Organic LETTERS
Letter
pubs.acs.org/OrgLett

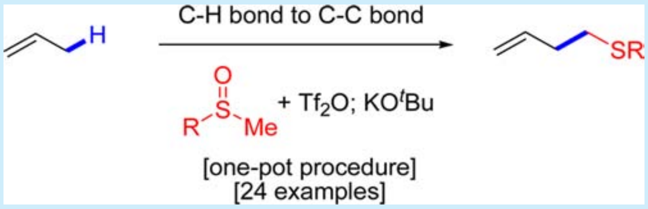
Sulfur Mediated Allylic C−H Alkylation of Tri- and Disubstituted Olefins

Gang Hu, Jiaxi Xu,* and Pingfan Li*

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, China

S Supporting Information

ABSTRACT: A novel transition-metal-free, sulfur mediated allylic C−H alkylation reaction through a one-pot procedure involving an ene-like step between simple olefins and activated sulfoxides to generate allylic sulfonium intermediates, and a subsequent [2,3]-sigmatropic rearrangement step under basic conditions to give allylic C−H alkylation products, has been developed. This method is applicable to tri- and disubstituted olefin substrates in both inter- and intramolecular fashions.

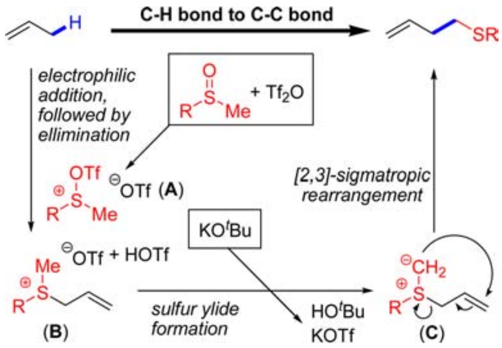


Recent advances in the field of transition-metal-catalyzed inert C−H bond functionalization have greatly expanded organic chemists' imagination for devising new synthetic routes toward complex molecular targets.[1] In the meantime, the unexplored potential of main group elements' chemistry deserves the community's attention toward providing alternative possibilities in methodology development.[2] Herein, we report a novel transition-metal-free, sulfur mediated allylic C−H alkylation reaction of olefins, which should complement well with the recently popularized transition-metal-catalyzed allylic C−H functionalization methods,[3,4] as well as the more traditional Tsuji−Trost type allylation.[5]

The well-known allylic C−H oxidation with selenium dioxide is generally thought to proceed through an initial ene reaction between an olefin substrate and SeO$_2$ to give an allylic selenic acid, followed by a subsequent [2,3]-sigmatropic rearrangement step to generate the corresponding selenium(II) intermediate, which is hydrolyzed to an allylic alcohol product.[6,7] Based on these mechanistic understandings, Sharpless et al. invented the imido selenium reagents, as well as related sulfur diimide reagents, to accomplish the allylic C−H amination of olefins.[8] On the other hand, although the call for "*pursuing the obvious extension of these unique bond forming processes with the goal of inserting carbon into allylic carbon−hydrogen bonds*" was explicitly noted in Sharpless' 1976 paper on imido selenium reagents (vide supra),[8a] realization of such a scenario was exceedingly rare, except for a single example reported by Moiseenkov et al.[9]

Currently, transition-metal-catalyzed oxidative coupling reactions represent the state-of-the-art for allylic C−H alkylation methods. Notable advances in this field include the copper/cobalt catalyst system reported by Li and Li in 2006,[10] as well as the palladium catalyst systems resembling Tsuji−Trost type allylation independently and almost simultaneously reported by the Shi group and White group in 2008.[11] While a number of important synthetic methods have been developed along this line of research,[12,13] including the first couple of examples for catalytic enantioselective allylic C−H alkylation reported by the Trost group and Gong group,[12d,i] most of these reactions still require the use of carbon nucleophiles containing two electron-withdrawing groups to couple with allylic C−H bonds from monosubstituted terminal olefins.

