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A Highly Nucleophilic Multifunctional Chiral Phosphane-Catalyzed Asymmetric Intramolecular Rauhut–Currier Reaction

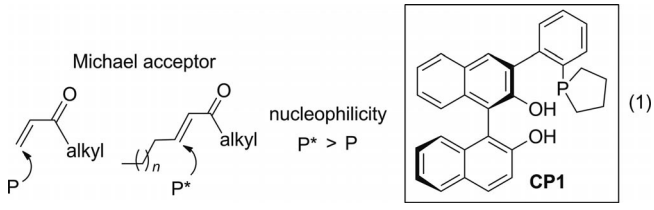
Xiao-Nan Zhang[a] and Min Shi*[a,b]

Keywords: Multifunctional chiral phosphanes / Rauhut-Currier reaction / Cyclopentene derivatives / Cyclohexene derivatives / Organocatalysis / Cyclization / Asymmetric synthesis

An asymmetric variant of the intramolecular Rauhut–Currier (RC) reaction can be achieved using a highly nucleophilic multifunctional chiral phosphane; the corresponding cyclopentene and cyclohexene derivatives are produced in moderate to good yields and with good to excellent enantioselectivities.

Introduction

The Rauhut–Currier (RC) reaction, also known as the vinylogous Morita–Baylis–Hillman (MBH) reaction, involves the coupling of one active alkene/latent enolate to a second Michael acceptor, producing a new C–C bond between the α-position of one activated alkene and the β-position of a second alkene; a nucleophilic catalyst is central to the reaction.[1] Since the first report by Rauhut and Currier in 1963 of the dimerization of electron-deficient alkenes catalyzed by a tertiary phosphane,[1a] the development of asymmetric intermolecular/intramolecular RC reactions has seen significant progress.[2,3] In particular, the asymmetric variant of the intramolecular RC reaction to afford corresponding carbocyclic derivatives with good *ee* values has been achieved in recent years.[4] During our ongoing investigations into the utilization of chiral multifunctional phosphanes in asymmetric MBH and related reactions, we realized that, in the case of a Michael acceptor bearing a substituent at the β-position, a highly nucleophilic phosphane is required to initiate the reaction due to steric issues [Equation (1)].[5,6] In this paper, we report the application of a highly nucleophilic multifunctional chiral phosphane **CP1** in the asymmetric intramolecular RC reaction, giving the corresponding cyclohexene and cyclopentene products in moderate to good yields and with good to high *ee* values under mild conditions.



(1)

Results and Discussion

We initiated our investigations by seeking a suitable chiral phosphane and the best conditions for the intramolecular RC reaction of bis(enone) **1a**. After screening of the catalysts, investigating the solvent effects and reaction temperature on the reaction outcomes, we found that toluene is a suitable solvent in this reaction, and the optimized reaction conditions involve performing the reaction in toluene/*tert*-amyl-OH (20:1) using **CP1** (20 mol-%) as the catalyst at room temperature (25 °C) for 48 h. Carried out under these conditions, the reaction affords desired product **2a** in 97% yield with 91% *ee* (Table 1, Entry 9) (see also Table SI-1 and reaction procedures in the Supporting Information for more details). Catalyst **CP2** was not as effective as **CP1** in this asymmetric reaction, and a less nucleophilic chiral phosphane **CP3**, developed by Sasai,[6d] had no catalytic activity in this reaction (Table 1, Entries 10 and 11). The dimethylated chiral phosphane **CP4** lacked the catalytic activity displayed by **CP1**, suggesting that the phenol groups are essential in this asymmetric RC reaction to achieve high *ee* value and good yield (Table 1, Entry 12).

Under the optimal reaction conditions, we next set out to examine the scope and limitations of this reaction using various bis(enone)s **1**; the results are summarized in Table 2. As can be seen from Table 2, all reactions proceeded smoothly to give the corresponding RC products **2** in moderate to good yields (76–97%) with good to high *ee* values (61–96%) as the (*R*) configuration[4b,4c] at 25 °C or 15 °C

[a] Laboratory for Advanced Materials & Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, P. R. China

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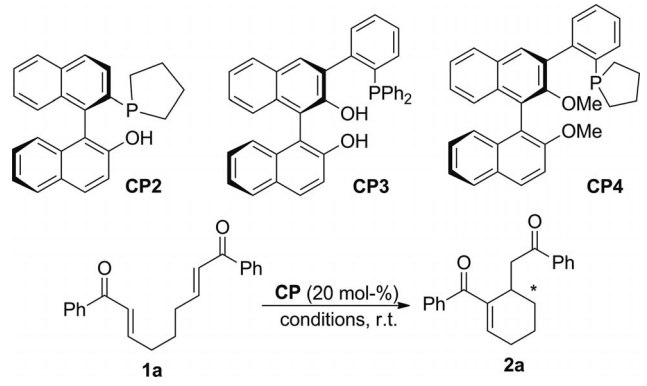
Table 1. Selected examples on the optimization of the reaction conditions.[a]



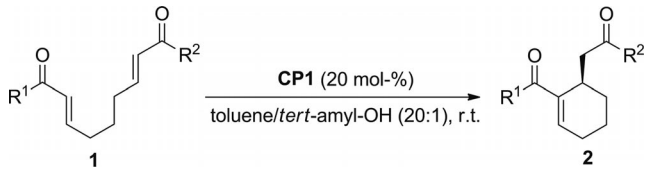
Entry	Solvent	CP	Time [d]	Yield [%][b]	*ee* [%][c]
1	THF	**CP1**	48	94	80
2	Et_2O	**CP1**	48	94	76
3	CH_2Cl_2	**CP1**	48	78	88
4	*t*BuOH	**CP1**	48	97	69
5	*t*BuOMe	**CP1**	48	98	82
6	toluene	**CP1**	48	74	91
7	*ortho*-xylene	**CP1**	48	52	90
8	toluene/*t*BuOH (20:1)	**CP1**	48	97	88
9	toluene/*tert*-amyl-OH (20:1)	**CP1**	48	97	91
10	toluene	**CP2**	48	45	3
11	toluene	**CP3**	48	n.r.	–
12	toluene	**CP4**	48	65	2

[a] Reactions were performed with **1a** (0.10 mmol) in the presence of 20 mol-% of CP in solvent (1 mL) at room temp. (25 °C). [b] Isolated yields. [c] Determined by chiral HPLC analysis.

or at –30 °C for 7 d when R^1 and R^2 are aromatic or heteroaromatic groups (Table 2, Entries 1–14). Using bis(enone)s **1i**–**1k** as substrates, in which the aromatic groups bare electron-donating substituents, 40 mol-% of **CP1** is required to give desired products in good yields (Table 2, Entries 9–11). In the case of unsymmetric bis(enone) **1o**, compound **2o** was formed as a single product in 74% yield and with 93% *ee*; isomeric material **2o′** (R^1 = 4-$NO_2C_6H_4$ and R^2 = 4-$MeOC_6H_4$) was not detected (Table 2, Entry 15). By contrast, in the case of **1p**, in which R^1 = C_6H_5 and R^2 = Me, two regioisomers **2p** and **2p′** were formed in good yield along with similar *ee* values upon heating (Table 2, Entry 16). As for aliphatic substrate **1q**, the desired product **2q** was obtained in 62% yield with 64% *ee* when the reaction was carried out at 80 °C (Table 2, Entry 17). Using diethyl (2*E*,7*E*)-nona-2,7-dienedioate (**1r**) as substrate, no reaction occurred, even when heated to 110 °C (Table 2, Entry 18).

