SUPPORTING INFORMATION: PART A

Iridium-catalyzed enantioselective direct vinylogous allylic alkylation of coumarins

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A. General information:

Infrared (FT-IR) spectra were recorded on a Bruker Alfa FT-IR, ν_{max} in cm^{-1} and the bands are characterized as broad (br), strong (s), medium (m), and weak (w). NMR spectra were recorded on Bruker Ultrashield spectrometer at 400 MHz (for ^{1}H-NMR) and 100 MHz (for ^{13}C-NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26, CD_3OD: δ 3.31 for ^{1}H-NMR and $CDCl_3$: δ 77.16, CD_3OD: δ 49.00 for ^{13}C-NMR). For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry was performed on Micromass Q-TOF Micro instrument. Optical rotations were measured on JASCO P-2000 polarimeter. Melting points were measured in open glass capillary using ANALAB μ-Thermocal 10 melting point apparatus and the values are uncorrected. Enantiomeric ratios were determined by Shimadzu LC-20AD HPLC instrument and SPD-20A UV/Vis detector using stationary phase chiral columns (25 cm × 0.46 cm) in comparison with authentic racemic compounds.

Unless stated otherwise, all reactions were carried out with distilled and dried solvents under an atmosphere of nitrogen or argon in oven (120 °C) dried glassware with standard vacuum-line techniques. Organic solvents used for carrying out reactions were dried using standard methods. $[Ir(COD)Cl]_2$, (*S*)-BINOL and (*R*)-BINOL were purchased from Combi-Blocks; (−)-bis[(*S*)-1-phenylethyl]amine was purchased from Alfa Aesar and used as received. All work up and purification were carried out with reagent grade solvents in air. Thin-layer chromatography was performed using Merck silica gel 60 F_{254} pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400 or 100-200 mesh). NMR yields were determined by using mesitylene as an internal standard. Unless otherwise noted, all reported yields of the Ir-catalyzed allylation reactions are isolated yields. Chiral ligands used in this work were prepared according to literature procedures.[1]

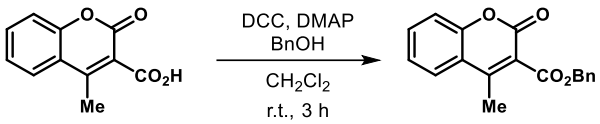
[1] a) L. A. Arnold, R. Imbos, A. Mandoli, A. H. M. de Vries, R. Naasz and B. L. Feringa, *Tetrahedron* 2000, **56**, 2865-2878; b) D. Polet and A. Alexakis, *Org. Lett.* 2005, **7**, 1621-1624; c) C. Defieber, M. A. Ariger, P. Moriel and E. M. Carreira, *Angew. Chem., Int. Ed.* 2007, **46**, 3139-3143.

B. Procedure for the synthesis of coumarins:

Substituted coumarins (**1a-o**) were prepared according to the previously reported procedure.[2]

Preparation of coumarin (1k):

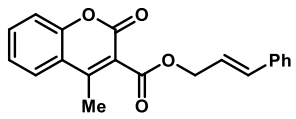
Coumarins (**1k-l**) were prepared according to the previously reported procedure.[2]



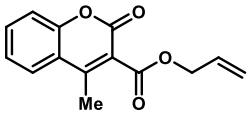
1l **1k**

In an oven dried 10 mL round-bottom flask, **1l** (100 mg, 0.490 mmol, 1.0 equiv.) was taken along with benzyl alcohol (80 mg, 0.735 mmol, 1.5 equiv.) in 1.6 mL of absolute CH_2Cl_2 at r.t. To this, DCC (111 mg, 0.540 mmol, 1.1 equiv.) and DMAP (6 mg, 0.050 mmol, 10 mol%) were added and the resulting solution was stirred at r.t. for 3 h. Solvent was removed under reduced pressure and the residue was purified by silica-gel flash column chromatography (CH_2Cl_2) to obtain **1k** as a colorless thick oil (123 mg, 0.418 mmol, 85% yield); **FT-IR (Thin film):** 1726 (s), 1609 (m), 1239 (s), 1024 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.55-7.51 (m, 1H), 7.44-7.42 (m, 2H), 7.37-7.26 (m, 5H), 5.37 (s, 2H), 2.36 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.7, 157.7, 152.8, 150.6, 135.1, 132.9, 128.6, 128.5, 128.4, 125.4, 124.8, 119.0, 117.1, 67.8, 16.0; **HRMS (ESI+):** Calcd. for $C_{18}H_{14}O_4Na$ ($[M+Na]^+$): 317.0790, Found: 317.0792.

Compound 1n: 1l (200 mg, 0.980 mmol, 1.0 equiv.), reaction time 21 h, purified by silica-gel flash column chromatography (10% EtOAc in petroleum ether); colorless thick oil (181 mg, 0.565 mmol, 58% yield); **FT-IR (Thin film):** 2924 (w), 2337 (m), 1723 (s), 1606 (m), 1239 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.56-7.52 (m, 1H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.31-7.22 (m, 5H), 6.76 (d, *J* = 15.9 Hz, 1H), 6.36 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.01 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.6, 157.7, 152.8, 150.5, 135.9, 135.0, 132.8, 128.6, 128.2, 126.6, 125.4, 124.7, 122.1, 120.9, 118.9, 117.0, 66.5, 16.1; **HRMS (ESI+):** Calcd. for $C_{20}H_{16}O_4Na$ ($[M+Na]^+$): 343.0946, Found: 343.0949.



Compound 1o: 1l (67 mg, 0.328 mmol, 1.0 equiv.), reaction time 14 h, purified by silica-gel flash column chromatography (10% EtOAc in petroleum ether); colorless thick oil (59 mg, 0.242 mmol, 80% yield); **FT-IR (Thin film):** 1725 (s), 1608 (m), 1239 (s), 1024 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.55-7.51 (m, 1H), 7.31-7.25 (m, 2H), 6.03-5.92 (m, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.82 (d, *J* = 5.8 Hz, 2H), 2.43 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.5, 157.7, 152.9, 150.6, 132.9, 131.3, 125.5, 124.8, 121.0, 119.4, 119.1, 117.1, 66.6, 16.1; **HRMS (ESI+):** Calcd. for $C_{14}H_{12}O_4Na$ ($[M+Na]^+$): 267.0633, Found: 267.0640.

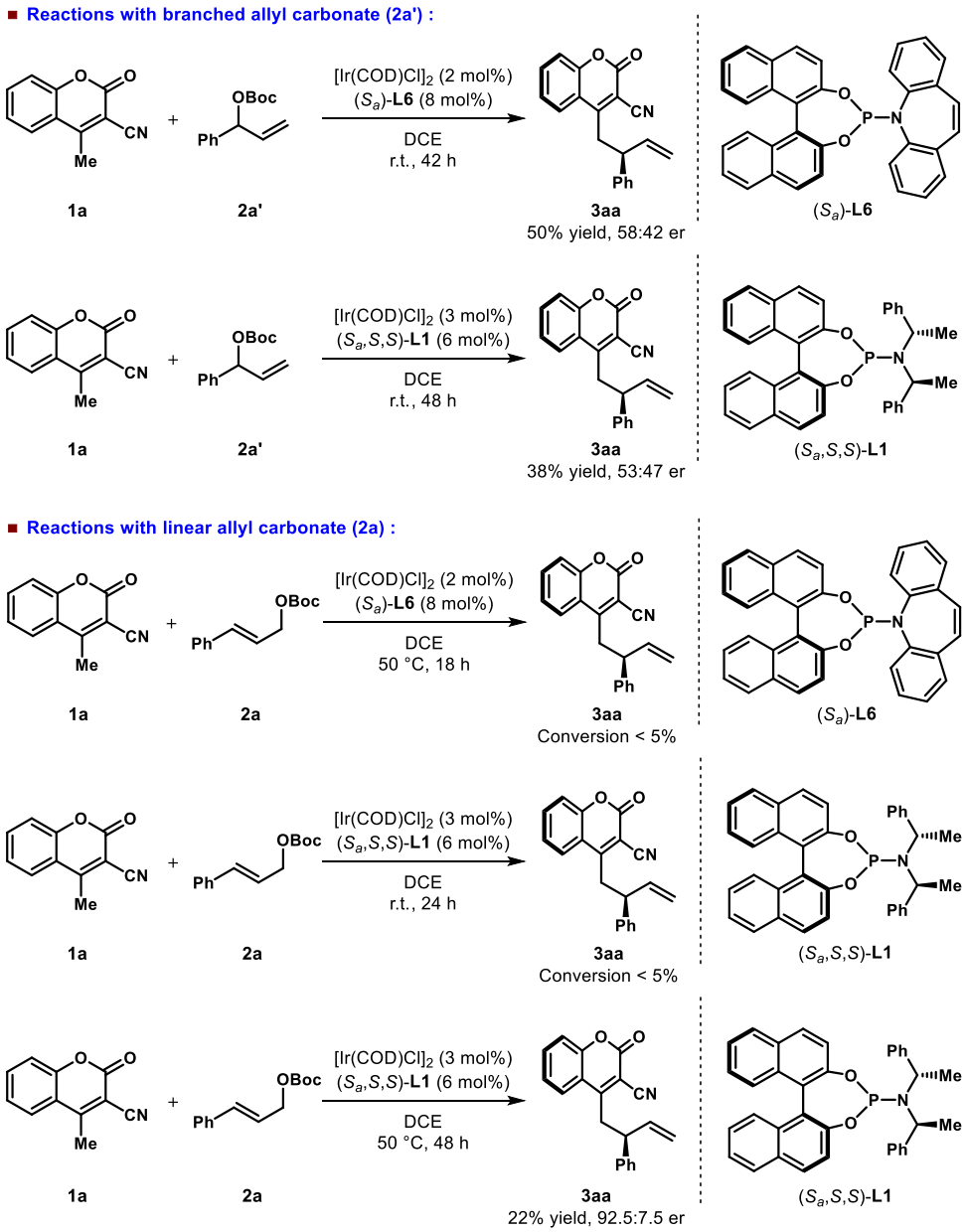


[2] C. C. J. Loh, M. Schmid, B. Peters, X. Fang and M. Lautens, *Angew. Chem., Int. Ed.* 2016, **55**, 4600-4604.

