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Heterogeneous Henry Reaction of Aldehydes: Diastereoselective Synthesis of Nitroalcohol Derivatives over Mg-Al Hydrotalcites.

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Abstract: Mg-Al Hydrotalcite (HT) has been found to catalyze the reaction between aldehydes and nitroalkanes very efficiently affording *threo* nitroalkanols in a highly diastereoselective manner. The ratios of *threo/erythro* isomers are determined from their respective ^{13}C-NMR spectra. A mechanism based on the transition state model for the predominant formation of *threo*-isomers is also described.

Keywords: Aldols; diastereoselection; catalysts; aldehydes.

INTRODUCTION

The Henry or nitroaldol reaction is one of the classical C-C bond forming processes by which diastereomeric mixtures of 2-nitroalcohols are formed on treatment of primary or secondary nitroalkanes and carbonyl derivatives with a base.[1] Since nitroalcohols can be hydrogenated over Raney-Ni with retention of configuration, they are useful intermediates in the elaboration of pharmacologically important β-aminoalcohols derivatives including chloramphenicol, ephedrine, norephedrine and anthracycline antibiotics.[2] Several base catalysts including alkali metal hydroxides, carbonates, alkoxides, anion-exchanged resins, organic amines, SiO_2/microwave have been employed to bring about the Henry reaction.[3] Since basic reagents are also catalysts for aldol condensations and for the Cannizzarro reactions when aldehydes are used as carbonyl sources, it is necessary to adopt experimental conditions to suppress these competitive reactions.[4] Hence, to obtain better yields and diastereoselectivity of 2-nitroalcohols, it is necessary to carefully control the basicity of the reaction medium. Furthermore, 2-nitroalcohols formed in the Henry reaction may undergo base catalyzed elimination of water to give α-nitroalkenes[5] which readily polymerize. This elimination is difficult to avoid when aryl aldehydes are used. Recently, several improved methods have been devised to overcome the many drawbacks of the Henry reaction by increasing their chemo-, regio-, and in specific cases, stereoselectivity. The Henry reaction performed using commercial chromatographic alumina in the absence of solvent gave mixtures of diastereomeric 2-nitroalcohols after 24 hours.[6] However, the lack of stereoselectivity is due to the reversibility of the reaction

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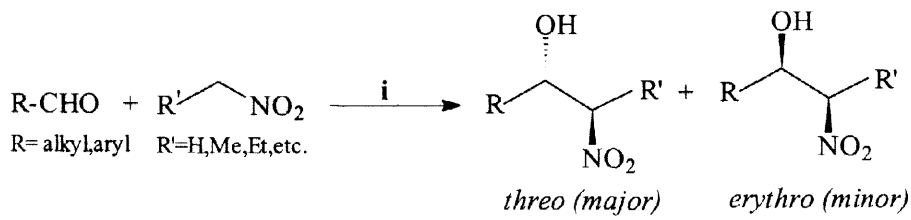
and easy epimerisation at the nitro-substituted C-atom.

Significant improvements to the Henry reaction have been achieved by using silyl nitronates in the presence of fluoride ion or alternatively α,α-doubly deprotonated primary nitroalkanes.[7] Both of these procedures discovered by the Seebach group, have proved to be useful for the stereoselective preparation of vicinal amino alcohols. However, the conditions reported are drastic and reduced diastereoselectivity is observed with aromatic aldehydes. A stereoselective synthesis of either of the *erythro* or *threo* isomers would be highly desirable. Hence to obtain better yields and diastereoselectivity of 2-nitroalcohols, it is necessary to develop new procedures employing heterogeneous catalysts with basic character. The development of new catalysts which can effectively overcome the problems experienced in the Henry reaction, should heighten the synthetic scope of the reaction. In this connection, the use of a heterogeneous catalyst in the liquid phase offers several advantages compared with their homogeneous counterparts, including ease of recovery, recycling and enhanced stability. We wish to report here in detail, our results on the diastereoselective synthesis of nitroalkanols from aldehydes and nitroalkanes catalyzed by Mg-Al hydrotalcite (Scheme 1).



