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ORIGINAL PAPER

Switching diastereoselectivity of direct Mannich-type reaction of cyclic ketones by polymeric laponite nanoclay catalyst

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Abstract A new polymeric laponite nanoclay heterogeneous catalytic system based on HPMC (hydroxypropyl methyl cellulose) was developed for direct Mannich-type reaction of ketones with substituted benzaldehydes and anilines to afford corresponding β-amino ketones in good to high yields. Interestingly, cyclic ketones exhibited different chemoselectivity. Cyclopentanone underwent aldol condensation to give crossed-aldol product, while cyclohexanone and cyclopentanone afforded corresponding Mannich adducts. In the case of cyclohexanone, stereoselectivity was changed depending on the nature of the substitution on benzaldehydes, in which, moderate electron-donating and electron-withdrawing groups afforded the *anti* isomer as major products, but strongly electron-donating substituted benzaldehydes led to *syn* isomer as the major Mannich adducts. Mannich reaction with cycloheptanone led to Mannich adducts with excellent *syn* selectivity.

Keywords Nanoclay · Polymeric catalyst · Mannich-type reaction · β-Amino ketones

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Introduction

Homogeneous catalysts, which are still being used in industrial chemical processes, are strong mineral or Lewis acids. These acids are highly toxic and dangerous to handle and transport, and corrosive to the storage containers. Also, the final products of the catalyzed reaction need to be separated from the catalyst generating a great volume of waste because frequently those acids are neutralized at the end of the reaction that causes environmental problems. To overcome these troublesome disadvantages, a large number of studies have been developed for application of heterogeneous catalysts. Therefore, the use of heterogeneous catalysts such as clays and zeolites has received great attention in organic synthesis. This has been attributed to their inexpensive nature, greater selectivity, environmental compatibility, recyclability, non-corrosiveness, simplicity in operation and ease of separation [1–10]. Especially, clay catalysts make the reaction process convenient, economic and act as Brønsted as well as Lewis acids enabling them to function as efficient catalysts for various organic transformations [11–16]. Polymer-supported catalysts have also attracted much attention and rapidly increasing numbers of new polymeric supports have recently been reported [17–30], since one of the major benefits of polymer-supported catalysis, is the recovery and reuse of immobilized species, which can be extremely expensive.

β-Amino carbonyl compounds are attractive targets for chemical synthesis because of their wide use as biologically active molecules [31]. Therefore, the development of new synthetic methods leading to β-amino carbonyl compounds or their derivatives has attracted much attention in organic synthesis. The Mannich reaction is a classical

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method for the preparation of β-amino ketones and aldehydes [31–33], and has been one of the most important basic reactions in organic chemistry for its use in natural product and pharmaceutical syntheses due to formation of carbon–carbon and carbon–nitrogen bonds, simultaneously. The classic Mannich reactions are usually carried out under acidic or basic conditions, which offer a number of serious disadvantages [32–35]. However, to avoid side reactions, occasionally encountered in the presence of a strong acid or a base, a number of alternative catalytic procedures for Mannich reactions have been developed [36–46]. Unfortunately, many of these procedures often require a large excess of reagents, long reaction time and drastic reaction conditions in organic solvents such as acetonitrile or 1,2-dichloroethane which are toxic. In some cases, a stoichiometric amount of Lewis acid is required.

In continuing with our research on Mannich reaction [39–41] and polymeric and solid support catalyst [47, 48], herein we report a new polymeric laponite nanoclay as a catalyst for the synthesis of β-amino carbonyl compounds via direct Mannich-type reaction.

Experimental

Preparation of polymeric laponite nanoclay

An amount of 0.5 g of laponite RD was dispersed in 30 mL of distilled water for 24 h. Then, 1 g of HPMC was added to laponite RD solution and was allowed to completely dissolve. Afterward, acrylamide monomer (3 g) and methylenebisacrylamide (MBA) (0.05 g) were added to the solution and the temperature of the solution was adjusted at 30 °C. The CAN initiator (0.1 g) was dissolved in 2 mL water and added to the solution to initiate the polymerization. After polymeric laponite nano composite formation, the product was cut into small pieces and immersed into excess deionized water to extract unreacted component. Then, the purified product was dried at 60 °C. The dried polymeric nano composite was ground and kept from moisture and light.

