Electronic Supplementary Material (ESI) for ChemComm.


# Supporting Information

## A rare three-dimensional POM-based inorganic polymer bonded by $CO_2$ with high catalytic performance for $CO_2$ cycloaddition

Weiwei Cheng,[‡] Yun-shan Xue,[‡] Ximing Luo, and Yan Xu*

### 1). Materials and Methods

All reagents were purchased from commercial sources and used without further purification.

Element analyses for C, H, and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

IR spectra were recorded on KBr pellets with a Nicolet Impact 410 FTIR spectrometer in the range of 4000-400 $cm^{-1}$.

Single crystal X-ray diffraction data was collected on a Bruker APEX II diffractometer using Mo-Kα monochromatized radiation (λ = 0.71073Å) at 296K. X-ray powder diffraction data were obtained on Bruker D8X diffractometer using Cu-Kα monochromatized radiation (λ = 1.5418 Å) in the 2θ range of 5-50° at room temperature.

TG measurement was carried out on a PerkinElmer, Diamond Thermogravimetric/Differential Thermal Analyzer under $N_2$ atmosphere from room temperature to 800 °C with a heating rate of 10 °C/min.

Gas chromatographic (GC) analysis was conducted by gas chromatography (GC-7920A, CEAU Light, China) with Thermal Conductivity Detector (TCD) and a TDX-01 column (2 m, 3 mm, 2mm). Experimental conditions were as follows: $N_2$ (99.99%) as Carrier gas; column temperature, 50°C; injector temperature, 100°C; TCD temperature, 100°C; carbon dioxide (99.5%) and air as quantitive analysis standard.

### 2). Syntheses of the compound 1

#### The synthesis of $(TBA)_2PMo_{12}O_{40}Zn_4(CO_2)$ (1)

A mixture of zinc chloride (0.28 g, 2 mmol), fumaric acid (0.058 g, 0.5 mmol) , 1,2,4-Triazole(0.035 g, 0.5 mmol), Mo powder 99.99% (0.060 g, 0.624 mmol), sodium molybdate dihydrate (0.847 g, 3.5 mmol), Phosphorous acid (0.040 g, 0.50 mmol), 40 wt % tetrabutylammonium hydroxide solution in water (200μL, 0.30 mmol) and 9 ml $H_2O$ was stirred for 20 min. The pH was adjusted to 4.0 with 2 M HCl. The mixture was heated to 180°C in 1 h, and the temperature was maintained for 72 h. After cooling to room temperature, black rod crystals of compound **1** were collected. The crystals were obtained in a 23% yield based on fumaric acid. Its purity was confirmed by X-ray power diffraction (XRD) (Fig. S1). Anal. Calcd (%) for compound **1**

$C_{33}H_{74}Mo_{12}N_2O_{42}PZn_4$ (*M*r = 2614.67): C, 15.16; H, 2.85; N, 1.07. Found: C, 15.37; H, 2.58; N, 1.17.

**Table S1**. Summary of Crystal Data and Structure Results for compound **1**.

| | |
|---|---|
| Compound | **1** |
| Chemical formula | $C_{33}H_{74}Mo_{12}N_2O_{42}PZn_4$ |
| Formula Mass | 2614.67 |
| Crystal system | monoclinic |
| a/(Å) | 26.704(8) |
| b/(Å) | 18.529(5) |
| c/(Å) | 17.539(10) |
| $\alpha$/(deg) | 90 |
| $\beta$/(deg) | 124.780(2) |
| $\gamma$/(deg) | 90 |
| Unit cell volume/(Å$^3$) | 7128(5) |
| Temperature/K | 296(2) |
| Space group | *C*2/*c* |
| No. of formula units per unit cell, *Z* | 4 |
| No. of reflections measured | 24158 |
| No. of independent reflections | 6272 |
| $R_{int}$ | 0.0923 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0708 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.1877 |
| Final $R_1$ values (all data) | 0.1189 |

