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ROOM TEMPERATURE, GREEN AND EFFICIENT SYNTHESIS OF 4,4'-(ARYLMETHYLENE)BIS(1H-PYRAZOL-5 OLS)

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Abstract
An eco-friendly and efficient pseudo three component method for the synthesis of 4,4'-(arylmethylene)bis(1H-pyrazol-5-ols) has been accomplished by tandem Knoevenagel–Michael reaction of various aromatic aldehydes with 5-methyl-2-phenyl- 2,4-dihydro-3H-pyrazol-3-one using inexpensive ammonium chloride catalyst in H_2O:EtOH at room temperature.

Keywords : 4,4'-(arylmethylene)bis(1H-pyrazol-5-ols), ammonium chloride, room temperature, inexpensive.

1. Introduction

Nitrogen containing heterocycles exhibit a great importance in organic and bioorganic chemistry both industrially as well as biologically. Among them pyrazoles are significant types of bio-active drug in pharmaceutical industry. Pyrazoles are the core structure of various biologically active compounds such as they represent anti-inflammatory, anti-anxiety, antipyretic, analgesic properties[i].

Bis(heterocyclyl)methanes represent an important class of compounds that constitute the building blocks of natural and synthetic porphyrins[ii]. These occur widely in various natural products and showed versatile biological and pharmacological activities[iii]. Among them 4,4´-(arylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s possesses a wide spectrum of biological activity like anti-inflammatory[iv], antidepressant[v], antipyretic[vi], antibacterial[vii], antifilarial agents[viii] and gastric secretion stimulatory[ix]. Some derivatives of 4,4´-(arylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s display agrochemical properties like pesticides[x], fungicides[xi] and insecticides[xii]. They are also used as dyestuffs[xiii], chelating and extracting reagents for different metal ions[xiv].

In recent years, to minimize the use and production of hazardous materials, green chemistry motivate chemists to design chemical procedures by using environmentally benign reagents that reduce and prohibit the pollution and ensure perpetual life on earth[xv].

3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one is a versatile building block with highly nucleophilic enolic carbon at 4-position. It has been recently used in several multi-component reactions (MCRs) for the synthesis of wide range of heterocycles[xvi].

The literature survey showed that the synthesis of 4,4'- (arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols) are accomplished by three methods: (i) Knoevenagel reaction of 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one with aldehydes to form the corresponding arylidene pyrazolones followed by base promoted Michael reaction with second equivalent of 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one[xvii], (ii) one-pot tandem Knoevenagel–Michael reaction of aldehydes with two equivalents of 3-methyl-1-phenyl-1Hpyrazol-5(4H)-one under various reaction conditions[xviii] and (iii) one-pot pseudo five component condensation of two equivalent of phenyl hydrazine derivatives and two equivalent of β-ketoesters with one equivalent of aromatic aldehydes[xvii]

The general approach to 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-pyrazol-5-ol) synthesis involve one-pot tandem Knoevenagel–Michael reaction of aryl aldehydes with 2 equivalent of 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one under variety of catalyst and reaction conditions(shown in Table 1). Although these protocols reported by others find certain merits of their own, still they suffered from a number of demerits such as harsh reaction conditions, a need of excess amounts of the reagent, the use of special reagent and time consuming product isolation procedures.

Ammonium chloride is an inexpensive and readily available reagent which has been reported as catalyst for the synthesis of various organic compounds. It is effectively promoted four component synthesis of pyrrolo[3,4-b]pyridinones and Ugi four-component reactions[xxxv]. Moreover ammonium chloride was effectively used as catalyst for Biginelli synthesis of 3,4-dihydropyrimidinones under solvent-free conditions, aliphatic Claisen rearrangement, reduction of azo compounds to corresponding hydrazines, reduction of nitrophenols in aqueous media and under ultrasound and reductive cleavage of azo compounds[xxxvi]. Such successful catalytic performance of ammonium chloride has encouraged us to investigate on its further application in other carbon–carbon bond forming reactions. Herein, we wish to extend the synthetic applicability of this unique and easily available catalyst in the synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-pyrazol-5-ol)s.

Table 1: Comparison efficiency of various catalysts in the synthesis of 4,4'-(aryl methylene)bis(3-methyl-1*H*-pyrazol-5-ol)s

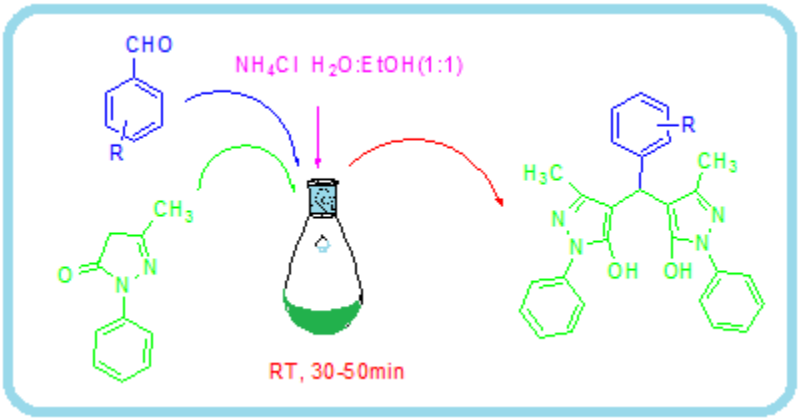
Entry	catalyst	condition	time	yield	ref
1	SDS	H_2O, Reflux	1 h	90	xix
2	[Cu(3,4-tmtppa)](MeSO$_4$)	H_2O, 90^{0}C	30 min	90	xx
3	SBSSA	EtOH, Reflux	50 min	90	xxi
4	SASPSPE	EtOH, Reflux	3 h	90	xxii
5	Cat. Free	H_2O,Reflux	6-8 h	76	xxiii
6	SSA	H2O/EtOH, 70^{0}C	1 h	93	xxiv
7	AP-SiO_2	CH_3CN, RT	10 min	98	xxv
8	Xanthane sulfuric acid	EtOH, Reflux	15 min	95	xxvi
9	Cat. free	Solv. Free, 120^{0}C MW	10 min 3 min	91 92	xxviii
10	DCDBTSD	Solv. Free 80^{0}C	40 min	80	xxix
11	Carbamoylhydrazine sulfonic/sulfamic acid	Sol. Free120^{0}C	10 min	95	xxx

12	C/TiO_2-SO_3H	H_2O 120^{0}C	30 min	92	xxxi
13	(HAP@AEPH_2-SO_3H)	Sol.free 80^{0}C	30 min	98	xxxii
14	(Mim)ClO_4	Sol.free 50^{0}C	20 min	96	xxxiii
15	Na+-MMT-[Pmim]HSO_4	100^{0}C	15 min	90	xxxiv
16	NH_4Cl	H_2O:EtOH (1:1),RT	30 min	95	**present work**

2. Experimental

2.1 Materials and instruments

All starting materials and chemical reagents were purchased from SD Fine Chemical Company and used without further purification. Melting points were determined in open capillaries using Electrothermal Mk3 apparatus. Infrared (IR) spectra in KBr pellets were recorded using a Perkin-Elmer FT-IR spectrometer. ^{1}H NMR spectra were recorded on 400 MHz FT-NMR spectrometer in DMSO-d6 as a solvent and chemical shift values were recorded in δ (ppm) relative to tetramethylsilane (Me_4Si) as an internal standard.



2.2 General procedure for the synthesis of

A mixture of aromatic aldehyde (1mmol), 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one (2 mmol) and ammonium chloride in catalytic amount was taken in 2 ml of solvent (EtOH : H_2O). Reaction mixture was stirred at room temperature for a period of 30-50 min (Scheme 1). The progress of reaction was monitored by thin layer chromatography (ethyl acetate: hexane 4:2). After completion of reaction, the obtained solid was filtered, washed with water and crude solid was recrystallized from hot ethanol to afford pure compound 3a–o. The products were confirmed by comparisons with authentic samples, melting points, IR, and ^{1}H NMR.

Table 2: **Synthesis of 4,4'-(phenylmethylene)bis(3-methyl-1*H*-pyrazol-5-ol) in the presence of ammonium chloride under optimized reaction conditions.**

Entry	R	Time (min)	Yield (%)	MP ^{0}C	Ref MP ^{0}C
a	4-Cl	25	96	211-213	213-215[xxii]
b	H	30	95	167-168	168-170 [xxii]
c	4-NO_2	25	98	229-230	229-231 [xxii]
d	3-OH	30	89	166-167	165-168 [xxiii]
e	3-NO_2	30	91	231-232	232-234 [xxii]
f	4-F	27	95	181-182	181-183 [xxiii]

g	4-Br	25	95	182-183	183-184 [xxiv]
h	2-OH	30	85	228-231	227-228 [xxii]
i	3-Cl	27	98	234-236	235-237 [xxiv]
j	4-OH	23	95	158-160	159-162[xxv]
k	4-OCH_3	30	95	175-178	174-176[xxv]
l	3-OCH_3	30	94	184-187	180-183[xxv]
m	4-CH_3	28	90	200-202	198-200[xxv]
n	2,4-dichloro	35	91	226-228	228-230[xxv]
o	3,4-di OMe	37	85	192-195	195-197[xxii]

2.3 Some selected spectral data of the products

2.3.1 4,4'-((4-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) **(3a).**
White cream solid; Yield 96 %; mp 211-213 °C; FT-IR (KBr) ν_{max} /cm^{-1} 3453, 3076, 2916, 1600 (C=N), 1579, 1500, 1407, 1373, 1296; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 2.3 (s, 6H, 2 CH_3), 4.92 (s, 1H, CH),7.2 (m, 6H, Ar-H), 7.4 (t, 4H, Ar-H), 7.7 (d, 4H, Ar-H), 12.37 (br s, 1H, OH), 13.80 (s, 1H, OH).

2.3.2 4,4'-((4-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) **(3c).**
White cream solid; Yield 98 %; mp 229-230 °C; FT-IR (KBr) ν_{max} /cm^{-1} 3411, 3080, 2920, 1598 (C=N), 1525, 1501, 1458, 1412, 1348, 1268. ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 2.3 (s, 6H, 2 CH_3), 5.0 (s, 1H, CH), 7.2 (t, 2H, Ar-H), 7.4 (t, 4H, Ar-H), 7.5 (t, 1H, Ar-H), 7.7 (d, 5H, Ar-H), 8.0 (d, 1H, Ar-H), 8.1 (d, 1H, Ar-H), 13.76 (s, 1H, OH).

2.3.3 4,4'-((3-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)) **(3e).**
Yellow solid; Yield 91 %; mp 231-232 °C; FT-IR (KBr) ν_{max} /cm^{-1} 3455, 2923, 1599 (C=N), 1524, 1502, 1457(C=C), 1413, 1349, 1268; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 2.30 (s, 6 H, 2 CH_3), 5.0 (s, 1 H, CH), 7.2 (t, 2H, Ar-H), 7.4 (t, 4H, Ar-H), 7.5 (t, 1H, Ar-H), 7.7 (d,5H, Ar-H), 8.0 (d, 1H, Ar-H), 8.1 (d, 1 H, Ar-H), 13.77 (s, 1H, OH).

2.3.4 4,4'-((4-flurophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)) **(3f).**
Yellow solid; Yield 95 %; mp 181-182 °C; FT-IR (KBr) ν_{max} /cm^{-1} 3440, 3066, 2921, 1599 (C=N), 1579, 1504, 1457(C=C), 1416, 1371, 1294, 1222, 1158; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 2.3 (s, 6H, 2 CH_3), 4.9 (s, 1H, CH), 7.0 (t, 2H, Ar-H), 7.2 (t, 4H, Ar-H), 7.4 (t, 4H, Ar-H), 7.7 (d, 4H, Ar-H), 13.83 (s, 1H, OH).

2.3.5 4,4'-((4-bromophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)) **(3g).**
Yellow solid; Yield 95 %; mp 182-183 °C; FT-IR (KBr) ν_{max} /cm^{-1} 3465, 2929, 1599 (C=N), 1579, 1500, 1404(C=C), 1297; ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 2.30 (s, 6H, 2 CH_3), 4.8 (s, 1H, CH), 7.2 (t, 4H, Ar-H), 7.3 (t, 6H, Ar-H), 7.7 (d, 4H, Ar-H), 13.73 (s,1H,OH).

2.3.6 4,4'-((4-hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)) **(3j).**
Yellow solid; Yield 95 %; mp 158-160 °C; FT-IR (KBr) ν_{max} /cm^{-1} 3430, 2922, 1598 (C=N), 1578, 1500, 1414(C=C), 1257, ^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 2.30 (s, 6H, 2 CH_3), 4.82 (s, 1H, CH), 6.64 (d, 2H, Ar-H), 7.05 (m, 2H, Ar-H), 7.22 (t, 2H, Ar-H), 7.41 (d, 4H, Ar-H), 7.71(d, 4H, Ar-H), 9.06 (s, 1H, OH), 12.11 (br s, 1H, OH), 13.86 (s, 1H, OH).

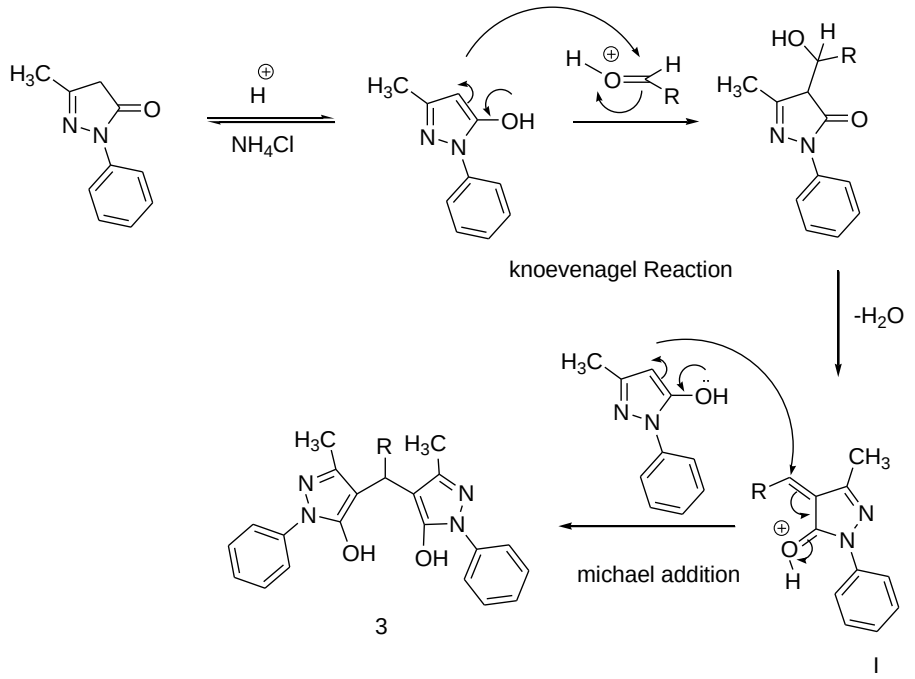
3. Result and discussion

To optimize the reaction conditions, we selected 4-chlorobenzaldehyde, 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one in presence of ammonium chloride as model reaction. For solvent optimization we carried out model reaction in polar protic solvents at room temperature. The results of the reaction are summarized in Table 3. As indicated, the reaction in CH_3OH and C_2H_5OH provided a relatively low yield and require long reaction time. As far as the solvents are concerned, water showed superiority over the other solvents. Moreover, excellent results were obtained when the reactions were performed with ammonium chloride as a catalyst using water: ethanol (1:1).

Table 3: optimization of solvent

Sr.no	Solvent	Time	yield
1	CH_3OH	2h	80
2	C_2H_5OH	2h	85
3	$C_2H_5OH:H_2O$ (2:1)	1.5h	86
4	$C_2H_5OH:H_2O$ (1:1)	30 min	96
5	$C_2H_5OH:H_2O$ (1:2)	1h	90

In order to determine % catalyst, we have carried out model reaction with different amount of catalyst and found that optimum catalyst loading of ammonium chloride to be 20mol % (Table 4). Decreasing the amount of catalyst to 5mol%, 10mol% and 15mol%, the yield of product 3a was reduced and took longer reaction time; however, by increasing the amount of catalyst from 20 to 25mol%, 30mol%, no appreciable change in the yield of product was observed. The percentage yields and the reaction time are considered the best results were obtained with ammonium chloride (20 mol %) in 2 ml of H_2O:EtOH (1:1) (see entry 5) as the reaction is completed within 30 min with 96% yield.



Scheme 2: plausible mechanism for the synthesis of 3

After optimization of the reaction conditions, in order to investigate the substrate scope of the reaction, different substituted benzaldehydes were used employing the present optimized reaction conditions. The yield and reaction were found to be fairly equal and good (Table 2).

On the basis of the above results and by referring to the literature, we propose a plausible mechanism for the formation of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-pyrazol-5-ol) (Scheme 2). First, the 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one and aldehyde is activated by ammonium chloride followed by knoevenagel reaction form intermediate I. Then nucleophilic attacks of another 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one on intermediate I converted to product 3.

Table 4: optimization of catalyst

Sr.no.	Amount of catalyst (mol %)	Time	Yield (%)
1	-----	8 h	60
2	5	4.5h	67
3	10	4h	70
4	15	2 h	82
5	20	30min	96
6	25	30min	95
7	30	30min	92

4. Conclusions:

In summary, ammonium chloride in EtOH: H_2O was developed as an efficient catalytic system for the greener synthesis of different 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-pyrazol-5-ol)s at lower reaction time at room temperature. The most remarkable point for the inexpensive and readily available ammonium chloride in EtOH: H_2O catalyst system was generation of the desired product in high yields without any unwanted side-products, besides the ease of work-up and purification.

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References:

i. McDonald, E.; Jones, K.; Brough, P.A.; Drysdale, M.J.; Workman, P.; Discovery and development of pyrazole-scaffold Hsp90 inhibitors; Curr. Top. Med.Chem.; 2006, 6, 1193.

ii. Sessler, J.L.; Seidel, D.; Synthetic Expanded Porphyrin Chemistry; Angew. Chem. Int. Ed; 2003, 42, 5134.

iii. Zheng J.; Wen R.; Luo X.; Lin G.; Zhang J.; Xu L.; Guo L.; Jiang H.; Design, synthesis, and biological evaluation of the N-diarylalkenyl-piperidinecarboxylic acid derivatives as GABA uptake inhibitors (I); Bioorg. Med. Chem. Lett; 2006, 16, 225.

iv. Sugiura S.; Ohno S.; Ohtani O.; Izumi K.; Kitamikado T.; Asai H.; Kato K.; Syntheses and antiinflammatory and hypnotic activity of 5-alkoxy-3-(N-substituted carbamoyl)-1-phenylpyrazoles; J. Med. Chem.; 1977, 20, 80.

v. Bailey D.M.; Hansen P.E.; Hlavac A.G.; Baizman E.R.; Pearl J.; Defelice A.F.; Feigenson M.E.; 3,4-Diphenyl-1H-pyrazole-1-propanamine antidepressants; J. Med. Chem.;1985, 28, 256.

vi. Behr L.C.; Fusco R.; Jarboe C.H.; Weissberger, A.; Ed. Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles And Condensed Rings, Interscience Publishers: New York; 1967.

vii. Mahajan R.N.; Havaldar F.H.; Fernandes P.S.; Syntheses and biological activity of heterocycles derived from 3-methoxy-i-phenyl-ih-pyrazole-5-carboxylate; J. Indian Chem. Soc.; 1991, 98, 245.

viii. Chauhan P.M.S.; Singh S.; Chatterjee R.K.; Antifilarial profile of substituted

pyrazoles: a new class of antifilarial agents; Indian J. Chem.; Sect. B: Org. Chem. Incl. Med. Chem.; 1993, 32, 858.

ix. Rosiere; C.E.; Grossman M. I.; An Analog of Histamine that Stimulates Gastric Acid Secretion without other Actions of Histamine; Science; 1951, 113, 651.

x. Londershausen M.; Review: Approaches to New Parasiticides, Pestic. Sci.; 1996, 48, 269- 292.

xi. Singh D.; Singh D.; Synthesis and antifungal activity of some 4-arylmetylene derivatives of substituted pyrazolones; J. Indian Chem. Soc.;1991, 68, 165.

xii. The Chemistry of Synthetic Dyes and Pigments; Lubs, H. A., Ed.; American Chemical Society: Washington D.C., (1970).

xiii. Uzoukwu A.B.; The synthesis and crystal structures of 1-phenyl-3-methyl-4-butanolypyrazol-5-one and of two pyrazolonato complexes of iron; Polyhedron; 1993, 12, 2719.

xiv. Maurya R.C.; Verma R.; Synthesis and characterizaton of some novel mixed-ligand cyanonitrosyl {MnNO}6 complexes of manganese (I) with biologically active oxygen donor 2- or 3-pyrazoline- 5-one derivatives; Indian J. Chem. Sec. A.; 1997, 36, 596.

xv. Tejedor D.; Garcia-Tellado F.; Chemo-differentiating ABB′ multicomponent reactions. Privileged building blocks; Chem. Soc. Rev.; 2007, 36, 484.

xvi. Simon C.; Constantieux T.; Rodriguez J.; Utilisation of 1,3-Dicarbonyl Derivatives in Multicomponent Reactions; Eur. J. Org. Chem; 2004, 4957.

xvii. Li X.L.; Wang Y.M.; Tian B.; Matsuura T.; Meng J.B.; The solid-state michael addition of 3-methyl-1-phenyl-5-pyrazolone; J. Heterocycl. Chem.; 1998, 35, 129.

xviii. Singh D.; Singh D.J; Syntheses of 1, 3-disubstituted 4-arylidenepyrazolin-5-ones and the keto and enol forms of 4, 4'-arylidenebis (1, 3-disubstituted pyrazolin-5-ones); J. Chem. Eng. Data; 1984, 29,355.

xix. Wang W.; Wang S.X.; Qin X.Y.; Li J.T.; Reaction of aldehydes and pyrazolones in the presence of sodium dodecyl sulfate in aqueous media; Synth. Commun.; 2005, 35 1263.

xx. Niknam K.; Saberi D.; Sadegheyan M.; Deris A.; Tetrahedron. Lett.; 2010, 5, 692.

xxi. Tayebi S.; Baghernejad M.; Saberi D.; Niknam K.; Sulfuric acid (3-(3-silicapropyl) sulfanyl] propyl) ester as a recyclable catalyst for the synthesis of 4, 4′-(arylmethylene) bis (1H-pyrazol-5-ols); J. Chin. Catal.; 2011, 32, 1477.

xxii. Tale N.P.; Tiwari G.B.; Karade N.N.; Un-catalyzed tandem Knoevenagel–Michael reaction for the synthesis of 4, 4′-(arylmethylene) bis (1H-pyrazol-5-ols) in aqueous medium; Chin. Chem. Lett.; 2011, 22, 1415.

xxiii. Niknam K.; Mirzaee S.; Silica Sulfuric Acid, an Efficient and Recyclable Solid Acid Catalyst for the Synthesis of 4,4′-(Arylmethylene)bis (1H-pyrazol-5-ols); Synth. Commun.; 2011, 41, 2403.

xxiv. Sobhani S.; Hasaninejad A.; Maleki M.F.; Parizi Z.P.; Tandem Knoevenagel–Michael Reaction of 1-Phenyl-3-methyl-5-pyrazolone with Aldehydes Using 3-Aminopropylated Silica Gel as an Efficient and Reusable Heterogeneous Catalyst; Synth. Commun.; 2012, 42, 2245.

xxv. Kuarm B.S.; Rajitha B.; Xanthan sulfuric acid: an efficient, biosupported, and recyclable solid acid catalyst for the synthesis of 4, 4′-(arylmethylene) bis (1H-pyrazol-5-ols); Synth. Commun.; 2012, 42, 2382.

xxvi. Hasaninejad A.; Kazerooni M.R.; Zare A.; Room temperature, catalyst-free, one-pot pseudo fivecomponent synthesis of 4,4-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols) under ultrasonic irradiation; ACS Sustainable Chem. Eng.; 2013, 6, 679.

xxvii. Gupta A.D.; Pal R., Mallik A.K.; Two efficient and green methods for synthesis of

4,4′-(arylmethylene)bis(1H-pyrazol-5-ols) without use of any catalyst or solvent; Green Chemistry Letters and Reviews; 2014,7, 404.

xxviii. Khazaei, A.; Abbasi F.; Moosavi-Zare A.R.; Tandem cyclocondensation-Knoevenagel–Michael reaction of phenyl hydrazine, acetoacetate derivatives and arylaldehydes; New J. Chem.; 2014, 38, 5287.

xxix. Zolfigol M.A.; Ayazi-Nasrabadi R. ; Baghery S. ; Synthesis and characterization of two novel biological-based nano organo solid acids with urea moiety and their catalytic applications in the synthesis of 4,4′-(arylmethylene)bis(1H-pyrazol-5-ol) coumarin-3-carboxylic acid and cinnamic acid derivatives under mild and green conditions; RSC Adv.; 2015, 5, 71942.

xxx. Kour M.; Paul S.; Sulfonated carbon/nano-metal oxide composites: a novel and recyclable solid acid catalyst for organic synthesis in benign reaction media; New J. Chem.; 2015, 39, 6338.

xxxi. Zarghani M. ; Akhlaghinia B. ; Sulfonated nanohydroxyapatite functionalized with 2-aminoethyl dihydrogen phosphate (HAP@AEPH2-SO3H) as a new recyclable and eco-friendly catalyst for rapid one-pot synthesis of 4,4′-(aryl methylene)bis(3-methyl-1H-pyrazol-5-ol)s; RSC Adv.; 2015, 5, 87769.

xxxii. Khaligh N.G.; Hamid S.B.A.; Titinchi S.J.J; Succinimide-N-sulfonic Acid as a Recyclable Brönsted Acid Catalyst for Synthesis of Pyrano[4,3-b]pyran Derivatives by Using Solar Energy Under Solvent-Free Conditions; Chinese Chemical Letters.; 2015.

xxxiii. Shirini F.; Seddighi M.; Mazloumi M.; Makhsous M.; Abedini M.; One-pot synthesis of 4,4′-(arylmethylene)-bis-(3-methyl-1-phenyl-1H-pyrazol-5-ols) catalyzed by Brönsted acidic ionic liquid supported on nanoporous Na+-montmorillonite; Journal of Molecular liquids; 2015, 208, 291.

xxxiv. Janvier P.; Sun X.; Bienayme H.; Zhu J.; Ammonium Chloride-Promoted Four-Component Synthesis of Pyrrolo[3,4-b]pyridin-5-one; J. Am. Chem. Soc.; 2002,124 11, 2560.

xxxv. Bonne D.; Dekhane M.; Zhu J.; Ammonium chloride promoted Ugi four-component, five-center reaction of α-substituted α-isocyano acetic acid: A strong solvent effect; Org. Lett.; 2004, 6, 4771.

xxxvi. Sridahara M.B.; Srinivasa G.R.; Gowada D.C.; Reductive cleavage of azo compounds by zinc and ammonium chloride; Synth. Commun.; 2004, 34, 1441.

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