Supporting Information
for
Dynamic Kinetic Asymmetric Allylic Alkylations of Allenes

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Experimental Procedures

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I. General Procedures

Flash chromatography was performed on silica gel (EM Science, Kieselgel 60, 230-400mesh, ASTM) or neutral alumina (Fluka, Aluminum Oxide, type 507, Brockmann grade III, 6% hydrate) using compressed air. TLC was performed using glass-backed plates coated with 0.2mm silica (Merck, DC-Platten, Kieselgel; 60 F_{254}) or plastic backed plates coated with 0.2mm neutral alumina (EM, 60 F_{254}, Type E). Chiral HPLC analysis was performed by comparison to racemic samples[1] on Daicel Chiralpack columns, eluting with a heptane and isopropanol mixture, using a Thermo Separation Products Spectra SERIES P100 or P200 instruments. NMR spectra were obtained on a Varian Gemini 200 (200 MHz), Gemini 300 (300 MHz), Mercury 400 (400 MHz), Unity 500 (500 MHz) or Unity 600 (600 MHz) instruments and are calibrated to TMS or residual solvent peaks: proton (benzene 7.15ppm, chloroform 7.26ppm, methanol 4.87ppm) and carbon (benzene 128.0ppm, chloroform 77ppm, methanol 49.15ppm). Optical rotation was measured on a Jasco DIP-1000 digital polarimeter in 5 cm cells at room temperature. $Pd_2dba_3CHCl_3$,[2] Trost ligand (S,S) **2**[3] were prepared by literature procedures. Solvents were

[1] Racemic allene products were prepared through the described Pd catalyzed allylic alkylation with triphenyl phosphine as the ligand instead of (S,S) **2.**

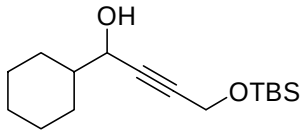
[2] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J.J.; Ibers, J.A. *J. Organomet. Chem.* **1974**, *65*, 253-266.

[3] Trost, B.M.; Bunt, R.C.; Lemoine, R.C.; Calkins, T.L. *J. Am. Chem. Soc.* **2000**, *122*, 5968-5976.

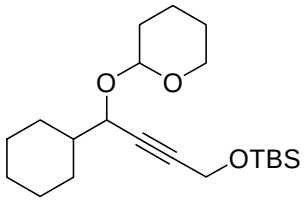
degassed by freeze-thaw techniques.[4] All compounds are >95% pure by proton NMR unless otherwise noted. All reagents were used as purchased unless otherwise noted.

II. Synthesis of Allene Substrates

Typical Procedure for the synthesis of acetates substrates (4-7)

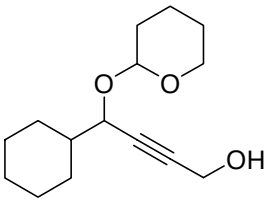


1-cyclohexyl-4-(tert-butyldimethylsilyloxy)-but-2-yne-1-ol (E1)
An anhydrous solution of *tert*-butyldimethyl-(2-propynyloxy)-silane (25 mmol, 4.2 g, 5.0 mL) in THF (80 mL) was slowly treated with n-BuLi (2.5 M in hexanes, 25 mol, 10 mL) at -78ºC under nitrogen. The homogenous solution was stirred for 10 minutes; at which point, cyclohexane carboxaldehyde (25 mmol, 2.8 g, 3.0 mL) was slowly added to the above solution. After stirring the above reaction for 30 minutes, the reaction was quenched at -78ºC by the slow addition of aqueous $NaHSO_4$ (1 M, 50 mL). The reaction while vigorously stirring was allowed to warm to room temperature. The mixture was diluted with water (100 mL) and extracted with ethyl acetate (3 x 75 mL). The combined organic portions were washed with water, brine, dried with $MgSO_4$, filtered and concentrated to an oil. The crude material was distilled under vacuum (0.5 torr) to provide the intended product **E1** as an oil (6.3g, 90%). **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 4.36 (d, *J*=1.6Hz, 2H), 4.18 (dt, *J*=4.8, 1.2Hz, 1H), 1.8-1.9 (m, 2H), 1.70-1.80 (m, 2H), 1.62-1.70 (m, 1H), 1.50-1.60 (m, 1H), 1.02-1.30 (m, 5H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H). **^{13}C NMR** ($CDCl_3$ 125 MHz) δ 84.79, 84.19, 67.13, 51.70, 44.00, 28.44, 28.04, 26.03, 25.82, 25.79, 25.74, 18.24, -5.17. **IR** (KBr-neat) 3424 b, 2929, 2856, 1472, 1463, 1390, 1365, 1255, 1127, 1086, 1008, 837, 778 cm^{-1}. **EA** calcd for $C_{16}H_{30}O_2Si$ C: 68.03, H: 10.70 found C: 68.96, H: 10.50.

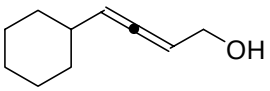


1-(*tert*-Butyldimethylsilyloxy)-4-cyclohexyl-4-(tetrahydro-2H-pyran-2-yloxy)-but-2-yne (E2)
A solution of compound **E1** (6.3 g, 0.022 mol) in dihydropyran (15 mL) was treated with p-toluenesulfonic acid monohydrate (22 mg, 0.11 mmol) in an ice bath. The exothermic reaction was allowed to warm to room temperature and stirred at room temperature for 45 minutes. The reaction was quenched with triethylamine (40 μL, 0.3 mmol), and the excess dihydropyran was removed *in vacuo*. The concentrated mixture of diastereomers was used in the next step without further purification. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 4.96 (t, *J*=3.6Hz, 0.5H), 4.70 (t, *J*=3.6Hz, 0.5H), 4.34 (dd, *J*=1.6, 4.4Hz, 2H), 4.19 (dt, *J*=6.8, 1.2Hz, 0.5H), 3.95-4.08 (m, 1.5H), 3.76-3.82 (m, 0.5H), 3.47-3.53 (m, 0.5H), 1.0-2.0 (m, 17H), 0.90 (s, 9H), 0.10 (s, 6H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 98.51, 95.16, 84.49, 83.76, 83.74, 82.68, 72.02, 69.49, 62.08, 51.83, 51.73, 42.57, 42.48, 30.40, 30.22, 29.08, 28.72, 28.15, 26.36, 25.90, 25.89, 25.86, 25.82, 25.73, 25.47, 25.38, 19.27, 19.93, 18.20, -5.15, -5.18. **IR** (KBr-neat) 2929, 2855, 1730, 1472, 1452, 1369, 1256, 1118, 1085, 1021, 974, 837, 816, 778 cm^{-1}. **EI-HRMS** calcd for $C_{21}H_{38}O_3Si$ $(M)^+$ 366.2590, $(M-C_4H_9)^+$ calcd 309.1886 found 309.1898, $(M-C_6H_{11})^+$ calcd 283.1729 found 283.1734, $(M-C_5H_9O)^+$ calcd 265.1988 found 265.1990. **ESI-LRMS** calcd for $C_{21}H_{38}O_3Si$ $(M)^+$ 366.3 found $(M+Na)^+$ 389.2.

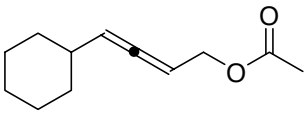
[4] Perrin, D.D.; Armarego, L.F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Elmsford, NY, 1988, pg 123.



4-Cyclohexyl-4-(tetrahydro-2H-pyran-2-yloxy)-but-2-yn-1-ol (E3)
A solution of all the crude oil from above **E2** (~22 mmol) in THF (30ml) was directly subjected to TBAF (1M in THF, 27 mL, 27 mmol). The reaction was stirred for 2.5 hours; at which point, the reaction was diluted with ethyl acetate (100 mL) and washed with water (3x75 mL), dried with $MgSO_4$, filtered and concentrated to an oil. Purification by silica chromatography (40-50% Et_2O in petroleum ether) provided the desired alcohol **E3** as a thick colorless oil and mixture of diastereomers (4.5 g, 71% for 2 steps). **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.00 (t, *J*=2.8Hz, 0.5H), 4.71 (t, *J*=3.6Hz, 0.5H), 4.30 (bs, 2H), 4.21 (dt, *J*=1.6, 6.8Hz, 0.5H), 4.0-4.1 (m, 1H), 3.78 (td, *J*=2.8, 9.2Hz, 0.5H), 3.55-3.59 (m, 1H), 2.48 (bs, 0.5H), 2.40 (bs, 0.5H), 1.48-1.98 (m, 13H), 1.02-1.32 (m, 4H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 99.11, 94.86, 84.57, 84.42, 83.63, 83.35, 77.21, 72.52, 69.33, 62.38, 61.85, 51.03, 50.94, 42.50, 42.44, 30.32, 30.29, 29.05, 28.73, 28.13, 26.36, 26.30, 25.87, 25.86, 25.83, 25.79, 25.42, 25.29, 19.11, 19.00. **IR** (KBr-neat) 3421 b, 2928, 2853, 1451, 1201, 1115, 1076, 1021, 974, 755 cm^{-1}. **EA** calcd for $C_{15}H_{24}O_3$ C: 71.39, H: 9.59 found C: 71.50, H: 9.54.

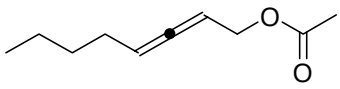


4-Cyclohexylbuta-2,3-dien-1-ol (E4)
Alcohol **E3** (2.0 g, 8.5 mmol) was added drop wise to a heterogeneous mixture of $LiAlH_4$ (1.3g, 34 mmol) in anhydrous diethyl ether (85 mL) at room temperature. The mixture was stirred at reflux for 1 hour. The reaction was cooled to 0ºC, quenched by the slow sequential addition of water (1.3 mL), 4M NaOH (1.3 mL) and water (2.6 mL). The mixture was allowed to warm to room temperature and vigorously stirred for 30 minutes. The mixture was diluted with diethyl ether (100 mL), dried with $NaSO_4$, filtered and concentrated to an oil. Purification by silica chromatography (35% diethyl ether in petroleum ether) provided the intended alcohol **E4** as a slightly yellow oil (530 mg, 41%). **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.37 (ddd, *J*=3.2, 6.4, 9.6Hz, 1H), 5.29 (ddd, *J*=3.2, 6.4,9.6Hz, 1H), 4.11 (dt, *J*= 2.8, 8.9Hz, 2H), 1.94-2.4 (m, 1H), 1.60-1.80 (m, 6H), 1.12-1.34 (m, 5H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 201.77, 100.04, 92.61, 60.78, 36.99, 33.01, 32.95, 26.01, 25.92, 25.90. **IR** (KBr-neat) 3320 b, 2925, 2851, 1961, 1448, 1012, 890, 695, 468 cm^{-1}. . **EI-HRMS** calcd for $C_{10}H_{16}O$ 152.1201 found 152.1194.



4-Cyclohexylbuta-2,3-dienyl acetate (5)
Pyridine (1.5 g, 1.6 mL, 20 mmol) was added to a solution of alcohol **E4** (470 mg, 3.1 mmol) and acetic anhydride (790 mg, 0.73 mL, 7.7 mmol) in anhydrous methylene chloride (30 mL). The reaction was stirred at room temperature for 3 days. After which, the reaction was diluted with ethyl acetate (100 mL), washed with phosphate buffer (2x 75 mL, 0.5M, pH = 5), brine (1x75 mL), dried with $MgSO_4$, filtered and concentrated to an oil. Purification by silica chromatography (7% ethyl ether in petroleum ether) provided the intended acetate **5** as a yellow oil (580 mg, 97%). **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.20-5.30 (m, 2H), 4.48-4.58 (m, 2H), 2.06 (s, 3H), 1.92-2.20 (m, 1H), 1.68-1.78 (m, 4H), 1.58-1.64 (m, 1H), 1.0-1.32 (m, 5H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 204.27, 170.80, 98.95, 87.69, 62.98, 36.81, 32.86, 32.84, 26.03, 25.91, 25.89, 20.99. **IR** (KBr-neat)2926, 2852, 1964, 1744 s, 1449, 1374, 1227, 1025, 959, 892, 869, 834, 727 cm^{-1}. **EA** calcd for $C_{12}H_{18}O_2$ C: 74.19, H: 9.34 found 74.09, H: 9.24.

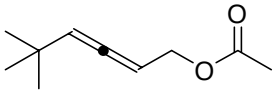
Octa-2,3-dienyl acetate (4)



Acetate **4** was prepared through an analogous synthesis as acetate **5** and isolated as a clear oil. **^{1}H NMR** ($CDCl_3$ 300 MHz) δ 5.20 – 5.30 (m, 2H), 4.50-4.60 (m, 2H), 2.07 (s, 3H), 2.01-2.05 (m,

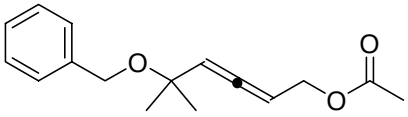
2H), 1.28-1.44 (m, 4H), 0.90 (t, *J*=7Hz, 3H). **^{13}C NMR** ($CDCl_3$ 125 MHz) δ 205.38, 170.79, 92.93, 86.77, 62.93, 31.07, 27.99, 22.05, 20.97, 13.83. **IR** (KBr – neat) 2959, 2932, 2874, 2661, 1967, 1744, 1458, 1444, 1375, 1227, 1026, 969, 869 cm^{-1}. **EA** calcd for $C_{10}H_{16}O_2$ C: 71.39, H: 9.59 found C: 71.40 H: 9.44.

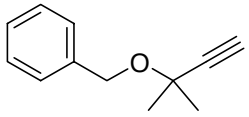
5,5-Dimethylhexa-2,3-dienyl acetate (6)



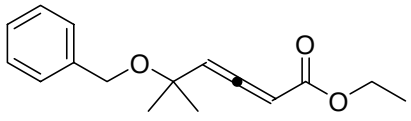
Acetate **6** was prepared through an analogous synthesis as acetate **5** and isolated as a clear oil. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.26-5.34 (m, 2H), 4.50-4.60 (m, 2H), 2.07 (s, 3H), 1.04 (9H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 202.74, 170.81, 104.88, 88.63, 62.90, 31.76, 30.01, 20.97. **IR** (KBr – neat) 2962, 2868, 1965, 1744, 1476, 1462, 1445, 1373, 1228, 1191, 1026, 975, 874 cm^{-1}. **ESI-LRMS** calcd for $C_{10}H_{16}O_2$ 168.1 found $(M+Na)^+$ 191.1. **EA** calcd for $C_{10}H_{16}O_2$ C: 71.39, H: 9.59 found C: 71.34, H: 9.36.

Synthesis of 5-(Benzyloxy)-5-methylhexa-2,3-dienyl acetate (7)





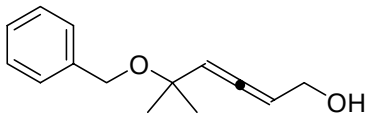
1-((2-Methylbut-3-yn-2-yloxy)methyl)benzene (E5)
2-Methyl-3-butyn-2-ol (8 mL, 9.94g, 8 3mmol) was added to a heterogeneous mixture of NaH (60% in mineral oil, 4g, 0.1 mol) in anhydrous THF (400 mL). After stirring the mixture for 1 hour under nitrogen at room temperature, tetrabutylammonium iodide (1.5g, 4 mmol) followed by benzyl bromide (12 mL, 17g, 0.1 mol) were added to the above alkoxide mixture. The mixture was stirred under nitrogen for 18 hours. After which, the reaction was diluted with diethyl ether (300 mL), washed with water (3x100 mL), brine (100 mL), dried with $MgSO_4$, filtered and concentrated to an oil. Silica chromatography (1.5% diethyl ether in petroleum ether) provided the intended ether **E5** as a clear oil (12.2g, 85%). **^{1}H NMR** ($CDCl_3$ 300 MHz) δ 7.20-7.40 (m, 5H), 4.63 (s, 2H), 2.47 (s, 1H), 1.55 (s, 6H). **^{13}C NMR** ($CDCl_3$ 75 MHz) δ 138.83, 128.27, 127.70, 127.35, 86.05, 72.25, 70.44, 66.49, 28.82. **IR** (KBr – neat) 3296, 2986, 1454, 1381, 1361, 1228, 1187, 1160, 1086, 1057, 1029, 736, 696, 636 cm^{-1}. **EI-HRMS** calcd for $C_{12}H_{14}O$ 174.1045 found 174.1025.



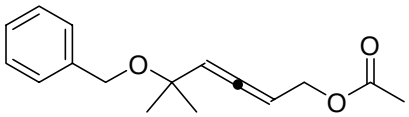
Ethyl 5-(benzyloxy)-5-methylhexa-2,3-dienoate (E6)
Alkyne **E5** was couple with ethyl diazoacetate according to the methodology published by Fu *et. al.*[5] A solution of alkyne **E5** (12.2g, 70 mmol) and ethyl diazoacetate (8.0g, 7.4 mL, 70mmol) in anhydrous acetonitrile (100 mL) was cannulated into a solution of CuI (670 mg, 3.5 mmol) in anhydrous acetonitrile (150 mL). The gently bubbling solution was stirred at room temperature for 24 hours. ^{1}H NMR analysis, of a concentrated aliquot, showed complete consumption of starting alkyne. The acetonitrile solvent was removed *in vacuo*, and the oily residue was taken up into chloroform (200 mL) and treated with triethylamine (9.75 mL, 7.1 g, 70 mmol). The isomerization reaction was stirred at room temperature for 18h hours. ^{1}H NMR analysis, of a concentrated aliquot, showed complete isomerization of the alkyne to the allene. Concentration *in vacuo* and silica chromatography (10% diethyl ether in petroleum ether)

[5] Suarez, A.; Fu, G.C. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*(27), 3580-3582.

provided the allenyl ester **E6** as a yellow clear oil (14.2g, 78%). **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 7.20-7.40 (m, 5H), 5.73 (d, *J*=6Hz, 1H), 5.69 (d, *J*=6Hz, 1H), 4.57 (d, *J*=11.2Hz, 1H), 4.48 (d, *J*=11.2Hz, 1H), 4.14-4.24 (m, 2H), 1.44 (s, 6H), 1.25 (t, *J*=7.2Hz, 3H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 211.30, 165.67, 139.06, 128.30, 127.51, 127.30, 101.79, 90.14, 75.07, 65.53, 60.92, 27.65, 26.28, 14.19. **IR** (KBr – neat) 2981, 1961, 1716 s, 1455, 1384, 1364, 1256, 1227, 1144, 1086, 1043, 1029, 875, 804, 736, 697 cm^{-1}. **EI-HRMS** calcd for $C_{16}H_{20}O_3$ 260.1412 found 260.1412.



5-(Benzyloxy)-5-methylhexa-2,3-dien-1-ol (E7)
DiBALH (1M in hexanes, 113 mL, 113 mmol) was added drop wise to an anhydrous solution of allenyl ester **E6** (14g, 54 mmol) in methylene chloride (400 mL) at -78ºC under nitrogen. The slightly yellow homogenous solution was stirred at -78ºC for 4 hours. At which point, the reaction was quenched by the slow addition of saturated aqueous NaF (100 mL). The mixture was vigorously stirred while allowing it to warm to room temperature. The mixture was diluted with methylene chloride (200 mL) and saturated aqueous Rochelle salt (400 mL). The mixture was vigorously stirred overnight at room temperature. The layers were separated, and the aqueous portion was extracted with methylene chloride (2x200 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated to an oil. Silica chromatography (45% diethyl ether in petroleum ether) provided the intended alcohol **E7** as a yellow oil (8.45g, 72%). **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 7.2-7.4 (m, 5H), 5.49 (quartet, *J*=6.4Hz, 1H), 5.40 (dt, *J*=6,3Hz, 1H), 4.47 (d, *J*=11.2Hz, 1H), 4.44 (d, *J*=11.2Hz, 1H), 4.14 (dd, *J*=6, 3Hz, 1H), 4.15 (dd, *J*=6, 3Hz, 1H), 1.65 (t, *J*=6Hz, 1H), 1.40 (s, 6H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 202.21, 139.30, 128.28, 127.42, 127.24, 100.35, 94.06, 74.79, 65.10, 60.58, 26.96, 26.93. **IR** (KBr – neat) 3396, 2978, 2931, 2869, 1962, 1381, 1362, 1188, 1144, 1085, 1055, 874, 738, 697 cm^{-1}. **ESI-LRMS** calcd for $C_{14}H_{18}O_2$ 218.1 found $(M+Na)^+$ 241.1. **EA** calcd for $C_{14}H_{18}O_2$ C: 77.03, H: 8.31 found C: 76.88, H: 8.07.



5-(Benzyloxy)-5-methylhexa-2,3-dienyl acetate (7)
Pyridine (3.0g, 3.1 mL, 38 mmol) was added to a neat solution of alcohol **E7** (8.2g, 38 mmol) in acetic anhydride (5.9 mL, 5.8g, 58 mmol) at 0ºC. The exothermic reaction was allowed to warm to room temperature and stirred in a room temperature water bath for 18 hours. The reaction was diluted with ethyl acetate (300 mL), washed with phosphate buffer (0.5M, pH=5, 3x125 mL), brine (100 mL), dried with $MgSO_4$, filtered and concentrated to an oil. Silica chromatography (12.5% diethyl ether in petroleum ether) and *in vacuo* (0.5 torr) removal of the residual acetic anhydride provided the intended acetate **7** as a yellow oil (9.3g, 94%). **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 7.2-7.4 (m, 5H), 5.44 (dd, *J*=13, 6.4Hz, 1H), 5.38-5.41 (m, 1H), 4.62 (ddd, *J*=8.4, 6.4, 2.8Hz, 1H), 4.57 (ddd, *J*=8.0 6.4, 2.8Hz, 1H), 4.47 (d, *J*=11.2Hz, 1H), 4.43 (d, *J*=11.2Hz, 1H), 2.06 (s, 3H), 1.394 (s, 3H), 1.391 (s, 3H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 204.11, 170.68, 139.28, 128.28, 127.45, 127.23, 99.88, 89.29, 74.73, 65.16, 62.13, 26.87, 26.80, 20.90. **IR** (KBr – neat) 2979, 2934, 2866, 1966, 1743, 1454, 1379, 1227, 1188, 1146, 1086, 1056, 1028, 964, 874, 737, 697 cm^{-1}. **ESI-LRMS** calcd for $C_{16}H_{20}O_3$ 260.1 found $(M+Na)^+$ 283.1. **EA** calcd for $C_{16}H_{20}O_3$ C: 73.82, H: 7.74 found C: 73.66, H: 7.57.

III Optimization Studies of the Ligand, Precatalyst, Solvent and Additive

Figure E1: The Trost Ligands

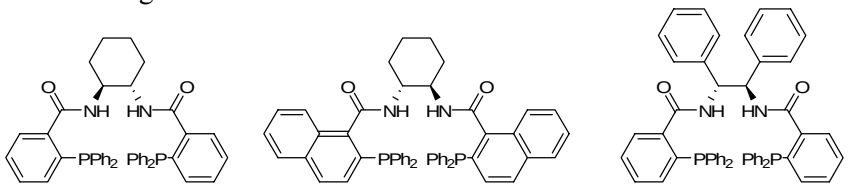
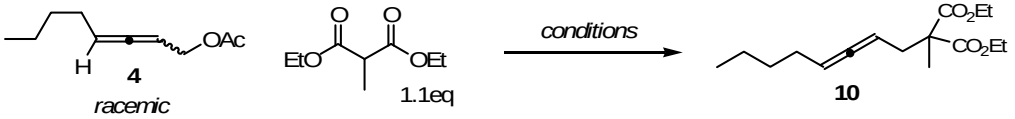


Table E1: Optimization Studies



entry	*palladium*[a]	*ligand*[b]	*additive*[c]	*solvent*[d]	*conv.*[d]	*yield*[e]	*ee*[f]
1	$(\eta^3C_3H_5PdCl)_2$	**(S,S) - 2**	*none*	THF	90%	50%	68%
2	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	*none*	THF	100%	90%	85%
3	$Pd_2dba_3CHCl_3$	**(R,R) - L_N**	*none*	THF	40%	ND	-39%
4	$Pd_2dba_3CHCl_3$	**(R,R) - L_A**	*none*	THF	0%	ND	ND
5	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	5% TBAT	THF	100%	81%	75%
6	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	2.5% THACl	THF	100%	85%	86%
7	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	5% THACl	THF	100%	85%	86-90%[g]
8	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	10% THACl	THF	100%	ND	88%
9	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	20% THACl	THF	100%	66%	71%
10	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	*none*	Tolune	100%	63%	60%
11	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	5% THACl	Tolune	100%	79%	84%
12	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	*none*	CH_2Cl_2	100%	84%	75%
13	$Pd_2dba_3CHCl_3$	**(S,S) - 2**	5% THACl	CH_2Cl_2	100%	76%	81%

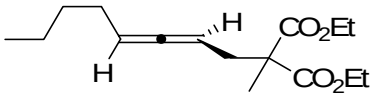
[a] 2.5 mol % palladium precatalyst to allene substrate. [b] 7.5 mol % of ligand to allene substrate. [c] percent by mole to substrate. [d] Conversion based on proton NMR with internal standard. [e] Isolated yields. [f] Enantiomeric excess determined by chiral HPLC. [g] Range of enantiomeric excesses over several reactions. Average enantiomeric excess between 86 and 87%. ND = not determined. TBAT = tetrabutylammonium triphenyldifluorosilicate. THACl = tetrahexylammonium chloride.

IV Dynamic Kinetic Asymmetric Addition of Malonates to Allenes

Typical procedure for the dynamic kinetic asymmetric addition of malonates to racemic allenes

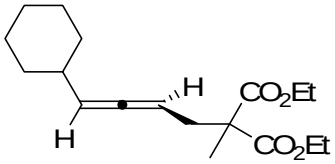
The nucleophile solution was prepared by the drop wise addition of LiHMDS (0.5M in THF, 1.1eq to allene) to a degassed and anhydrous solution of the malonate (1.1eq to allene) in THF (0.4M) at -78ºC under nitrogen followed by the slow warming to room temperature over 30 minutes. The deep orange catalyst solution was prepared by stirring for 15 minutes under nitrogen a degassed and anhydrous solution of $Pd_2dba_3CHCl_3$ (2.5% by mole to allene), (S,S) **2** (7.5% by mole to allene) and tetrahexylammonium chloride (5% by mole to allene) in THF (0.4M). After the addition of the allene substrate to the catalyst solution, the nucleophile solution was cannulated into the catalyst-allene solution under nitrogen at room temperature. The reaction was stirred in a nitrogen sealed vessel for 1 day at room temperature. Concentration *in vacuo* of the heterogeneous solution onto silica and direct silica chromatography provided the intended DYKAT product.

(S)-(+)-Diethyl 2-methyl-2-(octa-2,3-dienyl)malonate (10)



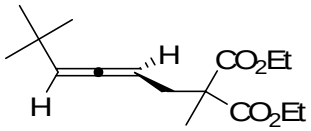
Chiral allene **10** was isolated as a clear oil (85%) after silica chromatography (5% diethyl ether in petroleum ether). $[\alpha]_D^{25.7}$ = +50º (c=1.7 in EtOH at 86% ee). Chiralpak AD **HPLC** (0.5% IPA in heptane, 1ml/min, 230nm) shows 86% ee in favor of 6.34 over 5.88min. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.08 (ddt, *J*=15.6, 9.2, 2.4Hz, 1H), 4.92-4.97 (m, 1H), 4.20 (quartet, *J*=7.2Hz, 4H), 2.60 (ddd, *J*=14,8,2.4Hz, 1H), 2.55 (ddd, *J*=14,8,2.4Hz, 1H), 1.95-2.02 (m, 2H), 1.43 (s, 3H), 1.32-1.44 (m, 4H), 1.25 (t, *J*=7.2Hz, 6H), 0.89 (t, *J*=7.6Hz, 3H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 205.85, 171.91, 171.83, 90.76, 85.05, 61.21, 61.19, 53.76, 35.85, 31.28, 28.42, 22.10, 19.56, 14.03, 13.87. **IR** (KBr – neat) 2985, 2980, 2934, 2874, 1963, 1732, 1434, 1378, 1366, 1298, 1271, 1241, 1190, 1107, 1024, 862 cm^{-1}. **EI-HRMS** calcd for $C_{16}H_{26}O_4$ 282.1831 found 282.1833.

(S)-(+)-Diethyl 2-(4-cyclohexylbuta-2,3-dienyl)-2-methylmalonate (11)



Chiral allene **11** was isolated as a clear oil (87%) after silica chromatography (5% diethyl ether in petroleum ether). $[\alpha]_D^{24.3}$ = +58º (c=1.2 in $CHCl_3$, 90% ee). Chiralpak AD **HPLC** (0.5% IPA in heptane, 1ml/min, 230nm) shows 90% ee in favor of 8.87 min over 8.27 min. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.06 (tt, *J*=6, 2.4Hz, 1H), 4.94-5.00 (m, 1H), 4.18 (quartet, *J*=7.2Hz, 4H), 2.54 (ddd, *J*=13.6, 7.6, 2.0Hz, 1H), 2.60 (ddd, *J*=13.6, 7.6, 2.0Hz, 1H), 1.90-2.0 (m, 1H), 1.60-1.78 (m, 5H), 1.43 (s, 3H), 1.25 (t, *J*=7.2Hz, 6H), 1.0-1.30 (m, 5H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 204.68, 171.86, 96.83, 86.01, 61.23, 61.20, 53.76, 37.10, 36.05, 33.00, 32.98, 26.09, 25.96, 19.67, 14.02. **IR** (KBr – neat) 2983, 2926, 2852, 1962, 1733, 1449, 1378, 1366, 1301, 1241, 1191, 1106, 1025, 891, 862, 731 cm^{-1}. **EI-HRMS** calcd for $C_{18}H_{28}O_4$ 308.1988 found 308.1990. **EA** calcd for $C_{18}H_{28}O_4$ C: 70.10, H: 9.11 found C: 70.06, H: 9.11.

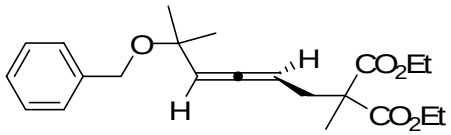
(S)-(+)-Diethyl 2-methyl-2-(5,5-dimethylhexa-2,3-dienyl)malonate (12)



Chiral allene **12** was isolated as a clear oil (89%) after silica chromatography (7.5% diethyl ether in petroleum ether). $[\alpha]_D^{25}$ = +47.9º (c=1.18 in $CHCl_3$, 89% ee). Chiralpak AD **HPLC** (0.5% IPA in heptane, 1ml/min, 210nm) shows 89% ee in favor of 7.15 over 6.76 minutes. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.09 (dt, *J*=6, 2.4Hz, 1H), 5.01 (quartet, *J*=7.6Hz, 1H), 4.18 (quartet, *J*=7.2Hz, 4H), 2.61 (ddd, *J*=14, 7.6, 2.8Hz, 1H), 2.55 (ddd, *J*=14, 7.6, 2.8Hz, 1H), 1.44 (s, 3H), 1.25 (t, *J*=7.2Hz, 6H), 1.02 (s, 9H).). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 203.09, 171.96, 171.85, 102.78, 87.02, 61.24, 61.21, 53.74, 36.18, 31.67, 30.11, 19.73, 14.03, 14.02. **IR** (KBr – neat) 2963, 2905, 2868, 1962, 1733, 1462, 1399, 1378, 1364, 1298, 1276, 1242, 1190,

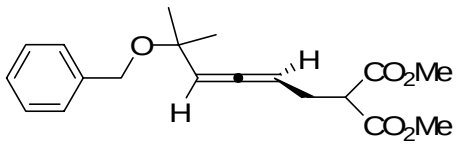
1106, 1025, 861 cm^{-1}. **EI-HRMS** calcd for $C_{16}H_{26}O_4$ 282.1831 found 282.1829. **EA** calcd for $C_{16}H_{26}O_4$ C: 68.06, H: 9.82 found C: 67.91, H: 9.61.

(S)-(+)-Diethyl 2-(5-(benzyloxy)-5-methylhexa-2,3-dienyl)-2-methylmalonate (13)



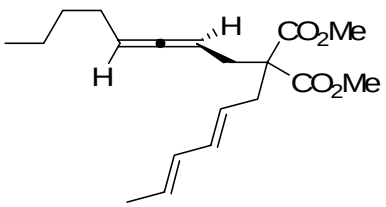
Chiral allene **13** was isolated as a clear oil (95%) after silica chromatography (10% diethyl ether in petroleum ether). $[\alpha]_D^{25}$ = +44.2º (c=1.46 in $CHCl_3$, 91% ee). Chiralpak AS **HPLC** (1% IPA in heptane, 1ml/min, 220nm) shows 91% ee in favor of 6.26 over 5.18 minutes. **^{1}H NMR** ($CDCl_3$ 300 MHz) δ 7.20-7.40 (m, 5H), 5.12-5.24 (m, 2H), 4.42 (s, 2H), 4.19 (quartet, *J*=6.9Hz, 4H), 2.61-2.65 (m, 2H), 1.45 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H), 1.25 (dt, *J*=1.2, 6.9Hz, 6H). **^{13}C NMR** ($CDCl_3$ 75 MHz) δ 204.76, 171.74, 171.66, 139.43, 128.25, 127.46, 127.17, 97.67, 87.76, 74.84, 65.08, 61.33, 53.64, 35.84, 26.97, 26.82, 19.78, 14.03. **IR** (KBr – neat) 2980, 2937, 2872, 1964, 1732, 1454, 1379, 1364, 1298, 1272, 1242, 1190, 1106, 1060, 1028, 861, 737. **EI-HRMS** calcd for $C_{22}H_{30}O_5$ 374.2093 found 374.2094.

(S)-(+)-Dimethyl 2-(5-(benzyloxy)-5-methylhexa-2,3-dienyl)malonate (14)



Chiral allene **14** was isolated as a clear oil (63 %) after silica chromatography (20% diethyl ether in petroleum ether), but 3 equivalents of dimethyl malonate was employed for the DYKAT reaction. $[\alpha]_D^{25}$ = +46º (c=0.78 in $CHCl_3$, 86% ee). Chiralpak AS **HPLC** (1% IPA in heptane, 1ml/min, 210nm) shows 86% ee in favor of 12.26 over 10.87 minutes. **^{1}H NMR** ($CDCl_3$ 500 MHz) δ 7.24-7.34 (m, 5H), 5.27-5.30 (m, 2H), 4.43 (s, 2H), 3.74 (s, 3H), 3.74 (s, 3H), 3.51 (t, *J*=7Hz, 1H), 2.65 (ddd, *J*=7.5, 6.5, 3.5Hz, 2H), 1.36 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** ($CDCl_3$ 125MHz) δ 203.09, 169.15, 169.10, 139.40, 128.22, 127.41, 127.15, 99.55, 89.75, 74.74, 65.07, 52.60, 52.58, 51.15, 28.05, 26.94, 26.53. **IR** (KBr – neat) 2978, 2955, 2865, 1964, 1738, 1454, 1436, 1380, 1361, 1341, 1233, 1190, 1149, 1086, 1059, 878, 738, 698 cm^{-1}. **EI-HRMS** calcd for $C_{19}H_{24}O_5$ 332.1624, $(M\text{-}CH_3)^+$ calcd 317.1389 found 317.1401. **ESI-LRMS** calcd for $C_{19}H_{24}O_5$ 332.2 found $(M+Na)^+$ 355.1.

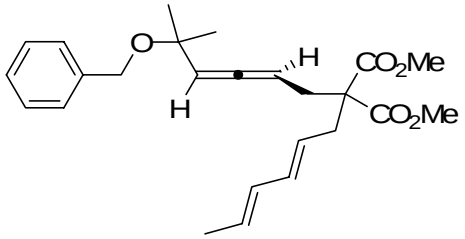
(S)-(+)- Dimethyl 2-((2E,4E)-hexa-2,4-dienyl)-2-(octa-2,3-dienyl)malonate (15)



Chiral allene **15** was isolated as a clear oil (74%) after silica chromatography (7.5% diethyl ether in petroleum ether). $[\alpha]_D^{25}$ = +49.3º (c=1.13 in $CHCl_3$, 87 %ee). Chiralpak OD-H

HPLC (0.5% IPA in Heptane, 1ml/min, 220nm) shows 87% ee in favor 9.63 over 10.61 minutes. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.95-6.07 (m, 2H), 5.60 (dq, *J*=14.4, 6.8Hz, 1H), 5.33 (dt, *J*=14.4, 7.6Hz, 1H), 5.04-5.10 (m, 1H), 4.84-4.91 (m, 1H), 3.70 (s, 6H), 2.68 (d, *J*=8.0Hz, 2H), 2.57 (dd, *J*=7.6, 1.6Hz, 2H), 1.95-1.98 (m, 2H), 1.72 (d, *J*=6.4Hz, 3H), 1.32-1.39 (m, 4H), 0.89 (t, *J*=6.8Hz, 3H). **^{13}C NMR** ($CDCl_3$ 100 MHz) δ 205.77, 171.18, 134.62, 131.15, 128.65, 124.21, 90.95, 84.58, 58.09, 52.39, 52.35, 35.57, 32.59, 31.36, 28.50, 22.13, 18.01, 13.88. **IR** (KBr – neat) 3019, 2956, 2931, 2857, 1963, 1738, 1437, 1285, 1235, 1203, 1157, 1076, 1028, 990, 875, 697 cm^{-1}. **EI-HRMS** calcd for $C_{19}H_{28}O_4$ 320.1988 found 320.1974. **EA** calcd for $C_{19}H_{28}O_4$ C: 71.22, H: 8.81 found C:71.00, H: 8.69.

(S)-(+)-Dimethyl 2-((S)-5-(benzyloxy)-5-methylhexa-2,3-dienyl)-2-((2E,4E)-hexa-2,4-dienyl)malonate (16)



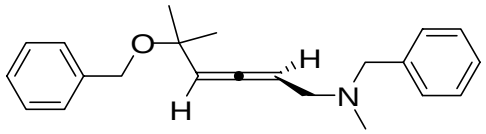
Chiral allene **16** was isolated as a clear oil (97%) after silica chromatography (15% diethyl ether in petroleum ether). **$[\alpha]_D^{25}$** = +49.2º (c=1.47 in $CHCl_3$, 90% ee). Chiralpak OD-H **HPLC** (1% IPA in heptane, 1ml/min, 220nm) shows 90% ee in favor of 11.08 over 11.92 minutes. . **^{1}H NMR** ($CDCl_3$ 500 MHz) δ 7.20-7.40 (m, 5H), 5.94-6.08 (m, 2H), 5.60 (qt, *J*=14.5, 7Hz, 1H), 5.32 (dt, *J*=15,7.6Hz, 1H), 5.21-5.22 (m, 1H), 5.09 (quartet, *J*=7Hz, 1H), 4.41 (s, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 2.70 (d, *J*=7.7Hz, 2H), 2.63-2.66 (m, 2H), 1.70 (d, *J*=7Hz, 3H), 1.36 (s, 6H). **^{13}C NMR** ($CDCl_3$ 125MHz) δ 204.70, 171.07, 171.02, 139.41, 134.83, 131.04, 128.93, 128.26, 127.46, 127.17, 123.85, 97.82, 87.30, 74.78, 65.10, 57.91, 52.51, 52.46, 35.75, 32.63, 26.87, 26.85, 17.99. **IR** (KBr – neat) 3021, 2977, 2983, 2932, 2857, 1963, 1736, 1437, 1380, 1362, 1322, 1277, 1236, 1203, 1147, 1082, 1061, 1028, 991, 878, 737, 698 cm^{-1}. **EI-HRMS** calcd for $C_{25}H_{32}O_5$ 412.2250 found 412.2254. **EA** calcd for $C_{25}H_{32}O_5$ C: 72.79 H: 7.82 found C: 73.00, H: 7.73.

V. Dynamic Kinetic Asymmetric Addition of Amines to Allenes

***Typical procedure for the dynamic kinetic asymmetric addition of amines to racemic allenes with 1.1 eq of amine and 3 eq of Cs_2CO_3* (Condition A)**

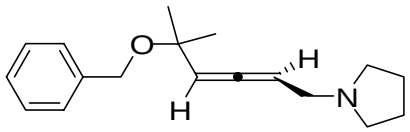
The catalyst solution was prepared by stirring for 15 minutes under nitrogen a degassed and anhydrous solution of Pd_2dba_3 $CHCl_3$ (2.5% by mole to allene), (S,S) **2** (7.5% by mole to allene) and tetrahexylammonium chloride (5% by mole to allene) in degassed and anhydrous THF (0.2M to allene). This solution was cannulated into a nitrogen flushed test tube of Cs_2CO_3 (3 eq to allene). Allene **7** followed by the amine (1.1 eq to allene) were added to the above heterogeneous catalyst solution. The heterogeneous reaction was stirred in a nitrogen sealed vessel for 1 day at room temperature. Concentration *in vacuo* of the heterogeneous solution and direct silica chromatography provided the intended addition product.

(S)-(+)- N-Benzyl-5-(benzyloxy)-N,5-dimethylhexa-2,3-dien-1-amine (19)



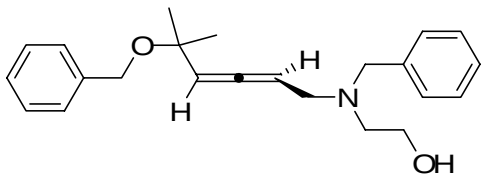
Chiral allene **19** was isolated as a clear oil (98%) after basic silica chromatography (25% diethyl ether in petroleum ether). $[\alpha]_D^{25}$ = +37.6º (c=1.35 in $CHCl_3$, 95% ee). Chiralpak OD-H **HPLC** (10% IPA in heptane, 1ml/min, 220nm) shows 95% ee in favor of 5.93 over 17.78 minutes. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 7.30-7.50 (m, 10H), 5.36 (quartet, *J*=6.8Hz, 1H), 5.26 (dt, *J*=6,2.4Hz, 1H), 4.54 (d, *J*=11.2Hz, 1H), 4.42 (d, *J*=11.2Hz, 1H), 3.57 (d, *J*=13.2Hz, 1H), 3.52 (d, *J*=13.2Hz, 1H), 3.15 (ddd, *J*=13.2, 6.8, 2.8Hz, 1H), 3.09 (ddd, *J*=13.2, 6.8, 2Hz, 1H), 2.26 (s, 3H), 1.38 (s, 6H). **^{13}C NMR** ($CDCl_3$ 100MHz) δ 204.05, 139.49, 138.82, 129.02, 128.26, 128.23, 127.48, 127.17, 127.01, 97.83, 90.32, 74.95, 65.06, 61.27, 56.62, 41.94, 27.13, 26.86. **IR** (KBr – neat) 3063, 3029, 2977, 2930, 2840, 2785, 1961, 1496, 1454, 1379, 1362, 1338, 1238, 1188, 1145, 1086, 1060, 1028, 877, 734, 697 cm^{-1}. **EA** calcd for $C_{22}H_{27}NO$ C: 82.20 H: 8.47 found C: 82.16, H: 8.58.

(S)-(+)-1-(5-(Benzyloxy)-5-methylhexa-2,3-dienyl)pyrrolidine (20)



Chiral allene **20** was isolated as a clear oil (86%) after basic silica chromatography (0.5% methanol, 0.5% (30% NH_3 in water) in diethyl ether). $[\alpha]_D^{25}$ = +39º (c=0.83 in $CHCl_3$, 89% ee). Chiralpak OD-H **HPLC** (10% IPA, 0.5% Et_2N in heptane, 1ml/min, 230nm) shows 89% ee in favor of 4.42 over 5.20 minutes. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 7.20-7.49 (m, 5H), 5.38 (quartet, *J*=7.2Hz, 1H), 5.25 (dt, *J*=6, 2.8Hz, 1H), 4.47 (d, *J*=11.2Hz, 1H), 4.43 (d, *J*=11.5Hz, 1H), 3.25 (ddd, *J*=12.8, 6.8, 2.8Hz, 1H), 3.08 (ddd, *J*=12.8, 6.8, 2.8Hz, 1H), 2.52-2.59 (m, 4H), 1.78-1.81 (m, 4H), 1.39 (s, 6H). **^{13}C NMR** ($CDCl_3$ 100MHz) δ 203.54, 139.47, 128.23, 127.48, 127.15, 97.87, 91.33, 74.95, 65.05, 55.25, 53.83, 30.26, 27.10, 26.81, 23.50. **IR** (KBr – neat) 2973, 2929, 2874, 2785, 1963, 1455, 1379, 1361, 1345, 1318, 1237, 1188, 1144, 1086, 1060, 1028, 873, 733, 696 cm^{-1}. **EI-HRMS** calcd for $C_{18}H_{25}NO$ 271.1936 found $[M-H]^+$ calcd 270.1858 found 270.1854, $[M+H]^+$ calcd 272.2014 found 272.2020.

(S)-(+)-2-(N-benzyl-N-(5-(benzyloxy)-5-methylhexa-2,3-dienyl)amino)ethanol (21)



Chiral allene **21** was isolated as a clear oil (89%) after basic silica chromatography (30% ethyl acetate in petroleum ether) but the reaction was stirred for 1 day at room temperature and at 60ºC for another day. $[\alpha]_D^{22.6}$ = +35.7º (c=0.624 in $CHCl_3$, 90% ee). Chiralpak OD-H **HPLC** (10% IPA, 0.5% Et_2N in heptane, 1ml/min, 235nm) shows 90% ee in favor of 10.10 over 13.40

minutes. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 7.26-7.33 (m, 10H), 5.27-5.35 (m, 2H), 4.42 (s, 2H), 3.70 (d, *J*=13.6Hz, 1H), 3.67 (d, *J*=13.6Hz, 1H), 3.60 (t, *J*=5.2Hz, 2H), 3.23 (ddd, *J*=6.7, 2.5, 1.5Hz, 2H), 2.73 (t, *J*=5.6Hz, 2H), 2.50 (bs, 1H), 1.38 (s, 6H). **^{13}C NMR** ($CDCl_3$ 100MHz) δ 204.17, 139.37, 138.51, 128.92, 128.42, 128.27, 127.45, 127.27, 127.20, 98.20, 89.11, 74.85, 65.06, 58.31, 57.57, 54.40, 52.35, 26.99, 26.96. **IR** (KBr – neat) 3442, 3029, 2976, 2930, 1959, 1496, 1454, 1380, 1362, 1329, 1238, 1188, 1144, 1084, 1059, 1028, 875, 733, 697 cm^{-1}. **EI-HRMS** calcd for $C_{23}H_{29}NO_2$ 351.2198 found $[M-H]^+$ calcd 350.2120 found 350.2124.

***Typical procedure for the dynamic kinetic asymmetric addition of amines to racemic allenes with 2.2 eq of amine* (Condition B)**

The catalyst solution was prepared by stirring for 15 minutes under nitrogen a degassed and anhydrous solution of Pd_2dba_3 $CHCl_3$ (2.5% by mole to allene), (S,S) **2** (7.5% by mole to allene) and tetrahexylammonium chloride (5% by mole to allene) in anhydrous and degassed THF (0.2M to allene). Allene **7** followed by the amine (2.2 eq to allene) were added to the above homogeneous catalyst solution. The reaction was stirred in a nitrogen sealed vessel for 18 hours at room temperature. Concentration *in vacuo* of the solution and direct silica chromatography provided the intended addition product.

(R)-(-)-N-Benzyl-5-(benzyloxy)-N,5-dimethylhexa-2,3-dien-1-amine (19)

Chiral allene **19** was isolated as a clear oil (91%) after basic silica chromatography (25% diethyl ether in petroleum ether). $[\alpha]_D^{23.7}$ = -24.6º (c=1.24 in $CHCl_3$, 65% ee). Chiralpak OD-H **HPLC** (10% IPA in heptane, 1ml/min, 220nm) shows 65% ee favoring 15.11 over 5.13 minutes.

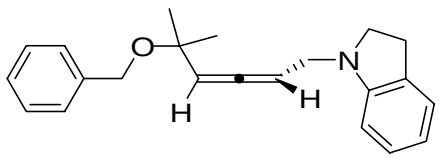
(R)-(-)-1-(5-(Benzyloxy)-5-methylhexa-2,3-dienyl)pyrrolidine (20)

Chiral allene **20** was isolated as a clear oil (90%) after basic silica chromatography (0.5% methanol, 0.5% (30% NH_3 in water) in diethyl ether). $[\alpha]_D^{22}$ = - 9.5º (c=0.90 in $CHCl_3$, 28% ee). Chiralpak OD-H **HPLC** (10% IPA, 0.5% Et_2N in heptane, 1ml/min, 230nm) shows 28% ee in favor of 5.55 over 4.77 minutes.

(R)-(-)-2-(N-benzyl-N-(5-(benzyloxy)-5-methylhexa-2,3-dienyl)amino)ethanol (21)

Chiral allene **21** was isolated as a clear oil (85%) after basic silica chromatography (30% ethyl acetate in petroleum ether) but the reaction was stirred for 1 day 60ºC. $[\alpha]_D^{23}$ = - 15º (c=0.52 in $CHCl_3$, 35% ee). Chiralpak OD-H **HPLC** (10% IPA, 0.5% Et_2N in heptane, 1ml/min, 235nm) shows 35% ee in favor of 14.28 over 10.89 minutes.

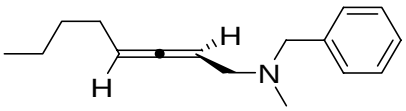
(R)-(-)-1-(5-(Benzyloxy)-5-methylhexa-2,3-dienyl)indoline (22) (Condition C)



The catalyst solution was prepared stirring a mixture of $Pd_2dba_3CHCl_3$ (5mg, 5μmol), (S,S)-**2** (10mg, 14μmol), and tetrahexylammonium chloride (4mg, 10μmol) in anhydrous and degassed THF (2ml) for 15 minutes under nitrogen at room temperature to afford a deep orange

homogeneous solution. Allene substrate **7** (50μL, 50mg, 0.192mmol) followed by indoline (24μL, 26mg, 0.21mmol) were added to the above catalyst solution under nitrogen. The resulting yellow homogeneous solution was stirred at room temperature in a nitrogen seal test tube for 1 day at room temperature and 1 day at 60ºC. The reaction was directly loaded onto a silica column and chromatographed (10% diethyl ether in petroleum ether) to provide the intended allene **22** as a clear and colorless oil (53.6mg, 88%) which gradually turns orange upon standing in air. $[\alpha]_D^{24.4}$ = - 19º (c=0.86 in EtOH, 84%ee). Chiralpak OD-H **HPLC** (1% IPA in heptane, 1ml/min, 254nm) shows 84% ee in favor of 22.86 over 17.25 minutes. **^{1}H NMR** (C_6D_6 400 MHz) δ 7.36-7.38 (m, 2H), 7.18-7.24 (m, 2H), 7.07-7.16 (m, 2H), 6.99-7.02 (m, 1H), 6.74 (dt, *J*=0.8, 7.2Hz, 1H), 6.44 (d, *J*=8.0Hz, 1H), 5.23 (td, *J*=2.8, 6.4Hz, 1H), 5.12 (quartet, *J*=6.0Hz, 1H), 4.43 (d, *J*=11.6Hz, 1H), 4.39 (d, *J*=11.6Hz, 1H), 3.61 (ddd, *J*=14.8, 6, 2.8Hz, 1H), 3.48 (ddd, *J*=14.8, 6.4, 2.4Hz, 1H), 3.15 (quartet, *J*=8.4Hz, 1H), 3.04 (quartet, *J*=8.4Hz, 1H), 2.65 (t, *J*=8.4Hz, 2H), 1.33 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** ($CDCl_3$ 100MHz) δ 203.68, 139.44, 130.24, 128.25, 127.43, 127.23, 127.17, 124.52, 117.81, 107.40, 98.85, 89.09, 74.88, 65.04, 52.69, 47.89, 28.47, 27.06, 26.76. **IR** (KBr – neat) 3028, 2976, 2926, 2849, 1961, 1607, 1607, 1488, 1471, 1458, 1439, 1379, 1361, 1330, 1307, 1269, 1239, 1187, 1144, 1085, 1059, 1028, 872, 743, 714, 696 cm^{-1}. **EI-HRMS** calcd for $C_{22}H_{25}NO$ 319.1936 found 319.1930. **EA** calcd for $C_{22}H_{25}NO$ C: 82.72, H: 7.89; found C: 82.90, H: 7.69.

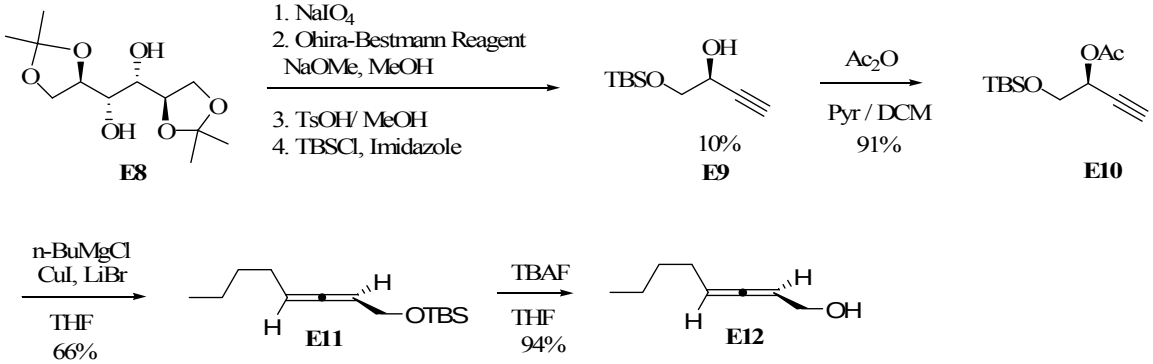
(S)-(+)-N-benzyl-N-methylocta-2,3-dien-1-amine (23) (Condition A)



An anhydrous and degassed suspension of $Pd_2dba_3CHCl_3$ (12.4mg, 12 μmol), (S,S) **2** (25mg, 36 μmol), and tetrahexylammonium chloride (9.4mg, 25 μmol) in degassed and anhydrous THF (6 mL) was stirred under nitrogen at room temperature for 20 minutes to afford the catalyst solution as an orange homogenous solution. This catalyst solution was cannulated to a test tube of Cs_2CO_3 (156mg, 0.48 mmol) under nitrogen. Allene acetate **4** (30 μL, 27mg, 0.16 mmol) followed by *N*-methyl-*N*-benzylamine (23 μL, 22mg, 0.18 mmol) were added to the catalyst and base suspension. The reaction was stirred in a nitrogen sealed test tube at room temperature for 24 hours. TLC at 24 hours showed complete conversion. The reaction was directly chromatographed through silica (pre-washed with methylene chloride and 5% triethylamine, eluted with 25% diethyl ether in petroleum ether) to afford the intended amine **23** contaminated with dba (dibenzylideneacetone). The mixture was purified by silica chromatography through a pipette column eluting 5% AcOH and 25 % diethyl ether in petroleum ether to remove the dba then 5% triethylamine and 25% diethyl ether in petroleum ether to elute the amine product contaminated with ammonium salts. The mixture was suspended in diethyl ether (10 mL), washed with 0.5M phosphate buffer pH=5 (2x2 mL), dried with Na_2SO_4, filtered and concentrated to the intended amine (S)-(+)-**23** as a yellow oil (20mg, 56%). $[\alpha]_D^{23}$ = +58º (c=0.99 in $CHCl_3$, ~90% +/- 10% ee). Enantiomers from a racemic sample are not separable by Chiralcel OB-H, OC, OD-H, OJ and Chiralpak AD and AS HPLC. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 7.22-7.32 (m, 5H), 5.10-5.20 (m, 2H), 3.56 (d, *J*=13Hz, 1H), 3.52 (d, *J*=13Hz, 1H), 3.09 (ddd, *J*=13, 7, 3Hz, 1H), 3.04 (ddd, *J*=13, 7, 2Hz, 1H), 2.24 (s, 3H), 2.03 (dd, *J*=7, 3Hz, 1H), 1.99 (dd, *J*=7, 3Hz, 1H), 1.30-1.42 (m, 4H), 0.89 (t, *J*=7Hz, 3H). **^{13}C NMR** ($CDCl_3$ 100MHz) δ 204.20, 138.97, 129.12, 128.19, 126.92, 90.97, 87.59, 61.03, 56.80, 41.81, 31.33, 28.46, 22.11, 13.90. **IR** (KBr – neat) 3027, 2957, 2927, 2872, 2783, 1961, 1494, 1454, 1365, 1131, 1021, 860, 738, 698 cm^{-1}. **EI-HRMS** calcd for $C_{16}H_{23}N$ 229.1830 found 229.1827.

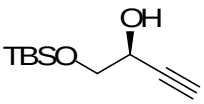
(S)-(+)-**23**, $[\alpha]_D^{23}$ = +38º (c=1.1 in $CHCl_3$), derived from alcohol (S)-(+)-**E12** (74% ee) has also a 74% ee. Amine (S)-(+)-**23** furnished from the DYKAT has an optical rotation of $[\alpha]_D^{23}$ = +58º (c=0.99 in $CHCl_3$) and considering the error in relation to determining optical purity from optical rotation, the ee of amine **23** from the DYKAT is ~90 +/- 10%.

VI. Determination of Absolute Stereochemistry



Scheme E1: Synthesis of (S)-(+)-**E12**

*Synthesis of alcohol (S)-(+)-**E12***



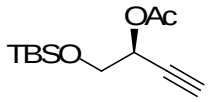
(S)-(+)-1-(*tert*-butyldimethylsilyloxy)-3-butyn-2-ol (E9)

Alcohol **E9** was prepared by a modified synthesis published by Gooding *et. al.*[6] (R)-2,2-Dimethyl-1,3-dioxolane-4-carbaldehyde was prepared from 1,2:5,6-di-*O*-isopropylidene-D-mannitol **E8** by the procedure published by Jackson.[7] Dimethyl(acetyldiazomethyl) phosphonate (4.0 g, 21 mmol) was added dropwise to a homogeneous solution of NaOMe (1.1g, 21mmol) in anhydrous THF (100 mL) and methanol (10 mL) at -78ºC. After stirring the resulting yellow solution for 5 minutes, (R)-2,2-Dimethyl-1,3-dioxolane-4-carbaldehyde (2.5g, 19 mmol) in anhydrous THF (50 mL) was cannulated into the above diazomethyl phosphonate solution at -78ºC. After 15 minutes, the reaction was allowed to slowly warm to room temperature, and after another 15 minutes, all starting aldehyde was consumed by TLC. The reaction was diluted with diethyl ether (400 mL), washed with water (3x250 mL), brine (100 mL), dried with $MgSO_4$, and filtered. To the organic filtrate was added methanol (400 mL) and TsOH-H_2O (5.4 g, 28 mmol). The homogeneous solution was stirred at room temperature for 13 hours at which point all starting material was consumed by TLC. The reaction was quenched with triethyl amine (8 mL, 57 mmol) and concentrated to an oily solid. The material was suspended in diethyl ether (500 mL), dried with $MgSO_4$, filtered and concentrated to a tan oil. *tert*-Butyldimethylsilyl chloride (2.17 g, 14 mmol) in anhydrous methylene chloride (75 mL) was added dropwise to an anhydrous solution of all of the crude diol from above and imidazole (2.01 g, 30 mmol) in methylene chloride (50 mL) at 0ºC under nitrogen. The reaction was allowed to warm to room temperature, and after 1 hour all of the starting diol was consumed by TLC. The reaction was diluted with diethyl ether (100 mL), washed with 0.5M phosphate buffer pH=5 (3x50 mL), brine (50 mL), dried with $MgSO_4$, filtered and concentrated to an oil. Silica chromatography provided the bis-TBS protected diol (1.09g, 18%) and the intended mono-TBS protected diol **E9:** (360mg, 10%) as a tan oil. **E9** $[\alpha]_D^{23.4}$ =

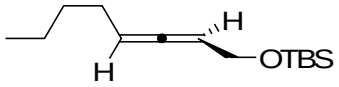
[6] Gooding, O.W.; Beard, C.C.; Jackson, D.Y.; Wren, D.L.; Cooper,G.F. *J. Org. Chem.* **1991**, *56*, 1083-1088.

[7] Jackson, D.Y. *Synth. Commun.* **1988**, *18*, 337-341.

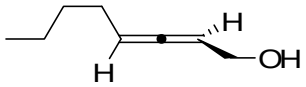
+16º (c=1.1 in $CHCl_3$, ee not determined). **^{1}H NMR** ($CDCl_3$ 500 MHz) δ 4.40-4.44 (m, 1H), 3.81 (dd, *J*=10, 4Hz, 1H), 3.69 (dd, *J*=10, 6.5Hz, 1H), 2.67 (d, *J*=5Hz, 1H), 2.45 (d, *J*=2.5Hz, 1H), 0.93 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H). **^{13}C NMR** ($CDCl_3$ 125MHz) δ 81.82, 73.44, 66.74, 62.87, 25.81, 18.31, -5.37. **IR** (KBr – neat) 3424, 3313, 2957, 2931, 2886, 2859, 2119, 1472, 1390, 1362, 1313, 1257, 1123, 1085, 1065, 1022, 1006, 962, 939, 881, 839, 780, 667, 632 cm^{-1}.



(S)-(+)-1-(*tert*-butyldimethylsilyloxy) but-3-yn-2-yl acetate (E10)
Pyridine (160 µL, 2.0 mmol) was added to a solution of alcohol **E9** (260 mg, 1.3 mmol) in acetic anhydride (3 mL) and methylene chloride (3 mL). After stirring the reaction for 3 hours, all alcohol was consumed by TLC. The reaction was diluted with diethyl ether (100 mL), washed with 0.5M phosphate buffer pH=5 (3x30 mL), $NaHCO_3$ saturated aqueous solution (3x30 mL), brine (30 mL), dried with $MgSO_4$, filtered and concentrated to an oil. Silica chromatography (10% diethyl ether in petroleum ether) provided the intended ester **E10** as a yellow oil (288mg, 91%). **$[\alpha]_D^{22.4}$** = +60.8º (c=1.24 in $CHCl_3$, ee not determined). **^{1}H NMR** ($CDCl_3$ 500 MHz) δ 5.43 (ddd, *J*=7, 5, 2Hz, 1H), 3.80-3.85 (m, 2H), 2.45 (d, *J*=2Hz, 1H), 2.11 (s, 3H), 0.89 (s, 9H), 0.081 (s, 3H), 0.078 (s, 3H). **^{13}C NMR** ($CDCl_3$ 125MHz) δ 169.83, 78.82, 74.28, 64.67, 64.59, 25.70, 20.88, 18.24, -5.36. **IR** (KBr – neat) 3312, 2956, 2931, 2886, 2859, 2126, 1749, 1473, 1464, 1372, 1228, 1134, 1089, 1050, 1029, 1007, 935, 838, 779, 668, 634 cm^{-1}. **ESI-LRMS** calcd for $C_{12}H_{22}O_3Si$ 242.1 found $[M+H]^+$ 243.1, $[M+Na]^+$ 265.1.



(S)-(+)-*tert*-Butyldimethyl(octa-2,3-dienyloxy)silane (E11)
The substitution was performed by the procedure published by Macdonald *et. al*[8] with inversion by the precedent of Gooding *et. al.*[6] and Gorins *et. al.*[9] n-BuMgCl (1.72M in THF, 4.1 mL, 7.1 mmol) was added drop wise to a suspension of CuI (1.4g, 7.1 mmol)[10] and LiBr (620 mg, 7.1 mmol)[10] in anhydrous THF (60 mL) at -78ºC under nitrogen. The mixture was stirred and allowed to slowly warm to 0ºC. After stirring for a further 15 minutes at OºC, a deep blue-purple solution was obtained. Acetate **E10** (286mg, 1.2 mmol) in anhydrous THF (10 mL) at -78ºC under nitrogen was added drop wise to the organocopper solution. The reaction was stirred at -78ºC for 2 hours; at which point no starting acetate was present by TLC. The reaction was allowed to warm to ~ -20ºC and poured into a mixture of diethyl ether (125 mL), brine (30 mL) and 0.5M phosphate buffer pH=5 (50 mL). The layeres were separated and the organic portion was washed with brine (2x50 mL). The combined aqueous layers were back extracted with diethyl ether (2x30 mL), and the combined organic portions were dried with $MgSO_4$, filtered and concentrated to an oil. Silica chromatography (2.5% diethyl ether in petroleum ether) provided the intended allene **E11** as a yellow oil (218mg, 77%). **$[\alpha]_D^{23}$** = +33º (c=1.0 in $CHCl_3$, ee not determined). **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.10-5.25 (m, 2H), 4.18 (d, *J*=3Hz, 1H), 4.16 (d, *J*=3Hz, 1H), 2.95-2.05 (m, 2H), 1.30-1.45 (m, 4H), 0.85-0.95 (m, 12H), 0.080 (s, 3H), 0.079 (s, 3H). **^{13}C NMR** ($CDCl_3$ 125MHz) δ 203.36, 92.33, 91.57, 62.12, 31.36, 28.33, 25.93, 22.13, 18.37, 13.89, -5.08. **IR** (KBr – neat) 2958, 2990, 2858, 1964, 1464, 1362, 1255, 1149, 1099, 1049, 1006, 837, 814, 776, 660 cm^{-1}.**EI-HRMS** calcd for $C_{14}H_{28}OSi$ 240.1909 found $[M+H]^+$ calcd 241.1988 found 241.1976, $[M-H]^+$ calcd 239.1831 found 239.1824.

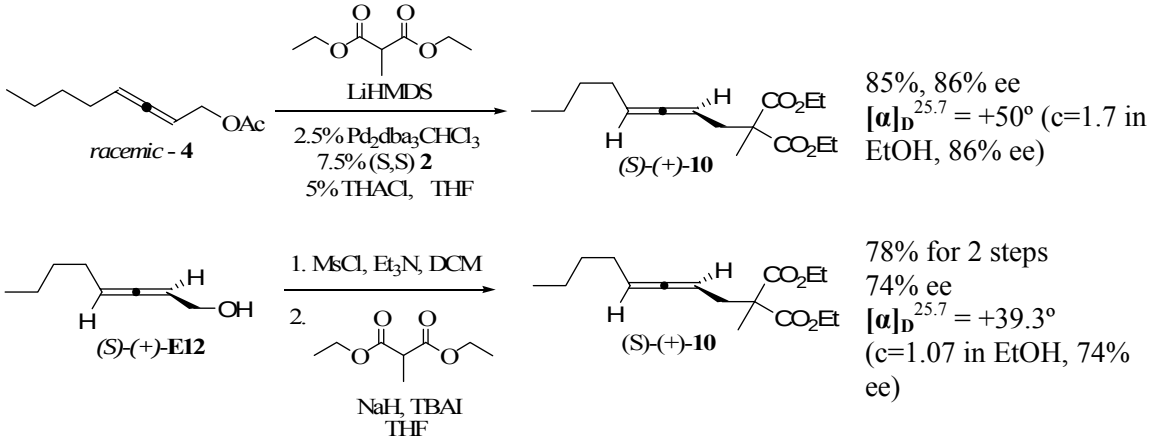


(S)-(+)-Octa-2,3-dien-1-ol (E12)

[8] Macdonald, T.L.; Reagen, D.R.; Brinkmeyer, R.S. *J. Org. Chem.* **1980**, *45*, 4740-4747.
[9] Gorins, G.; Kuhnert, L.; Johnson, C.R.; Marnett, L.J. *J. Med. Chem.* **1996**, *39*, 4871-4878.
[10] Purified by the procedure published in: Perrin, D.D.; Armarego, L.F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Elmsford, NY, 1988.

TBAF (1M in THF, 2.1 mL, 2.1 mmol) was added drop wise to a solution of silyl ether **E11** (475mg, 2.0 mmol) in THF (25 mL). The reaction was stirred at room temperature for 2 hours; at which point all starting silyl ether was consumed. The reaction was diluted with diethyl ether (100 mL), washed with water (2x30 mL), dried with $MgSO_4$, filtered and concentrated to an oil. Silica chromatography (35% diethyl ether in petroleum ether) provided the intended alcohol **E12** as a colorless oil (235mg, 94%). $[\alpha]_D^{24}$ = +64º (c=1.2 in $CHCl_3$, 74% ee).[11] **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.20-5.40 (m, 2H), 4.12 (dd, *J*=6, 3Hz, 1H), 4.11 (dd, *J*=6, 3Hz, 1H), 2.00-2.07 (m, 2H), 1.30-1.45 (m, 5H), 0.90 (t, *J*=7Hz, 3H). **^{13}C NMR** ($CDCl_3$ 100MHz) δ 200.94, 93.90, 91.67, 60.74, 31.19, 28.29, 22.07, 13.81. **IR** (KBr – neat) 3334, 2958, 2929, 2872, 1964, 1466, 1420, 1379, 1352, 1051, 1013, 867 cm^{-1}. **EI-HRMS** calcd for $C_8H_{14}O$ 126.1045 found 126.1039.

Determination of the absolute stereochemistry of the malonate products



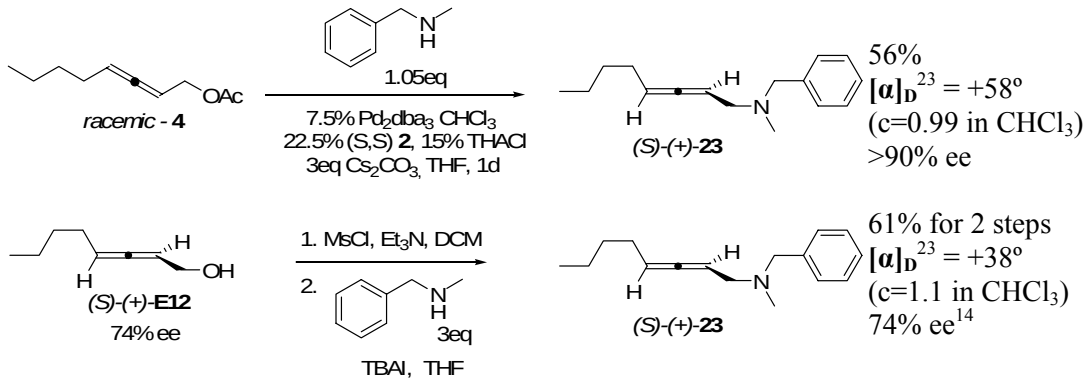
Methanesulfonyl chloride (12 µL, 17mg, 0.15 mmol) was added drop wise to an anhydrous solution of alcohol **E12** (17mg, 0.13mmol) and triethylamine (28 µL, 20mg, 0.20mmol) in methylene chloride (0.75 mL) at -20ºC under nitrogen. The reaction was stirred for 1.5 hours while allowing it to slowly warm to room temperature. The reaction was diluted with diethyl ether (10 mL), washed with 0.5M phosphate buffer pH=5 (2x2 mL), saturated aqueous $NaHCO_3$ (1x2 mL), brine (1x2 mL), dried with $MgSO_4$, filtered and concentrated to an oil. The mesylate of alcohol **E12** was obtained in reasonable purity and used in the next step without further purification. **^{1}H NMR** ($CDCl_3$ 400 MHz) δ 5.26-5.40 (m, 2H), 4.73 (d, *J*=2Hz, 1H), 4.71 (d, *J*=2Hz, 1H), 3.03 (s, 3H), 2.02-2.06 (m, 2H), 1.32-1.43 (m, 4H), 0.90 (t, *J*=7.2Hz, 3H). Diethyl methylmalonate (28 µL, 28mg, 0.16 mmol) was added to a suspension of NaH (60% dispersion in mineral oil, 6.4mg, 0.16 mmol) in anhydrous THF (3 mL). After stirring the gently bubbling mixture for 30 minutes, the above mesylate (all of the material from above) and tetrabutylammonium iodide (5mg, 14µmol) in anhydrous THF (3 mL) was added to the malonate solution. The reaction was stirred at 50ºC for 36 hours. The reaction was diluted with diethyl ether (50 mL), washed with water (2x15 mL), brine (1x15 mL), dried with $MgSO_4$, filtered and concentrated to an oil. Silica chromatography (7.5% diethyl ether in petroleum ether) provided the intended malonate (S)-(+)-**3** as a colorless oil (30mg, 78%). $[\alpha]_D^{23}$ = +35º (c=0.92 in $CHCl_3$, 74% ee). $[\alpha]_D^{23}$ = +39.3º (c=1.07 in EtOH, 74% ee). Chiralpak AD HPLC (0.5% isopropyl alcohol in heptane, 1ml/min, 220nm) showed 74% ee in favor of 7.85 over 6.82 minutes.[12] Spectroscopic properties match those listed above.

[11] Enantiomeric Excess deduced from the enantiomeric excess of the product of the malonate substitution of activated acohol **E12.**

[12] Racmic **3** Chiralpak AD HPLC (as listed above) showed enantiomers at 6.77 and 7.73 minutes.

The same product **10** derived from D-mannitol and the dynamic kinetic asymmetric additions of malonates have the same sign of the optical rotation and favor the same enantiomer by chiral HPLC. Therefore, the two compounds are the same enantiomer. Furthermore, the absolute configuration conforms to the Lowe-Brewester Rule.[13] By analogy, allene malonate products **11** to **16** possess the same absolute stereochemistry. (S)-(+)-**10** derived from (S)-(+)-**E12** has an ee of 74%, therefore the enantiomeric excess of alcohol (S)-(+)-**E12** is 74%.

Determination of the absolute stereochemistry of the amine products



*Formation of (S)-(+)-**23** from (S)-(+)-**E12***

Methanesulfonyl chloride (12 µL, 18mg, 0.15 mmol) was added drop wise to an anhydrous solution of alcohol (S)-(+)-**E12** (74% ee) (18mg, 0.14mmol) and triethylamine (30 µL, 22mg, 0.20mmol) in methylene chloride (0.75 mL) at -20ºC under nitrogen. The reaction was stirred for 1.5 hours while allowing it to slowly warm to room temperature. The reaction was diluted with diethyl ether (10 mL), washed with 0.5M phosphate buffer pH=5 (2x2 mL), saturated aqueous $NaHCO_3$ (1x2 mL), brine (1x2 mL), dried with $MgSO_4$, filtered and concentrated to an oil. The mesylate of alcohol **E12** was obtained in reasonable purity and used in the next step without further purification. ^{1}NMR corresponds to the mesylate above. *N*-Benzyl-*N*-methylamine (56 µL, 53mg, 0.43 mmol) was added to the anhydrous solution of the mesylate (all material from above) and tetrabutylammonium iodide (14 mg, 38 µmol) in THF (5 mL) under nitrogen. The reaction was stirred in a nitrogen sealed test tube at 60ºC for 18 hours. The reaction was concentrated and silica chromatography (22% diethyl ether in petroleum ether) provided the intended amine (S)-(+)-**23** as a yellow oil (20mg, 60%). $[\alpha]_D^{23}$ = +38º (c=1.1 in $CHCl_3$, 74% ee).[14] Spectroscopic properties correspond to material synthesized above.

The same product **23** derived from D-mannitol and the dynamic kinetic asymmetric additions of malonates under conditions of 1.1eq amine and 3eq Cs_2CO_3 have the same sign of the optical rotation. Therefore, the two compounds are the same enantiomer. Furthermore, the absolute configuration conforms to the Lowe-Brewester Rule.[13] By analogy, the allenamine products **19-21** under condition **A** have the same stereochemistry as (S)-(+)-**23**.

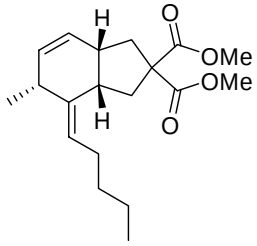
[13] (a) Lowe, G. *J. Chem. Soc. Commun.* **1965**, 411. (b) Brewster, J.H. *Topics in Stereochemistry* **1967**, *2*, 1.
[14] Enantiomeric Excess deduced from the enantiomeric excess of the starting alcohol **E12**.

VII. Rodium(I) catalyzed [4+2] cycloaddition of allenes and tethered dienes

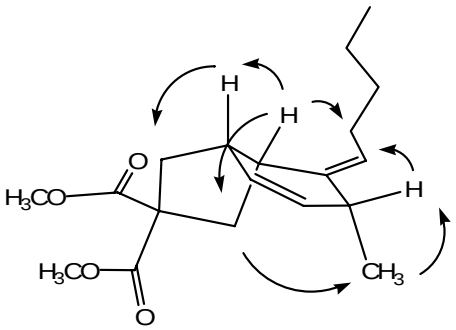
Typical Conditions for the Rhodium Catalyzed [4+2] Cycloadditions of Allenes with Dienes

The conditions and rhodium catalyst of Chung[15] and Wender[16] were used for the intramolecular [4+2] cycloaddition of allenes **15** and **16**. A degassed and anhydrous yellow solution of [(naphthalene)Rh(COD)]SbF_6 (2-3% by mole to allene) in dichloroethane (0.002M of catalyst) was cannulated into a degassed and anhydrous solution of allene in dichloroethane (0.1M of substrate) under nitrogen. The yellow homogeneous solution that gradually darkened was stirred at room temperature under nitrogen for 30 minutes. The reaction was directly chromatographed through silica gel to provide the intended product.

(3aS,6R,7Z,7aS)-(+)-Dimethyl 3,3a,7,7a-tetrahydro-6-methyl-7-pentylidene-1H-indene-2,2(6H)-dicarboxylate (24)



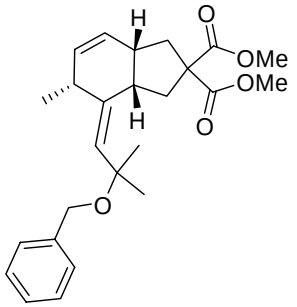
Cycloadduct **24** was isolated after silica chromatography (10% diethyl ether in petroleum ether) as a clear and colorless oil (93%). $[\alpha]_D^{25.8}$ = +21° (c=0.42 in $CHCl_3$, 87% ee). Chiralpak OD-H **HPLC** (0.5% IPA in heptane, 1ml/min, 210nm) shows 87% ee in favor of 13.64 over 7.98 minutes.[17] **^{1}H NMR** ($CDCl_3$ 500 MHz) δ 5.55 (ddt, *J*=2.5, 3.5, 10Hz, 1H), 5.41 (d, *J*=10Hz, 1H), 5.35 (t, *J*=7.5Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.18 (td, *J*=7.5, 12Hz, 1H), 2.74-2.82 (m, 1H), 2.62-2.68 (m, 1H), 2.55 (dd, *J*=8, 13.5Hz, 1H), 2.21-2.34 (m, 3H), 2.04-2.09 (m, 2H), 1.28-1.38 (m, 4H), 1.19 (d, *J*=7.5Hz, 3H), 0.90 (t, *J*=7Hz, 3H). **^{13}C NMR** ($CDCl_3$ 125MHz) δ 173.17, 172.58, 138.72, 131.41, 128.24, 127.44, 59.62, 52.76, 52.65, 40.60, 39.51, 39.16, 38.77, 35.94, 32.20, 26.67, 24.96, 22.24, 14.00. **IR** (KBr – neat) 2956, 2928, 2872, 1737, 1435, 1252, 1200, 1161, 1110, 1068 cm^{-1}. **EI-HRMS** calcd for $C_{19}H_{28}O_4$ 320.1988 found 320.1978. **EA** calcd for $C_{19}H_{28}O_4$ C: 71.22, H: 8.81 found C: 71.17, H: 8.68.



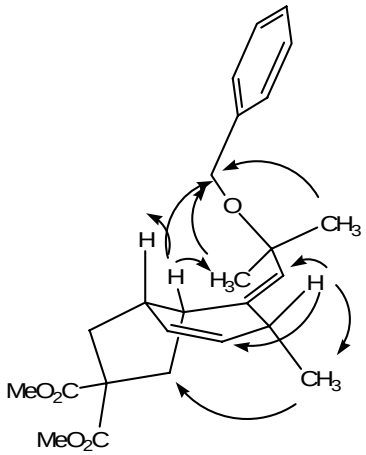
Scheme E1: Key ROSEY enhancements for diastereomer and stereochemistry assignment for compound **24**

[15] Paik, S-J.; Son, S.U.; Chung, Y.K. *Org. Lett.* **1999**, *1*(13), 2045-2047.
[16] Wender, P.A.; Williams, T.J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4550-4553.
[17] Eantiomeric excess was determined by comparison of racemic cycloadduct **23** or **24** by chiral HPLC.

(3aS,6R,7Z,7aS)-(+)-Dimethyl 7-(2-(benzyloxy)-2-methylpropylidene)-3,3a,7,7a-tetrahydro-6-methyl-1H-indene-2,2(6H)-dicarboxylate (25)



Cycloadduct **25** was isolated after silica chromography (20% diethyl ether in petroleum ether) as a clear and colorless oil (89%). $[\alpha]_D^{24.3}$ = +46º (c=0.34 in $CHCl_3$, 92% ee). Chiralpak OD-H **HPLC** (2% IPA in heptane, 1ml/min, 210nm) shows 91% ee in favor of 7.06 over 7.75 minutes.[17] **^{1}H NMR** ($CDCl_3$ 600 MHz) δ 7.29-7.32 (m, 4H), 7.20-7.23 (m, 1H), 5.52 (ddd, *J*=11, 4.2, 3Hz, 1H), 5.41 (s, 1H), 5.34 (d, *J*=10.8Hz, 1H), 4.45 (d, *J*=12Hz, 1H), 4.41 (d, *J*=12Hz, 1H), 3.81 (dt, *J*=12.6Hz, 7.2Hz, 1H), 3.69 (s, 3H), 3.67 (s, 3H), 2.76-2.79 (m, 1H), 2.44-2.48 (m, 1H), 2.37-2.43 (m, 1H), 2.33 (dd, *J*=13.2, 7.2Hz, 1H), 2.26 (dd, *J*=13.2, 1.2Hz, 1H), 1.47 (s, 3H), 1.43 (s, 3H), 1.23 (d, *J*=7.8Hz, 3H). **^{13}C NMR** ($CDCl_3$ 125MHz) δ 172.89, 172.63, 143.71, 139.85, 131.50, 131.05, 128.39, 128.17, 126.84, 126.70, 75.24, 64.44, 59.57, 52.72, 52.67, 40.36, 40.05, 38.73, 38.56, 36.63, 29.47, 28.52, 24.52. **IR** (KBr – neat) 2971, 2871, 1736, 1453, 1435, 1264, 1200, 1164, 1113, 1087, 1064, 1028, 735, 697 cm^{-1}. **EI-HRMS** calcd for $C_{25}H_{32}O_5$ 412.2250 found 412.2256. **EA** calcd for $C_{25}H_{32}O_5$ C: 72.79, H: 7.82 found C: 72.90, H: 7.67.



Scheme E2: Key ROSEY enhancements for diastereomer and stereochemistry assignment for compound **25**