ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Kim, C. Lee and C. Jun, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC04863K.

View Article Online
DOI: 10.1039/C8CC04863K

Journal Name

COMMUNICATION

Styrylsilane Coupling Reagents for Immobilization of Organic Functional Groups on Silica and Glass Surface

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

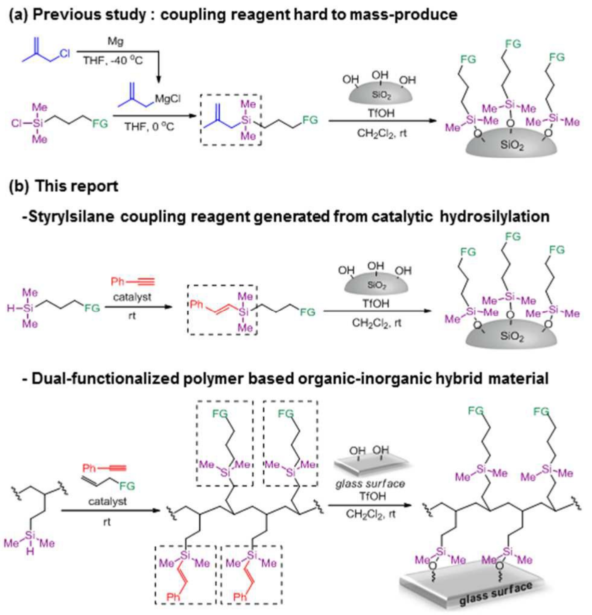
www.rsc.org/

Soo-Bin Kim,[§] Chang-Hee Lee[§] and Chul-Ho Jun*

Styrylsilanes serve as new coupling reagents for introducing organic functional groups on silica and glass surfaces. Functionalized styrylsilanes, which are readily prepared via catalytic hydrosilylation of the corresponding phenylacetylenes with silanes, are immobilized on silica through acid catalyzed processes under mild conditions.

Surface modifications of inorganic solids, such as silica or glass, utilizing covalent bond-forming reactions have received considerable attention because of their widespread applications in the fabrication of chemical and bio-sensor[1], drug delivery[2] and enzyme immobilization[3] systems, DNA probe films[4], and polymer brushes[5]. Among the various substances used in silica surface-grafting methods[6], alkoxysilanes[7] are the most common. Unfortunately, alkoxysilanes are unstable, moisture sensitive substances that are difficult to purify by employing chromatographic methods. Alkenylsilane such as allyl-[8], methallyl-[9] and vinyl-silanes[10] have been developed to overcome this problem. However, stoichiometric reactions of organometallic compounds such as Grignard reagents with chlorosilanes are required to prepare these silanes[8-10], and this limits their large-scale production (Fig. 1a).

Below, we describe the preparation and applications of novel styrylsilane coupling reagents for introducing organic functional groups on silica and glass surfaces. These substances are readily prepared in large quantities via catalytic hydrosilylation reactions of phenylacetylene with silanes. Using this protocol, various styrylsilanes were prepared and employed to generate functionalized silica and glass surfaces. In addition, styrylsilane moieties were linked the backbone of polybutadiene as part of a sequence to produce a unique organic-inorganic hybrid materials, which is stable toward hydrolysis because it possess robust multiple covalent bonds between the silyl groups on the polymer and hydroxy groups on the silica or glass surfaces (Fig. 1b).[10b] Finally, the new protocol was utilized to fabricate a recyclable sensor for aromatic nitro compound.


(a) Previous study : coupling reagent hard to mass-produce

(b) This report

-Styrylsilane coupling reagent generated from catalytic hydrosilylation

- Dual-functionalized polymer based organic-inorganic hybrid material

Fig. 1 (a) Previous approach using methallylsilane derivatives. (b) Conceptual basis of the new styrylsilane coupling reagent.

