Experimental

All reactions were performed under an inert atmosphere of dry nitrogen. (*R*)- (+)-styrene oxide, 2-cyclopentenone, 2-cyclohexenone, $LiAlH_4$, thiophenols, *p*-methyl thiophenols and benzyl mercaptan were purchased from E-Merck and used as such. Anhydrous THF was obtained by distillation over sodium-benzophenone ketyl All other reagents were purified by literature procedures.

The ^1H and ^{13}C NMR were recorded in $CDCl_3$ with JEOL 400 MHz (model GSX 400). ^1H-NMR and ^{13}C-NMR data are reported in parts per million (δ) downfield from tetramethylsilane. The following abbreviations are used for the resonance patterns: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. IR spectra were recorded with Shimadzu (model 470) IR spectrophotometer. Optical rotations were measured with a JASCO DIP-370 digital polarimeter (with 50 mm and 10 mm cell). Mass spectra (high and low resolution mass spectra) were obtained from Finnigan MAT (model 8230) High Resolution Mass Spectrometer. SEM photographs were scanned by LEICA STEREOSCAN 440 scanning electron microscopy. Waters HPLC with Waters 486 Tunable absorbance detector (λ) containing chiralcel OD column for studying enantiomeric excess. ICP–AES analysis was done by ARC 3410 ICP-AES with mini torch.

Synthesis of monomer

To a cooled solution of vinyl benzylamine (5 mmol) in 2 ml of methanol (*R*)-(+)-styrene oxide (10 mmol) in 4 ml methanol were added slowly drop by drop at 0^oC for 15 minutes, stirred for 1h and refluxed for 5 h. After completion of the reaction, the solvent was removed under reduced pressure to give a syrupy mass which on column chromatography (alumina) using ethylacetate : hexane (10:90) as eluent gave the product (yield 30%).

(*R*,*R*)-3-aza-3-*p*-vinylbenzyl-1,5-dihydroxy-1,5-diphenylpentane (**2**)

Yield 30%. ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.72-2.83 (m, 4H), 3.81 (bs, 2H, OH), 3.83 (dd, 2H, 13.2, & 51.8 Hz), 4.75 (d, 2H, 8.5 Hz), 5.25 (d, 1H, 11.2 Hz), 5.75 (d, 1H, 17.5 Hz), 6.68 (dd, 1H,17.5 & 11.2 Hz), 7.20-7.39 (m, 14H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 59.74, 62.53, 70.77, 114.07, 125.86, 127.41, 127.53, 128.50, 129.14, 138.03, 137.70, 142.10. IR (cm^{-1}, neat) 3376, 3024, 2832, 1946, 1875, 1805, 1491, 1446, 1292, 1056, 758, 701. MS (EI, m/z) 373 (M^+), 339, 270, 240, 208, 135, 107. HRMS (m/z) calculated 373.20418 and observed mass 373.0225. $[\alpha]_D = -118.01$, C = 2.1, $CHCl_3$.

Preparation of catalyst :

To one mole of (*R*,*R*)-3-aza-3-(*p*-vinylbenzyl)-1,5-diphenyl-1,5-dihydroxy pentane one mole of divinylbenzene and respective mole of styrene were added in the presence of 10 mg of benzoylperoxide and sealed at nitrogen atmosphere. Then the reaction mixture was heated at 70°C for 48 hours. The resulting polymer was washed with methanol and used as such. To 250 mg of **poly2a,** 10 mg of $LiAlH_4$ (0.268 mmol) in dry THF was added slowly at 0^oC and stirred for 30 minutes.

Estimation of evolution of hydrogen gas :

To 500 mg of **poly2a** in THF a solution of $LiAlH_4$ (10 mg, 0.268 mmol) in dry THF was added drop by drop at 0^oC. The hydrogen gas evolved, measured by usual displacement technique was 23.58 ml (calculated 23.74 ml).

ICP analysis :

To 580 mg of **poly2a** in dry THF a solution of $LiAlH_4$ (12 mg, 0.32 mmol) in dry THF was added and stirred for 30 minutes at 0^oC, after removal of the solvent 44 mg of the complex was weighed and made upto 10 ml using 1:1 mixture of water and conc. nitric acid. The aquous solution was filtered and this solution was used for ICP analysis. The metal contents were found to be Al : 63.20 mg/L (calculated 63.27 mg/L) and Li : 16.12 mg/L (calculated 16.27 mg/L).

Michael addition reaction of nitromethane to chalcone:

To the **LiAl-poly2a,** 0.5 mmol chalcone was added and then 0.5 mmol of nitromethane was added subsequently. After 7 hours it was quenched with 1N HCl, filtered the polymer ligand and the mixture was extracted with ethylacetate. The organic layer was washed successively with saturated $NaHCO_3$ solution, brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave a syrupy mass, which on flash chromatography using acetone : hexane (6 : 94) as eluent gave the product (yield 90%).

Nitro adduct (**3**)

Yield 90%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.38-3.5 (m, 2H), 4.18-4.24 (m, 1H), 4.63-4.83 (m, 2H), 7.20-7.9 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.42, 41.59, 79.61, 127.53, 127.92, 128.20, 128.74, 128.80, 129.12, 133.69, 136.44, 139.23. IR (CCl_4, cm^{-1}) 3056, 2944, 2864, 1692, 1596, 1558, 1491, 1449, 1372, 1225, 1200, 1177, 1097, 1027. MS (EI, m/z) 223 (M-46, NO_2). $[\alpha]_D$ = 21, ee = 51% C = 1.6, CH_2Cl_2 (lit: $[\alpha]_D$ = 11, ee = 27% C = 4.0, CH_2Cl_2)

Michael addition reaction of thiols to cycloalkenones:

To the **LiAl-poly2a** 0.5 mmol of cycloalkenones and 0.5 mmol of thiols were added subsequently. After 30 minutes it was quenched with 1N HCl, filtered the polymer ligand and the mixture was extracted with ethylacetate. The organic layer was washed successively with saturated $NaHCO_3$ solution, brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave a syrupy mass, which on flash chromatography using acetone : hexane (4 : 96) as eluent gave the product.

(*R*)-3-(phenylthio)cyclopentanone (**4**)

Yield 95%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.96-2.18 (m, 1H) 2.21-2.29 (m, 2H), 2.31-2.37 (m, 1H) 2.45 (dd, 1H, 6.8 & 18.0 Hz), 2.59 (dd, 1H, 6.8 & 18.5 Hz), 3.85-3.92 (m, 1H), 7.24-7.41 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 29.18, 36.62, 43.22, 45.09, 127.27, 128.98, 131.81, 134.08, 216.6. IR (CCl_4, cm^{-1}) 1748 (C=O). M.S (EI, m/z): 192 (M$^+$) 110, 83, 55. $[\alpha]_D$ = 3.3, ee = 41%, C = 1.0, CCl_4 (lit: $[\alpha]_D$ = 1.8, ee = 22.5%, C = 1.54, CCl_4)

(*R*)-3-(phenylthio) cyclohexanone (**5**)

Yield 90%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.67-1.78 (m, 2H), 2.10-2.15 (m, 2H), 2.28-2.40 (m, 3H), 2.66 (dd, 1H, 4.4 and 14.2 Hz), 3.39-3.45 (m, 1H), 7.25-7.32 (m, 3H), 7.4-7.43 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 23.9, 31.09, 40.75, 45.98,47.62, 127.66, 128.95, 132.92, 133.08, 208.61. IR (CCl_4,cm^{-1}) (C=O) 1715. MS (EI, m/z): 206 (M$^+$), 110, 97, 77, 55. $[\alpha]_D$ = 40.7, ee = 57% C = 1.6, benzene (lit: $[\alpha]_D$ = 16.4, ee = 22.5% C = 1.0, benzene.)

(*R*)-3-(p-methyl-phenylthio) cyclopentanone.(**6**)

Yield 90%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.94-2.20 (m, 1H), 2.14-2.30 (m, 2H), 2.34 (s, 3H), 2.46 (dd, 1H, 6.8 & 18.3 Hz), 2.55 (dd, 2H, 6.8 & 18.3 Hz) 3.77-3.89 (m, 1H), 7.12 (d, 2H, 8.5Hz), 7.3 (d, 3H, 8.5Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.08, 29.26, 36.73, 43.80, 45.14, 129.85, 130.26, 132.77, 137.71, 216.43. IR (CCL_4, cm^{-1}) 1747. MS (EI, m/z) 206 (M$^+$), 124.91, 55. $[\alpha]_D$ = 4.2, ee = 52 % C = 1.20, CCl_4 (lit: $[\alpha]_D$ = 1.8, ee = 22.8 % C = 2.00, CCl_4.)

(*R*)-3-(p-methyl-phenylthio)cyclohexanone (**7**)

Yield 90%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.65-1.72 (m, 2H) 2.09-2.15 (m, 2H), 2.32 (s,3H), 2.27-2.37 (m, 3H), 2.62-2.67 (dd, 1H, 4.4 & 14.2 Hz), 3.31-3.37 (m, 1H), 7.11 (d, 2H, 8.3 Hz), 7.32 (d, 2H, 8.3 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.00, 23.91, 31.12, 40.72, 46.33, 47.65, 129.70, 133.81, 137.98, 208.75. IR (CCl_4, cm^{-1}) 1718 (C=O). MS (EI, m/z) 220 (M$^+$), 124, 97, 79, 55. $[\alpha]_D$ = 23.2, ee = 33% C = 1.2, benzene (lit: $[\alpha]_D$ = +70, ee = 100% C = 2.0, benzene.)

(*R*)-3-(benzylmercapto)cyclopentanone (**8**)

Yield 85%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.64-1.69 (m, 2H), 2.04-2.06 (m, 2H), 2.27 (m, 1H), 2.37 (dd, 1H, 10.3 & 3.9 Hz), 2.62 (dd, 1H, 3.9 & 10.3 Hz), 2.91(m, 1H), 3.72(S, 2H), 7.22-7.29(m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 23.98, 31.12, 34.8, 40.87, 41.87, 47.66, 127.03, 128.39, 128.65, 137.84, 208.59. IR (neat,cm^{-1}) 1708 (C=O). MS (EI,m/z) 206 (M$^+$), 149, 135, 107, 91.

(*R*)-3-(benzylmercapto)cyclohexanone (**9**)

Yield 90%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.2-1.25 (m, 2H), 1.6-1.7 (m, 2H), 2.05-2.07 (m, 2H), 2.29 (m, 1H), 2.37 (dd, 1H, 10.3 & 3.9 Hz), 2.64 (dd, 1H, 10.3 & 3.9 Hz), 2.92 (m, 1H), 3.73 (S, 2H), 7.22-7.29 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 24.04, 31.2, 34.8, 40.87, 41.94, 47.73, 127.09, 128.44, 128.56, 137.87, 208.68. IR (neat, cm^{-1}) 1705 (C=O). MS (EI, m/z) 220 (M$^+$), 149, 135, 107, 91.

Michael addition reaction of benzylamine to ethylcinnamate:

To the LiAl-poly2a 0.5 mmol ethyl cinnamate was added and then 0.5 mmol of benzylamine was added subsequently. After 12 h it was quenched with 1N HCl, filtered the polymer ligand and the mixture was extracted with ethylacetate. The organic layer was washed successively with saturated $NaHCO_3$ solution, brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave a syrupy mass, which on flash chromatography using acetone : hexane (20 : 80) as eluent gave the product.

Amine adduct (**10**)

Yield 60%. ^{1}H NMR (Acetone –D_6, 400 MHz) δ: 1.33 (t, 3H, 7.3 Hz), 2.8 (dd, 2H), 3.1 (bs, 1H), 3.64 (t, 1H), 3.94 (s, 2H), 4.26 (q, 2H, 7.3 Hz), 7.34 (m, 10H). ^{13}C NMR (Acetone-D_6, 100 MHz) δ: 18.41, 33.81, 58, 59.2, 64.39, 126.8, 127.5, 127.9, 128.64, 128.84, 129.67, 130.22, 130.78, 171.8. IR (CCl_4, cm^{-1}) 3680, 3568, 3376, 2272, 1654, 1609, 1254, 1024, 732, 704, 646, 617. MS (EI, m/z) 283, 239, 148, 106, 91. $[\alpha]_D$ = 11.5, ee = 81 % C = 1.14, acetone (lit: $[\alpha]_D$ = 5.7, ee = 40 %, C = 0.5, acetone).