Z-Selective Synthesis of α,*β*-Unsaturated Amides with Triphenylsilylacetamides†

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With the purpose of developing a method of preparing *Z*-α,*β*-unsaturated amides, the Peterson reaction of the (triphenylsilyl)acetamide Ph_3SiCH_2COX (**1**, X = NBn_2; **3**, X = NMe_2) with various aldehydes was examined. The reaction of aromatic aldehydes gave selectivities up to >97:3. It was found that the selectivity was a function of the electronic nature of the aromatic ring and higher *Z* selectivity was attained with electron-rich aldehydes. With aliphatic aldehydes selectivities up to 92:8 were achieved, and unlike with analogous phosphorus reagents, less sterically hindered aldehydes gave higher *Z* selectivity. Also, **3**, which has a smaller amide group than **1**, tended to give rise to higher selectivity. A comparison with the reaction of trimethylsilyl analogues revealed the significance of the phenyl substituents on the silyl group.

Introduction

The versatility of geometry-defined olefins makes them good building blocks in organic synthesis. Of particular potential are olefins bearing carbon-based electron-withdrawing groups, such as the ester group, since not only are these groups viable of further functionalization but they also activate the double-bond moiety for reactions such as Michael addition and pericyclic reactions. In many such reactions, the stereochemistry of the product is dependent upon the geometry of the olefin. Among the methods of choice for obtaining such units with concomitant formation of a carbon−carbon bond are the Wittig reaction and the Horner−Wadsworth−Emmons (HWE) reaction, which utilize phosphorus,[1] and the Peterson reaction, which utilizes silicon.[2] Since disubstituted olefins bearing an electron-withdrawing group of *E* geometry are thermodynamically more stable than their *Z* counterparts, they are rather easy to come by, while methods available for moderate to highly selective preparation for the latter are rather limited. Although it is desirable to have a direct *Z*-selective method for the preparation of disubstituted α,*β*-unsaturated amides from aldehydes, no such method could be found among them, and we thus decided to seek for an efficient method. When the project was begun, the only methods available were preparative ones for olefins bearing the ester,[3−7] the cyano,[8−12] and methyl ketone group as the electron-withdrawing moiety.[13] To accomplish our objective, we decided to look into the Si platform. In Peterson olefination, reagents bearing a trimethylsilyl (TMS) group have been widely utilized to complement reagents of the Wittig type.[2] However, for reactions involving disubstituted olefin products with electron-withdrawing groups, geometric mixtures with low selectivity are usually obtained. Silicon differs greatly from its phosphorus counterpart, where high selectivity for both (*E*)- and (*Z*)-olefins has been established for certain electron-withdrawing groups. Previous amide formation with Peterson reagents bearing the TMS group is no exception.[14] To get around this problem, we decided to consider a more bulky and more electronegative silyl group, the triphenylsilyl group. This silyl group has proven to be relevant in combination with the cyano group for the preparation of *Z*-*β*-substituted acrylonitriles in earlier examinations by others.[8] In accordance with expectations, we have realized the first highly *Z*-selective preparation of α,*β*-unsaturated amides. We have also found that higher selectivity could be achieved with smaller substituents upon the nitrogen atom. Herein we describe our results.[15]

† Dedicated to Prof. B. M. Trost.

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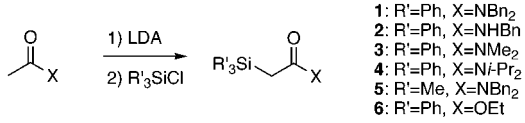
Scheme 1



Scheme 2

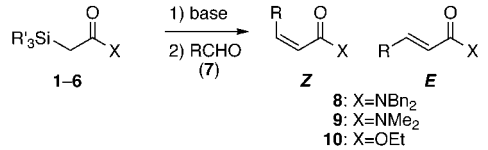


Table 1. Countercation Effect upon the Reaction of PhCHO[a]

entry	base	temp (°C)	*Z*:*E*[b]	yield (%)[c]
1	*n*-BuLi	−78 to 0	54:46	85
2	NaHMDS	−78	80:20	93
3	KHMDS	−78	>97:3	97

[a] All reactions were carried out at −78 °C. [b] Determined by 500 MHz ^{1}H NMR measurement of the crude mixture. [c] Combined isolated yield of (*E*)- and (*Z*)-olefins.

Results and Discussion

The Peterson reagents **1**−**4** (Scheme 1) examined for the reactions were prepared by treating the lithium enolate of *N*,*N*-dibenzylacetamide, *N*-benzylacetamide, *N*,*N*-dimethylacetamide, and *N*,*N*-diisopropylacetamide with triphenylsilyl chloride. The trimethylsilyl derivative **5** was prepared similarly with trimethylsilyl chloride. In all the cases, the yields were moderate to high (69−89%), indicating that regioselectively favored C-silylation over O-silylation.[16]

The reaction of reagent **1**, bearing potentially removable benzyl substituents, was first examined (Scheme 2). The geometry of the products was determined by the characteristic coupling constants between the two olefinic protons. For representative products, the NOE was measured between these protons to confirm our assignments. Since a countercation effect is usually observed for the analogous HWE reaction, the reaction with several metal-containing bases was carried out with benzaldehyde (**7a**) as substrate (Table 1). Whereas the reaction with *n*-BuLi was essentially unselective (entry 1), NaHMDS furnished the product with a fair 4:1 ratio (entry 2), and KHMDS gave the (*Z*)-amide **8a-*Z*** as the exclusive product (entry 3, >97:3), thus revealing that the effect of the countercation is quite significant. More common bases such as NaH and *t*-BuOK did not work.

The reaction of **1a** with 3-phenylpropionaldehyde (**7h**), an aliphatic aldehyde, was examined at −78 °C with KHMDS as the optimum base. This aldehyde was also found to be highly *Z* selective (91:9), although not exclusive. To improve the selectivity, an examination of solvents was carried out (Table 2). However, attempts to decrease (entry 3, ether) or increase (entry 4, THF−HMPA mixture) the solvent polarity did not prove rewarding. Lowering the reaction temperature did lead to a slight increase in selectivity (entry 5), but the yield turned out to be lower. The use of NaHMDS in place of KHMDS led surprisingly to identical selectivity (entry 2), in contrast to examinations with benzaldehyde.

Table 2. Solvent Effect upon the Reaction of $Ph(CH_2)_2CHO$[a]

entry	solvent	temp (°C)	*Z*:*E*[b]	yield (%)[c]
1	THF	−78	91:9	77
2	THF[d]	−78	91:9	53
3	ether	−78	74:26	15
4	THF/HMPA	−78	71:29	64
5	THF	−95	94:6	58

[a] The reactions were carried out with KHMDS as base unless noted otherwise. [b] Determined by 500 MHz ^{1}H NMR measurement of the crude mixture. [c] Combined isolated yield of (*E*)- and (*Z*)-olefins. [d] The reaction was carried out with NaHMDS as base.

Table 3. Reactions of 1 and 7 with KHMDS as Base[a]

entry	R	product	*Z*:*E*[b]	yield (%)[c]
1	Ph (**7a**)	**8a**	>97:3	88
2	*p*-$MeOC_6H_4$ (**7b**)	**8b**	>97:3	87
3	*o*-$MeOC_6H_4$ (**7c**)	**8c**	81:19	72
4	*p*-ClC_6H_4 (**7d**)	**8d**	88:12	91
5	2-furyl (**7e**)	**8e**	91:9	92
6	2-pyridyl (**7f**)	**8f**	59:41	47
7	(*E*)-PhCH=CH (**7g**)	**8g**	81:19	99
8	$PhCH_2CH_2$ (**7h**)	**8h**	91:9	77
9	cyclohexyl (**7i**)	**8i**	83:17	82
10	$Ph(CH_3)CH$ (**7j**)	**8j**		0
11	*t*-Bu (**7k**)	**8k**		0

[a] All reactions were carried out in THF at −78 °C with KHMDS as base. [b] Determined by 500 MHz ^{1}H NMR measurement of the crude mixture. [c] Combined isolated yield of (*E*)- and (*Z*)-olefins.

