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Chiral Biscinchona Alkaloid Promoted Asymmetric Allylic Alkylation of 3-Substituted Benzofuran-2(3*H*)-ones with Morita–Baylis–Hillman Carbonates

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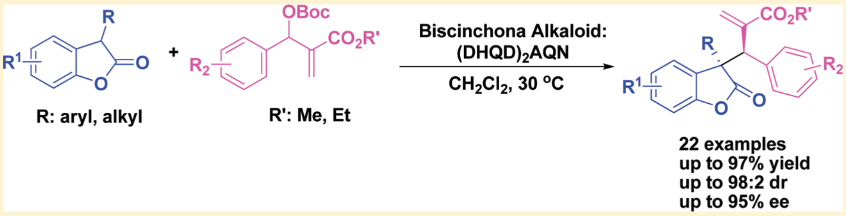
S *Supporting Information*

ABSTRACT:



A highly diastereo- and enantioselective asymmetric allylic alkylation reaction with respect to prochiral 3-substituted benzofuran-2(3*H*)-ones and MBH carbonate by a chiral biscinchona alkaloid catalyst was investigated. The corresponding adducts, containing a quaternary center at the C3-position of the benzofuran-2(3*H*)-one as well as a vicinal tertiary center, were generally obtained in high yields (up to 97%) with very good diastereo- (up to 98:2 dr) and enantioselectivities (up to 95% ee).

The 3,3′-disubstituted benzofuran-2(3*H*)-ones are important targets for asymmetric synthesis because of their significance in biological applications. A number of naturally occurring compounds that exhibit interesting medicinal properties contain chiral quaternary centers at the 3 position of the benzofuran-2(3*H*)-ones.[1−7] As a result, more and more efforts have been attracted to the total synthesis of corresponding benzofuran-2(3*H*)-ones type compounds in recent years.[8] Owing to its importance and versatility in the synthesis of these natural products and related analogues, a direct and valuable strategy for asymmetric synthesis of 3,3′-disubstituted benzofuran-2(3*H*)-ones framework is strongly desired. However, corresponding study for the synthesis of chiral 3,3′-disubstituted benzofuran-2(3*H*)-ones have been scarcely reported. To the best of our knowledge, only two bifunctional thiourea catalyzed Michael additions of 3-substituted benzofuran-2(3*H*)-ones with different electrophiles and two cascade reactions leading to enantiomerically pure spirocyclic benzofuranones have been devised.[9]

Asymmetric allylic alkylation (AAA) is one of the most widely used reactions that hold much promise for simplifying asymmetric total syntheses.[10] As a result, a great deal of efforts toward this strategy have been successfully attempted over the past decades.[11−13] Despite these advancements, very few allylic alkylation reactions allow the efficient stereocontrol in the process when two adjacent quaternary-tertiary stereogenic centers are created.

In recent years, catalytic α-allylic alkylation, in which MBH products were used as electrophile source, has been realized with a wide range of carbonyl compounds.[14] In this field of work, Chen has made a great contribution.[14g−m] Accordingly, many useful carbonyl type compounds, for example, oxindole[14h] and butenolide,[14i] have been successfully used as nucleophiles to realized the AAA strategy by Chen's group. Based on the above-mentioned work,[14h,i] we envisioned that the analogous transformation employing 3-substituted benzofuran-2(3*H*)-ones as nucleophiles could also be developed. This process would allow for the construction of a C−C bond at C3 in a catalytic fashion with the generation of two adjacent quaternary-tertiary stereogenic centers of benzofuran-2(3*H*)-ones. Owing to the synthetic importance of chiral 3,3-disubstituted benzofuran-2(3*H*)-one derivatives and based on our continuing interest in the construction of a structural core including a tetra-substituted stereogenic center by asymmetric catalysis,[9a,b,15] herein we disclose the first AAA reaction of 3-substituted benzofuran-2(3*H*)-ones using substituted MBH carbonates as electrophiles. As a result, a new range of chiral 3,3′-disubstituted benzofuran-2(3*H*)-one derivatives bearing vicinal quaternary-tertiary carbon centers were synthesized in high yields and with very good diastereo- and enantioselectivities (Scheme 1).

The key point of the proposed transformation was the selection of a chiral amine base, which can deprotonate the C3 methine proton of 3-substituted benzofuran-2(3*H*)-one to produce enough reactive enolate to overcome the steric encumbrance at this position. With this target, we initially examined the enantioselective alkylation reaction of 3-phenylbenzofuran-2(3*H*)-one **1a** with 2.0 equiv of Boc-protected MBH product **2a** in dichloromethane in the presence of some widely used natural cinchona alkaloids[16] **4a−d** (10 mol %) (Figure 1). Although the desired product **3a** can be isolated, unfortunately, very poor yields and only moderate selectivities of the product

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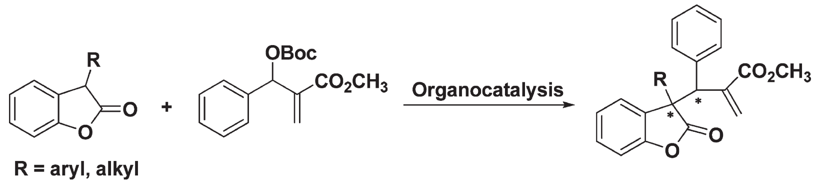
Scheme 1. AAA strategy of 3-Substituted Benzofuran-2(3*H*)-one



