DOI: 10.1002/ejoc.201201756

Phosphane-Catalyzed [3+2] Cycloaddition Reaction of Allenoate and Cyclic Imines: A Simple and Efficient Method for Synthesis of Benzo-Fused Cyclic Sulfamidate Heterocycles

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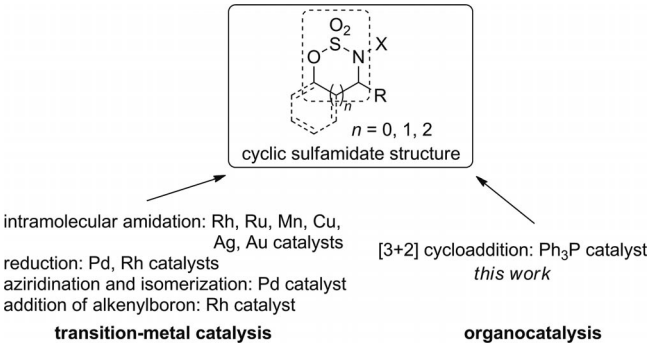
Keywords: Allenes / Cyclic sulfamidates / Cycloaddition / Organocatalysis / Phosphanes / Heterocycles

By using a phosphane as an organocatalyst, an efficient synthesis of benzo-fused cyclic sulfamidate heterocycles has been developed through a cycloaddition reaction of allenoate and cyclic imines including cyclic trifluoromethyl ketimine, which gave high yields (71–97 %). The reaction could also be conveniently performed on a gram scale. Furthermore, some simple transformations of the sulfamidate heterocycle products have been disclosed to obtain functional amines. An asymmetric variant of this reaction was also tried by screening several commercially available chiral phosphane ligands as organocatalysts, and up to 36 % *ee* was achieved.

Introduction

Cyclic sulfamidate heterocycles, 1,2,3-oxathiazolidine 2,2-dioxides,[1] play important roles in the synthesis of a wide variety of chemically and biologically important alkylamines, because they can undergo nucleophilic displacement with a carbon anion or other heteroatom nucleophile.[1,2] Such heterocycles have generally been synthesized by oxidation of their corresponding sulfamidites that could be assembled from amino alcohols or diols.[1] The use of synthetic methodologies, especially in the presence of catalysts, is particularly attractive when considering the economy and efficiency of a process. The Du Bois group initially reported the intramolecular amination of the saturated C–H bonds of sulfamate esters to afford cyclic sulfamidates by using dinuclear Rh catalysis.[3] Subsequently, the intramolecular amination of sulfamates esters was developed to efficiently and stereoselectively provide a series of cyclic sulfamidates catalyzed by Rh, Ru, Mn, Cu, Ag, and Au complexes.[4] The Pd-catalyzed asymmetric hydrogenation and Rh-catalyzed asymmetric transfer hydrogenation of cyclic sulfamidates have also been reported to result in cyclic sulfamidates.[5] A one-pot highly diastereoselective synthesis of cyclic sulfamidates containing a quaternary carbon center was realized by the combination of a sulfur-ylide-mediated aziridination and Pd^0-catalyzed isomerization.[6] Very recently, cyclic sulfamidates were synthesized through enantioselective Rh-catalyzed addition reactions of organic boron reagents to cyclic imines as reported by Lam[7a,7b] and one example by Nishimura and co-workers.[7c] Despite the impressive progress achieved, the use of a catalytic approach to cyclic sulfamidate heterocycles is still underexplored. These reactions are limited to the use of transition-metal catalysts, and at this time there are no descriptions of organocatalytic processes to generate cyclic sulfamidate heterocycles. Notably, benzo-fused sulfamidate heterocycles have received little attention.[3d,4e,5a,6,7] Therefore, it will be of interest to develop new and efficient organocatalytic methods for the synthesis of cyclic sulfamidate heterocycles (Scheme 1).



Scheme 1. Catalytic approach for the synthesis of cyclic sulfamidate heterocycles.

Phosphane-catalyzed [3+2] cycloaddition reactions of electron-deficient allenes or alkynes and imines, also known as the Lu reaction,[8] is a privileged method in organic synthesis and has attracted much attention.[9,10] This reaction allows the formation of new five-membered polyfunctionalized nitrogen heterocycles that may be valuable synthons

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201756.

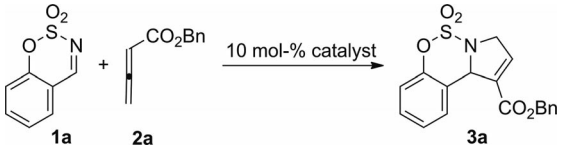
for fine chemistry. The imines used for this reaction are acyclic *N*-Ts- and *N*-(diphenyphosphinoyl)amide imines. Very recently, Ye et al. reported the phosphane-catalyzed [3+2] cycloaddition reaction of five-membered cyclic sulfonamide ketimines to give sultam-fused dihydropyrroles[10k] and used the same cyclic imines as electrophiles in [4+2] cycloaddition reactions catalyzed by phophanes to afford the corresponding tetrahydropyridines.[11] Here, we wish to report the synthesis of benzo-fused 1,2,3-benzoxathiazine 2,2-dioxide heterocycles through phosphane-catalyzed [3+2] cycloaddition reactions of allenoate (α-allenic ester) and cyclic imines **1**.

