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ARTICLE

Polymer Supported DMAP: An Easily Recyclable Organocatalyst for Highly Atom-economical Henry Reaction under Solvent-free Conditions

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Polymer supported catalyst is regarded as a borderline class of catalysts, which retains the advantages of homogeneous catalysts while securing the ease of recovery by simple filtration and workup of heterogeneous systems. Additionally, such catalysts are less hygroscopic due to the long polymer backbone. Here we have demonstrated that a catalytic amount of polymer supported DMAP (10 mol%) can lead to excellent conversion of an equimolar mixture of aldehyde and nitroalkane exclusively into *β*-nitroalcohols *via* the Henry reaction. Unlike most of the commonly used catalysts, polymer supported DMAP can be recovered by simple filtration and reused several times, thereby reducing the operational cost. High synthetic efficiency, total atom economy, near quantitative yields, mild reaction conditions, operational simplicity, easy recovery and reusability of the catalyst, solvent-free reaction conditions and avoidance of traditional reaction workup make the protocol highly significant from Green and Sustainable Chemistry perspectives.

Introduction

Over the last few years polymers have been widely utilized as a solid support material for the design of environmentally benign heterogeneous catalysts to address a variety of highly relevant economic and environmental issues. These types of 'quasi-homogeneous' catalytic systems possess uniformity and precisely engineered reactive sites similar to those of their homogeneous counterparts, and therefore combine the advantages of both homogeneous and heterogeneous catalytic reaction systems. Although solvents play a vital role in controlling the kinetic and thermodynamic parameters in most of the synthetic protocols, solvents are the main source of toxic waste; and their use bring about many undesired elements in industrial reaction design. The increasing concern of the effect of harmful chemicals on the environment and human body can be addressed by omission of organic solvents, the highest contributor to environmental factor[1] (E factor), from the reaction design. Hence, the application of organic reactions under solvent-free conditions has been getting immense attention in recent years.[2]

Henry reaction is one of the most important and economical C-C bond-constructing methodologies,[3-8] providing *β*-nitroalcohols which can lead to numerous valuable pharmaceutically important compounds[9] by manipulating the nitro and hydroxy groups. Traditional synthesis of nitroalcohols involves various base catalyzed additions of nitroalkane to carbonyl compound.[10-15] However, many other side reactions, such as aldol, Michael, Knoevenagel, Cannizaro and dehydration reactions take place under strong basic conditions.[16] Thus, careful control of the basicity of the reaction medium is crucial to achieve good yields of nitroalcohols. Such efforts often require longer reaction times. Additionally, removal of the base before workup is a difficult process as acidification of the reaction mixture may lead to the Nef reaction.[17] Apart from this, many reported literature are accompanied by low yield, requirement of moisture-free reaction conditions,[12] problems associated with recycling of homogeneous catalyst,[11] use of toxic solvents and tedious workup processes. Hence, a 'green' approach to chemical methods which stimulates the use of heterogeneous, stable and recyclable catalyst as a replacement of classical 'homogeneous' base catalyst for Henry reaction is highly desirable.

In the recent decades, organocatalysis[18] has evolved as an area for the development of new concepts in the field of synthetic chemistry. The term organocatalysis applies solely to the use of organic molecules, that is, metal-free catalysts, to realize a variety of reactions that were typically catalyzed by metal catalysts. Organocatalysis, as compared to metal and biocatalysis, represents a non-toxic, mild, robust nature, eco-friendly and cost-effective methodology for chemical synthesis, especially when metal traces are of real concern, particularly in the pharmaceutical and natural product synthesis.[19] However, most of the organocatalytic processes require high catalyst loading and rely on the tedious separation of the used organocatalyst from the synthesized product. As a result, 'heterogeneous organocatalyst' has recently attracted increased attention with an aim to develop simple purification procedure of the products and recyclable organocatalysts.[20]

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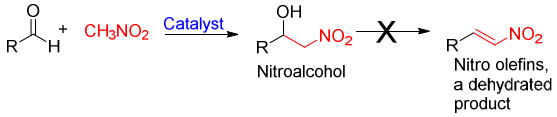
Presently, the environmental concerns associated with their toxicity, disposal and catalyst/product separation are limiting the applications of homogeneous catalyst in organic synthesis. Gratifyingly, solid-phase organic synthesis (SPOS) continues to evolve as a means to create and modify compound libraries via combinatorial chemistry.[21-23] The important advantages of solid phase synthesis over classical solution phase synthetic methods include purification of products by simple filtration of the polymer matrix, easy handling, low moisture susceptibility, minimum side reaction, and recovery and recyclability of the polymer matrix for repeated use.[24, 25, 21(a)] Interestingly, 4-DMAP has evolves as one the most frequently used catalyst in various organic transformation in recent years.[26] Here, we wish to report a simple and environmentally benign Henry reaction for the synthesis of nitroalcohols exclusively using polymer supported 4-DMAP (PS-DMAP) as a heterogeneous organocatalyst (Scheme 1).

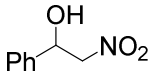
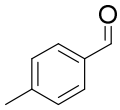
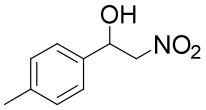
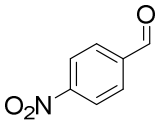
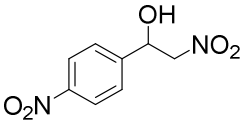
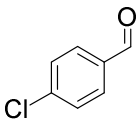
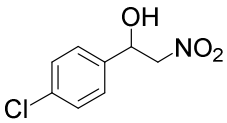
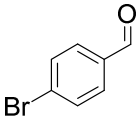
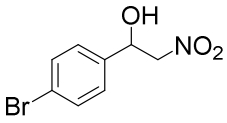
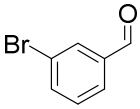
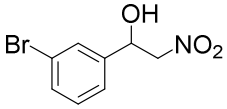


Scheme 1: Schematic representation of Henry reaction.

