Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Amine Functionalized Zn(II) MOF as an Efficient Multifunctional Catalyst for CO_2 Utilization and Sulfoxidation Reaction

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Experimental Section

Materials and General Methods

All reagents and solvents were purchased from commercial sources and were used without further purification. N-donor ligand (**L**) were synthesized according to our previous reports.[1] Distilled water was used for synthetic manipulations. CHNS analyses were done using elementar vario MICRO CUBE analyzer. IR spectra were recorded using KBr pellet method on a Perkin–Elmer GX FTIR spectrometer. For each IR spectra 10 scans were recorded at 4 cm^{-1} resolution. ^{1}H & ^{13}C NMR spectra for the ligands, cyclic bicarbonate and sulfoxide derivatives were recorded on JEOL, JNM-ECZ 600R (600 MHz) and Bruker, Avance II 500 (500 MHz) spectrometer at temperature 25 °C and was calibrated with respect to internal reference TMS.

TGA analysis was carried out using Mettler Toledo Star SW 8.10. TG analysis was performed in nitrogen environment while the heating rate was ramped from room temperature to 600 °C at 10°C/min. Powder X-ray diffraction (PXRD) data were collected using a PANalytical Empyrean (PIXcel 3D detector) system with CuK_{α} radiation. The CO_2 and N_2 adsorption desorption isotherm was measured on a Micromeritics, 3 Flex instrument. Field Emission-Scanning Electron Microscopy (FE-SEM) micrographs were recorded using a JEOL JSM-7100F instrument employing an 18-kV accelerating voltage. Single-crystal structures were determined using BRUKER SMART APEX (CCD) diffractometer. The cyclic carbonate and sulfoxide products were identified with a gas chromatograph (GC, Agilent HP 6890 A; equipped with a capillary column HP-5, 30m x 0.25 mm) using a flame ionization detector. NH_3-TPD profile measured on BELCAT II Version 0.4.5.16.

Conventional synthesis of Catalyst ZnMOF-1-NH_2

ZnMOF-1-NH_2 synthesized accoding to our previous reports.[2] **ZnMOF-1-NH_2** was synthesized *via* refluxing at *ca* 110 ^{o}C of 1 mmol of $Zn(NO_3)_2.6H_2O$, 1 mmol H_2**ATA**, 2 mmol KOH and 1 mmol **L**, in 40 mL methanol:water (1:1) solvent in a 100 mL round bottom flask for 6 h. The resulting precipitates were filtered and washed with methanol:water (1:1) followed by acetone then dried at 100 °C in oven (Yield ~88 % for **ZnMOF-1-NH_2**). For **ZnMOF-1-NH_2 $\{[Zn(ATA)(L).H_2O]\}_n$**: Elemental analysis (%) Cal.: C, 49.15; H, 3.51; N, 14.33; found (as synthesized): C, 48.95; H, 3.90; N, 14.27; IR cm^{-1} (KBr) (as synthesized): 3468 (br), 3365 (w), 3319 (w), 3225 (w), 3130 (w), 2925 (w), 2854 (w), 1692 (m), 1561 (s), 1497 (w), 1426 (m), 1382 (s), 1287 (m), 1147 (w), 1067 (w), 1015 (w), 947 (w), 828 (w), 773 (m), 698 (w), 572 (w).

Mechanochemical synthesis of Catalyst ZnMOF-1-NH_2

ZnMOF-1-NH$_2$ also synthesized via mechanochemical grinding method.[2] **ZnMOF-1-NH$_2$_G** was synthesized mechanochemically through manually grinding a mixture of 1 mmol of Zn(OAc)$_2$.2H$_2$O, 1 mmol H$_2$**ATA** and 1mmol **L** in a mortar and pestle for 25 min. The resulting solids were washed with methanol:water (1:1, 5mL) followed by acetone (5 mL) to remove any unreacted starting material and then dried at 100 °C for 24 h in oven (Yield ~83% for **ZnMOF-1-NH$_2$_G**). For **ZnMOF-1-NH$_2$_G {[Zn(ATA)(L1).H$_2$O]}$_n$**: Elemental analysis (%) Cal.: C, 49.15; H, 3.51; N, 14.33; found (as synthesized): C, 48.71; H, 3.50; N, 13.53; IR cm-1 (KBr): 3460 (br), 3366 (w), 3223 (w), 3071 (w), 2925 (w), 2848 (w), 1690 (m), 1572 (s), 1495 (w), 1423 (m), 1374 (s), 1288 (m), 1147 (w), 1067 (w), 1014 (w), 946 (w), 829 (w), 772 (w), 698 (m), 572 (w).

General Procedure for the Cycloaddition of CO$_2$ and Epoxide substrate

Cycloaddition of epoxide and CO$_2$ to form cyclic carbonate was carried out in 50 mL stainless-steel autoclave with a magnetic stirrer. For each operation, epoxide (20 mmol) and the **ZnMOF-1-NH$_2$** catalyst (1 mol%) and co-catalyst TBAB (2.5 mol%), wherever applicable were introduced into the reactor without solvent. The autoclave reactor was then pressurized with CO$_2$ to pre-set pressure at room temperature. The reaction mixture was then heated to the desired temperature, and stirring was set at 600 rpm. When the reaction time was elapsed, cycloaddition was stopped and the reaction was cooled to RT. The reaction mixture was centrifuged to separate the catalyst, 2 times washing with ethyl acetate and the products were isolated (in ethyl acetate) and identified with a gas chromatograph using dodecane as an internal standard (Bruker 450-GC; equipped with a capillary column HP-5, 30m × 0.25 mm; using a flame ionization detector).

General Procedure for the Sulfoxidation Reaction

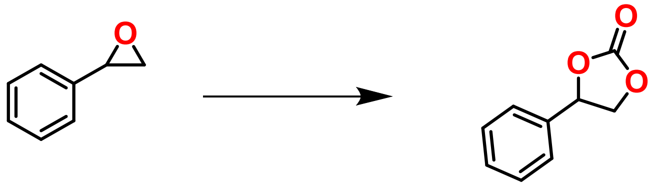
Oxidation of Sulfide derivatives to sulfoxide were carried out in 10 mL glass tube equipped with a magnetic stirring bar. For each reaction, sulfide (0.5 mmol) and the **ZnMOF-1-NH$_2$** catalyst (2.1 mol%) and oxidant (TBHP/H$_2$O$_2$/UHP, 1.0 mmol, wherever applicable) were introduced into the glass tube with DCM as solvent (4.0 mL). The reaction mixture was then set to the desired temperature (RT/40 ^{o}C) and stirred at 200 rpm. On completion of sulfoxidation, reaction was stopped and cooled to RT. The reaction mixture was centrifuged to separate the catalyst, 2 times washing with water and the products were isolated (in DCM) and identified with a gas chromatograph using dodecane as an internal standard (Bruker 450-GC; equipped with a capillary column HP-5, 30m × 0.25 mm; using a flame ionization detector).

Catalyst Recyclability

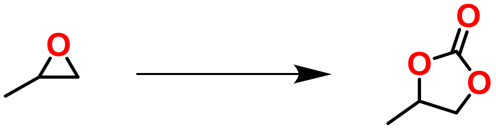
After each catalytic cycle, **ZnMOF-1-NH$_2$** catalyst was recovered by centrifugation, then rinsed with methanol/water, ethanol, and dried in vacuum at 100°C for the next catalytic cycle under the same reaction conditions up to 4 recycle. The recovered catalyst subject to PXRD, FTIR and FE-SEM analysis. For **ZnMOF-1-NH$_2$**: Elemental analysis (%) Cal.: C, 47.12; H, 3.95; N, 10.99; found (After 4th Catalytic cycle Cycloaddition): C, 47.40; H, 3.78; N, 13.82; IR cm^{-1} (KBr): 3464 (br), 3363 (w), 3319 (w), 3216 (w), 3127 (w), 2924 (w), 2852 (w), 1693 (m), 1568 (s), 1496 (w), 1428 (m), 1382 (s), 1286 (m), 1146 (w), 1065 (w), 1015 (w), 947 (w), 828 (w), 773 (m), 698 (w), 574 (w); found (After 4th Catalytic cycle Sulfoxidation): C, 47.50; H, 3.59; N, 13.85; IR cm^{-1} (KBr): 3465 (br), 3364 (w), 3320 (w), 3216 (w), 3128 (w), 2925 (w), 2852 (w), 1694 (m), 1569 (s), 1497 (w), 1430 (s), 1382 (s), 1286 (m), 1146 (w), 1065 (w), 1015 (w), 945 (w), 828 (w), 773 (m), 698 (w), 574 (w).

^{1}H & ^{13}C NMR analysis of cyclic carbonate and sulfoxide products

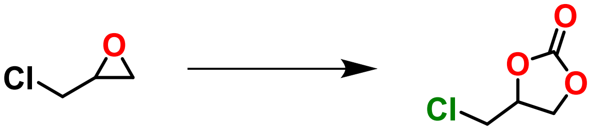
The cyclic carbonate and sulfoxide products involve in this study are all known compounds. ^{1}H and ^{13}C NMR spectra of products matched well with reported in the literature.[S3-S12] ^{1}H and ^{13}C NMR data of the cyclic carbonate and sulfoxide products are as follows.



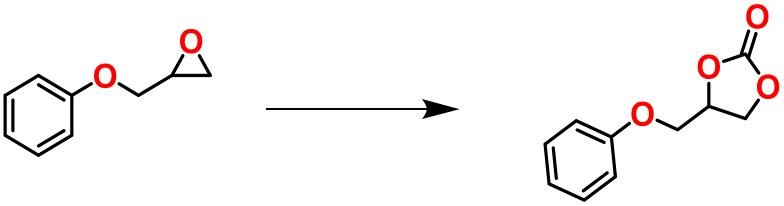
Styrene carbonate: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.39 (dd, J = 44.9, 6.4 Hz, 5H), 5.67 (t, J = 7.9 Hz, 1H), 4.80 (t, J = 8.2 Hz, 1H), 4.33 (t, J = 8.3 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.80, 135.71, 129.62, 129.12, 125.80, 71.09.



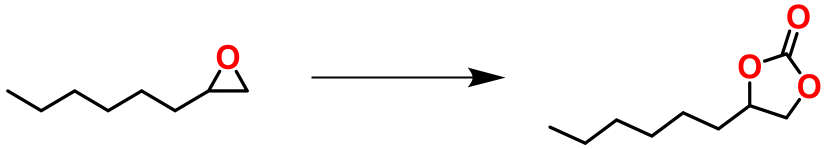
Propylene carbonate: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 4.94 – 4.87 (m, 1H), 4.63 – 4.56 (m, 1H), 4.06 (dd, *J* = 8.5, 7.2 Hz, 1H), 1.47 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.70, 73.30, 70.19, 18.48.



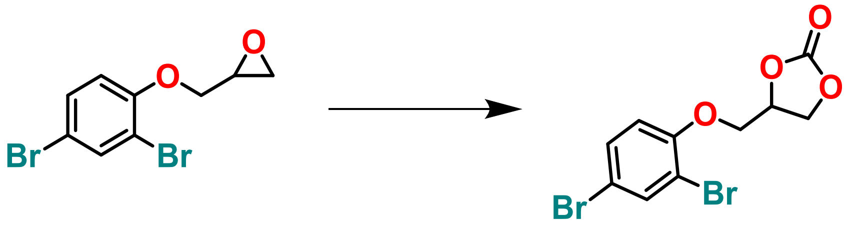
4-(chloromethyl)-1,3-dioxolan-2-one: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.05 – 5.01 (m, 1H), 4.63 – 4.60 (m, 1H), 4.42 (dd, J = 9.0, 5.7 Hz, 1H), 3.84 (dd, J = 12.1, 5.1 Hz, 1H), 3.75 (dd, J = 12.0, 3.7 Hz, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ = 154.29, 74.30, 66.83, 43.85.



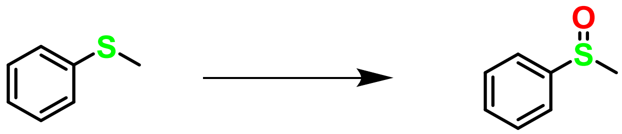
4-(phenoxymethyl)-1,3-dioxolan-2-one: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.31 – 7.29 (m, 2H), 7.02 – 6.90 (m, 3H), 5.02 (dd, *J* = 8.4, 5.3 Hz, 1H), 4.61 – 4.51 (m, 2H), 4.18 (ddd, *J* = 60.8, 10.6, 3.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 157.70, 154.68, 129.62, 121.89, 114.53, 74.12, 66.79, 66.15.



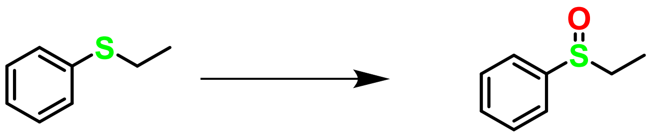
4-hexyl-1,3-dioxolan-2-one: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 4.66 (d, *J* = 5.2 Hz, 1H), 4.48 (d, *J* = 6.7 Hz, 1H), 4.02 (d, *J* = 6.6 Hz, 1H), 1.75 – 1.64 (m, 2H), 1.27 (d, *J* = 34.8 Hz, 8H), 0.89 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.04, 69.29, 33.67, 31.34, 28.62, 24.15, 22.28, 13.81.



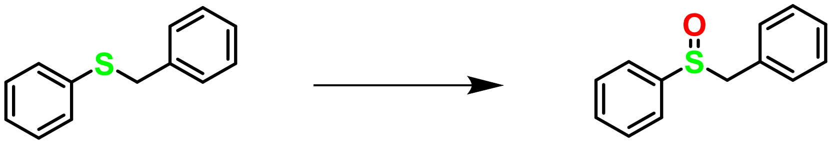
2-((2,4-dibromophenoxy)methyl)oxirane: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (s, 1H), 7.39 (d, J = 8.9 Hz, 1H), 6.78 (d, J = 8.8 Hz, 1H), 5.06 (ddd, J = 10.7, 7.1, 3.5 Hz, 1H), 4.65 (d, J = 7.1 Hz, 2H), 4.30 – 4.15 (m, 2H), ^{13}C NMR (151 MHz, $CDCl_3$) δ = 154.43, 153.48, 135.83, 131.39, 114.98, 114.73, 113.58, 73.71, 68.28, 66.02.



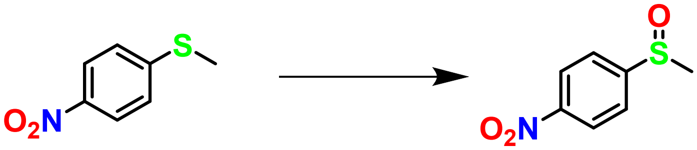
Phenyl methyl sulfoxide: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66-7.64 (m, 2H), 7.53-7.48 (m, 3H), 2.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.1, 130.5, 128.9, 123.0, 43.3.



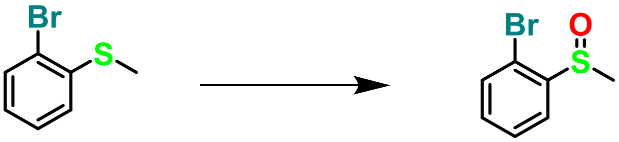
Ethyl Phenyl sulfoxide: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62-7.60 (m, 2H), 7.54-7.49 (m, 3H), 2.95-2.87 (m, 1H), 2.81-2.74 (m, 1H), 1.20 (t, 3H, J = 7.5) 13C (125 MHz, CDCl3): δ = 143.20, 130.94, 129.14, 124.17, 50.24, 5.95.



Benzyl phenyl sulfoxide: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46-7.37 (m, 5H), 7.29-7.23 (m, 3H), 6.98 (m, 2H), 4.12 (d, 1H, *J* = 12.5 Hz), 4.00 (d, 1H, *J* = 12.5 Hz) ^{13}C (125 MHz, $CDCl_3$): δ = 142.63, 131.16, 130.33, 129.06, 128.83, 128.42, 128.23, 124.43, 63.52.



4-Nitrophenyl methyl sulfoxide: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.40 (d, 2H, *J* = 8.5 Hz), 7.86 (d, 2H, *J* = 8.5 Hz), 2.81 (s, 3H), ^{13}C (125 MHz, $CDCl_3$): δ = 153.1, 149.4, 124.66, 124.49, 43.88.



2-Bromophenyl methyl sulfoxide: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98-7.93 (m, 1H), 7.62-7.49 (m, 2H), 7.42-7.34 (m, 1H), 2.83 (s, 3H), ^{13}C (125 MHz, $CDCl_3$): δ = 145.28, 132.90, 132.25, 128.73, 125.69, 118.39, 41.83.

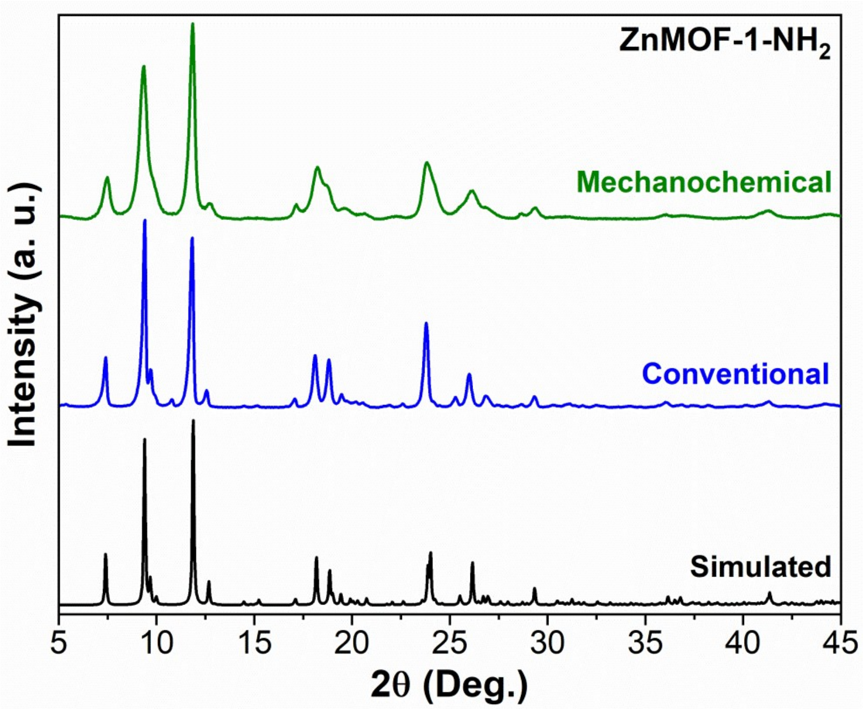


Figure S1. Comparison of PXRD data of **ZnMOF-1-NH$_2$** synthesized by conventional and mechanochemical routes with simulated from SXRD data obtained from CCDC database.

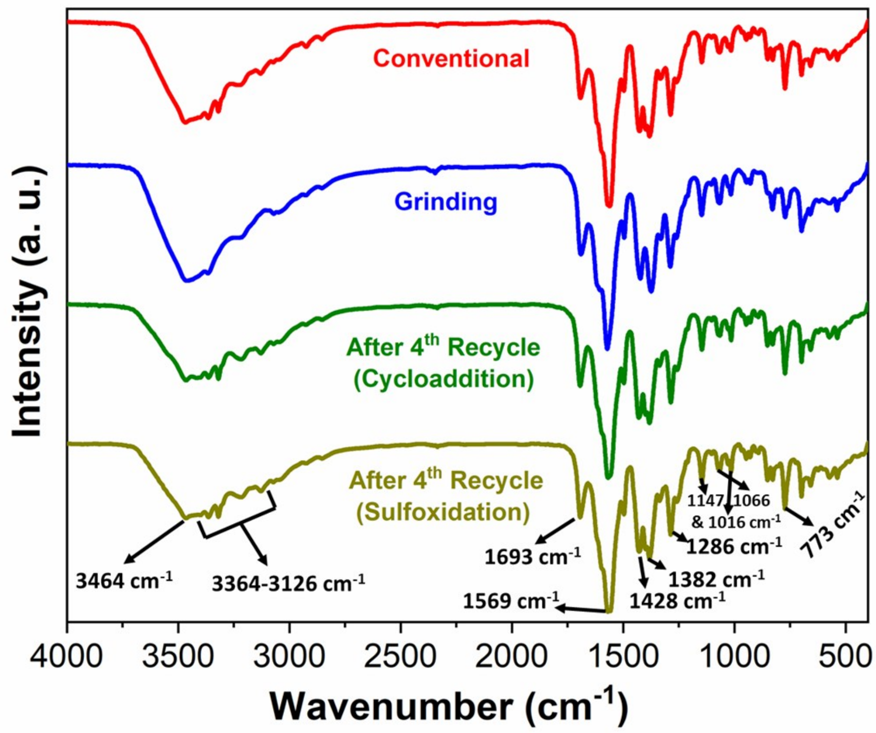


Figure S2. FTIR of **ZnMOF-1-NH$_2$**, synthesized by conventional route, synthesized by grinding, recovered after 4th catalytic cycle for cycloaddition and recovered after 4th catalytic cycle for sulfoxidation reaction respectively. (recorded for each compound dispersed in KBr pellets)

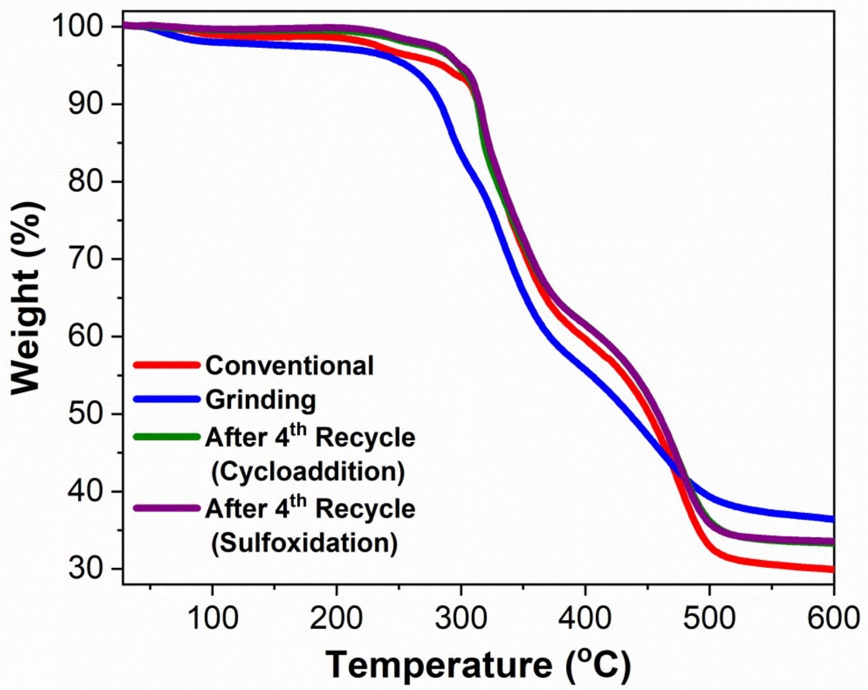


Figure S3. TGA plot for **ZnMOF-1-NH$_2$**, synthesized by conventional route, synthesized by grinding, recovered after 4th catalytic cycle for cycloaddition and recovered after 4th catalytic cycle for sulfoxidation reaction respectively.

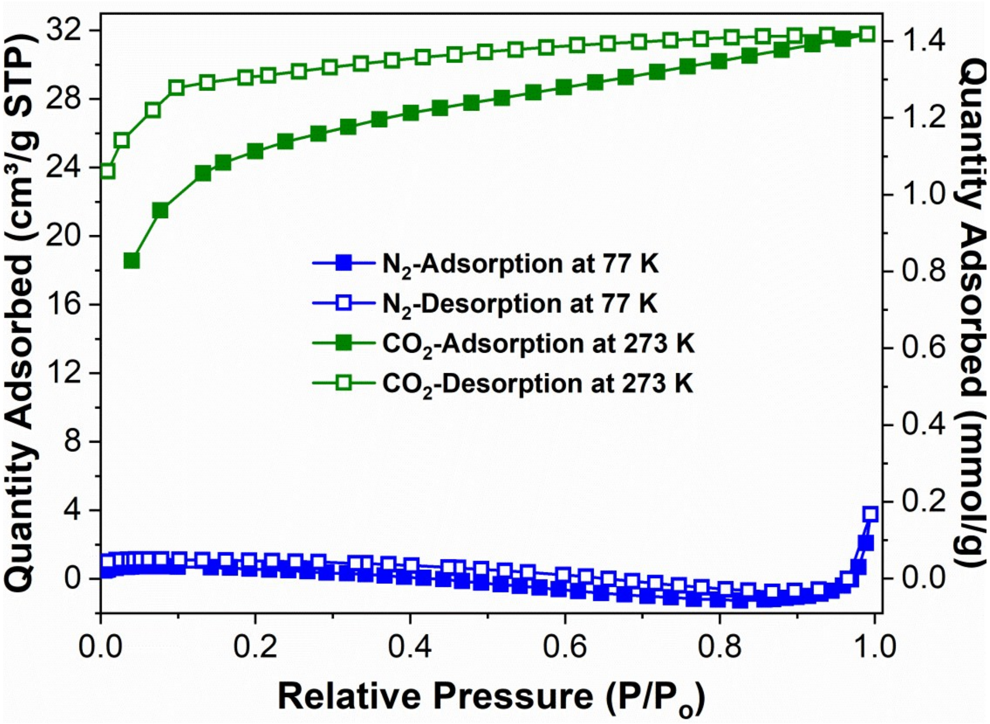


Figure S4. CO$_2$ and N$_2$ gas adsorption-desorption isotherm. (CO$_2$ at 273 K and N$_2$ at 77 K)

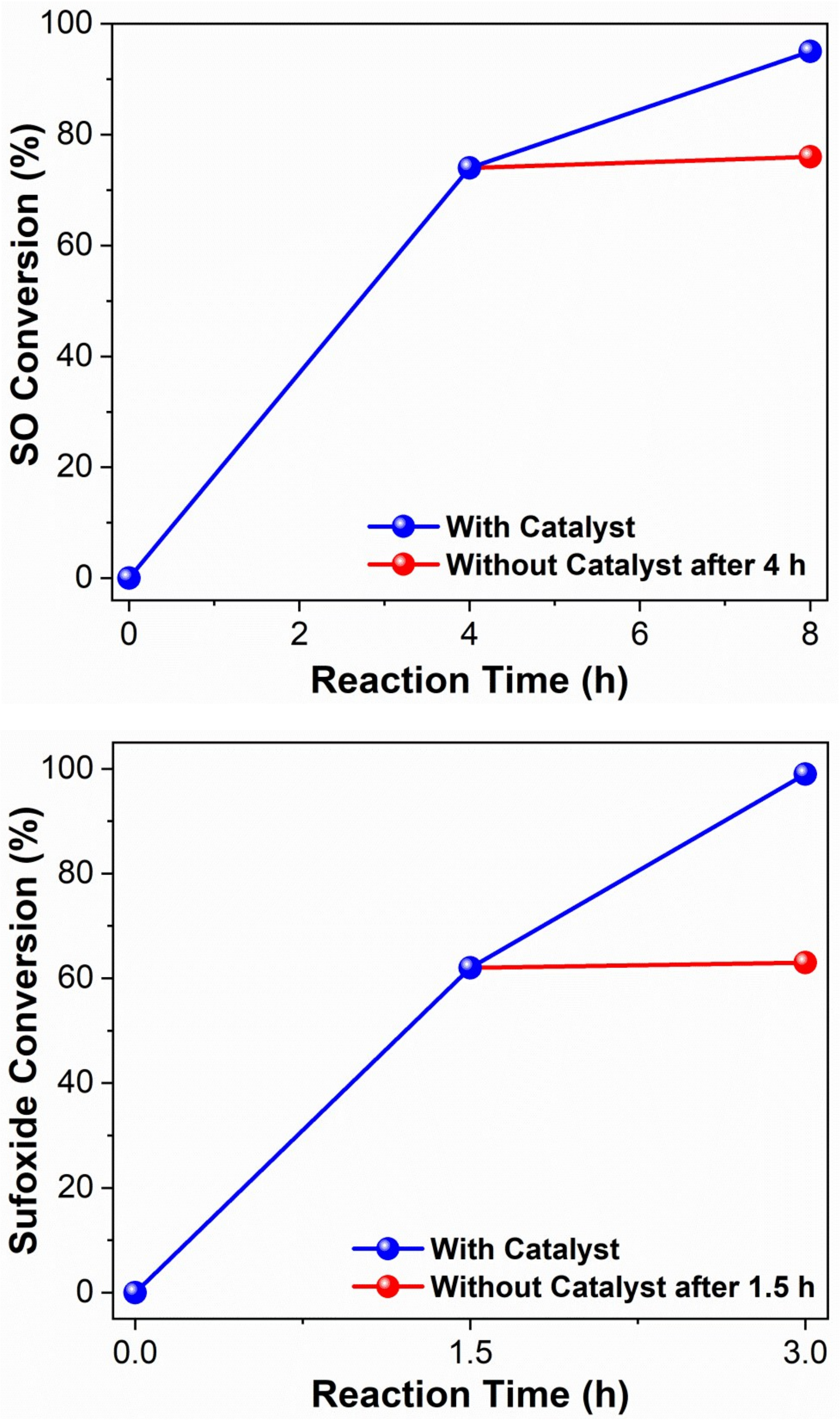


Figure S5. Hot filtration test for cycloaddition and sulfoxidation reactions for metal leaching. [Reaction Condition, cycloaddition: 1 mol% catalyst; 80 ^{o}C at 0.8 MPa CO_2. sulfoxidation: 2.1 mol% catalyst; 40 ^{o}C] Hot filtration was done at 50 % reaction time (4 h for cycloaddition and 1.5 h for sulfoxidation).

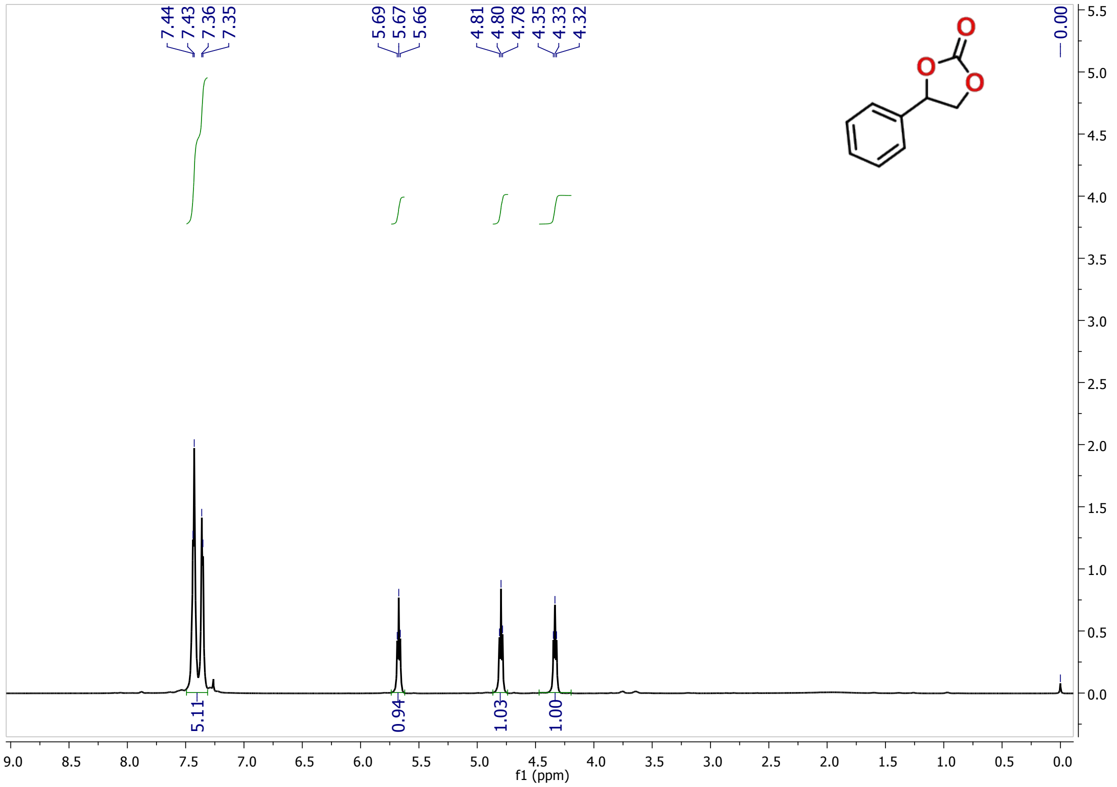


Figure S6. ^{1}H-NMR of the isolated styrene carbonate.

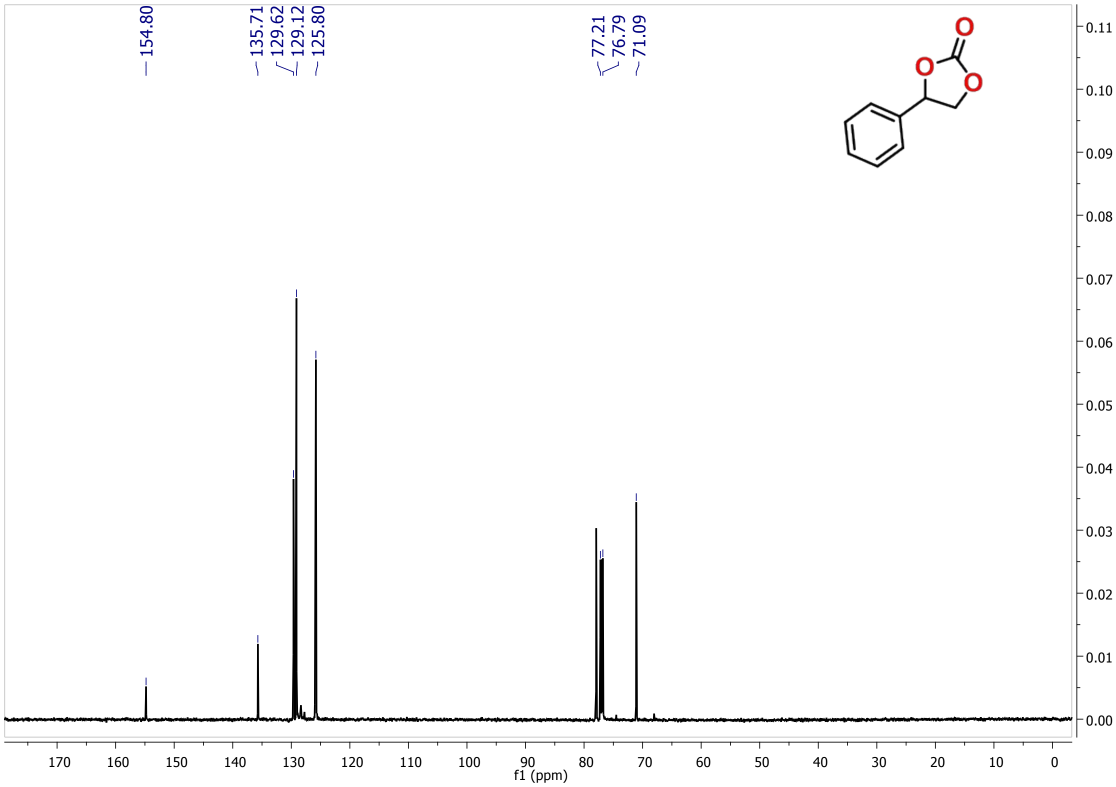


Figure S7. ^{13}C-NMR of the isolated styrene carbonate.

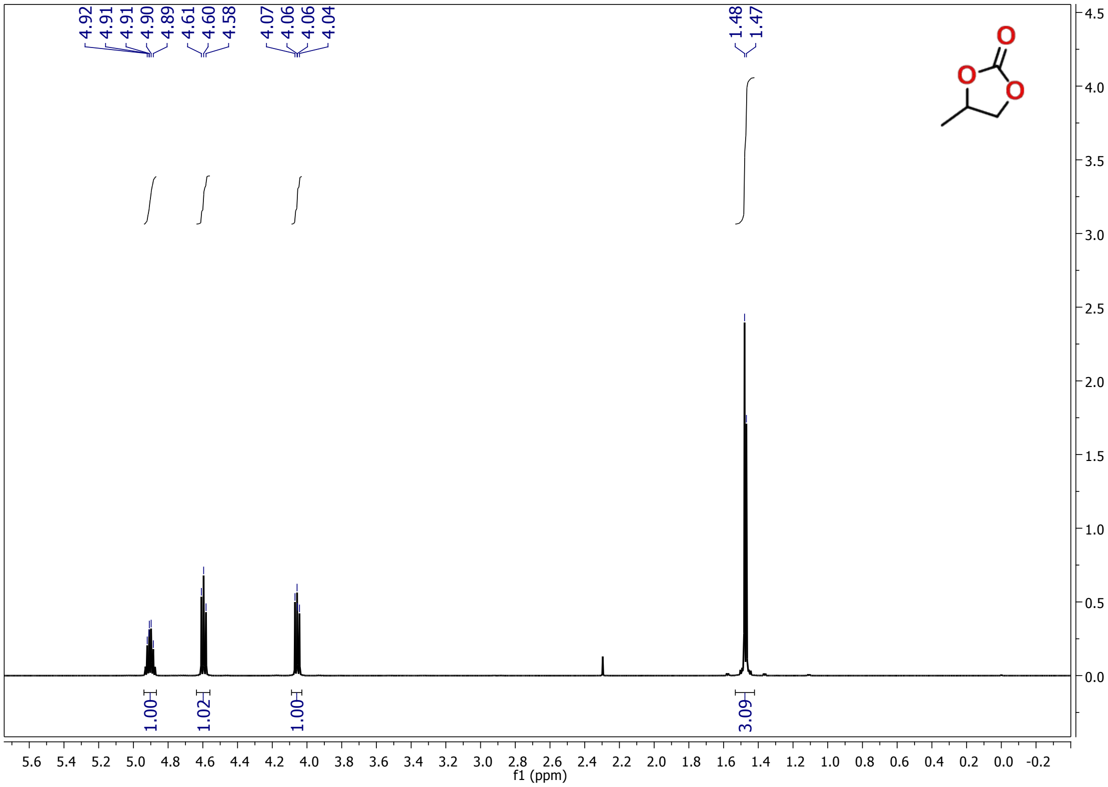


Figure S8. ^{1}H-NMR of the isolated propylene carbonate.

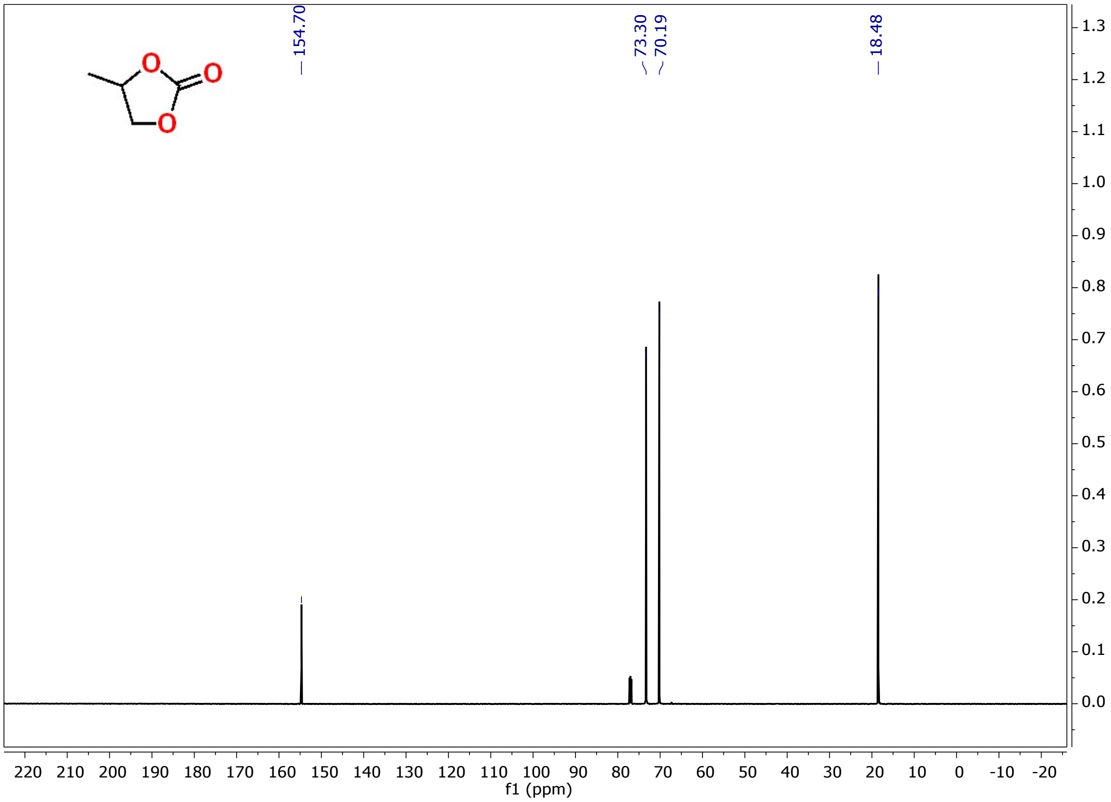


Figure S9. ^{13}C-NMR of the isolated propylene carbonate.

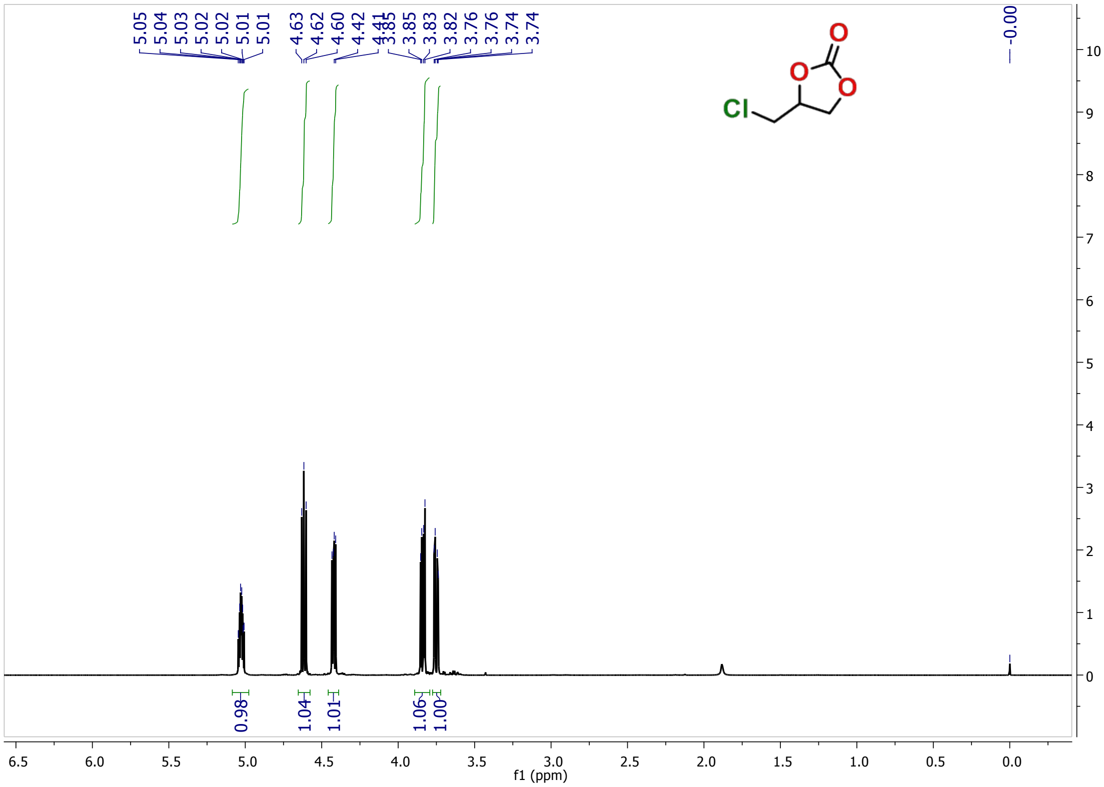


Figure S10. ^{1}H-NMR of the isolated 4-(chloromethyl)-1,3-dioxolan-2-one.

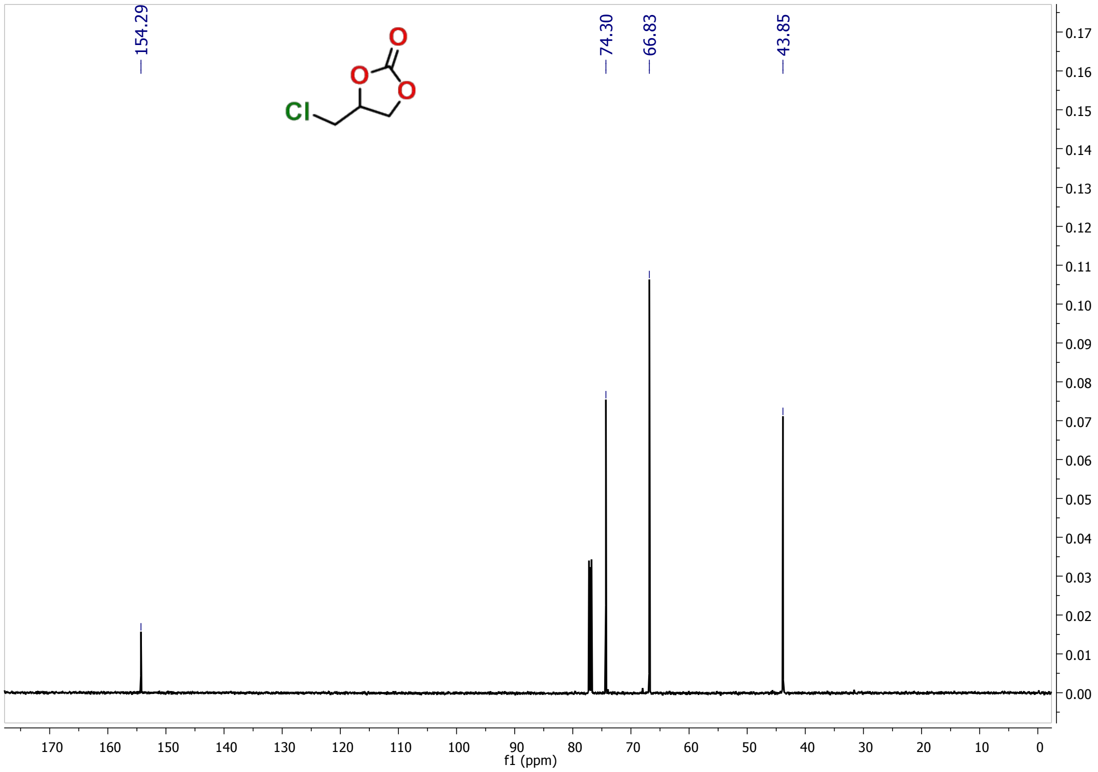


Figure S11. ^{13}C-NMR of the isolated 4-(chloromethyl)-1,3-dioxolan-2-one.

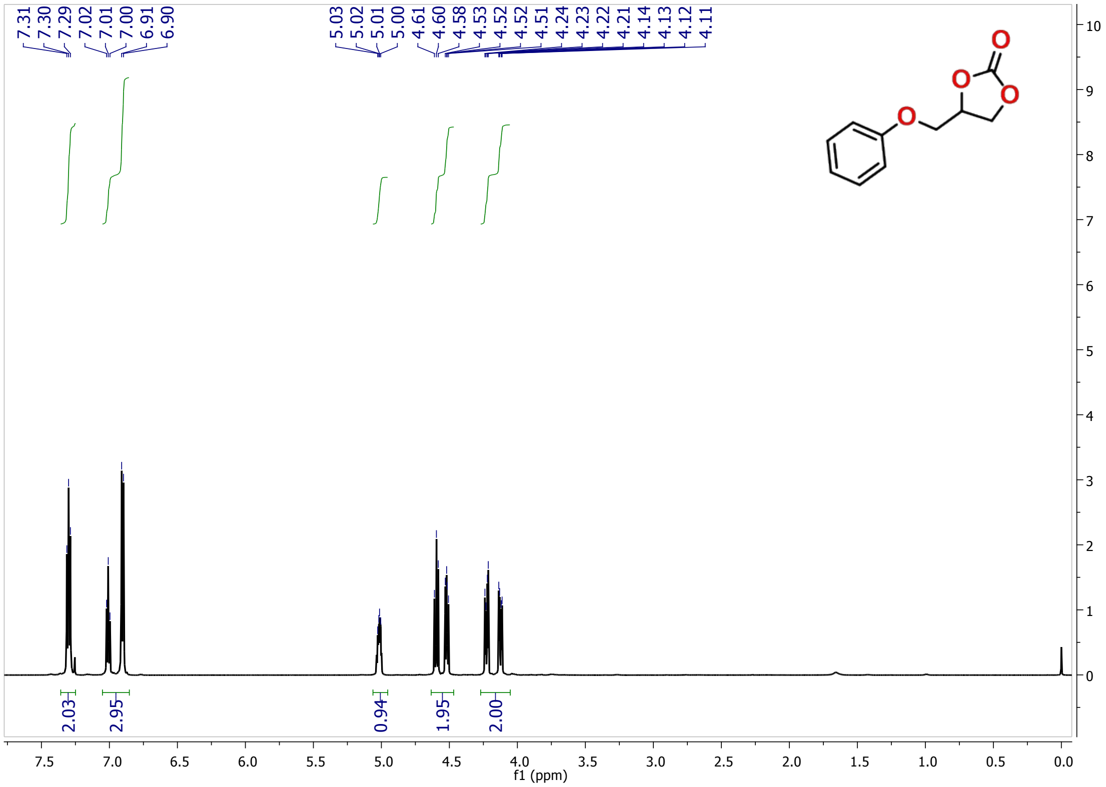


Figure S12. ^{1}H-NMR of the isolated 4-(phenoxymethyl)-1,3-dioxolan-2-one.

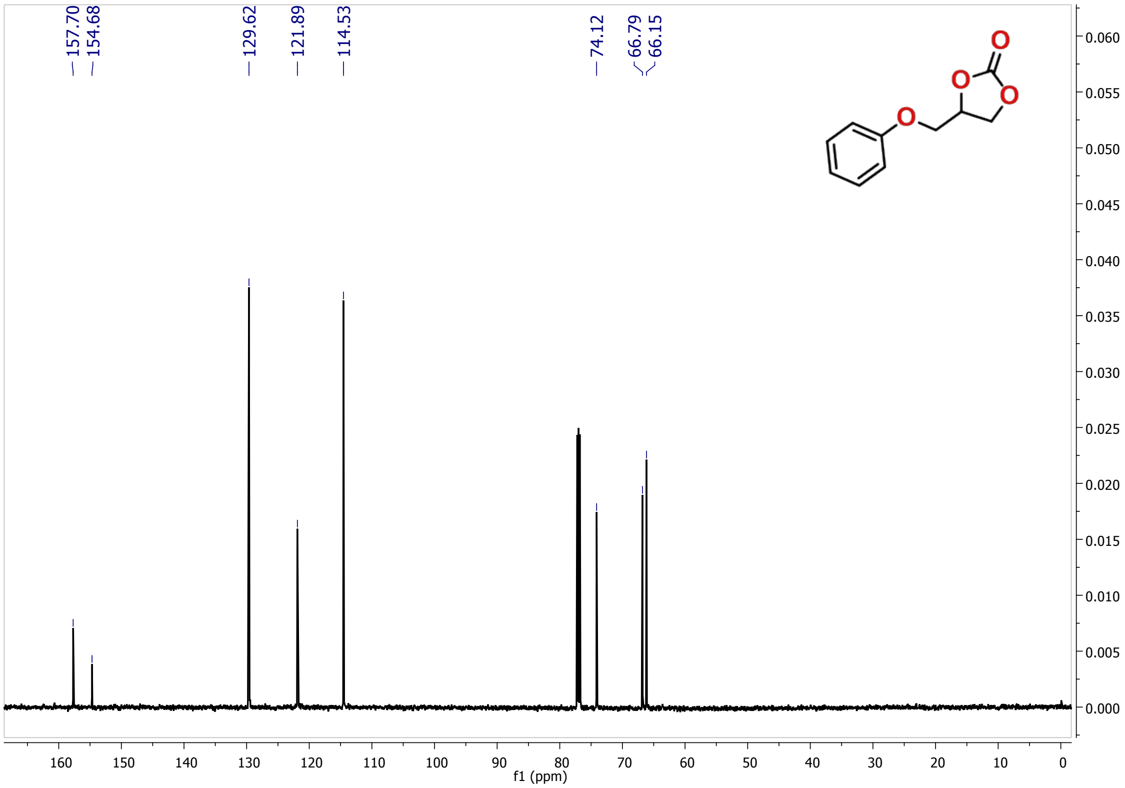


Figure S13. ^{13}C-NMR of the isolated 4-(phenoxymethyl)-1,3-dioxolan-2-one.

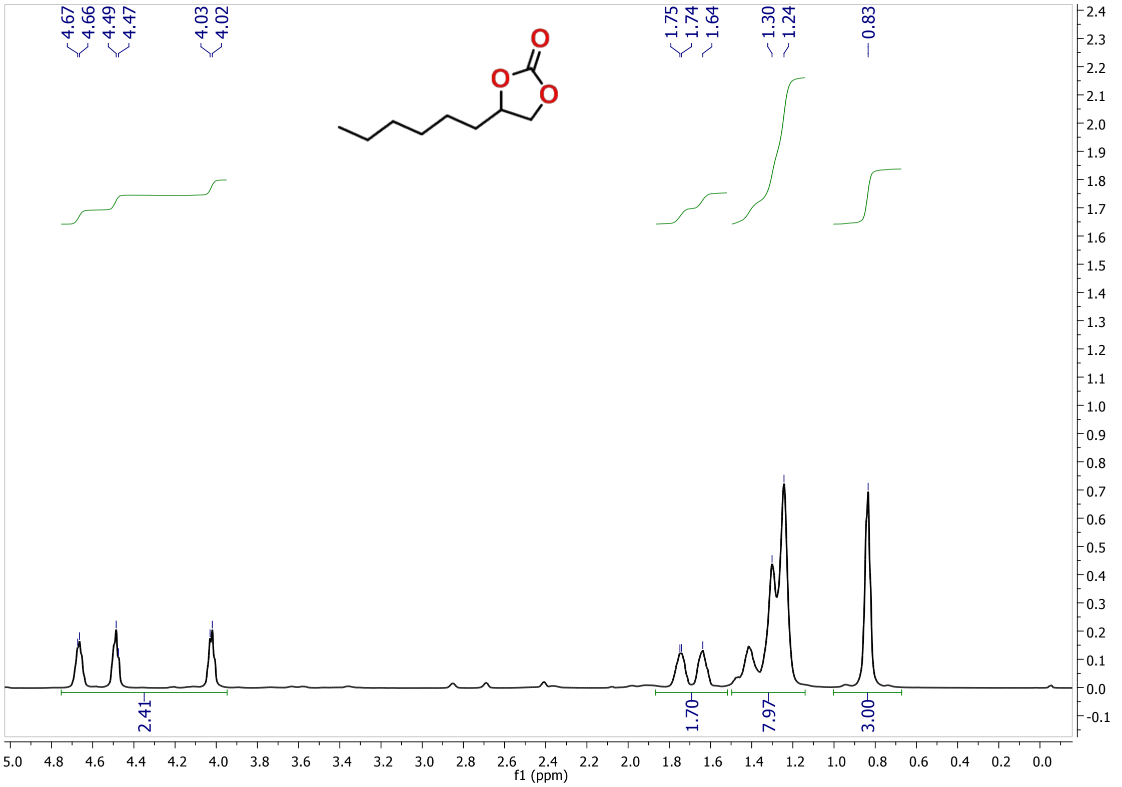


Figure S14. ^{1}H-NMR of the isolated 4-hexyl-1,3-dioxolan-2-one.

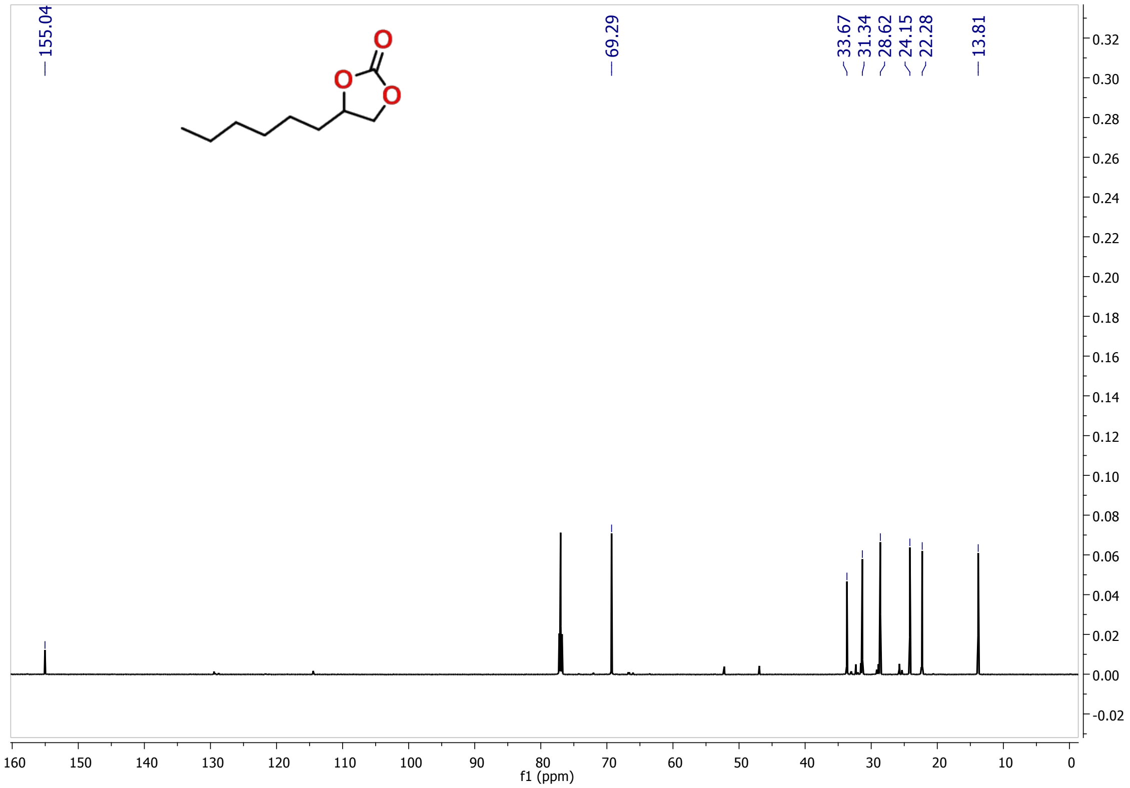


Figure S15. ^{13}C-NMR of the isolated 4-hexyl-1,3-dioxolan-2-one.

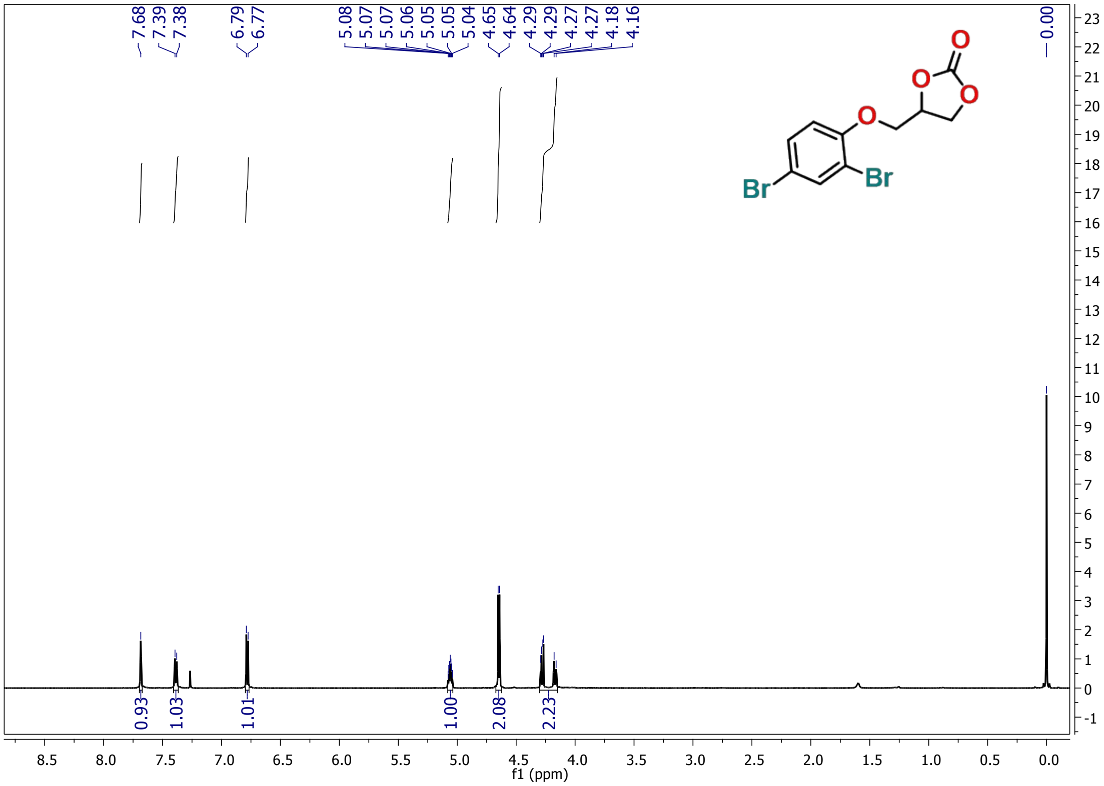


Figure S16. ^{1}H-NMR of the isolated 2-((2,4-dibromophenoxy)methyl)oxirane.

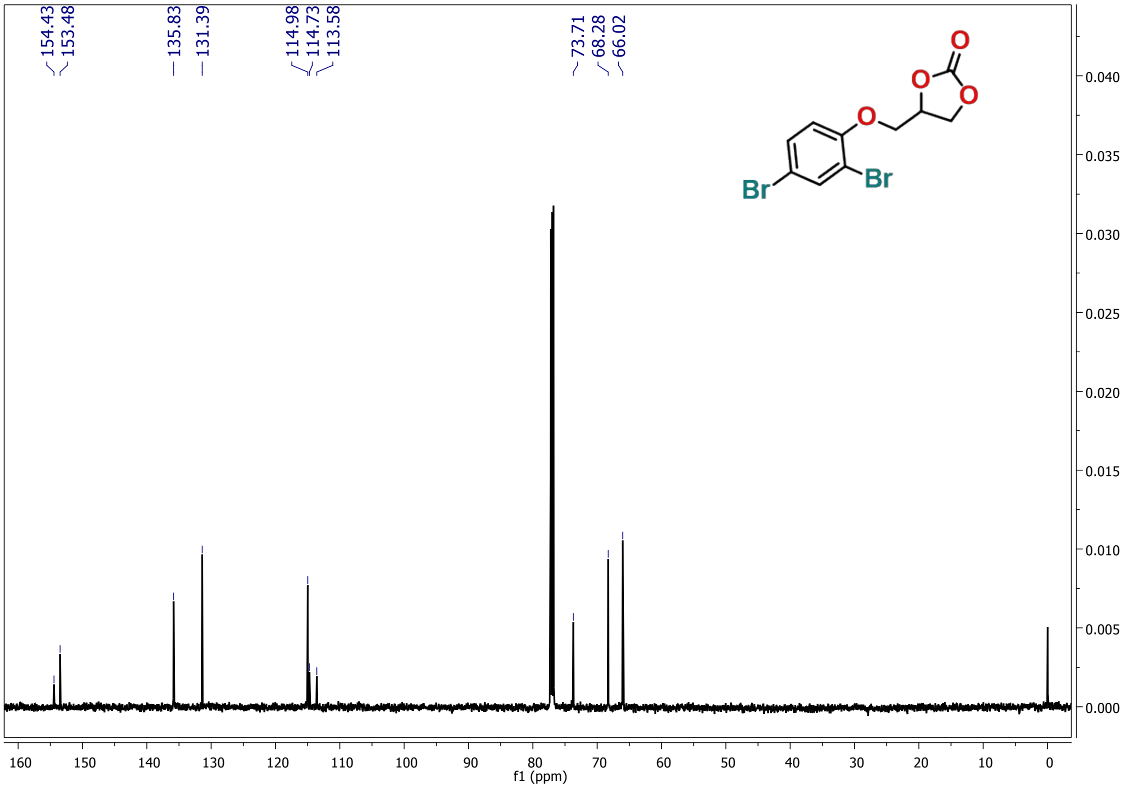


Figure S17. ^{13}C-NMR of the isolated 2-((2,4-dibromophenoxy)methyl)oxirane.

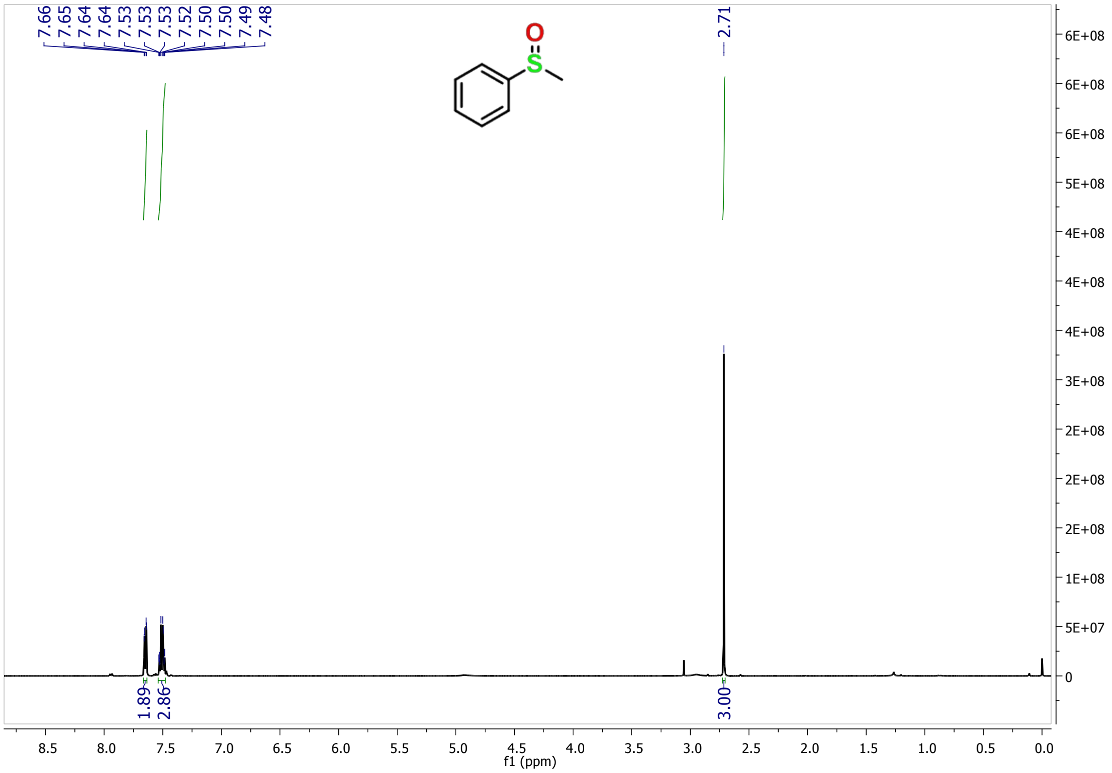


Figure S18. ^{1}H-NMR of the isolated Phenyl methyl sulfoxide.

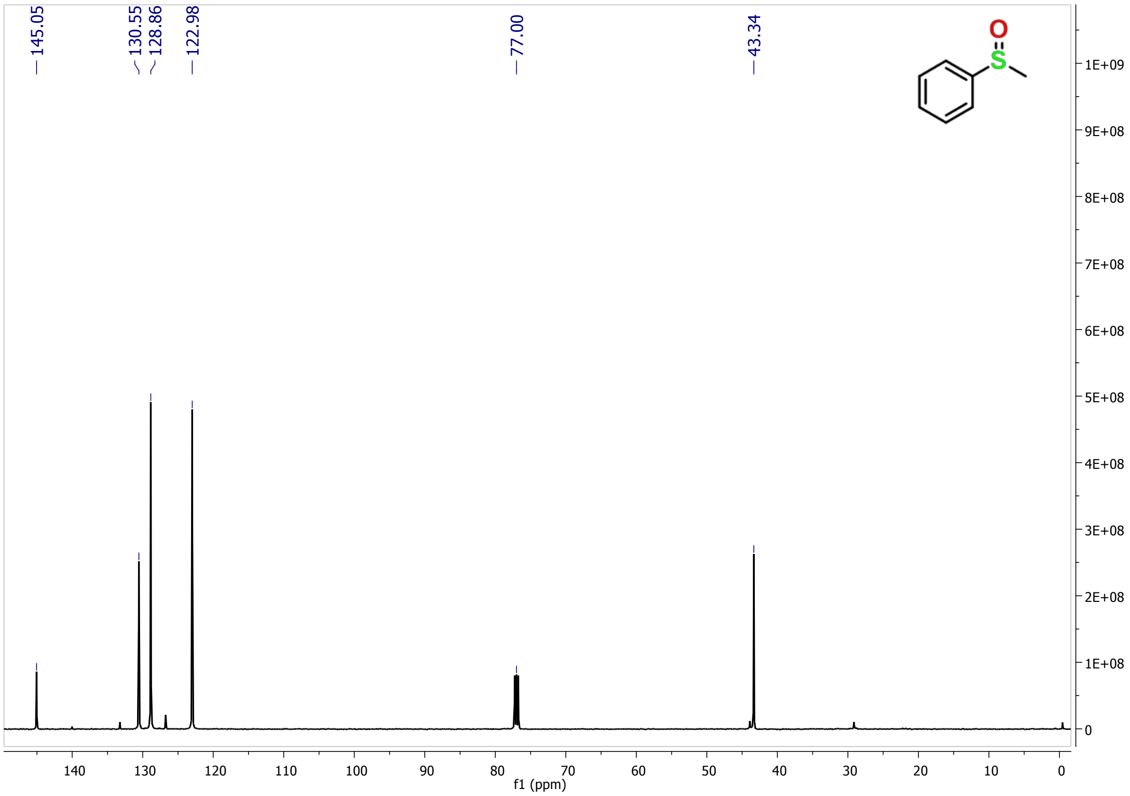


Figure S19. ^{13}C-NMR of the isolated Phenyl methyl sulfoxide.

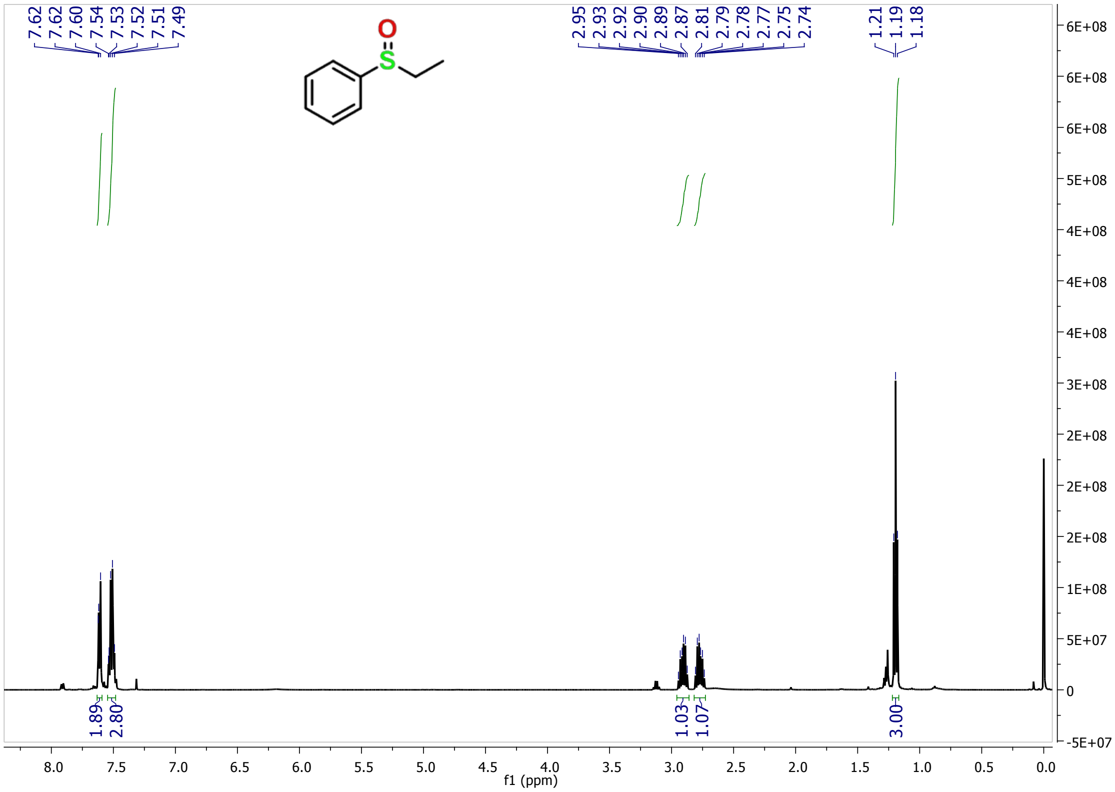


Figure S20. ^{1}H-NMR of the isolated Ethyl Phenyl sulfoxide.

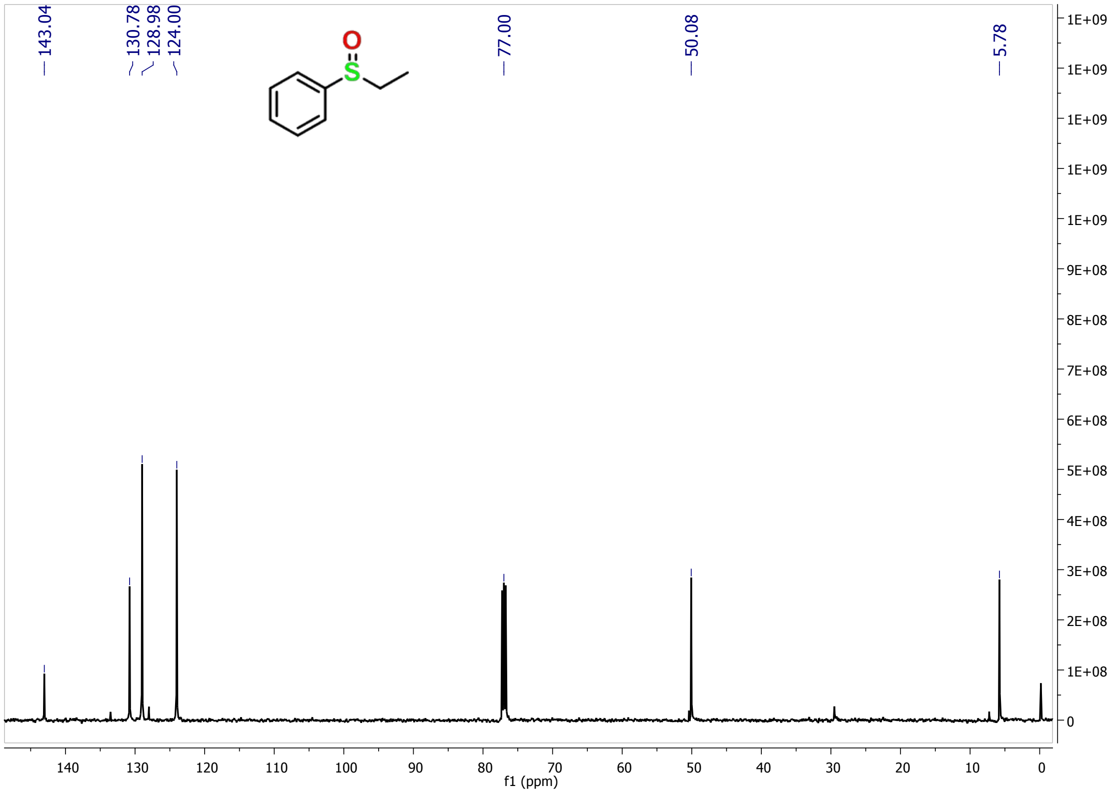


Figure S21. ^{13}C-NMR of the isolated Ethyl Phenyl sulfoxide.

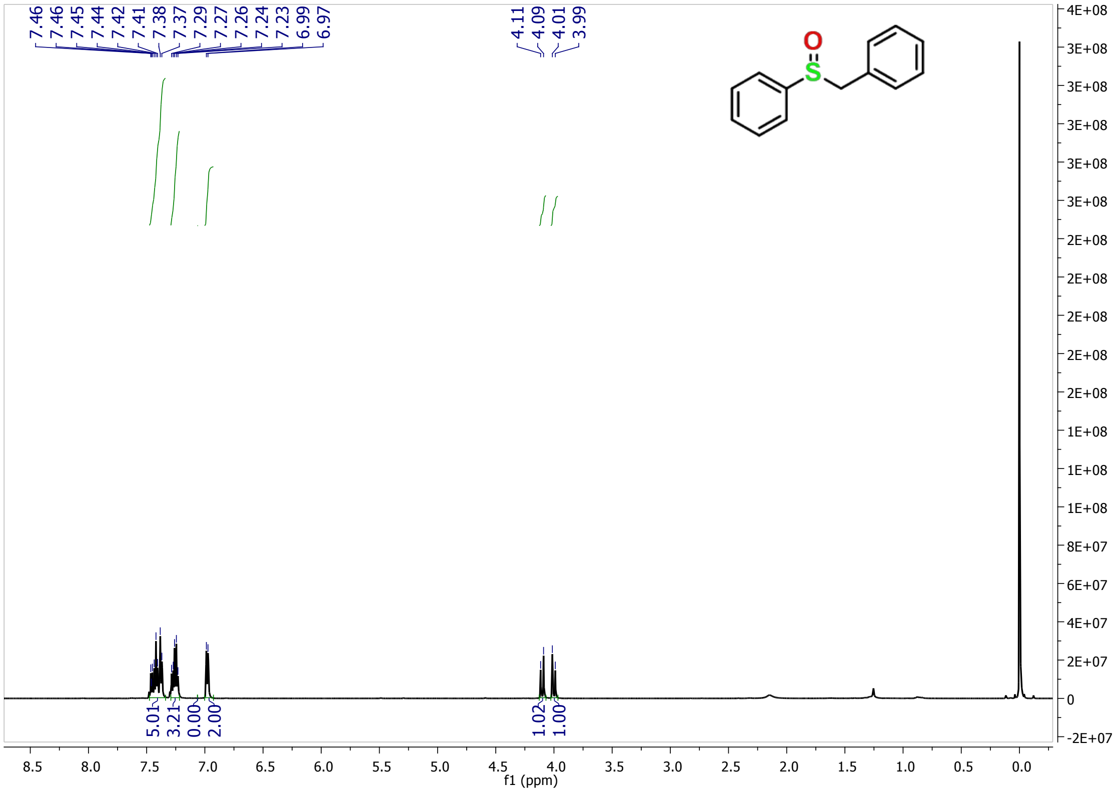


Figure S22. ^{1}H-NMR of the isolated Benzyl phenyl sulfoxide.

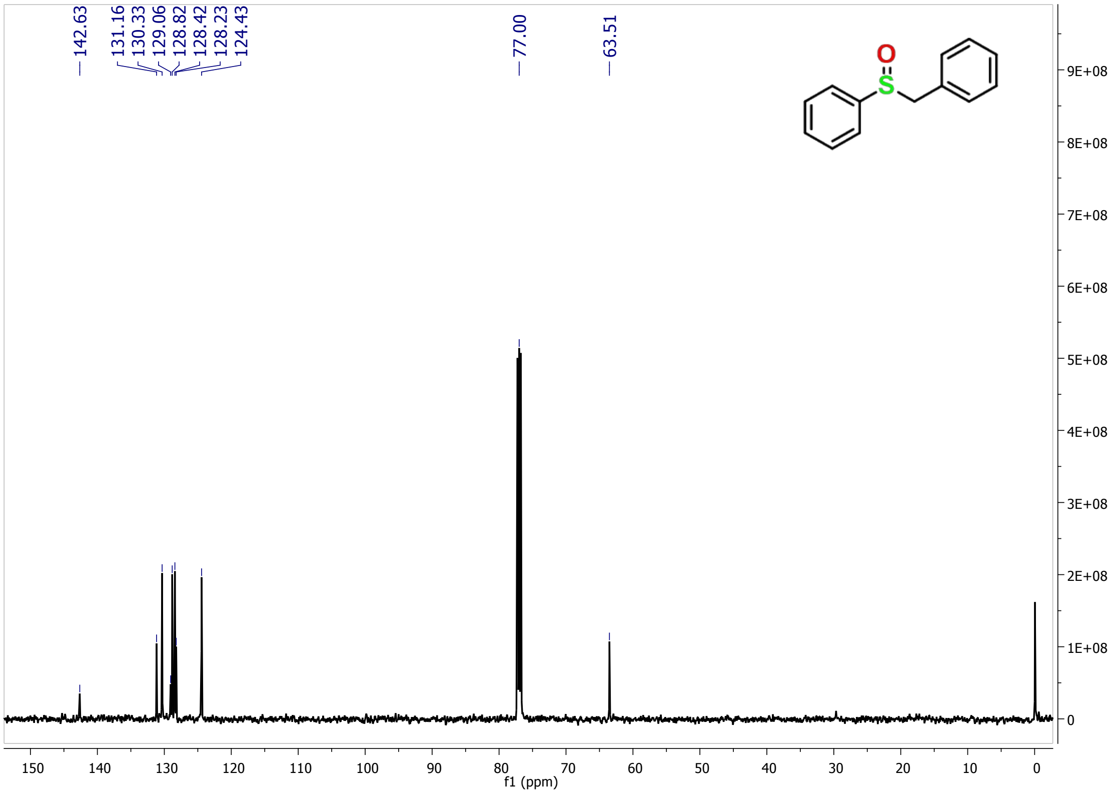


Figure S23. ^{13}C-NMR of the isolated Benzyl phenyl sulfoxide.

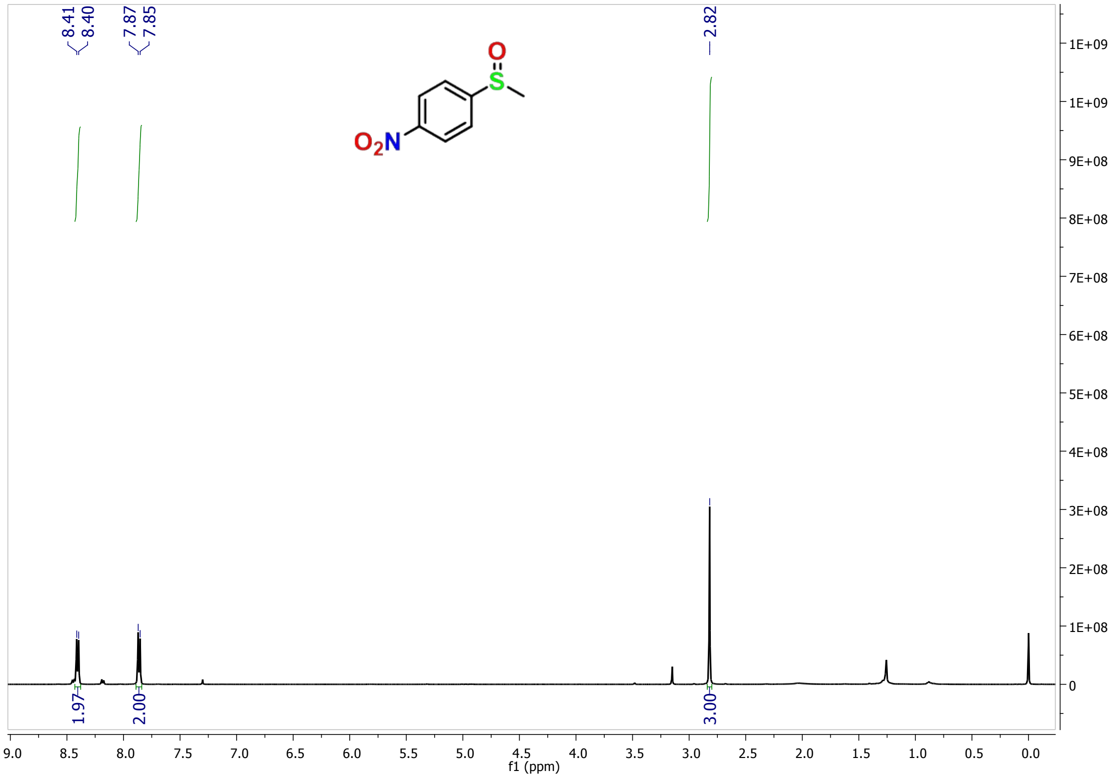


Figure S24. ^{1}H-NMR of the isolated 4-Nitrophenyl methyl sulfoxide.

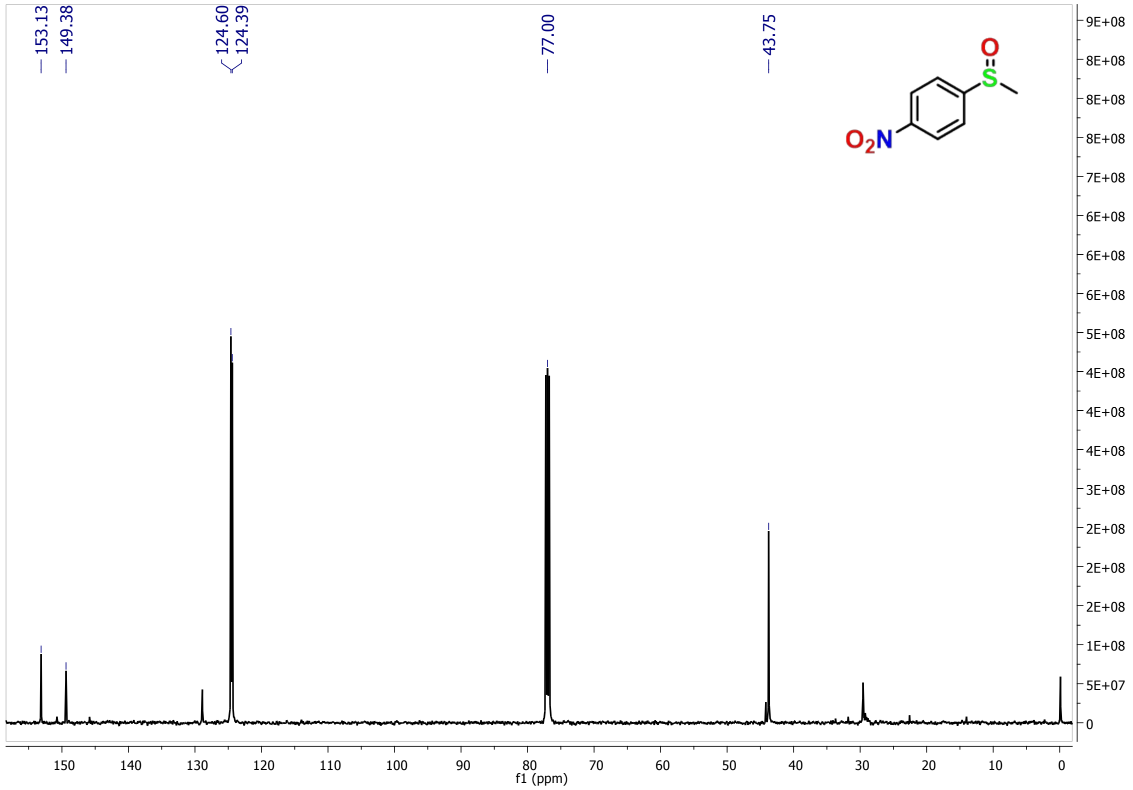


Figure S25. ^{13}C-NMR of the isolated 4-Nitrophenyl methyl sulfoxide.

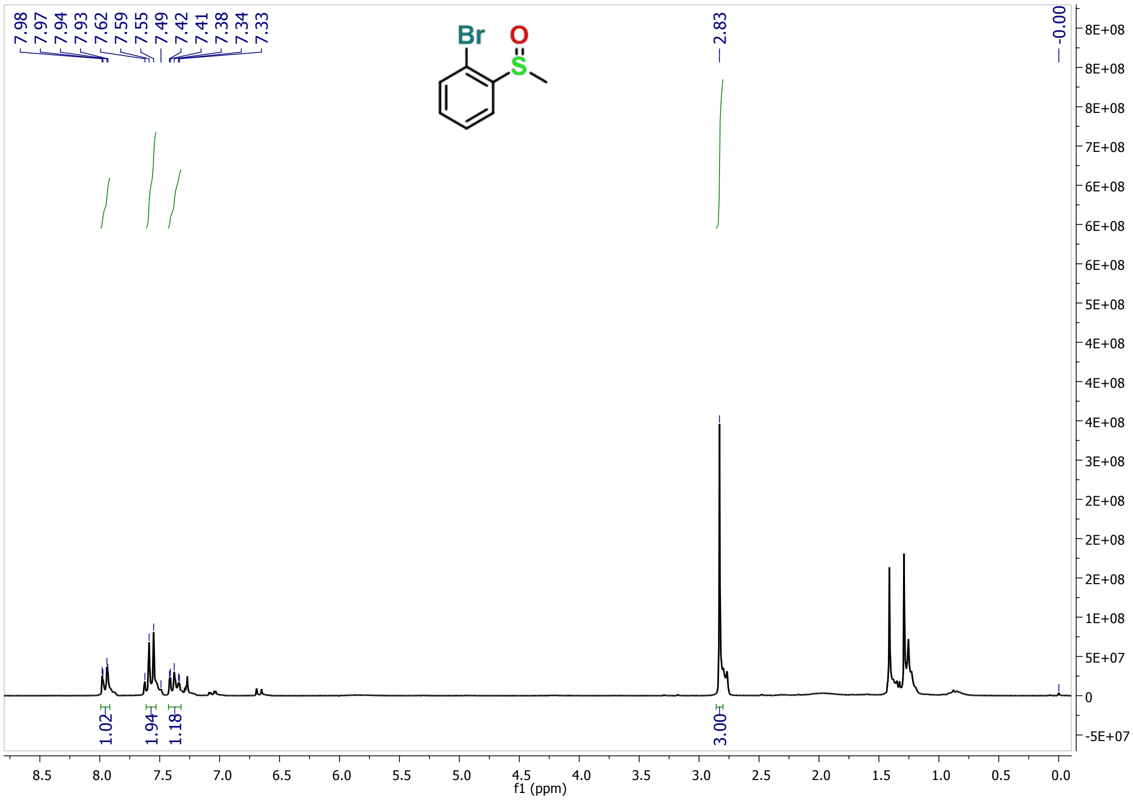


Figure S26. ^{1}H-NMR of the isolated 2-Bromophenyl methyl sulfoxide.

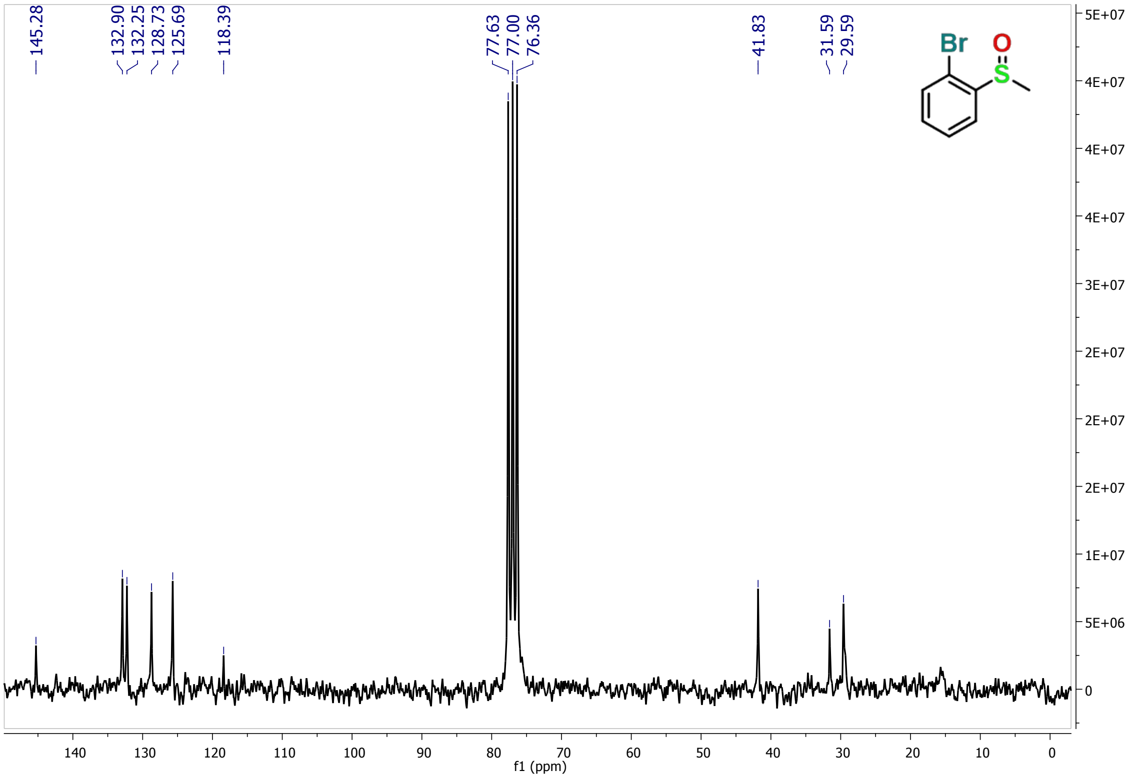


Figure S27. ^{13}C-NMR of the isolated 2-Bromophenyl methyl sulfoxide.

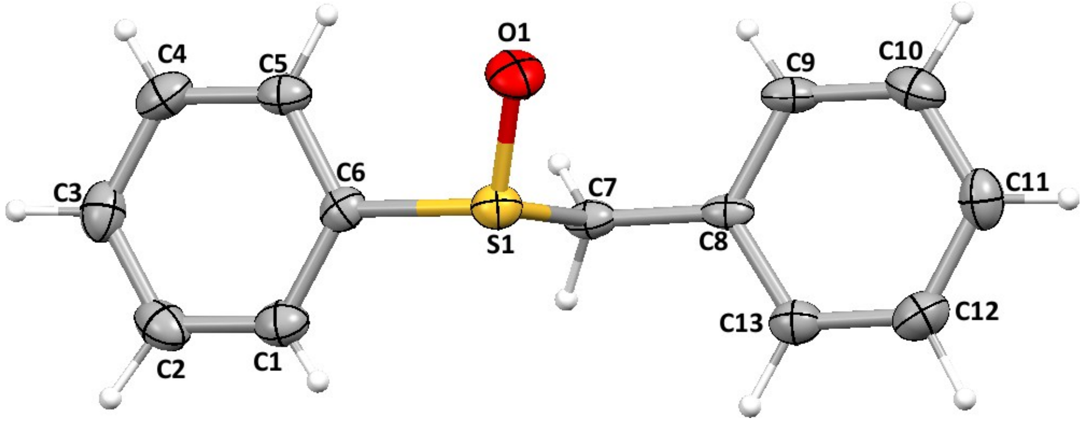


Figure S28. ORTEP depiction for sulfoxide product Benzyl phenyl sulfoxide with atom numbering scheme.[S13] (50% probability for the thermal ellipsoids)

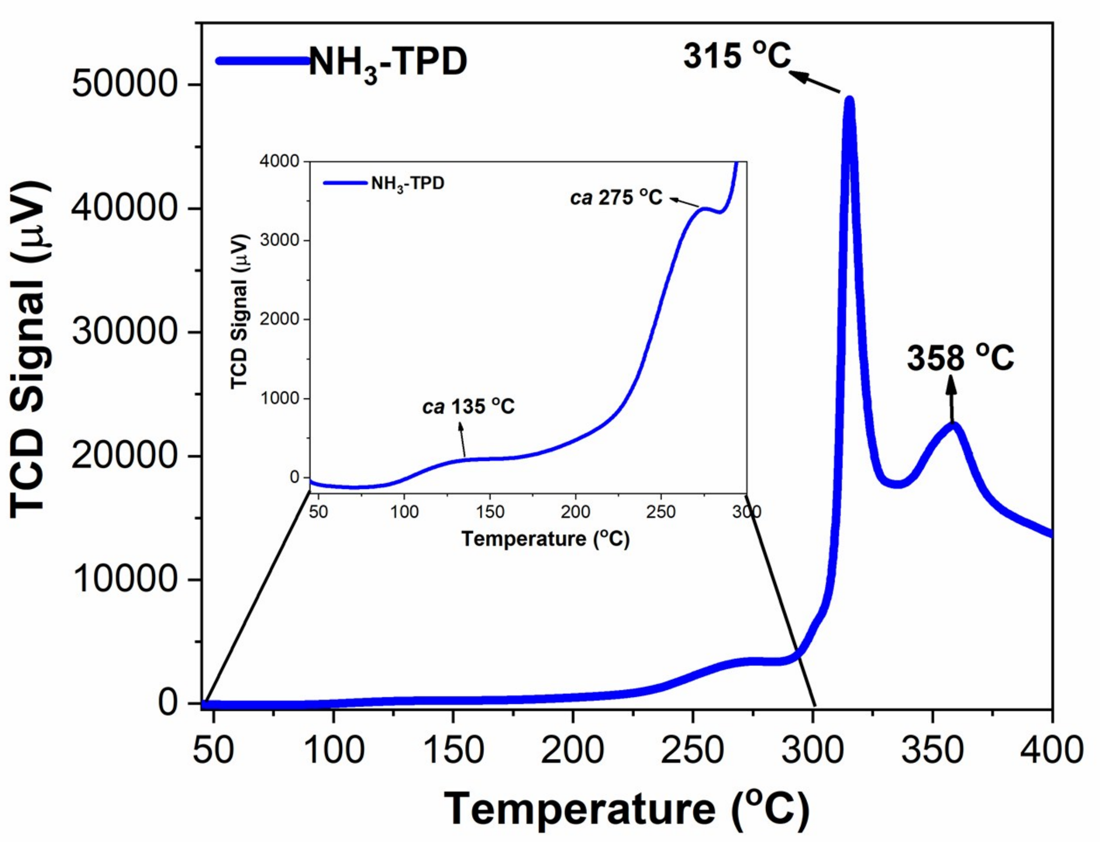


Figure S29. NH_3-TPD profiles of **ZnMOF-1-NH_2**.

References:

S1. B. Parmar, Y. Rachuri, K. K. Bisht and E. Suresh, *ChemistrySelect,* 2016, **1**, 6308-6315.

S2. B. Parmar, Y. Rachuri, K. K. Bisht and E. Suresh, *Inorg. Chem.,* 2017, **56**, 10939-10949.

S3. H. Zhou, G. -X. Wang, W. -Z. Zhang and X. -B. Lu, *ACS Catal.,* 2015, **5**, 6773-6779.

S4. Y. Kumatabara, M. Okada and S. Shirakawa, *ACS Sustainable Chem. Eng.,* 2017, **5**, 7295-7301.

S5. S. Kaneko and S. Shirakawa, *ACS Sustainable Chem. Eng.,* 2017, **5**, 2836-2840.

S6. S. Verma, R. I. Kureshy, T. Roy, M. Kumar, A. Das, N. H. Khan, S. H. R. Abdi and H. C. Bajaj, *Cat. Comm.,* 2015, **61**, 78-82.

S7. P. Patel, B. Parmar, R. I. Kureshy, N. H. Khan and E. Suresh, *ChemCatChem,* 2018, DOI: 10.1002/cctc.201800137.

S8. T. Fujihara, M. Inokuchi, T. Mizoe, K. Nogi, J. Terao and Y. Tsuji, *Chem. Lett.,* 2017, **46**, 968-969.

S9. J. Tang, P. Yao, F. Huang, M. Luo, Y. Wei and H. Bian, *Tetrahedron: Asymmetry,* 2017, **28**, 1700-1707.

S10. M. Ochiai, A. Nakanishi and T. Ito, *J. Org. Chem.,* 1997, **62**, 4253-4259.

S11. S. Gan, J. Yin, Y. Yao, Y. Liu, D. Chang, D. Zhu and L. Shi, *Org. Biomol. Chem.,* 2017, **15**, 2647-2654.

S12. C. A. Dannenberg, L. Fritze, F. Krauskopf and C. Bolm, *Org. Biomol. Chem.,* 2017, **15**, 1086-1090.

S13. A. L. Fuller, R. A. Aitken, B. M. Ryan, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Crystallogr.,* 2009, **39**, 407-415.