(Supporting Information)

Dehydrogenative Silylation of Cellulose in Ionic Liquid

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Chemicals

1-Ethyl-3-methylimidazolium hexafluorophasphate ($EmimPF_6$), 1-ethyl-3-methylimidazolium chloride (EmimCl), and 3-phenyl-1-propanol were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). 1-Allyl-3-methylimidazolium chloride (AmimCl), 1-ethyl-3-methylimidazolium trifluoroacetate (EmimTFA), dimethylphenylsilylchloride, triethylsilylchloride, dimethylphenylsilane, diphenylmethylsilane, triphenylsilane, and triethylsilane were purchased from Tokyo Chemical Industry (TCI, Tokyo, Japan). 1-Ethyl-3-methylimidazolium acetate (EmimOAc) was available from Nippon Nyukazai Co., Ltd. (Tokyo, Japan). Cellulose (Avicel®PH-101, particle size < 50 μm), tetrabutylammonium acetate (TBAOAc), and 1-butyl-3-methylimidazolium chloride (BmimCl) obtained from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA). The number-average degree of polymerization of Avicel was calculated to be 105.[1] 1-Methyl-2-phenyl-3-ethyl imidazolium acetate (EmpimOAc)[1] and dodecylammonium propionate (DDAP)[2] were synthesized according to conventional protocols. Other chemicals were obtained from commercial sources and were used as received unless otherwise stated.

Instruments

^{1}H NMR spectra were recorded using JNM-ECA 500 and 600 spectrometers (JEOL Ltd., Tokyo, Japan) in deuterated solvents, and the chemical shifts (δ, ppm) were referenced to either the residual solvent peak or tetramethylsilane [TMS, $\delta = 0$ (ppm)] as the internal standard. Fourier transform-infrared (FT-IR) spectra were recorded using a Thermo Fisher Scientific Nicolet IS10 (Thermo Fisher Scientific Inc., Tokyo, Japan) spectrometer equipped with an attenuated total reflection (ATR) unit, and JASCO FT/IR-4700 (JASCO Hachioji, Japan) for KBr pellet measurement. The size exclusion chromatography (SEC) measurements were performed with a JASCO PU-4180 liquid chromatograph equipped with a photo diode array (MD-4010) detector. All SEC measurements were carried out at 40 °C using Shodex (Tokyo, Japan) KF-805L, and tetrahydrofuran (THF) was used as an eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curves were obtained with polystyrene standards (Tosoh)

General procedure for the dehydrogenative silylation of cellulose.

Cellulose (120 mg, [OH] = 2.22 mmol) in EmimOAc (378 mg, 2.22 mmol) was dried for 3 h *in vacuo* at 80 °C. After the drying process was completed, dimethylsulfoxide (DMSO) (3.15 mL) was added and the mixture was stirred under Ar atmosphere. After 1 h, monohydrosilane (2.22 mmol) was added and the reaction mixture was stirred for 18 h at 60 °C. The resulting solution was poured into a large amount of MeOH. The polymer was washed with excess methanol and dried *in vacuo* overnight to give a white fiber of a corresponding cellulose silyl ether.

General procedure of cellulose silyl ether preparation using monochlorosilane

Cellulose (120 mg, [OH] = 2.22 mmol) in BmimCl (388 mg, 2.22 mmol) was dried for 3 h *in vacuo* at 80 °C. After the drying process was completed, dimethylsulfoxide (DMSO) (3.15 mL) was added and the mixture was stirred under Ar atmosphere. After 1 h, triethylamine (225 mg, 2.22 mmol) and monochlorosilane (2.22 mmol) were added and the reaction mixture was stirred for 18 h at 60 °C. The resulting solution was poured into a large amount of water. The polymer was reprecipitated from dichloromethane to 2-propanol, washed with excess 2-propanol and dried *in vacuo* overnight to give a corresponding cellulose silyl ether.

General procedure of per-acetylation of cellulose silyl ether

Cellulose silyl ether (50 mg, 1 equivalent as original cellulose) in EmimOAc (158 mg, 0.93 mmol) was dried for 3 h *in vacuo* at 80 °C. After the drying process was completed, dimethylsulfoxide (DMSO) (1.31 mL) was added and the mixture was stirred under Ar atmosphere. After 1 h, isopropenyl acetate (0.20 mL, 1.85 mmol) were added and the reaction mixture was stirred for 2 h at 80 °C. The resulting solution was poured into a large amount of methanol. The polymer was dried *in vacuo* at 70 °C overnight to give a corresponding per-acetylated cellulose silyl ether.

Stability test of cellulose triethylsilyl ether in EmimOAc (Figure S5).

Cellulose triethylsilyl ether (90 mg, DS = 2.27) were dissolved in EmimOAc (378 mg, 2.22 mmol) and dried for 3 h *in vacuo* at 80 °C, then dimethylsulfoxide (DMSO) (3.15 mL) was added and the mixture was stirred for 18 h at 60 °C under Ar atmosphere. The resulting solution was poured into a large amount of MeOH. The polymer was washed with excess methanol and dried *in vacuo* overnight to give a white fiber (54.0 mg, DS = 2.26).

Evaluation of the degree of substitution values of the cellulose esters.

The degree of substitution (DS) values of the cellulose silylethers were determined using ^{1}H NMR measurements in $CDCl_3$ or CD_2Cl_2 depending on the solubility of the product and overlap between the target and solvent peaks.

Generally, the DS values were calculated using the following equation

$$\mathbf{DS} = (\mathbf{I_{main}}/\mathbf{X})/(\mathbf{I_{AGU}}/\mathbf{7})$$

The DS values of cellulose dimethylphenylsilyl ether (typified in Table 2, entry 1), methyldiphenylsilyl ether (entry 3), triphenylsilyl ether (entry 4) and triethylsilyl ether (entry 6) of cellulose were calculated from the integrals of the corresponding peaks (I_{main}) at 0.1−0.7 ppm (X = 6), 0.1−0.8 ppm (X = 3), 6.6−7.7 ppm (X = 15), 0.3−0.7 ppm (X = 6), respectively, and the anhydroglucose unit (AGU) peaks (I_{AGU}) at around 2.7−5.0 ppm.

General procedure of model experiments: dehydrogenative silylation of monol (Table S3).

Catalyst (0.70 mmol) was dried for 3 h *in vacuo* at 80 °C. After the drying process was completed, dry dimethylsulfoxide (DMSO) (995 μL), 3-phenyl-1-propanol (**A**) (95.3 mg, 0.70 mmol), dimethylphenylsilane (**1**) (95.4 mg, 0.70 mmol) was added and the reaction mixture was stirred for 2 h at 60 °C. After adding trimethoxybenzene (16.8 mg, 0.10 mmol), a aliquot of reaction mixture was transferred to DMSO-d_6, and quantitative crude ^{1}H-NMR measurement was conducted to evaluate the yield of corresponding dimethyl(phenyl)(3-phenylpropoxy)silane (**B**). In the case of Table S3, entry 5 (EmimOAc was 0.07 mmol, and reaction time was 72 h), after quantitative crude ^{1}H-NMR measurement, the solvent was evaporated. Resulting solution was diluted by water and extracted by hexane. Combined organic layer was evaporated and resulting mixture was purified by silica gel column chromatography (Eluent: hexane/EtOAc) to afford dimethyl(phenyl)(3-phenylpropoxy)silane (**B**) as a colorless oil (71.2 mg, 0.263 mmol, 38%). ^{1}H NMR (500 MHz, DMSO-d_6, r.t.): δ 7.32–7.30 (m, 2H), 7.18–7.12 (m, 3H), 7.02–6.99 (m, 2H), 6.93–6.89 (m, 3H), 3.33 (t, J = 6.3 Hz, 2H), 2.34 (t, J = 7.7 Hz, 2H), 1.51 (t, J = 6.3, 7.7 Hz, 2H), 0.08 (s, 6H).

