DOI: 10.1002/ejoc.200600464

Organocatalytic Asymmetric Michael Addition of 2,2-Dimethyl-1,3-dioxan-5-one to Nitro Alkenes Employing Proline-Based Catalysts

Dieter Enders,*[a] and Sharon Chow[a]

Keywords: Asymmetric synthesis / Michael addition / Organocatalysis / Dioxanone / Nitro alkenes / Proline-based catalysts

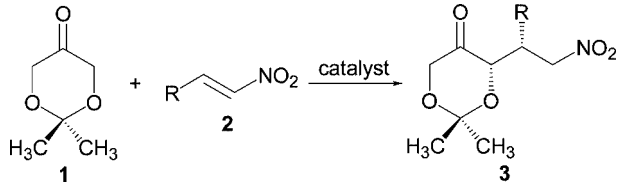
The organocatalytic asymmetric Michael addition of 2,2-dimethyl-1,3-dioxan-5-one (**1**) was performed with various nitro alkenes **2** using a number of proline-based catalysts (**A**–**M**) affording polyfunctional nitro ketones **3**. Reverse diastereoselectivity was observed with the diphenylprolinol catalyst **J**, and the best diastereo- and enantiomeric excesses were achieved with the sulfonamide catalyst **M** (*de* = 84–98 %, *ee* = 81–86 %).

Introduction

Enzyme catalysis is a fundamental process in nature. Its efficiency and excellent selectivity under physiological conditions attracted the chemists in mimicking mother nature in organic synthesis, which led to the development of enzymatic methods, organometallic catalysis and more recently organocatalysis.[1] Significant advancement in the latter field has been achieved during the last few years, in which the scope of organocatalytic reactions has been enormously expanded. In particular, asymmetric Michael additions[2] have been studied extensively due to their broad applicability with various substrates under carbon–carbon bond formation. Quite a number of Michael acceptors have already been used in organocatalysis, and nitro alkenes[3] are the most prominent ones,[4] because of their high acceptor reactivity and the ease in converting the nitro group to other different functionalities. The Michael donors vary from the typical aldehydes, ketones and malonates[4,5] to recently N-heterocycles,[6] unsaturated malononitriles[7] and nitro alkanes,[8] which all delivered good to excellent stereoselectivities depending on the organocatalysts. Herein, we would like to report our findings on the asymmetric Michael addition of 2,2-dimethyl-1,3-dioxan-5-one (dioxanone, **1**), the protected form of dihydroxyacetone, to various nitro alkenes **2** using some proline-based catalysts.

Results and Discussions

We recently summarized the rich chemistry and broad applicability of dioxanone **1** as an important C_3 unit in stoichiometric asymmetric synthesis employing our SAMP-/RAMP-hydrazone methodology.[9] Using the parent dioxanone itself as methylene component in proline-catalyzed aldol and Mannich reactions, we later developed a biomimetic organocatalytic $C_3 + C_n$ strategy for the de novo synthesis of carbohydrates and amino sugars.[10] In addition, we successfully applied the novel protocols in the organocatalytic asymmetric synthesis of phytosphingosines[11] and polyoxamic acid.[12] On the basis of our experience in organocatalytic Michael additions to nitro alkenes,[3e] we envisaged the proline-catalyzed 1,4-addition of dioxanone **1** to various nitroolefins **2** to afford the polyfunctionalized adducts **3** (Scheme 1).



Scheme 1. The organocatalytic asymmetric Michael addition of dioxanone **1** to nitro alkenes **2** resulting in the highly functionalized 1,4 adducts **3**.

Initial screenings of the catalysis were carried out by proline and derivatives (Figure 1) on dioxanone **1** and β-nitrostyrene (**2a**, R = Ph). The proline-catalyzed Michael addition to form the 1,4 adducts **3** proceeded with excellent diastereoselectivity ($de \geq 98\%$), but the enantioselectivity (*ee* = 43%) was barely acceptable (Entry 1, Table 1). A better enantioselectivity (*ee* = 58%) was obtained when the reaction was catalyzed by the substituted proline **B** at room temperature (Entry 2, Table 1). Unfortunately, the diastereoselectivity and the yield were reduced tremendously in comparison with the proline entry. The addition was attempted at a low temperature for stereoselectivity enhancement, but was proven fruitless due to the poor solubility of the catalyst **B** under such conditions. Despite the decent

[a] Institut für Organische Chemie, RWTH Aachen,
Landoltweg 1, 52074 Aachen, Germany
Fax: +49-241-8092127
E-mail: enders@rwth-aachen.de

Table 1. Asymmetric Michael additions of dioxanone **1** to β-nitrostyrene (**2a**) with the catalysts **A**–**G** to furnish the Michael adduct **3a** (R = Ph).[a]

Entry	Catalyst	Solvent	*T* [°C]	Yield [%]	*dr syn*/*anti*[b]	*ee* [%][b]
1	**A**	*i*PrOH	2	48	> 99:1	43
2	**B**	MeOH	20	< 10	57:43	58
3	**C**	MeCN	2	60	81:19	0
4	**D**	DMSO	2	10	93:7	14
5	**E**	MeOH	2	12	45:55	30
6	**F**	CH_2Cl_2	2	12	78:22	42
7	**G**	cyclohexane	2	28	67:33	54

[a] The reactions were performed with 2 equiv. of dioxanone **1**, 1 equiv. of β-nitrostyrene (**2a**) and 30 mol-% of the catalyst for 5–14 d. The solvents given are the best ones for each catalyst, respectively. [b] Determined by chiral stationary phase HPLC.

yield (60%) and diastereoselectivity, the enantioselectivity was virtually lost in the catalysis using the silyl-protected *trans*-hydroxyproline **C** (Entry 3, Table 1). Neither the proline amides **D** nor **E** resulted in any improvement in the enantioselectivity (Entries 4 and 5, Table 1). Whereas compatible and slightly improved *ee* values were detected with the prolinamine **F** and prolinol **G** (Entries 6 and 7, Table 1), their diastereoselectivities were not practical in comparison with the 1,4-additions catalyzed by proline itself.

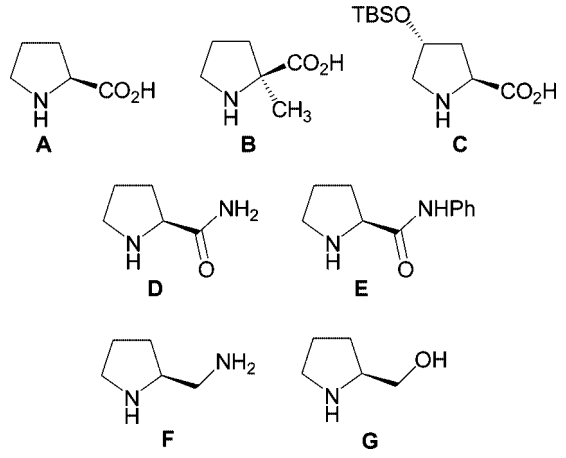


Figure 1. Catalysts **A**–**G**.

Interestingly, when the Michael addition was catalyzed by the disubstituted prolinols (**H** to **J**)[13] or its bicyclic derivative **K** shown in Figure 2, the reverse diastereoselectivity in favor of the *anti*-configuration was observed (Table 2). The enantiomeric excess was greatly enhanced, when the size of the substituents increased from methyl to phenyl (Entries 1 and 3, Table 2). As expected, all the selectivities were almost lost, when the hydroxy group was protected as a silyl ether (Entry 2, Table 2). In order to increase the steric hindrance in the catalyst, the bicyclic derivatives **K** and **L** were tested. The dimethylhydroxy system **K** delivered a better *ee* value (Entry 4, Table 2) than the monocyclic version

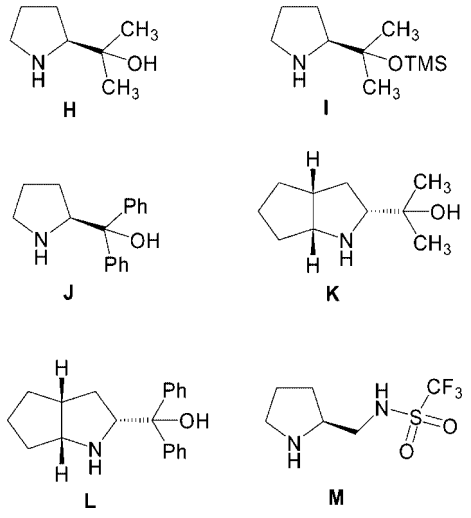


Figure 2. Catalysts **H** to **M**.

Table 2. Results of the Michael addition of dioxanone **1** to β-nitrostyrene (**2a**) to afford **3a** (R = Ph), using the catalysts **H** to **L**.[a]

Entry	Catalyst	Solvent	Additive	Yield [%]	*dr syn*/*anti*[b]	*ee* [%][b]
1	**H**	cyclohexane	–	37	29:71	18
2	**I**	cyclohexane	–	<10	45:55	5
3	**J**	cyclohexane	–	20	19:81	52
4	**K**	cyclohexane	–	42	38:62	41
5	**L**	CH_2Cl_2	–	0	–	–
6	**J**	$CHCl_3$	–	47	18:82	56
7	**J**	CH_2Cl_2	–	32	19:81	59
8	**J**	CH_2Cl_2	TsOH	0	–	–
9	**J**	CH_2Cl_2	CH_3CO_2H	0	–	–
10	**J**	CH_2Cl_2	$NH_4Cl + H_2O$	12	21:79	52

[a] The reactions were performed with 2 equiv. of dioxanone **1**, 1 equiv. of β-nitrostyrene (**2a**) and 30 mol-% of the catalyst for 9–14 d. In Entries 8–10, 1 equiv. of the additive was used. [b] Determined by chiral stationary phase HPLC.

of the catalyst. Nevertheless, no conversion was observed when the bulkier diphenyl bicyclic derivative **L** was used. The amine in **L** is probably overcrowded by all the substituents, and the formation of the corresponding enamine is prohibited.

Optimizations of the enantioselectivity were attempted utilizing the catalyst **J**, which exhibited the best diastereo- and enantioselectivity in the initial screening; however, the results were unsatisfactory. Further lowering the reaction temperature to –26 °C completely stopped the proceeding of the catalysis. Slight improvement in the yield and diastereoselectivity were observed using dichloromethane or chloroform as the solvent, but employing protic solvents, such as methanol for instance, led to side reactions of the β-nitrostyrene. In the cases with additives, acids like *p*-toluenesulfonic acid and acetic acid only promoted the decomposition of starting materials (Entries 8 and 9, Table 2). The addition of water and ammonium salt imposed no significant changes in the selectivities, but resulted in lower yield (Entry 10, Table 2).

The change in the diastereoselectivity from *syn*-**3a** to *anti*-**3a** with this group of amino catalysts can possibly be rationalized by the transition-state model illustrated in Figure 3. Instead of an intermolecular hydrogen bond between the donor and the acceptor with the proline-based catalysts, the steric hindrance from the side chain of the catalyst in the enamine intermediate forces the nitro alkene to approach the enamine at the *Re*-face. In addition, an attractive electrostatic interaction between the amine and the nitro group may lead to the relative topicity shown in Figure 3 explaining the *anti*-Michael product observed.

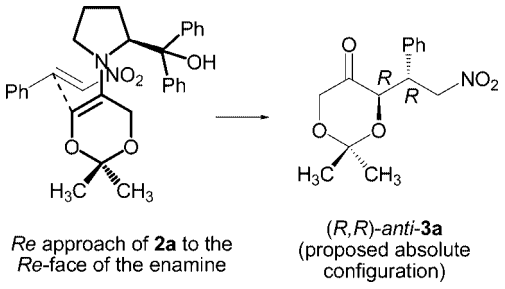


Figure 3. Proposed transition state explaining the *anti*-configuration of the Michael adducts.

During this work, a new pyrrolidinylsulfonamide-based catalyst **M**, which gave very high yields and selectivities in the asymmetric Michael addition of aldehydes with nitroolefins, was reported.[4k] This sulfonamide catalyst was prepared and then screened in our protocol. The first results with the aromatic nitro alkenes were encouraging (Table 3). Apart from the 2-furyl-substituted nitro alkene **2b** (Entry 2, Table 3), the other examples exhibited good diastereoselectivities and all the *ee* values were above 70%, despite the low chemical yields.

Table 3. Initial results of the Michael addition of dioxanone **1** to aromatic nitro alkenes **2a**–**e** to afford **3a**–**e** using the pyrrolidinylsulfonamide catalyst **M**.[a]

Entry	**2**,**3**	R	Yield [%]	*dr syn*/*anti*[b]	*ee* [%][b]
1	**a**	Ph	33	92:8	77
2	**b**	2-furyl	25	74:26	60
3	**c**	2-ClC_6H_4	16	88:12	81
4	**d**	3-ClC_6H_4	12	86:14	75
5	**e**	4-benzo[*d*][1,3]dioxolyl	14	93:7	71

[a] The reactions were performed with 2 equiv. of dioxanone **1**, 1 equiv. of nitro alkenes **2a**–**e**, and 25 mol-% of the catalyst **M** in 2-propanol as the best solvent for 13–16 d. [b] Determined by chiral stationary phase HPLC.

