DOI: 10.1002/adsc.200900552

Silver Acetate/TF-BiphamPhos-Catalyzed *endo*-Selective Enantioselective 1,3-Dipolar Cycloaddition of Azomethine Ylides with Vinyl Phenyl Sulfone

Gang Liang,[a] Min-Chao Tong,[a] and Chun-Jiang Wang[a,*]

[a] College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, People's Republic of China
Fax: (+86)-27-6875-4067; e-mail: cjwang@whu.edu.cn

Received: August 5, 2009; Revised: October 25, 2009; Published online: November 24, 2009

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.200900552.

Abstract: The first catalytic *endo*-selective 1,3-dipolar cycloaddition of azomethine ylides and vinyl phenyl sulfone has been developed successfully. The highly efficient silver acetate (AgOAc)/TF-BiphamPhos catalytic system exhibited high reactivity, excellent diastereoselectivity (>98:2), good enantioselectivity (67–92% *ee*) and broad substrate scope under mild conditions.

Keywords: asymmetric catalysis; azomethine ylides; cycloaddition; diastereoselectivity; enantioselectivity; vinyl phenyl sulfone

The asymmetric 1,3-dipolar cycloaddition of azomethine ylides to electron-deficient alkenes is a powerful and atom-economical carbon-carbon bond-forming reaction that can be used to create structurally and stereochemically rich pyrrolidines.[1] Because the resulting substituted pyrrolidines are prevalent in many natural alkaloids, compounds of pharmaceutical significance, organocatalysts, and biologically important building blocks in organic synthesis,[2] recent research has focused on the catalytic asymmetric version of the 1,3-dipolar cycloaddition of azomethine ylides. Since the original pioneering work of Grigg[3] employing stoichiometric amounts of a chiral metal complex and the first catalytic asymmetric version reported by Zhang[4] using the Ag(I)/xylyl-FAP system, various types of chiral metal catalysts [containing metals such as Ag(I),[4,5] Zn(II),[6] Cu(I/II),[7] Ni(II),[8] and Ca(II),[9]] and organocatalysts[10] have been developed to afford moderate to high enantio-/diastereoslectivities. Despite excellent results achieved for this transformation, most of the dipolarophiles applied in these reactions are the derivatives of conjugated unsaturated esters and maleimides.[3–10] In contrast, vinyl sulfones have been seldom studied in the catalytic asymmetric 1,3-dipolar cycloaddition[11] although the sulfonyl group possesses a high electron-withdrawing property and functional transformation versatility.[12] Two transition metal-catalyzed asymmetric 1,3-dipolar cycloadditions of azomethine ylides with vinyl phenyl sulfone have been reported by Carretero using the Cu(I)/Taniaphos complex[7a] and Fukuzawa using the Cu(I)/ClickFerrophos complex,[7c] both of which produced the *exo*-adducts with high diastereoselectivity and enantioselectivity (Figure 1). To the best of our knowledge, there are no reported methods which provide access to the *endo*-adducts with both high enantioselectivity and chemical efficiency for the catalytic asymmetric 1,3-dipolar cycloaddition of azomethine ylides with vinyl phenyl sulfone. Only one example reported by Grigg addressed that the *endo*-adduct and 70% *ee* were achieved for the reaction of vinyl phenyl sulfone with an azomethine ylide in the presence of a stoichiometric amount of a diphosphine-Ag(I) complex,[3a] however, no detailed data were given to support the relative and absolute configurations of the resulted adduct. Recently, we reported a novel family of readily available chiral TF-BiphamPhos ligands (**1**) (Figure 1), whose Cu(I) and Ag(I) complexes exhibited highly diastereoselectivity and excellent enantioselectivity in the asymmetric 1,3-dipolar cycloaddition of various azomethine ylides with conjugated carbonyl dipolarophiles.[13] Extending the interest in these ligands for asymmetric catalysis and filling up the literature gap, herein, we described that Ag(I)/TF-BiphamPhos served as an efficient catalyst for the highly *endo*-selective 1,3-dipolar cycloaddition of azomethine ylides and vinyl phenyl sulfone with high enantioselectivities of up to 92% *ee*.

