View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Chaudhary and P. Mohanty, *New J. Chem.*, 2018, DOI: 10.1039/C8NJ02174K.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

YAL SOCIETY CHEMISTRY

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Nitrogen enriched polytriazine as metal-free heterogeneous catalyst for the Knoevenagel reaction in mild condition

Monika Chaudhary and Paritosh Mohanty*

Nitrogen enriched (52 wt %) nanoporous polytriazine with high specific surface area up to 850 m² g⁻¹ is synthesized by an ultrafast (30 min reaction time) microwave assisted route using inexpensive precursors cyanuric chloride and melamine at 400 W. The metal-free highly electron rich material is used for the heterogeneous base catalysed Knoevenagel reaction with high yield of ~98% in a very short reaction time of 30 min at room temperature. The reaction condition was optimized and several aromatic aldehydes have been reacted with malononitrile with a minimum of 85 % yield under mild experimental conditions.

1. Introduction

The major developments in chemical industries for carrying out organic or inorganic transformations lie on the development of efficient catalysts.¹⁻³ This is one of the prominent research problems that draw attention from diverse research fields. Traditionally, metal based molecules and materials have dominated the research area, however, very recently there is a growing demand for the development of efficient metal-free organocatalysts owing to their environmental and cost benefits.⁴⁻⁸ Initially, the metal-free organocatalysis was focussed on the use of small organic molecules under homogeneous conditions.⁹⁻¹³ The catalyst recovery and recyclability are the two major concerns in homogenous catalysis that further encouraged to develop their solid catalyst counterparts to carry out the catalysis in the heterogeneous conditions. Some of the recently explored metal-free heterogeneous catalysts are functionalized porous aromatic frameworks,^{14,15} triazine based polymers,¹⁶ porous organic frameworks (POFs),¹⁷ and conjugated microporous polymers (CMPs).^{18,19}

Moreover, functionalization of various high surface area materials such as inorganic-organic hybrid materials, organic polymers, and mesoporous silicas and organosilicas with amine groups have shown superior adsorption and catalytic applications.²⁰⁻²⁷ Organic amine functionalized high surface area nanoporous materials have got tremendous interest of

This journal is © The Royal Society of Chemistry 20xx

late due to the control over the textural properties and functionality driven superior performance as organocatalyst, electrode materials for supercapacitors, adsorbents for capturing gases and removing heavy metals.^{22,24-34}

Among these, triazine based high surface area nanoporous polymers have received a lot of attention owing to their large nitrogen content, multiple methods of synthesis and interesting catalytic and adsorption applications.^{16,23,33-39} The versatile synthesis methods such as trimerization, Schiff-base reaction, substitution reaction (both nucleophilic and electrophilic), Yamamoto coupling, Sonogashira crosscoupling, Friedel-Craft's condensation reaction, polymerization, oxidative coupling and radical polymerization have made these materials an important class of polymers with wide range of applications.^{16,23,33-39} The basicity due to the lone pair of electrons in the nitrogen and the excess of active sites exposed have made these materials efficient for catalysis, sorption as electrode materials gas and for supercapacitors.^{16,23,33-39} The Knoevenagel reaction is considered as one of the very important base-catalysed reactions for the formation of C-C bond between the carbonyl compounds and compounds containing acidic methylene group. For the natural product synthesis, the Knoevenagel reaction is considered as a key step.¹⁶⁻¹⁸ Moreover, several molecules of therapeutic and pharmacological importance have been synthesized using the condensation. Various homogeneous and metal based catalysts have been explored, however, the recent environmental concerns encouraged the researchers to explore the organocatalysis pathway for the condensations.^{16-18,27} Mostly, electron rich amine functionalized organic molecules and materials have been investigated.^{4,18,32-40} In this article, we report the organocatalytic activity of one of the highly electron rich polymeric materials, polytriazine, for the Knoevenagel

Department of Chemistry, IIT Roorkee, Uttarakhand-247667, INDIA. E-mail: pmfcy@iitr.ac.in, paritosh75@gmail.com; Phone: +91-1332-284859; Fax: +91-1332-286202.

