Organic LETTERS

Letter

pubs.acs.org/OrgLett

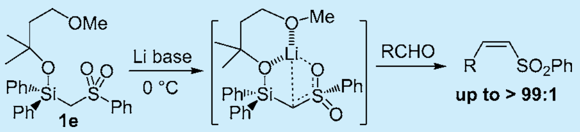
Stereoselective Synthesis of *Z*-*α*,*β*-Unsaturated Sulfones Using Peterson Reagents

Kaori Ando,* Tomohiro Wada, Miho Okumura, and Hiroshi Sumida

Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan

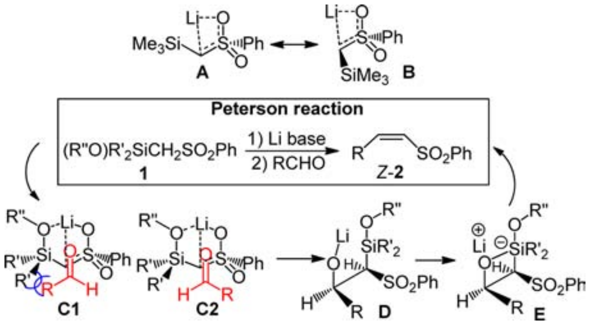
Supporting Information

ABSTRACT: New Peterson reagents were prepared by introducing alkyloxy groups on the silicon atom in order to fix the conformation of the sulfone anion. The reagents **1d** and **1e** reacted with a variety of aldehydes after the treatment with Li-base to give *Z*-*α*,*β*-unsaturated sulfones with up to >99:1 selectivity in good to excellent yields. For the reaction with aliphatic aldehydes, CPME (cyclopentyl methyl ether) is the choice of solvent, while DME (1,2-dimethoxyethane) gave higher selectivity for the reaction with aromatic aldehydes.



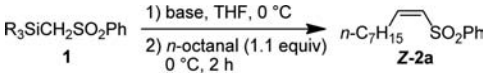
α,*β*-Unsaturated sulfones[1] are useful substrates in stereospecific reactions for the construction of chiral centers, such as the Michael reaction,[2] epoxidation,[3] and the Heck reaction.[4] In addition, some vinyl sulfones are known as cysteine protease inhibitors[5] and neuroprotective agents for Parkinson's disease therapy.[6] Therefore, the stereodefined synthesis of carbon–carbon double bonds with high selectivity is critically important. Although it is rather easy to obtain the thermodynamically stable *E*-*α*,*β*-unsaturated sulfones, there is no general method to obtain *Z*-isomers. For special cases, iodosulfonylation of terminal alkynes followed by reductive cleavage of the C–I bond,[7] nucleophilic addition of thiols to acetylene followed by oxidation,[8] and others[9] were reported. Mori and co-workers reported stereoselective epoxidation of *Z*-*α*,*β*-unsaturated sulfones having a chiral center at the *γ*-position, and the products were elegantly transformed to *trans*-fused tetrahydropyran rings which are frequently encountered cyclic units of marine toxins.[3] Unfortunately, they prepared the starting *Z*-*α*,*β*-unsaturated sulfones by the Peterson reaction[10] of $Me_3SiCH_2SO_2Ph$ with chiral aldehydes as a 1:1 mixture (*Z*/*E*) following Ley's procedure.[11] The reason for this non-stereoselectivity seems to be the presence of two conformers **A** and **B** for the sulfone anions[12] (Scheme 1). In order to fix the conformation of the sulfone anion, we planned to introduce an alkyloxy group on the silicon atom of the Peterson reagent. The anion derived from **1** would be expected to have a chelate structure. When that anion reacts with aldehyde, two plausible transition structures **C1** and **C2** could potentially arise. Moreover, if R′ is large, the structure **C1** would suffer from steric repulsion between the R group of the aldehyde and the R′ group on the silicon atom. Thus, reaction occurs via **C2** to give **D**, from which *Z*-*α*,*β*-unsaturated sulfone **2** would be obtained via the intermediate **E**.[13] In order to test this working hypothesis, the reagents **1** were prepared and the reactions of **1** with a variety of aldehydes were studied. Here, we wish to report the *Z*-selective preparation of *α*,*β*-unsaturated sulfones using new Peterson reagents **1**.

Scheme 1. Our Working Hypothesis for a New Peterson Reagent



In order to see the effects of the alkyloxy group, the reaction of the reagents **1** with *n*-octanal was performed (Table 1).

Table 1. Peterson Reaction of 1 with *n*-Octanal



entry	R_3Si, **1**	base (equiv)	yield (%)	*Z*/*E*
1	(*t*BuO)Ph_2Si, **1a**	*n*-BuLi (0.9)	92	81:19
2	Ph_3Si, **3**	*n*-BuLi (0.9)	32	22:78
3	(*t*BuO)Me_2Si, **1b**	*n*-BuLi (0.9)	89	64:36
4	**1a**	LiHMDS (1.3)	91	79:21
5	(Et_2CHO)Ph_2Si, **1c**	LiHMDS (1.3)	71	76:24

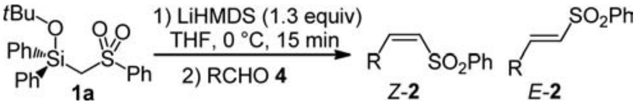
When the (*t*-BuO)Ph_2Si reagent **1a**[14,15] was treated with *n*-BuLi (0.9 equiv)[16] in THF at 0 °C for 30 min and the resulting anion reacted with *n*-octanal at 0 °C, *α*,*β*-unsaturated sulfone **2a** was obtained with 81:19 *Z*-selectivity in 92% yield (entry 1 in Table 1). For comparison, the same reaction was performed using $Ph_3SiCH_2SO_2Ph$ **3** instead of **1a**. The alkene **2a** was obtained in 32% yield with 22:78 *E*-selectivity (entry 2). Thus, we had

Received: October 17, 2015
Published: December 4, 2015

DOI: 10.1021/acs.orglett.5b03008
Org. Lett. 2015, 17, 6026–6029

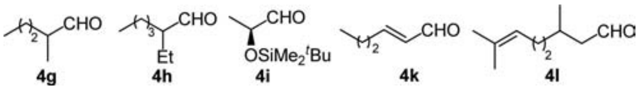
succeeded in the selective preparation of *Z*-**2a** by introducing a *t*-BuO group on the silicon atom of the Peterson reagent. The (*t*-BuO)Me_2Si reagent **1b** gave lower 64:36 selectivity by the same procedure (entry 3). The *Z*-selectivity of the (Et_2CHO)-Ph_2Si reagent **1c** using LiHMDS (1.3 equiv) was also lower than that of **1a** (entries 4 and 5), and the yield of **1c** was low probably due to the low stability of **1c**. From this screening, **1a** looked to be the most promising reagent tested here.

Table 2. Peterson Reactions of 1a with Aldehydes



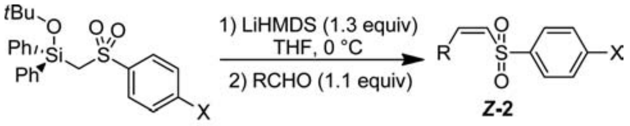
entry	4, R	conditions	2, yield (%)	*Z*/*E*
1[a]	Ph	−78 °C, 1 h	**2b**, 93	90:10
2	Ph	−78 °C, 1 h	**2b**, 76	90:10
3	Ph	0 °C, 2 h	**2b**, 81	91:9
4	*p*-MeC_6H_4	0 °C, 2 h	**2c**, 86	91:9
5	*p*-$MeOC_6H_4$	0 °C, 2 h	**2d**, 61	88:12
6[b]	*p*-ClC_6H_4	0 °C, 2 h	**2e**, 73	86:14
7	*p*-ClC_6H_4	−78 to 0 °C	**2e**, 90	82:18
8	*n*-C_7H_{15}	0 °C, 2 h	**2a**, 91	79:21
9	*n*-C_7H_{15}	−20 °C, 2 h	**2a**, 96	76:24
10	*n*-C_7H_{15}	rt, 2 h	**2a**, 70	74:26
11[a,b]	*n*-C_7H_{15}	0 °C, 2 h	**2a**, 92	81:19
12	*c*-Hex	0 °C, 2 h	**2f**, 97	94:6
13	**4g**	0 °C, 2 h	**2g**, 85	94:6
14	**4h**	0 °C, 2 h	**2h**, 85	96:4
15	**4i**	0 °C, 3 h	**2i**, 73	74:26
16[a,b]	*t*-Bu	0 °C, 4 h	**2j**, 55	69:31
17	**4k**	0 °C, 2 h	**2k**, 76	86:14

[a] *n*-BuLi was used as base. [b] 0.9 equiv of base was used.



Further optimization of the reaction conditions was performed using **1a**. When **1a** was treated with *n*-BuLi (1.3 equiv) in THF at 0 °C and the anion reacted with benzaldehyde at −78 °C, **2b** was obtained in 93% yield with 90:10 *Z*-selectivity (entry 1 in Table 2). Although the use of LiHMDS instead of *n*-BuLi gave the same selectivity at −78 °C, slightly higher selectivity (91:9) was obtained at 0 °C (entries 2 and 3). It is unclear why the Z-selectivity is higher at the higher temperature. Since the use of NaHMDS and KHMDS at −78 °C gave **2b** with *Z*/*E* = 76:24 and 35:65 ratio, respectively, it is important to use Li base. The use of toluene as solvent gave lower selectivity (*Z*/*E* = 36:64) in 40% yield along with the recovered **1a** (40%) at −78 °C. The reaction of **1b**, **1c**, and **3** with benzaldehyde gave **2b** with *Z*/*E* = 46:54 (62% yield), 51:49 (67% yield), and 21:79 (64% yield), respectively. The reactions of **1a** with *p*-tolualdehyde and *p*-anisaldehyde under the same conditions as entry 3 gave the corresponding alkenes **2c** and **2d** with 91:9 and 88:12 *Z*-selectivity, respectively (entries 4 and 5). The reaction with *p*-chlorobenzaldehyde under the same conditions (1.3 equiv of LiHMDS at 0 °C for 2 h) gave **2e** with 58:42 *Z*-selectivity (62% yield). When the same reaction was performed by using LiHMDS (0.9 equiv), an 86:14 ratio was obtained in 73% yield (entry 6). It seems that both decomposition and isomerization of **2e** occur in the presence of excess base at 0 °C or higher temperature. In fact, the reaction with *p*-chlorobenzaldehyde using LiHMDS (1.3 equiv) at room temperature gave 1:99 *E*-selectivity in 17% yield. The selectivity dropped to 82:18 at lower temperature in 90% yield (entry 7). Next, the reactions of **1a** with aliphatic aldehydes were studied. The reaction with *n*-octanal was also performed at 0 °C and gave 79:21 selectivity (entry 8). Interestingly, lower selectivity was obtained at both −20 °C and room temperature (entries 9 and 10). The highest selectivity was obtained by using *n*-BuLi (0.9 equiv) at 0 °C (81:19, 92% yield) (entry 11). The reaction of **1a** with cyclohexanecarbaldehyde gave **2f** in 97% yield with 94:6 *Z*-selectivity (entry 12). In the same procedure, the reactions with 2-methylpentanal **4g** and 2-ethylhexanal **4h** gave the corresponding alkenes with 94:6 and 96:4 *Z*-selectivity (entries 13 and 14). The reactions with more hindered **4i** and pivalaldehyde gave **2i** and **2j** with 74:26 and 69:31 *Z*-selectivity, respectively (entries 15 and 16). In addition, the reaction with *trans*-2-hexenal **4k** gave a moderate selectivity (86:14, entry 17). Thus, we succeeded in preparing *Z*-**2** by the reaction of **1a** with *α*-branched aldehydes highly selectively. However, there is still room for improvement for other types of aldehydes.

