

**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(1*H*-pyrazol-5-ol), coumarin-3-carboxylic acid and cinnamic acid derivatives under mild and green conditions**

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## Supplementary data:

**Fig. S1.** The IR spectrum of 2-carbamoylhydrazine-1-sulfonic acid as a novel nano structure organocatalyst (a) and semicarbazide hydrochloride (b).

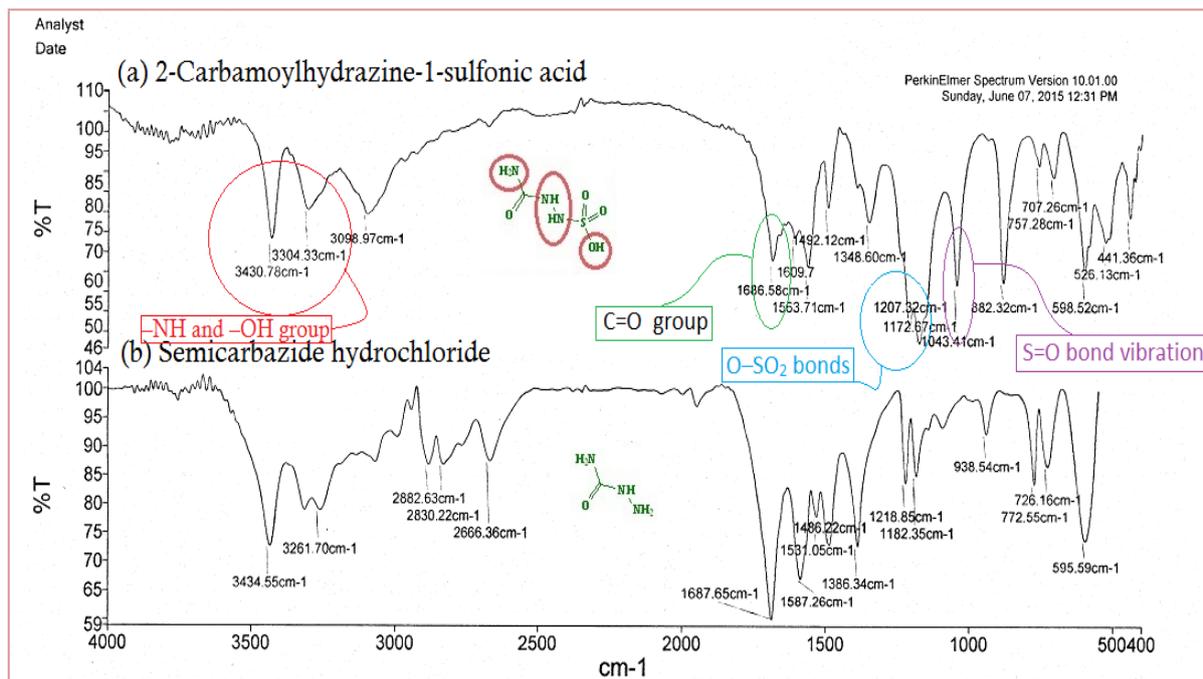
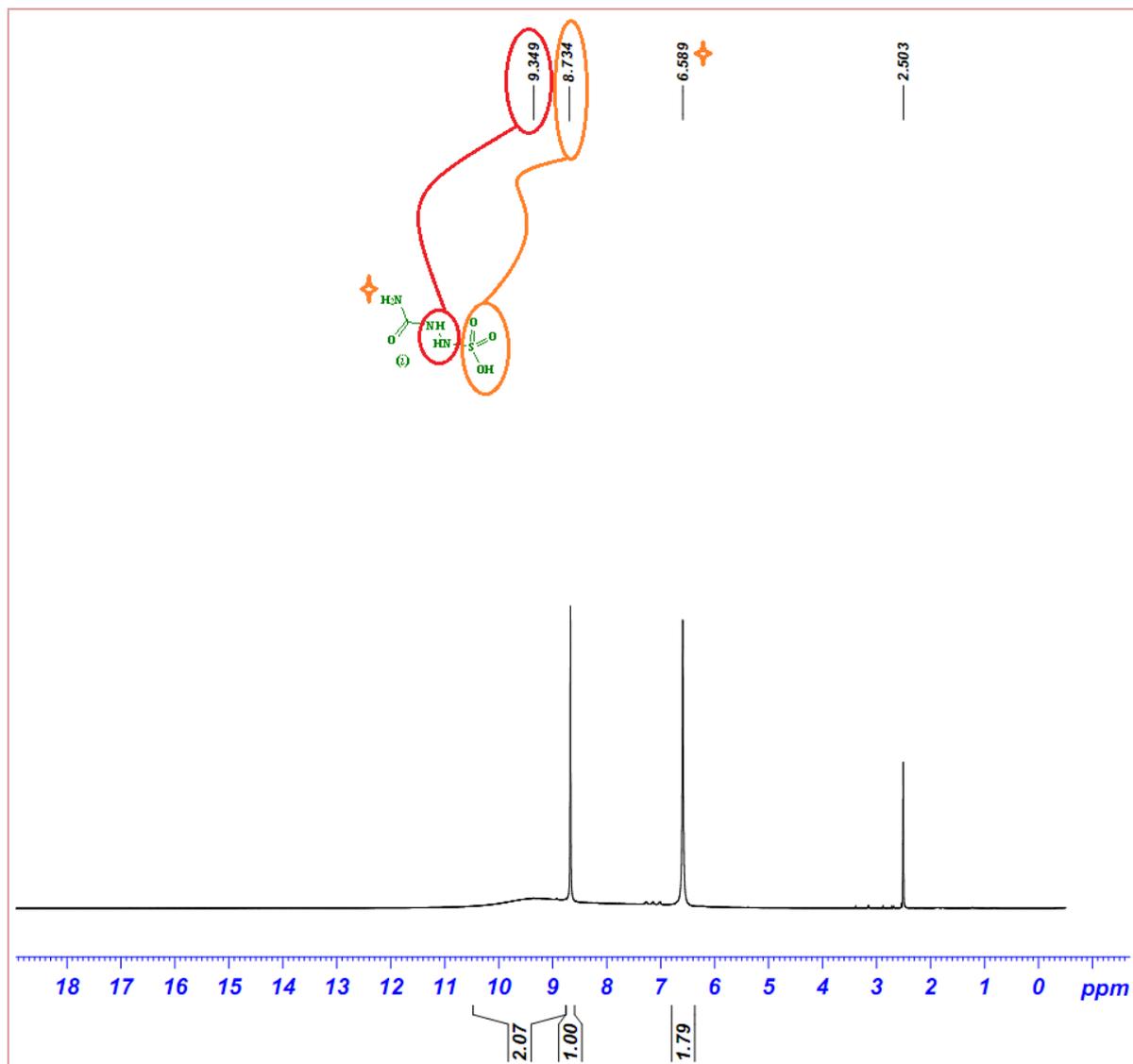
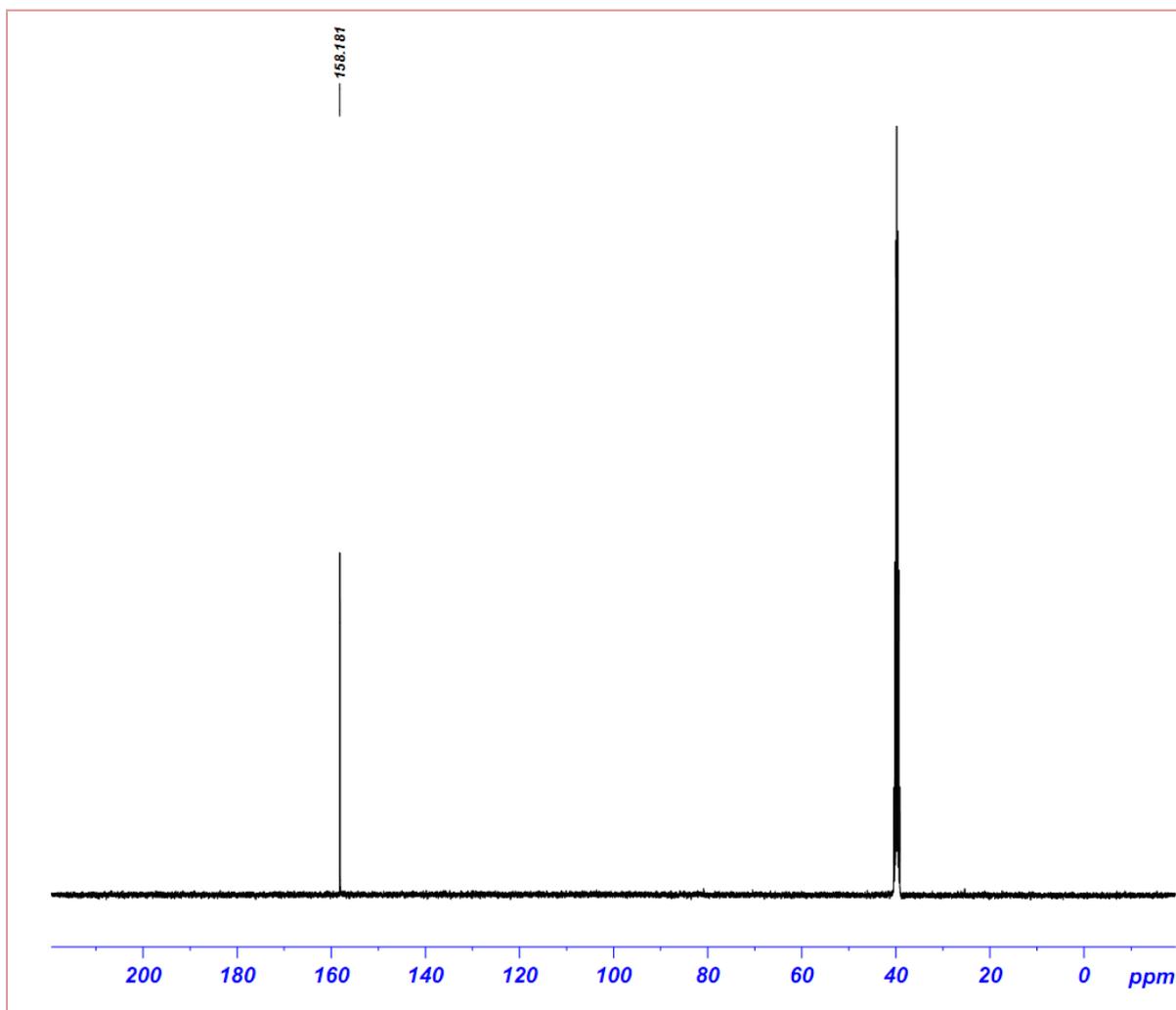


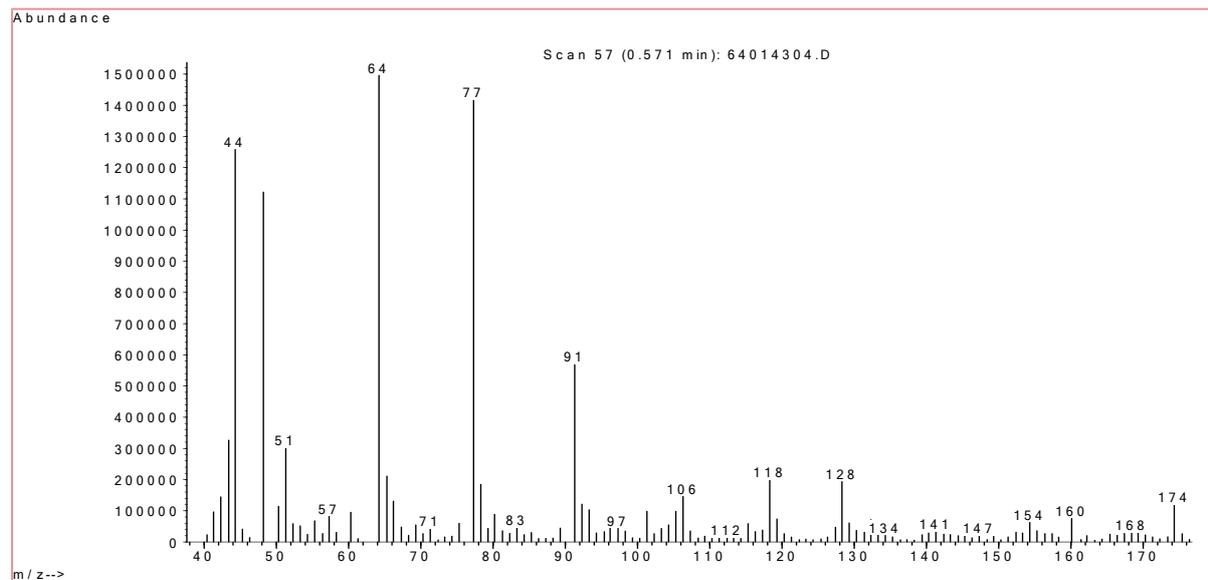
Fig. S2. The  $^1\text{H}$  NMR spectrum of the 2-carbamoylhydrazine-1-sulfonic acid as a novel nano structure organocatalyst.



