The commercial magnesium oxide (CM-MgO, S.A: 25 m²/g) was purchased from Aldrich. The conventionally prepared magnesium oxide (NanoActive™ MgO abbreviated as NA-MgO, S.A: 252 m²/g) and aerogel prepared magnesium oxide (NanoActive™ MgO Plus abbreviated as NAP-MgO: 590 m²/gm) samples were purchased from NanoScale Materials Inc, Manhattan, KS 66502, USA. All the samples were activated at 250 ºC before use. Benzaldehyde, substituted benzaldehydes, nitroalkanes and all chiral ligands were purchased from Aldrich and used as such. Silylated NAP-MgO, NA-MgO, protected –OH groups of binol were prepared according to the literature.1,2

General: ¹H spectra were recorded on a Varian Gemini 200 MHz Spectrometer. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. High Performance Liquid Chromatography (HPLC) was performed using the following apparatus; SHIMADZU LC-10AT (liquid Chromatograph), SHIMADZU SPD-10A (UV detector), and SHIMADZU C-R6A Chromatopac. TGA-DTA-MS thermograms were recorded on Mettler-Toledo TGA/SDTA 851® instrument coupled to MS Balzers Thermostar GSD 300T using open alumina crucibles, containing 8-10 mg of the sample with a linear heating in the temperature range of 25 -1000 ºC at a rate of 10 ºC/min in nitrogen atmosphere. ACME silica gel (100-200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F254 plates. Optical rotations were obtained on a Jasco P-1020 Polarimeter and reported as follows. [α] temperature wavelength, concentration (c = g/100 mL), and solvent. The absolute stereochemistry was assigned as (S) by comparison of the optical rotation with the literature values. X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about 10⁻⁹ Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using the Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species were first determined using the spectrum of a pure sample. The location and FWHM of the products, which were not
obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible to within $\pm 0.1$ eV.

**General procedure for the preparation of 1-phenyl-2-nitroethanol:** A mixture of nitromethane (5.0 mmol, 0.305 g), (S)-binol (0.139 mmol, 0.040 g) and catalyst (0.125 g) was introduced into a 50 mL round bottomed flask containing dry THF (10 mL) at $-78$ °C and stirred 1 h under nitrogen atmosphere. To the reaction mixture benzaldehyde (1 mmol, 0.1 mL) was added at that temperature. After completion of the reaction, (monitored by TLC), the reaction mixture was centrifuged to separate the catalyst and washed several times with ether. The combined organic layers were dried over MgSO$_4$ and the solvent was removed under reduced pressure. After purification by flash chromatography on silica gel using 5% ethyl acetate in petroleum ether, the Henry product was obtained.

**General procedure for the asymmetric Michael addition:** A mixture of nitromethane (50 mmol, 3.05 g), (1R, 2R)-(-)-1,2-diaminocyclohexane (0.25 mmol, 0.02854 g) and catalyst (0.125 g) was introduced into a 50 mL round bottomed flask containing dry THF (5 mL) at $-20$ °C and stirred 1 h under nitrogen atmosphere. To the reaction mixture, chalcone (1 mmol, 0.208 g) was added at that temperature and stirring was continued. After completion of the reaction, (monitored by TLC), the reaction mixture was centrifuged to separate the catalyst and washed several times with ether. The combined organic layers were dried over MgSO$_4$ and the solvent was removed under reduced pressure. After purification by flash chromatography on silica gel using 5% ethyl acetate in petroleum ether, the Michael adduct was obtained.

**Reuse of the catalysts:**

The reusability of the catalysts was checked by performing the AH of benzaldehyde on 10-mmol scale. NAP-MgO shows consistent activity for five cycles. After completion of the reaction of each cycle, the catalyst was recovered by centrifugation and activated under nitrogen flow for 1 h at 250 °C.

**Characterization of Products:** The following compounds are known compounds, and their spectra were in accordance with those reported in the literature. The absolute configuration of products was determined by comparison of the specific rotation with literature value. The enantiomeric excess of the nitroalcohol product and Michael adducts were determined by HPLC analysis with chiral stationary phases.

(S)-1-Phenyl-2-nitroethanol (3a): $[\alpha]_D^{25}$ + 31.8 (c 1.0, CH$_2$Cl$_2$) [Lit.$^3$ + 33.02 (c 3.71, CH$_2$Cl$_2$)]; $^1$H NMR $\delta$ 2.95 (d, 1 H, $J$=3.9 Hz), 4.42 (dd, 1 H, $J$=13.2, 2.9 Hz), 4.54-4.49 (dd, 1 H, $J$=13.2, 9.8 Hz), 5.45-5.42 (m, 1 H ), 7.42-7.35(m, 5 H); HPLC (Diacel Chiralcel OD, 3% isopropanol in hexane, flow rate 1.0 mL/min): $t_R$ =37.0 (minor), 43.8 (major).

(S)-1-(4-Nitrophenyl)-2-nitroethanol (3b): $[\alpha]_D^{25}$ + 39.7 (c 1.0, CH$_2$Cl$_2$) [Lit.$^4$ –31.6 (c 1.05, CH$_2$Cl$_2$)]; $^1$H NMR $\delta$ 3.09 (d, 1 H, $J$=4.0 Hz), 4.65-4.55 (m, 2 H), 5.62 (dd, 1H,
J=8.0, 4.0 Hz), 7.63-8.32(m, 4 H); HPLC (Diachel Chiralcel OD-H, 15% isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 19.6 \) (minor), 47.5 (major).

(S)-1-(2-Nitrophenyl)-2-nitroethanol (3c): \([\alpha]_D^{25} + 204 \) (c 1.0, CH\(_2\)Cl\(_2\)) [Lit.\(^4\)–227 (c 1.0, CH\(_2\)Cl\(_2\))]; \( ^1\)H NMR \( \delta 3.15\) (d, 1 H, \( J = 4.2\) Hz), 4.57 (dd, 1 H, \( J = 13.9, 8.8\) Hz), 4.9(dd, 1 H, \( J = 13.9, 2.2\) Hz), 6.07 (ddd,1 H, \( J = 8.8, 4.2, 2.2\) Hz ), 8.11-7.55(m, 4 H); HPLC (Diachel Chiralcel OD-H, 15% isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 19.6 \) (minor), 47.5 (major).

(S)-1-(4-Chlorophenyl)-2-nitroethanol (3d): \([\alpha]_D^{25} + 40.9 \) (c 2.0, CH\(_2\)Cl\(_2\)) [Lit.\(^4\)–37.6(c 2.03, CH\(_2\)Cl\(_2\))]; \( ^1\)H NMR \( \delta 3.14\) (d, 1 H, \( J = 4.0\) Hz), 4.48 (dd, 1 H, \( J = 13.3, 2.9\) Hz), 4.56 (dd, 1 H, \( J = 13.3, 9.5\) Hz), 5.44-5.41 (m, 1 H), 7.38-7.32(m,4 H); HPLC (Diachel Chiralcel OD-H, 15 % isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 11.1 \) (minor), 13.3(major).

(S)-1-(4-Methoxyphenyl)-2-nitroethanol (3e): \([\alpha]_D^{25} + 29.7 \) (c 1.0, CH\(_2\)Cl\(_2\)) [Lit. –31.65 (c 1.05, CH\(_2\)Cl\(_2\))]; \( ^1\)H NMR \( \delta 3.09\) (d, 1 H, \( J = 4.0\) Hz,), 3.8 (s, 3 H), 4.65-4.55 (m, 2 H), 5.62 (dd, 1 H, \( J = 8.0, 4.0\) Hz), 7.63-8.32(m, 4 H). HPLC (Diachel Chiralcel OD-H, 15% isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 23.6 \) (minor), 27.5 (major).

(S)-1-(2-Chlorophenyl)-2-nitroethanol (3f): \([\alpha]_D^{25} + 44.5 \) (c 1.21, CH\(_2\)Cl\(_2\)) [Lit. 4 –52.7(c 2.03, CH\(_2\)Cl\(_2\)); \( ^1\)H NMR \( \delta 3.01\) (d, 1 H, \( J = 4.4\) Hz), 4.43 (dd, 1 H, \( J = 13.7, 9.8\) Hz), 4.65 (dd, 1 H, \( J = 13.7, 3.3\) Hz), 5.84-5.81 (m, 1 H) , 7.64-7.27(m,4 H); HPLC (Diacel Chiralcel OD-H, 10 % isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 16.1 \) (minor), 20.3(major).

(S)-1-(2-Methoxyphenyl)-2-nitroethanol (3g): \([\alpha]_D^{25} + 33.5 \) (c 1.00,CH\(_2\)Cl\(_2\)) [Lit. 4 –31.6 (c 1.05, CH\(_2\)Cl\(_2\)); \( ^1\)H NMR \( \delta 3.12\) (d, 1 H, \( J = 6.1\) Hz.), 3.90 (s, 3 H, OCH \(_3\)), \( 4.65\) (dd, 1 H, \( J = 13.2, 9.0\) Hz), 4.67 (dd, 1 H, \( J = 13.2, 3.3\) Hz), 5.65 (ddd,1 H, \( J = 9.2, 6.1, 3.3\) Hz ), 6.93-7.46(m, 4 H); HPLC (Diacel Chiralcel OD-H, 10 % isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 13.5 \) (minor), 15.9 (major).

(S)-1-(4-Methylphenyl)-2-nitroethanol (3h): \([\alpha]_D^{25} + 32.4 \) (c 1.0, CH\(_2\)Cl\(_2\)) [Lit.5 –31.6 (c 1.05, CH\(_2\)Cl\(_2\))]; \( ^1\)H NMR \( \delta 2.3 \) ( s, 3 H), 3.09 (d, 1 H, \( J = 4.0\) Hz), 4.65-4.55 (m, 2 H), 5.62 (dd, 1 H, \( J = 8.0, 4.0\) Hz), 7.63-8.32(m, 4 H); HPLC (Diachel Chiralcel OD-H, 15% isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 27.6 \) (minor), 32.5 (major).

(S)-1-(2-Methylphenyl)-2-nitroethanol (3i): \([\alpha]_D^{25} + 32.3 \) (c 1.0, CH\(_2\)Cl\(_2\)) [Lit.\(^5\)–31.6 (c 1.05, CH\(_2\)Cl\(_2\))); \( ^1\)H NMR \( \delta 2.3 \) ( s, 3 H), 3.09 (d, 1 H, \( J = 4.0\) Hz), 4.65-4.55 (m, 2 H), 5.62 (dd, 1 H, \( J = 8.0, 4.0\) Hz), 7.63-8.32(m, 4 H); HPLC (Diachel Chiralcel OD-H, 15% isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 10.0 \) (minor), 14.3 (major).

(S)-1-Cyclohexyl-2-nitroethanol (3j): \([\alpha]_D^{25} + 16.0 \) (c 5.0, CHCl\(_3\)) [Lit.\(^4\) + 15.87 (c 5.01, CHCl\(_3\))]; \( ^1\)H NMR \( \delta 1.29-1.0\) (m, 5 H). 1.46-1.39 (m, 1 H), 1.70-1.62 (m, 2 H), 1.82-1.73 (m, 3 H), 2.77 (d, 1H, \( J = 4.9\) Hz), 4.0 (m, 1 H), 4.40 (dd, 1 H, \( J = 12.8, 9.0\)Hz), 4.46 (dd, 1 H, \( J = 12.8, 2.9\) Hz); HPLC (Diachel Chiralcel AD, 3% isopropanol in hexane, flow rate 0.8 mL /min): \( t_R = 26.0 \) (minor), 28.0 (major).
(S)-3,3-Dimethyl-1-nitrobutan-2-ol (3k): \([\alpha]_D^{25} + 27.0\) (c 1.0, CH2Cl2) [Lit.4 –21.6 (c 1.0, CH2Cl2)]; \(^1\)H NMR \(\delta\) 0.94-(s, 9 H), 2.6 (d, 1 H, J= 4.9 Hz), 4.0 (m, 1 H), 4.35 (dd, 1 H, J= 12.7, 9.8 Hz), 4.5(dd, 1 H, J= 12.7, 1.9 Hz); HPLC (Diaceg Chiralcel OD-H, 2% isopropanol in hexane, flow rate 0.8 mL/min): t\(_R\) =17.0 (minor), 19.9 (major).

(S)-1-Nitrohexan-2-ol (3l): \([\alpha]_D^{25} + 5.0\) (c 2.5, CH2Cl2) [Lit.4 –9.3 (c 2.73, CH2Cl2 )]; \(^1\)H NMR \(\delta\) 0.9 (t, 3 H, J= 6.3Hz), 1.30-1.58 (m, 6 H), 2.82 (bs, 1 H), 4.3 (m, 1 H), 4.36 (dd, 1 H, J= 13.1, 8.6 Hz), 4.42 (dd, 1 H, J= 13.1, 2.9 Hz); HPLC (Diacel Chiralcel AD, 2% isopropanol in hexane, flow rate 0.8 mL/min): t\(_R\) =33.6 (minor), 44.7 (major).

(S)-2-hydroxy-2-methyl-3-nitro-propionic acid ethyl ester (5a): \([\alpha]_D^{25} –11.0\) (c 1.0, CH2Cl2) [Lit.6 + 10.2 (c 1.19, CHCl3 )]; \(^1\)H NMR (CDCl3) \(\delta\) 1.33 (t, J= 7.2 Hz, 3H), 1.45 (s, 3H), 3.71 (s, 1H), 4.34 (m, 2H), 4.55 (d, J= 14 Hz, 1H), 4.83 (d, J= 14 Hz, 1H). HPLC (Diacel Chiralcel OD column, 3% isopropanol in hexane, flow rate 1.0mL/min, 215nm); tr 32.5(minor) , 44.75(major)

(S)-2-hydroxy-2-nitromethyl butyric acid ethyl ester (5b): \([\alpha]_D^{25} –22.0\) (c 1.0, CHCl3) [Lit.6 + 20.9 (c 1.19, CHCl3 )]; \(^1\)H NMR (CDCl3) \(\delta\) 0.89 (t, J= 7.2 Hz, 3H), 1.30 (t, J= 6.8 Hz, 3H), 1.68(m, 2H), 3.72 (s, 1H), 4.32 (m, 2H), 4.54 (d, J= 13.5 Hz, 1H), 4.81 (d, J= 14 Hz, 1H). HPLC (Diacel Chiralcel OD column, 3% isopropanol in hexane, flow rate 1.0mL/min, 215nm); tr 28.13(minor) , 46.27(major)

(R)– 4-Nitro-1,3-diphenyl-butane-1-one: (7a) \([\alpha]_D^{25} +25.5\) (c 1.0, CHCl3) [Lit.7 –9.3 (c 1.0, CHCl3 )]; \(^1\)H NMR (CDCl3) \(\delta\) 3.46 (d, J=5.2 Hz, 1H), 3.48 (s, 1H), 4.13-4.30 (m, 1H), 4.69 (dd, J=8.0 and 7.8 Hz, 1H), 4.85 (dd, J=6.6 and 6.6 Hz, 1H), 7.25-7.94 (m, 10 H)., HPLC (Diacel Chiralcel AS, 10% isopropanol in hexane, flow rate is 1.2 mL/min): t\(_R\) =12.7 (minor) 16.3 (major).

(R)– 3-(4-Chlorophenyl)-4-nitro-1-phenyl-butane-1-one:(7b): \([\alpha]_D^{25} +23.6\) (c 1.0, CHCl3) [Lit.7 –10.8 (c 1.0, CHCl 3 )]; \(^1\)H NMR (CDCl3) \(\delta\) 3.43 (d, J=7.0Hz, 2H), 4.14-4.30 (m, 1H ), 4.65 (dd, J= 8.0 and 8.0 Hz, 1H), 4.82 (dd, J=6.4 and 6.0 Hz, 1H), 7.21-7.91 (m, 9 H). HPLC (Diacel Chiralcel AD, 10% isopropanol in hexane, flow rate is 1.2 mL/min): t\(_R\) =16.8 (minor) 25.4 (major).

(R)– 3-Naphthalen-2-yl-4-nitro-1-phenyl-butane-1-one:(7c) \([\alpha]_D^{25} +16.0\) (c 1.0, CHCl3) [Lit.7 –7.4 (c 1.0, CHCl3 )]; \(^1\)H NMR (CDCl3) \(\delta\) 3.46 (d, J=7.0Hz, 2H), 4.14-4.30 (m, 1H ), 4.65 (dd, J= 8.0 and 8.0 Hz, 1H), 4.82 (dd, J=6.4 and 6.0 Hz, 1H), 7.21-7.96 (m, 12 H). HPLC (Diacel Chiralcel AD, 10% isopropanol in hexane, flow rate is 1.2 mL/min): t\(_R\) =15.8 (minor) 19.3(major).

(R)–4-Methyl-4-nitro-1,3-diphenylpentan-1-one (7d): \([\alpha]_D^{25} +80\) (c 1.0, CHCl3) [Lit.7 –30.5 (c 1.0, CHCl3 )]; \(^1\)H NMR (CDCl3) \(\delta\) 1.54 (s, 3 H), 1.63 (s, 3H ), 3.27 (dd, J= 3.2 and 3.6 Hz), 3.67 (dd, J=10.4 and 10.3 Hz, 1H), 4.15 (dd, J=3.4 and 3.4 Hz, 1H), 7.25-7.85 (m, 10 H). HPLC (Diacel Chiralcel OJ, 10% isopropanol in hexane, flow rate is 1.2 mL/min): t\(_R\) =25.8 (minor) 35.4 (major).
(R)-1-(4-Chlorophenyl)-4-methyl-4-nitro-3-phenylpentan-1-one: (7e): $[\alpha]_D^{25} +89.8$ (c 1.0, CH$_2$Cl$_2$) [Lit.$^8$ +58.5 (c 1.0, CH$_2$Cl$_2$)]; $^1$H NMR (CDCl$_3$) $\delta$ 1.46 (s, 3H), 1.55 (s, 3H), 3.16 (dd, J= 17.3, 3.1 Hz, 1H), 3.55 (dd, J= 17.3, 10.4 Hz, 1H), 4.04 (dd, 1H), 7.13-7.21 (m, 5H), 7.32 (d, 2H), 7.72 (d, 2H).

(R)-1-(4-Tolyl)-4-methyl-4-nitro-3-phenylpentan-1-one (7f): $[\alpha]_D^{25} +67$ (c 1.0, CH$_2$Cl$_2$) [Lit.$^8$ +65.7 (c 1.0, CH$_2$Cl$_2$)]; $^1$H NMR (CDCl$_3$) $\delta$ 1.54 (s, 3H), 1.63 (s, 3H), 2.40 (s, 3H), 3.25 (dd, J= 17.2 and 3.6 Hz, 1H), 3.67 (dd, J=17.2, 3.7 Hz, 1H), 4.15 (dd, J=3.4 and 3.4 Hz, 1H), 7.22-7.78 (m, 9H).

(R)-4-Methyl-4-nitro-3-(4-nitrophenyl)-1-phenylpentan-1-one: (7g) $[\alpha]_D^{25} +95.4$ (c 1.0, CH$_2$Cl$_2$) [Lit.$^8$ +99.8 (c 1.0, CH$_2$Cl$_2$)]; $^1$H NMR (CDCl$_3$) $\delta$ 1.60 (s, 3H), 1.65 (s, 3H), 3.40 (dd, J=17.7, 10.6 Hz, 1H), 3.71 (dd, J= 17.7, 3.2 Hz, 1H), 4.25 (dd, J=16.8, 3.2 Hz, 1H), 7.43-8.16 (m, 9H).

(R)-4-Methyl-4-nitro-3-(4-tolyl)-1-phenylpentan-1-one: (7h) $[\alpha]_D^{25} +77$ (c 1.0, CH$_2$Cl$_2$) [Lit.$^8$ +52.9 (c 1.0, CH$_2$Cl$_2$)]; $^1$H NMR (CDCl$_3$) $\delta$ 1.55 (s, 3H), 1.63 (s, 3H), 2.29 (s, 3H), 3.25 (dd, J=17.3, 3.3 Hz, 1H), 3.66 (dd, J= 17.3, 10.6 Hz, 1H), 4.12 (dd, 1H), 7.09-7.87 (m, 9H).

**Figure S1.** XPS high resolution narrow scans for Mg 2p (a) NAP-MgO and (b) nitromethane treated NAP-MgO.
Figure S2. DTA-TGA-MS of nitromethane treated NAP-MgO

References: