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Asymmetric Intramolecular Rauhut–Currier Reaction and Its Desymmetric Version via Double Thiol/Phase-Transfer Catalysis

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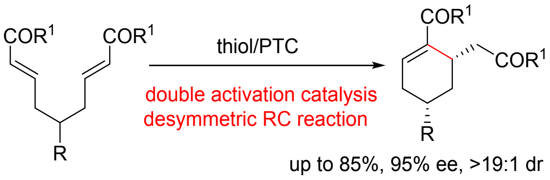


ABSTRACT

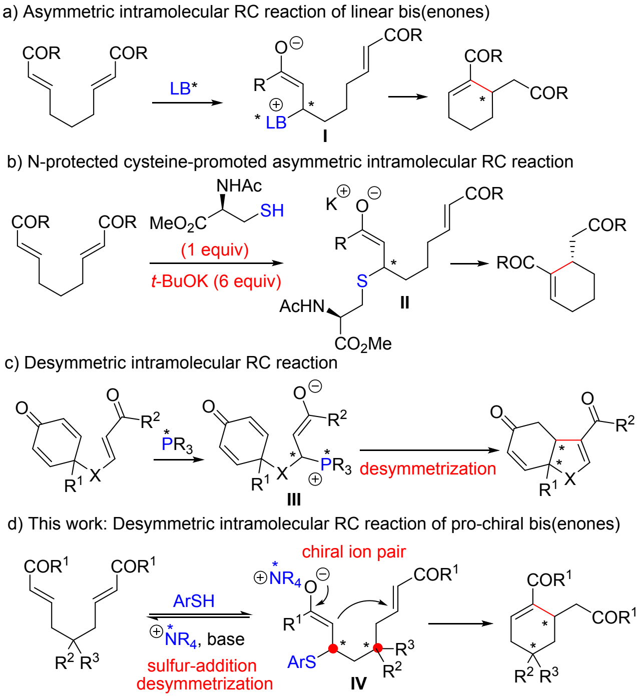
An asymmetric intramolecular Rauhut–Currier reaction of linear bis(enones) has been achieved via double activation catalysis of thiols and phase transfer substances, furnishing both enantioenriched cyclohexene and cyclopentene derivatives (up to 95% ee). Furthermore, the desymmetric version of pro-chiral substrates was developed under similar catalysis, producing the frameworks bearing an additional tertiary or even quaternary stereogenic center with moderate to excellent diastereo- and enantioselectivity (up to 95% ee, >19:1 dr).

Introduction

The intramolecular Rauhut–Currier (RC) reaction is an efficient protocol for the construction of cyclic compounds by forming a C–C bond between two electron deficient alkene groups.[1] It has gained much attention since the pioneering work reported simultaneously by Roush[2] and Krische.[3] It also has important application in the synthesis of many natural products.[4] The catalytic asymmetric RC reaction of linear bis(enones) substrates has been investigated extensively, mainly relying on the catalysis of chiral Lewis basic phosphines (Scheme 1a).[5] Besides, stoichiometric chiral *N*-protected cysteine was applied with excellent enantiocontrol, and excess strong bases were required for good conversions (Scheme 1b).[6] On the other hand, the Lu group designed a new kind of cyclohexadienone derivatives bearing a side enone motif, and realized an elegant intramolecular desymmetric RC reaction to construct fused frameworks under chiral phosphine catalysis (Scheme 1c).[7] Such a desymmetric strategy further enriches the structural diversity and complexity of the chiral RC adducts.[8]

Very recently, our group uncovered a double activation system by combining 2-mercaptobenzoic acid[9] and suitable chiral Brønsted bases, which efficiently catalyzed the asymmetric intermolecular cross-RC reaction of 2-cyclopentenone and activated alkenes.[9a] Considering the high efficiency of this novel catalytic system, we envisioned that it would be applicable to asymmetric intramolecular RC reaction of linear bis(enones) precursors.[5,10] Moreover, as outlined in Scheme 1d, the reversible sulfur-addition of thiol catalysts to pro-chiral bis(enones) would lead to the different early desymmetric generation of the key ion pair intermediates **IV** in a potentially stereoenriched manner under chiral phase-transfer catalysis (PTC), thus the following cyclization would deliver the expected cyclic products diastereoselectively, finally furnishing a previously unreported desymmetric intramolecular RC reaction process for linear bis(enones).

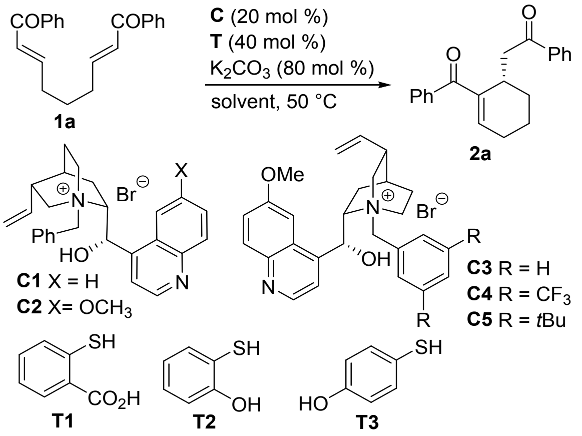
Scheme 1. Asymmetric Intramolecular Rauhut–Currier Reactions of Diverse Bis(enones) Substrates



Results and Discussion

Based on the above considerations, initially, we investigated the asymmetric intramolecular RC reaction of simple bis(enones) **1a** to establish the suitability of the double activation catalytic system.[5] It was pleasing that the combination of 2-mercaptobenzoic acid **T1** and chiral PTC **C1** derived from cinchonine could smoothly promote the conversion of substrate **1a** at 50 ºC, and the expected RC product **2a** was isolated in a moderate yield albeit with low enantioselectivity (Table 1, entry 1). Interestingly, the reaction was significantly improved by using 2-mercaptophenol **T2** as the catalytic partner (entry 2). It is also notable that the *ortho*-hydroxyl group of thiol **T2** is crucial for the reaction probably because it could assist the release of the thiol catalyst,[10] as no reaction occurred when 4-mercaptophenol **T3** was applied (entry 3). More PTCs in combination with thiol **T2** were tested (entries 4–7), and excellent enantioselectivity with a good yield could be achieved by employing PTC **C5** having a bulky 3,5-di-*t*-butylbenzyl substitution (entry 7). Slightly improved data were obtained at room temperature (entry 8), but incomplete conversion was observed at 4 °C even by extending the reaction time (entry 9). Inferior results were attained in other solvents (entries 10 and 11). In addition, the loadings of catalysts and bases were further investigated (entries 12−15), and the optimal data were afforded with 20 mol % **C5**, 40 mol % **T2** and 60 mol % K_2CO_3 (entry 14).

Table 1. Screening Conditions of Intramolecular RC Reactions of Bis(enones) 1a[a]



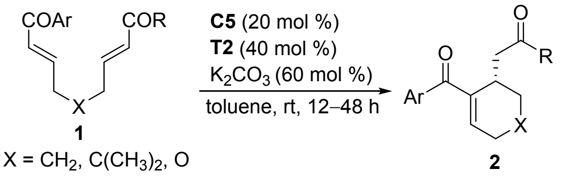
entry	C	T	solvent	*t* (h)	yield (%)[b]	ee (%)[c]
1	**C1**	**T1**	toluene	72	57	−9
2	**C1**	**T2**	toluene	24	79	−32
3	**C1**	**T3**	toluene	72	NR	/
4	**C2**	**T2**	toluene	24	83	−59
5	**C3**	**T2**	toluene	24	83	77
6	**C4**	**T2**	toluene	24	78	90
7	**C5**	**T2**	toluene	24	86	89
8[d]	**C5**	**T2**	toluene	48	91	91
9[e]	**C5**	**T2**	toluene	72	53	97
10[d]	**C5**	**T2**	EtOAc	48	95	83
11[d]	**C5**	**T2**	$CHCl_3$	48	89	84

12[d,f]	**C5**	**T2**	toluene	72	60	93
13[d,g]	**C5**	**T2**	toluene	48	91	87
14[d,h]	**C5**	**T2**	toluene	48	92	91
15[d,i]	**C5**	**T2**	toluene	48	80	89

[a] Unless noted otherwise, reactions were performed with **1a** (0.05 mmol), phase transfer catalysts **C** (20 mol %), thiol **T** (40 mol %) and K_2CO_3 (80 mol %) in solvent (1 mL) at 50 °C. [b] Yield of the isolated product. [c] Determined by chiral HPLC analysis on a chiral stationary phase. [d] At room temperature. [e] At 4 °C. [f] With **C5** (10 mol %). [g] With **T2** (20 mol %). [h] With K_2CO_3 (60 mol %). [i] With K_2CO_3 (40 mol %). NR = No reaction.

Consequently, we briefly investigated the substrate scope of this known reaction. As summarized in Table 2, bis(enones) **1** with different aryl and heteroaryl groups underwent the RC reaction smoothly to give the corresponding six-membered RC products **2a–i** in good to excellent results (Table 2, entries 1–9), even on a larger scale (entry 1, data in parentheses), whereas **C4** was employed instead of **C5** in some cases for better enantiocontrol. In addition, an unsymmetric bis(enones) bearing both an electron-withdrawing group and an electron-donating group afforded the corresponding **2j** as a single product with excellent regio- and stereocontrol, which is superior to that under phosphine catalysis (entry 10).[5] Moreover, an aromatic/aliphatic hybrid bis(enones) also proceeded smoothly to give product **2k** exclusively, albeit with lower enantioselectivity (entry 11).

Table 2. Substrate Scope for Intramolecular RC Reactions of Bis(enones) 1[a]



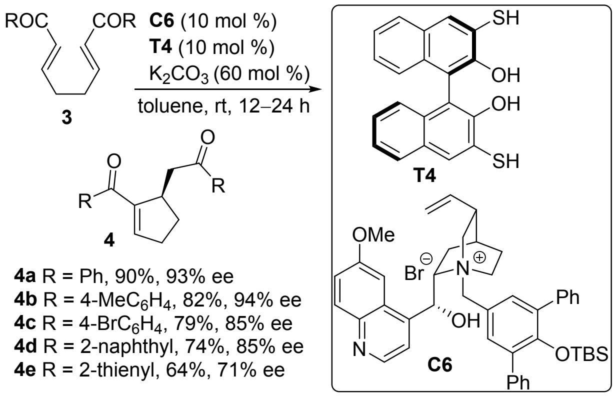
entry	Ar	R	X	n	*t* (h)	yield (%)[b]	ee (%)[c]

1[d]	Ph	Ph	CH_2	1	48	**2a**, 91 (73)	91 (91)[e]
2	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	CH_2	1	48	**2b**, 88	95
3	3-$CH_3OC_6H_4$	3-$CH_3OC_6H_4$	CH_2	1	48	**2c**, 83	92
4[f]	4-BrC_6H_4,	4-BrC_6H_4,	CH_2	1	24	**2d**, 91	84
5[f]	3-BrC_6H_4	3-BrC_6H_4	CH_2	1	24	**2e**, 72	79
6	2-naphthyl	2-naphthyl	CH_2	1	48	**2f**, 68	81
7	2-thienyl	2-thienyl	CH_2	1	48	**2g**, 81	82
8	Ph	Ph	$C(CH_3)_2$	1	48	**2h**, 65	83
9[f]	Ph	Ph	O	1	48	**2i**, 73	78
10	4-$NO_2C_6H_4$	4-$CH_3C_6H_4$	CH_2	1	48	**2j**, 92	93
11	Ph	CH_3	CH_2	1	48	**2k**, 73	80

[a]Unless noted otherwise, reactions were performed with bis(enones) **1** (0.1 mmol, X = CH_2, R^1 = R^2), PTC **C5** (20 mol %), thiol **T2** (40 mol %) and K_2CO_3 (60 mol %) in toluene (1 mL) at room temperature. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Data in parentheses were obtained on a 1.0 mmol scale. [e]The absolute configuration of product **2a** was determined by comparing rotation data with literature reports.[5] The other products were assigned by analogy. [f]With **C4** (20 mol %).

