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Supporting Information

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Allylsilane Vinylarene Cross Metathesis Enables a Powerful New Approach to Enantioselective Imine Allylation

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Supporting Information

General Information. All reactions were carried out in flame-dried glassware under an atmosphere of nitrogen with magnetic stirring unless otherwise indicated. Methylene chloride was obtained from Fisher and purified by degassing with argon followed by passage through an activated neutral alumina column. Benzene was purchased from Fisher and purified by degassing with argon followed by passage through both an activated neutral alumina column and Q5 reactant column. Toluene and triethylamine were purchased from Aldrich and purified by distillation from CaH_2 then stored under nitrogen. Pentane (HPLC grade) was purchased from Fisher and used as received. Anhydrous chloroform (stabilized with amylenes) and methanol were purchased from Aldrich and used as received. The Grubbs second generation and Hoveyda-Grubbs second-generation catalysts were obtained from Materia Inc. and used without purification. Allylamine and all ketone reagents were purchased from Aldrich and used as received. ^1H NMR spectra were recorded on Bruker DPX-300 (300 MHz) or DPX-400 (400 MHz) spectrometers. ^1H NMR chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane internal standard (0 ppm) or CD_3OD internal standard (3.31 ppm). Data are reported as follows: (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t = triplet, q = quartet, quint = quintet, dd = doublet of doublets, dq = doublet of quartets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, m = multiplet; integration; coupling constant in Hz; assignment). Proton decoupled ^{13}C NMR spectra were recorded on Bruker DPX-300 (75 MHz) or DPX-400 (100 MHz) spectrometers and are reported in ppm from $CDCl_3$ internal standard (77.1 ppm) or CD_3OD internal standard (49.0 ppm). ^{29}Si NMR spectra were recorded on a Bruker DPX-300 (60 MHz) spectrometer and are reported with tetramethylsilane (0 ppm) as an internal standard. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR or Nicolet Avatar 370 DTGS spectrometers. Optical rotations were recorded on a Jasco DIP-1000 digital polarimeter; the concentration *c* is reported in g/100mL. Low resolution mass spectra were obtained on a JEOL HX100 mass spectrometer in the Columbia University Mass Spectrometry Laboratory.

General Procedure for the Cross-Metathesis/Imine Cinnamylation Reactions Described in Table 1: To a solution of the vinylarene or vinylheteroarene (3.75 mmol) in either 1,2-dichloroethane (DCE), $CHCl_3$, or CH_2Cl_2 (5 mL) is added *(S,S)*-**2**[1] (0.750 mmol) followed by the second generation Grubbs catalyst (16.8 mg, 2.6 mol% based upon *(S,S)*-**2**). The resulting mixture is heated at reflux for 3.5 h (DCE) or 5 h ($CHCl_3$) or 7 h (CH_2Cl_2) and then cooled to room temperature. The imine (**3** or **4**) (0.50 mmol) is then added. The reaction mixture is then heated at reflux for 14 h and then cooled to room temperature and quenched by the addition of ethanol (0.5 mL). The resulting mixture is diluted with ethyl acetate (20 mL) and washed with water and brine (10 mL each). The organic layer is dried ($MgSO_4$), filtered, and concentrated. The residue is purified by flash chromatography on silica gel.

Characterization Data for the products in Table 1: Amines **5**, **6**, and **15** have been previously characterized.

Amine **5**, Table 1: The reaction was carried out in DCE according to the general procedure. Amine **5** has been previously characterized.[2]

Amine **6**, Table 1: The reaction was carried out in DCE according to the general procedure. Amine **6** has been previously characterized.[2]

Amine **7**, Table 1: The reaction was carried out in chloroform according to the general procedure. The product was purified by flash chromatography (15-20% ethyl acetate/hexane) to give 55.6 mg (65%) of amine **7**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23-7.08 (m, 8H, Ph-**H**, *o*-tolylAr**H**), 6.96 (t, *J* = 7.5 Hz, 1H, *o*-tolylAr-**H**), 6.90 (d, *J* = 7.5 Hz, 1H, phenolAr-**H**), 6.87 (m, 2H, phenolAr-**H**), 6.73 (t, *J* = 7.5 Hz, 1H, phenolAr-**H**), 6.07 (ddd, *J* = 10.0 Hz, 10.0 Hz, 17.0 Hz, Ph-CH-C**H**=CH$_2$), 5.24 (apparent d, *J* = 17.0 Hz, 1H, Ph-CH-CH=C**H$_2$**), 5.19 (apparent d, *J* = 10.0 Hz, 1H, Ph-CH-CH=C**H$_2$**), 3.92 (d, *J* = 10.0 Hz, 1H, N-C**H**), 3.87 (apparent t, *J* = 9.0 Hz, 1H, Ph-C**H**), 3.81 (d, *J* = 14.0 Hz, 1H, NC**H**$_2$), 3.63 (d, *J* = 14.0 Hz, 1H, NC**H**$_2$), 2.04 (s, 1H, ArC**H$_3$**); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 140.1, 139.5, 136.0, 130.6, 129.2, 128.8, 128.2, 128.0, 127.5, 126.6, 126.4, 123.3, 119.5, 118.3, 116.8, 67.5, 53.2, 51.0; IR (thin film): 3294, 3026, 1589, 1490, 1455, 1253, 1091, 914, 756, 727, 700 cm^{-1}; LRMS (FAB+): calculated for $C_{24}H_{25}NO$: 343, found: 344 (M+H); $[\alpha]_D^{23}$ = -49° (*c* 0.49, $CHCl_3$).

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(1) The large-scale (~150 g) preparation of (*S*,*S*)-**2** is described in the supporting information file associated with: Berger, R.; Rabbat, P. M.A.; Leighton, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 9596.

(2) See the supporting information file associated with: Huber, J. D.; Leighton, J. L. *J. Am. Chem. Soc.* **2007**, *129*, 14552.

Amine **8**, Table 1: The reaction was carried out in chloroform according to the general procedure. The product was purified by flash chromatography (15-20% ethyl acetate/hexane) to give 54.8 mg (65%) of amine **8**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.13 (m, 6H, Ph-**H**, phenolAr**H**), 7.05 (m, 1H, HetAr-**H**), 6.85 (m, 2H, phenolAr-**H**), 6.80 (m, 1H, HetAr-**H**), 6.73 (t, *J* = 7.5 Hz, 1H, phenolAr-**H**), 6.55 (d, *J* = 3.5 Hz, 1H, HetAr**H**), 6.07 (ddd, *J* = 9.0 Hz, 10.0 Hz, 17.0 Hz, Ph-CH-C**H**=CH_2), 5.24 (m, 2H, Ph-CH-CH=C$\mathbf{H_2}$), 3.89 (apparent t, *J* = 8.5 Hz, 1H, Ph-C**H**), 3.86 (d, *J* = 8.5 Hz, 1H, N-C**H**), 3.80 (d, *J* = 13.5 Hz, 1H, NC$\mathbf{H_2}$), 3.62 (d, *J* = 14.0 Hz, 1H, NC$\mathbf{H_2}$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 144.0, 139.8, 138.1, 129.3, 128.9, 128.8, 128.4, 128.2, 127.0, 125.2, 124.2, 123.2, 119.6, 119.0, 116.9, 68.2, 53.2, 51.1; IR (thin film): 3293, 3029, 2897, 2853, 1589, 1490, 1454, 1253, 757, 698 cm^{-1}; LRMS (FAB+): calculated for $C_{21}H_{21}NOS$: 335, found: 336 (M+H); $[\alpha]_D^{23}$ = -19° (*c* 0.75 $CHCl_3$).

Amine **9**, Table 1: The reaction was carried out in chloroform according to the general procedure. The product was purified by flash chromatography (15-35% ethyl acetate/hexane) to give 53.1 mg (57%) of amine **9**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 6.0 Hz, 1H, NO_2Ar-**H**), 7.85 (s, 1H, NO_2Ar-**H**), 7.29-7.14 (m, 6H, Ph-**H,** NO_2Ar-**H**), 7.06 (overlapping peaks, 2H, NO_2Ar-**H,** phenolAr**-H**), 6.86 (m, 2H, phenolAr-**H**), 6.75 (t, *J* = 7.6 Hz, 1H, phenolAr-**H**), 6.16 (ddd, *J* = 9.6 Hz, 9.6 Hz, 16.8 Hz, Ph-CH-C**H**=CH_2), 5.36-5.32 (m, 2H, Ph-CH-CH=C$\mathbf{H_2}$), 3.87 (d, *J* = 10.0 Hz, 1H, N-C**H**), 3.82 (d, *J* = 13.6 Hz, 1H, NC$\mathbf{H_2}$), 3.69 (apparent t, *J* = 9.6 Hz, 1H, Ph-C**H**), 3.64 (d, *J* = 13.6 Hz, 1H, NC$\mathbf{H_2}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 148.5, 143.4, 139.2, 137.9, 134.8, 129.6, 129.4, 129.2, 128.9, 128.5, 128.1, 123.3, 122.9, 122.1, 119.9, 119.7, 116.9, 67.2, 58.0, 51.0; IR (thin film): 3283, 3031, 2855, 1589, 1528, 1490, 1350, 1253, 760, 704 cm^{-1} ; LRMS (FAB+): calculated for $C_{23}H_{23}NO$: 374, found: 375 (M+H); $[\alpha]_D^{23}$ = -13° (*c* 1.0, $CHCl_3$).

Amine **10**, Table 1: The reaction was carried out in chloroform according to the general procedure. The product was purified by flash chromatography (15-25% ethyl acetate/hexane) to give 56.0 mg (65%) of amine **10**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.13 (m, 4H, Ph-**H**), 7.04 (m, 2H, *p*-FAr**H**), 6.91-6.78 (m, 6H, phenolAr-**H**, *p*-FAr**H**), 6.73 (t, *J* = 7.2 Hz, 1H, phenolAr-**H**), 6.12 (ddd, *J* = 9.6 Hz, 9.6 Hz, 17.2 Hz, Ph-CH-C**H**=CH_2), 5.24 (m, 2H, Ph-CH-CH=C$\mathbf{H_2}$), 3.79 (m, 2H, N-C**H**, NC$\mathbf{H_2}$), 3.62 (d, *J* = 13.6 Hz, 1H, N-C$\mathbf{H_2}$), 3.55 (apparent t, *J* = 9.2 Hz, 1H, PhC**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 160.8, 158.3, 139.8, 139.0, 136.9, 129.9, 129.8, 129.2, 128.9, 128.8, 128.2, 128.1, 123.1, 119.5, 118.6, 116.8, 115.6, 115.5, 67.5, 57.6, 51.0; IR (thin film): 3924, 3030, 2901, 2853, 1589, 1509, 1491, 1253, 1225, 912, 830, 758, 701 cm^{-1}; LRMS (FAB+): calculated for $C_{23}H_{22}FNO$: 347, found: 348 (M+H); $[\alpha]_D^{23}$ = -20° (*c* 0.77 $CHCl_3$).

Amine **11**, Table 1: The reaction was carried out in chloroform according to the general procedure. The product was purified by flash chromatography (10-35% ethyl acetate/hexane) to give 98.1 mg (54%) of amine **11**. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.13 (dd, *J* = 1.8 Hz, 4.5 Hz, 1H, pyr(6-pos)-**H**), 7.50 (dd, *J* = 1.8 Hz, 7.5 Hz, 1H, pyr(4-pos)-**H**), 7.28-7.17 (m, 6H, Ph-**H**, phenolAr-**H**), 7.10 (dd, *J* = 4.8 Hz, 7.8 Hz, 1H, pyr(5pos)-**H**), 6.88 (m, 2H, phenolAr-**H**), 6.78 (apparent dt, *J* = 0.9 Hz, 8.1 Hz, 1H, phenolAr-**H**), 6.10 (ddd, *J* = 9.9 Hz, 9.9 Hz, 17.1 Hz, 1H, C**H**=CH$_2$), 5.41-5.32 (m, 2H, CH=C**H$_2$**), 4.25 (apparent t, *J* = 9.3 Hz, 1H, PhC**H**), 4.03 (d, *J* = 9.6 Hz, 1H, NC**H**), 3.86 (d, *J* = 13.5 Hz, 1H, NC**H$_2$**), 3.64 (d, *J* = 13.8 Hz, 1H, NC**H$_2$**); ^{13}C NMR (75 MHz, CDCl$_3$): δ 158.1, 147.9, 139.0, 138.3, 136.7, 135.7, 129.4, 129.1, 128.9, 128.5, 128.0, 122.8, 120.4, 119.7, 116.9, 65.7, 53.2, 50.7; IR (thin film): 3029, 2854, 1588, 1563, 1490, 1455, 1408, 1253, 1183, 1059, 912, 847 cm^{-1}; LRMS (FAB+): calculated for $C_{22}H_{21}ClN_2O$: 364, found: 365 (M+H); $[\alpha]_D^{23}$ = -75° (*c* 0.92 CHCl$_3$).

Amine **12**, Table 1: The reaction was carried out in CH$_2$Cl$_2$ according to the general procedure. The product was purified by flash chromatography (5-15% ethyl acetate/hexane) to give 97.1 mg (58%) of amine **12**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.43-7.29 (m, 5H, Ph-**H**), 7.16 (appt. t, *J* = 7.0 Hz, 1H, phenolAr**H**), 6.86 (appt. t, *J* = 8.5 Hz, 2H, phenolAr-**H**), 6.74 (t, *J* = 7.0 Hz, 1H, phenolAr-**H**), 5.78 (ddd, *J* = 10.0 Hz, 10.0 Hz, 18.0 Hz, Ph-CH-C**H**=CH$_2$), 5.29 (appt. d, *J* = 10.0 Hz, 1H, Ph-CH-CH=C**H$_2$**), 5.13 (appt. d, *J* = 17.0 Hz, 1H, Ph-CH-CH=C**H$_2$**), 3.75 (d, *J* = 14.0 Hz, 1H, NC**H$_2$**), 3.66 (d, *J* = 10.0 Hz, 1H, NC**H**), 3.58 (d, *J* = 13.5 Hz, 1H, N-C**H$_2$**), 2.23 (appt. t, *J* = 9.0 Hz, 1H, Ph-C**H**), 1.70-1.58 (m, 4H, CyHex**H**), 1.36 (m, 1H, CyHex**H**), 1.16-0.96 (m, 6H, CyHex**H**); ^{13}C NMR (125 MHz, CDCl$_3$): δ 158.4, 141.4, 137.3, 129.2, 128.7, 128.1, 123.4, 120.0, 119.3, 116.7, 63.8, 57.2, 50.9, 38.3, 32.7, 27.9, 26.8; IR (thin film): 3296, 3027, 2925, 2852, 1616, 1589, 1490, 1452, 1254, 1093, 1034, 1002, 919, 755, 726, 701 cm^{-1}; LRMS (FAB+): calculated for $C_{23}H_{29}NO$: 335, found: 336 (M+H); $[\alpha]_D^{23}$ = -34° (*c* 1.5 CHCl$_3$).

Amine **13**, Table 1: The reaction was carried out in DCE according to the general procedure. The product was purified by flash chromatography (10-20% ethylacetate/hexane) to give 90.9 mg (55%) of amine **13**. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.33–7.16 (m, 9H, Ph-**H**, *o*-MePh-**H**), 6.66-6.60 (m, 3H, phenolAr-**H**), 6.47 (d, *J* = 7.5 Hz, 1H, phenolAr-**H**)**,** 5.94 (ddd, *J* = 8.1 Hz, 9.9 Hz, 17.1 Hz, 1H, Ph-CH-C**H**=CH$_2$), 5.04 (apparent d, *J* = 10.2 Hz, 1H, Ph-CH-CH=C**H**$_2$), 4.88 (partially buried apparent d, *J* = 17.1 Hz, 1H, Ph-CH-CH=C**H$_2$**), 4.88 (br s, 1H, N**H** or O**H**), 4.56 (d, *J* = 7.5 Hz, 1H, N-C**H**), 4.28 (brs, 1H, N**H** or O**H**), 4.04 (apparent t, *J* = 8.1 Hz, 1H, Ph-C**H**), 2.36 (s, 1H, ArC**H$_3$**); ^{13}C NMR (75 MHz, CDCl$_3$): δ 145.3, 142.0, 139.0, 138.1, 137.1, 135.8, 131.2, 128.6, 126.4, 127.8, 127.7, 127.6, 127.1, 126.7, 121.6, 119.3, 117.6, 115.9, 114.6, 63.2, 52.8; IR (thin film): 3524, 3420, 3062, 3028, 2978, 1610, 1512, 1449, 1267, 922, 739, 703 cm^{-1}; LRMS (FAB+): calculated for $C_{23}H_{23}NO$: 321, found: 322 (M+H); $[\alpha]_D^{23}$ = -93° (*c* 2.0, $CHCl_3$).

Amine **14**, Table 1: The reaction was carried out in DCE according to the general procedure. The product was purified by flash chromatography (10-25% ethyl acetate/hexane) to give 86.8 mg (54%) of amine **14**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20–7.04 (m, 5H, Ph-**H**), 6.87 (t, *J* = 3.6 Hz, 1H, phenolAr-**H**), 6.71 (d, *J* = 3.0 Hz, 1H, phenolAr-**H**), 6.63-6.46 (m, 4H, phenolAr-**H**, thiophene-**H**), 6.34 (d, *J* = 7.5 Hz, 1H, thiophene-**H**), 5.89 (ddd, *J* = 8.4 Hz, 10.2 Hz, 16.8 Hz, 1H, Ph-CH-C**H**=CH_2), 5.08-5.00 (m, 2H, Ph-CH-CH=C**H$_2$**), 4.81 (br s, 1H, N**H** or O**H**), 4.49 (d, *J* = 5.1 Hz, 1H, N-C**H**), 4.40 (br s, 1H, N**H** or O**H**), 4.00 (apparent t, *J* = 7.5 Hz, 1H, Ph-C**H**); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.7, 143.6, 141.1, 137.7, 135.6, 128.5, 128.0, 127.6, 127.6, 127.1, 125.8, 124.6, 121.9, 118.9, 118.0, 115.1, 114.6, 63.8, 52.5; IR (thin film): 3521, 3416, 3062, 1610, 1513, 1444, 1265, 741, 700 cm^{-1}; LRMS (FAB+): calculated for $C_{20}H_{19}NOS$: 321, found: 322 (M+H); $[\alpha]_D^{23}$ = -54° (*c* 0.70, $CHCl_3$).

Amine **15**, Table 1: The reaction was carried out in DCE according to the general procedure. Amine **15** has been previously characterized.[2]

Piperidine **16**: To a solution of amine **5** (200 mg, 0.60 mmol) in toluene (12 mL) in a 45 mL stainless steel Parr bomb equipped with a glass liner and magnetic stir bar was added $[Rh(OAc)_2]_2$ (7.2 mg, 0.015 mmol, 2.5 mol%) and XANTPHOS (26 mg, 0.045 mmol, 7.5 mol%) and the reaction apparatus was sealed and charged to 600 psi of 1:1 CO/H_2 with three cycles of filling and purging. The bomb was then heated at 100 °C (oil bath, external temperature) for 16 h. The reaction mixture was cooled to room temperature, the bomb was vented and the reaction mixture was concentrated. The residue was dissolved in ethanol (12 mL) and treated with $NaBH_4$ (46 mg, 1.2 mmol) and the resulting mixture was stirred for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (2 mL) and the mixture was partitioned between water (10 mL) and ethyl acetate (15 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (15 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (5% ethyl acetate/hexane) to give 178 mg (86%) of piperdine **16** as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.7-10.9 (br s, 1H, phenol O**H**), 7.12–7.00 (m, 9H, Ph-**H**), 6.93 (m, 2H, Ph-**H**, phenolAr-**H**), 6.85-6.78 (m, 2H, phenolAr-**H**), 6.70 (t, *J* = 7.5 Hz, 1H, phenolAr-**H**), 4.05 (d, *J* = 14.1 Hz, 1H, N-C**H**), 3.26 (apparent d, *J* = 10.5 Hz, 2H, NC**H$_2$**), 3.00 (apparent d, *J* = 13.8 Hz, 2H, NC**H$_2$**), 2.27-2.18 (m, 1H, Ph-C**H**), 2.07-2.04 (m, 1H, PhCHC**H$_2$**), 1.93-1.78 (m, 3H, PhCHC**H**$_2$, PhCHCH_2C**H$_2$**); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.8, 143.3, 140.6, 128.9, 128.7, 128.4, 128.3, 127.8, 126.6, 122.2, 119.4, 116.2, 75.6, 59.4, 53.6, 51.7, 33.4, 25.9; IR (thin film):

3029, 2933, 2813, 1589, 1490, 1255, 1081, 1033, 755, 698 cm^{-1}; LRMS (FAB+): calculated for $C_{24}H_{25}NO$: 343, found: 344 (M+H); $[\alpha]_D^{23}$ = +136° (*c* 0.73, $CHCl_3$).

Piperidine **17**: The procedure described above for the synthesis of **16** was employed starting with amine **8**. Data for **17**: ^{1}H NMR (300 MHz, $CDCl_3$): δ11.2 (s, 1H, phenol O**H**), 7.20–7.09 (m, 6H, Ph-**H**, thiopheneAr-**H**), 6.99 (d, *J* = 5.1 Hz, 1H, phenolAr-**H**), 6.86-6.79 (m, 2H, phenolAr-**H**), 6.74-6.67 (m, 2H, phenolAr-**H**, thiopheneAr-**H**), 6.37 (d, *J* = 3.6 Hz, 1H, thiopheneAr-**H**), 4.08 (d, *J* = 13.8 Hz, 1H, N-C**H**), 3.36-3.25 (m, 2H, NC**H2**CH2), 3.20 (d, *J* = 10.2 Hz, 1H, NC**H$_2$**), 3.01 (d, *J* = 14.1 Hz, 1H, NC**H$_2$**), 2.27-2.21 (m, 2H, thiopheneArC**H**, thiopheneArCHC**H$_2$**), 1.90-1.87 (m, 3H, thiopeheneArCHC**H**$_2$, thiopheneArCHCH$_2$C**H$_2$**); ^{13}C NMR (125 MHz, $CDCl_3$): δ157.8, 146.7, 140.7, 128.9, 128.7, 128.1, 126.6, 124.8, 123.4, 122.2, 119.5, 116.3, 76.8, 59.5, 53.4, 46.7, 34.8, 25.9; IR (thin film): 3029, 2946, 2914, 1852, 1588, 1492, 1409, 1255, 1099, 853, 758, 689cm^{-1}; LRMS (FAB+): calculated for $C_{22}H_{23}NOS$: 349, found: 350 (M+H); $[\alpha]_D^{23}$ = +127° (*c* 0.95, $CHCl_3$).

Piperidine **18**: The procedure described above for the synthesis of **16** was employed starting with amine **11**. Data for **18**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.0 (s, 1H, phenol-O**H**), 8.08 (dd, *J* = 1.8 Hz, 4.8 Hz, 1H, pyr-(6-pos)-**H**), 7.65 (d, *J* = 7.8 Hz, 1H, pyr-(4-pos)-**H**), 7.26-7.09 (m, 7H, pyr-(5-pos)-**H**, Ph-**H**, phenolAr-**H**), 6.86-6.78 (m, 2H, phenolAr-**H**), 6.71 (t, *J* = 7.5 Hz, 1H, phenolAr-**H**), 4.02 (d, *J* = 13.8 Hz, 1H, N-C**H**), 3.77 (apparent t, *J* = 9.6 Hz, 1H, NC**H$_2$**), 3.18 (apparent t, *J* = 11.1 Hz, 2H, NC**H$_2$**), 3.01 (d, *J* = 13.8 Hz, 1H, NC**H$_2$**), 2.26-1.90 (m, 4H, pyrC**H**, pyrCHC**H$_2$**, pyrCHCH$_2$C**H**$_2$), 1.60-1.53 (m, 1H, pyrCHCH$_2$C**H**$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7, 147.7, 138.9, 137.6, 137.1, 128.9, 128.8, 128.5, 122.7, 122.0, 119.5, 116.4, 74.3, 59.0, 53.6, 45.8, 33.4, 25.8; IR (thin film): 3031, 2935, 2855, 2819, 1589, 1563, 1488, 1410, 1255, 1183, 1102, 1081, 1058, 1034, 757, 700 cm^{-1}; LRMS (FAB+): calculated for $C_{23}H_{23}N_2O$: 378, found: 379 (75%), 381 (25%) (M+H for two chlorine isotopes); $[\alpha]_D^{23}$ = +42° (*c* 0.93, $CHCl_3$).

Piperidine **19**: To a solution of piperidine **16** (69 mg, 0.20 mmol) in MeOH (3 mL) was added $Pd(OH)_2$ on carbon (56 mg, 0.040 mmol, 20 mol%) followed by ammonium formate (315 mg, 5.0 mmol) and the reaction mixture was stirred for 16 h. Et_3N (0.5 mL) was then added and the reaction mixture was stirred 10 min before being filtered through a pad of celite. The celite was rinsed thoroughly with 1% Et_3N in MeOH and the combined filtrates were concentrated. The residue was purified by flash chromatography (0.5% Et_3N/5% ethyl acetate/94.5% hexane) to give 34 mg (72%) of the title compound as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.15–6.97 (m, 10H, Ph-**H**), 3.73 (d, *J* = 10.2 Hz, 1H, N-C**H**), 3.28 (m, 1H, NC**H$_2$**), 2.92-2.79 (m, 3H, NC**H$_2$**, PhC**H**, N**H**), 2.09-2.05 (m, 1H, PhCHC**H**$_2$), 1.88-1.79 (m, 3H, PhCHC**H**$_2$, PhCHCH$_2$C**H$_2$**); ^{13}C NMR (75 MHz, $CDCl_3$):

δ 143.8, 142.8, 128.3, 128.1, 127.5, 126.4, 68.5, 50.9, 47.8, 33.8, 26.7; IR (thin film): 3028, 2930, 2852, 2785, 1602, 1492, 1452, 1287, 1201, 1166, 1128, 756, 698 cm^{-1}; LRMS (FAB+): calculated for $C_{17}H_{19}N$: 237, found: 238 (M+H); $[\alpha]_D^{23}$ = +98° (*c* 0.84, $CHCl_3$).

Amine **23**: To a solution of (1*S*,2*R*)-**20**[3] (147 mg, 0.55 mmol) in benzene (3.7 mL) was added styrene (190 μL, 1.67 mmol) followed by the second generation Hoveyda-Grubbs catalyst (**21**) (14 mg, 0.02 mmol). The solution was heated at reflux for 2 h, and then cooled to room temperature. Aldimine **22** (50 mg, 0.37 mmol) was added and the reaction mixture was stirred for 14 h. Saturated sodium bicarbonate (2 mL) was added, and, after 15 minutes, the solution was diluted with 30% isopropanol in $CHCl_3$ (15 mL). Additional saturated sodium bicarbonate (10 mL) was added, the organic layer was separated, and the aqueous layer was extracted with 30% isopropanol/$CHCl_3$ solution (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (5% MeOH in CH_2Cl_2) to give 58 mg (62%) of amine **23** as a tan solid: $[\alpha]_D^{23}$ = -32.6° (*c* 1.2, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.23 (m, 3H, Ar-**H**), 7.19-7.17 (m, 2H, Ar-**H**), 6.99 (s, 2H, Imid-**H**), 6.04 (ddd, 1H, J = 17.4, 7.8, 2.4 Hz, C**H**=CH_2), 5.74-5.61 (m, 1H, C**H**=CH_2), 5.01-4.84 (m, 4H, CH=C**H**$_2$ x 2), 4.27 (d, 1H, J = 8.7 Hz, Imid-C**H**N), 3.63 (apparent triplet, 1H, J = 8.1 Hz, ArC**H**CH=CH_2), 3.05 (dd, 1H, J = 14.4, 5.4 Hz, one NC**H**$_2$), 2.97 (dd, 1H, J = 14.4, 6.6 Hz, one NC**H**$_2$); ^{13}C NMR (75 MHz, CD_3OD) δ 149.6, 142.3, 139.3, 136.9, 129.8, 129.2, 128.1, 122.5, 117.0, 116.9, 61.4, 57.1, 50.9; IR (KBr) 3096, 3026, 2970, 2906, 2870, 2807, 1453, 1099, 993, 916, 700 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{16}H_{19}N_3$ 253.3, found $(M+H)^+$ 254.2.

Amine **24**: To a solution of (1*S*,2*R*)-**20** (147 mg, 0.55 mmol) in benzene (3.7 mL) was added 2-chloro-3-vinylpyridine (232 mg, 1.66 mmol) followed by the second generation Hoveyda-Grubbs catalyst (**21**) (14 mg, 0.02 mmol). The solution was heated at reflux for 2 h, and then cooled to room temperature. Aldimine **22** (50 mg, 0.37 mmol) was added and the reaction mixture was stirred for 13 h. Saturated sodium bicarbonate (2 mL) was added, and, after 15 minutes, the solution was diluted with 30% isopropanol in $CHCl_3$ (15 mL). Additional saturated sodium bicarbonate (10 mL) was added, the organic layer was separated, and the aqueous layer was extracted with 30% isopropanol/$CHCl_3$ solution (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (3-4% MeOH in CH_2Cl_2) to give 62 mg (58%) of amine **24** as a tan solid: $[\alpha]_D^{23}$ = -49.2° (*c* 1.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, 1H, J

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(3) For the synthesis of **20**, see the supporting information file associated with: Perl, N. R.; Leighton, J. L. *Org. Lett.* **2007**, *9*, 3699.

= 4.4, 1.6 Hz, Ar-**H**), 7.37 (dd, 1H, J = 8.0, 1.2 Hz, Ar-**H**), 7.15 (dd, 1H, J = 7.6, 4.8 Hz, Ar-**H**), 6.99 (s, 2H, Imid-H), 6.12 (ddd, 1h, J = 17.6, 7.6, 2.4 Hz, C**H**=CH_2), 5.81-5.71 (m, 1H, C**H**=CH_2), 5.18-5.04 (m, 4H, 2 x CH=C**H**$_2$), 4.30-4.25 (m, 2H, overlapping Imid-C**H**N and Ar-C**H**CH=CH_2), 3.18 (dd, 1H, J = 14.4, 5.2 Hz, one NC**H**$_2$), 3.07 (dd, 1H, J = 4.4, 6.8 Hz, one NC**H**$_2$); ^{13}C NMR (75 MHz, CD_3OD) δ 152.1, 149.2, 148.5, 139.7, 137.4, 137.0, 136.7, 124.3, 122.5, 119.1, 117.1, 59.7, 52.3, 50.8; IR (neat) 3143, 3074, 2979, 2817, 1563, 1452, 1407, 1099, 1061 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{15}H_{17}ClN_4$ 288.8, found $(M+H)^+$ 289.2.

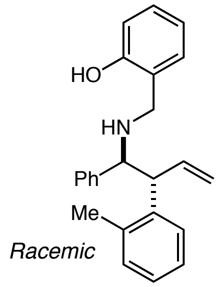
Amine **26**: To a solution of (1*S*,2*R*)-**20** (215 mg, 0.81 mmol) in benzene (5.4 mL) was added styrene (280 μL, 2.43 mmol) followed by the Grubbs second generation catalyst (27 mg, 0.03 mmol). The solution was heated at reflux for 2 h, and then cooled to room temperature. Aldimine **25** (100 mg, 0.54 mmol) was added, and the reaction mixture was stirred for 18 h. To ensure complete consumption of starting aldimine, the reaction mixture was heated at 45 °C for 45 min, and then recooled to room temperature. Additional second generation Grubbs catalyst (45 mg, 0.05 mmol) was added and the reaction mixture was heated at 45 °C for 24 h. The reaction mixture was cooled to room temperature and treated with saturated sodium bicarbonate (2 mL). After 15 minutes, the solution was diluted with 30% isopropanol in chloroform (15 mL). Additional saturated sodium bicarbonate (10 mL) was added, the organic layer was separated, and the aqueous layer was extracted with 30% isopropanol in chloroform (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (4% methanol in methylene chloride) to give 72 mg (48%) of amine **26** as a tan solid: $[\alpha]_D^{23}$ = +459.5° (*c* 0.9, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 7.38 (br s, 2H, Benzimid-**H**), 7.16-7.11 (m, 2H, Benzimid-**H**), 7.05-6.98 (m, 3H, Ar-**H**), 6.95-6.91 (m, 2H, Ar-**H**), 6.15-6.10 (m, 1H, one C**H**=CH), 6.01-5.91 (m, 1H, one CH=C**H**), 4.63 (d, 1H, J = 4.5 Hz, Benzimid-C**H**N), 3.86 (apparent br s, 1H, C**H**Ph), 3.74-3.59 (m, 2H, NC**H**$_2$CH=CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 139.4, 130.1, 128.2, 128.0, 127.3, 127.3, 122.5, 57.7, 46.4, 45.5, 45.5; IR (KBr) 3443, 3062, 3026, 2927, 2870, 2772, 1455, 1427, 1198, 1049, 734, 700 cm^{-1}; LRMS (FAB$^+$) calc'd for $C_{18}H_{17}N_3$ 275.4, found $(M+H)^+$ 276.2.

Stereochemical Proofs. The relative and absolute stereochemistry of products **5** and **6** have previously been rigorously established by single crystal X-ray diffraction analysis.[2] The stereochemistry of all products in Table 1 was assigned by analogy. The relative and absolute stereochemistry of products **23** and **24** were assigned by analogy, based upon previously determined similar structures.[3]

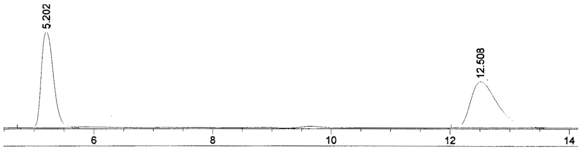
Determination of enantioselectivities: The enantiomeric excess (ee) of the products reported in this study was in every case determined by chiral HPLC analysis. Racemic samples were prepared by employing *rac*-**2** and *rac*-**20** in the reactions described in ths study. The *rac* allylsilanes were prepared by admixing the individual enantiomerically pure reagents, and slight deviations from 50:50 in the racemic HPLC traces may therefore be attributed to the error inherent in this procedure.

The assays for compounds **5** and **6** have previously been described in detail.[2]

7: Chiralpak AD-H, 90/10 Hexane/*i*-PrOH, 1.0mL/min, 220 nm.



Racemic



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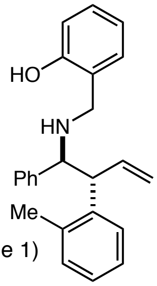
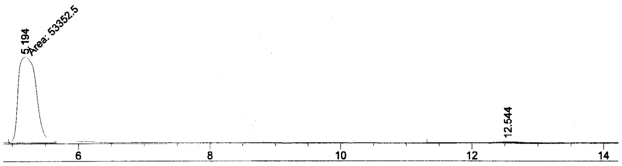


7 (Table 1)



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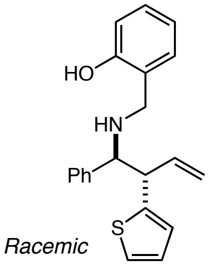
   1   5.194 MM    0.3153 5.33525e4  2820.21924  98.2300
   2  12.544 BV    0.4666  961.35352   30.99874   1.7700
```

8: Chiralpak AD-H, 90/10 Hexane/*i*-PrOH, 1.0mL/min, 220 nm.



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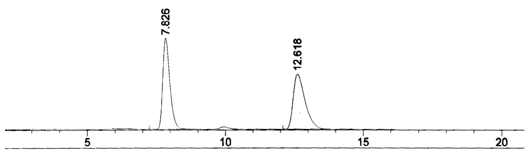

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   2  12.618 PB    0.4540 3.69607e4  1234.97705  50.1666
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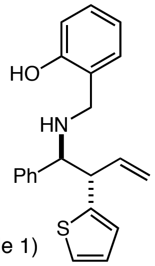
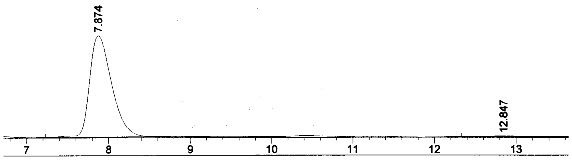


8 (Table 1)



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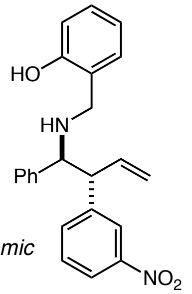
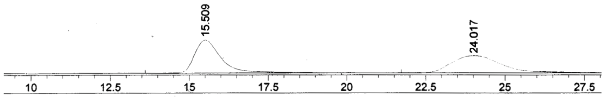
   1   7.874 VB    0.2890 6.01129e4  3201.10596  98.4348
   2  12.847 VP    0.4798  955.87213   30.69340   1.5652
```

9: Chiralpak AD-H, 90/10 Hexane/*i*-PrOH, 1.0mL/min, 220 nm.

Racemic





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   1  15.509 VB    0.9008 2.50505e4  422.84769  49.7486
   2  24.017 PPA   1.8161 2.53037e4  218.64476  50.2514
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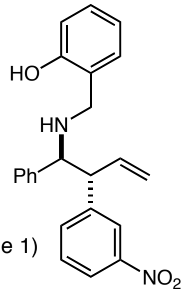
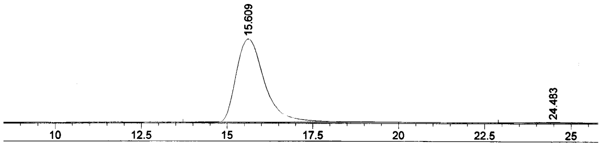
9 (Table 1)





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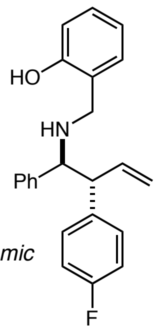
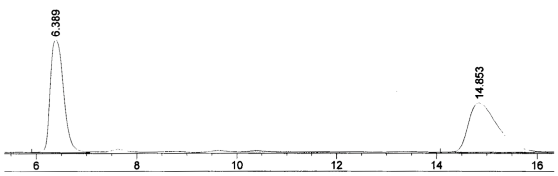
----|-------|----|-------|----------|----------|--------|
   1  15.609 VB    0.8924 6.31830e4 1079.73303  98.8427
   2  24.483 PV    1.5092  739.79907    7.91959   1.1573
```

10: Chiralpak AD-H, 90/10 Hexane/*i*-PrOH, 1.0mL/min, 220 nm.

Racemic





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----|-------|----|-------|----------|----------|--------|
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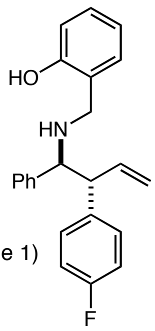
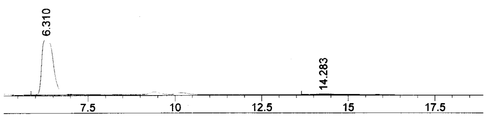
10 (Table 1)





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----|-------|----|-------|----------|----------|--------|
   1   6.310 VP    0.3700 6.39028e4 2811.47729  98.0750
   2  14.283 PV    0.5522 1254.29919   34.50867   1.9250
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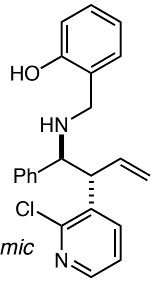
11: Chiralpak AD-H, 85/15 Hexane/*i*-PrOH, 1.0mL/min, 220 nm.



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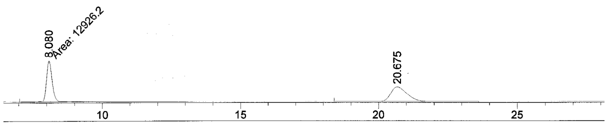

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----|-------|----|-------|----------|----------|--------|
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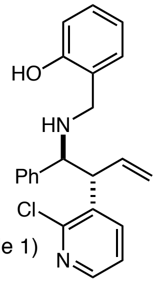
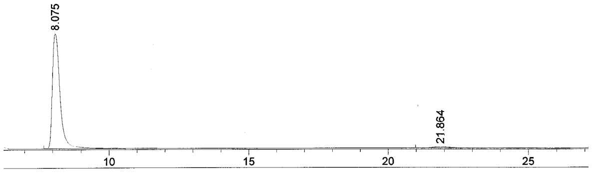
  2  20.675 VP     0.6322 1.28803e4   312.56812  49.9109
```



11 (Table 1)



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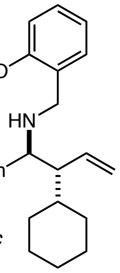
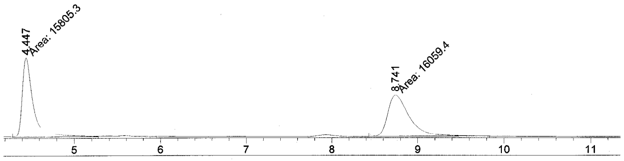
----|-------|----|-------|----------|----------|--------|
  1   8.075 MM     0.3193 4.87771e4  2545.98804  97.3735
  2  21.864 MM     0.7633 1315.69995   28.72978   2.6265
```

12: Chiralpak AD-H, 90/10 Hexane/*i*-PrOH, 1.0mL/min, 220 nm.



Racemic



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----|-------|----|-------|----------|----------|--------|
  1   4.447 MM     0.1489 1.58053e4  1768.96899  49.6013
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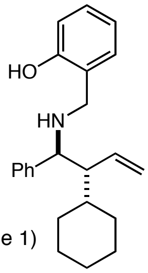
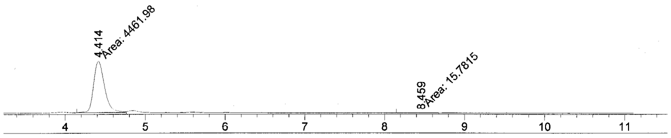


12 (Table 1)



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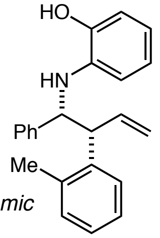
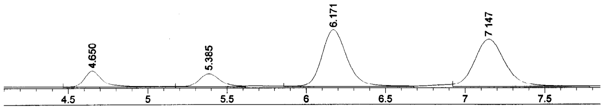
----|-------|----|-------|----------|----------|--------|
  1   4.414 MM     0.1575 4461.98389  472.22510  99.6476
  2   8.459 MM     0.3315   15.78150 7.93407e-1   0.3524
```

13: Chiralpak AD-H, 85/15 Hexane/*i*-PrOH, 1.0mL/min, 254 nm.



Racemic



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----|-------|----|-------|----------|----------|--------|
   1   4.650 VV     0.1264 2741.22534  328.67834   8.7797
   2   5.385 VV     0.1420 2492.95215  271.65445   7.9845
   3   6.171 VV     0.1706 1.29676e4  1165.15613  41.5332
   4   7.147 MM     0.2225 1.30205e4   975.46844  41.7026
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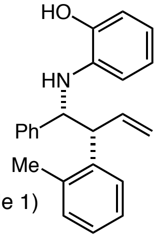
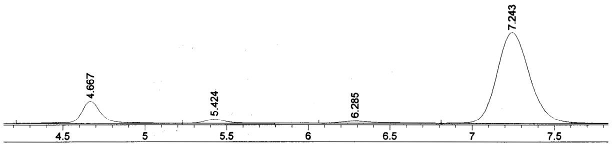


13 (Table 1)



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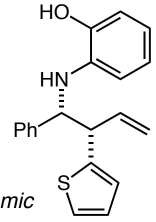
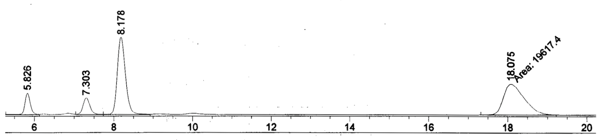
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   4.667 VV     0.1346 3963.90283  438.47693  12.9257
   2   5.424 VV     0.1558  826.37170   79.75767   2.6947
   3   6.285 VV     0.2410  789.13458   45.97749   2.5733
   4   7.243 VB     0.2135 2.50873e4  1816.51123  81.8063
```

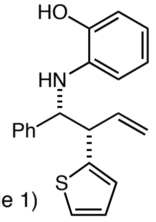
14: Chiralpak AD-H, 85/15 Hexane/*i*-PrOH, 1.0mL/min, 254 nm.



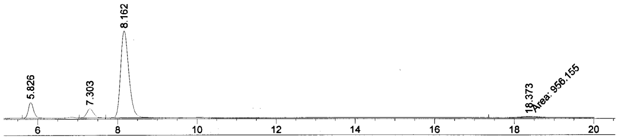
Racemic



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   5.826 VV     0.1487 3664.08008  375.63998   7.9172
   2   7.303 VV     0.1920 3620.75952  290.49191   7.8236
   3   8.178 VV     0.2198 1.93776e4  1350.33948  41.8706
   4  18.075 MM     0.6119 1.96174e4   534.32648  42.3886
```



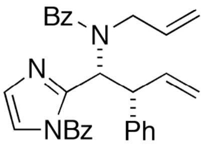
14 (Table 1)



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   5.826 VV     0.1432 3563.91992  384.05222   9.4531
   2   7.303 VV     0.1878 2788.78906  230.39818   7.3971
   3   8.162 VB     0.2209 3.03922e4  2104.15283  80.6136
   4  18.373 MM     0.5958  956.15460   26.74908   2.5361
```

15: The assay for this compound has previously been described in detail.[2]

23 (bis-benzamide): Chiralpak AD-H column, 15% EtOH/hexanes, 1.0 mL/min, 254 nm.



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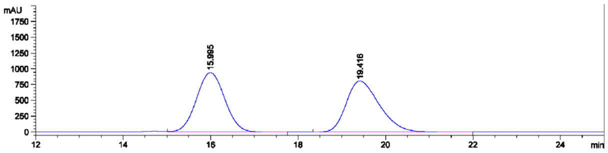
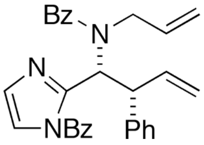
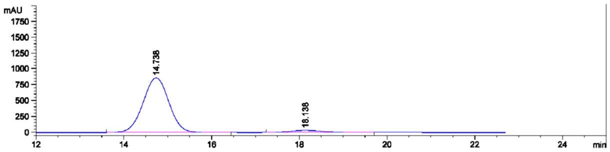


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  15.995 VB    0.7092 4.23141e4   944.24213  50.0372
  2  19.416 BB    0.8112 4.22512e4   803.94843  49.9628
```



Enantioenriched Product



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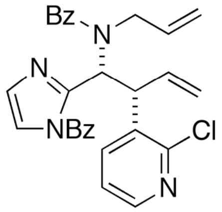
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------
  1  14.738 BB    0.6367 3.47797e4   856.69025  95.8791
  2  18.138 BB    0.7481 1494.84314   31.04731   4.1209
```

24 (bis-benzamide): Chiralpak AD-H column, 20% EtOH/hexanes, 1.0 mL/min, 254nm.



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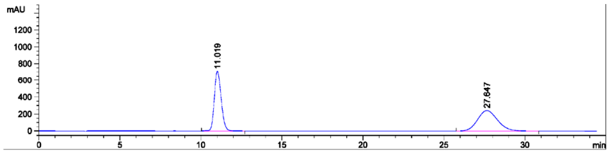

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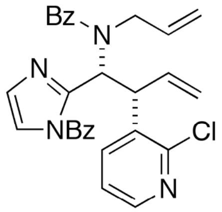
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  11.019 BB    0.4570 2.07255e4   710.03772  49.9563
  2  27.647 BB    1.3276 2.07618e4   241.87486  50.0437
```



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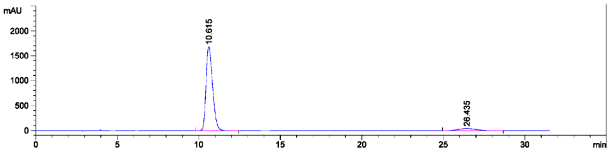
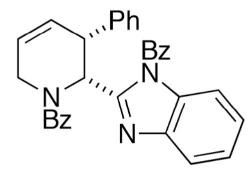


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  10.615 BB    0.4266 4.63599e4  1680.81567  93.7105
  2  26.435 BP    1.1931 3111.52661   40.77681   6.2895
```

26 (bis-benzamide): Chiralpak AD-H column, 7% IPA/hexanes, 1.0 mL/min, 254 nm.



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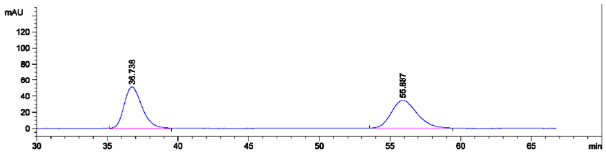
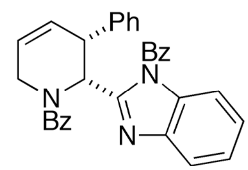
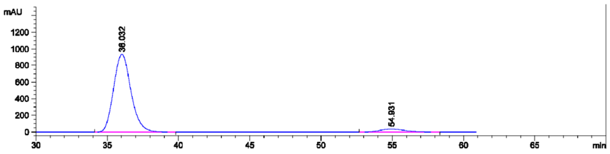


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU    *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  36.738 BB    1.3349 4486.86279   51.30058  50.4642
   2  55.887 BB    1.9386 4404.32178   34.34716  49.5358
```



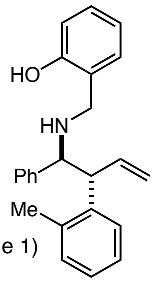
Enantioenriched Product



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU    *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  36.032 BB    1.3132 7.92808e4  937.07159  94.5489
   2  54.931 BB    1.9592 4570.87061  36.27749   5.4511
```

^{1}H NMR Spectra.

The ^{1}H NMR spectra of compounds **5**, **6**, and **15** have previously been published.[2]



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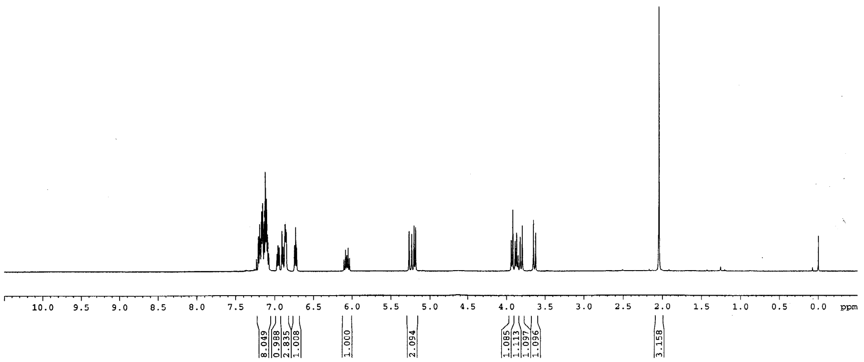

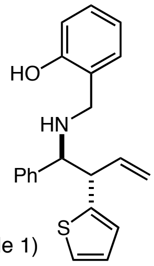

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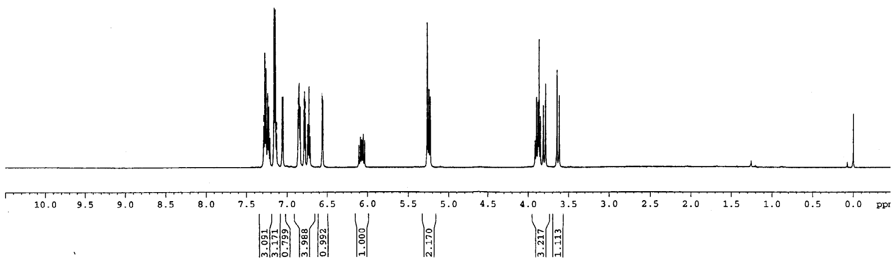

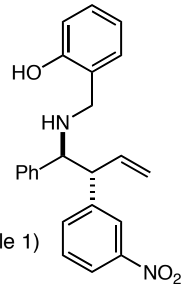

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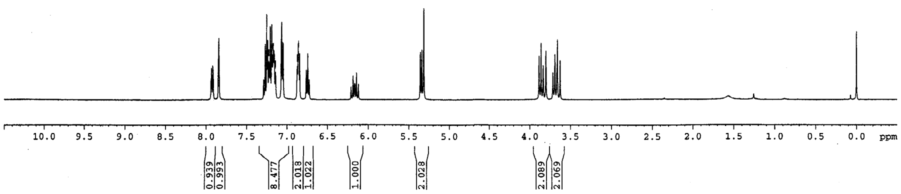

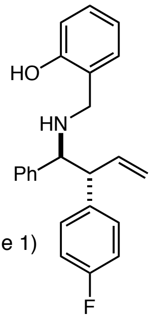

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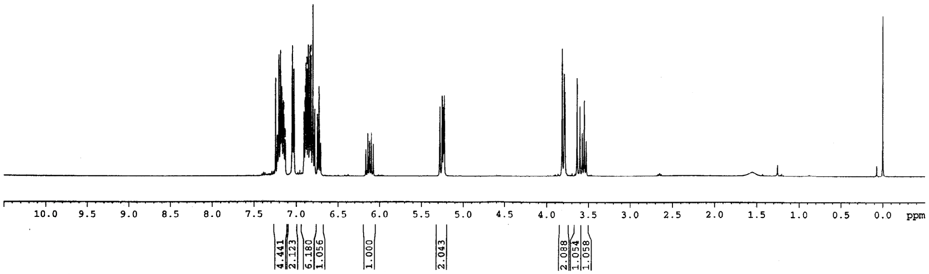

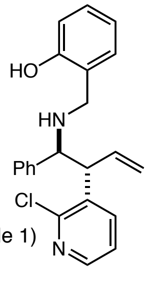

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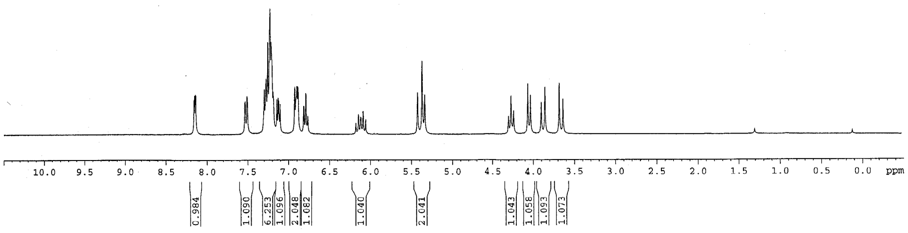

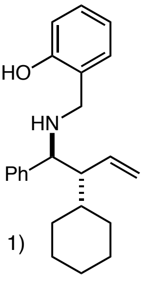

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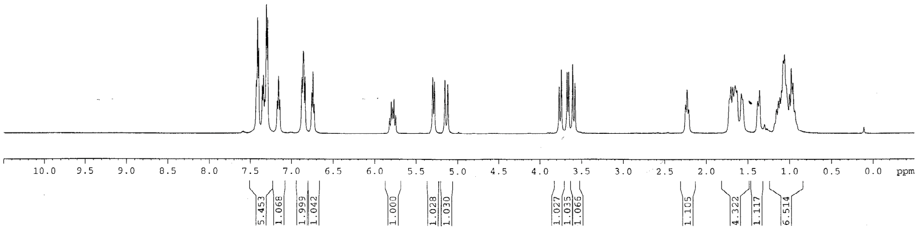

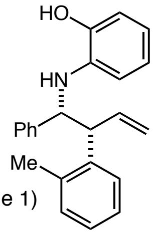

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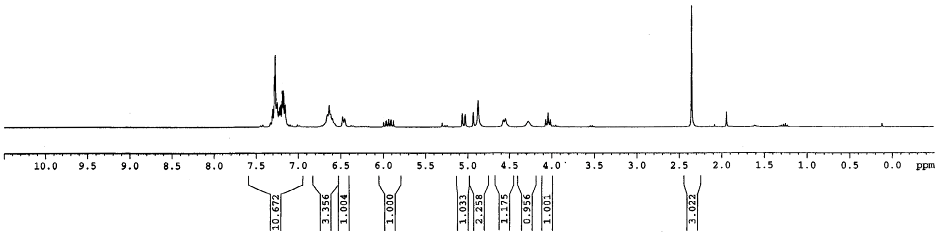

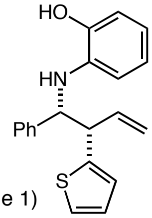

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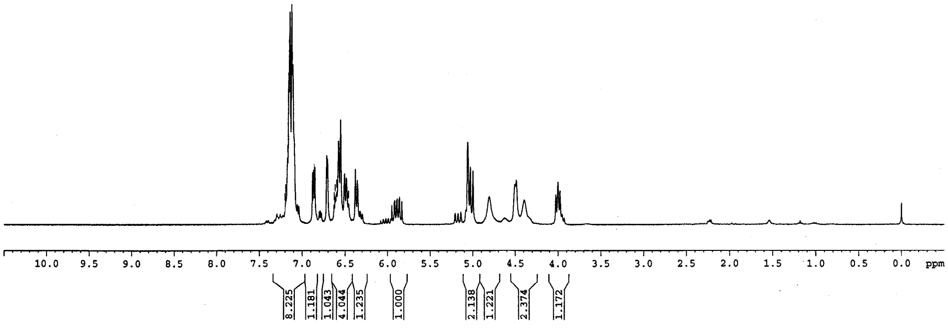
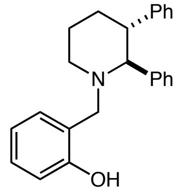
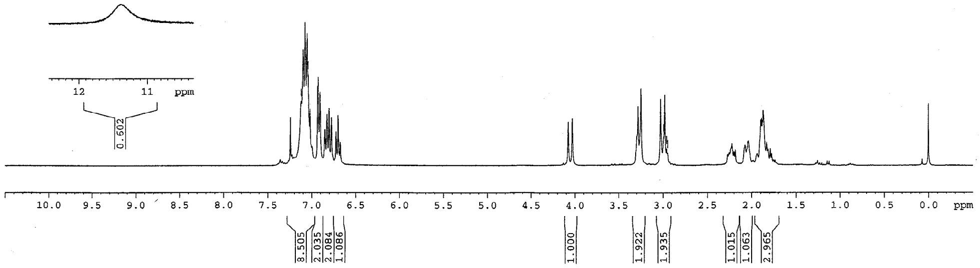
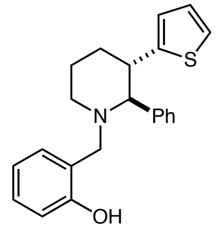




16 (Scheme 3)





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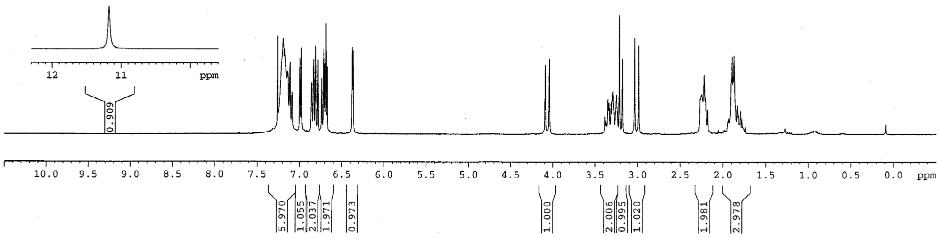

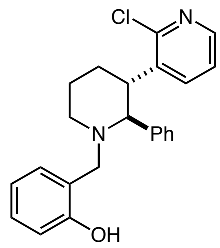

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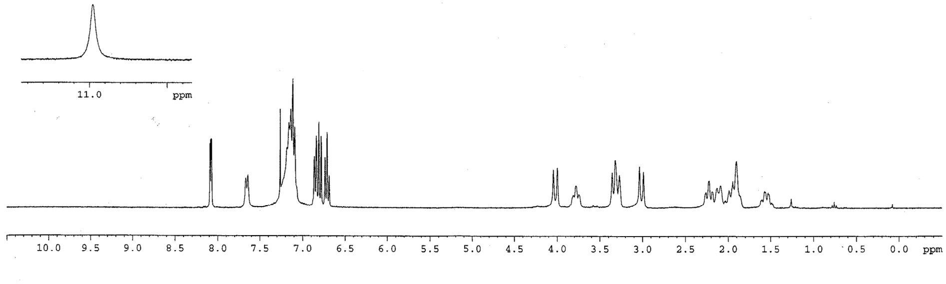

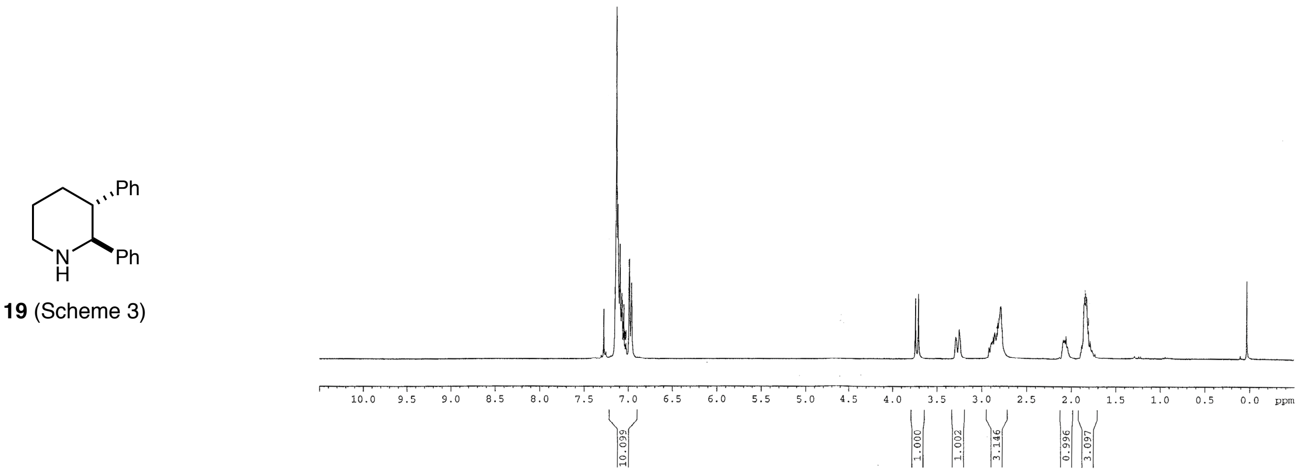

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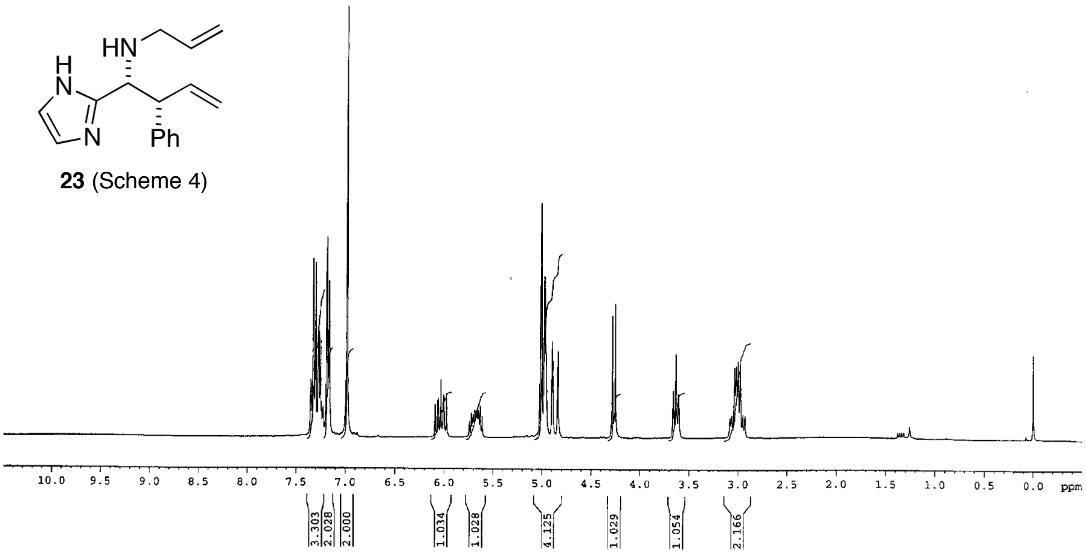
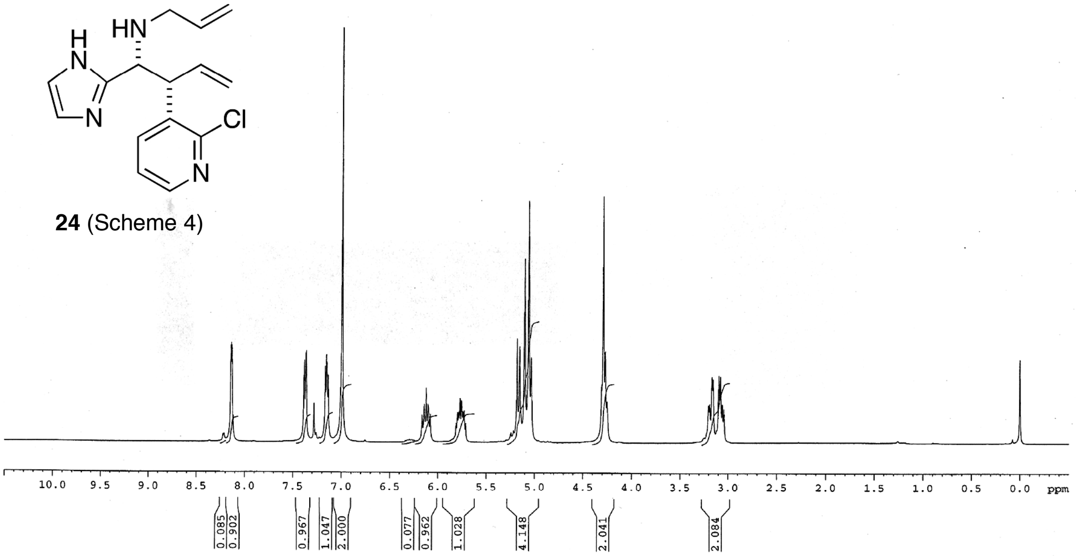
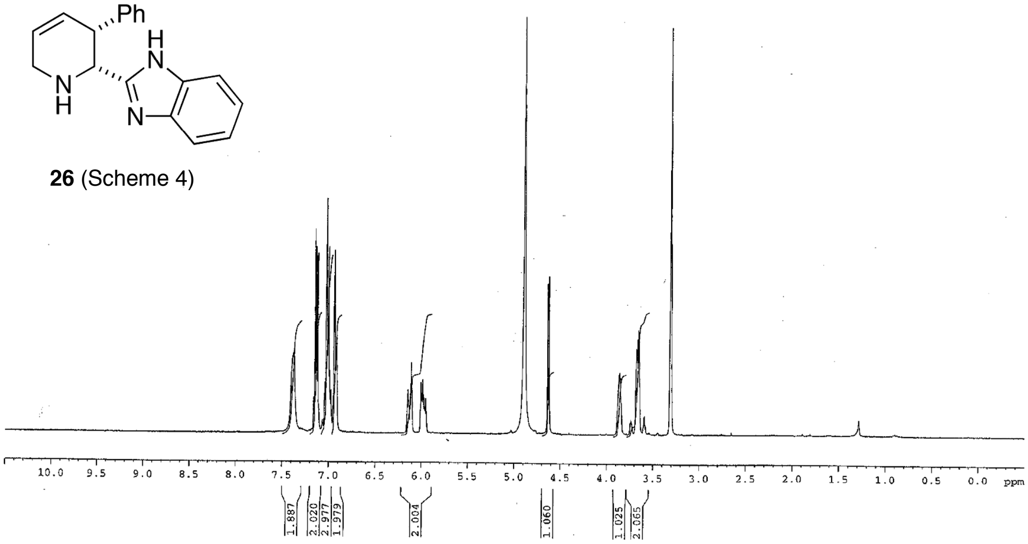


23 (Scheme 4)



24 (Scheme 4)



26 (Scheme 4)