Scheme 1. Working Hypothesis of Sulfur Mediated Allylic C−H Alkylation



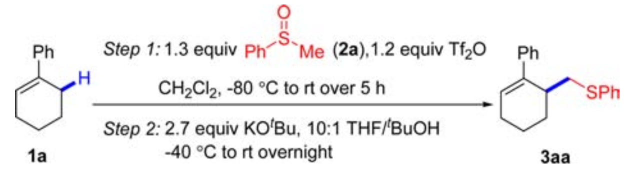
Our working hypothesis of sulfur mediated allylic C−H alkylation is shown in Scheme 1. We anticipate that a moderately electron-rich olefin could react with a highly electrophilic oxosulfonium reagent (**A**), generated by mixing a sulfoxide reagent with triflic anhydride (Tf$_2$O),[14] in an ene-like fashion (electrophilic addition, followed by elimination). If there is a regiochemistry issue, electrophilic addition should follow Markovnikov's rule (under electronic control). The elimination of H$^+$ by a triflate anion should then generate an allylic sulfonium intermediate (**B**)[15] and HOTf as a byproduct. The allylic functionalized sulfonium intermediate (**B**) could then be converted to the corresponding allyl-group-bearing sulfur ylide (**C**) under basic conditions (KO^{t}Bu), which then undergoes a

Received: October 27, 2014
Published: October 31, 2014

facile [2,3]-sigmatropic rearrangement to give the desired product.[16] The overall transformation would be a net allylic C−H alkylation reaction.

Gratifyingly, as depicted in Table 1, under our optimized reaction conditions (entry 1), this one-pot process can convert trisubstituted olefin **1a** and methyl phenyl sulfoxide (**2a**) to the desired product **3aa** in 60% yield. The influence of some reaction parameters is noteworthy. If DBU (entry 2) or sodium methoxide (entry 3), instead of potassium *tert*-butoxide, was used as a base in step 2, much lower yields were observed. The use of trifluoroacetic anhydride (entry 4) led to a very poor result, while the use of trichloroacetic anhydride (entry 5) or acetic anhydride (entry 6) only gave trace desired product, showcasing the advantage of using triflic anhydride to generate highly electrophilic oxosulfonium reagent (**A**). As discussed in Scheme 1, we expect the generation of one molecule of triflic acid in step 1. So it is very interesting to see that the use of 2-chloropyridine, a relatively non-nucleophilic base,[14h,17] as an acid scavenger is compatible with our present chemistry (entry 7), which should help the neutralization of the strong acid byproduct for avoiding side reactions on certain acid-labile substrates.

Table 1. Influence of Reaction Parameters on the Sulfur Mediated Allylic C−H Alkylation of Trisubstituted Olefin



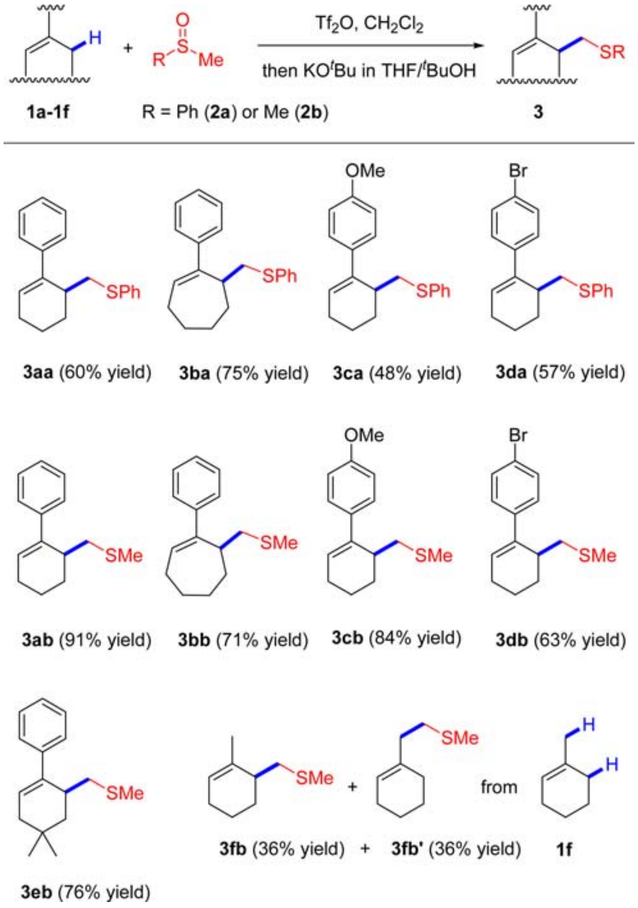
entry	variation from "standard" conditions	yield (%)[a]
1	none	60
2	use DBU instead of KO^{t}Bu as base in step 2	11
3	use NaOMe/MeOH as base in step 2	22
4	use $(CF_3CO)_2O$ instead of Tf_2O in step 1	<5
5	use $(CCl_3CO)_2O$ instead of Tf_2O in step 1	trace
6	use $(CH_3CO)_2O$ instead of Tf_2O in step 1	trace
7	use 2-chloropyridine as additive in step 1[b]	55