Results and Discussion

In our initial experiment, the reaction of cyclic imine **1a** and benzyl allenoate (**2a**) was carried out at 12 °C with Ph_3P (10 mol-%) as a catalyst in toluene. Full conversion could be observed as shown by TLC, and α-addition regioselective product **3a** was isolated in a quantitative yield (Table 1, Entry 1). The structure of the isolated product was characterized by ^1H and ^{13}C NMR spectroscopy as well as HRMS. The different product structures, such as [2+2] cycloadducts or Morita–Baylis–Hillman products, are possibly obtained from the reaction of allenoates and a C=N group, whereas only the *N*-substituent of the imines or catalysts were changed.[12] Therefore, it was necessary to clearly confirm the structure of compound **3a** by single-crystal X-ray diffraction analysis (Figure 1).[13] The analysis showed that an α-regioselective isomer of the [3+2] cycloadduct was obtained.

Next we investigated the influence of different factors related to reactivity as listed in Table 1. Firstly, solvent effects were studied. We stopped the reaction at the same time to evaluate the reactivity, and only toluene, as the best solvent, provided full conversion after 6 h (Table 1, Entries 1–6). The ratio of **1a/2a** also affected the reactivity (Table 1, Entries 7 and 8), and a slight excess of **2a** (1.2 equiv.) was chosen. Next, temperature increases were shown to considerably accelerate the rate of the reaction (Table 1, Entries 1 versus 7, and 8 versus 9), which is usually observed with chemical reactivity. Interestingly, the same product was observed by using other phosphane and amine catalysts (Table 1, Entries 10–13). However, a few by-products were seen by TLC and crude ^1H NMR analysis. When the concentration of imine **1a** was increased from 0.1 M to 0.2 M or more, the reaction activity improved significantly (Table 1, Entries 8 and 14–15). Considering the solubility of **1a** in toluene at a concentration of 0.5 M, we selected the optimal concentration of **1a** in toluene to be 0.2 M. The studies of catalyst loadings on the reaction revealed that the reaction rate decreased as the catalyst loading was reduced. With 2 mol-% of phosphane catalyst the reaction was still effective, although more time was required to complete the reaction. However, a further decrease in the catalyst loading to 1 mol-% rendered the reaction unacceptably slow (Table 1, Entries 16–18). From an operational perspective, the use of 5 mol-% of Ph_3P is optimal to ensure high reaction efficiency (93% yield) and maintain a reasonable reaction time (Table 1, Entry 16).

Table 1. Optimizaion of reaction conditions for the Ph_3P-catalyzed [3+2] cycloaddition reaction of allenoate **2a** and cyclic imine **1a**.



1a **2a** **3a**

Entry[a]	Catalyst	Solvent	Concentration[b]	*T* [°C]	Time [h]	Yield [%][c]
1	Ph_3P	toluene	0.1 M	12	6	99
2	Ph_3P	CH_2Cl_2	0.1 M	12	6	61
3	Ph_3P	THF	0.1 M	12	6	trace
4	Ph_3P	MeOH	0.1 M	12	6	13
5	Ph_3P	CH_3CN	0.1 M	12	6	39
6	Ph_3P	DMF	0.1 M	12	6	trace
7	Ph_3P	toluene	0.1 M	25	2.5	96
8	Ph_3P	toluene	0.1 M	25	4.5	92
9	Ph_3P	toluene	0.1 M	50	1	89
10	Ph_2PMe	toluene	0.1 M	25	5	64
11	Bu_3P	toluene	0.1 M	25	16	72
12	DBU	toluene	0.1 M	25	72	0
13	DBU	CH_2Cl_2	0.1 M	25	24	35
14	Ph_3P	toluene	0.2 M	25	2.5	93
15	Ph_3P	toluene	0.5 M	25	1.5	92
16[d]	Ph_3P	toluene	0.2 M	25	6	93
17[e]	Ph_3P	toluene	0.2 M	25	72	87
18[f]	Ph_3P	toluene	0.2 M	25	72	39

[a] General reaction conditions: 0.05 mmol scale: Ratio **1a/2a** = 1:1.5 for Entries 1–7, and 1:1.2 for Entries 8–18. [b] Concentration of imine **1a** in toluene. [c] Isolated yield. [d] Ph_3P (5 mol-%). [e] Ph_3P (2 mol-%). [f] Ph_3P (1 mol-%).

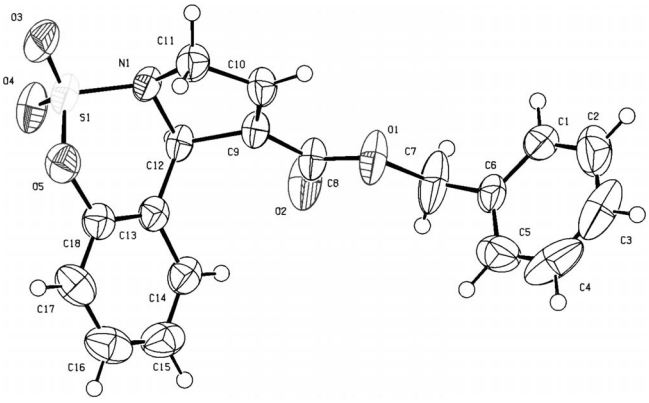
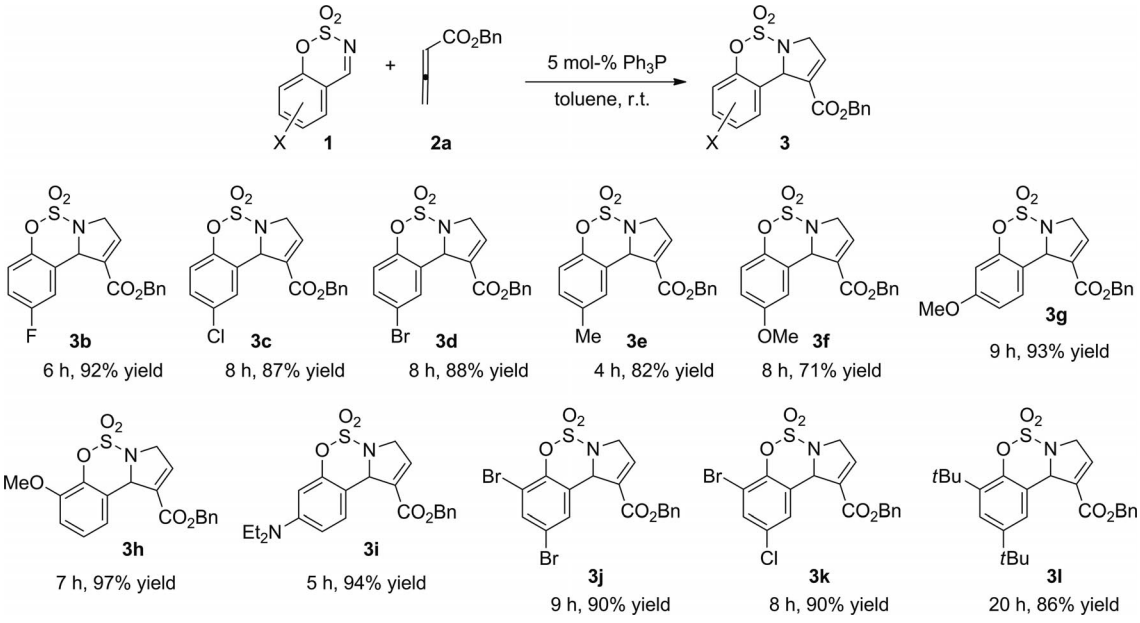


Figure 1. Single-crystal X-ray structure of **3a**.

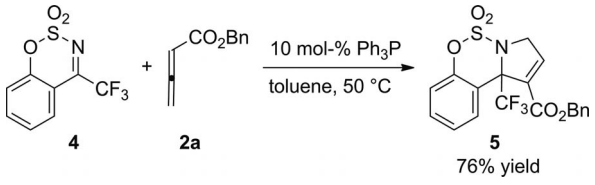
Under the optimized conditions, the reactions of allenoate **2a** and various cyclic imines **1**, which may be conveniently obtained from salicylaldehydes and chlorosulfonyl isocyanate in one step,[14] were conducted in the presence of Ph_3P in dry toluene at room temperature without any special handling. As shown in Scheme 2, the benzo-fused cyclic sulfamidate heterocycles **3**, with a variety of substituents at different positions on the aromatic ring, can be readily obtained in high isolated yields. For methoxy-substituted



Scheme 2. Cycloaddition reaction with various substrates **1**.

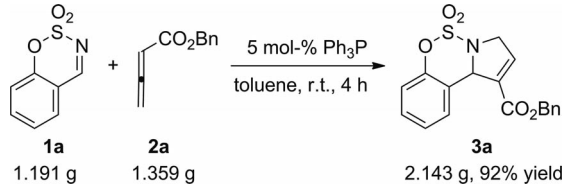
imine **1g**, a slightly lower yield was obtained. Interestingly, cycloadduct **1i** containing a tertiary amine group, which can act as a Lewis base owing to its nucleophilicity, was also obtained in 94% yield. Imines with two substituents leading to steric hindrance were also used and gave corresponding cyclic sulfamidate heterocycles **3j**, **3k**, and **3l** in high isolated yields.

Fluorine plays a key role in pharmaceutical, veterinary, agrochemical, and material sciences, and α-(trifluoromethyl)-substituted amines are essential structural motifs in a large number of pharmaceutical, agrochemical, and organic materials.[15] Consequently, there have been reports of preparing α-(trifluoromethyl)-substituted amines by means of a few catalytic addition reactions to cyclic trifluoromethyl ketimine.[16] We were attracted to the possibility of a Ph_3P-catalyzed cycloaddition reaction of allenoate **2** and cyclic trifluoromethyl ketimine **4**. It was found that the reaction proceeded smoothly to give α-(trifluoromethyl) quaternary carbon amine **5** in 76% yield at 50 °C, although no reaction occurred at room temperature (Scheme 3).



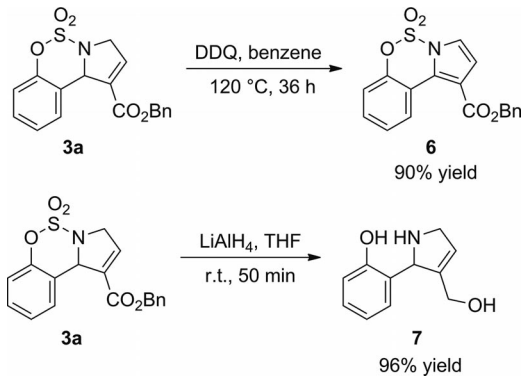
Scheme 3. Cycloaddition reaction with cyclic trifluoromethyl ketimine **4**.

To test the practicality of the current method, the cycloaddition reaction on a gram scale (1.191 g, 6.50 mmol of **1a**) was carried out in toluene at room temperature to give cyclic sulfamidates **3a** in 92% yield (Scheme 4).



Scheme 4. Gram-scale experiment.

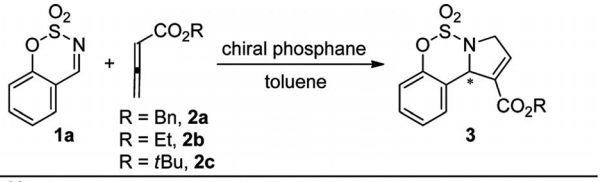
Benzo-fused cyclic sulfamidate heterocycles **3** are attractive synthetic intermediates as multifunctional compounds. Typical transformations for cyclic sulfamidates **3a** were carried out, and the results are illustrated in Scheme 5. When a mixture of cycloadduct **3a** and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene was heated to 120 °C for 1.5 d in a sealed tube, aromatization occurred smoothly, and a pyrrole derivative was obtained in 90% yield. With $LiAlH_4$ as the nucleophilic reagent, **3a** could be converted into aminophenol **7**, which is an important building block and useful structural unit in organic synthesis.

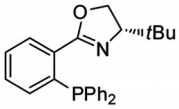


Scheme 5. Transformations of product **3a**.

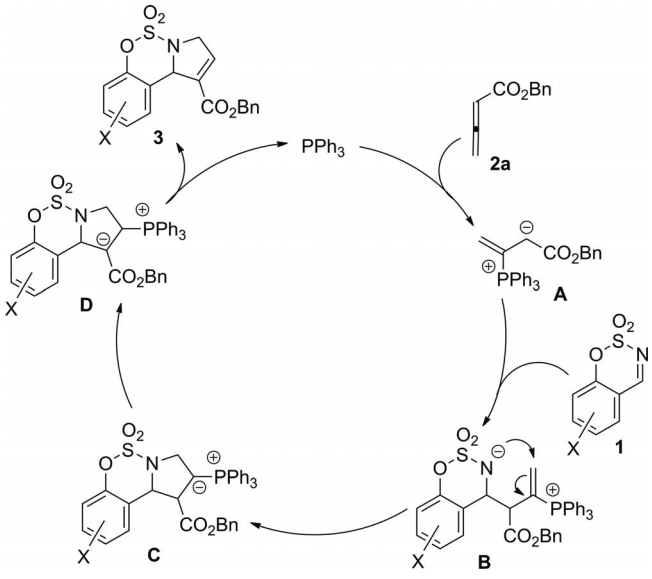
Some commercially available chiral phosphane ligands were screened for the reaction of **1a** with **2**. The results are listed in Table 2. (*R*)-SYNPHOS delivered the best result (66% yield, 27% *ee*). (*R*)-H_8-BINAP delivered the best enantioselectivity (36% *ee*) but with lower reactivity (24% yield). However, the reactivity decreased when ethyl allenoate (**2b**) was used instead of benzyl allenoate (**2a**), and no reaction was observed for *tert*-butyl allenoate (**2c**) with a sterically hindered group in the presence of (*R*)-SYNPHOS (Table 2, Entries 10 and 11).

Table 2. Screening of commercial chiral phosphane ligands as organocatalysts.



Entry[a]	Chiral phosphane	R/product	*T* [°C]	Time [h]	Yield [%]	*ee* [%]
1	(*R*)-BINAP	Bn/**3a**	25	60	78	24
2	(*R*)-H_8-BINAP	Bn/**3a**	25	72	24	36
3	(*R*)-SYNPHOS	Bn/**3a**	25	24	66	27
4[b]	(*R*)- SYNPHOS	Bn/**3a**	0	60	32	34
5	(*R*)-SEGPHOS	Bn/**3a**	25	20	81	15
6	(*R*)-MeOBIPHEP	Bn/**3a**	25	38	69	16
7	(*R,R*)-Me-DUPHOS	Bn/**3a**	25	48	NR	–
8	(S)-MOP	Bn/**3a**	25	48	95	15
9		Bn/**3a**	25	72	18	7
10	(*R*)-SynPhos	Et/**3m**[c]	0	168	13	26
11	(*R*)-SynPhos	*t*Bu/**3n**	25	48	NR	–

[a] General reaction conditions: 0.05 mmol scale, chiral phosphane (10 mol-%). [b] (*R*)-SYNPHOS (20 mol-%) was used. [c] Product **3m** in 89% yield was obtained with Ph_3P (5 mol-%) in toluene at room temperature for12 h.



Scheme 6. Proposed catalytic cycle.

Based on the widely accepted proposed mechanism for nucleophilic phosphane catalysis[9] and the experimental results from our current studies, a possible catalytic cycle for the above [3+2] annulation reactions is depicted in Scheme 6. The nucleophilic Ph_3P initially attacks the β-carbon atom of benzyl allenoate (**2a**) to yield allylic zwitterion **A**. Subsequently, the α-carbon atom of anionic allylic **A** may add to the C=N group of cyclic imine **1**, and then intramolecular Michael addition reaction of **B** affords cycloadduct **C**. The proton shift of intermediate **C** brings about final zwitterionic intermediate **D**, which dissociates to give product **3** and regenerates the Ph_3P catalyst.

Conclusions

We have developed a high-yielding method for the synthesis of benzo-fused cyclic sulfamidate heterocycles through the [3+2] cycloaddition reaction of allenoate and cyclic imines catalyzed by Ph_3P. This represents the first demonstration of an organocatalytic reaction to synthesize cyclic sulfamidate heterocycles, which are easily attacked by many nucleophiles to obtain functionalized amines. Further extensions of the utility of these new benzo-fused cyclic sulfamidate heterocycles, as well as the development of a highly enantioselective synthesis of nitrogen heterocycles, are underway in our laboratory.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded with Bruker DRX-400 spectrometers. The chemical shifts for ^1H NMR spectra were recorded relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$: δ = 7.26 ppm). The chemical shifts for ^{13}C NMR spectra were recorded relative to the central peak of deuteriochloroform (δ =77.0 ppm) as the internal standard. Flash column chromatography was performed with silica gel (200–300 mesh). TLC analysis was performed on glass-backed plates coated with 0.2 mm silica. After elution, the plate was visualized under 254 nm UV illumination, and further visualization was achieved by staining with basic $KMnO_4$ solution. All commercially available compounds were used as provided without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use, unless otherwise noted. Cyclic imines **1a**–**l** and **4** were prepared from the corresponding salicylaldehydes according to modified procedures reported in the literature.[14b] Benzyl allenoate (**2a**) was prepared according to a literature procedure.[17]

General Procedure for the [3+2] Cycloaddition Reaction of Cyclic Imines 1 Catalyzed by Ph_3P: Table 1 and Scheme 2. To allenoate **2a** (0.12 mmol) in anhydrous toluene (0.5 mL) was added cyclic imine **1** and triphenylphosphane (5 mol-%). The mixture was stirred at room temperature until the imine was shown to have reacted as monitored by TLC. The crude reaction mixture was directly charged on silica gel and purified by column chromatography (petroleum ether/ethyl acetate) to afford the desired product.

Benzyl 3,10b-Dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3a): R_f = 0.3 (petroleum ether/ethyl acet-

ate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, J = 10.4 Hz, 1 H), 7.39–7.26 (m, 6 H), 7.10 (dt, J = 1.4, 10.3 Hz, 1 H), 7.02 (dd, J = 1.3, 11.0 Hz, 1 H), 6.89 (s, 1 H), 6.15 (d, J = 4.4 Hz, 1 H), 5.31 (AB q, $\Delta\delta_{AB}$ = 0.09 ppm, J_{AB} = 16.2 Hz, 2 H), 4.49–4.35 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 149.8, 137.9, 135.2, 135.0, 129.5, 128.71, 128.68, 128.4, 127.3, 126.0, 120.7, 119.2, 67.3, 66.6, 55.9 ppm. HRMS (ESI): calcd. for $C_{18}H_{16}NO_5S$ $[M + H]^+$ 358.0744; found 358.0740.

Benzyl 9-Fluoro-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3b): R_f = 0.32 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.40 (m, 6 H), 7.01–6.99 (m, 2 H), 6.92 (s, 1 H), 6.09 (s, 1 H), 5.32 (AB q, $\Delta\delta_{AB}$ = 0.07 ppm, J_{AB} = 12.2 Hz, 2 H), 4.42 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0, 159.5 (d, $^1J_{C\text{-}F}$ = 244.5 Hz), 145.7 (d, $^4J_{C\text{-}F}$ = 2.8 Hz), 138.4, 134.8, 134.7, 128.8, 128.5, 122.2 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 120.8 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 116.5 (d, $^2J_{C\text{-}F}$ = 23.8 Hz), 114.2 (d, $^2J_{C\text{-}F}$ = 25.8 Hz), 109.9, 67.5, 66.5 (d, $^4J_{C\text{-}F}$ = 2.6 Hz), 56.0 ppm. HRMS (ESI): calcd. for $C_{18}H_{14}FNNaO_5S$ $[M + Na]^+$ 398.0469; found 398.0472.

Benzyl 9-Chloro-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3c): R_f = 0.26 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 1 H), 7.40–7.38 (m, 5 H), 7.26–7.24 (m, 1 H), 6.98–6.92 (m, 2 H), 6.09 (s, 1 H), 5.32 (AB q, $\Delta\delta_{AB}$ = 0.05 ppm, J_{AB} = 9.9 Hz, 2 H), 4.46–4.37 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 148.6, 138.6, 135.0, 134.9, 131.4, 129.8, 129.01, 129.00, 128.8, 127.6, 122.4, 120.8, 67.8, 66.6, 56.2 ppm. HRMS (ESI): calcd. for $C_{18}H_{18}ClN_2O_5S$ $[M + NH_4]^+$ 409.0620; found 409.0615.

Benzyl 9-Bromo-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3d): R_f = 0.24 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.41 (s, 6 H), 6.93–6.91 (m, 2 H), 6.10 (s, 1 H), 5.36–5.29 (m, 2 H), 4.42 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 148.9, 138.4, 134.8, 134.7, 132.6, 130.3, 128.82, 128.79, 128.60, 122.6, 120.9, 118.7, 67.6, 66.3, 56.0 ppm. HRMS (ESI): calcd. for $C_{18}H_{18}BrN_2O_5S$ $[M + NH_4]^+$ 453.0114; found 453.0108.

Benzyl 9-Methyl-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3e): R_f = 0.32 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.35 (m, 6 H), 7.07 (d, J = 8.3 Hz, 1 H), 6.92–6.89 (m, 2 H), 6.10 (s, 1 H), 5.33 (AB q, $\Delta\delta_{AB}$ = 0.08 ppm, J_{AB} = 12.2 Hz, 2 H), 4.45–4.36 (m, 2 H), 2.19 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 147.7, 137.9, 135.8, 135.3, 135.1, 130.1, 128.74, 128.71, 128.5, 127.4, 120.2, 118.9, 67.2, 66.6, 55.9, 20.8 ppm. HRMS (ESI): calcd. for $C_{19}H_{17}NNaO_5S$ $[M + Na]^+$ 394.0720; found 394.0713.

Benzyl 9-Methoxyl-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3f): R_f = 0.39 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (s, 5 H), 7.19 (s, 1 H), 6.96–6.91 (m, 2 H), 6.81 (d, J = 9.0 Hz, 1 H), 6.10 (s, 1 H), 5.30 (s, 2 H), 4.46–4.36 (m, 2 H), 3.62 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 157.1, 143.3, 138.2, 135.0, 128.70, 128.65, 128.4, 121.3, 120.1, 115.7, 111.2, 67.3, 66.7, 56.0, 55.5 ppm. HRMS (EI): calcd. for $C_{19}H_{17}O_6NS$ $[M]^+$ 387.0777; found 387.0777.

Benzyl 8-Methoxy-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3g): R_f = 0.44 (petroleum ether/ethyl acetate, 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.7 Hz, 1 H), 7.39 (s, 5 H), 6.86 (s, 1 H), 6.65 (d, J = 8.8 Hz, 1 H), 6.54 (s, 1 H), 6.07 (s, 1 H), 5.30 (AB q, $\Delta\delta_{AB}$ = 0.09 ppm, J_{AB} = 12.1 Hz, 2 H), 4.46–4.35 (m, 2 H), 3.77 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8, 160.9, 151.3, 138.2, 136.1, 135.7, 129.40, 129.35, 129.1, 128.8, 113.4, 113.1, 104.7, 67.9, 67.0, 56.6, 56.2 ppm. HRMS (ESI): calcd. for $C_{19}H_{18}NO_6S$ $[M + H]^+$ 388.0849; found 388.0851.

Benzyl 7-Methoxy-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3h): R_f = 0.30 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.36 (m, 5 H), 7.13 (d, J = 7.9 Hz, 1 H), 7.02 (t, J = 8.1 Hz, 1 H), 6.88–6.86 (m, 2 H), 6.14 (d, J = 4.1 Hz, 1 H), 5.30 (AB q, $\Delta\delta_{AB}$ = 0.08 ppm, J_{AB} = 12.2 Hz, 2 H), 4.49–4.36 (m, 2 H), 3.87 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1, 149.0, 139.5, 137.9, 135.2, 135.0, 128.70, 128.65, 128.4, 125.6, 121.6, 118.2, 111.9, 67.2, 66.7, 56.2, 56.0 ppm. HRMS (EI): calcd. for $C_{19}H_{17}O_6NS$ $[M]^+$ 387.0777; found 387.0774.

Benzyl 9-(Diethylamino)-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]-oxathiazine-1-carboxylate 5,5-Dioxide (3i): R_f = 0.50 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.33 (m, 6 H), 6.82 (s, 1 H), 6.39 (dd, J = 2.6, 8.9 Hz, 1 H), 6.22 (d, J = 2.6 Hz, 1 H), 6.03 (d, J = 3.9 Hz, 1 H), 5.30 (AB q, $\Delta\delta_{AB}$ = 0.08 ppm, J_{AB} = 12.2 Hz, 2 H), 4.41–4.33 (m, 2 H), 3.30 (q, J = 7.1 Hz, 4 H), 1.14 (t, J = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 150.9, 148.4, 137.0, 135.9, 135.1, 128.7, 128.5, 128.3, 127.8, 109.3, 106.0, 100.6, 67.0, 66.3, 55.9, 44.3, 12.4 ppm. HRMS (ESI): calcd. for $C_{22}H_{24}N_2O_5NaS$ $[M + Na]^+$ 451.1304; found 451.1307.

Benzyl 7,9-Dibromo-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3j): R_f = 0.29 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.68 (s, 1 H), 7.40 (s, 5 H), 6.94 (s, 1 H), 6.10 (s, 1 H), 5.35–5.29 (m, 2 H), 4.50–4.39 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 146.0, 138.6, 135.7, 134.7, 134.4, 129.4, 128.8, 128.6, 124.0, 118.6, 113.9, 67.6, 66.5, 56.2 ppm. HRMS (EI): calcd. for $C_{18}H_{13}O_5NBr_2S$ $[M]^+$ 512.8881; found 512.8886.

Benzyl 7-Bromo-9-chloro-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]-oxathiazine-1- carboxylate 5,5-Dioxide (3k): R_f = 0.32 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (s, 1 H), 7.54 (s, 1 H), 7.40 (s, 5 H), 6.94 (s, 1 H), 6.09 (s, 1 H), 5.32 (AB q, $\Delta\delta_{AB}$ = 0.05 ppm, J_{AB} = 12.1 Hz, 2 H), 4.39–4.50 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 145.5, 138.6, 134.7, 134.4, 132.9, 131.3, 128.8, 128.6, 126.5, 123.6, 113.6, 67.6, 66.6, 56.2 ppm. HRMS (EI): calcd. for $C_{18}H_{13}O_5NBrClS$ $[M]^+$ 468.9386; found 468.9390.

Benzyl 7,9-Di-*tert*-butyl-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]-oxathiazine-1-carboxylate 5,5-Dioxide (3l): R_f = 0.30 (petroleum ether/ethyl acetate, 10:1), identical to imine **1l**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, J = 1.8 Hz, 1 H), 7.38–7.33 (m, 5 H), 7.31 (d, J = 2.2 Hz, 1 H), 6.87 (s, 1 H), 6.15 (d, J = 4.2 Hz, 1 H), 5.29 (AB q, $\Delta\delta_{AB}$ = 0.14 ppm, J_{AB} = 12.2 Hz, 2 H), 4.51–4.37 (m, 2 H), 1.41 (s, 9 H), 1.22 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 148.0, 146.7, 139.4, 137.7, 135.6, 135.1, 128.7, 128.6, 128.5, 124.1, 122.1, 120.3, 67.2, 67.1, 56.3, 35.1, 34.7, 31.2, 30.0 ppm. HRMS (ESI): calcd. for $C_{26}H_{31}NO_5NaS$ $[M + Na]^+$ 492.1821; found 492.1828.

Cycloaddition Reaction with Cyclic Trifluoromethyl Ketimine 4: Scheme 3. To allenoate **2a** (0.225 mmol, 39.2 mg) in anhydrous toluene (0.75 mL) was added ketimine **4** (0.15 mmol, 37.7 mg) and Ph_3P (10 mol-%, 0.015 mmol, 4.0 mg). The mixture was stirred at room temperature for 1 h, but no reaction occurred as shown by TLC. Then the mixture was heated to 50 °C overnight (12 h), and analysis by using TLC indicated full conversion. After cooling to room temperature, the toluene solution was directly charged on silica gel and purified by column chromatography (petroleum ether/ethyl acetate) to afford the desired product (48.6 mg, 76% yield).

Benzyl 10b-(Trifluoromethyl)-3,10b-dihydrobenzo[*e*]pyrrolo[1,2-*c*]-[1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (5): R_f = 0.45 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.2 Hz, 1 H), 7.42–7.19 (m, 8 H), 7.07 (d, J = 8.2 Hz, 1 H), 5.15 (AB q, $\Delta\delta_{AB}$ = 0.04 ppm, J_{AB} = 12.2 Hz, 2 H), 4.81 (dd, J = 2.2, 18.2 Hz, 1 H), 4.51 (dd, J = 1.3, 18.2 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 150.2, 143.6, 134.7, 131.4, 130.9, 130.0 (q, J_{C-F} = 3.2 Hz), 128.7, 128.6, 128.4, 125.8, 123.8 (q, J_{C-F} = 285.4 Hz), 119.8, 116.2, 67.4, 57.4 ppm. HRMS (ESI): calcd. for $C_{19}H_{14}NO_5SF_3Na$ $[M + Na]^+$ 448.0442; found 448.0441.

Gram-Scale Procedure for [3+2] Cycloaddition Reaction of Allenoate 2a and Cyclic Imine 1a: Scheme 4. To allenoate **2a** (7.8 mmol, 1.359 g) in anhydrous toluene (13 mL) were added imine **1a** (1.191 g, 6.5 mmol) and triphenylphosphane (5 mol-%, 0.325 mmol, 85 mg). The mixture was stirred at room temperature for 4 h, and imine **1a** was shown to have reacted by using TLC. The crude reaction mixture was directly charged on silica gel and purified by column chromatography (petroleum ether/ethyl acetate). Recrystallisation from petroleum ether/ethyl acetate gave **3a** as a white solid (2.143 g, 92%).

