CHAPTER 4

Nitrogen bound polymers as heterogeneous basic catalysts for the synthesis of β-nitroaldol in aqueous medium

4.1 Introduction

The Henry reaction provides an efficient atom-economical route to prepare diastereomeric mixtures of β-nitroalcohols from the mixture of 1° or 2° nitroalkane with aldehydes or keto compounds in presence of a base [1-4]. The resulting β-nitroalcohols have been widely utilized as important precursors for the synthesis of other reaction intermediates such as 2-nitroketones, nitroalkenes, β-aminoalcohols, α-hydroxy carboxylic acids etc. [5-6]. As described earlier in **Chapter 1**, several groups have reported the use of various types of chiral and achiral catalysts for the stereoselective nitroaldol reactions using organic solvent as medium or in solvent-free condition [7-9]. In this point, it can be inferred that use of water as reaction medium instead of toxic solvents is quite important and necessary for the sustainable development and protection of the environment because it is cheap, safe, easy to operate, and environment friendly. Many base catalyzed nitroaldol reactions were associated with various competitive reactions and in many cases it transforms to nitroalkene by water elimination. Also by using achiral catalyst, the diastereoselectivity of this reaction was found to be poor [10-11]. Bulbule *et al.*, in 1999, reported the use of Mg-Al hydrotalcites as heterogeneous catalyst for diastereoselective synthesis of *threo*-nitroalcohol derivatives in THF under reflux condition in nitrogen atmosphere [12]. The first application of polymer-supported amines as heterogeneous catalyst for the nitroaldol reactions was observed with excess amount of nitroalkanes and aromatic aldehydes at room temperature and 60 °C under nitrogen atmosphere for longer reaction time (ranges within 3-96 hours) [13]. The discovery and development of better route, to obtain higher yields and diastereoselectivity of β-nitroalkanol, could always open a new era of achiral catalysts. The use of a heterogeneous catalyst offers many advantages, including simple separation of catalyst from the desired product by filtration and recycling of the catalyst.

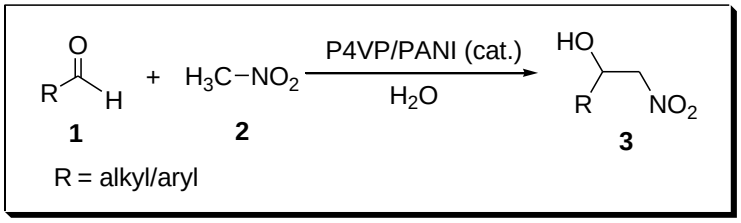
Now a day, different types of polymer-bound compounds have been utilized widely in organic synthesis as acidic or basic heterogeneous reagents/catalysts for various chemical transformations [14]. However, only few applications of nitrogen bound on polymer as Lewis base catalyst for

organic reactions were found in literature. Although most of the common organic amino bases are found to possess basic character in solution phase, recycling of such reactive catalysts are not possible in homogeneous medium. For this reason, the polymer-bound organic base can be applied as better alternative of these bases for the synthesis of libraries of complex and small molecules.

In view of this, the utilization of nitrogen containing polymer poly(4-vinylpyridine) has been studied as solid base catalyst for the diastereoselective synthesis of nitroalkanols from aromatic aldehydes and nitroalkanes in aqueous medium (**Scheme 4.1**).

4.2 Results and discussion

The synthesis of polyaniline salt (PANI) has been carried out according to the reported method as described in experimental section 4.4.2 [15]. The utilization of nitrogen bound polymer poly(4-vinylpyridine) (P4VP) and polyaniline salt (PANI) as heterogeneous catalyst has been studied from the reaction between alkyl or aryl aldehydes **1** and nitromethane **2** in water to obtain β-nitroaldol **3** as product in high yield (**Scheme 4.1**).



Scheme 4.1 Nitroaldol reaction of aldehydes with nitromethane

4.2.1 Optimization of reaction condition

At the outset, the efficiency of two nitrogen bound on polymers P4VP and PANI have been studied for nitroaldol reactions by the reaction between various substituted aromatic aldehydes with nitromethane in aqueous medium at room temperature (**Scheme 4.1**). To optimize the reaction condition, initially 0.005, 0.01, 0.02 and 0.04 g/mmol of P4VP as catalyst have been used

for the reaction of *o*-nitrobenzaldehyde (1 mmol) and nitromethane (5 mmol) in water (**Table 4.1**, entries 1-4). From the results in **Table 4.1**, it has been observed that 0.04 g/mmol of P4VP as catalyst provides the best condition against 5 mmol of nitromethane (**Table 4.1**, entry 4). When the same reaction was done using 3 mmol of nitromethane, the reaction took more time (3.5 h) to provide 85% yield of expected nitroaldol product (**Table 4.1**, entry 5). Proceeding with the above optimized amount of P4VP (0.04 g/mmol) and nitromethane (5 mmol), the efficiency of PANI for the nitroaldol reaction have been investigated for different aromatic aldhydes in water medium (**Table 4.1**, entries 6-9). The results demonstrated less basic properties of PANI as compared to P4VP.

Table 4.1 Studies on the efficiency of nitrogen bound polymers as catalysts for the nitroaldol reaction of various aromatic aldehydes and nitromethane in aqueous medium at room temperature

Entry	Catalyst[a] (g/mmol)	Aldehyde	Time (h)	Yield (%)[b] **3**
1	P4VP (0.005)	2-$NO_2C_6H_4CHO$	5	40
2	P4VP (0.01)	”	5	55
3	P4VP (0.02)	”	4	65
4	P4VP (0.04)	”	1	97
5	P4VP (0.04)	”	3.5	85[c]
6	PANI (0.04)	C_6H_5CHO	4	80
7	PANI (0.04)	2-$NO_2C_6H_4CHO$	4	75
8	PANI (0.04)	2-ClC_6H_4CHO	4	65
9	PANI (0.04)	4-ClC_6H_4CHO	4	75

[a] g/mmol indicates the amount of catalyst in g per mmol of aldehydes; [b] Isolated yield; [c] Using 3 mmol of nitromethane.

A solvent study has been performed using reactions of *o*-nitrobenzaldehyde with nitromethane as model reaction using P4VP as catalyst. From the **Table 4.2** it has been observed that when this reaction was performed in polar aprotic solvents like THF, acetonitrile the reaction took 4.5 and 4 h respectively to provide 50-52% yield (**Table 4.2**, entries 1-2). By using non polar solvent such as dichloromethane or chloroform the progress of the reaction showed similar results (**Table 4.2**, entries 3-4). The observation expressed a remarkable enhancement in rate and yield in water as compared to other solvents (**Table 4.2**, entry 7).

Table 4.2 Solvent effects for the nitroaldol reactions of *o*-nitrobenzaldehyde with nitromethane

Entry	Solvent	Time (h)	%Yield[a,b] **3b**
1	THF	4.5	50
2	CH_3CN	4	52
3	CH_2Cl_2	4	55
4	$CHCl_3$	4.5	49
5	EtOH	4	70
6	MeOH	4	68
7	H_2O	1	97
8	50% EtOH	3.5	90

[a]Reactions were carried out in the molar ratio of 1:5 aldehydes and nitromethane against 0.04 g/mmol of the catalyst at room temperature; [b]Isolated yield

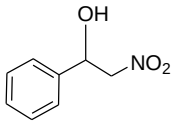
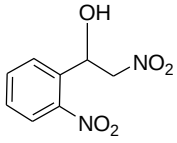
From the **Table 4.2** it has been found that using water as reaction medium the reaction completed within 1 h giving 97% yield. The reason is that in protic solvents, the miscible nitromethane molecules get easily solvated by H-bonding. This solvation process increases from alcohols (**Table 4.2**, entries 5-6) to water with increasing strength of H-bonding, which indirectly improve the reaction rate by abstracting the more acidic proton from nitromethane in protic solvents as compared to non-polar or polar aprotic solvents. These

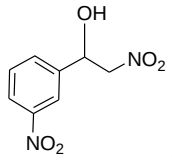
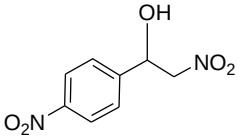
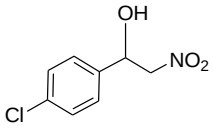
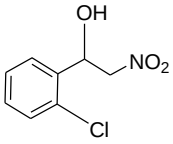
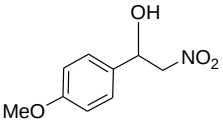
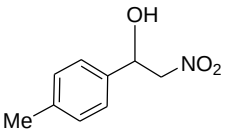
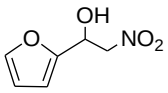
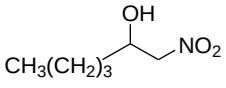
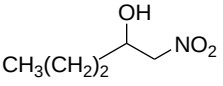
factors additionally affect the reaction progress along with the catalyst to accelerate the reaction rate and improve the percentage yield of β-nitroalkanols in water. From the above study it has been clear that the optimized reaction condition is the use of 0.04 g/mmol P4VP as catalyst in aqueous medium.

4.2.2 Reaction observation with nitromethane

It has been observed that treatment of *o*-nitrobenzaldehyde and nitromethane in water at room temperature with 0.04 g/mmol of P4VP as catalyst furnish 97% yield (**Table 4.2**, entry 7).The above optimized condition for nitroaldol reaction was extended with different aromatic/aliphatic aldehydes and nitromethane in aqueous medium at room temperature stirring. With the aromatic aldehydes containing different functional groups, the reactions completed within 1-2.5 h with good to better yields (**Table 4.3**, 74-97%). Aliphatic aldehydes provided moderate to good yield with this catalyst within 2-5 h reaction time (**Table 4.3**, entries 10-13).

Table 4.3 P4VP catalyzed synthesis of nitroalkanols from aldehydes with nitromethane (**2**) in aqueous medium

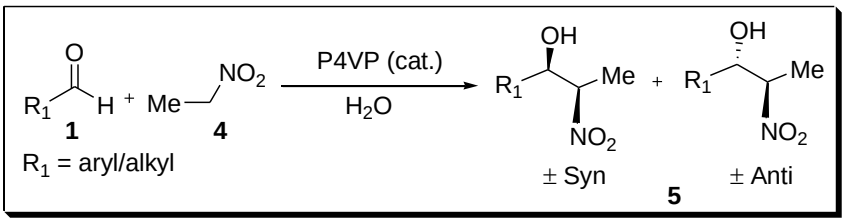
Entry	Substrate **1**	Product **3**	Time (h)	Yield (%)[a, b]
1	C_6H_5CHO	 **3a**	1	96
2	$2\text{-}NO_2C_6H_4CHO$	 **3b**	1	97

3	3-$NO_2C_6H_4CHO$	 **3c**	2	86
4	4-$NO_2C_6H_4CHO$	 **3d**	1.5	95
5	4-ClC_6H_4CHO	 **3e**	1.5	85
6	2-ClC_6H_4CHO	 **3f**	1.5	84
7	4-$MeOC_6H_4CHO$	 **3g**	2.5	74
8	4-MeC_6H_4CHO	 **3h**	2	82
9	Furaldehyde	 **3i**	1.5	80
10	$CH_3(CH_2)_3CHO$	 **3j**	2	48
11	$CH_3(CH_2)_3CHO$	**3j**	5	70
12	$CH_3(CH_2)_2CHO$	 **3k**	2	50
13	$CH_3(CH_2)_2CHO$	**3k**	5	76

[a]Isolated yields; [b]Reactions were carried out in the molar ratio of 1:5 aldehydes and nitromethane against 0.04 g/mmol of the catalyst.

4.2.3 Diastereoselective synthesis of β-nitroalkanol with nitroethane

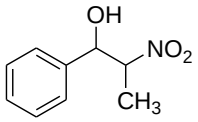
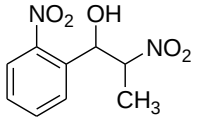
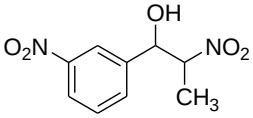
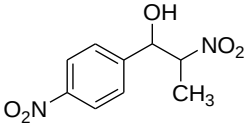
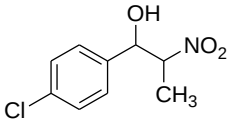
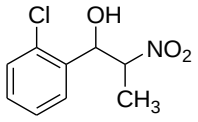
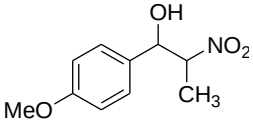
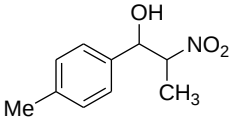
The diastereoselective synthesis of expected β-nitroalkanol was studied by performing the reaction of aldehydes and nitroethane in aqueous medium for 10 h stirring at room temperature using P4VP as Lewis base catalyst (**Scheme 4.2**).