Initial exploratory studies focussed on immobilization reactions of benzyldimethyl(styryl)silane (**1a**) on silica promoted by various acid catalysts **3** (Table 1). The results show that reaction of **1a** (0.08 mmol) with silica **2** (20 mg) in the presence of a catalytic amount of TfOH (**3a**, 5 mol%) at room temperature for 2 h, followed by washing with CH_2Cl_2, produces surface-modified silica **4a** (entry 1).[11] The amount of immobilized benzyl(dimethyl)silane moieties loaded on **4a** was determined by using elemental analysis to be 1.02 mmol/g, corresponding to 1.98 molecules/nm^2 of the surface density of the benzyl(dimethyl)silane moieties on silica **4a**.[12] Reactions

---

Department of Chemistry, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea. E-mail: junch@yonsei.ac.kr

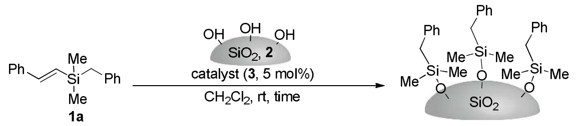
† Electronic Supplementary Information (ESI) available: [Experimental details and characterization of new materials]. See DOI: 10.1039/x0xx00000x

[§] These authors equally contributed to this work.

View Article Online
DOI: 10.1039/C8CC04863K

employing other acid catalysts generate modified silica with loading amounts that are lower than that of **4a** (entries 2-6). The reaction conducted in the absence of an acid catalyst leads to silica **4g** with a loading extent of only 0.17 mmol/g (entry 7). When the reaction time is increased from 2 h to 6 h under TfOH catalyst, the loading extent of immobilized silane moiety is increased to 1.11 mmol/g and a longer reaction times (eg., 12 h) do not cause a significant enhancement of the loading efficiency (entries 8 and 9).

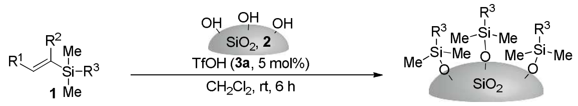
Table 1 Immobilization reactions with styrylsilane **1a** on silica **2** in the presence of the various acid catalysts **3**[a]



entry	catalyst	time (h)	loading extent[b] (mmol/g)
1	TfOH **3a**	2	1.02 (**4a**)
2	Acetic acid **3b**	2	0.18 (**4b**)
3	HCl in 1,4-dioxane **3c**	2	0.72 (**4c**)
4	$Cu(OTf)_2$ **3d**	2	0.21 (**4d**)
5	$Sc(OTf)_3$ **3f**	2	0.56 (**4e**)
6	$In(OTf)_3$ **3g**	2	0.85 (**4f**)
7	-	2	0.17 (**4g**)
8	**3a**	6	1.11 (**4h**)
9	**3a**	12	1.12 (**4i**)

[a] All reactions were carried out with **1a** (0.08 mmol), **2** (20 mg) and **3** (5 mol%) in 0.1 mL of CH_2Cl_2 at room temperature. [b] Determined by using the C value derived from elemental analysis.

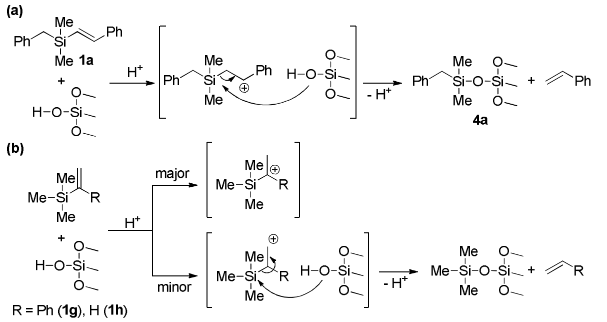
Table 2 Immobilization reactions with various alkenylsilane **1** on silica **2** in the presence of **3a**[a]



entry	silane **1** (R^1, R^2, R^3)	loading extent[b] (mmol/g)
1	**1b** (C_3H_7, H, Bn)	0.83 (**4j**)
2	**1c** (C_3H_7, C_3H_7, Bn)	0.73 (**4k**)
3	**1d** (Ph, Ph, Bn)	0.44 (**4l**)
4	**1e** (4-fluoro-Ph, H, Bn)	1.04 (**4m**)
5	**1f** (4-methoxy-Ph, H, Bn)	0.73 (**4n**)
6	**1g** (H, Ph, Me)	0.42 (**4o**)
7	**1h** (H, H, Me)	0.44 (**4p**)

