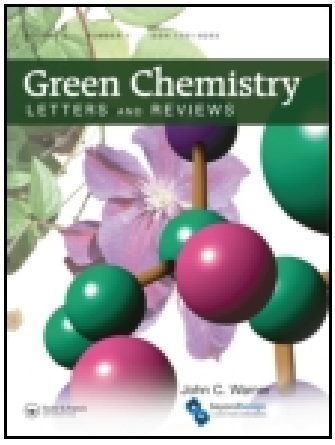

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A new sustainable protocol for the synthesis of nitroaldol derivatives via Henry reaction under solvent-free conditions

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A new sustainable protocol for the synthesis of nitroaldol derivatives via Henry reaction under solvent-free conditions

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A new protocol for the Henry addition of nitroalkanes to aryl- and alkyl-aldehydes promoted by PS-BEMP under solvent-free conditions (SolFC) is presented. The corresponding nitroaldol products were obtained in good yields and short times; furthermore minimization of the reaction waste was achieved by reducing the use of organic solvents. Extension of the protocol was obtained by setting up the tandem Michael-Henry reaction of α,β-unsaturated aldehydes and nitroalkane to yield the corresponding dinitro derivatives.

Keywords: Henry reaction; solvent-free condition; supported catalysis; nitro compounds; base catalysis

1. Introduction

The nitroaldol reaction or Henry reaction is a key transformation for the C-C bond forming that involves ready accessible nitroalkanes and carbonyl compound (*1*). The reaction products, namely nitroaldol compounds, are versatile intermediates to get access to nitroalkanes, 2-aminoalcohols and 2-nitroketones (*1*, *2*). Furthermore, many biologically and pharmacologically active compounds are synthesised via such intermediates (*3*–*8*) .

Usually a nitroaldol reaction is performed in the presence of a base (*1*, *9*–*15*) with the aid of an heterogeneous catalyst (*14*–*19*) or the enzymes (*20*) using an organic solvent. The Henry reaction is often complicated by the formation of undesired side products; therefore, many efforts have been directed to the development of mild reaction conditions to prevent the formation of such by-products (*15*, *21*, *22*).

In the last few years, we have focused our work on the optimization of synthetic procedures by employing eco-friendly reaction protocols based on the use of water (*23*), solvent-free conditions (SolFC) (*24*) and polymer-supported organocatalysts (*25*). The use of SolFC together with polymer-supported organocatalysts has been shown to increase the effectiveness of the catalysts, which are generally but not always (*26*) less efficient than their non-supported counterparts. In particular, we were able to optimise many base-catalysed reactions by employing 2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine supported on polystyrene (PS-BEMP), a very strong uncharged base (in MeCN pKa is 27.63) that has proved to be widely useful in many organic transformations (*25*a, b, d, g, *27*).

2. Results and discussion

As a continuation of our interest in the chemistry of nitro compounds and in the use of solid bases under SolFC, we have investigated the addition of nitroalkanes (2) to a variety of aryl- and alkyl-aldehydes (1) catalysed by PS-BEMP in SolFC. Here, we report our results on the use of PS-BEMP as an efficient and recoverable solid basic catalyst able to promote the reaction of aldehydes (1) with a variety of nitroalkanes (2) under SolFC.

Initially, we have compared the efficiency of PS-BEMP (5 mol%) to that of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine polymer-bound (PS-TBD; 5 mol%) in the reaction of equimolar amounts of benzaldehyde **1a** and nitroethane **2a** under SolFC at 30°C (Table 1). After 15 hours in the presence of 5 mol% of PS-BEMP, the conversion of **1a** was 75% giving exclusively the β-nitroaldol **3aa** (Table 1, entry 1), whereas a mixture of 70% of **3aa** and 16% of **4aa** was obtained when 5 mol% of PS-TBD was used (Table 1, entry 2). To confirm the efficiency and selectivity of PS-BEMP, we have also tested other solid-supported bases which were commercially available and the results are reported in Table 1. Polystyryl-supported 1,8-diazabicyclo[5.4.0]undec-7-ene (PS-DBU) gave only the product **3aa** with low conversion (34%; Table 1, entry 3) while polystyryl-supported 4-dimethylaminopyridine (PS-DMAP) gave a mixture of products **3aa**

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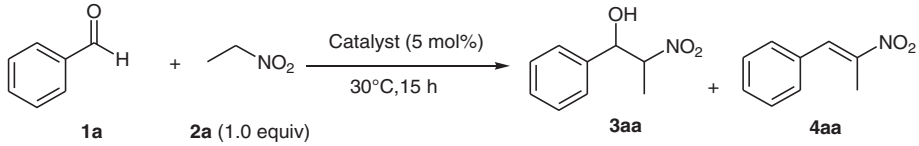
Table 1. PS-BEMP-catalysed Henry addition of nitroethane **2a** to benzaldehyde **1a**.



1a **2a** (1.0 equiv) **3aa** **4aa**

Entry	Catalyst	Solvent (M)	Conversion (%)[a]	
			3aa[b]	**4aa**
1	PS-BEMP	–	75	–
2	PS-TBD	–	70	16
3	PS-DBU	–	34	–
4	PS-DMAP	–	62	3
5	PS-BEMP	CH_2Cl_2 (0.5)	–	–
6	PS-BEMP	CH_3CN (0.5)	–	–
7	PS-BEMP[c]	–	74	–
8	PS-BEMP[d]	–	77	–

Notes: [a]Determined by 1H-NMR;
[b]Diasteroisomeric mixture syn/anti 1/1.6;
[c]Recovered and regenerated PS-BEMP;
[d]2 equiv. of **2a** were used.

and dehydrated **4aa** (Table 1, entry 4). The influence of the reaction medium is dramatic; although we have used the best organic solvents for swelling PS-BEMP (*27*), the results obtained were completely unsatisfactory compared to SolFC. In fact, in the presence of DCM or MeCN, no conversion to **3aa** or **4aa** was observed at all (Table 1, entries 5 and 6). The PS-BEMP was recovered and reused, after regeneration, giving the same conversion of the first run (Table 1, entry 7). By increasing the amount of nitroethane **2a**, no significant enhancement of the conversion of the reaction was observed (Table 1, entry 8).

In order to test the application range of the use of PS-BEMP in the nitroaldol addition of nitroalkanes to aldehydes, other substrates were considered. The results of the reactions of equimolar amounts of arylaldehydes **1a–d** and nitroalkanes **2a–d** are reported in Table 2. The reactions proceeded with 5 mol% of the catalyst and equimolar amounts of reactants under SolFC; benzaldehyde **1a** reacted satisfactorily with nitroethane **2a** and nitromethane **2b**, giving the corresponding products in good yields (Table 2, entries 1 and 2), but with more steric hindered 2-nitropropane **2c** no product was obtained (Table 2, entry 3). Surprisingly, benzaldehyde **1a** reacted satisfactorily with nitroalkane **2d** (Table 2, entry 4). As expected, p-chloro and p-nitrobenzaldehyde **1b** and **1c** reacted with nitroethane **2a** with good yields of the isolate products (Table 2, entries 5 and 6) whereas p-methoxybenzaldehyde **1d** didn't react with **2a** (Table 2, entry 7), according to the electronic properties of their substituents.

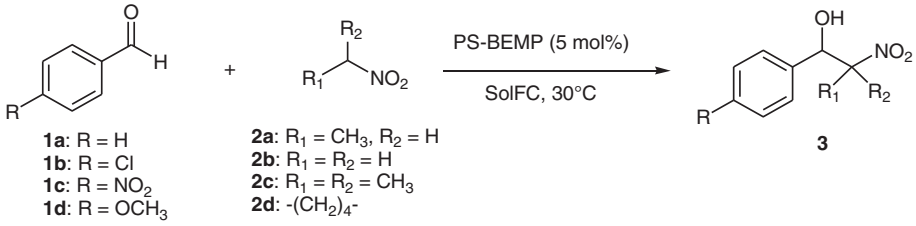
The applicability of this protocol was then tested in the nitroaldol addition of nitroalkanes **2a–d** to aliphatic aldehydes **1e–g**. Under SolFC, at 30°C and in the presence of 5–20 mol% of PS-BEMP, also for the aliphatic aldehydes, the only products detected were nitroaldols (**3**; Table 3), confirming the great selectivity of PS-BEMP as promoter for these reactions. Aliphatic aldehydes **1e–g** reacted efficiently with nitroethane **2a** in the presence of 5 mol% of PS-BEMP and gave the corresponding *β*-nitroaldols in very satisfactory yields (76–92%; Table 3, entries 1, 5 and 9).

