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Synthesis of 4,4´-(arylmethylene)bis(3-carboxymethyl-1-phenyl-1*H*-pyrazol-5-ol)s using ionic liquid attached to colloidal silica nanoparticles in water

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An efficient synthesis of 10 4,4´-(arylmethylene)bis(3-carboxymethyl-1-phenyl-1*H*-pyrazol-5-ol)s, eight of which are novel, was achieved by a one-pot three-component reaction of phenylhydrazine, dimethyl acetylenedicarboxylate and an arylaldehyde using bis(1(3-methoxysilylpropyl)-3-methyl-imidazolium) copper tetrachloride tethered to colloidal silica nanoparticles as catalyst under microwave irradiation in water. The advantages of the present process are atom economy, high catalytic activity, excellent yields, short reaction times and utilisation of microwave heating as a clean procedure. The catalyst was recyclable.

Keywords: ionic liquid, colloidal silica nanoparticles, multi-component reaction, bispyrazoles

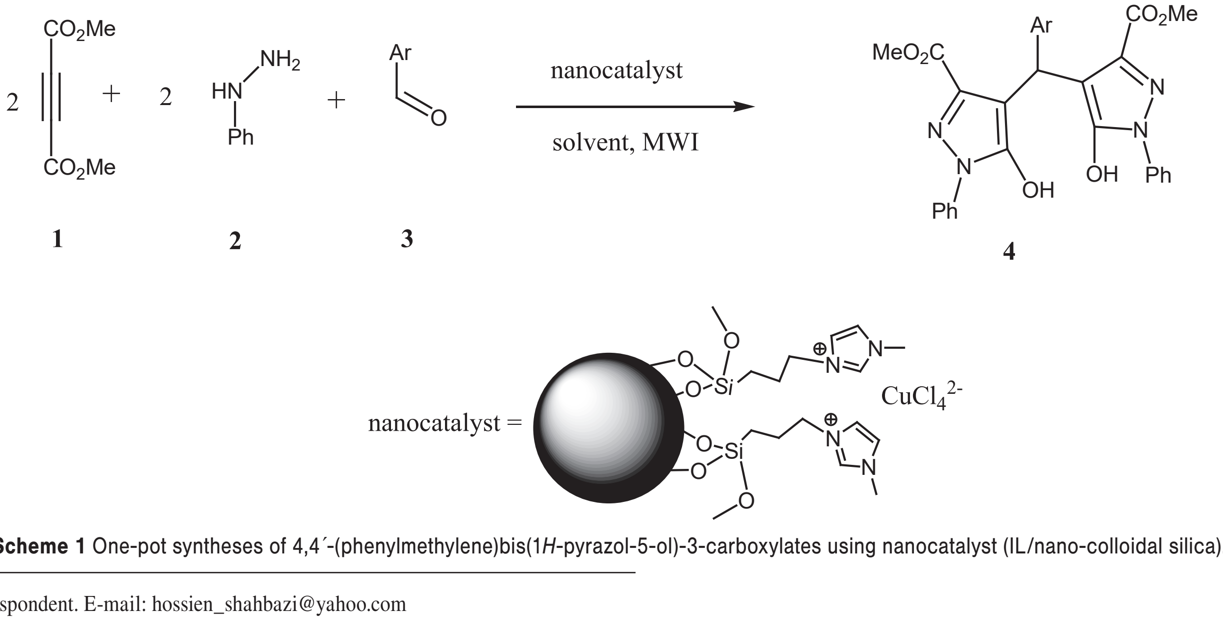
Introduction

Pyrazoles represent biological properties including anti-cancer,[1] antidepressants,[2] antiviral,[3] anti-inflammatory,[4] anti-malarial,[5] antibacterial,[6] and antiallergic,[7] activities. Efficient creation of complex molecules with chemical and biological importance is a challenging point and has gained substantial interest in recent years.[8,9]. A number of methods have been developed for the synthesis of 1-phenyl-1*H*-pyrazol-5-ols in the presence of diverse catalysts such as K_2CO_3,[10] silica-bonded S-sulfonic acid,[11] 1,3,5-tris(hydrogensulfato) benzene,[12] 1-sulfopyridinium chloride,[13] and acetic acid.[14] Some of the reported procedures endure drawbacks such as long reaction times, use of toxic and non-reusable catalyst and undesirable reaction conditions. Hence, to avoid these disadvantages, the finding of an effective method for the preparation of pyrazoles is still desirable. In recent years, synthesis and immobilisation of nanoparticles in ionic liquids (ILs) have been widely studied.[15,16] Ionic liquids can be considered as valuable key precursor compounds for catalysts.[17,18] The nature of cation–anion interactions in ambient temperature ionic liquids is an issue of increasing interest.[19,20] The structures of 1-ethyl-3-methylimidazolium (E_{mim}) and 1-butyl-3-methylimidazolium (B_{mim}) with transition metal chloride anions including $NiCl_4^{2-}$, $CoCl_4^{2-}$, and $PdCl_4^{2-}$ were investigated.[21-23] Here we report the use of bis(1-(3-methoxysilylpropyl)-3-methyl-imidazolium) copper tetrachloride ($CuCl_4^{2-}$) tethered to colloidal silica nanoparticles as an efficient catalyst for the synthesis of 4,4´-(arylmethylene) bis(3-carboxymethyl-1-phenyl-1*H*-pyrazol-5-ol)s.

