



## METAL PROLINE COMPLEX CATALYZED MICHAEL REACTIONS OF MERCAPTANS TO CHALCONES IN AQUEOUS MEDIUM

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### Abstract

Metal complexes of proline were developed and found to catalyze the Michael addition reaction of mercaptans and chalcone in aqueous medium at room temperature. Michael adducts with up to 90% yield were obtained under mild reaction conditions in the presence of efficient metal proline complexes as catalyst. The reaction was studied in different proportions of water and methanol an important solvent effect was noticed. The effect of water-methanol ratio on the reaction rate and yields of the products was also investigated.

**Keywords:** Michael Addition, Chalcones, Metal Proline Complex

### Introduction

In recent year's, the use of water as green solvent in various organic reactions has increased drastically [I-III]. Reaction in aqueous medium offer's advantages in organic synthesis because of the simplicity of catalyst-product separation and the safety of using water as the solvent. The aqueous medium with respect to organic solvent is environment friendly and less expensive [IV-V]. Various organic transformations such as Diels-Alders reaction [VI], Claisen-rearrangements [VII], Mannich reaction [VIII], Heck reaction [IX], Wittig reaction [X], oxidations [XI], allylation reactions [XII] and hydrogenation [XIII] of alkenes in organic synthesis have been successfully performed in aqueous medium.

Thia-Michael reaction is a carbon-sulphur bond forming reaction between electron deficient alkenes and mercaptans. The Michael addition reaction of mercaptans is one of most important process in organic synthesis especially for the synthesis of organosulphur compounds. The importance of organosulphur is well recognized by synthetic as well as biological chemists [XIV-XIX]. Many Lewis acid catalysts have been reported in the literature for this reaction including InBr<sub>3</sub> [XX], InCl<sub>3</sub> [XXI], Bi(OTf)<sub>3</sub> [XXII], Bi(NO<sub>3</sub>)<sub>3</sub> [XXIII], CdI<sub>2</sub> [XXIV], Hf(OTf)<sub>3</sub> [XXV] and I<sub>2</sub> [XXVI]. A number of procedure involving a variety of heterogeneous Catalysts such as zeolite [XXVII], phosphates [XXVIII], Nafion SAC-13 [XXIX], H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [XXX], fluorapatite [XXXI] and Na<sub>2</sub>CaP<sub>2</sub>O<sub>7</sub> [XXXII] have been reported. A literature survey revealed that preparation of heterogeneous catalysts is time consuming and also required a variety of additional reagents. Recently there were also some reports of this

reaction conducted in ionic liquid [XXXIII]. Very recently montmorillonite clays catalyzed Michael addition of mercaptans to  $\alpha,\beta$ -unsaturated ketones was reported [XXXIV]. Other method involves Copper (II) tetrafluoroborate [XXXV],  $\beta$ -cyclodextrin [XXXVI],  $\text{HClO}_4/\text{SiO}_2$  [XXXVII] polyethylene glycol [XXXVIII] and sodium dodecyl sulphate [XXXIX]. Most of the methodologies reported earlier require organic solvents although very few processes used aqueous medium. Unfortunately, many of these procedures often require an longer reaction time, high temperature, drastic reaction conditions, use of halogenated solvents, formation of undesirable side products, toxic chemicals, low yield, expensive catalyst etc. Therefore, there is still a need to develop alternative methods for this reaction.

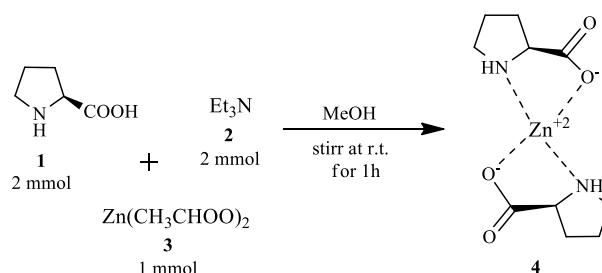
Metal complex of different amino acids such as  $\text{Zn}(\text{Pro})_2$ ,  $\text{Zn}(\text{Arg})_2$  and  $\text{Zn}(\text{Lys})_2$  are able to catalyze the direct aldol reaction of aldehydes and ketones in aqueous medium with moderate enantioselectivity [XXXX-XXXXI]. Very recently  $\text{Zn}(\text{Pro})_2$  catalyzed synthesis of 1,2-Disubstituted benzimidazole in moderate to excellent yield using water as a solvent at ambient temperature has been reported [XXXXII]. Zn-Proline complex also catalyzed pathway for the formation of sugars in water [XXXXIII]. For the increasing environmental and economical concerns in recent years, it is now essential for chemists to search environmentally benign catalytic reactions as many as possible. We noticed that only a few methodologies are reported for Michael addition of mercaptans using water as a reaction media. Here in, we reported a new entry in the catalytic Michael addition reaction of mercaptans and chalcones. using metal proline complex as efficient catalyst in aqueous medium (Scheme 2).

## Experimental

All reactions were carried out at room temperature 25-30<sup>0</sup>C. Unless otherwise specified, all the reagents were purchased from Sigma-Aldrich Chemical Co, Lancaster and were used directly without further any purification. Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer Rx1 FT-IR spectrophotometer as KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS, Coupling constant (J) in Hz. Mass analyses performed on THERMO FINNIGAN (LCQ Advantage MAX) Ion-Trap Mass spectrometer. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel plates visualized with UV light.

## Catalyst preparation

Two different metal complex of proline were prepared by similar method. Firstly  $\text{Zn}(\text{Pro})_2$  4 was prepared by stirring a mixture of proline (2 mmol), zinc acetate (1 mmol),  $\text{Et}_3\text{N}$  (2 mmol) in methanol (15 ml) for 1h at room temperature (Scheme 1). The complex precipitated as white solid. According to the same procedure silver-proline complex was prepared in good to moderate yield. While in case of copper-proline complex yield is low. The above metal complexes were stable in water and characterized by <sup>1</sup>H NMR, <sup>13</sup>C- NMR and mass spectroscopy.



**Scheme 1.** Synthesis of zinc proline complex

### Reaction procedure

1 mmol of chalcone, 2 mmol of metcaptan and 10 mol% of Zn(Pro)<sub>2</sub> were introduced in a 50ml of round bottom flask. Then 2ml of methanol was added and the reaction mixture was vigorously stirred at room temperature for the specified time (see Table 3). After completion of the reaction, as indicated by TLC, the solvent was removed under vacuum. The reaction mixture was then diluted with 10 ml of 5 N solution of HCl and the resulting mixture was extracted with 3×10 ml of ethyl acetate. The organic phase was then dried (Na<sub>2</sub>SO<sub>4</sub>), filtered, and the solvent was removed under vacuum to afford Michael adducts in 80- 90% yield.

### Spectral data of selected compounds

3-(4-Chloro-phenylsulfanyl)-1-(2-hydroxy-phenyl)-3-phenyl-propan-1-one (entry 1, Table 3) White solid; mp 112–115 °C; IR (KBr): 696, 820, 1230, 1336, 1677, 2894, 3062 v cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.3-3.8 (m, 2H), 4.8-5.0 (m, 1H), 7.1-7.4 (m, 8H), 7.4-7.5 (m, 3H), 7.9 (d, 2H, J= 9.0 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 43.27, 47.27, 126.22, 126.50, 126.79, 127.25, 127.37, 127.69, 131.37, 132.06, 132.54, 132.97, 135.42, 139.74, 195.46 ; m/z: 369 (M+H).

3-(4-Chloro-phenylsulfanyl)-3-(4-fluoro-phenyl)-1-phenyl-propan-1-one (entry 4, Table 3) White solid; mp 125–127 °C; IR (KBr): 684, 731, 823, 1225, 1511, 1682, 2896, 3061 v cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 3.4-3.8 (m, 2H), 4.8-5.1 (m, 1H), 6.8-7.1 (m, 2H), 7.1-7.4 (m, 6H), 7.4-7.7 (m, 3H), 7.89 (d, 2H, J= 7.11 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 43.31, 46.61, 98.71, 113.96, 114.24, 126.76, 127.41, 127.78, 128.06, 128.17, 131.04, 132.16, 132.78, 133.11, 135.31, 135.51, 195.28; m/z: 371 (M+H).

3-(4-Chloro-phenylsulfanyl)-3-(4-methoxy-phenyl)-1-phenyl-propan-1-one (entry 5, Table 3) White solid; mp 130–134 °C; IR (KBr): 691, 818, 1232, 1332, 1513, 1675, 2958, 3063 v cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.4-3.6 (m, 2H), 3.7-3.9 (m, 3H), 4.8-5.0 (m, 1H), 6.7-6.9 (m, 2H), 7.1-7.3 (m, 6H), 7.4-7.6 (m, 3H), 7.86 (d, 2H, J= 7.35 Hz); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 43.43, 46.72, 53.94, 112.62, 126.78, 127.36, 127.59, 127.69, 131.57, 131.65, 132.03, 132.43, 132.89, 135.45, 157.57, 195.63; m/z: 383 (M+H).

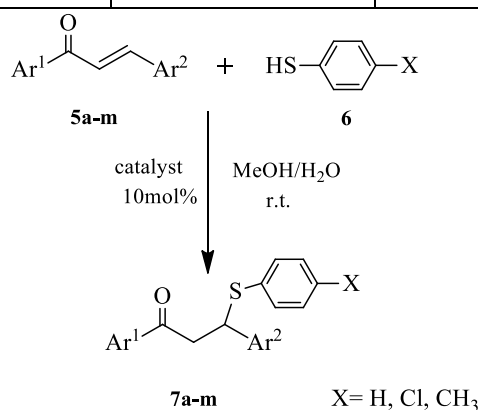
3-Naphthalen-2-yl-1-phenyl-3-phenylsulfanyl-propan-1-one (entry 10, Table 3) White solid; mp 155–158 °C; IR (KBr): 687, 739, 874, 1261, 1341, 1596, 1675, 2965, 3069 v cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 3.4-3.9 (m, 2H), 5.4-5.9 (m, 1H), 6.9-8.4 (m, 17H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 42.46, 43.57, 122.30, 124.11, 124.72, 125.35, 126.13, 126.47, 126.52, 127.07, 127.14, 127.59, 127.65, 127.79, 127.94, 128.03, 131.63, 132.24, 133.03, 140.74, 189.30, 196.07; m/z: 369 (M+H).

3-(4-Chloro-phenylsulfanyl)-3-naphthalen-2-yl-1-phenyl-propan-1-one (entry 13, Table 3) White solid; mp 166–168 °C; IR (KBr): 687, 779, 803, 1097, 1255, 1351, 1474, 1595, 1681, 2894, 3061 v cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.3-4.2 (m, 2H), 5.4-6.0 (m, 1H), 6.8-8.6 (m, 16H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 43.28, 43.55, 43.84, 44.11, 47.81, 126.63, 128.41, 128.61, 129.30, 129.92, 131.49, 131.74, 132.16, 132.37, 132.46, 134.28, 136.18, 136.91, 137.66, 139.69, 140.05, 200.31; m/z: 403 (M+H). Structure identification of all metal proline complexes was carried out by comparison with the reported <sup>1</sup>H and <sup>13</sup>C- NMR data.

### Results and discussion

In the presence of 20 mol% of different catalyst (**Table 1**, entries **1-6**) the Michael reaction of 1,3-Diphenyl-propenone (1mmol) with thiophenol (2mmol) in presence of water examined (Scheme 2). Table 1 summarizes the results. It was observed that all of the investigated metal proline complexes in different concentrations were able to catalyze the Michael addition of mercaptans to chalcones (Table 1, entries **4-9**). While no conversion was obtained when Zn(CH<sub>3</sub>COO)<sub>2</sub>, CH<sub>3</sub>COOAg and Cu(CH<sub>3</sub>COO)<sub>2</sub> were using as a catalyst in 20mol% (Table 1, entries **1-3**).