Result and discussion

Although there is wealth of methods available to synthesize *β*-nitroalcohols *via* the Henry reaction, only a few reports suit the '12 Principles of Green Chemistry' postulated by Anastas *et. al.*[27] In 1999, Choudary *et. al.* had described Henry reaction catalyzed by modified Mg-Al hydrotalcite. The solid catalyst was recovered by simple filtration and was reused.[28] In continuation of our on-going interest for the development of useful synthetic methodologies,[29] we assumed that if a mild base is used to abstract the *β*-hydrogen of nitroalkane, nitroalcohols could be easily accessed. We initially wanted to test our assumption in solution phase using soluble 4-DMAP as a base. At the onset, we took an equimolar mixture of benzaldehyde and nitromethane and stirred with 4-DMAP (10 mol%) at room temperature under solvent free condition (SolFC) as model reaction. To our delight, the formation of *β*-nitroalcohol was found to be completed in 20 mins to generate 93% isolated yield (Table 1, entry 1). We extended the method for the synthesis of a few more nitroalcohols starting from aromatic aldehydes with nitromethane as summarized in Table 1. In all the cases, we found good yield of the corresponding *β*-nitroalcohol without formation of any side product, particularly the dehydrated product (Scheme 1). These exclusive formation of the *β*-nitroalcohols may be attributed to the mild and selective nature of the organocatalyst (*i.e* 4-DMAP) used in the said transformation. No significant enhancement of the conversion of the reaction was observed by increasing the amount of nitroalkane (Table 1, entry 6).

Table 1: Synthesis of nitroalcohols in solution phase[a]

Entry	Aldehyde	Product	Time (mins)	Yield (%)[b]
1.			20	93
2.			30	89
3.			15	95
4.			15	91
5.			15	91
6.			20	92[c]

[a]Reaction conditions: Aldehyde (1 mmol), nitromethane (1 mmol), 4-DMAP (0.1 mmol, 10 mol%), solvent-free, room temperature; [b]Yields are calculated from pure isolated product after column chromatographic purification. [c]3 mmol of nitromethane was used.

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Encouraged by the result in solution phase synthesis, we wanted to use polymer supported 4-DMAP (PS-DMAP) as this will reduce our efforts in the purification of nitroalcohol from the reaction mixture. Here, we carried out the reaction of benzaldehyde with nitromethane under similar reaction conditions except for changing soluble DMAP with commercially available polymer supported DMAP (DMAP polymer-bound, ~3 mmol/g DMAP loading, matrix crosslinked with 2% DVB). Here it took comparatively longer time (25 min) to drive the reaction into completion and gave the desired product in 95% yield. Various solvents such as DCM, $CHCl_3$, THF, MeOH, CH_3CN, EtOAc, DMF and diethyl ether were tried to examine the influence of the solvent on the model reaction. However, we observed that the reaction was fastest and gave maximum yield of the product while working under solvent-free conditions. Results of various optimizations were as given in Table 2.

Table 2: Optimization of base for the model reaction

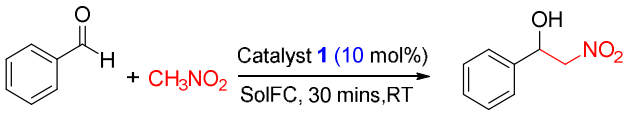
Entry	Base	Amount (mol%)	Time (mins)	Yield (%)
1.	KOH	20	40	56
2.	K_2CO_3	20	50	45
3.	CaCO3	20	50	51
4.	Na_2CO_3	20	50	48
5.	KI	20	40	54
6.	KF	20	40	56
7.	PS-TPP	10	50	<5
8.	DABCO	10	50	<5
9.	Pyridine	10	30	65
10.	Et_3N	10	30	67
11.	PS-DMAP	5	45	83
12.	PS-DMAP	10	25	95
13.	PS-DMAP	20	30	95

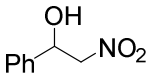
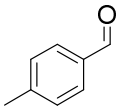
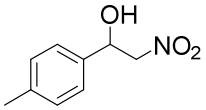
Reaction conditions: Benzaldehyde (1 mmol), nitromethane (1 mmol), solvent free, room temperature.

Further screening of both inorganic and organic base revealed that PS-DMAP was the optimal base for the said conversion. In the presence of inorganic base like KOH, K_2CO_3, $CaCO_3$, Na_2CO_3, KI or KF the reactions were sluggish, often resulted in the formation of base catalyzed dehydration to form nitro olefins and the yields of the corresponding *β*-nitroalcohol were relatively low (Table 2, entries 1-6). Only a trace amount of the desired product was observed when DABCO or polymer-supported triphenylphosphine (PS-TPP) was used as catalyst (Table 2, entries 7 and 8). Pyridine and Et_3N gave comparatively higher yields of 65% and 67% respectively (Table 2, entries 9-10). To our pleasure, used of 10 mol% of PS-DMAP gave the desired *β*-nitroalcohol in 95% yield (entry 12). Hence, taking PS-DMAP (denoted as catalyst **1**) as an excellent base for the reaction, the optimum catalyst loading was investigated. DMAP loadings of 5, 10 and 20 mol% were compared (Table 2, entries 11-13). Using 5 mol% of catalyst **1** the reaction took long time for complete conversion of the desired product and gave low yield (Table 2, entry 11). However, the use of more PS-DMAP (20 mol%) did not improve the yield (Table 2, entry 13). Hence, it was confirmed that, the optimal amount of catalyst loading was found to be 10 mol% (Table 2, entry 12). Since the formations of undesired olefinic compounds by dehydration were reported in several syntheses of *β*-nitroalcohols, we decided to investigate the limitations such reactions might have on our methodology. However, to our delight, under our optimized reaction conditions the formation of dehydrated product was not observed even after stirring the reaction for more than 2 hrs.

