Palladium-Catalyzed Decarboxylative Asymmetric Allylic Alkylation of Enol Carbonates

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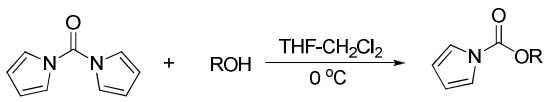
Supporting Information

Experimental

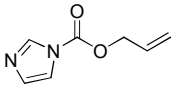
All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glasswares with magnetic stirring, unless otherwise indicated. 1,4-Dioxane for Pd-catalyzed reactions were freshly distilled from sodium. Other solvents were dried by J. C. Meyer's Solvent Purification System. Tris(dibenzylideneacetone)palladium(0) monochloroform complex, Pd_2dba_3•$CHCl_3$ was prepared by the procedure of Ibers.[1] Ligands were prepared by literature procedures.[2,3] All other reagents were used as obtained unless otherwise noted. Flash Chromatography was performed with EM Science silica gel (0.040-0.063µm grade). Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (E. Merck, DC-Plasrikfolien, kieselgel 60 F254). Proton nuclear magnetic resonance (^{1}H-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 (^{13}C-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 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 Pheonix, AZ. Chiral HPLC analyses were performed on a Themo Separation Products Spectra Series P-100 or 200 and UV100 (254 nm) using Chiralcel® columns (OD-H, OB-H, OJ, AD, As, OC, IA, IB or IC) 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.

General Procedure for the Synthesis of 5.[4]



To a clean oven-dried 250 mL flask with a magnetic stirring bar was charged with 2.43 g 1,1'-carbonyldiimidazole (15 mmol) and 100 mL of THF under nitrogen. The flask was cooled in a ice-water bath. A solution of allyl alcohol (10 mmol) in 30 mL of methylene chloride was added slowly and stirred for 2 h. Most solvent was removed *in vacuo* by

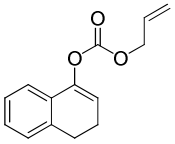
rotoevaporation and the crude product was purified by silica gel column chromatography eluting with ethyl acetate/petroleum ether.



Allyl 1*H*-pyrrole-1-carboxylate (**5a**) :

The general procedure for the synthesis of imidazolides was followed employing allyl alcohol 580 mg of (10 mmol), 1,1'-carbonyldiimidazole 2.43 g (15 mmol) in 100 mL of THF and 30 mL of DCM to produce 1.46 g product (96%) as colorless oil. Column chromatography on silica gel eluting with 1:1 ethyl acetate/petroleum ether. Spectra data matches the literature reported.[4]

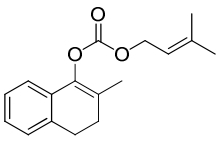
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (bs, 2H), 7.45 (bs, 1H), 7.08 (bs, 1H), 6.02 (m, 1H), 5.47 (m, 1H), 5.39 (m, 1H), 4.90 (m, 2H).



Allyl 3,4-dihydronaphthalen-1-yl carbonate (**7**):

To the solution of NaHMDS (460 mg, 2.4 mmol) in 5 mL of DME at -78 ^{o}C, 1-tetralone (292 mg, 2 mmol) was added in 2 mL of DME. The solution was stirred at -78 ^{o}C for 30 min. Meanwhile, another clean oven-dried 50 mL flask was charged with **5a** (365 mg, 2.4 mmol) in 5 mL of DME. The solution was cooled to -78 ^{o}C, to which was added boron trifluoride etherate (0.30 mL, 2.4 mmol) dropwise after stirring for 15 min., the above solution was transferred into the solution of enolate through a cannula under nitrogen and stirred for 30 min. One portion of saturated aqueous ammonium chloride (10 mL) was poured into the reaction mixture followed by diethyl ether (10 mL). The mixture was taken out from the bath and allowed to warm to ambient temperature. The organic layer was separated and the aqueous layer was extracted once with diethyl ether (10 mL). The organic layer was combined and dried over magnesium sulfate. After filtration and concentration *in vacuo* the crude material was purified by silica gel column chromatography eluting with 10% diethyl ether in petroleum ether to afford 392 mg of the title compound as a colorless oil (85%). The spectroscopic data match with the reported.[5]

R_f = 0.39 (Diethyl ether/petroleum ether 1:9); IR (film): 3068, 3024, 2941, 2890, 2836, 1760, 1659, 1489, 1452, 1428, 1360, 1293, 1244, 1225, 1186, 1013, 993, 944, 772, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.2 (m, 4H), 5.99 (m, 1H), 5.81 (t, *J* = 4.6 Hz, 1H), 5.42 (dq, *J* = 17.2 , 1.3 Hz, 1H), 5.32 (dq, *J* = 10.2, 1.3 Hz, 1H), 4.71 (dt, *J* = 5.6, 1.3 Hz, 2H), 2.86 (t, *J* = 8.2 Hz, 2H), 2.45 (m, 2H).

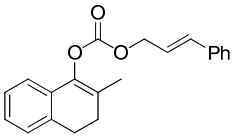


3-Methylbut-2-en-1-yl 2-methyl-3,4-dihydronaphthalen-1-yl carbonate (**9**):

The general procedure for the preparation of substituted allyl enol carbonates was followed employing 384.5 mg of 2-methyl-1-tetralone (2.4 mmol), 460 mg of NaHMDS (2.4 mmol), 360.4 mg of imidazolide (2.0 mmol) and 0.30 mL of BF_3

etherate (2.4 mmol) to yield 568 mg of product (100%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

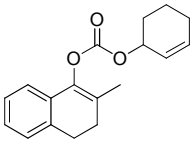
Colorless oil; R_f = 0.29 (Diethyl ether/petroleum ether 1:9); IR (film): 1760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.05 (m, 4H), 5.49-5.37 (m, 1H), 4.72 (d, *J* = 7.3 Hz, 2H), 2.85 (t, *J* = 8.1 Hz, 2H), 2.39 (ddd, *J* = 7.8, 6.3, 1.0 Hz, 2H), 1.82 (s, 3H), 1.79 (d, *J* = 0.8 Hz, 3H), 1.74 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 140.7, 140.5, 135.3, 130.9, 127.3, 127.0, 126.4, 124.4, 120.0, 117.8, 65.3, 28.9, 27.4, 25.8, 18.1, 16.6. Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40; Found: C, 75.10; H, 7.18.



2-Methyl-3,4-dihydronaphthalen-1-yl (2*E*)-3-phenylprop-2-en-1-yl carbonate (**10**):

The general procedure for the preparation of substituted allyl enol carbonates was followed employing 320 mg of 2-methyl-1-tetralone (2.0 mmol), 460 mg of NaHMDS (2.4 mmol), 548 mg of imidazolide (2.4 mmol), and 0.30 mL of BF_3 etherate (2.4 mmol) to yield 484 mg of white crystals after purification by silica gel chromatography eluting with 10% diethyl ether in petroleum ether (76%).

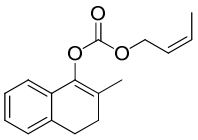
M.p. = 68-70 ^oC; R_f = 0.22 (Diethyl ether/petroleum ether 1:9); IR (film): 1769, 1749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.04 (m, 9H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.88 (dd, *J* = 6.4, 1.4 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.41 (t, *J* = 8.0 Hz, 2H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 140.8, 136.1, 135.3, 135.2, 130.9, 128.7, 128.4, 127.4, 127.2, 126.8, 126.5, 124.6, 122.2, 120.1, 69.1, 29.0, 27.5, 16.7. Anal. Calcd. for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29; Found: C, 79.00; H, 6.15.



Cyclohex-2-en-1-yl 2-methyl-3,4-dihydronaphthalen-1-yl carbonate (**11**):

The general procedure for the preparation of substituted allyl enol carbonates was followed employing 320 mg of 2-methyl-1-tetralone (2.0 mmol), 460 mg of NaHMDS (2.4 mmol), 462 mg of imidazolide (2.4 mmol) and 0.30 mL of BF_3 etherate (2.4 mmol) to yield 536 mg of product (94%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

Colorless oil; R_f = 0.22 (Diethyl ether/petroleum ether 1:9); IR (film): 1760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.07 (m, 4H), 6.02 (m, 1H), 5.83 (m, 1H), 5.18 (m, 1H), 2.86 (t, *J* = 8.1 Hz, 2H), 2.39 (dt, *J* = 8.1, 1.0 Hz, 2H), 2.20-1.60 (m, 6H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 140.8, 135.3, 133.7, 131.1, 127.3, 126.5, 124.8, 124.3, 120.1, 104.8, 72.7, 29.0, 28.2, 27.5, 24.9, 18.6, 16.7. Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09; Found: C, 75.93; H, 6.86.

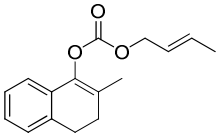


(2*Z*)-But-2-en-1-yl 2-methyl-3,4-dihydronaphthalen-1-yl carbonate (**12**):

The general procedure for the preparation of substituted allyl enol carbonates was followed employing 385 mg of 2-methyl-1-tetralone (2.4 mmol), 460 mg of NaHMDS (2.4 mmol), 479 mg of imidazolide (2.88 mmol), 0.36 mL of BF_3 etherate (2.88 mmol) to yield 550 mg of colorless oil after purification by silica gel chromatography eluting with 5% diethyl ether in petroleum ether (89%).

R_f = 0.33 (Diethyl ether/petroleum ether 1:9); IR (film): 1758 cm^{-1};

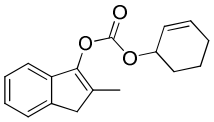
^1H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.07 (m, 4H), 5.80 (m, 1H), 5.65 (m, 1H), 4.79 (m, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.39 (dt, *J* = 8.1, 1.0 Hz, 2H), 1.82 (t, *J* = 1.0 Hz, 3H), 1.74 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 140.8, 135.3, 131.0, 130.8, 127.3, 127.1, 126.5, 124.5, 123.5, 120.1, 64.1, 29.0, 27.5, 16.6, 13.3. Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02; Found: C, 74.46; H, 6.86.



(2*E*)-But-2-en-1-yl 2-methyl-3,4-dihydronaphthalen-1-yl carbonate (**13**):

The general procedure for the preparation of substituted allyl enol carbonates was followed employing 385 mg of 2-methyl-1-tetralone (2.4 mmol), 460 mg of NaHMDS (2.4 mmol), 399 mg of imidazolide (2.4 mmol), and 0.30 mL of BF_3 etherate (2.4 mmol) to yield 595 mg of colorless oil was obtained after purification by silica gel chromatography eluting with 5% diethyl ether in petroleum ether (96%).

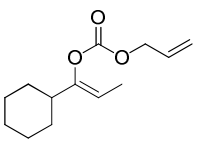
R_f = 0.32 (Diethyl ether/petroleum ether 1:9); IR (film): 1760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.07 (m, 4H), 5.89 (m, 1H), 5.67 (m, 1H), 4.64 (m, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 2.39 (dt, *J* = 8.1, 1.0 Hz, 2H), 1.82 (t, *J* = 1.0 Hz, 3H), 1.75 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 140.7, 135.3, 132.8, 131.0, 127.3, 127.1, 126.5, 124.44, 124.36, 120.1, 69.3, 29.0, 27.5, 17.9, 16.7. Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02; Found: C, 74.40; H, 6.89.



Cyclohex-2-en-1-yl 2-methyl-1*H*-inden-3-yl carbonate (**14**):

The general procedure for the preparation of substituted allyl enol carbonates was followed employing 350 mg of 2-methyl-1-indanone (2.4 mmol), 270 mg of KO^{t}Bu (2.4 mmol), 384.4 mg of imidazolide (2 mmol), and 0.28 mL of BF_3 etherate (2.2 mmol) to yield 474 mg of product was obtained as a white solid after purification by silica gel chromatography (88%).

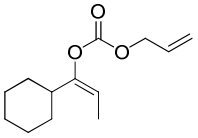
M.p. = 66-67 ^oC; R_f = 0.30 (Diethyl ether/petroleum ether 1:9); IR (film): 1756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (m, 1H), 7.25 (m, 1H), 7.15 (m, 2H), 6.05 (m, 1H), 5.87 (m, 1H), 5.23 (m, 1H), 3.32 (s, 2H), 2.03 (s, 3H), 2.20-1.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 144.6, 140.1, 139.6, 134.0, 128.3, 126.3, 124.6, 123.8, 117.3, 112.6, 73.1, 39.1, 28.2, 24.9, 18.6, 12.2. Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; Found: C, 75.55; H, 6.52.



(*Z*)-Allyl 1-cyclohexylprop-1-enyl carbonate (*Z*-15):

To an oven-dried flask with a stirring bar was added bis(dimethylphenylsilyl)amine (1.74 mL, 6.0 mmol) and 20 mL of dry THF. The solution was cooled to -78 ^{o}C and 2.5 M *n*-BuLi in hexane (2.4 mL, 6.0 mmol) was added slowly. The flask was taken out of the dry-ice bath after 5 min and put in an ice-water bath for 10 min with stirring. 1-Cyclohexyl-1-propanone (701 mg, 5 mmol) in 5 mL of THF was slowly dropped into the solution in 10 min. The reaction was stirred for 1.5 h at -78 ^{o}C and 0.64 mL of allyl chloroformate was added in one portion. The reaction mixture was stirred for 15 min and warmed to ambient temperature before quenching with saturated aqueous ammonium chloride solution. The mixture was extracted with diethyl ether, and The combined organic layers were dried over anhydride magnesium sulfate. After filtration and concentration, the crude product was analyzed by ^{1}H-NMR to be only the *Z* isomer. After purification by column chromatography eluting with 2% diethyl ether in petroleum ether, 630 mg of of ***Z*-15** was obtained (56%). Colorless oil; R_f = 0.55 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2929 (s), 2855 (s), 1760 (s), 1695 (m), 1450 (s), 1364 (m), 1296 (s), 1234 (s), 1187 (s), 1167 (s), 971 (s), 780 cm^{-1} (m); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 5.97 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.40 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.30 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 5.06 (qd, J_1 = 6.9 Hz, J_2 = 1.0 Hz, 1H), 4.67 (dt, J_1 = 5.8 Hz, J_2 = 1.2 Hz, 2H), 2.10 (m, 1H), 1.87 (m, 2H), 1.75 (m, 2H), 1.66 (m, 1H), 1.52 (dd, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 3H), 1.20 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 153.8, 152.9, 131.5, 119.0, 109.0, 68.7, 41.7, 30.6, 26.2, 26.1, 10.5. Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99; Found: C, 69.47; H, 8.79.

To an oven-dried flask with a stirring bar was added diisopropylamine (0.84 mL, 6.0 mmol) and 20 mL of dry THF. The solution was cooled to -78 ^{o}C and 2.5 M *n*-BuLi in hexane (2.4 mL, 6.0 mmol) was added. The flask was taken out of the dry-ice bath after 5 min and put in an ice-water bath for 10 min with stirring. TMEDA (0.91 mL, 6.0 mmol) was added and the solution then was cooled to -78 ^{o}C again. 1-Cyclohexyl-1-propanone (701 mg, 5 mmol) in 5 mL of THF was slowly dropped into the solution in 10 min. The reaction was stirred for 1 h at -78 ^{o}C and 0.64 mL of allyl chloroformate was added in one portion. The reaction mixture was stirred for 15 min and warmed to ambient temperature before quenching with saturated aqueous ammonium chloride solution. After extraction with ether, The combined organic layers were dried over anhydride magnesium sulfate. After concentration, the crude product was analyzed to be a mixture of *Z*/*E* isomers with a ratio of 1:0.6 by ^{1}H-NMR. The crude product was purified by column chromatography eluting with 2% diethyl ether in petroleum ether to yield 300 mg of of the *Z* isomer and 270 mg of of the *E* isomer and 450 mg of of mixture. The total yield is 1.02 g (91%).

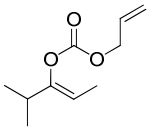


(*E*)-Allyl 1-cyclohexylprop-1-enyl carbonate (***E*-15**):

Colorless oil; R_f = 0.50 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2931 (s), 2856 (s), 1760 (s), 1688 (w), 1451 (m), 1386 (m), 1363 (m), 1295 (s), 1249 (s), 1229 (s), 1173 (s), 1058 (m), 977 (m), 781 cm^{-1} (m); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 5.96 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.38 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.29 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 5.17 (q, J = 7.2 Hz, 1H), 4.64 (dt, J_1 = 5.7 Hz, J_2 = 1.2 Hz, 2H), 2.50 (m, 1H), 1.76 (m, 2H), 1.68 (d, J_1 = 6.8 Hz, 3H), 1.66 (m, 3H), 1.4-1.1 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 154.4, 153.1, 131.6, 119.0, 111.5, 68.7, 38.5, 29.7, 26.3, 25.8, 11.4. Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99; Found: C, 69.71; H, 8.72.

Gereral Procedure for the Preparation of *Z*-isomer of Allyl Enol Carbonates.[6]

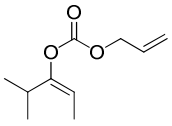
To a clean dry 100 mL flask with a magnetic stirring bar was loaded sodium hexamethyldisilazane (Aldrich, 97%, 1.15 g, 6.0 mmol) in a glove box under nitrogen. The flask was cooled in a dry-ice-acetone bath for 5 min and 20 mL of dry THF was transferred slowly to this flask with a syringe. The flask was warmed to 0 ^{o}C to make a clear solution and 0.91 mL of (6.0 mmol) TMEDA was added. The solution was cooled to -78 ^{o}C again and a solution of ketone (5.0 mmol) in 5 mL of THF was added slowly over 5 min. The reaction mixture was stirred for 1 h and transferred through a cannula into a solution of 0.64 mL of (6 mmol) allyl chloroformate in 5 mL of THF at -78 ^{o}C and stirred for 5 min. The reaction was quenched with aqueous ammonium chloride solution and transferred into a separating funnel. After dilution with 50 mL of diethyl ether and washed with brine once, the organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The product was purified by column chromatography on silica gel.



(*Z*)-Allyl 2-methylpent-3-en-3-yl carbonate (*Z*-**16**):

The general procedure for the synthesis of *Z*-enol carbonates was followed employing 2-methylpentan-3-one (1.0 g, 10 mmol) to yield product (1.40 g, 76%, *Z*/*E* > 98/2) after purification by flash column chromatography eluting with 2% diethyl ether in petroleum ether.

Colorless oil; R_f = 0.56 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2969 (s), 2877 (m), 1760 (s), 1697 (w), 1454 (m), 1366(m), 1298 (s), 1239 (s), 1193 (s), 973 (s), 781 cm^{-1} (w); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.99 (m, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.32 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 5.13 (qd, J_1 = 6.9 Hz, J_2 = 1.0 Hz, 1H), 4.70 (dt, J_1 = 5.8 Hz, J_2 = 1.2 Hz, 2H), 2.47 (m, 1H), 1.55 (dd, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 3H), 1.09 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.5, 152.8, 131.5, 119.0, 108.9, 68.7, 32.1, 20.2, 10.5. Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75; Found: C, 65.00; H, 8.98.

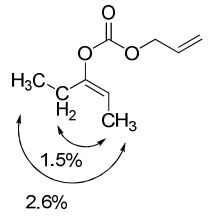


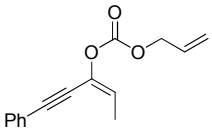
Allyl (*E*)-2-methylpent-3-en-3-yl carbonate (*E*-16): To a clean dry 250 mL flask was loaded TMP-HBr (1.155 g, 5.2 mmol) and 55 mL of DME. To this rapidly stirred suspension at 0°C and under argon was added a 2.4 M solution of n-Buli in hexanes (4.0 mL, 9.6 mmol) dropwise over a 3-min period. After being stirred for 20 min, the resulting pale yellow solution was cooled to -78°C and a solution of 2-methyl-3-pentanone (407 mg, 4 mmol) in 4 mL of DME was added dropwise over 3 min. After 15 min, TMEDA (1.5 mL, 10 mmol) was added dropwise along the inner flask wall over a 2-min period. After another 4 min a pre-cooled (-78°C) solution of allylchloroformate (970 mg, 8 mmol) in 1 mL of DME was added through a cannula at -78°C. After 30 min at -78°C the reaction was removed from the bath and was allowed to warm to room temperature. The reaction was quenched with 5% KH_2PO_4 aqueous solution and transferred into a separatory funnel. It was extracted twice with diethyl ether (40 mL). The combined organic layers were washed with water, brine, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. According to the NMR-data, the *E*/*Z* selectivity is 9:1 in the

crude product. The residue (956 mg of) was purified by silica gel column chromatography eluting with 2% diethyl ether in petroleum ether to afford 390 mg of colorless oil (53%, *E*/*Z* = 23/1).

R_f = 0.13 (diethyl ether/ petroleum ether 1:49); IR (film): $\tilde{\nu}_{max}$ = 3088 (w), 2972 (s), 2934 (m), 2876 (m), 1758 (s), 1688 (m), 1303 (s), 1242 (s), 1190 (s), 1160 (s), 989 (s), 940 (m), 782 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5,95 (ddt, J_1 = 17.2 Hz, J_2 = 10.5 Hz, J_3 = 5.8 Hz, 1H), 5.37 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.28 (dq, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1H), 5.17 (q, *J* = 7.2 Hz, 1H), 4.64 (m, 2H), 2.97 (sept, *J* = 6.9 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 154.5, 153.4, 131.7, 119.2, 111.4, 68.8, 28.2, 19.8, 11.5. HRMS (EI): $[M]^+$ calcd. for $C_{15}H_{14}O_3$, 184.1099; Found: 184.1092.

Allyl (*E*)-pent-2-en-3-yl carbonate (*E*-17): To a clean dry 100 mL flask was loaded TMP-HBr (500 mg, 2.25 mmol, 1.3 eq) and 25 mL of DME. To this rapidly stirred suspension at 0°C and under nitrogen was added a 2.4 M solution of n-Buli/hexanes (1.70 mL, 4.15 mmol, 2.4 eq) dropwise over a 3-min period. After being stirred for additional 15 min, the resulting pale yellow solution was cooled to -78°C and a solution of 3-pentanone (153 mg, 1.78 mmol, 1 eq) in 1.5 mL of DME was added dropwise. After 15 min, TMEDA (0.62 mL, 4.15 mmol, 2.4 eq) was added dropwise over a 3-min period. After another 15 min, a pre-cooled (-78°C) solution of allylchloroformate (241 mg, 2.00 mmol, 1.1 eq) in 1.4 mL of DME was added at -78°C. After 30 min at -78°C the reaction was removed from the bath and was allowed to warm to room temperature. The reaction was quenched with 5% KH_2PO_4 aqueous solution and transferred into a separatory funnel. It was extracted twice with 25 mL of diethyl ether. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified by silica gel column chromatography eluting with 2-3% diethyl ether in petroleum ether to afford 265 mg of colorless oil (90%). The *E*/*Z* ratio was determined by ^{1}H-NMR to be 18:1 [by the signal of the CH_3 at δ= 1.64 (d, *J* = 7.2 Hz, major) and 1.59 (dt, *J* = 6.9, 1.4 Hz, minor)]. R_f = 0.35 (diethyl ether/ petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2977 (m), 1756 (s), 1694 (m), 1459 (m), 1386 (m), 1365 (m), 1276 (s), 1245 (s), 1167 (s), 1031 (w), 983 (m), 942 (m), 916 (m), 783 (w), 734 cm^{-1} (m); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 5.95 (ddt, J_1 = 17.2 Hz, J_2 = 10.5 Hz, J_3 = 5.7 Hz, 1H), 5.37 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.28 (dq, J_1 = 10.5 Hz, J_2 = 1.1 Hz, 1H), 5.24 (q, *J* = 7.2 Hz, 1H), 4.64 (m, 2H), 2.31 (q, *J* = 7.6 Hz, 2H), 1.64 (d, *J* = 7.2 Hz, 3H), 1.04 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ= 153.8, 150.9, 131.5, 119.1, 111.8, 68.7, 21.8, 11.5, 11.4. The structure was further confirmed by NOE experiment.