Nitromethane **2b** has proven to be poorly reactive and in the reactions with aldehydes **1e** and **1f**, 2 equivalents of **2b** were required to obtain products with good yields (Table 3, entries 2 and 6). In the reactions with aldehydes **1e–g**, sterically demanding nitroalkanes **2c** and **2d** have required a larger amount of PS-BEMP (20 mol%) to give the desired products in moderate to good yields (Table 3, entries 3, 4, 7, 8, 11 and 12).

To prove the efficiency of our approach, we have also decided to perform tandem Michael-Henry reaction of *α*,*β*-unsaturated aldehydes **1h**, **i** to prepare dinitro alcohols **3hc**, **3ic** (Scheme 1) that can be easily converted into the correspondent diamino alcohols (*28–29*). Trans-cinnamaldehyde **1h** and crotonaldehyde **1i** were allowed to react with 2-nitropropane **2c**.

In the presence of 10 mol% of PS-BEMP, trans-cinnamaldehyde **1h** reacted with 2.2 equivalents of 2-nitropropane **2c** to give the desired product **3hc** at 30°C in 15 hours and in 92% yield. Similarly,

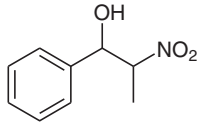
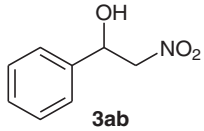
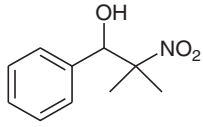
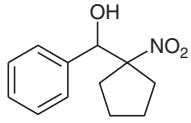
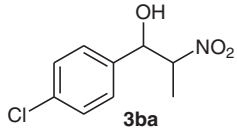
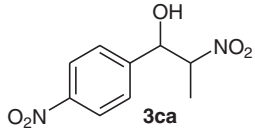
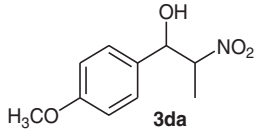
Table 2. PS-BEMP-catalysed Henry addition of nitroalkanes **2a–d** to benzaldehydes **1a–d**.



1a: R = H
1b: R = Cl
1c: R = NO_2
1d: R = OCH_3

2a: $R_1 = CH_3$, $R_2 = H$
2b: $R_1 = R_2 = H$
2c: $R_1 = R_2 = CH_3$
2d: $-(CH_2)_4-$

3

Entry	Aldehyde 1	Nitroalkane 2	t (h)	Product 3	Yield (%)[a]
1	**1a**	**2a**	15	 **3aa**	72[b]
2	**1a**	**2b**	7	 **3ab**	72
3	**1a**	**2c**	16	 **3ac**	–
4	**1a**	**2d**	15	 **3ad**	76
5	**1b**	**2a**	22	 **3ba**	63[c]
6	**1c**	**2a**	16	 **3ca**	75[c]
7	**1d**	**2a**	16	 **3da**	–

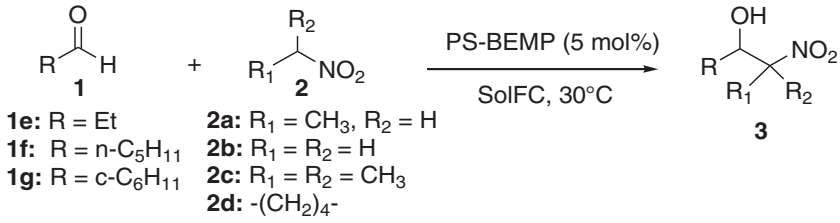
Notes: [a]Isolated yield of the pure product **3**;
[b]Diasteroisomeric mixture *syn*/*anti* 1/1.6;
[c]Diasteroisomeric mixture *syn*/*anti* 1/1.3.

crotonaldehyde **1i** reacted with 2.2 equivalents of nitroalkane **2c** in 15 hours, at 45°C to give the desired product **3ic** in 90% yield. In both cases, the pure products were obtained without any further purification. Variation of R group of the α,β-unsaturated aldehydes and use of different nitroalkanes will allow the efficient synthesis of highly functionalised molecules in a simple way.

