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Highly Diastereo- and Enantioselective Organocatalyzed Michael/Oxa-Michael Sequence: Asymmetric Synthesis of Pyranonaphthoquinone Derivatives

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An efficient asymmetric synthesis of pyranonaphthoquinones via Michael addition and oxo-Michael cyclization sequence of 2-hydroxy-1,4-naphthoquinone with (*E*)-2-nitroallylic acetates has been developed. The synthetically useful chiral pyranonaphthoquinone derivatives were obtained in moderate to high yields and high enantioselectivities. This approach offers a facile way to prepare chiral pyranonaphthoquinone derivatives with a wide range of functional group tolerance.

Keywords: 2-Hydroxy-1,4-naphthoquinones, 2-Nitroallylic acetates, Pyranonaphthoquinone, Organocatalysis

Introduction

2-Hydroxy-1,4-naphthoquinones serve as Michael donors for the conjugate addition to nitroalkenes, unsaturated carbonyl compounds, and β,γ-unsaturated α-oxo derivatives to afford carbocycles and heterocycles compounds which are precursors for the synthesis of various biologically active compounds.[1] The pyranonaphthoquinone skeleton is exist in many natural products and biologically active molecules.[2] Therefore, asymmetric synthesis of pyranonaphthoquinone derivatives is of great significance.[3] Recently, Namboothiri and Pericas groups reported the asymmetric synthesis of pyranonaphthoquinone via Michael and oxa-Michael cascade reactions of 2-hydroxy-1,4-naphthoquinones with (*E*)-2-nitroallylic acetates[4] catalyzed by cinchona-derived organocatalysts.[5] Although these approaches are moderately satisfying, new organocatalytic asymmetric Michael reaction and oxa-Michael cyclization of 2-hydroxy-1,4-naphthoquinones to (*E*)-2-nitroallylic acetates is highly desirable.

With our ongoing research interest for the development of synthetic methods for the enantioselective construction of stereogenic carbon centers,[6] we recently described asymmetric conjugated addition to nitroalkenes using chiral catalysts.[7] Herein, we report the asymmetric Michael addition of 2-hydroxy-1,4-naphthoquinones to (*E*)-2-nitroallylic acetates promoted by binaphthyl-modified organocatalyst (Figure 1).[8]

Results and Discussion

To determine optimal reaction conditions for the organocatalytic asymmetric Michael addition and oxa-Michael cyclization sequence of 2-hydroxy-1,4-naphthoquinone to (*E*)-2-nitroallylic acetates, we investigated a reaction system 2-hydroxynaphthalene-1,4-dione (**1**) and (*E*)-2-nitro-3-phenylallyl acetate (**2a**) in the presence of 10 mol % of organocatalyst. We initially evaluated the catalyst structure of bifunctional organocatalysts **I**–**VI** (Figure 1) on reactivity and selectivity in dichloromethane (Table 1, entries 1–6). Catalyst **VI**, which is a binaphthyl-derived tertiary amine-containing squaramide, was the best catalyst for this enantioselective Michael addition and oxa-Michael cyclization sequence (97% ee, Table 1, entry 6). Various solvents were surveyed in the presence of 10 mol% of binaphthyl-derived organocatalyst **VI** (Table 1, entries 6 and 7–15). Among the solvents tested, dichloromethane was found to be the best solvent, giving the desired product **3a** in 96% yield with >20:1 dr and 97% ee (Table 1, entry 6).

