Enantioselective Allylation of Ketone-Derived Benzoylhydrazones: Practical Synthesis of Tertiary Carbinamines

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Supporting Information

General Information. All reactions were carried out under an atmosphere of nitrogen in flame- or oven-dried glassware with magnetic stirring unless otherwise indicated. Degassed solvents were purified by passage through an activated alumina column. Toluene, hexanes, methanol and glacial acetic acid were purchased from Fisher and used as received. Anhydrous chloroform (stabilized with amylenes), anhydrous methylene chloride, benzoic hydrazide and all ketone reagents were purchased from Aldrich and used as received. ^1H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) spectrometer and are reported in ppm from either CDCl_3 internal standard (7.26 ppm) or $\text{DMSO}-d_6$ internal standard (2.49 ppm). Data are reported as follows: (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, tt = triplet of triplets, dq = doublet of quartets, ddt = doublet of doublet of triplets; coupling constant(s) in Hz; integration; assignment). Proton decoupled ^{13}C NMR spectra were recorded on a Bruker DPX-400 (100 MHz) and are reported in ppm from either CDCl_3 internal standard (77.0 ppm), $\text{DMSO}-d_6$ internal standard (39.5 ppm) or CD_3OD internal standard (49.0 ppm). Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer. Optical rotations were recorded on a Jasco DIP-1000 digital polarimeter.

Preparation of reagent (S,S)-1: The procedure for preparation and characterization data for this reagent may be found in the supporting information of our earlier work.¹

(1) (a) Kinnard, J. W. A.; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920-7921. (b) Berger, R.; Rabbat, P. M. A.; Leighton, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 7920-7921.

Preparation of benzoic acid (1-phenyl-ethylidene)-hydrazide (Table 1, Entry 1): Benzoic hydrazide (11.3 g, 83.3 mmol) was added to a stirred solution of acetophenone (10.0 g, 83.3 mmol) and glacial acetic acid (0.500 mL, 8.73 mmol) in methanol:hexanes (1:5) (70 mL). The resulting suspension was heated to reflux for 12 hr during which time all solids dissolved. After cooling to ambient temperature the mixture was concentrated and the residue recrystallized from toluene to yield benzoic acid (1-phenyl-ethylidene)-hydrazide (16.0 g, 80%) as a white solid.

Note: This procedure was used for the preparation of all benzoylhydrazones. Characterization data for substrates not previously reported are listed below.

Benzoic acid (1,2-diphenyl-ethylidene)-hydrazide (Table 1, Entry 3): Recrystallized from toluene (88% yield): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.99 (br s, 1H, N-H), 7.84 (br s, 2H, Ar-H), 7.72-7.74 (m, 2H, Ar-H), 7.45-7.56 (m, 3H, Ar-H), 7.37 (br s, 3H, Ar-H), 7.19-7.30 (m, 2H, Ar-H), 7.15-7.18 (m, 3H, Ar-H), 4.40 (s, 2H, $\text{CH}_2\text{-Ph}$), ^{13}C NMR (100 MHz, CDCl_3) δ 163.1, 135.1, 137.4, 133.9, 133.0, 131.6, 129.4, 128.3, 127.8, 127.4, 126.7, 34.2; IR (KBr): 3345, 3081, 3058, 3026, 2941, 2873, 1658, 1600, 1580, 1520, 1484, 1457, 1265, 1131, 1101, 1075 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$ 314, found $(\text{M}+\text{H})^+$ 315.

Benzoic acid (2-methyl-1-phenyl-propylidene)-hydrazide (Table 1, Entry 4): Recrystallized from toluene (68% yield): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) $\sim$ 10:1 mixture of rotamers: (major) δ 9.63 (br s, 1H, N-H), 7.33-7.81 (m, 10H, Ar-H), 2.90 (br s, 1H, $(\text{CH}_3)_2\text{C-H}$), 1.07-1.14 (m, 6H, $\text{CH-(CH}_3)_2$), (minor) δ 10.82 (br s, 1H, N-H), 7.33-7.81 (m, 10H, Ar-H), 3.61 (m, 1H, $(\text{CH}_3)_2\text{C-H}$), 1.07-1.14 (m, 6H, $\text{CH-(CH}_3)_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 163.1, 133.3, 132.3, 131.7, 130.3, 129.5, 128.6, 127.4, 127.1, 126.8, 36.5, 19.9; IR (KBr): 3359, 2969, 1670, 1505, 1480, 1464, 1440, 1307, 1292, 1259, 1118, 1073 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}$ 266, found $(\text{M}+\text{H})^+$ 267.

(Benzoyl-hydrazono)-phenyl-acetic acid methyl ester (Table 1, Entry 5): Recrystallized from toluene (70% yield): ^1H NMR (400 MHz, CDCl_3) δ 13.3 (br s, 1H, N-H), 7.91-8.01 (m, 2H, Ar-H), 7.62-7.68 (m, 2H, Ar-H), 7.50-7.62 (m, 3H, Ar-H), 7.35-7.43 (m, 3H, Ar-H), 3.95 (s, 3H, CO_2CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 162.9, 138.9, 134.0, 132.3, 132.1, 129.1, 128.7, 128.5, 127.8, 127.3, 52.8; IR (KBr):

3264, 3060, 3026, 2953, 1701, 1688, 1600, 1578, 1535, 1506, 1475, 1242, 1145 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3$ 282, found $(\text{M}+\text{H})^+$ 283.

