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Organocatalytic Asymmetric Michael/Hemiacetalization/Acyl Transfer Reaction of α-Nitroketones with o-Hydroxycinnamaldehydes: Synthesis of 2,4-Disubstituted Chromans

Rajendra Maity and Subhas Chandra Pan*

An organocatalytic asymmetric cascade Michael/ hemiketalization /acyl transfer reaction between *o*-hydroxycinnamaldehydes and *α*-nitroketones is developed. Prolinol TMS ether catalyst in combination with benzoic acid was found to be the most effective for this reaction which proceeds through an equibrium of lactols to provide a single diastereomer of enantiopure 2,4-disubstituted chromans.

Chiral chromans are one class of privileged structural motifs present in a plethora of natural products and synthetic analogs displaying a wide range of biological activities.[1] For example Cromakalim (**1**) was found to have vasodilatory or anti-hypertensive effects.[2] Sorbinil (**2**) uses to act as an addolase reductase inhibitor and has been shown to recover conduction velocity in daibatic patients.[3] Also natural phenol Catechin (**3**) prevents intestinal tumor formation and suppresses focal adhesion kinase activation in the min/t mouse (Figure 1).[4] Though a variety of organocatalytic routes has been reported in the last decade,[5] the development of efficient methods for the enantioselective construction of chroman rings having diverse substitutions is important for the finding of new chiral drugs and other utilities.

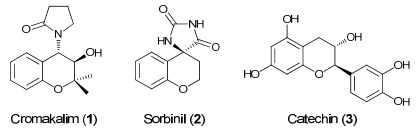
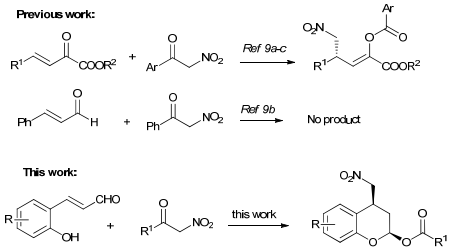


Figure 1 Biological active chroman derivatives.



Scheme 1 Organocatalytic asymmetric Michael-acyl transfer reaction between nitroketones and unsaturated carbonyl compounds.

In recent years, organocatalytic asymmetric Michael additions, particularly the Michael addition reaction-triggered cascade reactions, have been utilized in the enantioselective synthesis of a variety of complex molecules in a one-pot fashion.[6,7] Among which, considerable attention has been provided for the asymmetric Michael addition of nitroalkanes to *α,β*-unsaturated carbonyl compounds,[8] which is synthetically very useful as it provides highly functionalized synthetic intermediates such as *γ*-aminocarbonyl compounds and aminoalkanes as well as often initiates a variety of cascade reactions. However, the scope of nitro compounds are limited to nitroalkanes and nitro-esters and surprisingly *α*-nitroketones, another active nucleophiles, failed to provide products with cinnamaldehydes.[9b] Only the reactions of *α*-nitroketones with *β,γ*-unsaturated *α*-keto esters and unsaturated pyrazolones have been disclosed in the literature.[9] We envisioned that bidentate compounds like *o*-hydroxycinnamaldehydes[10] might be suitable substrate for the reaction with *α*-nitroketones. Realizing the potential of chroman compounds, we embark in developing an asymmetric Michael/hemiacetalization/acyl transfer reaction between α-nitroketones and o-hydroxycinnaldehydes (Scheme 1).

Initially, a model reaction between o-hydroxycinnamaldehyde (**1a**) and 2-nitro-1-phenylethanone (**2a**) was studied with α,α-diphenyl-2-pyrrolidinemethanol (**I**) in combination with benzoic acid in 1,2-dichloroethane solvent at room temperature (Table 1, entry 1). After stirring for two days, a product was isolated in 80% yield whose structure was determined to be chroman **3a** by 1H NMR (Table 1, entry 1). The relative structure of pure

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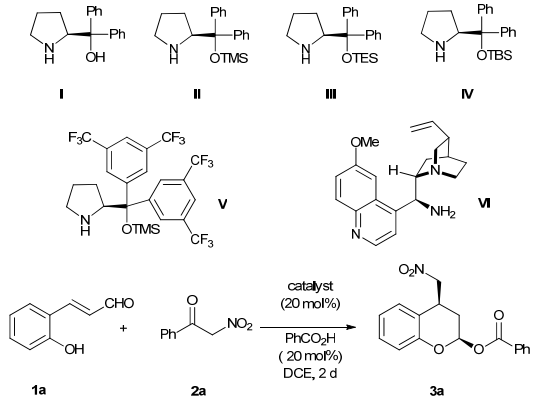
Table 1 Catalyst screening and optimization of reaction conditions



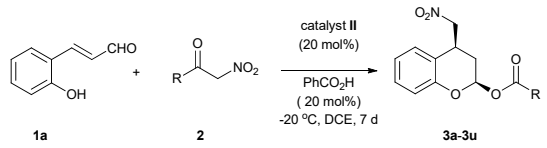
entry[a]	catalyst	temp	yield[b]	dr[c]	ee[d]
1	**I**	rt	80	>20:1	56
2	**II**	rt	85	>20:1	78
3	**III**	rt	84	>20:1	72
4	**IV**	rt	82	>20:1	78
5	**V**	rt	mixture	-	-
6	**VI**	rt	75	>20:1	52
7	**II**	0 °C	50	>20:1	90
8	**II**	-20 °C	40	>20:1	94
9[d]	**II**	-20 °C	85	>20:1	94

[a]Unless otherwise mentioned, reactions were carried out with 0.25 mmol of **1a** with 0.05 mmol of **2a** in 0.5 ml DCE using 20 mol% catalyst and 20 mol% $PhCO_2H$. [b]Isolated yield after silica gel column chromatography. [c]Determined by ^1H NMR. [d]Determined by chiral HPLC. [d]Reaction time 7 days.

single diastereomer **3a** was solved by 2D NMR analysis. However, the enantioselectivity was only moderate. A slight higher enantioselectivity was achieved with prolinol TMS ether catalyst **II** (entry 2).[11] To improve the enantioselectivity, other silyl ether catalysts **III** and **IV** were prepared but they failed to enhance the enantiomeric excess of the product (entries 3-4). Then catalyst **V** having aryl groups with bis-3,5 trifluromethyl substituents was engaged in the reaction, however only a complex mixture was attained (entry 5). Screening of other additives and solvents was also performed with catalyst **II** but good result was not achieved (see supporting information for details). Then we turned our attention on the reaction temperature and it proved to be beneficial. Lowering the temperature to 0 °C and -20 °C improved the enantiomeric excess significantly (entries 7-8) but the yield dropped. Pleasingly, a good yield of 85% was achieved by running the reaction for 7 days at -20 °C with enantiomeric excess unchanged (entry 9).

