Tetrahedron 67 (2011) 2081–2089

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Mesoporous aluminosilicate-catalyzed allylation of carbonyl compounds and acetals

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ARTICLE INFO

Article history:
Received 19 October 2010
Received in revised form 18 January 2011
Accepted 18 January 2011
Available online 25 January 2011

Keywords:
Al-MCM-41
Solid acid catalyst
Allylation
Homoallyl silyl ether
Homoallyl alkyl ether

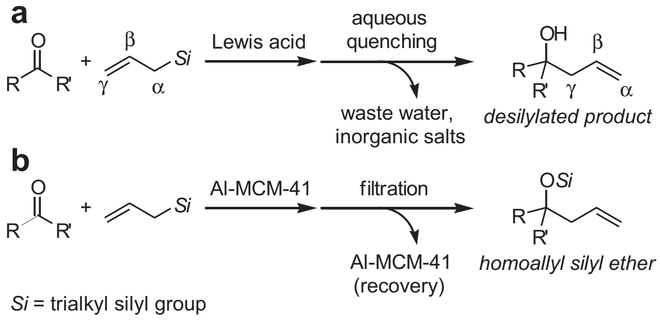
ABSTRACT

A mesoporous aluminosilicate (Al-MCM-41) was found to be an effective heterogeneous catalyst for the reaction of both carbonyl compounds and acetals with allylsilanes to afford the corresponding homoallyl silyl ethers and homoallyl alkyl ethers, respectively. Both the mesoporous structure and the presence of aluminum moiety were indispensable for the high catalytic activity of Al-MCM-41. Moreover, Al-MCM-41 could catalyze the reaction of acetals chemoselectively in the presence of the corresponding carbonyl compounds. The solid acid catalyst Al-MCM-41 could be recovered easily by filtration and could be reused three times without a significant loss of catalytic activity.

1. Introduction

Among the wide variety of carbon–carbon bond-forming reactions, Lewis acid-promoted allylations of aldehydes, ketones, and acetals with allylsilanes to afford homoallyl alcohol derivatives (Sakurai allylation) are valuable reactions in organic synthesis because of the high synthetic utility of the products. The new carbon–carbon bond is formed regioselectively at γ-carbon of allylsilanes (Scheme 1a). Usually, stoichiometric or sub-stoichiometric amounts of strong Lewis acids (e.g., $TiCl_4$, $BF_3 \cdot OEt_2$, and $AlCl_3$) are required to promote the reaction because a tight coordination of the product to the Lewis acid results in poor turnover of the acid.[1] Catalytic Sakurai allylation[2,3] was also investigated and many kinds of catalysts, such as $Sc(OTf)_3$,[2a,b,3f] $Yb(OTf)_3$,[2c] iodine,[2d] and $FeCl_3$,[2e,3d] have been found to date. However, the catalyst recycling is generally difficult in such homogeneous systems because the catalyst decomposes during aqueous workup, and the desilylated product is produced along with waste water and inorganic salts.

From an environmental and economical point of view, the development of heterogeneous organic reaction systems catalyzed by solid acid catalysts is important in the field of synthetic organic chemistry, recently.[4] Solid acids do not require an aqueous quenching and they could be recovered easily from a reaction mixture generally. Although metal cations-exchanged or proton-exchanged montmorillonites[5,6] and rare earth metals-exchanged zeolite-Y[7] have been reported as effective solid acid catalysts for Sakurai allylation, these catalytic systems sometimes have disadvantages, such as higher reaction temperature or low yields of the allylated products.



Scheme 1. Sakurai allylation of carbonyl compounds (a) promoted by a conventional Lewis acid and (b) catalyzed by Al-MCM-41.

On the other hand, mesoporous silicate MCM-41 and modified MCM-41s have become useful heterogeneous catalysts for wide variety of reactions due to its ordered pore structure, uniform pore diameter (2–10 nm), and high-surface area (>1000 m^2/g).[8] Moreover, it is well known that catalytic activity of MCM-41 increases by incorporating aluminum into its structure.[4b] Aluminum incorporated MCM-41 (Al-MCM-41) shows remarkable acidic properties, and has been found to catalyze several organic transformations under vapor

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doi:10.1016/j.tet.2011.01.055

phase or high-temperature reaction conditions.[9a–e] Furthermore, Al-MCM-41 could catalyze liquid-phase reactions under mild reaction conditions.[9f–i] In our preliminary communication, Al-MCM-41 was found to catalyze the allylation of aldehydes with allylsilanes under mild reaction conditions to afford the corresponding homoallyl silyl ether (Scheme 1b).[10a] The reaction of acetals was also catalyzed by Al-MCM-41.[10b] Herein, we describe the details of the Al-MCM-41-catalyzed allylation of aldehydes, ketones, and acetals with allylsilanes.

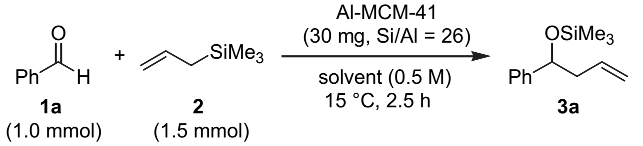
2. Results and discussion

According to a known procedure with slight modification,[11] Al-MCM-41s (Si/Al=23, 26, 34, and 48) were synthesized from cethyltrimethylammonium bromide, tetramethylammonium hydroxide, aluminum triisopropoxide, and tetraethyl orthosilicate.

To begin with, the effect of solvent was examined for the reaction of benzaldehyde (**1a**) (1.0 mmol) with allyltrimethylsilane (**2**) (1.5 mmol) in the presence of Al-MCM-41 (30 mg, Si/Al=26, dried prior to use at 120 °C for 1 h under vacuum). The best result was obtained when the reaction was carried out in dichloromethane at 15 °C for 2.5 h. After the reaction, the catalyst was removed by filtration. The filtrate was then concentrated and purified by silica-gel column chromatography to afford the corresponding homoallyl alcohol derivative **3a** in 93% yield. It should be noted that the product was obtained as trimethylsilyl ether because an aqueous workup is unnecessary (Table 1, entry 1). The use of toluene or nitromethane as a solvent also afforded the homoallyl silyl ether in good yields (entries 2 and 3). In contrast, the reaction did not take place in ether, THF, cyclohexane, or hexane (entries 4–7).

Next, to examine the effect of the mesoporous structure and presence of aluminum moiety, the reaction was carried out using various silica catalysts in place of Al-MCM-41 (Table 2). In the presence of amorphous silica/aluminas (JRC-SAH-1, JRC-SAL-2, and SiO$_2$/Al$_2$O$_3$), the reaction did not take place even though larger amount of catalysts were used to make the surface areas same (entries 2–4). Furthermore, aluminum-free mesoporous silicates (MCM-41 and SBA-15) could not catalyze the reaction (entries 5 and 6). These results suggest that the high catalytic activity of Al-MCM-41 is originated from the presence of both mesoporous structure and aluminum moiety in the catalyst. The superiority of Al-MCM-41 over amorphous silica/alumina is probably due to more efficient interaction between organic substrate and solid surface caused by concentration effect inside the ordered, hydrophobic mesopores with high-surface area. When the reaction was performed in dichloromethane at 30 °C, the reaction was completed in 1 h and the corresponding homoallyl silyl ether **3a** was obtained in 92% yield (entry 7).

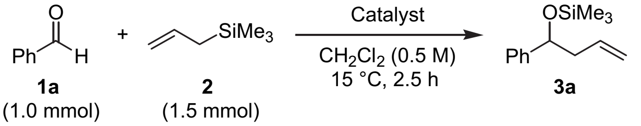
Table 1
Allylation of benzaldehyde with allyltrimethylsilane catalyzed by Al-MCM-41



Entry	Solvent	Yield[a](%)
1	CH$_2$Cl$_2$	93
2	Toluene	87
3	MeNO$_2$	85
4	Et$_2$O	N.R.
5	THF	N.R.
6	Cyclohexane	N.R.
7	Hexane	N.R.