3. Conclusion

We have proved that PS-BEMP is an efficient catalyst under SolFC for promoting the Henry addition of nitroalkanes **2** to aryl- and alkyl-aldehydes **1** to selectively yield the corresponding nitroaldol products in good yields and short times. The efficiency of this protocol is strictly related to the use of SolFC that is necessary for the feasibility

Table 3. PS-BEMP-catalysed Henry addition of nitroalkanes **2a–d** to alkyl-aldehydes **1e–g** under SolFC.



1

1e: R = Et
1f: R = n-C_5H_{11}
1g: R = c-C_6H_{11}

2

2a: R_1 = CH_3, R_2 = H
2b: R_1 = R_2 = H
2c: R_1 = R_2 = CH_3
2d: -$(CH_2)_4$-

3

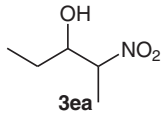
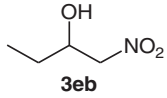
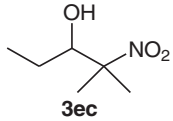
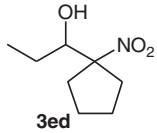
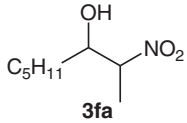
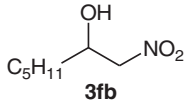
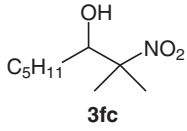
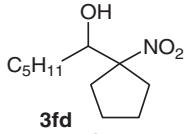
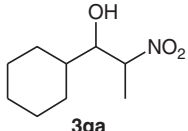
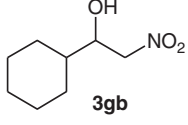
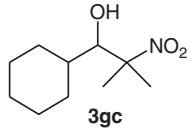
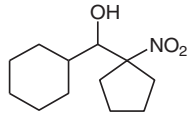
Entry	Aldehyde	Nitroalkane	t (h)	Product 3	Yield (%)[a]
1	**1e**	**2a**	16	 **3ea**	79[b]
2	**1e**	**2b**	16	 **3eb**	78[c]
3	**1e**	**2c**	50	 **3ec**	55[d]
4	**1e**	**2d**	50	 **3ed**	56[d]
5	**1f**	**2a**	3	 **3fa**	92[b]
6	**1f**	**2b**	28	 **3fb**	72[c]
7	**1f**	**2c**	3	 **3fc**	72[d]
8	**1f**	**2d**	3	 **3fd**	73[d]
9	**1g**	**2a**	3	 **3ga**	76[b]
10	**1g**	**2b**	3	 **3gb**	84

Table 3 (*Continued*)

Entry	Aldehyde	Nitroalkane	t (h)	Product 3	Yield (%)[a]
11	**1g**	**2c**	28	 **3gc**	37[d]
12	**1g**	**2d**	24	 **3gd**	80[d]

Notes: [a]Isolated yield of the pure product **3**;
[b]Diasteroisomeric mixture *syn*/*anti* 1/1.17;
[c]2 eq. of **2b** were used;
[d]20 mol% PS-BEMP.

Scheme 1. Polystyrene-supported organic base-catalysed tandem Michael-Henry reaction of 2-nitropropane **2c** and α,β-unsaturated aldehydes **1h–i**.

of the reactions and also allows to minimise the use of organic solvent, thus reducing the reaction waste. Further extension of the protocol was obtained by setting up the tandem Michael-Henry reaction of α,β-unsaturated aldehydes **1h,i** and nitroalkane **2c** in the presence of PS-BEMP as catalyst under SolFC to yield dinitro compounds **3hc** and **3ic** in high yields.

