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One-Pot Cascade Michael–Cyclization Reactions of *o*-Hydroxycinnamaldehydes: Synthesis of Functionalized 2,3-Dihydrobenzofuranes

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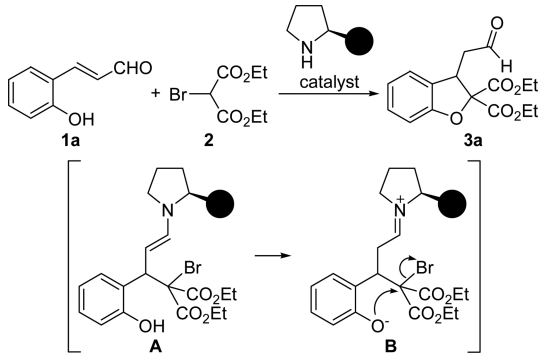
2,3-Dihydrobenzofurans are found in numerous biologically active natural products and synthetic compounds.[1] These are an attractive type of oxygenated compound because their basic core skeleton is present in neolignans,[2] pterocarpans,[3] and synthetic drugs used in the treatment of pulmonary hypertension, atherosclerotic peripheral arterial disease, and central nervous system trauma and ischemia.[4]

Owing to the importance of their structures, numerous synthetic methods for 2,3-dihydrobenzofurans have been developed, primarily: radical cyclizations,[5] Lewis acid promoted reactions,[6] anionic cyclizations,[7] and transition-metal catalyzed processes.[8] However, these methods cannot be generalized as much as is desirable, and they yielded poor chemo- and/or stereoselectivities. Hence, the development of an efficient enantioselective synthetic method for obtaining 2,3-dihydrobenzofuran scaffolds attracted our attention.

As part of the research program related to the development of synthetic methods for the enantioselective construction of stereogenic carbon centers, we recently developed a novel catalytic asymmetric 1,4-addition reaction of *o*-hydroxycinnamaldehydes using organocatalyst, which afforded enantio-enriched chroman derivatives.[9] Herein, we wish to describe the cascade Michael–cyclization reaction of *o*-hydroxycinnamaldehydes with diethyl α-bromomalonates, which allows efficient construction of 2,3-dihydrobenzofurans with high chemoselectivity.

Recently, Córdova and Wang have independently described the organocatalytic enantioselective cascade Michael-alkylation reactions of α,β-unsaturated aldehydes with bromomalonates.[10] This cascade reaction provides a highly attractive and convergent approach toward optically active cyclopropane compounds. Encouraged by these results, we envisioned that 2,3-dihydrobenzofurans could be synthesized if a 2-hydroxyaryl-α,β-unsaturated aldehyde was used instead of α,β-unsaturated aldehydes in the cascade reaction with bromomalonates (Scheme 1).[11] We conceived that the resulting tertiary bromide **A** from the Michael addition process could readily transform into intermediated **B** under proton transfer followed by S_N2 substitution to give 2,3-dihydrobenzofuran **3a** rather than undergo an intramolecular α-alkylation reaction to produce a cyclopropane.

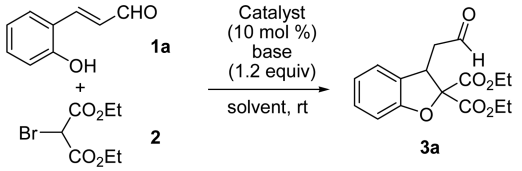
The conjugate addition-cyclization reaction of diethyl α-bromomalonate (**2**) to *o*-hydroxycinnamaldehyde (**1a**) was selected as the model reaction (Table 1). The α,α-diphenyl-D-prolinol TMS ether catalyst **I**[12] was initially examined as an organocatalyst in this reaction as this catalyst **I** has previously given the product in good yield with high enantioselectivity for the Michael–alkylation reactions of α,β-unsaturated aldehydes with bromomalonates.[10] The reaction took place in CH_2Cl_2 using 10 mol % catalyst **I** with an additive base. However, almost no reaction was observed when using sodium acetate as a base after 72 h at room temperature (entry 1). The reaction proceeded to furnish the corresponding 2,3-dihydrobenzofuran product **3a** in moderate yields with the use of K_2CO_3 as the base without the detection of cyclopropane compound (entry 2). The isolated yield was slightly increased when the reaction was performed in $CHCl_3$ using Et_3N as the base (entry 4). Under these conditions, pyrrolidinyl tetrazole catalyst **II** and L-proline **III** gave the similar results (entries 8 and 9). Moreover, the reaction from using K_2CO_3 as the base in acetone afforded the desired 2,3-dihydrobenzofuran product **3a** with good reactivity (entry 11). Unfortunately, catalysts **I**, **II** and **III** did not provide the chiral product **3a** in this reaction.[13] Additionally, we found that potassium carbonate alone could promote this reaction without **I**–**III** (entry 12).



