Sodium toluene-4-sulfonate as a reusable and ecofriendly catalyst for Greener Synthesis of 5-aminopyrazole-4-carbonitrile in aqueous medium

Aboli Sapkal, Santosh Kamble*

Department of Chemistry, Yashavantrao Chavan Institute of Science (Autonomous), Satara, Maharashtra, India

Email: santosh.san143@gmail.com

Abstract:

In these environmentally conscious days there is need to use eco-friendly greener technologies, such as solvent free, microwave, ultrasound and use of room temperature. Here report an efficient and green protocol for the synthesis of 5-aminopyrazole-4-carbonitrile from three component condensation of phenyl hydrazine, aldehyde, and malononitrile using NaPTS as catalyst in aqueous medium. Use of water has emerged as a versatile solvent for organic reaction; it is readily available, inexpensive, environmentally benign, neutral and natural solvent. Multicomponent reactions in water are of outstanding value in organic synthesis and green chemistry. The significant features of this article are short reaction time, provide excellent yield, removal of toxic solvent and use of water as green solvent.

Keywords: Green Synthesis, Hydrotrope, Aqueous medium, Pyrazole.

Introduction:

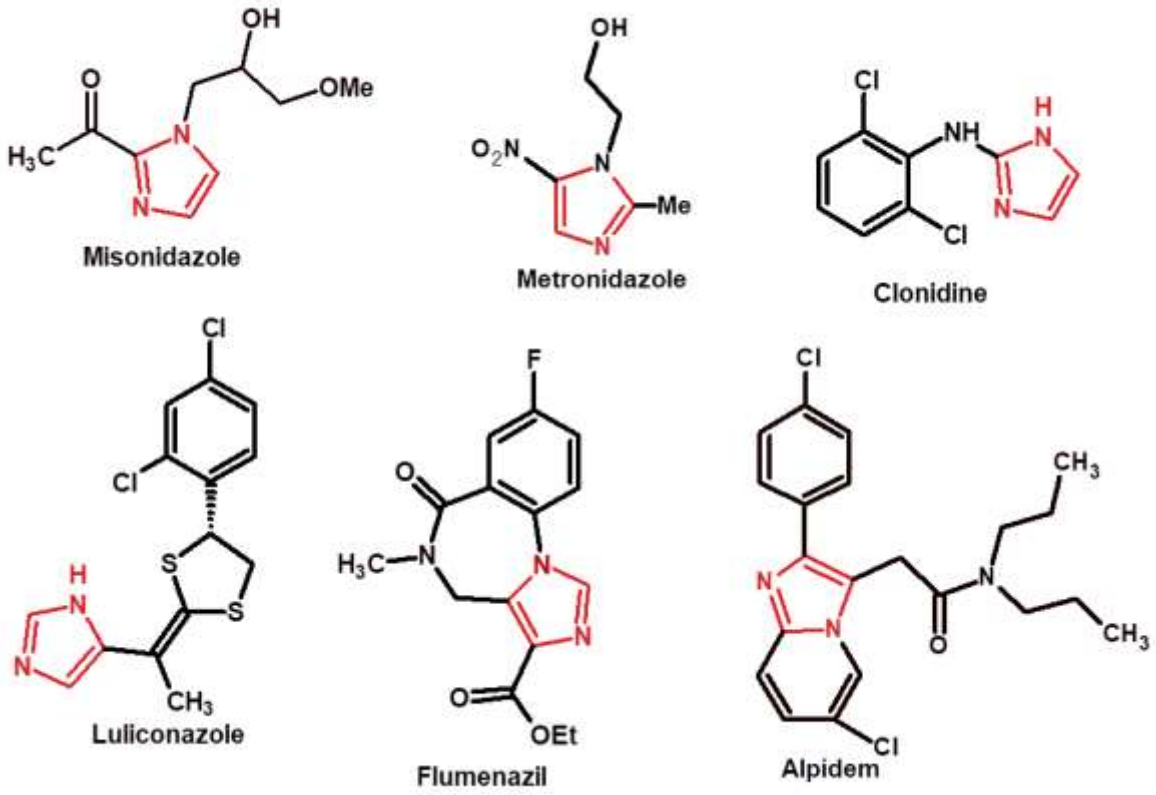
Heterocyclic compound having a significant & unique position in medicinal chemistry [1]. Synthesis of such heterocyclic compound have acquired high priority in the pharmaceutical field[2-4] because they shows a wide range of interesting biological activities, such as antimicrobial[5], anti-inflammatory[6], antioxidant[7] , antiviral[8], antibacterial[9], anticancer[10], anticonvulsant[11] , cardiovascular[12], antihypertensive[13], antipyretic[14], antibiotic[15], anti-hyperglycemic activity[16]. Among these heterocyclic compounds, the five membered heterocyclic aromatic ring compound having lots of applications in pharmaceutical field [17-18]. Out of which Nitrogen-containing five membered heterocyclic are abundant in natures and they

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/jhet.4077

are present in various biological motifs & they having great significance to life because of their structural units present in many natural products such as vitamins, nucleic acids, amino acid, herbicides, and dyes [19]. Therefore, for the synthesis of such heterocyclic compound several methods are presented including multi-component reactions (MCRs) [20-23]. Synthesis by MCRs is more accepted aspect because it is effective, required less energy, decrease cost, time & generation of by-products [24-28]. Therefore, the formation of new MCRs with green procedure has attracted more attention, especially in the field of medicinal chemistry, organic synthesis and material science [29-32]. Synthesis of heterocyclic scaffolds is performed via MCRs in the presence of various green tools & catalyst gives good results [33-38].

Out of which Pyrazole is one of the good example of Nitrogen containing heterocycles which is biologically active class of compound [39]. Therefore pyrazole derivatives are synthesized by many ways such as using sodium ascorbate [40], CuO/ZrO_2 recyclable catalyst [41], prepared by using 1,3 diketone, acid chloride in base and organic solvent[42], it is also prepared by using other catalyst such as $Sc(oTf)_3$[43], zirconium sulfophenyl phosphate [44] , Y-zeolite [45] , $Zn[L\text{-proline}]_2$ [46] , $H_3PW_{12}O_{40}$ [47], eosin-Y [48] & potassium phthalimide (PPI) [49]. All this reported methodologies require harsh reaction conditions viz. organic solvent, metal framework catalyst, acids and also bases but this reaction conditions are not sustainable to the environment, expensive, hazardous, time consuming. Therefore now days researchers focused on develop more eco-friendly, less hazardous, environmentally safe methodologies, such as ionic liquid [50], I_2 in water [51], 1-methylimidazolium trinitromethanide $\{[HMIM]C(NO_2)_3\}$as a nano ionic liquid (NIL) [52], PEG-400 and water under ultrasound waves [53] but preparation of ionic liquid & other solvent are also little costly & cause environmental issue therefore we use here hydrotrope in these synthesis which can full fill some of the conditions of green chemistry that is environmentally safe, less hazardous, cost effective, easy handling, no any toxic solvent, that is it is sustainable to environment [54].

Recent development shows Pyrazole derivatives have attracted more attention due to their interesting pharmacological properties. This type of hetrocycles can be traced in a number of well-established drugs belonging to different categories with diverse therapeutic activities. Some of these drugs mentioned as follows-



Experimental:

General:

All the chemicals required for synthesis were commercially sourced and were used without further purification. Melting points of products are measured on electrical melting point apparatuses. IR spectra were obtained with lambda FT-IR 750 spectrometer. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker 400MHZ spectrometer using $CDCl_3$as solvent and TMS is an internal standard.

2.1. General procedure for the synthesis of 5-amino-pyrazole-4-carbonitrile:

Take equimolar ratios of malononitrile (1mmol), phenyl hydrazine hydrochloride (1mmol) and substituted aldehyde (1mmol) in 10ml 40% aqueous NaPTS solution. This reaction mixture stirred at room temperature for few minutes until the completion of reaction is monitored by TLC in n-Hexane: Ethyl Acetate (7:3). The solid product separated by simple filtration. The separated solid product was recrystallized from suitable solvent.

Result and Discussion:

Hydrotropes increases the solubility of sparingly soluble organic compounds [55]. Hydrotropes are water- soluble and surface active compounds; they significantly increase the solubility of organic solutes such as esters, alcohols, ketones, aldehydes, hydrocarbons, and fats [56-58]. It acts as carrier for poorly soluble drugs & non-polar organic compounds [59]. The main feature is nature of hydrotropes on which reaction medium depends & its minimum hydrotropic concentration (MHC) above which maximum solubility of reactants. As the hydrotroe increases solubility of compounds there is direct interaction between reactants those are insoluble in aqueous medium. The mechanism by which insoluble & sparingly soluble compounds are soluble in water is aggregation & MHC [60]. There is difference between self aggregation of hydrotrope & micelle that is presence of minimum hydrotrope concentration (MHC) analogues to critical micelle concentration (CMC) [61]. Most hydrotropic solutions precipitate the solute on dilution with distilled water therefore recovery of product and re-use of hydrotropic solvent is easy [62]. Hydrotropes are used for many purposes such as drug solubilization, detergent formulations, health care, in household applications [63], also used as extracting agent. Overall hydrotrope has various advantages such as eco-friendly; non-flammable, less toxic, inexpensive that is hydrotrope follow the green chemistry principle. Therefore here use one of the hydrotrope is sodium paratoulenesulfonate (NaPTS) for synthesis of Pyrazole derivatives (Scheme-1).

Scheme 1. Synthesis of 5-amino-pyrazole-4-carbonitrile.

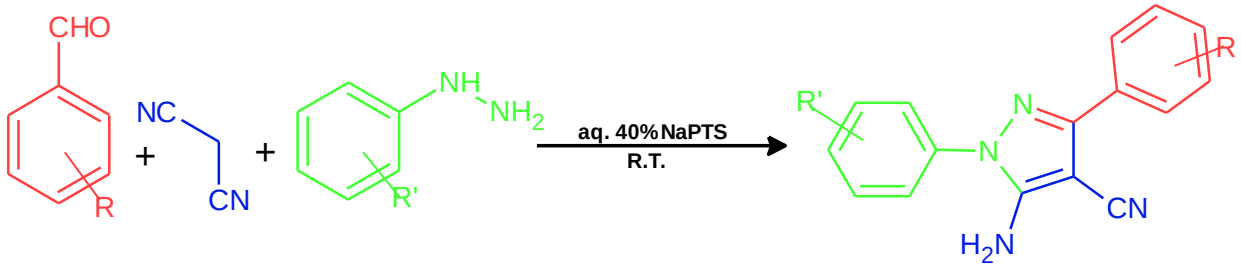


Table-1.1: Screening of conditions for synthesis of 5-amino-pyrazole-4-carbonitrile:

Entry	Solvent/ Catalyst	Time	Yield
1	Water	48hrs	trace
2	Ethanol	24hrs	trace
3	Water + Ethanol(1:1)	24hrs	40%
4	**Water + 40% NaPTS**	**30 min**	**92%**

Initially focused on selection of green methodology for synthesis of present scheme (Table1.1). Initially we use water as green solvent but yield was very low and also require long reaction time, then we choose the another solvent is water: ethanol(1:1) then also yield is poor due to lower solubility of organic compound in aqueous medium. Then we select hydrotrope that increase the solubility of sparingly soluble compounds in aqueous medium. Hydrotropes are surface active agent they increase solubility in many fold access. We select hydrotrope which is NaPTS at various concentrations out of which 40% NaPTS gives expected yield in 5-10 minutes at room temperature (Table 1.2). We screen the reaction condition by using reactant as aldehyde (1mmol), malononitrile (1mmol), and phenyl hydrazine (1mmol) and got the maximum yield in 5ml 40% aq. NaPTS at room temperature. Then use different derivatives of benzalaldehyde with electron donating and withdrawing group getting good to excellent yields of corresponding pyrazoles as shown in (Table 1.3).

Table-1.2: Optimization concentration of Hydrotrope for synthesis of 5-amino-pyrazole-4-carbonitrile:

SR. NO.	Hydrotrope (% w/v)	Temp.(^{0}C)	Time	Yield %
1.	10 % NaPTS	24^{0}C	24 hrs	-
2.	20 % NaPTS	24^{0}C	180 min	10
3.	30 % NaPTS	24^{0}C	100 min	50
4.	**40 % NaPTS**	**24^{0}C**	**30 min**	**92**
5.	50 % NaPTS	24^{0}C	100 min	90
6.	60 % NaPTS	24^{0}C	100 min	85
7.	40 % NaPTS	50^{0}C	60min	70
8.	40 % NaPTS	80^{0}C	80 min	70
9.	40 % NaPTS	100^{0}C	100 min	75

The plausible mechanism of the product formation is conceptualized in Fig1. The water added to hydrotrope, water molecules hydrate the hydrotrope head groups & decreasing the electrostatic attraction between these groups. The two head groups move apart and displace the water molecules interacting hydrophobic parts. This may be the driving force for two hydrophobic parts to interact and force the reactant molecule to solubilize & get interact with each other. Then water molecules get eliminated & easily absorbed by the hydrophilic head groups. As a result, of the overall effect there is a rate enhancement of the reaction & reaction proceeds in aqueous medium due to hydrotropism.

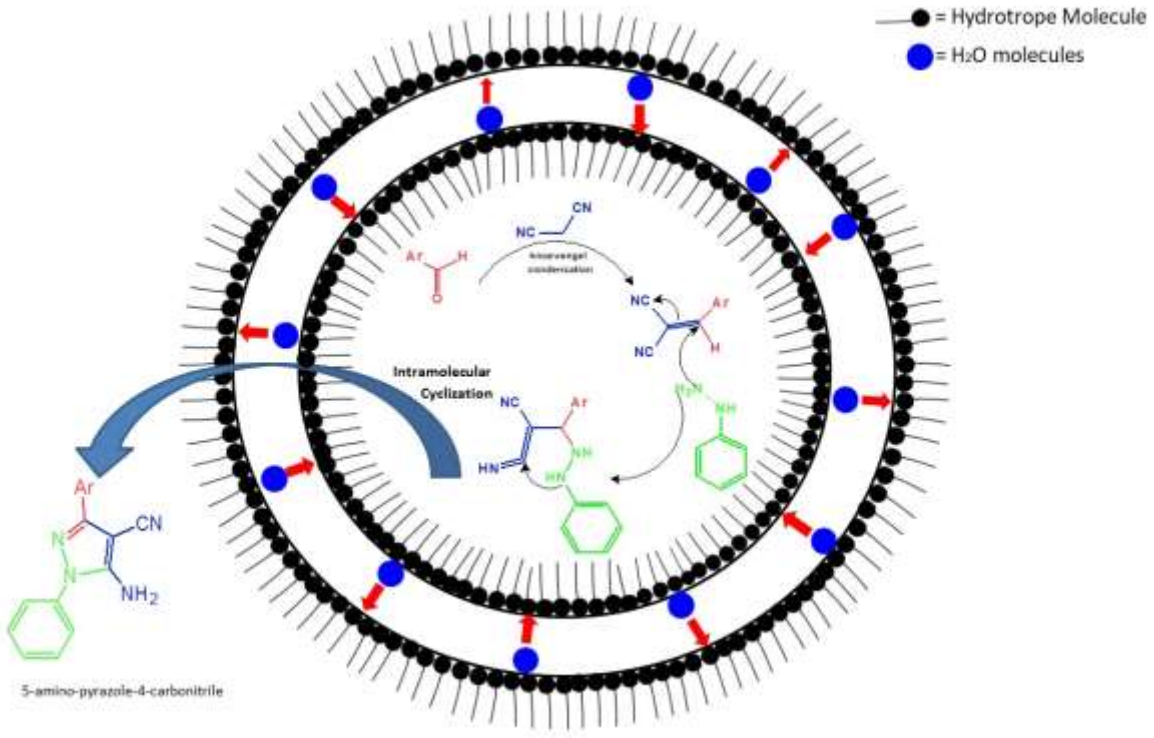


Fig.1. A Plausible reaction mechanism for synthesis of 5-amino-pyrazole-4-carbonitrile in aqueous hydrotropic medium.

Recyclability of Hydrotrope:

The reuse of catalyst is very important step in synthesis because reuse of catalyst directly effects on cost & also environment. Therefore easy recovery & reuse of catalyst is necessary these is possible by using hydrotrope, because it is reuse only after the reaction is complete, filter the product & give washing to product & collect the filtrate along with product because that filtrate contain the hydrotrope, then keep the filtrate for evaporation after that our catalyst i.e. hydrotrope is recover & which is ready for reuse. We check the recyclability of that hydrotrope by 5 times obtain the good result with loss of small amount of yield which is shown in fig. 2.

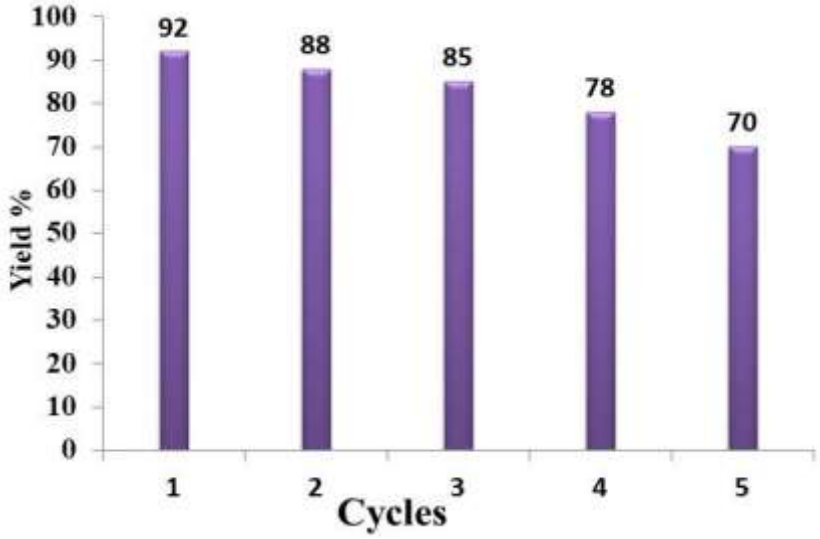
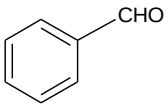
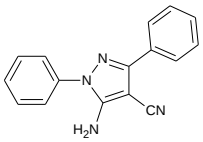
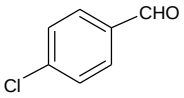
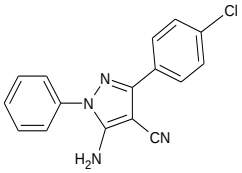
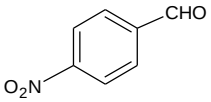
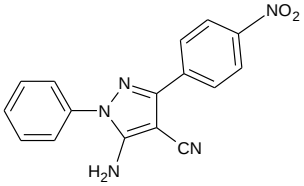
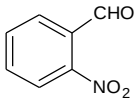
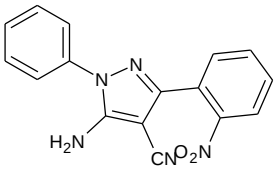
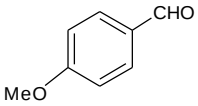
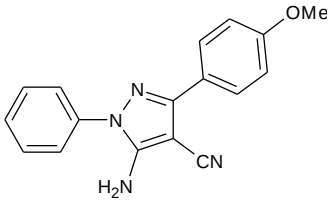
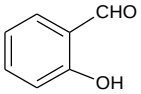
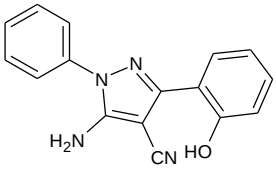
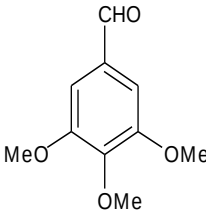
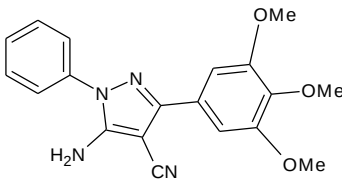
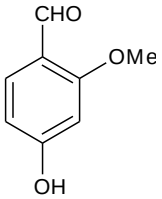
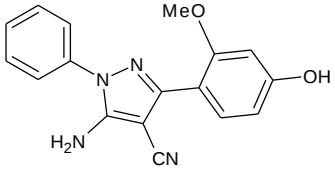
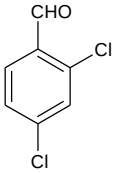
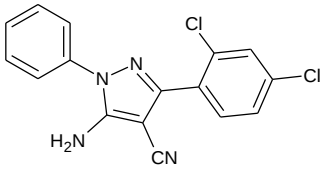
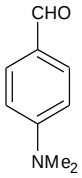
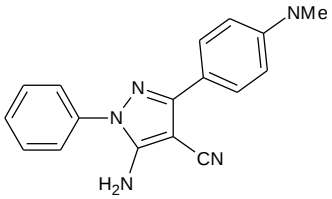
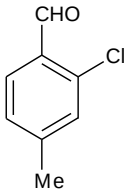
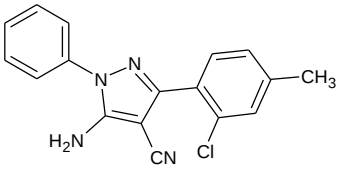
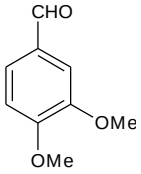
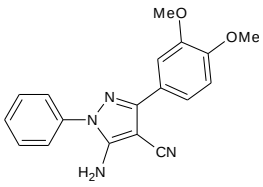
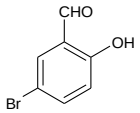
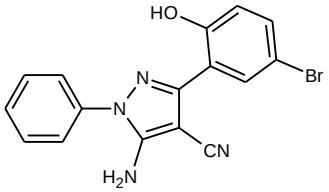


Fig.2 Recyclability of Hydrotrope.

Table-1.3: Synthesis of 5-amino-pyrazole-4-carbonitrile derivatives in 40% hydrotrope in aqueous medium.

Entry	Aldehyde	Product	M.P. (^{o}C)	Yield (%)
1			156-158	92
2			127-128	92
3			175-177	92
4			158-160	92
5			106-109	90
6			160-162	80

7			128-130	92
8			120-122	92
9			130-132	90
10			104-106	92
11			124-126	92
12			121-123	92

13			178-180	80

Spectroscopic data for some target compounds are as follows:

1) 5-Amino-1,3-diphenyl-1H-pyrazole-4-carbonitrile(1):

White solid, melting point: 156-158^{o}C. IR (KBr): $\bar{\upsilon}$ = 3320.82, 3290, 2930, 2210, 1580, 1600, 1240 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δppm 6.87 (d, 1H), 7.11(dd, 2H), 7.13-7.26(m, 5H), 7.37(d,1H), 7.65(S, 2H), 7.68(d,1H). ^{13}C NMR (100MHz $CDCl_3$): δppm 112.71, 120.07, 126.15, 128.40, 128.58, 129.28, 135.26, 137.24, 143.33, 144.61, 144.75, 146.80.

2) 5-amino-3-(2-hydroxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile(6):

Yellow solid, melting point: 160-162^{o}C. IR (KBr): υ= 3446.17, 3320.82, 3207.04, 2927, 2188.81, 1598.70, 112.79, 1150.01 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δppm 6.90-7.00 (m, 4H), 7.15-7.49 (m, 5H), 7.83 (s, NH_2), 10.84 (s, 1H). ^{13}C NMR (100MHz $CDCl_3$): δppm 112.58, 116.57, 118.46, 119.46, 120.86, 129.52, 129.53, 129.99, 135.26, 137.24, 141.17, 143.33, 146.61, 156.98.

3) 5-amino-3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile(3):

Red solid, melting point:175-177^{o}C. IR (KBr): υ 3467.38, 3303.43, 2950, 2360.11, 1580.70, 1210.05, 750.17 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δppm 6.95 (d, 1H), 7.15-7.26 (m, 5H), 7.78 (S, NH_2), 7.98 (d, 1H),8.23 (dd, 2H). ^{13}C NMR (100 MHz,$CDCl_3$): δppm 112.60, 119.81, 124.43, 125.76, 126.96, 127.52, 129.01,130.51, 130.74, 132.81, 144.54, 146.59.

4) 5-amino-1-phenyl-3-(3,4,5-trimethoxyphenyl)-1*H*-pyrazole-4-carbonitrile(7):

Cream colour solid, melting point:128-126^{o}C.IR (KBr): ῡ = 3413, 3364, 2930, 2220, 1610, 1245, 1140 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δppm 3.930 (s, 3H), 3.389 (s, 6H), 6.88 (d, 2H, ArH), 7.19-7.28 (m, 5H, ArH), 7.66(s, 2H). ^{13}C NMR (100MHz $CDCl_3$): δppm 112.60, 117.57, 119.46, 121.07, 127.2, 129.4, 130.7, 137.9, 143.2, 148.12, 150.0, 154.7.

5) 5-amino-3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile(5):

Light brawn solid, melting point:106-109^{o}C. IR (KBr): ῡ = 3446.17, 3320.82, 292741, 1598.17, 1480.17, 1272.78, 1159.01, 750.04. ^{1}H NMR (400 MHz, $CDCl_3$): δppm 3.910(S, 3H), 6.89(d, 2H, ArH), 7.60(d, 2H, ArH), 7.30-7.60(m, 5H, ArH), 7.71(s, 2H). ^{13}C NMR (100MHz $CDCl_3$): δppm 53.6, 112.60, 114.8, 116.34, 121.20, 126.2, 127.4, 129.01, 129.85, 130.07, 145.8, 152, 155.

6) 5-amino-3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole-4-carbonitrile(2):

Cream colour solid, melting point: 127-128^{o}C. IR (KBr): ῡ = 3446.17, 3313.11, 2229.11, 1594.84, 1488.78, 1255.43, 748.25. ^{1}H NMR (400MHz, $CDCl_3$): δppm 7.45-7.68 (m, 4H, ArH), 7.30-7.60 (m, 5H), 7.72 (s, 2H). ^{13}C NMR (100MHz,$CDCl_3$): δppm 118.45,120.86, 122.4, 126.5, 127.98, 129.25, 129.88, 130.45, 133.23, 144.46, 148.01, 153.01.

Conclusion:

The present protocol describe environmental friendly synthesis of 2-amino Pyrazole 5-carbonitrile. Due to harsh reaction conditions dangerous side effect on environment need to develop such safe methods therefore here we use hydrotrope in aqueous medium which is a green methodology. These methodogy having lot of advantages such as less hazardous, cost effective, time saving and mild reaction condition. Present protocol suggests a promising green approach for the synthesis of 5-aminopyrazole-4-carbonitrile.

SUPPORTING INFORMATION

Supporting information may be found online in the Supporting Information File of this article.

Acknowledgment:

We gratefully acknowledge the financial support from the Rayat Institute of Research and Development (RIRD) and Y.C.I.S. Satara (Autonomous). As well as Department of Science Technology–Science and Engineering Research Board (DST-SERB) and University Grants Commission (UGC) as major research project.

ORCID

Santosh B Kamble https://orcid.org/0000-002-4668-1628

References:

1] A. Majumder, R. Gupta & A. Jain. Green Chemistry Letters and Reviews 2013, 6, 151.

2] F. Hosseini & M. Mohammadi-Khanaposhtani & H. Azizian & A. Ramazani & M. B. Tehrani & H. Nadri & B. Larijani & M. Biglar & H. Adibi & M. Mahdavi. Structural chemistry 2020, 31, 999.

3] M. Khoobi, S. Emami, G. Dehghan, A. Foroumadi, A. Ramazani and A. Shafie. Arch. Pharm. Chem. Life Sci. 2011, 344, 588.

4] S. T. Fardooda, A. Ramazania, F. Moradniaa, Z. Afsharia, S. Ganjkhanlua, F. Y. Zarea. Chemical Methodologies 2019, 3, 632.

5] R. Nagamallu, A. K. Kariyappa. Bioorganic & Medicinal Chemistry Letters 2013, 23,6404.

6] S. Prekupec, D.Makuc, J. Plavec, L. Suman, M. Kralj, K. Pavelic, J. Balzarini, E.D. Clercq, M. Mintas, S. Raic-Malic, J. Med. Chem. 2007, 50, 3037.

7] N. Renuka , H. K. Vivek , G. Pavithra , and K. Ajay Kumar. Russian Journal of Bioorganic Chemistry 2017, 43, 197.

8] S.Mavel , J. L. Renou, C. Galtier , R. Snoeck, G. Andrei, J. Balzarini, E. D. Clercq, and A. Gueiffier . Arzneim.-Forsch./Drug Res. 2001, 51, 304.

9] S. Emami ,A. Foroumadi , M. A. Faramarzi , and N. Samadi. Arch. Pharm. Chem. Life Sci. 2008, 341, 42.

10] D. Havrylyuk , L. Mosula , B. Zimenkovsky , O. Vasylenko , A. Gzella , R. Lesyk. European Journal of Medicinal Chemistry 2010, 45, 5012.

11] S. N. pandeya , A. S. Raja. J Pharm Pharmaceut Sci. 2002, 5, 266.

12] A. V. Velikorodov, I. N. Tyurenkov, M. V. Timchenko and V. N. Perfilova. Pharmaceutical Chemistry Journal 2006, 40, 8.

13] A. Ma. Vela´zquez , L. Martı´nez , V. Abrego , M.A. Balboa , L.A. Torres , B. Camacho , S. Dı´az-Barriga , A. Romero , R. Lo´pez-Casta~nares , E. Angeles. European Journal of Medicinal Chemistry 2008, 43, 486.

14] N. Uramaru, H. Shigematsu, A. Toda, R. Eyanagi, S. Kitamura and S. Ohta. Journal of Medicinal Chemistry 2010, 53, 8727.

15] M. A. Wegman, M. H. A. Janssen, F. V. Rantwijk, R. A. Sheldon.Advance Synthetic Catalysis 2001, 343, 559.

16] G. R. Bebernitz, G. Argentieri, B. Battle, C. Brennan, B. Balkan, B. F. Burkey, Michele Eckhardt, Jiaping Gao, Prasad Kapa, R. J. Strohschein, H. F. Schuster, M. Wilson, and D. D. Xu. J. Med. Chem. 2001, 44, 2601.

17] I. Yavari and A. Ramazan. Synthetic Communications 1997, 27, 1385.

18] H. Aghahosseini, A. Ramazani, K. Ślepokura, T. Lis. Journal of Colloid and Interface Science 2018, 511, 222.

19] H. Aghahosseini, A. Ramazani, N. S. Jalayer, Z. Ranjdoost, A. Souldozi, K. Ślepokura and T. Lis. Org. Lett. 2019, 21, 22.

20] S. Gupta, M. Lakshman. Journal of Medicinal and Chemical Sciences 2019, 2, 51.

21] A. Ramazani, A. Rezaei, A. T. Mahyari, M. Rouhani, and M. Khoobi. Helvetica Chimica Acta 2010, 93, 2033.

22] A. Ramazani and A. R. Kazemizadeh. Current Organic Chemistry 2011, 15, 3986.

23] A. Ramazani, Y. Ahmadi, M. Rouhani, N. Shajari, and A. Souldozi. Heteroatom Chemistry 2010, 21, 368.

24] S. T. Fardood, A. Ramazani, Z. Golfar, S. W. Joo. Applied Organometallic chemistry 2017, 31, 3823.

25] Z. Hosseinzadeh & A. Ramazani & H. Ahankar & K. Ślepokura & T. Lis. Silicon 2018, 11, 2169.

26] A. Ramazani, A. T. Mahyari, M. Rouhani, A. Rezaei. Tetrahedron Letters 2009, 50,5625.

27] A. Ramazani, M. Rouhani, S. W. Joo. Ultrasonics Sonochemistry 2016, 28, 393.

28] A. Ramazania, S. T. Fardooda, Z. Hosseinzadeha, F. Sadrib, S. W. Joo. Iranian Journal of Catalysis 2017, 7, 181.

29] A. Ramazani, M. Khoobi, A. Torkaman, F. Z. Nasrabad, H. Forootanfar, M. Shakibaie, M. Jafari, A. Ameri, S. Emami, M. A. Faramarzi, A.Foroumadi, A. Shafiee. European Journal of Medicinal Chemistry 2014, 78, 151.

30] H. Ahankar, A. Ramazani, K. Ślepokura, T. Lisb and S. W. Joo. Green Chem. 2016,18, 3582.

31] J. Taran, A. Ramazani, H. Aghahosseini, F. Gouranlou, R. Tarasi, M. Khoobi & S. W. Joo. Phosphorus, Sulfur, and Silicon and the Related Elements 2017, 192, 776.

32] Z. Hosseinzadeh, A. Ramazani, N. Razzaghi-ASL3, K. Slepokura, T. LI. Turk. J. Chem. 2019, 43, 464.

33] H. Aghahosseinia, A. Ramazania. Eurasian Chem. Commun., 2020, 2, 410.

34] S. F. Motevalizadeh, M. Khoobia, A. Sadighic, M. Khalilvand-Sedagheha, M. Pazhouhandeh, A. Ramazani, M. A. Faramarzie, and A. Shafiee. Journal of Molecular Catalysis B: Enzymatic 2015, 120,75.

35] S. Rezayati, A. Ramazani. Res Chem Intermed. 2020, 46, 3757.

36] N. Varnaseri, F. Rouhani, A. Ramazania, A. Morsali. Dalton Transactions 2020, 49, 3234.

37] N. Fattahi, K. Triantafyllidis, R. Luque and A. Ramazani. Catalysts 2019, 9, 758.

38] E. Gholibegloo, T. Mortezazadeh, F. Salehian, H. Forootanfar, L. Firoozpour, A. Foroumadi, A. Ramazani, M. Khoobi. Journal of Colloid and Interface Science, 2019, 556, 128.

39] P. N. Kalaria, S. P. Satasia and D. K. Raval. RSC Adv. 2014, 4, 32353.

40] H. Kiyani , M. Bomdad. Res chem Intermed. 2018, 44, 2761.

41] S. Maddila, S. Rana, R. Pagadala, S. Kankala, S. Maddila, S. B. Jonnalagadda. Catalysis Communications 2015, 61, 26.

42] S. T. Heller & S. R. Natarajan.Organic Letters 2006, 6, 2675.

43] W. Xiong , J. X. Chen, M.C. Liu, J. C. Ding, H. Y. Wu, W. K. Su . J Braz.Chem.Soc. 2009, 20, 367.

44] M. Curini, O. Rosati, V. Campagna, F Montanari , G. Cravotto, M. Boccalini. Synlett 2005, 19, 2927.

45] R. Sreekumar, R. Padmakumar. Synthetic Communicaton 1998, 28, 1661.

46] M. Kidwai , A. Jain, R. Poddar . Journal of Organometallic Chemistry 2011,696, 1939.

47] X. Chen, J. She, Z. Shang, J. Wu, H. Wu, P. Zhang. Synthesis 2008, 21, 3478.

48] S. Yadav, P. Rai, M. Srivastava, J. Singh, K. P. Tiwaria and J. Singh. Tetrahedron Letters 2015, 56, 5831.

49] H. Kiyani & M. Bamdad. Hetrocycles 2017,94, 276.

50] M. Srivastava, P. Rai, J. Singh and J. Singh. RSC Adv. 2013, 3, 16994.

51] M. Srivastava, P. Rai, J. Singh and J. Singh. New J. Chem. 38, 302.

52] M. A. Zolfigol, F. Afsharnadery, S. Baghery, S. Salehzadeh and F. Maleki. RSC Advances 2012, 5, 7555.

53] F. Nemati, S. H. Nikkhah, A. Elhampour. Chinese Chemical Letters 2015, 26, 1397.

54] M. Barge ,S. Kamble , A. Kumbhar , G. Rashinkar , R. Salunkhe. Monatsh Chem. 2013,144, 1213.

55] S. B. Kamble, A. S. Kumbhar, S. N. Jadhav and R. S. Salunkhe. Procedia Material Science 2014, 6,1850.

56] V. G. Gaikar, P.V. Phathak. Sep. Sci. Technol. 1999, 34, 439.

57] S. E. Friberg, Hydrotropes. Surf. Sci. 1997, 2, 490.

58] X. Chen, J. C.Micheu. J. Colloid Interface Sci. 2002, 249,172.

59] N. S.Tavare, V. K. Jadhav. Chem. Eng. Data 1996, 41, 1196.

60] G. Horvath-Szabo, Q. Yin, S. E. Friberg. Colloid Interface Sci. 2001, 236, 52.

61] D. Balasubramanian, V. Shrinivas, V. G. Gaikar, M. M. Sharma. J. Phys. Chem. 1989, 93, 3865.

62] Mckee, H. Ralph. Journal of Industrial and Engineering Chemistry 1946, 38, 382.

63] S. E. Friberg, C. Brancewicz. Langmuir 1994,10, 2945.