Electronic Supplementary Information (ESI) available: [TEM, XRD, TGA, TGA, XRD of NENP-1 and characterization of the NENP-1 catalyzed Knoevenagel reaction products by FT-IR, CP-MAS ^{13}C NMR, ^1H NMR and GC-MS]. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C8NJ02174K Journal Name

ARTICLE

reaction. Two inexpensive precursors, melamine $(C_3N_6H_6)$ and cyanuric chloride $(C_3N_3Cl_3)$ were condensed to form a framework material as shown in Scheme-S1.

2. Material and methods

2.1. Synthesis of metal free organocatalyst NENP-1

Equimolar mixture of melamine (99 %, Sigma Aldrich, India) and cyanuric chloride (99 %, Sigma Aldrich, India) was reacted in 20 ml DMSO at 140 °C with a microwave power of 400 W and reaction time of 30 min in a microwave reactor in the presence of triethylamine (TEA) (Fisher Scientific, India) as a proton absorber. The synthesized product was filtered and severely washed with, distilled water, THF and dried at 100 at °C.

2.2. Characterization of metal free organocatalyst NENP-1

The obtained specimen (NENP-1) was investigated by FTIR (Perkin Elmer Spectrum Two spectrophotometer) and Cross polarization magic angle spinning (CP-MAS) 13 C NMR spectra (JEOL Resonance JNM-ECX-400II). XRD pattern was obtained using Rigaku Ultima IV with CuK_{\alpha} source. The microstructure of the specimen was studied by FESEM (TESCAN MIRA3) and TEM (TECNAI G 2 S-TWIN). The elemental analysis (C/H/N/S) was conducted using Thermo Flash 2000. TGA was performed on EXSTAR TG/DTA6300. The N_2 sorption was carried out using Autosorb-iQ2 (Quantachrome Instruments, USA).

2.3. Catalytic activity of metal free organocatalyst NENP-1 Here in, NENP-1 is used as a heterogeneous metal free organocatalyst for the Knoevenagel reaction of malononitrile with various aromatic aldehydes. In a model reaction, benzaldehyde (1 mmol) and malononitrile (1 mmol) were reacted in 1:1 volume ratio of dioxane-H₂O (total volume of the reaction mixture is 1 mL) at 25°C in the presence of 5 mg of NENP-1 and the product was isolated after recrystallization with ethanol (Scheme-S2). Various experimental parameters such as catalyst loading, reaction time and solvent ratio were varied to optimize the product yield. Total of eight aromatic aldehydes have been reacted with malononitrile to conclude the versatility of the metal free organocatalyst NENP-1. Synthesized products was characterized by FT-IR (Perkin Elmer Spectrum Two spectrophotometer) and Cross polarization magic angle spinning (CP-MAS) ¹³C NMR spectra, and ¹H NMR (JEOL Resonance JNM-ECX-400II). Purity of the products was investigated by GC (Perkin Elmer GC Clarus 680) and MS (Perkin Elmer MS Clarus SQ8T).

3. Results and discussion

The nitrogen enriched nanoporous polytriazine (NENP-1) framework has been synthesized by the condensation of cyanuric chloride and melamine using a microwave assisted route at 140 °C with a microwave power of 400 W and short reaction time of 30 min. The obtained specimen has been investigated by the ¹³C CPMAS NMR and FTIR spectroscopy. A strong signal at 166.7 ppm in the ¹³C CPMAS NMR spectrum in Figure 1a originated from the carbon of the triazine ring

confirms the condensation.^{33,38,41} Observation of a small signal at 149.5 ppm may be attributed to the side group functionalities originated from cyanuric chloride.^{24,38} Further, the observation of only broad band (instead of multiple bands observed for primary amine) above 3350 cm⁻¹ in the FTIR spectrum [Figure 1b] along with the absence of the band at 850 cm⁻¹ due to the C-Cl stretching vibration further corroborate the NMR results.^{33,38} The elemental composition estimated from the CHNSO analysis reveals the high nitrogen content of 52 wt% in the specimen (C:36.5, N:52.0, H:2.1, S:1.3). Nearly spherical inter-grown nanoparticles of average size of 220 nm could be seen in the FESEM image [Figure 1c]. The TEM image [Figure S1] further reveals the porous nature of the specimen with the pore size in the range of 2 to 6 nm. The XRD and SAED patterns (Figure S2 and inset of Figure S1) confirm the X-ray amorphous nature of the specimen.NENP-1 shows good thermal stability upto 350°C in air atmosphere [Figure S3].



