DOI: 10.1002/ejoc.201000818

Synthesis of Binaphthyl Sulfonimides and Their Application in the Enantioselective Michael Addition of Ketones to Nitroalkenes

Shurong Ban,[a,b] Da-Ming Du,*[a] Han Liu,[c] and Wen Yang[a]

Keywords: Sulfonamides / Organocatalysis / Enantioselectivity / Michael addition / Alkenes

Novel types of L-proline-based binaphthyl sulfonimides and sulfonamides were found to be efficient organocatalysts for the asymmetric Michael addition of ketones to nitroalkenes to provide optically active γ-nitroketone derivatives of synthetic and biological importance. After the fine optimization of solvents, temperature, and additive, good to excellent enantioselectivities and diastereoselectivities (71–96 % *ee*, up to >99:1 *dr*) can be achieved.

Introduction

In recent years, considerable attention has been focused on the development of efficient and operationally simple protocols for the formation of carbon–carbon bonds for the construction of valuable molecules. The Michael addition reaction is one of the most general and versatile methods for the construction of new carbon–carbon bonds in organic synthesis. The organocatalytic asymmetric Michael addition of ketones to *trans*-β-nitrostyrene, which provides optically active nitroalkane derivatives of synthetic and biological importance, was pioneered by List[1] and Barbas[2] independently, and since then great effort has been devoted to the development of more selective and efficient catalytic systems for this synthetically useful transformation.[3,4] Despite the excellent results that have been achieved by these systems, the design and development of novel backbones and efficient chiral organocatalysts remain major challenges in synthetic organic chemistry. During the past several years sulfonamide derivatives as organocatalysts or ligands have been successfully applied in asymmetric Michael additions,[5] asymmetric Aldol reactions,[6] asymmetric alkynylations of aldehydes,[7] asymmetric diethylzinc additions,[8] asymmetric cyclopropanations,[9] asymmetric reduction of ketones,[10] and asymmetric Nozaki–Hiyama–Kishi reactions,[11] but to the best of our knowledge, sulfonimide-catalyzed asymmetric reactions are rarely reported. Herein, we report the synthesis of novel L-proline-based binaphthyl sulfonimides and sulfonamides (**3a**–**d**) and their application in the asymmetric Michael addition of ketones to nitroalkenes to give the desired adducts in moderate to high yields with excellent enantioselectivities and diastereoselectivities (up to 97% yield, 96%*ee*, >99:1 *dr*) under mild conditions.

Results and Discussion

The synthetic route towards binaphthyl sulfonimides and sulfonamides **3a**–**d** is shown in Scheme 1. Our original research project is the synthesis of binaphthyl sulfonamide compounds **3b** and **3d** and their application in asymmetric Michael additions. However, the unexpected binaphthyl sulfonimides were obtained firstly and showed better catalytic performance.

Initially, one equivalent of (*R*)-1,1′-binaphthyl-2,2′-disulfonyl dichloride (**1**)[12,13] and two equivalents of (*S*)-*tert*-butyl 2-(aminomethyl)pyrrolidine-1-carboxylate (**2**)[14,15] were stirred in CH_2Cl_2. A new spot was observed by TLC (petroleum ether/ethyl acetate, 2:1; $R_f = 0.3$) after 12 h; thus, the mixture was purified by column chromatography and treated with TFA. Other than the expected binaphthyl sulfonamide catalyst, the new compound was determined to be the sulfonimide compound through NMR spectroscopy and MS characterization. Then, the mmol ratio of starting materials was adjusted to 1:1 and an improved yield of binaphthyl sulfonimide (**3a**) could be achieved. In our further experiments, when the amount of starting material **2** was increased to 3.6 equiv., the formation of a new product with significantly higher polarity could be observed (petroleum ether/ethyl acetate, 1:1; $R_f = 0.1$). After deprotection of the *N*-Boc group with TFA, binaphthyl sulfonamide **3b** was obtained in pure form. Catalysts **3c** and **3d** were prepared in similar ways. The detailed experimental procedures and the spectroscopic data are provided in the Experimental Section.

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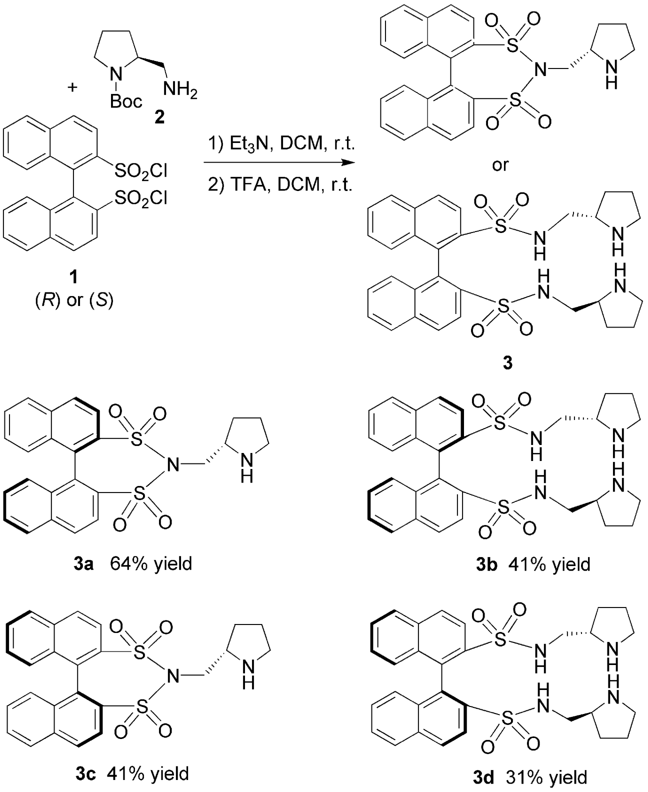
[a] School of Chemical Engineering and Environment, Beijing Institute of Technology,
Beijing 100081, People's Republic of China
Fax: +86-10-68914985
E-mail: dudm@bit.edu.cn
[b] School of Pharmaceutical Science, Shanxi Medical University,
Taiyuan 030001, People's Republic of China
[c] Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University,
Beijing 100871, People's Republic of China

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000818.



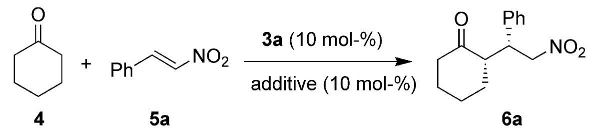
Scheme 1. Synthesis of binaphthyl sulfonimides and sulfonamides **3a**–**d**.

With the desired catalysts in hand, we immediately began to optimize the reaction conditions. Using **3a** as the catalyst, a number of parameters were screened in the model asymmetric Michael addition of cyclohexanone to β-nitrostyrene. The results are summarized in Table 1. Initially, the conjugate addition was examined in a few solvents at room temperature with *o*-nitrobenzoic acid as additive. In terms of enantioselectivity and diastereoselectivity, a variety of solvents were tolerated in this Michael addition reaction. Almost the same levels of enantioselectivity and diastereoselectivity were observed for solvent-free (Table 1, Entry 1; 97:3 *dr*, 92% *ee*), toluene (Table 1, Entry 2; 97:3 *dr*, 92% *ee*), EtOH (Table 1, Entries 3; 96:4 *dr*, 91% *ee*), and dichloromethane (Table 1, Entry 4; 97:3 *dr*, 92% *ee*). Considering both the reaction rate and atom economy, DCM is the best choice and was selected as the reaction solvent in the following reactions. Moreover, the additive carboxylic acid was found to be an essential factor to this reaction. In the absence of any carboxylic acid or in the presence of CF_3COOH, no product was obtained (Table 1, Entries 5 and 7). Almost the same level of enantioselectivity was observed for substituted benzoic acids such as *o*-nitrobenzoic acid (Table 1, Entry 4; 92% *ee*), *p*-bromobenzoic acid (Table 1, Entry 6; 92% *ee*), benzoic acid (Table 1, Entry 8; 93% *ee*), and *p*-methylbenzoic acid (Table 1, Entry 9; 93% *ee*). Benzoic acid is the suitable choice because of the higher diastereoselectivity and reaction rate. We also found that the stereoselectivity was increased by decreasing the reaction temperature from 20 to 0 °C (Table 1, Entry 10; 99:1 *dr*, 95% *ee*).

Other chiral catalysts **3b**–**d** were screened by employing these optimized conditions (Table 1, Entry 10), and the results are summarized in Table 2. Catalysts **3a**–**d** facilitated the asymmetric Michael addition of cyclohexanone to nitrostyrene with good to excellent stereoselectivities and yields. Sulfonimides **3a** and **3c** exhibited significantly higher enantioselectivities than sulfonamides **3b** and **3d**. (*S*)-1,1′-Binaphthyl-derived catalysts **3c** and **3d** demonstrated slight higher catalytic activity. Catalyst **3c** was the best catalyst and was selected in the following reactions.

With the optimized reaction conditions in hand, we next examined other nitroalkenes to expand the substrate scope of catalyst **3c**, and the results are summarized in Table 3. Various styrene-type nitroalkenes reacted smoothly with cyclohexanone to provide the corresponding adducts in moderate to excellent yields with excellent diastereoselectivities and enantioselectivities (Table 3, Entries 1–10). Excellent

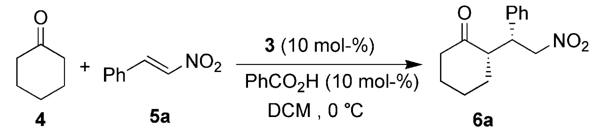
Table 1. Optimization of solvents, reaction temperature, and additive.[a]



Entry	Additive	Solvent	Temp. [°C]	Time [h]	Yield [%][b]	*dr* [*syn*/*anti*][c]	*ee* [%][d]
1	*o*-NO_2PhCO_2H	–	20	12	97	97:3	92
2	*o*-NO_2PhCO_2H	toluene	20	12	92	97:3	92
3	*o*-NO_2PhCO_2H	EtOH	20	12	81	96:4	91
4	*o*-NO_2PhCO_2H	DCM	20	12	97	97:3	92
5	–	DCM	20	12	0	–	–
6	*p*-$BrPhCO_2H$	DCM	20	12	94	97:3	92
7	CF_3CO_2H	DCM	20	12	0	–	–
8	$PhCO_2H$	DCM	20	12	97	98:2	93
9	*p*-CH_3PhCO_2H	DCM	20	12	74	97:3	93
10	$PhCO_2H$	DCM	0	24	97	99:1	95

[a] All reactions were carried out with cyclohexanone (**4**; 100 mg, 1.0 mmol) and nitrostyrene (**5a**; 18.7 mg, 0.13 mmol) in the presence of catalyst **3a** (10 mol-%) in DCM (0.2 mL). [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC on a Chiracel AS-H column with *n*-hexane and 2-propanol as eluents. [d] Determined by chiral HPLC analysis.

Table 2. Screening of catalysts.[a]

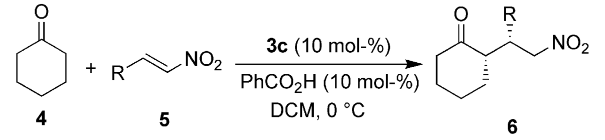


Entry	Catalyst	Time [h]	Yield [%][b]	*dr* [*syn*/*anti*][c]	*ee* [%][d]
1	**3a**	24	97	99:1	95.1
2	**3b**	24	94	97:3	88.0
3	**3c**	24	97	99:1	95.3
4	**3d**	24	95	98:2	93.0

[a] All reactions were carried out with cyclohexanone (**4**; 100 mg, 1.0 mmol) and nitrostyrene (**5a**; 18.7 mg, 0.13 mmol) in the presence of catalyst **3** (10 mol-%) and benzoic acid (10 mol-%) in DCM (0.2 mL). [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC. [d] Determined by chiral HPLC analysis.

diastereoselectivities (up to 99:1 *dr*) and enantioselectivities (93–96 %*ee*) were observed regardless of the electronic nature of the aromatic substituent R, whereas the nature of the substituent on the benzene ring exhibited a slight influence on the reaction activity. When an electron-donating substituent was introduced at the *para* position of the benzene ring, only low to moderate yields were obtained (Table 3, Entries 5 and 8), and this may be ascribed to the lower reactivity of these substrates as no other side reactions were observed. In addition, aliphatic-aldehyde-derived nitroalkenes do not appear to be good candidates for this asymmetric Michael addition reaction (Table 3, Entry 11; *syn*/*anti*, 67:33; 71 %*ee* for *syn* isomer).

