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PAPER

Synthesis of 2,3,5,6-tetrahydro-1-alkyl/aryl-1*H*-benzo[*f*]chromen-3-ol derivatives from β-tetralones and α,β-unsaturated aldehydes†

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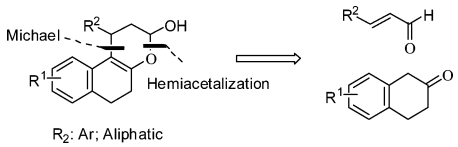
Organocatalytic domino Michael–hemiacetalization of β-tetralones with α,β-unsaturated aldehydes is presented. Treatment of β-tetralones with α,β-unsaturated aldehydes in the presence of diphenylprolinol silyl ether gave 2,3,5,6-tetrahydro-1-alkyl/aryl-1*H*-benzo[*f*]chromen-3-ol derivatives with high to excellent chemical yields (50–99%) and high levels of enantioselectivities (up to 96% ee).

Introduction

Six-membered oxygenated benzopyrans such as chromans, chromenes, and flavanones exhibit one of the most important structural motifs in natural products total synthesis.[1] The synthesis of functionalized derivatives for the study of diverse biological profiles has attracted attention in both academia and the pharmaceutical industry.[2] Asymmetric organocatalysis has proven to be a highly effective means of developing novel methodologies in organic synthesis.[3] In recent years, the scope of this field has been expanded to include multicomponent domino reactions for the preparation of complex molecules with more than one stereogenic center.[4] An organocatalytic cascade reaction of α,β-unsaturated aldehydes with various enolizable carbonyl compounds has been utilized to synthesize 3,4-dihydropyran,[5] hydroxyquinone,[6] 3,4-dihydropyranones,[7] chromene derivatives[8] and many other intermediates.[9] Benzochromenes are found in numerous natural products and are important pharmacophores of many biologically active compounds.[10]

Functionalization of β-tetralone at the benzylic position has been documented.[11] For example, treatment of cinnamaldehyde with β-tetralone under acidic conditions affords Michael–dehydration conjugate products.[12] To the best of our knowledge, the asymmetric synthesis of multifunctionalized 2,3,5,6-tetrahydro-1*H*-benzo[*f*]chromen-3-ol derivatives from β-tetralone and α,β-unsaturated aldehydes catalyzed by an organocatalyst has not been reported. This work describes the first organocatalytic reaction of β-tetralones with α,β-unsaturated aldehydes to construct optically enriched 2,3,5,6-tetrahydro-1-substituent-1*H*-benzo[*f*]chromen-3-ol derivatives through a domino Michael–hemiacetalization sequence.



Results and discussion

Investigations were begun using β-tetralone (**1a**) and *trans*-cinnamaldehyde (**2a**) as model substrates in the presence of a catalytic amount of diphenylprolinol silyl ether **I**.[13] The corresponding benzochromene product **3aa** was obtained under neat conditions with moderate stereoselectivity and low chemical yield (Table 1, entry 1). We next studied the solvent effects of the sequential process. No improvement was observed when weakly polar organic solvents were used (Table 1, entries 2–4). Both the reactivity and stereoselectivity of the products decreased when protic methanol was used (Table 1, entry 5). The reactivity was enhanced when the reaction was conducted in CH_3CN and further improved when DMSO was used (Table 1, entries 6–7). These effects may have been caused by the stabilization of the reaction intermediate by the polar aprotic solvents. Various L-proline derived organocatalysts were tested in the domino reaction. The incorporation of the sterically encumbered naphthalene group into organocatalysts **II**–**IV** resulted in high chemical yields and low enantioselectivities of the desired product **3aa** (Table 1, entries 8–10). Interestingly, the opposite enantiomer of **3aa** dominated when catalyst **II** was adopted (Table 1, entry 8).[14] The use of the camphor–pyrrolidine derived organocatalysts **V**–**VII**[15] failed to improve the stereoselectivity of the domino Michael–hemiacetalization reaction (Table 1, entries 11–13). The structure of benzo[*f*]chromenol **3aa** was characterized by IR, ^1H, ^{13}C NMR and DEPT NMR spectroscopy. The diastereo-/enantioselectivities were determined by chiral HPLC analyses. The ratio of the hemiacetal anomers typically ranges from 5 : 1 to 7 : 1. Organocatalyst **I** was the catalyst of choice for the process.

The reaction conditions were fine-tuned by examining the effects of additives. Various acidic and basic additives were studied.

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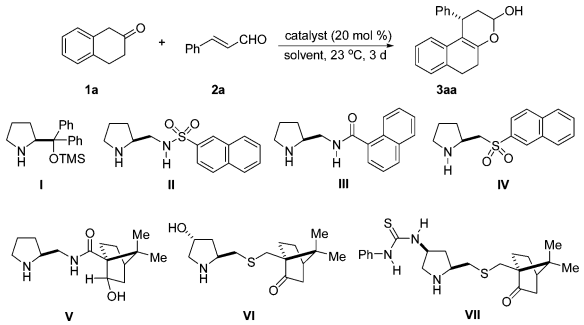
Table 1 Domino Michael–hemiacetalization: solvents and catalysts survey[a]

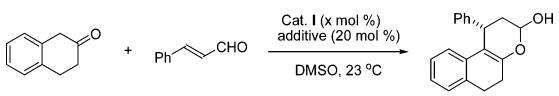


Entry	Catalyst	Solvent	Yield (%)[b]	ee (%)[c]
1	**I**	neat	41	63
2	**I**	toluene	34	35
3	**I**	CH_2Cl_2	59	60
4	**I**	$CHCl_3$	49	42
5	**I**	MeOH	39	17
6	**I**	CH_3CN	70	69
7	**I**	**DMSO**	**91**	**72**
8	**II**	DMSO	81	–40
9	**III**	DMSO	99	–2
10	**IV**	DMSO	98	15
11	**V**	DMSO	93	–4
12	**VI**	DMSO	79	15
13	**VII**	DMSO	94	33

[a] Reaction conditions: **1a** (0.20 mmol) and catalyst (20 mol%) were dissolved in the solvent (0.5 mL) indicated at 23 °C, then **2a** (0.80 mmol) was added. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

High enantioselectivities with low chemical yields were obtained when an acidic additive was employed in the reaction (Table 2, entries 1–3). Both the reactivity and the enantioselectivity dropped considerably when DBU was used but rebounded when DMAP was used instead (Table 2, entries 5 and 6). The reactivity increased when DABCO was used and the product was obtained with high stereoselectivity. Thus, in the presence of DABCO, the reaction

Table 2 Optimization of the domino reaction[a]



Entry	**Cat. I** (mol%)	Additive	Time (d)	Yield[b]	ee (%)[c]
1	20	NH_4Cl	3	39	81
2	20	PhCOOH	3	66	74
3	20	AcOH	3	66	71
4	20	TsOH	3	*trace*	—
5	20	DBU	1.5	27	0
6	20	DMAP	1.5	74	88
7	20	DABCO	1	97	88
8	25	DABCO	1	80	84
9	10	DABCO	1	94	88
10	5	DABCO	1	73	89
11[d]	20	DABCO	1	99	88
12[d]	**10**	**DABCO**	**1**	**97**	**90**

[a] Unless otherwise noted, the reaction was performed using **1a** (0.20 mmol), **Cat. I**, additive (20 mol%) and **2a** (0.80 mmol) in DMSO (0.5 mL) at 23 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The reaction was carried out at 0 °C.

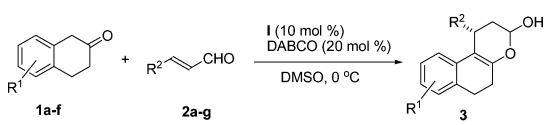
proceeded rapidly to give the corresponding **3aa** in 97% yield and 88% ee after 24 h (Table 2, entry 7).

Variations of catalyst loading were investigated to optimize the reaction conditions. Comparable stereoselectivity with decreased chemical yield was obtained when the reaction were carried out in the presence of 25 and 5 mol% of catalyst, respectively (Table 2, entries 8 and 10). The chemical yield was regained with comparable selectivity when 10 mol% of the catalyst was used (Table 2, entry 9). The selectivity was slightly improved by performing the reaction at 0 °C. Finally, the optimal reaction conditions were realized by using 10 mol% of catalyst **I** and 20 mol% of DABCO at 0 °C (Table 2, entry 12).

The scope and general utility of the organocatalytic Michael–hemiacetalization were exploited using various β-tetralones **1a–f** and α,β-unsaturated aldehydes **2a–g** (Table 3). Substituted β-tetralones reacted efficiently with **2a** to generate the corresponding products with excellent chemical yields and high enantioselectivities (Table 3, entries 1, 3–5). The use of 6-methoxy-β-tetralone **1c** resulted in a low chemical yield owing to the ready decomposition of the starting substrate (Table 3, entry 2).

Various α,β-unsaturated aldehydes were also tolerated with **1a** under the reaction conditions (Table 3, entries 7–11). However, 1,2-addition–dehydration products were observed when specific substrates were adopted.[16] Therefore, the use of *trans*-4-bromocinnamaldehyde with β-tetralone gave the desired product with 60% chemical yield together with 25% of the 1,2-addition–dehydration product (Table 3, entry 7).[17] The reaction was carried out at –20 °C to avoid the side reaction and failed. Comparable results were obtained when the starting enals **2d–e** were used with isolated yields of 15 and 40%, respectively (Table 3, entries 8, 9). The aliphatic α,β-unsaturated aldehydes were excellent substrates

Table 3 The scope of the domino Michael–hemiacetalization[a]



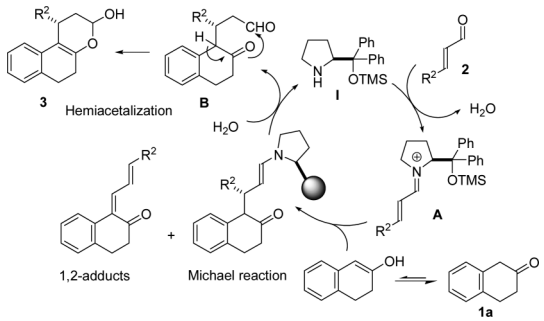
1a: R^1 = H; **1b**: R^1 = 5-OMe; **1c**: R^1 = 6-OMe; **1d**: R^1 = 6-Cl; **1e**: R^1 = 6-Br; **1f**: R^1 = 7-OMe
2a: R^2 = C_6H_5; **2b**: R^2 = 4-$OMeC_6H_4$; **2c**: R^2 = 4-BrC_6H_4; **2d**: R^2 = 4-$NO_2C_6H_4$; **2e**: R^2 = 2-furyl; **2f**: R^2 = Me; **2g**: R^2 = Et

Entry	R^1	R^2		Time (d)	Yield (%)[c]	d.r.	ee (%)[d]
1	5-OMe	C_6H_5	**3ba**	1	92	6 : 1	89
2	6-OMe	C_6H_5	**3ca**	1	77	5 : 1	88
3	6-Cl	C_6H_5	**3da**	1	95	4 : 1	90
4	6-Br	C_6H_5	**3ea**	1	99	4 : 1	91
5	7-OMe	C_6H_5	**3fa**	1	99	5 : 1	93
6	H	4-$OMeC_6H_4$	**3ab**	1	99	6 : 1	86
7[b]	H	4-BrC_6H_4	**3ac**	2	60 (25)[e]	4 : 1	80
8[b]	H	4-$NO_2C_6H_4$	**3ad**	2	67 (15)[e]	3 : 1	95
9	H	2-furyl	**3ae**	1	50 (40)[e]	9 : 1	83
10	H	Me	**3af**	1	99	2 : 1	93
11[b]	H	Et	**3ag**	2	62	3 : 1	93
12	5-OMe	Me	**3bf**	1	67	3 : 1	94
13	6-Cl	Me	**3df**	1	80	3 : 1	95
14	6-Br	Me	**3ef**	1	99	3 : 1	95
15	7-OMe	Me	**3ff**	1	77	3 : 1	96

[a] Reaction conditions: **1** (0.2 mmol), **Cat. I** (10 mol%) and DABCO (20 mol %) were dissolved in DMSO (0.5 mL) at 0 °C, then enals **2** (0.8 mmol) were added. [b] The reaction was carried out at –20 °C. [c] Isolated yield. [d] Determined by HPLC. [e] Yield of 1,2-addition–dehydration product (**4**).

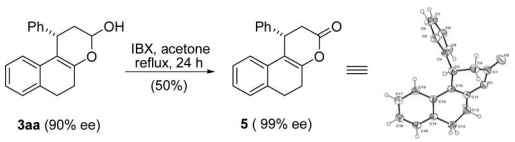
for use in the reaction. High enantioselectivities were observed when (*E*)-2-butenal and (*E*)-2-pentenal were used (Table 3, entries 10–11). (*E*)-2-Butenal also reacted smoothly with substituted β-tetralones. The corresponding benzochromene products **3bf–3ff** were achieved with good to excellent chemical yields and excellent levels of enantioselectivities (Table 3, entries 12–15).