4. Experimental

4.1 General information

GC-EIMS analyses were carried out by using a Hewett-Packard HP 6890 Series GC system/5973 Mass Selective Detector equipped with an electron impact ioniser at 70 eV. All ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100.6 MHz, respectively, using a Bruker DRX-ADVANCE 400 MHz spectromer. $CDCl_3$ was used as deuterated solvent. Chemical shift was reported in ppm and coupling constants in Hertz. All melting points were measured with Buchi Melting Point 510 apparatus and are uncorrected. Elemental analyses were realised by using a FISONS instrument EA 1108 CHN. Column chromatographies were performed by using silica gel 230–400 mesh and eluting as reported in the following characterization charts. Benzaldehyde **1a** was distilled before using. All other chemicals were purchased and used without any further purification. PS-BEMP (200-400 mesh, 2% DVB, 2.2 mmol BEMP/g) was purchased from Aldrich. Compounds **3aa** (*17a*), **3ab** (*30*), **3ba** (*31*), **3ca** (*31*), **3ea** (*32*), **3eb** (*17a*), **3ec** (*33*), **3fb** (*17a*), **3ga** (*15*), **3gb** (*30*), **3gc** (*33*), **3hc** (*29*) and **3ic** (*29*) are known compounds but essential characterization data (^{1}H NMR, ^{13}C NMR and GC-EIMS) were reported in the supplemental material for clarity, whereas products **3ad**, **3ed**, **3fa**, **3fc**, **3fd** and **3gd** are new compounds and therefore were fully characterised (see Supplemental material).

4.2 Representative batch procedure for Henry reaction of aromatic aldehydes 1a–d

In a screw-capped vial equipped with a magnetic stirrer, PS-BEMP (0.044 g, 0.05 mmol, 2.2 mmol/g), benzaldehyde (**1a**; 0.102 mL, 1.0 mmol) and nitroethane (**2a**; 0.072 mL, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 30°C. After 15 hours, dichloromethane (1 mL) was added, the catalyst was recovered by filtration and the solvent was removed under vacuum. The unreacted benzaldehyde was removed by chromatography (eluent: petroleum ether/AcOEt, 95:5) to give a 38/62 mixture of two diastereoisomers of

2-nitro-1-phenylpropan-1-ol (**3aa**) as a colorless oil (0.130 g, 72% yield).

4.3 Representative batch procedure for Henry reaction of aliphatic aldehydes 1e–g

In a screw-capped vial equipped with a magnetic stirrer, PS-BEMP (0.044 g, 0.05 mmol, 2.2 mmol/g), hexanal (**3f**; 0.120 mL, 1.0 mmol) and nitroethane (**2a**; 0.072 mL, 1.0 mmol) were consecutively added and the resulting mixture was left under stirring at 30°C. After 2 hours, dichloromethane (1 mL) was added, the catalyst was recovered by filtration and the solvent and unreacted reagents were removed under vacuum to give pure 2-nitrooctan-3-ol (**3fa**) as a colourless oil (0.160 g, 92% yield).

4.4 General procedure for regeneration of PS-BEMP

In a round bottom flask equipped with a magnetic stirrer, PS-BEMP (1.0 g, 2.2 mmol, 2.2 mmol/g) was suspended in a solution of BEMP (1.270 mL, 4.4 mmol) in AcOEt (4.4 mL) and stirred at room temperature. After one hour, the solvent was filtered off, and the PS-BEMP was washed twice with AcOEt and dried under high vacuum for 48 hours at room temperature.

4.5 Representative batch procedure for tandem Michael-Henry reaction of α,β-unsaturated aldehydes 1h–i

In a screw-capped vial equipped with a magnetic stirrer, PS-BEMP (0.088 g, 0.1 mmol, 2.2 mmol/g) and 2-nitropropane (**2c**; 0.2 mL, 2.2 mmol) were consecutively added, trans-cinnamaldehyde (**1h**; 0.126 mL, 1 mmol) was slowly added (the reaction was exotermic) and the resulting mixture was left under stirring at 30°C. After 15 hours, dichloromethane (1 mL) was added, the catalyst was recovered by filtration and the solvent was removed under vacuum to give pure 2,6-dimethyl-2,6-dinitro-5-phenylheptan-3-ol (**3hc**) as a white solid (0.285 g, 92% yield).

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Supplemental Material

All Supplemental Material is available alongside this article on www.tandfonline.com _ go to http://dx.doi.org/10.1080/17518253.2014.893028

References

(1) Ono, N. *The Nitro Group in Organic Synthesis*; Ed. Wiley-VCH: New York, **2001**.
(2) Rosini, G. In *Comprehensive Organic Synthesis*; Trost, B.M., Fleming, I., Heathcock, C.H., Eds.; Pergamon: New York, **1991**, 2, pp. 321–340.
(3) Kisanga, P.; Verkade, J. *J. Org. Chem*. **1999**, *64*, 4298–4303. doi:10.1021/jo9818733.
(4) Heffner, R.J.; Jiang, J.J.; Joullie, M.M. *J. Am. Chem. Soc*. **1992**, *114*, 10181–10189. doi:10.1021/ja00052a015.
(5) Ballini, R. *J. Chem. Soc., Perkin Trans*. **1991**, *1*, 1419–1421. doi:10.1039/p19910001419.
(6) Sakanaka, O.; Ohmori, T.; Kozaki, S.; Suami, T. *Bull. Chem. Soc. Jpn*. **1986**, *59*, 3523–3528. doi:10.1246/bcsj.59.3523.
(7) Suami, T.; Sasai, H.; Matsuno, K. *Chem. Lett*. **1983**, 819–822. doi:10.1246/cl.1983.819.
(8) Mikite, G.; Jakucs, E.; Kistamas, A.; Darvas, F.; Lopata, A. *Pestic. Sci*. **1982**, *13*, 557–562. doi:10.1002/ps.2780130515.
(9) (a)Ballini, R.; Bosica, G.; Parrini, M. *Chem. Lett*. **1999**, *28*, 1105–1106. (b) Akutu, K.; Kabashima, H.; Seki, T.; Hattori, H. *Appl. Cat. A: Gen*. **2003**, *247*, 65–74. doi:10.1246/cl.1999.1105.
(10) Jenner, G. *New J. Chem*. **1999**, *23*, 525–529. doi:10.1039/a900899c.
(11) Youn, S.W.; Kim, Y.H. *Synlett*. **2000**, 880–882.
(12) Bulbule, V.; Jnaneshwara, G.; Deshmukh, R.; Borate, H.; Deshpande, V. *Synth. Commun*. **2001**, *31*, 3623–3626. doi:10.1081/SCC-100107010.
(13) Li, H.; Wang, B.; Deng, L. *J. Am. Chem. Soc*. **2006**, 128, 732–733. doi:10.1021/ja0572371.
(14) Simoni, D.; Rondanin, R.; Morini, M.; Baruchello, R.; Invidiata, F. *Tetrahedron Lett*. **2000**, *41*, 1607–1610. doi:10.1016/S0040-4039(99)02340-0.
(15) Ballini, R.; Bosica, G. *J. Org. Chem*. **1997**, *62*, 425–427. doi:10.1021/jo961201h.
(16) Melot, J.M.; Texier-Boullet, F.; Foucraud, F. *Tetrahedron Lett*. **1986**, *27*, 493–496. doi:10.1016/S0040-4039(00)85513-6.
(17) (a)Bulbule, V.; Deshpande, V.; Velu, S.; Sudalai, A.; Sivasankar, S.; Sathe, V. *Tetrahedron* **1999**, *55*, 9325–9332. (b) Cwik, A.; Fuchs, A.; Hell, Z.; Clacens, J. *Tetrahedron* **2005**, *61*, 4015–4021. doi:10.1016/S0040-4020(99)00494-9.
(18) Ballini, R.; Bosica, G.; Forconi, P. *Tetrahedron* **1996**, *52*, 1677–1684. doi:10.1016/0040-4020(95)00996-5.
(19) Ballini, R.; Bosica, G. *Tetrahedron Lett*. **2003**, *44*, 2271–2273. doi:10.1016/S0040-4039(03)00274-0.
(20) Le, Z.-G.; Guo, L.-T.; Jiang, G.-F.; Yang, X.-B.; Liu, H.-Q. *Green Chem Lett. Rev*. **2013**, *6*, 277–281. doi:10.1080/17518253.2013.818721.
(21) Majhi, A.; Kadam, S.; Kim, S. *Bull. Korean Chem. Soc*. **2009**, *30*, 1767–1770. doi:10.5012/bkcs.2009.30.8.1767.
(22) Ballini, R.; Bosica, G.; Parrini, M. *Tetrahedron Lett*. **1998**, *39*, 7963–7964. doi:10.1016/S0040-4039(98)01730-4.
(23) Bonollo, S.; Lanari, D.; Pizzo, F.; Vaccaro, L. *Org. Lett*. **2011**, *13*, 2150–2152. doi:10.1021/ol200379r.

