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N-Heterocyclic Carbene-Catalyzed Internal Redox Reaction of Alkynals: An Efficient Synthesis of Allenoates

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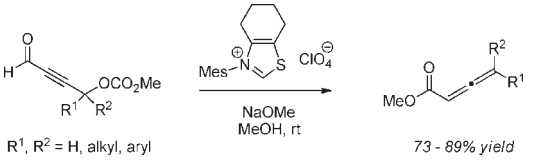
ABSTRACT



An efficient *N*-heterocyclic carbene (NHC)-catalyzed internal redox reaction of alkynals that bear a γ leaving group has been developed. This process provides a new access to a range of allenoates in good yields. Preliminary results demonstrate that the enantioselective variant can also be achieved.

Allenes represent an important structural motif that widely occurs in natural products and synthetic molecules with significant biological activity.[1] They also serve as versatile building blocks in organic synthesis.[2] Among them, allenoates have been demonstrated as a family of particularly useful synthetic intermediates due to their easy access to a variety of heterocycles and chiral molecules.[3] Although several methods are available for the synthesis of allenoates, such as base-catalyzed isomerization of 3-alkynoates,[4] transition-metal-catalyzed carbonylation of propargylic carbonates and tosylates,[5] etc.,[6] the most general and widely employed method is the olefination of ketenes, which can be generated in situ from acyl chlorides.[7] Drawbacks of this method include the use of

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(1) For some leading references, see: (a) *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982. (b) *Modern Allene Chemistry*; Krause, N., Hashimi, A. S. K., Eds.; Wiley-VCH: Weinheim, 2004. (c) Hoffmann-Röder, A.; Krause, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 1196.

(2) For reviews, see: (a) Rossi, R.; Diversi, P. *Synthesis* **1973**, 25. (b) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3590. (c) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067. (d) Marshall, J. A. *Chem. Rev.* **2000**, *100*, 3163. (e) Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12. (f) Sydnes, L. K. *Chem. Rev.* **2003**, *103*, 1133. (g) Tius, M. *Acc. Chem. Res.* **2003**, *36*, 284. (h) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701. (i) Wei, L.-L.; Xiong, H.; Hsung, R. P. *Acc. Chem. Res.* **2003**, *36*, 773. (j) Ma, S. *Chem. Rev.* **2005**, *105*, 2829. (k) Ma, S. *Aldrichimica Acta* **2007**, *40*, 91. (l) Ma, S. *Acc. Chem. Res.* **2009**, *42*, 1679.

(3) For recent examples, see: (a) Li, Y.; Zou, H.; Gong, J.; Xiang, J.; Luo, T.; Quan, J.; Wang, G.; Yang, Z. *Org. Lett.* **2007**, *9*, 4057. (b) Fang, Y.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2008**, *130*, 5660. (c) Smith, S. W.; Fu, G. C. *J. Am. Chem. Soc.* **2009**, *131*, 14231. (d) Yu, J.; Chen, W.; Gong, L. *Org. Lett.* **2010**, *12*, 4050. (e) Sun, J.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 4568. (f) Fujiwara, Y.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 12293. (g) Wang, X.; Fang, T.; Tong, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 5361.

(4) For seminal work, see: (a) Eglinton, G.; Jones, E. R. H.; Mansfield, G. H.; Whiting, M. C. *J. Chem. Soc.* **1954**, 3197. For a recent example, see: (b) Liu, H.; Leow, D.; Huang, K.; Tan, C. *J. Am. Chem. Soc.* **2009**, *131*, 7212.

(5) (a) Tsuji, J.; Sugiura, T.; Minami, I. *Tetrahedron Lett.* **1986**, *27*, 731. (b) Marshall, J. A.; Wolf, M. A.; Wallace, E. M. *J. Org. Chem.* **1997**, *62*, 367.

