JOC The Journal of Organic Chemistry

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Cu(II)-Catalyzed Allylic Silylation of Morita–Baylis–Hillman Alcohols via Dual Activation of Si–B Bond and Hydroxyl Group

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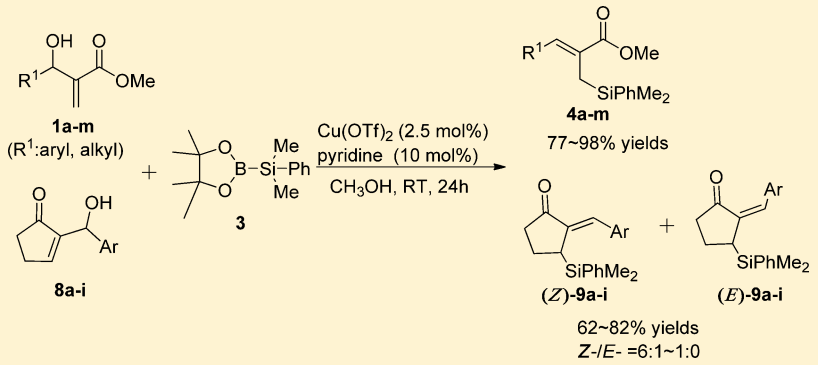
Supporting Information



ABSTRACT: The reaction of Morita–Baylis–Hillman (MBH) alcohols with $Me_2PhSiBpin$ under the catalysis of $Cu(OTf)_2$/pyridine in methanol has been developed. The direct silylation of allylic alcohols via dual activation of the Si–B bond and the hydroxyl group of the MBH alcohol provides an efficient and convenient method for the synthesis of functionalized allylsilanes.

Allylsilanes are important synthetic reagents and have been applied widely in the synthesis of natural products and bioactive compounds.[1] Many efficient methods for the synthesis of allylsilanes through silylations of allylic substrates by silylmetal reagents (silylmagnesium, silyllithium, silylcuprate, silylzincate, etc.) have been developed.[2] Recently, attention has been focused on the uses of interelement silicon–boron reagents for the synthesis of functionalized silanes.[3] Under mild conditions, silicon–boron reagents allow the catalytic transfer of a silicon nucleophile onto various electrophiles. Activation of the Si–B bond can be catalyzed by various transition metals [e.g., Pd(0),[3a,4] Rh(I),[3a,5] and Cu(I)[3a,6] complexes] and *N*-heterocyclic carbenes[7a] or achieved by the substrate itself[7b] to generate a silicon nucleophile. Oestreich and co-workers reported the allylic substitution of allylic precursors with Si–B compounds catalyzed by CuCN/NaOMe.[8] However, the allylic precursors were confined to functionalized allylic compounds such as allyl halides, allyl esters, allyl carbonates, and allyl phosphonates. For synthetic efficiency, it is much more desirable to generate allylsilanes directly from allyl alcohols. Although the direct substitution of alcohols with carbon and heteroatom nucleophiles is a significant chemical transformation,[9] the direct synthesis of allylsilanes from allylic alcohols has seldom been reported because of the poor leaving ability of the hydroxyl group. To the best of our knowledge, there is only one example of the direct synthesis of allylsilanes starting from allylic alcohols using disilane as a silylation reagent under the catalysis of $[Pd(MeCN)_4(BF_4)_2]$.[10]

Morita–Baylis–Hillman (MBH) adducts, which are densely functionalized (bearing both allyl and α,β-unsaturated carbonyl moieties) have been widely used as synthons in organic synthesis.[11] Kabalka and co-workers reported the synthesis of substituted allylsilanes from MBH acetates via a palladium-catalyzed cross-coupling reaction with disilane.[12] To date, however, there is still no direct synthesis of allylsilanes from MBH alcohols.

On the basis of our ongoing interest in the subsequent transformations of MBH adducts,[13] here we report the direct synthesis of functionalized allylsilanes through the γ-regioselective reaction of MBH alcohols with $Me_2PhSiBpin$ under the catalysis of $Cu(OTf)_2$/pyridine in methanol.

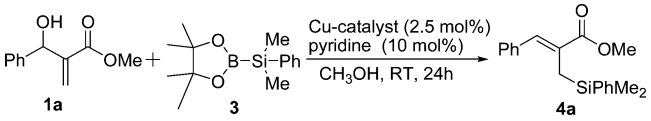
Initially, the reaction of the MBH alcohol 1-phenyl-2-methoxycarbonyl-2-propen-1-ol (**1a**, R^1 = phenyl) with hexamethyldisilane ($Me_3SiSiMe_3$, **2**) was carried out under the catalysis of $[Pd(MeCN)_4(BF_4)_2]$ in DMSO/MeOH.[10] Unfortunately, the desired silylation reaction did not occur. Recently, interelement Si–B reagents, especially dimethyl-

Received: August 9, 2013
Published: October 4, 2013

   dx.doi.org/10.1021/jo4016419 | J. Org. Chem. 2013, 78, 11076–11081

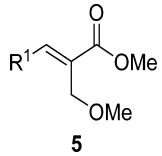
(phenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)silane (**3**), have attracted considerable attention,[3] and **3** has been employed in many Cu(I)-catalyzed allylic silylation reactions. As reported by Oestreich and co-workers, activation of the Si–B bond can be catalyzed by CuCN with NaOMe, releasing silicon nucleophiles for the subsequent silylation reactions.[8,14] However, the reaction of MBH alcohol **1a** with **3** in the presence of CuCN and NaOMe afforded only the etherification product **5** in 55% yield (Table 1, entry 1). Then we employed

Table 1. Reaction of 1a with 3 Catalyzed by Cupric Salt with Amine Base[a]