C. Procedure for the synthesis of allyl carbonates:

Allyl carbonates (**2a-u**, **2a′**) were prepared according to the previously reported procedure.[3]

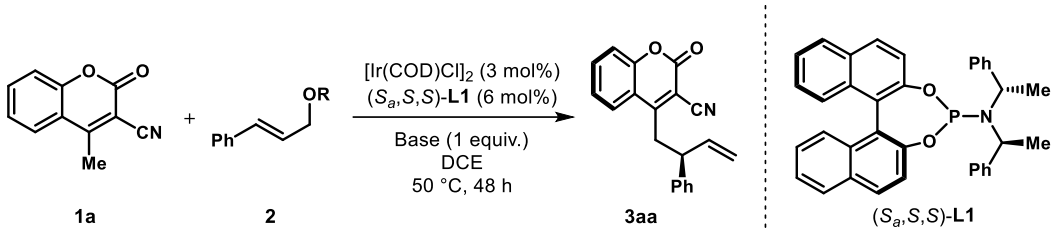
D. Preliminary studies on direct enantioselective vinylogous γ-allylic alkylation of coumarin 1a:



[3] a) L. M. Stanley, J. F. Hartwig, *Angew. Chem., Int. Ed.* 2009, **48**, 7841-7844; b) D. J. Weix, D. Marković, M. Ueda and J. F. Hartwig, *Org. Lett.* 2009, **11**, 2944-2947; c) J. Štambaský, A. V. Malkov and P. Kočovský, *J. Org. Chem.* 2008, **73**, 9148-9150.

E. Ligand and reaction conditions optimization for direct enantioselective vinylogous γ-allylic alkylation of coumarin:

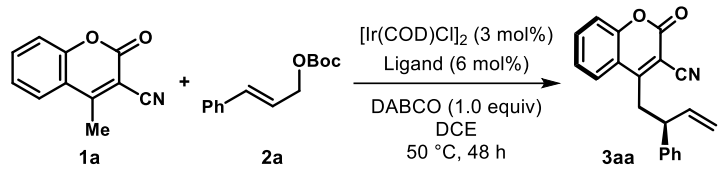
Table 1: Optimization of base[a]

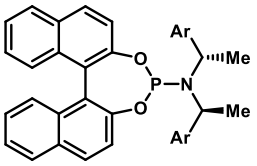


entry	R	ligand	base	yield (%)[b]	er
1	Boc	**L1**	-	(22)	92.5:7.5
2	Boc	**L1**	Cs_2CO_3	<5	n.d.
3	Boc	**L1**	KO*t*-Bu	<5	n.d.
4	Boc	**L1**	DBU	<5	n.d.
5	Boc	**L1**	*i*-Pr_2NEt	72	96:4
6[c]	Boc	**L1**	*i*-Pr_2NEt	25	97:3
7[d]	Boc	**L1**	*i*-Pr_2NEt	75	96:4
8	Boc	**L1**	Et_3N	74	97:3
9	CO_2Me	**L1**	*i*-Pr_2NEt	73	95:5
10	Boc	**L1**	*i*-Pr_2NH	76	97:3
11[e]	Boc	**L1**	*i*-Pr_2NH	33	97:3
12	Boc	**L1**	Et_2NH	4	n.d.
13	Boc	**L1**	*i*-Bu_2NH	23	96:4
14	Boc	**L1**	*n*-Pr_2NH	34	97:3
15	Boc	**L1**	Piperidine	24	98:2
16	Boc	**L1**	Pyrrolidine	8	98.5:1.5
17	Boc	**L1**	DABCO	84	97.5:2.5
18	Boc	**L1**	*n*-$PrNH_2$	13	96:4

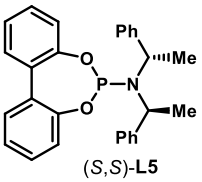
[a]Reaction conditions: 3 mol% $[Ir(COD)Cl]_2$, 6 mol% ligand, 0.240 mmol of **1a**, 0.200 mmol of **2** and 0.200 mmol of base in 0.6 mL DCE; The catalyst was prepared via *n*-$PrNH_2$ activation. [b]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard; Isolated yields are given in the parentheses. [c]Using 2.0 equiv. of base. [d]Using 1.2 equiv. of base. [e]Using 1.0 mL DCE as solvent. n.d. = Not determined.

Table 2: Ligand optimization[a]





(S_a,S,S)-**L1**: Ar = Ph
(R_a,S,S)-**L2**: Ar = Ph
(S_a,S,S)-**L3**: Ar = 2-OMeC_6H_4
(S_a,S,S)-**L4**: Ar = 1-Np

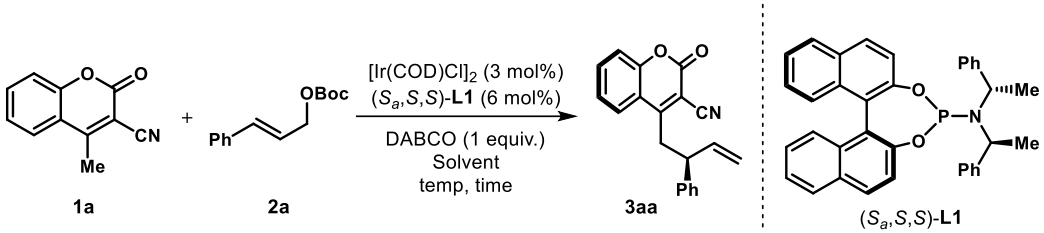


(*S*,*S*)-**L5**

entry	ligand	base	yield (%)[b]	er
1	**L1**	DABCO	84	97.5:2.5
2	**L2**	DABCO	n.r.	n.d.
3	**L3**	DABCO	11	98:2
4	**L4**	DABCO	n.r.	n.d.
5	**L5**	DABCO	28	92:8
6	**L3**	*i*-Pr_2NH	18	97:3
7	**L4**	*i*-Pr_2NH	36	97:3

[a]Reaction conditions: 3 mol% $[Ir(COD)Cl]_2$, 6 mol% ligand, 0.240 mmol of 1**a**, 0.200 mmol of 2**a** and 0.200 mmol of base in 0.6 mL DCE; The catalyst was prepared via *n*-$PrNH_2$ activation. [b]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard. n.r. = No reaction; n.d. = Not determined.

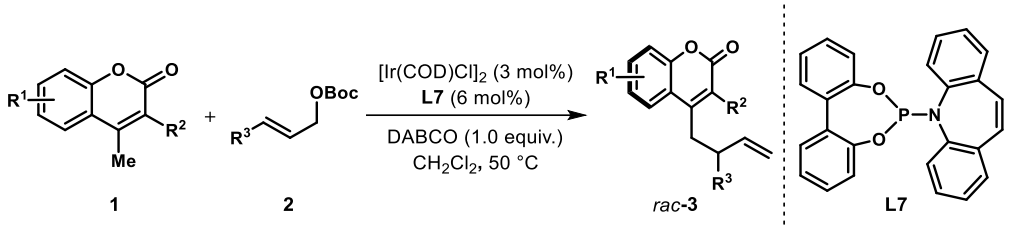
Table 3: Solvent optimization[a]



entry	Solvent	temp	Time (h)	yield (%)[b]	er
1	DCE	50 °C	48	84	97.5:2.5
2[c]	DCE	50 °C	48	23	97.5:2.5
3[d]	DCE	50 °C	48	27	98:2
4	DCE	r.t.	48	35	98:2
5[e]	DCE	50 °C	48	14	97.5:2.5
6	THF	50 °C	48	11	96:4
7	PhMe	50 °C	48	<5	n.d.
8	1,4-dioxane	50 °C	48	21	96:4
9	$CHCl_3$	50 °C	48	67	97:3
10	CH_2Cl_2	50 °C	36	88 (86%)	98:2
11[f]	CH_2Cl_2	50 °C	20	81	97.5:2.5
12[g]	CH_2Cl_2	50 °C	36	64	97.5:2.5
13	PhCl	50 °C	48	24	96:4
14	CH_3CN	50 °C	48	67	96.5:3.5
15	DMF	50 °C	48	39	97:3

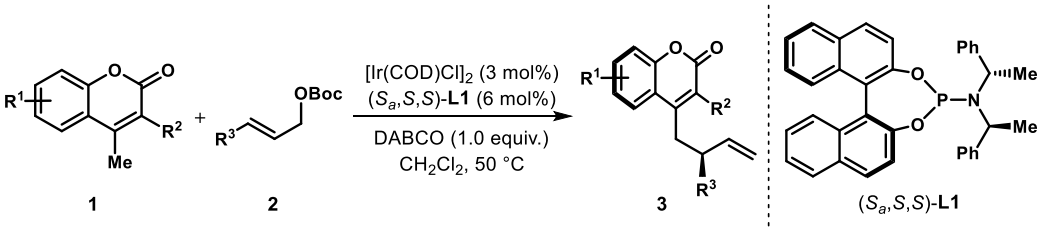
[a]Reaction conditions: 3 mol% $[Ir(COD)Cl]_2$, 6 mol% ligand, 0.240 mmol of **1a**, 0.200 mmol of **2a** and 0.200 mmol of base in 0.6 mL DCE; The catalyst was prepared via *n*-$PrNH_2$ activation. [b]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard; Isolated yields are given in the parentheses. [c]Using 0.5 mL DCE as solvent; [d]Using 1.0 mL DCE as solvent; [e]Using 2 mol% $[Ir(COD)Cl]_2$ and 4 mol% ligand; [f]Using 0.5 mL CH_2Cl_2 as solvent; [g]Using 0.200 mmol of **1a**, 0.240 mmol of **2a**.

F. General procedure for the preparation of racemic products (*rac*-3):



In a glass-vial $[Ir(COD)Cl]_2$ (0.003 mmol, 3 mol%) and ligand **L7** (0.006 mmol, 6 mol%) were taken with 0.2 mL of CH_2Cl_2, and the resulting solution was stirred at r.t. for 15 min. To this, was added **1** (0.120 mmol, 1.2 equiv.) followed by addition of **2** (0.100 mmol, 1.0 equiv.) in 0.1 mL CH_2Cl_2. The resulting suspension was stirred at 50 °C for 48 h. The crude mixture was purified by preparative TLC (Merck silica-gel 60 F_{254} pre-coated plates of 0.25 mm thickness) to obtain the racemic γ-allylated products (*rac*-**3**).

G. Typical procedure for Ir-catalyzed enantioselective allylation of coumarins with allyl carbonates:



In an oven and vacuum-dried reaction tube, $[Ir(COD)Cl]_2$ (0.006 mmol, 3 mol%) and ligand (*S*$_a$,*S*,*S*)-**L1** (0.012 mmol, 6 mol%) were taken with 0.5 mL of absolute THF under a positive argon pressure followed by addition of 0.3 mL dry *n*-$PrNH_2$. The solution was heated at 50 °C for 30 min, after which all volatiles were removed under vacuum to obtain a yellow solid. To this, coumarin **1** (0.240 mmol, 1.2 equiv.) and DABCO (22.4 mg, 0.200 mmol, 1.0 equiv.) were introduced under a positive argon pressure followed by 0.4 mL of absolute CH_2CL_2 and the suspension was stirred at 50 °C for 5 min. After 5 min, a solution of allyl carbonate **2** (0.200 mmol, 1.0 equiv.) in 0.2 mL absolute CH_2Cl_2 was added to it. The resulting mixture was purged with argon and the reaction tube was sealed with a glass stopper. The reaction was stirred at 50 °C until TLC (20% EtOAc in petroleum ether) revealed complete consumption of **2**. The reaction mixture was then allowed to attain ambient temperature, diluted with 2 mL of CH_2Cl_2 and 5 mL of 1 N HCl solution. Organic layer was separated from the aqueous layer. The aqueous layer was extracted with CH_2Cl_2 (3 × 4 mL). Combined organic layer was washed with brine (10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a reddish-brown oil. The crude reaction mixture was purified by silica-gel flash column chromatography (7-10% EtOAc in petroleum ether) to obtain **3**.

Compound 3aa: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (52 mg, 0.173 mmol, 86% yield); **m.p.** 148-150 °C; **FT-IR (Thin film):** 3028 (w), 2923 (w), 2229 (m), 1734 (s), 1602 (s), 1450 (m), 1366 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.71-7.68 (m, 2H), 7.42-7.39 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.23 (m, 3H), 6.14 (ddd, *J* = 17.7, 10.0, 8.2 Hz, 1H), 5.13 (d, *J* = 10.1 Hz, 1H), 5.02 (d, *J* = 17.0 Hz, 1H), 3.74 (dd, *J* = 15.4, 7.8 Hz, 1H), 3.54 (dd, *J* = 12.8, 8.4 Hz, 1H), 3.46 (dd, *J* = 12.6, 6.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.0, 156.8, 153.6, 141.3, 138.6, 135.2, 129.1, 127.6, 127.4, 126.1, 125.5, 118.1, 117.5, 116.8, 113.7, 103.1, 50.6, 38.3; **HRMS (ESI+):** Calcd. for $C_{20}H_{15}NO_2Na$ ($[M+Na]^+$): 324.1000, Found: 324.1000; The absolute configurations of **3aa** was assigned as (*S*) by comparing the specific rotation with the known compound.[4] **Optical rotation:** $[\alpha]_D^{22}$ –6.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er [Lit[4] +8.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er]. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 334 nm, τ_{major} = 15.3 min, τ_{minor} = 16.2 min). See Supporting Information: Part B for HPLC chromatograms.

Compound 3ab: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (55 mg, 0.174 mmol, 87% yield); **m.p.** 154-156 °C; **FT-IR (Thin film):** 2921 (w), 2361 (w), 2229 (m), 1734 (s), 1603 (m), 1450 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73-7.68 (m, 2H), 7.43-7.39 (m, 2H), 7.15-7.11 (m, 4H), 6.16-6.07 (m, 1H), 5.09 (d, *J* = 10.1 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 3.70 (dd, *J* = 15.4, 7.8 Hz, 1H), 3.52 (dd, *J* = 12.8, 7.8 Hz, 1H), 3.44 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.32 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.0, 156.8, 153.6, 138.9, 138.3, 137.3, 135.1, 129.7, 127.2, 126.1, 125.5, 118.1, 117.5, 116.6, 113.7, 103.1, 50.3, 38.4, 21.1; **HRMS (ESI+):** Calcd. for $C_{21}H_{17}NO_2Na$ ($[M+Na]^+$): 338.1157, Found: 338.1157; **Optical rotation:** $[\alpha]_D^{21}$ –11.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 298 nm, τ_{minor} = 13.7 min, τ_{major} = 15.2 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ab** was assigned in analogy with **3aa**.

[4] H. Xu, L. Laraia, L. Schneider, K. Louven, C. Strohmann, A. P. Antonchick and H. Waldmann, *Angew. Chem., Int. Ed.* 2017, **56**, 11232-11236.

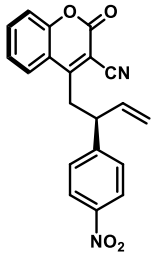
Compound 3ac: Purified by silica-gel flash column chromatography (7% EtOAc in petroleum ether); Off-white solid (55 mg, 0.160 mmol, 80% yield); **m.p.** 138-140 °C; **FT-IR (Thin film):** 2921 (m), 2854 (m), 2371 (m), 2228 (w), 1735 (s), 1599 (s), 1365 (m), 1022 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70-7.66 (m, 2H), 7.40-7.36 (m, 2H), 7.20-7.15 (m, 4H), 6.17-6.08 (m, 1H), 5.09 (d, *J* = 10.1 Hz, 1H), 4.99 (d, *J* = 16.9 Hz, 1H), 3.73-3.68 (m, 1H), 3.54-3.49 (m, 1H), 3.44 (dd, *J* = 12.8, 6.6 Hz, 1H), 2.91-2.84 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.2, 156.8, 153.6, 148.3, 138.8, 138.7, 135.1, 127.2, 127.1, 126.1, 125.4, 118.0, 117.6, 116.7, 113.7, 103.1, 50.5, 38.4, 33.8, 24.1; **HRMS (ESI+):** Calcd. for $C_{23}H_{21}NO_2Na$ ($[M+Na]^+$): 366.1470, Found: 366.1467; **Optical rotation:** $[\alpha]_D^{25}$ –7.0 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 214 nm, τ_{minor} = 11.6 min, τ_{major} = 13.6 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ac** was assigned in analogy with **3aa**.

Compound 3ad: Purified by silica-gel flash column chromatography (12% EtOAc in petroleum ether); Light yellow solid (66 mg, 0.198 mmol, 98% yield); **m.p.** 138-140 °C; **FT-IR (Thin film):** 2931 (w), 2362 (m), 2230 (m), 1734 (s), 1604 (s), 1512 (s), 1251 (s), 1034 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72-7.68 (m, 2H), 7.43-7.38 (m, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.10 (ddd, *J* = 17.2, 9.9, 8.1 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 4.99 (d, *J* = 16.9 Hz, 1H), 3.77 (s, 3H), 3.73-3.67 (m, 1H), 3.53-3.47 (m, 1H), 3.45-3.40 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.1, 158.9, 156.8, 153.6, 139.0, 135.1, 133.2, 128.4, 126.1, 125.5, 118.0, 117.5, 116.4, 114.4, 113.7, 103.0, 55.4, 49.8, 38.4; **HRMS (ESI+):** Calcd. for $C_{21}H_{17}NO_3Na$ ($[M+Na]^+$): 354.1106, Found: 354.1108; **Optical rotation:** $[\alpha]_D^{23}$ –30.4 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 285 nm, τ_{minor} = 47.1 min, τ_{major} = 50.2 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ad** was assigned in analogy with **3aa**.

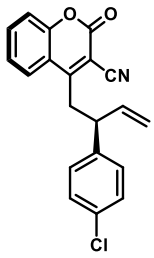
Compound 3ae: Purified by silica-gel flash column chromatography (10% EtOAc in petroleum ether); Off-white solid (51 mg, 0.138 mmol, 69% yield); **m.p.** 159-161 °C; **FT-IR (Thin film):** 2229 (w), 1735 (s), 1603 (m), 1326 (s), 1121 (w), 1071 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73-7.67 (m, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.42-7.38 (m, 4H), 6.15-6.06 (m, 1H), 5.16 (d, *J* = 10.1 Hz, 1H), 5.04 (d, *J* = 16.9 Hz, 1H), 3.84-3.79 (m, 1H), 3.58-3.53 (m, 1H), 3.49-3.44 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.4, 156.6, 153.7, 145.4, 137.7, 135.4, 129.9 (q, *J* = 32 Hz), 127.9, 126.1 (q, *J* = 4 Hz), 125.9, 125.6, 124.1 (q, *J* = 272 Hz), 118.2, 117.8, 117.4, 113.7, 103.3, 50.4,

37.9; **HRMS (ESI+):** Calcd. for $C_{21}H_{14}F_3NO_2Na$ ($[M+Na]^+$): 392.0874, Found: 392.0872; **Optical rotation:** $[\alpha]_D^{23}$ +3.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 320 nm, τ_{minor} = 12.8 min, τ_{major} = 15.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ae** was assigned in analogy with **3aa**.

Compound 3af: Purified by silica-gel flash column chromatography (12% EtOAc in petroleum ether); Off-white solid (49 mg, 0.141 mmol, 71% yield); **m.p.** 188-190 °C; **FT-IR (Thin film):** 2925 (s), 2854 (s), 2229 (m), 1730 (s), 1600 (s), 1517 (s), 1344 (s), 1017 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.75-7.68 (m, 2H), 7.45-7.42 (m, 4H), 6.10 (ddd, *J* = 17.3, 10.0, 8.2 Hz, 1H), 5.21 (d, *J* = 10.1 Hz, 1H), 5.08 (d, *J* = 17.00 Hz, 1H), 3.91-3.85 (m, 1H), 3.57 (dd, *J* = 13.0, 8.6 Hz, 1H), 3.48 (dd, *J* = 13.0, 6.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.9, 156.4, 153.8, 148.6, 147.4, 137.1, 135.5, 128.5, 125.8, 125.7, 124.4, 118.4, 118.4, 117.3, 113.6, 103.5, 50.2, 37.7; **HRMS (ESI+):** Calcd. for $C_{20}H_{14}N_2O_4Na$ ($[M+Na]^+$): 369.0851, Found: 369.0855; **Optical rotation:** $[\alpha]_D^{24}$ –4.4 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 300 nm, τ_{minor} = 17.6 min, τ_{major} = 21.2 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3af** was assigned in analogy with **3aa**.



Compound 3ag: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (53 mg, 0.158 mmol, 79% yield); **m.p.** 154-155 °C; **FT-IR (Thin film):** 3080 (w), 2924 (m), 2362 (w), 2230 (m), 1734 (s), 1602 (s), 1556 (s), 1367 (m), 1084 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73-7.67 (m, 2H), 7.43-7.39 (m, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.08 (ddd, *J* = 17.2, 10.0, 8.1 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 16.9 Hz, 1H), 3.76-3.70 (m, 1H), 3.50 (dd, *J* = 12.8, 8.4 Hz, 1H), 3.43 (dd, *J* = 12.9, 6.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.6, 156.7, 153.7, 139.7, 138.2, 135.3, 133.4, 129.2, 128.8, 126.0, 125.6, 118.2, 117.4, 117.3, 113.7, 103.2, 49.9, 38.1; **HRMS (ESI+):** Calcd. for $C_{20}H_{14}ClNO_2Na$ ($[M+Na]^+$): 358.0611, Found: 358.0614; **Optical rotation:** $[\alpha]_D^{23}$ –5.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 223 nm, τ_{minor} = 32.8 min, τ_{major} = 34.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ag** was assigned in analogy with **3aa**.



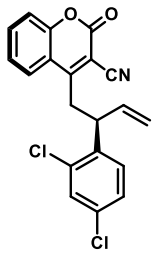
Compound 3ah: Purified by silica-gel flash column chromatography (10% EtOAc in petroleum ether); Off-white solid (69 mg, 0.181 mmol, 91% yield); **m.p.** 94-96 °C; **FT-IR (Thin film):** 3079 (w), 2923 (w), 2361 (m), 2230 (m), 1733 (s), 1602 (s), 1557 (m), 1367 (m), 1077 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73-7.67 (m, 2H), 7.44-7.39 (m, 4H), 7.23-7.17 (m, 2H), 6.07 (ddd, *J* = 17.0, 10.0, 8.2 Hz, 1H), 5.14 (d, *J* = 10.1 Hz, 1H), 5.01 (d, *J* = 16.9 Hz, 1H), 3.73-3.67 (m, 1H), 3.53-3.48 (m, 1H), 3.44 (dd, *J* = 12.9, 6.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.5, 156.6, 153.7, 143.6, 137.8, 135.3, 130.8, 130.7, 130.5, 126.1, 125.9, 125.6, 123.1, 118.2, 117.6, 117.4, 113.7, 103.3, 50.2, 37.9; **HRMS (ESI+):** Calcd. for $C_{20}H_{14}BrNO_2Na$ ($[M+Na]^+$): 402.0106, Found: 402.0107; **Optical rotation:** $[\alpha]_D^{23}$ +1.1 (*c* 2.3, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 288 nm, τ_{major} = 16.8 min, τ_{minor} = 21.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ah** was assigned in analogy with **3aa**.

Compound 3ai: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (50 mg, 0.157 mmol, 78% yield); **m.p.** 138-140 °C; **FT-IR (Thin film):** 3080 (w), 2923 (m), 2230 (m), 1733 (s), 1602 (s), 1449 (m), 1078 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73-7.68 (m, 2H), 7.44-7.40 (m, 2H), 7.32-7.27 (m, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.97-6.93 (m, 2H), 6.14-6.05 (m, 1H), 5.14 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 3.77-3.71 (m, 1H), 3.51 (dd, *J* = 12.9, 8.5 Hz, 1H), 3.44 (dd, *J* = 12.9, 6.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.5, 163.0 (d, *J* = 247.0 Hz), 156.7, 153.7, 143.8 (d, *J* = 6.9 Hz), 137.9, 135.3, 130.7, 125.9, 125.6, 123.1 (d, *J* = 2.62 Hz), 118.2, 117.5, 114.6 (d, *J* = 9.8 Hz), 114.4 (d, *J* = 10.7 Hz), 113.6, 103.2, 50.2, 38.0; **HRMS (ESI+):** Calcd. for $C_{20}H_{14}FNO_2Na$ ($[M+Na]^+$): 342.0906, Found: 342.0908; **Optical rotation:** $[\alpha]_D^{23}$ +0.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 304 nm, τ_{minor} = 19.8 min, τ_{major} = 21.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ai** was assigned in analogy with **3aa**.

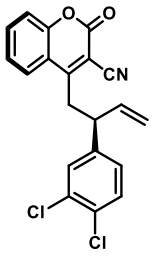
Compound 3aj: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (44 mg, 0.125 mmol, 62% yield); **m.p.** 120-122 °C; **FT-IR (Thin film):** 3074 (w), 2926 (m), 2361 (m), 2230 (m), 1734 (s), 1602 (s), 1556 (m), 1079 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.89 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.69-7.65 (m, 2H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.54-7.50 (m, 1H), 7.47-7.39 (m, 2H), 7.37-7.32 (m, 2H), 6.21 (ddd, *J* = 17.2, 10.1, 7.8 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 4.61-4.55

(m, 1H), 3.76 (dd, *J* = 12.7, 8.8 Hz, 1H), 3.56 (dd, *J* = 12.7, 6.2 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.0, 156.7, 153.6, 138.8, 137.5, 135.1, 134.0, 131.1, 129.3, 128.2, 126.4, 125.9, 125.8, 125.8, 125.5, 124.8, 122.5, 118.1, 117.7, 117.2, 113.8, 103.3, 45.1, 37.9; **HRMS (ESI+):** Calcd. for $C_{24}H_{17}NO_2Na$ ($[M+Na]^+$): 374.1157, Found: 374.1158; **Optical rotation:** $[\alpha]_D^{21}$ +8.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 69:31 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 280 nm, τ_{minor} = 9.2 min, τ_{major} = 10.9 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3aj** was assigned in analogy with **3aa**.

Compound 3ak: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (38 mg, 0.103 mmol, 51% yield); **m.p.** 138-140 °C; **FT-IR (Thin film):** 2925 (m), 2853 (m), 2231 (m), 1736 (s), 1602 (s), 1557 (m), 1079 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.82-7.80 (m, 1H), 7.74-7.69 (m, 1H), 7.45-7.40 (m, 3H), 7.35-7.31 (m, 2H), 6.09 (ddd, *J* = 17.0, 10.2, 8.0 Hz, 1H), 5.18 (d, *J* = 10.1 Hz, 1H), 5.05 (d, *J* = 16.9 Hz, 1H), 4.33-4.28 (m, 1H), 3.50 (dd, *J* = 12.5, 8.9 Hz, 1H), 3.41 (dd, *J* = 12.9, 6.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.9, 156.6, 153.7, 137.6, 136.7, 135.3, 133.9, 133.8, 129.8, 129.7, 128.2, 125.9, 125.6, 118.2, 118.1, 117.5, 113.7, 103.4, 45.5, 37.6; **HRMS (ESI+):** Calcd. for $C_{20}H_{13}Cl_2NO_2Na$ ($[M+Na]^+$): 392.0221, Found: 392.0220; **Optical rotation:** $[\alpha]_D^{23}$ –3.2 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 71:29 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 300 nm, τ_{minor} = 13.6 min, τ_{major} = 14.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ak** was assigned in analogy with **3aa**.



Compound 3al: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (55 mg, 0.149 mmol, 75% yield); **m.p.** 95-97 °C; **FT-IR (Thin film):** 2923 (m), 2854 (m), 2230 (m), 1733 (s), 1602 (s), 1556 (m), 1031 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74-7.68 (m, 2H), 7.45-7.34 (m, 4H), 7.12-7.10 (m, 1H), 6.08-5.99 (m, 1H), 5.15 (d, *J* = 10.1 Hz, 1H), 5.01 (d, *J* = 16.9 Hz, 1H), 3.72-3.70 (m, 1H), 3.49-3.47 (m, 1H), 3.46-3.44 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.2, 156.6, 153.7, 141.5, 137.5, 135.5, 133.1, 131.7, 131.0, 129.5, 126.8, 125.9, 125.7, 118.3, 117.9, 117.3, 113.7, 103.3, 49.6, 37.7; **HRMS (ESI+):** Calcd. for $C_{20}H_{13}Cl_2NO_2Na$ ($[M+Na]^+$): 392.0221, Found: 392.0221; **Optical rotation:** $[\alpha]_D^{20}$ –2.1 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IG column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 211 nm, τ_{minor} = 26.4 min, τ_{major} = 32.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3al** was assigned in analogy with **3aa**.



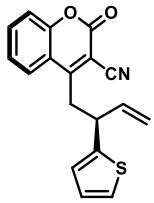
Compound 3am: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Light yellow solid (62 mg, 0.180 mmol, 90% yield); **m.p.** 145-147 °C; **FT-IR (Thin film):** 2922 (m), 2361 (m), 2230 (m), 1733 (s), 1603 (s), 1492 (s), 1245 (m), 1038 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72-7.68 (m, 2H), 7.43-7.38 (m, 2H), 6.73-6.71 (m, 2H), 6.64-6.62 (m, 1H), 6.08 (ddd, *J* = 17.3, 10.2, 8.0 Hz, 1H), 5.93 (s, 2H), 5.11 (d, *J* = 10.1 Hz, 1H), 5.01 (d, *J* = 17.0 Hz, 1H), 3.68-3.63 (m, 1H), 3.48 (dd, *J* = 12.8, 8.1 Hz, 1H), 3.40 (dd, *J* = 12.9, 7.1 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.9, 156.8, 153.7, 148.2, 147.0, 138.8, 135.2, 135.0, 126.0, 125.5, 120.6, 118.1, 117.5, 116.6, 113.7, 108.6, 107.8, 103.1, 101.3, 50.2, 38.4; **HRMS (ESI+):** Calcd. for $C_{21}H_{15}NO_4Na$ ([M+Na]$^+$): 368.0899, Found: 368.0907; **Optical rotation:** $[\alpha]_D^{22}$ –39.7 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 286 nm, τ_{minor} = 37.3 min, τ_{major} = 48.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3am** was assigned in analogy with **3aa**.

Compound 3an: Purified by silica-gel flash column chromatography (10% EtOAc in dichloromethane); Yellow thick oil (52 mg, 0.171 mmol, 86% yield); **FT-IR (Thin film):**, 2924 (m), 2853 (m), 2228 (m), 1733 (s), 1601 (s), 1556 (m), 1368 (m), 1082 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.51-8.42 (m, 2H), 7.72-7.66 (m, 3H), 7.44-7.38 (m, 2H), 7.30-7.26 (m, 1H), 6.14-6.05 (m, 1H), 5.17 (d, *J* = 10.0 Hz, 1H), 5.06 (d, *J* = 16.9 Hz, 1H), 3.81-3.75 (m, 1H), 3.57-3.52 (m, 1H), 3.48-3.43 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.1, 156.5, 153.7, 149.1, 148.9, 137.5, 136.7, 135.4, 134.9, 125.9, 125.7, 124.0, 118.2, 117.9, 117.3, 113.6, 103.3, 47.8, 37.8; **HRMS (ESI+):** Calcd. for $C_{19}H_{14}N_2O_2Na$ ([M+Na]$^+$): 325.0953, Found: 325.0954; **Optical rotation:** $[\alpha]_D^{21}$ +3.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 333 nm, τ_{minor} = 13.4 min, τ_{major} = 24.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3an** was assigned in analogy with **3aa**.

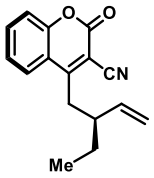
Compound 3ao: Purified by silica-gel flash column chromatography (9% EtOAc in petroleum ether); Off-white solid (43 mg, 0.148 mmol, 74% yield); **m.p.** 132-134 °C; **FT-IR (Thin film):** 3080 (w), 2924 (w), 2230 (m), 1734 (s), 1602 (s), 1556 (s), 1078 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74-7.67 (m, 2H), 7.42-7.35 (m, 3H), 6.29-6.27 (m, 1H), 6.10-6.02 (m, 2H), 5.19 (d, *J* = 10.1 Hz, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 3.86-3.81 (m, 1H), 3.63 (dd, *J* = 13.0, 6.7 Hz, 1H), 3.38 (dd, *J* = 12.9, 8.3 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.3, 156.7, 153.5, 142.1, 135.5, 135.1, 125.9, 125.5, 118.3, 117.9, 117.3, 113.4, 110.5, 106.5, 103.1, 44.1, 36.2; **HRMS (ESI+):** Calcd. for $C_{18}H_{13}NO_3Na$

([M+Na]$^+$): 314.0793, Found: 314.0796; **Optical rotation:** $[\alpha]_D^{21}$ –10.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 227 nm, τ_{minor} = 14.5 min, τ_{major} = 15.9 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ao** was assigned in analogy with **3aa**.

Compound 3ap: Purified by silica-gel flash column chromatography (10% EtOAc in petroleum ether); Light yellow solid (53 mg, 0.172 mmol, 86% yield); **m.p.** 140-142 °C; **FT-IR (Thin film):** 2923 (w), 2229 (m), 1733 (s), 1601 (s), 1555 (m), 1366 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.73-7.68 (m, 2H), 7.43-7.39 (m, 2H), 7.21 (dd, *J* = 5.1 Hz, 1.2 Hz, 1H), 6.96-6.94 (m, 1H), 6.90-6.89 (m, 1H), 6.09 (ddd, *J* = 16.9, 10.0, 8.4 Hz, 1H), 5.15 (d, *J* = 10.1 Hz, 1H), 5.04 (d, *J* = 16.9 Hz, 1H), 4.06-4.00 (m, 1H), 3.57 (dd, *J* = 12.9, 6.3 Hz, 1H), 3.50 (dd, *J* = 12.9, 8.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.2, 156.7, 153.7, 144.5, 138.0, 135.3, 127.3, 125.9, 125.6, 124.6, 124.5, 118.1, 117.5, 117.5, 113.6, 103.3, 45.8, 38.9; **HRMS (ESI+):** Calcd. for $C_{18}H_{13}NO_2SNa$ ([M+Na]$^+$): 330.0565, Found: 330.0566; **Optical rotation:** $[\alpha]_D^{23}$ –15.2 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 322 nm, τ_{minor} = 36.8 min, τ_{major} = 41.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ap** was assigned in analogy with **3aa**.



Compound 3aq: Purified by silica-gel flash column chromatography (7% EtOAc in petroleum ether); Off-white solid (24 mg, 0.094 mmol, 48% yield); **m.p.** 85-87 °C; **FT-IR (Thin film):** 2964 (m), 2921 (m), 2851 (m), 2229 (m), 1728 (s), 1599 (s), 1553 (s), 1367 (m), 1078 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72-7.67 (m, 2H), 7.44-7.38 (m, 2H), 5.69-5.60 (m, 1H), 5.00 (d, *J* = 9.9 Hz, 1H), 4.80 (d, *J* = 16.9 Hz, 1H), 3.22-3.18 (m, 1H), 3.07-3.02 (m, 1H), 2.38-2.36 (m, 1H), 1.66-1.62 (m, 1H), 1.59-1.55 (m, 1H), 0.98-0.94 (m, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.9, 156.9, 153.7, 139.3, 135.1, 126.2, 125.5, 118.1, 117.8, 117.4, 113.9, 102.9, 47.7, 37.5, 28.4, 11.9; **HRMS (ESI+):** Calcd. for $C_{16}H_{15}NO_2Na$ ([M+Na]$^+$): 276.1000, Found: 276.1003; **Optical rotation:** $[\alpha]_D^{20}$ –2.4 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 328 nm, τ_{minor} = 16.0 min, τ_{major} = 17.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3aq** was assigned in analogy with **3aa**.



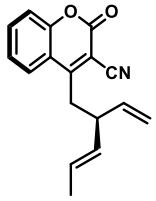
Compound 3ar: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (34 mg, 0.111 mmol, 55% yield); **m.p.** 150-152 °C; **FT-IR (Thin film):** 2925 (s), 2851 (m), 2229 (m), 1736 (s), 1602 (s), 1556 (m), 1077 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70-7.66 (m, 2H), 7.42-7.37 (m, 2H), 5.74-5.64 (m, 1H), 4.93 (d, *J* = 10.1 Hz, 1H), 4.62 (d, *J* = 16.9 Hz, 1H), 3.31 (dd, *J* = 12.8, 4.0 Hz, 1H), 3.00 (dd, *J* = 12.4, 11.0 Hz, 1H), 2.30-2.22 (m, 1H), 1.83-1.79 (m, 4H), 1.71-1.68 (m, 1H), 1.54-1.46 (m, 1H), 1.36-0.99 (m, 5H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 165.8, 157.0, 153.7, 137.6, 135.0, 126.1, 125.4, 118.1, 117.9, 117.8, 114.0, 103.0, 52.1, 42.6, 34.9, 31.2, 30.2, 26.5, 26.5, 26.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{21}NO_2Na$ ($[M+Na]^+$): 330.1470, Found: 330.1469; **Optical rotation:** $[\alpha]_D^{20}$ –5.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 93.5:6.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 341 nm, τ_{minor} = 11.8 min, τ_{major} = 12.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ar** was assigned in analogy with **3aa**.

Compound 3as: Purified by silica-gel flash column chromatography (6% EtOAc in petroleum ether); White solid (25 mg, 0.079 mmol, 40% yield); **m.p.** 111-113 °C; **FT-IR (Thin film):** 3072 (w), 2923 (m), 2853 (w), 2229 (m), 1734 (s), 1602 (m), 1555 (m), 1450 (m), 1077 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.65-7.61 (m, 1H), 7.38-7.34 (m, 3H), 7.30-7.24 (m, 4H), 7.17-7.15 (m, 1H), 5.85-5.76 (m, 1H), 5.01 (d, *J* = 10.1 Hz, 1H), 4.77 (d, *J* = 17.0 Hz, 1H), 3.19-3.15 (m, 1H), 3.03-2.96 (m, 2H), 2.82-2.76 (m, 1H), 2.75-2.69 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.6, 156.8, 153.7, 139.0, 138.9, 135.0, 129.4, 128.8, 127.0, 125.9, 125.4, 118.0, 117.6, 117.5, 114.0, 103.1, 48.0, 42.3, 36.5; **HRMS (ESI+):** Calcd. for $C_{21}H_{17}NO_2Na$ ($[M+Na]^+$): 338.1157, Found: 338.1154; **Optical rotation:** $[\alpha]_D^{21}$ +8.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IG column (95:5 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 294 nm, τ_{minor} = 34.0 min, τ_{major} = 37.1 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3as** was assigned in analogy with **3aa**.

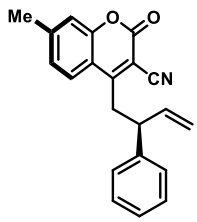
Compound 3at: Regioselectivity (rr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Off-white solid (50 mg, 0.176 mmol, 79% yield); **m.p.** 137-139 °C; **FT-IR (Thin film):** 3081 (w), 2925 (m), 2860 (w), 2361 (m), 2230 (m), 1733 (s), 1602 (s), 1556 (m), 1078 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.73-7.69 (m, 1H), 7.46-7.40 (m, 2H), 7.31-7.23 (m, 5H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.22 (dd, *J* = 15.6, 6.7 Hz, 1H), 6.00-5.92 (m, 1H), 5.14 (d, *J* = 10.0 Hz, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 3.39-3.34 (m, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.8, 156.8, 153.7, 138.1, 136.4, 135.2, 131.8, 129.3, 128.7, 127.9, 126.4, 126.1, 125.6, 118.1, 117.6, 116.9,

113.9, 103.1, 48.5, 37.3; **HRMS (ESI+):** Calcd. for $C_{22}H_{17}NO_2Na$ ($[M+Na]^+$): 350.1157, Found: 350.1159; **Optical rotation:** $[\alpha]_D^{24}$ –86.8 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{minor} = 16.8 min, τ_{major} = 18.2 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3at** was assigned in analogy with **3aa**.

Compound 3au: Regioselectivity (rr) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by silica-gel flash column chromatography (6% EtOAc in petroleum ether); Off-white solid (44 mg, 0.166 mmol, 83% yield); **m.p.** 105-107 °C; **FT-IR (Thin film):** 2923 (m), 2855 (w), 2228 (m), 1727 (s), 1600 (s), 1556 (m), 1449 (m), 1367 (m), 1078 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72-7.68 (m, 2H), 7.44-7.38 (m, 2H), 5.85 (ddd, *J* = 17.2, 9.9, 7.6 Hz, 1H), 5.51-5.38 (m, 2H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.97 (d, *J* = 17.0 Hz, 1H), 3.20-3.17 (m, 2H), 3.14-3.09 (m, 1H), 1.64 (d, *J* = 5.6 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.2, 156.9, 153.7, 138.8, 135.1, 130.9, 127.8, 126.2, 125.5, 118.1, 117.6, 116.2, 113.8, 103.0, 48.3, 37.5, 17.9; **HRMS (ESI+):** Calcd. for $C_{17}H_{15}NO_2Na$ ($[M+Na]^+$): 288.1000, Found: 288.1004; **Optical rotation:** $[\alpha]_D^{21}$ –17.0 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (99:1 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 322 nm, τ_{major} = 24.0 min, τ_{minor} = 29.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3au** was assigned in analogy with **3aa**.



Compound 3ba: Purified by silica-gel flash column chromatography (7% EtOAc in petroleum ether); Off-white solid (62 mg, 0.196 mmol, 98% yield); **m.p.** 114-116 °C; **FT-IR (Thin film):** 3029 (w), 2923 (m), 2362 (m), 2227 (m), 1731 (s), 1620 (s), 1545 (m), 1086 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, *J* = 8.2 Hz, 1H), 7.34-7.30 (m, 2H), 7.26-7.18 (m, 5H), 6.12 (ddd, *J* = 18.0, 9.9, 8.3 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 16.9 Hz, 1H), 3.75-3.70 (m, 1H), 3.49 (dd, *J* = 12.9, 8.7 Hz, 1H), 3.42 (dd, *J* = 12.9, 6.9 Hz, 1H), 2.50 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.0, 157.1, 153.7, 147.3, 141.3, 138.7, 129.0, 127.5, 127.3, 126.8, 125.8, 118.0, 116.7, 115.2, 113.9, 101.7, 50.6, 38.2, 22.0; **HRMS (ESI+):** Calcd. for $C_{21}H_{17}NO_2Na$ ($[M+Na]^+$): 338.1157, Found: 338.1180; **Optical rotation:** $[\alpha]_D^{24}$ –6.4 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 320 nm, τ_{minor} = 15.0 min, τ_{major} = 16.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ba** was assigned in analogy with **3aa**.



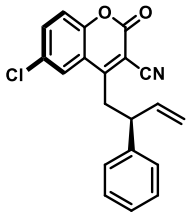
Compound 3ca: Purified by silica-gel flash column chromatography (7% EtOAc in petroleum ether); Off-white solid (62 mg, 0.196 mmol, 98% yield); **m.p.** 133-135 °C; **FT-IR (Thin film):** 3027 (m), 2925 (m), 2229 (m), 1732 (s), 1561 (s), 1493 (m), 1368 (m), 1081 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 8.2 Hz, 1H), 7.38 (s, 1H), 7.32-7.20 (m, 6H), 6.13 (ddd, *J* = 17.2, 10.0, 8.3 Hz, 1H), 5.11 (d, *J* = 10.1 Hz, 1H), 5.02 (d, *J* = 16.9 Hz, 1H), 3.74-3.69 (m, 1H), 3.49 (dd, *J* = 12.6, 8.2 Hz, 1H), 3.41 (dd, *J* = 12.8, 7.0 Hz, 1H), 2.42 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.0, 157.0, 151.8, 141.3, 138.7, 136.3, 135.4, 129.0, 127.5, 127.4, 125.7, 117.7, 117.2, 116.7, 113.8, 102.8, 50.5, 38.2, 21.1; **HRMS (ESI+):** Calcd. for $C_{21}H_{17}NO_2Na$ ($[M+Na]^+$): 338.1157, Found: 338.1154; **Optical rotation:** $[\alpha]_D^{23}$ –7.5 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 308 nm, τ_{major} = 11.9 min, τ_{minor} = 14.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ca** was assigned in analogy with **3aa**.

Compound 3da: Purified by silica-gel flash column chromatography (12% EtOAc in petroleum ether); Off-white solid (53 mg, 0.160 mmol, 80% yield); **m.p.** 102-104 °C; **FT-IR (Thin film):** 2926 (w), 2226 (m), 1729 (s), 1617 (s), 1381 (m), 1244 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 9.0 Hz, 1H), 7.34-7.30 (m, 2H), 7.26-7.22 (m, 3H), 6.92 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.82 (d, *J* = 2.5 Hz, 1H), 6.12 (ddd, *J* = 17.1, 10.1, 8.3 Hz, 1H), 5.11 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 16.9 Hz, 1H), 3.92 (s, 3H), 3.74-3.68 (m, 1H), 3.47 (dd, *J* = 12.8, 8.5 Hz, 1H), 3.38 (dd, *J* = 12.8, 6.9 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 165.4, 163.9, 157.5, 156.0, 141.4, 138.7, 129.1, 127.6, 127.4, 127.3, 116.8, 114.2, 111.3, 101.4, 99.2, 56.3, 50.7, 38.3; **HRMS (ESI+):** Calcd. for $C_{21}H_{17}NO_3Na$ ($[M+Na]^+$): 354.1106, Found: 354.1107; **Optical rotation:** $[\alpha]_D^{21}$ +4.8 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 246 nm, τ_{minor} = 8.8 min, τ_{major} = 9.8 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3da** was assigned in analogy with **3aa**.

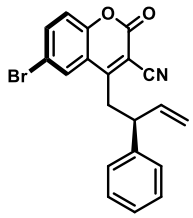
Compound 3ea: Purified by silica-gel flash column chromatography (12% EtOAc in petroleum ether); Off-white solid (53 mg, 0.166 mmol, 83% yield); **m.p.** 110-112 °C; **FT-IR (Thin film):** 3083 (w), 2923 (w), 2362 (m), 2230 (m), 1739 (s), 1611 (s), 1371 (m), 1025 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.70-7.66 (m, 1H), 7.34-7.30 (m, 2H), 7.26-7.21 (m, 3H), 7.15-7.08 (m, 2H), 6.13 (ddd, *J* = 17.1, 10.1, 8.0 Hz, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 3.74-3.68 (m, 1H), 3.51 (dd, *J* = 12.8, 8.3 Hz, 1H), 3.42 (dd, *J* = 12.9, 7.0 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 166.2 (d, *J* = 261.0 Hz), 163.6, 156.5, 155.1 (d, *J* = 13.4 Hz), 141.1, 138.5, 129.1,

128.3 (d, *J* = 10.8 Hz), 127.7, 127.4, 116.9, 114.4 (d, *J* = 2.6 Hz), 113.9 (d, *J* = 22.9 Hz), 113.5, 105.5 (d, *J* = 25.6 Hz), 101.9 (d, *J* = 2.6 Hz), 50.6, 38.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{14}FNO_2Na$ ($[M+Na]^+$): 342.0906, Found: 342.0907; **Optical rotation:** $[\alpha]_D^{21}$ –16.1 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 215 nm, τ_{minor} = 14.7 min, τ_{major} = 17.6 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ea** was assigned in analogy with **3aa**.

Compound 3fa: Purified by silica-gel flash column chromatography (6% EtOAc in petroleum ether); Off-white solid (66 mg, 0.196 mmol, 98% yield); **m.p.** 124-126 °C; **FT-IR (Thin film):** 3077 (w), 2924 (w), 2231 (w), 1739 (s), 1602 (m), 1553 (s), 1077 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.60 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.33-7.29 (m, 3H), 7.24-7.19 (m, 3H), 6.13 (ddd, *J* = 17.5, 10.0, 8.2 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 5.07 (d, *J* = 17.0 Hz, 1H), 3.74-3.68 (m, 1H), 3.49 (dd, *J* = 12.9, 8.2 Hz, 1H), 3.38 (dd, *J* = 12.9, 7.2 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.0, 156.1, 151.9, 140.9, 138.5, 134.9, 131.0, 129.1, 127.7, 127.4, 125.5, 119.4, 118.6, 116.9, 113.3, 104.0, 50.4, 38.3; **HRMS (ESI+):** Calcd. for $C_{20}H_{14}ClNO_2Na$ ($[M+Na]^+$): 358.0611, Found: 358.0607; **Optical rotation:** $[\alpha]_D^{21}$ –11.3 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 286 nm, τ_{minor} = 18.7 min, τ_{major} = 20.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3fa** was assigned in analogy with **3aa**.



Compound 3ga: Purified by silica-gel flash column chromatography (6% EtOAc in petroleum ether); Off-white solid (67 mg, 0.176 mmol, 88% yield); **m.p.** 128-130 °C; **FT-IR (Thin film):** 3076 (w), 2924 (m), 2230 (m), 1738 (s), 1598 (m), 1549 (m), 1275 (m), 1079 (m); **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.74 (d, *J* = 8.6 Hz, 1H), 7.70 (s, 1H), 7.33-7.26 (m, 4H), 7.23-7.21 (m, 2H), 6.20-6.11 (m, 1H), 5.17 (d, *J* = 10.2 Hz, 1H), 5.08 (d, *J* = 16.9 Hz, 1H), 3.74-3.68 (m, 1H), 3.53-3.48 (m, 1H), 3.42-3.37 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.0, 156.0, 152.4, 140.9, 138.5, 137.7, 129.2, 128.6, 127.8, 127.4, 119.7, 119.1, 118.3, 117.0, 113.2, 104.1, 50.5, 38.3; **HRMS (ESI+):** Calcd. for $C_{20}H_{14}BrNO_2Na$ ($[M+Na]^+$): 402.0106, Found: 402.0108; **Optical rotation:** $[\alpha]_D^{22}$ –5.2 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 224 nm, τ_{major} = 15.3 min, τ_{minor} = 20.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ga** was assigned in analogy with **3aa**.



Compound 3ha: Purified by silica-gel flash column chromatography (7% EtOAc in petroleum ether); Off-white solid (66 mg, 0.188 mmol, 94% yield); **m.p.** 103-105 °C; **FT-IR (Thin film):**, 2924 (m), 2852 (w), 2362 (m), 2229 (m), 1734 (s), 1540 (m), 1370 (m), 1092 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.56 (s, 1H), 7.32-7.31 (m, 2H), 7.26-7.22 (m, 4H), 6.18-6.10 (m, 1H), 5.15 (d, *J* = 10.0 Hz, 1H), 5.06 (d, *J* = 16.8 Hz, 1H), 3.75-3.69 (m, 1H), 3.50-3.45 (m, 1H), 3.40-3.35 (m, 1H), 2.50 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.1, 156.5, 151.9, 144.8, 141.1, 138.5, 131.6, 129.1, 127.7, 127.4, 125.7, 119.8, 116.9, 116.6, 113.5, 102.9, 50.5, 38.3, 21.0; **HRMS (ESI+):** Calcd. for $C_{21}H_{16}ClNO_2Na$ ([M+Na]$^+$): 372.0767, Found: 372.0764; **Optical rotation:** $[\alpha]_D^{21}$ – 9.8 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IF column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 300 nm, τ_{major} = 20.2 min, τ_{minor} = 21.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ha** was assigned in analogy with **3aa**.

Compound 3cq: Purified by silica-gel flash column chromatography (6% EtOAc in petroleum ether); Off-white solid (22 mg, 0.082 mmol, 41% yield); **m.p.** 127-129 °C; **FT-IR (Thin film):** 2924 (m), 2853 (m), 2230 (m), 1721 (s), 1560 (s), 1371 (m), 1083 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 8.3 Hz, 1H), 7.45 (s, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 5.70-5.61 (m, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 4.82 (d, *J* = 16.9 Hz, 1H), 3.17 (dd, *J* = 12.9, 5.5 Hz, 1H), 3.02 (dd, *J* = 12.7, 9.3 Hz, 1H), 2.47 (s, 3H), 2.41-2.32 (m, 1H), 1.71-1.63 (m, 1H), 1.59-1.50 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.8, 157.2, 151.9, 139.4, 136.2, 135.3, 125.8, 117.8, 117.5, 117.3, 114.1, 102.7, 47.6, 37.5, 28.4, 21.3, 11.9; **HRMS (ESI+):** Calcd. for $C_{17}H_{17}NO_2Na$ ([M+Na]$^+$): 290.1157, Found: 290.1161; **Optical rotation:** $[\alpha]_D^{21}$ +6.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96:4 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (99:1 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 365 nm, τ_{minor} = 20.1 min, τ_{major} = 22.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3cq** was assigned in analogy with **3aa**.

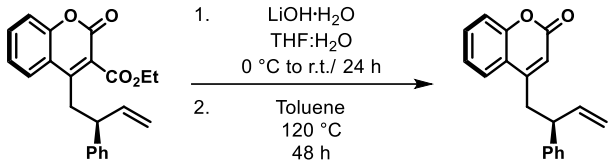
Compound 3ia: Purified by silica-gel flash column chromatography (4% EtOAc in CH_2Cl_2); Off-white solid (52 mg, 0.163 mmol, 81% yield); **m.p.** 152-154 °C; **FT-IR (Thin film):** 3399 (br), 2920 (m), 1710 (s), 1602 (s), 1452 (m), 1018 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.35-7.31 (m, 2H), 7.29-7.25 (m, 2H), 7.22-7.20 (m, 1H), 7.17-7.15 (m, 2H), 6.65 (bs, 1H), 6.11 (ddd, *J* = 17.5, 10.1, 7.7 Hz, 1H), 5.89 (bs, 1H), 5.07-5.00 (m, 2H), 3.88 (dd, *J* = 12.5, 7.1 Hz, 1H), 3.72-3.67 (m, 1H), 3.58 (dd, *J* = 12.4, 7.5 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 166.0, 159.9, 157.1, 153.0, 142.5, 139.8, 133.1, 128.8, 127.8, 127.1, 126.2, 124.9,

121.0, 119.2, 117.4, 115.6, 50.4, 35.0; **HRMS (ESI+):** Calcd. for $C_{20}H_{17}NO_3Na$ ($[M+Na]^+$): 342.1106, Found: 342.1105; **Optical rotation:** $[\alpha]_D^{21}$ –30.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 284 nm, τ_{minor} = 17.7 min, τ_{major} = 21.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ia** was assigned in analogy with **3aa**.

Compound 3ja: Purified by silica-gel flash column chromatography (10% EtOAc in petroleum ether); Yellow thick oil (56 mg, 0.160 mmol, 80% yield); **FT-IR (Thin film):** 2924 (w), 2852 (w), 2362 (w), 1722 (s), 1606 (m), 1243 (s), 1028 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.60-7.54 (m, 2H), 7.36-7.23 (m, 5H), 7.18 (d, *J* = 7.7 Hz, 2H), 6.10-6.01 (m, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 4.99 (d, *J* = 17.0 Hz, 1H), 4.42-4.36 (m, 1H), 4.33-4.27 (m, 1H), 3.74-3.69 (m, 1H), 3.39-3.28 (m, 2H), 1.36 (t, *J* = 7.7 Hz, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.9, 158.0, 153.3, 152.4, 142.3, 139.4, 132.7, 128.9, 127.5, 127.2, 125.9, 124.6, 122.0, 118.5, 117.5, 116.0, 62.2, 49.9, 35.5, 14.2; **HRMS (ESI+):** Calcd. for $C_{22}H_{20}O_4Na$ ($[M+Na]^+$): 371.1259, Found: 371.1258; **Optical rotation:** $[\alpha]_D^{20}$ –1.2 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 320 nm, τ_{major} = 9.0 min, τ_{minor} = 11.1 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ja** was assigned in analogy with **3aa**.

Compound 3ka: Purified by silica-gel flash column chromatography (8% EtOAc in petroleum ether); Yellow thick oil (70 mg, 0.170 mmol, 85% yield); **FT-IR (Thin film):** 2923 (w), 1722 (s), 1605 (m), 1452 (m), 1022 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.58-7.53 (m, 2H), 7.48-7.46 (m, 2H), 7.40-7.33 (m, 4H), 7.29-7.23 (m, 3H), 7.19-7.16 (m, 1H), 7.05-7.03 (m, 2H), 5.85 (ddd, *J* = 17.0, 10.1, 7.0 Hz, 1H), 5.39 (d, *J* = 12.2 Hz, 1H), 5.28 (d, *J* = 12.1 Hz, 1H), 4.94 (d, *J* = 10.1 Hz, 1H), 4.86 (d, *J* = 16.9 Hz, 1H), 3.64-3.59 (m, 1H), 3.30-3.25 (m, 1H), 3.24-3.20 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 164.7, 157.9, 153.3, 152.8, 142.3, 139.2, 135.2, 132.8, 128.9, 128.8, 128.7, 128.6, 127.4, 127.1, 125.8, 124.6, 121.7, 118.4, 117.5, 116.1, 67.9, 49.9, 35.4; **HRMS (ESI+):** Calcd. for $C_{27}H_{22}O_4Na$ ($[M+Na]^+$): 433.1416, Found: 433.1413; **Optical rotation:** $[\alpha]_D^{21}$ +13.4 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 306 nm, τ_{major} = 11.7 min, τ_{minor} = 13.9 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3ka** was assigned in analogy with **3aa**.

H. Procedure for the preparation of 3ma:

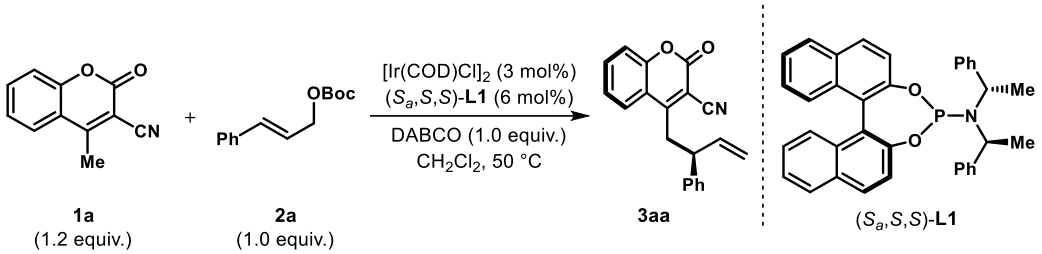


3ja (97.5:2.5 er) **3ma**

In a 10 mL round-bottom flask, **3ja** (51 mg, 0.147 mmol, 1.0 equiv.) was taken in 1 mL of a 1:1 mixture of THF and H_2O, and cooled to 0 °C. To this, was added $LiOH.H_2O$ (31 mg, 0.735 mmol, 5.0 equiv.), warmed to r.t. and the resulting solution was stirred for 24 h. The clear yellow solution was then diluted with 1 M HCl (1 mL) and Et_2O (5 mL). Organic phase was separated from the aqueous layer. The aqueous layer was extracted with Et_2O (3 × 5 mL). The combined organic layer was washed with brine (5 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain yellow oil. This residue was subjected for the next step without further purification.

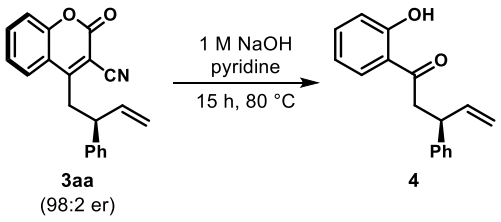
In an oven dried 10 mL round-bottom flask, equipped with a reflux condenser, the residue from the above step was taken in 2 mL absolute toluene under argon. The resulting solution was refluxed at 120 °C for 48 h. Solvent was removed under reduced pressure and the residue was purified by silica-gel flash column chromatography (3% EtOAc in petroleum ether) to obtain **3ma** as a colorless thick oil (24 mg, 0.087 mmol, 60% yield over 2 steps); **FT-IR (Thin film):** 2923 (w), 2350 (w), 1723 (s), 1608 (m), 1445 (m), 1179 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.55-7.51 (m, 1H), 7.35-7.28 (m, 4H), 7.25-7.22 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.09 (s, 1H), 6.07-6.00 (m, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 5.04 (d, *J* = 17.0 Hz, 1H), 3.73-3.67 (m, 1H), 3.22-3.17 (m, 1H), 3.16-3.11 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 160.7, 153.9, 153.5, 142.3, 140.0, 131.8, 129.0, 127.5, 127.2, 124.4, 124.3, 119.3, 117.6, 115.9, 115.8, 48.5, 37.9; **HRMS (ESI+):** Calcd. for $C_{19}H_{16}O_2Na$ ($[M+Na]^+$): 299.1048, Found: 299.1054; **Optical rotation:** $[\alpha]_D^{21}$ –39.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB column (99:1 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 208 nm, τ_{major} = 17.2 min, τ_{minor} = 19.0 min). See Supporting Information: Part B for HPLC chromatograms.

I. Large scale synthesis of 3aa:



In an oven dried 25 mL 2-necked round-bottom flask, equipped with a reflux condenser, $[Ir(COD)Cl]_2$ (101 mg, 0.150 mmol, 3 mol%) and ligand (S_a,*S*,*S*)-**L1** (162 mg, 0.300 mmol, 6 mol%) were taken with 12.5 mL of absolute THF under a positive argon pressure followed by addition of 7.5 mL dry *n*-$PrNH_2$. The solution was heated at 50 °C for 30 min, after which all volatiles were removed under vacuum to obtain a yellow solid. To this, coumarin **1a** (1.11 g, 6.000 mmol, 1.2 equiv.) and DABCO (561 mg, 5.000 mmol, 1.0 equiv.) were introduced under a positive argon pressure followed by 12.5 mL of absolute CH_2Cl_2 and the suspension was stirred at 50 °C for 5 min. After 5 min, a solution of allyl carbonate **2a** (1.17 g, 5.000 mmol, 1.0 equiv.) in 5.0 mL absolute CH_2Cl_2 was added to it. The resulting mixture was purged with argon and the reaction was refluxed at 50 °C until TLC (20% EtOAc in petroleum ether) revealed complete consumption of **2a**. After 36 h, the reaction mixture was allowed to attain ambient temperature, diluted with 10 mL of CH_2Cl_2 and 10 mL 1 N HCl solution. Organic layer was separated from the aqueous layer. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). Combined organic layer was washed with brine (20 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a reddish-brown oil. This oil was purified by silica-gel flash column chromatography (8-9% EtOAc in petroleum ether) to obtain **3aa** as off-white solid (1.32 g, 4.380 mmol, 88% yield) with 95:5 er. Isolated **3aa** was further recrystallized form EtOH to obtain 1.0 g of **3aa** with 98:2 er.

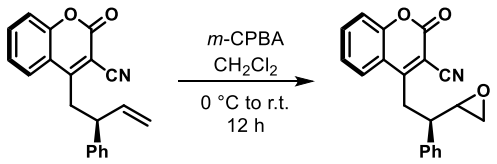
J. Procedure for the retro-Knoevanagel/hydrolysis reaction of 3aa:



In a 5 mL round-bottom flask, **3aa** (30 mg, 0.100 mmol, 1.0 equiv.) was suspended in 1 M NaOH solution (1 mL, 1.000 mmol, 10.0 equiv.). To this was added pyridine (9 µL, 0.110 mmol, 1.1 equiv.), purged with argon, sealed the flask with glass stopper and heated the reaction mixture at 80 °C for 15 h. The clear yellow solution was allowed to attain ambient temperature,

diluted with 1 M HCl (1 mL) and EtOAc (10 mL). Organic phase was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with brine (5 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether) to obtain **4** as a colorless thick oil (16 mg, 0.063 mmol, 63% yield); **FT-IR (Thin film):** 3029 (br), 2920 (w), 1640 (s), 1488 (s), 1447 (s), 1156 (m), 991 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 12.25 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.34-7.21 (m, 5H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.91-6.87 (m, 1H), 6.10-6.01 (m, 1H), 5.11-5.08 (m, 1H), 5.08-5.03 (m, 1H), 4.15-4.09 (m, 1H), 3.46 (dd, *J* = 16.5, 7.5 Hz, 1H), 3.39 (dd, *J* = 16.5, 6.8 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 204.5, 162.7, 142.8, 140.4, 136.5, 130.0, 128.8, 127.8, 126.9, 119.6, 119.0, 118.7, 115.1, 44.7, 43.7; **HRMS (ESI+):** Calcd. for $C_{17}H_{16}O_2Na$ ($[M+Na]^+$): 275.1048, Found: 275.1050; **Optical rotation:** $[\alpha]_D^{21}$ –27.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 4.3 min, τ_{minor} = 4.7 min). See Supporting Information: Part B for HPLC chromatograms.

K. Procedure for the epoxidation of 3aa:

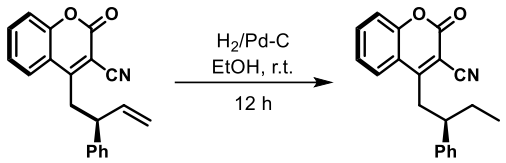


3aa (98:2 er) **5**

In an oven and vacuum-dried 10 mL round-bottom flask, **3aa** (30 mg, 0.100 mmol, 1.0 equiv.) was taken in 0.6 mL of abs. CH_2Cl_2 and cooled it to 0 °C. To this was added *m*-CPBA (41 mg, 55% assay, 0.130 mmol, 1.3 equiv.) and the resulting suspension was stirred at r.t. under argon. After 12 h, reaction mixture was diluted with 2 mL of sat. $Na_2S_2O_3$ solution and 5 mL of CH_2Cl_2. Organic phase was separated from aqueous phase, aqueous phase was extracted with additional CH_2Cl_2 (2 × 5 mL). Combined organic phase was washed with sat. $NaHCO_3$ solution (5 mL) and brine (5 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture (with 1.8:1 dr, as obtained from ^{1}H-NMR) was purified by silica-gel flash column chromatography (2-3% EtOAc in CH_2Cl_2) to obtain **5** as white solid (31 mg, 0.098 mmol, 98% yield); **FT-IR (Thin film):** 3063 (w), 2922 (m), 2852 (w), 2230 (m), 1734 (s), 1602 (s), 1557 (m), 1451 (m), 1367 (m), 1079 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** Signals corresponding to the major diastereomer: δ 7.78 (d, *J* = 7.1 Hz, 1H), 7.72-7.69 (m, 1H), 7.42-7.29 (m, 5H), 7.22-7.20 (m, 2H), 3.78 (dd, *J* = 13.1, 6.5 Hz, 1H), 3.54 (dd, *J* = 13.0, 8.0 Hz, 1H),

3.41 (ddd, *J* = 6.4, 3.6, 2.7 Hz, 1H), 2.80-2.78 (m, 1H), 2.70 (dd, *J* = 15.1, 8.2 Hz, 1H), 2.57 (dd, *J* = 4.5, 8.2 Hz, 1H); Representative signals corresponding to the minor diastereomer: δ 7.72-7.67 (m, 2H), 7.42-7.29 (m, 5H), 7.22-7.20 (m, 2H), 3.56-3.51 (m, 1H), 3.38-3.35 (m, 1H), 3.29 (dd, *J* = 12.9, 8.3 Hz, 1H), 3.18 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.89 (t, *J* = 4.21 Hz, 1H), 2.63 (dd, *J* = 4.4, 2.6 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.8, 163.4, 156.7, 156.6, 153.7, 138.1, 138.0, 135.4, 135.1, 129.3, 129.1, 128.3, 128.3, 128.1, 127.8, 126.2, 126.0, 125.7, 125.6, 118.1, 117.5, 117.3, 113.6, 113.3, 103.1, 55.6, 54.2, 50.7, 47.6, 47.4, 46.0, 36.9, 34.4; **HRMS (ESI+):** Calcd. for $C_{20}H_{15}NO_3Na$ ($[M+Na]^+$): 340.0950, Found: 340.0952; **Optical rotation:** $[\alpha]_D^{21}$ –86.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample (dr = 1.8:1) with 98:2 er for each of the diastereomer. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 320 nm, for major diasteromer τ_{minor} = 31.2 min, τ_{major} = 33.1 min, and for minor diasteromer τ_{minor} = 45.4 min, τ_{major} = 51.8 min). See Supporting Information: Part B for HPLC chromatograms.

L. Procedure for the selective reduction of the allylic double bond of 3aa:

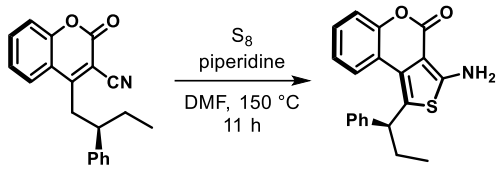


3aa (98:2 er) **6**

In an oven and vacuum-dried 10 mL two-necked round-bottom flask, a solution of **3aa** (90.4 mg, 0.300 mmol, 1.0 equiv.) in EtOH (3 mL), 10% Pd−C (16 mg, 0.015 mmol, 0.05 equiv.) was added. The resulting mixture was degassed and stirred under H_2 balloon pressure for 12 h at r.t. The reaction mixture was filtered over Celite® and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure to obtain crude. The crude reaction mixture was purified by silica-gel flash column chromatography (6-7% EtOAc in petroleum ether) to obtain **6** as white solid (86 mg, 0.283 mmol, 94% yield); **m.p.** 132-134 °C; **FT-IR (Thin film):** 2963 (w), 2922 (m), 2231 (w), 1738 (s), 1599 (m), 1453 (s), 1022 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68-7.63 (m, 2H), 7.38-7.34 (m, 2H), 7.28-7.24 (m, 2H), 7.21-7.17 (m, 1H), 7.13-7.11 (m, 2H), 3.46 (dd, *J* = 12.9, 6.9 Hz, 1H), 3.29 (dd, *J* = 12.9, 8.0 Hz, 1H), 2.98-2.91 (m, 1H), 1.96-1.84 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 165.0, 156.8, 153.5, 141.8, 135.1, 128.8, 127.5, 127.3, 126.3, 125.3, 117.9, 117.6, 113.7, 102.6, 48.8, 39.7, 28.7, 12.2; **HRMS (ESI+):** Calcd. for $C_{20}H_{17}NO_2Na$ ($[M+Na]^+$): 326.1157, Found: 326.1160; The absolute configurations of **6** was assigned as (*S*) by comparing specific rotation with the known compound.[4] **Optical rotation:** $[\alpha]_D^{22}$ –91.7 (*c* 0.85, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er [Lit[4] +78.4 (*c* 0.85, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er]. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IB

column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 12.3 min, τ_{minor} = 13.2 min). See Supporting Information: Part B for HPLC chromatograms.

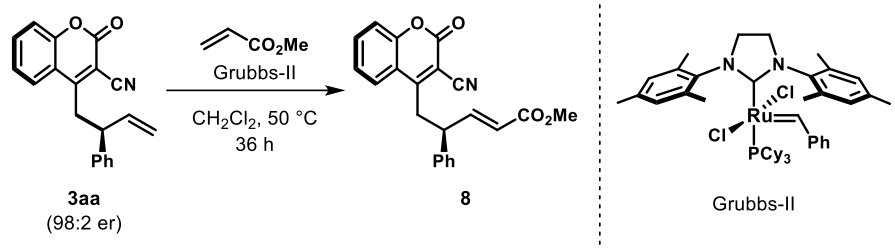
M. Procedure for the base-catalyzed cyclization of 6 with sulfur:



6 (99:1 er) **7**

In an oven dried 5 mL round-bottom flask, piperidine (5 mg, 0.060 mmol, 0.6 equiv.) was taken. Then **6** (30 mg, 0.100 mmol, 1.0 equiv.), sulfur (3.2 mg, 0.100 mmol, 1.0 equiv.) and dry DMF (150 µL) were added to the flask. Subsequently the flask was purged with argon, sealed with glass stopper and heated in an oil bath at 150 °C for 11 h. The clear brownish yellow solution was cooled down to ambient temperature, diluted with H_2O (5 mL) and EtOAc (10 mL). Organic phase was separated from the aqueous layer. The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layer was washed with brine (5 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel flash column chromatography (7% EtOAc in petroleum ether) to obtain **7** as a yellow thick oil (33 mg, 0.098 mmol, 98% yield); **FT-IR (Thin film):** 3415 (br), 3333 (br), 2925 (w), 1681 (s), 1591 (s), 1505 (s), 1270 (m), 1211 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 7.9 Hz, 1H), 7.34-7.28 (m, 5H), 7.25-7.22 (m, 2H), 7.16-7.12 (m, 1H), 6.26 (br s, 2H), 4.58 (t, *J* = 7.5 Hz, 1H), 2.14-2.06 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.4, 160.8, 151.8, 143.2, 128.8, 128.5, 127.9, 127.0, 125.6, 125.1, 124.2, 124.1, 119.2, 117.9, 101.6, 46.9, 31.2, 13.1; **HRMS (ESI+):** Calcd. for $C_{20}H_{17}NO_2SNa$ ($[M+Na]^+$): 358.0878, Found: 358.0874; The absolute configurations of **7** was assigned as (*S*) by comparing specific rotation with the known compound.[4] **Optical rotation:** $[\alpha]_D^{22}$ –68.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er [Lit[4] +12.8 (*c* 0.50, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er]. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AS-H column (95:5 *n*-Hexane/*i*-PrOH, 1.0 mL/min, 20 °C, 315 nm, τ_{major} = 36.3 min, τ_{minor} = 45.4 min). See Supporting Information: Part B for HPLC chromatograms.

N. Procedure for the cross-metathesis reaction of 3aa:



In an oven dried 10 mL 2-necked round-bottom flask, equipped with a reflux condenser, **3aa** (30 mg, 0.100 mmol, 1.0 equiv.) and Grubbs-II (4.3 mg, 0.005 mmol, 0.05 equiv.) were taken in 2 mL of absolute CH_2Cl_2 under argon and the resulting solution was heated to 50 °C. To this, was added methyl acrylate (53 µL, 0.500 mmol, 5.0 equiv.) at once and the resulting mixture was stirred at 50 °C for 36 h. Solvent was evaporated to obtain a yellow residue. The residue was purified by silica-gel flash column chromatography (2% EtOAc in CH_2Cl_2) to obtain **8** as a yellow thick oil (27 mg, 0.075 mmol, 75% yield); **FT-IR (Thin film):** 2955 (s), 2925 (s), 2854 (s), 2230 (m), 1732 (s), 1602 (s), 1454 (m), 1370 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.71-7.67 (m, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.40-7.36 (m, 2H), 7.33-7.22 (m, 4H), 7.20-7.17 (m, 2H), 5.85 (d, *J* = 15.6 Hz, 1H), 3.93-3.87 (m, 1H), 3.72 (s, 3H), 3.59 (dd, *J* = 13.0, 7.3 Hz, 1H), 3.51 (dd, *J* = 12.9, 8.0 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 166.2, 162.9, 156.5, 153.7, 147.6, 138.9, 135.4, 129.4, 128.3, 127.7, 125.9, 125.6, 122.5, 118.2, 117.3, 113.3, 103.3, 51.9, 48.7, 37.7; **HRMS (ESI+):** Calcd. for $C_{22}H_{17}NO_4Na$ ($[M+Na]^+$): 382.1055, Found: 382.1061; **Optical rotation:** $[\alpha]_D^{21}$ –26.2 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IA column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 302 nm, τ_{minor} = 39.2 min, τ_{major} = 48.0 min). See Supporting Information: Part B for HPLC chromatograms.