Bis(enone)s **3** are difficult substrates for asymmetric RC reactions, and *ee* values for such reactions have never exceeded 60% *ee*.[1b] Using bis(enone) **3a** as substrate, reactions were found to not be as effective as those involving bis(enone)s **1** in the presence of **CP1** in various solvents under the standard conditions (Table 3, Entries 1–5). Upon optimizing the reaction conditions, we found that lowering the reaction temperature significantly improved the *ee* value of **4a** in tetrahydrofuran (THF) along with a decrease in yield of **4a**, giving the corresponding product **4a** in 44% yield with 82% *ee* and 38% yield and 94% *ee* at 0 °C or –15 °C, respectively, in the presence of 35 mol-% of **CP1**

Table 2. Substrate scope of asymmetric intramolecular RC reaction.[a]

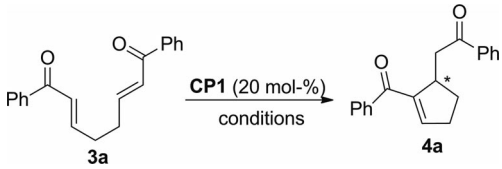


Entry	Substrate	R^1	R^2	Time [d]	Product, yield [%][b]	*ee* [%][c]
1	**1a**	C_6H_5	C_6H_5	2	**2a**, 97	91
2	**1b**	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	3	**2b**, 96	61
3	**1c**	4-FC_6H_4	4-FC_6H_4	4	**2c**, 94[d]	96[d]
4	**1d**	2-ClC_6H_4	2-ClC_6H_4	4	**2d**, 95[d] (76[e]	81[d] (91)[e]
5	**1e**	3-ClC_6H_4	3-ClC_6H_4	4	**2e**, 92[d]	89[d]
6	**1f**	4-ClC_6H_4	4-ClC_6H_4	4	**2f**, 94 (92[d]	89 (91)[d]
7	**1g**	3-BrC_6H_4	3-BrC_6H_4	4	**2g**, 90[d]	92[d]
8	**1h**	4-BrC_6H_4	4-BrC_6H_4	4	**2h**, 92[d]	91[d]
9	**1i**	4-MeC_6H_4	4-MeC_6H_4	4	**2i**, 45 (92)[f]	93 (93)[f]
10	**1j**	3-$MeOC_6H_4$	3-$MeOC_6H_4$	4	**2j**, 82[f]	89[f]
11	**1k**	4-$MeOC_6H_4$	4-$MeOC_6H_4$	4	**2k**, 91[f]	92[f]
12	**1l**	naphth-1-yl	naphth-1-yl	3	**2l**, 93	90
13	**1m**	naphth-2-yl	naphth-2-yl	3	**2m**, 93	90
14	**1n**	furan-2-yl	furan-2-yl	3	**2n**, 90[d]	90[d]
15	**1o**	4-$MeOC_6H_4$	4-$NO_2C_6H_4$	4	**2o**, 74	93
16	**1p**	C_6H_5	Me	2	**2p**, 45[g] (**2p′**,[h] 17[g])	66 (54)[g]
17	**1q**	Me	Me	2	**2q**, 62[g]	64[g]
18	**1r**	OEt	OEt	2	**2r**, 0[i]	–

[a] Reactions performed with **1a** (0.10 mmol) in the presence of 20 mol-% of **CP1** and *tert*-amyl-OH (50 μL) in toluene (1 mL) at room temp. [b] Isolated yields. [c] Determined by chiral HPLC analysis, and the absolute configuration of **2** has been assigned as (*R*) based on optical rotation comparisons to previously reported compounds. [d] Reaction conducted at 15 °C. [e] Reaction conducted at –30 °C in toluene (0.3 mL) for 7 d. [f] 40 mol-% of **CP1** was used. [g] Reaction conducted in toluene at 80 °C. [h] Regioisomer of **2p** (R^1 = C_6H_5, R^2 = Me) and **2p′** (R^1 = Me, R^2 = C_6H_5). [i] Reaction conducted in toluene at 111 °C.

(Table 3, Entries 6 and 7). Further reducing the reaction temperature failed to improve these results (Table 3, Entry 8).

Table 3. Optimization of the reaction conditions.[a]

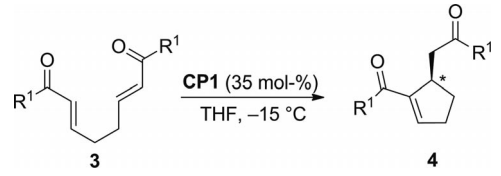


Entry	Solvent	Temp [°C]	Time [d]	Yield [%][b]	*ee* [%][c]
1	THF	25	2	72	60
2	Et_2O	25	2	32	45
3	CH_2Cl_2	25	2	56	27
4	*t*BuOMe	25	2	24	49
5	toluene	25	2	28	47
6[d]	THF	0	7	44	82
7[d]	THF	–15	7	38	94
8[d]	THF	–30	7	9	96

[a] Reactions were performed with **3a** (0.10 mmol) in the presence of 20 mol-% of **CP1** in solvent (1.0 mL). [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] 35 mol-% of **CP1** was used.

Using the optimized conditions, the substrate scope of the reaction was subsequently examined, and the results of these experiments are summarized in Table 4. The reactions produced corresponding products **4b**–**4i** in 18–53% yields along with 54–95% *ee* values (Table 4, Entries 1–8). As for bis(enone) **3b** having a *para*-fluoro substituent on the aromatic ring, corresponding products **4b** were formed in 18% yield, due to the poor substrate solubility in THF at –15 °C (Table 4, Entry 1). Carrying out the reaction at room temperature (25 °C) improved the yields of **4b** and **4d**–**4g**, but with significant decreases in *ee* for production of **4b** and **4d**–**4g**. The absolute configuration of product **4** has been unambiguously assigned as (*R*) on the basis of X-ray diffraction of **4a**. The ORTEP drawing of **4a** is shown in Figure 1 (see Supporting Information for details).[7]

Table 4. Substrate scope of asymmetric intramolecular RC reaction.[a]



Entry	Substrate	R^1	Time [d]	Product, yield [%][b]	*ee* [%][c]
1	**3b**	4-FC_6H_4	7	**4b**, 18 (70)[d]	82 (3)[d]
2	**3c**	2-ClC_6H_4	7	**4c**, 72	67
3	**3d**	3-ClC_6H_4	7	**4d**, 33 (74)[d]	57 (–6)[d]
4	**3e**	4-ClC_6H_4	7	**4e**, 22 (68)[d]	62 (–6)[d]
5	**3f**	4-BrC_6H_4	7	**4f**, 20 (62)[d]	60 (–7)[d]
6	**3g**	4-MeC_6H_4	7	**4g**, 28 (63)[d]	95 (24)[d]
7	**3h**	naphth-1-yl	7	**4h**, 53	54
8	**3i**	furan-2-yl	7	**4i**, 41	85

[a] Reactions were performed with **3** (0.10 mmol) in the presence of 35 mol-% of **CP1** in THF (1.0 mL) at –15 °C. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] Reactions were performed in the presence of 20 mol-% of **CP1** at room temp. (25 °C) for 3 d.

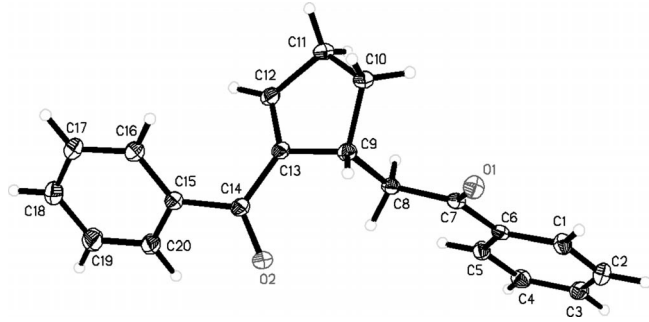


Figure 1. ORTEP drawing of **4a**.