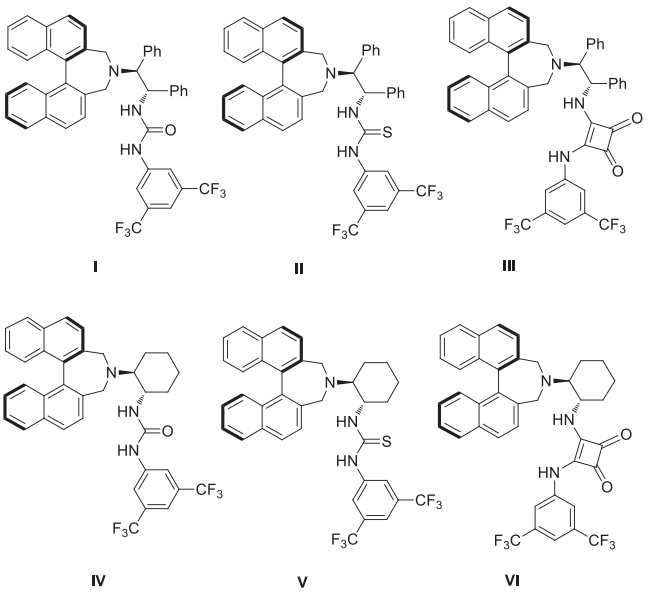
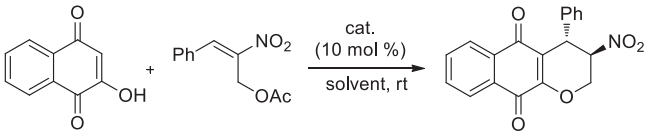


Figure 1. Structure of organocatalysts.

Table 1. Optimization of the reaction conditions.[a]



1 2a 3a

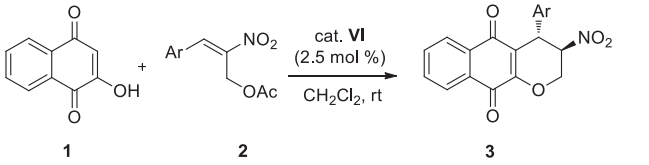
Entry	Cat.	Solvent	Time (h)	dr[b]	Yield (%)[c]	ee (%)[d]
1	**I**	CH_2Cl_2	21	17:1	50	85
2	**II**	CH_2Cl_2	20	14:1	88	91
3	**III**	CH_2Cl_2	27	15:1	93	90
4	**IV**	CH_2Cl_2	21	13:1	81	89
5	**V**	CH_2Cl_2	48	15:1	62	92
6	**VI**	CH_2Cl_2	21	>20:1	96	97
7	**VI**	$CHCl_3$	22	16:1	76	95
8	**VI**	DCE	22	34:1	69	94
9	**VI**	PhMe	16	20:1	54	97
10	**VI**	THF	22	13:1	78	87
11	**VI**	1,4-dioxane	24	15:1	74	81
12	**VI**	acetone	41	12:1	48	95
13	**VI**	EtOAc	46	16:1	96	75
14	**VI**	MeCN	21	15:1	56	93
15	**VI**	EtOH	19	13:1	91	81
16[e]	**VI**	CH_2Cl_2	23	>20:1	96	97
17[f]	**VI**	CH_2Cl_2	23	>20:1	97	97
18[g]	**VI**	CH_2Cl_2	115	19:1	85	97

[a] Reaction conditions: 2-hydroxy-1,4-naphthoquinones (**1**, 0.2 mmol) of (*E*)-2-nitro-3-phenylallyl acetate (**2a**, 0.2 mmol), and catalyst (10 mol %) in solvent (1.5 mL) at room temperature
[b] dr was determined by NMR analysis of crude mixture.
[c] Isolated yield.
[d] ee was determined by HPLC analysis using chiralpak AD-H column.
[e] 5 mol % of catalyst loading.
[f] 2.5 mol % of catalyst loading.
[g] 1.3 mol % of catalyst loading.

