Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 2595

www.rsc.org/greenchem

PAPER

Valorization of glycerol 1,2-carbonate as a precursor for the development of new synthons in organic chemistry

Julia Bensemhoun* and Sylvie Condon

Received 3rd May 2012, Accepted 29th June 2012
DOI: 10.1039/c2gc35678c

Conjugate addition reactions are efficiently performed by a very simple electrochemical method using nickel complexes as catalysts. In this paper, we reported a new method for the valorization of glycerol 1,2-carbonate. Firstly, we prepared the activated glycerol 1,2-carbonate derivatives (halogen or pseudo-halide derivatives), and secondly applied these halogen derivatives in coupling reactions by electrochemical methods with organic compounds and environment-friendly solvent (propylene carbonate). To our knowledge, this is the first report of creation of carbon–carbon bonds on the glycerol 1,2-carbonate and of the synthesis of these compounds.

1. Introduction

For several years, the manufacturing of raw materials resulted from chemicals obtained mainly from fossil resources, which are these days in the process of exhaustion. Moreover, these raw materials present a major inconvenience: their very slow biodegradation. Consequently, at the moment, their repercussions on the environment remain an increasing preoccupation. These last years, the use of renewable feedstocks[1,2] has presented a major interest in particular in the chemical industry. Among these renewable resources, the valorization of glycerol, which is the main co-product of the industry of vegetable oils (especially biodiesel) and broadly available at low prices, is a crucial challenge. Therefore, it is not surprising that much effort has been devoted to converting glycerol into high value-added chemicals.[3–5]

Indeed, chemists have become interested more and more in glycerol and in its by-products, which are synthesis intermediates, for the preparation of a large number of compounds *via* oxidation,[6] etherification,[7] esterification, transesterification,[8] polymerisation, *etc*.

In this context, our attention is focused on the development of new processes for the transformation and the valorization of glycerol and more particularly, due to its low toxicity, the ready accessibility[9,10] of glycerol 1,2-carbonate, an inexpensive compound, which has considerable potential for different transformations in fine chemistry, in order to be used as a precursor for the development of new synthons in organic chemistry.[11–14] Indeed, the presence of a cyclic carbonate group along with a primary hydroxylmethyl group implies that the molecule may react with aldehydes, anhydrides, and diamines[10,15] in order to form ester, ether, enol or urethane linkages.[16] Moreover, Rousseau *et al.* have shown the polymorphic reactivity of activated glycerol 1,2-carbonate in the presence of nucleophiles.[14,17] This compound may be also used as a protic solvent, and in cosmetic and pharmaceutical preparations.[18–21]

Modern organic chemistry has a real interest in being more environment-friendly. Within this context, electrochemistry can appear as a useful tool since electrons are cheap, clean and readily available reagents, whose concentration and activity are easily controlled. Significant progress has been made, notably in electroreduction, thus providing simple and efficient methodologies. Consequently, we report in this paper our preliminary results devoted to the creation of carbon–carbon bonds from halogenated or pseudo-halogenated glycerol 1,2-carbonate derivatives and electron deficient olefins based on an electrochemical process developed some years ago in our laboratory.[22,23] Another important point of our work consists of replacing organic solvents by more environment-friendly solvents. To our knowledge, this is the first example of creation of carbon–carbon bonds on the glycerol 1,2-carbonate.

2. Results and discussion

In this work, we focused on the activation of halogen or pseudo-halide derivatives of glycerol 1,2-carbonate mediated by nickel catalysis in conjunction with a consumable anode process, and then on their reaction with electrodeficient olefins. Firstly, we prepared the activated glycerol 1,2-carbonate derivatives (**2–5**) in order to examine their reactivity in electrochemical conjugate addition, and secondly applied these halogen derivatives in coupling reactions (Fig. 1).

