Supporting Information

Highly Efficient and Reusable Amorphous Pd(II)/Crystal Pd(0)-Grafted Porous Polymer Framework for Catalytic CO$_2$ Cycloaddition

Somnath Sarkar,[a] Swarbhanu Ghosh,[b] Titu Mondal,[a] Aslam Khan[c] and Sk. Manirul Islam[a],*

[a]*Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India*
[b]*Department of Chemistry, McGill University, Montréal, Québec H3A 0B8, Canada*
[c]*College of Science, King Saud University, Riyadh, 11451, Saudi Arabia*

*To whom correspondence should be addressed. E-mail: manir65@rediffmail.com

Number of pages: 13

Number of figures: 4

Number of Table: 1

Table of Contents

Materials and Equipments

All oxiranes were purchased from a commercial supplier. ^{1}H NMR spectra were recorded on Bruker DPX-300/500 NMR spectrometer at a temperature of 298 K.

A D8 Advance SWAX diffractometer from Bruker-AXS utilizing a constant current (40 mA) and voltage (40 kV) was used to obtain the PXRD pattern of the Pd nanoparticles decorated 3D PPF catalyst. The XRD machine was calibrated with silicon sample utilizing Ni-filtered Cu Kα radiation (λ=0.15406 nm). Quantachrome Autosorb-iQ (USA) surface area analyser was used for N_2 sorption analysis at 77 K. The sample was activated at 403 K for 12 h under high vacuum before the adsorption of gas. Pore size distribution was obtained by using NLDFT method employing the carbon/cylindrical pore model as reference. JEOL JEM 6700 field emission-scanning electron microscope (FE SEM) was employed to analyze particle size and morphology of Pd@3D PPF. FT-IR (Nicolet MAGNA-FT IR 750 spectrometer Series II) was used to understand the coordination. [1]H spectra of the desired products were kept on a Bruker DPX-300/500 NMR spectrometer.
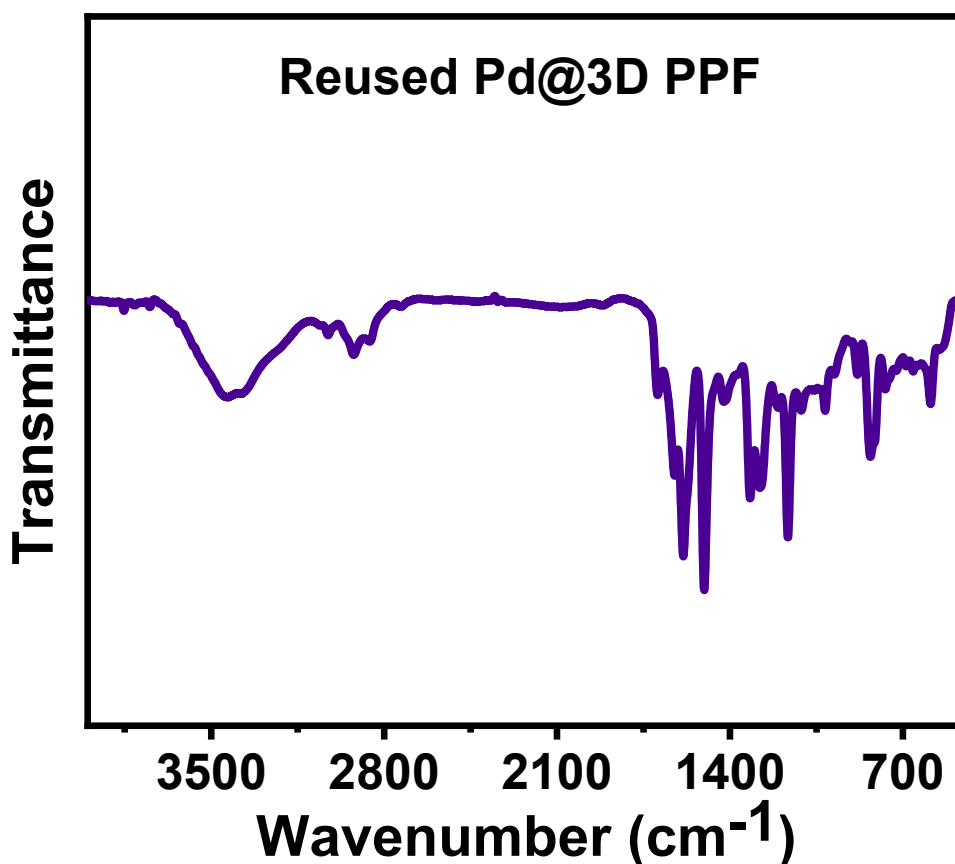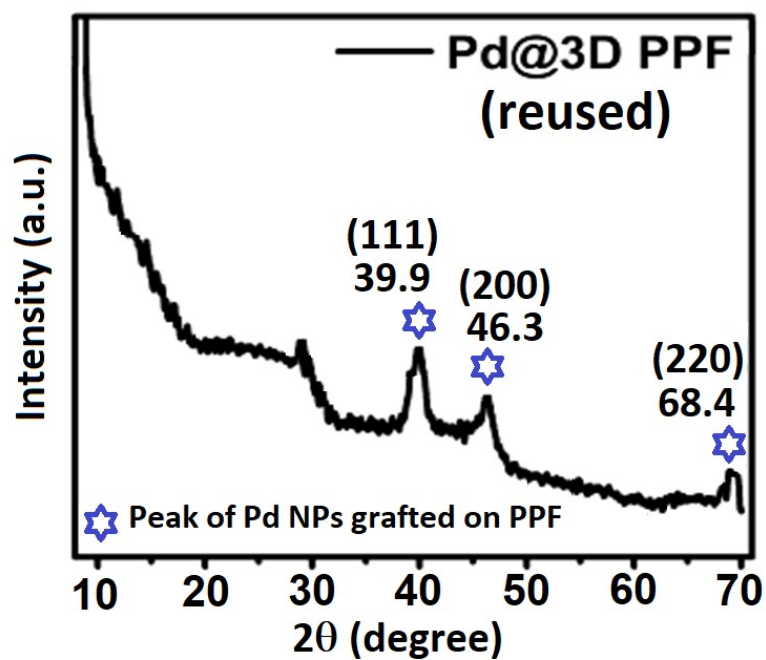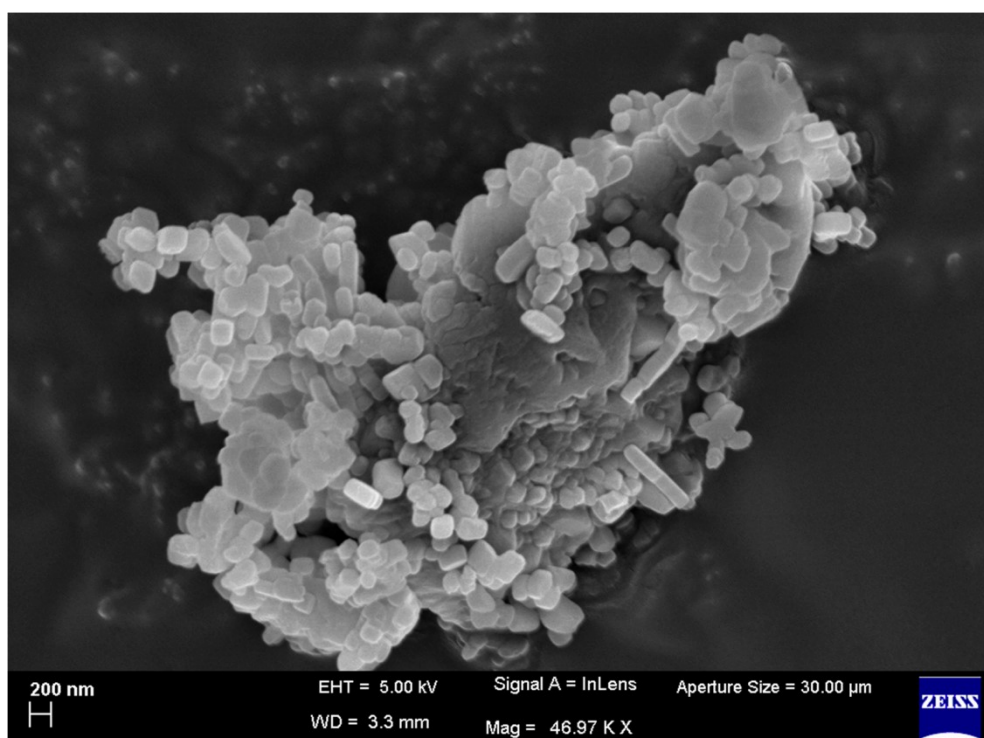