Scheme 1: i) Mg-Al hydrotalcite (20% w/w), THF, reflux 6-8 h.

HYDROTALCITE AS CATALYST

Hydrotalcites[8] (HT) – like anionic clays are a new family of interesting materials with applications as catalyst, catalyst support, anion exchangers and composite materials.[9] The structure of these compounds consists of brucite [$Mg(OH)_2$] type octahedral layers in which a part of the M(II) cations are isomorphously substituted by M(III) cations. The excess positive charge of the octahedral layers resulting from this substitution is

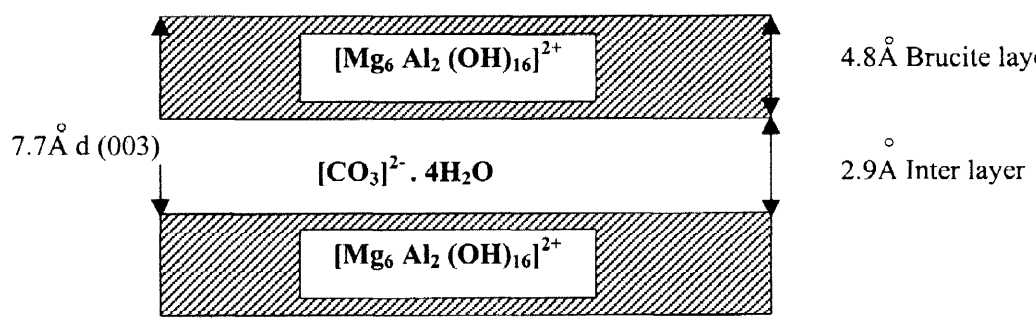


Fig 1: Schematic presentation of Mg-Al hydrotalcite

compensated for by interstitial layers built of anions such as CO_3^{2-} and crystal water. These compounds are represented by the general formula $[M(II)_{1-x}\ M(III)_{x}\ (OH)_2\ ]^{x+}\ [\ (A^{n-})_{x/n}\ Y\ H_2O\ ]^{x-}$ where M(II) is a divalent cation such as Mg, Cu, Ni, Co, Mn, Zn; M(III) is a trivalent cation such as Al, Fe, Cr, Ga, V, Ru, Rh and Y ; A^{n-}

is an interlayer anion such as CO_3^{2-}, NO_3^-, SO_4^{2-} and the value of x is in the range from 0.1 to 0.33. For example in hydrotalcite, $Mg_6 Al_2 (OH)_{16} CO_3 .4 H_2O$ (Mg:Al = 3:1), some of the Mg^{2+} are replaced by Al^{3+} in the brucite sheet resulting in a net positive charge on the clay sheets. The positively charged Mg-Al double hydroxide sheets (or layers) are charge-balanced by the carbonate anions residing in the interlayer section of the clay structure (Fig. 1).[10] Thermal calcination of these materials leads to interactive, high surface area, non-stoichiometric and well-dispersed mixed metal oxides which are efficiently used in many catalytic transformations such as Aldol condensation,[11] epoxidation,[12] cyanoethylation[13] and Meerwein-Ponndorf-Verley reduction.[14]

RESULTS AND DISCUSSION

When aldehydes were treated with an equimolar amount of nitroethane in the presence of a catalytic amount of Mg-Al- hydrotalcite under reflux in THF, the corresponding nitroalcohols were obtained in good to excellent yields. The results of the Henry reaction between 3-nitrobenzaldehyde and nitroethane over various hydrotalcites are presented in the Table 1. A comparison of the results in Table 1 shows that among the catalysts screened, Mg-Al (3:1) gives best results for the Henry reaction. The higher activity of this catalyst is due to the high surface area (176 $m^2 g^{-1}$) associated with this catalyst.

