

Highly Enantioselective Synthesis of Multifunctionalized Dihydrofurans by Copper-Catalyzed Asymmetric [4 + 1] Cycloadditions of α -Benzylidene- β -ketoester with Diazo Compound

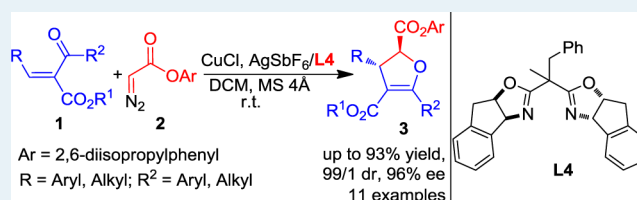
Jiao-Long Zhou, Li-Jia Wang, Hao Xu, Xiu-Li Sun, and Yong Tang*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

Supporting Information

ABSTRACT: Highly efficient synthesis of chiral tetrasubstituted 2,3-dihydrofuran derivatives has been realized by Cu-catalyzed asymmetric [4 + 1] cycloadditions of α -benzylidene- β -ketoester with a diazo compound. Following this methodology, a series of optically active multifunctionalized dihydrofurans were prepared in high yield with up to 96% ee and 99/1 dr.

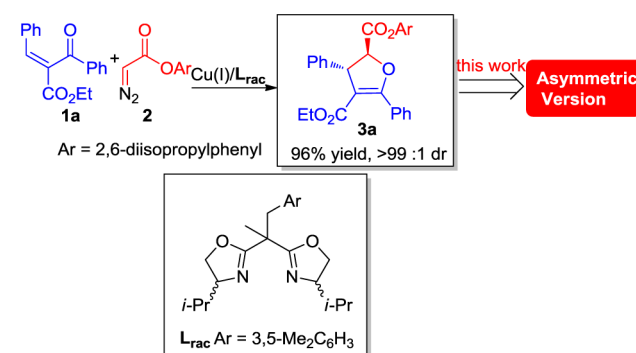
KEYWORDS: asymmetric, copper carbene, [4 + 1] cycloadditions, dihydrofurans



Synthesis of oxygenated heterocycles via transition-metal-catalyzed decomposition of diazo compounds generated by transient carbonyl ylides has proved to be one of the most efficient and practical protocols and has drawn considerable interest.^{1,2} Of those studies, the carbonyl ylides-involved 1,3-dipolar cycloaddition reactions have been well developed.^{3,4} However, [4 + 1] cycloadditions of α,β -unsaturated carbonyl compounds with diazo compounds, which provide a facile access to multifunctionalized 2,3-dihydrofurans, has been less explored. In 1967, Spencer et al. pioneered CuSO₄-catalyzed [4 + 1] cycloadditions of β -methoxy- α,β -unsaturated ketones with ethyl diazoacetate.⁵ Since then, great efforts have been devoted to the exploitation of such a cycloaddition,⁶ but none of these investigations has realized the enantioselective version until Fu's work in 2007,^{7a} leading to optically active 2,3,5-trisubstituted 2,3-dihydrofurans⁷ with good efficiency and stereoselectivity under the catalysis of the Cu(I)/[(-)-bpy*] complex. In view of dihydrofurans containing molecular skeletons being key subunits of various biologically active compounds as well as versatile intermediates for the construction of complex molecules,^{8,9} they are of considerable synthetic value, and efficient methodologies for the catalytic enantioselective synthesis of chiral multifunctionalized 2,3-dihydrofurans are still highly demanded.

In 2011, we developed a tunable carbonyl ylide reaction: in the presence of side-arm-modified *rac*-ⁱPrBox L_{rac}/Cu (I), the reaction of a α -benzylidene- β -dicarbonyl compound with a diazo 2,6-diisopropylphenyl ester can furnish 2,3,4,5-tetrasubstituted 2,3-dihydrofurans with high chemoselectivity in excellent yields and with high diastereocontrol (Scheme 1).¹⁰ Recently, our attempts on the asymmetric version achieved promising enantioselectivity to afford optically active 2,3,4,5-tetrasubstituted 2,3-dihydrofuran products. In this letter, we present our preliminary results on this subject.

