Regio- and Enantioselective Pd-Catalyzed Allylic Alkylation of Ketones through Allyl Enol Carbonates

Barry M. Trost* and Jiayi Xu

Department of Chemistry, Stanford University, Stanford, California 94305-5080.
bmtrost@stanford.edu

Supplemental Information

Experimental General

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated. Solvents were freshly purified by passage through an aluminum column before use. Solvents for Pd-catalyzed reactions were degassed by freeze-thaw techniques under vacuum¹. Tris(dibenzylideneacetone)palladium(0) monochloroform complex, Pd₂(dba)₃•CHCl₃ was prepared by the procedure of Ibers². Ligands **L1**, **L2**, **L3**, and **L4** were prepared by literature procedures^{3,4}. All other reagents were used as obtained unless otherwise noted.

Flash Chromatography was performed with EM Science silica gel (0.040-0.063 μm grade). Analytical thin-layer chromatography was performed with 0.2 mm coated commercial silica gel plates (E. Merck, DC-Plasikfolien, kieselgel 60 F254). Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Kugelrohr distillations were performed on a Büchi GKR-50 glass tube oven. Proton nuclear magnetic resonance (¹H-NMR) data were acquired on a Mercury 400 (400 MHz) or on a Varian Unity Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet, br, broad. Carbon-13 nuclear magnetic resonance (¹³C-NMR) data were acquired at 100 MHz on a Mercury 400 or at 125 MHz on a Varian Unity Inova-500 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.1 ppm for chloroform-*d*. Infrared (IR) data were recorded as films on sodium chloride plates or a potassium bromide (KBr) pellets on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm⁻¹). Elemental analyses (Anal.) were performed by M.-H.-W. Laboratories of Phoenix, AZ. Chiral GC analyses were performed on a HP 6890 series GC system using a Cyclosil B chiral column. GC analyses were performed on a HP 6850 series GC system using a Agilent Technologies HP-1 GC column (30 m length, 0.32 mm I.D., 0.25 μm film). Chiral HPLC analyses were performed on a Thermo Separation Products Spectra Series P-100 or 200 and UV100 (254 nm) using Chiralcel[®] columns (OD, OB-H, OJ, AD, As, or OC) eluting with heptane / *iso*-propanol mixtures indicated. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm cells and the sodium D line (589 nm) at ambient temperature in the solvent and concentration indicated.

The completed list of optimization studies of the Pd-catalyzed Asymmetric Allyl Alkylation of 2-methyl cyclohexanone^a.

Entry	Ln	Solvent	Temp. °C	Time h	Pd %	Ln%	Additive	ee ^b %	Yield ^c % of 3	Yield ^c % of 4
1	L1	CH ₃ CN	23	20	5	5.5		NA	<5	
2	L2	CH ₃ CN	23	20	5	5.5		NA	<5	
3	L3	CH ₃ CN	23	20	5	5.5		NA	<5	
4	L4	CH ₃ CN	23	20	5	5.5		NA	0	
5	L2	DCM	23	20	5	5.5		78	61	11

6	L3	DCM	23	20	5	5.5		64	90	9
7	L4	DCM	23	20	5	5.5		83	57	26
8	L4	DCM	23	20	5	5.5		84	64	26
9	L4	DCM	4	20	5	5.5		85	52	15
10	L4	DCM	23	20	5	5.5	50% Bu ₄ NCl	78	24	24
11	L4	DCM	23	20	5	5.5	50% Bu ₄ NBr	78	19	15
12	L4	DCM	23	20	5	5.5	50% Bu ₄ NBF ₄	77	18	13
13	L4	DCM	23	20	5	5.5	50% TBAT	NA	Trace	Trace
14	L1	Dioxane	23	20	5	5.5		49	87	3
15	L2	Dioxane	23	20	5	5.5		74	68	0
16	L3	Dioxane	23	20	5	5.5		66	92	3
17	L4	Dioxane	23	20	5	5.5		80	99	0
18	L1	DME	23	4	5	7.5		65	59*	
19	L2	DME	23	48	5	7.5		52	35*	
20	L3	DME	23	4	5	7.5		76	81*	
21	L4	DME	23	24	5	7.5		85	60*	
22	L1	DME	23	5	5	5.5		66	81	8
23	L2	DME	23	24	5	5.5		72	48	1
24	L3	DME	23	4	5	5.5		76	87	1.6
25	L4	DME	23	24	5	5.5		84	87	7
26	L4	DME	23	3	5	12.5		84	77	0.7
27	L4	DME	4	24	5	5.5		87	69	19
28	L4	DME 1% H ₂ O	23	24	5	5.5		NA	20	3.7
29	L3	DME 1% H ₂ O	23	24	5	5.5		NA	1.5	0
30	L1	DMSO	23	40	5	5.5		NA	0	
31	L2	DMSO	23	40	5	5.5		NA	0	
32	L3	DMSO	23	40	5	5.5		68	55	15.5
33	L4	DMSO	23	40	5	5.5		NA	0	
34	L2	THF	23	12	5	5.5		75	80	2
35	L3	THF	23	12	5	5.5		72	89	1