[a] Isolated yield for a 0.5 mmol scale reaction. [b] Instead of warming up to rt, step 1 was conducted at −80 °C for 4 h.

Several cyclohexene and -heptene derived trisubstituted olefins were converted to the corresponding allylic C−H alkylation products **3** in good yields (Scheme 2). Both methyl phenyl sulfoxide (**2a**), and dimethyl sulfoxide (**2b**) can functionalize olefins **1a**−**1d** to give homoallylic sulfides (**3aa** to **3da**, and **3ab** to **3db**) in 48% to 91% yields, which are otherwise difficult to access from simple precursors. Sterically more hindered substrate **1e** can also be converted to product **3eb** in 76% yield. For methylcyclohexene (**1f**), this reaction gave a 1:1 ratio mixture of two alkylation products **3fb** and **3fb′** in 72% combined yield, possibly due to the lack of regioselectivity in the ene-like step, which could give two different allylic sulfonium intermediates, and thus two isomers after rearrangement.

Disubstituted olefins **1g**−**1n** can also be successfully functionalized with this allylic C−H alkylation method (Scheme 3). With α-methylstytene (**1g**), alkylation products **3ga** and **3gb** were obtained in 61% and 72% yields, respectively. More electron-rich methoxy substituted α-methylstytene substrate **1h** gave only a 32% yield of **3hb**, while electron-deficient nitro substituted substrate **1i** gave a 73% yield of **3ib**. For alkenes with an exocyclic methylene group, reactions with **2a** gave products **3ja**, **3ka**, and **3la** in 67%, 74%, and 59% yields; however, reactions with **2b** can only give corresponding products **3jb**, **3kb**, and **3lb** in 75%, 22%, and 21% yields under our standard conditions (as shown in Table 1, entry 1). Switching to the more neutral reaction conditions (as shown in Table 1, entry 7) with 2-chloropyridine as an acid scavenger was found to be advantageous in these cases, leading to 92%, 80%, and 54% yields of **3jb**, **3kb**, and **3lb**. In addition to the above-mentioned *gem*-disubstituted olefins, electronically less polarized *vic*-disubstituted olefins were also competent substrates for this transformation. Cyclohexene (**1m**) can be converted to the desired product **3mb** in 58% yield. Acyclic *vic*-disubstituted olefins (*Z*)-oct-4-ene (***Z*-1n**) and (*E*)-oct-4-ene (***E*-1n**) both led to a 1:1 ratio mixture of *cis*- and *trans*-allylic C−H alkylation products **3nb** and **3nb′** in similar yields. Unfortunately, the use of 1-decene (not shown in Scheme 3) as a substrate to react with **2b** under our best reaction conditions (Table 1, entries 1 and 7) just gave less than a 20% yield of the desired product. Further development is necessary to make this chemistry applicable for allylic C−H alkylation of monosubstituted terminal olefins.

