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Highly enantioselective tandem cyclopropanation/Wittig reaction of α,β-unsaturated aldehydes with arsonium ylides catalyzed by recyclable dendritic catalyst

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Abstract—A novel tandem cyclopropanation/Wittig reaction of α,β-unsaturated aldehydes with arsonium ylides using a chiral 2-trimethylsilanyloxy-methyl-pyrrolidine-based dendritic catalyst is described. Good yields (up to 86%), and high diastereoselectivities (up to dr = 99:1) and enantioselectivities (up to 99% ee) were obtained under simple and mild reaction conditions. The catalyst can be recycled without any loss in activity.

1. Introduction

Cyclopropanes are useful building blocks for the synthesis of natural and synthetic products due to their unique structures and reactivities. They are also found as a basic structural unit in a wide range of biologically active compounds existing in plants and microorganisms.[1] As a result, the development of efficient methods for the asymmetric synthesis of cyclopropanes has attracted intensive research interest in recent years. The most important and useful methods for the preparation of cyclopropanes include the combination of ylides and electron-deficient olefins with the Michael-initiated ring closure (MIRC) strategy.[2] Various ylides including sulfonium,[3] telluronium,[4] ammonium[5] and arsonium ylides[6] have been successfully applied in the enantioselective cyclopropanation of electron-deficient olefins. On the other hand, as an important type of electron-deficient olefins, α,β-unsaturated aldehydes had remained a challenging target for enantioselective cyclopropanation until the development of a procedure involving stabilized sulfonium ylides and chiral amines[7] as the catalyst by MacMillan et al.[8] Thereafter, Arvidsson[9] developed (*S*)-(−)-indoline-2-yl-1H-tetrazole and novel aryl sulfonamides derived from L-proline as catalysts for this transformation, while Wang[10] and Córdova[11] reported that chiral amine catalyzed cyclopropanation reaction between halomalonates or 2-halo-β-keto esters and enals.

The studies of polymer-supported catalysts have attracted much attention over the past two decades.[12] Dendrimers as well-defined macromolecules with controllable structures have triggered increasing attention on their applications in catalysis, since dendritic catalysts have the advantages of good solubility and can be analyzed with routine spectroscopic techniques.[13] Moreover, the globular shapes of higher generation dendritic catalysts are suitable for either membrane filtration[14] or selective precipitation under specific conditions.[15] Recently, we reported the synthesis of a series of new dendritic catalysts and their application in catalytic asymmetric reactions.[16] As part of our ongoing research projects with regard to dendritic catalysts, we herein report a highly enantio- and diastereoselective cyclopropanation/Wittig reaction of α,β-unsaturated aldehydes with arsonium ylides using the polyether dendritic chiral 2-trimethylsilanyloxy-methyl-pyrrolidine derivative **3b** as a catalyst.

2. Results and discussion

Recently, we accomplished a highly enantioselective cyclopropanation of α,β-unsaturated aldehydes with arsonium ylides via MIRC using diphenylprolinol silylether as a

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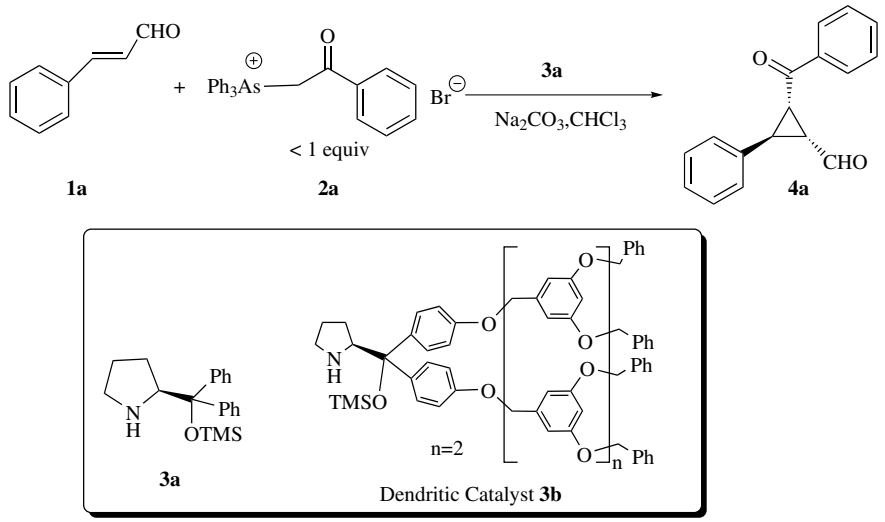
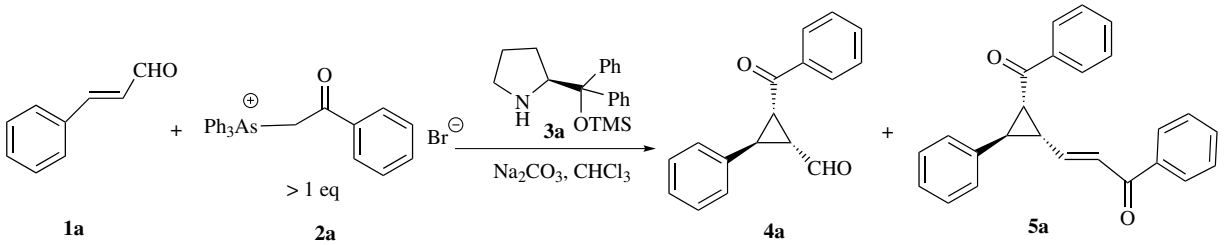


Scheme 1. Organocatalytic asymmetric cyclopropanation of α,β-unsaturated aldehydes with arsonium ylides.

catalyst (Scheme 1).[17] During the process of optimizing the reaction conditions, we isolated new compound **5a** as the major product instead of our desired product **4a** when we increased the amount of arsonium salts to 150 mol % or 200 mol % (Table 1, entries 2 and 3). Preliminary studies revealed that product **4a** could undergo further Wittig type reactions in the presence of excessive arsonium salt to form *E*-**5a**. Various reaction conditions were studied to optimize this tandem cyclopropanation/Wittig reaction, and the results are summarized in Table 1. No product **5** was

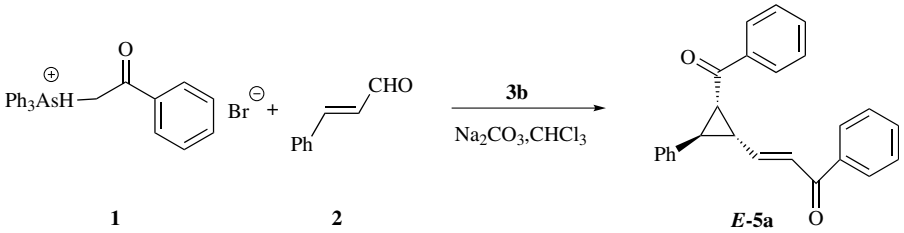
Table 1. Optimization of organocatalytic asymmetric tandem cyclopropanation/Wittig reaction of α,β-unsaturated aldehydes[a]



Entry	Solvent	Arsonium salt (equiv)	Yield[b] (%)		dr[c] (*E*-**5a**)	ee[d] (%) (**4a**/*E*-**5a**)
			4a	*E*-**5a**		
1[e]	$CHCl_3$	1.0	54	0	—	96/—
2[f]	$CHCl_3$	1.5	24	20	30:1	94/95
3	$CHCl_3$	2.0	Trace	60	19:1	—/95
4[g]	$CHCl_3$	2.5	Trace	54	10:1	—/98
5[h]	$CHCl_3$	3.0	—	45	7:1	—/98
6	Toluene	2.0	Trace	70	3:1	—/99
7	DCM	2.0	Trace	84	3:2	—/98
8	CH_3CN	2.0	Trace	65	99:1	—/90
9	EtOH	2.0	Trace	57	99:1	—/93
10	DMF	2.0	Trace	17	5:1	—/95
11	DMSO	2.0	Trace	16	2:1	—/94
12	THF	2.0	Trace	75	5:1	—/98
13	*n*-Hexane	2.0	Trace	77	2:1	—/94
14	DCE	2.0	Trace	41	3:1	—/95
15	DME	2.0	Trace	64	8:1	—/99

[a] See Section 4 for detailed conditions.
[b] Isolated yield.
[c] Determined by chiral HPLC or ^1H NMR analysis.
[d] Determined by chiral HPLC analysis.
[e] Na_2CO_3 0.5 equiv.
[f] Na_2CO_3 0.75 equiv.
[g] Na_2CO_3 1.25 equiv.
[h] Na_2CO_3 1.5 equiv.

Table 2. Tandem cyclopropanation of α,β-unsaturated aldehydes catalyzed by dendritic catalyst[a]



1 **2** ***E*-5a**

Entry	Catalyst (mol %)	Concentration	Yield[b] (%)	dr[c]	ee[d] (%)
1	5	1.0	31	99:1	97
2	10	1.0	60	99:1	98
3	15	1.0	43	99:1	98
4	20	1.0	30	99:1	98
5	10	2.0	34	99:1	98
6	10	0.5	26	99:1	99

[a] See Section 4 for detailed conditions.
[b] Isolated yield.
[c] Determined by chiral HPLC or ^{1}H NMR analysis.
[d] Determined by chiral HPLC analysis.

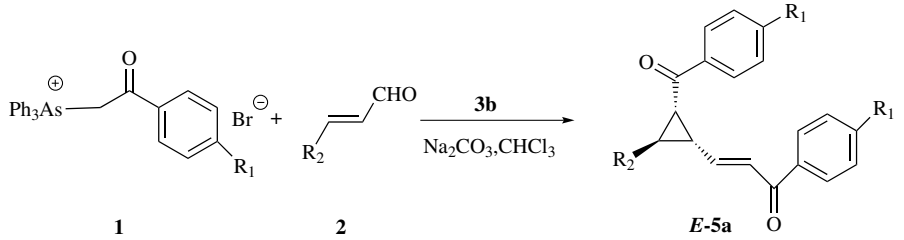
Table 3. Recycling of dendritic catalyst **3b**[a]

Run	Time (h)	Yield[b] (%)	dr[c]	ee[d] (%)
1	24	60	99:1	98
2	24	58	95:5	98
3	24	58	96:4	96
4	24	55	92:8	97

[a] See Section 4 for detailed conditions.
[b] Isolated yield.
[c] Determined by chiral HPLC or ^{1}H NMR analysis.
[d] Determined by chiral HPLC analysis.