Entry	CuXn (mol %)	Base (mol %)	Yield of **4a** (%)[b]
1	CuCN (5.0)	NaOMe	–[c]
2	CuCl (2.5)	pyridine (10)	22
3	CuOTf (2.5)	pyridine (10)	65
4	$CuSO_4$ (2.5)	pyridine (10)	39
5	$Cu(OAc)_2$ (2.5)	pyridine (10)	25
6	$Cu_3(PO_4)_2$ (2.5)	pyridine (10)	18
7	$CuCl_2$ (2.5)	pyridine (10)	15
8	$Cu(OTf)_2$ (2.5)	pyridine (10)	98
9	$Cu(OTf)_2$ (2.5)	DBU (10)	58
10	$Cu(OTf)_2$ (2.5)	DABCO (10)	62
11	$Cu(OTf)_2$ (2.5)	4-picoline (10)	48
12[d]	$Cu(OTf)_2$ (2.5)	pyridine (10)	19
13[e]	$Cu(OTf)_2$ (2.5)	pyridine (10)	70
14[f]	$Cu(OTf)_2$ (2.5)	pyridine (10)	10
15	$Cu(OTf)_2$ (2.5)	–	47
16	–	pyridine (10)	35
17	–	–	NR[g]

[a]The reactions were conducted with **1a** (0.1 mmol) and **3** (0.15 mmol) in CH_3OH (2 mL) under Ar at room temperature for 24 h, unless otherwise noted. [b]Isolated yields. [c]Compound **5** instead of the desired product was obtained in 55% yield.



5

[d]In water. [e]In ethanol. [f]Open to air. [g]No reaction.

CuCl and CuOTf (2.5 mol %) with an amine base (10 mol %) as a cocatalyst in the reaction of **1a** with **3**; to our delight, the desired silylation was observed, giving the product **4a** in reasonable yields of 22% and 65%, respectively (Table 1, entries 2 and 3). Subsequently, various Cu salts, including $CuSO_4$, $Cu(OAc)_2$, $Cu_3(PO_4)_2$, CuCl and $Cu(OTf)_2$, together with various amine bases, such as DBU, DABCO, 4-picoline, and pyridine, were employed in the reaction of **1a** with **3** (Table 1). To our delight, the reaction of **1a** with **3** in the presence of $Cu(OTf)_2$ (2.5 mol %) and pyridine (10 mol %) in methanol at room temperature under an argon atmosphere gave the desired product, allylsilane **4a**, in excellent yield (98%) with exclusive γ-regio- and (*Z*)-stereoselectivity (entry 8). Although there have been a few examples of Cu(II)-catalyzed silylation reactions with interelement Si–B reagents,[15] it was found that in the case of the silylation of MBH alcohols with **3**, $Cu(OTf)_2$ showed better catalytic efficiency than CuOTf (entry 8 vs 3). In addition, the catalytic efficiency was found to be strongly dependent on the counteranion of the Cu(II) salt (entries 4–8). The solvent effect was also examined. When 1,4-dioxane, $CHCl_3$, CH_2Cl_2, or toluene was used as the reaction medium, no reaction product was observed. When the reaction was carried out in THF, only a trace amount of the product was detected. When water was used as the solvent, the reaction provided a poor yield of **4a** (19%; entry 12), whereas the use of ethanol afforded a reasonable one (70%; entry 13). Methanol appeared to be the best solvent, providing product **4a** in 98% yield (entry 8). Thus, we concluded that an alcohol-type solvent was needed to perform the Cu(II)/amine base-catalyzed reaction of MBH alcohols with $Me_2PhSiBpin$ (**3**). When the reaction system was opened to air, only a 10% yield of the product was obtained (entry 14). Meanwhile, in the absence of pyridine or $Cu(OTf)_2$ in the catalyst system, the yields of **4a** decreased to 47% and 35%, respectively (entries 15 and 16). In the absence of $Cu(OTf)_2$ and pyridine, no reaction occurred at all (entry 17). Thus, the optimized conditions for the silylations of MBH alcohols with **3** include $Cu(OTf)_2$/pyridine as catalysts in CH_3OH under an argon atmosphere (entry 8).

Under the optimized reaction conditions, acyclic MBH alcohols **1a–k** offered excellent yields of the silylation products **4a–k**. The results are summarized in Table 2. In general, acyclic MBH alcohols with either electron-donating or electron-withdrawing groups in the phenyl group all furnished the desired products in good to excellent yields. The MBH alcohols derived from aliphatic aldehydes (**1l** and **1m**) also provided excellent yields (86–93%; entries 12 and 13).

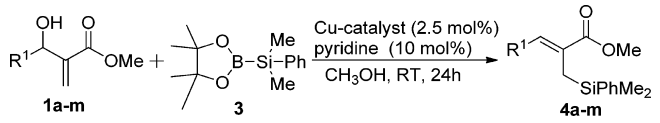
Interestingly, when 2-(aminoformyl)-1-phenyl-2-en-1-ol (**6**) or 2-methyl-1-phenylprop-2-en-1-ol (**7**) was reacted with **3** under the Cu(II) catalysis, no product was detected, and the starting MBH alcohol was recovered (Scheme 1). However, changing the methyl ester to *tert*-butyl 2-(hydroxy(phenyl)-methyl)acrylate (**1n**) gave the silylation product **4n** in 97% yield (Scheme 1). Thus, the ester carbonyl group of the MBH alcohol is essential and necessary for performing Cu(II)-catalyzed allylsilation of MBH alcohols with $Me_2PhSiBpin$ (**3**).

