Organocatalytic Domino Reactions

Organocatalytic Asymmetric Domino Knoevenagel/Diels–Alder Reactions: A Bioorganic Approach to the Diastereospecific and Enantioselective Construction of Highly Substituted Spiro[5,5]undecane-1,5,9-triones**

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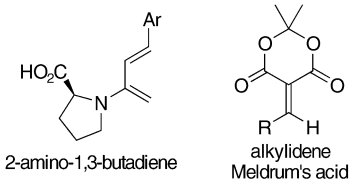
One of the ultimate goals in organic chemistry is the catalytic asymmetric assembly of simple and readily available precursor molecules into stereochemically complex products. In this regard, the Diels–Alder reaction is one of the most powerful synthetic methodologies for the construction of cyclic six-membered rings, and tremendous efforts have been directed to expand the scope of this cycloaddition reaction with various combinations of dienes, dienophiles, catalysts, and reaction conditions.[1] Recently organocatalysis has emerged as a promising synthetic tool for constructing C–C and C–N bonds in aldol,[2] Michael,[3] Mannich,[4] Diels–Alder,[5] and related reactions[6] with high diastereoselectivity and enantioselectivity. Structurally simple and stable chiral organoamines typically facilitate iminium- and enamine-based transformations with carbonyl compounds and may be used as catalysts in operationally simple, and in some cases environmentally friendly, experimental protocols. Previously we extended our studies of organoamine-catalyzed aldol,[2a–d] Michael,[3a,b] Mannich,[4a–f] and related reactions[6c,e] founded on enamine catalysis, and reported the first direct asymmetric Diels–Alder reactions of α,β-unsaturated ketones with nitro olefins.[5a]

In continuation of our interest in organocatalytic assembly or multicomponent reactions,[2c,d,4c,6e] we herein report the first organocatalytic diastereospecific and enantioselective direct asymmetric domino Knoevenagel/Diels–Alder reactions that produce highly substituted spiro[5,5]undecane-1,5,9-triones **5** from commercially available 4-substituted-3-buten-2-ones **1a–e**, aldehydes **2a–d**, and 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid, **3**; Scheme 1). Spirocyclic ketones **5** are attractive intermediates in the synthesis of natural products and in medicinal chemistry,[7] and are the starting materials for the synthesis of exotic amino acids which are used to modify the physical properties and biological activities of peptides, peptidomimetics, and proteins.[8]

In our reaction we envisioned that an amino acid would catalyze the domino Knoevenagel condensation[9] of aldehyde **2** with Meldrum's acid **3** to provide the alkylidene derivative of Meldrum's acid, which would then undergo a concerted [4+2] cycloaddition with a 2-amino-1,3-butadiene generated in situ from enone **1** and an amino acid to form substituted



spiro[5,5]undecane-1,5,9-triones **5** in a highly enantioselective and diastereospecific manner.[10] The domino Knoevenagel/Diels–Alder reaction would then generate a quaternary center with formation of three new carbon–carbon σ bonds through amino acid catalysis. This proposal was reflective of the pioneering studies of Tietze and Beifuss[11a,b] and our recent disclosure of the first direct asymmetric Knoevenagel/Michael reactions with ketones, aldehydes, and malonates involving alkylidene malonates generated under organocatalysis that subsequently react as electrophiles with ketone-derived enamines also generated under organocatalysis.[3a] In contrast to this early study where asymmetric induction was compromised by the use of the cyclic malonate Meldrum's acid, the alkylidene derivative of Meldrum's acid proved to be more efficient in the Diels–Alder reaction than the alkylidene formed from alkyl malonates.

We were pleased to find that the three-component reaction of *trans*-4-phenyl-3-buten-2-one (**1a**), 4-nitrobenzaldehyde (**2a**), and Meldrum's acid (**3**) with a catalytic amount of L-proline in methanol at ambient temperature furnished the Diels–Alder product **5aa** as a single diastereomer in 85% yield with 60% *ee* after 48 h (Table 1, entry 6). This product was accompanied by an unexpected symmetric spirocyclic ketone **6aa** in 7% yield.[12] The stereochemistry of products **5aa** and **6aa** was established by NMR analysis.

In the asymmetric three-component Diels–Alder (ATCDA) reaction of **1a**, **2a**, and **3** catalyzed directly by L-proline, we found that the solvent (dielectric constant) had a

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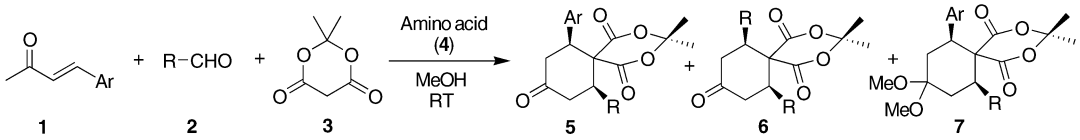


Scheme 1. Amino acid catalyzed asymmetric, three-component Diels–Alder reactions.

Table 1: Effect of solvent on the direct amino acid catalyzed ATCDA reaction of **1a**, **2a**, and **3**.[a]

Entry	Amino acid	Solvent	Dielectric constant [ε]	t [h]	Products	Yield [%][b]	Ratio[c] **5aa**:**6aa**	*ee* for **5aa** [%][d]
1	L-proline	C_6H_6	2.3	72	**5aa**	$\leq$10	100:0	nd[e]
2	L-proline	$CHCl_3$	4.8	72	**5aa**	24	100:0	71
3	L-proline	THF	7.6	72	**5aa**	70	100:0	65
4	L-proline	CH_2Cl_2	8.9	72	**5aa**	35	100:0	59
5	L-proline	C_2H_5OH	25	48	**5aa**, **6aa**	95	18:1	38
6	L-proline	CH_3OH	33	48	**5aa**, **6aa**	92	12:1	60
7	L-proline	CH_3CN	38	72	**5aa**	65	100:0	9
8	L-proline	[bmim]BF_4	–	24	**5aa**	95	100:0	6
9	thiaproline	*n*-C_3H_7OH	21.8	96	**5aa**, **6aa**	70	20:1	19
10	thiaproline	*iso*-C_3H_7OH	18.3	96	**5aa**, **6aa**	65	20:1	39
11[f]	DL-proline	(*S*)-$CH_3CHPhOH$	13	96	**5aa**	71	100:0	37

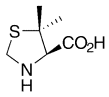
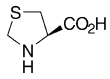
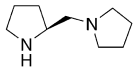
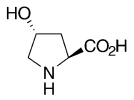
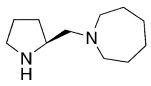
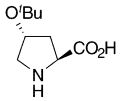
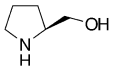
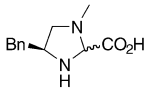
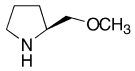
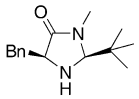
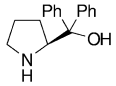
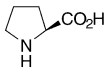
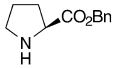
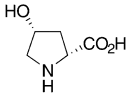
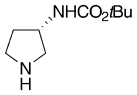
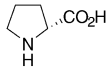
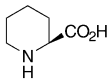
[a] Experimental conditions: Amino acid (0.1 mmol) was added to a stirred solution of enone (1 mmol), **2a** (0.5 mmol), and **3** (0.5 mmol) in the solvent (1 mL) at ambient temperature (see Supporting Information). [b] Yield refers to the purified product obtained by column chromatography. [c] Ratio based on isolated products. [d] Enantiomeric excesses determined by using chiral-phase HPLC. [e] not determined. [f] In this reaction, 0.75 mL of (*S*)-1-phenylethanol was used.

significant effect on the rates, yields, and *ee* values (Table 1). These results indicated that the domino Knoevenagel/Diels–Alder reaction catalyzed by L-proline produces products **5aa** and **6aa**[12] with low yields and good *ee* values in aprotic nonpolar solvents (Table 1, entries 2–4) and with excellent yields and good to moderate *ee* values in protic solvents (Table 1, entries 5 and 6). The same reaction in the ionic liquid [bmim]BF_4 (bmim = 1-butyl-3-methylimidazolium) provided **5aa** in 95% yield, albeit with a low *ee* value of 6% (Table 1, entry 8). The rates of both the Knoevenagel and Diels–Alder reactions catalyzed by L-proline were faster in protic/polar solvents than in nonprotic/nonpolar solvents presumably because of enhanced stabilization of charged intermediates and more-facile proton-transfer reactions. The transition state of the bimolecular Diels–Alder reaction is also effected by protic/polar solvents through hydrogen bonding.[1d,e]

To understand the role of solvent in this reaction aldehyde **2a**, Meldrum's acid (**3**), and enone **1a** were reacted in the chiral solvent (*S*)-1-phenylethanol, under DL-proline catalysis. The expected spiro product **5aa** was obtained in 71% yield, with an *ee* value of 37% (Table 1, entry 11). Thus, asymmetric induction can be effected by interactions with a chiral solvent. This finding supports a potential role of intermolecular hydrogen bonding, in standard achiral solvents, as a conduit for both transmission of chiral information from the prolyl-2-amino-1,3-butadiene and catalysis by lowering the activation barrier in a diastereotopic bimolecular Diels–Alder transition state. Intermolecular hydrogen bonding with the solvents serves these roles in the chiral protic solvent.