[a] Isolated yield after column chromatography.

Table 2
Allylation of benzaldehyde with allyltrimethylsilane in the presence of various silica catalysts

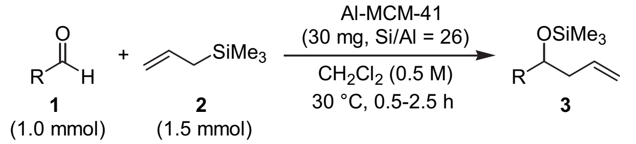


Entry	Catalyst (Si/Al)	Surface area (m^2/g)	Amount (mg)	Yield[a](%)
1	Al-MCM-41 (26)	1120	30	93
2	JRC-SAH-1 (2)	610	55	N.R.
3	JRC-SAL-2 (5)	570	59	N.R.
4	SiO$_2$/Al$_2$O$_3$ (31)	385	87	N.R.
5	MCM-41 (∞)	1080	30	N.R.
6	SBA-15 (∞)	925	30	N.R.
7[b]	Al-MCM-41 (26)	1120	30	92

[a] Isolated yield after column chromatography.
[b] Reaction was performed at 30 °C for 1 h.

The Al-MCM-41-catalyzed allylation was then applied to the reaction of various aldehydes with allyltrimethylsilane (Table 3). Electron-withdrawing groups (NO$_2^-$, Br$^-$, and Cl$^-$) on the aromatic ring accelerated the reaction, and the reaction was completed within 30 min to afford the corresponding homoallyl silyl ether in excellent yields (entries 1–6). Aromatic aldehydes bearing electron-donating groups were less reactive than benzaldehyde. The reaction of *o*-, *m*-, and *p*-tolualdehyde gave the allylated products in moderate to good yields (entries 7–10). When *o*- and *m*-anisaldehyde were used, the desired products were obtained in moderate yields (entries 12 and 13), whereas *p*-anisaldehyde gave only trace amount of the product (entry 11). In the case of naphthaldehydes, corresponding homoallyl silyl ethers were obtained in good yields although the reactivities

Table 3
Allylation of various aldehydes with allyltrimethylsilane catalyzed by Al-MCM-41



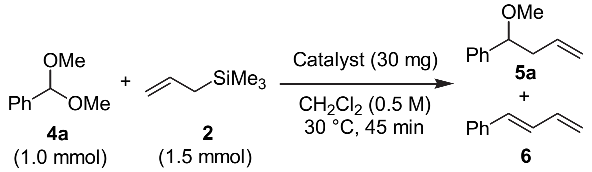
Entry	R	Time (h)	Yield[a](%)
1	4-NO$_2$C$_6$H$_4$	0.5	92
2	4-BrC$_6$H$_4$	0.5	97
3	4-ClC$_6$H$_4$	0.5	93
4	2-NO$_2$C$_6$H$_4$	0.5	90
5	2-BrC$_6$H$_4$	0.5	95
6	2-ClC$_6$H$_4$	0.5	93
7	4-MeC$_6$H$_4$	1	27
8[b]	4-MeC$_6$H$_4$	2.5	59
9	3-MeC$_6$H$_4$	1	70
10	2-MeC$_6$H$_4$	1	83
11	4-MeOC$_6$H$_4$	1	<3
12	3-MeOC$_6$H$_4$	1	24
13	2-MeOC$_6$H$_4$	1	41
14	2-Naphthyl	1	70
15[b]	2-Naphthyl	1	74
16	1-Naphthyl	1	61
17[b]	1-Naphthyl	1	67
18	PhCH$_2$CH$_2$	1	26[c] (20)[d]
19[b]	PhCH$_2$CH$_2$	1	60[c] (48)[d]
20	*c*-C$_6$H$_{11}$	1	54[c] (44)[d]
21[b]	*c*-C$_6$H$_{11}$	1	86[c] (73)[d]
22	*t*-Bu	1	85
23	(*E*)-PhCH=CH	1	7

[a] Isolated yield after column chromatography unless otherwise noted.
[b] Al-MCM-41 (50 mg) was used.
[c] Determined by ^{1}H NMR analysis using nitromethane as an internal standard.
[d] Isolated yield of the corresponding homoallyl alcohol after hydrolysis.

were slightly lower than that of benzaldehyde (entries 14–17). Although aromatic aldehydes, especially electron-rich aromatic aldehydes, are often diallylated by Lewis acid-catalyzed allylation with allylsilanes because of the stability of benzylic cation,[2b,e] the diallylated product was not detected in this catalytic system. The reaction of aliphatic aldehydes was also examined. In the case of 3-phenylpropanal and cyclohexanecarboxaldehyde, the formation of the corresponding silyl enol ethers[12] caused the decrease in the yield of the allylated products (entries 18 and 20). The yields were improved by increasing the amount of the catalyst (entries 19 and 21). The allylated products of these reactions were isolated after hydrolysis of the silyl ethers because the homoallyl silyl ether and the silyl enol ether were hard to separate by silica-gel column chromatography. Pivalaldehyde was allylated in 85% yield despite its steric hindrance (entry 22). The reaction did not proceed well with α,β-unsaturated aldehyde, and the 1,2-adduct was obtained in 7% yield from (*E*)-cinnamaldehyde (entry 23).

As good results were obtained in the reaction of aldehydes, Al-MCM-41-catalyzed allylation of acetals was examined (Table 4). In the presence of Al-MCM-41 (30 mg, Si/Al=26), the reaction of benzaldehyde dimethyl acetal (**4a**) (1.0 mmol) with **2** (1.5 mmol) in dichloromethane at 30 °C for 45 min afforded 4-methoxy-4-phenylbut-1-ene (**5a**) in 86% yield along with 7% yield of 1-phenylbuta-1,3-diene (**6**) (entry 1). The reaction did not occur in the presence of SiO_2/Al_2O_3 or MCM-41 as was observed in the case of allylation of aldehydes (entries 2 and 3).[13] By reducing the aluminum content of the catalyst, the amount of **6** produced in the reaction decreased and only **5a** was obtained in 96% yield by using Al-MCM-41 (Si/Al=48) (entries 4 and 5).

Table 4
Allylation of benzaldehyde dimethyl acetal with allyltrimethylsilane



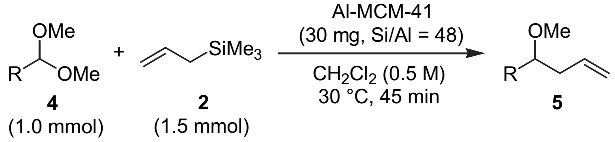
Entry	Catalyst	Si/Al	**5a**[a](%)	**6**[a](%)
1	Al-MCM-41	26	86	7
2	SiO_2–Al_2O_3	31	0	0
3	MCM-41	∞	0	0
4	Al-MCM-41	34	91	4
5	Al-MCM-41	48	96	Trace

[a] Determined by ^{1}H NMR analysis of the crude product using nitromethane as an internal standard.

In the presence of Al-MCM-41 (Si/Al=48), various dimethyl acetals were allylated effectively to afford the corresponding homoallyl methyl ethers (Table 5, entries 1–17). It should be noted that the yield of the allylated products was increased in most cases compared to the result of the corresponding aldehydes. Benzaldehyde diethyl acetal was allylated as well, and the corresponding homoallyl ethyl ether was obtained in 85% yield (entry 18).

