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LANTHANUM CHLORIDE CATALYSED NOVEL AND EFFICIENT PROTOCOL FOR SYNTHESIS OF SUBSTITUTED QUINOXALINE AT ROOM TEMPERATURE

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Abstract:

The novel protocol has been developed for the synthesis of variety of substituted quinoxalines by the condensation of aromatic 1,2-diamines with 1,2-diketones in the presence of lanthanum chloride in aqueous methanol at room temperature. Most of the reaction completed in less than one hour and required only 2mol% catalyst. High efficiency, inexpensiveness, and non toxicity are the interesting features of catalyst, which make it ecofriendly and highly attractive.

Keywords: Quinoxaline. 1,2-diamine, 1,2-diketone, lanthanum chloride, methanol.

Introduction

Quinoxaline are prevalent heterocyclic units in pharmaceuticals and bioactive natural products[i-iv]. The substituted quinoxalines derivatives not only constitute an important class of biologically active agents[v], but also find tremendous application in materials science such as luminescent materials[vi] and low bad gap polymers[vii]. They display a broad spectrum of biological activities such as antibacterial[viii-ix], antifungal[x], anticancer[xi-xii], antiinflammatory[xiii], antiviral[xiv], and also kinase inhibitor[xv-xvii]. Besides these pharmacological activities, quinoxaline derivatives are potential building block for the synthesis of organic semiconductor[xviii-]xix, DNA cleaving agents[xx], corrosion inhibitor[xxi], chemically controllable switches as well as practical applications such as copper(I) sensors[xxii], building blocks for den drimers[xxiii], ligands in metals complexes of supramolecular devices or DNA probes[xxiv-xxiii].

Due to their biomedical activities and ability to serve as valuable intermediate in organic synthesis, much effort has been devoted to development of new methodologies for the synthesis of substituted quinoxaline derivatives[xxix-xxxi]. Conventionally, quinoxalines can be synthesized by direct thermal condensation reaction between a 1,2-dicarbonyl compound and o-phenylene diamine[xxxii-xl]. Apart from these classical approaches, many other methods have also been developed for the oxidative cyclisation of alpha-hydroxy ketones or alpha-halide ketones with 1,2-diamines[xli-xlv].One of the major drawbacks of the above reported methods is that specially designed substrates are not readily available from commercial sources. Also,

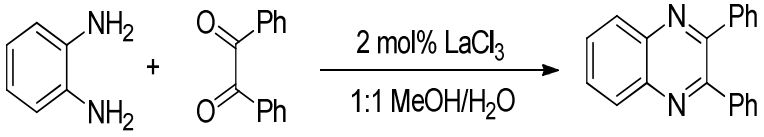
most of these oxidation methods require the usage of toxic oxidant, excess additives or high reaction temperature. In view of these, we have attempted to develop a new methodology for synthesis of quinoxaline derivatives which should be easy and efficient. In this context we report, herein, an novel and efficient protocol catalysed by lanthanum chloride for the synthesis of substituted quinoxaline by 1,2-dicarbonyl compounds and 1,2-diamine.

Lanthanum chloride is new type of lewis acids different from typical lewis acids such as $AlCl_3$, BF_3, and $SnCl_4$ etc. It is very stable, inexpensive, non-toxic, and highly effective in aqueous methanol, and reusable catalyst. It has broad application in synthetic organic chemistry which includes Friedal Craft acylation, Biginelli reaction, Knovengel condensation and Pechmann condensation.

Results and Discussion

In model condensation reaction, o-phenylene diamine and benzil were stirred at room temperature in the presence catalytic amount of lanthanum chloride (2 mol %) in aqueous methanolic medium **(Scheme 1)**. As expected, the reaction was completed within 30 min. In order to evaluate the optimimum concentration of lanthanum chloride required for this condensation, the reaction was carried out under varying concentrations of lanthanum chloride viz. 1, 2, 3, 5 and 10 mol%, in which we found that 2 mol% of lanthanum chloride is sufficient to do efficient transformation of this reaction. The screening experiment also showed that increasing the amount of lanthanum chloride did not enhance the yield and even after prolonging the reaction time to 12 h. When the reaction was conducted at a lower temperature, it proceeded with a lower yield, and higher reaction temperature did not increase the yield.