Table 1: Results of the Henry reaction between 3-nitrobenzaldehyde and nitroethane over various hydrotalcites[a]

Entry	Catalyst	Surface area ($m^2 g^{-1}$)[b]	Yield (%)[c]
1	MgAl 3.0 HT	176	95.5
2	MgAl 4.0 HT	125	72.2
3	MgAl 5.0 HT	150	81.5
4	ZnAl 3.0 HT	135	77.6
5	CuAl 3.0 HT	154	81.7

a: Reaction conditions: 3-Nitrobenzaldehyde (5mmol), nitroethane (5mmol), catalyst (20%w/w), THF (10ml), reflux 6-8h. b: Surface area determined by N_2 adsorption-desorption method. c:Isolated yield after column chromatographic purification.

Table 2 lists the results of various aldehydes that have been condensed with nitroalkanes to the corresponding nitroalkanols in high yields using Mg-Al (3:1) as a catalyst. Both aromatic and aliphatic aldehydes could be employed successfully for Henry reactions affording the corresponding nitroalkanols in high yields. High chemoselectivity is observed since several functionalities such as hydroxyl groups, tetrahydropyranyl, C-C double bond and furyl are preserved under these conditions. It is to be noted that both primary and secondary nitroalkanes can be employed. Contrary to other methods, the success of this approach is independent from the ratio of catalyst/substrate and does not need longer reaction time or dehydration of the 2-nitroalcohols into nitroalkenes even if aromatic aldehydes are used did not take place. Catalysts from the reaction mixture were recovered by simple filtration and were successfully reused, after activation at 450 °C, twice without losing its activity and stereoselectivity.

Table 2: Mg-Al hydrotalcite-catalyzed nitroaldol reaction between aldehydes and nitroalkanols.

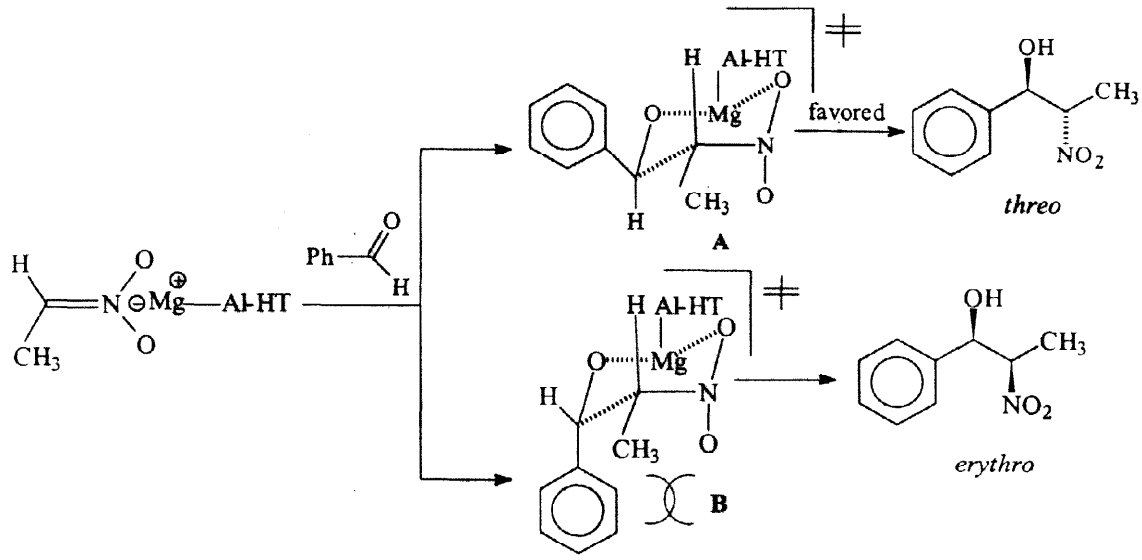
Entry	Substrates	Nitroalkanes	t/h	Products[a]	Yield[b]	*threo:erythro*[c]
1	Benzaldehyde	Nitroethane	6	1-Phenyl-2-nitropropan-1-ol	87	3.25:1
2	3-Nitrobenzaldehyde	Nitroethane	6	1-(3-Nitrophenyl)-2-nitropropan-1-ol	95	12.5:1
3	4-Nitrobenzaldehyde	1-Tetrahydro pyranoloxy-nitromethane	8	1-(4-Nitrophenyl)-2-nitro-3-tetrahydropyranoloxy-propan -1-ol	72	-
4	Salicylaldehyde	Nitroethane	8	1-(2-Hydroxyphenyl)-2-nitropropan-1-ol	45	-
5	4-Methoxy-benzaldehyde	Nitroethane	8	1-(4-Methoxyphenyl)-2-nitropropan-1-ol	62	1.23:1
6	2-Chloro-benzaldehyde	1-Nitropropane	6	1-(2-Chlorophenyl)-2-nitrobutan-1-ol	89	1.53 :1
7	4-Nitro-benzaldehyde	Nitroethane	6	1-(4-Nitrophenyl)-2-nitropropan-1-ol.	84	100:0
8	2-Chloro-benzaldehyde	Nitroethane	6	1-(2-Chlorophenyl)-2-nitropropan-1-ol	82	100:0
9	Furan 2-Carboxaldehyde	Nitroethane	6	1-(2-Furyl)-2-nitro-propan-1-ol.	74	1.5:1
10	2-Chloroqunoline-3-carboxaldehyde	Nitroethane	8	1-(2-Chloro-3-quiloline)-2-nitropropan-1-ol.	88	100:0
11	3-Nitrobenzaldehyde	2-Nitropropane	8	1-(m-Nitrophenyl)-2-nitro-2-methylpropan-1-ol	80	-
12	Cinnamaldehyde	Nitroethane	6	1-Styryl-2-nitropropan-1-ol	41	1.25:1
13	n-Hexanal	Nitromethane	6	1-Nitromethyl-1-hexanol	82	-
14	Propionaldehyde	Nitromethane	6	1-Nitromethylpropan-1-ol	77	-