Scheme 2. Effects of the Substituent on Aryl Sulfones

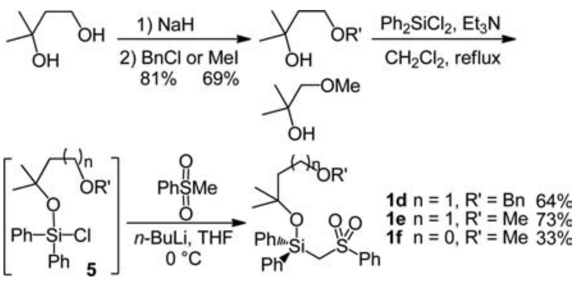


	X = H (**1a**)	Cl	Me	OMe	conditions
PhCHO	90:10	87:13	92:8	85:15	-78 °C, 2 h
n-octanal	79:21	74:26	85:15	79:21	0 °C, 2 h

The effect of the substituent on the aryl sulfones were also studied as shown in Scheme 2. When the reaction with benzaldehyde was performed at −78 °C, the *Z*/*E* ratios were 90:10, 87:13, 92:8, and 85:15 for the reagent having X = H, Cl, Me, OMe, respectively. The *p*-tolyl sulfone reagent gave the highest *Z*-selectivity (92:8) in a good yield (80%). A similar trend was observed for the reaction with *n*-octanal. Thus, the selectivity was slightly improved by using the *p*-tolyl sulfone reagent. In other words, our new method will be useful for various aryl sulfones due to the small substituent effect.

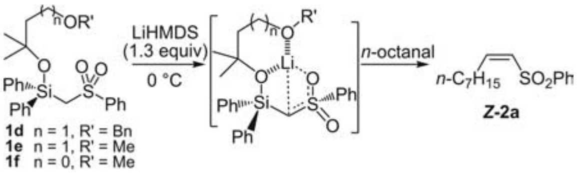
In order to improve the *Z*-selectivity, we prepared the reagents having alkoxyalkyloxy groups on the silicon atom, which were expected to have a stronger chelate structure when they were treated with Li base (Scheme 3). Monoprotection of 3-methylbutane-1,3-diol followed by the reaction with Ph_2SiCl_2 gave **5**. The reaction of the crude silyl chlorides **5** with the anion derived from $PhSO_2Me$ gave **1d** and **1e** in good yields.

Scheme 3. Preparation of New Peterson Reagents 1d,e,f



The reagent **1f** was obtained from commercially available 1-methoxy-2-methyl-2-propanol by the same procedure.

Table 3. Peterson Reactions of 1d–f with *n*-Octanal



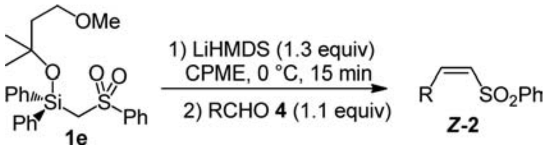
entry	1	solvent	conditions	yield (%)	*Z*/*E*
1[a]	**1d**	THF	0 °C, 2 h	79	82:18
2[a]	**1d**	toluene	0 °C, 4 h	60	92:8
3	**1d**	toluene	0 °C, 1 h	84	91:9
4[b]	**1d**	toluene	−78 °C, 3 h	77	93:7
5	**1d**	CPME	0 °C, 2 h	80	93:7
6[b]	**1d**	CPME	−78 °C, 3 h	78	95:5
7	**1e**	toluene	0 °C, 2 h	69	92:8
8	**1e**	CPME	0 °C, 2 h	90	93:7
9	**1e**	CPME	−78 °C, 2 h	85	97:3
10[a]	**1f**	toluene	0 °C, 2 h	56	80:20
11	**1f**	toluene	0 °C, 2 h	80	79:21

[a] *n*-BuLi (0.9 equiv) was used instead of LiHMDS (1.3 equiv). [b] Base was added at −78 °C.

When **1d** was treated with *n*-BuLi (0.9 equiv) in THF at 0 °C for 15 min followed by the addition of *n*-octanal at 0 °C, *Z*-**2a** was obtained in 79% yield and 82:18 ratio (entry 1 in Table 3). In toluene, the selectivity was improved to 92:8 and the use of LiHMDS instead of *n*-BuLi at −78 °C gave 93:7 *Z*-selectivity (entries 2–4). In cyclopentyl methyl ether (CPME), the *Z*-selectivity was further improved to 95:5 (entry 6). In order to see the effect of alkoxy group, R′O, the same reaction was performed using the methoxy reagent **1e** to give *Z*-**2a** with 97:3 selectivity in 85% yield (entry 9). The reaction of the one carbon shorter reagent **1f** gave **2a** with inferior *Z*-selectivity (80:20) even in toluene solvent (entry 10). Thus, extremely high *Z*-selectivity (97:3) was obtained from the reaction of **1e** with *n*-octanal, which reacted with **1a** to give **2a** in moderate *Z*-selectivity (entry 11 in Table 2).

The examples summarized in Table 4 demonstrate the versatility and the scope of our new reagent **1e** for the synthesis of *Z*-*α*,*β*-unsaturated sulfones **2** with various aliphatic aldehydes. Not only *n*-octanal but also *β*-branched aldehyde, citronellal **4l**, and 3-phenylpropionaldehyde reacted with **1e** at −78 °C to give **2l** and **2m** with high *Z*-selectivity (96:4 and 94:6, entries 2 and 4). The reactions of **1e** with *α*-branched aldehydes, cyclohexanecarbaldehyde, **4g**, and **4h** gave **2** with more than 99:1 *Z*-selectivity in 90–97% yields even at 0 °C (entries 5, 7, and 8). A similar result was obtained with **1d** (99:1, 84% yield, entry 6). The reaction with more hindered aldehyde **4i** gave slightly lower selectivity (91:9) in 68% yield (entry 9). The reaction of **1d** with **4i** gave similar results, and the selectivity was slightly higher at −78 °C (entries 10 and 11). With more bulky pivalaldehyde, **2j** was obtained with 88:12 selectivity from **1e** and 89:11 selectivity from **1d** (entries 12–14). The reaction with *α*,*β*-unsaturated aldehyde, *trans*-2-hexenal **4k** gave *Z*-**2k** with 94:6 *Z*-selectivity in 83% yield (entry 16).

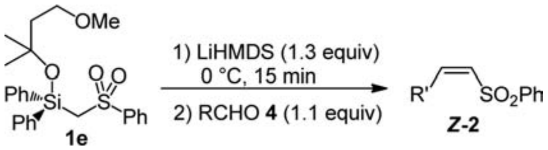
Table 4. Peterson Reactions of 1e with Aliphatic Aldehydes



entry	**4**, R	conditions	**2**, yield (%)	*Z*/*E*
1	*n*-C_7H_{15}	−78 °C, 2 h	**2a**, 85	97:3
2	**4l**	−78 °C, 2 h	**2l**, 92	96:4
3	**4l**	0 °C, 2 h	**2l**, 92	93:7
4	$Ph(CH_2)_2$	−78 °C, 3 h	**2m**, 64	94:6
5	*c*-Hex	0 °C, 2 h	**2f**, 97	99:1
6[a]	*c*-Hex	0 °C, 2 h	**2f**, 84	99:1
7	**4g**	0 °C, 2 h	**2g**, 90	99:1
8	**4h**	0 °C, 2 h	**2h**, 91	>99:1
9	**4i**	0 °C, 3 h	**2i**, 68	91:9
10[a]	**4i**	0 °C, 2 h	**2i**, 75	90:10
11[a]	**4i**	−78 °C, 3 h	**2i**, 69	91:9
12	*t*-Bu	0 °C, 2 h	**2j**, 79	88:12
13	*t*-Bu	rt, 2 h	**2j**, 92	86:14
14[a]	*t*-Bu	0 °C, 2 h	**2j**, 76	89:11
15	**4k**	0 °C, 2 h	**2k**, 90	92:8
16	**4k**	−78 °C, 2 h	**2k**, 83	94:6

[a] **1d** was used instead of **1e**.

Table 5. Peterson Reactions of 1e with Aromatic Aldehydes



entry	**4**, R	solvent	conditions	**2**, yield (%)	*Z*/*E*
1	Ph	CPME	−78 °C, 3 h	**2b**, 76	87:13
2	Ph	THF	0 °C, 1 h	**2b**, 76	90:10
3	Ph	THF	−78 °C, 1 h	**2b**, 97	90:10
4[a]	Ph	THF	0 °C, 1 h	**2b**, 71	92:8
5[a]	Ph	THF	−78 °C, 1 h	**2b**, 54	89:11
6	Ph	toluene	−78 °C, 3 h	**2b**, 35	74:26
7	Ph	DME	−55 °C, 3 h	**2b**, 90	94:6
8	*p*-MeC_6H_4	DME	−55 °C, 3 h	**2c**, 96	94:6
9	*p*-$MeOC_6H_4$	DME	−55 °C, 3 h	**2d**, 67	93:7
10	*p*-ClC_6H_4	DME	−55 °C, 4 h	**2e**, 64	87:13

[a] **1d** was used instead of **1e**.

The reactions of **1e** with aromatic aldehydes are summarized in Table 5. When **1e** was treated with LiHMDS (1.3 equiv) in CPME at 0 °C followed by the addition of benzaldehyde at −78 °C, **2b** was obtained in 76% yield and 87:13 *Z*-selectivity (entry 1). Since the selectivity is moderate under the best conditions for aliphatic aldehydes, further optimization of the reaction conditions was performed. In THF, slightly higher 90:10 *Z*-selectivity was obtained at both 0 and −78 °C (entries 2 and 3). Under the same conditions, **1d** gave 92:8 selectivity at 0 °C and 89:11 selectivity at −78 °C (entries 4 and 5). The *Z*-selectivity further improved to 94:6 in 1,2-dimethoxyethane (DME) at −55 °C, giving the products in 90% yield (entry 7). By using this procedure, *p*-tolualdehyde and *p*-anisaldehyde gave the corresponding alkenes with 94:6 and 93:7 *Z*-selectivity, respectively (entries 8 and 9). The selectivity was dropped to 87:13 for the reaction with *p*-chlorobenzaldehyde (entry 10).

In summary, we have developed new Peterson reagents for the synthesis of *Z*-*α*,*β*-unsaturated sulfones, which are useful synthetic intermediates in organic synthesis. In order to fix the conformation of the sulfone anion, we introduced an alkyloxy group on the silicon atom of the Peterson reagents. The reaction of the (*t*-BuO)Ph_2Si reagent **1a** with a variety of aldehydes gave *Z*-*α*,*β*-unsaturated sulfones with 69−96% selectivity in moderate to high yields. On the other hand, the Ph_3Si reagent **3** showed moderate *E*-selectivity. Further improvement was obtained by the introduction of alkoxyalkyloxy reagents **1d** and **1e**, which showed high *Z*-selectivity (generally 93−99% *Z*-selectivity) for a variety of aldehydes. This is the first *Z*-selective synthesis of *α*,*β*-unsaturated sulfones from aldehydes and can be applied to a broad range of substrates. Investigations into the detailed reaction mechanism and the synthetic applications of this methodology are actively being studied in this laboratory.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

This material is available free of charge via the Internet. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03008.

> Experimental procedures, compound characterization data, ^1H NMR spectra of compounds **1a−f**, **3**, **1a**(***p*-Me**), **1a**(***p*-MeO**), **1a**(***p*-Cl**), and **2a−m**, and ^{13}C NMR spectra of compounds **1a**,**b**,**d−f**, **3**, and **2a−m** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ando@gifu-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Prof. Natsuhisa Oka (Gifu University) for his assistance with the high-resolution mass spectra analysis. This work was supported financially by a Grant-in-Aid for Scientific Research on Innovative Areas.

■ REFERENCES

(1) For a review, see: (a) Meadows, D. C.; Gervay-Hague, J. *Med. Res. Rev.* **2006**, *26*, 793. (b) Simpkins, N. S. *Sulphones in Organic Synthesis*; Pergamon: Oxford, 1993.

(2) (a) Mauleón, P.; Carretero, J. C. *Org. Lett.* **2004**, *6*, 3195. (b) Llamas, T.; Arrayás, R. G.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 3329. (c) Desrosiers, J.-N.; Bechara, W. S.; Charette, A. B. *Org. Lett.* **2008**, *10*, 2315. (d) Bos, P. H.; Minnaard, A. J.; Feringa, B. L. *Org. Lett.* **2008**, *10*, 4219. (e) Li, H.; Song, J.; Deng, L. *Tetrahedron* **2009**, *65*, 3139. (f) Bos, P. H.; Maciá, B.; Fernández-Ibáñez, M. A.; Minnaard, A. J.; Feringa, B. L. *Org. Biomol. Chem.* **2010**, *8*, 47. (g) Moure, A. L.; Arrayás, R. G.; Carretero, J. C. *Chem. Commun.* **2011**, *47*, 6701. (h) Uraguchi, D.; Nakamura, S.; Sasaki, H.; Konakade, Y.; Ooi, T. *Chem. Commun.* **2014**, *50*, 3491.