Entry	Catalyst	Catalyst Loading mol%	Time (h)	Yield (%)
1	Zn(CH <sub>3</sub> COO) <sub>2</sub>	20mol%	48 h	5
2	CH <sub>3</sub> COOAg	20mol%	48 h	0
3	Cu(CH <sub>3</sub> COO) <sub>2</sub>	20mol%	48 h	0
4	Zn-proline	20mol%	2h	59
5	Ag-proline	20mol%	5h	42
6	Cu-proline	20mol%	28 h	25
7	Zn-proline	10mol%	1h	78
8	Ag-proline	10mol%	3h	62
9	Cu-proline	10mol%	52 h	15



**Scheme 2.** Michael addition of mercaptans to chalcones

**Table 1.** Results of screening of various metal proline complexes in the Michael addition of mercaptan to chalcone.

Longer reaction time and lower yields were obtained when this reaction was carried out using Zn-proline (20 mol%), Ag-proline (20 mol%) and Cu-proline (20 mol%) complexes as catalyst (Table 1, entries 4-6). However, the reactions were faster in the presence of Zn-proline (10mol%) and Ag-proline (10mol%) complexes (Table 1, entries 7 and 8). While in case of Cu-proline complex (10mol%) the reaction shows poor yield (15%) and required much longer reaction time (52h) as compare to other metal proline complexes (Table 1, entry 9). Best results were obtained when metal proline complex is used in 10mol% instead of 20mol% as catalyst. Therefore, Zn-proline (10mol%) and Ag-proline (10mol%) were used for the reaction of other model compounds.

We found that the Michael reaction of 1,3-Diphenyl-propenone (1mmol) with thiophenol (2mmol) in presence of water required longer time along with poor yield of the product. Lower yield is obtained due to poor solubility of reactants in water. To improve the yield of the products, we decided to extend the study of this reaction to various proportions of methanol

and water (Table 2, entries 2-10). When Michael reaction of mercaptans was carried out with different proportion of methanol and water using Zn-proline (10mmol%) as catalyst the yield obtained increased with a corresponding increase in the methanol content to some extent (Table 2, entries 2-6). However, there was dramatic increase in the yield along with a decrease in reaction time when the reaction was carried out in 7:3 proportions of methanol and water. Best results were obtained when the methanol water is used in the ratio of 7:3 and zn-proline complex (10mol%) as a catalyst for this reaction (Table 2, entry 8).

**Table 2.** Optimization of the reaction conditions for Michael addition by Screening of various solvent systems

Entry	Solvent system MeOH : H <sub>2</sub> O ml	Time (min)	Yields (%)
1	0 : 10	40	60
2	1 : 9	37	62
3	2 : 8	38	66
4	3 : 7	35	72
5	4 : 6	35	70
6	5 : 5	30	76
7	6 : 4	15	82
8	7 : 3	6	95
9	8 : 2	15	85
10	9 : 1	22	78
11	10 : 0	20	85

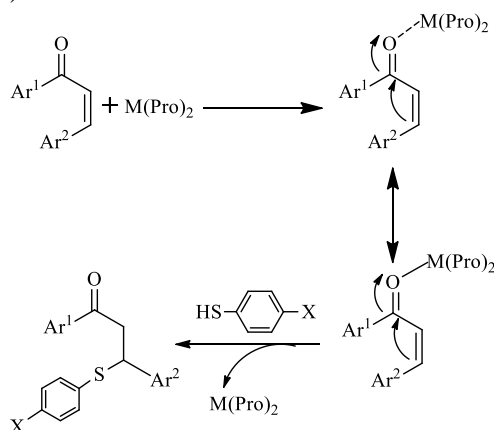
The scope and generality of this process is illustrated with respect to various mercaptans and chalcones. The results are summarized in Table 3. Both electron-donating and electron-withdrawing group at the aryl unit shows better results on performing reaction under optimized condition. All the synthesized compounds were characterised using <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR spectroscopic techniques.

**Table 3.** Michael reaction of mercaptans to chalcones catalyzed by Zn(L-Proline)<sub>2</sub> complex

Entry	Ar <sup>1</sup>	Ar <sup>2</sup>	X	Product <sup>b</sup>	Time (min)	Yields <sup>c</sup>
1	2-OH-C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	7a	25	85
2	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	7b	30	90
3	3-OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Naphthyl	H	7c	22	88
4	C <sub>6</sub> H <sub>5</sub>	4-F-C <sub>6</sub> H <sub>4</sub>	Cl	7d	15	92
5	C <sub>6</sub> H <sub>5</sub>	4-OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Cl	7e	40	82
6	2-OH-C <sub>6</sub> H <sub>4</sub>	Naphthyl	H	7f	28	88
7	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	7g	5	95
8	C <sub>6</sub> H <sub>5</sub>	Naphthyl	CH <sub>3</sub>	7h	10	94
9	C <sub>6</sub> H <sub>5</sub>	4-OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Cl	7i	20	87

10	C <sub>6</sub> H <sub>5</sub>	Naphthyl	H	7j	32	88
11	C <sub>6</sub> H <sub>5</sub>	Naphthyl	Cl	7k	10	90
12	C <sub>6</sub> H <sub>5</sub>	4-OCH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	H	7l	15	85
13	C <sub>6</sub> H <sub>5</sub>	Naphthyl	Cl	7m	30	92

A plausible mechanism for this metal proline catalyzed Michael reaction of the mercaptans and chalcones is proposed (fig 1).



**Fig 1.** Role of metal proline complex in the Michael addition reaction with metal acting as a Lewis acid catalyst

According to proposed mechanism metal act as a Lewis acid in water when metal proline complex is used as a catalyst. While proline act by enamine formation in methanol water system. Enamine formation is not favorable in aqueous medium that's why proline alone does not catalyze the reaction in water. A result shown in table 1 that metal acetates do not catalyze the Michael addition of mercaptans in water, which indicates that the both metal as well as proline, are necessary for catalysis. Thus, metal proline complex facilitates the Michael addition reaction via dual mechanism in methanol water system. Then, using the optimized reaction conditions we synthesized a series of Michael adducts (7a-m) from different chalcones (5a-m). The results of this study are summarized in (Table 3). To our gratified, all the reactions proceeded with reduced reaction time (Table 3, entries 1-13). Under the same conditions, the reaction of a mercapto-acetic acid with chalcones did not work very well.

## Conclusion

In summary, we have developed an economically and environmentally friendly procedure for Michael addition reaction of mercaptans to chalcones in aqueous medium with high yields and short reaction times, which involves the use of efficient catalysts metal proline complexes at room temperature. This method has some advantages over other methods since the reaction is easily operable in water under mild reaction conditions, as it uses no dried organic solvents. This procedure would be a convenient and practical method for the synthesis of thia-Michael adducts.

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## Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

## References

- i. D. Amantini, F. Fringuelli, O. Piermatti, F. Pizzo, L. Vaccaro, *Green Chemistry*. 3 (2001) 229.
- ii. V. Polshettiwar, R.S. Verma, *Tetrahedron Lett.* 48, (2007) 7343.
- iii. J.S. Yadav, B.V. Subba Reddy, S. Shubashree, K. Sadashiv, D. Krishna Rao, *Journal of Molecular Catalysis A: Chemical* 272, (2007) 128.
- iv. C.J. Li, T.H. Chan, *Organic Reactions in Aqueous Media*, John Wiley & Sons, New York, 1997.
- v. P.A. Ed. Grieco, *Organic Synthesis in Water*, Blackie Academic & Professional, London, 1998.
- vi. S. Otto, J.B.F.N. Engberts, *Pure Appl. Chem.* 72, (2000) 1365.
- vii. J.J. Gajewshi, *Acc. Chem. Res.* 30, (1997) 219.
- viii. N. Azizi, L. Torkiyan, M.R. Saidi, *Org. Lett.* 8, (2006) 2079.
- ix. L. Botella, C. Najera, *J. Org. Chem.* 70, (2005) 4360.
- x. J. Dambacher, W. Zhao, A. El-Batta, R. Anness, C. Jiang, M. Bergdahl, *Tetrahedron Lett.* 46, (2005) 4473.
- xi. V.V. Fokin, K.B. Sharpless, *Angew. Chem. Int. Ed. Engl.* 40, (2001) 3455.
- xii. W. Lu, T.H. Chan, *J. Org. Chem.* 66, (2001) 3467.
- xiii. U. Nagel, J. Albrecht, *Top. Catal.* 5, (1998) 3.
- xiv. P. Bakuzia, M. L. F. Bakuzis, *J. Org. Chem.* 46, (1981) 235.
- xv. J. P. Cherkauskas, T. Cohen, *J. Org. Chem.* 57, (1992) 6.
- xvi. S. Kobayashi, C. Ogawa, M. Kawamura, M. Sugiura, *Synlett* (2001) 983.
- xvii. E. Emori, T. Arai, H. Sasai, M. Shibasaki, *J. Am. Chem. Soc.* 120, (1998) 4043.
- xviii. A. Kumar, R.V. Salunkhe, R.A. Rane, S.Y. Dike, *J. Chem. Commun.* (1991) 485.
- xix. E. Fujita, Y. Nagao, *Bioorg. Chem.* 6, (1977) 287.
- xx. M. Bandini, P. G. Cozzi, M. Giacomini, P. Melchiorre, S. Selva, A. Umani-Ronchi, *J. Org. Chem.* 67, (2002) 3700.
- xxi. B. C. Ranu, S. S. Dey, S. Samanta, *ARKIVOC* 2005(iii) 44.
- xxii. M. M. Alam, R. Varala, S. R. Adapa, *Tetrahedron Lett.* 44, (2003) 5115.
- xxiii. N. Srivastava, B. K. Banik, *J. Org. Chem.* 68, (2003) 2109.
- xxiv. M. Saito, M. Nakajima, S. Hashimoto, *Tetrahedron* 56, (2000) 9589.
- xxv. S. Kobayashi, C. Ogawa, M. Kawamura, M. Sugiura, *Synlett* (2001) 983.
- xxvi. C. -M. Chu, S. Goa, M.N.V. Sastry, C. -F. Yao, *Tetrahedron Lett.* 46, (2005) 4971.
- xxvii. R. Sreekumar, P. Rugmini, R. Padmakumar, *Tetrahedron Lett.* 38, (1997) 6557.
- xxviii. Y. Abrouki, M. Zahouily, A. Rayadh, B. Bahlaouan, S. Sebti, *Tetrahedron Lett.* 43, (2002) 8951.
- xxix. T.C. Wabnitz, J.-Q. Yu, J.B. Spencer, *Synlett* (2003) 1070.
- xxx. H. Firouzabadi, N. Iranpoor, A.A. Jafari, *Synlett* (2005) 299.
- xxxi. M. Zahouily, Y. Abrouki, A. Rayadh, S. Sebti, H. Dhimane, M. David, *Tetrahedron Lett.* 44 (2003) 2463.
- xxxii. M. Zahouily, Y. Abrouki, A. Rayadh, *Tetrahedron Lett.* 43, (2002) 7729.

- xxxiii. P. Kotrusz, S. Toma, *Molecules* 11, (2006) 197.
- xxxiv. G. Sharma, R. Kumar, A. K. Chakraborti, *Journal of Molecular Catalysis A: Chemical* 263, (2007) 143.
- xxxv. S. K. Garg, R. Kumar, A. K. Chakraborti, *Tetrahedron Lett.* 46, (2005) 1721.
- xxxvi. N. S. Krisnaveni, K. Surendra, K. R. Rao, *Chem. Commun.* (2005) 669.
- xxxvii. A. T. Khan, S. Ghosh, L. H. Choudhury, *Eur. J. Org. Chem.* 9, (2006) 2226.
- xxxviii. A. Kamal, D. R. Reddy, Rajendra, *Tetrahedron Lett.* 46, (2005) 7951.
- xxxix. H. Firouzabadi, N. Iranpoor, A.A. Jafari, *Adv. Synth. Catal.* 347, (2005) 655.
- xl. T. Darbre, M. Machuqueiro, *Chem. Commun.* (2003) 1090.
- xli. R.F. Lopez, J. Kofoed, M. Machuqueiro, T. Darbre, *Eur. J. Org. Chem.* (2005) 5268.
- xlii. V. Ravi, E. Ramu, K. Vijay, A.S. Rao, *Chem. Pharm. Bull.* 55, (2007) 1254.
- xliii. J. Kofoed, M. Machuqueiro, J.-L. Reymond, T. Darbre, *Chem. Commun.* (2004) 1540.

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