a: Products were characterized by IR, ^{1}H, ^{13}C-NMR and M.S. b: Isolated yield after column chromatography.
c: Average ratios were calculated from ^{13} C- NMR signals (50.3 MHz)

MECHANISM AND DIASTEREOSELECTIVITY :

Mg-Al hydrotalcite materials upon thermal calcination at 450 °C give a highly active mixed oxide. The high activity of these materials is attributed to the presence of a large number of OH groups generated during rehydration of a thermally activated hydrotalcite, which act as Bronsted basic sites with pKas in the range of 10.7-13.3 and a few sites with pKa =16.5.[15] It is presumed that this basicity is responsible for the catalytic activity and selectivity by abstracting an acidic proton from the nitroalkanes followed by its addition onto the aldehydes. It is observed that in all 9 cases studied, the *threo* isomer is formed predominantly (Table 2). In the ^{13}C-NMR spectra of nitroaldols, the α-O-C signals of the major isomers lay at higher field and the α-O_2N-C signals at lower field than those of the minor isomers. The high field α-O-^{13}C signals and low field α-N-^{13}C signals are assigned to the *threo* isomers.[16] Particularly, in the case of the nitroaldols derived from 4-nitrobenzaldehyde, 2-chlorobenzaldehyde and 2-chloroquinoline-3-carboxaldehyde (entries 7,8 and 10), exclusive formation of the *threo* isomer was obtained based on their ^{1}H and ^{13}C-NMR and GLC analysis. In their ^{1}H-NMR spectra the vicinal coupling constants (7.3 Hz and 8.0 Hz) between the α-N-C-H and the α-O-C-H clearly confirm the formation of the *threo* isomers. These outcomes may be rationalized in terms of transition

state models based on closed chairlike structures involving coordination between the two oxygen atoms and the metal center (Scheme 2).



Scheme 2 : Transition state structures for the nitroaldol reaction

From scheme 2, it can be readily visualized that transition state **A** leading to the *threo* product is favored, whereas transition state **B** has steric interactions between the Ph and O groups leading to an energetically less favored species. Also if it is assumed that chelated products are likely to be thermodynamically more stable than nonchelated ones, this outcome may be rationalized by considering the Newmann projections **C** and **D** for two aldolates. For the *threo* aldolates, it can be seen that gauche interactions in C are minimized relative to conformation D of the *erythro* aldolate (Fig. 2).