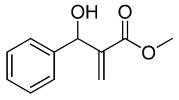
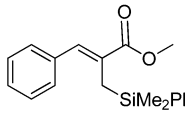
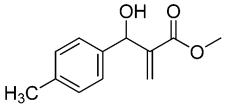
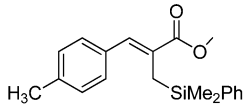
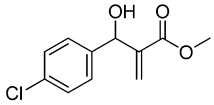
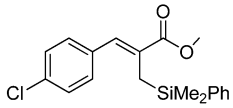
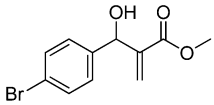
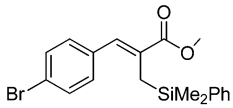
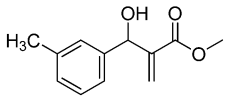
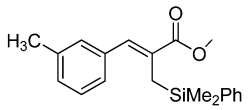
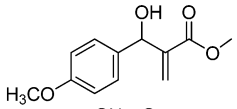
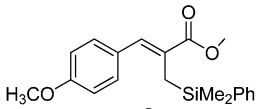
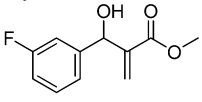
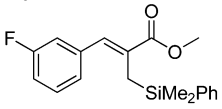
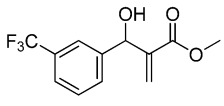
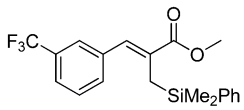
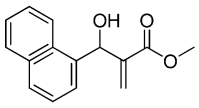
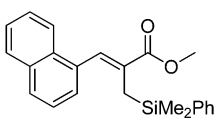
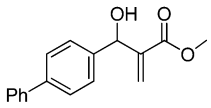
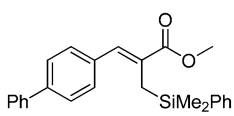
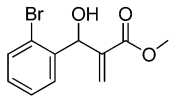
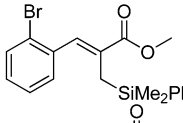
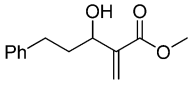
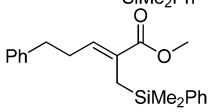
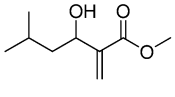
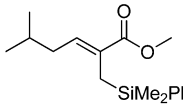
Cyclic MBH adducts derived from cyclic enones can also be used to construct fused cyclic frameworks and applied in the synthesis of heterocycles.[16] Unfortunately, an attempt to run the reaction of cyclic MBH alcohol **8a** (Ar = Ph) with disilane (**2**) under the catalysis of $[Pd(MeCN)_4(BF_4)_2]$[10] was not successful. Under the present optimized reaction conditions for silylation of acyclic MBH alcohols with **3**, the allylsilylation reactions of various cyclic MBH alcohols **8a–i** with **3** also proceeded well, and the results are summarized in Table 3. Cyclic MBH alcohols bearing either an electron-withdrawing or -donating group at the C-4 position of the phenyl ring (**8a–g**) or a 2-naphthyl substituent (**8h**) reacted with **3** smoothly to give the silylation products **9a–h** in 62–82% yield as mixtures of *Z* and *E* isomers (*Z*/*E* = 6:1 to 33:1) with exclusive γ-selectivity (entries 1–8). For 2-[1-(3,5-dimethoxyphenyl)-1-hydroxymethyl]cyclopenten-2-one (**8i**), the reaction with **3** provided (*Z*)-**9i** exclusively in 75% yield (entry 9).

A proposed mechanism for the $Cu(OTf)_2$-catalyzed reaction of MBH alcohols with the Si–B reagent is shown in Scheme 2.[15] The Si–B bond of $Me_2PhSiBpin$ (**3**) could be activated by $Cu(OTf)_2$/Py in MeOH (intermediate **A**), resulting in the formation of the active species **B** and the release of HOTf as well as CH_3OBpin, which was detected in the crude reaction

dx.doi.org/10.1021/jo4016419 | J. Org. Chem. 2013, 78, 11076–11081

Table 2. Cu(II)-Catalyzed Reactions of Acyclic MBH Alcohols 1a−m with 3[a]



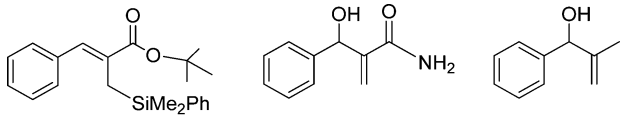
Entry	MBH alcohol	Product[b]	Yield (%)[c]
1	**1a** 	**4a** 	98
2	**1b** 	**4b** 	97
3	**1c** 	**4c** 	87
4	**1d** 	**4d** 	87
5	**1e** 	**4e** 	95
6	**1f** 	**4f** 	98
7	**1g** 	**4g** 	80
8	**1h** 	**4h** 	77
9	**1i** 	**4i** 	88
10	**1j** 	**4j** 	92
11	**1k** 	**4k** 	88
12	**1l** 	**4l** 	86
13	**1m** 	**4m** 	93

[a]All of the reactions were conducted with **1a** (0.1 mmol) and **3** (0.15 mmol) in CH_3OH (2 mL) under Ar at room temperature for 24 h. [b]Determined by NOESY analysis. [c]Isolated yields.

mixture before purification by GC. The hydroxyl group of the MBH alcohol (**1**) could be activated by the HOTf−pyridine complex through a hydrogen-bonding interaction. Then the nucleophilic silyl group released from **B** would be transferred onto the activated MBH alcohol **C** through an S_N2' substitution to afford the functionalized allylsilane (**4**).

dx.doi.org/10.1021/jo4016419 | J. Org. Chem. 2013, 78, 11076−11081

Scheme 1. Allylic Silylation of Other MBH Adducts with 3



*The data in parentheses are the yields of allylation of the corresponding MBH alcohols with **3**. NR = no reaction.