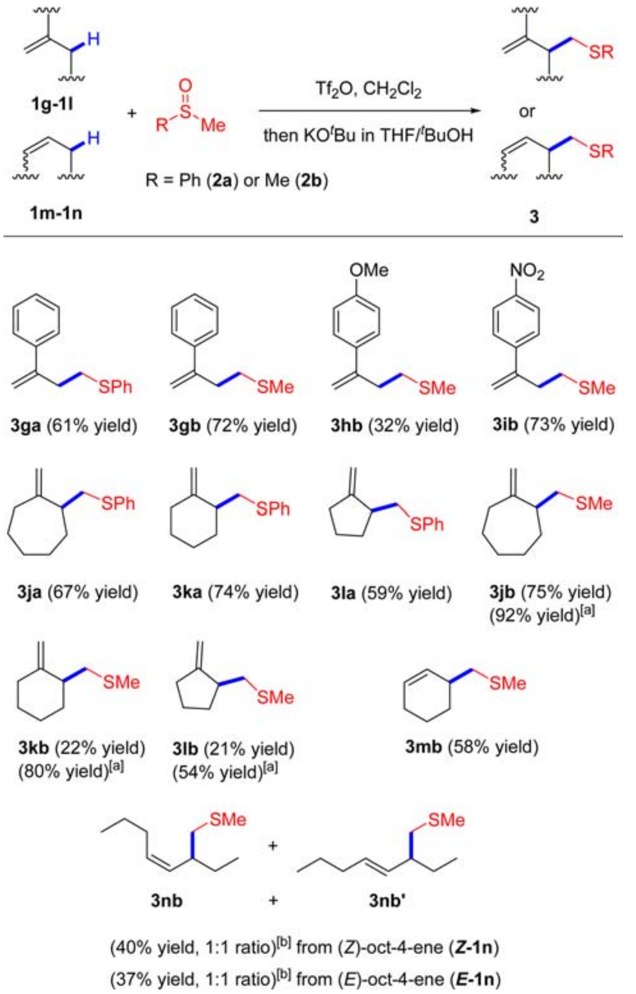
Scheme 2. Sulfur Mediated Intermolecular Allylic C−H Alkylation of Trisubstituted Olefins



In addition, we found this allylic C−H alkylation protocol can be realized in an intramolecular fashion (Scheme 4). For olefin **4** with a sulfoxide functional group, after sequential treatment of triflic anhydride and potassium *tert*-butoxide, the desired cyclization product **5** was obtained in 63% yield, most likely through a five-membered ring sulfonium intermediate.[18]

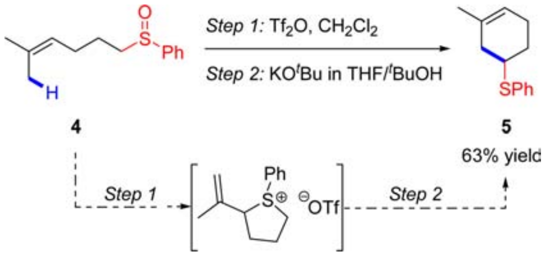
For product derivatization (Scheme 5), we were able to reduce the homoallylic sulfide **3aa** to **6** with Raney nickel. We could also oxidize **3aa** to corresponding sulfoxide **7** (in 1:1.63 dr) or sulfone

Scheme 3. Sulfur Mediated Intermolecular Allylic C−H Alkylation of *gem*- and *vic*-Disubstituted Olefins

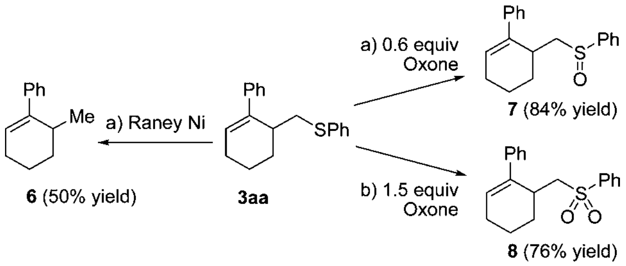


[a] Reaction conducted with 2-chloropyridine as acid scavenger. [b] Isolated as a mixture; ratio determined by ^{1}H NMR.

Scheme 4. Sulfur Mediated Intramolecular Allylic C−H Alkylation



Scheme 5. Derivatization of Homoallylic Sulfide Product



8 with Oxone in good yields,[19] which could potentially lead to many other types of derivatives through elimination, reduction, α-alkylation, or Julia olefination.

In conclusion, we have developed a novel sulfur mediated allylic C−H alkylation reaction to form C(sp^3)−C(sp^3) bonds from C−H bonds without the involvement of transition metal catalysts. This method is applicable to trisubstituted olefins, *gem*-disubstituted olefins, and *vic*-disubstituted olefins. The use of readily available reagents under robust reaction conditions is an attractive feature of this chemistry. The current scheme might also give us some new opportunity for designing enantioselective allylic C−H alkylation reactions. Exploration of the mechanism and synthetic applications is currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, characterization data, and copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: jxxu@mail.buct.edu.cn (J.X.).
*E-mail: lipf@mail.buct.edu.cn (P.L.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Dedicated to the memory of Prof. David Y. Gin (1967−2011). We thank Prof. Hisashi Yamamoto (Chubu University) for insightful discussions and Mr. Zhong Zhang (BUCT) for experimental assistance. This project was supported in part by the National Natural Science Foundation of China (21172017, 21372025, 21402005), National Basic Research Program of China (2013CB328905), and a start-up fund from the Public Hatching Platform for Recruited Talents of Beijing University of Chemical Technology.