36	L4	THF	23	12	5	5.5		81	85	1
37	L1	Toluene	23	2	5	5.5		31	73	0
38	L2	Toluene	23	16	5	5.5		61	73	2
39	L3	Toluene	23	16	5	5.5		60	85	1
40	L4	Toluene	23	16 (2)	5	5.5		85	88	0
41	L4	Toluene	4	16	5	5.5		87	91	2
42	L4	Toluene	4 (.3M)	16	5	5.5		85	94	4
43	L4	Toluene	-10	20	5	5.5		83	84	6
44	L4	Toluene	4 (.3M)	16	5	12.5		86	88	4
45	L4	Toluene	4 (.025M)	16	5	5.5		87	92	0
46	L4	Toluene	4 (.3M)	24	2	5		85	88	5

^a Unless otherwise indicated, all reactions were performed on a 0.3 mmol scale at 0.1 M; DCM stands for dichloromethane, DME stands for 1, 2-dimethoxyethane, THF stands for tetrahydrofuran. ^b The ee values were determined by chiral GC. ^c The yields were determined by quantitative GC analysis using decane as internal reference. * The yields were isolated yields.

General Procedure for the Pd-catalyzed Reaction of Carbonates.

The catalyst is sensitive to air and water and thus thorough degassing of the solvent needs to be performed. Two test tubes were connected with a double-end needle. One test tube was loaded with 2.5 mol% Pd₂(dba)₃CHCl₃ (**2**) and 5.5 mol% mmol ligand; the other one was loaded with 0.30 mmol carbonate. The system was evacuated and flushed with Argon three times at which point 1.5 ml degassed solvent was added to both of the test tubes. After stirred for 20 min the orange solution of catalyst was transferred into the test tube containing carbonate substrate. In most cases, the color of the reaction solution turned to light yellow within a few minutes and then turned back to orange in different time depending on the choice of ligand, substrate, solvent and temperature, indicating the completion of the reaction. For GC analysis, the reaction mixture was diluted with 3 ml 10% diethyl ether in petroleum ether and passed through a 3 cm layer of silica gel in a normal glass pipette. Otherwise, the reaction mixture was concentrated *in vacuo* and purified by column chromatography on silica gel eluted with 5% diethyl ether in petroleum ether.

(R)-(+)-2-Allyl-2-methylcyclohexanone (3)⁵: Colorless oil. *R*_f = 0.34 (Diethyl ether/petroleum ether 1:9); [α]_D²² = +49.6 (*c* = 2.9, CH₂Cl₂, 85% ee); GC (Cyclosil B column, 90 °C constant, 50:1 split ratio, 15.0 split flow, 1.3 flow rate; *t*₁ = 32.86 min (minor), *t*₂ = 34.95 min (major)); ¹H NMR (400 MHz, CDCl₃): δ = 5.70 (m, 1H), 5.08-5.01 (m, 2H), 2.38 (m, 3H), 2.23 (dd, *J*₁ = 14 Hz, *J*₂ = 7.6 Hz, 1H), 1.90-1.65 (m, 5H), 1.62-1.54 (m, 1H), 1.07 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 215.6, 133.9, 118.0, 48.5, 42.0, 38.9, 38.7, 27.5, 22.7, 21.1.

(R)-(-)-2-Allyl-1-tetralone (6)⁶: Colorless oil. *R*_f = 0.59 (Diethyl ether/petroleum ether 1:9); [α]_D²³ = -29.7 (*c* = 1.21, MeOH, 97% ee); HPLC (Chiralcel[®] OD column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL / min; *t*₁ = 21.87 min (minor), *t*₂ = 23.88 min (major)); IR (film): $\tilde{\nu}_{\text{max}}$ = 3073 (w), 2930 (m), 2862 (w), 1682 (s), 1640 (w), 1600 (s), 1455 (m), 1434 (m), 1359 (w), 1280 (m), 1220 (s), 1156 (m), 996 (m), 911

(m), 745 cm⁻¹ (s); ¹H NMR (400 MHz, CDCl₃): δ = 8.03 (d, *J* = 8.0 Hz, 1H), 7.45 (td, *J*₁ = 7.4 Hz, *J*₂ = 1.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 5.85 (m, 1H), 5.08 (m, 2H), 2.99 (dd, *J*₁ = 7.6 Hz, *J*₂ = 4.4 Hz, 2H), 2.76 (m, 1H), 2.55 (m, 1H), 2.25 (m, 2H), 1.86 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 199.5, 144.1, 136.3, 133.3, 132.6, 128.8, 127.5, 126.6, 116.9, 47.2, 34.1, 28.7, 28.0.

2, 2-Diallyl-1-tetralone (8)⁷: Colorless oil. *R*_f = 0.65 (Diethyl ether/petroleum ether 1:9); ¹H NMR (300 MHz, CDCl₃): δ = 8.03 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.23 (m, 2H), 5.85 (m, 2H), 5.08 (m, 4H), 2.99 (t, *J* = 6 Hz, 2H), 2.55 (dd, *J*₁ = 12.0 Hz, *J*₂ = 7.6 Hz, 2H), 2.25 (dd, *J*₁ = 12.0 Hz, *J*₂ = 7.6 Hz, 2H), 2.03 (t, *J* = 6 Hz, 2H).

(R)-(+)-2-Allylcyclohexanone (10)⁸: Colorless oil. *R*_f = 0.35 (Diethyl ether/petroleum ether 1:9); [α]_D²⁴ = +10.28 (c = 1.1, MeOH, 78% ee); ¹H NMR (400 MHz, CDCl₃): δ = 5.77 (m, 1H), 5.08 - 4.80 (m, 2H), 2.55 (m, 1H), 2.34 (m, 3H), 2.18 - 1.94 (m, 3H), 1.86 (m, 1H), 1.66 (m, 2H), 1.36 (m, 1H).

Determination of the ee value of **10**:

By our Chiral GC columns we had a hard time to separate the enantiomers of **10**. Therefore, **10** was reduced to alcohol **32** and **33** by NaBH₄ in MeOH in 1:2 ratio. **32** and **33** were separated by column chromatography on silica gel, eluted with 10% Et₂O in petroleum ether. **32** was dissolved in pyridine and treated with benzoyl chloride at room temperature. The reaction mixture was stirred for 2 h and most solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel eluted with 5% Et₂O in petroleum ether to yield **34**. Compound **34** was ready to be separated on chiral GC (Cyclosil B column, 150 °C constant, 50:1 split ratio, 15.0 split flow, 1.5 flow rate; *t*₁ = 50.48 min (minor), *t*₂ = 51.54 min (major)).

(R)-(+)-2-Allyl-2-methyl-1-tetralone (12)⁹: Colorless oil. *R*_f = 0.60 (Diethyl ether/petroleum ether 1:9); [α]_D²³ = +16.9 (c = 1.39, CH₂Cl₂, 100% ee); HPLC (Chiralcel[®] OB-H column; 97:3 Heptane / Isopropanol; flow rate = 1 mL / min; *t*₁ = 5.79 min (major), *t*₂ = 6.74 min (minor)); IR (film): $\tilde{\nu}_{\text{max}}$ = 3074 (w), 2966 (m), 2930 (s), 2856 (w), 1682 (s), 1640 (w), 1602 (m), 1455 (m), 1433 (w), 1375 (w), 1323 (w), 1287 (w), 1221 (s), 1156 (w), 1097 (w), 996 (w), 972 (w), 917 (m), 742 cm⁻¹ (s); ¹H NMR (400 MHz, CDCl₃): δ = 8.04 (d, *J* = 8.0 Hz, 1H), 7.45 (td, *J*₁ = 7.4 Hz, *J*₂ = 1.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 5.79 (m, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 5.06 (d, *J* = 5.6 Hz, 1H), 2.98 (m, 2H), 2.46 (dd, *J*₁ = 13.6 Hz, *J*₂ = 7.2 Hz, 1H), 2.27 (dd, *J*₁ = 13.6 Hz, *J*₂ = 7.6 Hz, 1H), 2.08 (m, 1H), 1.90 (m, 1H), 1.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 202.2, 143.6, 134.2, 133.3, 131.8, 128.9, 128.2, 126.9, 118.4, 44.8, 41.3, 33.6, 25.6, 22.1.

(-)-2-Allyl-2-methyl-1-benzosuberone (14)¹⁰: Colorless oil. $R_f = 0.49$ (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24} = -6.93$ ($c = 1.47$, CH_2Cl_2 , 91% ee); GC (Cyclosil B[®] column; 130 °C constant temperature; 50:1 split ratio; 15.0 split flow; 1.5 flow rate; $t_1 = 72.75$ min (minor), $t_2 = 74.49$ min (major)); IR (film): $\tilde{\nu}_{\text{max}} = 3073$ (w), 2933 (s), 2864 (m), 1682 (s), 1640 (w), 1600 (m), 1482 (w), 1453 (m), 1375 (w), 1300 (w), 1251 (m), 1192 (w), 1095 (w), 997 (w), 964 (m), 916 (m), 786 (w), 759 (m), 743 cm^{-1} (m); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.34$ (m, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.10 (t, $J = 7.6$ Hz, 1H), 5.72 (m, 1H), 5.06 – 5.00 (m, 2H), 2.77 (m, 2H), 2.32 (m, 2H), 1.91 (p, $J = 6.8$ Hz, 2H), 1.75 (m, 1H), 1.61 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 214.5$, 141.6, 137.3, 133.7, 130.8, 128.4, 127.2, 126.6, 118.4, 49.2, 43.9, 34.6, 32.9, 22.8, 22.3.

(+)-2-Allyl-2-methylindanone (16): Colorless oil. $R_f = 0.43$ (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{22} = +46.2$ ($c = 1.6$, CH_2Cl_2 , 76% ee); HPLC (Chiralcel[®] OB-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL / min; $t_1 = 9.49$ min (major), $t_2 = 12.62$ min (minor)); IR (film): $\tilde{\nu}_{\text{max}} = 3076$ (w), 2962 (m), 2926 (m), 2867 (w), 1715 (s), 1640 (w), 1609 (s), 1588 (w), 1465 (m), 1435 (m), 1372 (w), 1330 (w), 1296 (m), 1205 (w), 1152 (w), 1091 (w), 983 (m), 919 (m), 796 (m), 740 cm^{-1} (s); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.75$ (d, $J = 7.6$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.37 (t, $J = 7.6$ Hz, 1H), 5.66 (m, 1H), 5.12 – 4.98 (m, 2H), 3.17 (d, $J = 17.2$ Hz, 1H), 2.84 (d, $J = 17.2$ Hz, 1H), 2.39 (dd, $J_1 = 13.6$ Hz, $J_2 = 6.4$ Hz, 1H), 2.30 (dd, $J_1 = 8.2$ Hz, $J_2 = 6.4$ Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 210.9$, 152.7, 135.9, 135.0, 133.9, 127.5, 126.7, 124.3, 118.4, 48.9, 42.6, 39.4, 23.9; Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}$: C, 83.83; H, 7.58; Found: C, 84.16; H, 7.61.

(+)-5-Allyl-5-methyl-6,7-dihydrobenzofuran-4(5H)-one (18)¹⁰: Colorless oil. $R_f = 0.22$ (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23} = +8.6$ ($c = 1.4$, CH_2Cl_2 , 82% ee); HPLC (Chiralcel[®] AD column; 99.5:0.5 Heptane / Isopropanol; flow rate = 0.8 mL / min; $t_1 = 18.14$ min (minor), $t_2 = 20.70$ min (major)); IR (film): $\tilde{\nu}_{\text{max}} = 3150$ (w), 3074 (w), 2966 (w), 2933 (m), 2856 (w), 1677 (s), 1640 (w), 1603 (w), 1456 (m), 1440 (w), 1378 (w), 1356 (w), 1289 (w), 1253 (w), 1219 (w), 1121 (m), 1024 (w), 999 (w), 939 (w), 918 (w), 739 cm^{-1} (w); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.31$ (d, $J = 2.0$ Hz, 1H), 6.66 (d, $J = 2.0$ Hz, 1H), 5.77 (m, 1H), 5.12 – 5.03 (m, 2H), 2.88 (t, $J = 6.4$ Hz, 2H), 2.42 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.2$ Hz, 1H), 2.24 (dd, $J_1 = 14$ Hz, $J_2 = 7.6$ Hz, 1H), 2.12 (m, 1H), 1.92 (m, 1H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 198.5$, 165.4, 143.0, 134.1, 119.8, 118.3, 107.3, 45.2, 41.2, 33.4, 21.9, 20.7.

(+)-2-Allyl-6-benzylidene-2-methylcyclohexanone (20)⁹: Colorless oil. $R_f = 0.50$ (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24} = +22.9$ ($c = 2.75$, CH_2Cl_2 , 95% ee); HPLC (Chiralcel[®] OJ column; 97:3 Heptane / Isopropanol; flow rate = 1 mL / min; $t_1 = 6.43$ min (minor), $t_2 = 7.68$ min (major)); IR (film): $\tilde{\nu}_{\text{max}} = 3074$ (w), 3024 (w), 2966 (w), 2933 (s), 2870 (m), 1679 (s), 1639 (w), 1595 (s), 1573 (m), 1492 (m), 1446 (m), 1373 (w), 1317 (w), 1265 (m), 1145 (s), 1113 (w), 1030 (w), 996 (m), 917 (m), 857 (w), 762 (m), 695 cm^{-1} (s); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.37$ (m, 5H), 5.75 (m, 1H), 5.07 (m, 2H), 2.82 (m, 2H), 2.43 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.2$ Hz, 1H), 2.23 (dd, $J_1 = 14$ Hz, $J_2 = 7.6$ Hz, 1H), 1.91 (m, 1H), 1.73 (m, 3H), 1.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 206.9$, 137.0, 136.0, 135.6, 134.0, 130.2, 128.4, 128.3, 118.2, 47.1, 42.9, 35.1, 29.5, 24.2, 19.8.

(-)-3-Allyl-2,3-dihydrothiochromen-4-one (22)¹¹: Colorless oil. R_f = 0.47 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -98.83 (c = 1.27, CH_2Cl_2 , 93% ee); HPLC (Chiralcel[®] OB-H column; 99.5:0.5 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 10.68 min (major), t_2 = 11.87 min (minor)); IR (film): $\tilde{\nu}_{\text{max}}$ = 3075 (w), 3024 (w), 2917 (m), 2849 (w), 1682 (s), 1640 (w), 1588 (s), 1573 (m), 1459 (m), 1436 (s), 1342 (w), 1289 (m), 1211 (m), 1162 (w), 1118 (w), 1087 (w), 997 (w), 919 (m), 763 (m), 736, 695 cm^{-1} (m); ^1H NMR (400 MHz, CDCl_3): δ = 8.09 (m, 1H), 7.36 (m, 1H), 7.24 (m, 1H), 7.16 (m, 1H), 5.81 (m, 1H), 5.14 (m, 2H), 3.25 (dd, J_1 = 13.2 Hz, J_2 = 4.0 Hz, 1H), 3.08 (dd, J_1 = 13.2 Hz, J_2 = 10.0 Hz, 1H), 2.84 (m, 1H), 2.73 (m, 1H), 2.39 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 195.5, 141.8, 135.0, 133.1, 130.6, 129.6, 127.4, 124.9, 118.1, 46.5, 33.1, 30.3.

(-)-2-Allyl-6-methoxy-3,4-dihydronaphthalen-1(2H)-one (24): White solid, mp = 35 - 36 °C. R_f = 0.24 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = -55.88 (c = 3.8, CH_2Cl_2 , 100% ee); HPLC (Chiralcel[®] OD column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 48.72 min (minor), t_2 = 53.24 min (major)); IR (film): $\tilde{\nu}_{\text{max}}$ = 3075 (w), 3024 (w), 2917 (m), 2849 (w), 1674 (s), 1640 (w), 1601 (s), 1573 (m), 1494 (m), 1454 (m), 1359 (m), 1335 (m), 1251 (s), 1226 (m), 1155 (w), 1133 (m), 1029 (m), 913 (m), 851 (w), 830 cm^{-1} (w); ^1H NMR (400 MHz, CDCl_3): δ = 8.01 (d, J = 8.8 Hz, 1H), 6.81 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 5.84 (m, 1H), 5.14 - 5.04 (m, 2H), 3.85 (s, 3H), 2.94 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 2H), 2.75 (m, 1H), 2.49 (m, 1H), 2.23 (m, 2H), 1.84 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 198.3, 163.4, 146.6, 136.5, 129.9, 126.2, 116.8, 113.2, 112.5, 55.4, 46.8, 34.2, 29.0, 28.0; Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C, 77.75; H, 7.46; Found: C, 78.12; H, 7.60.

(-)-2-Allyl-7-methoxy-3,4-dihydronaphthalen-1(2H)-one (26): Colorless oil. R_f = 0.33 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = -50.2 (c = 2.1, CH_2Cl_2 , 97% ee); HPLC (Chiralcel[®] OC column; 99.5:0.5 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 25.23 min (major), t_2 = 30.86 min (minor)); IR (film): $\tilde{\nu}_{\text{max}}$ = 3074 (w), 3001 (w), 2932 (m), 2862 (w), 2836 (m), 1682 (s), 1640 (m), 1609 (s), 1496 (m), 1464 (m), 1422 (s), 1358 (m), 1322 (m), 1277 (s), 1249 (s), 1200 (m), 1173 (m), 1036 (m), 997 (w), 915 (m), 877 (m), 817 (w), 713 cm^{-1} (w); ^1H NMR (400 MHz, CDCl_3): δ = 7.51 (d, J = 2.8 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.04 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 5.84 (m, 1H), 5.14 - 5.04 (m, 2H), 3.83 (s, 3H), 2.92 (dd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, 2H), 2.75 (m, 1H), 2.53 (m, 1H), 2.23 (m, 2H), 1.84 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 199.7, 158.5, 136.9, 136.5, 133.5, 130.2, 121.8, 117.1, 109.5, 55.7, 47.2, 34.3, 28.4, 28.0; Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_2$: C, 77.75; H, 7.46; Found: C, 77.94; H, 7.21.

(+)-2-Allyl-1-indanone (28)¹²: Colorless oil. R_f = 0.27 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +95.8 (c = 4.0, CH_2Cl_2 , 81% ee); HPLC (Chiralcel[®] OB-H column; 90:10 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 6.27 min (minor), t_2 = 7.70 min (major)); IR (film): $\tilde{\nu}_{\text{max}}$ = 3077 (m), 2979 (w), 2919 (s), 2848 (w), 1714 (s), 1641 (m), 1610 (s), 1588 (m), 1474 (m), 1464 (s), 1435 (s), 1326 (m), 1296 (s), 1274 (s), 1211 (m), 1183 (w), 1151 (m), 1094 (m), 998 (s), 917 (s), 791 (w), 754 (s), 725 (m), 657 cm^{-1} (m); ^1H NMR (400 MHz, CDCl_3): δ = 7.76 (d, J = 7.6 Hz, 1H), 7.59 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 5.81 (m, 1H), 5.16 - 5.02 (m, 2H), 3.29 (dd, J_1 = 17.2 Hz, J_2 = 8.0 Hz, 1H), 2.87 (dd, J_1 = 17.2 Hz, J_2 = 4.0 Hz, 1H), 2.82 - 2.66 (m, 2H), 2.27 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 208.3, 153.9, 136.8, 135.6, 134.9, 127.4, 126.7, 124.0, 117.0, 46.6, 35.6, 32.1.

(+)-2-Allyl-1-benzosuberone (30)¹³: Colorless oil. R_f = 0.45 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +70.43 (c = 1.56, CH_2Cl_2 , 99% ee); HPLC (Chiralcel[®] OB-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 11.47 min (major), t_2 = 13.74 min (minor)); IR (film): $\tilde{\nu}_{\text{max}}$ = 3072 (m), 2935 (s), 2863 (m), 1682 (s), 1641 (m), 1599 (m), 1448 (m), 1375 (w), 1277 (m), 1246 (m), 1201 (m), 996 (w), 967 (m), 914 (s), 782 (w), 763 (m), 737 cm^{-1} (s); ^1H NMR (400 MHz, CDCl_3): δ = 7.64 (dd, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 7.37 (td, J_1 = 7.6 Hz, J_2 = 1.0 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 1H), 5.77 (m, 1H), 5.08 – 4.97 (m, 2H), 2.94 (m, 3H), 2.68 (m, 1H), 2.23 (p, J = 7.2 Hz, 1H), 2.06 (m, 1H), 1.96 (m, 1H), 1.69 (m, 1H), 1.59 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 206.9, 141.9, 140.0, 136.4, 131.3, 129.8, 128.3, 126.4, 116.5, 49.4, 35.4, 33.6, 29.7, 25.4.

- (1) Perrin, D. D. Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1988.
- (2) Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organometallic Chem.* **1974**, *65*, 253-266.
- (3) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327-9343.
- (4) Trost, B. M.; Bunt, R. C.; Lemoine, R. C.; Calkins, T. L. *J. Am. Chem. Soc.* **2000**, *122*, 5968-5976.
- (5) Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 4713-4714.
- (6) Imai, M.; Hagihara, A.; Kawasaki, H.; Manabe, K.; Koga, K. *Tetrahedron* **2000**, *56*, 179-185.
- (7) Diez-Barra, E.; Medrino, S.; Sanchez-Verdu, P.; Torres, J. *Tetrahedron* **1997**, *53*, 11437-11448.
- (8) Meyers, A. I.; Williams, D. R.; Erickson, G. W.; Whites, S.; Druehlinger, M. *J. Am. Chem. Soc.* **1981**, *103*, 3081-3087.
- (9) Trost, B. M.; Schroeder, G. M. *J. Am. Chem. Soc.* **1999**, *121*, 6759-6760.
- (10) Schroeder, G. M. Palladium Catalyzed Asymmetric Allylic Alkylation (AAA) of Prochiral Nucleophiles: Efforts toward the Synthesis of Erinacine A. Ph.D. Dissertation, Stanford University: Stanford, 2002.
- (11) Cid, J. M.; Romera, J. L.; Trabanco, A. A. *Tetrahedron Lett.* **2004**, *45*, 1133-1136.
- (12) Tsuda, T.; Okada, M.; Nishi, S.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 421-426.
- (13) Davies, H. J.; Main, B. G. *J. Chem. Soc. C-Organic* **1970**, 237.

Crossover Experiment:

Injection Date: 10/23/2004 10:38:55
 Injection Method: c:\star\gc 1 methods\gc 1 method
 Run Time (min): 27.929
 Instrument (Inj): GC 1

Sample Prep Info
 Manual injection

Peak No	Ret. Time (min)	Peak Area	Width 1/2 (sec)	Percent Area
1	3.512	526	1.8	8.82
2	4.046	76	2.1	1.27
3	5.374	277	1.4	4.64
4	5.792	2610	1.5	43.79
5	5.828	1063	1.3	17.84
6	6.198	476	1.4	7.98
7	6.319	253	1.2	4.25
8	6.575	30	1.4	0.50
9	7.439	17	1.1	0.28
10	7.463	25	1.2	0.42
11	7.626	117	1.2	1.96
12	7.771	22	1.5	0.37
13	8.318	470	1.8	7.88
Peak	Ret.	5962		100.00

GC#1 Method C

Method Notes
 No Method Notes

150 degree C, 3 min; ramp
 20 degree C/min; 250

Injection Date: 10/23/2004 10:15:03
Injection Method: c:\star\gc 1 methods\gc 1 method
Run Time (min): 8.965
Instrument (Inj): GC 1

Sample Prep Info
Manual injection

Peak No	Ret. Time (min)	Peak Area	Width 1/2 (sec)	Percent Area
1	5.383	1968	1.5	100.00
		1968		100.00

GC#1 Method C

Method Notes
No Method Notes

150 degree C, 3 min; ramp
20 degree C/min; 250

Injection Date: 10/23/2004 11:29:13
Injection Method: c:\star\gc 1 methods\gc 1 method
Run Time (min): 11.376
Instrument (Ini): GC 1

Sample Prep Info
 Manual injection

Peak No	Ret. Time (min)	Peak Area	Width 1/2 (sec)	Percent Area
1	5.775	776	1.4	100.00
		776		100.00

GC#1 Method C

Method Notes
 No Method Notes

150 degree C, 3 min; ramp
 20 degree C/min; 250

Injection Date: 10/23/2004 07:26:50
Injection Method: c:\star\gc 1 methods\gc 1 method
Run Time (min): 9.277
Instrument (Inj): GC 1

Sample Prep Info
Manual injection

Peak No.	Ret. Time (min)	Peak Area	Width 1/2 (sec)	Percent Area
1	3.527	2082	2.0	100.00
		2082		100.00

GC#1 Method C

Status Codes:
U - User defined peak endpoint(s)

Method Notes
No Method Notes

150 degree C, 3 min; ramp
20 degree C/min; 250

Injection Date: 10/23/2004 10:25:47
Injection Method: c:\star\gc 1 methods\gc 1 method
Run Time (min): 10.959
Instrument (Inj): GC 1

Sample Prep Info
Manual injection

Peak No.	Ret. Time (min)	Peak Area	Width 1/2 (sec)	Percent Area
1	4.045	3324	1.9	100.00
		3324		100.00

GC#1 Method C

Method Notes
No Method Notes

150 degree C, 3 min; ramp
20 degree C/min; 250

Injection Date: 10/23/2004 11:17:28
 Injection Method: c:\star\gc 1 methods\gc 1 method
 Run Time (min): 9.977
 Instrument (Ini): GC 1

Sample Prep Info
 Manual injection

Peak No	Ret. Time (min)	Peak Area	Width 1/2 (sec)	Percent Area
1	6.796	1879	1.3	100.00
		1879		100.00

GC#1 Method C

Method Notes
 No Method Notes

150 degree C, 3 min; ramp
 20 degree C/min; 250

Injection Date: 10/23/2004 09:59:06
Injection Method: c:\star\gc 1 methods\gc 1 method
Run Time (min): 13.737
Instrument (Inj): GC 1

Sample Prep Info
Manual injection

Peak No	Ret. Time (min)	Peak Area	Width 1/2 (sec)	Percent Area
1	7.279	336	1.3	100.00
		336		100.00

GC#1 Method C

Method Notes
No Method Notes

150 degree C, 3 min; ramp
20 degree C/min; 250

Injection Date: 10/23/2004 08:21:37
Injection Method: c:\star\gc 1 methods\gc 1 method
Run Time (min): 60.001
Instrument (Inj): GC 1

Sample Prep Info
 Manual injection

Peak No.	Ret. Time (min)	Peak Area	Width 1/2 (sec)	Percent Area
71	8.339	5771	1.9	100.00
		5771		100.00

GC#1 Method C

Method Notes
 No Method Notes

150 degree C, 3 min; ramp
 20 degree C/min; 250