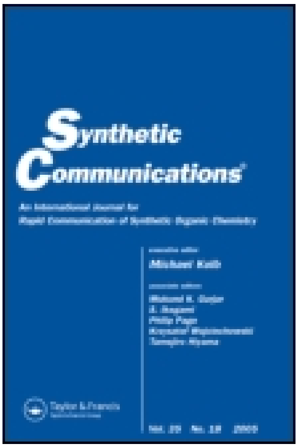

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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

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To cite this article: Sara Sobhani, Ali-Reza Hasaninejad, Mahdi Faal Maleki & Zahra Pakdin Parizi (2012): 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, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:15, 2245-2255

To link to this article: http://dx.doi.org/10.1080/00397911.2011.555589

Synthetic Communications®, 42: 2245–2255, 2012
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2011.555589

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

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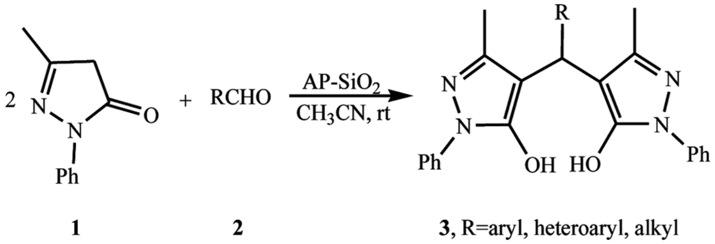
GRAPHICAL ABSTRACT



Abstract *3-Aminopropylated silica gel is introduced as an efficient, reusable, and thermally stable heterogeneous catalyst for tandem Knoevenagel–Michael reaction of 1-phenyl-3-methyl-5-pyrazolone with aldehydes. Short reaction times, mild reaction conditions, ease of recovery, and catalyst reusability make this method a new, economical, and waste-free chemical process for the efficient synthesis of bis(pyrazolyl)methanes.*

Keywords Bis(pyrazolyl)methane; heterogeneous catalysts; pyrazolone; silica-supported catalysts; solid bases

INTRODUCTION

Pyrazoles are an important class of bioactive drug targets in the pharmaceutical industry. They are the core structure of numerous biologically active compounds.[1] For example, they exhibit anti-anxiety, antipyretic, analgesic, and anti-inflammatory properties. 2,4-Dihydro-3*H*-pyrazol-3-one derivatives including 4,4′-(arylmethylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ols), which have a broad

Received July 5, 2010.

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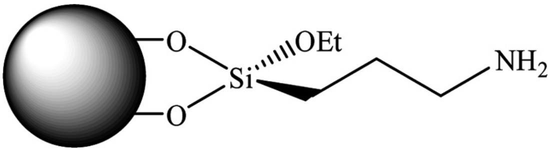


Figure 1. 3-Aminopropylated silica gel (AP-SiO_2).

spectrum of approved biological activity, are being used as anti-inflammatory, antipyretic, gastric secretion stimulatory, antidepressant, antibacterial, and antifilarial agents.[2] Moreover, the corresponding 4,4′-(arylmethylene)bis(1*H*-pyrazol-5-ols) are applied as fungicides, pesticides, insecticides, dyestuffs, and chelating and extracting reagents for different metal ions.[3] The conventional chemical approach to 4,4′-(arylmethylene)bis(3-methyl-1-phenyl-pyrazol-5-ols) involves the successive Knoevenagel synthesis of the corresponding arylidenepyrazolones and its base-promoted Michael reaction.[3a],[3b],[4] One-pot tandem Knoevenagell–Michael reaction of aldehydes with 2 equivalents of 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one, which can be performed under a variety of reaction conditions, is another approach for achieving these important scaffolds.[5] However, most of the methods suffer from at least one limitation that may include moderate yields, long reaction times, harsh reaction conditions, high temperature, use of unrecyclable catalyst, or tedious workup procedures.

Use of heterogeneous solid base catalysts is of current interest in chemistry and industry because solid bases offer many advantages such as simplicity in handling, more environmentally safe disposal, and less industrial corrosion problems.[6] Amine functionalized silica gel such as 3-aminopropylated silica gel (AP-SiO_2) is one of the organic–inorganic hybrid materials that have been applied as effective solid base catalysts in organic transformations.[7] In these types of solid base catalysts, the reactive centers are highly mobile, similar to those of homogeneous catalysts, and at the same time these species have the advantage of being recyclable in the same fashion as heterogeneous catalysts.

As part of our ongoing program directed toward the development of new methods in organic reactions,[8] herein we introduce 3-aminopropylated silica gel (AP-SiO_2)[7a],[9] (Fig. 1) as an efficient catalyst for tandem Knoevenagel–Michael reaction of 2 equivalents of 1-phenyl-3-methyl-5-pyrazolone with various aldehydes.

RESULTS AND DISCUSSIONS

At first, to find the best solvent, a series of reactions of benzaldehyde (1 equivalent) with 1-phenyl-3-methyl-5-pyrazolone (**1**, 2 equivalents) were studied in different solvents in the presence of AP-SiO_2(30 mol%) at room temperature (Table 1, Entries 2–6). Among solvents investigated, CH_3CN was the best medium for the present reaction (entry 2). Under the same reaction conditions, when 20 mol% of the catalyst was used, the desired product was obtained after a longer reaction time (entry 1). To show the role of the catalyst, similar reactions in the absence of the catalyst or in the presence of SiO_2 were examined. These reactions led to the formation of the desired product (**2a**) in good yields but after a long reaction time (Table 1, Entries 7 and 8).

Table 1. Effect of reaction media on the preparation of **3a** from tandem Knoevenagel–Michael reaction of 1-phenyl-3-methyl-5-pyrazolone (**2**) with benzaldehyde catalyzed by 3-aminopropylated silica gel (AP-SiO_2)

Entry	Catalyst	Solvent	Time	Yield[a] (%)
1	AP-SiO_2	CH_3CN	1.5 h	90[b]
2	AP-SiO_2	CH_3CN	10 min	98
3	AP-SiO_2	H_2O	24 h	90
4	AP-SiO_2	*n*-Hexane	20 h	75
5	AP-SiO_2	Toluene	1.5 h	90
6	AP-SiO_2	CH_2Cl_2	0.5 h	80
7	—	CH_3CN	24 h	70
8	SiO_2	CH_3CN	24 h	75

[a] Isolated yield. Conditions: benzaldehyde/pyrazolone/catalyst (AP-SiO_2) 1:2:0.3 (except for entry 1), room temperature.

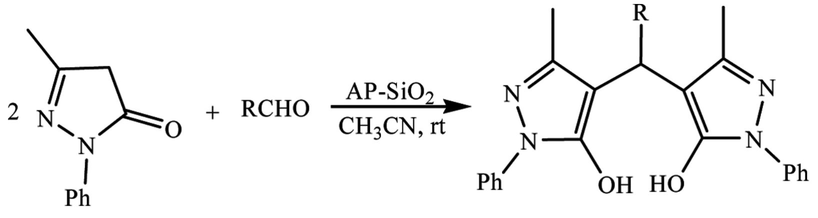
[b] Conditions: benzaldehyde/pyrazolone/catalyst (AP-SiO_2) 1:2:0.2.

Then, a range of different aldehydes (**2a–o**) were subjected to react with 1-phenyl-3-methyl-5-pyrazolone (**1**) under the optimized reaction conditions (Scheme 1, Table 2).

As shown in Table 2, different aromatic, heteroaromatic, and aliphatic aldehydes reacted with **1** in the presence of 30 mol% of 3-aminopropylated silica gel (AP-SiO_2) in short reaction times (5–45 min) to afford bis(pyrazolyl)methanes (**3a–o**) in good yields.

