Heteropoly acid/NaY zeolite as a reusable solid catalyst for highly efficient synthesis of *gem*-dihydroperoxides and 1,2,4,5-tetraoxanes

Kaveh Khosravi*, Mojgan Zendehdel, Shirin Naserifar, Fatemeh Tavakoli, Kobra Khalaji and Atefeh Asgari

Department of Chemistry, Faculty of Science, Arak University, Arak 38156-8-8349, Iran

gem-Dihydroperoxides and 1,2,4,5-tetraoxanes were synthesised from aldehydes and ketones catalysed by heteropoly acid/NaY zeolite (HPA/NaY) as a new, effective and reusable solid catalyst using 30% aqueous hydrogen peroxide at room temperature. The reactions proceeded with high rates and excellent yields.

Keywords: gem-dihydroperoxides, 1,2,4,5-tetraoxanes, heteropoly acid/NaY zeolite (HPA/NaY), antimalarial drugs, solid catalyst

gem-Dihydroperoxides are considered to be stable derivatives of ketones and aldehydes,¹ which have been of considerable interest because of their relevance to peroxidic antimalarial drugs.^{2,3} Also, gem-dihydroperoxides are significant central intermediates in the synthesis of different classes of peroxides such as tetraoxanes,4--6 silatetraoxanes,⁷ spirobisperoxyketals,^{8,9} bisperoxyketals¹⁰ and 1,2,4,5-tetraoxacycloalkanes.^{11,12} Additionally, due to the peroxidic bonds in gem-dihydroperoxides, these compounds have been used as initiators in radical polymerisations.¹³ Recently, they have been used as the appropriate solid oxidants in a variety of oxidative reactions such as oxidation of alcohols,14 oxidation of sulfides,15,16 epoxidation of α,β -unsaturated ketones,^{17,18} enantioselective oxidation of 2-substituted-1,4-naphtoquinones¹⁹ and other organic reactions.^{20–23} Commonly, the preparation of gem-dihydroperoxides has been accomplished using two reported methods, (1) the reaction of ketals with H₂O₂ in the presence of tungstic acid,²⁴ or BF₃.Et₂O,²⁵ HCl,¹⁰ methyltrioxorhenium (MeReO₂) in trifluoroethanol or AcOH as the solvent,¹¹ and (2) ozonolysis of ketone enol ethers or -olefines in the presence of aqueous H2O2.11,24-26 Unfortunately, these general methods have several drawbacks, such as the requirement for concentrated H₂O₂ and excess acid, limited substrate ranges and the production of mixtures of peroxidic products, poor yields and drastic reaction conditions.^{25,26} Also, low selectivity and limitations imposed by the presence of ozone-sensitive functional groups on the substrates are deficiencies in the ozonolysis reaction. Therefore, to eliminate these deficiencies, the synthesis of gem-dihydroperoxides has recently been carried out through peroxidation of aldehydes



R¹, R²= H, alkyl, cycloalkyl and aryl

Scheme 1 Peroxidation of aldehydes and ketones catalysed by HPA/NaY.

and ketones by aqueous H2O2 in the presence of molecular iodine as catalyst.^{27,28} Lately, various Lewis or Brønsted acids, such as ceric ammonium nitrate (CAN),29 camphor sulfuric acid (CSA),³⁰ NaHSO₄,SiO₂,³¹ Re₂O₂,³² PMA³³ and bismuth (III) trifluoromethanesulfonate³⁴ have been utilised as catalysts for the synthesis of this class of peroxides. Recently, both natural and modified zeolites have been considered as effective heterogeneous catalysts in many organic reactions.35,36-41 These compounds have shown high catalytic efficiency and selectivity, and they have been recovered and reused for many runs. Lately, heteropoly acid/NaY zeolite (HPA/NaY), a hybrid catalyst, has been synthesised and utilised as an efficient catalyst for the synthesis of perimidines.36 Therefore, because of the importance of gem-dihydroperoxides and 1,2,4,5-tetraoxanes as precursors in the preparation of antimalarial drugs, and due to the high efficiency, selectivity and reusability of zeolites, in continuation of our efforts to improve this methodology and utilise new and better catalysts,^{42,43} herein, we wish to report HPA/NaY as an effective, recoverable and cost-efficient solid catalyst in the synthesis of gem-dihydroperoxides via oxidation of various ketones and aldehydes using 30% aqueous H₂O₂ at room temperature (Scheme 1). Also in this paper, this hybrid catalyst has been used successfully for the facile synthesis of 1,2,4,5-tetraoxanes by the direct condensation of gem-dihydroperoxides obtained from different ketones (Scheme 2).

Results and discussion

First, $H_3PW_{12}O_{40}$ was selected as a useful heteropoly acid and was converted to HPA/NaY composite according to the method reported previously.³⁸ As shown in Table 1, we investigated the effects of several parameters contributing to the 1,1-dihydroperoxycyclohexane synthesis by the model reaction of cyclohexanone with 30% aqueous H_2O_2 under the catalytic effect of HPA/NaY at room temperature. Based on the results, it can be seen that using CH₃CN as the solvent and 0.01 g of the catalyst load gave a significant increase in yield and also led to a shorter reaction time (Table 1, entry 9).

To understand the scope of this reaction, we studied the reaction of various aldehydes and ketones under optimised conditions



Scheme 2 Synthesis of different 1,2,4,5-tetraoxanes catalysed by HPA/NaY.

^{*} Correspondent. E-mail: khosravi.kaveh@gmail.com

(aldehyde or ketone (1 mmol), aqueous 30% H₂O₂ (1 mL), 0.01 g catalyst, CH₃CN (3 mL, r.t.). The summarised results were obtained by investigating the synthesis of *gem*-dihydroperoxides in the presence of several side-chain aliphatic aldehydes and ketones (Table 2), cyclic aliphatic ketones (Table 3) and aromatic aldehydes and ketones (Table 2), the two observed that both side-chain and cyclic aliphatic ketones required shorter reaction times than aromatic ketones to produce the corresponding *gem*-dihydroperoxides. Among the cyclic ketones, cyclohexanone afforded 1,1-dihydroperoxycyclohexane faster than cyclopropane and in higher yield (Table 3, entries 2a and 2g). It was also noticed that powerful electron-withdrawing substituents on aromatic

 Table 1
 Screening of reaction parameters for formation of 1,1-dihydroperoxycyclohexane

0	H ₂ O ₂ (30%)	HOO	OOH
\frown	Cat	\geq	\leq
\bigtriangledown	rt	L	

Entry ^a	Solvent	HPA/NaY (g)	Time (min)	Yield (%) ^b
1	<i>n</i> -hexane	0.010	120	10
2		0.010	80	42
3	CHCI	0.010	60	51
4	CH,CĬ,	0.010	80	35
5	EtOAc	0.010	25	76
6	H,0	0.010	120	30
7	CH ₃ CN	0.005	30	65
8	CH ₃ CN	0.008	18	82
9	CH ₃ CN	0.010	10	97
10	CH ₃ CN	0.015	8	90
11	CH ₃ CN	0.020	8	71

^a1 mmol cyclohexanone (0.1 mL), amounts of H₂O₂ and solvent in all entries are 1 mL (9.8 mmol) and 3 mL, respectively. ^bIsolated yields.

 Table 2 Peroxidation of side-chain aliphatic ketones and aldehydes

ketones and aldehydes were unfavourable as long as very long reaction times were demanded, no reactions were carried out, or trace amounts of the products were obtained. Based on these results, 4-N,N-dimethylamino benzaldehyde required a shorter reaction time than 4-chlorobenzaldehyde (Table 4, entry 3q), while 4-nitro benzaldehyde was converted to gem-dihydroperoxide very slowly and at a very low conversion rate (12%) due to the powerful electron-withdrawing NO2 substituent, and it decomposed after 0.5 h (Table 4, entry 3n). Previously, Zmitek et al.^{27,28} reported that the negative reaction constant obtained from the Hammett equation $(\rho = -2.76)$ leads to a transition state with a more developed positive charge in the rate-determining step and suggests the electrophilic activation of the carbonyl group as a result of H⁺ generation by HPA/ NaY acting as a powerful acid. On the other hand, oxygen atoms in heteropoly acid and in the zeolite structure activate hydrogen peroxide via hydrogen bonding (Scheme 3).

In addition, and similar to our other studies reported previously, we noticed that the carbonyl group of aliphatic aldehydes carried out the reaction using only one molecule of hydrogen peroxide and 1,1-hydroxyhydroperoxide derivatives were produced instead of the related dihydroperoxides that were expected to be formed (Table 2, entries 1i and 1j, Scheme 4).



Scheme 3 Suggested transition state for catalytic zeolite and HPA effects.

Entrya	Ketone	Product ^b	Time (min)	Vield ^c (%)	M.p	. (°C)	Rof
	Kelolie	Floduct	Time (Tim)		Found	Reported	nei.
1a		HOO OOH	10	93	Oil	Oil	28
1b	o J	HOO OOH	10	94	Oil	Oil	37
1c	о Щ	HOO OOH	10	95	Oil	Oil	30
1d	o L	HOO OOH	8	94	Oil	Oil	37
1e	o L	НОО ООН	15	95	Oil	-	New
1f		HOOYOOH	12	93	Oil	Oil	28
1g		HOO OOH	9	92	31-33	30.1-30.5	28
1h	O U U U	HOO OOH	15	86	Oil	Oil	28
1i	o H	но оон	42	95	Oil	Oil	37
1j	O H H	но оон	37	96	Oil	Oil	37

^aReaction conditions: ketone and aldehyde (1 mmol), CH₃CN (3 mL), HPA/NaY (0.01 g), 30% aq. H₂O₂ (1 mL, 9.8 mmol), r.t.

^bThe structures of the products were established from their physical properties and spectral (¹H NMR, ¹³C NMR and IR) analysis and compared with the data reported in the literature. The amount of peroxide was determined by iodometric titration.

°lsolated yield.

Entrya	Ketone	Product ^b	Time (min)	Vield ^c (%)	M.p.	(°C)	Bef
	Retorie	Tioddol		Tield (70)	Found	Reported	
2a	0	ООН	10	97	Oil	Oil	37
2b		- ООН	9	97	Oil	Oil	30
2c		оон	13	90	Oil	Oil	30
2d	0	ООН	16	91	64-66	60-61	28
2e		ООН	11	95	Oil	Oil	8
2f		OOH COOH	30	84	138–140 (Decomposed)	137–138 (Decomposed)	28
2g		ООН	11	92	Oil	Oil	37

^aConditions: ketone and aldehyde (1 mmol), CH₃CN (3 mL), HPA/NaY (0.01 g), 30% aq. H₂O₂ (1 mL, 9.8 mmol), r.t.

^bThe structures of the products were established from their physical properties and spectral (¹H NMR, ¹³C NMR and IR) analysis and compared with the data reported in the literature. The amount of peroxide was determined by iodometric titration.

^clsolated vield.



Scheme 4 Production of 1,1-hydroxyhydroperoxide from aliphatic aldehydes.

For the first time, benzil and terephthalaldehyde (a dialdehyde) were successfully converted to their corresponding products, and we observed that both carbonyl groups were converted to *gem*-dihydroperoxide (Table 4, entries 3g and 3k). Also, pyridine-3-carbaldehyde and quinoline-2-carbaldehyde as heterocyclic compounds were successfully converted to their corresponding *gem*-dihydroperoxides without the formation of any by-products (Table 4, entries 3h and 3i). Moreover, as reported previously, unreactive benzophenone was recovered after 200 minutes (Table 4, entry 3f).

In addition, the synthesised *gem*-dihydroperoxides were used as the precursor for the preparation of 1,2,4,5-tetraoxanes as potential antimalarial drugs (Scheme 2) in the presence of HPA/ NaY as catalyst. HPA/NaY brought about electrophilic activation of the carbonyl group by protonating it. Then, the prepared *gem*dihydroperoxide as the nucleophile attacked the activated carbonyl compounds to produce 1,2,4,5-tetraoxanes in good yields (Table 5).

Catalyst recovery and reuse

The potential for recycling the catalyst was examined in the reaction of cyclohexanone with 30% aqueous H_2O_2 at room temperature in the presence of recovered HPA/NaY (Table 3, entry 2a). HPA/NaY was reused after washing with CHCl₃ and drying at 60 °C for 1 h. It was found that the catalyst could be reused for at least sixth cycles without significant loss of catalytic activity (Fig. 1).

Finally, to study the efficiency of this methodology in the peroxidation of cyclohexanone (Table 2, entry 1a), this method was compared with other reported methodologies (Table 6). It can be seen that our methodology has clearly improved reaction times, yields and reaction conditions.



Fig. 1 Recycling of HPA/NaY (0.01 g) in the peroxidation of cyclohexanone using H_2O_2 (9.8 mmol) at room temperature for 10 min.

Conclusions

In conclusion, HPA/NaY has been proved to be a costefficient, recoverable and environmentally benign solid catalyst that catalyses the synthesis of *gem*-dihydroperoxides and 1,2,4,5-tetraoxanes. Mild reaction conditions, shorter reaction times and higher yields are the notable advantages of this methodology.

Experimental

General

All chemicals were purchased from Merck and Fluka Company. Melting points were determined on an Electrothermal Digital Melting Point Apparatus. Final products were characterised with FTIR (Galaxy Series FTIR 5000 Spectrometer) and NMR spectra were recorded on JEOL FX 90Q and Bruker (300 MHz) spectrometers. Chemical shifts (ppm) were referenced to tetramethylsilane (TMS) as internal standard. Microanalyses were performed on an elemental analyser (Elemental,

M.p. (°C)					D-6		
Entryª	Ketone	Product	lime (min)	YIEIC° (%)	Found	Reported	Ket.
3a		ноо оон	120	68	75-77	75–77	37
3b	Cl Cl	HOO OOH	90	65	Oil	Oil	37
3c	MeO	HOO OOH MeO	85	69	Oil	Oil	37
3d	O L	HOO OOH	100	60	Oil	Oil	37
3e		HOO	60	90	Oil	Oil	37
3f	o L	-	300	-	-	-	-
3g		HOO HOO OOH	600	89	100–102	-	New
3h	O H H	HOO OOH H	130	73	165–170 (Decomposed)	160 < (Decomposed)	46
3i	K N N H	N HHOO OOH	140	75	142–144	138–140	46
3j	CHO	ООН	100	80	Oil	Oil	37
3k	онс — Сно	ноо	480	91	210-212	210-212	45
31	сі — Сно	ClOOH	110	80	72-74	72–74	37
3m	МеО — СНО	МеО — ООН	90	91	Oil	Oil	37
3n	02N — СНО	02N - OOH	240	12	Decomposed	Decomposed	37
30	— СНО		100	82	54-56	54-56	37
Зр		Ноо оон	20	94	99–101	-	New
3q	N-СНО	N - OOH OOH	90	75	Sticky oil	Oil	45

Table 4 Peroxidation of aromatic ketones and aldehydes

 a Conditions: ketone and aldehyde (1 mmol), CH $_{3}$ CN (3 mL), HPA/NaY (0.01 g), 30% aq. H $_{2}$ O $_{2}$ (1 mL, 9.8 mmol), r.t.

^bThe structures of the products were established from their physical properties and spectral (¹H NMR, ¹³C NMR and IR) analysis and compared with the data reported in the literature. The amount of peroxide was determined by iodometric titration.

^clsolated yield.

Table 9 Oynthesis of tetraoxanes using genr uniyutoperoxides	Table 5	Synthesis of	tetraoxanes	using	gem-dih	vdroperoxides
---	---------	--------------	-------------	-------	---------	---------------

Entry ^a	gem-dihydroperoxide	Ketone	Product ^b	Time (min)	Yield⁰ (%)	M.p. Found	(°C) Reported	Ref.
4a	оон			20	84	73-75	73-75	45
4b	ООН			18	86	78-80	78-80	45
4c	OOH OOH			15	83	101–103	101–102	45
4d	OOH OOH	t-Bu —	O-O O-O Bu-t	14	82	122-124	123-125	45
4e	ООН			22	71	61–63	60-64	44
4f	ClOOH			25	80	98–100	98-100	45
4g	СІ — ООН	t-Bu=0	$Cl \longrightarrow 0-0 \longrightarrow Bu-t$	13	81	114-116	114–116	44
4h	ClOOH			30	74	73-75	70-72	44
4i	оон			14	83	Oil	Oil	44
4j	оон			13	87	58-62	55-58	44
4k	ООН	t-Bu —	-Bu-t	12	84	131–133	134–136	44
41	оон			12	85	70-72	70-72	45
4m	ООН			11	88	86-88	86-88	44
4n	оон	t-BuO	O-O O-O Bu-t	10	87	102–104	100–102	44
40	- Сурон			10	90	153–155	153–154	45
4p	t-Bu - OOH	t-BuO	t-BuOBu-t	10	92	191–193	190–192	44

^aConditions: *gem*-dihydroperoxide (1 mmol), ketone (1 mmol, 9.8 mmol), CH₃CN (3 mL), HPA/NaY (0.01 g), r.t.

^bThe structures of the products were established from their physical properties and spectral (¹H NMR, ¹³C NMR and IR) analysis and compared with the data reported in the literature. The amount of peroxide was determined by iodometric titration.

°lsolated yield.

Table 6 Comparison of the results reported for different methods of synthesis of cyclohexane-1,1-dihydroperoxide

				.,,		
Entry	Catalyst	Condition	Solvent	Time (min)	Yield (%)	Ref.
1	(HPA/NaY)	r.t.	MeCN	10	95	This method
2	Silica sulfuric acid	r.t.	MeCN	20	98	47
3	Bi(OTf) ₃	r.t.	MeCN	18	78	34
4	Phosphomolybdic acid	r.t.	Et,0	150	95	33
5	Re ₂ 0 ₇	r.t.	MeCN	30	79	32
6	CAN reagent	r.t.	MeCN	120	87	29
7	$NaHSO_4 \cdot SiO_2$	r.t.	MeCN	20	98	31

Vario EL III) at Arak University. Reactions were monitored by TLC using silica gel F_{254} aluminium sheets (Merck). TLC was performed on SIL G/UV₂₅₄ plates. All known products were fully characterised by comparison with authentic samples (melting points) and their

¹H NMR, ¹³C NMR and IR spectra.^{9,28,30,42-47} All of the new products (**1e**, **3g** and **3p** compounds) were also fully characterised by ¹H NMR, ¹³C NMR and IR spectra and elemental analysis, the data for which are available in the supporting information file.

CAUTION: Although we did not encounter any problems with *gem*-dihydroperoxides and tetraoxanes, peroxides are potentially explosive and should be handled with extreme care and all necessary precautions taken. All reactions should be carried out behind a safety shield inside a fume hood and heating should be avoided.

Synthesis of HPA-NaY composite; general procedure

 $\rm H_3PW_{12}O_{40}~(10~g)$ was mixed with 6 mL zeolite gel (molar composition 16Na_2O:Al_2O_3:15SiO_2:320H_2O) prepared from mixing 16.13 g sodium alumina silicate (containing 19.80 wt% SiO_2, Merck), 13.20 mL sodium hydroxide (24 wt%) and 5.20 mL deionised water and aged at 32 °C for 32 h. The mixture was then placed in an autoclave at 100 °C for 24 h. After cooling the reaction mixture to room temperature, filtering, washing with water and drying in air, the solid product $\rm H_3PW_{12}O_{40}/NaY$ composite was recovered.³⁶

Synthesis of gem-dihydroperoxides; general procedure

To a solution of carbonyl compound (1 mmol) and HPA/NaY (0.01 g) in CH₃CN (3 mL), 30% aqueous H_2O_2 (1 mL, 9.8 mmol) was added and the mixture was stirred at room temperature for an appropriate time (Tables 2–4). After completion of the reaction, as monitored by TLC, the catalyst was separated by centrifuge and the solvent was evaporated under reduced pressure. The residue was purified by silica-packed column chromatography (hexane–EtOAc) to afford pure *gem*-dihydroperoxides (Tables 2–4, 60–97% yields). The products were characterised on the basis of their melting points, elemental analysis and IR, ¹H NMR and ¹³C NMR spectral analyses. Also, the amount of peroxide in the products was determined by iodometric titration.

Synthesis of 1,2,4,5-tetraoxanes; general procedure

To a mixture of carbonyl compound (1 mmol) and HPA/NaY (0.01 g) in CH_3CN (3 mL), *gem*-dihydroperoxide (1 mmol) was added and the mixture stirred at room temperature for the appropriate time (Table 5). After completion of the reaction, as monitored by TLC, the catalyst was separated by centrifuge and the solvent was evaporated under reduced pressure. The residue was purified by silica-packed column chromatography (hexane–EtOAc) to afford pure 1,2,4,5-tetraoxanes (Table 5, 71–92% yields). All of the products were characterised on the basis of IR, ¹H NMR and ¹³C NMR spectral analysis, elemental analysis and by their melting points.

Physical and spectroscopic characterisation data of the catalyst and the new compounds, including **1e**, **3g** and **3p**, are contained in the Electronic Supporting Information file and are also shown below.

2,2-*dihydroperoxypropane* (Table 2, entry 1e, 0.10 g, 95% yield): Oil; IR (v_{max} /cm⁻¹, KBr pellet): 3276, 2938, 2908, 2853, 1625, 1450, 1376, 1200, 1167, 829; ¹H NMR (CDCl₃, 90 MHz): δ = 9.15 (br, s, 2H, OOH), 1.79 (s, 6H); ¹³C NMR (DMSO-*d*₆, 75 MHz): δ = 107.6, 21.2; Anal. calcd for C₃H₈O₄; C, 33.34; H, 7.46; found: C, 33.40; H, 7.56%.

1,1,2,2-tetrahydroperoxy-1,2-diphenylethane (Table 4, entry 3g, 0.28 g, 89% yield): White solid, m.p.: 100–102 °C; IR (v_{max} /cm⁻¹, KBr pellet): 3304, 2924, 1614, 1513, 1457, 1375, 1115, 1033, 929; ¹H NMR (CDCl₃, 90 MHz): δ = 8.81 (br, s, 4H, OOH), 7.32–7.99 (m, 10H); ¹³C NMR (DMSO-*d*₆, 75 MHz): δ = 167.7, 133.3, 131.2, 129.7, 129.02; Anal. calcd for C₁₄H₄O₅: C, 54.20; H, 4.55; found: C, 54.15; H, 4.63%.

2,2-dihydroperoxy-1-phenylpropane (Table 4, entry 3p, 0.18 g, 94% yield): White-brown solid; m.p.: 99–101 °C; IR (ν_{max} /cm⁻¹, KBr pellet): 3427, 2953, 2924, 1633, 1457, 1375, 1212, 1167; ¹H NMR (90 MHz, CDCl₃), δ = 9.95 (bs, 2H, OOH), 6.7–7.3 (m, 5H, Ar), 2.2 (s, 2H, CH₂), 1.54 (s, 3H, CH₃); ¹³C NMR (100 MHz, DMSO- d_{0}): δ = 141.9, 128.8, 128.7, 128.5, 126.3, 110.0, 108.4; Anal. calcd for C₉H₁₂O₄: C, 58.69; H, 6.57; found: C, 58.33; H, 6.81%.

Acknowledgements

We are grateful to the Arak University Research Councils for financial support of this work.

Electronic Supplementary Information

Spectrum information for the new compounds available through: stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data

Received 12 September 2016; accepted 26 October 2016 Paper 1604316 doi: 10.3184/174751916X14792244600532 Published online: 23 November 2016

References

- 1 K. Zmitek, M. Zupan and J. Iskra, Org. Biomol. Chem., 2007, 5, 3895.
- 2 R. Oliveira, R.C. Guedes, P. Meireles, I.S. Albuquerque, L.M. Gonçalves, E. Pires, M.R. Bronze, J. Gut, P.J. Rosenthal, M. Prudêncio, R. Moreira, P.M. O'Neill and F. Lopes, *J. Med. Chem.*, 2014, **57**, 4916.
- 3 D. Bonnet-Delpon and J.P. Begue, *Tetrahedron Lett.*, 2003, 44, 6309.
- 4 Y.Q. Tang, Y.X. Dong and J.L. Vennerstrom, Med. Res. Rev., 2004, 24, 425.
- 5 Y. Dong, Mini-Rev. Med. Chem., 2002, 2, 113.
- 6 A.O. Terent'ev, A.V. Kutkin, Z.A. Starikova, M.Y. Antipin, Y.N. Ogibin, G.I. Nikishin and N.D. Zelinsky, *Synthesis*, 2004, 2356.
- 7 R. Amewu, A.V. Stachulski, S.A. Ward, N.G. Berry, P.G. Bray, J. Davies, G. Labat, L. Vivas and P.M. O'Neill, *Org. Biomol. Chem.*, 2006, **4**, 4431.
- 8 A.O. Terent'ev, M.M. Platonov, A.I. Tursina, V.V. Chernyshev and Ge.I. Nikishin, J. Org. Chem., 2008, 73, 3169.
- 9 P. Ghorai, P.H. Dussault and C. Hu, Org. Lett., 2008, 10, 2401.
- 10 Q. Zhang, Y. Li and Y.-K. Wu, Chin. J. Chem., 2007, 25, 1304.
- 11 Y. Hamada, H. Tokuhara, A. Masuyama, M. Nojima, H.-S. Kim, K. Ono, N. Ogura and Y. Wataya, J. Med. Chem., 2002, 45, 1374.
- 12 H.-S. Kim, Y. Nagai, K. Ono, K. Begum, Y. Wataya, Y. Hamada, K. Tsuchiya, A. Masuyama, M. Nojima and K.J. McCullough, J. Med. Chem., 2001, 44, 2357.
- 13 A. Masuyama, J.-M. Wu, M. Nojima, H.-S. Kim and Y. Wataya, <u>Mini-Rev. Med.</u> Chem., 2005, 5, 1035.
- 14 H. Hansma and A. Schroeder, AKZO NV, Belg. Patent 868,681, 1978, Chem. Abstr., 1979, 90, 153037a.
- 15 D. Azarifar, K. Khosravi and Z. Najminejad, J. Iran. Chem. Soc., 2013, 10, 979.
- D. Azarifar and K. Khosravi, *Eur. J. Chem.*, 2010, 1, 15.
 IP. Selvam V. Suresh K. Rajesh D. Chanti Babu, N. Survakiran and
- 17 J.P. Selvam, V. Suresh, K. Rajesh, D. Chanti Babu, N. Suryakiran and Y. Venkateswarlu, *Tetrahedron Lett.*, 2008, **49**, 3463.
- 18 K. Jakka, J. Liu and C.G. Zhao, Tetrahedron Lett., 2007, 48, 1395.
- 19 D. Aarifar and K. Khosravi, Synlett, 2010, 2755.