With the optimum reaction conditions in our hand, the reaction was generalized for diverse aldehydes to show the generality and scope of our method. The results were summarized in Table 3. We have found that the reaction of aldehydes with nitromethane in the presence of catalyst **1**was rapid and gave good to excellent yield in all the cases (Table 2, entries 1-19). In general, aromatic aldehydes bearing an electron-withdrawing substituent like nitro group ($-NO_2$) undergo faster reactions and furnished nitroalcohols in high yields (Table 3, entries 3, 8, 9). However, a few less electrophilic aldehydes, such as *m, p*-dimethoxybenzaldehyde (Table 3, entry 7) and *m, p*-methylenedioxybenzaldehyde (entry 12) gave product *β*-nitroalcohols in low yields of 59% and 54% respectively. These observations revealed that electron-withdrawing groups enhance the electrophilicity of carbonyl carbons in aldehydes which facilitate the reaction, while electron-donating groups render it less electrophilic which in turn retarded the reactions. We found that the reactions using aliphatic aldehydes were slower which probably is due to the electron donating tendency of alkyl group (entries 13-19). Interestingly, reactive groups like –OTBS (Table 3, entries 18) and –OTHP (Table 3, entries 19) remain unaffected which showed the mild nature of our protocol.

Table 3: Henry reactions of various aromatic and aliphatic aldehydes with nitromethane under solvent free conditions[a]



Entry	Aldehyde	Product	Time (mins)	Yield(%)[b]
1.			25	95
2.			36	94

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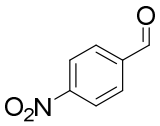
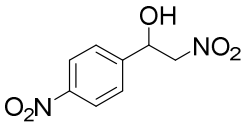
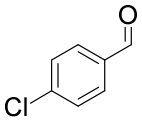
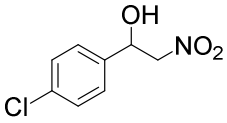
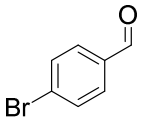
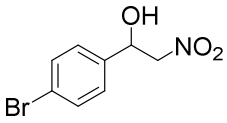
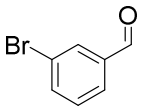
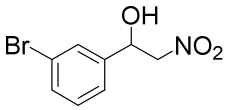
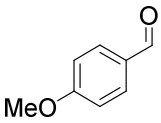
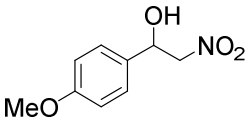
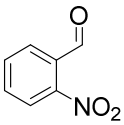
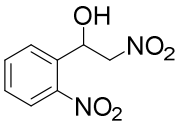
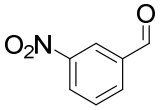
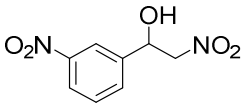
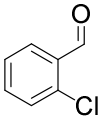
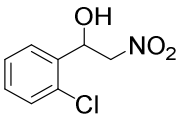
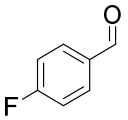
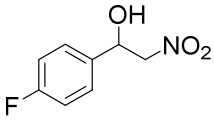
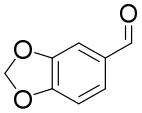
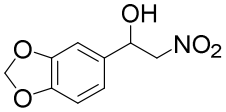
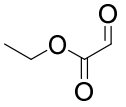
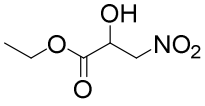
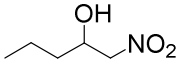
3.			20	100
4.			25	100
5.			25	93
6.			25	92
7.			75	59[c]
8.			20	96
9.			25	95
10.			23	88
11.			20	89
12.			65	54[c]
13.			30	85
14.			30	87

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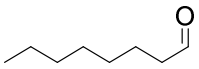
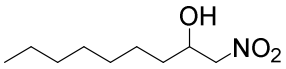
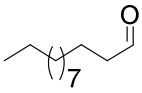
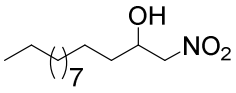
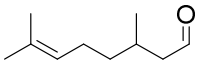
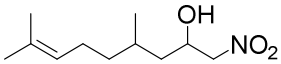
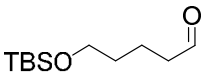
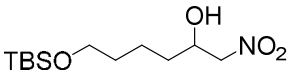
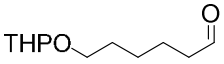
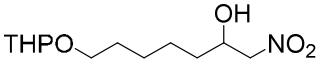
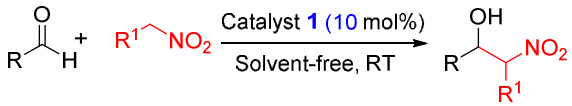
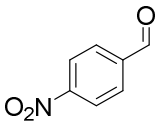
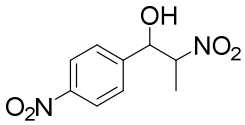
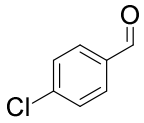
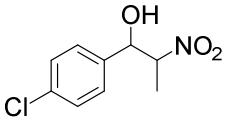
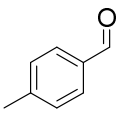
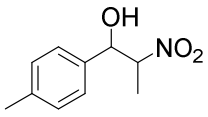
15.			35	91
16.			35	94
17.			30	89
18.			35	84
19.			35	85

[a]Reaction conditions: Aldehyde (1 mmol), nitromethane (1 mmol), catalyst **1** (0.1 mmol, 10 mol%) at room temperature; [b]Yields are calculated from pure isolated product. [c]Reaction was done at 45 °C

With an interest to perceive the effect of chain length and substitution pattern in the nitroalkane, we extended our reaction of aldehyde with nitroethane, nitropropane and 2-nitropropane as shown in Table 4. Under similar reaction conditions, the reactions of aldehyde with nitroethane gave excellent yields of the nitroalcohols (Table 4, entries 1-10). However, as compared to reaction with nitromethane, longer reaction times were required for completion. These may be attributed to the electronic effect and steric hindrance offered by the alkyl group of the nitroalkane. The effect was more pronounced while workings with bulky molecule like 2-nitropropane (Table 4, entries 13-15). Upon generalization, it was observed that the electronic effects of the substituent in the aromatic aldehydes affected the reactions in the same way as using nitromethane. As expected, 4-nitrobenzaldehyde, an aldehyde with electron-withdrawing group, gave an excellent yields with all the nitroalkanes. It gave quantitative yield (100%) with nitroethane (Table 4, entry 1), 96% with nitropropane (Table 4, entry 11) and quantitative yield with 2-nitropropane (Table 4, entry 13). Moreover, the aliphatic aldehydes on reacting with nitroethane and 2-nitropropane also gave nitroalcohols in high yields (Table 4, entries 5-8, 14, 15). To our delight, NMR analysis of all the products revealed exclusive formation of nitroalcohol. A plausible mechanistic pathways like our reactions, which involves 'hyper nucleophilic Lewis base' like DMAP was proposed by List *et al.*[30] and Zipse *et al.*[31]

Table 4: Henry reaction under solvent free conditions[a]



Entry	Aldehyde	Product	Time (mins)	Yield (%)[b]
1.			25	100
2.			30	95
3.			55	91

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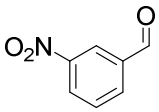
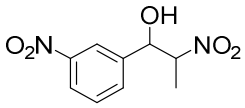
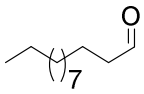
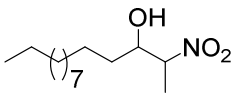
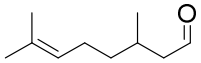
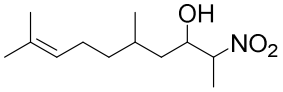
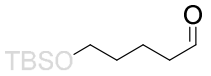
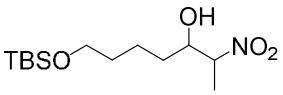
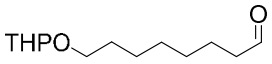
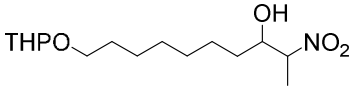
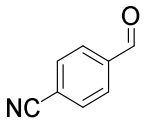
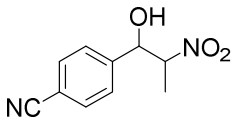
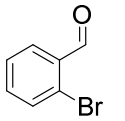
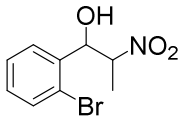
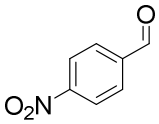
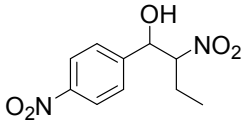
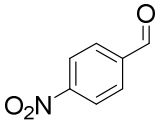
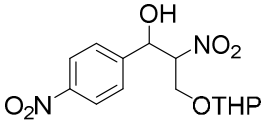
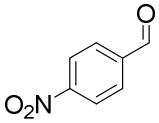
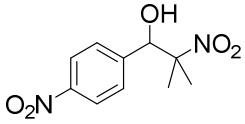
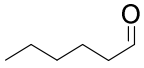
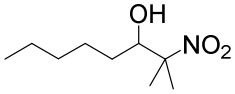
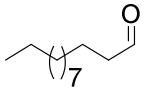
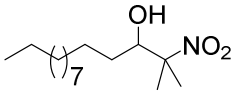
4.			3o	95
5.			45	89
6.			45	85
7.			45	88
8.			40	85
9.			35	96
10.			40	93
11.			30	96
12.			35	78
13.			35	100
14.			45	87
15.			50	89

[a]Reaction conditions: Aldehyde (1 mmol), nitroalkane (1 mmol), catalyst **1** (0.1 mmol, 10 mol%) at room temperature; [b]Yields are calculated from pure isolated product.

Recycling of the catalyst

The recyclability of catalyst **1** was investigated with consecutive Henry reaction using different substrates. Fig.1 depicts the results of consecutive runs performed by reusing the catalyst under our optimal reaction conditions. After each catalytic run, the catalyst were recovered by simple filtration, washed with ethyl acetate and then dried at 100 ^{o}C in Abderhalden apparatus under reduced pressure overnight before being used again in a new reaction. We have demonstrated that no depreciations of catalytic performance were observed in all the test reactions even after five catalytic cycles. Additionally, no difference in IR spectrum of the catalyst was observed after these repeated cycles.

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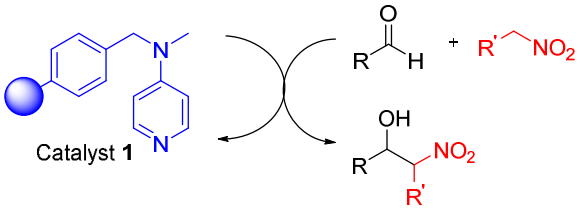
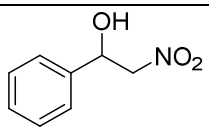
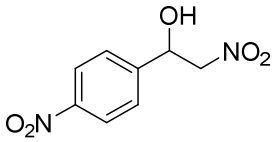
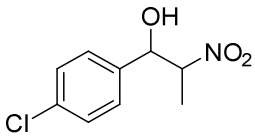
Figure 1: Recyclability test of catalyst 1 for the Henry reactions[a]



Entry	Products	Run/ Yield%
1.		run 1 2 3 4 5 yield (%) 95 94 93 93 94
2.		run 1 2 3 4 5 yield (%) 100 100 98 100 100
3.		run 1 2 3 4 5 yield (%) 100 100 98 98 100

[a]Reaction conditions: Aldehyde (1 mmol), nitroalkane (1 mmol), catalyst **1** (0.1 mmol, 10 mol%) at room temperature.

Conclusion

As "greener" reaction protocols gain popularity in academia and industries, the need for readily available, less toxic, stable, a heterogeneous and easily recyclable catalyst becomes a fundamental necessity. Here we have reported an exclusive synthesis of *β*-nitroalcohols *via* the Henry reaction using soluble and polymer supported DMAP at room temperature under solvent free conditions. The heterogeneous catalyst **1** was easily recovered by simple filtration and reused at least five times without any noticeable loss in its catalytic activities. It is noteworthy that the reaction medium was highly insensitivity towards moisture due to polymer backbone of the catalyst and reactive groups, including -OTBS, -OTHP were tolerated. Total atom economy of all the reactions and quantitative yields in many cases are the significant distinctive features of our method. In addition, ready availability of catalysts, solvent free conditions, products isolation by simple filtration avoiding tedious column chromatographic purification makes the procedure economical and environmentally benign.

Experimental

Materials and physical measurements

Polymer-supported 4-DMAP (~3 mmol/g DMAP loading, matrix crosslinked with 2% DVB (divinylbenzene)) was purchased from Sigma-Aldrich. Other reagents were obtained from SpectroChem. Progress of the reaction was monitored by thin layer chromatography (TLC) carried out on glass plates coated with silica gel G, using the solvent system EtOAc/hexane. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance II (400 MHz), Bruker Avance III (500 MHz) spectrometer using tetramethylsilane (TMS) as an internal reference. Elemental analyses of the products were performed on a Perkin-Elmer-2400 CHNS analyzer.

General procedure for the solution-phase Henry reaction using soluble DMAP

To a well-stirred mixture of aldehyde (1 mmol) and nitroalkane (1 mmol) in a sample vial was added 4-DMAP (10 mol%) at room temperature. Stirring was continued until completion of the reaction, as monitored by TLC. After completion of the reaction, the resultant mixture was purified by silica gel column chromatography (10% ethyl acetate in hexane) to give the corresponding nitroalcohol.

General procedure for the solid-phase Henry reaction using PS-DMAP

To a well-stirred mixture of aldehyde (1 mmol) and nitroalkane (1 mmol) in a sample vial, PS-DMAP (10 mol%) was added at ambient temperature. The reaction mixture was allowed to stir for the time specified in the table. The progress of the reaction was monitored using TLC. After completion of the reaction (as indicated by TLC), the resultant mixture was filtered and washes with ethyl acetate (20 ml). The filtrate was then concentrated to give desired product in high purity.

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The spectral (FT-IR, ^{1}H NMR, ^{13}C NMR) and analytical data for selected *β*-nitroalcohols are presented below:

2-Nitro-1-(p-tolyl)ethan-1-ol (Table 3, Entry 2):
Light yellow oil, IR (KBr, cm^{-1}): ν 3429, 3018, 2408, 1553, 1433, 1221, 1035, 963, 777, 677; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.27-7.26 (dd, J= 7.6 Hz, 1H), 7.20-7.18 (dd, J= 8 Hz, 1H), 7.10 (d, J= 8 Hz, 2H), 5.41-5.38 (m, 1H), 4.74-4.71 (m, 1H), 4.61-4.55 (m, 1H), 2.34 (s, 3H), 1.52 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 139.04, 138.89, 129.93, 129.67, 125.89, 70.90, 21.16; Elemental analysis for $C_9H_{11}NO_3$: Calculated; C 59.66; H 6.12; Found C 59.67; H 6.11.

2-Nitro-1-(4-nitrophenyl)ethan-1-ol (Table 3, Entry 3):
Yellowish liquid, IR (KBr, cm^{-1}): ν 3529, 3451, 3019, 1527, 1434, 1222, 1029, 937, 758, 768; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.27 (d, J= 8.8 Hz, 2H), 7.64 (d, J= 8.8 Hz, 2H), 5.63-5.60 (m, 1H), 4.87 (t, J= 6.8 Hz, 1H), 4.64-4.58 (m, 1H), 2.01 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 148.09, 145.02, 128.71, 126.96, 124.20, 69.95; Elemental analysis for $C_8H_8N_2O_5$: Calculated; C 45.29; H 3.80; Found C 45.28; H 3.81.

