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Abstract: β-Hydroxy nitroethanol ethers are prepared by selective alcoholysis of oxiranes. The best results are obtained using a clay (monmorillonite K10) or a π-acid (TCNE) as the catalyst.

Keywords: alcoholysis, nitroethanol ethers, oxiranes, TCNE

INTRODUCTION

The addition of alcohols to epoxides is a common synthetic process leading to β-hydroxy ethers and vic-diol mono ethers. This general reaction can be done under various experimental conditions, for instance, under basic conditions to generate the alcoholate by using a polymer-supported amine (PSTBD)[1] and under acid catalysis using TsOH.[2,3] The reaction also can proceed through an electron-transfer reaction using reagents such as cerium ammonium nitrate (CAN)[4,5] or 2-3-dichloro-5,6-dicyano-p-benzoquinone (DDQ).[6] The search for milder experimental conditions and efficacy led to many

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investigations on the use of a Lewis acid catalyst, such as, for instance, an Fe^{III} porphyrin complex,[7] $Fe(CF_3COO)_3$,[8] $BiCl_3$,[9] salen Co,[10] $Yb(OTf)_3$,[11] $Sc(OTf)_3$,[12] $CeCl_3$,[13] $CuBF_4$,[14] or $(ClBu_2Sn)_2O$.[15]

In the course of our studies on the bioactivity of terpene-related compounds, we were interested in introducing the nitroethoxy radical onto specifically designed structures. Ring opening of an epoxide by 2-nitroethanol appeared among the most convenient and versatile strategies to reach that goal.

However, the chemical nature of the nitro function limits the choice of the reagent and reaction conditions. For instance, standard basic conditions are ruled out because of the formation of a reactive nitronate anion. In addition, the alcoolate of the expected alcohol might further compete with nitroethanol to react with the epoxide. Radical reactions are of little interest because of the difficulty in controlling the process, as shown by the reaction involving CAN that led to the formation of polymers. Acidic conditions were first investigated in Russian laboratories[2,6–18] with some moderate success that can hardly be generalized. Low yields and polycondensation plagued the use of this simple route to more complex molecules.

The use of tetracyanoethylene (TCNE), a mild π-acid, turned out to efficiently catalyze ring opening of epoxides by alcohols, mostly methanol.[3,19,20] This method was put in use in the cleavage of caryophyllene oxide by nitroethanol along with a rearrangement of the terpene skeleton.[21,22]

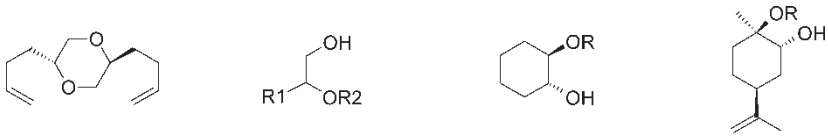
In this article, we report on the specific alcoholysis of oxiranes by nitroethanol, under several reaction conditions designed to limit the overall reaction to monocondensation, and give a general view on the scope and limits of this general reaction.

Basic Conditions

The condensation of the alcoolate of nitroethanol, formed with Na, NaH, and 1,4-diazabicyclo[2.2.2]octane (DABCO), led to no reaction at room temperature, then to a rapid polymerization upon heating.

We turned toward polymer-supported bases such as a polyaminophosphazene on polystyrene, a strong neutral nitrogen base, with no result. Finally, the reaction of various epoxides in nitroethanol (2 equivalents) at 60°C activated with 20% in weight of DOWEX monosphere 550A (OH) anion exchange resin, a strongly basic (type I) anion, afforded the expected β-hydroxy ether (Scheme 1). This reaction uses no solvent, is clean, and gives the corresponding diol as a main side product. Results are shown in Table 1. Using a solvent such as dry THF led to little reaction after 4 days under reflux, and refluxing in higher boiling dry dioxane gave only the corresponding diol.