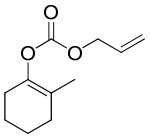




Allyl (*E*)-1-phenylpent-3-en-1-yn-3-yl carbonate (*E*-**18**):

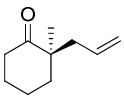
To a clean dry 250 mL flask was loaded TMP-HBr (1.16 g, 5.2 mmol) and 50 mL of DME. To this rapidly stirred suspension at 0°C and under argon was added 4.0 mL of a 2.4 M solution of n-BuLi/hexanes (9.6 mmol) dropwise over a 3-min period. After stirring for 15 min, the resulting pale yellow solution was cooled to –78°C and a solution of 667 mg of 1-phenyl-1-pentyn-3-one (4 mmol) in 4 mL of DME was added dropwise. After 15 min, 1.5 mL of TMEDA (10 mmol) was added dropwise along the inner flask wall over a 5-min period. After another 10 min, a precooled (-78°C) solution of 540 mg of allylchloroformate (4.4 mmol) in 3 mL of DME was added by a canula at –78°C. After 30 min at –78°C the reaction was taken out of the bath and was allowed to warm to room temperature. The reaction was quenched with 5% KH_2PO_4 aqueous solution and transferred into a seperatory funnel. It was extracted twice with 40 mL of diethylether. The combined organic layers were washed with water, brine, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue (1.1 g) was purified by silica gel column chromatography eluting with 3% diethyl ether in petroleum ether to afford 102 mg of of the starting marterial (16%) and 656 mg of brown yellow oil (68%). According to the ^{1}HNMR-data the *E*/*Z* selectivity is 14:1.

R_f = 0.39 (diethyl ether/ petroleum ether 1:9); IR (film): $\bar{\nu}_{max}$ = 3512 (w), 3060 (m), 2949 (m), 2219 (s), 1770 (s), 1651 (m), 1491 (s), 1443 (s), 1230 (s), 1151 (s), 757 (s), 681 (s) cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.47 (m, 2H), 7.36-7.31 (m, 3H), 5,95 (ddt, J_1 = 17.2 Hz, J_2 = 10.5 Hz, J_3 = 5.8 Hz, 1H), 5.89 (q, J = 7.26 Hz, 2H), 5.41 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.30 (dq, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1H), 4.71 (m, 2H), 1,93 (d, J = 7.26 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =153.4, 132.0, 131.8, 131.4, 129.2, 128.6, 124.2, 122.2, 119.6, 94.9, 81.1, 69.4, 13.7. HRMS (EI): $[M]^+$ calcd. for $C_{15}H_{14}O_3$, 242.0943; Found: 242.0950.



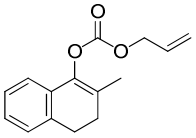
Allyl 2-methylcyclohex-1-enyl carbonate (**19**):

To a clean dry 200 mL three-neck flask with a magnetic stirring bar and a refluxing condenser was loaded a 60% suspension of sodium hydride in mineral oil (4.4 g , 110 mmol). The sodium hydride was washed three times with anhydrous hexane under nitrogen. TMEDA (15.1 mL) and 50 mL of anhydrous THF were added to the flask and the suspension was heated in an 80 ^{o}C oil bath. A solution of 2-methylcyclohexanone (10.4 mL, 100 mmol) in 50 mL of THF was added slowly *via* a cannula over 15 min. The reaction mixture was stirred for 1 h at 80 ^{o}C and then cooled to 0 ^{o}C in an ice-bath. The enolate solution was transferred through a cannula into a solution of allyl chloroformate (10.7 mL) in 50 mL of THF at 0 ^{o}C. After stirring for another 15 min, saturated aqueous ammonium chloride (100 mL) was poured into the reaction flask. The mixture was extracted with diethyl ether twice; the organic layer was combined and dried over anhydrous magnesium sulfate. After filtration and concentration the residue was purified by column chromatography eluting with 2% diethyl ether in petroleum ether to afford the title compound as a colorless liquid (6.4 g, 33%). R_f = 0.59 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3088 (m), 1756 (s), 1710 (m), 1446 (m), 1367 (m), 1249 (s), 1154 (m), 1037 (s), 995 (m), 937 (m), 862 (w), 785 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.96 (m, 1H), 5.38 (m, 1H), 5.28 (m, 1H), 4.65 (m, 2H), 2.15 (m, 2H), 2.06 (m, 2H), 1.72 (m, 2H), 1.60 (m, 2H), 1.58 (s, 3H). Spectral data was identical to the known compound.[7]



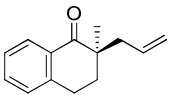
(*R*)-(+)-2-Allyl-2-methylcyclohexanone (2.10)[8]:

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing **19** (58.8 mg, 0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in toluene (3 mL) to produce the title compound as a volatile colorless oil (37.1-43.1 mg, 75-94%) after purification by column chromatography eluting with 2% diethyl ether in petroleum ether. R_f = 0.34 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{22}$ = +49.6 (c = 2.9, CH_2Cl_2); 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), 85% ee); ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.6, 133.9, 118.0, 48.5, 42.0, 38.9, 38.7, 27.5, 22.7, 21.1.



Allyl 2-methyl-3,4-dihydronaphthalen-1-yl carbonate (23)[9]:

The general procedure for the synthesis of enol carbonate was followed employing 2-methyl-1-tetralone (801 mg, 5 mmol) to produce the title compound as a colorless oil (800 mg, 66%) after purification by flash column chromatography eluting with 3% diethyl ether in petroleum. Colorless oil. R_f = 0.36 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3068 (w), 3024 (w), 2934 (m), 2888 (m), 2833 (m), 1760 (s), 1673 (m), 1488 (m), 1441 (m), 1366 (m), 1296 (m), 1228 (s), 1144 (m), 1034 (m), 986 (m), 941 (m), 770 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (m, 4H), 5.99 (m, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.32 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.72 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.86 (t, J = 8.0 Hz, 2H), 2.40 (t, J = 8.0 Hz, 2H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3, 140.9, 135.5, 131.6, 131.0, 127.5, 127.3, 126.7, 124.7, 120.2, 119.4, 69.2, 29.1, 27.6, 16.8. Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; Found: C, 73.90; H, 6.73.

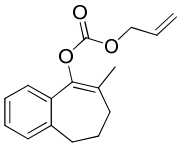


(*R*)-(+)-2-Allyl-2-methyltetralone (24):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 73.3 mg of carbonate **23** (0.30 mmol) $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in toluene (3 mL) to produce 53.0 mg of the title compound after purification by column chromatography eluting with 4% diethyl ether in petroleum ether (88%). Spectral data was identical to the known compound.[10]

Colorless oil; R_f = 0.60 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +16.9 (c = 1.39, CH_2Cl_2); HPLC (Chiralcel® OB-H column; 97:3 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 6.74 min (major), t_2 = 5.79 min (minor), 100% ee); IR (film): $\tilde{\nu}_{max}$ = 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); ^{1}H NMR (400 MHz, $CDCl_3$): 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 =

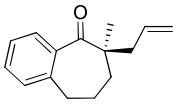
13.6 Hz, J_2 = 7.6 Hz, 1H), 2.08 (m, 1H), 1.90 (m, 1H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 143.6, 134.2, 133.3, 131.8, 128.9, 128.2, 126.9, 118.4, 44.8, 41.3, 33.6, 25.6, 22.1.



Allyl 6-methyl-8,9-dihydro-7*H*-benzo[7]annulen-5-yl carbonate (**25**):

The general procedure for the synthesis of enol carbonate was followed employing 871.2 mg of 2-methyl-1-benzosuberone (5.0 mmol) to produce 880 mg of the title compound after purification by flash column chromatography eluting with 2-4% diethyl ether in petroleum (68%).

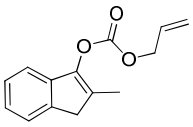
Colorless oil; R_f = 0.51 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3068 (w), 3024 (w), 2935 (s), 2859 (m), 1757 (s), 1678 (w), 1485 (w), 1441 (m), 1365 (m), 1295 (m), 1236 (s), 1179 (m), 1123 (m), 1083 (w), 970 (m), 943 (m), 774 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (m, 4H), 5.90 (m, 1H), 5.33 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.32 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.60 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.74 (t, J = 7.0 Hz, 2H), 2.17 (p, J = 7.2 Hz, 2H), 1.95 (t, J = 7.2 Hz, 2H), 1.913 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 141.2, 140.7, 136.0, 131.4, 128.9, 127.9, 126.5, 126.1, 125.5, 118.9, 68.8, 33.4, 32.3, 30.4, 17.6; Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02; Found: C, 74.60; H, 6.92.



(-)-2-Allyl-2-methylbenzosuberone (**26**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 77.5 mg of carbonate **25** (0.30 mmol) $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in toluene (3 mL) to produce 60.7 mg of the title compound after purification by column chromatography eluting with 2% diethyl ether in petroleum ether (94%). Spectral data was identical to the known compound.[11]

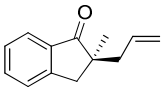
Colorless oil; R_f = 0.49 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = -6.93 (c = 1.47, CH_2Cl_2); GC (Cyclosil B® column; 130 °C constant temperature; 50:1 split ratio; 15.0 split flow; 1.5 flow rate; t_1 = 72.75 min (minor), t_2 = 74.49 min (major), 91% ee); IR (film): $\tilde{\nu}_{max}$ = 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); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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.



Allyl 2-methyl-3*H*-inden-1-yl carbonate (**27**):

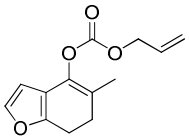
The general procedure for the synthesis of enol carbonate was followed employing 536 mg of 2-methyl-1-indanone (3.67 mmol) to produce 358 mg of product after purification by flash column chromatography (eluting with 5% diethyl ether in petroleum) and Kugelrohr distillation (45%).

Colorless oil; R_f = 0.38 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3068 (w), 3024 (w), 2914 (w), 2857 (w), 1766 (s), 1659 (m), 1485 (w), 1461 (m), 1396 (m), 1360 (m), 1295 (m), 1236 (s), 1170 (m), 1140 (w), 1088 (w), 1041 (m), 988 (m), 943 (m), 778 (w), 756 (m), 728 (w), 723 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 7.2 Hz, 1H), 7. 25 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 2H), 6.0 (m, 1H), 5.44 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.33 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.75 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 3.32 (s, 2H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 144.5, 140.1, 139.4, 131.2, 128.5, 126.4, 124.8, 123.8, 119.5, 117.1, 69.3, 39.0, 12.1;



(+)-2-Allyl-2-methylindanone (**28**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 65 mg of carbonate **27** (0.30 mmol) $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in toluene (3 mL) to produce 55 mg of the title compound after purification by column chromatography eluting with 2% diethyl ether in petroleum ether (98%). Colorless oil; R_f = 0.43 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{22}$ = +46.2 (c = 1.6, CH_2Cl_2); HPLC (Chiralcel® OB-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 9.49 min (major), t_2 = 12.62 min (minor), 76% ee); IR (film): $\tilde{\nu}_{max}$ = 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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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 $C_{13}H_{14}O$: C, 83.83; H, 7.58; Found: C, 84.16; H, 7.61.



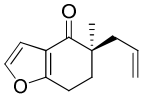
Allyl 5-methyl-6,7-dihydrobenzofuran-4-yl carbonate (**29**):

5-Methyl-6,7-dihydrobenzofuran-4(5*H*)-one was prepared by a literature procedure.[12,13] A clean and oven-dried 100 mL flask with a magnetic stirring bar was purged with nitrogen. It was charged 1.24 mL of diisopropylamine (8.81 mmol) and 30 mL of dry THF and was cooled to -20 ^oC by a dry-ice bath. To this solution was added 3.52 mL of 2.5 M *n*-butyllithium in hexane (8.81 mmol) slowly and was stirred for 10 min. To this fresh LDA solution was added slowly a solution of 1.2 g 6,7-dihydrobenzofuran-4(5*H*)-one (8.81 mmol) in 5 mL of dry THF. The reaction mixture was stirred for another 5 min and the flask was moved to an ice-bath and stirred for another 15 min. To the enolate solution was added a solution of 0.55 mL of iodomethane (8.81 mmol) in 5 mL of dry THF and the reaction mixture was stirred for 6 h while the bath temperature was allowed to rise to room temperature. The reaction mixture was poured into a separating funnel flask and diluted with 30 mL of diethyl ether. After it was washed with water once and brine once, the organic layer was separated and dried over anhydrous magnesium sulfate. After filtration and concentration by a rotaevaporator, the crude product was purified by column chromatography to yield 707 mg of colorless oil (53%).

The general procedure for the synthesis of enol carbonate was followed employing 600 mg of 5-Methyl-6,7-dihydrobenzofuran-4(5*H*)-one (4.0 mmol) to produce 190 mg of the title compound after purification by flash column chromatography eluting with 5% diethyl ether in petroleum as a colorless oil (20%).

The compound is not stable on silica gel. After concentration it rapidly turned yellow and a significant amount of decomposition was observed after stored one day at room temperature.

R_f = 0.38 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3068 (w), 3024 (w), 2938 (m), 1789 (s), 1716 (m), 1673 (m), 1499 (w), 1447 (m), 1386 (m), 1295 (s), 1238 (s), 1171 (s), 1132 (s), 1030 (s), 1041 (m), 954 (m), 783 (w), 756 (m), 729 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (m, 1H), 6.18 (d, J = 2.0 Hz, 1H), 5.99 (m, 1H), 5.41 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.32 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.71 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.85 (t, J = 9.4 Hz, 2H), 2.57 (t, J = 9.4 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 151.1, 141.4, 136.9, 131.4, 119.3, 116.0, 115.4, 105.4, 69.0, 29.9, 21.4, 15.3.

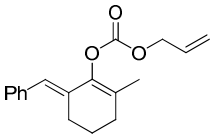


(+)-5-Allyl-5-methyl-6,7-dihydrobenzofuran-4(5*H*)-one (**30**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 70 mg of carbonate **29** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in toluene (3 mL) to produce 37 mg of the title compound after purification by column chromatography eluting with 2% diethyl ether in petroleum ether (64%). Spectral data was identical to the known compound.[11]

Colorless oil; R_f = 0.22 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +8.6 (c = 1.4, CH_2Cl_2); HPLC (Chiralcel® AD column; 99.5:0.5 Heptane / Isopropanol; flow rate = 0.8 mL of / min; t_1 = 18.14 min (minor), t_2 = 20.70 min (major), 82% ee); IR (film): $\tilde{\nu}_{max}$ = 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, $CDCl_3$): δ = 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, $CDCl_3$): δ = 198.5, 165.4, 143.0, 134.1, 119.8, 118.3, 107.3, 45.2, 41.2, 33.4, 21.9, 20.7.

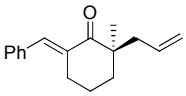


Allyl 6-benzylidene-2-methylcyclohex-1-enyl carbonate (**31**):

The general procedure for the synthesis of enol carbonate was followed employing 1.00 g (*E*)-2-benzylidene-6-methylcyclohexanone[13] (5.0 mmol) to produce 1.03 mg of product after purification by flash column chromatography (eluting with 5% diethyl ether in petroleum) and Kugelrohr distillation (72%).

Colorless oil; R_f = 0.44 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3068 (w), 3023 (w), 2933 (s), 2865 (m), 1760 (s), 1680 (m), 1650 (m), 1598 (m), 1494 (m), 1446 (s), 1364 (m), 1278 (s), 1234 (s), 1191 (s), 1135 (m), 1091 (w), 1046 (s), 995 (m), 928 (m), 874 (m), 756 (m), 699 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.3 (m, 5H), 6.44 (s, 1H), 5.98 (m, 1H),

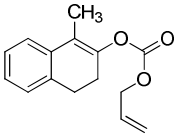
5.41 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.30 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.70 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.69 (m, 2H), 2.28 (t, J = 6 Hz, 2H), 1.75 (s, 3H), 1.71 (t, J = 6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 142.2, 137.5, 132.0, 131.5, 130.2, 129.4, 128.4, 128.1, 127.5, 126.4, 120.3, 119.1, 68.9, 31.1, 27.3, 22.4, 17.4;



(+)-2-Allyl-6-benzylidene-2-methylcyclohexanone (**32**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 85.3 mg of carbonate **31** (0.30 mmol) $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in toluene (3 mL) to produce 72 mg of the title compound after purification by column chromatography eluting with 2-5% diethyl ether in petroleum ether (99%). Spectral data was identical to the known compound.[10]

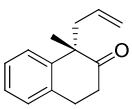
Colorless oil; R_f = 0.50 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +22.9 (c = 2.75, CH_2Cl_2); HPLC (Chiralcel® OJ column; 97:3 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 6.43 min (minor), t_2 = 7.68 min (major), 95% ee); IR (film): $\tilde{\nu}_{max}$ = 3074 (w), 3024 (w), 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); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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, $CDCl_3$): δ = 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.



Allyl 1-methyl-3,4-dihydronaphthalen-2-yl carbonate (**35**):

The general procedure for the synthesis of enol carbonate was followed employing 801 mg of 1-methyl-2-tetralone (5 mmol) to produce 950 mg of the title compound after purification by flash column chromatography eluting with 2% diethyl ether in petroleum and Kugelrohr distillation (78%);

Colorless oil; R_f = 0.44 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3070 (w), 2945 (m), 1756 (s), 1674 (m), 1488 (m), 1453 (s), 1365 (m), 1304 (s), 1245 (s), 1181 (s), 1019 (s), 988 (s), 943 (s), 760 (s), 693 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.2 (m, 4H), 5.98 (m, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.32 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.70 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.95 (t, J = 7.8 Hz, 2H), 2.53 (tq, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 2H), 1.98 (t, J = 1.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 148.7, 145.5, 136.8, 131.2, 130.2, 129.9, 123.0, 119.8, 119.5, 116.5, 69.6, 11.7; Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; Found: C, 73.78; H, 6.40.

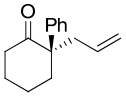


(*S*)-(-)-1-Allyl-1-methyl-3,4-dihydronaphthalen-2(1*H*)-one (**34**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 73.3 mg of carbonate **35** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 53.5 mg the title compound after purification by column chromatography eluting with 5% diethyl ether in petroleum ether (89%).

Colorless oil; R_f = 0.35 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{25}$ = -38.0 (c = 3.1, CH_2Cl_2); HPLC (Chiralcel® OJ column; 90:10 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 5.149 min (major), t_2 = 6.350 min (minor), 80% ee); IR (film): $\tilde{\nu}_{max}$ = 3075 (w), 2976 (m), 1715 (s), 1452 (m), 996 (m), 919 (m), 762 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25 (m, 4H), 5.39 (m, 1H), 4.92 (m, 2H), 3.04 (m, 2H), 2.78 (dd, J_1 = 14.0 Hz, J_2 = 6.8 Hz, 1H), 2.64 (m, 2H), 2.46 (m, 1H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.2, 141.5, 135.9, 133.7, 128.2, 127.0, 126.8, 126.4, 118.2, 51.8, 44.8, 38.4, 28.3, 26.2.

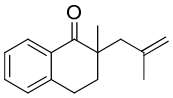
Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05; Found: C, 84.00; H, 7.94.



(*S*)-2-Allyl-2-phenylcyclohexanone (**37**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 77.5 mg of carbonate **4** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 62.8 mg of the title compound after purification by column chromatography eluting with 2% diethyl ether in petroleum ether (98%). Spectral data was identical to the known compound.[14]

Colorless oil; R_f = 0.43 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +242.2 (c = 1.38, CH_2Cl_2); HPLC (Chiralcel® ODH column; 99.9:0.1 Heptane / Isopropanol; flow rate = 0.8 mL of / min; t_1 = 10.429 min (major), t_2 = 11.543 min (minor), 81% ee); IR (film): $\tilde{\nu}_{max}$ = 2939 (s), 1708 (s), 1449 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35 (m, 2H), 7.24 (m, 1H), 7.15 (m, 2H), 5.44 (dddd, *J* = 16.9, 10.2, 8.1, 6.7 Hz, 1H), 4.96-4.84 (m, 2H), 2.67 (ddd, *J* =11.3, 2.8, 2.8 Hz, 1H), 2.55-2.20 (m, 4H), 1.94 (m, 1H), 1.82-1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.4, 140.8, 134.5, 129.0, 127.0, 126.95, 117.9, 57.0, 45.2, 40.3, 34.9, 28.5, 21.7.

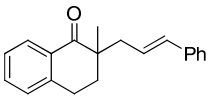


2-Methyl-2-(2-methylallyl)-3,4-dihydronaphthalen-1(2*H*)-one (**38**):

The general procedure for Pd catalyzed DAAA of enol carbonates was followed employing 52 mg of **8**, (0.2 mmol), 5.2 mg of (0.0075 mmol) $Pd_2(dba)_3CHCl_3$ and 9.2 mg of (*R,R*)-**L4** ligand (0.0165 mmol) ligand in 2 mL of dioxane to afford 38 mg of product was isolated (89%). Chromatography on silica gel, eluent: 3% diethyl ether in petroleum ether.

R_f = 0.44 (Diethyl ether/petroleum ether 1:9); Colorless oil; IR (film): 1682 cm^{-1}; $[\alpha]_D^{25}$ = +45.3 (c = 1.77, CH_2Cl_2, >99% ee); HPLC (Chiralcel® AD-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 15.1 min (minor), t_2 = 17.6 min (major)); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.04 (m, 1H), 7.46 (dt, *J* =7.5, 1.5 Hz, 1H), 7.30 (m, 1H), 7.24 (m, 1H), 4.83(m, 1H), 4.68 (m, 1H), 2.99 (t, *J* = 6.5 Hz, 2H), 2.66 (dd, *J* = 13.5, 0.7 Hz, 1H), 2.23 (dd, *J* = 13.5, 0.7 Hz, 1H), 2.10 (ddd, *J* = 13.9, 6.8, 6.8 Hz, 1H), 1.88 (ddd, *J* = 13.9, 5.8, 5.8 Hz, 1H), 1.65 (m, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz,

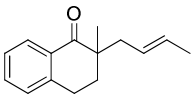
$CDCl_3$): δ = 202.2, 143.2, 142.5, 133.0, 131.8, 128.6, 128.1, 126.7, 114.9, 45.0, 44.7, 33.6, 25.5, 24.5, 23.3. Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47; Found: C, 84.32; H, 8.55.



2-Cinnamyl-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (**39**):

The general procedure for Pd catalyzed DAAA of enol carbonates was followed employing 64 mg of **10** (0.2 mmol), 5.2 mg of (0.0075 mmol) $Pd_2(dba)_3CHCl_3$ and 9.2 mg of (*R,R*)-**L4** ligand (0.0165 mmol) ligand in 2 mL of dioxane to afford 55.1 mg of product was isolated (99%). Chromatography on silica gel, eluent: 3% diethyl ether in petroleum ether.

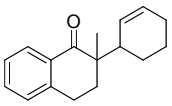
R_f = 0.37 (Diethyl ether/petroleum ether 1:9); Colorless oil; IR (film): 1682 cm^{-1}; $[\alpha]_D^{24}$ = +20.7.3 (c = 3.72, CH_2Cl_2, 92.5% ee); HPLC (Chiralcel® OD-H column; 98:2 Heptane / Isopropanol; flow rate = 0.8 mL of / min; t_1 = 9.6 min (major), t_2 = 10.7 min (minor)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 (dt, *J* =7.5, 1.5 Hz, 1H), 7.36-7.15 (m, 7H), 6.63 (d, *J* = 15.7 Hz, 1H), 6.21 (ddd, *J* = 15.7, 7.5, 7.5 Hz, 1H), 2.99 (dd, *J* = 6.1, 6.1 Hz, 2H), 2.65 (ddd, *J* = 13.7, 7.3, 1.2 Hz, 1H), 2.41 (ddd, *J* = 13.9, 7.8, 1.4 Hz, 1H), 2.14 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 1.94 (ddd, *J* = 13.7, 5.8, 5.8 Hz, 1H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0, 143.3, 137.4, 133.3, 133.1, 131.6, 128.7, 128.5, 128.0, 127.1, 126.7, 126.1, 125.8, 45.2, 40.5, 33.5, 25.4, 22.1.Anal. Calcd. for $C_{20}H_{20}O$: C, 86.92; H, 7.29; Found: C, 87.02; H, 7.12.