After the detection of the best optimized conditions, the scope and generality of the reaction was investigated. Initially a variety of α-nitroketones **1** having different aryl groups were tested (Table 2). It was found that a range of substituents can

Table 2 Scope of Nitroketones



entry[a]	R	3	yield[b]	dr[c]	ee[d]
1	Ph	**3a**	85	>20:1	94
2	4-MeC_6H_4	**3b**	76	>20:1	92
3	4-$^{i}PrC_6H_4$	**3c**	84	>20:1	90
4	4-$^{t}BuC_6H_4$	**3d**	68	>20:1	90
5	4-$OMeC_6H_4$	**3e**	90	>20:1	92
6	4-$OEtC_6H_4$	**3f**	70	>20:1	90
7	4-$O^{n}PrC_6H_4$	**3g**	84	>20:1	96
8	4-$O^{i}PrC_6H_4$	**3h**	78	>20:1	96
9	4-$O^{t}BuC_6H_4$	**3i**	86	>20:1	96
10	4-$OAllC_6H_4$	**3j**	60	>20:1	88
11	4-$OBnC_6H_4$	**3k**	84	>20:1	96
12	4-FC_6H_4	**3l**	76	>20:1	84
13	4-ClC_6H_4	**3m**	72	>20:1	82
14	4-BrC_6H_4	**3n**	70	>20:1	88
15	3-MeC_6H_4	**3o**	69	>20:1	86
16	3-ClC_6H_4	**3p**	78	>20:1	86
17	2-MeC_6H_4	**3q**	80	>20:1	96
18	2-$OMeC_6H_4$	**3r**	73	>20:1	90
19	2-FC_6H_4	**3s**	91	>20:1	84
20	2,4-$(Me)_2C_6H_3$	**3t**	91	>20:1	94
21	cyclohexyl	**3u**	47	>20:1	94

[a]Reactions were carried out with 0.5 mmol of **1a** and 0.1 mmol of **2** with 20 mol% catalyst **II** and 20 mol% $PhCO_2H$ in 1 mL DCE at -20 °C for 7 days. [b]Isolated yield after silica gel column chromatography of a single diastereomer. [c]Determined by ^1H NMR. [d]Determined by HPLC.

be incorporated in the *ortho*-, *meta*- and *para*-position of the aryl group and the corresponding products were achieved in high yields and enantioselectivities (entries 1-20). At first, 4-alkyl substituted aryl nitroketones **2b**-**d** were screened and the products **3b-d** were isolated in good yields with high enantioselectivities (entries 2-4). Then nitroketone **2e** with 4-anisyl group was employed in the reaction and the desired product **3e** was obtained in 92% ee (entry 5). Inspiring by this result, other 4-alkoxy substituted nitroketones were checked in the reaction and excellent results were observed (entries 6-11). 4-Halo substituted aryl nitroketones also participated in the reaction delivering the proudcts **3l**-**n** in good yields with acceptable enantioselectivities (entries 12-14). The reaction

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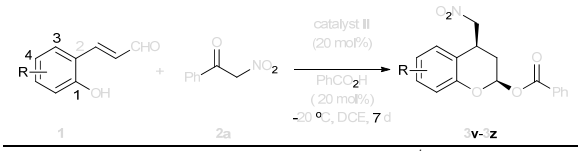
outcome was also gratifying for the *ortho*- and *meta*-substituted nitroketones (entries 15-19). A 2,4-disubstituted nitroketone **2t** also participated in the reaction (entry 20). Finally, *α*-nitroketone **2n** containing cyclohexyl group was screened and delightfully excellent enantioselectivity was maintained albeit the yield was moderate (entry 21).

The next stage of experiments involved screening of different *o*-hydroxyaromatic *α*,*β*-unsaturated aldehydes **1** in this method (Table 3). Thus different 4-halo and 4,6-dihalo substituted *α*,*β*-unsaturated aldehydes **1b-f** were prepared and employed in the reaction. Here also, the reaction progressed smoothly delivering the products in moderate to high yields and with high enantioselectivities. In particular the highest 96% ee was obtained for product **3z** having 4-Cl, 6-Br substitutions (entry 5). These halo group containing products are important as they can be converted to other derivatives *via* cross-coupling reactions. A methoxy group containing *o*-hydroxy cinnamaldehyde **1g** was also screened but lower enantioselectivity was obtained for product **3z**[1] (entry 6). Also, 4-methyl substituted *o*-hydroxycinnamaldehyde **1h** delivered the corresponding product **3z**[2] with excellent enantiomeric excess (entry 7). However, when *o*-hydroxy cinnamaldehyde having 4-nitro group **1i** was examined, the enantioselectivity was moderate for product **3z**[3] (entry 8). Then, 4,6-di^{t}butyl containing o-hydroxycinnamaldehyde **1j** was tested under the standard reaction condition; unfortunately, no product formation was observed possibly due to steric reason (entry 9).

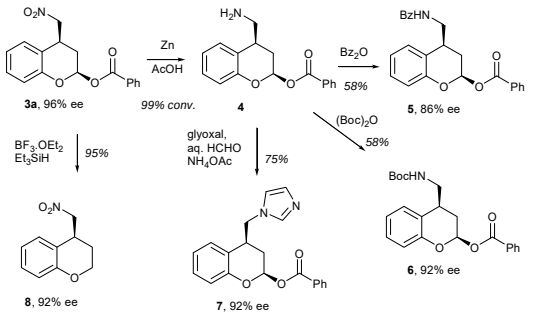
Table 3 Scope of *o*-Hydroxyaromatic-*α*,*β*-unsaturated aldehydes



entry[a]	R	3	yield[b]	dr[c]	ee[d]
1	4-Cl	**3v**	89	>20:1	90
2	4-Br	**3w**	93	>20:1	84
3	4,6-diCl	**3x**	81	>20:1	92
4	4,6-diBr	**3y**	51	>20:1	90
5	4-Cl, 6-Br	**3z**	60	>20:1	96
6	5-OMe	**3z**[1]	93	>20:1	60
7	4-Me	**3z**[2]	85	>20:1	90
8	4-NO_2	**3z**[3]	88	>20:1	68
9	4,6-di^{t}butyl	**3z**[4]	-	-	-

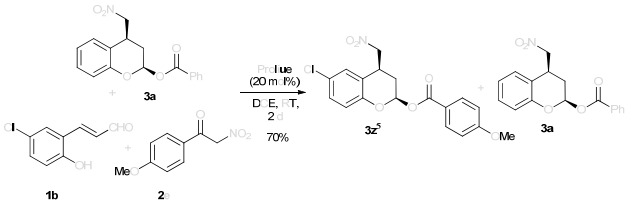
[a]Reactions were carried out with 0.5 mmol of **1** and 0.1 mmol of **2a** with 20 mol% catalyst **II** and 20 mol% $PhCO_2H$ in 1 mL DCE at -20 °C for 7 days. [b]Isolated yield after silica gel column chromatography. . [c]Determined by ^{1}H NMR. [d]Determined by HPLC.

Then the synthetic utility of our method was demonstrated by carrying out few reactions on **3a** (Scheme 2). Initially the reduction of **3a** using zinc and acetic acid was performed to provide amino group containing chroman **4** in 99% conversion. Chroman **4** was then subjected to a range of reactions.Protection of the amino group with benzoic anhydride leaded to the formation of **5** with slight reduction in enantiopurity. Gratifyingly, the enantiomeric excess was almost preserved for **6** having N-Boc protection. Then imidazole containing chroman **7** was synthesized by reaction of **4** with glyoxal, aq. formaldehyde and ammonium acetate[12] and here also the enantiomeric excess was nearly retained. Finally, 4-substituted chroman **8** was prepared in high yield and enantiopurity after treatment of **3a** with $BF_3.OEt_2$ and triethylsilane (Scheme 2).



Scheme 2 Synthetic transformations of **3a**.

To understand the mechanism of the reaction a cross-over experiment between product **3a**, nitroketone **2e** and *o*-hydroxycinnamaldehyde **1b** was carried out in DCE with proline catalyst (Scheme 3). After stirring the mixture for 2 days, only the new product **3z**[5] was detected along with unreacted **3a**. No cross-over product was found.



Scheme 3 Cross-over experiment.

The absolute configuration of the product **3p** was elucidated to be (2*R*,4*S*) by X-ray crystallography.[13] The absolute structure of other products are expected to be same by analogy. Based on the absolute configuration a plausible mechanism has been drawn in Scheme 4. It is believed that at first *o*-hydroxycinnamaldehyde **1a** reacts with catalyst **II** to provide iminium ion **A**. Since the *Si* face of the chiral iminium ion is blocked by bulky diphenylsiloxymethyl group, the addition of nitroketone **2a** occurs only from the *Re* face to generate intermediate **B** after hydrolysis. Intramolecular hemiacetalization provides two diastereomeric hemiacetals **C** and **D**. Since in **C**, further ketalization reaction cannot take place due to *trans*-orientation, only **D** participates in the ketalization step; and thus only **E** is obtained in good yield. Finally retro-Henry reaction of **E** generates chroman **3a**.

