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Supplementary Materials

Hercynite Silica Sulfuric Acid: A Novel Inorganic Sulfurous Solid Acid Catalyst for One-Pot Cascade Organic Transformations

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Abstract

Herein, we delignated the synthesis of a novel inorganic sulfurous magnetic solid acid catalyst by the immobilization of extremely high content of sulfuric acid functionalities on the amorphous silica-modified Hercynite nanomagnetic core-shell via a simple method. Silica sulfuric acid (SSA) modified Hercynite nanocomposite (Hercynite@SSA) combines excellent recoverability and stability characteristics of Hercynite (which can be regarded as a ferro spinel with Fd3m space group and cubic crystal structure) with the strong Brønsted acid properties of $–SO_3H$ groups. This nanomagnetic solid acid was found to be an efficient and facile strong solid acid catalyst for the synthesis of bis (pyrazolyl) methanes via two different one-pot multicomponent methodologies under green conditions. The Hercynite@SSA catalyst shows excellent catalytic activity and reusability in the ethanolic medium among different solid acid materials. A plausible reaction mechanism is proposed for this synthesis.

Keywords: Inorganic Bronsted Acid; Hercynite@SSA; Heterogeneous catalyst; Solid acid catalyst, Bis (pyrazolyl) methanes;

Experimental Section

2. Experimental Section

Supplementary Materials

Materials and methods

Chemicals such as $FeCl_2.4H_2O$, $Al(NO_3)_2.9H_2O$, NaOH, tetraethyl orthosilicate (TEOS), chlorosulfonic acid, phenylhydrazine, ethyl acetoacetat, 3-methyl,1-phenyl-H1-pyrazole-5-ol, aldehydes, PEG-400, ethanol, dichloromethane, acetonitrile, methanol, dimethylformamide, acetonitrile and dimethyl sulfoxide were purchased from Merck and Aldrich chemical companies and used as received. The products were characterized by comparison of their spectral data, TLC and physical data.

Typical Procedure for Hercynite@SSA Preparation

A convenient and inexpensive stepwise procedure was used to prepare Hercynite silica sulfuric acid magnetic nanocomposite. In the first step, Hercynite MNPs were prepared via the typical co-precipitation method, as reported by our group [43]. Afterward, the surface of Hercynite was modified using a silica shell according to the Stöber method [44]. Subsequently, 1 g of the obtained Hercynite@SiO_2 MNPs was dispersed in 50 mL of dry dichloromethane by sonication for 30 min. Thereafter, the solution was stirred in an ice bath for one hour and, then, 1.5 mL of chlorosulfuric acid reagent was added dropwise and stirred for 4 h at room temperature to ensure the complete consumption of the surface hydroxyl groups and assist the sulfuric acid immobilization. After completion of the reaction (when the release of HCL gas from the reaction vessel was stopped), The reaction mixture was separated using magnetic decantation and, then, washed thrice with dry dichloromethane. The obtained Hercynite@SSA MNPs were then dried at room temperature (Scheme 1).

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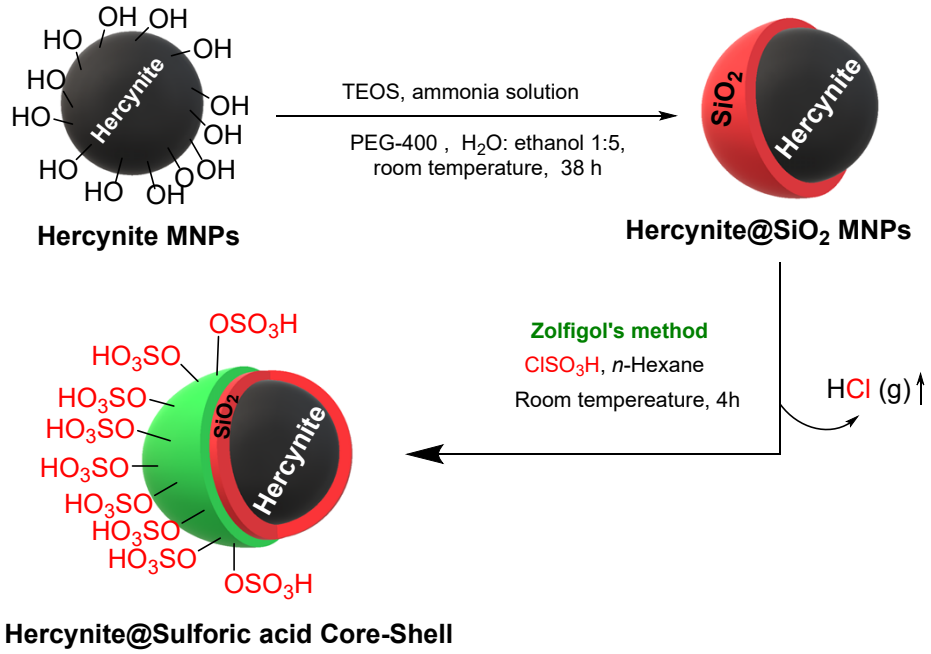

Scheme 1. Stepwise synthesis of Hercynite@SSA.

General Procedures for the Synthesis of bis (pyrazolyl) methanes

In a general reaction, 15 mg of Hercynite@SSA catalyst was added to a 5 ml ethanol solution of aryl aldehydes (1 mmol) and i) commercial 3-methyl,1-phenyl-H1-pyrazole-5-ol (2 mmol) (Pseudo-three-component, scheme 2a) or ii) synthetic mixture of phenylhydrazine (2 mmol) ethyl acetoacetate (2 mmol) (Pseudo-five-component, scheme2b) in 10 mL round bottom flask and, then, the resulting solution was stirred for the appropriate time at reflux conditions (80 °C). After completion of the reaction (probed by TLC), the Hercynite@SSA MNPs were separated from the boiling mixture using magnetic decantation. The precipitated bis(pyrazolyl) methanes were purified by recrystallization in ethanol thrice (Scheme 4). The isolated pure products, known in the literature, were authenticated by their corresponding melting points and also the performed ^{1}H-NMR spectroscopies.

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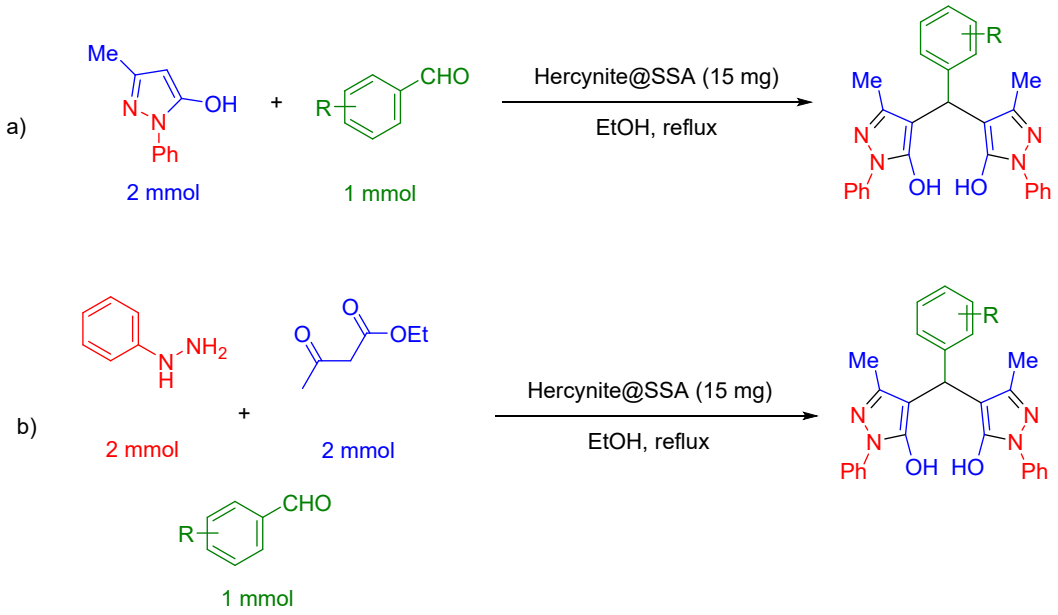
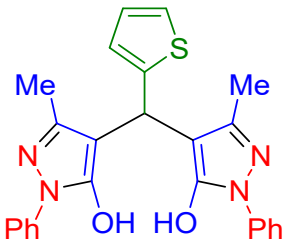


Scheme 2. The a) pseudo-three-component and b) pseudo-five-component synthesis of bis (pyrazolyl)methanes catalyzed by Hercynite@SSA.