Supporting Data

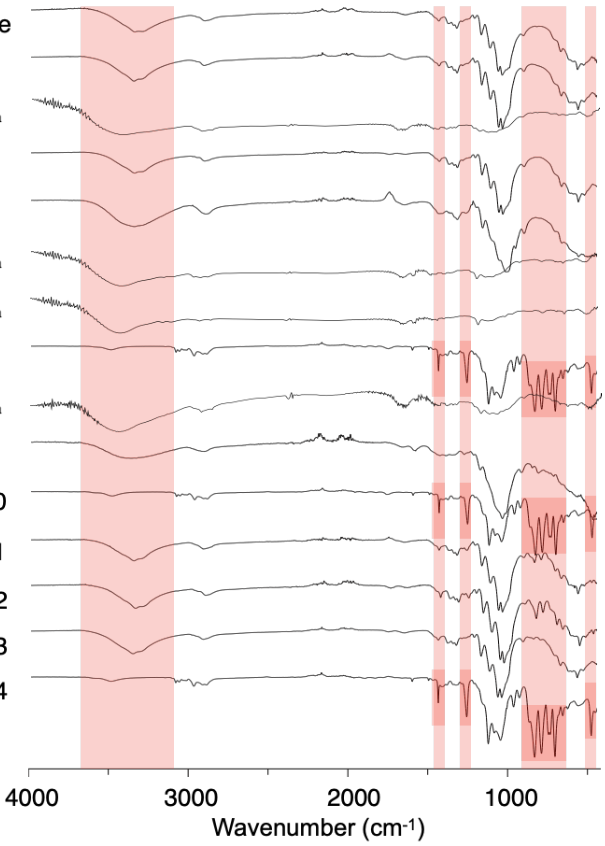


Figure S1. ATR-mode FT-IR spectra of original cellulose and the resulting cellulose silyl ether derivatives of Table 1. [a]Measured as KBr pellet (not ATR-mode FT-IR).

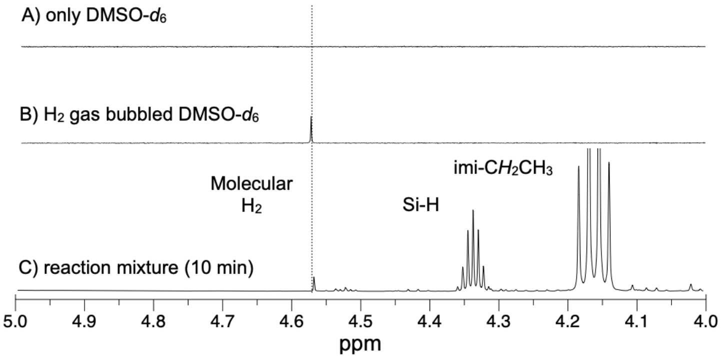


Figure S2. (A, B) ^{1}H NMR spectra of DMSO-d_6 before (A) and after (B) bubbling H_2 gas for 10 minutes at 25 °C. (C) ^{1}H NMR spectrum of reaction crude mixture (condition: Table S3, entry 4) after 10 min from the addition of **1**, measured in DMSO-d_6 at 25 °C.

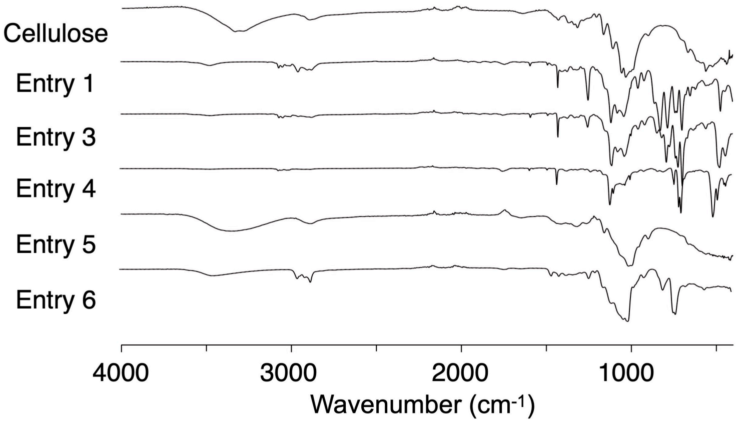


Figure S3. ATR-mode FT-IR spectra of resulting cellulose silyl ether derivatives of Table 2.

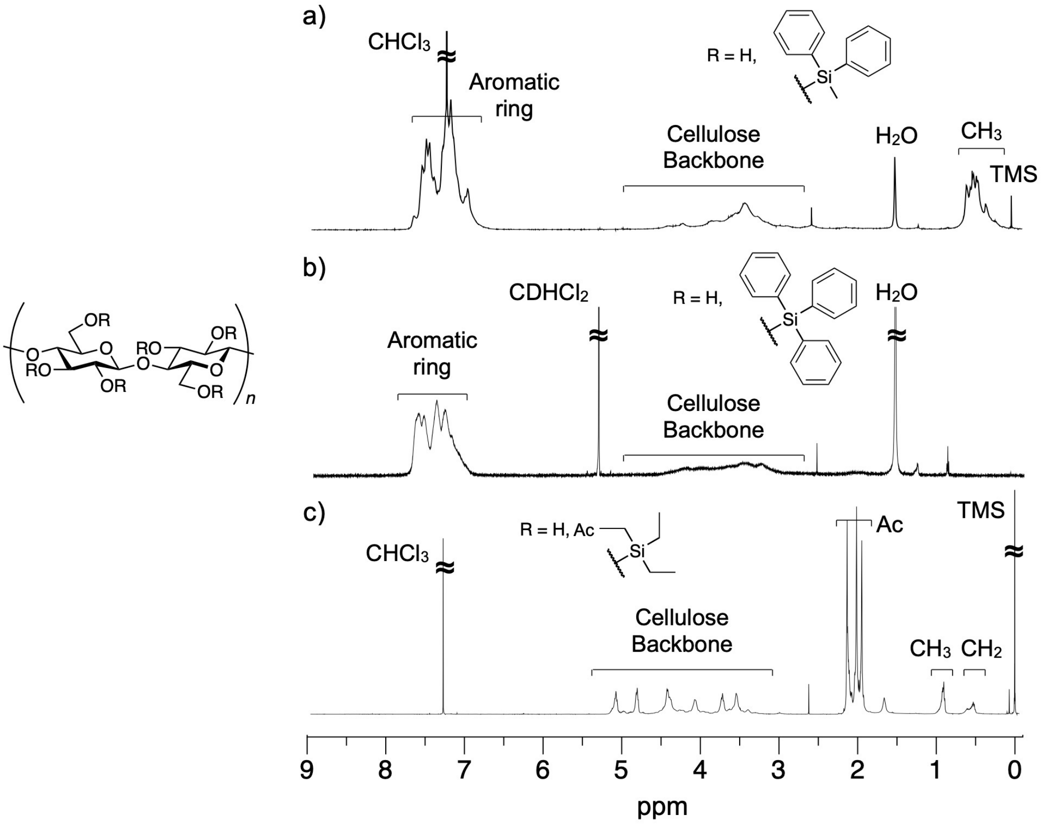


Figure S4. ^{1}H NMR spectra of cellulose methyldiphenylsilyl ether in $CDCl_3$ at room temperature (Table 2, entry 3, DS = 2.15) (a), cellulose triphenylsilyl ether in CD_2Cl_2 at room temperature (Table 2, entry 4, DS =1.53) (b) and per-acetylated cellulose triethylsilyl ether in $CDCl_3$ at room temperature (Table 2, entry 4, DS = 0.32) (c).

Cellulose dimethylphenylsilyl ether (DS = 2.57) [Table 2, entry 1]: 327 mg. ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.7–6.9 (br, aromatic ring), 5.0–2.7 (br, cellulose backbone), 0.7–0.1 (br, $\mathrm{C}H_3$).

Cellulose methyldiphenylsilyl ether (DS = 2.15) [Table 2, entry 3]: 341 mg. ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.8–6.5 (br, aromatic ring), 5.0–2.7 (br, cellulose backbone), 0.8–0.1 (br, $\mathrm{C}H_3$).

Cellulose triphenylsilyl ether (DS = 1.53) [Table 2, entry 4]: 629 mg. ^{1}H NMR (600 MHz, CD_2Cl_2, room temperature): δ 7.7–6.6 (br, aromatic ring), 5.0–2.7 (br, cellulose backbone).

Cellulose triethylsilyl ether (DS = 0.32) [Table 2, entry 6]: 140 mg (before acetylation). ^{1}H NMR (600 MHz, $CDCl_3$, room temperature [(after acetylation)]): δ 5.2–3.0 (br, cellulose backbone), 2.3–1.8 (br, Ac), 1.0–0.8 (br, $\mathrm{CH_2C}H_3$), 0.7–0.3 (br, $\mathrm{C}H_2$).

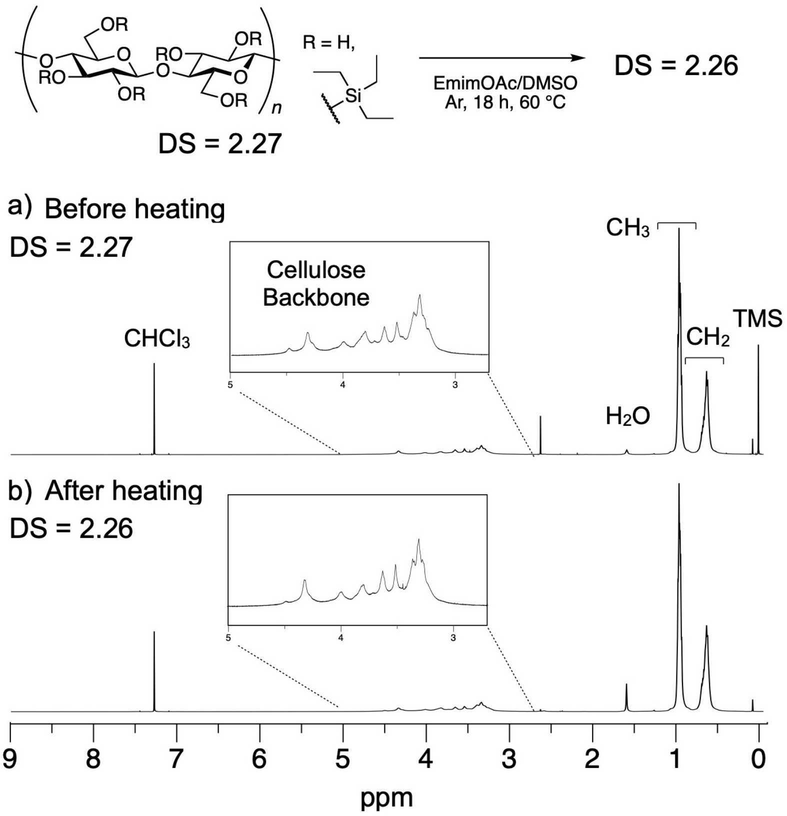


Figure S5. ^{1}H NMR spectra of cellulose triethylsilyl ether before (a) and after (b) annealing in EmimOAc/DMSO mixture for 18 h at 60 °C, measured in $CDCl_3$ at room temperature.

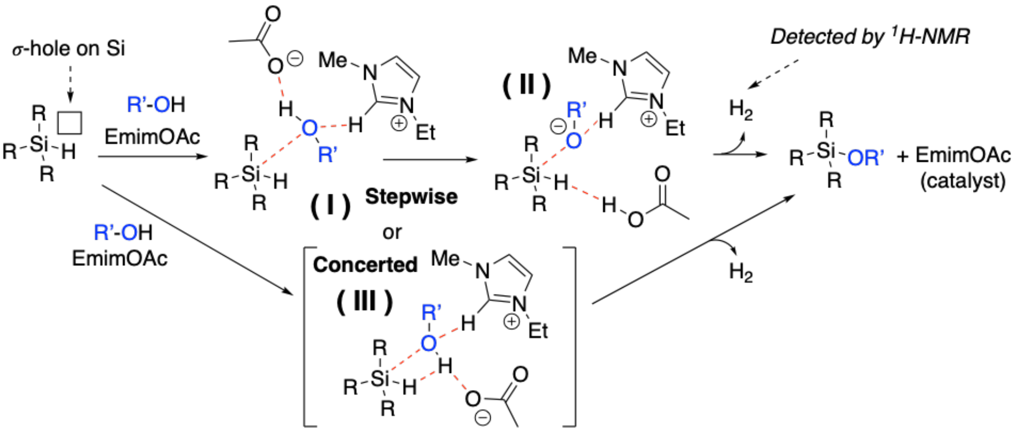


Figure S6. Tentative reaction mechanism of dehydrogenative silylation of alcohol catalyzed by EmimOAc.

Table S1. SEC Results of highly substituted (DS > 1.5) cellulose silyl ethers (Table 2).

	M_n (10^{-4})[a]	M_w/M_n [a]
Entry 1	3.5	3.9
Entry 3	3.6	3.9
Entry 4	3.1	3.9

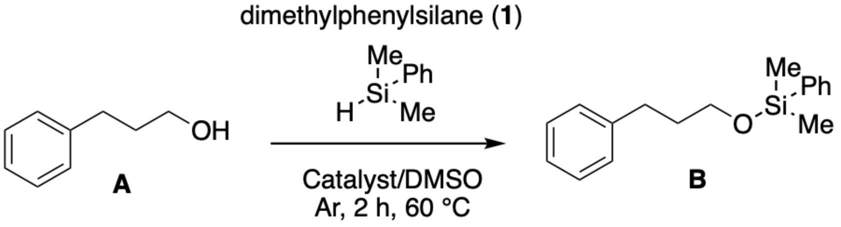
[a]Determined by SEC (eluent: THF, PSt standards).

Table S2. Solubility test (1.0 mg/mL) of resulting cellulose silyl ethers (Table 2) at room temperature.

	Toluene	$CHCl_3$	THF	Acetone	DMF	DMSO	MeOH	H_2O
Entry 1	○	○	○	X	X	X	X	X
Entry 3	○	○	○	X	X	X	X	X
Entry 4	X	○	○	X	X	X	X	X
Entry 6	X	X	X	X	△	○	X	X

○: Soluble, △: Partially soluble, X: Insoluble.

Table S3. Model Experiments: Initial Stage of Dehydrogenative Silylation of Monol (**A**)[a]



Entry	Catalyst	NMR Yield of **B** (%)
1	None	n.d.
2[b]	None	n.d.
3	BmimCl	n.d.
4	EmimOAc	34
5[c]	EmimOAc	50
6	EmimTFA	n.d.
7	DDAP	19
8	TBAOAc	27
9	KOAc	9

[a]Reaction conditions: [**A**]/[**1**]/[catalyst]/[DMSO] = 1:1:1:20 (molar ratio); 2 h; 60 °C; Ar atmosphere. [b]7 wt% LiCl containing DMA was used instead of DMSO. [c][**A**]/[**1**]/[catalyst][DMSO] = 1:1:0.1:20 (molar ratio); 72 h; 60 °C.

Reference

1. R. Kakuchi, R. Ito, S. Nomura, H. Abroshan, K. Ninomiya, T. Ikai, K. Maeda, H. J. Kim and K. Takahashi, *RSC Adv.*, 2017, **7**, 9423-9430.
2. J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *J. Organomet. Chem.*, 1978, **145**, C31-C33.