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A Rapid Tandem Knoevenagel/Michael Reaction Using Mohr's Salt as a Highly Efficient Catalyst: Green Synthesis of Bis(pyrazolyl)methanes

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Abstract: A convenient access to some new and known bis(pyrazolyl)methanes synthesis has been successfully achieved via an alternative Knoevenagel/Michael reaction of aromatic aldehydes and pyrazole-5-one in the presence of Mohr's salt as a green catalyst. This novel procedure has some advantages such as high efficiency, simplicity, high rate and environmental safety.

Keywords: Green synthesis, Knoevenagel condensation, Michael addition, aqueous media, bis(pyrazolyl)methane, Mohr's salt.

INTRODUCTION

Pyrazole derivatives have shown important pharmacological activity and chemical activity in medicinal and organic chemistry [1-3]. Pharmaceutically, they exhibit considerable antitubercular [4], antifungal [5], antibacterial [6], anti-inflammatory [7], and antitumor activities [8]. Synthetically, some pyrazole derivatives such as pyrazole-2-ones act as methylene active compounds for synthesis of various heterocycles [9-14]. Recently, some synthetic routes to bis(pyrazolyl)methanes under various conditions have been reported in the literature. The general method is tandem Knoevenagel and Michael addition reaction between aldehydes and pyrazolones in the presence of several catalytic systems including silica-bonded s-sulfonic acid [15], sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester [16], cellulose sulfuric acid [17], 2-hydroxyethylammonium acetate [18], nano *n*-propylsulphonated-γ-Fe_2O_3 [19], poly(ethylene glycol)-400 (PEG-400) [20], 1,3-disulfonic acid imidazolium tetrachloroaluminate [21], electrolysis [22], sodium dodecyl sulfate [23], ceric ammonium nitrate [24], PEG-SO_3H [25], lithium hydroxide [26], and sonication [27]. Despite the advantages of reported methods, some of them suffer from disadvantages such as toxicity, environmental pollution, low product yield, long reaction times, and use of extra tools and expensive catalysts.

In analytical chemistry, ferrous ammonium sulfate known as Mohr's salt is a common laboratory reagent preferred over other salts of iron for titration purposes as it is much less prone to oxidation by air to iron (III) [28]. Recently, Mohr's salt was reported as a new and powerful catalyst in organic synthesis by our research group [29]. Herein, we report a new application of Mohr's salt as a highly efficient catalyst for the green synthesis of some novel and known bis(pyrazolyl)methanes.

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RESULTS AND DISCUSSION

In continuation of our studies on the development of new strategies for the synthesis of organic compounds [30-35], herein, we wish to report a new access high efficient condensation between aromatic aldehydes **1**, and 3-methyl-1-phenyl-5-pyrazolone **2** to bis(pyrazolyl)methanes **3** synthesis in the presence of Mohr's salt as a green catalyst in aqueous media (Scheme **1**).

At first, in order to optimize reaction conditions, the reaction of benzaldehyde with 3-methyl-1-phenyl-5-pyrazolone was chosen as a model (compound **3a**).

We firstly evaluated required amount of the catalyst for this transformation. In the absence of catalyst, the reaction did not considerably proceed even for 90 min. By adding 1 mol% of the catalyst, the reaction showed an appreciable progress and completed in about 30 min. When 2 mol% of catalyst was used, the reaction efficiently proceeded and completed in less reaction time (20 min). By further increasing catalyst amount no appreciable improvement in the product yield and reaction time was observed.

Next, the model reaction was established at room temperature in the presence of Mohr's salt (2 mol%) as catalyst, but the reaction rate decreased and did not complete after 120 min.

A number of solvents such as EtOH, MeOH, CH_2Cl_2, H_2O, and THF were also tried with catalytic amount of Mohr's salt (2 mol%) and it was found that the use of protic solvents such as EtOH and MeOH dramatically reduces the reaction time with improved product yield at room temperature (Table **1**).

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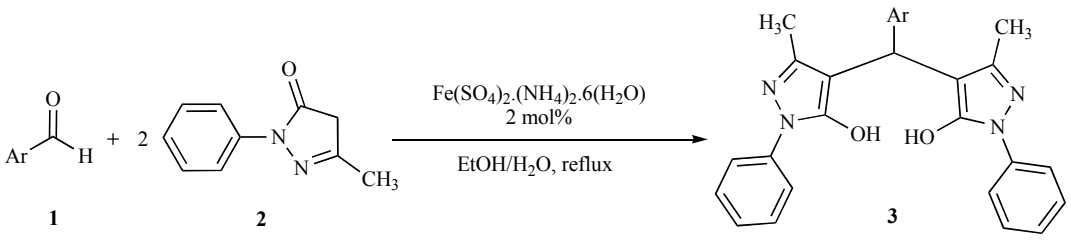

Scheme 1. Synthesis of bis(pyrazolyl)methanes using Mohr's salt.

Table 1. Solvent effect in the synthesis of model compound 3a.

Entry	Solvent	Time (min)	Yield (%)
1	CH_2Cl_2	120	25
2	THF	60	40
3	MeOH	30	80
4	EtOH	20	90
5	H_2O	120	70
6	EtOH/H_2O (1:1)	20	90

Table 2. Synthesis of bispyrazoles 3 using Mohr's salt (2 mol%).

Entry	Aldehyde	Product	Time (min)	Yield[a] (%) [Lit.]
1	C_6H_5CHO	**3a**	20	90 [20]
2	2,4-$(MeO)_2C_6H_3CHO$	**3b**	25	85
3	3-(EtO)-4-(HO)C_6H_3CHO	**3c**	30	87
4	1-NaphthylCHO	**3d**	30	88
5	4-$(C_6H_5)C_6H_4CHO$	**3e**	20	90
6	3-IndolylCHO	**3f**	30	88
7	2,4-$Cl_2C_6H_3CHO$	**3g**	20	85 [15]
8	3-$O_2NC_6H_4CHO$	**3h**	20	90 [20]
9	4-$O_2NC_6H_4CHO$	**3i**	20	92 [20]
10	4-MeC_6H_4CHO	**3j**	30	85 [20]
11	2-ClC_6H_4CHO	**3k**	20	90 [20]
12	4-$MeOC_6H_4CHO$	**3l**	20	85 [26]
13	3-BrC_6H_4CHO	**3m**	25	87 [20]

[a] Isolated yields.

From the economic and environmental point of view, an equal mixture of H_2O/EtOH was selected as medium for all further reactions. Therefore, the best reaction conditions were obtained by using 2 mol% of Mohr's salt as the catalyst under reflux in H_2O/EtOH (1:1).

By loading the reaction in achieved optimal conditions, a variety of novel and known bis(pyrazolyl)methanes **3** were successfully synthesized and results of this new procedure were shown in Table **2**. It is worthwhile to note that for purification of products **3a-3m**, a simple filtration and recrystallization from boiling EtOH is needed.

Reactions of aromatic aldehydes bearing electron-withdrawing/donating group with **2** gave the expected products in excellent yields under the same reaction conditions. Compounds **3a-m** are stable solids which their structures were confirmed by C H N analyses, IR, ^{1}H, and ^{13}C NMR spectroscopy. It should be also mentioned that our efforts on the use of aliphatic aldehydes instead of aromatic ones were

Table 3. Comparison of present work with other methods reported in the literature for synthesis of 3a.

Entry	Conditions	Time (min)	Yield[a] (%) [Lit.]
1	Mohr's salt (2 mol%), H_2O/EtOH, Reflux	20	90[b]
2	SBSSA[c] (0.1 g), EtOH, Reflux	120	80 [15]
3	SASPSPE[d] (0.1 g), EtOH, Reflux	180	90 [16]
4	Cellulose sulfuric acid (0.2 g), H_2O/EtOH, Reflux	120	74 [17]
5	2-HEAA[e] (5 mol%), EtOH, r.t.	15	90 [18]
6	NPS-γ-Fe_2O_3[f] (2 mol%), H_2O, r.t.	180	93 [19]
7	PEG-400[g], 110 °C	120	92 [20]
8	[Dsim]$AlCl_4$[h] (1 mol%), 50 °C	60	86 [21]
9	Electrolysis, EtOH, NaBr (0.1 g), 20 °C	33	82 [22]
10	Sodium dodecyl sulfate (5 mol%), H_2O, Reflux	60	87 [23]

[a] Isolated yields. [b] Present work. [c] Silica-bonded S-sulfonic acid. [d] Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl) ester. [e] 2-hydroxyethylammonium acetate. [f] Nano *n*-propylsulphonated-γ-Fe_2O_3. [g] Poly(ethylene glycol)-400. [h] 1,3-disulfonic acid imidazolium tetrachloroaluminate.

unsuccessful. We believe that it is a consequence of the enolization of aliphatic aldehydes and the lower electrophilicity of their carbonyl group.

In order to show the efficiency of the present work, Table **3** shows the results of some previously reported methods in the literature. According to the summarized data, the Mohr's salt catalyzed synthesis of **3** can be considered as an efficient, green and economical method due to the generation of desired product in high yield, short reaction time and environmentally safe conditions using a little amount of inexpensive catalyst in comparison with previous ones.

EXPERIMENTAL

General

Chemicals were purchased from Merck and Aldrich chemical companies. Melting points were measured on an electro thermal KSB1N apparatus. IR spectra were recorded in the matrix of KBr with a JASCO FT-IR-680 plus spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a FT-NMR Bruker Avance Ultra Shield Spectrometer at 400.13 MHz (300 and 250 MHz for some products) and 100.62 MHz (76.5 and 62.5 MHz for some products) in DMSO-d_6 as solvent in the presence of tetra methyl silane as internal standard. Elemental analyses were performed on a Heraeus CHN-O-Rapid analyzer. TLC was performed on TLC-Grade silica gel-G/UV 254 nm plates. All products were isolated, purified and deduced from IR, ^{1}H NMR, and ^{13}C NMR spectral data.

General Procedure to the Synthesis of Novel and Known Bispyrazols Using Mohr's Salt

A solution of the aromatic aldehyde **1** (1 mmol), the pyrazolone **2** (2 mmol) and Mohr's salt (2 mol%) in EtOH/H_2O (1:1, 10 mL) was stirred under reflux for a stipulated time. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled at room temperature and solvent was evaporated under reduced pressure. The precipitate was washed with cool distilled water to separate the catalyst. The pure product **3** was obtained after recrystallization from boiling EtOH and no further purification was needed.

Representative Spectral Data

4,4'-(Phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3a)

Light yellow crystals; mp 167-169 °C (lit.[20] 168-170 °C); FT-IR (KBr) (υ_{max}, cm^{-1}): 3424, 3062, 2917, 1598, 1498, 1415, 1284, 1186, 1027, 755, 692; ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 13.96 (s, 1H, OH), 12.39 (s, 1H, OH), 7.71 (d, J = 8.4 Hz, 4H, aromatic CH), 7.45 (t, J = 7.2 Hz, 4H, aromatic CH), 7.31-7.24 (m, 6H, aromatic CH), 7.20-7.17 (m, 1H, aromatic CH), 5.00 (s, 1H, CH), 2.33 (s, 6H, 2CH$_3$); ^{13}C NMR (100.62 MHz, DMSO-d_6) δ (ppm): 157.6, 146.4, 140.7, 136.9, 128.8, 128.3, 127.1, 126.4, 126.2, 121.3, 105.7, 33.6, 11.5.

4,4'-((2,4-Dimethoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3b)

Yellow crystals; mp 190-192 °C; FT-IR (KBr) (υ_{max}, cm^{-1}): 3428, 2996, 2958, 2839, 1613, 1503, 1460, 1406, 1294, 1209, 1122, 1041, 839, 757, 580; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ (ppm): 14.35 (s, 1H, OH), 12.38 (s, 1H, OH), 7.69 (d, J = 7.8 Hz, 4H, aromatic CH), 7.39-7.50 (m, 5H, aromatic CH), 7.22 (t, J = 6.9 Hz, 2H, aromatic CH), 6.46 (t, J = 9.6 Hz, 2H, aromatic CH), 5.09 (s, 1H, CH), 3.79 (s, 3H, OCH$_3$), 3.69 (s, 3H, OCH$_3$), 2.26 (s, 6H, 2CH$_3$); ^{13}C NMR (76.46 MHz, DMSO-d_6) δ (ppm): 158.8, 156.7, 146.1, 137.6, 137.4, 137.3, 137.1, 136.7, 133.6, 131.9, 128.8, 125.4, 122.9, 120.5, 104.1, 98.2, 55.4, 55.0, 26.9, 11.6. Anal. calcd for $C_{29}H_{28}N_4O_4$: C, 70.15; H, 5.68; N, 11.28; Found: C, 70.22; H, 5.62; N, 11.25%.

4,4'-((3-Ethoxy-4-hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3c)

Chocolate crystals; mp 212-213 °C; FT-IR (KBr) (υ_{max}, cm^{-1}): 3420, 3219, 2985, 2927, 1596, 1498, 1400, 1275,

1214, 1126, 1043, 811, 753, 691. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ (ppm): 13.97 (s, 1H, OH), 12.36 (s, 1H, OH), 8.67 (s, 1H, OH), 7.69 (d, J = 8.1 Hz, 4H, aromatic CH), 7.42 (t, J = 7.8 Hz, 4H, aromatic CH), 7.22 (t, J = 7.2 Hz, 2H, aromatic CH), 6.82 (s, 1H, CH), 6.66 (s, 2H, CH) 4.82 (s, 1H, CH), 3.90 (q, J = 6.9 Hz, 2H, CH_2), 2.29 (s, 6H, $2CH_3$), 1.25 (t, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR (76.46 MHz, DMSO-d_6) δ (ppm): 146.1, 145.1, 142.6, 137.3, 137.0, 133.1, 131.6, 128.9, 125.5, 120.5, 119.7, 115.2, 113.4, 63.9, 32.7, 14.7, 11.6. Anal. calcd for $C_{29}H_{28}N_4O_4$: C, 70.15; H, 5.68; N, 11.28; Found: C, 70.19; H, 5.57; N, 11.26%.

4,4'-(Naphthalen-1-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3d)

Navajo white crystals; mp 228-230 °C; FT-IR (KBr) (υ_{max}, cm^{-1}): 3419, 3062, 2922, 1608, 1542, 1497, 1402, 1370, 1132, 829, 783, 756, 689. ^{1}H NMR (300.13 MHz, DMSO-d_6) δ (ppm): 13.15 (s, 1H, OH), 12.19 (s, 1H, OH), 8.10-8.00 (m, 1H, aromatic CH), 7.92 (d, J = 6.6 Hz, 1H, aromatic CH), 7.80 (d, J = 7.2 Hz, 1H, aromatic CH), 7.62-7.75 (m, 5H, aromatic CH), 7.34-7.57 (m, 7H, aromatic CH), 7.15-7.25 (m, 2H, aromatic CH), 5.61 (s, 1H, CH), 2.25 (s, 6H, $2CH_3$). ^{13}C NMR (76.46 MHz, DMSO-d_6) δ (ppm): 146.0, 144.1, 140.6, 137.3, 136.7, 133.6, 130.7, 128.8, 128.7, 127.0, 125.9, 125.7, 125.3, 125.2, 123.5, 119.9, 105.6, 30.9, 11.9, 11.8. Anal. calcd for $C_{31}H_{26}N_4O_2$: C, 76.52; H, 5.39; N, 11.51; Found: C, 76.57; H, 5.33; N, 11.48%.

4,4'-([1,1'-Biphenyl]-4-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3e)

Navajo white crystals; mp 218-220 °C; FT-IR (KBr) (υ_{max}, cm^{-1}): 3444, 3026, 2922, 1599, 1580, 1499, 1405, 1294, 818, 751, 692; ^{1}H NMR (300.13 MHz, DMSO-d_6) δ (ppm): 14.05 (s, 1H, OH), 12.48 (s, 1H, OH), 7.74 (d, J = 7.8 Hz, 4H, aromatic CH), 7.55-7.62 (m, 4H, aromatic CH), 7.46-7.34 (m, 9H, aromatic CH), 7.23 (t, J = 7.2 Hz, 2H, aromatic CH), 5.01 (s, 1H, CH), 2.35 (s, 6H, $2CH_3$); ^{13}C NMR (76.46 MHz, DMSO-d_6) δ (ppm): 146.3, 141.5, 140.0, 137.9, 137.4, 137.3, 128.9, 128.8, 127.8, 127.1, 126.5, 125.5, 120.5, 104.9, 104.6, 32.8, 11.6. Anal. calcd for $C_{33}H_{28}N_4O_2$: C, 77.32; H, 5.51; N, 10.93; Found: C, 77.38; H, 5.43; N, 10.84%.

4,4'-((1H-Indol-3-yl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3f)

Yellow crystals; mp 242-244 °C; FT-IR (KBr) (υ_{max}, cm^{-1}): 3470, 3042, 2920, 1618, 1540, 1488, 1405, 1370, 1136, 830, 786, 755, 689; ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 12.65 (s, 2H, OH), 9.85 (s, 1H, NH), 8.13-8.11 (m, 2H, aromatic CH), 8.06 (s, 1H, aromatic CH), 8.05-8.01 (m, 2H, aromatic CH), 7.60-7.58 (m, 1H, aromatic CH), 7.44-7.40 (m, 4H, aromatic CH), 7.32-7.29 (m, 4H, aromatic CH), 7.17-7.13 (m, 1H, aromatic CH), 7.15-7.25 (m, 2H, aromatic CH), 3.49 (s, 1H, CH), 2.39 (s, 6H, $2CH_3$); ^{13}C NMR (100.62 MHz, DMSO-d_6) δ (ppm): 162.7, 150.8, 138.9, 138.2, 136.9, 136.4, 128.6, 128.1, 123.8, 123.4, 122.0, 118.5, 118.0, 112.8, 112.2, 18.5, 12.9. Anal. calcd for $C_{29}H_{25}N_5O_2$: C, 73.25; H, 5.30; N, 14.73; Found: C, 73.31; H, 5.23; N, 14.66%.

4,4'-((2,4-Dichlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3g)

Bisque crystals, mp 228-230 °C (lit.[15] 227–229 °C); FT-IR (KBr) (υ_{max}, cm^{-1}): 3420, 3057, 2920, 1597, 1572, 1500, 1470, 1380, 1298, 1189, 845, 792, 752, 690; ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 13.95 (s, 1H, OH), 12.67 (s, 1H, OH), 7.65-7.74 (m, 5H, aromatic CH), 7.53 (d, J = 2.0 Hz, 1H, aromatic CH), 7.36-7.44 (m, 5H, aromatic CH), 7.22 (t, J = 7.2 Hz, 2H, aromatic CH), 5.05 (s, 1H, CH), 2.26 (s, 6H, $2CH_3$); ^{13}C NMR (62.89 MHz, DMSO-d_6) δ (ppm): 148.3, 147.1, 146.0, 137.3, 134.9, 128.8, 125.4, 120.5, 119.2, 111.6, 111.5, 104.9, 104.6, 31.7, 11.6.

4,4'-((3-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3h)

Yellow crystals, mp 152-154 °C (lit.[20,16] 151-153 °C); FT-IR (KBr) (υ_{max}, cm^{-1}): 3420, 3068, 2920, 1598, 1579, 1524, 1500, 1415, 1348, 785, 753, 691. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 13.91 (s, 2H, OH), 8.06-8.10 (m, 2H, aromatic CH), 7.68-7.74 (m, 5H, aromatic CH), 7.60 (t, J = 8.3 Hz, 1H, aromatic CH), 7.45 (t, J = 7.6 Hz, 4H, aromatic CH), 7.26 (t, J = 7.3 Hz, 2H, aromatic CH), 5.14 (s, 1H, CH), 2.35 (s, 6H, $2CH_3$). ^{13}C NMR (100.62 MHz, DMSO-d_6) δ (ppm): 147.7, 146.3, 144.5, 137.3, 134.3, 129.7, 128.9, 125.8, 125.7, 121.7, 121.2, 120.6, 32.8, 11.5.

4,4'-((4-Nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3i)

Yellow crystals, mp 228-230 °C (lit.[20] 229-231 °C); FT-IR (KBr) (υ_{max}, cm^{-1}): 3068, 2920, 1598, 1579, 1524, 1500, 1415, 1348, 785, 753, 691. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 13.90 (s, 1H, OH), 12.49 (s, 1H, OH), 8.18 (d, J = 8.8 Hz, 2H, aromatic CH), 7.73 (d, J = 8.0 Hz, 4H, aromatic CH), 7.54 (d, J = 8.8 Hz, 2H, aromatic CH), 7.45 (t, J = 8.0 Hz, 4H, aromatic CH), 7.25 (t, J = 8.0 Hz, 2H, aromatic CH), 5.14 (s, 1H, CH), 2.37 (s, 6H, $2CH_3$); ^{13}C NMR (100.62 MHz, DMSO-d_6) δ (ppm): 150.3, 146.2, 145.8, 137.1, 129.1, 128.9, 128.5, 125.6, 123.3, 120.5, 104.0, 33.1, 11.5.

4,4'-((4-Methylphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3j)

White crystals, mp 203-205 °C (lit.[20] 201-203 °C); FT-IR (KBr) (υ_{max}, cm^{-1}): 3437, 2923, 1600, 1499, 1407, 1295, 1024, 803, 749, 690. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 13.92 (s, 1H, OH), 12.40 (s, 1H, OH), 7.08–7.71 (m, 14H, aromatic CH), 4.91 (s, 1H, CH), 2.31 (s, 6H, $2CH_3$), 2.24 (s, 3H, CH_3). ^{13}C NMR (100.62 MHz, DMSO-d_6) δ (ppm): 147.1, 140.0, 135.7, 129.8, 129.6, 127.9, 126.4, 121.4, 40.9, 33.6, 21.4, 12.5.

4,4'-((2-Chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3k)

White crystals, mp 238-240 °C (lit.[20,16] 236-237 °C); FT-IR (KBr) (υ_{max}, cm^{-1}): 3433, 3062, 2921, 1613, 1560, 1499, 1401, 747, 690. ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 13.92 (br, 2H, 2OH), 7.75-7.77 (m, 4H, aromatic CH), 7.41-7.43 (m, 8H, aromatic CH), 7.27-7.29 (m, 2H, aromatic CH), 5.08 (s, 1H, CH), 2.26 (s, 6H, $2CH_3$). ^{13}C NMR (100.62

MHz, DMSO-d_6) δ (ppm): 141.1, 140.6, 137.3, 135.9, 130.3, 129.4, 128.9, 128.0, 126.9, 123.6, 120.6, 32.4, 11.6.

4,4'-((4-Methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3l)

White crystals, mp 163-165 °C (lit.[26] 162-163 °C); FT-IR (KBr) (υ_{max}, cm^{-1}): 3433, 2924, 1601, 1507, 1406, 1245, 1030, 753, 692. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 13.85 (br, 2H, 2OH), 7.64 (d, J = 8.0 Hz, 4H, aromatic CH), 7.39 (d, J = 7.4 Hz, 4H, aromatic CH), 7.20 (t, J = 7.45 Hz, 2H, aromatic CH), 7.12 (d, J = 8.6 Hz, 2H, aromatic CH), 7.8 (d, J = 8.5 Hz, 2H, aromatic CH), 4.84 (s, 1H, CH), 3.85 (s, 3H, OCH_3), 2.46 (s, 6H, $2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 157.5, 146.1, 137.9, 134.6, 129.2, 128.9, 128.1, 125.4, 120.4, 113.5, 105.0, 54.9, 32.4, 11.6.

4,4'-((3-Bromophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (3m)

White crystals, mp 173-176 °C (lit.[20] 172-175 °C); FT-IR (KBr) (υ_{max}, cm^{-1}): 3066, 2973, 2918, 1595, 1500, 1416, 1297, 880, 754, 691. ^{1}H NMR (500 MHz, DMSO-d_6) δ (ppm): 13.92 (s, 1H, OH), 12.40 (s, 1H, OH), 6.82-7.71 (m, 14H, aromatic CH), 4.89 (s, 1H, CH), 2.30 (s, 6H, $2CH_3$). ^{13}C NMR (125 MHz, DMSO-d_6) δ (ppm): 154.4, 145.9, 140.4, 133.6, 132.4, 129.7, 128.7, 128.3, 127.7, 127.2, 125.4, 123.6, 117.9, 14.3, 10.0.

CONCLUSION

In summary, the present work discloses a rapid and expedient novel strategy for the condensation of aromatic aldehydes **1** and pyrazolone **2** in the presence of Mohr's salt as a green, available and powerful catalyst in H_2O/EtOH to afford new and known bis(pyrazolyl)methanes. The operational simplicity, short reaction times, excellent yields, and little environmental impact are notable advantages of this procedure.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's web site along with the published article.

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