(6) For examples of other methods, see: (a) Lee, P. H.; Mo, J.; Kang, D.; Com, D.; Park, C.; Lee, C.; Jung, Y. M.; Hwang, H. *J. Org. Chem.* **2011**, *76*, 312. (b) Bhowmick, M.; Lepore, S. *Org. Lett.* **2010**, *12*, 5078. (c) Gray, P. J.; Motherwell, W. B.; Sheppard, T. D.; Whitehead, A. J. *Synlett* **2008**, 2097. (d) Yu, X.; Ren, H.; Xiao, Y.; Zhang, J. *Chem.—Eur. J.* **2008**, *14*, 8481.

(7) For seminal reports, see: (a) Buono, G. *Tetrahedron Lett.* **1972**, *13*, 3257. (b) Lang, R. W.; Hansen, H. *Helv. Chim. Acta* **1980**, *63*, 438. For recent examples using this strategy for allenoate synthesis, see: (c) Fujiwara, Y.; Sun, J.; Fu, G. C. *Chem. Sci.* **2011**, *2*, 2196. (d) Chen, B.; Ma, S. *Chem.—Eur. J.* **2011**, *17*, 754. (e) Hopkinson, M. N.; Ross, J. E.; Giuffredi, G. T.; Gee, A. D.; Gouverneur, V. *Org. Lett.* **2010**, *12*, 4904. (f) Reference 3c–3f. (g) Hashmi, A. S. K.; Döpp, R.; Lothschütz, C.; Rudolph, M.; Riedel, D.; Rominger, F. *Adv. Synth. Catal.* **2010**, *352*, 1307.

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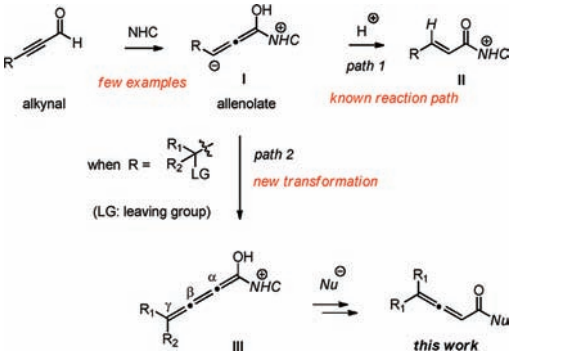
expensive phosphoranes as the stoichiometric olefinating reagent and the production of an equal amount of the phosphine oxide as waste. Here we report a new strategy for the synthesis of allenoates from alkynals by means of *N*-heterocyclic carbene (NHC) catalysis.

The use of NHCs for catalysis has emerged as an area of intense investigations in the past few years.[8,9] The majority of these catalytic reactions take advantage of the polarity reversal ("umpolung") process of the aldehyde functionality. For example, in the presence of a catalytic amount of NHC, aldehydes can serve as precursors for acyl anion equivalents, such as those in benzoin reactions and Stetter reactions.[10] Enals have also been demonstrated as convenient precursors for homoenolates, resulting in the development of numerous processes with new bond formation in the β position.[11] In contrast to the large number of publications on nonconjugated aldehydes and enals, reports on the use of *alkynals* to generate the corresponding allenolates are scarce (**I** in Scheme 1).[12] These isolated examples share a common feature, i.e., trapping the allenolate **I** with a proton to form the activated unsaturated acyl species **II** for further reactions with different nucleophiles.

Scheme 1. NHC-Catalyzed Reaction Patterns of Alkynals



We envisioned that allenolate **I**, which is difficult to generate by other strategies,[13] can be further utilized to expand the scope of NHC catalysis. For example, we hypothesized that if a leaving group is present in the γ position, the negative charge in the β position of **I** can trigger an elimination of the leaving group, forming a cumulative allenol **III** (Scheme 1, path 2). In the presence of a suitable nucleophile, **III** can be converted to activated allene products. The overall reaction is redox-neutral.[14] This process not only provides a new access to activated allenes but also represents a new platform for the discovery of other NHC-catalyzed reactions with alkynals. Also, the formation of allenoates can give useful insight into the question of whether an allenic species is involved in NHC-catalyzed reactions of alkynals.[15]