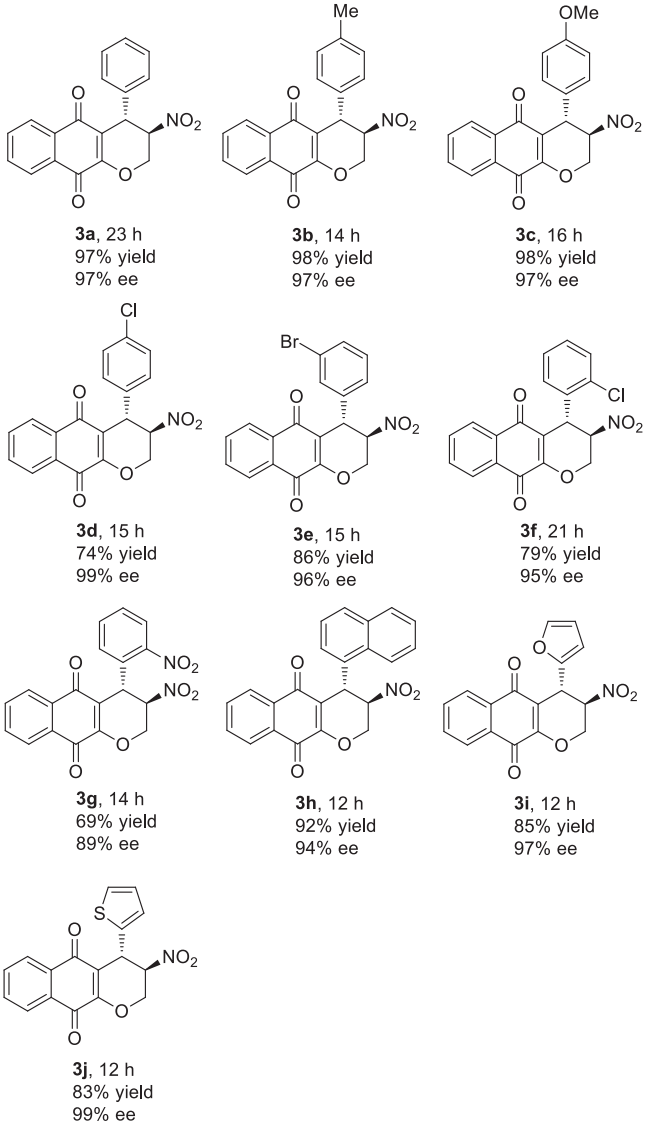
Finally, the effect of catalyst loading was examined (Table 1, entries 6 and 16–18), and excellent results were obtained when the catalyst loading was lowered to 2.5 mol % (Table 1, entry 17).

With the optimal reaction conditions established, we proceeded to investigate the scope of the asymmetric Michael addition and oxa-Michael cyclization sequence of 2-hydroxy-1,4-naphthoquinone (**1**) to (*E*)-2-nitroallylic acetates **2** in the presence of 2.5 mol% of catalyst **VI** in dichloromethane at room temperature (Table 2). A range of electron-donating and electron-withdrawing substitutions on the 3-aryl ring of the (*E*)-2-nitro-3-arylallyl acetate **2** provided desired products **3b-3g** in high yields and excellent enantioselectivities (69–98% yields and 89–99% ee). 3-Naphthyl- and heteroaryl-substituted (*E*)-2-nitroallylic acetates **2** provided corresponding products **3h-3j** with high selectivity (83–92% yields and 94–99% ee).

Table 2. Asymemetric synthesis of pyranonaphthoquinones **3**.[a-d]

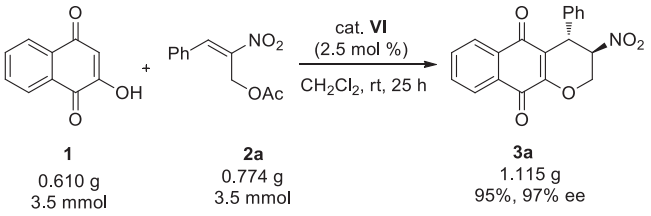


1 2 3



[a] Reaction conditions: 2-hydroxy-1,4-naphthoquinones (**1**, 0.2 mmol) of (*E*)-2-nitro-3-arylallyl acetate (**2**, 0.2 mmol), and catalyst **VI** (2.5 mol%) in CH_2Cl_2 (1.5 mL) at room temperature.
[b] dr was determined by NMR analysis of crude mixture.
[c] Isolated yield.
[d] ee was determined by HPLC analysis using chiralpak AD-H column.

To show the utility of the present transformation, we performed the asymmetric Michael addition and oxa-Michael cyclization sequence at the gram scale. As shown in Scheme 1, a gram scale synthesis of **3a** was performed with



Scheme 1. Gram scale synthesis of **3a**.