Figure 1. (a) 13 C CPMAS NMR spectrum, (b) FTIR spectra, (c) FESEM image (inset: HRTEM), (d) N₂ sorption isotherm of NENP-1. The 13 C NMR spectra of melamine and cyanuric chloride are given in the inset of Figure 1a and PSD in the inset of Figure 1d.

The N₂ sorption isotherm measured at 77 K as shown in Figure 1d is a type-I isotherm with sharp uptake at low pressure region. A narrow hysteresis extends from the low to high pressure range indicates the presence of both micro and mesopores in the specimen with a hierarchical pore structure. The PSD (inset of Figure 1d) is multimodal and the estimated pore sizes centered both in the micropore (1.3 nm) and mesopore (4.1 and 6.9 nm) regions. This confirms the hierarchy in the pore system. The specific BET surface area (SA_{BET}) of the specimen was estimated to be 850 m² g⁻¹ with a total pore volume of 0.89 cm³ g⁻¹.

Recently, various high surface area microporous materials have been explored as catalysts for different organic transformations.^{4,16-19,27,28,32-40} The major advantages of these high surface area heterogeneous catalysts are; (i) metal free catalysts hence, no chance of leaching out of metals, and (ii) ease of separation from the product compared to the homogenous catalysts (both metal based catalysts and organocatalysts).The above advantages made these Published on 25 June 2018. Downloaded by Kaohsiung Medical University on 7/1/2018 8:44:11 AM

Journal Name

heterogeneous nanoporous polymeric catalysts as safe, green, environmental friendly and cost effective alternatives to produce high quality molecules of significant importance.⁴²⁻⁴⁴ Further, the presence of nitrogen as electron rich entity in some of these materials have shown improved catalytic activities.¹⁶⁻¹⁹

The material synthesized in this research has high nitrogen content and superior textural properties. Moreover, the presence of both micropores and mesopores in the specimen forming a hierarchical pore system could be an additional advantage. These encouraged us to investigate the Knoevenagel reaction. The Knoevenagel reaction is a base catalysed reaction widely accepted as one of the most powerful method for carbon-carbon bond formation that produces fine chemicals of pharmaceutical importance.



Scheme 1. Proposed reaction mechanism for Knoevenagel reaction catalyzed over the metal-free heterogeneous organocatalyst NENP-1.

In this investigation, the NENP-1 was employed as a heterogeneous catalyst for the Knoevenagel reaction of malononitrile with various aromatic aldehydes. A model reaction of benzaldehyde (1 mmol) with malononitrile (1 mmol) was performed. Different experimental parameters such as reaction time, solvents and catalyst amount was varied to find out the optimum yield (Table-S1). The reactions were carried out using tetrahydrofuran (THF), methanol, dioxane and H₂O as co-solvents. It has been observed that a high yield could be achieved in the mixtures of the solvents such as THF- H_2O , methanol- H_2O and dioxane- H_2O at the 1:1 volume ratio. This could be mainly attributed to the better solubility of the reactant molecules in these mixtures of solvents.^{18,23} Moreover, the adsorption of water molecule on the N containing active sites further enhance the basicity of the system. Among these, a maximum yield was obtained in the dioxane-H₂O mixture and hence, used for further investigation. It was documented that a solvent mixture tunes the solubility of the reactants as well control the polarity, which in turn improve the reactivity and product yield by making available of the active sites on removing the intermediates if any and the products formed.^{18,23,43}

Effect of catalyst loading is investigated on the yield of product. It has been observed that a catalyst loading of 4.5

wt% in 1 ml of the dioxane-H₂O mixture (1:1) is ideal for the catalytic conversion of 1 mmol each of the reactants (Figure S7). A 98% yield could be achieved in a short reaction time of 30 min at 25 °C. To the best of our knowledge, the catalytic efficiency is the best among the reported literatures (Table-S2). The reaction time was further increased to 60 min to check if the yield could be increased. However, there is almost no change in the yield. Moreover, the product yield of 45 and 60% could be achieved within short reaction time of 2 and 5 min, respectively. Thus, 30 min is considered as the ideal reaction time to have an optimum yield. No product formation could be observed in the absence of the catalyst, under the identical experimental condition. The progress of the reaction was continuously monitored by TLC at regular interval. After the completion of the reaction in 30 min the catalyst was separated by filtration and the product was recrystallized using ethanol.

Spectroscopic investigations such as ¹H and ¹³C NMR, and FT-IR confirm the successful conversion of benzaldehyde into α - β unsaturated product as proposed in scheme-1. Absence of the signals due to the carbonyl carbon of the benzaldehyde and CH₂ group of malononitrile in the ¹H and ¹³C NMR spectra [Figure S5a & S5b] indicate the complete condensation of the reactants to form α - β unsaturated product.^{17,18} Moreover, the signal at 7.7(s) ppm in the 1H NMR attributed to the benzylic hydrogen further confirm the product formation.^{17,18} The FT-IR spectra further corroborate the results obtained from the NMR investigation as the carbonyl band at 1700 cm⁻¹ was absent and a new band at 2270 cm⁻¹ due to the CN stretching vibration was observed (Figure S4). Further, the product purity was investigated by GC-MS. The GC chromatograph reveals a single peak at retention time of 15.03 min and the molecular ion peak at m/z of 154 in mass spectrum are in good agreement with molecular weight of product [Figure S6a]. Systematic fragmentation pattern was observed in mass spectral analysis (Figure S6b). All of the spectra data fairly match with the recent reports.^{17,40} Thus, the metal-free catalyst used in this investigation has shown good performance for the carbon-carbon bond formation using the Knoevenagel reaction. In order to further investigate if the catalyst could be generalized, various aromatic aldehydes were condensed with malononitrile (Table-1) and the products of all these reactions were characterized by ¹H NMR, ¹³C NMR and GC-MS (Figure S8-S19). The superior efficiency of the catalyst could be observed as the minimum 80% yield were realized in a short time span of 30 min for whatever aldehyde may be condensed.

New Journal of Chemistry Accepted Manuscrip

DOI: 10.1039/C8NJ02174K Journal Name



Figure 2. Reusability test of catalyst: General conditions; Aromatic aldehyde (1.0 mmol), malononitrile (1.0 mmol) in the presence of 5 mg of NENP-1 in dioxane- H_2O at 25 °C. (% Yield of the isolated product obtained after recrystallization with ethanol).

 Table 1. Catalytic data of the NENP-1 catalysed Knoevenagel reaction with different aromatic aldehydes.

| Aldehyde | Active methylene | Time | Yield |
|------------------------|------------------|-------|-------|
| | compound | (min) | (%) |
| Benzaldehyde | Malononitrile | 30 | 98 |
| 4-Methoxy benzaldehyde | Malononitrile | 30 | 95 |
| 3-Methoxy benzaldehyde | Malononitrile | 30 | 92 |
| 2-Nitro benzaldehyde | Malononitrile | 30 | 87 |
| 4-Nitro benzaldehyde | Malononitrile | 30 | 86 |
| α-Napthaldehyde | Malononitrile | 30 | 81 |
| 4-Bromo benzaldehyde | Malononitrile | 30 | 97 |
| 2-Bromo benzaldehyde | Malononitrile | 30 | 96 |

Reaction conditions: Aromatic aldehyde (1.0 mmol), malononitrile (1.0 mmol) in the presence of 5 mg of NENP-1 in dioxane- H_2O (1:1) at 25 °C and Yield of the isolated product obtained after recrystallization from ethanol.

The catalyst was recycled for eight consecutive runs. It is important to note that no loss of activity was observed up to three consecutive cycles and a very minor loss of activity (~2%) could be seen even up to six cycles (Figure 2). The maximum yield of 92% could be realized even after eight cycles. This further indicates the superiority of this metal-free catalyst as compared to the metal based catalysts, where leaching of the metal ions during the catalytic activity is a very common problem.