Scheme 1. Synthesis of substituted quinoxaline from o-phenylene diamine and benzil in presence of lanthanum chloride



To study the effects of solvents, aqeuous methanol was replaced with several other solvents and optimise the effect of solvents **(Table 1)**. Among the various solvents tested methanol, ethanol, water, and acetonitrile were all effective, although affording the products with diminished yields and required long time for completion, and aqueous methanol appeared the best among them. Tetrahydrofuran, dimethyl sulphoxide, dichloromethane and toulene were also examined, but no product formation was observed. However, aqeuous methanol was considered as the best solvent because of it greener in nature for further studies.

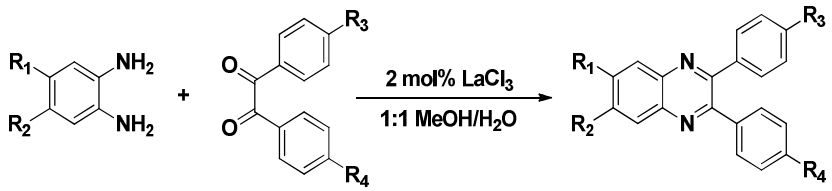
Table 1. Screened solvents for the condensation of o-phenylene diamine with benzil.

Entry	Solvent	Time	Yield[b] (%)
1	Ethanol	2 hr	70
2	Methanol	1.5 hr	80
3	Water	12 hr	47
4	Acetonitrile	3 hr	35
5	Dimethyl sulphoxide	12 hr	NR

6	Tetrahydrofuran	12 hr	NR
7	Dichloromethane	12 hr	NR
8	1:1 Aqueous methanol	30 min	98

However reaction conditions are optimized, to evaluate this methodology, various substituted 1,2-diamines were condensed with benzil in the presence of lanthanum chloride (2 mol%) at room temperature **(Table 2, entries 3a-3n**) in aqeuous methanol. An introduction of an electron releasing substituent on o-phenylene diamine, alter the reaction time and also incresed the observed yield **(Table 2, entries 3b-3d**). The halogen substituted aromatic diamines also undergoes condensation with benzil but it required 30-55 min for completion and decresed the observed yield **(Table 2, entries 3e-3f, 3j).** The nitro and cyano substituted 1,2-diamines was required high time for condensation and observed yield of product decreses amine **(Table 2, entriy 3h-3i).** Further, we extended our study by replacing benzil with 1,2-dicarbonyl compounds such as benzil containing the electron releasing substituents. The introduction of an electron releasing substituents on 1,2-dicarbonyl compounds also affect on reaction time and observed yield of products. The electron releasing substituents containing 1,2-dicarbonyl compounds was required 35-55 min for condensation with o-phenylene diamine and also observed yield of products decreases (**Table 2, entries 3k-3n)**. The incresing the concentration of lanthanum chloride for condensation of electron releasing substituents containing 1,2-dicarbonyl compounds with 1,2-diamines does not affect on rate of reaction. The lanthanum chloride is mild lewis acid catalyst and completely soluble in aqueous methanol. The lewic acid nature of lanthanum chloride, promotes the reaction by involving in both nucleophilic addition as well as in dehydration steps.

Table 2. Synthesis of various substituted quinoxaline via the condensation of 1,2-diamine with 1,2-diacabonyl compounds catalyzed by $LaCl_3$



Product	R_1	R_2	R_3	R_4	T/min	Yield%[b]
3a	H	H	H	H	30	94
3b	Me	H	H	H	25	96
3c	OMe	H	H	H	22	97
3d	Me	Me	H	H	15	98
3e	Br	H	H	H	35	87
3f	Cl	H	H	H	40	85
3g	F	H	H	H	47	83
3h	CN	H	H	H	60	72
3i	Cl	Cl	H	H	60	69
3j	H	H	H	H	45	77
3k	H	H	Me	Me	40	73
3l	H	H	OMe	OMe	55	71
3m	H	H	Br	Br	40	84
3n	H	H	Cl	Cl	45	82

Experimental

^{1}H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance Digital 400 spectrometer using TMS as an internal standard. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected. The isolation of pure products was carried out via column chromatography (silica gel, Merck).