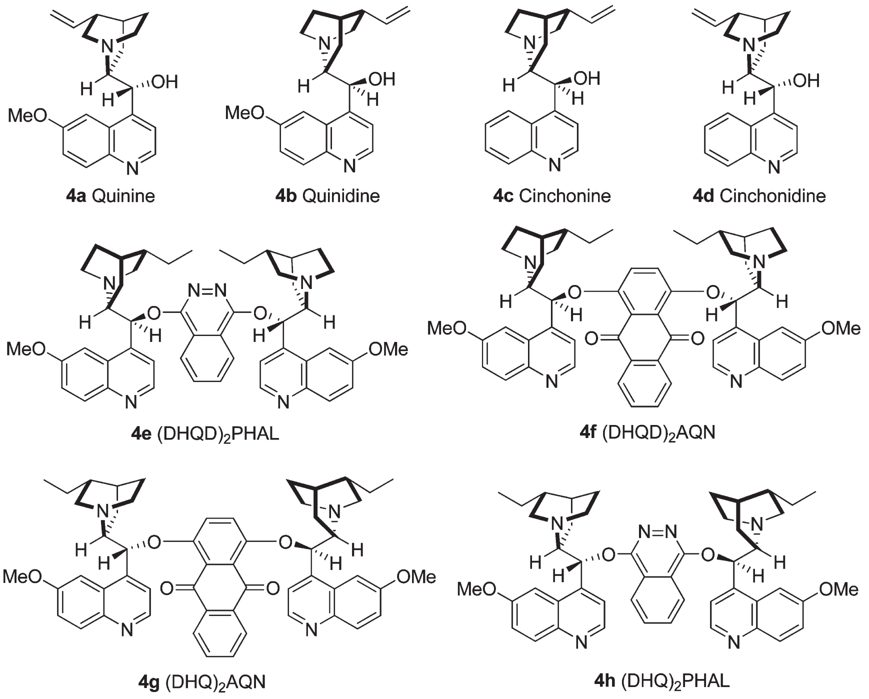


Figure 1. Catalysts screened in this study.

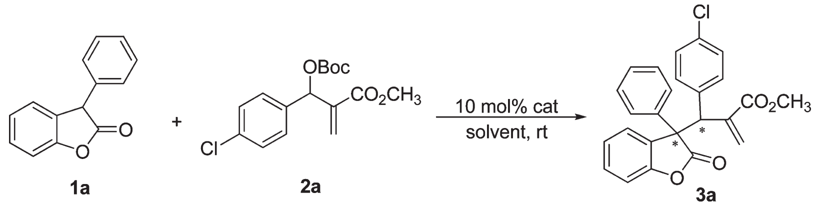
were obtained (entries 1−4 in Table 1). Four biscinchona alkaloids, **4e**−**h**[14g−m] (Figure 1), were screened for this reaction in the following test. To our delight, the catalysts exhibited high catalytic activities, and the alkylation products were isolated with very good yields (80−92%). Furthermore, the diastereoselectivities and enantioselectivities were also improved (entries 5−8 in Table 1). Among the catalysts tested, catalyst **4f** was found to give the optimal enantioselectivity (90% yield, 93:7 dr and 95% ee, entry 6 in Table 1).

Next, the influence of solvents was extensively studied. Interestingly, though different solvents were examined in the reaction of **1a** and **2a** with **4f**, very little change of the enantioinduction was observed, in which the enantioselectivities ranged from 90% to 95% ee for all of the test solvent systems (entries 6 and 9−14 in Table 1). With respect to both yield and stereoselectivity, the initial selected CH_2Cl_2 gives the best result yet (entry 6 in Table 1). When the reaction was catalyzed by **4f** at 30 °C, the yield was slightly increased (entry 15 in Table 1), and the results could not be further improved by adding 4 Å molecular sieves (24 h, 90% yield, 92:8 dr and 95% ee, entry 16 in Table 1). Lowering the catalyst loading led to a decrease of yield and enantioselectivity of the product, and a longer reaction time was required (entry 17 in Table 1).

Under the optimized conditions, the substrate scope was next explored (Table 2). First, six different substituted benzofuran-2(3*H*)-ones were investigated. As shown in Table 2 (entries 1−6), the desired allylic-alkylation products **3a**−**3f** were obtained with good to excellent yields (77−95%), very good diastereoselectivities (91:9−98:2 dr), and very good enantioselectivities (92−95% ee). Next, 10 different substituted MBH carbonates were examined in the current studied system (entries 7−16 in Table 2). The reactions were shown to work well with a range of MBH carbonates bearing either electron-withdrawing or electron-donating substituents, in which the corresponding products were obtained in high yields (80−97%), with moderate to very good diastereoselectivities (68:32−98:2 dr) and moderate to very good enantioselectivities (66−93% ee). It is obvious that the stereoselectivities are generally decreased for NO_2 substituted MBH carbonates (entries 13 and 14 in Table 2). A more accurate analysis of these results showed that the *ortho*- or *meta*-substituted MBH carbonates were also less effective in this AAA strategy, in which relatively lower enantioselectivities were obtained with 3-Cl, 3-Br, 3,4-2Cl and 2,4-2Cl substituted MBH carbonates (entries 10, 12, 15, and 16 in Table 2).

With the aim to expand the current synthetic strategy, reactions of ethyl MBH carbonate as electrophile to react with **1a** and **1c** were attempted in this study. To our delight, the examined two reactions did proceed smoothly and provided the desired products in very good yields with very good selectivities (Scheme 2, 92% yield, 91:9 dr and 94% ee for **3q**; 90% yield,

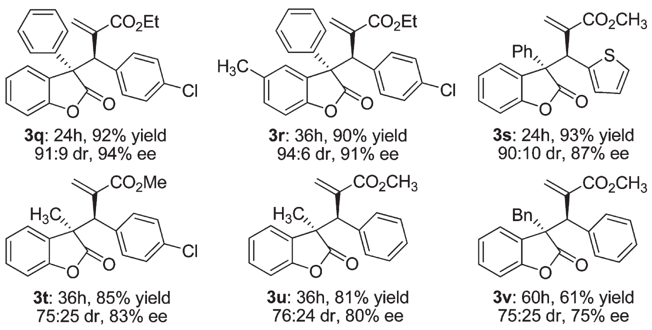
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	solvent	time (h)	yield[b] (%)	dr[c]	ee[d] (%)
1	**4a**	CH_2Cl_2	24	9	73:27	45
2	**4b**	CH_2Cl_2	24	12	80:20	26
3	**4c**	CH_2Cl_2	24	24	60:40	50
4	**4d**	CH_2Cl_2	24	15	77:23	47
5	**4e**	CH_2Cl_2	24	80	56:44	78
6	**4f**	CH_2Cl_2	24	90	93:7	95
7	**4g**	CH_2Cl_2	24	92	82:18	76
8	**4h**	CH_2Cl_2	24	83	59:41	43
9	**4f**	$CHCl_3$	24	80	89:11	94
10	**4f**	DCE	24	79	89:11	93
11	**4f**	benzene	24	40	87:13	96
12	**4f**	THF	24	49	84:16	94
13	**4f**	toluene	24	47	91:9	95
14	**4f**	CH_3CN	24	30	82:18	90
15[e]	**4f**	CH_2Cl_2	24	95	93:7	95
16[f]	**4f**	CH_2Cl_2	24	90	92:8	95
17[g]	**4f**	CH_2Cl_2	80	81	92:8	93

[a] The reaction was carried out on a 0.1 mmol scale in 500 μL of solvent at room temperature, and the molar ratio of **1a**/**2a** was 1:2. [b] Isolated yield. [c] Determined by HPLC analysis. [d] Determined by chiral HPLC. [e] The reaction was carried out on the general conditions at 30 °C. [f] The reaction was carried out on the general conditions with 4 Å molecular sieves at 30 °C. [g] Catalyst loading was 5 mol %.

