

## Supporting Information

### **Amine functionalized MCM-41 as an efficient catalyst for the synthesis of sulfur/dinitrogen-fused heterocycles via [3+3]- cycloaddition in water**

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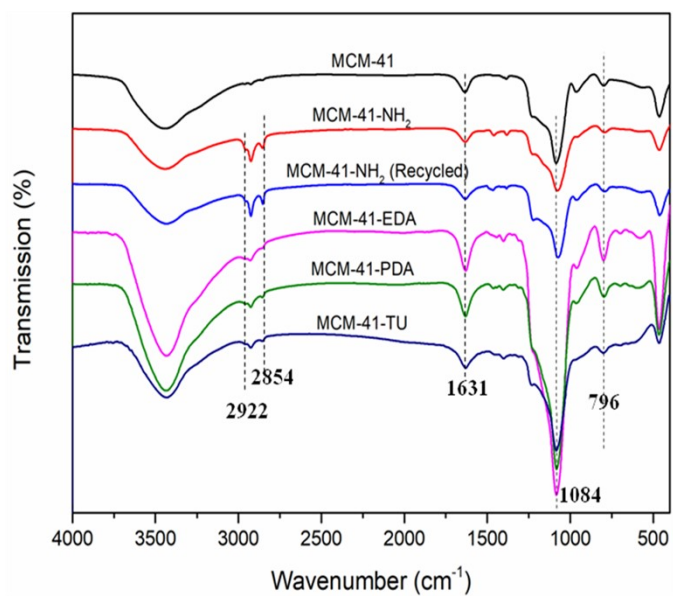
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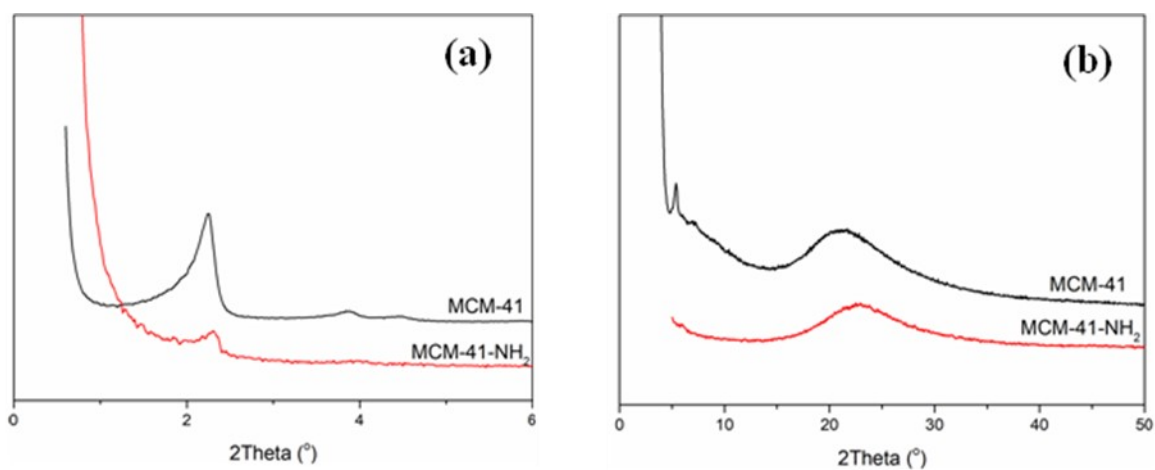
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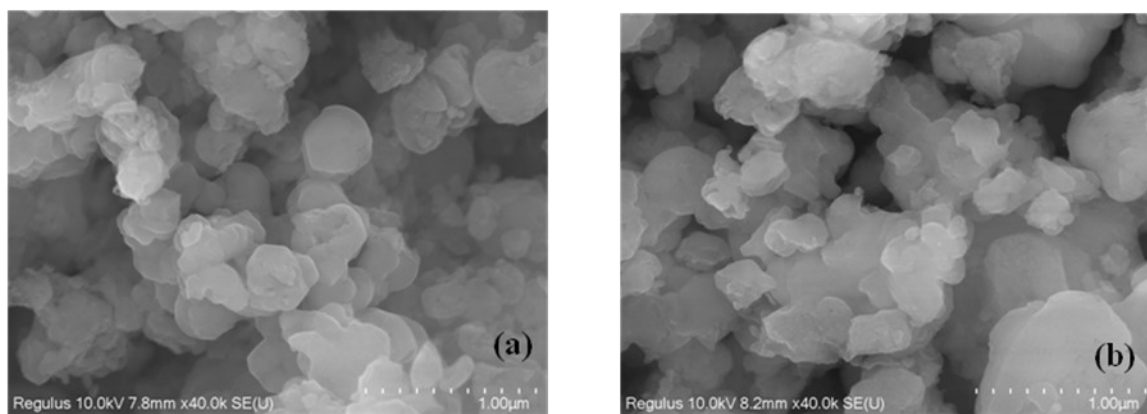
## Materials Characterization



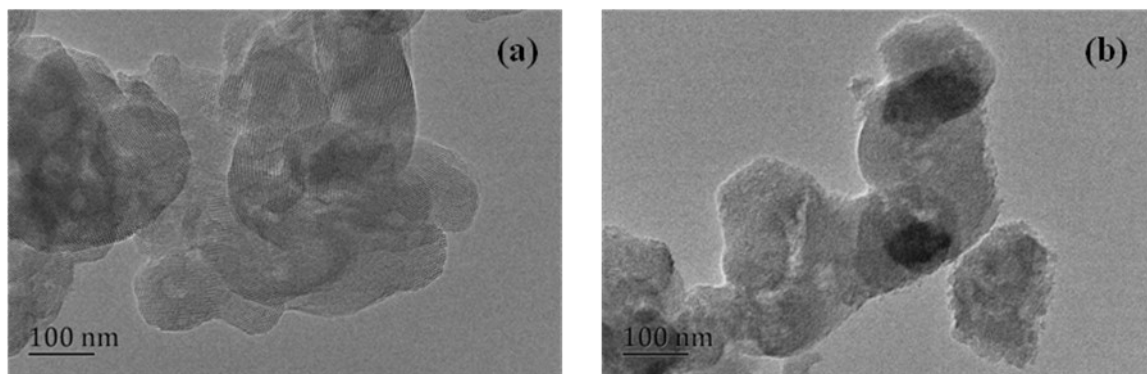
S1 FT IR images of MCM-41 and amine-functionalized MCM-41s



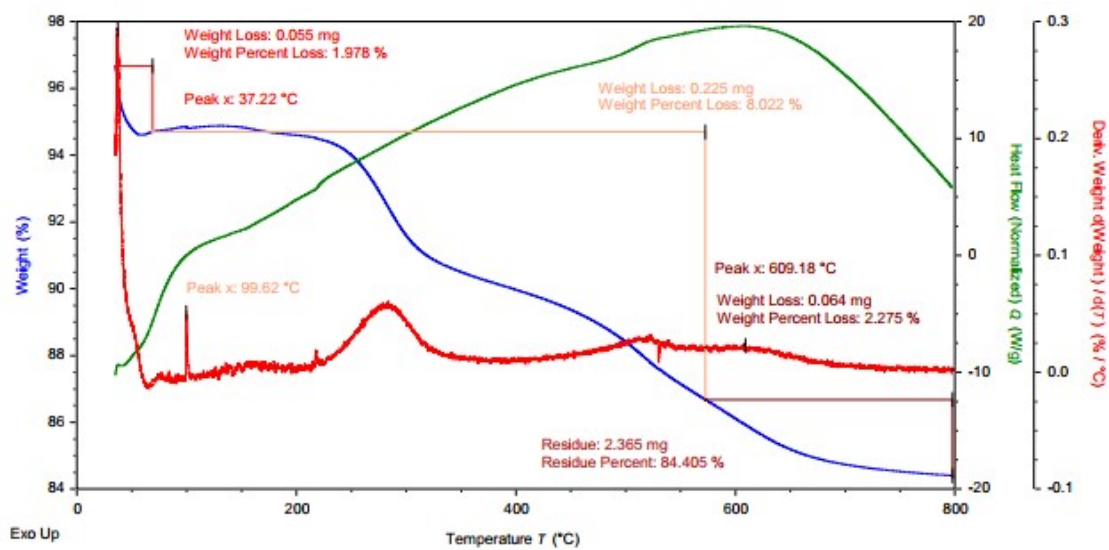
S2 Low-angle (a) and wide-angle (b) XRD patterns of MCM-41-NH<sub>2</sub>



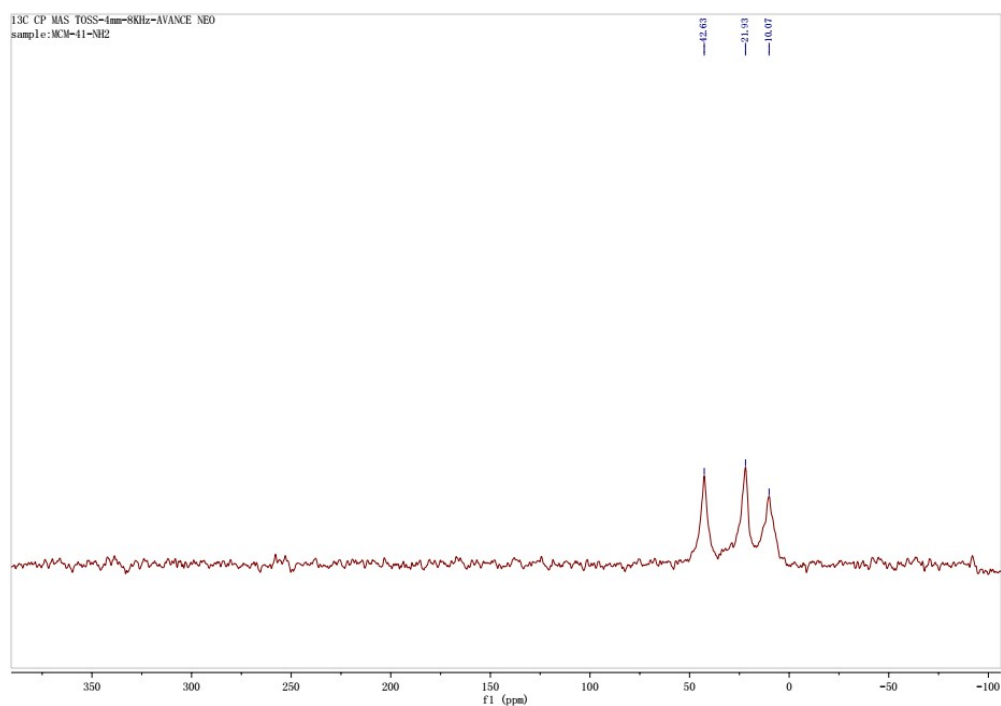
S3 SEM images of MCM-41 (a) and SEM images of MCM-41-NH<sub>2</sub> (b)



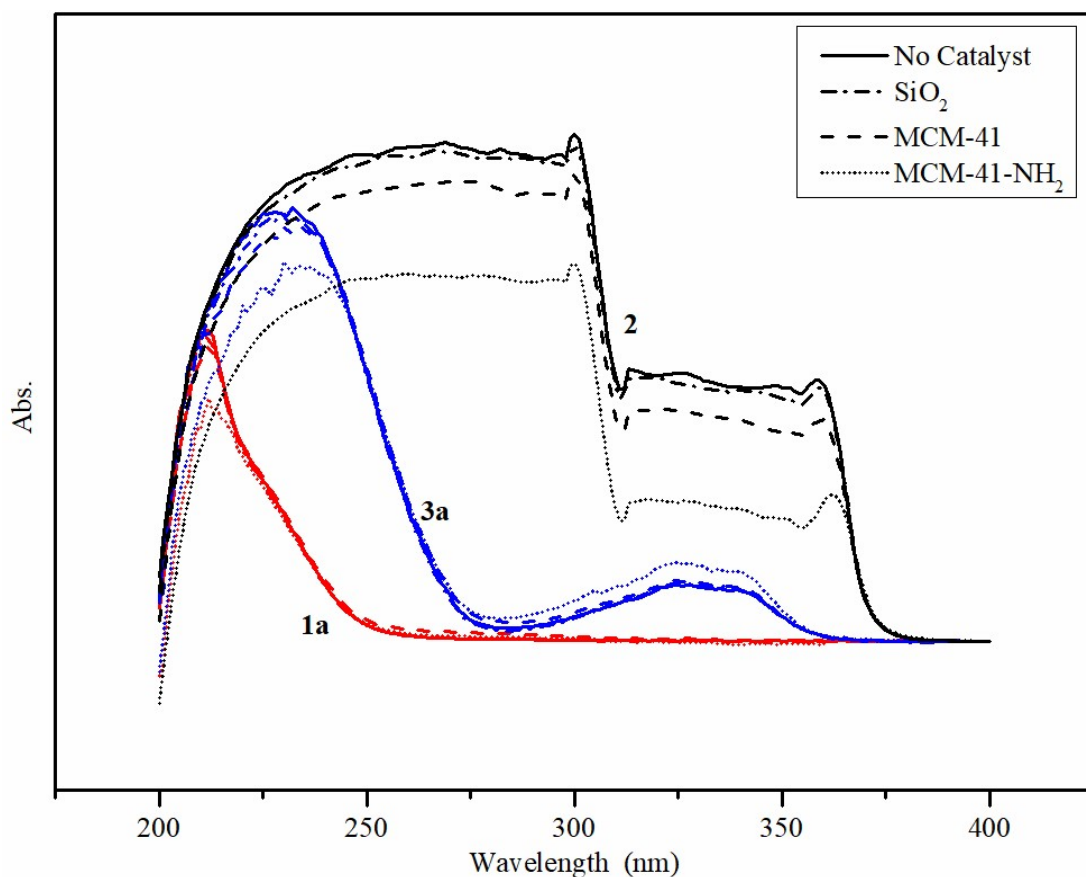
S4 TEM images of MCM-41 (a) and TEM images of MCM-41-NH<sub>2</sub> (b)



S5 TGA of activated MCM-41-NH<sub>2</sub>



S6 <sup>13</sup>C CP/MAS NMR of MCM-41-NH<sub>2</sub>

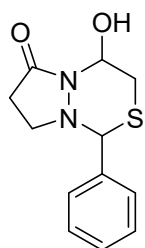


S7 The variations in concentration after the addition of different catalysts

## Experimental Section

### General procedure for the synthesis of 4-hydroxy-1-phenyltetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one (3a as an example)

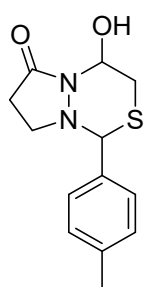
The reaction mixture of azomethine imine (17.4 mg, 0.1 mmol), 1,4-dioxane-2,5-dithiol (0.06 mmol) and amine functionalized MCM-41 (0.005 g) was stirred in water (0.5 mL) at room temperature for 10 mins. The process of the cyclo-condensation reaction was checked by thin-layer chromatography. After finishing the reaction, the solid product was extracted with ethyl acetate (5×5 mL) and the catalyst was separated. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by evaporation. The crude product was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = v/v) to give product **3a** (24.1 mg, 96%) as a white solid.



4-hydroxy-1-phenyltetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one(**3a**)

The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1).

White solid, m.p: 155-156 °C (Lit.<sup>1</sup> mp. 154 °C), 96% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.40-7.34 (m, 3H), 5.90 (s, 1H), 4.53 (s, 1H), 3.22-3.15 (m, 2H), 2.86 (dd, *J* = 13.6, 3.0 Hz, 1H), 2.60-2.33 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.53, 135.47, 129.51, 128.89, 128.09, 73.51, 70.71, 49.00, 35.87, 30.29.

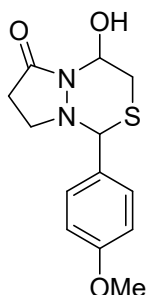


4-hydroxy-1-(p-tolyl)tetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-

one(**3b**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1).

White solid, m.p: 166-167 °C (Lit.<sup>1</sup> mp. 167 °C), 95% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 5.89 (s, 1H), 4.50 (s,

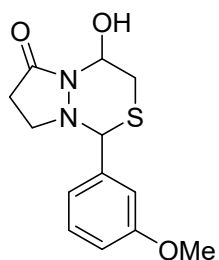
1H), 3.22-3.15 (m, 2H), 2.86 (dd, *J* = 13.5, 2.9 Hz, 1H), 2.60-2.35 (m, 6H).