In summary, an efficient and mild protocol for the direct synthesis of functionalized allylsilanes from both cyclic and acyclic MBH alcohols with $Me_2PhSiBpin$ under the catalysis of Cu(II)/pyridine in methanol at room temperature was successfully developed. The reaction proceeds via dual activation of the Si−B bond and the hydroxyl group, leading to the direct allylic silylation of MBH alcohols with exclusive γ-selectivity.

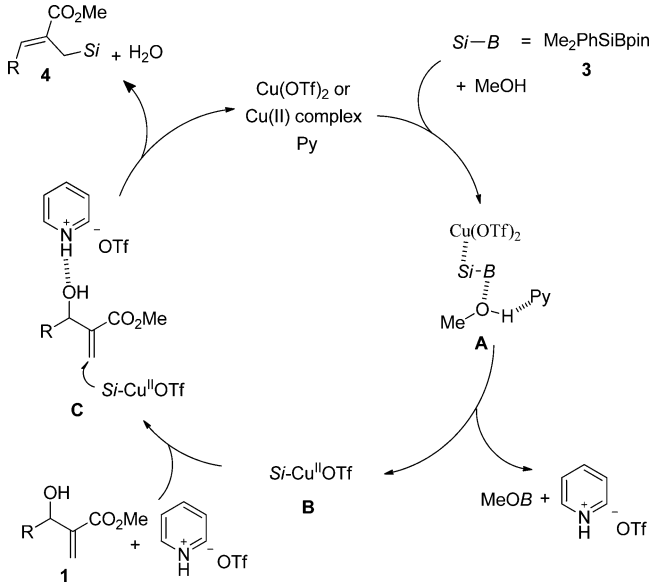
EXPERIMENTAL SECTION

General Procedure for Allylic Silylation of MBH Alcohols. $Cu(OTf)_2$ (0.9 mg, 2.5 mol %) and MBH alcohol **1a** (19.2 mg, 0.1 mmol) were weighed and added to a Schlenk tube, which was evacuated and backfilled with argon. Then methanol (2 mL), pyridine (0.8 μL, 10 mol %), and $Me_2PhSiBpin$ (**3**) (39 μL, 0.15 mmol) were added via syringe, and the reaction mixture was stirred for 24 h at room temperature. Then the organic solvent was evaporated, and the residue was subjected to flash column chromatography on silica gel (Et_2O/petroleum ether = 1:8) to give the allylsilylation product **4a** as a yellow oil (30.4 mg, 98%).

(*Z*)-Methyl 2-[Dimethyl(phenyl)silyl]methyl-3-phenylacrylate (4a). Yellow oil, 30.4 mg, yield 98%. IR (KBr, cm^{-1}): 1712, 1622, 1434, 1261, 1159, 1113, 1060, 838, 698. ^1H NMR (300 MHz, $CDCl_3$): δ 7.37−7.34 (m, 3H), 7.22−7.19 (m, 3H), 7.15−7.12 (m, 5H), 2.29 (s, 2H), 1.40 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 141.2, 139.0, 136.9, 135.9, 135.0, 131.4, 131.3, 130.6, 130.1, 129.8, 82.8, 30.4, 19.5, 0.0. HRMS (Orbitrap, MS, ESI): calcd for $C_{13}H_{17}O_2Si$ $[M - C_6H_5]^+$ 233.0992, found 233.0992.

(*Z*)-Methyl 2-[Dimethyl(phenyl)silyl]methyl-3-(*p*-tolyl)-acrylate (4b). Yellow oil, 31.4 mg, yield 97%. IR (KBr, cm^{-1}): 1708, 1606, 1510, 1463, 1253, 1176, 1112, 827, 731. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51 (s 1H), 7.48−7.45 (m, 2H), 7.33−7.29 (m, 3H), 7.22−7.16 (m, 2H), 3.66 (s, 3H), 2.39 (s, 2H), 2.32 (s, 3H), 0.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 141.3, 140.4, 138.2, 136.1, 135.9, 132.5, 131.7, 131.6, 131.3, 130.2, 54.3, 32.8, 20.0, 0.0. HRMS (Orbitrap, MS, ESI): calcd for $C_{14}H_{19}O_2Si$ $[M - C_6H_5]^+$ 247.1145, found 247.1149.

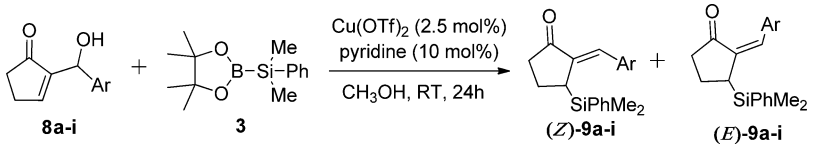
Scheme 2. Proposed Reaction Mechanism



(*Z*)-Methyl 3-(4-Chlorophenyl)-2-{[dimethyl(phenyl)silyl]-methyl}acrylate (4c). Yellow oil, 30.0 mg, yield 87%. IR (KBr, cm^{-1}): 1713, 1489, 1434, 1254, 1155, 1112, 838. ^1H NMR (300 MHz, $CDCl_3$): δ 7.45−7.41 (m, 3H), 7.35−7.31 (m, 3H), 7.25−7.19 (m, 2H), 7.15−7.12 (m, 2H), 3.69 (s, 3H), 2.35 (s, 2H), 0.25 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.1, 138.6, 136.6, 136.6, 133.5, 131.4, 130.1, 128.9, 128.3, 127.8, 127.7, 125.5, 0.0. HRMS (Orbitrap, MS, ESI): calcd for $C_{13}H_{16}O_2ClSi$ $[M - Ph]^+$ 267.0603, found 267.0600.