The ability to recycle and reuse AP-SiO_2 was also studied in this system. For this purpose, after performing the preparation reaction of bis(pyrazolyl)methane **3a** under the reaction conditions described in Table 2, the catalyst was recovered by filtration, washed with EtOH, and then reused for a consecutive run under similar conditions. The average isolated yield for the five consecutive runs was 92.6%, which clearly showed the practical reusability of this catalyst (Fig. 2). This reusability demonstrates the good stability and turnover of AP-SiO_2 under the employed conditions. It is worth to note that the recyclability test was stopped after five runs.

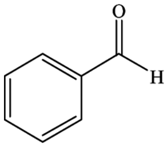
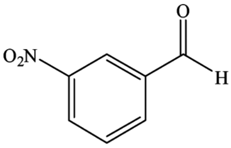
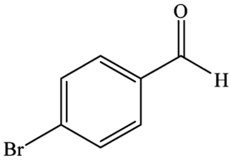
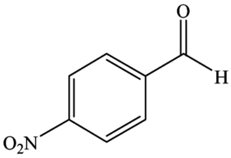
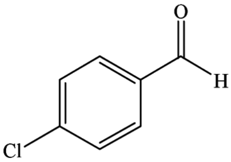
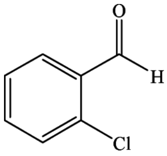
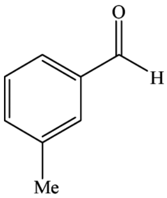
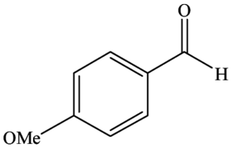
We propose a plausible mechanism for the formation of bis(pyrazolyl)-methanes **3** as the reaction of aldehydes with 1-phenyl-3-methyl-5-pyrazolone catalyzed by AP-SiO_2 (Scheme 2). The first step involves the formation of benzylidene **4**



1 **2** **3**, **R=aryl, heteroaryl, alkyl**

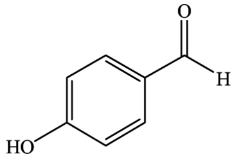
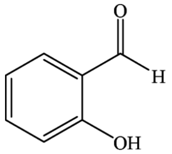
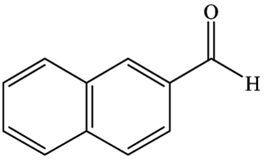
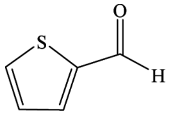
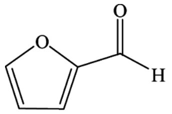
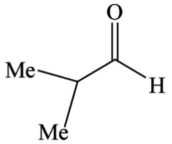
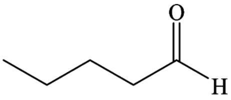
Scheme 1. Tandem Knoevenagel–Michael reaction of 1-phenyl-3-methyl-5-pyrazolone with aldehydes catalyzed by AP-SiO_2.

Table 2. Synthesis of bis(pyrazolyl)methanes **3a–o**

Entry	Aldehyde	Product	Time (min)	Yield[a] (%)
1		**3a**	10	98
2		**3b**	10	95
3		**3c**	5	95
4		**3d**	10	98
5		**3e**	5	97
6		**3f**	15	96
7		**3g**	15	96
8		**3h**	15	98

(*Continued*)

Table 2. Continued

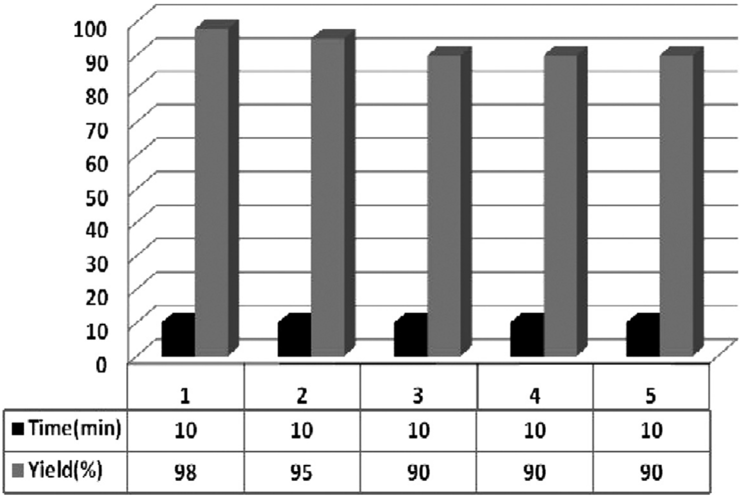
Entry	Aldehyde	Product	Time (min)	Yield[a] (%)
9		**3i**	30	97
10		**3j**	45	90
11		**3k**	10	95
12		**3l**	30	90
13		**3m**	15	90
14		**3n**	20	90
15		**3o**	10	95

[a] Isolated yield. Conditions: aldehyde/pyrazolone/catalyst (AP-SiO_2) 1:2:0.3, room temperature. All of the products are known.[5]

by the nucleophilic addition of 1-phenyl-3-methyl-5-pyrazolone to imine (formed by the reaction of aldehyde and AP-SiO_2) followed by dehydration. Then, the second molecule of 1-phenyl-3-methyl-5-pyrazolone is added to **4** in Michael addition fashion to give bis(pyrazolyl)methanes **3**.

CONCLUSION

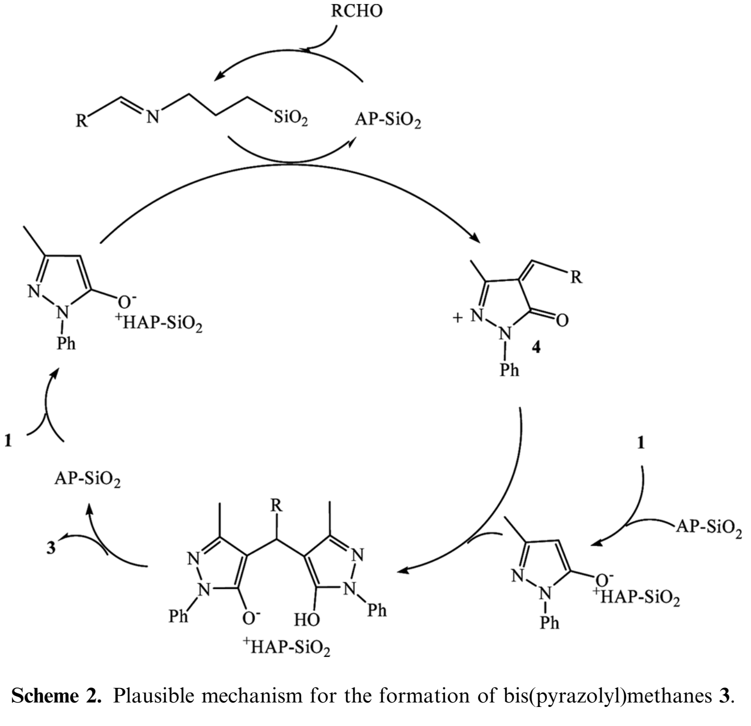
In conclusion, 3-aminopropylated silica gel (AP-SiO_2) is introduced as an efficient and heterogeneous catalyst for tandem Knoevenagel–Michael reaction of 1-phenyl-3-methyl-5-pyrazolone with various aldehydes. Ease of recovery and



	1	2	3	4	5
■ Time(min)	10	10	10	10	10
■ Yield(%)	98	95	90	90	90

Figure 2. Reusability of AP-SiO$_2$ as a catalyst for the preparation of bis(pyrazolyl)methane **3a**.

catalyst reusability make this method an economic and waste-free chemical process for the efficient synthesis of a variety of bis(pyrazolyl)methanes. Short reaction times, simple workup, and mild reaction conditions are the other advantageous of the present methodologies.



Scheme 2. Plausible mechanism for the formation of bis(pyrazolyl)methanes **3**.

EXPERIMENTAL

Chemicals were purchased from Merck and Fluka Chemical Companies. AP-SiO_2 was prepared by known procedures.[7] The loading of the organic groups was calculated from the nitrogen content (1.30%) by elemental analysis performed with a Heraeus CHN Rapid analyzer. Thermogravimetric analyses (TGA) revealed that the catalyst is thermally stable and thus does not release organic fragments almost until 125 °C. All of the products are known and were identified by their spectral data. Infrared (IR) spectra were run on a Perkin-Elmer 780 instrument. NMR spectra were recorded on Bruker Avance DPX 250, 400, and 500 instrument. Mass spectra were recorded on a Shimadzu GCMS-QP5050A instrument. The purity of the products and the progress of the reactions were accomplished by thin-layer chromatography (TLC) on silica-gel polygram SILG/UV_{254} plates.

General Procedure for the Synthesis of Bis(pyrazolyl)methanes

3-Aminopropylated silica gel (AP-SiO_2) (3.22 g, 0.93 mmol/g, 3 mmol) was added to a stirring solution of aldehyde (10 mmol) and pyrazolone **1** (20 mmol) in CH_3CN (10 mL). The mixture was stirred at room temperature for an appropriate time (Table 2). The catalyst was recovered by filtration, washed with EtOH, and then reused for a consecutive run under the same reaction conditions. The filtrate was concentrated under reduced pressure to give the crude product. The pure product (**3a–o**) was obtained by crystallization from ethanol.

Spectral Data for Selected Products

4,4′-(Phenylmethylene)bis(3-methyl-1-phenyl-pyrazol-5-ol) (3a). ^1H NMR (DMSO-d_6, 500 MHz): δ 2.30 (s, 6 H), 4.95 (s, 1 H), 7.17–7.27 (m, 1 H), 7.44 (t, 4 H, $J = 7.72$ Hz), 7.71 (d, 4 H, $J = 7.91$ Hz), 13.96 (brs, 2 H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.0, 33.5, 121.3, 126.4, 126.5, 127.7, 128.7, 129.5, 137.4, 142.5, 146.8 ppm; IR (KBr): υ 3430 (O–H) cm^{-1}; mp 168–170 °C; MS: m/z (%) = 436 (0.18), 262 (48), 174 (31).

4,4′-[(3-Nitrophenyl)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ol) (3b). ^1H NMR (DMSO-d_6, 400 MHz): δ 2.35 (s, 6 H), 5.14 (s, 1 H), 7.26 (t, 2 H, $J = 7.31$ Hz), 7.45 (t, 4 H, $J = 7.57$ Hz), 7.60 (t, 1 H, $J = 8.3$ Hz), 7.68–7.74 (m, 5 H), 8.06–8.10 (m, 2 H), 13.91 (brs, 2 H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 32.8, 120.6, 121.2, 121.7, 125.8, 125.8, 129.0, 129.7, 134.3, 137.4, 144.6, 146.3, 147.7 ppm; IR (KBr): 3420 (O–H) cm^{-1}; mp 151–153 °C; MS: m/z (%) = 307 (7.0), 174 (30.8).

4,4′-[(4-Bromophenyl)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ol) (3c). ^1H NMR (DMSO-d_6, 400 MHz): δ 2.32 (s, 6 H), 4.95 (s, 1 H), 7.19, 7.52 (d, 2 H, $J = 8.0$ Hz), 7.23–7.26 (m, 2 H), 7.42–7.48 (m, 6 H), 7.69 (d, 4 H, $J = 7.6$ Hz), 13.87 (brs, 2 H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 12.1, 33.0, 119.5, 121.0, 126.1, 129.34, 130.0, 131.4, 142.1, 146.7 ppm; mp 215 °C; MS: m/z (%) = 340 (10.5), 342 (10.5), 174 (29.5).

4,4′-[(4-Nitrophenyl)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ol) (3d). ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 2.35 (s, 6 H), 5.13 (s, 1 H), 7.25–7.27 (m, 2 H), 7.44 (t, 4 H, $J = 7.0$ Hz), 7.52 (d, 2 H, $J = 8.1$ Hz), 7.71 (d, 4 H, $J = 7.6$ Hz), 8.17 (d, 2 H, $J = 8.2$ Hz), 13.86 (brs, 2 H) ppm; ^{13}C NMR (DMSO-d$_6$, 125 MHz): δ 34.1, 56.9, 121.5, 124.2, 126.6, 129.5, 129.8, 146.8, 147.2, 151.2 ppm; IR (KBr): υ 3056 (O–H) cm^{-1}; mp 229–231 °C; MS: m/z (%) = 307 (9.2), 174 (18.3).

4,4′-[(4-Chlorophenyl)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ol) (3e). ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 2.32 (s, 6 H), 4.97 (s, 1 H), 7.26 (d, 4 H, $J = 8.2$ Hz), 7.34 (d, 2 H, $J = 8.0$ Hz), 7.44 (t, 4 H, $J = 7.1$ Hz), 7.71 (d, 4 H, $J = 7.6$ Hz), 12.40 (brs, 1 H), 13.87 (brs, 1 H) ppm; ^{13}C NMR (DMSO-d$_6$, 125 MHz): δ 33.4, 40.1, 121.4, 126.4, 128.9, 129.8, 130.0, 131.4, 142.0, 147.1 ppm; IR (KBr): υ 3044 (O−H) cm^{-1}; mp 212–214 °C; MS: m/z (%) = 296 (6.3), 174 (14.0).

4,4′-[(2-Chlorophenyl)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ol) (3f). ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 2.29 (s, 6 H), 5.14 (s, 1 H), 7.22–7.33 (m, 4 H), 7.40 (d, 1 H, $J = 7.8$ Hz), 7.44 (t, 4 H, $J = 7.6$ Hz), 7.70 (d, 4 H, $J = 7.6$ Hz), 7.80 (d, 1 H, $J = 7.1$ Hz), 13.92 (brs, 2 H) ppm; ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 32.4, 120.7, 123.6, 126.9, 128.0, 128.9, 129.4, 130.3, 135.9, 137.4, 140.6, 141.2 ppm; IR (KBr): υ 3450 (O−H) cm^{-1}; mp 235–237 °C; MS: m/z (%) = 296 (6.6), 185 (12.2).

4,4′-[(3-Methyl)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ol) (3g). ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ 2.25 (s, 3 H), 2.31 (s, 6 H), 4.91 (s, 1 H), 6.98 (d, 1 H, $J = 7.6$ Hz), 7.06 (s, 1 H), 7.07 (d, 1 H, $J = 6.8$ Hz), 7.16 (t, 1 H, $J = 7.2$ Hz),), 7.25 (t, 2 H, $J = 7.2$ Hz), 7.44 (t, 4 H, $J = 7.6$ Hz), 7.71 (d, 4 H, $J = 7.6$ Hz), 13.98 (brs, 2 H) ppm; ^{13}C NMR (DMSO-d$_6$, 100 MHz): δ 12.1, 21.7, 33.6, 121.0, 124.8, 126.0, 127.1, 128.2, 128.5, 129.4, 137.5, 142.7, 146.7 ppm; IR (KBr): υ 3023 (O−H) cm^{-1}; mp 193–194 °C; MS: m/z (%) = 276 (28.4), 174 (21.0).

4,4′-[(4-Methoxy)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ol) (3h). ^{1}H NMR (DMSO-d$_6$, 250 MHz): δ 2.12 (s, 6 H), 3.72 (s, 3 H), 4.73 (s, 1 H), 6.77 (d, 2 H, $J = 8.7$ Hz), 7.08–7.12 (m, 4 H), 7.21–7.28 (m, 4 H), 7.54 (d, 4 H, $J = 7.9$ Hz)) ppm; ^{13}C NMR (DMSO-d$_6$, 63 MHz): δ 11.6, 32.4, 54.9, 105.0, 113.5, 120.4, 125.4, 128.1, 128.9, 129.2, 134.6, 137.9, 146.1, 157.5 ppm; IR (KBr): υ 3060 (O−H) cm^{-1}; mp 176–177 °C; MS: m/z (%) = 466 (0.2, [M+]), 292 (100), 174 (32).

4,4′-[(4-Hydroxyphenyl)methylene]bis(3-methyl-1-phenyl-pyrazol-5-ol) (3i). ^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 2.31 (s, 6 H), 4.86 (s, 1 H), 6.67 (d, 2 H, $J = 8.0$), 7.06 (d, 2 H, $J = 8.5$ Hz), 7.24 (t, 2 H, $J = 7.0$ Hz), 7.44 (t, 4 H, $J = 8.0$ Hz),), 7.72 (d, 4 H, $J = 8.0$ Hz), 9.16 (brs, 1 H, OH), 12.40 (brs, 1 H, OH), 13.95 (brs, 1 H, OH) ppm ; ^{13}C NMR (DMSO-d$_6$, 125 MHz): δ 12.5, 33.2, 115.7, 121.4, 126.4, 128.9, 129.8, 133.2, 143.6, 147.0, 156.4 ppm; IR (KBr): υ 3420 (O−H) cm^{-1}; mp 150–151 °C; MS: m/z (%) = 296 (30.2), 174 (91.4).

4,4′-[(2-Hydroxyphenyl)methylene]bis(3-methyl-1-phenyl-pyrazol-5-ol) (3j). ^{1}H NMR (DMSO-d$_6$, 250 MHz): δ 2.28 (s, 6 H), 5.16 (s, 1 H), 6.66–6.75 (m, 2 H), 6.97 (t, 1 H, $J = 7.7$ Hz), 7.22 (t, 2 H, $J = 7.2$ Hz), 7.42 (t, 4 H, $J = 7.7$ Hz), 7.55 (d, 1 H, $J = 7.2$ Hz), 7.69 (d, 4 H, $J = 8.1$ Hz) ppm; ^{13}C NMR (DMSO-d$_6$, 63 MHz): δ 11.8, 27.3, 104.5, 114.9, 118.6, 120.6, 125.5, 126.9, 128.8, 128.9, 129.3, 137.5, 146.3, 153.9, 157.5 ppm; IR (KBr): υ 3064 (O–H) cm^{-1}; mp 230–231 °C; MS: *m*/*z* (%) = 452 (0.2, [M+]), 278 (5), 174 (34).

4,4′-[(2-Naphthyl)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ols) (3k). ^1H NMR (DMSO-d_6, 400 MHz): 2.49 (s, 6 H), 5.29 (s, 1 H), 7.35 (t, 2 H, *J* = 7.2 Hz), 7.42 (d, 1 H, *J* = 8.4 Hz), 7.45–7.48 (m, 2 H), 7.50 (t, 4 H, *J* = 7.6 Hz), 7.73 (d, 4 H, *J* = 7.6 Hz), 7.76 (s, 1 H), 7.84–7.88 (m, 3 H) ppm; ^{13}C NMR (DMSO-d_6, 100 MHz): δ 11.4, 33.1, 105.5, 122.3, 125.5, 126.1, 126.5, 126.7, 127.5, 127.8, 128.3, 128.4, 129.6, 132.2, 133.3, 135.9, 139.1, 146.5 ppm; IR (KBr): υ 3055 (O–H) cm^{-1}; mp 194 (dec.)°C. $C_{31}H_{26}N_4O_2$: calcd. C, 76.52; H, 5.39; N, 11.51. Found: C, 76.48; H, 5.39; N, 11.49.

4,4′-[(2-Thienyl)methylene] bis(3-methyl-1-phenyl-pyrazol-5-ol) (3 l). ^1H NMR (DMSO-d_6, 500 MHz): δ 2.38 (s, 6 H), 5.11 (s, 1 H), 6.90 (d, 2 H, *J* = 8.5 Hz), 7.09–7.48 (m, 7 H), 7.77–7.85 (m, 4 H), 13.56 (brs, 2 H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.5, 33.2, 121.3, 125.0, 125.1, 128.2, 128.6, 131.5, 131.9, 134.2, 139.8, 144.3, 154.9 ppm; IR (KBr): υ 3420 (O–H) cm^{-1}; mp 190–192 °C; MS: *m*/*z* (%) = 268 (100), 174 (71).

4,4′-[(2-Furyl)methylene]bis(3-methyl-1-phenyl-pyrazol-5-ol) (3 m). ^1H NMR (DMSO-d_6, 500 MHz): δ 2.27 (s, 6 H), 4.95 (s, 1 H), 6.09 (s, 1 H), 6.31 (s, 1 H), 7.20 (t, 2 H, *J* = 7.4 Hz), 7.39 (t, 4 H, *J* = 8.0 Hz), 7.47 (s, 1 H), 7.67 (d, 4 H, *J* = 8.0 Hz), (brs, 2 H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ 12.1, 28.8, 106.7, 110.9, 121.1, 126.2, 129.5, 142.1, 146.5, 154.7 ppm; IR (KBr): υ 3430 (O–H) cm^{-1}; mp 189–190 °C; MS: *m*/*z* (%) = 252 (100), 174 (64).

4,4′-[(*iso*-Propyl)methylene]bis(3-methyl-1-phenyl-pyrazol-5-ol) (3n). ^1H NMR (DMSO-d_6, 500 MHz): δ 0.84 (d, 6 H, *J* = 7.9 Hz), 2.21 (s, 6 H), 2.55–2.69 (m, 1 H), 7.40–7.48 (m, 4 H), 7.71–7.43 (m, 4 H), 11.93 (bs, 1 H), 13.64 (bs, 1 H) ppm; IR (KBr): υ 3428 (O–H) cm^{-1}; mp 210–212 °C; MS: *m*/*z* (%) = 228 (21), 174 (33), 77 (100).

4,4′-[(*N*-Buthyl)methylene]bis(3-methyl-1-phenyl-pyrazol-5-ol) (3o). ^1H NMR (DMSO-d_6, 400 MHz): δ 0.85 (t, 3 H, *J* = 7.2 Hz), 1.16–1.19 (m, 2 H), 1.27–1.32 (m, 2 H), 2.92 (s, 6 H), 2.50 (s, 1 H), 7.33 (t, 2 H, *J* = 7.2 Hz), 7.49 (t, 4 H, *J* = 8.0 Hz), 7.68 (d, 4 H, *J* = 8.0 Hz) ppm;^{13}C NMR (DMSO-d_6, 100 MHz): δ 10.9, 14.3, 22.4, 28.28, 30.0, 31.7, 106.4, 122.6, 127.9, 129.7, 135.0, 145.7, 158.6 ppm; IR (KBr): υ 3420 (O–H) cm^{-1}; mp 125–127 °C; MS: *m*/*z* (%) = 243 (23.3), 174 (100). $C_{25}H_{28}N_4O_2$: calcd. C, 72.09, H, 6.78, N, 13.45. Found: C, 72.12; H, 6.80; N, 13.40.

ACKNOWLEDGMENT

We are thankful to Birjand University Research Council and Persian Gulf University for their support.

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