■ REFERENCES

(1) For reviews, see: (a) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960. (b) Davies, H. M. L.; Bois, J. D.; Yu, J.-Q. *Chem. Soc. Rev.* **2011**, *40*, 1855. (c) Crabtree, R. H. *Chem. Rev.* **2010**, *110*, 575.

(2) For reviews and leading references, see: (a) *Main Group Metals in Organic Synthesis*; Yamamoto, H., Oshima, K., Eds.; Wiley: 2005. (b) *Frustrated Lewis Pairs I: Uncovering and Understanding; Frustrated Lewis Pairs II: Expanding the Scope. Topics in Current Chemistry*; Erker, G., Stephan, D. W., Eds.; Springer Verlag: 2013. (c) Bertrand, G. *Chem. Rev.* **2010**, *110*, 3851. (d) Bruckl, T.; Baxter, R. D.; Ishihara, Y.; Baran, P. S. *Acc. Chem. Res.* **2011**, *45*, 826. (e) Wang, T.; Jiao, N. *Acc. Chem. Res.* **2014**, *47*, 1137. (f) Uyanik, M.; Hayashi, H.; Ishihara, K. *Science* **2014**, *345*, 291. (g) Hashiguchi, B. G.; Konnick, M. M.; Bischof, S. M.; Gustafson, S. J.; Devarajan, D.; Gunsalus, N.; Ess, D. H.; Periana, R. A. *Science* **2014**, *343*, 1232. (h) Gui, J.; Zhou, Q.; Pan, C.-M.; Yabe, Y.; Burns, A. C.; Collins, M. R.; Ornelas, M. A.; Ishihara, Y.; Baran, P. S. *J. Am. Chem. Soc.* **2014**, *136*, 4853. (i) Bonet, A.; Odachowski, M.; Leonori, D.; Essafi, S.; Aggarwal, V. K. *Nat. Chem.* **2014**, *6*, 584. (j) Huang, X.; Patil, M.; Farès, C.; Thiel, W.; Maulide, N. *J. Am. Chem. Soc.* **2013**, *135*, 7312.

(3) For reviews on direct transition-metal-catalzyed allylic C−H functionalization, see: (a) Liron, F.; Oble, J.; Lorion, M. M.; Poli, G. *Eur. J. Org. Chem.* **2014**, 5863. (b) Li, H.; Li, B.-J.; Shi, Z.-J. *Catal. Sci. Technol.* **2011**, *1*, 191. (c) Engelin, C. J.; Fristrup, P. *Molecules* **2011**, *16*, 951.

(d) Liu, G.; Wu, Y. *Top. Curr. Chem.* **2010**, *292*, 195. (e) Jensen, T.; Fristrup, P. *Chem.—Eur. J.* **2009**, *15*, 9632.

(4) For one-pot procedures to realize asymmetric allylic C−H functionalization, see: (a) Covell, D. J.; White, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 6448. (b) Du, H.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2008**, *130*, 8590. (c) Zhao, B.; Du, H.; Fu, R.; Shi, Y. *Org. Synth.* **2010**, *87*, 263. (d) Bao, H.; Tambar, U. K. *J. Am. Chem. Soc.* **2012**, *134*, 18495. (e) Sharma, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2013**, *135*, 17983. (f) Bao, H.; Bayeh, L.; Tambar, U. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 1664.

(5) (a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, *6*, 4387. (b) Trost, B. M.; Fullerton, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 292. (c) Trost, B. M.; Vranken, D. L. V. *Chem. Rev.* **1996**, *96*, 395. (d) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (e) Mohr, J. T.; Stoltz, B. M. *Chem.—Asian J.* **2007**, *2*, 1476. (f) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258.

(6) Guillemonat, A. *Ann. Chim. Appl.* **1939**, *11*, 143.