1-(4-Chlorophenyl)-2-nitroethan-1-ol (Table 3, Entry 4):
Colorless liquid, IR (KBr, cm^{-1}): ν 3408, 3035, 2979, 2989, 2756, 1536, 1428, 1389, 1326, 1275, 1185, 1115, 840, 756; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.35 (d, J= 8.4 Hz, 2H), 7.18 (d, J= 8.4 Hz, 2H), 5.44-5.41 (m, 1H), 4.80 (t, J= 7.2 Hz, 1H), 4.56 (d, J= 3.6 Hz, 1H), 2.57 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 138.37, 132.67, 129.80, 129.18, 127.37, 70.29; Elemental analysis for $C_8H_8ClNO_3$: Calculated; C 47.66; H 4.00; Found C 47.68; H 3.98.

1-(4-Bromophenyl)-2-nitroethan-1-ol (Table 3, Entry 5):
Pale yellow oil, IR (KBr, cm^{-1}): ν 3415, 3025, 2939, 2889, 2787, 1550, 1440, 1381, 1331, 1280, 1184, 1120, 840; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.54 (d, J= 8.4 Hz, 2H), 7.29 (d, J= 8.4 Hz, 2H), 5.44-5.41 (m, 1H), 4.79 (t, J= 7.2 Hz, 1H), 4.57-4.50 (m, 1H), 2.03 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 138.05, 132.14, 129.12, 127.68, 122.89, 70.33; Elemental analysis for $C_8H_8BrNO_3$: Calculated; C 39.05; H 3.28; Found C 39.06; H 3.27.

2-Nitro-1-(2-nitrophenyl)ethan-1-ol (Table 3, Entry 8):
Oily liquid, IR (KBr, cm^{-1}): ν 3305, 3025, 2939, 2889, 2787, 1553, 1432, 1379, 1323, 1281, 1178, 1121, 845;^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.13 (d, J= 7.6 Hz, 1H), 8.07 (d, J= 8 Hz, 1H), 7.97 (d, J= 7.6 Hz, 1H), 7.56 (t, J= 8 Hz, 1H), 6.05 (d, J= 9.2 Hz, 1H), 4.87 (d, J= 13.6 Hz, 1H), 4.58-4.52 (m, 1H), 2.60 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 134.37, 134.16, 133.81, 131.31, 129.64, 128.77, 124.95, 66.79; Elemental analysis for $C_8H_8N_2O_5$: Calculated; C 45.29; H 3.80; Found C 45.27; H 3.82.

1-(4-Fluorophenyl)-2-nitroethan-1-ol (Table 3, Entry 11):
Light yellow liquid, IR (KBr, cm^{-1}): ν 3425, 3012, 2909, 2100, 1704, 1526, 1132, 879, 745; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.41-7.39 (dd, J= 8 Hz, 1H), 7.39-7.37 (dd, J= 8 Hz, 1H), 7.12 (d, J= 8.4 Hz, 2H), 5.47-5.44 (m, 1H), 4.78 (t, J= 6.8 Hz, 1H), 4.59-4.50 (m, 1H), 2.92 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 161.66, 133.86, 127.74, 116.14, 115.93, 70.32; Elemental analysis for $C_8H_8FNO_3$: Calculated; C 51.90; H 4.36; Found C 51.92; H 4.35.

1-Nitropentan-2-ol (Table 3, Entry 14):
Yellow liquid, IR (KBr, cm^{-1}): ν 3361, 2846, 1614, 1520, 1206, 1171, 853, 736; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 4.57-4.48 (m, 2H), 3.91 (s, 1H), 3.19 (s, 1H), 1.53-1.40 (m, 6H), 0.96 (t, J= 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 86.47, 65.19, 35.14, 18.89, 15.95; Elemental analysis for $C_5H_{11}NO_3$: Calculated; C 45.10; H 8.33; Found C 45.11; H 8.32

1-Nitrotridecan-2-ol (Table 3, Entry 16):
Solid, semi-solid, IR (KBr, cm^{-1}): ν 3402, 3018, 2932, 2866, 1527, 1438, 1222; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 4.46-4.31 (m, 3H), 2.58 (s, 1H), 1.64-1.04 (m, 20H), 0.88 (t, J= 6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 80.63, 68.66, 33.70, 31.90, 29.60, 29.51, 29.43, 29.33, 29.31, 25.17, 22.68, 14.12; Elemental analysis for $C_{13}H_{27}NO_3$: Calculated; C 63.64; H 11.09; Found C 63.66; H 11.07.

4,8-Dimethyl-1-nitronon-7-en-2-ol (Table 3, Entry 17):
Colorless liquid, IR (KBr, cm^{-1}): ν 3588, 3025, 2925, 1620, 1553, 1433, 1387, 1221; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 5.08 (t, J= 7.2 Hz, 2H), 4.45-4.31 (m, 6H), 2.71 (d, J= 4.8 Hz, 1H), 2.68 (d, J= 4.4 Hz, 1H), 2.06-1.91 (m, 4H), 1.73-1.55 (m, 2H), 1.68 (s, 6H), 1.60 (s, 6H), 1.47-1.37 (m, 4H), 1.20-1.12 (m, 4H), 0.96 (d, J= 6.8 Hz, 3H), 0.92 (d, J= 8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 131.71, 131.61, 124.27, 124.22, 81.14, 80.80, 66.98, 66.60, 40.89, 40.57, 37.53, 36.27, 28.87, 28.43, 25.73, 25.31, 25.19, 19.97, 18.81, 17.68; Elemental analysis for $C_{11}H_{21}NO_3$: Calculated; C 61.37; H 9.83; Found C 61.36; H 9.84.