Benzoic acid (1-furan-2-yl-ethylidene)-hydrazide (Table 1, Entry 10): Recrystallized from toluene (77% yield): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.67 (br s, 1H, N-H), 7.84-7.86 (m, 2H, Ar-H), 7.79 (br s, 1H, Ar-H), 7.47-7.58 (m, 3H, Ar-H), 6.96 (br s, 1H, Ar-H), 6.60 (br s, 1H, Ar-H), 2.27 (s, 3H, $\text{N}=\text{C}-\text{CH}_3$); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 151.4, 144.3, 133.7, 131.1, 127.9, 127.5, 111.7, 111.3, 13.9; IR (KBr): 3244, 3115, 3035, 1652, 1603, 1573, 1525, 1482, 1318, 1279, 1164, 1141, 1110, 1075, 1026 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_2$ 228, found $(\text{M}+\text{H})^+$ 229.

Benzoic acid (1-thiophen-2-yl-ethylidene)-hydrazide (Table 1, Entry 11): Recrystallized from (1:1) EtOAc:toluene (85% yield): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.75 (br s, 1H, N-H), 7.85-7.86 (m, 2H, Ar-H), 7.47-7.59 (m, 5H, Ar-H), 7.10 (br s, 1H, Ar-H), 2.37 (s, 3H, $\text{N}=\text{C}-\text{CH}_3$); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 163.6, 152.7, 143.2, 134.0, 131.5, 129.1, 128.4, 127.8, 127.6, 15.0; IR (KBr): 3209, 3066, 3025, 1650, 1540, 1517, 1488, 1435, 1307, 1275, 1234, 1139, 1050 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{OS}$ 244, found $(\text{M}+\text{H})^+$ 245.

3-[1-(Benzoyl-hydrazono)-ethyl]-indole-1-carboxylic acid *tert*-butyl ester (Table 1, Entry 12): Recrystallized from toluene (87% yield): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.77 (br s, 1H, N-H), 8.76 (br s, 1H, Ar-H), 8.00-8.20 (m, 2H, Ar-H), 7.90-7.92 (m, 2H, Ar-H), 7.50-7.61 (m, 3H, Ar-H), 7.33-7.39 (m, 2H, Ar-H), 2.42 (s, 3H, $\text{N}=\text{C}-\text{CH}_3$), 1.65 (s, 9H, $\text{COC}(\text{CH}_3)_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 135.7, 133.5, 131.7, 128.6, 127.6, 127.0, 126.6, 125.0, 119.8, 114.5, 84.4, 28.3, 13.5; IR (KBr): 3271, 3071, 2977, 2933, 1732, 1640, 1450, 1370, 1309, 1275, 1251, 1154, 1068 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_3$ 377, found $(\text{M}+\text{H})^+$ 378.

Benzoic acid (1-cyclohexyl-ethylidene)-hydrazide (Table 1, Entry 14): Recrystallized from toluene (82% yield): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 10.32 (br s, 1H, N-H), 7.79-7.81 (m, 2H, Ar-H), 7.46-7.52 (m, 3H, Ar-H), 2.23 (br s, 1H, Cy-H), 1.89 (s, 3H, $\text{N}=\text{C}-\text{CH}_3$), 1.63-1.75 (m, 5H, Cy-H), 1.17-1.31 (m, 5H, Cy-H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 163.5, 162.7, 133.9, 130.8, 127.9, 127.3, 46.5, 29.7, 28.5, 25.7, 25.6, 14.9; IR (KBr): 3219, 3031, 2928, 2850, 1653, 1628, 1581, 1542, 1446, 1290, 1146, 1129 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}$ 244, found $(\text{M}+\text{H})^+$ 245.

Benzoic acid *N*-methyl-*N'*-(1-phenyl-ethylidene)-hydrazide (Scheme 3, Compound 6):

Compound 6 was prepared by the same method as above using benzoic acid *N*-methyl-hydrazide in place of benzoic hydrazide. Recrystallized from toluene (80% yield): ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.70 (br s, 2H, Ar-**H**), 7.41-7.47 (br s, 8H, Ar-**H**), 3.25 (s, 3H, $\text{CH}_3\text{-NCOPh}$), 2.30 (br s, 3H, N=C-CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 169.8, 136.7, 135.2, 130.4, 129.9, 128.1, 126.7, 36.3 (br), 17.1; IR (KBr): 3055, 2948, 1637, 1609, 1573, 1446, 1422, 1346, 1303, 1057, 1023, 794, 716 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}$ 252, found $(\text{M}+\text{H})^+$ 253.

Representative procedure for the enantioselective allylation of benzoylhydrazones with (*S,S*)-1:

To a solution of the benzoylhydrazone (0.800 mmol) in CHCl_3 (5 mL) is added (*S,S*)-1 (320 mg, 1.20 mmol) and the resulting mixture is stirred at the indicated temperature for 24 h (see Table 1). The reaction is quenched with methanol (2 mL), the resulting mixture is stirred for 15 min, and then concentrated. The residue is diluted with EtOAc (5 mL) and H_2O (5 mL), the phases are separated, and the aqueous layer is extracted with EtOAc (2 x 5 mL). The combined organic layers are washed with brine (1 x 5 mL), dried (MgSO_4), filtered, and concentrated. Purification by flash chromatography on silica gel affords the pure hydrazide products in the yields and enantioselectivities reported in Table 1.

(*R*)-Benzoic acid *N'*-(1-methyl-1-phenyl-but-3-enyl)-hydrazide (Table 1, Entry 1): $[\alpha]_{\text{D}} = +78.5^\circ$ (*c* 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.60 (m, 4H, Ar-**H**), 7.47 (t, $J = 7.3$ Hz, 1H, Ar-**H**), 7.36-7.41 (m, 4H, Ar-**H**), 7.29 (t, $J = 7.3$ Hz, 1H, Ar-**H**), 7.08 (br s, 1H, PhCON-H), 5.63-5.72 (m, 1H, $\text{CH}_2\text{CH=CH}_2$), 5.44 (br s, 1H, ArC-N**H**), 5.07-5.12 (m, 2H, $\text{CH}_2\text{CH=CH}_2$), 2.62 (dd, $J = 13.7, 6.6$ Hz, 1H, one of $\text{CH}_2\text{CH=CH}_2$), 2.52 (dd, $J = 13.7, 8.0$ Hz, 1H, one of $\text{CH}_2\text{CH=CH}_2$), 1.56 (s, 3H, ArC-**CH**₃); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 144.2, 133.5, 132.7, 131.5, 128.5, 128.4, 127.0, 126.7, 126.4, 118.4, 62.4, 46.0, 22.6; IR (thin film) 3275, 3061, 2976, 2929, 1637, 1578, 1542, 1494, 1446, 1374, 1313 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}$ 280, found $(\text{M}+\text{H})^+$ 281.

(*R*)-Benzoic acid *N'*-(1-ethyl-1-phenyl-but-3-enyl)-hydrazide (Table 1, Entry 2): $[\alpha]_{\text{D}} = -16.7^\circ$ (*c* 2.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.58 (m, 4H, Ar-**H**), 7.47 (tt, $J = 7.3, 1.3$ Hz, 1H, Ar-**H**), 7.36-7.42 (m, 4H, Ar-**H**), 7.29 (t, $J = 7.3$ Hz, 1H, Ar-**H**), 7.01 (d, $J = 6.1$ Hz, 1H, PhCON-H), 5.86 (ddt, $J = 17.0, 10.0, 7.2$ Hz, 1H, $\text{CH}_2\text{CH=CH}_2$), 5.56 (d, $J = 7.3$ Hz, 1H, ArC-N**H**), 5.09-5.17 (m, 2H,

$\text{CH}_2\text{CH}=\text{CH}_2$), 2.62-2.71 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.79-1.93 (m, 2H, $\text{CH}_2\text{-CH}_3$), 0.83 (s, 3H, $\text{CH}_2\text{-CH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 142.7, 133.9, 132.7, 131.3, 128.4, 128.2, 126.8, 126.51, 126.47, 117.8, 65.0, 40.4, 29.3, 8.0; IR (thin film) 3279, 3058, 2974, 2933, 1638, 1578, 1538, 1447, 1432, 1312, 916 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$ 294, found $(\text{M}+\text{H})^+$ 295.

(S)-Benzoic acid *N'*-(1-benzyl-1-phenyl-but-3-enyl)-hydrazide (Table 1, Entry 3): $[\alpha]_{\text{D}} = +0.90^\circ$ (c 1.4, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.2$ Hz, 2H, Ar-H), 7.41-7.46 (m, 3H, Ar-H), 7.32-7.37 (m, 4H, Ar-H), 7.24-7.29 (m, 1H, Ar-H), 7.10-7.18 (m, 4H, Ar-H), 6.84-6.87 (m, 2H, Ar-H and PhCON-H), 5.97-6.08 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.67 (d, $J = 7.9$ Hz, 1H, ArC-NH), 5.15-5.22 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.12 (s, 2H, CH_2Ph), 2.80 (dd, $J = 14.8, 6.2$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.73 (dd, $J = 14.8, 7.7$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 142.1, 136.2, 134.1, 132.6, 131.2, 130.3, 128.3, 128.1, 127.6, 126.9, 126.8, 126.4, 126.3, 118.3, 65.6, 45.7, 39.9; IR (thin film) 3276, 3060, 3027, 2929, 1635, 1576, 1540, 1496, 1447, 1436, 1312, 1026, 920, 765 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}$ 356, found $(\text{M}+\text{H})^+$ 357.

(S)-Benzoic acid *N'*-(1-isopropyl-1-phenyl-but-3-enyl)-hydrazide (Table 1, Entry 4): $[\alpha]_{\text{D}} = +46.9^\circ$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.56-7.58 (m, 2H, Ar-H), 7.51-7.53 (m, 2H, Ar-H), 7.43-7.47 (m, 1H, Ar-H), 7.35-7.41 (m, 4H, Ar-H), 7.29 (t, $J = 7.3$ Hz, 1H, Ar-H), 7.21 (d, $J = 8.0$ Hz, 1H, PhCON-H), 5.99-6.09 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.67 (d, $J = 8.4$ Hz, 1H, ArC-NH), 5.20 (dd, $J = 17.0, 1.3$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 5.10 (d, $J = 10$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.80-2.90 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.03 (sep, $J = 6.8$ Hz, 1H, $\text{H-C}(\text{CH}_3)_2$), 0.89 (d, $J = 6.8$ Hz, 3H, one of $\text{CH}(\text{CH}_3)_2$), 0.85 (d, $J = 6.8$ Hz, 3H, one of $\text{CH}(\text{CH}_3)_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 164.9, 140.3, 134.7, 132.8, 131.3, 128.4, 127.9, 127.5, 126.6, 126.4, 117.6, 67.8, 38.6, 35.3, 17.8, 17.4; IR (thin film) 3284, 3065, 2963, 2876, 1637, 1579, 1535, 1492, 1447, 1427, 1307, 918 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}$ 308, found $(\text{M}+\text{H})^+$ 309.

(R)- 2-(*N'*-Benzoyl-hydrazino)-2-phenyl-pent-4-enoic acid methyl ester (Table 1, Entry 5): $[\alpha]_{\text{D}} = -36.0^\circ$ (c 1.15, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 6.4$ Hz, 1H, PhCON-H), 7.55-7.58 (m, 2H, Ar-H), 7.44-7.48 (m, 3H, Ar-H), 7.27-7.39 (m, 5H, Ar-H), 5.82-5.92 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.65 (d, $J = 6.7$ Hz, 1H, ArC-NH), 5.20 (d, $J = 17.0$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 5.15 (d, $J = 10.0$ Hz, 1H, one

of $\text{CH}_2\text{CH}=\text{CH}_2$), 3.80 (s, 3H, CO_2CH_3), 3.01 (dd, $J = 14.3, 7.4$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.94 (dd, $J = 14.3, 6.9$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$); ^{13}C NMR (100 MHz, CDCl_3) δ 173.4, 165.8, 138.4, 132.6, 132.4, 131.3, 128.3, 128.1, 127.9, 126.5, 126.4, 119.2, 71.0, 52.5, 41.0; IR (thin film) 3280, 3063, 3020, 2951, 1733, 1642, 1602, 1579, 1532, 1495, 1448, 1433, 1231, 698 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_3$ 324, found $(\text{M}+\text{H})^+$ 325.

(R)-Benzoic acid N'-(1-(4-bromophenyl)-1-methyl-but-3-enyl)-hydrazide (Table 1, Entry 6):

$[\alpha]_{\text{D}} = +91.8^\circ$ (c 1.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 7.8$ Hz, 2H, Ar-H), 7.37-7.51 (m, 7H, Ar-H), 7.09 (br s, 1H, PhCON-H), 5.58-5.67 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.41 (br s, 1H, ArC-NH), 5.10 (d, $J = 3.8$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 5.07 (s, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.57 (dd, $J = 13.7, 6.6$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.47 (dd, $J = 13.7, 8.0$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.53 (s, 3H, ArC- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 143.3, 132.8, 132.4, 131.5, 131.3, 128.4, 128.2, 126.5, 120.9, 118.8, 62.3, 46.1, 22.7; IR (thin film) 3274, 3071, 2977, 1638, 1578, 1540, 1487, 1449, 1395, 1314, 1008 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{18}\text{H}_{19}\text{BrN}_2\text{O}$ 358, found $(\text{M}+\text{H})^+$ 359.

(R)-Benzoic acid N'-(1-(4-methoxy-phenyl)-1-methyl-but-3-enyl)-hydrazide (Table 1, Entry 7):

$[\alpha]_{\text{D}} = +86.6^\circ$ (c 1.8, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.58-7.60 (m, 2H, Ar-H), 7.44-7.47 (m, 3H, Ar-H), 7.35-7.38 (m, 2H, Ar-H), 7.14 (br s, 1H, PhCON-H), 6.91 (d, $J = 8.8$ Hz, 2H, Ar-H), 5.61-5.72 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.39 (br s, 1H, ArC-NH), 5.05-5.10 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 3.81 (s, 3H, OCH_3), 2.60 (dd, $J = 13.7, 6.6$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.49 (dd, $J = 13.7, 8.0$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.52 (s, 3H, ArC- CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 166.1, 158.1, 135.8, 133.4, 132.6, 131.3, 128.3, 127.4, 126.5, 118.2, 113.5, 62.0, 55.2, 46.1, 22.8; IR (thin film) 3276, 3070, 2975, 2933, 2835, 1638, 1610, 1512, 1451, 1440, 1301, 1250, 1181, 1033 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}$ 310, found $(\text{M}+\text{H})^+$ 311.

(R)-Benzoic acid N'-(1-methyl-1-(3-nitrophenyl)-but-3-enyl)-hydrazide (Table 1, Entry 8):

$[\alpha]_{\text{D}} = +64.9^\circ$ (c 2.2, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.42 (t, $J = 2.0$ Hz, 1H, Ar-H), 8.10-8.13 (m, 1H, Ar-H), 7.90 (d, $J = 7.9$ Hz, 1H, Ar-H), 7.59-7.62 (m, 2H, Ar-H), 7.53 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.45-7.49 (m, 1H, Ar-H), 7.35-7.39 (m, 2H, Ar-H), 7.31 (d, $J = 7.5$ Hz, 1H, PhCON-H), 5.57-5.68 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.46 (d, $J = 7.8$ Hz, 1H, ArC-NH), 5.06-5.11 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.61 (dd, $J = 13.8,$

6.7 Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.52 (dd, $J = 13.8, 7.9$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.61 (s, 3H, $\text{ArC}-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 147.9, 146.6, 132.7, 132.2, 132.0, 131.5, 128.9, 128.3, 126.6, 121.8, 121.5, 119.1, 62.4, 45.8, 22.5; IR (thin film) 3275, 3083, 2981, 1627, 1448, 1348, 1312, 918, 865, 694 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_3$ 325, found $(\text{M}+\text{H})^+$ 326.

(R)-Benzoic acid *N'*-(1-methyl-1-naphthalen-2-yl-but-3-enyl)-hydrazide (Table 1, Entry 9): $[\alpha]_{\text{D}} = +105.3^\circ$ (c 1.25, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.84-7.93 (m, 4H, Ar-H), 7.77 (dd, $J = 8.6, 1.8$ Hz, 1H, Ar-H), 7.42-7.57 (m, 5H, Ar-H), 7.34 (t, $J = 7.5$ Hz, 2H, Ar-H), 7.11 (br s, 1H, $\text{PhCON}-\text{H}$), 5.63-5.73 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.55 (br s, 1H, $\text{ArC}-\text{NH}$), 5.12 (d, $J = 17.1$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 5.08 (d, $J = 10.1$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.72 (dd, $J = 13.6, 6.6$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.60 (dd, $J = 13.6, 8.0$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.67 (s, 3H, $\text{ArC}-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 141.5, 133.2, 133.0, 132.5, 132.2, 131.4, 128.4, 128.1, 128.0, 127.3, 126.5, 126.0, 125.8, 125.3, 124.5, 118.6, 62.6, 46.1, 22.8; IR (thin film) 3275, 3060, 2976, 1638, 1578, 1539, 1449, 1436, 1375, 1312.915 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}$ 330, found $(\text{M}+\text{H})^+$ 331.

(R)-Benzoic acid *N'*-(1-furan-2-yl-1-methyl-but-3-enyl)-hydrazide (Table 1, Entry 10): $[\alpha]_{\text{D}} = +37.9^\circ$ (c 1.5, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.67 (m, 2H, Ar-H), 7.49 (tt, $J = 7.4, 1.2$ Hz, 1H, Ar-H), 7.39-7.43 (m, 3H, Ar-H), 7.29 (br s, 1H, $\text{PhCON}-\text{H}$), 6.32 (dd, $J = 3.2, 1.8$ Hz, 1H, Ar-H), 6.23 (dd, $J = 3.2, 0.5$ Hz, 1H, Ar-H), 5.73 (ddt, $J = 17.0, 10.0, 7.6$ Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.24 (br s, 1H, $\text{ArC}-\text{NH}$), 5.08-5.15 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.73 (dd, $J = 13.7, 6.7$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.55 (dd, $J = 13.7, 7.8$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.48 (s, 3H, $\text{ArC}-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 156.5, 141.7, 133.0, 132.6, 131.4, 128.3, 126.6, 118.3, 109.9, 106.7, 59.8, 42.5, 21.5; IR (thin film) 3271, 3067, 2980, 1640, 1576, 1542, 1456, 1436, 1379, 1314, 1160, 1014 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_2$ 270, found $(\text{M}+\text{H})^+$ 271.

(R)-Benzoic acid *N'*-(1-methyl-1-thiophen-2-yl-but-3-enyl)-hydrazide (Table 1, Entry 11): $[\alpha]_{\text{D}} = +49.6^\circ$ (c 2.0, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.64-7.66 (m, 2H, Ar-H), 7.49 (t, $J = 7.4$ Hz, 1H, Ar-H), 7.39-7.42 (m, 2H, Ar-H), 7.25-7.28 (m, 2H, $\text{PhCON}-\text{H}$ and Ar-H), 6.96-7.00 (m, 2H, Ar-H), 5.78 (ddt, $J = 17.0, 10.0, 7.4$ Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.43 (br s, 1H, $\text{ArC}-\text{NH}$), 5.12-5.16 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.66 (dd, $J = 13.7, 6.7$ Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.59 (dd, $J = 13.7, 7.9$ Hz, 1H, one

of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.58 (s, 3H, $\text{ArC}-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 149.5, 132.9, 132.4, 131.5, 128.3, 126.6, 126.5, 124.5, 124.1, 118.6, 61.8, 46.5, 23.8; IR (thin film) 3273, 3071, 2977, 2932, 1638, 1587, 1540, 1450, 1435, 1372, 1312, 917 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{OS}$ 286, found $(\text{M}+\text{H})^+$ 287.

(R)-3-[1-(N'-Benzoyl-hydrazino)-1-methyl-but-3-enyl]-indole-1-carboxylic acid *t*-butyl ester (Table 1, Entry 12): $[\alpha]_{\text{D}} = +51.3^\circ$ (*c* 1.24, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1H, Ar-**H**), 8.16 (d, *J* = 8.0 Hz, 1H, Ar-**H**), 7.57-7.59 (m, 2H, Ar-**H**), 7.43-7.47 (m, 2H, Ar-**H**), 7.33-7.38 (m, 3H, Ar-**H**), 7.24-7.28 (m, 1H, Ar-**H**), 7.04 (br s, 1H, $\text{PhCON}-\text{H}$), 5.70-5.81 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.48 (br s, 1H, $\text{ArC}-\text{NH}$), 5.07-5.13 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.82 (dd, *J* = 13.5, 6.5 Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.66 (dd, *J* = 13.5, 8.0 Hz, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.69 (s, 9H, $\text{COC}(\text{CH}_3)_3$), 1.57 (s, 3H, $\text{ArC}-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 149.4, 135.9, 133.2, 132.4, 131.4, 128.3, 126.5, 124.2, 123.8, 123.6, 122.4, 121.8, 118.5, 115.1, 83.8, 60.6, 43.7, 28.3, 23.0; IR (thin film) 3242, 3052, 2979, 2931, 1734, 1654, 1559, 1451, 1370, 1309, 1281, 1243, 1153, 1066, 750 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{25}\text{H}_{29}\text{N}_3\text{O}_3$ 419, found $(\text{M}+\text{H})^+$ 420.

(R)-Benzoic acid N'-(1-methyl-1-phenethyl-but-3-enyl)-hydrazide (Table 1, Entry 13): $[\alpha]_{\text{D}} = +10.8^\circ$ (*c* 2.7, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.69-7.71 (m, 2H, Ar-**H**), 7.50 (tt, *J* = 7.3, 1.3 Hz, 1H, Ar-**H**), 7.41-7.45 (m, 2H, Ar-**H**), 7.15-7.29 (m, 6H, $\text{PhCON}-\text{H}$ and Ar-**H**), 5.97 (ddt, *J* = 17.0, 10.0, 7.3 Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.14-5.20 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.08 (br s, 1H, $\text{ArC}-\text{NH}$), 2.74 (t, *J* = 8.5 Hz, 2H, PhCH_2CH_2), 2.26-2.36 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.70-1.82 (m, 2H, PhCH_2CH_2), 1.18 (s, 3H, $\text{ArC}-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 166.8, 142.3, 134.1, 132.6, 131.4, 128.3, 128.1, 126.6, 125.5, 117.8, 59.5, 42.7, 39.7, 30.1, 23.0; IR (thin film) 3279, 3062, 3025, 2973, 2932, 2849, 1635, 1456, 1436, 1312, 913, 690 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}$ 308, found $(\text{M}+\text{H})^+$ 309.

(R)-Benzoic acid N'-(1-cyclohexyl-1-methyl-but-3-enyl)-hydrazide (Table 1, Entry 14): $[\alpha]_{\text{D}} = -9.78^\circ$ (*c* 1.25, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.70-7.73 (m, 2H, Ar-**H**), 7.41-7.52 (m, 3H, Ar-**H**), 7.26 (br s, 1H, $\text{PhCON}-\text{H}$), 6.02 (ddt, *J* = 17.0, 10.0, 7.1 Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.12-5.17 (m, 3H, $\text{CH}_2\text{CH}=\text{CH}_2$ and $\text{ArC}-\text{NH}$), 2.21-2.32 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.93 (d, *J* = 1.8 Hz, 1H, Cy-**H**), 1.79-1.87 (m, 3H, Cy-**H**), 1.68 (d, *J* = 1.4 Hz, 1H, Cy-**H**), 1.39-1.45 (m, 1H, Cy-**H**), 1.06-1.27 (m, 5H, Cy-**H**), 1.05

(s, 3H, ArC-CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 135.0, 132.8, 131.3, 128.3, 126.5, 117.1, 61.6, 44.2, 40.9, 27.4, 27.1, 27.04, 26.99, 26.7, 20.2 ; IR (thin film) 3287, 3070, 2926, 2851, 1635, 1549, 1450, 1375, 1313, 1159 cm⁻¹; LRMS (FAB+) calcd for C₁₈H₂₆N₂O 286, found (M+H)⁺ 287.

Procedure for the enantioselective allylation of benzoic acid (1-phenyl-ethylidene)-hydrazide with (*S,S*)-1 on a 5.0 g scale (Scheme 2): To a solution of (*S,S*)-1 (8.43 g, 31.5 mmol) in CHCl₃ (210 mL) was added benzoic acid (1-phenyl-ethylidene)-hydrazide (5.00 g, 21.0 mmol). The resulting solution was heated at 40 °C for 24 hours, then cooled to ambient temperature and quenched with methanol (40 mL). After 15 min, the solution was concentrated and the residue diluted with EtOAc (100 mL) and H₂O (200 mL). The phases were separated, and the aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed (2 x 100 mL H₂O, 1 x 100 mL brine), dried (MgSO₄), filtered and concentrated. The resulting red gum was dissolved in ether (100 mL) and HCl (2.0 M in Et₂O, 12 mL, 24 mmol) was added. A white precipitate formed immediately, and after 10 min was filtered and washed with ether (2 x 20 mL). The off-white solid was dried under vacuum to yield the crude product as the HCl salt. Recrystallization from absolute ethanol yielded the pure product (*R*)-Benzoic acid *N'*-(1-methyl-1-phenyl-but-3-enyl)-hydrazide-HCl (4.90 g, 74%) as a crystalline white solid. (The pseudoephedrine was recovered by the following procedure: the combined aqueous extracts from the above workup were basified with 3*N* aqueous NaOH and the cloudy suspension was extracted with EtOAc (3 x 75 mL). The combined organic layers were washed (2 x 25 mL H₂O, 1 x 100 mL brine), dried (MgSO₄), filtered and concentrated to yield pure (*S,S*)-pseudoephedrine as a white solid (5.10 g, 98% recovery)). [α]_D = -5.5° (c 1.64, CD₃OD); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.1 (br s, 1H, PhCON-**H**), 7.68-7.70 (m, 2H, Ar-**H**), 7.53-7.59 (m, 3H, Ar-**H**), 7.43 (t, *J* = 7.4 Hz, 2H, Ar-**H**), 7.25-7.36 (m, 3H, Ar-**H**), 5.37-5.47 (m, 1H, CH₂**CH**=CH₂), 5.06 (d, *J* = 16 Hz, 1H, one of CH₂CH=CH₂), 4.97-5.00 (m, 1H, one of CH₂CH=CH₂), 3.08 (dd, *J* = 13.8, 6.0 Hz, 1H, one of CH₂**CH**=CH₂), 2.73 (dd, *J* = 13.8, 8.0 Hz, 1H, one of CH₂**CH**=CH₂), 1.67 (s, 3H, ArC-CH₃); ¹³C NMR (100 MHz, CD₃OD) δ 167.8, 136.1, 134.1, 131.5, 131.0, 130.4, 129.8, 129.6, 128.8, 128.6, 121.0, 70.4, 42.6, 20.6; IR (thin film) 3129, 2949, 2903, 2559, 2489, 2359, 1690, 1550, 1528, 1448, 1390, 1375, 1287 cm⁻¹; LRMS (FAB+) calcd for (free base) C₁₈H₂₀N₂O 280, found (M+H)⁺ 281.

Note: A sample of the HCl salt was free-based and used for the determination of the enantiomeric excess of the recrystallized product. The following procedure was employed: To a stirred solution of the HCl salt (25 mg, 0.08 mmol) in MeOH was added solid NaOMe (4.8 mg, 0.09 mmol). After 5 min the reaction was concentrated and the residue diluted with EtOAc (2 mL)/H₂O (2 mL). The phases were separated and the aqueous layer extracted with EtOAc (2 x 2 mL). The combined organic layers were washed (2 x 2 mL H₂O, 1 x 2 mL brine), dried (MgSO₄), filtered and concentrated to yield the product (*R*)-Benzoic acid *N'*-(1-methyl-1-phenyl-but-3-enyl)-hydrazide (21 mg, 94%) as the free base. $[\alpha]_D = +89.9^\circ$ (*c* 0.93, CHCl₃).

Determination of absolute configuration: (*R*)-Benzoic acid *N'*-(1-methyl-1-phenyl-but-3-enyl)-hydrazide was reduced to yield the corresponding homoallylic amine (Scheme 1).² Comparison of the optical rotation to the lit. value³ established the (*R*) configuration of our product. All other absolute configurations of the products from Table 1 were assigned by analogy.

Scheme 1

(2) (a) Kobayashi, S.; Hirabayashi, R. *J. Am. Chem. Soc.* **1999**, *121*, 6942-6943. (b) Ogawa, C.; Sugiura, M.; Kobayashi, S. *J. Org. Chem.* **2002**, *67*, 5359-5364.

(3) Hua, D. H.; Miao, S. W.; Chen, J. S.; Iguchi, S. *J. Org. Chem.* **1991**, *56*, 4-6.

Preparation of reagent (*S,S*)-7: Triethylamine (27 mL, 0.19 mol) was added to a cooled (0 °C) solution of phenyltrichlorosilane (15 mL, 0.095 mol) in methylene chloride (200 mL) under argon. (1*S*,2*S*)-Pseudoephedrine (15 g, 0.091 mol) was then added portionwise over 15 min maintaining an internal temperature below 15 °C. After stirring with gradual warming to ambient temperature over 12 hours the methylene chloride was removed by distillation. The resulting residue was diluted with pentane (150 mL) and vigorously stirred for 4 hours to ensure complete precipitation of all triethylamine salts. Filtration of the suspension through a pad of celite and concentration of the filtrate by distillation afforded the crude product as a pale-orange oil. Purification by distillation under reduced pressure (bp ~138 °C, 0.5 mm Hg) gave (*S,S*)-7 (~2:1 mixture of diastereomers) as a colorless oil (20 g, 75%): ¹H NMR (400 MHz, CDCl₃) (major diastereomer) δ 7.85 (dd, *J* = 8.0, 1.3 Hz, 2H, Ar-**H**), 7.30-7.56 (m, 8H, Ar-**H**), 4.73 (d, *J* = 8.3 Hz, 1H, PhCH-**O**), 3.17 (dq, *J* = 8.3, 6.0 Hz, 1H, CH₃CH-**N**), 2.53 (s, 3H, CH₃-**N**), 1.20 (d, *J* = 6.0 Hz, 3H, CH₃-CHN); (minor diastereomer) δ 7.97 (dd, *J* = 8.0, 1.4 Hz, 2H, Ar-**H**), 7.30-7.56 (m, 8H, Ar-**H**), 4.86 (d, *J* = 7.2 Hz, 1H, PhCH-**O**), 3.34 (q, *J* = 6.2 Hz, 1H, CH₃CH-**N**), 2.53 (s, 3H, CH₃-**N**), 1.26 (d, *J* = 6.1 Hz, 3H, CH₃-CHN); ¹³C NMR (100 MHz, CDCl₃) δ 141.0, 140.6, 134.8, 134.7, 131.55, 131.48, 130.1, 128.2, 128.0, 127.94, 127.87, 127.8, 126.6, 126.2, 125.8, 85.8, 84.2, 63.9, 62.8, 29.7, 29.4, 17.4, 16.8; ²⁹Si NMR (60 MHz, CDCl₃) δ -12.44 (major diastereomer) and -13.85 (minor diastereomer); IR (CHCl₃) 3074, 3033, 2971, 2890, 2812, 1592, 1492, 1448, 1431, 1373, 1280, 1215, 1189, 1122 cm⁻¹.

Preparation of complex 11 (Figure 1): Hydrazone **8** (1.87 g, 8.36 mmol) was added to a solution of **7** (2.59 g, 8.52 mmol) in CH₂Cl₂ (10 mL) under an atmosphere of argon. The resulting mixture was stirred at ambient temperature for 15 min, and the CH₂Cl₂ was then removed by vacuum distillation. The ¹H NMR spectrum of this material is a mixture of 4 compounds, all displaying characteristics of complexes **9** and/or **10** (tentative structural assignments; the spectrum is reproduced below). The residue was diluted with toluene (10 mL) and the mixture stirred for 12 h under argon, during which time the precipitation of a white solid was observed. The suspension was transferred to an inert atmosphere glove box and filtered, washed (3 x 5 mL toluene), and dried under vacuum to yield the desired compound **11** (as a single compound) as a white solid (4.0 g, 90% yield). Crystals suitable for X-ray analysis were grown over 2 days by layering hexanes (3.0 mL) over a solution of compound **11** (175 mg, 0.33 mmol) in CH₂Cl₂ (1.0

mL). Data for **11**: ^1H NMR (400 MHz, CDCl_3) δ 9.92 (m, 1H, MeN-H), 8.52 (d, $J = 6.3$ Hz, 2H, Ar-H), 8.28 (d, $J = 7.3$ Hz, 2H, Ar-H), 7.89 (s, 1H, N=C-H), 7.58-7.68 (m, 8H, Ar-H), 7.45-7.55 (m, 8H, Ar-H), 5.47 (d, $J = 10.2$ Hz, 1H, PhCH-O), 3.04-3.15 (m, 1H, $\text{CH}_3\text{CH-N}$), 2.40 (d, $J = 5.4$ Hz, 3H, $\text{CH}_3\text{-N}$), 1.50 (d, $J = 6.4$ Hz, 3H, $\text{CH}_3\text{-CHN}$); ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 156.2, 137.8, 134.24, 134.18, 133.3, 132.5, 131.9, 131.3, 130.6, 129.1, 128.9, 128.7, 128.66, 128.60, 128.2, 127.0, 126.7, 126.3, 79.3, 61.9, 32.9, 11.2; ^{29}Si NMR (60 MHz, CDCl_3) δ -89.10.

Determination of enantioselectivity of homoallylic hydrazide products: All ee's were determined by chiral HPLC analysis. Racemic samples were prepared by the method of Kobayashi.⁴

Table 1, entry 1: Chiralpak AD-H Column, 20.0% EtOH/hexanes, 1.0 ml/min, 220 nm.

(4) Hirabayashi, R.; Ogawa, C.; Sugiura, M.; Kobayashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 9493-9499.

Table 1, entry 2: Chiralpak AD-H Column, 25.0% EtOH/hexanes, 1.0 ml/min, 220 nm. *Racemic* *Product from Table 1* **Table 1, entry 3:** Chiralpak AD-H Column, 15.0% EtOH/hexanes, 1.0 ml/min, 220 nm. *Racemic* *Product from Table 1*

Table 1, entry 4: Chiralpak AD-H Column, 5.0% EtOH/hexanes, 1.0 ml/min, 220 nm. **Table 1, entry 5:** Chiralpak AD-H Column, 10.0% IPA/hexanes, 1.0 ml/min, 220 nm.

Table 1, entry 6: Chiralpak AD-H Column, 15.0% IPA/hexanes, 1.0 ml/min, 220 nm. **Table 1, entry 7:** Chiralpak AD-H Column, 20.0% EtOH/hexanes, 1.0 ml/min, 220 nm.

Table 1, entry 8: Chiralpak AD-H Column, 20.0 % EtOH/hexanes, 1.0 ml/min, 220 nm. **Table 1, entry 9:** Chiralpak AD-H Column, 20.0% EtOH/hexanes, 1.0 ml/min, 220 nm.

Table 1, entry 10: Chiralpak AD-H Column, 20.0% EtOH/hexanes, 1.0 ml/min, 220 nm. *Racemic* *Product from Table 1* **Table 1, entry 11:** Chiralpak AD-H Column, 15.0% IPA/hexanes, 1.0 ml/min, 220 nm. *Racemic* *Product from Table 1*

Table 1, entry 12: Chiralpak AD-H Column, 25.0% EtOH/hexanes, 0.4 ml/min, 220 nm. **Table 1, entry 13:** Chiralpak AD-H Column, 3.0% MeOH:EtOH (1:1)/hexanes, 1.0 ml/min, 220 nm,

Table 1, entry 14: Chiralpak AD-H Column, 7.0% IPA/hexanes, 1.0 ml/min, 220 nm *Racemic* *Product from Table 1* **Scheme 2** (reaction in CHCl_3): Chiralpak AD-H Column, 25.0% EtOH/hexanes, 1.0 ml/min, 220 nm. *Racemic* *Product from Scheme 2*

^1H NMR (400 MHz, CDCl_3) spectra of the allylation products from Table 1:

^1H NMR (400 MHz, $\text{DMSO}-d_6$) spectrum of the scale-up allylation product:

^1H NMR (400 MHz, CDCl_3) spectrum of silane **7**:

^{29}Si NMR (60 MHz, CDCl_3) spectrum of silane **7**:

^1H NMR (400 MHz, CDCl_3) spectrum of **9** and/or **10** (tentative structural assignment; the spectrum is consistent with the amine of the pseudoephedrine being protonated):

^1H NMR (400 MHz, CDCl_3) spectrum of **11**:

^{29}Si NMR (60 MHz, CDCl_3) spectrum of silane **11**: