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Cetyltrimethylammonium hydroxide (CTAOH) as a general, ecofriendly catalyst for the formation of carbon–carbon bond through nitroalkanes

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Abstract—Nitroalkanes have been found to give good yields in Michael and nitroaldol (Henry) reactions by the use of a catalytic amount (10 mol%) of CTAOH, at room temperature and under solvent free conditions and in very short reaction times. The methods do not need a large excess of the nitroalkanes and show good chemoselectivity toward further functionalities.

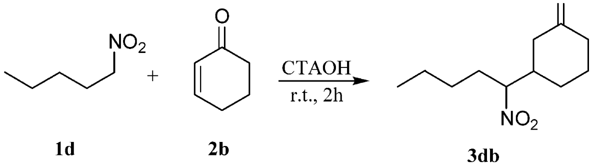
1. Introduction

Carbon–carbon bond formation is the essence of organic synthesis and nitroalkanes are very important starting materials in this context.[1,3] This is mainly due to their easy conversion into the corresponding nitronate anions because the high electron-withdrawing power of the nitro group that provides an outstanding enhancement of the acidity of α-hydrogens atoms. Therefore, nitronate salts can act as carbon nucleophiles with a range of electrophiles such as aldehydes, giving the nitroaldol (Henry reaction),[4,5] or with electron poor alkenes, giving the conjugate addition (Michael) reaction.[6] As routine procedures the Henry and Michael reactions are performed in the presence of different bases in homogeneous solutions of organic solvent or water or, alternatively, under heterogeneous catalysis[6,7] and, for these purposes, even the help of sonication[8] or high pressure[9,10] have been proposed. Although each of the above procedures have been widely studied, very often these suffer from different drawbacks such as: (i) for the nitroaldol reaction, low yields, retroaldol reaction, the formation of side products due to the aldol condensation and/or Cannizzaro reaction of aldehydes or olefin formation, and (ii), for the Michael reaction, low yields, efficiency restricted to a class of electrophilic olefins, the need of ultrasound, and/or a large excess of the nitroalkane that, for valuable nitro derivatives, is a serious economic drawback.

Thus, considering that over the past few years, a significant amount of research has been directed towards the development of new technologies for environmentally benign processes (green chemistry). An important area of the green chemistry deals with solvent minimization,[11–13] and new efficient, economical and environmentally friendly catalytic processes for both Henry and Michael reactions, are desirable.

2. Results and discussion

In this context, we report herein a new catalytic approach developed in our laboratory, and carried out with cetyltrimethylammonium hydroxide (CTAOH, 10% water solution) as ecofriendly catalyst. First, we investigated the Michael reaction and, in order to verify the best substrates/catalyst ratio, the method was tested (Scheme 1) through the reaction of 1-nitropentane **1d** with an hindered electrophilic alkene such as 2-cyclohexen-1-one **2b**.



Scheme 1.

The choice of this model reaction is due to the well known behaviour of the conjugate additions of nitroalkanes to **2b** that, generally, need long reaction times and the Michael adducts are generally obtained in low to satisfactory yields, probably due to the steric hindrance of the acceptor.[2,6] The reaction was performed by adding the Michael acceptor **2b**

Keywords: Henry reaction; Michael reaction; Nitroalkanes; β-Nitroalcohol; CTAOH.

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Table 1. Study of Michael addition of 1-nitropentane **1d** to 2-cyclohexen-2-one **2b** with different amount of CTAOH (reaction time 2 h)

% of CTAOH	Yield (%) of **3db**
2.5	30
5	65
10	90
15	91
20	90

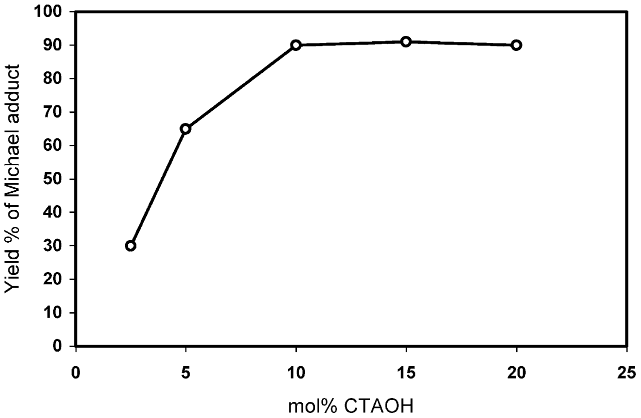
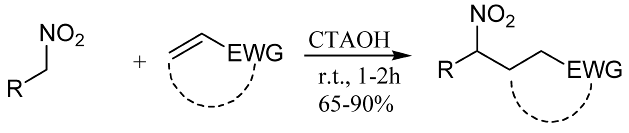


Figure 1. Trend of Michael adduct **3db** with different amount of CTAOH.

to an equimolar amount of a stirred mixture of **1d** and in the presence of different quantities of CTAOH (Table 1, Fig. 1).

As reported in Figure 1, 10 mol% of the catalyst was found to be most appropriate and the Michael adduct **3db** was obtained in excellent yield (90%) and in a very short reaction time (2 h, Table 1).

Thus, a number of different nitroalkanes **1** and electron poor alkenes **2** were chosen to assess the scope of the reaction (Scheme 2).

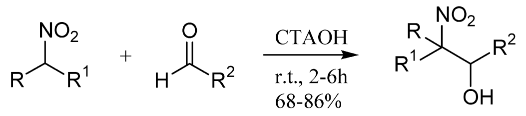


1 **2** **3**

Scheme 2.

All the reactions were carried out in the presence of a minimum amount of water (due to the use of 10% water solution of the catalyst) and involved simple mixing stoichiometric amounts of **1** (1 mmol) and **2** (mmol) with 10% mol% of CTAOH (10% water solution), at room temperature, and leaving the mixture for further 1–2 h.

The synthetic results of the reactions are presented in Table 2. Under this method simple and functionalized nitroalkanes easily react with a variety of electrophilic alkenes, and the yields seem to be fairly independent of the degree of electron-deficiency of the alkene and of steric hindrance (**3bb**,**db**). It is worthy of note that this procedure affords compounds **3** in good yields (65–90%). Encouraged by these excellent results, we applied the same reaction conditions to the nitroaldol reaction investigating the reactivity of a series of linear and cyclic nitroalkanes **1** with an array of both aliphatic and aromatic aldehydes **4** (Scheme 3).



1 **4** **5**

Scheme 3.

Although these reactions are slower than the conjugate additions (2–6 h vs 1–2 h), we found that the β-nitro-alcohols **5** are produced in good yields (68–86%, Table 3) and contrary to other methods, the very mild reaction conditions needed prevent the typical side reactions such as retro-aldol reaction or dehydration of the 2-nitro alcohol into nitroalkenes, even if aromatic aldehydes are used.[14,15]

3. Conclusion

In summary, we have reported general catalytic method for the formation of carbon–carbon bond using nitroalkanes with several electrophilic alkenes (such as α,β-unsaturated ketones, α,β-unsaturated esters, α,β-unsaturated suphones, and α,β-unsaturated nitriles) and both aromatic and aliphatic aldehydes. All the reactions work well with short reaction times, mild reaction conditions (room temperature and 10% of the catalyst), in the presence of a minimum amount of water. High chemoselectivity is observed since further functionalities are preserved under these conditions. It is noteworthy that our method avoids the need for a large excess of the nitroalkanes and uses organic solvents during the work up only. Thus, because an important area of green chemistry deals with solvents[16,17] and by products minimization our results represent an improved, inexpensive and ecological process.

4. Experimental

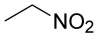
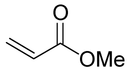
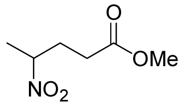
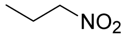
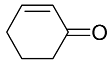
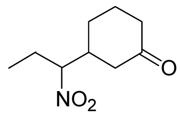
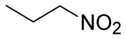
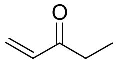
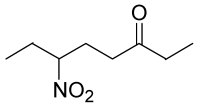
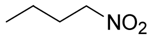
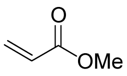
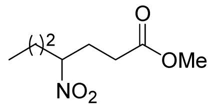
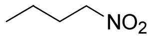
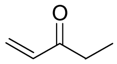
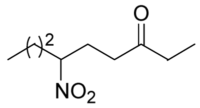
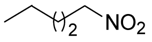
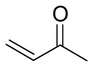
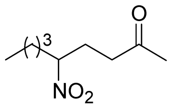
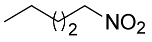
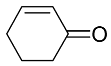
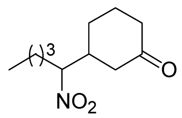
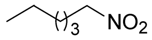
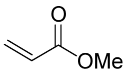
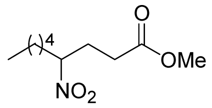
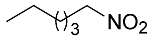
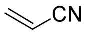
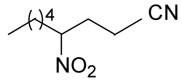
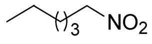
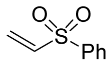
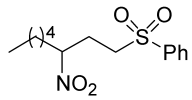
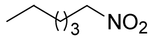
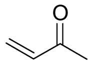
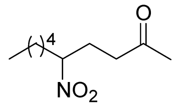
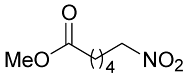
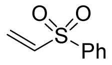
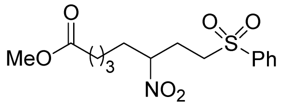
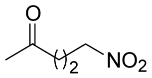
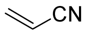
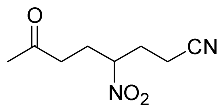
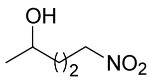
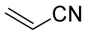
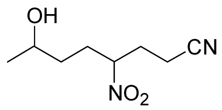
4.1. General

^1H NMR were recorded at 300 MHz on a Varian VXR300 in $CDCl_3$ as solvent. ^{13}C NMR were recorded at 75 MHz in $CDCl_3$ as solvent. Microanalyses were performed with a CHNS-O analyser MODEL EA 1108 from Fisons Instruments. IR spectra were recorded with a Perkin–Elmer Paragon 500 FT-IR. GLC analyses were performed on a fised silica (0.32 mm×25 m), stationary phase SE54. Mass spectra were performed on a Hewlett–Packard GC/MS 5970 by means of the EI technique (70 eV). CTAOH was supplied by Fluka as a 10% water solution.

4.2. General procedure for the Michael reaction

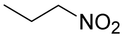
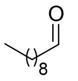
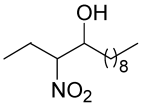
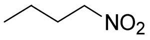
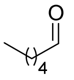
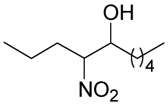
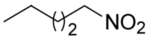
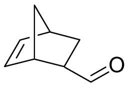
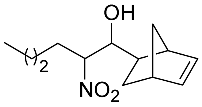
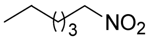
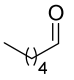
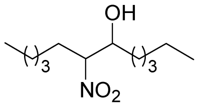
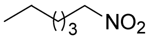
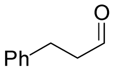
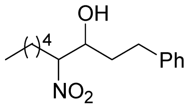
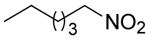
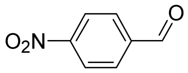
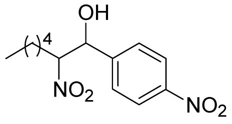
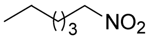
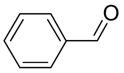
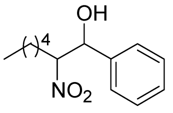
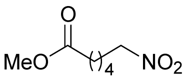
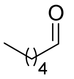
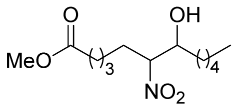
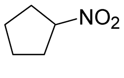
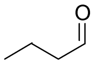
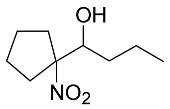
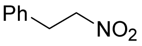
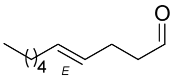
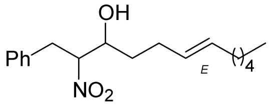
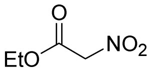
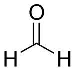
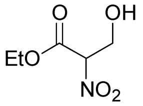
The Michael acceptor **2** (1 mmol) was added to a stirred mixture of nitrocompound **1** (1 mmol; when the nitroalkanes **1a** and **1b** were employed 1.2 mmol were utilised) in a 10% water solution of hexadecyltrimethyl ammonium

Table 2. Michael addition of nitro compounds **1** to α,β-unsaturated systems **2**

Nitro compound **1**		α,β-Unsaturated compound **2**		Michael adduct **3**		Time (h)	Yield (%)[a]
1a		**2a**		**3aa**		1	78
1b		**2b**		**3bb**		1	80
1b		**2c**		**3bc**		1	83
1c		**2a**		**3ca**		1	77
1c		**2c**		**3cc**		1	75
1d		**2d**		**3dd**		1	74
1d		**2b**		**3db**		2	90
1e		**2a**		**3ea**		1	87
1e		**2e**		**3ee**		1	70
1e		**2f**		**3ef**		1	70
1e		**2d**		**3ed**		1	77
1f		**2f**		**3ff**		2	73
1g		**2e**		**3ge**		2	65
1h		**2e**		**3he**		1	72

[a] Yields of pure, isolated compounds.

Table 3. Addition of nitro compounds **1** to aldehydes **4**

Nitro compound **1**		Aldehyde **4**		Nitroalcohol **5**		Time (h)	Yield (%)[a]
1b		**4a**		**5ba**		3	82
1c		**4b**		**5cb**		2	83
1d		**4c**		**5dc**		3	85
1e		**4b**		**5eb**		3	81
1e		**4d**		**5ed**		4	75
1e		**4e**		**5ee**		4	76
1e		**4f**		**5ef**		6	68
1f		**4b**		**5fb**		3	77
1i		**4g**		**5ig**		4	83
1j		**4i**		**5ji**		3	86
1k		**4h**		**5kh**		4	75

[a] Yields of pure, isolated compounds.

hydroxide (CTAOH, 0.300 mL). The reaction progress was monitored by withdrawing aliquots which were analyzed by GC and TLC. Then the solution was treated with brine (10 mL) and extracted by CH_2Cl_2 (3×25 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated under vacuum to afford the crude product **3**, that was purified on flash cromatography (cyclohexane–ethyl acetate).

4.2.1. Methyl-4-nitropentanoate (3aa). Yield 78% of yellow oil. Spectroscopic data corresponds to that reported in the literature.[18]

4.2.2. 3-(1-Nitropropyl)-1-cyclohexanone (3bb). (Diastereomeric mixture, 1:1). Yield 80% of yellow oil. Spectroscopic data corresponds to that reported in the literature.[19]

4.2.3. 6-Nitro-3-octanone (3bc). Yield 83% of colourless oil. Spectroscopic data corresponds to that reported in the literature.[20]

4.2.4. Methyl-4-nitroheptanoate (3ca). Yield 77% of yellow oil; IR (cm^{-1}, neat) 1364, 1560, 1740; ^1H NMR δ (ppm) 0.95 (t, 3H, J=7.3 Hz), 1.28–1.47 (m, 2H), 1.61–1.81 (m, 1H), 1.90–2.42 (m, 5H), 3.70 (s, 3H), 4.52–4.65 (m, 1H); ^{13}C NMR δ (ppm) 13.5, 19.1, 28.7, 30.0, 35.9, 52.0, 87.6, 172.5; EI-MS: m/z=190, 172, 158, 143, 127, 111, 83, 69, 55 (100), 41. Anal. calcd for $C_8H_{15}NO_4$

(189.21) C, 50.78; H, 7.99; N, 7.40. Found: C, 50.93; H, 8.12; N, 7.29.

4.2.5. 6-Nitro-3-nonanone (3cc). Yield 75% of colourless oil; IR (cm^{-1}, neat) 1363, 1548, 1717; ^{1}H NMR δ (ppm) 0.95 (t, 3H, J=7.3 Hz), 1.07 (t, 3H, J=6.4 Hz), 1.22–1.43 (m, 2H), 1.60–1.79 (m, 1H), 1.89–2.18 (m, 3H), 2.38–2.52 (m, 4H), 4.42–4.60 (m, 1H); ^{13}C NMR δ (ppm) 7.7, 13.1, 18.9, 29.4, 34.5, 36.0, 40.1, 83.0, 208.5; EI-MS: *m*/*z*=188, 157, 141, 127, 110, 83, 69, 57 (100), 41. Anal. calcd for $C_9H_{17}NO_3$ (187.24) C, 57.73; H, 9.15; N, 7.48. Found: C, 57.88; H, 9.06; N, 7.39.

4.2.6. 5-Nitro-2-nonanone (3dd). Yield 74% of colourless oil. Spectroscopic data corresponds to that reported in the literature.[20]

4.2.7. 3-(1-Nitropentyl)-1-cyclohexanone (3db). (Diastereomeric mixture, 1:1). Yield 90% of yellow oil. Spectroscopic data corresponds to that reported in the literature.[20]

4.2.8. Methyl-4-nitrononanoate (3ea). Yield 87% of yellow oil. Spectroscopic data corresponds to that reported in the literature.[18]

4.2.9. 4-Nitrononanenitrile (3ee). Yield 70% of yellow oil. Spectroscopic data corresponds to that reported in the literature.[21]

4.2.10. 3-Nitro-1-(phenylsulfonyl)octane (3ef). Yield 70% of yellow oil. Spectroscopic data corresponds to that reported in the literature.[21]

4.2.11. 5-Nitro-2-decanone (3ed). Yield 77% of colourless oil. Spectroscopic data corresponds to that reported in the literature.[22]

4.2.12. Methyl-6-nitro-8-(phenylsulfonyl)octanoate (3ff). Yield 73% of yellow oil; IR (cm^{-1}, neat) 1308, 1556, 1732; ^{1}H NMR δ (ppm) 1.22–1.41 (m, 2H), 1.58–1.82 (m, 3H), 1.90–2.09 (m, 1H), 2.21–2.39 (m, 4H), 3.11 (t, 2H, J=7.4 Hz), 3.67 (s, 3H), 4.58–4.67 (m, 1H), 7.58–7.93 (m, 5H); ^{13}C NMR δ (ppm) 24.2, 25.2, 26.6, 33.5, 33.6, 51.8, 52.5, 86.5, 128.2, 129.8, 134.4, 138.8, 173.7; EI-MS: *m*/*z*=265, 171, 143, 123, 95, 77 (100), 67, 55, 41. Anal. calcd for $C_{15}H_{21}NO_6S$ (343.39) C, 52.47; H, 6.16; N, 4.08. Found: C, 52.59; H, 6.30; N, 3.99.

4.2.13. 4-Nitro-7-oxooctanenitrile (3ge). Yield 65% of yellow oil; IR (cm^{-1}, neat) 1363, 1560, 1729, 2249; ^{1}H NMR δ (ppm) 2.02–2.25 (m, 6H), 2.33–2.60 (m, 5H), 4.57–4.70 (m, 1H); ^{13}C NMR δ (ppm) 14.4, 27.2, 29.4, 30.2, 38.8, 85.9, 117.9, 206.2; EI-MS: *m*/*z*=185, 155, 113, 95, 71, 55, 43 (100). Anal. calcd for $C_8H_{12}N_2O_3$ (184.24) C, 52.17; H, 6.57; N, 15.21. Found: C, 52.31; H, 6.66; N, 15.08.

4.2.14. 7-Hydroxy-4-nitrooctanenitrile (3he). (Diastereomeric mixture 1:1). Yield 72% of yellow oil; IR (cm^{-1}, neat) 1376, 1552, 2250, 3422; ^{1}H NMR δ (ppm) 1.21 (d, 3H, J=6.2 Hz), 1.41–1.55 (m, 2H), 1.71–1.82 (bs, 1H), 1.95–2.49 (m, 6H), 3.71–3.92 (m, 1H), 4.58–4.76 (m, 1H); ^{13}C NMR δ (ppm) 14.5, 24.0, 24.1, 29.2, 29.4, 29.8, 30.3, 34.5, 34.9, 66.8, 67.4, 86.6, 87.2, 118.1; EI-MS: *m*/*z*=171, 122, 96, 82, 67, 55, 45 (100), 39. Anal. calcd for $C_8H_{14}N_2O_3$ (186.21) C, 51.60; H, 7.58; N, 15.04. Found: C, 51.77; H, 7.66; N, 14.95.

4.3. General procedure for the Henry reaction

The aldehyde **4** (1 mmol) was added to a stirred mixture of nitrocompound **1** (1 mmol) in a 10% water solution of hexadecyltrimethyl ammonium hydroxide (0.300 mL). The reaction progress was monitored by withdrawing aliquots which were analyzed by TLC. Then the solution was treated with brine (10 mL) and extracted by CH_2Cl_2 (3×25 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated under vacuum to afford the crude product **5**, that was purified on flash cromatography (cyclohexane–ethyl acetate).

4.3.1. 3-Nitro-4-tridecanol (5ba). Yield 82% of yellow oil; IR (cm^{-1}, neat) 1377, 1559, 3435; ^{1}H NMR δ (ppm) 0.83–0.90 (m, 3H), 0.93–1.02 (m, 3H), 1.18–1.56 (m, 16H), 1.78–2.19 (m, 2H), 2.46–2.52 (m, 0.5H), 2.58–2.62 (m, 0.5H), 3.82–3.92 (m, 0.5H), 3.94–4.02 (m, 0.5H), 4.30–4.41 (m, 1H); ^{13}C NMR δ (ppm) 10.4, 10.7, 14.3, 21.8, 22.9, 24.1, 25.5, 25.8, 29.4, 29.5, 29.6, 29.7, 29.8, 32.1, 33.5, 33.7, 72.0, 72.4, 94.2, 94.7. Anal. calcd for $C_{13}H_{27}NO_3$ (245.36) C, 63.64; H, 11.09; N, 5.71. Found: C, 63.75; H, 11.20; N, 5.58.

4.3.2. 4-Nitro-5-decanol (5cb). Yield 83% of colourless oil; IR (cm^{-1}, neat) 1380, 1560, 3436; ^{1}H NMR δ (ppm) 0.82–1.01 (m, 6H), 1.22–1.57 (m, 10H), 1.62–1.85 (m, 1H), 1.95–2.15 (m, 1H), 2.20–2.38 (m, 0.5H), 2.35–2.40 (m, 0.5H), 3.80–3.90 (m, 0.5H), 3.93–4.05 (m, 0.5H), 4.41–4.55 (m, 1H); ^{13}C NMR δ (ppm) 13.6, 13.7, 14.2, 19.3, 19.5, 22.7, 25.2, 25.5, 30.1, 31.7, 31.8, 32.7, 33.4, 33.8, 72.3, 72.6, 92.3, 92.9. Anal. calcd for $C_{10}H_{21}NO_3$ (203.28) C, 59.09; H, 10.41; N, 6.89. Found: C, 59.23; H, 10.55; N, 6.77.

4.3.3. 1-Bicyclo[2.2.1]hept-5-en-2-yl-nitrohexan-1-ol (5dc). Yield 85% of white solid, mp 43–45 °C; IR (cm^{-1}, neat) 1365, 1543, 1625, 3040, 3420; ^{1}H NMR δ (ppm) 0.83–1.05 (m, 3H), 1.22–1.57 (m, 7H), 1.70–2.38 (m, 5H), 2.82–2.94 (m, 1H), 3.02–3.12 (m, 1H), 4.38–4.76 (m, 2H), 5.82–6.27 (m, 2H); ^{13}C NMR δ (ppm) 13.9, 22.3, 28.0, 28.1, 28.4, 29.6, 29.8, 30.7, 42.6, 44.4, 49.1, 49.2, 50.1, 50.2, 75.8, 76.0, 91.3, 91.4, 132.5, 132.6, 138.3, 138.5. Anal. calcd for $C_{13}H_{21}NO_3$ (239.31) C, 65.25; H, 8.84; N, 5.85. Found: C, 65.39; H, 8.99; N, 5.77.

4.3.4. 7-Nitro-6-dodecanol (5eb). Yield 81% of colourless oil; IR (cm^{-1}, neat) 1379, 1561, 3447; ^{1}H NMR δ (ppm) 0.82–1.05 (m, 6H), 1.19–1.90 (m, 15H), 2.01–2.42 (m, 2H) 3.80–3.91 (m, 0.5H), 3.93–4.12 (m, 0.5H), 4.38–4.59 (m, 1H); ^{13}C NMR δ (ppm) 13.7, 14.3, 21.9, 23.0, 24.3, 28.4, 28.5, 30.1, 31.0, 31.2, 33.8, 33.9, 72.9, 73.1, 92.9, 93.0. Anal. calcd for $C_{12}H_{25}NO_3$ (231.33) C, 62.30; H, 10.89; N, 6.05. Found: C, 62.15; H, 11.00; N, 5.98.

4.3.5. 4-Nitro-1-phenyl-3-nonanol (5ed). Yield 75% yellow oil; IR (cm^{-1}, neat) 1376, 1560, 1603, 3027, 3448; ^{1}H NMR δ (ppm) 0.83–0.99 (m, 3H), 1.21–1.40 (m, 6H), 1.68–2.17 (m, 4H) 2.38–2.45 (m, 0.5H), 2.51–2.56 (m, 0.5H), 2.62–3.01 (m, 2H), 3.82–4.11 (m, 1H), 4.41–4.57

(m, 1H), 7.18–7.37 (m, 5H); ^{13}C NMR δ (ppm) 14.0, 14.1, 22.5, 25.5, 25.8, 28.2, 30.6, 31.3, 31.4, 31.8, 32.0, 35.0, 35.5, 71.5, 71.8, 92.6, 93.2, 126.5, 128.7, 128.8, 141.0, 141.1. Anal. calcd for $C_{15}H_{23}NO_3$ (265.35) C, 67.90; H, 8.74; N, 5.28. Found: C, 68.03; H, 8.86; N, 5.19.

4.3.6. 2-Nitro-1-(4-nitrophenyl)-1-heptanol (5ee). Yield 76% of yellow oil; IR (cm^{-1}, neat) 1349, 1520, 1556, 1607, 3082, 3522; ^{1}H NMR δ (ppm) 0.81–0.97 (m, 3H), 1.09–1.40 (m, 6H), 1.62–2.13 (m, 2H), 3.03 (bs, 1H), 4.61–4.77 (m, 1H), 5.05–5.10 (m, 0.5H), 5.13–5.18 (m, 0.5H), 7.60 (d, 2H, J=8.3 Hz), 8.22 (d, 2H, J=8.3 Hz); ^{13}C NMR δ (ppm) 13.9, 22.4, 25.4, 25.6, 27.5, 27.7, 30.4, 31.0, 31.1, 73.6, 74.7, 92.9, 93.3, 124.1, 124.3, 128.0, 145.9, 148.5. Anal. calcd for $C_{13}H_{18}N_2O_5$ (282.29) C, 55.31; H, 6.43; N, 9.92. Found: C, 55.44; H, 6.24; N, 9.85.

4.3.7. 2-Nitro-1-phenyl-1-heptanol (5ef). Yield 68% of yellow oil. Spectroscopic data corresponds to that reported in the literature.[23]

4.3.8. Methyl-7-hydroxy-6-nitrododecanoate (5fb). Yield 77% of yellow oil; IR (cm^{-1}, neat) 1371, 1556, 1731, 3497; ^{1}H NMR δ (ppm) 0.83–0.97 (m, 3H), 1.22–1.91 (m, 12H), 1.92–2.21 (m, 2H), 2.27–2.39 (m, 2H), 2.44–2.51 (m, 0.5H), 2.58–2.62, (m, 0.5H), 3.65 (s, 3H), 3.77–3.91 (m, 0.5H), 3.92–4.02 (m, 0.5H), 4.32–4.49 (m, 1H); ^{13}C NMR δ (ppm) 14.1, 22.7, 24.4, 25.1, 25.4, 25.7, 27.9, 30.2, 33.4, 33.7, 33.8, 51.8, 72.2, 72.5, 92.3, 92.9, 173.9, 174.0. Anal. calcd for $C_{13}H_{25}NO_5$ (275.34) C, 56.71; H, 9.15; N, 5.09. Found: C, 56.84; H, 9.03; N, 4.98.

4.3.9. 1-(1-Nitrocyclopentyl)-1-butanol (5ig). Yield 83% of colourless oil; IR (cm^{-1}, neat) 1357, 1537, 3445; ^{1}H NMR δ (ppm) 0.92 (t, 3H, J=7.0 Hz), 1.22–1.91 (m, 9H), 2.03–2.20 (m, 1H), 2.37–2.62 (m, 3H), 3.79–3.91 (m, 1H); ^{13}C NMR δ (ppm) 14.0, 19.7, 24.8, 25.0, 33.8, 34.7, 35.6, 75.7, 103.8. Anal. calcd for $C_9H_{17}NO_3$ (187.24) C, 57.73; H, 9.15; N, 7.48. Found: C, 57.89; H, 9.27; N, 7.33.

4.3.10. (*E*)-2-Nitro-1-phenyl-6-dodecen-3-ol (5ji). Yield 86% of yellow oil; IR (cm^{-1}, neat) 1377, 1560, 1605, 3031, 3066, 3544; ^{1}H NMR δ (ppm) 0.9 (t, 3H, J=6.9 Hz), 1.21–1.39 (m, 6H), 1.57–1.71 (m, 2H), 1.93–2.05 (m, 2H), 2.09–2.30 (m, 2H), 2.38–2.42 (m, 0.5H), 2.48–2.53, (m, 0.5H), 3.13–3.38 (m, 2H), 3.83–3.94 (m, 0.5H), 4.08–4.17 (m, 0.5H), 4.68–4.77 (m, 1H), 5.30–5.59 (m, 2H), 7.16–7.37 (m, 5H); ^{13}C NMR δ (ppm) 14.3, 22.7, 28.7, 28.9, 29.3, 31.6, 32.7, 33.1, 33.8, 34.6, 36.8, 71.1, 72.1, 93.6, 93.7, 127.6, 127.7, 129.0, 129.1, 132.6, 132.8, 135.3, 136.0. Anal. calcd for $C_{18}H_{27}NO_3$ (305.42) C, 70.79; H, 8.91; N, 4.59. Found: C, 70.91; H, 9.01; N, 4.47.

4.3.11. Ethyl-3-hydroxy-2-nitropropanoate (5kh). Yield 75% of yellow oil. Spectroscopic data corresponds to that reported in the literature.[24]

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