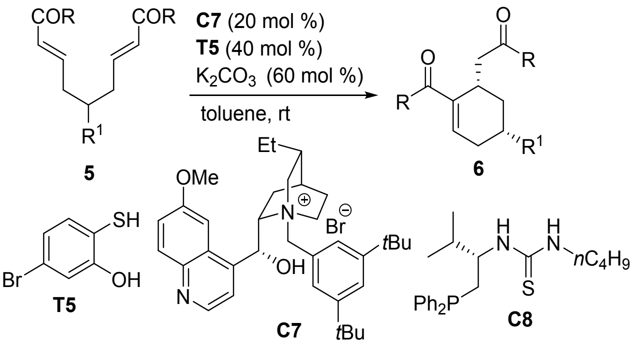
On the other hand, compared to bis(enones) **1** from glutaraldehyde-type precursors, succinaldehyde-derived ones **3** have been less investigated, and the related asymmetric RC reactions usually suffered from low reactivity and enantioselectivity.[5a,c] In contrast, we pleasingly found that the intramolecular RC reaction of such a type of substrates **3** proceeded very well under the double activation of an axial chiral thiol **T4** derived from *R*-BINOL[10a] and chiral PTC **C6**,[11] and a few five-membered ring products **4a–e** were efficiently constructed in moderate to excellent enantioselectivity (Scheme 2).

Scheme 2. Substrate Scope for Intramolecular RC Reactions of Bis(enones) 3[a]



Inspired by the promising results based on the easily tunable thiol-PTC system, we intended to explore the more challenging desymmetric RC reaction with linear bis(enones) having a δ-substitution. Under the catalysis of thiol **T5** and PTC **C7**,[11] pro-chiral bis(enones) **5a** delivered the diastereomerically pure product **6a** with excellent enantioselectivity (Table 3, entry 1), whereas slightly lower diastereocontrol was observed on a larger scale (entry 2). For comparison, much lower catalytic efficacy was obtained by using a bifunctional phosphine **C8** (entry 3),[5b] further showing the superiority of the current double activation system. As summarized in Table 3, an array of bis(enones) **5** bearing diverse substituents were investigated, and the corresponding desymmetric RC products **6b–m** were generally obtained with good to excellent stereoselectivity (entries 4–15), whereas inferior data were observed for the substrates with electron-withdrawing or heteroaryl groups, probably due to the electronic effects (entries 6, 7 and 9).

Table 3. Substrate Scope of Desymmetric Intramolecular RC Reaction of Bis(enones) 5[a]



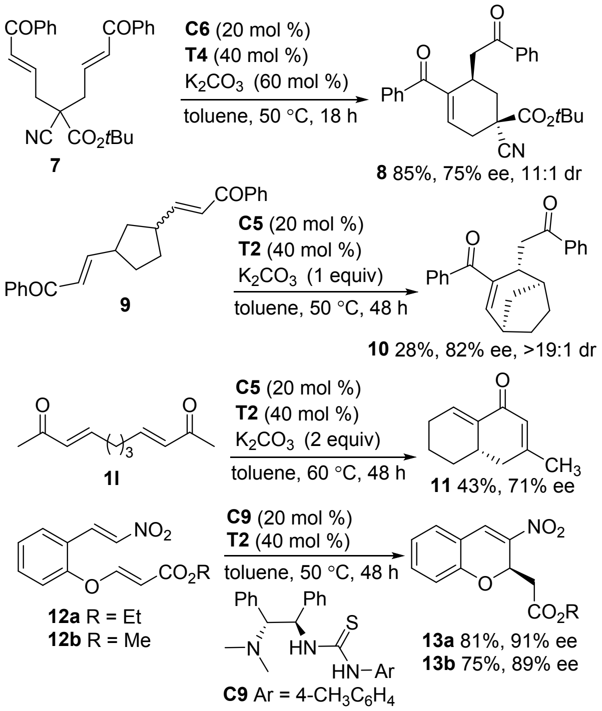
entry	R, R^1	*t* (h)	yield (%)[b]	ee (%)[c]	dr[d]
1	Ph, CH_3	72	**6a**, 76	92	>19:1
2[e]	Ph, CH_3	72	**6a**, 78	90	14:1
3[f]	Ph, CH_3	96	**6a**, 34	97	>19:1
4	4-$CH_3C_6H_4$, CH_3	72	**6b**, 66	94	>19:1
5	3-$CH_3OC_6H_4$, CH_3	72	**6c**, 75	95	>19:1
6	4-BrC_6H_4, CH_3	48	**6d**, 66	79	13:1
7	3-ClC_6H_4, CH_3	24	**6e**, 82	70	14:1
8	2-naphthyl, CH_3	72	**6f**, 75	80	>19:1
9	2-thienyl, CH_3	72	**6g**, 62	75	3:1
10	Ph, Ph	48	**6h**, 73	84	>19:1
11	Ph, 4-ClC_6H_4	48	**6i**, 82	86	>19:1
12	Ph, CO_2Et	48	**6j**, 82	85	>19:1
13	Ph, OTBS	36	**6k**, 75	83	10:1
14	Ph, *i*Bu	36	**6l**, 85	84	>19:1
15[g]	2-naphthyl, 4-ClC_6H_4	48	**6m**, 70	81	>19:1

[a]Unless noted otherwise, reactions were performed with bis(enones) **5** (0.1 mmol), PTC **C7** (20 mol %), thiol **T5** (40 mol %) and K_2CO_3 (60 mol %) in toluene (1 mL) at room temperature. [b]Yield of the isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Determined by ^1H NMR analysis. [e]With **5a** (0.5 mmol). [f]With phosphine **C8**. [g]In $CHCl_3$; the absolute configuration of product **6m** was determined by X-ray analysis after conversion to product **15** (see Scheme 4).[12] The other products were assigned by analogy.

In addition, a bis(enones) **7** having a *δ,δ*-disubstituted pattern underwent the desymmetric RC reaction smoothly under the double catalysis of PTC **C6** and thiol

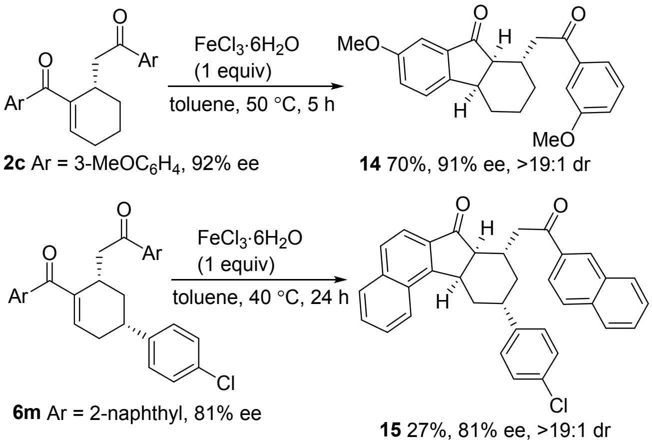
T4,[11] producing product **8** bearing a quaternary stereogenic center in a good yield with moderate stereocontrol (Scheme 3). Even the highly challenging desymmetric RC reaction of substrate **9** (as an inseparable *cis*/*trans* mixture) could be realized, and the bridged product **10** was obtained with good stereoselectivity under the catalysis of PTC **C5** and thiol **T2**, albeit in a fair yield, probably because the *trans*-precursor could not undergo the cyclization.[13] Interestingly, the substrate **1l** could undergo intramolecular RC reaction followed by a cascade aldol process under similar catalytic conditions, and a bicyclic framework **11** was furnished in a fair yield with moderate enantioselectivity.[14] Finally, our thiol-based double activation strategy was applicable to the asymmetric RC reaction of substrates **12**;[15] in this case, a bifunctional thiourea-tertiary amine **C9** was found to be a more reliable choice,[11] and the desired products **13a** and **13b** were constructed in good yields with high ee values.

Scheme 3. More Exploration on Intramolecular RC Reactions of Diversely Structured Substrates



As illustrated in Scheme 4, the multifunctional RC adduct **2c** could undergo Nazarov cyclization to afford the fused hexahydro-9*H*-fluoren-9-one architecture **14** in a moderate yield with exclusive diastereocontrol promoted by $FeCl_3 \cdot 6H_2O$.[16] Besides, product **6m** was similarly transformed to framework **15**, albeit in a fair yield.

Scheme 4. Transformation of RC Products 2c and 6m



In conclusion, we have further developed the double activation system combining thiols and phase transfer catalysts, which was successfully applied to the asymmetric intramolecular Rauhut–Currier reaction of linear bis(enones) substrates, including the previously unreported desymmetric version for the unsaturated substrates with pro-chiral centers. This easily tunable catalytic system is highly efficient under mild conditions, and enables straightforward access to a broad spectrum of six- and five-membered frameworks with structural diversity in moderate to high yields with fair to excellent stereoselectivity. We believe that this catalytic strategy could be applicable to more challenging asymmetric reactions. The results will be reported in due course.

EXPERIMENTAL SECTION

General Method. Unless otherwise noted, all reactions were carried out under ambient atmosphere; when the reactions required heating, the heat source was oil bath. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian INOVA-400/54, Agilent DD2-600/54 or Bruker Ascend^{TM} 400 instruments. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. High resolution mass spectra (HRMS) was recorded on a Waters SYNAPT G2 or Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using an electrospray (ESI) ionization source. X-ray diffraction experiments were carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre. In each case, diastereomeric ratio was determined by ^{1}H NMR analysis and enantiomeric ratio was determined by HPLC (Agilent Technologies: 1220 Infinity Ⅱ, 1200 Series, 1260 Infinity) analysis on a chiral column in comparison with the authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralpak IC Column (250 × 4.6 mm), Chiralpak ID Column (250 × 4.6 mm), Chiralpak IH Column (250 × 4.6 mm), Chiralpak OD-H Column (250 × 4.6 mm); UV detection was monitored at 254 nm. Optical rotation was obtained from Rudolph Research Analytical Autopol Ⅰ automatic polarimeter in $CHCl_3$ solution at 25 °C. The melting point was obtained from WRX-4 Mel-Temp apparatus. Column chromatography was performed on silica gel (200-300 mesh) eluting with EtOAc and petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and EtOAc were distilled. THF was freshly distilled from sodium/benzophenone before use. Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet.

The bis(enones) **1** and **3** were synthesized according to the literature procedures.[5b,c,17] The axial chiral mercaptophenol **T4** was synthesized following the literature procedures.[10a] The substituted mercaptophenol **T5**, **T14** and **T15** were synthesized according to the literature procedures.[18] The bis(enones) **9** was synthesized according to the literature procedures.[19] The absolute configuration of chiral **2a**, **4a** and **13b** was assigned by comparison with the experimental data in the literatures.[5b,5c,6,15]

General Procedure for preparation of bis(enones) 5 and 7. *General procedure A:* A solution of 3-substituted glutaric acid (10 mmol) in anhydrous THF (20 mL) was added dropwise to a cooled suspension of $LiAlH_4$ (20 mmol, 2.0 equiv) in anhydrous THF (20 mL) at 0 ºC. The mixture was heated to 60 °C and monitored by TLC. After completion, the mixture was cooled to 0 °C, and quenched by NaOH (1 M). The precipitate was filtered, and the filtrate was extracted with EtOAc. The combined organic layers were washed with brine, dried and evaporated to provide the diol without further purification.

Oxalyl chloride (30 mmol, 3.0 equiv) was added dropwise to a solution of DMSO (50 mmol, 5.0 equiv) in DCM (30 mL) at −78 °C. The mixture was stirred at −78 °C for 15 min, and a solution of the obtained diol (10 mmol) in DCM (20 mL) was added dropwise. The mixture was stirred at −78 °C for 30 min and then triethylamine (70 mmol, 7.0 equiv) was added. The mixture was allowed to warm to room temperature for 30 min, and sodium bicarbonate solution was added. The mixture was extracted with DCM. The combined organic layers were washed with brine, dried and evaporated to provide 3-substituted glutaric dialdehyde without further purification.

A solution of 3-substituted glutaric dialdehyde in THF (20 mL) was added to a solution of the ylide reagent (25 mmol, 2.5 equiv) in THF (20 mL). Then magnesium sulfate (40 mmol, 4.0 equiv) was added. The mixture was stirred under reflux and monitored by TLC. After removing the precipitate and solvent, the residue was purified by column chromatography (petroleum ether/EtOAc = 15/1) to afford the 5-substituted bis(enones) **5**.

General procedure B: The 4-substituted 1,6-heptadiene (5 mmol) was dissolved in *t*BuOH/H_2O (1:1, 50 mL), and $K_2OsO_4 \cdot 2H_2O$ (0.025 mmol, 0.005 equiv) and $NaIO_4$ (25 mmol, 5.0 equiv) were added. The mixture was stirred at room temperature overnight. The reaction was quenched with saturated NaS_2O_3, and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated to provide 3-substituted glutaric dialdehyde without further purification. Subsequently, the 5-substituted bis(enones) **5** was similarly prepared with the ylide reagent.

Bis(enones) **5a–i**, **5m** were obtained according to the general procedure A, and bis(enones) **5j**, **5k** and **7** were obtained according to the general procedure B.

(2E,7E)-5-Methyl-1,9-diphenylnona-2,7-diene-1,9-dione ***(5a)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **5a**: 670 mg,

42% yield (for three steps), colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.96–7.87 (m, 4H), 7.58–7.52 (m, 2H), 7.50–7.41 (m, 4H), 7.10–6.99 (m, 2H), 6.96–6.86 (d, J = 14.8 Hz, 2H), 2.43–2.34 (m, 2H), 2.29–2.20 (m, 2H), 2.04–1.89 (m, 1H), 1.02 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 190.5, 147.5, 137.8, 132.8, 128.59, 128.55, 127.6, 39.8, 32.5, 19.7; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{22}H_{22}O_2Na$ 341.1512; found 341.1518.

*(2E,7E)-5-Methyl-1,9-di-p-tolylnona-2,7-diene-1,9-dione (**5b**).* Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **5b**: 504 mg, 29% yield (for three steps), colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.84 (d, J = 7.9 Hz, 4H), 7.28–7.23 (d, J = 7.9 Hz, 4H), 7.08–6.98 (m, 2H), 6.91 (d, J = 15.4 Hz, 2H), 2.41 (s, 6H), 2.39–2.34 (m, 2H), 2.28–2.18 (m, 2H), 2.02–1.89 (m, 1H), 1.02 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$): δ (ppm) 189.0, 146.9, 143.6, 135.3, 129.3, 128.7, 127.5, 39.7, 32.5, 21.6, 19.7; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{24}H_{26}O_2Na$ 369.1825; found 369.1818.

*(2E,7E)-1,9-Bis(3-methoxyphenyl)-5-methylnona-2,7-diene-1,9-dione (**5c**).* Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) gave **5c**: 336 mg, 18% yield (for three steps), colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.53–7.44 (m, 4H), 7.37 (t, J = 7.9 Hz, 2H), 7.14–7.08 (m, 2H), 7.08–6.99 (m, 2H), 6.94–6.86 (m, 2H), 3.86 (s, 6H), 2.46–2.33 (m, 2H), 2.30–2.18 (m, 2H), 2.03–1.92 (m, 1H), 1.03 (d, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 190.2, 159.9, 147.5, 139.2, 129.5, 127.6, 121.1, 119.3, 112.8, 55.5, 39.8, 32.5, 19.7; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{24}H_{26}O_4Na$ 401.1723; found 401.1717.

(2E,7E)-1,9-Bis(4-bromophenyl)-5-methylnona-2,7-diene-1,9-dione ***(5d)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/25) gave **5d**: 150 mg, 32% yield (for three steps), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.75 (m, 4H), 7.67–7.55 (m, 4H), 7.12–7.00 (m, 2H), 6.87 (d, J = 15.3 Hz, 2H), 2.46–2.34 (m, 2H), 2.31–2.21 (m, 2H), 2.04–1.93 (m, 1H), 1.03 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 189.2, 147.9, 136.5, 131.9, 130.0, 127.9, 127.1, 39.8, 32.5, 19.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{20}Br^{79}Br^{81}O_2Na$ 498.9702; found 498.9695; calcd for $C_{22}H_{20}Br^{79}{}_2O_2Na$ 496.9722; found 496.9721; calcd for $C_{22}H_{20}Br^{81}{}_2O_2Na$ 500.9681; found 500.9691.

(2E,7E)-1,9-Bis(3-chlorophenyl)-5-methylnona-2,7-diene-1,9-dione ***(5e)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/30) gave **5e**: 297 mg, 16% yield (for three steps), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.90 (t, J = 1.9 Hz, 2H), 7.80 (dt, J = 7.8, 1.3 Hz, 2H), 7.58–7.50 (m, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.14–7.02 (m, 2H), 6.92–6.84 (m, 2H), 2.45–2.35 (m, 2H), 2.32–2.22 (m, 2H), 2.05–1.93 (m, 1H), 1.05 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 189.0, 148.4, 139.4, 134.9, 132.7, 129.9, 128.6, 127.1, 126.6, 39.9, 32.5, 19.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{20}Cl^{35}{}_2O_2Na$ 409.0733; found 409.0721; calcd for $C_{22}H_{20}Cl^{35}Cl^{37}O_2Na$ 411.0703; found 411.0705.

(2E,7E)-5-Methyl-1,9-di(naphthalen-2-yl)nona-2,7-diene-1,9-dione ***(5f)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **5f**: 444 mg, 19% yield (for three steps), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.44 (d, J = 1.7 Hz, 2H), 8.03 (dd, J = 8.6, 1.8 Hz, 2H), 7.98–7.73 (m, 6H),

7.65–7.55 (m, 2H), 7.55–7.45 (m, 2H), 7.22–7.00 (m, 4H), 2.52–2.40 (m, 2H), 2.37–2.26 (m, 2H), 2.10–1.97 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$): *δ* (ppm) 190.2, 147.4, 135.5, 135.1, 132.5, 130.0, 129.5, 128.5, 128.4, 127.8, 127.5, 126.8, 124.5, 39.8, 32.6, 19.8; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{30}H_{26}O_2Na$ 441.1825; found 441.1826.

(2E,7E)-5-Methyl-1,9-di(thiophen-2-yl)nona-2,7-diene-1,9-dione (***5g***). Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **5g**: 253 mg, 15% yield (for three steps), colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) 7.76 (dd, *J* = 3.8, 1.1 Hz, 2H), 7.66 (dd, *J* = 4.9, 1.1 Hz, 2H), 7.18–7.13 (m, 2H), 7.13–7.05 (m, 2H), 6.87–6.80 (m, 2H), 2.44–2.34 (m, 2H), 2.30–2.20 (m, 2H), 2.04–1.93 (m, 1H), 1.04 (d, *J* = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): *δ* (ppm) 182.0, 146.6, 145.1, 133.8, 131.9, 128.2, 127.1, 39.5, 32.5, 19.7; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{18}H_{18}S_2O_2Na$ 353.0640; found 353.0645.

(2E,7E)-1,5,9-Triphenylnona-2,7-diene-1,9-dione (***5h***). Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/15) gave **5h**: 976 mg, 28% yield (for three steps), colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$): *δ* (ppm) 7.82–7.70 (m, 4H), 7.55–7.47 (m, 2H), 7.44–7.35 (m, 4H), 7.35– 7.29 (m, 2H), 7.23–7.16 (m, 3H), 6.95–6.84 (m, 2H), 6.79 (d, *J* = 15.5 Hz, 2H), 3.09–2.97 (m, 1H), 2.76–2.62 (m, 4H); ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$): *δ* (ppm) 190.6, 146.5, 142.8, 137.7, 132.7, 128.8, 128.6, 128.5, 128.0, 127.6, 126.9, 44.6, 39.4; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{27}H_{24}O_2Na$ 403.1669; found 403.1675.

(2E,7E)-5-(4-Chlorophenyl)-1,9-diphenylnona-2,7-diene-1,9-dione (***5i***).

Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) gave **5i**: 564 mg, 28% yield (for three steps), as a white solid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.83–7.77 (m, 4H), 7.57–7.51 (m, 2H), 7.47–7.40 (m, 4H), 7.33–7.28 (m, 2H), 7.17– 7.11 (m, 2H), 6.92–6.83 (m, 2H), 6.79 (d, *J* = 15.4 Hz, 2H), 3.08–2.98 (m, 1H), 2.78–2.58 (m, 4H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): *δ* (ppm) 190.4, 145.8, 141.2, 137.6, 132.8, 132.6, 128.9, 128.6, 128.51, 128.48, 128.1, 44.1, 39.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{23}Cl^{35}O_2Na$ 437.1279; found 437.1284; calcd for $C_{27}H_{23}Cl^{37}O_2Na$ 439.1249; found 439.1260.

*(E)-Ethyl 6-oxo-2-((E)-4-oxo-4-phenylbut-2-en-1-yl)-6-phenyl hex-4-enoate (**5j**).* Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) gave **5j**: 108 mg, 15% yield (in two steps), colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): *δ* (ppm) 7.97–7.86 (m, 4H), 7.60–7.53 (m, 2H), 7.52–7.42 (m, 4H), 7.02–6.91 (m, 4H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.87–2.80 (m, 1H), 2.75–2.68 (m, 2H), 2.61–2.54 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 194.9, 178.3, 149.5, 142.3, 137.6, 133.33, 133.27, 132.8, 65.7, 48.3, 39.4, 19.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{24}O_4Na$ 399.1567; found 399.1571.

*(2E,7E)-5-Isobutyl-1,9-diphenylnona-2,7-diene-1,9-dione (**5l**).* Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **5l**: 560 mg, 31% yield (for three steps), white semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.96–7.90 (m, 4H), 7.59–7.52 (m, 2H), 7.50–7.42 (m, 4H), 7.12–7.01 (m, 2H), 6.93 (d, *J* = 15.3 Hz, 2H), 2.44–2.26 (m, 4H), 2.03–1.90 (m, 1H), 1.76–1.67 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): *δ* (ppm)

190.3, 147.5, 137.8, 132.8, 128.6, 128.5, 127.6, 43.2, 37.1, 34.8, 25.2, 22.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{28}O_2Na$ 383.1982; found 383.1987.

(2E,7E)-5-(4-Chlorophenyl)-1,9-di(naphthalen-2-yl)nona-2,7-diene-1,9-dione ***(5m)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) gave **5m**: 539 mg, 21% yield (for three steps), white solid; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28 (s, 2H), 8.00–7.80 (m, 8H), 7.64–7.49 (m, 4H), 7.40–7.31 (m, 2H), 7.24–7.18 (m, 2H), 7.04–6.86 (m, 4H), 3.16–3.07 (m, 1H), 2.86–2.66 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 190.2, 145.7, 141.3, 135.5, 134.9, 132.7, 132.5, 130.1, 129.5, 129.0, 128.6, 128.5, 128.2, 127.8, 126.8, 124.4, 44.2, 39.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{27}Cl^{35}O_2Na$ 537.1592; found 537.1591; calcd for $C_{35}H_{27}Cl^{37}O_2Na$ 539.1562; found 539.1604.

tert-Butyl (E)-2-cyano-6-oxo-2-((E)-4-oxo-4-phenylbut-2-en-1-yl)-6-phenylhex-4-enoate (7). Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) gave **7**: 359 mg, 28% yield (for two steps), white semisolid; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98–7.88 (m, 4H), 7.61–7.53 (m, 2H), 7.52–7.42 (m, 4H), 7.07 (d, J = 15.5 Hz, 2H), 7.02–6.89 (m, 2H), 2.93 (dd, J = 14.2, 7.4 Hz, 2H), 2.82 (dd, J = 14.1, 7.3 Hz, 2H), 1.47 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 189.7, 166.0, 138.9, 137.2, 133.2, 130.9, 128.74, 128.68, 117.9, 85.6, 48.9, 39.5, 27.8; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{27}NO_4Na$ 452.1832; found 452.1835.

General procedure for intramolecular RC reaction of bis(enones) 1. Bis(enones) **1** (0.1 mmol), 2-mercaptophenol **T2** (0.04 mmol), catalyst **C5** or **C4** (0.02 mmol) and K_2CO_3 (0.06 mmol) were added into a vial equipped with a magnetic stir bar. Toluene (1.0 mL) was added. The mixture was stirred at room temperature for 24 to 72 h. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1:40) gave the product **2**.

The racemic products were prepared following the general procedure, using an achiral TBAB as the phase transfer catalyst.

*(S)-2-(2-Benzoylcyclohex-2-en-1-yl)-1-phenylethanone (**2a**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **2a**: 27.6 mg, 91% yield, colorless oil; $[\alpha]_D^{25} = -30.6$; [$c = 0.85$ in $CHCl_3$; data in the references: 95% ee, $[\alpha]_D^{25} = -38.6$ ($c = 0.76$ in $CHCl_3$);[6] –99% ee, $[\alpha]_D^{25} = +30.0$ ($c = 0.35$ in $CHCl_3$);[5b] –91% ee, $[\alpha]_D^{20} = +25.1$ ($c = 0.90$ in $CHCl_3$)[5c]]; 91% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 8.63 min, t (minor) = 12.69 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11–8.01 (m, 2H), 7.73–7.63 (m, 2H), 7.54–7.35 (m, 6H), 6.64–6.56 (m, 1H), 3.58–3.46 (m, 1H), 3.39 (dd, $J = 15.0, 3.2$ Hz, 1H), 2.84 (dd, $J = 15.0, 10.5$ Hz, 1H), 2.38–2.24 (m, 1H), 2.22–2.09 (m, 1H), 1.79–1.66 (m, 3H), 1.66–1.53 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.5, 197.9, 144.8, 141.5, 138.8, 136.9, 132.9, 131.6, 129.2, 128.6, 128.4, 128.1, 42.4, 30.3, 26.6, 26.1, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{20}O_2Na$ 327.1356; found 327.1355.

*(S)-2-(2-(4-Methylbenzoyl)cyclohex-2-en-1-yl)-1-(p-tolyl) ethanone (**2b**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **2b**: 29.2 mg, 88% yield, colorless oil; $[\alpha]_D^{25} = -15.8$ ($c = 0.33$ in $CHCl_3$); 95% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0

mL/min, λ = 254 nm, t (major) = 11.17 min, t (minor) = 18.53 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.97 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.32–7.19 (m, 4H), 6.63–6.55 (m, 1H), 3.53–3.43 (m, 1H), 3.38 (dd, *J* = 14.6 Hz, 3.2 Hz, 1H), 2.76 (dd, *J* = 14.5 Hz, 10.8 Hz, 1H), 2.42 (s, 3H), 2.41(s, 3H), 2.38–2.29 (m, 1H), 2.25–2.14 (m, 1H), 1.81–1.68 (m, 3H), 1.67−1.57 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 199.5, 198.0, 143.9, 143.8, 142.4, 141.6, 136.0, 134.3, 129.6, 129.3, 128.9, 128.7, 42.5, 30.7, 26.5, 26.1, 21.7, 21.6, 18.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{24}O_2Na$ 355.1669; found 355.1670.

*(S)-2-(2-(3-Methoxybenzoyl)cyclohex-2-en-1-yl)-1-(3-methoxyphenyl)ethanone (**2c**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **2c**: 30.2 mg, 83% yield, colorless oil; $[\alpha]_D^{25}$ = −21.7 (*c* = 0.41 in $CHCl_3$); 92% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 12.51 min, t (minor) = 16.10 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.67 (d, *J* = 7.6 Hz, 1H), 7.62–7.57 (m, 1H), 7.41–7.29 (m, 2H), 7.28–7.16 (m, 2H), 7.13–7.00 (m, 2H), 6.68–6.59 (m, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.53–3.43 (m, 1H), 3.38 (dd, *J* = 14.8, 3.2 Hz, 1H), 2.76 (dd, *J* = 14.8, 10.7 Hz, 1H), 2.40–2.26 (m, 1H), 2.26–2.11 (m, 1H), 1.79–1.67 (m, 3H), 1.65–1.57 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): *δ* (ppm) 199.5, 197.7, 159.8, 159.4, 145.1, 141.4, 140.1, 138.0, 129.6, 129.1, 121.8, 121.2, 119.8, 117.7, 114.0, 112.4, 55.5, 55.4, 42.7, 30.5, 26.4, 26.1, 18.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{24}O_4Na$ 387.1567; found 387.1565.

*(S)-2-(2-(4-Bromobenzoyl)cyclohex-2-en-1-yl)-1-(4-bromophenyl) ethanone (**2d**)*.

Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/60) gave **2d**: 41.8 mg, 91% yield, colorless oil; $[\alpha]_D^{25}$ = +8.44 (*c* = 0.45 in $CHCl_3$); 84% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 9.27 min, t (minor) = 12.15 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.94 (d, *J* = 8.4 Hz, 2H), 7.67–7.50 (m, 6H), 6.68–6.57 (m, 1H), 3.50–3.38 (m, 1H), 3.34 (dd, *J* = 14.8 Hz, 3.2 Hz, 1H), 2.80 (dd, *J* = 14.8 Hz, 10.3 Hz, 1H), 2.43–2.30 (m, 1H), 2.29–2.17 (m, 1H), 1.80–1.69 (m, 3H), 1.68–1.62 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 198.7, 196.9, 145.6, 141.2, 137.4, 135.4, 132.0, 131.5, 130.9, 130.1, 128.3, 126.6, 42.4, 30.4, 26.5, 26.2, 18.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{18}Br^{79}Br^{81}O_2Na$ 484.9545; found 484.9548; calcd for $C_{21}H_{18}Br^{79}{}_2O_2Na$ 482.9566; found 482.9568; calcd for $C_{21}H_{18}Br^{81}{}_2O_2Na$ 486.9525; found 486.9535.

(S)-2-(2-(3-Bromobenzoyl)cyclohex-2-en-1-yl)-1-(3-bromophenyl)ethanone (***2e***). Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/60) gave **2e**: 33.1 mg, 72% yield, colorless oil; $[\alpha]_D^{25}$ = −17.1 (*c* = 0.46 in $CHCl_3$); 79% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 8.70 min, t (minor) = 11.00 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.17 (t, *J* = 1.8 Hz, 1H), 8.01 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.78 (t, *J* = 1.8 Hz, 1H), 7.72–7.62 (m, 2H), 7.58 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 6.70–6.62 (m, 1H), 3.51–3.40 (m, 1H), 3.32 (dd, *J* = 15.2, 3.3 Hz, 1H), 2.84 (dd, *J* = 15.2, 10.2 Hz, 1H), 2.45–2.31 (m, 1H), 2.30–2.17 (m, 1H), 1.80–1.69 (m, 3H), 1.70–1.63 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 198.1,

196.3, 146.4, 141.1, 140.6, 138.5, 135.9, 134.5, 132.0, 131.4, 130.3, 129.8, 127.8, 127.1, 123.0, 122.4, 42.4, 30.1, 26.5, 26.3, 18.0; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{18}Br^{79}Br^{81}O_2Na$ 484.9545; found 484.9559; calcd for $C_{21}H_{18}Br^{79}{}_2O_2Na$ 482.9566; found 482.9572; calcd for $C_{21}H_{18}Br^{81}{}_2O_2Na$ 486.9525; found 486.9524.

(S)-2-(2-(2-Naphthoyl)cyclohex-2-en-1-yl)-1-(naphthalen-2-yl) ethanone ***(2f)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **2f**: 27.4 mg, 68% yield, colorless oil; $[\alpha]_D^{25}$ = +13.6 (*c* = 0.25 in $CHCl_3$); 81% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 13.31 min, t (minor) = 19.60 min]; ^1H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.69 (s, 1H), 8.19 (s, 1H), 8.11 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.98–7.78 (m, 6H), 7.63–7.46 (m, 4H), 6.76–6.67 (m, 1H), 3.69–3.55 (m, 2H), 3.02–2.91 (m, 1H), 2.47–2.31 (m, 1H), 2.31–2.15 (m, 1H), 1.88–1.74 (m, 3H), 1.72–1.63 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 199.8, 198.1, 144.9, 141.8, 136.1, 135.6, 134.9, 134.1, 132.7, 132.3, 130.5, 130.3, 129.8, 129.2, 128.41, 128.38, 128.2, 127.9, 127.8, 127.7, 126.7, 126.6, 125.7, 124.2, 42.8, 30.9, 26.7, 26.3, 18.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{29}H_{24}O_2Na$ 427.1669; found 427.1670.

(S)-1-(Thiophen-2-yl)-2-(2-(thiophene-2-carbonyl)cyclohex-2-en-1-yl)ethanone ***(2g)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **2g**: 25.6 mg, 81% yield, colorless oil; $[\alpha]_D^{25}$ = −19.0 (*c* = 0.21 in $CHCl_3$); 82% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 10.44 min, t (minor) = 17.52 min]; ^1H NMR (400

MHz, $CDCl_3$): δ (ppm) 7.92 (d, J = 4.0 Hz, 1H), 7.63 (d, J = 4.8 Hz, 1H), 7.62–7.56 (m, 2H), 7.15–7.05 (m, 2H), 6.87–6.81 (m, 1H), 3.55–3.40 (m, 1H), 3.27 (dd, J = 14.2, 3.1 Hz, 1H), 2.68 (dd, J = 14.2, 10.8 Hz, 1H), 2.42–2.29 (m, 1H), 2.27–2.15 (m, 1H), 1.77–1.71 (m, 3H), 1.68–1.60 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 192.5, 189.3, 144.3, 143.9, 141.7, 141.5, 133.6, 133.34, 133.26, 132.8, 128.3, 127.7, 43.2, 31.6, 26.5, 26.0, 18.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{17}H_{16}O_2S_2Na$ 339.0484; found 339.0483.

(S)-2-(2-Benzoyl-5,5-dimethylcyclohex-2-en-1-yl)-1-phenylethanone (***2h***). Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **2h**: 21.6 mg, 65% yield, colorless oil; $[\alpha]_D^{25}$ = −80.0 (c = 0.25 in $CHCl_3$); 83% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 10.03 min, t (minor) = 13.41 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07–7.97 (m, 2H), 7.82–7.72 (m, 2H), 7.59–7.51 (m, 2H), 7.50–7.40 (m, 4H), 6.53–6.43 (m, 1H), 3.52 (dd, J = 15.3, 3.1 Hz, 1H), 3.46–3.34 (m, 1H), 2.83 (dd, J = 15.3, 9.5 Hz, 1H), 2.26–2.16 (m, 1H), 2.02–1.90 (m, 1H), 1.73–1.63 (m, 1H), 1.47–1.35 (m, 1H), 1.00 (s, 3H), 0.87 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.7, 198.2, 142.2, 140.9, 138.5, 136.9, 133.0, 132.0, 129.6, 128.6, 128.3, 128.2, 42.4, 41.7, 39.8, 31.3, 30.6, 29.4, 25.3; IR (CH_2Cl_2) ν 2961, 2923, 1680, 1597, 1579, 1448, 1365, 1261, 754, 691 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{24}O_2Na$ 355.1669; found 355.1670.

*(S)-2-(4-Benzoyl-3,6-dihydro-2H-pyran-3-yl)-1-phenylethanone (**2i**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/10) gave **2i**: 22.2

mg, 73% yield, colorless oil; $[\alpha]_D^{25}$ = –9.35 (*c* = 0.54 in $CHCl_3$); 78% ee, determined by HPLC analysis: [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 12.74 min, t (minor) = 17.47 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.04–7.94 (m, 2H), 7.72–7.62 (m, 2H), 7.59–7.49 (m, 2H), 7.50–7.38 (m, 4H), 6.63–6.55 (m, 1H), 4.42 (dd, *J* = 19.1, 3.3 Hz, 1H), 4.32–4.22 (m, 1H), 4.07–4.00 (m, 1H), 3.72–3.64 (m, 1H), 3.51–3.43 (m, 1H), 3.35–3.27 (m, 1H), 3.27–3.20 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): *δ* (ppm) 198.7, 195.9, 141.8, 138.7, 137.9, 136.9, 133.1, 132.0, 129.2, 128.6, 128.3, 128.2, 67.7, 65.3, 39.9, 29.9; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{18}O_3Na$ 329.1148; found 329.1150.

(S)-2-(2-(4-Nitrobenzoyl)cyclohex-2-en-1-yl)-1-(p-tolyl)ethanone ***(2j)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **2j**: 33.4 mg, 92% yield, colorless oil; $[\alpha]_D^{25}$ = –5.30 (*c* = 0.42 in $CHCl_3$); 93% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 15.41 min, t (minor) = 21.42 min]; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.33–8.24 (m, 2H), 7.98–7.90 (m, 2H), 7.85–7.76 (m, 2H), 7.27 (d, *J* = 7.0 Hz, 2H), 6.64–6.56 (m, 1H), 3.53–3.41 (m, 1H), 3.33 (dd, *J* = 15.0, 3.7 Hz, 1H), 2.93 (dd, *J* = 15.0, 9.7 Hz, 1H), 2.41 (s, 3H), 2.39–2.31 (m, 1H), 2.30–2.18 (m, 1H), 1.84–1.70 (m, 3H), 1.70–1.62 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): *δ* (ppm) 199.2, 196.0, 149.3, 147.1, 144.4, 144.0, 141.8, 134.4, 130.0, 129.4, 128.5, 123.4, 42.0, 30.1, 26.6, 26.4, 21.7, 18.0; IR (CH_2Cl_2) ν 2921, 2851, 1679, 1604, 1524, 1347, 1270, 1183, 967, 805, 721 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{21}NO_4Na$ 386.1363; found 386.1361.

(S)-1-(2-benzoylcyclohex-2-en-1-yl)propan-2-one ***(2k)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/30) gave **2k**: 18.0 mg, 73% yield, colorless oil; $[\alpha]_D^{25}$ = –62.8 (*c* = 0.96 in $CHCl_3$); 80% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 10.17 min, t (minor) = 11.17 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.68–7.62 (m, 2H), 7.54–7.48 (m, 1H), 7.45–7.39 (m, 2H), 6.59–6.53 (m, 1H), 3.41–3.32 (m, 1H), 2.70 (dd, *J* = 15.7, 3.6 Hz, 1H), 2.46 (dd, *J* = 15.7, 9.7 Hz, 1H), 2.37–2.26 (m, 1H), 2.25–2.17 (m 1H), 2.17 (s, 3H), 1.82–1.72 (m, 1H), 1.70–1.64 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 208.2, 197.9, 144.5, 141.3, 138.7, 131.7, 129.3, 128.1, 47.4, 29.9, 29.3, 27.0, 26.1, 18.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{18}O_2Na$ 265.1199; found 265.1168.

Asymmetric reaction of 2a on a large scale. (2*E*,7*E*)-1,9-Diphenylnona-2,7-diene-1,9-dione (304.0 mg, 1 mmol), 2-mercaptophenol **T2** (50.4 mg, 0.4 mmol), catalyst **C5** (125.2 mg, 0.2 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) were stirred in toluene (10 mL) at rt for 72 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **2a**: 221.0 mg, 73% yield, colorless oil; 91% ee.

General procedure for intramolecular RC reaction of bis(enones) 3. Bis(enones) **3** (0.1 mmol), chiral thiol **T4** (0.01 mmol), catalyst **C6** (0.01 mmol) and K_2CO_3 (0.06 mmol) were added into a vial equipped with a magnetic stir bar. Toluene (1.0 mL) was added. The mixture was stirred at room temperature for 24 h. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1:40) gave the product

4.

*(R)-2-(2-Benzoylcyclopent-2-en-1-yl)-1-phenylethanone (**4a**).* Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **4a**: 26.0 mg, 90% yield, colorless oil; $[\alpha]_D^{25}$ = +91.1 [*c* = 0.38 in $CHCl_3$; data in the reference: 94% ee, $[\alpha]_D^{20}$ = +108.1 (*c* = 0.60 in $CHCl_3$)[5c]]; 93% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 9.64 min, t (major) = 19.14 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08–7.99 (m, 2H), 7.80–7.71 (m, 2H), 7.57–7.49 (m, 2H), 7.49–7.39 (m, 4H), 6.61–6.53 (m, 1H), 3.80–3.68 (m, 2H), 2.89–2.76 (m, 1H), 2.75–2.60 (m, 1H), 2.59–2.44 (m, 1H), 2.39–2.23 (m, 1H), 1.86–1.70 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.7, 194.2, 147.9, 146.2, 139.0, 137.0, 133.0, 132.0, 128.9, 128.6, 128.3, 128.2, 42.4, 41.7, 32.7, 29.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{20}H_{18}O_2Na$ 313.1199; found 313.1201.

*(R)-2-(2-(4-Methylbenzoyl)cyclopent-2-en-1-yl)-1-(p-tolyl) ethanone (**4b**).* Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **4b**: 25.9 mg, 82% yield, colorless oil; $[\alpha]_D^{25}$ = +44.4 (*c* = 0.73 in $CHCl_3$); 94% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 12.50 min, t (major) = 25.22 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96–7.87 (m, 2H), 7.70–7.60 (m, 2H), 7.29–7.15 (m, 4H), 6.58–6.48 (m, 1H), 3.78–3.64 (m, 2H), 2.80–2.69 (m, 1H), 2.69–2.59 (m, 1H), 2.57–2.45 (m, 1H), 2.41 (s, 3H), 2.38 (s,3H), 2.34–2.23 (m, 1H), 1.82–1.69 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.5, 194.0, 146.9, 146.3, 143.7, 142.7, 136.4,

134.5, 129.3, 129.1, 128.9, 128.5, 42.4, 41.9, 32.6, 29.5, 21.62, 21.58; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{22}H_{22}O_2Na$ 341.1512; found 341.1511.

*(R)-2-(2-(4-Bromobenzoyl)cyclopent-2-en-1-yl)-1-(4-bromophenyl) ethanone **(4c)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **4c**: 35.1 mg, 79% yield, colorless oil; $[\alpha]_D^{25}$ = +21.3 (*c* = 1.48 in $CHCl_3$); 85% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.59 min, t (major) = 16.20 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94–7.86 (m, 2H), 7.67–7.55 (m, 6H), 6.61–6.54 (m, 1H), 3.74–3.62 (m, 2H), 2.79 (dd, *J* = 16.2, 10.6 Hz), 2.74–2.62 (m, 1H), 2.61–2.48 (m, 1H), 2.38–2.25 (m, 1H), 1.82–1.70 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 198.6, 193.0, 148.3, 145.8, 137.6, 135.5, 131.9, 131.6, 130.4, 129.8, 128.2, 127.0, 42.2, 41.5, 32.7, 29.5; HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{20}H_{16}Br^{79}Br^{81}O_2Na$ 470.9389; found 470.9392; calcd for $C_{20}H_{16}Br^{79}{}_2O_2Na$ 468.9409; found 468.9415; calcd for $C_{20}H_{16}Br^{81}{}_2O_2Na$ 472.9368; found 472.9383.

*(R)-2-(2-(2-Naphthoyl)cyclopent-2-en-1-yl)-1-(naphthalen-2-yl) ethanone **(4d)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **4d**: 28.8 mg, 74% yield, colorless oil; $[\alpha]_D^{25}$ = –8.00 (*c* = 0.75 in $CHCl_3$); 85% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 14.32 min, t (major) = 26.77 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.62 (s, 1H), 8.27 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 8.00–7.84 (m, 7H), 7.66–7.50 (m, 4H), 6.71–6.64 (m, 1H), 4.03–3.91 (m, 1H), 3.91–3.80 (m, 1H), 3.01 (dd, *J* = 15.6, 10.2 Hz), 2.82–2.68 (m, 1H), 2.68–2.53 (m, 1H), 2.47–2.34 (m, 1H),

2.00–1.82 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.8, 194.3, 147.9, 146.4, 136.3, 135.6, 135.2, 134.2, 132.6, 132.3, 130.3, 130.2, 129.7, 129.3, 128.42, 128.37, 128.3, 128.0, 127.8, 127.7, 126.74, 126.66, 125.1, 124.1, 42.6, 42.0, 32.8, 29.7; IR (CH_2Cl_2) ν 2941, 1676, 1627, 1469, 1355, 1277, 1186, 751 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{22}O_2Na$ 413.1512; found 413.1505.

*(R)-1-(Thiophen-2-yl)-2-(2-(thiophene-2-carbonyl)cyclopent-2-en-1-yl) ethanone (**4e**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **4e**: 19.3 mg, 64% yield, colorless oil; $[\alpha]_D^{25} = +33.9$ (*c* = 1.12 in $CHCl_3$); 71% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 11.46 min, t (major) = 25.33 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89–7.81 (m, 1H), 7.71–7.66 (m, 1H), 7.65–7.55 (m, 2H), 7.16–7.05 (m, 2H), 6.84–6.76 (m, 1H), 3.75–3.68 (m, 1H), 3.64 (dd, *J* = 14.9, 3.0 Hz), 2.71 (dd, *J* = 14.8, 10.3 Hz, 1H), 2.68–2.63 (m, 1H), 2.60–2.50 (m, 1H), 2.35–2.21 (m , 1H), 1.88–1.75 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 192.7, 185.1, 145.9, 145.3, 144.4, 144.2, 133.5, 133.1, 132.7, 132.6, 128.2, 127.8, 43.0, 42.6, 32.7, 29.3; IR (CH_2Cl_2) ν 3097, 2936, 1655, 1618, 1515, 1413, 722 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{16}H_{14}O_2S_2Na$ 325.0327; found 325.0330.

General procedure for desymmetric intramolecular RC reaction of bis(enones) 5. Bis(enones) **5** (0.1 mmol), 2-mercaptophenol **T5** (0.04 mmol), catalyst **C7** (0.02 mmol) and K_2CO_3 (0.06 mmol) were added into a vial equipped with a magnetic stir bar. Toluene (1.0 mL) was added. The mixture was stirred at room temperature for 24 to 72 h. Purification by flash chromatography on silica gel

(EtOAc/petroleum ether = 1/40) gave the product **6**.

((1S,5R)-2-Benzoyl-5-methylcyclohex-2-en-1-yl)-1-phenylethanone ***(6a)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6a**: 24.2 mg, 76% yield, colorless oil; $[\alpha]_D^{25} = -97.4$ (c = 1.77 in $CHCl_3$); >19:1 dr; 92% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 10.11 min, t (minor) = 12.28 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.06–7.96 (m, 2H), 7.79–7.70 (m, 2H), 7.57–7.48 (m, 2H), 7.48–7.37 (m, 4H), 6.52–6.46 (m, 1H), 3.52 (dd, J = 15.1, 3.1 Hz, 1H), 3.45–3.33 (m, 1H), 2.73 (dd, J = 15.1, 9.8 Hz, 1H), 2.30–2.17 (m, 1H), 1.98–1.87 (m, 2H) , 1.71–1.56 (m, 1H), 1.20 (q, J = 12.1 Hz, 1H), 0.96 (d, J = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz,$CDCl_3$): δ (ppm) 199.8, 198.3, 142.7, 142.0, 138.5, 136.9, 133.0, 132.1, 129.6, 128.6, 128.4, 128.2, 42.8, 37.6, 34.6, 33.5, 28.1, 21.7; IR (CH_2Cl_2) ν 3058, 2908, 1680, 1640, 1597, 1579, 1447, 1369, 1258, 753, 734, 711, 690 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{22}O_2Na$ 341.1512; found 341.1512.

((1S,5R)-5-Methyl-2-(4-methylbenzoyl)cyclohex-2-en-1-yl)-1-(p-tolyl)ethanone ***(6b)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6b**: 22.8 mg, 66% yield, colorless oil; $[\alpha]_D^{25} = -93.5$ (c = 0.62 in $CHCl_3$); >19:1 dr; 94% ee, determined by HPLC analysis: [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 18.90 min, t (major) = 19.81 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97–7.87 (m, 2H), 7.73–7.65 (m, 2H), 7.29–7.21 (m, 4H), 6.50–6.42 (m, 1H), 3.48 (dd, J = 14.8 Hz, 2.3 Hz, 1H), 3.44–3.33 (m, 1H), 2.65 (dd, J = 14.2 Hz, 10.2 Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H), 2.29–2.16 (m, 1H), 1.99–1.85 (m,

2H), 1.69–1.59 (m, 1H), 1.27–1.13 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) *δ* (ppm): 199.4, 198.1, 143.6, 142.7, 142.0, 141.5, 135.6, 134.3, 129.7, 129.2, 128.8, 128.4, 42.8, 37.5, 34.4, 33.7, 28.0, 21.7, 21.6, 21.5; IR (CH_2Cl_2) ν 2923, 1678, 1642, 1605, 1572, 1454, 1375, 1263, 1180, 807, 747 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{26}O_2Na$ 369.1825; found 369.1831.

*((1S,5R)-2-(3-Methoxybenzoyl)-5-methylcyclohex-2-en-1-yl)-1-(3-methoxyphenyl) ethanone (**6c**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6c**: 28.3 mg, 75% yield, colorless oil; $[\alpha]_D^{25}$ = −122.3 (*c* = 0.27 in $CHCl_3$); >19:1 dr; 95% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 38.96 min, t (minor) = 44.92 min]; ^1H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.62 (d, *J* = 7.7 Hz, 1H), 7.60–7.52 (m, 1H), 7.39–7.27 (m, 4H), 7.14–7.03 (m, 2H), 6.55–6.49 (m, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.50 (dd, *J* = 14.9, 3.1 Hz, 1H), 3.46–3.34 (m, 1H), 2.68 (dd, *J* = 14.9, 9.9 Hz, 1H), 2.29–2.17 (m, 1H), 2.00–1.85 (m, 2H), 1.69–1.61 (m, 1H), 1.18 (q, *J* = 12.1 Hz, 1H), 0.96 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 199.6, 198.0, 159.9, 159.5, 142.7, 142.0, 139.8, 138.2, 129.6, 129.2, 122.3, 121.1, 119.8, 118.3, 114.1, 112.3, 55.49, 55.46, 43.1, 37.6, 34.5, 33.6, 28.1, 21.7; IR (CH_2Cl_2) ν 2923, 1680, 1640, 1596, 1580, 1485, 1452, 1263, 1031, 794, 764, 745 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{26}O_4Na$ 401.1723; found 401.1723.

*((1S,5R)-2-(4-Bromobenzoyl)-5-methylcyclohex-2-en-1-yl)-1-(4-bromophenyl) ethanone (**6d**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/60) gave **6d**: 31.2 mg, 66% yield, yellow oil; $[\alpha]_D^{25}$ = −84.2 (*c* = 0.36 in

$CHCl_3$); 13:1 dr; 79% ee, determined by HPLC analysis: [Daicel chiralpak IH, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, λ = 254 nm, t (minor) = 11.27 min, t (major) = 17.90 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89–7.84 (m, 2H), 7.65–7.56 (m, 6H), 6.52–6.46 (m, 1H), 3.43 (dd, J = 15.3, 3.2 Hz, 1H), 3.39–3.28 (m, 1H), 2.77 (dd, J = 15.3, 9.2 Hz, 1H), 2.31–2.19 (m, 1H), 2.00–1.88 (m, 2H), 1.71–1.60 (m, 1H), 1.28–1.16 (m, 1H), 0.98 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 198.7, 197.0, 143.2, 141.6, 137.1, 135.6, 131.9, 131.5, 131.1, 129.9, 128.3, 127.1, 42.4, 37.6, 34.5, 33.4, 28.1, 21.7; IR (CH_2Cl_2) ν 2951, 2922, 1682, 1642, 1584, 1395, 1260, 1069, 1010, 814, 751 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{20}Br^{79}Br^{81}O_2Na$ 498.9702; found 498.9714; calcd for $C_{22}H_{20}Br^{79}{}_2O_2Na$ 496.9722; found 496.9737; calcd for $C_{22}H_{20}Br^{81}{}_2O_2Na$ 500.9681; found 500.9697.

*((1S,5R)-2-(3-Chlorobenzoyl)-5-methylcyclohex-2-en-1-yl)-1-(3-chlorophenyl) ethanone (**6e**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6e**: 31.6 mg, 82% yield, colorless oil; $[\alpha]_D^{25}$ = −118.5 (c = 0.13 in $CHCl_3$); 14:1 dr; 70% ee, determined by HPLC analysis: [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 13.72 min, t (minor) = 15.23 min]; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.99–7.95 (m, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.74–7.70 (m, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.0 Hz, 2H), 7.43–7.37 (m, 2H), 6.57–6.52 (m, 1H), 3.44 (dd, J = 15.6 Hz, 3.0 Hz, 1H), 3.41–3.34 (m, 1H), 2.83 (dd, J = 15.6 Hz, 9.2 Hz, 1H), 2.32–2.23 (m, 1H), 2.01−1.93 (m, 2H), 1.72–1.63 (m, 1H), 1.21 (q, J = 12.2 Hz, 1H), 1.00 (d, J = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 198.6, 196.9, 144.3, 141.9, 140.4, 138.8, 135.3, 134.7, 133.3,

132.3, 130.3, 129.9, 129.8, 128.7, 128.0, 126.8, 42.9, 38.0, 34.9, 33.5, 28.4, 22.0; IR (CH_2Cl_2) ν 2923, 1686, 1645, 1569, 1420, 1254, 1076, 797, 740, 701, 680 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{20}Cl^{35}{}_2NaO_2$ 409.0733; found 409.0733; calcd for $C_{22}H_{20}Cl^{35}Cl^{37}O_2Na$ 411.0703; found 411.0714.

*((1S,5R)-2-(2-Naphthoyl)-5-methylcyclohex-2-en-1-yl)-1-(naphthalen-2-yl) ethanone (**6f**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6f**: 31.4 mg, 75% yield, colorless oil; $[\alpha]_D^{25}$ = –54.4 (*c* = 0.45 in $CHCl_3$); >19:1 dr; 80% ee, determined by HPLC analysis: [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 14.41 min, t (minor) = 15.31 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.63– 8.57 (m, 1H), 8.31–8.26 (m, 1H), 8.08 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.01–7.94 (m, 2H), 7.94–7.81 (m, 5H), 7.64–7.48 (m, 4H), 6.64–6.56 (m, 1H), 3.71 (dd, *J* = 14.9, 3.2 Hz, 1H), 3.63–3.48 (m, 1H), 2.92 (dd, *J* = 14.9, 9.8 Hz, 1H), 2.35–2.21 (m, 1H), 2.09–1.94 (m, 2H), 1.76–1.65 (m, 1H), 1.37–1.28 (m, 1H), 1.00 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.8, 198.3, 142.5, 142.2, 135.7, 135.6, 135.2, 134.2, 132.6, 132.3, 131.0, 130.3, 129.8, 129.4, 128.41, 128.36, 128.2, 128.1, 127.8, 127.7, 126.7, 126.6, 125.6, 124.1, 43.0, 37.7, 34.6, 34.0, 28.2, 21.8; IR (CH_2Cl_2) ν 2923, 1653, 1619, 1515, 1412, 1265, 722 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{26}O_2Na$ 441.1825; found 441.1828.

*((1S,5R)-5-Methyl-2-(thiophene-2-carbonyl)cyclohex-2-en-1-yl)-1-(thiophen-2-yl) ethan-1-one (**6g**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6g**: 20.5 mg, 62% yield, yellow oil; $[\alpha]_D^{25}$ = –43.2 (*c* = 0.81 in $CHCl_3$); 3:1 dr; 75% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-

hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 16.11 min, t (minor) = 24.30 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.86 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.66–7.62 (m, 2H), 7.60 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.15–7.07 (m, 2H), 6.74–6.66 (m, 1H), 3.45–3.32 (m, 2H), 2.66–2.55 (m, 1H), 2.34–2.22 (m, 1H), 2.02–1.88 (m, 2H), 1.74–1.62 (m, 1H), 1.28–1.16 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 192.6, 189.8, 144.4, 144.0, 141.8, 139.9, 133.8, 133.7, 133.6, 132.8, 128.3, 127.8, 43.4, 37.5, 34.4, 34.3, 28.1, 21.7; IR (CH_2Cl_2) ν 3100, 2923, 1653, 1619, 1515, 1412, 1265, 722 (cm^{-1}); HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{18}H_{18}O_2S_2Na$ 353.0640; found 353.0635.

((1R,3S)-4-Benzoyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)-1-phenylethanone ***(6h)***. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6h**: 27.7 mg, 73% yield, colorless oil; $[\alpha]_D^{25}$ = −84.2 (*c* = 0.43 in $CHCl_3$); >19:1 dr; 84% ee, determined by HPLC analysis: [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 14.82 min, t (major) = 16.21 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.03–7.95 (m, 2H), 7.85–7.78 (m, 2H), 7.60–7.50 (m, 2H), 7.50–7.41 (m, 4H), 7.34–7.27 (m, 2H), 7.25–7.19 (m, 3H), 6.64–6.58 (m, 1H), 3.63–3.50 (m, 2H), 2.89 (dd, *J* = 15.9 Hz, 10.0 Hz, 1H), 2.85–2.76 (m, 1H), 2.54–2.45 (m, 2H), 2.26–2.15 (m, 1H), 1.89–1.74 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 199.5, 198.2, 145.4, 142.1, 142.0, 138.3, 136.8, 133.1, 132.2, 129.6, 128.62, 128.58, 128.31, 128.30, 126.9, 126.5, 42.5, 39.5, 36.3, 34.2, 34.1; IR (CH_2Cl_2) ν 2922, 1677, 1640, 1605, 1571, 1263, 1180, 807, 747 (cm^{-1}); HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{27}H_{24}O_2Na$ 403.1669; found 403.1668.

*((1R,3S)-4-Benzoyl-4'-chloro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)-1-phenyl ethanone (**6i**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **6i**: 33.9 mg, 82% yield, colorless oil; $[\alpha]_D^{25} = -77.3$ ($c = 0.67$ in $CHCl_3$); >19:1 dr; 86% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 9.16 min, t (major) = 10.11 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99 (d, $J = 7.6$ Hz, 2H), 7.81 (d, $J = 7.4$ Hz, 2H), 7.59–7.51 (m, 2H), 7.50–7.41 (m, 4H), 7.27 (d, $J = 8.3$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 6.63–6.55 (m, 1H), 3.63–3.49 (m, 2H), 2.92 (dd, $J = 15.8$ Hz, 9.6 Hz, 1H), 2.86–2.74 (m, 1H), 2.50–2.41 (m, 2H), 2.24–2.13 (m, 1H), 1.78 (q, $J = 12.5$ Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.4, 198.0 143.8, 142.1, 141.5, 138.2, 136.8, 133.1 132.3, 132.1, 129.6, 128.7, 128.6, 128.31, 128.28, 128.2, 42.3, 38.9, 36.1, 34.1, 34.0; IR (CH_2Cl_2) ν 2923, 1680, 1642, 1596, 1492, 1447, 1263, 1091, 1013, 821, 754, 690 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{23}Cl^{35}O_2Na$ 437.1279; found 437.1271; calcd for $C_{27}H_{23}Cl^{37}O_2Na$ 439.1249; found 439.1255.

*Ethyl-(1R,5S)-4-benzoyl-5-(2-oxo-2-phenylethyl)cyclohex-3-ene-1-carboxylate (**6j**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **6j**: 30.8 mg, 82% yield, colorless oil; $[\alpha]_D^{25} = -93.5$ ($c = 0.77$ in $CHCl_3$); >19:1 dr; 85% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 34.29 min, t (major) = 45.75 min]; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.01–7.93 (m, 2H), 7.81–7.74 (m, 2H), 7.58–7.51 (m, 2H), 7.50–7.40 (m, 4H), 6.55–6.48 (m, 1H), 4.19–4.06 (m, 2H), 3.52–3.40 (m, 2H), 2.97–2.88 (m, 1H), 2.64–2.53 (m, 2H), 2.52–2.43 (m, 1H), 2.39–2.32 (m, 1H), 1.74–1.66 (m, 1H), 1.23 (t, $J = 7.2$ Hz, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 198.9, 197.7, 174.8, 141.7, 140.3, 138.0, 136.8, 133.0, 132.2, 129.6, 128.6, 128.3, 128.2, 60.7, 41.9, 38.6, 32.4, 31.4, 28.2, 14.1; IR (CH_2Cl_2) ν 2925, 1727, 1683, 1644, 1597, 1579, 1448, 1374, 1263, 1176, 755, 692 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{24}H_{24}O_4Na$ 399.1567; found 399.1571.

*((1S,5R)-2-Benzoyl-5-((tert-butyldimethylsilyl)oxy)cyclohex-2-en-1-yl)-1-phenyl ethanone (**6k**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **6k**: 32.6 mg, 75% yield, colorless oil; $[\alpha]_D^{25} = -51.4$ ($c = 0.42$ in $CHCl_3$); 10:1 dr; 83% ee, determined by HPLC analysis: [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 5.81 min, t (major) = 8.14 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01–7.92 (m, 2H), 7.80–7.72 (m, 2H), 7.58–7.50 (m, 2H), 7.49–7.38 (m, 4H), 6.44–6.36 (m, 1H), 4.02–3.90 (m, 1H), 3.61–3.49 (m, 1H), 3.36 (dd, $J = 16.3$ Hz, 3.1 Hz, 1H), 3.14 (dd, $J = 16.3$ Hz, 9.5 Hz, 1H), 2.50–2.27 (m, 2H), 2.14–1.99 (m, 1H), 1.81–1.66 (m, 1H), 0.86 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 199.2, 197.8, 141.6, 139.9, 138.4, 137.1, 132.9, 132.1, 129.5, 128.5, 128.2, 128.1, 66.7, 42.2, 36.9, 35.6, 31.5, 25.9, 18.1, −4.6, −4.7; IR (CH_2Cl_2) ν 2925, 1686, 1597, 1579, 1448, 1201, 1070, 1025, 756, 699 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{34}O_3SiNa$ 457.2169; found 457.2173.

*((1S,5R)-2-Benzoyl-5-isobutylcyclohex-2-en-1-yl)-1-phenylethanone (**6l**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6l**: 32.4 mg, 85% yield, colorless oil; $[\alpha]_D^{25} = -110.0$ ($c = 0.76$ in $CHCl_3$); >19:1

dr; 84% ee, determined by HPLC analysis: [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 9.91 min, t (major) = 11.30 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.05–7.97 (m, 2H), 7.80–7.73 (m, 2H), 7.57–7.50 (m, 2H), 7.49–7.41 (m, 4H), 6.55–6.48 (m, 1H), 3.51 (dd, *J* = 15.2, 3.1 Hz, 1H), 3.46–3.34 (m, 1H), 2.77 (dd, *J* = 15.2, 9.6 Hz, 1H), 2.32–2.22 (m, 1H), 2.03–1.95 (m, 1H), 1.95–1.85 (m, 1H), 1.71–1.64 (m, 1H), 1.63–1.59 (m, 1H), 1.23–1.16 (m, 1H), 1.17–1.12 (m, 2H), 0.84 (t, *J* = 6.5 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 199.8, 198.3, 142.7, 142.2, 138.4, 136.9, 133.0, 132.1, 129.6, 128.6, 128.3, 128.2, 46.1, 42.8, 36.1, 33.4, 32.9, 30.6, 24.8, 23.1, 22.5; IR (CH_2Cl_2) ν 3060, 2953, 2906, 1681, 1642, 1597, 1579, 1447, 1366, 1259, 753, 691 (cm^{-1}); HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{25}H_{28}O_2Na$ 383.1982; found 383.1988.

*((1R,3S)-4-(2-Naphthoyl)-4'-chloro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3-yl)-1-(naphthalen-2-yl)ethan-1-one (**6m**)*. Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/30) gave **6m**: 40.0 mg, 70% yield, white semisolid; $[\alpha]_D^{25}$ = −13.0 (*c* = 2.24 in $CHCl_3$); >19:1 dr; 81% ee, determined by HPLC analysis: [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 18.44 min, t (major) = 32.60 min]; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.55 (s, 1H), 8.32 (s, 1H), 8.06–7.80 (m, 8H), 7.64–7.47 (m, 4H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.72–6.61 (m, 1H), 3.77–3.63 (m, 2H), 3.06 (dd, *J* = 15.8, 9.9 Hz, 1H), 2.89–2.77 (m, 1H), 2.54–2.42 (m, 2H), 2.29–2.18 (m, 1H), 1.93–1.80 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* (ppm) 199.4, 198.0, 143.9, 142.3, 141.3, 135.6, 135.4, 135.3, 134.1, 132.6, 132.3, 132.1, 131.1, 130.2, 129.7, 129.4, 128.7, 128.5, 128.4, 128.3,

128.24, 128.20, 127.8, 127.7, 126.8, 126.7, 125.6, 124.0, 42.5, 39.0, 36.2, 34.4, 34.1; IR (CH_2Cl_2) ν 3057, 2921, 1671, 1625, 1595, 1492, 1467, 1353, 1276, 1263, 1123, 816, 734 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{27}Cl^{35}O_2Na$ 537.1592; found 537.1588; calcd for $C_{35}H_{27}Cl^{37}O_2Na$ 539.1562; found 539.1579.

Asymmetric reaction of 5a on a large scale. (2*E*,7*E*)-5-Methyl-1,9-diphenylnona-2,7-diene-1,9-dione **5a** (159.0 mg, 0.5 mmol), 5-Br-2-mercptophenol **T5** (41.0 mg, 0.2 mmol), catalyst **C7** (62.8 mg, 0.1 mmol) and K_2CO_3 (41.4 mg, 0.3 mmol) were stirred in toluene (5 mL) at rt for 72 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **6a**: 124.2 mg, 78% yield, colorless oil; 90% ee, 14:1 dr.

Procedure for the synthesis of tert-butyl (1S,5R)-4-benzoyl-1-cyano-5-(2-oxo-2-phenylethyl)cyclohex- 3-ene-1-carboxylate (8). *tert*-Butyl (*E*)-2-cyano-6-oxo-2-((*E*)-4-oxo-4-phenyl but-2-en-1-yl)-6-phenylhex-4-enoate **7** (42.9 mg, 0.1 mmol), (*R*)-bis-*ortho*-mercaptophenol **T4** (14.1 mg, 0.04 mmol), catalyst **C6** (15.6 mg, 0.02 mmol) and K_2CO_3 (8.4 mg, 0.06 mmol) were stirred in toluene (1 mL) at 50 °C for 18 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave **8**: 36.5 mg, 85% yield, white solid, mp 140–146 °C; $[\alpha]_D^{25} = +21.9$ (*c* = 1.95 in $CHCl_3$); 11:1 dr; 75% ee, determined by HPLC analysis: [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (major) = 10.38 min, t (minor) = 13.82 min]; ^1H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.94–7.86 (m, 2H), 7.80–7.73 (m, 2H), 7.58–7.49 (m, 2H), 7.49–7.37 (m, 4H), 6.47–6.39 (m, 1H), 3.74–3.60 (m, 1H), 3.41 (dd, J = 17.2, 3.1 Hz, 1H), 3.26 (dd, J = 17.2, 8.0 Hz, 1H), 3.02–2.90 (m, 1H), 2.79–2.65 (m, 1H), 2.53–2.41 (m, 1H), 2.15–2.03 (m, 1H), 1.50 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 198.3, 196.8, 167.2, 141.6, 137.6, 136.6, 135.1, 133.4, 132.5, 129.7, 128.7, 128.4, 128.1, 118.7, 84.5, 43.2, 40.4, 34.7, 32.7, 30.5, 27.8; IR (CH$_2$Cl$_2$) ν 2980, 2931, 1733, 1683, 1647, 1597, 1579, 1448, 1370, 1261, 1153, 754, 735, 701, 690 (cm^{-1}); HRMS (ESI-TOF) *m/z*: [M + Na]$^+$ calcd for $C_{27}H_{27}NO_4Na$ 452.1832; found 452.1829.

Procedure for the synthesis of 2-((1S,2R,5R)-3-benzoylbicyclo[3.2.1]oct-3-en-2-yl)-1-phenylethan-1-one (10). 3,3'-(Cyclopentane-1,3-diyl)bis(1-phenylprop-2-en-1-one) **9** (33.0 mg, 0.1 mmol, as a *cis*/*trans* mixture, but the ratio might be various from different preparation reactions), 2-mercaptophenol **T2** (5.2 mg, 0.04 mmol), catalyst **C5** (12.6 mg, 0.02 mmol) and K$_2$CO$_3$ (13.8 mg, 0.1 mmol) were stirred in toluene (1 mL) at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **10**: 9.2 mg, 28% yield, colorless oil; $[\alpha]_D^{25}$ = –31.2 (c = 0.78 in CHCl$_3$); >19:1 dr; 82% ee, determined by HPLC analysis: [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (major) = 12.53 min, t (minor) = 14.97 min]; ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.04–7.94 (m, 2H), 7.68–7.59 (m, 2H), 7.52–7.44 (m, 2H), 7.44–7.33 (m, 4H), 6.70–6.61 (m, 1H), 3.72–3.62 (m, 1H), 3.42 (dd, J = 15.0, 3.6 Hz, 1H), 2.73 (dd, J = 15.0, 11.3 Hz, 1H), 2.56–2.47 (m, 1H), 2.44–2.32 (m, 1H), 1.98–1.82 (m, 2H), 1.82–1.72 (m, 1H), 1.72–1.61 (m, 2H), 1.61–1.54 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 199.9, 198.4, 149.9, 138.9, 138.5, 136.9, 133.0, 132.0, 129.5, 128.6, 128.4, 128.2, 41.4, 38.7, 36.6, 36.5, 36.1, 33.8, 23.7; IR (CH_2Cl_2) ν 3059, 2942, 1680, 1634, 1597, 1578, 1447, 1370, 1266, 748, 697 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{22}O_2Na$ 353.1512; found 353.1516.

Procedure for the synthesis of (S)-3-methyl-4a,5,6,7-tetrahydronaphthalen-1(4H)-one (11). (3*E*,8*E*)-Undeca-3,8-diene-2,10-dione **1l** (18.0 mg, 0.1 mmol), 2-mercaptophenol **T2** (5.2 mg, 0.04 mmol), catalyst **C5** (12.6 mg, 0.02 mmol) and K_2CO_3 (27.6 mg, 0.2 mmol) were stirred in toluene (1 mL) at 60 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) to give **11**: 7.8 mg, 43% yield, colorless oil; $[\alpha]_D^{25} = +108.4$ ($c = 0.55$ in $CHCl_3$); 71% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 8.62 min, t (minor) = 9.82 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.93–6.84 (m, 1H), 6.00–5.93 (m, 1H), 2.75–2.59 (m, 1H), 2.31 (dd, $J = 17.4, 5.8$ Hz, 1H), 2.26–2.17 (m, 2H), 2.15–2.06 (m, 1H), 2.05–1.98 (m, 1H), 1.96 (s, 3H), 1.83–1.75 (m, 1H), 1.58–1.44 (m, 1H), 1.40–1.26 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 188.2, 161.2, 136.2, 135.3, 127.1, 38.1, 35.0, 29.9, 25.9, 24.6, 21.1; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{11}H_{14}ONa$ 185.0937; found 185.0942.

General procedure for intramolecular RC reaction of nitroolefin enoate 12. Nitroolefin enoate **12** (0.1 mmol), 2-mercaptophenol **T2** (5.2 mg, 0.04 mmol), catalyst **C9** (7.8 mg, 0.02 mmol) were dissolved in toluene (1.0 mL). Then the mixture was stirred at 50 °C for 48 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **13**.

*Ethyl (R)-2-(3-nitro-2H-chromen-2-yl)acetate (**13a**).* Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **13a**: 21.3 mg, 81% yield, yellow oil; $[\alpha]_D^{25} = -67.0$ ($c = 0.88$ in $CHCl_3$); 91% ee, determined by HPLC analysis: [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 15.02 min, t (major) = 16.51 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (s, 1H), 7.43–7.35 (m, 1H), 7.30 (dd, J = 7.6, 1.7 Hz, 1H), 7.09–7.01 (m, 1H), 6.98–6.92 (m, 1H), 6.05 (dd, J = 9.4, 3.5 Hz, 1H), 4.18 (q, J = 7.1, 2H), 2.86 (dd, J = 15.1, 9.4 Hz, 1H), 2.71 (dd, J = 15.1, 3.6 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 168.9, 152.8, 140.8, 134.5, 130.5, 129.4, 123.0, 117.8, 117.6, 69.8, 61.2, 37.9, 14.1, HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{13}NO_5Na$ 286.0686; found 286.0681.

*Methyl (R)-2-(3-nitro-2H-chromen-2-yl)acetate (**13b**).* Purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave **13b**: 18.7 mg, 75% yield, yellow solid; $[\alpha]_D^{25} = -75.0$ [$c = 0.20$ in $CHCl_3$; data in the reference: 98% ee, $[\alpha]_D^{16} = -97.87$ ($c = 1.10$ in $CHCl_3$)[15]]; 89% ee, determined by HPLC analysis: [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, λ = 254 nm, t (minor) = 14.40 min, t (major) = 19.36 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (s, 1H), 7.39 (td, J = 7.6, 1.7 Hz, 1H), 7.30 (dd, J = 7.6, 1.7 Hz, 1H), 7.05 (td, J = 7.5, 1.1 Hz, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.05 (dd, J = 9.4, 3.5 Hz, 1H), 3.73 (s, 3H), 2.88 (dd, J = 15.2, 9.5 Hz, 1H), 2.72 (dd, J = 15.2, 3.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 169.3, 152.7, 140.7, 134.5, 130.5, 129.4, 123.0, 117.8, 117.7, 69.7, 52.2, 37.6; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_{11}NO_5Na$ 272.0529; found 272.0531.

Procedure for the synthesis of (1S,4aR,9aS)-7-methoxy-1-(2-(3-methoxyphenyl)-2-oxoethyl)-1,2,3,4,4a,9a-hexahydro-9H-fluoren-9-one (14). (*S*)-2-(2-(3-Methoxybenzoyl)cyclohex-2-en-1-yl)-1-(3-methoxyphenyl)ethan-1-one **2c** (36.4 mg, 0.1 mmol), $FeCl_3{\cdot}6H_2O$ (27.0 mg, 0.1 mmol) were stirred in toluene (1 mL) at 50 °C for 5 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40) gave product **14**: 25.4 mg, 70% yield, colorless oil; $[\alpha]_D^{25} = -5.23$ ($c = 0.65$ in $CHCl_3$); 91% ee, determined by HPLC analysis: [Daicel chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 47.40 min, t (major) = 49.70 min]; ^1H NMR (400 MHz, CDCl3): δ (ppm) 7.59 (d, $J = 7.7$ Hz, 1H), 7.50 (t, $J = 2.1$ Hz, 1H), 7.41–7.32 (m, 2H), 7.23–2.14 (m, 2H), 7.09 (dd, $J = 8.3$, 2.7 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.78–3.70 (m, 1H), 3.42 (q, $J = 6.3$ Hz, 1H), 2.91 (dd, $J = 16.2$, 9.6 Hz, 1H), 2.58 (dd, $J = 9.5$, 6.5 Hz, 1H), 2.33–2.20 (m, 1H), 2.01–1.89 (m, 1H), 1.88–1.71 (m, 2H), 1.66–1.60 (m, 1H), 1.46–1.32 (m, 1H), 1.28–1.14 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 207.5, 199.4, 159.8, 159.4, 149.7, 138.5, 137.1, 129.6, 125.3, 123.5, 120.9, 119.6, 112.3, 105.8, 55.6, 55.4, 53.5, 43.5, 37.5, 31.7, 29.3, 27.7, 20.4; IR (CH_2Cl_2) ν 2924, 1710, 1683, 1597, 1583, 1455, 1279, 1257, 1025, 786, 687 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{24}O_4Na$ 387.1567; found 387.1571.

Procedure for the synthesis of (7aS,8S,10S,11aR)-10-(4-chlorophenyl)-8-(2-(naphthalen-2-yl)-2-oxoethyl)-7a,8,9,10,11,11a-hexahydro-7H-benzo[c]fluoren-7-one (15). 2-((1*R*,3*S*)-4-(2-nNaphthoyl)-4'-chloro-1,2,3,6- tetrahydro-[1,1'-biphenyl]-3-yl)-1-(naphthalen-2-yl)ethan-1-one **6m** (51.4 mg, 0.1 mmol), $FeCl_3{\cdot}6H_2O$ (27.0 mg, 0.1

mmol) were stirred in toluene (1.0 mL) at 40 °C for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20) gave product **15**: 13.8 mg, 27% yield, white solid, mp 137–147 °C; $[\alpha]_D^{25} = +2.63$ ($c = 0.84$ in $CHCl_3$); 81% ee, determined by HPLC analysis: [Daicel chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, $\lambda = 254$ nm, t (major) = 26.82 min, t (minor) = 41.20 min]; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.73–8.67 (m, 1H), 8.13 (dd, $J = 8.6$, 1.7 Hz, 1H), 8.07–8.01 (m, 1H), 7.96 (d, $J = 8.3$ Hz, 2H), 7.94–7.87 (m, 2H), 7.87–7.79 (m, 2H), 7.68–7.55 (m, 4H), 7.35–7.30 (m, 2H), 7.30–7.26 (m, 2H), 4.31–4.21 (m, 2H), 3.17 (dd, $J = 16.0$, 9.8 Hz, 1H), 3.06–2.96 (m, 1H), 2.93 (dd, $J = 9.7$, 7.1 Hz, 1H), 2.82–2.70 (m, 1H), 2.50–2.40 (m, 1H), 2.35–2.23 (m, 1H), 1.99–1.88 (m, 1H), 1.63–1.58 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ (ppm) 207.8, 199.8, 158.4, 146.0, 137.5, 136.0, 134.6, 134.5, 133.0, 132.3, 130.7, 130.12, 130.09, 129.7, 129.42, 129.39, 129.2, 128.8, 128.6, 128.1, 127.6, 127.1, 124.8, 124.4, 120.1, 53.2, 45.1, 37.7, 36.3, 36.2, 35.9, 31.9; IR (CH_2Cl_2) ν 3057, 2925, 1696, 1678, 1625, 1591, 1458, 1377, 1266, 1091, 1013, 821, 736 (cm^{-1}); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{35}H_{27}Cl^{35}O_2Na$ 537.1592; found 537.1598; calcd for $C_{35}H_{27}Cl^{37}O_2Na$ 539.1562; found 539.1587.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Complete screening conditions and experimental procedures; NMR, HRMS spectra and HPLC chromatograms (PDF); cif files of enantiopure **8** and **15**.

Accession Codes

CCDC 2002926 (**8**) and 2002927 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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