2.1. Formation of pseudo-halogen and halogen glycerol 1,2-carbonate

As described in the literature,[24] the primary hydroxyl group of glycerol 1,2-carbonate **1** was activated by tosylation in order to

Equipe Electrochimie et Synthèse Organique, Institut de Chimie et des Matériaux Paris-Est, 2-5 rue Henri Dunant, 94320 Thiais, France. E-mail: julia.bens@gmail.com; Fax: +33 149781148; Tel: +33 149781126

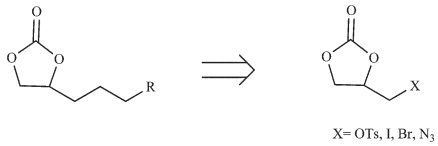


Fig. 1 Creation of carbon–carbon bonds.

obtain compound **2** in 98% yield. Because of its accessibility and versatility, 3-*O*-tosyl glycerol 1,2-carbonate **2** was first prepared as an intermediate to get halides **3**, **4** (I, Br) and azide **5** derivatives (Fig. 2).

The compound **2** reacted with an excess of tetra-*n*-butylammonium bromide or iodide in anhydrous acetone leading to compounds **3** and **4** with 90% yield (Fig. 2). This reaction proved to be the most efficient compared to the use of sodium iodide. Moreover, the excess of tetra-*n*-butylammonium bromide or iodide can be recycled.

Compound **5** (Fig. 2) was prepared as described in the literature but the purification method is different.[17]

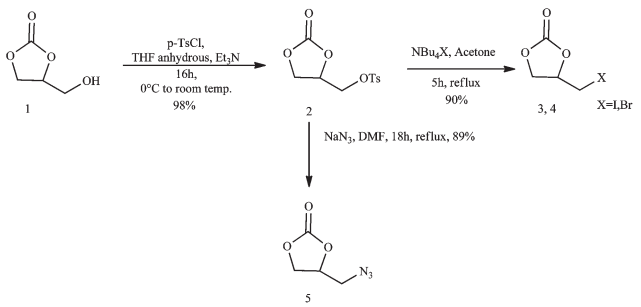


Fig. 2 Formation of tosylated, halides and azide glycerol 1,2-carbonate.

2.2. Creation of carbon–carbon bonds by indirect electrolysis

In the case of indirect electrolysis, where the species reduced at the cathode is a catalytic precursor, we generate the catalyst in solution. The principle is described in Fig. 3.

The reported previous work on the conjugate addition reaction by nickel catalysis associated with the consumable anode process developed in our laboratory is characterized by its simplicity and its high functional compatibility to the reaction. Indeed, in order to create carbon–carbon bonds, our first investigation on this reaction was studied with various aryl halides and electrodeficient or electrodonator groups which are tolerated.[22] It has also been demonstrated that this reaction is regioselective and compatible with the presence of functional groups (CN, CO) (Fig. 4).

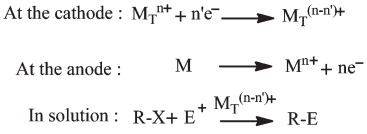


Fig. 3 Principle of the indirect electrolysis reaction.

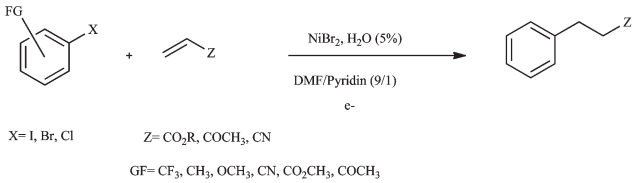


Fig. 4 Creation of carbon–carbon bonds between halogen aryls and activated olefins.

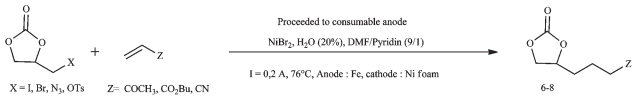


Fig. 5 Creation of carbon–carbon bonds from activated glycerol 1,2-carbonate.

However, to this day, activation of alkyl halides has not been achieved.

The first attempt has been realized between iodide glycerol 1,2-carbonate and various electrodeficient olefins such as methylvinylacetone (MVK), butyl acrylate (ABu) and acrylonitrile (ACN) (Fig. 5).