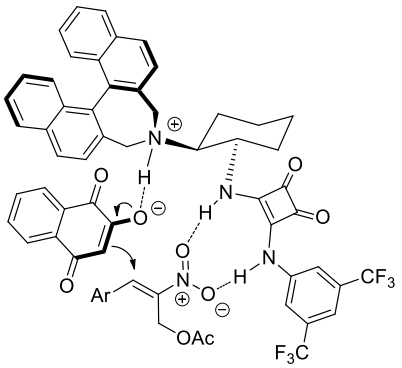


Figure 2. Proposed stereochemical model.

maintained efficiency and stereoselectivity. This reaction affords practical access to chiral pyranonaphthoquinone derivatives.

Based on the experiments and previous studies,[8] possible stereochemical model was proposed to elucidate the stereocontrol. We suppose that (*E*)-2-nitroallylic acetates **2** is activated by the chiral binaphthyl-derived squaramide **VI** by hydrogen-bonding interaction. Then, enolate of 2-hydroxy-1,4-naphthoquinone (**1**) attacks the *re*-face of (*E*)-2-nitroallylic acetates **2** (Figure 2).

Conclusion

In summary, we have developed highly diastereo- and enantioselective organocatalyzed Michael addition and oxo-Michael cyclization sequence of 2-hydroxy-1,4-naphthoquinone (**1**) with (*E*)-2-nitroallylic acetates **2**. This reaction is catalyzed by binaphthyl-derived squaramide catalyst **VI** with low catalyst loading (2.5 mol %). The corresponding products were formed in high yields (74–98%) with moderate to excellent diastereo- and enantioselectivities (>20:1 dr and 94–99% ee). This reaction would afford a practical access to chiral pyranonaphthoquinone derivatives.

Experimental

General. All commercial reagents and solvents were used without purification. TLC analyses were carried out on precoated silica gel plates with F_{254} indicator. Purification of reaction products was carried out by flash chromatography using E. Merck silica gel 60 (230–400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz respectively, on a Jeol ECS 400 MHz NMR spectrometer. Chemical shift values (δ) are reported in ppm relative to Me_4Si as the internal references and $PhCF_3$ as the external references. Mass spectra (MS-EI, 70 eV) were conducted on GC–MS Shimadzu QP2010.