General procedure for the synthesis of substituted quinoxalines : To a stirred solution of o-phenylene diamine (1 mmol) in aqueous methanol (1:1, 10 ml) was added benzil (1 mmol) and reaction mixture was stirred a vigorously at room temperature. The progress of reaction was monitored by TLC. When all the starting material had been consumed, the reaction mixture was quenched with water (10 ml) and extracted with ethyl acetate (2 x 10 ml). The organic phase was separated and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give crude product. The pure product was isolated by silica gel column chromatography using (EtOAc/hexane, 1:9)

2,3-diphenylquinoxaline (**3a**). This compound was obtained as beige solid, yield: 95% mp 125-128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.35 (m, 6H), 7.50-7.52 (m, 4H), 7.73-7.75 (m, 2H), 8.16-8.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.3, 128.8, 129.2, 129.8, 129.9, 139.1, 141.2, 153.4.

6-methyl-2,3-diphenylquinoxaline (**3b**).This compound was obtained as pale yellow solid, yield: 97% mp 137-138°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 7.26-7.32 (m, 6H), 7.50 (t, J = 6 Hz,1.2 Hz, 4H), 7.53 (d, J = 8.8 Hz, 1H), 7.92 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 128.0, 128.2, 128.6, 128.7, 129.90, 129.92, 1132.3, 139.2, 139.7, 140.4, 141.3, 152.5, 153.3.

6-methoxy-2,3-diphenylquinoxaline (**3c**).This compound was obtained as pale yellow solid, yield: 97%, mp 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (s, 3H), 7.32-7.34 (m, 6H), 7.41-7.44 (m, 2H), 7.47-7.51 (m, 5H), 8.06 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 106.4, 123.4, 128.2, 128.3, 128.5, 128.7, 129.8. 130.1, 137.4, 139.2, 139.29, 142.7, 150.9, 153.3, 160.8.

6,7-Dimethyl-2,3-diphenylquinoxaline (**3d**). This compound was obtained as white solid, yield: 80%, mp 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2 H), 7.50-7.52 (m, 2H), 7.27-7.36 (m, 2H), 2.53 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 127.3, 128.4, 128.7, 129.2, 138.4, 140.3, 147.3, 153.6.

6-bromo-2,3-diphenylquinoxaline (**3e**). This compound was obtained as pale yellow solid, yield: 89%, mp 120-122 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.40 (m, 6H), 7.51 (d, J = 6.8 Hz, 4H), 7.69-7.27 (m, 1H), 8.11 (d, J = 8.8 Hz, 1H), 8.17 (d, J = 2.0 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.0, 128.3, 129.0, 129.1, 129.8, 129.9, 130.4, 130.9, 135.6, 138.6, 138.7, 139.7, 141.4, 153.5, 154.2.

6-chloro-2,3-diphenylquinoxaline (**3f**). This compound was obtained as pale yellow solid, yield: 90%, mp 115-116 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.39 (m, 6H), 7.51 (d, J = 6.4 Hz, 4H), 7.84 (m, 1H), 8.03 (d, J = 8.8 Hz, 1H), 8.36 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.8, 128.3, 129.0, 129.1, 129.7, 129.8, 130.5, 131.4, 133.5, 138.6, 138.7, 139.9, 141.7, 153.7, 154.2.

6-fluoro-2,3-diphenylquinoxaline (3g). This compound was obtained as White solid; yield: 89%, mp = 130-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, J = 5.7 Hz & 9.2 Hz, 1H), 7.79 (dd, J = 2.7 Hz & 9.2 Hz, 1H), 7.48-7.54 (m, 5H), 7.23-7.37 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.8, 119.3, 127.3, 128.5, 129.7, 129.9, 130.8,131.4, 131.8, 138.4, 139.4, 142.5, 154.6, 156.7, 164.2.

6-Nitro-2,3-diphenylquinoxaline (3h). This compound was obtained as White solid; yield:

89%, mp = 190-911°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, J = 2.4 Hz, 1H), 8.55 (dd, J = 2.5 Hz & 9.2 Hz, 1H), 7.31(d, J = 9.1 Hz, 1H), 7.55-7.59 (m, 4H), 7.36-7.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.4, 123.2, 127.3, 127.5, 128.7, 128.9, 129.3, 129.6, 138.3, 138.6, 141.3, 141.6, 144.8, 157.3. 159.3.

2,3-Diphenylquinoxaline-6-carbonitrile (3i). This compound was obtained as White solid; yield: 89%, mp = 184-185°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (d, J = 2.4 Hz, 1H), 8.55 (dd, J = 2.5 Hz & 9.2 Hz, 1H), 7.31(d, J = 9.1 Hz, 1H), 7.55-7.59 (m, 4H), 7.36-7.46 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.5, 118.9, 127.2, 127.6, 128.3, 128.6, 129.2, 129.5, 129.7, 130.2, 135.4, 138.2, 138.6, 140.6, 142.9, 158.2, 158.6.

6,7-Dichloro-2,3-diphenylquinoxaline (3j). This compound was obtained as White solid; yield: 89%, mp = 148-149°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 2H), 7.48-7.51 (m, 2H), 7.32-7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.8, 128.8, 129.4, 129.7, 136.6, 138.6, 139.6, 156.5.

2,3-bis(tolyl)quinoxaline (**3k**). This compound was obtained as pale white solid, yield: 69%, mp 143-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31(s, 6H), 7.15 (d, J = 7.6 Hz, 4H), 7.42 (d, J = 8.0 Hz, 4H), 7.73-7.75 (m, 2H), 8.13-8.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 128.9, 129.9, 129.1, 129.63, 129.74, 130.0, 136.4, 138.7, 141.1, 153.5.

2,3-bis(4-methoxyphenyl)quinoxaline (**3l**). This compound was obtained as pale white solid, yield: 83%, mp 149-150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (d, J = 1.6 Hz, 6H), 6.78-6.81 (m, 4H), 7.40-7.42 (m, 4H), 7.63-7.65 (m, 2H), 8.03-8.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 55.6, 113.7, 114.3, 129.0, 129.5, 129.9, 131.2, 131.4, 131.6, 132.0, 141.0, 153.0, 160.1, 164.5

2,3-bis(4-bromophenyl)quinoxaline (3m). This compound was obtained as pale yellow solid, yield: 84%, mp 191-193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.0 Hz , 3H), 7.50-7.53(m, 5H), 7.55-7.57 (m, 2H), 7.59-7.60 (m, 1H), 7.80-7.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.7, 124.0, 127.9, 129.2, 130.2, 130.4, 131.4, 131.6, 131.9, 132.2, 133.1, 137.7, 141.2, 151.9.

2,3-bis(4-chlorophenyl)quinoxaline (3n). This compound was obtained as pale white solid, yield: 88%, mp 188-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.37 (m, 2H), 7.39-7.42 (m, 3H), 7.44-7.48 (m, 3H), 7.78-7.81 (m, 1H), 7.90 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 8.15-8.17(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.7, 128.8, 128.9, 129.1,129.2, 129.5, 129.7, 129.9, 130.1, 130.3, 131.1, 131.3, 131.8, 132.7, 135.3, 135.8, 137.2, 140.1,140.3, 141.2.

Conclusion

In summary, we present here a highly efficient and facile methodology for preparation of substituted quinoxalines from various 1,2-dicarbonyl compounds and aromatic 1,2-diamine promoted by lanthanum chloride in methanol at room temperature. Compare to previous reported methodologies, the present protocol features operationally straightforward, mild, efficient and eco-friendly, which make this method a useful and attractive strategy in the view of economic and environmental advantages.

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References and notes

i. L. E. Seitz, W. J. Suling, R. C. Reynolds, *J. Med. Chem*., **2002**, *45*, 5604.

ii. F. Palacios, A. M. Ochoa de Retana, J. I. Gil, R. Lopezde Munain, *Org. Lett*., **2002**,

4, 2405.
iii. A. Jaso, B. Zarranz, I. Aldana, A. Monge, *J. Med. Chem*., **2005**, 48, 2019.
iv. M. Sato, M. Nakazawa, Y. Tsunematsu, K. Hotta, K. Watanabe, *Curr.Opin. Chem. Biol.,* **2013**, 17, 537.
v. L. Yan, L, F. W. Liu, G. F. Dai, H. M. Liu, *Bioorg. Med. Chem. Lett*., **2007**, 17, 609.
vi. S. Achelle, C. Baudequin, N. Ple, *Dye Pigm.,* **2013**, 98, 575.
vii. S. Zhang, J. Zou, H. L. Yip, K. S. Chen, D. F. Zeigler, Y. Sun, A. K. Jen, *Chem.Mater*., **2011,** 23, 2289.
viii. M. M. Badran, K. A. Abonzid, M.H. Hussein, *Arch. Pharm. Res*., **2003**, 26, 107.
ix. L. E. Seitz, W. J. Suling, R. C. Reynolds, *J. Med. Chem*., **2002**, 45, 5604.
x. J. R. Kerr, G. W. Taylor, A. Rutman, N. Hoiby, P. J. Cole, R. Wilson, *J. Clin. Pathol*., **1999,** 52, 385.
xi. J. Brueggen, P. Chene, P. Drueckes, D. Erdmann, P. Furet, M. Gerspacher, M. Lang, D. Ledieu, L. Nolan, S. Ruetz, J. Trappe, E. Vanghrevelinghe, M. Wartmann, L. Wyder, F. Hofmann, T. Mol. Radimerski, *Cancer Ther*., **2010,** 9, 1945.
xii. S. B. Lee, Y. I. Park, M. S. Dong, Y. D.Gong, *Bioorg. Med. Chem. Lett*., **2010**, 20, 5900.
xiii. A. A. Abu-Hashem, M. A. Gouda, F. A. Badria, *Eur. J. Med. Chem.,* **2010,** 45, 1976.
xiv. E. S. H. El-Ashry, A. A. H. Abdel-Rahman, N. Rashed, H. A. Rasheed, *Pharmazie*., **1999**, 54, 893-897.
xv. S. N. Khattab, S. Y. Hassan, A. A. Bekhit, A. M. El Massry, V. Langer, *Eur. J. Med. Chem*., **2010**, 45, 4479.
xvi. C. Srinivas, C. N. S. P. Kumar, V. J. Rao, S .J. Palaniap pan, *Mol. Catal. A: Chem*., **2007**, 26, 227.
xvii. L. G. Frohlich, P. Kotsonis, H. Traub, S. Taghavi- Moghadam, N. Al-Masoudi, H, Hofmann, H. Strobel, H. Matter, W. Pfleiderer, H.H.H.W. Schmid, *J.Med.Chem*., **1999**, 42, 4108.
xviii. S. Dailey, J. W. Feast, R. J. Peace, I. C. Sage, S. Till, E. L. Wood, *J. Mater. Chem*., **2001**, 11, 2238.
xix. D. O'Brien, M. S. Weaver, D. G. Lidzey, D. D. C. Bradley, *Appl. Phys. Lett*., **1996**, 69, 881.
xx. P. K. Sasmal, R. Majumdar, R. R. Dighe, A. R. Chakravorty, *Dalton Trans*., **2010**, 39, 7104.
xxi. A. Zarrouk, A. Dafali, B. Hammouti, H. Zarrok, S. Boukhris, M. Zertoubi, *Int. J. Electrochem. Sci.*, **2010**, 5, 46.
xxii. J. C. Crossley, L. A. Johnston, *Chem. Commun*., **2002**, 10, 1122.
xxiii. W. I. Stephen, P. C. Uden, *Anal. Chim. Acta*., **1967**, 39, 357.
xxiv. M. Mastalerz, V. Fisher, Ma, Ch.-Q, R. A. J. Janssen, P. Baurele, *Org. Lett*., **2009,** 11, 4500.
xxv. R. E. Holmlin, J. A. Barton, *Inorg. Chem*., **1995**, 34, 7.
xxvi. V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res*., **1998**, 31, 26.
xxvii. V. Balzani, M. Gomez-Loez, J. F. Stoddart, *Acc. Chem. Res*., **1998,** 31, 405.
xxviii. M. Du, X. J. Zhao, *Acta Crystallogr. Sect. C*., **2003**, 59, 403.
xxix. P. P. Castro, G. Zhao, G. A. Masangkay, C. Hernandez, L. M. Gutierrez-Tunstad, *Org. Lett.,* **2004,** 6, 333.
xxx. J. L. Sessler, H. Maeda, T. Mizuno,V. M. Lynch, H. Furuta, *J. Am. Chem. Soc*., **2002**, 124, 13474.