(24) (a)Costantino, U.; Curini, M.; Marmottini, F.; Rosati, O.; Pisani, E. *Chem. Lett*. **1994**, 2215–2218. (b) Lanari, D.; Ballini, R.; Palmieri, A.; Pizzo, F.; Vaccaro, L. *Eur. J. Org. Chem*. **2011**, 2874–2884. doi:10.1246/cl.1994.2215.

(25) (a)Ballini, R.; Barboni, L.; Castrica, L.; Fringuelli, F.; Lanari, D.; Pizzo, F.; Vaccaro, L. *Adv. Synth. Catal*. **2008**, *350*, 1218–1224. (b) Zvagulis, A.; Bonollo, S.; Lanari, D.; Pizzo, F.; Vaccaro, L. *Adv. Synth. Catal*. **2010**, *352*, 2489. (c) Fringuelli, F.; Lanari, D.; Pizzo, F.; Vaccaro, L. *Green Chem*. **2010**, *12*, 1301–1305. (d) Angelini, T.; Fringuelli, F.; Lanari, D.; Pizzo, F.; Vaccaro, L. *Tetrahedron Lett*. **2010**, *51*, 1566–1569. (e) Lanari, D.; Ballini, R.; Bonollo, S.; Palmieri, A.; Pizzo, F.; Vaccaro, L. *Green Chem*, **2011**, *13*, 3181–3186. (f) Bonollo, S.; Lanari, D.; Angelini, T.; Pizzo, F.; Marrocchi, A.; Vaccaro, L. *J. Catal*. **2012**, *285*, 216–222. (g) Bonollo, S.; Lanari, D.; Longo, J.; Vaccaro, L. *Green Chem*. **2012**, *14*, 164–169. doi:10.1002/adsc.200800117.

(26) Aranda, C.; Cornejo, A.; Fraile, J.; Garcia-Verdugo, E.; Gil, M.; Luis, S.; Mayoral, J.; Martinez-Merino, V.; Ochoa, Z. *Green Chem*. **2011**, *13*, 983–990. doi:10.1039/c0gc00775g.

(27) Schwesinger, R.; Schlempler, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; Putzas, D.; Rotter, H.W.; Bordwell, F.G.; Satish, A.V.; Ji, G.Z.; Peters, E.M.; Peters, K.; vonSchnering, H.G.; Walz, L. *Liebigs Ann*. **1996**, 1055–1081.

(28) Luzzio, F.A. *Tetrahedron* **2001**, *57*, 915–945. doi:10.1016/S0040-4020(00)00965-0.

(29) Peera, A.; Tomlinson, I. *Tetrahedron Lett*. **2012**, *53*, 3322–3324. doi:10.1016/j.tetlet.2012.04.078.

(30) Liu, S.; Wolf, C. *Org. Lett*. **2008**, *10*, 1831–1834. doi:10.1021/ol800442s.

(31) Palacios, F.; Santos, J.M.; Aparicio, D. *Arkivoc* **2005**, 405. doi:10.3998/ark.5550190.0006.934.

(32) Bhattacharya, A.; Purohit, V.C. *Org. Process Res. & Dev*. **2003**, *7*, 254. doi:10.1021/op020222c.

(33) Crich, D.; Ranganathan, K.; Rumthao, S.; Shirai, M. *J. Org. Chem*. **2003**, *68*, 2034. doi:10.1021/jo026707g.