

# Supporting Information for

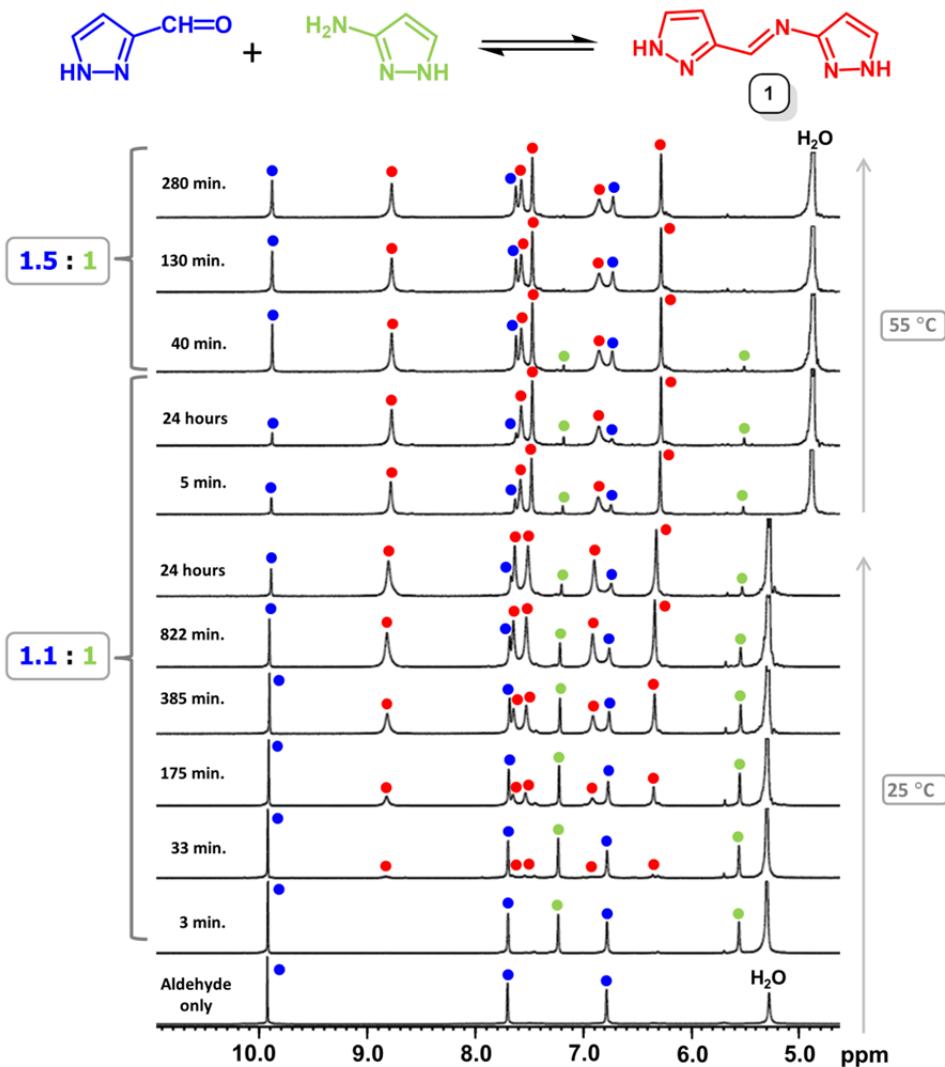
## **Reaction of Amines with Aldehydes and Ketones Revisited: Access to a Class of Non-Scorpionate Tris(pyrazolyl)methane and Related Ligands**

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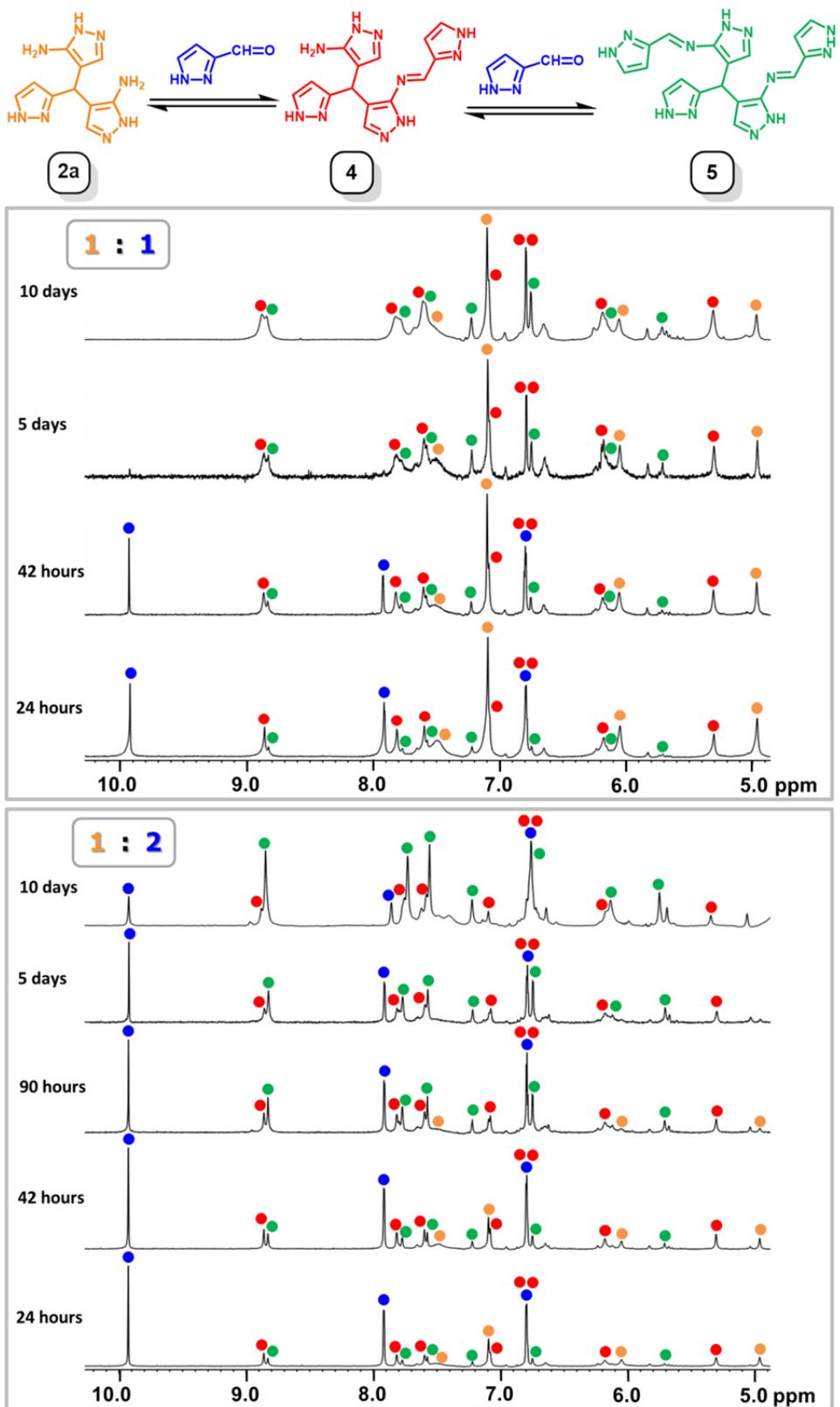
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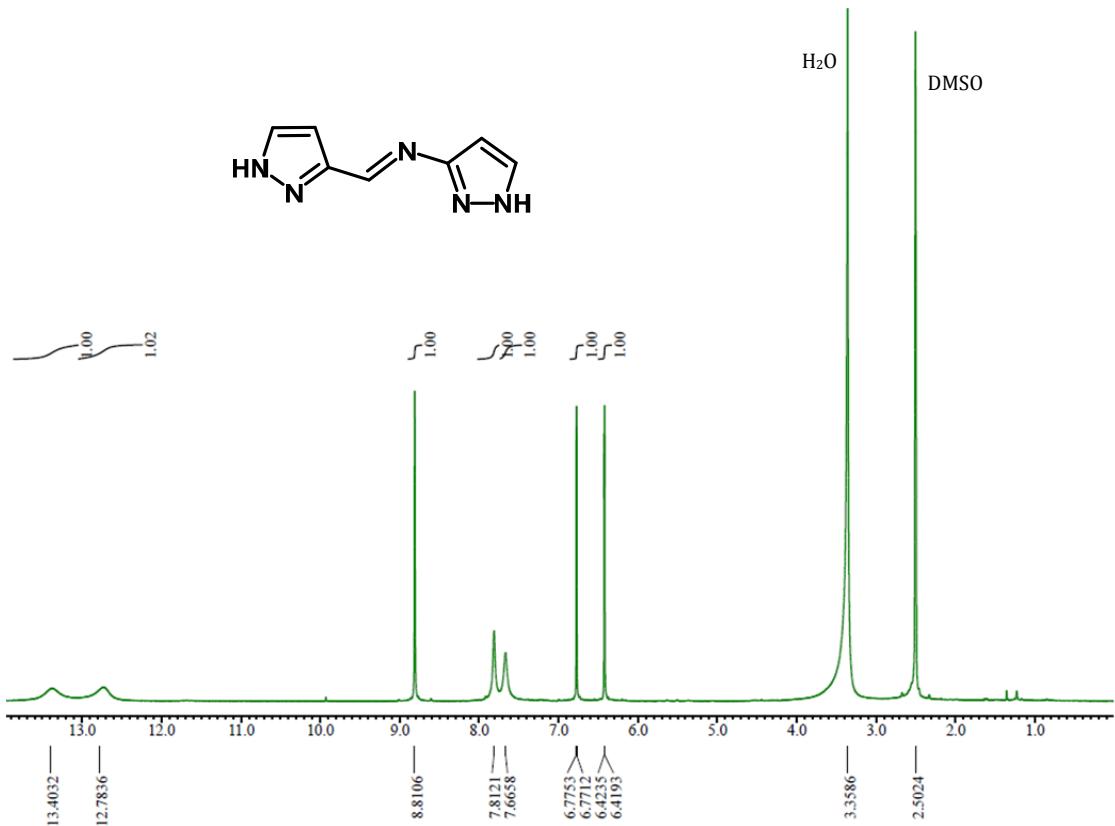
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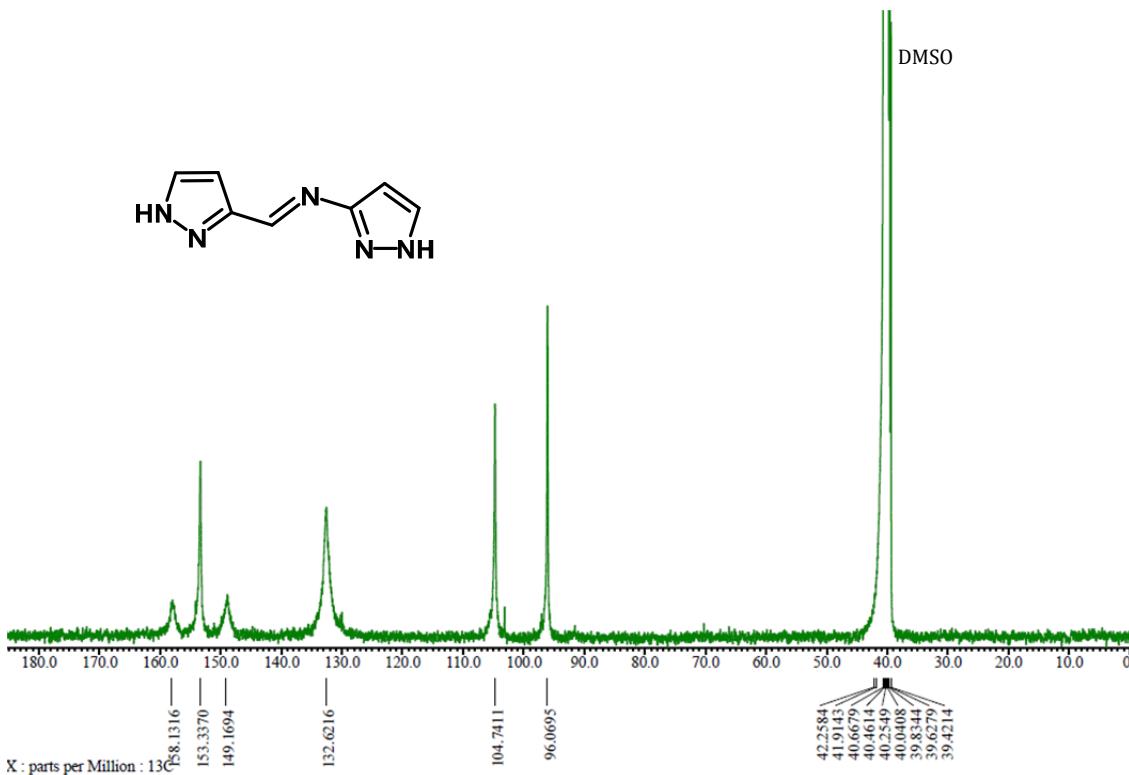
**Figure S1.** Reaction of pyrazole-3(5)-carbaldehyde and 3(5)-aminopyrazole (1.1:1 then 1.5:1 molar ratio) monitored over time by <sup>1</sup>H NMR in ethanol-*d*<sub>6</sub> (in the absence of acid). 10% excess aldehyde is insufficient for driving the equilibrium reaction to completion; with a 50% excess, the reaction is practically complete.



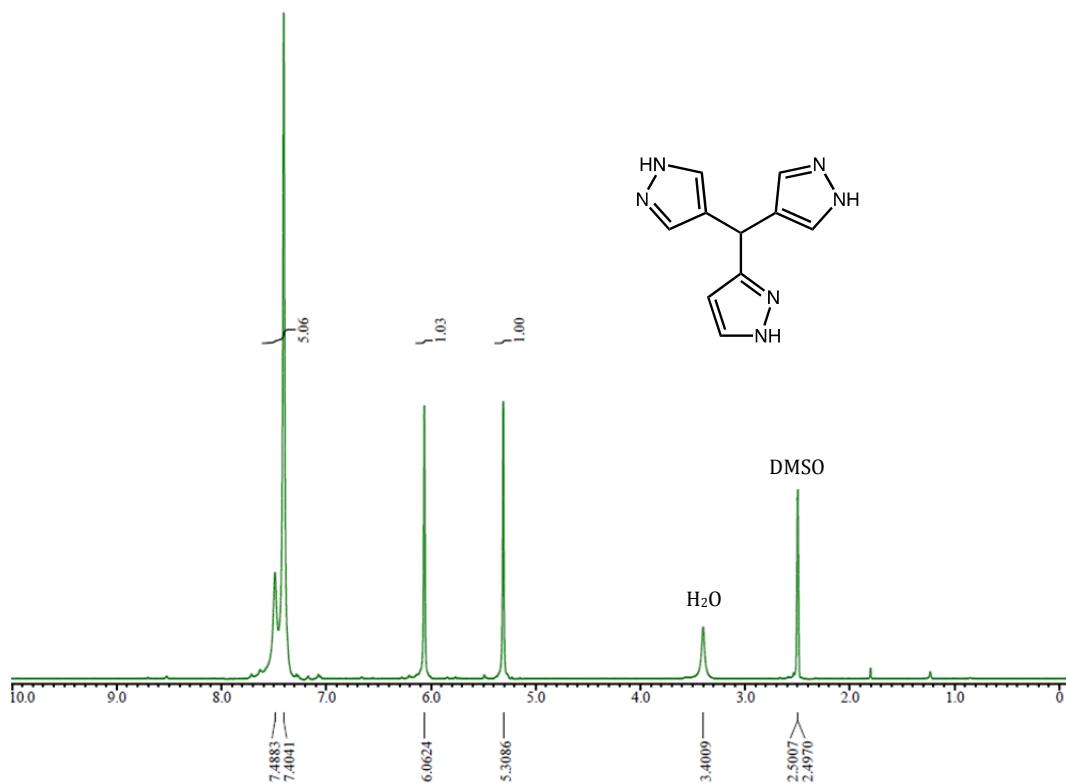
**Figure S2.** Reaction of **2a** with pyrazole-3(5)-carbaldehyde (1:1 and 1:2 molar ratio) in ethanol (in the absence of acid) monitored periodically by  $^1\text{H}$  NMR (in  $\text{DMSO}-d_6$ ).



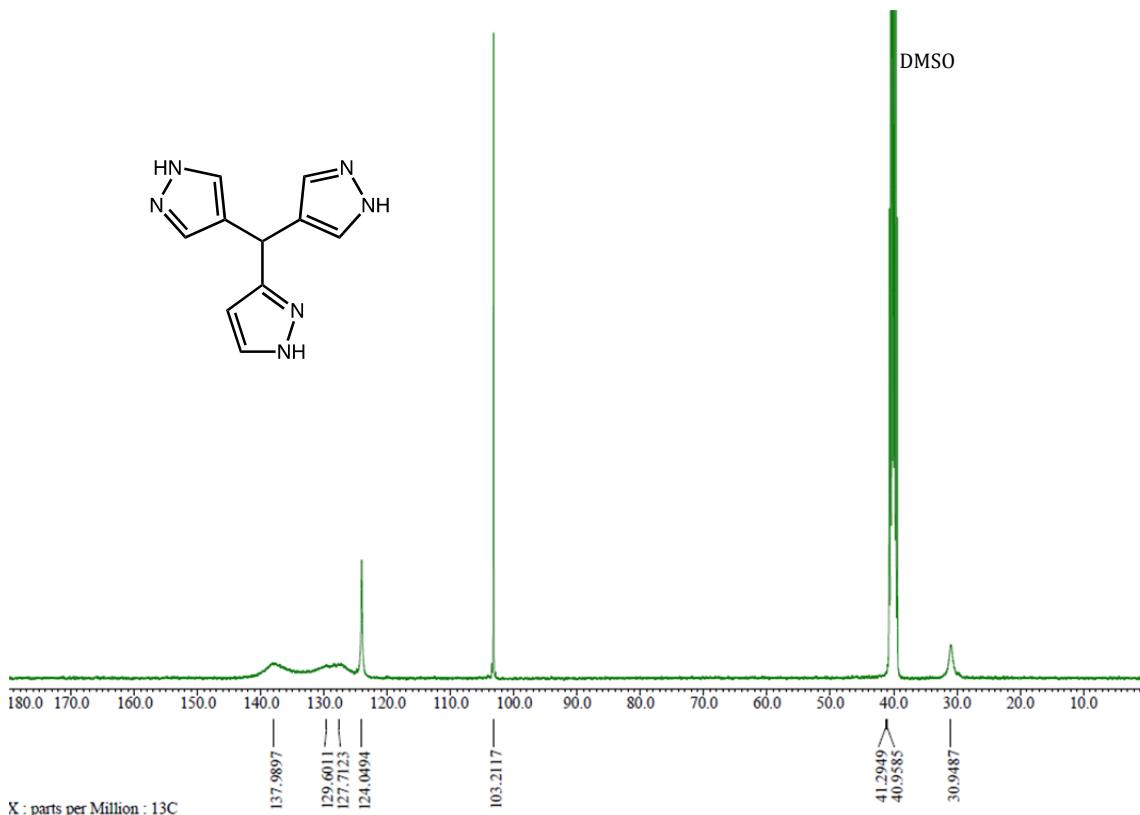
**Figure S3.** <sup>1</sup>H NMR spectrum of *N*,1-bis(pyrazol-3(5)-yl)methanimine (**1**) in DMSO-*d*<sub>6</sub>.



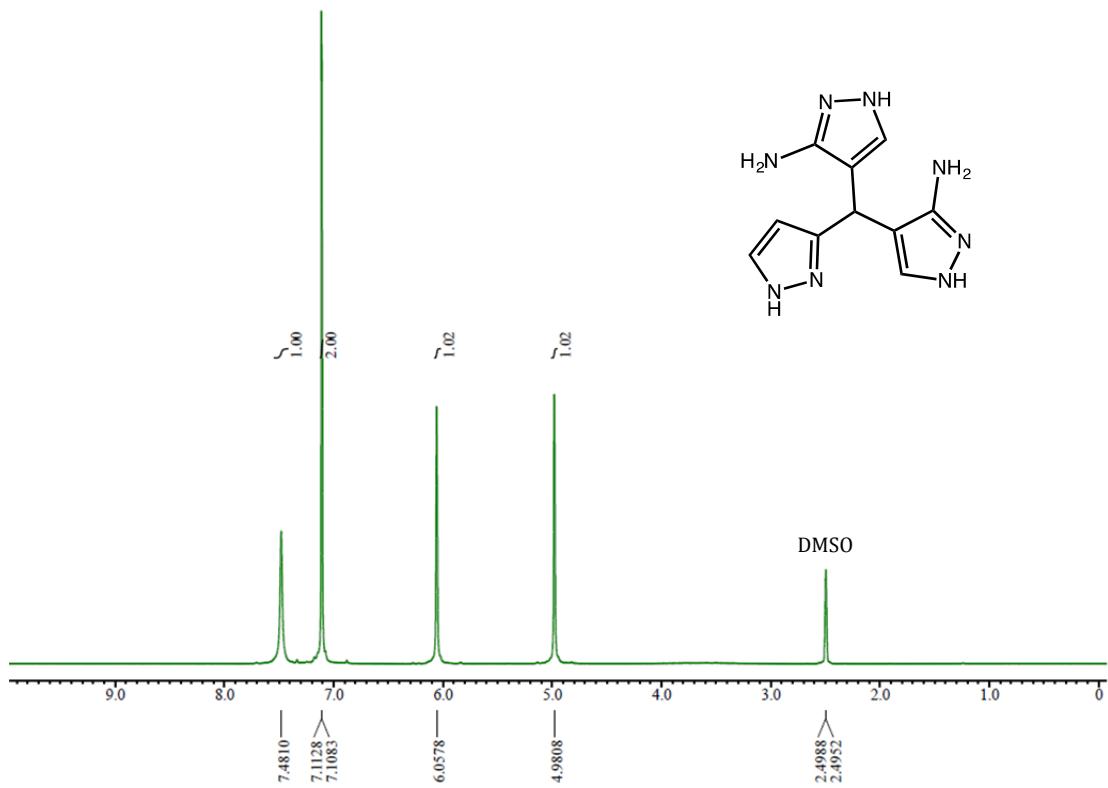
**Figure S4.** <sup>13</sup>C NMR spectrum of *N*,1-bis(pyrazol-3(5)-yl)methanimine (**1**) in DMSO-*d*<sub>6</sub>.



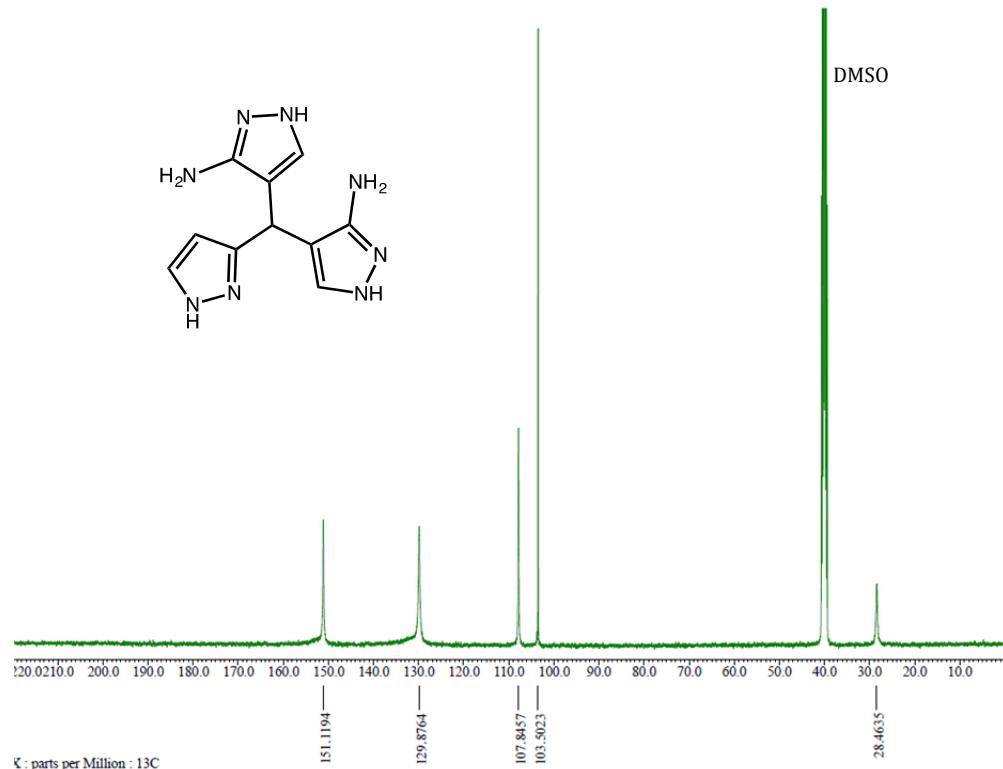
**Figure S5.** <sup>1</sup>H NMR spectrum of bis(pyrazol-4-yl)-pyrazol-3(5)-yl-methane (**2**) in DMSO-*d*<sub>6</sub>.



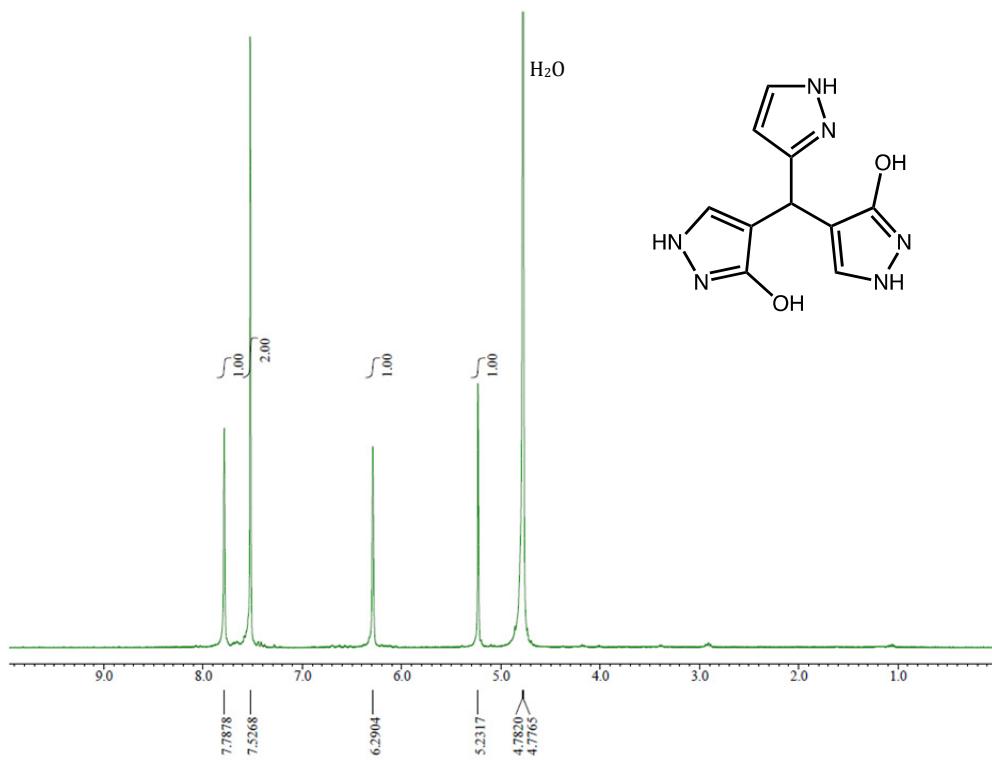
**Figure S6.** <sup>13</sup>C NMR spectrum of bis(pyrazol-4-yl)-pyrazol-3(5)-yl-methane (**2**) in DMSO-*d*<sub>6</sub>.



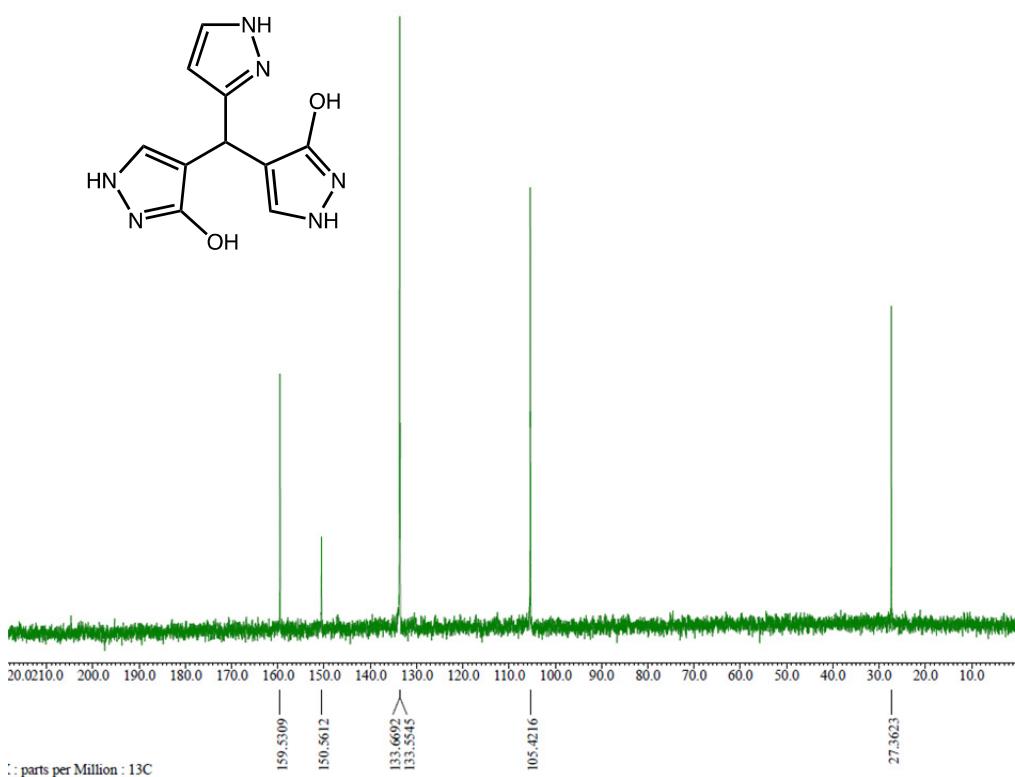
**Figure S7.**  $^1\text{H}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-pyrazol-3(5)-yl-methane (**2a**) in  $\text{DMSO}-d_6$ .



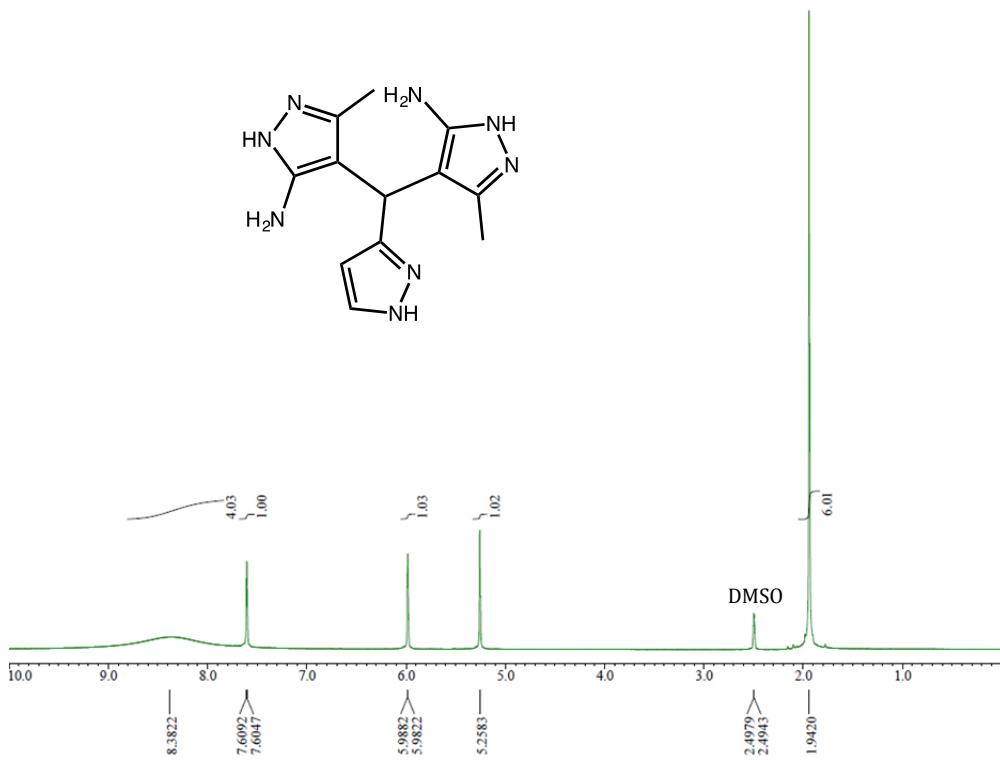
**Figure S8.**  $^{13}\text{C}$  NMR of bis(3(5)-aminopyrazol-4-yl)-pyrazol-3(5)-yl-methane (**2a**) in  $\text{DMSO}-d_6$ .



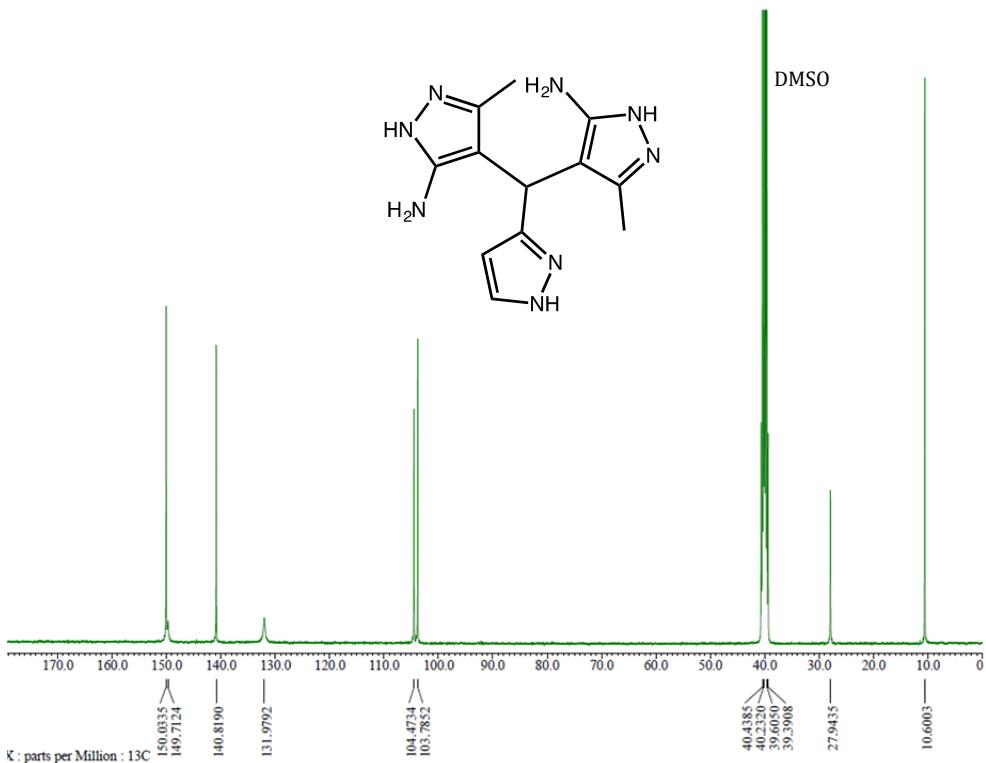
**Figure S9.**  $^1\text{H}$  NMR spectrum of bis(3(5)-hydroxypyrazol-4-yl)-pyrazol-3(5)-yl-methane (**2b**) in  $\text{D}_2\text{O}$ .



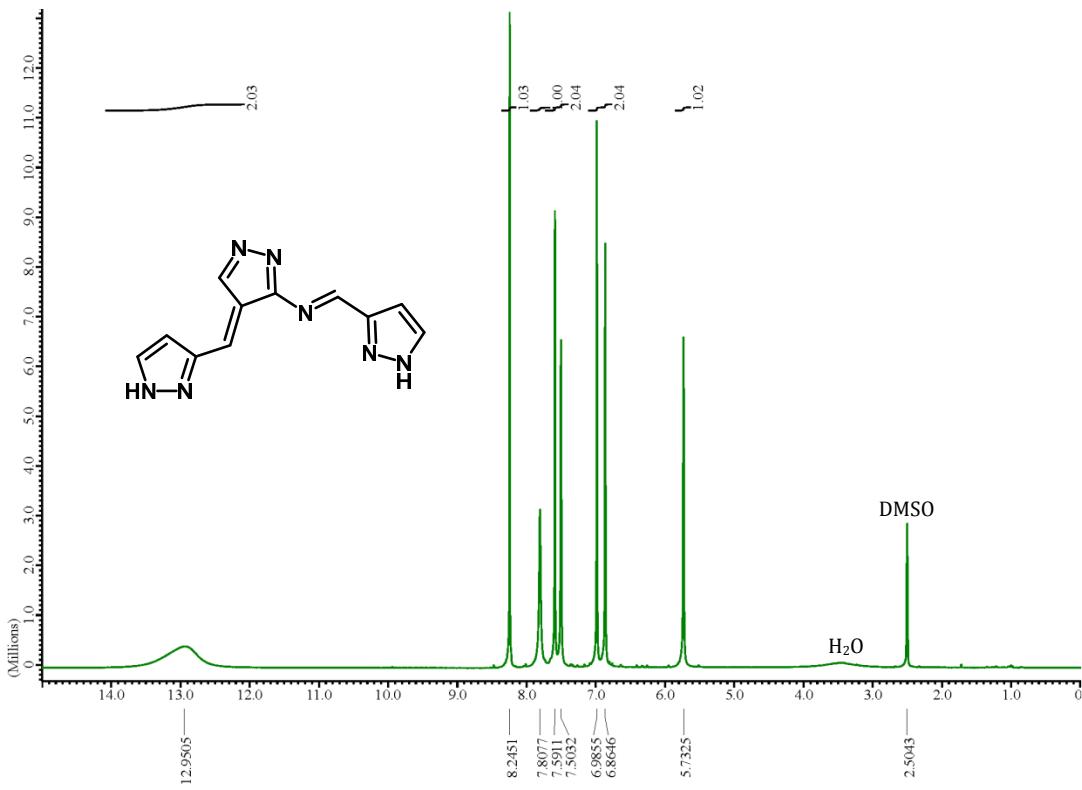
**Figure S10.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-hydroxypyrazol-4-yl)-pyrazol-3(5)-yl-methane (**2b**) in  $\text{D}_2\text{O}$ .



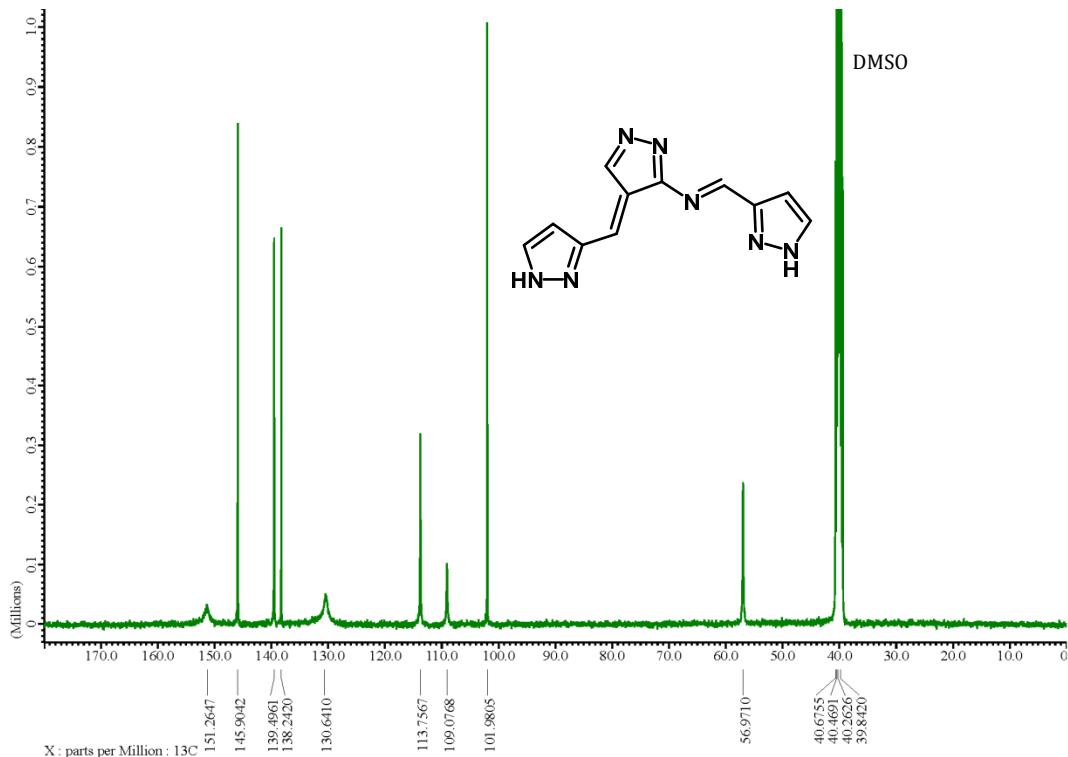
**Figure S11.**  $^1\text{H}$  NMR spectrum of bis(3(5)-amino-5(3)-methylpyrazol-4-yl)-pyrazol-3(5)-ylmethane (**2c**) in  $\text{DMSO}-d_6$ .



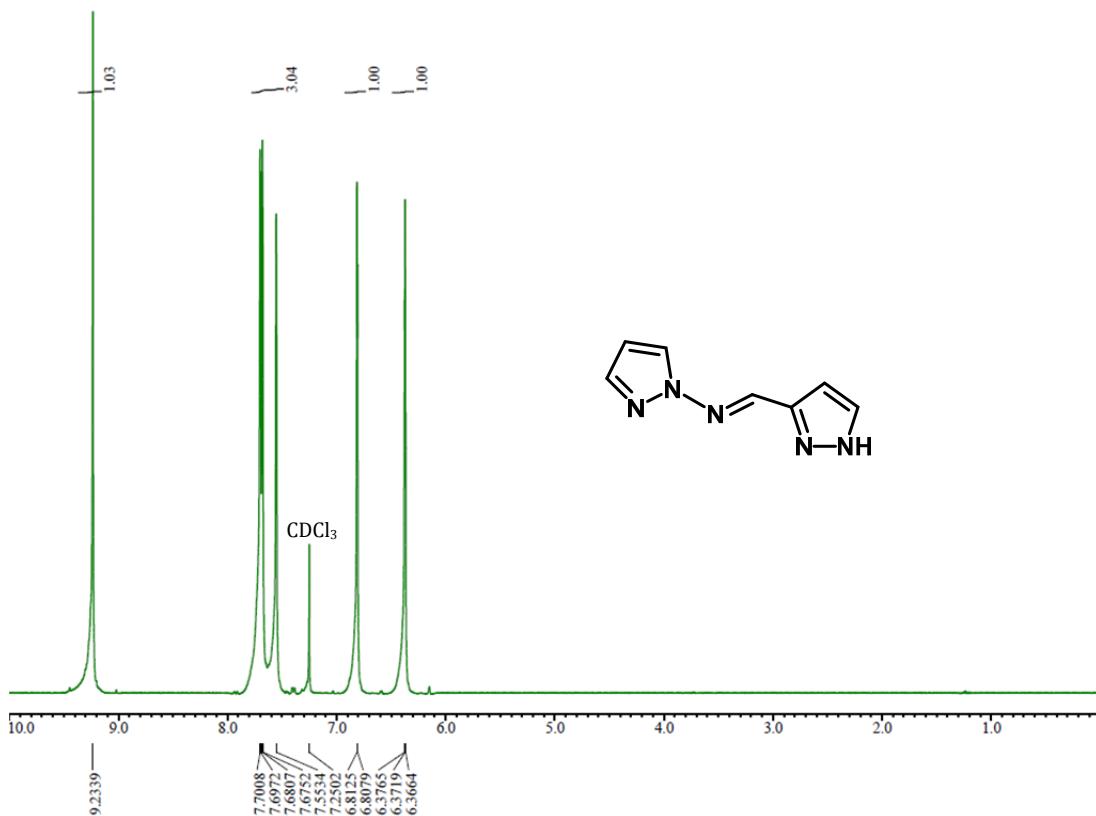
**Figure S12.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-amino-5(3)-methylpyrazol-4-yl)-pyrazol-3(5)-ylmethane (**2c**) in  $\text{DMSO}-d_6$ .



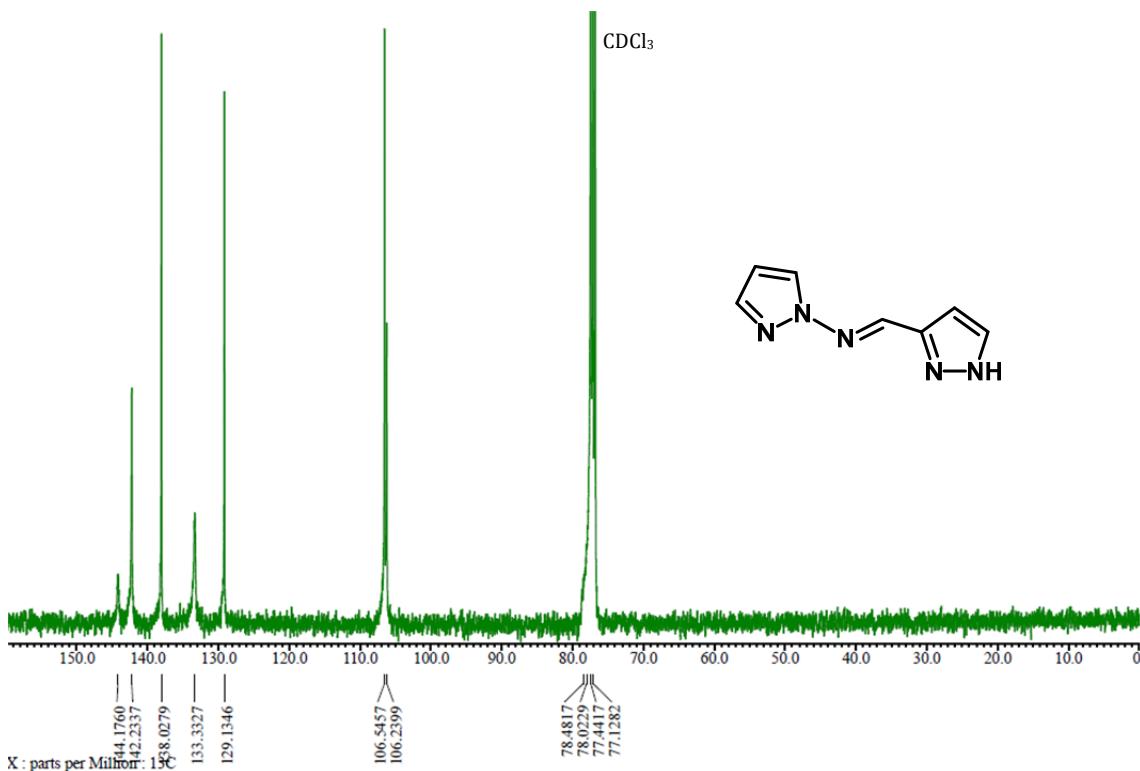
**Figure S13.**  $^1\text{H}$  NMR spectrum of compound 6 in  $\text{DMSO}-d_6$ .



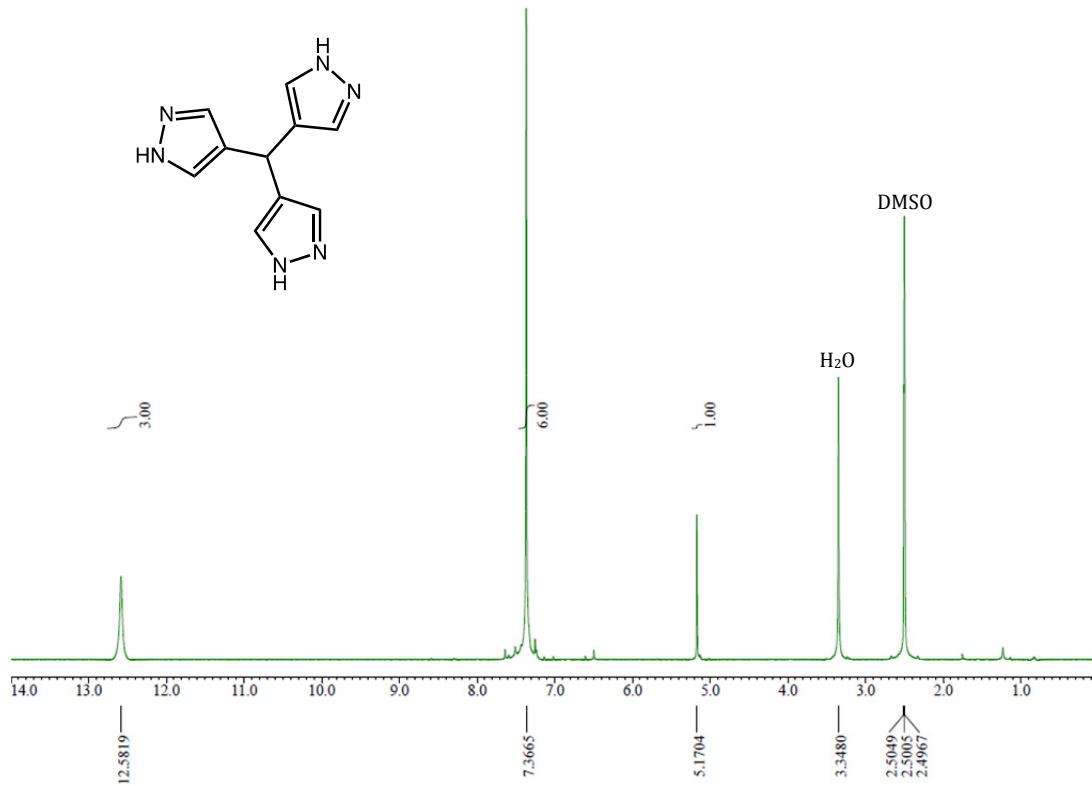
**Figure S14.**  $^{13}\text{C}$  NMR spectrum of compound 6 in  $\text{DMSO}-d_6$ .



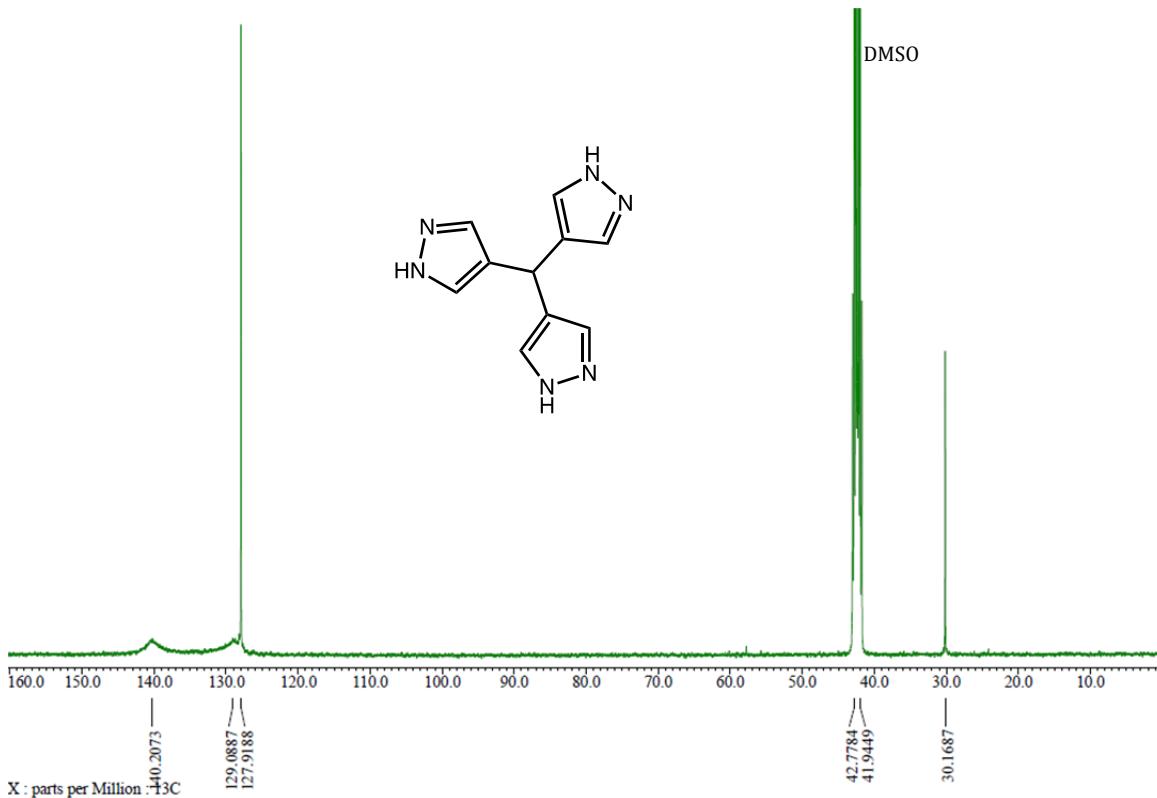
**Figure S15.**  $^1\text{H}$  NMR spectrum of N-(pyrazol-1-yl)-1-(pyrazol-3(5)-yl)methanimine (**7**) in  $\text{CDCl}_3$ .



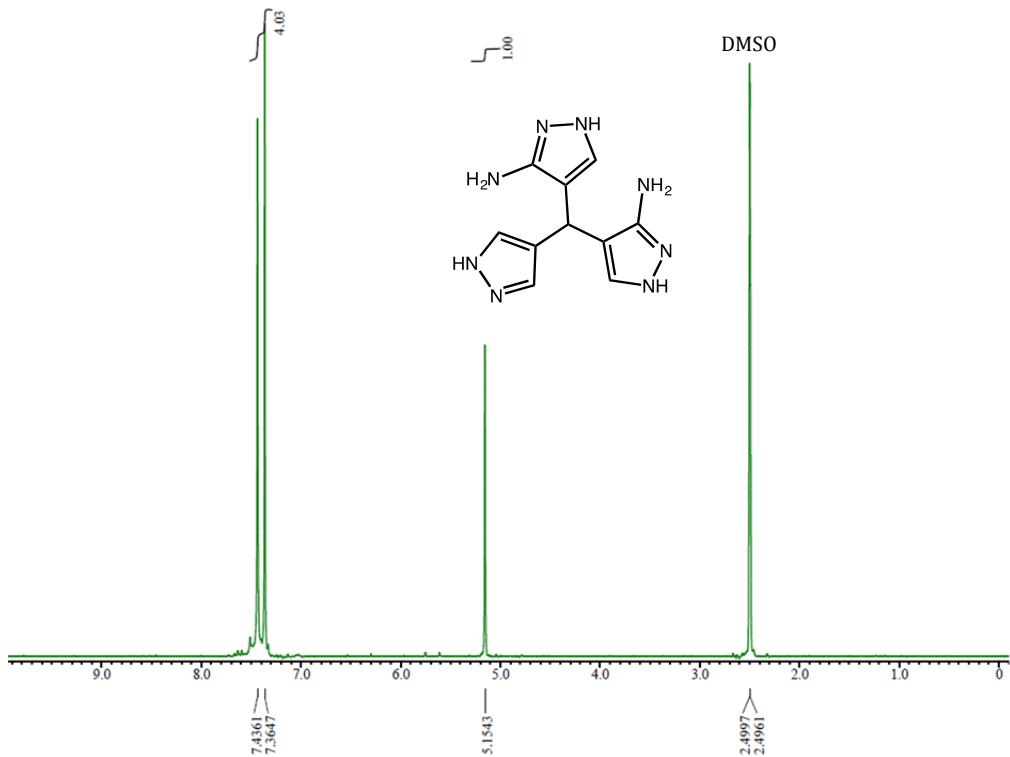
**Figure S16.**  $^{13}\text{C}$  NMR spectrum of N-(pyrazol-1-yl)-1-(pyrazol-3(5)-yl)methanimine (**7**) in  $\text{CDCl}_3$ .



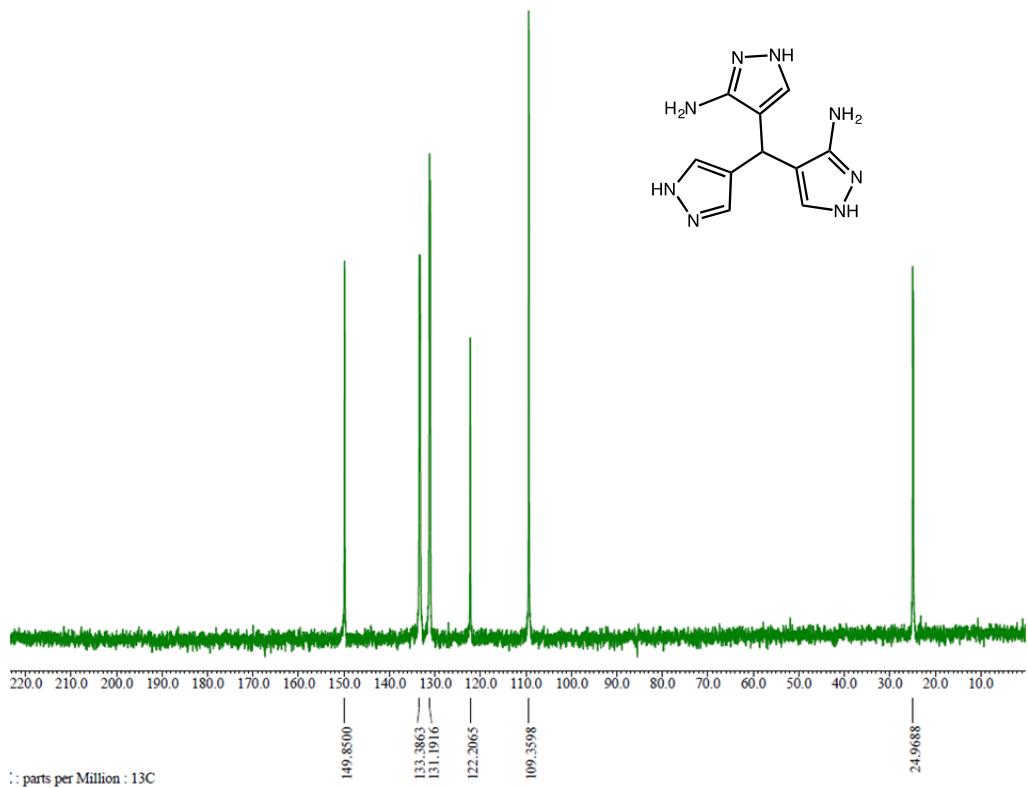
**Figure S17.**  $^1\text{H}$  NMR spectrum of tris(pyrazol-4-yl)methane (**8**) in  $\text{DMSO}-d_6$ .



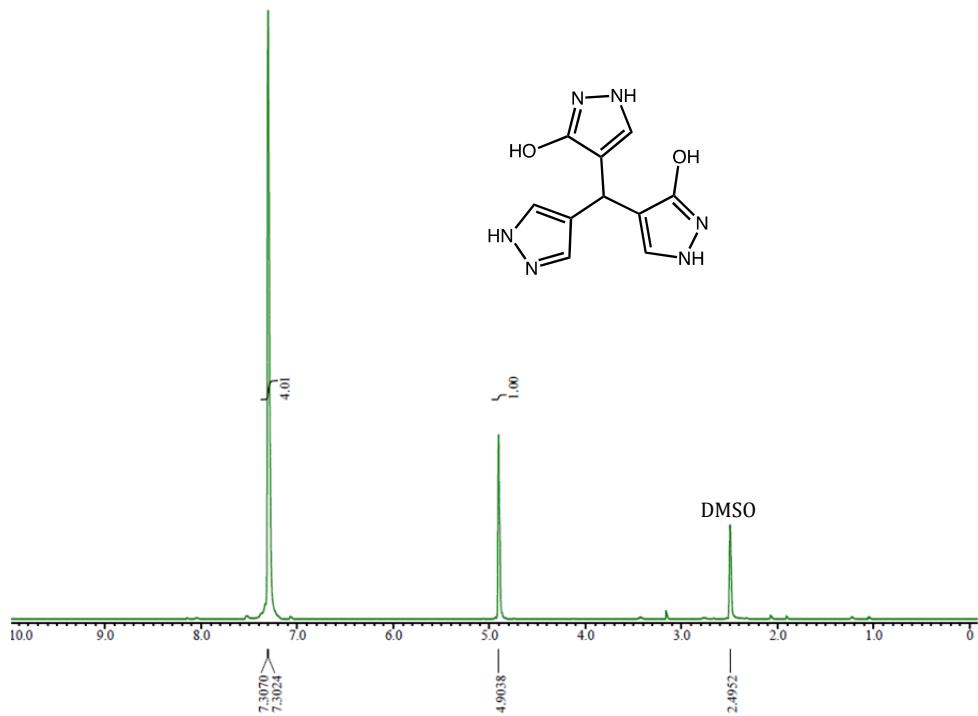
**Figure S18.**  $^{13}\text{C}$  NMR spectrum of tris(pyrazol-4-yl)methane (**8**) in  $\text{DMSO}-d_6$ .



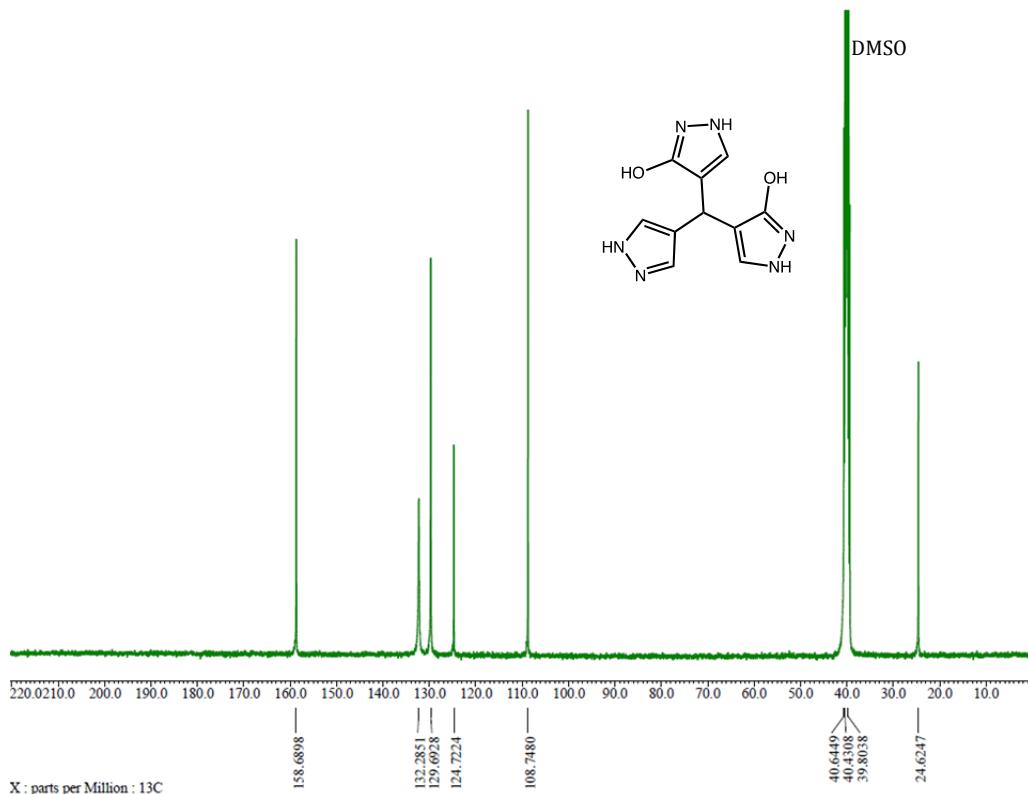
**Figure S19.**  $^1\text{H}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-pyrazol-4-yl-methane (**8a**) in  $\text{DMSO}-d_6$ .



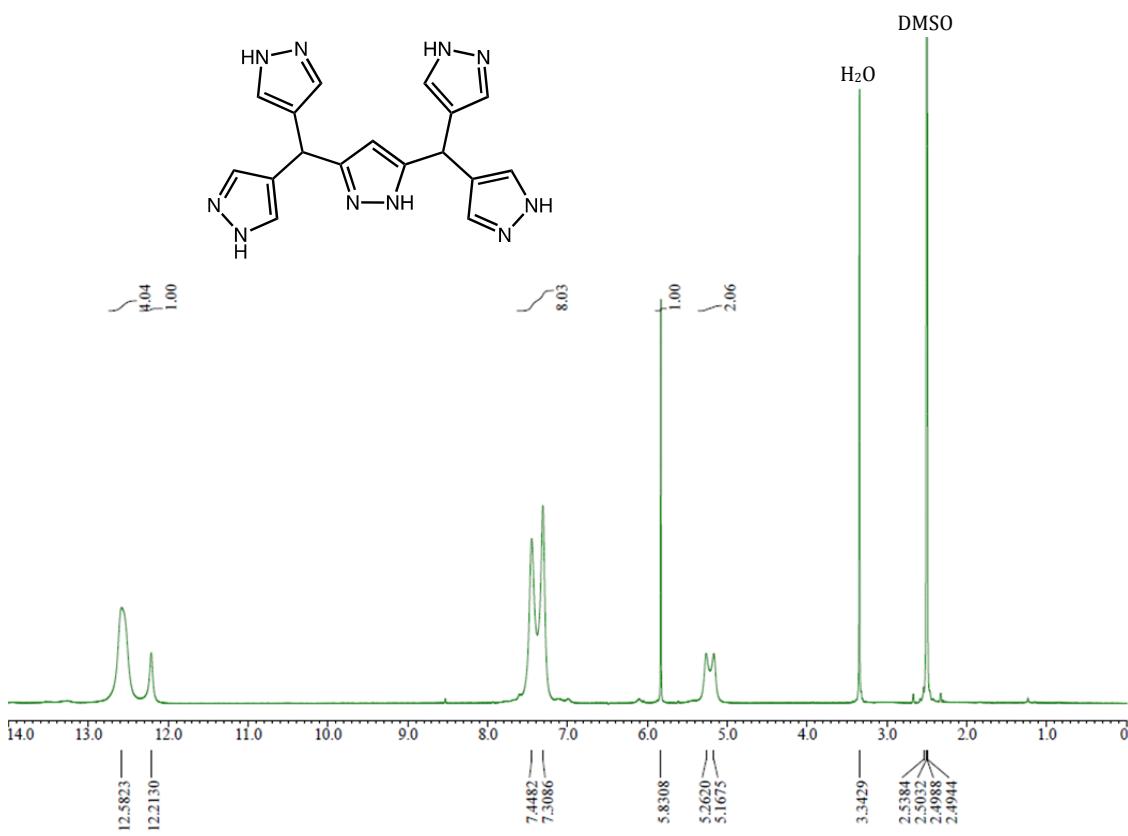
**Figure S20.**  $^{13}\text{C}$  NMR of bis(3(5)-aminopyrazol-4-yl)-pyrazol-4-yl-methane (**8a**) in  $\text{D}_2\text{O}$ .



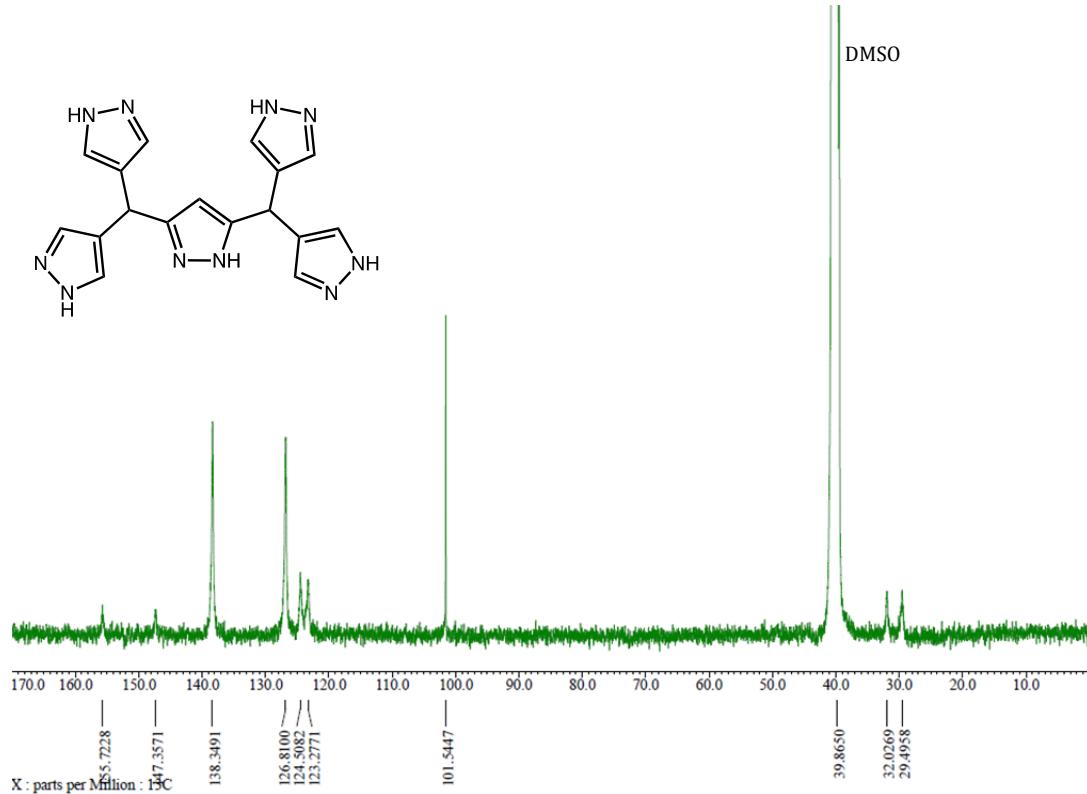
**Figure S21.**  $^1\text{H}$  NMR spectrum of bis(3(5)-hydroxypyrazol-4-yl)-pyrazol-4-yl-methane (**8b**) in  $\text{DMSO}-d_6$ .



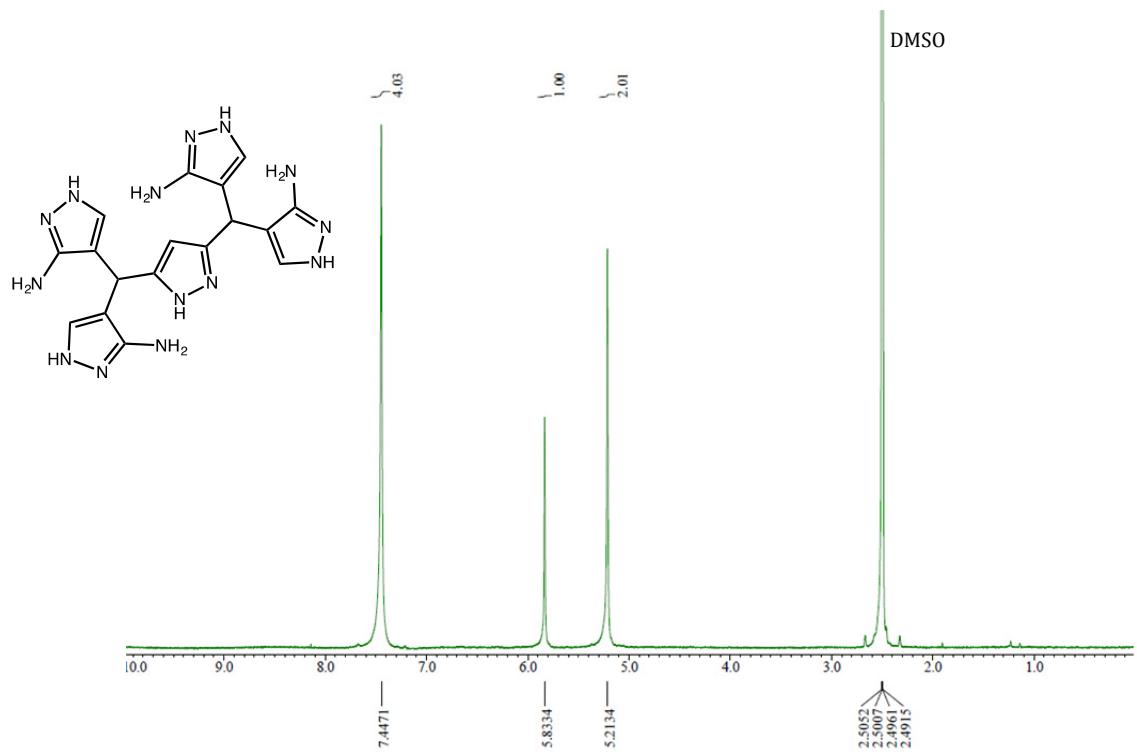
**Figure S22.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-hydroxypyrazol-4-yl)-pyrazol-4-yl-methane (**8b**) in  $\text{DMSO}-d_6$ .



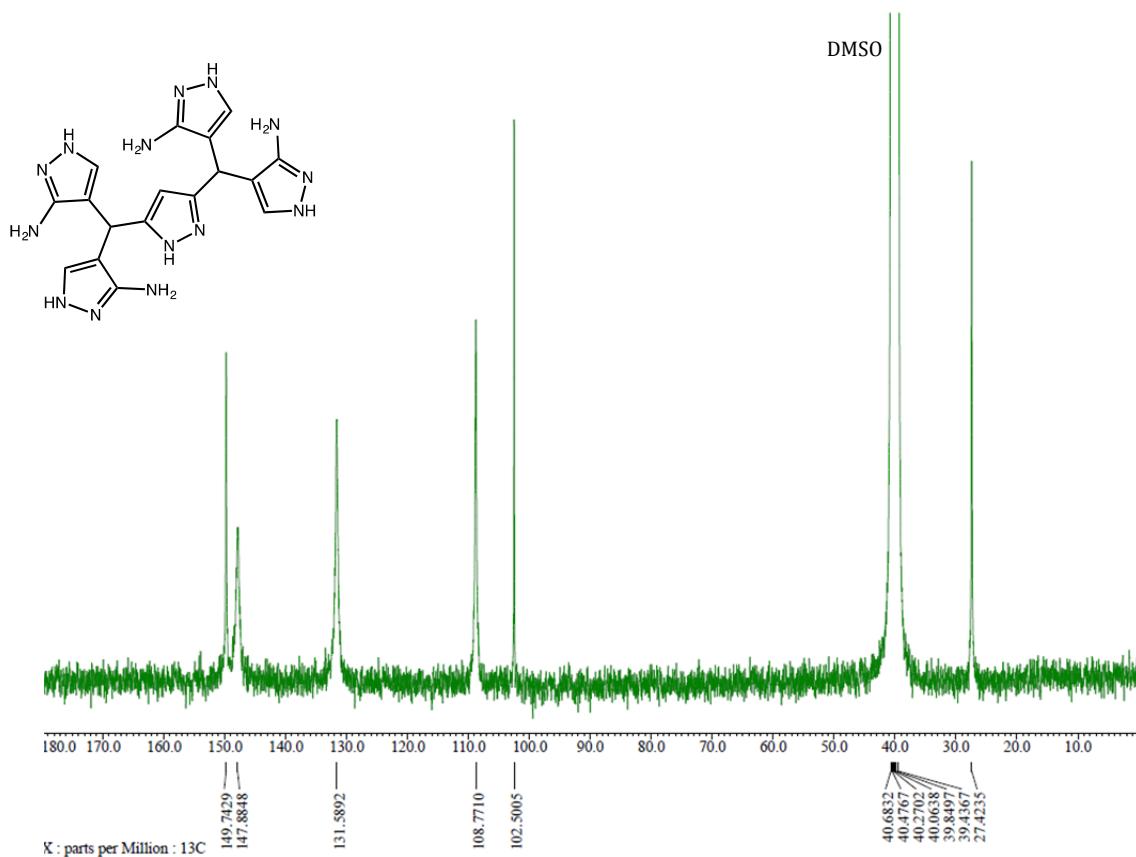
**Figure S23.** <sup>1</sup>H NMR spectrum of 3,5-bis(bis(pyrazol-4-yl)methyl)pyrazole (**9**) in DMSO-d<sub>6</sub>.



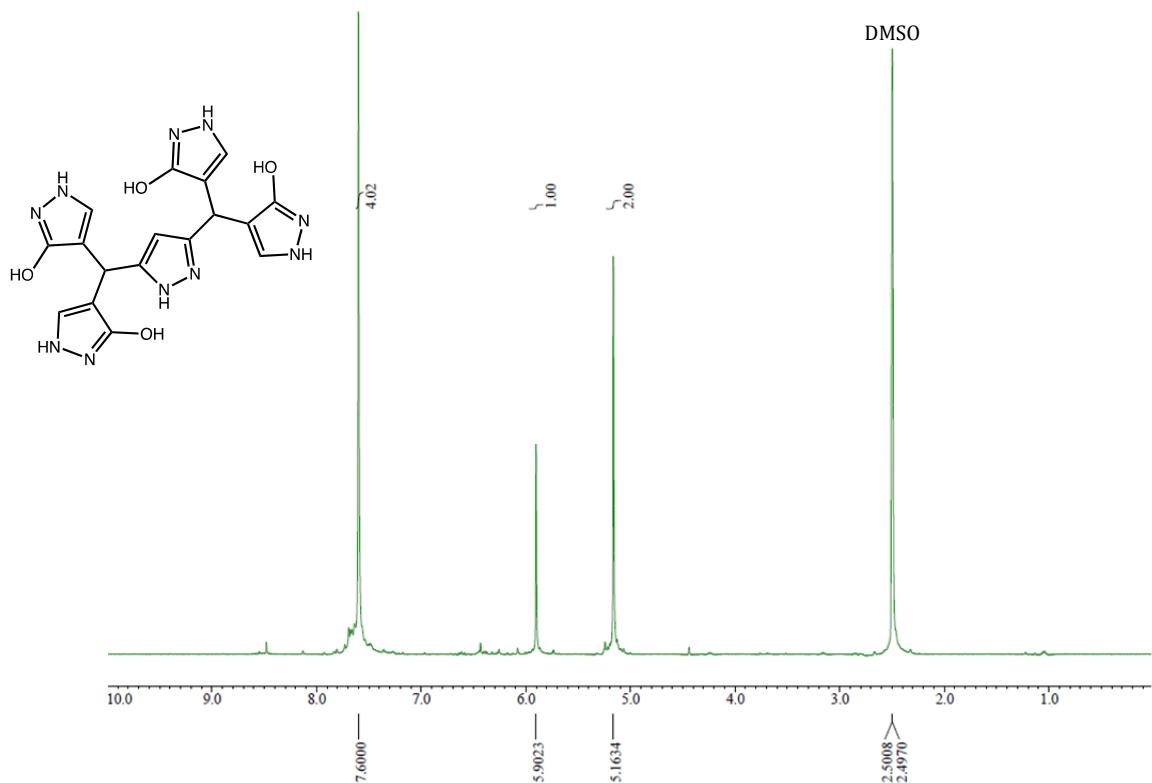
**Figure S24.** <sup>13</sup>C NMR spectrum of 3,5-bis(bis(pyrazol-4-yl)methyl)pyrazole (**9**) in DMSO-d<sub>6</sub>.



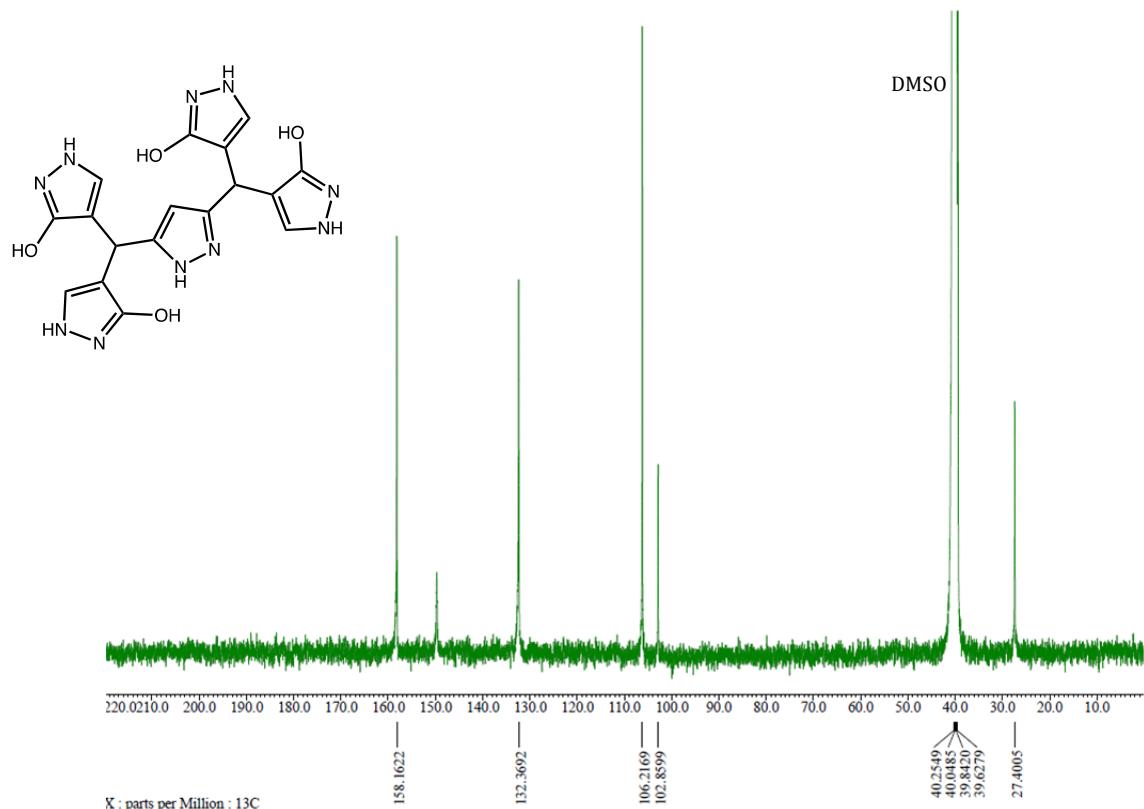
**Figure S25.** <sup>1</sup>H NMR spectrum of 3,5-bis(bis(3(5)-aminopyrazol-4-yl)methyl)pyrazole (**9a**) in DMSO-*d*<sub>6</sub>.



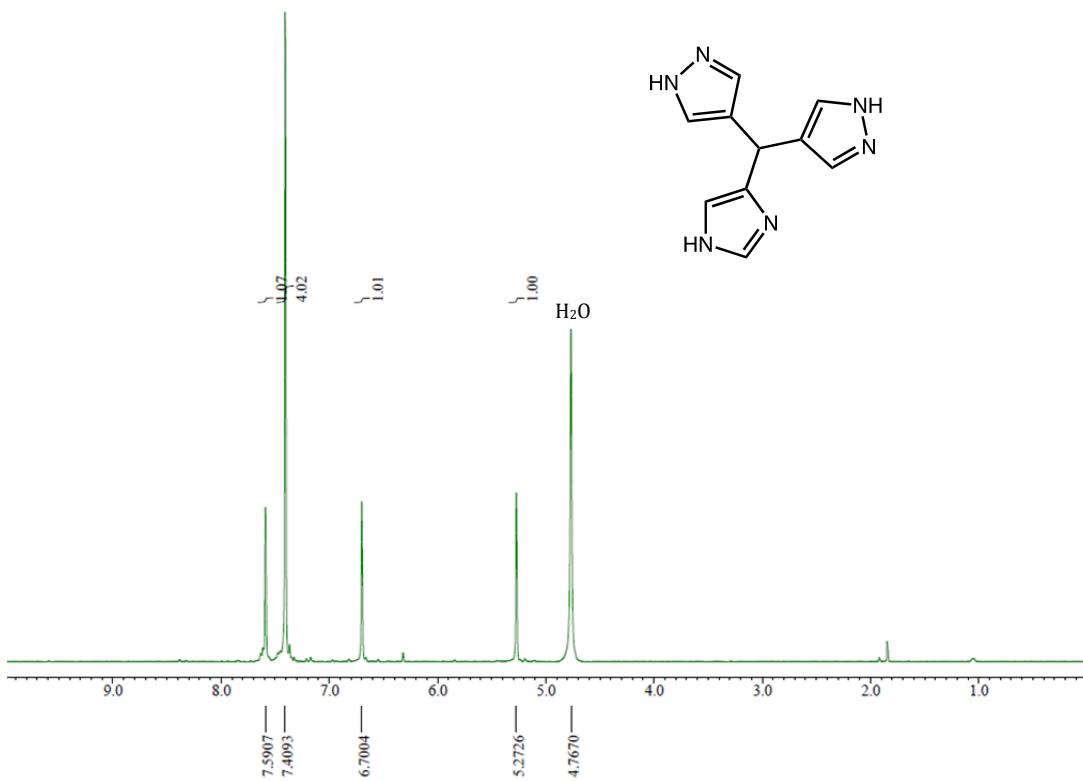
**Figure S26.** <sup>13</sup>C NMR spectrum of 3,5-bis(bis(3(5)-aminopyrazol-4-yl)methyl)pyrazole (**9a**) in DMSO-*d*<sub>6</sub>.



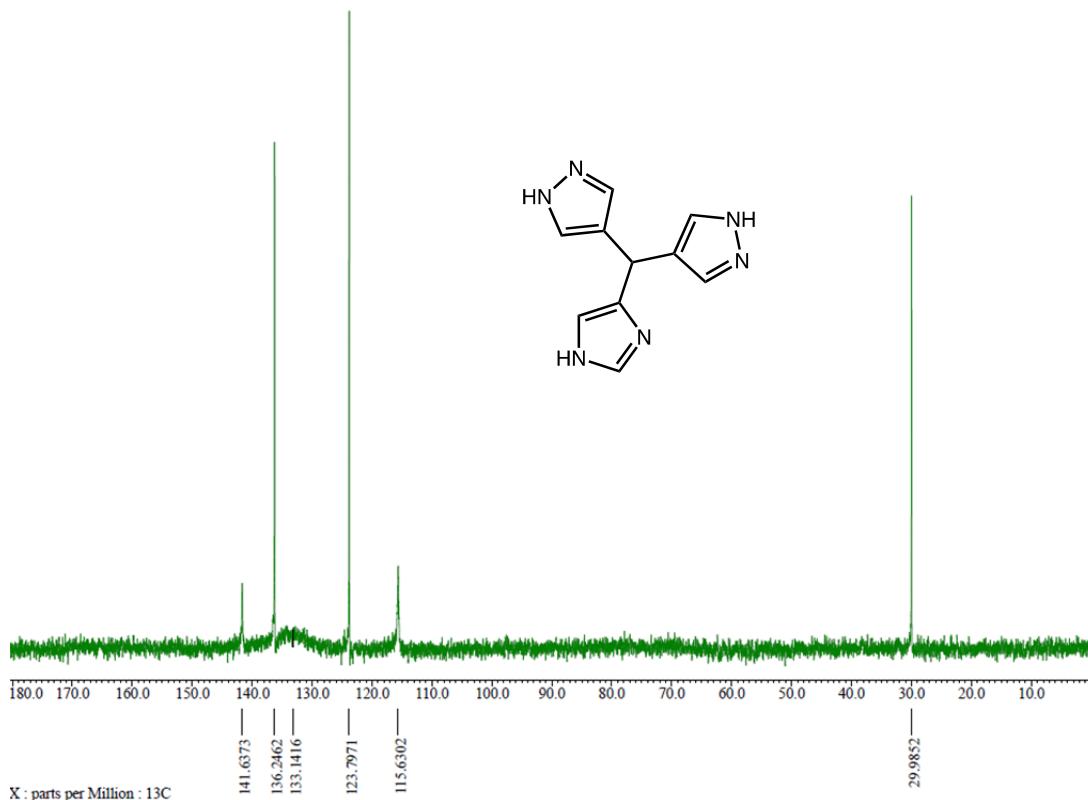
**Figure S27.**  $^1\text{H}$  NMR spectrum of 3,5-bis(bis(3(5)-hydroxypyrazol-4-yl)methyl)pyrazole (**9b**) in  $\text{DMSO}-d_6$ .



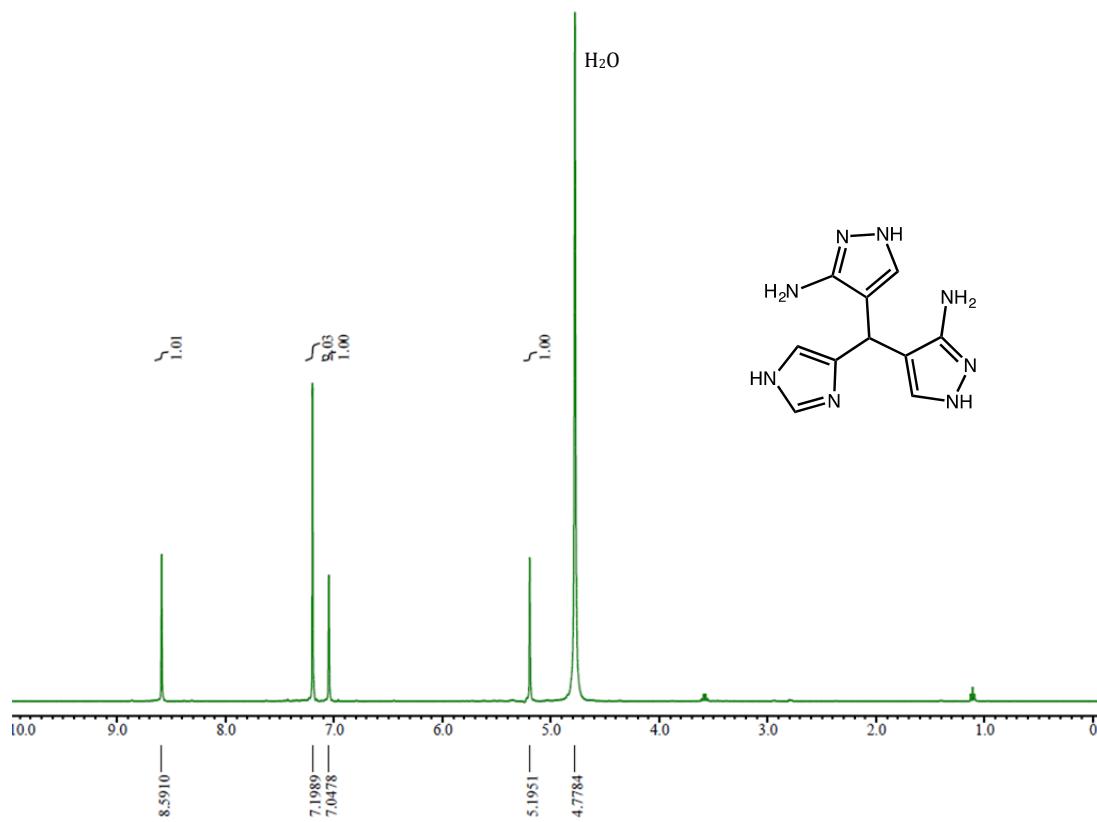
**Figure S28.**  $^{13}\text{C}$  NMR spectrum of 3,5-bis(bis(3(5)-hydroxypyrazol-4-yl)methyl)pyrazole (**9b**) in  $\text{DMSO}-d_6$ .



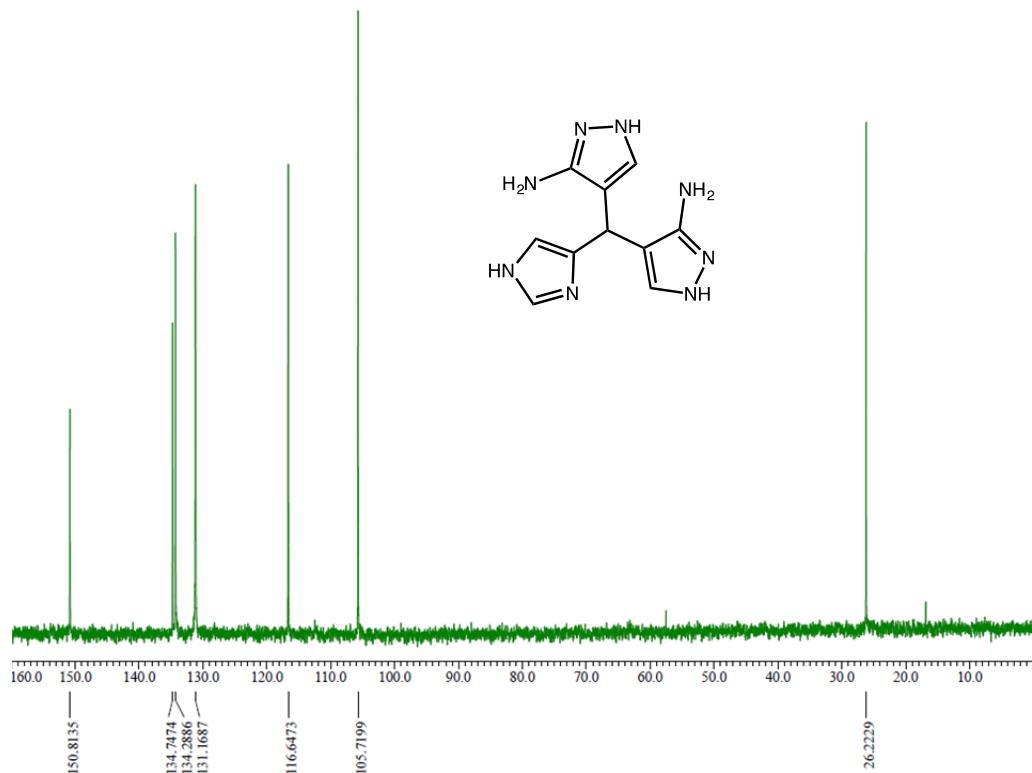
**Figure S29.** <sup>1</sup>H NMR spectrum of imidazol-4-yl-bis(pyrazol-4-yl)methane (**10**) in  $\text{D}_2\text{O}$ .



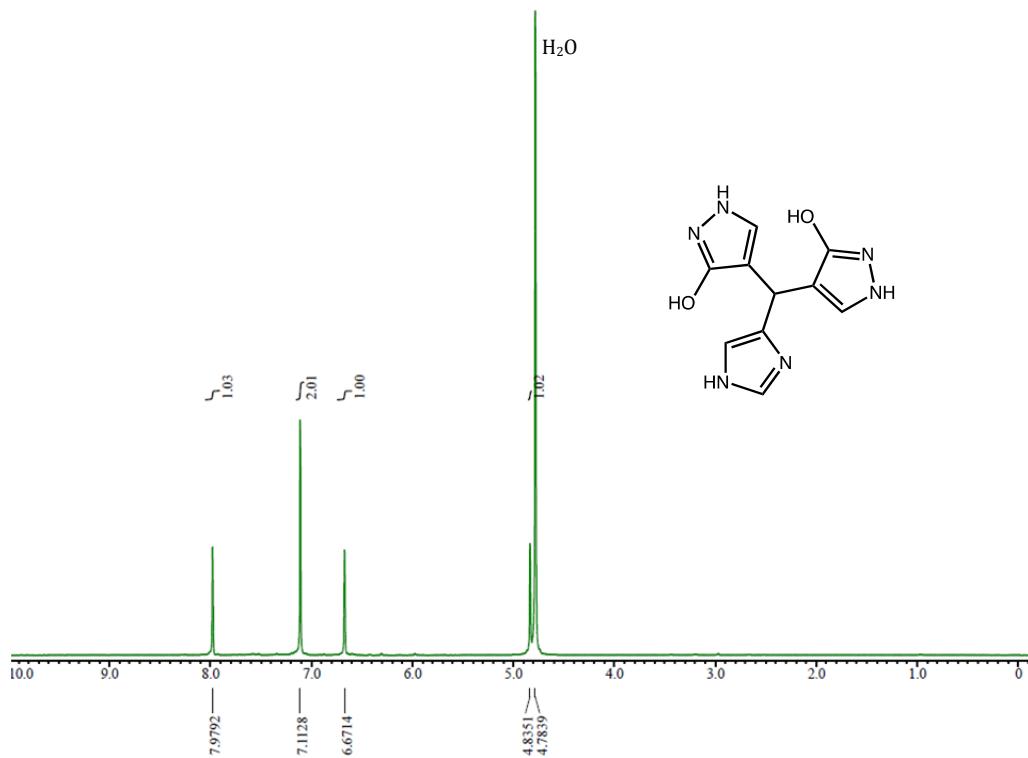
**Figure S30.** <sup>13</sup>C NMR spectrum of imidazol-4-yl-bis(pyrazol-4-yl)methane (**10**) in  $\text{D}_2\text{O}$ .



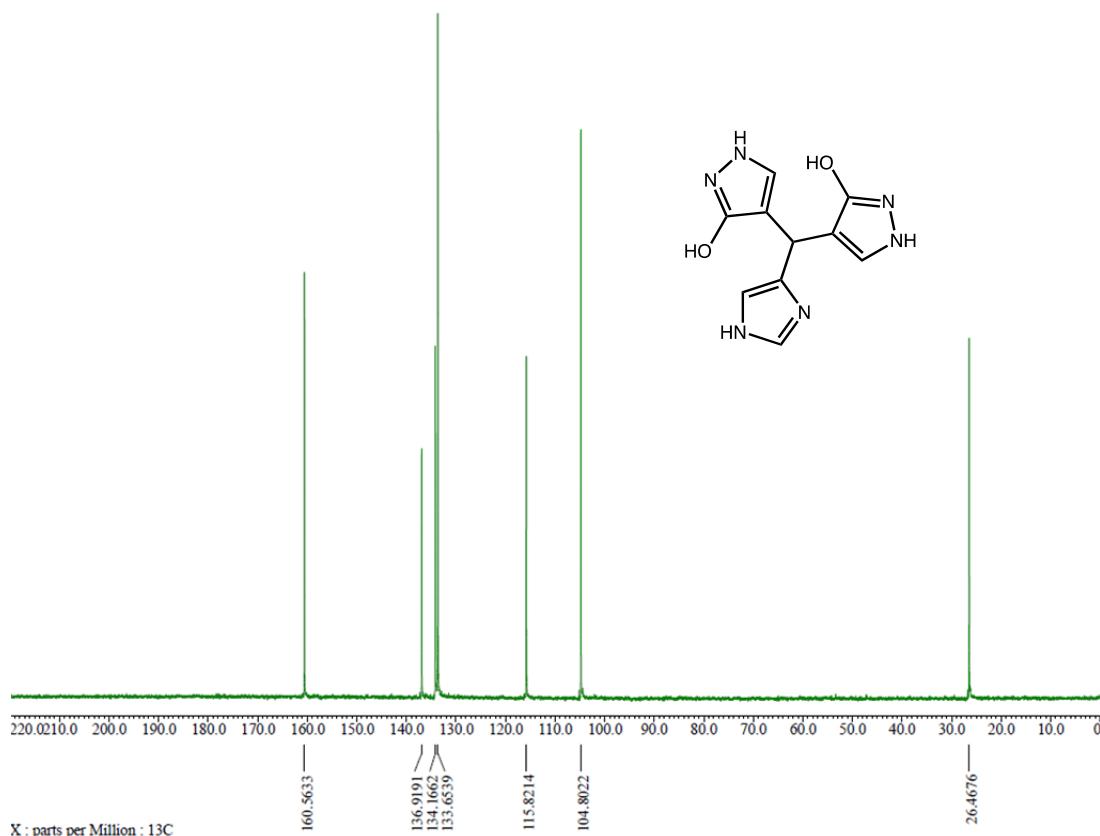
**Figure S31.**  $^1\text{H}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-imidazol-2-yl-methane (**10a**) in  $\text{D}_2\text{O}$ .



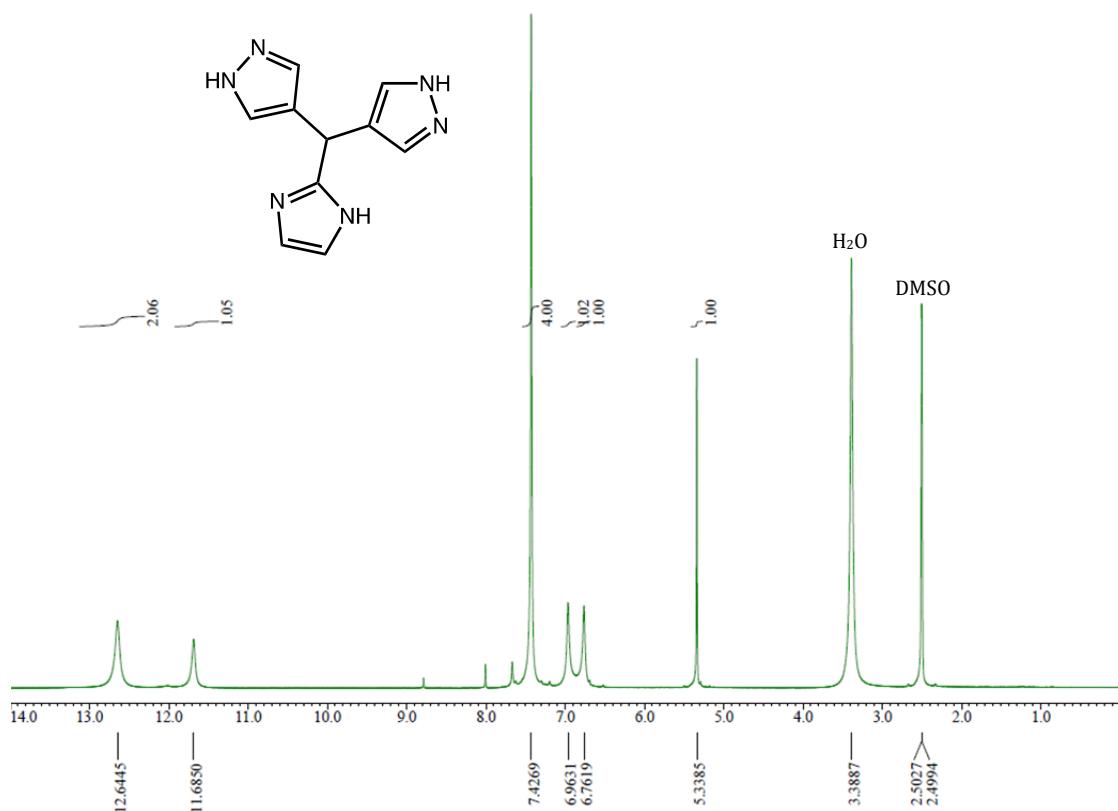
**Figure S32.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-imidazol-2-yl-methane (**10a**) in  $\text{D}_2\text{O}$ .



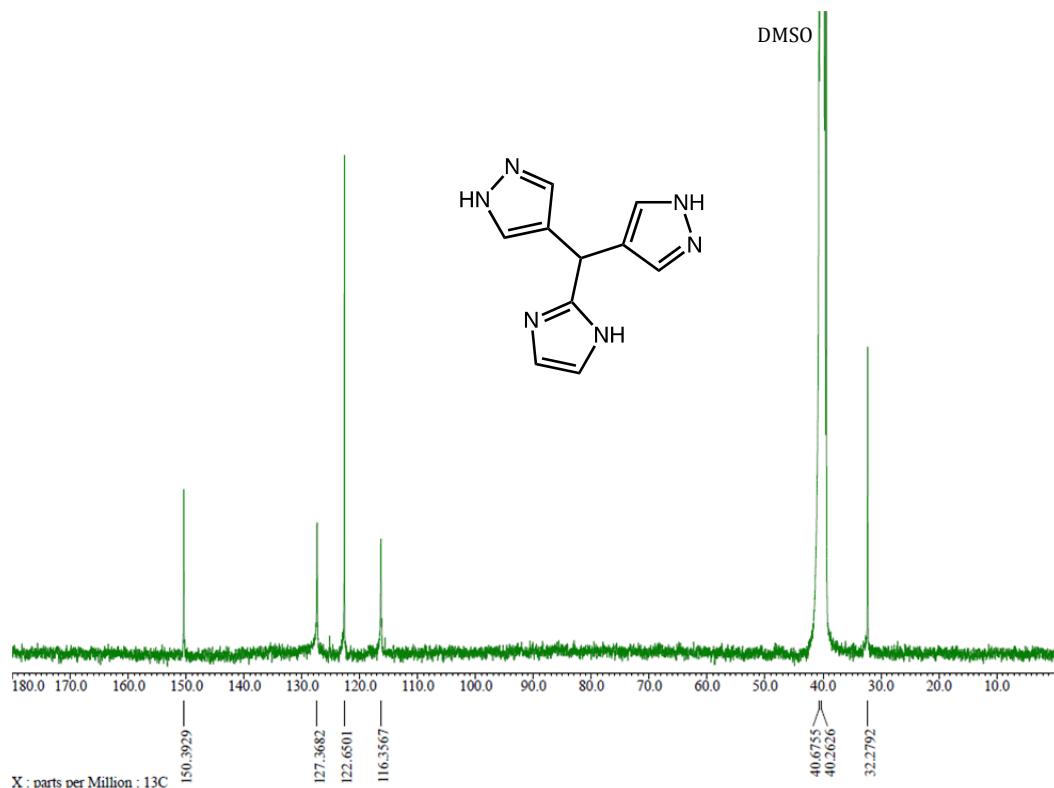
**Figure S33.**  $^1\text{H}$  NMR spectrum of bis(3(5)-hydroxypyrazol-4-yl)-imidazol-2-yl-methane (**10b**) in  $\text{D}_2\text{O}$ .



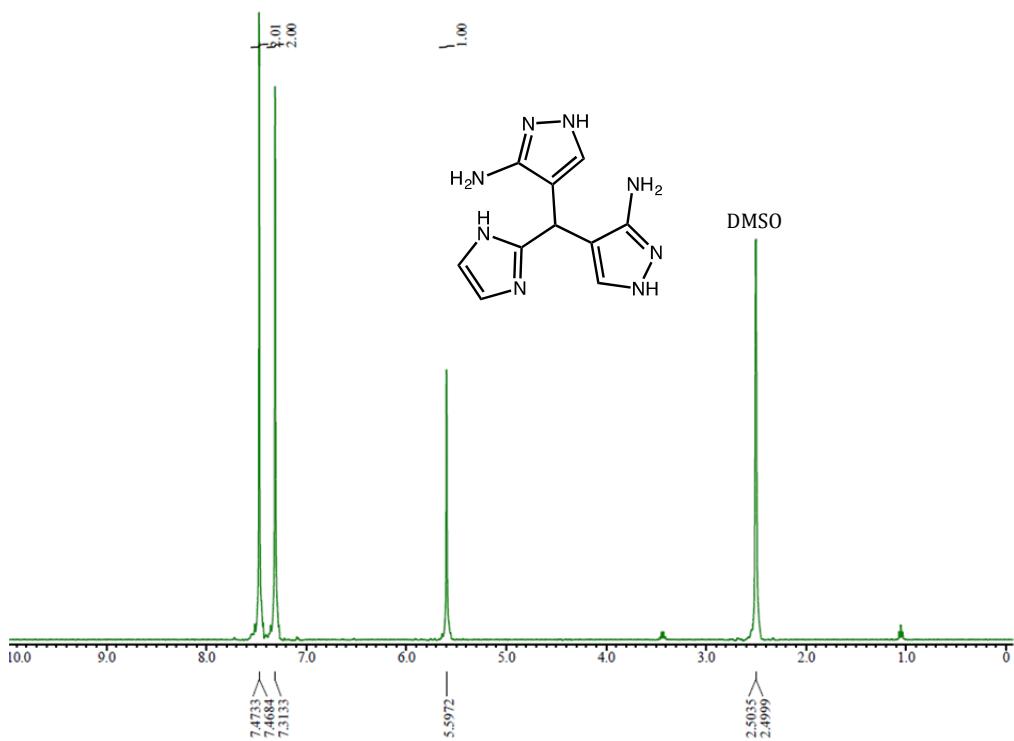
**Figure S34.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-hydroxypyrazol-4-yl)-imidazol-2-yl-methane (**10b**) in  $\text{D}_2\text{O}$ .



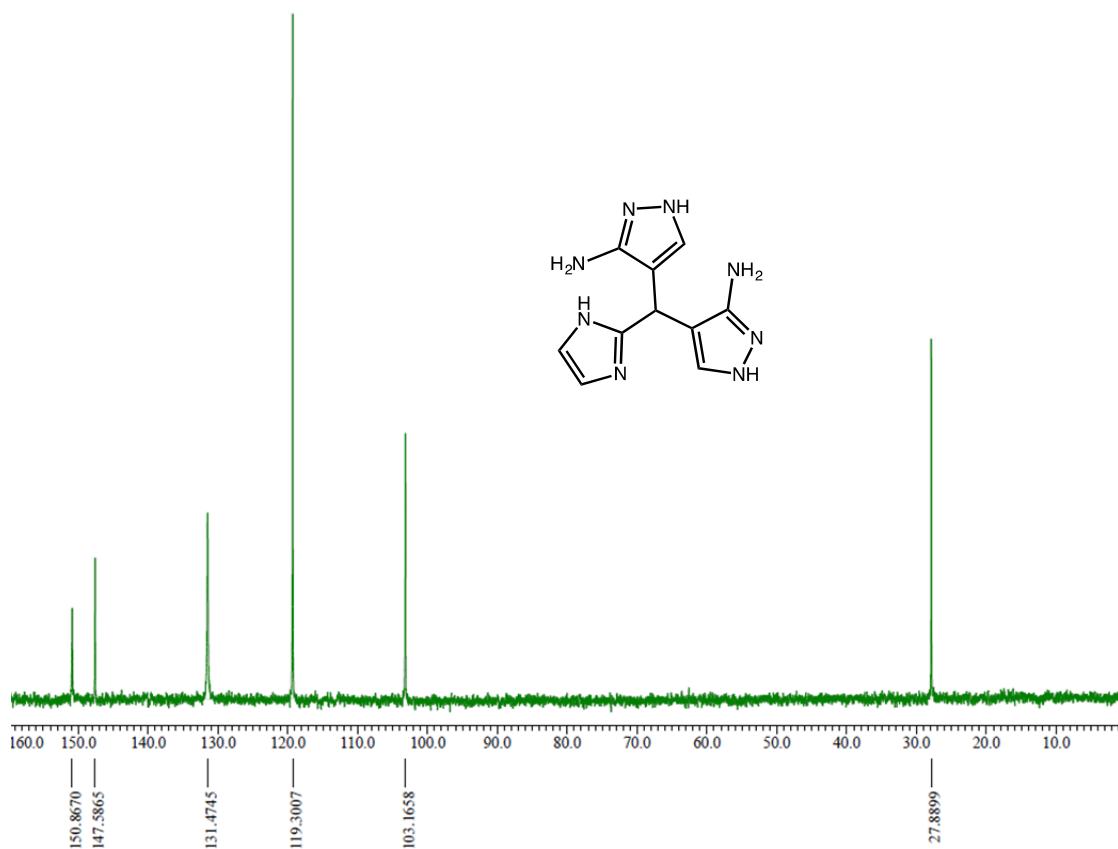
**Figure S35.**  $^1\text{H}$  NMR spectrum of imidazol-2-yl-bis(pyrazol-4-yl)methane (**11**) in  $\text{DMSO}-d_6$ .



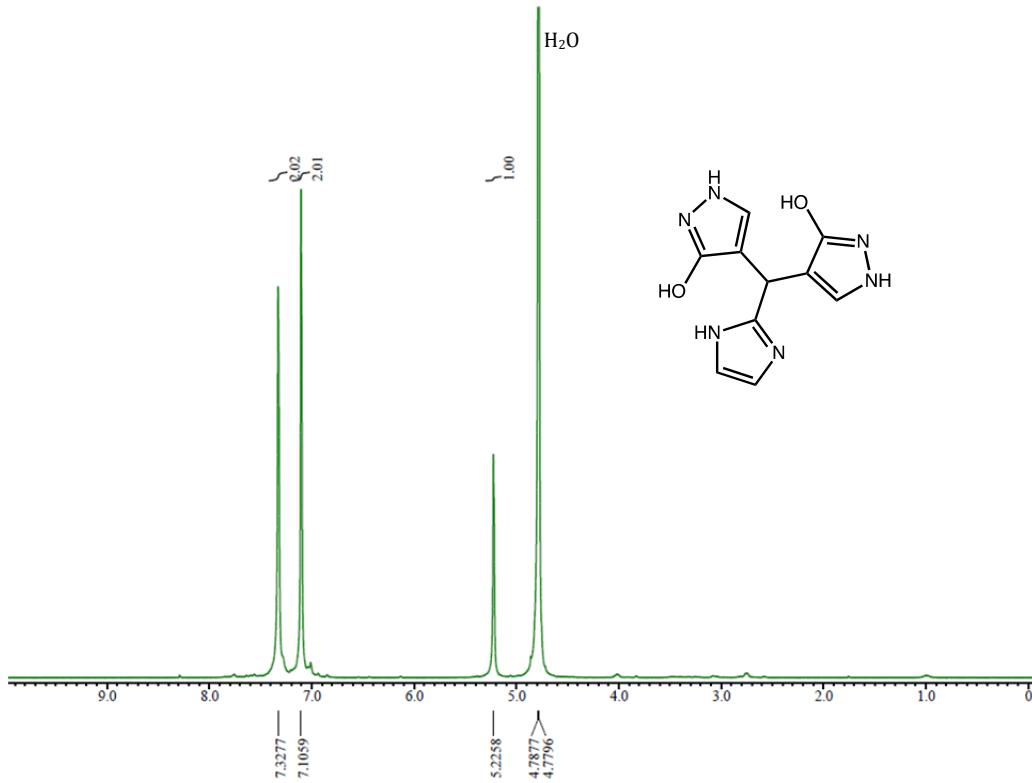
**Figure S36.**  $^{13}\text{C}$  NMR spectrum of imidazol-2-yl-bis(pyrazol-4-yl)methane (**11**) in  $\text{DMSO}-d_6$ .



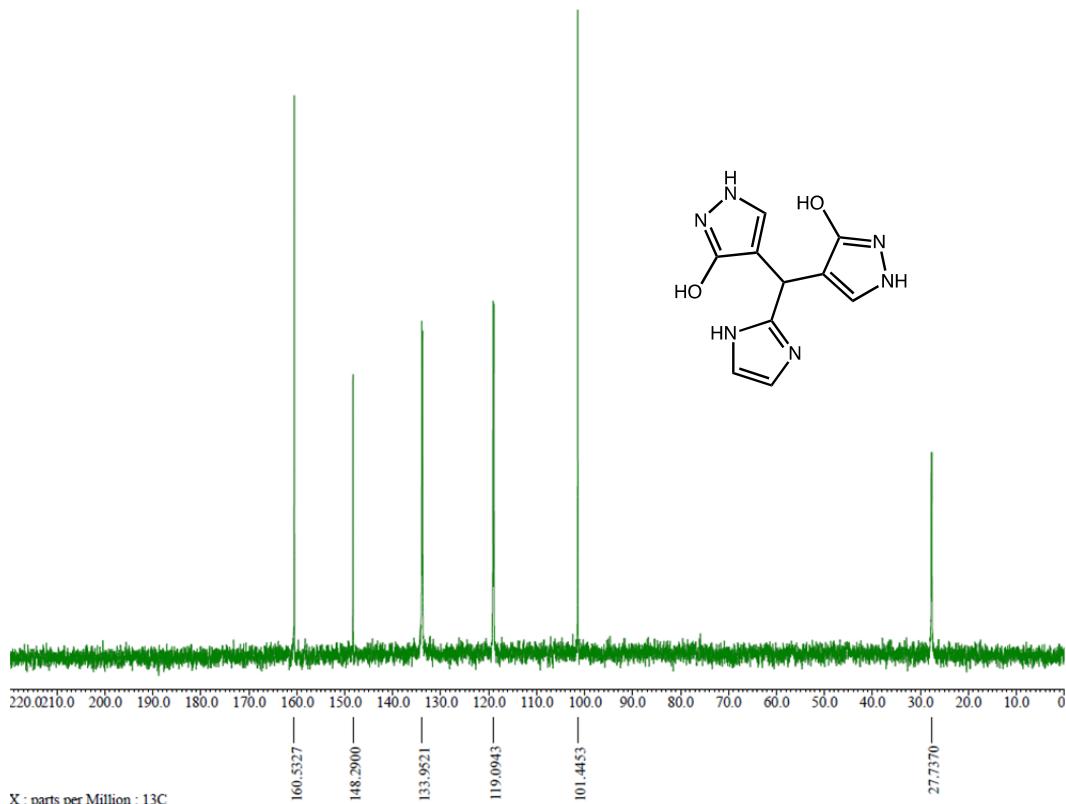
**Figure S37.**  $^1\text{H}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-imidazol-4-yl-methane (**11a**) in  $\text{DMSO}-d_6$ .



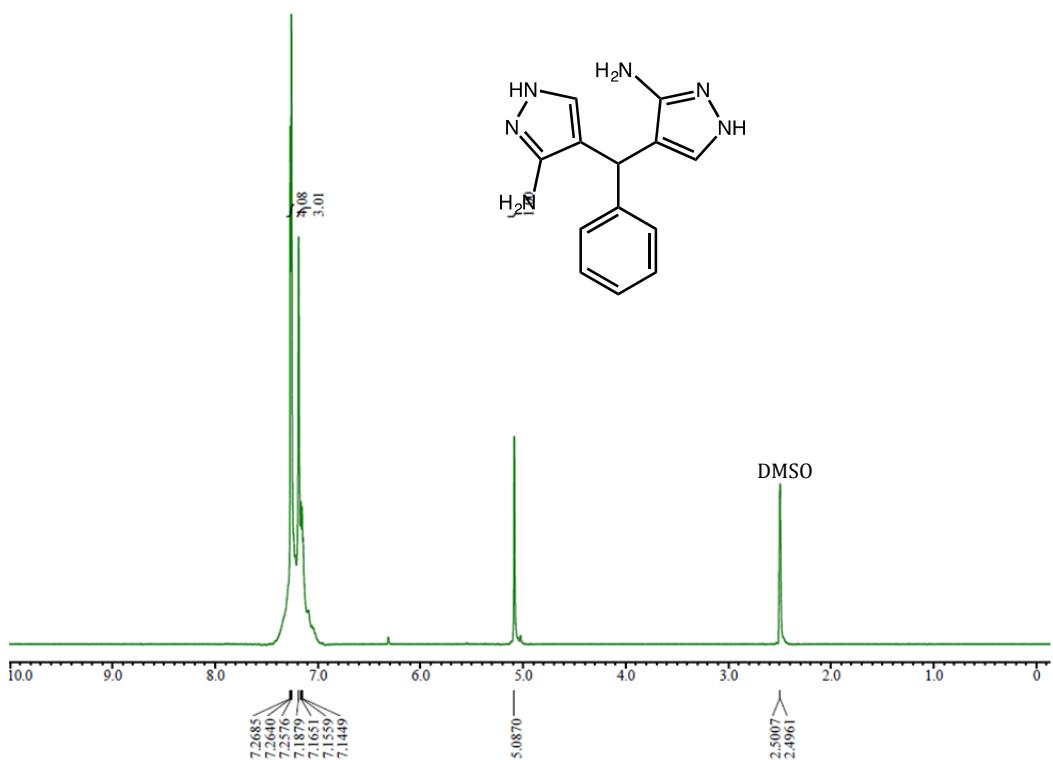
**Figure S38.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-imidazol-4-yl-methane (**11a**) in  $\text{D}_2\text{O}$ .



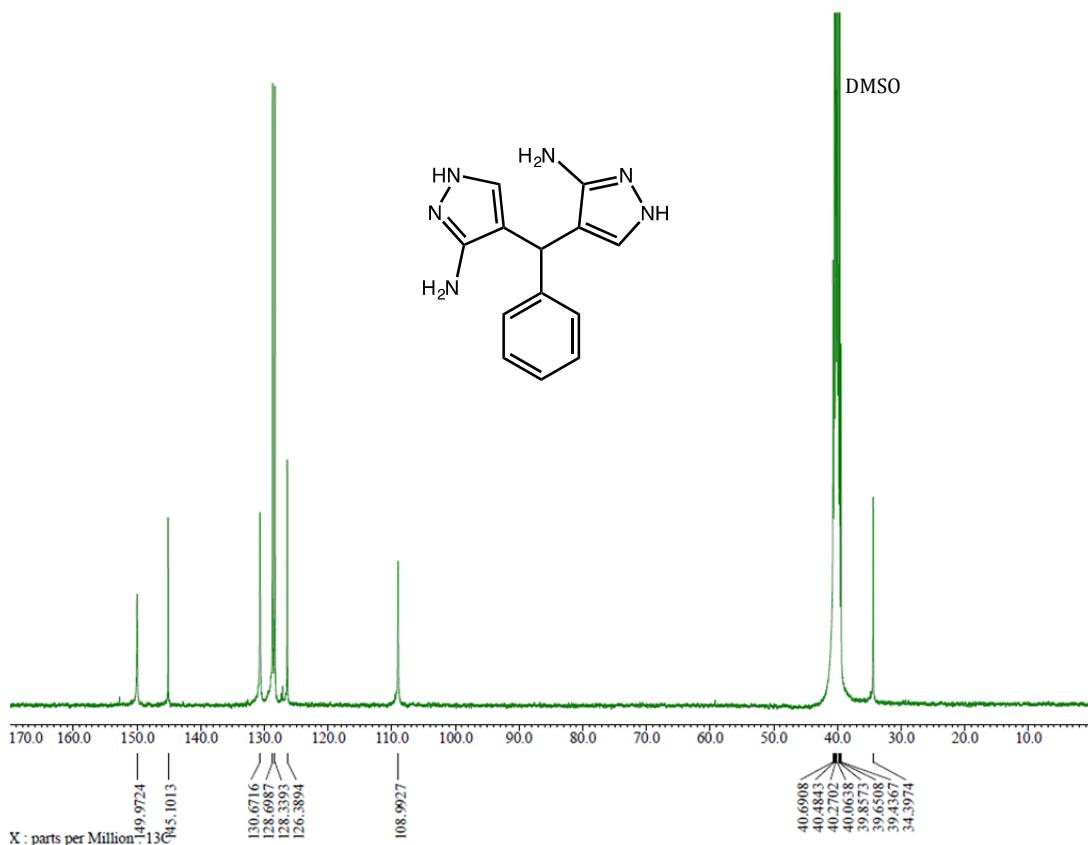
**Figure S39.** <sup>1</sup>H NMR spectrum of bis(3(5)-hydroxypyrazol-4-yl)-imidazol-4-yl-methane (**11b**) in D<sub>2</sub>O.



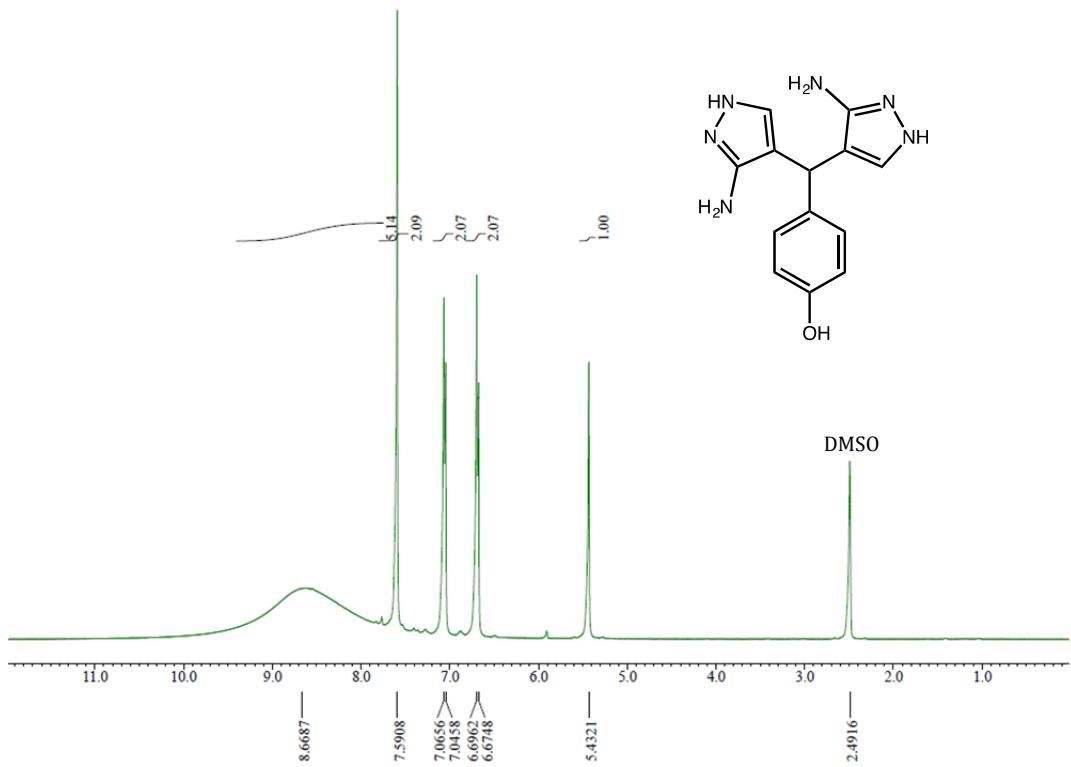
**Figure S40.** <sup>13</sup>C NMR spectrum of bis(3(5)-hydroxypyrazol-4-yl)-imidazol-4-yl-methane (**11b**) in D<sub>2</sub>O.



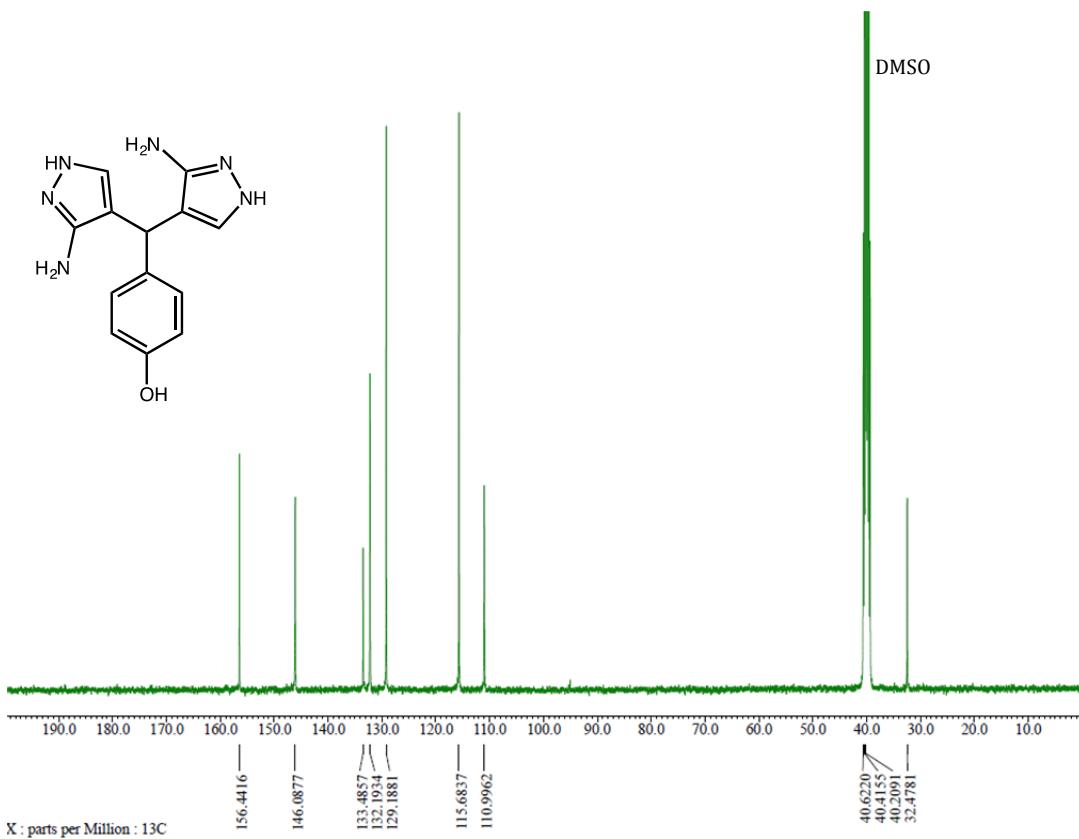
**Figure S41.**  $^1\text{H}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-phenyl-methane (**12a**) in  $\text{DMSO}-d_6$ .



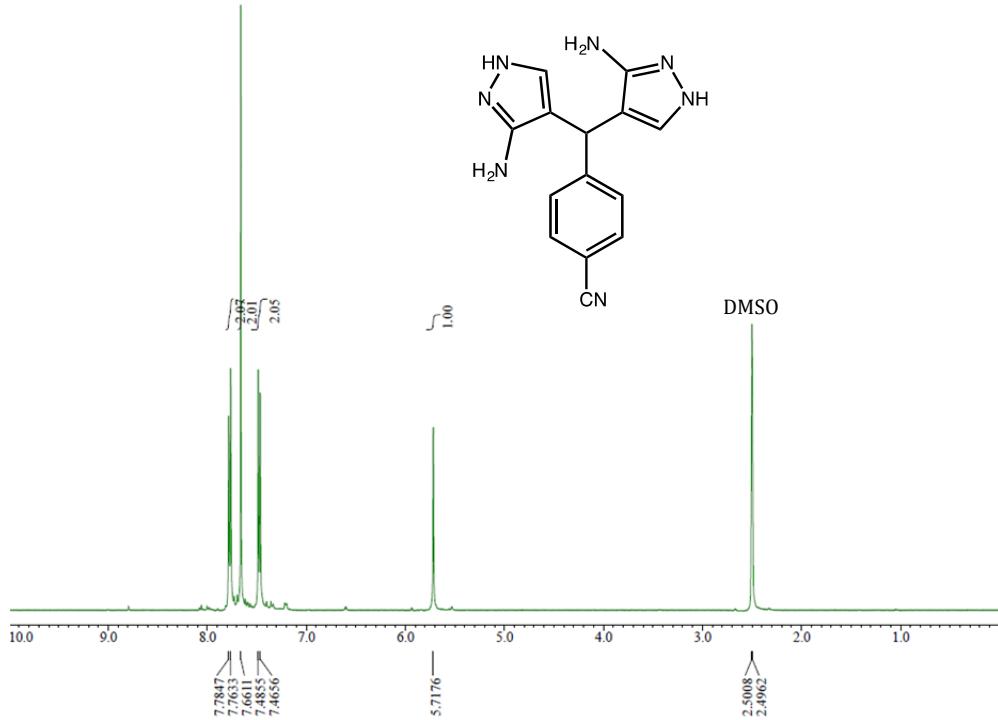
**Figure S42.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-phenyl-methane (**12a**) in  $\text{DMSO}-d_6$ .



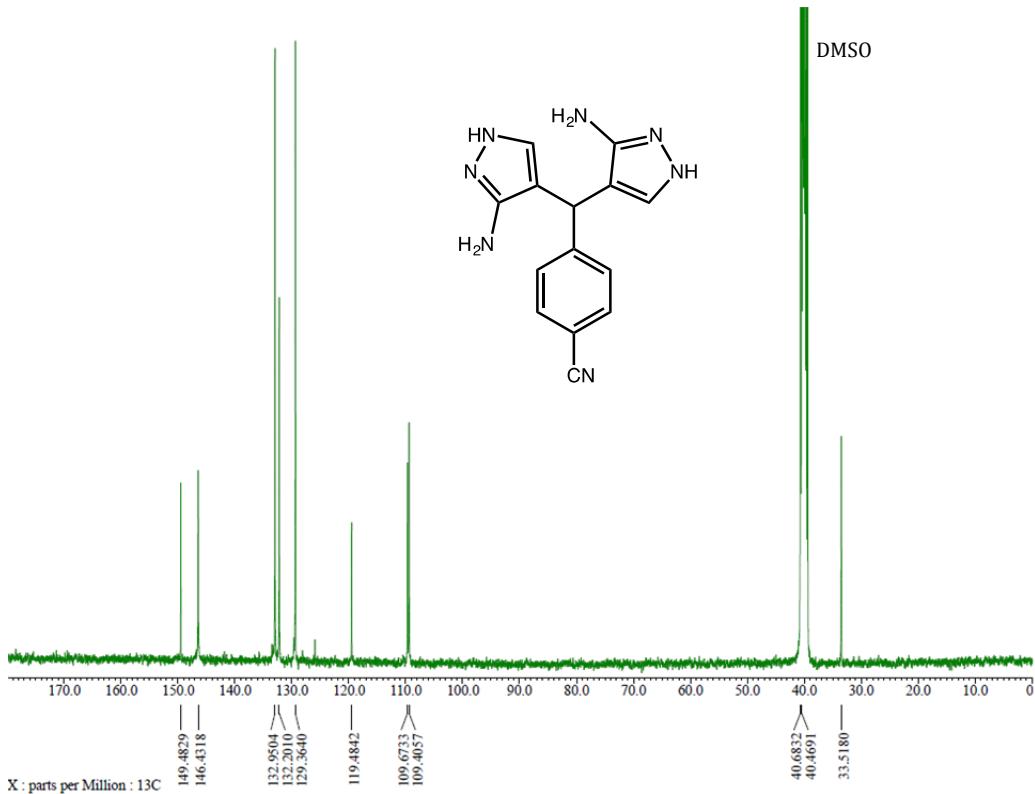
**Figure S43.**  $^1\text{H}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-4-hydroxyphenyl-methane (**13a**) in  $\text{DMSO}-d_6$ .



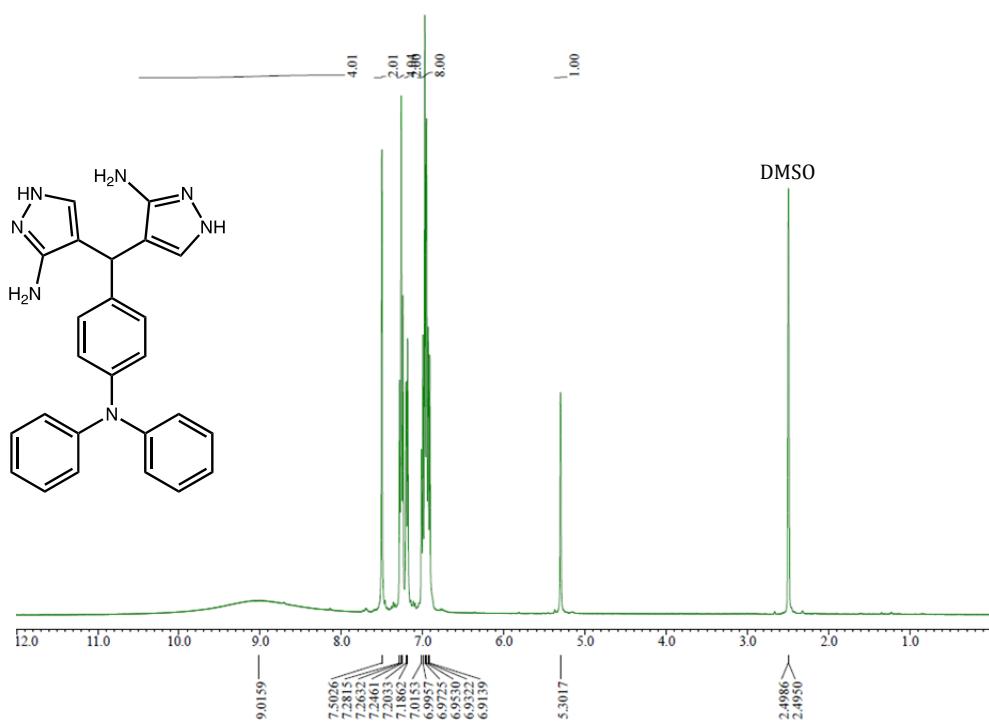
**Figure S44.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-4-hydroxyphenyl-methane (**13a**) in  $\text{DMSO}-d_6$ .



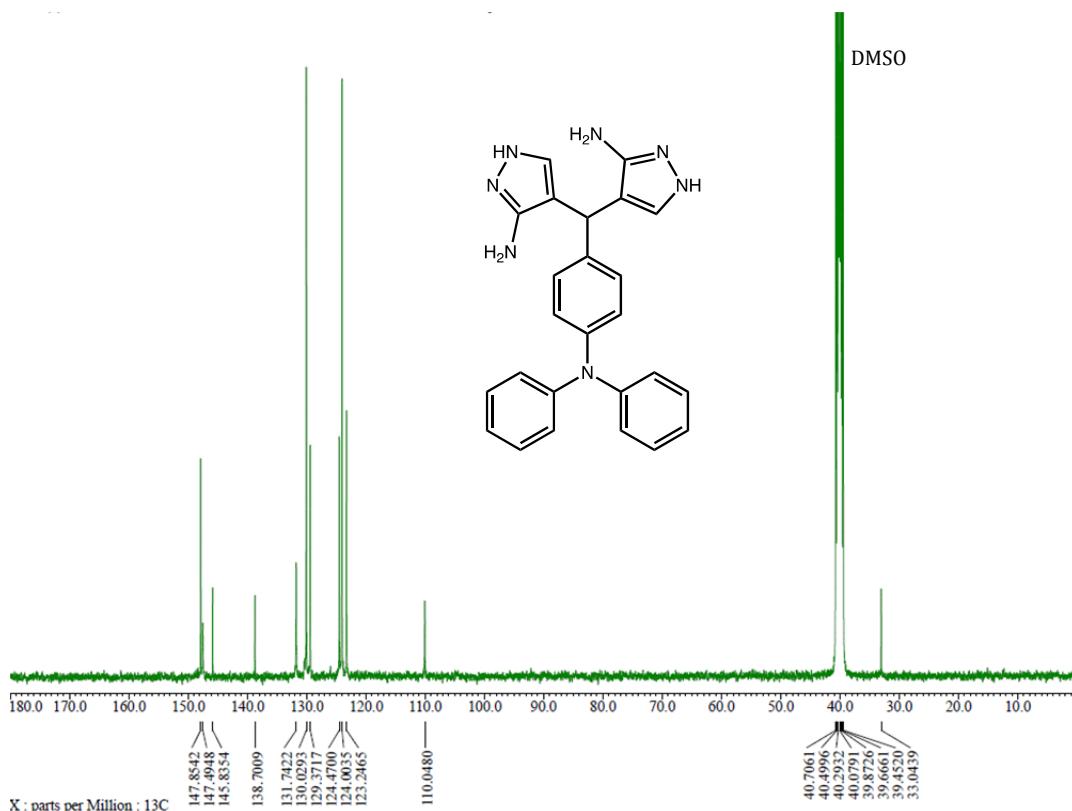
**Figure S45.**  $^1\text{H}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-4-cyanophenyl-methane (**14a**) in  $\text{DMSO}-d_6$ .



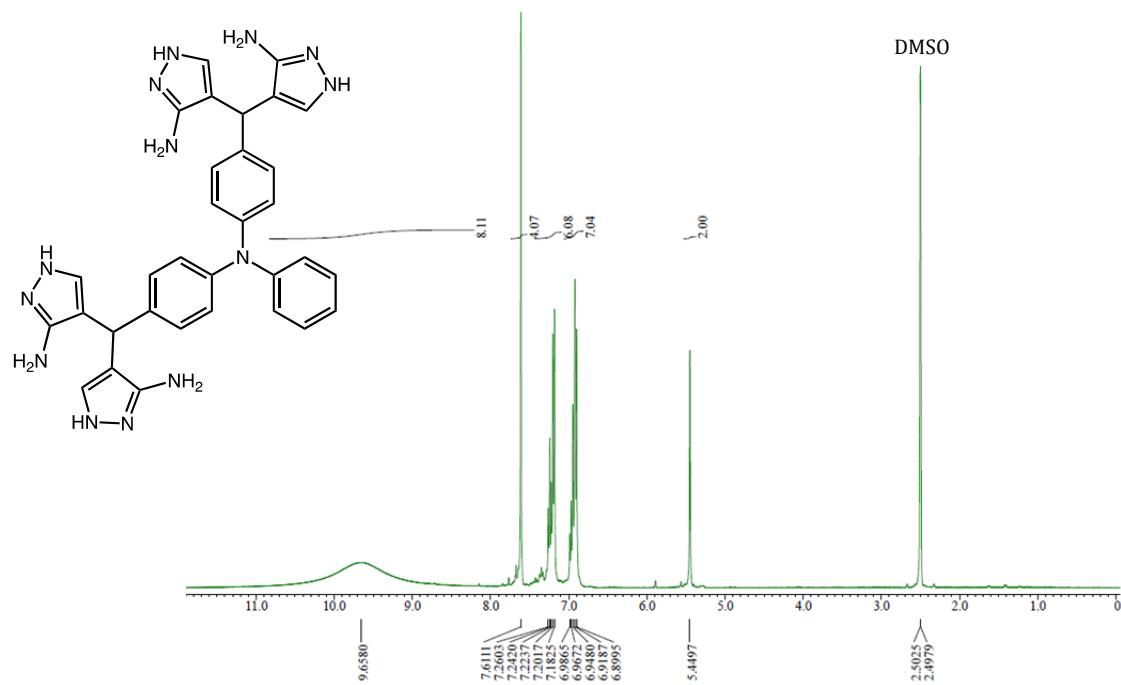
**Figure S46.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-4-cyanophenyl-methane (**14a**) in  $\text{DMSO}-d_6$ .



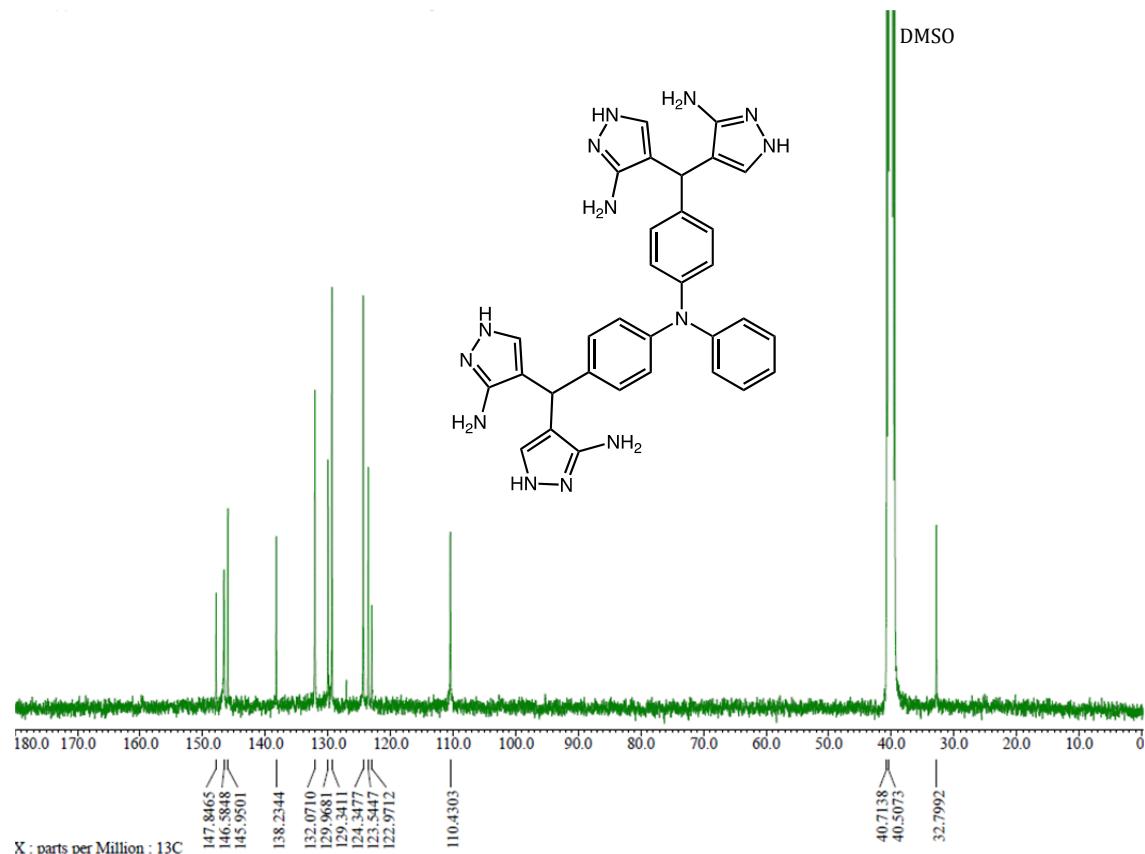
**Figure S47.** <sup>1</sup>H NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-4-(N,N-diphenylamino)phenylmethane (**15a**) in DMSO-d<sub>6</sub>.



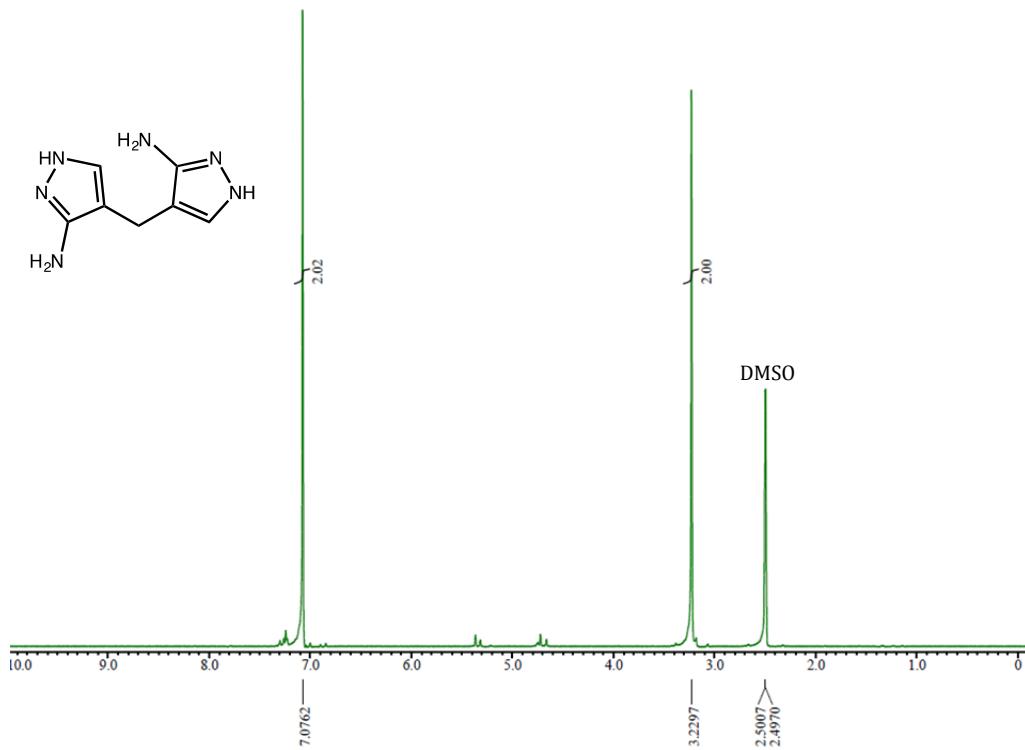
**Figure S48.** <sup>13</sup>C NMR spectrum of bis(3(5)-aminopyrazol-4-yl)-4-(N,N-diphenylamino)phenylmethane (**15a**) in DMSO-d<sub>6</sub>.



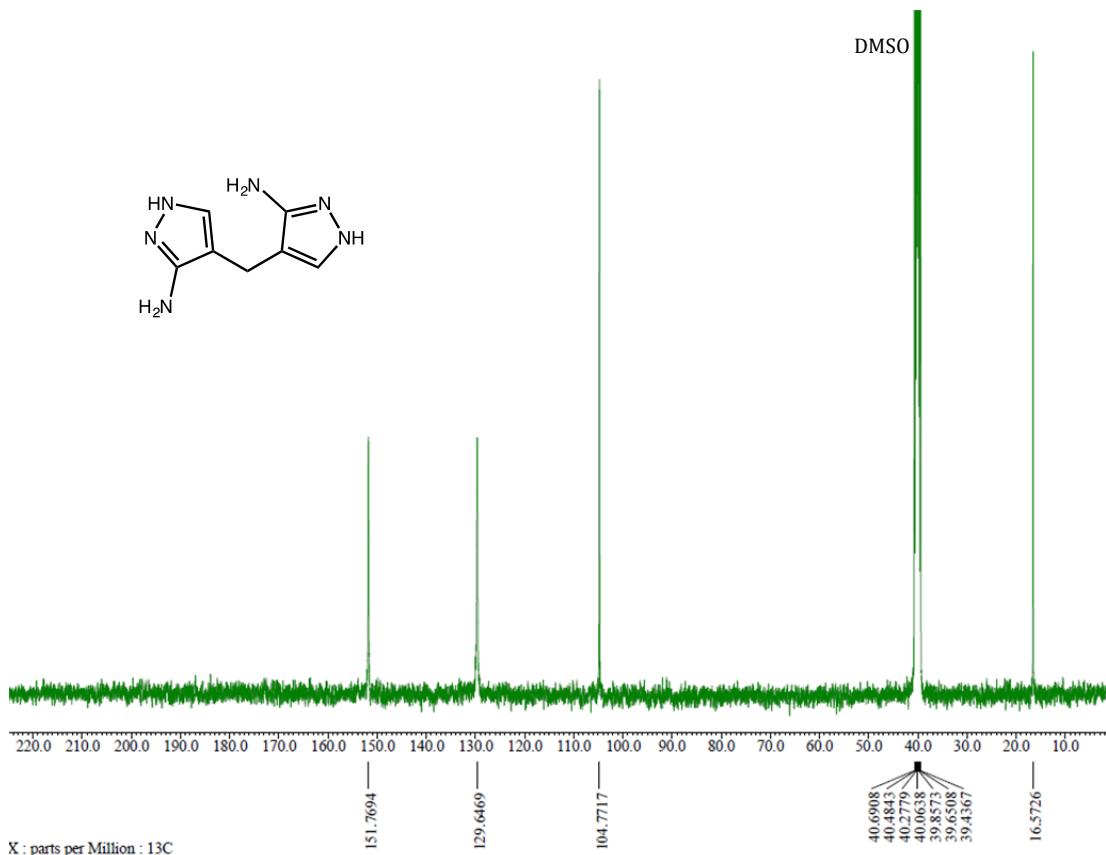
**Figure S49.**  $^1\text{H}$  NMR spectrum of  $N,N$ -bis(bis(3(5)-aminopyrazol-4-yl)methylphenyl)aniline (**16a**) in  $\text{DMSO-d}_6$ .



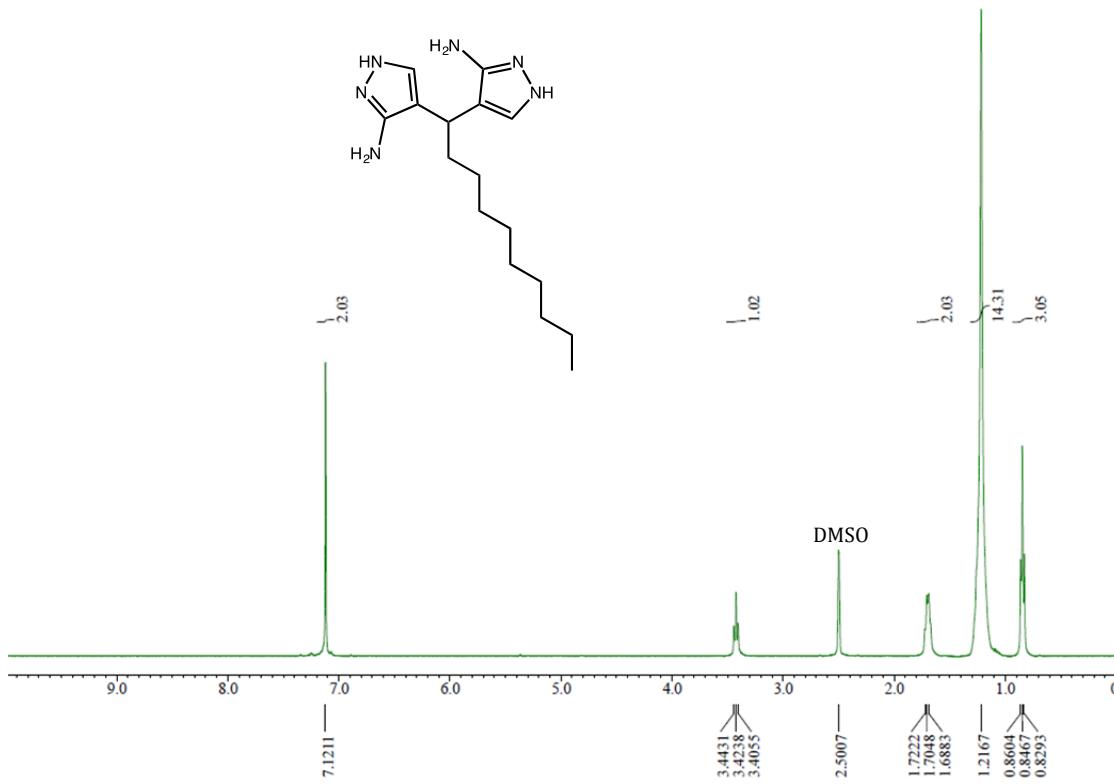
**Figure S50.**  $^{13}\text{C}$  NMR spectrum of  $N,N$ -bis(bis(3(5)-aminopyrazol-4-yl)methylphenyl)aniline (**16a**) in  $\text{DMSO-d}_6$ .



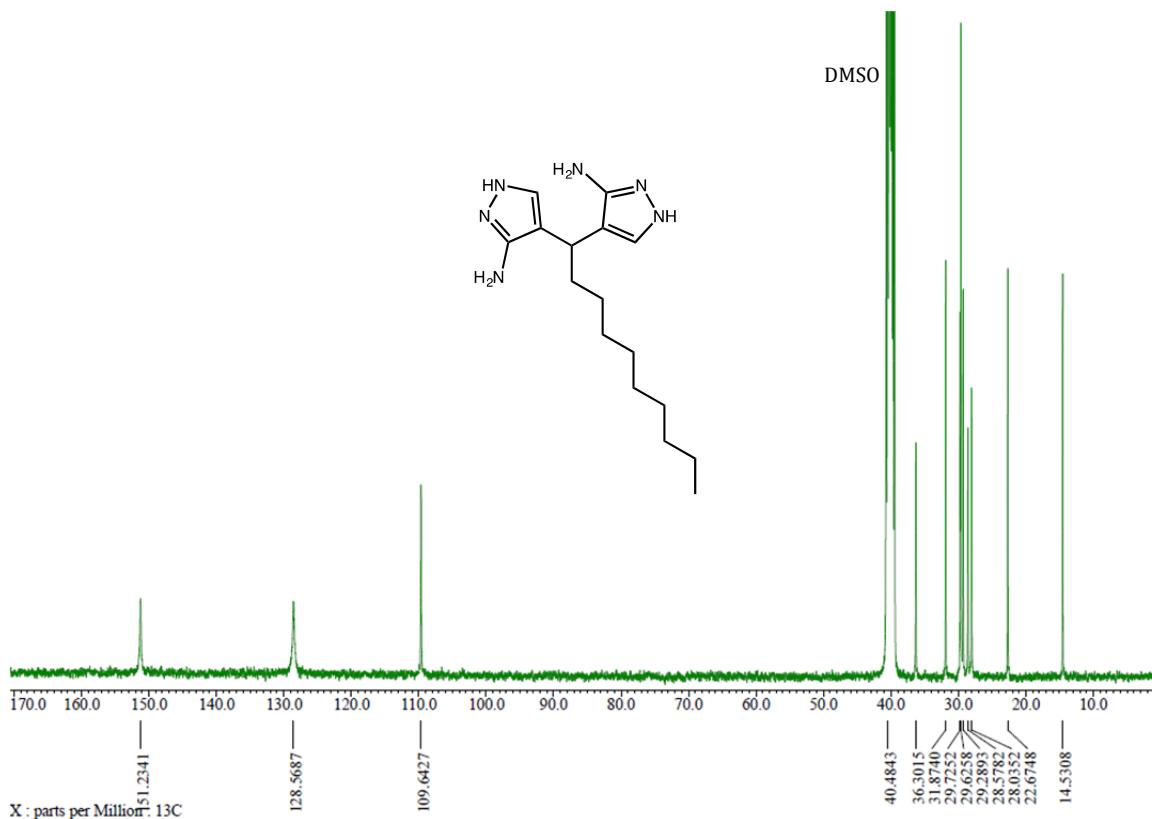
**Figure S51.**  $^1\text{H}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)methane (**17a**) in  $\text{DMSO}-d_6$ .



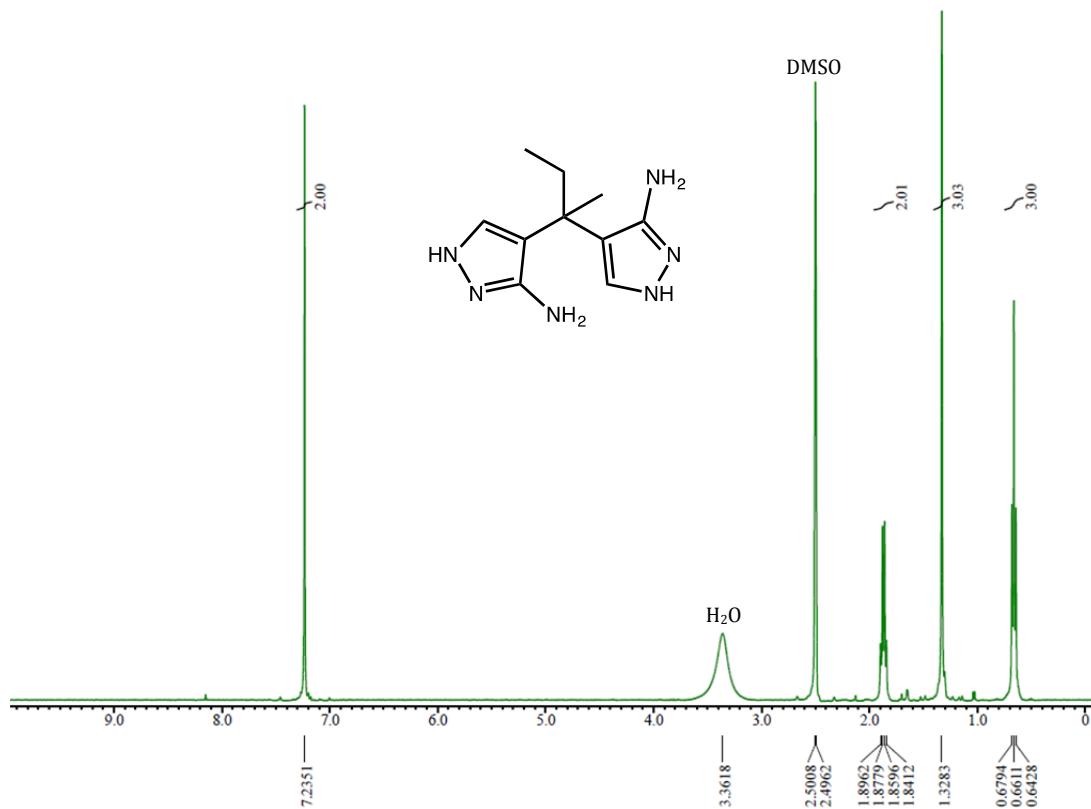
**Figure S52.**  $^{13}\text{C}$  NMR spectrum of bis(3(5)-aminopyrazol-4-yl)methane (**17a**) in  $\text{DMSO}-d_6$ .



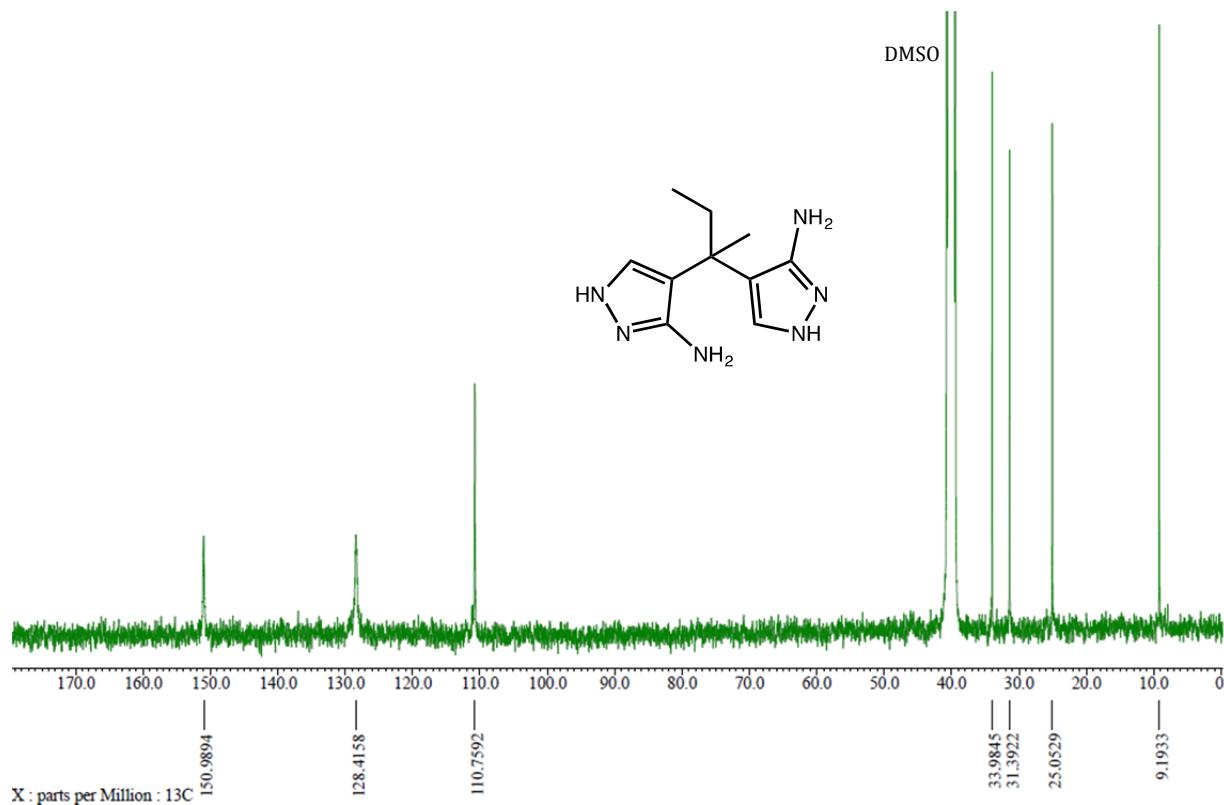
**Figure S53.**  $^1\text{H}$  NMR of 1,1-bis(3(5)-aminopyrazol-4-yl)decane (**18a**) in  $\text{DMSO}-d_6$ .



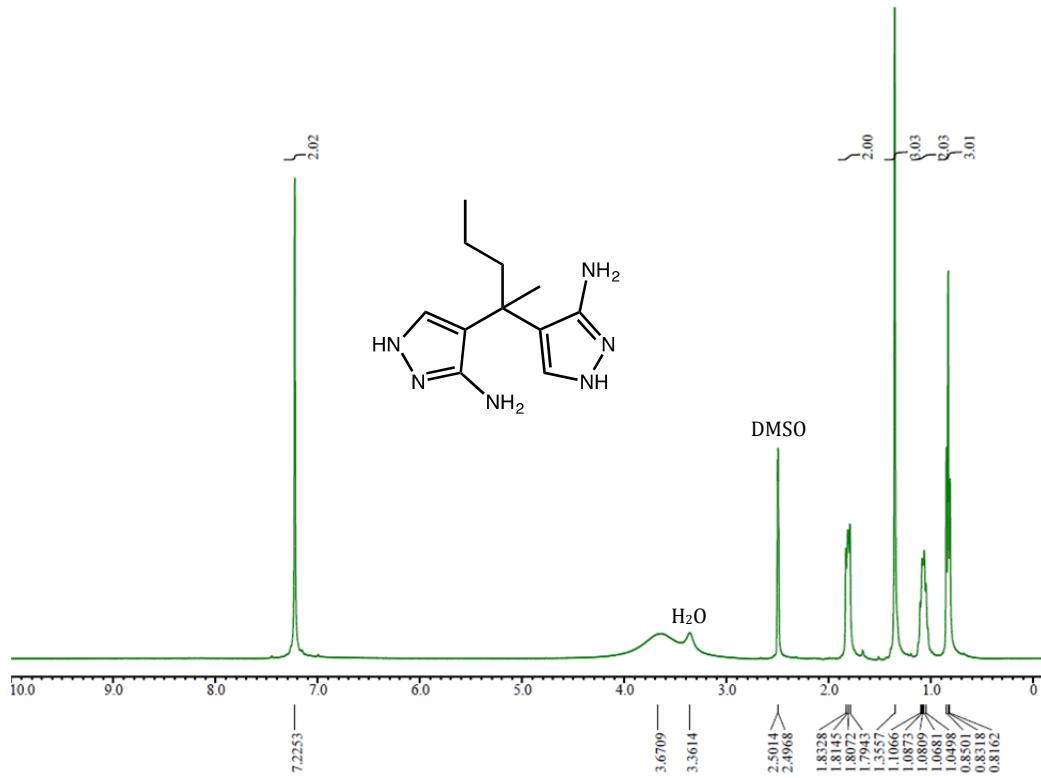
**Figure S54.**  $^{13}\text{C}$  NMR of 1,1-bis(3(5)-aminopyrazol-4-yl)decane (**18a**) in  $\text{DMSO}-d_6$ .



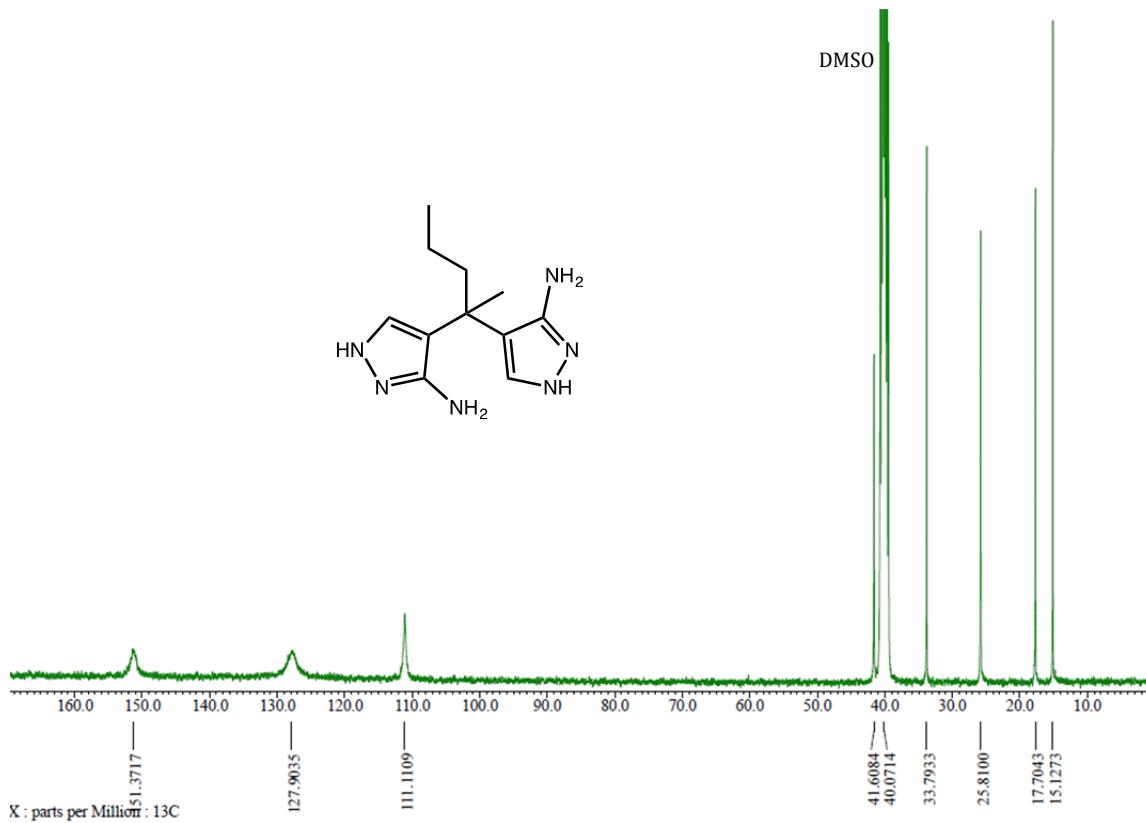
**Figure S55.**  $^1\text{H}$  NMR spectrum of 2,2-bis(3(5)-aminopyrazol-4-yl)butane (**19a**) in  $\text{DMSO}-d_6$ .



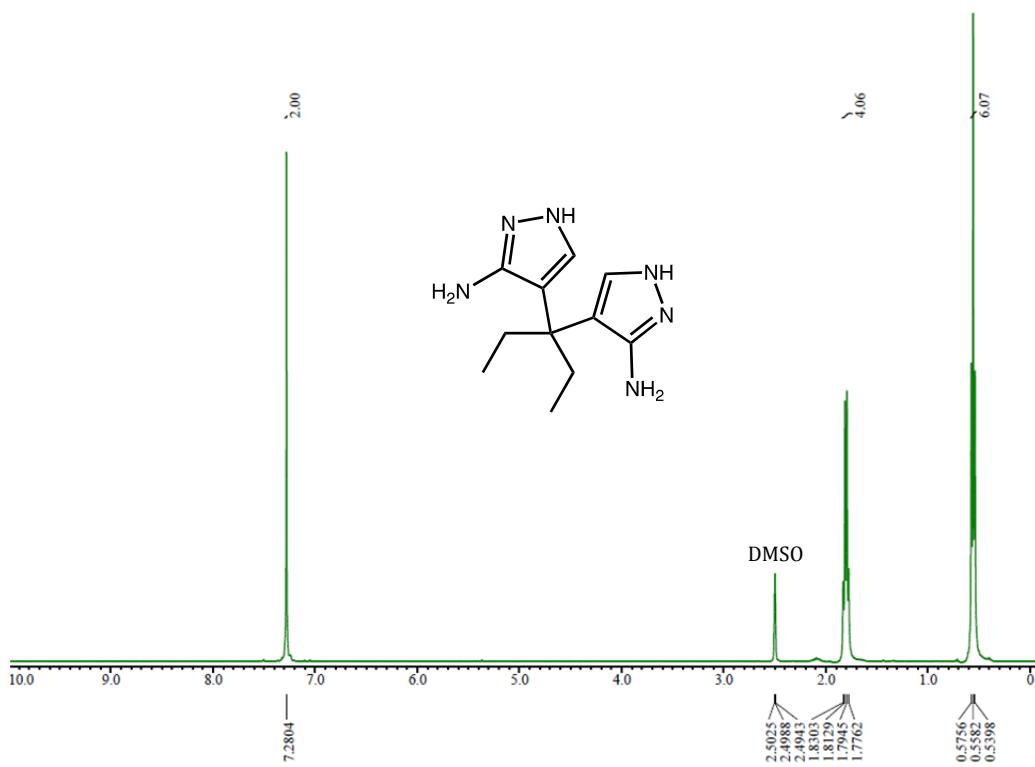
**Figure S56.**  $^{13}\text{C}$  NMR spectrum of 2,2-bis(3(5)-aminopyrazol-4-yl)butane (**19a**) in  $\text{DMSO}-d_6$ .



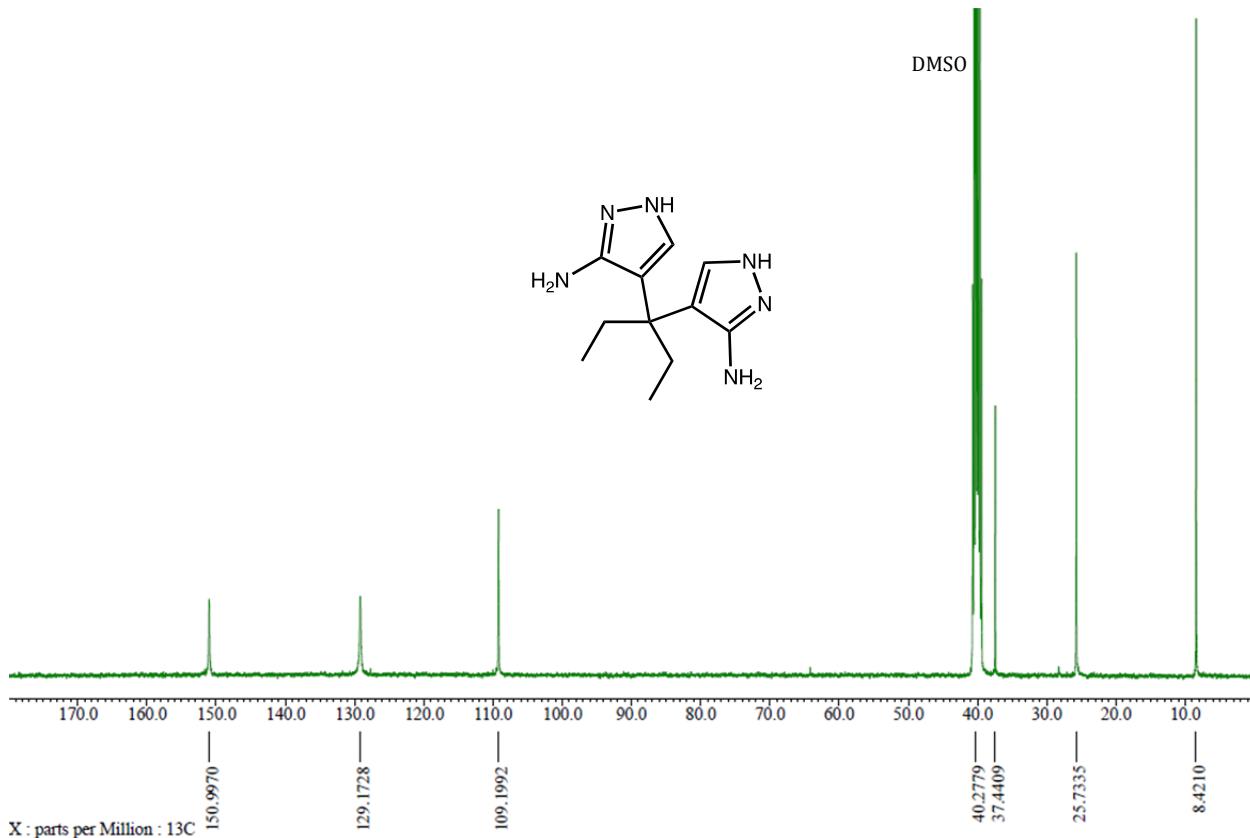
**Figure S57.**  $^1\text{H}$  NMR spectrum of 2,2-bis(3(5)-aminopyrazol-4-yl)pentane (**20a**) in  $\text{DMSO}-d_6$ .



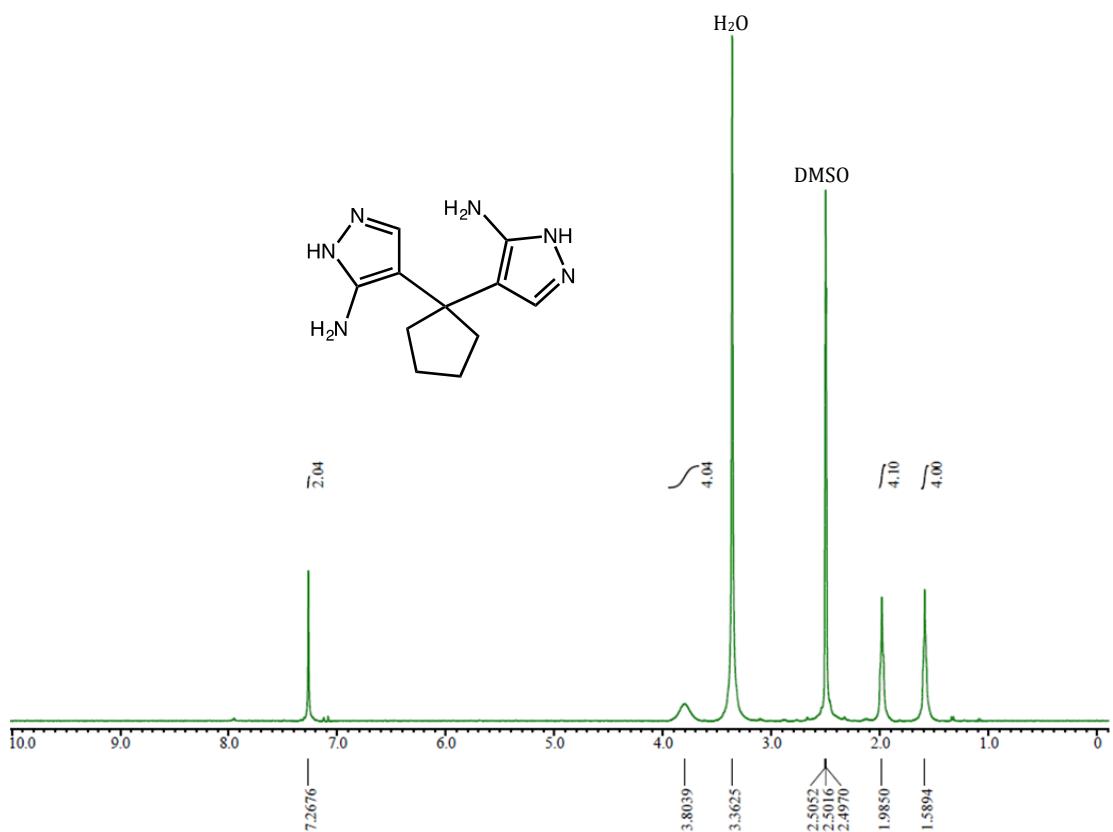
**Figure S58.**  $^{13}\text{C}$  NMR spectrum of 2,2-bis(3(5)-aminopyrazol-4-yl)pentane (**20a**) in  $\text{DMSO}-d_6$ .



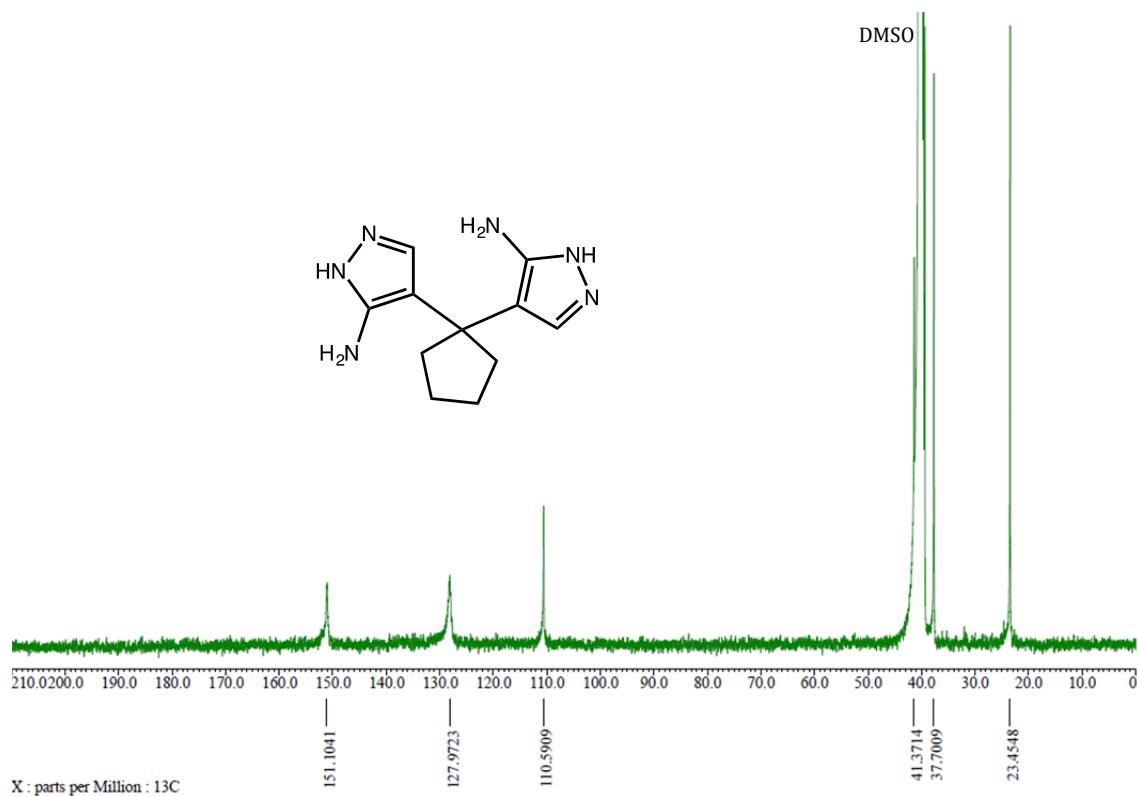
**Figure S59.**  $^1\text{H}$  NMR spectrum of 3,3-bis(3(5)-aminopyrazol-4-yl)pentane (**21a**) in  $\text{DMSO}-d_6$ .



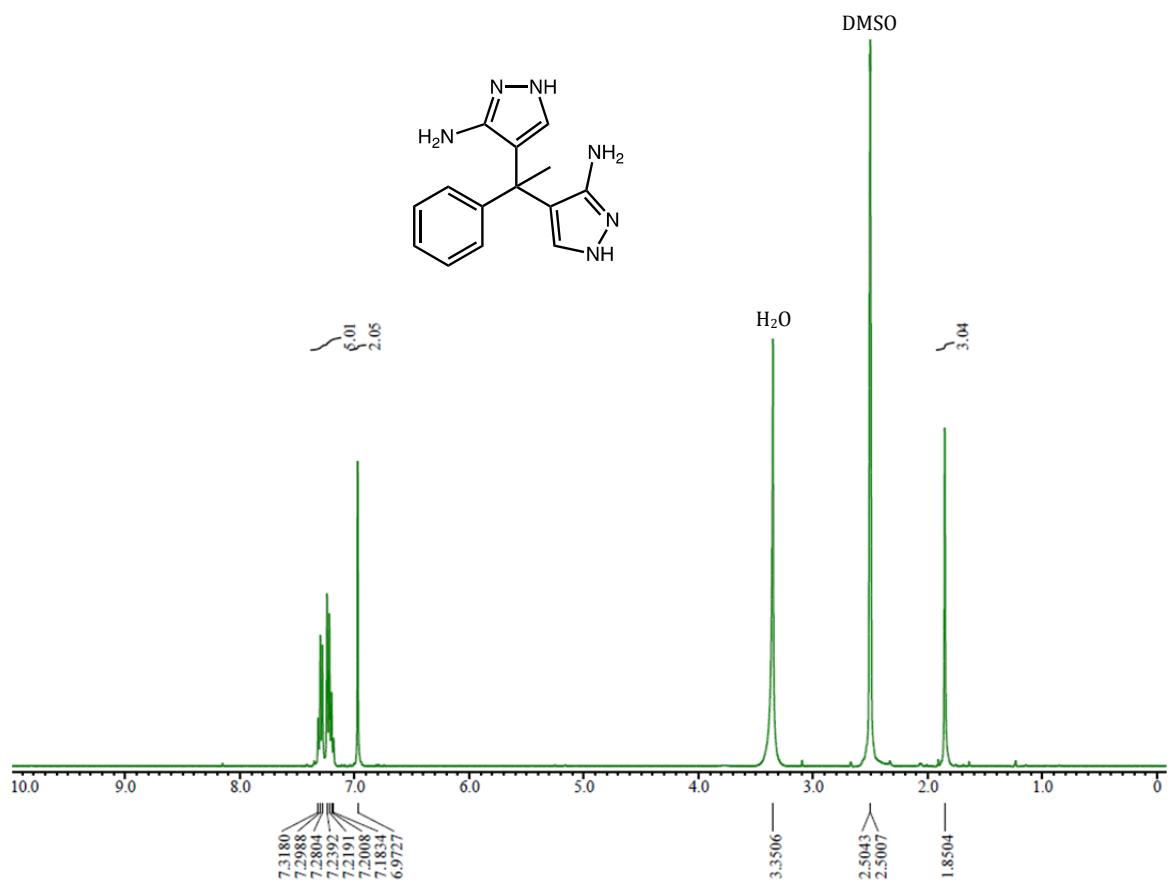
**Figure S60.**  $^{13}\text{C}$  NMR spectrum of 3,3-bis(3(5)-aminopyrazol-4-yl)pentane (**21a**) in  $\text{DMSO}-d_6$ .



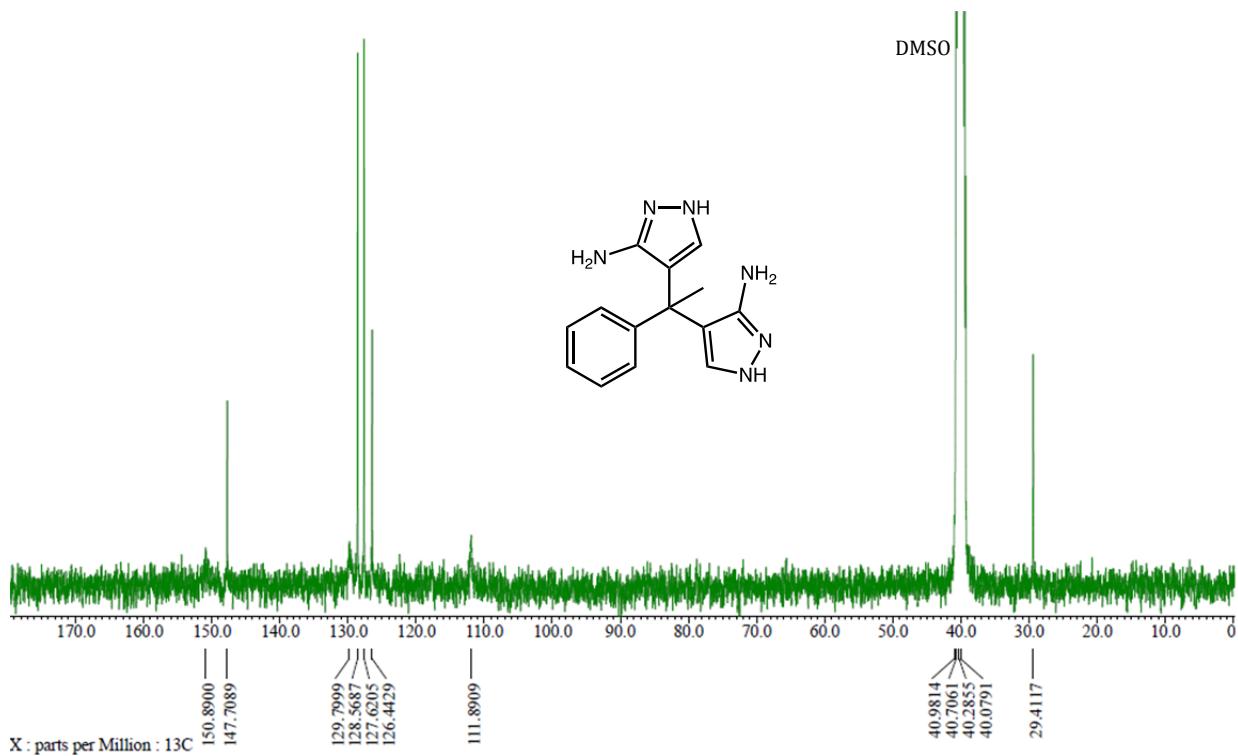
**Figure S61.** <sup>1</sup>H NMR spectrum of 1,1-bis(3(5)-aminopyrazol-4-yl)cyclopentane (**22a**) in DMSO-*d*<sub>6</sub>.



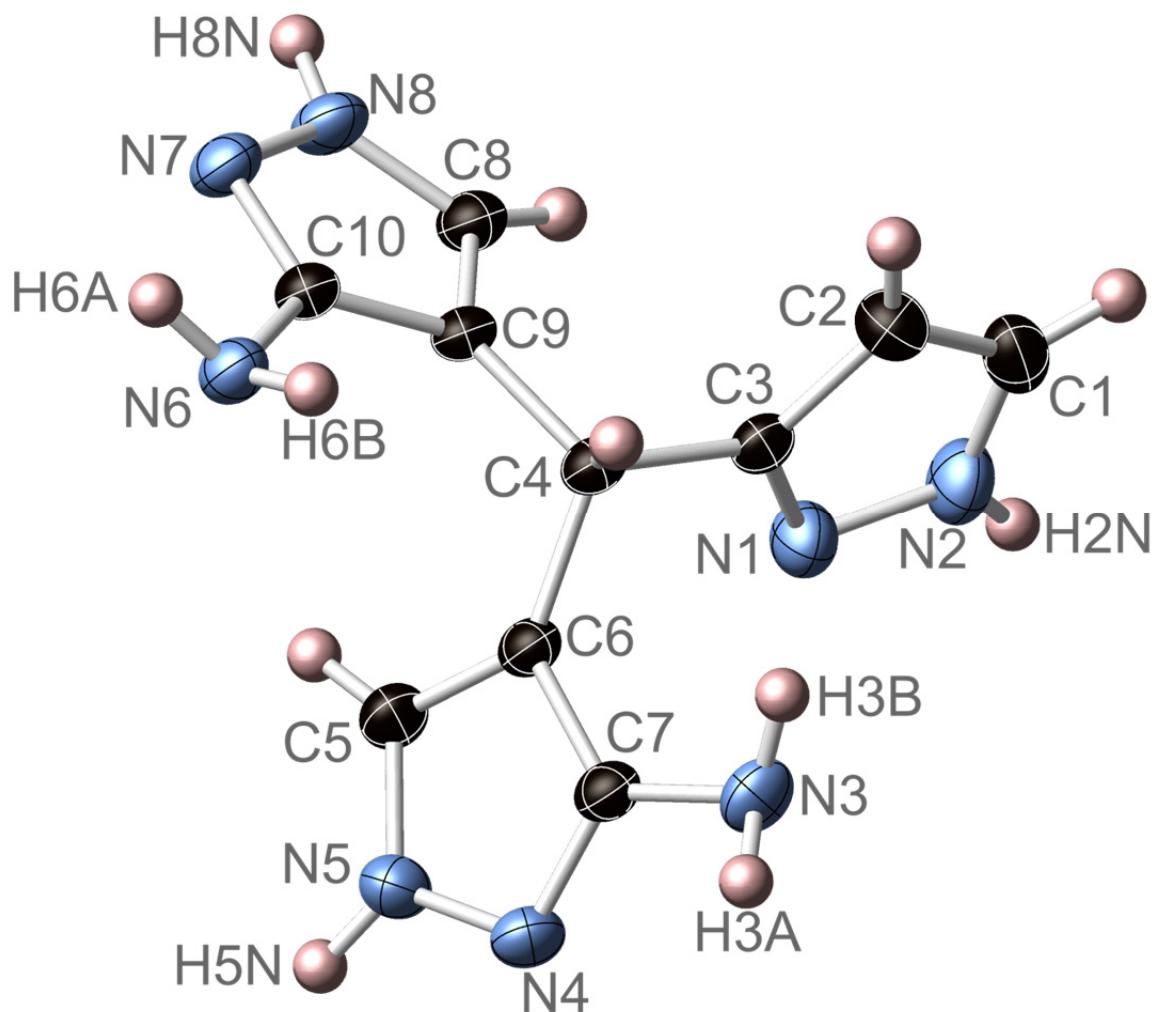
**Figure S62.** <sup>13</sup>C NMR spectrum of 1,1-bis(3(5)-aminopyrazol-4-yl)cyclopentane (**22a**) in DMSO-*d*<sub>6</sub>.



**Figure S63.** <sup>1</sup>H NMR spectrum of 1,1-bis(3(5)-aminopyrazol-4-yl)-1-phenyl-ethane (**23a**) in DMSO-*d*<sub>6</sub>.



**Figure S64.** <sup>13</sup>C NMR spectrum of 1,1-bis(3(5)-aminopyrazol-4-yl)-1-phenyl-ethane (**23a**) in DMSO-*d*<sub>6</sub>.



**Figure S65.** Thermal ellipsoid plot (50% probability level) of the crystal structure of **2a**.