(*Z*)-Methyl 3-(4-Bromophenyl)-2-{[dimethyl(phenyl)silyl]-methyl}acrylate (4d). Yellow oil, 33.8 mg, yield 87%. IR (KBr, cm^{-1}): 1713, 1621, 1487, 1434, 1259, 1156, 1112, 824. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44−7.41 (m, 3H), 7.38−7.37 (m, 1H), 7.35−7.33 (m, 4H), 7.31−7.25 (m, 2H), 3.67 (s, 3H), 2.34 (s, 2H), 0.25 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 138.3, 135.2, 134.2, 133.5, 131.7, 131.5, 130.6, 129.2, 127.8, 121.8, 52.0, 17.7, −2.62. HRMS (Orbitrap, MS, ESI): calcd for $C_{13}H_{16}O_2BrSi$ $[M - C_6H_5]^+$ 311.0098, found 311.0092.

Table 3. $Cu(OTf)_2$-Catalyzed Reactions of Cyclic MBH Alcohols 8a−i with 3[a]



Entry	MBH alcohol (Ar)	Product (Ar)	Z/E[b]	Yield (%)[c]
1	**8a** (Ph)	**9a** (Ph)	20:1	65
2	**8b** (4-FC_6H_4)	**9b** (4-FC_6H_4)	10:1	75
3	**8c** (4-ClC_6H_4)	**9c** (4-ClC_6H_4)	10:1	80
4	**8d** (4-BrC_6H_4)	**9d** (4-BrC_6H_4)	6:1	62
5	**8e** (4-$NO_2C_6H_4$)	**9e** (4-$NO_2C_6H_4$)	6:1	63
6	**8f** (4-$CH_3C_6H_4$)	**9f** (4-$CH_3C_6H_4$)	33:1	80
7	**8g** (4-$CF_3C_6H_4$)	**9g** (4-$CF_3C_6H_4$)	10:1	65
8	**8h** (2-naphthyl)	**9h** (2-naphthyl)	10:1	82
9	**8i** (3,5-$(OMe)_2C_6H_3$)	**9i** (3,5-$(MeO)_2C_6H_3$)	1:0[d]	75

[a]All of the reactions were conducted with MBH alcohol (0.1 mmol) and **3** (0.15 mmol) in CH_3OH (2 mL) under Ar at room temperature for 24 h. [b]Determined by ^1H NMR analysis of the product mixture; the configuration was determined by NOESY analysis. [c]Isolated yields of the mixtures of *E* and *Z* isomers. [d]The *Z* isomer was formed exclusively.

dx.doi.org/10.1021/jo4016419 | J. Org. Chem. 2013, 78, 11076−11081

(*Z*)-Methyl 2-[Dimethyl(phenyl)silyl]methyl-3-(*m*-tolyl)-acrylate (4e). Yellow oil, 30.8 mg, yield 95%. IR (KBr, cm^{-1}): 1713, 1489, 1254, 1112, 834. ^1H NMR (300 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.38−7.33 (m, 2H), 7.31−7.23 (m, 3H), 7.17−7.09 (m, 2H), 7.08−7.05 (m, 2H), 3.69 (s, 3H), 2.23 (s, 2H), 2.19 (s, 3H), 0.18 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.1, 138.6, 136,6, 135.6, 135.3, 133.5, 131.4, 130.1, 128.9, 128.3, 127.8, 127.7, 125.5, 51.8, 19.9, 16.9, −2.61. HRMS (Orbitrap, MS, ESI): calcd for $C_{20}H_{24}O_2NaSi$ ([M + Na]$^+$) 347.1438, found 347.1438.

(*Z*)-Methyl 2-[Dimethyl(phenyl)silyl]methyl-3-(4-methoxyphenyl)acrylate (4f). Yellow oil, 33.3 mg, yield 98%. IR (KBr, cm^{-1}): 1708, 1605, 1510, 1253, 1112, 827. ^1H NMR (300 MHz, $CDCl_3$): δ 7.50−7.46 (m, 3H), 7.33−7.31 (m, 3H), 7.26−7.23 (m, 2H), 6.81 (s, 1H), 6.78 (s, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 0.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 159.3, 138.9, 135.4, 133.6, 130.8, 129.0, 128.8, 128.8, 128.7, 55.3, 51.8, 17.4, −2.53. HRMS (Orbitrap, MS, ESI): calcd for $C_{20}H_{24}O_3NaSi$ ([M + Na]$^+$) 363.1387, found 363.1387.

(*Z*)-Methyl 2-[Dimethyl(phenyl)silyl)]methyl-3-(3-fluorophenyl)acrylate (4g). Yellow oil, 26.2 mg, yield 80%. IR (KBr, cm^{-1}): 1714, 1582, 1434, 1273, 1234, 1146, 1112, 833, 699. ^1H NMR (300 MHz, $CDCl_3$): δ 7.45−7.42 (m, 3H), 7.34−7.30 (m, 3H), 7.28−7.18 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 162.6 (d, $^1J_{CF}$ = 244.5 Hz), 138.5 (d, $^3J_{CF}$ = 8.23 Hz), 138.2, 134.2, 133.5, 132.2, 129.8 (d, $^3J_{CF}$ = 8.25 Hz), 129.1, 127.8, 124.8 (d, $^4J_{CF}$ = 2.25 Hz), 115.6 (d, $^2J_{CF}$ = 21.8 Hz), 114.6 (d, $^2J_{CF}$ = 21.0 Hz), 52.0, −2.63. HRMS (Orbitrap, MS, ESI): calcd for $C_{13}H_{16}O_2FSi$ ([M − C_6H_5]$^+$) 251.0898, found 251.0895.

