Supporting Information

Palladium-Catalyzed Asymmetric Arylation, Vinylation and Allenylation of *tert*-Cyclobutanols via Enantioselective C–C Bond Cleavage

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General Methods. NMR spectra were recorded on JEOL EX-400 (^1H NMR, 400 MHz; ^{13}C NMR, 100 MHz; ^{31}P NMR, 161.9 MHz), JNM AL-300 (^1H NMR, 300 MHz; ^{13}C NMR, 75.5 MHz) and JEOL GSX-270 (^1H NMR, 270 MHz; ^{13}C NMR, 67.5 MHz) instruments for solutions in CDCl_3 with Me_4Si as an internal standard: the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. FT-IR spectra (thin film for liquids, KBr disk for solids) were recorded on a Nicolet Impact 400 spectrometer. Melting points are uncorrected. Recycling preparative high performance liquid chromatography (HPLC) was performed on a JAI LC-908-G30 instrument (600 mm $\times$ 20 mm $\times$ 2, JAIGEL-1H and JAIGEL-2H dual styrene polymer columns) equipped with ultraviolet (UV) and refractive-index (RI) detector and CHCl_3 as an eluent. HPLC analyses were performed on a L-7000 instrument (HITACHI) using Daicel Chiralcel[®] AD and OD columns (4.6 $\times$ 250 mm) at 25 °C. Mass spectra were measured on a JEOL JMS600H mass spectrometer. Column chromatography on SiO_2 was performed with Merck silica gel 60. Elemental analysis was carried out at the Microanalytical Center of Kyoto University.

Materials. Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by the known method before use. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (dba = dibenzylideneacetone) was synthesized by the literature method.⁴⁴ Cyclobutanols **1–10** and 1-phenylcyclobutanol were prepared according to the reported procedures from the corresponding cyclobutanones and Grignard reagents or alkyllithiums. (*R*)-MeO-MOP, (*S*)-H-MOP³⁴ and PPFA derivatives **D–M**³⁶ were prepared according to the reported procedures. Vinyl triflate were prepared according to the reported

procedures⁴⁵ from the corresponding ketones and trifluoromethanesulfonic anhydride, while vinyl bromides are commercial products. Propargylic acetates and propargylic carbonates were prepared according to known procedures^{40b} from the corresponding propargylic alcohols.

Preparation of *Cis*-rich *tert*-Cyclobutanols: A typical procedure to prepare *cis*-rich *tert*-cyclobutanol **1** is as follows: to a mixture of **1**, pyridine (3.0 equiv), and a catalytic amount of 4-*N,N*-dimethylaminopyridine in CH₂Cl₂, was added acetic anhydride (0.7–0.8 equiv) at 0 °C and the resulted mixture was stirred for 6 h. After the general workup, the produced acetate ester of **1** (*cis/trans* = 98/2) was separated from unreacted **1** and isolated in a pure form by column chromatography on SiO₂. Deacetylation of the ester was performed by the known method (excess K₂CO₃ in MeOH at room temperature). *Cis*-rich **1** was obtained after column chromatography on SiO₂ in ca. 45% yield from the initial **1**.

1,3-Diphenyl-1-cyclobutanol (1**, *cis/trans* = 98/2).** White solid; mp 81.0–81.8 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.31 (s, OH, 1H), 2.48–2.60 (m, 2H), 2.98–3.12 (m, 3H), 7.16–7.35 (m, 6H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.61 (d, *J* = 7.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 29.9, 44.5, 72.4, 76.7, 77.0, 77.3, 125.4, 126.0, 126.6, 127.5, 128.3, 128.6, 144.6, 145.3. Anal. Calcd for C₁₆H₁₆O: C, 85.68; H, 7.19. Found: C, 85.40; H, 7.12. Other alcohols **2**, **3**, **4**, **6**, **7** and **8** were prepared by the same procedure, except for **5**, which could be purified in the alcohol form by column chromatography on SiO₂. Each of the alcohols *cis*-**9** and *trans*-**9** was separated by HPLC, while each of the alcohols *cis*-**10** and *trans*-**10** was separated by column chromatography on SiO₂. The ratio of *cis* and *trans* isomers of each substrate was determined by ¹H NMR. The exact stereochemistry of **1** was determined to be *cis* by X-ray single crystal analysis of 4-chlorobenzoic acid ester of **1**.

***cis*-4-Chlorobenzoic acid 1,3-diphenylcyclobutyl ester (ester-1).** White solid; mp 92.8–93.1 °C; IR (KBr) 2985, 1720 (C=O), 1595, 1485, 1277, 1235, 1104, 943, 843, 760, 750, 700, 530 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.75–2.93 (m, 2H), 3.21–3.42 (m, 3H), 7.15–7.48 (m, 10H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.94 (d, *J* = 7.7 Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 31.9, 42.6, 78.6, 126.0, 126.3, 126.5, 127.8, 128.5, 128.5, 128.6, 129.1, 131.0, 139.3, 141.8, 143.9, 164.1. Anal. Calcd for C₂₃H₁₉ClO₂: C, 76.13; H, 5.28. Found: C,

76.18; H, 5.47.

X-ray Crystallographic Studies of ester-1. Colorless crystals of **ester-1** suitable for X-ray analysis were obtained by recrystallization from CH₂Cl₂–*n*-hexane. The single crystal was sealed in a Pyrex glass capillary under N₂ atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-K α radiation. Details of crystal and data collection parameters are summarized in Table S1. The positions of non-hydrogen atoms were determined by direct methods (SIR97) and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of **ester-1** is shown in Figure S1.

Table S1. Crystallographic Data for **ester-1**.

formula	C ₂₃ H ₁₉ ClO ₂
formula weigh	362.85
cryst size (mm ³)	0.60 x 0.20 x 0.10
cryst system	monoclinic
space group	P2 ₁ /a (#14)
cryst color	colorless
<i>a</i> (Å)	16.3301(8)
<i>b</i> (Å)	6.0079(3)
<i>c</i> (Å)	19.615(1)
β (°)	107.257(1)
<i>V</i> (Å ³)	1837.8(2)
<i>Z</i>	4
<i>d</i> _{calc} (g cm ⁻³)	1.311
<i>F</i> (000)	760.00
μ _{calc} (cm ⁻¹)	2.22
no. of unique data	4202
no. of data used (<i>I</i> > 3 σ (<i>I</i>))	2070
no. of params refined	312
<i>R</i> ^a	0.036
<i>R</i> _w ^b	0.035
goodness of fit indicator	1.07
maximum residuals (e Å ⁻³)	2.27

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}$.

Figure S1. Crystal structure of ester-1.

3-Hexyl-1-phenyl-1-cyclobutanol (2, *cis/trans* = 96/4). Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.88 (t, $J = 7.1$ Hz, 3H), 1.08–1.35 (m, 8H), 1.47–1.54 (m, 2H), 1.76–1.88 (sept, $J = 8.2$ Hz, 1H), 1.95–2.05 (m, 3H), 2.68–2.75 (m, 2H), 7.24–7.30 (m, 1H), 7.35–7.40 (m, 2H), 7.51–7.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.6, 25.5, 27.4, 29.2, 31.9, 37.2, 43.4, 73.0, 125.2, 127.2, 128.4, 146.3. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}$: C, 82.70; H, 10.41. Found: C, 82.60; H, 10.70.

3-*tert*-Butyl-1-phenyl-1-cyclobutanol (3, *cis/trans* = 97/3). White solid; mp 45.8–46.2 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 0.86 (s, 9H), 1.65–1.75 (m, 1H), 1.99 (s, OH, 1H), 2.08–2.16 (m, 2H), 2.40–2.52 (m, 2H), 7.24–7.42 (m, 3H), 7.56 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 26.6, 30.9, 36.1, 38.1, 71.4, 76.7, 77.0, 77.3, 125.4, 127.3, 128.5, 146.0. Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}$: C, 82.30; H, 9.87. Found: C, 82.06; H, 10.03.

1-Methyl-3-phenyl-1-cyclobutanol (4, *cis/trans* = 97/3). Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 1.50 (s, 3H), 1.69 (br s, OH, 1H), 2.14–2.27 (m, 2H), 2.46–2.58 (m, 2H), 3.04 (quint, $J = 8.8$ Hz, 1H), 7.13–7.35 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.1, 30.0, 45.4, 68.9, 126.0, 126.6, 128.3, 145.0. Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: C, 81.44; H, 8.70.