Next we probed the structure and reactivity relationships among a family of 19 pyrrolidine-based catalysts by monitoring the reaction yields and *ee* values of the ATCDA reaction of **1a**, **2a**, and **3** in methanol (Table 2). The structurally simple amine pyrrolidine catalyzed the ATCDA reaction to produce **5aa** in 14% yield and **6aa** in 17% yield (Table 2, entry 1). An imidazoline-type catalyst also catalyzed the ATCDA reaction (Table 2, entry 15). Among the catalysts screened, 5,5-dimethyl thiazolidinium-4-carboxylate (DMTC) proved to be the most efficient catalyst with respect to yield, and provided **5aa** in 88% yield and 86% *ee* (Table 2, entry 11), which is significantly better than L-proline in both respects (Table 2, entry 17). The overall structure/activity relationship garnered from the catalyst screen of the ATCDA reaction was similar to that which we reported for the aldol,[2b] with optimal yield and enantioselectivity being provided by pyrrolidine-amines substituted at the α-position with an acid functionality, that is, proline-like catalysts. Notable improvement in the enantioselectivity of the reaction beyond L-proline catalysis was found in the ATCDA reactions catalyzed by L-thiaproline, L-DMTC, and *trans*-4-hydroxy-L-proline. These amino acids catalyze the preferential addition of the in situ generated benzylidene derivative of Meldrum's acid **8** to the *exo* face of the in situ generated 2-amino-1,3-butadiene. It should

Table 2: Effect of the structure/reactivity of the amino acid on the direct amino acid catalyzed ATCDA reaction of **1a**, **2a**, and **3** in methanol at 25 °C.[a]

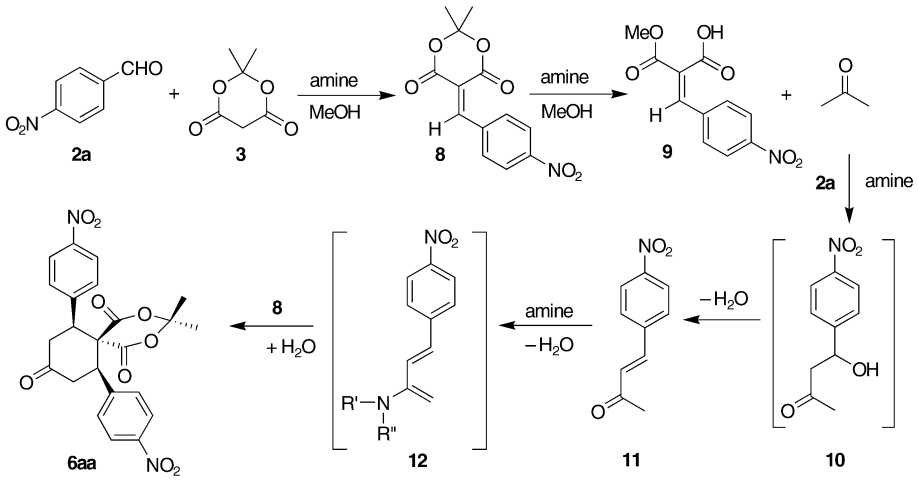
Entry	Amine	*t* [h]	Yield [%][b] **5aa**	Yield [%][b] **6aa**	*ee* for **5aa** [%][c]	Entry	Amine	*t* [h]	Yield [%][b] **5aa**	Yield [%][b] **6aa**	*ee* for **5aa** [%][c]
1		48	14	17	–	11		72	88	trace	86
2		120	10	8	41	12		84	65	trace	89
3[d]		72	56	12	45	13		96	50	4	91
4		72	80	13	24	14		84	84	trace	76
5		96	12	17	68	15[e]		96	64	14	70
6		120	12	17	65	16		72	–	–	–
7		120	10	9	32	17		48	85	7	60
8		96	23	trace	35	18		84	70	trace	60
9		48	40	34	40	19		72	80	trace	34
10		120	7	17	60						

[a] See Supporting Information. [b] Yield refers to the column purified product. [c] Enantiomeric excesses were determined by using chiral-phase HPLC. [d] Reaction was performed in THF. [e] Reaction performed at 4 °C.

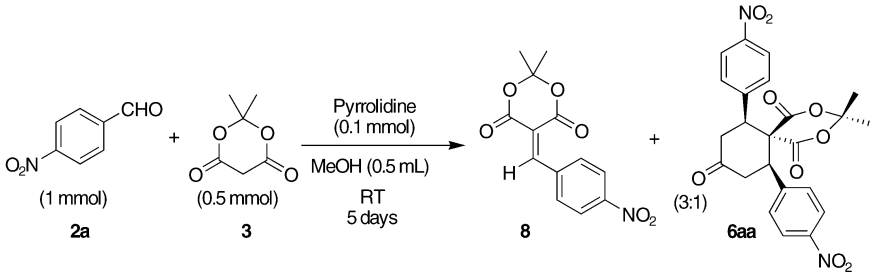
be noted that L-DMTC was also found to be generally more efficient than L-proline in aldol reactions involving aromatic acceptors.[2b]

Formation of the unexpected symmetric triketone **6aa** in the reaction of **1a**, **2a**, and **3** can be explained as shown in Scheme 2. Amine-catalyzed Knoevenagel condensation of **2a** with **3** provides the 4-nitrobenzelidene derivative of Meldrum's acid **8**, which undergoes a Diels–Alder or a double Michael reaction with the soft nucleophilic 2-amino-1,3-butadiene generated in situ from enone **1a** and an amine to produce product **5aa.** Otherwise the in situ generated hard nucleophile methoxide (MeO^-) can react with **8** to regenerate acetone; the yield of this regeneration will depend on the basicity of the amine catalyst. Acetone undergoes amine-catalyzed aldol condensation with aldehyde **2a** to furnish enone **11**, which reacts with an amine to form reactive 2-amino-1,3-butadiene **12**, which undergoes a diastereospecific Diels–Alder reaction with dienophile **8** to furnish the ketone **6aa**. Regeneration of acetone and formation of prochiral ketone **6aa** were confirmed by the pyrrolidine-catalyzed reaction between **2a** and **3** in methanol (Scheme 3).

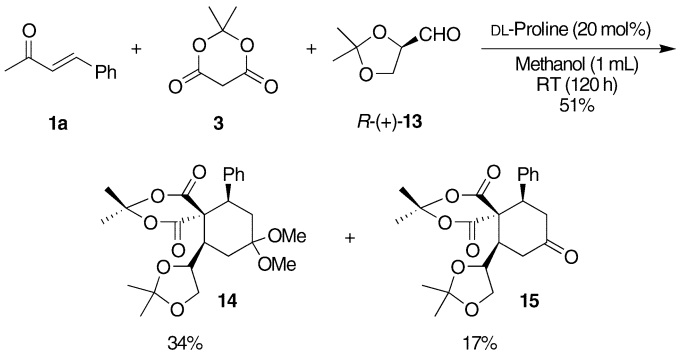
We further explored the scope of the DMTC-catalyzed ATCDA reaction with various aldehydes **2a–d** and enones **1a–e**. The spirotriones **5** were obtained as single diastereomers with good yields and excellent *ee* values together with the accompanying corresponding acetals **7**[13] in low yields. The reaction of benzaldehyde (**2c**), piperonal (**2d**), and Meldrum's acid (**3**) with enones **1a** and **1b** furnished the prochiral spirotriones **5ac** and **5bd**, respectively, in excellent yields (Table 3, entry 1 and 2). In the same manner, the reaction of *para*-substituted benzaldehydes **2a–b** and Meldrum's acid (**3**) with a variety of enones **1a–e** in methanol



Scheme 2. Proposed reaction mechanism for the formation of the unexpected product: prochiral cyclohexanone **6aa**.



Scheme 3. Formation of prochiral spirocyclic ketone **6aa** from 4-nitrobenzaldehyde (**2a**) and Meldrum's acid (**3**).



Scheme 4. Proline-catalyzed diastereoselective three-component Diels–Alder reaction of enone **1a** and Meldrum's acid (**3**) with chiral aldehyde **13**.

Table 3: Direct DMTC-catalyzed ATCDA reaction of different aldehydes **2a–d** and enones **1a–e** with Meldrum's acid (**3**).[a]

Entry	Enone	Aldehyde	*t* [h]	Products	Yield [%][b]	Ratio **5**:**7**	*ee* for **5** [%][c]
1[d]	**1a**	**2c**	96	**5ac**, **7ac**	85	16:1	prochiral
2[d]	**1b**	**2d**	96	**5bd**	99	>100:1	prochiral
3	**1a**	**2a**	72	**5aa**, **7aa**	95	13:1	86
4	**1a**	**2b**	96	**5ab**, **7ab**	85	16:1	84
5	**1c**	**2a**	72	**5ca**	93	>100:1	99
6	**1d**	**2a**	72	**5da**, **7da**	92	12:1	88
7	**1e**	**2a**	72	**5ea**, **7ea**	80	15:1	99

[a] See Supporting Information. [b] Yield of the combined isolated products. [c] Enantiomeric excesses were determined using chiral-phase HPLC. [d] Reaction catalyzed by L-proline (0.1 mmol).

furnished the spirotriones **5** as single diastereomers in good yields with excellent *ee* values together with the corresponding acetals **7** in low yields (Table 3). Formation of acetals **7** from ketones **5** is most likely the result of acid or base catalysis of the bifunctional acid/base catalyst DMTC in methanol. Spirotrione **5bd** should be an attractive starting material for the synthesis of endothelin receptor antagonists.[7d]

The diastereoselective ATCDA reaction of α,β-unsaturated ketone **1a** and Meldrum's acid (**3**) with chiral aldehyde (*R*)-2,2-dimethyl-[1,3]dioxolane-4-carbaldehyde (**13**) in methanol at room temperature produced the expected Diels–Alder product acetal **14** and ketone **15** as the major products (Scheme 4). Thus, optically pure aldehydes can be used to effect diastereoselective synthesis of chiral, substituted cyclohexanones under organocatalysis.

The absolute configuration of product **5aa** prepared under DMTC catalysis was established by using X-ray crystallography.[14] Product **5aa** was obtained as colorless, block-shaped crystals from hexane-chloroform. Crystallization enriched the *ee* value to 99%. On the basis of X-ray structural analysis and AM1 calculations we propose a transition state for the DMTC-catalyzed direct ATCDA reaction (Figures 1 and 2).

In summary, we have developed the first direct ATCDA reaction catalyzed by an amino acid. This experimentally simple and environmentally friendly approach can be used to construct highly substituted spiro[5,5]undecane-1,5,9-triones in a diastereospecific and enantioselective fashion. Selective reactions of this type inspire analogies with enzyme-catalyzed reaction and compliment traditional Diels–Alder reactions. As we have suggested previously, the synthesis of polyfunctionalized molecules under organocatalysis provides a unique and under-

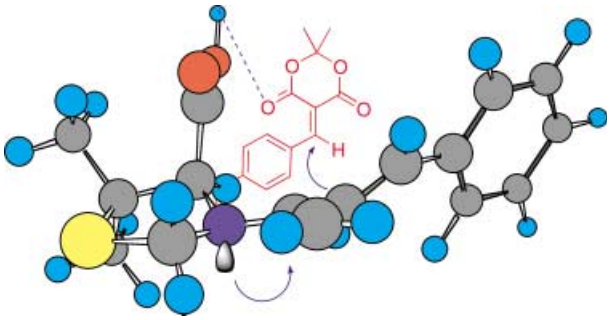


Figure 1. Proposed transition state for the DMTC-catalyzed ATCDA reaction based on AM1 calculations.

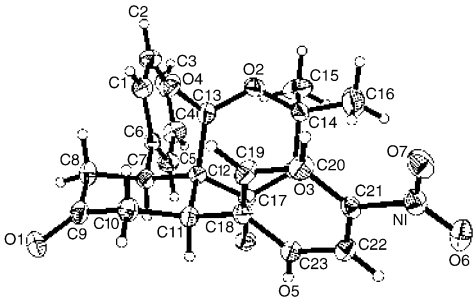


Figure 2. X-ray crystal structure of chiral spiro[5,5]undecane-1,5,9-trione **5aa**.

explored perspective on prebiotic synthesis. Given the efficiency of the organocatalysis of the Diels–Alder reaction, consideration should be given to the utilization of these types of reaction mechanisms in extant biological systems.

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[12] Symmetric ketone **6aa** was generated only in alcoholic solvents and in low yields.

[13] Compounds **7da** and **7ea** are mixtures of acetal and methyl enol ethers (see Supporting Information).

[14] Crystal structure data for **5aa**: $C_{23}H_{21}NO_7$, $M_r = 423.41$, monoclinic, space group $P2_1/c$ (No. 14, C_{2h}^5), $a = 18.571(3)$, $b = 9.6564(16)$, $c = 11.9942(19)$ Å, $\alpha = 90$, $\beta = 106.511(3)$, $\gamma = 90°$, $V = 2062.2(6)$ Å^3, $T = 296(2)$ K, 17946 reflections collected. CCDC-205429 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