(*Z*)-Methyl 2-[Dimethyl(phenyl)silyl)]methyl-3-[3-(trifluoromethyl)phenyl]acrylate (4h). Yellow oil, 29.1 mg, yield 77%. IR (KBr, cm^{-1}): 1716, 1436, 1331, 1259, 1166, 1278, 1074, 833, 699. ^1H NMR (300 MHz, $CDCl_3$): δ 7.50−7.47 (m, 3H), 7.42−7.39 (m, 2H), 7.37−735 (m, 2H), 7.34−7.24 (m, 3H), 3.70 (s, 3H), 2.36 (s, 2H), 0.26 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 135.1 (d, $^3J_{CF}$ = 1.5 Hz), 133.6, 133.5, 132.1, 131.4, 130.2, 128.6 (q, $^2J_{CF}$ = 30 Hz), 127.7, 127.6, 126.0 (q, $^3J_{CF}$ = 5.3 Hz), 124.0 (d, $^1J_{CF}$ = 272.3 Hz), 52.0, 17.6, −2.7. HRMS (Orbitrap, MS, ESI): calcd for $C_{14}H_{16}O_2F_3Si$ ([M − C_6H_5]$^+$) 301.0866, found 301.0862.

(*Z*)-Methyl 2-[Dimethyl(phenyl)silyl]methyl-3-(naphthalen-2-yl)acrylate (4i). Yellow oil, 31.7 mg, yield 88%. IR (KBr, cm^{-1}): 1713, 1622, 1434, 1252, 1161, 1112, 832, 801, 784. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.49−7.46 (m, 2H), 7.36−7.34 (m, 1H), 7.31−7.28 (m, 3H), 7.25−7.16 (m, 4H), 3.74 (s, 3H), 2.24 (s, 2H), 0.12 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 138.5, 134.3, 133.7, 133.5, 135.5, 133.1, 131.5, 128.9, 128.5, 128.1, 127.6, 126.2, 126.1, 126.0, 125.1, 124.9, 51.9, 17.7, −2.6. HRMS (Orbitrap, MS, ESI): calcd for $C_{23}H_{24}O_2NaSi$ ([M + Na]$^+$) 383.1438, found 383.1437.

(*Z*)-Methyl 3-(1,1′-Biphenyl-4-yl)-2-{[dimethyl(phenyl)silyl]-methyl}acrylate (4j). Yellow oil, 35.5 mg, yield 92%. IR (KBr, cm^{-1}): 1709, 1619, 1487, 1269, 1155, 1112, 829. ^1H NMR (300 MHz, $CDCl_3$): δ 7.61−7.57 (m, 1H), 7.52−7.42 (m, 6H), 7.38−7.24 (m, 8H), 3.69 (s, 3H), 2.45 (s, 2H), 0.28 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 140.5, 140.5, 138.6, 135.3, 135.2, 133.6, 130.9, 129.7, 129.1, 128.8, 127.8, 127.5, 127.0, 127.0, 51.9, −2.5. HRMS (Orbitrap, MS, ESI): calcd for $C_{25}H_{26}O_2NaSi$ ([M + Na]$^+$) 409.1594, found 409.1595.

(*Z*)-Methyl 3-(2-Bromophenyl)-2-{[dimethyl(phenyl)silyl]-methyl}acrylate (4k). Yellow oil, 34.2 mg, yield 88%. IR (KBr, cm^{-1}): 1716, 1434, 1255, 1158, 1112, 1063, 838, 699. ^1H NMR (300 MHz, $CDCl_3$): δ 7.57−7.51 (m, 2H), 7.41−7.38 (m, 2H), 7.36−7.24 (m, 3H), 7.18−7.07 (m, 3H), 3.69 (s, 3H), 2.24 (s, 2H), 0.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 138.5, 136.8, 135.0, 133.5, 132.8, 132.6, 130.0, 129.1, 129.0, 127.7, 127.0, 124.2, 51.2, 17.3, −2.73. HRMS (Orbitrap, MS, ESI): calcd for $C_{13}H_{16}O_2BrSi$ ([M − C_6H_5]$^+$) 311.0098, found 311.0092.

(*Z*)-Methyl 2-{[Dimethyl(phenyl)silyl]methyl}-5-phenylpent-2-enoate (4l). Yellow oil, 29.2 mg, yield 86%. IR (KBr, cm^{-1}): 1714, 1636, 1454, 1427, 1167, 1113, 835, 699. ^1H NMR (300 MHz, $CDCl_3$): δ 7.43−7.40 (m, 2H), 7.27−7.25 (m, 3H), 7.22−7.11 (m, 3H), 7.03−7.00 (m, 2H), 6.58−6.54 (t, J = 7.2 Hz, 2H), 3.54 (s, 3H), 3.55−3.50 (t, J = 7.9 Hz, 2H), 2.19−2.11 (q, J = 7.8 Hz, 4H), 1.92 (s, 2H), 0.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 141.3, 138.7, 138.2, 133.6, 129.8, 129.1, 128.4, 128.3, 127.4, 126.0, 51.6, 34.8, 30.8, 17.2, −2.83. HRMS (Orbitrap, MS, ESI): calcd for $C_{15}H_{21}O_2Si$ ([M − C_6H_5]$^+$) 261.1305, found 261.1301.