Initially, the asymmetric 1,3-dipolar cycloaddition of *N*-benzylidene glycine methyl ester **3a** with vinyl phenyl sulfone **2** was examined using different metal salts as Lewis acids and TF-BiphamPhos as chiral

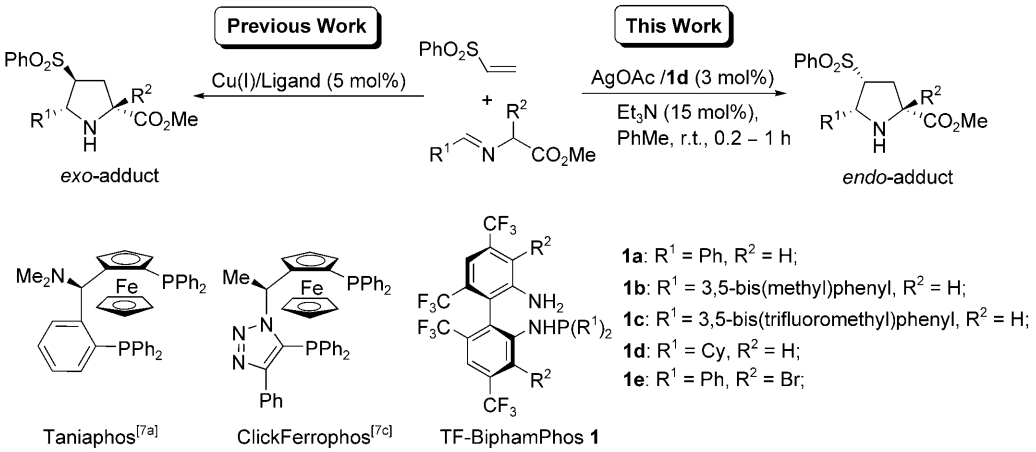
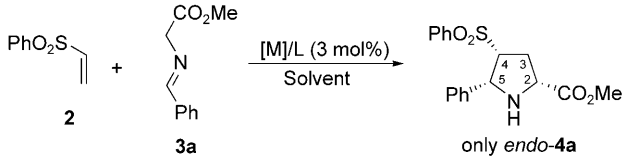


Figure 1. Catalytic asymmetric 1,3-dipolar cycloaddition of vinyl phenyl sulfone with azomethine ylides.

ligand in the presence of triethylamine at room temperature, and the representative results are summarized in Table 1. Except for the inactivity of $Cu(OTf)_2$, monovalent copper or silver metal precursors, such as $Cu(CH_3CN)_4ClO_4$, $Cu(CH_3CN)_4BF_4$, AgOAc, $AgSbF_6$, AgOTf and $AgClO_4$, combined with TF-BiphamPhos **1a** showed high reactivities, and the reactions were finished in less than 30 min at room temperature using PhMe as the solvent (Table 1, entries 1–8). To our delight, *endo*-**4a** was obtained as the

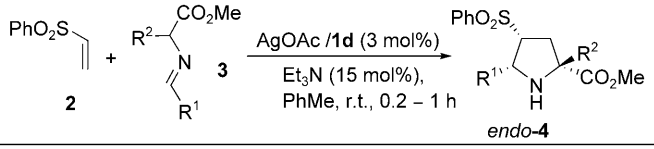
Table 1. Screening studies of the asymmetric 1,3-dipolar cycloaddition of vinyl phenyl sulfone **2** with azomethine ylide **3a**.[a]