A reasonable mechanism is proposed in Scheme 1. α,β-Unsaturated aldehydes **2** reacted with amine catalyst **I** to form the intermediary iminium ion (**A**). The enol derived from the β-tetralone **1a** attacked the iminium ion on the less hindered side to give the Michael adduct. Protonation and hydrolysis of the intermediate produced keto aldehyde **B**. This process was followed by hemiacetalization to complete the domino sequence. The amine catalyst **I** was regenerated and participated in the next catalytic cycle.



Scheme 1 The proposed mechanism of the domino Michael–hemiacetalization.

To determine the absolute stereochemistry of the newly generated stereogenic centers, several attempts to derivatize the products were made and unsuccessful. Finally, treatment of benzochromene acetal **3aa** with IBX gave 2,3,5,6-tetrahydro-1-phenyl-1*H*-benzo[*f*]chromen-3-one (**5**) with excellent optical purity (Scheme 2). The structure of compound **5** was verified by X-ray analysis.[17]



Scheme 2 The synthesis of 2,3,5,6-tetrahydro-1-phenyl-1*H*-benzo[*f*]chromen-3-one (**5**) and its X-ray crystal structure (30% probability).[18]

Conclusions

In summary, the organocatalytic enantioselective domino Michael–hemiacetalization of β-tetralones with α,β-unsaturated aldehydes to give 2,3,5,6-tetrahydro-1-alkyl/aryl-1*H*-benzo[*f*]chromen-3-ol derivatives has been presented. The functionalized products were obtained with high to excellent chemical yields and good to high enantioselectivities. This process provides a useful synthesis for the preparation of important benzo[*f*]chromenols and their derivatives. Further exploration is underway.

Experimental

Measurement: ^{1}H and ^{13}C NMR spectra were measured, and spectral data are reported in *ppm* relative to tetramethylsilane (TMS) as an internal standard using $CDCl_3$ as solvent; stereoselectivities were determined by chiral High-Performance Liquid Chromatography analysis; optical rotation was measured on a polarimeter.

Typical procedure

To a stirred solution of catalyst **I** (0.02 mmol) and DABCO (0.04 mmol) in DMSO (0.5 mL) was added β-tetralone **1a–f** (0.21 mmol) at appropriate temperature (0 °C or –20 °C). The mixture was stirred for 5 min and then α,β-unsaturated aldehydes **2a–g** (0.85 mmol) were added slowly. Stirring was continued until the starting material had completely disappeared, as determined by TLC. The reaction mixture was quenched with H_2O (3 mL) and extracted with dichloromethane (5 mL). The combined organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent, a crude residue was purified by flash column chromatography on silica gel (eluted with hexanes–ethyl acetate = 4 : 1 ~ 6 : 1) to give the corresponding benzo[*f*]chromen-3-ol (**3**).

(1*S*)-2,3,5,6-Tetrahydro-1-phenyl-1*H*-benzo[*f*]chromen-3-ol (3aa). 90% ee, $[\alpha]_D^{20}$ = +80.6 (*c* = 1.0 in $CHCl_3$); colorless oil; R_f 0.25 (4 : 1 Hex–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.24 (m, 4H, both diastereomers), 7.20–7.15 (m, 1H, both diastereomers), 7.08–7.06 (m, 1H, both diastereomers), 6.95–6.89 (m, 2H, both diastereomers), 6.70–6.65 (m, 1H, both diastereomers), 5.38 (br s, 1H, minor), 5.28 (d, *J* = 7.4 Hz, 1H, major), 4.06 (t, *J* = 7.0 Hz, 1H, minor), 4.01 (t, *J* = 5.1 Hz, 1H, major), 3.03–2.86 (m, 3H, both diastereomers), 2.56–2.47 (m, 2H, both diastereomers), 2.25 (ddd, *J* = 16.4, 7.8, 5.9 Hz, 1H, both diastereomers), 2.17 (ddd, *J* = 16.4, 4.4, 2.6 Hz, 1H, both diastereomers); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 152.3, 144.4, 143.7, 134.9, 134.6, 133.0, 132.8, 128.8, 128.6, 127.9, 127.3, 126.9 (×2), 126.4, 126.3, 126.2, 126.1, 124.3 (×2), 122.9, 122.7, 106.7, 105.6, 93.5, 91.3, 39.3, 38.3, 36.6, 36.4, 28.5 (×2), 27.4, 27.1 ppm; FTIR (ν/cm^{-1}): 3404, 3061, 3026, 2936, 1646, 1601, 1488, 1451, 1240, 1115, 1040; HRMS (EI) *m*/*z* calcd. for $C_{19}H_{18}O_2$ 278.1307; found 278.1302.

(1*S*)-2,3,5,6-Tetrahydro-7-methoxy-1-phenyl-1*H*-benzo[*f*]chromen-3-ol (3ba). 89% ee, $[\alpha]_D^{18}$ = +105.3 (*c* = 1.0 in $CHCl_3$); yellow oil; R_f 0.28 (3 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.19 (m, 4H, both diastereomers), 7.19–7.11 (m, 1H, both diastereomers), 6.87 (t, *J* = 8.0 Hz, 1H, both diastereomers), 6.57 (d, *J* = 8.2 Hz, 1H, both diastereomers), 6.36 (d, *J* = 7.9 Hz, 1H, major), 6.33 (d, *J* = 7.8 Hz, 1H, minor), 5.36 (dd, *J* = 5.9, 2.5 Hz, 1H, minor), 5.24 (dd, *J* = 8.4, 2.5 Hz, 1H, major), 4.04 (t, *J* = 6.7 Hz, 1H, minor), 3.98 (t, *J* = 4.5 Hz, 1H, major), 3.79 (s, 3H, both diastereomers), 3.16–2.75 (m, 2H, both diastereomers), 2.53–2.41 (m, 3H, both diastereomers), 2.25–2.18 (m, 1H, both diastereomers), 2.15 (ddd, *J* = 13.1, 4.2, 2.7 Hz, 1H, both diastereomers); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8 (×2), 152.8, 152.6, 144.7, 143.9, 136.3, 136.1, 128.9, 128.6, 127.9, 127.4, 126.5 (×2), 126.4, 126.3, 120.7, 120.5, 116.1, 116.0, 107.4 (×2), 106.1, 105.3, 93.4, 91.3, 55.4 (×2), 39.0, 38.4, 37.0, 36.2, 26.8, 26.5, 20.6, 20.4 ppm; FTIR (ν/cm^{-1}): 3417, 2960, 2930, 2898, 2834,

1649, 1598, 1572, 1470, 1439, 1261, 1153, 1122, 1054; HRMS (EI) *m*/*z* calcd. for $C_{20}H_{20}O_3$ 308.1412; found 308.1414.

(1*S*)-2,3,5,6-Tetrahydro-8-methoxy-1-phenyl-1*H*-benzo[*f*]chromen-3-ol (3ca). 88% ee, $[\alpha]_D^{20}$ = +46.2 (*c* = 1.0 in $CHCl_3$); yellow oil; R_f 0.20 (4 : 1 Hex–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.23 (m, 4H, both diastereomers), 7.22–7.16 (m, 1H, both diastereomers), 6.67–6.66 (m, 1H, both diastereomers), 6.60–6.56 (m, 1H, both diastereomers), 6.46 (dd, *J* = 8.5, 2.7 Hz, 1H, both diastereomers), 5.39–5.33 (m, 1H, minor), 5.31–5.20 (m, 1H, major), 4.04–4.01 (m, 1H, minor), 3.98–3.95 (m, 1H, major), 3.72 (s, 3H, minor), 3.70 (s, 3H, major), 3.05–2.81 (m, 3H, both diastereomers), 2.50 (td, *J* = 7.6, 1.4 Hz, 2H, both diastereomers), 2.27–2.12 (m, 2H, both diastereomers); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7 (×2), 150.7, 150.5, 144.6, 143.8, 134.8, 134.7, 128.9, 128.6, 128.0, 127.8, 127.6, 127.4, 126.5, 126.4, 123.8, 123.7, 113.7, 113.6, 110.8, 110.7, 106.1, 105.2, 93.4, 91.2, 55.2 (×2), 39.2, 38.5, 36.8, 36.3, 29.0, 28.9, 27.3, 27.0 ppm; FTIR (ν/cm^{-1}): 3420, 3057, 3023, 2932, 2835, 1649, 1609, 1572, 1499, 1453, 1252, 1119, 1054.

(1*S*)-2,3,5,6-Tetrahydro-8-chloro-1-phenyl-1*H*-benzo[*f*]chromen-3-ol (3da). 90% ee, $[\alpha]_D^{18}$ = +60.3 (*c* = 1.0 in $CHCl_3$); yellow oil; R_f 0.28 (3 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.24 (m, 2H, both diastereomers), 7.22–7.18 (m, 3H, both diastereomers), 7.05–7.04 (m, 1H, both diastereomers), 6.86 (dd, *J* = 8.4, 2.1 Hz, 1H, both diastereomers), 6.58 (d, *J* = 8.4 Hz, 1H, major), 6.55 (d, *J* = 8.4 Hz, 1H, minor), 5.38 (ddd, *J* = 8.3, 6.2, 2.2 Hz, 1H, minor), 5.31–5.27 (m, 1H, major), 4.01 (td, *J* = 7.3, 1.8 Hz, 1H, minor), 3.96 (t, *J* = 5.4 Hz, 1H, major), 3.00 (d, *J* = 6.2 Hz, 1H, major), 3.01–2.98 (m, 1H, minor), 2.97–2.81 (m, 2H, both diastereomers), 2.52–2.48 (m, 2H, both diastereomers), 2.26 (ddd, *J* = 13.6, 7.8, 6.0 Hz, 1H, both diastereomers), 2.19–2.13 (m, 1H, both diastereomers); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 152.5, 144.1, 143.3, 135.0, 134.8, 133.5, 133.3, 129.6, 129.5, 129.0, 128.7, 127.8, 127.3, 127.0 (×2), 126.7, 126.6, 126.1, 126.0, 124.1, 124.0, 106.0, 105.3, 93.5, 91.3, 39.1, 38.3, 36.4, 36.3, 28.4 (×2), 27.2, 27.0 ppm; FTIR (ν/cm^{-1}): 3417, 3028, 2930, 2852, 1646, 1598, 1484, 1451, 1241, 1122, 1054; HRMS (EI) *m*/*z* calcd. for $C_{19}H_{17}ClO_2$ 312.0917; found 312.0912.

(1*S*)-2,3,5,6-Tetrahydro-8-bromo-1-phenyl-1*H*-benzo[*f*]chromen-3-ol (3ea). 91% ee, $[\alpha]_D^{18}$ = +51.3 (*c* = 1.1 in $CHCl_3$); yellow oil; R_f 0.28 (3 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.23 (m, 2H, both diastereomers), 7.21–7.17 (m, 4H, both diastereomers), 7.00 (dd, *J* = 8.4, 2.0 Hz, 1H, both diastereomers), 6.52 (d, *J* = 8.4 Hz, 1H, major), 6.49 (d, *J* = 8.4 Hz, 1H, minor), 5.37 (t, *J* = 5.6 Hz, 1H, minor), 5.30–5.26 (m, 1H, major), 4.00 (td, *J* = 6.9, 2.0 Hz, 1H, minor), 3.95 (t, *J* = 5.4 Hz, 1H, major), 3.11 (d, *J* = 5.3 Hz, 1H, major), 3.03 (d, *J* = 8.7 Hz, 1H, minor), 3.00–2.80 (m, 2H, both diastereomers), 2.51–2.46 (m, 2H, both diastereomers), 2.27–2.22 (m, 1H, both diastereomers), 2.17–2.12 (m, 1H, both diastereomers); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 152.7, 144.1, 143.2, 135.3, 135.1, 134.0, 133.8, 129.8 (×2), 129.1 (×2), 129.0, 128.7, 127.8, 127.3, 126.7, 126.6, 124.4 (×2), 117.6, 117.5, 106.1, 105.3, 93.5, 91.4, 39.1, 38.3, 36.4, 36.2, 28.3 (×2), 27.2, 27.0 ppm; FTIR (ν/cm^{-1}): 3392, 3028, 2926, 2858, 1646, 1555, 1482, 1450, 1377, 1238, 1159, 1122, 1054; HRMS (EI) *m*/*z* calcd. for $C_{19}H_{17}BrO_2$ 356.0412; found 356.0404.

(1*S*)-2,3,5,6-Tetrahydro-9-methoxy-1-phenyl-1*H*-benzo[*f*]chromen-3-ol (3fa). 93% ee, $[\alpha]_D^{20}$ = +48.2 (*c* = 1.0 in $CHCl_3$); yellow oil; R_f 0.25 (3 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.22 (m, 4H, both diastereomers), 7.18–7.11 (m, 1H, both diastereomers), 6.97 (d, *J* = 8.1 Hz, 1H, minor), 6.96 (d, *J* = 8.2 Hz, 1H, major), 6.46 (dd, *J* = 8.2, 2.6 Hz, 1H, both diastereomers), 6.27 (d, *J* = 2.6 Hz, 1H, major), 6.24 (d, *J* = 2.6 Hz, 1H, minor), 5.34 (d, *J* = 4.7 Hz, 1H, minor), 5.28 (dd, *J* = 7.9, 2.0 Hz, 1H, major), 4.02 (td, *J* = 7.0, 1.8 Hz, 1H, minor), 3.96 (td, *J* = 4.8, 1.0 Hz, 1H, major), 3.51 (s, 3H, minor), 3.50 (s, 3H, major), 3.39–3.26 (br s, 1H, major), 3.26–3.16 (br s, 1H, minor), 2.98–2.77 (m, 2H, both diastereomers), 2.50–2.45 (m, 2H, both diastereomers), 2.26–2.20 (m, 1H, both diastereomers), 2.18–2.10 (m, 1H, both diastereomers); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2, 158.1, 153.3, 153.0, 144.4, 143.6, 136.2, 136.0, 128.9, 128.7, 127.9, 127.5, 127.4, 127.3, 126.6, 126.4, 125.4, 125.2, 109.8, 109.6, 109.0, 108.9, 106.7, 105.7, 93.5, 91.3, 55.0 (×2), 39.3, 38.3, 36.7, 36.5, 27.8, 27.7, 27.6, 27.5 ppm; FTIR (ν/cm^{-1}): 3426, 3023, 2932, 2835, 1646, 1606, 1575, 1493, 1453, 1244, 1215, 1150, 1122, 1045; HRMS (EI) *m*/*z* calcd. for $C_{20}H_{20}O_3$ 308.1412; found 308.1404.

(1*S*)-2,3,5,6-Tetrahydro-1-(4-methoxyphenyl)-1*H*-benzo[*f*]chromen-3-ol (3ab). 86% ee, $[\alpha]_D^{21}$ = +59.9 (*c* = 1.0 in $CHCl_3$); yellow oil; R_f 0.23 (3 : 1 Hex–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.14 (m, 2H, both diastereomers), 7.08–7.06 (m, 1H, both diastereomers), 6.95–6.90 (m, 2H, both diastereomers), 6.82–6.79 (m, 2H, both diastereomers), 6.73–6.67 (m, 1H, both diastereomers), 5.38 (tt, *J* = 5.8, 2.8 Hz, 1H, minor), 5.26 (tt, *J* = 5.9, 2.5 Hz, 1H, major), 4.00 (t, *J* = 6.5 Hz, 1H, minor), 3.95 (t, *J* = 4.7 Hz, 1H, major), 3.76 (s, 3H, major), 3.74 (s, 3H, minor), 3.01–2.87 (m, 3H, both diastereomers), 2.56–2.43 (m, 2H, both diastereomers), 2.25–2.18 (m, 1H, both diastereomers), 2.14 (ddd, *J* = 13.0, 4.0, 2.8 Hz, 1H, both diastereomers); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2, 158.1, 152.4, 152.3, 136.5 (×2), 135.3, 135.0, 133.1, 132.9, 128.9, 128.4, 127.0 (×2), 126.3, 126.2, 124.4, 124.3, 122.8 (×2), 114.4, 114.0, 106.5, 105.8, 93.4, 91.4, 55.2 (×2), 38.8, 38.6, 35.9, 34.8, 28.6 (×2), 27.4, 27.1 ppm; FTIR (ν/cm^{-1}): 3420, 3063, 3017, 2932, 2835, 1646, 1609, 1510, 1487, 1453, 1246, 1178, 1116, 1059; HRMS (EI) *m*/*z* calcd. for $C_{20}H_{20}O_3$ 308.1412; found 308.1406.

(1*S*)-2,3,5,6-Tetrahydro-1-(4-bromophenyl)-1*H*-benzo[*f*]chromen-3-ol (3ac). 80% ee, $[\alpha]_D^{30}$ = +58.1 (*c* = 1.0 in $CHCl_3$); yellow oil; R_f 0.23 (4 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (dt, *J* = 8.5, 2.4 Hz, 2H, major), 7.35 (dt, *J* = 8.4, 2.6 Hz, 2H, minor), 7.15–7.09 (m, 2H, both diastereomers), 7.09–7.05 (m, 1H, both diastereomers), 6.97–6.89 (m, 2H, both diastereomers), 6.63 (dd, *J* = 6.8, 2.2 Hz, 1H, major), 6.61 (dd, *J* = 7.1, 1.3 Hz, 1H, minor), 5.40–5.36 (m, 1H, minor), 5.29–5.22 (m, 1H, major), 4.02 (td, *J* = 7.3, 2.6 Hz, 1H, minor), 3.97 (t, *J* = 5.2 Hz, 1H, major), 3.09 (br s, 1H, both diastereomers), 3.03–2.82 (m, 2H, both diastereomers), 2.53–2.45 (m, 2H, both diastereomers), 2.28–2.21 (m, 1H, both diastereomers), 2.13–2.05 (m, 1H, both diastereomers); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 152.7, 143.6, 142.9, 134.6, 134.4, 133.1, 133.0, 131.9, 131.8, 129.7, 129.3, 127.1 (×2), 126.3, 126.2, 124.6, 124.5, 122.9, 122.7, 120.2, 120.1, 106.3, 105.4, 93.3, 91.1, 39.1, 38.2, 36.0 (×2), 28.6, 28.5, 27.4, 27.2 ppm; FTIR (ν/cm^{-1}): 3415, 3063, 3023, 2932, 2898, 2858, 1646, 1601, 1569, 1487, 1241, 1150, 1119, 1057; HRMS (EI) *m*/*z* calcd. for $C_{19}H_{17}BrO_2$ 356.0412; found 356.0415.

(1*S*)-2,3,5,6-Tetrahydro-1-(4-nitrophenyl)-1*H*-benzo[*f*]chromen-3-ol (3ad). 95% ee, $[\alpha]_D^{21}$ = +40.1 (*c* = 1.0 in $CHCl_3$); yellow oil; R_f 0.16 (3 : 1 Hex–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.6 Hz, 2H, major), 8.08 (d, *J* = 8.6 Hz, 2H, minor), 7.42–7.37 (m, 2H, both diastereomers), 7.09 (d, *J* = 7.1 Hz, 1H, both diastereomers), 6.94 (t, *J* = 7.1 Hz, 1H, both diastereomers), 6.89 (t, *J* = 7.5 Hz, 1H, both diastereomers), 6.54 (d, *J* = 7.5 Hz, 1H, both diastereomers), 5.43 (d, *J* = 6.2 Hz, 1H, minor), 5.30 (d, *J* = 6.2 Hz, 1H, major), 4.16–4.13 (m, 1H, both diastereomers), 3.41 (br s, 1H, major), 3.26 (br s, 1H, minor), 3.07–2.84 (m, 2H, both diastereomers), 2.59–2.41 (m, 2H, both diastereomers), 2.36–2.29 (m, 1H, both diastereomers), 2.12–2.06 (m, 1H, both diastereomers); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.3, 153.0, 152.5, 152.2, 146.7, 146.6, 134.2, 134.1, 133.2, 133.0, 128.8, 128.6, 127.3 (×2), 126.3 (×2), 124.8, 124.7, 124.0, 123.9, 122.6 (×2), 105.8, 105.1, 93.0, 90.8, 38.5, 37.9, 36.6, 36.0, 28.5 (×2), 27.4 (×2) ppm; FTIR (ν/cm^{-1}): 3432, 2926, 2852, 1646, 1603, 1518, 1487, 1348, 1238, 1113, 1057; HRMS (EI) *m*/*z* calcd. for $C_{19}H_{17}NO_4$ 323.1158; found 323.1150.

(1*R*)-2,3,5,6-Tetrahydro-1-(furan-2-yl)-1*H*-benzo[*f*]chromen-3-ol (3ae). 83% ee, $[\alpha]_D^{18}$ = +54.8 (*c* = 0.36 in $CHCl_3$); yellow oil; R_f 0.25 (4 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, *J* = 1.1 Hz, 1H, minor), 7.33–7.32 (m, 1H, major), 7.11–7.07 (m, 1H, both diastereomers), 7.05–7.02 (m, 1H, both diastereomers), 7.01–6.96 (m, 1H, both diastereomers), 6.89–6.87 (m, 1H, both diastereomers), 6.24–6.22 (m, 1H, both diastereomers), 6.00 (d, *J* = 3.2 Hz, 1H, minor), 5.96 (d, *J* = 3.2 Hz, 1H, major), 5.44 (d, *J* = 7.5 Hz, 1H, minor), 5.32 (d, *J* = 8.2 Hz, 1H, major), 4.10–4.04 (m, 1H, both diastereomers), 3.54 (d, *J* = 10.6 Hz, 1H, minor), 3.15 (br s, 1H, major), 3.02–2.86 (m, 2H, both diastereomers), 2.54 (dt, *J* = 14.0, 3.1 Hz, 1H, minor), 2.51–2.43 (m, 2H, both diastereomers), 2.40 (dt, *J* = 13.0, 2.6 Hz, 1H, major), 2.30 (ddd, *J* = 14.0, 6.8, 3.1 Hz, 1H, minor), 2.06 (ddd, *J* = 13.0, 9.3, 5.7 Hz, 1H, major); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 156.4, 152.3, 151.6, 142.1, 141.4, 134.8, 134.5, 132.9, 132.8, 127.2, 127.1, 126.4 (×2), 124.7, 124.6, 121.8, 121.6, 110.6, 110.3, 107.1, 106.5, 104.0, 103.6, 92.3, 92.1, 34.7, 32.9, 31.1, 28.5, 28.3, 27.7, 27.2, 27.0 ppm; FTIR (ν/cm^{-1}): 3415, 3063, 2932, 2892, 2852, 1646, 1601, 1504, 1487, 1453, 1272, 1241, 1150, 1119, 1057; HRMS (ESI) *m*/*z* calcd. for $C_{17}H_{16}O_3$ $[M - H]^-$ 267.1099; found 267.1090.

(1*S*)-2,3,5,6-Tetrahydro-1-methyl-1*H*-benzo[*f*]chromen-3-ol (3af). 93% ee, $[\alpha]_D^{23}$ = −85.9 (*c* = 1.0 in $CHCl_3$); colorless oil; R_f 0.28 (4 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17–7.14 (m, 1H, both diastereomers), 7.10–7.04 (m, 2H, both diastereomers), 7.01 (qd, *J* = 7.4, 1.2 Hz, 1H, both diastereomers), 5.43 (d, *J* = 5.1 Hz, 1H, major), 5.26 (d, *J* = 6.5 Hz, 1H, minor), 3.40 (br s, 1H, both diastereomers), 2.95–2.85 (m, 2H, both diastereomers), 2.78–2.68 (m, 1H, both diastereomers), 2.50–2.37 (m, 1H, both diastereomers), 2.30–2.19 (m, 1H, both diastereomers), 2.00–1.91 (m, 2H, both diastereomers), 1.78 (dt, *J* = 13.5, 7.6 Hz, 1H, minor), 1.22 (d, *J* = 5.8 Hz, 3H, minor), 1.20 (d, *J* = 6.9 Hz, 3H, major); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 149.7, 134.9, 134.8, 133.8, 133.4, 127.3, 127.2, 126.3, 126.1, 124.3 (×2), 122.2, 121.6, 110.6, 109.7, 93.7, 91.4, 38.1, 36.8, 28.6, 28.5, 27.2, 26.9, 24.9, 23.8, 21.0, 20.4 ppm; FTIR (ν/cm^{-1}): 3415, 2955, 2932, 2892, 2835, 1643, 1601, 1569, 1487, 1453, 1235, 1122, 1085; HRMS (EI) *m*/*z* calcd. for $C_{14}H_{16}O_2$ 216.1150; found 216.1149.

(1*S*)-2,3,5,6-Tetrahydro-1-ethyl-1*H*-benzo[*f*]chromen-3-ol (3ag). 93% ee, $[\alpha]_D^{17}$ = −86.9 (*c* = 1.0 in $CHCl_3$); colorless oil; R_f 0.30 (4 : 1 Hex–EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17–7.14 (m, 1H, both diastereomers), 7.11–7.07 (m, 1H, both diastereomers), 7.05–6.99 (m, 2H, both diastereomers), 5.40 (dd, *J* = 8.0, 2.0 Hz, 1H, major), 5.22 (dd, *J* = 7.7, 1.8 Hz, 1H, minor), 3.58–3.21 (m, 1H, both diastereomers), 2.93–2.83 (m, 1H, both diastereomers), 2.78–2.70 (m, 1H, both diastereomers), 2.68–2.63 (m, 1H, both diastereomers), 2.51–2.35 (m, 1H, both diastereomers), 2.22 (ddd, *J* = 16.0, 6.9, 3.8 Hz, 1H, both diastereomers), 2.10 (ddd, *J* = 13.4, 4.0, 2.6 Hz, 1H, both diastereomers), 1.90–1.73 (m, 2H, both diastereomers), 1.44–1.22 (m, 1H, both diastereomers), 0.97 (t, *J* = 7.4 Hz, 3H, major), 0.90 (t, *J* = 7.4 Hz, 3H, minor); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 150.1, 135.0, 134.9, 133.8, 133.5, 127.3, 127.2, 126.3, 126.1, 124.3 (×2), 122.0, 121.4, 109.8, 108.8, 94.1, 91.7, 34.6, 32.8, 31.4, 30.6, 28.6 (×2), 27.3, 27.0, 26.8, 26.0, 11.5, 10.7 ppm; FTIR (ν/cm^{-1}): 3415, 3063, 3023, 2960, 2932, 2875, 1643, 1601, 1569, 1484, 1456, 1235, 1125, 1110, 1085, 1014; HRMS (FAB) *m*/*z* calcd. for $[M - H]^+$ $C_{15}H_{17}O_2$ 229.1229; found 229.1226.

(1*S*)-2,3,5,6-Tetrahydro-7-methoxy-1-methyl-1*H*-benzo[*f*]chromen-3-ol (3bf). 94% ee, $[\alpha]_D^{24}$ = −45.9 (*c* = 1.0 in $CHCl_3$); colorless oil; R_f 0.23 (4 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (t, *J* = 8.0 Hz, 1H, both diastereomers), 6.78 (d, *J* = 7.8 Hz, 1H, major), 6.74 (d, *J* = 7.8 Hz, 1H, minor), 6.68 (d, *J* = 8.0 Hz, 1H, minor), 6.67 (d, *J* = 8.0 Hz, 1H, major), 5.44–5.42 (m, 1H, major), 5.28 (dd, *J* = 7.1, 2.0 Hz, 1H, minor), 3.82 (s, 3H, minor), 3.82 (s, 3H, major), 3.16 (ddd, *J* = 15.5, 6.5, 2.6 Hz, 1H, minor), 3.09 (ddd, *J* = 16.0, 7.1, 4.5 Hz, 2H, major), 2.95–2.89 (m, 1H, both diastereomers), 2.65–2.46 (m, 1H, both diastereomers), 2.44–2.27 (m, 1H, both diastereomers), 2.23 (ddd, *J* = 16.0, 7.3, 4.5 Hz, 1H, both diastereomers), 2.00–1.92 (m, 2H, both diastereomers), 1.79 (dt, *J* = 13.5, 7.3 Hz, 1H, minor), 1.21 (d, *J* = 6.5 Hz, 3H, minor), 1.20 (d, *J* = 6.8 Hz, 3H, major); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.1, 156.0, 150.1, 149.9, 136.4, 136.3, 126.6, 126.4, 121.4, 121.0, 115.4, 114.8, 109.4, 107.5, 93.6, 91.4, 55.5 (×2), 38.0, 36.9, 26.5, 26.3, 25.0, 24.2, 21.2, 20.6, 20.5, 20.3 ppm; FTIR (ν/cm^{-1}): 3420, 2960, 2926, 2858, 1649, 1586, 1575, 1473, 1439, 1263, 1130, 1093, 1028; HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{18}O_3$ $[M - H]^-$ 245.1256; found 245.1244.

(1*S*)-2,3,5,6-Tetrahydro-8-chloro-1-methyl-1*H*-benzo[*f*]chromen-3-ol (3df). 95% ee, $[\alpha]_D^{25}$ = −64.6 (*c* = 1.0 in $CHCl_3$); colorless oil; R_f 0.18 (4 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14–7.11 (m, 1H, both diastereomers), 7.08 (s, 1H, minor), 7.07 (s, 1H, major), 6.99 (d, *J* = 8.3 Hz, 1H, major), 6.95 (d, *J* = 8.3 Hz, 1H, minor), 5.43 (d, *J* = 6.5 Hz, 1H, major), 5.28 (d, *J* = 6.5 Hz, 1H, minor), 3.24 (br s, 1H, both diastereomers), 2.90–2.83 (m, 2H, both diastereomers), 2.75–2.65 (m, 1H, both diastereomers), 2.48–2.35 (m, 1H, both diastereomers), 2.28 (ddd, *J* = 13.5, 7.2, 2.4 Hz, 1H, minor), 2.26–2.19 (m, 1H, both diastereomers), 2.01–1.91 (m, 2H, major), 1.79 (dt, *J* = 13.5, 7.4 Hz, 1H, minor), 1.19 (d, *J* = 6.2 Hz, 3H, minor), 1.18 (d, *J* = 6.9 Hz, 3H, major); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 149.9, 135.6, 135.3, 133.5, 133.4, 129.5 (×2), 127.3, 127.2, 126.2, 126.0, 123.3, 122.7, 110.0, 109.2, 93.6, 91.4, 37.8, 36.7, 28.4, 28.3, 26.9, 26.7, 24.7, 23.7, 20.8, 20.3 ppm; FTIR (ν/cm^{-1}): 3420, 2955, 2932, 1643, 1595, 1484, 1450, 1238, 1125, 1088; HRMS (ESI) *m*/*z* calcd. for $C_{14}H_{15}ClO_2$ $[M - H]^-$ 249.0761; found 249.0731.

(1*S*)-2,3,5,6-Tetrahydro-8-bromo-1-methyl-1*H*-benzo[*f*]chromen-3-ol (3ef). 95% ee, $[\alpha]_D^{26} = -40.6$ ($c = 1.0$ in $CHCl_3$); colorless oil; R_f 0.25 (4 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–7.25 (m, 1H, both diastereomers), 7.22 (s, 1H, minor), 7.21 (s, 1H, major), 6.94 (d, $J = 8.3$ Hz, 1H, major), 6.89 (d, $J = 8.3$ Hz, 1H, minor), 5.43 (d, $J = 5.7$ Hz, 1H, major), 5.28 (d, $J = 6.2$ Hz, 1H, minor), 3.31 (br s, 1H, both diastereomers), 2.90–2.83 (m, 2H, both diastereomers), 2.75–2.65 (m, 1H, both diastereomers), 2.47–2.35 (m, 1H, both diastereomers), 2.27 (ddd, $J = 13.5$, 7.2, 2.3 Hz, 1H, minor), 2.21 (ddd, $J = 16.1$, 7.0, 4.5 Hz, 1H, both diastereomers), 2.00–1.90 (m, 2H, major), 1.78 (dt, $J = 13.5$, 7.4 Hz, 1H, minor), 1.19 (d, $J = 6.8$ Hz, 3H, minor), 1.18 (d, $J = 7.0$ Hz, 3H, major); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 150.0, 136.0, 135.6, 134.0, 133.9, 130.1, 130.0, 129.1, 129.0, 123.7, 123.1, 117.5, 117.4, 110.1, 109.2, 93.7, 91.4, 37.7, 36.6, 28.3, 28.2, 26.9, 26.7, 24.7, 23.7, 20.8, 20.2 ppm; FTIR (ν/cm^{-1}): 3572, 2959, 2930, 2893, 2841, 1642, 1558, 1480, 1373, 1233, 1119, 1086; HRMS (ESI) m/z calcd. for $C_{14}H_{15}BrO_2$ $[M+K]^+$ 333.0255; found 333.0176.

(1*S*)-2,3,5,6-Tetrahydro-9-methoxy-1-methyl-1*H*-benzo[*f*]chromen-3-ol (3ff). 96% ee, $[\alpha]_D^{27} = -73.0$ ($c = 1$ in $CHCl_3$); colorless oil; R_f 0.18 (4 : 1 Hex–EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02–6.99 (m, 1H, both diastereomers), 6.69 (d, $J = 2.6$ Hz, 1H, major), 6.64 (d, $J = 2.5$ Hz, 1H, minor), 6.58–6.55 (m, 1H, both diastereomers), 5.43 (dd, $J = 6.6$, 3.6 Hz, 1H, major), 5.27 (dd, $J = 6.9$, 1.5 Hz, 1H, minor), 3.79 (s, 3H, both diastereomers), 3.27 (br s, 1H, both diastereomers), 2.92–2.86 (m, 1H, both diastereomers), 2.82 (td, $J = 14.6$, 6.8 Hz, 1H, both diastereomers), 2.74–2.64 (m, 1H, both diastereomers), 2.48–2.35 (m, 1H, both diastereomers), 2.28 (ddd, $J = 13.5$, 7.2, 2.3 Hz, 1H, minor), 2.24–2.18 (m, 1H, both diastereomers), 1.99–1.92 (m, 2H, major), 1.78 (dt, $J = 13.5$, 7.5 Hz, 1H, minor), 1.23 (d, $J = 8.1$ Hz, 3H, minor), 1.21 (d, $J = 7.1$ Hz, 3H, major); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 158.3, 150.5 (×2), 136.3, 136.2, 127.7, 127.6, 126.1, 125.7, 110.5, 109.6, 109.4, 108.8, 108.3, 108.2, 93.7, 91.4, 55.3 (×2), 37.9, 36.8, 27.7, 27.6, 27.5, 27.3, 24.8, 23.9, 21.0, 20.4 ppm; FTIR (ν/cm^{-1}): 3420, 2960, 2926, 2858, 1643, 1609, 1572, 1493, 1456, 1238, 1212, 1125, 1042; HRMS (ESI) m/z calcd. for $C_{15}H_{18}O_3$ $[M - H]^-$ 245.1256; found 245.1245.

(*E*)-1-((*E*)-3-(4-Nitrophenyl)allylidene)-3,4-dihydronaphthalen-2(1*H*)-one (4). yellow crystal; R_f 0.28 (6 : 1 Hex–EtOAc); mp (°C) 190–191; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, $J = 8.8$ Hz, 2H), 7.58 (d, $J = 8.8$ Hz, 2H), 7.50–7.44 (m, 3H), 7.40–7.33 (m, 3H), 7.15 (ddd, $J = 11.8$, 10.0, 10.0 Hz, 1H), 3.01 (t, $J = 6.5$ Hz, 2H), 2.65 (t, $J = 6.5$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.3, 147.5, 142.8, 139.5, 138.6, 135.8, 133.2, 133.1, 129.2, 128.9, 128.6, 128.1, 127.6, 126.9, 124.2, 37.0, 27.8 ppm; FTIR (ν/cm^{-1}): 1680, 1592, 1507, 1337, 1241, 1167, 1110; HRMS (EI) m/z calcd. for $C_{19}H_{15}NO_3$ 305.1052; found 305.1059.

(*S*)-1-Phenyl-5,6-dihydro-1*H*-benzo[*f*]chromen-3(2*H*)-one (5). >99% ee, $[\alpha]_D^{20} = +95.6$ ($c = 1$ in $CHCl_3$); colorless crystal; R_f 0.25 (6 : 1 Hex–EtOAc); mp (°C) 159–160; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (t, $J = 7.2$ Hz, 2H), 7.25–7.20 (m, 3H), 7.14 (d, $J = 6.7$ Hz, 1H), 7.10–7.03 (m, 2H), 6.93 (dd, $J = 7.0$, 1.5 Hz, 1H), 4.15 (d, $J = 7.5$ Hz, 1H), 3.14 (dd, $J = 15.7$, 7.5 Hz, 1H), 3.10–3.05 (m, 1H), 2.99 (dt, $J = 15.7$, 6.7 Hz, 1H), 2.92 (dd, $J = 15.7$, 1.7 Hz, 1H), 2.79 (ddd, $J = 18.9$, 12.4, 7.2 Hz, 1H), 2.62–2.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0, 150.8, 140.3, 133.2, 132.5, 129.3, 127.6 (×2), 126.8 (×2), 126.5, 122.7, 111.9, 38.2, 37.8, 28.3, 25.4 ppm; FTIR (ν/cm^{-1}): 3063, 3028, 2949, 2892, 2841, 1771, 1669, 1601, 1490, 1450, 1244, 1178, 1130; HRMS (EI) m/z calcd. for $C_{19}H_{16}O_2$ 276.1150; found 276.1144.

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