

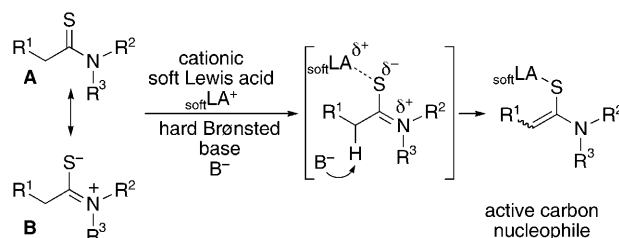
## Direct Catalytic Asymmetric Mannich-Type Reaction of Thioamides\*\*

Yuta Suzuki, Ryo Yazaki, Naoya Kumagai,\* and Masakatsu Shibasaki\*

Thioamides are widely utilized as useful precursors for the synthesis of a broad range of heterocyclic compounds by exploiting their ambident nucleophilic character at both the sulfur and nitrogen atoms.<sup>[1]</sup> They are, however, rarely recognized as carbon pronucleophiles in enantioselective C–C bond-forming reactions. Yoshida and co-workers disclosed that the exposure of thioamides to a stoichiometric amount of strong base selectively generated a *Z* enolate, thus affording *syn*-aldol products upon the addition of aldehydes.<sup>[2]</sup> Lithium thioamide enolates and thioketene *S*-silyl *N,S*-acetals were successively reported as activated nucleophiles for Michael,<sup>[3]</sup> aldol,<sup>[4]</sup> and Mannich-type reactions.<sup>[5]</sup> Later the aldol reaction was rendered asymmetric under stoichiometric conditions, although only one example with benzaldehyde was described.<sup>[6]</sup> In this context, there are no reports on the catalytic generation of active carbon nucleophiles from thioamides and their integration into enantioselective C–C bond-forming processes. Such an approach would be more advantageous than the preceding stoichiometric reactions in terms of both atom and step economy.<sup>[7]</sup> Herein, we report a direct catalytic asymmetric Mannich-type reaction of thioamides and *N*-diphenylphosphinoyl (Dpp) imines<sup>[8]</sup> under proton-transfer conditions by soft Lewis acid/hard Brønsted base cooperative catalysis, to afford enantiomerically enriched  $\beta$ -amino thioamides. Divergent transformation of the thioamides ensures the synthetic utility of the product.

The direct catalytic asymmetric Mannich-type reaction has attracted much attention as a useful protocol to provide optically active  $\beta$ -amino carbonyl units under proton-transfer conditions.<sup>[9]</sup> We recently reported a catalytic system comprising  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4/(R,R)\text{-Ph-BPE/LiOAr}$  that was particularly effective for catalytic generation of nucleophiles from otherwise unreactive pronucleophiles bearing soft Lewis basic functionality.<sup>[10]</sup> We envisioned employing thioamides as carbon pronucleophiles in this catalytic system. The thioamide functionality has an even larger rotational barrier and dipole moment than the corresponding amides, although the C=S bond, unlike the C=O bond, is intrinsically not polar-

ized.<sup>[11]</sup> A commonly accepted interpretation is the greater contribution of the canonical structure B in Scheme 1, where more pronounced charge transfer from N to S is antici-