Benzyl Benzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (6): Scheme 5. A mixture of **3a** (0.2 mmol, 71 mg) and DDQ (0.4 mmol, 91 mg) in benzene (3 mL) was heated to 120 °C for 36 h in a sealed tube. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and filtered through a short pad of silica gel. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate) to afford **6** as colorless oil (90%). If the reaction mixture was heated to reflux for 3 d in an open flask, the yield obtained was 78%. R_f = 0.52 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (dd, J = 1.7, 7.8 Hz, 1 H), 7.48–7.31 (m, 9 H), 6.97 (d, J = 3.4 Hz, 1 H), 5.36 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.1, 147.7, 135.7, 131.0, 130.8, 129.2, 128.6, 128.4, 128.2. 127.4, 118.8, 116.94, 116.88, 116.6, 115.3, 66.7 ppm. HRMS (EI): calcd. for $C_{18}H_{13}O_5NS$ $[M]^+$ 355.0514; found 355.0518.

2-[3-(Hydroxymethyl)-2,5-dihydro-1*H*-pyrrol-2-yl]phenol (7): (Scheme 5) To a solution of **3a** (0.2 mmol, 71 mg) in tetrahydrofuran (THF; 4 mL) was added lithium aluminum hydride (1.2 mmol, 45.5 mg), and the mixture was stirred at room temperature for 50 min. TLC indicated full conversion of the starting materials, and the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate (3×) and the combined organic phases were washed with brine and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate) on silica gel to a afford a colorless oil (36.6 mg, 96%). R_f = 0.21 (petroleum ether/ethyl acetate, 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (dd, J = 1.2, 8.1 Hz, 1 H), 7.36–7.32 (m, 1 H), 7.29–7.25 (m, 1 H), 6.58 (s, 1 H), 5.12 (t, J = 6.5 Hz, 1 H), 4.29 (d, J = 0.8 Hz, 2 H), 3.40 (AB q, $\Delta\delta_{AB}$ = 0.02 ppm, J_{AB} = 6.5 Hz, 2 H), 2.18–2.15 (m, 2 H), 2.15 (br., 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.2, 141.6, 131.6, 129.9, 128.8, 126.9, 124.5, 123.5, 66.5, 42.6, 31.4 ppm. HRMS (EI): calcd. for $C_{11}H_{13}O_2N$ $[M]^+$ 191.0946; found 191.0939.

Procedure for the [3+2] Cycloaddition Reaction of Cyclic Imine 1a by Using Chiral Phosphane Ligands as Organocatalysts: Table 2. To benzyl allenoate (**2a**) (20.9 mg, 0.12 mmol) in anhydrous toluene (0.25 mL) was added cyclic imine **1a** (0.05 mmol) followed by chiral phosphane (0.005 mmol, 10 mol-%). The mixture was stirred at room temperature. The crude reaction mixture was directly charged on silica gel and purified by column chromatography (petroleum ether/ethyl acetate) to afford the desired product. The enantiomeric excess was determined by HPLC (Chiralcel AD-H column, *i*PrOH/hexane, 18:82, 1.0 mL/min, 220 nm): t_1 = 10.2 min, t_2 = 13.5 min.

Ethyl 3,10b-Dihydrobenzo[*e*]pyrrolo[1,2-*c*][1,2,3]oxathiazine-1-carboxylate 5,5-Dioxide (3m): R_f = 0.35 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.8 Hz, 1 H), 7.32–7.28 (m, 1 H), 7.17 (dt, J = 1.3, 7.8 Hz, 1 H), 7.03 (dd, J = 1.2, 8.2 Hz, 1 H), 6.86–6.85 (m, 1 H), 6.14 (d, J = 3.9 Hz, 1 H), 4.44–4.41 (m, 2 H), 4.38–4.30 (m, 2 H), 1.36 (t, J = 7.1 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4, 149.8, 137.4, 135.4, 129.4, 127.3, 126.0, 120.7, 119.2, 66.6, 61.6, 55.9, 14.1 ppm. HRMS (EI): calcd. for $C_{13}H_{13}O_5NS$ $[M]^+$ 295.0514; found 295.0517. HPLC (Chiralcel AD-H column, *i*PrOH/hexane, 18:82, 1.0 mL/min, 220 nm): t_1 = 7.3 min, t_2 = 8.2 min.

Supporting Information (see footnote on the first page of this article): Data for cyclic imines, X-ray structure for product **3a** and copies of the ^{1}H and ^{13}C NMR spectra for all new compounds.

Acknowledgments

We are grateful for the financial support from the National Natural Science Foundation of China (No. 21002022), the Chinese Ministry of Education (the Scientific Research Foundation for the Returned Overseas Chinese Scholars), and the postdoctoral science foundation supports of Henan province in China. We also thank Professor Yong-Gui Zhou (DICP, CAS, China) for helpful suggestions and support in experiments.

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Received: December 28, 2012
Published Online: April 22, 2013