Yields were not optimized, and it is noteworthy that the regioselectivity was excellent in this addition. Addition of nitroethanol occurred at the most substituted carbon on the oxirane. Because limonene oxide was used as a mixture of stereomers, **9** should arise from the major isomer having the



2

3: R1 = Ph, R2 = 2-nitroethyl
4: R1 = Ph, R2 = H
5: R1 = PhO, R2 = 2-nitroethyl
6: R1 = PhO, R2 = H

7: R = 2-nitroethyl
8: R = H

9: R = 2-nitroethyl
10: R = H

Scheme 1.

oxirane trans to the isopropylidene group. Diol **10** mainly arises from the cleavage of the corresponding cis isomer on the least substituted carbon, probably due to the size of the resin. The stereochemistry of **10** is based on the coupling constants measured in the ^{1}H NMR spectra. Ether **9** was contaminated by a minor regioisomer.

Brønsted Acids

Brønsted acids have been used in the alcoholysis of epoxides, and we refluxed cyclohexenoxide in CH_2Cl_2 along with *p*-TsOH · H_2O (0.05 equivalent) for 4 h to obtain a complex mixture of compounds. At room temperature, the reaction was much cleaner and complete after 48 h, affording ether **11** as the main product. No or little expected addition of nitroethanol occurred, and we observed the simple hydrolysis of cyclohexene oxide followed by condensation onto a second epoxide (Scheme 2).

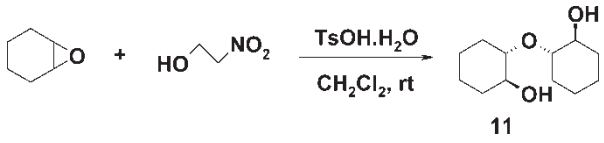
This strategy thus turned out to be of little interest when applied to nitroethanol.

Lewis Acids

The use of Lewis acids provides a mild method for the alcoholysis of epoxides, but there is no reagent that can be generally applied to all cases. Rather, there

Table 1. Reaction of epoxides with 2-nitroethanol activated by Dowex, 20% in weight

Epoxide	Time	Products, yield (%)
1,2-Epoxy-5-hexene	3 d	**1**: hex-5-ene-1,2-diol, 55; **2**, 10
Styrene oxide	2 d	**3**, 57; **4**, 38
1,2-Epoxy-3-phenoxypropane	2.5 d	**5**, 40; **6**, 42
Cyclohexene oxide	2 d	**7**, 52; **8**, 38
Limonene oxide	3 d	**9**, 45; **10**, 37



Scheme 2.

is a set of candidates from which an appropriate acid might solve a given problem. The reaction usually gives a mixture of regioisomers.

Strong Lewis acids such as $BF_3 \cdot Et_2O$ gave a complex mixture of products, even at low temperature ($-78^\circ C$) and low catalyst concentration (5%). Milder Lewis acids such as $Yb(OTf)_3$ also led to the same complex mixture of products, synthetically useless.

Finally, styrene oxide reacted with nitroethanol (3 equivalents) at rt for 30 h in the presence of $CeCl_3 \cdot 7H_2O$ to give both regioisomers with the secondary ether favored. Anhydrous $CeCl_3$ led to the same result albeit much faster (3 h). An even faster addition was obtained using $BiCl_3$ (5%), leading to hydroxyether **3** in 45% yield. The reaction alternatively can be run at $0^\circ C$ for 72 h in CH_2Cl_2 as the solvent with the same result (Scheme 3).

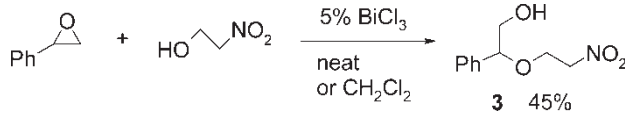
This positive result encouraged us to investigate even milder acids such as clays and π-acids.

Clays and π-Acids

Montmorillonite K is a mineral adsorbent that promotes reactions catalyzed by Brønsted or Lewis acids, and TCNE is a π-acid that has been used for the methanolysis of epoxides. Both reagents gave satisfactory results in the addition of nitroethanol to most of the epoxides that were involved: alkyl, ring fused, and functionalized.

The additions were run at room temperature without solvent, using instead 3 equivalents of nitroethanol, and they are followed by an easy workup. Results are gathered in Table 2 and Scheme 4.

Under those conditions, the reaction is rather highly regioselective, favoring the addition of nitroethanol on the most substituted carbon atom of the oxirane, except for isophorone oxide (entries 15 and 16). In that case, the addition mainly leads to C-α substitution, and the anti-β-



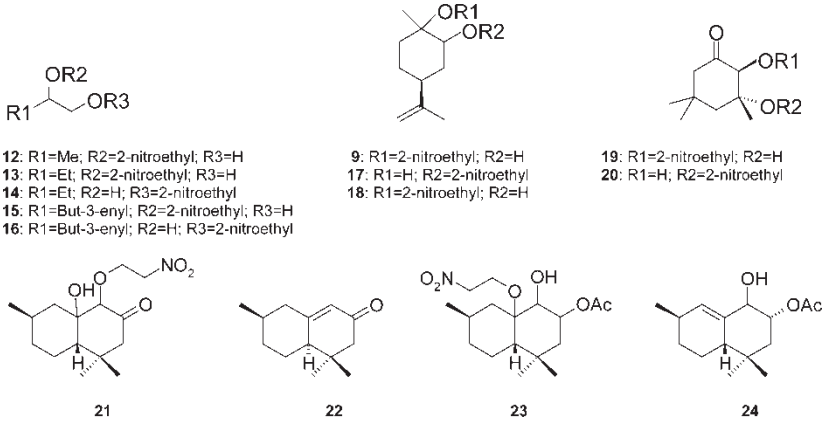
Scheme 3.

Table 2. K10- and TCNE-catalyzed reaction of epoxides with 2-nitroethanol

Epoxide	Entry	Catalyst	Time (h)	Products, yield (%)
1,2-Epoxy propane	1	K10	4	**12**, 10[a]
	2	TCNE	3	**12**, 15[a]
1,2-Epoxy butane	3	K10	3	**13**, 36; **14**, 18
	4	TCNE	6	**13**, 37; **14**, 15
1,2-Epoxy-5-hexene	5	K10	28	**15**, 58; **16**, 34
	6	TCNE	28	**15**, 58
Styrene oxide	7	K10	3.5	**3**, 98
	8	TCNE	4	**3**, 84
1,2-Epoxy-3-phenoxypropane	9	K10	48	**5**, 92
	10	TCNE	44	**5**, 96
Cyclohexene oxide	11	K10	4	**7**, 60
	12	TCNE	18	**7**, 58
Limonene oxide	13	K10	1.5	**9**, 65; **17**, 15[b]
	14	TCNE	18	**9**, 31; **17**, 8; **18**, 9[b]
Isophorone oxide	15	K10	22	**19**, 36; **20**, 10
	16	TCNE	24	**19**, 30; **20**, 10
25	17	K10	24	**21**, 20;[b] **22**, 60
26	18	K10	24	**23**, 19; **24**, 58[b]

[a]Volatile compound that was simply characterized.
[b]Stereochemistry not attributed.

hydroxycompound **19** is obtained as the major regioisomer. This latter regioselectivity applied to the terpene-like compound **25** shown in entry 17. The addition of nitroethanol was accompanied with opening of the oxirane, followed by dehydration and conjugation to enone **22** (epi pulegonacetone).



Scheme 4.

In entry 18, the addition to **26** is accompanied by hydrolysis of the oxirane, leading to olefine **22** after dehydration of the tertiary alcohol.

CONCLUSION

The nitroethanol monoethers of some vic-diols are of some biological interest, and they can be synthesized by ring opening of epoxides. If needed, the reaction can be done with acceptable yields under basic conditions using a DOWEX resin. $CeCl_3$ and $BiCl_3$ were among the few Lewis acids to reasonably afford the expected ethers. Most satisfactory results were obtained using either montmorillonite K or TCNE as the catalyst. The experimental procedure is simple, and the reaction proved highly regioselective, mostly giving addition onto the most substituted carbon of the epoxide.

EXPERIMENTAL

Typical Procedure for the Alcoholysis of Epoxides

The catalyst (montmorillonite or TCNE) is added to a solution of the epoxide in nitroethanol (3 equiv.) under Ar. The mixture is magnetically stirred at room temperature until the epoxide has vanished. After dilution with CH_2Cl_2, the medium is neutralized by addition of solid $NaHCO_3$. The solution is filtered off and concentrated under vacuum to afford a crude product from which isomers are further purified by column chromatography over silica gel.

Diols **1**, **4**, **6**, and **8** are identical to the commercially available compounds.

Data

Dioxane **2:** ^{1}H NMR (300 MHz, $CDCl_3$): 5.80 (1H, ddt, $J = 17.2, 10.3, 6.6$); 5.08 (1H, dd, $J = 17.2, 1.6$); 5.02 (1H, dd, $J = 10.2, 1.6$); 4.42 (1H, dd, $J = 8.0, 7.5$); 4.40 (1H, d, $J = 7.2$); 4.34 (1H, m); 2.70 (OH, bs); 2.25 (2H, m); 1.60 (2H, m). ^{13}C NMR (50.3, $CDCl_3$): 137.6; 116.6; 81.1; 68.68; 33.3; 29.9. Anal. calcd. for $C_{12}H_{20}O_2$ (%): C, 73.43; H, 10.27. Found: C, 73.36; H, 10.37.

β-Hydroxy nitroethanol ether **3:** ^{1}H NMR (300 MHz, $CDCl_3$): 7.45–7.25 (5H, m); 4.55 (2H, m); 4.49 (1H, dd, $J = 8.5, 3.6$); 3.94 (2H, m); 3.72 (1H, dd, $J = 12.0, 8.3$); 3.62 (1H, dd, $J = 12.0, 3.8$); 2.30 (OH, bs). ^{13}C NMR (50.3, $CDCl_3$): 137.9; 129.3; 129.1; 127.4; 84.2; 75.8; 67.4; 65.0. Anal. calcd. for $C_{10}H_{13}NO_4$ (%): C, 50.87; H, 6.20; N, 6.63. Found: C, 50.79; H, 6.30, N, 6.58.

β-Hydroxy nitroethanol ether **5:** ^{1}H NMR (300 MHz, $CDCl_3$): 7.30 (2H, m); 7.00 (1H, m); 6.92 (2H, m); 4.56 (2H, m); 4.14 (1H, m); 4.08 (2H, AB, $J = 5.4$); 4.03 (2H, dd, $J = 6.6$); 3.74 (1H, dd, $J = 10.0, 4.5$); 3.68 (1H, dd, $J = 10.0, 5.2$); 2.60 (OH, bs). ^{13}C NMR (50.3, $CDCl_3$): 158.8; 129.9; 121.6; 114.9; 75.3; 72.6; 69.4; 68.9; 67.0. Anal. calcd. for $C_6H_{13}NO_4$ (%): C, 44.17; H, 8.03; N, 8.58. Found: C, 44.01; H, 8.13, N, 8.52.

β-Hydroxy nitroethanol ether **15:** ^{1}H NMR (300 MHz, $CDCl_3$): 5.80 (1H, m); 5.01 (1H, d, $J = 18.7$); 4.96 (1H, d, $J = 10.2$); 4.12 (2H, m); 3.65 (1H, dd, $J = 11.0, 2.5$); 3.50 (1H, dd, $J = 11.0, 6.3$); 3.43 (1H, m); 2.51 (OH, bs); 2.06 (2H, m); 1.61 (2H, m). ^{13}C NMR (50.3, $CDCl_3$): 138.5; 115.9; 81.03; 76.0; 65.8; 65.1; 30.5; 30.0. Anal. calcd. for $C_8H_{15}NO_4$ (%): C, 50.78; H, 7.99; N, 7.40. Found: C, 50.71; H, 8.09; N, 7.43.

β-Hydroxy nitroethanol ether **16:** ^{1}H NMR (300 MHz, $CDCl_3$): 5.76 (1H, m); 5.01 (1H, d, $J = 18.7$); 4.94 (1H, d, $J = 10.2$); 4.50 (2H, m); 4.07 (1H, m); 3.67 (1H, dd, $J = 11.0, 2.5$); 3.60 (1H, dd, $J = 11.0, 6.3$); 2.51 (OH, bs); 2.11 (2H, m); 1.51 (2H, m). ^{13}C NMR (50.3, $CDCl_3$): 138.4; 115.4; 76.0; 70.0; 67.0; 59.0; 32.4; 30.0. Anal. calcd. for $C_8H_{15}NO_4$ (%): C, 50.78; H, 7.99; N, 7.40. Found: C, 50.74; H, 8.03; N, 7.38.

β-Hydroxy nitroethanol ether **7:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.56 (2H, m); 4.16 (1H, ddd, $J = 10.0, 7.0, 3.0$); 3.98 (1H, ddd, $J = 10.0, 6.6, 3.5$); 3.41 (1H, m); 3.11 (1H, m); 2.70 (OH, bs); 2.01 (4H, m); 1.68 (4H, m). ^{13}C NMR (50.3, $CDCl_3$): 85.2; 76.2; 74.3; 65.2; 32.9; 29.8; 24.8; 24.5. Anal. calcd. for $C_8H_{15}NO_4$ (%): C, 50.78; H, 7.99; N, 7.40. Found: C, 50.75; H, 8.03; N, 7.41.

β-Hydroxy nitroethanol ether **9:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.69 (2H, bs); 4.49 (2H, m, $J = 5.1$); 3.88 (2H, dd, $J = 5.3$); 3.64 (1H, bs); 2.23 (1H, m, $J = 11.7$); 1.83 (2H, m, $J = 13.0, 2.7$); 1.69 (3H, s); 1.7–1.21 (5H, m); 1.19 (3H, s). ^{13}C NMR (50.3, $CDCl_3$): 150.2; 109.7; 76.7; 76.5; 72.8; 57.8; 38.0; 34.4; 29.9; 26.5; 21.4; 21.3. Anal. calcd. for $C_{12}H_{21}NO_4$ (%): C, 59.24; H, 8.70; N, 5.76. Found: C, 59.17; H, 8.74, N, 5.72.

β-Hydroxy nitroethanol ether **17:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.71 (2H, bs); 4.55 (2H, m, $J = 5.1$); 4.10–3.90 (2H, m); 3.21 (1H, bs); 2.25 (1H, m); 2.0–1.0 (6H, m); 1.74 (3H, s); 1.17 (3H, s). ^{13}C NMR (50.3, $CDCl_3$): 149.1; 109.3; 82.9; 76.2; 71.1; 57.8; 37.8; 35.3; 28.4; 26.4; 21.7; 15.5. Anal. calcd. for $C_{12}H_{21}NO_4$ (%): C, 59.24; H, 8.70; N, 5.76. Found: C, 59.15; H, 8.76, N, 5.71.

β-Hydroxy nitroethanol ether **18:** ^{13}C NMR (50.3, $CDCl_3$): stereomers, selected signals: 148.7; 109.5; 79.6.

β-hydroxy nitroethanol ethers **12:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.50 (2H, m); 3.95 (2H, m); 3.40 (4H, m); 1.14 (3H, m).

β-Hydroxy nitroethanol ether **13:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.56 (2H, m); 4.18 (1H, m); 4.05 (1H, m); 3.70 (2H, m); 3.50 (OH); 3.30 (1H, m); 1.50

(2H, m); 0.95 (3H, m). ^{13}C NMR (50.3, $CDCl_3$): 81.0; 77.6; 66.9; 64.7; 19.9; 15.9. Anal. calcd. for $C_6H_{13}NO_4$ (%): C, 44.17; H, 8.03; N, 8.58. Found: C, 44.10; H, 8.09, N, 8.56.

β-Hydroxy nitroethanol ether **14:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.53 (2H, m); 4.13 (2H, m); 3.50 (6H, m); 1.50 (2H, m); 0.95 (3H, m). ^{13}C NMR (50.3, $CDCl_3$): 76.9; 75.8; 66.8; 65.8; 19.8; 18.8. Anal. calcd. for $C_6H_{13}NO_4$ (%): C, 44.17; H, 8.03; N, 8.58. Found: C, 44.11; H, 8.08, N, 8.56.

Diol **10:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.73 (2H, bs); 3.63 (1H, dd, $J = 3.5$, 3.3); 2.26 (1H, m); 1.93 (1H, ddd, $J = 14.0$, 11.7, 2.8); 1.79–1.49 (7H, m); 1.73 (3H, s); 1.27 (3H, s). ^{13}C NMR (50.3, $CDCl_3$): 149.7; 109.3; 74.3; 71.6; 37.8; 34.4; 34.0; 28.1; 26.6; 21.4. Anal. calcd. for $C_{10}H_{18}O_2$ (%): C, 70.55; H, 10.66. Found: C, 70.45; H, 10.71.

β-Hydroxy nitroethanol ether **19:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.54 (1H, ddd, $J = 13.4$, 6.0, 4.1); 4.47 (1H, ddd, $J = 13.4$, 6.0, 4.2); 4.23 (1H, s), 3.6 (OH); 2.35 (1H, d, $J = 13.3$); 2.25 (1H, dd, $J = 13.3$, 2.3); 1.95 (1H, d, $J = 14.4$); 1.80 (1H, dd, $J = 14.3$, 2.3); 1.14 (3H, s); 1.12 (3H, s); 0.93 (3H, s). ^{13}C NMR (50.3, C_6D_6): 208.8; 81.6; 81.5; 75.8; 59.3; 50.7; 49.0; 33.2; 32.9; 27.4; 18.3. Anal. calcd. for $C_{11}H_{19}NO_5$ (%): C, 53.87; H, 7.81; N, 5.71. Found: C, 53.84; H, 7.83; N, 5.68.

β-Hydroxy nitroethanol ether **20:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.53 (2H, m); 4.13 (2H, m); 4.02 (1H, s); 3.40 (OH); 2.32 (1H, d, $J = 8.0$); 2.26 (1H, d, $J = 9.0$); 1.85 (1H, d, $J = 15.2$); 1.70 (1H, d, $J = 15.2$); 1.42 (3H, s); 1.06 (3H, s); 0.99 (3H, s). ^{13}C NMR (50.3, $CDCl_3$): 209.3; 82.9; 82.1; 76.3; 60.8; 52.6; 36.7; 34.4; 28.4; 22.9. Anal. calcd. for $C_{11}H_{19}NO_5$ (%): C, 53.87; H, 7.81; N, 5.71. Found: C, 53.81; H, 7.86, N, 5.67.

β-Hydroxy nitroethanol ether **21** (mixture of diastereomers): ^{1}H NMR (300 MHz, $CDCl_3$) (selected signals): 4.6 (2H, m); 4.25 (2H, m); 4.0 (1H, s); 3.4 (OH); 2.25 (1H, d, $J = 14$); 2.45 (H, d, $J = 13$); 2.34 (H, d, $J = 14$); 2.19 (1H, d, $J = 13$); 1.02 (3H, s); 0.94 (3H, d, $J = 13$); 0.91 (3H, s). ^{13}C NMR (50.3, $CDCl_3$): 210.2 (211.4); 86.5 (81.7); 76.7 (76.4); 76.6 (75.8); 61.6 (59.9); 50.3 (49.6); 50.0 (44.2); 46.4 (39.8); 39.5 (35.1); 31.9 (31.5); 30.0 (31.2); 27.4 (28.2); 26.6 (26.9); 22.8 (25.5); 20.6 (18.0). Anal. calcd. for $C_{15}H_{25}NO_5$ (%): C, 60.18; H, 8.42; N, 4.68. Found: C, 60.14; H, 8.46, N, 4.65.

Enone **22:** ^{1}H NMR (300 MHz, $CDCl_3$): 5.9 (1H, d, $J = 5.7$); 2.3 (1H, m); 2.2 (1H, m); 1.8 (1H, dd, $J = 12.4$, 3.2); 1.7 (1H, m); 1.6 (2H, m); 1.52 (1H, dd, $J = 12.4$, 3.2); 1.4 (1H, m); 1.2 (2H, m); 1.14 (3H, s); 1.04 (3H, s); 0.97 (3H, d, $J = 6.7$). ^{13}C NMR (50.3, $CDCl_3$): 198.0; 145.0; 130.2; 48.9; 45.2; 35.5; 35.4; 35.0; 32.8; 29.6; 27.4; 23.2; 22.3. Anal. calcd. for $C_{13}H_{20}O$ (%): C, 81.20; H, 10.48. Found: C, 81.23; H, 10.52.

β-Hydroxy nitroethanol ether **23:** ^{1}H NMR (300 MHz, $CDCl_3$): 5.22 (1H, ddd, $J = 12.6$, 4.3, 2.8); 4.0 (1H, m); 3.99 (OH); 3.99 (1H, m); 3.96 (1H, m); 2.12

(1H, m); 2.06 (3H, s); 1.99–1.10 (7H, m); 1.17 (3H, s); 0.91 (3H, s); 0.87 (3H, d, $J = 6.4$). ^{13}C NMR (50.3, $CDCl_3$): 170.6; 80.6; 76.2; 74.0; 71.8; 57.1; 47.9; 44.7; 35.0; 34.7; 34.1; 31.6; 31.1; 29.6; 26.6; 23.3; 21.6. Anal. calcd. for $C_{17}H_{29}NO_6$ (%): C, 59.46; H, 8.51; N, 4.08. Found: C, 59.41; H, 8.54; N, 4.05.

Alcohol **24:** ^{1}H NMR (300 MHz, $CDCl_3$): 5.68 (1H, bs); 5.02 (1H, ddd, $J = 12.3$, 4.7, 2.4); 3.86 (1H, bs); 2.47 (1H, m); 2.14 (1H, m); 2.04 (3H, s); 1.97 (1H, m); 1.77–0.90 (6H, m); 1.10 (3H, s); 1.08 (3H, s); 0.88 (3H, d, $J = 6.6$). ^{13}C NMR (50.3, $CDCl_3$): 170.7; 139.7; 121.8; 74.1; 73.0; 39.4; 36.5; 35.2; 34.8; 33.4; 29.1; 27.8; 26.1; 21.6; 20.8. Anal. calcd. for $C_{15}H_{24}O_3$ (%): C, 71.39; H, 9.59. Found: C, 71.62; H, 9.62.

Diol **11:** ^{1}H NMR (300 MHz, $CDCl_3$): 4.27 (2H, m); 3.59 (2H, m); 3.33 (OH); 1.99 (4H, m); 1.65 (4H, m); 1.20 (8H, m). ^{13}C NMR (50.3, $CDCl_3$): 86.7; 72.0; 32.3; 30.8; 23.9; 23.2. Anal. calcd. for $C_{12}H_{22}O_3$ (%): C, 67.26; H, 10.35. Found: C, 67.23; H, 10.36.

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