- 20 A. Bunge, H.-J. Hamann, E. McCalmont and J. Liebscher, *Tetrahedron Lett.*, 2009, 50, 4629.
- 21 K. Khosravi, Res. Chem. Intermed., 2015, 41, 5253.
- 22 K. Khosravi, A. Mobinikhaledi, S. Kazemi, D. Azarifar and P. Rahmmani, *Iran. J. Catal.*, 2014, 4, 25.
- 23 K. Khosravi and S. Kazemi, Chin. Chem. Lett., 2012, 23, 387.
- 24 T. Ito, T. Tokuyasu, A. Masuyama, M. Nojima and K.J. McCullough, *Tetrahedron*, 2003, 59, 525.
- 25 A.O. Terent'ev, A.V. Kutkin, N.A. Troizky, Y.N. Ogibin and G.I. Nikishin, Synthesis, 2005, 13, 2215.
- 26 C.W. Jefford, W. Li, A. Jaber and J. Boukouvalas, Synth. Commun., 1990, 20, 2589.
- 27 K. Zmitek, K. Zupan, S. Stavber and J. Iskra, J. Org. Chem., 2007, 72, 6534.
- 28 K. Zmitek, K. Zupan, S. Stavber and J. Iskra, Org. Lett., 2006, 8, 2491.
- 29 B. Das, B. Veeranjaneyulu, M. Krishnaiah, B. Veeranjaneyulu and B. Ravikanth, *Tetrahedron Lett.*, 2007, 48, 6286.
- 30 A. Bunge, H.-J. Hamann and J. Liebscher, Tetrahedron Lett., 2009, 50, 524.
 - 31 B. Das, B. Veeranjaneyulu, M. Krishnaiah and P. Balasubramanyam, J. Mol. Catal. A: Chem., 2008, 284, 116.
- 32 P. Ghorai and P.H. Dussault, Org. Lett., 2008, 10, 4577.
- 33 Y. Li, H.-D. Hao, Q. Zhan and Y. Wu, Org. Lett., 2009, 11, 1615.
- 34 K.V. Sashidhara, S.R. Avula, L.R. Singh and G.R. Palnati, *Tetrahedron Lett.*, 2012, 53, 4880.
- 35 R.S. Varma, Sustainable Chemical Processes, 2014, 2, 11.
- 36 M. Zendehdel, A. Mobinikhaledi, H. Alikhani and N. Jafari, <u>J. Chin. Chem.</u> Soc., 2010, 57, 683.
- 37 F. Zamani, M. Zendehdel, A. Mobinikhaledi and M. Azarkish, *Microporous and Mesoporous Materials*, 2015, 212, 18.
- 38 M. Zendehdel, G. Cruciani, F. Sahra Kar and A. Barati, J. Environ. Health Sci. & Eng., 2014, 12, 35.
- 39 M. Zendehdel, F. Hoseini, A. Zendehnam and M. Azarkish, *Polym. Bull.*, 2015, 72, 1281.
- 40 S.M. Sajadi, M. Maham and S.A. Mahmoud, J. Chem. Res., 2013, 37, 853.
- 41 K.D. Safa, L. Sarchami, M. Allahvirdinesbat, A. Feyzi and P. Nakhostin Panahi, J. Chem. Res., 2014, 38, 515.
- 42 K. Khosravi and S. Kazemi, J. Chin. Chem. Soc., 2012, 59, 641.
- 43 K. Khosravi, F. Pirbodaghi, S. Kazemi and A. Asgari, J. Iran. Chem. Soc., 2015, 12, 1333.
- 44 P. Ghorai and P.H. Dussault, Org. Lett., 2009, 11, 213.
- 45 K. Khosravi and A. Asgari, J. Advanc. Chem., 2015, 11, 3381.
- 46 D. Azarifar, O. Badalkhani, K. Khosravi and Y. Abbasi, J. Adv. Chem., 2015, 11, 3452.
- 47 D. Azarifar, Z. Najminejad and K. Khosravi, Synth. Commun., 2013, 43, 826.