(*Z*)-Methyl 2-{[Dimethyl(phenyl)silyl]methyl}-5-methylhex-2-enoate (4m). Yellow oil, 26.9 mg, yield 93%. IR (KBr, cm^{-1}): 1715, 1636, 1287, 1256, 1068, 836, 731, 699. ^1H NMR (300 MHz, $CDCl_3$): δ 7.52−7.49 (m, 2H), 7.35−7.33 (m, 3H), 6.66−6.61 (t, J = 7.2 Hz, 1H), 3.61 (s, 3H), 2.01 (s, 2H), 1.83−1.78 (t, J = 7.1 Hz, 2H), 1.68−1.55 (quintet, J = 6.6 Hz, 1H), 0.86 (s, 3H), 0.84 (s, 3H), 0.27 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 138.9, 138.5, 133.6, 129.7, 129.0, 127.7, 51.5, 38.0, 28.2, 22.5, 17.0, −2.8. HRMS (Orbitrap, MS, ESI): calcd for $C_{11}H_{21}O_2Si$ ([M − C_6H_5]$^+$) 213.1305, found 213.1303.

(*Z*)-*tert*-Butyl 2-((Dimethyl(phenyl)silyl)methyl)-3-phenylacrylate (4n). Yellow oil, 33.8 mg, yield 97%. IR (KBr, cm^{-1}): 1719, 1632, 1262, 832, 801. ^1H NMR (300 MHz, $CDCl_3$): δ 7.39−7.34 (m, 3H), 7.22−7.21 (m, 2H), 7.20−7.19 (m, 1H), 7.18−7.10 (m, 5H), 2.29 (s, 2H), 0.15 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 141.2, 139.0, 136.9, 135.9, 135.0, 131.4, 131.3, 130.6, 130.1, 129.8, 82.8, 30.4, 19.5, 0.0. HRMS (Orbitrap, MS, ESI): calcd for $C_{22}H_{28}NaO_2Si$ ([M + Na]$^+$) 375.17508, found 375.17513.

2-Benzylidene-3-[dimethyl(phenyl)silyl]cyclopentanone (9a). Yellow oil, 19.9 mg, yield 65%. IR (KBr, cm^{-1}): 1712, 1622, 1446, 1434, 1261, 1159, 1112, 1060, 834, 731, 698. ^1H NMR (300 MHz, $CDCl_3$): δ 7.47−7.44 (m, 2H), 7.36−7.25 (m, 7H), 3.41−3.39 (t, 3H), 2.26−2.08 (m, 3H), 1.85−1.72 (m, 1H), 0.26 (s, 3H), 0.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.8, 138.9, 137.0, 136.0, 133.7, 130.2, 129.6, 129.2, 128.6, 128.5, 128.0, 35.9, 31.0, 21.9, −3.3, −3.6. HRMS (Orbitrap, MS, ESI): calcd for $C_{20}H_{23}OSi$ ([M + H]$^+$) 307.1513, found 307.1518.

3-[Dimethyl(phenyl)silyl]-2-(4-fluorobenzylidene)cyclopentanone (9b). Yellow solid, mp 59−61 °C, 24.3 mg, yield 75%. IR (KBr, cm^{-1}): 1709, 1613, 1597, 1505, 1424, 1220, 1173, 1150, 1112, 895, 828, 703. ^1H NMR (300 MHz, $CDCl_3$): δ 7.58−7.56 (m, 4H), 7.48−7.40 (m, 4H), 7.16−7.10 (m, 1H), 7.46−7.45 (m, 3H), 2.41−2.22 (m, 3H), 2.01−1.88 (m, 1H), 0.40 (s, 3H), 0.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.7, 162.5 (d, $^1J_{CF}$ = 248.3 Hz), 138.4, 136.8, 133.7, 132.16 (d, $^3J_{CF}$ = 3 Hz), 131.9, 131.8, 129.7, 128.0, 115.6 (d, $^2J_{CF}$ = 21.8 Hz), 35.9, 30.9, 21.9, −3.4, −3.5. HRMS (Orbitrap, MS, ESI): calcd for $C_{20}H_{22}FOSi$ [M + H]$^+$ 325.1419, found 325.1419.

2-(4-Chlorobenzylidene)-3-[dimethyl(phenyl)silyl]cyclopentanone (9c). Yellow solid, mp 70−72 °C, 27.3 mg, yield 80%. IR (KBr, cm^{-1}): 1714, 1607, 1487, 1403, 1249, 1169, 1085, 820, 703, 516. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44−7.35 (m, 4H), 7.33−7.27 (m, 4H), 7.25−7.23 (m, 2H), 3.33−3.32 (m, 3H), 2.28−2.09 (m, 3H), 1.89−1.75 (m, 1H), 0.26 (s, 3H), 0.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.6, 139.4, 136.7, 134.5, 134.3, 133.7, 131.2, 129.7, 128.7, 128.0, 127.7, 35.9, 31.2, 21.9, −3.4, −4.5. HRMS (Orbitrap, MS, ESI): calcd for $C_{20}H_{22}ClOSi$ ([M + H]$^+$) 341.1123, found 341.1124.

2-(4-Bromobenzylidene)-3-[dimethyl(phenyl)silyl]cyclopentanone (9d). Yellow solid, mp 91−93 °C, 23.9 mg, yield 62%. IR (KBr, cm^{-1}): 1710, 1609, 1486, 1399, 1168, 1071, 823, 703, 511. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44−7.40 (m, 4H), 7.37−7.33 (m, 2H), 7.32−7.27 (m, 2H), 7.26−7.25 (m, 1H), 7.21−7.20 (m, 1H), 3.32−3.31 (m, 3H), 2.28−2.10 (m, 3H), 1.90−1.80 (m, 1H), 0.26 (s, 3H), 0.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.6, 139.6, 136.7, 134.9, 133.7, 131.7, 131.5, 129.7, 128.0, 127.7, 122.6, 35.9, 31.3, 21.9, −3.4, −3.5. HRMS (Orbitrap, MS, ESI): calcd for $C_{20}H_{22}BrOSi$ ([M + H]$^+$) 385.0618, found 385.0619.