Scheme 2. Examination of Other Substrates



3q: 24h, 92% yield
91:9 dr, 94% ee

3r: 36h, 90% yield
94:6 dr, 91% ee

3s: 24h, 93% yield
90:10 dr, 87% ee

3t: 36h, 85% yield
75:25 dr, 83% ee

3u: 36h, 81% yield
76:24 dr, 80% ee

3v: 60h, 61% yield
75:25 dr, 75% ee

94:6 dr and 91% ee for **3r**). When heterocyclic MBH carbonate was selected as electrophile to react with **1a**, a satisfactory result was also obtained (Scheme 2, 93% yield, 90:10 dr and 87% ee for **3s**). Furthermore, 3-alkyl benzofuran-2(3*H*)-ones, such as 3-methyl benzofuran-2(3*H*)-one and 3-benzyl benzofuran-2(3*H*)-one, were also examined as nucleophiles in the current AAA strategy. As a result, the corresponding products were obtained in moderate to very good yield with moderate dr and very good enantioselectivities (Scheme 2, 85% yield, 75:25 dr and 83% ee for **3t**; 81% yield, 76:24 dr and 80% ee for **3u**; 61% yield, 75:25 dr and 75% ee for **3v**).

We obtained the X-ray crystal structure of product **3b** (Figure 2), which proved the absolute configuration for **3b**.[17]

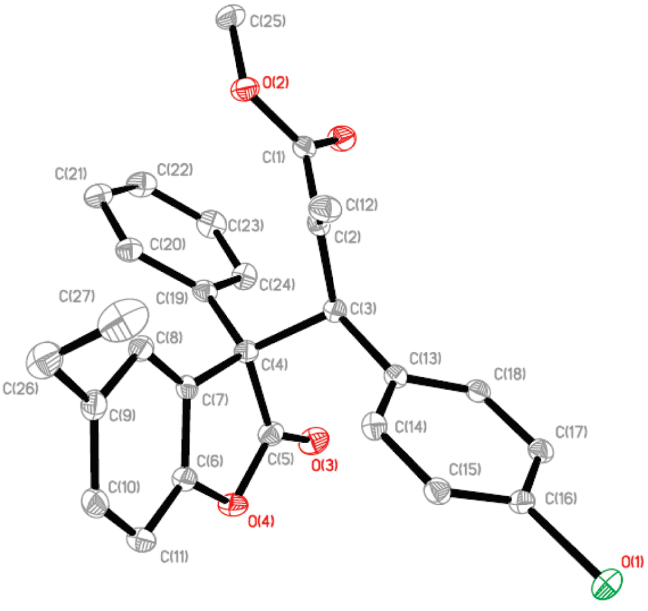
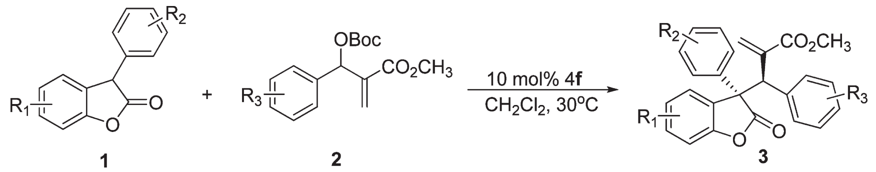


Figure 2. X-ray crystal structure of **3b**.

The absolute configurations of other products can therefore be determined by analogy.

In summary, we have developed a biscinchona alkaloid catalyzed asymmetric allylic-alkylation reaction with benzofuran-2(3*H*)-ones

Table 2. Substrate Scope[a]



entry	R_1	R_2	R_3	reaction time (h)	yield[b] (%)	dr[c]	ee[d] (%)
1	H	H	4-Cl	24	**3a**: 95	98:2	95
2	4-Et	H	4-Cl	36	**3b**: 79	92:8 (99:1)[e]	92 (>99)[e]
3	4-Me	H	4-Cl	24	**3c**: 85	91:9	93
4	8-MeO	H	4-Cl	48	**3d**: 91	94:6	93
5	4-Me	4-Cl	4-Cl	48	**3e**: 77	94:6	94
6	H	4-Cl	4-Cl	18	**3f**: 92	92:8	94
7	H	H	4-Me	48	**3g**: 80	93:7	93
8	H	H	H	24	**3h**: 89	88:12	85
9	H	H	4-F	36	**3i**: 87	88:12 (90:10)[e]	87 (93)[e]
10	H	H	3-Cl	24	**3j**: 85	86:14	86
11	H	H	4-Br	24	**3k**: 90	93:7	90
12	H	H	3-Br	24	**3l**: 88	86:14 (86:14)[e]	85 (86)[e]
13	H	H	4-NO_2	18	**3m**: 97	75:25	67
14	H	H	3-NO_2	24	**3n**: 90	68:32	66
15	H	H	3,4-2Cl	24	**3o**: 88	94:6	84
16	H	H	2,4-2Cl	24	**3p**: 85	98:2	73

[a] The reaction was carried out on a 0.1 mmol scale in 500 μL CH_2Cl_2 at 30 °C, and the molar ratio of **1**/**2** is 1:2. [b] Isolated yield. [c] Determined by HPLC analysis. [d] Determined by chiral HPLC. [e] Data in the parentheses were obtained through a single recrystallization from isopropanol.

and MBH carbonates that proceeds with high diastereo- and enantioselectivity. The reaction scope is substantial, and a number of aryl or alkyl 3-substituted benzofuran-2(3*H*)-ones and substituted MBH carbonates could be successfully applied to give multifunctional chiral benzofuran-2(3*H*)-ones compounds bearing an adjacent all-carbon-substituted quaternary stereocenter and a tertiary stereocenter. In the case of substituted MBH carbonates, the selectivity of the reaction is sensitive toward the electronic variation and substituted position of the aryl group. Further application of benzofuran-2(3*H*)-ones as nucleophiles in other asymmetric strategies is ongoing in our laboratory.