observed when 1.0 equiv of arsonium salt was used (Table 1, entry 1). When increasing the amount of arsonium salt, the amount of product **4a** decreased, along with a gradual increase in the amount of product *E*-**5a**. When the amount of arsonium salt was increased to 2.0 equiv, product **4a** disappeared and only product *E*-**5a** was isolated in 60% yield with 95% ee (Table 1, entry 3). Increasing the concentration of base, the ee values remained almost the same, but the diastereoselectivity decreased dramatically (Table 1, entries 2–5). A study of the solvent effect revealed that chloroform was optimal for this tandem process. The reaction

Table 4. Scope of the organocatalytic enantioselective cyclopropanation reaction of α,β-unsaturated aldehydes[a]



1 **2** ***E*-5a**

Entry	R_1	R_2	Product (*E*-)	Yield[b] (%)	dr[c]	% ee[d]
1	H	Ph	**5a**	60	99:1	98
2	F	Ph	**5b**	56	91:1	99
3	Cl	Ph	**5c**	64	80:20	99
4	Br	Ph	**5d**	70	83:17	93
5	Me	Ph	**5e**	86	93:7	99
6	MeO	Ph	**5f**	68	95:5	94
7	H	4-$MeOC_6H_4$	**5g**	60	98:2	92
8	Br	4-$MeOC_6H_4$	**5h**	73	74:26	87
9	H	Me	**5i**	51	90:10	71
10	H	*n*-Pr	**5j**	61	92:8	80

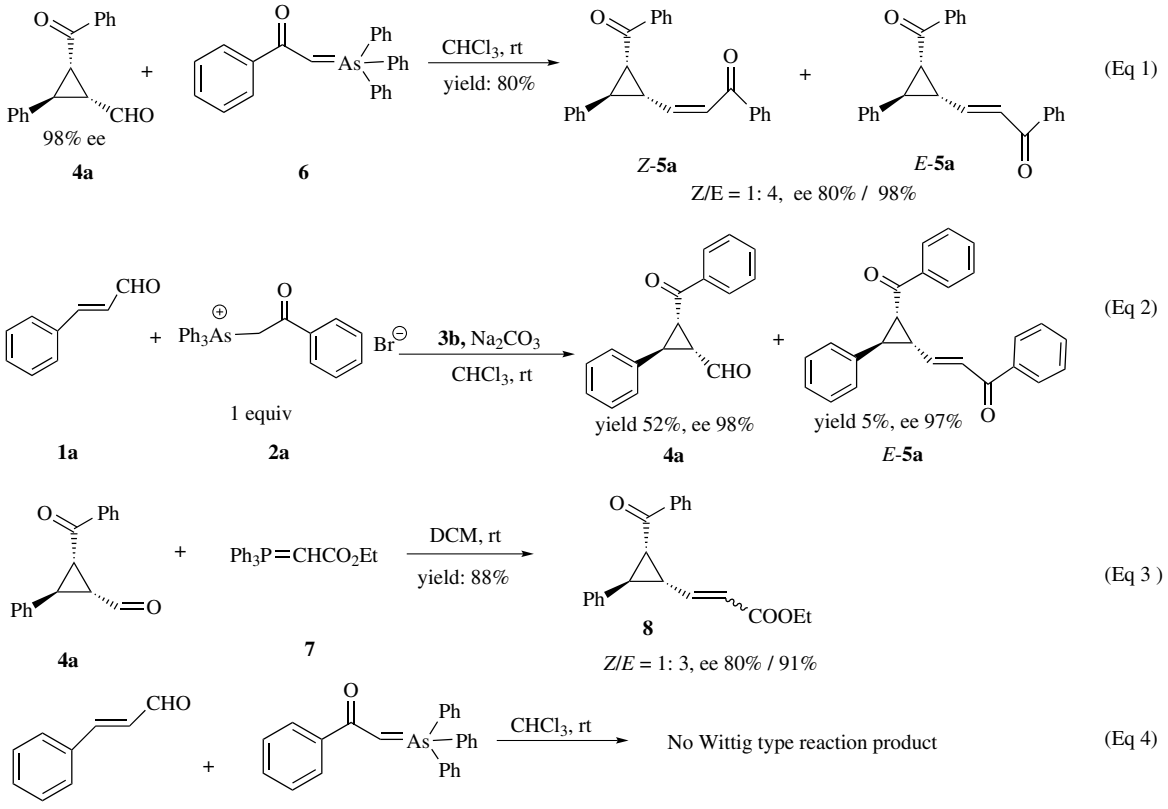
[a] See Section 4 for detailed conditions.
[b] Isolated yield.
[c] Determined by chiral HPLC or ^{1}H NMR analysis.
[d] Determined by chiral HPLC analysis.

performed with 20 mol % catalyst **3a**, 100 mol % cinnamaldehyde, 200 mol % arsonium salt, and 100 mol % sodium carbonate in chloroform gave a good result providing product *E*-**5a** in 60% yield with up to 95% ee and a good dr value (19:1).

For the sake of comparison, we became interested in the study of using dendritic catalyst **3b** instead of organocatalyst **3a**. As shown in Table 2, the reactions catalyzed by dendritic catalyst **3b** were more efficient than homogeneous catalyst **3a** with higher stereoselectivities (98–99% ee and almost single diastereomer) and required less catalyst loading. Most importantly, we only obtained the *E*-isomer of **5a**. These experiments showed that 10 mol % catalyst loading was the optimal amount, which provided products *E*-**5a** in high enantiomeric excess (98%) and excellent diastereomeric excess (99:1). Increasing or decreasing the concentration of the reaction system resulted in low yields (Table 2, entries 5 and 6). As mentioned above, the most important advantage of the dendritic catalyst is that it could be recovered easily. After the reaction completed, dry methanol was added to the reaction mixture. Catalyst **3b** precipitated and was recovered almost quantitatively after filtration. As shown in Table 3, the recovered catalyst was reused for at least four times almost without any loss in activity.