The conjugate addition reactions were conducted in an undivided cell fitted with an iron rod as the anode and a nickel grid as the cathode, under Ar, in commercial solvents used without purification. The first step of this reaction is the ionic conductivity which is ensured by employing NBu_4Br and NBu_4I as supporting electrolytes. A short pre-electrolysis was conducted at room temperature, leading to an improvement in faradic and chemical yields as well as the oxidation of the iron anode along with the reduction of 1,2-dibromoethane in DMF–pyridine (9 : 1) prior to the electrolysis run at 76 °C under a constant current intensity of 0.2 A, until full consumption of the alkyl halide. The postulated reaction mechanism (Fig. 6) includes (i) the electrochemical reduction of $NiBr_2$ into $Ni^{(0)}$ which is stabilized in the solution by complexation to weak ligands (pyridine) along with the release of iron ions from the anodic oxidation, (ii) the oxidative addition of the alkyl halide to $Ni^{(0)}$, (iii) the insertion of the activated olefin into an R–Ni bond, (iv) iron ions released by the oxidation of the anode may undergo a transmetallation reaction, and this could explain the positive effect of both the use of iron as the anode and the need for the pre-electrolysis to optimize the process.[22]

The first attempt led respectively to compounds **6** (55%), **7** (50%) and **8** (45%) (Fig. 5).

In order to improve these yields, some parameters, such as the temperature, nickel quantity as well as activated olefin amounts, were modified. The best results were obtained using the following parameters: T = 76 °C, $NiBr_2$, H_2O (20%), DMF–pyridine (9 : 1), 2.7 equiv. activated olefins leading to yields of about 75%.

Under these reaction conditions, other derivatives of glycerol 1,2-carbonate bearing an active group were tested on these same electrodeficient olefins (Fig. 5) and the results are reported in Table 1.

Table 1 shows that good results were as well obtained with iodide, bromide or azide. It is worth noting that the

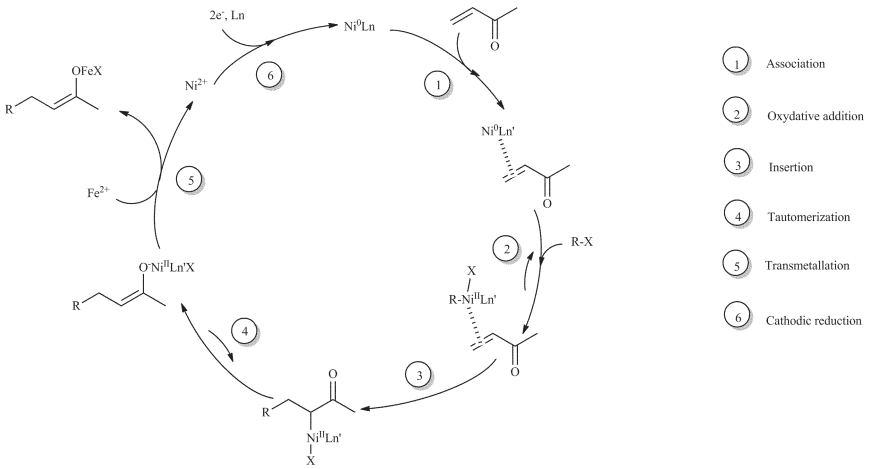
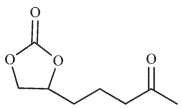
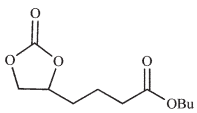
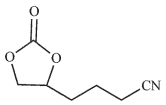


Fig. 6 Mechanism of the conjugate addition reaction by indirect electrolysis.

Table 1 Yields of coupling products **6–8**

Entry	X	Z	Coupling products	Isolated yield (%)
1	I	$COCH_3$		75
2	Br			72
3	N_3			72
4	OTs			68
5	I	CO_2Bu		73
6	Br			70
7	N_3			67
8	OTs			68
9	I	CN		70
10	Br			66
11	N_3			64
12	OTs			66

secondary product is always propylene carbonate (PC) with about 10% yields. Moreover, the excess of olefins can be recycled.

However, one of the main objectives of this work was to save steps in the preparation of the activated product. We wished to bypass the halogenation step and consequently save time, energy and solvents. We realized the same coupling reactions in the optimized reaction conditions with tosylated glycerol 1,2-carbonate (Fig. 5).