Found: C, 81.21; H, 8.76.

1-Butyl-3-phenyl-1-cyclobutanol (5, *cis/trans* = 99/1). Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.96 (t, $J = 7.1$ Hz, 3H), 1.30–1.50 (m, 5H), 1.65–1.75 (m, 2H), 2.07–2.20 (m, 2H), 2.50–2.61 (m, 2H), 3.02 (quint, $J = 8.9$ Hz, 1H), 7.13–7.36 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 23.2, 25.9, 30.3, 39.4, 43.7, 71.1, 125.8, 126.5, 128.2, 145.1. Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}$: C, 82.30; H, 9.87. Found: C, 82.21; H, 9.87.

1-*tert*-Butyl-3-phenyl-1-cyclobutanol (6, *cis/trans* = 99/1). White solid; mp 61.5–62.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.02 (s, 9H), 1.99 (s, OH, 1H), 2.00–2.15 (m, 2H), 2.75–2.88 (m, 2H), 3.01 (quint, $J = 8.9$ Hz, 1H), 7.16–7.20 (m, 1H), 7.24–7.37 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 23.9, 29.9, 35.6, 40.2, 76.4, 125.7, 126.6, 128.2, 146.2. Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}$: C, 82.30; H, 9.87. Found: C, 82.05; H, 10.15.

1-(1-Naphthyl)-3-phenyl-1-cyclobutanol (7, *cis/trans* = 98/2). White solid; mp 75.0–76.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.46 (br s, OH, 1H), 2.66–2.77 (m, 2H), 2.96 (quint, $J = 9.0$ Hz, 1H), 3.25–3.36 (m, 2H), 7.14–7.23 (m, 1H), 7.24–7.35 (m, 5H), 7.41–7.55 (m, 3H), 7.68 (d, $J = 7.3$ Hz, 1H), 7.89 (d, $J = 9.3$ Hz, 1H), 8.35 (d, $J = 9.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 31.5, 44.4, 73.6, 122.9, 124.6, 125.6, 125.7, 126.0, 126.3, 126.6, 128.3, 129.0, 129.0, 130.8, 134.9, 138.8, 144.4. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}$: C, 87.56; H, 6.61. Found: C, 87.33; H, 6.72.

1-(2-Naphthyl)-3-phenyl-1-cyclobutanol (8, *cis/trans* = 99/1). White solid; mp 122.0–122.7 °C; ^1H NMR (400 MHz, CDCl_3) δ 2.23 (br s, OH, 1H), 2.54–2.75 (m, 2H), 3.05–3.29 (m, 3H), 7.17–7.43 (m, 5H), 7.46–7.61 (m, 2H), 7.76 (d, $J = 8.6$ Hz, 1H), 7.83–7.98 (m, 3H), 8.05 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 30.1, 44.5, 72.6, 123.5, 124.4, 126.1, 126.2, 126.3, 126.7, 127.6, 128.2, 128.4, 128.8, 132.8, 133.1, 142.4, 144.6. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}$: C, 87.56; H, 6.61. Found: C, 87.37; H, 6.64.

3-Methyl-1,3-diphenyl-1-cyclobutanol (*cis*-9, *cis/trans* = 99/1). White solid; mp 96.0–96.8 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.27 (s, 3H), 1.83 (br s, OH, 1H), 2.89 (d, $J = 12.7$ Hz, 2H), 2.97 (d, $J = 12.7$ Hz, 2H), 7.17–7.23 (m, 1H), 7.29–7.44 (m, 7H), 7.54–7.58 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 31.4, 34.3, 48.9, 72.5, 125.3, 125.5, 125.7, 127.5, 128.4, 128.6, 146.4, 151.6. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: C, 85.67; H, 7.61. Found: C, 85.39; H,

7.65.

3-Methyl-1,3-diphenyl-1-cyclobutanol (*trans*-9, *cis/trans* = 1/99). White solid; mp 97.0–98.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 1.72 (s, 3H), 1.93 (br s, OH, 1H), 2.62 (dd, J = 11.0, 2.7 Hz, 2H), 3.00 (dd, J = 11.0, 2.7 Hz, 2H), 7.10–7.35 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 32.7, 36.0, 48.4, 72.9, 124.7, 125.1, 125.3, 127.0, 128.2, 128.4, 147.4, 151.6. The exact stereochemistry of *cis*-9 and *trans*-9 was determined by X ray single crystal analysis of 4-chlorobenzoate ester of *trans*-9.

***trans*-4-Chlorobenzoic acid 3-methyl-1,3-diphenylcyclobutyl ester (ester-*trans*-9).** White solid; mp 157.0–157.5 °C; IR (KBr) 2964, 1720 (C=O), 1595, 1496, 1278, 1119, 1091, 1014, 851, 762, 697 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.63 (s, 3H), 3.00–3.11 (m, 2H), 3.18–3.30 (m, 2H), 7.11–7.47 (m, 12H), 8.02 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 32.7, 36.9, 46.2, 80.5, 125.0, 125.6, 125.6, 127.3, 128.1, 128.3, 128.7, 129.4, 131.0, 139.4, 143.0, 150.6, 164.3. Anal. Calcd for $\text{C}_{23}\text{H}_{21}\text{ClO}_2$: C, 76.13; H, 5.28. Found: C, 76.36; H, 5.58.

X-ray Crystallographic Studies of ester-*trans*-9. Colorless crystals of ester-*trans*-9 suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2 –*n*-hexane. The single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo- $\text{K}\alpha$ radiation. Details of crystal and data collection parameters are summarized in Table S2. The positions of non-hydrogen atoms were determined by direct methods (SIR97) and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of ester-*trans*-9 is shown in Figure S2.

Table S2. Crystallographic Data for **ester-trans-9**.

formula	C ₂₄ H ₂₁ ClO ₂
formula weigh	376.88
cryst size (mm ³)	0.60 x 0.10 x 0.10
cryst system	monoclinic
space group	C2/c (#15)
cryst color	colorless
<i>a</i> (Å)	20.812(6)
<i>b</i> (Å)	5.862(2)
<i>c</i> (Å)	33.049(1)
β (°)	101.782(7)
<i>V</i> (Å ³)	3947.3(2)
<i>Z</i>	8
<i>d</i> _{calc} (g cm ⁻³)	1.268
<i>F</i> (000)	1584.00
μ _{calc} (cm ⁻¹)	2.09
no. of unique data	4177
no. of data used (<i>I</i> > 3 σ (<i>I</i>))	2290
no. of params refined	266
<i>R</i> ^{<i>a</i>}	0.040
<i>R</i> _w ^{<i>b</i>}	0.043
goodness of fit indicator	0.85
maximum residuals (e Å ⁻³)	1.49

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$$

$$^b R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2]^{1/2}.$$

Figure S2. Crystal structure of **ester-trans-9**.

1-Butyl-3-methyl-3-phenyl-1-cyclobutanol (*cis*-10, *cis/trans* = 99/1). Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.95 (t, J = 7.1 Hz, 3H), 1.33–1.42 (m, 4H), 1.40 (s, 3H), 1.45 (br s, OH, 1H), 1.68–1.76 (m, 2H), 2.38 (d, J = 13.5 Hz, 2H), 2.49 (d, J = 13.5 Hz, 2H), 7.13–7.34 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 23.1, 25.5, 32.4, 33.8, 42.2, 48.8, 70.8, 125.2, 128.2, 152.3. Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}$: C, 82.52; H, 10.16. Found: C, 82.63; H, 10.26.

1-Butyl-3-methyl-3-phenyl-1-cyclobutanol (*trans*-10, *cis/trans* = 1/99). Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 0.82 (t, J = 7.0 Hz, 3H), 1.15–1.28 (m, 4H), 1.32–1.42 (m, 2H), 1.47–1.61 (m, 1H), 1.52 (s, 3H), 2.20 (d, J = 12.5 Hz, 2H), 2.54 (d, J = 12.5 Hz, 2H), 7.08–7.33 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 22.8, 25.2, 34.0, 35.3, 41.9, 47.8, 71.3, 125.2, 125.4, 128.2, 151.3. The stereochemistry of *cis*-10 and *trans*-10 was assumed to be so by comparison with ^1H NMR of *cis*-9 and *trans*-9 whose exact stereochemistry was clarified by X-ray single crystal analysis.

Preparation of (*R*)-*N,N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-PPFA] derivatives. PPFA derivatives were prepared according to the reported procedures from (*R*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl acetate [(*R*)-(*S*)-PPFOAc] and the corresponding amines.³⁶ A typical procedure to prepare ligand **D** is as follows: a mixture of PPFOAc and diethylamine (30 equiv) in MeOH (0.2 M) was stirred for 6 h at reflux temperature. The solvent was evaporated, and the crude residue was purified by column chromatography on SiO_2 to afford the desired product **D** as a yellow solid. Other ligands **E–M** were prepared by the same procedure. Ligands **H–M** are new compounds and their spectral data are shown below.

(*R*)-*N*-[(*S*)-1-Phenylethyl]-*N*-methyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine [(*S*)-(*R*)-(*S*)-H**].** Yellow solid; mp 34.0–34.5 °C; $[\alpha]_{\text{D}}^{25} = -297.4$ (c = 0.5, CHCl_3); IR (KBr) 3058, 2974, 2776, 1443, 1370, 1245, 1172, 1073, 911, 823, 744, 700, 546, 507, 489 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.88 (d, J = 5.4 Hz, 3H), 1.19 (d, J = 6.3 Hz, 3H), 1.73 (s, 3H), 1.82 (br s, 1H), 3.30–3.48 (m, 1H), 3.81 (s, 5H), 4.12 (s, 1H), 4.23 (s, 1H), 4.37 (s, 1H), 7.09–7.69 (m, 15H); ^{31}P NMR (161.9 MHz, CDCl_3) δ -26.1. Anal. Calcd for

C₃₃H₃₄FeNP: C, 74.58; H, 6.45; N, 2.64. Found: C, 74.77; H, 6.44; N, 2.44.

(R)-N-[(R)-1-Phenylethyl]-N-methyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine [(R)-(R)-(S)-I]. Yellow solid; mp 143.0–144.0 °C; $[\alpha]_D^{25} = -244.8$ (c = 0.5, CHCl₃); IR (KBr) 2969, 2359, 1640, 1450, 1433, 1366, 1245, 816, 745, 698, 485 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (d, *J* = 6.8 Hz, 3H), 1.37 (d, *J* = 6.3 Hz, 3H), 1.53 (s, 3H), 3.40 (q, *J* = 6.3 Hz, 1H), 3.81–3.90 (m, 1H), 3.94 (s, 5H), 4.28 (s, 1H), 4.43 (s, 1H), 4.75–4.84 (m, 1H), 6.57 (d, *J* = 7.3 Hz, 2H), 6.88 (t, *J* = 7.3 Hz, 2H), 6.98 (t, *J* = 7.1 Hz, 1H), 7.08–7.70 (m, 10H); ³¹P NMR (161.9 MHz, CDCl₃) δ -31.4. Anal. Calcd for C₃₃H₃₄FeNP: C, 74.58; H, 6.45; N, 2.64. Found: C, 74.28; H, 6.33; N, 2.56.

(R)-N-Cyclohexyl-N-methyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine [(R)-(S)-J]. Yellow solid; mp 159.2–160.0 °C; $[\alpha]_D^{25} = -286.9$ (c = 0.5, CHCl₃); IR (KBr) 2956, 2939, 2774, 1446, 1433, 818, 749, 739, 696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.49–1.58 (m, 10H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.65 (s, 3H), 2.15–2.30 (m, 1H), 3.70 (s, 1H), 3.73–4.26 (m, 3H), 3.94 (s, 5H), 7.01–7.70 (m, 10H); ³¹P NMR (161.9 MHz, CDCl₃) δ -31.3. Anal. Calcd for C₃₁H₃₆FeNP: C, 73.09; H, 7.12; N, 2.75. Found: C, 73.02; H, 7.07; N, 2.82.

(R)-N-tert-Butyl-N-methyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine [(R)-(S)-K]. Yellow solid; mp 118.0–118.6 °C; $[\alpha]_D^{25} = -286.2$ (c = 0.5, CHCl₃); IR (KBr) 3075, 2976, 2876, 1480, 1435, 1370, 1230, 1050, 1005, 813, 751, 741, 696, 510 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.80 (s, 9H), 1.34 (d, *J* = 5.9 Hz, 3H), 1.72 (s, 3H), 3.73 (s, 1H), 3.95 (s, 5H), 4.23 (s, 1H), 4.38 (s, 1H), 4.68–4.78 (m, 1H), 7.01–7.60 (m, 10H); ³¹P NMR (161.9 MHz, CDCl₃) δ -26.0. Anal. Calcd for C₂₉H₃₄FeNP: C, 72.05; H, 7.09; N, 2.90. Found: C, 71.77; H, 7.02; N, 2.81.

(R)-N-(1-Adamantyl)-N-methyl-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethylamine [(R)-(S)-L]. Yellow solid; mp 182 °C (dec); $[\alpha]_D^{25} = -243.3$ (c = 0.5, CHCl₃); IR (KBr) 3065, 2916, 2369, 1435, 1360, 1240, 1110, 1075, 915, 816, 751, 739, 699, 507 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.24–1.33 (m, 4H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.40–1.63 (m, 8H), 1.74 (s, 3H), 1.90 (br s, 3H), 3.70 (s, 1H), 3.95 (s, 5H), 4.19–4.23 (m, 1H), 4.37 (s, 1H), 4.72–4.80 (m, 1H), 7.03–7.10 (m, 2H), 7.31–7.37 (m, 3H), 7.48–7.56 (m, 2H); ³¹P NMR (161.9 MHz,

CDCl₃) δ -26.3. Anal. Calcd for C₃₅H₄₀FeNP: C, 74.86; H, 7.18; N, 2.49. Found: C, 74.58; H, 7.16; N, 2.24.

(*R*)-*N*-(2-Adamantyl)-*N*-methyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine [(*R*)-(*S*)-M**].** Yellow solid; mp 191 °C (dec); $[\alpha]_D^{25} = -275.0$ (*c* = 0.5, CHCl₃); IR (KBr) 3075, 2906, 2846, 2777, 2369, 1440, 1245, 1110, 1005, 821, 741, 696, 495 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.44–0.76 (m, 2H), 1.12–1.94 (m, 16H), 2.18 (s, 1H), 2.27 (s, 1H), 2.56 (br s, 1H), 3.77 (s, 1H), 3.96 (s, 5H), 4.27 (s, 1H), 4.43 (s, 1H), 4.50 (s, 1H), 6.85–7.74 (m, 10H); ³¹P NMR (161.9 MHz, CDCl₃) δ -26.5. HRMS (FAB) calcd for C₃₅H₄₀FeNP (*M*⁺) 561.2248, found 561.2245. Anal. Calcd for C₃₅H₄₀FeNP: C, 74.86; H, 7.18; N, 2.49. Found: C, 74.42; H, 7.18; N, 2.41.

Typical Procedure for Palladium-Catalyzed Asymmetric Arylation of *tert*-Cyclobutanols. A mixture of Pd(OAc)₂ (0.01 mmol), (*R*)-(*S*)-**L** (0.02 mmol), Cs₂CO₃ (0.24 mmol) and toluene (0.5 mL) in a 10-mL two-necked round-bottomed flask was stirred at room temperature under N₂. After 0.5 h, a mixture of aryl bromide (0.24 mmol) and alcohol (0.20 mmol) in toluene (0.5 mL) was added and the resulted mixture was stirred at 50 °C until the reaction had reached completion by monitoring with TLC analysis. The reaction mixture was cooled to room temperature and then filtered through a pad of Florisil. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO₂ with EtOAc-hexane (2/98) as eluent. The enantiomeric excess was determined by HPLC.