Entry	L	[M]	Et_3N (mol%)	Solvent	Temp. [°C]	Time [h]	Yield [%][c]	*ee* [%][d]
1	**1a**	$Cu(OTf)_2$	15	PhMe	r.t.	24	–	–
2	**1a**	$CuClO_4$[b]	15	PhMe	r.t.	0.2	90	67
3	**1a**	$CuBF_4$[b]	15	PhMe	r.t.	0.2	90	63
4	**1a**	AgOAc	15	PhMe	r.t.	0.2	98	80
5	**1a**	AgOAc	0	PhMe	r.t.	5	45	80
6	**1a**	$AgClO_4$	15	PhMe	r.t.	0.2	98	80
7	**1a**	$AgSbF_6$	15	PhMe	r.t.	0.2	98	78
8	**1a**	AgOTf	15	PhMe	r.t.	0.2	93	75
9	**1a**	AgOAc	15	DCM	r.t.	0.2	92	74
10	**1a**	AgOAc	15	Et_2O	r.t.	0.5	84	64
11	**1a**	AgOAc	15	THF	r.t.	0.5	77	58
12	**1a**	AgOAc	15	Xylene	r.t.	0.2	95	80
13	**1b**	AgOAc	15	PhMe	r.t.	0.5	90	74
14	**1c**	AgOAc	15	PhMe	r.t.	0.5	84	53
15	**1d**	AgOAc	15	PhMe	r.t.	0.2	98	92
16	**1e**	AgOAc	15	PhMe	r.t.	3	63	48
17	**1d**	AgOAc	15	PhMe	0	0.5	97	88
18	**1d**	AgOAc	15	PhMe	–20	6	89	89

[a] The reactions were carried out with 0.33 mmol of **2** and 0.40 mmol of **3a** in 2 mL of solvent.
[b] $CuClO_4 = Cu(CH_3CN)_4ClO_4$, $CuBF_4 = Cu(CH_3CN)_4BF_4$.
[c] Isolated yield.
[d] Determined by HPLC analysis.

Table 2. Asymmetric 1,3-dipolar cycloaddition of vinyl phenyl sulfone **2** with various azomethine ylides **3** catalyzed by AgOAc/**1d**.[a]



Entry	R^1	R^2	4	Yield [%][b]	*ee* (%)[c,d]
1	Ph (**3a**)	H	**4a**	98	92(99)
2	*p*-Me-C_6H_4 (**3b**)	H	**4b**	87	84
3	*p*-MeO-C_6H_4 (**3c**)	H	**4c**	95	82
4	*p*-F-C_6H_4 (**3d**)	H	**4d**	91	89
5	*p*-Cl-C_6H_4 (**3e**)	H	**4e**	98	84
6	*o*-Me-C_6H_4 (**3f**)	H	**4f**	82	79 (99)
7	1-Naphthyl (**3g**)	H	**4g**	84	85
8	2-Naphthyl (**3h**)	H	**4h**	98	86
9[e]	Cy (**3i**)	H	**4i**	77	67
10	Ph (**3j**)	Me	**4j**	90	82

[a] The reactions were carried out with 0.33 mmol of **2** and 0.40 mmol of **3** in 2 mL PhMe.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis.
[d] Data in parentheses were achieved after recrystallization.
[e] In 6 h.