Similar results were obtained; we observed and isolated compounds **6–8** with yields of *ca.* 70% (Table 1). These results are particularly interesting and unprecedented to this day because the same reaction realized with the tosylated octanol and the electrodeficient olefins has never led to the conjugate addition product unlike iodooctane which gave 88% of yield (Fig. 7).

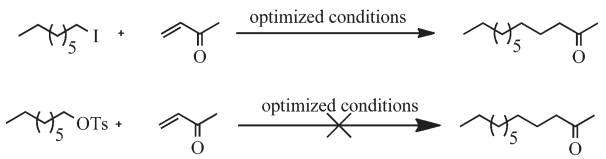


Fig. 7 Reaction from tosylated octanol and iodooctane.

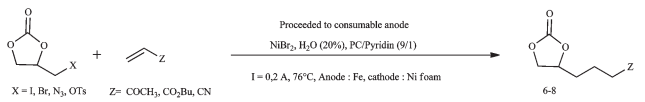
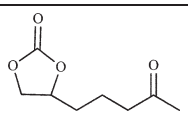
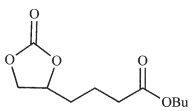
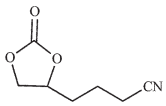


Fig. 8 Creation of carbon–carbon bonds from activated glycerol 1,2-carbonate using PC as a solvent.

Table 2 Yields of coupling products **6–8** with PC

Entry	X	Z	Coupling products	Isolated yield (%)
1	I	$COCH_3$		73
2	Br			74
3	N_3			64
4	OTs			68
5	I	CO_2Bu		66
6	Br			65
7	N_3			64
8	OTs			68
9	I	CN		60
10	Br			60
11	N_3			55
12	OTs			63

Another important point of our work consists of replacing DMF by a more environment-friendly solvent. So, we chose propylene carbonate (PC), which is a derivative of glycerol 1,2-carbonate, as a green solvent, we realized the same reactions in this solvent using the optimized reaction conditions (Fig. 8). Coupling products **6–8** were observed and isolated. Table 2 shows the obtained results.

Table 2 indicates that the PC led to good results. The coupling products were obtained with similar yields. This solvent is a good alternative to the use of DMF.

3. Conclusions

This research has shown that the activation of halogen or pseudo-halide derivatives of glycerol 1,2-carbonate mediated by

nickel catalysis is effective and leads to the creation of new carbon–carbon bonds with electron deficient olefins. One step electrochemical procedures then remain of high interest. Indeed, in organic synthesis, conjugate additions are often used. In the chemical routes, the use of either organocuprate reagents, or organometallic reagents in the presence of copper salt, are the classical methods of regioselective 1,4-addition. These procedures require, as the preliminary step, the preparation of air- and/or moisture-sensitive organometallic reagents (such as organomagnesium). Problems in functional compatibility are encountered when the organometallic reagent is from a precursor bearing sensitive functional groups such as a ketone. Thus, the sacrificial anode-based electroreductive process is a very efficient method which is compatible with the presence of functional groups and more particularly carbonate function, for this one is not modified during the reaction. Moreover, we have also shown that the tosylated glycerol 1,2-carbonate gives good results and the secondary product obtained through these coupling reactions can be used as an environment-friendly solvent. The use of tosylated glycerol 1,2-carbonate is very interesting because this compound is easily obtained in one step. To our knowledge, this is the first report of creation of carbon–carbon bonds on the glycerol 1,2-carbonate and of the synthesis of these compounds.

These coupling reactions have also been tested on the other by-products of glycerol, and more particularly on the solketal, giving good preliminary results with *ca.* 40% yields for each of the conjugate addition products (X = I, Br, N_3, OTs and Z = $COCH_3$, CO_2Bu, CN). We can thus confirm that the coupling reaction by electrochemical methods is compatible with the presence of functional groups. However, this reaction ought to be optimized.

Preliminary tests using the diethylcarbonate, solketal and glycerol 1,2-carbonate as environment-friendly solvents have led to encouraging results. These conjugate addition reactions will be optimized and tested in the other green solvents and realized on other by-products of glycerol.