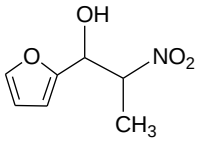
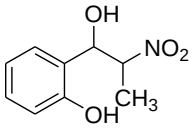
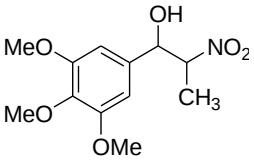
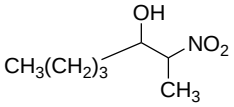
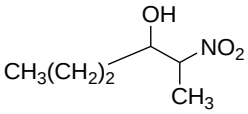


Scheme 4.2 Diastereoselective synthesis of nitroalcohol using P4VP

The reactions were studied by using various aryl aldehydes and found diastereoselective nature of the products with excellent yields (**Table 4.4**). In this case, the reaction consumes longer time than nitromethane. The reason may be the increasing one carbon atom in nitroethane slightly effect the solvation process in water as compared to nitromethane. In addition, the methyl group in nitroethane decreases the acidity of methylene protons through +I inductive effect due to which the catalyst takes more time for abstraction of acidic proton from nitroethane in aqueous medium. The *syn/anti* diastereoselectivity of β-nitroalkanols were determined from spectral analysis (^{1}H NMR and ^{13}C NMR). From these results, it has been observed that in all cases *syn*-isomers are formed in major amount than *anti* isomer. The observed absorption at δ_H 4.94 ppm as a doublet with coupling constant $^3J_{HH}$ = 9.2Hz and at δ_H 5.33 ppm ($^3J_{HH}$ = 3.6Hz) for methylene proton bonded to hydroxyl group clearly confirm the formation of *syn* selective nitroaldol product (**Table 4.4**, entry 1) [13, 16]. When the reactions were carried out using aliphatic aldehydes moderate yields were obtained (60-65%) but no diastereoselectivity was observed (**Table 4.4**, entries 12-13).

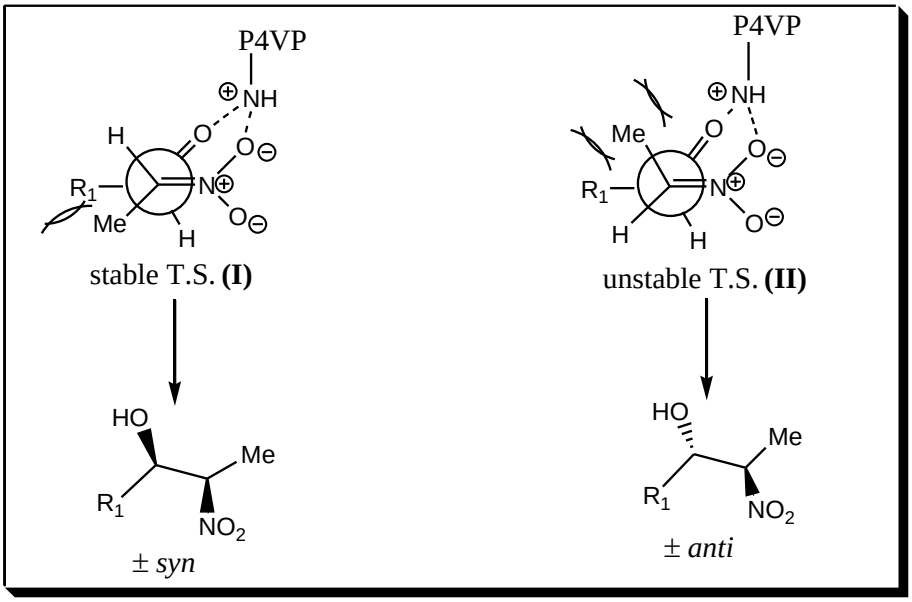
Table 4.4 P4VP catalyzed diastereoselective synthesis of nitroalkanols from aldehydes and nitroethane (**4**) in aqueous medium at room temperature

Entry	Substrate	Product	Yield (%)[a,b]	Diastereoselectivity *syn/anti* (%)[c]	de[d]
1	C_6H_5CHO	 **5a**	89	61.5/38.5	23
2	2-$NO_2C_6H_4CHO$	 **5b**	87	60.8/39.2	21.6
3	3-$NO_2C_6H_4CHO$	 **5c**	85	56.1/43.9	12.2
4	4-$NO_2C_6H_4CHO$	 **5d**	86	58.4/41.6	16.8
5	4-ClC_6H_4CHO	 **5e**	87	63/37	26
6	2-ClC_6H_4CHO	 **5f**	80	57/43	14
7	4-$MeOC_6H_4CHO$	 **5g**	70	-	-
8	4-MeC_6H_4CHO	 **5h**	82	64.5/35.5	29

9	Furaldehyde	 **5i**	73	73.6/26.4	47.2
10	2-OHC_6H_4CHO	 **5j**	74	74/26	48
11	3,4,5-$(MeO)_3C_6H_2CHO$	 **5k**	80	68.1/31.9	36.2
12	$CH_3(CH_2)_3CHO$	 **5l**	65	--	--
13	$CH_3(CH_2)_2CHO$	 **5m**	60	--	--

[a] All products were characterized by FT-IR, ^{1}H NMR and ^{13}C NMR techniques and also their comparison with authentic sample [12-13, 17]; [b] Isolated yield after purification; [c] The ratios were determined from ^{1}H NMR signals; [d] Diastereomeric excess of the *syn* product.

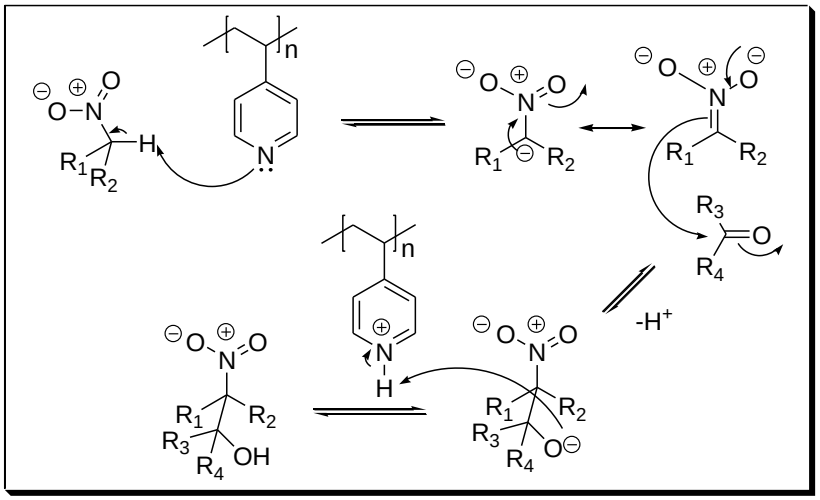
A plausible mechanism has been proposed to justify the *syn*-selectivity of the reaction in **Scheme 4.3** [18]. The six-membered cyclic transition state (I) for *syn* isomer is more stable than the transition state for *anti*-isomer (II) due to less steric hindrance which leads to the formation of major amount of *syn*-selective product.



Scheme 4.3 A plausible mechanism for the diastereoselective synthesis of β-nitroalkanol

4.2.4 General mechanism of nitroaldol reaction

The mechanism of Henry reaction involves base initiated deprotonation of the acidic α proton of the nitroalkane to give carbanion which is in tautomerism with nitronate **(Scheme 4.4)**. Nitronate eventually reacts with carbonyl compound followed by proton abstraction to form nitroaldol.



Scheme 4.4 Mechanism of Henry reaction catalyzed by P4VP

4.2.5 Reusability of catalyst

The reusability of the catalyst P4VP was studied with the reaction between *o*-nitrobenzaldehyde (1 mmol) and nitromethane (1 mmol) in water (**Figure 4.1**).

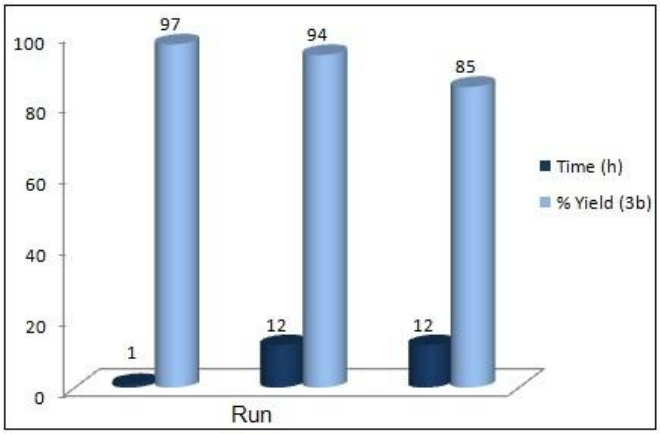


Figure 4.1 Recycling of catalyst P4VP without reactivation

It has been observed that for next cycles of reaction the catalyst requires more time to give better results which indicates that some active sites of the catalyst may loss in first cycle of reaction. This was again confirmed by the changing pattern of fingerprint region of IR spectra of fresh P4VP (a), P4VP used in 1st run (b) and P4VP used in 2nd run (c) as shown in **Figure 4.2**.

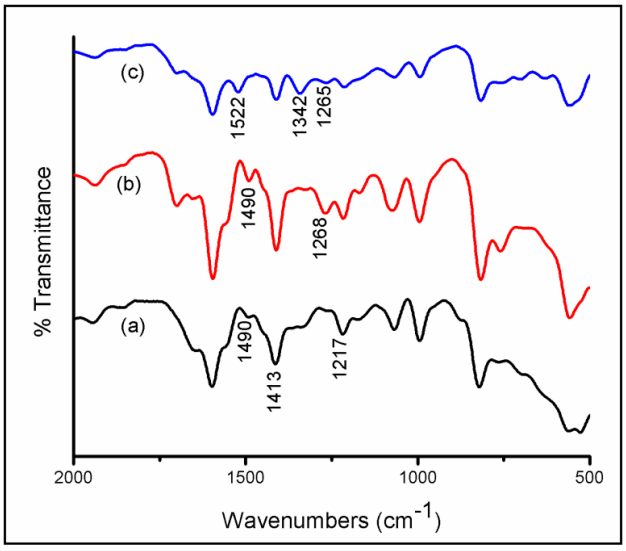


Figure 4.2 FT-IR spectra of fresh P4VP (a), P4VP used in 1st run (b) and P4VP used in 2nd run (c)

Therefore, the reactivation of catalyst was done by treatment with an aqueous solution of sodium bicarbonate for 1 hour and reused for the reaction of *o*-nitrobenzaldehyde and nitromethane in one hour with 95% yield.

4.3 Conclusion

In this chapter two nitrogen containing basic polymers (P4VP & PANI) were investigated as heterogeneous catalysts for the nitroaldol reaction in aqueous medium at room temperature stirring without any added base. It has been found that poly(4-vinylpyridine) (P4VP) acted an efficient recyclable heterogeneous Lewis base catalyst for the diastereoselctive synthesis of *syn*-nitroalkanols from aromatic aldehydes and nitroethane. Furthermore, the catalyst also works efficiently with the reaction of aldehyde and nitromethane in aqueous solution at room temperature. This protocol has several greener components such as water as reaction medium, high yields, simple separation of reusable polymer catalyst and mild reaction condition.

4.4 Experimental section

4.4.1 General information

The used chemicals are commercially available and were used without further purification. The products were identified by comparison of their FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic data with those of authentic compounds (prepared by known method) and literature reported data [12-13, 17].

4.4.2 Preparation of polyaniline catalyst (PANI)

In a 2 L round-bottomed flask, 700 mL of water was taken and stirred after adding 30 mL of H_2SO_4. To this solution, 10 mL of aniline was added and the solution was kept under constant stirring at 5–10 °C for 15–20 min. To the stirred solution 250 mL aqueous solution of sodium persulfate (23.8 g) was added and then allowed to continue the reaction for 4 h at 5–10 °C. The

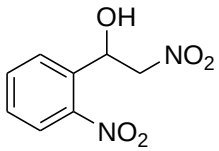
precipitated polyaniline powder was filtered and washed with 5 L distilled water followed by 500 mL acetone and dried at 100 °C till a constant weight [15].

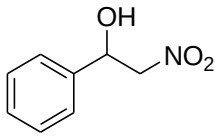
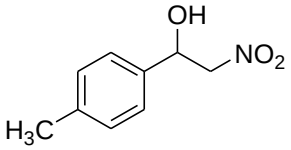
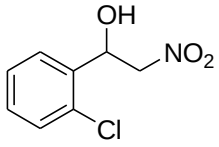
4.4.3 General experimental procedure

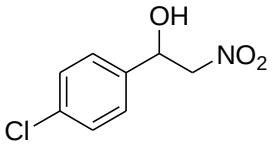
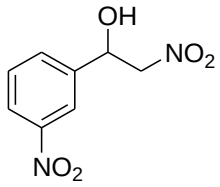
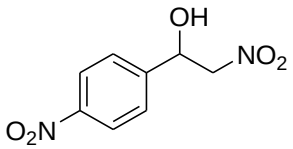
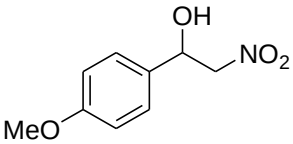
A mixture of aldehyde (1 mmol), nitroalkane (5 mmol) and P4VP (0.04 g/mmol) was charged with 2 ml of distilled water in a 50 ml round bottom flask and this heterogeneous reaction mixture was stirred at ambient temperature for the specified reaction period. The completion of the reaction was monitored by TLC. After completion the aqueous solution was filtered for removal of poly(4-vinylpyridine) catalysts from the reaction mixture. The product was extracted with 12 ml (3×4 ml) of ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and filtered. The ethyl acetate extract was distilled under reduced pressure to get the crude product. The crude mixture was further purified by column chromatography using different ratio of ethyl acetate and *n*-hexane as effluent to get the desired analytically pure products.

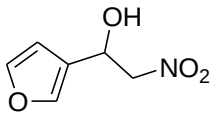
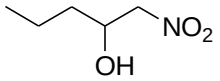
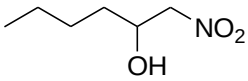
4.5 Spectral data of β-nitroalkanols

4.5.1 Compounds given in Table 4.3

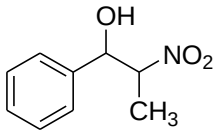
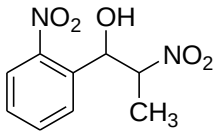
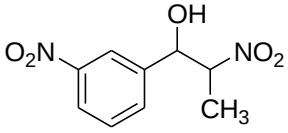
Compounds	Spectral data
 2-Nitro-1-(2-nitro-phenyl)-ethanol **Table-4.3**, entry-1, (**3a**)	Yellow oil FT-IR (KBr): 3526, 3107, 2923, 1530, 1348,1191, 1091, 901, 791 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 3.42 (s, 1H), 4.52 (dd, *J* = 9.2, 13.8Hz, 1H), 4.83 (dd, *J* = 2.3, 13.7Hz, 1H), 6.03 (dd, *J* = 2.2, 9.2Hz, 1H), 7.53-7.55 (m, 1H), 7.71-7.75 (m, 1H), 7.92 (d, *J* = 7.8Hz, 1H), 8.03 (dd, *J* = 1.4, 8.2Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 65.8, 79.1, 124.0, 127.7, 128.7, 133.1, 133.4, 146.2; Elemental analysis

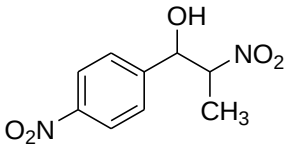
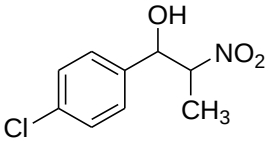
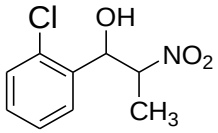
	for $C_8H_8N_2O_5$: Cal. C 45.29, H 3.80, N 13.20; Found: C 45.35, H 3.84, N 13.26.
 2-Nitro-1-phenyl-ethanol **Table-4.3**, entry-2, (**3b**)	Colourless oil FT-IR (KBr): 3410, 3035, 2923, 1553, 1378, 1201, 1066, 901, 702 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ (ppm) = 2.93 (s, 1H), 4.53 (dd, *J* = 2.8, 13.2Hz, 1H), 4.60 (dd, *J* = 9.2, 13.2Hz, 1H), 5.44 (dd, *J* = 2.8, 9.2Hz, 1H), 7.40-7.41 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 70.0, 80.3, 124.9, 127.9, 128.0, 137.2; Elemental analysis for $C_8H_9NO_3$: Cal. C 57.48, H 5.43, N 8.38; Found: C 57.53, H 5.48, N 8.40.
 2-Nitro-1-p-tolyl-ethanol **Table-4.3**, entry-3, (**3c**)	Yellow oil FT-IR (KBr): 3450, 3027, 2923, 1684, 1554, 1421, 1378, 1207, 1075, 899, 816 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ (ppm) = 2.42 (s, 3H), 3.31 (s, 1H), 4.48 (dd, *J* = 3.2, 13.5Hz, 1H), 4.57 (dd, *J* = 9.6, 12.8Hz, 1H), 5.39 (d, *J* = 9.6Hz, 1H), 7.25 (d, *J* = 7.8Hz, 2H), 7.31 (d, *J* = 7.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 20.8, 69.9, 80.3, 128.6, 128.9, 129.2, 133.1, 134.4, 137.7; Elemental analysis for $C_9H_{11}NO_3$: Cal. C 59.66, H 6.12, N 7.73; Found: C 59.69, H 6.19, N 7.82.
 1-(2-Chlorophenyl)-2-nitro ethanol **Table-4.3**, entry-4, (**3d**)	Colourless oil FT-IR (KBr): 3526, 3070, 2923, 1937, 1556, 1468, 1427, 1380, 1288, 1205, 1042, 900, 756 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ (ppm) = 3.08 (s, 1H), 4.38 (dd, *J* = 9.6, 13.7Hz, 1H), 4.58 (dd, *J* = 2.0, 13.7Hz, 1H), 5.78 (d, *J* = 9.6Hz, 1H), 7.22-7.31 (m, 3H) 7.59 (d, *J* = 7.4Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 66.8, 78.3, 126.5, 126.6, 128.7, 128.9, 130.5, 134.9; Elemental analysis for $C_8H_8ClNO_3$: Cal. C 47.66, H 4.00, N 6.95; Found: C 47.72, H 4.06, N 6.98.

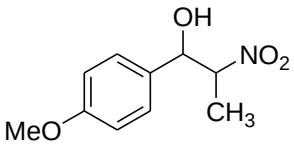
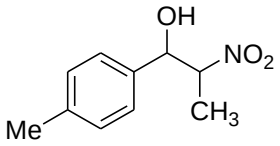
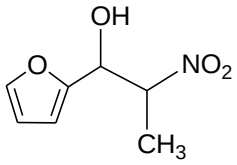
 1-(4-Chlorophenyl)-2-nitro ethanol **Table-4.3**, entry-5, (**3e**)	Colourless oil FT-IR (KBr): 3464, 2921, 1911, 1554, 1494, 1381, , 1340, 1264, 1200, 1086, 1018, 897, 824 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ (ppm) = 2.94 (brs, 1H), 4.50 (dd, *J* = 3.2, 13.2Hz, 1H), 4.59 (dd, *J* = 9.6, 13.2Hz, 1H), 5.45 (dd, *J* = 3.2, 9.6Hz, 1H), 7.31-7.39 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 69.3, 79.7, 126.3, 128.2, 128.8, 129.3, 133.8, 135.5; Elemental analysis for $C_8H_8ClNO_3$: Cal. C 47.66, H 4.00, N 6.95; Found: C 47.71, H 4.05, N 6.98.
 2-Nitro-1-(3-nitrophenyl) ethanol **Table-4.3**, entry-6, (**3f**)	Yellow oil FT-IR (KBr): 3438, 2854, 1914, 1559, 1492, 1385, 1268, 1087, 764 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ (ppm) = 3.72 (s, 1H), 4.52 (dd, *J* = 3.2, 13.6Hz, 1H), 4.56 (dd, *J* = 9.6, 13.6Hz, 1H), 5.63 (dd, *J* = 3.2, 9.6Hz, 1H), 7.56 (m, 1H), 7.77 (d, *J* = 8.2Hz, 1H), 8.20 (d, *J* = 8.2Hz, 1H), 8.28 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 70.6, 78.9, 121.6, 123.5, 129.4, 132.5, 140.8, 148.6; Elemental analysis for $C_8H_8N_2O_5$: Cal. C 45.29, H 3.80, N 13.20; Found: C 45.33, H 3.84, N 13.28.
 2-Nitro-1-(4-nitrophenyl) ethanol **Table-4.3**, entry-7, (**3g**)	Yellow oil FT-IR (KBr): 3507, 2925, 1939, 1603, 1551, 1348, 1200, 1087, 903, 855, 742 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ (ppm) = 3.24 (s, 1H), 4.58-4.64 (m, 2H), 5.59 (dd, *J* = 4.2, 6.8Hz, 1H), 7.54 (d, *J* = 7.8Hz, 2H), 8.19 (d, *J* = 7.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 68.2, 78.5, 124.5, 125.9, 146.3, 147.8; Elemental analysis for $C_8H_8N_2O_5$: Cal. C 45.29, H 3.80, N 13.20; Found: C 45.37, H 3.86, N 13.28.
	Colourless oil FT-IR (KBr): 3529, 2913, 1926, 1514, 1520, 1317, 1210, 1089, 825 cm^{-1}; ^1H NMR (400MHz, $CDCl_3$): δ (ppm) = 3.02 (s, 1H), 3.82 (s, 3H), 4.45 (dd, *J* = 3.2,

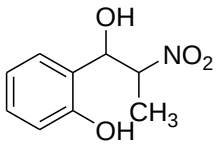
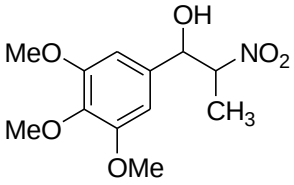
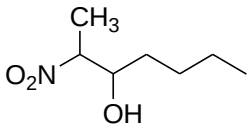
1-(4-Methoxyphenyl)-2-nitro ethanol **Table-4.3**, entry-8, (**3h**)	13.2Hz, 1H), 4.53 (dd, *J* = 9.6, 13.3Hz, 1H), 5.60 (dd, *J* = 3.2, 9.6Hz, 1H), 6.86-6.92 (m, 2H), 7.28-7.34 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 57.5, 71.4, 82.2, 114.2, 127.2, 130.7, 160.2; Elemental analysis for $C_9H_{11}NO_4$: Cal. C 54.82, H 5.62, N 7.10; Found: C 54.88, H 5.67, N 7.17.
 1-(Furan-3-yl)-2-nitro ethanol **Table-4.3**, entry-9, (**3i**)	Brown oil FT-IR (KBr): 3412, 2962, 1560, 1407, 1260, 1091, 1024, 802, 693 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 3.32 (s, 1H), 4.68 (dd, *J* = 3.2, 13.2Hz, 1H), 4.82 (dd, *J* = 9.6, 13.2Hz, 1H), 5.49 (dd, *J* = 3.2, 9.6Hz, 1H), 6.38-6.44 (m, 2H), 7.42 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 65.5, 80.2, 108.5, 110.3, 143.5, 150.3; Elemental analysis for $C_6H_7NO_4$: Cal. C 45.86, H 4.49, N 8.91; Found: C 45.89, H 4.54, N 8.88.
 1-Nitropentan-2-ol **Table-4.3**, entry-10, (**3j**)	Colourless oil FT-IR (KBr): 3512, 2960, 1548, 1463, 1316, 1254, 1076, 765 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 0.97 (t, *J* = 6.8Hz, 3H), 1.42-1.57 (m, 4H), 2.56 (brs, 1H), 4.29-4.37 (m, 1H), 4.43-4.49 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 14.3, 18.7, 36.5, 67.7, 81.3; Elemental analysis for $C_5H_{11}NO_3$: Cal. C 45.10, H 8.33, N 10.52; Found: C 45.17, H 8.37, N 10.62.
 1-Nitrohexane-2-ol **Table-4.3**, entry-12, (**3k**)	Colourless oil FT-IR (KBr): 3420, 2952, 1554, 1467, 1352, 1250, 1089, 746 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 0.92 (t, *J* = 7.3Hz, 3H), 1.32-1.39 (m, 3H), 1.47-1.54 (m, 3H), 2.57 (s, 1H), 4.25-4.35 (m, 1H), 4.38-4.46 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 13.8, 21.8, 27.2, 32.7, 68.7, 80.6; Elemental analysis for $C_6H_{13}NO_3$: Cal. C 48.97, H 8.90, N 9.52; Found: C 48.95, H 8.96, N 9.64.

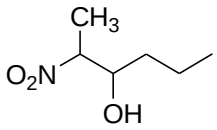
4.5.2 Compounds given in Table 4.4

Compounds	Spectral data
 1-Phenyl-2-nitropropan-1-ol **Table-4.4**, entry-1, (**5a)**	Colourless Viscous liquid FT-IR (KBr): 3504, 2961, 1961, 1702, 1548, 1448, 1397, 1262, 1050, 866 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.25 (d, *J* = 6.4Hz, 3H), 1.44 (d, *J* = 6.8Hz, 3H), 2.4 (brs, 1H), 4.70 (m, 2H), 4.94 (d, *J* = 9.2Hz, 1H), 5.33 (d, *J* = 3.6Hz, 1H), 7.32 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$,): δ = 11.0, 15.4, 75.2, 86.4, 87.4, 124.9, 125.9, 127.7, 128.0, 137.2, 137.4; Elemental analysis for $C_9H_{11}NO_3$: Cal. C 59.66, H 6.12, N 7.73; Found: C 59.76, H 6.23, N 7.78.
 2-Nitro-1-(2-nitrophenyl) propan-1-ol **Table-4.4**, entry-2, (**5b)**	Yellow viscous liquid FT-IR (KBr): 3465, 2962, 1554, 1460, 1381, 1087, 824 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.52 (d, *J* = 6.9Hz, 3H), 1.56 (d, *J* = 6.9Hz, 3H), 3.2 (brs, 1H), 4.98-5.0 (m, 2H), 5.72 (d, *J* = 6.4Hz, 1H), 6.1 (m, 1H), 7.77-7.79 (m, 2H), 7.93 (m, 1H), 8.10 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 11.3, 68.5, 86.7, 123.8, 128.7, 128.9, 130.6, 132.9, 133.4, 152.3; Elemental analysis for $C_9H_{10}N_2O_5$: Cal. C 47.79, H 4.46, N 12.39; Found: C 47.85, H 4.54, N 12.41
 1-(3-Nitrophenyl)-2-nitropropan-1-ol **Table-4.4**, entry-3, (**5c)**	Yellow viscous liquid FT-IR (KBr): 3526, 2995, 1700, 1540, 1453, 1351, 1204, 1055, 898 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.27 (d, *J* = 6.6Hz, 3H), 1.43 (d, *J* = 6.8Hz, 3H), 3.70 (brs, 1H), 4.71-4.69 (m, 2H), 5.11 (d, *J* = 8.6Hz, 1H), 5.46 (d, *J* = 2.3Hz, 1H), 7.67-7.51 (m, 2H), 8.15 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 12.2, 16.4, 73.2, 75.3, 87.2, 88.3, 121.5, 123.2, 123.6, 124.2, 130.1, 130.4, 132.6, 133.5, 141.0, 141.4, 148.6; Elemental analysis for $C_9H_{10}N_2O_5$: Cal.

	C 47.79, H 4.46, N 12.39; Found: C 47.87, H 4.53, N 12.45
 2-Nitro-1-(4-nitrophenyl) propan-1-ol **Table-4.4**, entry-4, (**5d)**	Yellow viscous liquid FT-IR (KBr): 3464, 3000, 1603, 1550, 1341, 1188, 1102, 1058, 1000, 856, 709 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.40 (d, *J* = 6.8Hz, 3H), 1.50 (d, *J* = 6.8Hz, 3H), 3.07 (s, 1H), 4.77-4.79 (m, 2H), 5.19 (d, *J* = 8.2Hz, 1H), 5.56 (m, 1H), 7.60 (d, *J* = 8.7Hz, 2H), 8.26 (d, *J* = 8.7Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 11.9, 16.2, 72.9, 75.0, 87.7, 124.0, 124.3, 127.0, 127.9, 145.5, 148.3; Elemental analysis for $C_9H_{10}N_2O_5$: Cal. C 47.79, H 4.46, N 12.39; Found: C 47.83, H 4.50, N 12.47
 1-(4-Chlorophenyl)-2-nitropropan-1-ol **Table-4.4**, entry-5, (**5e)**	Yellow viscous liquid FT-IR (KBr): 3492, 2949, 1558, 1424, 1331, 1041, 815 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.32 (d, *J* = 6.9Hz, 3H), 1.47 (d, *J* = 6.9Hz, 3H), 2.93 (brs, 1H), 4.72-4.74 (m, 2H), 5.02 (d, *J* = 8.7Hz, 1H), 5.37 (d, *J* = 3.6Hz, 1H), 7.32 (d, *J* = 6.8Hz, 2H), 7.36 (d, *J* = 6.8Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 11.0, 15.3, 72.2, 74.5, 86.2, 87.2, 126.4, 127.2, 128.2, 134.0, 135.8; Elemental analysis for $C_9H_{10}ClNO_3$: Cal. C 50.13, H 4.67, N 6.50; Found: C 50.19, H 4.72, N 6.55
 1-(2-Chlorophenyl)-2-nitropropan-1-ol **Table-4.4**, entry-6, (**5f)**	Yellow viscous liquid FT-IR (KBr): 3465, 2962, 1554, 1474, 1381, 1087, 824 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.42 (d, *J* = 6.8Hz, 3H), 1.44 (d, *J* = 6.8Hz, 3H), 2.38 (brs, 1H), 4.85-4.86 (m, 2H), 5.59 (d, *J* = 8.3Hz, 1H), 5.83 (d, *J* = 2.0Hz, 1H), 7.24-7.38 (m, 2H), 7.54 (m, 1H), 7.65 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 11.2, 16.0, 70.4, 71.8, 83.9, 88.0, 127.3, 127.7, 128.2, 129.6, 130.0, 133.4, 137.3; Elemental analysis for $C_9H_{10}ClNO_3$: Cal. C 50.13, H 4.67, N 6.50;

	Found: C 50.15, H 4.69, N 6.53
 1-(4-Methoxyphenyl)-2-nitropropan-1-ol **Table-4.4**, entry-7, (**5g)**	Yellow viscous liquid FT-IR (KBr): 3492, 2991, 1598, 1560, 1389, 1158, 886 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.31 (d, *J* = 6.9Hz, 3H), 1.53 (d, *J* = 6.9Hz, 3H), 3.88 (s, 3H), 4.68-4.72 (m, 2H), 5.20 (d, *J* = 9.6Hz, 1H), 5.53 (m, 1H), 6.93 (d, *J* = 8.7Hz, 2H), 7.02 (d, *J* = 8.7Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 11.3, 54.7, 75.2, 87.8, 113.7, 114.9, 128.8, 129.6, 132.3, 157.8; Elemental analysis for $C_{10}H_{13}NO_4$: Cal. C 56.86, H 6.20, N 6.63; Found: C 56.89, H 6.24, N 6.65
 1-(4-Methylphenyl)- 2-nitropropan-1-ol **Table-4.4**, entry-8, (**5h)**	Yellow viscous liquid FT-IR (KBr): 3447, 2991, 2925, 1697, 1551, 1449, 1363, 1045, 816 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.24 (d, *J* = 6.9Hz, 3H), 1.44 (d, *J* = 6.9Hz, 3H), 2.28 (brs, 1H), 2.35 (s, 3H), 4.70-4.60 (m, 2H), 4.92 (d, *J* = 8.7Hz, 1H), 5.27 (d, *J* = 3.7Hz, 1H), 7.18 (d, *J* = 7.8Hz, 2H), 7.92 (d, *J* = 7.7Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 11.2, 15.5, 20.1, 20.7, 75.1, 75.6, 86.5, 87.4, 124.8, 125.8, 128.4, 128.7, 129.2, 134.3, 138.1, 143.5; Elemental analysis for $C_{10}H_{13}NO_3$: Cal. C 61.53, H 6.71, N 7.18; Found: C 61.56, H 6.73, N 7.24
 1-(Furan-2-yl)-2-nitropropan-1-ol **Table-4.4**, entry-9, (**5i)**	Brown viscous liquid FT-IR (KBr): 3424, 2992, 1637, 1554, 1452, 1387, 1302, 1146, 1015, 880, 815, 749 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.34 (d, *J* = 6.8Hz, 3H), 1.54 (d, *J* = 6.8Hz, 3H), 2.76 (brs, 1H), 4.91-4.80 (m, 2H), 4.99 (d, *J* = 8.6Hz, 1H), 5.27 (m, 1H), 6.34-6.31 (m, 2H), 7.36 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 12.2, 15.2, 67.9, 68.5, 83.9, 85.2, 108.4, 109.6, 142.3, 150.2; Elemental analysis for $C_7H_9NO_4$: Cal. C 49.12, H 5.30, N 8.18; Found:

	C 49.10, H 5.32, N 8.16
 2-(1-Hydroxy-2-nitropropyl) phenol **Table-4.4**, entry-10, (**5j)**	Yellow viscous liquid FT-IR (KBr): 3434, 2989, 2924, 1690, 1551, 1446, 1362, 1043, 813 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) =1.24 (d, *J* = 6.9Hz, 3H), 1.45 (d, *J* = 6.9Hz, 3H), 2.38 (brs, 1H), 4.86-4.88 (m, 2H), 5.60 (d, *J* = 8.3Hz, 1H), 5.84 (m, 1H), 6.85 (m, 1H), 6.96-7.00 (m, 1H), 7.24-7.28 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 13.2, 65.7, 86.7, 114.9, 119.9, 128.1, 129.3, 134.3, 153.4; Elemental analysis for $C_9H_{11}NO_4$: Cal. C 54.82, H 5.62, N 7.10; Found: C 54.85, H 5.66, N 7.08
 1-(3,4,5-Trimethylphenyl)2-nitropropan-1-ol **Table-4.4**, entry-11, (**5k)**	Yellow viscous liquid FT-IR (KBr): 3476, 2939, 2842, 1685, 1590, 1461, 1328, 1235, 1126, 989, 842 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 1.35 (d, *J* = 6.8Hz, 3H), 3.94 (s, 9H), 4.69-4.71 (m, 1H), 4.74-4.78 (m, 1H), 6.59 (s, 1H), 7.14 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 12.3, 16.6, 56.2, 61.0, 76.5, 88.4, 106.6, 131.6, 134.0, 143.5, 153.4, 153.6; Elemental analysis for $C_{12}H_{17}NO_3$: Cal. C 64.55, H 7.67, N 6.27; Found: C 64.59, H 7.70, N 6.29
 2-Nitroheptane-3-ol **Table-4.4**, entry-12, (**5l)**	Yellow viscous liquid FT-IR (KBr): 3490, 2949, 2830, 1632, 1525, 1404, 1315, 1087, 789 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 0.97 (d, *J* = 6.9Hz, 3H), 1.30-1.35 (m, 4H), 1.43-1.45 (m, 2H), 1.47 (d, *J* = 6.8Hz, 3H), 1.5 (d, *J* = 6.8Hz, 3H), 2.37 (brs, 1H), 4.46-4.52 (m, 2H), 5.08 (m, 1H), 5.25 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 12.2, 14.6, 24.7, 26.6, 34.2, 73.5, 86.7; Elemental analysis for $C_7H_{15}NO_3$: Cal. C 52.16, H 9.38, N 8.69; Found: C 52.18, H 9.43, N 8.63

 2-Nitrohexane-3-ol **Table-4.4**, entry-13, (**5m)**	Yellow viscous liquid FT-IR (KBr): 3439, 2979, 2832, 1690, 1565, 1431, 1325, 1125, 810 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm) = 0.89 (d, *J* = 6.8Hz, 3H), 1.25-1.34 (m, 4H), 1.48 (d, *J* = 6.8Hz, 3H), 1.50 (d, *J* = 6.8Hz, 3H), 2.37 (brs, 1H), 4.45-4.49 (m, 2H), 5.07 (m, 1H), 5.24 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 12.4, 13.9, 18.5, 36.6, 72.7, 87.9; Elemental analysis for $C_6H_{13}NO_3$: Cal. C 48.97, H 8.90, N 9.52; Found: C 48.95, H 8.93, N 9.55

References:

[1] Kurti, L. & Czako, B. *Strategic Applications of Named Reactions in Organic Synthesis*, Elsevier Academic Press: Burlington, MA, 2005, 202--203.

[2] Palomo, C., et al. *Chem. Soc. Rev.* **33** (2), 65--75, 2004.

[3] Palomo, C., et al. *Eur. J. Org. Chem.* **2007** (16), 2561--2574, 2007.

[4] Boruwa, J., et al. *Tetrahedron: Asymmetry* **17** (24), 3315--3326, 2006.

[5] Ballini, R. & Petrini, M. *Tetrahedron* **60** (5), 1017--1047, 2004.

[6] Luzzio, F.A., et al *Tetrahedron* **57** (6), 915--945, 2001.

[7] Ji, Y.Q., et al. *Tetrahedron: Asymmetry* **22** (24), 2065--2070, 2011.

[8] Sasai, H., et al. *Tetrahedron Lett*. **34** (5), 855--854, 1993.

[9] Trost, B.M., et al. *Org. Lett*. **4** (16), 2621--2623, 2002.

[10] Sasai, H., et al. *Tetrahedron Lett*. **35** (33), 6123--6126, 1994.

[11] Ma, D., et al. *Tetrahedron Lett.* **43** (51), 9401--9403, 2002.

[12] Bulbule, V.J., et al. *Tetrahedron* **55** (30), 9325--9332, 1999.

[13] Palacios, F., et al. *Arkivo*c (ix), 405--414, 2005.

[14] Benaglia, M., et al. *Chem. Rev.***103** (9), 3401--3429, 2003.

[15] Gangadasu, B., et al. *J. Appl. Poly. Sc.* **102** (2), 1741--1745, 2006.

[16] Kanagaraj, K., et al. *Org. Lett*. **12** (18), 4070--4073, 2010.

[17] Evans, D.A., et al. *J. Am. Chem. Soc.* **125** (42), 12692--12693, 2003.

[18] Arai, T., et al. *J. Org. Chem*. **73** (13), 4903--4906, 2008.