Plausible transition states for the formation of (*R*)-**2a** and (*R*)-**4a** shown in Figure 2 may be invoked to rationalize the reaction outcomes. During formation of five- or six-membered ring products, **TS-1** is favored due to the steric repulsions inherent to **TS-2**; corresponding products **2a** or **4a** are thus obtained in possessing the (*R*) configuration. Intramolecular hydrogen bonding between the phenol group and the enolate generated in situ are envisioned to play a significant role in both cases.[5a,5h,6d]

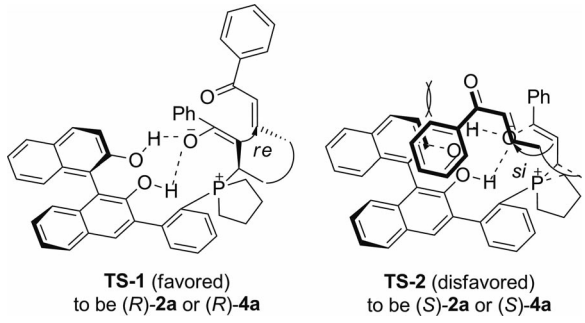
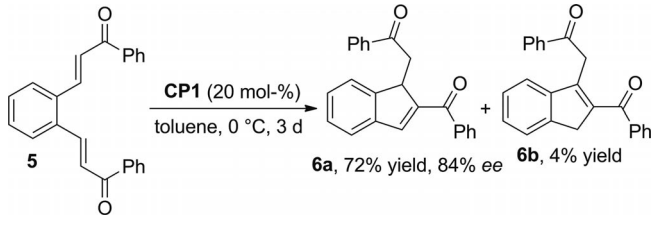


Figure 2. Proposed transition state en route to five- and six-membered ring products catalyzed by **CP1**.

This asymmetric catalytic system can also be used in the intramolecular RC reaction of (2E,2′*E*)-3,3′-(1,2-phenylene)bis(1-phenylprop-2-en-1-one) (**5**), giving the desired product **6a** in 72% yield with 84% *ee* in toluene at 0 °C along with achiral product **6b** in 4% yield (Scheme 1). It should also be noted that in protic solvents such as *tert*-amyl-OH, achiral product **6b** could be formed as the major product using **CP1** as the catalyst under otherwise identical conditions.



Scheme 1. Intramolecular RC reaction of **5** catalyzed by **CP1**.

Conclusions

We have developed a novel and highly nucleophilic multifunctional chiral phosphane **CP1** catalyzed asymmetric intramolecular RC reaction that uses mild conditions and enables facile access to corresponding cyclopentene and cyclohexene derivatives in moderate to good yields with good to excellent enantioselectivities. Further studies on the mechanistic details of this catalytic system along with the development of new asymmetric catalytic reactions with these highly nucleophilic multifunctional chiral phosphanes are currently underway in our laboratory.

Experimental Section

General Remarks: Melting points were determined with a digital melting point apparatus, and temperatures are uncorrected. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin–Elmer-341 MC digital polarimeter. $[\alpha]_D$ values are given in units of 10 $deg^{-1} cm^2 g^{-1}$. ^1H NMR spectra were recorded with Bruker AM-300 and AM-400 spectrometers for solutions in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants J are given in Hz. ^{13}C NMR spectra were recorded with Bruker AM-300 and AM-400 spectrometers (75 or 100 MHz) with complete proton decoupling ($CDCl_3$: δ = 77.0 ppm). Infrared spectra were recorded using a Perkin–Elmer PE-983 spectrometer with absorptions reported in cm^{-1}. Flash column chromatography was performed using 300–400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Chiral HPLC was performed with a Waters 2487 series with chiral columns [Chiralpak AD-H columns 4.6 × 250 mm (Daicel Chemical Ind., Ltd.)]. Mass spectra were recorded by EI, ESI, MALDI, and HRMS was measured with an HP-5989 instrument. The preparations of chiral phosphanes **CP1**, **CP2**, and **CP4** are reported in the Supporting Information. Chiral **CP3** was prepared according to previous literature.[6d] Bis(enone)s **1** and **3** were also synthesized according to previous literature (see Supporting Information).

Compound CP1: A white solid, 55.6 mg. 62% yield. M.p. 114–116 °C. IR (KBr): $\tilde{\nu}$ = 3519, 3058, 2935, 2856, 1731, 1619, 1595, 1465, 1421, 1382, 1265, 1140, 740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.59–2.05 (m, 8 H, 4 CH_2), 5.17 (s, 1 H, OH), 5.93 (s, 1 H, OH), 7.13–7.20 (m, 1 H, ArH), 7.27–7.52 (m, 10 H, ArH), 7.83–7.94 (m, 4 H, ArH) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz, 85% H_3PO_4): δ = –21.33, –22.69 ppm. MS (EI) m/z (%): 448 (3.09) $[M]^+$, 433(6.77), 432 (36.29), 431 (100), 430 (11.58), 373 (3.99), 172 (3.97), 144 (5.67). HRMS (EI): calcd. for $C_{30}H_{25}O_2P^+$ $[M]^+$ 448.1592, found 448.1595. $[\alpha]_D^{20}$ = +137.0 (c = 0.25, $CHCl_3$).

Compound CP2: A yellowish solid, 46.3 mg, 65% yield. M.p. 188–190 °C. IR (KBr): $\tilde{\nu}$ = 3506, 3425, 3054, 2933, 2856, 1619, 1594, 1514, 1501, 1345, 1265, 1203, 1143, 866, 812, 735, 683 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.25–1.43 (m, 2 H, CH_2), 1.64–1.88 (m, 5 H, 3 CH_2), 2.00–2.08 (m, 1 H, CH_2), 4.84 (s, 1 H, OH), 6.92 (d, J = 8.4 Hz, 1 H, ArH), 7.20–7.25 (m, 2 H, ArH), 7.26–7.34 (m, 2 H, ArH), 7.36 (d, J = 8.8 Hz, 1 H, ArH), 7.48 (td, J = 8.0, 1.2 Hz, 1 H, ArH), 7.70 (dd, J = 2.4, 8.8 Hz, 1 H, ArH), 7.87 (d, J = 8.0 Hz, 1 H, ArH),7.92 (d, J = 8.0 Hz, 1 H, ArH), 7.95 (d, J = 8.8 Hz, 1 H, ArH), 7.98 (d, J = 8.8 Hz, 1 H, ArH) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz, 85% H_3PO_4): δ = –21.71 ppm. MS (EI) m/z (%): 356 (34.94) $[M]^+$, 355 (18.83), 340 (27.25), 399 (100), 281 (14.69), 268 (29.67), 252 (17.67), 239 (20.96). HRMS (EI): calcd. for $C_{24}H_{21}OP^+$ $[M]^+$ 356.1330, found 356.1324. $[\alpha]_D^{20}$ = –120.6 (c = 1.0, $CHCl_3$).

Compound (*R*)-CP4: White solid, 55.3 mg, 58% yield. M.p. 96–98 °C. IR (KBr): $\tilde{\nu}$ = 3053, 2934, 2857, 2836, 1621, 1593, 1509, 1456, 1403, 1267, 1247, 1089, 1018, 807, 745, 611 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.58–2.01 (m, 8 H, 4 CH_2), 3.02 (s, 1.1 H, OCH_3), 3.08 (s, 1.9 H, OCH_3), 3.81 (s, 3 H, OCH_3), 7.13–7.24 (m, 2 H, ArH), 7.26 (dd, J = 3.2, 8.4 Hz, 1 H, ArH), 7.29–7.40 (m, 4 H, ArH), 7.44–7.54 (m, 4 H, ArH), 7.84–7.90 (m, 3 H, ArH), 7.98 (d, J = 8.8 Hz, 1 H, ArH) ppm. ^{31}P NMR ($CDCl_3$, 121.5 MHz, 85% H_3PO_4): δ = –20.19, –22.45 ppm. MS (EI) m/z (%): 476 (0.24) $[M]^+$, 447 (7.53), 446 (35.97), 445 (100), 444 (3.95), 429 (6.44), 230 (3.99), 215 (4.37). HRMS (EI): calcd. for $C_{32}H_{29}O_2P^+$ $[M]^+$ 476.1905, found 476.1906. $[\alpha]_D^{20}$ = +121.2 (c = 0.2, $CHCl_3$).

General Procedure A: To a solution of compound **CP1** (0.02 mmol) in toluene (1.0 mL) were added the corresponding bis(enone) (0.1 mmol) and *tert*-amyl-OH (50 μL) at room temp. The reaction mixture was stirred at room temp. (25 °C) until the reaction was completed (monitoring by TLC). Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to afford the desired cyclic product.

General Procedure B: To a solution of compound **CP1** (0.02 mmol) in toluene (1.0 mL) were added the corresponding bis(enone) (0.1 mmol) and *tert*-amyl-OH (50 μL) at room temp. The reaction mixture was stirred at 15 °C until the reaction completed (monitoring by TLC). Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to afford the desired cyclic product.