Scheme 1. Organocatalytic Cascade Michael–Cyclization Reactions of *o*-Hydroxycinnamaldehyde to Diethyl α-Bromomalonate.

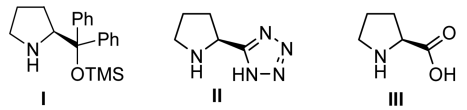
Although this conjugate addition-cyclization reaction does not achieve enantiocontrol, the desired 2,3-dihydrobenzofuran was mainly obtained as we expected and then we

Table 1. Organocatalytic conjugate addition–cyclization of *o*-hydroxycinnamaldehyde (**1a**) to diethyl α-bromomalonate (**2**)[a]



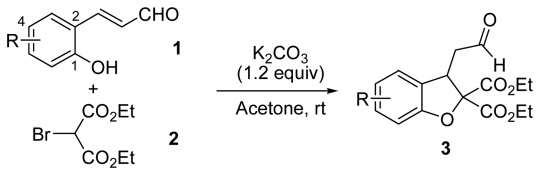
Entry	Catalyst	Base	Solvent	Time (h)	Yield (%)[b]
1	**I**	NaOAc	CH_2Cl_2	72	5
2	**I**	K_2CO_3	CH_2Cl_2	24	28
3	**I**	Et_3N	CH_2Cl_2	24	35
4	**I**	Et_3N	$CHCl_3$	24	42
5	**I**	Et_3N	toulene	24	30
6	**I**	Et_3N	EtOH	24	25
7	**I**	Et_3N	CH_3CN	24	32
8	**II**	Et_3N	$CHCl_3$	24	36
9	**III**	Et_3N	$CHCl_3$	48	27
10	**I**	K_2CO_3	THF	24	45
11	**I**	K_2CO_3	acetone	6	54
12	-	K_2CO_3	acetone	6	65

[a]Unless otherwise specified, the reaction was carried out in solvent (0.2 M) with 1.2 equiv of diethyl α-bromomalonate (**2**) relative to the *o*-hydroxycinnamaldehyde (**1a**) in the presence of 10 mol % catalyst and 1.2 equiv of base. [b]Isolated yield after chromatographic purification.



decided to explore the scope of this new process. This reaction proved to be general for a wide variety of *o*-hydroxyaromatic α,β-unsaturated aldehydes **1**. As shown in Table 2, the reactions proceeded with good yields for all *o*-hydroxyaromatic α,β-unsaturated aldehydes. The conjugate addition–cyclization reaction of diethyl α-bromomalonate (**2**) to *o*-hydroxyaromatic α,β-unsaturated aldehydes was tolerant to several functional groups in the 4-, 5-, or 6-position of the aromatic ring. Therefore, variation of the substituent on the aromatic ring is allowed in this reaction while good reactivity is preserved, regardless of the nature of the substituent is electron- donating (entries 2-C5) or electron- withdrawing (entries 6-C10).

Table 2. Organocatalytic conjugate addition–cyclization reaction of *o*-hydroxyaromatic α,β-unsaturated aldehydes **1** to diethyl α-bromomalonate (**2**)[a]



Entry	R	Product	Time (h)	Yield (%)[b]
1	H	**3a**	6	65
2	4-Me	**3b**	4	68
3	4-MeO	**3e**	6	75
4	5-MeO	**3d**	24	72
5	6-MeO	**3e**	8	87
6	4-Br	**3f**	4	80
7	4-Cl	**3g**	4	78
8	4,6-diBr	**3h**	24	86
9	4,6-diCl	**3i**	24	92
10	4-NO_2	**3j**	24	68

[a]Unless otherwise specified, the reaction was carried out in solvent (0.2 M) with 1.2 equiv of diethyl α-bromomalonate (**2**) relative to the *o*-hydroxycinnamaldehydes (**1**) in the presence of 1.2 equiv of K_2CO_3. [b]Isolated yield after chromatographic purification.

In summary, we described the cascade Michael–cyclization reaction of *o*-hydroxycinnamaldehydes with diethyl α-bromomalonate promoted by potassium carbonate. The reactions provided functionalized 2,3-dihydrobenzofurans in good yields for a variety of *o*-hydroxyaromatic α,β-unsaturated aldehydes. Current work focuses on expanding the scope of this reaction to other substrates such as sulfur yields, and on developing an efficient catalytic asymmetric variant.

Experiments

General Procedure for the Cascade Michael–Cylization Reaction of *o*-Hydroxyaromatic α,β-Unsaturated Aldehydes 1 with Diethyl α-Bromomalonate (2). To a mixture of *o*-hydroxycinnamaldehyde **1a** (37 mg, 0.25 mmol) and K_2CO_3 (41 mg, 0.30 mmol) in acetone (1.2 mL) was added diethyl α-bromomalonate (**2**, 72 mg, 0.30 mmol) at room temperature. The resulting mixture was stirred at constant temperature for 6 h. The solvent was removed and the resulting mixture was directly purified by silica gel chromatography (20% EtOAc/hexanes) to afford the desired compound **3a** as pale yellow oil (50 mg, 65% yield).

Diethyl 3-(Formylmethyl)benzofuran-2,2(3*H*)-dicarboxylate (3a): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.21 (dd, J = 7.6, 8.0 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 6.93-6.98 (m, 2H), 4.85 (t, J = 6.8 Hz, 1H), 4.20-4.34 (m, 4H), 2.87 (ddd, J = 1.2, 6.0, 18.0 Hz, 1H), 2.80 (ddd, J = 1.2, 7.6, 18.0 Hz, 1H), 1.29-1.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 167.2, 166.5, 129.3, 127.3, 124.4, 122.3, 110.3, 91.2, 62.9, 62.6, 45.5, 42.0, 14.0, 13.9; MS *m/z* (%) 306 (M^+, 6), 233 (11), 186 (100), 159 (97), 131 (33); Anal. Calcd for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.52; H, 6.04.

Diethyl 3-(Formylmethyl)-5-methylbenzofuran-2,2(3*H*)-dicarboxylate (3b): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.93 (s, 1H), 6.85 (d, J = 8.0 Hz, 1H), 4.80 (t, J = 6.8 Hz, 1H), 4.26-4.40 (m, 4H), 2.87 (ddd, J = 1.2, 6.4, 18.0 Hz, 1H), 2.79 (ddd, J = 1.2, 7.6, 18.0 Hz, 1H), 2.28 (s, 3H), 1.32 (dt, J = 2.4, 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 167.3, 166.5, 155.2, 131.8, 129.6, 127.3, 124.8, 109.8, 91.4, 62.9, 62.6, 45.5, 42.0, 20.9, 14.0, 13.9; MS *m/z* (%) 320 (M^+, 11), 228 (14), 200 (100), 173 (91), 145 (34), 115 (21); Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.80; H, 6.42.

Diethyl 3-(Formylmethyl)-5-methoxybenzofuran-2,2(3*H*)-dicarboxylate (3c): Pale yellow oil; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 9.82 (t, J = 1.2 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.69-6.74 (m, 2H), 4.79 (t, J = 6.8 Hz, 1H), 4.25-4.39 (m, 4H), 3.74 (s, 3H), 2.87 (ddd, J = 1.2, 6.0, 18.0 Hz, 1H), 2.79 (ddd, J = 1.2, 7.6, 18.0 Hz, 1H), 1.31 (dt, J = 0.8, 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 167.3, 166.5, 155.3, 151.2, 128.3, 114.3, 110.4, 91.6, 62.9, 62.6, 55.9, 45.4, 42.3, 14.0, 13.9.

Diethyl 3-(Formylmethyl)-6-methoxybenzofuran-2,2(3*H*)-dicarboxylate (3d): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (t, J = 1.2 Hz, 1H), 7.00 (dd, J = 0.8, 8.4 Hz, 1H), 6.55 (d, J = 2.0 Hz, 1H), 6.48 (dd, J = 2.0, 8.4 Hz, 1H), 4.76 (t, J = 6.8 Hz, 1H), 4.28-4.40 (m, 4H), 3.77 (s, 3H), 2.84 (ddd, J = 1.2, 6.0, 18.0 Hz, 1H), 2.75 (ddd, J = 1.2, 8.0, 18.0 Hz, 1H), 1.31 (dt, J = 2.0, 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 167.2, 166.4, 161.1, 158.5, 124.6, 119.1, 108.1, 92.0, 62.9, 62.6, 55.5, 45.8, 41.5, 14.0, 13.9; MS *m/z* (%) 336 (M^+, 14), 244 (12), 216 (100), 189 (34), 161 (14); Anal. Calcd for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found: C, 60.67; H, 6.09.

Diethyl 3-(Formylmethyl)-7-methoxybenzofuran-2,2(3*H*)-dicarboxylate (3e): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 6.91 (dd, J = 7.6, 8.0 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 7.6 Hz, 1H), 4.87 (t, J = 6.8 Hz, 1H), 4.17-4.42 (m, 4H), 3.90 (s, 3H), 2.88 (ddd, J = 0.8, 6.4, 18.0 Hz, 1H), 2.79 (ddd, J = 0.8, 7.6, 18.0 Hz, 1H), 1.25-1.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 167.2, 166.4, 145.7, 144.6, 128.4, 123.0, 116.1, 112.4, 91.6, 62.9, 62.6, 56.0, 45.4, 42.6, 14.0, 13.9.

Diethyl 5-Bromo-3-(formylmethyl)benzofuran-2,2(3*H*)-dicarboxylate (3f): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.23-7.31 (m, 2H), 6.83 (d, J = 8.8 Hz, 1H), 4.80 (dd, J = 5.6, 7.6 Hz, 1H), 4.26-4.38 (m, 4H), 2.92 (ddd, J = 0.8, 5.6, 18.0 Hz, 1H), 2.79 (ddd, J = 0.8, 8.0, 18.0 Hz, 1H), 1.24-1.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 166.8, 166.1, 156.5, 132.1, 129.9, 127.6, 114.2, 111.8, 91.6, 63.1, 62.8, 45.3, 41.8, 14.0, 13.9; MS *m/z* (%) 384 (M^+, 22), 312 (33), 266 (100), 237 (92), 209 (34), 131 (44); Anal. Calcd for $C_{16}H_{17}BrO_6$: C, 49.89; H, 4.45. Found: C, 50.08; H, 4.64.

Diethyl 5-Chloro-3-(formylmethyl)benzofuran-2,2(3*H*)-dicarboxylate (3g): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.10-7.17 (m, 2H), 6.88 (d, J = 8.4 Hz, 1H), 4.80 (dd, J = 5.6, 8.0 Hz, 1H), 4.26-4.40 (m, 4H), 2.92 (ddd, J = 0.8, 6.0, 18.4 Hz, 1H), 2.80 (ddd, J = 0.8, 8.0, 18.4 Hz, 1H), 1.25-1.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 166.8, 166.1, 156.0, 129.4, 129.2, 127.1, 124.8, 111.2, 91.7, 63.1, 62.8, 45.3, 41.8, 14.0, 13.9.

Diethyl 5,7-Dibromo-3-(formylmethyl)benzofuran-2,2(3*H*)-dicarboxylate (3h): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.51 (d, J = 2.0 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 4.89 (dd, J = 5.6, 8.4 Hz, 1H), 4.33-4.43 (m, 4H), 2.96 (ddd, J = 0.8, 5.6, 18.4 Hz, 1H), 2.82 (ddd, J = 0.8, 8.4, 18.4 Hz, 1H), 1.27-1.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 166.4, 166.0, 154.4, 134.5, 130.7, 126.7, 114.4, 103.8, 91.5, 63.2, 63.0, 45.1, 42.7, 14.0, 13.9.

Diethyl 5,7-Dichloro-3-(formylmethyl)benzofuran-2,2(3*H*)-dicarboxylate (3i): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.23 (d, J = 2.0 Hz, 1H), 7.01 (d, J = 2.0 Hz, 1H), 4.87 (dd, J = 5.6, 8.4 Hz, 1H), 4.30-4.42 (m, 4H), 2.97 (ddd, J = 0.8, 5.2, 18.4 Hz, 1H), 2.82 (ddd, J = 0.8, 8.4, 18.4 Hz, 1H), 1.27-1.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 166.4, 165.6, 152.5, 130.5, 129.3, 127.4, 123.3, 116.2, 91.8, 63.3, 63.0, 45.1, 42.5, 14.0, 13.9; MS *m/z* (%) 374 (M^+, 7), 282 (22), 254 (100), 227 (98), 199 (21), 136 (11); Anal. Calcd for $C_{16}H_{16}Cl_2O_6 \cdot 1/2H_2O$: C, 50.02; H, 4.46. Found: C, 50.06; H, 4.42.

Diethyl 3-(Formylmethyl)-5-nitrobenzofuran-2,2(3*H*)-dicarboxylate (3j): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.20 (dd, J = 2.4, 8.8 Hz, 1H), 8.04 (dd, J = 1.2, 2.4 Hz, 1H), 7.04 (d, J = 8.8 Hz, 1H), 4.87 (dd, J = 5.6, 6.8 Hz, 1H), 4.25-4.41 (m, 4H), 3.05 (ddd, J = 0.8, 5.2, 18.4 Hz, 1H), 2.90 (ddd, J = 0.8, 8.0, 18.4 Hz, 1H), 1.27-1.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 166.2, 165.6, 162.5, 143.3, 129.3, 126.6, 121.1, 110.3, 92.6, 63.4, 63.2, 45.0, 41.4, 14.0, 13.9.

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13. Catalyst **I**: 4% ee, catalyst **II**: 2% ee, catalyst **III**: 7% ee.