Scheme 1. Synthesis of 2,3,4,5-Tetrasubstituted 2,3-dihydrofurans

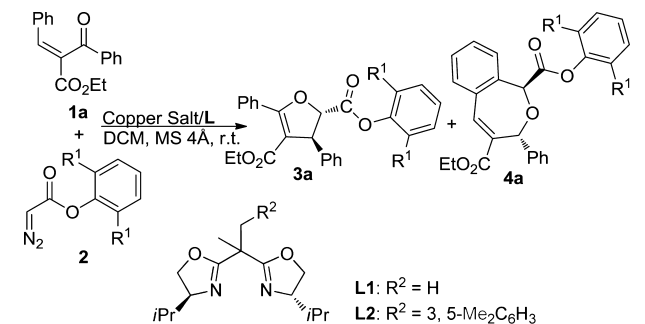


Initially, a control experiment was carried out with non-side arm ⁱPrBox L1 and side arm-modified ⁱPrBox L2, which indicated that installing an aryl side arm at the bridge of the bisoxazoline ligand could increase the enantioselectivity of this reaction obviously (Table 1, entry 1 vs 2). In the case of L2 as a ligand, we examined the cycloadditions of α -benzylidene- β -ketoester **1a** with diazo compound **2** in the presence of a variety of commonly used copper salts. As shown in Table 1, the reaction was carried out smoothly in good yield with 88% ee for the major diastereoisomer when CuPF₆(CH₃CN)₄ was used, but 14% yield of **4a** was also detected by ¹H NMR analysis (entry 2).¹⁰ Both CuBARf (CuCl + NaBARf) and CuSbF₆ (CuCl + AgSbF₆) could give the desired 2,3-dihydrofuran **3a** in excellent yields with high enantioselectivities (92% yield with 90% ee and 94% yield with 91% ee,

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Table 1. Optimization of Reaction Conditions^a

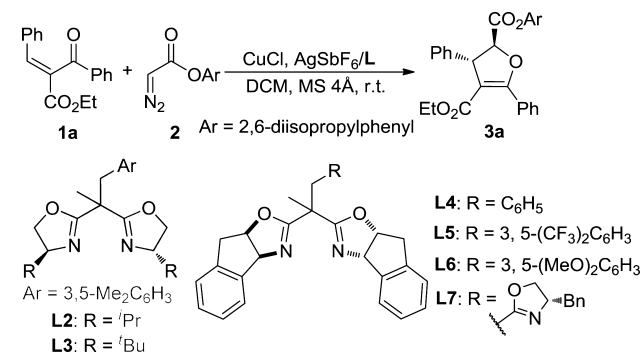
entry	copper salt	R ¹	L	yield of 3a (%) ^b	ee (%) ^c
1	CuPF ₆ (MeCN) ₄	ⁱ Pr	L1	90	75
2	CuPF ₆ (MeCN) ₄	ⁱ Pr	L2	85 ^d	88
3	CuCl + NaBARF ^f	ⁱ Pr	L2	94 (92) ^e	90
4	CuCl + AgSbF ₆	Me	L2	90	89
5	CuCl + AgSbF ₆	^t Bu ^g	L2	94	89
6	CuCl + AgSbF ₆	ⁱ Pr	L2	94 (94) ^e	91

^aReaction conditions: Copper salt (5 mol %), L (5.2 mol %), MS 4 Å (100 mg/mL), DCM, r.t., 1a (0.5 mmol), 2 (2.0 mmol). ^bDetermined by ¹H NMR. ^cFor major diastereomer; determined by chiral HPLC. ^d4a was observed from ¹H NMR in 14% yield with 53% ee. ^eIsolated yield. ^fBARF⁻ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. ^gDiazo 2,6-di-^tBu-4-Me-Phenyl ester and (E)-ethyl 2-benzoyl-3-(4-chlorophenyl)acrylate used.

respectively, entries 3 and 6). The impact of the diazo ester was next investigated, and it was found that the nature of the diazo compounds influences the yield and stereoselectivity.¹¹ Further study showed that the diazo 2,6-diisopropylphenyl ester provided the best combination of both yield and ee (94% yield, 91% ee, entry 6).