From a synthetic point of view, allylation of cyclic acetals obtained from the corresponding aldehydes with 1,3-propanediol is useful since the conversion of homoallyl 3-hydroxypropyl ethers to the corresponding homoallyl alcohols is easier than that of homoallyl alkyl ethers.[14] As shown in Scheme 2, the reaction of 2-phenyl-1,3-dioxane (**7**) with **2** in dichloromethane at 30 °C for 2 h gave homoallyl 3-(trimethylsiloxy)propyl ether **8**. Desilylation followed by oxidation and β-elimination gave 1-phenylbut-3-en-1-ol (**9**) in 85% yield from **7**.

Table 5
Allylation of various acetals with allyltrimethylsilane catalyzed by Al-MCM-41

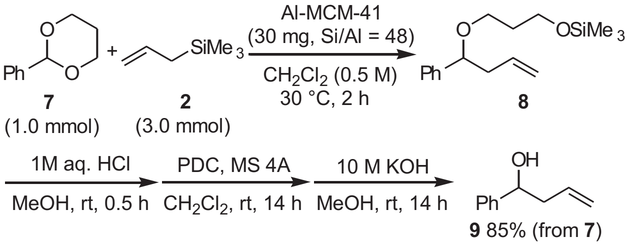


Entry	R	Yield[a](%)
1	Ph	93
2	4-$NO_2C_6H_4$	98
3	4-BrC_6H_4	90
4	2-BrC_6H_4	92
5	4-ClC_6H_4	96
6	3-ClC_6H_4	86
7	2-ClC_6H_4	92
8	4-MeC_6H_4	93
9	3-MeC_6H_4	92
10	2-MeC_6H_4	95
11[b]	4-$MeOC_6H_4$	76
12	2-$MeOC_6H_4$	88
13	2-Naphthyl	89
14	1-Naphthyl	80
15	(*E*)-PhCH=CH	74
16	*c*-C_6H_{11}	93
17	$PhCH_2CH_2$	93
18[c]	Ph	85

[a] Isolated yield.

[b] Allyltrimethylsilane (3.0 mmol) was used.

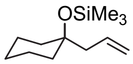
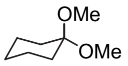
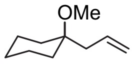
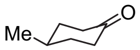
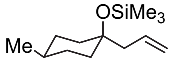
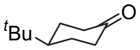
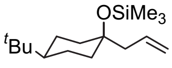
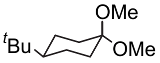
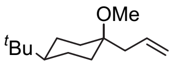
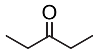
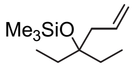
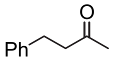
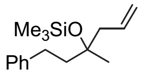
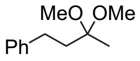
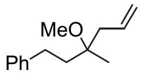
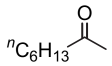
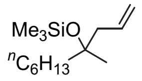
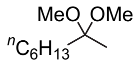
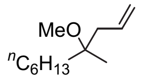
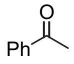
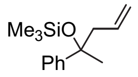
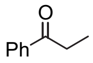
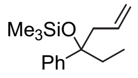
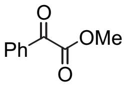
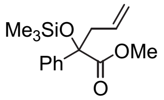
[c] Benzaldehyde diethyl acetal was used.



Scheme 2. Synthesis of 1-phenylbut-3-en-1-ol from 2-phenyl-1,3-dioxane.

The allylation of ketones is more difficult than that of aldehydes usually due to the steric hindrance and electron density of their carbonyl carbon. The reaction of ketones and ketals with allyltrimethylsilane was carried out in the presence of Al-MCM-41 (Si/Al=23 for ketones, Si/Al=48 for ketals). The results are summarized in Table 6. The reaction of cyclohexanone with 3.0 equiv of allyltrimethylsilane gave the corresponding homoallyl silyl ether in 89% yield (entry 1). A ketal, cyclohexanone dimethyl ketal, afforded the allylated product in 95% yield (entry 2). Allylation of 4-methylcyclohexanone and 4-*tert*-butylcyclohexanone proceeded preferentially from the equatorial direction and the allylated products were obtained in high yields (entries 3 and 4). Dimethyl ketal of 4-*tert*-butylcyclohexanone also allylated successfully and the diastereomeric ratio was almost the same as the result of 4-*tert*-butylcyclohexanone (entry 5). Allylation of acyclic dialkyl ketones were also examined (entries 6, 7, and 9). The formation of the corresponding self aldol product decreased the yields of the allylated products in the case of alkyl methyl ketones (entries 7 and 9). Dimethyl ketals of benzylacetone and 2-octanone were less reactive even by using larger amount of the catalyst, and the yields of the allylated products were 41% and 33%, respectively (entries 8 and 10). The reaction of acetophenone gave the allylated product in 18% yield along with the corresponding self aldol product in 33% yield (entry 11). Allylation of propiophenone afforded the corresponding homoallyl silyl ether in 23% yield, and the silyl enol ether of propiophenone, (*Z*)-1-phenyl-1-trimethylsiloxypropene, was obtained

Table 6
Allylation of various ketones and ketals with allyltrimethylsilane catalyzed by Al-MCM-41[a]

Entry	Substrate	Time (h)	Product	Yield[b](%)
1		1.5		89
2		1.5		95
3		2	 dr = 59:20[c]	79
4		2	 dr = 66:14[c]	80
5		2	 dr = 66:11[c]	77
6[d]		2		74
7		2		67 (16)[e]
8[f]		24		41
9		2		40 (39)[e]
10[f]		24		33
11		24		18 (33)[e]
12		24		23 (63)[g]
13[h]		24		86

[a] In the presence of Al-MCM-41 (30 mg, Si/Al=23 and 48 were used for ketones and ketals, respectively), the reaction of a substrate (1.0 mmol) with allyltrimethylsilane (3.0 mmol) was carried out in dichloromethane (0.5 M) at 30 °C.

[b] Isolated yield after column chromatography.

[c] Isolated yield of each diastereomers. The structure of major isomer is shown.

[d] Allyltrimethylsilane (5.0 equiv) was used.

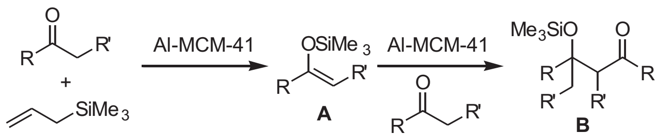
[e] Isolated yield of the corresponding self aldol adduct.

[f] Al-MCM-41 (50 mg) was used.

[g] Isolated yield of (*Z*)-1-phenyl-1-trimethylsiloxypropene.

[h] Reaction was carried out in toluene (0.5 M) at 60 °C.

in 63% yield (entry 12). The formation of the self aldol adduct could be explained as shown in Scheme 3. Initially, Al-MCM-41 promotes the formation of the silyl enol ether **A** from enolizable ketone and allyltrimethylsilane. When R′ was hydrogen, Al-MCM-41-catalyzed self aldol reaction of **A** with another molecule of the ketone occurred to give β-siloxy ketone **B** (entries 7, 9, and 11). When R′ was methyl group, silyl enol ether **A** was isolated (entry 12). This is probably because the higher steric hindrance inhibited the self aldol reaction. Methyl benzoylformate was allylated in toluene at 60 °C for 24 h to give the desired product in 86% yield (entry 13).

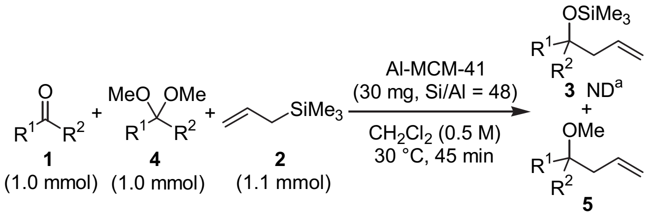


Scheme 3. Self aldol reaction of ketones catalyzed by Al-MCM-41.

