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LETTER ARTICLE

Cu-Fe Spinels: First Heterogeneous and Magnetically Recoverable Catalyst for the Ferrier Rearrangement of 2-Nitroglycals

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Abstract: Cu-Fe spinels promoted the Ferrier rearrangement of 2-nitroglycals with several *O*-nucleophiles. 2,3-Unsaturated carbohydrate derivatives were prepared by the reaction of 3,4,6-tri-*O*-acetyl-2-nitroglucal and alcohols in the presence of 5 % of $CuFe_2O_4$. After separation of the catalyst with an external magnet, the reaction products were obtained in good yields and high stereo and regioselectivity. Also, S- and heterocyclic C-3 substituted 2-nitro-*endo*-glycals could be prepared by this method.

Keywords: 2-Nitroglycals, Cu-Fe spinels, Ferrier rearrangement, magnetically recoverable catalyst, unsaturated heterocycle, carbohydrate.

1. INTRODUCTION

2-Nitroolefins derived from carbohydrates (2-nitroglycals) have emerged as important building blocks in the recent past years [1]. The combination of a conjugated nitroolefin and an enol ether moiety provides a wide range of capabilities for structural transformations by well-known synthetic methods [2-4]. Moreover, the nitro substituent can be converted into other useful substructures or removed [5]. This reactivity profile converts 2-nitroglycals into very useful substrates for the synthesis of biologically relevant 2-deoxy-2-amino substituted glycosides [6] such as D-lividosamine [7], a component of several antibiotics and antigens [8].

Magnetic separation is an attractive alternative to filtration or centrifugation as it prevents loss of catalyst and enhances reusability, ideal qualities for "green chemistry" applications [9]. Copper-iron spinels have been recognized in the last years as a useful catalyst in organic synthesis [10]. As part of our ongoing efforts in the development of environmentally friendly catalytic methods for the synthesis of biologically active carbohydrates derivatives [11], we decided to investigate the reactivity of 2-nitroglycals with *O*- and *S*-nucleophiles and copper/iron oxide spinels as a heterogeneous catalyst.

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In the last decade, 2-nitroglycals and their reactivity have emerged as a key theme in the synthesis of 2-*N*-glycosides. Promising results were achieved, nevertheless, the reactions of acetylated 2-nitroglycals were poorly investigated. Several reaction pathways may be involved when nucleophiles react with the nitroacetate derivatives in the presence of a base catalyst. Michael type addition or Ferrier rearrangement at C-1 or the less common C-3 addition may occur. The Ferrier rearrangement of acetylated 2-nitroglycals was reported recently for the first time [12].

2. RESULTS AND DISCUSSION

Initially, to investigate the catalyst effect, a model reaction was conducted at room temperature, and a series of different base promoters was tested. First, we attempted the reaction of 1,2-dideoxy-2-nitro-D-*arabino*-hex-1-enopyranose 3,4,6-triacetate (**1**) and methanol using Et_3N as a base, expecting that methanol might add to the nitroglycal **1** in a Michael addition fashion. Unfortunately, as happened with tBuOK, the reaction was slow and after certain time, we observed the partial deprotection of the sugar **1**. Next, we examined two organocatalysts 4-dimethylamino pyridine (DMAP) and 4-pyrrolodinopyridine (PPY). In full agreement with previously published results [12] both catalysts promote Michael type addition when the nitrosugar **2** was protected with benzyl groups and the Ferrier rearrangement when acetyl moieties were present, as in **1** (Table **1**).

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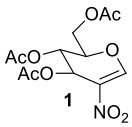
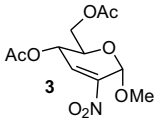
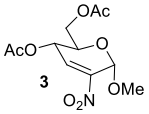
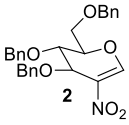
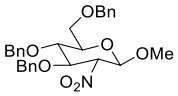
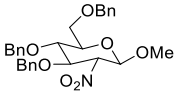
Table 1. Reactions of 2-nitroglycals 1 and 2 with MeOH and different base catalysts[a].

Entry	Glycal	Cat.	Product	Yield (%)[b]
1		Et_3N	---[c]	<20[c]
2	-	tBuOK	---[c]	<15[c]
3		DMAP		65
4		PPY		61
5		DMAP		82
6	-	PPY		81

[a]Reagents and conditions: 2-nitroglycal (1 eq), methanol (1.2 eq), and catalyst (10 mol %) CH_2Cl_2, rt, under Ar atmosphere.

[b]Yields calculated after purification by column chromatography.

[c]A complex mixture of products were obtained as seen by thin layer chromatography (TLC) analysis, including the desired product and more polar glycosides. The yields declared for entries 1 and 2 represent an estimation after NMR analysis.

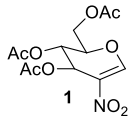
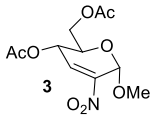
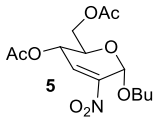
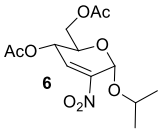
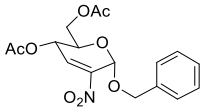
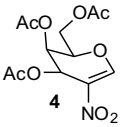
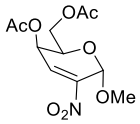
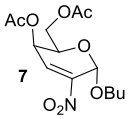
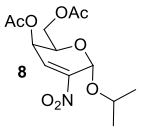
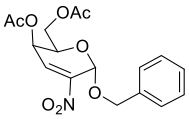
Table 2. Model reaction, 3,4,6-tri-*O*-acetyl-2-nitroglucal 1 with 1.2 eq of MeOH, using different solvents and catalysts amounts.

Entry	Catalyst	Solvent	Catalyst (%)	Yield (%)
1	DMAP	CH_2Cl_2	10	65
2	$CuFe_2O_4$	CH_2Cl_2	5	70
3	$CuFe_2O_4$	CH_2Cl_2	10	59
4	$CuFe_2O_4$	CH_2Cl_2	20	30
5	$CuFe_2O_4$	toluene	5	52
6	$CuFe_2O_4$	CH_3CN	5	45

Unfortunately, DMAP and its derivatives exhibit acute dermal toxicity [13] and their use is discouraged in terms of green chemistry protocols. Because of their unique properties, magnetic particles have emerged as a useful group of heterogeneous catalysts, hence we have investigated the possible use of Cu-Fe spinels as a catalyst. These catalysts were recently reported as Michael addition reaction promoters [14]. To the best of our knowledge, this is the first report that applies the novel and efficient magnetic catalysis methods in the transformations of 2-nitroglycals.

Surprisingly the reaction within 3,4,6-tri-*O*-acetyl-2-nitroglucal **1**, methanol and $CuFe_2O_4$ produces, with good yields, the corresponding 2,3-unsaturated glycoside **3**. The results presented in Table **2** show the optimum reaction conditions. The use of 5 mol % of catalyst leads selectively to Ferrier product **3**, ^1H and ^{13}C NMR spectra of the crude mixture, as well as TLC analysis, indicates the complete absence of the direct addition or other secondary products.

Table 3. Reactions of 2-nitroglycals 1 and 4 with several nucleophiles promoted by $CuFe_2O_4$[a].

Entry	Glycal	Alcohol	Product	Yield (%)[b]
1		MeOH		70
2	-	nBuOH		75
3	-	iPrOH		64
4		BnOH		60
5		MeOH		77
6	-	nBuOH		73
7	-	iPrOH		65
8		BnOH		60

[a]Reagents and conditions: 2-nitroglycal (1 eq), alcohol (1.2 eq), $CuFe_2O_4$ (5 mol %), CH_2Cl_2, rt, under Ar atmosphere.

[b]Yields calculated after purification by column chromatography.

The scope of the reaction was explored using a series of alcohols as nucleophiles: the results, including reaction conditions and yields, are depicted in Table **3**.

It is well known that in some cases, the orientation and protective groups on the hydroxyl moieties drastically affect the selectivity of the reaction [15]. To investigate this topic, we used the same reaction conditions, alcohols and D-galactose derivative **4** as substrate. As seen in Table **3**, entries 5-8, the results obtained were similar when the C-4 OAc changes spatial orientation. After purification by column chromatography, we determined the structure of the products by gCOSY, gHSQC, ^1H and ^{13}C NMR spectra. To the best of our knowledge, products **5**-**8** are first described in this paper. In all cases presented, the α anomeric selectivity was determined and unambiguously assigned as expected and in full accordance with published results [16].

Heterogeneous catalysis offers interesting methodology advantages [17]. Separation and reutilization of the catalyst represent their major benefits. After the reaction was completed, the spinels were placed at the bottom of the flask by an external magnet. The reaction mixture was taken, and the separated catalyst was washed successively two times with

dichloromethane and then dried under high vacuum. In a typical recycling procedure, more than 85 % of spinels could be recovered. No significant loss of the initial catalytic activity was observed up to three cycles (Table **4**).

Table 4. Recyclability of Cu-Fe spinels.

Cycle	Catalyst Recovery	Yield (%)
Native	89	90
2	87	85
3	86	83

The native and used spinels were analyzed by powder XRD, SEM-EDAX and IR. It was observed that the catalyst remains intact after the reaction process (Fig. **1**).

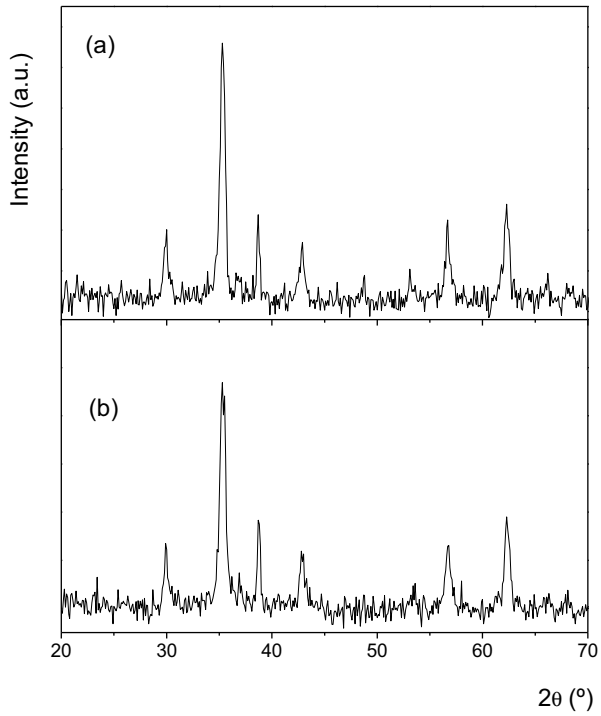


Fig. (1). X-ray diffraction patterns of $CuFe_2O_4$ catalyst before (a) and after (b) the reaction of 2-nitroglucal **1** with MeOH.

As represented in Scheme **1** different reaction pathways take place when S-nucleophiles are used. 3,4,6-Tri-*O*-acetyl-2-nitroglucal **1** was dissolved in dried CH_2Cl_2 and 1.5 eq of thiophenol and $CuFe_2O_4$ (5 mol %) were added. The mixture was stirred at room temperature until the reaction was completed as indicated by TLC. After purification, performed by flash column chromatography, and spectral analysis (^{1}H and ^{13}C NMR, gCOSY and gHSQC) we noticed that thiophenol was added to the C-3 position to give [(*R,R,R*)-3-acetoxy-3,4-dihydro-5-nitro-4-(phenylthio)-2*H*-pyran-2-yl]methyl acetate (**9**) in 72 % yield. Even by changing the reaction conditions including solvent, molar relations and amount of catalyst, the regioselectivity of the reaction was maintained.

In accordance with previous results reported and the Pearson´s HSAB (Hard Soft Acid Base) concept, the regioselectivity of the reaction was explained [18]. Contrary to the results obtained with oxygen nucleophiles, thiophenol, a soft base, prefers the soft acid C-3 site.

Finally, we studied the selectivity towards *N*-heterocyclic nucleophiles. An interesting result was achieved when imidazole was used as a nucleophile. Following the methodology previously described, a 2-nitro-3-imidazole carbohydrate derivative **10** was obtained in a regio- and stereoselective manner in enantiopure form with 42 % yield (Scheme **2**).

The complete analysis by ^{1}H, ^{13}C NMR and gHSQC, gCOSY and NOESY experiments confirms the selectivity of the product formed. This novel *endo*-glycal derivative **10** presents an interesting capability of transformation through the double bond and nitro moieties besides the biologically relevant presence of the heterocycle at C-3. Further work expanding on the scope of the substrates and suitability of the protocol to prepare C-3 nucleosides is underway in our laboratory.

3. EXPERIMENTAL SECTION

TLC was performed on Merck 60 F254 plates. Reactions were monitored by TLC on silica gel, with detection by UV light (254 nm) or by charring with sulfuric acid. Flash chromatography was performed using silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVIII (600 and 150 MHz, respectively) in $CDCl_3$. HSQC and COSY spectra were used to establish peak assignments in ^{1}H and ^{13}C NMR. All reactions sensitive to moisture were carried out under an argon atmosphere using oven-dried glassware.

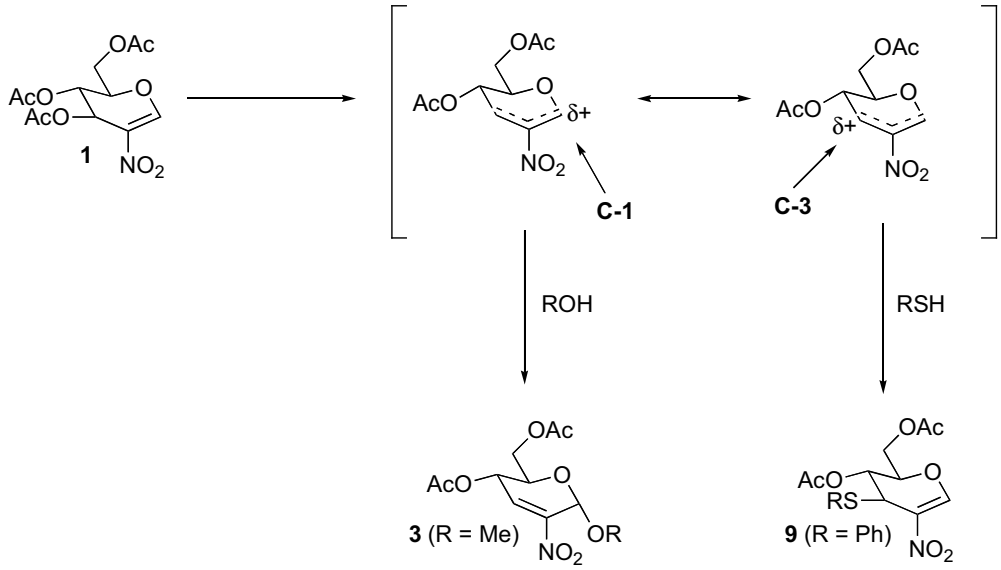
3.1. $CuFe_2O_4$ Catalyst Preparation and Characterization

$CuFe_2O_4$ catalyst was prepared by a co-precipitation method at reduced temperatures. A known amount of $Cu(NO_3)_2.3H_2O$ and 2 eq of $Fe(NO_3)_3.9H_2O$ were dissolved in distilled water, then added into 4 M NaOH solution followed by heating at 90 °C for 2 h, then filtered, washed with water and dried at 80 °C overnight. The solid product was ground and heated in a furnace at 700 °C.

The samples were fully characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) [11]. XRD patterns were performed on a Philips PW 1732/10 equipment by using Cu Ka radiation (k = 1.5404 Å). The FTIR spectra were measured using a Magna 550 Nicolet instrument equipped with CsI optics using the KBr pellets technique.

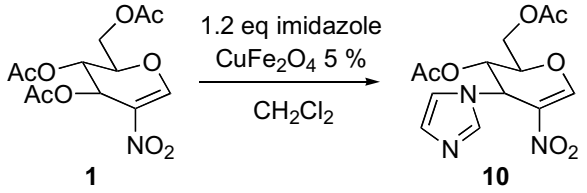
3.2. General Procedure for the Synthesis of 2-Nitroglycals

A solution in dry CH_2Cl_2 (5 mL) was prepared with 0.2 mmol of the glycal and 1.2 eq of tetrabutylammonium nitrate salt under Ar atmosphere. The mixture was cooled at 0°C and 1.2 eq of trifluoroacetic anhydride was added dropwise. The reaction mixture was then stirred for 2 h at room temperature. The reaction vessel was again cooled to 0°C and 1 eq of Et_3N was added dropwise with a syringe during 10 min. The reaction was completed after 1 h, then 5 mL of cold