Figure S1. FT-IR spectrum of the recovered catalyst (Pd@3D PPF) after 5th run.

Figure S2. PXRD pattern of the recovered Pd@3d PPF after 5th run.

The PXRD pattern of the recovered Pd@3D PPF catalyst confirms the retention of its original structural Integrity.

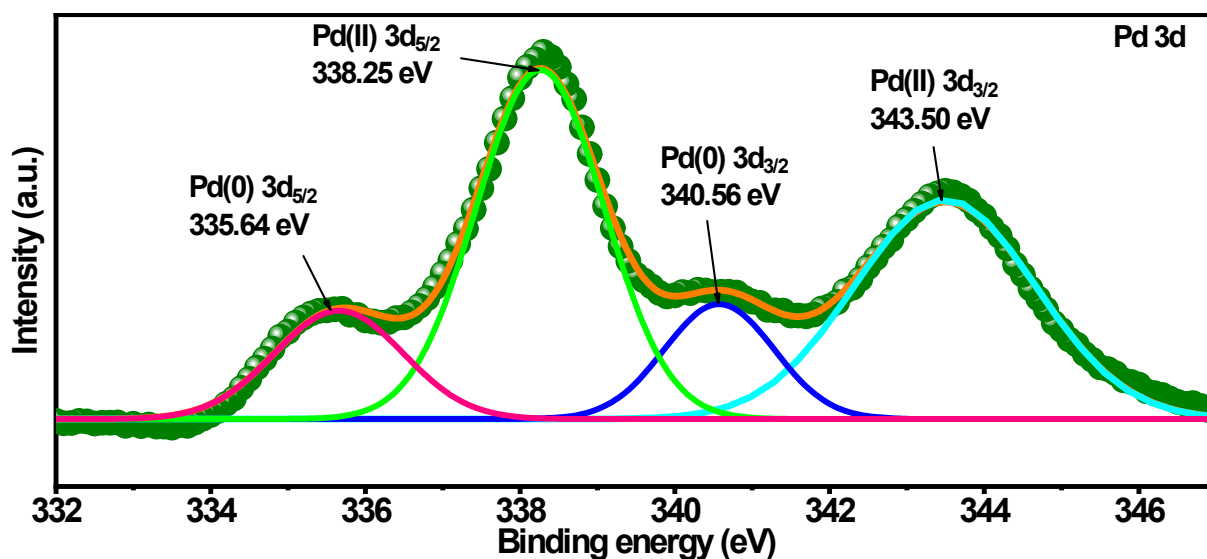**Figure S3.** SEM image of the recovered Pd@3D PPF after 1st run

Figure S4. XPS spectra of the recovered catalyst

Table S1. Comparison of Pd@3D PPF with other heterogeneous catalysts for the coupling of epichlorohydrin and CO_2

Entry	Catalyst	Pressure (MPa)	Cocatalyst	Temperature (^0C)	Time (h)	yield (%)	References
1	MOF-Zn-1	1.0	TBAB	100	3	97	1
2	UiO-66-OH	1.0	TBAI	140	2	90	2
3	Gd-MOF	2.0	TBAB	80	5	99.1	3
4	MOF-5	0.1	TBAB	50	12	93	4
5	F-IRMOF-3	2.0		140	1.5	80	5
6	UMCM-1-NH$_2$	1.2	TBAB	rt	24	78	6
7	Pd@3D PPF	0.1	TBAB	rt	10	99	This work