sole product, which was totally different from the *exo* preference achieved by Cu(I)/Taniaphos[7a] and Cu(I)/ClickFerrophos[7c] complexes. The apparent differences of the proton chemical shifts were observed through comparing the ^{1}H NMR spectra of *exo*-adduct **4a** and *endo*-adduct **4a**: H-2 and H-4 of the pyrrolidine ring in *exo*-**4a** appear around 4.18 ppm and 3.66 ppm, respectively;[7a] however, the signal peaks of the corresponding protons in *endo*-**4a** merge together and appear around 4.00 ppm (see Supporting Information for more information). The catalytic ability and asymmetric induction of the Cu(I)/**1a** complex was generally inferior to that of the Ag(I)/**1a** complex, which was opposite to the trend exhibited in the cases reported by Carretero[7a] and Fukuzawa.[7c] Although the examined four silver salts gave the similar results in terms of yields and enantio-/diastereoselectivity, AgOAc was chosen as the best metal precursor due to the economy and easy handling. The reaction rate was reduced remarkably without Et_3N as the extra base although the enantioselecivity remained at the same level (Table 1, entries 4 and 5). We then conducted the reaction using other TF-BiphamPhos ligands. When the phenyl group on the phosphorus atom of ligand **1a** was replaced by a xylyl group (**1b**) or a 3,5-bis(trifluoromethyl)phenyl group (**1c**), the enantioselectivity decreased from 80% to 74% and 53%, respectively (Table 1, entries 5, 13 and 14). Ligand **1e** bearing two bromines at the 3,3′-positions of the TF-Bipham backbone, which exhibited the excellent reactivity and substrate scope for the 1,3-dipolar cycloaddition of azomethine ylides with various conjugated carbonyl dipolarophiles,[13] unexpectedly showed the lowest asymmetric induction and catalytic ability in this transformation (Table 1, entry 16). Strikingly, ligand **1d** containing the bulky cyclohexyl group on the phosphorus atom, which provided unsatisfactory result in former studies, emerged as the most effective chiral ligand in this reaction and provided *endo*-**4a** as the sole product in high yield and excellent enantioselectivity of 92% within 20 min (Table 1, entry 15). A preliminary screening of solvent effects showed that toluene and xylene were the best solvents, other solvents such as dichloromethane, diethyl ether, tetrahydrofuran gave lower enantioselectivities (Table 1, entries 4, 9–12). Reducing the temperature from room temperature to 0 °C or −20 °C did not improve the enantioselectivity (Table 1, entry 15 *versus* entries 17 and 18). Thus, the optimized reaction conditions were established as 3 mol% of AgOAc/**1d** and 15 mol% Et_3N in PhMe or xylene at room temperature.

Having established the optimal reaction condition, we then investigated a series of representative imino esters **3** derived from glycinate to test the substrate scope. As shown in Table 2, a wide array of imino esters derived from aromatic aldehyde reacted smoothly with vinyl phenyl sulfone **2** to afford the corresponding *endo*-adducts exclusively in high yields and good enantioselectivities (Table 2, entries 1–6). It appears that the position and the electronic properties of the substituents on the aromatic rings have very

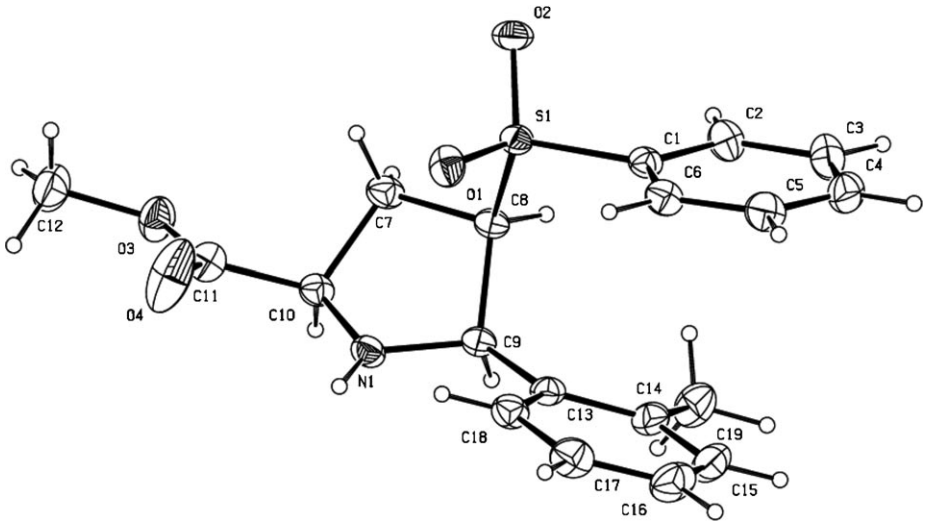


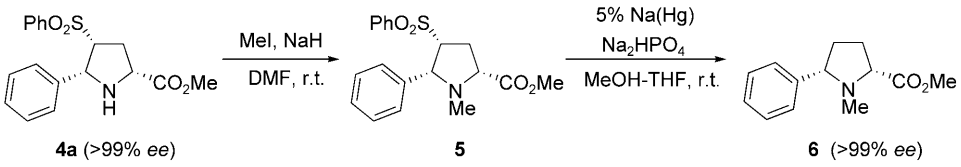
Figure 2. X-ray crystal structure of *endo*-**4f** (relative configuration).

limited effects on the enantioselectivities. Azomethine ylides from α- or β-naphthylaldehyde also worked well in this transformation producing the *endo*-**4g** and **4h** with 85% and 86% *ee*, respectively (Table 2, entries 7 and 8). An azomethine ylide from an aliphatic aldehyde has been seldom studied in the asymmetric 1,3-dipolar cycloaddition reaction probably due to its lower reactivity. Remarkably, azomethine ylide **3i** from the aliphatic cyclohexanecarbaldehyde was tolerated in this reaction, and the *endo*-adduct **4i** could be obtained in 77% yield and 67% *ee* (Table 2, entry 9). Notably, azomethine ylide **3j** derived from the α-substituted amino acid alanine also worked well in this transformation producing the *endo*-**4j** bearing a nitrogen-substituted quaternary stereogenic center[14] with 82% *ee* in 90% yield (Table 2, entry 10). Fortunately, all the products are solid, and enantioenriched compounds can be easily obtained by simple recrystallization of the crude products (Table 2, entries 1 and 6).

The relative configuration of the adducts **4f** and **4g** was determined to be *endo* by X-ray diffraction analysis of the corresponding racemic adducts,[15,16] which were achieved by using racemic TF-BiphamPhos **1a** as the ligand (Figure 2 and Supporting Information). However, high quality crystals of enantiomerically enriched *endo*-adducts for determining the absolute configuration have not been achieved yet. The absolute configuration of **4a** was assigned as (2*R*,4*R*,5*R*) through the highly efficient desulfonylation of the *N*-methyl derivative **5** and then optical rotation comparison of the obtained **6** with the data in a literature report[7a] (Scheme 1). Those of other adducts were tentatively proposed on the basis of these results.

Based on the relative and absolute configurations of **4a**, **4f** and **4g**, the high *endo*-selectivity observed in the AgOAc/(*S*)-TF-BiphamPhos-catalyzed asymmetric 1,3-dipolar cycloaddition reaction of azomethine ylides with vinyl phenyl sulfone can be rationalized by the proposed tetracoordinated complex[5c,j] shown in Figure 3. The *in situ*-formed azomethine ylide is coordinated to the metallic center and oriented in such a transition state because of the steric repulsion between the phenyl group in the ylide and the cyclohexyl rings on the phosphorus atom of the chiral ligand, and the highly steric congestion imposed by the latter effectively blocks the dipolarophile approach from the *Re* (C=N) face of the azomethine ylide and forms the *endo*-(2*R*,4*R*,5*R*) product through *Si* face attack (See Supporting Information for more information).

In conclusion, we have reported the first catalytic *endo*-selective 1,3-dipolar cycloaddition of azomethine ylides and vinyl phenyl sulfone catalyzed by the efficient AgOAc/TF-BiphamPhos. This catalytic system exhibited high reactivity, excellent diastereoselectivity, good enantioselectivity (67–92% *ee*) and



4a (>99% *ee*) **5** **6** (>99% *ee*)

Scheme 1. Determination of the absolute configuration of **4a** through desulfonylation of methylated compound **5**.

