

## Supplementary material:

# **Cu(OH)<sub>x</sub>: Clay catalyst promoted synthesis of 4,5-dihydro-1,2,4-oxadiazole at room temperature**

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### **1. Experimental**

The X-ray diffraction(XRD) analysis of Cu(II)-clay catalyst was obtained on a Rigaku Miniflex diffractometer, using Ni-filtered Cu Ka (0.15418 nm) radiation source. The sample was scanned over the range 10.00–78.99 on 2 $\theta$  scale with steps 0.0118 and step time 13.6 s. To study the morphology, Scanning Electron microscopy (SEM) of the catalyst was carried out using JEOL.JEM100CXII ELECTRON MICROSCOPE with ASID Accelerating Voltage 40.0 KV

#### **1.1 Preparation of Clay encapsulated Cu(OH)<sub>x</sub> catalyst**

To volume 200 mL distilled water 2.012 grams of CuCl<sub>2</sub>.2H<sub>2</sub>O were added and dissolved, followed by drop wise addition of 0.2 molar aqueous NaOH with vigorous stirring till pH of the mixture reaches 6.0-6.5. The resulting oligomer was kept stirring for 8 h. 5 g montmorillonite-KSF with was added to 200 mL distilled water and stirred vigorously at 80 °C for 2 h. Copper oligomer (Cu(OH)<sub>x</sub> (prepared by base hydrolysis of cupric chloride keeping OH/Cu molar ratio equal to 2.0) was added drop wise to this suspension to get encapsulated Cu(OH)<sub>x</sub> with 15 wt% of copper loading the suspension thus formed was stirred at 90 °C for 8 h. Heating causes expansion of clay

interlayer and makes the intercalation of Cu-oligomer easy. The suspension was filtered and washed with distilled water a number of times. The solid residue was dried at room temperature and then at 110° C for 12 h. The catalyst was calcined at different temperatures ranging from 200-425 °C and effect of calcination on the rate of reaction was studied.

### **1.2 Synthesis of 4,5-dihydro-1,2,4-oxadiazoles(General procedure)**

In a 100 mL volume round bottom flask, a mixture of benzohydroximoyl chloride (1mmol) and dichloromethane (DCM = 3 mL) was taken. To this, Cu(OH)x-Clay (10 mg) was added with vigorous stirring. 1mmol imine (prepared insitu) was added to the reaction mixture and stirring was continued for 5-6 h. On finishing point of the reaction, as monitored by thin layer chromatography (TLC), the mixture was centrifuged to remove the catalyst. After concentrating the filtrate under high vacuum, the reaction mixture was extracted with DCM. Washing the organic layer with water and drying over sodium sulphate, the crude mixture achieved was purified by column chromatography on silica gel, where hexane-ethyl acetate (8.5: 1.5) was used as an eluent. The purified products were characterized by NMR, HRMS and IR. The spectral data were found to be reliable with authentic samples.

### **1.3 Spectral analysis of some representative compounds**

*1S.3.1 Compound b:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.68 (s, 3H), 3.79 (s, 3H), 6.79 (s, 1H), 6.49- 6.79 (m, 3H), 6.99-7.11 (m, 5H), 7.69-7.79 (m, 2H), 8.19-8.26 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 54.96, 55.89, 98.58, 109.68, 110.69, 115.97, 120.79, 122.96, 123.82, 125.58, 126.77, 126.94, 128.56, 140.67, 144.89, 147.92, 150.98, 154.87; *m/z*: 405 (M<sup>+</sup>); IR(KBr): ν 1619, 1547, 1245, 1354 cm<sup>-1</sup>

*1S.3.2 Compound c:* <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.47 (s, 1H), 6.99 (d, 2H), 7.09-7.18 (m, 5H), 7.49 (d,2H), 7.73 (d,2H), 8.18 (d,2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 99.01, 122.99, 123.99, 125.00, 127.00, 127.96, 129.01, 129.57, 130.38, 136.84, 140.55, 145.29, 148.62, 154.44; *m/z*: 379 (M<sup>+</sup>),

381 (M+2)<sup>+</sup> in 3:1 ratio; IR(KBr):  $\nu$  1630, 1570, 1350 cm<sup>-1</sup>. 1S3.3.3

Compound e: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.80 (s, 3H), 6.57 (s, 1H), 6.84

(m, 3H), 7.14-7.25 (m, 4H), 7.54 (d, 2H), 7.79 (d, 2H), 8.30 (d, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  54.87, 97.87, 113.87, 115.99, 123.29, 123.43, 124.67,

125.89, 127.96, 128.37, 129.44, 129.61, 141.18, 145.84, 148.62, 155.01,

161.51;  $m/z$ : 375 (M<sup>+</sup>); IR(KBr):  $\nu$  1613, 1512, 1214, 1335 cm<sup>-1</sup>

3.3.4 Compound o: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.78 (s, 3H), 3.58 (s, 3H),

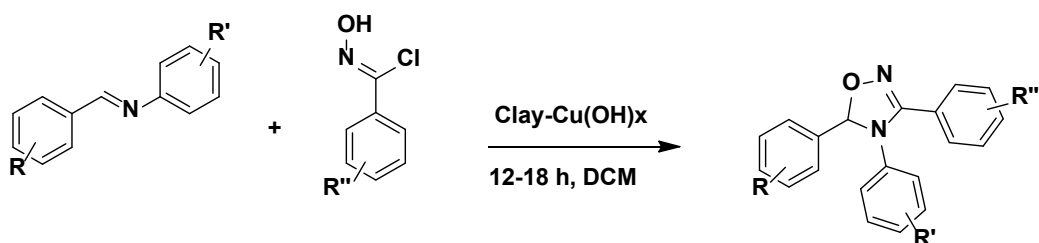
6.61 (s, 1H), 6.81 (m, 4H), 7.24 (d, 2H), 7.08-7.19 (m, 3H), 7.51 (m, 4H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  55.29, 98.87, 113.98, 114.11, 117.67, 124.05,

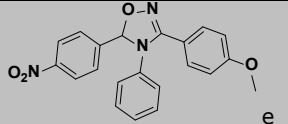
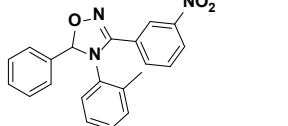
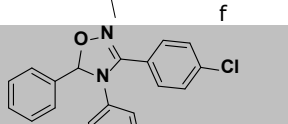
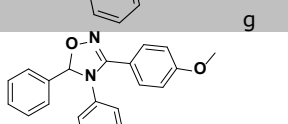
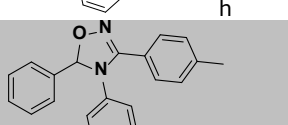
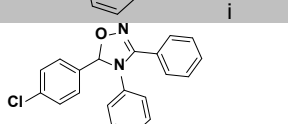
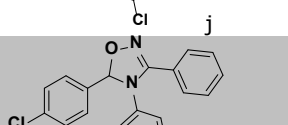
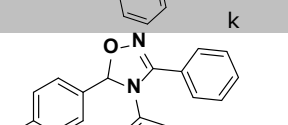
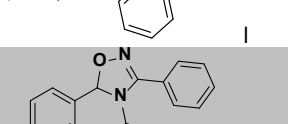
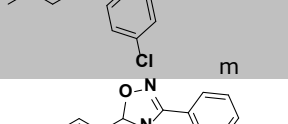
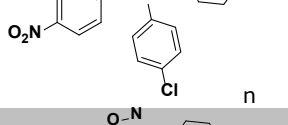
125.33, 128.54, 129.11, 129.67, 131.09, 140.97, 149.85, 154.80, 160.63,

161.19;  $m/z$ : 360 (M<sup>+</sup>); IR(KBr):  $\nu$  1611, 1245 cm<sup>-1</sup>;

**Table 1S.** Cu(OH)<sub>x</sub>-Clay-catalyzed synthesis of 4, 5-dihydro-1,2,4-oxadiazoles<sup>a</sup>



Entry	R	R'	R''	Product	Yield (%)
1	H	H	4-OMe		87
2	4-NO <sub>2</sub>	H	2, 4-OMe (2,3-dimethoxy)		63
3	4-NO <sub>2</sub>	H	4-Cl		68
4	H	H	3-NO <sub>2</sub>		66

<b>5</b>	4-NO <sub>2</sub>	H	4-OMe		71
<b>6</b>	H	2,3- Me (2,3-dimethyl)	3-NO <sub>2</sub>		63
<b>7</b>	H	H	4Cl		92
<b>8</b>	H	H	4-OMe		90
<b>9</b>	H	H	4-Me		92
<b>10</b>	4-Cl	H	H		96
<b>11</b>	4-Cl	H	H		91
<b>12</b>	4-CH <sub>3</sub>	H	H		87
<b>13</b>	4-CH <sub>3</sub>	4-Cl	H		94
<b>14</b>	4-NO <sub>2</sub>	4-Cl	H		77
<b>15</b>	4-OMe	H	4-OMe		85

<sup>a</sup>Reaction condition: benzohydroximoyl chloride (1mmol), imine (1mmol), solvent (3 mL), Cu(OH)x-Clay (10 mg) at 25 °C.