General procedure for Mannich-type reaction

To a mixture of 0.5 mmol of benzaldehyde, 0.5 mmol of aniline and three equiv. of cyclohexanone, was added 0.04 g of polymeric laponite nanoclay and stirred at room temperature for appropriate time. After completion of the reaction, monitored by TLC, 5 mL EtOH was added and catalyst was removed by filtration, and filtrate was concentrated under reduced pressure. The obtained crud product was recrystallized from EtOH. All products are known and characterized by comparison of ^{1}H NMR with authentic samples.

X-ray crystal structure determination

Single crystals, suitable for X-ray crystallography, were obtained via slow evaporation in EtOH. X-ray data were collected on a STOE IPDS 2 diffractometer with a graphite monochromator and Mo K_α radiation ($\lambda = 0.71073$ Å) by the rotation method scans at 296 K. The structure was solved using direct methods with SHELXS97 [49] and refined on F^2 by full-matrix least squares with anisotropic displacements parameters for all non-hydrogen atoms with SHELXL-97 [49]. All carbon-bonded hydrogen atoms were geometrically fixed with C—H = 0.93, 0.97, and 0.98 Å for aromatic, methylene and methine H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The nitrogen H atoms were located from the difference Fourier map and allowed to refine freely. The crystals data and pertinent details of the experimental conditions are summarized in Table 1.

Results and discussion

Polymeric laponite nanoclay was synthesized via grafting of acryl amide (AAm) onto HPMC using laponite RD nanoclay as filler. The grafting was carried out using ceric ammonium nitrate (CAN). It has been reported that the anhydroglucose units are predominantly oxidized through C_2–C_3 bond cleavage induced by Ce^{4+} ions and oxidizing corresponding bonds induce free radicals onto HPMC. AAm monomer can graft onto HPMC backbones through produced free radicals and cross-linking reaction can occur in the presence of MBA cross-linker and finally a three-dimensional network is produced. The dispersed laponite sheets will be captured in the HPMC-g-PAAm networks (Scheme 1).

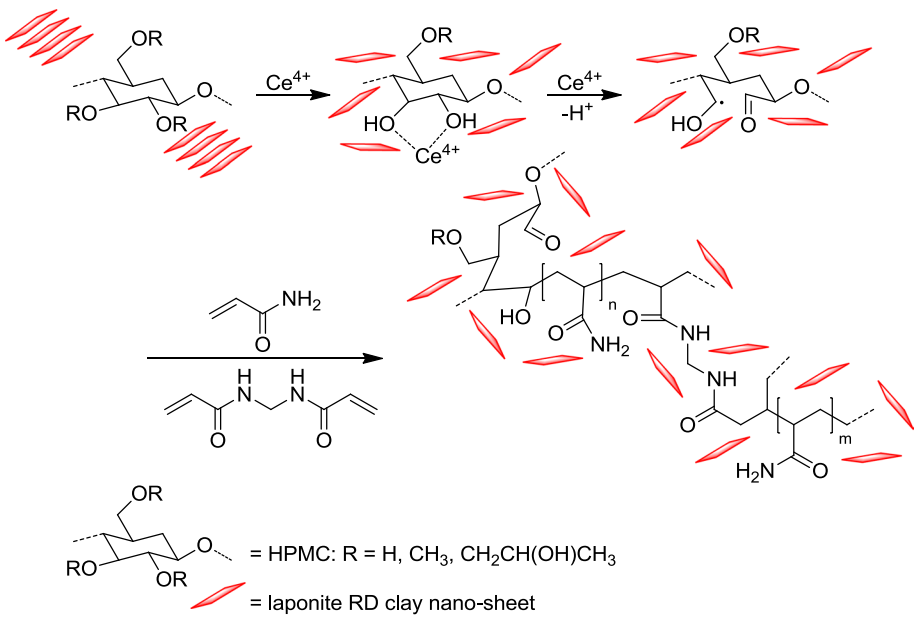
The XRD patterns of pristine laponite RD and polymeric laponite nanoclay were studied at $2\theta = 2.5$–15° and are illustrated in Fig. 1. According to data, the XRD profile of pristine laponite (a) shows a broad peak from $2\theta = 2.5$ to $2\theta = 9.1$ with a diffraction peak at about $2\theta = 4.32$ corresponding to the distance of clay sheets with d spacing 20.4 Å. Stirring of laponite for 5 h subsequently in situ graft copolymerization of AAm onto biopolymer in the presence of laponite nanoclay leads to corresponding nano-composite that the XRD profile of the sample was shown in Fig. 1, b. No diffraction peak was observed in polymeric laponite nanoclay and it can be concluded that the clay layers are completely exfoliated.

The crosslinked HPMC-based polymeric laponite nanoclay dispersed in water (0.1 g/100 mL water) and spread onto copper grid. After air-drying, the TEM micrograph was studied and the result was shown in Fig. 2. The micrograph of polymeric laponite nanoclay showed plates with

Table 1 Crystal data and structure refinement for 2-[(4-chlorophenylamino)(*p*-tolyl)methyl]cyclohexanone **I**, and 2-[phenyl(phenylamino)methyl]cycloheptanone **II**

CCDC deposit no.	**I** (CCDC 895762) [50]	**II** (CCDC 1043140) [50]
Empirical formula	$C_{20}H_{22}ClNO$	$C_{20}H_{23}NO$
Formula weight (g mol^{-1})	327.84	293.39
Temperature (K)	296	296
Habitus, color	Prism, colorless	Prism, colorless
Crystal size [mm^3]	0.57 × 0.42 × 0.34	0.72 × 0.56 × 0.27
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)	$a = 12.9387$ (9) $b = 9.1452$ (7) $c = 18.3327$ (14) $\beta = 126.110$ (4)	$a = 5.7534$ (4) $b = 16.1336$ (8) $c = 18.1980$ (13) $\beta = 99.371$ (6)
Volume ($Å^3$)	1752.5 (2)	1666.65 (19)
Z	4	4
D_c (gcm^{-1})	1.243	1.169
$F(000)$	696	632
Diffractometer	STOE IPDS2	STOE IPDS2
Data collection method	Rotation method scans	Rotation method scans
Radiation type, wavelength (Å)	Mo K_α, 0.71073	Mo K_α, 0.71073
Absorption coefficient (mm^{-1})	0.22	0.07
θ range for data collection (°)	2.0–26.5	1.7–28.0
Reflections collected	21,741	10,757
Independent reflections (Rint)	3626 (0.036)	3449 (0.041)
Observed reflections	2462 [$I > 2\sigma(I)$]	2170 [$I > 2\sigma(I)$]
Index ranges	$-16 \le h \ge 16$ $-11 \le k \ge 11$ $-22 \le l \ge 22$	$-7 \le h \ge 7$ $-20 \le k \ge 20$ $-22 \le l \ge 18$
Refinement	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data, restraints, parameters	3626, 0, 213	3449, 0, 203
R [$F^2 > 2\sigma(F^2)$], wR(F^2), S	0.050, 0.137, 1.03	0.048, 0.136, 1.01
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.50, −0.17	0.26, −0.13

Scheme 1 Preparation of polymeric laponite nanoclay catalyst



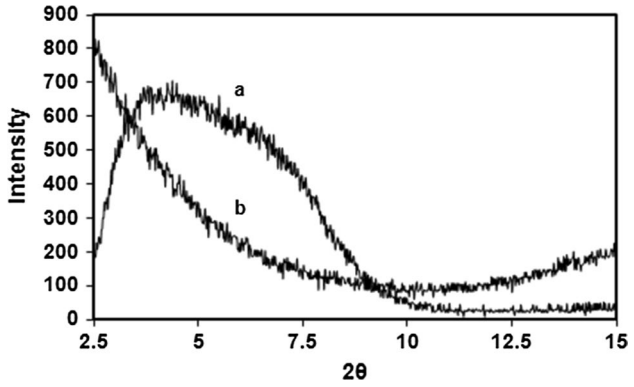


Fig. 1 XRD patterns of **a** pristine laponite RD and **b** polymeric nano-laponite

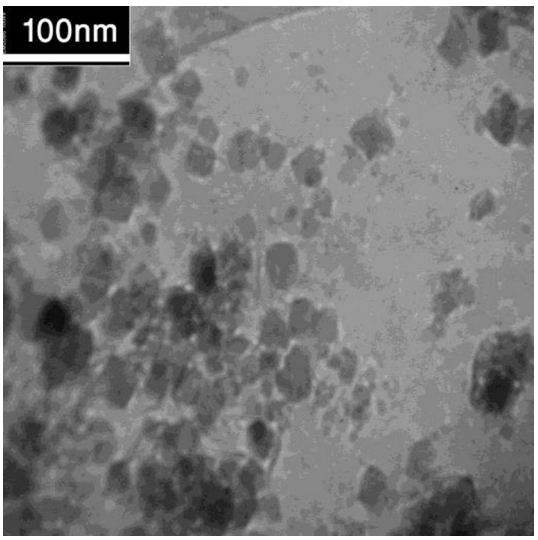


Fig. 2 TEM image of polymeric laponite nanoclay

undefined shape, which the size of plates were less than 30 nm. The data confirmed the presence of nanometric laponite RD in polymeric matrix.

We first studied the catalytic activity of polymeric laponite nanoclay in direct Mannich-type reaction of cyclohexanone with aniline and 2-chlorobenzaldehyde under different conditions (Scheme 2). When 1 equiv. of cyclohexanone was used, the reaction proceeded slowly and afforded the desired Mannich adduct in low yield. So, the optimum amount of cyclohexanone was determined to be 3 equiv. which furnished the corresponding Mannich product in acceptable yield with excellent *anti* selectivity. Also, we carried out the same reactions using different amount of catalysts, and 0.04 g of polymeric laponite nanoclay per 0.5 mmol of 2-chlorobenzaldehyde was determined as an optimum amount of catalyst. Also, different solvents were examined and according to environmental view, we carried out the reaction in water and solvent-free conditions, and the Mannich adduct was obtained in good yield with excellent *anti* selectivity under solvent-free conditions and compared with conditions in which water was used as solvent. Also, the catalytic activity of polymeric laponite nanoclay was investigated using HPMC as catalyst, in which only corresponding imine was obtained, however, laponite RD nanoclay led to Mannich adduct in good yield with low diastereoselectivity. Moreover, the recyclability of the polymeric laponite nanoclay catalyst was investigated. In these experiments the product was isolated by filtration, the solid residues were washed with dichloromethane, and the remaining catalyst was dried under vacuum and then at 60 °C for 1 h, and reloaded with fresh reagents for further runs. No considerable decrease in the yield and stereoselectivity was observed over four runs, demonstrating that polymeric laponite nanoclay can be reused as a catalyst in direct Mannich-type reactions.

The scope of the reaction was investigated using different anilines, benzaldehydes and ketones using polymeric laponite nanoclay as catalyst under solvent-free conditions at room temperature. The reaction was carried out by adding of 0.04 g of polymeric laponite nanoclay to a mixture of 0.5 mmol of benzaldehyde, 0.5 mmol of aniline and three equiv. of ketones and stirring at room temperature to appropriate time. The structures and yields of products are summarized in Table 2.

As shown in Table 2, polymeric laponite nanoclay catalyzed direct Mannich type reactions of cyclohexanone exhibited interesting stereoselectivity depending on the nature of the substituent on benzaldehydes. Benzaldehydes with moderated electron-donating substituents (Me, entry 7) and electron-withdrawing substituents (Cl, NO_2, entries

Scheme 2 Polymeric laponite nanoclay catalyzed Mannich-type reaction of cyclohexanone with aniline and 2-chlorobenzaldehyde

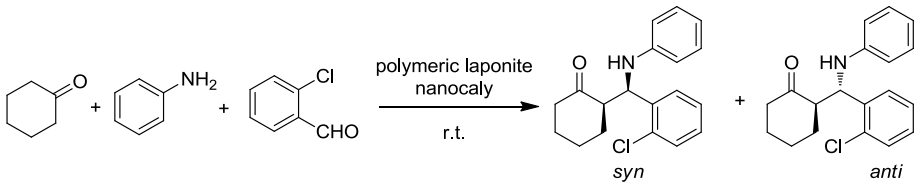
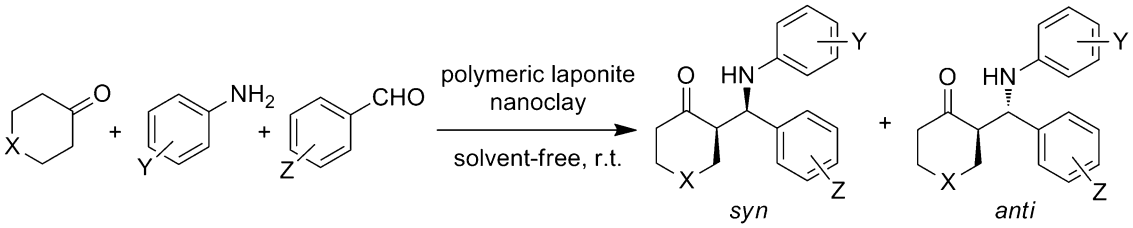


Table 2 Direct Mannich-type reaction of cyclic ketones, anilines and benzaldehydes using polymeric laponite nanoclay as catalyst

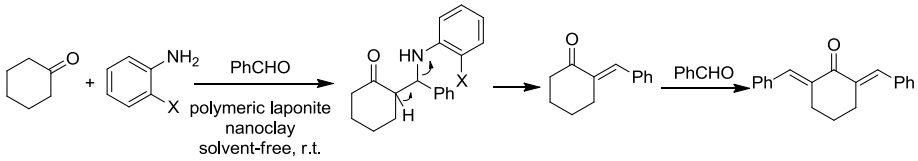


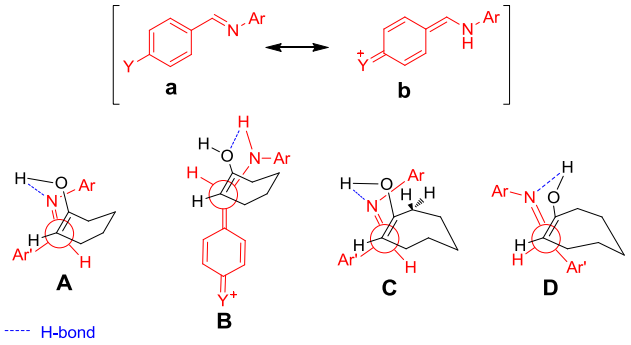
Entry	*X*, *Y*, *Z*	Time (h)	Yield (%)[a]	*anti*/*syn*[b]
1	CH_2, H, H	24	64	>99/1
2	CH_2, H, 2-NO_2	24	62	>99/1
3	CH_2, H, 2-Cl	2	75, 72, 72, 68[c]	98/2, 98/2, 97/3, 98/2
4	CH_2, H, 4-NMe_2	5	80	32/68
5	CH_2, 4-Cl, H	19	60	>99/1
6	CH_2, 4-Cl, 2-Cl	1.5	57	98/2
7	CH_2, 4-Cl, 4-Me	24	56	91/9
8	CH_2, 4-Cl, 4-OH-3-MeO	6	60	<1/99
9	CH_2, 4-Br, H	2.5	50	86/14
10	CH_2, 2-Cl, H	24	–[d]	–
11	CH_2, 2-Me, H	24	–[d]	–
12	CH_2CH_2, H, H	24	60	6/94
13	CH_2CH_2, H, 4-Me		41	2/98
14	CH_2CH_2, 4-Cl, H	2	70	<1/99
15	S, H, 2-Cl	3	59	98/2

[a] Yields refer to isolated products. [b]*Anti*/*syn* ratio was determined using ^{1}H NMR spectra [39]. [c]Catalyst was used over four runs. [d]The crossed aldol product was obtained

2, 3 and 6) afforded the Mannich adducts with excellent *anti* selectivity, while the strongly electron-donating substituted benzaldehydes such as 4-Me_2N and 3-HO-4-MeO (entries 4 and 8) furnished the Mannich adducts with high to excellent *syn* selectivity. Also, aniline as well as *para*-substituted anilines worked well in polymeric laponite nanoclay catalyzed direct Mannich type reaction and afforded the corresponding *β*-amino ketones in good to high yields. But, in the case of *ortho*-substituted anilines such as 2-Cl and 2-Me (entries 10 and 11) the crossed aldol product was obtained as sole product (Scheme 3). Further investigation revealed that, initially obtained Mannich adducts underwent removing of an aniline molecules to give aldol product. This can be attributed to steric repulsion which was introduced by Cl and Me groups on *ortho* position. Another switching in selectivity was shown when cycloheptanon was used as ketone component in Mannich type reaction in the presence of polymeric laponite nanoclay under solvent free conditions, which afforded the corresponding *β*-amino ketones in good yields with excellent *syn* selectivity (entries 12–14). The structures of all products were established by NMR in compared with reported ones in the literature.

Scheme 3 Crossed aldol condensation in the case of *ortho*-substituted anilines

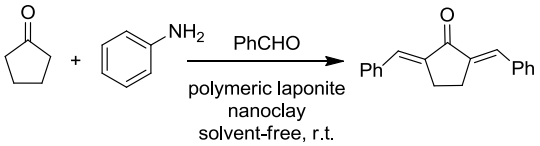




Scheme 4 Proposed transition states in Mannich reaction of cyclohexanone and cycloheptanone

The plausible reaction mechanism involves the nucleophilic addition of enol form of the ketones onto the in situ generated imines. As shown in Scheme 4, reaction of cyclohexanone with imines **a**, derived from moderately electron-donating and electron-withdrawing substituted benzaldehydes, proceeded via transition state **A**, in which the minimal steric repulsions are exist and led to *anti* stereoisomers [39]. While, in the case of strongly electron donating substitutions (OH and Me_2N) at *para* position of benzaldehyde, enamine **b** is participated in the reaction and the transition state **B** is overcoming, and *syn* isomer is produced as major stereoisomer. In the case of cycloheptanone, also two transition states are possible; **C** led to *anti* and **D** afforded *syn* stereoisomer. Due to the steric repulsion between aryl group of imine and methylene of cycloheptanone ring in the transition state **C**, reactions proceeded via transition state **D**, and afforded *syn* stereoisomer as major product.

An ORTEP view of 2-[(4-chlorophenylamino)(*p*-tolyl) methyl]cyclohexanone **I** and 2-[phenyl(phenylamino) methyl]cycloheptanone **II** with atomic labelling is shown in Fig. 3. The X-ray single crystal structures analysis revealed that the major isomer of **I** possesses *anti* stereochemistry, with 173.44 (18)° and −66.4 (2)° torsion angles of C_6─C_1─C_7─N_1 and C_2─C_1─C_7─N_1, respectively, and



Scheme 5 Crossed aldol condensation of cyclopentanone with benzaldehyde

the relative configuration of the two stereocentres is *R*,*S*. While, in the case of Mannich base **II**, the major isomer has *syn* stereochemistry with 55.55 (19)° and 175.01 (14)° torsion angles of C_7─C_1─C_8─N_1 and C_2─C_1─C_8─N_1, respectively, and the relative configuration of the two stereocentres is *R*,*R*.

In the case of cyclopentanone, reactions occurred rapidly, and chemoselectively, corresponding crossed-aldol products were obtained in high yields (Scheme 5). This can be attributed to the high acidity of the proton adjacent to the carbonyl group of cyclopentanone that underwent elimination reaction.

An attempt to Mannich-type reaction of *n*-butanal, an aliphatic aldehyde, and aniline with cyclohexanone in the presence of catalytic amount of polymeric laponite nanoclay at room temperature was failed. Similarly, Mannich reactions of aldehydes and anilines with acyclic ketones such as acetone and acetophenone derivatives were investigated. The overall reaction is shown in Scheme 6.

Conclusion

In summary, a new heterogeneous catalytic system based on HPMC-laponite nano composite was developed for three-component direct Mannich type reactions of aldehydes, anilines, and ketones at room temperature under solvent-free conditions. Reactions of cyclic ketones exhibited interesting chemoselectivity and stereoselectivity depending on the ring sizes of ketones and nature of the substituent on the benzaldehydes. In the case of cyclopentanone, chemoselectively, aldol condensation reaction took place

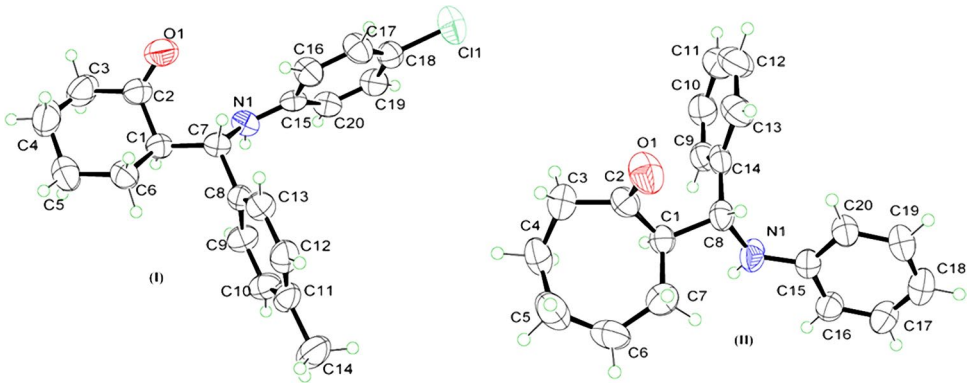
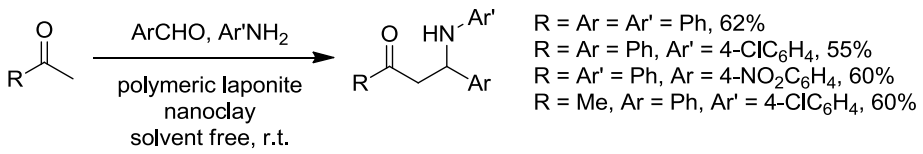


Fig. 3 ORTEP representations (45 % probability level) of the crystal structures of 2-[(4-chlorophenylamino)(*p*-tolyl) methyl]cyclohexanone **I**, and 2-[phenyl(phenylamino)methyl] cycloheptanone **II**

Scheme 6 Mannich-type reaction of acyclic ketones



to afford corresponding crossed-aldol products, but reaction with cyclohexanone and cycloheptanone led to the formation of corresponding Mannich adducts. In the case of Mannich reaction of cyclohexanone, stereoselectivity was dependent on the nature of substitution on benzaldehydes, which, with moderate electron-donating and electron-withdrawing groups, *anti*-stereoisomers were obtained as major isomer, while with strongly electron-donating groups, the *syn* isomers were the major products. When cycloheptanone was used as ketone component, stereoselectively, *syn* isomers were produced. Also polymeric laponite nanoclay catalytic system catalyzed the Mannich reaction of acyclic ketones to afford corresponding β-amino ketones in good yields.

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50. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 895762 (**I**) and CCDC 1043140 (**II**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)