6-((*tert*-Butyldimethylsilyl)oxy)-1-nitrohexan-2-ol (Table 3, Entry 18):
Colorless oil, IR (KBr, cm^{-1}): ν 1753, 1628, 1528, 1201, 1119, 865, 769, 678; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 5.25 (s, 1H), 4.51-4.41 (m, 1H), 4.14-4.11 (m, 1H), 3.89 (t, J= 7.2 Hz, 2H), 3.64-3.57 (m, 1H), 1.49-1.39 (m, 6H), 0.83 (s, 9H), 0.26 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 80.60, 68.58, 62.83, 36.01, 33.35, 32.13, 25.95, 21.66, -5.31; Elemental analysis for $C_{12}H_{27}NO_4Si$: Calculated; C 51.95; H 9.81; Found C 51.97; H 9.79.

2-Nitro-1-(4-nitrophenyl)propan-1-ol (Table 4, Entry 1):
Reddish liquid, IR (KBr, cm^{-1}): ν 3435, 3330, 3025, 2889, 2789, 1547, 1440, 1320, 1284, 1223, 1185;^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.24-8.23 (dd, J= 4.4 Hz, 1H), 8.22-8.21 (dd, J= 4 Hz, 1H), 7.62 (d, J= 4.8 Hz, 2H), 5.21 (d, J= 8.4 Hz, 1H), 4.82-4.71 (m,1H), 3.26 (s, 1H), 1.48-1.46 (dd, J= 6.8 Hz, 1.5 H), 1.38-1.36 (dd, J= 6.8 Hz, 1.5H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 148.11, 147.71, 128.01, 124.36, 87.88, 75.03, 16.16; Elemental analysis for $C_9H_{10}N_2O_5$: Calculated; C 47.79; H 4.46; Found C 47.77; H 4.48.

1-(4-Chlorophenyl)-2-nitropropan-1-ol (Table 4, Entry 2):
Colorless oil, IR (KBr, cm^{-1}): ν 3401, 3025, 2949, 2889, 2786, 1546, 1438, 1381, 1323, 1281, 1179, 1121, 845, 786; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.81 (d, J= 7.6 Hz, 2H), 7.52 (d, J= 7.6 Hz, 2H), 5.01 (d, J= 8.8 Hz, 1H), 4.75-4.69 (m, 1H), 2.64 (s, 1H), 1.47 (d, J= 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 136.87, 131.47, 128.32, 127.40, 88.25, 31.77, 16.33; Elemental analysis for $C_9H_{10}ClNO_3$: Calculated; C 50.13; H 4.67; Found C 50.14; H 4.66.

2-Nitro-1-(p-tolyl)propan-1-ol (Table 4, Entry 3):
Colorless liquid, IR (KBr, cm^{-1}):ν3354, 3015, 2929, 2898, 2780, 1550, 1441, 1377, 1345, 1284, 1179, 1110;^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.24 (d, J= 8 Hz, 2H), 7.20 (d, J= 7.2 Hz, 2H), 5.30 (s, 1H), 4.96 (d, J= 8.8 Hz, 1H), 4.77-4.70 (m, 1H), 2.35 (s, 1H), 1.48-1.47 (dd, J= 6.8 Hz, 1.5H), 1.29-1.27 (dd, J= 6.8 Hz, 1.5H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 129.16, 128.89, 126.35, 125.40, 87.98, 75.62, 20.69, 15.95; Elemental analysis for $C_{10}H_{13}NO_3$: Calculated; C 61.53; H 6.71; Found C 61.55; H 6.69.

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2-Nitro-1-(3-nitrophenyl)propan-1-ol (Table 4, Entry 4):
Reddish liquid, IR (KBr, cm^{-1}): ν 3445, 3310, 3055, 2819, 2779, 1536, 1441, 1327, 1282, 1242, 1158; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.69 (s, 1H), 8.50 (d, J= 7.6 Hz, 1H), 7.78 (d, J= 7.6 Hz, 1H), 7.64-7.58 (dd, = 8.4 Hz, 1H), 5.56 (s, 1H), 5.22 (d, J= 8.4 Hz, 1H), 4.85-4.77 (m, 1H), 1.50-1.48 (dd, J= 6 Hz, 1.5H), 1.39-1.37 (dd, J= 6 Hz, 1.5H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 148.38, 140.83, 135.00, 133.21, 123.84, 121.95, 88.0, 74.97, 16.11; Elemental analysis for $C_9H_{10}N_2O_5$: Calculated; C 47.79; H 4.46; Found C 47.80; H 4.47.

2-Nitrotetradecan-3-ol (Table 4, Entry 5):
Colorless liquid, IR (KBr, cm^{-1}): ν 1850, 1622, 1547, 1450, 1386, 1225, 1024, 848; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 4.18-4.15 (m, 1H), 3.91-3.88 (m, 1H), 2.44 (s, 1H), 1.54-1.37 (m, 20H), 0.89 (t, J= 6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 86.17, 72.90, 33.05, 33.92, 31.71, 29.52, 29.32, 24.92, 22.65, 16.13, 14.09; Elemental analysis for $C_{14}H_{29}NO_3$: Calculated; C 64.83; H 11.27; Found C 64.82; H 11.28.

5,9-Dimethyl-2-nitrodec-8-en-3-ol (Table 4, Entry 6):
Colorless liquid, IR (KBr, cm^{-1}): ν 3540, 3025, 2925, 1620, 1553, 1454, 1381, 1215; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 5.10-5.06 (m, 2H), 4.55-4.45 (m, 2H), 4.34-4.25 (m, 1H), 4.03-3.94 (m, 1H), 2.46-2.40 (m, 1H), 2.39-2.35 (m, 1H), 2.02-1.95 (m, 4H), 1.73-1.55 (m, 2H), 1.68 (s, 6H), 1.60 (s, 6H), 1.49-1.06 (m, 8H), 1.54 (t, *J* = 6.4, 6H), 0.96 (dd, *J* = 6.4, 3.2 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 131.6, 131.5, 124.3, 88.4, 87.9, 86.8, 86.3, 71.1, 70.8, 70.1, 69.8, 40.4, 40.1, 40.0, 37.8, 37.6, 36.1, 35.7, 29.1, 28.8, 28.6, 28.4, 25.7, 25.3, 25.19, 25.14, 20.3, 20.0, 18.7, 18.6, 17.6, 10.2, 10.1; Elemental analysis for $C_{12}H_{23}NO_3$: Calculated; C 62.85; H 10.11; found: C 62.71, H 9.98.

4-(1-Hydroxy-2-nitropropyl)benzonitrile (Table 4, Entry 9):
Light green liquid, IR (KBr, cm^{-1}):ν3555, 3059, 2914, 2055, 1976, 1528, 1448, 1280, 845; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 8.01 (d, J= 8 Hz, 2H), 7.86 (d, J= 8 Hz, 2H), 5.48 (s, 1H), 5.12 (d, J= 8.8 Hz, 1H), 4.77-4.66 (m, 1H), 1.47-1.45 (dd, J= 6.8 Hz, 1.5H), 1.35-1.33 (dd, J= 6.8 Hz, 1.5H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 143.87, 132.50, 126.92, 118.43, 112.07, 87.93, 73.13, 15.95; Elemental analysis for $C_{10}H_{10}N_2O_3$: Calculated; C 58.25; H 4.89; Found C 58.27; H 4.87.

1-(2-Bromophenyl)-2-nitropropan-1-ol (Table 4, Entry 10):
Yellow liquid, IR (KBr, cm^{-1}): ν 3351, 2957, 2863, 1527, 1379, 883; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 7.59 (d, J= 7.6 Hz, 1H), 7.55 (t, J= 7.2 Hz, 1H), 7.45 (d, J= 6.8 Hz, 1H), 7.2 (t, J= 5.2 Hz, 1H), 5.75 (s, 1H), 5.55 (d, J= 6.8 Hz, 1H), 4.87-4.81 (m, 1H), 1.40-1.38 (dd, J= 6.8 Hz, 1.5H), 1.37-1.36 (dd, J= 4 Hz, 1.5H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 137.98, 132.92, 130.32, 129.94, 121.53, 88.32, 73.91, 16.01; Elemental analysis for $C_9H_{10}BrNO_3$: Calculated; C 41.56; H 3.88; Found C 41.57; H 3.87.

2-Nitro-1-(4-nitrophenyl)-3-[(tetrahydro-2H-pyran-2-yl)oxy]propan-1-ol (Table 4, Entry 12):
Colorless semi-solid, IR (KBr, cm^{-1}):ν 3456, 3018, 2932, 1533, 1440, 1361, 1215, 1036; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 8.28-8.25 (m, 2H), 7.63-7.60 (m, 2H), 5.45-5.40 (m, 1H), 4.92-4.87 (m, 1H), 4.57-4.53 (m, 1H), 4.11-3.95 (m, 2H), 3.56-3.45 (m, 3H), 1.75-1.52 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): 148.23, 145.34, 145.12, 127.71, 127.55, 127.41, 127.11, 124.15, 124.04, 99.92, 99.42, 98.68, 91.33, 91.26, 90.89, 90.52, 72.33, 71.62, 71.35, 71.32, 65.17, 64.80, 64.38, 64.19, 63.17, 62.70, 62.62, 62.16, 30.23, 30.18, 29.96, 29.72, 25.03, 19.38, 19.15, 19.06, 18.76; Elemental analysis for $C_{14}H_{18}N_2O_7$: Calculated; C 51.53; H 5.56; Found: C 51.56, H 5.53.

2-Methyl-2-nitrotetradecan-3-ol (Table 4, Entry 15):
Colorless liquid; IR (KBr, cm^{-1}): ν 3343, 3018, 2932, 2859, 1527, 1540, 1460; ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): 4.00 (m, 1H), 3.89 (m, 1H), 2.30-2.25 (m, 1H), 2.07-2.01 (m, 1H), 1.89-1.85 (m, 1H), 1.69-1.28 (m, 16H), 1.56 (s, 3H), 1.55 (s, 3H), 0.88 (t, J = 6.4 Hz, 3H), , ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): 94.32, 92.22, 71.82, 33.54, 31.91, 31.44, 29.61, 29.54, 29.46, 29.36, 26.40, 25.26, 23.90, 23.79, 22.70, 20.19, 14.15, 10.22; Elemental analysis for $C_{15}H_{31}NO_3$: Calculated; C 65.89; H 11.43; found: C 65.93; H 11.39.

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Graphical Abstract