The scope of the reaction using **1** was examined under the standard conditions of using THF and KHMDS, which proved to be commonly effective for both benzaldehyde and 3-phenylpropionaldehyde, at a temperature of −78 °C (Table 3). For 4-substituted benzaldehyde derivatives, complete *Z* selectivity was achieved (entry 2), with *p*-anisaldehyde (**7b**) bearing the electron-donating MeO group, whereas a dropoff in selectivity was observed with the electronegative Cl substituent of **7d** (entry 4). Although, generally in HWE reactions, sterically hindered 2-substituted aromatic aldehydes are more *Z* selective than their 4-substituted counterparts, the Peterson reaction here gave lower selectivity with the 2-MeO substrate **7c** than for the 4-MeO substrate **7b** (entry 3). With heterocyclic aldehydes, the highly electronegative 2-pyridylaldehyde (**7f**) showed low selectivity (entry 6), whereas the reaction of furfural (**7e**) was highly *Z* selective (entry 5). The conjugated (*E*)-cinnamaldehyde (**7g**) also furnished the *Z* product as the predominant isomer (entry 7).

As for aliphatic aldehydes, cyclohexanecarboxaldehyde (**7i**), an α-branched olefin, reacted to give the (*Z*)-olefin as the major product (entry 9). Here again as in the case of *o*- and *p*-anisaldehyde, sterics seemed to have caused lower selectivity. In contrast to cyclohexanecarboxaldehyde (**7i**), 2-phenylpropionaldehyde (**7j**) did not give any desired product. This indicates that with readily enolizable aldehydes, enolization is favored over the olefination reaction. Apparently due to steric factors, pivalaldehyde (**7k**) was unreactive, as were other carbonyl compounds such as ketones and cyclic acid anhydrides.

The electronic effect observed in aromatic aldehydes with KHMDS as base was more obvious upon using *n*-BuLi as the base (Table 4), with the *Z* selectivity

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Table 4. Reactions of 1 and 7 with *n*-BuLi as Base[a]

entry	R	product	*Z*:*E*[b]	yield (%)[c]
1	*p*-$MeOC_6H_4$ (**7b**)	**8b**	69:31	94
2	Ph (**7a**)	**8a**	54:46	85
3	*p*-ClC_6H_4 (**7d**)	**8d**	43:57	95

[a] All reactions were carried out in THF at −78 °C for 1 h and then the temperature was raised slowly to 0 °C. [b] Determined by 500 MHz ^{1}H NMR measurement of the crude mixture. [c] Combined isolated yield of (*E*)- and (*Z*)-olefins.

Table 5. Reactions of 3 and 7 with KHMDS as Base[a]

entry	R	product	*Z*:*E*[b]	yield (%)[c]
1	Ph (**7a**)	**9a**	>97:3	78
2	*p*-$MeOC_6H_4$ (**7b**)	**9b**	>97:3	99
3	*o*-$MeOC_6H_4$ (**7c**)	**9c**	78:22	53
4	*p*-ClC_6H_4 (**7d**)	**9d**	97:3	66
5	$PhCH_2CH_2$ (**7h**)	**9h**	92:8	72
6	cyclohexyl (**7i**)	**9i**	88:12	44
7	$Ph(CH_3)CH$ (**7j**)	**9j**		0

[a] All reactions were carried out in THF at −78 °C with KHMDS as base. [b] Determined by 500 MHz ^{1}H NMR measurement of the crude mixture. [c] Combined isolated yield of (*E*)- and (*Z*)-olefins.

Table 6. Reactions of 3 and 7 with *n*-BuLi as Base[a]

entry	R	product	*Z*:*E*[b]	yield (%)[c]
1	*p*-$MeOC_6H_4$ (**7b**)	**9b**	>97:3	95
2	Ph (**7a**)	**9a**	90:10	87
3	*p*-ClC_6H_4 (**7d**)	**9d**	90:10	54

[a] All reactions were carried out in THF at −78 °C for 1 h and then the temperature was raised slowly to 0 °C. [b] Determined by 500 MHz 1H NMR measurement of crude mixture. [c] Combined isolated yield of (*E*)- and (*Z*)-olefins.

decreasing from 69:31 (*p*-$MeOC_6H_4CHO$) down to 43:57 (*p*-ClC_6H_4CHO) with increasing electronegativity of the aryl group.

Products with a secondary amide substituent were envisioned to expand the utility of this system, and thus, attempts with **2**, which bears only one benzyl substituent, were also carried out. However, under no conditions could olefin formation be observed. The major reaction path in this case was decomposition of the Peterson reagent, evident from the nearly quantitative recovery of desilylated acetamide from the reaction mixture.

We next turned our attention toward the size of the alkyl substituents upon the nitrogen atom. To assess our amide reagents, the reaction of **3** was examined under standard conditions (Table 5). A large increase in *Z* selectivity was observed for *p*-ClC_6H_4CHO (**7d**) (entry 4), thus indicating that the less sterically hindered amide is favorable for higher selectivity. As for aliphatic aldehydes, a slight increase was seen for the hindered cyclohexylcarboxaldehyde **7i** (entry 6).

The steric effect of the nitrogen substituents was more obvious with the use of *n*-BuLi as base (Table 6). For the three aromatic aldehydes (**7a**,**b**,**d**) examined, all gave much higher *Z* selectivity than **1**, while the same substituent effect order was retained as for **1**. Especially with *p*-anisaldehyde (**7b**), complete selectivity was attained. This represents a rare case of high *Z* selectivity using a lithium reagent in double-bond-forming chemistry.

Reactions for extremely sterically hindered **4** with isopropyl groups were sluggish, and decomposition of reagent was found to be the predominantly followed route.

The efficacy of the triphenylsilyl group was demonstrated by a comparison with the reactions of trimethylsilyl reagent **5** using KHMDS as base, as shown in Table 7.[10] The reaction of **5** with benzaldehyde (**7a**) resulted in a complete turnaround in selectivity, favoring (*E*)-olefin formation (entry 2), while that with 3-phenylpropionaldehyde (**7h**) gave no olefin product (entry 6). The effect of having an amide in the place of an ester group was next checked out with the ester analogue **6**, which bears the same triphenylsilyl group. The reaction of **6** with benzaldehyde (**7a**) (entry 3) and 3-phenylpropionaldehyde (**7h**) (entry 7) with KHMDS as base gave the corresponding electron-deficient olefins as *Z*:*E* = 71:29 and 77:23 mixtures, respectively. These ratios are clearly inferior compared with those of the corresponding amide (entries 1 and 5). These results imply that the electronic nature of the amide group has a bearing on the selectivity. In contrast to the amide reagents, *t*-BuOK could be used as base with the ester reagent **6**, albeit leading to somewhat lower selectivity (entries 4 and 8). Another point to note is that the Si-based reagent **1** gave higher *Z* selectivity than the corresponding HWE reagent (an analogue of the Ando ester reagent) carrying the same dibenzylamide group (i.e., 94:6 for benzaldehyde). Especially significant was the reaction of aliphatic aldehydes, where selectivity was low or in some cases even *E* selective for the HWE reagent (i.e. the highest selectivity was only 67:33 for 3-phenylpropionaldehyde).[17,18]