4. Experimental

4.1. General

All chemicals were purchased from Aldrich, TCI or Acros Organics. Solvents were commercially available and used as received without any further purification. Reactions were monitored by TLC analysis on precoated silica gel plates (Kieselgel 60F254, E. Merck); spots were visualized with UV light and charring after a vanillin solution spray.

The electrochemical reaction was followed by GC until complete conversion of the substrate.

Column chromatography was performed on alumina (neutral, Merck) using mixtures of *n*-heptane and ethyl acetate or deactivated silica gel Si 60 (43–60 mm; Merck) using mixtures of CH_2Cl_2–MeOH or by size exclusion chromatography on Sephadex LH-20 eluting with *n*-heptane–CH_2Cl_2–MeOH (2 : 1 : 1) then CH_2Cl_2–MeOH (1 : 1) and finally 100% MeOH.

^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz (Bruker). Chemical shifts are given in ppm downfield from internal standard TMSCl (δ = 0 ppm). High-resolution mass spectra (HRMS) were performed on a Bruker maXis mass spectrometer by the "Fédération de Recherche" ICOA/CBM (FR2708) platform.

3-*O*-Tosyl glycerol 1,2-carbonate **2** was prepared according to ref. 24; NMR spectra are in agreement with literature data.

4.2. Standard procedure for the synthesis of 3 and 4

A solution of 3-*O*-tosyl glycerol 1,2-carbonate **2** (0.272 g, 1 mmol) and tetra-*n*-butylammonium iodide or bromide (7 equiv.) in anhydrous acetone (5 mL) was heated under reflux for 3 h. The reaction was monitored by GC and stopped after the 3-*O*-tosyl glycerol 1,2-carbonate was consumed. After cooling and evaporating, the mixture was diluted with ethyl acetate and water and the aqueous phase was extracted three times with ethyl acetate. The organic phase was washed with water, brine and dried over $MgSO_4$. After filtration and concentration of the solution *in vacuo*, the residue was purified by column chromatography on Sephadex LH-20 eluting with *n*-heptane–CH_2Cl_2–MeOH (2 : 1 : 1) then CH_2Cl_2–MeOH (1 : 1) and finally 100% MeOH leading to compounds **3** or **4** with 90% yield.

4.2.1. 4-(Iodomethyl)-1,3-dioxolan-2-one.[15,17] Compound **3** was isolated by *n*-heptane–CH_2Cl_2–MeOH (2 : 1 : 1) in 90% yield as a white solid. NMR, MS and IR spectra are in agreement with literature data.

4.2.2. 4-(Bromomethyl)-1,3-dioxolan-2-one. Compound **4** was isolated by *n*-heptane–CH_2Cl_2–MeOH (2 : 1 : 1) in 90% yield as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 4.96 (m, 1H, H-3), 4.59 (t, 1H, J = 8.8 Hz, H-2a), 4.34 (dd, 1H, J = 6.2 Hz, H-2b), 3.58 (m, 2H, $BrCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.27 (CO), 74.10 (C-3), 68.24 (C-2), 31.57 (CH_2Br). IR 1776 (CO).

4.3. Synthesis of 4-(azidomethyl)-1,3-dioxolan-2-one 5[17,25]

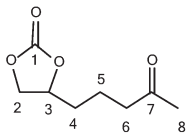
To a solution of tosylated glycerol 1,2-carbonate **2** (0.5 g, 1.836 mmol) in 4 mL of anhydrous DMF, 2 equiv. of NaN_3 was added and the reaction mixture was heated for 18 h at 70 °C. After cooling and evaporating, the mixture was washed with pentane and diluted with dichloromethane and water. The aqueous phase was extracted three times with dichloromethane and the organic phase was washed with water, brine and dried over $MgSO_4$. After filtration and concentration of the solution *in vacuo*, compound **2** was isolated in 89% yield as a colorless oil. NMR spectra are in agreement with literature data.

4.4. Standard procedure for the synthesis of compounds 6–8

Under Ar, in an undivided cell equipped with a nickel grid (area 30 cm^2) as the cathode and an iron rod as the anode, tetrabutylammonium bromide (0.35 mmol) and tetrabutylammonium iodide (0.21 mmol) were dissolved as supporting electrolytes in a mixture of DMF (24 mL) (or environment-friendly solvent) and pyridine (2.5 mL). A short electrolysis was conducted in the presence of 1,2-dibromoethane (0.90 mmol) at constant current density (0.2 A dm^{-2}) and at r.t. within 15 min to generate a small amount of iron ions. Then the current was turned off. $NiBr_2{\cdot}3H_2O$ (0.70 mmol, 153 mg), the activated olefin

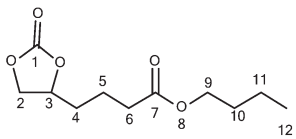
(18.9 mmol) and the activated glycerol 1,2-carbonate (7 mmol) were added. The mixture was then heated at 76 °C. The electrosynthesis was run at constant current density (0.2 A dm^{-2}). The reaction was monitored by GC and stopped after the activated glycerol 1,2-carbonate was consumed. After concentration of the solution *in vacuo*, the crude product was thus subjected to column chromatography to give the purified compounds **6–8**.

4.4.1. Synthesis of compound 6.



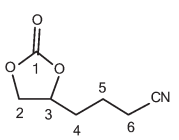
The electrodeficient olefin used for the synthesis of **6** was MVK. The compound **6** was purified by column chromatography on Sephadex LH-20 eluting with *n*-heptane–CH_2Cl_2–MeOH (2 : 1 : 1) and CH_2Cl_2–MeOH (1 : 1) or by deactivated silica gel Si 60 using mixtures of CH_2Cl_2–MeOH. The compound was obtained as a yellow oil on sephadex with *n*-heptane–CH_2Cl_2–MeOH (2 : 1 : 1) and CH_2Cl_2–MeOH (1 : 1) or by deactivated silica gel Si 60 with 30% MeOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.69 (m, 1H, H-3), 4.54 (t, 1H, J = 8.2 Hz, H-2a), 4.09 (dd, 1H, J = 8.4, 7.2 Hz, H-2b), 2.54 (t, 2H, J = 5.3 Hz, H-6), 2.16 (s, 3H, H-8), 1.75 (m, 4H, H-4 and H-5). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.90 (CO-7), 155.01 (CO-1), 76.90 (C-3), 69.40 (C-2), 42.55 (C-6), 33.30 (C-4), 30.14 (C-8), 18.68 (C-5). ESI-HRMS calcd for $C_8H_{12}O_4Na$: 195.1688. Found: 195.06278, IR 1780 (CO).

4.4.2. Synthesis of compound 7.



The electrodeficient olefin used for the synthesis of **7** was ABu. The compound **7** was obtained as a yellow oil by column chromatography on Sephadex LH-20 eluting with *n*-heptane–CH_2Cl_2–MeOH (2 : 1 : 1) and CH_2Cl_2–MeOH (1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (m, 1H, H-3), 4.59 (m, 1H, H-2a), 4.41 (m, 1H, H-2b), 3.75 (t, 2H, J = 7.6 Hz, H-9), 2.31 (m, 2H, H-6), 1.58 (m, 6H, H-4, H-5 and H-10), 1.36 (m, 2H, H-11), 0.92 (t, 3H, J = 7.2 Hz, H-12). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.59 (CO-7), 154.17 (CO-1), 74.39 (C-3), 67.19 (C-2), 64.53 (C-9), 43.76 (C-6), 30.71 (C-4), 29.77 (C-10), 19.18 (C-11 and C-5), 13.80 (C-12). ESI-HRMS calcd for $C_{11}H_{18}O_5Na$: 253.2482. Found: 253.1030, IR 1778 (CO).

4.4.3. Synthesis of compound 8.



The electrodeficient olefin used for the synthesis of **8** was ACN. The compound **8** was purified on an alumina column eluted with *n*-heptane–ethyl acetate mixtures of increasing polarity and obtained as a yellow oil with 30% ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (m, 1H, H-3), 4.58 (t, 1H, J = 8.3 Hz, H-2a), 4.10 (dd, 1H, J = 8.3, 7.2 Hz, H-2b), 2.45 (m, 2H, H-6), 1.91 (m, 4H, H-4 and H-5). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.60 (CO-1), 118.09 (CN), 76.00 (C-3), 69.23 (C-2), 32.98 (C-4), 21.18 (C-5), 17.05 (C-6). ESI-HRMS calcd for $C_7H_9O_3NNa$: 178.1421. Found: 178.0475, IR 2210 (CN), 1776 (CO).

Acknowledgements

We are grateful to the "Fédération de Recherche" ICOA/CBM (FR2708) platform for spectral data measurement and to Dr I. Lachaise for her help.

Notes and references

1 A. Corma, S. Iborra and A. Veity, *Chem. Rev.*, 2007, **107**, 2411.
2 J. H. Clark, V. Budarin, F. E. I. Deswarte, J. J. E. Hardy, F. M. Kerton, A. J. Hunt, R. Luque, D. J. Macquarrie, K. Milkowski, A. Rodriguez, O. Samuel, S. J. Tavener, R. J. White and A. J. Wilson, *Green Chem.*, 2006, **8**, 853.
3 C. H. Zhou, J. N. Beltramini, Y. X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527.
4 R. De Sousa, C. Thurier, C. Len, Y. Pouilloux, J. Barrault and F. Jérôme, *Green Chem.*, 2011, **13**, 1129.
5 A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13.
6 L. Prati, P. Spontoni and A. Gaiassi, *Top. Catal.*, 2009, **52**, 288.
7 A. M. Ruppert, J. D. Meeldijk, B. W. M. Kuipers, B. H. Erné and B. M. Weckhuysen, *Chem.–Eur. J.*, 2008, **14**, 2016.
8 A. Corma, S. B. Abd Hamid, S. Iborra and A. Veity, *J. Catal.*, 2005, **234**, 340.
9 C. Vieville, J. Yoo, S. Pelet and Z. Mouloungui, *Catal. Lett.*, 1998, **56**, 245.
10 H. R. Pfaendler and F. X. Müller, *Synthesis*, 1992, 350.
11 F. R. Pfeiffer, C. K. Miao and J. A. Weisbach, *J. Org. Chem., Commun.*, 1990, **20**, 1631.
12 M. Pallavicini, E. Valoti, L. Villa and O. Piccolo, *J. Org. Chem.*, 1994, **59**, 1751.
13 S. Jegham, A. Nedelec, Ph. Burnier, Y. Guminski, F. Puech, J. J. Koenig and P. George, *Tetrahedron Lett.*, 1998, **39**, 4453.
14 A.-C. Simão, B. Lynikaite-Pukleviciene, C. Rousseau, A. Tatibouët, S. Cassel, A. Sackus, A. P. Rauter and P. Rollin, *Lett. Org. Chem.*, 2006, **3**, 744.
15 A. G. Olivero, J. M. Cassel and J. R. Poulsen, *PCT Int. Appl.*, WO9322451, 1993.
16 H. R. Gillis and D. Stanssens, US 5703136, 1997.
17 J. Rousseau, C. Rousseau, B. Lynikaite, A. Sackus, C. de Leon, P. Rollin and A. Tatibouët, *Tetrahedron*, 2009, **65**, 8571.
18 A. Murase, JP 6222709, 1987.
19 D. Randall and R. De Vos, *Eur. Pat.*, EP 419114, 1991.
20 M. Weuthen and U. Hees, *Ger. Pat.*, DE 4335947, 1995.
21 P. G. Jessop, *Green Chem.*, 2011, **13**, 1391.
22 S. Condon and J. Y. Nédelec, *Synthesis*, 2004, 3070.
23 J. Chaussard, J. C. Folest, J. Y. Nédelec, J. Périchon, S. Sibille and M. Troupel, *Synthesis*, 1990, 369.
24 A. G. Olivero, J. M. Cassel and J. R. Poulsen, *U.S.Pat.*, 5,326,885, 1994.
25 R. M. Hanson, *Chem. Rev.*, 1991, **91**, 437.