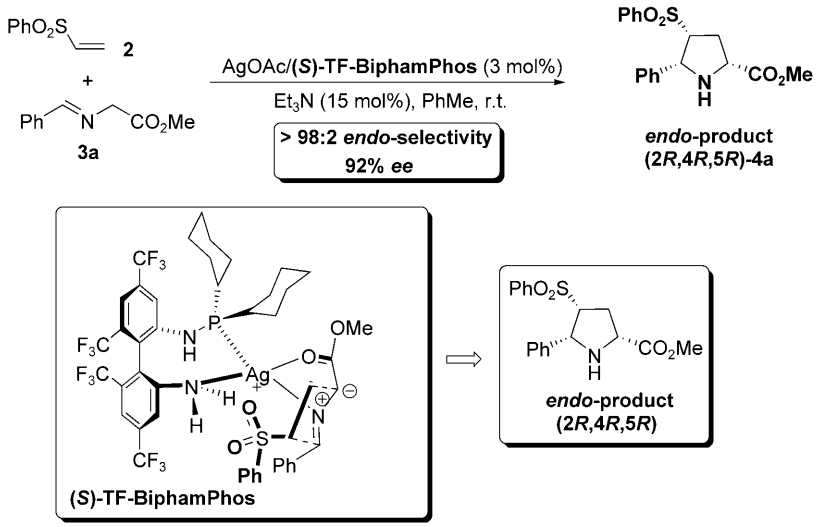


Figure 3. Proposed transition state leading to the *endo*-adduct when using vinyl phenyl sulfone as the dipolarophile.

broad substrate scope under mild conditions. Further investigations on the mechanism and applications of TF-BiphamPhos in asymmetric catalysis are ongoing in our laboratory and will be reported in due course.

Experimental Section

General Procedure

Under an argon atmosphere a solution of ligand (*S*)-TF-BiphamPhos **1d** (7.7 mg, 0.01 mmol) and AgOAc (1.67 mg, 0.01 mmol) in 1 mL toluene was stirred at room temperature for about 1 h. Then, imine substrate (0.40 mmol) was added as a solution in 1 mL toluene followed by Et_3N (0.05 mmol) and phenyl vinyl sulfone (37.0 mg, 0.33 mmol). Once the starting material had been consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. The crude product was analyzed by ^1H NMR to determine the *endo*/*exo* ratio, and then the residue was purified by column chromatography to give the corresponding cycloaddition product as a white solid, which was then directly analyzed by chiral HPLC to determine the enantiomeric excess.

Acknowledgements

This work was supported by National Natural Science Foundation of China and the startup fund from Wuhan University.

References

[1] For recent reviews about 1,3-dipolar cycloaddition reactions of azomethine ylides, see: a) L. M. Stanley, M. P. Sibi, *Chem. Rev.* **2008**, *108*, 2887; b) H. Pellisier, *Tetrahedron* **2007**, *63*, 3235; c) G. Pandey, P. Banerjee, S. R. Gadre, *Chem. Rev.* **2006**, *106*, 4484; d) T. M. V. D. Pinho e Melo, *Eur. J. Org. Chem.* **2006**, 2873; e) M. Bonin, A. Chauveau, L. Micouin, *Synlett* **2006**, 2349; f) C. Nájera, J. M. Sansano, *Angew. Chem.* **2005**, *117*, 6428; *Angew. Chem. Int. Ed.* **2005**, *44*, 6272; g) I. Coldham, R. Hufton, *Chem. Rev.* **2005**, *105*, 2765; h) K. V. Gothelf, in: *Cycloaddition Reactions in Organic Synthesis*, (Eds.: S. Kobayashi, K. A. Jørgensen), Wiley-VCH, Weinheim, **2002**; i) I. Coldham, R. Hufton, *Chem. Rev.* **2005**, *105*, 2765; j) V. Nair, T. D. Suja, *Tetrahedron* **2007**, *63*, 12247; k) H. Pellissier, *Tetrahedron* **2007**, *63*, 3235; l) S. Husinec, V. Savic, *Tetrahedron: Asymmetry* **2005**, *16*, 2047; m) M. Alvarez-Corral, M. Munoz-Dorado, I. Rodriguez-Garcia, *Chem. Rev.* **2008**, *108*, 3174.

[2] a) S. G. Pyne, A. S. Davis, N. J. Gates, J. Nicole, J. P. Hartley, K. B. Lindsay, T. Machan, M. Tang, *Synlett* **2004**, 2670; b) L. M. Harwood, R. J. Vickers, in: *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*, (Eds.: A. Padwa, W. Pearson), Wiley & Sons, New York, **2002**.

[3] a) R. Grigg, *Tetrahedron: Asymmetry* **1995**, *6*, 2475; b) P. Allway, R. Grigg, *Tetrahedron Lett.* **1991**, *32*, 5817.

[4] J. M. Longmire, B. Wang, X. Zhang, *J. Am. Chem. Soc.* **2002**, *124*, 13400.

[5] a) C. Nájera, M. D. G. Retamosa, J. M. Sansano, *Org. Lett.* **2007**, *9*, 4025; b) W. Zeng, Y.-G. Zhou, *Tetrahedron Lett.* **2007**, *48*, 4619; c) W. Zeng, G.-Y. Chen, Y.-G. Zhou, Y.-X. Li, *J. Am. Chem. Soc.* **2007**, *129*, 750; d) M. Nyerges, D. Bendell, A. Arany, D. E. Hibbs, S. J. Coles, M. B. Hursthouse, P. W. Groundwater, O. Meth-Cohn, *Tetrahedron* **2005**, *61*, 3745; e) R. Stohler, F. Wahl, A. Pfaltz, *Synthesis* **2005**, 1431; f) W. Zeng, Y.-G. Zhou, *Org. Lett.* **2005**, *7*, 5055; g) C. Alemparte, G. Blay, K. A. Jørgensen, *Org. Lett.* **2005**, *7*, 4569; h) T. F. Knöpfel, P. Aschwanden, T. Ichikawa, T. Watanabe, E. M. Carreira, *Angew. Chem.* **2004**, *116*, 6097; *Angew. Chem. Int. Ed.* **2004**, *43*, 5971; i) C. Chen, X. Li, S. L. Schreiber, *J. Am. Chem. Soc.* **2003**, *125*, 10174; j) C.

Nájera, M. D. G. Retamosa, J. Sansano, *Angew. Chem.* **2008**, *120*, 6144; *Angew. Chem. Int. Ed.* **2008**, *47*, 6055; k) S.-B. Yu, X.-P. Hu, J. Deng, D.-Y. Wang, Z.-C. Duan, Z. Zheng, *Tetrahedron: Asymmetry* 2009, 20, 621.

[6] a) A. S. Gothelf, K. V. Gothelf, R. G. Hazell, K. A. Jørgensen, *Angew. Chem.* **2002**, *114*, 4410; *Angew. Chem. Int. Ed.* **2002**, *41*, 4236; b) O. Dogan, H. Koyuncu, P. Garner, A. Bulut, W. J. Youngs, M. Panzner, *Org. Lett.* **2006**, *8*, 4687.

[7] a) T. Liamas, R. G. Arrayás, J. C. Carretero, *Org. Lett.* **2006**, *8*, 1795; b) S. Cabrera, R. G. Arrayás, B. Martín-Matute, F. P. Cossío, J. C. Carretero, *Tetrahedron* **2007**, *63*, 6587; c) S.-i. Fukuzawa, H. Oki, *Org. Lett.* **2008**, *10*, 1747; d) X.-X. Yan, Q. Peng, Y. Zhang, K. Zhang, W. Hong, X.-L. Hou, Y.-D. Wu, *Angew. Chem.* **2006**, *118*, 2013; *Angew. Chem. Int. Ed.* **2006**, *45*, 1979; e) S. Cabrera, R. G. Arrayás, J. C. Carretero, *J. Am. Chem. Soc.* **2005**, *127*, 16394; f) Y. Oderaotoshi, W. Cheng, S. Fujitomi, Y. Kasano, S. Minakata, M. Komatsu, *Org. Lett.* **2003**, *5*, 5043; g) W. Gao, X. Zhang, M. Raghunath, *Org. Lett.* **2005**, *7*, 4241; h) B. Martín-Matute, S. I. Pereira, E. Peña-Cabrera, J. Adrio, A. M. S. Silva, J. C. Carretero, *Adv. Synth. Catal.* 2007, 349, 1714; i) M. Shi, J.-W. Shi, *Tetrahedron: Asymmetry* 2007, 18, 645; j) A. López-Pérez, J. Adrio, J. C. Carretero, *J. Am. Chem. Soc.* **2008**, *130*, 10084; k) J. Hernández-Toribio, R. G. Arrayás, B. Martín-Matute, J. C. Carretero, *Org. Lett.* **2009**, *11*, 393.