(*S*)-(-)-1,3,4-Triphenyl-1-butanone (1a**).** White solid; mp 114.7–115.0 °C; $[\alpha]_D^{25} = -41.9$ (*c* = 0.5, CHCl₃, 98% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), *t*₁ = 19.2 min (major), *t*₂ = 26.9 min (minor); IR (KBr) 3024, 1678 (C=O), 1560, 1494, 1449, 1374, 1226, 760, 746, 702, 684, 544, 526 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.95 (dd, *J* = 13.4, 7.8 Hz, 1H), 3.00 (dd, *J* = 13.4, 7.3 Hz, 1H), 3.26 (dd, *J* = 17.1, 6.6 Hz, 1H), 3.34 (dd, *J* = 17.1, 7.1 Hz, 1H), 3.67 (tt, *J* = 7.3, 7.3 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 2H), 7.10–7.26 (m, 8H), 7.35–7.42 (m, 2H), 7.46–7.52 (m, 1H), 7.81–7.85 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 43.0 (t), 43.0 (d), 44.1 (t), 126.1 (d), 126.4 (d), 127.7 (d), 128.0 (d), 128.2 (d), 128.3 (d), 128.5 (d), 129.3 (d), 132.9 (d), 137.2 (s),

139.8 (s), 144.1 (s), 198.9 (s). Anal. Calcd for C₂₂H₂₀O: C, 87.96; H, 6.71. Found: C, 87.91; H, 6.85.

(-)-4-(2-Methoxyphenyl)-1,3-diphenyl-1-butanone (1b). White solid; mp 80.5–81.2 °C; $[\alpha]_D^{25} = -7.1$ (c = 0.5, CHCl₃, 75% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 50.9$ min (major), $t_2 = 58.2$ min (minor); IR (KBr) 2939, 1680 (C=O), 1598, 1493, 1244, 1178, 1027, 765, 748, 698, 689, 516 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 2.99 (d, $J = 6.6$ Hz, 2H), 3.25 (dd, $J = 16.5, 6.4$ Hz, 1H), 3.34 (dd, $J = 16.5, 7.9$ Hz, 1H), 3.69 (s, 3H), 3.74 (t, $J = 7.3$ Hz, 1H), 6.72–6.84 (m, 2H), 6.95 (d, $J = 6.3$ Hz, 1H), 7.07–7.28 (m, 6H), 7.38 (t, $J = 7.4$ Hz, 2H), 7.50 (t, $J = 7.3$ Hz, 1H), 7.81 (t, $J = 7.6$ Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 37.3 (t), 41.5 (d), 44.0 (t), 55.1 (q), 110.2 (d), 120.2 (d), 126.2 (d), 127.6 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.4 (d), 131.0 (d), 132.7 (d), 137.3 (s), 144.7 (s), 157.6 (s), 199.1 (s). Anal. Calcd for C₂₃H₂₂O₂: C, 83.60; H, 6.71. Found: C, 83.45; H, 6.64.

(-)-4-(3-Methoxyphenyl)-1,3-diphenyl-1-butanone (1c). White solid; mp 99.3–100.1 °C; $[\alpha]_D^{25} = -29.6$ (c = 0.5, CHCl₃, 92% ee). The enantiomeric excess was measured by HPLC (AD column, 1.0 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 28.2$ min (major), $t_2 = 35.7$ min (minor); IR (KBr) 3043, 2939, 1678 (C=O), 1596, 1490, 1465, 1259, 1229, 1163, 1040, 991, 762, 747, 694, 575 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.93 (dd, $J = 13.4, 7.7$ Hz, 1H), 2.98 (dd, $J = 13.4, 7.3$ Hz, 1H), 3.27 (dd, $J = 16.7, 6.6$ Hz, 1H), 3.34 (dd, $J = 16.7, 7.2$ Hz, 1H), 3.67 (tt, $J = 7.2, 7.2$ Hz, 1H), 3.69 (s, 3H), 6.58 (s, 1H), 6.64–6.75 (m, 2H), 7.17–7.31 (m, 6H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.51 (t, $J = 7.3$ Hz, 1H), 7.84 (d, $J = 7.3$ Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) δ 42.9 (d), 43.2 (t), 44.1 (t), 55.1 (q), 111.8 (d), 114.7 (d), 121.7 (d), 126.4 (d), 127.7 (d), 128.0 (d), 128.4 (d), 128.5 (d), 129.1 (d), 132.9 (d), 137.2 (s), 141.4 (s), 144.1 (s), 159.4 (s), 198.9 (s). Anal. Calcd for C₂₃H₂₂O₂: C, 83.60; H, 6.71. Found: C, 83.55; H, 6.67.

(-)-4-(4-Methoxyphenyl)-1,3-diphenyl-1-butanone (1d). White solid; mp 79.3–80.0 °C; $[\alpha]_D^{25} = -34.7$ (c = 0.5, CHCl₃, 90% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 50.1$ min (major), $t_2 = 75.0$ min (minor); IR (KBr) 2923, 1681 (C=O), 1610, 1511, 1448, 1247, 1033,

813, 764, 745, 699, 689, 531 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.89 (dd, $J = 13.6, 7.7$ Hz, 1H), 2.94 (dd, $J = 13.6, 7.2$ Hz, 1H), 3.26 (dd, $J = 16.7, 6.8$ Hz, 1H), 3.32 (dd, $J = 16.7, 7.0$ Hz, 1H), 3.62 (tt, $J = 7.2, 7.1$ Hz, 1H), 3.75 (s, 3H), 6.74 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 7.11–7.29 (m, 5H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.51 (t, $J = 7.3$ Hz, 1H), 7.84 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 42.1 (t), 43.2 (d), 44.1 (t), 55.2 (q), 113.6 (d), 126.4 (d), 127.7 (d), 128.0 (d), 128.3 (d), 128.5 (d), 130.2 (d), 131.9 (s), 132.9 (d), 137.2 (s), 144.2 (s), 157.9 (s), 199.0 (s). Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{O}_2$: C, 83.60; H, 6.71. Found: C, 83.38; H, 6.68.

(–)-4-(4-Chlorophenyl)-1,3-diphenyl-1-butanone (1e). White solid; mp 97.3–97.8 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} = -51.8$ ($c = 0.5$, CHCl_3 , 88% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 18.9$ min (major), $t_2 = 29.8$ min (minor); IR (KBr) 2927, 1678 (C=O), 1489, 1448, 1266, 1213, 1091, 983, 817, 755, 743, 699, 686, 566 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.88 (dd, $J = 13.4, 8.5$ Hz, 1H), 3.01 (dd, $J = 13.7, 6.3$ Hz, 1H), 3.28 (dd, $J = 17.3, 7.6$ Hz, 1H), 3.34 (dd, $J = 17.3, 7.1$ Hz, 1H), 3.63 (tt, $J = 7.3, 7.1$ Hz, 1H), 6.82–7.02 (d, $J = 8.3$ Hz, 2H), 7.03–7.58 (m, 10H), 7.87 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 42.1 (t), 42.9 (d), 44.2 (t), 126.5 (d), 127.6 (d), 128.0 (d), 128.2 (d), 128.4 (d), 128.6 (d), 130.6 (d), 131.8 (s), 133.0 (d), 137.1 (s), 138.3 (s), 143.6 (s), 198.7 (s). Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{ClO}$: C, 78.91; H, 5.72. Found: C, 78.84; H, 5.97.

(–)-1,3-Diphenyl-4-(*p*-tolyl)-1-butanone (1f). White solid; mp 99.8–100.0 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} = -32.9$ ($c = 0.5$, CHCl_3 , 91% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 16.2$ min (major), $t_2 = 22.2$ min (minor); IR (KBr) 2925, 1676 (C=O), 1595, 1448, 1263, 1212, 983, 812, 761, 746, 700, 688, 587, 507 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.28 (s, 3H), 2.94 (d, $J = 7.3$ Hz, 2H), 3.25 (dd, $J = 16.6, 6.3$ Hz, 1H), 3.32 (dd, $J = 16.6, 7.3$ Hz, 1H), 3.65 (tt, $J = 7.2, 7.1$ Hz, 1H), 6.91–7.55 (m, 12H), 7.83 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 21.0 (q), 42.5 (t), 43.0 (d), 44.1 (t), 126.3 (d), 127.7 (d), 128.0 (d), 128.5 (d), 128.9 (d), 129.1 (d), 132.9 (d), 135.5 (s), 136.7 (s), 137.2 (s), 144.3 (s), 199.0 (s). Anal. Calcd for $\text{C}_{23}\text{H}_{22}\text{O}$: C, 87.86; H, 7.05. Found: C, 87.64; H, 7.13.

