Supporting Information for

A Highly Enantio- and Diastereoselective Molybdenum-Catalyzed Asymmetric Allylic Alkylation of Cyanoesters

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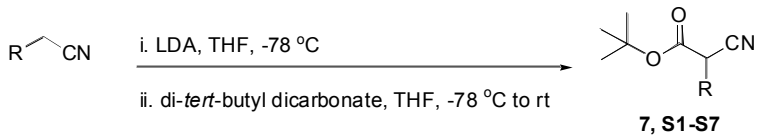
I. General Information

Glassware was oven-dried for at least 8 h at 150 ^{o}C or flame dried under vacuum immediately prior to use. All reactions were carried out in oven-dried flasks or pyrex test tubes under a positive pressure of argon for Mo-catalyzed AAA and nitrogen for all other reactions. Anhydrous solvents were obtained from elution through alumina column, except for THF, which was distilled from Na-benzophenone ketyl and freeze pump thawed under argon before use. $Mo(CO)_6$ was purchased from Aldrich and used directly. TLC analysis of reaction mixtures was performed on 0.2 mm coated silica gel plates (EM 60-F254). Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (EMD, TLC Silica Gel 60 F254); visualization of the developed chromatogram was performed by fluorescence and staining with potassium permanganate. Flash Chromatography was performed with Acros silica gel (0.035-0.070 μm grade). All nuclear magnetic resonance (NMR) spectra were obtained at ambient temperature using Inova-300, Mercury-400, or Unity-500 Varian spectrometers. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual protiated solvent. Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). ^{13}C NMR chemical shifts (δ) are reported in ppm relative to the carbon resonance of the deuterated solvent. Infrared (IR) spectra were recorded as a thin film on NaCl salt plates with a Thermo Scientific Nicolet IR100 FTIR. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Enantiomeric excess was determined using a Thermo Separation Products Spectra Series P-100 chiral HPLC equipped with a spectrophotometric detector (220 or 254 nm). Melting points were determined using a Thomas-Hoover capillary melting point apparatus. Optical rotation data was acquired on a Jasco DIP-360 digital polarimeter or P-2000 polarimeter at the sodium D-line (589 nm) in the solvent, concentration, and temperature indicated. Mass spectra were acquired by the Vincent Coates Foundation Mass Spectrometry Laboratory, Stanford University Mass Spectrometry (http://mass-spec.stanford.edu) on a Micromass Q-Tof API-US mass spectrometer (Waters Corporation, Milford, MA).

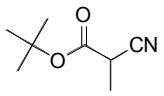
II. Synthesis of Substrates

a. General Procedure for Synthesis of Cyanoester Nucleophiles.



7, S1-S7

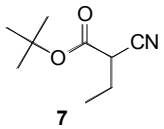
A solution of nitrile **3a-g** (5.0 mmol, 1.0 equiv.) in 15mL THF is added dropwise to a solution of LDA (12.5 mmol, 2.5 equiv.) in THF cooled to -78 °C. The reaction mixture is allowed to stir at -78 °C for 30 min. and then at room temperature for an additional 30 minutes. The reaction mixture is then cooled to -78 °C and a solution of di-*tert*-butyl dicarbonate (1.146 g, 5.25 mmol, 1.05 equiv.) in 10mL of THF is added *via* syringe. The reaction mixture is stirred at -78 °C for 2.5 hours. The reaction mixture is quenched with 10 mL saturated ammonium chloride and extracted with 75 mL diethyl ether. The ether is washed with 10% HCl (2x 30 mL), brine (30 mL) and dried with $MgSO_4$. The solvent is removed under reduced pressure and the resulting crude oil is purified using silica gel chromatography (3% EtOAc: PE) to yield the desired cyanoester **7, S1-S7**. Yields and characterization data are listed for the cyanoesters synthesized.



S1

***tert*-butyl 2-cyanopropanoate (S1).**

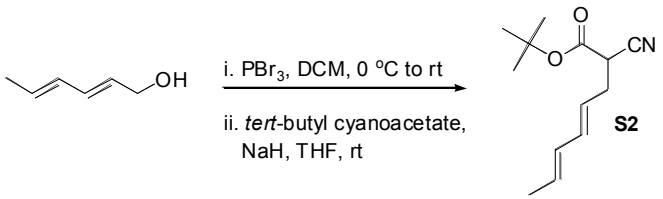
Obtained as a clear oil (0.652 g, 4.20 mmol, 84% yield) which was identical to the reported characterization data.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (q, *J* = 7.4 Hz, 1H), 1.52 (d, *J* = 7.4 Hz, 3H), 1.47 (s, 9H). R_f = 0.13 (2% EtOAc: PE).



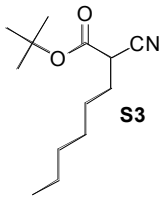
7

***tert*-butyl 2-cyanobutanoate (7).**

Obtained as a clear oil (0.846 g, 5.0 mmol, 100% yield) which was identical to the reported characterization data.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.36 (t, *J* = 7.5 Hz, 1H), 1.96 (q, J = 7.5 Hz, 2H), 1.48 (s, 9H), 1.10 (t, *J* = 7.5 Hz, 3H). R_f = 0.13 (2% EtOAc: PE).



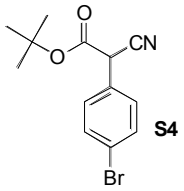
(4E,6E)-tert-butyl 2-cyanoocta-4,6-dienoate (S2). To a solution of sorbic alcohol (0.981 g, 10.0 mmol, 1.0 equiv.) in DCM (2.0 mL) was added PBr_3 (0.32 mL, 3.4 mmol, 0.34 equiv.) in DCM (2.0 mL) dropwise at 0 °C over 10 min under an atmosphere of N_2. The solution was allowed to warm to rt and stir for 2 h before being quenched with H_2O (10 mL) and extracted with DCM (3 x 20 mL). The combined organics were dried over $MgSO_4$ and concentrated under vacuum. The crude residue was dissolved in anhydrous THF (5.0 mL) and added slowly over 2 h to a pre-stirred suspension of NaH (0.303 g, 12.0 mmol, 1.20 equiv.) and *tert*-butylcyanoacetate (1.40 mL, 10.0 mmol, 1.0 equiv.) in THF (25.0 mL) at rt under N_2. The reaction mixture was allowed to stir an additional 7 h at rt before being quenched with H_2O (20 mL) and extracted with EtOAc (3 x 30 mL). The combined organics were washed with sat. aqueous NaCl (30 mL), dried over $MgSO_4$, and concentrated in vacuo. Chromatography on the residue (2% to 10% EtOAc: PE) furnished S2 (2.21 g, 6.19 mmol, 62% yield) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.15 (dd, *J* = 14.9, 10.2 Hz, 1H), 6.05 – 5.96 (m, 1H), 5.74 – 5.64 (m, 1H), 5.49 (dt, *J* = 14.8, 7.4 Hz, 1H), 3.45 – 3.39 (m, 1H), 2.64 (t, *J* = 7.0 Hz, 2H), 1.74 (d, *J* = 6.8 Hz, 3H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 135.4, 130.7, 130.5, 123.4, 116.8, 84.3, 39.1, 33.3, 28.0, 18.3. IR (film): υ_{max}/cm^{-1}: 1278, 2937, 2242, 1736, 1556, 1370, 1253, 1157, 840, 741 HRMS: Expected: 222.1494 (H+), Found: 222.1489 (H+). R_f = 0.21 (2% EtOAc: PE).



***tert*-butyl 2-cyanooctanoate (S3).**

Obtained as a clear oil (1.070 g, 4.75 mmol, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.38 (t, *J* = 7.0 Hz, 1H), 1.93 – 1.85 (m, 2H), 1.48 (s, 9H), 1.37 – 1.24 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 165.5, 117.2, 84.0, 38.8, 31.6, 30.1, 28.7, 28.0, 26.9, 22.7, 14.2. IR (film): υ_{max}/cm^{-1}: 2929, 2861, 2249, 1741, 1459, 1371, 1258, 1155, 840. HRMS: Expected: 226.1807 (H+), Found: 226.1802 (H+). R_f = 0.19 (2% EtOAc: PE).



S4

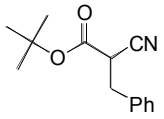
***tert*-butyl 2-(4-bromophenyl)-2-cyanoacetate (S4).**

Obtained as a clear oil (1.481 g, 5.0 mmol, 100% yield) which was identical to the reported characterization data.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.57 (s, 1H), 1.44 (s, 9H). R_f = 0.09 (2% EtOAc: PE).

S5

***tert*-butyl 2-cyano-2-methoxyacetate (S5).**

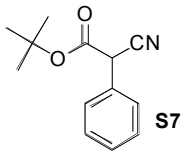
Obtained as a clear oil (0.4535g, 2.65 mmol, 53%) which was identical to the reported characterization data.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (s, 1H), 3.75 (s, 3H), 1.48 (s, 9H). R_f = 0.11 (10% EtOAc: PE).



S6

***tert*-butyl 2-cyano-3-phenylpropanoate (S6).**

Obtained as a clear oil (1.156 g, 5.0 mmol, 100% yield) which was identical to the reported characterization data.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.20 (m, 5H), 3.63 (dd, *J* = 8.3, 6.0 Hz, 1H), 3.32 - 3.14 (m, 2H), 1.44 (s, 9H). R_f = 0.09 (2% EtOAc: PE).

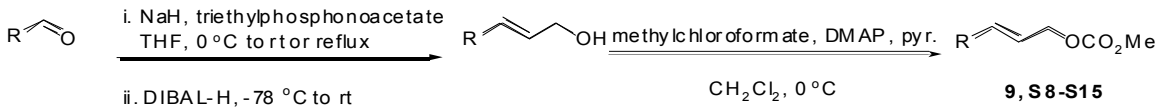


S7

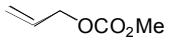
***tert*-butyl 2-cyano-2-phenylacetate (S7).**

Obtained as a clear oil (1.086 g, 5.0 mmol, 100% yield) which was identical to the reported characterization data.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.29 (m, 5H), 4.61 (s, 0.5H), 3.75 (s, 0.5H), 1.44 (s, 9H). R_f = 0.13 (2% EtOAc: PE).

b. General Procedure for Synthesis of Allyl Carbonates



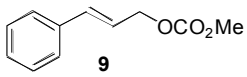
To a stirred suspension of NaH (60% disp., 0.440 g, 11.0 mmol, 1.10 equiv.) in THF (10 mL) under N_2 was added triethylphosphonoacetate (2.24 g, 10.0 mmol, 1.0 equiv.) at 0 °C and allowed to stir 20 min before being added with the appropriate aldehyde (10.0 mmol, 1.0 equiv.) and allowed to warm to rt and stir for the indicated temperature. In some cases the solution was heated to reflux and added with a small amount of DMF (1 to 5 mL) to solubilize the reaction. After cooling to 0 °C the reaction was carefully quenched with H_2O (10 mL) and extracted with EtOAc (3 x 25 mL). The combined organics were washed with brine (20 mL), dried over $MgSO_4$ and concentrated. The residue was dissolved in Et_2O (10 mL) and stirred at -78 °C under N_2 when DIBAL-H (1.0M toluene, 21.0 mL 21.0 mmol, 2.10 equiv.) was added dropwise. The solution was allowed to warm to rt and stir for 3-5 h before being quenched with sat Rochelle's salts (25 mL) very slowly followed by H_2O (10 mL) and diluted with Et_2O (30 mL) and stirred for h when the layers were separated and the aqueous layer extracted with Et_2O (3 x 20 mL). The combined organics were washed with brine (30 mL), dried over $MgSO_4$, and concentrated. Chromatography on the residue (10% to 20% to 50% EtOAc: PE) gave the allylic alcohol. Finally, the residue was dissolved in CH_2Cl_2 (50 mL) under N_2 and added with DMAP (0.244 g, 2.00 mmol, 0.20 equiv.) and pyridine (3.21 mL, 40.0 mmol, 4.0 equiv.) and stirred at 0 °C for 20 min before methyl chloroformate (2.32 mL, 30.0 mmol, 3.0 equiv.) was added dropwise over 20 min and then allowed to warm to rt and stir for 17 h before being quenched with 1M H_3PO_4 (30 mL) and the organics were separated and washed with H_2O (20 mL), brine (20 mL) and dried over $MgSO_4$. The solvent was removed under vacuum and the crude residue was purified by chromatography (5% to 10% EtOAc: PE) to yield the desired allyl carbonate **9**, **S8-S15**. Yields and characterization data are listed for the allyl carbonates synthesized.



S8

Allyl methyl carbonate (S8).

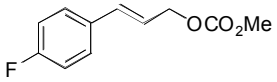
Obtained as a clear oil (1.0915 g, 9.40 mmol, 94% yield, one step) which was identical to the reported characterization data.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.33 (dddd, *J* = 41.7, 10.4, 2.7, 1.4 Hz, 2H), 4.66 – 4.63 (m, 2H), 3.80 (s, 3H). R_f = 0.47 (10% EtOAc: PE).



9

(E)-Cinnamyl methyl carbonate (9).

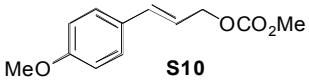
Obtained as a clear oil (1.6146 g, 8.40 mmol, 84% yield, one step) which was identical to the reported characterization data.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.25 (m, 5H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.82 (dd, *J* = 6.4, 1.3 Hz, 2H), 3.83 (s, 3H). R_f = 0.42 (10% EtOAc: PE).



S9

(E)- 4-Fluorocinnamyl methyl carbonate (S9).

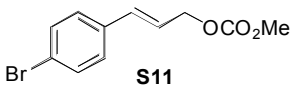
Obtained as a white solid (1.2822 g, 6.10 mmol, 61% yield, three steps) having m.p. 38 ^{o}C which was identical to the reported characterization data.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 8.5, 5.4 Hz, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.24 (dt, *J* = 12.9, 6.7 Hz, 1H), 4.80 (dd, *J* = 6.4, 1.3 Hz, 2H), 3.83 (s, 3H). R_f = 0.39 (10% EtOAc: PE).



S10

(E)-4-Methoxycinnamyl methyl carbonate (S10).

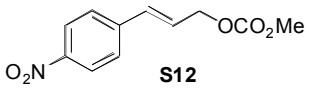
Obtained as a white solid (1.200 g, 5.40 mmol, 54% yield, three steps) having m.p. 88 ^{o}C, lit. 81 -83 ^{o}C which was identical to the reported characterization data.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.32 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.20 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.79 (d, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H). R_f = 0.32 (10% EtOAc: PE).



S11

(E)-4-Bromocinnamyl methyl carbonate (S11).

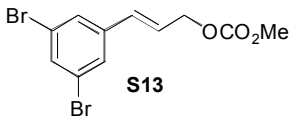
Obtained as a white solid (1.6267 g, 6.00 mmol, 60% yield, three steps) having m.p. 74-75 ^{o}C which was identical to the reported characterization data.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 6.65 (d, *J* = 16.1 Hz, 1H), 6.37 – 6.26 (dt, *J* = 12.9, 6.7 Hz, 1H), 4.81 – 4.79 (m, 2H), 3.83 (s, 3H). R_f = 0.42 (10% EtOAc: PE).



S12

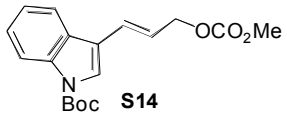
(E)-4-Nitrocinnamyl methyl carbonate (S12).

Obtained as a yellow solid (1.3284 g, 5.60 mmol, 56% yield, three steps) having m.p. 100-101 ^{o}C which was identical to the reported characterization data.[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.49 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.87 (dd, *J* = 6.0, 1.5 Hz, 2H), 3.86 (s, 3H). R_f = 0.21 (10% EtOAc: PE).



S13

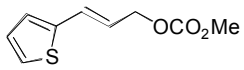
3,5-dibromocinnamyl methyl carbonate (S13). Obtained as a white solid having m.p. 91-92 ^{o}C (1.7150 g, 4.90 mmol, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.45 (s, 2H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 15.8, 5.9 Hz, 1H), 4.78 (d, *J* = 5.9 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 139.8, 133.6, 131.5, 128.6, 125.9, 123.4, 67.8, 55.2. IR (film): υ_{max}/cm^{-1}: 3068, 2957, 1747, 1583, 1550, 1452, 1270, 1105, 935, 856, 791, 743. HRMS: Expected: 274.8894 ($-C_2H_3O_3$ + H+), Found: 274.8889 ($-C_2H_3O_3$ + H+). R_f = 0.42 (10% EtOAc: PE).



S14

(E)-3-(1-(tert-butoxycarbonyl)-1H-indol-3-yl)allylmethyl carbonate (S14).

Obtained as a thick yellow oil (1.557 g, 4.70 mmol, 47% yield, three steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.35 (m, 2H), 6.83 (d, *J* = 16.1 Hz, 1H), 6.46 – 6.37 (m, 1H), 4.85 (dd, *J* = 6.6, 1.2 Hz, 2H), 3.84 (s, 3H), 1.71 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 155.9, 136.9, 129.0, 126.8, 125.0, 123.8, 122.7, 120.4, 120.1, 117.1, 115.8, 84.8, 69.2, 55.0, 28.3. IR (film): υ_{max}/cm^{-1}: 360, 2980, 1737, 136, 1452, 1369, 1263, 1155, 1095, 944, 856, 745. HRMS: Expected: 332. 1498 (H+), Found: 332.1129 (H+). R_f = 0.42 (10% EtOAc: PE).



S15

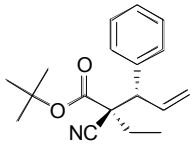
(E)-3-(thiophen-2-yl)allyl methyl carbonate (S15).

Obtained as an orange oil (0.8326 g, 4.20 mmol, 42% yield, three steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 5.0 Hz, 1H), 7.03 – 7.01 (m, 1H), 7.00 – 6.97 (m, 1H), 6.83 (ddd, *J* = 15.7, 1.3, 0.6 Hz, 1H), 6.19 – 6.09 (m, 1H), 4.77 (dd, *J* = 6.5, 1.3 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 141.2, 128.2, 127.7, 127.1, 125.4, 122.0, 68.3, 55.1. IR (film): υ_{max}/cm^{-1}: 3484, 3108, 2956, 1747, 1444, 1381, 1262, 949, 791, 703. HRMS: Expected: 199.0429 (H+), Found: 199.0424 (H+). R_f = 0.42 (10% EtOAc: PE).

III. Molybdenum-catalyzed Asymmetric Allylic Alkylation (Mo-AAA)

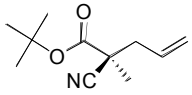
General Procedure for the Molybdenum-catalyzed Asymmetric Allylic Alkylation of Cyanoester Nucleophiles (Both Preparation of Active catalyst and Preparation of Nucleophile).

N-((1R,2R)-2-(4-methoxypyridine-2-carboxamido)cyclohexyl)-4-methoxypyridine-2-carboxamide (R, R-L-OMe) (0.0058 g, 0.015 mmol, 0.15 equiv.) and $Mo(CO)_6$ (0.0026 g, 0.010 mmol, 0.10 equiv.) in THF (0.50 mL, freshly distilled and freeze pump thawed) was stirred under argon stream (schlenk line) in a sealed pyrex microwave vial in a preheated oil bath (75 ^{o}C) for 45 min turning the solution from clear to dark crimson over this time. This indicated the generation of the active catalyst which is very sensitive to air and moisture. In a different sealed pyrex microwave vial was added the cyanoester nucleophile (0.22 mmol, 2.20 equiv.) and BSA (0.049 mL, 0.20 mmol, 2.00 equiv.) in THF (1.0 mL, freshly distilled and freeze pump thawed). To this was added NaH (0.0002 g, 0.01 mmol, 0.010 equiv.) and the resulting solution was stirred for 20 min before the catalyst solution prepared above was transferred via cannula and transferred to a preheated oil bath at 65 ^{o}C (external). To this dark red solution was added the appropriate electrophile (0.10 mmol, 1.00 equiv.) and the resulting solution was stirred at 65 ^{o}C (external) for 5-17 h depending on the substrate. After cooling to rt the solvent was removed in vacuo and loaded directly onto a preparative TLC plate and eluted with EtOAc: PE to yield the desired branched cyanoester products **8-24**.



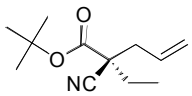
8

(2S,3S)-tert-butyl 2-cyano-2-ethyl-3-phenylpent-4-enoate (8). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **9** (0.0265 g, 0.093 mmol, 93% yield, >20:1 b/l, 12.0:1 dr, 95% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.31 (m, 5H), 6.40-6.29 (m, 1H), 5.25-5.20 (m, 2H), 3.71 (d, J = 9.3 Hz, 1H), 1.87-1.79 (m, 2H), 1.54 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 137.3, 134.4, 129.3, 129.2, 128.8, 119.9, 84.6, 55.9, 49.4, 25.2. IR (film): υ_{max}/cm^{-1}: 2981.8, 2935, 1736, 1454, 1371, 1259, 1160, 1122, 731. HRMS: Expected 286.1807 (H+), Found: 286.1802 (H+). $[\alpha]^{D}_{20}$ -31.3° (*c* = 1.55, CH_2Cl_2). R_f = 0.28 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 11.07 min, major 10.25 min (major diastereomer).



9

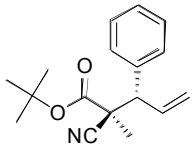
(S)-tert-butyl 2-cyano-2-methylpent-4-enoate (9). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **9** (0.0194 g, 0.100 mmol, 99% yield, 99% ee) as a clear oil and identical to the previously reported characterization data.[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 – 5.76 (m, 1H), 5.31 – 5.20 (m, 2H), 2.66 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.49 (ddd, *J* = 13.8, 7.4 Hz, 1H), 1.56 (s, 3H), 1.52 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 131.1, 121.0, 120.2, 84.2, 44.5, 42.4, 28.0, 22.9. IR (film): υ_{max}/cm^{-1}: 2983, 2938, 2243, 1739, 1458, 1371, 1252, 1148, 842. HRMS: Expected: 196.1337 (H+), Found: 196.1332 (H+). $[\alpha]^{D}_{20}$° -5.90 (*c* = 1.13, CH_2Cl_2). R_f = 0.43 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 8.38 min, major 8.90 min (major diastereomer). Identical to the reported characterization data while reported optical rotation confirms *S* configuration in our product.



10

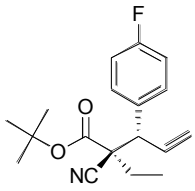
(S)-tert-butyl 2-cyano-2-ethylpent-4-enoate (10). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **10** (0.0201 g, 0.096 mmol, 96% yield, 98% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 – 5.76 (m, 1H), 5.30 – 5.19 (m, 2H), 2.61 (dd, *J* = 13.8,

7.5 Hz, 1H), 2.50 (dd, *J* = 13.9, 7.0 Hz, 1H), 2.01 – 1.89 (m, 2H), 1.51 (s, 9H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 131.2, 120.7, 119.4, 84.2, 41.4, 30.6, 28.1, 23.9, 9.90. IR (film): υ_{max}/cm^{-1}: 2979, 2938, 2245, 1738, 1460, 1371, 1254, 1156, 841. HRMS: Expected: 210.1494 (H+), Found: 210.1489 (H+). $[\alpha]^{D}_{20}$° -9.36 (*c* = 0.10, CH_2Cl_2). R_f = 0.43 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 4.69 min major 5.40 min (major diastereomer).



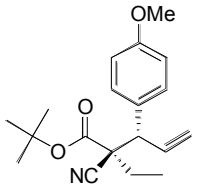
11

(2R,3S)-*tert*-butyl 2-cyano-2-methyl-3-phenylpent-4-enoate (11). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **11** (0.0260 g, 0.096 mmol, 96% yield, >20:1 b/l, 16.8:1 dr, 93% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.30 (m, 5H), 6.39 – 6.24 (m, 1H), 5.34 – 5.18 (m, 2H), 3.71 (d, *J* = 9.0 Hz, 1H), 1.53 (s, 9H), 1.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 137.6, 135.6, 129.2, 129.0, 128.9, 128.2, 119.2, 84.5, 55.9, 49.8, 28.1, 22.7. IR (film): υ_{max}/cm^{-1}: 2982, 2935, 2241, 1736, 1454, 1371, 1259, 1160, 1122, 840, 704. HRMS: Expected: 272.1650 (H+), Found: 272.1645 (H+). $[\alpha]^{D}_{20}$ -36.45° (*c* 0.84, CH_2Cl_2). R_f = 0.29 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 10.04 min, 10.47 major min (major diastereomer).



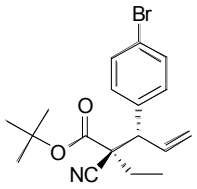
12

(2R,3S)-*tert*-butyl 3-(4-fluorophenyl)-2-cyano-2-ethylpent-4-enoate (12). Prepared using the general procedure. Preparative TLC on the residue (5% EtOAc: PE) yielded the title compound **12** (0.0303 g, 0.100 mmol, >99% yield, >20:1 b/l, >20::1 dr, 91% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.11 – 7.02 (m, 2H), 6.35 – 6.20 (m, 1H), 5.27 – 5.17 (m, 2H), 3.71 (d, *J* = 9.1 Hz, 1H), 1.84 – 1.79 (m, 2H), 1.53 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 162.7 (d, $J_{C\text{-}F}$ = 247 Hz), 135.4, 130.7 (d, $J_{C\text{-}F}$ = 8.8 Hz), 119.3, 118.6, 115.9 (d, $J_{C\text{-}F}$ = 21.4 Hz), 84.7, 56.5, 55.2, 30.2, 28.1, 9.9. IR (film): υ_{max}/cm^{-1}: 2979, 2939, 2242, 1735, 1511, 1371, 1251, 1161, 840. HRMS: Expected: 304.1713 (H+), Found: 304.1707 (H+). $[\alpha]^{D}_{20}$ -7.75° (*c* = 3.70, CH_2Cl_2). R_f = 0.43 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 10.46 min, major 12.09 min (major diastereomer).



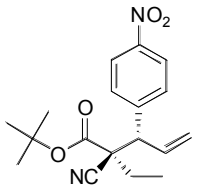
13

(2R,3S)-*tert*-butyl 3-(4-methoxyphenyl)-2-cyano-2-ethylpent-4-enoate (13). Prepared using the general procedure. Preparative TLC on the residue (10% EtOAc: PE) yielded the title compound **13** (0.0267 g, 0.085 mmol, 85% yield, >20:1 b/l, 12.2:1 dr, 89% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.34 – 6.21 (m, 1H), 5.25 – 5.19 (m, 2H), 3.82 (s, 3H), 3.66 (d, *J* = 9.0 Hz, 1H), 2.03 – 1.94 (m, 2H), 1.52 (s, 9H), 1.14 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 159.5, 135.9, 130.2, 129.8, 118.9, 118.7, 114.3, 84.5, 56.7, 55.5, 40.3, 30.2, 28.2, 9.9. IR (film): υ_{max}/cm^{-1}: 2977, 2937, 2241, 1735, 1514, 1370, 1249, 1160, 1035, 837. HRMS: Expected: 316.1912 (H+), Found: 316.1907 (H+). $[\alpha]^{D}_{20}$ -7.07° (*c* = 2.30, CH_2Cl_2). R_f = 0.29 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor min 21.56, major 26.40 min (major diastereomer).



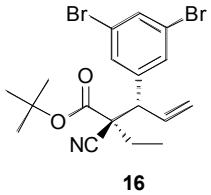
14

(2R,3S)-*tert*-butyl 3-(4-bromophenyl)-2-cyano-2-ethylpent-4-enoate (14). Prepared using the general procedure. Preparative TLC on the residue (5% EtOAc: PE) yielded the title compound **14** (0.0335 g, 0.092 mmol, 92% yield, >20:1 b/l, 13.7:1 dr, 97% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.26 (ddd, *J* = 16.9, 10.2, 9.1 Hz, 1H), 5.27 – 5.19 (m, 2H), 3.68 (d, *J* = 9.2 Hz, 1H), 1.83-1.77 (m, 2H), 1.53 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 136.8, 135.1, 132.1, 130.8, 122.3, 119.5, 118.6, 84.8, 55.4, 30.2, 28.1, 27.8, 9.9. IR (film): υ_{max}/cm^{-1}: 2977, 2937, 2241, 1735, 1489, 1370, 1252, 1156, 1011, 839. HRMS: Expected: 364.0912 (H+), Found: 364.0908 (H+). $[\alpha]^{D}_{20}$° -65.4° (*c* = 0.79, CH_2Cl_2). R_f = 0.43 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 11.37 min, major 14.85 min (major diastereomer).



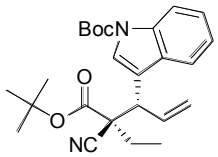
15

(2R,3S)-*tert*-butyl 2-cyano-2-ethyl-3-(4-nitrophenyl)pent-4-enoate (15). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **15** (0.0274 g, 0.083 mmol, 83% yield, >20:1 b/l, 11.1:1 dr, 92% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J = 7.5* Hz, 2H), 7.29 (d, *J = 7.5,* 2H), 6.24 (tdd, *J* = 13.7, 10.0, 6.0 Hz, 1H), 5.28 – 5.18 (m, 2H), 3.68 (d, *J* = 9.2 Hz, 1H), 1.85 – 1.74 (m, 1H), 1.53 (s, 9H), 1.44 – 1.34 (m, 1H), 0.99 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 135.7, 129.4, 129.1, 129.0, 128.5, 127.9, 116.9, 84.5, 40.8, 36.0, 31.8, 28.0, 19.6. IR (film): υ_{max}/cm^{-1}: 3382, 2978, 2936, 2243, 1735, 1524, 1348, 1252, 1156, 840. HRMS: Expected: 331.1658 (H+), Found: 331.1652 (H+). $[\alpha]^{D}_{20}$ -58.7° (*c* = 0.57, CH_2Cl_2). R_f = 0.19 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 30.94 min, 52.57 major min (major diastereomer).



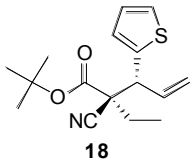
16

(2R,3S)-*tert*-butyl-3-(3,5-dibromophenyl)-2-cyano-2-ethylpent-4-enoate (16). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **16** (0.0417 g, 0.094 mmol, 94% yield, >20:1 b/l, 14.0:1 dr, 97% ee) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H), 6.26 – 6.10 (m, 1H), 5.23 (m, 2H), 3.60 (d, *J* = 9.1 Hz, 1H), 1.89 – 1.74 (m, 2H), 1.50 (s, 9H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 141.8, 134.3, 133.9, 130.9, 128.3, 123.4, 120.3, 85.0, 56.1, 55.2, 30.2, 28.1, 9.9. IR (film): υ_{max}/cm^{-1}: 2977, 2935, 2243, 1736, 1582, 1555, 1370, 1252, 1157, 841, 742. HRMS: Expected: 443.9997 (H+), Found: 443.9992 (H+). $[\alpha]^{D}_{20}$ -21.1° (*c* = 0.71, CH_2Cl_2). R_f = 0.44 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 7.51 min major 8.07 min (major diastereomer).



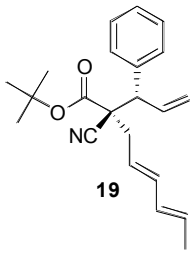
17

(2R,3S)-*tert*-butyl 3-(4-(*tert*-butoxycarbonyl)-4-cyanohex-1-en-3-yl)-1H-indole-1-carboxylate (17). Prepared using the general procedure. Preparative TLC on the residue (20% EtOAc: PE) yielded the title compound **17** (0.0424 g, 0.100 mmol, >99% yield, >20:1 b/l, 11.0:1 dr, 97% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.13 (m, 1H), 7.79 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.30 – 7.29 (m, 1H), 6.30 – 6.19 (m, 1H), 5.24 (m, 2H), 4.08 (d, *J* = 9.3 Hz, 1H), 1.95 (d, *J* = 6.5 Hz, 1H), 1.63 – 1.58 (m, 1H), 1.56 (s, 9H), 0.98 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 149.7, 135.3, 130.5, 125.0, 124.2, 122.9, 119.0, 118.9, 118.6, 117.3, 115.6, 84.7, 84.3, 59.8, 57.7, 46.8, 38.4, 31.5, 30.0, 28.4, 28.2, 27.6, 10.1. IR (film): υ_{max}/cm^{-1}: 2979, 2938, 2243, 1738, 1454, 1370, 1254, 1157, 1095, 840, 747. HRMS: Expected: 425.2436 (H+), Found: 425.2440 (H+). $[\alpha]^{D}_{20}$ -30.8° (*c* = 1.33, CH_2Cl_2). R_f = 0.18 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 8.53 min, 9.47 major min (major diastereomer).



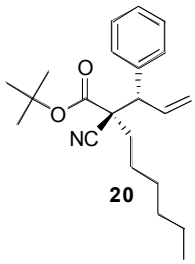
18

(2R,3S)-*tert*-butyl 2-cyano-2-ethyl-3-(thiophen-2-yl)pent-4-enoate (18). Prepared using the general procedure. Preparative TLC on the residue (10% EtOAc: PE) yielded the title compound **18** (0.0271 g, 0.093 mmol, 93% yield, >20:1 b/l, >20:1 dr, 98% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 5.1, 0.6 Hz, 1H), 7.16 – 7.14 (m, 1H), 7.04 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.24 (dd, *J* = 13.4, 2.4 Hz, 2H), 4.02 (d, *J* = 9.1 Hz, 1H), 1.92 – 1.80 (m, 1H), 1.66 – 1.57 (m, 1H), 1.53 (s, 9H), 1.02 (t, *J = 7.4 Hz*, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 135.5, 129.9, 129.4, 127.4, 126.4, 125.1, 119.1, 84.7, 57.0, 51.4, 30.1, 28.1, 9.9. IR (film): υ_{max}/cm^{-1}: 2977, 2936, 2240, 1736, 1459, 1370, 1251, 1157, 841. HRMS: Expected: 292.1371 (H+), Found: 292.1366 (H+). $[\alpha]^{D}_{20}$ -3.87° (*c* = 1.94, CH_2Cl_2). R_f = 0.50 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 9.92 min, 10.40 major min (major diastereomer).



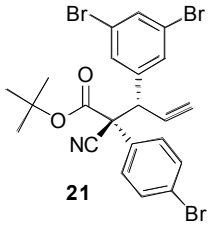
19

(2R,3S,4'E,6'E)-*tert*-butyl 2-cyano-2-(1-phenylallyl)octa-4',6'-dienoate (19). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **19** (0.0307 g, 0.091 mmol, 91% yield, >20:1 b/l, 6.5:1 dr, 98% ee) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 6.28 (ddd, *J* = 16.7, 10.3, 9.2 Hz, 1H), 6.06 – 5.90 (m, 2H), 5.61 (dd, *J* = 14.3, 7.2 Hz, 1H), 5.55-5.42 (m, 1H), 5.25 – 5.15 (m, 2H), 3.72 (d, *J* = 9.1 Hz, 1H), 2.45 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.09 (dd, *J* = 13.8, 6.7 Hz, 1H), 1.71 (d, *J* = 6.8 Hz, 3H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 136.0, 135.4, 130.9, 130.1, 129.2, 129.0, 128.3, 122.4, 84.5, 55.7, 39.9, 28.1, 18.3, 14.4. IR (film): υ_{max}/cm^{-1}: 2978, 2923, 2241, 1733, 1369, 1253, 1153, 988, 706. HRMS: Expected: 338.2120 (H+), Found: 338.2115 (H+). $[\alpha]^{D}_{20}$ -8.91° (*c* = 0.410, CH_2Cl_2). R_f = 0.40 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 8.80 min, major 11.32 min (major diastereomer).



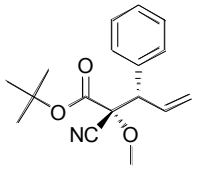
20

(2R,3S)-*tert*-butyl 2-cyano-2-(1-phenylallyl)octanoate (20). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **20** (0.0335 g, 0.098 mmol, 98% yield, >20:1 b/l, 15.7:1 dr, >99% ee) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.49 (s, 3H), 6.20 (dd, *J* = 18.2, 8.8 Hz, 1H), 5.37 – 5.14 (m, 3H), 3.63 (d, *J* = 9.1 Hz, 1H), 1.90 – 1.77 (m, 2H), 1.53 (s, 9H), 1.51 – 1.36 (m, 8H), 1.02 (t, *J* = 7.3 Hz, 3H). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.39 (m, 3H), 7.35 – 7.25 (m, 2H), 7.13 (d, *J* = 1.7 Hz, 2H), 6.39 – 6.11 (m, 1H), 5.39 (dd, *J* = 13.6, 10.7 Hz, 2H), 4.21 (d, *J* = 8.3 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 137.9, 134.7, 129.7, 129.5, 129.6, 128.0, 82.3, 56.3, 43.0, 36.4, 31.8, 29.2, 28.2, 25.7, 22.4, 15.0. IR (film): υ_{max}/cm^{-1}: 3079, 2978, 2937, 2241, 1736, 1556, 1370, 1253, 1157, 839, 741. HRMS: Expected: 342.2433 (H+), Found: 342.2428 (H+). $[\alpha]^{D}_{20}$ -19.1° (*c* = 1.05, CH_2Cl_2). R_f = 0.42 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 7.32 min, 8.17 major min (major diastereomer).



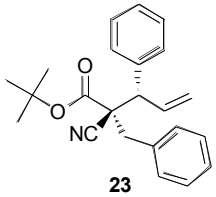
21

(2R,3S)-*tert*-butyl-3-(3,5-dibromophenyl)-2-(4-bromophenyl)-2-cyanopent-4-enoate (21). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **21** (0.0574 g, 0.089 mmol, 89% yield, >20:1 b/l, >20:1 dr, 99% ee) as a clear oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 3H), 7.30 (d, *J* = 9.0 Hz, 3H), 7.13 (d, *J* = 1.7 Hz, 2H), 6.35 – 6.16 (m, 1H), 5.39 (dd, *J* = 13.6, 10.7 Hz, 2H), 4.21 (d, *J* = 8.3 Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 140.8, 134.2, 133.6, 132.3, 131.6, 130.9, 128.5, 123.6, 122.9, 121.3, 117.0, 85.9, 59.7, 55.9, 27.9. IR (film): υ_{max}/cm^{-1}: 3074, 2981, 2246, 1740, 1556, 1255, 1152, 1011, 837, 741. HRMS: Expected: 567.9122 (H+), Found: 567.9119(H+). $[\alpha]^{D}_{20}$ +6.48° (*c* = 0.17, CH_2Cl_2). R_f = 0.45 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 11.67 min, 17.02 major min (major diastereomer).



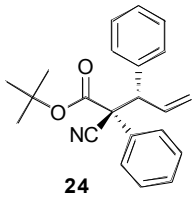
22

(2R,3S)-*tert*-butyl 2-cyano-2-methoxy-3-phenylpent-4-enoate (22). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **22** (0.0227 g, 0.079 mmol, 79% yield, >20:1 b/l, >20:1 dr, 88% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.28 (m, 5H), 6.32-6.20 (m, 1H), 5.32-5.14 (m, 2H), 3.89 (d, J = 9.24 Hz, 1H), 3.53 (s, 1.5H), 3.50 (s, 1.5H), 1.44 (s, 4.5H), 1.31 (s, 4.5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 136.2, 134.3, 129.8, 128.8, 120.8, 120.1, 115.7, 85.3, 83.7, 57.2, 56.2, 55.9, 27.8. IR (film): υ_{max}/cm^{-1}: 2982, 2936, 2245, 1730, 1371, 1302, 1262, 1154, 926. HRMS: Expected: 288.1599 (H+), Found: 288.1594 (H+). $[\alpha]^{D}_{20}$ -32.4° (*c* = 3.1, CH_2Cl_2). R_f = 0.19 (10% EtOAc: PE). HPLC: Chiralcel OD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 8.07 min, 18.40 major min (major diastereomer).



23

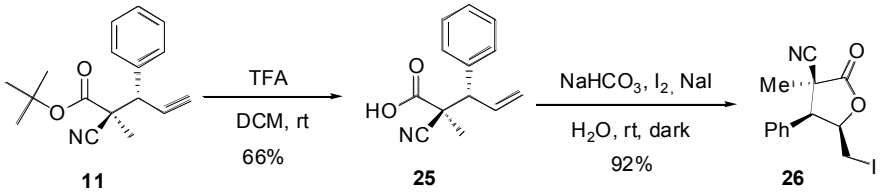
(2R,3S)-*tert*-butyl 2-benzyl-2-cyano-3-phenylpent-4-enoate (23). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **23** (0.0323 g, 0.093 mmol, 93% yield, >20:1 b/l, >20:1 dr, 98% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.19 (m, 10H), 6.37-6.29 (m, 1H), 5.25-5.21 (m, 2H), 3.86 (d, *J = 9.2 Hz*, 1H), 3.01 (d, *J = 13.6 Hz*, 1 Hz), 2.56 (d, *J = 13.4 Hz*, 1H), 1.27 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 137.6, 135.4, 134.6, 130.4, 129.3, 129.2, 128.6, 128.4, 127.8, 119.4, 118.8, 84.7, 56.8, 42.3, 27.9. IR (film): υ_{max}/cm^{-1}: 3030, 2979, 2929, 2241, 1731, 1369, 1256, 1153, 702. HRMS: Expected: 348.1963 (H+), Found: 348.1958 (H+). $[\alpha]^{D}_{20}$ +1.35° (*c* = 1.39, CH_2Cl_2). R_f = 0.30 (10% EtOAc: PE). HPLC: Chiralcel OD-H Column, 99.0:1.0 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 13.13 min, 14.15 major min (major diastereomer).



24

(2R,3S)-*tert*-butyl-2-cyano-2,3-diphenylpent-4-enoate (24). Prepared using the general procedure. Preparative TLC on the residue (3% EtOAc: PE) yielded the title compound **24** (0.0317 g, 0.095 mmol, 95% yield, >20:1 b/l, >20:1 dr, >99% ee) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.36 (m, 5H), 7.11-7.03 (m, 5), 6.42-6.32 (m, 1H), 5.38-5.32 (m, 2H), 4.31 (d, J = 8.4 Hz, 1H), 1.47 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 137.2, 135.9, 133.1, 129.3, 128.8, 128.7, 128.3, 127.6, 126.9, 119.8, 118.0, 85.0, 60.6, 56.8, 27.9. IR (film): υ_{max}/cm^{-1}: 3032, 2978, 2927, 2244, 1736, 1369, 1252, 1151, 697. HRMS: Expected: 334.1807 (H+), Found: 334.1802 (H+). $[\alpha]^{D}_{20}$ +19.0° (*c*= 0.70, CH_2Cl_2). R_f = 0.28 (10% EtOAc: PE). HPLC: Chiralcel AD-H Column, 99.5:0.5 heptane: *i*PrOH, flow rate 0.8 mL/min, Tr minor 14.24 min, 18.95 major min (major diastereomer).

IV. Conversion of 11 into iodolactone 26



(3S,4S,5R)-tetrahydro-5-(iodomethyl)-3-methyl-2-oxo-4-phenylfuran-3-carbonitrile (26). To a solution of **11** (0.0238 g, 0.08 mmol, 1.0 equiv.) in DCM (1.0 mL) was added TFA (1.0 mL) under N_2 at rt and the reaction mixture was stirred for 2 h before concentrated in vacuo and purified by flash chromatography (CH_2Cl_2 to 5% MeOH: CH_2Cl_2) to yield **25** (0.0125 g, 66%) as a clear oil. To a suspension of **25** (0.0125 g, 0.058 mmol, 1.0 equiv) and $NaHCO_3$ (0.0146 g, 0.174 mmol, 3.0 equiv.) in H_2O (1.0 mL) was added NaI (0.0522 g, 0.3483 mmol, 6.0 equiv.) followed by I_2 (0.0162 g, 0.0638 mmol, 1.0 equiv.) under N_2 and the flask was covered was covered with aluminum foil and the reaction mixture stirred in the dark for 5 h before being uncovered to reveal a brown precipitate. The reaction was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organics were washed with 10% $Na_2S_2O_8$ (2 x 10 mL), 10% $NaHCO_3$ (1 x 10 mL), and brine (10 mL). The combined organics were combined and dried over $MgSO_4$ and concentrated under vacuum covering the flask with aluminum foil. The crude residue yielded analytically pure 26 (0.0182 g, 92%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.32 – 7.22 (m, 2H), 5.10 (dd, *J* = 5.6, 3.0 Hz, 1H), 3.76 (d, *J* = 5.3 Hz, 1H), 3.30 (dd, *J* = 10.2, 6.0 Hz, 1H), 2.78 (dd, *J* = 10.1, 8.8 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 132.4, 129.8, 129.6, 129.1, 116.8, 81.3, 55.4, 48.0, 22.5. IR (film): υ_{max}/cm^{-1}: 3034, 2923, 2851, 2250, 1786, 1457, 1171, 1116, 992, 941, 802, 705. HRMS: Expected: 341.9991 (H+), Found: 341.9985 (H+). $[\alpha]^{D}_{20}$ +13.9° (*c*= 1.03, CH_2Cl_2), R_f = 0.15 (20% EtOAc: PE).

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