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Enantioselective Synthesis of Optically Active 3,3-Diarylpropanoates by Conjugate Hydrosilylation with Chiral Rh-bis(oxazolinyl)phenyl Catalysts

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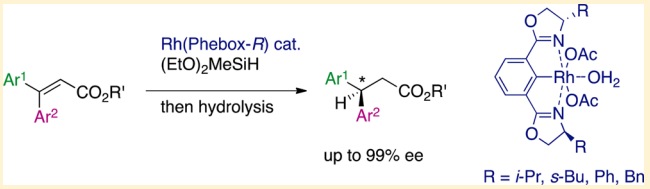
Supporting Information

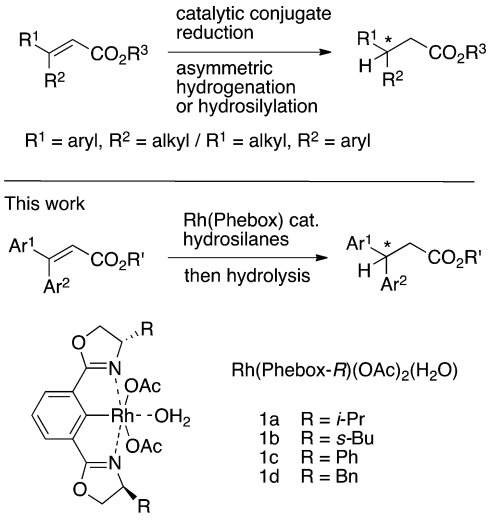
ABSTRACT: Conjugate hydrosilylation of 3,3-diarylacrylate derivatives catalyzed by chiral rhodium-bis(oxazolinyl)phenyl complexes (1 mol %) at 60 °C for 2 h was investigated to prepare optically active 3,3-diarylpropanoate derivatives in high yields up to 99% yield and high enantioselectivities up to 99%.



INTRODUCTION

Asymmetric conjugate reduction of 3,3-disubstituted α,β-unsaturated carbonyl compounds has been extensively studied to obtain optically active propanoates having a chiral carbon center at the β-position (Scheme 1).[1] For example, such a conjugate reduction was realized by catalytic hydrosilylation using a variety of metal catalysts.[2,3] We have reported the conjugate hydrosilylation of α,β-unsaturated esters using chiral rhodium-bis(oxazolinyl)phenyl acetate complexes (**1**) [Rh(Phebox)$(OAc)_2(H_2O)$] as catalysts and hydrosilanes as reducing agents.[4] In the reaction, we adopted linear β,β-aryl,alkyl- or alkyl,alkyl-substituted unsaturated compounds as substrates.

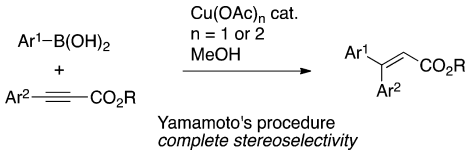
Scheme 1. Asymmetric Conjugate Reduction of 3,3-Disubstituted Acrylates



Methods in organic synthesis often depend on the supply of starting substrates. Once a new substrate can stably be supplied, new routes for synthesizing fine chemicals such as pharmaceutical compounds or functional materials can lead to the development of new reagents or reactions.

Yamamoto et al. recently discovered a method for synthesizing 3,3-diarylacrylates with stereoselective control of *cis* and *trans* isomers by copper-catalyzed conjugate addition of an arylboronic acid to alkynoates (Scheme 2).[5] Therefore, we adopted this method to prepare 3,3-diarylacrylate substrates, which are subsequently subjected to asymmetric conjugate reduction to afford optically active 3,3-diarylpropanoates, as precursors for various pharmaceutical compounds (Figure 1).[6]

Scheme 2. Completely Stereoselective Preparation of 3,3-Diaryl Substituted Acrylates Developed by Yamamoto



In terms of the asymmetric conjugate reduction, Yun et al. successfully demonstrated copper-catalyzed hydrosilylation of 3,3-diaryl-substituted acrylonitriles to produce 3,3-diarylpropionitriles in high enantioselectivities.[7] Yun et al. adopted the Horner–Wadsworth–Emmons olefination reaction[7a] and also Yamamoto's method for stereoselective preparation of the starting 3,3-diaryl-substituted nitriles.[7b,c] Andersson et al. employed an iridium-catalyzed asymmetric hydrogenation reaction for trisubstituted olefins including 3,3-diarylacrylate, which afforded a little lower enantioselectivity compared to that of alkyl- or aryl-substituted olefins where the unsaturated olefin substrate was prepared by Heck reaction.[8] In 2011, Correia et al. reported stereoselective synthesis of 3,3-diaryl-substituted

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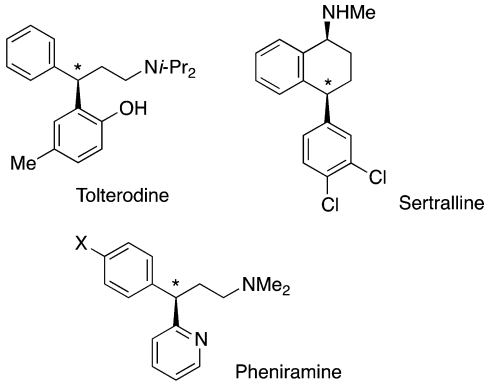


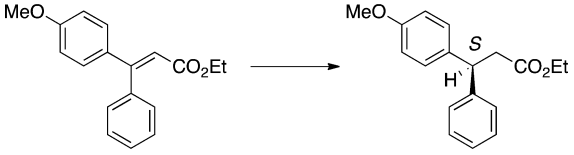
Figure 1. Diaryl substituted chiral carbon atoms in pharmaceutical compounds.

acrylates by Heck–Matsuda reaction followed by a conjugate reduction to afford a psychoactive compound.[9]

RESULTS AND DISCUSSION

Conjugate hydrosilylation of (*E*)-3-(*p*-methoxyphenyl) and 3-(phenyl) disubstituted acrylate **2a** (1.0 mmol scale) was examined with 1 mol % of Rh(Phebox-*R*) complexes **1** and diethoxymethylsilane (1.5 mmol) in toluene at 60 °C (Table 1). The desired reaction took place within 1 h. After acidic workup, the desired conjugate reduction product, 3,3-diarylpropanoate **3a**, was obtained in 97% yield with 95% ee (entry 1). Triethoxysilane gave almost the same result (entry 2). The reduction of gram scale substrate was carried out with 0.2 mol % (TON 500) of the catalyst **1a** at 60 °C to proceed for 10 h, giving the corresponding product in 97% and 96% ee (entry 3). The secondary butyl catalyst **1b** gave almost the same results as those with the isopropyl catalyst **1a** (entries 4 and 5). The phenyl catalyst **1c** retarded the reduction to give similar yield and enantioselectivity (entry 6). The benzyl catalyst **1d** gave decreased enantioselectivity (entry 7).

Table 1. Asymmetric Conjugate Hydrosilylation of (*E*)-Ethyl 3-(*p*-Methoxyphenyl)-3-phenylacrylate 2a with Rh(Phebox-*R*) Complexes 1[a]



2a **3a**

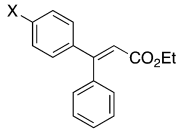
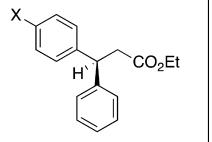
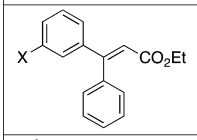
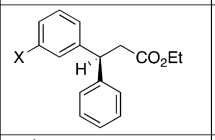
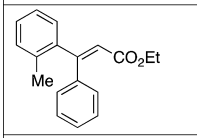
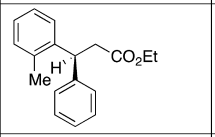
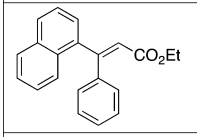
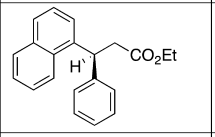
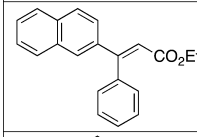
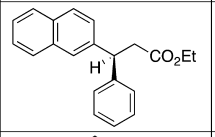
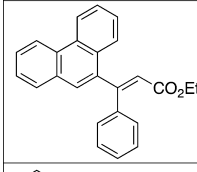
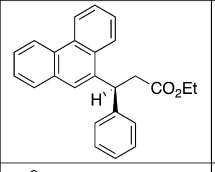
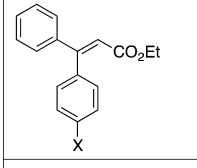
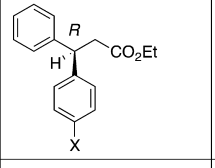
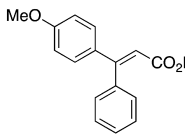
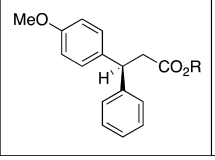
Rh(Phebox-*R*) cat. **1** 1.0 mol %
$(EtO)_2MeSiH$ (1.5 equiv.)
toluene, 60 °C, then H_3O^+

entry	cat. (*R*)	time (h)	yield (%)	ee (%)
1	**1a** (*ip*)	2	97	95
2[b]	**1a** (*ip*)	2	94	95
3[c]	**1a** (*ip*)	10	97	96
4	**1b** (*sb*)	2	96	94
5[b]	**1b** (*sb*)	2	96	94
6[d]	**1c** (*ph*)	12	90	93
7	**1d** (*bn*)	2	94	79

[a]Acrylate **2a** (1.0 mmol), Rh(Phebox-R) cat. **1** (1 mol %), $(EtO)_2MeSiH$ (1.5 mmol), toluene (2 mL) at 60 °C, then acidic workup. [b]$(EtO)_3SiH$ (1.5 mmol). [c]Acrylate **2a** (5.0 mmol, 1.41 g), Rh(Phebox-ip) cat. **1a** (0.2 mol %, 0.01 mmol, 5.4 mg), $(EtO)_2MeSiH$ (7.5 mmol), toluene (10 mL) at 60 °C, 10 h, then acidic workup. [d]Catalyst **1d** (2 mol %).

Next, the substrate scope was examined using ethyl acrylates under the standard conditions as described in entry 1 of Table 1; 1.0 mmol of the acrylate, 1.5 equiv of diethoxymethylsilane, 1 mol % of the catalyst **1a**, 60 °C, 2 h (Table 2). Reduction of the substrates substituted at the *para*-position (**2b–2e**), at the *meta*-position (**2f–2i**), and at the *ortho*-position (**2j**) proceeded smoothly to give the corresponding propanoates **3b–3j** in over 90% yields with 95–98% ee's. Large steric effects of the substituents on the yields and ee's were not observed. Reduction of the bulky 1-naphthyl acrylate **2k** proceeded smoothly under the same condition to give the highest ee of

Table 2. Asymmetric Conjugate Hydrosilylation of (*E*)-Ethyl 3-(Substituted aryl)-3-phenylacrylates 2 with Rh(Phebox-*ip*) Complex 1a[a]

Substrate		Product	yield (%), ee
	**2b** X = Me **2c** X = Cl **2d** X = EtO_2C **2e** X = CF_3		**3b** 90%, 98% ee **3c** 93%, 98% ee **3d** 90%, 98% ee **3e** 95%, 97% ee
	**2f** X = MeO **2g** X = Me **2h** X = Cl **2i** X = EtO_2C		**3f** 94%, 97% ee **3g** 94%, 95% ee **3h** 91%, 97% ee **3i** 95%, 98% ee
	**2j**		**3j** 92%, 97% ee
	**2k**		**3k** 96%, 99% ee
	**2l**		**3l** 96%, 95% ee
	**2m**		**3m** 99%, 97% ee
	**4** X = MeO **5** X = CF_3		**3a** 92%, 97% ee **3e** 96%, 97% ee
	**6** X = Me **8** X = *i*-Pr		**7** 95%, 98% ee **9** 98%, 97% ee

[a]Acrylate **2** (1.0 mmol), Rh(Phebox-*ip*) cat. **1a** (1 mol %), $(EtO)_2MeSiH$ (1.5 mmol), toluene (2 mL), at 60 °C, 2 h, then acidic workup.

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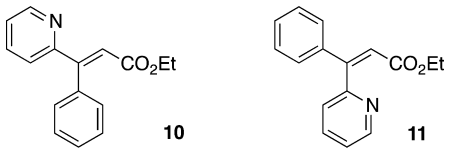
99%, in comparison to that of 95% ee for 2-naphthyl one **2l**. 9-Phenanthrenyl acrylate **2m** was also reduced, giving the product with a high ee of 97%. Next, the *Z*-acrylates **4** and **5** were reduced under the same standard conditions with catalyst **1a**. The absolute configurations of products **3a** and **3e** were confirmed to be *R*, which is opposite to those of the corresponding propanoates **3a** and **3e** derived from *E*-acrylates **2a** and **2e**, respectively. This phenomenon can be explained by the fact that the Rh(Phebox) catalyst differentiates the prochiral face of the α-carbon atom, but not that of the β-carbon atom. Replacement of the ethyl ester, with the methyl and isopropyl esters **6** and **8** gave similar high enantioselectivity for the products **7** and **9**, respectively (up to 98% ee). Comparing to the case of asymmetric hydrogenation of the methyl ester **6**, even Andersson's excellent iridium-catalyst system giving high enantioselectivity resulted in 69% ee.[8a]

Heteroaromatic substituted esters were expected as raw materials for some of the pharmaceutical compounds. However, the starting pyridyl substituted esters, **10** and **11**, were not successfully synthesized by Yamamoto's method. Therefore, these esters were synthesized by the Horner–Wadsworth–Emmons method, followed by separation of the *Z* and *E* isomers by column chromatography. Unfortunately, the conjugate hydrosilylation of both isomers did not smoothly proceed under the standard conditions.



Finally, a proposed hydride attack transition structure is shown in Figure 2, in which the hydride attacks the *re* face of the acrylate ($Ar^1 > Ar^2$) to form the *S* absolute configuration.

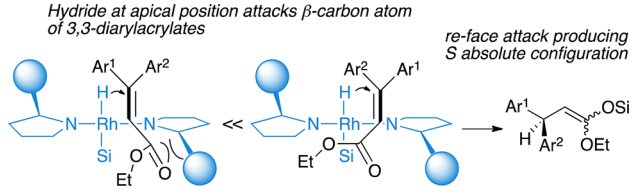


Figure 2. Hypothetical course of the hydride attack to 3,3-diarylacrylate forming *S* absolute configuration.

Thus we have found highly enantioselective conjugate reduction of 3,3-diaryl-substituted acrylates by hydrosilylation with Rh(Phebox) complexes to produce optically active 3,3-diaryl propanoates. Study is now underway on substrate scope toward the corresponding enones, amides, and nitriles having heteroaromatic rings.

EXPERIMENTAL SECTION

^{1}H and ^{13}C NMR were measured at 300 and 75 MHz in $CDCl_3$, respectively. HRMS were obtained on a double-focusing magnetic sector mass spectrometer.

Typical Method for Preparation of Substrate 3,3-Diaryl Acrylates. (*E*)-Ethyl 3-(4-Methoxyphenyl)-3-phenylacrylate (2a).[5] A mixture of ethyl phenylpropiolate (1.80 g, 10.3 mmol), *p*-methoxyphenylboronic acid (2.52 g, 16.6 mmol), and CuOAc (7.2 mg, 0.059 mmol) in 20 mL of methanol was stirred overnight at room temperature. The mixture was filtered through Celite-545, and the filtrate was concentrated under vacuum pressure. The residue was purified by silica gel column chromatography with EtOAc and hexane (1/10) to give **2a** as white solids (2.56 g, 9.08 mmol, 88% yield); mp 48 °C; IR (KBr) ν 1717, 1600, 1255, 1154, 1034, 834 cm^{-1}; ^{1}H NMR δ 1.11 (t, J = 7.2 Hz, 3H), 3.82 (s, 3H), 4.04 (q, J = 7.2 Hz, 2H), 6.31 (s, 1H, C=C*H*), 6.84 (d, J = 9.0 Hz, 2H), 7.18–7.22 (m, 2H), 7.30 (d, J = 9.2 Hz, 2H), 7.35–7.40 (m, 3H) ppm; ^{13}C NMR δ 14.2, 55.4, 59.9, 113.6, 115.2, 127.6, 127.8, 128.8, 129.5, 132.8, 139.0, 156.0, 160.4, 165.9 ppm; HRMS-FAB (m/z, M = $C_{18}H_{18}O_3$) 305.1157 [M + Na]$^+$, calcd 305.1154.

(*E*)-Ethyl 3-Phenyl-3-(*p*-tolyl)acrylate (2b).[5] Colorless oil; IR (KBr) ν 1723, 1608, 1266, 1160, 1038, 820, 700 cm^{-1}; ^{1}H NMR δ 1.11 (t, J = 7.2 Hz, 3H), 2.36 (s, 3H), 4.04 (q, J = 7.2 Hz, 2H), 6.35 (s, 1H), 7.10–7.25 (m, 6 H), 7.37–7.42 (m, 3H) ppm; ^{13}C NMR δ 14.3, 21.6, 60.1, 116.4, 127.7, 127.9, 128.1, 128.9, 129.0, 137.8, 139.0, 139.5, 156.4, 166.0 ppm; HRMS-FAB (m/z, M = $C_{18}H_{19}O_2$) 267.1398 [M + H]$^+$, calcd 267.1385.

(*E*)-Ethyl 3-(4-Chlorophenyl)-3-phenylacrylate (2c).[5] Colorless oil; IR (KBr) ν 1720, 1617, 1488, 1265, 1163, 1092, 1035, 830, 700 cm^{-1}; ^{1}H NMR δ 1.12 (t, J = 7.2 Hz, 3H), 4.05 (q, J = 7.2 Hz, 2H), 6.34 (s, 1H), 7.15–7.33 (m, 6H), 7.35–7.43 (m, 3H) ppm; ^{13}C NMR δ 14.2, 60.2, 117.6, 127.8, 128.1, 128.4, 128.8, 129.3, 135.2, 138.2, 139.0, 154.8, 165.5 ppm; HRMS-FAB (m/z, M = $C_{17}H_{15}ClO_2$) 309.0672 [M + Na]$^+$, calcd 309.0658.

(*E*)-Ethyl 4-(3-Ethoxy-3-oxo-1-phenylprop-1-en-1-yl)-benzoate (2d). Colorless oil; IR (KBr) ν 1719, 1614, 1274, 1165, 1105, 1022, 776, 700 cm^{-1}; ^{1}H NMR δ 1.13 (t, J = 6.9 Hz, 3H), 1.40 (t, J = 7.05 Hz, 3H), 4.07 (q, J = 7.1 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 6.41 (s, 1H), 7.10–7.20 (m, 2H), 7.30–7.40 (m, 5H), 7.99 (d, J = 6.9 Hz, 2H) ppm; ^{13}C NMR δ 14.1, 14.5, 60.3, 61.1, 118.9, 127.8, 128.0, 128.1, 128.8, 129.3, 130.7, 138.0, 144.7, 154.8, 165.4, 165.7 ppm; HRMS-FAB (m/z, M = $C_{20}H_{20}O_4$) 347.1249 [M + Na]$^+$, calcd 347.1259.

(*E*)-Ethyl 3-Phenyl-3-(4-(trifluoromethyl)phenyl)acrylate (2e). Colorless oil; IR (KBr) ν 1724, 1325, 1169, 1127, 1068, 842, 700 cm^{-1}; ^{1}H NMR δ 1.13 (t, J = 7.1 Hz, 3H), 4.08 (q, J = 7.1 Hz, 2H), 6.39 (s, 1H), 7.18–7.22 (m, 2H), 7.38–7.42 (m, 5H), 7.58 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR δ 14.2, 60.4, 119.2, 125.1 (CF_3), 127.9, 128.3, 128.4, 128.8, 130.6, 131.1, 137.9, 144.1, 154.4, 165.4 ppm; HRMS-FAB (m/z, M = $C_{18}H_{15}F_3O_2$) 340.0915 [M + Na]$^+$, calcd 343.0922.