■ EXPERIMENTAL SECTION

General Experimental AAA Reaction Procedure. To a stirred solution of 3-substituted benzofuran-2(3*H*)-one (0.1 mmol) and MBH carbonate (2.0 equiv) in dry CH_2Cl_2 (500 μL) was added biscinchona alkaloid catalyst (0.1 equiv) at 30 °C. After the reaction was complete, the reaction solution was concentrated *in vacuo*, and the crude was purified by flash chromatography to afford the product.

Characterization of 3a. The AAA product was synthesized according to the general procedure as a colorless oil in 95% overall yield. R_f = 0.25 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −329.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (1H, d, J = 7.52 Hz, 1 CH Ar), 7.48 (2H, d, J = 7.65 Hz, 2 CH Ar), 7.38−7.22 (5H, m, 5 CH Ar), 7.06 (2H, d, J = 8.44 Hz, 2 CH Ar), 7.02 (1H, d, J = 8.18 Hz, 1 CH Ar), 6.91 (2H, d, J = 8.44 Hz, 2 CH Ar), 6.28 (1H, s, CH), 5.57 (1H, s, CH=), 5.36 (1H, s, CH=), 3.46 (3H, s, CO_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.3, 167.4, 153.1, 139.2, 136.4, 135.6, 133.4, 131.1, 129.7, 129.0, 128.8, 128.7, 128.5, 128.2, 128.1, 127.6, 127.4, 127.1, 124.0, 111.2, 59.4, 53.0, 52.1 ppm; HRMS (ESI$^+$) calcd for $[C_{25}H_{19}ClO_4 + Na]^+$ 441.0864, found 441.0859. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 8.6 min (major), 30.5 min (minor).

Characterization of 3b. The AAA product was synthesized according to the general procedure as white solid in 79% overall yield. R_f = 0.30 (ethyl acetate/petroleum ether = 1:30); mp 95−97 °C; $[\alpha]^{15}_D$ −270.1 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (2H, d, J = 7.38 Hz, 2 CH Ar), 7.40 (1H, s, 1 CH Ar), 7.35−7.24 (3H, m, 3 CH Ar), 7.16 (2H, d, J = 8.73 Hz, 2 CH Ar), 7.06 (1H, d, J = 8.40 Hz, 1 CH Ar), 6.91 (3H, d, J = 8.73 Hz, 3 CH Ar), 6.29 (1H, s, CH), 5.59 (1H, s, CH=), 5.34 (1H, s, CH=), 3.46 (3H, s, CO_2CH_3), 2.75−2.68 (2H, m, CH_3CH_2−), 1.30−1.26 (3H, t, J = 15.19 Hz, CH_3CH_2−); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.7, 167.5, 151.1, 140.2, 139.3, 136.6, 135.8, 133.3, 131.2, 131.1, 1q29.0, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 126.4, 110.8, 110.7, 59.6, 52.9, 52.1, 28.8, 16.2 ppm; HRMS (ESI$^+$) calcd for $[C_{27}H_{23}ClO_4 + Na]^+$ 469.1177, found 469.1182. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 7.9 min (major), 11.7 min (minor).

Characterization of 3c. The AAA product was synthesized according to the general procedure as colorless oil in 85% overall yield. R_f = 0.28 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −312.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (2H, d, J = 7.73 Hz, 2 CH Ar), 7.39 (1H, s, 1 CH Ar), 7.32−7.26 (3H, m, 3 CH Ar), 7.14 (2H, d, J = 8.26 Hz, 2 CH Ar), 7.06 (1H, d, J = 8.26 Hz, 1 CH Ar), 6.91 (3H, t, J = 9.14 Hz, 3 CH Ar), 6.28 (1H, s, CH), 5.56 (1H, s, CH=), 5.35 (1H, s, CH=), 3.46 (3H, s, CO_2CH_3), 2.43 (3H, s, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.6, 167.5, 151.0, 139.3, 136.6, 135.7, 133.6, 133.3, 131.1, 130.2, 128.6, 128.2, 128.1, 128.0, 127.6, 127.4, 110.8, 59.5, 53.0, 52.1, 21.4 ppm; HRMS (ESI$^+$) calcd for $[C_{26}H_{21}ClO_4 + Na]^+$ 455.1021, found 455.1020. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 6.6 min (major), 15.5 min (minor).

Characterization of 3d. The AAA product was synthesized according to the general procedure as colorless oil in 91% overall yield. R_f = 0.25 (ethyl acetate/petroleum ether = 1:20); $[\alpha]^{15}_{D}$ −206.0 (*c* 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (2H, d, *J* = 7.39 Hz, 2 CH Ar), 7.32−7.23 (3H, m, 3 CH Ar), 7.22−7.16 (2H, m, 2 CH Ar), 7.07 (2H, d, *J* = 8.26 Hz, 2 CH Ar), 6.94 (3H, d, *J* = 8.26 Hz, 3 CH Ar), 6.28 (1H, s, CH), 5.59 (1H, s, CH═), 5.35 (1H, s, CH═), 3.85(3H, s, CH$_3$O), 3.47 (3H, s, CO$_2$*CH$_3$*); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 175.9, 167.4, 144.4, 141.7, 139.1, 136.4, 135.5, 133.3, 131.2, 128.6, 128.2, 127.6, 124.5, 118.8, 113.3, 59.7, 56.4, 52.9, 52.1 ppm; HRMS (ESI$^+$) calcd for [C$_{26}$H$_{21}$ClO$_5$+H]$^+$ 449.1150, found 449.1154. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 2:98), 1.0 mL/min; t_R = 36.1 min (major), 83.4 min (minor).

Characterization of 3e. The AAA product was synthesized according to the general procedure as colorless oil in 77% overall yield. R_f = 0.31 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_{D}$ −255.2 (*c* 0.5, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 (2H, d, *J* = 8.09 Hz, 2 CH Ar), 7.28 (1H, s, 1 CH Ar), 7.20 (2H, d, *J* = 8.26 Hz, 2 CH Ar), 7.09 (1H, d, *J* = 8.26 Hz, 1 CH Ar), 7.01 (2H, d, *J* = 8.09 Hz, 2 CH Ar), 6.83 (3H, d, *J* = 8.09 Hz, 3 CH Ar), 6.22 (1H, s, CH), 5.49 (1H, s, CH═), 5.21 (1H, s, CH═), 3.41(3H, s, CO$_2$*CH$_3$*), 2.36 (3H, s, CH$_3$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 176.3, 167.4, 151.0, 139.0, 135.4, 135.1, 134.3, 133.8, 133.5, 131.1, 130.4, 129.1, 128.7, 128.3, 128.2, 127.3, 127.0, 111.0, 59.0, 53.0, 52.2, 21.5 ppm; HRMS (ESI$^+$) calcd for [C$_{26}$H$_{20}$Cl$_2$O$_4$ + Na]$^+$ 489.0631, found 489.0630. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 6.6 min (major), 14.5 min (minor).

Characterization of 3f. The AAA product was synthesized according to the general procedure as colorless oil in 92% overall yield. R_f = 0.30 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_{D}$ −245.6 (*c* 0.5, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (1H, d, *J* = 7.73 Hz, 1 CH Ar), 7.43 (2H, d, *J* = 8.79 Hz, 2 CH Ar), 7.37 (1H, d, *J* = 8.09 Hz, 1 CH Ar), 7.27 (3H, d, *J* = 8.79 Hz, 3 CH Ar), 7.07 (2H, d, *J* = 8.44 Hz, 2 CH Ar), 7.03 (1H, d, *J* = 7.91 Hz, 1 CH Ar), 6.89 (2H, d, *J* = 8.61 Hz, 2 CH Ar), 6.29 (1H, s, CH), 5.57 (1H, s, CH═), 5.30 (1H, s, CH═), 3.48 (3H, s, CO$_2$*CH$_3$*); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 176.0, 167.3, 153.0, 138.9, 135.2, 134.9, 134.4, 133.6, 131.0, 130.0, 129.1, 129.0, 128.8, 128.4, 128.3, 128.1, 127.1, 127.0, 124.2, 111.4, 58.9, 53.1, 52.2 ppm; HRMS (ESI$^+$) calcd for [C$_{25}$H$_{20}$Cl$_2$O$_4$ + Na]$^+$ 475.0474, found 475.0481. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 8.9 min (major), 13.9 min (minor).

Characterization of 3g. The AAA product was synthesized according to the general procedure as colorless oil in 80% overall yield. R_f = 0.25 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_{D}$ −142.2 (*c* 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (1H, d, *J* = 7.56 Hz, 1 CH Ar), 7.28 (2H, d, *J* = 7.21 Hz, 2 CH Ar), 7.39 (1H, t, *J* = 7.74 Hz, 1 CH Ar), 7.36−7.27 (4H, m, 4 CH Ar), 7.04 (1H, d, *J* = 8.09 Hz, 1 CH Ar), 6.93 (2H, d, *J* = 8.09 Hz, 2 CH Ar), 6.84 (2H, d, *J* = 8.09 Hz, 2 CH Ar), 6.27 (1H, s, CH), 5.59 (1H, s, CH═), 5.38 (1H, s, CH═), 3.45 (3H, s, CO$_2$*CH$_3$*), 2.25 (3H, s, CH$_3$); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 176.4, 167.9, 153.3, 139.8, 137.1, 136.6, 134.0, 129.5, 128.9, 128.5, 128.0, 127.9, 127.8, 127.4, 123.8, 111.1, 59.4, 53.5, 52.0, 21.0 ppm; HRMS (ESI$^+$) calcd for [C$_{26}$H$_{22}$O$_4$ + Na]$^+$ 421.1410, found 421.1405. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 2:98), 1.0 mL/min; t_R = 31.1 min (major), 44.6 min (minor).

Characterization of 3h. The AAA product was synthesized according to the general procedure as colorless oil in 89% overall yield. R_f = 0.25 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_{D}$ −194.6 (*c* 0.5, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (1H, d, *J* = 7.73 Hz, 1 CH Ar), 7.53 (2H, d, *J* = 7.73 Hz, 2 CH Ar), 7.37−7.23 (5H, m, 5 CH Ar), 7.12−7.07 (3H, m, 3 CH Ar), 6.99 (1H, d, *J* = 8.09 Hz, 1 CH Ar), 6.95 (2H, d, *J* = 7.03 Hz, 2 CH Ar), 6.27 (1H, s, CH), 5.57 (1H, s, CH═), 5.39 (1H, s, CH═), 3.43 (3H, s, CO$_2$*CH$_3$*); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 176.4, 167.7, 153.2, 139.6, 137.1, 136.6, 129.7, 129.6, 128.7, 128.5, 128.1, 128.1, 127.8, 127.7, 127.4, 123.8, 111.1, 59.5, 53.8, 52.0 ppm; HRMS (ESI$^+$) calcd for [C$_{25}$H$_{20}$O$_4$+H]$^+$ 385.1434, found 385.1425. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 2:98), 1.0 mL/min; t_R = 18.8 min (major), 11.7 min (minor).

Characterization of 3i. The AAA product was synthesized according to the general procedure as white solid in 87% overall yield. R_f = 0.35 (ethyl acetate/petroleum ether = 1:30); mp 123−125 °C; $[\alpha]^{15}_{D}$ −193.2 (*c* 0.5, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (1H, d, *J* = 7.03 Hz, 1 CH Ar), 7.49 (2H, d, *J* = 6.33 Hz, 2 CH Ar), 7.37−7.26 (5H, m, 5 CH Ar), 7.01 (1H, d, *J* = 8.09 Hz, 1 CH Ar), 6.93 (2H, s, 2 CH Ar), 6.78 (2H, t, *J* = 7.73 Hz, 2 CH Ar), 6.27 (1H, s, CH), 5.57 (1H, s, CH═), 5.38 (1H, s, CH═), 3.46 (3H, s, CO$_2$*CH$_3$*); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 176.4, 167.6, 163.2, 153.1, 139.4, 136.4, 132.7, 131.4, 131.3, 129.7, 128.8, 128.6, 128.2, 127.9, 127.7, 127.6, 127.4, 127.2, 124.0, 115.1, 114.9, 111.2, 59.6, 53.0, 52.1 ppm; HRMS (ESI$^+$) calcd for [C$_{25}$H$_{19}$FO$_4$ + Na]$^+$ 425.1160, found 425.1155. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 13.3 min (major), 20.5 min (minor).

Characterization of 3j. The AAA product was synthesized according to the general procedure as colorless oil in 85% overall yield. R_f = 0.28 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_{D}$ −189.3 (*c* 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62 (1H, d, *J* = 7.56 Hz, 1 CH Ar), 7.50 (2H, d, *J* = 8.26 Hz, 2 CH Ar), 7.39−7.24 (5H, m, 5 CH Ar), 7.10 (1H, d, *J* = 8.09 Hz, 1 CH Ar), 7.03 (2H, t, *J* = 8.26 Hz, 2 CH Ar), 6.92−6.90 (2H, m, 2 CH Ar), 6.30 (1H, s, CH), 5.58 (1H, s, CH═), 5.36 (1H, s, CH═), 3.46 (3H, s, CO$_2$*CH$_3$*); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 176.2, 167.4, 153.1, 139.2, 138.9, 137.4, 136.3, 133.9, 129.8, 129.3, 128.8, 128.7, 128.6, 128.2, 127.9, 127.7, 127.6, 127.5, 127.4, 127.2, 124.0, 111.2, 59.3, 53,3, 52.7, 52.4, 52.1 ppm; HRMS (ESI$^+$) calcd for [C$_{25}$H$_{19}$ClO$_4$ + Na]$^+$ 441.0864, found 441.0863. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 1:199), 1.0 mL/min; t_R = 55.4 min (major), 75.5 min (minor).

Characterization of 3k. The AAA product was synthesized according to the general procedure as colorless oil in 90% overall yield. R_f = 0.25 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_{D}$ −298.0 (*c* 0.5, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 (1H, d, *J* = 7.59 Hz, 1 CH Ar), 7.48 (2H, d, *J* = 7.41 Hz, 2 CH Ar), 7.36 (1H, t, *J* = 7.78 Hz, 1 CH Ar), 7.31−7.25 (4H, m, 4 CH Ar), 7.22 (2H, d, *J* = 7.78 Hz, 2 CH Ar), 7.02 (1H, d, *J* = 7.96 Hz, 1 CH Ar), 6.85 (2H, d, *J* = 8.14 Hz, 2 CH Ar), 6.27 (1H, s, CH), 5.57 (1H, s, CH═), 5.35 (1H, s, CH═), 3.46 (3H, s, CO$_2$*CH$_3$*); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 176.3, 167.4, 153.1, 139.2, 136.4, 136.2, 131.4, 131.2, 129.8, 128.7, 128.2, 128.1, 127.6, 127.1, 124.0, 121.6, 111.2, 59.4, 53.1, 52.1 ppm; HRMS (ESI$^+$) calcd for [C$_{25}$H$_{19}$BrO$_4$ + Na]$^+$ 485.0359, found 485.0364. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 9.4 min (major), 33.8 min (minor).

Characterization of 3l. The AAA product was synthesized according to the general procedure as white solid in 88% overall yield. R_f = 0.34 (ethyl acetate/petroleum ether = 1:30); mp 110−113 °C; $[\alpha]^{15}_{D}$ −180.6 (*c* 1.0, CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ7.62 (1H, d, *J* = 7.61 Hz, 1 CH Ar), 7.50 (2H, d, *J* = 7.45 Hz, 2 CH Ar), 7.39−7.24 (6H, m, 6 CH Ar), 7.05−6.97 (4H, m, 4 CH Ar), 6.30 (1H, s, CH), 5.58 (1H, s, CH═), 5.35 (1H, s, CH═), 3.46 (3H, s, CO$_2$*CH$_3$*); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 176.2, 167.4, 153.1, 139.4, 138.9, 136.2, 132.9, 132.7, 130.8, 130.6, 129.8, 129.7, 129.6, 129.2, 128.8, 128.7, 128.6, 128.4, 128.2, 127.7, 127.5, 127.4, 127.2, 126.7, 124.0, 123.9, 122.1, 121.8, 111.2, 59.3, 53.3, 52.8, 52.4, 52.2 ppm; HRMS (ESI$^+$) calcd for

$[C_{25}H_{19}BrO_4 + Na]^+$ 485.0359, found 485.0360. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 1:99), 1.0 mL/min; t_R = 29.3 min (major), 38.3 min (minor).

Characterization of 3m. The AAA product was synthesized according to the general procedure as colorless oil in 97% overall yield. R_f = 0.22 (ethyl acetate/petroleum ether = 1:20); $[\alpha]^{15}_D$ −167.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (2H, d, *J* = 8.39 Hz, 2 CH Ar), 7.46 (2H, t, *J* = 8.54 Hz, 2 CH Ar), 7.36−7.15 (6H, m, 6 CH Ar), 7.05−6.95 (3H, m, 3 CH Ar), 6.36 (1H, s, CH), 5.65 (1H, s, CH=), 5.52 (1H, s, CH=), 3.49 (3H, s, CO_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.1, 167.0, 166.5, 152.8, 152.6, 147.4, 147.0, 144.8, 143.2, 138.4, 137.8, 137.1, 136.2, 130.8, 130.0, 129.9, 129.5, 129.1, 128.9, 128.4, 128.2, 127.5, 127.4, 127.3, 126.8, 126.2, 124.3, 124.2, 123.1, 122.9, 111.3, 59.4, 53.1, 52.9, 52.4, 52,3 ppm; HRMS (ESI^+) calcd for $[C_{25}H_{19}NO_6 + Na]^+$ 452.1105, found 452.1108. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 1:9), 1.0 mL/min; t_R = 29.1 min (major), 19.4 min (minor).

Characterization of 3n. The AAA product was synthesized according to the general procedure as colorless oil in 90% overall yield. R_f = 0.23 (ethyl acetate/petroleum ether = 1:20); $[\alpha]^{15}_D$ −195.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (1H, d, *J* = 8.08 Hz, 1 CH Ar), 7.78 (1H, s, 1 CH Ar), 7.66 (1H, d, *J* = 6.83 Hz, 1 CH Ar), 7.47 (2H, d, J=5.86 Hz, 2 CH Ar), 7.36−7.29 (6H, m, 6 CH Ar), 7.20−7.14 (1H, m, 1 CH Ar), 7.03 (1H, t, *J* = 8.08 Hz, 1 CH Ar), 6.38 (1H, s, CH), 5.67 (1H, s, CH=), 5.50 (1H, s, CH=), 3.50 (3H, s, CO_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.1, 167.0, 166.5, 152.8, 152.6, 147.7, 147.6, 139.2, 138.4, 137.8, 137.7, 137.0, 136.2, 136.0, 135.8, 130.1, 130.0, 129.6, 129.0, 128.9, 128.7, 128.5, 128.4, 128.0, 127.5, 127.4, 127.3, 126.9, 126.2, 124.7, 124.6, 124.4, 124.3, 122.8, 122.5, 111.3, 59.4, 59.3, 53.1, 52.7, 52.5, 52.3 ppm; HRMS (ESI^+) calcd for $[C_{25}H_{19}NO_6 + Na]^+$ 452.1105, found 452.1105. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 16.6 min (major), 107.6 min (minor).

Characterization of 3o. The AAA product was synthesized according to the general procedure as colorless oil in 88% overall yield. R_f = 0.28 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −90.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (1H, d, *J* = 7.46 Hz, 1 CH Ar), 7.43 (2H, d, *J* = 7.46 Hz, 2 CH Ar), 7.39−7.33 (2H, m, 2 CH Ar), 7.26−7.23 (5H, m, 5 CH Ar), 7.10 (1H, d, *J* = 8.08 Hz, 1 CH Ar), 7.01 (1H, d, *J* = 8.07 Hz, 1 CH Ar), 6.27 (1H, s, CH), 5.88 (1H, s, CH=), 5.42 (1H, s, CH=), 3.36 (3H, s, CO_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.0, 166.9, 152.4, 139.1, 136.4, 135.9, 134.7, 133.6, 131.7, 130.1, 129.7, 128.8, 128.6, 128.1, 127.6, 127.3, 127.1, 126.9, 126.6, 124.1, 111.1, 59.0, 52.0, 48.5, ppm; HRMS (ESI^+) calcd for $[C_{25}H_{18}Cl_2O_4 + Na]^+$ 475.0474, found 475.0475. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 10.5 min (major), 9.2 min (minor).

Characterization of 3p. The AAA product was synthesized according to the general procedure as colorless oil in 85% overall yield. R_f = 0.33 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −175.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (1H, d, *J* = 7.61 Hz, 1 CH Ar), 7.47 (2H, d, *J* = 7.46 Hz, 2 CH Ar), 7.39−7.25 (5H, m, 5 CH Ar), 7.19−7.16 (1H, m, 1 CH Ar), 7.08−7.04 (2H, m, 2 CH Ar), 6.88 (1H, d, *J* = 8.39 Hz, 1 CH Ar), 6.31 (1H, s, CH), 5.59 (1H, s, CH=), 5.34 (1H, s, CH=), 3.48 (3H, s, CO_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.2, 167.2, 153.0, 138.7, 137.4, 136.1, 132.1, 131.7, 131.6, 130.0, 129.2, 129.1, 129.0, 128.8, 128.7, 128.3, 127.6, 127.5, 127.4, 127.0, 126.5, 124.2, 124.1, 111.4, 59.3, 52.7, 52.5, 52.2 ppm; HRMS (ESI^+) calcd for $[C_{25}H_{18}Cl_2O_4 + Na]^+$ 475.0474, found 475.0474. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 2:98), 1.0 mL/min; t_R = 16.5 min (major), 10.8 min (minor).

Characterization of 3q. The AAA product was synthesized according to the general procedure as colorless oil in 92% overall yield. R_f = 0.30 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −224.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, d, *J* = 7.61 Hz, 1 CH Ar), 7.47 (2H, d, *J* = 7.46 Hz, 2 CH Ar), 7.36−7.22 (5H, m, 5 CH Ar), 7.06 (2H, d, *J* = 8.23 Hz, 2 CH Ar), 7.00 (1H, d, *J* = 8.08 Hz, 1 CH Ar), 6.92 (2H, d, *J* = 8.23 Hz, 2 CH Ar), 6.29 (1H, s, CH), 5.57 (1H, s, CH=), 5.39 (1H, s, CH=), 4.02−3.81 (2H, m, CO_2CH_2-), 1.07 (3H, t, *J* = 7.15 Hz, CH_3CH_2−); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.4, 167.0, 153.1, 139.4, 136.6, 135.8, 133.3, 131.2, 131.1, 129.7, 128.8, 128.7, 128.2, 128.0, 127.7, 127.6, 127.4, 127.2, 124.0, 111.2, 61.2, 59.6, 52.8, 13.9 ppm; HRMS (ESI^+) calcd for $[C_{26}H_{21}ClO_4 + Na]^+$ 455.1021, found 455.1026. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 2:98), 1.0 mL/min; t_R = 8.3 min (major), 22.3 min (minor).

Characterization of 3r. The AAA product was synthesized according to the general procedure as colorless oil in 90% overall yield. R_f = 0.33 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −207.0 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (2H, d, *J* = 7.46 Hz, 2 CH Ar), 7.39 (1H, s, 1 CH Ar), 7.32−7.24 (3H, m, 3 CH Ar), 7.13 (1H, d, *J* = 8. 93 Hz, 1 CH Ar), 7.06 (2H, d, *J* = 8.31 Hz, 2 CH Ar), 6.93 (2H, d, *J* = 8.39 Hz, 2 CH Ar), 6.88 (1H, d, *J* = 8.23 Hz, 1 CH Ar), 6.28 (1H, s, CH), 5.56 (1H, s, CH=), 5.36 (1H, s, CH=), 3.99−3.82 (2H, m, CO_2CH_2-), 2.43(3H, s, CH_3), 1.07 (3H, t, *J* = 7.15 Hz, CH_3CH_2−); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 176.7, 167.0, 151.0, 139.5, 136.8, 135.9, 133.6, 133.2, 131.2, 130.1, 128.7, 128.1, 128.0, 127.9, 127.6, 127.4, 110.8, 61.2, 59.7, 52.7, 21.5, 13.9 ppm; HRMS (ESI^+) calcd for $[C_{27}H_{23}ClO_4 + Na]^+$ 469.1177, found 469.1180. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 6.1 min (major), 9.6 min (minor).

Characterization of 3s. The AAA product was synthesized according to the general procedure as colorless oil in 93% overall yield. R_f = 0.25 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −16.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (3H, d, J=7.86 Hz, 3 CH Ar), 7.43 (1H, t, J=7.43 Hz, 1 CH Ar), 7.34−7.26 (4H, m, 4 CH Ar), 7.10−7.06 (2H, m, 2 CH Ar), 6.79 (1H, t, *J* = 4.33 Hz, 1 CH Ar), 6.56 (1H, d, J = 3.53 Hz, 1 CH Ar), 6.32 (1H, s, CH), 5.70 (2H, d, J=6.58 Hz, CH=), 3.39 (3H, s, CO_2CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 175.9, 167.5, 153.7, 139.4, 135.2, 129.9, 129.2, 128.4, 128.3, 128.1, 127.4, 126.6, 125.2, 123.7, 111.2, 59.0, 52.0, 48.8 ppm; HRMS (ESI^+) calcd for $[C_{23}H_{18}O_4S + Na]^+$ 413.0818, found 413.0816. The enantiomeric excess was determined by HPLC with an AD-H column at 210 nm (2-propanol/hexane = 3:97), 1.0 mL/min; t_R = 24.1 min (major), 17.0 min (minor).

Characterization of 3t. The AAA product was synthesized according to the general procedure as colorless oil in 85% overall yield. R_f = 0.28 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −261.0 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.33−7.06 (7H, m, 7 CH Ar), 6.80 (1H, d, *J* = 7.14 Hz, 1 CH Ar), 6.38 (1H, s, CH), 5.58 (1H, s, CH=), 4.66 (1H, s, CH=), 3.66 (3H, s, CO_2CH_3), 1.51(3H, s,CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 179.0, 166.6, 152.6, 139.2, 136.2, 134.6, 133.8, 131.6, 131.1, 130.6, 129.2, 128.5, 128.3, 127.6, 126.8, 124.6, 124.2, 124.1, 123.7, 111.0, 52.4, 51.2, 50.7, 50.1, 25.7, 24.8 ppm; HRMS (ESI^+) calcd for $[C_{20}H_{17}ClO_4 + Na]^+$ 379.0708, found 379.0700. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 2:98), 1.0 mL/min; t_R = 9.1 min (major), 14.5 min (minor).

Characterization of 3u. The AAA product was synthesized according to the general procedure as colorless oil in 81% overall yield. R_f = 0.30 (ethyl acetate/petroleum ether = 1:40); $[\alpha]^{15}_D$ −134.0 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.31 (4H, m, 4 CH Ar), 7.25−7.22 (2H, m, 2 CH Ar), 7.10−7.08 (2H, m, 2 CH Ar), 6.80 (1H, d, *J* = 7.14 Hz, 1 CH Ar), 6.38 (1H, s, CH), 5.58 (1H, s, CH=), 4.66 (1H, s, CH=), 3.66 (3H, s, CO_2CH_3), 1.54(3H, s, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 179.4, 166.7, 152.6, 139.6, 139.4, 137.8, 135.9, 131.2, 130.8, 130.4, 129.7, 129.1, 129.0, 128.3, 128.1, 127.8, 127.6, 126.5, 125.0, 124.1, 124.0, 123.8, 111.8, 110.7, 52.3, 51.8, 51.1, 50.3, 50.1, 27.8, 25.9, 24.8 ppm; HRMS (ESI$^+$) calcd for $[C_{20}H_{18}O_4 + Na]^+$ 345.1097, found 345.1105. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 2:98), 1.0 mL/min; t_R = 13.8 min (major), 14.7 min (minor).

Characterization of 3v. The AAA product was synthesized according to the general procedure as colorless oil in 61% overall yield. R_f = 0.21 (ethyl acetate/petroleum ether = 1:50); $[\alpha]^{15}_{D}$ −56.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (2H, d, J = 8.20 Hz, 2 CH Ar), 7.27 (3H, d, J = 6.15 Hz, 3 CH Ar), 7.22−7.19 (1H, m, 1 CH Ar), 7.14−6.98 (4H, m, 4 CH Ar), 6.93 (1H, d, J = 7.43 Hz, 1 CH Ar), 6.78 (1H, d, J = 7.95 Hz, 1 CH Ar), 6.69 (2H, d, J = 7.43 Hz, 2 CH Ar), 6.40 (1H, s, CH), 5.56 (1H, s, CH═), 4.91 (1H, s, CH═), 3.71 (3H, s, CO_2CH_3), 3.46 (1H, d, J= 12.82 Hz, 1 CH_2), 3.03 (1H, d, J= 12.82 Hz, 1 CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 177.8, 166.5, 153.1, 139.4, 134.6, 133.9, 131.8, 131.4, 129.9, 129.8, 129.3, 128.6, 128.4, 128.0, 127.9, 127.6, 127.1, 127.0, 125.5, 124.4, 123.8, 123.7, 111.7, 110.6, 57.2, 57.0, 52.5, 52.4, 51.1, 50.6, 45.1, 44.1, 29.7, 28.9 ppm; HRMS (ESI$^+$) calcd for $[C_{26}H_{22}O_4 + Na]^+$ 421.1410, found 421.1406. The enantiomeric excess was determined by HPLC with an OD-H column at 210 nm (2-propanol/hexane = 2:98), 1.0 mL/min; t_R = 16.1 min (major), 37.6 min (minor).

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details, analytical data for all new compounds, and X-ray crystallography data of **3b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) CCDC 815934 contains the supplementary crystallographic data for compound **3b**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif. For details of the crystallographic data of **3b**, also see Table S1 in Supporting Information.