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Helical Chiral 2,2′-Bipyridine *N*- Monoxides as Catalysts in the Enantioselective Propargylation of Aldehydes with Allenyltrichlorosilane

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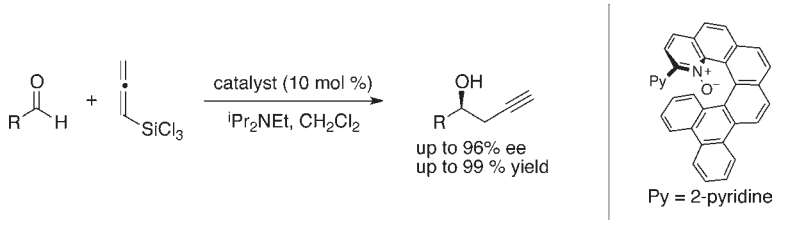
ABSTRACT



A highly enantioselective synthesis of homopropargylic alcohols is achieved by using the new helical chiral 2,2′-bipyridine *N*-monoxide catalyst and allenyltrichlorosilane. This method can be further extended to the enantio- and regioselective propargylation of *N*-acylhydrazones.

Optically active homopropargylic alcohols are highly useful chiral building blocks in organic synthesis due to the synthetic versatility of an acetylene unit.[1] The asymmetric propargylation of aldehydes provides direct access to this class of compounds.[2] Significant progress has been made in the development of chiral propargylation reagents and diastereoselective additions of propargylic anion equivalents to chiral aldehydes.[2,3] Enantioselective catalytic approaches include Barbier type additions,[1a,b,4] Lewis acid or base catalysis with metalloallene reagents,[5] and the Cu-catalyzed propargylation with a propargyl borolane.[6] Despite these creative efforts, the catalytic asymmetric

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(2) For selected reviews, see: (a) Marshall, J. A. *J. Org. Chem.* **2007**, *72*, 8153–8166. (b) Gung, B. W. *Org. React.* **2004**, *64*, 1–113. (c) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31–47. (d) Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, U. K., 1991; Vol. 2, p 81−98.

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(4) For selected references, see: (a) Usanov, D. L.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 8169–8172. (b) Inoue, M.; Nakada, M. *Org. Lett.* **2004**, *6*, 2977–2980. (c) Bandini, M.; Cozzi, P. G.; Melchiorre, P.; Tino, R.; Umani-Ronchi, A. *Tetrahedron: Asymmetry* **2001**, *12*, 1063–1069. (d) Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Polyhedron* **2000**, *19*, 537–539.

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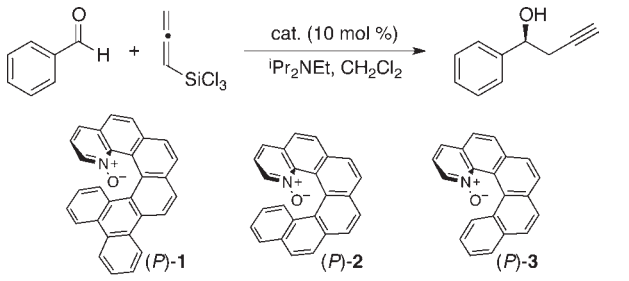
propargylation of aldehydes remains a challenge. Some of these methods suffer from difficulties associated with low regioselectivity (competing allenylation) and/or reactivity. In some instances, the protocol requires the use of toxic reagents, such as tin compounds.

Chiral Lewis base catalysis of polychlorosilane-mediated transformations was pioneered by Denmark and co-workers, and such Lewis base catalysts have been shown to promote several synthetically useful reactions, providing valuable implication for further study.[7] Allenyltrichlorosilane is an attractive candidate as a nucleophilic partner in C=O and C=N propargylation reactions because of its mildness, regiospecificity, and low toxicity, although it is considerably less reactive than analogous allyltrichlorosilane.[8,9] However, to our knowledge, the report by Nakajima and co-workers is the only example of the use of this reagent in asymmetric catalysis (20 mol % of axial chiral 3,3′-dimethyl-2,2′-biquinoline *N,N*′-dioxide,[10] 35−65% yields, 23−52% ees).[11a] Herein, we report the discovery of a new bidentate Lewis base that efficiently catalyzes the addition of allenyltrichlorosilane to aromatic aldehydes with high levels of enantioselectivity and yields. The proposed stereochemical models that account for the observed levels and trends in enantioselectivity are provided.

Recently, we reported that helical chiral pyridine *N*-oxides **1**−**3** (Table 1) efficiently activate $SiCl_4$, and the chirality of an helicene can indeed be communicated effectively to the putative hypervalent silicate complex.[12,13] In light of this observation, we were interested in exploring the reactivity of allenyltrichlorosilane in Lewis base-catalyzed addition to aldehydes since it represents a more challenging substrate as mentioned above.

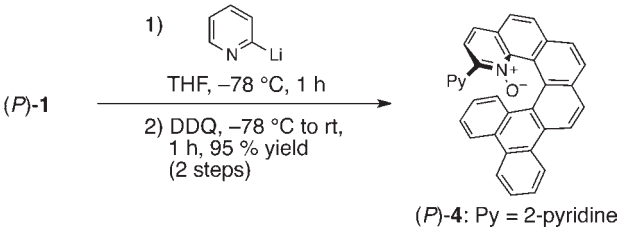
Table 1. Evaluation of Catalysts[a]



entry	cat.	temp (°C)	time (h)	yield (%)[b]	ee[c]
1	**1**	−78	24	7	68
2	**1**	−40	24	48	54
3	**1**	−20	24	80	48
4	**2**	−20	24	85	48
5	**3**	−20	24	90	34
6	**4**[d]	**−78**	**3**	**99**	**84**

[a] Allenyltrichlorosilane (1.5 equiv) was used. [b] Yield of the isolated product. [c] Ee value was determined by HPLC analysis on a chiral phase. [d] See Scheme 1.

Scheme 1. Synthesis of a New Bidentate Catalyst



(*P*)-**4**: Py = 2-pyridine

We initiated our investigation by evaluating the reaction of allenyltrichlorosilane with benzaldehyde using catalyst **1** (Table 1). To our delight, **1** did catalyze the reaction and provided the product with good enantioselectivity although the yield was poor (entry 1). Higher reaction temperature was necessary to increase the yield, but it adversely affected the enantioselectivity (entries 2 and 3). Sterically less demanding catalysts **2** and **3** did not improve the reactivity much (entries 4 and 5). Mechanistically, this reaction is thought to involve coordination of one or two Lewis bases to allenyltrichlorosilane to generate a more Lewis acidic species capable of activating aldehyde toward propargylation, analogous to other reactions involving Lewis bases and polychlorosilanes.[14] Thus, the reaction

(5) For selected references, see: (a) Hanawa, H.; Uraguchi, D.; Konishi, S.; Hashimoto, T.; Maruoka, K. *Chem.—Eur. J.* **2003**, *9*, 4405–4413. (b) Konishi, S.; Hanawa, H.; Maruoka, K. *Tetrahedron: Asymmetry* **2003**, *14*, 1603–1605. (c) Yu, C.-M.; Kim, J.-M.; Shin, M.- S.; Cho, D. *Tetrahedron Lett.* **2003**, *44*, 5487–5490. (d) Evans, D. A.; Sweeney, Z. K.; Rovis, V; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 12095–12096. (e) Denmark, S. E.; Wynn, T. *J. Am. Chem. Soc.* **2001**, *123*, 6199–6200. (f) Yu, C.-M.; Yoon, S.-K.; Choi, H.-S.; Baek, K. *Chem. Commun.* **1997**, 763–764. (g) Keck, G. E.; Krishnamurthy, D.; Chen, X. *Tetrahedron Lett.* **1994**, *55*, 8323–8324.

(6) (a) Fandrick, D. R.; Fandrick, K. R.; Reeves, J. T.; Tan, Z.; Tang, W.; Capacci, A. G.; Rodriguez, S.; Song, J. J.; Lee, H.; Yee, N. K.; Senanayake, C. H. *J. Am. Chem. Soc.* **2010**, *132*, 7600–7601. For a related copper catalyzed asymmetric propargylation of ketones, see: (b) Shi, S.-L.; Xu, L.-W.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 6638–6639.

(7) For selected reviews, see: (a) Denmark, S. E.; Beutner, G. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 1560–1638. (b) Benaglia, M.; Guizzetti, S.; Pignataro, L. *Coord. Chem. Rev.* **2008**, *252*, 492–512. (c) Malkov, A. V.; Kocovsky, P. *Eur. J. Org. Chem.* **2007**, 29–36. (d) Orito, Y.; Nakajima, M *Synthesis* **2006**, *9*, 1391–1401.

(8) (a) Schneider, U.; Sugiura, M.; Kobayashi, S. *Adv. Synth. Catal.* **2006**, *348*, 323–329. (b) Schneider, U.; Sugiura, M.; Kobayashi, S. *Tetrahedron* **2006**, *62*, 496–502. (c) Kobayashi, S.; Nishio, K. *J. Am. Chem. Soc.* **1995**, *117*, 6392–6393.

(9) For discussions, see: (a) Curtis-Long, M. J.; Aye, Y. *Chem.—Eur. J.* **2009**, *15*, 5402–5416. (b) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763–2793. Allenylstannanes are considerably less reactive than allylstannanes. see:(c) Lequan, M.; Guillerm, et G. *J. Organomet. Chem.* **1973**, *54*, 153–164.

(10) 3,3′-Dimethyl-2,2′-biquinoline *NN*′-dioxide developed by Nakajima and co-workers is among the most successful catalysts reported to date for allylation of aldehydes with allyltrichlorosilane. (a) Nakajima, M.; Saito, M.; Shiro, M.; Hashimoto, S. *J. Am. Chem. Soc.* **1998**, *120*, 6419–6420. Also see(b) Malkov, A. V.; Bell, M.; Castelluzzo, F.; Kocovsky, P. *Org. Lett.* **2005**, *7*, 3219–3222 and ref 7c.

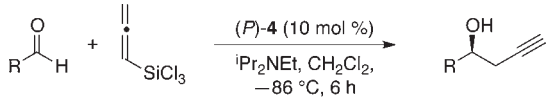
(11) (a) Nakajima, M.; Saito, M.; Hashimoto, S. *Tetrahedron: Asymmetry* **2002**, *13*, 2449–2452. For a related allenylation of aldehydes, see: (b) Iseki, K.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron: Asymmetry* **1998**, *9*, 2889–2894.

(12) (a) Chen, J.; Takenaka, N. *Chem.—Eur. J.* **2009**, *15*, 7268–7276. (b) Takenaka, N.; Sarangthem, R. S.; Captain, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 9708–9710.

(13) For azahelicenes as asymmetric catalysts, see: (a) Takenaka, N.; Chen, J.; Captain, B.; Sarangthem, R. S.; Chandrakumar, A. *J. Am. Chem. Soc.* **2010**, *132*, 4536–4537. (b) Samai, M.; MiSek, J.; Stara, I. G.; Stary, I. *Collect. Czech. Chem. Commun.* **2009**, *74*, 1151–1159.

can be either first or second order in a monodentate Lewis base catalyst. Since the beneficial effects of bidentate catalysts were described for some analogous reactions,[14,15] we decided to pursue the possibility that 2-pyridine substituted *N*-oxide **4** (Scheme 1) might serve as a bidentate Lewis base catalyst[16] (i.e., first order in the catalyst). Catalyst **4** was readily derived from **1** in high yield.[17] To our surprise, **4** displayed *significantly* increased reactivity and selectivity, completing the reaction at −78 °C in only 3 h (entry 6).[18]

Table 2. Asymmetric Propargylation of Aldehydes[a]



entry	R	yield (%)[b]	ee[c]
1[d]	Ph	87	86
2[d]	2-naphthyl	86	84
3[d]	4-Br-Ph	95	92
4	4-Cl-Ph	90	92
5	4-F-Ph	93	88
6[f]	4-NO_2−Ph	55[e]	92
7	4-CF_3−Ph	80	90
8	4-MeO-Ph	80	74
9	4-Me-Ph	85	82
10[d]	2-Br-Ph	93	96
11	2-Cl-Ph	97	96
12	2-F-Ph	98	92
13	2-NO_2−Ph	87	96
14[f]	2-CF_3−Ph	95	94
15	2-MeO-Ph	78	94
16	2-Me-Ph	90	86
17[f]	2-Br-4-Me-Ph	92	96
18[g]	Cy	61[h](80)[i]	59

[a] Allenyltrichlorosilane (1.5 equiv)was used. [b] Yield of the isolated product. [c] Ee value was determined by HPLC analysis on a chiral phase. [d] Absolute configurations were determined. See Supporting Information. [e] Low yield is presumably due to the poor solubility of the aldehyde. [f] (*M*)-4 catalyst was used. [g] (*R*)-Isomer is major. [h] Twelve hour reaction. [i] Thirty-six hour reaction.