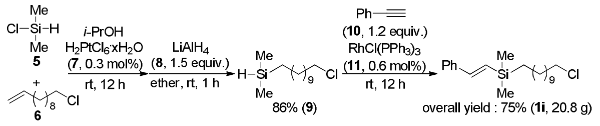
[a] All reactions were carried out with **1** (0.08 mmol), **2** (20 mg) and **3a** (5 mol%) in 0.1 mL of CH_2Cl_2 at room temperature. [b] Determined by using the C value derived from elemental analysis.

The efficiencies of loading other alkenylsilane moieties on silica were also determined (Table 2, entries 1-7). Immobilization reaction of 1-pentenylsilane **1b**, using TfOH (**3a**, 5 mol%) at room temperature for 2 h, takes place to form benzyl(dimethyl)silane modified silica **4j** with a loading extent of 0.83 mmol/g (entry 1). Reactions of α,β-disubstituted alkenylsilanes **1c** and **1d** lead to lower loading amounts (0.73 and 0.44 mmol/g) (entries 2 and 3). Reaction of the *p*-electron withdrawing group substituted (F) styrylsilane **1e** leads to higher loading efficiency than that of the *p*-electron donating substituted (MeO) styrylsilane **1f** (entries 4 and 5). Compared to those of β-substituted vinylsilanes (entries 1 and 4-5), reactions of the α-phenyl-substituted vinylsilane **1g** and vinylsilane **1h** generate modified silica with very low loading amounts (0.42 and 0.44 mmol/g) (entries 6 and 7). The low reactivities of **1g** and **1h** might be caused by the propensity of reactions of **1g** and **1h** with acids to form α-silyl carbocations intermediates which would resist substitution reaction at Si by a silanol silophile (see below).

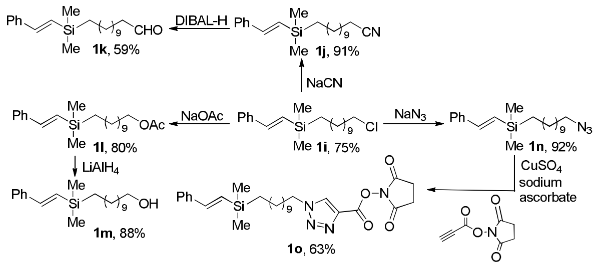


Scheme 1 (a) Proposed mechanism of immobilization with **1a**. (b) Proposed mechanism of immobilization with α-phenyl-substituted vinylsilane **1g** and vinylsilane **1h**.

A plausible mechanism for the immobilization reaction of styrylsilane **1a**, displayed in Scheme 1a, begins with protonation of the styryl group to form a β-silyl cation. Regioselective formation of this intermediate occurs because of the higher stabilities of benzyl[13] and β-silyl cations.[14] The β-silyl carbocation then undergoes substitution at silicon with silanol groups on silica or glass serving as the nucleophile.[8b] This step generates surface modified silica **4a** and styrene. In contrast, protonation of α-phenyl-substituted vinylsilane **1g** and vinylsilane **1h** should preferentially occur to generate respective *tert*- and *sec*-carbocations, both of which are α-silyl cations that should not readily undergo substitution at their Si centers (Scheme 1b).



Scheme 2 Large-scale production of (11-chloroundecyl)dimethyl(styryl)silane (**1i**).



Scheme 3 Chemical transformation of the functional groups of **1i**.

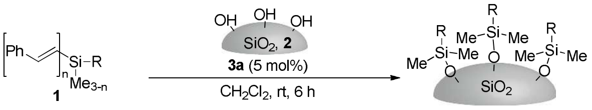
Functionalized styrylsilane coupling reagents can be readily prepared in large-scale by sequences involving catalytic

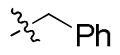
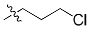
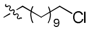
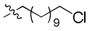
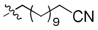
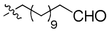
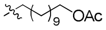
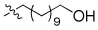
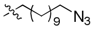
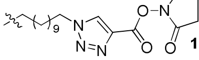
View Article Online
DOI: 10.1039/C8CC04863K

hydrosilylation of phenylacetylene with the corresponding silanes, which are generated by reactions of chlorodimethylsilanes with alkenyl chlorides. This approach is exemplified by preparation of the (11-chloroundecyl) substituted styrylsilane **1i** (Scheme 2) and its derivatives (Scheme 3). The routes begin with reaction of chlorodimethylsilane (**5**, 15.0 g) with 11-chloroundec-1-ene (**6**, 15.0 g) in the presence of the Pt catalyst **7** (0.3 mol%) to produce chloro(11-chloroundecyl)dimethylsilane, which is reduced using $LiAlH_4$ (4.5 g) to form (11-chloroundecyl)dimethylsilane **9** in 86% isolated yield. Silane **1i** is then generated in 75% overall yield (20.8 g) by hydrosilylation reaction of **9** (17.0 g) and phenylacetylene using Rh catalyst **11** (0.6 mol%).

Chloride **1i** can be transformed into various functionallized silanes in good yields (Scheme 3). This is demonstrated by reactions of **1i** with sodium cyanide, sodium acetate and sodium azide, which produce the respective silanes **1j**, **1l** and **1n** in 91%, 80%, and 92% yields. Moreover, reduction reactions of **1j** and **1l** using DIBAL-H and $LiAlH_4$ produce the aldehyde and alcohol functionalized styrylsilanes **1k** and **1m** in 59% and 88% respective yields. Finally, Cu(I)-promoted [3+2]-cycloaddition reaction of azide **1n** with 2,5-dioxopyrrolidin-1-yl propiolate forms the triazole linked, NHS-ester (N-hydroxysuccinimide ester) functionalized styrylsilane **1o** in 63% yield. Notably, the styrylsilyl group is preserved in these processes and the resulting styrylsilanes can be readily purified by using column chromatography.

Table 3 Immobilization reactions of various functional group containing styrylsilanes[a]

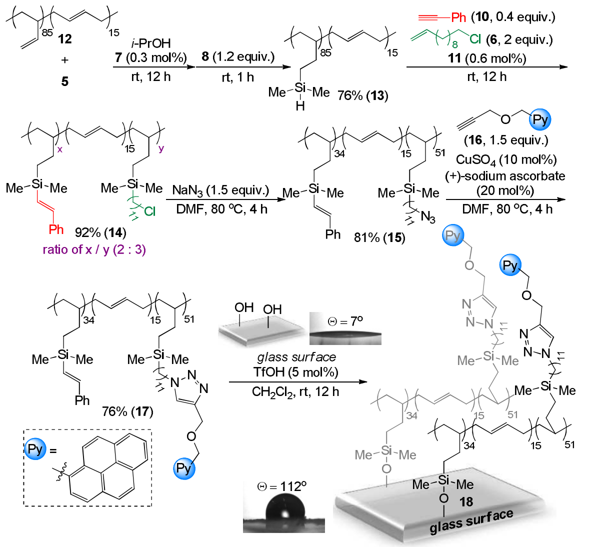


entry	n	R		loading extent[b] (mmol/g)
1	1		**1a**	1.11 (**4q**)
2	1		**1p**	1.06 (**4r**)
3	1		**1i**	0.77 (**4s**)
4[c]	2		**1q**	0.84 (**4t**)
5	1		**1j**	0.61 (**4u**)
6	1		**1k**	0.98 (**4v**)
7	1		**1l**	0.68 (**4w**)
8	1		**1m**	0.49 (**4x**)
9	1		**1n**	0.70 (**4y**)
10	1		**1o**	0.56 (**4z**)

[a] All reactions were carried out using **1** (0.08 mmol), **2** (20 mg), **3a** (5 mol%) in 0.1 mL of CH_2Cl_2 at room temperature. [b] Determined by using derived from C value from elemental analysis. [c] **1q** contains 15% α-phenyl-substituted vinylsilane isomer.

Immobilization reactions of styrylsilanes were performed to incorporate various functional groups on silica **2** (Table 3). Reactions of styrylsilanes **1p** and **1i** produce the respective immobilized silica **4r** and **4s** with moderate loading extents (1.06 and 0.77 mmol/g, respectively) (entries 2 and 3). Use of the distyrylsilane coupling reagent **1q** in this process leads to formation of functionalized silica **4t** with the higher loading extent of 0.84 mmol/g (entry 4).

Many other types of functionalized silica surfaces can be generated using this protocol (entries 5-10). Reactions of the nitrile, aldehyde, acetate ester and azide containing styrylsilanes **1j-1l** and **1n** were found to produce the respective immobilized products **4u-4w** and **4y** with moderate loading extents (0.61, 0.98, 0.68, and 0.70 mmol/g, respectively) (entries 5-7 and 9). Interestingly, reaction of the hydroxyl group-functionalized styrylsilane **1m** with silica forms the corresponding functionalized silica with a low loading (0.49 mmol/g) (entry 8). Finally, the NHS-ester group-functionalized silica **4z** for enzyme immobilization is produced with a 0.56 mmol/g loading extent (entry 10).[9b,9d]



Scheme 4 Preparation of pyrene group containing polymer **17** and immobilization reaction of **17** on glass surface.

A new strategy for introducing organic functional groups on solid surfaces, which uses styrylsilyl-impregnated polybutadiene was explored (Scheme 4). For this purpose, the dimethylsilyl group-imbedded polymer **13** was first generated in 76% overall yield by Pt-catalyzed hydrosilylation reaction of polybutadiene **12** with chlorodimethylsilane (**5**) followed by reduction with $LiAlH_4$. Hydrosilylation of **13** with a mixture of phenylacetylene (**10**, 0.4 equiv. based on the number of silane groups in **13**) and 11-chloroundec-1-ene (**6**, 2 equiv.) using Rh catalyst **11** produces polymer **14** (92%), which contains both appended styrylsilane and chloroalkyl groups. ^{1}H NMR analysis shows that this dual-functionalized polymer contains a 2:3 ratio of styrylsilyl and chloroalkyl groups. Reaction of **14** with sodium azide forms the azide functionalized polybutadiene **15**, which undergoes Cu(I)-promoted [3+2]-cycloaddition reaction[15] with 1-(propargyloxymethyl)pyrene (**16**) to form the dual-functionalized polybutadiene **17** (76%) containing both pyrenyl and styrylsilyl groups. Finally, reaction of piranha solution-treated glass with **17** in the presence of TfOH

View Article Online
DOI: 10.1039/C8CC04863K

produces glass **18**, which has a surface that is significantly more hydrophobic than that of untreated glass (contact angles of surface before and after reaction are 7° and 112°, respectively).

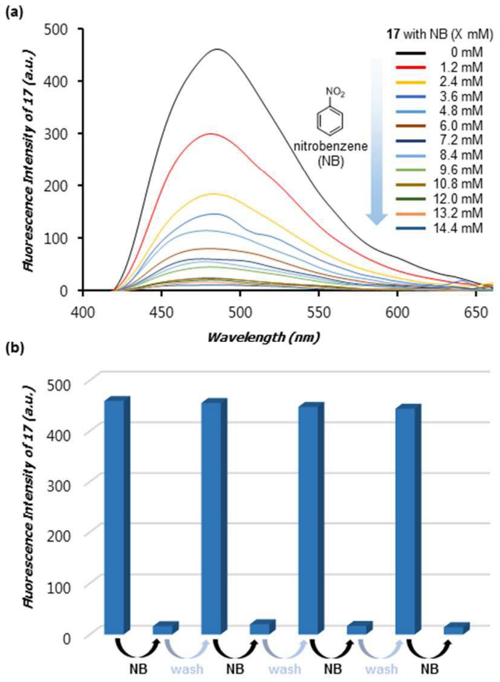


Fig. 2 (a) Fluorescence spectra of solutions of **18** in CH_2Cl_2 with different concentrations of nitrobenzene (NB) (excitation at 330 nm). (b) Fluorescence intensities of solutions of **18** in CH_2Cl_2 at 482 nm following addition of nitrobenzene (14.4 mM) and washing with CH_2Cl_2

It is known that aromatic nitro compounds are efficient electron transfer quenchers of fluorescent aromatic compounds.[16] To demonstrate potential applications of the immobilization strategy described above, pyrenyl group-immobilized glass **18** was utilized as a recyclable fluorescence sensor of the potential explosive simulant, nitrobenzene (NB). Inspection of the fluorescence spectra displayed in Fig. 2a shows that **18** has strong fluorescence with a maximum at 482 nm. Upon addition of NB to a solution of **18** in CH_2Cl_2, the intensity of fluorescence at 482 nm decreases, leading to complete quenching when the concentration of NB reaches 14.4 mM. Pyrenyl group-immobilized glass **18** can be separated, washed and used for NB detection multiple times (Fig. 2b).

In the investigation described above, we demonstrated that styrylsilanes serve as a new family of coupling reagents for immobilization of organic functional groups on solid surfaces. Styrylsilanes with high purities can be produced on large scales utilizing catalytic hydrosilylation reactions. This new protocol enables fabrication of unique functionalized materials, as exemplified by the preparation of a polymer-based organic-inorganic hybrid material that serves as a recyclable sensor.

This work was supported by a grant from the National Research Foundation of Korea (NRF) (Grant 2016-R-1-A2b4009460).

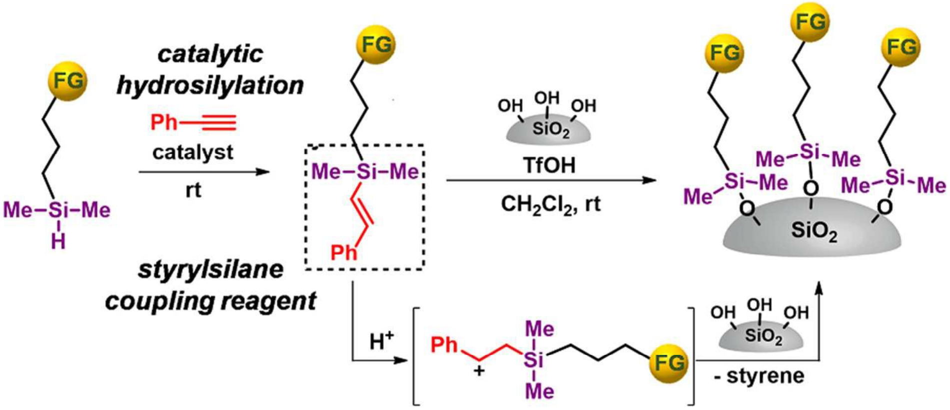
Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (a) S. Flink, F. C. J. M. van Veggel and D. N. Reinhoudt, *Adv. Mater.*, 2000, **12**, 1315; (b) Z. Farka, T. Juřík, D. Kovář, L. Trnková and P. Skládal, *Chem. Rev.*, 2017, **117**, 9973.
2 (a) Y. Chen, H. Chen and J. Shi, *Adv. Mater.*, 2013, **25**, 3144; (b) E. Aznar, M. Oroval, L. Pascual, J. R. Murguía, R. Martínez-Máñez and F. Sancenón, *Chem. Rev.*, 2016, **116**, 561.
3 U. Hanefeld, L. Gardossi and E. Magner, *Chem. Soc. Rev.*, 2009, **38**, 453.
4 R. Georgiadis, K. P. Peterlinz and A. W. Peterson, *J. Am. Chem. Soc.*, 2000, **122**, 3166.
5 (a) M. Krishnamoorthy, S. Hakobyan, M. Ramstedt and J. E. Gautrot, *Chem. Rev.*, 2014, **114**, 10976; (b) H. Jiang and F.-J. Xu, *Chem. Soc. Rev.*, 2013, **42**, 3394.
6 (a) R. J. Klein, D. A. Fischer and J. L. Lenhart, *Langmuir,* 2011, **27**, 12423; (b) V. Dugas and Y. Chervalier, *Langmuir*, 2011, **27**, 14188; (c) J.-W. Park, Y. J. Park and C.-H. Jun, *Chem. Commun.,* 2011, **47**, 4860; (d) N. Moitra, S. Ichii, T. Kamei, K. Kanamori, Y. Zhu, K. Takeda, K. Nakanishi and T. Shimada, *J. Am. Chem. Soc.*, 2014, **136**, 11570; (e) J. Escorihuela, S. P. Pujari and H. Zuilhof, *Langmuir*, 2017, **33**, 2185.
7 (a) K. B. Yoon, *Acc. Chem. Res.,* 2007, **40**, 29; (b) F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angew. Chem. Int. Ed.*, 2006, **45**, 3216; (c) S. K. Vashist, E. Lam, S. Hrapovic, K. B. Male and J. H. T. Luong, *Chem. Rev.,* 2014, **114**, 11083; (d) C. M. Crudden, M. Sateesh and R. Lewis, *J. Am. Chem. Soc.,* 2005, **127**, 10045.
8 (a) T. Shimada, K. Aoki, Y. Shinoda, T. Nakamura, N. Tokunaga, S. Inagaki and T. Hayashi, *J. Am. Chem. Soc.*, 2003, **125**, 4688; (b) Y. Maegawa, N. Mizoshita, T. Tani, T. Shimada and S. Inagaki, *J. Mater. Chem.*, 2011, **21**, 14020.
9 (a) Y.-R. Yeon, Y. J. Park, J.-S. Lee, J.-W. Park, S.-G. Kang and C.-H. Jun, *Angew. Chem. Int. Ed.*, 2008, **47**, 109; (b) Y.-K. Sim, J.-W. Park, B.-H. Kim and Jun, C.-H. *Chem. Commun.*, 2013, **49**, 11170; (c) Y. R. Han, J.-W. Park, H. Kim, H. Ji, S. H. Lim and C.-H. Jun, *Chem. Commun.,* 2015, **51**, 17084; (d) R.-Y. Choi, C.-H. Lee and C.-H. Jun, Org. Lett., 2018, **20**, 2972.
10 (a) J.-W. Park and C.-H. Jun, *J. Am. Chem. Soc.,* 2010, **132**, 7268. (b) J.-W. Park, D.-S. Kim, M.-S. Kim, J.-H. Choi and C.-H. Jun, *Polym. Chem.,* 2015, **6**, 555.
11 The surface structure of modified silica and its purity were also examined with ^{13}C CP-MAS NMR and elemental analysis with washing experiment (see ESI†).
12 The surface density (molecules/nm^2) of benzyl(dimethyl)-silane moiety loaded on **4a** can be estimated by using [loading extent (mmol/g) x N_A x 10^{-21} / SA (m^2/g)], where N_A is Avogadro's number and SA is the surface area (310 m^2/g) of the silica **2**.
13 J. McMurry, *Organic Chemistry*, Brooks/Cole, Pacific Grove, CA, 5th edn, 2000. pp. 407.
14 M. A. Brook, M. A. Hadi and A. Neuy, *J. Chem. Soc., Chem. Commun.*, 1989, 957.
15 Q. Wang, T. R. Chan, R. Hilgraf, V. V. Fokin, K. B. Sharpless and M. G. Finn, *J. Am. Chem. Soc.*, 2003, **125**, 3192.
16 (a) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153; (b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (c) Y. R. Han, S.-H. Shim, D.-S. Kim and C.-H. Jun, *Org. Lett.*, 2018, **20**, 264.

View Article Online
DOI: 10.1039/C8CC04863K



251x126mm (96 x 96 DPI)