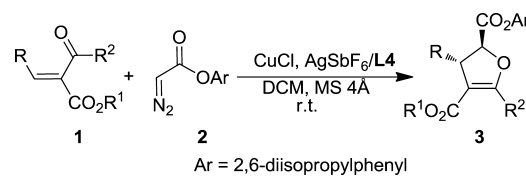
Further investigation was focused on the ligand effects of modified bisoxazolines on the enantioselectivity.^{12,13} As outlined in Table 2, comparing with the ⁱPrBox L2 and ^tBu-Box L3, ligands L4–L7 with indane skeletons gave a better result. For example, the enantioselectivity could be increased to 96% ee with a slight decrease in the isolated yield when InBox L4 was employed (entry 3). By the use of chiral InBox L5 with a 3,5-ditrifluoromethylbenzyl group as a side arm, 95% ee could also be afforded (entry 4). In contrast, chiral ligand L6 with 3,5-dimethoxybenzyl, which contains an electron-rich side arm, led to an obvious decline in the ee value (84% ee, entry 5). In addition, good enantioselectivity could also be achieved with the chiral In-TOX ligand L7 (94% ee, entry 6).

Under the optimized conditions, we evaluated the generality of the current asymmetric reaction. As shown in Table 3, a variety of substrates were examined. When R and R² were a phenyl or substituted phenyl group, the reaction displayed excellent stereoselectivity and chemoselectivity. All substrates completed the reaction smoothly to afford optically active 2,3-dihydrofuran derivatives in up to 96% yield with extremely high diastereoselectivities (>99/1) as well as excellent enantioselectivities (90–96%), regardless of the electronic nature and the position of the substituent on phenyl group R (entries 1–7). Further studies show that alkyl-substituted substrates are suitable to this catalysis. For instance, when R² was ⁱPr, the reaction could furnish the desired 3h with 79% yield in up to 99/1 dr and 89% ee (entry 8). Using the Me group instead of the ⁱPr group, the high diastereoselectivity and enantioselectivity were maintained, albeit with a slight decrease in the yield

Table 2. Survey of Ligands^a

entry	ligand	yield (%) ^b	ee (%) ^c
1	L2	94 (94) ^d	91
2	L3	45 ^e	99
3	L4	93 (82) ^d	96
4	L5	88	95
5	L6	88	84
6	L7	86 ^f	94

^aReaction conditions: CuCl (2.5 mg, 0.025 mmol, 5 mol %), AgSbF₆ (8.7 mg, 0.025 mmol, 5 mol %), ligand (0.026 mmol, 5.2 mol %), MS 4 Å (100 mg/mL), DCM, r.t., 1a (0.5 mmol), 2 (2.0 mmol). ^bDetermined by ¹H NMR. ^cFor major diastereomer; determined by chiral HPLC. ^dIsolated yield. ^e4a was observed by ¹H NMR in 55% yield with 24% ee. ^f4a was observed by ¹H NMR in 13% yield with 38% ee.

Table 3. Substrate Scope^a

entry	substrate (R, R ¹ , R ²)	yield ^b	dr ^c	ee ^d (%)
1	1a (Ph, Et, Ph)	3a, 82%	99/1	96
2	1b (o-Me-C ₆ H ₄ , Et, Ph)	3b, 71%	99/1	95
3	1c (p-Me-C ₆ H ₄ , Et, Ph)	3c, 89%	99/1	95
4 ^e	1d (p-MeO-C ₆ H ₄ , Et, Ph)	3d, 85%	99/1	90
5	1e (p-CF ₃ -C ₆ H ₄ , Et, Ph)	3e, 82%	99/1	90
6	1f (p-Cl-C ₆ H ₄ , Et, Ph)	3f, 93%	99/1	96
7	1g (p-Br-C ₆ H ₄ , Et, Ph)	3g, 81%	99/1	96
8	1h (Ph, Me, ⁱ Pr)	3h, 79%	99/1	89
9	1i (Ph, Et, Me)	3i, 65%	99/1	90
10 ^f	1j (n-C ₈ H ₁₇ , Et, Ph)	3j, 68%	90/10	81
11 ^f	1k (n-C ₁₂ H ₂₅ , Et, Ph)	3k, 74%	92/8	78

^aReaction conditions: CuCl (2.5 mg, 0.025 mmol, 5 mol %), AgSbF₆ (8.7 mg, 0.025 mmol, 5 mol %), ligand (0.026 mmol, 5.2 mol %), MS 4 Å (100 mg/mL) and DCM, r.t., 1 (0.5 mmol), 2 (2.0 mmol). ^bIsolated yield. ^cDetermined by ¹H NMR. ^dDetermined by chiral HPLC. ^eLigand = L3. ^fLigand = L7, 10 mol % catalyst.

(entry 9). When R was n-C₈H₁₇ and n-C₁₂H₂₅, good stereoselectivities and isolated yields were obtained, giving 68% yield with 90/10 dr and 81% ee and 74% yield with 92/8 dr and 78% ee, respectively (entry 10 and 11). The absolute configuration of 3g was established as 2S, 3S by X-ray crystallography (Figure 1).¹⁴

Previous study of the structure of side-armed BOX–metal complexes showed that the pendant aryl groups of BOX–metal complexes always bend toward the metal center.¹⁵ In

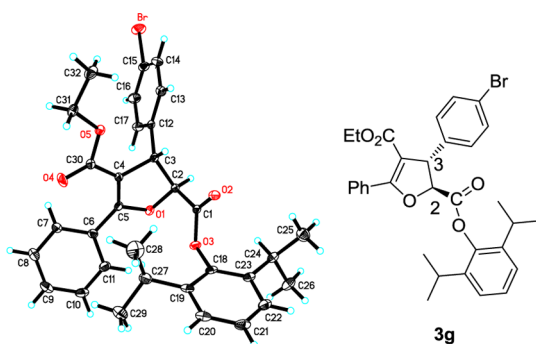
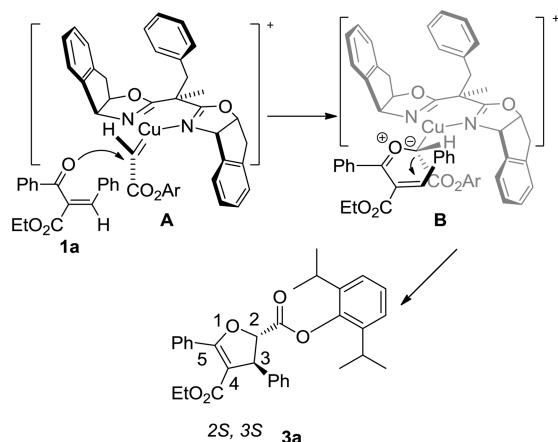


Figure 1. X-ray crystal structure of **3g**.

combination with our previous computational study¹⁰ and the aforementioned experimental results, the stereoinductive model shown in Scheme 2 was proposed to account for the observed

Scheme 2. Proposed Stereochemical Model



enantioselectivity. In this model, the top of the Cu(I)/oxazoline ring square is blocked by the phenyl-ring side arm, and the top left corner as well as the lower right corner are blocked by an indanyl ring. We proposed that in the presence of the Cu(I) complex, the diazo compound decomposed to form copper carbene **A** first, followed by the formation of the accepted metal-associated carbonyl ylide **B** by attack of the carbonyl group from the lower left corner of the copper carbene with a less steric hindrance. Consequently, 1,5-cyclization takes place by the ylide attack from the *si* face of the benzylidene plate (Scheme 2). To our delight, this model is consistent with stereochemical results.

In conclusion, we have developed an efficient and practical protocol to construct chiral multifunctionalized 2,3-dihydrofurans by combining a α -benzylidene- β -ketoester with a diazo compound. Following this methodology, a series of optically active tetrasubstituted 2,3-dihydrofurans were achieved with good to excellent stereoselectivity (90/10–99/1 dr and 78–96% ee) in good to excellent yields (65–93%). In addition, a rational stereoinductive model was developed. The present reaction will be helpful for the understanding of the Cu(I)/side-armed BOX-catalyzed reactions and provide useful information for the rational design of new ligands to control selectivities in related asymmetric reactions.

ASSOCIATED CONTENT

Supporting Information

¹H NMR and ¹³C NMR spectroscopic data of new compounds and analytic data of the compounds **3** are included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: tangy@mail.sioc.ac.cn.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) For reviews, see: (a) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon Press: New York, 1995; Vol. 12, p 421. (b) Padwa, A.; Weigarten, M. D. *Chem. Rev.* **1996**, *96*, 223. (c) Mehta, G.; Muthusamy, S. *Tetrahedron* **2002**, *58*, 9477. (d) McMills, M. C.; Wright, D. In *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*; Padwa, A., Pearson, W. H., Eds.; Wiley: New York, 2002; Vol. 59, p 253. (e) Padwa, A. *Chem. Soc. Rev.* **2009**, *38*, 3072. (f) Zhao, X.; Zhang, Y.; Wang, J. *Chem. Commun.* **2012**, *48*, 10162.
- (2) For selected examples on carbonyl ylide in total synthesis, see: (a) Hodgson, D. M.; Bailey, J. M.; Villalonga-Barber, C.; Drew, M. G. B.; Harrison, T. J. *Chem. Soc., Perkin Trans. 1* **2000**, 3432. (b) Wood, J. L.; Thompson, B. D.; Yusuff, N.; Pflum, D. A.; Matthäus, M. S. P. *J. Am. Chem. Soc.* **2001**, *123*, 2097. (c) Graening, T.; Friedrichsen, W.; Lex, J.; Schmalz, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1524. (d) Geng, Z.; Chen, B.; Chiu, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 6197. (e) Nakamura, S.; Sugano, Y.; Kikuchi, F.; Hashimoto, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 6532. (f) Mejía-Oneto, J. M.; Padwa, A. *Org. Lett.* **2006**, *8*, 3275. (g) Kim, C. H.; Jang, K. P.; Choi, S. Y.; Chung, Y. K.; Lee, E. *Angew. Chem., Int. Ed.* **2008**, *47*, 4009.
- (3) For selected examples on carbonyl ylide-involved 1,3-dipolar cycloadditions, see: (a) Ibata, T.; Toyoda, J.; Sawada, M.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1266. (b) Suga, H.; Kakehi, A.; Ito, S.; Inoue, K.; Ishida, H.; Ibata, T. *Org. Lett.* **2000**, *2*, 3145. (c) Padwa, A.; Snyder, J. P.; Curtis, E. A.; Sheehan, S. M.; Worsencroft, K. J.; Kappe, C. O. *J. Am. Chem. Soc.* **2000**, *122*, 8155. (d) Suga, H.; Kakehi, A.; Ito, S.; Inoue, K.; Ishida, H.; Ibata, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1115. (e) Torssell, S.; Kienle, M.; Somfai, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 3096. (f) Nair, V.; Mathai, S.; Mathew, S. C.; Rath, N. P. *Tetrahedron* **2005**, *61*, 2849. (g) Diev, V. V.; Kostikov, R. R.; Gleiter, R.; Molchanov, A. P. *J. Org. Chem.* **2006**, *71*, 4066. (h) Muthusamy, S.; Krishnamurthi, J.; Babu, S. A.; Suresh, E. *J. Org. Chem.* **2007**, *72*, 1252. (i) England, D. B.; Eagan, J. M.; Merrey, G.; Anag, O.; Padwa, A. *Tetrahedron* **2008**, *64*, 988. (j) DeAngelis, A.; Panne, P.; Yap, G. P. A.; Fox, J. M. *J. Org. Chem.* **2008**, *73*, 1435. (k) DeAngelis, A.; Taylor, M. T.; Fox, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 1101. (l) Rout, L.; Harned, A. M. *Chem.—Eur. J.* **2009**, *15*, 12926.
- (4) For selected examples on carbonyl ylide-involved asymmetric 1,3-dipolar cycloadditions, see: (a) Suga, H.; Inoue, K.; Inoue, S.; Kakehi, A. *J. Am. Chem. Soc.* **2002**, *124*, 14836. (b) Hodgson, D. M.; Brückl, T.; Glen, R.; Labande, A. H.; Selden, D. A.; Dossetter, A. G.; Redgrave, A. *J. Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5450. (c) Garca Ruano, J. L.; Fraile, A.; Rosario Martín, M.; Núñez, A. *J. Org. Chem.* **2006**, *71*,

6536. (d) Suga, H.; Ishimoto, D.; Higuchi, S.; Ohtsuka, M.; Arikawa, T.; Tsuchida, T.; Kakehi, A.; Baba, T. *Org. Lett.* **2007**, *9*, 4359. (e) Shimada, N.; Anada, M.; Nakamura, S.; Nambu, H.; Tsutsui, H.; Hashimoto, S. *Org. Lett.* **2008**, *10*, 3603.