xxxi. Z. Chen, J. Zhu, H. Xie, S. Li, Y. Wu, Y. Gong, *Adv. Synth. Cata*l., **2010**, 352, 1296.
xxxii. Q. Tang, Z. Liang, Liu, J. Xu, J, Q. Miao, *Chem. Commun*., **2010**, 46, 2977.
xxxiii. M. Tingoli, M. Mazzella, B. Panunzi, A. Tuzi, *Eur. J. Org. Chem*., **2011**, 399.
xxxiv. S. Naskar, P. Paira, R. Paira, S. Mondal, A. Maity, A. Hazra, K. B. Sahu, P. Saha, S. Banerjee, P. Luger, M. Webe, N. B. Mondal, *Tetrahedron.,* **2010**, 66, 5196.
xxxv. S. V. More, M.N.V. Sastry, C. F. Yao, Green Chem., **2006,** 8, 91.
xxxvi. A. Dhakshinamoorthy, K. Kanagaraj, K. K. Pitchumani, *Tetrahedron Lett.*, **2011**, 52, 69.
xxxvii. S. V. More, M. N. V. Sastry, C. C. Wang, C. F. Yao, *Tetrahedron Lett*., **2005**, 46, 6345.
xxxviii. R. S. Bhosale, S. R. Sarda, S. S. Ardhapure, W. N. Jadhav, S. R. Bhusare, R. P. Pawar, *Tetrahedron Lett*., **2005**, 46, 7183.
xxxix. E. E. Merkul, J. Dohe, C. Gers, F. Rominger, T.J.I. Müller, *Angew. Chem*., **2011**, 50, 2966.
xl. A. R. Katritzky, D. Zhang, K. Kirichenko, *J. Org. Chem.*, **2005**, 70, 3271.
xli. J. P. Wan, S. F. Gan, J. M. Wu, Y. Pan, *Green Chem*., **2009**, 11, 1633.
xlii. B. Madhav, S. Narayana Murthy, V. Prakash Reddy, K. Rama Rao, Y. V. D. Nageswar, *Tetrahedron Lett*., **2009**, 50, 6025.
xliii. H. M. Meshram, G. Santosh Kumar, P. Ramesh, B. Chennakesava Reddy, *Tetrahedron Lett.*, **2010**, 51, 2580.
xliv. S. Y. Kim, K. H. Park, Y. K. Chung, *Chem. Commun*., **2005**, 1321–1323.
xlv. S. A. Raw, C. D. Wilfre, R. J. K. Taylor, *Org. Biomol. Chem*., 2004, 2, 788.

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