(3) Mori, Y.; Yaegashi, K.; Furukawa, H. *J. Am. Chem. Soc.* **1996**, *118*, 8158.

(4) Mauleón, P.; Alonso, I.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 1291.

(5) (a) Roush, W. R.; Gwaltney, S. L., II; Cheng, J.; Scheidt, K. A.; McKerrow, J. H.; Hansell, E. *J. Am. Chem. Soc.* **1998**, *120*, 10994. (b) Dunny, E.; Doherty, W.; Evans, P.; Malthouse, J. P. G.; Nolan, D.; Knox, A. J. S. *J. Med. Chem.* **2013**, *56*, 6638.

(6) Woo, S. Y.; Kim, J. H.; Moon, M. K.; Han, S.; Yeon, S. K.; Choi, J. W.; Jang, B. K.; Song, H. J.; Kang, Y. G.; Kim, J. W.; Lee, J.; Kim, D. J.; Hwang, O.; Park, K. D. *J. Med. Chem.* **2014**, *57*, 1473.

(7) (a) Truce, W. E.; Muldoon, C. A.; Sinclar, J. *J. Org. Chem.* **1971**, *36*, 1727. (b) Edwards, G. L.; Muldoon, C. A.; Sinclair, D. J. *Tetrahedron* **1996**, *52*, 7779.

(8) Truce, W. E.; Simms, J. A. *J. Am. Chem. Soc.* **1956**, *78*, 2756.

(9) Ohnuma, T.; Hata, N.; Fujiwara, H.; Ban, Y. *J. Org. Chem.* **1982**, *47*, 4713.

(10) (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. (b) Staden, L. F.; Gravestock, D.; Ager, D. J. *Chem. Soc. Rev.* **2002**, *31*, 195.

(11) Craig, D.; Ley, S. V.; Simpkins, N. S.; Whitham, G. H.; Prior, M. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1949.

(12) The metallated carbon is nearly pyramidal in $PhSCH_2Li$ and nearly planar in $PhSOCH_2Li$, and $PhSO_2CH_2Li$ is in an intermediate hybridization state. See: (a) Chassaing, G.; Marquet, A. *Tetrahedron* **1978**, *34*, 1399. (b) Chassaing, G.; Marquet, A. *J. Organomet. Chem.* **1982**, *232*, 293. (c) Ohno, A.; Higaki, M.; Oka, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1721. In addition, our DFT study (B3LYP/6-31G*) on the anion derived from **1a** shows strong interactions with both one of the sulfone oxygens and the metallated carbon, which caused the carbanion carbon to have a rather flat pyramidal structure. The energy difference between two conformers **A** and **B** is only 0.1 kcal/mol.

(13) Kawashima, T.; Iwama, N.; Okazaki, R. *J. Am. Chem. Soc.* **1992**, *114*, 7598.

(14) The reagent **1a** was prepared in 91% yield from the reaction of $MeSO_2Ph$ and (*t*-BuO)Ph_2SiCl, which was prepared by following the literature procedure: Gillard, J. W.; Fortin, R.; Morton, H. E.; Yoakim, C.; Quesnelle, C. A.; Daignault, S.; Guindon, Y. *J. Org. Chem.* **1988**, *53*, 2602.

(15) The nitrile reagent (*t*-BuO)Ph_2SiCH_2CN was reported to give *Z*-*α*,*β*-unsaturated nitriles: Kojima, S.; Fukuzaki, T.; Yamakawa, A.; Murai, Y. *Org. Lett.* **2004**, *6*, 3917.

(16) When 1.3 equiv of *n*-BuLi was used and the reaction with *n*-octanal was performed at 0 °C, only a trace amount of **2a** was obtained. When isolated **2a** (*Z*/*E* = 85:15) was treated with *n*-BuLi (0.2 equiv) in THF at 0 °C for 3 h, 7% of **2a** (*Z*/*E* = 82:18) was recovered along with deconjugated sulfones and some Michael addition products.