(8) For leading reviews on NHC organocatalysis, see: (a) Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606. (c) Marion, N.; Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988. (d) Phillips, E. M.; Chan, A.; Scheidt, K. A. *Aldrichimica Acta* **2009**, *42*, 55. (e) de Alaniz, J. R.; Rovis, T. *Synlett* **2009**, 1189. (f) Moore, J. L.; Rovis, T. *Top. Curr. Chem.* **2010**, *291*, 77. (g) Vora, H. U.; Rovis, T. *Aldrichimica Acta* **2011**, *44*, 3. (h) Hirano, K.; Piel, I.; Glorius, F. *Chem. Lett.* **2011**, *40*, 786. (i) Biju, A. T.; Kuhl, N.; Glorius, F. *Acc. Chem. Res.* **2011**, *44*, 1182. (j) Campbell, C. D.; Ling, K. B.; Smith, M. D. In *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*; Cazin, C. S. J., Ed.; Springer: 2011; p 263. (k) Cohen, D. E.; Scheidt, K. A. *Chem. Sci.* **2012**, *3*, 53. (l) Nair, V.; Vellalath, S.; Babu, B. P. *Chem. Soc. Rev.* **2008**, *37*, 2691. (m) Nair, V.; Menon, R. S.; Biju, A. T.; Sinu, C. R.; Paul, R. R.; Jose, A.; Sreekumar, V. *Chem. Soc. Rev.* **2011**, *40*, 5336. (n) Chiang, P.; Bode, J. W. *TCI Mail* **2011**, *149*, 2. (o) Rong, Z.; Zhang, W.; Yang, G.; You, S. *Curr. Org. Chem.* **2011**, *15*, 3077.

(9) For a review on the physicochemical properties of NHCs, see: Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940.

(10) For detailed reviews on NHC-catalyzed benzoin and Stetter reactions, see ref 8b and 8e−8g.

(11) For reviews on homoenolates generated by NHC-catalyzed reactions of enals, see ref 8l−8m.

(12) To our knowledge, there are isolated examples on NHC-catalyzed reactions of alkynals: (a) Zeitler, K. *Org. Lett.* **2006**, *8*, 637. (b) Kaeobamrung, J.; Mahatthananchai, J.; Zheng, P.; Bode, J. W. *J. Am. Chem. Soc.* **2010**, *132*, 8810. (c) Zhu, Z.; Xiao, J. *Adv. Synth. Catal.* **2010**, *352*, 2455. (d) Zhu, Z.; Zheng, X.; Jiang, N.; Wan, X.; Xiao, J. *Chem. Commun.* **2011**, *47*, 8670.

(13) We are not aware of other strategies for this type of allenolate formation. For examples of normal allenolate reactivity, see: (a) González-Cruz, D.; Tejedor, D.; de Armas, P.; García-Tellado, F. *Chem.—Eur. J.* **2007**, *13*, 4823. (b) Wei, H.; Hu, J.; Jasoni, R. L.; Li, G.; Paré, P. W. *Helv. Chim. Acta* **2004**, *87*, 2359. (c) Schultz-Fademrecht, C.; Tius, M. A.; Grimme, S.; Wibbeling, B.; Hoppe, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1532.

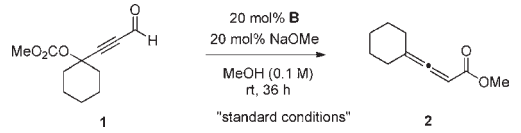
(14) For selected examples of NHC-catalyzed redox reactions, see: (a) Reynolds, N. T.; de Alaniz, J. R.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 9518. (b) Vora, H. U.; Rovis, T. *J. Am. Chem. Soc.* **2010**, *132*, 2860. (c) Vora, H. U.; Rovis, T. *J. Am. Chem. Soc.* **2007**, *129*, 13796. (d) Ling, K. B.; Smith, A. D. *Chem. Commun.* **2011**, *47*, 373. (e) Wang, L.; Thai, K.; Gravel, M. *Org. Lett.* **2009**, *11*, 891. (f) Chow, K. Y.; Bode, J. W. *J. Am. Chem. Soc.* **2004**, *126*, 8126. (g) Chan, A.; Scheidt, K. A. *Org. Lett.* **2005**, *7*, 905. (h) Kawanaka, Y.; Phillips, E. M.; Scheidt, K. A. *J. Am. Chem. Soc.* **2009**, *131*, 18028. (i) Sohn, S. S.; Bode, J. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 6021. (j) Lv, H.; Mo, J.; Fang, X.; Chi, Y. R. *Org. Lett.* **2011**, *13*, 5366. (k) Li, G.; Li, Y.; Dai, L.; You, S. *Org. Lett.* **2007**, *9*, 3519. (l) Li, G.; Li, Y.; Dai, L.; You, S. *Adv. Synth. Catal.* **2008**, *350*, 1258. (m) Li, G.; Dai, L.; You, S. *Org. Lett.* **2009**, *11*, 1623. (n) Wu, Y.; Yao, W.; Pan, L.; Zhang, Y.; Ma, C. *Org. Lett.* **2010**, *12*, 640. (o) Sun, F.; Sun, L.; Ye, S. *Adv. Synth. Catal.* **2011**, *353*, 3134. (p) Gerson, M. H.; Uc, G. J.; Bode, J. W. *J. Am. Chem. Soc.* **2006**, *128*, 10588. (q) Kobayashi, S.; Kinoshita, T.; Uehara, H.; Sudo, T.; Ryu, I. *Org. Lett.* **2009**, *11*, 3934. (r) Sohn, S. S.; Bode, J. W. *Org. Lett.* **2005**, *7*, 3873. (s) Bode, J. W.; Sohn, S. S. *J. Am. Chem. Soc.* **2007**, *129*, 13798.

(15) For a leading reference on the investigations and discussions of the mechanism of NHC-catalyzed reactions of alkynals, see: Mahatthananchai, J.; Zheng, P.; Bode, J. W. *Angew. Chem., Int. Ed.* **2011**, *50*, 1673.

(16) For examples using thiazolidenes as effective catalysts, see: (a) Stetter, H.; Dambkes, G. *Synthesis* **1977**, 403. (b) Stetter, G.; Dambkes, G. *Synthesis* **1980**, 309. (c) Sheehan, J. C.; Hunnemann, D. H. *J. Am. Chem. Soc.* **1966**, *88*, 3666. (d) Sheehan, J. C.; Hara, T. *J. Org. Chem.* **1974**, *39*, 1196. (e) Tagaki, W.; Tamura, Y.; Yano, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 478. (f) Marti, J.; Castells, J.; López-Calahorra, R. *Tetrahedron Lett.* **1993**, *34*, 521. (g) Knight, R. L.; Leeper, F. J. *Tetrahedron Lett.* **1997**, *38*, 3611. (h) Dvorak, C. A.; Rawal, V. H. *Tetrahedron Lett.* **1998**, *39*, 2925. (i) Stetter, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 639. (j) Reference 14f. (k) Murry, J. A.; Frantz, D. E.; Soheili, A.; Tillyer, R.; Grabowski, E. J. J.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9696. (l) Frantz, D. E.; Morency, L.; Soheili, A.; Murry, J. A.; Grabowski, E. J. J.; Tillyer, R. D. *Org. Lett.* **2004**, *6*, 843. (m) Noonan, C.; Baragwanath, L.; Connon, S. J. *Tetrahedron Lett.* **2008**, *49*, 4003. (n) Mattson, A. E.; Bharadwaj, A. R.; Scheidt, K. A. *J. Am. Chem. Soc.* **2004**, *126*, 2314. (o) Mattson, A. E.; Bharadwaj, A. R.; Zuhl, A. M.; Scheidt, K. A. *J. Org. Chem.* **2006**, *71*, 5715. (p) Hirano, K.; Piel, I.; Glorius, F. *Adv. Synth. Catal.* **2008**, *350*, 984. (q) Hirano, K.; Biju, A. T.; Piel, I.; Glorius, F. *J. Am. Chem. Soc.* **2009**, *131*, 14190. (r) Rose, C. A.; Zeitler, K. *Org. Lett.* **2010**, *12*, 4552. (s) Biju, A. T.; Wurz, N. E.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 5970. (t) Sánchez-Larios, E.; Holmes, J. M.; Daschner, C. L.; Gravel, M. *Org. Lett.* **2010**, *12*, 5772. (u) Padmannaban, M.; Biju, A. T.; Glorius, F. *Org. Lett.* **2011**, *13*, 98. (v) Padmanaban, M.; Biju, A. T.; Glorius, F. *Org. Lett.* **2011**, *13*, 5624. (w) Wu, K.; Li, G.; Li, Y.; Dai, L.; You, S. *Chem. Commun.* **2011**, *47*, 493. (x) Piel, I.; Pawelczyk, M. D.; Kirano, K.; Fröhlich, R.; Glorius, F. *Eur. J. Org. Chem.* **2011**, 5475.

A brief experimental survey of different leaving groups, e.g. OTs, OMe, and OAc, reveals that the methyl carbonate group (OCO_2Me) is superior. Thus, we used alkynal **1**, which bears a methyl carbonate group in the γ position, for our further optimization (Table 1). To our delight, the

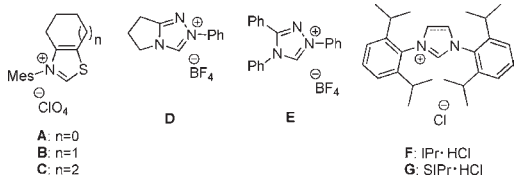
Table 1. Effect of Reaction Parameters on the NHC-Catalyzed Reaction of Alkynal **1**



1 2

entry	change from the "standard conditions"	yield (%)[a]
1	none	77
2	no **B**	0
3	**A** instead of **B**	39
4	**C** instead of **B**	71
5	**D** instead of **B**	70
6	**E** instead of **B**	31
7	**F** instead of **B**	10
8	**G** instead of **B**	<5
9	DBU instead of NaOMe	65
10	Cs_2CO_3 instead of NaOMe	68
11	$KOBu^t$ instead of NaOMe	54
12	KHMDS instead of NaOMe	44
13	1.0 instead of 0.2 equiv of NaOMe	35
14	DCM instead of MeOH	<5
15	DCM as solvent, and 3.0 equiv of MeOH	<5
16	EtOH in stead of MeOH	–[b]
17	40 °C instead of rt	71

[a] Determined by ^1H NMR analysis with dibromomethane as an internal standard. [b] Ethyl allenoate was observed in 35% yield.

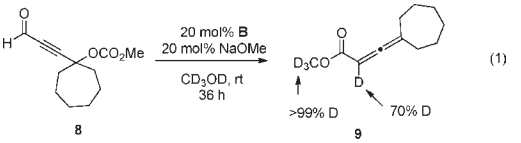


reaction proceeds smoothly in the presence of 20 mol % of thiazolium salt **B** and 20 mol % of NaOMe in methanol at rt, providing the desired allenoate **2** in 77% yield (Table 1, entry 1).[16] In the absence of **B**, no desired **2** is formed, indicating that the reaction is catalyzed by NHC instead of a base (entry 2). NHCs derived from other precatalysts, e. g. thiazoliums **A**, **C**, triazoliums **D**, **E**, imidazolium **F**, and dihydroimidazolium **G**, proved to be less effective (entries 3–8). With regard to the choice of base, NaOMe is better than other bases, such as DBU, Cs_2CO_3, KO^tBu, and KHMDS (entries 9–12). While 20 mol % of NaOMe is sufficient to promote the reaction with high efficiency, excess base is detrimental to the product yield (entry 13). It is worth noting that the use of methanol as solvent is critical to the success of the reaction. In fact, when DCM is used as solvent, either with 3.0 equiv of MeOH or without MeOH, the reaction gives a trace of desired product **2** (entries 14, 15). The use of ethanol instead of methanol as solvent results in the formation of the corresponding ethyl allenoate product, albeit in low yield (entry 16).[17] Finally, although the reaction proceeds faster at 40 °C than that at rt, the product is obtained in slightly diminished yield (entry 17), presumably due to the increased side reactions or decomposition of the allenoate at an elevated temperature.