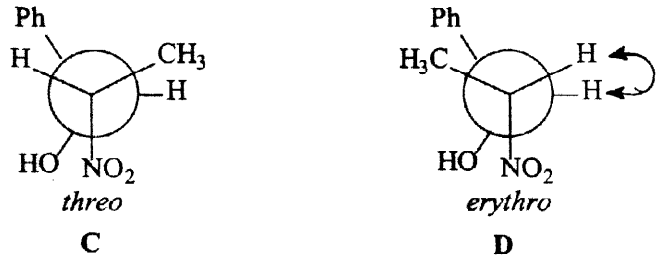


Fig. 2:Newman projections of *threo* and *erythro* aldolates

CONCLUSION:

In summary, we have shown that Mg-Al hydrotalcite is an effective and convenient catalyst for the condensation of nitroalkanes producing *threo*-nitroaldols in high yields and high diastereoselectivity. We have also shown that this new solid base catalyst is a practical alternative to soluble bases in Henry reactions in view of the following advantages: high catalytic activity under mild liquid phase conditions, easy separation of the catalyst by simple filtration, waste minimization and possibility of reuse.

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EXPERIMENTAL

All mps reported are uncorrected. IR spectra were recorded as neat or Nujol mulls (in the case of solid samples) on Perkin-Elmer Infrared model 137-E. ^{1}H NMR spectra were taken on a Varian FT 80A, Bruker FT 90, 200 MHz instruments. ^{13}C-NMR spectra were obtained on a Bruker 50.3 MHz instrument. The chemical shifts were reported with TMS as the internal standard. The mass spectra (MS) were recorded on an automated Finnigan MAT 1020 C mass spectrometer using ionization energy of 70 eV.

Preparation of the Mg-Al hydrotalcite (3:1) catalyst:
Two separate solutions namely solution A containing $Mg(NO_3)_2.6H_2O$ (115.38 g, 0.45 moles) and $Al(NO_3)_3.9H_2O$ (56.27 g, 0.15 moles) in 300 ml of distilled water and solution B containing NaOH (30 g, 0.75 moles) and Na_2CO_3 (15g, 0.141 moles) in 200 ml of distilled water, were prepared at room temperature. The rate of addition of metal nitrates was maintained at about 60 ml/h, while the pH of the reaction mixture was maintained by adjusting the flow rate of solution B. After completion of addition of solution A, the resulting slurry was digested at 65 °C for 30 min. with constant stirring. The resulting precipitate was washed with distilled water several times until the pH of the filtrate was 7.0. The catalyst was then dried 100 °C and calcined at 450 °C respectively for 8 h in air. The other ratio of the above catalyst, Mg-Al 4.0, 5.0 were prepared by following the above procedure similarly, other catalysts Zn-Al 3.0, Cu-Al 3.0 were prepared using $Zn(NO_3)_2$ and $Cu(NO_3)_2$ respectively.

General procedure for the preparation of 2-nitroalcohols:
In a typical reaction experimental procedure, 3-nitrobenzaldehyde (500 mg; 2 mmol), nitroethane (151 mg; 2 mmol) and MgAl-HT (100 mg 20%w/w) in THF (10 ml) was refluxed under nitrogen atmosphere for 6 h. The progress of the reaction was monitored by TLC (10% EtOAc in pet ether) the catalyst was filtered off and the product purified by flash chromatography (6% EtOAc in pet ether as eluent) to afford 1-(3-nitrophenyl)-2-nitropropan-1-ol (666 mg; 95%).

1-Phenyl 2-nitropropan-1-ol (1)[16] :Viscous liquid; IR (Neat): 3528, 1552, 1494, 1390, 1022, 908, 870, 766, 610 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.3 (d, J= 7.3Hz, 3H), 1.5 (d, J= 7.3 Hz, 3H), 2.7 (d, J= 4.8 Hz, 1H), 2.85 (d, J= 4.8 Hz, 1H), 4.6-4.9 (m, 3H), 5.1 (dd, J=5.8 Hz, each,1H), 7.4 (s, Ar, 5H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 12.3, 16.6, 74.1, 76.4, 87.6, 88.6, 126.1, 127.1, 128.9, 129.3, 138.6; MS: m/z (rel. intensity %) 181 (M^+, 5), 107 (100), 91 (25), 77(77), 57 (65).