(-)-4-(4-*tert*-Butylphenyl)-1,3-diphenyl-1-butanone (1g). White solid; mp 103.0–103.8 °C; $[\alpha]_{\text{D}}^{25} = -24.0$ ($c = 0.5$, CHCl_3 , 94% ee). The enantiomeric excess was measured by HPLC (AD column, 1.0 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 9.8$ min (major), $t_2 = 15.2$ min (minor); IR (KBr) 2964, 1681 (C=O), 1598, 1449, 1228, 874, 815, 748, 703, 689, 568, 550 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.28 (s, 9H), 2.92 (dd, $J = 13.7$, 8.3 Hz, 1H), 2.98 (dd, $J = 13.7$, 6.8 Hz, 1H), 3.25 (dd, $J = 16.7$, 6.1 Hz, 1H), 3.32 (dd, $J = 16.7$, 7.8 Hz, 1H), 3.66 (quint, $J = 7.2$ Hz, 1H), 7.04 (d, $J = 8.3$ Hz, 2H), 7.11–7.29 (m, 7H), 7.38 (t, $J = 7.6$ Hz, 2H), 7.50 (t, $J = 7.3$ Hz, 1H), 7.76–7.84 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 31.5 (q), 34.4 (s), 42.6 (t), 43.0 (d), 44.1 (t), 125.0 (d), 126.2 (d), 127.5 (d), 127.8 (d), 128.2 (d), 128.3 (d), 128.7 (d), 132.7 (d), 136.5 (s), 137.0 (s), 144.3 (s), 148.7 (s), 198.6 (s). Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{O}$: C, 87.60; H, 7.92. Found: C, 87.41; H, 8.01.

(-)-4-(4-*N,N*-Dimethylaminophenyl)-1,3-diphenyl-1-butanone (1h). White solid; mp 113.2–114.0 °C; $[\alpha]_{\text{D}}^{25} = -33.1$ ($c = 0.5$, CHCl_3 , 95% ee). The enantiomeric excess was measured by HPLC (AD column, 1.0 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 22.3$ min (major), $t_2 = 32.3$ min (minor); IR (KBr) 3065, 2936, 2886, 1680 (C=O), 1620, 1525, 1445, 1350, 1270, 1215, 983, 970, 803, 746, 701, 579, 527 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 2.81–2.96 (m 2H), 2.90 (s, 6H), 3.25 (dd, $J = 16.7$, 6.8 Hz, 1H), 3.31 (dd, $J = 16.5$, 7.3 Hz, 1H), 3.62 (quint, $J = 7.2$ Hz, 1H), 6.67 (br s, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 7.11–7.30 (m, 5H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.46–7.55 (m, 1H), 7.78–7.88 (m, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 40.8 (q), 42.1 (t), 43.2 (d), 43.9 (t), 112.8 (d), 126.2 (d), 127.7 (d), 128.0 (d), 128.3 (d), 128.4 (d), 129.9 (d), 132.8 (d), 137.2 (s), 144.5 (s), 149.0 (s), 199.2 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}$: C, 83.93; H, 7.34; N, 4.08. Found: C, 83.64; H, 7.25; N, 4.05.

(-)-4-(1-Naphthyl)-1,3-diphenyl-1-butanone (1i). White solid; mp 93.8–94.5 °C; $[\alpha]_{\text{D}}^{25} = -25.0$ ($c = 0.5$, CHCl_3 , 77% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 39.7$ min (major), $t_2 = 45.2$ min (minor); IR (KBr) 3059, 3027, 2935, 1680 (C=O), 1595, 1448, 1229, 1201, 988, 775, 762, 749, 701, 688, 545 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.29 (dd, $J = 13.7$, 8.3 Hz, 1H), 3.37 (dd, $J = 17.0$, 7.1 Hz, 1H), 3.43 (dd, $J = 17.0$, 6.8 Hz, 1H), 3.56 (dd, $J = 13.7$, 6.8 Hz, 1H), 3.86 (tt, $J = 7.3$, 7.1 Hz, 1H), 7.03 (d, $J = 6.8$ Hz, 1H), 7.10–7.26 (m, 6H), 7.38 (t, $J =$

7.6 Hz, 2H), 7.43–7.57 (m, 3H), 7.66 (d, $J = 8.3$ Hz, 1H), 7.78–7.86 (m, 3H), 8.23 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 40.4 (t), 42.0 (d), 44.7 (t), 124.1 (d), 125.1 (d), 125.5 (d), 126.0 (d), 126.4 (d), 127.0 (d), 127.5 (d), 128.0 (d), 128.4 (d), 128.5 (d), 128.7 (d), 132.1 (s), 132.9 (d), 133.9 (s), 135.9 (s), 137.2 (s), 144.4 (s), 199.0 (s). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{O}$: C, 89.11; H, 6.33. Found: C, 88.96; H, 6.41.

(–)-4-(2-Naphthyl)-1,3-diphenyl-1-butanone (1j). White solid; mp 104.8–105.5 °C; $[\alpha]_{\text{D}}^{25} = -40.9$ ($c = 0.5$, CHCl_3 , 81% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 31.7$ min (major), $t_2 = 44.7$ min (minor); IR (KBr) 3025, 2929, 1678 (C=O), 1597, 1494, 1448, 1350, 1230, 993, 825, 766, 742, 700, 688, 541, 482 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.10 (dd, $J = 13.7, 7.9$ Hz, 1H), 3.17 (dd, $J = 13.7, 7.2$ Hz, 1H), 3.30 (dd, $J = 16.9, 7.2$ Hz, 1H), 3.37 (dd, $J = 16.9, 7.0$ Hz, 1H), 3.79 (quint, $J = 7.2$ Hz, 1H), 7.10–7.28 (m, 6H), 7.33–7.44 (m, 4H), 7.45–7.54 (m, 2H), 7.64–7.78 (m, 3H), 7.79–7.87 (m, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 42.9 (d), 43.1 (t), 44.1 (t), 125.2 (d), 125.8 (d), 126.4 (d), 127.5 (d), 127.5 (d), 127.6 (d), 127.7 (d), 127.8 (d), 128.0 (d), 128.4 (d), 128.5 (d), 132.1 (s), 132.9 (d), 133.4 (s), 137.1 (s), 137.3 (s), 144.0 (s), 198.9 (s). Anal. Calcd for $\text{C}_{26}\text{H}_{22}\text{O}$: C, 89.11; H, 6.33. Found: C, 89.16; H, 6.30.

(+)-4-(9-Anthracenyl)-1,3-diphenyl-1-butanone (1k). Pale yellow solid; mp 167.0–168.0 °C; $[\alpha]_{\text{D}}^{25} = +39.4$ ($c = 0.5$, CHCl_3 , 48% ee). The enantiomeric excess was measured by HPLC (OD column, 1.0 mL/min, 5% 2-propanol/hexane, 254 nm), $t_1 = 10.2$ min (minor), $t_2 = 14.0$ min (major); IR (KBr) 3065, 2896, 1676 (C=O), 1450, 1350, 1235, 1015, 883, 761, 746, 732, 702, 689, 604, 542 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.27 (dd, $J = 16.5, 5.7$ Hz, 1H), 3.55 (dd, $J = 16.5, 7.9$ Hz, 1H), 3.84 (dd, $J = 13.3, 6.3$ Hz, 1H), 3.97 (quint, $J = 7.0$ Hz, 1H), 4.10 (dd, $J = 13.3, 8.4$ Hz, 1H), 7.07–7.27 (m, 6H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.37–7.54 (m, 4H), 7.67 (d, $J = 7.3$ Hz, 2H), 7.91–8.04 (m, 2H), 8.21–8.35 (m, 2H), 8.34 (s, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 34.9 (t), 43.0 (d), 43.9 (t), 124.6 (d), 124.7 (d), 125.6 (d), 126.4 (d), 126.5 (d), 127.4 (d), 127.9 (d), 128.4 (d), 129.1 (d), 130.4 (s), 131.5 (s), 132.1 (s), 132.8 (d), 136.9 (s), 144.3 (s), 198.8 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{O}$: C, 89.97; H, 6.04. Found: C, 89.69; H, 6.16.

(+)-3-Benzyl-4,4-dimethyl-1-phenyl-1-pentanone (2a). White solid; mp 82.8–83.1 °C; $[\alpha]_{\text{D}}^{25} = +39.3$ ($c = 0.5$, CHCl_3 , 75% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 10.8$ min (minor), $t_2 = 11.8$ min (major); IR (KBr) 2596, 1687 (C=O), 1595, 1445, 1365, 1290, 1225, 1000, 758, 745, 723, 698, 685, 519 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.97 (s, 9H), 2.30 (dd, $J = 13.7, 10.7$ Hz, 1H), 2.52–2.60 (m, 1H), 2.70 (dd, $J = 17.1, 4.9$ Hz, 1H), 3.02 (dd, $J = 17.1, 6.3$ Hz, 1H), 3.03 (dd, $J = 13.7, 2.9$ Hz, 1H), 7.05–7.12 (m, 1H), 7.14–7.20 (m, 4H), 7.31–7.37 (m, 2H), 7.44–7.49 (m, 1H), 7.66–7.70 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.8 (q), 33.9 (s), 37.3 (t), 39.3 (t), 45.0 (d), 125.8 (d), 127.8 (d), 128.2 (d), 128.3 (d), 129.3 (d), 132.4 (d), 137.4 (s), 141.3 (s), 200.3 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.63; H, 8.60.

(+)-3-Benzyl-1-phenyl-1-nonanone (3a). Colorless oil; $[\alpha]_{\text{D}}^{25} = +14.1$ ($c = 0.5$, CHCl_3 , 82% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 2% 2-propanol/hexane, 254 nm), $t_1 = 11.2$ min (major), $t_2 = 11.9$ min (minor); IR (neat) 2926, 2855, 1805, 1683 (C=O), 1598, 1448, 1217, 742, 699, 691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, $J = 6.5$ Hz, 3H), 1.20–1.40 (m, 10H), 2.30–2.45 (m, 1H), 2.57 (dd, $J = 13.4, 7.3$ Hz, 1H), 2.73 (dd, $J = 13.5, 6.5$ Hz, 1H), 2.82 (dd, $J = 16.0, 6.3$ Hz, 1H), 2.89 (dd, $J = 16.0, 6.1$ Hz, 1H), 7.10–7.60 (m, 8H), 7.75–7.90 (m, 2H); ^{13}C NMR (67.8 MHz, CDCl_3) δ 14.1 (q), 22.6 (t), 26.8 (t), 29.4 (t), 29.7 (t), 31.8 (t), 33.9 (t), 36.4 (d), 40.5 (t), 42.6 (t), 125.9 (d), 128.0 (d), 128.2 (d), 128.5 (d), 129.3 (d), 132.8 (d), 137.4 (s), 140.6 (s), 200.4 (s). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}$: C, 85.66; H, 9.15. Found: C, 85.70; H, 9.15.

(-)-4,5-Diphenyl-2-pentanone (4a). White solid; mp 38.1–38.5 °C; $[\alpha]_{\text{D}}^{25} = -37.4$ ($c = 0.5$, CHCl_3 , 64% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 2% 2-propanol/hexane, 254 nm), $t_1 = 21.2$ min (major), $t_2 = 23.4$ min (minor); IR (KBr) 3027, 2913, 1710 (C=O), 1494, 1453, 1373, 1356, 1030, 760, 700, 548, 526 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.97 (s, 3H), 2.71 (dd, $J = 16.7, 6.5$ Hz, 1H), 2.79 (dd, $J = 16.7, 8.2$ Hz, 1H), 2.88 (d, $J = 7.6$ Hz, 2H), 3.45 (quint, $J = 7.3$ Hz, 1H), 7.04 (d, $J = 7.2$ Hz, 2H), 7.09–7.30 (m, 8H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 30.6 (q), 42.9 (d), 43.1 (t), 49.1 (t), 126.1 (d), 126.4 (d), 127.5 (d), 128.2 (d), 128.4 (d), 129.2 (d), 139.6 (s), 143.8 (s), 207.6 (s).

Anal. Calcd for C₁₇H₁₈O: C, 85.67; H, 7.61. Found: C, 85.82; H, 7.79.

(S)-(-)-1,2-Diphenyl-4-octanone (5a). White solid; mp 65.2–66.0 °C; $[\alpha]_D^{25} = -23.3$ (c = 0.5, CHCl₃, 66% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 2% 2-propanol/hexane, 254 nm), $t_1 = 11.6$ min (major), $t_2 = 12.7$ min (minor); IR (KBr) 3025, 2946, 2927, 2867, 2359, 1709 (C=O), 1490, 1454, 1405, 1370, 761, 700, 553, 528 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.81 (t, $J = 7.3$ Hz, 3H), 1.09–1.22 (m, 2H), 1.40 (quint, $J = 7.3$ Hz, 2H), 2.12–2.30 (m, 2H), 2.68 (dd, $J = 16.3, 6.3$ Hz, 1H), 2.76 (dd, $J = 16.3, 8.1$ Hz, 1H), 2.88 (d, $J = 7.3$ Hz, 2H), 3.47 (quint, $J = 7.3$ Hz, 1H), 6.97–7.27 (m, 10H); ¹³C NMR (67.8 MHz, CDCl₃) δ 13.8 (q), 22.2 (t), 25.6 (t), 42.9 (d), 43.0 (t), 43.2 (t), 48.3 (t), 126.1 (d), 126.4 (d), 127.6 (d), 128.1 (d), 128.3 (d), 129.2 (d), 139.7 (s), 144.0 (s), 209.9 (s). Anal. Calcd for C₂₀H₂₄O: C, 85.67; H, 8.63. Found: C, 85.51; H, 8.63.

(-)-2,2-Dimethyl-5,6-diphenyl-3-hexanone (6a). White solid; mp 70.0–70.5 °C; $[\alpha]_D^{25} = -15.1$ (c = 0.5, CHCl₃, 36% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 2% 2-propanol/hexane, 254 nm), $t_1 = 11.1$ min (major), $t_2 = 12.2$ min (minor); IR (KBr) 2924, 1696 (C=O), 1494, 1449, 1373, 1076, 776, 756, 701, 545, 527 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.99 (s, 9H), 2.73 (dd, $J = 17.3, 6.3$ Hz, 1H), 2.79–2.97 (m, 3H), 3.53 (tt, $J = 7.2, 7.2$ Hz, 1H), 7.04 (d, $J = 7.0$ Hz, 2H), 7.08–7.27 (m, 8H); ¹³C NMR (75.5 MHz, CDCl₃) δ 26.1 (q), 42.4 (d), 42.6 (t), 44.1 (s), 125.9 (d), 126.2 (d), 127.7 (d), 128.1 (d), 128.2 (d), 129.2 (d), 140.0 (s), 144.3 (s), 214.2 (s). Anal. Calcd for C₂₀H₂₄O: C, 85.67; H, 8.63. Found: C, 85.41; H, 8.61.

(+)-1-(1-Naphthyl)-3,4-diphenyl-1-butanone (7a). White solid; mp 76.5–77.2 °C; $[\alpha]_D^{25} = +14.4$ (c = 0.5, CHCl₃, 86% ee). The enantiomeric excess was measured by HPLC (AD column, 1.0 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 13.4$ min (major), $t_2 = 15.8$ min (minor); IR (KBr) 3050, 2936, 1667 (C=O), 1506, 1453, 1230, 1099, 950, 798, 763, 694, 617, 542 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.00 (d, $J = 7.5$ Hz, 2H), 3.34 (dd, $J = 16.5, 6.8$ Hz, 1H), 3.40 (dd, $J = 16.5, 7.2$ Hz, 1H), 3.70 (tt, $J = 7.3, 7.3$ Hz, 1H), 7.08 (d, $J = 6.4$ Hz, 2H), 7.11–7.28 (m, 8H), 7.34–7.52 (m, 3H), 7.59 (d, $J = 6.8$ Hz, 1H), 7.77–7.86 (m, 1H), 7.91 (d, $J = 8.1$ Hz, 1H), 8.13–8.22 (m, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 43.1 (t), 43.6 (d), 47.9 (t), 124.2 (d), 125.7 (d), 126.2 (d), 126.4 (d), 126.5 (d), 126.8 (d), 127.6 (d), 127.7 (d),

128.2 (d), 128.4 (d), 129.3 (d), 129.9 (s), 132.2 (d), 133.8 (s), 136.7 (s), 139.7 (s), 143.8 (s), 203.5 (s). Anal. Calcd for C₂₆H₂₂O: C, 89.11; H, 6.33. Found: C, 89.19; H, 6.29.

(-)-1-(2-Naphthyl)-3,4-diphenyl-1-butanone (8a). White solid; mp 114.9–115.5 °C; $[\alpha]_D^{25} = -29.8$ (c = 0.5, CHCl₃, 93% ee). The enantiomeric excess was measured by HPLC (AD column, 1.0 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 27.1$ min (major), $t_2 = 35.8$ min (minor); IR (KBr) 2962, 1669 (C=O), 1452, 1375, 1261, 1096, 1023, 823, 801, 765, 751, 699, 544, 477 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 2.94–3.13 (m, 2H), 3.44 (d, $J = 6.8$ Hz, 2H), 3.64–3.81 (m, 1H), 7.06–7.35 (m, 10H), 7.48–7.65 (m, 2H), 7.79–8.00 (m, 4H), 8.31 (s, 1H); ¹³C NMR (75.5 MHz, CDCl₃) δ 43.0 (t), 43.3 (d), 44.2 (t), 123.9 (d), 126.1 (d), 126.4 (d), 126.7 (d), 127.7 (d), 128.2 (d), 128.4 (d), 129.3 (d), 129.5 (d), 129.6 (d), 132.5 (s), 134.5 (s), 135.5 (s), 139.9 (s), 144.1 (s), 198.8 (s). Anal. Calcd for C₂₆H₂₂O: C, 89.11; H, 6.33. Found: C, 88.92; H, 6.21.

(-)-3-Methyl-1,3,4-triphenyl-1-butanone [(-)-9a]. Colorless oil; $[\alpha]_D^{25} = -16.9$ (c = 0.5, CHCl₃, 90% ee). The enantiomeric excess was measured by HPLC (OD column, 1.0 mL/min, 15% *tert*-butyl methyl ether/hexane, 254 nm), $t_1 = 17.5$ min (major), $t_2 = 23.7$ min (minor); IR (neat) 3059, 3026, 1691 (C=O), 1597, 1496, 1447, 1355, 1217, 766, 749, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.49 (s, 3H), 3.13 (d, $J = 12.9$ Hz, 1H), 3.18 (d, $J = 12.9$ Hz, 1H), 3.26 (d, $J = 16.4$ Hz, 1H), 3.54 (d, $J = 16.4$ Hz, 1H), 6.81–6.87 (m, 2H), 7.09–7.18 (m, 4H), 7.21–7.30 (m, 4H), 7.36–7.42 (m, 2H), 7.47–7.53 (m, 1H), 7.80–7.86 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 25.1 (q), 41.4 (s), 47.8 (t), 49.1 (t), 125.8 (d), 126.2 (d), 126.2 (d), 127.6 (d), 127.9 (d), 128.0 (d), 128.4 (d), 130.7 (d), 132.7 (d), 138.0 (s), 138.3 (s), 146.9 (s), 198.7 (s). Anal. Calcd for C₂₃H₂₂O: C, 87.86; H, 7.05. Found: C, 87.64; H, 7.11.

(+)-3-Methyl-1,3,4-triphenyl-1-butanone [(+)-9a]. $[\alpha]_D^{25} = +9.5$ (c = 0.5, CHCl₃, 55% ee).

(-)-2-Methyl-1,2-diphenyl-4-octanone [(-)-10a]. Colorless oil; $[\alpha]_D^{25} = -3.6$ (c = 0.5, CHCl₃, 22% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 2% 2-propanol/hexane, 254 nm), $t_1 = 12.5$ min (major), $t_2 = 20.1$ min (minor); IR (neat) 3035, 2966, 2876, 1715 (C=O), 1500, 1455, 1380, 1035, 768, 701, 552 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.80 (t, $J = 7.3$ Hz, 3H), 1.08–1.20 (m, 2H), 1.30–1.44 (m, 2H), 1.40 (s,

3H), 2.02–2.19 (m, 2H), 2.61 (d, $J = 15.1$ Hz, 1H), 2.97 (d, $J = 15.1$ Hz, 1H), 3.04 (s, 2H), 6.78–6.85 (m, 2H), 7.08–7.33 (m, 8H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 13.8 (q), 22.2 (t), 24.4 (q), 25.6 (t), 41.3 (s), 44.3 (t), 49.0 (t), 53.0 (t), 126.0 (d), 126.1 (d), 126.3 (d), 127.6 (d), 128.1 (d), 130.6 (d), 137.9 (s), 146.5 (s), 210.0 (s). Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{O}$: C, 85.67; H, 8.90. Found: C, 85.59; H, 8.84.

Typical Procedure for Palladium-Catalyzed Asymmetric Vinylation and Allenylation of *tert*-Cyclobutanols. A mixture of $\text{Pd}(\text{OAc})_2$ (0.01 mmol), (*R*)-(*S*)-**L** (0.02 mmol), Cs_2CO_3 (0.24 mmol) and toluene (0.5 mL) in a 10-mL schlenk tube was stirred at room temperature under N_2 . After 0.5 h, a mixture of alcohol (0.20 mmol) and vinylic bromide (0.24 mmol) or propargylic compound (0.24 mmol) in toluene (0.5 mL) was added and the resulted mixture was stirred at 50 °C until the reaction had reached completion by monitoring with TLC analysis. The reaction mixture was cooled to room temperature and then filtered through a pad of Florisil. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (2/98) as eluent. The enantiomeric excess was determined by HPLC.

(+)-4-(3,4-Dihydro-1-naphthalenyl)-1,3-diphenyl-1-butanone (11). Colorless oil; $[\alpha]_{\text{D}}^{25} = +3.6$ ($c = 0.83$, CHCl_3 , 73% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 25.0$ min (major), $t_2 = 27.1$ min (minor); IR (neat) 3359, 3034, 2932, 2831, 1684 (C=O), 1597, 1496, 1451, 1273, 1218, 1197, 1076, 814, 756, 700, 553 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.01–2.18 (m, 2H), 2.50–2.66 (m, 2H), 2.70 (dd, $J = 13.9$, 7.6 Hz, 1H), 2.89 (dd, $J = 13.9$, 7.6 Hz, 1H), 3.28 (dd, $J = 16.7$, 7.3 Hz, 1H), 3.40 (dd, $J = 16.7$, 6.6 Hz, 1H), 3.64 (quint, $J = 7.2$ Hz, 1H), 5.66 (t, $J = 4.4$ Hz, 1H), 6.98–7.31 (m, 8H), 7.32–7.45 (m, 3H), 7.50 (t, $J = 7.3$ Hz, 1H), 7.85 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 23.0 (t), 28.3 (t), 39.5 (d), 40.4 (t), 44.6 (t), 122.7 (d), 125.9 (d), 126.2 (d), 126.3 (d), 127.2 (d), 127.3 (d), 127.7 (d), 127.8 (d), 128.0 (d), 128.1 (d), 132.5 (d), 134.0 (s), 134.1 (s), 136.4 (s), 136.8 (s), 144.2 (s) 198.5 (s). HRMS (FAB) calcd for $\text{C}_{26}\text{H}_{24}\text{O}$ (M^+) 352.1827, found 352.1825. Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{O}$: C, 88.60; H, 6.86. Found: C, 88.07; H, 6.99.

(+)-4-(1-Cyclohexenyl)-1,3-diphenyl-1-butanone (1m). Colorless oil; $[\alpha]_{\text{D}}^{25} = +14.4$ ($c = 0.5$, CHCl_3 , 63% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 14.5$ min (major), $t_2 = 22.2$ min (minor); IR (neat) 3034, 2939, 2844, 1683 (C=O), 1607, 1498, 1451, 1242, 1009, 919, 744, 701, 689, 564, 540 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.37–1.62 (m, 4H), 1.70–2.04 (m, 4H), 2.19–2.37 (m, 2H), 3.19 (dd, $J = 16.6, 7.3$ Hz, 1H), 3.31 (dd, $J = 16.6, 6.3$ Hz, 1H), 3.59 (quint, $J = 7.2$ Hz, 1H), 5.35 (s, 1H), 7.10–7.30 (m, 5H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.53 (t, $J = 7.3$ Hz, 1H), 7.90 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 22.4 (t), 23.0 (t), 25.4 (t), 28.3 (t), 39.3 (d), 44.6 (t), 46.0 (t), 124.0 (d), 126.0 (d), 127.3 (d), 127.9 (d), 128.1 (d), 128.3 (d), 132.6 (d), 135.4 (s), 137.2 (s), 145.1 (s), 198.7 (s). Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{O}$: C, 86.80; H, 7.95. Found: C, 86.54; H, 8.05.

(+)-6-Methyl-1,3-diphenyl-5-hepten-1-one (1n). Colorless oil; $[\alpha]_{\text{D}}^{25} = +0.6$ ($c = 0.5$, CHCl_3 , 73% ee). The enantiomeric excess was measured by HPLC (AD column, 1.0 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 18.8$ min (major), $t_2 = 23.1$ min (minor); IR (neat) 3435, 2974, 2912, 1683 (C=O), 1600, 1449, 1376, 1271, 1209, 979, 840, 754, 701, 570, 539 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.52 (s, 3H), 1.61 (s, 3H), 2.25–2.48 (m, 2H), 3.24 (dd, $J = 16.6, 7.6$ Hz, 1H), 3.30 (dd, $J = 16.6, 6.2$ Hz, 1H), 3.40 (quint, $J = 6.9$ Hz, 1H), 4.98–5.10 (m, 1H), 7.12–7.32 (m, 5H), 7.37–7.57 (m, 3H), 7.89 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 17.8 (q), 25.7 (q), 35.0 (t), 41.5 (d), 44.5 (t), 122.0 (d), 126.2 (d), 127.5 (d), 128.0 (d), 128.3 (d), 128.5 (d), 132.8 (d), 133.4 (s), 137.3 (s), 144.9 (s), 199.2 (s). Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}$: C, 86.29; H, 7.97. Found: C, 86.12; H, 8.02.

(S)-(+)-1,3-Diphenyl-5-hexen-1-one (1o).^{S1} Colorless oil; $[\alpha]_{\text{D}}^{20} = +7.0$ ($c = 0.4$, CHCl_3 , 73% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 18.2$ min (major), $t_2 = 24.5$ min (minor); ^1H NMR (300 MHz, CDCl_3) δ 2.42–2.51 (m, 2H), 3.28 (d, $J = 1.5$ Hz, 1H), 3.30 (s, 1H), 3.48 (quint, $J = 7.0$ Hz, 1H), 4.91–5.07 (m, 2H), 5.60–5.78 (m, 1H), 7.13–7.32 (m, 5H), 7.38–7.59 (m, 3H), 7.86–7.93 (m, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 40.7 (t), 40.7 (d), 44.5 (t), 116.8 (t), 126.4 (d), 127.6 (d), 128.0 (d), 128.4 (d), 128.5 (d), 132.9 (d), 136.3 (d), 137.2 (s), 144.3 (s), 198.9 (s).

(+)-1,3,5-Triphenyl-5-hexen-1-one (1p). Colorless oil; $[\alpha]_{\text{D}}^{25} = +1.4$ ($c = 0.5$, CHCl_3 , 82% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm), $t_1 = 17.9$ min (major), $t_2 = 20.1$ min (minor); IR (neat) 3045, 2926, 1685 ($\text{C}=\text{O}$), 1605, 1500, 1450, 1270, 1225, 900, 781, 753, 699, 552 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.84 (dd, $J = 14.2, 7.8$ Hz, 1H), 2.98 (dd, $J = 14.2, 7.3$ Hz, 1H), 3.25 (dd, $J = 16.6, 7.8$ Hz, 1H), 3.34 (dd, $J = 16.6, 6.3$ Hz, 1H), 3.48 (quint, $J = 7.3$ Hz, 1H), 4.94 (s, 1H), 5.21 (s, 1H), 7.18–7.42 (m, 12H), 7.47–7.53 (m, 1H), 7.77–7.83 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 39.7 (d), 42.6 (t), 44.7 (t), 114.8 (t), 126.2 (d), 126.2 (d), 127.4 (d), 127.4 (d), 127.8 (d), 128.2 (d), 128.3 (d), 132.7 (d), 136.9 (s), 140.4 (s), 144.0 (s), 146.1 (s), 198.6 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{O}$: C, 88.31; H, 6.79. Found: C, 88.27; H, 6.75.

(+)-7-Methyl-1,3,5-triphenyl-octa-5,6-dien-1-one (1q). Colorless oil; $[\alpha]_{\text{D}}^{20} = +9.8$ ($c = 0.4$, CHCl_3 , 78% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm) $t_1 = 8.6$ min (major), $t_2 = 11.5$ min (minor); IR (neat) 3035, 2936, 1965, 1690 ($\text{C}=\text{O}$), 1605, 1500, 1455, 1365, 1275, 1220, 985, 910, 756, 699, 599, 559 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.51 (s, 3H), 1.57 (s, 3H), 2.74 (dd, $J = 14.8, 8.7$ Hz, 1H), 2.89 (dd, $J = 14.8, 6.8$ Hz, 1H), 3.31 (dd, $J = 16.9, 7.5$ Hz, 1H), 3.42 (dd, $J = 16.9, 6.4$ Hz, 1H), 3.64 (quint, $J = 7.1$ Hz, 1H), 7.06–7.59 (m, 13H), 7.87 (d, $J = 7.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.9 (q), 20.1 (q), 36.9 (t), 39.3 (d), 45.5 (t), 98.0 (s), 100.9 (s), 125.8 (d), 125.9 (d), 127.3 (d), 127.5 (d), 127.6 (d), 127.7 (d), 128.1 (d), 128.4 (d), 132.5 (d), 136.8 (s), 137.5 (s), 144.3 (s), 198.4 (s), 202.4 (s). HRMS (FAB) calcd for $\text{C}_{27}\text{H}_{26}\text{O}$ (M^+) 366.1984, found 366.1978. Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{O}$: C, 88.48; H, 7.15. Found: C, 87.48; H, 7.23.

(+)-4-Methyl-2-(4-oxo-2,4-diphenylbutyl)penta-2,3-dienoic acid methyl ester (1r). White solid; mp 92.0–93.0 $^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{20} = +19.3$ ($c = 0.4$, CHCl_3 , 84% ee). The enantiomeric excess was measured by HPLC (AD column, 0.5 mL/min, 3% 2-propanol/hexane, 254 nm) $t_1 = 55.6$ min (major), $t_2 = 68.2$ min (minor); IR (KBr) 3453, 2946, 1960, 1710 ($\text{C}=\text{O}$), 1685 ($\text{C}=\text{O}$), 1440, 1265, 1195, 1110, 985, 763, 749, 701, 691, 559 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.49 (s, 3H), 1.54 (s, 3H), 2.62 (dd, $J = 15.0, 8.9$ Hz, 1H), 2.69 (dd, $J = 15.0, 6.2$ Hz, 1H), 3.26 (dd, $J = 17.0, 6.8$ Hz, 1H), 3.32 (dd, $J = 17.0, 6.9$

Hz, 1H), 3.52–3.64 (m, 1H), 3.67 (s, 3H), 7.09–7.16 (m, 1H), 7.18–7.29 (m, 4H), 7.41 (t, J = 7.5 Hz, 2H) 7.52 (t, J = 7.3 Hz, 1H), 7.83–7.91 (m, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 19.4 (q), 35.0 (t), 39.7 (d), 45.7 (t), 51.9 (q), 96.0 (s), 100.0 (s), 126.3 (d), 127.7 (d), 128.0 (d), 128.4 (d), 128.5 (d), 132.9 (d), 137.2 (s), 144.2 (s), 168.4 (s), 198.6 (s), 208.8 (s). Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{O}_3$: C, 79.28; H, 6.94. Found: C, 79.04; H, 6.92.

Table S3.

<p> 1 (98/2) (0.1 mmol) + PhBr (0.12 mmol) $\xrightarrow[\text{toluene (0.5 mL), 80 } ^\circ\text{C, 4 h}]{\text{Pd(dba)}_2, \text{ ligand L, Cs}_2\text{CO}_3 \text{ (0.12 mmol)}}$ 1a </p>					
entry	Pd(dba)_2	ligand L	Pd/L	isolated yield (%)	ee (%)
1	5 mol%	10 mol%	1/2	68	91
2	5 mol%	none	—	no reaction	—
3	10 mol%	5 mol%	2/1	71	88

(S1) Nudelman, N. S.; Garcia, G. V. *J. Org. Chem.* **2001**, *66*, 1387.