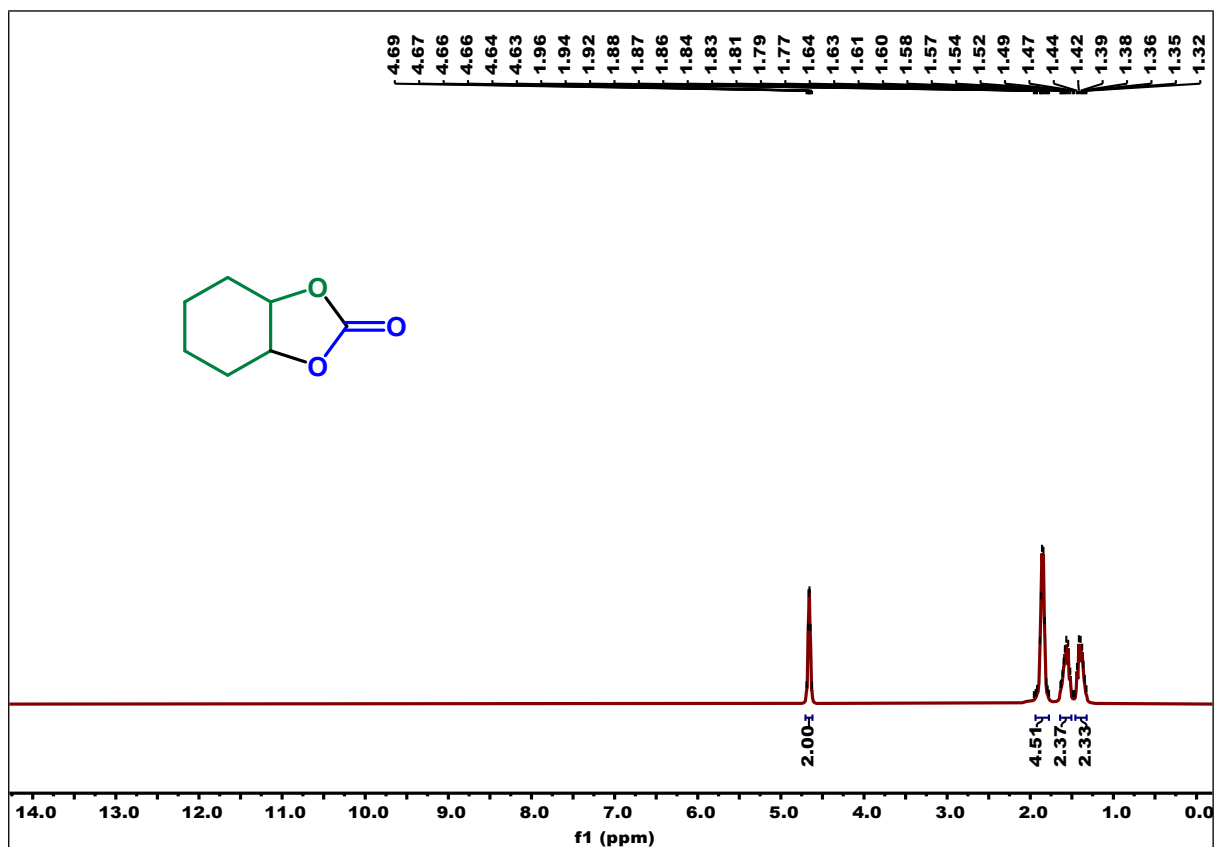**¹H NMR spectra of 4-(chloromethyl)-1,3-dioxolan-2-one (2c):** [7]
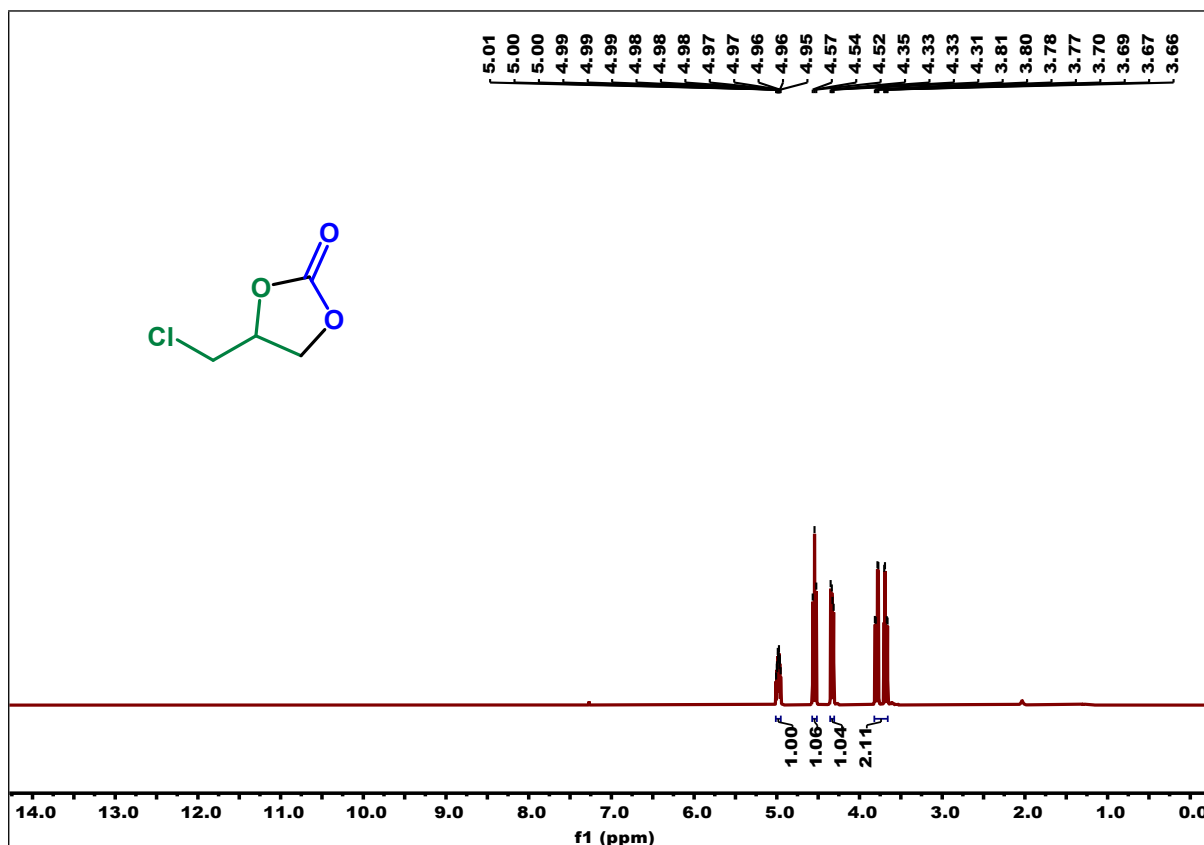
¹H NMR (400 MHz, CDCl₃): δ 5.01 – 4.95 (m, 1H), 4.57 – 4.52 (m, 1H), 4.33 (dd, J = 8.9, 5.7 Hz, 1H), 3.81 – 3.66 (m, 2H).

¹H NMR spectra of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (2e):[7]
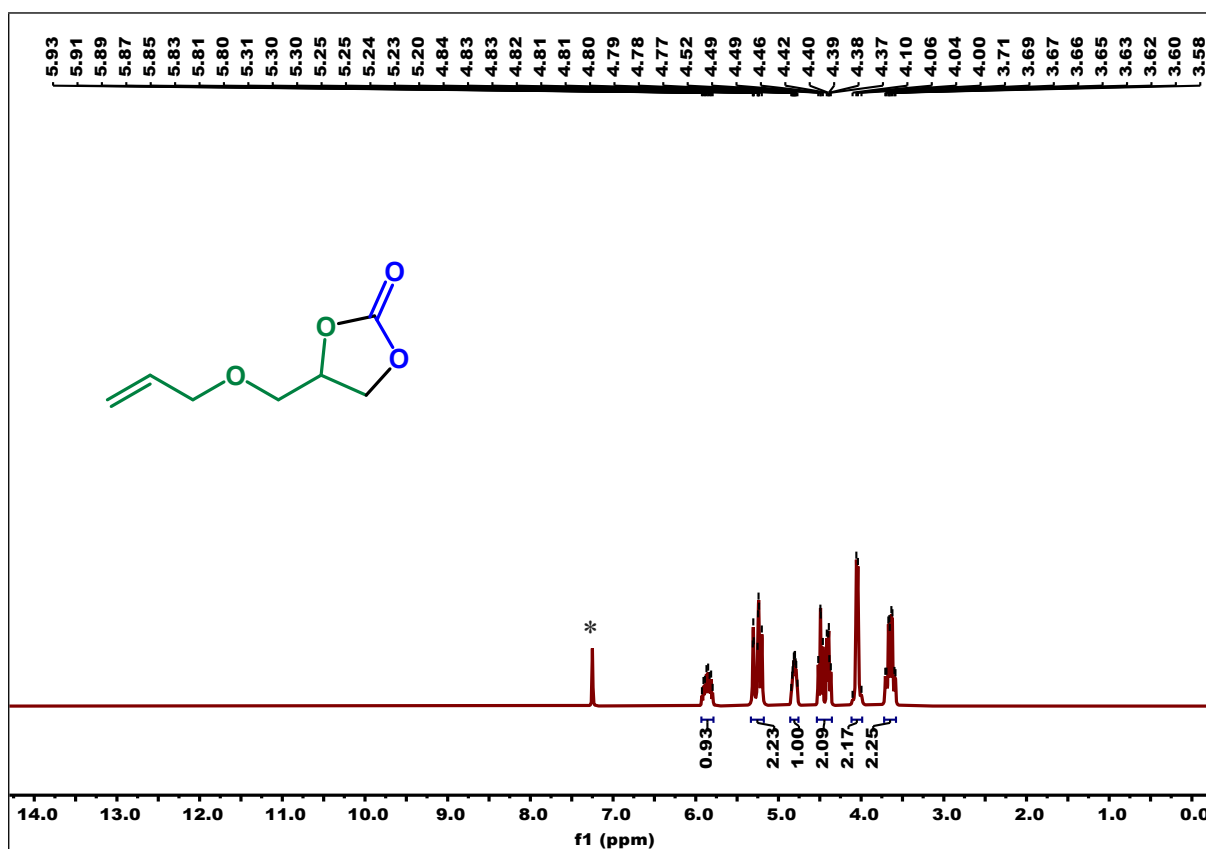
¹H NMR (400 MHz, CDCl₃ (*)): δ 5.86 (ddt, $J = 16.3, 10.8, 5.6$ Hz, 1H), 5.31 – 5.20 (m, 2H), 