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Supporting Information

69451 Weinheim, Germany

Indium Mediated Asymmetric Allylation of Acylhydrazones using a Chiral Urea Catalyst

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General Procedures. All reactions were performed in oven dried scintillation vials unless otherwise stated. The vessels were fitted with rubber septa and stir bars and the reactions were performed under a positive pressure of nitrogen. Stainless steel needles were used to transfer air and moisture sensitive liquids. Flash chromatography was performed using silica gel 60 (230-400 mesh) from EM Science.

Materials. Commercial reagents were purchased from Sigma Aldrich, Fluka, Alfa Aesar, or Lancaster, and used as received with the following exceptions diethyl ether, tetrahydrofuran, and toluene were distilled from sodium at 760 torr, and dichloromethane was distilled from calcium hydride at 760 torr. Allyl bromide was purified through a plug of basic alumina prior to use in order to remove any acidic impurities. Indium powder (100 mesh) was purchased from Aldrich, and was stored in a glove box. The following compounds were prepared by literature procedures: (1R, 2R)-1-(*N*-*t*-butyloxycarbonylamino)-2-amniocyclohexane,[1] HCl-(*S*)-amino-3,3,*N*,*N*,-tetramethyl-butryamide (**10**),[2] HCl•(1R, 2R)-diamino cyclohexane (**12**).[3]

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian Mercury-400 (400 MHz), Inova-500 (500 MHz), or Inova-600 (600 MHz) NMR spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethyl silane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants in Hertz (Hz). Infrared (IR) spectra were obtained using a Mattson Galaxy Series FTIR 3000 spectrophotometer referenced to a polystyrene standard. Data are represented as follows: frequency of absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak). Optical rotations were measured using a 2 mL cell with a 1 dm path length on a Jasco DIP 370 digital polarimeter. The mass spectroscopic data were obtained at the Harvard University mass spectrometry facility. Chiral HPLC analysis was performed on a Shimadzu VP-series instrument. Chiral SFC analysis was performed on a Berger instrument.

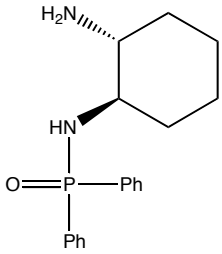
General Procedure for the synthesis of benzoylhydrazones.

Hydrazones were prepared according to a procedure published by Kobayashi and co-workers.[4] To a round bottom flask was added benzoic hydrazide (1.0 equiv) and methanol (0.25 M in benzoic hydrazide). The aldehyde (1.2 equiv) was added to this mixture followed by several drops of acetic acid. After several hours, the reaction had reached completion and the methanol was removed in vacuo. The resulting solid was crystallized from the appropriate solvent (methanol or ethyl acetate/hexanes). In many

cases titration with ethyl acetate/ hexanes was sufficient to obtain highly pure hydrazones.

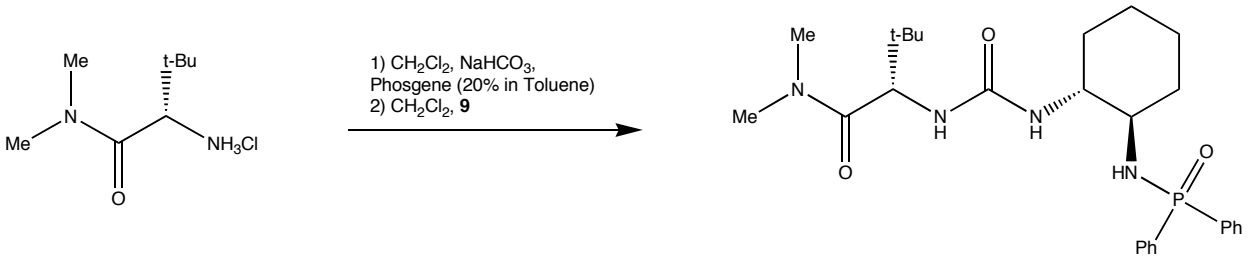
Catalyst Preparation

(1*R*, 2*R*)-*N*-(diphenylphosphinyl)-cyclohexane-1,2-diamine (9):



To a round bottom flask was added (1*R*, 2*R*)-1-(*N*-*t*-butyloxycarbonylamino)-2-aminocyclohexane (415 mg, 1.94 mmol) in CH_2Cl_2 (15 mL). The vessel was cooled to −30 °C and diisopropylethylamine (592 μL, 3.40 mmol) and diphenylphosphinic chloride (406 μL, 2.13 mmol) was added. The reaction vessel was warmed to room temperature and stirred for 2 h. The reaction was diluted with CH_2Cl_2 (30 mL). The organic layer was washed with 1N HCl (1 x 15 mL), $NaHCO_3$ (sat.) (1 x 15 mL), H_2O (1 x 15 mL), brine (1 x 15 mL). The organic layer was dried and concentrated. Purification of the crude material by SiO_2 column chromatography (2.5% MeOH/CH_2Cl_2) yielded a pale yellow solid (740 mg, 92% yield). The product (700mg, 1.69 mmol) was added to a round bottom flask in CH_2Cl_2 (15 mL). Trifluroacetic acid (2.0 mL, 33.8 mmol) was added, and the reaction solution was stirred. After the reaction reached completion, triethylamine (4.7 mL) was added at 0 °C. The reaction was diluted with CH_2Cl_2 (75 mL), and the organic layer was washed with H_2O (2 x 50 mL). The organic layer was dried and concentrated in vacuo, and the crude residue was purified by SiO_2 column chromatography (10% MeOH/CH_2Cl_2 → 0.5% TEA + 10% MeOH/CH_2Cl_2) yielding a white solid (413 mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00-7.90 (m, 4H), 7.56-7.45 (m, 6H), 3.28-3.21 (br s, 1H), 2.69-2.65 (m, 2H), 2.58-2.46 (m, 1H), 2.11 (d br, 1H, *J*= 12), 2.00 (d br, 1H, *J*= 13.2), 1.67 (d br, 2H, *J*= 12.6) 1.35-1.09 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 133.0 (d, *J*= 129.0), 132.6 (d, *J*= 130.5), 132.2 (d, *J*= 9.2), 131.7 (d, *J*= 10.0), 131.7, 131.6, 128.4 (d, *J*= 14.1), 58.5 (d, *J*= 2.3), 56.6 (d, *J*= 4.6), 35.1 (d, *J*= 4.6), 34.6, 25.2, 24.8. IR (NaCl): 3162.1 (br), 2927.8, 2856.4, 1437.8, 1182.3, 1121.5, 1110.9. HRMS: Calc'd for $C_{18}H_{23}N_2OP$ $[M+H]^+$: 315.1626. Found: 315.1616.

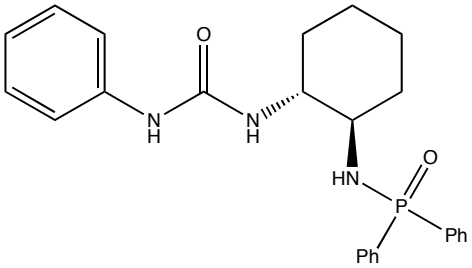
(*S*)-3,3,*N*,*N*-tetramethyl-2-[3-((1*R*,2*R*)-2-(N-diphenylphosphinyl)-cyclohexyl)-ureido)-butyramide (4):



To a round bottom flask was added HCl-(*S*)-amino-3,3,*N*,*N*,-tetramethyl-butryamide (400 mg, 2.05 mmol), CH_2Cl_2 (30 mL), and $NaHCO_3$ (30 mL). The reaction mixture was cooled to 0 °C. Without stirring, phosgene (1.19 mL, 2.26 mmol, 20% in toluene) was added directly into the CH_2Cl_2 layer. The reaction was stirred at 500 rpm for 45 min. The aqueous layer as extracted with CH_2Cl_2 (2 x 30 mL). The organic layers were pooled, dried with Na_2SO_4, filtered and concentrated. The product could be used directly in the next reaction or purified by column chromatography. Rapid purification by SiO_2 column chromatography (30% EtOAc/hexanes) yielded a white solid (171 mg, 45% yield).

To a round bottom flask was added (*S*)-2-isocyanato-3,3,*N,N*-tetramethyl-butyramide (**10**) (50 mg, 0.271 mmol) followed by CH_2Cl_2 (2.5 mL). At room temperature (1*R*, 2*R*)-*N*-(diphenylphosphinyl)-cyclohexane-1,2-diamine (**9**) (94 mg, 0.298 mmol) was added, and the reaction solution was stirred for ~3h. The crude solution was directly loaded onto a SiO_2 column and was purified (2.5% → 5% MeOH/CH_2Cl_2). A white solid was isolated (132 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, 1H, *J*= 7.0), 7.96 (d, 1H, *J*= 7.2). 7.78 (d, 1H, *J*= 7.2), 7.76 (d, 1H, *J*= 7.8), 7.59-7.29 (m, 6H), 6.32 (br s, 1H), 5.60 (br d, 1H, *J*= 9.0), 4.75 (d, 1H, *J*= 8.9), 3.36 (t, 1H, *J*= 10.0), 3.19 (dd, 1H, *J*=9.4, 10.3), 3.14 (s, 3H), 2.96 (s, 3H), 2.84-2.80 (m, 1H), 2.21 (m, 1H), 2.11 (m, 1H), 1.67 (m, 2H), 1.39-1.28 (m, 2H), 1.21-1.14 (m, 2H), 1.05 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$), 172.6, 159.0, 132.9 (d, *J*= 130.6), 132.2 (d, *J*= 9.2), 132.6 (d, *J*= 125.8), 131.7 (d, *J*= 9.2), 131.6, 131.6, 128.4 (d, *J*= 12.2), 128.3 (d, *J*= 13.0), 55.5 (br, 2 carbons), 55.0, 38.1, 35.9, 35.4, 35.4, 33.7, 26.4, 25.1, 24.7. IR(NaCl): 3336.7 (br), 2931.6, 2859.3, 1642.3 (s), 1562.2, 1187.1. HRMS: Calc'd for $C_{27}H_{39}N_4O_3P$ $[M+H]^+$: 499.2838. Found: 499.2833.

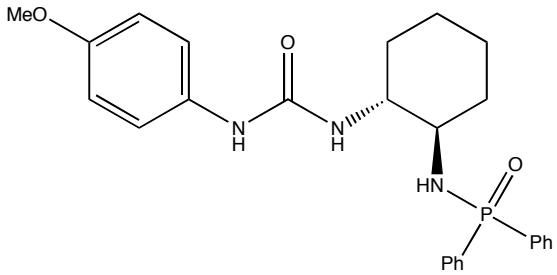
1-((1*R*,2*R*)-2-(*N*-diphenylphosphinyl)-cyclohexyl)-3-phenyl-urea (5):



To a vial was added phenyl isocyanate (23 mg, 0.191 mmol) and CH_2Cl_2 (0.25 mL). Compound **9** (50 mg, 0.159 mmol) in CH_2Cl_2 (1 mL) was then added. After 3 h the reaction was quenched with MeOH, and the crude reaction mixture was concentrated in vacuo. The resulting residue was purified by column chromatography (2%

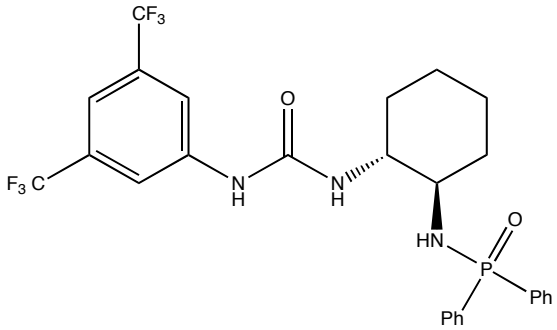
MeOH/CH_2Cl_2), yielding a white solid (63 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.97 (d, 1H, *J* = 7.0) 7.95 (d, 1H, *J* = 7.0), 7.61 (d, 1H, *J* = 7.3), 7.60 (d, 1H, *J* =4.4), 7.60-7.55 (m, 1H), 7.55-7.49 (m, 2H), 7.35 (1H, td, *J* = 7.3, 1.2), 7.15-7.11 (m, 4H), 7.07-7.04 (m, 3H), 6.87 (t, 1H, *J*= 7.3), 4.02 (t, 1H, *J* = 9.1), 3.68-3.64 (m, 1H), 2.95-2.75 (m, 1H), 2.10 (br d, 1H, *J* = 12.3), 1.88 (br d, 1H, *J* = 12.3), 1.67-1.62 (m, 2H), 1.45-1.05 (m, 4H). ^{13}C NMR (100 Mhz, $CDCl_3$): δ 157.5, 140.1, 132.7 (d, *J* = 124.4), 133.0 (d, *J* = 9.8), 132.1, 132.2 (d, *J* = 124), 131.9, 130.9 (d, *J* = 10.7), 128.5 (d, *J* = 6.8), 128.5, 128.4 (d, *J* = 5.3), 121.4, 118.6, 56.9, 54.3, 35.5, 33.5, 25.3, 25.0. IR (NaCl): 3317.4 (br), 2926.8, 2855.4, 1555.5 (s), 1177.5, 906.5 (w). HRMS: Calc'd for $C_{25}H_{28}N_3O_2P$ $[M+H]^+$: 434.1997. Found: 434.2012.

1-((1*R*,2*R*)-2-(*N*-diphenylphosphinyl)-cyclohexyl)-3-(4-methoxy-phenyl)-urea (**6**).



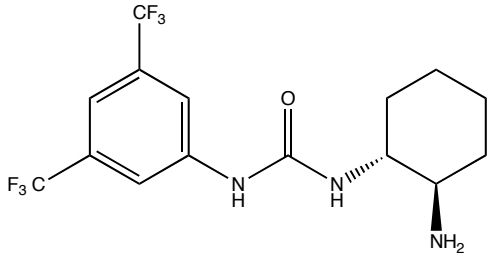
To a vial was added **9** (33 mg, 0.105 mmol) and CH_2Cl_2 (1 mL), followed by (4-methoxy)-phenyl) isocyanate (17 μL, 0.126 mmol) in CH_2Cl_2 (0.5 mL). After stirring for 2 h, the crude reaction was loaded directly on a SiO_2 column and was purified (1 → 2.5 % MeOH/CH_2Cl_2), yielding a white solid (40 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (br s, 1H), 7.96 (d, 1H, *J*= 7.0), 7.93 (d, 1H, *J*= 7.0), 7.63 (d, 1H, *J*= 7.0), 7.60 (d, 1H, *J*= 7.3), 7.54 (t, 1H, *J*= 7.3), 7.49-7.44 (m, 2H), 7.35 (t, 1H, *J*= 7.3), 7.17-7.13 (m, 2H), 6.99 (d, 2H, *J*= 8.8), 6.94 (br s, 1H), 6.58 (d, 2H, *J*= 9.1), 4.30 (br s, 1H), 3.72 (s, 3H), 3.72-3.60 (m, 1H), 3.00-2.80 (m, 1H), 2.06 (br d, 1H, *J*= 12.1), 1.85 (br d, 1H, 12.8), 1.66-1.58 (m, 2H), 1.36-1.25 (m, 2H), 1.12-0.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 154.5, 132.8 (d, *J*= 124.4), 133.5, 133.0 (d, *J*= 9.9), 131.9, 131.8, 131.0 (d, *J*= 10.7), 128.5 (d, *J*= 8.3), 128.4 (d, *J*= 8.4), 120.4, 113.7, 57.1, 55.4, 54.1, 35.5, 33.4, 25.2, 25.0. IR(NaCl): 3311.6 (br), 2933.6, 2855.4, 1678.0, 1556.5, 1511.1 (s), 1241.1, 1179.4, 1110.0. LRMS (ESI) = 464.2 (100%) $[M+H]^+$, 927.4 (25%) $[Dimer]^+$.

(*R*)-1-(3,5-bis-trifluoromethyl-phenyl)-3-((*R)*-2-(*N*-diphenylphosphinyl)-cyclohexyl) urea (7).



To a round bottom flask was added (1*R*, 2*R*)-*N*-(diphenylphosphinyl)-cyclohexane-1,2-diamine (**9**) (75 mg**,** 239 mmol) in CH_2Cl_2 (1 mL). 3,5-(bis-triflurometh yl)phenyl isocyanate (49 μL, 0.286 mmol) was then added. The crude reaction mixture was loaded directly on a SiO_2 column and was purified (1.5% MeOH/CH_2Cl_2), yielding a white solid (116 mg, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.98 (d, 1H, *J*= 7.0), 7.94 (d, 1H, *J*= 7.0), 7.71-7,66 (m, 4H), 7.57 (t, 1H, *J*= 7.3), 7.52-7.44 (m, 3H), 7.32-7.20 (m, 4H), 4.31 (dd, 1H, *J*=9.1, 6.2), 3.78-3.71 (m, 1H), 2.77-2.72 (m, 1H), 1.98 (br d, 1H, *J*=12.1), 1.87 (br d, 1H, *J*= 12.4), 1.65 (br d, 2H, *J*= 12.4), 1.45-1.26 (m, 2H), 1.05-0.88 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$): δ 157.4, 142.0, 133.4 (d, *J*= 10.0), 132.3, 132.1 (d, *J*= 128.2), 131.5 (q, *J*= 32.9), 131.1 (d, *J*= 122.9), 130.4 (d, *J*= 9.9), 128.7 (d, *J*= 13.0), 128.5 (d, *J*= 12.2), 123.2 (q, *J*= 273.1), 116.6 (br), 114.0 (br), 58.10, 54.0, 35.5 (d, *J*= 4.5), 33.4, 25.3, 25.1. IR(NaCl): 3307.7 (br), 3091.7, 2934.5, 2857.4, 1697.3, 1581.5, 1393.5, 1279.7 (s), 1175.5, 1126.4. LRMS (ESI) = 570.2 (100%) $[M+H]^+$.

1-((1*R*,2*R*)-2-amino-cyclohexyl)-3-(3,5-bis-trifluoromethyl-phenyl)-urea (11):



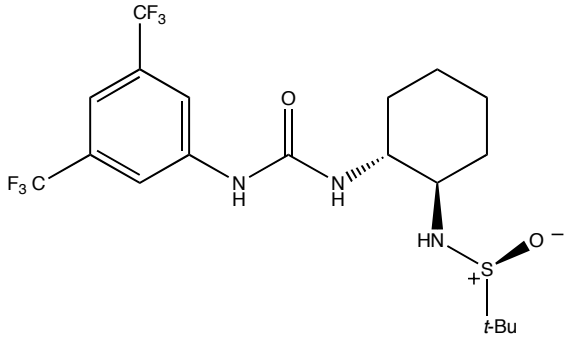
To a round bottom flask was added HCl•(1*R*, 2*R*)-diaminocyclohexane (**12**) (5.0 g, 33 mmol) and CH_2Cl_2 (125 mL). The reaction mixture was cooled to 0 °C and a solution 3,5-bis(triflurometh yl)phenyl isocyanate (5.0 g, 20 mmol) in CH_2Cl_2 (20 mL) was added at a rate of 2 mL/h via syringe pump. After the addition was complete, the reaction was stirred for 3 h then was diluted with 1.1N NaOH (20 mL), and stirred for several minutes. The crude biphasic mixture was filtered to remove any insoluble material. The mixture was diluted further with H_2O (50 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2. The organic layers were pooled together, dried with Na_2SO_4, filtered, and concentrated. The resulting residue was purified by SiO_2 column chromatography (5%→10% MeOH/CH_2Cl_2 → 10% MeOH/CH_2Cl_2 + 1% NH_4OH). After pooling the column fractions the organic layer was dried with Na_2SO_4. The organic layer was filtered and concentrated in vacuo, yielding a white solid (4.75g, 66% yield). (note: often the purified product is a viscous oil; by suspending the residue in hexanes and adding CH_2Cl_2 slowly with agitation with a spatula causes a white solid to form.) ^{1}H NMR (400 MHz, CD_3OD): δ 8.00 (s, 2H), 7.46 (s, 1H), 3.38 (dt, 1H, *J*= 4.4, 10.2), 2.48 (dt, 1H, *J*= 4.03, 10.6), 1.99-1.75 (m, 2H), 1.76-1.72 (m, 2H), 1.38-1.20 (m, 4H). ^{13}C NMR (100 MHz, CD_3OD): δ 157.4, 143.5, 133.1 (q, *J*= 32.8), 124.9 (q, *J*= 271.7), 119.1 (br), 115.4 (br), 57.0, 56.0, 35.0, 33.8, 26.2, 25.9. IR (NaCl): 3319.3 (br), 2936.4, 2862.2, 1661.6, 1568.0, 1388.7, 1277.8 (s), 1177.5, 1129.3. HRMS: Calc'd for $C_{15}H_{17}F_6N_3O$ $[M+H]^+$: 370.1354. Found: 370.1362.

(*R*)-2-methyl-propane-2-sulfinic acid {(1*R*,2*R*)-2-[3-(3,5-bis-trifluoromethyl-phenyl)-ureido]-cyclohexyl}-amide (8b):

To a flame dried round bottom flask was added THF (50 mL). The flask was cooled to −78 °C and *tert*-butylsulfinyl chloride (984 mg, 7.00 mmol), diisopropylethylamine (1.5 mL, 8.6 mmol) and DMAP (155 mg, 1.27 mmol) were added. After stirring for 5 min, **11** (2.29 g, 6.20 mmol) was added as a solid in a single portion. The reaction mixture was stirred at −78 °C for 4 h, then the reaction was allowed to warm slowly to room temperature over ~7 h. After quenching with MeOH, the THF was removed in vacuo. The crude residue was dissolved with ethyl acetate (50 mL),and the organic layer was washed with 1N HCl (1 x 25 mL) and $NaHCO_3$ (sat.) (1 x 25 mL). The organic layer was dried and concentrated. Catalysts **8a** and **8b** were separated by SiO_2 column chromatography (0.75% → 3% MeOH/CH_2Cl_2), affording catalyst **8a** as a white solid (29% yield, 840 mg), and catalyst **8b** as a white solid (1.69 g, 57% yield). Note: **8b** elutes first off the column.

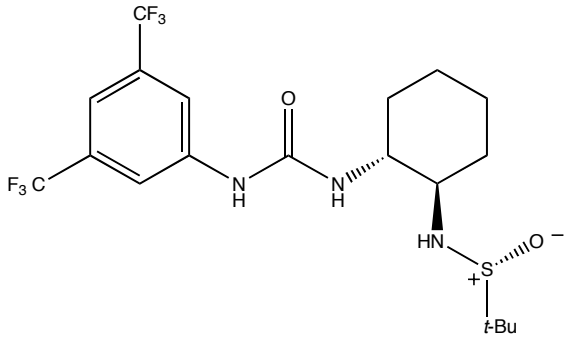
Spectroscopic data for 8a

(*S*)-2-methyl-propane-2-sulfinic acid {(1*R*,2*R*)-2-[3-(3,5-bis-trifluoromethyl-phenyl)-ureido]-cyclohexyl}-amide (8a):



^{1}H NMR (600 MHz, CD_3OD): δ 7.97 (s, 2H), 7.47 (s, 1H), 3.60-3.50 (m, 1H), 2.93 (td, 1H, *J*= 4.1, 11.4), 2.20-2.15 (m, 1H), 1.99-1.96 (m, 1H), 1.77-1.74 (m, 2H), 1.56-1.48 (m, 1H), 1.40-1.30 (m, 3H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, CD_3OD): ∂ 157.1, 143.3, 133.1 (q, *J*= 32.8), 124.8 (q, *J*= 272.4), 119.0, 115.5, 63.5, 57.4, 54.7, 36.4, 34.2, 26.1, 26.0, 23.1. $[\alpha]_D^{23}$ = 15.4, c = 1.06. HRMS: Calc'd for $C_{19}H_{25}F_6N_3O_2S$ $[M+H]^+$: 474.1650. Found: 474.1635.

Spectroscopic data for 8b



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.57 (s, 2H), 7.12 (s, 1H), 6.47 (d, 1H, *J*= 6.6), 6.14 (d, 1H, *J*= 2.9), 3.64-3.52 (m, 1H), 2.92-2.80 (m, 1H), 2.17 (br d, 1H, *J*= 12.1),

2.04 (br d, 1H, *J*= 13.2), 1.83 (m, 2H), 1.55-1.15 (m, 4H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 141.0, 131.8 (q, *J*= 32.6), 123.0 (q, *J*= 270.8), 116.9 (br), 114.5 (br), 63.6, 55.8, 52.8, 35.0, 33.0, 24.9, 24.6, 22.8. IR (NaCl): 3324.1, 3191.0. 3112.0, 2937.4, 2862.2, 1690.5, 1577.7, 1279.7, 1030.9. $[\alpha]_D^{23}$ = –5.7, c = 0.965. HRMS: Calc'd for $C_{19}H_{25}F_6N_3O_2S$ $[M+H]^+$: 474.1650. Found: 474.1636.

General procedure for screening catalysts.

To a vial was added benzoic acid benzylidene hydrazide (10.0 mg, 0.045 mmol), indium (7.6 mg, 0.67 mmol), and catalyst (0.0045 mmol). The vessel was purged with nitrogen for 20 mins., then toluene (0.5 mL) was added. The reaction mixture was cooled to 0 °C and allyl bromide (9 μL, 0.1 mmol, purified through an alumina plug) was added. The reaction was stirred in a cold room (4°C) for 14 h. The reaction mixture was quenched with 1N HCl (1 mL). The reaction mixture was diluted with EtOAc (~2 mL), and the aqueous layer was basified with 4N NaOH. The organic layer was filtered through a plug of SiO_2, and eluted with 1:1 EtOAc/Hexanes. A stock solution of 4-benzoylpyridine (0.093 M,100 μL, 0.0093 mmol) was added. The organic fractions were concentrated in vacuo and analyzed by SFC using commercial chiral stationary phase (Chiralpak AS-H, 25% methanol/CO_2, 4 mL/min^{-1}, 30 °C, 234 nm; t_r(standard): 1.09 min; t_r (minor): 1.81, t_r(major): 1.59 min.

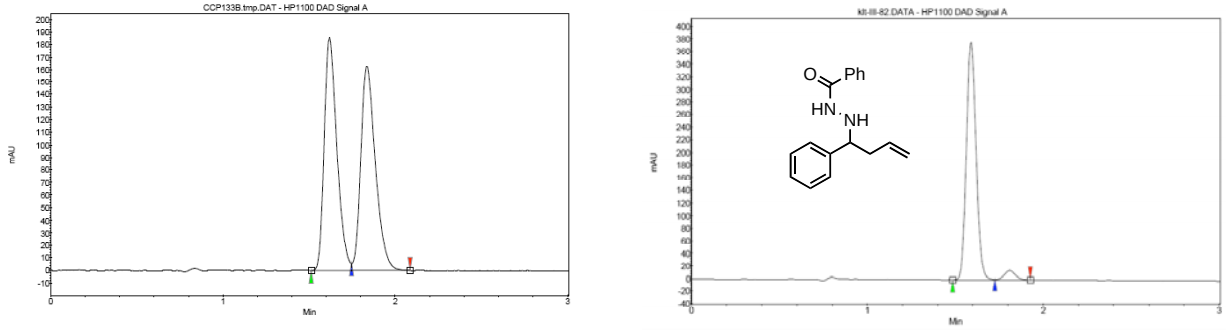
General procedure for the allylation of acylhydrazones catalyzed by 8b:

Benzoic acid *N*'-(1-phenyl-but-3-enyl)-hydrazide (Table 2, entry 1). To a 20mL scintillation vial was added benzoic acid benzylidene hydrazide (224 mg, 1.00 mmol, 1 equiv), indium powder (200 mg, 1.74 mmol, 1.74 equiv), and **8b** (47mg, 0.10 mmol, 0.1 equiv). The vial was purged with N_2 for ~20 min, then toluene (10 mL) was added. The reaction mixture was cooled to –78 °C and allyl bromide was added (228 μL, 2.63 mmol, 2.63 equiv, purified through an alumina plug). The reaction mixture was stirred vigorously at –20 °C for 15 h. The reaction mixture was removed from the cold bath and was immediately quenched with 1N HCl (4 mL) at room temperature. The mixture was diluted with ethyl acetate (25 mL) and 0.67 N NaOH (60 mL). The aqueous layer was extracted with ethyl acetate (2 x 25 mL). The organic layer was dried with Na_2SO_4, filtered, and concentrated. The resulting residue was purified by SiO_2 column chromatography (20% ethyl acetate/hexanes), yielding a white solid (231 mg, 0.87 mmol, 87% yield). The enantiomeric excess was determined to be 92% by SFC using commercial chiral stationary phase (Chiralpak AS-H, 25% methanol/CO_2, 4 mL/min^{-1}, 30 °C, 254 nm; t_r (minor): 1.81 min, t_r (major): 1.59 min; $[\alpha]_D^{23}$ = –152.1° (*c* = 0.955, $CHCl_3$).

Note: The reaction was stirred with a 7/8'' x 3/16'' polygon stir bar at a setting between 8-9 on a IKA RCT-basic. At higher stir rates allyl indium formation was more rapid resulting in the reaction mixture turning light brown in color; furthermore, upon quenching the reaction mixture, it was observed that almost all of the indium metal had been consumed. Under these conditions, a decrease in enantioselectivity and an

increase in yield were observed (see paper for results). At lower stir rates, conversion to product was slower, but high enantioselectivities were maintained.

Spectroscopic Data: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, 2H, *J*= 7.3), 7.48 (t, 1H, *J*= 7.3), 7.41-7.34 (m, 6H), 7.31-7.28 (m, 2H), 5.89-5.83 (m, 1H), 5.26 (br s, 1H), 5.20 (dd, 1H, *J*= 1.1, 17.0), 5.13 (d, 1H, *J*= 10.3), 4.18 (t, 1H, *J*= 7.0), 2.60-2.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 141.6, 134.4, 132.8, 131.7, 128.54, 128.50, 127.7, 127.6, 126.8, 118.0, 63.8, 40.3. IR (NaCl): 3274.0, 1639.4, 1453.3. LRMS (ESI)= 267.2 (100%) $[M+H]^+$.



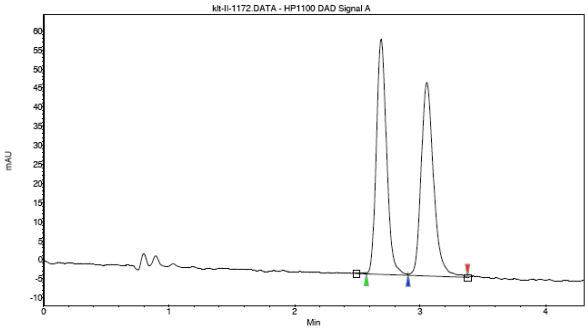
Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	1.59	375.82	24.05	95.805
2	1.81	14.40	1.05	4.195
Total			25.11	100.000

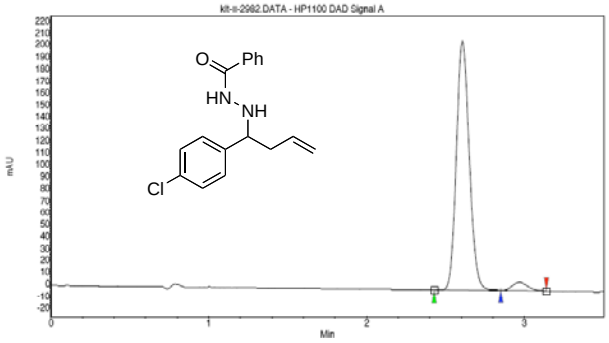
Allylation of 1 on 10 mmol scale
(Note: An octagon 2'' x 5/16'' stirbar was used to stir the reaction mixture.)

To a 250 mL Erylenmeyer flask was added **1** (2.24 g, 10 mmol), **8b** (474 mg, 1.0 mmol), and indium powder (2.0 g, 17.5 mmol). The vessel was fitted with a rubber septum, and was purged with N_2 for 25 min. Toluene (100 mL) was added and the vessel was cooled to −78 °C. Allylbromide (2.28 mL, 26.3 mmol) was then added, and the vessel was stirred at −20 °C for 2 days. The reaction mixture was removed from the cold bath and immediately quenched at room temperature with 1N HCl (30 mL). The reaction mixture was partitioned between ethyl acetate (200 mL) and 0.19 N NaOH (210 mL). The aqueous layer as extracted with ethyl acetate (200 mL). The organic layers were pooled and washed with Brine (200 mL). The organic layer was dried with Na_2SO_4, and was filtered and concentrated. After SiO_2 column chromatography (20% → 50% ethyl acetate/hexanes), the product was isolated as a white solid in 94% yield (2.49 g) and 89% enantiomeric excess. 448 mg of catalyst was recovered after column chromatography as a white solid (95% recovery).

(*S*)-Benzoic acid *N*'-[1-(4-chloro-phenyl)-but-3-enyl]-hydrazide (Table 2, entry 2):
The general procedure for allylation of hydrazones was followed except that 1.35 equiv of indium powder and 2.00 equiv of allyl bromide were used. After SiO_2 column chromatography (20% ethyl acetate/hexanes), the product was isolated as a white solid

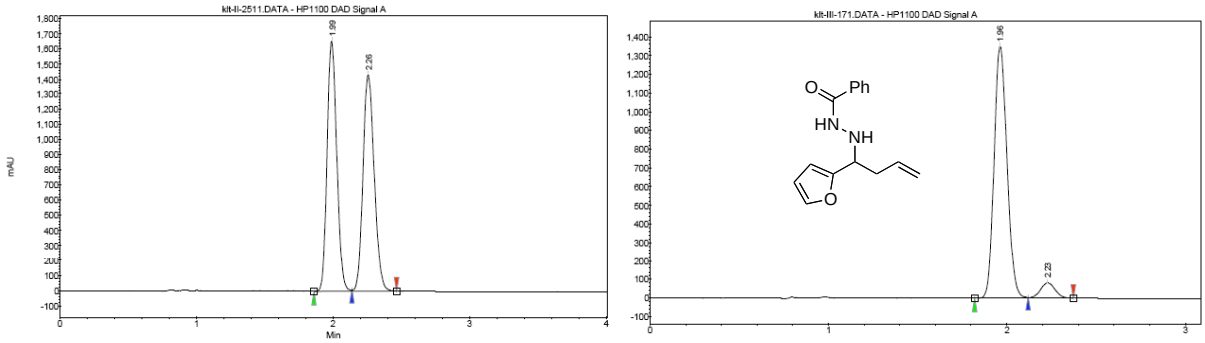
in 83% yield (250 mg) and 92% enantiomeric excess, as determined by SFC (Chiralpak AS-H, 15% MeOH/CO_2, 4 mL/min, 30 °C, 254 nm; t_r(minor) = 2.97 min, t_r(major) = 2.61 min). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, *J*= 7.3, 2H), 7.49 (t, *J*= 7.6, 1H), 7.39 (dd, *J*= 7.9, 7.3, 2H), 7.33 (m, 4H), 7.30 (br d, *J*= 6.4, 1H), 5.90-5.75 (m, 1H), 5.22 (br d, *J*= 5.3, 1H), 5.18 (d, *J*= 17.9, 1H), 5.14 (d, *J*= 10.3, 1H), 4.17 (td, *J*= 7.1,1.8, 1H), 2.55-2.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ 167.3, 140.2, 134.0, 133.2, 132.6, 131.8, 129.0, 128.64, 128.60, 126.8, 118.3, 63.2, 40.3. $[\alpha]_D^{23}$ = -181.3°, c = 0.535. (Literature value: $[\alpha]_D$ = –136.1°, c = 0.535, $CHCl_3$, 89% ee (S)).[5] LRMS (ESI)= 301.1 (100%), 303.1 (33%) $[M+H]^+$.ESI(M+1).





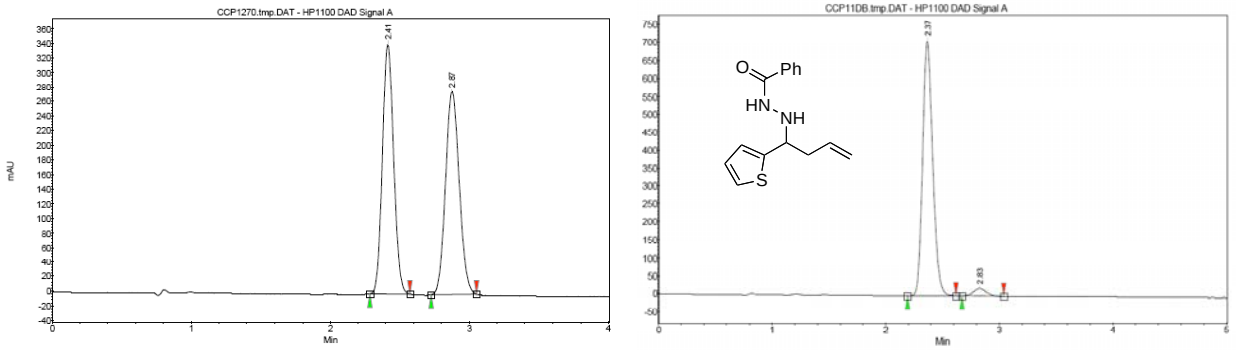
Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	2.61	208.16	19.67	96.053
2	2.97	7.22	0.81	3.947
Total			20.48	100.000

Benzoic acid *N*'-(1-furan-2-yl-but-3-enyl)-hydrazide (Table 2, entry 3):
The general procedure for allylation of hydrazones was followed. After SiO_2 column chromatography (20% ethyl acetate/hexanes), the product was isolated as a white solid in 90% yield (230 mg) and 87% enantiomeric excess, as determined by SFC (Chiralpak AD-H, 15% MeOH/CO_2, 4 mL/min, 30 °C, 254 nm; t_r(minor) = 2.23 min, t_r(major) = 1.96 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (br s, 1H), 7.69-7.66 (m, 2H), 7.49 (t, *J*= 7.7, 1H) 7.42-7.36 (m, 3H), 6.31 (dd, *J*= 1.8, 3.3, 1H), 6.23 (d, *J*= 2.9, 1H), 5.90-5.74 (m, 1H), 5.25-5.18 (m, 2H), 5.13 (d, *J*= 11.7, 1H), 5.10 (d, *J*= 10.2, 1H), 4.23 (t, *J*= 7.00, 1H), 2.66-2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 154.0, 142.2, 133.9, 132.7, 131.8, 128.6, 126.8, 118.1, 110.0, 107.8, 57.5, 36.8. IR (NaCl): 3273.0, 1641.3, 1461.0. $[\alpha]_D^{23}$ = –132.3°, c = 0.720. LRMS (ESI)= 257.2 (100%) $[M+H]^+$.



Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	1.96	1350.15	113.16	93.534
2	2.23	81.91	7.82	6.466
Total			120.98	100.000

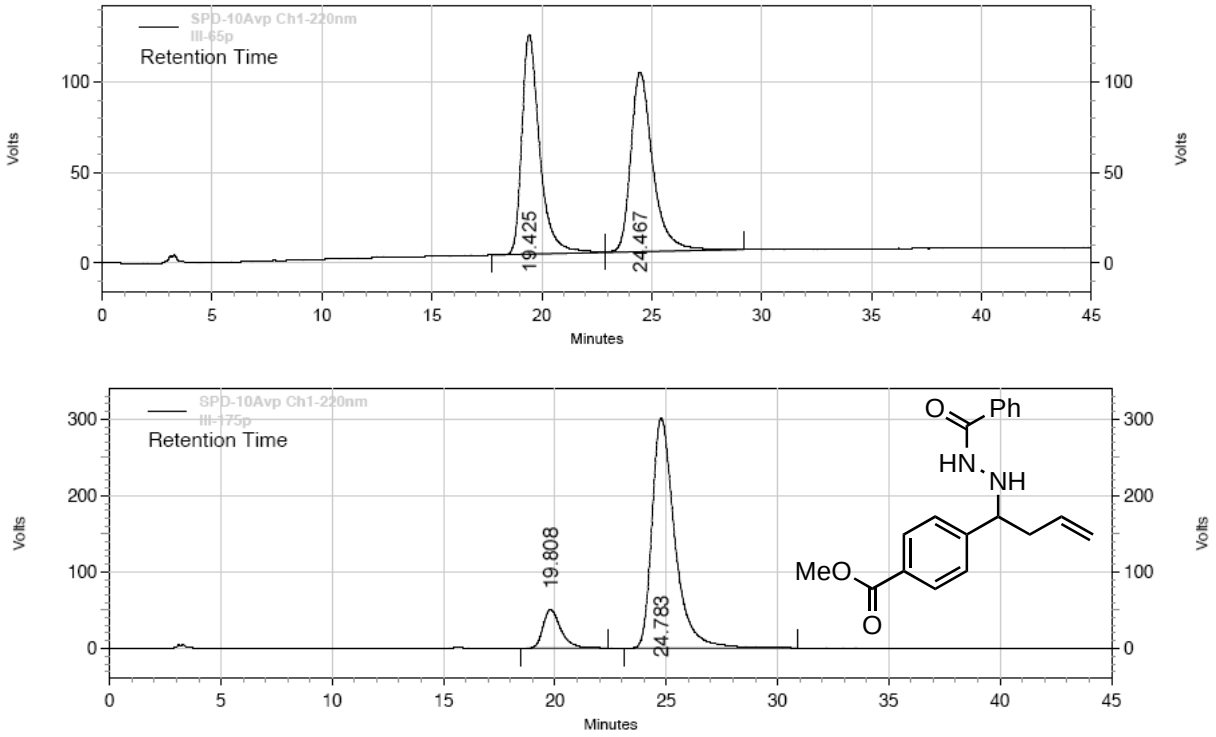
Benzoic acid N'-(1-thiophen-2-yl-but-2-enyl)-hydrazide (Table 2, entry 4):
The general procedure for allylation of hydrazones was followed. After SiO_2 column chromatography (20% ethyl acetate/hexanes), the product was isolated as a white solid in 82% yield (223 mg) and 93% enantiomeric excess, as determined by SFC (Chiralpak AD-H, 35% MeOH/CO_2, 4 mL/min, 30 °C, 254 nm; t_r(minor) = 2.83 min, t_r(major) = 2.37 min). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64 (d, 2H, *J*= 7.0), 7.50 (t, 1H, *J*= 7.6), 7.46 (s, 1H), 7.41(dd, 2H, *J*= 7.6, 7.9), 7.28 (dd, 1H, *J*= 1.8, 4.7), 6.98-6.96 (m, 2H), 5.94-5.84 (m, 1H), 5.30 (br s, 1H), 5.22 (dd, 1H, *J*= 1.2, 17.0), 5.16 (d, 1H, *J*= 10.3), 4.51 (t, 1H, *J*= 7.0), 2.75-2.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 167.3, 145.5, 133.9, 132.7, 131.8, 128.6, 126.8, 126.6, 125.5, 124.7,118.4, 59.5, 41.0. IR (NaCl): 3274.0, 1640.4(s), 1461.0. $[\alpha]_D^{23}$ = –136.9° , c = 0.515. LRMS (ESI)= 273.1(100%) $[M+H]^+$, .



Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
2	2.37	709.84	74.66	96.650
1	2.83	20.78	2.59	3.350
Total			77.25	100.000

4-[1-(N'-Benzoyl-hydrazino)-but-3-enyl-benzoic acid methyl ester (Table 2, entry 5):

The general procedure for allylation of hydrazones was followed. After SiO_2 column chromatography (20% ethyl acetate/hexanes), the product was isolated as a white solid in 92% yield (297 mg) and 76% enantiomeric excess, as determined by HPLC (Chiralpak AD, 10% *i*-PrOH/Hexanes, 1 mL/min, 30 °C, 254 nm; t_r(minor) = 19.808 min, t_r(major) = 24.783 min). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, 2H, *J*= 8.2), 7.57 (d, 2H, *J*= 7.0), 7.50-7.46 (m, 3H), 7.38 (t, 2H, *J*= 7.6), 7.30 (br s, 1H), 5.85-5.80 (m, 1H), 5.25 (br, s, 1H), 5.19 (dd, 1H, *J*= 1.2, 17.0), 5.14 (d, 1H, *J*= 10.0), 4.27 (dd, 1H, *J*= 6.7, 7.7), 3.92 (s, 3H), 2.60-2.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.4, 166.9, 147.1, 133.8, 132.5, 131.8, 129.8, 129.4, 128.5, 127.6, 126.8, 118.4, 63.6, 52.0, 40.3. IR(NaCl): 3284.6 (br), 1721.4 (s), 1641.3, 1279.7. $[\alpha]_D^{23}$ = –155.3°, c = 0.815. LRMS (ESI)= 325.2 (100%) $[M+H]^+$, 366.2 (8%) $[M+CH_3CN]$.

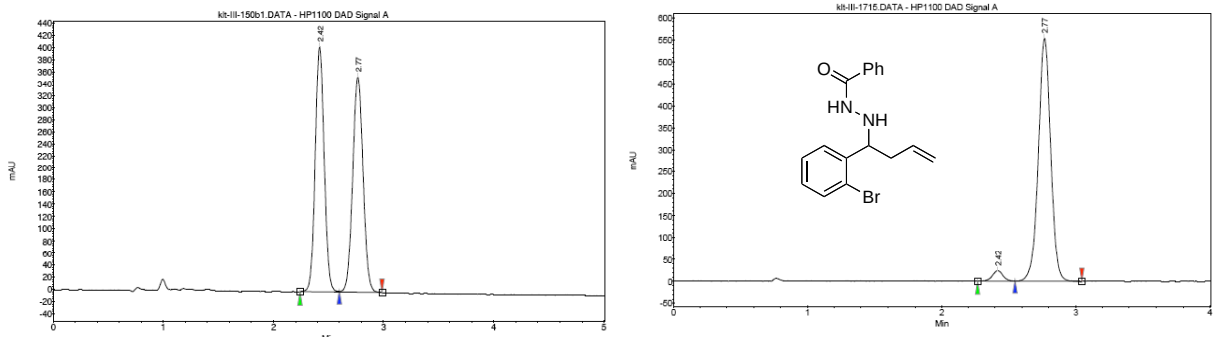


SPD-10Avp
Ch2-254nm
Results

Retention Time	Area	Area %	Height	Height %
19.808	1674027	11.73	30321	14.51
24.783	12599949	88.27	178699	85.49
Totals	14273976	100.00	209020	100.00

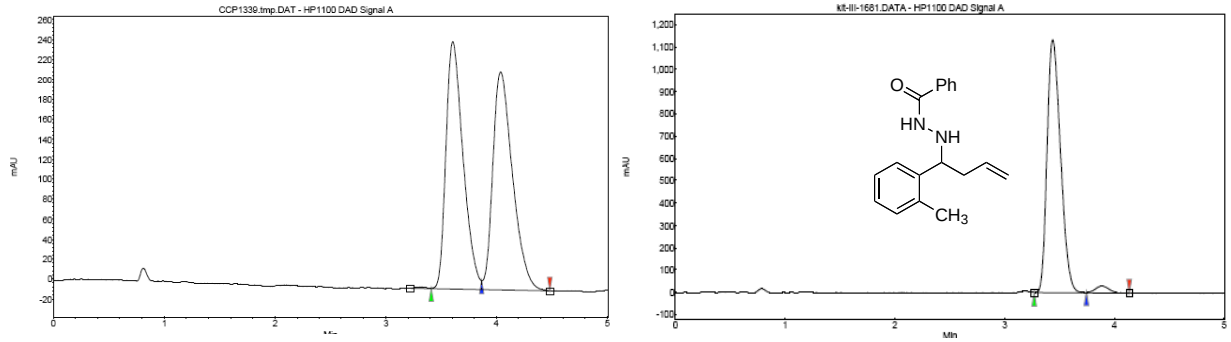
Benzoic acid *N*'-[1-(2-bromo-phenyl)-but-3-enyl]-hydrazide (Table 2, entry 6):
The general procedure for allylation of hydrazones was followed. After SiO_2 column chromatography (20% ethyl acetate/hexanes), the product was isolated as a white solid in 78% yield (270 mg) and 93% enantiomeric excess, as determined by SFC (Chiralpak

OD-H, 15% MeOH/CO_2, 4 mL/min, 30 °C, 254 nm; t_r(major) = 2.77 min, t_r(minor) = 2.42 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, 1H, *J*= 1.8, 7.7), 7.62-7.58 (m, 2H), 7.54 (dd, 1H, *J*= 1.1, 7.7), 7.50-7.40 (m, 2H), 7.39-7.31 (m, 3H), 7.13 (dt, 1H, *J*= 1.8, 8.1), 5.97-5.88 (m, 1H), 5.31 (dd, 1H, *J*= 2.6, 7.0), 5.21 (dd, 1H, *J*= 2.1, 17.2), 5.17 (d, 1H, *J*= 10.6), 5.8-5.6 (m, 1H), 2.6-2.5 (m, 1H), 2.40 (app dt, 1H, *J*= 8.4, 14.3,). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 140.7, 134.0, 133.0, 132.8, 131.7, 128.8, 128.6, 128.3, 127.7, 126.8, 124.5, 118.4, 62.1, 39.3. IR(NaCl): 3282.7 (br), 3064.7, 1638.4 9 (s), 1467.7 cm^{-1}. $[\alpha]_D^{23}$ = –106.9°, c = 0.730. LRMS (ESI)= 345.1 (100%) $[M+H]^+$, and 347.1 (98%) $[M+H]^+$.



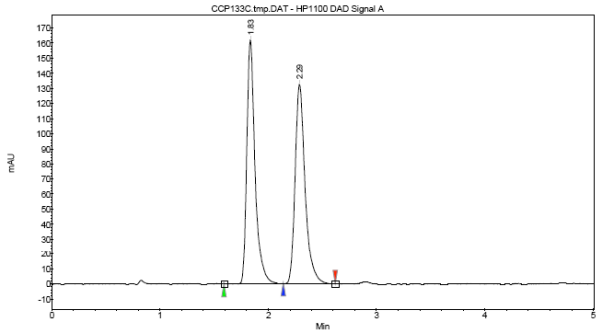
Index	Time [Min]	Height [mAU]	Area [mAU*min]	Area [%]
1	2.42	23.70	2.24	3.633
2	2.77	554.22	59.30	96.367
Total			61.54	100.000

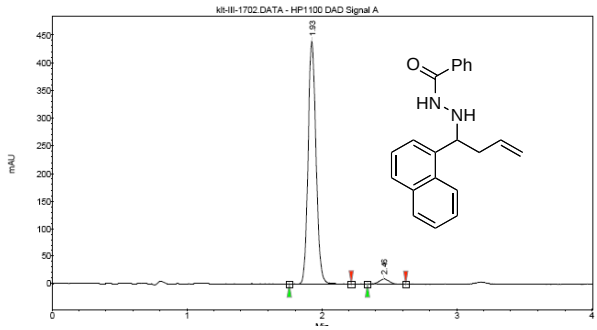
Benzoic acid *N*'-(1-*o*-tolyl-but-3-enyl)-hydrazide (Table 2, entry 7):
The general procedure for allylation of hydrazones was followed. After SiO_2 column chromatography (20% ethyl acetate/hexanes), the product was isolated as a white solid in 89% yield (249 mg) and 95% enantiomeric excess, as determined by SFC (Chiralpak AS-H, 10% MeOH/CO_2, 4 mL/min, 30 °C, 254 nm; t_r(minor) = 3.89 min, t_r(major) = 3.44 min). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60-7.58 (m, 3H), 7.48 (dd, 1H, *J*= 7.0, 7.6), 7.38 (t, 2H, *J*= 7.6), 7.33 (s, 1H), 7.26 (dd, 1H, *J*= 7.0, 7.9), 7.18 (t, 1H, *J*= 7.3), 7.15 (d, 1H, *J*= 7.6), 5.90-5.80 (m, 1H), 5.26 (br s, 1H), 5.21 (d, 1H, *J*= 17.0), 5.14 (d, 1H, *J*= 10.3), 4.53 (t, 1H, *J*= 7.0), 2.48 (t, 2H, *J*= 7.0), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 139.6, 136.5, 134.5, 132.8, 131.7, 130.5, 128.6, 127.1, 126.7, 126.3, 118.0, 59.0, 39.7, 19.4. IR(NaCl): 3282.7 (br), 3065.7, 1638.4 (s), 1462.0 cm^{-1}. $[\alpha]_D^{23}$ = –146.4°, c = 0.675. LRMS (ESI)= 281.2 (100%) $[M+H]^+$, 322.2 (8%) $[M+CH_3CN]^+$.



Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	3.44	1133.91	160.96	97.374
2	3.89	29.54	4.34	2.626
Total			165.30	100.000

Benzoic acid *N*'-(1-naphthanlen-1-yl-but-3-enyl)-hydrazide (Table 2, entry 8):
The general procedure for allylation of hydrazones was followed. After SiO_2 column chromatography (20% ethyl acetate/hexanes), the product was isolated as a white solid in 89% yield (280 mg) and 95% enantiomeric excess, as determined by SFC (Chiralpak AD-H, 35% MeOH/CO_2, 4 mL/min, 30 °C, 254 nm; t_r(minor) = 2.46 min, t_r(major) = 1.93 min). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (br s, 1H), 7.87 (dd, 1H, *J*= 2.0, 7.3), 7.81 (d, 2H, *J*= 8.2), 7.68-7.46 (m, 5H), 7.43 (t, 1H, *J*= 7.6), 7.39 (br s, 1H), 7.35-7.31 (m, 2H), 6.02-5.93 (m, 1H), 5.47 (br s, 1H), 5.26 (dd, 1H, *J*= 17.0), 5.18 (d, 1H, *J*= 10.0), 5.07 (br s, 1H), 2.80-2.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 137.2, 134.6, 133.9, 132.6, 131.7, 131.6, 128.8, 128.5, 127.9, 126.7, 126.1, 125.5, 125.4, 124.3 (br), 123.2 (br), 118.1, 59.5 (br), 39.9. IR(NaCl): 3282.7 (br), 3065.7, 1637.5, 1460.0, 798.5, 777.3 cm^{-1}. $[\alpha]_D^{23}$ = −112.3°, c = 0.815. LRMS (ESI)= 317.2 (65%) $[M+H]^+$, 181.2 (100%) $[M-(NH\text{-}NHCOC_6H)]^+$.

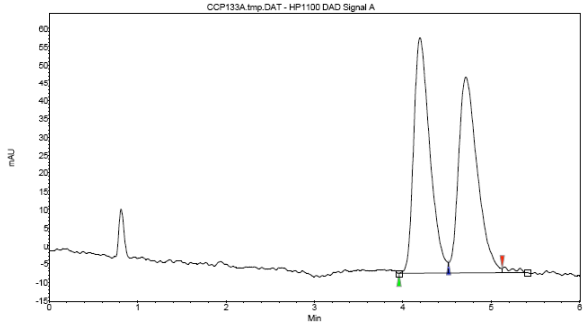


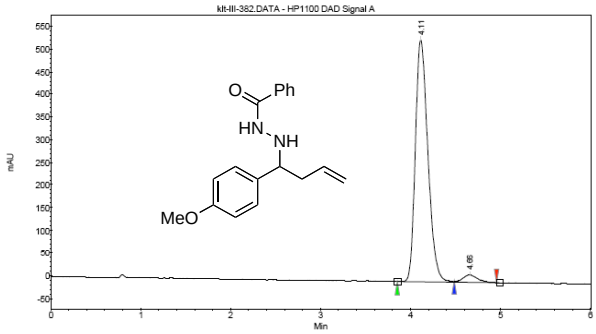


Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	1.93	440.39	30.51	97.485
2	2.46	9.06	0.79	2.515
Total			31.29	100.000

(*S*)-Benzoic acid *N*'-[1-(4-methoxy-phenyl)-but-3-enyl]-hydrazide (Table 2, entry 9):
The general procedure for allylation of hydrazones was followed except that 1.35 equiv of indium powder and 2.00 equiv of allyl bromide were used. After SiO_2 column chromatography (20% ethyl acetate/hexanes), the product was isolated as a white solid in 79% yield (235 mg) and 92% enantiomeric excess, as determined by SFC (Chiralpak AS-H, 10% MeOH/CO_2, 4 mL/min, 30 °C, 254 nm; t_r(minor) = 4.64 min, t_r(major) = 4.11 min). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, *J*=7.3, 2H), 7.48 (t, *J*= 7.6, 1H), 7.39 (dd, *J*= 7.9, 7.6, 2H), 7.31 (m, 3H), 6.89 (d, *J*= 8.5, 2H), 5.90-5.75 (m, 1H), 5.3-5.2 (br s, 1H), 5.19 (d, *J*= 17.0, 1H), 5.12 (d, *J*=10.3, 1H), 4.13 (t, 1H, *J*= 6.4), 3.82 (s, 3H), 2.60-2.40 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 159.0, 134.5, 133.4, 132.8, 131.7, 128.7,

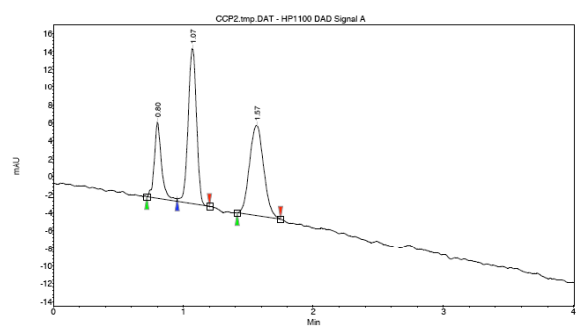
128.5, 126.8, 117.8, 113.8, 63.2, 55.1, 40.2. $[\alpha]_D^{23}$ = –188.2°, c = 0.535. (Literature value: $[\alpha]_D$ = –118.8° (c = 0.510, $CHCl_3$, 77% ee (S)).[2] LRMS (ESI)= 297 (100%) $[M+H]^+$.

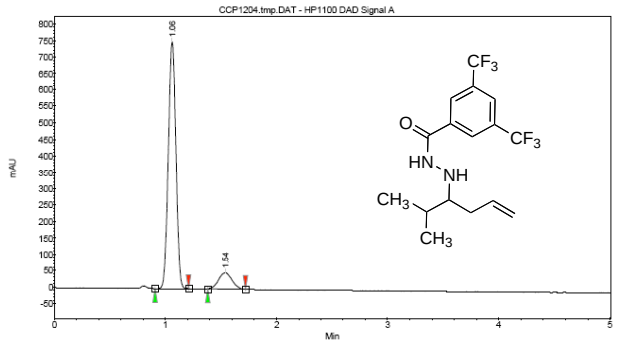




Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	4.11	534.10	85.87	96.634
2	4.66	15.85	2.99	3.366
Total			88.86	100.000

3,5-bis-trifluoromethyl-benzoic acid-*N*'-(1-isopropyl-but-3-enyl)-hydrazide: The general procedure for allylation of hydrazones was followed with the exception that the reaction was stirred at –40 °C for 38 h. After SiO_2 column chromatography (10% ethyl acetate/hexanes), the product was isolated as a white solid in 55% yield (203 mg) and 80% enantiomeric excess, as determined by SFC (Chiralpak AD-H, 5% MeOH/CO_2, 4 mL/min, 30 °C, 254 nm; t_r(minor) = 1.54 min, t_r(major) = 1.06 min). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 2H), 8.00 (s, 1H), 7.96 (s br, 1H), 6.00-5.90 (m, 1H), 5.19 (dd, 1H, *J*=1.1, 17.2), 5.14 (d, 1H, *J*= 10.2), 4.98 (br, s, 1H), 2.89 (dt, 1H, *J*= 4.0, 8.8), 2.35-2.27 (m, 1H), 2.11 (dt, 1H, *J*= 8.4, 14.6), 1.93-1.86 (m, 1H) 0.97 (d, 6H, *J*= 7.0). ^{13}CNMR (100 MHz, $CDCl_3$): δ 164.1, 136.4, 135.0, 132.2 (q, *J*= 34.2), 127.2 (br s), 125.2 (br s), 124.7 (q, *J*= 271.6), 117.3, 64.6, 33.8, 29.5, 18.7, 17.4. IR (NaCl): 3269.2 (br), 3092.7, 1643.3, 1274.9, 1135.0. $[\alpha]_D^{23}$ = –30.5°, c = 0.550. HRMS: Calc'd for $C_{16}H_{18}F_6N_2O$ $[M+H]^+$: 369.1401. Found: 369.1413.





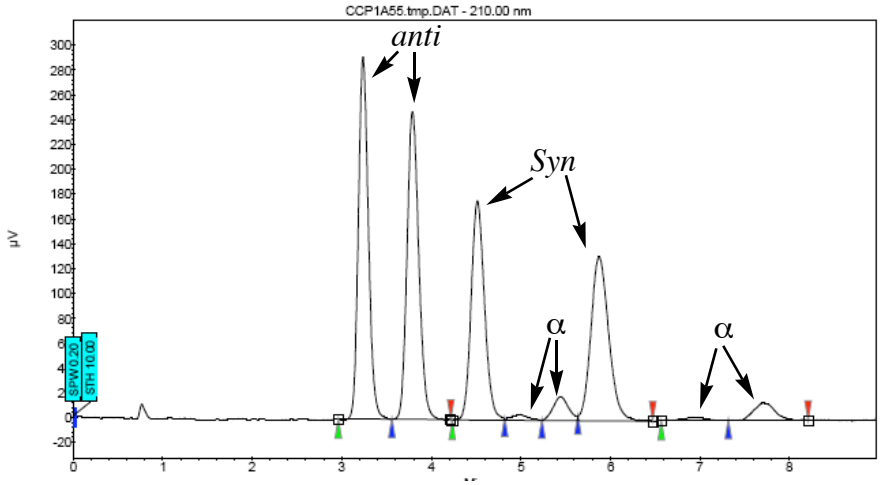
Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	1.06	751.19	59.39	89.725
2	1.54	48.70	6.80	10.275
Total			66.19	100.000

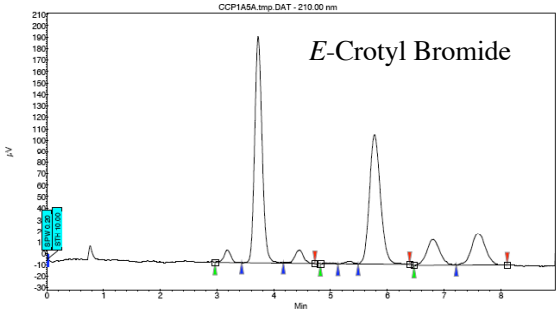
Benzoic acid *N'*-(2-methyl-1-phenyl-but-3-enyl) hydrazide

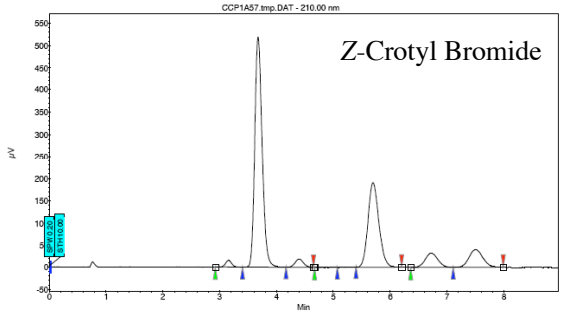
The general procedure for allylation of hydrazones was followed with the exception that crotyl bromide was used in place of allyl bromide. Employing (*E*)-crotyl bromide the product was obtained as a white solid (109 mg, 70% yield), after SiO_2 column chromatography (20% ethyl acetate/hexanes). The *anti*-, *syn*-, and α-addition products were formed in a ratio of 1.10 : 1.00 : 0.40, respectively, as judged by ^{1}H NMR. The enantiomeric excess was determined to be 90% ee (*anti*), 85% ee (*syn*), >90% (α) by SFC (Chiralpak OD-H, 5% MeOH/CO_2, 4 mL/min, 30 °C, 210 nm; t_r(*anti*-minor) = 3.18 min, t_r(*anti*-major) = 3.72 min, t_r(*syn*-minor) = 4.45 min, t_r(*syn*-major) = 5.77 min, t_r(α-minor) = 5.01 min, t_r(α-major) = 6.80 min, t_r(α-minor) = 5.13 min, t_r(α-major) = 7.59 min.

Employing (*Z*)-crotyl bromide, the product was obtained as a white solid (90 mg, 71% yield), after SiO_2 column chromatography (20% ethyl acetate/hexanes). The *anti*-, *syn*-, and α-addition products were formed in a ratio of 1.57 : 1.00 : 0.38, respectively, as judged by ^{1}H NMR. The enantiomeric excess was determined to be 95% ee (*anti*), 86% ee (*syn*), >90% (α) by SFC (Chiralpak OD-H, 5% MeOH/CO_2, 4 mL/min, 30 °C, 210 nm; t_r(*anti*-minor) = 3.15 min, t_r(*anti*-major) = 3.67 min, t_r(*syn*-minor) = 4.41 min, t_r(*syn*-major) = 5.70 min, t_r(α-minor) = 4.91 min, t_r(α-major) = 6.72 min, t_r(α-minor) = 5.07 min, t_r(α-major) = 7.51 min. Spectroscopic data for the products matched the reported spectra in the literature.[6]

(Note: authentic racemic crotylation products were made by performing the reaction under standard conditions with the exception that triphenylphosphine oxide was used as the catalyst and the reaction was performed at 0 °C.)







Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.96	3.18	3.43	0.00	2.10	10.9	1.5	2.096
2	UNKNOWN	3.43	3.72	4.17	0.00	40.84	199.0	30.2	40.836
3	UNKNOWN	4.17	4.45	4.72	0.00	2.86	11.4	2.1	2.857
4	UNKNOWN	4.82	5.01	5.13	0.00	0.19	1.0	0.1	0.195
5	UNKNOWN	5.13	5.35	5.49	0.00	0.53	2.5	0.4	0.528
6	UNKNOWN	5.49	5.77	6.39	0.00	34.59	114.3	25.5	34.586
7	UNKNOWN	6.47	6.80	7.21	0.00	8.17	22.6	6.0	8.169
8	UNKNOWN	7.21	7.59	8.11	0.00	10.73	27.8	7.9	10.734
Total						100.00	389.5	73.9	100.000

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	2.92	3.15	3.40	0.00	1.20	14.7	1.7	1.196
2	UNKNOWN	3.40	3.67	4.16	0.00	53.86	519.6	78.0	53.856
3	UNKNOWN	4.16	4.41	4.65	0.00	2.24	18.6	3.2	2.241
4	UNKNOWN	4.67	4.91	5.07	0.00	0.01	0.6	0.0	0.013
5	UNKNOWN	5.07	5.33	5.40	0.00	0.07	1.1	0.1	0.074
6	UNKNOWN	5.40	5.70	6.20	0.00	29.22	190.6	42.3	29.223
7	UNKNOWN	6.36	6.72	7.11	0.00	5.70	32.1	8.3	5.704
8	UNKNOWN	7.11	7.51	7.99	0.00	7.69	39.9	11.1	7.692
Total						100.00	817.2	144.9	100.000

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