(*E*)-Ethyl 3-(3-Methoxyphenyl)-3-phenylacrylate (2f). Colorless oil; IR (KBr) ν 1718, 1598, 1277, 1162, 1040 cm^{-1}; ^{1}H NMR δ 1.12 (t, J = 7.2 Hz, 3H), 3.78 (s, 3H), 4.05 (q, J = 7.2 Hz, 2H), 6.36 (s, 1H, C=C*H*), 6.83–6.92 (m, 3H), 7.18–7.25 (m, 3H), 7.35–7.42 (m, 3H) ppm; ^{13}C NMR δ 14.2, 55.3, 60.1, 113.7, 114.6, 117.4, 120.7, 127.6, 127.9, 128.8, 129.1, 138.6, 141.9, 156.0, 159.1, 165.7 ppm; HRMS-FAB (m/z, M = $C_{18}H_{18}O_3$) 305.1141 [M + Na]$^+$, calcd 305.1154.

(*E*)-Ethyl 3-Phenyl-3-(*m*-tolyl)acrylate (2g). Colorless oil; IR (KBr) ν 1722, 1599, 1271, 1203, 1038, 699 cm^{-1}; ^{1}H NMR δ 1.22 (t, J = 7.2 Hz, 3H), 2.33 (s, 3H), 4.05 (q, J = 7.2 Hz, 2H), 6.35 (s, 1H), 7.10–7.30 (m, 6H), 7.35–7.43 (m, 3H) ppm; ^{13}C NMR δ 14.4, 21.7, 60.2, 117.3, 125.5, 127.8, 128.0, 128.2, 128.8, 129.0, 130.1, 137.9, 138.9, 140.7, 156.6, 165.9 ppm; HRMS-FAB (m/z, M = $C_{18}H_{19}O_2$) 267.1376 [M + H]$^+$, calcd 267.1385.

(*E*)-Ethyl 3-(3-Chlorophenyl)-3-phenylacrylate (2h). Colorless oil; IR (KBr) ν 1723, 1257, 1161, 1036, 874, 788 cm^{-1}; ^{1}H NMR δ 1.12 (t, J = 7.2 Hz, 3H), 4.05 (q, J = 7.2 Hz, 2H), 6.34 (s, 1H), 7.15–7.45 (m, 9H) ppm; ^{13}C NMR δ 14.2, 60.2, 118.4, 126.2, 127.8, 128.0, 128.2, 128.8, 129.1, 129.4, 134.2, 138.0, 142.4, 154.6, 165.4 ppm; HRMS-FAB (m/z, M = $C_{17}H_{15}ClO_2$) 309.0649 [M + Na]$^+$, calcd 309.0658.

(*E*)-Ethyl 3-(3-Ethoxy-3-oxo-1-phenylprop-1-en-1-yl)-benzoate (2i). Colorless oil; IR (KBr) ν 1719, 1614, 1274, 1165, 1105, 1022, 776, 700 cm^{-1}; ^{1}H NMR δ 1.13 (t, J = 7.2 Hz, 3H), 1.39 (t, J = 7.2 Hz, 3H), 4.07 (q, J = 7.1 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 6.40 (s, 1H), 7.20 (m, 2H), 7.36–7.45 (m, 5H), 8.00–8.10 (m, 2H) ppm; ^{13}C NMR δ 14.1, 14.5, 60.2, 61.2, 118.2, 127.7, 128.1, 128.2, 128.6, 128.8, 130.0, 130.5, 132.5, 138.1, 140.9, 155.4, 165.5, 165.7 ppm; HRMS-FAB (m/z, M = $C_{20}H_{20}O_4$) 347.1249 [M + Na]$^+$, calcd 347.1259.

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(*E*)-Ethyl 3-Phenyl-3-(*o*-tolyl)acrylate (2j). Colorless oil; IR (KBr) ν 1722, 1617, 1256, 1162, 1034, 763, 730 cm^{-1}; ^1H NMR δ 1.18 (t, J = 7.2 Hz, 3H), 2.07 (s, 3H), 4.12 (q, J = 7.1 Hz, 2H), 6.00 (s, 1H), 7.12−7.35 (m, 9H) ppm; ^{13}C NMR δ 14.2, 20.5, 60.2, 119.9, 125.5, 127.4, 128.15, 128.17, 128.9, 129.3, 130.4, 135.7, 138.5, 141.6, 156.4, 166.0 ppm; HRMS-FAB (m/z, M = $C_{18}H_{18}O_2$) 289.1195 [M + Na]$^+$, calcd 289.1204.

(*E*)-Ethyl 3-(Naphthalen-1-yl)-3-phenylacrylate (2k). White solid; mp 55 °C; IR (KBr) ν 1720, 1614, 1275, 1162, 1032, 776, 699 cm^{-1}; ^1H NMR δ 1.20 (t, J = 6.9 Hz, 3H), 4.17 (q, J = 7.1 Hz, 2H), 6.20 (s, 1H), 7.27−7.44 (m, 9H), 7.85 (d, J = 7.8 Hz, 2H), 7.94 (d, J = 0.9 Hz, 1H) ppm; ^{13}C NMR δ 14.2, 60.3, 121.1, 124.9, 125.5, 125.7, 126.2, 127.0, 127.6, 128.1, 128.3, 128.68, 128.70, 130.9, 133.5, 139.1, 139.5, 154.9, 165.9 ppm; HRMS-FAB (m/z, M = $C_{21}H_{18}O_2$) 325.1209 [M + Na]$^+$, calcd 325.1204.

(*E*)-Ethyl 3-(Naphthalen-2-yl)-3-phenylacrylate (2l). White solid; mp 84 °C; IR (KBr) ν 1687, 1590, 1367, 1279, 1254, 1037, 823, 751, 700 cm^{-1}. ^1H NMR δ 1.14 (t, J = 7.2 Hz, 3H), 4.08 (q, J = 7.2 Hz, 2H), 6.50 (s, 1H), 7.20−7.80 (m, 12 H) ppm; ^{13}C NMR δ 14.2, 60.1, 117.6, 124.9, 126.3, 126.7, 127.3, 127.7, 127.8, 128.0, 128.4, 128.6, 129.0, 132.7, 133.4, 137.8, 138.7, 156.1, 165.8 ppm; HRMS-FAB (m/z, M = $C_{21}H_{18}O_2$) 325.1209 [M + Na]$^+$, calcd 325.1204.

(*E*)-Ethyl 3-(Phenanthren-9-yl)-3-phenylacrylate (2m). White solid; mp 83 °C; IR (KBr) ν 1715, 1614, 1159, 750, 699 cm^{-1}; ^1H NMR δ 1.22 (t, J = 7.1 Hz, 3H), 3.85 (s, 3H), 4.19 (q, J = 7.1 Hz, 2H), 6.30 (s, 1H), 7.28−7.30 (m, 3H), 7.39−7.49 (m, 3H), 7.57−7.72 (m, 4H), 7.88−7.92 (m, 2H), 8.66−8.71 (m, 4H) ppm; ^{13}C NMR δ 14.2, 60.4, 121.0, 122.3, 122.7, 126.4, 126.5, 126.6, 126.7, 127.0, 127.6, 127.7, 128.4, 128.7, 128.8, 129.9, 130.2, 130.4, 130.8, 138.2, 138.5, 155.0, 166.0 ppm; HRMS-FAB (m/z, M = $C_{25}H_{20}O_2$) 375.1370 [M + Na]$^+$, calcd 375.1361.

(*Z*)-Ethyl 3-(4-Methoxyphenyl)-3-phenylacrylate (4). Ethyl *p*-methoxyphenylpropiolate (682 mg, 3.34 mmol), phenylboronic acid (647 mg, 5.31 mmol), $Cu(OAc)_2$ (16.3 mg, 0.089 mmol), MeOH (20 mL), **4** (826 mg, 2.93 mmol, 88%); colorless oil; IR (KBr) ν 1720, 1607, 1510, 1248, 834, 772 cm^{-1}; ^1H NMR δ 1.18 (t, J = 7.1 Hz, 3H), 3.85 (s, 3H), 4.10 (q, J = 7.2 Hz, 2H), 6.28 (s, 1H), 6.91 (d, J = 9.0 Hz, 2H), 7.16 (t, J = 9.0 Hz, 2H), 7.28−7.40 (m, 5H) ppm; ^{13}C NMR δ 14.3, 55.2, 60.0, 113.0, 116.6, 128.0, 128.3, 129.0, 130.6, 130.7, 141.2, 156.2, 159.3, 165.9 ppm; HRMS-FAB (m/z, M = $C_{18}H_{18}O_3$) 305.1149 [M + Na]$^+$, calcd 305.1154.

(*Z*)-Ethyl 3-Phenyl-3-(4-(trifluoromethyl)phenyl)acrylate (5). Ethyl *p*-trifluoromethylphenylpropiolate (1.12 g, 4.61 mmol), phenylboronic acid (841 mg, 6.89 mmol), $Cu(OAc)_2$ (17.6 mg, 0.097 mmol), MeOH (15 mL), **5** (580 mg, 1.81 mmol, 39%); brown solid; mp 58 °C; IR (KBr) ν 1721, 1613, 1324, 1162, 1118, 837, 774 cm^{-1}; ^1H NMR δ 1.13 (t, J = 7.2 Hz, 3H), 4.06 (q, J = 7.1 Hz, 2H), 6.44 (s, 1H), 7.24−7.28 (m, 2H), 7.32−7.34 (m, 5H), 7.65 (d, J = 7.8 Hz, 2H) ppm; ^{13}C NMR δ 14.1, 60.3, 118.0, 122.1, 124.7 (CF_3), 126.7, 127.9, 128.4, 129.2, 129.5, 139.6, 142.5, 154.8, 165.3 ppm; HRMS-FAB (m/z, M = $C_{18}H_{15}F_3O_2$) 343.0929 [M + Na]$^+$, calcd 343.0922.

(*Z*)-Methyl 3-(4-Methoxyphenyl)-3-phenylacrylate (6). Methyl phenylpropiolate (748 mg, 4.67 mmol), *p*-methoxyphenylboronic acid (1.0 g, 6.59 mmol), CuOAc (8.69 mg, 0.071 mmol), MeOH (20 mL), the product acrylate (1.02 g, 3.80 mmol, 81%); white solid; mp 70 °C; IR (KBr) ν 1724, 1597, 1269, 1158, 834, 700 cm^{-1}; ^1H NMR δ 3.60 (s, 3H), 3.82 (s, 3H), 6.29 (s, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.20−7.40 (m, 6H) ppm; ^{13}C NMR δ 51.2, 55.4, 113.6, 114.5, 127.6, 127.9, 128.8, 129.6, 132.8, 138.8, 156.6, 160.5, 166.2 ppm; HRMS-FAB (m/z, M = $C_{17}H_{16}O_3$) 291.0991 [M + Na] $^+$, calcd 291.0997.

(*Z*)-Isopropyl 3-(4-Methoxyphenyl)-3-phenylacrylate (8). Isopropyl phenylpropiolate (1.05 g, 5.56 mmol), *p*-methoxyphenylboronic acid (1.2 g, 7.88 mmol), $Cu(OAc)_2$ (9.95 mg, 0.0548 mmol), MeOH (15 mL), **8** (1.10 g, 3.70 mmol, 67%); colorless oil; IR (KBr) ν 1715, 1600, 1510, 1254, 1166, 834, 700 cm^{-1}; ^1H NMR δ 1.09 (d, J = 6.3 Hz, 6H), 3.82 (s, 3H), 4.91 (q, J = 6.3 Hz, 1H), 6.29 (s, 1H), 6.84 (d, J = 9.0 Hz, 2H), 7.18−7.26 (m, 4H), 7.36−7.39 (m, 3H) ppm; ^{13}C NMR δ 21.8, 55.3, 67.1, 113.5, 115.8, 127.56, 127.63, 128.8, 129.4, 132.8, 139.1, 155.3, 160.3, 165.5 ppm; HRMS-FAB (m/z, M = $C_{19}H_{20}O_3$) 319.1312 [M + Na]$^+$, calcd 319.1310.

Typical Procedure for the Conjugate Hydrosilylation of 3,3-Diarylacrylates. Reduction of (*E*)-Ethyl 3-(*p*-Methoxyphenyl)-3-phenylacrylate 2a (Table 1, entry 1). To a solution of **2a** (282 mg, 1.0 mmol) and Rh(Phebox-*ip*) **1a** (5.4 mg, 0.01 mmol) in toluene (2.0 mL) was added diethoxymethylsilane (202 mg, 1.5 mmol) at 60 °C. The mixture was stirred for 2 h. At 0 °C, THF (1 mL), MeOH (1 mL), and hydrochloric acid (1 N, 1 mL) were then added, and the mixture was stirred for 1 h. The mixture was extracted with EtOAc, and the extract was washed with aq $NaHCO_3$ and saturated brine. The organic layer was dried over $MgSO_4$ and then concentrated to give the residual oil, which was purified by silica gel column chromatography with hexane and EtOAc (10/1) to give **3a** as colorless oil (274 mg, 0.97 mmol, 97% yield); DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 7.9 min for *R* and 9.2 min for *S*, 95% ee; $[\alpha]^{27}_D$ = −2.09 (*c* 1.00, $CHCl_3$). For entry 3 of Table 1: **2a** (1.41 g, 5.00 mmol), Rh(Phebox-*ip*) **1a** (5.34 mg, 0.0099 mmol), toluene (10 mL), $(EtO)_2MeSiH$ (1.01 g, 7.50 mmol), 60 °C, 10 h, the product **3a** (1.38 g, 4.85 mmol, 97%), 96% ee.

(*S*)-Ethyl 3-(4-Methoxyphenyl)-3-phenylpropanoate (3a).[10] IR (KBr) ν 1732, 1510, 1250, 1154, 1033, 830 cm^{-1}; ^1H NMR δ 1.12 (t, J = 6.9 Hz, 3H), 3.02 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 4.04 (q, J = 7.2 Hz, 2H), 4.50 (t, J = 8.1 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.17−7.36 (m, 7H) ppm; ^{13}C NMR δ 14.2, 41.1, 46.3, 55.2, 60.4, 113.7, 126.2, 127.3, 128.2, 128.4, 135.3, 143.5, 157.8, 171.5 ppm; HRMS-FAB (m/z, M = $C_{18}H_{20}O_3$) 307.1322 [M + Na]$^+$, calcd 307.1310. The racemic propanoate was prepared by hydrogenation of acrylates with Pd/C catalyst under hydrogen atmosphere (1 atm) in ethanol.

(*S*)-Ethyl 3-Phenyl-3-(*p*-tolyl)propanoate (3b).[11] **2b** (270 mg, 1.02 mmol), **3b** (246 mg, 0.92 mmol, 90% yield); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 99:1, 1 mL/min, 27 °C, t_R = 5.2 min for *R* and 6.1 min for *S*, 98% ee; $[\alpha]^{27}_D$ = +1.72 (*c* 0.99, $CHCl_3$); IR (KBr) ν 1735, 1254, 1154, 700 cm^{-1}. ^1H NMR δ 1.13 (t, J = 7.2 Hz, 3H), 2.31 (s, 3H), 3.05 (d, J = 7.8 Hz, 2H), 4.05 (q, J = 7.2 Hz, 2H), 4.53 (t, J = 7.8 Hz, 1H), 7.08−7.33 (m, 9H) ppm; ^{13}C NMR δ 14.4, 21.3, 41.1, 46.9, 60.6, 126.4, 127.5, 127.6, 128.4, 129.2, 135.9, 140.4, 143.6, 171.7 ppm; HRMS-FAB (m/z, M = $C_{18}H_{20}O_2$) 269.1533 [M + H]$^+$, calcd 269.1542.

(*S*)-Ethyl 3-(4-Chlorophenyl)-3-phenylpropanoate (3c).[12] **2c** (287 mg, 1.00 mmol), **3c** (268 mg, 0.927 mmol, 93% yield); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 99:1, 1 mL/min, 27 °C, t_R = 9.7 min for *R* and 13.1 min for *S*, 98% ee; $[\alpha]^{20}_D$ = −1.58 (*c* 1.00, $CHCl_3$); IR (KBr) ν 1733, 1491, 1253, 1156, 1093, 1015, 823 cm^{-1}; ^1H NMR δ 1.13 (t, J = 7.2 Hz, 3H), 3.02 (d, J = 8.1 Hz, 2H), 4.04 (q, J = 7.2 Hz, 2H), 4.53 (t, J = 8.1 Hz, 1H), 7.15−7.40 (m, 9H) ppm; ^{13}C NMR δ 14.3, 40.8, 46.5, 60.6, 126.5, 127.3, 128.4, 128.8 (Cx2), 132.1, 141.7, 142.7, 171.2 ppm; HRMS-FAB (m/z, M = $C_{17}H_{17}ClO_2$) 311.0815 [M + Na]$^+$, calcd 311.0815.

(*S*)-Ethyl 4-(3-Ethoxy-3-oxo-1-phenylpropyl)benzoate (3d). **2d** (326 mg, 1.00 mmol), **3d** (294 mg, 0.899 mmol, 90%); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 9.8 min for *R* and 11.5 min for *S*, 98% ee; $[\alpha]^{20}_D$ = 8.39 (*c* 1.00, $CHCl_3$); IR (KBr) ν 1718, 1609, 1277, 1105, 1022, 704 cm^{-1}; ^1H NMR δ 1.12 (t, J = 7.2 Hz, 3H), 1.37 (t, J = 7.1 Hz, 3H), 3.07 (d, J = 7.8 Hz, 2H), 4.04 (q, J = 7.1 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.61 (t, J = 7.95 Hz, 1H), 7.19−7.33 (m, 7H), 7.96 (d, J = 8.7 Hz, 2H) ppm; ^{13}C NMR δ 14.2, 14.5, 40.5, 47.0, 60.6, 60.9, 126.6, 127.4, 127.5, 128.4, 128.6, 129.6, 142.4, 148.3, 166.0, 171.1 ppm; HRMS-FAB (m/z, M = $C_{20}H_{22}O_4$) 349.1426 [M + Na]$^+$, calcd 349.1416.

(*S*)-Ethyl 3-Phenyl-3-(4-(trifluoromethyl)phenyl)propanoate (3e). **2e** (321 mg, 1.00 mmol), **3e** (308 mg, 0.95 mmol, 95%); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 5.7 min for *R* and 6.5 min for *S*, 97% ee; $[\alpha]^{20}_D$ = −2.56 (*c* 1.00, $CHCl_3$); IR (KBr) ν 1735, 1326, 1164, 1119, 1069, 700 cm^{-1}; ^1H NMR δ 1.13 (t, J = 6.9 Hz, 3H), 3.07 (d, J = 7.8 Hz, 2H), 4.05 (q, J = 7.0 Hz, 2H), 4.61 (t, J = 7.9 Hz, 1H), 7.20−7.37 (m, 7H), 7.54 (d, J = 8.1 Hz, 2H) ppm; ^{13}C NMR δ 14.2, 40.5, 46.9, 60.7, 122.1, 125.3 (CF_3), 126.7, 127.4, 127.8, 128.4, 128.5, 142.2, 147.2, 171.0 ppm; HRMS-FAB (m/z, M = $C_{18}H_{17}F_3O_2$) 345.1069 [M + Na]$^+$, calcd 345.1078.

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(*S*)-Ethyl 3-(3-Methoxyphenyl)-3-phenylpropanoate (3f).[12] **2f** (282 mg, 1.00 mmol), the product (268 mg, 0.945 mmol, 94% yield); colorless oil; DAICEL CHIRALCEL AS-H, hexane/ipa = 99:1, 1 mL/min, 27 °C, t_R = 10.1 min for *R* and 12.4 min for *S*, 97% ee; $[\alpha]^{27}_D$ = +2.36 (*c* 1.01, $CHCl_3$); IR (KBr) ν 1733, 1597, 1489, 1257, 1155, 1042, 868 cm^{-1}; ^1H NMR δ 1.12 (t, *J* = 7.2 Hz, 3H), 3.04 (d, *J* = 7.8 Hz, 2H), 3.76 (s, 3H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.52 (t, *J* = 7.9 Hz, 1H), 6.70−6.90 (m, 3H), 7.15−7.33 (m, 6H) ppm;[12] ^{13}C NMR δ 14.3, 40.8, 47.1, 55.1, 60.5, 111.3, 113.6, 119.8, 126.3, 127.4, 128.3, 129.3, 143.0, 144.8, 159.3, 171.4 ppm; HRMS-FAB (*m*/*z*, M = $C_{18}H_{20}O_3$) 307.1306 $[M + Na]^+$, calcd 307.1310.

(*S*)-Ethyl 3-Phenyl-3-(*m*-tolyl)propanoate (3g). **2g** (270 mg, 1.00 mmol), **3g** (253 mg, 0.94 mmol, 94% yield); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 99:1, 1 mL/min, 27 °C, t_R = 8.0 min for *R* and 8.4 min for *S*, 95% ee; $[\alpha]^{27}_D$ = +2.37 (*c* 1.11, $CHCl_3$); IR (KBr) ν 1736, 1255, 1155, 706 cm^{-1}; ^1H NMR δ 1.12 (t, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 3.04 (d, *J* = 8.1 Hz, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.52 (t, *J* = 8.1 Hz, 1H), 6.97−7.10 (m, 3H), 7.13−7.34 (m, 6H) ppm; ^{13}C NMR δ 14.4, 21.8, 41.1, 47.2, 124.5, 126.4, 127.2, 127.6, 128.3, 128.4, 138.0, 143.3, 143.5, 171.7 ppm; HRMS-FAB (*m*/*z*, M = $C_{18}H_{20}O_2$) 269.1546 $[M + H]^+$, calcd 269.1542.

(*S*)-Ethyl 3-(3-Chlorophenyl)-3-phenylpropanoate (3h). **2h** (286 mg, 1.00 mol), **3h** (261 mg, 0.906 mmol, 91% yield); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 6.4 min for *R* and 7.9 min for *S*, 97% ee; $[\alpha]^{24}_D$ = 0.54 (*c* 0.99, $CHCl_3$); IR (KBr) ν 1733, 1252, 1157, 1082, 1029, 781, 701 cm^{-1}; ^1H NMR δ 1.13 (t, *J* = 7.2 Hz, 3H), 3.03 (d, *J* = 8.1 Hz, 2H), 4.05 (q, *J* = 7.2 Hz, 2H), 4.52 (t, *J* = 7.9 Hz, 1H), 7.10−7.33 (m, 9H) ppm; ^{13}C NMR δ 14.2, 40.6, 46.8, 60.6, 125.7, 126.5, 126.6, 127.4, 127.7, 128.4, 129.6, 134.1, 142.4, 145.2, 171.8 ppm; HRMS-FAB (*m*/*z*, M = $C_{17}H_{17}ClO_2$) 311.0811 $[M + Na]^+$, calcd 311.0815.

(*S*)-Ethyl 3-(3-Ethoxy-3-oxo-1-phenylpropyl)benzoate (3i). **2i** (327 mg, 1.01 mmol), **3i** (311 mg, 0.954 mmol, 95%); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 11.3 min for *R* and 12.5 min for *S*, 98% ee; $[\alpha]^{20}_D$ = 3.53 (*c* 1.00, $CHCl_3$); IR (KBr) ν 1721, 1280, 1186, 1105, 753, 701 cm^{-1}; ^1H NMR δ 1.12 (t, *J* = 7.2 Hz, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 3.09 (d, *J* = 8.1 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.61 (t, *J* = 8.0 Hz, 1H), 7.16−7.45 (m, 6H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.96 (s, 1H) ppm;[13] ^{13}C NMR δ 14.2, 14.5, 40.7, 46.9, 60.6, 61.0, 126.5, 127.4, 127.6, 128.36, 128.41, 130.5, 132.1, 142.6, 143.5, 166.2, 171.2 ppm; HRMS-FAB (*m*/*z*, M = $C_{20}H_{22}O_4$) 349.1426 $[M + Na]^+$, calcd 349.1416.

(*S*)-Ethyl 3-Phenyl-3-(*o*-tolyl)propanoate (3j). **2j** (267 mg, 1.00 mmol), **3j** (247 mg, 0.922 mmol, 92% yield); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 5.8 min for *S* and 7.1 min for *R*, 97% ee; $[\alpha]^{24}_D$ = +71.4 (*c* 1.01, $CHCl_3$); IR (KBr) ν 1734, 1253, 1155, 752, 700 cm^{-1}. ^1H NMR δ 1.12 (t, *J* = 7.1 Hz, 3H), 2.30 (s, 3H), 3.03 (d, *J* = 7.2 Hz, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 4.74 (t, *J* = 8.0 Hz, 1H), 7.10−7.30 (m, 9H) ppm; ^{13}C NMR δ 14.2, 20.0, 41.3, 43.1, 60.4, 125.8, 126.0, 126,1, 126.3, 127.7, 128.2, 130.4, 136.1, 140.9, 142.8, 171.5 ppm; HRMS-FAB (*m*/*z*, M = $C_{18}H_{20}O_2$) 291.1351 $[M + Na]^+$, calcd 291.1361.

(*S*)-Ethyl 3-(Naphthalen-1-yl)-3-phenylpropanoate (3k). **2k** (302 mg, 1.00 mol), **3k** (293 mg, 0.961 mmol, 96%); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 9.7 min for *R* and 17.5 min for *S*, 99% ee; $[\alpha]^{24}_D$ = +16.8 (*c* 1.01, $CHCl_3$); IR (KBr) ν 1731, 1250, 1155, 1029, 779, 700 cm^{-1}; ^1H NMR δ 1.11 (t, *J* = 7.2 Hz, 3H), 3.15−3.25 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 5.38 (t, *J* = 7.9 Hz, 1H), 7.13−7.30 (m, 5H), 7.39−7.50 (m, 4H), 7.74 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 9.6 Hz, 1H), 8.14 (d, *J* = 9.6 Hz, 1H) ppm; ^{13}C NMR δ 14.3, 41.5, 42.7, 60.5, 123.5, 123.9, 125.0, 125.3, 125.9, 126.3, 127.2, 127.6, 128.3, 128.6, 131.3, 133.8, 138.6, 143.1, 171.5 ppm; HRMS-FAB (*m*/*z*, M = $C_{21}H_{20}O_2$) 327.1365 $[M + Na]^+$, calcd 327.1361.

(*S*)-Ethyl 3-(Naphthalen-2-yl)-3-phenylpropanoate (3l). **2l** (303 mg, 1.00 mmol), the product (294 mg, 0.966 mmol, 96%); white solid; mp 75 °C; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 8.2 min for *R* and 11.2 min for *S*, 95% ee; $[\alpha]^{25}_D$ = +38.8 (*c* 1.01, $CHCl_3$); IR (KBr) ν 1723, 1373, 1267, 1151, 1017, 750, 703 cm^{-1}; ^1H NMR δ 1.11 (t, *J* = 7.1 Hz, 3H), 3.17 (m, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.73 (t, *J* = 8.0 Hz, 1H), 7.16−7.50 (m, 8H), 7.70−7.83 (m, 4H) ppm; ^{13}C NMR δ 14.3, 40.8, 47.2, 60.5, 125.38, 125.42, 125.8, 126.3, 126.4, 127.3, 127.5, 127.6, 128.0, 128.3, 132.0, 133.2, 140.6, 143.0, 171.4 ppm; HRMS-FAB (*m*/*z*, M = $C_{21}H_{20}O_2$) 327.1365 $[M + Na]^+$, calcd 327.1361.

(*S*)-Ethyl 3-(Phenanthren-9-yl)-3-phenylpropanoate (3m). **2m** (353 mg, 1.00 mmol), **3m** (353 mg, 0.99 mmol, 99%); white solid; mp 74 °C; DAICEL CHIRALCEL AD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 7.1 min for *R* and 7.9 min for *S*, 97% ee; $[\alpha]^{27}_D$ = +157.9 (*c* 1.00, $CHCl_3$); IR (KBr) ν 1714, 1297, 1267, 1148, 1026, 748, 701 cm^{-1}; ^1H NMR δ 1.12 (t, *J* = 7.1 Hz, 3H), 3.13−3.34 (m, 2H), 4.01−4.12 (m, 2H), 5.37 (t, *J* = 7.8 Hz, 1H), 7.14−7.35 (m, 4H), 7.51−7.66 (m, 4H), 7.69 (s, 1H), 7.87 (m, 1H), 8.15 (m, 1H), 8.65 (m, 1H), 8.70 (m, 1H) ppm; ^{13}C NMR δ 14.3, 41.6, 43.1, 60.6, 122.2, 122.9, 124.4, 124.8, 126.0, 126.3, 126.4, 126.47, 126.50, 127.7, 128.3, 128.4, 129.6, 130.5, 130.7, 131.1, 136.6, 142.9, 171.5 ppm; HRMS-FAB (*m*/*z*, M = $C_{25}H_{22}O_2$) 377.1509 $[M + Na]^+$, calcd 377.1517.

(*R*)-Ethyl 3-(4-Methoxyphenyl)-3-phenylpropanoate ((*R*)-3a). **4** (282 mg, 1.00 mmol), **3a** (262 mg, 0.924 mmol, 92% yield); colorless oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 7.7 min for *R* and 9.4 min for *S*, 97% ee; $[\alpha]^{27}_D$ = +3.18 (*c* 1.00, $CHCl_3$).

(*R*)-Ethyl 3-Phenyl-3-(4-(trifluoromethyl)phenyl)propanoate ((*R*)-3e). **5** (321 mg, 1.00 mmol), **3e** (310 mg, 0.963 mmol, 96% yield); brown oil; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 5.7 min for *R* and 6.8 min for *S*, 97% ee; $[\alpha]^{26}_D$ = +2.18 (*c* 1.00, $CHCl_3$).

(*S*)-Methyl 3-(4-Methoxyphenyl)-3-phenylpropanoate (7).[13] **6** (269 mg, 1.00 mmol), **7** (258 mg, 0.95 mmol, 95% yield); white solid; mp 49 °C; DAICEL CHIRALCEL OD-H, hexane/ipa = 97:3, 1 mL/min, 27 °C, t_R = 9.6 min for *R* and 12.9 min for *S*, 98% ee; $[\alpha]^{28}_D$ = −3.16 (*c* 1.01, $CHCl_3$); Lit[13] $[\alpha]^{20}_D$ = −14.3 (*c* 0.51, $CHCl_3$) for *R*; IR (KBr) ν 1736, 1511, 1257, 1156, 1026, 831, 700 cm^{-1}; ^1H NMR δ 3.04 (d, *J* = 8.1 Hz, 2H), 3.59 (s, 3H), 3.77 (s, 3H), 4.52 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 7.10−7.35 (m, 7H) ppm; ^{13}C NMR δ 40.8, 46.2, 51.7, 55.2, 113.7, 126.2, 127.3, 128.30, 128.34, 135.3, 143.5, 157.7, 172.0 ppm; HRMS-FAB (*m*/*z*, M = $C_{17}H_{18}O_3$) 293.1145 $[M + Na]^+$, calcd 293.1154.

(*S*)-Isopropyl 3-(4-Methoxyphenyl)-3-phenylpropanoate (9). **8** (297 mg, 1.00 mmol), **9** (293 mg, 0.98 mmol, 98% yield); colorless oil; DAICEL CHIRALCEL AD-H, hexane/ipa = 99:1, 1 mL/min, 27 °C, t_R = 9.5 min for *S* and 10.3 min for *R*, 97% ee; $[\alpha]^{26}_D$ = −2.92 (*c* 1.01, $CHCl_3$). IR (KBr) ν 1728, 1511,1251, 1107, 828, 700 cm^{-1}; ^1H NMR δ 1.08 (d, *J* = 6.0 Hz, 6H), 2.99 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 3H), 4.48 (t, *J* = 8.3 Hz, 1H), 4.89 (q, *J* = 6.0 Hz, 1H), 6.81(d, *J* = 8.7 Hz, 2H), 7.13−7.29 (m, 7H) ppm; ^{13}C NMR δ 21.8, 41.4, 46.8, 55.2, 67.7, 113.6, 126.2, 127.4, 128.2, 128.4, 135.3, 143.5, 157.7, 171.0 ppm; HRMS-FAB (*m*/*z*, M = $C_{19}H_{22}O_3$) 321.1472 $[M + Na]^+$, calcd 321.1467.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectra and HPLC charts of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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