General Procedure C: To a solution of compound **CP1** (0.02 mmol) in toluene (0.3 mL) were added the corresponding bis(enone) (0.1 mmol) and *tert*-amyl-OH (50 μL) at room temp. The reaction mixture was stirred at –30 °C for 7 d. Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to afford the desired cyclic product.

General Procedure D: To a solution of compound **CP1** (0.04 mmol) in toluene (1.0 mL) were added the corresponding bis(enone) (0.1 mmol) and *tert*-amyl-OH (50 μL) at room temp. The reaction mixture was stirred at room temp. until the reaction was completed (monitoring by TLC). Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to afford the desired cyclic product.

General Procedure E: To a solution of compound **CP1** (0.02 mmol) in toluene (1.0 mL) was added the corresponding bis(enone) (0.1 mmol) at room temp. The reaction mixture was stirred at 80 °C for 2 d. Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to afford the desired cyclic product.

General Procedure F: To a solution of compound **CP1** (0.035 mmol) in THF (1.0 mL) was added the corresponding bis(enone) (0.1 mmol) at room temp. The reaction mixture was stirred at –15 °C for 7 d. Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to afford the desired cyclic products.

General Procedure G: To a solution of compound **CP1** (0.02 mmol) in toluene (0.5 mL) was added the compound **5** (0.1 mmol) at room temp. The reaction mixture was stirred at 0 °C for 3 d. Then the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography to afford the desired cyclic products **6a** and **6b**.

Compound 2a: General Procedure A; yield 29 mg, 97%; this is a known compound.[8] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.60–1.81 (m, 4 H, CH_2, CH_2), 2.15–2.24 (m, 1 H, CH_2), 2.31–2.37 (m, 1 H, CH_2), 2.82 (dd, J = 10.8, 14.8 Hz, 1 H, CH_2), 3.42 (dd, J = 3.2, 14.8 Hz, 1 H, CH_2), 3.49–3.52 (m, 1 H, CH), 6.62–6.64 (m, 1 H, =CH), 7.41–7.57 (m, 6 H, ArH), 7.67–7.69 (m, 2 H, ArH), 8.06–8.09 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 18.1, 26.1, 26.4, 30.3, 42.5, 128.1, 128.5, 128.6, 129.2, 131.6, 133.0, 136.7, 138.8, 141.5, 145.0, 198.1, 199.7 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 23.40 min, t_{major} = 31.89 min; *ee* = 91%; $[\alpha]_D^{20}$ = +25.1 (c = 0.90, $CHCl_3$)].

Compound 2b: General Procedure A; yield 38 mg, 96%; this is a known compound.[4b] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.70–1.78 (m, 4 H, CH_2, CH_2), 2.25–2.31 (m, 1 H, CH_2), 2.39–2.45 (m, 1 H, CH_2), 2.99 (dd, J = 9.6, 15.2 Hz, 1 H, CH_2), 3.42 (dd, J = 3.6, 15.2 Hz, 1 H, CH_2), 3.44–3.47 (m, 1 H, CH), 6.70 (t, J = 3.6 Hz, 1 HCH), 7.79 (d, J = 8.4 Hz, 2 H, ArH), 8.23 (d, J = 8.4 Hz, 2 H, ArH), 8.28–8.34 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.7, 26.3, 26.5, 29.8, 42.8, 123.4, 123.9, 129.4, 129.9, 140.9, 141.0, 144.2, 148.3, 149.3, 150.3, 196.0, 197.9 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.75 mL/min; t_{minor} = 86.05 min, t_{major} = 92.42 min; *ee* = 61%; $[\alpha]_D^{20}$ = –10.0 (c = 0.65, $CHCl_3$)].

Compound 2c: General Procedure B; yield 32 mg, 94%; this is a known compound.[4f] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.62–1.80 (m, 4 H, CH_2, CH_2), 2.17–2.27 (m, 1 H, CH_2), 2.32–2.39 (m, 1 H, CH_2), 2.79 (dd, J = 10.0, 14.8 Hz, 1 H, CH_2), 3.35 (dd, J = 3.6, 14.8 Hz, 1 H, CH_2), 3.44–3.47 (m, 1 H, CH), 6.60–6.62 (m, 1 H, =CH), 7.10–7.16 (m, 4 H, ArH), 7.71–7.74 (m, 2 H, ArH), 8.08–8.12 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 18.1, 26.1, 26.5, 30.5, 42.3, 115.2 (d, J = 21.7 Hz), 115.6 (d, J = 22.5 Hz), 131.1 (d, J = 9.5 Hz), 131.7 (d, J = 8.9 Hz), 133.1 (d, J = 3.0 Hz), 134.7 (d, J = 3.6 Hz), 141.2, 144.7, 164.9 (d, J = 251.2 Hz), 165.7 (d, J = 252.3 Hz), 196.6, 198.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ = –105.45, –107.27 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 49.21 min, t_{major} = 66.33 min; *ee* = 96%; $[\alpha]_D^{20}$ = +24.7 (c = 1.5, $CHCl_3$)].

Compound 2d: General Procedure C; yield 28 mg, 76%; this is a known compound.[4f] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.65–1.87 (m, 4 H, CH_2, CH_2), 2.14–2.32 (m, 2 H, CH_2), 2.98 (dd, J = 10.4, 16.8 Hz, 1 H, CH_2), 3.38 (dd, J = 2.8, 16.8 Hz, 1 H, CH_2), 3.47–3.50 (m, 1 H, CH), 6.56 (t, J = 3.6 Hz, 1 HCH), 7.23–7.25 (m, 1 H, ArH), 7.27–7.29 (m, 1 H, ArH), 7.32–7.43 (m, 5 H, ArH), 7.61–7.63 (m, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.4, 26.2, 26.4, 28.4, 46.0, 126.4, 126.9, 128.6, 129.1, 129.7, 130.4, 130.5, 130.86, 130.89, 131.5, 139.03, 139.09, 141.7, 148.9, 196.2, 202.2 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.75 mL/min; t_{minor} = 18.00 min, t_{major} = 21.57 min; *ee* = 91%; $[\alpha]_D^{20}$ = +5.0 (c = 1.00, $CHCl_3$)].

Compound 2e: General Procedure B; yield 34 mg, 92%; this is a known compound.[4f] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.62–1.77 (m, 4 H, CH_2, CH_2), 2.19–2.28 (m, 1 H, CH_2), 2.33–2.42 (m, 1 H, CH_2), 2.85 (dd, J = 10.4, 15.2 Hz, 1 H, CH_2), 3.33 (dd, J = 3.2, 15.2 Hz, 1 H, CH_2), 3.45–3.47 (m, 1 H, CH), 6.66 (t, J = 3.6 Hz, 1 H, =CH), 7.36–7.44 (m, 2 H, ArH), 7.48–7.55 (m, 3 H, ArH), 7.63 (t, J = 1.6 Hz, 1 H, ArH), 7.95–7.98 (m, 1 H, ArH), 8.02 (t, J = 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.9, 26.2, 26.5, 30.0, 42.4, 126.6, 127.3, 128.3, 129.0, 129.5, 129.9, 131.5, 132.9, 134.2, 134.9, 138.3, 140.3, 141.0, 146.2, 196.2, 198.0 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 31.93 min, t_{major} = 36.00 min; *ee* = 89%; $[\alpha]_D^{20}$ = +19.5 (c = 0.90, $CHCl_3$)].

Compound 2f: General Procedure B; yield 34 mg, 92%; this is a known compound.[4f] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.62–1.79 (m, 4 H, CH_2, CH_2), 2.19–2.25 (m, 1 H, CH_2), 2.33–2.38 (m, 1 H, CH_2), 2.81 (dd, J = 10.4, 14.8 Hz, 1 H, CH_2), 3.34 (dd, J = 3.2, 14.8 Hz, 1 H, CH_2), 3.42–3.44 (m, 1 H, CH), 6.61–6.63 (m, 1 H, =CH), 7.41 (d, J = 8.4 Hz, 2 H, ArH), 7.43 (d, J = 8.4 Hz, 2 H, ArH), 7.63 (d, J = 8.4 Hz, 2 H, ArH), 8.00 (d, J = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.9, 26.0, 26.4, 30.2, 42.3, 128.3, 128.8, 129.8, 130.6, 134.9, 136.8, 137.9, 139.4, 141.1, 145.3, 196.6, 198.3 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 254 nm; eluent: hexane/2-propanol = 90:10; flow rate: 1.0 mL/min; t_{minor} = 18.39 min, t_{major} = 23.98 min; *ee* = 91%; $[\alpha]_D^{20}$ = +8.6 (c = 1.65, $CHCl_3$)].

Compound 2g: General Procedure B; yield 42 mg, 90%; this is a known compound.[4f] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.63–1.77 (m, 4 H, CH_2, CH_2), 2.19–2.28 (m, 1 H, CH_2), 2.34–2.44 (m, 1 H, CH_2), 2.84 (dd, J = 10.5, 15.3 Hz, 1 H, CH_2), 3.33 (dd, J = 3.0, 15.3 Hz, 1 H, CH_2), 3.44–3.47 (m, 1 H, CH), 6.67 (t, J = 3.6 Hz, 1 H, CH), 7.27–7.39 (m, 2 H, ArH), 7.58 (d, J = 7.2 Hz, 1 H, ArH), 7.63–7.70 (m, 2 H, ArH), 7.78 (s, 1 H, ArH), 8.02 (d, J = 7.8 Hz, 1 H, ArH), 8.17 (s, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.9, 26.1, 26.4, 29.9, 42.3, 122.3, 122.9, 127.0, 127.7, 129.7, 130.1, 131.3, 131.9, 134.4, 135.8, 138.4, 140.5, 141.0, 146.3, 196.1, 198.0 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 27.63 min, t_{major} = 32.40 min; *ee* = 92%; $[\alpha]_D^{20}$ = +10.0 (c = 1.00, $CHCl_3$)].

Compound 2h: General Procedure B; yield 43 mg, 92%; this is a known compound.[4b] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.62–1.77 (m, 4 H, CH_2, CH_2), 2.18–2.25 (m, 1 H, CH_2), 2.32–2.38 (m, 1 H, CH_2), 2.80 (dd, J = 10.4, 14.8 Hz, 1 H, CH_2), 3.33 (dd, J = 3.2, 14.8 Hz, 1 H, CH_2), 3.41–3.43 (m, 1 H, CH), 6.62 (t, J = 3.6 Hz, 1 H, CH), 7.53–7.64 (m, 6 H, ArH), 7.92 (d, J = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.9, 26.1, 26.4, 30.2, 42.3, 126.5, 128.2, 129.9, 130.7, 131.3, 131.8, 135.3, 137.2, 141.0, 145.5, 196.8, 198.6 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 74.87 min, t_{major} = 95.27 min; *ee* = 91%; $[\alpha]_D^{20}$ = –10.6 (c = 1.45, $CHCl_3$)].

Compound 2i: General Procedure D; yield 31 mg, 92%; this is a known compound.[4f] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.59–1.79 (m, 4 H, CH_2, CH_2), 2.14–2.23 (m, 1 H, CH_2), 2.29–2.36 (m, 1 H, CH_2), 2.39 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3), 2.75 (dd, J = 10.4, 14.4 Hz, 1 H, CH_2), 3.37 (dd, J = 3.2, 14.8 Hz, 1 H, CH_2), 3.46–3.49 (m, 1 H, CH), 6.58 (t, J = 3.6 Hz, 1 H, CH), 7.23–7.27 (m, 4 H, ArH), 7.61 (d, J = 8.4 Hz, 2 H, ArH), 7.96 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 18.1, 21.4, 21.5, 26.0, 26.4, 30.5, 42.4, 128.5, 128.7, 129.2, 129.4, 134.2, 135.9, 141.5, 142.2, 143.6, 143.7, 197.8, 199.3 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column [λ = 254 nm; eluent: hexane/2-propanol = 90:10; flow rate: 1.0 mL/min; t_{minor} = 11.17 min, t_{major} = 12.83 min; *ee* = 93%; $[\alpha]_D^{20}$ = +12.2 (c = 0.70, $CHCl_3$)].

Compound 2j: General Procedure D; yield 30 mg, 82%; colorless oil. IR (KBr): $\tilde{\nu}$ = 2928, 1685, 1676, 1638, 1484, 1459, 1430, 1274, 1042, 788, 754, 685 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.61–1.78 (m, 4 H, CH_2, CH_2), 2.16–2.23 (m, 1 H, CH_2), 2.31–2.37 (m, 1 H, CH_2), 2.79 (dd, J = 10.4, 14.8 Hz, 1 H, CH_2), 3.40 (dd, J = 3.2, 14.8 Hz, 1 H, CH_2), 3.49–3.51 (m, 1 H, CH), 3.84 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.65 (t, J = 3.6 Hz, 1 H, CH), 7.04–7.11 (m, 2 H, ArH), 7.21–7.25 (m, 2 H, ArH), 7.31–7.39 (m, 2 H, ArH), 7.61 (s, 1 H, ArH), 7.68 (d, J = 8.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 18.0, 26.1, 26.4, 30.4, 42.6, 55.38, 55.44, 112.4, 114.0, 117.7, 119.7, 121.1, 121.8, 129.0, 129.6, 138.0, 140.1, 141.4, 145.0, 159.4, 159.8, 197.7, 199.4 ppm. MS (EI) m/z (%): 364 (44.05) $[M]^+$, 229 (48.60), 214 (17.53), 135 (100), 121 (28.41), 107 (57.55), 92 (35.59), 77 (68.86). HRMS (EI): calcd. for $C_{23}H_{24}O_4^+$ $[M]^+$ 364.1675, found 364.1679. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 21.98 min, t_{major} = 26.49 min; ee = 89%; $[\alpha]_D^{20}$ = +17.0 (c = 0.70, $CHCl_3$)].

Compound 2k: General Procedure D; yield 33 mg, 91%; this is a known compound.[4b] ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.59–1.81 (m, 4 H, CH_2, CH_2), 2.14–2.22 (m, 1 H, CH_2), 2.29–2.36 (m, 1 H, CH_2), 2.70 (dd, J = 10.8, 14.4 Hz, 1 H, CH_2), 3.33 (dd, J = 2.8, 14.4 Hz, 1 H, CH_2), 3.45–3.47 (m, 1 H, CH), 3.85 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.52–6.54 (m, 1 H, =CH), 6.92–6.95 (m, 4 H, ArH), 7.72–7.76 (m, 2 H, ArH), 8.03–8.07 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 18.3, 25.9, 26.6, 31.1, 42.3, 55.38, 55.40, 113.4, 113.7, 129.8, 130.8, 131.1, 131.7, 141.6, 142.3, 162.7, 163.4, 197.0, 198.3 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.75 mL/min; t_{minor} = 28.25 min, t_{major} = 41.05 min; ee = 92%; $[\alpha]_D^{20}$ = –4.2 (c = 0.40, $CHCl_3$)].

Compound 2l: General Procedure A; yield 37 mg, 93%; colorless oil. IR (KBr): $\tilde{\nu}$ = 3060, 2929, 2864, 1679, 1644, 1508, 1282, 1245, 1143, 803, 780, 734 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.64–1.90 (m, 4 H, CH_2, CH_2), 2.09–2.17 (m, 1 H, CH_2), 2.21–2.29 (m, 1 H, CH_2), 3.01 (dd, J = 10.8, 15.2 Hz, 1 H, CH_2), 3.63–3.66 (m, 1 H, CH), 3.75 (dd, J = 2.8, 15.2 Hz, 1 H, CH_2), 6.64 (t, J = 3.6 Hz, 1 H, =CH), 7.45–7.47 (m, 2 H, ArH), 7.48–7.62 (m, 5 H, ArH), 7.86–7.92 (m, 3 H, ArH), 7.96–8.00 (m, 2 H, ArH), 8.18 (dd, J = 1.2, 7.6 Hz, 1 H, ArH), 8.71 (d, J = 8.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.7, 26.4, 26.5, 30.0, 45.8, 124.3, 124.6, 125.4, 125.9, 126.30, 126.31, 126.39, 127.0, 127.9, 128.3, 128.4, 128.5, 130.3, 130.4, 130.9, 132.6, 133.6, 134.0, 135.3, 137.3, 143.3, 148.3, 199.3, 204.0 ppm. MS (EI) m/z (%): 404 (29.45) $[M]^+$, 250 (12.91), 249 (62.72), 234 (19.95), 155 (68.04), 128 (15.55), 127 (100), 126 (13.38). HRMS (EI): calcd. for $C_{29}H_{24}O_2^+$ $[M]^+$ 404.1776, found 404.1773. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column [λ = 254 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 47.76 min, t_{major} = 51.40 min; ee = 90%; $[\alpha]_D^{20}$ = +63.0 (c = 1.85, $CHCl_3$)].

Compound 2m: General Procedure A; yield 37 mg, 93%; this is a known compound.[4f] ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.64–1.82 (m, 4 H, CH_2, CH_2), 2.16–2.25 (m, 1 H, CH_2), 2.33–2.41 (m, 1 H, CH_2), 2.98 (dd, J = 10.4, 14.4 Hz, 1 H, CH_2), 3.60 (dd, J = 3.2, 14.4 Hz, 1 H, CH_2), 3.62–3.66 (m, 1 H, CH), 6.70 (t, J = 3.6, Hz, 1 H, =CH), 7.48–7.59 (m, 4 H, ArH), 7.81–7.95 (m, 6 H, ArH), 8.00 (d, J = 7.6 Hz, 1 H, ArH), 8.10 (dd, J = 1.6, 8.4 Hz, 1 H, ArH), 8.19 (s, 1 H, ArH), 8.68 (s, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 18.2, 26.2, 26.6, 30.8, 42.7, 124.1, 125.6, 126.6, 126.7, 127.7, 127.8, 127.9, 128.1, 128.35, 128.37, 129.2, 129.8, 130.3, 130.5, 132.3, 132.6, 134.0, 134.9, 135.5, 136.0, 141.7, 144.9, 198.1, 199.7 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column [λ = 254 nm; eluent: hexane/2-propanol = 90:10; flow rate: 1.0 mL/min; t_{minor} = 15.89 min, t_{major} = 24.59 min; ee = 90%; $[\alpha]_D^{20}$ = –29.4 (c = 1.90, $CHCl_3$)].

Compound 2n: General Procedure B; yield 26 mg, 90%; this is a known compound.[4f] ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.65–1.77 (m, 4 H, CH_2, CH_2), 2.21–2.28 (m, 1 H, CH_2), 2.33–2.40 (m, 1 H, CH_2), 2.67 (dd, J = 10.8, 14.8 Hz, 1 H, CH_2), 3.10 (dd, J = 3.2, 14.8 Hz, 1 H, CH_2), 3.45–3.48 (m, 1 H, CH), 6.51–6.54 (m, 2 H, ArH), 6.99–7.02 (m, 1 H, =CH), 7.11–7.12 (m, 1 H, ArH), 7.40–7.42 (m, 1 H, ArH), 7.56–7.57 (m, 1 H, ArH), 7.63–7.64 (m, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.9, 26.0, 26.3, 30.6, 42.2, 111.8, 112.1, 118.2, 119.2, 140.8, 142.1, 146.4, 146.5, 152.27, 152.31, 183.6, 188.2 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.75 mL/min; t_{minor} = 22.73 min, t_{major} = 32.25 min; ee = 90%; $[\alpha]_D^{20}$ = –6.9 (c = 1.10, $CHCl_3$)].

Compound 2o: General Procedure A; yield 28 mg, 74%; this is a known compound.[4b] ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.62–1.84 (m, 4 H, $2CH_2$, $2CH_2$), 2.19–2.27 (m, 1 H, CH_2), 2.34–2.43 (m, 1 H, CH_2), 2.87 (dd, J = 9.6, 14.8 Hz, 1 H, CH_2), 3.31 (dd, J = 3.6, 14.4 Hz, 0.5 H, CH_2), 3.32 (dd, J = 3.6, 14.8 Hz, 1 H, CH_2), 3.42–3.51 (m, 1 H, CH), 3.87 (s, 3 H, CH_3), 6.60–6.62 (m, 1 H, =CH), 6.95 (d, J = 8.8 Hz, 2 H, ArH), 7.81 (d, J = 8.8 Hz, 2 H, ArH), 8.05 (d, J = 8.8 Hz, 2 H, ArH), 8.29 (d, J = 8.8 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 17.8, 26.33, 26.40, 30.2, 41.8, 55.4, 113.7, 123.3, 129.8, 129.9, 130.6, 141.7, 144.3, 147.2, 149.2, 163.4, 195.9, 198.0 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.75 mL/min; t_{minor} = 44.37 min, t_{major} = 47.58 min; ee = 93%; $[\alpha]_D^{20}$ = –6.1 (c = 0.85, $CHCl_3$)].

Compound 2p: General Procedure E; yield 15 mg, 62%; this is a known compound (a mixture of **2p** and **2p′**).[9] ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.45–1.81 (m, 5.7 H, 2 CH_2, 2 CH_2), 2.11–2.37 (m, 7.7 H, CH_2, CH_3, CH_2, CH_3), 2.46 (dd, J = 10.0, 16.0 Hz, 1 H, CH_2), 2.65–2.72 (m, 1.5 H, CH_2, CH_2), 3.33–3.38 (m, 1.8 H, CH, CH, CH_2), 6.56 (t, J = 4.0 Hz, 1 H, =CH), 7.01 (t, J = 4.0, Hz, 0.4 H, =CH), 7.39–7.50 (m, 4.2 H, ArH, ArH), 7.64–7.66 (m, 2 H, ArH), 8.10–8.13 (m, 0.8 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 16.7, 18.1, 25.52, 25.54, 25.9, 26.1, 26.9, 28.7, 29.1, 29.8, 42.5, 47.3, 128.0, 128.40, 128.44, 129.1, 131.5, 132.8, 136.6, 138.5, 141.2, 142.2, 143.0, 144.3, 197.8, 199.0, 199.8, 208.0 ppm. Enantiomeric excess of **2p** was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 25.32 min, t_{major} = 28.40 min; ee = 54%]; enantiomeric excess of **2p′** was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 23.54 min, t_{major} = 41.23 min; ee = 66%; $[\alpha]_D^{20}$ = –5.5 (c = 1.25, $CHCl_3$)] (a mixture of **2p** and **2p′**).

Compound 2q: General Procedure E; yield 11 mg, 62%; this is a known compound.[4b] ^1H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.50–1.68 (m, 4 H, $2CH_2$), 2.17 (s, 3 H, CH_3), 2.19–2.33 (m, 6 H, CH_2, CH_3, CH_2), 2.60 (dd, J = 2.8, 15.6 Hz, 1 H, CH_2), 3.16–3.19 (m, 1 H, CH), 6.96 (t, J = 4.0, Hz, 1 H, =CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 16.9, 25.5, 26.0, 26.1, 27.6, 29.6, 47.5, 142.0, 142.5, 198.7, 208.2 ppm. Enantiomeric excess was de-

termined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.60 mL/min; t_{minor} = 25.17 min, t_{major} = 26.91 min; *ee* = 64%; $[\alpha]_D^{20}$ = –6.9 (*c* = 0.55, $CHCl_3$)].

Compound 4a: General Procedure F; colorless oil, yield 11 mg, 38%; this is a known compound.[4a] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.73–1.82 (m, 1 H, CH_2), 2.27–2.36 (m, 1 H, CH_2), 2.47–2.57 (m, 1 H, CH_2), 2.62–2.72 (m, 1 H, CH_2), 2.82 (dd, *J* = 11.2, 16.4 Hz, 1 H, CH_2), 3.70–3.78 (m, 2 H, CH, CH_2), 6.56–6.57 (m, 1 H, =CH), 7.41–7.46 (m, 4 H, ArH), 7.50–7.55 (m, 2 H, ArH), 7.74–7.77 (m, 2 H, ArH), 8.03–8.05 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 29.5, 32.6, 41.6, 42.4, 128.2, 128.3, 128.6, 128.9, 132.0, 132.9, 136.9, 139.0, 146.1, 147.9, 194.2, 199.7 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 9.37 min, t_{major} = 12.03 min; *ee* = 94%; $[\alpha]_D^{20}$ = +108.1 (*c* = 0.60, $CHCl_3$)].

Compound 4b: General Procedure F; a yellowish solid, yield 6 mg, 18%. M.p. 87–88 °C. IR (KBr): $\tilde{\nu}$ = 3076, 2936, 1683, 1639, 1597, 1505, 1408, 1359, 1228, 1156, 1097, 993, 836, 757, 614, 594 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.73–1.82 (m, 1 H, CH_2), 2.26–2.36 (m, 1 H, CH_2), 2.50–2.58 (m, 1 H, CH_2), 2.64–2.73 (m, 1 H, CH_2), 2.77–2.84 (m, 1 H, CH_2), 3.68–3.73 (m, 2 H, CH, CH_2), 6.56–6.57 (m, 1 H, =CH), 7.08–7.14 (m, 4 H, ArH), 7.78–7.82 (m, 2 H, ArH), 8.04–8.08 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 29.5, 32.6, 41.7, 42.1, 115.3 (d, *J* = 20.5 Hz), 115.5 (d, *J* = 21.9 Hz), 130.9 (d, *J* = 9.0 Hz), 131.4 (d, *J* = 8.8 Hz), 133.3 (d, *J* = 3.0 Hz), 135.1 (d, *J* = 3.0 Hz), 145.9, 147.6, 165.1 (d, *J* = 251.8 Hz), 165.6 (d, *J* = 254.3 Hz), 192.5, 197.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ = –110.32, –111.50 ppm. MS (ESI): *m*/*z* (%) = 327.3 (100) $[M + H]^+$. HRMS (ESI): calcd. for $C_{20}H_{17}F_2O_2^+$ $[M + H]^+$ 327.1191, found 327.1196. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 10.48 min, t_{major} = 13.75 min; *ee* = 82%; $[\alpha]_D^{20}$ = +51.0 (*c* 0.50, $CHCl_3$)].

Compound 4c: General Procedure F; a yellowish oil, yield 26 mg, 72%. IR (KBr): $\tilde{\nu}$ = 3062, 2922, 2851, 1697, 1650, 1608, 1590, 1469, 1432, 1360, 1287, 1057, 758 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.79–1.87 (m, 1 H, CH_2), 2.35–2.44 (m, 1 H, CH_2), 2.46–2.56 (m, 1 H, CH_2), 2.59–2.69 (m, 1 H, CH_2), 3.01 (dd, *J* = 10.4, 17.6 Hz, 1 H, CH_2), 3.67–3.72 (m, 2 H, CH+CH_2), 6.41–6.43 (m, 1 H, =CH), 7.29–7.43 (m, 6 H, ArH), 7.54–7.56 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 30.0, 32.5, 39.8, 46.4, 126.4, 126.9, 128.5, 128.9, 130.0, 130.5, 130.66, 130.75, 130.83, 131.5, 139.41, 139.42, 146.9, 151.4, 193.0, 202.5 ppm. MS (ESI): *m*/*z* (%) = 359.2 (100) $[M + H]^+$. HRMS (ESI): calcd. for $C_{20}H_{17}Cl_2O_2^+$ $[M + H]^+$ 359.06001, found 359.0610. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 10.91 min, t_{major} = 11.97 min; *ee* = 67%; $[\alpha]_D^{20}$ = +45.0 (*c* = 1.0, $CHCl_3$)].

Compound 4d: General Procedure F; colorless oil, yield 12 mg, 33%. IR (KBr): $\tilde{\nu}$ = 3067, 2932, 1688, 1642, 1605, 1567, 1420, 1356, 1285, 1257, 1198, 1077, 789, 738, 723, 681 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.72–1.80 (m, 1 H, CH_2), 2.30–2.39 (m, 1 H, CH_2), 2.52–2.61 (m, 1 H, CH_2), 2.65–2.75 (m, 1 H, CH_2), 2.85 (dd, *J* = 10.4, 16.0 Hz, 1 H, CH_2), 3.66–3.73 (m, 2 H, CH + CH_2), 6.61–6.62 (m, 1 H, =CH), 7.37–7.43 (m, 2 H, ArH), 7.50–7.53 (m, 2 H, ArH), 7.61–7.64 (m, 1 H, ArH), 7.70–7.71 (m,1 H, ArH), 7.90–7.93 (m, 1 H, ArH), 7.98 (t, *J* = 2.0 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 29.5, 32.7, 41.3, 42.2, 126.4, 126.9, 128.3, 128.8, 129.6, 129.9, 131.9, 132.9, 134.4, 134.9, 138.4, 140.4, 145.6, 148.9, 192.5, 198.2 ppm. MS (ESI): *m*/*z* (%) = 359.2 (100) $[M + H]^+$. HRMS (ESI): calcd. for $C_{20}H_{17}Cl_2O_2^+$ $[M + H]^+$ 359.06001, found 359.0594. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 8.90 min, t_{major} = 9.97 min; *ee* = 57%; $[\alpha]_D^{20}$ = +39.0 (*c* = 0.70, $CHCl_3$)].

Compound 4e: General Procedure F; colorless oil, yield 8 mg, 22%. IR (KBr): $\tilde{\nu}$ = 3078, 2927, 1684, 1641, 1586, 1569, 1486, 1400, 1281, 1174, 1091, 1013, 991, 833, 753 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.72–1.81 (m, 1 H, CH_2), 2.27–2.36 (m, 1 H, CH_2), 2.50–2.60 (m, 1 H, CH_2), 2.64–2.74 (m, 1 H, CH_2), 2.80 (dd, *J* = 10.8, 16.4 Hz, 1 H, CH_2), 3.67–3.72 (m, 2 H, CH+CH_2), 6.57–6.58 (m, 1 H, =CH), 7.41–7.44 (m, 4 H, ArH), 7.69–7.72 (m, 2 H, ArH), 7.96–7.98 (m, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 29.4, 32.6, 41.5, 42.1, 128.5, 128.8, 129.7, 130.2, 135.1, 137.1, 138.4, 139.4, 145.7, 148.1, 192.8, 198.3 ppm. MS (ESI): *m*/*z* (%) = 359.2 (100) $[M + H]^+$. HRMS (ESI): calcd. for $C_{20}H_{17}Cl_2O_2^+$ $[M + H]^+$ 359.06001, found 359.0604. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 13.17 min, t_{major} = 18.27 min; *ee* = 62%; $[\alpha]_D^{20}$ = +34.0 (*c* = 0.50, $CHCl_3$)].

Compound 4f: General Procedure F; white solid, yield 9 mg, 20%. M.p. 74–76 °C. IR (KBr): $\tilde{\nu}$ = 3065, 2926, 1685, 1637, 1584, 1566, 1481, 1395, 1283, 1175, 1070, 1010, 990, 828, 748 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.70–1.81 (m, 1 H, CH_2), 2.25–2.38 (m, 1 H, CH_2), 2.48–2.61 (m, 1 H, CH_2), 2.62–2.72 (m, 1 H, CH_2), 2.80 (dd, *J* = 10.5, 15.9 Hz, 1 H, CH_2), 3.66–3.72 (m, 2 H, CH+CH_2), 6.57–6.59 (m, 1 H, =CH), 7.57–7.64 (m, 6 H, ArH), 7.90 (d, *J* = 8.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 29.4, 32.6, 41.4, 42.1, 127.0, 128.1, 129.8, 130.4, 131.5, 131.8, 135.4, 137.5, 145.7, 148.3, 192.9, 198.5 ppm. MS (ESI): *m*/*z* (%) = 449.2 (100) $[M + H]^+$. HRMS (ESI): calcd. for $C_{20}H_{17}Br_2O_2^+$ $[M + H]^+$ 446.95898, found 446.9600. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 15.82 min, t_{major} = 22.32 min; *ee* = 60%; $[\alpha]_D^{20}$ = +38.0 (*c* = 0.45, $CHCl_3$)].

Compound 4g: General Procedure F; white solid, yield 9 mg, 28%. M.p. 86–88 °C. IR (KBr): $\tilde{\nu}$ = 3070, 2922, 1680, 1637, 1605, 1569, 1455, 1406, 1356, 1283, 1198, 1179, 1115, 979, 813, 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.72–1.80 (m, 1 H, CH_2), 2.24–2.35 (m, 1 H, CH_2), 2.40 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 2.48–2.58 (m, 1 H, CH_2), 2.62–2.71 (m, 1 H, CH_2), 2.75 (dd, *J* = 10.8, 16.4 Hz, 1 H, CH_2), 3.66–3.76 (m, 2 H, CH_2+CH), 6.54–6.56 (m, 1 H, =CH), 7.24–7.26 (m, 4 H, ArH), 7.68 (d, *J* = 8.0 Hz, 2 H, ArH), 7.94 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.56, 21.61, 29.5, 32.6, 41.8, 42.4, 128.4, 128.9, 129.1, 129.2, 134.4, 136.3, 142.7, 143.7, 146.2, 147.0, 194.0, 199.5 ppm. MS (EI): *m*/*z* (%) = 318 (16.71) $[M]^+$, 199 (24.22), 185(6.42), 184 (18.17), 120 (9.27), 119 (100), 91 (51.8), 65 (13.67). HRMS (EI): calcd. for $C_{22}H_{22}O_2^+$ $[M]^+$ 318.1620, found 318.1618. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 17.52 min, t_{major} = 27.07 min; *ee* = 95%; $[\alpha]_D^{20}$ = +90.0 (*c* = 0.40, $CHCl_3$)].

Compound 4h: General Procedure F; yellowish oil, yield 21 mg, 53%. IR (KBr): $\tilde{\nu}$ = 3131, 2941, 1671, 1630, 1564, 1467, 1392, 1299, 1166, 1083, 1013, 883, 796, 761, 595 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.88–1.96 (m, 1 H, CH_2), 2.33–2.51 (m, 2 H,

CH_2 + CH_2), 2.58–2.67 (m, 1 H, CH_2), 3.07 (dd, J = 10.8, 16.0 Hz, 1 H, CH_2), 3.85–3.87 (m, 1 H, CH), 3.99 (dd, J = 2.8, 16.0 Hz, 1 H, CH_2), 6.44–6.45 (m, 1 H, =CH), 7.42–7.61 (m, 7 H, ArH), 7.86 (d, J = 7.6 Hz, 2 H, ArH), 7.91 (d, J = 8.4 Hz, 1 H, ArH), 7.96 (dd, J = 8.4 Hz, 1 H, ArH), 8.03–8.12 (m, 2 H, ArH), 8.68 (d, J = 9.2 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 29.8, 32.6, 41.2, 45.8, 124.3, 124.6, 125.4, 125.9, 126.37, 126.40, 126.9, 127.1, 127.9, 128.1, 128.4, 128.5, 130.3, 130.5, 130.8, 132.6, 133.7, 134.1, 135.8, 137.3, 148.3, 150.6, 195.8, 204.1 ppm. MS (ESI): m/z (%) = 391.4 (100) $[M + H]^+$. HRMS (ESI): calcd. for $C_{28}H_{23}O_2^+$ $[M + H]^+$ 391.16926, found 391.1683. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 96:4; flow rate: 0.75 mL/min; t_{minor} = 33.82 min, t_{major} = 40.58 min; ee = 54%; $[\alpha]_D^{20}$ = +59.0 (c = 0.85, $CHCl_3$)].

Compound 4i: General Procedure F; yield 11 mg, 41%; this is a known compound.[4a] IR (KBr): $\tilde{\nu}$ = 3056, 2926, 1681, 1643, 1592, 1574, 1507, 1435, 1351, 1278, 1101, 947, 781, 737 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.75–1.83 (m, 1 H, CH_2), 2.20–2.29 (m, 1 H, CH_2), 2.53–2.62 (m, 1 H, CH_2), 2.65–2.75 (m, 2 H, CH_2+CH_2), 3.47 (dd, J = 3.2, 15.2 Hz, 1 H, CH_2), 3.65–3.75 (m, 1 H, CH), 6.52 (dd, J = 1.6, 3.6 Hz, 1 H, ArH), 6.55 (dd, J = 1.6, 3.6 Hz, 1 H, ArH), 7.10–7.11 (m, 1 H, =CH), 7.20 (dd, J = 0.8, 3.6 Hz, 1 H, ArH), 7.33 (dd, J = 0.8, 3.6 Hz, 1 H, ArH), 7.57 (dd, J = 0.8, 3.6 Hz, 1 H, ArH), 7.62 (dd, J = 0.8, 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 28.7, 32.8, 41.8, 42.2, 112.0, 112.1, 117.8, 118.2, 145.0, 146.2, 146.40, 146.42, 152.5, 153.0, 179.4, 188.6 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 80:20; flow rate: 0.70 mL/min; t_{minor} = 11.55 min, t_{major} = 14.92 min; ee = 85%; $[\alpha]_D^{20}$ = +28.0 (c = 0.5, $CHCl_3$)].

Compound 6a: General Procedure G; yield 24 mg, 72%; this is a known compound.[9] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 3.18 (dd, J = 9.6, 16.8 Hz, 1 H, CH_2), 4.05 (dd, J = 2.8, 16.8 Hz, 1 H, CH_2), 4.67–4.69 (m, 1 H, CH), 7.30–7.36 (m, 2 H, =CH+ArH), 7.43–7.60 (m, 9 H, ArH), 7.83 (d, J = 8.0 Hz, 2 H, ArH), 8.02 (d, J = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 39.4, 45.2, 124.0, 124.4, 127.3, 128.1, 128.2, 128.5, 128.8, 131.8, 133.0, 136.7, 139.1, 141.5, 144.1, 147.3, 149.3, 192.8, 198.3 ppm. Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column [λ = 214 nm; eluent: hexane/2-propanol = 70:30; flow rate: 0.80 mL/min; t_{minor} = 19.31 min, t_{major} = 23.63 min; ee = 84%; $[\alpha]_D^{20}$ = –240.8 (c = 0.8, $CHCl_3$)].

Compound 6b: General Procedure G; yield 1.4 mg, 4%; this is a known compound.[9] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 3.91 (s, 2 H, CH_2), 4.46 (s, 2 H, CH_2), 7.32–7.46 (m, 8 H, ArH), 7.51–7.57 (m, 2 H, ArH), 7.74 (d, J = 7.2 Hz, 2 H, ArH), 7.91 (d, J = 7.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 37.4, 40.7, 121.7, 124.0, 126.8, 127.7, 128.0, 128.3, 128.4, 128.5, 131.9, 133.2, 136.4, 139.9, 140.9, 143.4, 144.3, 146.0, 194.9, 195.7 ppm.

Supporting Information (see footnote on the first page of this article): Spectroscopic data and chiral HPLC traces of the compounds (Tables S1, S2, S3, and S4), detailed descriptions of experimental procedures and crystal structure of **4a**.

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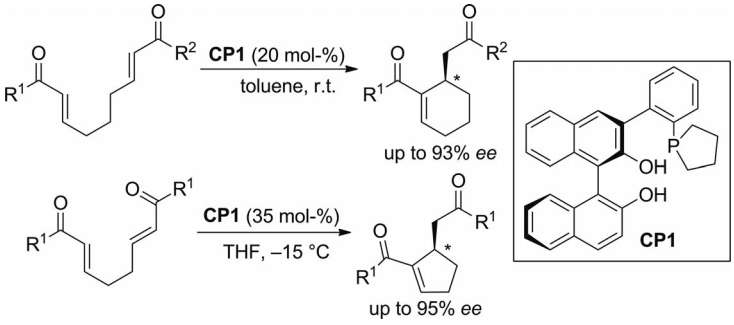

A highly nucleophilic multifunctional chiral phosphane enables asymmetric intramolecular Rauhut–Currier (RC) reactions to afford corresponding cyclopentene and cyclohexene derivatives in moderate to good yields with good to excellent enantioselectivities.

Keywords: Multifunctional chiral phosphanes / Rauhut-Currier reaction / Cyclopentene derivatives / Cyclohexene derivatives / Organocatalysis / Cyclization / Asymmetric synthesis