(*E*)-2-(But-2-enyl)-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (**40**):

The general procedure for Pd catalyzed DAAA of enol carbonates was followed employing 52 mg of **13** (0.2 mmol), 5.2 mg of (0.0075 mmol) $Pd_2(dba)_3CHCl_3$ and 9.2 mg of (*R,R*)-**L4** ligand (0.0165 mmol) ligand in 2 mL of dioxane to afford a mixture linear (**40**, 20:1 dr) and branched (**41**, 7:1 dr) products (l/b = 7.4:1).The title product (38 mg, 89%) was isolated by purification by chromatography on silica gel eluting with 3% diethyl ether in petroleum ether.

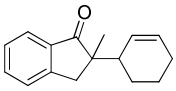
Colorless oil; R_f = 0.38 (Diethyl ether/petroleum ether 1:9); IR (film): 1682 cm^{-1}; $[\alpha]_D^{25}$ = +17.4 (c = 2.1, CH_2Cl_2); HPLC (Chiralcel® OD-H column; 2000:1 Heptane / Isopropanol; flow rate = 0.8 mL of / min; t_1 = 17.1 min (minor), t_2 = 17.9 min (major)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (m, 1H), 7.45 (dt, *J* =7.5, 1.5 Hz, 1H), 7.29 (m, 1H), 7.21 (m, 1H), 5.55-5.34 (m, 2H), 2.97 (m, 2H), 2.39 (m, 1H), 2.18 (m, 1H), 2.06 (m, 1H), 1.88 (m, 1H), 1.62 (dq, *J* = 5.0, 1.2 Hz, 3H), 1.16 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 143.4, 133.0, 131.7, 128.7, 128.7, 128.0, 126.6, 126.2, 44.9, 39.8, 33.3, 25.4, 22.0, 18.1; Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47; Found: C, 83.88; H, 8.36.



2-(Cyclohex-2-enyl)-2-methyl-3,4-dihydronaphthalen-1(2H)-one (**42**):

The general procedure for Pd catalyzed DAAA of enol carbonates was followed employing 57 mg of **11** (0.2 mmol), 5.2 mg of (0.0075 mmol) $Pd_2(dba)_3CHCl_3$ and 9.2 mg of (*R,R*)-**L4** ligand (0.0165 mmol) ligand in 2 mL of dioxane to afford 32 mg of the title compound (67%) was isolated as a mixture two diastereomers (dr = 20:1). Chromatography on silica gel, eluent: 3% diethyl ether in petroleum ether.

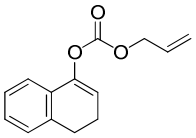
Colorless oil; R_f = 0.38 (Diethyl ether/petroleum ether 1:9); IR (film): 1681 cm^{-1}; $[\alpha]_D^{24}$ = +55.7 (c = 1.77, CH_2Cl_2, 99% ee the major one); HPLC (Chiralcel® AD-H column; 99.5:0.5 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 10.7 min (minor), t_2 = 11.7 min (major)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.44 (dt, *J* =7.5, 1.5 Hz, 1H), 7.30 (m, 1H), 7.20 (m, 1H), 5.76 (m, 1H), 5.49 (m, 1H), 2.99 (m, 1H), 2.90 (m, 1H), 2.65 (m, 1H), 2.15 (m, 1H), 2.0-1.74 (m, 5H), 1.53 (m, 1H), 1.36 (m, 1H), 1.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 143.3, 132.9, 129.2, 128.6, 128.1, 127.4, 126.6, 47.3, 38.4, 31.4, 25.2, 25.1, 24.3, 22.6, 19.0.



2-(Cyclohex-2-enyl)-2-methyl-2,3-dihydro-1H-inden-1-one (**43**):

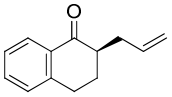
The general procedure for Pd catalyzed DAAA of enol carbonates was followed employing 54.5 mg of **14** (0.2 mmol) 5.2 mg of (0.0075 mmol) $Pd_2(dba)_3CHCl_3$ and 9.2 mg of (*R,R*)-**L4** ligand (0.0165 mmol) ligand in 2 mL of dioxane to afford 35.6 mg of product was isolated as a mixture of two diastereomers (79%). The ratio of the two diastereomers was measured to be 5:1 according to the integrations of the vinyl proton peaks in both diastereomers in the ^{1}HNMR. Chromatography on silica gel, eluent: 5% diethyl ether in petroleum ether.

White solid; mp = 48-56 °C; R_f = 0.30 (Diethyl ether/petroleum ether 1:9); IR (film): 1712 cm^{-1}; Major diastereomer: 98% ee, HPLC (Chiralcel® IC column; 99:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 10.0 min (major), t_2 = 12.1 min (minor)); Minor diastereomer: 93% ee, HPLC (Chiralcel® IC column; 99:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 11.4 min (minor), t_2 = 16.9 min (major)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (m, 1H), 7.58 (m, 1H), 7.42 (m, 1H), 7.36 (m, 1H), 5.85 (m, 1H, major), 5.75 (m, 1H, major), 5.66 (m, 1H, minor), 5.07 (m, 1H, minor), 3.15 (d, *J* = 17.6 Hz, 1H, minor), 3.10 (d, *J* = 17.6 Hz, 1H, major), 2.71 (m, 1H, minor), 2.70 (d, *J* = 17.6 Hz, 1H, major), 2.68 (d, *J* = 17.6 Hz, 1H, major), 2.54 (m, 1H, major), 2.40-1.35 (m, 5H), 1.29 (s, 3H, major), 1.26 (m, 1H, minor), 1.19 (s, 3H, minor), 0.84 (m, 1H, major).



Allyl 3,4-dihydronaphthalen-1-yl carbonate (**44**)[15]:

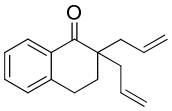
The general procedure for the synthesis of enol carbonate was followed employing 730 mg of 1-tetralone (5 mmol) to produce 1.03 g the title compound after purification by flash column chromatography eluting with 5% diethyl ether in petroleum (90%). Colorless oil; R_f = 0.39 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3068 (w), 3024 (w), 2941 (m), 2890 (w), 2836 (w), 1760 (s), 1659 (m), 1489 (m), 1452 (m), 1428 (m), 1360 (m), 1293 (m), 1244 (s), 1225 (s), 1186 (m), 1013 (m), 993 (m), 944 (m), 772 (m), 744 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7. 2 (m, 4H), 5.99 (m, 1H), 5.81 (t, *J* = 4.6 Hz, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.32 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.71 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.86 (t, *J* = 8.2 Hz, 2H), 2.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 146.1, 136.4, 131.2, 130.1, 128.1, 127.6, 126.5, 120.6, 119.4, 115.2, 69.1, 27.4, 22.0. Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13; Found: C, 73.58; H, 6.43.



(*R*)-(-)-2-Allyltetralone (**45**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 69 mg of carbonate **44** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 45 mg of the title compound after purification by column chromatography eluting with 2-5% diethyl ether in petroleum ether (81%). Spectral data was identical to the known compound.[16]

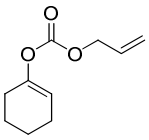
Colorless oil; R_f = 0.59 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -29.7 (c = 1.21, MeOH); HPLC (Chiralcel® OD column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 21.87 min (minor), t_2 = 23.88 min (major), 97% ee); IR (film): $\tilde{\nu}_{max}$ = 3073 (w), 2930 (m), 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, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 (47):

Isolated from the reaction of **44** as a minor product.

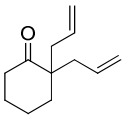
Colorless oil. R_f = 0.65 (Diethyl ether/petroleum ether 1:9); ^1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.23 (m, 2H), 5.85 (m, 2H), 5.08 (m, 4H), 2.99 (t, *J* = 6 Hz, 2H), 2.55 (dd, J_1 = 12.0 Hz, J_2 = 7.6 Hz, 2H), 2.25 (dd, J_1 = 12.0 Hz, J_2 = 7.6 Hz, 2H), 2.03 (t, *J* = 6 Hz, 2H). Spectral data was identical to the known compound.[17]



Allyl cyclohexenyl carbonate (**48**):

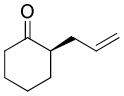
To a clean dry 100 mL of three-neck flask with a magnetic stirring bar and a refluxing condenser was loaded 0.96 g (24 mmol) suspension of 60% sodium hydride in mineral oil and was purged with nitrogen. The sodium hydride was washed three times with anhydrous hexane under nitrogen. 3.6 mL of TMEDA and 20 mL of anhydrous THF was added into the flask and the suspension was heated in a 80 ^oC oil bath. A solution of 2.07 mL of cyclohexanone (20 mmol) in 10 mL of THF was added slowly via a cannula over 15 min. The reaction mixture was stirred for 1 h at 80 ^oC and then cooled to 0 ^oC in an ice-bath. The enolate solution was transferred through a cannula into a solution of 2.56 mL of allyl chloroformate in 10 mL of THF at 0 ^oC. After stirring for another 15 min, 50 mL of saturated aqueous ammonium chloride was poured into the reaction flask. The mixture was extracted with diethyl ether twice; the organic layer was combined and dried over anhydrous magnesium sulfate. After filtration and concentration the residue was purified by column chromatography eluting with 2% diethyl ether in petroleum ether to afford 0.90 g colorless liquid (25%).

Colorless oil; R_f = 0.57 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3088 (w), 3024 (w), 2939 (s), 2862 (m), 1756 (s), 1659 (m), 1450 (m), 1363 (m), 1296 (m), 1244 (s), 1236 (s), 1153 (m), 1052 (m), 1033 (m), 995 (m), 972 (m), 926 (m), 783 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 5.96 (m, 1H), 5.49 (m, 1H), 5.40 (dq, J_1 = 18.4 Hz, J_2 = 1.5 Hz, 1H), 5.32 (m, 1H), 4.65 (m, 2H), 2.19 (m, 2H), 2.11 (m, 2H), 1.75 (m, 2H), 1.60 (m, 2H). Spectral data was identical to the known compound.[7]



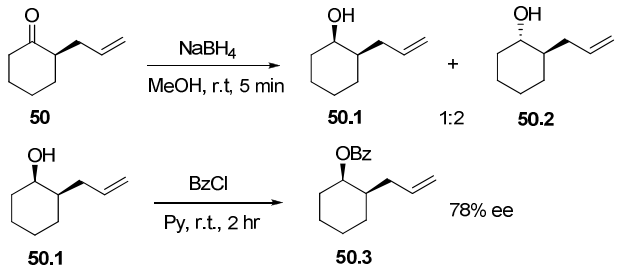
2,2-Diallylcyclohexanone (**49**):

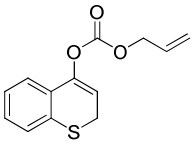
The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 54.7 mg of carbonate **48** (0.3 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and dppe (12 mg, 0.030 mmol) in toluene (3 mL) to produce 25 mg of the title compound after purification by column chromatography eluting with 5% diethyl ether in petroleum ether (47%).
Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.67 (m, 2H), 5.09-5.00 (m, 4H), 2.37 (dd, J_1 = 13.4, J_1 = 6.5, 4H), 2.26 (dd, J_1 = 14.1, J_1 = 7.1, 2H), 1.88 – 1.66 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 214.2, 133.7, 118.1, 51.5, 39.4, 39.3, 36.0, 27.1, 20.8.



(*R*)-(+)-2-Allylcyclohexanone (**50**):

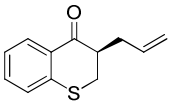
The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 54.7 mg of carbonate **48** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 32.2 mg of the title compound after purification by column chromatography eluting with 5% diethyl ether in petroleum ether (78%). The compound is volatile. Spectral data was identical to the known compound[18].
Colorless oil; R_f = 0.35 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +10.28 (c = 1.1, MeOH); ^1H NMR (400 MHz, $CDCl_3$): δ = 5.77 (m, 1H), 5.08 - 4.80 (m, 2H), 2.55 (m, 1H), 2.34 (m, 2H), 2.18 – 1.94 (m, 3H), 1.86 (m, 1H), 1.66 (m, 2H), 1.4 – 1.2 (m, 2H), 1.86 (m, 1H).
Determination of the ee value of **50**:
By our Chiral GC columns we had a hard time to separate the enantiomers of **50**. Therefore, it was reduced to alcohol **50.1** and **50.2** by $NaBH_4$ in MeOH in 1:2 ratio. They were separated by column chromatography on silica gel, eluting with 10% Et_2O in petroleum ether. **50.1** 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 eluting with 5% Et_2O in petroleum ether to yield **50.3**. Compound **50.3** was ready to be separated on chiral GC (Cyclosil B column, 150 ^oC 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), 78% ee).





Allyl 2*H*-thiochromen-4-yl carbonate (**51**):

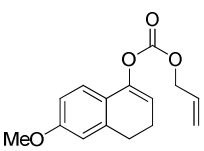
The general procedure for the synthesis of enol carbonate was followed employing 821 mg of thiochroman-4-one (5.0 mmol) to produce 670 mg of the title compound after purification by flash column chromatography eluting with 5% diethyl ether in petroleum (90%). Colorless oil; R_f = 0.30 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3062 (m), 3024 (w), 2953 (m), 2889 (m), 1766 (s), 1661 (m), 1589 (m), 1471 (m), 1436 (m), 1366 (m), 1232 (s), 1162 (m), 1140 (m), 993 (m), 945 (m), 763 (m), 726 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7. 24 (m, 2H), 7.11 (m, 2H), 5.95 (m, 1H), 5.80 (t, J = 5.4 Hz, 1H), 5.39 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.30 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.69 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 3.55 (d, J = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 147.2, 133.6, 131.0, 128.9, 128.7, 127.2, 125.6, 122.7, 119.5, 110.4, 69.2, 24.3.



(-)-3-Allyl-2,3-dihydrothiochromen-4-one (**52**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 74.5 mg of carbonate **51** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 54.4 mg of **52** after purification by column chromatography eluting with 5% diethyl ether in petroleum ether (89%). Spectral data was identical to the known compound.[19]

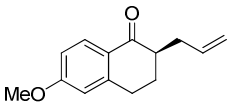
Colorless oil; R_f = 0.47 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -98.83 (c = 1.27, CH_2Cl_2); HPLC (Chiralcel® OB-H column; 99.5:0.5 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 10.68 min (major), t_2 = 11.87 min (minor), 93% ee); IR (film): $\tilde{\nu}_{max}$ = 3075 (w), 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); ^{1}H 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.



Allyl 6-methoxy-3,4-dihydronaphthalen-1-yl carbonate (**53**):

The general procedure for the synthesis of enol carbonate was followed employing 881 mg of 6-methoxy-1-tetralone (5 mmol) to produce 330 mg of the title compound after purification by flash column chromatography eluting with 5% diethyl ether in petroleum (25%). The low yield blames the poor quality of the specific bottle of NaHMDS.

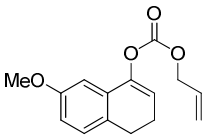
Colorless oil; R_f = 0.24 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3068 (w), 3024 (w), 2940 (m), 2890 (m), 2837 (m), 1760 (s), 1659 (m), 1609 (s), 1573 (s), 1530 (s), 1464 (s), 1452 (m), 1429 (s), 1360 (s), 1307 (s), 1223 (s), 1161 (m), 1143 (s), 1108 (m), 1043 (s), 1009 (s), 947 (m), 873 (m), 822 (m), 782 (m), 734 (w), 699 (w), 672 cm^{-1} (w); ^1H NMR (500 MHz, $CDCl_3$): δ = 7. 11 (d, J = 8.5 Hz, 1H), 6.71 (m, 2H), 5.98 (m, 1H), 5.67 (t, J = 4.8 Hz, 1H), 5.41 (dq, J_1 = 17.5 Hz, J_2 = 1.5 Hz, 1H), 5.32 (dq, J_1 = 10.5 Hz, J_1 = 1.5 Hz, 1H), 4.71 (dt, J_1 = 5.5 Hz, J_2 = 1.5 Hz, 2H), 3.79 (s, 3H), 2.83 (t, J = 8.0 Hz, 2H), 2.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.5, 153.4, 146.1, 138.4, 131.3, 123.2, 122.0, 119.4, 114.0, 112.5, 111.1, 69.0, 55.3, 27.9, 22.0; Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20; Found: C, 69.48; H, 6.12.



(-)-2-Allyl-6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (**54**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 78 mg of carbonate **54** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 58 mg of the title compound after purification by column chromatography eluting with 5% diethyl ether in petroleum ether (90%).

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); HPLC (Chiralcel® OD column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 48.72 min (minor), t_2 = 53.24 min (major), 100% ee); IR (film): $\tilde{\nu}_{max}$ = 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 $C_{14}H_{16}O_2$: C, 77.75; H, 7.46; Found: C, 78.12 ; H, 7.60.

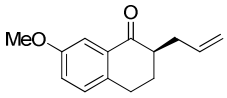


Allyl 7-methoxy-3,4-dihydronaphthalen-1-yl carbonate (**55**):

The general procedure for the synthesis of enol carbonate was followed employing 881 mg of 7-methoxy-1-tetralone (5 mmol) to produce 1.13 g the title compound after purification by flash column chromatography eluting with 5% diethyl ether in petroleum (87%).

Colorless oil; R_f = 0.24 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3084 (w), 2998 (w), 2941 (s), 2889 (m), 2836 (m), 1766 (s), 1659 (m), 1607 (s), 1574 (s), 1494 (s), 1463 (s), 1452 (m), 1426 (s), 1369 (s), 1332 (s), 1248 (s), 1174 (m), 1045 (s), 1016 (m), 994 (m), 948 (m), 886 (m), 813 (m), 782 (m), 734 (w), 700 cm^{-1} (w); ^1H NMR (400 MHz, $CDCl_3$): δ =

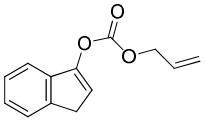
7.06 (d, J = 8.4 Hz, 1H), 6.77 (d, J = 2.4 Hz, 1H), 6.72 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 5.98 (m, 1H), 5.82 (t, J = 4.8 Hz, 1H), 5.42 (dd, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.32 (dd, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.71 (dt, J_1 = 5.4 Hz, J_2 = 1.3 Hz, 2H), 3.77 (s, 3H), 2.79 (t, J = 8.0 Hz, 2H), 2.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.4, 153.4, 146.0, 131.3, 131.2, 128.5, 128.4, 119.4, 115.9, 112.9, 107.0, 69.1, 55.4, 26.5, 22.4; Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20; Found: C, 69.02; H, 6.05.



(-)-2-Allyl-7-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (**56**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 78 mg of carbonate **55** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 63 mg of the title after purification by column chromatography eluting with 5% diethyl ether in petroleum ether (97%).

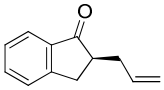
White solid; mp = 32-43 ^{o}C; R_f = 0.33 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = -50.2 (c = 2.1, CH_2Cl_2); HPLC (Chiralcel® OC column; 99.5:0.5 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 25.23 min (major), t_2 = 30.86 min (minor), 97% ee); IR (film): $\tilde{\nu}_{max}$ = 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); ^{1}H 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 $C_{14}H_{16}O_2$: C, 77.75; H, 7.46; Found: C, 77.94 ; H, 7.21.



Allyl 3H-inden-1-yl carbonate (**57**):

The general procedure for the synthesis of enol carbonate was followed employing 661 mg of 1-indanone (5 mmol) to produce 864 mg of the title compound after purification by flash column chromatography eluting with 5% diethyl ether in petroleum (80%).

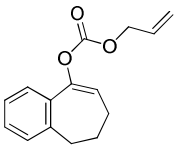
Colorless oil; R_f = 0.49 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 3029 (w), 2953 (w), 2892 (m), 1770 (s), 1651 (w), 1620 (m), 1604 (m), 1579 (m), 1462 (m), 1399 (m), 1361 (s), 1295 (s), 1230 (s), 1175 (m), 1015 (m), 993 (m), 944 (m), 761 (s), 717 cm^{-1} (w); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (m, 4H), 6.35 (t, J = 2.4 Hz, 1H), 6.01 (m, 1H), 5.45 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.32 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.71 (dt, J_1 = 5.4 Hz, J_2 = 1.3 Hz, 2H), 3.42 (d, J = 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 149.3, 141.8, 138.5, 131.1, 126.4, 125.8, 124.1, 119.6, 118.1, 114.4, 69.2, 34.8; Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59; Found: C, 72.26; H, 5.47.



(+)-2-Allyl-1-indanone (**58**):

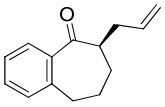
The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 65 mg of carbonate **57** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 48.5 mg of the title compound after purification by column chromatography eluting with 5% diethyl ether in petroleum ether (94%). Spectral data was identical to the known compound.[20]

Colorless oil; R_f = 0.27 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +95.8 (c = 4.0, CH_2Cl_2); HPLC (Chiralcel® OB-H column; 90:10 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 6.27 min (minor), t_2 = 7.70 min (major), 81% ee); IR (film): $\tilde{\nu}_{max}$ = 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.



Allyl 8,9-dihydro-7H-benzo[7]annulen-5-yl carbonate (**59**):

The general procedure for the synthesis of enol carbonate was followed employing 801 mg of 1-benzosuberone (5 mmol) to produce 850 mg of the title compound after purification by flash column chromatography eluting with 5% diethyl ether in petroleum (74%). Colorless oil; R_f = 0.43 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3064 (w), 3022 (w), 2934 (s), 2897 (m), 2861 (m), 1760 (s), 1660 (m), 1491 (m), 1450 (s), 1426 (m), 1366 (s), 1241 (s), 1213 (s), 1177 (m), 1125 (m), 994 (s), 969 (s), 773 (s), 747 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37 (m, 1H), 7.20 (m, 3H), 5.94 (m, 2H), 5.35 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.28 (dq, J_1 = 10.2 Hz, J_1 = 1.3 Hz, 1H), 4.62 (dt, J_1 = 5.4 Hz, J_2 = 1.3 Hz, 2H), 2.82 (m, 2H), 2.17 (m, 2H), 2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.0, 146.1, 141.9, 133.9, 131.4, 129.2, 128.4, 126.2, 125.4, 119.8, 119.1, 68.9, 33.7, 30.9, 25.3; Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; Found: C, 73.17; H, 6.26.

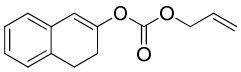


(+)-2-Allyl-1-benzosuberone (**60**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 73.3 mg of carbonate **59** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 55.6 mg of the title compound after purification by column chromatography eluting with 2% diethyl ether in petroleum ether (92%). Spectral data was identical to the known compound.[21]

Colorless oil; R_f = 0.45 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +70.43 (c = 1.56, CH_2Cl_2); HPLC (Chiralcel® OB-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 11.47 min (major), t_2 = 13.74 min (minor), 99% ee); IR (film): $\tilde{\nu}_{max}$ = 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),

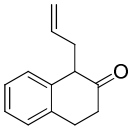
5.08 – 4.97 (m, 2H), 2.94 (m, 3H), 2.68 (m, 1H), 2.23 (p, *J* = 7.2 Hz, 1H), 2.06 (m, 1H), 1.96 (m, 1H), 1.69 (m, 1H), 1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.9, 141.9, 140.0, 136.4, 131.3, 129.8, 128.3, 126.4, 116.5, 49.4, 35.4, 33.6, 29.7, 25.4.



Allyl 3,4-dihydronaphthalen-2-yl carbonate (**61**):

The general procedure for the synthesis of enol carbonate was followed employing 731 mg of 2-tetralone (5 mmol) to produce 817 mg of the title compound after purification by flash column chromatography eluting with 5% diethyl ether in petroleum (71%).

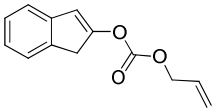
Colorless oil; R_f = 0.45 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2945 (s), 1756 (s), 1668 (s), 1455 (m), 1363 (m), 1225 (s), 1145 (s), 1034 (m), 985 (m), 759 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15-6.95 (m, 4H), 6.31 (s, 1H), 5.96 (m, 1H), 5.40 (m, 1H), 5.30 (m, 1H), 4.69 (m, 2H), 2.99 (dd, *J* = 8.2, 8.2 Hz, 2H), 2.56 (dd, *J* = 8.2, 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 150.8, 133.1, 132.9, 131.2, 127.3, 127.1, 126.7, 126.4, 119.4, 114.5, 69.0, 28.6, 25.9. Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13; Found: C, 72.88; H, 6.01.



1-Allyl-3,4-dihydronaphthalen-2(1*H*)-one (**62**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 69 mg of carbonate **61** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 47.3 mg of the title compound after purification by column chromatography eluting with 2% diethyl ether in petroleum ether (85%). Spectral data was identical to the known compound.[22]

Colorless oil; R_f = 0.25 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3076 (m), 2915 (m), 1715 (s), 1640 (m), 1490 (m), 1456 (m), 1147 (m), 918 (m), 747 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.13 (m, 4H), 5.74 (ddt, *J* = 16.8, 10.0, 6.8 Hz, 1H), 5.02 (m, 2H), 3.51 (dd, *J* = 6.8, 6.8 Hz, 1H), 3.13 (m, 1H), 3.02 (m, 1H), 2.77-2.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.8, 136.7, 136.6, 135.0, 128.0, 127.8, 126.9, 126.8, 117.4, 53.2, 37.9, 35.8, 27.9.

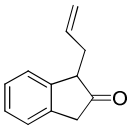


Allyl 1H-inden-2-yl carbonate (**63**):

The general procedure for the synthesis of enol carbonate was followed employing 661 mg of 2-indanone (5 mmol) to produce 650 mg of the title compound after purification by flash column chromatography eluting with 2% diethyl ether in petroleum (60%).

Colorless oil; R_f = 0.56 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3032 (m), 2952 (m), 1766 (s), 1608 (s), 1461 (s), 1365 (m), 1224 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.4-7.1 (m, 4H), 6.61 (m, 1H), 5.97 (ddt, *J* = 17.2, 11.2, 5.6 Hz, 1H), 5.43 (ddd, *J* = 17.2, 5.6, 5.6 Hz, 1H), 5.30 (ddd, *J* = 10.8, 5.6, 5.6Hz, 1H), 4.72 (ddd, *J* = 5.6, 1.6, 1.6 Hz, 2H),

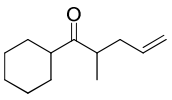
3.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 152.1, 142.6, 137.1, 131.0, 126.8, 124.5, 123.5, 121.1, 119.7, 114.3, 69.2, 37.5. Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59; Found: C, 72.46; H, 5.59.



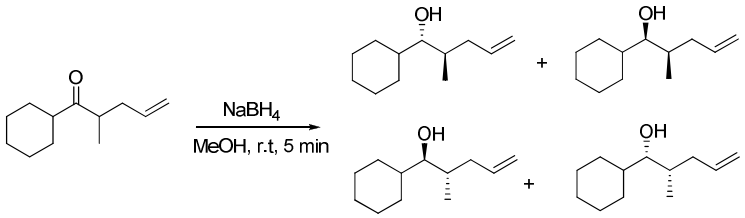
1-Allyl-1*H*-inden-2(3*H*)-one (**64**):

The general procedure for the Pd-catalyzed DAAA of enol carbonates was followed employing 65 mg of carbonate **63** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to produce 46.3 mg of the title compound after purification by column chromatography eluting with 5% diethyl ether in petroleum ether (90%). Spectral data was identical to the known compound.[23]

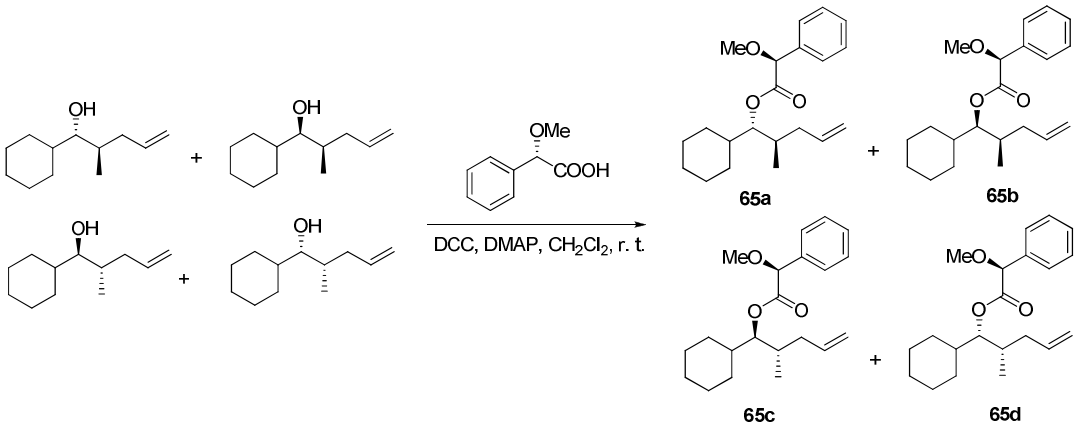
IR (film): $\tilde{\nu}_{max}$ = 3076 (m), 2908 (m), 1750 (s), 1480 (m), 1147 (m), 918 (m), 747 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.4-7.2 (m, 4H), 5.72 (m, 1H), 5.10-4.98 (m, 2H), 3.6-3.4 (m, 3H), 2.72 (m, 1H), 2.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 217.1, 141.5, 136.9, 134.4, 127.5, 127.4, 124.89, 124.87, 117.8, 52.7, 43.4, 35.7.



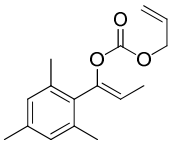
(-)-1-Cyclohexyl-2-methyl-4-penten-1-one (**65**): The general procedure for the Pd catalyzed DAAA reaction in dioxane was followed employing 67.3 mg of *E*-**15** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 51 mg of product (94%). Colorless oil; R_f = 0.58 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{22}$ = -30.8 (c = 2.35, CH_2Cl_2, 97% ee); IR (film): $\tilde{\nu}_{max}$ = 3078 (w), 2932 (s), 2855 (s), 1708 (s), 1642 (w), 1450 (s), 1375 (m), 993 (s), 914 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.70 (m, 1H), 5.01 (m, 2H), 2.74 (sextet, *J* = 6.9 Hz, 1H), 2.45 (m, 1H), 2.37 (m, 1H), 2.05 (m, 1H), 1.78 (m, 4H), 1.67 (m, 1 H), 1.30 (m, 5H), 1.05 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 217.0, 136.1, 116.7, 50.0, 44.3, 37.4, 28.6, 28.4, 25.9, 25.81, 25.78, 16.5. Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18; Found: C, 80.20; H, 10.99. Ee of **65** was determined by the following procedure:



To the solution of 46 mg of **65** (0.26 mmol) in 1 mL of methanol was added 48 mg of sodium borohydride at room temperature. After stirring for 5 min, most of solvent was removed *in vacuo* and the crude product was purified by column chromatography on silica gel eluting with 10% ether in petroleum ether to yield a mixture of *syn*- and *anti*- (1:1.1) 1-cyclohexyl-2-methylpent-4-en-1-ol, 35 mg of (75%), as a colorless oil.



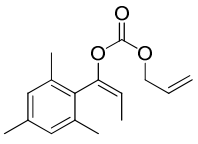
1-Cyclohexyl-2-methylpent-4-en-1-ol (20 mg, 0.11 mmol), 22 mg of (0.13 mmol) (*S*)-(+)-2-methoxy-2-phenylacetic acid (aldrich, 99+% ee), DMAP (3.4 mg of , 0.03 mmol) and DCC (27 mg of , 0.13 mmol) was mixed with 1 mL of dichloromethane. The reaction was stirred at room temperature for 1 h and filtered through a short pad silica gel eluting with 10% diethyl ether in petroleum ether to yield 34 mg of (94%) colorless oil as a mixture of *O*-methyl mandelic esters **65a-d**, which gave no separation by TLC. HPLC (Chiralcel® AD column; 97:3 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 5.444 min, t_2 = 6.741 min, t_3 = 7.525 min, t_4 = 9.140 min). de of **65a** and **65c** or **65b** and **65d** reflects the ee of **65**.



(*Z*)-Allyl 1-mesityl-1-propenyl carbonate (*Z*-**66**):

To an oven-dried flask with a stirring bar was added HMDS (2.54 mL, 12.0 mmol) and 20 mL of dry THF. The solution was cooled to -78 ^{o}C and 2.2 M *n*-BuLi in hexane (5.5 mL, 12.1 mmol) was added. The flask was removed from the dry-ice bath after 5 min and put in an ice-water bath for 10 min with stirring. The solution then was cooled to -78 ^{o}C again and 2',4',6'-trimethylpropiophenone (1.76 g, 10.0 mmol)in 5 mL of THF was added dropwise to the solution over 10 min. The reaction was stirred for 1 h at -78 ^{o}C and 1.28 mL of allyl chloroformate was added in one portion. The reaction mixture was stirred for 1 h and warmed to ambient temperature for another 20 min before the quenching with ammonium chloride saturated aqueous solution. After extraction with ether, the combined organic layers were dried over anhydride magnesium sulfate. Concentration *in vacuo* and purification by column chromatography gave 1.37 g (53%) colorless oil as a mixture of isomers with a *Z*/*E* ratio of 96/4 by ^{1}HNMR.

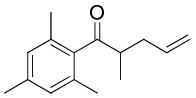
R_f = 0.47 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2921 (s), 2863 (w), 1758 (s), 1446 (m), 1224 (s), 1162 (m), 966 (s), 926 (m), 852 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.86 (s, 2H), 5.90 (m, 1H), 5.32 (dq, J_1 = 17.4 Hz, J_2 = 1.4 Hz, 1H), 5.29 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 5.22 (q, J = 7.0 Hz, 1 H), 4.58 (dt, J_1 = 5.8 Hz, J_2 = 1.2 Hz, 2H), 2.37 (s, 6H), 2.27 (s, 3H), 1.80 (d, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.5, 145.4, 138.1, 137.8, 131.9, 131.5, 128.4, 119.0, 117.0, 68.7, 21.1, 20.4, 11.1. Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74; Found: C, 74.00 ; H, 7.86.



(*E*)-Allyl 1-mesityl-1-propenyl carbonate (*E*-**66**):

To an oven-dried flask with a stirring bar was added 0.84 mL of diisopropylamine (6 mmol) and 5 mL of dry THF. The solution was cooled to -78 ^{o}C and 2.6 mL of 2.3 M *n*-BuLi in hexane was added. The flask was removed from the dry-ice bath after 5 min and put in an ice-water bath for 10 min with stirring. The solution then was cooled to -78 ^{o}C again and 881 mg of (5 mmol) 2',4',6'-trimethylpropiophenone in 2 mL of THF was added dropwise to the solution over 10 min. The reaction was stirred for 1 h at -78 ^{o}C and 1.28 mL of allyl chloroformate was added in one portion. The reaction mixture was stirred for 2 h and warmed to 0 ^{o}C for another 20 min before the quenching with ammonium chloride saturated aqueous solution. After extraction with ether the combined organic layers were dried over anhydride magnesium sulfate. Concentration *in vacuo* and purification by column chromatography eluting with 2% diethyl ether in petroleum ether gave 0.83 g (64%) colorless oil as a mixture of isomers with a *Z*/*E* ratio of 5/95 by proton NMR.

R_f = 0.47 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2920 (s), 2862 (w), 1758 (s), 1612 (m), 1449 (m), 1381 (m), 1363 (m), 1239 (s), 1198 (s), 1158 (s), 993 (s), 932 (s), 851 cm^{-1} (m); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 6.87 (s, 2H), 5.87 (m, 1H), 5.73 (q, J = 7.2 Hz, 1 H), 5.31 (dq, J_1 = 17.4 Hz, J_2 = 1.4 Hz, 1H), 5.23 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.55 (dt, J_1 = 5.7 Hz, J_2 = 1.3 Hz, 2H), 2.32 (s, 6H), 2.28 (s, 3H), 1.46 (d, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ= 153.3, 146.0, 138.4, 138.1, 131.5, 129.1, 128.3, 119.0, 115.6, 68.6, 21.2, 19.9, 12.2. Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74; Found: C, 73.94 ; H, 7.68.

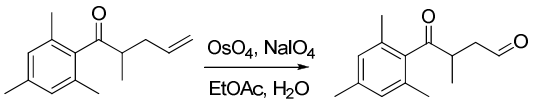


(+)-1-Mesityl-2-methyl-4-penten-1-one (**67**):

The general procedure for the Pd catalyzed DAAA reaction in dioxane was followed employing 78 mg of *E*-**66** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 64 mg of product after purification by flash column chromatography (99%);

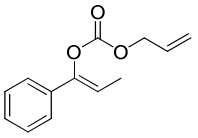
Colorless oil. R_f = 0.47 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +0.5 (c = 2.47, $CHCl_3$, 96% ee);

IR (film): $\tilde{\nu}_{max}$ = 2969 (s), 2921 (s), 1694 (s), 1611 (m), 1456 (m), 1378 (w), 973 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 6.82 (s, 2H), 5.76 (m, 1H), 5.05 (m, 2H), 2.92 (m, 1H), 2.54 (m, 1H), 2.26 (s, 3H), 2.18 (s, 6H), 2.10 (m, 1H), 1.12 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 213.1, 138.8, 138.5, 136.0, 133.5, 128.8, 117.1, 47.3, 36.3, 21.1, 19.8, 15.2. Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32; Found: C, 83.56; H, 9.07. The ee value was determined by the following procedure:



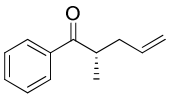
To the solution of 33 mg of **67** (0.15 mmol) in 1 mL of ethyl acetate was added sodium periodate (71 mg of , 0.33 mmol), 4% (w/w) OsO_4 in water (0.1 mL, 0.016 mmol) and 1 mL of water. The reaction mixture was stirred at room temperature for 2 h and then transferred to a separating funnel. After extraction with ether, the combined organic layers were dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography on silica gel eluting with 10% ethyl acetate in petroleum ether to yield 24 mg of 4-mesityl-3-methyl-4-oxobutanal (73%) as colorless oil.

R_f = 0.58 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{24}$ = +24 (c = 24, CH_2Cl_2); HPLC (Chiralcel® OJ column; 99:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 21.43 min (minor), t_2 = 26.84 min (major), 96% ee); IR (film): $\tilde{\nu}_{max}$ = 2973 (s), 2920 (s), 2729 (m), 1732 (s), 1694 (s), 1611 (s), 1456 (m), 1381 (m), 1234 (m), 975 (s), 853 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 9.86 (s, 1H), 6.95 (s, 1H), 3.50 (sextet, J = 7.2 Hz, 1H), 3.02 (ddd, J_1 = 17.7 Hz, J_2 = 6.4 Hz, J_3 = 0.8 Hz, 1H), 2.51 (ddd, J_1 = 17.7 Hz, J_2 = 6.4 Hz, J_3 = 1.2 Hz, 1H), 2.28 (s, 3H), 2.22 (s, 6H), 1.17 (d, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 211.4, 200.5, 138.8, 137.5, 133.6, 128.9, 45.5, 42.5, 21.1, 19.8, 16.1. Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31; Found: C, 76.89; H, 8.17.



(*Z*)-Allyl 1-phenyl-1-propenyl carbonate (**68**):

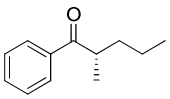
The general procedure for the synthesis of *Z*-enol carbonates was followed employing 2.68 g of propiophenone (20 mmol) to yield 2.22 g product (51%) after purification by flash column chromatography eluting with 2% diethyl ether in petroleum ether. Colorless oil; R_f = 0.50 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3061 (m), 2920 (m), 1760 (s), 1673 (m), 1496 (s), 1446 (s), 1366 (s), 1227 (s), 1186 (s), 966 (s), 765 (s), 693 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.5-7.2 (m, 5H), 5.94 (m, 1H), 5.86 (q, J = 7.2 Hz, 1H), 5.40 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.29 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.68 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 1.77 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.3, 147.4, 134.8, 131.3, 128.6, 128.2, 124.3, 119.2, 113.0, 69.0, 11.3. Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47; Found: C, 71.67 ; H, 6.33.



(*S*)-(+)-2-Methyl-1-phenyl-4-penten-1-one (**69**):

The general procedure for Pd catalyzed DAAA was followed employing 65.5 mg of **68** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 50 mg of product after purification by flash column chromatography eluting with 2% diethyl ether in petroleum ether (96%). Spectral data was identical to the known compound.[24]

Colorless oil; R_f = 0.59 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{25}$ = +39.7 (c = 1.5, CH_2Cl_2); HPLC (Chiralcel® OD-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 14.68 min (minor), t_2 = 16.25 min (major), 94% ee); IR (film): $\tilde{\nu}_{max}$ = 3078 (w), 2976 (m), 2933 (w), 1682 (s), 1642 (w), 1448 (m), 1209 (s), 976 (s), 917 (m), 704 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.96 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 5.79 (m, 1H), 5.03 (m, 2H), 3.54 (sextet, J = 6.8 Hz, 1H), 2.56 (m, 1H), 2.20 (m, 1H), 1.21 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 203.7, 136.5, 135.9, 133.0, 128.7, 128.3, 116.8, 40.5, 37.7, 17.1.

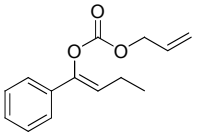


(*S*)-(+)-2-Methyl-1-phenylpentan-1-one:

Carbonate **68** (50 mg, 0.29 mmol) was dissolved in 2 mL of methanol and was added 10 mg of 5% Pd on $CaCO_3$. The reaction flask was sealed and purged with H_2 three times. The reaction mixture was stirred under H_2 balloon at room

temperature for 2 hours. Most solvent was removed *in vacuo* and the crude product was purified by silica gel column chromatography eluting with 2% diethyl ether in petroleum ether. 42 mg of (82%) of colorless oil was obtained. Spectral data was identical to the known compound.[25]

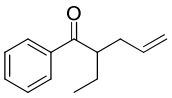
R_f = 0.55 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{25}$ = +25.7 (c = 2.83, EtOH, 94% ee); lit. (*R*)-isomer $[\alpha]_D^{25}$ = -15.8 (EtOH).[26] IR (film): $\tilde{\nu}_{max}$ = 3064 (w), 2961 (s), 2933 (s), 2874 (m), 1682 (s), 1596 (m), 1448 (m), 1241 (m), 1212 (s), 973 (s), 704 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.96 (m, 2H), 7.55 (m, 1H), 7.46 (m, 2H), 3.49 (sextet, *J* = 6.9 Hz, 1H), 1.78 (m, 1H), 1.36 (m, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 204.8, 1367.0, 133.0, 128.8, 128.5, 40.5, 36.1, 20.8, 17.4, 14.4.



(*Z*)-Allyl 1-phenyl-1-butenyl carbonate (**70**):

The general procedure for the synthesis of enol carbonates was followed employing 1.48 g butyrophenone (10 mmol) to yield 2.13 g product (91%) after purification by flash column chromatography eluting with 2% diethyl ether in petroleum ether.

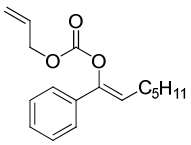
Colorless oil; R_f = 0.51 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3061 (m), 2970 (s), 2937 (m), 1760 (s), 1668 (w), 1496 (m), 1448 (m), 1300 (m), 1225 (s), 1186 (m), 973 (s), 775 (m), 693 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.5-7.2 (m, 5H), 5.94 (m, 1H), 5.78 (t, *J* = 7.2 Hz, 1H), 5.38 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.28 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.67 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.22 (q, *J* = 7.2 Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.0, 146.0, 134.8, 131.3, 128.6, 128.2, 124.3, 120.1, 119.2, 69.0, 19.4, 13.5. Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94; Found: C, 72.59 ; H, 6.81.



(-)-2-Ethyl-1-phenyl-4-penten-1-one (**71**):

The general procedure for the Pd catalyzed DAAA reaction in dioxane was followed employing 70 mg of **70** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 53 mg of product (94%). Spectral data was identical to the known compound.[27]

Colorless oil; R_f = 0.58 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{26}$ = -0.93 (c = 1.95, CH_2Cl_2); HPLC (Chiralcel® OD-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 12.289 min (minor), t_2 = 13.465 min (major), 94% ee); IR (film): $\tilde{\nu}_{max}$ = 3078 (w), 2965 (m), 2929 (m), 1682 (s), 1448 (m), 1222 (m), 1208 (m), 913 (m), 734 (m), 703 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.95 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.75 (m, 1H), 5.00 (m, 2H), 3.45 (pentet, *J* = 6.0 Hz, 1H), 2.52 (m, 1H), 2.27 (m, 1H), 1.81 (m, 1H), 1.61 (m, 1H), 0.88 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 203.7, 137.5, 136.0, 133.0, 128.7, 128.3, 116.7, 47.4, 35.9, 25.0, 11.7.

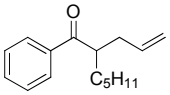


(*Z*)-Allyl 1-phenyl-1-heptenyl carbonate (**72**):

The general procedure for the synthesis of enol carbonates was followed employing 951 mg of 1-phenyl-1-heptanone (5 mmol) to yield 1.29 g product (91%) after purification by flash column chromatography eluting with 2% diethyl ether in petroleum ether.

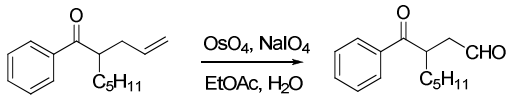
Colorless oil; R_f = 0.49 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2957 (s), 2930 (s), 2859 (s), 1761 (s), 1668 (w), 1496 (m), 1448 (m), 1365.1 (m), 1226 (s), 1186 (m), 965 (s), 770 (m), 693 cm^{-1} (m);

^1H NMR (400 MHz, $CDCl_3$): δ= 7.5-7.2 (m, 5H), 5.95 (m, 1H), 5.79 (t, J = 7.2 Hz, 1H), 5.38 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.29 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.67 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.20 (q, J = 7.2 Hz, 2H), 1.46 (p, J = 7.2 Hz, 2H), 1.33 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.0, 146.4, 134.9, 131.3, 128.6, 128.3, 124.4, 119.2, 118.8, 69.0, 31.6, 28.7, 25.9, 22.5, 14.1. Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08; Found: C, 74.62 ; H, 8.26.



(+)-2-Allyl-1-phenyl-1-heptanone (**73**):

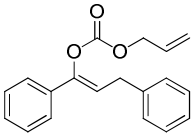
The general procedure for the Pd catalyzed DAAA reaction in dioxane was followed employing 82.3 mg of **72** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 60.5 mg of product (93%) was isolated by column chromatograph and preparative TLC developed with 3% diethyl ether in petroleum ether. Colorless oil. R_f = 0.61 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +1.64 (c = 1.35, CH_2Cl_2, 92% ee); IR (film): $\tilde{\nu}_{max}$ = 3078 (m), 2927 (s), 2858 (s), 1682 (s), 1642 (m), 1448 (m), 1226 (m), 1207 (m), 915 (m), 707 (s), 688 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.95 (m, 2H), 7.56 (tt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.47 (m, 2H), 5.75 (m, 1H), 4.99 (m, 2H), 3.51(m, 1H), 2.51 (m, 1H), 2.26 (m, 1H), 1.77 (m, 1H), 1.53 (m, 1H), 1.25 (m, 6H), 0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 203.9, 137.5, 136.0, 133.0, 128.7, 128.3, 116.7, 45.9, 36.4, 32.02, 31.99, 27.1, 22.5, 14.1. Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63; Found: C, 83.50; H, 9.89. The ee value of **73** was determined by the following procedure:



To the solution of 44 mg of **73** (0.19 mmol) in 1 mL of ethyl acetate was added 96 mg of sodium periodate (0.45 mmol), 0.13 mL of 4% (w/w) OsO_4 in water and 1 mL of water. The reaction mixture was stirred at room temperature for 2 h and then transferred into a separatory funnel . Extracted with ether and the organic layer was combined, dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography on silica gel eluting with 10% ethyl acetate in petroleum ether to yield 30 mg of 3-benzoyloctanal (67%) as colorless oil.

R_f = 0.45 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{25}$ = -51.3 (c = 1.9, CH_2Cl_2); HPLC (Chiralcel® OC column; 90:10 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 8.625 min (major), t_2 = 10.461 min (minor), 92% ee); IR (film): $\tilde{\nu}_{max}$ = 3063 (w), 2931 (s), 2859 (s), 1723 (s), 1682 (s), 1597 (w), 1448 (m), 1385 (m), 1239 (m), 976 (m), 698 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 9.80 (s, 1H), 7.98 (m, 2H), 7.58 (tt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.48 (m, 2H), 3.95 (m, 1H), 3.17 (dd, J_1 = 18.6 Hz, J_2 = 8.8 Hz, 1H), 2.66 (dd, J_1 = 18.6 Hz, J_2 = 4.2 Hz, 1H), 1.70 (m, 1H), 1.48 (m, 1H), 1.24 (m, 6H),

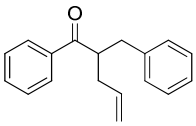
0.84 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 202.6, 200.8, 136.4, 133.2, 128.7, 128.4, 45.4, 40.1, 32.3, 31.7, 26.8, 22.4, 14.0. Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; Found: C, 77.40; H, 8.47.



(*Z*)-allyl 1,3-diphenylprop-1-enyl carbonate (**74**):

The general procedure for the synthesis of enol carbonates was followed employing 1.05 g 1,3-diphenylpropan-1-one (5 mmol) to yield 1.27 g product was obtained (86%) after purification by flash column chromatography eluting with 2% diethyl ether in petroleum ether.

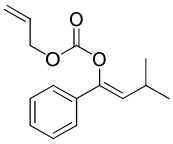
Colorless oil; R_f = 0.36 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3061 (m), 3028 (m), 2949 (w), 1760 (s), 1668 (w), 1495 (s), 1454 (s), 1365 (s), 1294 (s), 1227 (s), 1186 (s), 956 (s), 768 (s), 745 (s), 698 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.5-7.2 (m, 10H), 5.94 (m, 1H), 5.86 (q, J = 7.2 Hz, 1H), 5.38 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.29 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.68 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 3.56 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.9, 146.9, 139.5, 134.5, 131.2, 128.6, 128.5, 126.4, 124.6, 119.4, 117.1, 69.2, 32.2. Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16; Found: C, 77.70 ; H, 5.91.



(-)-2-Benzyl-1-phenylpent-4-en-1-one (**75**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 88.3 mg of **74** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 56 mg of product (75%). Colorless oil; R_f = 0.49 (Diethyl ether/petroleum ether 1:9);

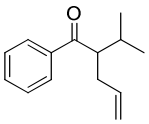
$[\alpha]_D^{24}$ = -44.2 (c = 1.93, $CHCl_3$); HPLC (Chiralcel® AD column; 99:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 7.873 min (minor), t_2 = 8.698 min (major), 88% ee); IR (film): $\tilde{\nu}_{max}$ = 3063 (w), 2923 (w), 2874 (m), 1682 (s), 1448 (m), 1236 (m), 919 (m), 699 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.86 (m, 2H), 7.52 (tt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.41 (m, 2H), 7.3-7.1 (m, 5H), 5.73 (m, 1H), 5.01 (m, 2H), 3.80 (m, 1H), 3.10 (dd, J_1 = 13.7 Hz, J_2 = 7.6 Hz, 1H), 2.81 (dd, J_1 = 13.7 Hz, J_2 = 6.4 Hz, 1H), 2.32 (m, 1H), 2.53 (m, 1H), 2.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 203.1, 139.7, 137.2, 135.3, 133.0, 129.1, 128.6, 128.46, 128.27, 126.3, 117.3, 48.1, 37.7, 36.3. Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25; Found: C, 86.50; H, 7.24.



(*Z*)-Allyl 3-methyl-1-phenyl-1-butenyl carbonate (**76**):

The general procedure for the synthesis of enol carbonates was followed employing 3-methyl-1-phenyl-1-butanone (811 mg, 5 mmol) to yield 1.13 g product was obtained (92%) after purification by flash column chromatography eluting with 2% diethyl ether in petroleum ether.

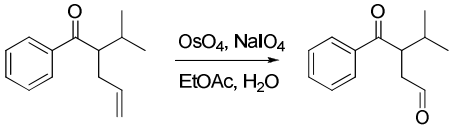
Colorless oil; R_f = 0.54 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2961 (s), 2871 (w), 1761 (s), 1669 (w), 1496 (w), 1448 (w), 1300 (m), 1228 (s), 1188 (m), 973 (s), 771 (m), 693 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.5-7.2 (m, 5H), 5.95 (m, 1H), 5.61 (d, J = 9.6 Hz, 1H), 5.38 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.29 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.67 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 2.74 (m, 1H), 1.07 (d, J = 6.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.1, 144.8, 134.9, 131.3, 128.6, 128.2, 125.4, 124.5, 119.2, 69.0, 26.0, 22.6. Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37; Found: C, 72.90 ; H, 7.20.



2-Allyl-3-methyl-1-phenyl-1-butanone (**77**):

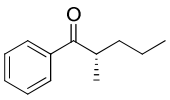
The general procedure for the Pd catalyzed DAAA reaction was followed employing 74 mg of **76** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 60 mg of product (99%). Spectral data was identical to the known compound.[28]

Colorless oil; R_f = 0.60 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3078 (w), 2963 (s), 2874 (m), 1682 (s), 1448 (m), 1209 (m), 1002 (m), 913 (m), 696 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.94 (m, 2H), 7.55 (tt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.46 (m, 2H), 5.71 (m, 1H), 5.01 (m, 1H), 4.91 (m, 1H), 3.36 (m, 1H), 2.56 (m, 1H), 2.32 (m, 1H), 2.06 (m, 1H), 0.94 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 203.9, 138.3, 136.3, 132.9, 128.7, 128.3, 116.4, 52.3, 33.1, 30.5, 29.8, 21.3, 19.5.



To the solution of 36 mg of 2-allyl-3-methyl-1-phyenyl-1-butanone (0.18 mmol) in 1 mL of ethyl acetate was added 85 mg of sodium periodate (0.40 mmol), 0.12 mL of 4% (w/w) OsO_4 in water and 1 mL of water. The reaction mixture was stirred at room temperature for 2 h and then transferred into a separatory funnel . Extracted with ether and the organic layer was combined, dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography on silica gel eluting with 10% ethyl acetate in petroleum ether to yield 35 mg of 3-benzoyl-4-methylpentanal (95%) as colorless oil.

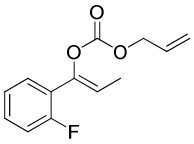
R_f = 0.44 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{22}$ = -30.9 (c = 1.1, CH_2Cl_2, 32% ee); HPLC (Chiralcel® OC column; 90:10 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 10.658 min (major), t_2 = 13.146 min (minor)); IR (film): $\tilde{\nu}_{max}$ = 3062 (w), 2964 (s), 2875 (m), 2729 (m), 1716 (s), 1682 (s), 1597 (m), 1448 (m), 1392 (s), 1248 (s), 1200 (s), 978 (m), 696 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 9.82 (s, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.3 Hz, 2H), 3.87 (ddd, J_1 = 10.2 Hz, J_2 = 4.8 Hz, J_3 = 3.2 Hz, 1H), 3.22 (dd, J_1 = 18.4 Hz, J_2 = 10.2 Hz, 1H), 2.61 (dd, J_1 = 18.4 Hz, J_2 = 3.0 Hz, 1H), 2.10 (m, 1H), 0.98 (d, J = 6.9 Hz, 3H), 0.81 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 202.4, 201.1, 137.1, 133.0, 128.7, 128.4, 45.9, 41.5, 29.8, 21.3, 18.4. Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; Found: C, 76.35; H, 7.90.



(*S*)-(+)-2-Methyl-1-phenylpentan-1-one (**78**):

Carbonate **69** (50 mg of , 0.29 mmol) was dissolved in 2 mL of methanol and was added 10 mg of 5% Pd on $CaCO_3$. The reaction flask was sealed and purged with H_2 three times. The reaction mixture was stirred under H_2 balloon at room temperature for 2 hours. Most solvent was removed *in vacuo* and the crude product was purified by silica gel column chromatography eluting with 2% diethyl ether in petroleum ether. 42 mg of (82%) of colorless oil was obtained. Spectral data was identical to the known compound.[25]

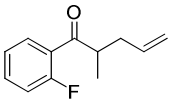
R_f = 0.55 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{25}$ = +25.7 (c = 2.83, EtOH, 94% ee); lit. (*R*)-**3.5** $[\alpha]_D^{25}$ = -15.8 (EtOH).[26] IR (film): $\tilde{\nu}_{max}$ = 3064 (w), 2961 (s), 2933 (s), 2874 (m), 1682 (s), 1596 (m), 1448 (m), 1241 (m), 1212 (s), 973 (s), 704 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.96 (m, 2H), 7.55 (m, 1H), 7.46 (m, 2H), 3.49 (sextet, *J* = 6.9 Hz, 1H), 1.78 (m, 1H), 1.36 (m, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 204.8, 1367.0, 133.0, 128.8, 128.5, 40.5, 36.1, 20.8, 17.4, 14.4.



(*Z*)-Allyl 1-(2'-fluorophenyl)-1-propenyl carbonate (**79**):

The general procedure for the synthesis of enol carbonates was followed employing 761 mg of 2'-fluoropropiophenone (5 mmol) to yield 1.09 g product (93%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

Colorless oil; R_f = 0.45 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3080 (w), 2921 (w), 1763 (s), 1491 (m), 1452 (m), 1365 (w), 1228 (s), 968 (m), 769 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.4-7.0 (m, 4H), 5.95 (m, 2H), 5.38 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.29 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.68 (dt, J_1 = 6.0 Hz, J_2 = 1.3 Hz, 2H), 1.80 (dd, J_1 = 6.8 Hz, J_2 = 0.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 160.8, 158.3, 152.7, 142.14, 142.10, 131.2, 129.65, 129.56, 127.75, 127.72, 124.18, 124.14, 123.0, 119.2, 118.4, 118.3, 116.4, 116.2, 69.1, 11.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ= -114.6. Anal. Calcd. for $C_{13}H_{13}FO_3$: C, 66.09; H, 5.55; F, 8.04; Found: C, 66.00; H, 5.77; F, 8.26.

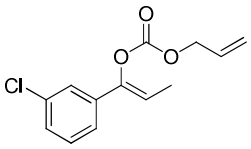


(+)-1-(2'-Fluorophenyl)-2-methyl-4-penten-1-one (**80**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 71 mg of **79** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 46 mg of product (80%).

Colorless oil; R_f = 0.51 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +22 (c = 1.55, CH_2Cl_2); HPLC (Chiralcel® OB-H column; Heptane; flow rate = 1 mL of / min; t_1 = 9.53 min (major), t_2 = 13.96 min (minor), 94% ee); IR (film): $\tilde{\nu}_{max}$ = 3080 (w), 2979 (w), 2936 (w), 1688 (s), 1610 (s), 1480 (m), 1452 (s), 1274 (m), 1211 (m), 976 (s), 977 (m), 756 cm^{-1} (m); ^1H

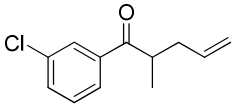
NMR (400 MHz, $CDCl_3$): δ= 7.77 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.50 (m, 1H), 7.24 (m, 1H), 7.12 (ddd, J_1 = 11.6 Hz, J_2 = 8.4 Hz, J_3 = 2.0 Hz, 1H), 5.78 (m, 1H), 5.04 (m, 2H), 3.42 (m, 1H), 2.56 (m, 1H), 2.16 (m, 1H), 1.19 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 202.63, 202.59, 162.5, 160.0, 135.8, 134.2, 134.1, 131.0, 130.9, 126.1, 126.0, 124.61, 124.58, 116.9, 116.8, 116.5, 45.23, 45.17, 37.3, 16.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ=-111.6. Anal. Calcd. for $C_{12}H_{13}FO$: C, 74.98; H, 6.82; F, 9.88; Found: C, 75.30; H, 6.62; F, 9.69.



(*Z*)-Allyl 1-(3'-chlorophenyl)-1-propenyl carbonate (**81**):

The general procedure for the synthesis of enol carbonates was followed employing 843 mg of of 3'-chloropropiophenone (5 mmol) to yield 1.12 g product (89%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

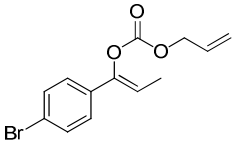
Colorless oil; R_f = 0.35 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3068 (w), 2921 (w), 1761 (s), 1596 (m), 1568 (m), 1365 (m), 1226 (s), 976 (m), 785 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.5-7.2 (m, 4H), 5.97 (m, 1H), 5.89 (q, J = 7.6 Hz, 1H), 5.40 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.31 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.70 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 1.78 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.7, 146.1, 136.7, 134.7, 131.1, 129.9, 128.3, 124.6, 122.5, 119.4, 114.6, 69.2, 11.4. Anal. Calcd. for $C_{13}H_{13}ClO_3$: C, 61.79; H, 5.19; Cl, 14.03; Found: C, 61.85; H, 4.93; Cl, 13.88.



(+)-1-(3'-Chlorophenyl)-2-methyl-4-penten-1-one (**82**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 76 mg of **81** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 61 mg of product (97%).

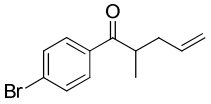
Colorless oil; R_f = 0.65 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +32.7 (c = 2.2, CH_2Cl_2); HPLC (Chiralcel® OJ column; Heptane; flow rate = 1 mL of / min; t_1 = 8.87 min (minor), t_2 = 9.839 min (major), 93% ee); IR (film): $\tilde{\nu}_{max}$ = 3077 (w), 2977 (w), 2934 (w), 1688 (s), 1571 (w), 1237 (w), 1205 (m), 993 cm^{-1} (w); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.92 (t, J = 2.0 Hz, 1H), 7.82 (m, 1H), 7.53 (ddd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, J_3 = 1.2 Hz, 1H), 7.42 (m, 1H), 5.77 (m, 1H), 5.04 (m, 2H), 3.48 (sextet, J = 6.4 Hz, 1H), 2.55 (m, 1H), 2.20 (m, 1H), 1.21 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 202.4, 138.1, 135.5, 135.1, 132.9, 130.1, 128.5, 126.4, 117.1, 40.7, 37.5, 17.0. Anal. Calcd. for $C_{12}H_{13}ClO$: C, 69.07; H, 6.28; Cl, 16.99; Found: C, 68.96; H, 6.13; Cl, 17.16.



(*Z*)-Allyl 1-(4'-bromophenyl)-1-propenyl carbonate (**83**):

The general procedure for the synthesis of enol carbonates was followed employing 1.06 g of 4'-bromopropiophenone (5 mmol) to yield 1.42 g product (98%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

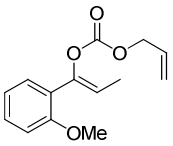
Colorless oil; R_f = 0.34 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3086 (w), 2919 (w), 1760 (s), 1671 (w), 1590 (m), 1487 (s), 1365 (m), 1224 (s), 966 (s), 825 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.46 (dt, J_1 = 9.2 Hz, J_2 = 2.2 Hz, 2H), 7.29 (dt, J_1 = 9.2 Hz, J_2 = 2.2 Hz, 2H), 5.96 (m, 1H), 5.86 (q, J = 7.6 Hz, 1H), 5.40 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.31 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.68 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 1.76 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.7, 146.5, 133.8, 131.7, 131.1, 126.0, 122.3, 119.4, 113.9, 69.2, 11.4. Anal. Calcd. for $C_{13}H_{13}BrO_3$: C, 52.55; H, 4.41; Br, 26.89; Found: C, 52.70; H, 4.41; Br, 27.00.



(+)-1-(4'-Bromophenyl)-2-methyl-4-penten-1-one (**84**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 89 mg of **83** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 71.5 mg of product (94%).

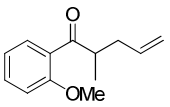
Colorless oil; R_f = 0.56 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{26}$ = +21.8 (c = 1.5, CH_2Cl_2); HPLC (Chiralcel® OJ column; Heptane; flow rate = 1 mL of / min; t_1 = 12.35 min (minor), t_2 = 14.35 min (major), 93% ee); IR (film): $\tilde{\nu}_{max}$ = 3077 (w), 2977 (w), 2934 (w), 1682 (s), 1585 (s), 1397 (m), 1206 (m), 1071 (m), 976 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.82 (m, 2H), 7.62 (m, 2H), 5.76 (m, 1H), 5.04 (m, 2H), 3.47 (sextet, J = 6.8 Hz, 1H), 2.54 (m, 1H), 2.20 (m, 1H), 1.20 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 202.7, 135.6, 135.2, 132.0, 129.9, 128.2, 117.0, 40.5, 37.6, 17.0. Anal. Calcd. for $C_{12}H_{13}BrO$: C, 56.94; H, 5.18; Br, 31.57; Found: C, 57.08; H, 5.08; Br, 31.80.



(*Z*)-Allyl 1-(2'-methoxyphenyl)-1-propenyl carbonate (**85**):

The general procedure for the synthesis of enol carbonates was followed employing 1.27 g of 2'-methoxypropiophenone (7.7 mmol) to yield 1.12 g product (59%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

Colorless oil; R_f = 0.22 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3078 (m), 2947 (s), 1760 (s), 1599 (m), 1494 (s), 1456 (s), 1366 (m), 1223 (s), 964 (m), 754 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.34 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.26 (m, 1H), 6.90 (m, 2H), 5.94 (m, 2H), 5.37 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.27 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.66 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 3.17 (s, 3 H), 1.77 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 156.8, 152.8, 144.8, 131.5, 129.4, 128.5, 124.0, 120.5, 118.9, 116.9, 111.2, 68.8, 55.6, 11.5. Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50; Found: C, 67.57; H, 6.65.

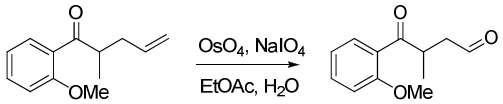


(-)-1-(2-Methoxyphenyl)-2-methyl-4-penten-1-one (**86**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 61 mg of **85** (0.30 mol) to yield 50 mg of product (99%).

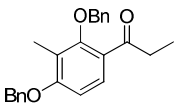
Colorless oil; R_f = 0.32 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -0.33 (c = 5.0, CH_2Cl_2, 98% ee);

IR (film): $\tilde{\nu}_{max}$ = 3076 (m), 2976 (m), 2921 (m), 1674 (s), 1597 (s), 1485 (s), 1464 (s), 1285 (s), 1245 (s), 1024 (m), 976 (m), 755 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.23 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.43 (m, 1H), 6.97 (m, 2H), 5.77 (m, 1H), 5.00 (m, 2H), 3.88 (s, 3H), 3.50 (m, 1H), 2.52 (m, 1H), 1.12 (m, 1H), 1.14 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 207.1, 157.9, 136.4, 132.9, 130.2, 129.0, 120.8, 116.4, 111.4, 55.5, 45.1, 37.5, 16.0. Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; Found: C, 76.46; H, 8.01. The ee value was determined by the following procedure:



To the solution of 50 mg of **87** (0.24 mmol) in 1 mL of ethyl acetate was added 113 mg of sodium periodate (0.53 mmol), 0.15 mL of 4% (w/w) OsO_4 in water and 1 mL of water. The reaction mixture was stirred at room temperature for 2 h and then transferred into a separatory funnel . Extracted with ether and the organic layer was combined, dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography on silica gel eluting with 10% ethyl acetate in petroleum ether to yield 21 mg of 3-benzoyl-4-methylpentanal (42%) as colorless oil.

R_f = 0.31 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{23}$ = +38.3 (c = 2.1, CH_2Cl_2); HPLC (Chiralcel® OC column; 90:10 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 22.601 min (major), t_2 = 29.465 min (minor), 98% ee); IR (film): $\tilde{\nu}_{max}$ = 2972 (m), 2934 (m), 1726 (s), 1667 (s), 1598 (s), 1485 (s), 1463 (s), 1285 (s), 1245 (s), 1022 (m), 979 (m), 756 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.82 (t, J = 1.2 Hz, 1H), 7.65 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.47 (ddd, J_1 = 10 Hz, J_2 = 7.6 Hz, J_3 = 2.0 Hz,, 1H), 7.00 (m, 2H), 3.98 (sextet, J = 7.2 Hz, 1H), 3.90 (s, 3H), 3.01 (ddd, J_1 = 17.2 Hz, J_2 = 10.8 Hz, J_3 = 1.2 Hz, 1H), 2.50 (ddd, J_1 = 17.2 Hz, J_2 = 6.4 Hz, J_3 = 1.6 Hz, 1H), 1.19 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 204.8, 201.2, 158.0, 133.5, 130.7, 127.5, 120.9, 111.5, 55.6, 46.9, 40.3, 16.9. Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; Found: C, 69.68; H, 6.69.

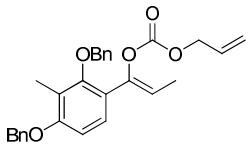


1-(2,4-Bis(benzyloxy)-3-methylphenyl)propan-1-one:

1.81 g 2',4'-Dihydroxy-3'-methylpropiophenone (10 mmol) was dissolved in 50 mL of anhydrous DMF and the resulting solution was stirred in an ice-bath for 5 min. To the solution was added 840 mg of sodium hydride (21 mmol, 60% in mineral oil) in small portions and was stirred for another 10 min. Benzyl bromide (2.5 mL, 21 mmol) was added to the reaction mixture and stirred for 4 h at 0 °C. It was warmed to room temperature and stirred overnight. The reaction mixture was diluted with 150 mL of water and extracted three times with 100 mL of diethyl ether. The combined organic layers were washed with 100 mL of water and 100 mL of brine twice. It was dried over anhydrous $MgSO_4$ and concentrated. The

residue was purified with flash column chromatography eluting with 10% ethyl acetate in petroleum ether to afford 3.54 g of a colorless oil (98%).

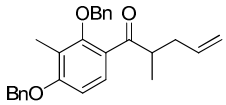
H NMR (400 MHz, $CDCl_3$): δ= 7.50 (d, *J* = 8.7 Hz, 1H), 7.46-7.30 (m, 10H), 6.75 (d, *J* = 8.7 Hz, 1H), 5.13 (s, 2H), 4.83 (s, 2H), 2.96 (q, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.1, 160.6, 157.1, 136.8, 136.7, 128.6, 128.6, 128.2, 128.1, 128.0, 127.1, 126.9, 121.0, 107.3, 76.9, 70.2, 35.6, 9.5, 8.7.



(Z)-Allyl 1-(2,4-bis(benzyloxy)-3-methylphenyl)prop-1-enyl carbonate (**87**):

The general procedure for the synthesis of allyl enol carbonate was followed employing 1-(2,4-bis(benzyloxy)-3-methylphenyl)propan-1-one (1.38 g, 3.83 mmol) to produce 1.22 g product (72%) after the purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

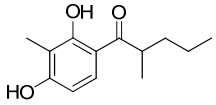
Colorless oil; R_f = 0.27 (diethylether/ petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2919 (s), 1756 (s), 1598 (s), 1497 (s), 1454 (s), 1373 (s), 1310 (s), 1227 (s), 1184 (s), 1100 (s), 974 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.50-7.28 (m, 10 H), 7.20 (d, *J* = 8.7 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 5.99-5.87 (m, 2H), 5.36 (ddd, *J* = 17.2, 1.4, 1.4 Hz, 1H), 5.26 (ddd, *J* = 10.4, 1.4, 1.4 Hz, 1H), 5.07 (s, 2H), 4.91 (s, 2H), 4.62 (m, 2H), 2.21 (s, 3H), 1.74 (d, *J* = 7.0 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 155.2, 153.0, 144.2, 137.7, 137.2, 131.4, 128.6, 128.4, 128.3, 127.9, 127.9, 127.1, 125.5, 121.9, 121.3, 118.9, 115.4, 107.3, 74.2, 70.1, 68.8, 11.4, 9.5. Anal. Calcd. for $C_{28}H_{28}O_5$: C, 75.65; H, 6.35; Found: C, 75.65; H, 6.35.



(+)-1-(2,4-Bis(benzyloxy)-3-methylphenyl)-2-methylpent-4-en-1-one (**88**):

The general procedure for the Pd catalyzed DAAA of enol carbonates was followed employing 133.4 mg of **87** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to afford 93.7 mg of product was isolated (78%).

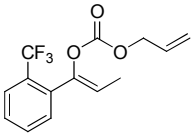
Colorless oil; R_f = 0.19 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +2.5 (c, 2.08, DCM); HPLC (Chiralcel® AD column; 97:3 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 12.65 min (major), t_2 = 13.79 min (minor), 92% ee); IR (film): $\tilde{\nu}_{max}$ = 2974 (s), 1682 (s), 1592 (s), 1455 (s), 1372 (s), 1273 (s), 1247 (s), 1102 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.47-7.30 (m, 11 H), 6.60 (d, *J* = 8.7 Hz, 1H), 5.68 (m, 1H), 5.12 (s, 2H), 4.96 (m, 2H), 4.81 (s, 2H), 3.54 (m, 1H), 3.47 (q, *J* = 7.0 Hz, 1H), 2.44 (m, 1H), 2.22 (s, 3H), 2.08 (m, 1H), 1.21 (t, *J* = 7 Hz, 1H), 1.08 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.38, 160.45, 156.79, 136.81, 136.73, 136.12, 128.67, 128.60, 128.27, 128.26, 128.10, 128.07, 127.20, 126.86, 121.05, 116.65, 107.40, 77.14, 70.26, 65.92, 44.24, 37.55, 16.42, 15.35, 9.54. Anal. Calcd. for $C_{27}H_{28}O_3$: C, 80.97; H, 7.05; Found: C, 81.08; H, 6.97.



1-(2,4-Dihydroxy-3-methylphenyl)-2-methylpentan-1-one (**99**):

A flask was charged with a magnetic stirring bar, 68 mg of **88** (0.17 mmol), 18 mg of 10%(w/w) Pd/C and 2 mL of methanol. It was purged with nitrogen three times then hydrogen three times. The reaction was vigorously stirred for 4 h under a hydrogen balloon at room temperature. The reaction mixture was filtered through a short pad of celite and concentrated. The residue was purified by flash column chromatography on silica gel eluting with 15% ethyl acetate in petroleum ether to yield 37 mg of product (98%).

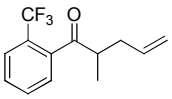
Colorless oil; R_f = 0.0.5 (30% ethyl acetate in petroleum); $[\alpha]_D^{27}$ = +28.2 (c, 1.65; DCM, 94% ee); IR (film): $\tilde{\nu}_{max}$ = 3367 (s), 2960 (s), 1614 (s), 1502 (s), 1252 (s), 1093 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$): δ= 7.58 (d, *J* = 8.8 Hz, 1H), 6.38 (d, *J* = 8.8 Hz, 1H), 5.55 (s, 1H), 3.44 (sextet, *J* = 6.8 Hz, 1H), 3.47 (q, *J* = 7.0 Hz, 1H), 2.14 (s, 3H), 1.77 (m, 1H), 1.45 (m, 1H), 1.33 (m, 2H), 1.20 (d, *J* = 6.8 Hz, 1H), 0.91 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 209.5, 163.8, 160.1, 128.9, 112.9, 111.4, 106.8, 39.5, 36.3, 20.6, 17.7, 14.2, 7.4.



(*Z*)-Allyl 1-(2'-(trifluoromethyl)phenyl)-1-propenyl carbonate (**89**):

The general procedure for the synthesis of enol carbonates was followed employing 1.01 g of 2'-trifluoromethylpropiophenone (5 mmol) to yield 1.24 g product (87%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

Colorless oil; R_f = 0.32 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3078 (w), 2921 (w), 1760 (s), 1450 (s), 1366 (s), 1316 (s), 1232 (s), 1171 (s), 1133 (s), 968 (s), 769 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.7-7.4 (m, 4H), 5.89 (m, 1H), 5.49 (q, *J* = 7.0 Hz, 1H), 5.33 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.25 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.60 (dt, J_1 = 6.0 Hz, J_2 = 1.3 Hz, 2H), 1.79 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.8, 145.6, 132.1, 131.9, 131.4, 129.0, 126.54, 126.48, 126.43, 122.4, 119.3, 118.1, 69.2, 11.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ= -60.1. Anal. Calcd. for $C_{14}H_{13}F_3O_3$: C, 58.74; H, 4.58; F, 19.91; Found: C, 59.00; H, 4.36; F, 20.21.

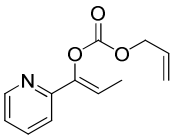


(+)-2-Methyl-1-(2'-(trifluoromethyl)phenyl)-4-penten-1-one (**90**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 86 mg of **89** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 68 mg of product (94%).

Colorless oil; R_f = 0.37 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{22}$ = +11.1 (c = 2.40, $CHCl_3$); HPLC (Chiralcel® OD-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 22.792 min (minor), t_2 = 24.434 min (major), 92% ee); IR (film): $\tilde{\nu}_{max}$ = 3080 (w), 3079 (w), 2980 (m), 2937 (w), 1705 (s), 1458 (m), 1314 (s), 1274 (m), 1170 (s), 1135 (s), 1063 (m), 975 (m), 769 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.72 (dd, J_1 = 7.6 Hz, J_2 = 0.5 Hz, 1H), 7.58 (m, 1H), 7.43 (dd, J_1 = 7.2 Hz, J_2 = 1.0 Hz, 1H), 5.76 (m, 1H), 5.08 (m, 2H), 3.16 (sextet, *J* = 7.0 Hz, 1 H), 2.54 (m, 1H), 2.15 (m, 1H), 1.16 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 207.2, 135.7, 131.9, 130.3, 127.6, 127.23, 127.17, 127.13, 122.4,

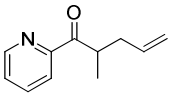
117.5, 45.8, 36.9, 16.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ=-58.3. Anal. Calcd. for $C_{13}H_{13}F_3O$: C, 64.46; H, 5.41; F, 23.53; Found: C, 64.52; H, 5.26; F, 23.68.



(*Z*)-Allyl 1-(2-pyridinyl)-1-propenyl carbonate (**91**):

The general procedure for the synthesis of enol carbonates was followed employing 1.27 g of 676 mg of of 1-(2-pyridinyl)-1-propanone[29] (5 mmol) to yield 700 mg of product (64%) after purification by flash column chromatography eluting with 10-20% ethyl acetate in petroleum ether.

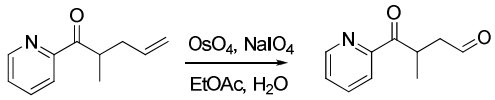
Colorless oil; R_f = 0.36 (30% EtOAc in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3056 (w), 2949 (w), 1760 (s), 1675 (m), 1585 (m), 1471 (m), 1434 (m), 1282 (s), 1230 (s), 976 (s), 781 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.56 (m, 1H), 7.66 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.17 (ddd, J_1 = 7.6 Hz, J_2 = 5.0 Hz, J_3 = 1 Hz, 1H), 6.64 (q, J = 7.4 Hz, 1 H), 5.98 (m, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.31 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.72 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 1.84 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.9, 151.9, 149.4, 146.5, 136.7, 122.7, 119.3, 118.3, 116.5, 69.2, 11.4. Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39; Found: C, 65.62; H, 5.89; N, 6.52.



(+)-2-Methyl-1-(2-pyridinyl)-4-penten-1-one (**92**):

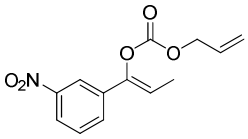
The general procedure for the Pd catalyzed DAAA reaction was followed employing 66 mg of **91** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 50 mg of product (95%).

Colorless oil; R_f = 0.33 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +26.3 (c = 2.4, CH_2Cl_2, 73% ee); IR (film): $\tilde{\nu}_{max}$ = 3077 (m), 2976 (s), 2934 (m), 1694 (s), 1583 (m), 1455 (m), 1436 (m), 1355 (m), 1266 (m), 1216 (m), 996 (s), 981 (s), 746 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.69 (m, 1H), 8.04 (m, 1H), 7.84 (ddd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, J_3 = 1.8 Hz, 1H), 7.47 (m, 1H), 5.80 (m, 1H), 5.00 (m, 2H), 4.18 (sextet, J = 7.2 Hz, 1 H), 2.56 (m, 1H), 2.23 (m, 1H), 1.20 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 204.9, 153.0, 149.0, 137.0, 136.1, 127.0, 122.5, 116.5, 38.9, 37.2, 16.5. Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99; Found: C, 75.21; H, 7.45; N, 7.76. The ee value was determined by the following procedure:



To the solution of 23 mg of 2-methyl-1-(2-pyridinyl)-4-penten-1-one (0.13 mmol) in 1 mL of ethyl acetate was added 61mg sodium periodate (0.28 mmol), 0.085 mL of 4% (w/w) OsO_4 in water and 1 mL of water. The reaction mixture was stirred at room temperature for 2 h and then transferred into a separatory funnel . Extracted with ether and the organic layer was combined, dried over magnesium sulfate and concentrated. The crude product was purified by column chromatography on silica gel eluting with 10% ethyl acetate in petroleum ether to yield 19 mg of 3-methyl-4-oxo-4-(pyridin-2-yl)butanal (87%) as colorless oil.

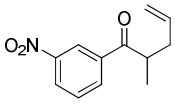
R_f = 0.28 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{23}$ = +1.6 (c = 0.7, CH_2Cl_2); HPLC (Chiralcel® OC column; 90:10 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 18.79 min (major), t_2 = 22.55 min (minor), 73% ee); IR (film): $\tilde{\nu}_{max}$ = 3056 (w), 2972 (m), 2934 (m), 2829 (m), 2727 (m), 1716 (s), 1698 (s), 1583 (s), 1456 (s), 1378 (s), 1267 (m), 1233 (s), 996 (s), 747 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.80 (s, 1H), 8.71 (dq, J_1 = 4.8 Hz, J_2 = 0.9 Hz, 1H), 8.05 (m, J_1 = 8.0 Hz, J_2 = 0.9 Hz, 1H), 7.85(td, J_1 = 7.6 Hz, J_2 = 1.8 Hz, 1H), 7.48 (ddd, J_1 = 7.5 Hz, J_2 = 4.8 Hz, J_3 = 1.2 Hz, 1H), 4.54 (m, 1H), 3.12 (ddd, J_1 = 18.2 Hz, J_2 = 8.4 Hz, J_3 = 0.8 Hz, 1H), 2.63 (ddd, J_1 = 18.2 Hz, J_2 = 5.4 Hz, J_3 = 1.2 Hz, 1H), 1.27 (d, J = 8.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 203.4, 200.8, 152.3, 149.1, 137.1, 127.6, 122.7, 47.2, 34.3. 17.4. Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90; Found: C, 68.00; H, 6.50; N, 8.06.



(*Z*)-Allyl 1-(3'-nitrophenyl)-1-propenyl carbonate (**93**):

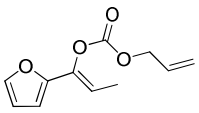
The general procedure for the synthesis of enol carbonates was followed employing 896 mg of 3'-nitropropiophenone (5 mmol) to yield 1.23 g product (94%) after purification by flash column chromatography eluting with 10% diethyl ether in petroleum ether.

Colorless oil; R_f = 0.17 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3089 (w), 2901 (w), 1760 (s), 1671 (w), 1532 (s), 1447 (m), 1352 (s), 1223 (s), 976 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.28 (t, J = 2.0 Hz, 1H), 8.14 (ddd, J_1 = 8.3 Hz, J_2 = 2.1 Hz, J_2 = 1 Hz, 1H), 7.74 (ddd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, J_2 = 1.1 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 6.05 (q, J = 7.0 Hz, 1H), 5.88 (m, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.33 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.72 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 1.83 (d, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.6, 148.5, 145.3, 136.6, 131.0, 130.0, 129.7, 122.8, 119.6, 119.3, 116.3, 69.4, 11.5. Anal. Calcd. for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32; Found: C, 59.10; H, 4.88; N, 5.12.



(+)-2-Methyl-1-(3'-nitrophenyl)-4-penten-1-one (**94**):

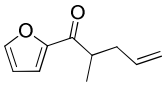
The general procedure for the Pd catalyzed DAAA reaction was followed employing 79 mg of **93** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 54 mg of product (83%). Colorless oil; R_f = 0.31 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +27.2 (c = 1.3, $CHCl_3$); HPLC (Chiralcel® AD column; 99:1 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 10.65 min (minor), t_2 = 12.69 min (major), 82% ee); IR (film): $\tilde{\nu}_{max}$ = 3082 (w), 2978 (w), 2935 (w), 1694 (s), 1614 (m), 1532 (s), 1350 (s), 1208 (m), 1001 (m), 919 (m), 716 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.28 (t, J = 2.0 Hz, 1H), 8.13 (ddd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, J_3 = 1.0 Hz, 1H), 7.74 (ddd, J_1 = 7.9 Hz, J_2 = 1.8 Hz, J_3 = 1.0 Hz, 1H), 7.52 (t, J = 8.2 Hz, 1H), 6.05 (q, J = 7.0 Hz, 1H), 5.96 (m, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.33 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.72 (dt, J_1 = 5.8 Hz, J_2 = 1.4 Hz, 1H), 1.83 (d, J = 7.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 201.4, 148.6, 137.8, 135.2, 134.0, 130.1, 127.3, 123.2, 117.5, 40.9, 37.5, 17.0. Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39;; Found: C, 66.00; H, 5.86; N, 6.45.



(*Z*)-Allyl 1-(2-furanyl)-1-propenyl carbonate (**95**):

The general procedure for the synthesis of enol carbonates was followed employing 621 mg of 1-(2-furanyl)-1-propanone (5 mmol) to yield 0.86 g product (83%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

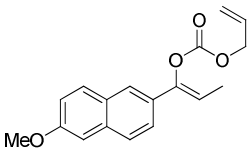
Colorless oil; R_f = 0.43 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3156 (w), 2987 (w), 2920 (w), 2862 (w), 1770 (s), 1686 (w), 1494 (m), 1448 (m), 1365 (m), 1224 (s), 1162 (s), 978 (s), 739 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.34 (d, J = 1.8 Hz, 1H), 6.36 (dd, J_1 = 3.4 Hz, J_2 = 1.8 Hz, 1H), 6.26 (d, J = 3.4 Hz, 1H), 5.97 (m, 1H), 5.89 (q, J = 7.3 Hz, 1H), 5.41 (dq, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 5.32 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.72 (dt, J_1 = 5.6 Hz, J_2 = 1.3 Hz, 2H), 1.74 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.7, 148.8, 142.5, 139.5, 131.2, 119.4, 111.9, 111.3, 106.8, 69.3, 10.7. Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81; Found: C, 63.24; H, 5.62.



(+)-1-(2-Furanyl)-2-methyl-4-penten-1-one (**96**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 62.5 mg of **95** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 44 mg of product (89%).

Colorless oil; R_f = 0.29 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +30.2 (c = 2.64, CH_2Cl_2); GC (Cyclosil B® column; 90 °C isothermal; 1.2 flow rate; t_1 = 47.567 min (minor), t_2 = 48.202 min (major), 88% ee); IR (film): $\tilde{\nu}_{max}$ = 3134 (w), 3079 (w), 2976 (m), 2934 (m), 1672 (s), 1567 (s), 1467 (s), 1395 (m), 1262 (m), 1015 (m), 983 (m), 761 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.57 (dd, J_1 = 1.7 Hz, J_2 = 0.8 Hz, 1H), 7.18 (dd, J_1 = 3.5 Hz, J_2 = 0.8 Hz, 1H), 6.51 (dd, J_1 = 3.5 Hz, J_2 = 1.7 Hz, 1H), 5.74 (m, 1H), 5.00 (m, 2H), 3.30 (sextet, J = 7.0 Hz, 1 H), 2.52 (m, 1H), 2.18 (m, 1H), 1.18 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 192.7, 152.4, 146.4, 135.7, 117.4, 116.9, 112.2, 41.3, 37.4, 16.7. Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37; Found: C, 72.96; H, 7.37.

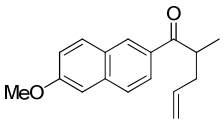


(*Z*)-Allyl 1-(6'-methoxy-2-naphthalenyl)-1-propenyl carbonate (**97**):

The general procedure for the synthesis of enol carbonates was followed employing 11.07 g 1-(6-methoxy-2-naphthalenyl)-1-propanone (5 mmol) to yield 1.45 g product (97%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

White crystals; Mp = 86 °C; R_f = 0.33 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2941 (w), 1761 (s), 1228 (s), 1192 (s), 1168 (m), 981 (m), 858 (m), 820 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.77 (s, 1H), 7.70 (dd, J_1 = 11.6 Hz, J_2 = 8.8 Hz, 2H), 7.54 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.12 (m, 2H), 5.98 (m, 1H), 5.95 (q, J = 7.6 Hz, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 0.8 Hz, 1H), 5.31 (dq, J_1 = 10.4 Hz, J_2 = 0.8 Hz, 1H), 4.71 (d, J = 6.0 Hz, 2H), 3.90 (s, 3H), 1.82 (d, J = 7.2

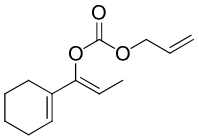
Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 158.0, 152.9, 147.5, 134.4, 131.3, 129.95, 129.91, 128.7, 127.2, 123.05, 123.00, 119.3, 119.2, 112.7, 105.7, 69.1, 55.4, 11.5. Anal. Calcd. for $C_{18}H_{18}O_3$: C, 72.47; H, 6.08; Found: C, 72.62 ; H, 6.15.



(+)-1-(6'-Methoxy-2-naphthalenyl)-2-methyl-4-penten-1-one (**98**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 89.5 mg of **97** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 69 mg of product (90%).

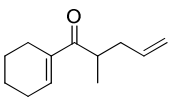
Colorless oil; R_f = 0.25 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +7.4 (c = 1.54, CH_2Cl_2); HPLC (Chiralcel® OJ column; 90:10 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 14.17 min (major), t_2 = 18.47 min (minor), 95% ee); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2974 (m), 2935 (m), 1674 (s), 1626 (s), 1482 (s), 1269 (s), 1196 (s), 1030 (m), 916 (m), 812 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.40 (d, *J* = 1.6 Hz, 1H), 8.01 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.20 (dd, J_1 = 8.8 Hz, J_2 = 1.8 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 5.83 (m, 1H), 5.04 (m, 2H), 3.94 (s, 3H), 3.68 (sextet, *J* = 6.8 Hz, 1H), 2.62 (m, 1H), 2.25 (m, 1H), 1.26 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 203.4, 159.8, 137.3, 136.0, 131.8, 131.2, 129.7, 127.9, 127.3, 125.1, 119.8, 116.8, 105.7, 55.5, 40.3, 37.9, 17.4. Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13; Found: C, 80.48; H, 6.99.



(*Z*)-Allyl 1-cyclohexenyl-1-propenyl carbonate (**2**):

The general procedure for the synthesis of enol carbonates was followed employing 520 mg of 1-cyclohexenyl-1-propanone (3.76 mmol). However, instead of transferring the enolate into allyl chloroformate, allyl chloroformate was added rapidly in one portion into the enolate solution. 0.70 g product was obtained (84%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

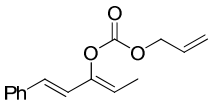
Colorless oil; R_f = 0.41 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3047 (w), 2931 (s), 2861 (s), 1760 (s), 1664 (m), 1448 (s), 1364 (s), 1304 (s), 1248 (s), 1216 (s), 977 (s), 928 (s), 805 (s), 781 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.97 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.87 (bs, 1H), 5.40 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.35 (qd, J_1 = 7.0 Hz, J_2 = 0.8 Hz, 1H), 5.30 (dq, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1H), 4.69 (dt, J_1 = 5.8 Hz, J_2 = 1.4 Hz, 2H), 2.13 (m, 4H), 1.71-1.54 (m, 4H), 1.64 (dd, J_1 = 7.2 Hz, J_2 = 0.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 153.1, 148.7, 131.7, 130.4, 123.7, 119.2, 110.2, 69.0, 25.4, 24.8, 22.6, 22.2, 11.2. Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16; Found: C, 70.50; H, 7.97.



(+)-1-Cyclohexenyl-2-methyl-4-penten-1-one (**100**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 67 mg of **2** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 45.6 mg of product (85%).

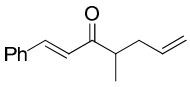
Colorless oil; R_f = 0.57 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{22}$ = +29.8 (c = 3.1, CH_2Cl_2); HPLC (Chiralcel® OB-H column; 97:3 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 4.710 min (major), t_2 = 5.709 min (minor), 88% ee); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2973 (s), 2934 (s), 2861 (s), 1665 (s), 1637 (s), 1450 (m), 1435 (m), 1387 (w), 1197 (s), 988 (s), 912 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 6.90 (m, 1H), 5.72 (m, 1H), 5.00 (m, 2H), 3.24 (sextet, *J* = 6.9 Hz, 1H), 2.40 (m, 1H), 2.24 (m, 4H), 2.07 (m, 1H), 1.62 (m, 4H), 1.07 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 204.8, 139.4, 138.6, 136.3, 116.3, 38.8, 38.1, 26.2, 23.4, 22.1, 21.6, 17.6. Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18; Found: C, 81.08; H, 10.40.



Allyl (1*E*,3*Z*)-1-phenylpenta-1,3-dien-3-yl carbonate (**101**):

The general procedure for the synthesis of enol carbonates was followed employing 801 mg of (*E*)-1-phenyl-1-penten-3-one (5 mmol). However, instead of transferring the enolate into allyl chloroformate, allyl chloroformate was added rapidly in one portion into the enolate solution. 1.10 g product was obtained (90%) after purification by flash column chromatography eluting with 5% diethyl ether in petroleum ether.

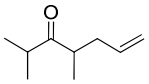
Colorless oil; The Z/E ratio is 25/1 by ^1H-NMR. R_f = 0.33 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3026 (m), 2948 (m), 1760 (s), 1660 (m), 1449 (s), 1366 (s), 1231 (s), 957 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.39 (m, 2H), 7.31 (m, 2H), 7.22 (m, 1H), 6.62 (d, *J* = 16 Hz, 1H), 6.54 (d, *J* = 16 Hz, 1H), 6.00 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.52 (q, *J* = 7.2 Hz, 1H), 5.44 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.33 (dq, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1H), 4.74 (dt, J_1 = 5.8 Hz, J_2 = 1.4 Hz, 2H), 1.73 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ= 152.5, 147.2, 136.5, 131.3, 128.7, 127.9, 127.3, 126.7, 122.8, 119.3, 117.8, 69.1, 11.5. Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; Found: C,73.78; H, 6.41.



(*E*)-4-Methyl-1-phenyl-1,6-heptadien-3-one (**102**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 73.3 mg of **101** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in dioxane (3 mL) to yield 56 mg of product (93%).

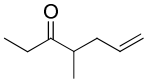
Colorless oil; R_f = 0.37 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -20.0 (c = 3.3, CH_2Cl_2, 91% ee); HPLC (Chiralcel® OD-H column; 99.5:0.5 Heptane / Isopropanol; flow rate = 1 mL of / min; t_1 = 18.680 min (minor), t_2 = 21.179 min (major)); IR (film): $\tilde{\nu}_{max}$ = 3079 (m), 2974 (s), 2932 (m), 1688 (s), 1661 (s), 1613 (s), 1577 (s), 1450 (s), 1187 (s), 1054 (s), 990 (s), 916 (s), 762 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.61 (d, *J* = 16.0 Hz, 1H), 7.56 (m, 2H), 7.39 (m, 3H), 6.81 (d, *J* = 16.0 Hz, 1H), 5.78 (m, 1H), 5.05 (m, 2H), 2.93 (sextet, *J* = 6.9 Hz, 1H), 2.51 (m, 1H), 2.18 (m, 1H), 2.07 (m, 1H), 1.18 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 203.0, 142.7, 135.8, 134.7, 130.5, 129.0, 128.4, 124.9, 116.8, 44.4, 37.3, 16.4. Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05; Found: C, 83.71; H, 8.25.



(-)-2,4-Dimethylhept-6-en-3-one (**103**):

The general procedure for the Pd catalyzed DAAA of enol carbonates was followed employing 56 mg of *E*-**16** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in toluen (3 mL) to afford 13.9 mg of product was isolated (33%) as volatile colorless oil. Spectral data was identical to the known compound.[30]

R_f = 0.25 (diethylether/ petroleum ether 1:49); $[\alpha]_D^{24.5}$ = -33.6 (c, 0.59; CH_2Cl_2); Chiral GC (Cyclo Sil-B; 55°C; 1.2 mL/ min flow rate; t_1 = 27.49 min (major), t_2 = 28.74 min (minor), 94% ee); IR (film): $\bar{\nu}_{max}$ = 3079 (w), 2970 (s), 2933 (s), 2876 (s), 2361 (w), 1747 (w), 1712 (s), 1641 (m), 1466 (s), 1383 (m), 1259 (w), 1014 (m), 915 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ= 5.70 (m, 1H), 5.05- 4.95 (m, 2H), 2.80- 2.67 (m, 2H), 2.37 (m, 1H), 2.05 (m, 1H), 1.08- 1.04 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 218.0, 136.1, 116.9, 44.4, 39.9, 37.6, 18.5, 18.3, 16.8.

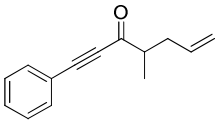


4-Methylhept-6-en-3-one (**104**):

The general procedure for the Pd catalyzed DAAA reaction was followed employing 85.1 mg of *E*-**17** (0.5 mmol). Since the product is very volatile toluene was used as solvent so that after the reaction the reaction mixture was directly purified by column chromatography eluting with 2% diethyl ether. The product was contaminated with 16% allyl alcohol. Spectral data matches the literature.[31]

^1H NMR (500 MHz, $CDCl_3$): δ= 5.76 (ddt, J_1 = 17.2 Hz, J_2 = 10.5 Hz, J_3 = 5.7 Hz, 1H), 5.02 (m, 2H), 2.60 (m, 1H), 2.48 (m, 2H), 2.40 (m, 1H), 2.05 (m, 1H), 1.04 (d, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H);

Chiral GC (CycloSil-B; 40°C; 3 mL/ min flow rate; t_1 = 26.4 min (major), t_2 = 29.0 min (minor));

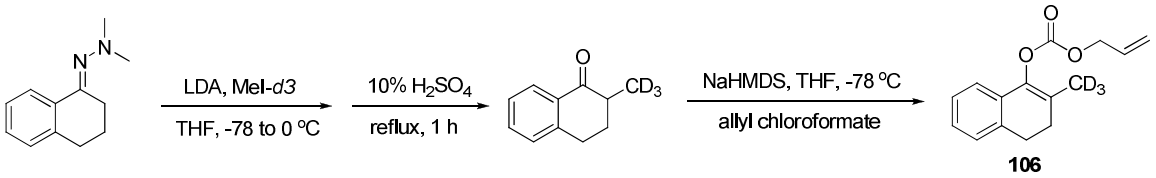


4-Methyl-1-phenylhept-6-en-1-yn-3-one (**105**):

The general procedure for the Pd catalyzed DAAA of enol carbonates was followed employing 82 mg of *E*-**18** (0.30 mmol), $Pd_2(dba)_3CHCl_3$ (7.8 mg, 0.0075 mmol) and (*R*,*R*)-**L4** (13.6 mg, 0.0165 mmol) in toluene (3 mL) to afford 61 mg of product was isolated (91%).

Yellow oil; R_f=0.47 (diethylether/ petroleum ether 1:9); $[\alpha]_D^{22}$ = -1.3 (c, 1.46; CH_2Cl_2, 81% ee); HPLC (Chiralcel® OD-H column; 99.9:0.1 Heptane / 2-Propanol; flow rate = 0.8 mL of / min; t_1 = 24.98 min (major), t_2 = 26.36 min (minor)); IR (film): $\bar{\nu}_{max}$ = 3316 (w), 3080 (m), 2977 (s), 2933 (m), 2200 (s), 1668 (s), 1490 (s), 1456 (m), 1444 (m), 1282 (m), 1169 (m), 1050 (s), 988 (m), 919 (m), 759 (s), 689 cm^{-1} (s);

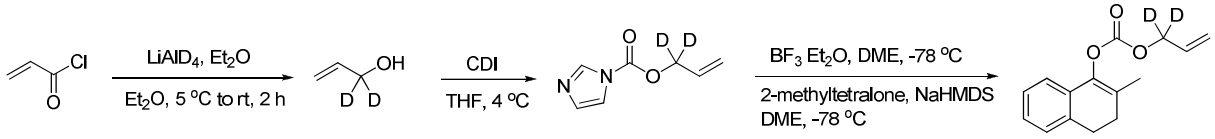
^1H NMR (400 MHz, $CDCl_3$): δ= 7.60- 7.56 (m, 2H), 7.50- 7.36 (m, 3H), 5.78 (m, 1H), 5.05- 5.15 (m, 2H), 2.76 (m, 1H), 2.62 (m, 1H), 2.28 (m, 1H), 1.25 (d, *J* = 6.96, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 135.2, 133.2, 130.9, 128.8, 120.2, 117.5, 92.0, 87.1, 48.3, 37.1, 15.8. HRMS (EI): $[M]^+$ calcd. for $C_{14}H_{14}O$, 198.1045; Found: 198.1051.



106

A solution of the hydrazone (941.5 mg, 5 mmol) in 5 mL of anhydrous THF was added to a freshly prepared LDA solution in 20 mL of THF (6 mmol) at -78 °C stirring for 20 min. MeI-*d3* (0.37 mL, 6 mmol) was added to the enolate and stirred for 20 min. The reaction was allowed to warm to 0 °C and stirred for another 15 min. The reaction mixture was diluted with ether (20 mL) and washed with brine (20 mL). The organic layer was concentrated and the residue was refluxed in 10% H_2SO_4 aqueous solution (30 mL) for 1 h. The mixture was extracted with ether (20 mL) twice. The combined organic layers were washed with brine (20 mL) and dried over $MgSO_4$. After concentration, the residue was purified by column chromatography eluting with 10% diethyl ether in petroleum ether to afford deuterated 2-methyl-*d3*-1-tetralone (0.78 g, 96%). To the solution of 750 mg of 2-methyl-*d3*-1-tetralone (4.6 mmol) in THF (10 mL) was added NaHMDS (1 M in THF, 5.5 mL, 5.5 mmol) at -78 °C. After stirring for 30 min, allylcholorformate (0.59 mL) was added to the enolate solution and was stirred for 5 min. To reaction mixture was added 5% KH_2PO_4 (20 mL) and the mixture was extracted with ether (20 mL) twice. The combined organic layers were dried over $MgSO_4$. After concentration the residue was purified by flash column chromatography eluting with 2% diethyl ether in petroleum ether to afford the title compound (850 mg, 75%) as a colorless oil.

IR (film): $\tilde{\nu}_{max}$ = 3069, 3022, 2934, 2886, 2832, 2237, 2196, 2058, 1766, 1683, 1487, 1365, 1224 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.05 (m, 4H), 5.99 (ddt, J_1 = 17.1 Hz, J_2 = 10.4, J_3 = 5.8 Hz, 1H), 5.42 (dq, J_1 = 17.0 Hz, J_2 = 1.5 Hz, 1H), 5.31 (dq, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1H), 4.71 (m, 2H), 2.86 (t, J = 8.0 Hz, 2H), 2.39 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 135.3, 131.4, 130.8, 127.3, 127.1, 126.5, 124.4, 124.4, 120.0, 119.2, 69.0, 28.8, 27.4.



107

To a clean dry 500 mL three-neck flask was charged with a stirring bar and $LiAlD_4$ (2.45 g, 58.3 mmol). The flask was purged with nitrogen and was added 100 mL of anhydrous diethyl ether. The suspension was cooled by an ice-water bath and a solution of acryloyl chloride (9.05 g, 0.10 mol) in 10 mL of diethyl ether was added to the reaction mixture very slowly. The reaction was stirred for 1 h and then removed from the bath and allowed to warm to rt stirring for another 2 h. The reaction mixture was quenched by addition of sequential 3 mL of water, 3 mL of sodium hydroxide (15%) and 3 mL of water, and then stirred vigorously for 3 h. The white solid was filtrated and the filtrate was concentrated on a rotoevaporator with care. The residue was distilled to afford allyl acohol-*d2* (1.6 g, 27%). The product was dissolved in 50 mL of anhydrous THF and cooled to 4 °C. Carbonyldiimidazole (6.5 g, 40 mmol) was added to the solution and stirred for 2 h. Most solvent was removed and the residue was purified by column chromatography eluting with 50% ethyl acetate in petroleum ether to afford the imidazolide (3.13 g, 65%).

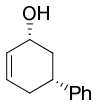
In a dry clean 100 mL flask was purged with nitrogen and was added 2-methyl-1-tetralone (550 mg, 3.43 mmol) and 10 mL anhydrous DME. The solution cooled to -78 °C and was added a solution of NaHMDS in THF (1 M, 4.1 mL, 4.1 mmol). In

another 25 mL flask under nitrogen were added the above imidazolide (632 mg, 4.1 mmol) and 5 mL anhydrous THF. The solution cooled to -78 ^{o}C was added BF_3 etherate (0.52 mL, 4.1 mmol) stirring for 5 min. The enolate solution was transferred to the imidazolide-BF_3 complex through a cannula. The reaction was stirred for 10 min at -78 ^{o}C and allowed to rt before the addition of 5% KH_2PO_4 (20 mL). The mixture was extracted with ether (20 mL) twice and the combined organic layers were dried over magnesium sulfate and concentrate. The residue was purified with 2% diethyl ether in petroleum ether to afford the title compound (742 mg, 88%, contaminated with a little 2-methyltetralone) as a slight yellow oil.

IR (film): $\tilde{\nu}_{max}$ = 3068, 3022, 2932, 2833, 1759, 1678, 1487, 1440, 1257, 1182, 1142, 1072 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20-7.05 (m, 4H), 5.99 (dd, J_1 = 17.1 Hz, J_2 = 10.4 Hz, 1H), 5.42 (m, 1H), 5.32 (m, 1H), 2.86 (t, J = 8.0 Hz, 2H), 2.40 (t, J = 8.0 Hz, 2H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 140.7, 135.3, 131.2, 130.8, 127.3, 127.1, 126.5, 124.5, 120.0, 119.4, 28.9, 27.4, 16.6.

Crossover experiment:

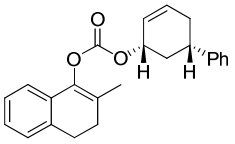
The procedure for Pd catalyzed DAAA reaction was followed employing a mixture of **106** (37 mg, 0.15 mmol) and **107** (37 mg, 0.15 mmol), 7.8 mg of $Pd_2(dba)_3CHCl_3$ (0.0075 mmol) and 13.6 mg of (*R,R*)-**L4** (0.0165 mmol) in dioxane (3 mL) at rt for 10 min. Most solvent was removed and the residue was purified by column chromatography eluting with 5% diethyl ether in petroleum ether. The product was analyzed by a GC-MS. The MS of the whole GC signal of the product shows roughly the same amount of four isotopic compounds with m/z = 200, 202, 203 and 205.



***cis*-5-Phenylcyclohex-2-enol**:

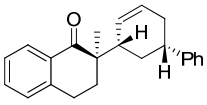
A literature reported procedure was followed.[32] A solution of 5-phenyl-1,3-cyclohexanedione (5.0 g, 26.50 mmol), *p*-toluenesulfonic acid (68 mg) in 60 mL of isobutyl alcohol and 60 mL of benzene was heated to reflux with a Dean-Stark trap for 3 h. The solution was cooled to room temperature and concentrated *in vacuo*. The residue was dissolved in 100 mL diethyl ether and washed with 30 mL 2 N sodium hydroxide aqueous solution 3 times and then washed with 50 mL of brine twice. The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration and concentration *in vacuo*, the residue yellow oil was dried under high vacuum. It was dissolved in 150 mL of anhydrous diethyl ether and the resulting solution was cooled to 0 ^{o}C. $LiAlH_4$ (780 mg, 20.5 mmol) was added in portions to the solution and stirred for 30 min. The reaction flask was removed from the ice-bath and warmed to room temperature in the air while stirring for another 30 min. To the reaction flask 100 mL of 10% aqueous HCl solution was slowly added with vigorous stirring. The reaction mixture was transferred into a separatory funnel and the organic layer was separated. The aqueous layer was extracted with 100 mL of diethyl ether once. The organic layer was combined and washed with brine twice. The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration and concentration the residue was dried under high vacuum and was dissolved together with 10 g $CeCl_3 \cdot 7H_2O$ in 200 mL of methanol. To the solution, cooled to 0 ^{o}C, was added in small portions $NaBH_4$ (1.0 g, 26 mmol). The reaction mixture was stirred for another 5 min. Most solvent was rota-evaporated *in vacuo*. The residue was dissolved in diethyl ether and washed with 1 N HCl, and then brine. The organic layer was dried over anhydrous sodium sulfate. After filtration and concentration the crude product was purified by silica gel

column chromatography using gradient elution with 10-20% ethyl acetate in petroleum to afford 4.0 g of white crystals (87%). M.p. = 43-44 ^{o}C.



***cis*-2-Methyl-3,4-dihydronaphthalen-1-yl-5-phenylcyclohex-2-enyl carbonate** (**110**):

A clean and oven-dried flask was charged with 2.8 mL 20% wt solution of phosgene in toluene and cooled to -78 ^{o}C by a dry-ice-acetone bath. A solution of *cis*-5-phenylcyclohex-2-enol (630 mg, 3.6 mmol) in 2 mL THF was slowly added to the phosgene solution and stirred for 1 h. The dry-ice bath was remove and the reaction solution was allowed to warm to room temperature. A nitrogen stream was bubbled into the solution for 1 h, with a base trap at the end to absorb the excess phosgene removed by the nitrogen stream. The solution was cooled to -78 ^{o}C before use. Meanwhile, 0.83 g (4.5 mmol) NaHMDS was weighted to a clean oven-dried flask in a dry-box and cooled in a dry-ice-acetone bath. To the solid was added 10 mL of dry-THF re-distilled TMEDA (0.68 mL) and 2-methyl-1-tetralone (481 mg, 3.0 mmol) in 5 mL THF slowly and the resulting solution was stirred at -78 ^{o}C for 1 h. The enolate solution then was transferred to the chlorocarbonate solution through a cannula and stirred for 5 min before the dry-ice bath was removed and the reaction flask was allowed to warm to room temperature in the air. The reaction mixture was quenched with ammonium chloride aqueous solution and transferred with 50 mL of diethyl ether into a separatory funnel. The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration and concentration, the residue was purified by silica gel column chromatography eluting with 2% diethyl ether in petroleum to afford 870 mg of white solid (80%). M.p. = 122-124 ^{o}C; R_f = 0.47 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3030 (m), 2931 (m), 2834 (m), 1755 (s), 1673 (w), 1490 (m), 1454 (m), 1242 (s), 1209 (s), 1028 (s), 984 (s), 911 (m), 759 (s), 734 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.07 (m, 9H), 5.99 (m, 1H), 5.81 (m, 1H), 5.48 (m, 1H), 2.98 (dddd, J_1 = 13.6 Hz, J_2 = 11.1 Hz, J_3 = 5.3 Hz, J_4 = 1.7 Hz, 1H), 2.86 (t, J = 8.0 Hz, 2H), 2.48-2.10 (m, 3H), 2.39 (t, J = 8.4 Hz, 2H), 1.97 (dddd, J_1 = 23.5 Hz, J_2 = 22.1 Hz, J_3 = 11.9 Hz, J_4 = 10.2 Hz, 1H), 1.82 (s, 3H);. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.1, 144.9, 140.7, 135.3, 131.1, 130.9, 128.7, 127.3, 127.1, 126.8, 126.6, 126.5, 126.3, 124.5, 120.0, 75.6, 39.0, 35.0, 33.4, 28.9, 27.5, 16.8. HRMS (EI): M^+ calcd. For $C_{24}H_{24}O_3$, 360.1725; Found: 360.1721.



(+)-2-Methyl-2-(5-phenyl-cyclohex-2-enyl)-3,4-dihydro-2*H*-naphthalen-1-one (**111**):

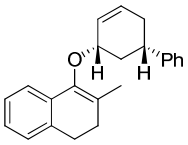
Two test tubes were connected with a double-end needle. One test tube was loaded with 5.2 mg of $Pd_2(dba)_3CHCl_3$ (0.005 mmol) and 9.2 mg of **L4** (0.011 mmol) and the other one was loaded with **110** (72 mg, 0.20 mmol). The system was evacuated and flushed with argon three times at which point 1.0 mL of dry 1,4-dioxane 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 substrate stirring 1 h at rt. Most of the solvent was evaporated *in vacuo* and the residue was suspended in 10% diethyl ether in petroleum ether (5 mL) and filtrated through a short pepette silica gel column and eluting with another 5 mL 10% diethyl ether in petroleum ether. The solution was concentrated and dried under high vacuum. The ^{1}HNMR of the crude product suggested a mixture of

unreacted **110** and **111** in 1:1 ratio, as well as 6% of O-alkylated product **112**. The mixture was separated by silica gel column chromatography eluting with 2% diethyl ether in petroleum ether to give 26.4 mg (-)-**110** (37%, 99.5% ee). HPLC Chiralcel® OD-H column; 90:10 heptane: isopropanol; flow rate = 0.8 ml/min; t_1 = 9.596 min (minor), t_2 = 10.663 min (major) and $[\alpha]_D^{23}$ = -16.9 (c = 2.6, CH_2Cl_2).

From the above reaction 25 mg **111** was isolated (40%) as white crystals.

M.p. = 126-127 °C (petroleum ether), R_f = 0.55 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = +73.7 (c = 1.1, CH_2Cl_2, 100% ee); HPLC (Chiralcel® AD column; 99:1 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 9.047 min (major), t_2 = 10.40 min (minor)); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03 (ddd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, J_3 = 0.5 Hz, 1H), 7.45 (td, J_1 = 7.3 Hz, J_2 = 1.5 Hz, 1H), 7.30 (m, 3H), 7.21 (m, 4H), 5.86 (ddt, J_1 = 10.2 Hz, J_2 = 4.8 Hz, J_3 = 2.2 Hz, 1H), 5.58 (ddq, J_1 = 10.2 Hz, J_2 = 2.8 Hz, J_3 = 1.5 Hz, 1H), 3.0 (ddd, J_1 = 17.3 Hz, J_2 = 9.3 Hz, J_3 = 4.8 Hz, 1H), 2.88 (m, 3H), 2.24 (m, 1H), 2.15 (m, 2H), 1.94 (m, 2H), 1.64 (q, J = 12.0 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.3, 147.0, 143.3, 133.0, 132.0, 128.6, 128.5, 128.3, 127.3, 127.0, 126.8, 126.3, 47.2, 40.9, 39.9, 33.7, 32.0, 31.5, 25.3, 19.0. HRMS (EI): M^+ calcd. for $C_{23}H_{24}O$, 316.1827; found 316.1824.

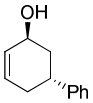
Single crystals for X-ray analysis were obtained by recrystalization from petroleum ether. See Appendix.



***cis*-3-Methyl-4-(5-phenyl-cyclohex-2-enyloxy)-1,2-dihydro-naphthalene** (**112**):

From the above reaction **108** was isolated as a minor side product in 4.2 mg (6.7%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (m, 3H), 7.20 (m, 4H), 7.11 (m, 2H), 5.96 (m, 1H), 5.88 (m, 1H), 4.56 (m, 1H), 2.81 (m, 1H), 2.73 (t, J = 7.8 Hz, 2H), 2.37-2.16 (m, 5H), 2.01 (ddd, J_1 = 22.1 Hz, J_2 = 12.0 Hz, J_3 = 10.2 Hz, 1H), 1.91 (s, 3H).



***trans*-5-Phenyl-cyclohex-2-enol**:

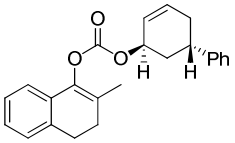
cis-5-Phenylcyclohex-2-enol (1.1 g, 6.3 mmol) and triphenyl phosphine (2.5 g, 9.5 mmol) were dissolved in 20 mL of dry THF and cooled to 0 °C. To the solution was added DIAD (1.62 ml, 8.2 mmol) and acetic acid (0.47 ml, 8.2 mmol). The reaction was stirred for 5 min and transferred into a separatory funnel with 20 mL of diethyl ether. After washing with water once and brine once, the organic layer was separated and dried over magnesium sulfate. After filtration and concentration, the crude product was purified by silica gel column chromatograph eluting with 5% diethyl ether in petroleum ether to give 1.1 g colorless oil (81%) as a 6:1 *trans*:*cis* mixture.

R_f = 0.32 (Diethyl ether/petroleum ether 1:9); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (m, 2H), 7.23 (m, 3H), 6.12 (ddd, J_1 = 9.9 Hz, J_2 = 5.3 Hz, J_3 = 2.2 Hz, 1H), 5.88 (m, 1H), 5.35 (m, 1H), 2.41 (m, 1H), 2.12 (m, 2H), 2.07 (s, 3H), 1.97 (ddd, J_1 = 14.2 Hz, J_2 = 12.9 Hz, J_3 = 4.3 Hz, 1H).

The above compound (725 mg, 3.35 mol) was stirred in 10 mL methanol and 10 mL water mixture with 0.46 g potassium carbonate for overnight. The reaction mixture was transferred into a separatory funnel and extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After filtration and concentration the crude product was purified by

silica gel column chromatography eluting with 10% ethyl acetate in petroleum ether to afford 550 mg white solid (94% as a mixture of 5:1 *trans*:*cis* isomers).

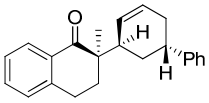
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (m, 2H), 7.23 (m, 3H), 6.00 (ddd, J_1 = 9.9 Hz, J_2 = 5.2 Hz, J_3 = 1.8 Hz, 1H), 5.92 (m, 1H), 4.29 (s, 1H), 3.04 (m, 1H), 2.36 (dt, J_1 = 17.9 Hz, J_2 = 5.1 Hz, 1H), 2.10 (m, 2H), 1.92 (td, J_1 = 13.0 Hz, J_2 = 4.0 Hz, 1H), 1.70 (m, 1H).



***trans*-2-Methyl-3,4-dihydronaphthalen-1-yl-5-phenylcyclohex-2-enyl carbonate** (**114**):

Following the same procedure as the preparation of **110** employing 2-methyltetralone (320.4 mg, 2 mmol), 100 mg of white solid was isolated (14%).

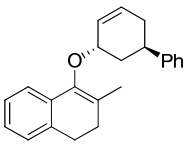
M.p. = 93-95 ^{o}C; IR (film): $\tilde{\nu}_{max}$ = 2923 (m), 1752 (s), 1489 (m), 1454 (m), 1244 cm^{-1} (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33 (m, 2H), 7.24 (m, 3H), 7.12 (m, 4H), 6.18 (ddd, J_1 = 9.9 Hz, J_2 = 5.2 Hz, J_3 = 2.2 Hz, 1H), 5.99 (m, 1H), 5.27 (m, 1H), 3.12 (dddd, J_1 = 16.1 Hz, J_2 = 13.8 Hz, J_3 = 4.9 Hz, J_4 = 3.0 Hz, 1H), 2.86 (t, J = 8.0 Hz, 2H), 2,45 (m, 1H), 2.41 (t, J = 8.4 Hz, 2H), 2.25 (d, J = 14.3 Hz, 1H), 2.17 (ddq, J_1 = 21.6 Hz, J_2 = 11.4 Hz, J_3 = 2.5Hz, 1H), 2.01 (ddd, J_1 = 15.3 Hz, J_2 =13.2 Hz, J_3 = 4.2 Hz, 1H), 1.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.0, 145.4, 140.8, 135.3, 134.4, 131.0, 128.6, 127.3, 127.1, 127.0, 126.5, 124.4, 123.4, 120.1, 71.9, 35.2, 35.0, 33.4, 29.0, 27.5, 16.7. MS (ESI): $[M+Na]^+$ calcd. for $C_{24}H_{24}NaO_3$, 383.2; found 383.2.



2-Methyl-2-(5-phenyl-cyclohex-2-enyl)-3,4-dihydro-2*H*-naphthalen-1-one (**111**):

Compound **110** (72 mg, 0.20 mmol) was subjected to the palladium catalyzed decarboxylation-alkylation reaction in dioxane at room temperature overnight. Most of the solvent was evaporated *in vacuo* and the residue was suspended in 5 mL 10% diethyl ether in petroleum ether followed by filtration through a short pepette silica gel column and eluting with another 5 mL 10% diethyl ether in petroleum ether. The solution was concentrate and dried under high vacuum. The ^{1}HNMR of the crude product suggested a mixture of unreacted **114**, desired product **113**, O-alkylated product **116** and 2-methyltetralone in 1.4:1.4:1:1 ratio. The mixture was separated by silica gel column chromatography eluting with 2% diethyl ether in petroleum ether to afford 22 mg **113** (35%).

White crystals; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (dd, J_1 = 7.9 Hz, J_2 = 1.3 Hz, 1H), 7.41 (td, J_1 = 7.4 Hz, J_2 = 1.5 Hz, 1H), 7.34-7.11 (m, 7H), 5.97 (m, 1H), 5.61 (dq, J_1 = 10.2 Hz, J_2 = 2.6 Hz, 1H), 3.0 (m, 1H), 2.84 (m, 2H), 2.67 (m, 1H), 2.36 (m, 1H), 2.2 (m, 2H), 1.94 (m, 2H), 1.83 (dt, J_1 = 13.5 Hz, J_2 = 4.5 Hz, 1H), 1.20 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.1, 146.1, 143.2, 133.0, 128.8, 128.6, 128.3, 128.2, 127.2, 127.0, 126.7, 126.1, 48.3, 37.4, 35.6, 31.6, 31.4, 31.1, 25.2, 20.1. HRMS (EI): M^+ calcd. for $C_{23}H_{24}O$, 316.1827; found 316.1829.



***trans*-3-Methyl-4-(5-phenyl-cyclohex-2-enyloxy)-1,2-dihydro-naphthalene (116)**:

Compound **116** was isolated from the above reaction (11 mg, 17%).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.4-7.1 (m, 9H), 6.12 (ddd, J_1 = 10.0 Hz, J_2 = 5.4 Hz, J_3 = 1.8 Hz, 1H), 6.06 (m, 1H), 4.32 (s, 1H), 3.29 (m, 1H), 2.71 (m, 2H), 2.43 (dt, J_1 = 17.9 Hz, J_2 = 5.1 Hz, 1H), 2.35-2.10 (m, 4H), 1.91 (s, 3H), 1.74 (td, J_1 = 13.7 Hz, J_2 = 4.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.4, 145.6, 136.8, 132.6, 132.2, 128.6, 127.3, 127.2, 126.3, 126.0, 123.3, 121.3, 72.0, 35.6, 35.2, 33.8, 29.3, 28.1, 17.3.

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Appendix

Experimental

Data Collection

A colorless plate crystal of C23 H24 O having approximate dimensions of 0.52 x 0.1 x 0.1 mm was mounted on a quartz fiber using Paratone N hydrocarbon oil. All measurements were made on a Bruker-Siemens SMART[1] CCD area detector with monochromatic radiation of wavelength 0.71073 Å.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the measured positions of 605 centered reflections with $I > 10\sigma(I)$ in the range $2.2° < \theta < 19.62°$, corresponded to a primitive monoclinic cell with dimensions:

a = 10.102(10) Å	α = 90º
b = 5.802(6) Å	β = 103.938(17)º
c = 15.213(15) Å	γ = 90º
V = 865.3(15) Å^3	

For Z = 2 and $F.W.$ = 316.42, the calculated density is 1.214 g/cm^3.

Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

$P\ 2_1$ (#4)

The data were collected at a temperature of 168 K. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3º counted for a total of 10 seconds per frame.

Data Reduction

Data were integrated by the program SAINT[2] with box parameters of 1.6 x 1.6 x 1.6º to a maximum θ value of 26.30º. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ, for 0.71073 Å radiation is 0.072 mm^{-1}. Data were analyzed for agreement and possible absorption using SADABS[3]. A semi-empirical absorption correction based on 5.41 reflections with $I > 5\sigma(I)$ was applied that resulted in normalized transmission factors ranging from 0.79 to 0.99. Of the 4807 reflections that were collected, 1916 were unique (R_{int} = 0.0386); equivalent reflections were merged, including Friedel mates. No decay correction was deemed necessary.

Structure Solution and Refinement

The structure was solved by direct methods (Sir-2002)[4] and expanded using Fourier techniques[5]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located on the difference Fourier map, but were positioned using the HFIX command (idealized positions via a riding refinement). The final cycle of full-matrix least-squares refinement[6] was based on 1916 reflections (all data) and 219 variable parameters and converged (largest parameter shift was 0.000 times its esd) with conventional unweighted and weighted agreement factors of:

$$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o| = 0.0446 \text{ for 1454 data with } F_o > 4\sigma(F_o)$$

$$wR_2 = [(\Sigma w (|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^2)]^{1/2} = 0.1024$$

The standard deviation of an observation of unit weight (S)[7] was 1.037. Sheldrick weights[6] were used; where applicable, weights were refined to convergence. Absolute configuration was manually assigned based on the known configuration of a synthetic precursor. The Flack parameter[5b] was not refined but was assigned an arbitrary value of 0. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.19 and -0.18 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[8]. Anomalous dispersion effects were included in Fcalc[9]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[10]. The values for the mass attenuation coefficients were those of Creagh and Hubbel[11]. All calculations were performed using the Crystal Structure[12] crystallographic software package.

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(6) Least-Squares:

Function minimized: $\Sigma w (|F_o|^2 - |F_c|^2)^2$

$w=1/[\sigma^2(F_o^2)+(0.0090P)^2+0.1734P]$ where $P=(F_o^2+2F_c^2)/3$

Sheldrick weights: G. M. Sheldrick (1997)

(7) Standard deviation of an observation of unit weight:

$S = [\Sigma w (|F_o|^2 - |F_c|^2)^2/(N_o - N_v)]^{1/2}$

where: N_o = number of observations

N_v = number of variables

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EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C23 H24 O
Formula Weight	316.42
Crystal Color, Habit	colorless, plate
Crystal Dimensions	0.52 x 0.1 x 0.1 mm
Crystal System	monoclinic
Lattice Type	primitive
Lattice Parameters	a = 10.102(10) Å b = 5.802(6) Å c = 15.213(15) Å α = 90º β = 103.938(17)º γ = 90º V = 865.3(15) Å^3
Space Group	$P\,2_1$
Z value	2
d_{calc}	1.214 g/cm^3
F_{000}	340
μ(0.71073 Å radiation)	0.07 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker-Siemens SMART CCD
Radiation	λ = 0.71073 Å graphite monochromated
Exposure Time	10 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
θ_{max}	26.30º
Data Collection Temperature	168 K
No. of Reflections Measured	Total: 4807 Unique: 1916 (R_{int} = 0.0386)
Corrections	Lorentz-polarization Absorption: T_{max} = 0.99 T_{min} = 0.79

C. Structure Solution and Refinement

Structure Solution	Direct (SIR-2002)
Refinement	Full-matrix least-squares (SHELXS-97)
Function Minimized	$\Sigma w(\|F_o\|^2 - \|F_c\|^2)^2$
Least Squares Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0090P)^2+0.1734P]$ where $P=(F_o^2+2F_c^2)/3$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($F_o > 4\sigma(F_o)$)	1454
No. Variables	219
Reflection/Parameter Ratio	8.75
Residuals: R_1; wR_2	0.0446; 0.1024
Goodness of Fit Indicator (S)	1.037
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.19 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.18 $e^-/Å^3$

Table 1. Atomic coordinates, U_{iso}/U_{eq}, and occupancy for jxu72

atom	*x*	*y*	*z*	U_{eq}	occ
O1	0.6866(2)	0.3440(4)	0.1867(1)	0.038(1)	1
C1	0.7488(3)	0.4645(5)	0.1445(2)	0.028(1)	1
C2	0.8636(3)	0.6255(5)	0.1931(2)	0.026(1)	1
C3	0.8646(3)	0.8402(6)	0.1334(2)	0.032(1)	1
C4	0.8815(3)	0.7804(6)	0.0390(2)	0.033(1)	1
C5	0.7854(3)	0.5940(5)	-0.0069(2)	0.031(1)	1
C6	0.7221(3)	0.4463(5)	0.0442(2)	0.029(1)	1
C7	0.6338(3)	0.2722(6)	0.0005(2)	0.034(1)	1
C8	0.6101(3)	0.2409(6)	-0.0919(2)	0.043(1)	1
C9	0.6724(4)	0.3868(7)	-0.1425(2)	0.046(1)	1
C10	0.7578(3)	0.5614(6)	-0.1001(2)	0.040(1)	1
C11	0.8431(3)	0.6875(6)	0.2886(2)	0.029(1)	1
C12	0.7096(3)	0.8137(5)	0.2872(2)	0.028(1)	1
C13	0.6979(3)	0.8795(6)	0.3828(2)	0.029(1)	1
C14	0.8155(3)	1.0401(6)	0.4280(2)	0.036(1)	1
C15	0.9495(3)	0.9746(7)	0.4074(2)	0.038(1)	1
C16	0.9617(3)	0.8204(6)	0.3460(2)	0.036(1)	1
C17	0.9962(3)	0.4839(6)	0.2022(2)	0.037(1)	1
C18	0.5582(3)	0.9830(6)	0.3803(2)	0.028(1)	1
C19	0.4645(3)	0.8649(6)	0.4176(2)	0.028(1)	1
C20	0.3353(3)	0.9549(6)	0.4119(2)	0.034(1)	1
C21	0.2968(3)	1.1634(6)	0.3695(2)	0.035(1)	1
C22	0.3896(3)	1.2830(6)	0.3331(2)	0.035(1)	1
C23	0.5191(3)	1.1949(6)	0.3388(2)	0.032(1)	1
H3A	0.7798	0.9239	0.1277	0.039	1
H3B	0.9386	0.9409	0.1631	0.039	1
H4A	0.8660	0.9180	0.0017	0.040	1
H4B	0.9746	0.7305	0.0437	0.040	1
H7	0.5908	0.1769	0.0342	0.041	1
H8	0.5529	0.1232	-0.1202	0.052	1
H9	0.6567	0.3671	-0.2048	0.055	1
H10	0.7977	0.6591	-0.1348	0.048	1
H11	0.8390	0.5409	0.3198	0.035	1
H12A	0.6334	0.7156	0.2591	0.033	1
H12B	0.7046	0.9522	0.2508	0.033	1
H13	0.7067	0.7377	0.4188	0.034	1
H14A	0.7926	1.1967	0.4075	0.044	1

H14B	0.8258	1.0368	0.4930	0.044	1
H15	1.0282	1.0472	0.4399	0.046	1
H16	1.0484	0.7917	0.3376	0.043	1
H17A	0.9995	0.3633	0.2459	0.056	1
H17B	1.0737	0.5832	0.2217	0.056	1
H17C	0.9975	0.4174	0.1446	0.056	1
H19	0.4888	0.7245	0.4465	0.034	1
H20	0.2739	0.8738	0.4369	0.040	1
H21	0.2100	1.2224	0.3656	0.042	1
H22	0.3649	1.4237	0.3046	0.042	1
H23	0.5806	1.2782	0.3146	0.038	1

U_{eq} is defined as one third of the orthogonalized U_{ij} tensor

Table 2. Anisotropic Displacement Parameters for jxu72

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.050(1)	0.031(1)	0.040(1)	0.001(1)	0.022(1)	-0.009(1)
C1	0.026(2)	0.027(2)	0.034(2)	0.003(2)	0.012(1)	0.009(2)
C2	0.025(2)	0.024(2)	0.030(2)	0.004(1)	0.008(1)	0.004(1)
C3	0.038(2)	0.024(2)	0.036(2)	-0.001(1)	0.012(2)	-0.003(2)
C4	0.039(2)	0.030(2)	0.034(2)	0.000(1)	0.015(1)	-0.004(2)
C5	0.030(2)	0.033(2)	0.033(2)	0.003(1)	0.011(1)	0.005(1)
C6	0.026(2)	0.025(2)	0.034(2)	0.005(1)	0.006(1)	0.006(1)
C7	0.027(2)	0.035(2)	0.039(2)	0.006(2)	0.005(1)	0.000(2)
C8	0.038(2)	0.042(2)	0.040(2)	0.001(2)	-0.007(2)	-0.003(2)
C9	0.051(2)	0.051(2)	0.031(2)	0.001(2)	0.002(2)	-0.002(2)
C10	0.044(2)	0.041(2)	0.036(2)	0.004(2)	0.013(2)	-0.006(2)
C11	0.029(2)	0.030(2)	0.028(2)	0.004(1)	0.007(1)	0.003(1)
C12	0.026(2)	0.027(2)	0.030(2)	0.001(1)	0.009(1)	0.002(1)
C13	0.029(2)	0.029(2)	0.029(2)	0.004(1)	0.009(1)	0.004(1)
C14	0.034(2)	0.042(2)	0.034(2)	-0.009(2)	0.008(2)	-0.007(2)
C15	0.027(2)	0.055(2)	0.031(2)	-0.005(2)	0.002(1)	-0.006(2)
C16	0.024(2)	0.053(2)	0.030(2)	0.003(2)	0.005(1)	0.004(2)
C17	0.033(2)	0.039(2)	0.040(2)	-0.001(2)	0.011(2)	0.009(2)
C18	0.029(2)	0.032(2)	0.023(2)	-0.004(1)	0.006(1)	-0.001(2)
C19	0.031(2)	0.029(2)	0.025(2)	0.000(1)	0.005(1)	-0.004(1)
C20	0.025(2)	0.045(2)	0.031(2)	0.001(2)	0.006(1)	-0.008(2)
C21	0.026(2)	0.046(2)	0.032(2)	-0.002(2)	0.005(1)	0.003(2)
C22	0.039(2)	0.032(2)	0.033(2)	-0.001(2)	0.008(2)	0.004(2)
C23	0.034(2)	0.030(2)	0.032(2)	0.000(1)	0.011(1)	-0.001(2)

The general temperature factor expression:
$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 3. Bond Lengths (Å) for jxu72

atom	atom	distance	atom	atom	distance	
O1	C1	1.220(3)	C1	C6	1.489(4)	C1
	C2	1.533(4)	C2	C3	1.543(4)	C2
	C17	1.549(4)	C2	C11	1.559(4)	C3
	C4	1.527(4)	C3	H3A	0.9700	C3
	H3B	0.9700	C4	C5	1.507(4)	C4
	H4A	0.9700	C4	H4B	0.9700	C5
	C10	1.391(5)	C5	C6	1.409(4)	C6
	C7	1.405(4)	C7	C8	1.380(5)	C7
	H7	0.9300	C8	C9	1.393(5)	C8
	H8	0.9300	C9	C10	1.385(5)	C9
	H9	0.9300	C10	H10	0.9300	C11
	C16	1.513(5)	C11	C12	1.530(4)	C11
	H11	0.9800	C12	C13	1.536(4)	C12
	H12A	0.9700	C12	H12B	0.9700	C13
	C18	1.526(4)	C13	C14	1.536(4)	C13
	H13	0.9800	C14	C15	1.510(4)	C14
	H14A	0.9700	C14	H14B	0.9700	C15
	C16	1.320(5)	C15	H15	0.9300	C16
	H16	0.9300	C17	H17A	0.9600	C17
	H17B	0.9600	C17	H17C	0.9600	C18
	C19	1.394(4)	C18	C23	1.395(5)	C19
	C20	1.389(4)	C19	H19	0.9300	C20
	C21	1.381(5)	C20	H20	0.9300	C21
	C22	1.385(4)	C21	H21	0.9300	C22
	C23	1.388(4)	C22	H22	0.9300	C23
	H23	0.9300				

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond Angles (º) for jxu72

atom	atom	atom	angle	atom	atom	atom	angle	
O1	C1	C6	120.6(3)	O1	C1	C2	121.4(3)	C6
	C1	C2	117.8(2)	C1	C2	C3	108.7(3)	C1
	C2	C17	104.9(2)	C3	C2	C17	110.7(2)	C1
	C2	C11	109.6(2)	C3	C2	C11	112.5(2)	C17
	C2	C11	110.2(2)	C4	C3	C2	112.8(3)	C4
	C3	H3A	109.0	C2	C3	H3A	109.0	C4
	C3	H3B	109.0	C2	C3	H3B	109.0	H3A
	C3	H3B	107.8	C5	C4	C3	113.2(2)	C5
	C4	H4A	108.9	C3	C4	H4A	108.9	C5
	C4	H4B	108.9	C3	C4	H4B	108.9	H4A
	C4	H4B	107.8	C10	C5	C6	118.2(3)	C10
	C5	C4	121.2(3)	C6	C5	C4	120.6(3)	C7
	C6	C5	119.8(3)	C7	C6	C1	118.3(3)	C5
	C6	C1	121.8(3)	C8	C7	C6	120.7(3)	C8
	C7	H7	119.6	C6	C7	H7	119.6	C7
	C8	C9	119.5(3)	C7	C8	H8	120.2	C9
	C8	H8	120.2	C10	C9	C8	120.1(3)	C10
	C9	H9	119.9	C8	C9	H9	119.9	C9
	C10	C5	121.6(3)	C9	C10	H10	119.2	C5
	C10	H10	119.2	C16	C11	C12	109.7(3)	C16
	C11	C2	113.0(2)	C12	C11	C2	114.3(2)	C16
	C11	H11	106.4	C12	C11	H11	106.4	C2
	C11	H11	106.4	C11	C12	C13	112.0(2)	C11
	C12	H12A	109.2	C13	C12	H12A	109.2	C11
	C12	H12B	109.2	C13	C12	H12B	109.2	
H12A	C12	H12B	107.9	C18	C13	C12	110.9(2)	C18
	C13	C14	112.5(3)	C12	C13	C14	110.3(2)	C18
	C13	H13	107.6	C12	C13	H13	107.6	C14
	C13	H13	107.6	C15	C14	C13	112.9(3)	C15
	C14	H14A	109.0	C13	C14	H14A	109.0	C15
	C14	H14B	109.0	C13	C14	H14B	109.0	
H14A	C14	H14B	107.8	C16	C15	C14	124.0(3)	C16
	C15	H15	118.0	C14	C15	H15	118.0	C15
	C16	C11	123.9(3)	C15	C16	H16	118.1	C11
	C16	H16	118.1	C2	C17	H17A	109.5	C2
	C17	H17B	109.5	H17A	C17	H17B	109.5	C2
	C17	H17C	109.5	H17A	C17	H17C	109.5	
H17B	C17	H17C	109.5	C19	C18	C23	118.1(3)	C19
	C18	C13	120.7(3)	C23	C18	C13	121.1(3)	C20
	C19	C18	120.6(3)	C20	C19	H19	119.7	C18

C19	H19	119.7	C21	C20	C19	120.9(3)	C21
C20	H20	119.6	C19	C20	H20	119.6	C20
C21	C22	118.9(3)	C20	C21	H21	120.5	C22
C21	H21	120.5	C21	C22	C23	120.6(3)	C21
C22	H22	119.7	C23	C22	H22	119.7	C22
C23	C18	120.8(3)	C22	C23	H23	119.6	C18
C23	H23	119.6					

Symmetry transformations used to generate equivalent atoms:

Table 5. Torsion Angles (º) for jxu72

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle	
O1	C1	C2	C3	-147.5(3)	C6	C1	C2	C3	36.9(3)	O1
	C1	C2	C17	94.1(3)	C6	C1	C2	C17	-81.5(3)	O1
	C1	C2	C11	-24.2(4)	C6	C1	C2	C11	160.2(2)	C1
	C2	C3	C4	-57.2(3)	C17	C2	C3	C4	57.5(3)	C11
	C2	C3	C4	-178.8(2)	C2	C3	C4	C5	49.2(4)	C3
	C4	C5	C10	161.6(3)	C3	C4	C5	C6	-19.0(4)	C10
	C5	C6	C7	0.0(4)	C4	C5	C6	C7	-179.4(3)	C10
	C5	C6	C1	178.2(3)	C4	C5	C6	C1	-1.2(4)	O1
	C1	C6	C7	-6.2(4)	C2	C1	C6	C7	169.5(3)	O1
	C1	C6	C5	175.6(3)	C2	C1	C6	C5	-8.8(4)	C5
	C6	C7	C8	1.2(4)	C1	C6	C7	C8	-177.1(3)	C6
	C7	C8	C9	-1.3(5)	C7	C8	C9	C10	0.2(5)	C8
	C9	C10	C5	1.0(5)	C6	C5	C10	C9	-1.1(5)	C4
	C5	C10	C9	178.3(3)	C1	C2	C11	C16	172.4(3)	C3
	C2	C11	C16	-66.5(3)	C17	C2	C11	C16	57.5(4)	C1
	C2	C11	C12	-61.1(3)	C3	C2	C11	C12	59.9(3)	C17
	C2	C11	C12	-176.0(3)	C16	C11	C12	C13	-49.4(3)	C2
	C11	C12	C13	-177.5(3)	C11	C12	C13	C18	-174.3(2)	C11
	C12	C13	C14	60.4(3)	C18	C13	C14	C15	-163.3(3)	C12
	C13	C14	C15	-38.9(4)	C13	C14	C15	C16	10.3(5)	C14
	C15	C16	C11	-0.5(5)	C12	C11	C16	C15	20.0(4)	C2
	C11	C16	C15	148.8(3)	C12	C13	C18	C19	111.6(3)	C14
	C13	C18	C19	-124.4(3)	C12	C13	C18	C23	-66.7(4)	C14
	C13	C18	C23	57.4(4)	C23	C18	C19	C20	1.0(4)	C13
	C18	C19	C20	-177.3(3)	C18	C19	C20	C21	-0.2(4)	C19
	C20	C21	C22	-0.4(4)	C20	C21	C22	C23	0.2(4)	C21
	C22	C23	C18	0.7(5)	C19	C18	C23	C22	-1.3(4)	C13
	C18	C23	C22	177.0(3)						

Symmetry transformations used to generate equivalent atoms: