Article

JOURNAL OF THE CHINESE
CHEMICAL SOCIETY

Nanomagnetic-supported Sulfonic Acid: Simple and Rapid Method for the Synthesis of α,α′-Bis-(substituted-benzylidene) Cycloalkanones

Ali Amoozadeh,* Eskandar Kolvari, Nadiya Koukabi and Somayeh Otokesh
Department of Organic Chemistry, Semnan University, Semnan, Iran

(Received: Sept. 7, 2014; Accepted: Dec. 26, 2014; Published Online: Apr. 17, 2015; DOI: 10.1002/jccs.201400377)

Nanomagnetic-supported sulfonic acid is found to be a powerful and reusable heterogeneous catalyst for the rapid synthesis of α,α′-bis-(substituted-benzylidene)cycloalkanones under conventional heating and solvent free conditions. High yield, simple work up and easy recovery of the catalyst are the most obvious advantages of this procedure.

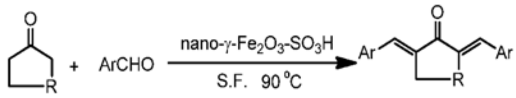
Keywords: Nanomagnetic-supported sulfonic acid; Heterogeneous catalyst; Solvent-free route; α,α′-Bis-(substituted-benzylidene)cycloalkanones.

INTRODUCTION

The α,α′-bis-(substituted-benzylidene) cycloalkanones motif is a versatile pharmacophore. This structure has been widely found in many important biologically active compounds. These compounds have shown activities including cytotoxicty,[1] cholesterol-lowering,[2] HIV-1 integrate inhibition,[3] cancer chemoprevention[4] and antioxidant.[5] Recently, bis-benzylidene cycloalkanones have been reported to possess drug resistance reversal.[6] They are frequently used for the synthesis a range of organic molecules with many applications such as precursors to potentially bioactive pyrimidine derivatives[7] and bis-spiropyrrolidines with antimicrobial and antifungal properties,[8] liquid-crystalline polymers.[9] For these reasons, the synthesis of titled compounds has attracted much more attention from organic and medicinal chemistry.

Commonly these compounds are synthesized by cross-aldol condensation and classically carried out using strong acid or base. However, in recent years a number of various catalysts have been used for this reactions such as wet 2,4,6-trichloro[1,3,5]triazine (TCT),[10] (SiO_2-R-SO_3H),[11] solid base SiO_2-OK,[12] polymer-supported sulphonic acid (NKC-9),[13] solid NaOH,[14] NaOAc,[15] ethanolic KOH[16] and ionic liquids.[17] But all them suffer from reverse and side reactions resulting low yields of the products. Consume minimal energy, reagents or auxiliaries and minimize waste are the principles of "Green Chemistry" for catalyzed organic reactions. Catalysts, in turn, could meet these goals. With the advent nanomagnetic catalysts, these goals can be achieved due to the high activity, easy separation, and protection of the environment. Magnetic nanoparticles have emerged as viable alternatives to porous materials for use as robust, readily available, high surface area heterogeneous catalysts in organic synthesis. Also insoluble and paramagnetic nature of these particles enables magnetically recoverable which facilitates reaction work-up and rapid sample processing, and most importantly reduces solvent consumption.[18-23] For these reasons, it is of interest to use nanomagnetic-supported sulfonic acid (γ-Fe_2O_3-SO_3H) for synthesis of α,α′-bis-(substituted-benzylidene) cycloalkanones under thermal condition (Scheme 1). Nano-γ-Fe_2O_3-SO_3H has been prepared by the reaction of chlorosulfonic acid with nano magnetite previously and was characterized thoroughly and has been used as catalyst in organic synthesis.[24]

Scheme 1 Preparation of α,α′-bis-(substituted-benzylidene) cycloalkanones



RESULTS AND DISCUSSION

In this paper, we used for the first time nano magnetic supported sulfonic acid catalyst for the synthesis of benzylidene. At the first glance, in order to optimize the conditions, the reaction of benzaldehyde, cyclopentanone was chosen as a model system under thermal conditions (Table 1). The nano-sized particles increase the exposed surface area of the active component of the catalyst, thereby enhancing the contact between reactants so the reaction process must be better with nano magnetic catalyst. We tested

---

* Corresponding author. Tel.: +982333366177; Fax: +98 (23) 33354082; E-mail: aamozadeh@semnan.ac.ir

Supporting information for this article is available on the www under http://dx.doi.org/10.1002/jccs.201400377

Table 1. Iron-based catalyzed synthesis of α,α′-bis-(substituted-benzylidene) cycloalkanones[a]

Entry	Catalyst (0.05 g)	Time (min)	Yield (%)[b]
1	Fe	20	-
2	$FeCl_3.6H_2O$	20	Trace
3	Bulk-Fe_2O_3	20	35
4	Bulk-Fe_2O_3-SO_3H	20	55
5	γ-Fe_2O_3-SO_3H	20	88

[a] Benzaldehyde-cyclopentanone = 2:1, Solvent-free, at 90 °C.
[b] Yields refer to isolated products.

Table 2. Influence of the amount of nano-γ-Fe_2O_3-SO_3H on the synthesis of α,α′-bis-(substituted-benzylidene) cycloalkanones[a]

Entry	γ-Fe_2O_3-SO_3H (g)	Time (min)	Yield (%)[b]
1	0.0125	20	64
2	0.025	20	74
3	0.05	20	88
4	0.07	20	82
5	0.1	20	80
6	0.15	20	73

[a] Benzaldehyde-cyclopentanone = 2:1, Solvent-free, at 90 °C.
[b] Yields refer to isolated products.

Table 3. The effect of temperature on the synthesis of α,α′-bis-(substituted-benzylidene) cycloalkanones[a]

Entry	Temperature (°C)	Time (min)	Yield (%)[b]
1	60	20	67
2	80	20	80
3	90	20	88
4	100	20	75

[a] Benzaldehyde-cyclopentanone = 2:1, Solvent-free.
[b] Yields refer to isolated products.

Table 4. Effect of the solvent on the synthesis of the α,α′-bis-(substituted-benzylidene) cycloalkanones[a]

Entry	Solvent	Time (min)	Yield (%)[b]
1	$CHCl_3$	20	42
2	EtOH	20	76
3	CH_3CN	20	76
4	CH_2Cl_2	20	65
5	H_2O	20	45
6	Solvent free	20	88

[a] Benzaldehyde-cyclopentanone = 2:1 at 90 °C.
[b] Yields refer to isolated products.

the model reaction in the present of different iron-based catalyst. As indicated from Table 1, the yield of product increases to 88% when used nano-γ-Fe_2O_3-SO_3H instead of Bulk-Fe_2O_3-SO_3H that shows the impact of nano particles on the reaction. No activity was observed in the presence of Fe and pure bulk-Fe_2O_3 (Table 1, Entries 1 and 3). A trace amount of product also observed when catalyzed by $FeCl_3.6H_2O$ (Entry 2). The reaction was clean and fairly rapid. No side products were detected in these reactions.

The amount of the catalyst is a main factor affecting the synthesis procedure. To study the required catalyst load, we explore different reaction condition under solvent free condition and results are summarized in Table 2. The results show that the product **3a** could be obtained in yield range 64 to 88%. Hence 0.05 g of nano-γ-Fe_2O_3-SO_3H can be catalyze aldol condensation for synthesis of α,α′-bis-(substituted-benzylidene) cycloalkanones (Table 2, Entry 3). It be should noted that more increasing catalyst amount did not affect the total yield (Table 2, Entries 4-6).

Afterwards, we investigated the effect of temperature on the reaction rate as well as the yields of products. To study the effect of temperature, we explored some reaction conditions for aldol condensation of cyclopentanone and benzaldehyde in the presence of 0.05 g nano-γ-Fe_2O_3-SO_3H under solvent free condition. The results are summarized in Table 3. According to the obtained results, 90 °C was selected for synthesis procedure (Table 3, Entry 3).

After determining the appropriate amount of catalyst and the optimum temperature and for making sure that solvent free conditions provide the best yields, we have examined the effect of different solvents by using the same reaction conditions, as shown in Table 4. Moreover, when the reaction was carried out in solvent-free condition, good conversion was achieved (Table 4, Entry 5).

It is important to note that the ferromagnetic property of nano-γ-Fe_2O_3-SO_3H made easy isolation and reuse of catalyst. After completion of reaction, mixture turned clear and catalyst was deposited on the magnetic bar, which was easily removed using an external magnet. After being washed with acetone and dried in air, the nano-γ-Fe_2O_3-SO_3H can be directly reused without any deactivation even after five rounds of synthesis of products (Table 5).

In this method under the optimized conditions, we also examined scope of the reaction by using various aryl aldehydes with electron-donating and electron-withdrawing groups and cyclic ketones (cyclopentanone, cyclohexanone, tert-butylcyclohexanone) and condensation products produced in good yields, the results are summarized in Table 6. As shown, the reaction works easily for a variety

Table 5. Reusability of nano-γ-Fe_2O_3-SO_3H in the synthesis of α,α′-bis-benzylidenecycloalkanone[a]

Run	Time (min)	Yield (%)[b]
1	20	88
2	20	86
3	20	84
4	20	81
5	20	77

[a] Benzaldehyde-cyclopentanone = 2:1, Solvent-free, at 90 °C.

[b] Yields refer to isolated products.

of aldehydes with both electron-donating and electron-withdrawing groups to give corresponding α,α′-bis(substitutedbenzylidene) cyclohexanones in good to excellent yields. It is important to note that nature of the substituted on the aromatic ring had effect on this reaction. In general, aromatic aldehydes carrying electron-donating groups (such as methyl and methoxy) (Table 6, Entries 2, 3 and 8, 9) gave cleaner reaction in shorter times than aromatic aldehydes carrying electron-withdrawing groups (Table 6, Entries 4, 5, 6 and 10, 11, 12). Steric effects can play an important role in rate and yield of reaction, substituent on the ring at the *para* position (Table 6, Entries 6, 12 and 17) react faster than *ortho* position (Table 6, Entries 4, 10 and 11). It would be interesting to test the reaction on acyclic ketones as well, but it falls outside the scope of the investigation. On the other hand, compared to different ketones, cyclohexanone (Table 6, Entries 7-11) reacts faster than cyclopentanone (Table 6, Entries 1-5).

Table 7 compares the efficiency of our method with the efficiency of other published results of the same aldol reaction. As indicated in Table 7, our method provides high yield (88%) within 20 minutes (Table 7 Entry 18). The main advantages of our method are fast reaction time, clean and environmentally benign reagents and ease of separation of catalyst with external magnet.

EXPERIMENTAL

General: The IR spectra were recorded on a Perkin-Elmer model 783 spectrophotometer (Waltham, MA, USA). The NMR spectra were obtained on a Bruker AMX-300 (300 MHz) spectrometer (Ettlingen, Germany). The solvent was $CDCl_3$. Tetra methyl silane (TMS) was used as internal reference.

Typical reaction for the synthesis of 2,5-dibenzylidene-cyclopentanone (Table 6, Entry 1): A mixture of benzaldehyde (2 mmol), cyclopentanone (1 mmol), and nano-γ-Fe_2O_3-SO_3H (0.05 g) was heated at 90 °C. After completion of the reaction, hot ethanol (5 mL) was added to the mixture. In the presence of a

Table 6. Preparation of α,α′-bis-benzylidenecycloalkanone derivatives by nano-γ-Fe_2O_3-SO_3H[a]

Entry	Ar	R	Product	Time (min)	Yield (%)[b]	M.p. (°C)
1	C_6H_5	CH_2	3a	20	88	190-191
2	p-MeC_6H_4	CH_2	3b	20	87	245-246
3	p-$MeOC_6H_4$	CH_2	3c	20	85	211-213
4	o-ClC_6H_4	CH_2	3d	35	83	162-163
5	o-$O_2NC_6H_4$	CH_2	3e	40	87	168-170
6	p-ClC_6H_4	CH_2	3f	35	89	225-226
7	C_6H_5	CH_2CH_2	3g	15	91	114-116
8	p-MeC_6H_4	CH_2CH_2	3h	15	87	162-163
9	p-$MeOC_6H_4$	CH_2CH_2	3i	20	94	163-165
10	o-ClC_6H_4	CH_2CH_2	3j	27	87	103-107
11	o-$O_2NC_6H_4$	CH_2CH_2	3l	35	90	158-159
12	p-$O_2NC_6H_4$	CH_2CH_2	3k	30	95	160-162
13	2,6-diClC_6H_4	CH_2CH_2	3m	60	88	181-183
14	p-FC_6H_4	CH_2CH_2	3n	32	96	152-154
15	p-BrC_6H_4	CH_2CH_2	3o	15	91	165-168
16	$Me_2NC_6H_4$	CH_2CH_2	3p	30	85	250-252
17	p-ClC_6H_4	CH_2CH_2	3q	30	93	146-148
18	p-NCC_6H_5	CH_2CH_2	3r	60	85	208-211
19	C_6H_5	$CH_2CHC(CH_3)_3$	3s	60	83	124-127
20	o-$O_2NC_6H_4$	$CH_2CHC(CH_3)_3$	3t	80	80	208-211
21	C_6H_5	$CO(CH_3)_2$	3u	100	84	109-111

[a] Aromatic aldehyde-ketone = 2:1, Solvent-free, at 90 °C.

[b] Yields refer to isolated products, which were characterized by comparison of their spectroscopic and physical data with those of samples synthesized by reported procedures [16, 25,10].

Table 7. Comparison of the results obtained for the synthesis α,α′-bis-(substituted-benzylidene) cyclopentanone catalyzed by nano-γ-Fe_2O_3-SO_3H with those recently reported catalysts

Entry	Catalyst	Condition	Time (min)	Yield (%)	Ref.
1	I_2	CH_2Cl_2/r.t.	270	89	[26]
2	KOH	Ethanol/40 °C	5	98	[16]
3	SiO_2-R-SO_3H	S.F./90 °C	90	85	[11]
4	KF/Al_2O_3	MW/450W	5	73	[27]
5	NKC-9	$CHCl_3$/80 °C	240	90	[13]
6	NaOAc	HOAc/120 °C	420	86	[15]
7	NaOH	Grinding	5	98	[14]
8	Si_2OK	Ethanol/Reflux	180	87	[12]
9	TCT	S.F./90 °C	20	92	[10]
10	$[N_{2222}][EtNHC_3SO_3]$	water/60 °C	360	94	[28]
11	$LiClO_4$	$TMSNEt_2$/r.t.	7	97	[29]
12	SmI_3	THF/Reflax	360	85	[30]
13	$AlCl_3$	PEG/r.t.	120	94	[25]
14	BDMS	S.F./r.t.	3	96	[31]
15	NH_4Cl	EtOH/Reflux	300	93	[32]
16	KF/Al_2O_3	MeOH/ultra son.	40	89	[33]
17	$FeCl_3.6H_2O$	[bmim][BF_4]/80 °C	360	92	[34]
18	γ-Fe_2O_3-SO_3H	S.F./90 °C	20	88	This work

magnetic stirrer bar, nano-γ-Fe_2O_3-SO_3H moved onto the stirrer bar steadily and the reaction mixture turned clear within 10 s. The catalyst can be isolated by simple decantation and the crude product was recrystallized from hot EtOH to give a pure product.

Spectra Data

α,α′-Bis-(4-cyano-benzylidene)cyclohexanone (3r): Yellow powder; M.p. = 208-211 °C ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.75 (2H, sbr), 7.70 (4H, dbr, J = 8.20 Hz), 7.53 (4H, dbr, J = 8.35 Hz), 2.91 (4H, m), 1.83 ppm (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.29, 140.20, 138.23, 135.22, 135.18, 132.14, 130.57, 118.51, 112.00, 28.30, 22.56 ppm. IR (KBr): 2223, 1666, 1577, 1500, 1139 cm^{-1}. Anal. calc. for $C_{22}H_{16}N_2O$: C 81.49; H 4.93; N 8.63 %; found: C 81.10; H 4.88; N 8.56 %. **α,α′-bis-(2-nitro-benzylidene)cyclopentanone (3e)**: Yellow powder; M.p. = 168-170° C ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.86 (2H, sbr), 7.52 (4H, J = 6 Hz), 8.11 (4H, J = 6 Hz), 2.88 (4H, sbr), ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.33, 148.86, 140.14 130.59, 125.03, 25.98 ppm. IR (KBr): 3080, 2914, 1691, 1517, 1473 cm^{-1}. Anal. calc. for $C_{19}H_{14}N_2O_5$: C, 65.14; H, 4.03; N, 8.00; O, 22.84%. found: C, 65.11; H, 3.89; N, 7.93; O, 22.75 %. **α,α′-bis-benzylidene-4-(tert-butyl)cyclohexanone (3s):** Yellow powder; M.p. = 124-127 °C ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.78 (2H, sbr), 7.33-7.49 (4H, m), 2.49 (2H, m), 3.20 (2H, m), 1.4-1.6 (1H, m), 0.96 (9H, m), ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.64, 136.85, 25.98 ppm. IR (KBr): 3083, 2867, 1660, 1490, 1446 cm^{-1}. Anal. calc. for $C_{24}H_{26}O$: C, 87.23; H, 7.93; O, 4.84%. found: C, 86.98; H, 7.71; O, 4.79%. **α,α′-bis-(2-nitrobenzylidene)-4-(tert-butyl)cyclohexanone (3t):** Yellow powder; M.p. = 208-211 °C ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ 7.9 (2H, sbr), 7.37-7.69 (4H, m), 2.18 (2H, m), 2.77 (2H, m) 1.4-1.6 (1H, m), 0.7 (4H, sbr), ^{13}C NMR (75 MHz, $CDCl_3$): 188.82, 148.19, 137.28, 29.02 ppm. IR (KBr): 3075, 2960, 1674, 1519, 1440 cm^{-1}. Anal. calc. for $C_{24}H_{24}N_2O_5$: C, 68.56; H, 5.75; N, 6.66; O, 19.03%. found: C, 68.33; H, 5.58; N, 6.62; O, 18.93% .

CONCLUSIONS

In conclusion, an efficient, sustainable and green procedure for synthesis of α,α′-bis-(substituted-benzylidene)cycloalkanones has been developed using a magnetically separable and easily recyclable nano-γ-Fe_2O_3-SO_3H catalyst in solvent free medium under thermal condition. Easy magnetic separation of the catalyst eliminates the requirement of catalyst filtration after completion of the reaction which is an additional greener attribute of this reaction.

ACKNOWLEDGEMENTS

We thank the Department of Chemistry of Semnan University for supporting this work.

REFERENCES

1. (a) Dimmock, J. R.; Padmanilayam, M. P.; Zello, G. A.; Nienaber, K. H.; Allen, T. M.; Santos, C. L.; De Clercq, E.; Balzarini, J.; Manavathu, E. K.; Stables, J. P. *Eur. J. Med.*

Chem. **2003**, *38*, 169-177. (b) Modzelewska, A.; Pettit, C.; Achanta, G.; Davidson, E. N.; Huang, P.; Khan, S. R. *Bioorg. Med. Chem.* **2006,** *14*, 3491-3495.

2. Piantadosi, C.; Hall, I. H.; Irvine, J. L.; Carlson, G. L. *J. Med. Chem*. **1973**, *16*, 770-775.
3. Costi, R.; Santo, R. D.; Artico, M.; Massa, S.; Ragno, R.; Loddo, R.; La Colla, M.; Tramontano, E.; La Colla, P.; Pani, A. *Bioorg. Med. Chem*. **2004**, *12*, 199-215.
4. Gafner, S.; Lee, S. K.; Cuendet, M.; Barthelemy, S.; Vergnes, L.; Labidalle, S. R.; Mehta, G.; Boone, C. W.; Pezzuto, J. M. *Phytochemistry* **2004**, *65*, 2849-2859.
5. Weber, W. M.; Hunsaker, L. M.; Abcouwer, S. F.; Deck, L. M.; Vander Jagt, L. M. *Bioorg. Med. Chem*. **2005**, *13*, 3811-3820.
6. Das, U.; Kawase, M.; Sakagami, H.; Ideo, A.; Shimada, J.; Molnár, J.; Baráth, Z.; Bata, Z.; Dimmock, J. R. *Bioorg. Med. Chem.* **2007**, *15*, 3373-3380.
7. Fosun, R. C.; San, T.; Deikmann, J. *J. Org. Chem.* **1962**, *27*, 1221-1223.
8. Raj, A. A.; Raghunathan, R.; SrideviKumari, M. R.; Raman, N. *Med. Chem.* **2003**, *11*, 407-419.
9. Kishore, K. *Polymer*. **1995**, *36*, 1903-1910.
10. Bigdeli, M. A.; Mahdavinia, G. H.; Safari, S.; Hazarkhani, H. *Catal. Commun*. **2007**, *8*, 2229-2231.
11. Habibi, A.; Sheikhhosseini, E.; Bigdeli, M.; Balalaie, S.; Farrokhi, E. *Int. J. Org. Chem*. **2011**, *1*, 143-147.
12. Jin, T.; Zaho, Y.; Liu, L.; Li, T. *Indian J. Chem. Sect B*. **2006**, *45B*, 1965-1967.
13. An, L. T.; Zou, J. P.; Zhang, L. L. *Catal. Commun.* **2008**, *9*, 349-354.
14. Rahman, A. F. M. M.; Ali. R.; Jahng, Y.; Kadi A, A. *Molecules* **2012**, *17*, 571-583.
15. Rahman, A. F. M. M.; Jeong, B. S.; Kim, D. H.; Park, J. K.; Lee, E. S.; Jahng, Y. *Tetrahedron* **2007**, *63*, 2426-2431.
16. Mahdavinia, G. H.; Mirzazadeh, M. *E- J. Chem*. **2012**, *9*, 49-54.
17. Wang, C.; Liu, X.; Yang, M.; Ma, H.; Yan, P.; Slattery, J. M.; Gao, Y. *RSC Adv.* **2013**, *3*, 8796-8804.
18. Nasir Baig, R. B.; Varma Rajender, S. *Chem. Commun*. **2013**, *49*, 752-770.
19. Sheykan, M.; Mohammadnejad, H.; Akbari, J.; Heydari, A. *Tetrahedron Lett*. **2012**, *53*, 2959-2964.
20. Gawande, M. B.; Rathi, A. K.; Branco, P. S.; Varma, R. S. *Appl. Sci*. **2013**, *3*, 656-674.
21. Baig, R. B. N.; Varma, R. S. *Green Chem*. **2013**, *15*, 398-417.
22. Polshettiwar, V.; Varma, R. S. *Chem. Eur. J*. **2009**, *15*, 1582-1586.
23. Luque, R.; Baruwati, B.; Varma, R. S. *Green Chem*. **2010**, *12*, 1540-1543.
24. (a) Koukabi, N.; Kolvari, E.; Zolfigol, M. A.; Khazaei, A.; Shirmardi-Shaghasemi, B.; Fasahati, B. *Adv. Synth. Catal*. **2012**, *354*, 2001-2008. (b) Koukabi, N.; Kolvari, E.; Khazaei, A.; Zolfigol, M. A.; Shirmardi-Shaghasemi, B.; Khavasi, H. R. *Chem. Commun*. **2011**, *47*, 9230–9232. (c) Kolvari, E.; Koukabi, N.; Armandpour, O. *Tetrahedron*. **2014**, *70*, 1383-1386. (d) Kolvari, E.; Amoozadeh, A.; Koukabi, N.; Otokesh, S.; Isari, M. *Tetrahedron Lett*. **2014**, *55*, 3648-3651.
25. Amoozadeh, A.; Rahmani, S.; Nemati, F. *S. Afr. J. Chem*. **2010**, 72-74.
26. Das, B.; Thirupathi, P.; Mahender, I.; Ravinder Reddy, K. *J. Mol. Catal. A: Chem*. **2006**, *247*, 182-185.
27. Wang, J. X.; Liqin, K.; Yuai, H.; Bangguo, G. *Syn. Commun*. **2002**, *32*, 1691-1696.
28. Wang, C.; Liu, X.; Yang, M.; Ma, H.; Yan, P.; Slatteryb, J.; Gao, Y. *RSC Adv.* **2013**, *3*, 8796-8804.
29. Abaee, M. S.; Mojtahedi, M. M.; Sharifi, R.; Zahedi, M. M.; Abbasi, H.; Tabar-Heidar, K. *J. Iran. Chem. Soc*. **2006**, *3*, 293-296.
30. Bao, W-L.; Zhang, Y. M.; Taokai, Y. K. *Synth. Commun*. **1996**, *26*, 503-507.
31. Zhao, C. Y.; Liu, J. Y.; Wang, Y.; Zhao, X. J.; Yuan, B.; Yue, M. M. *Synth. Commun*. **2014**, *44*, 827-835.
32. Teimouri, F.; Hadi Khezri, S.; Miri, Z.; Eftekhari-Sis, B.; Azizian, J. *J. Sci. I. A. U.* **2009**, *19*, 103-108.
33. Li, J. T.; Yang, W. Z.; Chen, G. F.; Li, T. S. *Synth. Commun*. **2003**, *33*, 2619-2625.
34. Zhang, X. Y.; Fan, X. S.; Niu, H. Y.; Wang, J. J. *Chin. Chem. Lett.* **2003**, *14*, 1005-1007.