(7) (a) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154. (b) Arigoni, D.; Vasella, A.; Sharpless, K. B.; Jensenls, H. P. *J. Am. Chem. Soc.* **1973**, *95*, 7917. (c) Jensen, H. P.; Sharpless, K. B. *J. Org. Chem.* **1975**, *40*, 264. (d) Stephenson, L. M.; Speth, D. R. *J. Org. Chem.* **1979**, *44*, 4683. (e) Singleton, D. A.; Hang, C. *J. Org. Chem.* **2000**, *65*, 7554.

(8) (a) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. O. *J. Am. Chem. Soc.* **1976**, *98*, 269. (b) Sharpless, K. B.; Hori, T. *J. Org. Chem.* **1976**, *41*, 176. (c) Schönberger, N.; Kresze, G. *Justus Liebigs Ann. Chem.* **1975**, *1975*, 1725. (d) Kresze, G.; Muensterer, H. *J. Org. Chem.* **1983**, *48*, 3561. (e) Katz, T. J.; Shi, S. *J. Org. Chem.* **1994**, *59*, 8297. (f) Bruncko, M.; Khuong, T.-A. V.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 454.

(9) To the best of our knowledge, the work by Moiseenkov et al. was the only precedent, which received virtually no citation since their publication. (a) Veselovsky, V. V.; Dragan, V. A.; Moiseenkov, A. M. *Tetrahedron Lett.* **1988**, *29*, 6637. (b) Moiseenkov, A. M.; Dragan, V. A.; Veselovskii, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 365.

(10) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 56.

(11) (a) Lin, S.; Song, C.-X.; Cai, G.-X.; Wang, W.-H.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 12901. (b) Young, A. J.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 14090. (c) Hegedus, L. S.; Hayashi, T.; Darlington, W. H. *J. Am. Chem. Soc.* **1978**, *100*, 7747.

(12) (a) Young, A. J.; White, M. C. *Angew. Chem., Int. Ed.* **2011**, *50*, 6824. (b) Trost, B. M.; Hansmann, M. M.; Thaisrivongs, D. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4950. (c) Trost, B. M.; Thaisrivongs, D. A.; Hansmann, M. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 11522. (d) Trost, B. M.; Thaisrivongs, D. A.; Donckele, E. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 1523. (e) Li, L.; Chen, Q.-Y.; Guo, Y. *Chem. Commun.* **2013**, *49*, 8764. (f) Howell, J. M.; Liu, W.; Young, A. J.; White, M. C. *J. Am. Chem. Soc.* **2014**, *136*, 5750. (g) Wang, G.-W.; Zhou, A.-X.; Li, S.-X.; Yang, S.-D. *Org. Lett.* **2014**, *16*, 3118. (h) Tang, S.; Wu, X.; Liao, W.; Liu, K.; Liu, C.; Luo, S.; Lei, A. *Org. Lett.* **2014**, *16*, 3584. (i) Wang, P.-S.; Lin, H.-C.; Zhai, Y.-J.; Han, Z.-Y.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 12218. (j) Engelin, C.; Jensen, T.; Rodriguez-Rodriguez, S.; Fristrup, P. *ACS Catal.* **2013**, *3*, 294.

(13) For other mechanistically related work on allylic C−H trifluorometylation, arylation, or carbonylation reactions, see: (a) Parsons, A. T.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 9120. (b) Xu, J.; Fu, Y.; Luo, D.-F.; Jiang, Y.-Y.; Xiao, B.; Liu, Z.-J.; Gong, T.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 15300. (c) Wang, X.; Ye, Y.; Zhang, S.; Feng, J.; Xu, Y.; Zhang, Y.; Wang, J. *J. Am. Chem. Soc.* **2011**, *133*, 16410. (d) Chu, L.; Qing, F.-L. *Org. Lett.* **2012**, *14*, 2106. (e) Sekine, M.; Ilies, L.; Nakamura, E. *Org. Lett.* **2013**, *15*, 714. (f) Jiang, H.; Yang, W.; Chen, H.; Li, J.; Wu, W. *Chem. Commun.* **2014**, *50*, 7202. (g) Chen, H.; Cai, C.; Liu, X.; Li, X.; Jiang, H. *Chem. Commun.* **2011**, *47*, 12224.