The internal redox reaction proceeds efficiently with an array of alkynals (Table 2). Thus, cyclic and acyclic allenoate products are all obtained in good yields. The catalytic process is also compatible with a variety of functional groups, including cyanides and ethers (entries 4, 5). It is noteworthy that steric hindrance in the γ position does not affect the reaction efficiency (entry 2). Moreover, alkynals with aryl substitutions in the γ position are compatible with the reaction conditions (entry 3).

While the reactions of alkynals with a quaternary γ carbon center proceed to form allenoates as the sole product, the reaction of alkynals with a tertiary γ carbon center may give a mixture of two isomers, i.e., allenoate **6** and alkynoate **7** (Table 3), with the allenoate as the major product. The ratio of the allenoate and alkynoate products varies with different substituents at the γ position. For example, moderate allenoate/alkynoate ratios are observed for substrates with phenyl-, phenylethyl-, *n*-decyl-, and 9-decenyl substitutions (entries 1–4), but improved ratios can be obtained with sterically more demanding substituents (entries 5, 6). In fact, with *tert*-butyl substitution, essentially only the allenoate product is formed. Finally, all these reactions proceed with high efficiency in terms of overall yield.

To gain more insight into the reaction mechanism, we conducted the reaction of alkynal **8** in CD_3OD as solvent under otherwise identical conditions (eq 1). We observed almost complete deuterium incorporation for the methyl group of the allenoate product **9** based on ^1H NMR. Also, there is significant deuterium incorporation at the α position of the allenoate product, which is consistent with the proposed mechanism (*vide infra*), in which a Breslow intermediate is involved.[18]



8 9

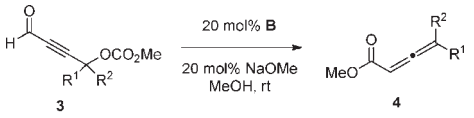
A plausible reaction mechanism is depicted in Scheme 2. The catalytic cycle begins with nucleophilic addition of the NHC to the carbonyl group of alkynal **3**, which is predominantly in its trimer form in methanol.[19] Next, electron-pushing from the nitrogen lone pair of the resulting Breslow intermediate **10**, along the conjugated π-system, triggers the elimination of methyl carbonate group to form cumulative allenol **11**. Subsequent steps involve tautomerization to form allene **12** and then nucleophilic acyl substitution by MeO^- to form the observed allenoate **4** and regenerate the NHC catalyst.

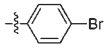
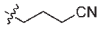
(17) We believe that the allenic acyl intermediates, e.g., **12** in Scheme 2, are quite unstable. Tapping with MeOH is relatively faster than that with EtOH.

(18) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719.

(19) On the basis of ^1H and ^{13}C NMR spectra, alkynal **3** exists as a monomer in $CDCl_3$. In contrast, it exists as a trimer in CD_3OD.

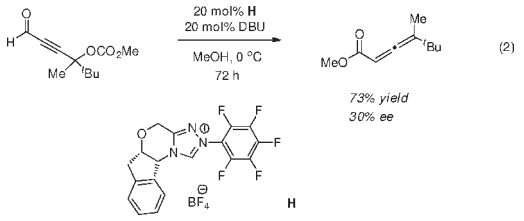
Table 2. NHC-Catalyzed Reactions of Alkynals: Scope of Alkynals with a Quaternary γ Carbon



entry	R^1	R^2	time (h)	yield (%)[a]
1	Me	*n*-Pr	45	83
2	Me	*t*-Bu	48	87
3	Me		26	73
4	Me		48	87
5	Me		48	89
6	—$CH_2CH_2CH_2$—		72	76
7			32	79
8			48	82

[a] Yield of purified product.