4. Conclusions

In summary, polytriazine as a high surface area metal-free nitrogen enriched catalyst was synthesized that demonstrates a superior catalytic activity for the Knoevenagel reaction of aromatic aldehydes with malononitrile. The superior catalytic performance could be attributed to the large nitrogen content of 52 wt% in the framework coupled with the controlled textural properties. The formation of a single product with high yield (up to 98 %) along with very minor loss on recyclability up to eight cycles, wide substrate adaptability and low cost, make this catalyst as a potential candidate for practical applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was financially supported by DST, Govt. of India with Grant No. DST/TDT/TDP-03/ 2017(G).

References

- 1 A. P. Wight and M. E. Davis, *Chem. Rev.*, 2002, **102**, 3589-3614.
- 2 L. L. Chng, N. Erathodiyil and J. Y. Ying, *Acc. Chem. Res.*, 2013, **46**, 1825-1837.
- 3 P. Munnik, P. E. d. Jongh and K. P. D. Jong, Chem. Rev., 2015, 115, 6687-6718.
- 4 M. B. Ansari, H. Jin, M. N. Parvin and S. Park, *Catal. Today*, 2012, **185**, 211-216.
- X. Zhou, H. P. Zhang, G. Y. Wang, Z. G. Yao, Y. R. Tang and S. S. Zheng, J. Mol. Catal. A: Chem., 2013, 366, 43-47.
- 6 H. Sardon, A. Pascual, D. Mecerreyes, D. Taton, H. Cramail and J. L. Hedrick, *Macromol.*, 2015, 48, 3153-3165.
- 7 S. Y. Park, I. Hwang, H. J. Lee and C. E. Song, *Nat. Comm.* 2017, **8**, 14877 (1-8).
- 8 L. Zhu, X. Liu, H. Jiang and L. Sun, Chem. Rev., 2017, 117, 8129-8176.
- C. V. Doorslaer, J. Wahlen, P. Mertens, K. Binnemans and D. D. Vos, *Dalton Trans.*, 2010, **39**, 8377-8390.
- 10 N. Mase and T. Horibe, Org. Lett., 2013, 15, 1854-1857.
 11 D. M. Flanigan, F. R. M., N. A. White and T. Rovis, Chem. Rev.,
- 2015, **115**, 9307-9387.
 X. Gu, Y. Tang, X. Zhang, Z. Luo and H. Lu, New J. Chem., 2016, **40**, 6580-6583.
- 13 A. M. F. Phillips and A. J. L. Pombeiro, Org. Biomol. Chem., 2017, **15**, 2307-2340.57
- 14 M. G. Goesten, A. Szecsenyi, M. F. D. Lange, A. V. Bavykina, K. B. S. S. Gupta, F. Kapteijn and J. Gascon, *ChemCatChem*, 2016, **8**, 961-967.
- 15 Y. Yang, X. Zou, P. Cui, Y. Zhou, S. Zhao, L. Wang, Y. Yuan, and G. Zhu, ACS Appl. Mater. Interfaces, 2017, 9, 30958–30963.
- 16 P. Puthiaraj, Y. Lee, S. Zhang and W. Ahn, J. Mater. Chem. A, 2016, 4, 16288-16311.
- 17 Y. Zhang, S. A, Y. Zou, X. Luo, Z. Li, H. Xia, X. Liu and Y. Mua, J. Mater. Chem. A, 2014, **2**, 13422-13430.
- 18 S. K. Dey, N. D. S. Amadeu and C. Janiak, *Chem. Commun.*, 2016, **52**, 7834-7837.
- 19 Y. B. Zhou, Y. Q. Wang, L. C. Ning, Z. C. Ding, W. L. Wang, C. K. Ding, R. H. Li, J. J. Chen, X. Lu, Y. J. Ding and Z. P. Zhan, *J. Am. Chem. Soc.*, 2017, **139**, 3966-3969.
- 20 P. Mohanty and K. Landskron, J. Mater. Chem., 2009, 19, 2400-2406.
- 21 Y. Tang and K. Landskron, J. Phys. Chem. C, 2010, **114**, 2494-2498.
- 22 P. Mohanty, L. D. Kull and K. Landskron, Nat. Commun., 2011, 2, 401-406.
- 23 S. K. Kundu and A. Bhaumik, RSC Adv., 2015, 5, 32730-32739.

4 | J. Name., 2012, 00, 1-3

This journal is $\ensuremath{\mathbb{C}}$ The Royal Society of Chemistry 20xx

Published on 25 June 2018. Downloaded by Kaohsiung Medical University on 7/1/2018 8:44:11 AM

Journal Name

- 24 P. Pandey, A. P. Katsoulidis, I. Eryazici, Y. Wu, M. G. Kanatzidis and S. T. Nguyen, *Chem. Mater.*, 2010, **22**, 4974-4979
- 25 P. Rekha, V. Sharma and P. Mohanty, *Microporous Mesoporous Mater.* 2016, **219**, 93-102.
- 26 P. Rekha, R. Muhammad, V. Sharma, M. Ramteke and P. Mohanty, *J. Mater. Chem. A*, 2016, **4**, 17866-17874.
- 27 R. Muhammad, P. Rekha and P. Mohanty, *Greenhouse Gas* Sci. Technol., 2016, **6**, 150-157.
- 28 R. Muhammad, M. Chaudhary and P. Mohanty, J. CO₂ Util., 2018, 25, 302-309.
- 29 Z. Xiang and D. Cao, Macromol. Rapid Commun., 2012, **33**, 1184-1190.
- 30 D. Rath, S. Rana and K. M. Parida, RSC Adv., 2014, 4, 57111-57124.
- 31 G. Sneddon, A. Greenaway and H. H. P. Yiu, Adv. Energy Mater., 2014, 4, 1301873 (1-19).
- 32 D. Elhamifar, S. Kazempoor and B. Karimi, *Catal. Sci. Technol.*, 2016, **6**, 4318-4326.
- 33 M. G. Schwab, B. H. Fassbender, W. Spiess, A. Thomas, X. Feng and K. Mullen, J. Am. Chem. Soc., 2009, 131, 7216-7217.
- 34 S. Ren, R. Dawson, A. Laybourn, J. -X. Jiang, Y. Khimyak, D. J. Adams and A. I. Cooper, *Polym. Chem.*, 2012, **3**, 928-934.
- 35 L. Zhang, H. Wang, W. Shen, Z. Qin, J. Wang and W. Fan, J. Catal. 2016, 344, 293-302.
- 36 P. Puthiaraj, S. S. Kim and W. S. Ahn, Chem. Engg. J., 2016, 283, 184-192.
- 37 L. Jiao, Y. Hu, H. Ju, C. Wang, M. Gao, Q. Yang, J. Zhu, S. Yu and H. Jiang, J. Mater. Chem. A, 2017, 5, 23170-23178.
- 38 M. Chaudhary, A. K. Nayak, R. Muhammad, D. Pradhan and P. Mohanty, ACS Sustainable Chem. Engg., 2018. 6, 5895-5902.
- 39 I. Janica, V. Patroniak, P. Samor and A. Ciesielski, *Chem. Asian J.*, 2018, **13**, 465-481.
- 40 B. Liu, T. Ben, J. Xu, F. Deng and S. Qiu, New J. Chem., 2014, 38, 2292-2299.
- 41 G. Li, B. Zhang and Z. Wang, *Macromol.*, 2016, **49**, 2575-2581.
- 42 Y. Zhang and S. N. Riduan, *Chem. Soc. Rev.*, 2012, **41**, 2083-2094.
- 43 P. Pollet, E. A. Davey, E. E. U. Benavides, C. A. Eckerta and C. L. Liotta, *Green Chem.*, 2014, **16**, 1034-1055.
- 44 M. Taherimehr, B. V. de Voorde, L. H. Wee, J. A. Martens, D. D. Vos and P. P. Pescarmona, *ChemSusChem*, 2017, **10**, 1283-1291.

Nitrogen enriched polytriazine as metal-free heterogeneous catalyst for the Knoevenagel reaction in mild condition

Monika Chaudhary and Paritosh Mohanty*

Functional Materials Laboratory, Department of Chemistry, IIT Roorkee, Uttarakhand-

247667, India

E-mail: pmfcy@iitr.ac.in, paritosh75@gmail.com

Graphical abstract:

Ultra-fast Knoevenagel products with high-yield at ambient condition is reported using nitrogen-enriched nanoporous polytriazine as metal-free heterogeneous organocatalyst.

