

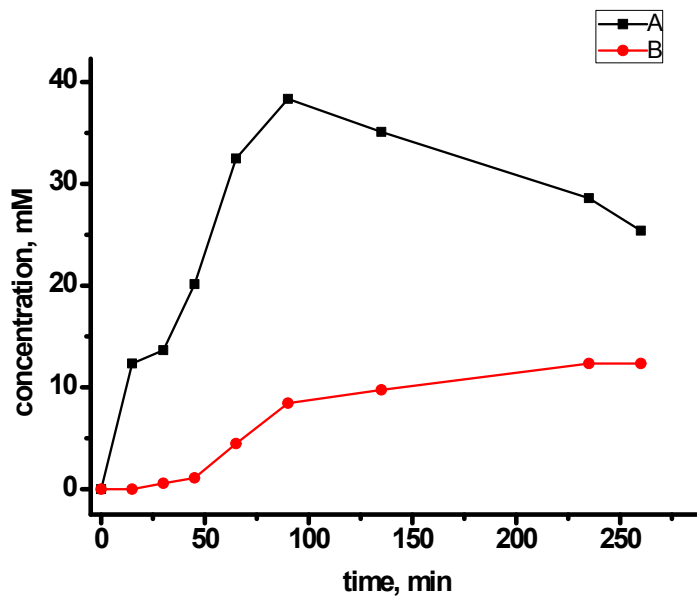
Electronic Supplementary Information

A Regioselective Synthesis of the Dephospho Ditholene Protected Molybdopterin

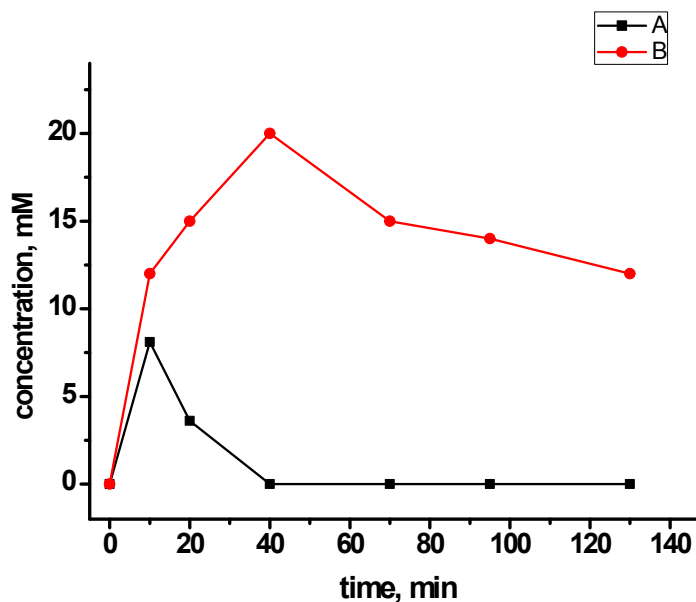
**by**

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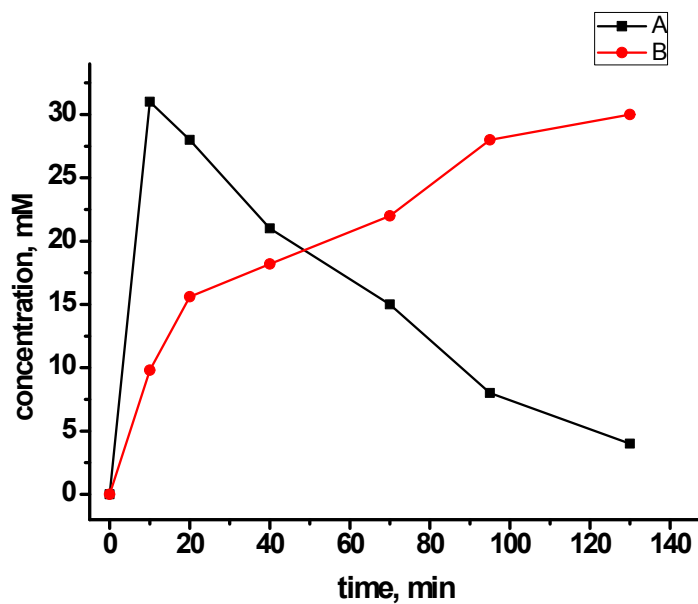
**In situ microscale synthesis and optimization of condensation reaction of 4a with 3a.** Small amount of **4a** and **3a** in 1 mL of DMSO-d<sub>6</sub>, with or without Na<sub>2</sub>SO<sub>3</sub>, in presence of 1,4-dimethoxybenzene as an internal standard for quantitative determination of concentration. The reaction mixture was heated with stirring in water bath (100 °C) or oil bath (130, 160 °C), with periodic probing by <sup>1</sup>H NMR.



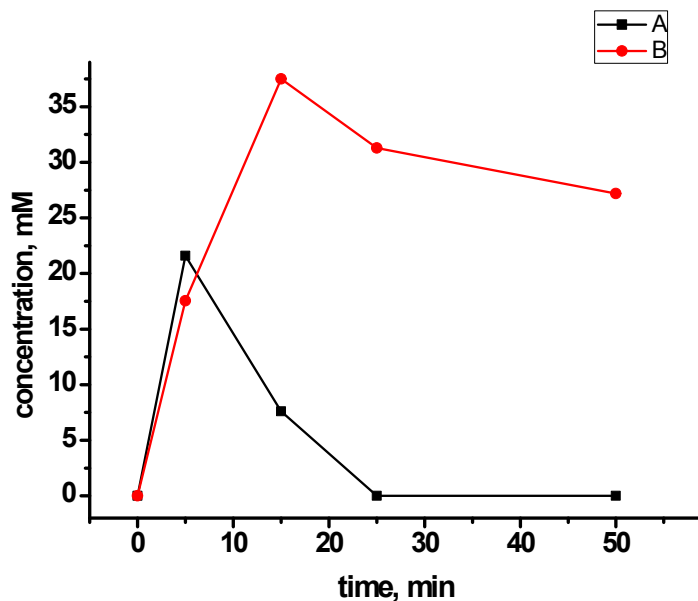
**Figure S1.** Change of concentrations of compound **8** (A) and compound **9** (B) during the condensation reaction (in situ microscale synthesis) of **4a** with **3a** in presence of Na<sub>2</sub>SO<sub>3</sub> at 100 °C.



**Figure S2.** Change of concentrations of compound **8** (A) and compound **9** (B) during the condensation reaction (in situ microscale synthesis) of **4a** with **3a** at 130 °C.



**Figure S3.** Change of concentrations of compound **8** (A) and compound **9** (B) during the condensation reaction (in situ microscale synthesis) of **4a** with **3a** in presence of  $\text{Na}_2\text{SO}_3$  at 130 °C.



**Figure S4.** Change of concentrations of compound **8** (A) and compound **9** (B) during the condensation reaction (in situ microscale synthesis) of **4a** with **3a** in presence of  $\text{Na}_2\text{SO}_3$  at 130 °C.

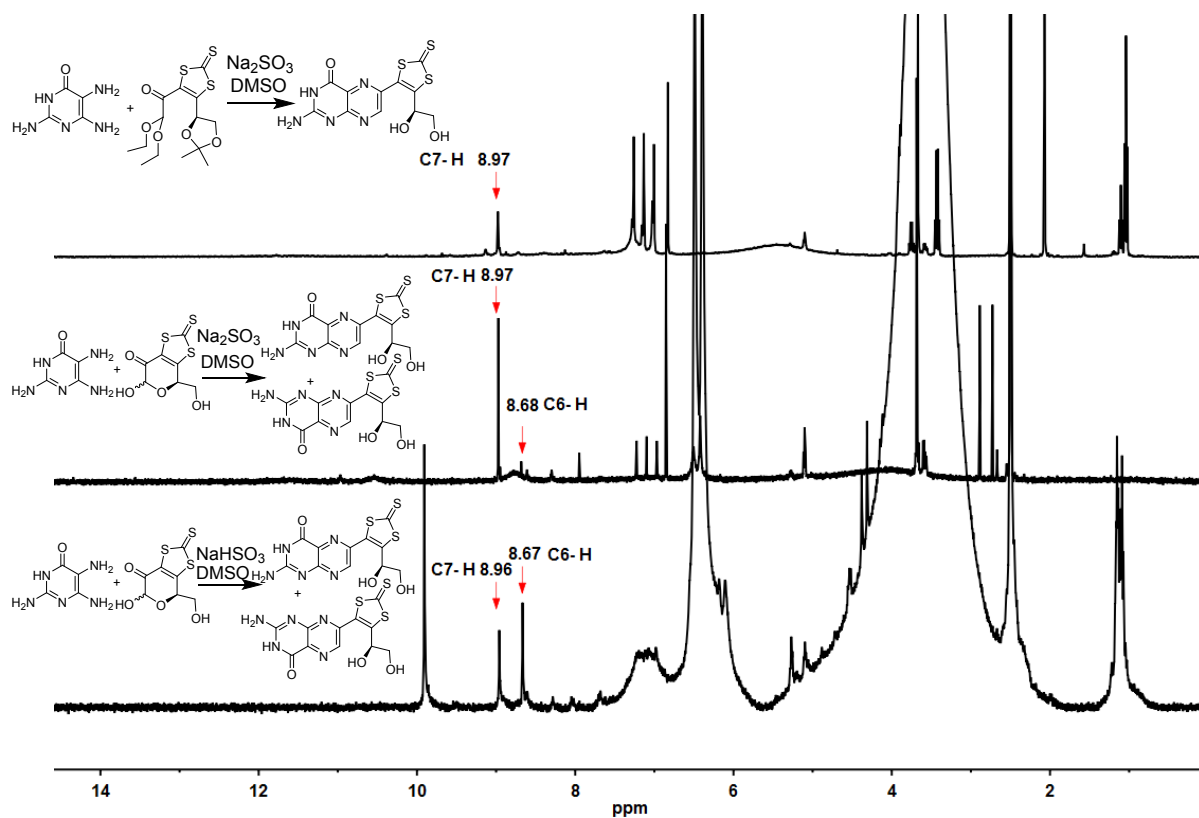


Figure S5.  $^1\text{H}$  NMR spectra of three different reaction mixtures indicating the the formation of only 6-isomer (top), and mixture of 6- and 7-isomers in the other two. The large broad peak in the bottom spectrum is due water present in  $\text{NaHSO}_3$ .