Typical Procedure for the Asymmetric Synthesis of 3a. To a stirred solution of (*E*)-2-nitro-3-phenylallyl acetate (**2a**, 44.2 mg, 0.2 mmol) and catalyst **VI** (3.4 mg, 5 μmol) in methylene chloride (1.5 mL) was added 2-hydroxy-1,-4-naphthoquinone (**1**, 34.8 mg, 0.2 mmol) at room temperature. The reaction mixture was stirred for 23 h at room temperature. After completion of the reaction, the reaction mixture was purified by column chromatography (ethyl acetate: *n*-hexane = 1:4) on silica gel directly to give (*3R,4S*)-3-nitro-4-phenyl-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3a**, 65.1 mg, 97%)[5]: Yellow solid, m.p. 218–220°C; $[\alpha]^{28}_D = -116.0$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 5.8 Hz, J = 3.2 Hz, 1H), 8.03 (dd, J = 6.0 Hz, J = 4.0, 1H), 7.75 (dd, J = 5.6 Hz, J = 3.2, 2H), 7.41–7.29 (m, 5H), 5.07 (m, 2H), 4.82 (q, J = 2.0 Hz, 1H), 4.36 (dd, J = 12.8 Hz, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.47, 178.47, 154.26, 138.77, 134.57, 133.78, 131.69, 130.76, 129.56, 128.41, 127.88, 126.71, 126.61, 118.72, 81.80, 63.09, 37.44; EI-MS: m/z = 335.1 [M^+];The ee value was 97%, t_R (major) = 13.70 min, t_R (minor) = 79.02 min (Chiralpak AD-H, λ = 230 nm, 20% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*R*)-3-Nitro-4-*p*-tolyl-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3b**)[5]: Yellow solid, m.p. 164–167°C; $[\alpha]^{28}_D = -85.6$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 6.0 Hz, J = 3.2 Hz, 1H), 8.03 (dd, J = 6.0 Hz, J = 3.2, 1H), 7.74 (dd, J = 5.6 Hz, J = 3.2, 2H), 7.17 (q, J = 8.4 Hz, 4H), 5.06 (m, 2H), 4.82 (q, J = 2.4 Hz, 1H), 4.36 (dt, J = 13.2 Hz, J = 2.8 Hz, 1H), 2.33(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.65, 178.66, 154.30, 138.46, 135.95, 134.67, 133.77, 131.85, 130.90, 130.34, 127.89, 126.81, 126.75, 119.09, 82.04, 63.24, 37.22, 21.18; EI-MS: m/z = 349.1 [M^+]; The ee value was 97%, t_R (major) = 11.81 min, t_R (minor) = 58.74 min (Chiralpak AD-H, λ = 230 nm, 20% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*R*)-4-(4-Methoxyphenyl)-3-nitro-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3c**)[5]: Yellow solid, m.p. 118–121°C; $[\alpha]^{28}_D = -60.4$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (m, 1H), 8.02 (m, 1H), 7.74 (dd, J = 5.6 Hz, J = 2.4 Hz, 2H), 7.19 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.07(m, 2H), 4.78 (q, J = 1.6 Hz, 1H), 4.36 (dd, J = 13.2 Hz, J = 2.4 Hz, 1H), 3.78(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.50, 178.52, 159.49, 154.08, 134.54, 133.65, 131.73, 130.69, 129.93, 129.01, 126.68, 126.61, 119.03, 114.89, 81.93, 63.07, 55.36, 36.69; EI-MS: m/z = 365.1 [M^+]; The ee value was 97%, t_R (major) = 22.93 min, t_R (minor) = 167.32 min (Chiralpak AD-H, λ = 230 nm, 20% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*S*)-4-(4-Chlorophenyl)-3-nitro-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3d**)[5]: Yellow solid, m.p. 175–179°C; $[\alpha]^{28}_{D}$ = −108.200 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 5.2 Hz, *J* = 3.2 Hz, 1H), 8.03 (dd, *J* = 4.8 Hz, *J* = 3.2 Hz, 1H), 7.75 (dd, *J* = 8.0 Hz, *J* = 3.6 Hz, 2H), 7.37–7.22 (m, 4H), 5.04–5.12 (m, 2H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.32 (dd, *J* = 16.0 Hz, *J* = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.40, 178.30, 154.37, 137.28, 134.66, 134.53, 133.81, 131.60, 130.74, 129.76, 129.25, 126.78, 126.64, 118.36, 81.58, 63.02, 36.94; EI-MS: *m/z* = 369.0 [M^+]; The ee value was 99%, t_R (major) = 18.46 min, t_R (minor) = 126.49 min (Chiralpak AD-H, λ = 230 nm, 20% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*R*)-4-(3-Bromophenyl)-3-nitro-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3e**)[5]: Yellow solid, m.p. 129–132°C; $[\alpha]^{28}_{D}$ = −137.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.15 (m, 1H), 8.05–7.99 (m, 1H), 7.76 (dd, *J* = 5.2 Hz, *J* = 2.8 Hz, 2H), 7.46 (dt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.42 (t, *J* = 2 Hz, 1H), 7.31–7.22(m, 2H), 5.15–5.08 (m, 2H), 4.81 (q, *J* = 2.4 Hz, 1H), 4.34 (dd, *J* = 12.8 Hz, *J* = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.36, 178.29, 154.41, 141.00, 134.67, 133.82, 131.65, 131.05, 130.92, 130.72, 126.80, 126.61, 118.00, 81.45, 63.02, 37.06; EI-MS: *m/z* = 413.0 [M^+]; The ee value was 96%, t_R (major) = 15.75 min, t_R (minor) = 102.22 min (Chiralpak AD-H, λ = 230 nm, 20% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*S*)-4-(2-Chlorophenyl)-3-nitro-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3f**)[5]: Pale yellow solid, m.p. 212–216°C; $[\alpha]^{28}_{D}$ = −95.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20–8.16 (m, 1H), 8.06–8.03 (m, 1H), 7.76 (dd, *J* = 5.2 Hz, *J* = 3.2 Hz, 2H), 7.52 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 7.30 (dt, *J* = 8 Hz, *J* = 2 Hz, 1H), 7.23 (dt, *J* = 8 Hz, *J* = 1.2 Hz, 1H), 7.04 (dd, *J* = 8 Hz, *J* = 2 Hz, 1H), 5.48 (s, 1H), 5.11 (dt, *J* = 12.8 Hz, *J* = 2 Hz, 1H), 4.91 (q, *J* = 5.6 Hz, 1H), 4.27 (dd, *J* = 13.4 Hz, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.21, 178.27, 154.98, 135.85, 134.65, 133.78, 133.57, 131.62, 130.66, 129.77, 129.30, 127.63, 126.77, 126.64, 118.42, 79.46, 63.45, 34.88; EI-MS: *m/z* = 369.0 [M^+]; The ee value was 95%, t_R (major) = 15.65 min, t_R (minor) = 90.66 min (Chiralpak AD-H, λ = 230 nm, 20% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*R*)-3-Nitro-4-(2-nitrophenyl)-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3g**)[5]: Yellow solid, m.p. 225–232°C; $[\alpha]^{28}_{D}$ = −343.2 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.17 (m, 2H), 8.00–7.97 (m, 1H), 7.78–7.74 (m, 2H), 7.70–7.47 (m, 3H), 5.53(s, 1H), 5.20–5.17 (m, 2H) 4.42 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.22, 178.16, 155.16, 148.48, 134.76, 134.07, 133.93, 133.72, 131.47, 130.73, 130.30, 129.55, 126.85, 126.61, 126.34, 118.60, 80.62, 63.91, 33.87; EI-MS: m/z = 380.1 [M^+]; The ee value was 89%, t_R (major) = 19.59 min, t_R (minor) = 62.86 min (Chiralpak AD-H, λ = 230 nm, 30% *i*PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*R*)-4-(Naphthalen-1-yl)-3-nitro-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3h**)[5]: Yellow solid, m.p. 217–223°C; $[\alpha]^{28}_{D}$ = −130.0 (c = 1,0 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.4 Hz, 1H), 8.20–8.22 (m, 1H), 8.02–8.01 (m, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.74–7.77 (m, 3H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 6.8 Hz, 1H), 7.16 (d, *J* = 6.8 Hz, 1H), 5.93 (s, 1H), 5.10 (d,, *J* = 12.8 Hz, 1H) 4.93 (d, *J* = 1.2 Hz, 1H), 4.32 (d, *J* = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.35, 178.44, 154.94, 134.60, 134.47, 134.34, 133.71, 131.75, 130.83, 129.99, 129.62, 129.39, 127.92, 126.77, 126.67, 126.07, 125.20, 121.86, 118.62, 80.00, 63.04, 34.07; EI-MS: *m/z* = 385.1 [M^+]; The ee value was 94%, t_R (major) = 12.73 min, t_R (minor) = 84.81 min (Chiralpak AD-H, λ = 230 nm, 30% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*S*)-4-(Furan-2-yl)-3-nitro-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3i**)[5]: Yellow solid, m.p. 159–164°C; $[\alpha]^{28}_{D}$ = −69.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–8.14 (m, 1H), 8.10–8.07 (m, 1H), 7.77–7.73 (m, 2H), 7.38 (dd, *J* = 1.6 Hz, *J* = 0.8 Hz, 1H), 6.34 (m, 1H), 6.26 (d, *J* = 3.2 Hz, 1H), 5.19 (m, 2H), 5.02 (q, *J* = 2.0 Hz, 1H), 4.55 (dt, *J* = 13.2 Hz, *J* = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.34, 178.44, 153.89, 150.20, 143.07, 134.58, 133.69, 131.65, 130.70, 126.73, 126.60, 117.02, 111.04, 109.37, 78.85, 64.40, 31.31; EI-MS: *m/z* = 325.1 [M^+]; The ee value was 97%, t_R (major) = 32.64 min, t_R (minor) = 44.14 min (Chiralpak AD-H, λ = 230 nm, 20% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

(3*R*,4*R*)-3-Nitro-4-(thiophen-2-yl)-3,4-dihydro-2*H*-benzo[*g*]chromene-5,10-dione (**3j**)[5]: Yellow solid, m.p. 153–161°C; $[\alpha]^{28}_{D}$ = −83.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.15 (m, 1H), 8.09–8.04 (m, 1H), 7.77–7.42 (m, 2H), 7.30–7.28 (m, 1H), 7.00–6.96 (m, 2H), 5.34 (s, 1H), 5.16 (dt, *J* = 13.2 Hz, *J* = 2.4 Hz, 1H), 4.91 (q, *J* = 2.0 Hz, 1H), 4.54 (dd, *J* = 12.8 Hz, *J* = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.29, 178.47, 153.44, 141.50, 134.63, 133.73, 131.62, 130.69, 127.70, 126.84, 126.74, 126.65, 126.09, 119.03, 81.26, 63.54, 32.28; EI-MS: *m/z* = 341.0 [M^+]; The ee value was 99%, t_R (major) = 10.53 min, t_R (minor) = 42.08 min (Chiralpak AD-H, λ = 230 nm, 30% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

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References

1. For selected recent examples, see: (a) S. B. Woo, D. Y. Kim, *Beilstein J. Org. Chem.* **2012**, *8*, 699. (b) K. Pinar, R. E. Carles, A. P. Miquel, *Org. Lett.* **2013**, *15*, 3498. (c) B. V. S. Reddy, M. Swain, S. M. Reddy, J. S. Yadav, *RSC Adv.* **2013**, *3*, 8756. (d) J. H. Lee, D. Y. Kim, *Bull. Korean Chem. Soc.* **2013**, *34*, 1619. (e) B. V. S. Reddy, S. M. Reddy, M. Swain, *RSC Adv.*

2013, *3*, 930. (f) H. Klare, J. M. Neudörfl, B. Goldfuss, *Beilstein J. Org. Chem.* **2014**, *10*, 224. (g) N. Molletia, V. K. Singh, *Org. Biomol. Chem.* **2015**, *13*, 5243. (h) V. P. R. Gajulapalli, K. Lokesh, M. Vishwanath, V. Kesavan, *RSC Adv.* **2016**, *6*, 12180. (i) Y. Liu, W. H. Ge, Y. Q. Zhu, H. Y. Hu, H. Fan, Y. H. Shi, H. Wu, *Eur. J. Org. Chem.* **2017**, *2017*, 551.