Next, we systematically examined a series of aromatic aldehydes using catalyst **4**. The results are summarized in Table 2, from which certain trends were gleaned. (1) In the case of 4-substituted aldehydes, electron-deficient aldehydes (entries 3−7) are better substrates than electron-rich aldehydes (entries 8 and 9) in terms of enantioselectivity. (2) For 2-substituted counterparts, both electron-deficient and electron-rich aldehydes provided excellent enantioselectivities (entries 10−17). (3) 2-substituted aldehydes always provided higher enantioselectivities than 4-substituted counterparts did regardless of the kind of functional groups. An aliphatic aldehyde was also found to be a good substrate for the present catalyst although somewhat longer reaction time was required (entry 18). At the end of these reactions, the catalysts were recovered (ca. 80%) and reused without loss in activity and selectivity.

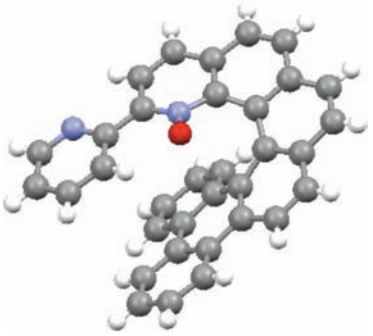


Figure 1. Solid-state structure of (*P*)-**4**.

Collectively considering all the data we have obtained so far, including the crystal structure of **4** (Figure 1), we were able to propose the stereochemical models[19] that are consistent with the observed sense of enantioselection and the aforementioned trends (Scheme 2). The *Si* face addition is favored due to the expected π-stacking between the bound aldehyde and the helicene framework. In contrast, the 11, 12- benzo unit is very close to the aldehyde bound in the *Re* face addition mode (steric repulsion). This expected steric repulsion is also consistent with the large enantioselectivity difference between 4- and 2-MeO substituted aldehydes whose π-stacking interactions with the helicene framework should not be efficient (Table 2, entries 8 and 15). For comparison, we synthesized catalyst **5** and tested it (Scheme 2, eq 1). It was equally reactive but significantly less selective than **4** as predicted by the stereochemical models. While a definitive answer regarding the mode of 2-pyridine substituted catalyst **4** is still to be firmly

(14) For selected references, see: (a) Denmark, S. E.; Eklov, B. M.; Yao, P. J.; Eastgate, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 11770–11787. (b) Malkov, A. V.; Ramirez-Lopez, P.; Biedermannova, L.; Rulfiek, L.; Dufkova, L.; Kotora, M.; Zhu, F.; Kocovsky, P. *J. Am. Chem. Soc.* **2008**, *130*, 5341–5348. (c) Denmark, S. E.; Fu, J.; Coe, D. M.; Su, X.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **2006**, *71*, 1513–1522. (d) Denmark, S. E.; Fu, J.; Lawler, M. J. *J. Org. Chem.* **2006**, *71*, 1523–1536. (e) Malkov, A. V.; Dufkova, L.; Farrugia, L.; Kocovsky, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3674–3677. (f) Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2000**, *122*, 12021–12022.

(15) For selected references, see: (a) Pu, X.; Qi, X.; Ready, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 10364–10365. (b) Chelucci, G.; Baldino, S.; Pinna, G. A.; Benaglia, M.; Buffa, L.; Guizzetti, S. *Tetrahedron* **2008**, *64*, 7574–7582. (c) Nakajima, M.; Saito, M.; Uemura, M.; Hashimoto, S. *Tetrahedron Lett.* **2002**, *43*, 8827–8829.