Table 7. Differently Substituted Reagents 1, 5, and 6[a]

entry	reagent	R	product	*Z*:*E*[b]	yield (%)[c]
1	$Ph_3SiCH_2CONBn_2$ (**1**)	Ph (**7a**)	**8a**	>97:3	88
2	$Me_3SiCH_2CONBn_2$ (**5**)	Ph (**7a**)	**8a**	27:73	63
3	$Ph_3SiCH_2CO_2Et$ (**6**)	Ph (**7a**)	**10a**	71:29	82
4	$Ph_3SiCH_2CO_2Et$ (**6**)[d]	Ph (**7a**)	**10a**	58:42	80
5	$Ph_3SiCH_2CONBn_2$ (**1**)	$PhCH_2CH_2$ (**7h**)	**8h**	91:9	77
6	$Me_3SiCH_2CONBn_2$ (**5**)	$PhCH_2CH_2$ (**7h**)	**8h**		0
7	$Ph_3SiCH_2CO_2Et$ (**6**)	$PhCH_2CH_2$ (**7h**)	**10h**	77:23	78
8	$Ph_3SiCH_2CO_2Et$ (**6**)[d]	$PhCH_2CH_2$ (**7h**)	**10h**	62:38	68

[a] All reactions were carried out in THF at −78 °C with KHMDS as base unless noted otherwise. [b] Determined by 500 MHz ^{1}H NMR measurement of the crude mixture. [c] Combined isolated yield of (*E*)- and (*Z*)-olefins. [d] *t*-BuOK was used as base.

Table 8. Competition Reactions[a]

entry	reagent	R	*Z*:*E*[b]	yield (%)[c]
1	$Ph_3SiCH_2CONMe_2$ (**3**)	$PhCH_2CH_2$ (**7h**)	91:9	33
		Ph (**7a**)	>97:3	56
2	$(PhO)_2P(O)CH_2CO_2Et$ (**11**)	$PhCH_2CH_2$ (**7h**)	85:15	67
		Ph (**7a**)	88:12	32
3	$Ph_3SiCH_2CONMe_2$ (**3**)	$PhCH_2CH_2$ (**7h**)	91:9	60
		$Ph(CH_3)CH$ (**7j**)		0
4	$(PhO)_2P(O)CH_2CO_2Et$ (**11**)	$PhCH_2CH_2$ (**7h**)	82:18	59
		$Ph(CH_3)CH$ (**7j**)	87:13	40

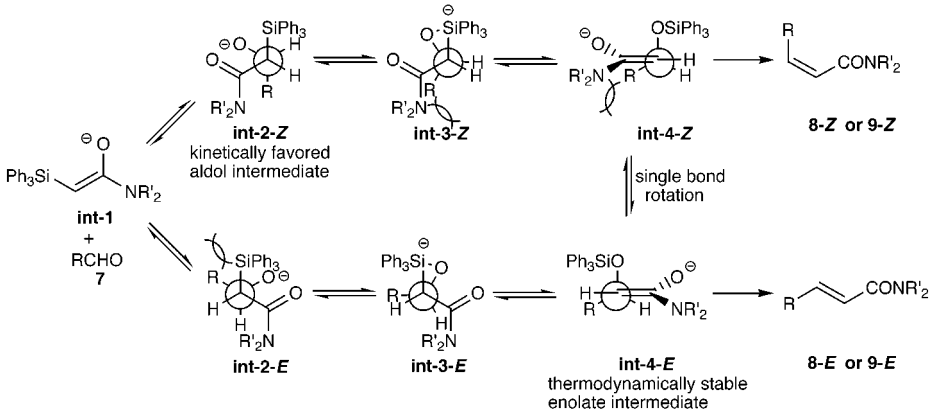
[a] All reactions were carried out in THF at −78 °C with KHMDS as base. The ratio was reagent:base:aldehyde **7h**:aldehyde **7a** (or **7j**) = 1:1:1:1. [b] Determined by 500 MHz ^{1}H NMR measurement of the crude mixture. [c] Combined isolated yield of (*E*)- and (*Z*)-olefins.

Since several aspects indicated that our Peterson reagent differed from the *Z*-selective Ando reagent (**9**) based on esters, we examined the chemoselectivity by carrying out competitive reactions (Table 8). Thus, the reaction with a reagent:aliphatic aldehyde **7h**:aromatic

(17) Kojima, S.; Hidaka, T.; Ohba, Y.; Ohkata, K. *Phosphorus, Sulfur, Silicon* **2002**, *177*, 729−732.

(18) Prof. Ando of the University of the Ryukyus has recently reported on similar amide reagents (no examples on *N*,*N*-dibenzyl amide) based on the Wadsworth−Emmons reaction: Ando, K. *Synlett* **2000**, 1272−1274.

Scheme 3



aldehyde **7a** reactant ratio of 1:1:1 for **11** slightly favored the product from the aliphatic aldehyde (entry 2). This is in line with expectations from a electronic standpoint. However, **3** turned out to slightly favor the aromatic aldehyde (entry 1). A comparison between an unbranched aldehyde and an α-branched aldehyde for **11** revealed that the aldehydes are hardly differentiated (entry 4). With **3**, as expected from the above independent reactions, only the unbranched aldehyde gave rise to product. A decrease in yield compared with the result when the aldehyde was used alone implies that when an enolizable compound is present, enolization could compete to some extent with olefination.

On the basis of empirical results, the general mechanism for the Peterson reaction can be depicted as in Scheme 3.[2,20] The kinetic aldol products of the initial addition of enolates to aldehydes in the Peterson reaction with reagents bearing electron-withdrawing groups have been determined to be erythro intermediates (corresponding to **int-2-*Z***) upon examinations of aldol adducts in the reaction of $Me_3SiCH_2CO_2R$.[3] The same has been assumed in HWE reactions.[19] In contrast to HWE reactions, however, the retro-aldol reaction leading back to enolate **int-1** and aldehyde in the Peterson reaction has generally been considered to be of less significance.[2,3] Intramolecular ring closure of the oxide **int-2-*Z*** gives the pentacoordinated intermediate **int-3-*Z***. In HWE reactions, it is commonly accepted that olefin is formed directly from the pentacoordinated oxidophosphorane intermediate (corresponding to intermediates **int-3** in Scheme 2) in a concerted manner. However, to account for the generally low selectivity, it has been suggested in the Peterson reaction that olefin formation is stepwise from the pentacoordinated silicate such as **int-3**. That is, the cleavage of the Si−C bond in **int-3** gives an enolate such as **int-4** as a short-lived intermediate and elimination of the silyloxide group follows to give the product.[2,19] The presence of an intermediate such as **int-4** allows C−C single-bond rotation to compete with the ensuing elimination step, thus opening the opportunity for intermediates such as **int-4-*Z*** to change conformation to the thermodynamically favored **int-4-*E***, the precursor to the (*E*)-olefin.

The results we have obtained here can be nicely rationalized with this mechanism. If we can assume that the substitution of Me groups with Ph on Si does not facilitate the retro-aldol reaction from **int-2-*Z***, then the unexpectedly high *Z* selectivity (for a Peterson type reaction) disclosed here can be rationalized by consideration of **int-4-*Z***. The Ph groups raise the nucleofugacity of the silyloxy group, and this in turn raises the rate of olefin formation relative to single-bond rotation, thus leading to higher *Z* content in the olefinic product. This also accounts for the fact that (*Z*)-olefins are favored even with ester reagents, as compared with corresponding trimethylsilyl reagents.[2] The presence of the amide group works in an additive manner. Since the electron-donating ability of nitrogen compared with that of oxygen leads to destabilization of the enolate anion **int-4-*Z***, compared with the ester group, the extrusion of silyl oxide becomes more facile, whereas the rate of single-bond rotation should remain essentially the same, whether the electron-withdrawing group be an amide or an ester. Electron-donating aryl groups (MeO compared with Cl) and localized charge in the enolate due to the difference in countercations (K^+ compared with Li^+) should further assist in destabilizing **int-4-*Z***, resulting in facilitated olefin formation and thus *Z* selectivity. With Li^+, the retro processes could also be more important, thus explaining the lower selectivity in general.