Results and discussion

Our plan was to react dimethyl acetylenedicarboxylate **1** (2 equiv) and phenylhydrazine **2** (2 equiv.) with an arylaldehyde **3** (1 equiv.) under microwave irradiation in a solvent in the presence of a nanocatalyst (Scheme 1). We chose phenylhydrazine (2 mmol), dimethyl acetylenedicarboxylate (2 mmol) and 4-nitrobenzaldehyde **3** (Ar = 4-NO_2–C_6H_4) (1 mmol) as the standard substrates to search for the optimum reaction conditions. Various catalysts, solvents and microwave microwave (MW) conditions were evaluated and the results are shown in Table 1. Yields were determined for reaction in the presence of various catalysts such as oxides of Zn, Mg, Ni, Cu and Sn in water, MeCN, EtOH, or $CHCl_3$, but yields of 4,4′-(4-nitrophenylmethylene)bis(3-carboxymethyl-1-phenyl-1*H*-pyrazol-5-ol) **4** (Ar = 4-NO_2–C_6H_4) were moderate 19–43% (entries 1–7). $CoAl_2O_4$ NPs were a slight improvement at 55% (entry 8), but much improved yields were obtained using a nanocatalyst composed of the IL propyl-3-methyl-imidazolium chloride and $CuCl_4^{2-}$ tethered to colloidal silica nanoparticles (IL/nano-colloidal silica) (Scheme 1) (entries 9–15). Water was a better solvent than MeCN or EtOH (entries 8–10), and the best yield of 96% was obtained using a loading of 14 mg of IL/nano-colloidal silica (not improved using 16 mg) and a MW power of 400 W (entry 12). Thus we had established the optimum conditions.

Using these optimised conditions, we examined the scope of this multicomponent reaction by using various easily available



Scheme 1 One-pot syntheses of 4,4´-(phenylmethylene)bis(1*H*-pyrazol-5-ol)-3-carboxylates using nanocatalyst (IL/nano-colloidal silica).

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Table 1 Optimisation of the reaction conditions (catalyst, catalyst loading, solvent, duration of reaction) for the synthesis of 4,4´-(4-nitrophenylmethylene)bis(3-carboxymethyl-1-phenyl-1*H*-pyrazol-5-ol) 4 (Ar = 4-NO$_2$–C$_6$H$_4$) from dimethyl acetylenedicarboxylate **1**, phenyl hydrazine **2**, and 4-nitrobenzaldehyde **3** (Ar = 4-NO$_2$–C$_6$H$_4$) (Scheme 1)[a]

Entry	Conditions	Catalyst	Time (min)	Yield[b] (%)
1	CHCl$_3$ (300 W)	ZnO (3 mol%)	100	19
2	EtOH (400 W)	MgO (4 mol%)	50	35
3	H$_2$O (600 W)	NiO (3 mol%)	65	44
4	EtOH (500 W)	CuO (4 mol%)	45	31
5	H$_2$O (500 W)	SnO (3 mol%)	55	34
6	H$_2$O (400 W)	ZnO (3 mol%)	45	55
7	CH$_3$CN (400 W)	ZnO (3 mol%)	45	43
8	H$_2$O (400 W)	CoAl$_2$O$_4$ NPs (3 mol%)	40	55
9	CH$_3$CN (300 W)	IL/nano-colloidal silica (16 mg)	15	60
10	EtOH (400 W)	IL/nano-colloidal silica (16 mg)	15	73
11	H$_2$O (300 W)	IL/nano-colloidal silica (14 mg)	10	87
12	H$_2$O (400 W)	IL/nano-colloidal silica (14 mg)	10	96
13	H$_2$O (500 W)	IL/nano-colloidal silica (14 mg)	10	94
14	H$_2$O (400 W)	IL/nano-colloidal silica (12 mg)	10	89
15	H$_2$O (400 W)	IL/nano-colloidal silica (16 mg)	10	96

[a]Reaction conditions: a mixture of dimethyl acetylenedicarboxylate **1** (2 mmol), phenyl hydrazine **2** (2 mmol), 4-nitrobenzaldehyde **3** (Ar = 4-NO$_2$–C$_6$H$_4$) (1 mmol) and a catalyst in a solvent (15 mL) was irradiated (MW) for various times and at various wattages.

[b]Isolated yield.

aldehydes and the results are shown in Table 2. Aldehydes containing electron-withdrawing groups generally gave yields of the corresponding bispyrazole **4** of 87–96% in 10 min (entries 1–3, 6, 8, 9), but those with electron-donating groups gave slightly lower yields 82–84% in a longer reaction time of 15 min (entries 4, 7, 10). Two of the compounds prepared **4a**,**b** were known, but eight **4c**–**j** were novel.

We also considered reusability of the IL/nano-colloidal silica as catalyst under microwave irradiation in water for the synthesis of product **4a** and it was found that product yields reduced to a small extent on each reuse (runs 1–5: 96, 96, 95, 95, 94%). After completion of the reaction (TLC), ethyl acetate was added. The catalyst was insoluble in ethyl acetate and it could therefore be recycled by an easy filtration. The solvent was evaporated and the solid obtained recrystallised from ethanol to afford the pyrazoles. The recovered IL/nano-colloidal silica was washed four to six times with ethanol and dried at room temperature for 14 h.

In conclusion, we have described an efficient and one-pot synthesis of 4,4′-(phenylmethylene)bis(1*H*-pyrazol-5-ol)-3-carboxylates by the three-component reaction of phenylhydrazine, acetylenedicarboxylates, and aromatic aldehydes in the presence of bis (1(3-methoxysilylpropyl)-3-methyl-imidazolium) copper tetrachloride tethered to colloidal silica nanoparticles under microwave irradiation in water. The advantages offered by this method include short reaction times, utilising microwave as a clean procedure, high atom economy, excellent yields, use of non toxic organic solvent, and the employment of a cost-effective catalyst.

Experimental

Reagent grade chemicals were purchased from Sigma-Aldrich or Merck and were used without further purification. The products were isolated and characterised by physical and spectral data. NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer (^{1}H NMR at 400 Hz, ^{13}C NMR at 100 Hz) in CDCl$_3$ or DMSO-d_6 using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) are given in Hz. The IR spectra were recorded on FT-IR Magna 550 apparatus using with KBr plates. Melting points were determined on Electro thermal 9200, and are not corrected. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyser. We used the Milestone microwave (Microwave Labstation, MLS GmbH- ATC-FO 300) for synthesis.

Table 2 Yields of a series of 4,4´-(arylmethylene)bis(3-carboxymethyl-1-phenyl-1*H*-pyrazol-5-ol)s **4** (Ar = various) prepared from dimethyl acetylenedicarboxylate 1, phenyl hydrazine **2**, and an araldehyde **3** (Ar = various) using IL/nano-colloidal silica under microwave irradiation in water (Scheme 1)[a]

Entry	Aldehyde (Ar)	Product	Time (min)	Yield[b] (%)	M. p. (°C)	M.p. (°C) [ref.]
1	4-NO$_2$–C$_6$H$_4$	**4a**	10	96	215–216	216–217 [14]
2	4-Cl–C$_6$H$_4$	**4b**	10	94	223–225	226–228 [14]
3	2-3-Cl–C$_6$H$_3$	**4c**	10	90	204–205	–
4	2-Me–C$_6$H$_4$	**4d**	15	84	186–187	–
5	C$_6$H$_5$	**4e**	10	88	285–286	–
6	2-Cl–C$_6$H$_4$	**4f**	10	87	267–269	–
7	4-Me–C$_6$H$_4$	**4g**	15	82	192–194	–
8	3-NO$_2$–C$_6$H$_4$	**4h**	10	92	248–250	–
9	2-Br–C$_6$H$_4$	**4i**	10	90	230–232	–
10	4-OMe–C$_6$H$_4$	**4j**	15	82	217–219	–

[a] Reaction conditions: a mixture of dimethyl acetylenedicarboxylate **1** (2 mmol), phenyl hydrazine **2** (2 mmol), an araldehyde **3** (Ar = various) (1 mmol) and IL/nano-colloidal silica (14 mg) in water (15 mL) was heated for periods of 10–15 min under microwave irradiation (400 W).

[b]Isolated yield.

Synthesis of ionic liquid/nano-colloidal silica

In a typical procedure, based on a reported method,[24,25] colloidal silica nanoparticles (LUDOX SM colloidal silica 30 wt% suspension in H$_2$O) (0.098 mL) were diluted in deionised water (3 mL), and 1-(3-trimethoxysilylpropyl)-3-methyl-imidazolium chloride (IL) (1.8 mmol) was added slowly with continuous stirring during one hour. Then, CuCl$_2$.2H$_2$O (0.15 g) was added and the mixture refluxed for 24 h. IL functionalised silica nanoparticles were separated by centrifugation and washed with acetone and methanol four times and dried by lyophilisation/freeze-drying. The purity of the resultant IL/Cu^{2+}/SiO$_2$ was confirmed using ^{1}H NMR spectroscopy. The Cu loading (4.7 wt%) was measured using XRF.

*Synthesis of 4,4′-(phenylmethylene)bis(1*H*-pyrazol-5-ol)3-carboxylates; general procedure*

A mixture of dimethyl acetylenedicarboxylate (2 mmol) phenylhydrazine (2 mmol), arylaldehydes (1 mmol) and bis (1(3-methoxysilylpropyl)-3-methyl imidazolium) copper tetrachloride tethered to silica nanoparticles (nanocatalyst) (14 mg) in 15 mL of water were added and the mixture was irradiated in microwave oven at 50°C and 400 W. After completion of the reaction (TLC), ethyl acetate was added. The catalyst was insoluble in ethyl acetate and it could therefore be recycled by an easy filtration. The solvent was evaporated and the solid obtained recrystallised from ethanol to afford the pyrazoles.

Physical and spectroscopic data

*Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(4-nitrophenyl)methyl) -5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4a**): Golden powder; m.p. 215–216 °C; IR (KBr): ν = 3432, 3073, 2954, 1731, 1600, 1515, 1443, 1344, 1213, 1113, 842 cm^{-1} ; ^{1}H NMR (DMSO-d_6): δ (ppm) = 3.85 (s, 6H, 2OCH$_3$), 4.83 (2OH exchanged with water of DMSO-d_6), 6.92 (s, 1H, CH), 7.29-7.43 (t, *J* = 7.6 Hz, 6H, ArH), 7.52 (d, *J* = 8Hz, 2H, ArH), 7.77–7.86 (m, 4H, ArH), 8.14 (d, *J* = 7.6 Hz, 2H, ArH); ^{13}C NMR (DMSO-d_6): δ (ppm) = 31.2, 51.4, 107.3, 122.2, 125.3, 127.6, 128.0, 129.9, 130.5, 137.3, 139.7, 142.2, 159.5, 165.3; Anal. calcd for C$_{29}$H$_{23}$N$_5$O$_8$: C, 61.16; H, 4.07; N, 12.30; found: C, 61.10; H, 4.12; N, 12.43%.

*Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(4-chlorophenyl) methyl)-5-hydroxy-1-phenyl-1*H*-pyrazole-3- carboxylate* (**4b**): White powder; m.p. 223–225 °C; IR (KBr): ν = 3429, 3068, 2952, 1718, 1599, 1492 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ (ppm) = 3.94 (s, 6H, 2OCH$_3$), 6.17 (s, 1H, CH), 7.23 (m, 2H, ArH), 7.26 (m, 2H, ArH), 7.35 (m, 2H, ArH), 7.46 (m, 4H, ArH), 7.84 (m, 4H, ArH), 10.59 (2OH); ^{13}C NMR (DMSO-d_6): δ (ppm) = 32.2, 52.3, 106.3, 123.2, 124.3, 127.6, 128.1, 129.9, 133.5, 138.3, 139.7, 144.2, 159.4, 164.9; Anal. calcd for $C_{29}H_{23}ClN_4O_6$: C, 62.31; H, 4.15; N, 10.02; found: C, 62.22; H, 4.25; N, 9.87%.

*Methyl4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(2,3-dichloro phenyl) methyl)-5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4c**): White powder; m.p. 204–205 °C; IR (KBr): ν = 3443, 2925, 1725, 1593, 1499, 1208, 1112 cm^{-1}; ^{1}HNMR (DMSO-d_6): δ (ppm) = 3.76 (s, 6H, 2OCH$_3$), 4.65 (2OH exchanged with water of DMSO-d_6), 6.73 (s, 1H, CH), 7.12-7.75 (m, 13 H, ArH); ^{13}CNMR (DMSO-d_6): δ (ppm) = 31.1, 52.0, 105.2, 122.4, 122.6, 126.8, 127.0, 129.1, 129.2, 129.5, 131.5, 131.9, 133.8, 138.3, 157.2, 162.8; Anal. calcd for $C_{29}H_{22}Cl_2N_4O_6$: C, 58.70; H, 3.74; N, 9.44; found: C, 58.63; H, 3.80; N, 9.51%.

*Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(2-methyl phenyl) methyl)-5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4d**): Green powder; m.p. 186–187 °C; IR (KBr): ν = 3429, 3027, 2954, 1722, 1600, 1494, 1122, 863, 762 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ (ppm) = 2.20 (s, 3H, CH$_3$), 3.88 (s, 6H, 2OCH$_3$), 4.86 (2OH exchanged with water of DMSO-d_6), 6.75 (s, 1H, CH), 6.93-7.76 (m,14H, ArH); ^{13}CNMR (DMSO-d_6): δ (ppm) = 31.0, 31.9, 52.3, 107.9, 122.8, 123.3, 124.8, 126.9, 127.4, 128.3, 128.4, 129.3, 137.4, 137.5, 138.5, 142.6, 162.4; Anal. calcd for $C_{30}H_{26}N_4O_6$: C, 66.91; H, 4.87; N, 10.40; found: C 66.98, H, 4.96; N 10.32%.

*Methyl 4- ((3- (methoxycarbonyl) -5- hydroxy-1- phenyl-1*H *-pyrazol-4-yl)(phenyl)methyl)-5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4e**): Brown powder; m.p. 285–286°C; IR (KBr): ν = 3427, 2954, 1707, 1599, 1575, 759, 697 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ (ppm) 3.36 (s, 6H, 2OCH$_3$), 3.78 (2OH, exchanged with water of DMSO-d_6), 6.67 (s, CH, 1H), 7.08-7.93 (m, 15H, ArH); ^{13}C NMR (DMSO-d_6): δ (ppm) = 32.2, 51.4, 105.3, 121.2, 125.3, 125.6, 128.0, 128.9, 130.5, 137.3, 139.7, 140.2, 158.5, 164.3; Anal. calcd for $C_{29}H_{24}N_4O_6$: C, 66.41; H, 4.61; N, 10.68; found: C, 66.46; H, 4.72; N, 10.58%.

*Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(2-chlorophenyl) methyl)-5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4f**): White powder; m.p. 267–269 °C; IR (KBr): ν = 3420, 2957, 1723, 1595, 1552, 1207, 1131, 765 cm^{-1}; ^{1}HNMR (DMSO-d_6): δ (ppm) = 3.75 (s, 6H, 2OCH$_3$), 4.65 (2OH exchanged with water of DMSO-d_6), 7.362 (s, 1H, CH), 7.512 (m, 6H, ArH), 7.770 (m, 8H, ArH); ^{13}C NMR (DMSO-d_6): δ (ppm) = 31.1, 51.6, 102.0, 122.5, 122.8, 127.3, 127.8, 129.3, 129.5, 131.4, 131.9, 133.2, 138.7, 141.0, 151.9, 162.9; Anal. calcd for $C_{29}H_{23}ClN_4O_6$: C, 62.31; H, 4.15; N, 10.02; found: C, 62.25; H, 4.08; N, 10.08%.

*Methyl 4-((3-(methoxycarbonyl) -5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(4-methylphenyl) methyl)-5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4g**): Green powder; m.p. 192–194 °C; IR (KBr): ν = 3432, 3063, 2952, 1729, 1602, 1506, 1447, 1207, 1122 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ (ppm) = 2.17 (s, 3H, CH$_3$), 3.74 (s, 6H, 2OCH$_3$), 4.35 (2OH exchanged with water of DMSO-d_6), 6.68 (s, 1H, CH), 6.75-7.76 (m, 14H, ArH); ^{13}C NMR (DMSO-d_6): δ (ppm) = 29.3, 31.5, 51.6, 113.8, 122.8, 123.3, 124.8, 125.6, 126.9, 127.4, 128.4, 129.3, 138.5, 142.6, 162.4; Anal. calcd for $C_{30}H_{26}N_4O_6$: C, 66.91; H, 4.87; N, 10.40; found: C, 66.97; H, 4.95; N, 10.34%.

*Methyl4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(3-nitrophenyl)methyl)-5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4h**): White powder; m.p. 248–250 °C; IR (KBr): ν = 3423, 2949, 1720, 1590, 1555, 1320, 1207, 1131 cm^{-1}; ^{1}HNMR (DMSO-d_6): δ (ppm) = 3.78 (s, 6H, 2OCH$_3$), 4.64 (2OH exchanged with water of DMSO-d_6), 7.42 (s, 1H, CH), 7.515 (m, 6H, ArH), 7.784 (m, 8H, ArH); ^{13}C NMR(DMSO-d_6): δ (ppm) = 32.1, 52.6, 105.0, 123.5, 123.8, 127.3, 128.8, 129.3, 129.5, 132.4, 133.9, 134.2, 139.6, 141.2, 151.9, 165.0; Anal. calcd for $C_{29}H_{23}N_5O_8$: C, 61.16; H, 4.07; N, 12.30; found: C, 61.03; H, 3.95; N, 12.14%.

*Methyl4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(2-bromophenyl) methyl) -5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4i**): White powder; m.p. 230–232 °C; IR (KBr): ν = 3424, 2955, 1720, 1594, 1554, 1206, 1132, 764 cm^{-1}; ^{1}HNMR (DMSO-d_6): δ (ppm) = 3.77 (s, 6H, 2OCH$_3$), 4.64 (2OH exchanged with water of DMSO-d_6), 7.365 (s, 1H, CH), 7.522 (m, 6H, ArH), 7.740 (m, 8H, ArH); ^{13}C NMR(DMSO-d_6): δ (ppm) = 31.2, 52.6, 104.1, 122.1, 122.9, 128.3, 128.8, 129.4, 130.5, 131.4, 131.9, 134.2, 137.7, 142.1, 153.9, 158.9; Anal. calcd for $C_{29}H_{23}BrN_4O_6$: C, 57.72; H, 3.84; N, 9.28; found: C, 57.58; H, 3.73; N, 9.15%.

*Methyl 4-((3-(methoxycarbonyl)-5-hydroxy-1-phenyl-1*H*-pyrazol-4-yl)(4-methoxyphenyl) methyl)-5-hydroxy-1-phenyl-1*H*-pyrazole-3-carboxylate* (**4j**): Green powder; m.p. 217–219 °C; IR (KBr): ν = 3429, 3052, 2950, 1727, 1600, 1508, 1444, 1206, 1125 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ (ppm) = 3.70 (s, 6H, 2OCH$_3$), 3.92 (s, 3H, OCH$_3$) 4.38 (2OH exchanged with water of DMSO-d_6), 6.702 (s, 1H, CH), 6.755-7.865 (m, 14H, ArH); ^{13}C NMR (DMSO-d_6): δ (ppm) = 31.4, 51.6, 54.3, 109.8, 121.8, 124.3, 124.8, 125.3, 126.5, 127.4, 128.5, 129.7, 138.5, 142.6, 162.4; Anal. calcd for $C_{30}H_{26}N_4O_7$: C, 64.98; H, 4.73; N, 10.10; found: C, 64.78; H, 4.65; N, 10.02%.

Electronic Supplementary Information

Some characteristics of the nanocatalyst are described in the ESI available through: http://ingentaconnect.com/content/stl/jcr/2017/00000041/00000008

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