Optimizations of enantioselectivity, carried out at a lower temperature while increasing the concentration of the dioxanone **1**, resulted in a marginally improvement of the enantiomeric excess, but the yield was further diminished even with the prolongation of the reaction time. The catalyses with the aliphatic nitro alkene **2f** (R = Et) gave better selectivities and yields, especially when 30 mol-% of catalyst was used (Entry 5, Table 4). Nevertheless, the reaction did not proceed when a more sterically demanding aliphatic nitro alkene (**2g** and **2h**) was engaged in the catalysis (Entries 7 and 8, Table 4).

Interestingly, the initial result of utilizing water as an additive (4.0 equiv.) in the catalysis appeared to have accelerated the reaction, and furnished a promising yield of 62% in 6 d, still with the good stereoselectivities (Entry 5, Table 5). To explore this effect further, different amounts of water were used and the catalyses were monitored by gas chromatography. Figure 4 illustrates the plot of the ratio of the product **3f** and dioxanone **1** against the reaction time. Not surprisingly, the reaction proceeded very sluggishly without any water addition. With the addition of 10 equiv.

Table 4. Optimization results with the sulfonamide catalyst **M** in 2-propanol using nitro alkenes **2a** and **2f**.

Entry	**2**,**3**	R	**1** [equiv.]	**M** [mol-%]	*T* [°C]	Time [d]	Yield [%]	*dr syn*/*anti*[a]	*ee* [%][a]
1	**A**	Ph	2	25	20	13	33	92:8	77
2	**A**	Ph	2	25	2	19	10	92:8	78
3	**a**	Ph	4	25	2	21	12	89:11	81
4	**f**	Et	2	30	20	5	35	99:1	85
5	**f**	Et	2	30	20	28	48	97:3	83
6	**f**	Et	2	20	2	14	traces	[b]	[b]
7	**g**	*i*Pr	4	30	20	21	0	–	–
8	**h**	*t*Bu	4	30	20	21	0	–	–

[a] Determined by chiral stationary phase HPLC. [b] Not determined.

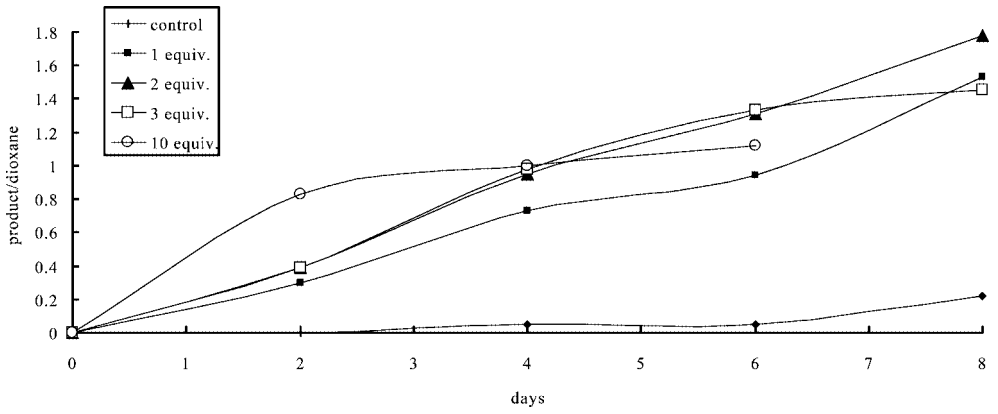


Figure 4. The effect of adding different equivalents of water on the reaction rate of the 1,4-addition of dioxanone **1** to nitro alkene **2f** catalyzed by the sulfonamide **M**.

of water, the conversion was the fastest for the first two days, and then decreased afterwards. Whereas, the rest of the trials started off at a slower rate, but increased steadily during the monitoring period, except when 3 equiv. of water was engaged. In this particular case, the conversion rate seemed to level out after 6 d of stirring. The yield, other than Entry 2 (Table 5), improved greatly with a shorter reaction time, and the high level of selectivities was maintained in all cases. It is worthy to note that some unnecessary solvent evaporation occurred in Entries 3 and 5 (Table 4). This increase in the concentrations of the reactions may have caused the slight decrease in the diastereo- and enantioselectivity of the products.

Table 5. Effect of water on the Michael addition of **1** to the nitro alkene **2f** to form **3f** catalyzed by the sulfonamide **M**.[a]

Entry	H_2O [equiv.]	Yield [%]	*dr syn/anti*[b]	*ee* [%][b]
1	0	21[c]	99:1	80
2	1	47	97:3	83
3	2	24	91:9	81
4	3	58	97:3	84
5	4	62	91:9	81
6	10	47	98:2	85

[a] The reactions were performed with 2 equiv. of dioxanone **1**, 1 equiv. of nitro alkene **2f** and 20 mol-% of the catalyst **M** in 2-propanol for 6–8 d. [b] Determined by chiral stationary phase HPLC. [c] 2 Equiv. of water were added on day 6 and the reaction was stirred for 28 d.

The high stereoselectivities observed in these examples employing the sulfonamide catalyst **M** could be governed by the transition state illustrated in Figure 5.[4k] The sulfonamide moiety, with a highly electron-withdrawing triflate substituent, may provide hydrogen bonding to the nitro alkene and possibly to the pyrrolidine backbone. This tighter transition state may impose a stronger directing effect of the acceptor to the enamine, and thus resulting in higher diastereo- and enantioselectivities.

A few other examples with aliphatic nitro alkenes have been performed with the aid of water (Table 6). The yields were more decent (Entries 1 and 2, Table 6), and the products were all obtained with excellent *syn*/*anti* diastereoselectivities, and high enantiomeric excesses of up to 86%. In the

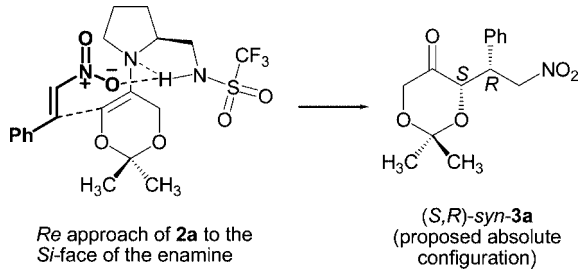


Figure 5. The proposed transition state and absolute configuration employing the sulfonamide catalyst **M**.

case of Entries 2 and 3, the protected alcohol substituent on the nitro alkene masked the opportunity for further functionalization at this position. Nevertheless, the yield of the catalysis with nitro alkene **2k** needs further optimization.