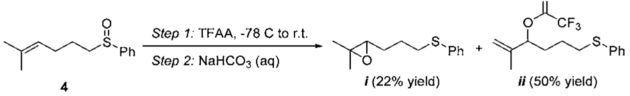
(14) For selected early examples using sulfoxide/triflic anhydride combination, see: (a) Hendrickson, J. B.; Schwartzman, S. M. *Tetrahedron Lett.* **1975**, 273. (b) Kahne, D.; Walker, S.; Cheng, Y.; Van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 6881. (c) Umemoto, T.; Ishihara, S. *J. Am. Chem. Soc.* **1993**, *115*, 2156. (d) Yan, L.; Kahne, D. *J. Am. Chem. Soc.* **1996**, *118*, 9239. (e) Corey, E. J.; Gin, D. Y.; Kania, R. S. *J. Am. Chem. Soc.* **1996**, *118*, 9202. (f) Nenajdenko, V. G.; Vertelezkij, P. V.; Gridnev, I. D.; Shevchenko, N. E.; Balenkova, E. S. *Tetrahedron* **1997**, *53*, 8173. For a review, see: (g) Nenajdenko, V. G.; Balenkova, E. S. *Russ. J. Org. Chem.* **2003**, *39*, 323. For the development of Gin glycosylation using sulfoxide/triflic anhydride combination, see: (h) Garcia, B. A.; Poole, J. L.; Gin, D. Y. *J. Am. Chem. Soc.* **1997**, *119*, 7597. (i) Di Bussolo, V.; Kim, Y.-J.; Gin, D. Y. *J. Am. Chem. Soc.* **1998**, *120*, 13515. (j) Di Bussolo, V.; Liu, J.; Huffman, J. L. G.; Gin, D. Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 204. (k) Garcia, B. A.; Gin, D. Y. *J. Am. Chem. Soc.* **2000**, *122*, 4269. (l) Nguyen, H. M.; Poole, J. L.; Gin, D. Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 414. (m) Liu, J.; Gin, D. Y. *J. Am. Chem. Soc.* **2002**, *124*, 9789. (n) Gin, D. Y. *J. Carbohydr. Chem.* **2002**, *21*, 645. (o) Galonic, D. P.; Gin, D. Y. *Nature* **2007**, *446*, 1000. For a recent review on mechanistically related Pummerer-type reactions, see: (p) Smith, L. H. S.; Coote, S. C.; Sneddon, H. F.; Procter, D. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 5832.

(15) See Supporting Information for the crude ^{1}H NMR and high resolution mass spectrometry data for the corresponding allylic sulfonium intermediate generated by mixing 1-phenylcycohexene (**1a**), DMSO (**2b**), Tf$_2$O, and then aqueous workup.

(16) For original works, see: (a) Bates, R. B.; Feld, D. *Tetrahedron Lett.* **1968**, *9*, 417. (b) Blackburn, G. M.; Ollis, W. D.; Plackett, J. D.; Smith, C.; Sutherland, I. O. *Chem. Commun.* **1968**, 186. (c) Baldwin, J. E.; Hackler, R. E.; Kelly, D. P. *Chem. Commun.* **1968**, 537−538. (d) Baldwin, J. E.; Hackler, R. E.; Kelly, D. P. *J. Am. Chem. Soc.* **1968**, *90*, 4758. For reviews, see: (e) Sulfur-Mediated Rearrangement II. In *Topics in Current Chemistry*; Schaumann, E., Eds.; Springer: 2007. (f) Vedejs, E. *Acc. Chem. Res.* **1984**, *17*, 358. (g) Vedejs, E. *J. Org. Chem.* **2004**, *69*, 5159. (h) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. (i) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341. (j) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (k) Zhang, Y.; Wang, J. *Coord. Chem. Rev.* **2010**, *254*, 941.

(17) Myers, A. G.; Tom, N. J.; Fraley, M. E.; Cohen, S. B.; Madar, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 6072.

(18) In a mechanistically related work, it was reported that when **4** was treated with trifluoroacetic anhydride and then aquoeus NaHCO$_3$, a mixture of epoxide ***i*** and trifluoroacetate ***ii*** was obtained: Zhang, Y.; Lee, J. H.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 752.



(19) Yu, B.; Liu, A.-H.; He, L.-N.; Li, B.; Diao, Z.-F.; Li, Y.-N. *Green Chem.* **2012**, *14*, 957.