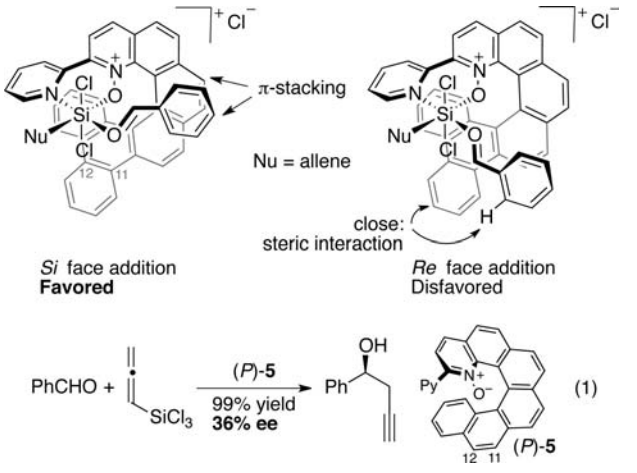
(16) For selected references for 2,2′-bipyridine *N*-monoxides as Lewis base catalysts, see: (a) Malkov, A. V.; Orsini, M.; Pernazza, D.; Muir, K. W.; Langer, V.; Meghani, P.; Kocovsky, P. *Org. Lett.* **2002**, *4*, 1047–1049. (b) Malkov, A. V.; Bell, M.; Orsini, M.; Pernazza, D.; Massa, A.; Herrmann, P.; Meghani, P.; KoCovsky, P. *J. Org. Chem.* **2003**, *68*, 9659–9668.

(17) Tagawa, Y.; Nomura, M.; Yamashita, H.; Goto, Y.; Hamana, M. *Heterocycles* **1999**, *51*, 2385–2397.

(18) For comparison, we tested the corresponding *p*-tol analogue of **4** (Py = *p*-tol). It hardly produced the product even after 24 h at ambient temperature.

(19) The proposed stereochemical models in Scheme 2 respect the stereoelectronic effect, which dictates that the Lewis-basic *N*-oxide oxygen be positioned *trans* to the allenyl group to enhance its nucleophilicity. For discussions, see: refs 14f, 16 and Traverse, J. F.; Zhao, Y.; Hoveyda, A. H.; Snapper, M. L. *Org. Lett.* **2005**, *7*, 3151–3154.

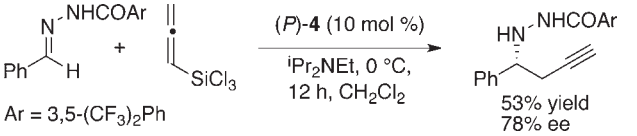
Scheme 2. Proposed Stereochemical Models



established, and while we would like to refrain from speculating on the reason for its remarkably high reactivity at the current stage, we can not completely rule out a possibility of the stabilizing cation-π type interaction[20] between the silicate and the helicene framework due to its unique architecture. This would increase the concentration of a reactive silicate species in the reaction.

Encouraged by the excellent reactivity observed with catalyst **4**, we wondered whether it could add allenyltrichlorosilane to an acylhydrazone.[8a] Interestingly, it did catalyze the reaction and provided the product in good enantioselectivity (Scheme 3).[21,22] It is worthy of mention that substoichiometric enantioinduction has not been

Scheme 3. Propargylation of an Acylhydrazone[a]



[a] Allenyltrichlorosilane (1.5 equiv) was used. The reaction was not optimized.

reported, to our knowledge, for the Lewis base-promoted additions of not only allenyltrichlorosilane but also more reactive allyltrichlorosilane to *N*-acylhydrazones.[23]

In summary, we have developed a highly enantioselective propargylation of aromatic aldehydes with allenyltrichlorosilane. In the course of this study, we have identified new helical chiral 2,2′-bipyridine *N*-monoxides that exhibited excellent reactivity for the relatively unreactive allenyltrichlorosilane. Ongoing studies include mechanistic study of new catalysts, and expansion of the scope and utility of the reaction.

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Supporting Information Available. Experimental procedures, characterization data, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

(20) For selected review, see: Ma, J. C; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303–1324.

(21) For selected references for the asymmetric synthesis of homopropargylic amines, see: (a) Fandrick, D. R.; Johnson, C. S.; Fandrick, K. R.; Reeves, J. T.; Tan, Z.; Lee, H.; Song, J. J.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2010**, *12*, 748–751. (b) Brawn, R. A.; Panek, J. S. *Org. Lett.* **2009**, *11*, 4362–4365. (c) Gonzalex, A. Z.; Soderquist, J. A. *Org. Lett.* **2007**, *9*, 1081–1084.

(22) For catalytic enantioselective propargylation of C=N electrophiles, see: (a) Wisniewska, H. M.; Jarvo, E. R. *Chem. Sci.* **2011**, DOI: 10.1039/c0sc00613k. (b) Kagoshima, H.; Uzawa, T.; Akiyama, T. *Chem. Lett.* **2002**, 298–299.

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