4.84 – 4.77 (m, 1H), 4.52 – 4.37 (m, 2H), 4.05 (d, $J = 5.6$ Hz, 2H), 3.64 (ddt, $J = 14.8, 11.1, 5.3$ Hz, 2H).
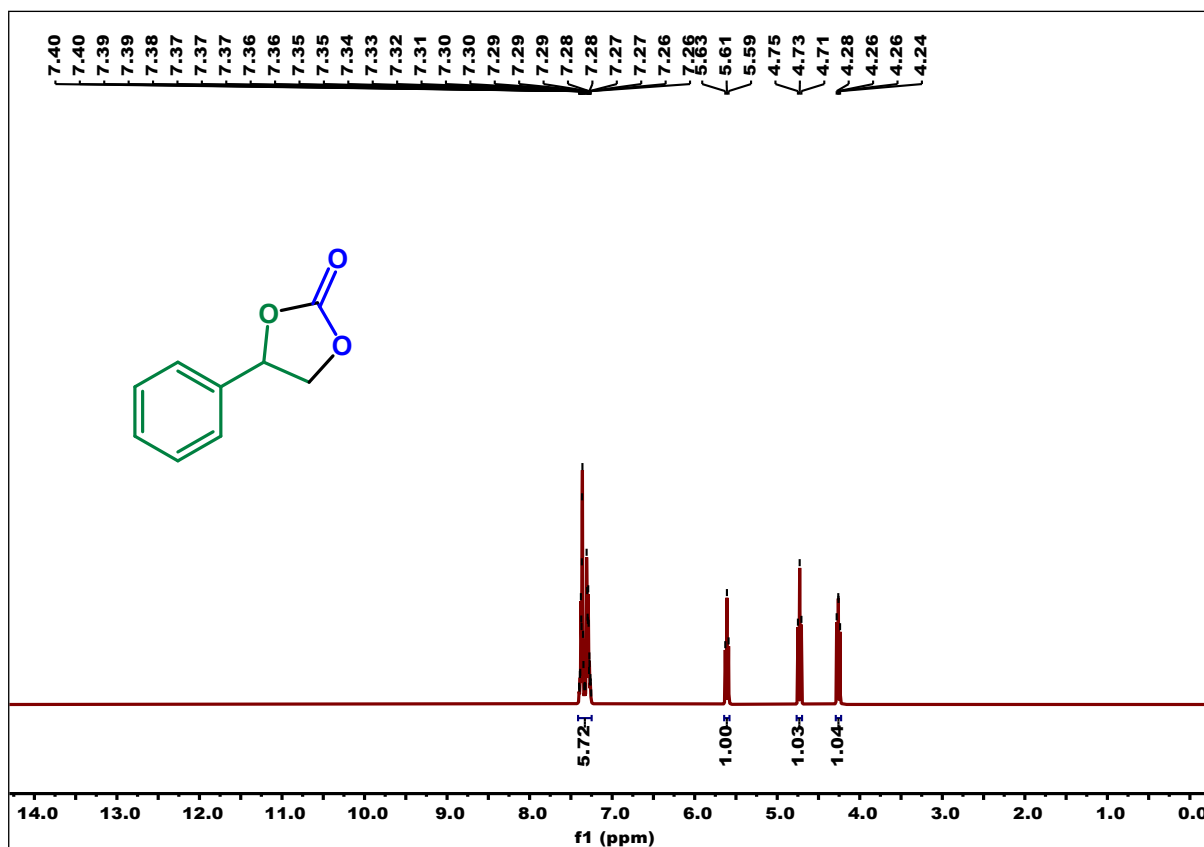
¹H NMR spectra of Hexahydro-benzo[1,3]dioxol-2-one (2f):[8]

¹H NMR (400 MHz, CDCl₃): δ 4.69 – 4.63 (m, 2H), 1.96 – 1.77 (m, 4H), 1.57 (dq, *J* = 14.2, 5.9 Hz, 2H), 1.39 (dt, *J* = 10.2, 5.8 Hz, 2H).
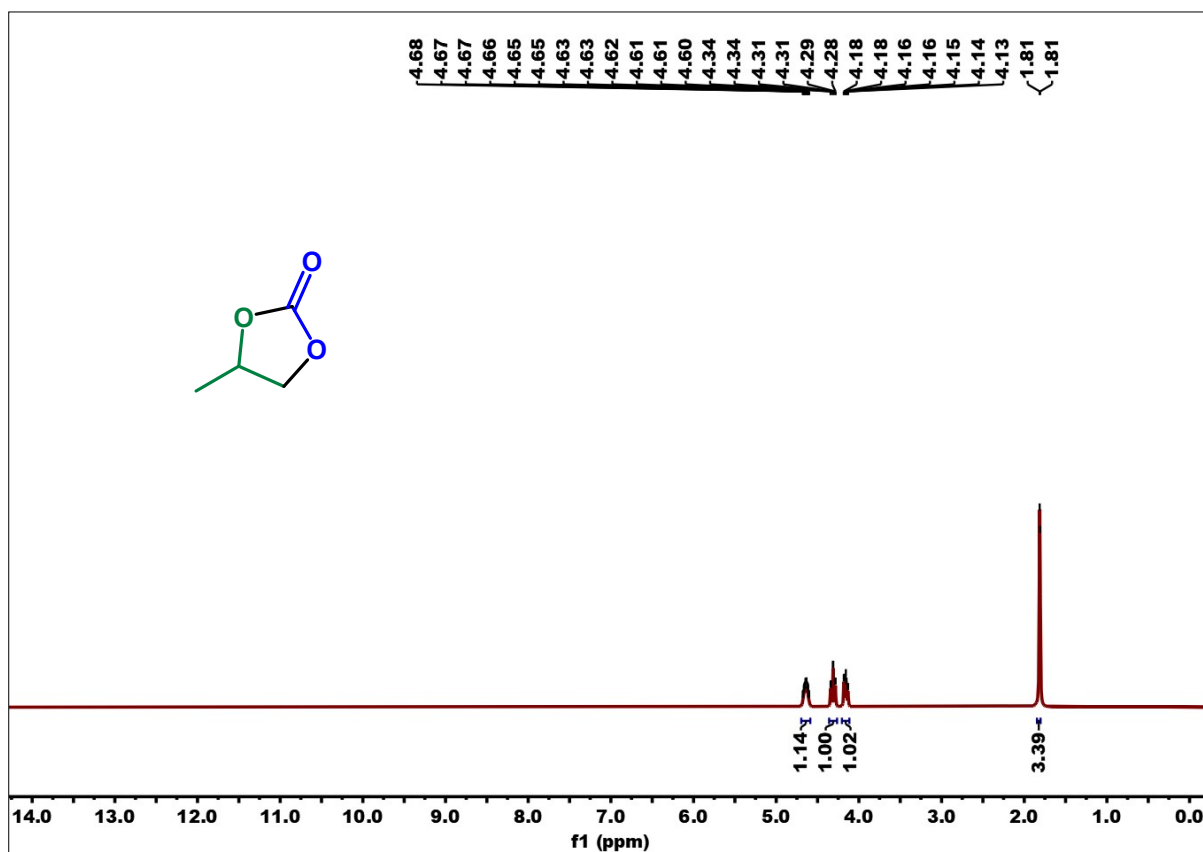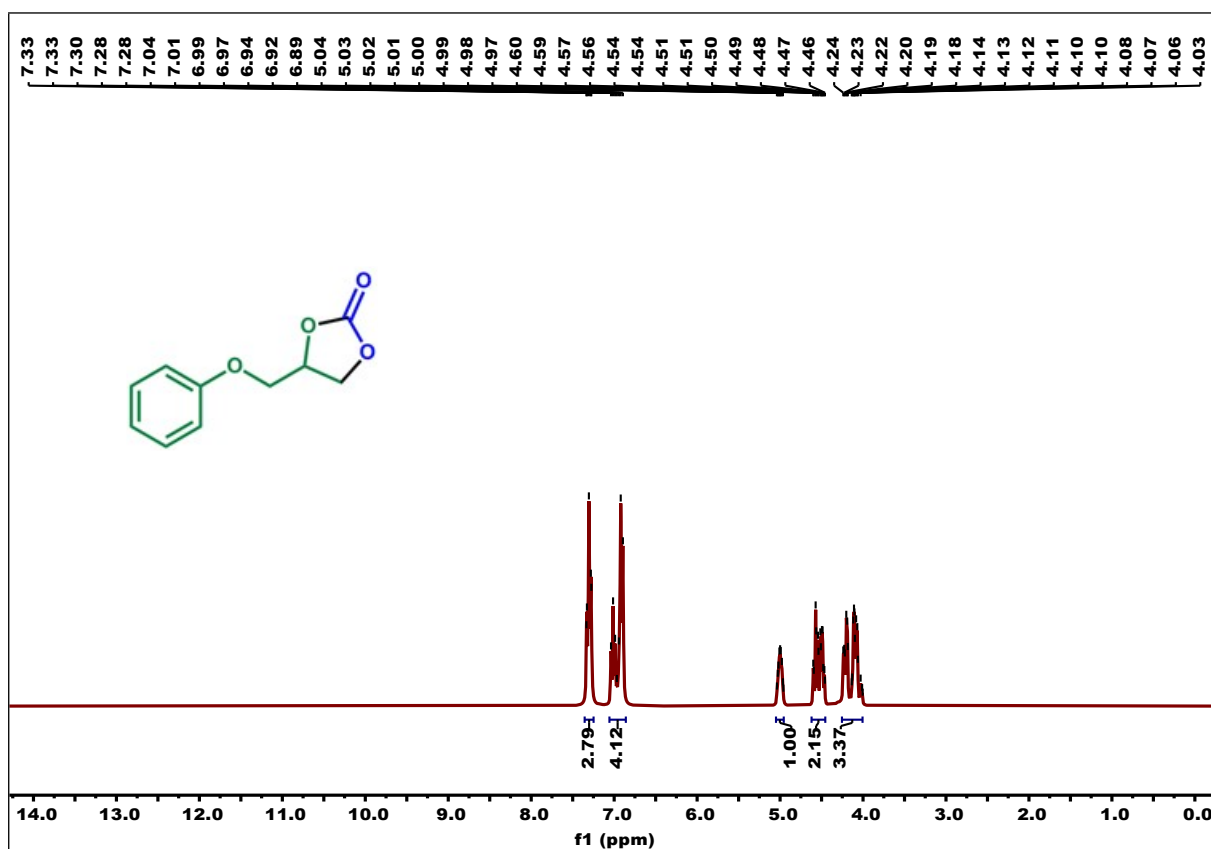
¹H NMR spectra of 4-phenyl-1,3-dioxolan-2-one (2g):[7]

¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.26 (m, 5H), 5.61 (t, J = 8.0 Hz, 1H), 4.73 (t, J = 8.4 Hz, 1H), 4.26 (dd, J = 8.7, 7.8 Hz, 1H).

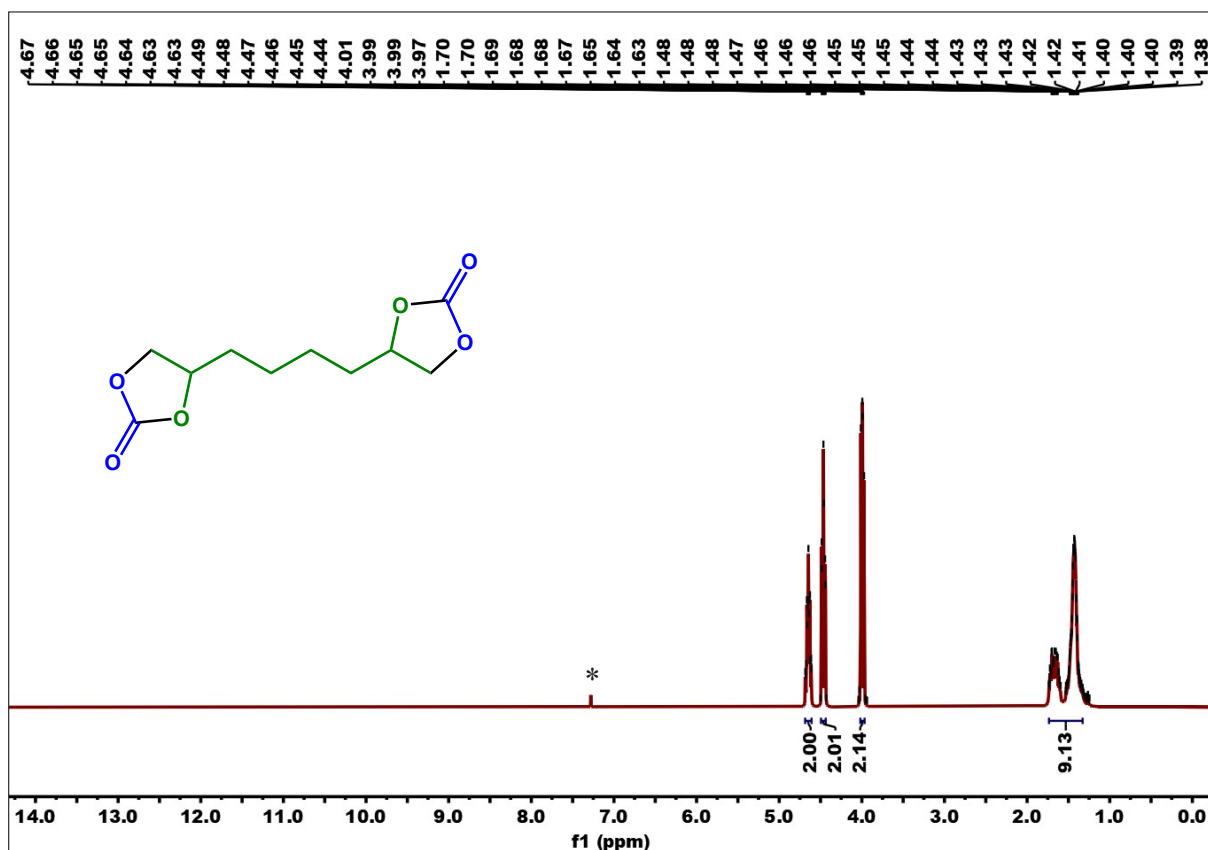**¹H NMR spectra of 4-methyl-1,3-dioxolan-2-one (2a):[8]**

¹H NMR (400 MHz, CDCl₃): δ 4.68 – 4.60 (m, 1H), 4.31 (td, *J* = 8.4, 1.3 Hz, 1H), 4.16 (ddd, *J* = 8.1, 5.9, 1.3 Hz, 1H), 1.81 (d, *J* = 1.6 Hz, 3H).

¹H NMR spectra of 4-(phenoxymethyl)-1,3-dioxolan-2-one (2i):[8]

¹H NMR (400 MHz, CDCl₃): δ 7.33 – 7.28 (m, 2H), 7.04 – 6.89 (m, 3H), 5.04 – 4.97 (m, 1H), 4.60 – 4.46 (m, 2H), 4.24 – 4.03 (m, 2H).

¹H NMR spectra of 4-(4-(oxiran-2-yl)butyl)-1,3-dioxolan-2-one (2b):[9]

¹H NMR (400 MHz, CDCl₃ (*)): δ 4.67-4.63 (m, 2H), 4.46 (td, *J* = 8.2, 2.3 Hz, 2H), 4.01 – 3.97 (m, 2H), 1.70 – 1.38 (m, 8H).

References:

1.   J. Lan, M. Liu, X. Lu, X. Zhang and J. Sun, *ACS Sustainable Chem. Eng.*, 2018, **6**, 8727-8735.

2.   J. Noh, Y. Kim, H. Park, J. Lee, M. Yoon, M. H. Park, Y. Kim and M. Kim, *J. Ind. Eng. Chem.*, 2018, **64**, 478-483.

3.   Z. Xue, J. Jiang, M.-G. Ma, M.-F. Li and T. Mu, *ACS Sustainable Chem. Eng.*, 2017, **5**, 2623-2631.

4.   J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang and B. Han, *Green Chem.*, 2009, **11**, 1031-1036.

5.   X. Zhou, Y. Zhang, X. Yang, L. Zhao and G. Wang, *J. Mol. Catal. A: Chem.*, 2012, **361**, 12-16.

6.   R. Babu, A. C. Kathalikkattil, R. Roshan, J. Tharun, D.-W. Kim and D.-W. Park, *Green Chem.*, 2016, **18**, 232-242.

7.   S. Motokucho, Y. Takenouchi, R. Satoh, H. Morikawa and H. Nakatani, *ACS Sustainable Chem. Eng.*, 2020, **8**, 4337-4340.

8.   S. Sarkar, S. Ghosh and S. M. Islam, *Org. Biomol. Chem.*, 2022, **20**, 1707-1722.

9.   J. Steinbauer and T. Werner, *ChemSusChem*, 2017, **10**, 3025-3029.