We have begun to develop an enantioselective variant of this process. We anticipated that this might be challenging, due to issues such as potential generation of mixtures of *E*/*Z* isomers of the key intermediate **11** and the difficulty in controlling facial selectivity of the proton transfer in the tautomerization to **12**. Yet we were pleased to find that the chiral NHC generated from precatalyst **H** can catalyze the synthesis of an allenoate with promising enantioselectivity (30% ee; eq 2).[20,21]



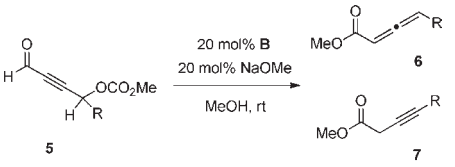
(2)

In summary, we have developed an efficient internal redox process of alkynals, which is now added to the small family of known reactions of alkynals with NHC catalysis. This first successful exploitation of an allenolate **I** intermediate for allenoate formation provides a versatile platform for further development of new NHC-catalyzed reactions of alkynals. Without the use of transition metals and the production of phosphine oxide waste, this process serves as a green alternative for the synthesis of allenoates.

(20) The NHC derived from precatalyst **H** has been employed in a range of catalytic asymmetric processes. For some selected examples, see: (a) Kerr, M. S.; Rovis, T. *J. Am. Chem. Soc.* **2004**, *126*, 8876. (b) Reynolds, N. T.; Rovis, T. *J. Am. Chem. Soc.* **2005**, *127*, 16406. (c) Ozboya, K. E.; Rovis, T. *Chem. Sci.* **2011**, *2*, 1835.

(21) For examples of enantioselective synthesis of allenoates, see: (a) Li, C.; Wang, X.; Sun, X.; Tang, Y.; Zheng, J.; Xu, Z.; Zhou, Y.; Dai, L. *J. Am. Chem. Soc.* **2007**, *129*, 1494. (b) Zhang, W.; Zheng, S.; Liu, N.; Werness, J. B.; Guzei, I. A.; Tang, W. *J. Am. Chem. Soc.* **2010**, *132*, 3664. (c) Li, C.; Zhu, B.; Ye, L.; Jing, Q.; Sun, X.; Tang, Y.; Shen, Q. *Tetrahedron* **2007**, *63*, 8046. (d) Reference 4.

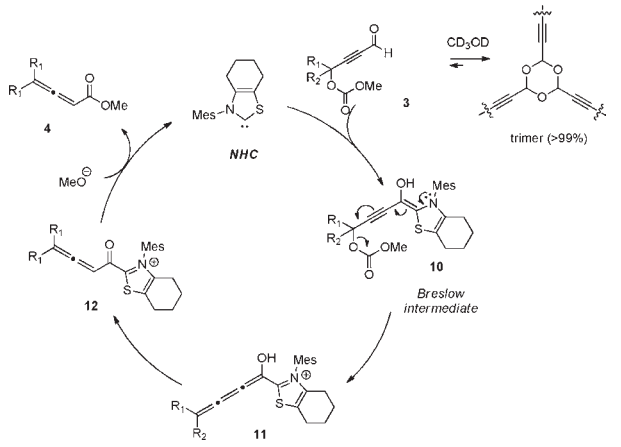
Table 3. NHC-Catalyzed Reactions of Alkynals: Scope of Alkynals with a Tertiary γ Carbon



entry	R	ratio (**6**:**7**)[a]	time (h)	yield (%)[b]
1	Ph	5.4:1	41	71
2	$PhCH_2CH_2$	2.7:1	41	81
3	*n*-$C_{10}H_{21}$	2.7:1	41	76
4		3.1:1	40	74
5		8.8:1	39	87[c]
6	*t*-Bu	>99:1	39	79

[a] Ratio was determined by ^{1}H NMR. [b] Isolated total yield of allenoate and alkynoate. [c] The starting alkynal is a mixture of two diastereomers (dr = 3.9:1), and the dr of the allene product is ~1:1.

Scheme 2. Proposed Mechanism



Preliminary studies have also shown that an enantioselective variant can be achieved.

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Supporting Information Available. Experimental procedures and compound characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.