Conclusion

In summary, we have developed a highly geometry selective method of preparing *Z*-unsaturated amides based upon the Peterson reaction using the triphenylsilyl group. Through the examination of substituent effects upon the nitrogen atom of the amide moiety, it was revealed that the selectivity and reactivity were sensitive to the size of the substituents, with higher selectivity for the smaller groups. It was also found that the use of phenyl groups in the place of methyl groups upon silicon was essential.

Experimental Section

General Considerations. Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-LA500 spectrometer with $CDCl_3$ as solvent. ^1H NMR chemical shifts are given in relative ppm from either internal TMS (δ 0.0) or residual $CHCl_3$ (δ 7.26). ^{13}C NMR chemical shifts are given in relative ppm from internal $CDCl_3$ (δ 77.0). High-resolution mass spectra were measured on a JEOL JMS-SX102A spectrometer under electron ionization conditions (70 eV). Elemental analyses (CHN) were carried out on a Perkin-Elmer 2400CHN elemental analyzer.

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(20) Yamamoto, K.; Tomo, Y.; Suzuki, S. *Tetrahedron Lett.* **1980**, *21*, 2861−2864.

All reactions were carried under N_2. THF and ether were freshly distilled from Na−benzophenone prior to use. Liquid aldehydes were distilled before use. Silica gel column chromatography was carried out using Merck 7734 (63−200 mesh) or 9385 (230−400 mesh). Preparative thin-layer chromatography was carried out with plates prepared with Merck 7730.

***N,N*-Dibenzyl(triphenylsilyl)acetamide (1).** To dibenzylamine (4.04 mL, 21.0 mmol) and triethylamine (3.22 mL, 23.1 mmol) in THF (50 mL) was added acetyl chloride (1.49 mL, 21.0 mmol) at 0 °C. After it was stirred for 3 h at room temperature, the solution was quenched with aqueous $NaHCO_3$. After the usual workup, crude *N,N*-dibenzylacetamide was obtained as a liquid. Without further purification, this was dissolved in THF (10 mL) and added at −78 °C to LDA prepared from *n*-butyllithium (1.50 M in hexane, 28.8 mL, 43.2 mmol) and diisopropylamine (6.0 mL, 42.8 mmol). After it was warmed to 0 °C, the resulting solution was recooled to −78 °C, and triphenylsilyl chloride (6.10 g, 20.7 mmol) in THF (10 mL) was added at this temperature. The solution was quenched with saturated NH_4Cl after stirring for 2 h at room temperature. After the usual workup, the product was subjected to column chromatography (silica gel, 10/1 v/v hexane/ethyl acetate) and then recrystallized (hexane/CH_2Cl_2) to give *N,N*-dibenzyl(triphenylsilyl)acetamide (**1**) in 76% yield (7.9 g) as colorless crystals. Mp: 111−114 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.59−6.90 (m, 25H), 4.49 (s, 2H), 4.10 (s, 2H), 2.88 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.9, 137.2, 136.6, 135.0, 133.7, 129.8, 128.8, 128.5, 128.3, 127.9, 127.4, 127.1, 126.4, 50.7, 48.2, 22.6. HRMS: calcd for $C_{34}H_{31}NOSi$ 497.2175, found 497.2177. Anal. Calcd for $C_{34}H_{31}NOSi$: C, 82.05; H, 6.28; N, 2.81. Found: C, 82.11; H, 6.36; N, 2.79.

***N*-Benzyl(triphenylsilyl)acetamide (2).** A procedure similar to that for **1** was applied. Benzylamine (1.5 mL, 14 mmol), triethylamine (2.2 mL, 15 mmol), and acetyl chloride (1.0 mL, 14 mmol) gave *N*-benzylacetamide as a crude product, which was treated with LDA from *n*-butyllithium (1.53 M in hexane, 20.1 mL, 31 mmol) and diisopropylamine (4.1 mL, 31 mmol), followed by triphenylsilyl chloride (4.13 g, 14 mmol), to give *N*-benzyl(triphenylsilyl)acetamide (**2**) in 79% yield (4.5 g) as colorless crystals. Mp: 155−157 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57−7.33 (m, 15H), 7.20−7.17 (m, 3H), 6.92−6.89 (m, 2H), 5.23 (bs, 1H), 4.19 (s, 1H), 4.18 (s, 1H), 2.64 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.4, 138.0, 135.7, 133.3, 130.0, 128.5, 128.1, 127.7, 127.2, 43.8, 26.3. HRMS: calcd for $C_{27}H_{25}NOSi$ 407.1705, found 407.1716. Anal. Calcd for $C_{27}H_{25}NOSi$: C, 79.57; H, 6.18; N, 3.44. Found: C, 79.50; H, 6.06; N, 3.42.

***N,N*-Dimethyl(triphenylsilyl)acetamide (3).** A procedure similar to that for **1** was applied. From *N,N*-dimethylacetamide (0.56 mL, 6.0 mmol), LDA from *n*-butyllithium (1.53 M in hexane, 4.7 mL, 7.2 mmol), diisopropylamine (1.0 mL, 7.8 mmol), and triphenylsilyl chloride (1.70 g, 6.0 mmol) was obtained *N,N*-dimethyl(triphenylsilyl)acetamide (**3**) in 69% yield (1.43 g) as colorless crystals. Mp: 116−118 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61−7.59 (m, 6H), 7.42−7.35 (m, 9H), 2.80 (s, 2H), 2.73 (s, 3H), 2.54 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.1, 135.7, 133.6, 129.7, 127.8, 38.1, 35.1, 22.5. HRMS: calcd for $C_{22}H_{23}NOSi$ 345.1549, found 345.1582. Anal. Calcd for $C_{22}H_{23}NOSi$: C, 76.48; H, 6.71; N, 4.05. Found: C, 76.56; H, 6.82; N, 4.11.

***N,N*-Bis(methylethyl)(triphenylsilyl)acetamide (4).** A procedure similar to that for **1** was applied. From *N,N*-diisopropylacetamide (1.00 g, 7.00 mmol), LDA from *n*-butyllithium (1.6 M in hexane, 8.80 mL, 14.0 mmol), diisopropylamine (2.00 mL, 14.2 mmol), and triphenylsilyl chloride (2.47 g, 8.39 mmol) was obtained *N,N*-dimethyl(triphenylsilyl)acetamide **4** in 45% yield (1.27 g) as a colorless solid. This compound gradually decomposed upon standing. Mp: 139−141 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67−7.58 (m, 6H), 7.46−7.33 (m, 9H), 3.71 (sept, J = 6.7 Hz, 1H), 3.33 (bs, 1H), 2.77 (s, 2H), 1.22 (d, J = 6.7 Hz, 6H), 0.83 (d, J = 6.7 Hz, 6H). HRMS: calcd for $C_{26}H_{31}NOSi$ 401.2175, found 401.2178.

***N,N*-Dibenzyl(trimethylsilyl)acetamide (5).** A procedure similar to that of **1** was applied. From *N,N*-dibenzylacetamide (0.72 g, 3.0 mmol), LDA from *n*-butyllithium (1.53 M in hexane, 2.35 mL, 3.6 mmol), diisopropylamine (0.51 mL, 3.9 mmol), and trimethylsilyl chloride (0.38 mL, 3.0 mmol) was obtained *N,N*-dibenzyl(trimethylsilyl)acetamide **5** in 89% yield (0.79 g) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39−7.16 (m, 10H), 4.59 (s, 2H), 4.39 (s, 2H), 2.11 (s, 2H), 0.14 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.9, 137.8, 136.6, 128.8, 128.4, 128.3, 127.5, 127.2, 126.4, 50.6, 47.6, 25.5, −0.9. Anal. Calcd for $C_{19}H_{25}NOSi$: C, 73.26; H, 8.09; N,4.50. Found: C, 73.34; H, 8.08; N, 4.56.

General Procedures for the Peterson Reaction, Given as Examples of the Reaction of Benzaldehyde. With KHMDS as Base (Method A). To a solution of *N,N*-dibenzyl(triphenylsilyl)acetamide (**1**; 206 mg, 0.415 mmol) in THF (4 mL) cooled to −78 °C was added KHMDS (0.5 M in toluene, 0.98 mL, 0.49 mmol). After it was stirred for 30 min at 0 °C, the solution was recooled to −78 °C. To this solution was added benzaldehyde (**7a**; 39.0 mg, 0.368 mmol) in THF (2.5 mL), and stirring was continued for 3 h. Water was then added to quench the solution, and extraction was carried out with ether. After the usual workup and chromatographic purification by preparative TLC (SiO_2, 5/1 hexane/ethyl acetate), (*Z*)-*N,N*-dibenzylcinnamamide (**8a**) was obtained in 88% yield (106 mg, Z:E = >97:3).

With *n*-BuLi as Base (Method B). To a solution of *N,N*-dibenzyl(triphenylsilyl)acetamid (**1**; 206 mg, 0.415 mmol) in THF (5 mL) cooled to −78 °C was added *n*-BuLi (1.53 M in hexane, 0.27 mL, 0.42 mmol). After it was stirred for 30 min at 0 °C, the solution was recooled to −78 °C. To this solution was added benzaldehyde (**7a**; 38.8 mg, 0.366 mmol) in THF (2 mL), and stirring was continued for 1 h, after which the solution was slowly warmed to 0 °C. Water was then added to quench the reaction, and extraction was carried out with ether. After the usual workup and chromatographic purification by preparative TLC (SiO_2, 5/1 hexane/ethyl acetate), a mixture of (*Z*)- and (*E*)-*N,N*-dibenzylcinnamamide (**8a**) was obtained in 85% yield (102 mg, Z:E = 54:46). The isomers were separated by TLC (SiO_2, 5/1 hexane/ethyl acetate).

***(Z)*-*N,N*-Dibenzyl-3-phenylprop-2-enamide (8a-*Z*).** Pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39−7.20 (m, 13H), 7.06 (d, J = 6.7 Hz, 2H), 6.66 (d, J = 12.8 Hz, 1H), 6.18 (d, J = 12.8 Hz, 1H), 4.59 (s, 2H), 4.38 (s, 2H). NOE: 9.9%. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.3, 136.6, 136.3, 135.4, 134.0, 129.1, 128.9, 128.6, 128.6, 128.6, 127.7, 127.6, 127.2, 127.2, 123.2, 50.6, 46.8. HRMS: calcd for $C_{23}H_{21}NO$ 327.1623, found 327.1633.

***(E)*-*N,N*-Dibenzyl-3-phenylprop-2-enamide (8a-*E*).** Colorless solid. Mp: 128−131 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86 (d, J = 15.5 Hz, 1H), 7.47−7.21 (m, 15H), 6.90 (d, J = 15.5 Hz, 1H), 4.72 (s, 2H), 4.61 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 144.0, 137.5, 136.8, 135.3, 129.8, 129.1, 128.9, 128.8, 128.5, 128.0, 127.9, 127.6, 126.7, 117.4, 50.2, 49.0. HRMS: calcd for $C_{23}H_{21}NO$ 327.1623, found 327.1626.

***(Z)*-*N,N*-Dibenzyl-3-(4-methoxyphenyl)prop-2-enamide (8b-*Z*).** Following method A, **1** (176 mg, 0.353 mmol), KHMDS (0.5 M in toluene, 0.88 mL, 0.44 mmol), and *p*-methoxybenzaldehyde (**7b**; 38.1 mg, 0.280 mmol) gave (*Z*)-*N,N*-dibenzyl-3-(4-methoxyphenyl)prop-2-enamide in 87% yield (86.6 mg, Z:E = >97:3) as an oil.

Following method B, **1** (176 mg, 0.353 mmol), *n*-BuLi (1.53 M in hexane, 0.23 mL, 0.35 mmol), and *p*-methoxybenzaldehyde (**7b**; 39.3 mg, 0.289 mmol) gave *N,N*-dibenzyl-3-(4-methoxyphenyl)prop-2-enamide (**8b**) in 94% yield (97 mg, Z:E = 69:31) as an oil. The *E* and *Z* isomers could not be separated. **8b-*Z***: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36−7.27 (m, 10H), 7.09 (d, J = 8.5 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 12.6 Hz, 1H), 6.05 (d, J = 12.6 Hz, 1H), 4.59 (s, 2H), 4.39 (s, 2H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) d 169.3, 159.7, 136.5, 136.3, 133.6, 130.0, 129.0, 128.7, 128.5, 127.9, 127.5, 127.4, 127.1, 120.7, 113.7, 55.1, 50.4, 46.6; HRMS calcd for $C_{24}H_{23}NO_2$ 357.1729, found 357.1716.

***(E)*-*N,N*-Dibenzyl-3-(4-methoxyphenyl)prop-2-enamide (8b-*E*).** ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82 (d, J = 15.5 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H), 7.39−7.22 (m, 10H), 6.86 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 15.5 Hz, 1H), 4.71 (s, 2H), 4.60 (s, 2H), 3.81 (s, 3H).

(*Z*)-*N*,*N*-Dibenzyl-3-(2-methoxyphenyl)prop-2-enamide (8c-*Z*). Following method A, **1** (176 mg, 0.353 mmol), KHMDS (0.5 M in toluene, 0.88 mL, 0.44 mmol), and *o*-methoxybenzaldehyde (**7c**; 38.6 mg, 0.284 mmol) gave *N*,*N*-dibenzyl-3-(2-methoxyphenyl)prop-2-enamide (**8c**) in 72% yield (72.6 mg, *Z*:*E* = 81:19) as an oil. The *E* and *Z* isomers could not be separated. **8c-*Z***: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.45 (dd, J = 7.6, 1.5 Hz, 1H), 7.31−7.23 (m, 9H), 7.19−7.15 (m, 1H), 7.07−7.03 (m, 1H), 6.97 (d, J = 12.5 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.79 (t, J = 7.6 Hz, 1H), 6.18 (d, J = 12.5 Hz, 1H), 4.54 (s, 2H), 4.35 (s, 2H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.5, 156.8, 136.5, 136.3, 129.8, 129.7, 129.4, 128.8, 128.7, 128.4, 127.5, 127.3, 127.1, 124.5, 122.7, 120.4, 110.4, 55.3, 50.3, 46.5; HRMS calcd for $C_{24}H_{23}NO_2$ 357.1729, found 357.1723.

(*E*)-*N*,*N*-Dibenzyl-3-(2-methoxyphenyl)prop-2-enamide (8c-*E*). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.08 (d, J = 15.5 Hz, 1H), 7.40−7.22 (m, 10H), 7.19−7.15 (m, 2H), 7.05 (d, J = 15.5 Hz, 1H), 7.07−7.03 (m, 1H), 6.92−6.87 (m, 1H), 4.72 (s, 2H), 4.60 (s, 2H), 3.80 (s, 3H).

(*Z*)-*N*,*N*-Dibenzyl-3-(4-chlorophenyl)prop-2-enamide (8d-*Z*). Following method A, **1** (206 mg, 0.413 mmol), KHMDS (0.5 M in toluene, 0.85 mL, 0.425 mmol), and *p*-chlorobenzaldehyde (**7d**, 38.9 mg, 0.276 mmol) gave *N*,*N*-dibenzyl-3-(4-chlorophenyl)prop-2-enamide (**8d**) in 91% yield (91.2 mg, *Z*:*E* = 88:12). The isomers were separated by TLC (SiO_2, 5/1 hexane/ethyl acetate).

Following method B, **1** (365 mg, 0.733 mmol), *n*-BuLi (1.53 M in hexane, 0.50 mL, 0.765 mmol), and *p*-chlorobenzaldehyde (**7d**; 51.5 mg, 0.366 mmol) gave *N*,*N*-dibenzyl-3-(4-chlorophenyl)prop-2-enamide (**8d**) in 95% yield (126 mg, *Z*:*E* = 43:57) as an oil. The isomers were separated by TLC (SiO_2, 5/1 hexane/ethyl acetate). **8d-*Z***: colorless solid; mp 68−70 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36−7.25 (m, 10 H), 7.18 (d, J = 8.5 Hz, 2H), 7.07 (m, 2H), 6.60 (d, J = 12.5 Hz, 1H), 6.20 (d, J = 12.5 Hz, 1H), 4.57 (s, 2H), 4.38 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.7, 136.3, 136.0, 134.3, 133.7, 132.8, 129.8, 128.9, 128.8, 128.6, 128.5, 127.7, 127.6, 127.0, 123.7, 50.4, 46.7; HRMS calcd for $C_{23}H_{20}{}^{37}ClNO$ 363.1204, found 363.1207; HRMS calcd for $C_{23}H_{20}{}^{35}ClNO$ 361.1233, found 361.1225.

(*E*)-*N*,*N*-Dibenzyl-3-(4-chlorophenyl)prop-2-enamide (8d-*E*). Mp: 131−134 °C. Colorless solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80 (d, J = 15.5 Hz, 1H), 7.39−7.26 (m, 12H), 7.21 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 15.5 Hz, 1H), 4.71 (s, 2H), 4.60 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 142.4, 137.2, 136.6, 135.5, 133.6, 129.0, 129.0, 128.9, 128.6, 128.3, 127.7, 127.5, 126.5, 117.8, 50.0, 48.9. HRMS: calcd for $C_{23}H_{20}{}^{37}ClNO$ 363.1204, found 363.1217. HRMS: calcd for $C_{23}H_{20}{}^{35}ClNO$ 361.1233, found 361.1232.

(*Z*)-*N*,*N*-Dibenzyl-3-(2-furyl)prop-2-enamide (8e-*Z*). Following method A, **1** (164 mg, 0.330 mmol), KHMDS (0.5 M in toluene, 0.67 mL, 0.335 mmol), and furfural (**7e**; 20.8 mg, 0.217 mmol) gave *N*,*N*-dibenzyl-3-(2-furyl)prop-2-enamide (**8e**) in 92% yield (63.4 mg, *Z*:*E* = 91:9). The isomers were separated by TLC (SiO_2, 5/1 hexane/ethyl acetate). **8e-*Z***: off-white solid; mp 59−61 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40−7.24 (m, 9H), 7.14 (d, J = 7.0 Hz, 2H), 6.64 (d, J = 3.4 Hz, 1H), 6.48 (d, J = 12.8 Hz, 1H), 6.37 (dd, J = 3.4, 1.8 Hz, 1H), 6.03 (d, J = 12.8 Hz, 1H), 4.63 (s, 2H), 4.45 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.7, 150.8, 143.3, 136.9, 136.4, 129.0, 128.8, 128.4, 127.6, 127.4, 127.0, 122.1, 119.0, 112,7, 111.7, 50.5, 46.7; HRMS calcd for $C_{21}H_{19}NO_2$ 317.1416, found 317.1421.

(*E*)-*N*,*N*-Dibenzyl-3-(4-furyl)prop-2-enamide (8e-*E*). Off-white oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, J = 14.9 Hz, 1H), 7.41−7.19 (m, 11H), 6.84 (d, J = 14.9 Hz, 1H), 6.56 (d, J = 3.4 Hz, 1H), 6.43 (dd, J = 3.4, 1.8 Hz, 1H), 4.69 (s, 2H), 4.59 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.30, 151.77, 144.19, 135.14, 130.76, 130.24, 129.09, 128.77, 128.48, 128.07, 127.57, 126.89, 114.81, 114.31, 112.32, 50.15, 48.80. HRMS: calcd for $C_{21}H_{19}NO_2$ 317.1416, found 317.1411.

(*Z*)-*N*,*N*-Dibenzyl-3-(2-pyridyl)prop-2-enamide (8f-*Z*). Following method A, **1** (205 mg, 0.412 mmol), KHMDS (0.5 M in toluene, 0.84 mL, 0.42 mmol), and 2-pyridylaldehyde (**7f**; 39.1 mg, 0.365 mmol) gave *N*,*N*-dibenzyl-3-(2-pyridyl)prop-2-enamide (**8f**) in 47% yield (56.1 mg, *Z*:*E* = 59:41). The isomers were separated by TLC (SiO_2, 5/1 hexane/ethyl acetate). **8f-*Z***: off-white solid; mp 71−72 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.45 (d, J = 5.1 Hz, 1H), 7.57 (td, J = 7.3, 1.8 Hz, 1H), 7.45 (d, J = 7.3 Hz, 2H), 7.39−7.28 (m, 7H), 7.15−7.13 (m, 3H), 6.67 (d, J = 12.5 Hz, 1H), 6.32 (d, J = 12.5 Hz, 1H), 4.64 (s, 2H), 4.43 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.6, 153.6, 149.3, 136.8, 136.6, 136.5, 132.0, 129.1, 128.8, 128.4, 127.5, 127.3, 127.1, 126.7, 123.7, 122.8, 50.5, 46.6; HRMS calcd for $C_{22}H_{20}N_2O$ 328.1576, found 328.1583.

(*E*)-*N*,*N*-Dibenzyl-3-(2-pyridyl)prop-2-enamide (8f-*E*). Viscous off-white oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.57 (d, J = 4.3 Hz, 1H), 7.82 (d, J = 15.0 Hz, 1H), 7.68 (td, J = 7.6, 1.5 Hz, 1H), 7.59 (d, J = 15.0 Hz, 1H), 7.46−7.03 (m, 12H), 4.69 (s, 2H), 4.65 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.9, 153.3, 149.8, 142.1, 137.1, 136.9, 136.5, 128.9, 128.6, 128.3, 127.7, 127.4, 126.9, 124.9, 123.9, 121.5, 50.0, 48.3. HRMS: calcd for $C_{22}H_{20}N_2O$ 328.1576, found 328.1584.

(*Z*,*E*)-*N*,*N*-Dibenzyl-5-phenylpenta-2,4-dienamide (8g-*Z*). Following method A, **1** (181 mg, 0.363 mmol), KHMDS (0.5 M in toluene, 0.72 mL, 0.36 mmol), and *trans*-cinnamaldehyde (**7g**; 38.5 mg, 0.291 mmol) gave *N*,*N*-dibenzyl-5-phenylpenta-2,4-dienamide in 99% yield (103 mg, *E*,*Z*:*E*,*E* = 81:19). The isomers were separated by TLC (SiO_2, 5/1 hexane/ethyl acetate). **8g-*Z***: colorless solid; mp 89−90 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.88 (ddd, J = 15.8, 11.3, 1.2 Hz, 1H), 7.50−7.19 (m, 15H), 6.76 (d, J = 15.8 Hz, 1H), 6.62 (ddd, J = 11.3, 11.3, 1.2 Hz, 1H), 6.11 (d, J = 11.3 Hz, 1H), 4.68 (s, 2H), 4.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.0, 140.6, 139.2, 137.5, 136.7, 136.7, 129.1, 128.8, 128.8, 128.7, 128.5, 127.8, 127.6, 127.4, 126.8, 125.4, 119.4, 50.6, 47.9; HRMS calcd for $C_{25}H_{23}NO$ 353.1780, found 353.1783.

(*E*,*E*)-*N*,*N*-Dibenzyl-5-phenylpenta-2,4-dienamide (8g-*E*). Colorless solid. Mp: 104−106 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (ddd, J = 14.6, 9.4, 0.9 Hz, 1H), 7.50−7.15 (m, 15H), 6.88 (t, J = 14.6 Hz, 1H), 6.87 (d, J = 9.4 Hz, 1H), 6.47 (d, J = 14.6 Hz, 1H), 4.69 (s, 2H), 4.56 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.3, 143.9, 139.5, 136.3, 135.0, 130.1, 129.0, 128.7, 128.6, 128.4, 127.9, 127.7, 127.4, 127.1, 126.9, 126.5, 120.4, 50.0, 48.8. HRMS: calcd for $C_{25}H_{23}NO$ 353.1780, found 353.1771.

(*Z*)-*N*,*N*-Dibenzyl-5-phenylpent-2-enamide (8h-*Z*). Following method A, **1** (178 mg, 0.358 mmol), KHMDS (0.5 M in toluene, 0.72 mL, 0.36 mmol), and 3-phenylpropionaldehyde (**7h**; 41.3 mg, 0.308 mmol) gave *N*,*N*-dibenzyl-5-phenylpent-2-enamide (**8h**) in 77% yield (84.1 mg, *Z*:*E* = 91:9) as an oil. The *E* and *Z* isomers could not be separated. The replacement of KHMDS with NaHMDS resulted in 54% yield and an identical selectivity of *Z*:*E* = 91:9. **8h-*Z***: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36−7.09 (m, 15H), 6.08 (dt, J = 11.6, 1.5 Hz, 1H), 5.96 (dt, J = 11.6, 7.0 Hz, 1H), 4.57 (s, 2H), 4.25 (s, 2H), 2.80−2.77 (m, 4H); NOE 6.2%; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.0, 141.4, 141.1, 137.0, 136.2, 128.7, 128.4, 128.3, 128.2, 128.1, 127.4, 127.2, 126.4, 125.7, 122.3, 49.9, 47.0, 35.0, 30.9; HRMS calcd for $C_{25}H_{25}NO$ 355.1909, found 355.1922.

(*E*)-*N*,*N*-Dibenzyl-5-phenylpent-2-enamide (8h-*E*). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67 (dt, J = 16.7, 1.5 Hz, 1H), 7.42−7.08 (m, 15H), 6.24 (dt, J = 14.9, 1.5 Hz, 1H), 4.62 (s, 2H), 4.42 (s, 2H), 2.75 (t, J = 7.3 Hz, 2H), 2.51 (td, J = 7.3, 1.5 Hz, 2H).

(*Z*)-*N*,*N*-Dibenzyl-3-cyclohexylprop-2-enamide (8i-*Z*). Following method A, **1** (120 mg, 0.242 mmol), KHMDS (0.5 M in toluene, 0.48 mL, 0.24 mmol), and cyclohexanecarboxaldehyde (**7i**; 22.8 mg, 0.203 mmol) gave *N*,*N*-dibenzyl-3-cyclohexylprop-2-enamide (**8i**) in 83% yield (56.0 mg, *Z*:*E* = 83:17). The isomers were separated by TLC (SiO_2, 10/1 hexane/ethyl acetate). **8i-*Z***: pale yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37−7.21 (m, 8H), 7.15 (d, J = 7.3 Hz, 2H), 5.99 (d, J = 11.5 Hz, 1H), 5.75 (dd, J = 11.5, 9.7 Hz, 1H), 4.60 (s, 2H), 4.46 (s, 2H), 2.88−2.79 (m, 1H), 1.79−1.67 (m, 5H), 1.39−1.28 (m, 2H), 1.21−1.14 (m, 1H), 1.14−1.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.7, 147.8, 135.1, 129.0, 128.7, 128.5, 128.0, 127.7, 127.5, 126.9, 120.0, 50.6, 47.2, 38.3, 32.7, 26.1, 25.7; HRMS calcd for $C_{23}H_{27}NO$ 333.2093, found 333.2082.

(*E*)-*N*,*N*-Dibenzyl-3-cyclohexylprop-2-enamide (8i-*E*). Pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.39−7.21 (m,

8H), 7.17 (d, J = 7.3 Hz, 2H), 7.02 (dd, J = 15.2, 7.3 Hz, 1H), 6.23 (dd, J = 15.2, 1.2 Hz, 1H), 4.64 (s, 2H), 4.50 (s, 2H), 2.15−2.07 (m, 1H), 1.76−1.68 (m, 4H), 1.67−1.60 (m, 1H), 1.31−1.07 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.7, 153.1, 137.6, 136.9, 129.0, 128.6, 128.5, 127.7, 127.4, 126.7, 117.7, 50.0, 48.6, 40.9, 32.1, 26.0, 25.8. HRMS: calcd for $C_{23}H_{27}NO$ 333.2093, found 333.2083.

(*Z*)-*N*,*N*-Dimethyl-3-phenylprop-2-enamide (9a-*Z*). Following method A, **3** (143 mg, 0.415 mmol), KHMDS (0.5 M in toluene, 0.98 mL, 0.49 mmol), and benzaldehyde (**7a**; 40.2 mg, 0.379 mmol) gave *N*,*N*-dimethyl-3-phenylprop-2-enamide (**9a**) in 78% yield (51.5 mg, *Z*:*E* = >97:3) as an oil.

Following method B, **3** (156 mg, 0.452 mmol), *n*-butyllithium (1.53 M in hexane, 0.30 mL, 0.452 mmol), and benzaldehyde (**7a**; 38.5 mg, 0.363 mmol) gave *N*,*N*-dimethyl-3-phenylprop-2-enamide (**9a**) in 87% yield (55.3 mg, *Z*:*E* = 90:10) as an oil. The *E* and *Z* isomers could not be separated. **9a-*Z***: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36−7.26 (m, 5H), 6.65 (d, J = 12.5 Hz, 1H), 6.05 (d, J = 12.5 Hz, 1H), 2.98 (s, 3H), 2.83 (s, 3H). NOE 5.7%. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.8, 135.5, 133.1, 128.4, 128.3, 128.0, 123.3, 37.3, 34.2; HRMS calcd for $C_{11}H_{13}NO$ 175.0997, found 175.1013.

(*E*)-*N*,*N*-Dimethyl-3-phenylprop-2-enamide (9a-*E*). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67 (d, J = 15.5 Hz, 1H), 7.54−7.52 (m, 2H), 7.38−7.30 (m, 3H), 6.89 (d, J = 15.5 Hz, 1H), 3.16 (br s, 3H), 3.09 (br s, 3H).

(*Z*)-*N*,*N*-Dimethyl-3-(4-methoxyphenyl)prop-2-enamide (9b-*Z*). Following method A, **3** (122 mg, 0.353 mmol), KHMDS (0.5 M in toluene, 0.88 mL, 0.44 mmol), and *p*-methoxybenzaldehyde (**7b**; 40.2 mg, 0.295 mmol) gave *N*,*N*-dimethyl-3-(4-methoxyphenyl)prop-2-enamide (**9b**) in 99% yield (60.1 mg, *Z*:*E* = >97:3) as an oil.