1-(3-Nitrophenyl)-2-nitropropan-1-ol (2): solid; m.p. 74 °C; IR (Nujol): 3510, 1520, 1352, 1210, 1050, 900, 816, 740 cm^{-1} ;^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.4 (d, J= 7.3 Hz, 3H), 1.5 (d, J= 5.8 Hz, 3H), 3.4 (d, J= 10.8 Hz, 1H), 4.7-4.85 (m, 1H), 5.2 (dd, J= 5.4 Hz, each 1H), 7.55-7.8 (m, 2H), 8.2 (m, 2H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 16.29, 73.0, 75.1, 87.0, 88.0, 122.0, 124.0, 130.2, 133.2, 140.7, 148.5; MS: m/z (rel. intensity %) 226 (M^+, 3), 179 (44), 149 (100), 105 (40), 90 (10), 77 (51). Anal. Calcd. for $C_9H_{10}N_2O_5$ C, 47.79; H, 4.45; N, 12.38%. Found C, 47.51; H, 4.58; N, 12.52%.

1-(4-Nitrophenyl)-2-nitro-3-tetrahydropyranoloxypropan-1-ol (3): Viscous Liquid; IR (Neat): 3404, 1558, 1524, 1458, 1350, 1258, 1122, 1074, 964, 832, 758 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.4-1.9 (m, 6H), 3.3-3.8 (m, 2H), 3.9-4.1 (m, 1H), 4.1-4.2 (m, 1H), 4.5-4.6 (m, 1H), 4.8-4.9 (m, 1H), 5.35-5.6 (m, 1H), 7.65 (d, J= 8.0 Hz, 2H), 8.25 (d, J= 8.0 Hz, 2H). Anal. Calcd. for $C_{14}H_{18}N_2O_7$ C, 51.53; H, 5.55; N, 8.58%. Found C, 51.01; H, 5.78; N, 8.03%.

1-(2-Hydroxyphenyl)-2-nitropropan-1-ol (4): Viscous Liquid; IR (Neat): 3652, 3332, 1664, 1552, 1458, 1388, 1302, 1234, 1152, 1048, 912, 758 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.35 (d, J=7Hz 3H), 3.9 (bs, 1H),4.45 (q,

J= 4.5 Hz, 1H), 4.9-5.1 (m,1H), 6.8-7.5 (m, 4H); MS: m/z (rel. intensity %) 197 (M^+, 5), 179 (2), 132 (15), 123 (73), 121(100), 105 (16), 93 (10), 77 (15), 66 (10). Anal. Calcd. for $C_9H_{11}NO_4$ C, 54.82; H, 5.61; N, 7.1 %. Found C, 54.20; H, 5.8; N, 7.3 %.

1-(4-Methoxyphenyl)–2-nitropropan-1-ol (5): Viscous Liquid; IR (Neat): 3478, 1670, 1552, 1454, 1360, 1250, 1118, 1028, 912, 782, 734 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.3 (d, J= 8.1 Hz, 3H), 1.5 (d, J= 6.5 Hz, 3H), 3.85 (s, 3H), 4.6-4.85 (m, 1H), 4.9 (d, J= 10.8 Hz 1H), 5.35 (d, J= 5.4 Hz 1H), 6.9 (d, J= 7.5 Hz, 2H), 7.35 (d, J= 8.0 Hz, 2H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 12.4, 16.4, 55.2, 73.8, 75.8, 87.5, 88.5, 114.3, 127.2, 128.1, 130.4, 130.6, 159.6, 160.1; MS: m/z (rel. intensity %) 211 (M^+, 5), 137 (100), 135 (35) 109 (28), 94 (18), 77 (40), 65 (15). Anal. Calcd. for $C_{10}H_{13}NO_4$ C, 56.89; H, 6.20; N, 6.63 %. Found C, 56.32; H, 6.82; N, 6.28 %.

1-(2-Chlorophenyl)-2-nitrobutan-1-ol (6): Viscous Liquid; IR (Neat): 3514, 1552, 1464, 1372, 1270, 1196, 1102, 928, 806, 700 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.9, (m, 3H), 1.5-1.8 (m, 2H), 2.0-2.25 (m, 1H), 2.9 (b. s, –OH), 4.7 (m,1H), 5.6 (m, 1H), 7.2-7.6 (m, 4H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 10.4, 10.6, 19.9, 23.6, 71.1, 71.2 91.7, 94.9, 127.4, 127.8, 128.3, 129.8, 130.0, 130.1, 132.8, 135.9, 136.6; MS: m/z (rel. intensity %) 229 (M^+, 5), 182 (8), 143 (28), 141 (100), 125 (25), 111 (32), 91 (15), 77 (95), 57 (41). Anal. Calcd. for $C_{10}H_{12}NO_3Cl$ C, 52.29; H, 5.26; N, 6.09; Cl, 15.45%. Found C, 52.56; H, 5.42; N, 6.7; Cl, 15.32%.

1-(4-Nitrophenyl)-2-nitropropan-1-ol (7) [3a]**:** Solid m. p. 91 °C; IR (Nujol): 3540, 1550, 1340, 1200, 840, 730, 660 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.27 (d, J=10.5 Hz, 3H), 1.42 (d, J=10.0 Hz, 3H), 3.5 (s, -OH), 4.81 (m, 1H), 5.21 (d, J=10.0 Hz, 2H), 7.48 (d, J=10.0 Hz, 2H), 8.22 (d, J= 10.0 Hz 2H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 16.4, 754.2, 88.0, 124.2, 128.1, 145.5, 148.5; MS: m/z (rel. intensity %) 226 (M^+, 5), 179 (32), 151 (100), 134 (15), 115 (12), 105 (48), 77 (42).

1-(2-Chlorophenyl)-2-nitropropan-1-ol (8) : Viscous Liquid; IR (Neat): 3512, 1548, 1462, 1282, 1196, 1098, 1050, 992, 884, 700 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.4 (d, J=9.0 Hz, 3H), 2.85 (d, J= 4.0 Hz, -OH), 4.85 (q, J= 4.0 Hz 1H), 5.6 (m, 1H), 7.2-7.4 (m, 3H), 7.5 (d, 1H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 16.1, 72.0, 88.3, 127.8, 128.4, 130.0, 130.2, 132.9, 136.4; MS: m/z (rel. intensity %) 215 (M^+, 5), 168 (10), 144 (100), 138 (52), 110 (18), 76 (8). Anal. Calcd. for $C_9H_{10}NO_3Cl$ C, 50.12; H, 4.66; N, 6.49; Cl, 16.46%. Found C, 50.51; H, 4.85; N, 6.83; Cl, 16.43%.

1-(2-Furyl)-2-nitropropan-1-ol (9)[3a] **:** Viscous Liquid; IR (Neat): 3500, 1530, 1340, 1200, 1010, 740, 510 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.4 (d, J=7.2 Hz, 3H), 1.7 (d, J=6.2 Hz, 3H), 2.8 (d, J=4.8 Hz 1H), 2.9 (d, J=4.8 Hz, 1H), 4.8-5.0 (m,1H), 6.45 (m, 2H) 7.45 (d, J= 4.3 Hz, 1H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 13.2, 16.2, 69.0, 69.5, 85.1, 86.5, 108.2, 109.5, 110.7, 142.9, 143.4, 150.9, 151.5; MS: m/z (rel. intensity %) 171 (M^+, 5), 124 (121), 108 (5), 97 (100), 83 (42).

1-(2-Chloro-3-quinoline)-2-nitropropan-1-ol (10): Solid, m.p. 88 °C; IR (Nujol): 3540, 1540, 1360, 1200, 1040, 940 cm^{-1} ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.5 (d, J=7.2 Hz, 3H), 3.65 (s, 1H), 5.05 (q, J= 4.8 Hz 1H), 5.95 (s, 1H) 7.6-8.05 (m, 4H), 8.5 (s, 1H).^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 11.1, 70.3, 83.9, 127.3, 127.9, 128.3, 130.4, 131.4, 138.0, 147.5; MS: m/z (rel. intensity %) 266 (M^+, 5), 219 (42), 192 (95), 127 (100), 100 (45), 74 (60), 57 (42). Anal. Calcd. for $C_{12}H_{11}N_2O_3Cl$ C, 54.03; H, 4.15; N, 10.50; Cl, 13.30%. Found C, 54.53; H, 4.32; N, 10.83; Cl, 13.63%.

1-(3-Nitrophenyl)-2-nitro-2-methylpropan-1-ol (11)[17] **:** Solid, m.p. 151 °C (Literature m.p. 154-156 °C) IR (Nujol): 3642, 1552, 1464, 1354, 1272, 1126, 1004, 888, 742 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.49 (s, 3H), 1.58 (s, 3H), 3.1 (br. s –OH), 5.4 (s, 1H) 7.5-7.8 (m, Ar, 2H), 8.1-8.3 (m, 2H); MS: m/z (rel. intensity %) 240 (M^+, 5), 194 (25), 151(42), 105 (45), 89 (78), 77 (100), 74 (33), 65 (12), 57 (12).

1-Styryl-2-nitropropan-1-ol (12) [16]**:** Viscous Liquid, IR (Neat): 3438, 1550, 1496, 1390, 1300, 1026, 972, 872, 696 cm^{-1} ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.7 (d, J=8.1 Hz, 3H), 2.5 (m, 1H), 4.75 (m, 1H), 4.9 (m, 1H) , 6.2 (dd, J=14.0 Hz, 4.0 Hz, 1H), 6.8 (d, J=14.0 Hz, 1H) 7.35 (m, 5H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): δ 13.0, 16.1, 73.4,

74.8, 77.2, 77.9,86.3, 87.4, 125.4, 126.8, 126.6, 128.8, 129.0, 133.7, 134.8, 135.8. MS: m/z (rel. intensity %) 207 (M^+, 5), 160 (25), 133(52), 115(45), 103 (38), 91 (100), 77 (55), 65 (5), 55 (81).

1-Nitromethyl-1-hexanol (13): Viscous Liquid, IR (Neat): 3492, 1570, 1496,1296, 1210, 1132, 1090, 944, 884, 726 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 0.9 (b t, J = 6.4 Hz 3H), 1.1-1.2 (b s, 4H), 1.5-1.6 (b s, 4H), 2.6 (b s, 1H), 4.1-4.3 (m, 1H), 4.5-4.6 (m, 2H). MS: m/z (rel. intensity %) 161 (M^+, 5), 97 (15), 90 (22), 81 (40), 69 (45), 55 (100), 54 (75). Anal. Calcd. for $C_7H_{15}NO_3$ C, 52.16; H, 9.37; N, 8.68%. Found C, 52.08; H, 9.70; N, 8.12%.

1-Nitromethylpropan-1-ol (14): Viscous Liquid, IR (Neat): 3490, 1716, 1636, 1556, 1422, 1358, 1280, 1130, 1082, 990, 844, 728 cm^{-1}; ^{1}H-NMR (200 MHz, $CDCl_3$): δ 1.05 (t, J= 8.1 Hz, 3H), 1.6 (q, J= 6.4 Hz, 2H), 2.7 (b s, 1H), 4.22-4.3 (m, 1H), 4.4-4.55 (m, 1H); MS: m/z (rel. intensity %) 119 (M^+, 5), 99 (10), 90 (40), 75 (55), 62 (70), 55 (100). Anal. Calcd. for $C_4H_9NO_3$ C, 40.33; H, 7.60; N, 11.75%. Found C, 39.83; H, 7.23; N, 12.26%.

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