**Scheme 1.** Catalytic generation of the thioamide enolate by soft Lewis acid/hard Brønsted base cooperative catalysis.

pated.<sup>[12]</sup> Higher acidity of the  $\alpha$  proton of thioamides compared to that of amides may also be ascribed to better accommodate the negative charge at the sulfur atom.<sup>[13]</sup> We hypothesized that chemoselective coordination of the sulfur atom to a cationic soft Lewis acid would accommodate the partial negative charge and enhance the acidity of the  $\alpha$  proton of thioamides, thus leading to a facile catalytic generation of thioamide enolates by a mild Brønsted base (Scheme 1). Initially, we selected *N,N*-dimethylthioacetamide (**2a**), which is a commercially available thioamide pronucleophile,<sup>[14]</sup> and it was subjected to a direct Mannich-type reaction with *N*-Dpp imine **1a** (Table 1). The catalyst prepared from  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ , (*R,R*)-Ph-BPE, and  $\text{Li}(\text{OC}_6\text{H}_4\text{-}p\text{-OMe})$  showed better catalytic turnover than that prepared from  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ , and afforded **3aa** with encouraging enantioselectivity (Table 1, entries 1 and 2). The reaction in  $\text{CH}_2\text{Cl}_2$  or DME resulted in a lower yield despite the higher solubility of **1a** (Table 1, entries 3 and 4). Toluene offered a suitable reaction medium for the present catalysis in terms of both catalytic turnover and *ee* value (Table 1, entry 5). The reaction in the absence of the  $\text{Cu}^{\text{I}}$  salt or base did not proceed at all, thus verifying the crucial cooperative nature of the soft Lewis acid and hard Brønsted base to generate the active nucleophile from **2a** (Table 1, entries 6 and 7). The reaction can be carried out in the presence of 1 mol % of catalyst at  $-20^\circ\text{C}$  without any loss of enantioselectivity (Table 1, entry 8).

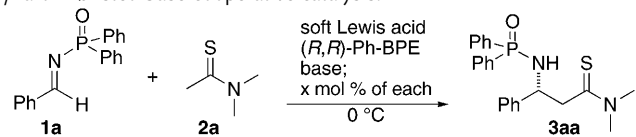
The investigation of the substrate scope with the present system was our next focus. *N,N*-diallyl **2b** and *N,N*-bisPMB **2c** variants, whose nitrogen substituents can be removed at the product elaboration stage, were used as thioamide pronucleophiles. In the reaction using **2b**,  $\beta$  elimination of the *N*-Dpp group occurred occasionally at  $0^\circ\text{C}$ , which was circumvented by lowering the reaction temperature to  $-20^\circ\text{C}$  and using  $\text{Li}(\text{OC}_6\text{H}_4\text{-}o\text{-OMe})$  as the base.<sup>[15]</sup> The reaction of **1a** and **2b** proceeded smoothly with 3 mol % of the catalyst, and

[\*] Y. Suzuki, R. Yazaki, Dr. N. Kumagai, Prof. Dr. M. Shibasaki  
Graduate School of Pharmaceutical Sciences  
The University of Tokyo  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 (Japan)  
Fax: (+81) 3-5684-5206  
E-mail: nkumagai@mol.f.u-tokyo.ac.jp  
mshibasa@mol.f.u-tokyo.ac.jp  
Homepage: [http://www.f.u-tokyo.ac.jp/~kanai/e\\_index.html](http://www.f.u-tokyo.ac.jp/~kanai/e_index.html)

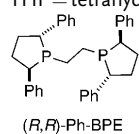
[\*\*] This work was financially supported by a Grant-in-Aid for Scientific Research (S) and a Grant-in-Aid for Young Scientist (B). Dr. M. Shiro at Rigaku Corporation is gratefully acknowledged for technical assistance with the X-ray crystallographic analysis of **3ab**.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.200901588>.

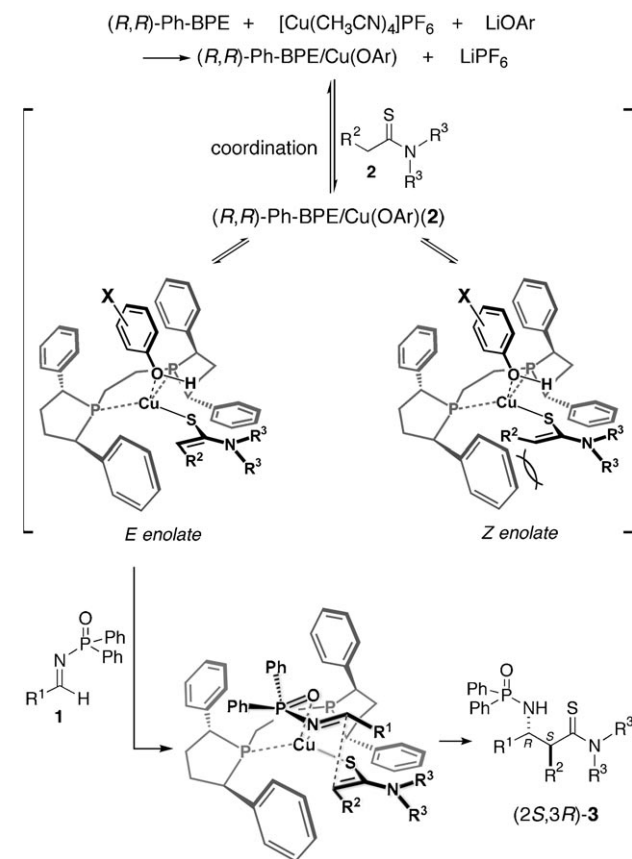
**Table 1:** Direct catalytic asymmetric Mannich-type reaction of *N*-Dpp imine **1a** and thioamides **2a** with soft Lewis acid/hard Brønsted base cooperative catalysis.<sup>[a]</sup>

							
Entry	Soft Lewis acid	Base	Solvent	x [mol %]	t [h]	Yield [%] <sup>[b]</sup>	ee [%]
1	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]ClO <sub>4</sub>	Li(OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe)	THF	10	20	60	87
2	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]PF <sub>6</sub>	Li(OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe)	THF	10	20	72	89
3	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]PF <sub>6</sub>	Li(OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe)	DME	10	20	60	93
4	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]PF <sub>6</sub>	Li(OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe)	CH <sub>2</sub> Cl <sub>2</sub>	10	20	46	88
5	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]PF <sub>6</sub>	Li(OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe)	toluene	10	20	95	95
6 <sup>[c]</sup>	—	Li(OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe)	toluene	10	20	0	—
7 <sup>[c]</sup>	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]PF <sub>6</sub>	—	toluene	10	20	0	—
8 <sup>[d]</sup>	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]PF <sub>6</sub>	Li(OC <sub>6</sub> H <sub>4</sub> - <i>p</i> -OMe)	toluene	1	72	88 <sup>[e]</sup>	96

[a] **1a** (0.2 mmol), **2a** (0.24 mmol). [b] Determined by <sup>1</sup>H NMR with Bn<sub>2</sub>O as an internal standard. [c] In the absence of (*R,R*)-Ph-BPE. [d] Run with 1.5 equivalents of **2a** at −20 °C. [e] Yield of isolated product. THF = tetrahydrofuran, DME = 1,2-dimethoxyethane.



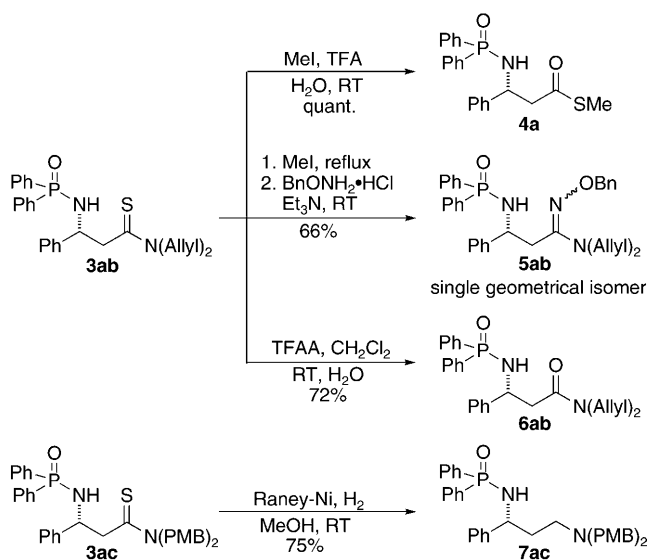
the reaction also reached completion with as little as 1 mol % of catalyst over an extended period of time (Table 2, entries 1 and 2).<sup>[16]</sup> The methyl group at the *ortho* position of the imine did not interfere with the enantioselectivity (Table 2, entry 3), whereas an imine derived from 1-naphthaldehyde gave a



**Scheme 2.** Proposed transition state.

lower enantioselectivity (Table 2, entry 4). Excellent enantioselectivity was maintained with imines bearing either bromide or methoxy substituents in the *para* position (Table 2, entries 5 and 6). Notably, high enantioselectivity was observed even for imines bearing soft Lewis basic 2-thienyl or 2-pyridyl groups (Table 2, entries 8 and 9). Although the yield was moderate with **1h** likely owing to a competitive coordination to Cu<sup>I</sup>. In view of the synthetic utility of the product, a Mannich-type reaction was conducted with imines bearing aliphatic or alkenyl substituents and reasonable enantioselectivities were observed (Table 2, entries 10 and 11). Thioamide **2c** also served as a suitable pronucleophile to afford **3ac** in excellent yield and enantioselectivity (Table 2, entry 12). The reactions using thio-

amides **2d,e** derived from propionic or butyric acids were sluggish and required Li(OC<sub>6</sub>H<sub>4</sub>-*p*-OMe) as a stronger base, and afforded the product in high *anti*-diastereoselectivity and in moderate to good enantioselectivity (Table 2, entries 13–16). A plausible transition state model is depicted in Scheme 2. The (*R,R*)-Ph-BPE/Cu(OC<sub>6</sub>H<sub>4</sub>-*o*-OMe) complex, which would be formed by mixing (*R,R*)-Ph-BPE, [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>, and Li(OC<sub>6</sub>H<sub>4</sub>-*o*-OMe),<sup>[17]</sup> serve as a soft Lewis acid and a hard Brønsted base to generate thioamide enolates, which would be in equilibrium between *E/Z* isomers through protonation/deprotonation. Taking severe steric constraint into account, the reaction would proceed through the transition state where the *N,N*-dialkyl and *C*-alkyl groups



**Scheme 3.** Transformation of the Mannich products. TFA = trifluoroacetic acid, TFAA = trifluoroacetic anhydride.

**Table 2:** Direct catalytic asymmetric Mannich-type reaction of *N*-Dpp imine **1** and thioamides **2**.<sup>[a]</sup>

Entry	Imine <b>1</b>	R <sup>1</sup>	Thioamide <b>2</b>	x [mol %]	Product	T [°C]	t [h]	anti/syn <sup>[b]</sup>	Yield [%] <sup>[c]</sup>	ee [%]
1	<b>1a</b>		<b>2b</b>	3	<b>3ab</b>	-20	20	—	95	97
2	<b>1a</b>		<b>2b</b>	1	<b>3ab</b>	-20	72	—	99	95
3	<b>1b</b>		<b>2b</b>	3	<b>3bb</b>	-20	48	—	88	95
4	<b>1c</b>		<b>2b</b>	3	<b>3cb</b>	-20	20	—	96	84
5	<b>1d</b>		<b>2b</b>	3	<b>3db</b>	-20	20	—	94	95
6	<b>1e</b>		<b>2b</b>	3	<b>3eb</b>	-20	48	—	89	95
7	<b>1f</b>		<b>2b</b>	3	<b>3fb</b>	-20	48	—	95	93
8	<b>1g</b>		<b>2b</b>	3	<b>3gb</b>	-20	48	—	90	90
9	<b>1h</b>		<b>2b</b>	3	<b>3hb</b>	-20	48	—	54	88
10	<b>1i</b>		<b>2b</b>	3	<b>3ib</b>	-20	48	—	60	78
11	<b>1j</b>		<b>2b</b>	3	<b>3jb</b>	-20	48	—	66	81
12	<b>1a</b>		<b>2c</b>	3	<b>3ac</b>	-20	48	—	99	94
13 <sup>[d,e]</sup>	<b>1a</b>		<b>2d</b>	10	<b>3ad</b>	-20	72	89/11	57	88 <sup>[f]</sup>
14 <sup>[d,e]</sup>	<b>1a</b>		<b>2d</b>	10	<b>3ad</b>	0	72	90/10	89	74 <sup>[f]</sup>
15 <sup>[d,e]</sup>	<b>1a</b>		<b>2e</b>	10	<b>3ae</b>	0	72	90/10	84	53 <sup>[f]</sup>
16 <sup>[d,e]</sup>	<b>1d</b>		<b>2d</b>	10	<b>3dd</b>	0	42	89/11	89	71 <sup>[f]</sup>

[a] **1** (0.2 mmol), **2** (0.3 mmol). [b] Determined by <sup>1</sup>H NMR analysis. [c] Yield of isolated product. [d] Li(OC<sub>6</sub>H<sub>4</sub>-*p*-OMe) was used instead of Li(OC<sub>6</sub>H<sub>4</sub>-*o*-OMe). [e] THF was used as the solvent. [f] Enantioselectivity of the *anti* diastereomer. PMB = *p*-methoxybenzyl.

of the *E* enolate and the *P,P*-diphenyl groups of **1** occupy the vacant space of the asymmetric architecture provided by (*R,R*)-Ph-BPE, thereby affording (2*S*,3*R*)-**3** predominantly.

The rich chemistry of thioamides enabled functional group manipulation of the Mannich product (Scheme 3). Treatment of **3ab** with MeI in the presence of H<sub>2</sub>O under acidic conditions gave methyl thioester **4a** in quantitative yield.<sup>[18]</sup> Meanwhile, anhydrous conditions and the addition of HCl·NH<sub>2</sub>OBn provided benzyloxyamidine **5ab** as a single geometric isomer. Facile conversion into amide **6ab** was achieved by TFAA in CH<sub>2</sub>Cl<sub>2</sub>.<sup>[19]</sup> Desulfurization of **3ac** with Raney-Ni generated the *N,N*-bisPMB-protected diamine **7ac** in 75 % yield.

In summary, we have developed a direct catalytic asymmetric Mannich-type reaction of *N*-Dpp imines and thioamides. A soft Lewis acid/hard Brønsted base cooperative system worked efficiently to generate the active carbon nucleophile from thioamides by exploiting the soft Lewis basic nature of the sulfur atom. The reaction can be performed with as little as 1 mol % of catalyst and excellent enantioselectivity as well as high *anti*-diastereoselectivity was observed. Divergent transformation of thioamide functionality highlights the utility of the methodology presented here.

### Experimental Section

A typical procedure for the direct catalytic asymmetric Mannich-type reaction of *N*-Dpp imine **1a** and thioamide **2b** described in Table 2, entry 1: A flame-dried 20 mL test tube equipped with a magnetic stirring bar was charged *N*-Dpp imine **1a** (61.1 mg, 0.2 mmol) and was dried under vacuum for 10 min. The test tube was back-filled with argon and dry toluene (2.0 mL) was added in an argon atmosphere. Then a premixed solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> and (*R,R*)-Ph-BPE in THF (60 μL, 0.006 mmol, 0.1 M) was added at room temperature. After cooling the reaction mixture to -20 °C, Li(OC<sub>6</sub>H<sub>4</sub>-*o*-OMe) (30 μL, 0.006 mmol, 0.2 M/THF) and thioamide **2b** (47.7 μL, 0.3 mmol) were subsequently added. After stirring at the same temperature for 20 h, 1 N HCl (1.0 mL) was added and the resulting biphasic mixture was extracted with AcOEt three times. The combined organic layers were washed with saturated aqueous NaHCO<sub>3</sub> and brine, then dried over Na<sub>2</sub>SO<sub>4</sub>. The volatiles were removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel to give Mannich product **3ab** as a colorless solid (87.5 mg, 0.19 mmol, 95 % yield). The enantioselectivity was determined by HPLC on a chiral stationary phase using a Daicel Chiralcel OD-H column (φ 0.46 × 25 cm); eluent: *n*-hexane/2-propanol = 4/1; flow rate: 0.5 mL min<sup>-1</sup>; detection at 254 nm; *t*<sub>R</sub> = 12.0 min ((*S*) minor), 16.6 ((*R*) major).

