Toward a Universal Allylation Reagent: Practical, Enantioselective Allylation of Acylhydrazones Using Strained Silacycles

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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. Absolute ethanol was purchased from Pharmco Inc. and used without purification. Acetic hydrazide, (1*S*,2*S*)-pseudoephedrine and all aldehyde reagents were purchased from Aldrich and used as received. ¹H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer at 100 °C and are reported in ppm from 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, m = multiplet, dd = doublet of doublets, td = triplet of doublets; coupling constant(s) in Hz; integration; assignment). Proton decoupled ¹³C NMR spectra were recorded on a Bruker DPX-300 (75 MHz) at 50 °C and are reported in ppm from CDCl₃ internal standard (77.0 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.

Large scale preparation of reagent (*S,S*)-1: To a cooled (0 °C) solution of allyltrichlorosilane (101 mL, 0.696 mol) in methylene chloride (1.8 L) was added triethylamine (170 mL, 1.21 mol). (1*S*, 2*S*)-pseudoephedrine (100 g, 0.605 mol) was added portionwise over 30 min, maintaining an internal temperature below 15 °C. The reaction mixture was stirred for 12 hours and was then concentrated. The residue was treated with pentane (1.5 L) and vigorously stirred for 12 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 unpurified product as a pale yellow oil. Purification by distillation under reduced pressure (bp ~120 °C, 5 mm Hg) afforded (*S,S*)-1 (149 g, 92%)

as a colorless oil. Characterization data for this reagent may be found in the supporting information of our earlier work.¹

Preparation of *cis*-crotylsilane reagent (*S,S*)-5a**:** The above procedure for the preparation of (*S,S*)-**1** was followed exactly using the following reagents: *cis*-crotyltrichlorosilane² (5.0 g, 26.4 mmol), (*S,S*)-pseudoephedrine (3.64 g, 22 mmol) and triethylamine (6.13 mL, 44 mmol). Upon distillation under reduced pressure, (*S,S*)-**5a** was obtained as a colorless oil (4.93 g, 79%, b.p. 111-116°C @ 0.5 mm Hg, 2.6:1 mixture of diastereomers). ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.25 (m, 5H, Ar-**H**, (both diastereomers)), 5.63-5.40 (m, 2H, R₃SiCH₂CH=CHCH₃, (both diastereomers)), 4.66 (d, 1H, *J* = 7.4 Hz, OCHPh (minor)), 4.53 (d, 1H, *J* = 7.4 Hz, OCHPh (major)), 3.17-3.07 (apparent quintet, 1H, *J* = 7.1 Hz, NCHMe (minor)), 3.02-2.92 (doublet of quartets, 1H, *J* = 8.2, 6.0 Hz, NCHMe (major)), 2.55 (br s, 3H, NCH₃ (minor)), 2.48 (br s, 3H, NCH₃ (major)), 2.08 (apparent d, 1H, *J* = 7.5 Hz, SiCH₂CH=CHMe (minor)), 2.02 (apparent d, 1H, *J* = 7.5 Hz, SiCH₂CH=CHMe (major)), 1.68-1.62 (m, 3H, NCHCH₃), 1.13 (d, 3H, *J* = 5.1 Hz, SiCH₂CH=CHMe (minor)), 1.08 (d, 3H, *J* = 6Hz, SiCH₂CH=CHMe (major)); ¹³C NMR (75 MHz, CDCl₃) δ 141.2, 141.1, 128.4, 128.3, 128.0 (two peaks), 126.7, 126.6, 125.4, 125.2, 121.6, 121.3, 85.6, 84.3, 63.4, 63.1, 30.1, 29.1, 18.0, 17.9, 16.7, 16.5, 12.8, 12.7; ²⁹Si NMR (60 MHz, CDCl₃) δ -5.72, -7.00; IR (neat): 3086, 3063, 3024, 2969, 2885, 2810, 2636, 1652, 1604, 1493, 1454, 1372, 1280, 1214, 1186, 1014, 941, 918, 900, 965, 782; LRMS (EI) calc'd for C₁₄H₂₀ClNOSi 281.10, found 281.15.

Preparation of *trans*-crotylsilane reagent (*S,S*)-5b**:** The above procedure for the preparation of (*S,S*)-**1** was followed exactly using the following reagents: *trans*-crotyltrichlorosilane^{2b,c,3} (5.0 g, 26.4

(1) Kinnard, J. W. A.; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920-7921.

(2) (a) Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143-2146. (b) Kira, M.; Hino, T.; Sakurai, H. *Tetrahedron Lett.* **1989**, *30*, 1099-1102. (c) Iseki, K.; Kuroki, Y.; Takahashi, M.; Kishimoto, S.; Kobayashi, Y. *Tetrahedron* **1997**, *53*, 3513-3526.

(3) Furuya, N.; Sukawa, T. *J. Organomet. Chem.* **1975**, *96*, C1-C3.

mmol), (*S,S*)-pseudoephedrine (3.64 g, 22 mmol) and triethylamine (6.13 mL, 44 mmol). Upon distillation under reduced pressure, (*S,S*)-**5b** was obtained as a colorless oil (3.46 g, 59%, b.p. 116-120°C @ 0.5 mm Hg, 2.3:1 mixture of diastereomers). ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.27 (m, 5H, Ar-**H**, (both diastereomers)), 5.59-5.40 (m, 2H, R₃SiCH₂CH=CHCH₃, (both diastereomers)), 4.67 (d, 1H, *J* = 7.3 Hz, OCHPh (minor)), 4.53 (d, 1H, *J* = 8.2 Hz, OCHPh (major)), 3.12 (apparent quintet, 1H, *J* = 6.1 Hz, NCHMe (minor)), 3.02-2.92 (doublet of quartets, 1H, *J* = 8.2, 6.0 Hz, NCHMe (major)), 2.54 (br s, 3H, NCH₃ (minor)), 2.48 (br s, 3H, NCH₃ (major)), 2.02 (m, 1H, SiCH₂CH=CHMe (minor)), 1.95 (m, 1H, SiCH₂CH=CHMe (major)), 1.72-1.67 (m, 3H, NCHCH₃), 1.13 (d, 3H, *J* = 3.1 Hz, SiCH₂CH=CHMe (minor)), 1.08 (d, 3H, *J* = 3.1 Hz, SiCH₂CH=CHMe (major)); ¹³C NMR (75 MHz, CDCl₃) δ 141.9, 141.6, 128.8, 128.4, 127.6, 127.0, 127.2, 127.0, 123.1, 122.5, 86.0, 84.7, 64.1, 63.6, 30.4, 29.5, 22.7, 18.5, 17.3, 17.0; ²⁹Si NMR (60 MHz, CDCl₃) δ -4.98, -6.51; LRMS (EI) calc'd for C₁₄H₂₀ClNOSi 281.10, found 281.15.

Preparation of acetic acid benzylidene-hydrazide: Benzaldehyde (3.5 mL, 34 mmol) was added to a stirred solution of acetic hydrazide (2.50 g, 33.8 mmol) in ethanol (70 mL). The resulting solution was stirred for 12 hours, during which time a white solid precipitated. The mixture was concentrated and the residue was purified by flash chromatography on silica gel (10%-15% acetone/CH₂Cl₂) to give acetic acid benzylidene-hydrazide (5.32 g, 97 %) as a white solid. ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 10.85 (br s, 1H, N-**H**), 8.08 (br s, 1H, ArCH=N), 7.62–7.66 (m, 2H, Ar-**H**), 7.38–7.44 (m, 3H, Ar-**H**), 2.12 (br s, 3H, COCH₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 173.8, 143.6, 133.9, 129.8, 128.5, 127.0, 20.5; IR (KBr) 3178, 3082, 2977, 2866, 1668, 1600, 1395, 1343, 1139, 1023 cm⁻¹; LRMS (FAB+) calcd for C₉H₁₀N₂O 162, found (M+H)⁺ 163.

Note: This procedure was used for the preparation of all other substrates.

Acetic acid (2-methyl-benzylidene)-hydrazide: ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 10.80 (br s, 1H, N-**H**), 8.34 (br s, 1H, ArCH=N), 7.69 (d, 1H, *J* = 8.1 Hz, Ar-**H**), 7.26 (m, 3H, Ar-**H**), 2.43 (s, 3H, ArCH₃), 2.13 (br s, 3H, COCH₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 174.4, 143.5, 137.4, 132.4, 131.4, 130.0, 127.8, 126.5, 20.5; IR (KBr): 2972, 1664, 1614, 1504, 1394, 1336, 1305, 1175, 1135, 1106, 1018, 954, 934, 903, 812, 772, 633, 572, 508 cm⁻¹; LRMS (FAB+) calcd for C₁₀H₁₂N₂O 176, found (M+H)⁺ 177.

Acetic acid (4-bromo-benzylidene)-hydrazide: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.93 (br s, 1H, N-**H**), 8.05 (br s, 1H, ArCH=N), 7.59 (br s, 4H, Ar-**H**), 2.11 (br s, 3H, COCH₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 174.2, 142.6, 133.0, 132.0, 128.5, 124.3, 20.2; IR (KBr) 3185, 3079, 2974, 2861, 1678, 1610, 1392, 1331, 1007, 812 cm⁻¹; LRMS (FAB+) calcd for C₉H₉BrN₂O 240, found (M+H)⁺ 241.

Acetic acid (4-methoxy-benzylidene)-hydrazide: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.71 (br s, 1H, N-**H**), 8.02 (br s, 1H, ArCH=N), 7.58 (d, 2H, J = 8.7 Hz, Ar-**H**), 6.97 (d, 2H, J = 8.7 Hz, Ar-**H**), 3.81 (s, 3H, ArOCH₃), 2.09 (br s, 3H, COCH₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 173.9, 161.3, 143.6, 128.6, 126.9, 114.3, 55.3, 20.2; IR (KBr) 3190, 3087, 2965, 2926, 1664, 1610, 1506, 1401, 1305, 1250, 1177, 1033, 822 cm⁻¹; LRMS (FAB+) calcd for C₁₀H₁₂N₂O₂ 192, found (M+H)⁺ 193.

Acetic acid benzo[1,3]dioxol-5-ylmethylene-hydrazide: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.75 (br s, 1H, N-**H**), 7.99 (br s, 1H, ArCH=N), 7.21 (br s, 1H, Ar-**H**), 7.08 (dd, 1H, J = 8.0, 1.6 Hz, Ar-**H**), 6.91 (d, 1H, J = 8.0 Hz, Ar-**H**), 6.04 (s, 2H, O-CH₂-O), 2.10 (br s, 3H, COCH₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 173.5, 148.8, 147.9, 142.9, 128.7, 123.5, 108.7, 106.0, 101.8, 20.6; IR (KBr) 2968, 1681, 1496, 1452, 1405, 1331, 1264, 1199, 1143, 1119, 1036, 948, 932, 873, 806, 790, 611, 566, 514, 467 cm⁻¹; LRMS (FAB+) calcd for C₁₀H₁₀N₂O₃ 206, found (M+H)⁺ 207.

Acetic acid naphthalen-2-ylmethylene-hydrazide: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.96 (br s, 1H, N-**H**), 8.24 (br s, 1H, ArCH=N), 8.04 (s, 1H, Ar-**H**), 7.87-7.96 (m, 4H, Ar-**H**), 7.50-7.56 (m, 2H, Ar-**H**), 2.16 (br s, 3H, COCH₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 173.8, 143.7, 134.4, 133.3, 131.7, 128.8, 128.6, 127.9, 127.1, 126.7, 122.8, 20.3; IR (KBr) 3182, 3057, 2957, 2852, 1673, 1606, 1381, 1345, 1320, 1137, 1019, 948, 831 cm⁻¹; LRMS (FAB+) calcd for C₁₃H₁₂N₂O 212, found (M+H)⁺ 213.

Acetic acid furan-2-ylmethylene-hydrazide: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.83 (br s, 1H, N-**H**), 7.99 (br s, 1H, ArCH=N), 7.71 (d, 1H, J = 1.8 Hz, Ar-**H**), 6.78 (d, 1H, J = 3.4 Hz, Ar-**H**), 6.57 (dd, 1H, J = 3.4, 1.8 Hz, Ar-**H**), 2.08 (br s, 3H, COCH₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 174.7, 149.9, 144.7, 134.4, 113.0, 112.1, 20.4; IR (KBr) 2960, 2852, 1670, 1386, 1344, 1325, 1221, 1155, 1138, 1071, 1016, 942, 928, 883, 763, 629, 594 cm⁻¹; LRMS (FAB+) calcd for C₇H₈N₂O₂ 152, found (M+H)⁺ 153.

Acetic acid furan-3-ylmethylene-hydrazide: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.72 (br s, 1H, N-**H**), 8.03 (br s, 1H, ArCH=N), 7.96 (br s, 1H, Ar-**H**), 7.65 (br s, 1H, Ar-**H**), 6.73 (br s, 1H, Ar-**H**), 2.07 (br s, 3H, COCH₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 174.5, 144.4, 144.3, 136.8, 122.9, 107.8, 20.4; IR (KBr) 3126, 2952, 1665, 1520m 1404, 1330, 1160, 1132, 1085, 1025, 976, 938, 868, 793, 644, 627, 594 cm⁻¹; LRMS (FAB+) calcd for C₇H₈N₂O₂ 152, found (M+H)⁺ 153.

Acetic acid thiophen-2-ylmethylene-hydrazide: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.82 (br s, 1H, N-**H**), 8.27 (br s, 1H, ArCH=N), 7.54 (d, 1H, J = 5.0 Hz, Ar-**H**), 7.34 (d, 1H, J = 3 Hz, Ar-**H**), 7.08 (dd, 1H, J = 5.0, 3 Hz, Ar-**H**), 2.06 (br s, 3H, COCH₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 174.2, 139.0, 138.5, 129.5, 127.8, 127.4, 20.1; IR (KBr) 3185, 3027, 2846, 1664, 1595, 1565, 1367, 1279, 1098, 672 cm⁻¹; LRMS (FAB+) calcd for C₇H₈N₂OS 168, found (M+H)⁺ 169.

3-(Acetyl-hydrazonomethyl)-indole-1-carboxylic acid *tert*-butyl ester: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.84 (br s, 1H, N-**H**), 8.24 (br s, 2H, ArCH=N and one of Ar-**H**), 8.10 (d, 1H, J = 8.1 Hz, Ar-**H**), 7.97 (s, 1H, Ar-**H**), 7.30- 7.42 (m, 2H, Ar-**H**), 2.18 (br s, 3H, COCH₃), 1.67 (s, 9H, COC(CH₃)₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 173.5, 149.2, 138.5, 136.3, 128.9, 127.0, 125.6, 123.7, 122.4, 116.4, 115.2, 84.6, 28.2, 20.5; IR (KBr) 3171, 3082, 2974, 1739, 1661, 1553, 1455, 1379, 1343, 1236, 1159, 1093, 1016 cm⁻¹; LRMS (FAB+) calcd for C₁₆H₁₉N₃O₃ 301, found (M+H)⁺ 302.

Acetic acid (6-chloro-pyridin-3-ylmethylene)-hydrazide: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 11.10 (br s, 1H, N-**H**), 8.60 (d, 1H, J = 2 Hz, Ar-**H**), 8.09 (dd, 1H, J = 8.3, 2 Hz, Ar-**H**), 8.09 (br s, 1H, ArCH=N), 7.50 (d, 1H, J = 8.3 Hz, Ar-**H**), 2.13 (br s, 3H, COCH₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 174.6, 152.5, 148.7, 139.5, 135.8, 129.0, 124.5, 20.1; IR (KBr) 3190, 3089, 3058, 2979, 2871, 1675, 1609, 1468, 1397, 1352, 1336, 1142, 1100, 1022 cm⁻¹; LRMS (FAB+) calcd for C₈H₈ClN₃O 197 found (M+H)⁺ 198.

2-(Acetyl-hydrazonomethyl)-pyrrole-1-carboxylic acid *tert*-butyl ester: ^1H NMR (300 MHz, 100 °C, DMSO- d_6) δ 10.88 (br s, 1H, N-**H**), 8.52 (br s, 1H, ArCH=N), 7.31 (dd, 1H, J = 3.5, 1.7 Hz, Ar-**H**), 6.72-6.73 (m, 1H, Ar-**H**), 6.26 (t, 1H, J = 3.5 Hz, Ar-**H**), 2.05 (br s, 3H, COCH₃), 1.60 (s, 9H, COC(CH₃)₃); ^{13}C NMR (75 MHz, 50 °C, CDCl₃) δ 173.3, 149.0, 137.1, 130.0, 123.7, 113.9, 111.5, 84.9,

28.0, 20.1; IR (KBr) 3189, 3106, 2984, 2945, 1737, 1668, 1463, 1394, 1337, 1150, 1114, 851, 727 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_3$ 251, found $(\text{M}+\text{H})^+$ 252.

Acetic acid (2,2-dimethyl-propylidene)-hydrazide: ^1H NMR (300 MHz, 100 $^\circ\text{C}$, $\text{DMSO}-d_6$) δ 10.32 (br s, 1H, N-H), 7.32 (br s, 1H, ArCH=N), 1.98 (br s, 3H, COCH_3), 1.06 (s, 9H, $(\text{CH}_3)_3\text{CH}=\text{N}$); ^{13}C NMR (75 MHz, 50 $^\circ\text{C}$, CDCl_3) δ 173.9, 154.7, 34.6, 27.4, 20.1; IR (KBr) 3209, 3029, 2961, 2870, 1972, 1587, 1375, 1300, 1274, 1091, 1007, 916 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_7\text{H}_{14}\text{N}_2\text{O}$ 142, found $(\text{M}+\text{H})^+$ 143.

Representative procedure for the enantioselective allylation of acetylhydrazones with (*S,S*)-1: To a cooled (10 $^\circ\text{C}$) solution of the acetylhydrazone (0.616 mmol) in CH_2Cl_2 (5 mL) is added (*S,S*)-1 (250 mg, 0.925 mmol). The resulting solution is stirred for 16 hours and then quenched with methanol (2 mL). After 15 min the solution is concentrated and 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 (brine, 1 x 5 mL), dried (MgSO_4), filtered and concentrated. The residue is purified by flash chromatography on silica gel to afford the pure hydrazide products in the yields and enantioselectivities indicated in Tables 1 and 2.

(*R*)-Acetic acid *N'*-(1-phenyl-but-3-enyl)-hydrazide (Table 1, Entry 1): $[\alpha]_D^{25} = +193.6^\circ$ (c 1.0, CHCl_3); ^1H NMR (300 MHz, 100 $^\circ\text{C}$, $\text{DMSO}-d_6$) δ 8.83 (br s, 1H, $\text{CH}_3\text{CON}-\text{H}$), 7.20- 7.31 (m, 5H, Ar-H), 5.63-5.77 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.93- 5.04 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.87- 4.90 (m, 1H, ArCHN-H), 3.92 (br s, 1H, ArCH-NH), 2.43-2.50 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.30-2.39 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.73 (br s, 3H, COCH_3); ^{13}C NMR (75 MHz, 50 $^\circ\text{C}$, CDCl_3) δ 169.2, 141.8, 134.4, 128.5, 127.7, 127.5, 117.8, 63.8, 40.4, 21.0; IR (KBr) 3225, 3076, 2981, 2926, 2585, 1643, 1623, 1555, 1480, 1371, 767 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}$ 204, found $(\text{M}+\text{H})^+$ 205.

(*R*)-Acetic acid *N'*-(1-*o*-tolyl-but-3-enyl)-hydrazide (Table 1, Entry 2): $[\alpha]_D^{25} = +163.9^\circ$ (c = 0.905, CHCl_3); ^1H NMR (300 MHz, 100 $^\circ\text{C}$, $\text{DMSO}-d_6$) δ 8.85 (br s, 1H, $\text{CH}_3\text{CON}-\text{H}$), 7.42 (d, 1H, J = 7.3 Hz, Ar-H), 7.21-7.10 (m, 3H, Ar-H), 5.79-5.63 (ddt, 1H, J = 17.2, 10.2, 6.8, $\text{CH}_2-\text{CH}=\text{CH}_2$), 5.06-4.98 (ddt, 1H, J = 17.2, 2.1, 1.5 Hz, $\text{CH}_2-\text{CH}=\text{CH}_2$), 4.98-4.93 (ddt, 1H, J = 10.2, 2.1, 1.2 Hz, $\text{CH}_2-\text{CH}=\text{CH}_2$), 4.85 (br s, 1H, ArCHN-H), 4.25 (apparent t, 1H, J = 6.8 Hz), 2.50-2.30 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.30 (s, 3H, ArCH₃), 1.74 (br s, 3H, COCH_3); ^{13}C NMR (75 MHz, 50 $^\circ\text{C}$, CDCl_3) δ 169.6, 140.2, 136.8, 134.8, 130.8,

127.4, 126.8, 126.6, 118.0, 59.5, 40.0, 21.3, 19.6; IR (thin film): 3270, 3074, 2928, 1642, 1536, 1492, 1462, 1372, 1291, 1133, 1036, 993, 916, 758, 727, 598 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}$ 218, found $(\text{M}+\text{H})^+$ 219.

(R)-Acetic acid N'-[1-(4-bromo-phenyl)-but-3-enyl]-hydrazide (Table 1, Entry 3): $[\alpha]_{\text{D}} = +146.6^\circ$ (*c* 0.5, CHCl_3); ^1H NMR (300 MHz, 100 $^\circ\text{C}$, $\text{DMSO}-d_6$) δ 8.83 (br s, 1H, $\text{CH}_3\text{CON}-\text{H}$), 7.47 (d, 2H, $J = 8.5$ Hz, Ar-**H**), 7.26 (d, 2H, $J = 8.5$ Hz, Ar-**H**), 5.62-5.74 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.93-5.04 (m, 3H, $\text{CH}_2\text{CH}=\text{CH}_2$ and ArCHN-**H**), 3.93 (br s, 1H, ArCH-NH), 2.41-2.50 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.27-2.37 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.72 (br s, 3H, COCH_3); ^{13}C NMR (75 MHz, 50 $^\circ\text{C}$, CDCl_3) δ 169.4, 140.9, 133.9, 131.6, 129.4, 121.4, 118.1, 63.3, 40.3, 21.0; IR (thin film) 3270, 3071, 2981, 2930, 1645, 1536, 1485, 1368, 1298, 1073, 1010 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{12}\text{H}_{15}\text{BrN}_2\text{O}$ 282, found $(\text{M}+\text{H})^+$ 283.

(R)-Acetic acid N'-[1-(4-methoxy-phenyl)-but-3-enyl]-hydrazide (Table 1, Entry 4): $[\alpha]_{\text{D}} = +175.9^\circ$ (*c* 2.6, CHCl_3); ^1H NMR (300 MHz, 100 $^\circ\text{C}$, $\text{DMSO}-d_6$) δ 8.79 (br s, 1H, $\text{CH}_3\text{CON}-\text{H}$), 7.21 (d, 2H, $J = 8.5$ Hz, Ar-**H**), 6.87 (d, 2H, $J = 8.5$ Hz, Ar-**H**), 5.62-5.75 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.92-5.03 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.82 (br s, 1H, ArCHN-**H**), 3.81-3.87 (m, 1H, ArCH-NH), 3.75 (s, 3H, ArOCH_3), 2.41-2.50 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.27-2.37 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.73 (br s, 3H, COCH_3); ^{13}C NMR (75 MHz, 50 $^\circ\text{C}$, CDCl_3) δ 169.2, 159.2, 134.5, 133.8, 128.7, 117.6, 114.0, 63.2, 55.2, 21.0; IR (thin film) 3277, 3074, 2999, 2931, 2833, 1646, 1612, 1515, 1247, 1175, 1035 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_2$ 234, found $(\text{M}+\text{H})^+$ 235.

(R)-Acetic acid N'-(1-benzo[1,3]dioxol-5-yl-but-3-enyl)-hydrazide (Table 1, Entry 5): $[\alpha]_{\text{D}} = +152.5^\circ$ (*c* 0.93, CHCl_3); ^1H NMR (300 MHz, 100 $^\circ\text{C}$, $\text{DMSO}-d_6$) δ 8.81 (br s, 1H, $\text{CH}_3\text{CON}-\text{H}$), 6.87 (apparent dt, 1H, $J = 1.6, 0.4$ Hz, Ar-**H**), 6.80 (dd, 1H, $J = 7.9, 0.4$ Hz, Ar-**H**), 6.75 (ddd, 1H, $J = 7.9, 1.6, 0.4$, Ar-**H**), 5.78-5.63 (ddt, 1H, $J = 17.1, 10.2, 6.9$ Hz, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.06-4.94 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.88-4.81 (br s, 1H, , ArCHN-**H**), 3.91-3.82 (m, 1H, ArCH-NH), 2.50-2.25 $\text{CH}_2\text{CH}=\text{CH}_2$), 1.74 (br s, 3H, COCH_3); ^{13}C NMR (75 MHz, 50 $^\circ\text{C}$, CDCl_3) δ 169.6, 148.3, 147.4, 136.1, 134.7, 121.5, 118.1, 108.4, 108.0, 101.3, 63.9, 40.8, 21.4. IR (thin film) 3273, 3074, 2897, 1652, 1503, 1407, 1441, 1373, 1244, 1038, 929, 809 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_3$ 248, found $(\text{M}+\text{H})^+$ 249.

(R)-Acetic acid N'-(1-naphthalen-2-yl-but-3-enyl)-hydrazide (Table 1, Entry 6): $[\alpha]_D^{25} = +219.8^\circ$ (c 1.3, CHCl₃); ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 8.87 (br s, 1H, CH₃CON-**H**), 7.83-7.87 (m, 3H, Ar-**H**), 7.78 (s, 1H, Ar-**H**), 7.43-7.52 (m, 3H, Ar-**H**), 5.66-5.81 (m, 1H, CH₂CH=CH₂), 4.93-5.06 (m, 3H, CH₂CH=CH₂ and ArCHN-**H**), 4.11 (br s, 1H, ArCHN-**H**), 2.40-2.61 (m, 2H, CH₂CH=CH₂), 1.72 (br s, 3H, COCH₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 169.3, 139.3, 134.3, 133.5, 133.2, 128.3, 127.9, 127.7, 126.7, 126.1, 125.8, 125.5, 117.9, 64.0, 40.4, 21.0; IR (thin film) 3273, 3056, 2930, 1646, 1539, 1507, 1437, 1371, 1320, 994 cm⁻¹; LRMS (FAB+) calcd for C₁₆H₁₈N₂O 254, found (M+H)⁺ 255.

(R)-Acetic acid N'-(1-furan-2-yl-but-3-enyl)-hydrazide (Table 1, Entry 7): $[\alpha]_D^{25} = +123.8^\circ$ (c 0.966, CHCl₃); ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 8.92 (br s, 1H, CH₃CON-**H**), 7.51 (br s, 1H, Ar-**H**), 6.36 (dd, 1H, *J* = 3.2, 1.8 Hz, Ar-**H**), 6.26-6.24 (m, 1H), 5.82-5.67 (ddt, 1H, *J* = 17.2, 10.3, 6.9 Hz, CH₂-CH=CH₂), 5.11-5.02 (ddt, 1H *J* = 17.2, 2.1, 1.5 Hz, CH₂-CH=CH₂), 5.02-4.96 (ddt, 1H, *J* = 10.3, 2.1, 1.2 Hz, CH₂-CH=CH₂), 4.92 (br s, 1H, ArCHN-**H**), 4.01 (apparent t, 1H, *J* = 6.9 Hz), 2.50-2.44 (m, 2H, CH₂CH=CH₂), 1.77 (s, 3H, COCH₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 169.6, 154.8, 142.4, 134.3, 118.2, 110.4, 107.8, 58.0, 37.2, 21.3; IR (thin film): 3266, 3077, 2936, 1656, 1536, 1504, 1440, 1372, 1298, 1152, 1074, 1010, 920, 884, 806, 736, 599 cm⁻¹; LRMS (FAB+) calcd for C₁₀H₁₄N₂O₂ 194, found (M+H)⁺ 195.

(R)-Acetic acid N'-(1-furan-3-yl-but-3-enyl)-hydrazide (Table 1, Entry 8): $[\alpha]_D^{25} = +89.9^\circ$ (c 1.01, CHCl₃); ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 8.79 (br s, 1H, CH₃CON-**H**), 7.52 (t, 1H, *J* = 1.7 Hz, Ar-**H**), 7.49-7.47 (m, 1H, Ar-**H**), 6.45 (br s, 1H, Ar-**H**), 5.84-5.71 (ddt, 1H *J* = 17.1, 10.3, 6.9 Hz, CH₂-CH=CH₂), 5.10-4.95 (m, 2H, CH₂-CH=CH₂), 4.70 (br s, 1H, ArCHN-**H**), 3.89 (apparent t, 1H, *J* = 6.9 Hz), 2.50-2.27 (partly buried m, 2H, CH₂CH=CH₂), 1.71 (s, 3H, COCH₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 169.6, 143.5, 140.7, 134.7, 126.1, 118.0, 109.6, 55.9, 39.4, 21.3; IR (thin film): 3269, 2918, 1652, 1503, 1436, 1372, 1160, 1036, 1022, 995, 920, 874, 790, 730, 602 cm⁻¹; LRMS (FAB+) calcd for C₁₀H₁₄N₂O₂ 194, found (M+H)⁺ 195.

(R)-Acetic acid N'-(1-thiophen-2-yl-but-3-enyl)-hydrazide (Table 1, Entry 9): $[\alpha]_D^{25} = +152.8^\circ$ (c 1.0, CHCl₃); ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 8.93 (br s, 1H, CH₃CON-**H**), 7.34-7.37 (m, 1H, Ar-**H**), 6.94-6.96 (m, 2H, Ar-**H**), 5.68-5.82 (m, 1H, CH₂CH=CH₂), 4.97-5.08 (m, 3H, CH₂CH=CH₂ and

ArCHN-**H**), 4.23 (br s, 1H, ArCH-NH), 2.48-2.58 (m, 1H, one of CH₂CH=CH₂), 2.33-2.42 (m, 1H, one of CH₂CH=CH₂), 1.77 (br s, 3H, COCH₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 169.4, 145.8, 133.9, 126.6, 125.3, 124.6, 118.1, 59.6, 41.0, 21.0; IR (KBr) 3237, 3185, 3064, 2981, 2861, 1626, 1558, 1482, 1369, 1312 cm⁻¹; LRMS (FAB+) calcd for C₁₀H₁₄N₂OS 210, found (M+H)⁺ 211.

(R)-3-[1-(N'-Acetyl-hydrazino)-but-3-enyl]-indole-1-carboxylic acid *tert*-butyl ester (Table 1, Entry 10): [α]_D = +102.4° (c 1.9, CHCl₃); ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 8.95 (br s, 1H, CH₃CON-**H**), 8.04 (d, *J* = 8.0 Hz, 1H, Ar-**H**), 7.75 (d, *J* = 8.0 Hz, 1H, Ar-**H**), 7.53 (s, 1H, Ar-**H**), 7.30 (td, *J* = 7.5, 1.2 Hz, 1H, Ar-**H**), 7.21 (td, *J* = 7.5, 1.2 Hz, 1H, Ar-**H**), 5.73-5.86 (m, 1H, CH₂CH=CH₂), 4.95-5.08 (m, 3H, CH₂CH=CH₂ and ArCHN-**H**), 4.23 (br s, 1H, ArCH-NH), 2.48-2.64 (m, 2H, CH₂CH=CH₂), 1.75 (br s, 3H, COCH₃), 1.65 (s, 9H, COC(CH₃)₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 169.4, 149.7, 136.0, 134.6, 129.4, 124.5, 123.8, 122.5, 120.8, 120.2, 117.7, 115.4, 83.7, 56.7, 38.6, 28.2, 21.0; IR (KBr) 3421, 3290, 2978, 1735, 1653, 1452, 1374, 1256, 1156, 1157 cm⁻¹; LRMS (FAB+) calcd for C₁₉H₂₅N₃O₃ 343, found (M+H)⁺ 344.

(R)-Acetic acid N'-[1-(6-chloro-pyridin-3-yl)-but-3-enyl]-hydrazide (Table 1, Entry 12): [α]_D = +152.4° (c 1.2, CHCl₃); ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 8.88 (br s, 1H, CH₃CON-**H**), 8.30 (d, *J* = 2.4 Hz, 1H, Ar-**H**), 7.75 (dd, *J* = 8.2, 2.5 Hz, 1H, Ar-**H**), 7.40 (d, *J* = 8.2 Hz, 1H, Ar-**H**), 5.65-5.78 (m, 1H, CH₂CH=CH₂), 4.97-5.04 (m, 3H, CH₂CH=CH₂ and ArCHN-**H**), 4.03 (br s, 1H, ArCH-NH), 2.48-2.55 (m, 1H, one of CH₂CH=CH₂), 2.32-2.41 (m, 1H, one of CH₂CH=CH₂), 1.71 (br s, 3H, COCH₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 169.8, 150.6, 149.4, 138.3, 136.4, 133.1, 124.1, 118.8, 61.0, 39.9, 20.9; IR (thin film) 3271, 3077, 2983, 2933, 1653, 1568, 1457, 1371, 1103 cm⁻¹; LRMS (FAB+) calcd for C₁₁H₁₄ClN₃O 239, found (M+H)⁺ 240.

(R)-2-[1-(N'-Acetyl-hydrazino)-but-3-enyl]-pyrrole-1-carboxylic acid *tert*-butyl ester (Table 1, Entry 14): [α]_D = + 27.2° (c 0.8, CHCl₃); ¹H NMR (300 MHz, 100 °C, DMSO-*d*₆) δ 8.76 (br s, 1H, CH₃CON-**H**), 7.14-7.16 (m, 1H, Ar-**H**), 6.20 (br s, 1H, Ar-**H**), 6.08 (t, *J* = 3.2 Hz, 1H, Ar-**H**), 5.74-5.88 (m, 1H, CH₂CH=CH₂), 5.16 (br s, 1H, ArCHN-**H**), 4.95-5.07 (m, 2H, CH₂CH=CH₂), 4.54-4.60 (m, 1H, ArCH-NH), 2.37-2.50 (m, 2H, CH₂CH=CH₂), 1.70 (br s, 3H, COCH₃), 1.57 (s, 9H, COC(CH₃)₃); ¹³C NMR (75 MHz, 50 °C, CDCl₃) δ 168.7, 149.5, 135.2, 122.0, 117.0, 113.9, 112.0, 110.2, 109.8, 83.9, 57.0,

37.8, 28.0, 21.0; IR (KBr) 3294, 3200, 3064, 2978, 2932, 2870, 1734, 1646, 1370, 1335, 167, 1119, 1067 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{15}\text{H}_{23}\text{N}_3\text{O}_3$ 293, found $(\text{M}+\text{H})^+$ 294.

(*R*)-Acetic acid *N'*-(1-*tert*-butyl-but-3-enyl)-hydrazide (Table 1, Entry 15): $[\alpha]_{\text{D}} = -99.5^\circ$ (*c* 1.6, CHCl_3); ^1H NMR (300 MHz, 100 $^\circ\text{C}$, $\text{DMSO}-d_6$) δ 8.77 (br s, 1H, $\text{CH}_3\text{CON}-\text{H}$), 5.89-6.02 (m, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.92-5.05 (m, 2H, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.57 (br s, 1H, $\text{ArCHN}-\text{H}$), 2.49 (m, 1H, $\text{ArCH}-\text{NH}$), 2.23-2.32 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 2.01-2.11 (m, 1H, one of $\text{CH}_2\text{CH}=\text{CH}_2$), 1.77 (br s, 3H, COCH_3), 0.92 (s, 9H, $(\text{CH}_3)_3\text{CH}$); ^{13}C NMR (75 MHz, 50 $^\circ\text{C}$, CDCl_3) δ 168.6, 138.3, 115.7, 68.6, 34.9, 34.4, 26.9, 21.1; IR (KBr) 3251, 3077, 2957, 2867, 1642, 1550, 1497, 1473, 1431, 1364, 1303, 910 cm^{-1} ; LRMS (FAB+) calcd for $\text{C}_{10}\text{H}_{20}\text{N}_2\text{O}$ 184 found $(\text{M}+\text{H})^+$ 185.

Procedure for the enantioselective allylation of acetic acid benzylidene-hydrazide with (*S,S*)-1 on a 5.0 g scale (Scheme 3): To a cooled (10 $^\circ\text{C}$) solution of (*S,S*)-1 (9.90 g, 37.0 mmol) in CH_2Cl_2 (300 mL) was added acetic acid benzylidene-hydrazide (5.00 g, 30.8 mmol). The resulting solution was stirred for 16 hours and quenched with methanol (40 mL). After 15 min the solution was concentrated and the residue was diluted with EtOAc (150 mL) and H_2O (500 mL). The phases were separated and the aqueous layer was extracted with EtOAc (2 x 150 mL). The combined organic layers were washed (2 x 200 mL H_2O , 1 x 200 mL brine), dried (MgSO_4), filtered and concentrated. The resulting white solid was dissolved in boiling toluene (80 mL) and the solution was then cooled to room temperature. Pentane (350 mL) was layered on top of the toluene solution and the resulting mixture was maintained at room temperature overnight. The solid precipitate was filtered, washed with pentane:toluene (5:1), and dried to yield the product (*R*)-acetic acid *N'*-(1-phenyl-but-3-enyl)-hydrazide (5.04 g, 80%) as a crystalline white solid. $[\alpha]_{\text{D}} = +212.4^\circ$ (*c* 1.5, CHCl_3).

Procedure for the enantioselective allylation of acetic acid thiophen-2-ylmethylene-hydrazide with (*S,S*)-1 on a 5.0 g scale (Scheme 3): The same procedure as above was used except the reaction time was 40 h to ensure complete conversion. The residue was dissolved in boiling toluene (50 mL) and cooled to room temperature. Pentane (200 mL) was layered on top of the toluene solution and the resulting mixture was maintained at room temperature overnight. The solid precipitate was filtered,

washed with pentane:toluene (5:1), and dried to yield (*R*)-Acetic acid *N*-(1-thiophen-2-yl-but-3-enyl)-hydrazide (4.94 g, 79%) as a crystalline white solid. $[\alpha]_D = +178.0^\circ$ (*c* 1.0, CHCl_3).

Determination of absolute configuration: (*R*)-acetic acid *N*-(1-phenyl-but-3-enyl)-hydrazide was reduced to yield the corresponding homoallylic amine (Scheme 1).⁴ The optical rotation was compared to the lit. value⁵ to establish the (*R*) configuration of our product. The absolute configurations of the products derived from aromatic and heterocyclic substrates (entries 2-14, Table 1) were assigned by analogy.

Scheme 1

To establish the absolute configuration of the product of entry 15, Table 1 we used the benzoylhydrazide product, as it was more amenable to reduction with SmI_2 (Scheme 2). A synthesis of authentic tosylamide was developed starting from commercial (*S*)-*tert*-leucinol. Comparison of optical rotations of the tosylamides established the absolute configuration of the benzoylhydrazide product.

Scheme 2

Data for the tosylamide: $[\alpha]_D = +8.32$ (*c*=1.0, CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.75 (m, 2H, ArH), 7.26 (br d, *J* = 8.0 Hz, 2H, ArH), 4.38 (br d, *J* = 9.6 Hz, NHTs), 3.06 (dt, *J* = 9.4, 2.9 Hz, Me_3CCH), 2.41 (s, 3H, ArCH₃), 1.42-1.58 (m, 1H, one of CH_2CH_2), 1.29-0.98 (m, 3H, three of CH_2CH_2), 0.82-0.72 (m, 12H, Me_3C and CH_2CH_3); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 143.2, 139.8, 129.8, 127.3, 63.8,

(4) Denmark, S.E.; Nicaise, O.; Edwards, J.P. *J. Org. Chem.* **1990**, 55, 6219-6223.

(5) Chen, G.-M.; Ramachandran, P.V.; Brown, H.C. *Angew. Chem. Int. Ed.* **1999**, 38, 825-826.

35.4, 34.3, 27.2, 21.9, 20.5, 14.5; IR (KBr pellet): 3284, 2960, 2872, 1428, 1318, 1157, 1096, 1027, 926, 817 cm^{-1} ; MS (FAB+) calc'd for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{S}$ 283.16, found 284.05 ($\text{M}+1$).

Determination of enantioselectivity of homoallylic hydrazide products: All ee's were determined by chiral HPLC analysis. Racemic samples were prepared by method of Kobayashi.⁶

Table 1, entry 1: Chiralpak AD-H Column, 2.5% IPA/hexanes, 1.0 ml/min, 220 nm.

Table 1, entry 2: Chiralpak AD-H Column, 4% IPA/hexanes, 1.0 ml/min, 220 nm.

(6) (a) Kobayashi, S.; Hirabayashi, R. *J. Am. Chem. Soc.* **1999**, *121*, 6942-6943. (b) Hirabayashi, R.; Ogawa, C.; Sugiura, M.; Kobayashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 9493-9499.

Table 1, entry 3: Chiralpak AD-H Column, 2.5% IPA/hexanes, 1.0 ml/min, 220 nm. **Table 1, entry 4:** Chiralpak AD-H Column, 5.0% IPA/hexanes, 1.0 ml/min, 220 nm.

Table 1, entry 5: Chiralpak AD-H Column, 8.0% IPA/hexanes, 1.0 ml/min, 220 nm, *Racemic* *Product from Table 1* **Table 1, entry 6:** Chiralpak AD-H Column, 4.0% IPA/hexanes, 1.0 ml/min, 220 nm. *Racemic* *Product from Table 1*

Table 1, entry 7: Chiralpak AD-H Column, 4.0% IPA/hexanes, 1.0 ml/min, 220 nm. *Racemic* *Product from Table 1* **Table 1, entry 8:** Chiralpak AD-H Column, 4.0% IPA/hexanes, 1.0 ml/min, 220 nm. *Racemic* *Product from Table 1*

Table 1, entry 9: Chiralpak AD-H Column, 4.0% IPA/hexanes, 1.0 ml/min, 220 nm. **Table 1, entry 10:** Chiralpak AD-H Column, 5.0% IPA/hexanes, 0.4 ml/min, 220 nm.

Table 1, entry 12: Chiralcel OD Column, 2.5% EtOH/hexanes, 1.0 ml/min, 220 nm. **Table 1, entry 14:** Chiralpak AD-H Column, 5.0% IPA/hexanes, 1.0 ml/min, 220 nm

Table 1, entry 15: Chiralpak AD-H Column, 2.5% EtOH/hexanes, 1.0 ml/min, 220 nm. **Scheme 3, First reaction:** Chiralcel AD-H Column, 2.5% IPA/hexanes, 1.0 ml/min, 220 nm.

Scheme 3, Second reaction: Chiracel AD-H Column, 4.0% IPA/hexanes, 1.0 ml/min, 220 nm.

Racemic

Product from Scheme 3

Mixture (94:6) of racemic hydrazides 6a and 6b: Chiralpak AD-H Column, 6.0% IPA/hexanes, 1.0 ml/min, 254 nm.

Authentic 94:6 mixture of anti:syn crotylation products, racemic.

Scheme 5, hydrazide 6a: Chiralpak AD-H Column, 6.0% IPA/hexanes, 1.0 ml/min, 254 nm.

Scheme 5, hydrazide 6b: Chiralpak AD-H Column, 6.0% IPA/hexanes, 1.0 ml/min, 254 nm.

^1H NMR (300 MHz, CDCl_3) spectrum of (*S,S*)-**5a**:

^1H NMR (500 MHz, CDCl_3) spectrum of (*S,S*)-**5b**:

^1H NMR (300 MHz, 100 $^\circ\text{C}$, $\text{DMSO}-d_6$) spectra of the allylation products:

^1H NMR (300 MHz, CDCl_3) spectra of the tosylamide: