CHAPTER II

EXPERIMENTAL

2.1 General

The weight of all chemical substances was determined on a Mettler AE200 electrical balance. Melting points were recorded on an Electrothermal 9100 melting point apparatus. Evaporation of solvents was carried out on a Büchi Rotavapor R-114 equipped with a Büchi B-480 Waterbath and a water aspirator. The progress of the reactions was followed by Thin Layer Chromatography (TLC) performed on Merck D.C. silica gel 60 F_{254} 0.2 mm precoated aluminium plates and visualized using either UV light (254 nm), ninhydrin, or potassium permanganate reagents. Flash column chromatography was performed on Merck 230-400 mesh silica gel using a medium pressure of 2–3 atm provided by a domestic air-pump.

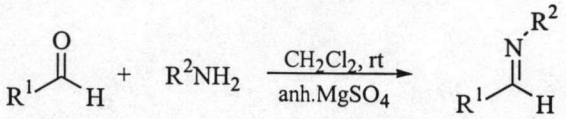
Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ACF200 spectrometer operating at 200 MHz (^{1}H) and 50 MHz (^{13}C) in $CDCl_3$ (unless otherwise stated). Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane using the residual protonated solvent signal as a reference. Coupling constants (J) are for proton-proton coupling unless otherwise noted and are reported in Hertz (Hz).

Optical rotations were measured in a Bellingham + Stanley Ltd. ADP220 polarimeter. The ESITOF mass spectra were obtained from a Micromass LCT mass spectrometer.

2.2 Materials

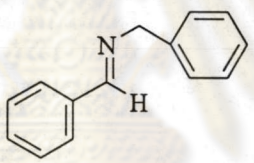
Indium powder > 99.99 % containing 1.2 % Mg was purchased from Aldrich Chemicals Co., Ltd. and *R*(-)-α-phenylglycinol (> 99 % *ee*) was purchased from Fluka. All other chemicals were purchased from Fluka, Merck or Aldrich Chemicals Co., Ltd. and were used as received without further purification. Commercial grade solvents for column chromatography were distilled before use. Solvents for reactions were AR grade and used without further purification.

2.3 General procedure for the preparation of imines



To a 25 mL round bottom flask was added the amine (1 mmol) and 5 mL of dichloromethane, followed by addition of the aldehyde (1 mmol) and anhydrous magnesium sulfate (10 mg) at room temperature. After leaving overnight, the magnesium sulfate was removed by filtration. The filter cake was washed with dichloromethane, the filtrate was collected and the solvent was removed *in vacuo* to obtain the desired product which was used for the next step without further purification.

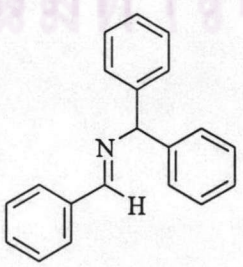
2.3.1 *N*-Benzylidenebenzylamine



I-1

Colorless oil, 94.7 % yield (1 mmol scale); ^{1}H-NMR ($CDCl_3$, 200 MHz); δ 4.87 (2H, s, C<u>H</u>$_2$Ph), 7.38 (8H, m, aromatic C<u>H</u>), 7.83 (2H, m, aromatic C<u>H</u>), 8.41 (1H, s, <u>H</u>C=N); ^{13}C-NMR ($CDCl_3$, 50 MHz); δ 65.1 (C<u>H</u>$_2$Ph), 127.1, 128.0, 128.4, 128.6, 128.7, 130.8, 136.2, 139.4 (aromatic <u>C</u>H), 162.0 (H<u>C</u>=N)

2.3.2 *N*-Benzylidene diphenylmethylamine

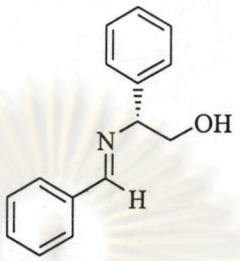


I-5

Colorless oil, 95.7 % yield (1 mmol scale); ^{1}H-NMR ($CDCl_3$, 200 MHz); δ 5.64 (1H, s, C<u>H</u>Ph$_2$), 7.30 (13H, m, Ar), 7.86 (2H, m, Ar), 8.46 (1H, s, <u>H</u>C=N);

^{13}C-NMR ($CDCl_3$, 50 MHz); δ 78.0 (C<u>H</u>Ph_2), 127.1, 127.7, 128.5, 128.6, 130.8, 136.3, 143.9 (Ar), 160.9 (H<u>C</u>=N)

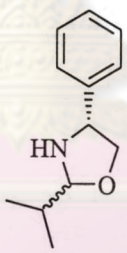
2.3.3 *N*-benzylidene-(*R*)-2-amino-1-phenylethanol



I-19

Colorless oil, 95 % yield (1 mmol scale); ^{1}H-NMR ($CDCl_3$, 200 MHz); δ 3.93 (2H, m, C<u>H</u>$_2$OH), 4.50 (1H, m, PhC<u>H</u>CH$_2$OH), 7.24-7.89 (10H, m, aromatic C<u>H</u>), 8.36 (1H, s, <u>H</u>C=N)

2.3.4 2-Isopropyl-4-(*R*)-phenyloxazolidine

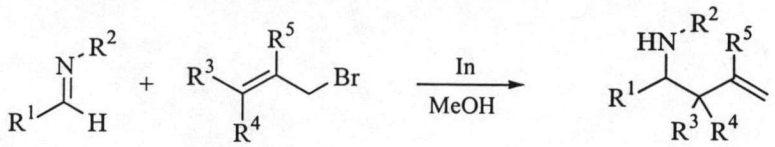


I-31

Colorless oil, 100 % yield (1 mmol scale); ^{1}H-NMR ($CDCl_3$, 200 MHz); δ 0.99 (6H, m, (C<u>H</u>$_3$)$_2$CH), 1.85 (1H, m, (CH$_3$)$_2$C<u>H</u>), 2.68 (1H, br s, N<u>H</u>), 3.55 (1H, m, 1×C<u>H</u>$_2$OH), 4.08 (1H, t *J*=7.6 Hz, 1×C<u>H</u>$_2$OH), 4.20 (1H, t *J*=7.6 Hz, PhC<u>H</u>CH$_2$OH), 4.26 (1H, d *J*=9.5 Hz, ^{i}PrC<u>H</u>), 7.20-7.30 (5H, m, aromatic C<u>H</u>)

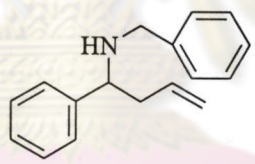
Other imines derived from phenylglycinol were used without characterization.

2.4 General procedure for the allylation of imines



To a mixture of the imine (1.0 mmol) and indium powder (288 mg, 2.0 mmol) in an appropriate alcoholic solvent (5 mL) was added allyl bromide (3.0 mmol). The reaction was stirred vigorously at room temperature until all the metal had dissolved (30 min - 2 h), at which time TLC indicated complete reaction. The reaction mixture was diluted with 10 % aqueous $NaHCO_3$ and extracted with ethyl acetate (10 mL x 3). The combined organic extracts were dried ($MgSO_4$), evaporated and the residue was purified by flash column chromatography on silica gel using hexane-ethylacetate as eluent.

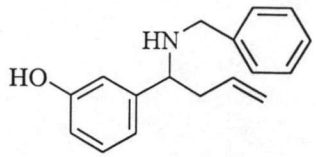
2.4.1 *N*-benzyl-1-phenylbut-3-enamine



II-1

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a yellow oil 0.17 g, 72 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.80 (1H, br s, NH), 2.42 (2H, m, CH_2 allyl), 3.50 (1H, d *J*=13.3, CH_aH_bPh), 3.65 (2H, m, CH_aH_bPh and Ar-CH), 5.01 (2H, m, $CH=CH_2$), 5.70 (1H, m, $CH=CH_2$), 7.30 (m, 10 H, aromatic CH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 43.0 (CH_2 allyl), 51.4 (CH_2Ph), 61.5 (ArCH), 117.5 ($CH=CH_2$), 126.8, 127.0, 127.3, 128.1, 128.3, 128.4, 135.4 ($CH=CH_2$), 140.5, 143.7; LRMS (ESI+) *m/z* 238.2 ($M{\cdot}H^+$)

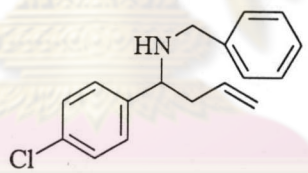
2.4.2 *N*-benzyl-1-(3′-hydroxyphenyl)but-3-enamine



II-2

Purified by flash column chromatography (10 % ethyl acetate-hexane) to give a yellow oil 0.17 g, 66 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.48 (2H, m, C$\underline{H}_2$ allyl), 3.64 (1H, m, C$\underline{H}_a$H$_b$Ph), 3.68 (2H, m, CH$_a\underline{H}_b$Ph and ArC$\underline{H}$), 5.06 (2H, m, CH=C$\underline{H}_2$), 5.66 (1H, m, C$\underline{H}$=CH$_2$), 6.82 (2H, m, ArC$_{2'}\underline{H}$ and ArC$_{4'}$C$\underline{H}$), 7.25 (10H, m, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 42.1 (C$\underline{H}_2$ allyl), 51.1 (C$\underline{H}_2$Ph), 61.5 (ArC$\underline{H}$), 114.4, 115.2, 118.1, 119.7 (CH=C$\underline{H}_2$), 127.3, 128.6, 129.8, 135.0 (C$\underline{H}$=CH$_2$), 139.2, 144.1, 156; LRMS (ESI+) *m/z* 254.2 $(M{\cdot}H)^+$

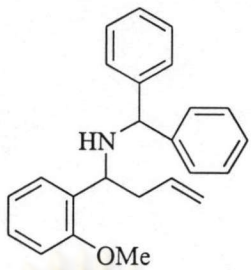
2.4.3 *N*-benzyl-1-(4′-cholrophenyl)but-3-enamine



II-3

Purified by flash column chromatography (10 % ethyl acetate-hexane) to give a yellow oil 0.19 g, 69 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.88 (1H, br s, N$\underline{H}$), 2.43 (2H, m, C$\underline{H}_2$ allyl), 3.56 (1H, d, *J*=13.3, C$\underline{H}_a$H$_b$Ph), 3.73 (2H, m, CH$_a\underline{H}_b$Ph and ArC$\underline{H}$), 5.15 (2H, m, CH=C$\underline{H}_2$), 5.73 (1H, m, C$\underline{H}$=CH$_2$), 7.36 (m, 9H, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 43.2 (C$\underline{H}_2$ allyl), 51.5 (C$\underline{H}_2$Ph), 61.0 (ArC$\underline{H}$CH$_2$), 118.0 (CH=C$\underline{H}_2$), 127.0, 128.2, 128.5, 128.7, 128.8, 132.7, 135.1 (C$\underline{H}$=CH$_2$), 140.5, 142.5; HRMS (ESI+) calcd for $C_{17}H_{18}ClN{\cdot}H^+$ 271.1128, found *m/z* 272.1207 $(M{\cdot}H)^+$

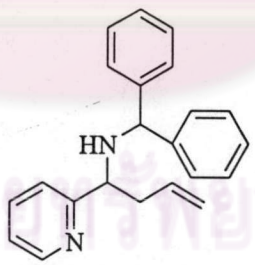
2.4.4 *N*-diphenylmethyl-1-(2′-methoxyphenyl)but-3-enamine



II-6

Purified by flash column chromatography (10 % ethyl acetate-hexane) to give a yellow oil 0.25 g, 72 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.35 (1H, br s, NH), 2.62 (2H, t *J*=7.0 Hz, CH_2 allyl), 3.76 (3H, s, OCH_3), 3.99 (1H, t *J*=7.0 Hz, ArCH), 4.73 (1H, s, $CHPh_2$), 5.09 (1H, m, $CH=CH_2$), 5.85 (1H, m, $CH=CH_2$), 7.02 (2H, 2×d *J*=7.4, 19.1, $ArC_{3'}H$ and $ArC_{6'}H$), 7.33 (12 H, m, aromatic CH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 40.9 ($CH_2CH=CH_2$), 55.2 (ArCH), 55.8 (CH_3O), 64.0 ($CHPh_2$), 110.8, 116.5 ($CH=CH_2$), 120.6, 126.8, 126.9, 127.5, 128.0, 128.4, 128.8, 131.4, 136.6 ($CH=CH_2$), 143.9, 145.2, 157.8

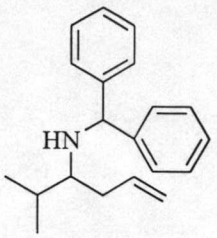
2.4.5 *N*-diphenylmethyl-1-(2′-pyridyl)but-3-enamine



II-7

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a yellow oil 0.25 g, 79 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.56 (3H, t *J*=9.6 Hz, CH_2 allyl and NH), 3.75 (1H, t *J*=6.8 Hz, ArCH), 4.62 (1H, s, $CHPh_2$), 5.04 (2H, 2×d *J*=16.8, 6.3 Hz, $CH=CH_2$), 5.73 (1H, m, $CH=CH_2$), 7.29 (m, 13H, Ph-CH and Py-CH), 8.62 (1H, m, Py-$C_{6'}$H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 41.5 (CH_2 allyl), 60.8 (ArCH), 64.2 (Ph_2CH), 117.2 ($CH=CH_2$), 122.0, 122.6, 126.9, 127.1, 127.4, 127.9, 128.3, 128.5, 135.5 ($CH=CH_2$), 136.1, 143.4, 144.6, 149.7, 163.1; LRMS (ESI+) *m/z* 315.2 $(M{\cdot}H)^+$

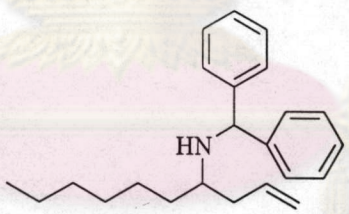
2.4.6 *N*-diphenylmethyl-1-isopropylbut-3-enamine



II-8

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a yellow oil 0.17 g, 61 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.99 (6H, d *J*=7.8 Hz, $(C\underline{H}_3)_2CH$), 1.55 (1H, s, N<u>H</u>), 1.93 (1H, m, $(CH_3)_2C\underline{H}$), 2.27 (2H, m, ^{i}PrCHC<u>H</u>$_2$), 2.45 (1H, m, ^{i}PrC<u>H</u>), 5.07 (s, 1H, C<u>H</u>Ph$_2$), 5.18 (2H, m, CH=C<u>H</u>$_2$), 5.85 (1H, m, C<u>H</u>=CH$_2$), 7.35 (m, 10 H, CH<u>Ph</u>$_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 18.4 and 18.8 [$(\underline{C}H_3)_2CH$], 29.9 [$(CH_3)_2\underline{C}H$], 34.5 ($\underline{C}H_2CH=CH_2$), 59.0 (^{i}PrC<u>H</u>), 64.2 (<u>C</u>HPh$_2$), 116.9 (CH=<u>C</u>H$_2$), 126.9, 127.0, 127.6, 127.8, 128.4, 128.5, 136.5 (<u>C</u>H=CH$_2$), 144.6, 144.9; LRMS (ESI+) *m/z* 280.2 $(M{\cdot}H)^+$

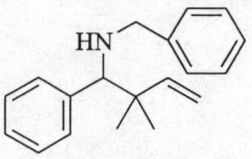
2.4.7 *N*-diphenylmethyl-1-hexylbut-3-enamine



II-9

Purified by flash column chromatography (2 % ethyl acetate-hexane) to give a yellow oil 0.06 g, 20 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.89 [3H, m, $C\underline{H}_3(CH_2)_6$], 1.25 [12H, s, $CH_3(C\underline{H}_2)_6$], 1.40 (1H, s, N<u>H</u>), 2.27 (2H, m, C<u>H</u>$_2$ allyl), 2.62 (1H, m, $CH_3(CH_2)_6C\underline{H}$), 5.05 (1H, d *J*=11.6 Hz, CH=C<u>H</u>$_a$H$_b$), 5.10 (1H, d *J*=4.8 Hz, CH=CH$_a$<u>H</u>$_b$), 5.75 (1H, m, C<u>H</u>=CH$_a$H$_b$), 7.25 (12 H, m, CH<u>Ph</u>$_2$); ^{13}C-NMR (50 MHz, $CDCl_3$)δ 14.2 ($\underline{C}H_3CH_2CH_2CH_2CH_2CH_2CH$), 22.7 ($CH_3\underline{C}H_2CH_2CH_2CH_2CH_2CH$), 25.6 ($CH_3CH_2\underline{C}H_2CH_2CH_2CH_2CH$), 29.3 ($CH_3CH_2CH_2\underline{C}H_2CH_2CH_2CH$), 29.7 ($CH_3CH_2CH_2CH_2\underline{C}H_2CH_2CH$), 31.9 ($CH_3CH_2CH_2CH_2CH_2\underline{C}H_2CH$), 33.4 ($\underline{C}H_2CH=CH_2$), 54.3 [$(C_6H_{13})\underline{C}H$], 64.1 (<u>C</u>HPh$_2$), 117.5 (CH=<u>C</u>H$_2$), 127.2, 127.7, 127.8, 128.5, 135.4 (<u>C</u>H=CH$_2$)

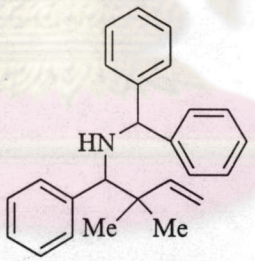
2.4.8 *N*-benzyl-1-phenyl-2,2-dimethylbut-3-enamine



II-10

Purified by flash column chromatography (4 % ethyl acetate-hexane) to give a yellow oil 0.08 g, 30 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.91 [3H, s, 1×($C\underline{H}_3$)$_2$CCH], 0.95 [3H, s, 1×($C\underline{H}_3$)$_2$CCH], 3.36 (2H, d, m, $C\underline{H}_aH_b$Ph and PhC$\underline{H}$), 3.63 (2H, d *J*=13.5 Hz, $CH_a\underline{H}_b$Ph), 5.06 (2H, 2×d *J*=17.3, 10.9 Hz, CH=C$\underline{H}_2$), 5.82 (1H, dd *J*=17.3, 10.9 Hz, C$\underline{H}$=CH_2), 7.27 (10H, m, 2×Ph); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 20.8, 26.6 (2×CH_3), 41.3 $(CH_3)_2\underline{C}$, 51.7 ($\underline{C}H_2$Ph), 113.0 (CH=$\underline{C}H_2$), 126.7, 127.0, 127.5, 128.1, 128.2, 129.5 ($\underline{C}$H=CH_2), 140.4, 141.0, 146.6; LRMS (ESI+) *m/z* 266.2 $(M{\cdot}H)^+$

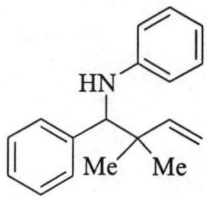
2.4.9 *N*-diphenylmethyl-1-phenyl-2,2-dimethylbut-3-enamine



II-11

Purified by flash column chromatography (4 % ethyl acetate-hexane) to give a yellow oil 0.10 g, 30 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.03 [3H, s, 1×($C\underline{H}_3$)$_2$C], 1.08 [3H, s, 1×($C\underline{H}_3$)$_2$C], 2.18 (1H, br s, N$\underline{H}$), 3.35 (1H, s, ArC$\underline{H}$), 4.54 (1H, s, C$\underline{H}$Ph$_2$), 5.12 (2H, 2×d *J*=10.6, 17.3 Hz, CH=C$\underline{H}_2$), 5.85 (1H, dd *J*=10.9, 17.3 Hz, C$\underline{H}$=CH_2), 7.35 (15 H, m, CH$\underline{\text{Ph}}_2$ and $\underline{\text{Ar}}$-CH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 22.5 [1×($C\underline{H}_3$)$_2$C], 26.3 [1×($C\underline{H}_3$)$_2$C], 41.3 [$\underline{C}(CH_3)_2$], 63.4 ($\underline{C}$HPh$_2$), 67.8 (Ar$\underline{C}$H), 113.2 (CH=$\underline{C}H_2$), 126.8, 127.0, 127.4, 127.7, 128.1, 128.3, 128.4, 128.9, 129.4, 130.2 ($\underline{C}$H=CH_2), 140.5, 143.6, 145.0, 145.2, 146.2

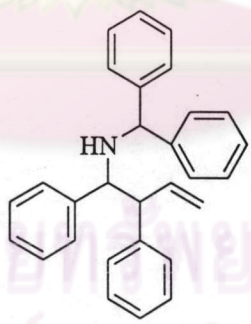
2.4.10 *N*-phenyl-1-phenyl-2,2-dimethylbut-3-enamine



II-12

Purified by flash column chromatography (0.5 % ethyl acetate-hexane) to give a yellow oil 0.14 g, 55 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.03 [3H, s, 1×($C\underline{H}_3$)$_2$CCH], 1.19 [3H, s, 1×($C\underline{H}_3$)$_2$C], 4.11 (1H, s, ArC$\underline{H}$), 4.28 (1H, br s, N$\underline{H}$), 5.22 (2H, 2×d *J*=17.0, 11.1 Hz, CH=C$\underline{H}_2$), 5.92 (1H, dd *J*=11.1, 17.0 Hz, C$\underline{H}$=CH_aH_b), 6.50 (2H, d *J*=7.9 Hz, PhNH *ortho* C$\underline{H}$), 6.67 (1H, t, PhNH *para* C$\underline{H}$), 7.08 (2H, t, PhNH *meta* C$\underline{H}$), 7.30 (6H, m, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 23.1 [1×($C\underline{H}_3$)$_2$C], 25.9 [1×($C\underline{H}_3$)$_2$C], 41.4 [$\underline{C}(CH_3)_2$], 65.9 (Ar$\underline{C}$H), 113.4 ($\underline{C}H=CH_2$), 113.9, 117.1, 127.1, 127.8, 128.7, 128.8, 129.1 (CH=$\underline{C}H_2$), 140.4, 145.1, 147.7; LRMS (ESI+) *m/z* 252.2 $(M{\cdot}H)^+$

2.4.11 *N*-diphenylmethyl-1,2-diphenylbut-3-enamine



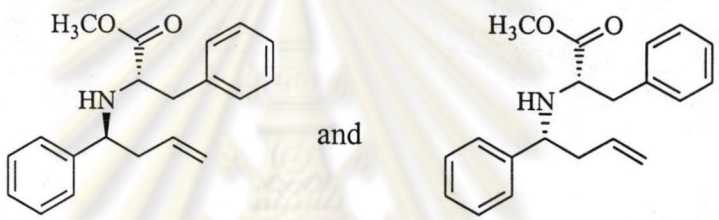
II-13

Purified by flash column chromatography (1 % ethyl acetate-hexane) to give a colourless oil 0.24 g, 62 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds* = 83:17 as determined by ^{1}H-NMR). Major isomer: ^{1}H -NMR (200 MHz, $CDCl_3$) δ 3.71 (1H, t, C$\underline{H}$CH=CH_2), 3.72 (1H, d *J*=9.3 Hz, C$\underline{H}$Ph), 4.47 (1H, s, C$\underline{H}Ph_2$), 4.95 (2H, 2×d *J*=21.0, 10.2 Hz, CH=C$\underline{H}_2$), 5.85 (1H, m, C$\underline{H}$=CH_2), 6.88-7.37 (20 H, m, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 57.7 ($\underline{C}$HPh), 62.8 ($\underline{C}HPh_2$), 64.2

[Ar<u>C</u>HC(CH_3)$_2$], 116.2 (CH=<u>C</u>H_2), 126.6, 126.8, 126.9, 127.3, 127.6, 128.1, 128.2, 128.3, 128.5, 128.6, 139.1 (<u>C</u>H=CH_2), 141.5, 141.9, 142.9, 144.5

Minor isomer: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 3.58 (1H, t, C<u>H</u>CH=CH_2), 3.72 (1H, d *J*=9.3 Hz, C<u>H</u>Ph), 4.68 (1H, s, C<u>H</u>Ph_2), 5.33 (2H, m, CH=C<u>H</u>$_2$), 6.28 (1H, m, C<u>H</u>=CH_2), 6.98-7.46 (20 H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 58.7 (<u>C</u>HPh), 62.8 (<u>C</u>HPh_2), 64.2 [Ar<u>C</u>HC(CH_3)$_2$], 117.2 (CH=<u>C</u>H_2), 126.7, 127.0, 127.1, 127.4, 128.2, 128.3, 128.4, 128.7, 139.2 (<u>C</u>H=CH_2), 141.6, 142.1, 143.1, 144.6

2.4.12 Methyl-2-benzyl-2-(1′-phenylbut-3′-enylamino)acetate (diasteromeric ratio = 75:25)

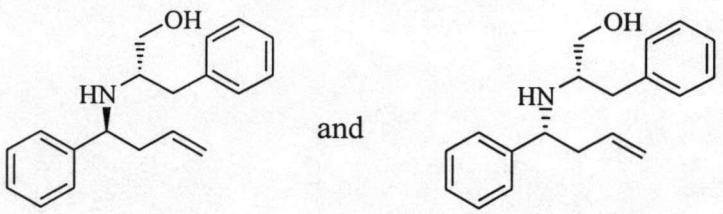


II-15a **II-15b**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give the major isomer (**II-15a**) a yellow oil 0.09 g, 28 % yield (1 mmol scale): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.07 (1H, br s, N<u>H</u>), 2.36 (2H, m, C<u>H</u>$_2$ allyl), 2.88 (2H, m, C<u>H</u>$_2$Ph), 3.31 (1H, t, C<u>H</u>COOMe), 3.63 (3H, s, OC<u>H</u>$_3$), 5.12 (2H, m, CH=C<u>H</u>$_2$), 5.75 (1H, m, C<u>H</u>=CH_2), 7.08-7.28 (m, 10H, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 40.2 (<u>C</u>H_2 allyl), 43.7 (<u>C</u>H_2Ph), 51.5 (O<u>C</u>H_3), 60.0 (Ar<u>C</u>HCH_2), 60.4 (<u>C</u>HCOOMe), 117.8 (CH=<u>C</u>H_2), 126.6, 127.1, 127.3, 128.2, 128.3, 129.4, 135.1, 137.5, 143.2 (<u>C</u>H=CH_2), 174.5 (<u>C</u>OOMe)

The minor isomer (**II-15b**) was determined as a yellow oil 0.03 g, 10 % yield: ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.90 (1H, br s, N<u>H</u>), 2.36 (2H, m, C<u>H</u>$_2$ allyl), 2.93 (2H, m, C<u>H</u>$_2$Ph), 3.39 (3H, s, OC<u>H</u>$_3$), 3.47-3.60 (2H, m, C<u>H</u>COOMe and ArC<u>H</u>), 4.93 (2H, m, CH=C<u>H</u>$_2$), 5.56 (1H, m, C<u>H</u>=CH_2), 7.12-7.34 (m, 10H, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 39.1 (<u>C</u>H_2 allyl), 42.2 (<u>C</u>H_2Ph), 51.5 (O<u>C</u>H_3), 61.2 (Ar<u>C</u>HCH_2), 61.6 (<u>C</u>HCOOMe), 117.5 (CH=<u>C</u>H_2), 117.5, 126.7, 127.3, 127.5, 128.3, 128.4, 129.3, 135.0, 137.2, 143.0 (<u>C</u>H=CH_2), 174.6 (<u>C</u>OOMe)

2.4.13 2-Benzyl-2-(1′-phenylbut-3′-enylamino)ethanol

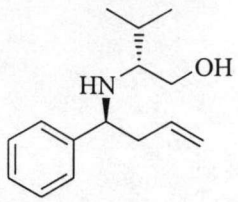


II-16a and **II-16b**

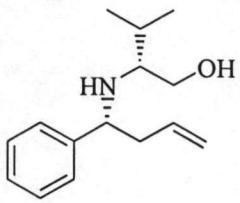
Purified by flash column chromatography (10 % ethyl acetate-hexane) to give a yellow oil 0.11 g, 40 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds* = 67:33 as determined by ^{1}H-NMR). Major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.38 (2H, m, C$\underline{H}_2$ allyl), 2.76 (2H, m, C$\underline{H}_2$Ph), 3.33 (1H, m, 1×C$\underline{H}_2$OH), 3.67 (1H, m, 1×C$\underline{H}_2$OH), 3.75 (1H, dd *J*=11.9, 5.2 Hz, ArC$\underline{H}$), 5.04 (1H, 2×d *J*=17.7, 10.4 Hz, CH=C$\underline{H}_2$), 5.65 (1H, m, C$\underline{H}$=CH$_2$), 6.94-7.38 (10H, m, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 38.9 (C$\underline{H}_2$ allyl), 42.7 (C$\underline{H}_2$Ph), 56.5, 59.5, 61.7 (Ar$\underline{C}$H, Ph$\underline{C}$H$_2$CH and PhCH$\underline{C}$H$_2$OH), 117.4 (CH=$\underline{C}$H$_2$), 126.4, 126.8, 127.1, 128.5, 129.3, 135.2, 138.5 ($\underline{C}$H=CH$_2$)

Minor isomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.38 (2H, m, C$\underline{H}_2$ allyl), 2.87 (2H, dd *J*=13.1, 6.1 Hz, C$\underline{H}_2$Ph), 3.22 (1H, dd *J*=10.7, 6.4 Hz, 1×C$\underline{H}_2$OH), 3.67 (1H, m, 1×C$\underline{H}_2$OH), 3.75 (1H, m, ArC$\underline{H}$), 5.04 (1H, 2×d *J*=17.7, 10.4 Hz, CH=C$\underline{H}_2$), 5.59 (1H, m, C$\underline{H}$=CH$_2$), 6.94-7.38 (10H, m, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 38.0 (C$\underline{H}_2$ allyl), 43.4 (C$\underline{H}_2$Ph), 58.0, 60.2, 63.9 (Ar$\underline{C}$H, Ph$\underline{C}$H$_2$CH and PhCH$\underline{C}$H$_2$OH), 118.0 (CH=$\underline{C}$H$_2$), 126.4, 126.8, 127.1, 128.5, 129.3, 135.2, 138.5 ($\underline{C}$H=CH$_2$)

2.4.14 2-Isopropyl-2-(1′-phenylbut-3′-enylamino)ethanol



and

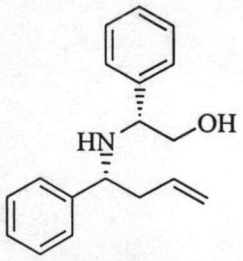


II-17a **II-17b**

Purified by flash column chromatography (10 % ethyl acetate-hexane) to give a yellow oil 0.15 g, 51 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds* = 90:10 as determined by ^{1}NMR). Major isomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.80 (6H, 2×d *J*=7.0 Hz, [$(C\underline{H}_3)_2CH$], 1.66 (1H, m, [$(CH_3)_2C\underline{H}$], 2.24 (1H, m, ^{i}Pr$C\underline{H}$NH), 2.44 (2H, m, $C\underline{H}_2$ allyl), 3.37 (1H, dd *J*=10.8, 4.4 Hz, 1×$C\underline{H}_aH_bOH$), 3.58 (1H, dd *J*=10.9, 4.3 Hz, 1×$CH_a\underline{H}_bOH$), 3.71 (1H, t *J*=6.7 Hz, Ar$C\underline{H}$), 5.00 (2H, 2×d *J*=17.1,9.1 Hz, CH=$C\underline{H}_2$), 5.65 (1H, m, $C\underline{H}$=CH_2), 7.19-7.31 (m, 5H, aromatic $C\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 18.9, 19.4 [$(\underline{C}H_3)_2CH$], 29.4 [$(CH_3)_2\underline{C}H$], 42.7 ($\underline{C}H_2$ allyl), 59.9 (Ar$\underline{C}HCH_2$), 60.1 ($\underline{C}HCH_2OH$), 61.1 ($CH\underline{C}H_2OH$), 117.3 (CH=$\underline{C}H_2$), 127.1, 127.3, 128.4, 135.4 ($\underline{C}H$=CH_2), 143.9

Minor isomer: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.86 (6H, 2×d *J*=7.0 Hz, [$(C\underline{H}_3)_2CH$], 1.89 (1H, m, [$(CH_3)_2C\underline{H}$)], 2.24 (1H, m, ^{i}Pr$C\underline{H}$NH), 2.33 (2H, m, $C\underline{H}_2$ allyl), 3.16 (1H, m, 1×$C\underline{H}_aH_bOH$), 3.30 (1H, dd *J*=10.9, 4.5 Hz, 1×$CH_a\underline{H}_bOH$), 3.76 (1H, dd *J*=8.5, 5.2 Hz, Ar$C\underline{H}$), 5.09 (2H, 2×d *J*=17.7, 9.1 Hz, CH=$C\underline{H}_2$), 5.72 (1H, m, $C\underline{H}$=CH_2), 7.19-7.31 (m, 5H, aromatic $C\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 17.5, 19.4 [$(\underline{C}H_3)_2CH$], 28.2 [$(CH_3)_2\underline{C}H$], 43.6 ($\underline{C}H_2$ allyl), 59.9 (Ar$\underline{C}HCH_2$), 60.1 ($\underline{C}HCH_2OH$), 60.8 ($CH\underline{C}H_2OH$), 118.2 (CH=$\underline{C}H_2$), 127.1, 127.3, 128.4, 135.4 ($\underline{C}H$=CH_2), 143.9

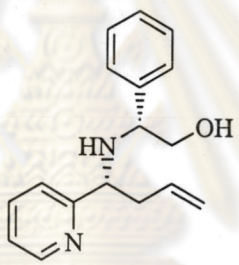
2.4.15 (2*R*)-2-phenyl-2-[(1′*R*)-1′-phenylbut-3′-enylamino]ethanol



II-19

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a colourless oil 0.24 g, 89 % yield (1 mmol scale); $[\alpha]^{23}_D$ = -35.2 (*c* = 1.052, $CHCl_3$), lit[21] $[\alpha]^{29}_D$ = -42.3 (*c* = 4.00, $CHCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.46 (2H, m, NH, CH_2 allyl), 3.53 (1H, dd *J*=10.7, 9.0 Hz, 1×CH_2OH), 3.73 (2H, 2×d *J*=3.4, 4.6 Hz, Ar$CHCH_2$ and 1×CH_2OH), 3.85 (1H, dd *J*=6.9, 4.6 Hz, Ph$CHCH_2OH$), 4.99 (1H, m, $CH=CH_2$), 5.65 (1H, m, $CH=CH_2$), 7.18-7.37 (m, 10H, aromatic CH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 41.3 (CH_2 allyl), 59.8, 61.4, 65.6 (Ar$CHCH_2$, $CHCH_2OH$ and $CHCH_2OH$), 117.5 ($CH=CH_2$), 125.9, 127.2, 127.4, 127.5, 128.4, 128.6, 134.9 ($CH=CH_2$), 141.1, 143.5; LRMS (ESI+) *m/z* 268.2 $(M\cdot H)^+$. Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.86; H, 7.98; N, 5.23 %

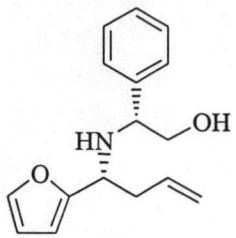
2.4.16 (2*R*)-2-phenyl-2-[(1′*R*)-1-(2″-pyridyl)but-3′-enylamino]ethanol



II-21

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a yellow oil 0.26 g, 98 % yield (1 mmol scale); $[\alpha]^{24}_D$ = -15.2 (*c* = 0.99, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.53 (2H, t, *J*=6.8 Hz, CH_2 allyl), 2.74 (1H, br s, NH), 3.54 (1H, dd *J*=10.6, 7.6 Hz, 1×CH_2OH), 3.75 (3H, m, Py$CHCH_2$, Ph$CHCH_2OH$ and 1×CH_2OH), 5.01 (2H, m, $CH=CH_2$), 5.66 (1H, m, $CH=CH_2$), 7.15 (7H, m, aromatic CH), 7.45 (1H, t *J*=7.9 Hz, Py-C_4H) 8.43 (1H, m, Py-C_6H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 40.5 (CH_2 allyl), 61.3, 62.8, 66.1 (Ar$CHCH_2$, $CHCH_2OH$ and $CHCH_2OH$), 117.6 ($CH=CH_2$), 121.8, 122.3, 127.2, 127.4, 128.3, 128.5, 134.8 ($CH=CH_2$), 136.1, 141.0, 149.0, 162.4; HRMS (ESI+) calcd for $C_{17}H_{20}N_2O\cdot H^+$ 269.1654, found *m/z* 269.1649 $(M\cdot H)^+$. Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44. Found: C, 74.83; H, 7.75; N, 10.36 %

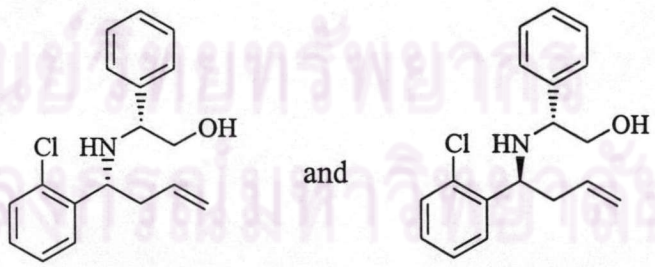
2.4.17 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(2″-furyl)but-3′-enylamino]ethanol



II-22

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a yellow oil 0.20 g, 79 % yield (1 mmol scale); $[\alpha]^{24}_{D}$ = -5.71 (*c* = 1.05, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.54 (2H, m, C<u>H</u>$_2$ allyl), 2.74 (1H, br s, N<u>H</u>), 3.53 (1H, dd *J*=10.8, 7.4 Hz, 1×C<u>H</u>$_2$OH), 3.68 (1H, dd *J*=10.8, 4.5 Hz, 1×C<u>H</u>$_2$OH), 3.84 (2H, m, ArC<u>H</u>, PhC<u>H</u>CH$_2$OH), 5.03 (2H, m, CH=C<u>H</u>$_2$), 5.76 (1H, m, C<u>H</u>=CH$_2$), 6.05 (1H, d *J*=3.1 Hz, furyl C$_3$<u>H</u>), 6.19 (1H, m, furyl C$_4$<u>H</u>), 7.25 (6H, m, aromatic C<u>H</u> and furyl C$_5$<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 38.3 (<u>C</u>H$_2$ allyl), 53.7, 61.8, 66.0 (furyl <u>C</u>HCH$_2$, <u>C</u>HCH$_2$OH and CH<u>C</u>H$_2$OH), 106.5, 109.9, 117.7 (CH=<u>C</u>H$_2$) 127.2, 127.5, 128.5, 134.5 (<u>C</u>H=CH$_2$), 140.8, 141.5 (CH=<u>C</u>H$_2$), 155.9; LRMS (ESI+) *m/z* 258.1 $(M{\cdot}H)^+$. Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.72; H, 7.43; N, 5.45 %

2.4.18 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(2″-chlorophenyl)but-3′-enylamino]ethanol and (2*R*)-2-phenyl-2-[(1′*S*)-1′-(2″-chlorophenyl)but-3′-enylamino]ethanol



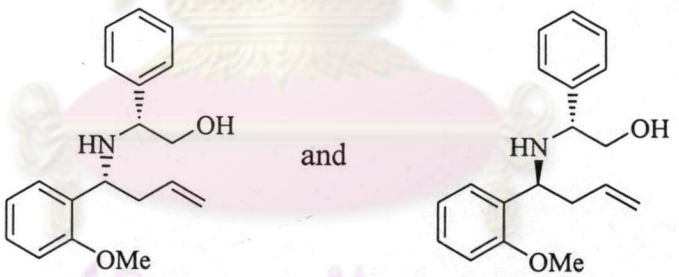
II-23a and **II-23b**

Purified by flash column chromatography (20 % ethyl acetate-hexane) to give a white solid 0.28 g, 94 % yield (1 mmol scale) (inseparable mixture of diastereomer; d.r.= 94:6 as determined by ^{1}H-NMR): (m.p. 67-68 °C); $[\alpha]^{26}_{D}$ = -36.2 (*c* = 1.02, $CHCl_3$). Major isomer (2*R*,1*S*): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.72 (1H, br s, N<u>H</u>),

2.45 (2H, m, C$\underline{H}_2$ allyl), 3.55 (1H, dd J=10.4, 6.1 Hz, 1×C$\underline{H}_2$OH), 3.71 (2H, m, PhC$\underline{H}$CH$_2$OH and 1×C$\underline{H}_2$OH), 4.31 (1H, t J=6.4 Hz, ArC$\underline{H}$), 5.04 (2H, m, CH=C$\underline{H}_2$), 5.71 (1H, m, C$\underline{H}$=CH$_2$), 7.21 (m, 9H, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 40.5 (C$\underline{H}_2$ allyl), 56.3, 62.0, 65.5 (Ar$\underline{C}$HCH$_2$, $\underline{C}$HCH$_2$OH and CH$\underline{C}$H$_2$OH), 117.9 (CH=$\underline{C}$H$_2$), 127.3, 128.4, 129.7, 133.2, 134.5 ($\underline{C}$H=CH$_2$), 140.9, 141.3

Minor isomer (2*R*,1*R*): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.72 (1H, br s, N$\underline{H}$), 2.24 (2H, m, C$\underline{H}_2$ allyl), 3.47 (1H, m, C$\underline{H}$CH$_2$OH), 3.71 (2H, m, PhC$\underline{H}$CH$_2$OH and 1×C$\underline{H}_2$OH), 4.07 (1H, m, ArC$\underline{H}$), 5.04 (2H, m, CH=C$\underline{H}_2$), 5.63 (1H, m, C$\underline{H}$=CH$_2$), 7.21 (m, 9H, aromatc-C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 42.1 (C$\underline{H}_2$ allyl), 56.3, 65.5, 69.6 (Ar$\underline{C}$HCH$_2$, $\underline{C}$HCH$_2$OH and CH$\underline{C}$H$_2$OH), 118.2 (CH=$\underline{C}$H$_2$), 126.8, 128.0, 133.3, 134.5 ($\underline{C}$H=CH$_2$), 134.7, 140.8; HRMS (ESI+) calcd for $C_{18}H_{20}ClNO \cdot H^+$ 302.1312, found *m/z* 302.1311 $(M \cdot H)^+$. Anal. Calcd for $C_{18}H_{20}ClNO$: C, 71.63; H, 6.68; N, 4.64. Found: C, 71.46; H, 6.88; N, 4.64 %.

2.4.19 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(2″-methoxyphenyl)but-3′-enylamino]ethanol and (2*R*)-2-phenyl-2-[(1′*S*)-1′-(2″-methoxyphenyl)but-3′-enylamino]ethanol



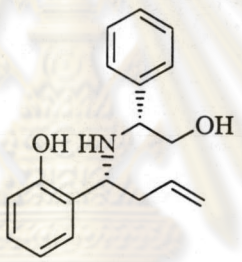
II-24a **II-24b**

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a yellow oil 0.24 g, 82 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds*= 80:20 as determined by ^{1}H-NMR); $[\alpha]^{24}_D$ = -45.2 (*c* = 1.04, $CHCl_3$). Major isomer (2*R*,1*R*): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.87 (1H, br s, N$\underline{H}$), 2.51 (2H, m, C$\underline{H}_2$ allyl), 3.49 (1H, dd J=10.4, 6.4 Hz, PhC$\underline{H}$CH$_2$OH), 3.64 (3H, s, OC$\underline{H}_3$), 3.66 (1H, m, ArC$\underline{H}$CH$_2$), 4.00 (2H, t, C$\underline{H}_2$OH), 5.00 (1H, m, CH=C$\underline{H}_2$), 5.73 (1H, m, C$\underline{H}$=CH$_2$), 6.71, 6.84, 7.14 (d, t, m, 9H, aromatic-C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 39.9 (C$\underline{H}_2$ allyl), 55.0 (O$\underline{C}$H$_3$), 56.6, 61.7, 65.2 (Ar$\underline{C}$HCH$_2$, $\underline{C}$HCH$_2$OH and CH$\underline{C}$H$_2$OH), 110.5,

116.7 ($CH=\underline{C}H_2$), 120.4, 127.6, 128.3, 131.1, 136.0 ($\underline{C}H=CH_2$), 141.8, 157.1 ($\underline{C}OCH_3$)

Minor isomer (2*R*,1*S*): ^{1}H-NMR (500 MHz, $CDCl_3$); δ 1.85 (1H, br s, N$\underline{H}$), 2.38 (2H, m, C$\underline{H}_2$ allyl), 3.54 (1H, m, C$\underline{H}CH_2OH$), 3.72 (3H, s, OC$\underline{H}_3$), 3.90 (1H, dd *J*=8.5, 5.5 Hz, ArC$\underline{H}CH_2$), 4.00 (2H, t, C$\underline{H}_2$OH), 5.00 (1H, m, $CH=C\underline{H}_2$), 5.64 (1H, m, C$\underline{H}=CH_2$), 6.71, 6.94, 7.30 (d, t, m, 9H, Ph-C$\underline{H}$ and Ph-OCH$_3$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 41.1 ($\underline{C}H_2$ allyl), 55.2 (O$\underline{C}H_3$) 59.0, 61.5, 67.2 (Ar$\underline{C}HCH_2$, $\underline{C}HCH_2OH$ and $CH\underline{C}H_2OH$), 110.8, 116.9 ($CH=\underline{C}H_2$), 120.7, 127.6, 128.3, 131.1, 136.2 ($\underline{C}H=CH_2$), 141.1, 157.6 ($\underline{C}OCH_3$); LRMS (ESI+) *m/z* 298.1 $(M{\cdot}H)^+$. Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71. Found: C, 76.67; H, 7.65; N, 4.72 %

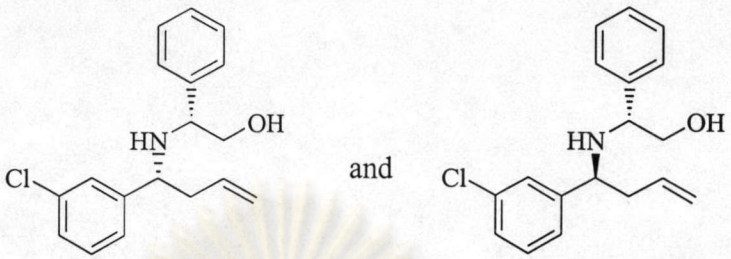
2.4.20 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(2″-hydroxyphenyl)but-3′-enylamino]ethanol



II-25

Purified by flash column chromatography (25 % ethyl acetate-hexane) to give a colourless oil 49 % yield (1 mmol scale); $[\alpha]^{24}_D$ = -63.1 (*c* = 0.89, $CHCl_3$). ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.56 (2H, m, C$\underline{H}_2$ allyl), 3.71 – 3.95 (m, ArC$\underline{H}$, PhC$\underline{H}$, C$\underline{H}_2$OH), 5.20 (2H, m, $CH=C\underline{H}_2$), 5.74 (1H, m, C$\underline{H}=CH_2$), 6.67 (2H, m, Ar$C_4\underline{H}$ and Ar$C_6\underline{H}$), 6.80 (1H, d, *J*=7.5 Hz, Ar$C_3\underline{H}$), 7.05 (1H, t, *J*=7.5 Hz, Ar$C_5\underline{H}$), 7.20 (5H, m, C_6H_5); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 40.1 ($\underline{C}H_2$ allyl), 60.4, 61.2, 64.2 (Ar$\underline{C}H$, Ph$\underline{C}HCH_2OH$ and $\underline{C}H_2OH$), 116.9 ($CH=\underline{C}H_2$), 119.0, 125.5, 127.3, 127.7, 128.0, 128.4, 128.6, 128.9, 134.4 ($\underline{C}H=CH_2$), 139.3, 157.2; HRMS (ESI+) calcd for $C_{18}H_{21}NO_2{\cdot}H^+$ 284.1651, found *m/z* 284.1638 $(M{\cdot}H)^+$. Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.08; H, 7.45; N, 4.97 %

2.4.21 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(3′-chlorophenyl)but-3′-enylamino]ethanol and (2*R*)-2-phenyl-2-[(1′*S*)-1′-(3″-chlorophenyl)but-3′-enylamino]ethanol

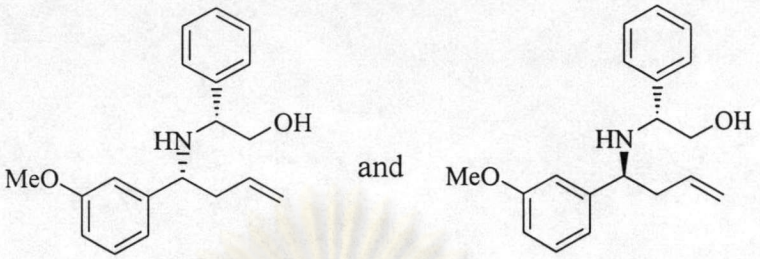


II-26a **II-26b**

Purified by flash column chromatography (20 % ethyl acetate-hexane) to give a white solid 0.21 g, 71 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds*= 94:6 as determined by ^{1}H-NMR): (m.p. 67-68 °C); $[\alpha]^{23}_D$ = -22.1 (*c* = 1.13, $CHCl_3$). Major isomer (2*R*,1*R*): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.32 (1H, br s, NH), 2.52 (2H, m, CH_2 allyl), 3.59 (1H, dd *J*=11.0, 7.1 Hz, 1×CH_2OH), 3.76 (2H, m, PhC<u>H</u>CH_2OH and 1×CH_2OH), 3.88 (1H, dd *J*=2.4, 7.0 Hz, ArCH), 5.09 (2H, m, CH=CH_2), 5.71 (1H, m, CH=CH_2), 7.21 (m, 9H, aromatic CH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 41.2 (CH_2 allyl), 59.8, 62.1, 65.9 (Ar<u>C</u>HCH_2, <u>C</u>HCH_2OH and CH<u>C</u>H_2OH), 118.0(<u>C</u>H=CH_2), 125.4, 127.2, 127.4, 128.5, 129.6, 134.4 (CH=<u>C</u>H_2), 140.9, 145.9

Minor isomer (2*R*,1*S*): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.32 (1H, br s, NH), 2.52 (2H, m, CH_2 allyl), 3.55 (1H, m, 1×CH_2OH), 3.76 (2H, m, PhC<u>H</u>CH_2OH and 1×CH_2OH), 3.88 (1H, m, ArCH), 5.15 (2H, m, CH=CH_2), 5.71 (1H, m, CH=CH_2), 7.11 (m, 9H, aromatic CH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 43.1 (CH_2 allyl), 58.5, 61.2, 67.1 (Ar<u>C</u>HCH_2, <u>C</u>HCH_2OH and CH<u>C</u>H_2OH), 118.3 (<u>C</u>H=CH_2), 125.4, 127.2, 127.4, 128.5, 129.6, 134.4 (CH=<u>C</u>H_2), 139.5, 145.9; Anal. Calcd for $C_{18}H_{20}ClNO$: C, 71.63; H, 6.68; N, 4.64. Found: C, 70.68; H, 6.54; N, 4.66 %

2.4.22 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(3″-methoxyphenyl)but-3′-enylamino]ethanol and (2*R*)-2-phenyl-2-[(1′*S*)-1′-(3″-methoxyphenyl)but-3′-enylamino]ethanol

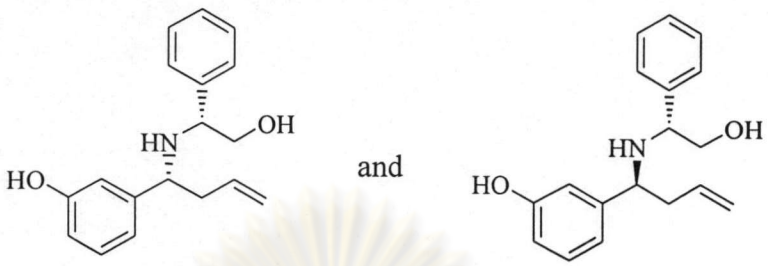


II-27a **II-27b**

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a yellow oil 0.16 g, 51 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds*= 80:20 as determined by ^{1}H-NMR); $[\alpha]^{24}_D$ = -45.2 (*c* = 1.04, $CHCl_3$). Major isomer (2*R*,1*R*): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.28 (1H, br s, NH), 2.51 (2H, m, CH_2 allyl), 3.56 (1H, dd *J*=11.7, 4.0 Hz, PhC<u>H</u>CH_2OH), 3.72 (1H, t, ArC<u>H</u>CH_2), 3.77 (3H, s, OCH_3), 3.86 (2H, dd *J*=7.0, 2.1 Hz, CH_2OH), 5.05 (1H, m, CH=C<u>H</u>$_2$), 5.70 (1H, m, C<u>H</u>=CH_2), 6.79 (4H, m, Ph-OCH_3), 7.21 (5H, m, Ph-C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 41.3 (<u>C</u>H_2 allyl), 55.2 (O<u>C</u>H_3), 60.0, 61.2, 65.7 (Ar<u>C</u>HCH_2, <u>C</u>HCH_2OH and $CH\underline{C}H_2OH$), 112.5, 117.5 127.3, 128.5, 129.4, 134.5 (CH=<u>C</u>H_2), 141.3, 145.4 (<u>C</u>H=CH_2), 159.6 (<u>C</u>OCH_3)

Minor isomer (2*R*,1*S*): ^{1}H-NMR (500 MHz, $CDCl_3$) of a minor product; δ 1.85 (1H, br s, NH), 2.38 (2H, m, CH_2 allyl), 3.54 (1H, m, C<u>H</u>CH_2OH), 3.72 (3H, s, OCH_3), 3.90 (1H, dd *J*=8.5, 5.5 Hz, ArC<u>H</u>CH_2), 4.00 (2H, t, CH_2OH), 5.00 (1H, m, CH=C<u>H</u>$_2$), 5.64 (1H, m, C<u>H</u>=CH_2), 6.71, 6.94, 7.30 (d, t, m, 9H, aromatic-C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 43.0 (<u>C</u>H_2 allyl), 55.1 (O<u>C</u>H_3), 59.0, 61.2, 66.9 (Ar<u>C</u>HCH_2, <u>C</u>HCH_2OH and $CH\underline{C}H_2OH$), 112.9, 117.9 (CH=<u>C</u>H_2), 127.4, 128.5, 129.4, 136.0, 141.1, 154.4 (<u>C</u>H=CH_2), 159.6 (<u>C</u>OCH_3); Anal. Calcd for $C_{19}H_{23}NO_2 \cdot 0.6H_2O$: C, 74.04; H, 7.91; N, 4.54. Found: C, 73.89; H, 7.70; N, 4.60 %

2.4.23 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(3″-hydroxyphenyl)but-3′-enylamino]ethanol and (2*R*)-2-phenyl-2-[(1′*S*)-1′-(3″-hydroxyphenyl)but-3′-enylamino]ethanol

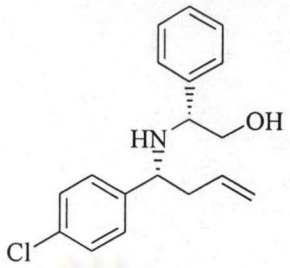


II-28a and **II-28b**

Purified by flash column chromatography (30 % ethyl acetate-hexane) to give a colourless oil 0.22 g, 78 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds*= 94:6 as determined by ^{1}H-NMR); $[\alpha]^{24}_D$ = -36.1 (*c* = 0.97, $CHCl_3$). Major isomer (2*R*,1*R*): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.44 (2H, m, C$\underline{H}_2$ allyl), 2.78 (1H, br s, N$\underline{H}$), 3.53 (1H, dd *J*=10.7, 7.0 Hz, 1×C$\underline{H}_2$OH), 3.65 (1H, t *J*=6.4 Hz, PhC$\underline{H}$CH$_2$OH), 3.74 (1H, 2×d *J*=10.7, 4.6 Hz, 1×C$\underline{H}_2$OH), 3.84 (1H, m, ArC$\underline{H}$), 5.00 (2H, 2×d *J*=18.3, 10.4 Hz, CH=C$\underline{H}_2$), 5.63 (1H, m, C$\underline{H}$=CH$_2$), 6.80 (3H, m, aromatic CH), 7.24 (6H, m, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 40.7 (C$\underline{H}_2$ allyl), 59.6 61.2, 65.4 (ArC$\underline{H}$CH$_2$, C$\underline{H}$CH$_2$OH and CHC$\underline{H}_2$OH), 114.3, 114.6, 117.6, 119.2, 127.3, 127.7, 128.6, 129.6, 134.8 (C$\underline{H}$=CH$_2$), 140.4, 144.9, 156.4

Minor isomer (2*R*,1*S*): ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.32 (2H, m, C$\underline{H}_2$ allyl), 2.78 (1H, br s, N$\underline{H}$), 3.47 (1H, m, C$\underline{H}$CH$_2$OH), 3.65 (1H, t *J*=6.4 Hz, PhC$\underline{H}$CH$_2$OH), 3.74 (1H, 2×d *J*=10.7, 4.6 Hz, 1×C$\underline{H}_2$OH), 3.84 (1H, m, ArC$\underline{H}$), 5.07 (2H, 2×d *J*=17.1, 11.0 Hz, CH=C$\underline{H}_2$), 5.63 (1H, m, C$\underline{H}$=CH$_2$), 6.80 (3H, m, aromatic C$\underline{H}$), 7.24 (6H, m, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 42.9 (ArCH$\underline{C}$H$_2$), 58.4, 60.9, 66.5 (Ar$\underline{C}$HCH$_2$, $\underline{C}$HCH$_2$OH and CH$\underline{C}$H$_2$OH), 113.7, 114.6, 118.1, 119.9, 127.3, 127.7, 128.6, 129.6, 135.1 ($\underline{C}$H=CH$_2$), 140.0, 144.6, 156.7; HRMS (ESI+) calcd for $C_{18}H_{21}NO_2 \cdot H^+$ *m/z* 284.1651, found *m/z* 284.1661 $(M \cdot H)^+$

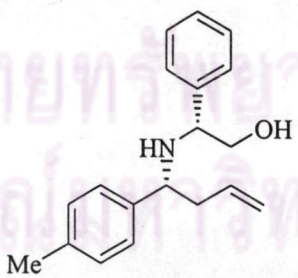
2.4.24 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(4″-chlorophenyl)but-3′-enylamino]ethanol



II-29

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.27 g, 91 % yield (1 mmol scale): (m.p. 68-70 °C); $[\alpha]^{23}_{D}$ = -18.3 (*c* = 1.04, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.99 (1H, br s, NH), 2.42 (2H, m, CH_2 allyl), 3.51 (1H, dd *J*=10.4, 6.8 Hz, 1×CH_2OH), 3.75 (3H, m, ArCH, 1×CH_2OH and $PhCHCH_2OH$), 5.03 (2H, m, $CH=CH_2$), 5.63 (1H, m, $CH=CH_2$), 7.21 (m, 9H, aromatic CH); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 41.4 (CH_2 allyl), 59.4, 61.6, 65.8 (ArCH, $PhCHCH_2OH$ and $PhCHCH_2OH$), 117.8 ($CH=CH_2$), 127.1, 127.5, 128.4, 128.6, 132.7, 134.5 ($CH=CH_2$), 140.9, 142.2; LRMS (ESI+) *m/z* 302.1 $(M{\cdot}H)^+$. Anal. Calcd for $C_{18}H_{20}ClNO$: C, 71.63; H, 6.68; N, 4.64. Found: C, 71.61; H, 6.70; N, 4.65 %

2.4.25 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(4″-methylphenyl)but-3′-enylamino]ethanol

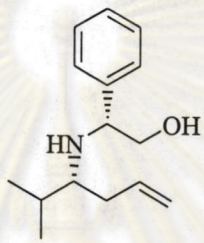


II-30

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.37 g, 98 % yield (1 mmol scale): (m.p. 66-68 °C); $[\alpha]^{26}_{D}$ = -28.5 (*c* = 1.01, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.32 (3H, s, CH_3-4′), 2.41 (1H, br s, NH), 2.48 (2H, m, CH_2 allyl), 3.51 (1H, dd *J*=10.6, 6.9 Hz, 1×CH_2OH), 3.70 (2H, m, ArCH and 1×CH_2OH), 3.82 (1H, m, $PhCHCH_2OH$), 4.98 (1H, d *J*=9.1 Hz,

CH=C$\underline{H}_a\underline{H}_b$), 5.07 (1H, d J=10.4 Hz, CH=CH$_a\underline{H}_b$), 5.65 (1H, m, C$\underline{H}$=CH$_a$H$_b$), 7.10 (4H, s, 4×ArC$\underline{H}$) 7.22 (m, 5H, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 21.1 ($\underline{C}H_3$-4′), 41.3 ($\underline{C}H_2$ allyl), 59.3, 61.2, 65.5 (Ar$\underline{C}$H), Ph$\underline{C}$HCH$_2$OH and PhCH$\underline{C}$H$_2$OH), 117.3 (CH=$\underline{C}$H$_2$), 127.0, 127.2, 127.4, 128.6, 129.1, 135.1 ($\underline{C}$H=CH$_2$), 136.7, 140.6, 141.3; LRMS (ESI+) *m/z* 382.2 $(M{\cdot}H)^+$ Anal. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 80.90; H, 8.41; N, 5.10 %

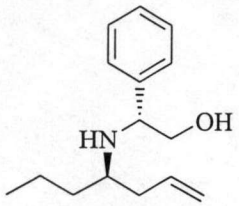
2.4.26 (2*R*)-2-phenyl-2-[(1′*R*)-1′-isopropylbut-3′-enylamino]ethanol



II-31

Purified by flash column chromatography (20 % ethyl acetate-hexane) to give a yellow solid 0.23 g, 98 % yield (1 mmol scale): (m.p. 52-53 °C); $[\alpha]^{24}_D$ = -116.1 (*c* = 1.042, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.78 [6H, 2×d J=6.8 Hz, ($C\underline{H}_3$)$_2$CH],1.63 [1H, m, (CH$_3$)$_2$C$\underline{H}$], 2.06 (1H, br s, N$\underline{H}$), 2.18 (2H, m, C$\underline{H}_2$ allyl), 2.30 (1H, m, ^{i}PrC$\underline{H}$), 3.46 (1H, dd J=10.5, 8.5 Hz, 1×C$\underline{H}_2$OH), 3.63 (1H, dd J=10.6, 4.5 Hz, 1×C$\underline{H}_2$OH), 3.86 (1H, dd J=9.0, 4.5 Hz, PhC$\underline{H}$CH$_2$OH), 5.03 (1H, d J=9.1 Hz, CH=C$\underline{H}_a\underline{H}_b$), 5.08 (1H, d J=15.8 Hz, CH=CH$_a\underline{H}_b$), 5.82 (1H, m, C$\underline{H}$=CH$_2$), 7.32 (m, 5H, aromatic C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 18.2, 18.8 [($\underline{C}H_3$)$_2$CH], 30.5 [(CH$_3$)$_2\underline{C}$H], 35.1 ($\underline{C}H_2$ allyl), 59.5, 61.9, 66.9 [(CH$_3$)$_2\underline{C}$HCH$_2$, $\underline{C}$HCH$_2$OH and CH$\underline{C}$H$_2$OH], 116.8 (CH=$\underline{C}$H$_2$), 127.4, 127.5, 128.5, 136.1 ($\underline{C}$H=CH$_2$), 141.4; LRMS (ESI+) *m/z* 234.2 $(M{\cdot}H)^+$. Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93; N, 6.00. Found: C, 77.03; H, 9.90; N, 5.95 %

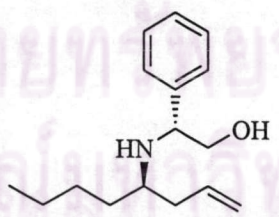
2.4.27 (2*R*)-2-phenyl-2-[(1′*R*)-1′-*n*-propylbut-3′-enylamino]ethanol



II-32

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a colourless oil 0.12 g, 51 % yield (1 mmol scale); $[\alpha]^{31}_{D}$ = -94.2 (*c* = 1.35, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.77 (3H, m, $(CH_2)_2C\underline{H}_3$), 1.25 (4H, m, $(C\underline{H}_2)_2CH_3$), 2.17 (2H, m, $C\underline{H}_2$ allyl), 2.25 (1H, br s, N<u>H</u>), 2.49 (1H, m, $CH_3(CH_2)_2C\underline{H}$), 3.46 (1H, m, 1×$C\underline{H}_2OH$), 3.63 (1H, dd *J*=10.5, 4.5, 1×$C\underline{H}_2OH$), 3.86 (1H, dd *J*=8.6, 4.5 Hz, $PhC\underline{H}CH_2OH$), 5.08 (2H, m, $CH{=}C\underline{H}_2$), 5.56 (1H, m, $C\underline{H}{=}CH_2$), 7.27 (m, 5H, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 14.1 [$(CH_2)_2\underline{C}H_3$], 19.0, 37.0 [$(\underline{C}H_2)_2CH_3$], 37.8 ($\underline{C}H_2$ allyl), 53.5, 61.6, 65.8 [$CH_3(CH_2)_2\underline{C}HCH_2$, $\underline{C}HCH_2OH$ and $CH\underline{C}H_2OH$], 117.2 ($CH{=}\underline{C}H_2$), 127.2, 127.5, 128.6, 135.2 ($\underline{C}H{=}CH_2$), 141.3; LRMS (ESI+) *m/z* 234.2 $(M{\cdot}H)^+$. Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93; N, 6.00. Found: C, 77.51; H, 10.26; N, 5.71 %

2.4.28 (2*R*)-2-phenyl-2-[(1′*R*)-1′-*n*-butylbut 3′-enylamino]ethanol

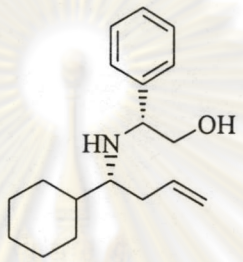


II-33

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a colourless oil 0.08 g, 33 % yield (1 mmol scale); $[\alpha]^{31}_{D}$ = -76.3 (*c* = 0.47, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.80 [3H, m, $(CH_2)_3C\underline{H}_3$], 1.25 [6H, m, $(C\underline{H}_2)_3CH_3$], 2.17 (2H, m, $C\underline{H}_2$ allyl), 2.34 (1H, br s, N<u>H</u>), 2.47 [1H, m, $(CH_2)_3C\underline{H}$], 3.47 (1H, m, 1×$C\underline{H}_2OH$), 3.63 (1H, dd *J*=10.6, 4.6, 1×$C\underline{H}_2OH$), 3.86 (1H, dd *J*=8.6, 4.5 Hz, $PhC\underline{H}CH_2OH$), 5.08 (2H, m, $CH{=}C\underline{H}_2$), 5.76 (1H, m, $C\underline{H}{=}CH_2$), 7.31 (m, 5H,

aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 14.0 [$(CH_2)_3\underline{C}H_3$], 22.7, 28.0, 34.4 [$\underline{C}H_2)_3CH_3$], 37.7 ($\underline{C}H_2$ allyl), 53.7, 61.7, 66.8 [$CH_3(CH_2)_2\underline{C}HCH_2$, $\underline{C}HCH_2OH$ and $CH\underline{C}H_2OH$], 117.2 ($\underline{C}H{=}CH_2$), 127.2, 127.5, 128.6, 135.2, 141.2 ; LRMS (ESI+) *m/z* 248.2 $(M{\cdot}H)^+$. Anal. Calcd for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.51; H, 10.26; N, 5.72 %

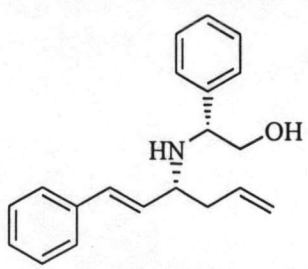
2.4.29 (2*R*)-2-phenyl-2-[(1′*R*)-1′-cyclohexylbut-3′-enylamino]ethanol



II-34

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a colourless oil 0.21 g, 78 % yield (1 mmol scale); $[\alpha]^{24}_D$ = -78.9 (*c* = 1.07, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.80–1.69 (11H, m, (^{c}Hex C<u>H</u>), 2.15 (2H, m, $C\underline{H}_2$ allyl) 2.24 (1H, m, ^{c}Hex C<u>H</u>), 3.40 (1H, dd *J*= 10.52, 8.56 Hz, 1×$C\underline{H}_2OH$), 3.56 (1H, dd *J*= 10.48, 4.64 Hz, 1×$C\underline{H}_2OH$), 3.78 (1H, dd *J*=8.56, 4.6 Hz, $PhC\underline{H}CH_2OH$), 5.00 (2H, m, $CH{=}C\underline{H}_2$), 5.72 (1H, m, $C\underline{H}{=}CH_aH_b$), 7.20 (m, 5H, aromatic C<u>H</u>); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 26.3, 26.4, 26.6, 26.8, 29.2, 34.8 (^{c}Hex <u>C</u>H), 40.8 ($\underline{C}H_2$ allyl), 58.7, 61.8, 66.8 [$(CH_2)_5\underline{C}HCH_2$, $\underline{C}HCH_2OH$ and $CH\underline{C}H_2OH$], 116.7 ($CH{=}\underline{C}H_2$), 127.3, 127.4, 128.4, 136.0 ($\underline{C}H{=}CH_2$), 141.3; HRMS (ESI+) calcd for $C_{18}H_{27}NO{\cdot}H^+$ 274.2171, found *m/z* 274.2192 $(M{\cdot}H)^+$

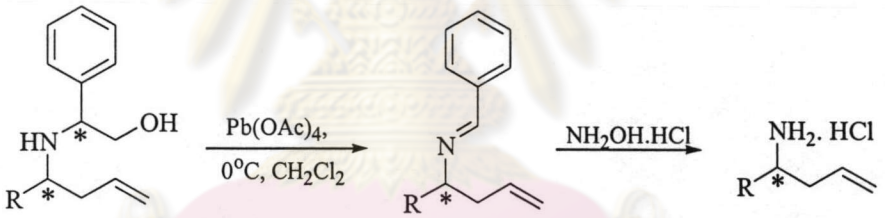
2.4.30 (2*R*)-2-phenyl-2-[(1′*R*)-1′-(2″-phenylethenyl)but-3′-enylamino]ethanol



II-35

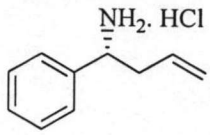
Purified by flash column chromatography (20 % ethyl acetate-hexane) to give a yellow oil 0.25 g, 87 % yield (1 mmol scale); $[\alpha]^{24}_{D}$ = +26.0 (*c* = 1.00, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.26 (1H, br s, NH), 2.37 (2H, m, CH_2 allyl, $ArCHCH_2$), 3.34 (1H, dd *J*=13.9, 5.8 Hz, RCH), 3.56 (1H, dd *J*=10.7, 7.6, 1×CH_2OH), 3.72 (1H, dd *J*=10.8, 4.6 Hz, 1×CH_2OH), 3.90 (1H, dd *J*=7.4, 4.5 Hz, $PhCHCH_2OH$), 5.08 (1H, d *J*=10.1 Hz, $CH=CH_aH_b$), 5.14 (1H, d *J*=18.6 Hz, $CH=CH_aH_b$), 5.84 (1H, m, $CH=CH_2$), 5.94 (1H, d *J*= 8.0 Hz, ArCH=CH), 5.94 (1H, d *J*=15.9 Hz, ArCH=CH), 7.25 (m, 10H, aromatic CH); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 39.7 (CH_2 allyl), 58.1, 61.4, 65.9 ($ArCHCH_2$, $CHCH_2OH$ and $CHCH_2OH$), 117.5 ($CH=CH_2$), 126.2, 127.2, 127.3, 127.4, 128.4, 128.5, 130.5, 132.6 ($CH=CH_2$), 136.8, 141.5 ; HRMS (ESI+) calcd for $C_{20}H_{23}NO{\cdot}H^+$ 294.1858, found *m/z* 294.1871 $(M{\cdot}H)^+$

2.5 General procedure for the preparation of homoallyl amine hydrochloride salts



The homoallyl amine bearing the phenylglycinol auxiliary was treated with a slight excess of $Pb(OAc)_4$ in 1:1 CH_2Cl_2/MeOH at 0 °C for 2 hours. Large excess of methanolic solution of hydroxylamine hydrochloride (10 eq) was then directly added to affect the cleavage of the resulting imine. The reaction was followed by TLC which indicated complete cleavage within 1 h at 0 °C. The mixture was adjusted to pH=1 with 10 % aqueous HCl and was extracted with diethyl ether to remove non-basic impurities. The aqueous phase was adjusted to pH=12 with aqueous 15 % NaOH and was extracted with diethyl ether. The dried ether phase was treated with excess amount of methanolic HCl (prepared *in situ* from acetyl chloride methanol at 0 °C). The solvent was evaporated and the residue was dried under vacuum to give the homoallyl amine as a hydrochloride salt.

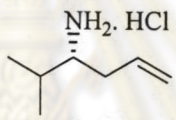
2.5.1 (*R*)-1-phenyl-but-3-enamine hydrochloride



V-6

A white solid 0.14 g, 78 % yield (1 mmol scale); $[\alpha]^{24}_{D}$ = -1.18 (*c* = 0.85, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.78 (2H, m, C<u>H</u>$_2$ allyl), 4.17 (1H, m, ArC<u>H</u>, 5.01 (2H, m, CH=C<u>H</u>$_2$), 5.49 (1H, m, C<u>H</u>=CH$_2$), 7.31 (5H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 38.6 (C<u>H</u>$_2$ allyl), 55.8 (Ar<u>C</u>H), 120.0 (CH=<u>C</u>H$_2$), 127.7, 129.0, 131.6, 135.8 (<u>C</u>H=CH$_2$); LRMS (ESI+) *m/z* 148.1 $(M{\cdot}H)^+$

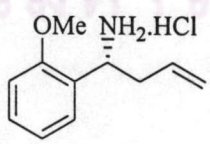
2.5.2 (*R*)-1-isopropyl-but-3-enamine hydrochloride



V-7

A yellow solid 0.11 g, 74 % yield (1 mmol scale); $[\alpha]^{24}_{D}$ = -4.8 (*c* = 0.834, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.80 [6H, d, (C<u>H</u>$_3$)$_2$CH], 1.79 [1H, m, (CH$_3$)$_2$C<u>H</u>], 2.26 [2H, m, (CH$_3$)$_2$CHC<u>H</u>$_2$], 3.98 (1H, m, ^{i}PrC<u>H</u>) 5.05 (2H, m, CH=C<u>H</u>$_2$), 5.60 (1H, m, C<u>H</u>=CH$_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 17.8 [(<u>C</u>H$_3$)$_{2a}$CH], 18.5 [(<u>C</u>H$_3$)$_{2b}$CH], 29.5 [(CH$_3$)$_2$C<u>H</u>], 34.2 (<u>C</u>H$_2$ allyl), 57.4 (^{i}Pr<u>C</u>H), 120.0 (CH=<u>C</u>H$_2$), 132.2 (<u>C</u>H=CH$_2$) HRMS (ESI+) calcd for $C_7H_{15}N{\cdot}H^+$ *m/z* 114.1283, found *m/z* 114.1215 $(M{\cdot}H)^+$

2.5.3 (*R*)-1-(2′-methoxyphenyl)but-3-enamine hydrochloride

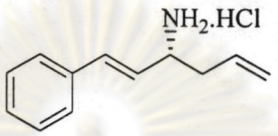


V-8

A white solid 0.17 g, 82 % yield (1 mmol scale); $[\alpha]^{22}_{D}$ = -6.91 (*c* = 1.04, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.80 (2H, m, C<u>H</u>$_2$ allyl), 3.80 (3H, s, OC<u>H</u>$_3$), 4.56 (1H, m, ArC<u>H</u>), 5.02 (2H, dd *J*=17.2, 10.2, CH=C<u>H</u>$_2$), 5.58 (1H, m, C<u>H</u>=CH$_2$),

6.89, 7.30 (4H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 36.8 (<u>C</u>H_2 allyl), 55.4 (O<u>C</u>H_3), 58.1 (Ar<u>C</u>H), 110.8, 119.4 (CH=<u>C</u>H_2), 120.7, 123.6, 127.6, 128.8, 130.0, 132.3 (<u>C</u>H=CH_2), 156.9 (<u>C</u>OCH_3); HRMS (ESI+) calcd for $C_{11}H_{15}NO{\cdot}H^+$ 178.1232, found *m/z* 178.1236 $(M{\cdot}H)^+$

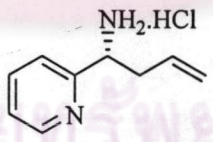
2.5.4 (*R*)-1-(2′-phenylethenyl)but-3-enamine hydrochloride



V-9

A yellow oil 0.15g, 73 % yield (1 mmol scale); $[\alpha]^{24}_D$ = +23.1 (*c* = 0.78, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.61 (2H, m, C<u>H</u>$_2$ allyl), 3.78 (1H, m, RC<u>H</u>NH_2), 5.08 (2H, m, CH=C<u>H</u>$_2$), 5.62 (1H, m, C<u>H</u>=CH_2), 6.18 (1H, dd *J*=15.9, 8.1, PhCH=C<u>H</u>), 6.63 (1H, d *J*=15.9, PhC<u>H</u>=CH), 7.24 (5H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 37.7 (<u>C</u>H_2 allyl), 53.8 (Ar<u>C</u>H), 120.1 (CH=<u>C</u>H_2), 123.8, 126.9, 128.4, 128.6, 131.5, 135.5, 135.8 (<u>C</u>H=CH_2); HRMS (ESI+) calcd for $C_{12}H_{15}N{\cdot}H^+$ 174.1283, found *m/z* 174.1284 $(M{\cdot}H)^+$

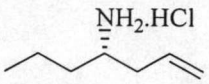
2.5.5 (*R*)-1-(2′-pyridyl)but-3-enylamine hydrochloride



V-10

A yellow oil 0.14 g, 75 % yield (1 mmol scale); $[\alpha]^{27}_D$ = +20.29 (*c* = 1.02, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.55 (2H, m, C<u>H</u>$_2$ allyl), 4.29 (1H, m, Ar<u>C</u>H), 4.96 (2H, m, CH=C<u>H</u>$_2$), 5.55 (1H, m, C<u>H</u>=CH_2), 6.94-7.59 (3H, m, Pyridyl C_3-<u>H</u>, C_4-<u>H</u>, C_5-<u>H</u>), 8.43 (1H, m, Pyridyl C_6-<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 40.2 (<u>C</u>H_2 allyl), 55.4 (Ar<u>C</u>H), 119.3 (CH=<u>C</u>H_2), 122.4, 122.9, 132.8, 136.9, 149.1 (<u>C</u>H=CH_2), 158.5. HRMS (ESI+) calcd for $C_9H_{12}N_2$+$2H^+$ 150.1157, found *m/z* 150.08 $[M+2H]^+$

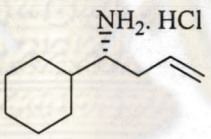
2.5.6 (*R*)-1-propyl-but-3-enamine hydrochloride



V-11

A colourless oil 0.12 g, 82 % yield (1 mmol scale); $[\alpha]^{27}_{D}$ = -0.16 (*c* = 1.10, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.88 [3H, m, $(CH_2)_2C\underline{H}_3$], 1.36 (2H, m, $CH_2C\underline{H}_2CH_3$), 1.61 (2H, m, $C\underline{H}_2CH_2CH_3$), 2.40 (2H, m, $C\underline{H}_2$ allyl), 3.26 (1H, m, ^{n}PrC$\underline{H}$NH$_2$), 5.19 (2H, m, CH=C$\underline{H}_2$), 5.70 (1H, m, C$\underline{H}$=CH$_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 13.8 ($CH_2CH_2\underline{C}H_3$), 18.7 ($CH_2\underline{C}H_2CH_3$), 34.3 ($C\underline{H}_2CH_2CH_3$), 35.9 ($\underline{C}H_2$ allyl), 51.9 (^{n}Pr$\underline{C}$H), 120.4 (CH=$\underline{C}H_2$), 131.8 ($\underline{C}$H=CH$_2$); HRMS (ESI+) calcd for $C_7H_{15}N{\cdot}H^+$ 114.1283, found *m/z* 114.1206 $(M{\cdot}H)^+$

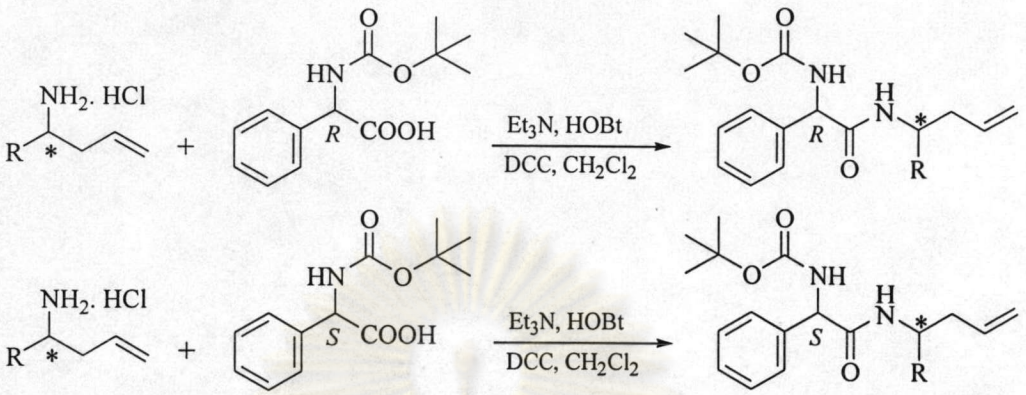
2.5.7 (*R*)-1-cyclohexyl-but-3-enamine hydrochloride



V-12

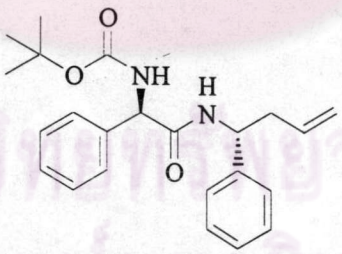
A colourless oil 0.11 g, 56 % yield (1 mmol scale); $[\alpha]^{27}_{D}$ = -0.16 (*c* = 1.10, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.22 (5H, m, $(C\underline{H}_2)_2C\underline{H}$), 1.70 (5H, m, $(C\underline{H}_2)_2C\underline{H}$), 2.48 (2H, m, $C\underline{H}_2$ allyl), 3.10 (1H, m, ^{c}HexC$\underline{H}$), 5.22 (2H, m, CH=C$\underline{H}_2$), 5.77 (C$\underline{H}$=CH$_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 25.9, 27.9, 28.9, 31.5, 34.3 ($\underline{C}_6H_{11}$), 39.0 ($\underline{C}H_2$ allyl), 56.7 (^{c}Hex$\underline{C}$H), 119.8 (CH=$\underline{C}H_2$), 132.5 ($\underline{C}$H=CH$_2$); HRMS (ESI+) calcd for $C_{10}H_{19}N{\cdot}H^+$ 154.1596, found *m/z* 154.1597 $(M{\cdot}H)^+$

2.6 General procedure for the coupling of Boc-phenylglycine to the homoallyl amine



A suspension of the homoallyl amine hydrochloride salt in dichloromethane was stirred with Et_3N (1 eq) to liberated the free amine. The free amine was then treated with (*R*)- or (*S*)-Boc-phenylglycine (1 eq), 1-hydroxybenzotriazole monohydrate ($HOBt{\cdot}H_2O$) (1 eq) and dicyclohexylcarbadi-imide (DCC) (1 eq) until the reaction was judged complete by TLC. The reaction mixture was filtered to remove the dicyclohexylurea, and the amide was purified by flash chromatography on silica gel using hexane/ethyl acetate as eluent.

2.6.1 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-phenylbut-3-enamine

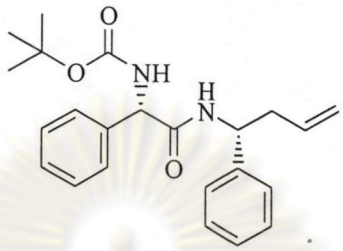


(*R,R*)-**XI-1**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.19 g, 52 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.37 (9H, m, $(C\underline{H}_3)_3CO$), 2.45 (2H, m, $C\underline{H}_2$ allyl), 5.10 (4H, m, $CH{=}C\underline{H}_2$, $ArC\underline{H}CH_2$ allyl and Phegly $C_\alpha\underline{H}$), 5.58 (1H, m, $C\underline{H}{=}CH_2$), 5.83 (1H, m, $N\underline{H}CHCH_2$ allyl), 6.20 (1H, d, N<u>H</u> Phegly), 6.92 (2H, m, aromatic C<u>H</u>), 7.35 (8H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [$(\underline{C}H_3)_3CO$], 40.5 ($C\underline{H}_2$ allyl), 52.5 ($ArC\underline{H}CH_2$ allyl), 58.6 (Phegly $C_\alpha\underline{H}$), 80.1 [$(CH_3)_3\underline{C}O$], 118.5 ($CH{=}\underline{C}H_2$), 126.0, 127.3, 128.4, 129.0, 133.6

(C<u>H</u>=CH$_2$), 138.3, 141.2, 155.2 (Boc<u>C</u>O), 169.4 (Phegly <u>C</u>ONH); HRMS (ESI+) calcd for $C_{23}H_{28}N_2O_3 \cdot Na^+$ 403.1998, found *m/z* 403.1996 $(M \cdot Na)^+$

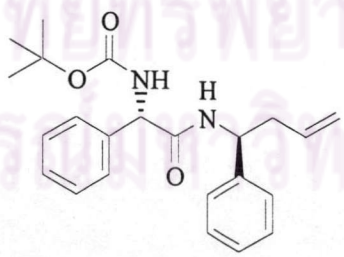
2.6.2 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*S*)-phenylglycyl]-(*R*)-1-phenylbut-3-enamine



(*S,R*)-**XI-1**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.23 g, 61 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.37 [9H, m, (C<u>H</u>$_3$)$_3$CO], 2.37 (2H, m, C<u>H</u>$_2$ allyl), 4.77 (1H, d *J*=16.7, CH=C<u>H</u>$_a$H$_b$), 4.84 (1H, d *J*=9.0, CH=CH$_a$<u>H</u>$_b$), 5.00 (1H, m, ArC<u>H</u>CH$_2$ allyl), 5.15 (1H, d, Phegly C$_\alpha$<u>H</u>), 5.43 (1H, m, C<u>H</u>=CH$_2$), 5.87 (1H, d, N<u>H</u>CHCH$_2$ allyl), 6.29 (1H, d, N<u>H</u> Phegly), 7.16 (10H, m, Aromatic-C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 28.3 [(<u>C</u>H$_3$)$_3$CO], 40.4 (C<u>H</u>$_2$ allyl), 52.7 (ArC<u>H</u>CH$_2$ allyl), 58.4 (Phegly C$_\alpha$<u>H</u>), 79.8 [(CH$_3$)$_3$<u>C</u>O], 118.1 (CH=<u>C</u>H$_2$), 126.5, 127.2, 128.1, 128.5, 128.8, 133.5 (<u>C</u>H=CH$_2$), 138.6, 141.3, 155.2 (Boc<u>C</u>O), 169.8 (Phegly <u>C</u>ONH); HRMS (ESI+) calcd for $C_{23}H_{28}N_2O_3 \cdot Na^+$ 403.1998, found *m/z* 403.1998 $(M \cdot Na)^+$

2.6.3 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*S*)-phenylglycyl]-(*S*)-1-phenylbut-3-enamine

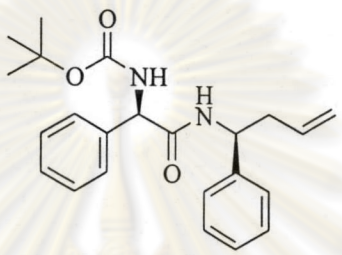


(*S,S*)-**XI-1**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.20 g, 52 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.38 [9H, m, (C<u>H</u>$_3$)$_3$CO], 2.46 (2H, m, C<u>H</u>$_2$ allyl), 5.07 (4H, m, CH=C<u>H</u>$_2$ and ArC<u>H</u>CH$_2$ allyl), 5.59 (1H, m, C<u>H</u>=CH$_2$), 5.82 (1H, m, Phegly C$_\alpha$<u>H</u>), 6.20 (1H, m, N<u>H</u> Phegly),

6.92-7.34 (10H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [(<u>C</u>H_3)$_3$CO], 40.5 (<u>C</u>H_2 allyl), 53.1 (ArC<u>H</u>CH_2 allyl), 58.4 (Phegly C_α<u>H</u>), 70.5 [$(CH_3)_3$<u>C</u>O], 118.5 (<u>C</u>H=CH_2), 126.0, 127.3, 128.4, 129.0, 133.6 (CH=<u>C</u>H_2), 138.3, 140.2, 155.2 (Boc<u>C</u>O), 169.4 (Phegly <u>C</u>ONH); HRMS (ESI+) calcd for $C_{23}H_{28}N_2O_3 \cdot Na^+$ 403.1998, found *m/z* 403.1992 $(M \cdot Na)^+$

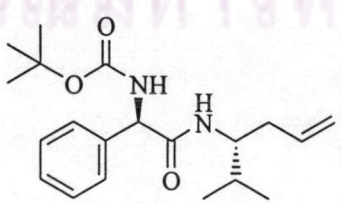
2.6.4 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*S*)-1-phenylbut-3-enamine



(*R,S*)-**XI-1**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 56 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.37 [9H, m, (C<u>H</u>$_3$)$_3$CO], 2.38 (2H, m, C<u>H</u>$_2$ allyl), 4.77 (1H, dd *J*=17.2, 9.0 Hz, CH=C<u>H</u>$_2$), 5.04 (2H, m, ArC<u>H</u>CH_2 allyl, N<u>H</u> and Phegly C_α<u>H</u>), 5.43 (1H, m, C<u>H</u>=CH_2), 5.87 (1H, m, Phegly C_α<u>H</u>), 6.20 (1H, m, N<u>H</u>), 7.16 (10H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [(<u>C</u>H_3)$_3$CO], 39.0 (<u>C</u>H_2 allyl), 52.5 (ArC<u>H</u>CH_2 allyl), 58.4 (Phegly C_α<u>H</u>), 79.5 [$(CH_3)_3$<u>C</u>O], 118.5 (<u>C</u>H=CH_2), 125.5, 127.3, 128.4, 129.0, 133.6 (CH=<u>C</u>H_2), 137.3, 141.2, 155.2 (Boc<u>C</u>O), 169.4 (Phegly <u>C</u>ONH); HRMS (ESI+) calcd for $C_{23}H_{28}N_2O_3 \cdot Na^+$ 403.1998, found *m/z* 403.1998 $(M \cdot Na)^+$

2.6.5 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-isopropylbut-3-enamine

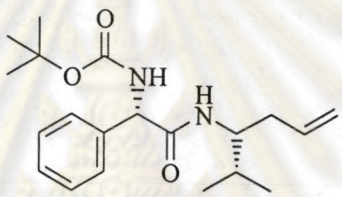


(*R,R*)-**XI-2**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a yellow oil 0.17 g, 50 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.66

[6H, 2×d *J*=6.8 Hz, $(C\underline{H}_3)_2CH$], 1.28 [9H, m, $(C\underline{H}_3)_3CO$], 1.58 [1H, m, $(CH_3)_2C\underline{H}$], 2.15 (2H, m, $C\underline{H}_2$ allyl), 3.83 (1H, m, $^{i}PrC\underline{H}CH_2$ allyl), 5.05 (3H, m, Phegly $C_{\alpha}\underline{H}$ and $CH=C\underline{H}_2$), 5.49 (1H, m, $N\underline{H}CHCH_2$ allyl), 5.68 (1H, m, $C\underline{H}=CH_2$), 5.82 (1H, m, $N\underline{H}$ Phegly), 7.29 (5H, m, aromatic $C\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 17.3, 19.1 $[(\underline{C}H_3)_2CH]$, 28.3 $[(\underline{C}H_3)_3CO]$, 31.2 $[(CH_3)_2\underline{C}HCH]$, 36.6 ($\underline{C}H_2$ allyl), 53.9 $[(CH_3)_2CH\underline{C}H]$, 60.0 (Phegly $\underline{C}_{\alpha}H$), 80.0 $[(CH_3)_3\underline{C}O]$, 117.5 ($CH=\underline{C}H_2$), 127.1, 128.3, 128.9, 134.6 ($\underline{C}H=CH_2$), 138.9, 155.1 (Boc$\underline{C}O$), 169.6 (Phegly $\underline{C}ONH$); LRMS (ESI+) *m/z* 369.1 $(M{\cdot}Na)^+$

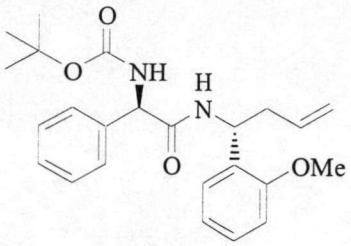
2.6.6 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*S*)-phenylglycyl]-(*R*)-1-isopropylbut-3-enamine



(*S,R*)-**XI-2**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a yellow oil 0.23 g, 68 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.86 [6H, 2×d *J*=7.0 Hz, $(C\underline{H}_3)_2CH$], 1.37 [9H, m, $(C\underline{H}_3)_3CO$], 1.67 [1H, m, $(CH_3)_2C\underline{H}$], 1.99 (2H, m, $C\underline{H}_2$ allyl), 3.76 (1H, m, $^{i}PrC\underline{H}CH_2$ allyl), 4.65 (1H, d *J*=18.4 Hz, $CH=C\underline{H}_aH_b$), 4.72 (1H, d *J*=10.1 Hz, $CH=CH_a\underline{H}_b$), 5.05 (1H, m, Phegly $C_{\alpha}\underline{H}$), 5.41 (2H, m, $C\underline{H}=CH_2$ and $N\underline{H}CHCH_2$ allyl), 5.85 (1H, m, $N\underline{H}$ Phegly), 7.29 (5H, m, aromatic $C\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 18.2, 19.2 $[(\underline{C}H_3)_2CH]$, 28.3 $[(\underline{C}H_3)_3CO]$, 31.3 $[(CH_3)_2\underline{C}HCH]$, 36.3 ($\underline{C}H_2$ allyl), 54.1 $^{i}PrC\underline{H}CH_2$ allyl), 58.8 (Phegly $\underline{C}_{\alpha}H$), 79.9 $[(CH_3)_3\underline{C}O]$, 117.7 ($CH=\underline{C}H_2$), 127.2, 128.2, 128.9, 133.7 ($\underline{C}H=CH_2$), 138.9, 155.2 (Boc$\underline{C}O$), 169.6 ($\underline{C}ONH$); LRMS (ESI+) *m/z* 369.15 $(M{\cdot}Na)^+$

2.6.7 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-(2'-methoxyphenyl) but-3-enamine

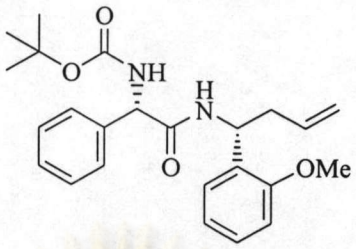


(*R,R*)-**XI-3**

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a white solid 0.21 g, 51 % yield (1 mmol scale); (inseparable mixture of diastereomer; *ds* = 85:15 as determined by ^{1}H-NMR); Major isomer (*R,R*): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.36 [9H, m, $(C\underline{H}_3)_3CO$], 2.48 (2H, m, $C\underline{H}_2$ allyl), 3.60 (3H, s, $OC\underline{H}_3$), 5.05 (4H, m, $CH{=}C\underline{H}_2$, $ArC\underline{H}CH_2$ allyl and Phegly $C_\alpha\underline{H}$), 5.60 (1H, m, $C\underline{H}{=}CH_2$), 5.85 (1H, m, $N\underline{H}CHCH_2$ allyl) 6.55 (1H, m, $N\underline{H}$ Phegly), 6.84 (3H, m, aromatic $C\underline{H}$), 7.10-7.34 (6H, m, aromatic $C\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [$(\underline{C}H_3)_3CO$], 39.4 ($\underline{C}H_2$ allyl), 51.5 ($Ar\underline{C}HCH_2$ allyl), 55.0 ($O\underline{C}H_3$), 58.7 (Phegly $\underline{C}_\alpha H$), 79.9 [$(CH_3)_3\underline{C}O$], 117.6 ($\underline{C}H{=}CH_2$), 120.5 (*R*), 127.3, 128.1, 128.3, 128.4, 128.9, 134.5 ($CH{=}\underline{C}H_2$), 138.7, 155.1 ($\underline{C}OMe$) 156.7 (Boc$\underline{C}O$), 168.9 (Phegly $\underline{C}ONH$).

Minor isomer (*R,S*): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.36 [9H, m, $(C\underline{H}_3)_3CO$], 2.35 (2H, m, $C\underline{H}_2$ allyl), 3.75 (3H, s, $OC\underline{H}_3$), 4.77 (4H, m, $CH{=}C\underline{H}_2$, $ArC\underline{H}CH_2$ allyl and Phegly $C_\alpha\underline{H}$), 5.42 (1H, m, $C\underline{H}{=}CH_2$), 5.85 (1H, m, $N\underline{H}CHCH_2$ allyl) 6.55 (1H, m, $N\underline{H}$ Phegly), 6.73 (3H, m, aromatic $C\underline{H}$), 7.10-7.34 (6H, m, aromatic $C\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [$(\underline{C}H_3)_3CO$], 39.4 ($\underline{C}H_2$ allyl), 51.5 ($Ar\underline{C}HCH_2$ allyl), 55.0 ($O\underline{C}H_3$), 58.7 (Phegly $\underline{C}_\alpha H$), 79.9 [$(CH_3)_3\underline{C}O$], 117.6 ($\underline{C}H{=}CH_2$), 120.8, 127.3, 128.1, 128.3, 128.4, 128.9, 134.1, 138.7 ($CH{=}\underline{C}H_2$), 155.2 ($\underline{C}OMe$) 156.7 (Boc$\underline{C}O$), 168.9 (Phegly $\underline{C}ONH$); LRMS (ESI+) *m/z* 433.2 $(M{\cdot}Na)^+$

2.6.8 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*S*)-phenylglycyl]-(*R*)-1-(2′-methoxyphenyl) but-3-enamine

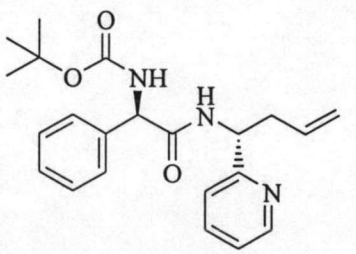


(*S,R*)-**XI-3**

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a white solid 0.16 g, 40 % yield (1 mmol scale); (inseparable mixture of diastereomer; *ds* = 89:11 as determined by ^{1}H-NMR); Major isomer (*S,R*): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.36 (9H, m, $(C\underline{H}_3)_3CO$), 2.34 (2H, m, $C\underline{H}_2$ allyl), 3.76 (3H, s, $OC\underline{H}_3$), 4.78 (2H, m, $CH=C\underline{H}_2$), 5.06 (1H, m, $ArC\underline{H}CH_2$ allyl and Phegly $C_\alpha\underline{H}$), 5.44 (1H, m, $C\underline{H}=CH_2$), 5.95 (1H, m, $N\underline{H}CHCH_2$ allyl), 6.70 (1H, m, N<u>H</u> Phegly), 6.91 (2H, m, aromatic C<u>H</u>), 7.07-7.35 (8H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 28.3 [$(\underline{C}H_3)_3CO$], 39.5 ($\underline{C}H_2$ allyl), 51.6 ($\underline{C}H_2$ allyl), 55.2 ($O\underline{C}H_3$), 58.8 (Phegly $\underline{C}_\alpha H$), 79.8 [$(CH_3)_3\underline{C}O$], 117.6 ($CH=\underline{C}H_2$), 120.8, 127.3, 128.2, 128.4, 128.7, 128.9, 134.1 ($\underline{C}H=CH_2$), 139.1, 155.2 (<u>C</u>OMe) 156.8 (Boc<u>C</u>O), 168.8 (Phegly <u>C</u>ONH)

Minor isomer (*S,S*): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.36 (9H, m, $(C\underline{H}_3)_3CO$), 2.45 (2H, m, $C\underline{H}_2$ allyl), 3.59 (3H, s, $OC\underline{H}_3$), 4.78 (2H, m, $CH=C\underline{H}_2$), 5.06 (1H, m, $ArC\underline{H}CH_2$ allyl and Phegly $C_\alpha\underline{H}$), 5.44 (1H, m, $C\underline{H}=CH_2$), 5.95 (1H, m, $N\underline{H}CHCH_2$ allyl), 6.70 (1H, m, N<u>H</u> Phegly), 6.91 (2H, m, aromatic C<u>H</u>), 7.07-7.35 (8H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$); δ 28.3 [$(\underline{C}H_3)_3CO$], 39.5 ($\underline{C}H_2$ allyl), 51.7 ($\underline{C}H_2$ allyl), 55.2 ($O\underline{C}H_3$), 58.8 (Phegly $\underline{C}_\alpha H$), 79.8 [$(CH_3)_3\underline{C}O$], 117.5 ($CH=\underline{C}H_2$), 120.5, 127.3, 128.2, 128.4, 128.7, 128.9, 134.5 ($\underline{C}H=CH_2$), 139.0, 155.1 (<u>C</u>OMe) 156.9 (Boc<u>C</u>O), 168.8 (Phegly <u>C</u>ONH); LRMS (ESI+) *m/z* 433.2 $(M{\cdot}Na)^+$

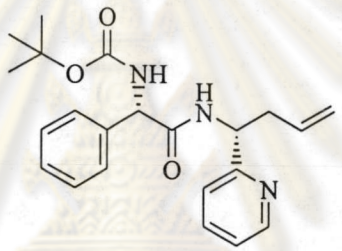
2.6.9 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-(2′-pyridyl)but-3-enamine



(*R,R*)-**XI-4**

Purified by flash column chromatography (20 % ethyl acetate-hexane) to give a white solid 0.21 g, 56 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.22 (9H, m, $(C\underline{H}_3)_3CO$), 2.56 (2H, m, $C\underline{H}_2$ allyl), 4.93 (4H, m, $CH{=}C\underline{H}_2$, $C\underline{H}$-Py and Phegly $C_\alpha\underline{H}$), 5.56 (1H, m, $C\underline{H}{=}CH_2$), 5.82 (1H, m, N$\underline{H}$ Phegly), 6.97-7.51 (9H, m, $C_6\underline{H}_5$ and $C_5\underline{H}_4$), 8.36 (1H, m, Py-$C_6\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.2 [$(\underline{C}H_3)_3CO$], 40.3 ($\underline{C}H_2$ allyl), 53.6 (Ar$\underline{C}$HCH$_2$ allyl), 58.8 (Phegly $\underline{C}_\alpha$H), 79.9 [$(CH_3)_3\underline{C}O$], 118.3 ($\underline{C}H{=}CH_2$), 121.7, 122.3, 127.2, 128.1, 128.8, 133.4 ($CH{=}\underline{C}H_2$), 136.5, 138.3, 148.9, 155.0, 158.7 (Boc$\underline{C}$O), 169.5 (Phegly $\underline{C}$ONH); HRMS (ESI+) calcd for $C_{22}H_{27}N_3O_3{\cdot}H^+$ 382.2131, found *m/z* 382.2125 $(M{\cdot}H)^+$

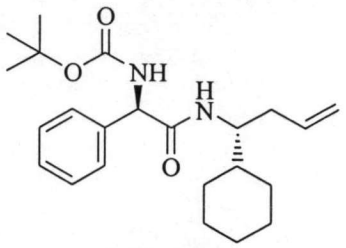
2.6.10 *N*-[1-*N*′-(*tert*-butoxycarbonyl)-(*S*)-phenylglycyl]-(*R*)-1-(2′-pyridyl)but-3-enamine



(*S,R*)-**XI-4**

Purified by flash column chromatography (20 % ethyl acetate-hexane) to give a white solid 0.19 g, 50 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.24 [9H, m, $(C\underline{H}_3)_3CO$], 2.41 (2H, m, $C\underline{H}_2$ allyl), 4.70 (2H, m, $CH{=}C\underline{H}_2$), 5.09 (1H, m, $C\underline{H}$-Py), 5.20 (1H, m, Phegly $C_\alpha\underline{H}$), 5.36 (1H, m, $C\underline{H}{=}CH_2$), 5.95 (1H, m, N$\underline{H}$ Phegly), 7.08-7.40 (9H, m, aromatic C$\underline{H}$), 7.55 (1H, t, *J*=7.7 Hz, Py-$C_2\underline{H}$), 8.45 (1H, d *J*=4.8 Hz, Py-C$\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [$(\underline{C}H_3)_3CO$], 40.2 ($\underline{C}H_2$ allyl), 53.4 (Py$\underline{C}$HCH$_2$ allyl), 58.6 (Phegly $\underline{C}_\alpha$H), 79.8 [$(CH_3)_3\underline{C}O$], 118.3 ($CH{=}\underline{C}H_2$), 122.0, 122.4, 127.2, 128.1, 128.8, 132.8 ($\underline{C}H{=}CH_2$), 136.6, 138.7, 149.0, 155.0, 158.8 (Boc$\underline{C}$O), 169.5 (Phegly $\underline{C}$ONH); HRMS (ESI+) calcd for $C_{22}H_{27}N_3O_3{\cdot}H^+$ 382.2131, found *m/z* 382.2052 $(M{\cdot}H)^+$

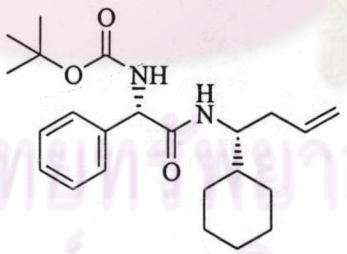
2.6.11 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-cyclohexylbut-3-enamine



(*R,R*)-**XI-5**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.23 g, 59 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.66-1.16 [8H, m, $(C\underline{H}_2)_4CH_2CH$], 1.43 [9H, m, $(C\underline{H}_3)_3OCO$], 1.60 [2H, m, $CH_2(C\underline{H}_2)_4CH$], 2.20 (2H, m, $C\underline{H}_2$ allyl), 3.85 (1H, m, $RC\underline{H}CH_2$ allyl), 5.09 (3H, m, $CH{=}C\underline{H}_2$, Phegly $C_\alpha\underline{H}$), 5.54 (1H, m, $N\underline{H}CHCH_2$ allyl), 5.74 (1H, m, $C\underline{H}{=}CH_2$), 5.84 (1H, m, N<u>H</u> Phegly), 7.33 (5H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 25.9, 26.0, 26.2 [$(\underline{C}H_2)_3C_3H_5$], 27.7 [$(\underline{C}H_3)_3CO$], 28.3, 29.6, 36.4 [$(\underline{C}_3H_5)CHCH_2$], 41.2 ($\underline{C}H_2$ allyl), 53.2 [$(C_6H_{11})\underline{C}HCH_2$], 58.9 (Phegly $\underline{C}_\alpha H$), 80.0 [$(CH_3)_3\underline{C}O$], 117.5 ($CH{=}\underline{C}H_2$), 127.2, 128.2, 128.9, 134.6, 138.9 ($\underline{C}H{=}CH_2$), 155.1 (Boc<u>C</u>O), 169.5 (Phegly <u>C</u>ONH); LRMS (ESI+) *m/z* 409.2 $(M{\cdot}Na)^+$

2.6.12 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*S*)-phenylglycyl]-(*R*)-1-cyclohexylbut-3-enamine

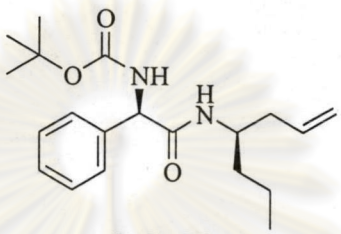


(*S,R*)-**XI-5**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.24 g, 62 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.80-1.41 [9H, m, $(C\underline{H}_3)_3CO$], 1.66 [8H, m, $CH_2(C\underline{H}_2)_4CH$], 2.00 [4H, m, $C\underline{H}_2$ allyl and $C\underline{H}_2(CH_2)_5$], 3.75 (1H, m, $C\underline{H}CH_2$ allyl), 4.70 (1H, d J=15.0 Hz, $CH{=}C\underline{H}_aH_b$), 4.75 (1H, d J=10.0 Hz, $CH{=}CH_a\underline{H}_b$), 5.05 (1H, m, Phegly $C_\alpha\underline{H}$), 5.44 (2H, m, $C\underline{H}{=}CH_2$ and $N\underline{H}CHCH_2$ allyl) 5.90 (1H, m, N<u>H</u> Phegly), 7.28 (5H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 26.0, 26.3 ($(\underline{C}H_2)_2C_4H_7$), 28.3 [$(\underline{C}H_3)_3CO$], 28.8, 29.6,

36.0 [($\underline{C}_3H_5$)CHCH$_2$]1, 41.0 ($\underline{C}H_2$ allyl), 53.4 ((C_6H_{11})$\underline{C}$HCH$_2$), 58.7 (Phegly $\underline{C}_\alpha$H), 79.9 [(CH_3)$_3\underline{C}$O], 117.7 (CH=$\underline{C}H_2$), 127.2, 128.2, 128.9, 133.7 ($\underline{C}$H=CH$_2$), 138.9, 155.2 (Boc$\underline{C}$O), 169.6 (Phegly $\underline{C}$ONH); LRMS (ESI+) *m/z* 409.2 (M·Na)$^+$

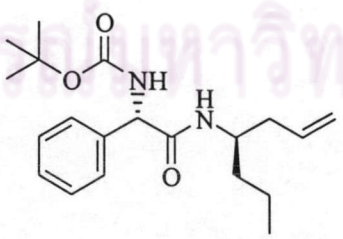
2.6.13 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-*n*-propylbut-3-enamine



(*R,R*)-**XI-6**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a colourless oil 0.21 g, 61 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.73 [3H, m, (CH_2)$_2$C$\underline{H}_3$], 1.15 [4H, m, (C$\underline{H}_2$)$_2$CH$_3$], 1.42 [9H, m, (C$\underline{H}_3$)$_3$CO], 2.15 (2H, m, C$\underline{H}_2$ allyl), 3.91 (1H, m, RC$\underline{H}$CH$_2$ allyl), 5.00 (2H, m, CH=C$\underline{H}_2$), 5.68 (4H, m, C$\underline{H}$=CH$_2$, Phegly C$_\alpha\underline{H}$, and N$\underline{H}$×2), 7.30 (5H, m, aromatic C$\underline{H}$), ^{13}C-NMR (50 MHz, $CDCl_3$) δ 13.7 (CH_2)$_2\underline{C}$H$_3$), 18.7 [($\underline{C}H_2$)$_2$CH$_3$], 28.3 [($\underline{C}H_3$)$_3$CO], 36.2 [($\underline{C}H_2$)$_2$CH$_3$], 39.2 ($\underline{C}H_2$ allyl), 48.8 ($C_3H_7\underline{C}$H), 58.7 (Phegly $\underline{C}_\alpha$H), 80.0 [(CH_3)$_3\underline{C}$O], 117.9 (CH=$\underline{C}H_2$), 127.1, 128.2, 128.9, 134.2 ($\underline{C}$H=CH$_2$), 138.7, 155.1 (Boc$\underline{N}$H), 169.6 (Phegly $\underline{C}$ONH); HRMS (ESI+) calcd for $C_{20}H_{23}N_2O_3$·Na$^+$ 369.2154, found *m/z* 369.2152 (M·Na)$^+$

2.6.14 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*S*)-phenylglycyl]-(*R*)-1-*n*-propylbut-3-enamine

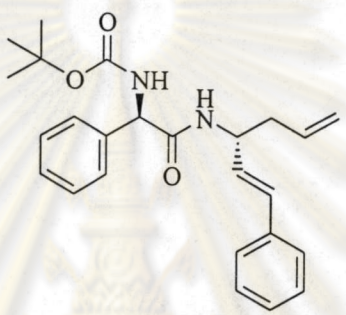


(*S,R*)-**XI-6**

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a colourless oil 63 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.87 [3H, m, (CH_2)$_2$C$\underline{H}_3$], 1.31 [13H, m, (C$\underline{H}_3$)$_3$CO and (C$\underline{H}_2$)$_2$CH$_3$], 2.05 (2H, m, C$\underline{H}_2$ allyl), 3.95

(1H, m, RC<u>H</u>CH$_2$ allyl), 4.69 (1H, d *J*=17.2 Hz, CH=C<u>H$_a$</u>H$_b$), 4.76 (1H, d *J*=10.2 Hz, CH=CH$_a$<u>H$_b$</u>), 5.05 (1H, m, Phegly <u>C$_\alpha$</u>H), 5.50 (2H, m, C<u>H</u>=CH$_2$ and N<u>H</u>CHCH$_2$ allyl), 5.85 (1H, m, N<u>H</u> Phegly), 7.27 (5H, m, aromatic C<u>H</u>), ^{13}C-NMR (50 MHz, $CDCl_3$) δ 13.9 (<u>C</u>H$_3$CH$_2$CH$_2$), 19.2 (CH$_3$<u>C</u>H$_2$CH$_2$), 28.3 [(<u>C</u>H$_3$)$_3$CO], 36.4 (CH$_3$CH$_2$<u>C</u>H$_2$), 38.8 (<u>C</u>H$_2$ allyl), 48.7 (R<u>C</u>H), 58.6 (Phegly <u>C$_\alpha$</u>H), 79.9 [(CH$_3$)$_3$<u>C</u>O], 118.0 (CH=<u>C</u>H$_2$), 127.2, 128.2, 128.9, 133.4 (<u>C</u>H=CH$_2$), 138.8, 155.1 (Boc<u>C</u>O), 169.5 (<u>C</u>ONH); HRMS (ESI+) calcd for $C_{20}H_{23}N_2O_3 \cdot Na^+$ 369.2154, found *m/z* 369.2159 $(M \cdot Na)^+$

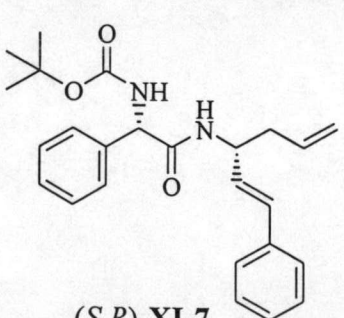
2.6.15 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-(2′-phenylethenyl) but-3-enamine



(*R,R*)-**XI-7**

Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a white solid 87 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.39 (9H, s, (C<u>H</u>$_3$)$_3$CO), 2.36 (2H, m, C<u>H</u>$_2$ allyl), 3.21 (1H, m, R<u>C</u>HCH$_2$ allyl), 4.70 (1H, m, CH=C<u>H$_a$</u>H$_b$), 5.07 (2H, m, CH=CH$_a$<u>H$_b$</u>, Phegly C$_\alpha$<u>H</u>), 5.75 (1H, m, C<u>H</u>=CH$_2$), 5.99 (3H, m, N<u>H</u> Phegly, PhCH=C<u>H</u> and PhC<u>H</u>=CH), 7.12-7.39 (10H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [(<u>C</u>H$_3$)$_3$CO], 39.3 (<u>C</u>H$_2$ allyl), 50.0 (Phegly <u>C$_\alpha$</u>H), 58.6 (Phegly <u>C$_\alpha$</u>H), 80.0 [(CH$_3$)$_3$<u>C</u>O], 118.6 (<u>C</u>H=CH$_2$), 126.3, 127.2, 127.5, 128.4, 129.9, 133.6, 136.4, 138.7 (CH=<u>C</u>H$_2$), 155.2 (Boc<u>C</u>O), 169.5 (<u>C</u>ONH); LRMS (ESI+) *m/z* 429.2 $(M \cdot Na)^+$

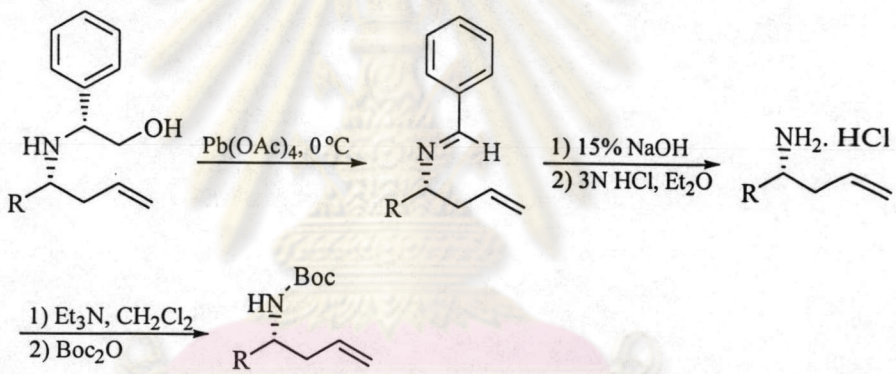
2.6.16 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*S*)-phenylglycyl]-(*R*)-1-(2′-phenylethenyl) but-3-enamine



(*S,R*)-**XI-7**

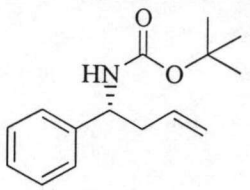
Purified by flash column chromatography (15 % ethyl acetate-hexane) to give a white solid 0.22 g, 55 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.41 [9H, s, $(C\underline{H}_3)_3CO$], 2.23 (2H, m, $C\underline{H}_2$ allyl), 4.70 (2H, m, $CH=C\underline{H}_aH_b$ and $RC\underline{H}CH_2$ allyl), 4.85 (1H, m, $CH=CH_a\underline{H}_b$), 5.28 (1H, s, Phegly $C_\alpha\underline{H}$), 5.50 (1H, m, $CH_2C\underline{H}=CH_2$), 6.07 (2H, m, $PhCH=C\underline{H}$ and $N\underline{H}CHCH_2$ allyl), 6.44 (2H, m, $PhC\underline{H}=CH$ and $N\underline{H}$ Phegly), 7.29 (10H, m, aromatic $C\underline{H}$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [$(\underline{C}H_3)_3CO$], 39.2 ($\underline{C}H_2$ allyl), 50.3 (Phegly $C_\alpha\underline{H}$), 58.7 (Phegly $\underline{C}_\alpha H$), 80.0 [$(CH_3)_3\underline{C}O$], 118.6 ($CH=\underline{C}H_2$), 126.4, 127.2, 127.7, 128.3, 130.8, 133.0 ($\underline{C}H=CH_2$), 136.5, 138.6, 155.2 (Boc$\underline{C}O$), 169.5 (Phegly $\underline{C}ONH$); LRMS (ESI+) *m/z* 429.2 $(M\cdot Na)^+$

2.7 Oxidative cleavage of phenylglycinol auxiliary followed by Boc-protection[4]



To a solution of the amino alcohol in CH_2Cl_2/MeOH (2:1) at 0 °C was added, in one portion, 1 eq of lead tetraacetate [$Pb(OAc)_4$]. The reaction mixture was stirred for 2-20 min, whereupon 5 mL of 15 % NaOH was added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase were evaporated *in vacuo*. The crude product was then dissolved in ether and stirred for 4-16 h with an equal volume of 3 N aqueous HCl solution and extracted with ether. The aqueous phase was devaporated *in vacuo* to give the hydrocholride salt of the homoallylic amine which is hygroscopic. The crude amine salt was protected by *t*-butoxycarbonyl (Boc) group as follows: to a solution of the amine in CH_2Cl_2 was added 2 equiv of triethylamine (Et_3N) and 1.1 eq of Boc_2O. The reaction mixture was stirred for 2 h and then evaporated *in vacuo*. The crude Boc-protected amine was purified by flash column chromatography.

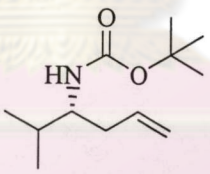
2.7.1 *N-tert*-butoxycarbonyl-(*R*)-1-phenylbut-3-enamine



X-6

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.09 g, 38 % yield (1 mmol scale); $[\alpha]^{24}_{D}$ = -9.8 (*c* = 0.626, $CHCl_3$) (40 % *ee* determined by ^{1}H-NMR from the coupling of Boc-phenylglycine **section 2.8**); ^{1}H-NMR (200 MHz, $CHCl_3$) δ 1.41 [9H, s, $(C\underline{H}_3)_3CO$], 2.50 (2H, t, $C\underline{H}_2$ allyl), 4.72 (1H, br s, C<u>H</u>NH), 4.84 (1H, br s, CHN<u>H</u>), 5.08 (2H, dd *J*=8.8, 17.9 Hz, CH=C<u>H</u>$_2$), 5.64 (1H, m, C<u>H</u>=CH_2), 7.26 (5H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.3 [$(\underline{C}H_3)_3CO$], 40.5 ($\underline{C}H_2$ allyl), 54.1 (<u>C</u>HNH), 79.5 [$(CH_3)_3\underline{C}O$], 118.2 (<u>C</u>H=CH_2), 126.2, 127.1, 128.5, 134.0 (CH=<u>C</u>H$_2$), 155.2 (Boc<u>C</u>O)

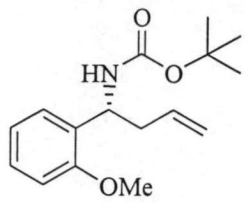
2.7.2 *N-tert*-butoxycarbonyl-(*R*)-1-isopropylbut-3-enamine



X-7

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.03 g, 13 % yield (1 mmol scale); $[\alpha]^{24}_{D}$ = -7.9 (*c* = 1.004, $CHCl_3$) (60 % *ee* determined by ^{1}H-NMR from the coupling of Boc-phenylglycine **section 2.8**); ^{1}H-NMR (200 MHz, $CHCl_3$) δ 0.87 [6H, 2×d, $CH(C\underline{H}_3)_2$], 1.40 [9H, s, $(C\underline{H}_3)_3CO$], 1.69 [2H, m, $C\underline{H}(CH_3)_2$], 2.14 (1H, m, $C\underline{H}_2$ allyl), 3.45 (1H, m, C<u>H</u>NH), 4.27 (1H, m, CHN<u>H</u>), 5.05 (2H, m, CH=C<u>H</u>$_2$), 5.73 (1H, m, C<u>H</u>=CH_2); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 18.2, 19.2 [$(\underline{C}H_3)_2CH$], 27.5, 28.3 [$(\underline{C}H_3)_3CO$], 31.5 [$(CH_3)_2\underline{C}H$], 37.8 ($\underline{C}H_2$ allyl), 54.1 (<u>C</u>HNH), 79.5 [$(CH_3)_3\underline{C}O$], 118.2 (CH=<u>C</u>H$_2$), 134.0 (<u>C</u>H=CH_2), 147.0 (Boc<u>C</u>O)

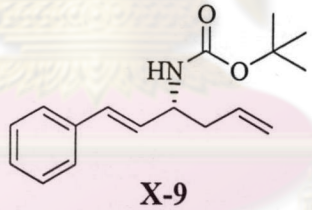
2.7.3 *N-tert*-butoxycarbonyl-(*R*)-1-(2′-methoxyphenyl)but-3-enamine



X-8

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid. 0.07 g, 0.31 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CHCl_3$) δ 1.39 [9H, s, $(C\underline{H}_3)_3CO$], 2.50 (2H, t, $C\underline{H}_2$ allyl), 3.82 (3H, s, $OC\underline{H}_3$), 4.96 (1H, br s, C<u>H</u>NH), 5.01 (2H, m, CH=C<u>H</u>$_2$), 5.64 (1H, m, C<u>H</u>=CH$_2$), 6.82-7.24 (4H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.4 [$(\underline{C}H_3)_3CO$], 39.9 ($\underline{C}H_2$ allyl), 52.0 (<u>C</u>HNH), 55.3 ($O\underline{C}H_3$), 79.5 [$(CH_3)_3\underline{C}O$], 110.7 (CH=<u>C</u>H$_2$), 117.2, 120.5, 128.2, 134.9 (<u>C</u>H=CH$_2$)

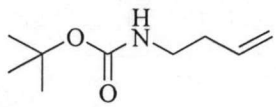
2.7.4 *N-tert*-butoxycarbonyl-(*R*)-1-(2′-phenylethenyl)but-3-enamine



X-9

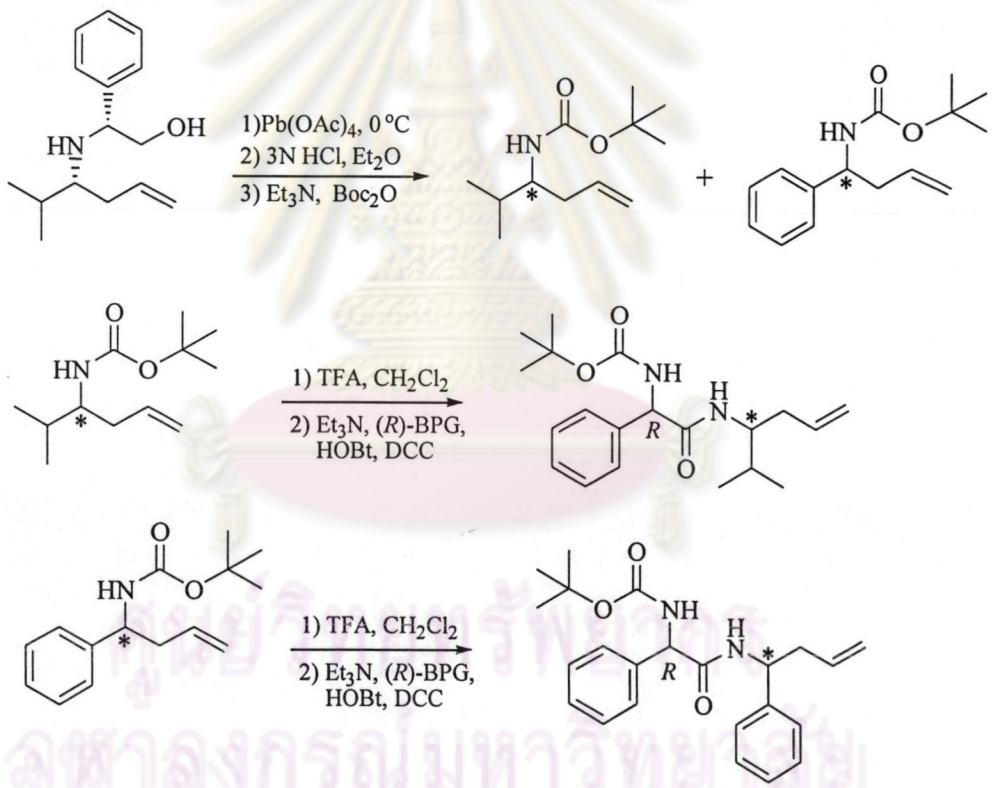
Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.04 g, 14 % yield (1 mmol scale); ^{1}H-NMR (200 MHz, $CHCl_3$) δ 1.42 [9H, s, $(C\underline{H}_3)_3CO$], 2.37 (2H, t, $C\underline{H}_2$ allyl), 4.35 (1H, br s, C<u>H</u>NH), 4.65 (1H, br s, CHN<u>H</u>), 5.14 (2H, dd *J*=7.9, 18.6 Hz, CH=C<u>H</u>$_2$), 5.73 (1H, m, C<u>H</u>=CH$_2$), 6.11 (1H, dd *J*=5.9, 15.9 Hz, PhCH=C<u>H</u>), 6.50 (1H, d *J*=15.9 Hz, PhC<u>H</u>=CH), 7.28 (5H, m, aromatic C<u>H</u>); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 28.4 [$(\underline{C}H_3)_3CO$], 39.8 ($\underline{C}H_2$ allyl), 51.7 (<u>C</u>HNH), 79.5 [$(CH_3)_3\underline{C}O$], 118.3 (CH=<u>C</u>H$_2$), 126.2, 126.4, 127.1, 127.5, 128.5, 129.9, 130.1, 133.8, 136.8 (<u>C</u>H=CH$_2$), 155.3 (Boc<u>C</u>O)

2.7.5 *N-tert*-butoxycarbonyl-1-but-3-enamine

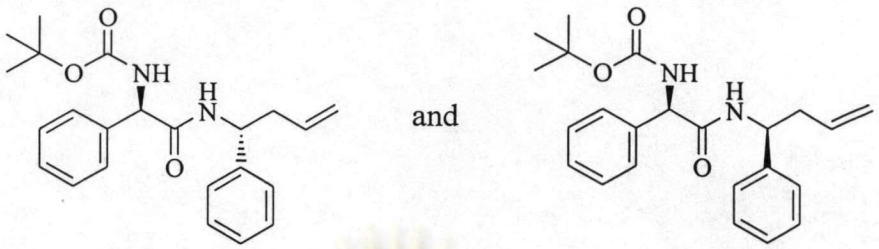


Inseparable from the reaction mixture; ^{1}H-NMR (200 MHz, $CHCl_3$) δ 1.35 [9H, s, $(C\underline{H}_3)_3CO$], 2.22 (2H, m, $C\underline{H}_2$ allyl), 3.15 (2H, m, $NHC\underline{H}_2$), 5.01 (2H, m, $CH=C\underline{H}_2$), 5.63 (1H, m, $C\underline{H}=CH_2$)

2.8 The coupling of Boc-phenylglycine to the homoallyl amine derived from the oxidative cleavage by $Pb(OAc)_4$ and HCl.



2.8.1 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-phenylbut-3-enamine (from acid hydrolysis)

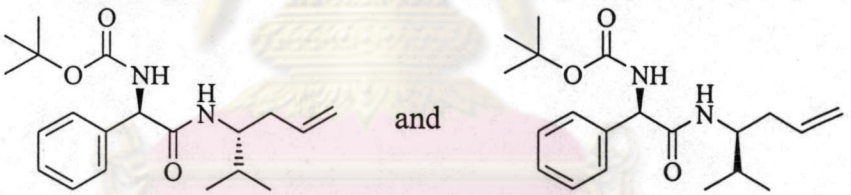


major and minor

XI-1

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.17 g, 44 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds* = 70:30 as determined by ^{1}H-NMR). Characterization by ^{1}H-NMR indicated that the major isomer is the same as **2.6.2** and the minor isomer is **2.6.1**.

2.8.2 *N*-[1-*N'*-(*tert*-butoxycarbonyl)-(*R*)-phenylglycyl]-(*R*)-1-isopropylbut-3-enamine (from acid hydrolysis)



major and minor

XI-2

Purified by flash column chromatography (5 % ethyl acetate-hexane) to give a white solid 0.19 g, 54 % yield (1 mmol scale) (inseparable mixture of diastereomer; *ds* = 80:20 as determined by ^{1}H-NMR). Characterization by ^{1}H-NMR indicated that the major isomer is the same as **2.6.5** and the minor isomer is **2.6.6**.