In summary, we have developed an efficient Michael-hemiacetalization-acyl transfer reaction between *α*-nitroketones and *o*-hydroxycinnamaldehydes. This reaction delivered single

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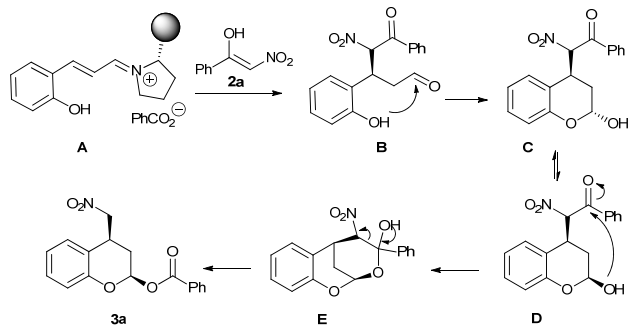

Scheme 4 Proposed mechanism.

diastereomer of 2,4-disubstituted chroman compounds in good to high yields and with excellent enantioselectivities. Also selective functionalizations for the synthesis of different di-substituted as well as mono-substituted chromans are appealing. Given the high pharmaceutical significance of chroman compounds our method might be beneficial to synthesize these compounds in a convenient way.

Experiment section:

General Information: Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H NMR spectra were recorded on 400 MHz and 600 MHz spectrometer.^{13}C NMR spectra were recorded on 100MHz and 150MHz. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.23). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet),ddd (doublet doublet of doublet), dt (doublet of triplet). Coupling constants were reported in Hertz (Hz). HRMS spectra were recorded using ESI mode. Enantiomeric ratios were determined by HPLC analysis using Dionex (Ultimate 3000) instrument with chiral columns in comparison with authentic racemic materials. For single crystal X-ray analysis the intensity data we recollected using Bruker Smart Apex-II. All solvent were purified using standard procedure and store under MS 4 A^o .Silica gel (60-120 mesh) was used for column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25mm).

General procedure for the synthesis of compound (3):

To a solution of o-hydroxycinnamaldehyde **1** (0.5 mmol) in 1 ml DCE were added **II** (20 mol%) and $PhCO_2H$ (20 mol%) at -20 ^{o}C, after 2 hr *α*-nitroketones **2** (0.1 mmol) was added. The reaction mixture was stirred at -20 ^{o}C for 7 days. After completion of reaction, the products were purified by silica gel column chromatography (hexane/ethyl acetate).

(2*R*,4S)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl benzoate (3a):

White solid (85%, 27 mg, >20:1 dr); MP-115 ^{o}C; Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 6.7 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.84 (t, *J* = 2.5 Hz, 1H), 5.04 (dd, *J* = 12.5, 10.3 Hz, 1H), 4.78 (dd, *J* = 12.5, 5.8 Hz, 1H), 3.93 – 3.85 (m, 1H), 2.45 (ddd, *J* = 15.2, 6.6, 3.2 Hz, 1H), 2.37 (dt, *J* = 15.3, 2.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.5, 151.3, 133.9, 130.0, 129.8, 129.4, 129.2, 128.9, 122.6, 118.8, 118.3, 90.4, 80.3, 30.7, 27.1; **ESI-MS**: m/z calcd. for $C_{17}H_{19}N_2O_5^+$ $[M+NH_4^+]^+$ 331.1288, found 331.1291; **FT-IR (KBr)**: 3437, 2925, 1731, 1604, 1584, 1547, 1491, 1451, 1424, 1374, 1270, 1215, 1176, 1137, 1055 cm^{-1}; The ee value 94% (t_{major} = 20.52 min, t_{minor} = 23.40 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 ^{o}C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-methylbenzoate (3b):

White solid (76%, 25 mg, >20:1 dr); MP-146 ^{o}C; Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.27 (s, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 2.3 Hz, 1H), 5.05 (dd, *J* = 12.5, 10.3 Hz, 1H), 4.79 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.92 – 3.86 (m, 1H), 2.45 (ddd, *J* = 15.3, 6.6, 3.2 Hz, 1H), 2.42 (s, 3H), 2.37 (dt, *J* = 15.2, 1.7 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.5, 151.4, 144.8, 130.0, 129.8, 129.6, 129.2, 126.7, 122.5, 118.8, 118.4, 90.3, 80.3, 30.7, 27.2, 21.9; **ESI-MS**: m/z calcd. for $C_{18}H_{21}N_2O_5^+$ $[M+NH_4^+]^+$ 345.1445, found 345.1442**; FT-IR (KBr)**: 3436, 2924, 2853, 1730, 1610, 1582, 1548, 1490, 1426, 1375, 1331, 1274, 1215, 1175, 1091, 1074 cm^{-1}; The ee value 92% (t_{major} = 29.78 min, t_{minor} = 37.72 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 ^{o}C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-isopropylbenzoate (3c):

Colourless sticky oil (84%, 30 mg, >20:1 dr); Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 2.3 Hz, 1H), 5.06 (dd, *J* = 12.6, 10.3 Hz, 1H), 4.78 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.92 – 3.86 (m, 1H), 2.95 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.44 (ddd, *J* = 15.2, 6.6, 3.2 Hz, 1H), 2.36 (dt, *J* = 15.2, 1.9 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.5, 155.5, 151.3, 130.2, 129.8, 129.2, 127.0, 127.0, 122.5, 118.8, 118.4, 90.2, 80.3, 34.5, 30.7, 27.2, 23.8, 23.8; **ESI-MS**: m/z calcd. for $C_{20}H_{25}N_2O_5^+$ $[M+NH_4^+]^+$ 373.1758, found 373.1762; **FT-IR (KBr)**: 3458, 2963, 2927, 2871, 1730, 1610, 1586, 1552, 1490, 1458, 1421, 1379, 1268, 1216, 1180, 1075 cm^{-1}; The ee value 90% (t_{major} = 28.01 min, t_{minor} = 33.01 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 ^{o}C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-*tert*-butylbenzoate (3d):

White semisolid (68%, 25 mg, >20:1 dr); Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.83 (s, 1H), 5.07 (dd, *J* = 12.5, 10.3 Hz, 1H), 4.78 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.94 –

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3.84 (m, 1H), 2.44 (ddd, *J* = 15.2, 6.6, 3.1 Hz, 1H), 2.36 (d, *J* = 15.2 Hz, 1H), 1.32 (s, 9H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.4, 157.7, 151.3, 129.9, 129.8, 129.2, 126.6, 125.9, 122.5, 118.8, 118.4, 90.1, 80.4, 35.4, 31.3, 30.7, 27.2; **ESI-MS**: m/z calcd. for $C_{21}H_{27}N_2O_5^+$ $[M+NH_4^+]^+$ 387.1914, found 387.1918; **FT-IR (KBr)**: 3438, 2960, 2925, 1732, 1607, 1587, 1489, 1458, 1435, 1407, 1379, 1267, 1184, 1214, 1184, 1131 cm^{-1}; The ee value 90% (t_{major} = 22.39 min, t_{minor} = 24.75 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-methoxybenzoate (3e):

White solid (90%, 31 mg, >20:1 dr); MP-120 °C; Rf value 0.3 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 6.8 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.81 (t, *J* = 2.3 Hz, 1H), 5.04 (dd, *J* = 12.6, 10.3 Hz, 1H), 4.78 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.89 (dd, *J* = 10.4, 5.5 Hz, 1H), 3.86 (s, 3H), 2.43 (ddd, *J* = 15.2, 6.5, 3.2 Hz, 1H), 2.35 (dt, *J* = 15.2, 1.9 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.1, 164.1, 151.4, 132.1, 129.8, 129.1, 122.5, 121.6, 118.9, 118.4, 114.1, 90.1, 80.3, 55.7, 30.7, 27.2; **ESI-MS**: m/z calcd. for $C_{18}H_{21}N_2O_6^+$ $[M+NH_4^+]^+$ 361.1394, found 361.1399; **FT-IR (KBr)**: 2924, 2851, 1727, 1605, 1548, 1512, 1491, 1452, 1425, 1377, 1326, 1214, 1185, 1165, 1134, 1091 cm^{-1}; The ee value 92% (t_{major} = 38.43 min, t_{minor} = 47.84 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-ethoxybenzoate (3f):

White semisolid (70%, 25 mg, >20:1 dr); Rf value 0.3 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.96 (d, *J* = 8.9 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.81 (t, *J* = 2.3 Hz, 1H), 5.04 (dd, *J* = 12.6, 10.3 Hz, 1H), 4.78 (dd, *J* = 12.6, 5.8 Hz, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.88 (dt, *J* = 11.0, 6.1 Hz, 1H), 2.43 (ddd, *J* = 15.1, 6.6, 3.2 Hz, 1H), 2.37 – 2.32 (m, 1H), 1.43 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.1, 163.5, 151.4, 132.1, 129.8, 129.1, 122.5, 121.4, 118.8, 118.4, 114.6, 90.1, 80.3, 64.0, 30.7, 27.3, 14.8; **ESI-MS**: m/z calcd. for $C_{19}H_{23}N_2O_6^+$ $[M+NH_4^+]^+$ 375.1551, found 375.1548; **FT-IR (KBr)**: 2984, 2925, 2854, 1724, 1606, 1583, 1549, 1511, 1491, 1455, 1423, 1378, 1378, 1324, 1258, 1214, 1168, 1135, 1113, 1075 cm^{-1}; The ee value 90% (t_{major} = 33.46 min, t_{minor} = 44.58 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-propoxybenzoate (3g):

Yellow semisolid (84%, 31 mg, >20:1 dr); Rf value 0.3 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.96 (d, *J* = 8.9 Hz, 2H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.81 (t, *J* = 2.2 Hz, 1H), 5.04 (dd, *J* = 12.6, 10.3 Hz, 1H), 4.77 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 2H), 3.91 – 3.85 (m, 1H), 2.43 (ddd, *J* = 15.1, 6.4, 3.1 Hz, 1H), 2.35 (d, *J* = 15.2 Hz, 1H), 1.85 – 1.79 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.2, 163.7, 151.4, 132.1, 129.8, 129.1, 122.4, 121.3, 118.8, 118.4, 114.6, 90.1, 80.3, 70.0, 30.7, 27.3, 22.6, 10.6; **ESI-MS**: m/z calcd. for $C_{20}H_{25}N_2O_6^+$ $[M+NH_4^+]^+$ 389.1707, found 389.1703; **FT-IR (KBr)**: 3418, 2966, 2876, 1723, 1604, 1548, 1510, 1492, 1456, 1422, 1377, 1314, 1259, 1214, 1165, 1056 cm^{-1}; The ee value 96% (t_{major} = 28.97 min, t_{minor} = 39.23 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 254 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-isopropoxybenzoate (3h):

Colorless sticky oil (78%, 29 mg, >20:1 dr); Rf value 0.3 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.81 (s, 1H), 5.04 (dd, *J* = 12.3, 10.5 Hz, 1H), 4.78 (dd, *J* = 12.6, 5.8 Hz, 1H), 4.63 (dt, *J* = 12.0, 6.0 Hz, 1H), 3.88 (dd, *J* = 13.2, 8.6 Hz, 1H), 2.43 (ddd, *J* = 15.1, 6.5, 3.1 Hz, 1H), 2.34 (d, *J* = 15.2 Hz, 1H), 1.35 (dd, *J* = 5.9, 3.1 Hz, 6H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.1, 162.6, 151.4, 132.1, 129.8, 129.1, 122.4, 121.1, 118.7, 118.4, 115.5, 90.1, 80.3, 70.4, 30.7, 27.3, 22.1, 22.0; **ESI-MS**: m/z calcd. for $C_{20}H_{25}N_2O_6^+$ $[M+NH_4^+]^+$ 389.1707, found 389.1709; **FT-IR (KBr)**: 3444, 2924, 2854, 1875, 1725, 1606, 1551, 1508, 1489, 1457, 1426, 1380, 1313, 1256, 1165, 1110, 1072 cm^{-1}; The ee value 96% (t_{major} = 28.68 min, t_{minor} = 36.92 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-isobutoxybenzoate (3i):

White semisolid (86%, 33 mg, >20:1 dr); Rf value 0.3 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.81 (t, *J* = 2.3 Hz, 1H), 5.04 (dd, *J* = 12.6, 10.3 Hz, 1H), 4.77 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.91 – 3.85 (m, 1H), 3.76 (d, *J* = 7.8 Hz, 2H), 2.43 (ddd, *J* = 15.1, 6.5, 3.2 Hz, 1H), 2.37 – 2.32 (m, 1H), 2.09 (dt, *J* = 13.3, 6.6 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.2, 163.9, 151.4, 132.1, 129.8, 129.1, 122.5, 121.3, 118.9, 118.4, 114.6, 90.1, 80.3, 74.8, 30.7, 28.4, 27.3, 19.4; **ESI-MS**: m/z calcd. for $C_{21}H_{27}N_2O_6^+$ $[M+NH_4^+]^+$ 403.1864, found 403.1862; **FT-IR (KBr)**: 3421, 2923, 2854, 1722, 1605, 1549, 1511, 1492, 1465, 1377, 1259, 1215, 1165, 1113, 1090 cm^{-1}; The ee value 96% (t_{major} = 22.37 min, t_{minor} = 29.95 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-(allyloxy)benzoate (3j):

White semisolid (60%, 22 mg, >20:1 dr); Rf value 0.35 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.23 (t, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.81 (t, *J* = 2.4 Hz, 1H), 6.03 (ddd, *J* = 22.5, 10.5, 5.3 Hz, 1H), 5.41 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 9.3 Hz, 1H), 5.04 (dd, *J* = 12.6, 10.3 Hz, 1H), 4.77 (dd, *J* = 12.6, 5.8 Hz, 1H), 4.59 (d, *J* = 5.3 Hz, 2H), 3.91 – 3.85 (m, 1H), 2.43 (ddd, *J* = 15.2, 6.6, 3.3 Hz, 1H), 2.34 (dt, *J* = 15.2, 1.9 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.1, 163.1, 151.4, 132.6, 132.1, 129.8, 129.2, 122.5, 121.8, 118.8, 118.5, 118.4, 114.9, 90.2, 80.3, 69.1, 30.8, 27.2; **ESI-MS**: m/z calcd. for $C_{20}H_{23}N_2O_6^+$ $[M+NH_4^+]^+$ 387.1551, found 387.1550; **FT-IR (KBr)**: 3074, 2924,

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2854, 1724, 1606, 1582, 1549, 1510, 1489, 1456, 1424, 1379, 1258, 1214, 1133, 1073 cm^{-1}; The ee value 88% (t_{major} = 35.34 min, t_{minor} = 47.62 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-(benzyloxy)benzoate (3k):

Yellow semisolid (84%, 35 mg, >20:1 dr); Rf value 0.3 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.38 (m, 4H), 7.34 (t, *J* = 7.0 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.1 Hz, 3H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.81 (s, 1H), 5.12 (s, 2H), 5.03 (dd, *J* = 12.5, 10.3 Hz, 1H), 4.77 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.91 – 3.85 (m, 1H), 2.43 (ddd, *J* = 15.1, 6.5, 3.2 Hz, 1H), 2.34 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.0, 163.2, 151.4, 136.2, 132.1, 129.8, 129.1, 128.9, 128.5, 127.6, 122.5, 121.9, 118.8, 118.4, 115.0, 90.2, 80.3, 70.4, 30.7, 27.2; **ESI-MS**: m/z calcd. for $C_{24}H_{25}N_2O_6^+$ $[M+NH_4^+]^+$ 437.1707, found 437.1703; **FT-IR (KBr)**: 3484, 2923, 1724, 1605, 1547, 1510, 1455, 1378, 1260, 1215, 1169, 1087, 999, 946 cm^{-1}; The ee value 96% (t_{major} = 55.84 min, t_{minor} = 75.63 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-fluorobenzoate (3l):

Yellow semisolid (76%, 25 mg, >20:1 dr); Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.05 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 6.8 Hz, 1H), 7.13 (t, *J* = 8.6 Hz, 2H), 7.02 (t, *J* = 7.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.81 (t, *J* = 2.5 Hz, 1H), 5.00 (dd, *J* = 12.5, 10.7 Hz, 1H), 4.76 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.92 – 3.85 (m, 1H), 2.44 (ddd, *J* = 15.3, 6.6, 3.2 Hz, 1H), 2.35 (dt, *J* = 15.3, 2.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 167.2, 165.5, 164.5, 151.3, 132.6 (d, *J* = 9 Hz), 129.9, 129.2, 125.7 (d, *J* = 3 Hz), 122.6, 118.7, 118.4, 116.1 (d, *J* = 22.5 Hz), 90.6, 80.2, 30.7, 27.1; **ESI-MS**: m/z calcd. for $C_{17}H_{18}FN_2O_5^+$ $[M+NH_4^+]^+$ 349.1194, found 349.1193**; FT-IR (KBr)**: 3436, 2924, 2853, 1731, 1603, 1550, 1507, 1490, 1453, 1426, 1375, 1272, 1237, 1154, 1055 cm^{-1}; The ee value 84% (t_{major} = 26.13 min, t_{minor} = 31.26 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-chlorobenzoate (3m):

White solid (72%, 25 mg, >20:1 dr); MP-125 °C; Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 2.1 Hz, 1H), 4.98 (dd, *J* = 12.4, 10.7 Hz, 1H), 4.76 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.92 – 3.85 (m, 1H), 2.44 (ddd, *J* = 15.3, 6.5, 3.2 Hz, 1H), 2.35 (dt, *J* = 15.3, 1.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.7, 151.2, 140.4, 131.3, 129.9, 129.3, 129.2, 127.9, 122.7, 118.6, 118.4, 90.7, 80.2, 30.7, 27.0; **ESI-MS**: m/z calcd. for $C_{17}H_{18}ClN_2O_5^+$ $[M+NH_4^+]^+$ 365.0899, found 365.0898; **FT-IR (KBr)**: 3436, 2973, 2924, 1729, 1590, 1548, 1488, 1452, 1400, 1375, 1329, 1274, 1215, 1170, 1136, 1095, 1057, 1008 cm^{-1}; The ee value 82% (t_{major} = 27.65 min, t_{minor} = 32.06 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 4-bromobenzoate (3n):

White solid (70%, 27 mg, >20:1 dr); MP-157 °C; Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.89 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 6.9 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.81 (t, *J* = 2.4 Hz, 1H), 4.98 (dd, *J* = 12.4, 10.7 Hz, 1H), 4.75 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.92 – 3.85 (m, 1H), 2.44 (ddd, *J* = 15.3, 6.5, 3.2 Hz, 1H), 2.35 (dt, *J* = 15.3, 1.9 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.8, 151.2, 132.3, 131.4, 129.9, 129.2, 129.1, 128.3, 122.7, 118.6, 118.4, 90.8, 80.2, 30.7, 27.0; **ESI-MS**: m/z calcd. for $C_{17}H_{18}BrN_2O_5^+$ $[M+NH_4^+]^+$ 409.0394, found 409.0394; **FT-IR (KBr)**: 3436, 2922, 2847, 1729, 1588, 1543, 1488, 1429, 1377, 1332, 1271, 1217, 1134, 1071, 1010, 934 cm^{-1}; The ee value 88% (t_{major} = 30.48 min, t_{minor} = 34.88 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 3-methylbenzoate (3o):

Yellow semisolid (69%, 23 mg, >20:1 dr); Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.85 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 2.3 Hz, 1H), 5.06 (dd, *J* = 12.6, 10.4 Hz, 1H), 4.77 (dd, *J* = 12.7, 5.8 Hz, 1H), 3.92 – 3.86 (m, 1H), 2.44 (ddd, *J* = 15.2, 6.5, 3.2 Hz, 1H), 2.40 (s, 3H), 2.36 (dt, *J* = 15.2, 1.9 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.6, 151.4, 138.8, 134.6, 130.6, 129.8, 129.3, 129.2, 128.8, 127.1, 122.5, 118.8, 118.4, 90.4, 80.2, 30.7, 27.2, 21.4; **ESI-MS**: m/z calcd. for $C_{18}H_{21}N_2O_5^+$ $[M+NH_4^+]^+$ 345.1445, found 345.1449; **FT-IR(KBr)**: 3059, 2918, 2855, 1731, 1608, 1548, 1487, 1457, 1434, 1382, 1329, 1298, 1276, 1217, 1188, 1130, 1112, 1070, 1051 cm^{-1}; The ee value 86% (t_{major} = 23.69 min, t_{minor} = 27.79 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 3-chlorobenzoate (3p):

White solid (78%, 27 mg, >20:1 dr); MP-127 °C, Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.03 (t, *J* = 1.6 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.1 Hz, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 2.3 Hz, 1H), 4.99 (dd, *J* = 12.4, 10.8 Hz, 1H), 4.77 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.92 – 3.86 (m, 1H), 2.44 (ddd, *J* = 15.3, 6.5, 3.2 Hz, 1H), 2.36 (dt, *J* = 15.3, 2.0 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.4, 151.2, 135.1, 133.9, 131.2, 130.2, 130.1, 129.9, 129.2, 128.0, 122.7, 118.6, 118.4, 90.9, 80.2, 30.7, 27.0; **ESI-MS**: m/z calcd. for $C_{17}H_{18}ClN_2O_5^+$ $[M+NH_4^+]^+$ 365.0899, found 365.0894; **FT-IR (KBr)**: 2920, 2844, 1734, 1579, 1548, 1488, 1461, 1435, 1382, 1330, 1287, 1254, 1209, 1136, 1117, 1069, 1051 cm^{-1}; The ee value 86% (t_{major} = 25.81 min, t_{minor} = 28.60 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 2-methylbenzoate (3q):

Yellow semisolid (80%, 26 mg, >20:1 dr); Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.42

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(t, *J* = 7.5 Hz, 1H), 7.28 – 7.22 (m, 4H), 7.17 (t, *J* = 9.8 Hz, 1H), 7.00 (dd, *J* = 17.5, 7.9 Hz, 2H), 6.81 (t, *J* = 2.5 Hz, 1H), 4.98 (dd, *J* = 12.4, 10.4 Hz, 1H), 4.72 (dd, *J* = 12.5, 5.6 Hz, 1H), 3.89 – 3.83 (m, 1H), 2.60 (s, 3H), 2.44 (ddd, *J* = 15.2, 6.6, 3.1 Hz, 1H), 2.37 (dt, *J* = 15.2, 2.0 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.8, 151.4, 141.2, 132.8, 132.1, 130.3, 129.8, 129.2, 128.8, 126.1, 122.5, 118.9, 118.3, 90.0, 80.3, 30.8, 27.2, 21.7; **ESI-MS**: m/z calcd. for $C_{17}H_{21}N_2O_5^+$ [M+NH$_4^+$]$^+$ 345.1445, found 345.144; **FT-IR (KBr)**: 2923, 2853, 1726, 1587, 1550, 1488, 1454, 1432, 1377, 1331, 1249, 1214, 1191, 1128, 1065, 1037 cm^{-1}; The ee value 96% (t_{major} = 19.05 min, t_{minor} = 32.28 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 2-methoxybenzoate (3r):

Colorless sticky oil (73%, 25 mg, >20:1 dr); Rf value 0.3 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.80 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.48 (t, *J* = 8.7 Hz, 1H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.01 – 6.96 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.85 (t, *J* = 2.2 Hz, 1H), 5.09 (dd, *J* = 13.0, 9.2 Hz, 1H), 4.79 (dd, *J* = 13.0, 6.0 Hz, 1H), 3.85 (dd, *J* = 14.7, 6.8 Hz, 1H), 3.72 (s, 3H), 2.45 (ddd, *J* = 15.1, 6.8, 3.1 Hz, 1H), 2.38 (d, *J* = 15.1 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.4, 159.2, 151.4, 134.5, 132.4, 129.6, 129.2, 122.4, 120.6, 119.4, 119.3, 118.4, 112.2, 89.7, 80.3, 55.9, 30.5, 27.5; **ESI-MS**: m/z calcd. for $C_{18}H_{21}N_2O_6^+$ [M+NH$_4^+$]$^+$ 361.1394, found 361.1390; **FT-IR (KBr)**: 2923, 2852, 1726, 1603, 1550, 1490, 1462, 1436, 1380, 1297, 1251, 1212, 1185, 1037, 946 cm^{-1}; The ee value 90% (t_{major} = 41.06 min, t_{minor} = 33.79 min) was determined by HPLC using Daicel Phenomenex Lux Amalyse-A2 with hexane/i-PrOH (90:10) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 2-fluorobenzoate (3s):

White semisolid (91%, 30 mg, >20:1 dr); Rf value 0.5 (5:95 EA in hex**); ^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.98 (t, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 12.6, 6.3 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.15 – 7.10 (m, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.87 (s, 1H), 5.14 – 5.05 (m, 1H), 4.75 (dd, *J* = 12.9, 5.8 Hz, 1H), 3.86 (dd, *J* = 15.0, 6.3 Hz, 1H), 2.46 (ddd, *J* = 15.2, 6.6, 3.1 Hz, 1H), 2.40 (d, *J* = 15.3 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 163.3, 162.8, 161.1, 151.1, 135.5 (d, *J* = 9 Hz), 132.8, 129.7, 129.3, 124.6 (d, *J* = 3 Hz), 122.7, 119.2, 118.3, 118.0 (d, *J* = 10.5 Hz), 117.4 (d, *J* = 22.5 Hz), 117.3, 90.3, 80.2, 80.1, 30.4, 27.4; **ESI-MS**: m/z calcd. for $C_{17}H_{18}FN_2O_5^+$ [M+NH$_4^+$]$^+$ 349.1194, found 349.1199; **FT-IR (KBr)**: 3463, 2925, 2853, 1744, 1723, 1612, 1583, 1547, 1489, 1454, 1374, 1330, 1292, 1252, 1161, 1138 cm^{-1}; The ee value 84% (t_{major} = 26.44 min, t_{minor} = 35.42 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl 2,4-dimethylbenzoate (3t):

White solid (91%, 31 mg, >20:1 dr); MP-112 °C, Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.08 – 6.97 (m, 4H), 6.79 (t, *J* = 2.4 Hz, 1H), 4.98 (dd, *J* = 12.5, 10.3 Hz, 1H), 4.72 (dd, *J* = 12.5, 5.7 Hz, 1H), 3.89 – 3.83 (m, 1H), 2.57 (s, 3H), 2.43 (ddd, *J* = 15.1, 6.7, 3.1 Hz, 1H), 2.37 (t, *J* = 1.9 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.7, 151.5, 143.5, 141.5, 132.9, 130.5, 129.7, 129.2, 126.9, 125.8, 122.5, 119.0, 118.3, 89.8, 80.3, 30.8, 27.3, 21.7, 21.6; **ESI-MS**: m/z calcd. for $C_{19}H_{23}N_2O_5^+$ [M+NH$_4^+$]$^+$ 359.1601, found 359.1601; **FT-IR (KBr)**: 2961, 2931, 1726, 1610, 1582, 1548, 1457, 1429, 1337, 1256, 1217, 1151, 1070, 1044 cm^{-1}; The ee value 94% (t_{major} = 17.84 min, t_{minor} = 28.59 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 274 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl cyclohexanecarboxylate (3u):

Colorless sticky oil (47%, 15 mg, >20:1 dr); Rf value 0.55 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.23 (t, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.61 (t, *J* = 2.3 Hz, 1H), 4.92 (dd, *J* = 12.6, 10.3 Hz, 1H), 4.69 (dd, *J* = 12.6, 5.8 Hz, 1H), 3.84 – 3.77 (m, 1H), 2.34 – 2.28 (m, 2H), 2.19 (dt, *J* = 15.2, 1.9 Hz, 1H), 1.95 – 1.89 (m, *J* = 7.5, 3.5, 1.8 Hz, 1H), 1.88 – 1.83 (m, 1H), 1.77 – 1.70 (m, 2H), 1.65 – 1.61 (m, 1H), 1.46 – 1.39 (m, 2H), 1.30 – 1.27 (m, 1H), 1.24 – 1.18 (m, 2H); **^{13}C NMR (150 MHz, CDCl3)** δ 174.5, 151.3, 129.7, 129.2, 122.4, 118.9, 118.3, 89.2, 80.3, 43.4, 30.7, 29.00, 28.9, 27.1, 25.8, 25.5; **ESI-MS**: m/z calcd. for $C_{17}H_{25}N_2O_5^+$ [M+NH$_4^+$]$^+$ 337.1758, found 337.1757; **FT-IR (KBr)**: 3445, 2931, 2855, 1748, 1586, 1552, 1490, 1454, 1379, 1221, 1158, 1116, 1076 cm^{-1}; The ee value 94% (t_{major} = 13.69 min, t_{minor} = 15.63 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-6-chloro-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl benzoate (3v):

White solid (89%, 31 mg, >20:1 dr); MP-110 °C, Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 6.9 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.19 (dd, *J* = 16.4, 2.4 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.83 (t, *J* = 2.3 Hz, 1H), 5.04 (dd, *J* = 12.7, 10.4 Hz, 1H), 4.76 (dd, *J* = 12.7, 5.7 Hz, 1H), 3.91 – 3.83 (m, 1H), 2.42 (ddd, *J* = 15.3, 6.5, 3.1 Hz, 1H), 2.36 (dt, *J* = 15.3, 2.0 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.3, 149.9, 134.0, 130.0, 129.9, 129.2, 128.9, 128.8, 127.4, 120.4, 119.8, 90.2, 79.9, 30.5, 26.9; **ESI-MS**: m/z calcd. for $C_{17}H_{14}ClNaNO_5$ [M+Na] 370.0458, found 370.0446; **FT-IR (KBr)**: 3438, 3046, 2922, 1732, 1582, 1549, 1482, 1549, 1485, 1452, 1411, 1379, 1266, 1215, 1179, 1137, 1056 cm^{-1}; The ee value 90% (t_{major} = 26.43 min, t_{minor} = 34.29 min) was determined by HPLC using Daicel Chiralpak IB with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-6-bromo-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl benzoate (3w):

White solid (93%, 36 mg, >20:1 dr); MP-125 °C, Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.31 (m, 2H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.83 (s, 1H), 5.04 (dd, *J* = 12.7, 10.4 Hz, 1H), 4.76 (dd, *J* = 12.7, 5.6 Hz, 1H), 3.90 – 3.84 (m, 1H), 2.42 (ddd, *J* = 15.3, 6.5, 3.2 Hz, 1H), 2.36 (dt, *J* = 15.3, 2.0 Hz, 1H); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 165.3, 150.5, 134.0, 132.8, 131.7, 130.0, 129.2, 129.0, 120.9, 120.2, 114.6, 90.2, 79.9, 30.5, 26.9; **ESI-MS**: m/z calcd. for $C_{17}H_{18}BrN_2O_5^+$ [M+NH$_4^+$]$^+$ 409.0394, found 409.0386; **FT-IR (KBr)**: 3436, 2923, 2853, 1731, 1579,

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1549, 1481, 1451, 1429, 1379, 1265, 1213, 1178, 1137, 1053 cm^{-1}; The ee value 84% (t_{major} = 34.03 min, t_{minor} = 32.45 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-6,8-dichloro-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl benzoate (3x):

White solid (81%, 31mg); MP-130 °C, Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.3 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 6.94 (t, *J* = 2.4 Hz, 1H), 5.00 (dd, *J* = 12.8, 10.0 Hz, 1H), 4.76 (dd, *J* = 12.8, 5.9 Hz, 1H), 3.93 – 3.87 (m, 1H), 2.44 (ddd, *J* = 15.3, 6.3, 3.1 Hz, 1H), 2.39 (dt, *J* = 15.3, 2.1 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 164.8, 146.3, 134.1, 130.3, 130.0, 129.0, 129.0, 127.3, 127.1, 124.3, 121.8, 90.3, 79.7, 30.7, 27.1; **ESI-MS**: m/z calcd. for $C_{17}H_{17}Cl_2N_2O_5^+$ $[M+NH_4^+]^+$ 399.0509, found 399.0504; **FT-IR (KBr)**: 3446, 3070, 2925, 1737, 1646, 1552, 1458, 1376, 1319, 1266, 1181, 1128, 1070, 1020 cm^{-1}; The ee value 92% (t_{major} = 41.38 min, t_{minor} = 46.01 min) was determined by HPLC using Daicel Chiralpak IB with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-6,8-dibromo-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl benzoate (3y):

Yellow semisolid (51%, 24mg); Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.64 (s, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.28 (s, 1H), 6.93 (s, 1H), 5.00 (dd, *J* = 12.6, 10.2 Hz, 1H), 4.75 (dd, *J* = 12.8, 5.8 Hz, 1H), 3.95 – 3.83 (m, 1H), 2.43 (ddd, *J* = 15.2, 6.1, 3.1 Hz, 1H), 2.38 (d, *J* = 15.3 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.8, 147.7, 135.9, 134.1, 130.9, 130.0, 129.0, 129.0, 122.2, 114.5, 113.5, 90.5, 79.7, 30.7, 27.1; **ESI-MS**: m/z calcd. for $C_{17}H_{17}Br_2N_2O_5^+$ $[M+NH_4^+]^+$ 486.9484, found 486.9469; **FT-IR (KBr)**: 3438, 2923, 2853, 1731, 1635, 1549, 1450, 1374, 1314, 1266, 1224, 1162, 1128, 1071, 1046 cm^{-1}; The ee value 90% (t_{major} = 76.60 min, t_{minor} = 53.67 min) was determined by HPLC using Daicel Chiralpak IC with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-8-bromo-6-chloro-3,4-dihydro-4-(nitromethyl)-2*H*-chromen-2-yl benzoate (3z):

White solid (60%, 25 mg , >20:1 dr); MP-130 °C; Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.49 (dd, *J* = 16.5, 8.8 Hz, 3H), 7.15 (d, *J* = 2.3 Hz, 1H), 6.93 (s, 1H), 5.00 (dd, *J* = 12.8, 10.0 Hz, 1H), 4.76 (dd, *J* = 12.8, 5.9 Hz, 1H), 3.94 – 3.84 (m, 1H), 2.44 (ddd, *J* = 15.3, 6.3, 3.1 Hz, 1H), 2.39 (d, *J* = 15.3 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 164.8, 147.2, 134.1, 133.2, 130.0, 129.0, 129.0, 128.0, 127.6, 121.7, 113.1, 90.5, 79.7, 30.8, 27.1; **ESI-MS**: m/z calcd. for $C_{17}H_{17}BrClN_2O_5^+$ $[M+NH_4^+]^+$ 443.0004, found 443.0001; **FT-IR (KBr)**: 3444, 2920, 2853, 1732, 1601, 1549, 1454, 1375, 1314, 1268, 1224, 1206, 1171, 1122, 1084, 1066 cm^{-1}; The ee value 96% (t_{major} = 126.00 min, t_{minor} = 106.66 min) was determined by HPLC using Daicel Chiralpak IB with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-7-methoxy-4-(nitromethyl)chroman-2-yl benzoate (3z^1):

White sticky solid (93%, 33 mg, >20:1 dr); Rf value 0.5 (5:95 EA in hex) **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.81 (s, 1H), 6.59 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 5.00 (dd, *J* = 12.3, 10.3 Hz, 1H), 4.74 (dd, *J* = 12.4, 5.8 Hz, 1H), 3.81 (d, *J* = 8.7 Hz, 1H), 3.75 (s, 3H), 2.42 (ddd, *J* = 15.2, 6.6, 3.1 Hz, 1H), 2.34 (d, *J* = 15.2 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.5, 160.7, 152.1, 133.9, 129.9, 129.8, 129.4, 128.9, 110.7, 109.9, 102.6, 90.4, 80.4, 55.6, 30.2, 27.2; **ESI-MS**: m/z calcd. for $C_{18}H_{21}N_2O_6^+$ $[M+NH_4^+]^+$ 361.1394, found 361.1390; **FT-IR (KBr)**: 2923, 2852, 1726, 1603, 1550, 1490, 1462, 1436, 1380, 1297, 1251, 1212, 1185, 1037, 946 cm^{-1}; The ee value 60% (t_{major} = 26.01 min, t_{minor} = 33.49 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-6-methyl-4-(nitromethyl)-2*H*-chromen-2-yl benzoate (3z^2):

White semisolid (85%, 27 mg >20:1 dr); Rf value 0.5 (5:95 EA in hex); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.97 (s, 1H), 6.90 – 6.78 (m, 2H), 5.03 (dd, *J* = 12.4, 10.5 Hz, 1H), 4.77 (dd, *J* = 12.5, 5.6 Hz, 1H), 3.90 – 3.77 (m, 1H), 2.48 – 2.31 (m, 2H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.5, 149.1, 133.8, 132.0, 130.5, 130.0, 129.5, 129.3, 128.9, 118.4, 118.1, 90.5, 80.4, 30.7, 27.2, 20.7; **ESI-MS**: m/z calcd. for $C_{18}H_{21}N_2O_5^+$ $[M+NH_4^+]^+$ 345.1445, found 345.1443; **FT-IR (KBr)**: 2925, 2853, 1727, 1551, 1500, 1450, 1378, 1318, 1272, 1172, 1142, 1026 cm^{-1}; The ee value 90% (t_{major} = 23.82 min, t_{minor} = 21.75 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-3,4-dihydro-6-nitro-4-(nitromethyl)-2*H*-chromen-2-yl benzoate (3z^3):

Yellow semisolid (88%, 31 mg >20:1 dr); Rf value 0.5 (7:93 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.19 – 8.11 (m, 2H), 8.01 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 9.0 Hz, 1H), 6.91 (t, *J* = 2.5 Hz, 1H), 5.08 (dd, *J* = 12.8, 10.5 Hz, 1H), 4.84 (dd, *J* = 12.9, 5.7 Hz, 1H), 4.00 (dd, *J* = 6.6, 3.5 Hz, 1H), 2.51 – 2.42 (m, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.0, 156.6, 142.7, 134.3, 130.0, 129.0, 128.8, 125.6, 125.5, 119.7, 119.3, 90.3, 79.4, 30.6, 26.8; **ESI-MS**: m/z calcd. for $C_{17}H_{18}N_3O_7^+$ $[M+NH_4^+]^+$ 376.1139, found 376.1140; **FT-IR (KBr)**: 2922, 2855, 1727, 1623, 1586, 1545, 1481, 1446, 1419, 1345, 1270, 1227, 1086, 1022 cm^{-1}; The ee value 68% (t_{major} = 93.50 min, t_{minor} = 90.17 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97.5:2.5) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-4-((benzamido)methyl)-3,4-dihydro-2*H*-chromen-2-yl benzoate (5):