Scheme (1). Reaction of 2-nitroglycal **1** with *S*- and *O*-nucleophiles.

water was added. The aqueous phase was extracted with 3 x 10 mL of CH_2Cl_2. The combined organic extracts were washed twice with 10 mL of water and then dried and concentrated in vacuo. The product was purified by flash column chromatography with highly compacted silica to obtain the pure 2-nitroglycal as a viscous oil. NMR data for 1,2-dideoxy-2-nitro-D-*arabino*-hex-1-enopyranose 3,4,6-triacetate (**1**) was in full accordance with previously reported results: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (s, 1H), 5.79 (m, 1H), 5.20 (t, 1H, J = 2.5 Hz), 4.69–4.77 (m, 1H), 4.36 (dd, 1H, J = 4.8, 11.9 Hz), 4.10 (dd, 1H, J = 8.5, 11.9 Hz), 2.15 (s, 6H), 2.09 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170-169 (3), 155.2, 126.4, 75.2, 64.6, 61.5, 60.5, 21.0, 20.9, 20.8.



Scheme (2). Catalyzed reaction of 2-nitroglycal **1** with imidazole.

3.3. General Procedure for the Ferrier Rearrangement of 2-Nitroglycals

The 2-nitroglycal (100 mg) and 1.2 eq of the alcohol were dissolved in dried CH_2Cl_2 (2 mL) and then $CuFe_2O_4$ (5 mol %) was added. The mixture was stirred at ambient temperature until the reaction was completed as indicated by TLC. An external magnet was used to separate the catalyst from the reaction mixture. The magnetic catalyst was washed twice with 5 mL of CH_2Cl_2 and the combined extracts were evaporated, then, the residue was dried under high vacuum. The purification was performed by flash column chromatography (hexane/EtOAc 8:2).

3.3.1. Methyl 2,3-dideoxy-2-nitro-α-D-erythro-hex-2-enopyranoside 4,6-diacetate (3)

Yield: 70%. Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (d, J = 2.1 Hz, 1H), 5.57−5.30 (m, 2H), 4.30−4.16 (m, 3H), 3.43 (s, 3H), 2.15 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 169.7, 148.2, 132.7, 128.1, 92.5, 65.1, 64.5, 61.9, 57.0, 20.3, 20.1. HRMS calcd for $C_{11}H_{16}NO_8$ $[M + H]^+$ 290.0876, found 290.0879.

3.3.2. Butyl 2,3-dideoxy-2-nitro-α-D-erythro-hex-2-enopyranoside 4,6-diacetate (5)

Yield: 75%. Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, J = 2.1 Hz, 1H), 5.87-5.61 (m, 2H), 4.35-4.21 (m, 3H), 3.81-3.66 (m, 1H), 3.53-3.49 (m, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 1.52-1.40 (m, 2H), 1.33-1.24 (m, 2H), 1.10 (t, J = 4.9Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 170.5, 148.7, 133.1, 131.8, 94.3, 67.1, 65.5, 62.8, 60.1, 30.2, 21.3, 21.0, 19.4, 14.6. HRMS calcd for $C_{14}H_{21}NNaO_8$ $[M + Na]^+$ 354.1165, found 354.1162.

3.3.3. Isopropyl 2,3-dideoxy-2-nitro-α-D-erythro-hex-2-enopyranoside 4,6-diacetate (6)

Yield: 64%. Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, J = 2.0 Hz, 1H), 5.66-5.50 (m, 2H), 4.29-4.18 (m, 3H), 3.87 (seven lines, J = 6.3 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 1.18 (d, J = 6.3 Hz, 3H), 1.11 (d, J = 6.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 169.9, 148.7, 132.2, 127.9, 92.9, 70.1, 66.8, 65.4, 63.2, 23.5, 22.0, 21.0, 20.8. HRMS calcd for $C_{13}H_{19}NNaO_8$ $[M + Na]^+$ 340.1008, found 340.1007.

3.3.4. Butyl 2,3-dideoxy-2-nitro-α-D-threo-hex-2-enopyranoside 4,6-diacetate (7)

Yield: 73%. Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, J = 5.7 Hz, 1H), 5.76-5.35 (m, 2H), 4.42-4.23 (m, 3H), 3.85-3.56 (m, 1H), 3.47-3.29 (m, 1H), 2.12 (s, 3H),

2.09 (s, 3H), 1.50-1.38 (m, 2H), 1.32-1.25 (m, 2H), 1.10 (t, J = 4.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 170.0, 147.2, 134.0, 129.7, 93.3, 67.5, 67.0, 63.2, 60.1, 31.1, 22.0, 21.5, 19.3, 14.1. HRMS calcd for $C_{14}H_{21}NNaO_8$ $[M + Na]^+$ 354.1165, found 354.1164.

3.3.5. Isopropyl 2,3-dideoxy-2-nitro-α-D-threo-hex-2-enopyranoside 4,6-diacetate (8)

Yield: 65%. Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (d, J = 5.6 Hz, 1H), 5.72-5.48 (m, 2H), 4.33-4.21 (m, 3H), 3.79 (seven lines, J = 6.2 Hz, 1H), 2.11 (s, 3H), 2.08 (s, 3H), 1.17 (d, J = 6.2 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 169.0, 148.3, 131.9, 128.5, 92.6, 70.1, 65.6, 64.1, 63.2, 24.5, 22.0, 21.0, 20.9. HRMS calcd for $C_{13}H_{19}NNaO_8$ $[M + Na]^+$ 340.1008, found 340.1005.

3.4. Synthesis of C-3 Substituted 2-Nitro-*endo*-glycals 9 and 10

Tri-*O*-acetyl-2-nitroglucal **1** (100 mg) and 1.2 eq of the thiophenol or imidazole were dissolved in dried CH_2Cl_2 (2 mL) and then $CuFe_2O_4$ (5 mol %) was added. The mixture was stirred at ambient temperature until the reaction was completed as indicated by TLC. An external magnet was used to separate the catalyst from the reaction mixture. The magnetic catalyst was washed twice with 5 mL of CH_2Cl_2 and the combined extracts were evaporated, then, the residue was dried under high vacuum. The purification was performed by flash column chromatography (hexane/EtOAc 9:1).

3.4.1. [(R,R,R)-3-Acetoxy-3,4-dihydro-5-nitro-4-(phenylthio)-2H-pyran-2-yl]methyl acetate (9)

Yield: 72%. Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.65-7.60 (m, 2H), 7.41-7.33 (m, 3H), 5.20 (d, J = 1.3 Hz, 1H), 4.80-4.75 (m, 1H), 4.36 (s, 1H), 4.34-4.25 (m, 2H), 2.09 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 169.2, 152.6, 132.0-129.8, 73.0, 65.8, 62.0, 42.8, 21.0, 20.7. HRMS calcd for $C_{16}H_{18}NO_7S$ $[M + H]^+$ 368.0804, found 368.0804.

3.4.2. [(2R,3S,4R)-3-Acetoxy-5-nitro-4-(1H-imidazol-1-yl)-3,4-dihydro-2H-pyran-2-yl)methyl acetate (10)

Yield: 42%. Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.58 (s, 1H), 7.07-7.05 (m, 2H), 5.10-4.19 (m, 5H), 2.11-2.09 (two s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 169.6, 155.4, 135.9, 129.2, 128.3, 120.2, 72.1, 64.9, 61.0, 55.1, 20.3, 20.1. HRMS calcd for $C_{13}H_{15}N_3NaO_7$ $[M + Na]^+$ 348.0808, found 348.0807.

CONCLUSION

A new and facile method was developed for the synthesis of alkyl 2,3-dideoxy-2-nitro-α-D-*erythro*(or *threo*)-hex-2-enopyranosides 4,6-diacetates. The results obtained are very useful since this kind of carbohydrate derivatives represent an important class of intermediates for the synthesis of several biologically active compounds. Moreover, S- and heterocyclic C-3 substituted 2-nitro-*endo*-glycals could be prepared by this method. Cu-Fe spinels were proven to be excellent catalysts for the nucleophilic addition to 2-nitroglycals due to the yields and selectivity obtained. $CuFe_2O_4$ is easy to prepare and presents some interesting advantages over traditional catalysts: low costs, magnetic separation, reusability, no toxicity and easy manipulation represent its major benefits.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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