[8] J.-W. Shi, M.-X. Zhao, Z.-Y. Lei, M. Shi, *J. Org. Chem.* **2008**, *73*, 305.

[9] a) S. Saito, T. Tsubogo, S. Kobayashi, *J. Am. Chem. Soc.* **2007**, *129*, 5364; b) T. Tsubogo, S. Saito, K. Seki, Y. Yamashita, S. Kobayashi, *J. Am. Chem. Soc.* **2008**, *130*, 13321.

[10] a) J. L. Vicario, S. Reboredo, D. Badía, L. Carrillo, *Angew. Chem.* **2007**, *119*, 5260; *Angew. Chem. Int. Ed.* **2007**, *46*, 5168; b) I. Ibrahem, R. Rios, J. Vesely, A. Co'rdova, *Tetrahedron Lett.* **2007**, *48*, 6252; c) X.-H. Chen, W.-Q. Zhang, L.-Z. Gong, *J. Am. Chem. Soc.* **2008**, *130*, 5652; d) C. Guo, M.-X. Xue, M.-K. Zhu, L.-Z. Gong, *Angew. Chem.* **2008**, *120*, 3462; *Angew. Chem. Int. Ed.* **2008**, *47*, 3414; e) Y.-K. Liu, H. Liu, W. Du, L. Yue, Y.-C. Chen, *Chem. Eur. J.* **2008**, *14*, 9873.

[11] For some scattered examples in the literature, see: a) M.-A. Plancquaert, M. Redon, Z. Janousek, H. G. Viehe, *Tetrahedron* **1996**, *52*, 4383; b) R. B. Clark, W. H. Pearson, *Org. Lett.* **1999**, *1*, 349; c) C. Wittland, N. Risch, *J. Prakt. Chem.* **2000**, *342*, 311; d) F. Laduron, H. G. Viehe, *Tetrahedron* **2002**, *58*, 3543.

[12] a) N. S. Simpkins, *Sulfones in Organic Synthesis*, Pergamon Press, Oxford, **1993**; b) P. L. Fuchs, T. F. Braish, *Chem. Rev.* **1986**, *86*, 903; c) C. Nájera, M. Yus, *Tetrahedron* **1999**, *55*, 10547.

[13] a) C.-J. Wang, G. Liang, Z.-Y. Xue, F. Gao, *J. Am. Chem. Soc.* **2008**, *130*, 17250; b) C.-J. Wang, Z.-Y. Xue, G. Liang, Z. Lu, *Chem. Commun.* **2009**, 2905.

[14] a) *Quaternary Stereocenters: Challenges and Solution for Organic Synthesis*, (Eds.: J. Christoffers, A. Baro), Wiley-VCH, Weinheim, **2005**; b) K. Juji, *Chem. Rev.* **1993**, *93*, 2037; c) M. Chavarot, J. J. Byrne, P. Y. Chavant, Y. Vallee, *Tetrahedron: Asymmetry* **2001**, *12*, 1147; d) S. Masumoto, H. Usuda, M. Suzuki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2003**, *125*, 5634.

[15] Crystal data for *endo*-**4f**: $C_{19}H_{21}NO_4S$, $M_r = 359.43$, $T = 293$ K, orthorhombic, space group *Pbca*, $a = 11.9819(12)$, $b = 11.1860(12)$, $c = 27.029(3)$ Å, $V = 3622.7(6)$ Å^3, $Z = 8$, 3554 unique reflections, final $R_1 = 0.0398$ and $wR_2 = 0.1071$ for 2823 observed [$I > 2\sigma(I)$] reflections. CCDC 740802 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 [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)-1223-336-033; or deposit@ccdc.cam.ac.uk).

[16] Crystal data for *endo*-**4g**: $C_{21}H_{22}NO_4S$, $M_r = 395.46$, $T = 293$ K, monoclinic, space group *P21/c*, $a = 12.3249(14)$, $b = 12.7741(15)$, $c = 12.7222(15)$ Å, $V = 1952.2(4)$ Å^3, $Z = 4$. CCDC 740803 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 [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)-1223-336-033; or deposit@ccdc.cam.ac.uk].