White semisolid (58%, 22 mg); Rf value 0.3 (10:90 EA in hex); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.40 (m, 4H), 7.28 (d, *J* = 9.4 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 17.4, 7.9 Hz, 2H), 6.83 (s, 1H), 6.39 (s, 1H), 4.06 – 3.97 (m, 1H), 3.95 – 3.87 (m, 1H), 3.41 (s, 1H), 2.39 (d, *J* = 2.4 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 167.9, 165.6, 151.5, 134.5, 133.8, 131.9, 130.0, 129.7, 129.3, 128.9, 128.8, 128.8, 127.0, 122.7, 122.1, 117.9, 91.5, 45.4, 31.8, 28.3; **ESI-MS**: m/z calcd. for $C_{17}H_{14}NaNO_5$ [M+Na] 410.1368, found 410.1364; **FT-IR (KBr)**: 3336, 2922, 2851, 1732, 1639, 1580, 1487, 1380, 1451, 1311,

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1270, 1214, 1187, 1073 cm^{-1}; The ee value 86% (t_{major} = 25.92 min, t_{minor} = 29.42 min) was determined by HPLC using Daicel Chiralpak IC with hexane/i-PrOH (88:12) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

***tert*-butyl((2*R*,4*S*)-2-(benzoyloxy)-3,4-dihydro-2*H*-chromen-4-yl)methylcarbamate (6):**

Yellow semisolid (58%, 22 mg); Rf value 0.5 (10:90 EA in hex); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.10 (m, 2H), 7.03 – 6.95 (m, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.80 (s, 1H), 4.81 (s, 1H), 3.76 – 3.65 (m, 1H), 3.51 (s, 1H), 3.21 (s, 1H), 2.32 (s, 2H), 1.46 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.6, 156.2, 151.5, 133.7, 130.0, 129.7, 129.3, 128.8, 128.6, 122.7, 122.0, 117.7, 91.4, 79.7, 46.1, 32.1, 28.6, 27.8; **ESI-MS**: m/z calcd. for $C_{17}H_{15}BrNO_5^+$ $[M+H^+]^+$ 384.1805, found 384.1810; **FT-IR (KBr)**: 3389, 2977, 2926, 1735, 1692, 1528, 1488, 1450, 1371, 1274, 1218, 1174, 1073, 1030 cm^{-1}; The ee value 92% (t_{major} = 25.82 min, t_{minor} = 31.04 min) was determined by HPLC using Daicel Chiralpak IA with hexane/i-PrOH (97:3) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2*R*,4*S*)-4-((1*H*-imidazol-1-yl)methyl)-3,4-dihydro-2*H*-chromen-2-yl benzoate (7):

Colorless sticky oil (75%, 25 mg); Rf value 0.5 (50:50 EA in hex); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.41 (s, 1H), 7.25 – 7.20 (m, 1H), 7.11 (s, 1H), 6.96 (t, *J* = 7.3 Hz, 3H), 6.87 (t, *J* = 2.8 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 4.46 – 4.42 (m, 2H), 3.33 (d, *J* = 7.6 Hz, 1H), 2.31 (ddd, *J* = 15.0, 6.9, 3.2 Hz, 1H), 2.16 (dt, *J* = 15.0, 2.4 Hz, 1H; **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.4, 151.1, 137.8, 134.0, 130.2, 129.9, 129.5, 129.3, 129.3, 129.0, 122.3, 120.6, 119.2, 90.8, 52.6, 34.1, 29.9, 27.2; **ESI-MS**: m/z calcd. for $C_{20}H_{19}N_2O_3^+$ $[M+H^+]^+$ 335.1390, found 335.1388; FT-IR (KBr): 3419, 2923, 2853, 1723, 1583, 1489, 1451, 1366, 1266, 1214, 1133, 1050, 995, 936 cm^{-1}; The ee value 92% (t_{major} = 47.05 min, t_{minor} = 38.38 min) was determined by HPLC using Daicel Chiralpak IC with hexane/i-PrOH (70:30) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(*S*)-3,4-dihydro-4-(nitromethyl)-2*H*-chromene (8):

Colorless sticky oil (95%, 18 mg); Rf value 0.5 (3:97 EA in hex); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.18 (t, *J* = 7.1 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 4.71 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.55 (dd, *J* = 12.2, 10.8 Hz, 1H), 4.27 (dt, *J* = 11.4, 4.3 Hz, 1H), 4.20 – 4.13 (m, 1H), 3.72 (td, *J* = 9.9, 4.7 Hz, 1H), 2.24 – 2.16 (m, 1H), 1.96-1.92 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 155.1, 129.2, 129.0, 121.1, 119.6, 117.9, 80.1, 62.5, 33.0, 25.1; **ESI-MS**: m/z calcd. for $C_{10}H_{11}NaNO_3$ [M+Na] 216.0637, found 216.1251; **FT-IR (KBr)**: 3445, 2923, 2853, 1740, 1582, 1551, 1490, 1456, 1379, 1263, 1226, 1118, 1038 cm^{-1}; The ee value 92% (t_{major} = 11.57 min, t_{minor} = 22.38 min) was determined by HPLC using Daicel Chiralpak IB with hexane/i-PrOH (98:2) as the eluent, flow: 1.0 mL/min, 220 nm, 25 °C.

(2R,4S)-6-chloro-4-(nitromethyl)chroman-2-yl 4-methoxybenzoate ($3z_5$):

White solid (70%, 26mg); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.00 – 7.92 (m, 2H), 7.20 – 7.15 (m, 2H), 6.92 (dd, *J* = 13.7, 7.8 Hz, 3H), 6.80 (t, *J* = 2.5 Hz, 1H), 5.02 (dd, *J* = 12.8, 10.2 Hz, 1H), 4.76 (dd, *J* = 12.8, 5.7 Hz, 1H), 3.88 – 3.83 (m, 4H), 2.40 (ddd, *J* = 15.2, 6.5, 3.2 Hz, 1H), 2.34 (dt, *J* = 15.3, 2.1 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 165.0, 164.2, 150.1, 132.1, 129.9, 128.7, 127.3, 121.4, 120.4, 119.8, 114.2, 90.0, 79.9, 55.7, 30.6, 27.0.

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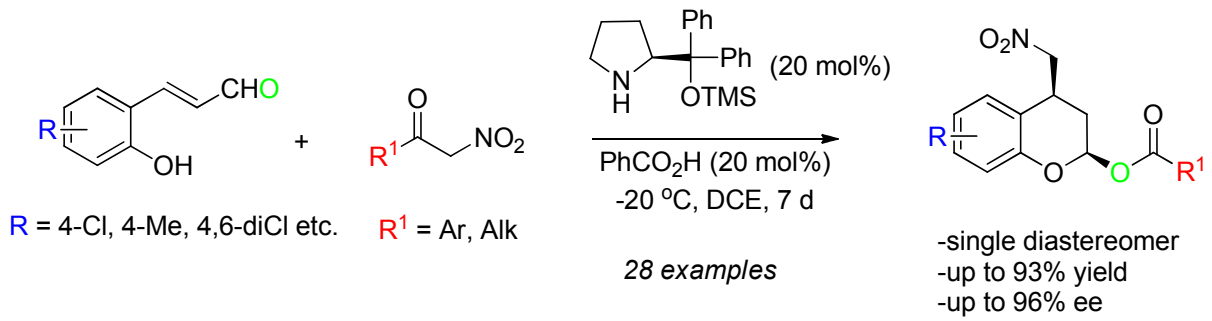

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