Following method B, **3** (122 mg, 0.353 mmol), *n*-butyllithium (1.53 M in hexane, 0.23 mL, 0.353 mmol), and *p*-methoxybenzaldehyde (**7b**; 39.2 mg, 0.288 mmol) gave *N*,*N*-dimethyl-3-(4-methoxyphenyl)prop-2-enamide (**9b**) in 95% yield (56.0 mg, *Z*:*E* = >97:3) as an oil. The *E* and *Z* isomers could not be separated. **9b-*Z***: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.58 (d, J = 12.5 Hz, 1H), 5.93 (d, J = 12.5 Hz, 1H), 3.81 (s, 3H), 2.99 (s, 3H), 2.87 (s, 3H); NOE 5.7%; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.1, 159.5, 132.8, 129.6, 128.2, 121.1, 113.8, 55.1, 37.4, 34.2; HRMS calcd for $C_{12}H_{15}NO_2$ 205.1103, found 205.1105.

(*Z*)-*N*,*N*-Dimethyl-3-(2-methoxyphenyl)prop-2-enamide (9c-*Z*). Following method A, **3** (134 mg, 0.390 mmol), KHMDS (0.5 M in toluene, 0.78 mL, 0.390 mmol), and 2-methoxybenzaldehyde (**7c**; 40.5 mg, 0.297 mmol) gave *N*,*N*-dimethyl-3-(2-methoxyphenyl)prop-2-enamide (**9c**) in 53% yield (32.2 mg, *Z*:*E* = 78:22) as a pale yellow oil. The *E* and *Z* isomers could not be separated. **9c-*Z***: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35−7.22 (m, 2H), 6.96−6.83 (m, 2H), 6.93 (d, J = 12.5 Hz, 1H), 6.02 (d, J = 12.5 Hz, 1H), 3.82 (s, 3H), 2.91 (s, 3H), 2.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.2, 156.8, 129.7, 129.0, 128.7, 124.8, 122.9, 120.5, 110.5, 55.4, 37.4, 34.3; HRMS (FAB) calcd for $C_{12}H_{16}NO_2$ 206.1181, found 206.1187.

(*E*)-*N*,*N*-Dimethyl-3-(2-methoxyphenyl)prop-2-enamide (9c-*E*). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.91 (d, J = 15.5 Hz, 1H), 7.49 (dd, J = 7.62, 1.22 Hz, 1H), 7.35−7.22 (m, 1H), 7.00 (d, J = 15.5 Hz, 1H), 6.96−6.83 (m, 2H), 3.86 (s, 3H), 3.14 (s, 3H), 3.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.3, 158.1, 137.7, 130.5, 128.9, 124.3, 120.5, 118.4, 111.1, 55.4, 37.3, 35.8.

(*Z*)-*N*,*N*-Dimethyl-3-(4-chlorophenyl)prop-2-enamide (9d-*Z*). Following method A, **3** (152 mg, 0.440 mmol), KHMDS (0.5 M in toluene, 0.90 mL, 0.45 mmol), and *p*-chlorobenzaldehyde (**7d**; 43.3 mg, 0.308 mmol) gave *N*,*N*-dimethyl-3-(4-chlorophenyl)prop-2-enamide (**9d**) in 66% yield (42.3 mg, *Z*:*E* = 97:3) as an oil. Following method B, **3** (138 mg, 0.399 mmol), *n*-butyllithium (1.54 M in hexane, 0.26 mL, 0.400 mmol), and *p*-chlorobenzaldehyde (**7d**, 28.4 mg, 0.202 mmol) gave *N*,*N*-dimethyl-3-(4-chlorophenyl)prop-2-enamide (**9d**) in 54% yield (22.8 mg, *Z*:*E* = 90:10) as an oil. The *E* and *Z* isomers could not be separated. **9d-*Z***: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.31 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 12.5 Hz, 1H), 6.07 (d, J = 12.5 Hz, 1H), 2.98 (s, 3H), 2.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.4, 134.1, 134.0, 132.0, 129.4, 128.6, 123.9, 37.4, 34.3; HRMS calcd for $C_{11}H_{12}{}^{37}ClNO$ 211.0578, found 211.0572; HRMS calcd for $C_{11}H_{12}{}^{35}ClNO$ 209.0607, found 209.0606.

(*E*)-*N*,*N*-Dimethyl-3-(4-chlorophenyl)prop-2-enamide (9d-*E*). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61 (d, J = 15.5 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 15.5 Hz, 1H), 3.17 (s, 3H), 3.07 (s, 3H).

(*Z*)-*N*,*N*-Dimethyl-5-phenylpent-2-enamide (9h-*Z*). Following method A, **3** (113 mg, 0.328 mmol), KHMDS (0.5 M in toluene, 0.78 mL, 0.39 mmol), and 3-phenylpropionaldehyde (**7h**; 40.3 mg, 0.300 mmol) gave *N*,*N*-dimethyl-5-phenylpent-2-enamide (**9h**) in 72% yield (44 mg, *Z*:*E* = 92:8) as an oil. The *E* and *Z* isomers could not be separated. **9h-*Z***: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28−7.25 (m, 2H), 7.21−7.16 (m, 3H), 5.99 (dt, J = 11.6, 1.5 Hz, 1H), 5.91 (dt, J = 11.6, 7.0 Hz, 1H), 2.91 (s, 6H), 2.77−2.67 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.7, 141.3, 139.9, 128.4, 128.2, 125.8, 122.6, 37.4, 35.1, 34.5, 30.6; HRMS calcd for $C_{13}H_{17}NO$ 203.1310, found 203.1343.

(*E*)-*N*,*N*-Dimethyl-5-phenylpent-2-enamide (9h-*E*). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.30−7.27 (m, 2H), 7.20−7.17 (m, 3H), 6.89 (dt, J = 15.2, 7.0 Hz, 1H), 6.22 (dt, J = 15.2, 1.2 Hz, 1H), 2.99 (s, 6H), 2.78 (t, J = 7.3 Hz, 2H), 2.53 (tdd, J = 7.3, 7.0, 1.2 Hz, 2H).

(*Z*)-*N*,*N*-Dimethyl-3-cyclohexylprop-2-enamide (9i-*Z*). Following method A, **3** (153 mg, 0.443 mmol), KHMDS (0.5 M in toluene, 0.90 mL, 0.45 mmol), and cyclohexanecarboxaldehyde (**7i**; 34.2 mg, 0.305 mmol) gave *N*,*N*-dimethyl-3-cyclohexylprop-2-enamide (**9i**) in 44% yield (24.4 mg, *Z*:*E* = 88:12). The isomers were separated by TLC (SiO_2, 4/1 hexane/ethyl acetate). **9i-*Z***: pale yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.87 (d, J = 11.6 Hz, 1H), 5.70 (dd, J = 11.6, 9.8 Hz, 1H), 3.02 (s, 3H), 2.98 (s, 3H), 2.77−2.65 (m, 1H), 1.76−1.60 (m, 5H), 1.38−1.24 (m, 2H), 1.22−1.01 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 168.1, 146.7, 119.9, 38.0, 37.9, 34.7, 32.6, 26.0, 25.5; HRMS calcd for $C_{11}H_{19}NO$ 181.1467, found 181.1476.

(*E*)-*N*,*N*-Dimethyl-3-cyclohexylprop-2-enamide (9i-*E*). Pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.83 (dd, J = 15.2, 7.0 Hz, 1H), 6.18 (dd, J = 15.2, 1.5 Hz, 1H), 3.07 (s, 3H), 3.00 (s, 3H), 2.18−2.08 (m, 1H), 1.81−1.72 (m, 4H), 1.71−1.63 (m, 1H), 1.35−1.24 (m, 2H), 1.24−1.11 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.4, 151.5, 117.8, 40.9, 37.5, 35.9, 32.2, 26.2, 26.0.

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