Table 6. 1,4-Additions using the aliphatic nitro alkenes **2i**–**k** and the sulfonamide catalyst **M** to furnish **3i**–**k**.[a]

Entry	**2,3**	R	Yield [%]	*dr syn/anti*[b]	*ee* [%]
1	**i**	Me	52	> 97:3	85[c]
2	**j**	CH_2OTBS	60	> 98:2	[d]
3	**k**	CH_2OAc	15	97:3[d]	86[e]

[a] The reactions were performed with 2 equiv. of dioxanone **1**, 1 equiv. of nitro alkene **2i-k**, 2 equiv. of water and 20 mol-% of the catalyst **M** in 2-propanol for 6–8 d. [b] Determined by ^1H NMR spectroscopy. [c] Determined by chiral stationary phase HPLC. [d] *rac*-**3J** could not be measured by CSP GC and thus the *ee* of **3j** could not be accurately determined. [e] Determined by chiral stationary phase GC.

Conclusions

In summary, we have worked out a protocol to obtain high to excellent *syn* diastereoselectivities and relatively good enantiomeric excesses (81–86%) in the organocatalytic asymmetric Michael addition of the dioxanone **1** to various nitro alkenes **2** catalyzed by the sulfonamide **M**. The addition of water employing catalyst **M** accelerated the conversion and provided a better yield with shorter reaction time. In addition, the studies with the diphenylprolinol cata-

lyst **J** revealed the reversal in the diastereoselectivity, favoring the *anti* configuration.

Experimental Section

General: All solvents were dried prior to use: THF and ethyl acetate were distilled from potassium hydroxide; dichloromethane, DMSO, methanol and 2-propanol were distilled from CaH_2. Analytical glass-backed TLC plates (silica gel 60 F_{254}) and silica gel (60, 40–63 μm) were purchased from Merck. Mass spectra were obtained with a Varian MAT 212, EI 70 eV, 1 mA. ^1H, ^{13}C and two-dimensional NMR spectra were recorded with a Varian VXR 300, Gemini 300 or Varian Inova 400 with residual chloroform (δ_H = 7.26 and δ_C = 77.0 ppm) as the internal standard. Optical rotations were measured with a Perkin–Elmer P241 polarimeter. Microanalyses were obtained with a Heraeus CHN-O-RAPID, Vario EL elemental analyser. IR spectra were recorded with a Perkin–Elmer FT/IR 1760 spectrometer. High-resolution mass spectra were measured with a Finnigan MAT 95.

General Catalysis Procedure 1 (without additive): Dioxanone **1** (0.67 mmol, 2 equiv. or 1.34 mmol, 4 equiv.) and the catalyst (**A**–**M**, 20–30 mol-%) were mixed in the solvent (0.4 mL) and then stirred for 30 min at room temperature in a closed flask to initiate the formation of the enamine. A pale yellow color was observed in most cases. This was followed by the addition of the nitro alkene **2** (0.33 mmol) and the reaction was stirred at either room temperature or 2 °C until the disappearance of the nitro alkene **2**. The reaction was quenched according to the catalyst used in the Michael addition (see work-up procedure).

General Catalysis Procedure 2 (with additive): Dioxanone **1** (0.67 mmol, 2 equiv. or 1.34 mmol, 4 equiv.) and the catalyst (**A**–**M**, 20–30 mol-%) were mixed in the solvent (0.4 mL) and then stirred for 30 min at room temperature in a closed flask to initiate the formation of the enamine. A pale yellow color was observed in most cases. This was followed by the addition of the nitro alkene **2** (0.33 mmol) and the additive (1 equiv.), respectively. The reaction was stirred at either room temperature or 2 °C until the disappearance of the nitro alkene **2**. The reaction was quenched according to the catalyst used in the Michael addition (see work-up procedure).

Work-up Procedure A: (for the catalysts **A**–**L**) The reaction was quenched with the addition of aqueous saturated NH_4Cl solution (2 mL) and stirred for 5 min, followed by the extraction with ethyl acetate (3 × 3 mL). The combined organic layers were washed with brine (2 mL), and dried with Na_2SO_4. Upon filtration and concentration, the crude product was purified by flash chromatography.

Work-up Procedure B: (for the catalyst **M**) The reaction was concentrated under reduced pressure and the crude product was then subjected to flash chromatography.

3a (R = phenyl): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 10% diethyl ether in pentane as a *syn*/*anti* mixture). ***syn* Isomer:** ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.34–7.26 (m, 5 H, Ph-H), 4.91 (dd, $^{2,3}J_{H,H}$ = 12.9 and 8.5 Hz, 1 H, CH_2NO$_2$), 4.66 (dd, $^{2,3}J_{H,H}$ = 12.9 and 6.8 Hz, 1 H, CH_2NO$_2$), 4.59 (dd, $^{2,4}J_{H,H}$ = 3.7 and 1.1 Hz, 1 H, C*H*), 4.13 (ddd, $^3J_{H,H}$ = 8.5, 6.8 and 3.7 Hz, 1 H, C*H*CH$_2$NO$_2$), 3.87 (s, 2 H, CH_2), 1.46 (s, 3 H, CCH_3), 1.45 (s, 3 H, CCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 206.5, 134.7, 129.3 (2 C), 128.4 (2 C), 127.9, 101.1, 76.3, 74.6, 67.0, 43.3, 24.1, 23.3 ppm. MS (EI): *m*/*z* (%) = 264 (1) [M$^+$ – 15 (CH$_3$)], 221 (1), 191 (2), 174 (7), 145 (9), 129 (35), 115 (17), 104 (100), 91 (24), 77 (17), 72 (92), 59 (25). ***anti* Isomer:** ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.28 (m, 5 H, Ph-H), 4.90 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2NO$_2$), 4.53 (dd, $^{2,4}J_{H,H}$ = 3.0 and 1.5 Hz, 1 H, 4-H), 4.29 (dd, $^{2,4}J_{H,H}$ = 17.3 and 1.5 Hz, 1 H, C*H*H), 4.19 (dt, $^3J_{H,H}$ = 7.4 and 3.0 Hz, 1 H, C*H*CH$_2$NO$_2$), 4.05 (d, $^2J_{H,H}$ = 17.3 Hz, 1 H, CH*H*), 1.48 (s, 3 H, CCH_3), 1.39 (s, 3 H, CCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 206.8, 137.5, 128.9 (2 C), 128.1 (3 C), 101.6, 76.4, 75.8, 66.8, 41.8, 23.5 (2 C) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3065, 3031, 2991, 2940, 2886, 1750, 1603, 1555, 1496, 1455, 1430, 1380, 1175, 1112, 1060, 1008, 866, 759, 703 cm^{-1}. $C_{14}H_{17}NO_5$ (279.3): calcd. C 60.21, H 6.14, N 5.02; found C 60.68, H 6.35, N 5.69. The *ee* and *dr* were determined by chiral stationary phase HPLC (Daicel AW for the *syn* enantiomers and Daicel AD for the *anti* enantiomers) using *n*-heptane/2-propanol (95:5 and 98:2, respectively) with a flow rate of 1 and 0.7 mL/min, respectively. Retention times relative to the racemic sample: 9.1 min for the major *syn* isomer and 7.5 min for the minor isomer; 22.0 min for the major *anti* isomer and 17.4 min for the minor isomer.

3b (R = 2-furyl): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 10% diethyl ether in pentane). ***syn* Isomer:** ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.34 (m, 1 H, OC*H*=CH), 6.30 (m, 1 H, OCH=C*H*), 6.24 (m, 1 H, OCR=C*H*), 4.81 (dd, $^{2,3}J_{H,H}$ = 13.1 and 8.4 Hz, 1 H, CH_2NO$_2$), 4.72 (dd, $^{2,3}J_{H,H}$ = 13.1 and 6.7 Hz, 1 H, CH_2NO$_2$), 4.56 (dd, $^{3,4}J_{H,H}$ = 3.7 and 1.5 Hz, 1 H, CH), 4.29 (m, 1 H, C*H*CH$_2$NO$_2$), 4.14 (dd, $^{2,4}J_{H,H}$ = 17.1 and 1.5 Hz, 1 H, C*H*H), 3.98 (d, $^2J_{H,H}$ = 17.1 Hz, 1 H, CH*H*), 1.45 (s, 3 H, CCH_3), 1.43 (s, 3 H, CCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 206.5, 148.7, 110.5, 108.7, 101.8, 74.2, 73.3, 66.8, 37.4, 23.7, 23.2 ppm. MS (EI): *m*/*z* (%) = 269 (2) [M$^+$], 254 (2), 222 (6), 191 (3), 151 (8), 129 (100), 122 (11), 94 (31), 72 (19), 59 (10). IR ($CHCl_3$): $\tilde{\nu}$ = 3023, 2992, 1752, 1557, 1429, 1380, 1224, 1112, 866, 757 cm^{-1}. $C_{12}H_{15}NO_6$ (269.3): calcd. C 53.53, H 5.62, N 5.20; found C 53.66, H 6.17, N 6.18. The *ee* and *dr* were determined by chiral stationary phase HPLC (Daicel AD) using *n*-heptane/2-propanol (98:2) with a flow rate of 1 mL/min. Retention times relative to the racemate: 30.7 min for the major *syn* isomer and 36.6 min for the minor isomer; 34.2 min and 42.9 min for the *anti* isomers.

3c (R = 2-ClC_6H_4): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 10% diethyl ether in pentane). ***syn* Isomer:** ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.59 (m, 1 H, Ar-H), 7.38 (m, 1 H, Ar-H), 7.22 (m, 2 H, Ar-H), 4.86 (dd, $^{2,3}J_{H,H}$ = 12.9 and 8.2 Hz, 1 H, CH_2NO$_2$), 4.76 (dd, $^{2,4}J_{H,H}$ = 5.0 and 1.4 Hz, 1 H, CH), 4.74 (dd, $^{2,3}J_{H,H}$ = 12.9 and 6.6 Hz, 1 H, CH_2NO$_2$), 4.65 (m, 1 H, C*H*CH$_2$NO$_2$), 4.13 (dd, $^{2,4}J_{H,H}$ = 17.0 and 1.4 Hz, 1 H, C*H*H), 3.97 (d, $^2J_{H,H}$ = 17.0 Hz, 1 H, CH*H*), 1.49 (s, 3 H, CCH_3), 1.47 (s, 3 H, CCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 206.8, 134.6, 133.2, 130.1, 129.2, 129.1, 127.1, 101.5, 76.1, 74.5, 73.6, 39.3, 23.9, 23.3 ppm. MS (EI): *m*/*z* (%) = 298 (1) [M$^+$ – 15 (CH$_3$)], 255 (14), 213 (4), 169 (3), 167 (6), 140 (22), 138 (83), 129 (29), 115 (14), 102 (20), 100 (18), 77 (10), 72 (100), 59 (20). IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 1750, 1556, 1477, 1437, 1380, 1224, 1114, 1038, 864, 759 cm^{-1}. $C_{14}H_{16}ClNO_5$ (313.7): calcd. C 53.60, H 5.14, N 4.46; found C 53.61, H 5.59, N 4.89. The *ee* and *dr* were determined by chiral stationary phase GC (Varian CP-Chirasil-dex CB 25 m × 0.25 mm ID, the temperature program: 100 – 10 iso – 1 – 120 – 3 – 180 – 60iso). Retention times relative to the racemate: 59.1 min for the major *syn* isomer and 58.5 min for the minor isomer; 60.0 min and 60.9 min for the *anti* isomers.

3d (R = 3-ClC_6H_4): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 10% diethyl ether in pentane). ***syn* Isomer:** ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.37 (m, 1 H, Ar-H), 7.29–7.21 (m, 3 H, Ar-H), 4.87 (dd, $^{2,3}J_{H,H}$ = 12.9

and 8.5 Hz, 1 H, CH_2NO_2), 4.65 (dd, $^{2,3}J_{H,H}$ = 12.9 and 7.1 Hz, 1 H, CH_2NO_2), 4.58 (dd, $^{2,4}J_{H,H}$ = 3.6 and 1.1 Hz, 1 H, CH), 4.11 (ddd, $^{3}J_{H,H}$ = 8.5 and 7.1 and 3.6 Hz, 1 H, CHCH_2NO_2), 3.95 (dd, $^{2,4}J_{H,H}$ = 17.0 and 1.1 Hz, 1 H, CHH), 3.89 (d, $^{2}J_{H,H}$ = 17.0 Hz, 1 H, CHH), 1.47 (s, 6 H, C(CH_3)$_2$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 206.3, 136.7, 134.2, 129.6, 129.4, 128.2, 127.7, 101.2, 76.1, 74.3, 66.9, 42.8, 23.8, 23.4 ppm. MS (EI): *m*/*z* (%) = 298 (1) [M^+ – 15 (CH_3)], 257 (4), 255 (13), 210 (4), 208 (13), 167 (13), 140 (29), 138 (100), 100 (29), 72 (79), 59 (16). IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 1749, 1556, 1432, 1379, 1223, 1113, 1089, 869, 759 cm^{-1}. $C_{14}H_{16}ClNO_5$ (313.7): calcd. C 53.60, H 5.14, N 4.46; found C 53.45, H 5.45, N 4.90. The *ee* and *dr* were determined by chiral stationary phase HPLC (Daicel OD) using *n*-heptane/2-propanol (9:1) with a flow rate of 1 mL/min. Retention times relative to the racemate: 12.2 min for the major *syn* isomer and 16.3 min for the minor isomer; 10.1 min and 14.2 min for the *anti* isomers.

3e (R = 4-benzo[*d*][1,3]dioxolyl): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 20% diethyl ether in pentane). ***syn* Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.86 (m, 1 H, Ar-H), 6.78 (m, 1 H, Ar-H), 6.71 (m, 1 H, Ar-H), 5.92 (s, 2 H, OCH_2O), 4.83 (dd, $^{2,3}J_{H,H}$ = 12.8 and 8.7 Hz, 1 H, CH_2NO_2), 4.61 (dd, $^{2,3}J_{H,H}$ = 12.8 and 7.0 Hz, 1 H, CH_2NO_2), 4.52 (dd, $^{2,4}J_{H,H}$ = 3.7 and 1.2 Hz, 1 H, CH), 4.05 (m, 1 H, CHCH_2NO_2), 3.97 (dd, $^{2,4}J_{H,H}$ = 16.1 and 1.2 Hz, 1 H, CHH), 3.87 (d, $^{2}J_{H,H}$ = 16.7 Hz, 1 H, CHH), 1.48 (s, 3 H, CCH_3), 1.47 (s, 3 H, CCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 206.6, 147.6, 147.3, 128.2, 123.1, 109.5, 108.2, 101.2 (2 C), 76.6, 74.6, 67.0, 42.9, 24.0, 23.2 ppm. MS (EI) *m*/*z* (%) = 323 (21) [M^+], 265 (4), 218 (3), 194 (15), 176 (5), 148 (100), 129 (26), 103 (4), 89 (5), 77 (4), 72 (7), 59 (6). IR ($CHCl_3$): $\tilde{\nu}$ = 2991, 2929, 1750, 1555, 1492, 1445, 1380, 1041, 936, 864, 818, 758 cm^{-1}. HRMS: *m*/*z* calcd. for $C_{15}H_{17}NO_7$ 323.1005; found: 323.1006. The *ee* and *dr* were determined by chiral stationary phase HPLC (Daicel OD) using *n*-heptane/2-propanol (9:1) with a flow rate of 1 mL/min. Retention times relative to the racemate: 16.6 min for the major *syn* isomer and 25.3 min for the minor isomer; 14.5 min and 20.3 min for the *anti* isomers.

3f (R = Et): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 10% diethyl ether in pentane). ***syn* Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.50 (dd, $^{2,3}J_{H,H}$ = 12.4 and 8.4 Hz, 1 H, CH_2NO_2), 4.45 (dd, $^{2,3}J_{H,H}$ = 12.4 and 5.8 Hz, 1 H, CH_2NO_2), 4.36 (dd, $^{2,4}J_{H,H}$ = 3.7 and 1.7 Hz, 1 H, CH), 4.24 (dd, $^{2,4}J_{H,H}$ = 17.1 and 1.7 Hz, 1 H, CHH), 4.01 (d, $^{2}J_{H,H}$ = 17.1 Hz, 1 H, CHH), 2.88 (m, 1 H, CHCH_2NO_2), 1.48 (m, 2 H, CH_2CH_3), 1.45 (s, 3 H, CCH_3), 1.43 (s, 3 H, CCH_3), 0.95 (t, $^{3}J_{H,H}$ = 7.7 Hz, 1 H, CH$_2$CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 208.2, 101.1, 75.4, 73.9, 67.0, 39.2, 23.7, 23.3, 20.2, 14.0 ppm. MS (EI): *m*/*z* (%) = 231 (1) [M^+], 216 (1), 173 (9), 143 (4), 127 (8), 114 (7), 111 (15), 84 (55), 72 (100), 59 (31), 55 (14). IR (neat): $\tilde{\nu}$ = 2985, 2940, 2883, 1749, 1554, 1463, 1432, 1381, 1225, 1157, 1117, 1093, 867 cm^{-1}. $C_{10}H_{17}NO_5$ (231.3): calcd. C 51.94, H 7.41, N 6.06; found C 51.98, H 7.57, N 6.54. The *ee* was determined by chiral stationary phase HPLC (Daicel OD) using *n*-heptane/2-propanol (98:2) with a flow rate of 0.5 mL/min. Retention times for the *syn*-enantiomer peaks: 16.6 min for the major isomer and 15.3 min for the minor. $[a]_D^{25}$ = +15.2 (*c* = 1.40, $CHCl_3$) from the sample of Entry 3 in Table 5 with the *ee* and de values of 81 and 82%, respectively.

3i (R = Me): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 10% diethyl ether in pentane). ***syn* Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.50 (dd, $^{2,3}J_{H,H}$ = 12.4 and 8.2 Hz, 1 H, CH_2NO_2), 4.35 (dd, $^{2,3}J_{H,H}$ = 12.4 and 6.4 Hz, 1 H, CH_2NO_2), 4.31 (dd, $^{2,4}J_{H,H}$ = 3.0 and 1.5 Hz, 1 H, CH), 4.22 (dd, $^{2,4}J_{H,H}$ = 17.1 and 1.5 Hz, 1 H, CHH), 4.01 (d, $^{2}J_{H,H}$ = 17.1 Hz, 1 H, CHH), 3.00 (m, 1 H, CHCH_2NO_2), 1.44 (s, 6 H, CCH_3), 1.00 (d, $^{3}J_{H,H}$ = 7.0 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 207.9, 101.1, 74.0, 67.0, 32.4, 23.6, 23.4, 11.8 ppm. MS (EI): *m*/*z* (%) = 202 (3) [M^+ – 15 (CH_3)], 159 (19), 129 (8), 113 (13), 100 (31), 72 (100), 59 (31), 55 (8). IR ($CHCl_3$): $\tilde{\nu}$ = 2989, 2941, 2888, 1749, 1554, 1460, 1433, 1382, 1224, 1118, 1091, 1069, 1020, 867 cm^{-1}. $C_9H_{15}NO_5$ (217.2): calcd. C 49.76, H 6.96, N 6.45; found C 49.89, H 6.95, N 6.33. The *ee* was determined by chiral stationary phase HPLC (Daicel IA) using *n*-heptane/2-propanol (95:5) and with a flow rate of 0.6 mL/min. Retention time of the peaks relative to the *syn* isomers: the major isomer at 13.1 min and the minor one at 15.6 min. $[a]_D^{25}$ = –15.6 (*c* = 2.00, $CHCl_3$) from the sample of Entry 1 in Table 6 with the *ee* and de values of 85 and 94%, respectively.

3j (R = CH$_2$OTBS): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 3% diethyl ether in pentane). ***syn* Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 4.61 (d, $^{3}J_{H,H}$ = 6.7 Hz, 2 H, CH_2OTBS), 4.41 (dd, $^{2,4}J_{H,H}$ = 4.7 and 1.5 Hz, 1 H, CH), 4.27 (dd, $^{2,4}J_{H,H}$ = 17.1 and 1.5 Hz, 1 H, CHH), 3.99 (d, $^{2}J_{H,H}$ = 17.1 Hz, 1 H, CHH), 3.69 (dd, $^{2,3}J_{H,H}$ = 10.1 and 5.7 Hz, 1 H, CH_2NO_2), 3.64 (dd, $^{2,3}J_{H,H}$ = 10.1 and 6.7 Hz, 1 H, CH_2NO_2), 3.00 (m, 1 H, CHCH_2NO_2), 1.44 (s, 3 H, CCH_3), 1.42 (s, 3 H, CCH_3), 0.88 (s, 9 H, SiC(CH_3)$_3$), 0.06 (s, 3 H, SiCH_3), 0.04 (s, 3 H, SiCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 207.8, 101.2, 73.5, 71.9, 66.8, 59.2, 40.4, 25.8 (3 C), 23.7, 23.3, 18.2, –5.6 (2 C) ppm. IR (neat): $\tilde{\nu}$ = 2989, 2933, 2888, 2859, 1749, 1556, 1470, 1380, 1225, 1098, 841, 780 cm^{-1}. MS [EI, m/z (%)]: 332 (3) [M^+ – 15 (CH_3)], 290 (49), 232 (23), 201 (55), 185 (100), 173 (46), 172 (45), 157 (26), 142 (51), 129 (30), 117 (47), 104 (38), 99 (14), 75 (45), 59 (22). $C_{15}H_{29}NO_6Si$ (347.5): calcd. C 51.58, H 8.41, N 4.03; found C 51.45, H 8.18, N 4.87. The *ee* and *dr* were determined by GC (CP-Chirasil-dex CB 25 m × 0.25 mm ID, the temperature program: 120 – 10 iso – 1 – 140 – 3 – 180 – 50iso). Retention times relative to the racemate: 41.9 min for the *syn* major isomer and 42.2 min for the minor isomer (signals of the minor *syn* isomer overlap with those of one of the *anti* enantiomers).

3k (R = CH$_2$OAc): This compound was obtained as a pale yellow oil after flash chromatography (silica gel, 15% diethyl ether in pentane). ***syn* Isomer:** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.61 (dd, $^{2,3}J_{H,H}$ = 13.0 and 7.4 Hz, 1 H, CH_2NO_2), 4.56 (dd, $^{2,3}J_{H,H}$ = 13.0 and 6.0 Hz, 1 H, CH_2NO_2), 4.43 (dd, $^{2,4}J_{H,H}$ = 3.9 and 1.6 Hz, 1 H, CH), 4.27 (dd, $^{2,4}J_{H,H}$ = 17.0 and 1.6 Hz, 1 H, CHH), 4.25 (dd, $^{2,3}J_{H,H}$ = 11.5 and 7.4 Hz, 1 H, CH_2OAc), 4.07 (dd, $^{2,3}J_{H,H}$ = 11.5 and 3.0 Hz, 1 H, CH_2OAc), 4.04 (d, $^{2}J_{H,H}$ = 17.0 Hz, 1 H, CHH), 3.22 (m, 1 H, CHCH_2NO_2), 2.03 [s, 3 H, C(O)CH_3], 1.43 (s, 3 H, CCH_3), 1.42 (s, 3 H, CCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 207.0, 170.2, 101.4, 73.6, 72.3, 66.8, 60.6, 36.9, 23.6, 23.4, 20.7 ppm. MS [EI, *m*/*z* (%)]: 260 (1) [M^+ – 15 (CH_3)], 217 (22), 157 (28), 129 (10), 127 (10), 101 (27), 72 (100), 59 (21). IR ($CHCl_3$): $\tilde{\nu}$ = 2982, 1746, 1558, 1380, 1232, 1049, 862 cm^{-1}. HRMS: *m*/*z* calcd. for [$C_{11}H_{17}NO_7$ – (CH_3)$_2$CO] 217.0586; found: 217.0587. The *ee* and *dr* were determined by GC (Varian CP-Chirasil-dex CB 25 m × 0.25 mm ID column, the temperature program: 100 – 10 iso – 1 – 120 – 3 – 180 – 20iso). Retention times relative to the racemate: 46.6 min for the major *syn* isomer and 47.1 min for the minor one; 47.4 min and 47.9 min for the *anti* isomers.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm 1179 Organokatalyse and Graduiertenkol-

leg 440, S. C. thanks for a fellowship) and the Fonds der Chemischen Industrie. We thank BASF AG, Degussa AG and Bayer AG for the donation of chemicals.

[1] a) Review: P. I. Dalko, L. Moisan, *Angew. Chem.* **2004**, *116*, 5248–5286; *Angew. Chem. Int. Ed.* **2004**, *43*, 5138–5175; b) *Asymmetric Organocatalysis* (Eds.: A. Berkessel, H. Gröger), Wiley-VCH, Weinheim, **2005**.

[2] Review: N. Krause, A. Hoffmann-Röder, *Synthesis* **2001**, 171–196.

[3] a) Review: O. M. Berner, L. Tedeschi, D. Enders, *Eur. J. Org. Chem.* **2002**, 1877–1894; for the first asymmetric organocatalytic Michael additions to nitro alkenes, see: b) B. List, P. Pojarliev, H. J. Martin, *Org. Lett.* **2001**, *3*, 2423–2425; c) J. M. Betancort, K. Sakthivel, R. Thayumanavan, C. F. Barbas III, *Tetrahedron Lett.* **2001**, *42*, 4441–4444; d) J. M. Betancort, C. F. Barbas III, *Org. Lett.* **2001**, *3*, 3737–3740; e) D. Enders, A. Seki, *Synlett* **2002**, 26–28.

[4] For recent examples, see: a) S. Tsogoeva, S. Wei, *Chem. Commun.* **2006**, 1451–1453; b) M.-K. Zhu, L.-F. Cun, A.-Q. Mi, Y.-Z. Jiang, L.-Z. Gong, *Tetrahedron: Asymmetry* **2006**, *17*, 491–493; c) N. Mase, K. Watanabe, H. Yoda, K. Takabe, F. Tanaka, C. F. Barbas III, *J. Am. Chem. Soc.* **2006**, *128*, 4966–4967; d) M. Terada, H. Ube, Y. Yaguchi, *J. Am. Chem. Soc.* **2006**, *128*, 1454–1455; e) A. Lattanzi, *Tetrahedron: Asymmetry* **2006**, *17*, 837–841; f) Y. Xu, A. Córdova, *Chem. Commun.* **2006**, 460–462; g) Y. Xu, W. Zou, H. Sundén, I. Ibrahem, A. Córdova, *Adv. Synth. Catal.* **2006**, *348*, 418–424; h) T. Okino, Y. Hoashi, T. Furukawa, X. Xu, Y. Takemoto, *J. Am. Chem. Soc.* **2005**, *127*, 119–125; i) S. H. McCooey, S. J. Connon, *Angew. Chem.* **2005**, *117*, 6525–6528; *Angew. Chem. Int. Ed.* **2005**, *44*, 6367–6370; j) Y. Hayashi, H. Gotoh, T. Hayashi, M. Shoji, *Angew. Chem.* **2005**, *117*, 4284–4287; *Angew. Chem. Int. Ed.* **2005**, *44*, 4212–4215; k) W. Wang, J. Wang, H. Li, *Angew. Chem.* **2005**, *117*, 1393–1395; *Angew. Chem. Int. Ed.* **2005**, *44*, 1369–1371; l) C. E. T. Mitchell, A. J. A. Cobb, S. V. Ley, *Synlett* **2005**, 611–614; m) A. J. A. Cobb, D. M. Shaw, D. A. Longbottom, J. Gold, S. V. Ley, *Org. Biomol. Chem.* **2005**, *8*, 84–93; n) J. Wang, H. Li, W. Duan, L. Zu, W. Wang, *Org. Lett.* **2005**, *7*, 4713–4716; o) J. Ye, D. J. Dixon, P. S. Hynes, *Chem. Commun.* **2005**, 4481–4483; p) D. Terakado, M. Takano, T. Oriyama, *Chem. Lett.* **2005**, *34*, 962–963; q) S. B. Tsogoeva, D. A. Yalalov, M. J. Hateley, C. Weckbecker, K. Huthmacher, *Eur. J. Org. Chem.* **2005**, 4995–5000.

[5] a) O. Andrey, A. Alexakis, A. Tomassini, G. Bernardinelli, *Adv. Synth. Catal.* **2004**, *346*, 1147–1168; b) T. Ishii, S. Fujioka, Y. Sekiguchi, H. Kotsuki, *J. Am. Chem. Soc.* **2004**, *126*, 9558–9559; c) A. J. A. Cobb, D. A. Longbottom, D. M. Shaw, S. V. Ley, *Chem. Commun.* **2004**, 1808–1809; d) N. Mase, R. Thayumanavan, F. Tanaka, C. F. Barbas III, *Org. Lett.* **2004**, *6*, 2527–2530; e) J. M. Betancort, K. Sakthivel, R. Thayumanavan, F. Tanaka, C. F. Barbas III, *Synthesis* **2004**, *9*, 1509–1521; f) P. Kotrusz, S. Toma, H.-G. Schmalz, A. Adler, *Eur. J. Org. Chem.* **2004**, 1577–1583; g) T. Okino, Y. Hoashi, Y. Takemoto, *J. Am. Chem. Soc.* **2003**, *125*, 12672–12673; h) A. Alexakis, O. Andrey, G. Bernardinelli, *Org. Lett.* **2003**, *5*, 2559–2561; i) A. Alexakis, O. Andrey, *Org. Lett.* **2002**, *4*, 3611–3614.

[6] J. Wang, H. Li, L. Zu, W. Wang, *Org. Lett.* **2006**, *8*, 1391–1394.

[7] a) T. B. Poulsen, K. A. Jørgensen, *Org. Biomol. Chem.* **2006**, *4*, 63–70; b) D. Xue, Y.-C. Chen, Q.-W. Wang, L.-F. Cun, J. Zhu, J.-G. Deng, *Org. Lett.* **2005**, *7*, 5293–5296; c) S. Hanessian, S. Govindan, J. S. Warrier, *Chirality* **2005**, *17*, 540–543.

[8] a) B. Vakulya, S. Varga, A. Csámpai, T. Soós, *Org. Lett.* **2005**, *7*, 1967–1969; b) A. Prieto, N. Halland, K. A. Jørgensen, *Org. Lett.* **2005**, *7*, 3897–3900; c) S. Hanessian, V. Pham, *Org. Lett.* **2000**, *2*, 2975–2978.

[9] Review: D. Enders, M. Voith, A. Lenzen, *Angew. Chem.* **2005**, *117*, 1330–1351; *Angew. Chem. Int. Ed.* **2005**, *44*, 1304–1325.

[10] a) C. Grondal, D. Enders, *Tetrahedron* **2006**, *62*, 329–337; b) D. Enders, C. Grondal, *Angew. Chem.* **2005**, *117*, 1235–1238; *Angew. Chem. Int. Ed.* **2005**, *44*, 1210–1212; c) D. Enders, C. Grondal, M. Vrettou, G. Raabe, *Angew. Chem.* **2005**, *117*, 4147–4151; *Angew. Chem. Int. Ed.* **2005**, *44*, 4079–4083; for related publications see: d) B. Westermann, C. Neuhaus, *Angew. Chem.* **2005**, *117*, 4145–4147; *Angew. Chem. Int. Ed.* **2005**, *44*, 4077–4079; e) J. T. Suri, S. Mitsumori, K. Albertshofer, F. Tanaka, C. F. Barbas III, *J. Org. Chem.* **2006**, *71*, 3822–3828; f) J. T. Suri, D. B. Ramachary, C. F. Barbas III, *Org. Lett.* **2005**, *7*, 1383–1385; g) I. Ibrahem, A. Córdova, *Tetrahedron Lett.* **2005**, *46*, 3363–3367.

[11] D. Enders, J. Paleček, C. Grondal, *Chem. Commun.* **2006**, 655–657.

[12] D. Enders, M. Vrettou, *Synthesis* **2006**, 2155–2158.

[13] a) H. Kipphardt, Dissertation, RWTH Aachen, **1986**; b) D. Enders, H. Kipphardt, P. Gerdes, L. J. Breña-Valle, V. Bhushan, *Bull. Soc. Chim. Belg.* **1988**, *97*, 691–704; c) E. J. Corey, R. K. Bakshi, S. Shibata, *J. Am. Chem. Soc.* **1987**, *109*, 5551–5553.

Received: May 29, 2006
Published Online: August 18, 2006

