Supplementary Materials:

On the Exceptionally High Loading of L-proline on Multi-wall Carbon Nanotubes

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1. Experimental procedures

1.1 Typical procedure of Mannich reaction.

L-proline/MWCNTs (0.050 g, containing 0.29 mmol of L-proline), 4-nitrobenzaldehyde (0.151 g, 1.0 mmol) and *p*-methoxyaniline (0.135 g, 1.1 mmol) were mixted in a round bottom flask, and then 10 mL of acetol in DMSO (acetol:DMSO = 1:9) was injectedwith stirring under Ar. After the reaction was complete, the mixture was treated following the similar procedure as above Aldol reaction. The obtained crude product was purified by column chromatography (hexane/ethyl acetate, 1:4). The conversion yields of product were determined by high performance liquid chromatography.

1.2 Typical procedure of Michael reaction.

L-proline/MWCNTs (0. 050 g, containing 0.29 mmol of L-proline) and 2-nitroviny benzene (0.149 g, 1.0 mmol) were mixed in a small sample bottle, followed by the addition of cyclohexane (2.0 mL) and isopropanol (0.5 mL). With stirring, *n*-pentanal (0.258 g, 3.0 mmol) was added in one portion. After the reaction was complete, the mixture was treated following the similar procedure as above Aldol reaction. The obtained crude product was purified by column chromatography (hexane/ethyl acetate, 1:6). The conversion yields of product were determined by high performance liquid chromatography.

1.3 Typical procedure of α-oxyamination reaction.

L-Proline/MWCNTs (0.050 g, containing 0.29 mmol of L-proline) and cyclohexanone (0.196 g, 2.0 mmol) were mixed in DMF (4.0 mL), followed by the addition of a solution of nitrosobenzene (0.107 g, 1.0 mmol) in DMF (2.0 mL) dropwise with stirring. After the reaction was complete, the mixture was treated following the similar procedure as above Aldol reaction. The obtained crude product was purified by column chromatography (hexane/ethyl acetate, 1:6). The conversion yields of product were determined by high performance liquid chromatography.

1.4 Typical procedure of Knoevenagel condensation.

L-proline/MWCNTS (0.050 g, containing 0.29 mmol of L-proline), benzaldehyde (0.106 g, 1.0mmol) and diethyl malonate (0.240 g, 1.5 mmol) were mixed in 2.0 mL of DMF at room temperature with stirring. After the reaction was complete, the mixture was treated following the similar procedure as above Aldol reaction. The obtained crude product was purified by column chromatography (hexane/ethyl acetate, 1:6). The conversion yields of product were determined by high performance liquid chromatography.

2. Supplementary data and figures

2.1 L-proline/MWCNTs

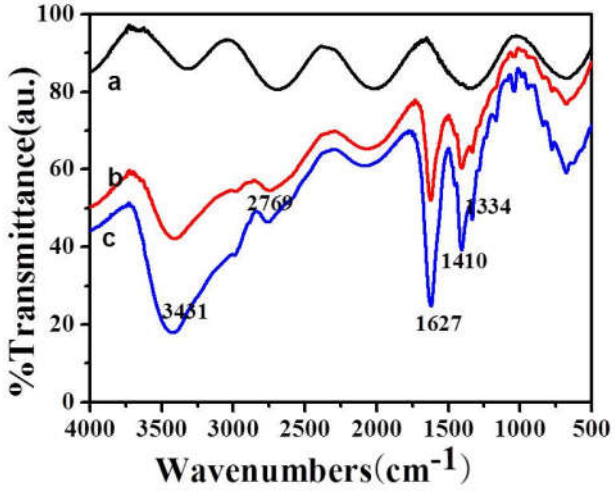


Figure S1. Infrared spectra of (a) MWCNTs, (b) L-proline, and (c) L-proline/MWCNTs.

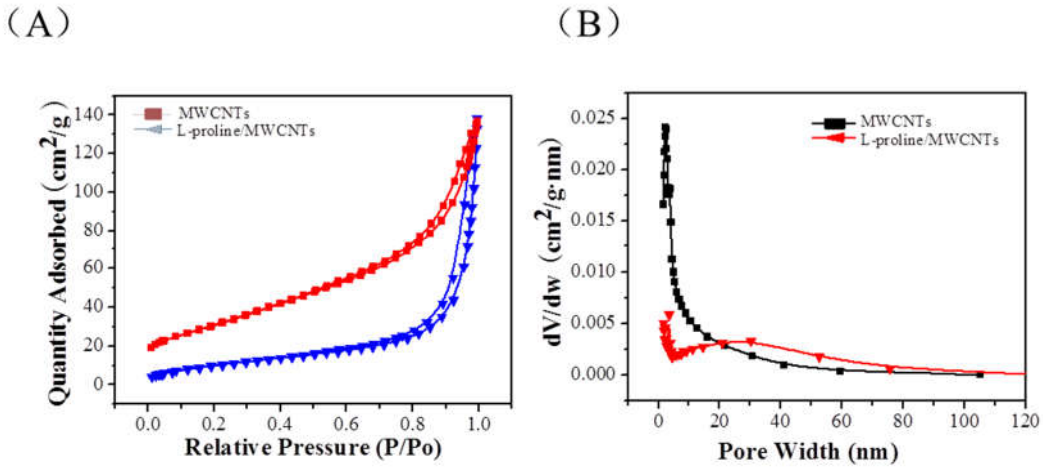


Figure S2. (A) N_2 adsorption and desorption curves of MWCNTs (red trace) and L-proline/MWCNTs (blue trace), (B) The pore size distribution of MWCNTs (black trace) and L-proline/MWCNTs (red trace).

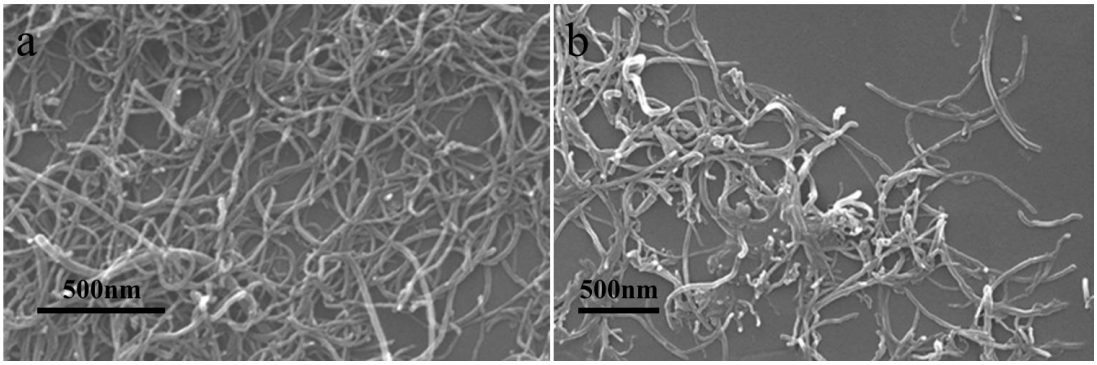


Figure S3. SEM of (a) MWCNTs and (b) L-proline/MWCNTs.

2.2 Thermogravimetric analysis (TGA)

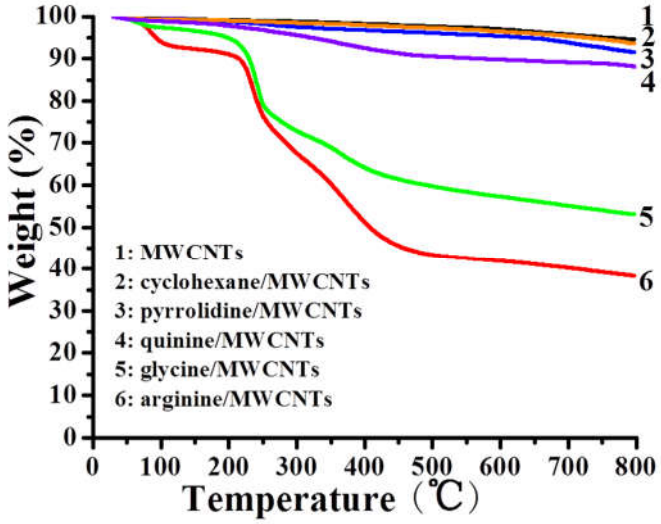


Figure S4. TGA of (1) MWCNTs, (2) cyclohexane/MWCNTs, (3) pyrrolidine/MWCNTs, (4) quinine/MWCNTs , (5) glycine/MWCNTs, (6) arginine/MWCNTs.

2.3 Aldol reaction

The product was isolated and determined as 4-hydroxy-4-(4-nitrophenyl)-butan-2-one with ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.21-8.19 (m, 2H), 7.54-7.51 (m, 2H), 5.27-5.24 (m, 1H), 3.58 (s, 1H), 2.89-2.83 (m, 2H), 2.21 (s, 3H). The conversion yield was determined by HPLC (i-PrOH/hexane = 7:93, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 12.02 min). Enantiomeric excess of product was determined by HPLC with a Chiralpak OJ-H column (i-PrOH/hexane = 10:90, 254 nm, 1.0 ml/min; t_R = 31.8 min (major) and 36.8 min (minor)). HR-MS m/z: calcd. For $C_{10}H_{11}NO_4$ $(M + Na)^+$ 232.0586, found 232.0555.

^{1}H NMR of product in $CDCl_3$:

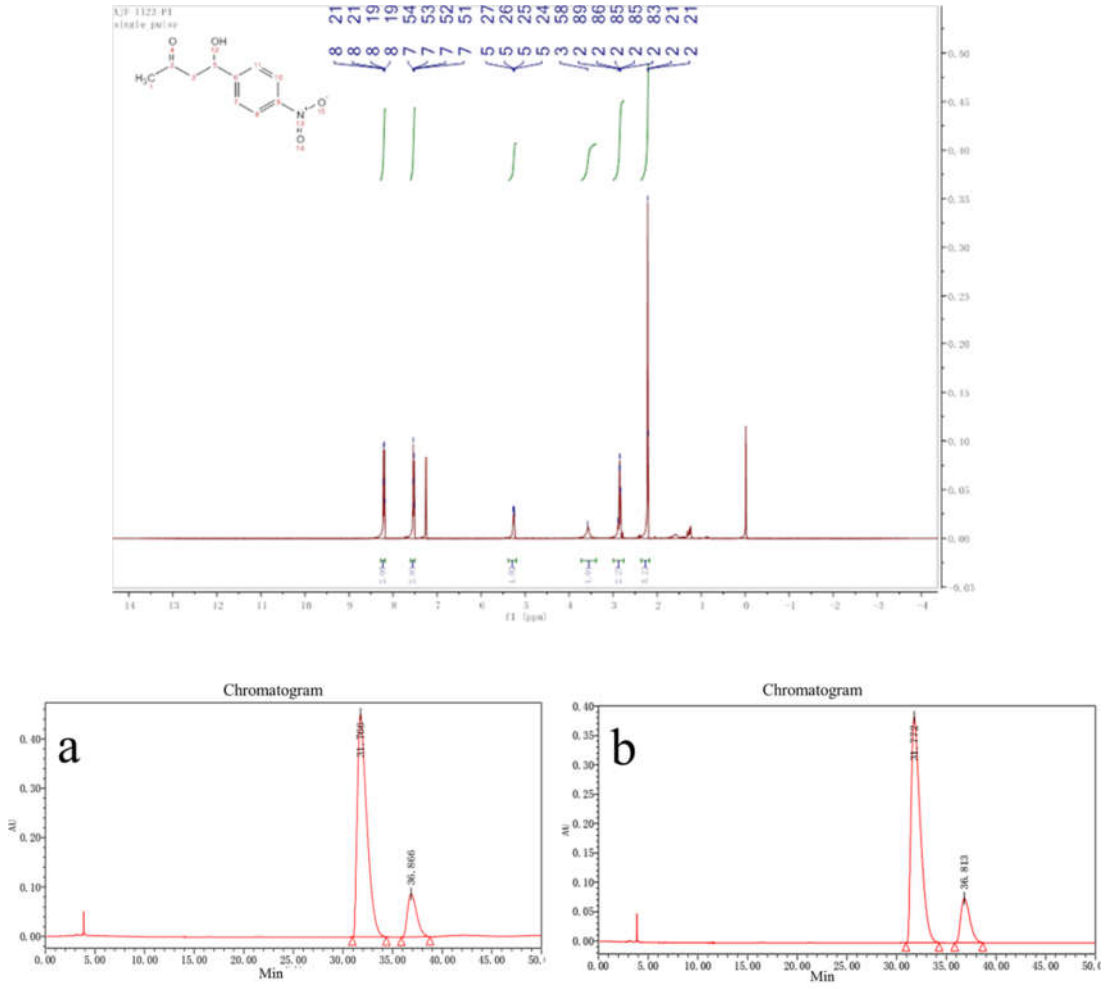


Figure S5. Chiral HPLC of product when (a) L-proline/MWCNTs and (b) L-proline applied.

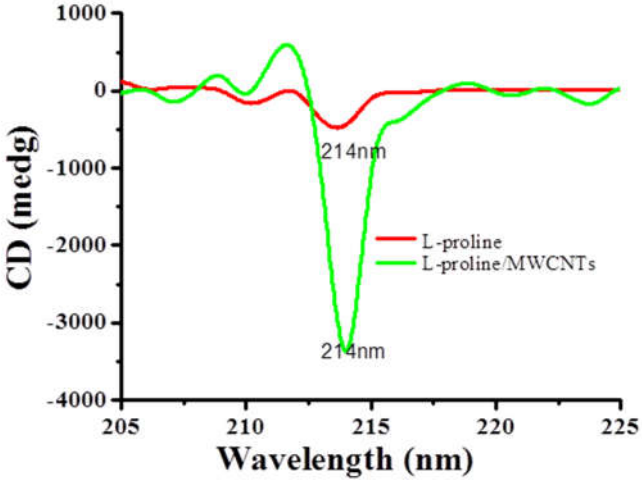


Figure S6. Circular dichroism spectra of L-proline/MWCNTs (green) and neat L-proline (red). The solid samples were tested by potassium bromide tablet at room temperature and 999.985 V.

Filtration test: The solution of 0.05 g of L-proline/MWCNTs catalysts in 5 mL of acetone was stirred at room temperature for 30 min, and then the solid catalysts were removed by filtration. To the solution was added 0.1 mmol of *p*-nitrobenzaldehyde, and the reaction was stirred for 8 h at room temperature. After concentration, the crude mixture was analyzed by HPLC (i-PrOH/hexane = 7:93, flow rate = 1.0 mL/min, λ = 254 nm, t_R = 3.66 min (*p*-nitrobenzaldehyde) and 11.85 min (product)) to determine the conversion yield.

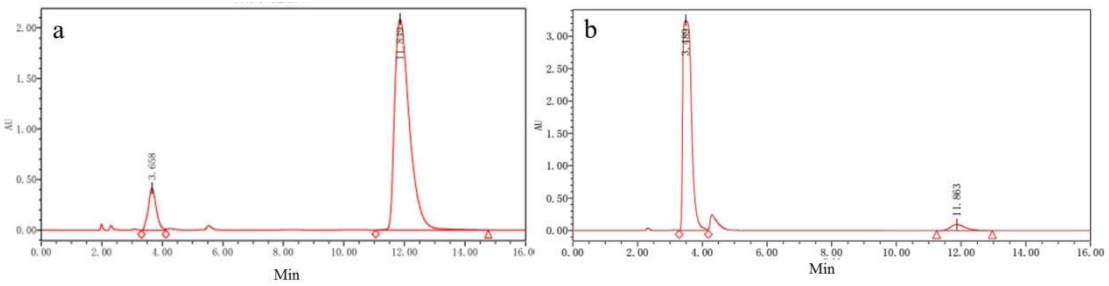
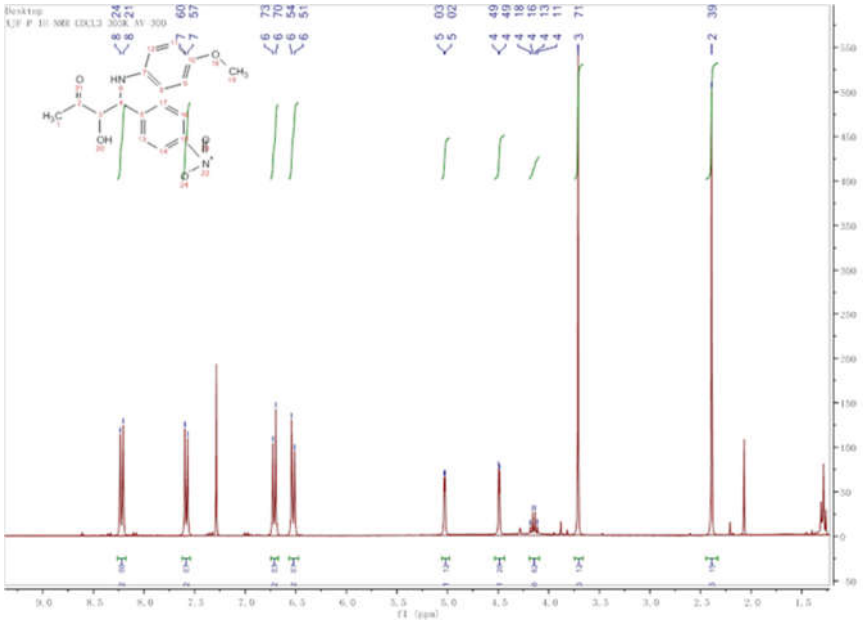


Figure S7. HPLC of product without (a) and with (b) filtration treatment.

2.4 Mannich reaction

In Mannich reaction, the product of 3-hydroxy-4-((4-methoxyphenyl)amino)-4-(4-nitrophenyl)butan-2-one was obtained with ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24-8.21 (d, *J* = 9Hz, 2H), 7.60-7.57 (d, *J* = 9Hz, 2H), 6.73-6.70 (d, *J* = 9Hz, 2H), 6.54-6.51 (d, *J* = 9Hz, 2H), 5.03-5.02 (d, *J* = 3Hz, 1H), 4.49 (s, 1H), 4.18-4.11 (t, *J* = 9Hz, 1H), 3.71(s, 3H), 2.39(s, 3H). The conversion yield was determined by HPLC (i-PrOH/hexane = 4:96, flow rate = 1.0 mL/min, λ = 245 nm, t_R = 14.58 min). HR-MS m/z: calcd. For $C_{17}H_{18}N_2O_5$ $(M + Na)^+$ 353.1113, found 353.1152.

^{1}H NMR of product in $CDCl_3$:



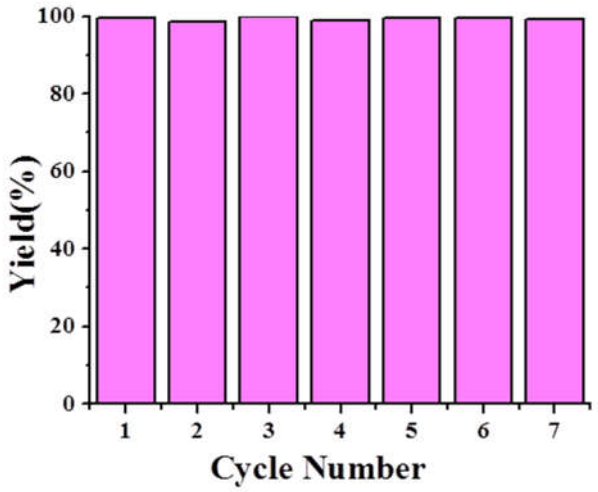
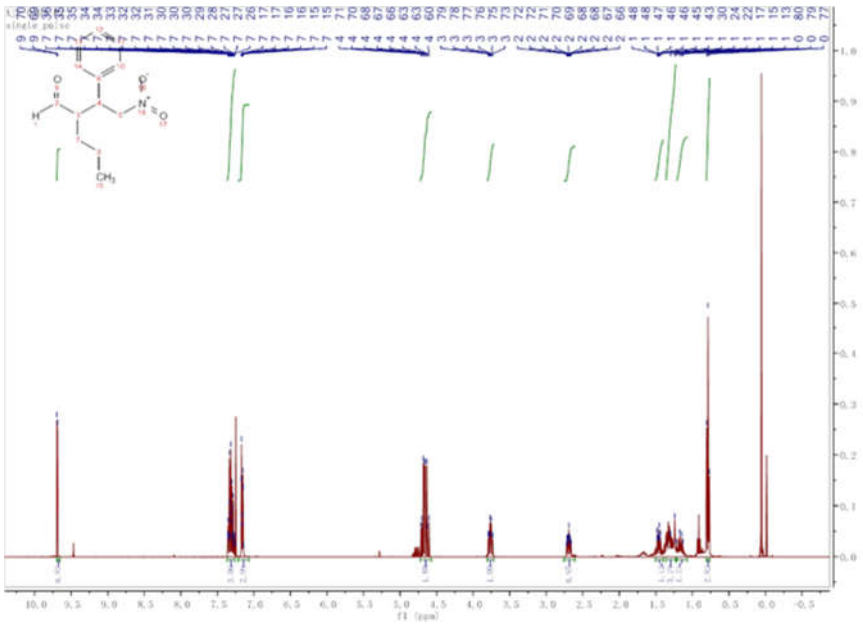


Figure S8. Recycling and reuse of L-proline/MWCNTs catalyst in Mannich reaction.

2.5 Michael reaction

In Michael reaction, the product was determined as 2-propyl-4-nitro-3-phenylbutanal with ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.70-9.69 (d, *J* = 4Hz, 1H), 7.36-7.26 (m, 3H), 7.17-7.14 (m, 2H), 4.70-4.60 (m, 2H), 3.79-3.73 (m, 1H), 2.72-2.66 (m, 1H), 1.48-1.45 (m, 1H), 1.22-1.43 (m, 3H), 1.13-1.17 (m, 1H), 0.80-0.77 (t, *J* = 8Hz, 3H). The conversion yield was determined by HPLC (i-PrOH/hexane = 6:94, flow rate = 1.0 mL/min, λ = 220 nm, t_R = 2.84 min). HR-MS m/z: calcd. For $C_{13}H_{17}NO_3$ $(M+Na)^+$ 258.0950, found 258.0895.

^{1}H NMR of product in $CDCl_3$:



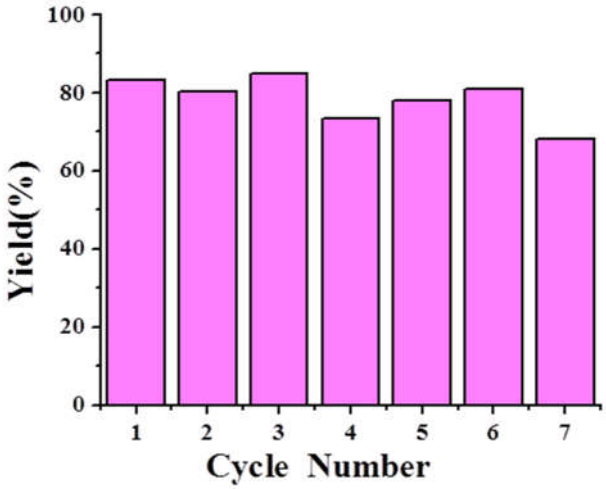
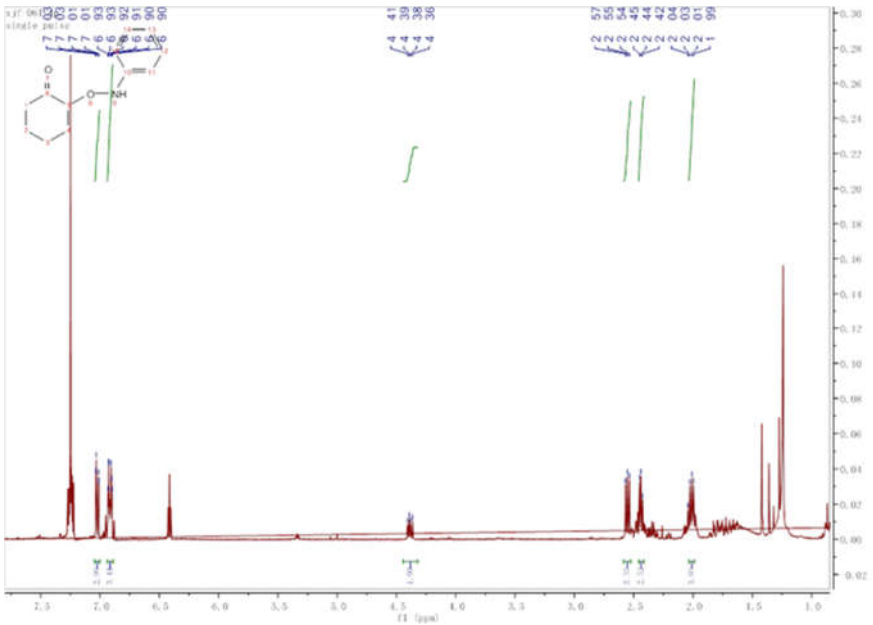


Figure S9. Recycling and reuse of L-proline/MWCNTs catalyst in Michael reactions.

2.6 α-oxyamination reaction

In α-oxyamination reaction of cyclohexanone with nitrosobenzene, the product was determined as 2-((phenylamino)oxy)cyclohexan-1-one with ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.03-7.01 (m, 2H), 6.93-6.90 (m, 3H), 4.41-4.36 (m, 1H), 2.57-2.54 (m, 2H), 2.45-2.42 (m, 3H), 2.04-1.99 (m, 3H). The conversion yield was determined by HPLC (i-PrOH/hexane = 5:95, flow rate = 1.0 mL/min, λ = 244 nm, t_R = 3.11 min). HR-MS m/z: calcd. For $C_{12}H_{15}NO_2$ $(M + Na)^+$ 228.1000, found 228.0817.

^{1}H NMR of product in $CDCl_3$:



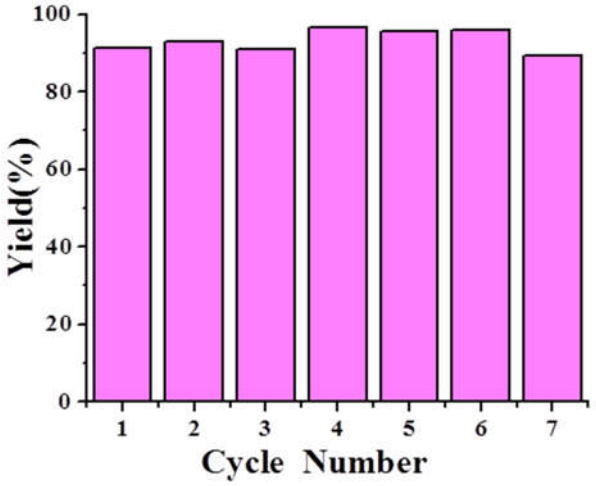
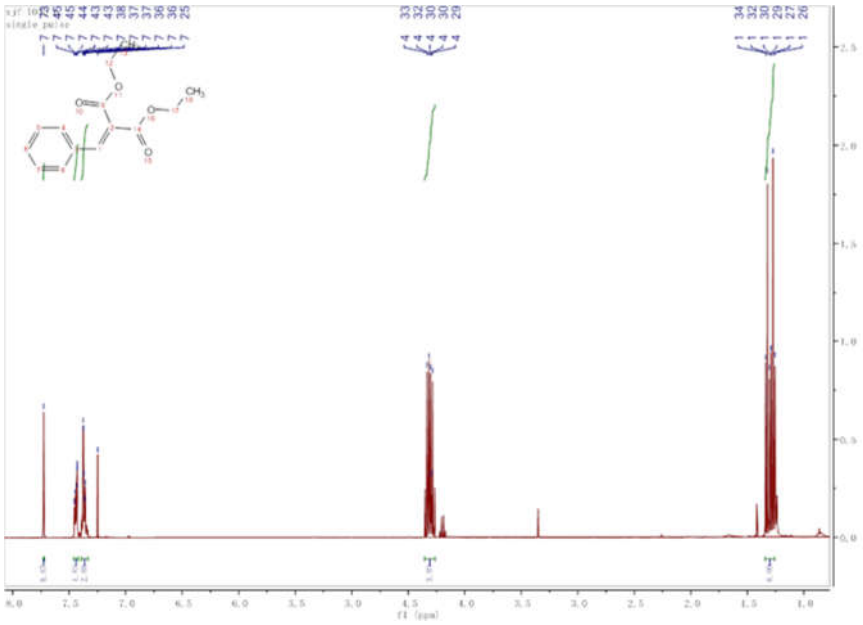


Figure S10. Recycling and reuse of L-proline/MWCNTs catalyst in α-oxyamination reaction.

2.7 Knoevenagel condensation reaction

In Knoevenagel condensation reaction, the product was determined as diethyl 2-benzylidenemalonate with ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.72 (m, 1H), 7.45-7.43 (m, 2H), 7.38-7.36 (m, 3H), 4.33-4.29 (m, 4H), 1.34-1.26 (m, 6H). The conversion yield was determined by HPLC (i-PrOH/hexane = 5:95, flow rate = 0.5 mL/min, λ = 254 nm, t_R = 4.93 min). HR-MS m/z: calcd. For $C_{14}H_{16}O_4$ $(M+Na)^+$ 271.0946, found 271.1037.

^{1}H NMR of product in $CDCl_3$:



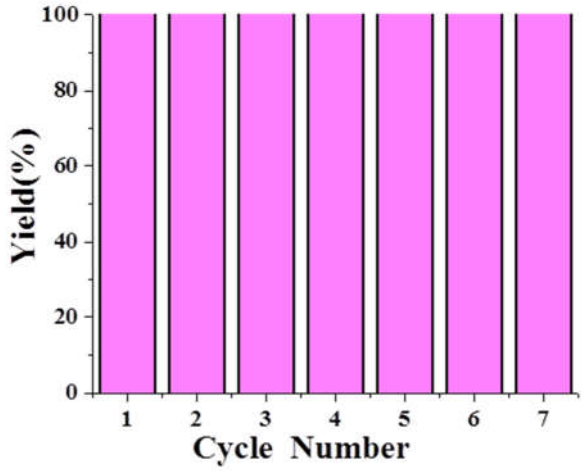


Figure S11. Recycling and reuse of L-proline/MWCNTs catalyst in Knoevenagel condensation.

Table S1. Elemental analysis of L-proline/MWCNTs.[a]

NAME	N	C	H	O
L-proline/MWCNTs -1	8.15	57.34	5.98	27.41
L-proline/MWCNTs -2	8.20	57.48	6.22	27.68
L-proline/MWCNTs -3	8.21	57.38	6.14	27.09

[a] Elemental analysis data from three parallel experiments.

Calculation of the molar loading of L-proline on the MWCNTs

From the elemental analysis results: The mean value of the N element content in the sample is 8.17 wt%, which is only coming from L-proline. So the molar content of N element is equal to that of L-proline. From calculation as following (1.0 g of sample), $\frac{8.17\ \text{wt\%}}{14.0\ \text{g/mol}}$= 5.84 mmol/g, the molar loading of L-proline on the MWCNTs is obtained.

From TGA analysis (Figure 1): In thermogravimetric analysis, the weight of initial sample is 17.166 mg and the weight loss during the decomposition temperature of L-proline between 229 ℃ and 347 ℃ is 11.437 mg. The proportion of L-proline in the sample is equal to 67 wt% (11.437 mg/17.166 mg). From calculation as following (1.0 g of sample), $\frac{11.437\ \text{mg}}{115.13\frac{\text{g}}{\text{mol}} \times 17.166\ \text{mg}}$ = 5.82 mmol/g, the molar loading of L-proline on the MWCNTs is obtained.