**Fig. S3.** The  $^{13}\text{C}$  NMR spectrum of the 2-carbamoylhydrazine-1-sulfonic acid as a novel nano structure organocatalyst.



**Fig. S4.** The mass spectrum of the 2-carbamoylhydrazine-1-sulfonic acid as a novel nano structure organocatalyst.



**Fig. S5.** The UV/Vis spectra of 2-carbamoylhydrazine-1-sulfonic acid as organocatalyst (a), reaction mixture (b), 1-phenyl-3-methylpyrazol-5-one (c) and 4-chlorobenzaldehyde (d) at room temperature.

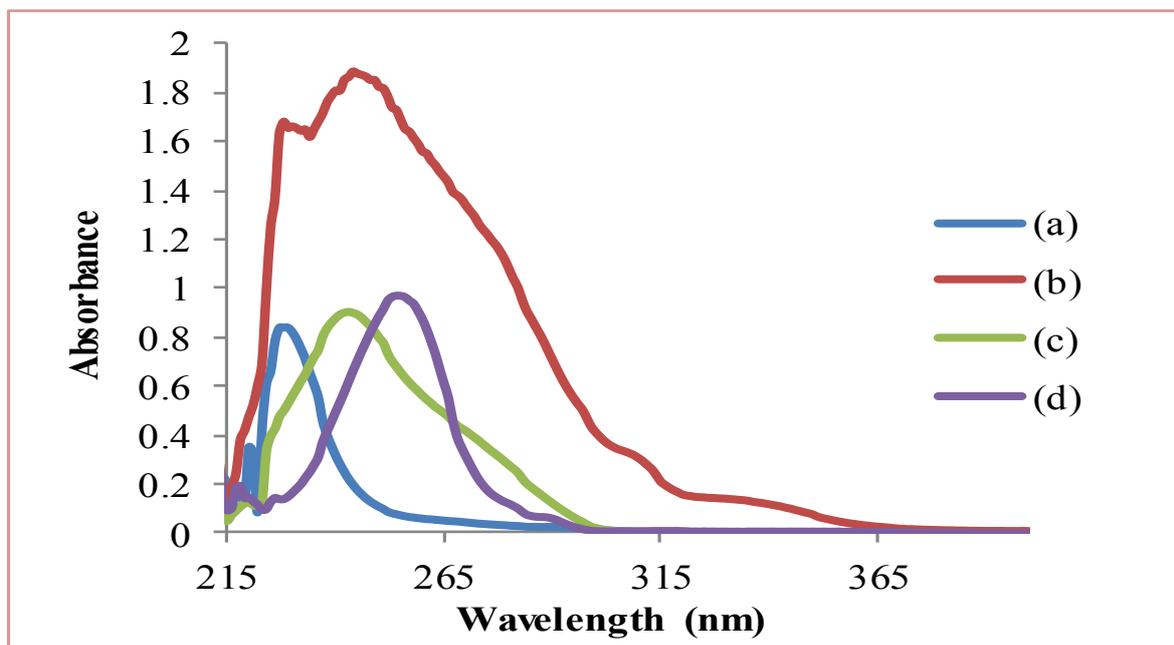


Fig. S6. The IR spectrum of carbamoylsulfamic acid as a novel nano structure organocatalyst (a) and urea (b).

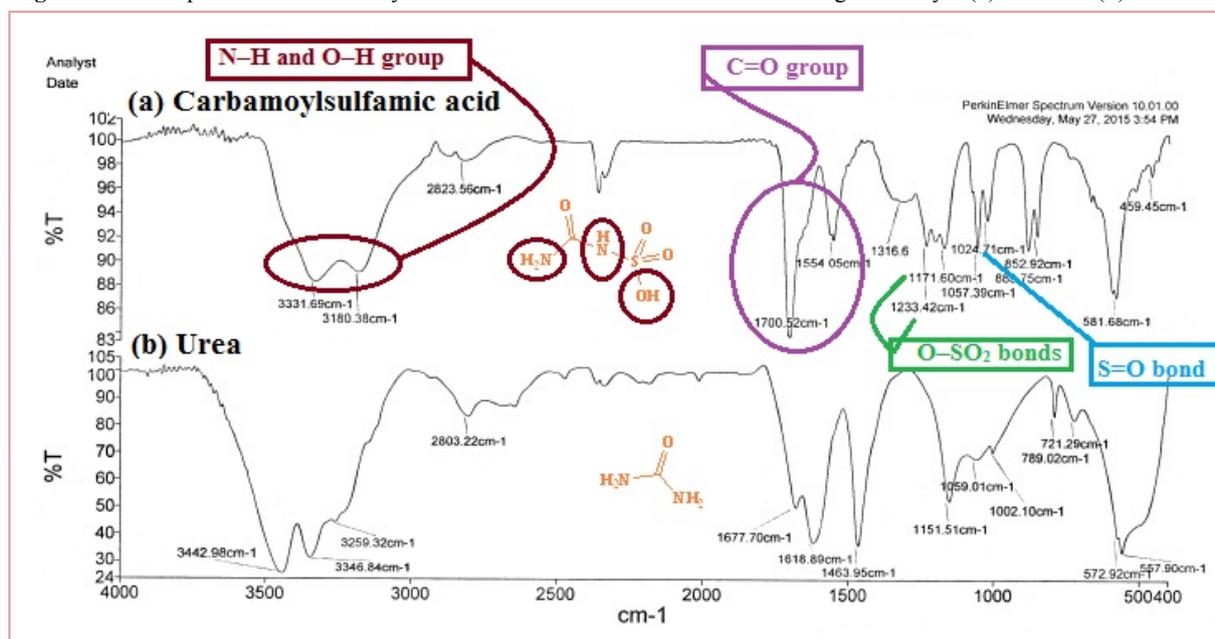
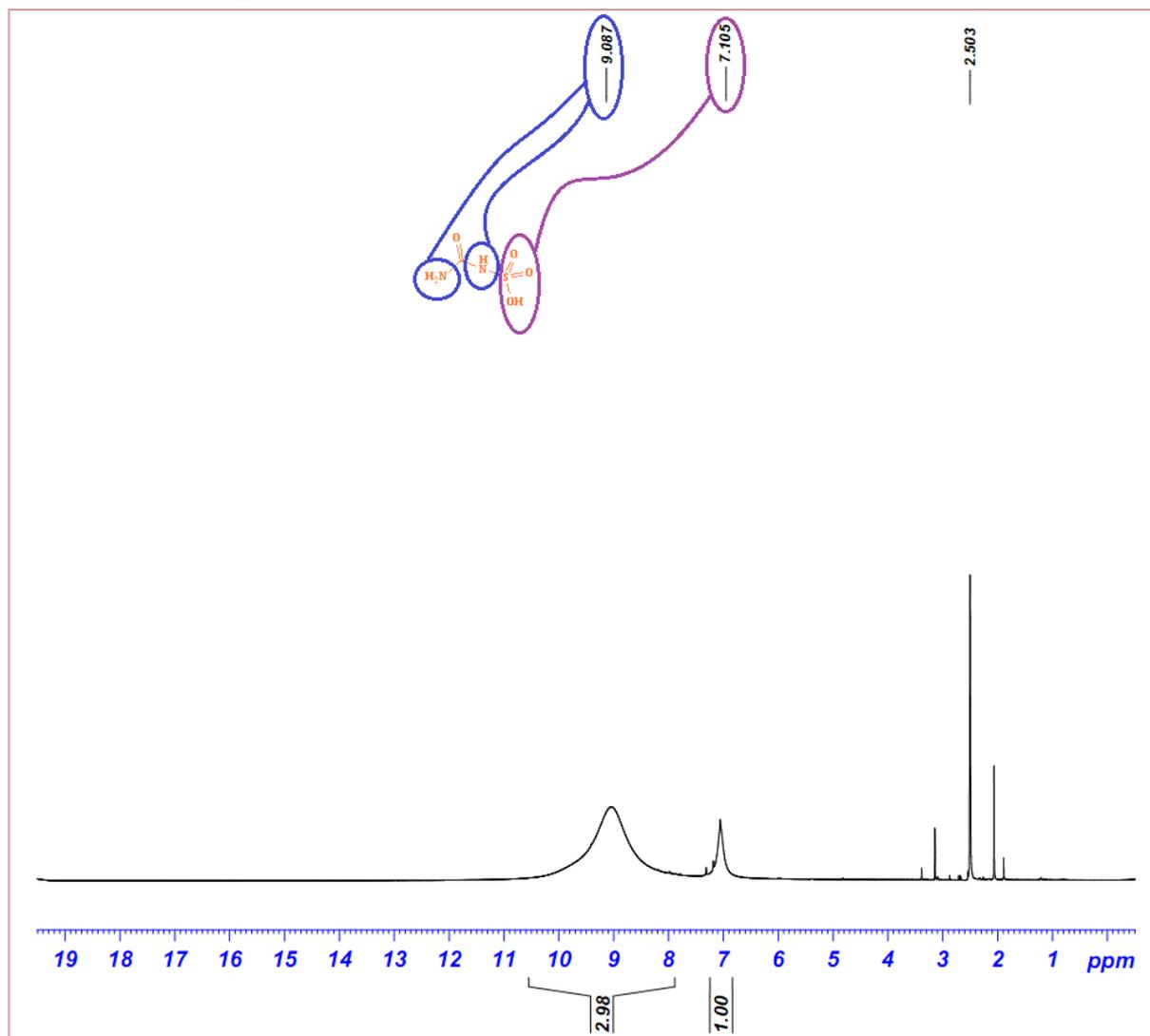
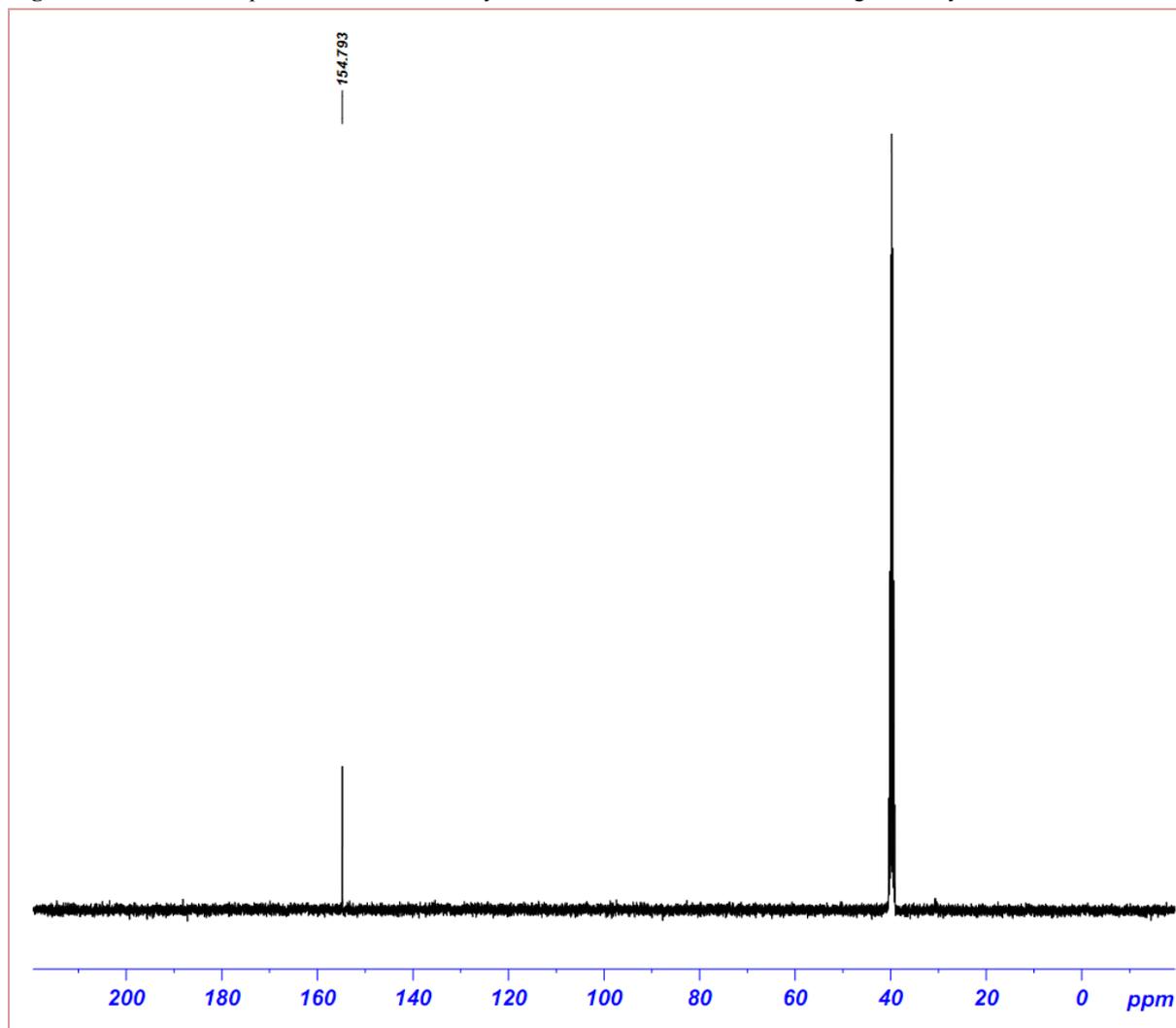


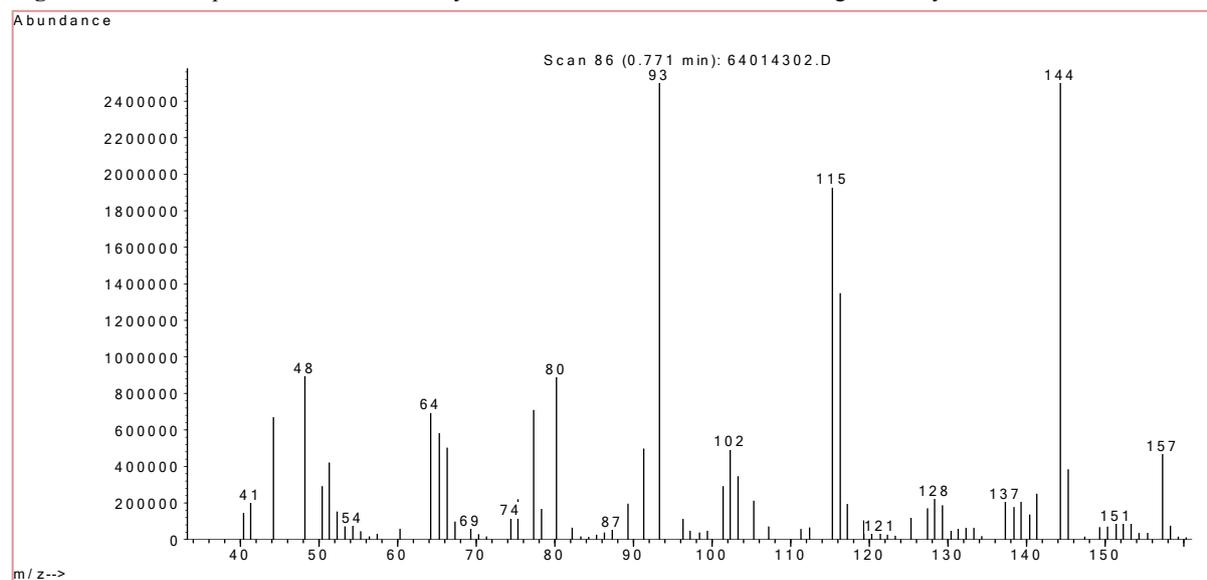
Fig. S7. The  $^1\text{H}$  NMR spectrum of the carbamoylsulfamic acid as a nano structure organocatalyst.



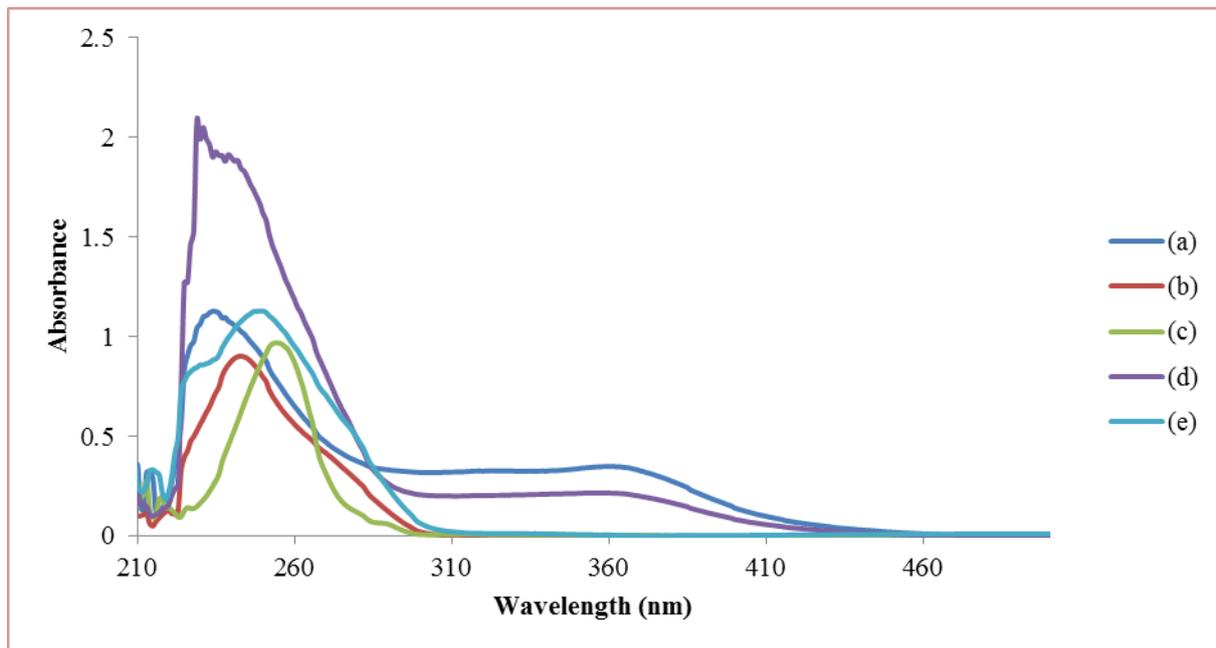
**Fig. S8.** The  $^{13}\text{C}$  NMR spectrum of the carbamoylsulfamic acid as a nano structure organocatalyst.



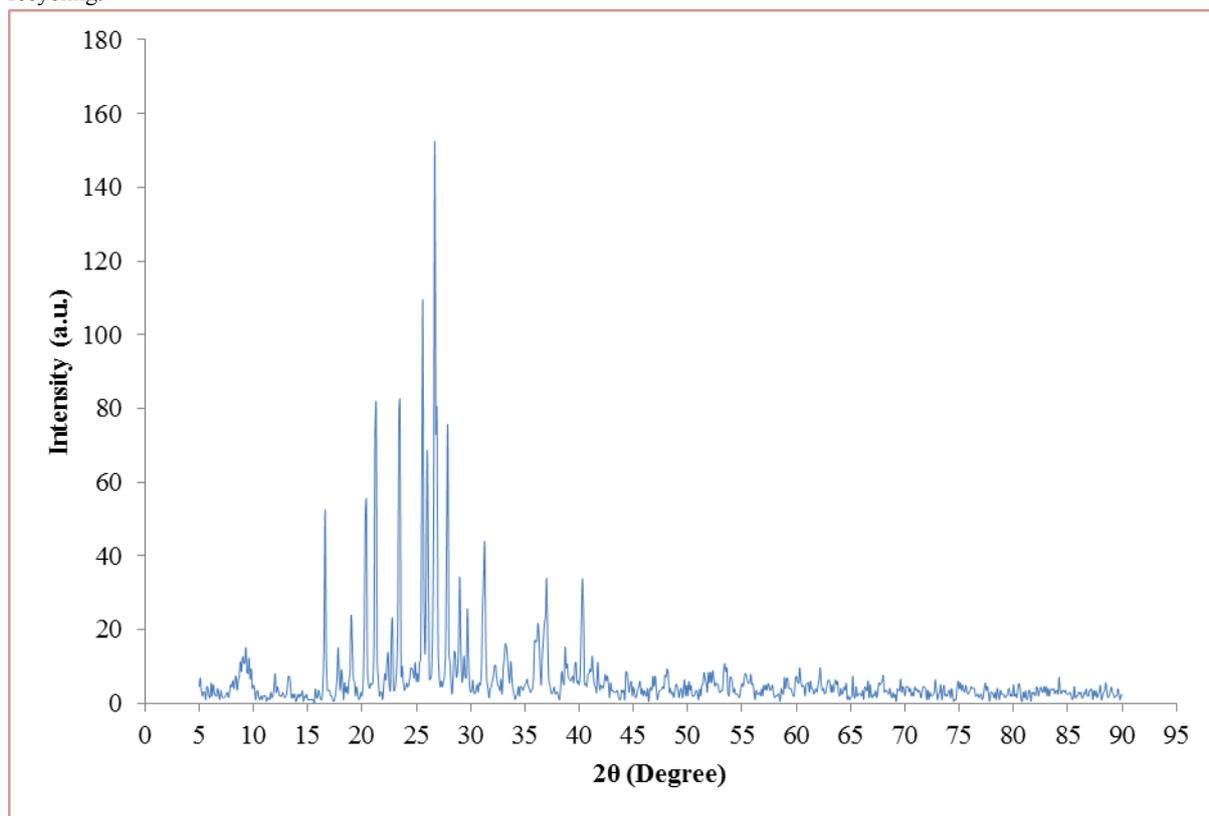
**Fig. S9.** The mass spectrum of the carbamoylsulfamic acid as a nano structure organocatalyst.



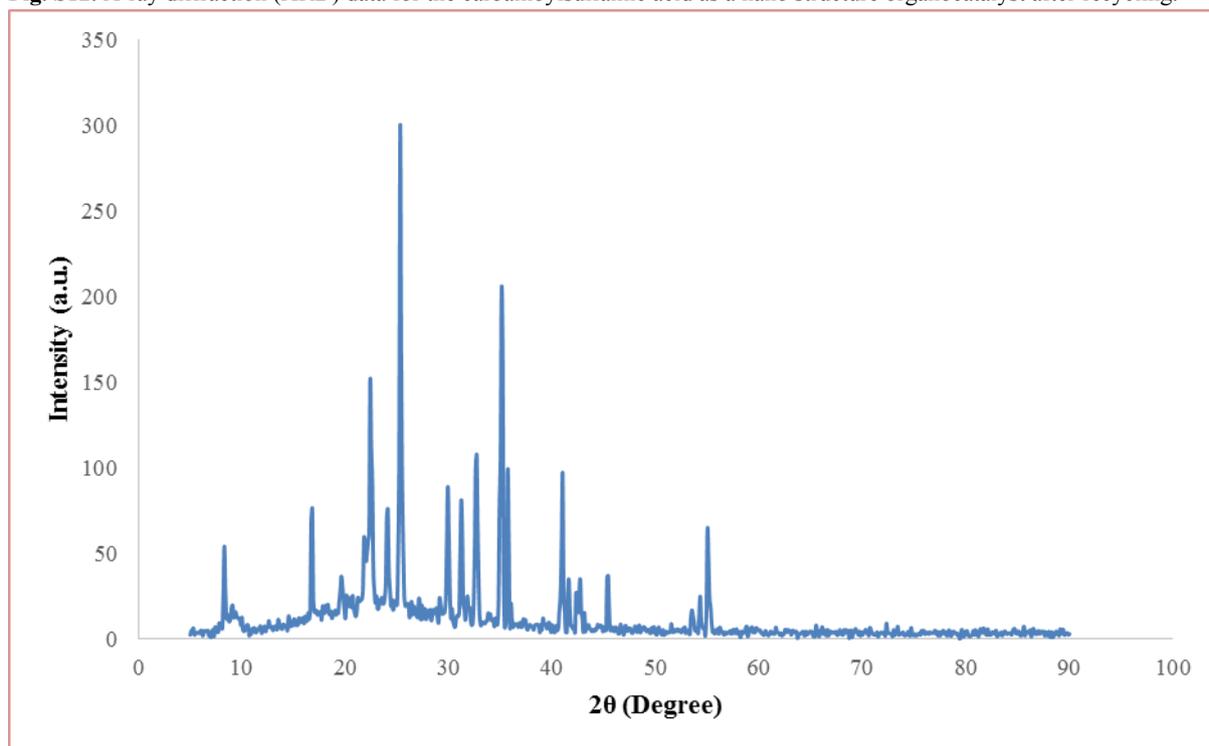
**Fig. S10.** The UV/Vis spectra of carbamoylsulfamic acid as organocatalyst (a), 1-phenyl-3-methylpyrazol-5-one (b), 4-chlorobenzaldehyde (c), reaction mixture (d) and product (e) at room temperature.



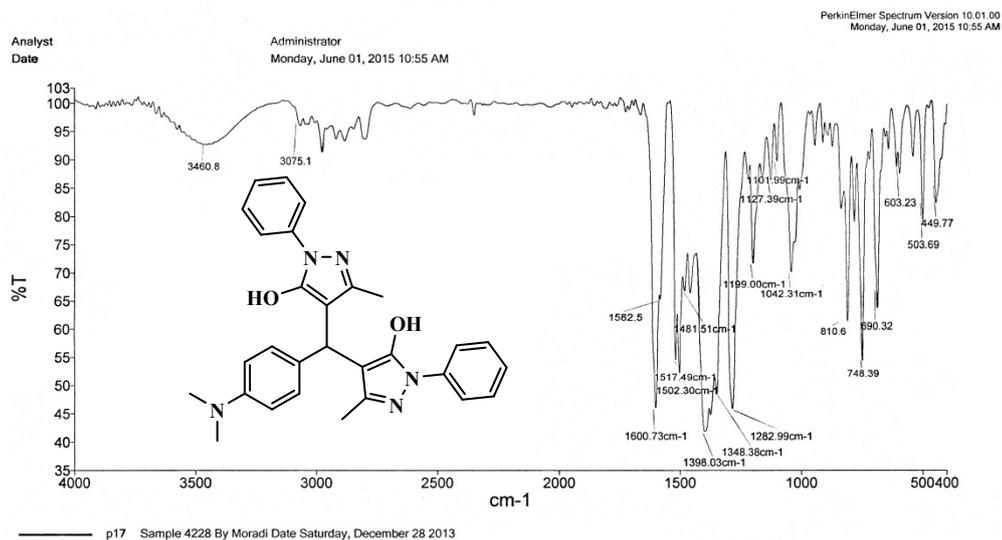
**Fig. S11.** X-ray diffraction (XRD) data for the 2-carbamoylhydrazine-1-sulfonic acid as a nano structure organocatalyst after recycling.



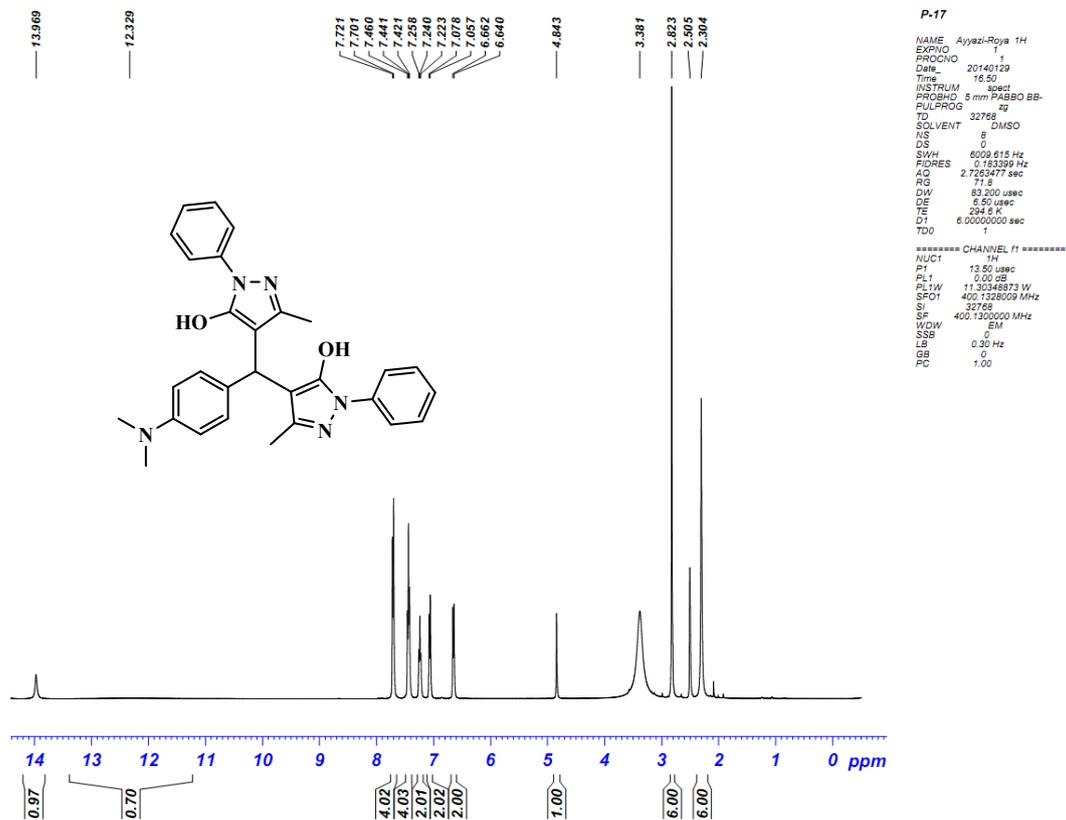
**Fig. S12.** X-ray diffraction (XRD) data for the carbamoylsulfamic acid as a nano structure organocatalyst after recycling.



**Fig. S13.** The IR spectrum of 4-((4-(dimethylamino)phenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 1).

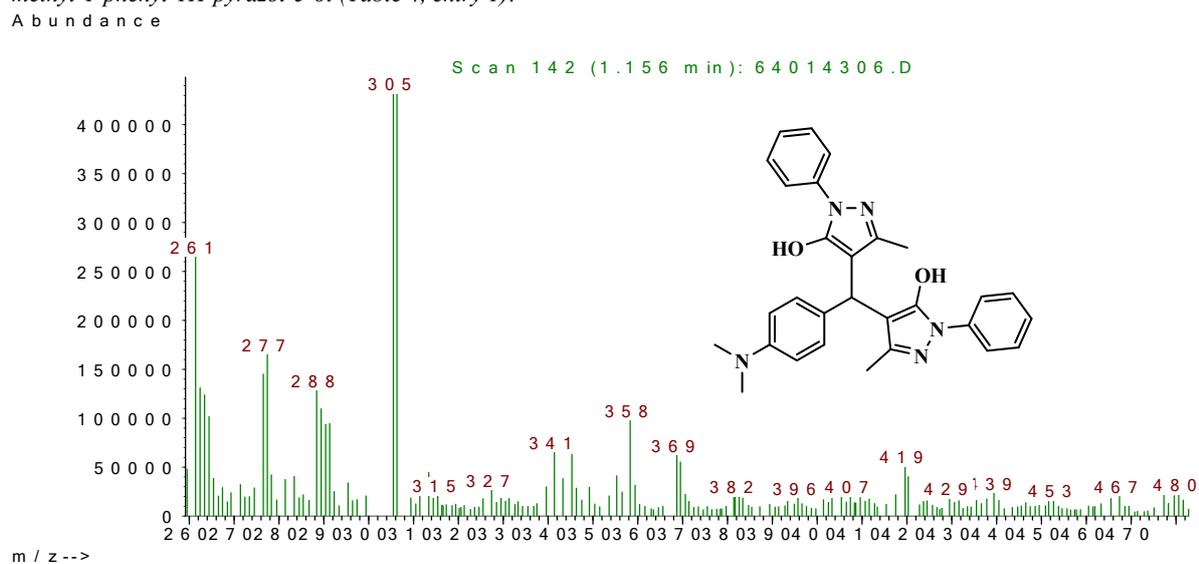


**Fig. S14.** The  $^1\text{H}$  NMR spectrum of 4-((4-(dimethylamino)phenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 1).

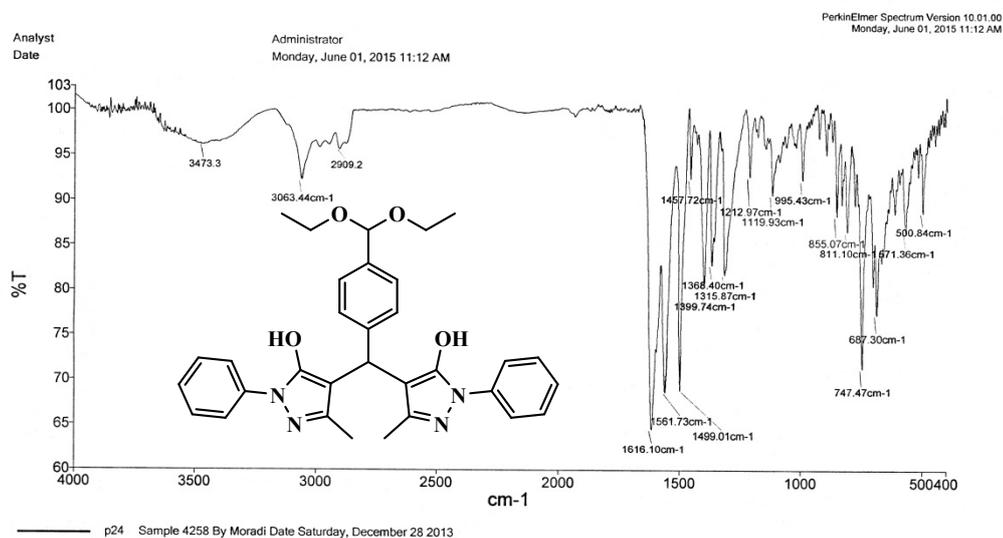




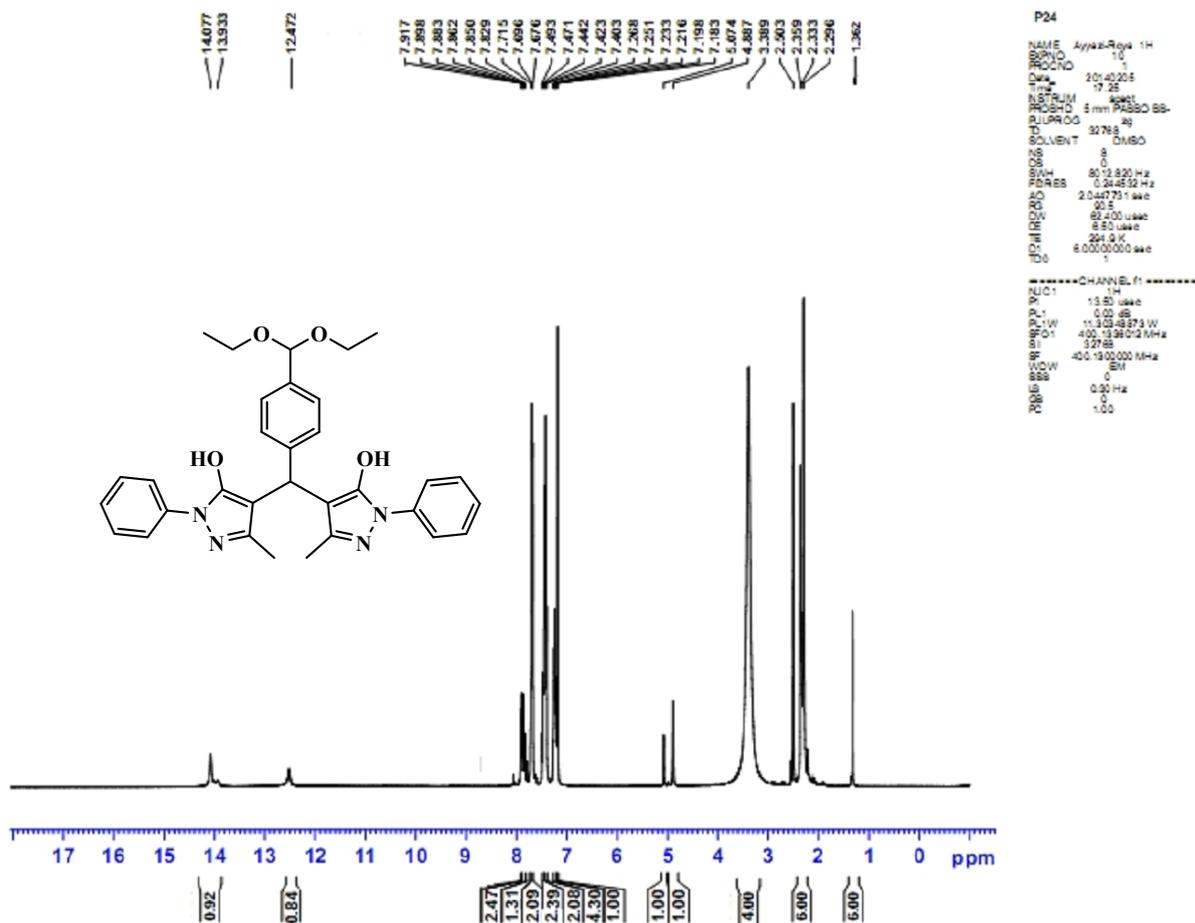
**Fig. S16.** The mass spectrum of 4-((4-(dimethylamino)phenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 1).



**Fig. S17.** The IR spectrum of 4,4'-((4-(diethoxymethyl)phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 4, entry 6).



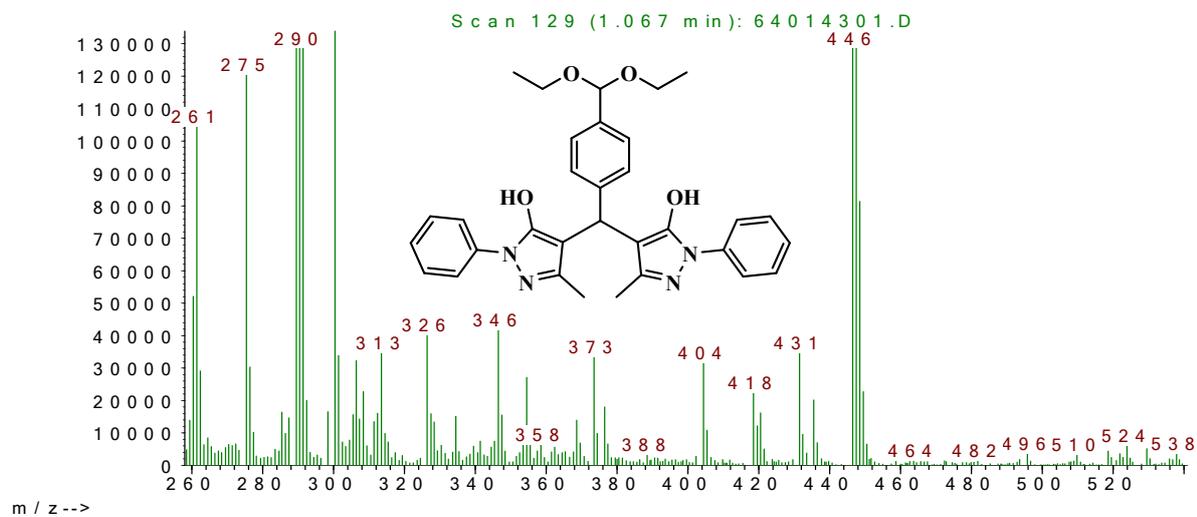
**Fig. S18.** The <sup>1</sup>H NMR spectrum of 4,4'-((4-(diethoxymethyl)phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 4, entry 6).



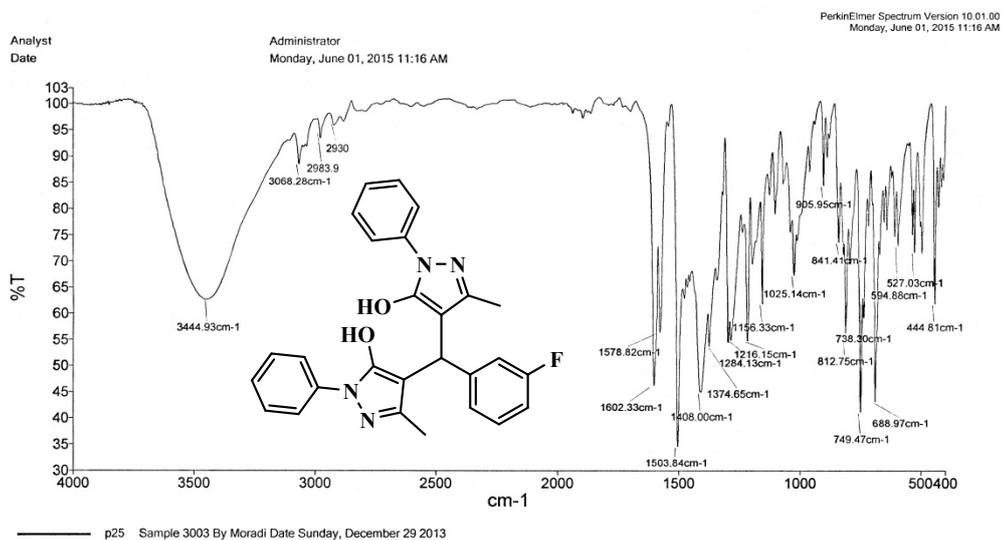


**Fig. S20.** The mass spectrum of 4,4'-((4-(diethoxymethyl)phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 4, entry 6).

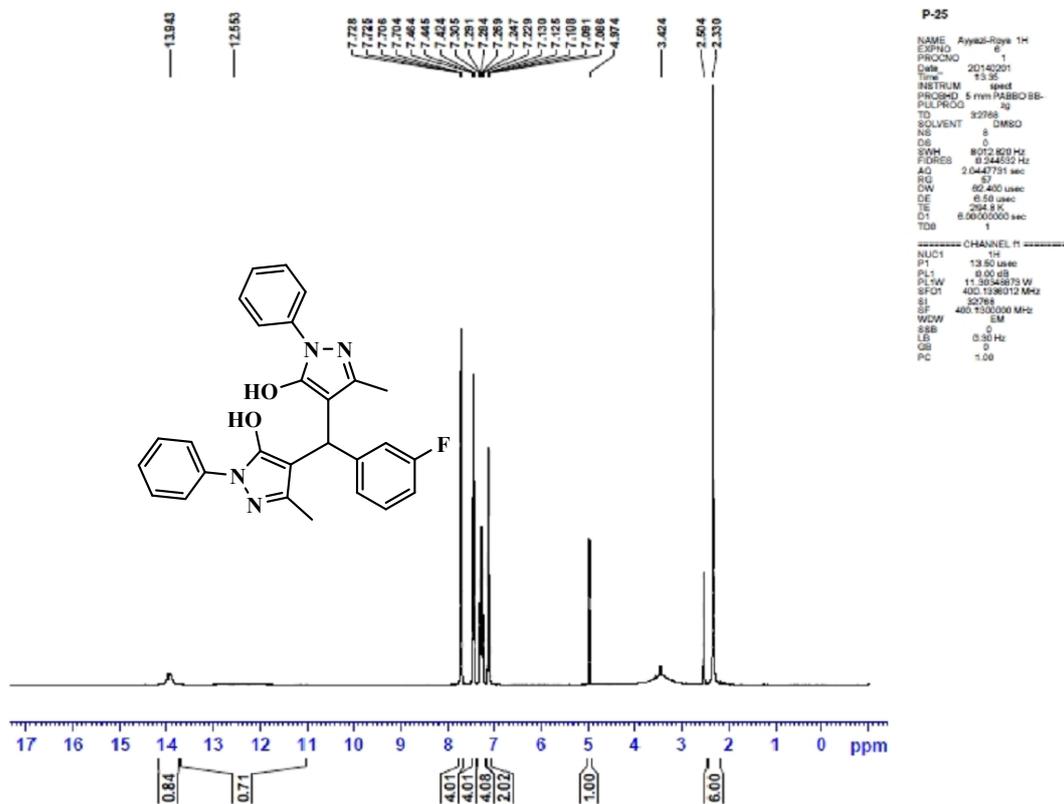
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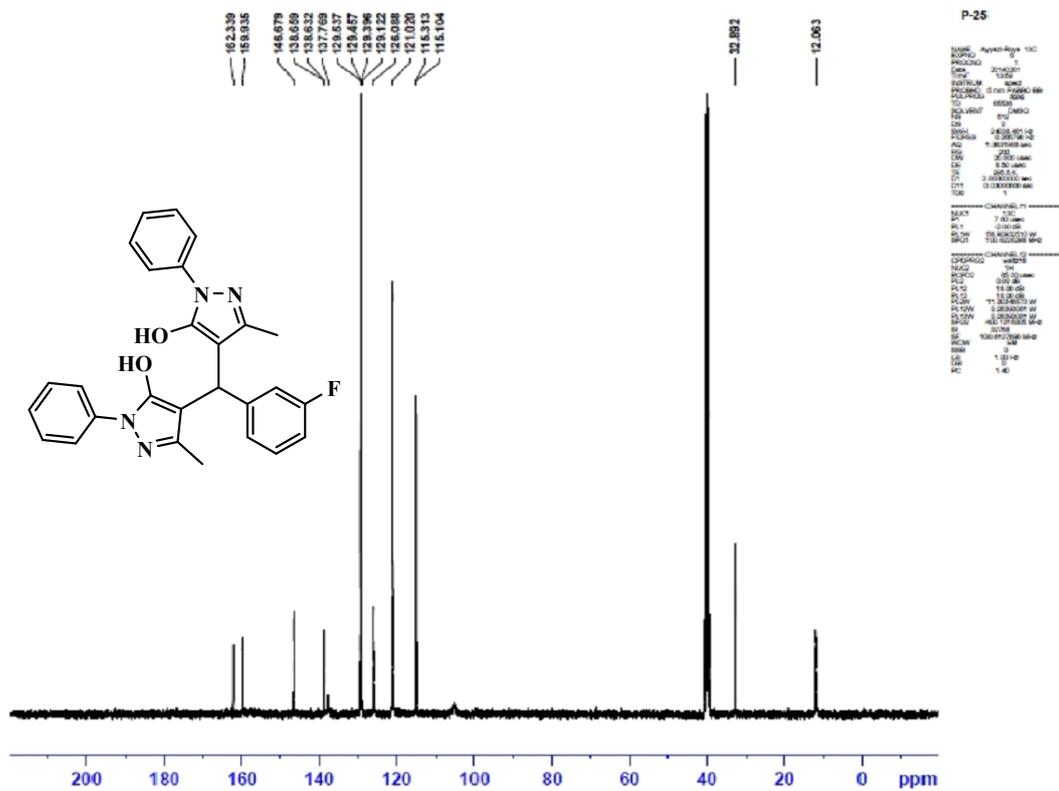
**Fig. S21.** The IR spectrum of 4-((3-fluorophenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (table 4, entry 7).



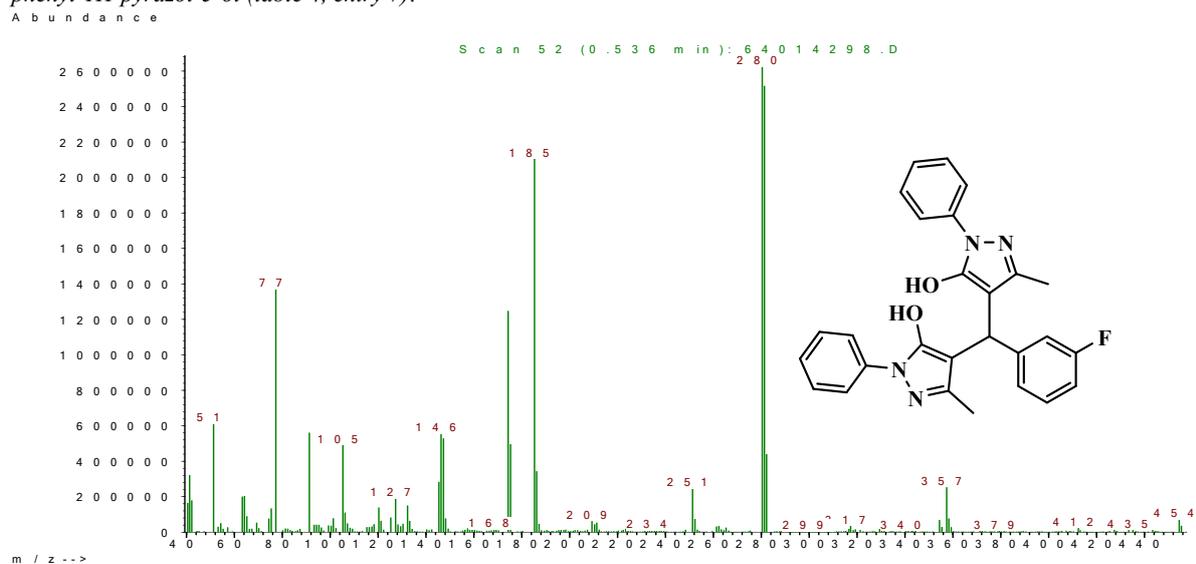
**Fig. S22.** The  $^1\text{H}$  NMR spectrum of 4-((3-fluorophenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (table 4, entry 7).



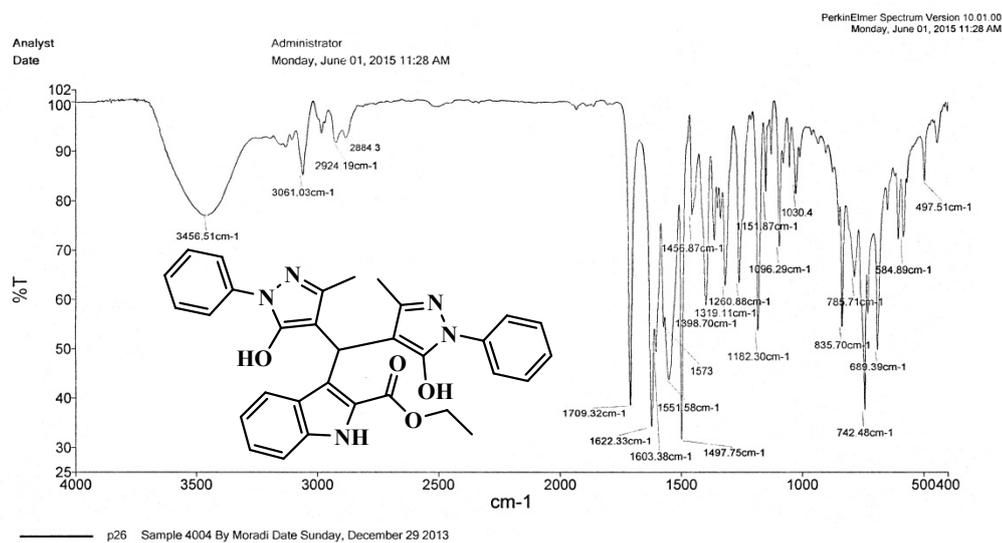
**Fig. S23.** The  $^{13}\text{C}$  NMR spectrum of 4-((3-fluorophenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (table 4, entry 7).



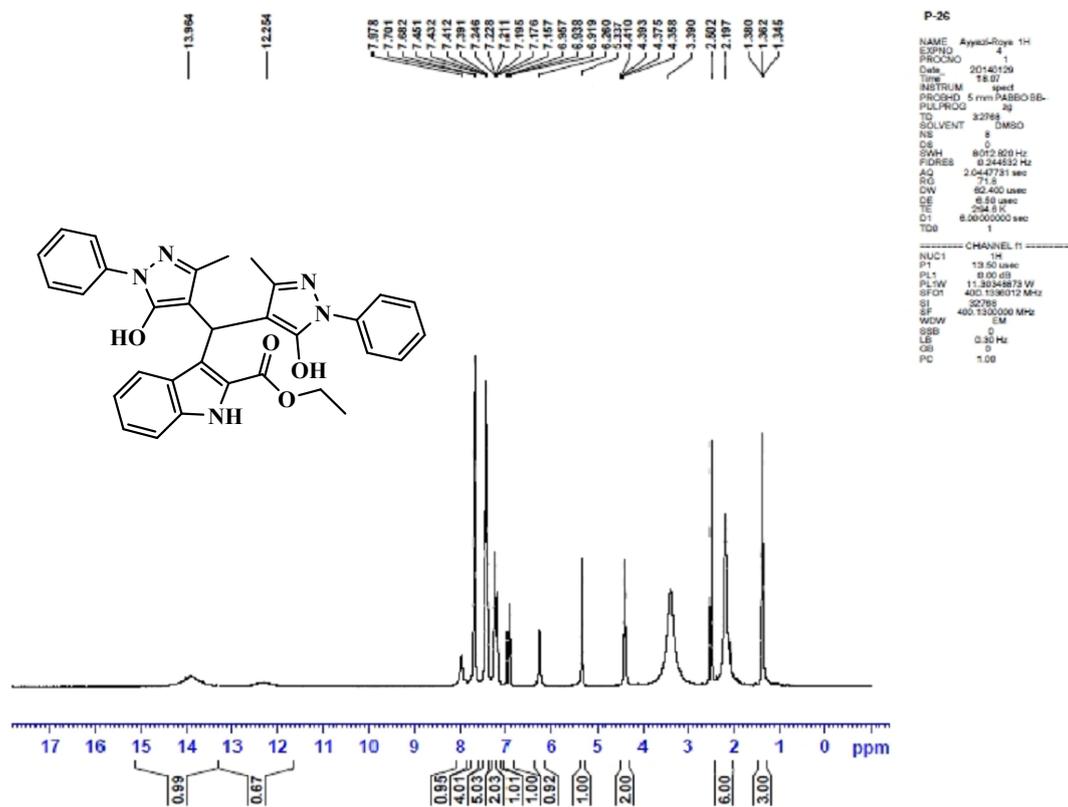
**Fig. S24.** The mass spectrum of 4-((3-fluorophenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (table 4, entry 7).



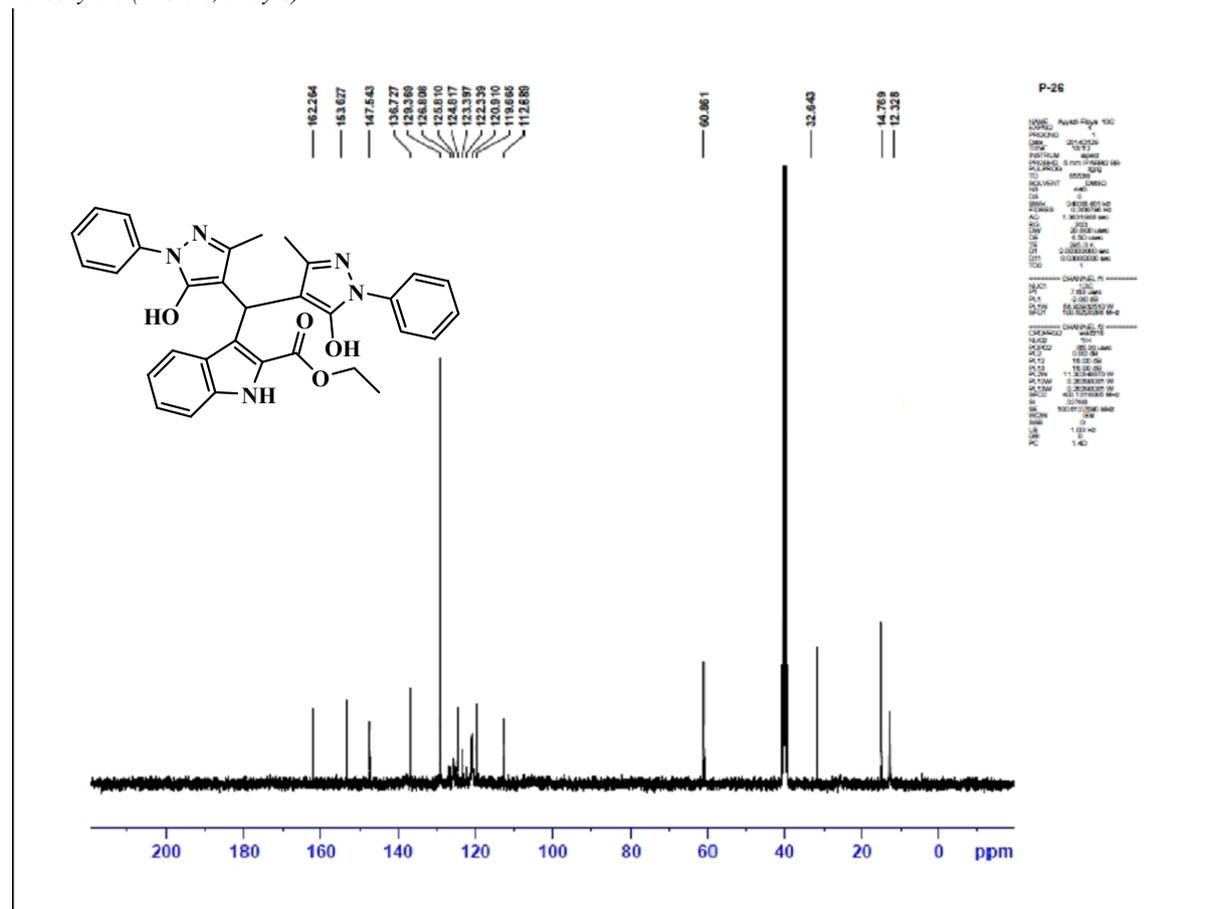
**Fig. S25.** The IR spectrum of *ethyl 3-(bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-1H-indole-2-carboxylate* (Table 4, entry 8).



**Fig. S26.** The  $^1\text{H}$  NMR spectrum of *ethyl 3-(bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-1H-indole-2-carboxylate* (Table 4, entry 8).



**Fig. S27.** The  $^{13}\text{C}$  NMR spectrum of *ethyl 3-(bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-1H-indole-2-carboxylate* (Table 4, entry 8).



**Fig. S28.** The mass spectrum of *ethyl 3-(bis(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-1H-indole-2-carboxylate* (Table 4, entry 8).

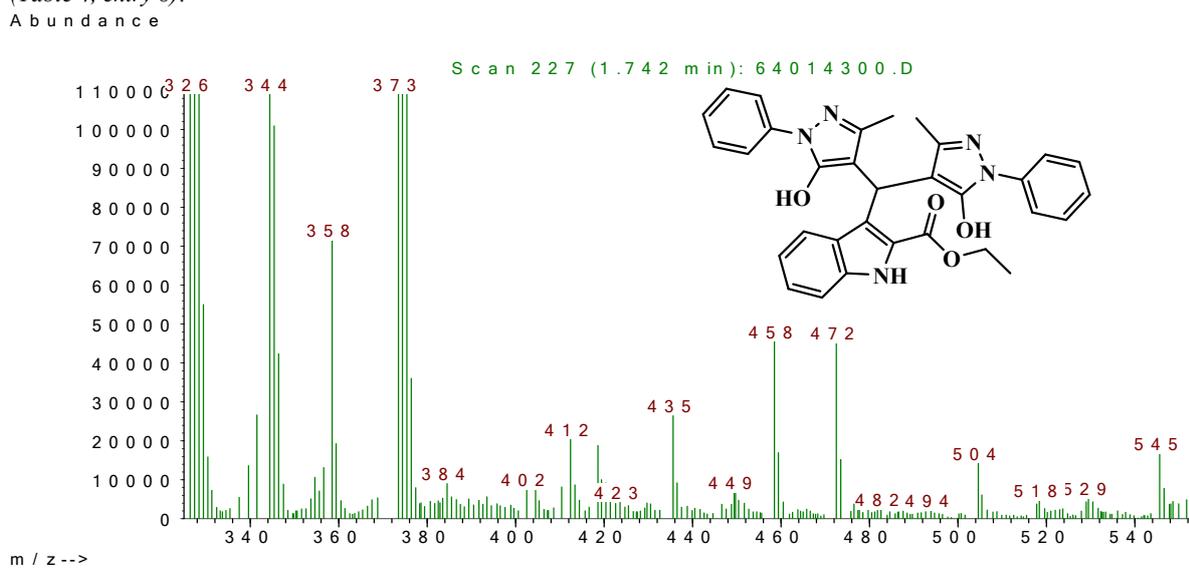
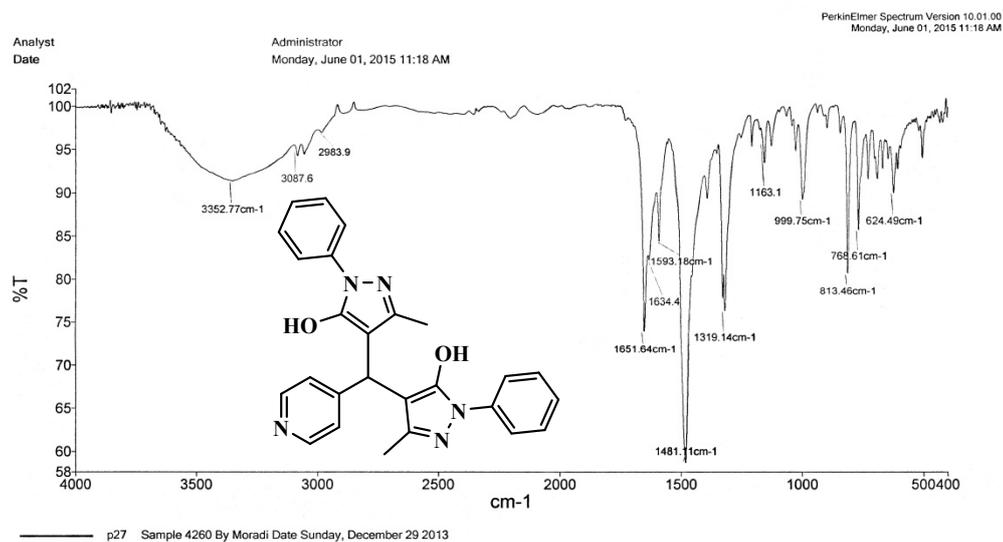


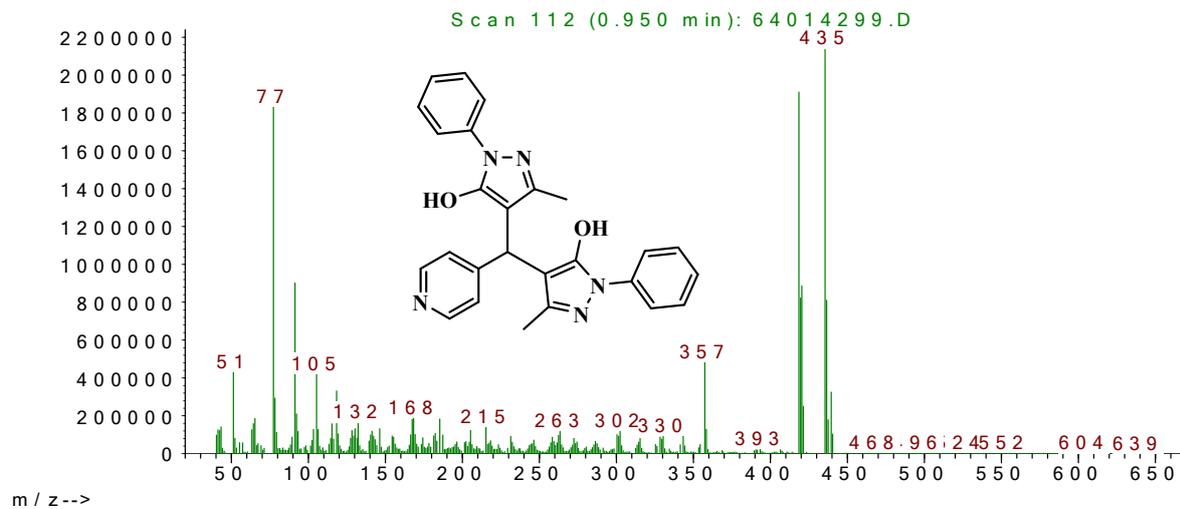
Fig. S29. The IR spectrum of 4,4'-(pyridin-4-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 4, entry 9).



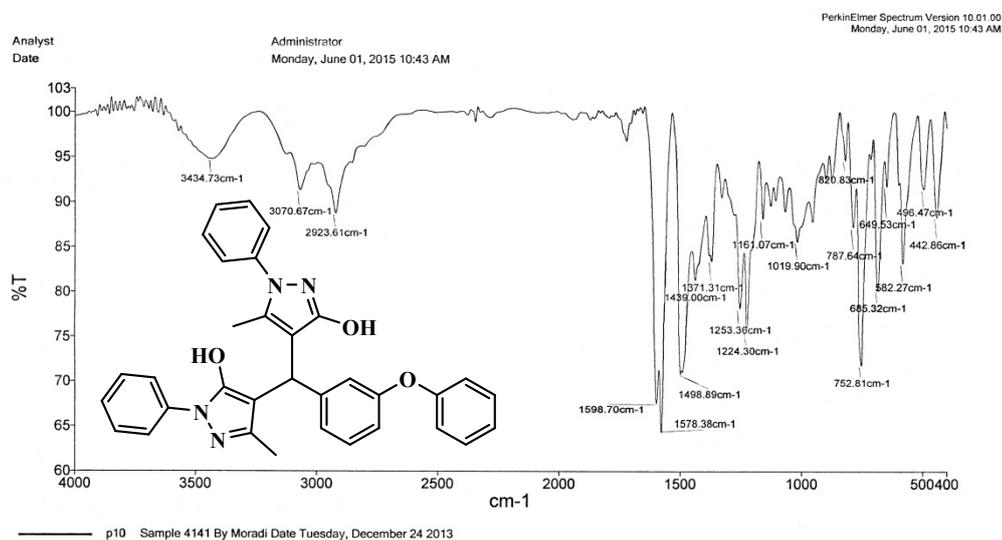




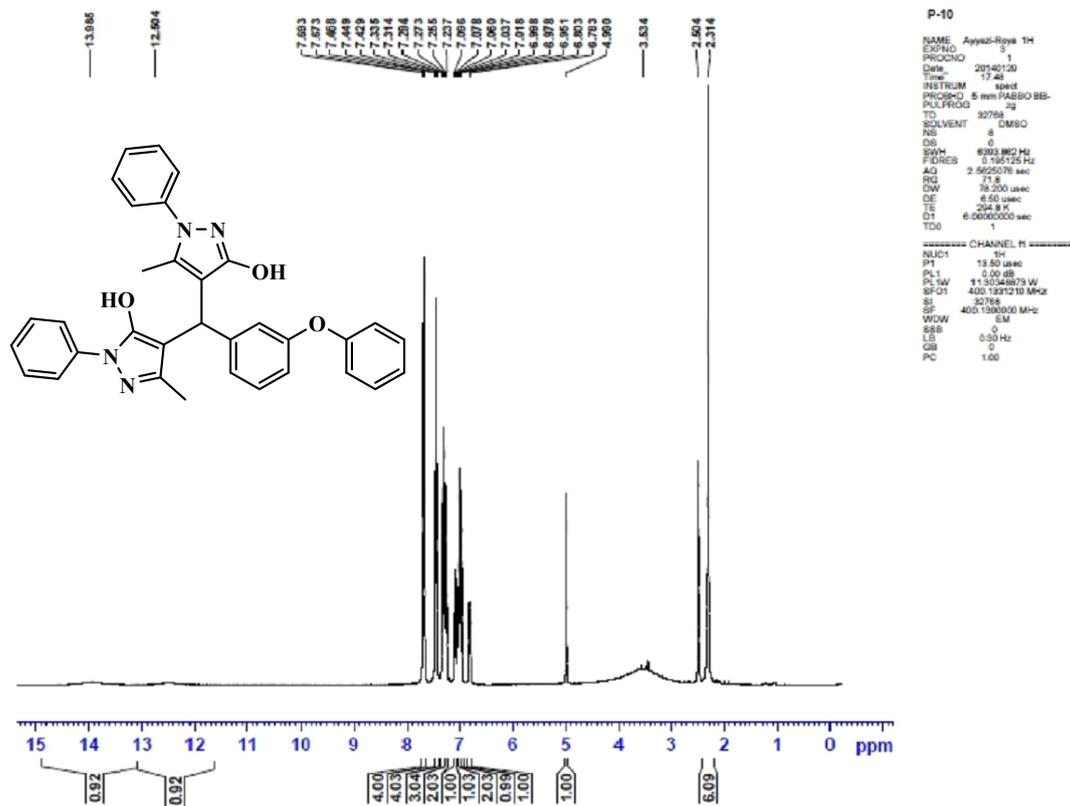
**Fig. S32.** The mass spectrum of 4,4'-(pyridin-4-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table 4, entry 9).



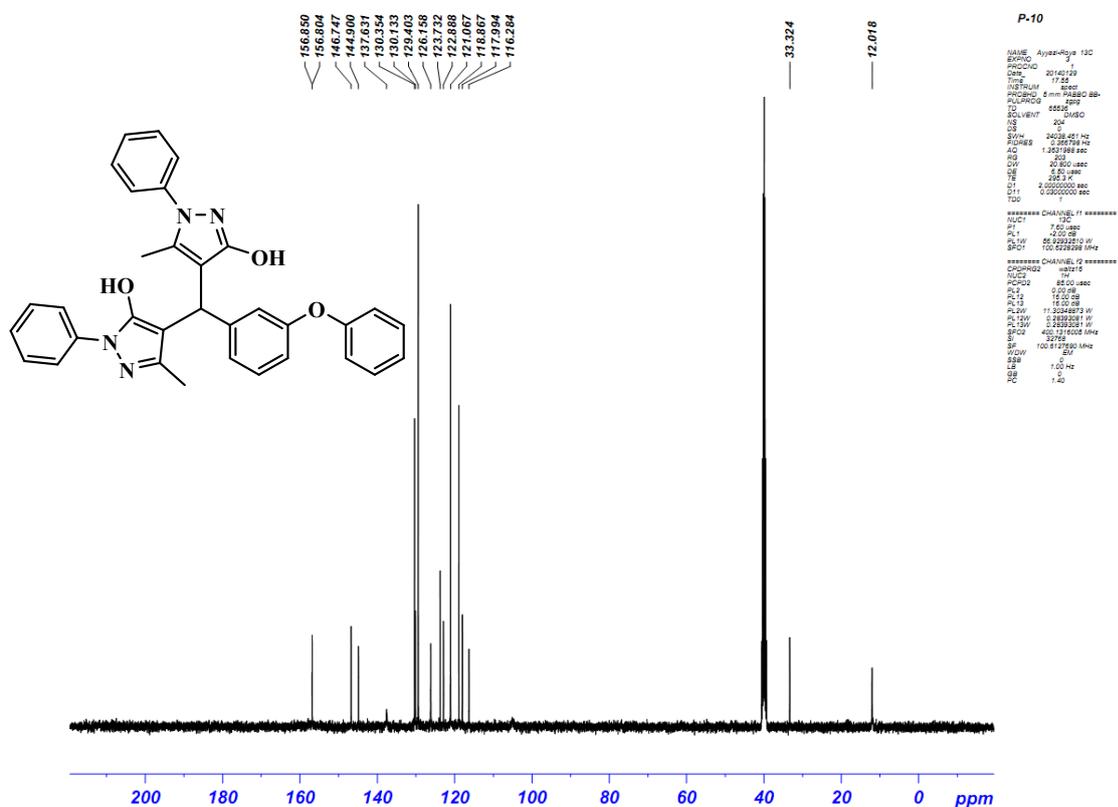
**Fig. S33.** The IR spectrum of 4-((3-hydroxy-5-methyl-1-phenyl-1H-pyrazol-4-yl)(3-phenoxyphenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 19).



**Fig. S34.** The <sup>1</sup>H NMR spectrum of 4-((3-hydroxy-5-methyl-1-phenyl-1H-pyrazol-4-yl)(3-phenoxyphenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 19).

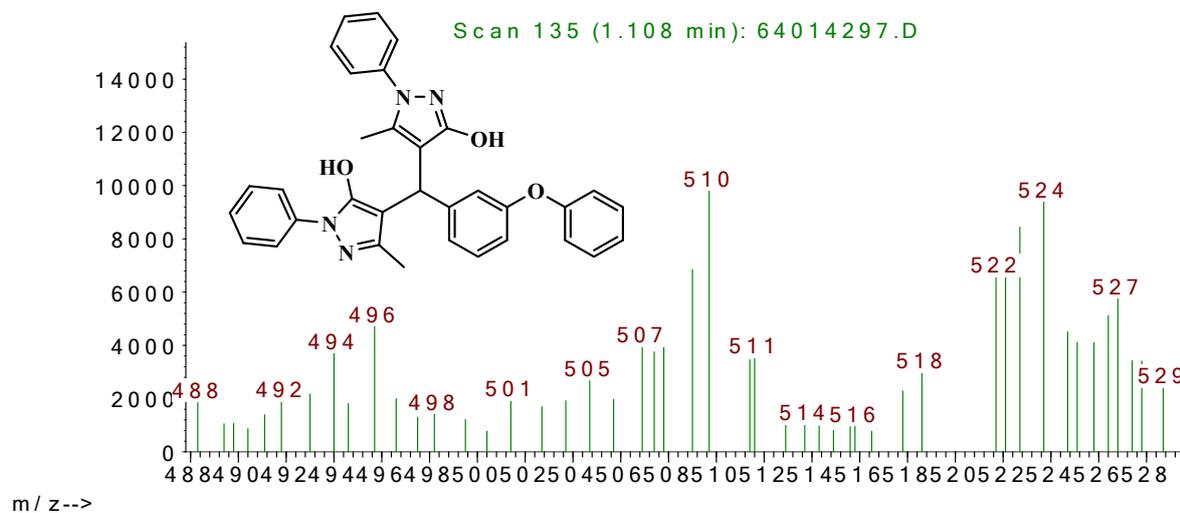


**Fig. S35.** The  $^{13}\text{C}$  NMR spectrum of 4-((3-hydroxy-5-methyl-1-phenyl-1H-pyrazol-4-yl)(3-phenoxyphenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 19).

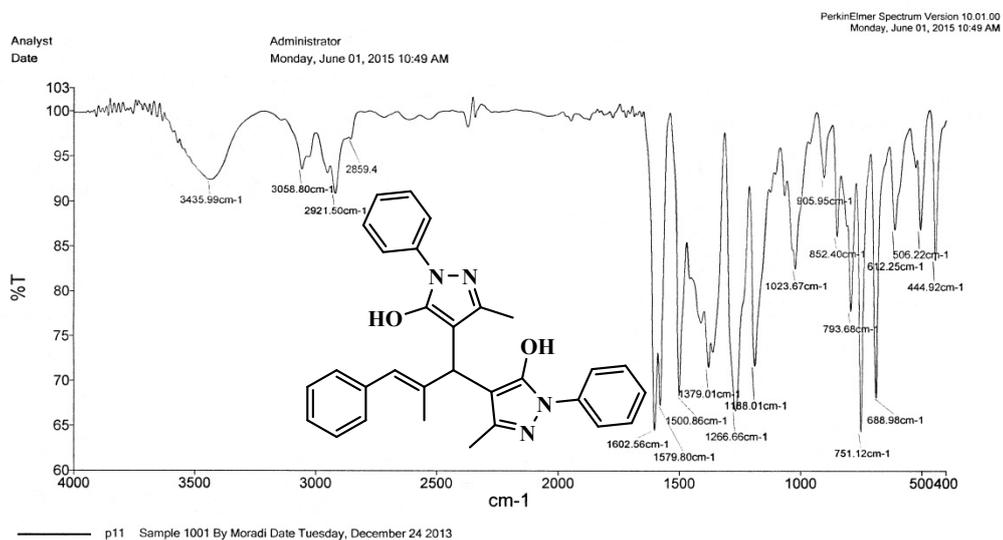


**Fig. S36.** The mass spectrum of 4-((3-hydroxy-5-methyl-1-phenyl-1H-pyrazol-4-yl)(3-phenoxyphenyl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 19).

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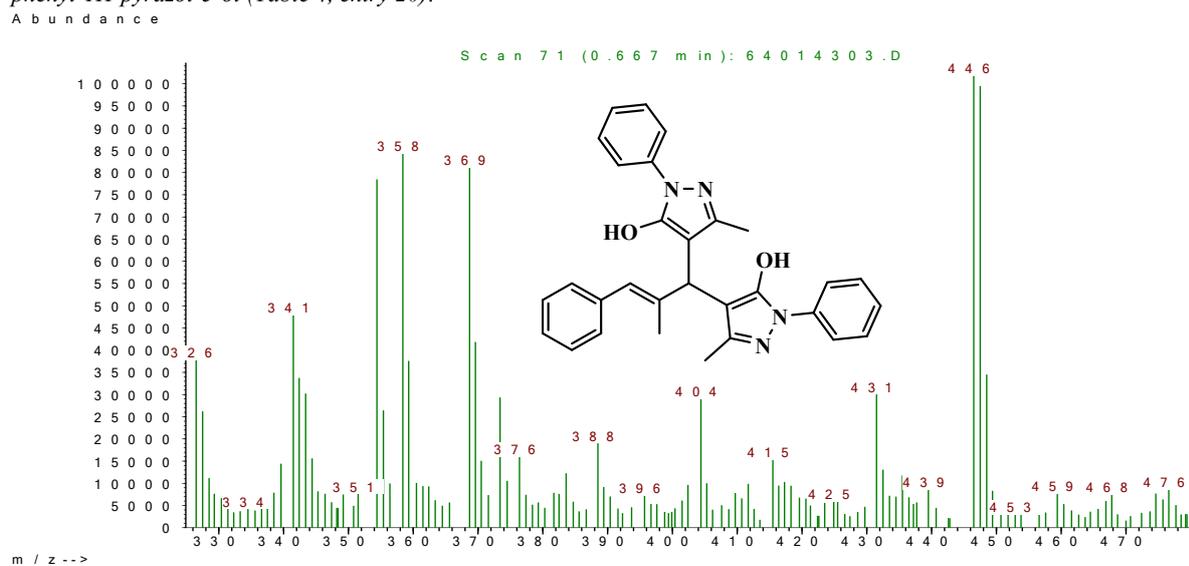
**Fig. S37.** The IR spectrum of 4-(1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-methyl-3-phenylallyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 20).



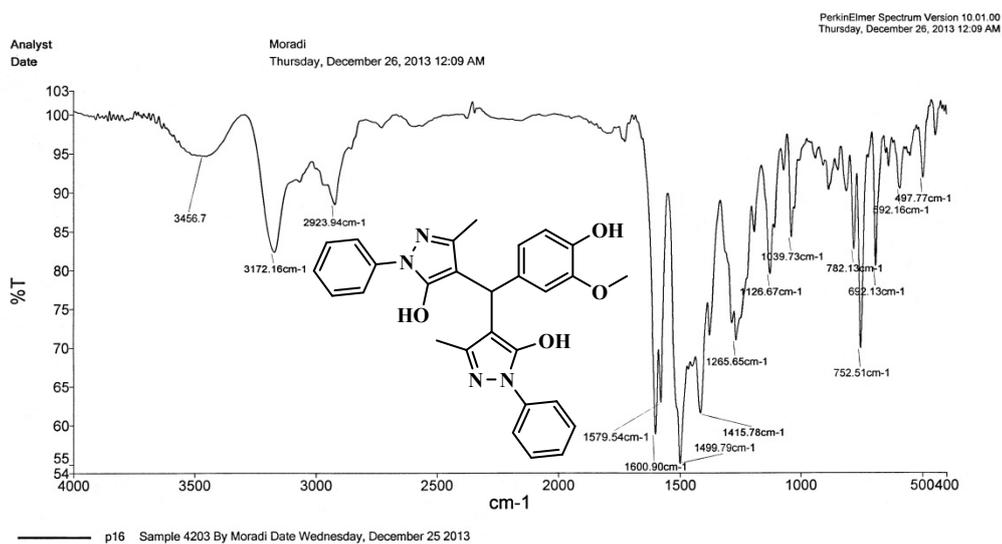




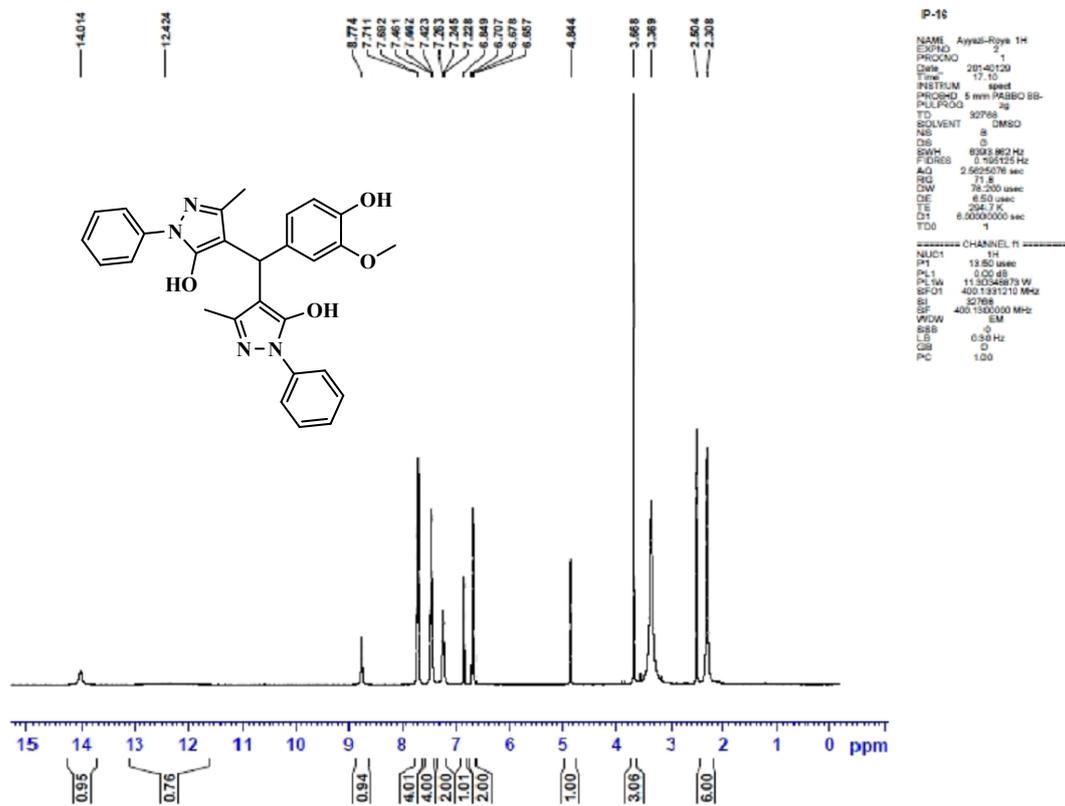
**Fig. S40.** The mass spectrum of *4-(1-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-methyl-3-phenylallyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol* (Table 4, entry 20).



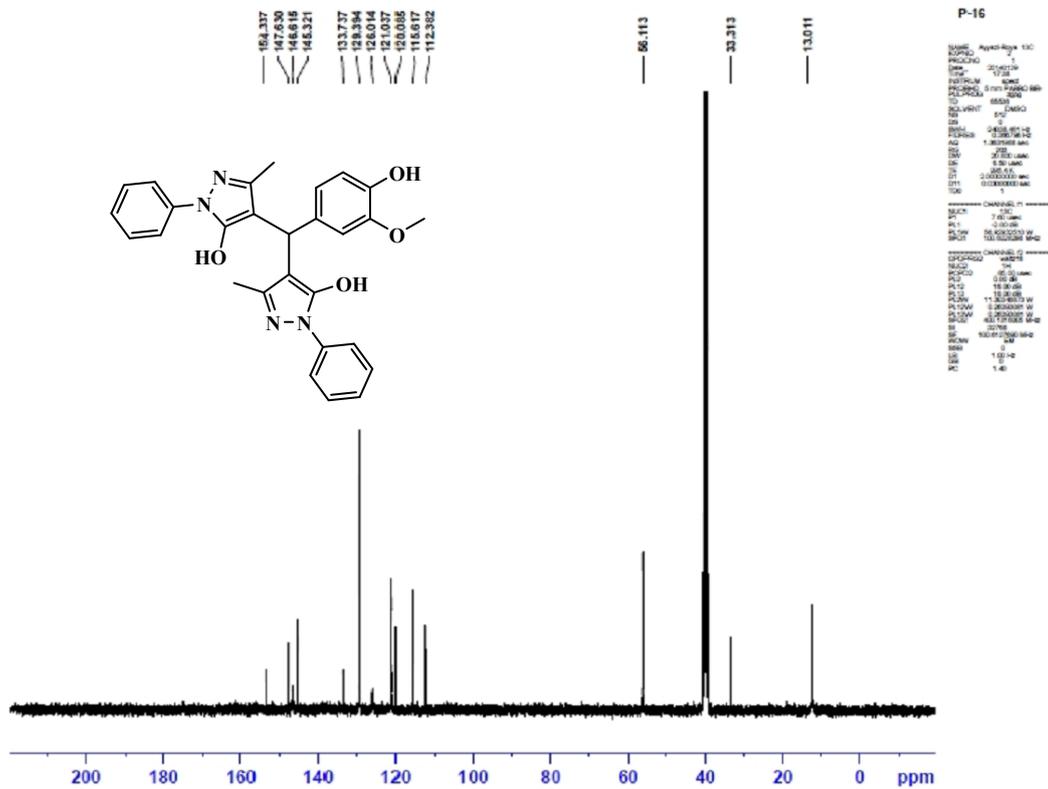
**Fig. S41.** The IR spectrum of 4-((4-hydroxy-3-methoxyphenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 24).



**Fig. S42.** The <sup>1</sup>H NMR spectrum of 4-((4-hydroxy-3-methoxyphenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 24).



**Fig. S43.** The  $^{13}\text{C}$  NMR spectrum of 4-((4-hydroxy-3-methoxyphenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 24).



**Fig. S44.** The mass spectrum of 4-((4-hydroxy-3-methoxyphenyl)(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol (Table 4, entry 24).

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