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

**Table S2.** Selected bond lengths (Å) and angles (°) for compound **1**

| | | | |
|---|---|---|---|
| Mo(1)-O(15) | 1.674(10) | Mo(4)-O(7) | 1.993(8) |
| Mo(1)-O(18) | 1.822(9) | Mo(4)-O(2)#2 | 2.014(8) |
| Mo(1)-O(17) | 1.844(8) | Mo(4)-O(20) | 2.014(9) |
| Mo(1)-O(1) | 2.015(9) | Mo(5)-O(11) | 1.680(9) |
| Mo(1)-O(1)#1 | 2.040(9) | Mo(5)-O(5) | 1.940(9) |
| Mo(1)-Mo(1)#1 | 3.209(2) | Mo(5)-O(4) | 1.982(9) |
| Mo(2)-O(14) | 1.676(9) | Mo(5)-O(17) | 1.987(9) |
| Mo(2)-O(4) | 1.956(9) | Mo(5)-O(12)#1 | 2.082(8) |
| Mo(2)-O(5) | 1.967(8) | Mo(6)-O(19) | 1.697(10) |
| Mo(2)-O(2)#2 | 1.998(8) | Mo(6)-O(20) | 1.808(9) |
| Mo(2)-O(16) | 2.031(10) | Mo(6)-O(16) | 1.818(9) |
| Mo(2)-Mo(5) | 2.6178(17) | Mo(6)-O(10)#1 | 2.006(9) |
| Mo(3)-O(9) | 1.672(9) | Mo(6)-O(10) | 2.015(8) |

| | | | |
|---|---|---|---|
| Mo(3)-O(3) | 1.960 (8) | Zn(1)-O(1) | 1.943(9) |
| Mo(3)-O(7) | 1.972(8) | Zn(1)-O(2) | 1.965(8) |
| Mo(3)-O(18)#1 | 1.998(9) | Zn(1)-O(4) | 1.971(9) |
| Mo(3)-O(12) | 2.091(9) | Zn(1)-O(3) | 1.986(8) |
| Mo(3)-Mo(4) | 2.6233(18) | Zn(2)-O(21) | 1.929(7) |
| Mo(4)-O(13) | 1.666(9) | Zn(2)-O(10) | 1.935(9) |
| Mo(4)-O(3) | 1.970(8) | Zn(2)-O(7) | 1.947(9) |
| Zn(2)-O(5)#1 | 1.974(9) | O(5)-Zn(2)#1 | 1.981(9) |
| O(1)-Mo(1)#1 | 2.036(9) | O(10)-Mo(6)#1 | 2.004(9) |
| O(2)-Mo(2)#2 | 2.002(8) | O(12)-Mo(5)#1 | 2.090(8) |
| O(2)-Mo(4)#2 | 2.016(8) | O(18)-Mo(3)#1 | 1.998(9) |
| O(15)-Mo(1)-O(18) | 103.7(4) | O(15)-Mo(1)-Mo(1)#1 | 99.8(3) |
| O(15)-Mo(1)-O(17) | 104.1(4) | O(18)-Mo(1)-Mo(1)#1 | 124.9(3) |
| O(18)-Mo(1)-O(17) | 96.9(4) | O(17)-Mo(1)-Mo(1)#1 | 124.3(3) |
| O(15)-Mo(1)-O(1) | 103.4(4) | O(1)-Mo(1)-Mo(1)#1 | 37.8(2) |
| O(18)-Mo(1)-O(1) | 150.5(4) | O(1)#1-Mo(1)-Mo(1)#1 | 37.3(2) |
| O(17)-Mo(1)-O(1) | 87.6(4) | O(14)-Mo(2)-O(4) | 106.1(4) |
| O(15)-Mo(1)-O(1)#1 | 102.9(4) | O(14)-Mo(2)-O(5) | 105.2(4) |
| O(18)-Mo(1)-O(1)#1 | 88.7(4) | O(4)-Mo(2)-O(5) | 93.2(4) |
| O(17)-Mo(1)-O(1)#1 | 150.2(4) | O(14)-Mo(2)-O(2)#2 | 97.9(4) |
| O(1)-Mo(1)-O(1)#1 | 74.1(4) | O(4)-Mo(2)-O(2)#2 | 86.2(4) |
| O(5)-Mo(2)-O(2)#2 | 156.0(3) | O(4)-Mo(2)-Mo(5) | 48.8(3) |
| O(14)-Mo(2)-O(16) | 99.4(4) | O(5)-Mo(2)-Mo(5) | 47.6(3) |
| O(4)-Mo(2)-O(16) | 154.2(4) | O(2)#2-Mo(2)-Mo(5) | 134.6(3) |
| O(5)-Mo(2)-O(16) | 83.5(4) | O(16)-Mo(2)-Mo(5) | 130.7(3) |
| O(2)#2-Mo(2)-O(16) | 86.7(4) | O(9)-Mo(3)-O(3) | 107.5(4) |
| O(14)-Mo(2)-Mo(5) | 99.3(3) | O(9)-Mo(3)-O(7) | 105.1(4) |
| O(3)-Mo(3)-O(7) | 94.0(3) | O(5)-Mo(5)-O(17) | 151.9(3) |
| O(9)-Mo(3)-O(18)#1 | 101.7(4) | O(4)-Mo(5)-O(17) | 85.0(4) |
| O(3)-Mo(3)-O(18)#1 | 84.6(3) | O(11)-Mo(5)-O(12)#1 | 97.3(4) |
| O(7)-Mo(3)-O(18)#1 | 152.2(4) | O(5)-Mo(5)-O(12)#1 | 84.0(4) |
| O(9)-Mo(3)-O(12) | 96.8(4) | O(4)-Mo(5)-O(12)#1 | 155.2(3) |
| O(3)-Mo(3)-O(12) | 155.2(3) | O(17)-Mo(5)-O(12)#1 | 86.0(4) |
| O(7)-Mo(3)-O(12) | 84.1(4) | O(11)-Mo(5)-Mo(2) | 100.6(4) |
| O(18)#1-Mo(3)-O(12) | 85.8(4) | O(5)-Mo(5)-Mo(2) | 48.6(2) |
| O(9)-Mo(3)-Mo(4) | 100.5(3) | O(4)-Mo(5)-Mo(2) | 47.8(3) |
| O(3)-Mo(3)-Mo(4) | 48.2(2) | O(17)-Mo(5)-Mo(2) | 132.0(3) |
| O(7)-Mo(3)-Mo(4) | 48.9(2) | O(12)#1-Mo(5)-Mo(2) | 132.2(3) |
| O(18)#1-Mo(3)-Mo(4) | 132.0(2) | O(19)-Mo(6)-O(20) | 104.8(4) |
| O(12)-Mo(3)-Mo(4) | 132.6(3) | O(19)-Mo(6)-O(16) | 104.7(4) |
| O(13)-Mo(4)-O(3) | 106.8(4) | O(20)-Mo(6)-O(16) | 97.2(4) |
| O(13)-Mo(4)-O(7) | 105.3(4) | O(19)-Mo(6)-O(10)#1 | 102.8(4) |
| O(3)-Mo(4)-O(7) | 92.9(3) | O(20)-Mo(6)-O(10)#1 | 149.6(4) |
| O(13)-Mo(4)-O(2)#2 | 99.4(4) | O(16)-Mo(6)-O(10)#1 | 87.8(4) |

| | | | |
|---|---|---|---|
| O(3)-Mo(4)-O(2)#2 | 86.5(4) | O(19)-Mo(6)-O(10) | 102.6(4) |
| O(7)-Mo(4)-O(2)#2 | 154.4(3) | O(20)-Mo(6)-O(10) | 89.5(4) |
| O(13)-Mo(4)-O(20) | 100.8(4) | O(16)-Mo(6)-O(10) | 149.2(4) |
| O(3)-Mo(4)-O(20) | 152.2(4) | O(10)#1-Mo(6)-O(10) | 72.2(4) |
| O(7)-Mo(4)-O(20) | 83.2(3) | O(1)-Zn(1)-O(2) | 124.2(4) |
| O(2)#2-Mo(4)-O(20) | 85.5(4) | O(1)-Zn(1)-O(4) | 108.5(4) |
| O(13)-Mo(4)-Mo(3) | 100.1(3) | O(2)-Zn(1)-O(4) | 105.8(4) |
| O(3)-Mo(4)-Mo(3) | 47.9(2) | O(1)-Zn(1)-O(3) | 109.3(4) |
| O(7)-Mo(4)-Mo(3) | 47.9(2) | O(2)-Zn(1)-O(3) | 109.4(4) |
| O(2)#2-Mo(4)-Mo(3) | 134.0(3) | O(4)-Zn(1)-O(3) | 95.9(4) |
| O(20)-Mo(4)-Mo(3) | 130.4(2) | O(21)-Zn(2)-O(10) | 119.4(7) |
| O(11)-Mo(5)-O(5) | 105.9(4) | O(21)-Zn(2)-O(7) | 107.7(7) |
| O(11)-Mo(5)-O(4) | 107.1(4) | O(10)-Zn(2)-O(7) | 115.0(3) |
| O(5)-Mo(5)-O(4) | 93.2(4) | O(21)-Zn(2)-O(5)#1 | 98.7(6) |
| O(11)-Mo(5)-O(17) | 101.4(4) | O(10)-Zn(2)-O(5)#1 | 113.2(4) |
| O(3)-Mo(3)-O(7) | 94.0(3) | O(7)-Zn(2)-O(5)#1 | 100.1(4) |

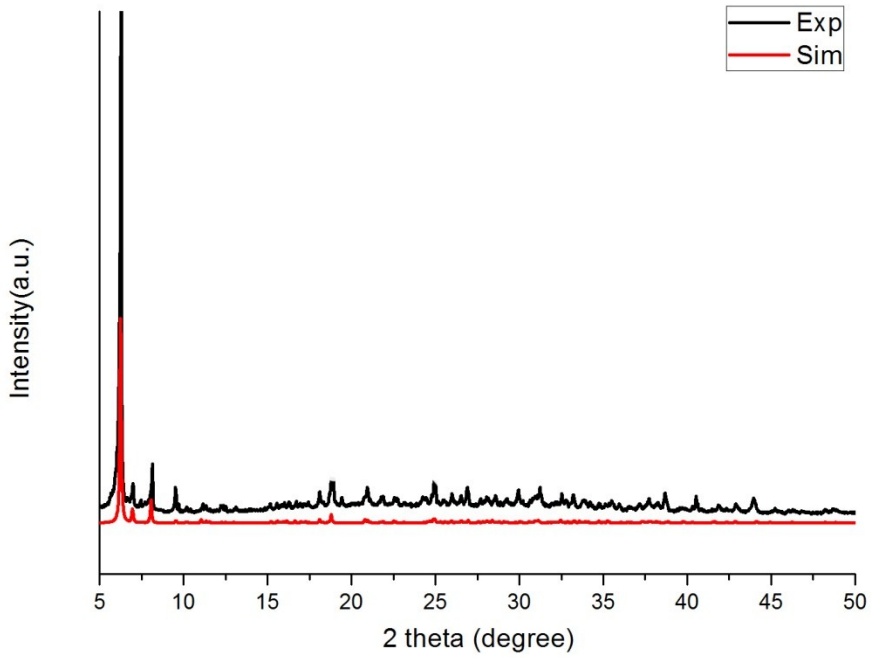


**Fig. S1** Simulated and measured XRD powder pattern for compound **1**

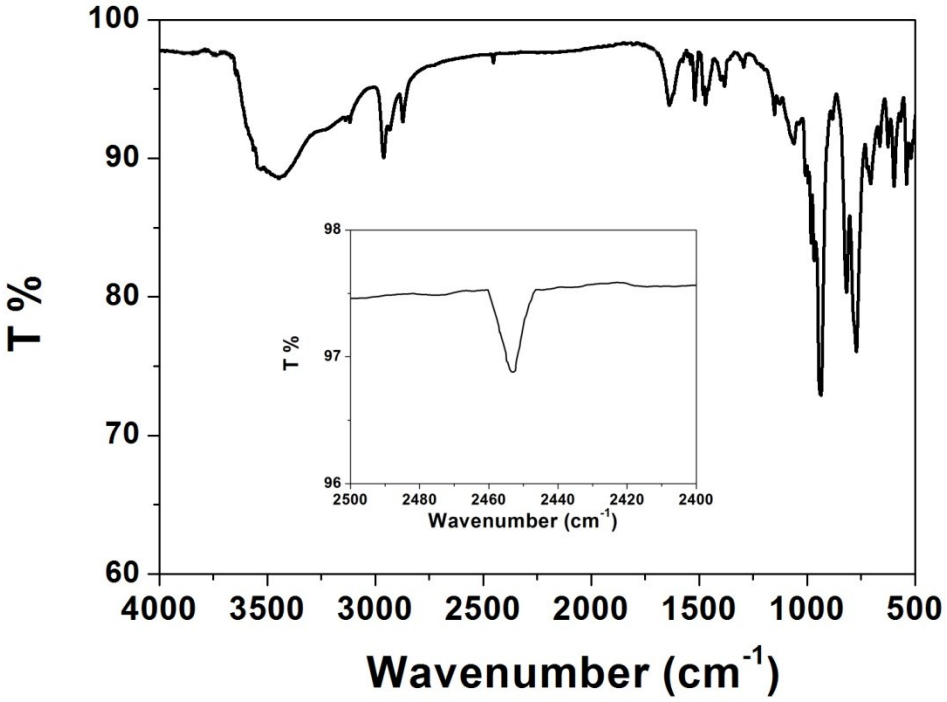


**Fig. S2** The IR spectra of compound **1**

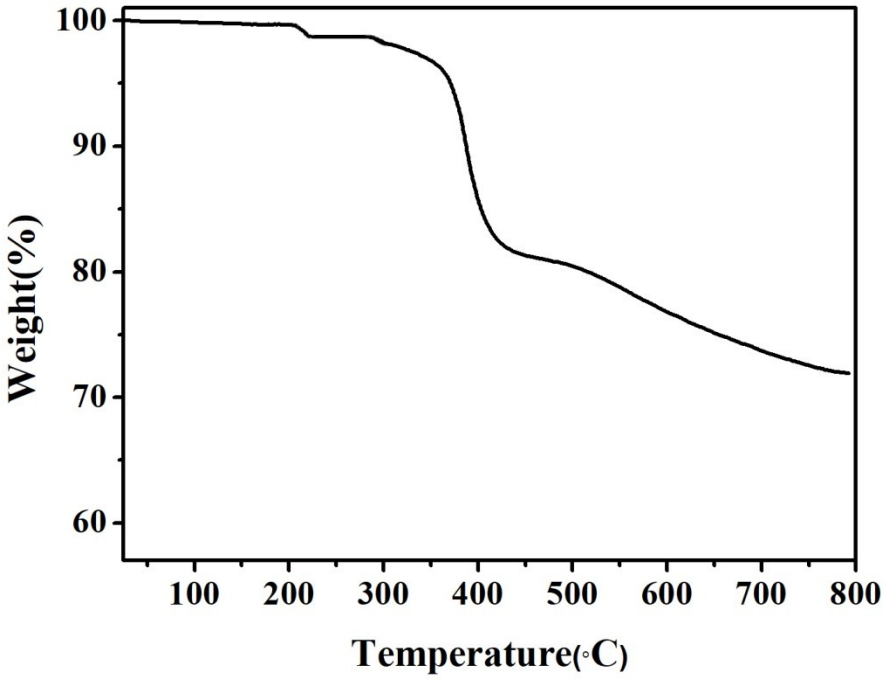


**Fig. S3** The TGA diagram of compound **1**

The TGA analysis of compound **1** was carried out, shown in Fig. S3. The TGA diagram shows two main weight losses in the curves. The first step (25-221°C) corresponds to the release of $CO_2$ ligand. The observed weight loss of 1.4% is very close to the calculated values (1.7%). From 221 °C to 445°C, the weight lost 20.22% immediately due to the splitting of $TBA^+$ ions with the calculated 19.6% at 445 °C. With the further increasing of temperature, the final residuals contained ZnO and $MoO_3$.

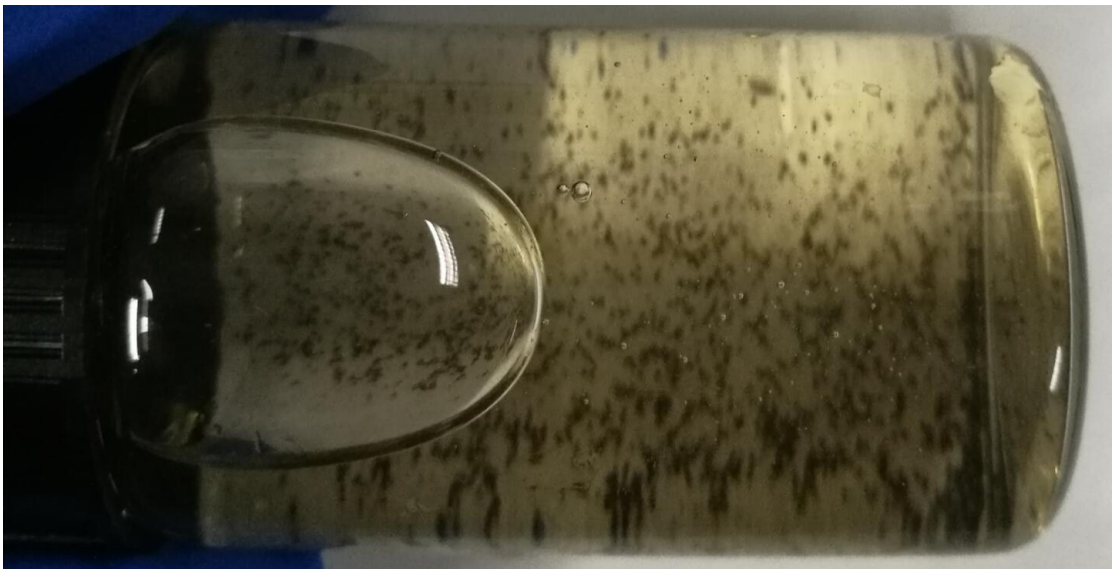

**Fig. S4** The samples of compound **1** immersed in water with concentrated $H_2SO_4$ (40μL).

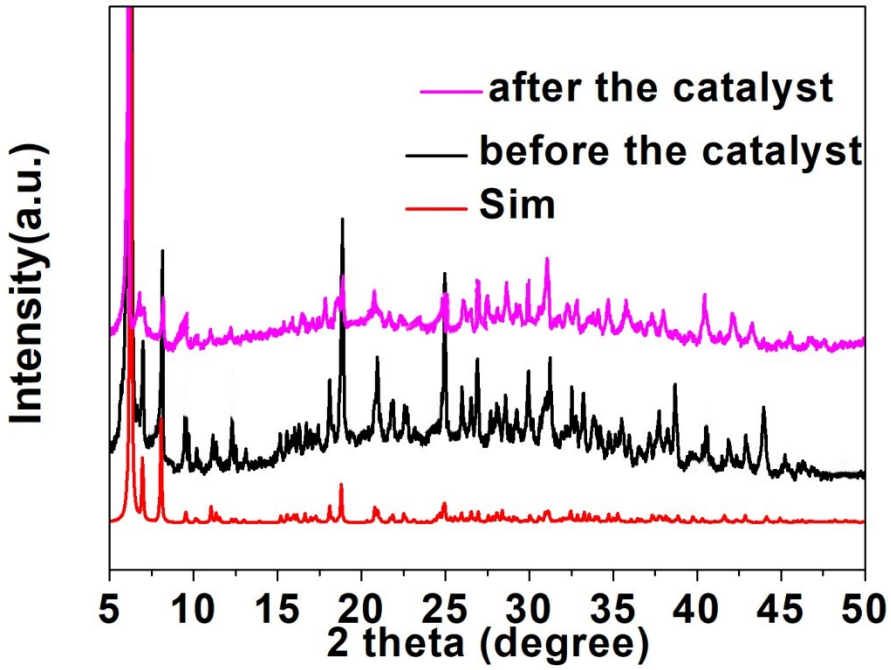


**Fig. S5** The PXRD pattern of recycled samples before the catalyst and after catalyst.

**$^{1}$ H NMR characterization data**:

4-Methyl-1.3-dioxolan-2-one:

$^{1}$H NMR ($CDCl_3$, 400 MHz) δ 1.48 (d, 3H), 3.99-4.03 (m, 1H), 4.53-4.57 (m, 1H), 4.81-4.90 (m, 1H).

4-Chloromethyl-1,3-dioxolan-2-one:

$^{1}$H NMR ($CDCl_3$, 400 MHz) δ 3.70-3.80 (m, 2H), 4.42 (q, 1H), 4.59 (t, 1H), 4.93-4.99 (m, 1H).

4-Phenyl-1,3-dioxolan-2-one:

$^{1}$H NMR ($CDCl_3$, 400 MHz) δ 4.33 (t, 1H), 4.82 (t, 1H), 5.69 (t, 1H), 7.26-7.29 (m, 2H), 7.31-7.37 (m, 3H).

4-Ethyl-1,3-dioxolan-2-one:

$^{1}$H NMR ($CDCl_3$, 400 MHz) δ 1.02 (t, 3H), 1.80 (m, 2H), 4.08 (dd, 1H), 4.52 (t, 1H), 4.62-4.69 (m, 1H).

Hexahydrobenzo[d][1,3]dioxol-2-one:

$^{1}$H NMR ($CDCl_3$, 400 MHz) δ 1.37-1.49 (m, 4H), 1.87-1.97 (m, 4H), 5.29 (m, 2H).