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Supporting information

Macroporous Polystyrene Degraded and Functionalized Chromium MPS-Cr(lll)-alen Complex as a Sustainable Porous Catalyst for CO_2 Fixation under Atmospheric Pressure and Selective Oxidation of Aromatic Alkenes

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Materials

Chloromethylated polystyrene was purchased from Sigma-Aldrich Chemical Company, USA. 2-hydroxy-4-methylbenzaldehyde, diethylenetriamine and Chromium chloride ($CrCl_3$) were obtained from Spectrochem, India. Other reagents were purchased from E-Merck, India.

Characterization techniques

Transmission electron microscopy (TEM) image of the material was obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. Scanning electron microscopy (SEM) measurements were performed with a JEOL JEM 6700F field-emission scanning electron microscope. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. FT-IR spectra of the samples were recorded on KBr pellets by using a Perkin-Elmer FT-IR 783 spectrophotometer. Thermogravimetry (TG) analysis of the samples was done by using Mettler Toledo TGA/DTA 851e. The reaction products were analyzed through a Varian 3400 gas chromatograph equipped with a 30 m CP-SIL 8CB capillary column and a flame ionization detector. The isolated products were monitored by ^{1}H NMR spectroscopy. The products were purified by performing column chromatography (Petroleum Ether/ethyl acetate=9:1).

Preparation of macroporous polymer supported Schiff base ligand (MPS-alen)

The synthesis of polymer supported Schiff base ligand named as MPS-alen was involved two steps synthetic process. In Step (I), the Schiff base was prepared by a literature procedure.[1] In a 50 ml round bottom flask, 2-hydroxy-4-methylbenzaldehyde (30 mmol) and diethylenetriamine (15 mmol) were taken in 20 ml ethanol and the mixture was refluxed for 24 h. Then the solution was cooled to room temperature and the solvent was evaporated under reduced pressure to yield an orange-yellow liquid product. The resulting Schiff base was then dried under vacuum. In Step (II), the polymer supported Schiff base ligand (MPS-alen) was prepared by stirring 1 g of Chloromethylated polystyrene with the Schiff base of Step (I) (10 mmol, 3.39 g) using tetrahydrofuran (20 mL) as a solvent for 48 h at RT. A yellow solid product was obtained, which was filtered and washed with de-ionized water followed by ethanol. Then the resulting product was dried under vacuum.

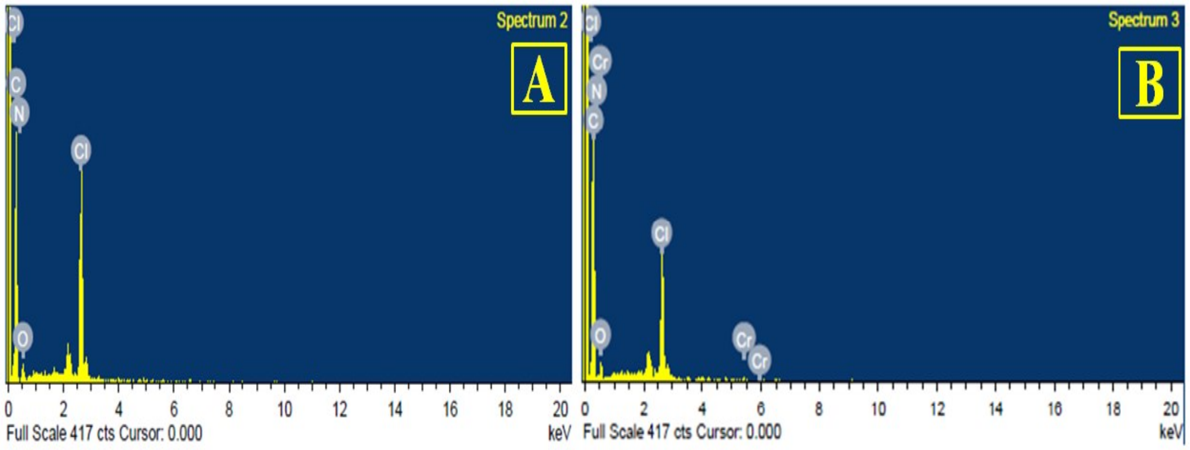


Fig. S1 EDAX images of (A) MPS-alen ligand and (B) MPS-Cr(III)-alen catalyst.

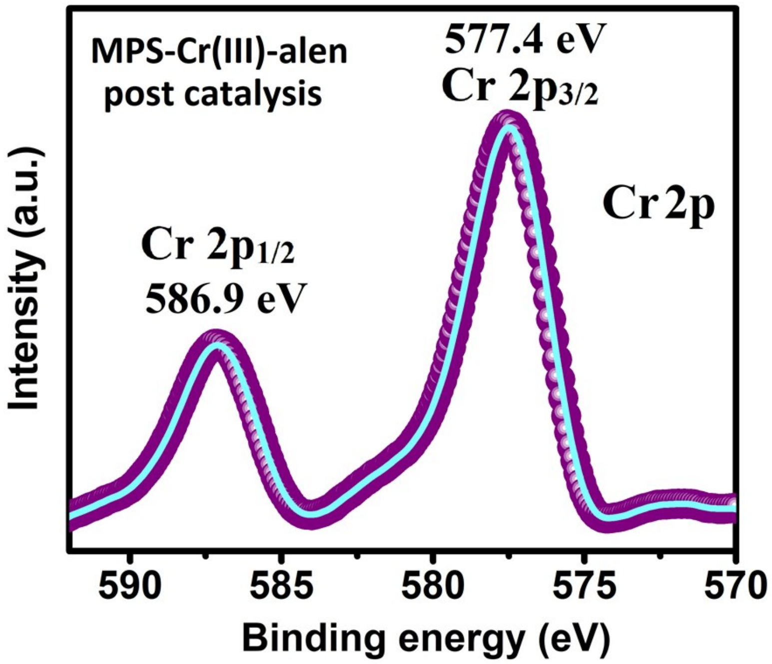


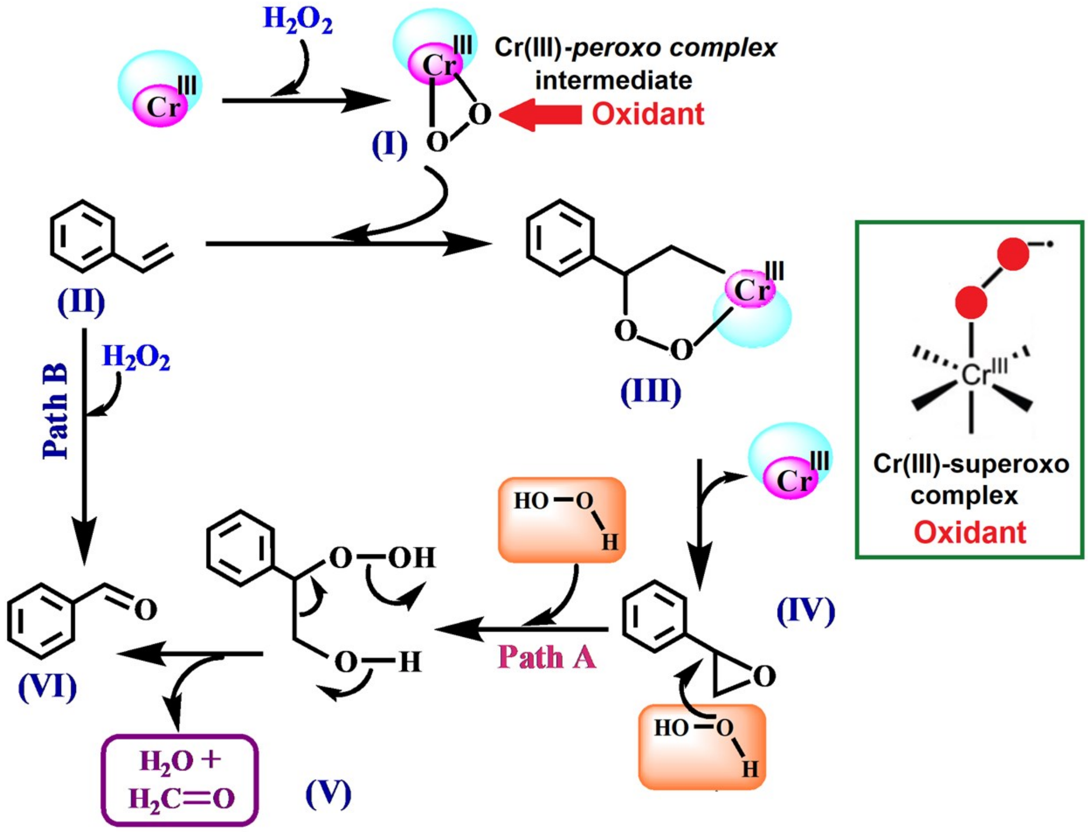
Fig. S2 XPS spectrum of reused MPS-Cr(III)-alen material illustrating the bands corresponding to chromium featuring certain oxidation state (Cr^{3+}) after five runs.

Hot filtration and leaching tests with ICP analysis

Hot filtration test is performed for both catalytic cyclic carbonate synthesis and selective oxidation of aromatic alkene in order to check the heterogeneous nature of the catalyst. The cyclic carbonate synthesis reaction is carried out by taking epichlorohydrin (2 mmol), TBAB (1 mmol), MPS-Cr(III)-alen catalyst (50 mg) in presence of CO_2 gas (1 atm.) at room temperature under solvent free condition. The reaction is performed for 8 h in presence of catalyst and then after removing the catalyst by simple filtration, the reaction is continued for another 16 h. After the first 8 h and the next 16 h, the conversion of epichlorohydrin was almost same. Again same methodology is applied in case of selective oxidation of aromatic alkene by using styrene (5 mmol), styrene:H_2O_2 molar ratio 3, ACN (10 mL), MPS-Cr(III)-alen catalyst (50 mg), at 60 ˚C. Initially the reaction is carried out in presence of catalyst for 3 h; then another 5 h the reaction is continued in absence of catalyst. After the first 3 h and the next 5 h, the conversion of styrene was almost same. From this leaching limit studied with the help of AAS instrument we can demonstrate that after the first run, Cr leaching was observed in inconsiderable quantity in ppm scale. The AAS analysis recorded that after multiple reaction runs, a very inconsiderable quantity of Cr was leached out in our experiment compared to the other previously reported works. For additional authentication we have conducted ICP-AES experiments of the filtrate and the recovered MPS-Cr(III)-alen catalytic system. We did not detect any noticeable Cr trace in the filtrate and in MPS-Cr(III)-alen catalyst, which retains almost the same Cr loading as that of fresh catalyst (≈2.83 wt%). All these experimental data obviously confirmed the heterogeneous nature of MPS-Cr(III)-alen catalyst. The outcomes obtained from AAS were in good agreement with ICP-AES experiments because only low amounts of leached Cr in the filtrate collected by hot filtration test were detected (≈3 ppm). These results obtained undoubtedly demonstrated that the as-prepared MPS-Cr(III)-alen catalytic system is a true heterogeneous in nature for the title reactions.

Plausible Reaction mechanism for selective oxidation of aromatic alkenes

The proposed mechanistic pathway, based on some reported articles[2-5] for the selective oxidation of styrene to benzaldehyde using MPS-Cr(III)-alen catalyst and hydrogen peroxide is shown in Scheme S1. In the first step, oxygen transfer from a donor (H_2O_2) to a MPS-Cr(III)-alen material occurred, leading to the formation of M^{III}-peroxo complex under the interaction with H_2O_2. Afterwards, styrene was bound with one of the metal-peroxo bonds to produce the peroxo-metallocycle (the second step). In the third step, the peroxo-metallocycle is broken and styrene oxide was produced; simultaneously, the H_2O_2 is consumed. Therefore, the catalyst restores its initial state due to the loss of an oxygen atom. A further nucleophilic attack of H_2O_2 on the styrene oxide leads to the final product, benzaldehyde (the fourth step). Benzaldehyde can also be resulted from the direct oxidative cleavage of styrene side chain double bond by a radical mechanism pathway (Path B).



Scheme S1. Plausible mechanism of MPS-Cr(III)-alen catalyzed selective aromatic alkene oxidation reaction

Optimization of reaction conditions:

Table S1: Optimization of TBAB and catalyst for the synthesis of epichlorohydrin carbonate[a]

Entry	Catalyst	Amount of TBAB (mmol)	Conversion (%)[b]
1	Cr(III)-alen	1.0	30
2	Cr(III)-alen	-	Trace
3	Macroporous polymer without Cr	-	Trace
4	MPS-Cr(III)-alen	-	Trace
5	**MPS-Cr(III)-alen**	**1.0**	**99**

[a]**Reaction conditions:** epichlorohydrin (2 mmol), TBAB, catalyst (50 mg, 2.75 wt% Cr loading), CO_2 gas (1 atm.), time 24 h, room temperature. [b]Determined by GC.

Hot filtration test

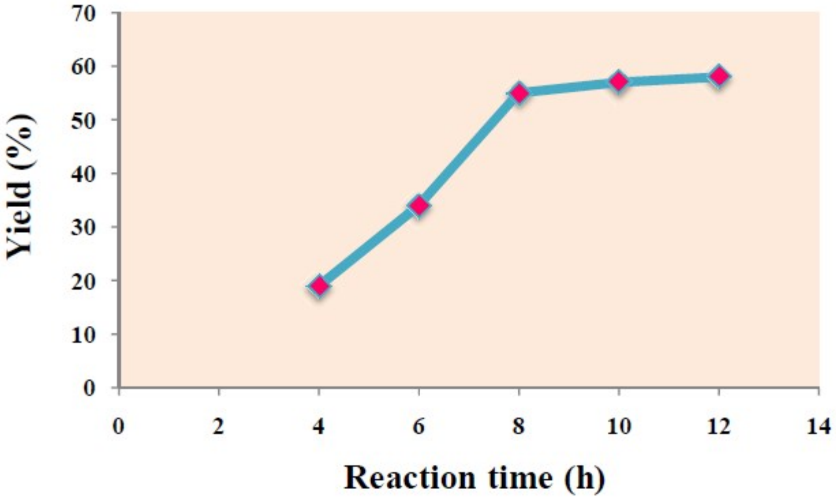
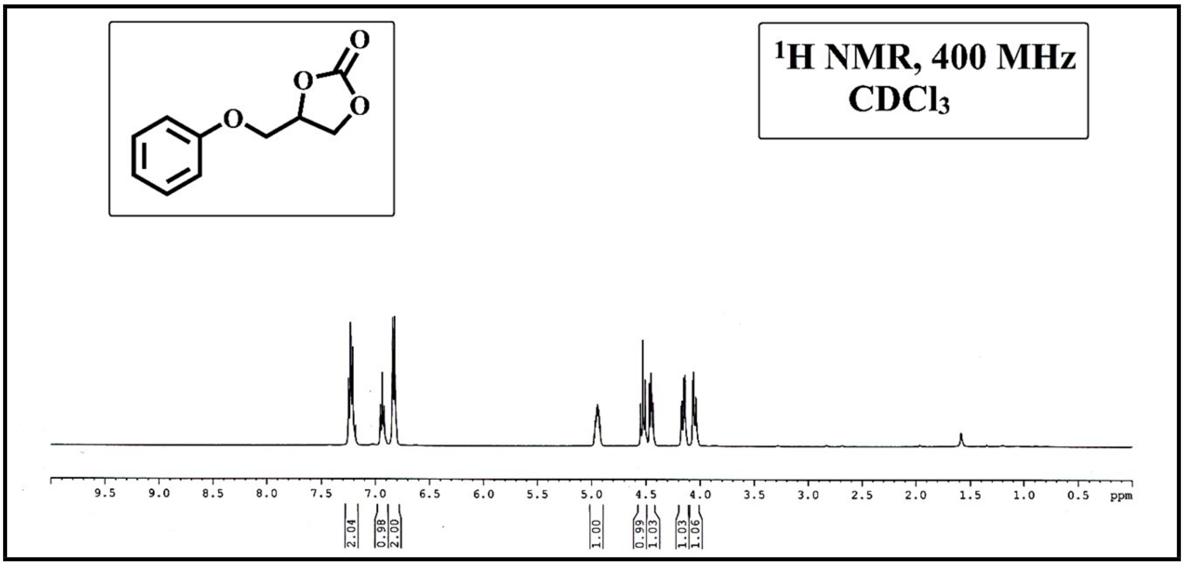


Fig. S3 Hot filtration test for synthesis of cyclic carbonate.

NMR Spectra

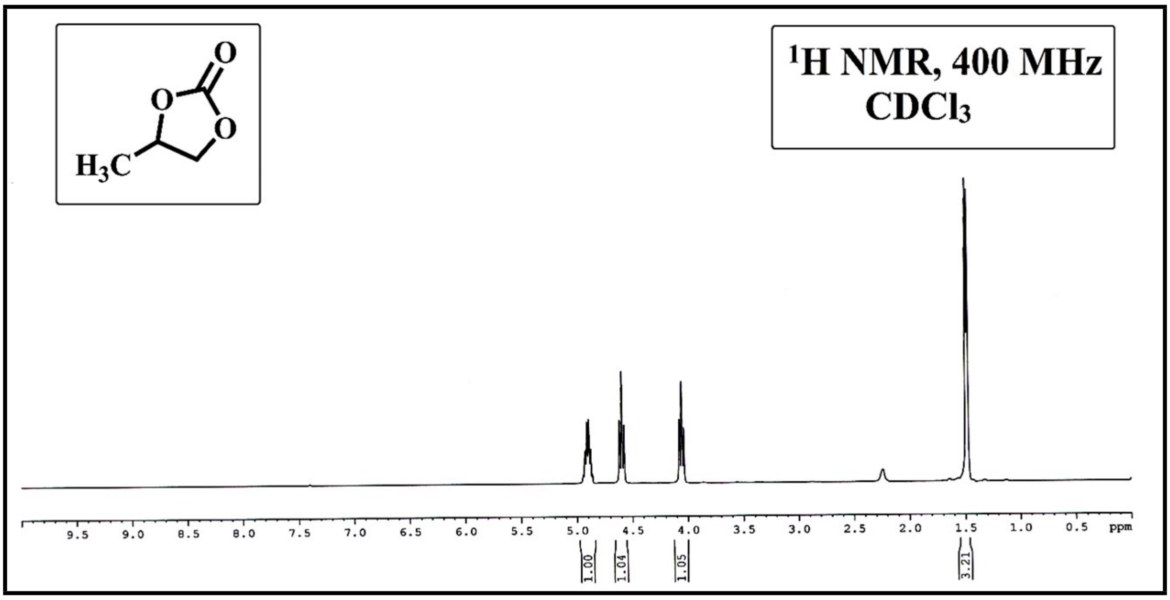
4-Phenoxymethyl-[1,3]dioxolan-2-one

^{1}H NMR spectra (400 MHz, CDCl$_3$): δ 4.03-4.18(m, 2H), 4.43-4.55 (m, 2H), 4.92-4.98 (m, 1H), 6.82-6.95 (m, 3H), 7.18-7.25 (m, 2H) ppm.



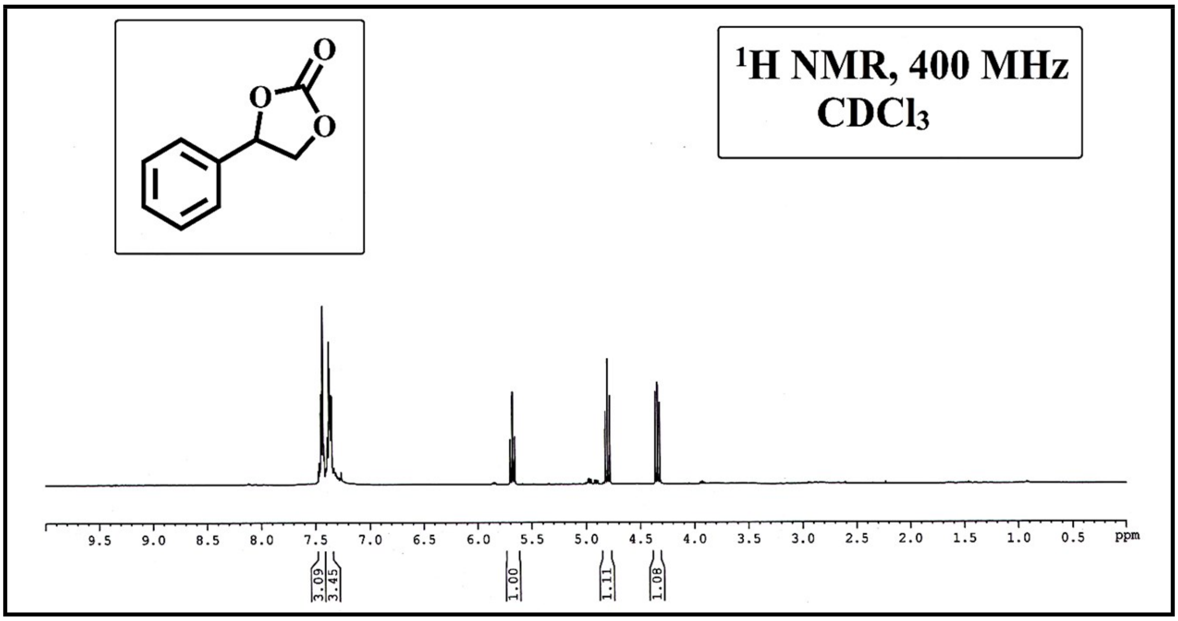
4-methyl-1,3-dioxolan-2-one

^{1}H NMR spectra (400 MHz, CDCl$_3$): δ 1.47-1.49 (d, 3H), 4.03-4.07 (t, 1H), 4.57-4.61 (t, 1H), 4.87-4.92 (m, 1H) ppm.



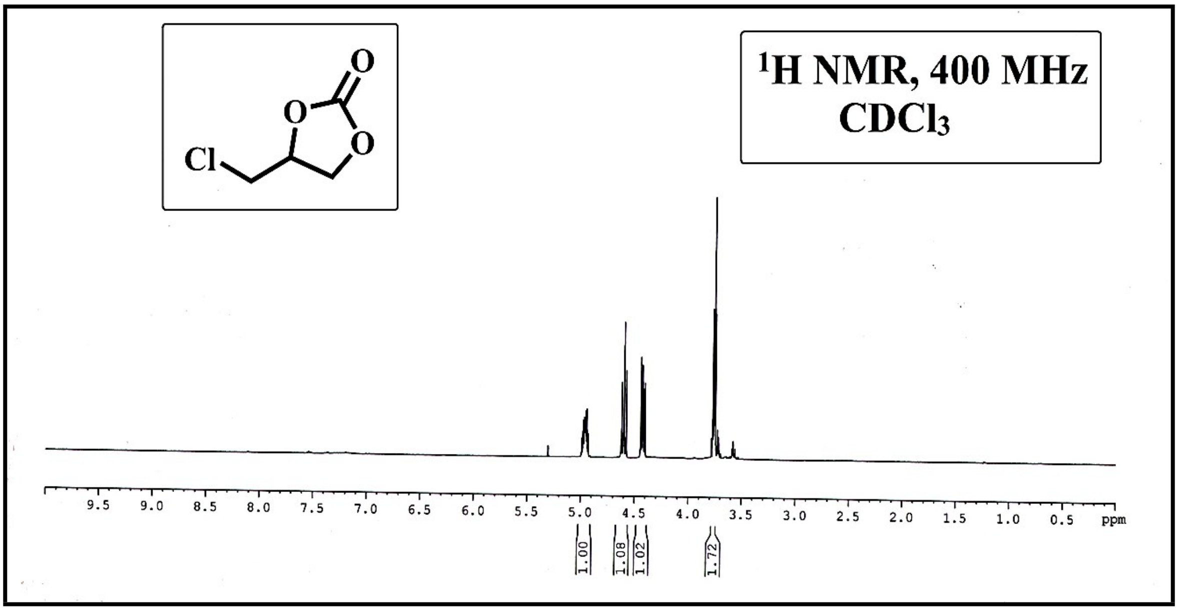
4-phenyl-1,3-dioxolan-2-one

^{1}H NMR spectra (400 MHz, CDCl$_3$): δ 4.32-4.36 (t, 1H), 4.78-4.82 (t, 1H), 5.66-5.70 (t, 1H), 7.33-7.37 (m, 2H), 7.39-7.46 (m, 3H) ppm.



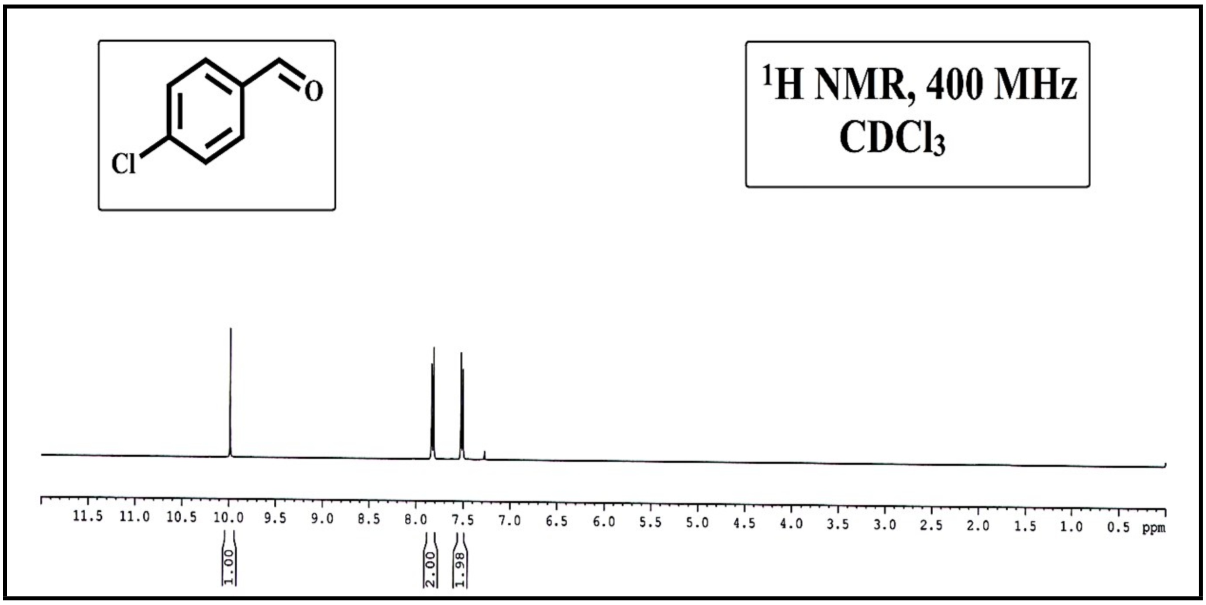
4-(chloromethyl)-1,3-dioxolan-2-one

^{1}H NMR spectra (400 MHz, CDCl$_3$): δ 3.74-3.77 (m, 2H), 4.40-4.44 (m, 1 H), 4.57-4.62 (m, 1 H), 4.93-5.01 (m, 1H) ppm.



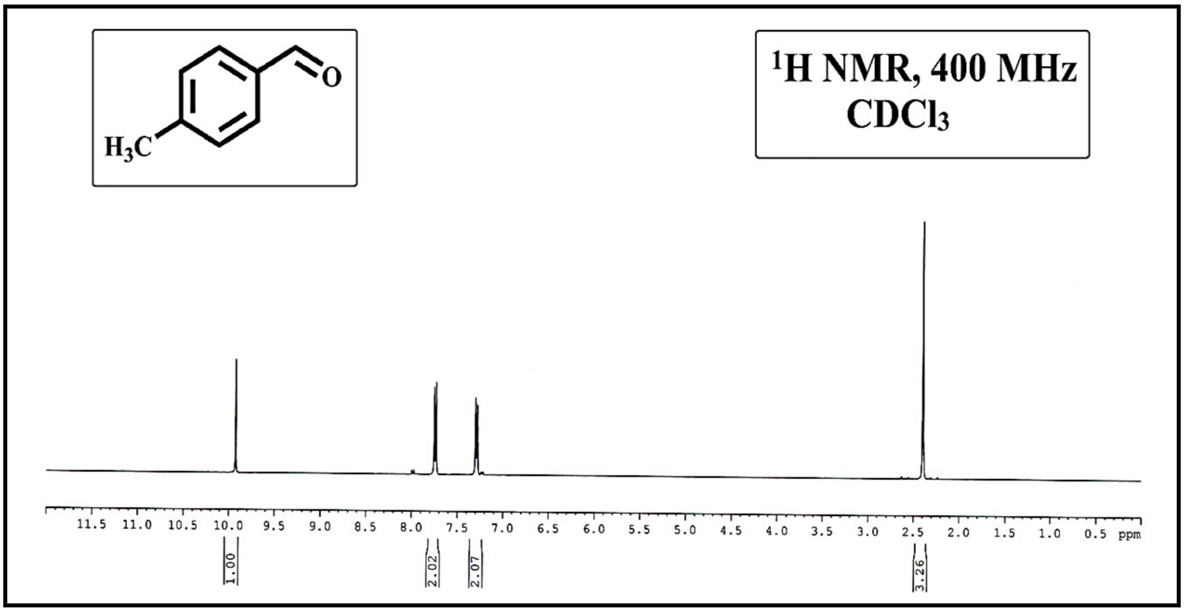
4-chloro benzaldehyde

^{1}H NMR spectra (400 MHz, CDCl$_3$): δ 7.50-7.53 (d, 2H), 7.82-7.84 (d, 2H), 9.98 (s, 1H) ppm.



4-methyl benzaldehyde

^{1}H NMR spectra (400 MHz, CDCl$_3$): δ 2.39 (s, 3H), 7.28-7.30 (d, 2H), 7.73-7.75 (d, 2H), 9.92 (s, 1H) ppm.



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