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COMMUNICATION

Triethanolamine-catalyzed expeditious and greener synthesis of 2-amino-4*H*-chromenes

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Triethanolamine (TEOA), an inexpensive and eco-friendly base, was used to efficiently catalyze the three-component condensation reaction of heterocyclic/aromatic aldehyde, (α/β)-naphthol, and malononitrile in water to give the corresponding substituted 2-amino-4*H*-chromene derivatives with excellent yields.

KEYWORDS

2-amino-4*H*-chromene, green synthesis, multicomponent reaction, triethanolamine (TEOA), water medium

1 | INTRODUCTION

In the last two decades, considerable effort has been made for the development of multicomponent reactions (MCRs) in aqueous media.[1] Because of the associated environmental and economic advantages, such as the less number of steps, high atom economy, operational simplicity, and low waste generation, MCRs complies with the principles of green chemistry.[2] On the other hand, reactions in aqueous media may circumvent the problems associated with many of the traditional methods, which are largely based on the use of toxic or hazardous organic solvents. In this context, reactions using water as the medium have emerged as a useful alternative for numerous organic transformations.[3] Besides being cheap, nontoxic, nonflammable, and environmentally benign, aqueous solutions possess the other physicochemical characteristic like high heat capacity required to be an alternative reaction medium.[4] Consequently, a number of MCRs have been reported in aqueous media, providing easy access to a variety of bioactive chemical entities such as pyrido[2,3-*d*]pyrimidines,[5] dihydropyrano[2,3-*c*]pyrazole,[6] 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione,[7] thiopyrano[2,3-*b*]indole-3-carbonitrile,[8] pyrazolo[3,4-*b*]quinolin-5-one,[9] 3-methyl-isoxazol-5(4*H*)-one,[10] 1,2-dihydro[1,6]naphthyridine,[11] and others.[12]

Chromenes are considered medicinally important heterocycles found in many natural products and pigments.[13] Of these, substituted 2-amino-4*H*-chromenes exhibit a wide range of biological properties including, antimicrobial,[14] antiviral,[15] anticoagulant,[16] potassium channel regulating,[17] antispasmolitic,[18] anti-inflammatory,[19] antiproliferative,[20] and central nervous system (CNS) activities.[21] There is renewed interest on 2-amino-4*H*-chromenes due to their potent anticancer activity through vascular disruption[22] and inhibition of the Bcl-2 protein,[23] which reflects the potential of this class of derivatives as drug candidates.

A widely used protocol for the synthesis of 2-amino-4*H*-chromenes is by refluxing aldehyde, malononitrile, and activated phenol in the presence of organic bases such as piperidine, triethylamine, pyridine, so forth. for several hours.[24–27] Moreover, other catalysts such as methanesulfonic acid,[28] imidazole,[29] porous organic polymers (POPs),[30] potassium phthalimide,[31] L-proline-melamine,[32] sodium malonate,[33] and Na_2CO_3[34] have also been utilized for this transformation. In recent years, several new green methods have been reported using cetyltrimethylammonium chloride,[35] KF/Al_2O_3,[36] basic γ–alumina,[37] MgO,[38] $CuSO_4{\cdot}5H_2O$,[39] DBU,[40] CTABr/ultrasound irradiation,[41] nanocatalyst,[42] bael fruit extract (BFE),[43] water extract of lemon fruit shell ash (WELFSA),[44] and poly(ethylene glycol) (PEG) in water.[45] Although various procedures for the synthesis of 2-amino-4*H*-chromenes are known, many of these methods have disadvantages such as expensive and unique catalysts, long reaction times, utilization

of microwave or ultrasonic irradiation, and affording only moderate yields.[46] Moreover, organic bases (piperidine, triethylamine, pyridine, etc.) used for this MCR as catalysts are toxic and harmful to the environment.[47] Hence, the development of inexpensive, mild, and efficient green synthetic methodologies is of great interest.

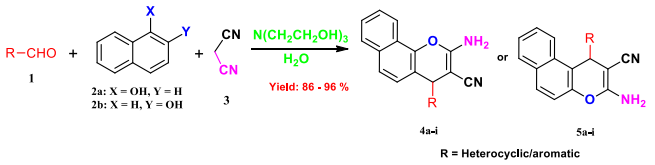
Triethanolamine (TEOA) has been utilized as surfactant and an emulsifier in many consumer products such as detergents, dishwashing, hand cleaners, polishes, paints, shaving creams, and printing inks.[48] Recent reports have demonstrated the efficiency of TEOA as catalyst in several organic transformations[49] including phosphate-free Heck reactions,[50] and Knoevenagel-type cyclocondensation,[51] and as a reusable reaction medium for the synthesis of aryl sulfones.[52] From the green chemistry perspective, we hoped that replacing conventional organic bases (TEA, piperidine, or pyridine) with TEOA in water can be an effective strategy for the synthesis of 2-amino-4*H*-chromenes.

In continuation of our ongoing research on the development of simple and efficient synthetic methods for various heterocycles,[53] here we report on TEOA as an economical, ingenious, and eco-friendly base catalyst for the synthesis of 2-amino-4*H*-chromene derivatives in water (Scheme 1).

2 | RESULT AND DISCUSSION

Initially, a mixture of benzaldehyde, malononitrile, and α-naphthol in water was stirred at room temperature (RT) using 20 mol% of TEOA as catalyst. We found that the reaction took a long time (24 hr) with only moderate yield of the corresponding 2-amino-4*H*-chromene derivative **4a** (Table 1, entry 1). When reaction temperature and catalyst loading were raised from RT to 90°C and 20–30 mol%, respectively, the reaction gave superior results, providing **4a** within 1 hr in excellent yield (96%). Contrarily, under catalyst-free condition, the yield of compound **4a** was poor (Table 1, entry 6), thus underlining the crucial role of TEOA for this transformation.

The possible role of TEOA as a base catalyst in the formation of 2-amino-4*H*-chromene derivatives is shown in Scheme 2. Initially, the reaction of benzaldehyde and malononitrile undergoes Knoevenagel condensation in the presence of TEOA to furnish the intermediate 2-benzylidenemalononitrile (**I**). The enolate intermediate (**II**) generated from the interaction of α-naphthol with TEOA reacts with **I** and undergoes heterocyclization via the intermediate (**III**), resulting in the desired product.

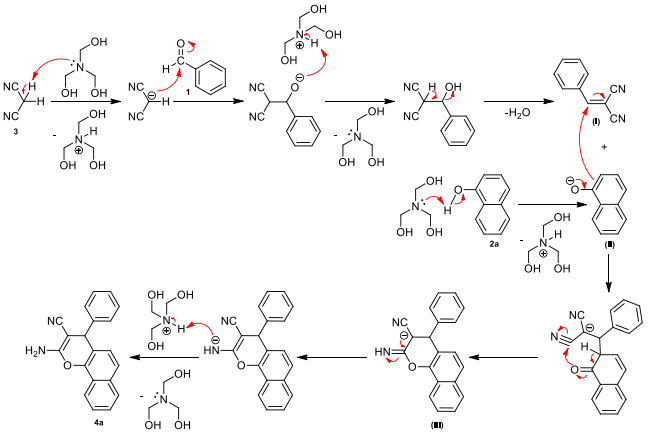


SCHEME 1 Synthesis of 2-amino-4*H*-chromenes

TABLE 1 Reaction optimization for triethanolamine (TEOA)-catalyzed synthesis of 2-amino-4*H*-chromene (**4a**)[a]

Entry	TEOA (Mol%)	Reaction temperature (°C)	Reaction time (hr)	Yield (%)[b]
1	20	RT	24	62
2	30	50	8	70
3	30	75	4	83
4	**30**	**90**	**1**	**96**
5	15	90	3	80
6	Free	90	16	15

[a] *Reaction conditions*: benzaldehyde (3.0 mmol), α-naphthol (3.0 mmol), malononitrile (3.0 mmol), TEOA in water (10 mL).
[b] Isolated yield after crystallization from MeOH.
Note. Bold value represents optimal reaction condition.



SCHEME 2 Plausible mechanism for the synthesis of representative derivative (**4a**) of 2-amino-4*H*-chromenes using TEOA

Several other organic bases were employed, such as piperidine, pyridine, and triethylamine, under aqueous condition for a comparative study (Table 2). From these results, it was evident that TEOA showed superior catalytic activity for the synthesis of 2-amino-4*H*-chromene derivatives in aqueous medium over the others.

The structure of the product **4a** was confirmed by comparison of the melting points and through thin-layer chromatography (TLC) with an authentic sample prepared by following a reported method[39,51] and also by spectral data (IR, mass spectrometry, and ^{1}H NMR).

With the optimized protocol, we examined the generality of this method by varying the aldehyde and naphthol components under same reaction condition (Table 3). It

TABLE 2 Synthesis of 2-amino-4*H*-chromene (**4a**) using different organic catalysts in water[a]

Entry	Catalyst	Reaction time (hr)	Yield (%)[b]
1	Piperidine	4	78
2	Pyridine	6	62
3	Triethylamine	4	82
4	**TEOA**	**1**	**96**

[a] *Reaction conditions*: benzaldehyde (3.0 mmol), α-naphthol (3.0 mmol), malononitrile (3.0 mmol), different base catalysts (30 mol %) in water (10 mL).
[b] Isolated yield after crystallization from MeOH.
Note. Bold value represents optimal reaction condition.

TABLE 3 Synthesis of substituted 2-amino-4*H*-chromenes (**4a–i** or **5a–i**) catalyzed by TEOA in water[a]

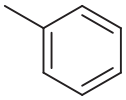
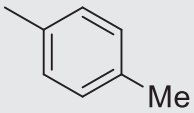
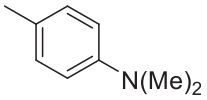
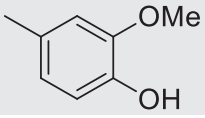
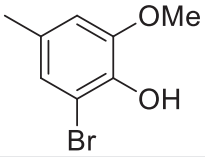
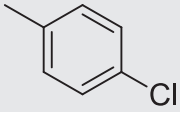
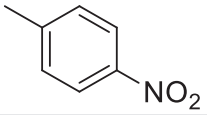
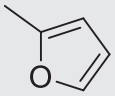
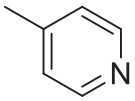
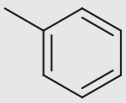
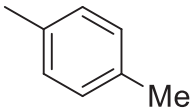
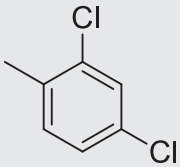
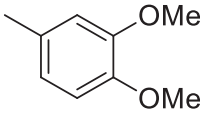
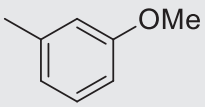
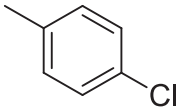
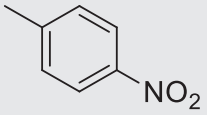
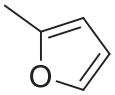
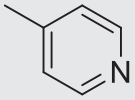
Entry	R	Naphthol	Time (min)	Product[b]	Yield (%)[c]	M.p. (°C) Found	M.p. (°C) Reported[ref]
1		**2a**	60	**4a**	96	205–206	207–208[54]
2		**2a**	45	**4b**	90	204–205	205–206[55]
3		**2a**	60	**4c**	93	202–203	203–205[56]
4		**2a**	60	**4d**	90	138–140	136–138[55]
5		**2a**	90	**4e**	91	203–204	—
6		**2a**	60	**4f**	92	230–231	231–232[55]
7		**2a**	45	**4g**	96	232–233	230–231[55]
8		**2a**	45	**4h**	92	167–168	169–171[55]
9		**2a**	90	**4i**	88	198–199	199–200[35]
10		**2b**	60	**5a**	90	278–279	280[28]
11		**2b**	90	**5b**	87	254–255	256–257[54]
12		**2b**	60	**5c**	91	240–242	242–243[39]
13		**2b**	90	**5d**	90	141–143	148–150[39]
14		**2b**	90	**5e**	86	263–264	262–263[57]

TABLE 3 (Continued)

Entry	R	Naphthol	Time (min)	Product[b]	Yield (%)[c]	M.p. (°C) Found	M.p. (°C) Reported[ref]
15		**2b**	60	**5f**	89	210–212	210–212[20]
16		**2b**	60	**5g**	90	183–185	186[28]
17		**2b**	60	**5h**	94	222–224	225–226[57]
18		**2b**	90	**5i**	89	231–232	229–231[20]

[a] *Reaction condition*: aldehyde (3.0 mmol), α- or β-naphthol (3.0 mmol), malononitrile (3.0 mmol), triethanolamine (30 mol%) in water (10 mL) at 90°C.
[b] All products were characterized by their m.p. and IR, mass, and ^{1}H NMR spectra and compared with reported data.
[c] Isolated yields after crystallization from MeOH.

was revealed that the reaction is also applicable to different aromatic aldehydes and weakly reactive β-naphthols as well, giving the desired 2-aminochromene derivatives (**4a–i** or **5a–i**) in very high yields. Moreover, the yields were independent of the electronic effect of substituents present on the aromatic aldehyde (Table 3). It is noteworthy that the product isolation and purification procedure were extremely simple in this protocol. Moreover, easy recovery of the catalyst from filtrate underlines the convenience of this method.

3 | CONCLUSIONS

In summary, we have developed a greener and expeditious methodology for the synthesis of 2-amino-4*H*-chromenes via a three-component condensation reaction catalyzed by TEOA. Several advantages of this method, such as the use of an inexpensive catalyst, short reaction time, use of water as solvent, and easy purification technique, imply that this method may have industrial applicability.

4 | EXPERIMENTAL SECTION

4.1 | General information

The melting points of all compounds were recorded in open capillary tubes and are uncorrected. IR spectra were recorded on an alpha FT-IR (Bruker) spectrophotometer using the KBr pallet technique. ^{1}H NMR spectra were recorded on a Bruker-400 MHz FT-NMR spectrometer in DMSO-d_6 as solvent, and the chemical shift values are reported in units of δ (ppm) relative to tetramethylsilane as the internal standard. The mass spectra were recorded on an Agilent GC-MS-5977A spectrometer. Reaction monitoring was carried out using TLC on aluminum silica gel 60 F_{254} (Merck, Germany) and detected by UV light (254 nm).

4.2 | General procedure for the synthesis of substituted 2-amino-4*H*-chromenes (4a–i or 5a–i) catalyzed by TEOA in water

In a Teflon septa-capped reaction vessel, a mixture of the appropriate aldehyde (**1**, 3.0 mmol), α or β-naphthol (**2a** or **2b**, 3.0 mmol), malononitrile (**3**, 3.0 mmol), and TEOA (0.9 mmol) in water (10 mL), was heated and stirred at 90°C for an appropriate time (as mentioned in Table 3). The progress of the reaction was monitored by TLC (ethyl acetate/hexane 3:1). After the starting material was completely consumed, the reaction mixture was cooled to RT, and the separated solid product was collected by Buchner filtration and crystallized from methanol to give the corresponding 2-amino-4*H*-chromenes (**4a–i**, **5a–i**).

4.2.1 | Catalyst separation and purification procedure

The filtrate (containing TEOA) collected after Buckner filtration, as describe above, was extracted sequentially with diethyl ether (5 mL) and hexane (5 mL) in order to remove the absorbed organic substrates. The remaining aqueous medium was evaporated under reduced pressure to obtain sufficiently pure TEOA for further use. The recovery of TEOA was about 95%.

All the synthesized compounds **4a–i** and **5a–i** were characterized by IR, mass spectrometry, and ^{1}H NMR spectroscopy. Also, the melting points determined were compared with those in the literature and found to be matching (Table 3). The spectral data for selected compounds are listed below.

4.3 | 2-Amino-4-phenyl-4*H*-benzo[*h*]chromene-3-carbonitrile (4a)

IR (KBr) (ν_{max}, cm^{-1}): 3433, 3340, 3021, 2183, 1639, 1590, 1411, 1233, 1171, 1028, 815, 752; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.89 (s, 1H, CH), 7.1 (s, 2H, NH_2), 7.10–7.19 (m, 6H, ArH), 7.53–7.66 (m, 3H, ArH), 7.92 (d, J = 8 Hz, 1H, ArH), 8.23 (d, J = 8 Hz, 1H, ArH). GC–MS: *m/z* 298 (M^+).

4.4 | 2-Amino-4-(3-bromo-4-hydroxy-5-methoxyphenyl)-4*H*-benzo[*h*]chromene-3-carbonitrile (4e)

IR (KBr) (ν_{max}, cm^{-1}): 3416, 3354, 3055, 2188, 1658, 1374, 1278, 1198, 794, 768; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.79 (s, 3H, OMe), 4.90 (s, 1H, CH), 6.88 (s, 1H, ArH), 6.93 (s, 1H, ArH), 7.16 (s, 1H, ArH), 7.18 (s, 2H, NH_2), 7.56–7.66 (m, 3H, ArH), 7.90 (d, J = 8.1 Hz, 1H, ArH), 8.23 (d, J = 8.1 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 30.56, 57.05, 59.38, 111.63, 112.42, 115.44, 120.36, 123.50, 124.04, 125.56, 126.13, 126.24, 126.65, 127.25, 129.13, 133.50, 134.56, 139.87, 143.62, 149.66, 159.92. GC–MS: *m/z* 422 $(M-1)^+$.

4.5 | 2-Amino-4-phenyl-4*H*-benzo[*f*]chromene-3-carbonitrile (5a)

IR (KBr) (ν_{max}, cm^{-1}): 3440, 3345, 2180, 1631, 1560, 1279, 1102, 800, 760; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 5.18 (s, 1H, CH), 6.59 (s, 2H, NH_2), 7.16–7.32 (m, 6H, ArH), 7.39–7.42 (m, 3H, ArH), 7.75 (d, J = 8.1 Hz, 1H, ArH), 7.83 (d, J = 8.1 Hz, 1H, ArH). GC–MS: *m/z* 298 (M^+).

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REFERENCES

[1] Y. Gu, *Green Chem.* **2012**, *14*, 2091.
[2] M. O. Simon, C. J. Li, *Chem. Soc. Rev.* **2012**, *41*, 1415.
[3] a) R. N. Butler, A. G. Coyne, *Chem. Rev.* **2010**, *110*, 6302. b) S. Kobayashi, *Pure Appl. Chem.* **2007**, *79*, 235.
[4] Y. Jung, R. A. Marcus, *J. Am. Chem. Soc.* **2007**, *129*, 5492.
[5] S.-H. Li, Y.-H. Shen, N. Gao, J.-T. Li, *Egypt. J. Chem.* **2010**, *7*, 779.
[6] M. M. Heravi, A. Ghods, F. Derikvand, K. Bakhtiari, F. F. Bamoharram, *J. Iran. Chem. Soc.* **2010**, *7*, 615.
[7] D. S. Raghuvanshi, K. N. Singh, *Tetrahedron Lett.* **2011**, *52*, 5702.
[8] K. C. Majumdar, S. Ponra, T. Ghosh, *RSC Adv.* **2012**, *2*, 1144.
[9] A. Y. Andriushchenko, S. M. Desenko, V. N. Chernenko, V. A. Chebanov, *J. Heterocycl. Chem.* **2011**, *48*, 365.
[10] Q. Liu, Y.-N. Zhang, *Bull. Korean Chem. Soc.* **2011**, *32*, 3559.
[11] C. Mukhopadhyay, P. Das, R. J. Butcher, *Org. Lett.* **2011**, *13*, 4664.
[12] a) X.-S. Wang, J. Zhou, K. Yang, M.-M. Zhang, *Synth. Commun.* **2010**, *40*, 1065. b) G.-P. Lu, L.-Y. Zeng, C. Cai, *Green Chem.* **2011**, *13*, 998. c) M. Hadjebi, M. S. Hashtroudi, H. R. Bijanzadeh, S. Balalaie, *Helv. Chim. Acta* **2011**, *94*, 382. d) A. Alizadeh, A. Rezvanian, L.-G. Zhu, *J. Org. Chem.* **2012**, *77*, 4385. e) S. M. Rajesh, B. D. Bala, S. Perumal, J. C. Menéndez, *Green Chem.* **2011**, *13*, 3248. f) Y. Zou, H. Wu, Y. Hu, H. Liu, X. Zhao, H. Ji, D. Shi, *Ultrason. Sonochem.* **2011**, *18*, 708. g) S. A. El-Assaly, *Der. Pharm. Chem.* **2011**, *3*, 81.
[13] G. P. Ellis, in *The Chemistry of Heterocyclic Compounds. Chromenes, Chromanes, and Chromones* (Eds: A. Weissberger, E. C. Taylor), John Wiley, New York **1977**, p. 11.
[14] a) K. Hiramoto, A. Nasuhara, K. Michiloshi, T. Kato, K. Kikugawa, *Mutat. Res.* **1997**, *395*, 47. b) A. M. El-Agrody, M. H. El-Hakim, M. S. Abd El-Latif, A. H. Fakery, E. S. M. El-Sayed, K. A. El-Ghareab, *Acta Pharm.* **2000**, *50*, 111.
[15] a) P. W. Smith, S. L. Sollis, P. D. Howes, P. C. Cherry, I. D. Starkey, K. N. Cobley, H. Weston, J. Scicinski, A. Merritt, A. Whittington, P. Wyatt, N. Taylor, D. Green, R. Bethell, S. Madar, R. J. Fenton, P. J. Morley, T. Pateman, A. Beresford, *J. Med. Chem.* **1998**, *41*, 787. b) A. Martínez-Grau, J. Marco, *Bioorg. Med. Chem. Lett.* **1997**, *7*, 3165.
[16] L. Bonsignore, G. Loy, D. Secci, A. Calignano, *Eur. J. Med. Chem.* **1993**, *28*, 517.
[17] T. S. Jin, A. Q. Wang, X. Wang, J. S. Zhang, T. S. Li, *Synlett* **2004**, *5*, 871.
[18] R. W. DeSimone, K. S. Currie, S. A. Mitchell, J. W. Darrow, D. A. Pippin, *Comb. Chem. High Throughput Screening* **2004**, *7*, 473.
[19] A. A. Patchett, R. P. Nargund, *Annu. Rep. Med. Chem.* **2000**, *35*, 289.
[20] M. Sudershan Rao, B. S. Chhikara, R. Tiwari, S. A. Nasrolahi, K. Parang, A. Kumara, *Chem. Bio. Interface* **2012**, *2*, 362.
[21] F. Eiden, F. Denk, *Arch. Pharm.* **1991**, *324*, 353.
[22] a) W. Kemnitzer, S. Kasibhatla, S. Jiang, H. Zhang, Y. Wang, J. Zhao, S. Jia, J. Herich, D. Labreque, R. Storer, K. Meerovitch, D. Bouffard, R. Rej, R. Denis, C. Blais, S. Lamothe, G. Attardo, H. Gourdeau, B. Tseng, J. Drewe, S. X. Cai, *J. Med. Chem.* **2004**, *47*, 6299. b) S. Kasibhatla, H. Gourdeau, K. Meerovitch, J. Drewe, S. Reddy, L. Qiu, H. Zhang, F. Bergeron, D. Bouffard, Q. Yang, J. Herich, S. Lamothe, S. X. Cai, B. Tseng, *Mol. Cancer Ther.* **2004**, *3*, 1365.
[23] J. Wang, D. Liu, Z. Zhang, S. Shan, X. Han, S. Srinivasula, C. Croce, E. Alnemri, Z. Huang, *Proc. Natl. Acad. Sci. U. S. A.* **2000**, *97*, 7124.
[24] A. F. Harb, A. M. Hesien, S. A. Metwally, M. H. Elnagdi, *Liebigs Ann. Chem.* **1989**, *24*, 585.
[25] N. Martin, C. Pascual, C. Seoane, J. L. Soto, *Heterocycles* **1987**, *26*, 2811.
[26] A. G. A. Elagamay, F. M. A. El-Taweel, *Indian J. Chem. Sect. B: Org. Chem. Incl. Med. Chem.* **1990**, *29B*, 885.
[27] S. E. Zayed, E. I. AbouEImaged, S. A. Metwally, M. H. Elnagdi, *Collect. Czech. Chem. Commun.* **1991**, *56*, 2175.
[28] M. M. Heravi, B. Baghernejad, H. A. Oskooie, *J. Chin. Chem. Soc.* **2008**, *55*, 659.
[29] M. N. Khan, S. Pal, S. Karamthulla, L. H. Choudhury, *RSC Adv.* **2014**, *4*, 3732.
[30] S. K. Kundu, A. Bhaumik, *RSC Adv.* **2015**, *5*, 32730.
[31] H. Kiyani, F. Ghorbani, *Chem. Pap.* **2014**, *68*, 1104.
[32] S. Nagaraju, B. Paplal, K. Sathish, S. Giri, D. Kashinath, *Tetrahedron Lett.* **2017**, *58*, 4200.
[33] H. Kiyani, M. Tazari, *Res. Chem. Intermed.* **2017**, *43*, 6639.
[34] I. B. Masesane, S. O. Mihigo, *Synth. Commun.* **2015**, *45*, 1546.
[35] R. Ballini, G. Bosica, M. L. Conforti, R. Maggi, A. Mazzacani, P. Righi, G. Sartori, *Tetrahedron* **2001**, *57*, 1395.
[36] X.-S. Wang, D.-Q. Shi, G.-F. Wang, S.-J. Tu, *Synth. Commun.* **2004**, *34*, 509.
[37] R. Maggi, R. Ballini, G. Sartori, *Tetrahedron Lett.* **2004**, *45*, 2297.
[38] D. Kumar, V. B. Reddy, B. G. Mishra, R. K. Rana, M. N. Nadagouda, R. S. Varma, *Tetrahedron* **2007**, *63*, 3093.
[39] F. K. Behbahani, S. Maryam, *J. Korean Chem. Soc.* **2013**, *57*, 357.
[40] V. A. Osyanin, D. V. Osipov, Y. N. Klimochkin, *Tetrahedron* **2012**, *68*, 5612.
[41] T. S. Jin, J. C. Xiao, S. J. Wang, T. S. Li, *Ultrason. Sonochem.* **2004**, *11*, 393.
[42] a)A. Maleki, R. Ghalavand, R. F. Haji, *Appl. Organomet. Chem.* **2018**, *32*, e3916. b) A. Mobinikhaledi, H. Moghanian, M. Ghanbari, *Appl. Organomet. Chem.* **2018**, *32*, e4108. c) H. Naeimi, M. F. Zarabi, *Appl. Organomet.*

Chem. **2018**, *32*, e4225. d) R. Tayebee, A. Pejhan, H. Ramshini, B. Maleki, N. Erfaninia, Z. Tabatabaie, E. Esmaeili, *Appl. Organomet. Chem.* **2018**, *32*, e3924. e) M. H. Sarvari, S. S. Haghighi, *Collect. Czech. Chem. Commun.* **2011**, *76*, 1285.

[43] S. Shinde, S. Damate, S. Morbale, M. Patil, S. S. Patil, *RSC Adv.* **2017**, *7*, 7315.

[44] K. Kantharaju, S. Y. Khatavi, *ChemistrySelect* **2018**, *3*, 5016.

[45] N. V. Shitole, K. F. Shelke, S. A. Sadaphal, B. B. Shingate, M. S. Shingare, *Green Chem. Lett. Rev.* **2010**, *3*, 83.

[46] a) M. Fujiwara, M. Sakamoto, K. Komeyama, H. Yoshida, K. Takaki, *J. Heterocycl. chem.* **2015**, *52*, 59. b) N. J. Thumar, M. P. Patel, *ARKIVOC* **2009**, *xiii*, 363.

[47] a) A. M. Shestopalov, Y. M. Emelianova, V. N. Nesterov, *Russ. Chem. Bull.* **2002**, *51*, 2238. b) R. A. Mekheimer, K. U. Sadek, *J. Heterocycl. chem.* **2009**, *46*, 149.

[48] R. D. Ashford, *Ashford's Dictionary of Industrial Chemicals*, 3rd ed., Wavelength Publications, Saltash, UK **2011**, p. 9252.

[49] B. Maleki, M. Baghayeri, S. Sheikh, S. Babaee, S. Farhadi, *Russ. J. Gen. Chem.* **2017**, *87*, 1064.

[50] H. J. Li, L. Wang, *Eur. J. Org. Chem.* **2006**, *62*, 5099.

[51] A. Khoraamabadi-zad, M. Azadmanesh, R. Karamian, M. Asadbegy, M. Akbari, *RSC Adv.* **2014**, *4*, 47721.

[52] K. Srinivas, P. K. Dubey, *Chem. Sci. Trans.* **2014**, *3*, 375.

[53] a) N. Kapuriya, R. Kakadiya, M. M. Savant, A. M. Pansuriya, C. V. Bhuva, J. Singh, A. S. Patel, P. V. Pipaliya, V. B. Audichya, S. Gangadharaiah, S. M. Anandalwar, S. J. Prasad, A. Shah, Y. Naliapara, *Indian J. Chem. Sect. B: Org. Chem. Incl. Med. Chem.* **2012**, *51B*, 1032. b) M. M. Savant, N. Gowda, A. M. Pansuriya, C. V. Bhuva, N. Kapuriya, S. M. Anandalwar, S. J. Prasad, A. Shah, Y. T. Naliapara, *Tetrahedron Lett.* **2011**, *52*, 254. c) M. M. Savant, A. M. Pansuriya, C. V. Bhuva, N. Kapuriya, Y. T. Naliapara, *Org. Chem. Int.* **2014**, 4.

[54] H. Kiyani, F. Ghorbani, *Res. Chem. Intermed.* **2015**, *41*, 7847.

[55] L. Chen, X. J. Huang, Y. Q. Li, M. Y. Zhou, W. J. Zheng, *Monatsh. Chem.* **2009**, *140*, 45.

[56] T. S. Jin, J. C. Xiao, S. J. Wang, T. S. Li, X. R. Song, *Synlett* **2003**, *13*, 2001.

[57] X. S. Wang, G. S. Yang, G. Zhao, *Tetrahedron: Asymmetry* **2008**, *19*, 709.

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