(5) (a) Storm, D. L.; Spencer, T. A. *Tetrahedron Lett.* **1967**, *8*, 1865. (b) Spencer, T. A.; Villarica, R. M.; Storm, D. L.; Weaver, T. D. R.; Friary, J.; Posler, J.; Shafer, P. R. *J. Am. Chem. Soc.* **1967**, *89*, 5497. (c) Murayama, S. T.; Spencer, T. A. *Tetrahedron Lett.* **1969**, *10*, 4479.

(6) (a) Paulissen, R.; Hayez, E.; Hubert, A. J.; Teyssie, P. *Tetrahedron Lett.* **1974**, *15*, 607. (b) Anac, O.; Daut, A. *Liebigs Ann./Recl.* **1997**, 1249. (c) Anac, O.; Ozdemir, A. D.; Sezer, O. *Helv. Chim. Acta* **2003**, *86*, 290. (d) Anac, O.; Guengor, F. S.; Kahveci, C.; Cansever, M. S. *Helv. Chim. Acta* **2004**, *87*, 408. (e) Celik, M. A.; Yurtsever, M.; Tüzün, N. Ş.; Güngör, F. Ş.; Sezer, Ö.; Anaç, O. *Organometallics* **2007**, *26*, 2978. (f) Anaç, O.; Sezer, Ö.; Candan, Ö.; Güngör, F. Ş.; Cansever, M. Ş. *Tetrahedron Lett.* **2008**, *49*, 1062.

(7) (a) Son, S.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 1046. For leading references for the asymmetric synthesis of dihydrofurans, see: (b) Davis, H. M. L.; Ahmed, G.; Calvo, R. L.; Churchill, M. R.; Churchill, D. G. *J. Org. Chem.* **1998**, *63*, 2641. (c) Evans, D. A.; Sweeney, Z. K.; Rovis, T.; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 12095. (d) Garzino, F.; Méou, A.; Brun, P. *Eur. J. Org. Chem.* **2003**, 1410. (e) Xia, W.; Yang, C.; Patrick, B. O.; Scheffer, J. R.; Scott, C. J. *Am. Chem. Soc.* **2005**, *127*, 2725. (f) Calter, M. A.; Phillips, R. M.; Flaschenriem, C. J. *Am. Chem. Soc.* **2005**, *127*, 14566. (g) Bowman, R. K.; Johnson, J. S. *Org. Lett.* **2006**, *8*, 573. (h) Zheng, J.-C.; Zhu, C.-Y.; Sun, X.-L.; Tang, Y.; Dai, L.-X. *J. Org. Chem.* **2008**, *73*, 6909.

(8) (a) Barton, D. H. R.; Chung, H. T.; Gross, A. D.; Jackman, L. M.; Martin-Smith, M. J. *Chem. Soc.* **1961**, 5061. (b) Steyn, P. S.; Vlegaar, R. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2250. (c) Von Dreele, R. B.; Pettit, G. R.; Ode, R. H.; Perdue, R. E., Jr.; White, J. D.; Manchand, P. S. *J. Am. Chem. Soc.* **1975**, *97*, 6236. (d) Ley, S. V.; Santafianos, D.; Blaney, W. M.; Simmonds, M. S. *J. Tetrahedron Lett.* **1987**, *28*, 221. (e) Merritt, A. T.; Ley, S. V. *Nat. Prod. Rep.* **1992**, *9*, 243. (f) Kilroy, T. G.; O'Sullivan, T. P.; Guiry, P. J. *Eur. J. Org. Chem.* **2005**, 4929.

(9) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. (b) Faul, M. M.; Huff, B. E. *Chem. Rev.* **2000**, *100*, 2407. (c) Garzino, F.; Meou, A.; Brun, P. *Synthesis* **2003**, S98. (d) Pettigrew, J. D.; Wilson, P. D. *Org. Lett.* **2006**, *8*, 1427.

(10) Zhou, J.-L.; Liang, Y.; Deng, C.; Zhou, H.-L.; Wang, Z.; Sun, X.-L.; Zheng, J.-C.; Yu, Z.-X.; Tang, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 7874 (the reaction mechanism for the formation of **4a** was discussed in the literature).