3-[Dimethyl(phenyl)silyl]-2-(4-nitrobenzylidene)cyclopentanone (9e). Yellow solid, mp 109−111 °C, 22.1 mg, yield 63%. IR (KBr, cm^{-1}): 1713, 1609, 1590, 1340, 1174, 1111, 835, 704, 693. ^1H NMR (300 MHz, $CDCl_3$): δ 8.11 (s, 1H), 8.08 (s, 1H), 7.55 (s, 1H), 7.52 (s, 1H), 7.39−7.37 (m, 2H), 3.41−3.39 (m, 3H), 2.36−2.16 (m, 3H), 1.96−1.87 (m, 1H), 0.27 (s, 1H), 0.24 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.1, 146.8, 142.9, 142.8, 136.1, 133.7, 130.2, 129.8, 128.1, 126.0, 123.6, 35.8, 32.0, 21.8, −3.5, −3.6. HRMS

dx.doi.org/10.1021/jo4016419 | J. Org. Chem. 2013, 78, 11076−11081

(Orbitrap, MS, ESI): calcd for $C_{20}H_{21}O_3NNaSi$ ([M + Na]$^+$) 374.1183, found 374.1183.

3-[Dimethyl(phenyl)silyl]-2-(4-methylbenzylidene)cyclopentanone (9f). Yellow oil, 25.7 mg, yield 80%. IR (KBr, cm^{-1}): 1713, 1617, 1330, 1166, 1126, 831, 834, 697. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.46 (m, 3H), 7.42 (s, 1H), 7.36−7.25 (m, 4H), 7.16−7.13 (m, 2H), 3.38−3.36 (t, J = 27 Hz, 3H), 2.36 (s, 3H), 2.24−2.07 (m, 3H), 1.84−1.74 (m, 1H), 0.27 (s, 3H), 0.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.9, 138.9, 137.8, 137.1, 133.7, 133.1, 130.3, 129.6, 129.3, 129.2, 128.0, 35.9, 31.0, 21.9, 21.4, −3.2, −3.5. HRMS (Orbitrap, MS, ESI): calcd for $C_{21}H_{25}OSi$ ([M + H]$^+$) 321.16692, found 321.16677.

3-[Dimethyl(phenyl)silyl]-2-[3-(trifluoromethyl)benzylidene]cyclopentanone (9g). Yellow oil, 24.3 mg, yield 65%. IR (KBr, cm^{-1}): 1716, 1436, 1330, 1258, 1199, 1166, 1272, 834, 699. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.62−7.59 (d, J = 9 Hz, 2H), 7.51−7.48 (d, J = 9 Hz, 1H), 7.44−7.39 (m, 3H), 7.31−7.23 (m, 4H), 7.39−7.37 (m, 2H), 2.30−2.11 (m, 3H), 2.10−1.78 (m, 1H), 0.26 (s, 3H), 0.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.4, 140.6, 136.89, 136.29, 133.7, 133.4, 130.8 (q, $^2J_{CF}$ = 32.3 Hz), 129.7, 129.0, 128.0, 127.1, 126.0 (q, $^3J_{CF}$ = 3.8 Hz), 124.9 (q, $^3J_{CF}$ = 3.8 Hz), 124.0 (d, $^1J_{CF}$ = 270.8 Hz), 35.8, 31.5, −3.5, −3.8. HRMS (Orbitrap, MS, ESI): calcd for $C_{21}H_{22}F_3OSi$ ([M + H]$^+$) 375.1387, found 375.1386.

3-[Dimethyl(phenyl)silyl]-2-[(naphthalen-2-yl)methylene]-cyclopentanone (9h). Yellow solid, mp 93−95 °C, 29.3 mg, yield 82%. IR (KBr, cm^{-1}): 1705, 1603, 1198, 1174, 1112, 814, 704. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.81−7.74 (m, 4H), 7.65−7.62 (m, 1H), 7.49−7.46 (m, 5H), 7.30−7.24 (m, 2H), 7.54−7.52 (m, 1H), 2.30−2.13 (m, 3H), 1.92−1.78 (s, 1H), 0.27 (s, 3H), 0.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.8, 139.1, 137.0, 134.0, 133.7, 133.6, 133.3, 133.2, 130.6, 129.6, 129.3, 128.4, 128.0, 127.6, 127.1, 126.8, 126.4, 35.9, 31.4, 22.0, −3.2, −3.5. HRMS (Orbitrap, MS, ESI): calcd for $C_{24}H_{25}OSi$ ([M + H]$^+$) 357.1669, found 357.1669.

2-(3,5-Dimethoxybenzylidene)-3-[dimethyl(phenyl)silyl]-cyclopentanone (9i). Yellow solid, mp 88−90 °C, 27.5 mg, yield 75%. IR (KBr, cm^{-1}): 1706, 1609, 1196, 1174, 1112, 814, 704. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.46−7.44 (m, 2H), 7.35−7.27 (m, 3H), 7.23−7.22 (m, 1H), 6.69−6.68 (m, 2H), 6.42−6.41 (t, J = 1.9 Hz, 1H), 3.78 (s, 6H), 3.39−3.38 (m, 3H), 2.25−2.07 (m, 3H), 1.83−1.69 (m, 1H), 0.28 (s, 3H), 0.19 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.8, 160.7, 139.3, 137.9, 136.9, 133.7, 129.6, 129.2, 127.9, 108.3, 101.1, 55.4, 35.9, 31.2, 21.8, −3.2, −3.5. HRMS (Orbitrap, MS, ESI): calcd for $C_{22}H_{27}O_3Si$ ([M + H]$^+$) 367.1724, found 367.1719.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China, the Ministry of Science and Technology (973 Program, 2011CB808600), and the Chinese Academy of Sciences for supporting our research.

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