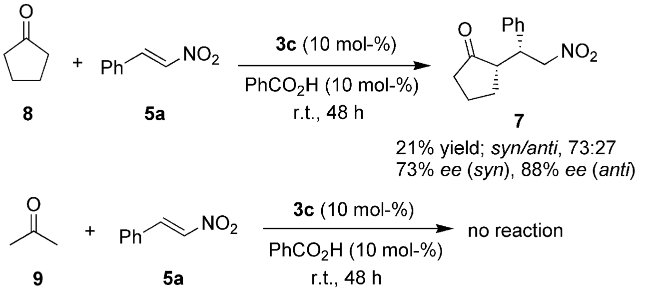
Table 3. Catalytic asymmetric Michael addition of cyclohexanone to nitroalkenes.[a]



Entry	R	Time [h]	Yield [%][b]	*dr* [*syn*/*anti*[c]]	*ee* [%][d]
1	Ph	24	97	99:1	95
2	2-MeOC$_6$H$_4$	24	87	>99:1	96
3	2-ClC$_6$H$_4$	24	81	>99:1	96
4	4-ClC$_6$H$_4$	36	57	99:1	96
5	4-MeC$_6$H$_4$	48	47	>99:1	95
6[e]	3-NO$_2$C$_6$H$_4$	48	88	98:2	96
7	2-furyl	48	50	99:1	94
8[e]	3,4-(MeO)$_2$C$_6$H$_3$	96	42	99:1	96
9	2-thienyl	70	63	98:2	93
10	4-FC$_6$H$_4$	70	78	99:1	96
11	PhCH$_2$CH$_2$	70	30	67:33	71

[a] All reactions were carried out with cyclohexanone (**4**; 100 mg, 1.0 mmol) and nitroalkene **5** (0.13 mmol) in the presence of catalyst **3c** (10 mol-%) and benzoic acid (10 mol-%) in DCM (0.2 mL). [b] Yield of the isolated product after chromatography on silica gel. [c] Determined by chiral HPLC. [d] Determined by chiral HPLC analysis, the configuration was assigned according to ref.[4] [e] Reaction at room temperature.

Cyclopentanone and acetone were subsequently examined in the **3c**-catalyzed Michael addition with nitrostyrene (**5a**). Unfortunately, as depicted in Scheme 2, the results were not satisfactory. Cyclopentanone gave low yield and moderate enantioselectivities, and no product was obtained for acetone.



Scheme 2. Michael addition of ketones to **5a**.

On the basis of the configuration of the product, the possible transition state for the **3c**-catalyzed Michael addition is illustrated in Figure 1. The pyrrolidine ring will first react with the carbonyl compound to form an enamine with the aid of the acidic cocatalyst. Subsequently, the oxygen atom of the sulfonimide as well as the Brønsted acid additive will orientate the nitro group through a hydrogen bonding interaction so that the enamine will nucleophilically attack the nitroalkene from the *Re* face to give the highly enantio- and diastereoselective product.

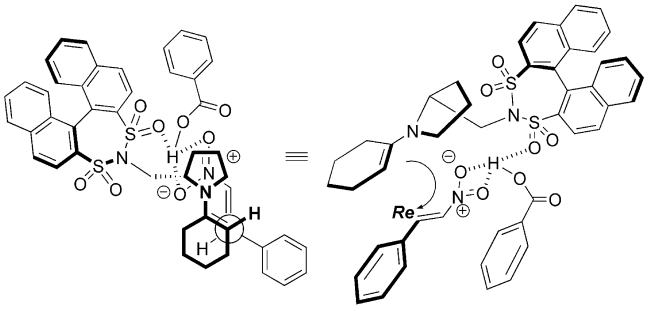


Figure 1. Possible transition state.

Conclusions

In conclusion, we have developed new L-proline-based binaphthyl sulfonimides and sulfonamides **3** as highly efficient and stereoselective organocatalysts for the asymmetric Michael addition of ketones to nitroalkenes. Moderate to excellent diastereoselectivities and enantioselectivities were obtained for the addition of cyclohexanone to a variety of nitroalkenes under the catalysis of **3c**. The presence of a brønsted acid with proper acidity, such as PhCO$_2$H, proved to be critical for the excellent performance of this catalyst system. The application of this new type of organocatalyst in other asymmetric reactions is underway in our laboratory.