Under the optimized reaction conditions, the scope of this asymmetric tandem cyclopropanation catalyzed by dendritic catalyst **3b** was investigated extensively. The results are summarized in Table 4. Generally, the reactions provided the cyclopropane products in moderate to good yields and excellent ee values. For example, arsonium salts **1** bearing electron-donating groups (EDG) (R_1 = EDG) gave the corresponding cyclopropanes **5** in good yields (entries 5 and 6), while arsonium salts **1** bearing electron-withdrawing groups (EWG) (R_1 = EWG) usually provided slightly lower yields of cyclopropanes **5** (Table 3, entries 2–4). In addition, as shown in Table 4, the reactions of aromatic α,β-unsaturated aldehyde worked well to provide the corresponding products with high enantioselectivities (93–99% ee, entries 1–7), while the use of crotonaldehyde as a substrate resulted in low yield and with moderate enantioselectivity (71% ee, entry 7). The absolute configuration of **5f** is determined unambiguously as *E*-3-(1*R*,2*R*,3*R*) by X-ray diffraction (Fig. 1).[18]

In our previous report,[17] a reasonable mechanism was proposed for explaining the Wittig type[19] cyclopropanation. In order to confirm that this tandem cyclopropanation product **5a** was generated from intermediate **4a**, several experiments were performed using intermediate **4a** as a reactant (Eqs. 1–4; Scheme 2). Cyclopropyl aldehyde **4a** reacted with an arsonium ylide to afford a mixture of *Z* and *E*-isomers **5**a in good yields and with high ee values. We believe that the dendritic catalyst performs some effects on the stereoselectivity of the reaction procedure. While a Wittig reaction product was not observed in the reaction of cinnamaldehyde and arsonium ylide. Cyclopropyl aldehyde **4a** can also react with a phosphonium ylide to provide β-cyclopropyl-α,β-unsaturated ester **8** in excellent yield and



Scheme 2. The Wittig reaction of cyclopropyl aldehydes with arsonium ylides.

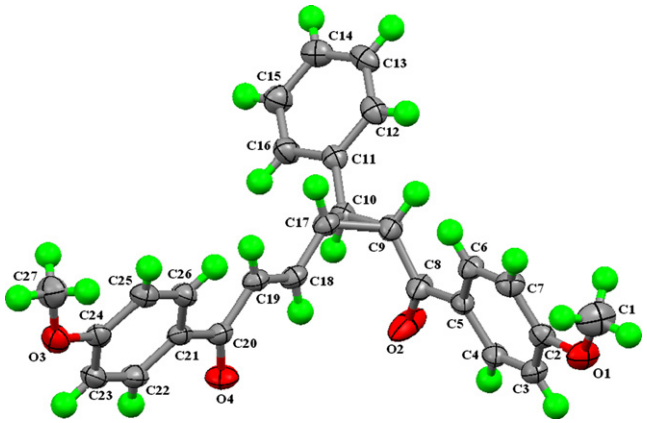


Figure 1. X-ray crystal structure of *E*-**5f**.

with good ee value. These results clearly indicated that **4a** was the intermediate of this reaction to afford product **5a**.

3. Conclusion

We have developed a novel tandem cyclopropanation of α,β-unsaturated aldehydes using a chiral 2-trimethylsilanyloxy-methyl-pyrrolidine-based dendrimer **3b** as the catalyst. The reactions were carried out under mild conditions and provided the corresponding cyclopropanes *E*-**5** with excellent enantioselectivities. The dendritic catalyst is recoverable and reusable without any loss in activity. Further applications of this new process in asymmetric synthesis are currently in progress.

4. Experimental

4.1. General

Analytical TLC was performed on precoated silica gel plates. Column chromatography was conducted with 300–400 mesh silica gel. NMR spectra were recorded at 400 MHz for ^{1}H NMR using $SiMe_4$ as an internal standard in $CDCl_3$ and 100 MHz for ^{13}C NMR. Enantiomeric excesses were determined by chiral HPLC analysis. Optical rotations were measured on a JASCO 1030 polarimeter. All solvents were used directly without further purification.

4.2. General procedure for the organocatalytic asymmetric cyclopropanation

Dendritic Catalyst (36 mg, 0.02 mmol) was added to a solution of α,β-unsaturated aldehydes (0.2 mmol) in chloroform ($CHCl_3$, 4 mL) and the mixture was stirred for about 30 min at room temperature. Then, 0.4 mmol of the arsonium salts and sodium carbonate (21.2 mg, 0.2 mmol) were added to the reaction mixture. The mixture was stirred at room temperature for 24 h until the starting material disappeared. The mixture was then treated with methanol (5 mL) and filtered. The dendritic catalyst was washed several times with methanol and 31 mg (86%) catalyst was recovered; the filtrate was concentrated at the reduced pressure. Then, H_2O (5 mL) was added to the reaction mixture and extracted with DCM (3 × 10 mL). The combined organic solution was washed with the saturated NaCl solution, dried over anhydrous Na_2SO_4 and concentrated at reduced pressure. The crude product was purified by column chromatography (silica, 12:1 hexane/EtOAc) to afford the pure product **5**.

4.3. (*E*)-3-((1*R*,2*R*,3*R*)-2-Benzoyl-3-phenylcyclopropyl)-1-phenylprop-2-en-1-one *E*-5a

White solid, mp 146–147 °C (EtOAc–hexane), $[\alpha]_D^{25} = -36.0$ (*c* 1.0, $CHCl_3$). IR (film) 3060, 1668, 1608, 1579, 1448, 1372, 1260, 1227, 1177, 1007, 740, 695 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 8.14 (d, $J = 8.7$ Hz, 2H), 7.98 (d, $J = 8.7$ Hz, 2H), 7.70–7.12 (m, 13H), 3.66–3.61 (dd, $J = 6.0$, 5.7 Hz, 1H), 3.48 (t, $J = 6.0$, 9.0 Hz, 1H), 2.68 (ddd, $J = 6.0$, 6.0, 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 195.5, 190.5, 145.3, 138.8, 138.0, 137.9, 133.5, 132.8, 129.0, 128.9, 128.8, 128.7, 128.5, 127.6, 127.3, 126.7, 36.9, 36.3, 34.1; MS *m*/*z* 353.3 (M^++1); Elemental Anal. Calcd for $C_{25}H_{20}O_2$: C 85.20, H 5.72; Found: C 84.98, H 6.04. The enantiomeric ratio was determined by HPLC analysis using a Chiracel OD-H column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 1.0 mL/min); $t_{major} = 14.3$ min, $t_{minor} = 17.0$ min.

4.4. (*Z*)-3-((1*R*,2*R*,3*R*)-2-Benzoyl-3-phenylcyclopropyl)-1-phenylprop-2-en-1-one *Z*-5a

White solid, mp 130–131 °C (EtOAc–hexane), $[\alpha]_D^{25} = +81.3$ (*c* 1.0, $CHCl_3$). IR (film) 3053, 1655, 1609, 1578, 1448, 1416, 1364, 1335, 1262, 1225, 1172, 1009, 734, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) 8.02 (d, $J = 8.7$ Hz, 2H), 7.91 (d, $J = 8.7$ Hz, 2H), 7.54–7.26 (m, 11H), 6.92 (d, $J = 12.0$ Hz, 1H), 6.53–6.45 (dd, $J = 10.5$, 11.7 Hz, 1H), 4.22–4.14 (ddd, $J = 6.3$, 5.7, 9.3 Hz, 1H), 3.49–3.44 (dd, $J = 5.7$, 9.3 Hz, 1H), 3.32–3.28 (t, $J = 5.7$, 6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 196.7, 191.8, 145.4, 138.9, 138.1, 133.4, 133.0, 128.9, 128.8, 128.6, 128.5, 127.2, 127.0, 124.9, 37.4, 35.3, 33.5; MS *m*/*z* 375.2 (M^++Na); Elemental Anal. Calcd for $C_{25}H_{20}O_2$: C 85.20, H 5.72; Found: C 85.04, H 6.08. The enantiomeric ratio was determined by HPLC analysis using a Chiracel OD column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 0.75 mL/min); $t_{major} = 25.4$ min, $t_{minor} = 37.6$ min.

4.5. (*E*)-3-((1*R*,2*R*,3*R*)-2-(4-Fluorobenzoyl)-3-phenylcyclopropyl)-1-(4-fluorophenylprop)-2-en-1-one *E*-5b

White solid, mp 108–110 °C (EtOAc–hexane), $[\alpha]_D^{25} = +7.7$ (*c* 1.0, $CHCl_3$). IR (film) 3070, 2926, 1669, 1599, 1507, 1422, 1338, 1262, 1229, 1156, 1009, 753, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.07–8.03 (dd, $J = 3.3$, 6.6 Hz, 2H), 7.93–7.88 (dd, $J = 5.4$, 8.7 Hz, 2H), 7.38–6.99 (m, 11H), 3.48–3.43 (dd, $J = 6.0$, 9.0 Hz, 1H), 3.36–3.32 (t, J=5.7, 6.0 Hz, 1H), 2.81–2.73 (ddd, $J = 5.7$, 6.0, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 193.5, 188.4, 167.2, 164.2, 144.9, 138.4, 134.1, 131.9, 131.1, 130.9, 128.8, 128.7, 127.2, 115.7, 115.5, 115.4, 36.4, 35.9, 33.9; LRMS (ESI) *m*/*z* 389.2 (M^++1); HRMS (ESI) 411.1169 $[M+Na]^+$ calcd for $C_{25}H_{18}F_2O_2Na^+$ 411.1167. The

enantiomeric ratio was determined by HPLC analysis using a Chiracel OD-H column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 1 mL/min); $t_{major} = 15.1$ min, $t_{minor} = 19.8$ min.

