SUPPORTING INFORMATION: PART A

Iridium-catalyzed enantioselective olefinic C(sp^2)–H allylic alkylation

Rahul Sarkar, and Santanu Mukherjee*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, INDIA

*Corresponding author: E-mail: sm@iisc.ac.in

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A. General information:

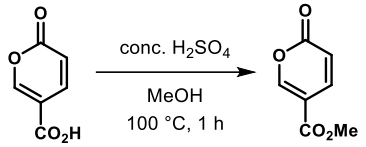
Infrared (FT-IR) spectra were recorded on a Bruker Alfa FT-IR, ν_{max} in cm^{-1} and the bands are characterized as broad (br), strong (s), medium (m), and weak (w). NMR spectra were recorded on Bruker Ultrashield spectrometer at 400 MHz (for ^{1}H-NMR) and 100 MHz (for ^{13}C-NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard [$CDCl_3$: δ 7.26, CD_3OD: δ 3.31, $(CD_3)_2SO$: δ 2.50 for ^{1}H-NMR and $CDCl_3$: δ 77.16, CD_3OD: δ 49.00, $(CD_3)_2SO$: δ 39.52 for ^{13}C-NMR]. For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, ddd = doublet of doublet of doublets, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry was performed on Waters XEVO G2-XS QTof instrument. Optical rotations were measured on JASCO P-2000 polarimeter. Melting points were measured in open glass capillary using Buchi M-560 melting point apparatus and the values are uncorrected. Enantiomeric ratios were determined by Shimadzu LC-20AD HPLC instrument and SPD-20A Diode Array 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, Inc.; (−)-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 the literature procedure.[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. General procedure for the synthesis of coumalates:

Coumalic acid was purchased from Sigma Aldrich and used as received. Methyl coumalate **1a** was prepared from coumalic acid according to the following procedure:

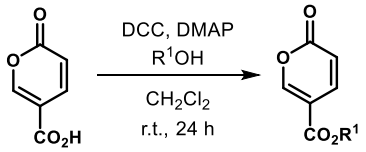


1a

In an oven dried 10 mL 2-necked round-bottom flask, equipped with a reflux condenser, coumalic acid (1.0 g, 7.140 mmol, 1.0 equiv.) was taken along with conc. H_2SO_4 (1.1 mL, 19.640 mmol, 2.8 equiv.). To this mixture, MeOH (1.3 mL, 31.27 mmol, 4.4 equiv.) was added and the resulting solution was refluxed at 100 °C for 1 h. The reaction mixture was cooled to r.t. and poured into 20 mL of H_2O. Solid was removed by filtering through a cotton plug and washed with Et_2O. The organic layer was separated from the aqueous layer. The aqueous layer was extracted with Et_2O (3 × 20.0 mL). Combined organic layer was washed with brine (20.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a reddish-brown oil. This residue was purified by silica-gel flash column chromatography (15% EtOAc in petroleum ether) to obtain **1a** as a white solid (689 mg, 4.471 mmol, 63% yield). **m.p.** 71-72 °C; **FT-IR (Thin film):** 2957 (w), 1760 (s), 1723 (s), 1447 (m), 1236 (m), 1156 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.25 (dd, *J* = 2.6, 1.0 Hz, 1H), 7.74 (dd, *J* = 9.8, 2.6 Hz, 1H), 6.29 (dd, *J* = 9.8, 1.0 Hz, 1H), 3.83 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.4, 159.8, 158.2, 141.7, 115.3, 112.0, 52.5; **HRMS (ESI+):** Calcd. for $C_7H_6O_4H$ ($[M+H]^+$): 155.0344, Found: 155.0349.

Preparation of coumalates 1b-1d:

Compound **1b**-**1d** was prepared according to the following procedure:



1

In an oven dried round-bottom flask, coumalic acid (1.0 equiv.) was taken along with alcohol (1.5 equiv.) in 12.0 mL of absolute CH_2Cl_2 at r.t. To this solution, DCC (1.1 equiv.) and DMAP (0.1 equiv.) were added and the resulting solution was stirred at r.t. for 24 h. Solid was removed by filtering through a cotton plug and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by silica-gel flash column chromatography (4-7% EtOAc in petroleum ether) to obtain **1**.

Compound 1b: Starting from coumalic acid (1.0 g, 7.140 mmol, 1.0 equiv.), purified by silica-gel flash column chromatography (4% EtOAc in petroleum ether); white solid (494.0 mg, 2.518 mmol, 35% yield); **m.p.** 67-68 °C; **FT-IR (Thin film):** 2980 (m), 1765 (s), 1716 (s), 1309 (s), 1235 (s), 1155 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.20 (dd, *J* = 2.4, 0.9 Hz, 1H), 7.75 (dd, *J* = 9.8, 2.6 Hz, 1H), 6.31 (dd, *J* = 9.8, 0.9 Hz, 1H), 1.55 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.0, 160.2, 157.7, 142.1, 115.0, 113.4, 82.7, 28.1; **HRMS (ESI+):** Calcd. for $C_{10}H_{12}O_4H$ ($[M+H]^+$): 197.0814, Found: 197.0816.

Compound 1c: Starting from coumalic acid (500.0 mg, 3.570 mmol, 1.0 equiv.), purified by silica-gel flash column chromatography (4% EtOAc in petroleum ether); light yellow solid (460.0 mg, 2.525 mmol, 71% yield); **m.p.** 45-46 °C; **FT-IR (Thin film):** 2984 (s), 2938 (m), 1773 (s), 1707 (s), 1429 (s), 1152 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.24-8.23 (m, 1H), 7.74 (dd, *J* = 9.8, 2.5 Hz, 1H), 6.28 (d, *J* = 9.8 Hz, 1H), 5.15 (septet, *J* = 6.2 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.5, 160.0, 157.9, 141.9, 115.1, 112.5, 69.5, 21.8; **HRMS (ESI+):** Calcd. for $C_9H_{10}O_4H$ ($[M+H]^+$): 183.0657, Found: 183.0648.

Compound 1d: Starting from coumalic acid (500.0 mg, 3.570 mmol, 1.0 equiv.), purified by silica-gel flash column chromatography (2% EtOAc in CH_2Cl_2); white solid (253.0 mg, 1.099 mmol, 31% yield); **m.p.** 91-92 °C; **FT-IR (Thin film):** 2945 (m), 1773 (s), 1705 (s), 1378 (s), 1306 (m), 1160 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.31-8.30 (m, 1H), 7.79 (dd, *J* = 9.8, 2.6 Hz, 1H), 7.39-7.33 (m, 5H), 6.32 (d, *J* = 9.8 Hz, 1H), 5.30 (s, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.9, 159.8, 158.4, 141.7, 135.1, 128.8, 128.7, 128.5, 115.3, 112.0, 67.3; **HRMS (ESI+):** Calcd. for $C_{13}H_{10}O_4H$ ($[M+H]^+$): 231.0657, Found: 231.0664.

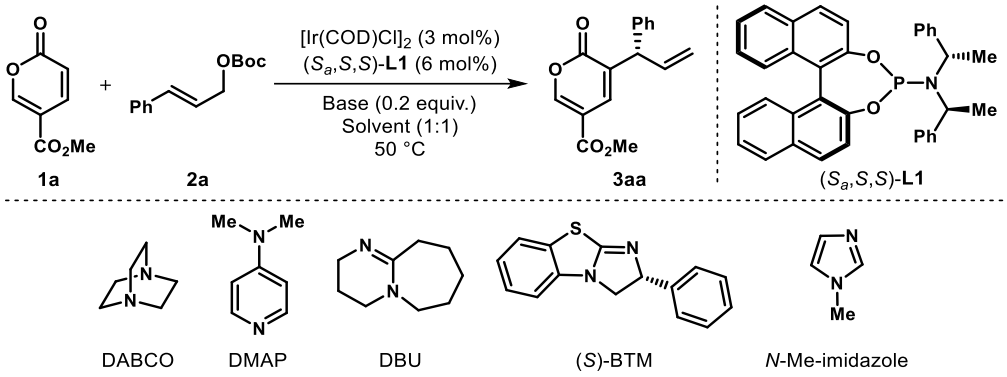
C. Procedure for the synthesis of allylic carbonates:

Allylic carbonates (**2a-t**) were prepared according to the previously reported procedure.[2]

[2] (a) C.-Y. Shi, J.-Z. Xiao and L. Yin, *Chem. Commun.* 2018, **54**, 11957-11960; (b) M. Chen and J. F. Hartwig, *Angew. Chem., Int. Ed.* 2014, **53**, 12172-12176; (c) L. M. Stanley and J. F. Hartwig, *Angew. Chem., Int. Ed.* 2009, **48**, 7841-7844; (d) D. J. Weix, D. Marković, M. Ueda and J. F. Hartwig, *Org. Lett.* 2009, **11**, 2944-2947.

D. Ligand and reaction conditions optimization for enantioselective α-C(sp²–H) allylic alkylation of coumalates:

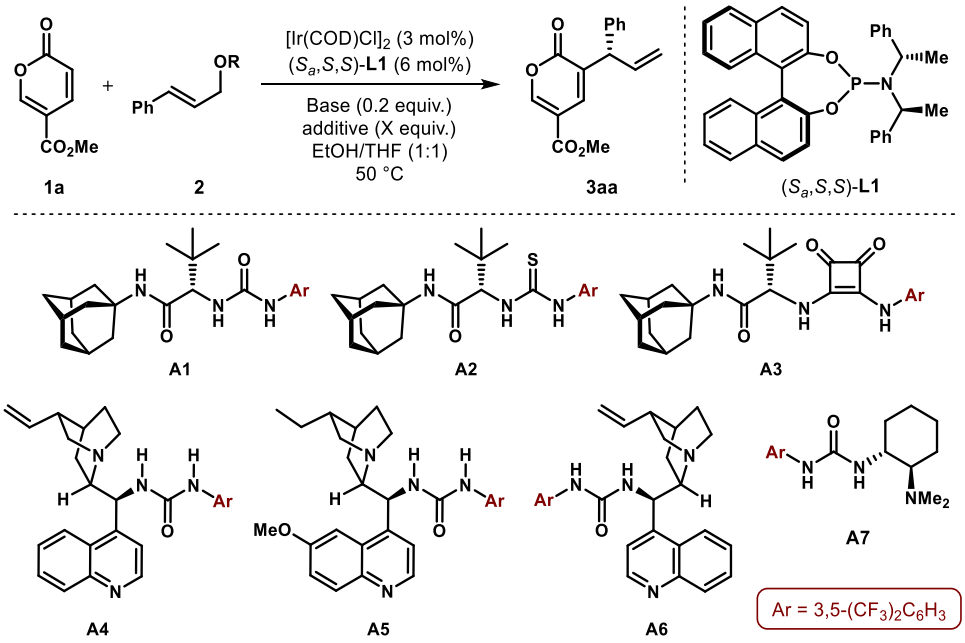
Table 1: Optimization of base and solvent[a]



entry	base	solvent	*t* (h)	yield (%)[b]	er[c]
1	DABCO	DCE	24	<5	n.d.
2	DABCO	THF	24	<5	n.d.
3	DMAP	DCE	24	<5	n.d.
4	PBu_3	DCE	24	<5	n.d.
5[d]	*i*-Pr_2NH	DCE	60	<5	n.d.
6[e]	EtOH	DCE	60	<5	n.d.
7	DMAP	EtOH	60	11	83:17
8	PBu_3	EtOH	48	<5	n.d.
9	DABCO	EtOH	40	11	88:12
10	DABCO	MeOH	48	<5	n.d.
11	DABCO	*t*-BuOH	48	<5	n.d.
12	DABCO	CF_3CH_2OH	48	<5	n.d.
13	DABCO	EtOH/DCE (1:1)	72	7	88:12
14	DABCO	EtOH/THF (1:1)	72	10	92.5:7.5
15	DABCO	*t*-BuOH/THF (1:1)	36	<5	n.d.
16	Et_3N	EtOH/THF (1:1)	48	<5	n.d.
17	PPh_3	EtOH/THF (1:1)	60	<5	n.d.
18	*i*-Pr_2NEt	EtOH/THF (1:1)	60	<5	n.d.
19	DMAP	EtOH/THF (1:1)	60	5	n.d.
20	DBU	EtOH/THF (1:1)	48	<5	n.d.
21	(*S*)-BTM	EtOH/THF (1:1)	48	<5	n.d.
22	*N*-Me-imidazole	EtOH/THF (1:1)	48	<5	n.d.

[a]Reaction conditions: 3 mol% $[Ir(COD)Cl]_2$, 6 mol% ligand, 0.10 mmol of **1a**, 0.12 mmol of **2a** and 0.02 mmol of base in 1.0 mL of solvent; The catalyst was prepared via *n*-$PrNH_2$ activation. [b]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard. [c]Enantiomeric ratios (er) were determined by HPLC analysis on a chiral stationary phase. [d]Using 2.0 equiv. of *i*-Pr_2NH as a base. [e]Using 2.0 equiv. of EtOH as a base. n.d. = Not determined.

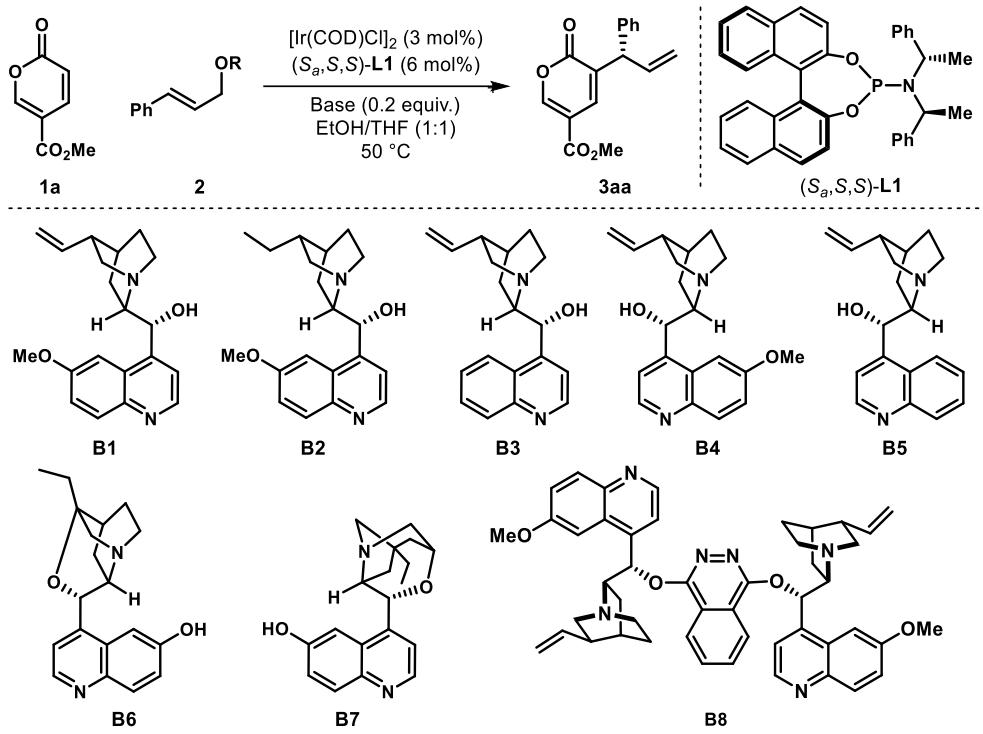
Table 2: Screening of additive[a]



entry	R	base	additive (X equiv.)	*t* (h)	yield (%)[b]	er[c]
1	Boc	DABCO	-	72	10	92.5:7.5
2	Ac	DABCO	-	48	<5	n.d.
3	CO_2Me	DABCO	-	48	16	95:5
4	CO_2Me	DABCO	K_2CO_3 (1.0)	72	<5	n.d.
5	CO_2Me	DABCO	Cs_2CO_3 (1.0)	72	<5	n.d.
6	CO_2Me	DABCO	**A1** (0.10)	48	12	95:5
7	CO_2Me	DABCO	**A2** (0.10)	48	<5	n.d.
8	CO_2Me	DABCO	**A3** (0.10)	48	<5	n.d.
9	CO_2Me	DABCO	**A4** (0.10)	72	17	92:8
10	CO_2Me	-	**A4** (0.20)	48	14	97:3
11	CO_2Me	-	**A5** (0.20)	48	5	95.5:4.5
12	CO_2Me	-	**A6** (0.20)	48	8	96.5:3.5
13	CO_2Me	-	**A7** (0.20)	48	<5	n.d.

[a]Reaction conditions: 3 mol% $[Ir(COD)Cl]_2$, 6 mol% ligand, 0.10 mmol of **1a**, 0.12 mmol of **2** and 0.02 mmol of base in 1.0 mL EtOH/THF (1:1). The catalyst was prepared via *n*-$PrNH_2$ activation. [b]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard. [c]Enantiomeric ratios (er) were determined by HPLC analysis on a chiral stationary phase. n.d. = Not determined.

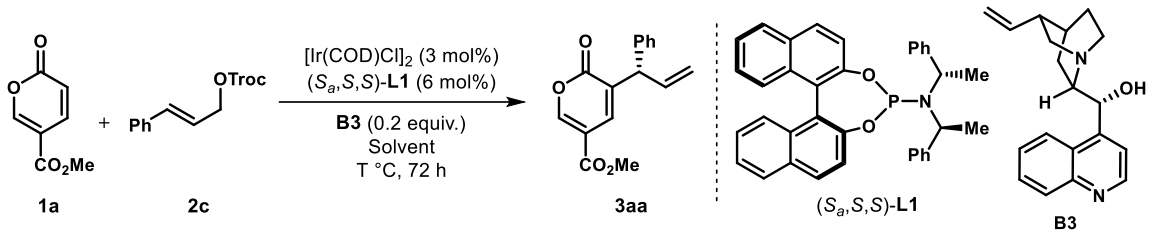
Table 3: Screening of cinchona alkaloid derived base[a]



entry	R	base	*t* (h)	yield (%)[b]	er[c]
1	CO_2Me	**B1**	48	14	97:3
2	Boc	**B1**	72	13	94:6
3	$P(O)(OEt)_2$	**B1**	60	<5	n.d.
4	Troc	**B1**	72	32	97:3
5	Troc	**B2**	72	21	97:3
6	Troc	**B3**	72	42	98:2
7[d]	Troc	**B3**	72	22	97.5:2.5
8	Troc	**B4**	72	38	97:3
9	Troc	**B5**	72	25	97:3
10	Troc	**B6**	72	29	97:3
11	Troc	**B7**	72	21	98:2
12	Troc	**B8**	72	25	98:2
13	Troc	DABCO	48	25	96.5:3.5
14[e]	Troc	DABCO	48	<5	56.5:43.5
15	Troc	DMAP	48	13	94.5:5.5
16	Troc	Et_3N	48	24	96.5:3.5

[a]Reaction conditions: 3 mol% $[Ir(COD)Cl]_2$, 6 mol% ligand, 0.10 mmol of **1a**, 0.12 mmol of **2** and 0.02 mmol of base in 1.0 mL EtOH/THF (1:1). The catalyst was prepared via *n*-$PrNH_2$ activation. [b]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard. [c]Enantiomeric ratios (er) were determined by HPLC analysis on a chiral stationary phase. [d]Using 0.1 equiv. of **B3** as a base. [e]Using 1.0 equiv. of DABCO as a base. n.d. = Not determined.

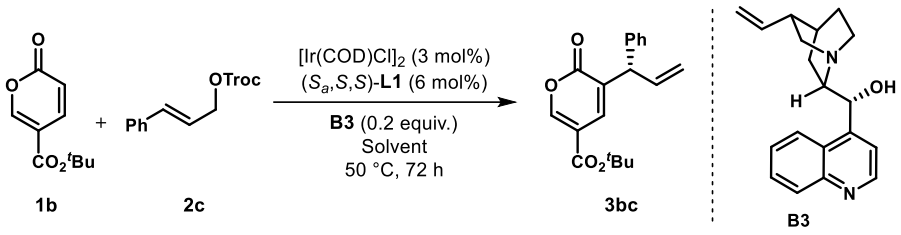
Table 4: Optimization of solvent and concentration in the presence of **B3**[a]

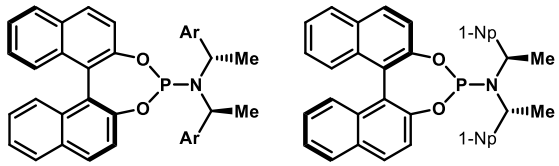


entry	solvent	conc. (M)	*T* (°C)	yield (%)[b]	er[c]
1	EtOH/THF (1:1)	0.1	50 °C	42	98:2
2	EtOH/THF (1:1)	0.05	50 °C	29	97:3
3	EtOH/THF (1:1)	0.20	50 °C	34	97:3
4	EtOH/THF (1:1)	0.1	30 °C	15	97:3
5	EtOH/THF (1:1)	0.1	80 °C	30	97:3
6	*t*-BuOH/THF (1:1)	0.1	50 °C	<5	n.d.
7	CF_3CH_2OH/THF (1:1)	0.1	50 °C	17	84.5:15.5
8	$MeOCH_2CH_2OH$/THF (1:1)	0.1	50 °C	43	97.5:2.5
9	EtOH/THF (9:1)	0.1	50 °C	27	98:2
10	EtOH/2-MeTHF (1:1)	0.1	50 °C	15	98:2
11	EtOH/CPME (1:1)	0.1	50 °C	35	97:3
12	EtOH/TBME (1:1)	0.1	50 °C	23	98:2
13	EtOH/1,4-dioxane (1:1)	0.1	50 °C	38	97:3
14	EtOH/CH_3CN (1:1)	0.1	50 °C	<5	n.d.
15[d]	EtOH/THF (1:1)	0.1	50 °C	28	97:3
16[e]	EtOH/THF (1:1)	0.1	50 °C	42	97.5:2.5

[a]Reaction conditions: 3 mol% $[Ir(COD)Cl]_2$, 6 mol% ligand, 0.10 mmol of **1a**, 0.12 mmol of **2c** and 0.02 mmol of base in 1.0 mL solvent. The catalyst was prepared via *n*-$PrNH_2$ activation. [b]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard. [c]Enantiomeric ratios (er) were determined by HPLC analysis on a chiral stationary phase. [d]Using 0.10 mmol of **1a** and 0.10 mmol of **2c**. [e]Using 0.20 mmol of **1a** and 0.10 mmol of **2c**. n.d. = Not determined.

Table 5: Optimization of ligand and stoichiometry of reactants[a]





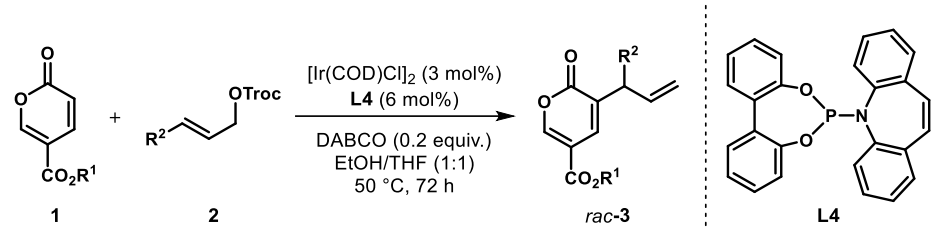
(*Sa*,*S*,*S*)-**L1**: Ar = Ph
(*Sa*,*S*,*S*)-**L2**: Ar = 2-OMeC$_6$H$_4$

(*Ra*,*R*,*R*)-**L3**: Ar = 1-Np

entry	ligand	1b/2c	solvent	yield (%)[b]	er[c]
1	**L1**	1:1.2	EtOH/THF (1:1)	44	98:2
2	**L2**	1:1.2	EtOH/THF (1:1)	42	98:2
3	**L3**	1:1.2	EtOH/THF (1:1)	40	97:3
4[d]	**L1**	1.5:1	EtOH/THF (1:1)	51	97.5:2.5
5[e]	**L1**	2:1	EtOH/THF (1:1)	54	97:3
6[f]	**L1**	2:1	$MeOCH_2CH_2OH$ /THF (1:1)	53	97:3
7	**L1**	2:1	EtOH/PhMe (1:1)	47	97:3
8	**L1**	2:1	*n*-PrOH/THF (1:1)	32	98:2
9	**L1**	2:1	*n*-BuOH/THF (1:1)	47	98:2
10[g]	**L1**	2:1	$MeOCH_2CH_2OH$ /THF (1:1)	22	98:2
11[h]	**L1**	2:1	$MeOCH_2CH_2OH$ /THF (1:1)	43	97:3
12[i]	**L1**	2:1	$MeOCH_2CH_2OH$ /THF (1:1)	53	96:4

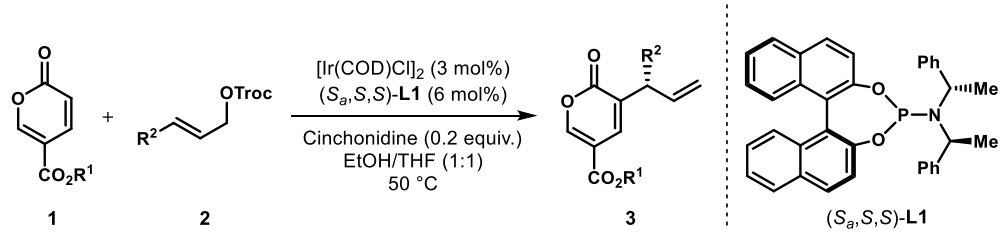
[a]Reaction conditions: 3 mol% $[Ir(COD)Cl]_2$, 6 mol% ligand, 0.10 mmol of **1b**, 0.12 mmol of **2c** and 0.02 mmol of **B3** in 1.0 mL solvent. The catalyst was prepared via *n*-$PrNH_2$ activation. [b]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard. [c]Enantiomeric ratios (er) were determined by HPLC analysis on a chiral stationary phase. [d]Using 0.15 mmol of **1b** and 0.10 mmol of **2c**. [e]Using 0.20 mmol of **1b** and 0.10 mmol of **2c**. [f]Using 0.20 mmol of **1b**, 0.10 mmol of **2c** and $MeOCH_2CH_2OH$/THF (1:1) as the solvent. [g]Using 0.1 equiv. of **B3** as a base. [h]Using 0.3 equiv. of **B3** as a base. [i]Using 0.5 equiv. of **B3** as a base. n.d. = Not determined.

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



In a glass-vial, $[Ir(COD)Cl]_2$ (0.0015 mmol, 6 mol%) and ligand **L4** (0.006 mmol, 24 mol%) were taken with 0.3 mL of THF, and the resulting solution was stirred at r.t. for 15 min. To this solution, was added **1** (0.050 mmol, 2.0 equiv.) and DABCO (0.010 mmol, 0.2 equiv.) followed by **2** (0.025 mmol, 1.0 equiv.) in 0.3 mL EtOH. The resulting suspension was stirred at 50 °C for 72 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 C(sp^2)–H allylated product (*rac*-**3**) samples for HPLC analysis.

F. General procedure for Ir-catalyzed enantioselective allylic alkylation of coumalates 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 in 0.5 mL of absolute THF under positive argon pressure, followed by the addition of 0.3 mL dry *n*-$PrNH_2$. The resulting solution was heated at 50 °C for 30 min, after which all volatiles were removed under vacuum to obtain a yellow solid. To this residue, coumalates **1** (0.400 mmol, 2.0 equiv.) and allyl carbonate **2** (0.200 mmol, 1.0 equiv.) were introduced under positive argon pressure, followed by 1.6 mL of absolute THF/EtOH (1:1) and the suspension was stirred at 50 °C. After 5 min, a solution of cinchonidine (0.040 mmol, 0.2 equiv.) in 0.4 mL absolute THF/EtOH (1:1) was added. The resulting mixture was purged with argon and the reaction tube was sealed with a glass stopper. The reaction mixture was stirred at 50 °C until TLC (10% EtOAc in petroleum ether) revealed complete consumption of **2**. The reaction mixture was then allowed to attain ambient temperature, concentrated under reduced pressure and diluted with 2.0 mL of CH_2Cl_2 and 5.0 mL of 1 N HCl solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 4.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh.

Na_2SO_4 and concentrated under reduced pressure to obtain a reddish-brown oil. This residue was purified by silica-gel flash column chromatography (1-2% EtOAc in petroleum ether) to obtain **3**.

Compound 3bc: Reaction performed in $MeOCH_2CH_2OH$/THF (1:1) as solvent; purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (32.0 mg, 0.102 mmol, 51% yield); **FT-IR (Thin film):** 2980 (m), 2927 (m), 2365 (w), 1743 (s), 1715 (s), 1370 (m), 1311 (m), 1154 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 2.3 Hz, 1H), 7.57-7.56 (m, 1H), 7.34-7.30 (m, 2H), 7.26-7.21 (m, 3H), 6.19 (ddd, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 4.80 (d, *J* = 6.7 Hz, 1H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.5, 160.8, 155.5, 139.7, 137.8, 137.4, 130.3, 128.8, 128.6, 127.2, 118.0, 113.5, 82.7, 49.1, 28.2; **HRMS (ESI+):** Calcd. for $C_{19}H_{20}O_4Na$ ($[M+Na]^+$): 335.1259, Found: 335.1257; **Optical rotation:** $[\alpha]_D^{21}$ +27.5 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 290 nm, τ_{minor} = 4.8 min, τ_{major} = 5.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bc** was assigned in analogy with **5** (see below).

Compound 3bd: Reaction performed in $MeOCH_2CH_2OH$/THF (1:1) as solvent; purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (41.0 mg, 0.126 mmol, 63% yield); **FT-IR (Thin film):** 2979 (w), 2928 (m), 2364 (m), 1746 (s), 1715 (s), 1369 (m), 1309 (s), 1150 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.56-7.55 (m, 1H), 7.14-7.09 (m, 4H), 6.17 (ddd, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 4.76 (d, *J* = 6.7 Hz, 1H), 2.32 (s, 3H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.6, 160.8, 155.4, 137.7, 137.6, 136.8, 136.7, 130.5, 129.5, 128.5, 117.8, 113.5, 82.6, 48.7, 28.2, 21.2; **HRMS (ESI+):** Calcd. for $C_{20}H_{22}O_4Na$ ($[M+Na]^+$): 349.1416, Found: 349.1412; **Optical rotation:** $[\alpha]_D^{21}$ +29.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 252 nm, τ_{major} = 5.1 min, τ_{minor} = 5.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bd** was assigned in analogy with **5** (see below).

Compound 3be: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Light yellow oil (48.0 mg, 0.135 mmol, 68% yield); **FT-IR (Thin film):** 2966 (m), 2926 (m), 1747 (s), 1715 (s), 1369 (m), 1309 (s), 1153 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.56-7.55 (m, 1H), 7.19-7.13 (m, 4H), 6.18 (ddd, *J* = 17.1, 10.1, 6.9 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.77 (d, *J* = 6.9 Hz, 1H), 2.93-2.83 (m, 1H), 1.53 (s, 9H), 1.23 (d, *J* = 6.9 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.5, 160.9, 155.4, 147.7, 137.7, 137.6, 137.0, 130.5, 128.5, 126.8, 117.7, 113.6, 82.6, 48.7, 33.8, 28.2, 24.1; **HRMS (ESI+):** Calcd. for $C_{22}H_{26}O_4Na$ ($[M+Na]^+$): 377.1729, Found: 377.1729; **Optical rotation:** $[\alpha]_D^{21}$ +21.2 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 96.5:3.5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 252 nm, τ_{major} = 4.5 min, τ_{minor} = 5.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3be** was assigned in analogy with **5** (see below).

Compound 3bf: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (33.0 mg, 0.096 mmol, 48% yield); **FT-IR (Thin film):** 2978 (w), 2931 (w), 1747 (s), 1714 (s), 1369 (m), 1308 (s), 1149 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.54-7.53 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.17 (ddd, *J* = 17.0, 10.4, 6.8 Hz, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 4.75-4.74 (m, 1H), 3.78 (s, 3H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.6, 160.8, 158.8, 155.4, 137.7, 137.6, 131.7, 130.5, 129.7, 117.7, 114.2, 113.5, 82.7, 55.4, 48.3, 28.2; **HRMS (ESI+):** Calcd. for $C_{20}H_{22}O_5Na$ ($[M+Na]^+$): 365.1365, Found: 365.1362; **Optical rotation:** $[\alpha]_D^{22}$ +24.9 (*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 IB column (95:5 *n*-Hexane/EtOH, 0.5 mL/min, 20 °C, 295 nm, τ_{minor} = 12.7 min, τ_{major} = 13.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bf** was assigned in analogy with **5** (see below).

Compound 3bg: Purified by silica-gel flash column chromatography (3% EtOAc in petroleum ether); Colorless oil (32.0 mg, 0.084 mmol, 42% yield); **FT-IR (Thin film):** 2981 (w), 2929 (w), 2368 (w), 1746 (s), 1716 (s), 1370 (m), 1326 (s), 1163 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 2.3 Hz, 1H), 7.62-7.61 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.17 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.33 (d, *J* = 10.2 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.83 (d, *J* = 6.7 Hz, 1H), 1.55 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.4, 160.6, 155.8, 143.9, 138.1, 136.6, 129.6 (q, 32.3 Hz), 129.5, 128.9, 125.7 (q, *J* = 3.7 Hz), 122.9 (q, *J* = 272.6 Hz), 118.9, 113.5, 82.9, 49.1, 28.2; **HRMS (ESI+):** Calcd. for $C_{20}H_{19}F_3O_4H$ ($[M+H]^+$): 381.1314, Found: 381.1312;

Optical rotation: $[\alpha]_D^{21}$ +47.6 (*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 Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 290 nm, τ_{major} = 4.5 min, τ_{minor} = 5.2 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bg** was assigned in analogy with **5** (see below).

Compound 3bh: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (28.0 mg, 0.078 mmol, 39% yield); **FT-IR (Thin film):** 2980 (w), 2933 (w), 1744 (s), 1714 (s), 1522 (s), 1347 (m), 1310 (s), 1155 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.18-8.16 (m, 3H), 7.66-7.65 (m, 1H), 7.39 (d, *J* = 8.6 Hz, 2H), 6.18 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.37 (d, *J* = 10.2 Hz, 1H), 5.05 (d, *J* = 17.1 Hz, 1H), 4.85 (d, *J* = 6.8 Hz, 1H), 1.55 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.3, 160.4, 156.0, 147.4, 147.2, 138.4, 136.0, 129.4, 128.9, 123.9, 119.5, 113.6, 83.1, 49.2, 28.3; **HRMS (ESI+):** Calcd. for $C_{19}H_{19}NO_6H$ ($[M+H]^+$): 358.1291, Found: 358.1290; **Optical rotation:** $[\alpha]_D^{22}$ +57.0 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 95.5:4.5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 252 nm, τ_{major} = 10.4 min, τ_{minor} = 11.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bh** was assigned in analogy with **5** (see below).

Compound 3bi: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (38.0 mg, 0.097 mmol, 49% yield); **FT-IR (Thin film):** 2978 (w), 2929 (w), 2364 (m), 1745 (s), 1715 (s), 1369 (m), 1308 (s), 1151 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 2.3 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.14 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.73 (d, *J* = 6.6 Hz, 1H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.4, 160.6, 155.7, 138.8, 137.9, 136.9, 131.9, 130.3, 129.8, 121.2, 118.6, 113.5, 82.8, 48.6, 28.3; **HRMS (ESI+):** Calcd. for $C_{19}H_{19}BrO_4H$ ($[M+H]^+$): 391.0545, Found: 391.0541; **Optical rotation:** $[\alpha]_D^{21}$ +40.3 (*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 Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 247 nm, τ_{major} = 5.5 min, τ_{minor} = 6.2 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bi** was assigned in analogy with **5** (see below).

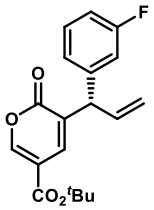
Compound 3bj: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (38.0 mg, 0.109 mmol, 55% yield); **FT-IR (Thin film):** 2978 (w), 2928 (w), 2364 (m), 1746 (s), 1714 (s), 1368 (w), 1309 (s), 1152 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 2.4 Hz, 1H), 7.57-7.56 (m, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.15 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.75 (d, *J* = 6.5 Hz, 1H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.4, 160.6, 155.6, 138.2, 137.9, 136.9, 133.1, 129.9, 129.8, 128.9, 118.5, 113.5, 82.8, 48.6, 28.2; **HRMS (ESI+):** Calcd. for $C_{19}H_{19}ClO_4Na$ ($[M+Na]^+$): 369.0870, Found: 369.0871; **Optical rotation:** $[\alpha]_D^{21}$ +49.1 (*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 Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 252 nm, τ_{major} = 5.4 min, τ_{minor} = 5.9 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bj** was assigned in analogy with **5** (see below).

Compound 3bk: Purified by silica-gel flash column chromatography (1% EtOAc in petroleum ether); Colorless oil (41.0 mg, 0.126 mmol, 63% yield); **FT-IR (Thin film):** 2979 (w), 2929 (w), 1747 (s), 1714 (s), 1370 (m), 1310 (s), 1153 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.06-6.99 (m, 3H), 6.18 (ddd, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.27 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 4.76 (d, *J* = 6.7 Hz, 1H), 2.33 (s, 3H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.6, 160.8, 155.4, 139.7, 138.4, 137.8, 137.6, 130.4, 129.3, 128.6, 128.0, 125.6, 117.9, 113.6, 82.7, 49.0, 28.3, 21.6; **HRMS (ESI+):** Calcd. for $C_{20}H_{22}O_4Na$ ($[M+Na]^+$): 349.1421, Found: 349.1421; **Optical rotation:** $[\alpha]_D^{22}$ +25.3 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 96.5:3.5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 5.1 min, τ_{minor} = 5.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bk** was assigned in analogy with **5** (see below).

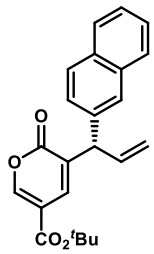
Compound 3bl: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (39.0 mg, 0.100 mmol, 50% yield); **FT-IR (Thin film):** 2977 (w), 2926 (w), 2365 (m), 1745 (s), 1714 (s), 1368 (w), 1309 (s), 1152 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14-8.13 (m, 1H), 7.58-7.57 (m, 1H), 7.38-7.37 (m, 1H), 7.33 (s, 1H), 7.21-7.14 (m, 2H), 6.14 (ddd, *J* = 17.1, 10.1, 6.8 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.74 (d, *J* = 6.8 Hz, 1H), 1.55 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.4, 160.6, 155.7, 142.1, 138.1, 136.7, 131.5, 130.4, 130.3, 129.6, 127.4, 122.9, 118.8, 113.6, 82.9, 48.9, 28.3; **HRMS (ESI+):** Calcd. for $C_{19}H_{19}BrO_4Na$ ($[M+Na]^+$): 413.0364, Found: 413.0367; **Optical rotation:** $[\alpha]_D^{21}$ +39.4 (*c* 0.8,

$CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 5.7 min, τ_{minor} = 6.4 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bl** was assigned in analogy with **5** (see below).

Compound 3bm: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (28.0 mg, 0.085 mmol, 43% yield); **FT-IR (Thin film):** 2979 (w), 2930 (w), 2365 (m), 1746 (s), 1714 (s), 1369 (w), 1310 (s), 1153 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 2.3 Hz, 1H), 7.58-7.57 (m, 1H), 7.31-7.27 (m, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.96-6.90 (m, 2H), 6.15 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.78 (d, *J* = 6.7 Hz, 1H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.0 (d, *J* = 246.4 Hz), 162.4, 160.7, 155.7, 142.3 (d, *J* = 6.8 Hz), 138.0, 136.8, 130.2 (d, *J* = 8.2 Hz), 129.7, 124.3 (d, *J* = 2.8 Hz), 118.6, 115.5 (d, *J* = 21.9 Hz), 114.2 (d, *J* = 21.1 Hz), 113.5, 82.8, 48.8, 28.2; **HRMS (ESI+):** Calcd. for $C_{19}H_{19}FO_4Na$ ($[M+Na]^+$): 353.1165, Found: 353.1166; **Optical rotation:** $[\alpha]_D^{23}$ +36.9 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 250 nm, τ_{major} = 5.5 min, τ_{minor} = 6.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bm** was assigned in analogy with **5** (see below).



Compound 3bn: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (41.0 mg, 0.113 mmol, 57% yield); **FT-IR (Thin film):** 2978 (w), 2930 (w), 2365 (w), 1746 (s), 1713 (s), 1368 (w), 1309 (s), 1150 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 2.4 Hz, 1H), 7.81-7.79 (m, 3H), 7.67-7.63 (m, 2H), 7.47-7.45 (m, 2H), 7.35-7.32 (m, 1H), 6.27 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.33 (d, *J* = 10.2 Hz, 1H), 5.07 (d, *J* = 17.1 Hz, 1H), 4.97 (d, *J* = 6.6 Hz, 1H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.5, 160.8, 155.5, 137.9, 137.4, 137.2, 133.6, 132.7, 130.2, 128.5, 127.9, 127.8, 127.2, 126.9, 126.3, 125.9, 118.4, 113.6, 82.7, 49.1, 28.2; **HRMS (ESI+):** Calcd. for $C_{23}H_{22}O_4Na$ ($[M+Na]^+$): 385.1416, Found: 385.1416; **Optical rotation:** $[\alpha]_D^{24}$ +33.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 230 nm, τ_{major} = 6.8 min, τ_{minor} = 7.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bn** was assigned in analogy with **5** (see below).



Compound 3bo: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (38.0 mg, 0.100 mmol, 50% yield); **FT-IR (Thin film):** 2979 (w), 2930 (w), 2365 (w), 1745 (s), 1714 (s), 1369 (w), 1309 (s), 1154 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.14 (d, *J* = 2.2 Hz, 1H), 7.60-7.59 (m, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.06 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.12 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.33 (d, *J* = 10.2 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 4.71 (d, *J* = 6.6 Hz, 1H), 1.55 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.3, 160.5, 155.9, 140.0, 138.1, 136.3, 132.8, 131.4, 130.7, 130.4, 129.2, 128.1, 119.1, 113.5, 82.9, 48.4, 28.3; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}Cl_2O_4H$ ($[M+H]^+$): 381.0660, Found: 381.0658; **Optical rotation:** $[\alpha]_D^{23}$ +53.0 (*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 Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 247 nm, τ_{major} = 5.3 min, τ_{minor} = 6.3 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bo** was assigned in analogy with **5** (see below).

Compound 3bp: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (34.0 mg, 0.095 mmol, 48% yield); **FT-IR (Thin film):** 2978 (w), 2929 (w), 2365 (w), 1748 (s), 1714 (s), 1368 (w), 1310 (m), 1154 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.55-7.54 (m, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.68-6.67 (m, 2H), 6.13 (ddd, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.93 (s, 2H), 5.27 (d, *J* = 10.2 Hz, 1H), 5.02 (d, *J* = 17.1 Hz, 1H), 4.70 (d, *J* = 6.5 Hz, 1H), 1.54 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.5, 160.8, 155.5, 147.9, 146.8, 137.7, 137.5, 133.5, 130.3, 121.8, 117.9, 113.5, 109.1, 108.5, 101.2, 82.7, 48.7, 28.3; **HRMS (ESI+):** Calcd. for $C_{20}H_{20}O_6Na$ ($[M+Na]^+$): 379.1158, Found: 379.1158; **Optical rotation:** $[\alpha]_D^{21}$ +25.2 (*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-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 288 nm, τ_{major} = 7.8 min, τ_{minor} = 8.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bp** was assigned in analogy with **5** (see below).

Compound 3bq: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Light yellow oil (28.0 mg, 0.093 mmol, 46% yield); **FT-IR (Thin film):** 2979 (w), 2929 (w), 2365 (w), 1748 (s), 1715 (s), 1370 (w), 1311 (m), 1155 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 2.4 Hz, 1H), 7.53-7.52 (m, 1H), 7.36 (s, 1H), 6.33-6.32 (m, 1H), 6.17 (d, *J* = 3.1 Hz, 1H), 6.08 (ddd, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.27 (d, *J* = 10.1 Hz, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 4.87 (d, *J* = 7.0 Hz, 1H), 1.53 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.4, 160.6, 155.7, 152.8, 142.4, 138.2, 134.7, 127.8, 118.4, 113.7, 110.5, 107.9, 82.7, 42.9, 28.3; **HRMS (ESI+):** Calcd. for

$C_{17}H_{18}O_5Na$ ([M+Na]$^+$): 325.1052, Found: 325.1051; **Optical rotation:** $[\alpha]_D^{22}$ –11.3 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 90:10 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (95:5 *n*-Hexane/EtOH, 0.5 mL/min, 20 °C, 252 nm, τ_{minor} = 13.0 min, τ_{major} = 13.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bq** was assigned in analogy with **5** (see below).

Compound 3br: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Light yellow oil (40.0 mg, 0.126 mmol, 63% yield); **FT-IR (Thin film):** 2978 (w), 2930 (w), 1747 (s), 1715 (s), 1369 (w), 1310 (m), 1153 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 2.3 Hz, 1H), 7.59-7.58 (m, 1H), 7.22-7.20 (m, 1H), 6.98-6.95 (m, 1H), 6.89-6.88 (m, 1H), 6.18 (ddd, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.28 (d, *J* = 10.1 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.04 (d, *J* = 7.0 Hz, 1H), 1.53 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.3, 160.6, 155.7, 143.1, 137.9, 136.8, 129.9, 127.1, 125.9, 124.9, 118.0, 113.6, 82.8, 44.2, 28.2; **HRMS (ESI+):** Calcd. for $C_{17}H_{18}O_4SNa$ ([M+Na]$^+$): 341.0823, Found: 341.0824; **Optical rotation:** $[\alpha]_D^{21}$ +9.4 (*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 IB column (95:5 *n*-Hexane/*i*-PrOH, 0.4 mL/min, 20 °C, 195 nm, τ_{minor} = 17.0 min, τ_{major} = 17.6 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3br** was assigned in analogy with **5** (see below).

Compound 3bs: Regioselectivity (r.r.) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (31.0 mg, 0.092 mmol, 46% yield); **FT-IR (Thin film):** 2978 (w), 2929 (w), 2365 (w), 1744 (s), 1714 (s), 1369 (w), 1308 (m), 1153 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 2.4 Hz, 1H), 7.62 (d, *J* = 2.2 Hz, 1H), 7.38-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.20 (m, 1H), 6.52 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 15.9, 7.4 Hz, 1H), 6.03 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.27-5.21 (m, 2H), 4.32 (m, 1H), 1.55 (m, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.5, 160.7, 155.5, 137.3, 137.0, 136.8, 132.6, 129.6, 128.7, 127.9, 127.7, 126.5, 117.5, 113.7, 82.7, 46.5, 28.2; **HRMS (ESI+):** Calcd. for $C_{21}H_{22}O_4Na$ ([M+Na]$^+$): 361.1416, Found: 361.1415; **Optical rotation:** $[\alpha]_D^{21}$ +5.3 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 95.5:4.5 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 252 nm, τ_{major} = 5.6 min, τ_{minor} = 6.1 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bs** was assigned in analogy with **5** (see below).

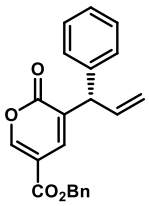
Compound 3bt: Regioselectivity (r.r.) > 20:1 was determined by ^{1}H NMR analysis of the crude reaction mixture. Purified by silica-gel flash column chromatography (1% EtOAc in petroleum ether); Colorless oil (31.0 mg, 0.112 mmol, 56% yield); **FT-IR (Thin film):** 2926 (w), 2368 (w), 1746 (s), 1716 (s), 1369 (m), 1308 (m), 1154 (m), 1116 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.10 (d, *J* = 2.4 Hz, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 5.91 (ddd, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.64-5.50 (m, 2H), 5.18-5.09 (m, 2H), 4.12-4.09 (m, 1H), 1.71 (d, *J* = 5.7 Hz, 3H) 1.55 (m, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.6, 160.8, 155.3, 137.4, 137.0, 130.1, 129.2, 128.5, 116.8, 113.6, 82.6, 46.2, 28.3, 18.1; **HRMS (ESI+):** Calcd. for $C_{16}H_{20}O_4Na$ ($[M+Na]^+$): 299.1259, Found: 299.1259; **Optical rotation:** $[\alpha]_D^{21}$ +7.0 (*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-2 column (85:15 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 295 nm, τ_{major} = 5.0 min, τ_{minor} = 5.5 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3bt** was assigned in analogy with **5** (see below).

Compound 3aa: Purified by silica-gel flash column chromatography (4% EtOAc in petroleum ether); Colorless oil (20.0 mg, 0.074 mmol, 37% yield); **FT-IR (Thin film):** 2955 (w), 2923 (w), 2365 (w), 1748 (s), 1721 (s), 1442 (m), 1302 (m), 1151 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.22 (d, *J* = 2.4 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.34-7.30 (m, 2H), 7.26-7.21 (m, 3H), 6.19 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.30 (d, *J* = 10.3 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.80 (d, *J* = 6.8 Hz, 1H), 3.86 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.9, 160.6, 156.1, 139.8, 137.5, 137.4, 130.8, 128.9, 128.7, 127.4, 118.3, 112.3, 52.7, 49.2; **HRMS (ESI+):** Calcd. for $C_{16}H_{14}O_4H$ ($[M+H]^+$): 271.0971, Found: 271.0970; **Optical rotation:** $[\alpha]_D^{21}$ +41.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 282 nm, τ_{minor} = 7.1 min, τ_{major} = 7.9 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3aa** was assigned in analogy with **5** (see below).

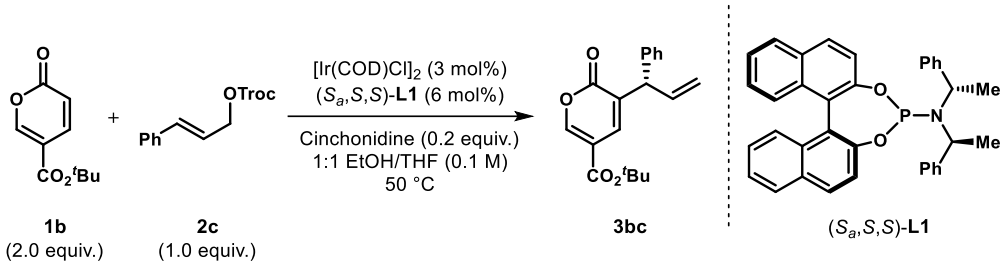
Compound 3cc: Purified by silica-gel flash column chromatography (1% EtOAc in petroleum ether); Colorless oil (26.0 mg, 0.087 mmol, 44% yield); **FT-IR (Thin film):** 2984 (w), 2926 (m), 1717 (s), 1414 (w), 1296 (m), 1151 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.19 (d, *J* = 2.4 Hz, 1H), 7.60-7.59 (m, 1H), 7.34-7.30 (m, 2H), 7.26-7.21 (m, 3H), 6.20 (ddd, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 5.23-5.14 (m, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.80 (d, *J* = 6.6 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.9, 160.7, 155.7, 139.7, 137.6, 137.4, 130.5, 128.8, 128.6, 127.3, 118.1, 112.7, 69.5, 49.2, 21.9; **HRMS (ESI+):** Calcd. for $C_{18}H_{18}O_4Na$ ($[M+Na]^+$): 321.1103, Found: 321.1100; **Optical rotation:** $[\alpha]_D^{22}$ +34.6 (*c* 1.0, $CHCl_3$) for an

enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 300 nm, τ_{minor} = 5.2 min, τ_{major} = 6.0 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3cc** was assigned in analogy with **5** (see below).

Compound 3dc: Purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether); Colorless oil (28.0 mg, 0.081 mmol, 40% yield); **FT-IR (Thin film):** 2960 (w), 2924 (m), 1721 (s), 1454 (w), 1293 (m), 1154 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.24 (d, *J* = 2.4 Hz, 1H), 7.61-7.60 (m, 1H), 7.39-7.36 (m, 5H), 7.34-7.31 (m, 2H), 7.27-7.25 (m, 1H), 7.23-7.21 (m, 2H), 6.19 (ddd, *J* = 17.1, 10.2, 6.8 Hz, 1H), 5.30 (s, 2H), 5.30-5.28 (m, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.80 (d, *J* = 6.7 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.3, 160.4, 156.1, 139.6, 137.4, 137.3, 135.3, 130.7, 128.9, 128.8, 128.6, 128.5, 127.3, 118.2, 112.2, 67.4, 49.1; **HRMS (ESI+):** Calcd. for $C_{22}H_{18}O_4Na$ ($[M+Na]^+$): 369.1103, Found: 369.1100; **Optical rotation:** $[\alpha]_D^{23}$ +29.4 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 300 nm, τ_{minor} = 11.3 min, τ_{major} = 15.7 min). See Supporting Information: Part B for HPLC chromatograms. The absolute stereochemistry of the product **3dc** was assigned in analogy with **5** (see below).

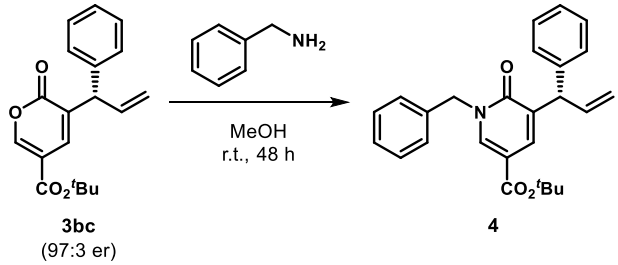


G. Scale-up procedure for C(sp²)–H allylic alkylation of coumalate 1b:



In an oven dried 25 mL round-bottom flask, $[Ir(COD)Cl]_2$ (20.0 mg, 0.030 mmol, 3 mol%) and ligand (*S*$_a$,*S*,*S*)-**L1** (32.4 mg, 0.060 mmol, 6 mol%) were taken with 2.5 mL of absolute THF under a positive argon pressure followed by addition of 1.5 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 residue, coumalate **1b** (392.4 mg, 2.000 mmol, 2.0 equiv.) and allyl carbonate **2c** (260.2 mg, 1.000 mmol, 1.0 equiv.) were introduced under positive argon pressure, followed by 9.0 mL of absolute THF/EtOH (1:1). The resulting suspension was stirred at 50 °C for 5 min. After 5 min, a solution of cinchonidine (59 mg, 0.200 mmol, 0.2 equiv.) in 1.0 mL absolute THF/EtOH (1:1) was added. The resulting mixture was purged with argon and the reaction flask was sealed with a glass stopper. The reaction mixture was stirred at 50 °C for 72 h. The reaction mixture was then allowed to attain ambient temperature, concentrated under reduced pressure, and diluted with 5.0 mL of CH_2Cl_2 and 5.0 mL of 1 N HCl solution. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 5.0 mL). Combined organic layer was washed with brine (10.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a reddish-brown oil. This residue was purified by silica-gel flash column chromatography (2% EtOAc in petroleum ether) to obtain **3bc** as light yellow oil (179 mg, 0.573 mmol, 57% yield) with 97:3 er.

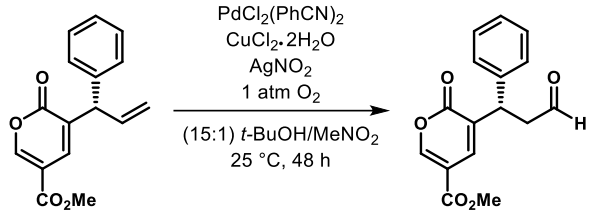
H. Procedure for the preparation of 2-pyridone derivative 4:



In an oven dried 10 mL round-bottom flask, **3bc** (31.0 mg, 0.100 mmol, 1.0 equiv.) was taken in 0.5 mL of absolute MeOH under a positive argon pressure. To this solution, was added benzyl amine (33.0 µL, 0.300 mmol, 3.0 equiv.) and stirred at r.t. for 48 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica-gel flash column

chromatography (6% EtOAc in petroleum ether) to obtain **4** as a colorless oil (27.0 mg, 0.067 mmol, 67% yield); **FT-IR (Thin film):** 2976 (w), 2930 (m), 2365 (w), 1708 (s), 1656 (s), 1454 (w), 1313 (s), 1155 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.01 (d, *J* = 2.1 Hz, 1H), 7.68 (d, *J* = 1.8 Hz, 1H), 7.36-7.19 (m, 10H), 6.23 (ddd, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.24-5.22 (m, 2H), 5.05-4.96 (m, 3H), 1.51 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.8, 162.0, 141.2, 140.2, 138.9, 135.8, 135.7, 134.0, 129.1, 128.7, 128.5, 128.4, 128.3, 126.7, 117.0, 111.1, 81.6, 53.3, 48.8, 28.3; **HRMS (ESI+):** Calcd. for $C_{26}H_{27}NO_3H$ ($[M+H]^+$): 402.2069, Found: 402.2070; **Optical rotation:** $[\alpha]_D^{19}$ –12.7 (*c* 0.9, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (95:5 *n*-Hexane/EtOH, 0.5 mL/min, 20 °C, 338 nm, τ_{minor} = 15.5 min, τ_{major} = 16.5 min). See Supporting Information: Part B for HPLC chromatograms.

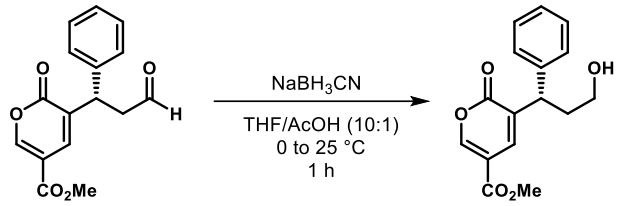
I. Procedure for the regioselective Wacker oxidation of 3aa & 3bc:



3aa (97:3 er) **5**

In an oven dried 10 mL round-bottom flask, $PdCl_2(PhCN)_2$ (6.5 mg, 0.017 mmol, 0.12 equiv.), $CuCl_2.2H_2O$ (3.0 mg, 0.017 mmol, 0.12 equiv.) and $AgNO_2$ (1.3 mg, 0.008 mmol, 0.06 equiv.) were taken in 0.2 mL $MeNO_2$ under a positive oxygen pressure. To this mixture, a solution of **3aa** (38.0 mg, 0.140 mmol, 1.0 equiv.) in 2.6 mL *t*-BuOH was added and the reaction mixture was stirred at 25 °C under balloon pressure of O_2 for 48 h. The reaction mixture was diluted with 5.0 mL of H_2O and 5.0 mL of CH_2Cl_2. The organic phase was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5.0 mL). Combined organic layer was washed with brine (5.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography (16-17% EtOAc in petroleum ether) to obtain **5** as a light yellow sticky liquid (18.0 mg, 0.063 mmol, 45% yield); **FT-IR (Thin film):** 2958 (w), 2924 (w), 1719 (s), 1443 (m), 1296 (m), 1156 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.73 (t, *J* = 1.4 Hz, 1H), 8.20 (d, *J* = 2.4 Hz, 1H), 7.56 (dd, *J* = 2.6, 0.9 Hz, 1H) 7.35-7.25 (m, 5H), 4.62 (t, *J* = 7.6 Hz, 1H), 3.85 (s, 3H), 3.29 (ddd, *J* = 17.6, 7.3, 0.8 Hz, 1H), 3.12 (ddd, *J* = 17.5, 7.8, 1.4 Hz, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.7, 163.7, 160.4, 156.1, 139.6, 136.9, 130.3, 129.1, 128.1, 127.7, 112.2, 52.6, 46.9, 40.3; **HRMS (ESI+):** Calcd. for $C_{16}H_{14}O_5Na$ ($[M+Na]^+$): 309.0739, Found: 309.0737; **Optical rotation:** $[\alpha]_D^{22}$ +26.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er.

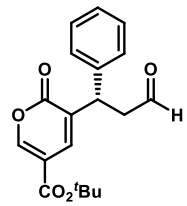
To determine the enantiomeric ratio, compound **5** was converted to the corresponding alcohol **5′** according to the following procedure:



5 (97:3 er) **5′**

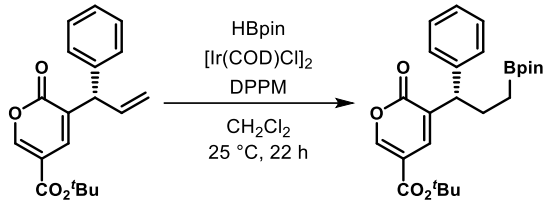
In an oven dried 10 mL round-bottom flask, **5** (10.0 mg, 0.035 mmol, 1.0 equiv.) was taken in 0.3 ml THF/AcOH (10:1) and cooled to 0 °C. Then $NaBH_3CN$ (1.3 mg, 0.021 mmol, 0.6 equiv.) was added and the resulting solution was stirred at r.t. for 1 h under argon atmosphere. The reaction mixture was diluted with 5.0 mL of EtOAc and 5 ml of brine. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 5.0 mL). Combined organic layer was washed with brine (5.0 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica-gel flash column chromatography (25-27% EtOAc in petroleum ether) to obtain **5′** as colorless oil (7.0 mg, 0.031 mmol, 88% yield); **FT-IR (Thin film):** 3746 (m), 2924 (m), 1712 (s), 1647 (m), 1292 (m), 1153 (w), 1115 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.18 (d, *J* = 2.4 Hz, 1H), 7.63 (dd, *J* = 2.2, 0.5 Hz, 1H), 7.33-7.28 (m, 4H), 7.25-7.21 (m, 1H), 4.24 (t, *J* = 7.7 Hz, 1H), 3.86 (s, 3H), 3.65-3.55 (m, 2H), 2.28-2.18 (m, 2H), 1.74 (s, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 163.9, 161.0, 155.7, 140.7, 136.2, 131.8, 128.9, 128.3, 127.3, 112.2, 60.5, 52.6, 41.8, 36.4; **HRMS (ESI+):** Calcd. for $C_{16}H_{16}O_5Na$ ($[M+Na]^+$): 311.0895, Found: 311.0894; **Optical rotation:** $[\alpha]_D^{19}$ +9.1 (*c* 0.7, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-2 column (60:40 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 300 nm, τ_{major} = 11.2 min, τ_{minor} = 17.3 min). See Supporting Information: Part B for HPLC chromatograms.

Compound 6: Reaction was performed on a 0.300 mmol scale of **3bc**; purified by silica-gel flash column chromatography (9% EtOAc in petroleum ether); Light yellow sticky liquid (67.0 mg, 0.204 mmol, 68% yield); **FT-IR (Thin film):** 2977 (w), 2929 (m), 2364 (w), 1714 (s), 1454 (w), 1309 (m), 1155 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 9.73 (t, *J* = 1.5 Hz, 1H), 8.09 (d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 2.2, 0.6 Hz, 1H, 7.35-7.28 (m, 4H), 7.27-7.23 (m, 1H), 4.62 (t, *J* = 7.6 Hz, 1H), 3.28 (ddd, *J* = 17.5, 7.2, 1.1 Hz, 1H), 3.10 (ddd, *J* = 17.5, 8.0, 1.6 Hz, 1H), 1.52 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.8, 162.3, 160.7, 155.5, 139.7, 137.3, 129.9, 129.0, 128.1, 127.6, 113.5, 82.8, 46.9, 40.3, 28.2; **HRMS (ESI+):** Calcd. for $C_{19}H_{20}O_5H$ ($[M+H]^+$): 329.1389, Found: 329.1389; **Optical rotation:** $[\alpha]_D^{21}$ +18.9 (*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 IG column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 254 nm, τ_{major} = 14.2 min, τ_{minor} = 15.4 min). See Supporting Information: Part B for HPLC chromatograms.

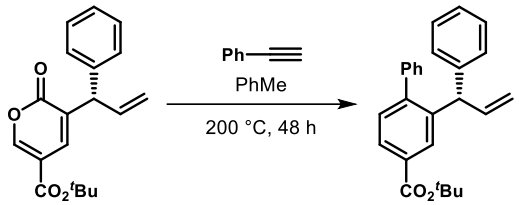
J. Procedure for the Ir-catalyzed hydroboration of 3bc:



3bc (97:3 er) **7**

In an oven dried 10 mL round-bottom flask, **3bc** (36.0 mg, 0.115 mmol, 1.0 equiv.) was taken along with $[Ir(COD)Cl]_2$ (2.4 mg, 0.004 mmol, 0.03 equiv.) and bis(diphenylphosphino)methane (DPPM; 2.7 mg, 0.007 mmol, 0.06 equiv.) under a positive argon pressure. Then 1.2 mL CH_2Cl_2 was added followed by the addition of HBpin (34 µL, 0.230 mmol, 2.0 equiv.) and the resulting solution was stirred at r.t. for 22 h under argon atmosphere. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica-gel flash column chromatography (4% EtOAc in petroleum ether) to obtain **7** as a thick colorless oil (32.0 mg, 0.073 mmol, 63% yield); **FT-IR (Thin film):** 2978 (m), 2929 (m), 1715 (s), 1371 (s), 1309 (s), 1148 (s), 1115 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.06 (d, *J* = 2.4 Hz, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.30-7.24 (m, 4H), 7.21-7.17 (m, 1H), 3.96-3.92 (m, 1H), 2.13-1.97 (m, 2H), 1.54 (s, 9H), 1.22 (s, 12H), 0.76-0.71 (m, 2H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 162.7, 161.2, 155.0, 141.6, 135.9, 131.8, 128.6, 128.4, 126.9, 113.6, 83.3, 82.6, 47.5, 28.3, 28.2, 25.0; **HRMS (ESI+):** Calcd. for $C_{25}H_{33}BO_6Na$ ($[M+Na]^+$): 463.2298, Found: 463.2297; **Optical rotation:** $[\alpha]_D^{23}$ +10.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-1 column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 258 nm, τ_{minor} = 5.6 min, τ_{major} = 6.7 min). See Supporting Information: Part B for HPLC chromatograms. [*Note*: This compound is sensitive to silica-gel and rapid chromatographic purification is necessary.]

K. Procedure for [4+2]-cycloaddition/decarboxylation of 3bc:

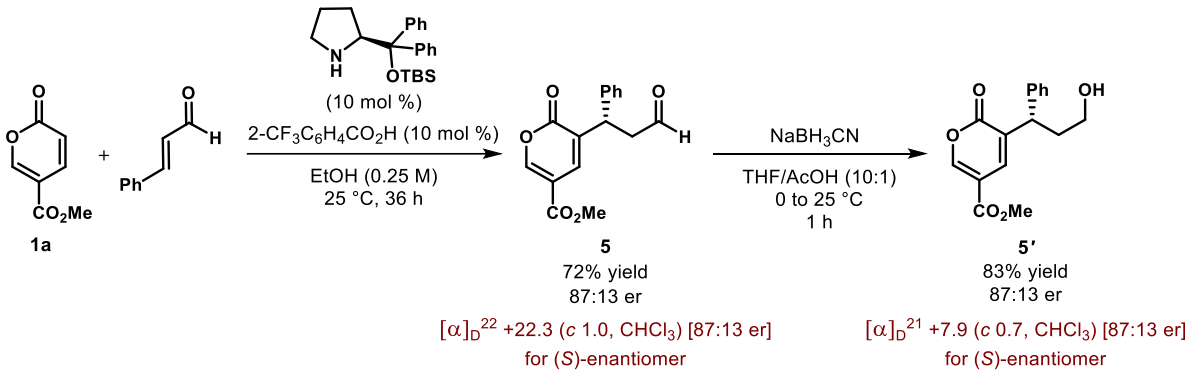


3bc (97:3 er) **8**

In an oven and vacuum-dried seal tube, **3bc** (20.0 mg, 0.064 mmol, 1.0 equiv.) was taken in 0.64 mL absolute toluene. To this solution, phenyl acetylene (35.0 µL, 0.320 mmol, 5.0 equiv.) was added and the resulting mixture was stirred for 48 h at 200 °C. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica-gel flash column chromatography (1% EtOAc in petroleum ether) to obtain **8** as a light yellow oil (10.0 mg, 0.027 mmol, 42% yield); **FT-IR (Thin film):** 2925 (s), 2852 (m), 2367 (w), 1713 (s), 1453 (m), 1298 (m) 1164 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.94 (d, *J* = 1.1 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.37-7.36 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24-7.16 (m, 5H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.26 (ddd, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.22 (d, *J* = 10.2 Hz, 1H), 4.86 (d, *J* = 6.4 Hz, 1H), 4.81 (d, *J* = 17.1 Hz, 1H), 1.59 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 165.9, 146.5, 143.2, 141.0, 140.9, 140.8, 131.3, 130.4, 130.3, 129.1, 128.7, 128.4, 128.2, 127.6, 127.2, 126.4, 117.0, 81.1, 50.7, 28.4; **HRMS (ESI+):** Calcd. for $C_{26}H_{26}O_2Na$ ($[M+Na]^+$): 393.1830, Found: 393.1834; **Optical rotation:** $[\alpha]_D^{19}$ –11.0 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Phenomenex Cellulose-3 column (99:1 *n*-Hexane/*i*-PrOH, 0.3 mL/min, 20 °C, 248 nm, τ_{major} = 13.2 min, τ_{minor} = 18.6 min). See Supporting Information: Part B for HPLC chromatograms.

L. Determination of the absolute configuration of the products:

The absolute configuration of **5** was previously established by Zu *et al*.[3] However, the optical rotation of **5** was not reported. The aldehyde **5** and the corresponding alcohol **5′** were prepared according to the literature report,[3] as shown in the scheme below, and their optical rotations were measured:



The optical rotations of **5** and **5′**, prepared by Ir-catalyzed enantioselective allylic alkylation and aldehyde-selective Wacker oxidation (as discussed above), are:

Optical rotation of 5: $[\alpha]_D^{22}$ +26.1 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er.

Optical rotation of 5′: $[\alpha]_D^{19}$ +9.1 (*c* 0.7, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er.

Considering the consistencies in the sign and specific rotation values of both set of samples, the absolute configuration of **5** and **5′** was assigned as (*S*).

The absolute stereochemistry of allylic alkylation products was assigned in analogy with **5** and **5′**.

[3] Q. Liu and L. Zu, *Angew. Chem., Int. Ed.* 2018, **57**, 9505-9509.