Selected Spectral data

4,4´-(Thiophen-2-ylmethylene)bis(3-methyl-1-phenyl-1Hpyrazol-5-ol):



^{1}H NMR (400 MHz, DMSO-d_6) δ 14.01 (s, 1H), 12.51 (s, 1H), 7.71 (d, J = 8.0 Hz, 4H), 7.45 (t, J = 7.8 Hz, 4H), 7.31 – 7.23 (m, 3H), 6.91 (dd, J = 5.1, 3.5 Hz, 1H), 6.78 – 6.73 (m, 1H), 5.14 (s, 1H), 2.32 (s, 6H) ppm.

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

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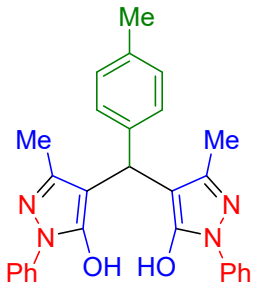
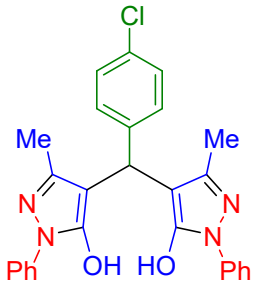


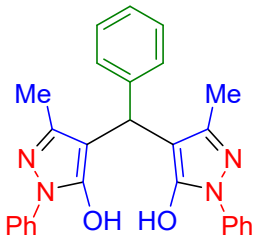
^{1}H NMR (400 MHz, DMSO-d_6) δ 13.94 (s, 1H), 12.44 (s, 1H), 7.71 (d, J = 7.9 Hz, 4H), 7.45 (t, J = 7.8 Hz, 4H), 7.25 (t, J = 7.6 Hz, 2H), 7.15 – 7.07 (m, 4H), 4.92 (s, 1H), 2.32 (s, 6H), 2.25 (s, 3H).

4,4'-(4-chlorophenylmethylene)-bis-(3-methyl-1-phenyl-1H-pyrazol-5-ol):



^{1}H NMR (400 MHz, DMSO-d_6) δ 13.89 (s, 1H), 12.53 (s, 1H), 7.70 (s, 4H), 7.45 (s, 4H), 7.34 (s, 2H), 7.26 (s, 4H), 4.98 (s, 1H), 2.33 (s, 6H).

4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-pyrazol-5-ol):



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^{1}H NMR (400 MHz, DMSO-d_6) δ 13.94 (s, 1H), 12.42 (s, 1H), 7.71 (d, J = 8.0 Hz, 4H), 7.44 (t, J = 7.8 Hz, 4H), 7.25 (t, J = 7.6 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 8.2 Hz, 3H), 4.90 (s, 1H), 2.31 (s, 6H).

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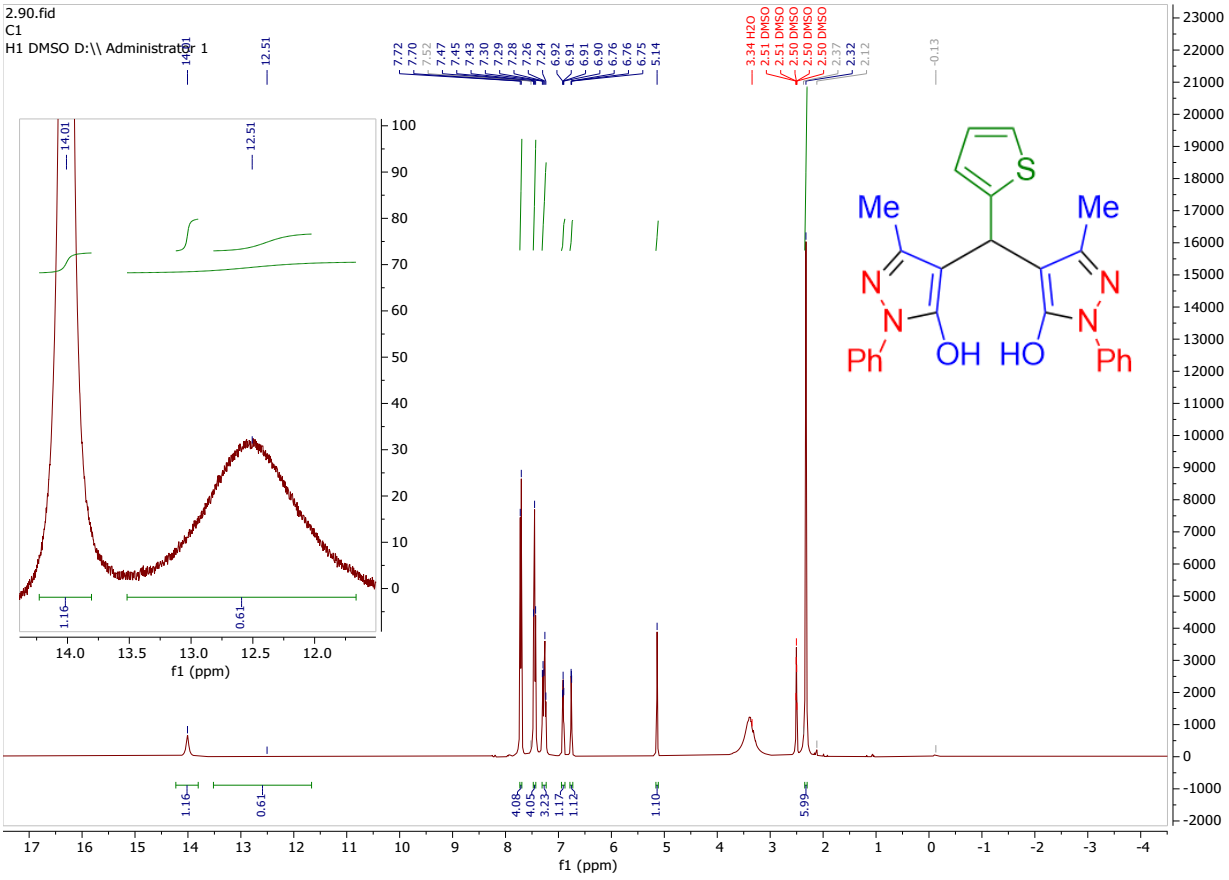

S.1. *^{1}H NMR of 4,4′-(Thiophen-2-ylmethylene)bis(3-methyl-1-phenyl-1Hpyrazol-5-ol).*

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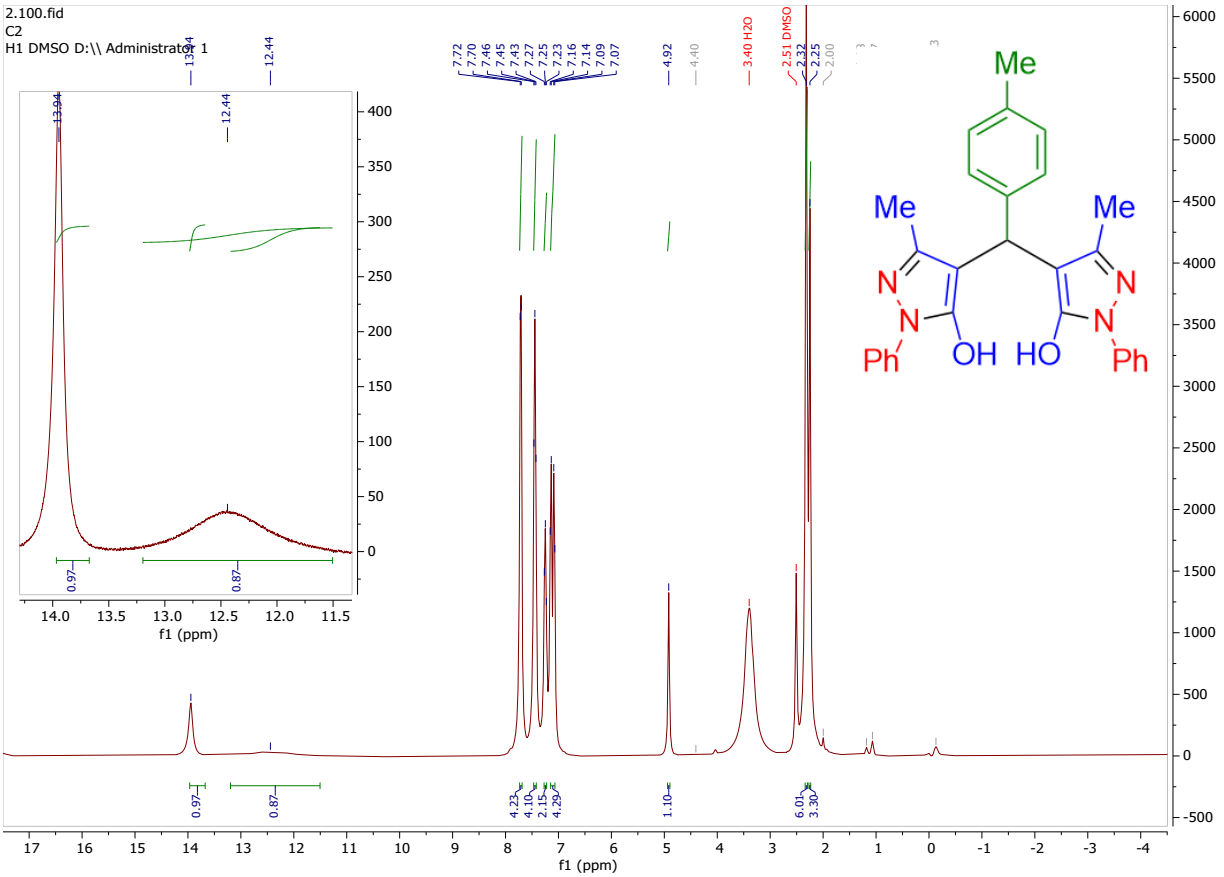

S.2. *^{1}H NMR of 4,4'-((4-methylphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol).*

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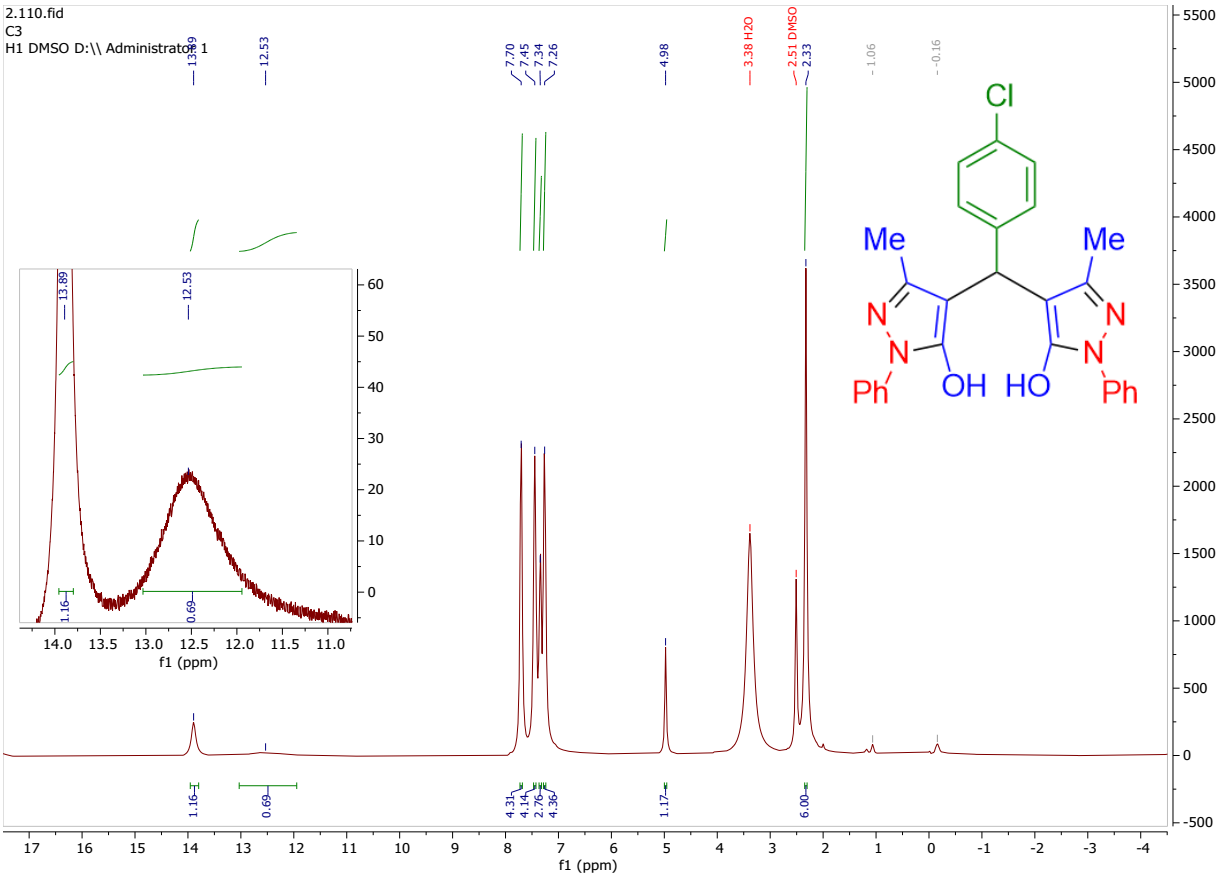

S.3. *^{1}H NMR of* 4,4'-(4-chlorophenylmethylene)-bis-(3-methyl-1-phenyl-1H-pyrazol-5-ol):

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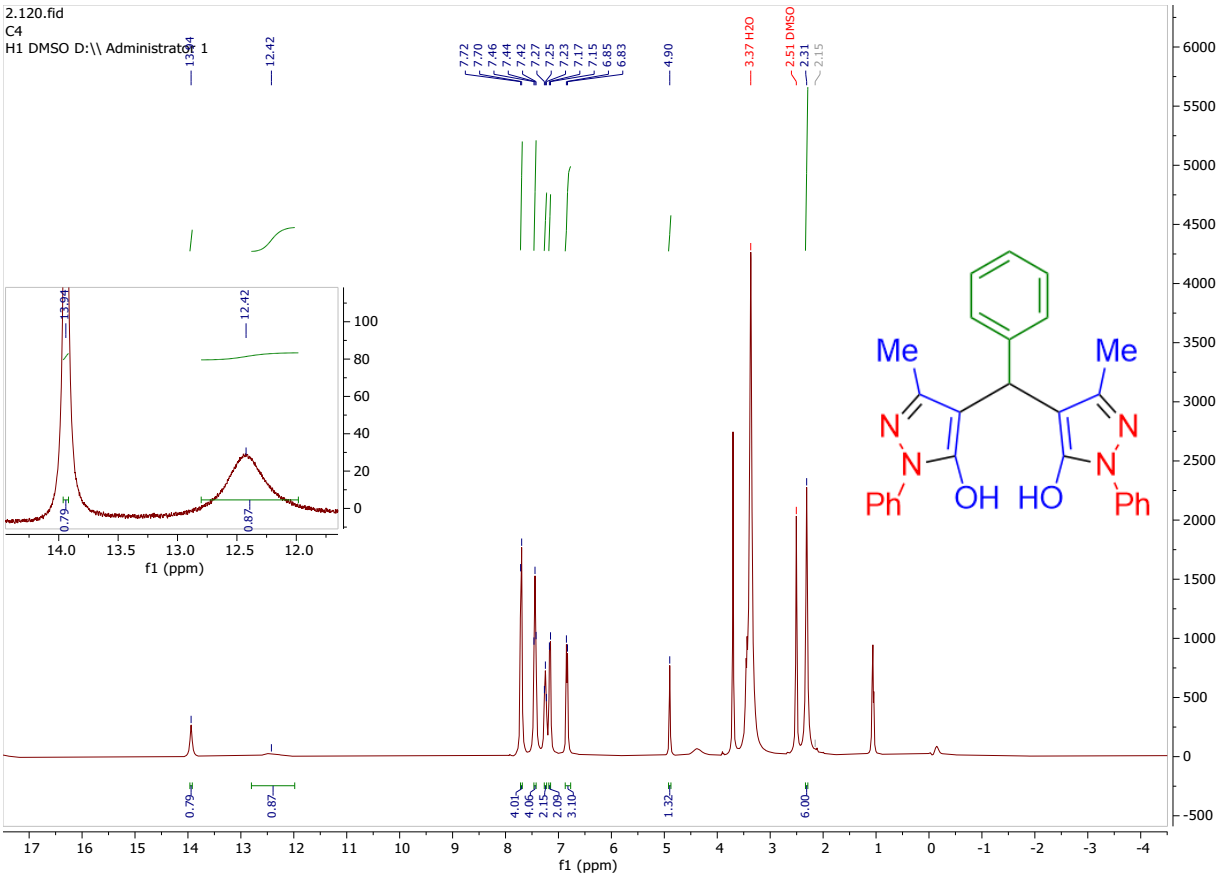

S.4. *[1]H NMR of 4,4'-(phenylmethylene)bis(3-methyl-1-phenyl-pyrazol-5-ol):*