4.6. (*E*)-3-((1*R*,2*R*,3*R*)-2-(4-Chlorobenzoyl)-3-phenylcyclopropyl)-1-(4-chlorophenylprop)-2-en-1-one 5c

White solid, mp 140–141 °C (EtOAc–hexane), $[\alpha]_D^{25} = -21.3$ (*c* 1.0, $CHCl_3$). IR (film) 3071, 2920, 1667, 1606, 1588, 1558, 1424, 1336, 1260, 1229, 1093, 1009, 757, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.96 (d, $J = 8.1$ Hz, 2H), 7.81 (d, $J = 8.1$ Hz, 2H), 7.47–6.98 (m, 11H), 3.48–3.43 (dd, $J = 6.0$, 9.0 Hz, 1H), 3.36–3.32 (t, $J = 5.7$, 6.0 Hz, 1H), 2.81–2.73 (ddd, $J = 5.7$, 6.0, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 193.9, 188.7, 145.2, 139.8, 139.1, 138.2, 136.1, 130.0, 129.8, 129.1, 129.0, 128.9, 128.8, 127.2, 127.0, 126.4, 36.5, 35.9, 34.8; LRMS (ESI) *m*/*z* 421.2 (M^++1); HRMS (ESI) 421.0765 $[M+H]^+$ calcd for $C_{25}H_{18}Cl_2O_2H^+$ 421.0757. The enantiomeric ratio was determined by HPLC analysis using a Chiracel OD-H column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 1 mL/min); $t_{major} = 17.4$ min, $t_{minor} = 35.1$ min.

4.7. (*E*)-3-((1*R*,2*R*,3*R*)-2-(4-Bromobenzoyl)-3-phenylcyclopropyl)-1-(4-bromophenylprop)-2-en-1-one *E*-5d

White solid, mp 158–160 °C (EtOAc–hexane), $[\alpha]_D^{25} = -31.2$ (*c* 1.0, $CHCl_3$). IR (film) 3068, 2921, 1666, 1605, 1583, 1505, 1418, 1259, 1228, 1176, 1071, 1007, 755, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.89–7.86 (d, $J = 8.7$ Hz, 2H), 7.75–7.72 (d, $J = 8.7$ Hz, 2H), 7.63–6.97 (m, 11H), 3.47–3.42 (dd, $J = 6.0$, 9.0 Hz, 1H), 3.36–3.32 (t, $J = 5.7$, 6.0 Hz, 1H), 2.81–2.73 (ddd, $J = 5.7$, 6.0, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 194.2, 188.9, 145.2, 138.2, 136.5, 136.4, 132.2, 132.0, 131.8, 130.1, 129.7, 128.8, 127.7, 127.2, 127.0, 126.4, 36.6, 35.9, 34.2; LRMS (ESI) *m*/*z* 511.2 (M^++1); HRMS (ESI) 508.9739 $[M+H]^+$ calcd for $C_{25}H_{18}Br_2O_2H^+$ 508.9746. The enantiomeric ratio was determined by HPLC analysis using a Chiracel AD column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 1 mL/min); $t_{major} = 63.5$ min, $t_{minor} = 54.9$ min.

4.8. (*E*)-3-((1*R*,2*R*,3*R*)-2-(4-Methylbenzoyl)-3-phenylcyclopropyl)-1-(4-methylphenylprop)-2-en-1-one *E*-5e

White solid, mp 129–130 °C (EtOAc–hexane), $[\alpha]_D^{25} = -10.2$ (*c* 1.0, $CHCl_3$). IR (film) 3031, 2919, 2852, 1661, 1608, 1568, 1557, 1423, 1373, 1337, 1264, 1228, 1175, 1009, 733, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.93 (d, $J = 8.1$ Hz, 2H), 7.77 (d, $J = 8.1$ Hz, 2H), 7.36–6.98 (m, 11H), 3.50–3.45 (dd, $J = 6.0$, 9.0 Hz, 1H), 3.35–3.32 (t, $J = 5.7$, 6.0 Hz, 1H), 2.77–2.69 (ddd, $J = 5.7$, 6.0, 9.0 Hz, 1H), 2.40 (s, 1H), 2.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 194.6, 189.8, 144.6, 144.1, 143.3, 138.8, 135.3, 129.5, 129.3, 129.0, 128.7, 128.6, 128.4, 127.4, 127.0, 126.5, 36.5, 35.9, 33.6, 21.6; LRMS (ESI) *m*/*z* 381.2 (M^++1); HRMS (ESI) 381.1853 $[M+H]^+$ calcd for $C_{27}H_{24}O_2H^+$ 381.1849. The enantiomeric ratio was determined by HPLC analysis using a Chiracel AD column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 1 mL/min); $t_{major} = 55.2$ min, $t_{minor} = 38.2$ min.

4.9. (*E*)-3-((1*R*,2*R*,3*R*)-2-(4-Methoxylbenzoyl)-3-phenylcyclopropyl)-1-(methoxylphenylprop)-2-en-1-one *E*-5f

White solid, mp 129–131 °C (EtOAc–hexane), $[\alpha]_D^{25} = 55.2$ (*c* 1.0, $CHCl_3$). IR (film) 3050, 2918, 2848, 1660, 1601, 1575, 1506, 1455, 1428, 1339, 1255, 1223, 1169, 1030 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.03 (d, $J = 8.7$ Hz, 2H), 7.90 (d, $J = 8.7$ Hz, 2H), 7.31–6.84 (m, 11H), 4.16–4.09 (ddd, $J = 5.7$, 6.0, 9.0 Hz, 1H), 4.07 (s, 3H), 3.85 (s, 3H), 3.42–3.37 (dd, $J = 6.0$, 9.0 Hz, 1H), 3.28–3.23 (t, $J = 5.7$, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 194.6, 190.3, 171.7, 163.6, 163.3, 144.3, 139.1, 131.6, 131.0, 130.6, 128.6, 126.8, 126.0, 124.6, 114.2, 113.8, 55.5, 55.4, 36.8, 34.6, 32.9; LRMS (ESI) *m*/*z* 413.3 (M^++1); HRMS (ESI) 435.1556 $[M+H]^+$ calcd for $C_{27}H_{24}O_4Na^+$ 435.1566. The enantiomeric ratio was determined by HPLC analysis using a Chiracel AD-H column (23 °C, 254 nm, 60:40 hexanes/2-propanol, 0.7 mL/min); $t_{major} = 39.8$ min, $t_{minor} = 34.6$ min.

4.10. (*E*)-3-((1*R*,2*R*,3*R*)-2-Benzoyl-3-(4-methoxylphenyl)-cyclopropyl)-1-phenylprop-2-en-1-one *E*-5g

White solid, mp 128–130 °C (EtOAc–hexane), $[\alpha]_D^{25} = -10.2$ (*c* 1.0, $CHCl_3$). IR (film) 3031, 2919, 2852, 1661, 1608, 1568, 1557, 1423, 1373, 1337, 1264, 1228, 1175, 1009, 733, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.01 (d, $J = 8.7$ Hz, 2H), 7.86 (d, $J = 8.7$ Hz, 2H), 7.84–6.86 (m, 12H), 3.80 (s, 1H), 3.47–3.42 (dd, $J = 6.0$, 9.0 Hz, 1H), 3.33–3.29 (t, $J = 5.7$, 6.0 Hz, 1H), 2.75–2.67 (ddd, $J = 5.7$, 6.0, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 195.3, 190.3, 158.8, 145.3, 137.8, 133.2, 132.5, 130.6, 130.1, 128.8, 128.5, 128.4, 128.2, 127.6, 127.3, 114.2, 55.4, 36.5, 35.9, 33.5; LRMS (ESI) *m*/*z* 383.2 (M^++1); HRMS (ESI) 383.1645 $[M+H]^+$ calcd for $C_{26}H_{22}O_3H^+$ 383.1642. The enantiomeric ratio was determined by HPLC analysis using a Chiracel OD-H column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 1 mL/min); $t_{major} = 14.8$ min, $t_{minor} = 16.2$ min.

4.11. (*E*)-3-((1*R*,2*R*,3*R*)-2-(4-Bromobenzoyl)-3-(4-methoxylphenyl)-cyclopropyl)-1-(4-bromo-phenylprop)-2-en-1-one *E*-5h

White solid, mp 135–136 °C (EtOAc–hexane), $[\alpha]_D^{25} = -29.7$ (*c* 1.0, $CHCl_3$). IR (film) 3060, 2926, 2819, 1665, 1604, 1583, 1514, 1446, 1335, 1260, 1222, 1175, 1071, 1005, 657 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.88 (d, $J = 8.4$ Hz, 2H), 7.74 (d, $J = 8.4$, Hz, 2H), 7.63–7.56 (dd, $J = 9.0$, 11.4 Hz, 4H), 7.26–6.86 (m, 6H), 3.80 (s, 1H), 3.40–3.35 (dd, $J = 6.0$, 9.0 Hz, 1H), 3.31–3.27 (t, $J = 5.7$, 6.0 Hz, 1H), 2.75–2.67 (ddd, $J = 5.7$, 6.0, 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 194.3, 189.0, 158.9, 145.5, 136.5, 136.4, 132.0, 131.8, 130.2, 130.1, 129.7, 128.5, 127.7, 127.6, 126.9, 114.2, 55.4, 36.5, 35.9, 33.8; LRMS (ESI) *m*/*z* 541.1 (M^++1); HRMS (ESI) 538.9848 $[M+H]^+$ calcd for $C_{26}H_{20}Br_2O_3H^+$ 538.9852. The enantiomeric ratio was determined by HPLC analysis using a Chiracel OD-H column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 0.7 mL/min); $t_{major} = 20.1$ min, $t_{minor} = 33.2$ min.

4.12. (*E*)-3-((1*R*,2*R*,3*R*)-2-Benzoyl-3-methyl-cyclopropyl)-1-phenylprop-2-en-1-one 5i

White solid, mp 114–115 °C (EtOAc–hexane), $[\alpha]_D^{25} = -22.2$ (*c* 1.0, $CHCl_3$). IR (film) 3060, 2961, 2924, 2852, 1665, 1605, 1578, 1514, 1449, 1375, 1333, 1263, 1228, 1169, 993, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.96 (d, $J = 8.7$ Hz, 2H), 7.83 (d, $J = 8.7$ Hz, 2H), 7.58–7.39 (m, 6H), 6.97–6.94 (m, 2H), 2.94 (t, $J = 6.6$, 7.2 Hz, 1H), 2.25–2.21 (m, 1H), 1.31 (d, $J = 5.4$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 196.3, 190.5, 146.6, 138.1, 133.5, 132.9, 132.4, 128.8, 128.6, 128.4, 128.3, 126.9, 36.3, 35.9, 25.2, 17.5; LRMS (ESI) *m*/*z* 291.2 (M^++1); HRMS (ESI) 313.1202 $[M+Na]^+$ calcd for $C_{20}H_{18}O_2Na^+$ 313.1199. The enantiomeric ratio was determined by HPLC analysis using a Chiracel AD column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 1 mL/min); $t_{major} = 17.9$ min, $t_{minor} = 21.9$ min.

4.13. (*E*)-3-((1*R*,2*R*,3*R*)-2-Benzoyl-3-propyl-cyclopropyl)-1-phenylprop-2-en-1-one *E*-5j

White solid, mp 140–141 °C (EtOAc–hexane), $[\alpha]_D^{25} = -33.2$ (*c* 1.0, $CHCl_3$). IR (film) 3063, 2954, 2923, 2872, 1686, 1664, 1603, 1578, 1554, 1449, 1374, 1267, 1223, 1014, 996, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.99 (d, $J = 7.2$ Hz, 2H), 7.83 (d, $J = 7.2$, Hz, 2H), 7.56–7.39 (m, 6H), 6.99–6.90 (m, 2H), 2.99–2.94 (dd, $J = 6.6$, 8.7 Hz, 1H), 2.28–2.22 (m, 2H), 1.54–1.48 (m, 4H), 0.95 (t, $J = 6.6$, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 196.3, 190.5, 146.7, 138.1, 137.9, 132.9, 132.4, 128.6, 128.4, 128.1, 126.8, 35.3, 34.9, 34.4, 30.7, 22.0, 13.8; LRMS (ESI) *m*/*z* 319.2 (M^++1); HRMS (ESI) 341.1510 $[M+Na]^+$ calcd for $C_{22}H_{22}O_2Na^+$ 341.1512. The enantiomeric ratio was determined by HPLC analysis using a Chiracel AD column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 1 mL/min); $t_{major} = 32.6$ min, $t_{minor} = 23.7$ min.

4.14. Preparation of ethyl 3-(1*R*,2*R*,3*R*)-2-benzoyl-3-phenyl-cyclopropyl acrylate 8

Phosphonium ylide **7** (0.12 mmol) was added to a solution of cycloproyl aldehyde **4a** (0.1 mmol) in DCM (1 mL) and the mixture was stirred for 4 h at room temperature. The reaction was monitored by TLC. After completion, the solution was concentrated at the reduced pressure. The crude product was purified by column chromatography (silica, 12:1 hexane/EtOAc) to give product **8a** (in 66% yield) and **8b** (in 22% yield).

4.15. Ethyl (*E*)-3-(1*R*,2*R*,3*R*)-2-benzoyl-3-phenyl-cyclopropyl acrylate *E*-8a

White solid, mp 102–104 °C (EtOAc–hexane), $[\alpha]_D^{25} = -38.5$ (*c* 1.0, $CHCl_3$). IR (film) 2918, 1710, 1671, 1648, 1641, 1597, 1449, 1367, 1251, 1227, 1172, 1133, 1035, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 8.01 (d, $J = 7.8$ Hz, 2H), 7.58–6.99 (m, 9H), 6.05–5.99 (d, $J = 15.9$ Hz, 1H), 4.17–4.12 (m, 2H), 3.46–3.41 (dd, $J = 6.0$, 8.7 Hz, 1H), 3,28 (t, $J = 5.7$, 6.3 Hz, 1H), 2.66–2.63 (dd, $J = 5.4$, 9.0 Hz, 1H), 1.26 (t, $J = 7.2$, 14.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 195.4, 165.9, 144.1, 138.5, 137.7, 133.2, 128.7, 128.6, 128.2, 127.0, 126.4, 122.7, 60.3, 35.9, 35.5, 33.6, 14.2; LRMS (ESI) *m*/*z* 321.1 (M^++1); HRMS (EI) exact mass calcd for ($C_{21}H_{20}O_3$) requires *m*/*z* 320.1412, found *m*/*z* 320.1402. The enantiomeric ratio was determined by HPLC analysis using a Chiracel OD column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 0.75 mL/min); $t_{major} = 28.5$ min, $t_{minor} = 23.9$ min.

4.16. Ethyl (*Z*)-3-(1*R*,2*R*,3*R*)-2-benzoyl-3-phenyl-cyclopropyl acrylate *Z*-8b

White solid, mp 96–98 °C (EtOAc–hexane), $[\alpha]_D^{25} = +44.4$ (*c* 1.0, $CHCl_3$). IR (film) 2924, 2853, 1718, 1670, 1648, 1642, 1588, 1570, 1449, 1371, 1252, 1227, 1185, 1136, 1035, 737, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 8.05 (d, $J = 7.2$ Hz, 2H), 7.65–7.29 (m, 8H), 6.49–6.40 (dd, $J = 10.8$, 15.6 Hz, 1H), 6.07 (d, $J = 15.6$ Hz, 1H), 4.16–4.09 (dd, $J = 6.6$, 14.1 Hz, 2H), 3.41–3.34 (m, 2H), 2.81–2.73 (ddd, $J = 4.5$, 10.5, 13.8 Hz, 1H), 1.23 (t, $J = 7.2$, 14.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 197.0, 165.9, 145.1, 137.3, 135.3, 133.4, 128.9, 128.7, 128.6, 128.1, 127.3, 122.7, 60.2, 35.6, 34.1, 32.3, 14.2; LRMS (ESI) *m*/*z* 321.1 (M^++1); HRMS (EI) exact mass calcd for ($C_{21}H_{20}O_3$) requires *m*/*z* 320.1412, found *m*/*z* 320.1402. The enantiomeric ratio was determined by HPLC analysis using a Chiracel OD column (23 °C, 254 nm, 80:20 hexanes/2-propanol, 0.75 mL/min); $t_{major} = 21.8$ min, $t_{minor} = 18.1$ min.

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