Experimental Section

***N*-{[(*S*)-Pyrrolidin-2-yl]methyl}-(*R*)-1,1′-binaphthyl-2,2′-disulfonimide (3a):** To a solution of (*R*)-1,1′-binaphthyl-2,2′-disulfonyl dichloride (197 mg, 0.44 mmol) in dichloromethane was added dropwise a mixture of (*S*)-*tert*-butyl 2-(aminomethyl)pyrrolidine-1-carboxylate (105 mg, 0.52 mmol) and triethylamine (2 mL). The reaction mixture was stirred at room temperature overnight. The mixture was separated directly by silica gel column chromatography (dichloromethane) to give a white solid, which was then dissolved in a mixture of trifluoroacetic acid (0.28 mL) and dichloromethane (10 mL). The mixture was stirred for 4 h at room temperature. The pH of the mixture was adjusted to about 8 with saturated $NaHCO_3$. The mixture was extracted with dichloromethane (3 × 20 mL) and dried with anhydrous Na_2SO_4. After removal of the solvent, the product was obtained as a white solid (133 mg, 64% yield). M.p. >270 °C. $[\alpha]_D^{20}$ = –4.2 (*c* = 0.5, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3457, 3060, 2951, 2868, 1584, 1504, 1449, 1340, 1281, 1182, 1138, 1106, 1027, 877, 820, 776, 751, 728, 671, 656 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (s, 4 H, ArH), 8.04 (d, *J* = 8.2 Hz, 2 H, ArH), 7.67 (t, *J* = 7.4 Hz, 2 H, ArH), 7.26–7.41 (m, 4 H, ArH), 3.91 (dd, *J* = 7.8 Hz, *J* = 15.0 Hz, 1 H, CH_2), 3.74 (dd, *J* = 5.1 Hz, *J* = 15.1 Hz, 1 H, CH_2), 3.60–3.66 (m, 1 H, CH), 3.05–3.11 (m, 1 H, CH), 2.92–3.00 (m, 1 H, CH_2), 2.82 (br. s, 1 H, NH), 1.67–1.99 (m, 3 H, CH_2), 1.52–1.61 (m, 1 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.3, 135.2, 134.0, 131.2, 130.5, 129.1, 128.4, 127.9, 127.8, 122.8, 58.4, 49.7, 45.5, 28.4, 24.1 ppm. HRMS (ESI): calcd. for $C_{25}H_{23}N_2O_4S_2$ [M + H]$^+$ 479.10938; found 479.10908.

***N*,*N*′-{[(*S*)-Pyrrolidin-2-yl]methyl}-(*R*)-1,1′-binaphthyl-2,2′-disulfonamide (3b):** To a solution of (*S*)-*tert*-butyl 2-(aminomethyl)pyrrolidine-1-carboxylate (300 mg, 1.50 mmol) and triethylamine (3 mL) in dichloromethane (10 mL) was added dropwise (*R*)-1,1′-binaphthyl-2,2′-disulfonyl dichloride (188 mg, 0.42 mmol). The reaction mixture was stirred at room temperature overnight. The mixture was separated directly by silica gel column chromatography (petroleum ether/ethyl acetate, 1:1) to give a white solid, which was dissolved in a mixture of trifluoroacetic acid (0.50 mL) and dichloromethane (10 mL). The mixture was then stirred for 4 h at room temperature. The pH of the mixture was adjusted to about 8 with saturated $NaHCO_3$. The mixture was extracted with dichloromethane (3 × 30 mL) and dried with anhydrous Na_2SO_4. After removal of the solvent, the product was obtained as a white solid (100 mg, 41% yield). M.p. 172–173 °C. $[\alpha]_D^{20}$ = +221.2 (*c* = 0.5, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3425, 3060, 2960, 2873, 1588, 1503, 1424, 1330, 1170, 1149, 1135, 1123, 879, 817, 752, 697, 683 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (s, 4 H, ArH), 7.94 (d, *J* = 8.1 Hz, 2 H, ArH), 7.55 (t, *J* = 7.4 Hz, 2 H, ArH), 7.29 (t, *J* = 7.3 Hz, 2 H, ArH), 7.02 (d, *J* = 8.5 Hz, 2 H, ArH), 4.22 (br. s, 4 H, NH), 3.12–3.16 (m, 2 H, CH_2), 2.99 (dd, *J* = 4.5 Hz, *J* = 12.3 Hz, 2 H, CH_2), 2.77–2.85 (m, 6 H, CH_2 + CH), 1.58–1.77 (m, 6 H, CH_2),1.24–1.33 (m, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.2, 134.8, 134.3, 133.3, 129.3, 128.2, 128.1, 127.5, 124.4, 57.9, 47.3, 46.0, 28.8, 25.3 ppm. HRMS (ESI): calcd. for $C_{30}H_{35}N_4O_4S_2$ [M + H]$^+$ 579.20942; found 579.20957.