Received: March 23, 2009

Published online: May 26, 2009

**Keywords:** asymmetric catalysis · copper · Mannich reactions · proton transfer · thioamides

- [1] T. S. Jagodzinski, *Chem. Rev.* **2003**, *103*, 197, and references therein.
- [2] a) Y. Tamaru, T. Harada, S.-I. Nishi, M. Mizutani, T. Hioeki, Z.-I. Yoshida, *J. Am. Chem. Soc.* **1980**, *102*, 7806; b) Y. Tamaru, T. Hioeki, Z.-I. Yoshida, *Tetrahedron Lett.* **1984**, *25*, 5793.
- [3] C. Goasdoue, N. Goasdoue, M. Gaudemar, M. Mladenova, *J. Organomet. Chem.* **1982**, *226*, 209.
- [4] a) C. Goasdoue, N. Goasdoue, M. Gaudemar, *Tetrahedron Lett.* **1983**, *24*, 4001; b) C. Goasdoue, N. Goasdoue, M. Gaudemar, *Tetrahedron Lett.* **1984**, *25*, 537.
- [5] C. Goasdoue, M. Gaudemar, *Tetrahedron Lett.* **1985**, *26*, 1015.
- [6] N. Iwasawa, T. Yura, T. Mukaiyama, *Tetrahedron* **1989**, *45*, 1197.
- [7] a) B. M. Trost, *Science* **1991**, *254*, 1471; b) P. A. Wender, V. A. Verma, T. J. Paxton, T. H. Pillow, *Acc. Chem. Res.* **2008**, *41*, 40.
- [8] For the utility of *N*-diphenylphosphinoyl imines, see: a) S. M. Weinreb, R. K. Orr, *Synthesis* **2005**, 1205; b) G. K. Friestad, A. K. Mathies, *Tetrahedron* **2007**, *63*, 2541.
- [9] For recent reviews on direct Mannich(-type) reactions, see: a) M. M. B. Marques, *Angew. Chem.* **2006**, *118*, 356; *Angew. Chem. Int. Ed.* **2006**, *45*, 348; b) A. Ting, S. E. Schaus, *Eur. J. Org. Chem.* **2007**, 5797; c) J. M. M. Verkade, L. J. C. van Hemert, P. J. L. M. Quaedflieg, F. P. J. T. Rutjes, *Chem. Soc. Rev.* **2008**, *37*, 29; for general reviews on catalytic asymmetric Mannich reactions, see: d) S. Kobayashi, M. Ueno in *Comprehensive Asymmetric Catalysis, Supplement 1* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, **2004**, Chapter 29.5, p. 143; e) G. Friestad, A. K. Mathies, *Tetrahedron* **2007**, *63*, 2541.
- [10] a) Y. Suto, R. Tsuji, M. Kanai, M. Shibasaki, *Org. Lett.* **2005**, *7*, 3757; b) Y. Asano, K. Hara, H. Ito, M. Sawamura, *Org. Lett.* **2007**, *9*, 3901; c) R. Yazaki, T. Nitabaru, N. Kumagai, M. Shibasaki, *J. Am. Chem. Soc.* **2008**, *130*, 14477; d) R. Yazaki, N. Kumagai, M. Shibasaki, *J. Am. Chem. Soc.* **2009**, *131*, 3195; for selected examples of catalytic asymmetric formation of C–C or C–B bonds using Cu/alkoxides, see: e) B. L. Pagenkopf, J. Krüger, A. Stojanovic, E. M. Carreira, *Angew. Chem.* **1998**, *110*, 3312; *Angew. Chem. Int. Ed.* **1998**, *37*, 3124; f) H. Ito, C. Kawakami, M. Sawamura, *J. Am. Chem. Soc.* **2005**, *127*, 16034; g) R. Wada, T. Shibusguchi, S. Makino, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2006**, *128*, 7687; h) J.-E. Lee, J. Yun, *Angew. Chem.* **2008**, *120*, 151; *Angew. Chem. Int. Ed.* **2008**, *47*, 145.