To estimate the chemoselectivity of Al-MCM-41-catalyzed allylation, the reaction of benzaldehyde (1.0 mmol) and its dimethyl acetal (1.0 mmol) with 1.1 equiv of **2** was carried out under the same reaction conditions given in Table 5. Only the acetal reacted with **2** to afford the corresponding homoallyl methyl ether in 92% yield, and the allylated product of benzaldehyde was not obtained (Table 7, entry 1). Moreover, all acetals and a ketal examined in entries 2–7 were also allylated chemoselectively in the presence of the corresponding carbonyl compounds, although the yield of the products was affected by the reactivity of the substrates. With regard to the chemoselectivity of the reaction, typical strong Lewis acids (e.g., $TiCl_4$, $BF_3 \cdot OEt_2$, and $AlCl_3$) are known to show poor chemoselectivity.[15] Among the catalysts that activate both carbonyl compounds and acetals in Sakurai allylation, no catalyst has been reported to exhibit high acetal selectivity in the reaction, to the best of our knowledge. High acetal selectivity achieved by Al-MCM-41 may be attributed to the preferential adsorption of acetals on the surface of Al-MCM-41. Adsorbed acetals should be irreversibly allylated since the reaction affords methoxytrimethylsilane as a thermodynamically stable by-product.[16]

The reaction of aldehydes with other silanes was then examined. Bulkier silyl ethers are often useful than trimethylsilyl ether as protective groups of alcohols. Allyltriethylsilane, allyl*tert*-butyldimethylsilane, and allyl*tert*-butyldiphenylsilane were synthesized

Table 7
Chemoselective allylation of acetals in the presence of carbonyl compounds



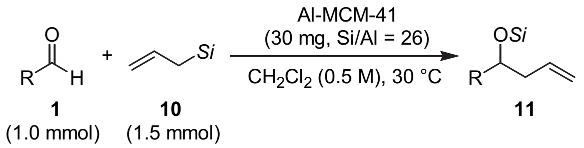
Entry	R¹	R²	Yield of **5**[b] (%)
1	Ph	H	92
2	4-BrC_6H_4	H	96
3	4-MeC_6H_4	H	94
4	2-Naphthyl	H	79
5	(*E*)-PhCH=CH	H	49
6	$PhCH_2CH_2$	H	61
7	$-(CH_2)_5-$		29

[a] Not detected.

[b] Based on **4**. Determined by ^{1}H NMR analysis using nitromethane as an internal standard.

from the corresponding silyl chloride and allylmagnesium chloride in refluxing THF.[17–19] The reaction of 4-nitrobenzaldehyde with allyltriethylsilane or allyl*tert*-butyldimethylsilane under the same reaction conditions given in Table 3 afforded the corresponding homoallyl silyl ethers in 93% and 91% yields, respectively (Table 8, entries 1 and 2). Although the reactivity of allyl*tert*-butyldiphenylsilane was relatively low, the reaction of 4-nitrobenzaldehyde with allyl*tert*-butyldiphenylsilane afforded the desired product in 57% yield by using increased amount of the catalyst (entry 3). Benzaldehyde and pivalaldehyde were also allylated with allyl*tert*-butyldimethylsilane in 86% and 87% yields, respectively (entries 4 and 5).

Table 8
Allylation of aldehydes with various allylsilanes catalyzed by Al-MCM-41



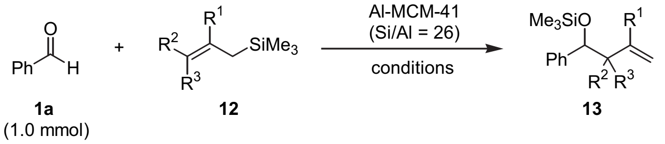
Entry	R	Si[a]	Time (h)	Yield[b](%)
1	4-$NO_2C_6H_4$	TES	0.5	93
2	4-$NO_2C_6H_4$	TBDMS	0.5	91
3[c]	4-$NO_2C_6H_4$	TBDPS	0.5	57
4	Ph	TBDMS	1	86
5	*t*-Bu	TBDMS	1	87

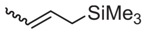
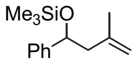
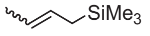
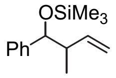
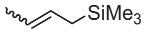
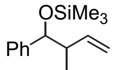
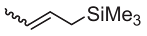
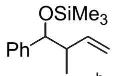
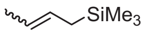
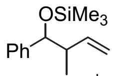
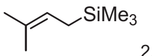
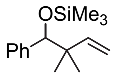
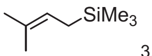
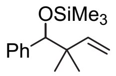
[a] TES=triethylsilyl, TBDMS=*tert*-butyldimethylsilyl, TBDPS=*tert*-butyldiphenylsilyl.
[b] Isolated yield after column chromatography.
[c] Al-MCM-41 (50 mg) was used.

Substituted allylsilanes, methallyltrimethylsilane, crotyltrimethylsilane, and trimethylprenylsilane, were synthesized according to the literature procedure[20–22] and their reactivity was examined in the reaction with benzaldehyde (Table 9). The reaction of benzaldehyde with methallyltrimethylsilane was completed in 1 h under the same reaction conditions given in Table 3 to give the corresponding product in 89% yield (entry 1), whereas crotyltrimethylsilane did not react under the reaction conditions (entry 2). When the reaction was carried out in toluene at 60 °C, the addition of crotylsilane to benzaldehyde occurred at γ-position of the silane to afford the corresponding adduct in 35% yield as a diastereomer mixture (*syn*/*anti*=1:1) (entry 3). The yield was increased to 47% by using a larger amount of catalyst (entry 4), and the γ-adduct was obtained in 88% yield by using 2.0 equiv of crotylsilane (entry 5). The reaction of benzaldehyde with prenylsilane under the same reaction conditions used in entry 5 afforded the γ-adduct in 13% yield (entry 6). The product was obtained in 58% yield by using 3.0 equiv of prenylsilane at 90 °C (entry 7), and the decomposition of the product occurred at a higher temperature or by using a larger amount of the silane. From these results, Al-MCM-41-catalyzed allylation with allylsilane was found to occur at γ-carbon of the silane like traditional Lewis acid-promoted reactions[1] and the steric hindrance of the γ-carbon had a large influence on the reaction.

The following experiment was carried out to examine whether the reaction occurs on the surface of Al-MCM-41 or not. A suspension of Al-MCM-41 (30 mg, Si/Al=26, dried prior to use at

Table 9
Allylation of benzaldehyde with substituted allylsilanes catalyzed by Al-MCM-41



Entry	Silane (equiv)	Al-MCM-41 (mg)	Solvent (0.5 M)	Temp (°C)	Time (h)	Product	Yield[a](%)
1	 E:Z = 1:3[b] 1.5	30	CH_2Cl_2	30	1		89
2	 E:Z = 1:3[b] 1.5	30	CH_2Cl_2	30	1		N.R.
3	 E:Z = 1:3[b] 1.5	30	Toluene	60	4.5	 dr = 1:1[b]	35
4	 E:Z = 1:3[b] 1.5	100	Toluene	60	4.5	 dr = 1:1[b]	47
5	 E:Z = 1:3[b] 2.0	100	Toluene	60	1	 dr = 1:1[b]	88
6	 2.0	100	Toluene	60	4.5		13
7	 3.0	100	Toluene	90	3.5		58

[a] Isolated yield after column chromatography.
[b] Determined by ^1H NMR analysis.

120 °C for 1 h under vacuum), benzaldehyde (1.0 mmol), and allyltrimethylsilane (1.5 mmol) in dichloromethane (2.0 mL) was stirred at 30 °C. After 30 min, Al-MCM-41 was removed by filtration. The reaction was not completed at that time. The filtrate was stirred at the same temperature and monitored by TLC analysis. The TLC analysis showed that benzaldehyde remained and the product did not increase after 24 h, whereas the reaction was completed in 1 h when the catalyst was not removed (Table 2, entry 7). This result indicates that the Al-MCM-41 catalyzes the reaction as a heterogeneous catalyst, and any homogeneous species, such as a trimethylsilyl cation generated in situ or an active aluminum species leached from the catalyst, are not the real catalyst of the reaction. The recovery and reuse of the catalyst were also examined in the reaction of 4-nitrobenzaldehyde with allyltrimethylsilane (Table 10). The catalyst was recovered by filtration and washed with dichloromethane. The recovered catalyst was then dried at 70 °C for 15 min, treated at 120 °C for 1 h under vacuum, and used in a next run. The catalyst could be reused three times without a significant loss of catalytic activity.

Table 10
Reuse of Al-MCM-41[a]

Run	Al-MCM-41 (mg)	$4\text{-}NO_2C_6H_4CHO$ (mmol)	Yield[b](%)
1	60	2.0	92
2	53	1.8	94
3	38	1.3	94
4	25	0.8	93

[a] In the presence of Al-MCM-41 (30 mg/mmol, Si/Al=26), the reaction of 4-nitrobenzaldehyde with 1.5 equiv of allyltrimethylsilane was carried out in dichloromethane (0.5 M) at 30 °C for 0.5 h.

[b] Isolated yield after column chromatography.

Finally, the amount of active site on Al-MCM-41 was estimated by the addition of triethylamine to a reaction mixture (Fig. 1). To an activated Al-MCM-41 (30 mg, Si/Al=23, dried prior to use at 120 °C for 1 h under vacuum), benzaldehyde (1.0 mmol) and triethylamine (0.001–0.01 mmol) in dichloromethane (1.5 mL) was added at 30 °C. Allyltrimethylsilane (1.5 mmol) in dichloromethane (0.5 mL) was then added to the stirred suspension and the mixture was stirred at 30 °C for 1 h. As shown in Fig. 1, only 0.005 mmol of triethylamine was enough to deactivate Al-MCM-41 completely. The result indicates that Al-MCM-41 acts as a catalyst in the reaction and its turnover number is 200. As for aluminum content of Al-MCM-41 (Si/Al=23), there are 0.021 mmol of aluminum atoms in 30 mg of the catalyst. Therefore, the active site of Al-MCM-41 is about 25% of all aluminum moieties. They probably exist on the surface of mesopores.

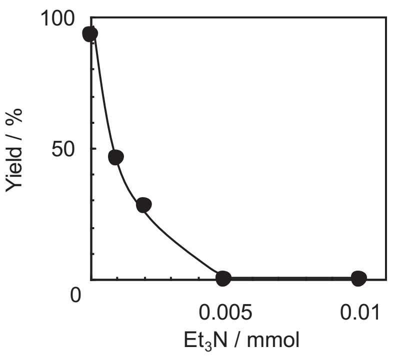


Fig. 1. Poisoning effect of triethylamine on Al-MCM-41-catalyzed allylation of benzaldehyde with allyltrimethylsilane.

3. Conclusion

In conclusion, Al-MCM-41 was found to act as an effective heterogeneous catalyst for Sakurai allylation of both carbonyl compounds and acetals to afford the corresponding homoallyl alcohol derivatives. The remarkable high catalytic activity of Al-MCM-41 over amorphous silica/alumina and aluminum-free mesoporous silicate was observed in the reaction. Moreover, Al-MCM-41 became the first catalyst that exhibits high acetal selectivity over carbonyl compound among the catalyst that activates both acetals and carbonyl compounds in Sakurai allylation. The reaction of aldehyde with substituted allylsilanes took place regioselectively at the γ-carbon of allylsilanes, and the steric hindrance of the γ-carbon strongly affected the reactivity of allylsilanes. Furthermore, it became apparent that the reactants were activated by catalytic amount of active sites on the surface of Al-MCM-41, and the catalyst was reusable without a significant loss of catalytic activity.

4. Experimental section

4.1. General

The structures of mesoporous materials were characterized by using X-ray diffraction (XRD). XRD patterns were recorded on a Mac Science M3X Model 1030 diffractometer equipped with a Cu Kα X-ray source (40 kV, 20 mA). Nitrogen adsorption–desorption measurements were carried out at 77 K using a gas adsorption analyzer (Belsorp 28SA, Bel Japan). The specific surface areas (S_{BET}) were estimated using the Brunauer–Emmett–Teller (BET) method. The average pore-size of the mesoporous materials was obtained from the adsorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method. The contents of Al in aluminosilicates were measured by using inductively coupled plasma spectrometer (ICP, ICP-8000E, Shimadzu). JRC-SAH-1 (Si/Al=2, S_{BET}: 528 m^2/g) and JRC-SAL-2 (Si/Al=5, S_{BET}: 617 m^2/g) were obtained from Catalysis Society of Japan as reference catalysts. All air-sensitive experiments were carried out under an atmosphere of argon. IR spectra were recorded on an HORIBA FT-730 spectrometer. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-EX270, JEOL JNM-AL400 or Brucker DRX-300 spectrometer using $CDCl_3$ as a solvent. Tetramethylsilane (0.00 ppm) served as an internal standard in ^1H NMR and $CDCl_3$ (77.0 ppm) in ^{13}C NMR. TLC analyses were done on silica-gel 60 F_{254}-precoated aluminum backed sheets (E. Merck). Toyo filter paper No.1 was used for filtration. Wakogel C-200 and Silica-gel 60N (spherical, neutral, 63–210 μm) were used for column chromatography. Diethyl ether (Et_2O) (dehydrated) and tetrahydrofuran (THF) (dehydrated, stabilizer free), were purchased from Kanto Chemical Co., Inc. Other solvents were purified and dried according to standard procedures. All aldehydes, ketones, and allyltrimethylsilane were commercially available. All acetals,[23] allyltriethylsilane,[17] allyl*tert*-butyldimethylsilane,[18] allyl*tert*-butyldiphenylsilane,[19] methallyltrimethylsilane,[20] crotyltrimethylsilane,[21] and trimethylprenylsilane[22] were synthesized according to the literature procedure and fully characterized by IR and ^1H, ^{13}C NMR spectroscopy.

4.2. Preparation of catalysts

4.2.1. Synthesis of Al-MCM-41[11]. To a stirred suspension of cetyltrimethylammonium bromide (CTMABr; 8.75 g, 24.0 mmol) in water (350 mL) at 50 °C, tetramethylammonium hydroxide (TMAOH; 26.3 g, 72.0 mmol) in water (99 mL) and aluminum triisopropoxide ($Al(O^iPr)_3$; 1.36 g, 6.67 mmol) were added. Tetraethyl orthosilicate (TEOS; 41.7 g, 200 mmol) was then slowly added to the suspension and stirred at 35 °C for 4 h (input Si/Al atomic ratio was 30). The mixture was heated at 100 °C in an oven for 4 days without stirring and then filtered off, washed with water, and dried at 100 °C to give 17.8 g of as-synthesized sample. This sample (17.0 g) was heated to 130 °C for 50 min, heated at 130 °C for 5 h. The temperature was raised to 550 °C for 5 h and the sample was calcined at that temperature for 10 h to afford Al-MCM-41 (10.2 g, Si/Al=26) as a white powder. The Si/Al atomic ratio was determined to be 26 by ICP analysis. The specific surface area (S_{BET}) and the average pore diameter (BJH) of Al-MCM-41 were 1120 m^2/g and 2.7 nm, respectively. Al-MCM-41 (Si/Al=23, S_{BET}: 1031 m^2/g, BJH: 2.7 nm) was obtained in a next batch. There was no difference in catalytic activity between Al-MCM-41 (Si/Al=26) and Al-MCM-41 (Si/Al=23).

Al-MCM-41 (Si/Al=34, S_{BET}: 1101 m^2/g, BJH: 2.7 nm) and Al-MCM-41 (Si/Al=48, S_{BET}: 1135 m^2/g, BJH: 2.7 nm) were synthesized by changing the input Si/Al atomic ratio from 30 to 50 and 70, respectively.

4.2.2. Synthesis of SiO_2/Al_2O_3. Amorphous silica/alumina (SiO_2/Al_2O_3) was synthesized according to the same procedure as the one used in the synthesis of Al-MCM-41 without the addition of the surfactant, CTMABr. The Si/Al atomic ratio was determined to be 31 by ICP analysis. The specific surface area (S_{BET}) was 385 m^2/g.

4.2.3. Synthesis of MCM-41. Aluminum-free MCM-41 was synthesized according to the same procedure as the one used in the synthesis of Al-MCM-41 without the addition of aluminum source, Al(O^{i}Pr)$_3$. The specific surface area (S_{BET}) and the average pore diameter (BJH) were 1080 m^2/g and 2.6 nm, respectively.

4.2.4. Synthesis of SBA-15[24]. Triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123; 38.4 g, 6.62 mmol) was dissolved in a mixture of water (1010 g) and concentrated hydrochloric acid (256 g) with stirring at 35 °C. To the resulting solution, TEOS (81.9 g, 393 mmol) was added and stirred at 35 °C for 20 h. The mixture was then heated at 100 °C in an oven for 20 h without stirring. The mixture was filtered off, washed with water and air-dried at room temperature to yield 23.2 g of as-synthesized sample. This sample was calcined at 550 °C for 10 h (heating rate=1.4 K/min), resulting in a white powder. The specific surface area (S_{BET}) and the average pore diameter (BJH) were 925 m^2/g and 7.0 nm, respectively.

4.3. Typical experimental procedure for Al-MCM-41-catalyzed allylation of carbonyl compounds (Table 2, entry 7)

Under an atmosphere of argon, to a mixture of benzaldehyde (0.106 g, 1.0 mmol) and Al-MCM-41 (30 mg, Si/Al=26, dried prior to use at 120 °C for 1 h under vacuum) in dichloromethane (1.5 mL), allyltrimethylsilane (0.172 g, 1.5 mmol) in dichloromethane (0.5 mL) was added through a syringe at 30 °C. The reaction mixture was stirred at 30 °C for 1 h. The catalyst was removed by filtration and washed with dichloromethane (40 mL). After the filtrate was concentrated under reduced pressure, crude product was purified by silica-gel column chromatography (hexane/Et_2O=20:1) to afford 4-trimethylsiloxy-4-phenyl-1-butene[25] as a colorless oil (0.203 g, 92%); IR (neat): ν_{max} 2957, 1641, 1493, 1454, 1252, 1089, 840 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.20–7.35 (m, 5H), 5.69–5.85 (m, 1H), 4.99–5.07 (m, 2H), 4.66 (dd, J=7.6, 5.3 Hz, 1H), 2.34–2.54 (m, 2H), 0.04 (s, 9H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ (ppm) 144.7, 135.2, 128.0, 126.9, 125.8, 116.7, 74.9, 45.1, 0.3.

Desilylation was performed to characterize the products because all desilylated products are known compounds. To a stirred solution of 4-trimethylsiloxy-4-phenyl-1-butene (0.220 g, 1.0 mmol) in MeOH (2 mL), 1 M aq HCl (2 mL) was added and the mixture was stirred at room temperature for 10 min. After the reaction was completed, ethyl acetate and water were added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, crude product was purified by silica-gel column chromatography (hexane/ethyl acetate=8:1) to give 1-phenylbut-3-en-1-ol[26a] as a colorless oil (0.133 g, 90%); IR (neat): ν_{max} 3369, 1641, 1494, 1454, 1049, 916, 758, 700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.24–7.37 (m, 5H), 5.74–5.89 (m, 1H), 5.12–5.21 (m, 2H), 4.71–4.77 (m, 1H), 2.43–2.58 (m, 2H), 2.05 (d, J=3.3 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ (ppm) 143.7, 134.3, 128.1, 127.2, 125.6, 117.9, 73.2, 43.6. All desilylated products exhibited spectroscopic data consistent with the previously reported ones in the literature.[26]

4.4. Typical experimental procedure for Al-MCM-41-catalyzed allylation of acetals (Table 5, entry 1)

Under an atmosphere of argon, to a mixture of benzaldehyde dimethyl acetal (0.152 g, 1.0 mmol) and Al-MCM-41 (30 mg, Si/Al=48, dried prior to use at 120 °C for 1 h under vacuum) in dichloromethane (1.5 mL), allyltrimethylsilane (0.172 g, 1.5 mmol) in dichloromethane (0.5 mL) was added through a syringe at 30 °C. The reaction mixture was stirred at 30 °C for 45 min. The catalyst was removed by filtration and washed with dichloromethane (40 mL). After the filtrate was concentrated under reduced pressure, almost pure homoallyl methyl ether was obtained. Further purification by silica-gel column chromatography (hexane to hexane/Et_2O=10:1) afforded 4-methoxy-4-phenylbut-1-ene[27a] as a colorless oil (0.151 g, 93%); IR (neat): ν_{max} 3028, 2980, 2936, 2821, 1641, 1454, 1357, 1100, 914, 701 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.26–7.35 (m, 5H), 5.69–5.85 (m, 1H), 5.00–5.09 (m, 2H), 4.17 (t, J=5.9 Hz, 1H), 3.22 (s, 3H), 2.52–2.62 (m, 1H), 2.36–2.46 (m, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ (ppm) 141.4, 134.6, 128.1, 127.4, 126.5, 116.7, 83.5, 56.4, 42.5. All allylated products are known compounds and characterized by IR and ^1H, ^{13}C NMR spectroscopy.[3d,f,27]

4.5. Synthesis of 1-phenylbut-3-en-1-ol (Scheme 2)

Under an atmosphere of argon, to a mixture of 2-phenyl-1,3-dioxane (**7**) (0.164 g, 1.0 mmol) and Al-MCM-41 (30 mg, Si/Al=48, dried prior to use at 120 °C for 1 h under vacuum) in dichloromethane (1.5 mL), allyltrimethylsilane (0.343 g, 3.0 mmol) in dichloromethane (0.5 mL) was added through a syringe at 30 °C. The reaction mixture was stirred at 30 °C for 2 h. The catalyst was removed by filtration and washed with dichloromethane (40 mL). After the filtrate was concentrated under reduced pressure, the crude product **8** was dissolved in MeOH (3 mL), and 1 M aq HCl (1 mL) was added. The reaction mixture was stirred at room temperature for 30 min. Water and Et_2O were added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the crude alcohol was obtained and used in a next step without further purification.

To a stirred suspension of crushed 4 Å MS (0.90 g) and pyridinium dichromate (0.376 g, 1.0 mmol) in dichloromethane (12 mL), the crude alcohol in dichloromethane (9.0 mL) was added. The reaction mixture was stirred at room temperature for 14 h and the resulting precipitates were removed by silica-gel column chromatography (hexane/Et_2O=4:1). After removal of the solvent under reduced pressure, the residue was dissolved in MeOH (15 mL). To the solution, 10 M aq KOH (5 mL) was added. The reaction mixture was stirred at room temperature for 14 h. Water and Et_2O were added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the crude product was purified by silica-gel column chromatography (hexane/Et_2O=4:1) to afford 1-phenylbut-3-en-1-ol (**9**)[26a] as a colorless oil (0.126 g, 85%).

4.6. Typical experimental procedure for chemoselective allylation (Table 7, entry 1)

Under an atmosphere of argon, to a mixture of benzaldehyde (0.106 g, 1.0 mmol), benzaldehyde dimethyl acetal (0.152 g, 1.0 mmol), and Al-MCM-41 (30 mg, Si/Al=48, dried prior to use at 120 °C for 1 h under vacuum) in dichloromethane (1.5 mL), allyltrimethylsilane (0.126 g, 1.1 mmol) in dichloromethane (0.5 mL) was added through a syringe at 30 °C. The reaction mixture was stirred at 30 °C for 45 min. The catalyst was removed by filtration and washed with dichloromethane (40 mL). After the filtrate was concentrated under reduced pressure, nitromethane (61.0 mg, 1.0 mmol) in $CDCl_3$ was added to the crude product as an internal standard. ^1H NMR analysis of the crude product showed 92% yield of 4-methoxy-4-phenylbut-1-ene, and 4-trimethylsiloxy-4-phenyl-1-butene was not detected.

4.7. Reuse of Al-MCM-41 (Table 10)

The reaction of 4-nitrobenzaldehyde (0.302 mg, 2.0 mmol) with allyltrimethylsilane (0.343 mg, 3.0 mmol) was carried out in the presence of Al-MCM-41 (60 mg, Si/Al=26) according to the typical experimental procedure for carbonyl compounds. After the reaction, the recovered catalyst was dried at 70 °C for 15 min. The catalyst (53 mg) was then dried at 120 °C for 1 h under vacuum and used in a second run.

Acknowledgements

Y.K. thanks New Energy and Industrial Technology Development Organization (NEDO) for financial support.

Supplementary data

Characterization data (IR and ^1H, ^{13}C NMR spectra) of synthesized compounds are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.01.055. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

1. (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295–1298; (b) Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1976**, 941–942; (c) Fleming, I.; Dunoguès, J.; Smithers, R. *Org. React.* **1989**, *37*, 57–575; (d) Deleris, G.; Dunoguès, J.; Calas, R. *Tetrahedron Lett.* **1976**, 2449–2450.
2. For catalytic allylation of carbonyl compounds, see (a) Aggarwal, V. K.; Vennall, G. P. *Tetrahedron Lett.* **1996**, *37*, 3745–3746; (b) Aggarwal, V. K.; Vennall, G. P. *Synthesis* **1998**, 1822–1826; (c) Yang, Y.; Wang, M.; Wang, D. *Chem. Commun.* **1997**, 1651–1652; (d) Yadav, J. S.; Chand, P. K.; Anjaneyulu, S. *Tetrahedron Lett.* **2002**, *43*, 3783–3784; (e) Watahiki, T.; Oriyama, T. *Tetrahedron Lett.* **2002**, *43*, 8959–8962; (f) Davis, A. P.; Jaspars, M. *Ang. Chem., Int. Ed.* **1992**, *31*, 470–471; (g) Davis, A. P.; Jaspars, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2111–2118; (h) Komatsu, N.; Uda, M.; Suzuki, H.; Takahashi, T.; Domae, T.; Wada, M. *Tetrahedron Lett.* **1997**, *38*, 7215–7218; (i) Marx, A.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 178–181; (j) Onishi, Y.; Ito, T.; Yasuda, M.; Baba, A. *Eur. J. Org. Chem.* **2002**, 1578–1581; (k) Fang, X.; Watkin, J. G.; Warner, B. P. *Tetrahedron Lett.* **2000**, *41*, 447–449.
3. For catalytic allylation of acetals, see (a) Spafford, M. J.; Anderson, E. D.; Lacey, J. R.; Palma, A. C.; Mohan, R. S. *Tetrahedron Lett.* **2007**, *48*, 8665–8667; (b) Arai, S.; Sudo, Y.; Nishida, A. *Tetrahedron* **2005**, *61*, 4639–4642; (c) Jung, M. E.; Maderna, A. *Tetrahedron Lett.* **2004**, *45*, 5301–5304; (d) Watahiki, T.; Akabane, Y.; Mori, S.; Oriyama, T. *Org. Lett.* **2003**, *5*, 3045–3048; (e) Wieland, L. C.; Zerth, H. M.; Mohan, R. S. *Tetrahedron Lett.* **2002**, *43*, 4597–4600; (f) Yadav, J. S.; Subba Reddy, B. V.; Srihari, P. *Synlett* **2001**, 673–675; (g) Kamata, M.; Yokoyama, Y.; Karasawa, N.; Kato, M.; Hasegawa, E. *Tetrahedron Lett.* **1996**, *37*, 3483–3486; (h) Trehan, A.; Vij, A.; Walia, M.; Kaur, G.; Verma, R. D.; Trehan, S. *Tetrahedron Lett.* **1993**, *34*, 7335–7338; (i) Sakurai, H.; Sasaki, K.; Hosomi, A. *Tetrahedron Lett.* **1981**, *22*, 745–748; (j) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 71–74.
4. (a) Sartori, G.; Ballini, R.; Bigi, F.; Bosica, G.; Maggi, R.; Righi, P. *Chem. Rev.* **2004**, *104*, 199–250; (b) Corma, A.; García, H. *Chem. Rev.* **2003**, *103*, 4307–4365; (c) Okuhara, T. *Chem. Rev.* **2002**, *102*, 3641–3665.
5. Kawai, M.; Onaka, M.; Izumi, Y. *Chem. Lett.* **1986**, 381–384.
6. Kawabata, T.; Kato, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Chem.—Eur. J.* **2005**, *11*, 288–297.
7. Sasidharan, M.; Tatsumi, T. *Chem. Lett.* **2003**, *32*, 624–625.
8. (a) Kresge, C. T.; Lenowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710–712; (b) Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216–3251; (c) Xiao, F.-S. *Top. Catal.* **2005**, *35*, 9–24; (d) Ziolek, M. *Catal. Today* **2004**, *90*, 145–150; (e) Wight, A. P.; Davis, M. E. *Chem. Rev.* **2002**, *102*, 3589–3614; (f) Corma, A. *Top. Catal.* **1997**, *4*, 249–260.
9. (a) Ratnamala, A.; Subrahmanyam, M.; Kumari, V. D. *Appl. Catal., A* **2004**, *264*, 219–224; (b) Shanmugapriya, K.; Palanichamy, M.; Murugesan, V. *Catal. Commun.* **2006**, *7*, 47–51; (c) Ratnamala, A.; Lalitha, K.; Reddy, J. K.; Kumari, V. D.; Subrahmanyam, M. *J. Mol. Catal. A: Chem.* **2008**, *279*, 112–118; (d) Katada, N.; Fujinaga, H.; Nakamura, Y.; Okumura, K.; Nishigaki, K.; Niwa, M. *Catal. Lett.* **2002**, *80*, 47–51; (e) Ajaikumar, S.; Pandurangan, A. *J. Mol. Catal. A: Chem.* **2007**, *266*, 1–10; (f) Iwanami, K.; Choi, J.-C.; Lu, B.; Sakakura, T.; Yasuda, H. *Chem. Commun.* **2008**, 1002–1004; (g) Iwanami, K.; Seo, H.; Choi, J.-C.; Sakakura, T.; Yasuda, H. *Tetrahedron* **2010**, *66*, 1898–1901; (h) Murata, H.; Ishitani, H.; Iwamoto, M. *Tetrahedron Lett.* **2008**, *49*, 4788–4791; (i) Ito, S.; Yamaguchi, H.; Kubota, Y.; Asami, M. *Chem. Lett.* **2009**, *38*, 700–701.
10. (a) Ito, S.; Yamaguchi, H.; Kubota, Y.; Asami, M. *Tetrahedron Lett.* **2009**, *50*, 2967–2969; (b) Ito, S.; Hayashi, A.; Komai, H.; Kubota, Y.; Asami, M. *Tetrahedron Lett.* **2010**, *51*, 4243–4245.
11. Chen, C.-Y.; Li, H.-X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 17–26.
12. Silyl enol ethers were formed from enols of the aliphatic aldehydes with allyltrimethylsilane, which is known to act as a silylating reagent of hydroxy groups in the presence of acid catalysts. (a) Morita, T.; Okamoto, Y.; Sakurai, H. *Synthesis* **1981**, 745–746; (b) Onaka, M.; Hosokawa, Y.; Higuchi, K.; Izumi, Y. *Tetrahedron Lett.* **1993**, *34*, 1171–1172.
13. Recently, an allylation of acetals by allylsilanes using silica–alumina was reported. It required higher reaction temperature and longer reaction time than Al-MCM-41 catalyzed reaction Motokura, K.; Yoneda, H.; Miyaji, A.; Baba, T. *Green Chem.* **2010**, *12*, 1373–1375.
14. (a) Hosokawa, T.; Shinohara, T.; Ooka, Y.; Murahashi, S.-I. *Chem. Lett.* **1989**, 2001–2004; (b) Chen, S.-H.; Sun, X.; Boyer, R.; Paschal, J.; Zeckner, D.; Current, W.; Zweifel, M.; Rodriguez, M. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 2107–2110.
15. Ooi, T.; Tayama, E.; Takahashi, M.; Maruoka, K. *Tetrahedron Lett.* **1997**, *38*, 7403–7406.
16. Li, W.-D. Z.; Zhang, X.-X. *Org. Lett.* **2002**, *4*, 3485–3488.
17. Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998–6004.
18. (a) Murakami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2009**, *74*, 1415–1417; (b) Morita, T.; Okamoto, Y.; Sakurai, H. *Tetrahedron Lett.* **1980**, *21*, 835–838.
19. Imazeki, S.; Sugawara, H.; Sano, A.; Akiyama, T. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 623–629.
20. Li, L.-H.; Wang, D.; Chan, T. H. *Tetrahedron Lett.* **1991**, *32*, 2879–2882.
21. (a) Hosomi, A.; Iguchi, H.; Sakurai, H. *Chem. Lett.* **1982**, 223–226; (b) Hosomi, A.; Shirahata, A.; Sakurai, H. *Chem. Lett.* **1978**, 901–904.
22. Lipshutz, B. H.; Hackmann, C. *J. Org. Chem.* **1994**, *59*, 7437–7444.
23. (a) Ladepeche, A.; Tam, E.; Ancel, J.-E.; Ghosez, L. *Synthesis* **2004**, 1375–1380; (b) Miura, K.; Izumi, H.; Kinoshita, H.; Ichikawa, J.; Hosomi, A. *Chem. Lett.* **2009**, *38*, 1204–1205; (c) Wiles, C.; Watts, P.; Haswell, S. J. *Tetrahedron* **2005**, *61*, 5209–5217; (d) Fukuzumi, T.; Bode, J. W. *J. Am. Chem. Soc.* **2009**, *131*, 3864–3865; (e) Myles, L.; Gore, R.; Špulák, M.; Gathergood, N.; Connon, S. J. *Green Chem.* **2010**, *12*, 1157–1162; (f) Tateiwa, J.; Horiuchi, H.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 4039–4043; (g) Sakai, N.; Moritaka, K.; Konakahara, T. *Eur. J. Org. Chem.* **2009**, 4123–4127; (h) Das, P.; McNulty, J. *Eur. J. Org. Chem.* **2010**, 3587–3591; (i) Gregg, B. T.; Golden, K. C.; Quinn, J. F. *Tetrahedron* **2008**, *64*, 3287–3295; (j) Kropp, P. J.; McNeely, S. A.; Davis, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 6907–6915; (k) Baghdasarian, G.; Woerpel, K. A. *J. Org. Chem.* **2006**, *71*, 6851–6858; (l) Gasparrini, F.; Giovannoli, M.; Misiti, D.; Palmieri, G. *Tetrahedron* **1984**, *40*, 1491–1500; (m) Bassetti, M.; Floris, B. *J. Chem. Soc., Perkin Trans. 2* **1988**, 227–233.
24. (a) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024–6036; (b) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548–552.
25. Comins, D. L.; Dinsmore, J. M.; Marks, L. R. *Chem. Commun.* **2007**, 4170–4171.
26. (a) Denmark, S. E.; Nguyen, S. T. *Org. Lett.* **2009**, *11*, 781–784; (b) Nowrouzi, F.; Thadani, A. N.; Batey, R. A. *Org. Lett.* **2009**, *11*, 2631–2634; (c) Kim, I. S.; Ngai, M.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 6340–6341; (d) Bower, J. F.; Skucas, E.; Patman, R. L.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 15134–15135; (e) Shen, K.-H.; Yao, C.-F. *J. Org. Chem.* **2006**, *71*, 3980–3983; (f) Li, G.-l.; Zhao, G. *Org. Lett.* **2006**, *8*, 633–636; (g) Traverse, J. F.; Zhao, Y.; Hoveyda, A. H.; Snapper, M. L. *Org. Lett.* **2005**, *7*, 3151–3154; (h) Canales, E.; Prasad, K. G.; Soderquist, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 11572–11573; (i) Hirayama, L. C.; Gamsey, S.; Knueppel, D.; Steiner, D.; DeLaTorre, K.; Singaram, B. *Tetrahedron Lett.* **2005**, *46*, 2315–2318; (j) Goujon, J.-Y.; Zammattio, F.; Chrétien, J.-M.; Beaudet, I. *Tetrahedron* **2004**, *60*, 4037–4049; (k) Buchmann, B.; Marschall-Weyerstahl, H.; Weyerstahl, P. *Tetrahedron* **1984**, *40*, 3393–3398; (l) Boldrini, G. P.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1983**, *48*, 4108–4111; (m) Mani, N. S.; Mapes, C. M.; Wu, J.; Deng, X.; Jones, T. K. *J. Org. Chem.* **2006**, *71*, 5039–5042.
27. (a) Jung, M. E.; Maderna, A. *J. Org. Chem.* **2004**, *69*, 7755–7757; (b) Barbero, M.; Bazzi, S.; Cadamuro, S.; Dughera, S.; Piccinini, C. *Synthesis* **2010**, 315–319; (c)

Olivero, S.; Perriot, R.; Dunach, E.; Baru, A. R.; Bell, E. D.; Mohan, R. S. *Synlett* **2006**, 2021–2026; (d) Cui, Y.-M.; Huang, Q.-Q.; Xu, J.; Chen, L.-L.; Li, J.-Y.; Ye, Q.-Z.; Li, J.; Nan, F.-J. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 4130–4135; (e) Anzalone, P. W.; Baru, A. R.; Danielson, E. M.; Hayes, P. D.; Nguyen, M. P.; Panico, A. F.; Smith, R. C.; Mohan, R. S. *J. Org. Chem.* **2005**, *70*, 2091–2096; (f) Suga, S.; Suzuki, S.; Yamamoto, A.; Yoshida, J. *J. Am. Chem. Soc.* **2000**, *122*, 10244–10245; (g) Torii, S.; Inokuchi, T.; Takagishi, S.; Horike, H.; Kuroda, H.; Uneyama, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2173–2188; (h) Kamata, M.; Nagai, S.; Kato, M.; Hasegawa, E. *Tetrahedron Lett.* **1996**, *37*, 7779–7782; (i) Hermans, B.; Hevesi, L. *J. Org. Chem.* **1995**, *60*, 6141–6147.