(11) The steric demand of the diazoester has been discussed by Prof. G. C. Fu et al. in their published work. For details, see ref 7a.

(12) For selected examples on the box ligand in asymmetric catalysis, see reviews: (a) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339. (b) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1. (c) Jørgensen, K. A.; Johannsen, M.; Yao, S.; Audrain, H.; Thorhauge, J. *Acc. Chem. Res.* **1999**, *32*, 605. (d) Johnson, J. S.; Evans, D. A. *Acc. Chem. Res.* **2000**, *33*, 325. (e) McManus, H. A.; Guiry, P. J. *Chem. Rev.* **2004**, *104*, 4151. (f) Desimoni, G.; Faita, G.; Jørgensen, K. A. *Chem. Rev.* **2006**, *106*, 3561. (g) Hargaden, G. C.; Guiry, P. J. *Chem. Rev.* **2009**, *109*, 2505. For leading references, see: (h) Lowentahl, R. E.; Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1990**, *31*, 6005. (i) Lowentahl, R. E.; Masamune, S. *Tetrahedron Lett.* **1991**, *32*, 7373. (j) Corey, E. J.; Imai, N.; Zhang, H. Y. *J. Am. Chem. Soc.* **1991**, *113*, 728. (k) Corey, E. J.; Ishihara, K. *Tetrahedron Lett.* **1992**, *33*, 6807. (l) von Matt, P.; Lloyd-Jones, G. C.; Minidis, A. B. E.; Pfaltz, A.; Macko, L.; Neuburger, M.; Zehnder, M.; Rüegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **1995**, *78*, 265. (m) Mazet, C.; Köhler, V.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4888.

(13) For selected examples on enantioselective reactions with side arm-modified bisoxazolines, see: (a) Zhou, J.; Tang, Y. *J. Am. Chem. Soc.* **2002**, *124*, 9030. (b) Ye, M. C.; Zhou, J.; Huang, Z. Z.; Tang, Y. *Chem. Commun.* **2003**, 2554. (c) Huang, Z. Z.; Kang, Y. B.; Zhou, J.; Ye, M. C.; Tang, Y. *Org. Lett.* **2004**, *6*, 1677. (d) Foltz, C.; Stecker, B.; Marconi, G.; Bellemin-Lapponnaz, S.; Wadepohl, H.; Gade, L. H. *Chem. Commun.* **2005**, 5115. (e) Seitz, M.; Capacchione, C.; Bellemin-

Lapponnaz, S.; Wadepohl, H.; Ward, B. D.; Gade, L. H. *Dalton. Trans.* **2006**, 193. (f) Foltz, C.; Enders, M.; Bellemin-Lapponnaz, S.; Wadepohl, H.; Gade, L. H. *Chem.—Eur. J.* **2007**, *13*, 5994. (g) Xu, Z. H.; Zhu, S. N.; Sun, X. L.; Tang, Y.; Dai, L. X. *Chem. Commun.* **2007**, 1960. (h) Schatz, A.; Rasappan, R.; Hager, M.; Gissibl, A.; Reiser, O. *Chem.—Eur. J.* **2008**, *14*, 7259. (i) Gaab, M.; Bellemin-Lapponnaz, S.; Gade, L. H. *Chem.—Eur. J.* **2009**, *15*, 5450. (j) Cao, P.; Deng, C.; Zhou, Y. Y.; Sun, X. L.; Zheng, J. C.; Xie, Z.; Tang, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 4463. (k) Rendina, V. L.; Moebius, D. C.; Kingsbury, J. S. *Org. Lett.* **2011**, *13*, 2004. (l) Sawada, T.; Nakada, M. *Tetrahedron: Asymmetry* **2012**, *23*, 350. (m) Li, J.; Liao, S.-H.; Xiong, H.; Zhou, Y.-Y.; Sun, X.-L.; Zhang, Y.; Zhou, X.-G.; Tang, Y. *Angew. Chem. Int. Ed.* **2012**, *51*, 8838. (n) Deng, C.; Wang, L.-J.; Zhu, J.; Tang, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 11620.

(14) CCDC 915948 (**3g**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See the Supporting Information.

(15) See refs 13e, 13f, 13m, and 13n.