- [11] Sulfur has an electronegativity close to that for carbon: a) L. Pauling in *The Nature of Chemical Bond*, 3rd ed., Cornell University, Ithaca, NY, **1960**, pp. 88; for rotational barriers of thioamides, see: b) C. M. Lee, W. D. Kumler, *J. Org. Chem.* **1962**, *27*, 2052; c) K. A. Jensen, *Acta Chem. Scand.* **1963**, *17*, 551; d) A. Loewenstein, A. Melera, P. Rigny, W. Walter, *J. Phys. Chem.* **1964**, *68*, 1597; e) W. E. Stewart, T. H. Siddall III, *Chem. Rev.* **1970**, *70*, 517.
- [12] a) K. B. Wiberg, P. R. Rablen, *J. Am. Chem. Soc.* **1995**, *117*, 2201; b) D. Lauvergnat, P. C. Hiberty, *J. Am. Chem. Soc.* **1997**, *119*, 9478; c) B. Galabov, S. Ilieva, B. Hadjieva, E. Dincheva, *J. Phys. Chem. A* **2003**, *107*, 5854.
- [13] *H*-CH<sub>2</sub>C(S)NMe<sub>2</sub> (*pK<sub>a</sub>* = 25.7 in DMSO; F. G. Bordwell, H. E. Fried, *J. Org. Chem.* **1991**, *56*, 4218) compared to the corresponding amide *H*-CH<sub>2</sub>C(O)NEt<sub>2</sub> (*pK<sub>a</sub>* = 35 in DMSO; M. L. Hlavinka, J. F. Greco, J. R. Hagadorn, *Chem. Commun.* **2005**, 5304).
- [14] As of May 2009, this commercially available C2 unit sells for €85.7 per 5 g from A Better Choice for Research Chemicals.
- [15] Lower basicity of LiOC<sub>6</sub>H<sub>4</sub>-*o*-OMe (*pK<sub>a</sub>* = 17.8 in DMSO) compared with LiOC<sub>6</sub>H<sub>4</sub>-*p*-OMe (*pK<sub>a</sub>* = 19.1 in DMSO) would avoid undesirable β elimination.
- [16] The absolute configuration of **3ab** was determined by single X-ray crystallographic analysis. *Mr* = 475.67, colorless block; *a* = 13.9241(3), *b* = 19.8931(4), *c* = 21.3053(4) Å, *α* = 64.6031(10)°, *β* = 118.497(7)°, *γ* = 88.5534(11)°. *V* = 5228.95(19) Å<sup>3</sup>, *T* = 103 K, triclinic, space group *P*1, *Z* = 8, Rigaku RAXIS-RAPID, λ(Cu Kα) = 1.54187 Å, *θ*<sub>max</sub> = 68.25°. The crystallographic data (CCDC-720992) can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [17] Mixing three catalyst components would afford Ph-BPE/Cu(OC<sub>6</sub>H<sub>4</sub>-*o*-OMe) and LiPF<sub>6</sub>. For the formation of CuOAr upon addition of an alkali metal aryloxide to Cu<sup>I</sup> salt, see: P. G. Eller, G. J. Kubas, *J. Am. Chem. Soc.* **1977**, *99*, 4346.
- [18] D. C. Harrowven, M. C. Lucas, P. D. Howes, *Tetrahedron* **1999**, *55*, 1187.
- [19] R. Masuda, M. Hojo, T. Ichi, S. Sasano, T. Kobayashi, C. Kuroda, *Tetrahedron Lett.* **1991**, *32*, 1195.