***N*-{[(*S*)-Pyrrolidin-2-yl]methyl}-(*S*)-1,1′-binaphthyl-2,2′-disulfonimide (3c):** Compound **3c** was prepared according to the method outlined for **3a** by using (*S*)-1,1′-binaphthyl-2,2′-disulfonyl dichloride (201 mg, 0.45 mmol) and (*S*)-*tert*-butyl 2-(aminomethyl)pyrrolidine-1-carboxylate (107 mg, 0.53 mmol). A white solid (88 mg, 41% yield) was obtained. M.p. 249–251 °C. $[\alpha]_D^{20}$ = –30.2 (*c* = 0.5, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3448, 3058, 2955, 2874, 1718, 1623, 1584, 1504, 1450, 1341, 1280, 1182, 1138, 1106, 1028, 877, 821, 781, 750, 728, 672, 656 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.18 (s, 4 H, ArH), 8.00 (d, *J* = 8.2 Hz, 2 H, ArH), 7.63 (t, *J* = 6.4 Hz, 2 H, ArH), 7.35 (d, *J* = 6.5 Hz, 4 H, ArH), 3.88 (dd, *J* = 6.5 Hz, *J* = 14.9 Hz, 1 H, CH_2), 3.73 (dd, *J* = 6.6 Hz, *J* = 15.0 Hz, 1 H, CH_2), 3.58–3.65 (m, 1 H, CH), 2.90–3.05 (m, 3 H, CH_2 + NH), 1.65–1.91 (m, 4 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.5, 134.4, 131.4, 130.8, 129.4, 128.6, 128.2, 128.0, 122.9, 58.1, 50.2, 46.0, 28.6, 24.6 ppm. HRMS (ESI): calcd. for $C_{25}H_{23}N_2O_4S_2$ [M + H]$^+$ 479.10938; found 479.10907.

***N*,*N*′-{[(*S*)-Pyrrolidin-2-yl]methyl}-(*S*)-1,1′-binaphthyl-2,2′-disulfonamide (3d):** Compound **3d** was prepared according to the method outlined for **3b** by using (*S*)-1,1′-binaphthyl-2,2′-disulfonyl dichloride (140 mg, 0.31 mmol) and (*S*)-*tert*-butyl 2-(aminomethyl)pyrrolidine-1-carboxylate (224 mg, 1.12 mmol). A white solid (55 mg, 31% yield) was obtained. M.p. 181–183 °C. $[\alpha]_D^{20}$ = –208.0 (*c* = 0.5, DMSO). IR (KBr): $\tilde{\nu}$ = 3434, 3060, 2922, 2871, 1646, 1586, 1502, 1407, 1321, 1258, 1171, 1136, 1083, 1025, 952, 906, 819, 750, 698, 682, 638 cm^{-1}. ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 8.17 (d, *J* = 8.5 Hz, 2 H, ArH), 8.02 (d, *J* = 8.4 Hz, 4 H, ArH), 7.54 (t, *J* = 7.0 Hz, 2 H, ArH), 7.28 (t, *J* = 7.2 Hz, 2 H, ArH), 6.80 (d, *J* = 8.2 Hz, 2 H, ArH), 4.79 (br. s, 4 H, NH), 2.91–2.93 (m, 2 H, CH_2), 2.61–2.71 (m, 8 H, CH_2 + CH), 1.49–1.60 (m, 6 H, CH_2), 1.18 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $[D_6]$DMSO): δ = 137.1, 134.6, 133.7, 132.8, 128.9, 128.0, 127.9, 127.3, 126.9, 123.9, 57.4, 47.2, 45.5, 28.7, 24.7 ppm. HRMS (ESI): calcd. for $C_{30}H_{35}N_4O_4S_2$ [M + H]$^+$ 579.20942; found 579.20969.

General Procedure for 3-Catalyzed Asymmetric Michael Addition of Ketone to Nitroalkenes: A solution of catalyst **3** (0.013 mmol) and cyclohexanone (0.1 mL, 0.1 mmol) in DCM (0.2 mL) was stirred at room temperature for 30 min. Then, benzoic acid (1.5 mg, 0.013 mmol) was added, and the reaction mixture was stirred for 15 min. To the resulting mixture was added the nitroalkene (0.13 mmol) at the required temperature. Upon completion of the reaction (monitored by TLC), the mixture was purified by column chromatography on silica gel (200–300 mesh; petroleum ether/ethyl acetate, 10:1) to afford the pure product.

Supporting Information (see footnote on the first page of this article): General remarks; ^1H NMR, ^{13}C NMR, IR, and mass spectra of the new organocatalysts; spectra data and HPLC diagrams for the Michael addition adducts.

Acknowledgments

We are grateful to the National Natural Science Foundation of China (Grant No. 20772006) and the Development Program for Distinguished Young and Middle-Aged Teachers of Beijing Institute of Technology for financial support.

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Received: June 8, 2010