2. (a) T. Kimachi, E. Torii, R. Ishimoto, A. Sakue, M. Ju-ichi, *Tetrahedron Asymmetry* **2009**, *20*, 1683. (b) S. Pethuan, P. Duangkaew, S. Sarapusit, E. Srisook, P. Rongnoparut, *J. Med. Entomol.* **2012**, *49*, 993.
3. (a) C. D. Donner, *Tetrahedron* **2013**, *69*, 377. (b) M. A. Brimble, N. P. S. Hassan, B. J. Naysmith, J. Sperry, *J. Org. Chem.* **2014**, *79*, 7169. (c) F.-F. Pan, W. Yu, Z.-H. Qi, C. Qiao, X.-W. Wang, *Synthesis* **2014**, *46*, 1143. (d) N. P. S. Hassan, B. J. Naysmith, J. Sperry, M. A. Brimble, *Tetrahedron* **2015**, *71*, 7137.
4. (a) T. Shu, Q. Ni, X. Song, K. Zhao, T. Wu, R. Puttreddy, K. Rissanen, D. Enders, *Chem. Commun.* **2016**, *52*, 2609. (b) W. Xiao, X. Yin, Z. Zhou, W. Du, Y. C. Chen, *Org. Lett.* **2016**, *18*, 116. (c) Y. Zheng, L. Cui, Y. Wang, Z. Zhou, *J. Org. Chem.* **2016**, *81*, 4340. (d) J. Xie, F. Sha, X. Y. Wu, *Tetrahedron* **2016**, *72*, 4047. (e) Y. J. Liu, J. Zhao, J. L. Zhang, P. F. Xu, *Org. Lett.* **2017**, *19*, 1846. (f) Y. J. Liu, C. X. Yang, H. Lu, Y. C. Gu, P. F. Xu, *Org. Lett.* **2018**, *20*, 2190.
5. (a) D. K. Nair, R. F. S. Menna-Barreto, E. N. da Silva Júnior, S. M. Mobin, I. N. N. Namboothiri, *Chem. Commun.* **2014**, *50*, 6973. (b) G. A. M. Jardim, T. T. Guimarães, M. C. F. R. Pinto, B. C. Cavalcanti, K. M. de Farias, C. Pessoa, C. C. Gatto, D. K. Nair, I. N. N. Namboothiri, E. N. da Silva Júnior, *Med. Chem. Commun.* **2015**, *6*, 120.
6. For a selection of our recent works on asymmetric catalysis, see: (a) D. Y. Kim, S. M. Kim, K. O. Koh, J. Y. Mang, K. Lee, *Bull. Korean Chem. Soc.* **2003**, *24*, 1425. (b) Y. K. Kang, H. J. Lee, H. W. Moon, D. Y. Kim, *RSC Adv.* **2013**, *3*, 1332. (c) S. B. Woo, C. W. Suh, K. O. Koh, D. Y. Kim, *Tetrahedron Lett.* **2013**, *54*, 3359. (d) Y. K. Kang, D. Y. Kim, *Adv. Synth. Catal.* **2013**, *355*, 3131. (e) C. W. Suh, D. Y. Kim, *Org. Lett.* **2014**, *16*, 5374. (f) C. W. Suh, S. B. Woo, D. Y. Kim, *Asian J. Org. Chem.* **2014**, *3*, 399. (g) S. J. Kwon, D. Y. Kim, *J. Fluorine Chem.* **2015**, *180*, 201. (h) C. W. Suh, S. J. Kwon, D. Y. Kim, *Org. Lett.* **2017**, *19*, 1334. (i) H. J. Jeong, D. Y. Kim, *Org. Lett.* **2018**, *20*, 2944.
7. (a) H. J. Lee, S. B. Woo, D. Y. Kim, *Tetrahedron Lett.* **2012**, *53*, 3374. (b) H. J. Lee, S. M. Kim, D. Y. Kim, *Tetrahedron Lett.* **2012**, *53*, 3437. (c) H. W. Moon, D. Y. Kim, *Tetrahedron Lett.* **2012**, *53*, 6569. (d) H. J. Sung, J. Y. Mang, D. Y. Kim, *J. Fluorine Chem.* **2015**, *178*, 40. (e) H. J. Jeong, S. J. Kwon, D. Y. Kim, *Bull. Korean Chem. Soc.* **2015**, *36*, 1516. (f) H. J. Jeong, D. Y. Kim, *Bull. Korean Chem. Soc.* **2015**, *36*, 2936. (g) Y. Kim, Y. J. Kim, H. I. Jung, D. Y. Kim, *J. Fluorine Chem* **2017**, *201*, 43.
8. For a selection of our recent works on organocatalysis, see:(a) H. J. Lee, S. B. Woo, D. Y. Kim, *Molecules* **2012**, *17*, 7523. (b) H. J. Lee, D. Y. Kim, *Bull. Korean Chem. Soc.* **2012**, *33*, 3171. (c) H. J. Lee, D. Y. Kim, *Bull. Korean Chem. Soc.* **2012**, *33*, 3537. (d) C. W. Suh, C. W. Chang, K. W. Choi, Y. J. Lim, D. Y. Kim, *Tetrahedron Lett.* **2013**, *54*, 3651. (e) H. S. Jang, Y. Kim, D. Y. Kim, *Beilstein J. Org. Chem.* **2016**, *12*, 1551. (f) Y. H. Kim, J. H. Yoon, M. Y. Lee, D. Y. Kim, *Bull. Korean Chem. Soc.* **2017**, *38*, 1242. (g) Y. S. Kim, M. H. Lee, D. Y. Kim, *Bull. Korean Chem. Soc.* **2018**, *39*, 579.

