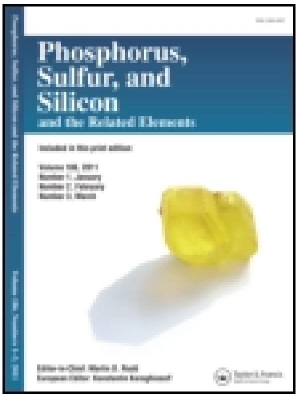

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Heterogeneous and Catalytic Thiocyanation of Aromatic Compounds in Aqueous Media

Mohammad Ali Zolfigol [a] , Ardeshir Khazaei [a] , Mohammad Mokhlesi [a] , Hoshang Vahedi [b] , Sami Sajadifar [a] [b] & Mahtab Pirveysian [a]
[a] Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran
[b] Chemistry Department, Payame Noor University, 19395-4697, Tehran, I. R. of Iran

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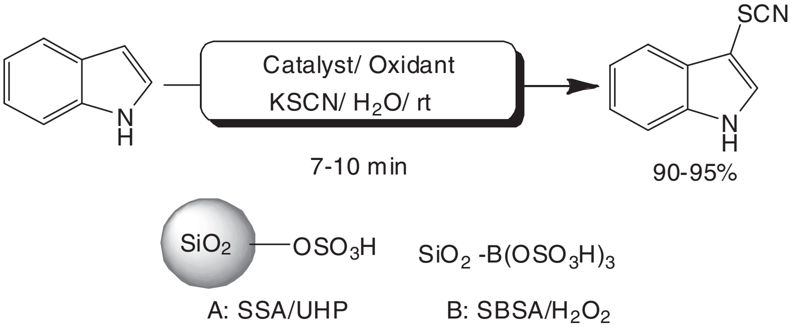
HETEROGENEOUS AND CATALYTIC THIOCYANATION OF AROMATIC COMPOUNDS IN AQUEOUS MEDIA

Mohammad Ali Zolfigol,[1] Ardeshir Khazaei,[1] Mohammad Mokhlesi,[1] Hoshang Vahedi,[2] Sami Sajadifar,[1,2] and Mahtab Pirveysian[1]
[1]*Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran*
[2]*Chemistry Department, Payame Noor University, 19395-4697 Tehran, I. R. of Iran*

GRAPHICAL ABSTRACT



Abstract *This article describes a highly efficient heterogeneous catalytic thiocyanation of indoles, substituted anilines (electron rich and electron deficient) and N-substituted aromatic amines in water under mild and green conditions. The reaction of substrates with KSCN in the presence of silica sulfuric acid (SSA) and silica boron sulfonic acid (SBSA) as heterogeneous catalysts and H_2O_2 or UHP (urea hydrogen peroxide) as green oxidants produces aryl thiocyanates in short reaction times and high yields. Moreover, in this article, some novel aryl thiocyanates were synthesized.*

Keywords Silica sulfuric acid; silica boron sulfonic acid; thiocyanation; water; heterogeneous

INTRODUCTION

One of the useful reactions for the introduction of sulfur into aromatic systems is thiocyanation. Thiocyanate is a versatile synthon that can be readily transferred to

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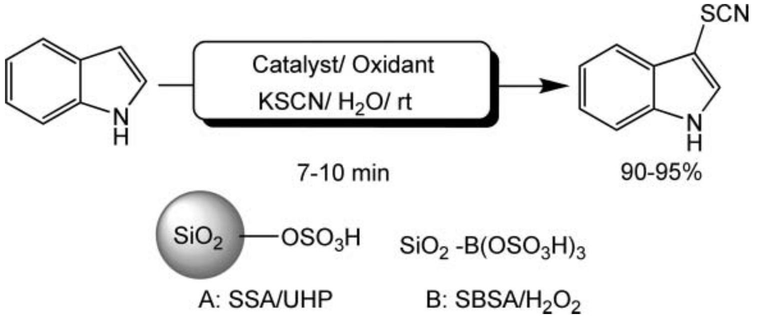
Address correspondence to Mohammad Ali Zolfigol, Faculty of Chemistry, Bu-Ali Sina University, P.O. Box 6517838683, Hamedan, Iran. E-mail: zolfi@basu.ac.ir

other functional groups such as sulfide,[1] aryl nitrile,[2] thiocarbamate,[3] and thionitrile.[4] Therefore, it is important to find new, safe, fast, and useful methods for the synthesis of aryl thiocyanates.[5–11] Various methods have been reported for the thiocyanation of aromatic and heteroaromatic systems such as, *N*-thiocyanatosuccinimide,[12] iodine/methanol,[13] diethyl azodicarboxylate,[14] IL-$OPPh_2$,[15] I_2O_5,[16] pentavalent iodine,[17] IBX,[18] and Selectfluor^{TM}.[19] However, most of the reported methods for the synthesis of aryl thiocyanates are associated with one or more of the following drawbacks: (1) low yields, (2) long reaction times, (3) the use of a large amount of catalyst, (4) the use of toxic or expensive catalysts, (5) a tedious work-up procedure, and (6) performances under certain special conditions. Thus, finding an efficient, inexpensive, and nonpolluting method for the synthesis of this class of compounds is still of practical importance.

In recent years, the application of eco-friendly applicable industrial and green catalysts has received considerable interest.[20] Thus, green chemistry has been defined as a set of principles that reduces or eliminates the use or generation of hazardous substances and catalysts throughout the entire life of chemical materials. Along this line, using heterogeneous catalysts as green, inexpensive and nontoxic catalysts, have found more attention. They have been used as an efficient acidic catalyst in organic synthesis. For example, they have efficiently catalyzed oxidation of sulfides,[21] thioacetalization of carbonyl compounds,[22] von Pechmann Reaction,[23] thioacetalization of carbonyl compounds,[24] synthesis of benzimidazoles,[25] synthesis of 3,4-dihydropyryimidinones,[26] α-bromination of carbonyl compouns,[27] and acetalization of carbonyl compounds.[28]

According to our previously reported results on the applications of heterogeneous catalysts such as silica sulfuric acid (SSA) in organic reactions,[29,30] now, we wish to report an efficient and convenient procedure for the thiocyanation of aromatic compounds using silica supported catalysts in conjunction with UHP (urea hydrogen peroxide) or hydrogen peroxide under green conditions (Scheme 1).



Scheme 1

RESULT AND DISCUSSION

For the synthesis of aryl thiocyanate, conversion of indole into its corresponding indole thiocyanate has been considered as a model reaction. At first, the reaction was examined in the presence of some different catalysts such as SiO_2, p-Tol-SO_3H, SSA, and silica boron sulfonic acid (SBSA) at room temperature. The results are summarized in Table 1. As Table 1 indicates, in the absence of a catalyst, when indole was treated with hydrogen peroxide and KSCN, no product was obtained. If SiO_2 was directly used as catalyst, the

Table 1 The thiocyanation of indole using different catalysts

Entry	Catalyst	Time (min)	Yield (%)[a]
>1	—	180	No reaction
2	SiO_2[b]	180	15
3	4-Me-Ph-SO_3H (5%)	180	30
4	4-Me-Ph-SO_3H (10%)	180	50
5	4-Me-Ph-SO_3H (15%)	180	60
6	4-Me-Ph-SO_3H (20)	100	75
7	SSA (0.05 g)	180	40
8	SSA (0.1 g)	30	92
9	SSA (0.2g)	7	95
10	SBSA (0.01 g)	90	89
11	SBSA (0.05 g)	10	90

[a]Isolated yields. [b]SiO_2 (50–60 mesh).

yield of product was 15% (entry 2). The use of *p*-tol-SO_3H was also examined whereby a moderate yield of product was obtained but it needs a long reaction time (entries 3–6). Then, we examined heterogeneous catalysts, and as shown in Table 1, higher yields and shorter reaction times were obtained when SSA and SBSA were utilized as catalysts (Table 1, entries 7–11). The optimal amounts of the catalysts were 10 mol% (0.2 g) and 5 mol% (0.05 g) respectively.

In the next step, we examined the effect of solvents on the reaction. Water, methanol, ethanol, and acetonitrile were used as solvents and surprisingly the same results were obtained (Table 2, entries 1–4). In other organic solvents reaction were proceeded in longer reaction time (Table 2, entries 5–7). Therefore, water was chosen as the preferred solvent.

In continuation, a wide range of aromatic and hetero-aromatic compounds were used for the thiocyanation. The reaction was mild and clean for hetero aromatics, electron rich, and deficient anilines and *N*-substituted amines. High regioselectivity, excellent yields and short reaction times were obtained in all cases (Table 3). As shown in Table 3, in two methods, indole and its derivatives as electron rich heterocycles, are produced as the product with good to excellent yields (Table 3, 1a–1d). Also, 5-bromoindole reacted with KSCN to afford the corresponding 5-bromo-3- thiocyanato indole in good yields, but required longer

Table 2 Optimization of solvent for thiocyanation reaction

		Time (min)		Yield (%)[a]	
Entry	Solvent	A	B	A	B
1	H_2O	7	10	95	90
2	MeOH	<5	<5	91	94
3	EtOH	<5	<5	91	89
4	CH_3CN	< 5	< 5	95	93
5	CH_2Cl_2	90	90	55	45
6	$CHCl_3$	90	90	45	30
7	EtOAc	90	90	75	50

[a]Isolated yields.

Table 3 Thiocyanation of heterocycle compounds in aqueous media

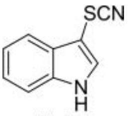
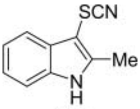
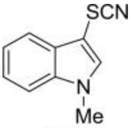
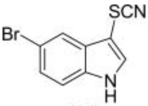
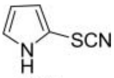
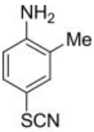
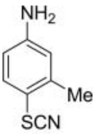
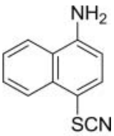
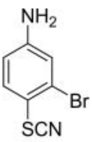
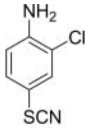
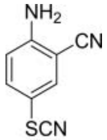
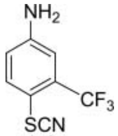
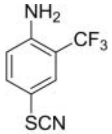
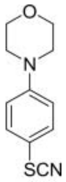
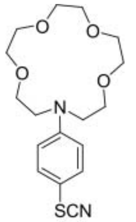
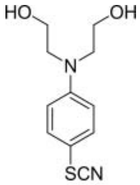
	SSA/UHp		SBSA/H_2O_2		Melting point
Product	Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]	Found (lit)
 (1a)	7	95	10	90	(70–72) (71–73)[8]
 (1b)	50	84	20	80	(97–99) (99–101)[6]
 (1c)	15	85	10	87	(79–81) (83–84)[6]
 (1d)	45	78	25	87	113–115) (127–129)[6]
 (1e)	40	88	10	91	liquid (liquid)[6]
 (1f)	15	90	45	92	(62–64) (–)[b]
 (1g)	10	94	40	89	(70–71) (–)[b]
 (1h)	45	89	45	83	(191–194) (–)[b]
 (1i)	40	86	50	90	(69–71) (71–73)[8]

Table 3 Thiocyanation of heterocycle compounds in aqueous media *(Continued)*

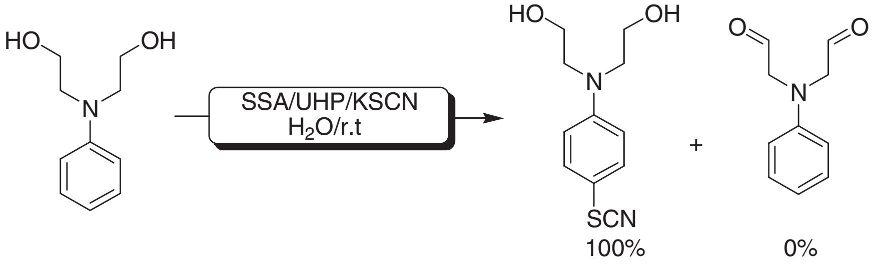
	SSA/UHp		SBSA/H_2O_2		Melting point
Product	Time (min)	Yield (%)[a]	Time (min)	Yield (%)[a]	Found (lit)
 (1j)	35	90	55	85	(58–60) (60–61)[6]
 (1k)	55	88	60	82	(58–60) (–)[b]
 (1l)	75	79	3.5 (h)	71	(97–99) (–)[b]
 (1m)	70	71	4.5 (h)	76	(148–150) (–)[b]
 (1n)	40	91	60	89	(74–76) (–)[b]
 (1o)	10	95	60	85	(77–80) (–)[b]
 (1p)	45	83	4 (h)	79	(66–69) (–)[b]

[a] Isolated yields. [b] This compound is new.

reaction times (Table 3, 1d). This observation can be attributed to the lower electron density of such substrates.

Thiocyanation of pyrrole was also investigated. In two methods, pyrrole was produced the 2-thiocyanato pyrrole in short reaction time and high efficiency (Table 3, 1e).

After our investigation of the thiocyanation reaction of heterocycles, we examined the ability of aromatic amines in the thiocyanation reaction (Scheme 2). In all cases, the substitution was highly regioselective at the para-position of the aromatic ring. The reaction of potassium thiocyanate with electron rich amines such as *o*-toluidine, *m*-toluidine, and 1-amino naphthalene, occurred under the same conditions (Table 3, entries 1f–1h). Our studies showed that electron deficient amines are also converted in this reaction, but they need more time (Table 3, 1i–1m). In accord, on reaction times, we investigated the effect of halogens and inductive and resonance withdrawing groups. As shown in Table 3, in the presence of halogens groups such as Cl and Br, the reactions took place at longer time but in good yields (Table 3, 1i, 1j). Similarly, the effect of inductive and resonance withdrawing groups such as CF_3 and CN was studied. In both, the reaction times were longer but the yields are as acceptable as other substrates (Table 3, 1k–1m). In the case of *N*-substituted amines, when *N*-phenyl morpholine and *N*-phenyl-15-crown-5 were used as the substrate, the products were produced in a short reaction time and excellent yields.



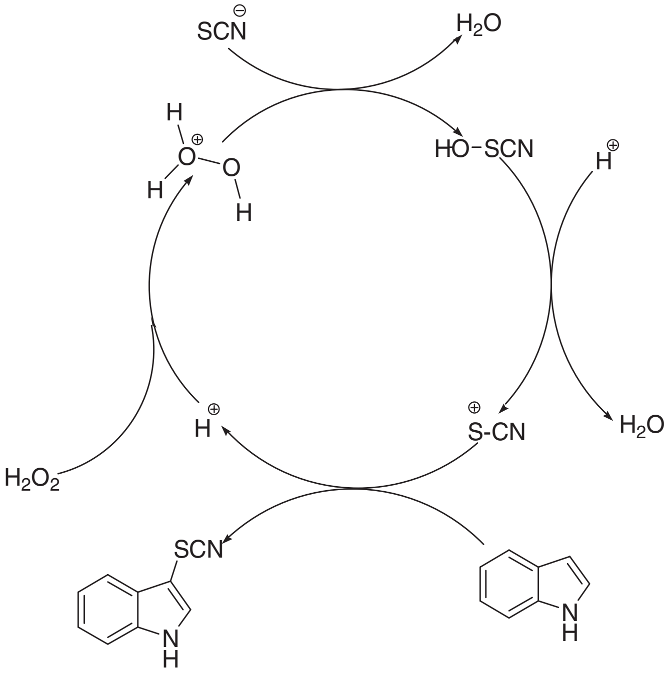
Scheme 2

Oxidizable functional groups such as alcoholic hydroxyl group remain intact under the reaction conditions (Scheme 2). For example, *N*-phenyl-2, 2-iminodiethanol, in the presence of KSCN, UHP and SSA, was converted to 4-thiocyanato *N*-phenyl-2, 2-iminodiethanol and oxidation of the hydroxyl to aldehyde did not occur. The above mentioned fact was proven by spectroscopy techniques. In its infrared spectrum, the presence of a sharp and single peak at 2153 cm^{-1} confirmed the presence of the SCN group.

Furthermore, a broad peak related to the OH group exists in 3300 cm^{-1}. Around 1650–1800 cm^{-1}, the C=O group peak was not observed.

A proposed reaction mechanism is shown in Scheme 3. In the first step, H_2O_2 reacts with H^+ and generates the hydrogen peroxonium ion ($H_3O_2{}^+$) in situ.[31] Subsequently, reaction of this cation with SCN^- generates HOSCN,[32] which in the presence of H^+ is able to produce thiocyanium ion $(S\text{-}CN)^+$ and H_2O. In the last step, the thiocyanium ion $(S\text{-}CN)^+$ attacks indole and produces the corresponding indole thiocyanate.

Finally, we compared our results with other reported methods using other reagents that require refluxing conditions, ultrasonic irradiation, toxic solvent, or oxidant. As shown in Table 4, the described methods in this article occurred under mild and green reaction conditions.



Scheme 3

In conclusion, we have developed an efficient, simple, and green mediated thiocyanation of aromatic compounds with high regioselectivity. The described methods have advantages such as simple work-up, short reaction time, metal free, mild reaction conditions, and clean production of the desired products in high yields.

EXPERIMENTAL

Preparation of Silica Boron Sulfonic Acid

A 50 mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. Boric acid (1.55 g, 25 mmol) was charged in the flask and chlorosulfonic

Table 4 Thiocyanation of indole in various systems

Entry	System	Time (min)	Yield% [Ref.]
1	SSA/UHP	7	95 (This work)
2	SBSA/H_2O_2	10	90 (This work)
3	I_2/MeOH	50	85 [13]
4	DDQ	50	94 [5]
5	DEAD	45	85 [14]
6	$Mn(OAc)_3$	2 (h)	83 [14]
7	Oxone	43	98 [8]
8	m.K10clay, 8 0 °C	2 (h)	85 [6]

acid (8.74 g, *ca.* 5 mL, 75 mmol) in CH_2Cl_2 (5 mL) was added dropwise over a period of 1 h at room temperature under N_2 gas. HCl evolved immediately. After completion of the addition, the mixture was shaken for 85 min, while the residual HCl was eliminated by suction.[33] Then, the mixture was washed with diethyl ether to remove the unreacted chlorosulfonic acid and then SiO_2 was added (14.4 g) and mixed. Finally, dried and a grayish solid material was obtained in 95.6% yield (21.6 g).

General Procedure for the Preparation of Aryl Thiocyanate Using SBSA and H_2O_2

A suspension of substrate (1 mmol), potassium thiocyanate (0.228 g, 3 mmol) and SBSA (0.05g) in H_2O (5–7 mL) was stirred at room temperature for 10 min. Then, a solution of H_2O_2 (30%, 0.282 g, 3 mmol) was added dropwise (2–5 min). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with $CHCl_3$ (2 × 10 mL). Anhydrous Na_2SO_4 (2 g) was added to the organic layer and filtered off after 20 min. The chloroform was removed under vacuum. The crude product was adsorbed onto silica and purified by short column chromatography on silica gel using n-hexane/EtOAc to afford pure product.

General Procedure for the Preparation of Aryl Thiocyanate Using SSA and UHP

A suspension of substrate (1 mmol), potassium thiocyanate (0.291 g, 3 mmol) and SSA (0.2g) in H_2O (5–7 mL) was stirred at room temperature for 10 min. Then, the solution of UHP (0.282 g, 3 mmol in 3–5 mL H_2O) was added dropwise (2–5 min). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with $CHCl_3$ (2 × 10 mL). Anhydrous Na_2SO_4 (2 g) was added to the organic layer and filtered off after 20 min. $CHCl_3$ was removed and further purification was achieved by silica gel short column chromatography hexane/EtOAc.

Note: compounds **1f**, **1h**, **1k**, **1l**, **1m**, **1n**, **1o**, and **1p** are previously unreported.

SELECTED SPECTRAL DATA

2-Methyl-4-thiocyanato Aniline (1f)

IR (KBr): 2153, 3369, 3456 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 6.64–7.37 (m, 3H), 3.99 (s, br, 2H, NH_2), 2.12 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 147.3, 135.1, 132.1, 123.9, 115.8, 112.8, 108.8, 17.2. MS: $m/z = 164$ (M^+).

3-Methyl-4-thiocyanato Aniline (1g)

IR (KBr): 2146, 3219, 3337 cm^{-1}, ^{1}H NMR ($CDCl_3$): δ 6.64–7.37 (m, 3H), 3.98 (s, br, 2H, NH_2), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 149.7,143, 136.3, 117.3, 112.4, 108.4, 21.2. MS: $m/z = 164$ (M^+).

4-Thiocyanato-1-naphthyl Amine (1h)

IR (KBr): 2146, 3358, 3442 cm^{-1}, ^{1}H NMR (CDCl$_3$): δ 6.71–7.85 (m, 6H), 4.58 (s, br, 2H). ^{13}C NMR (CDCl$_3$): δ 136.2, 128.2, 125.8, 125.6, 121.6, 108.9. MS: *m/z* = 200 (M$^+$).

2-Cyano-4-thiocyanato aniline (1k)

IR (KBr): 2156, 2222, 3360 cm^{-1}, 3444, ^{1}H NMR (CDCl$_3$): δ 7.28–7.58 (m, 2H), 6.83 (s, 1H), 4.96 (s, br, 2H, NH$_2$). ^{13}C NMR (CDCl$_3$): δ 151.7, 138.4, 137.2, 117.8, 116, 111.3, 109.3, 96.7. MS: *m/z* = 175 (M$^+$).

3-Triflouro methyl-4-thiocyanato Aniline (1l)

IR (KBr): 2160, 3275, 3369 cm^{-1}, ^{1}H NMR (CDCl$_3$): δ 7.33–7.82 (m, 3H), 4.01 (s, br, 2H, NH$_2$). ^{13}C NMR (CDCl$_3$): δ 144.6, 135.3, 125.5, 118.8, 117.4, 115.1, 111.7. MS: *m/z* = 218 (M$^+$).

2-Triflouro methyl-4-thiocyanato Aniline (1m)

IR (KBr): 2158, 3395, 3435 cm^{-1}, ^{1}H NMR (CDCl$_3$): δ 7.28–7.68 (m, 2H), 6.809 (s, 1H), 4.574 (s, br, 2H, NH$_2$). ^{13}C NMR (CDCl$_3$): δ 146.7, 137.5, 131.9, 125.6, 114.3, 111.6, 109.2. MS: *m/z* = 218 (M$^+$).

4-Thiocyanato *N*-phenyl Morpholine (1n)

IR (KBr): 2156 cm^{-1}, ^{1}H NMR (CDCl$_3$): δ 7.48 (d, 2H, J = 8.29 Hz), 6.92 (d, 2H, J = 8.42 Hz), 3.88 (t, 4H, J = 4.69 Hz), 3.24–3.21 (t, 4H, J = 4.83 Hz). ^{13}C NMR (CDCl$_3$): δ 152.5, 133.7, 116.1, 111.9, 111.1, 67.1, 48.1. MS: *m/z* = 200 (M$^+$).

4-Thiocyanato N-phenyl 15-crown-5 (1o)

IR (KBr): 2147, 1094 cm^{-1}, ^{1}H NMR (CDCl$_3$): δ 7.35 (d, 2H, J = 5.5 Hz), 6.64 (d, 2H, J = 6 Hz), 3.57–3.72 (m, 20H). ^{13}C NMR (CDCl$_3$): δ 149.3, 134.7, 112.8, 105.9, 112.6, 71.2, 70.2, 69.9, 68.0, 52.6. MS: *m/z* = 352 (M$^+$).

4-Thiocyanato N-phenyl-2,2-iminodiethanol (1p)

IR (KBr): 2153, 3300 cm^{-1}, ^{1}H NMR (CDCl$_3$): δ 7.43 (d, 2H, J = 6.5 Hz), 6.70 (d, 2H, J = 7.1 Hz), 3.75–3.60 (m, 4H), 3.55–3.35 (m 4H), 2.15 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 151.8, 132.1, 116.5, 114.3, 111.7, 58.7, 55.9. MS: *m/z* = 238 (M$^+$).

REFERENCES

1. (a) Billard, T.; Langlois, B. R.; Medebielle, M. *Tetrahedron Lett.* **2001,** 42, 3463-3465; (b) Nguyen, T.; Rubinstein, M.; Wakselman, C. *J. Org. Chem.* **1981,** 46, 1938-1940; (c) Large, T. S.; Langlois, B. R. *Tetrahedron Lett.* **1997,** 38, 65-68; (d) Grieco, P. A.; Yokoyama, Y.; Williams, E. *J. Org. Chem.* **1978,** 43, 1283-1285.

2. Zhang, Z. H.; Liebeskind, L. S. *Org. Lett.* **2006,** 8, 4331-4333.
3. Riemschneider, R.; Wojahn, F.; Orlick, G. *J. Am. Chem. Soc.* **1951,** 73, 5905-5907.
4. Lee, Y. T.; Choi, S. Y.; Chung, Y. K. *Tetrahedron Lett.* **2007,** 48, 5673-5677 and references cited therein.
5. Memarian, H. R.; Mohammadpoor-Baltork, I.; Nikoofar, K. *Ultrasonics Sonochem.* **2008,** 15, 456-462.
6. Chakrabarty, M.; Sarkar, S. *Tetrahedron Lett.* **2003,** 44, 8131-8133.
7. Grant, M. S.; Snyder, H. R. *J. Am. Chem. Soc.* **1960,** 82, 2742-2744.
8. Wu, G.; Liu, Q.; Shen, Y.; Wu, W.; Wu, L. *Tetrahedron Lett.* **2005,** 46, 5831-5834.
9. Yadav, J. S.; Reddy, B. V. S.; Krishna, A. D.; Suresh Reddy, Ch.; Narsaiah, A. V. *Synthesis* **2005**, 961-971.
10. Kumar, A.; Ahamd, P.; Maurya, R. A. *Tetrahedron Lett.* **2007,** 48, 1399-1401.
11. Nair, V.; George, T. G.; Nair, L. G.; Panicker, S. B. *Tetrahedron Lett.* **1999,** 40, 1195-1196.
12. Toste, F. D.; Stefano, V. D.; Still, I. V. J. *Synth. Commun.* **1995,** 25, 1277-1286.
13. Yadav, J. S.; Reddy, B. V. S.; Shubashree, S.; Sadashiv, K. *Tetrahedron Lett.* **2004,** 45, 2951-2954.
14. Iranpoor, N.; Firouzabadi, H.; Khalili, D.; Shahin, R. *Tetrahedron Lett.* **2010,** 51, 3508-3510.
15. Iranpoor, N.; Firouzabadi, H.; Azadi, R. *Tetrahedron Lett.* **2006,** 47, 5531-5534.
16. Wu, J.; Wu, G. L.; Wu, L. M. *Synth. Commun.* **2008,** 38, 2367-23739.
17. Bhalerao, D. S.; Akamanchi, K. G. *Synlett.* **2007**, 2815-2818.
18. Yadav, J. S.; Reddy, B. V.; Krishna, B. B. M. *Synthesis.* **2008**, 3779-3782.
19. Yadav, J. S.; Reddy, B. V. S.; Reddy, Y. J. *Chem. Lett.* **2008,** 37, 652-658.
20. (a) Corma, A. *Chem. Rev.* **1995,** 95, 559-614; (b) Corma, A.; Garcia, H. *Catal. Today* **1997,** 38, 257-308.
21. Karimi, B.; Ghoreishi-Nezhad, M.; Clark, J. H. *Org. Lett.* **2005,** 7, 4693-4695.
22. Karimi, B.; Ghoreishi-Nezhad, M. *J. Mole. Catal. A. Chem.* **2007,** 277, 262-265.
23. Karimi, B.; Zareyee, D. *Org. Lett.* **2008,** 10, 3989-3992.
24. Karimi, B.; Khalkhali, M. *J. Mol. Cat. A.Chem.* **2007,** 271, 75-79.
25. Das, B.; Kanth, B. S.; Reddy, K. R.; Kumar, A. S. *J. Heterocycl. Chem.* **2008,** 45, 1499-1505.
26. Gupta, R.; Paul, S.; Loupy, A. *J. Mol. Catal. A. Chem.* **2006,** 266, 50-54.
27. Das, B.; Venkateswarlu, K.; Holla, H.; Krishnaiah, M. *J. Mol. Catal. A: Chem.* **2006,** 253, 107-111.
28. Shimizu, K.; Hayashi, E.; Hatamachi, Y.; Kodama, T.; Kitayama, Y. *Tetrahedron Lett.* **2004,** 45, 5135-5138.
29. Mokhlesi, M. *Synlett (Spothlight)* **2010,** 318, 1574-1575.
30. (a) Ghorbani-Choghamarani, A.; Zolfigol, M. A.; Hajjami, M.; Mallakpour, S. *J. Iran. Chem. Soc.* **2010,** 7, 834-839; (b) Ghorbani-Choghamarani, A.; Zolfigol, M. A.; Hajjami, M.; Rastgoo, S.; Mallakpour, S. *Lett. Org. Chem.* **2010,** 7, 249-254; (c) Ghorbani-Choghamaran, A.; Zolfigol, M. A.; Rastegar, T. *Chin. J. Catal.* **2009,** 30, 273-275; (d) Habibi, D.; Zolfigol, M. A.; Safaiee, M.; Shamsian, A.; Ghorbani-Choghamarani, A. *Catal. Commun.* **2009,** 10, 1257-1260; (e) Salehi, P.; Zolfigol, M. A.; Shirini, F.; Baghbanzadeh, M. *Cur. Org. Chem.* **2006,** 10, 2171-2189.
31. Olah, G. A.; Prakash, G. K. S.; Jean. Sommer; Molnar, A. *Superacid Chemistry*, 2rd ed.; John Wiley & Sons, Inc., 2008; pp. 661-665.
32. Wilson, I. R.; Harris, G. M. *J. Am. Chem Soc.* **1960,** 82, 4515-4517.
33. Kiasat, A. R.; Fallah-Mehrjardi, M. *J. Braz. Chem. Soc.* **2008,** 19, 1595-1599.