Est. 1984

ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2020, Vol. 36, No.(5):
Pg. 843-849

Bismuth (III) Triflate: A Mild, Efficient Promoter for the Synthesis of Trisubstituted Alkenes through Knoevenagel Condensation

ARUP DATTA

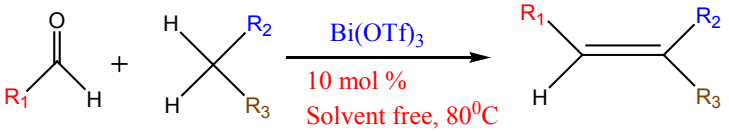
Department of Chemistry, Shibpur Dinobundhoo Institution (College), 412/1, G. T. Road (South), Shibpur, Howrah-711102, West Bengal, India.
Corresponding author E-mail: arupdattadb@gmail.com

http://dx.doi.org/10.13005/ojc/360507

(Received: September 19, 2020; Accepted: October 20, 2020)

ABSTRACT

In this work, smooth efficient and eco-friendly two component coupling method is reported for the synthesis of Knoevenagel Condensation product in presence of $Bi(OTf)_3$ catalyst under solvent free condition. Catalyst has participated in condensation between substituted aldehydes (aromatic and hetero-aromatic) and active methylene compounds (ethyl cyanoacetate, malononitrile and cyanoacetamide) effectively to generate an excellent yield of the product. $Bi(OTf)_3$ catalyst is stable, inexpensive and easily available was used for four times in this reaction without loss of catalytic activity.



$R_2 = CN$, $R_3 = CO_2CH_2CH_3$,

$R_2 = CN$, $R_3 = CN$,

$R_2 = CONH_2$, $R_3 = CO_2CH_2CH_3$

Keywords: Knoevenagel Condensation, Different aldehydes, Various active methylene compounds, $Bi(OTf)_3$, Heterogeneous Catalyst.

INTRODUCTION

The Knoevenagel reaction first reported in 1890 by Emil Knoevenagel which is an Aldol type condensation is extensively applied to the formation of the carbon–carbon double bond in synthetic organic chemistry. This important methodology has been used to produce different α,β-unsaturated acids like cinnamic acid.[1] This reaction is assisted for the production of such compounds which have immense biological significance[2] that is therapeutic activity and drug discovery.[3,4] In addition these compounds are used for production of polymers,[5,6] cosmetics,[7] perfumes[8] and natural products.[9] Malononitrile, ethyl cyanoacetate, cyanoacetamide are active methylene compounds and usually used in the string

of carbon-carbon double bond formation in organic transformation.[6]

A large no of methods for the synthesis of Knoevenagel Condensation products has been reported because of their immense biological activity and synthetic viewpoint. Bases such as amines (piperidine and N methyl piperidine), metal alkoxides, metal hydroxide and pyridine catalyzed Knoevenagel condensation reaction in either solvent free or organic solvents were reported.[10] Ammonium salts[10] and amino acids[10] were also used to construct this condensation product. These catalysts are homogeneous and very effective to increase the reaction rate but some disadvantages of these catalysts were (a) toxic to human[11] (b) difficult to separate from the reaction mixture because of homogeneity and can't be recycled and (c) neutralization was required at the end of the process. In many published papers green methodology was used to develop the Knoevenagel condensation product.[12,13] Analysis of the literature reveals that many Lewis acid catalysts for Knoevenagel condensation were used compared to bases as catalysts in huge numbers to overcome the above difficulties. Some Lewis acid catalysts such as TiCl4,[14] MgO,[15] Al_2O_3,[16] $ZnCl_2$,[17] $LaCl_3$[18] and $NbCl_5$[19] were used to construct this reaction in presence of hazardous organic solvents in few cases. Heteropoly acid catalyst $Na_8H[PW_9O_{34}]$[20] was used to create the Knoevenagel Condensation product to improve the methodology in solvent free medium.[21] Knoevenagel Condensation in green solvents like ionic liquids[22a] and water[22b] was documented in literature in different conditions in presence of different catalyst. Now a days solvent free technique is more popular because it maintains the green reaction conditions. Solvent free reaction is more attractive if it is carried out by using readily available non toxic and inexpensive reagent. Scientists are very interested in using Lewis acids like lanthanide triflate because they have certain characteristics.[23] Lanthanide triflates are used as an alternative to conventional Lewis acids because of the following advantages like low toxicity, high catalytic activity, air tolerance and reusability.[24] However large scale synthesis of this catalyst is inadequate because they are costly, so cheap and efficient catalysts are required to develop this reaction. Bismuth (III) triflate shows remarkable catalytic activity like lanthanide triflate in an organic transformation.[25] $Bi(OTf)_3$ is very cheap compare to lanthanide triflate and can be prepared in large scale by the reaction between Bi_2O_3 and triflic acid.[26] This catalyst was successfully used to synthesize the Substituted 2-Alkenylfurans in nitro methane solvent[27] and 2-aryl-1-arylmethyl benzimidazole derivatives in water.[28]

So my aim was to search an environmentally benign catalyst to build up a scheme for the synthesis of Knoevenagel Condensation products and for this purpose herein, I explore a scheme in presence of Bismuth (III) triflate catalyst under solvent free condition.

EXPERIMENTAL

Chemicals were purchased from SRL India and Spectrochem Pvt. Ltd. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz instrument. From Aldrich chemical company NMR solvents $CDCl_3$, DMSO-d_6 and TMS as the internal standard were purchased. Electrical melting point apparatus were used to determine the melting point. Perkin Elmer Spectrophotometer was used to study FT-IR spectra. Thin layer chromatography was used to monitor the reaction. For recrystallisation, distilled ethyl acetate-petroleum ether was used as solvents.

General procedure

An active methylene compound 2 (2.2 mmol), aldehyde 1 (2 mmol) and $Bi(OTf)_3$ (0.10 mmol) were taken and mixed in a 50 mL Erlenmeyer flask with a condenser containing ice water circulation and it was heated in an oil bath at 80^{0}C with a specific time period. The reaction was monitored by TLC time to time. After the complete conversion of the reaction indicated by brown spot in TLC then the crude product was cooled and diluted with 10 mL water stirred and filtered. After the separation of organic portion the crude product was crystallized from minimum volume of distilled ethylacetate-petroleum ether to get pure product. All ^{1}H-NMR and ^{13}C-NMR spectral data of all known compounds (3a-u) were checked with the data of authentic known compounds.

Selected characterization data for synthesized compounds

Ethyl-(E)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (3b)

White color solid, FT-IR (KBr, cm^{-1}): 3417, 2990, 1718, 1582, 1264 and 1181, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.17 (s, 1H, =CH), 8.01 (dd, 2H, C_2 and C_6 protons), 7.01 (dd, 2H, C_3 and C_5 protons), 4.37 (q, 2H,

OCH_2 CH_3), 3.90 (s, 3H, OMe), 1.23 (t, 3H, OCH_2CH_3), ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 163.9, 163.2, 154.3, 133.5, 124.4, 116.3, 114.8, 99.6, 62.4, 55.6, 14.2, Analytical calculation for $C_{13}H_{13}NO_3$(%): C: 67.52; H: 5.67; N: 6.06; Found: C: 67.36; H: 5.48; N: 5.82.

Ethyl-(E)-2-cyano-3-(4-hydroxy-3-methoxyphenyl)-2-propenoate (3c)

White color solid, FT-IR (KBr, cm^{-1}): 3376, 1707, 1578, 1510, 1276 and 1177, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.14 (s, 1H, OH), 7.86 (d, 1H, C_2 proton), 7.38 (dd, 1H, C_6 proton), 7.00 (d, 1H, C_5 proton), 6.26 (s, 1H, =CH), 4.37 (q, 2H, OCH_2CH_3), 3.97 (s, 3H, OMe), 1.39 (t, 3H, OCH_2CH_3), ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 163.2, 154.8, 150.8, 146.8, 128.9, 124.3, 116.5, 114.9, 111.2, 99.2, 62.4, 56.3, 14.2, Analytical calculation for $C_{13}H_{13}NO_4$(%): C: 63.15; H: 5.30; N: 5.67; Found: C: 63.00; H: 5.15; N: 5.52.

Ethyl-(E)-2-cyano-3-(4-hydroxyphenyl)-2-propenoate (3e)

White color solid, FT-IR (KBr, cm^{-1}): 3319, 2228, 1716, 1586, 1444, 1285, 1207 and 1172, ^{1}H NMR (300 MHz, DMSO-d_6) δ: 10.84 (brs, 1H, OH), 8.14 (s, 1H, =CH), 8.00 (dd, 2H, C_2 and C_6 protons), 6.96 (dd, 2H, C_3 and C_5 protons), 4.29 (q, 2H, OCH_2CH_3), 1.29 (t, , 3H, OCH_2CH_3), ^{13}C NMR (75 MHz, DMSO-d_6) δ: 163.4, 163.1, 155.2, 134.4, 123.0, 116.9, 97.5, 62.4, 14.5, Analytical calculation for $C_{12}H_{11}NO_3$(%): C: 66.35; H: 5.10; N: 6.45; Found: C: 66.28; H: 4.92; N: 6.31

Ethyl-(E)-2-cyano-3-(3-furanylphenyl)-2-propenoate (3l)

White color solid, FT-IR (KBr, cm^{-1}): 3038, 1716, 1617 and 1267, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.01 (s, 1H, =CH), 7.74 (d, 1H, furanyl proton), 7.39 (d, 1H, furanyl proton), 6.66 (dd, 1H, furanyl proton), 4.35 (q, 2H, OCH_2CH_3), 1.37 (t, 3H, OCH_2CH_3), ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.5, 148.7, 148.2, 139.4, 121.6, 115.3, 113.8, 98.7, 62.5, 14.1, Analytical calculation for $C_{10}H_9NO_3$(%): C: 62.82; H: 4.74; N: 7.33; Found: C: 62.69; H: 4.61; N: 7.20.

2-(2-Nitrophenylmethylene) malononitrile (3o)

White color solid, FT-IR (KBr, cm-^{1}): 2366, 1568, 1522 and 1344, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.45 (s, 1H, =CH), 8.35 (dd, , 1H, C_3 proton), 7.91-7.78 (m, 3H, C_4, C_5 and C_6 protons), ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.6, 134.9, 133.4, 130.4, 129.5, 126.7, 125.8, 112.2, 110.9, 88.6, Analytical calculation for $C_{10}H_5N_3O_2$ (%): C: 60.31; H: 2.53; N: 21.10; Found: C: 60.20; H: 2.41; N: 20.93.

2-(4-Chlorophenylmethylene) malononitrile (3n)

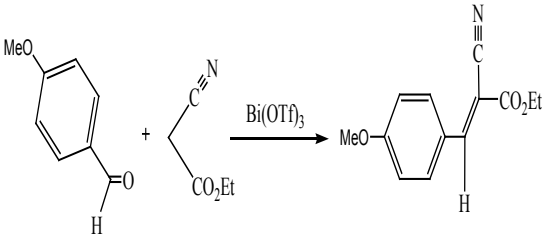
White color solid, FT-IR (KBr, cm^{-1}): 2221, 1578, 1484, 1408, 1215 and 1091, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.85 (td, 2H, C_2 and C_6 protons), 7.75 (s, 1H, =CH), 7.52 (td, 2H, C_3 and C_5 protons), ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 158.2, 141.1, 131.9, 130.1, 129.3, 113.4, 112.4, 83.4, Analytical calculation for $C_{10}H_5ClN_2$(%): C: 63.68; H: 2.67; N: 14.85; Found: C: 63.53; H: 2.42; N: 14.67.

(E)-2-Cyano-3-phenyl-2-propenamide (3s)

White color solid, FT-IR (KBr, cm^{-1}): 3398, 3161, 1691, 1595 and 1371, ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.32 (s, 1H, =CH), 7.95-7.91 (m, 2H, Ar protons), 7.56-7.45 (m, 3H, Ar protons), 6.42 (brs, 2H, $CONH_2$), ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 162.2, 154.0, 133.1, 131.6, 130.8, 129.2, 116.8, 103.2, Analytical calculation for $C_{10}H_8N_2$ (%): C: 69.76; H: 4.68; N: 16.27; Found: C: 69.63; H: 4.52; N: 16.15.

RESULT AND DISCUSSIONS

In order to investigate the effect of catalyst, solvent, time and yield; a model reaction had been chosen for this purpose. Initially 4-methoxybenzaldehyde (2 mmol) and ethyl cyanoacetate (2.2 mmol) were taken as model substrate and reagent under different conditions to focus the feasibility of the catalyst in solvent free medium at suitable temperature.



Scheme 1. Study of optimization of Knoevenagel Condensation product in presence of $Bi(OTf)_3$

The reaction was performed systematically and results were shown in Table 1. Mixture of the reaction was warmed with different amount of $Bi(OTf)_3$ (BT) catalyst in solvent free condition at changeable temperature and it was noticeable that the product yield depends on the amount of BT

catalyst and as well as temperature. The reaction sluggish without catalyst in solvent less condition at 80^{0}C and no yield was isolated when 10 mol% of BT catalyst was used at room temperature although reaction was continually monitored for 6 h (Entry 1, Table 1). When the mol% of the catalyst was varied from 1 to 10, the yield of the product gradually increased. 5 mol% of the catalyst at 80^{0}C gave only 60% yield of the product (Entry 4, Table 1). Increasing the amount of the catalyst from 5 to 10 mol% resulted in a drastic increase of the yield to 90% (Entry 6, Table 1). More over in presence of 10 mol% of catalyst at 90^{0}C no improved yield was observed (Entry 7, Table 1). More than 10 mol% of the catalyst that means 15 and 20 mol% of the catalyst at 80^{0}C did not improve the yield of the product (Entries 8 and 10, Table 1) and at comparatively high temperature (90^{0}C) no better result was observed (Entries 9 and 11, Table 1). So I came to the point that only 10 mol% of catalyst was adequate to complete the reaction at 80^{0}C (Entry 6, Table 1) with excellent yield of the product.

Table 1: Study of the optimization condition of the Knoevenagel Condensation in different mol% of $Bi(OTf)_3$ catalyst

Entry	BT(mol%)	[a]Conditions	Time (h)	Yield[b](%)
1	0	Oil bath 80^{0}C, solvent free	6	25
2	10	Room temp, solvent free	6	00
3	2.5	Oil bath 80^{0}C, solvent free	6	30
4	5.0	Oil bath 80^{0}C, solvent free	6	60
5	7.5	Oil bath 80^{0}C, solvent free	6	75
6	10	Oil bath 80^{0}C, solvent free	6	90
7	10	Oil bath 90^{0}C, solvent free	6	88
8	15	Oil bath 80^{0}C, solvent free	6	90
9	15	Oil bath 90^{0}C, solvent free	6	90
10	20	Oil bath 80^{0}C, solvent free	6	88
11	20	Oil bath 90^{0}C, solvent free	6	90

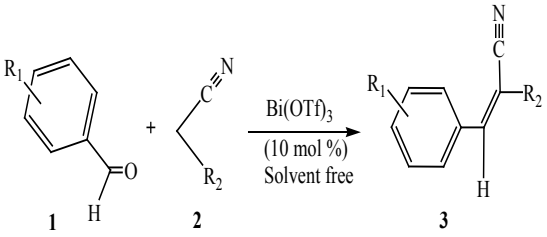
[a]Reaction Conditions: p-methoxy benzaldehyde (2mmol) and ethylcyanoacetate (2.2 mmol), [b]Isolated Yield.

Table 2: Study of solvent effect for the formation of Knoevenagel compound at 80^{0}C

Entry	Solvent(5mL)	[a]Conditions	Time (h)	[b]Yield(%)
1	THF	Oil bath, 80^{0}C	6	30
2	Toluene	Oil bath, 80^{0}C	6	35
3	DMSO	Oil bath, 80^{0}C	6	45
4	MeCN	Oil bath, 80^{0}C	6	40
5	EtOH	Oil bath, 80^{0}C	6	50
6	Aqueous EtOH	Oil bath, 80^{0}C	6	55
7	H_2O	Oil bath, 80^{0}C	6	68
8	none	Oil bath, 80^{0}C	6	90

[a]Reaction conditions: *p*-methoxy benzaldehyde(2mmol), ethylcyanoacetate (2.2 mmol) and 10mol% of BT catalyst, [b]Isolated Yield

Then I have studied the influence of the solvent effect on Knoevenagel condensation product catalyzed by 10 mol% of BT using the model substrate 4-methoxy benzaldehyde and reagent ethylcyanoacetate at 80^{0}C temperature and the results were shown in Table 2. In presence of less polar solvent (Entries 1 and 2, Table 2) the yield was very low even after 6 h of the continuous heating of the reaction mixture. Polar aprotic solvent increases the yield slightly (Entries 3 and 4, Table 2) but the reaction gave moderate yield in polar protic solvent (Entries 5, 6 and 7, Table 2). Under solvent free condition 90% yield of the product was determined, so I can conclude that BT catalyst worked well under solvent less condition (Entry 8, Table 2) than protic solvent to generate high yield of the condensation product. In solvent free condition the substrates and reagents are very close to each other and that's why high yield was observed under this conditions.



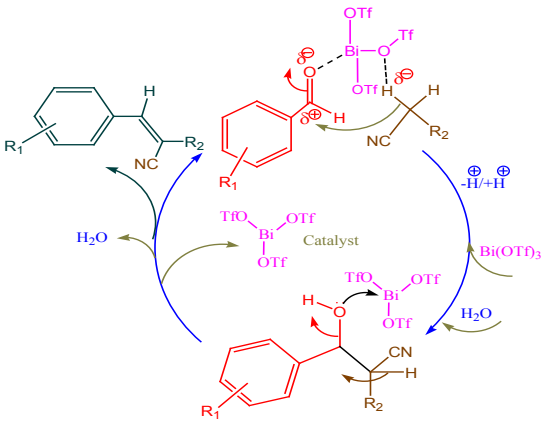
Scheme 2. Synthesis of Knoevenagel Condensation Product in presence of BT catalyst under solvent free condition at 80^{0}C

From the analysis of the reported data in Table 3, I can say that electron pulling group like NO_2, Cl, Br present in the aromatic aldehyde increases the electrophilicity of the aldehyde group and then enol form of the active methylene compound reacted with the aldehyde group smoothly and it was reflected in the yield of the products. Temperature was required to complete the dehydration step of the reaction. Electron donating group like OMe, NMe_2 gave slightly lower yield because of lower electrophilicity of aldehyde group (Entries 2 and 10, Table 3). However, all the substrates reacted very fine and produce excellent yields of the products. Beside this, it was also observed that when 4-bromobenzaldehyde was reacted separately with three different active methylene compound then different time was required to complete the reaction so the reactivity order is malanonitrile>ethyl cyanoacetate>cyanoacetamide of three active methylene compounds. Lewis acid catalysed mechanism was reported in many

previously published papers. Here Bi (III) acts as a Lewis acid catalyst which polarizes the aldehyde group by the formation of Lewis acid-Lewis base complex and beside this, catalyst helps to generate the nucleophilic activity of the active methylene compound by enolisation and then nucleophilic addition to aldehyde take place rapidly. In recent published paper where they shown the mechanism of the reaction.[39] I have represented here the details mechanism in Scheme 3 like that paper. In the previous published paper the products configuration was Trans.[31] According to this information all the products obtained through this methodology were Trans in nature.

Table 3: BT catalysed Knoevenagel Condensation

Entry	Aldehyde(R_1), (1)	Methylene Comp. R_2(2)	Product (3)	Time (h)	Yield(%)	Melting Point(°C) Observed	Melting Point(°C) Reported	Ref
1	4-Cl-C_6H_4	$CO_2CH_2CH_3$	3a	4.5	92	86	86-87	29
2	4-OMe-C_6H_4	$CO_2CH_2CH_3$	3b	6.0	90	82-84	80-84	30
3	4-OH-3OMe-C_6H_3	$CO_2CH_2CH_3$	3c	5.5	85	98	97-98	31
4	C_6H_5	$CO_2CH_2CH_3$	3d	5.0	84	50	49-50	31
5	4-OH-C_6H_4	$CO_2CH_2CH_3$	3e	6.0	86	170	170-171	31
6	4-NO_2-C_6H_4	$CO_2CH_2CH_3$	3f	5.0	88	167-169	167-169	29
7	2- NO_2-C_6H_4	$CO_2CH_2CH_3$	3g	5.0	82	96	96	29
8	2-OMe-C_6H_4	$CO_2CH_2CH_3$	3h	6.0	80	70-71	69	32
9	3-OH-C_6H_4	$CO_2CH_2CH_3$	3i	6.0	86	82	80-82	32
10	4-N,NMe_2-C_6H_4	$CO_2CH_2CH_3$	3j	6.0	82	121-122	122-123	31
11	4-Br-C_6H_4	$CO_2CH_2CH_3$	3k	4.5	88	85-86	86-88	32
12	2-Furanyl	$CO_2CH_2CH_3$	3l	5.0	86	92-93	91-93	29
13	4-OH-C_6H_4	CN	3m	4.0	90	183-184	184	33
14	4-Cl-C_6H_4	CN	3n	3.5	92	160	159-161	34
15	2-NO_2-C_6H_4	CN	3o	4.0	85	136-138	137-138	34
16	4-Br-C_6H_4	CN	3p	3.5	88	153-154	153-155	34
17	2-cinnamyl	CN	3q	4.0	86	128	126-128	35
18	3-Br-C_6H_4	$CONH_2$	3r	5.5	85	133-134	135	36
19	C_6H_5	$CONH_2$	3s	5.0	82	82	82-83	37
20	4-Br-C_6H_4	$CONH_2$	3t	5.5	88	223-224	222-224	38
21	2-cinnamyl	$CONH_2$	3u	5.0	85	136-137	135-137	37



Scheme 3. Plausible reaction mechanism of Knoevenagel Condensation Product

Recycling experiment of the catalyst always gets importance in industrial method and for this purpose an experiment was carried out to check the reusability of the catalyst in the present work. After complete conversion of the reaction the isolated crude product was incubated in 10 mL of water then stirred and filtered. Then aqueous layer was dried and regenerated catalyst was reused for next reaction under the same reaction condition. It was observed that no loss of efficiency of the catalyst even after using four times in the reaction and it is clearly represented graphically in Figure 1.

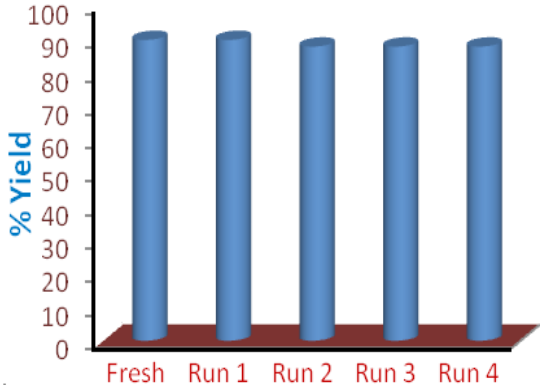


Fig. 1. Study of the reusability of the catalyst for the formation of the Knoevenagel condensation product (3b, Table 3)

CONCLUSION

In outline, it is clear that catalyst proves it efficiency and effectiveness towards the synthesis of trisubstituted alkene and provides a new synthetic methodology. Catalyst is inexpensive, easily obtainable and shows its eco friendly behavior. Moreover, the protocol offers some advantages with operational simplicity, clean reaction conditions, high yields with three different active methylene compounds under solvent less condition and causes less environmental pollution which makes the method more useful and interesting.

ACKNOWLEDGEMENT

Author is very much grateful to his PhD supervisor Professor Chhanda Mukhopadhyay, Department of Chemistry, University of Calcutta for providing him laboratory facility and financial support.

Conflict of Interest

No conflict of interest regarding this article.

REFERENCES

1. List, B.; *Angew. Chem.*, **2010**, *49*, 1730–1734.
2. Lavanya, G.; Padmavathi, V.; Padmaja, A.; *J. Braz. Chem. Soc.*, **2014**, *25*, 1200-1207.
3. Kaminskyy, D.; Den Hartog, G. J. M.; Wojtyra, M.; Lelyukh, M.; Gzella, A.; Bast, A.; Lesyk, R.; *Eur. J. Med. Chem.*, **2016**, *112*, 180-195.
4. Patel, R. V.; Kumari, P.; Rajani, D. P.; Chikhalia, K. H.; *Med. Chem. Res.*, **2013**, *22*, 195-210.
5. Birzan, L.; Cristea, M.; Draghici, C. C.; Tecuceanu, V.; Maganu, M.; Hanganu, A.; Razus, A. C.; Buica, G. O.; Ungureanu, E. M.; *Dyes Pigm.*, **2016**, *131*, 246-255.
6. Zhuang, X.; Zhao, W.; Zhang, F.; Cao, Y.; Liu, F.; Bi, S.; Feng, X.; *Polym. Chem.*, **2016**, *7*, 4176-4181.
7. De, P.; Koumba Yoya, G.; Constant, P.; Bedos-Belval, F.;Duran, H.; Saffon, N.; Daffé, M.; Baltas, M.; *J. Med. Chem.,* **2011**, *54*, 1449–1461.
8. Kwak, G.; Fujiki, M.; *Macromolecules.*, **2004**, *37*, 2021–2025.
9. Tan, H.; Chen, X.; Chen, H.; Liu, H.; Qiu, S.; *Eur. J. Org. Chem.*, **2015**, *39*, 4956.
10. (a)Saeed, B.; Morteza, B.; Shohreh, H.; Peyman, S.; *Synth. Commun.*, **2006**, *36*, 3703-3711.(b) Junjie, H.; Yanfen, J.; Yingpeng, S.; Xuegog, S.; Xinfu, P.; *Catal. Commun.*, **2008**, *9*, 2077-2079. (c) Zhou, Z; Sun, Y. *Synth. Commun.*, **2011**, *41*, 3162-3168.
11. Green, B. T.; Lee, S. T.; Panter, K. E.; Brown, D. R.; *Food Chem. Toxicol.*, **2012**, *50*, 2049-2055.
12 (a) Jafari, A. A.; Ghadami, M.; *Environ. Chem. Lett.*, **2016**, *14*, 215-221. (b) Dandia, A.; Parewa, V.; Kumari, S.; Bansal, S.; Sharma, A.; *Green Chem.*, **2016**, *18*, 2488-2499.
13. Lenardão, E. J.; Freitag, R. A.; Dabdoub, M. J.; Batista, A. C. F.; Silveira, C. D. C.; *Quim. Nova.*, **2003**, *26*, 123.
14. Lehnert, W.; *Tetrahedron Lett.,* **1970**, *54*, 4723.
15. Gawande, M. B.; Jayaram, M. V.; *Catal Commun.*, **2006**, *7*(12) , 931-935.
16. Texier-Boullet, F.; Faucaud, A.; *Tetrahedron Lett.*, **1982**, *23*, 4927-4928.
17. Yazdani, H.; Bazgir, A.; *Synthesis.*, **2019**, *51*, 1669-1679.
18. Narasiah, A.V.; Nagaih, K.; *Synth. Commun.,* **2003**, *33*, 3825-3832.
19. Leelavathi, P.; Ramesh Kumar, S.; *J. Mol. Catal., A: Chem.*, **2005**, *240*, 99-102.
20. Zhao, S.; Chen, Y.; Song, YF.; *App. Catalysis A: Genl.*, **2014**, *475*, 140-146.
21. Bartoli, G.; Bosco, M.; Carlone, A.; Dalpozzo, R.; Galzerano, P.; Melchiorre, P.; Sambri, L.; *Tetrahedron Lett.*, **2008**, *49*, 2555-2557. (b) Miaoa, Z.; Yangb, F.; Luanb, Y.; Shuc, X.; Ramella, D.; *J. Solid State Chem.,* **2017**, *256*, 27–32.
22. (a) Keithellakplm, S; Moirangthem, N; Lationjam, W.S.; *Indian J. Chem.*, **2015**, *54*B, 1157-1161. (b) De Paula, B. R. S.; Zampieri, D. S.; Zukerman-Schpector, J.; Tiekink; E. R. T.; Rodrigues, J. A. R.; Moran, P. J. S.; *J. Braz. Chem. Soc.*, **2012**, *23*, 825-830.
23. Xie, W.; Jin, Y.; Wang, P.G.; *Chemtech.,* **1999**, *29*, 23.
24. (a) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W.W. L.; *Chem. Rev.*, **2002**, *102*, 2227-2302. (b) Kobayashi, S.; *Eur. J. Org.Chem.,* **1999**, 15-27. (c) Kobayashi, S.; *Synlett.*, **1994**, *9*, 689-701.
25. Gaspard-Houghmane, H.; Le Roux, C.; *Eur. J. Org.Chem.*, **2004**, 2517-2532. (b) Leonard, M. N.; Wieland, L.C.; Mohan, R.S.; *Tetrahedron.,* **2002**, *58*, 8373-8397.

26. Repichet, S.; Zwick, A.; Vendier, L.; Le Roux, C.; Dubac, J.; *Tetrahedron Lett.*, **2002**, *43*, 993-995.
27. Nitsch, D.; Bach, T.; *J. Org. Chem.,* **2014**, *79*(13), 6372–6379.
28. Yadav, J. S.; Subba Reddy, B.V.; Premalatha, K.; Shiva, S. K.; *Can. J. Chem.*, **2008**, *86*, 124-128.
29. Oskooie, H. A.; Roomizadeh, E.; Heravi, M. M.; *J. Chem. Res.*, **2006**, 246.
30. Cabello, J. A.; Campelo, J. M.; Garcia, A.; Luna, D.; Marinas, J. M.; *J. Org. Chem.,* **1984**, *49*, 5195.
31. Lu, Y. Y.; Ren, Z. J.; Cao, W. G.; Tong, W. K.; Gao, M. F.; *Synth. Commun.*, **2004**, *34*, 2047.
32. Mukhopadhyay, C.; Datta, A; *Synth. Commun.,* **2008**, *38*, 2103–2112.
33. Zhang, M.; Zhong, A. Q.; Chen, H. H.; Chen, J.; Chen, H. Y.; *Synth. Commun.,* **2006**, *36*, 3441-3445.
34. Rong, L.; Li, X.; Wang, H.; Shi, D. Tu, S.; Zhuang, Q.; *Synth. Commun.*, **2006**, *36*, 2407-2412.
35. Deb, M. L.; Bhuyan, P.; *Tetrahedron Lett.,* **2005**, *46*, 6453-6456.
36. Sun, Q.; Shi, L. X.; Ge, Z. M.; Cheng, T. M.; Li, R. T.; *Chin. J. Chem.*, **2005**, *23*, 745.
37. Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O.; Tsadjout, A.; *Synth. Commun.*, **2002**, *32*, 355.
38. Ibrador, E.; Castro, M.; Tamariz, J.; Zepeda, G.; Miranda, R.; Delgado, F.; *Synth. Commun.*, **1998**, *28*, 4649-4663.
39. Ilangovan, A.; Muralidharan, S.; Maruthamuthu, S.; *J. Korean Chem. Soc.*, **2011**, *55*, 1000-1006.