4-hydroxy-1-(4-methoxyphenyl)tetrahydro-1H,6H-pyrazolo[1,2-

c][1,3,4]thiadiazin-6-one(**3c**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 3/1).

White solid, m.p: 144-145 °C (Lit.<sup>1</sup> mp. 142 °C), 94% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.88 (s, 1H), 4.49 (s, 1H), 3.81 (s, 3H), 3.21-3.14 (m, 2H), 2.85 (dd, *J* = 13.5, 2.9 Hz, 1H), 2.61-2.51 (m, 1H), 2.50-2.36 (m, 2H).

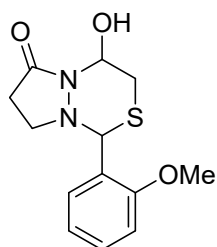


4-hydroxy-1-(3-methoxyphenyl)tetrahydro-1H,6H-pyrazolo[1,2-

c][1,3,4]thiadiazin-6-one(**3d**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1 and 2/1).

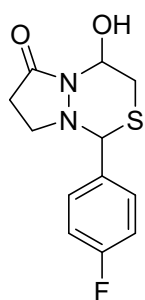
White solid, m.p: 146-147 °C, 95% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (t, *J* = 8.0 Hz, 1H), 7.09-7.02 (m, 2H), 6.91 (dd, *J* = 7.5, 1.7 Hz, 1H), 5.89 (s, 1H), 4.50 (s, 1H), 3.83 (s, 3H), 3.26-3.14 (m, 2H), 2.87 (dd, *J* = 13.5, 2.9 Hz, 1H), 2.64-2.53 (m, 1H), 2.51-2.36

(m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.54, 159.91, 136.87, 129.96, 120.41, 115.12, 113.48, 73.55, 70.74, 55.37, 48.99, 35.87, 30.31.



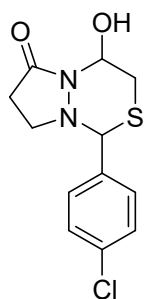
4-hydroxy-1-(2-methoxyphenyl)tetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one(**3e**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1).

White solid, m.p: 139-140 °C, 93% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.32 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.00 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.90 (dd, *J* = 8.4, 0.8 Hz, 1H), 5.89 (s, 1H), 5.17 (s, 1H), 3.85 (s, 3H), 3.24-3.15 (m, 2H), 2.84 (dd, *J* = 13.5, 2.9 Hz, 1H), 2.60 (dd, *J* = 11.4, 10.0 Hz, 1H), 2.42 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.41, 156.41, 130.26, 129.19, 123.51, 121.14, 110.83, 70.78, 65.02, 55.66, 48.39, 35.92, 30.33.



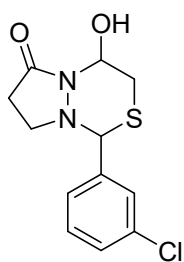
1-(4-fluorophenyl)-4-hydroxytetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one(**3f**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 3/1).

White solid, m.p: 126-127 °C, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54-7.44 (m, 2H), 7.08 (t, *J* = 8.7 Hz, 2H), 5.89 (s, 1H), 4.52 (s, 1H), 3.22-3.13 (m, 2H), 2.87 (dd, *J* = 13.6, 2.9 Hz, 1H), 2.58-2.37 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.59, 161.96, 131.41, 129.96, 116.15 (s), 115.93, 72.68, 70.73, 49.07, 35.88, 30.32.



1-(4-chlorophenyl)-4-hydroxytetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one(**3g**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 3/1).

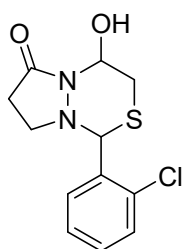
White solid, m.p: 142-143 °C, 91% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 6.20 (d, *J* = 6.6 Hz, 1H), 5.75-5.66 (m, 1H), 4.76 (s, 1H), 3.03 (dd, *J* = 12.7, 3.0 Hz, 2H), 2.77 (dd, *J* = 13.6, 2.9 Hz, 1H), 2.55 (dd, *J* = 19.2, 9.6 Hz, 1H), 2.50-2.40 (m, 1H), 2.25 (dd, *J* = 16.5, 9.7 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 171.20, 136.36, 133.58, 130.14, 128.84, 70.58, 70.06, 48.39, 34.24, 29.88.



1-(3-chlorophenyl)-4-hydroxytetrahydro-1H,6H-pyrazolo[1,2-

c][1,3,4]thiadiazin-6-one (**3h**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1 and 2/1).

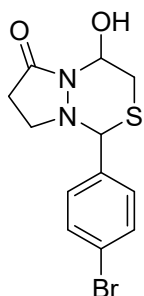
White solid, m.p: 139-140 °C (Lit.<sup>1</sup> mp. 142 °C), 89% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.52 (t, *J* = 1.7 Hz, 1H), 7.39-7.29 (m, 3H), 5.90 (s, 1H), 4.50 (s, 1H), 3.21 (dd, *J* = 15.9, 2.7 Hz, 2H), 2.88 (dd, *J* = 13.6, 2.9 Hz, 1H), 2.59-2.38 (m, 3H).



1-(2-chlorophenyl)-4-hydroxytetrahydro-1H,6H-pyrazolo[1,2-

c][1,3,4]thiadiazin-6-one (**3i**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1 and 2/1).

White solid, m.p: 137-138 °C (Lit.<sup>1,2</sup> mp. 138 °C), 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.41-7.27 (m, 3H), 5.92 (t, *J* = 2.5 Hz, 1H), 5.16 (s, 1H), 3.23 (dd, *J* = 12.0, 2.8 Hz, 2H), 2.87 (dd, *J* = 13.6, 2.9 Hz, 1H), 2.62 (dd, *J* = 11.4, 8.5 Hz, 1H), 2.46 (m, 2H).

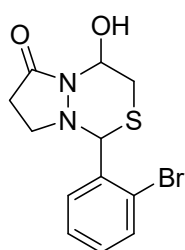


1-(4-bromophenyl)-4-hydroxytetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-

6-one (**3j**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 3/1).

White solid, m.p: 169-170 °C (Lit.<sup>1</sup> mp. 166 °C), 89% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 5.89 (s, 1H), 4.50 (s, 1H), 3.19 (dd, *J* = 11.9, 2.7 Hz, 2H), 2.87 (dd, *J* = 13.6, 2.9 Hz, 1H), 2.57-2.37 (m,

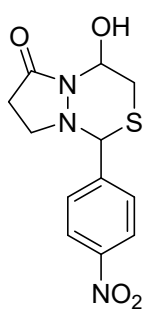
3H).



1-(2-bromophenyl)-4-hydroxytetrahydro-1H,6H-pyrazolo[1,2-

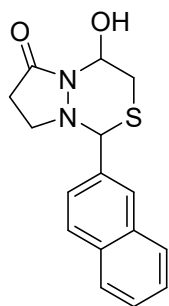
c][1,3,4]thiadiazin-6-one (**3k**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1 and 2/1).

White solid, m.p: 164-165 °C, 91% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 6.7 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.40-7.34 (m, 1H), 7.27-7.19 (m, 1H), 5.91 (s, 1H), 5.14 (s, 1H), 3.23 (dd, *J* = 10.8, 2.8 Hz, 2H), 2.86 (dd, *J* = 13.6, 2.9 Hz, 1H), 2.63 (dd, *J* = 11.0, 8.6 Hz, 1H), 2.51 (dd, *J* = 16.9, 3.4 Hz, 1H), 2.39 (dd, *J* = 16.9, 9.3 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 172.24, 134.79, 133.14, 130.66, 130.15, 128.21, 123.45, 71.28, 70.73, 48.62, 35.70, 30.28.



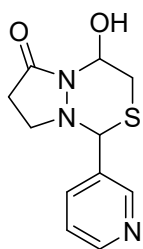
4-hydroxy-1-(4-nitrophenyl)tetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one (**3l**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 1/1).

Yellow solid, m.p: 188-190 °C, 98% yield. <sup>1</sup>H NMR (400 MHz, DMSO- d<sub>6</sub>) δ 8.30-8.22 (m, 2H), 7.86-7.80 (m, 2H), 6.29 (d, *J* = 6.2 Hz, 1H), 5.76-5.68 (m, 1H), 4.96 (s, 1H), 3.14-3.01 (m, 2H), 2.82 (dd, *J* = 13.6, 3.1 Hz, 1H), 2.60-2.46 (m, 2H), 2.27 (dd, *J* = 16.5, 9.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, DMSO- d<sub>6</sub>) δ 171.13, 147.84, 144.75, 129.63, 124.00, 70.13, 48.54, 34.01, 29.83.



4-hydroxy-1-(naphthalen-2-yl)tetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one (**3m**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 5/1).

White solid, m.p: 127-129 °C (Lit.<sup>1</sup> mp. 128 °C), 92% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 0.8 Hz, 1H), 7.90-7.82 (m, 3H), 7.63 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.55-7.50 (m, 2H), 5.95 (s, 1H), 4.71 (s, 1H), 3.27-3.17 (m, 2H), 2.91 (dd, *J* = 13.5, 2.9 Hz, 1H), 2.62 (dd, *J* = 11.9, 8.5 Hz, 1H), 2.53-2.35 (m, 2H).

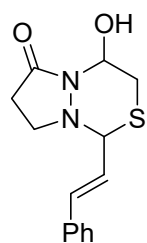


4-hydroxy-1-(pyridin-3-yl)tetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one (**3n**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1 and 2/1).

White solid, m.p: 144-146 °C (Lit.<sup>1</sup> mp. 148 °C), 82% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.72-8.60 (m, 2H), 7.89 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.35 (dd, *J* = 7.9, 4.8

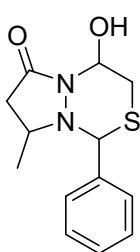


Hz, 1H), 5.93 (t,  $J = 2.5$  Hz, 1H), 4.58 (s, 1H), 3.23-3.15 (m, 2H), 2.90 (dd,  $J = 13.6, 2.9$  Hz, 1H), 2.60-2.51 (m, 1H), 2.50-2.34 (m, 2H).



(E)-4-hydroxy-1-styryltetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one (**3o**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 6/1).

White solid, m.p: 179-180 °C (Lit.<sup>1</sup> mp. 180 °C), 88% yield. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.51-7.41 (m, 2H), 7.35-7.19 (m, 3H), 6.95 (d,  $J = 6.9$  Hz, 1H), 5.50 (d,  $J = 3.9$  Hz, 1H), 4.92 (dd,  $J = 6.8, 3.4$  Hz, 1H), 4.80 (d,  $J = 11.1$  Hz, 1H), 4.26 (t,  $J = 8.0$  Hz, 2H), 3.63-3.48 (m, 2H), 2.88 (dd,  $J = 11.3, 1.0$  Hz, 1H), 2.44 (dd,  $J = 16.1, 7.9$  Hz, 2H). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  182.98, 139.46, 136.68, 128.67, 128.19, 127.70, 73.99, 56.39, 55.79, 51.38, 30.28.



4-hydroxy-8-methyl-1-phenyltetrahydro-1H,6H-pyrazolo[1,2-c][1,3,4]thiadiazin-6-one (**3p**) The title compound was purified by column chromatography on silica gel (petroleum ether and petroleum ether/ethyl acetate = 3/1).

White solid, m.p: 124-125 °C (Lit.<sup>1</sup> mp. 122 °C), 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53-7.45 (m, 2H), 7.41-7.36 (m, 3H), 5.89 (s, 1H), 4.45 (s, 1H), 3.34-3.15 (m, 2H), 2.91-2.84 (m, 1H), 2.55-2.39 (m, 1H), 2.12 (dd,  $J = 12.5, 9.3$  Hz, 1H), 1.16 (d,  $J = 7.0$  Hz, 3H).

## References:

- [1] X. Fang, J. Li, H. Y. Tao, and C. J. Wang, *Org. Lett.* 2013, **15**, 5554-5557.
- [2] L. Wei, Z. F. Wang, L. Yao, G. F. Qiu, H. Y. Tao, H. Li, and C. J. Wang, *Adv. Synth. Catal.*, 2016, **358**, 3955-3959.

