

## Supplementary Information

### Multivalent Cobalt Nanoparticles Supported on Silica for Efficient and Sustainable Methanolysis of Commercial Polyethylene Terephthalate Waste Bottles

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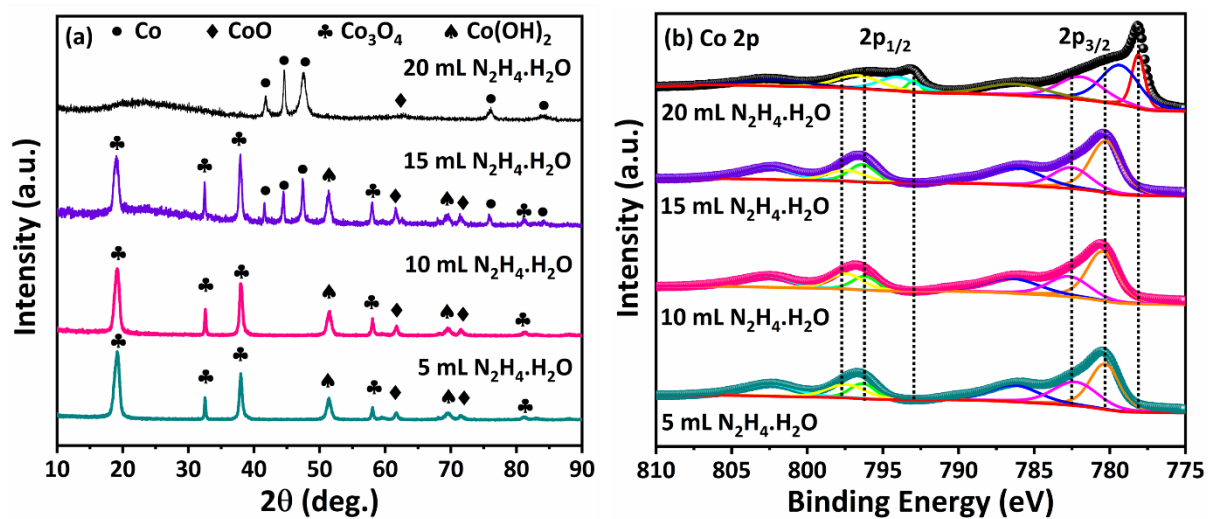
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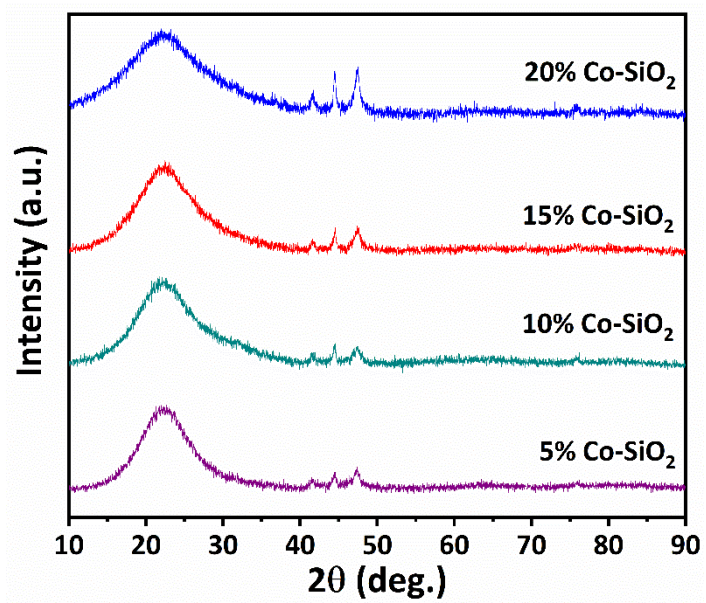
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## S1. Materials characterization

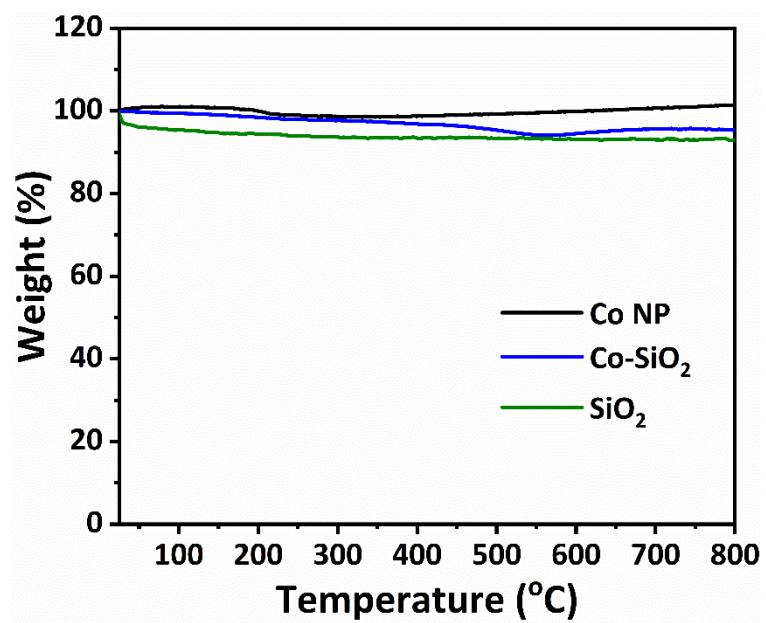
Various instruments were used to perform different characterizations of the developed catalysts. The powder X-ray diffraction (PXRD) measurements of the catalysts were performed using 9 kW Rigaku Smart Lab rotating anode X-ray diffractometer equipped with Ni-filtered Cu K $\alpha$  irradiation source having  $\lambda = 1.542 \text{ \AA}$  working at 45 kV and 100 mA. All the measurements were done at a scattering range of  $2\theta = 10^\circ$  to  $90^\circ$  with a scanning rate of  $2^\circ$  per min and scan step size of  $0.02^\circ$ . The crystalline phases of the catalysts were identified by JCPDS data obtained from X'Pert HighScore software. An Agilent K8002AA Cary 660 instrument was used to perform Fourier-transform infrared spectroscopy (FTIR) measurements. The thermogravimetric analysis (TGA) of the samples was done using PerkinElmer Pyris 1 instrument. All samples were heated in a nitrogen atmosphere with a flow rate of  $20 \text{ mL min}^{-1}$  from  $25^\circ\text{C}$  to  $800^\circ\text{C}$  with the ramp rate of  $10^\circ\text{C min}^{-1}$ . The FEI Nova SEM-450 scanning electron microscope (SEM) was utilized for the morphological investigation of the catalyst. The samples were prepared by dispersing 2 mg of catalyst in ethanol, sonicating them for 30 min and drop casting them onto a small piece of silicon wafer. The nanoscale morphological analysis of the samples was performed using a transmission electron microscope (TEM), FEI Tecnai G2 20 S-twin microscope operating at 200 kV accelerating voltage and the d-spacing were calculated using Gatan software. The samples were prepared by dispersing the catalyst in ethanol by ultrasonication for 30 min and drop casting them onto a copper grid having carbon coating. X-ray photoelectron spectroscopy (XPS) studies on the samples were conducted using a Thermo Fisher Scientific NEXSA photoemission spectrometer equipped with 1486.6 eV Al-K $\alpha$  X-ray radiation source. The samples were prepared by making pellets of the powdered catalyst and the data obtained was deconvoluted using Avantage software. Brunauer–Emmett–Teller (BET) specific surface area was measured on a Quantachrome ASiQwin instrument at 77.35 K temperature. The samples were degassed under vacuum by heating at  $120^\circ\text{C}$  with heating rate of  $5^\circ\text{C min}^{-1}$  before measuring the surface area. Using BELCAT II TPR/TPD, Quanta Chrome instrument the temperature programmed desorption (TPD) study was carried out. Nuclear magnetic resonance (NMR) experiments were performed using a JEOL-USA (JNMECX500) spectrometer in  $\text{CDCl}_3$  solvent having tetramethyl silane (TMS) as an internal standard and the chemical shifts are reported in ppm. The  $^1\text{H}$  NMR spectra was recorded at 500 MHz and  $^{13}\text{C}$  NMR spectra was recorded at 125 MHz frequency and the data obtained was analyzed using MestReNova software.



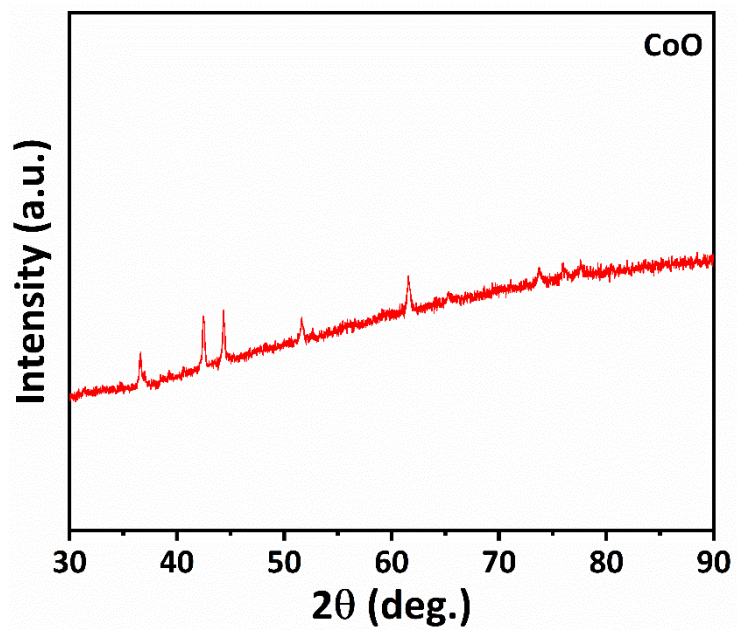
**Figure S1.** Variation in amount of hydrazine hydrate for Co NP synthesis; (a) PXRD plot, (b) XPS spectrum of Co 2p.



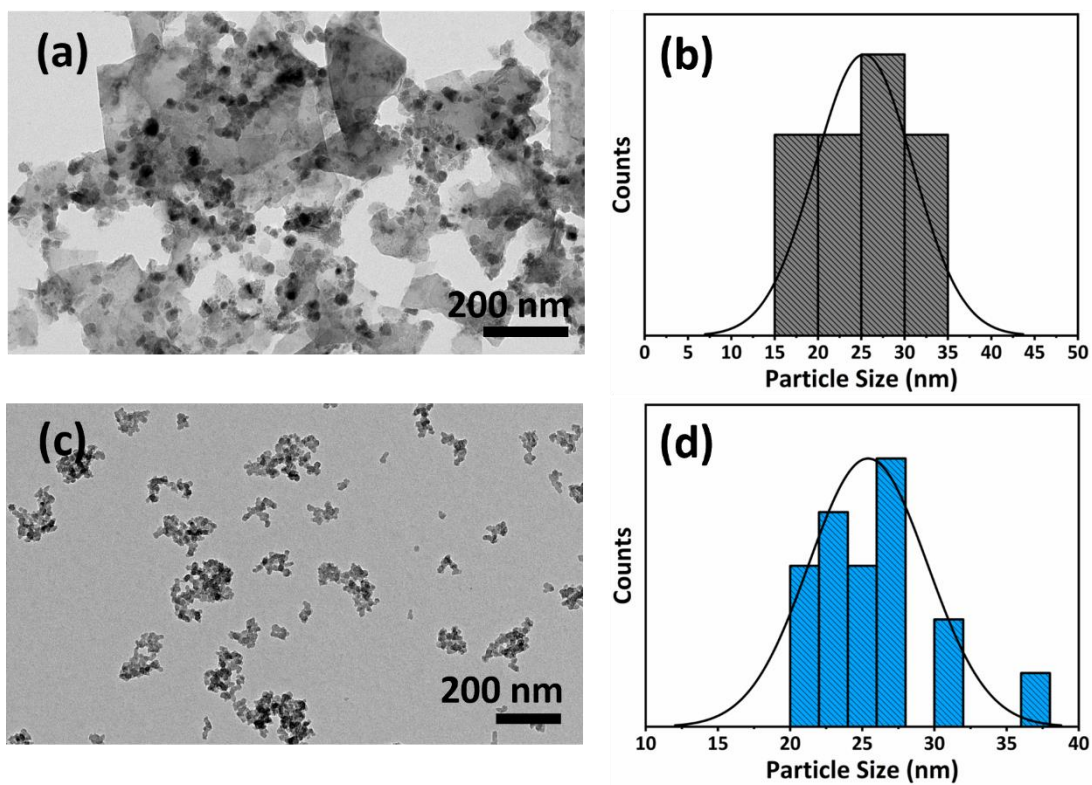
**Figure S2.** PXRD plots of different wt% loading of Co-SiO<sub>2</sub> catalysts.



**Figure S3.** TGA plot of Co NP, SiO<sub>2</sub> and Co-SiO<sub>2</sub> catalyst.



**Figure S4.** PXRD plots of post TGA sample of Co NP, indicating the conversion of Co NP to CoO.

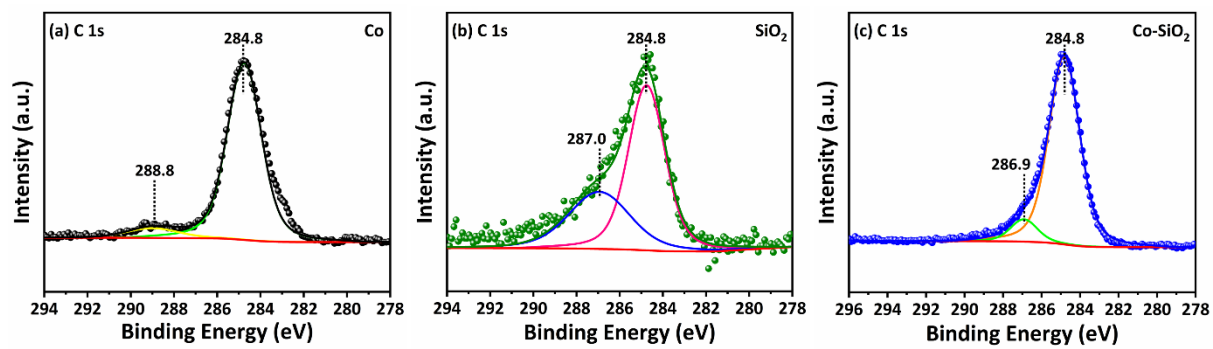


**Figure S5.** (a) TEM image of Co NP, (b) particle size distribution of Co NP, (c) TEM image of Co-SiO<sub>2</sub>, and (d) particle size distribution of Co-SiO<sub>2</sub>.

**Table S1.** Atomic percentage of constituent elements in Co and SiO<sub>2</sub> and Co-SiO<sub>2</sub> catalysts from XPS analysis.

Sl. No.	Elements	Atomic percentage of constituent elements (%)		
		Co	SiO <sub>2</sub>	Co-SiO <sub>2</sub>
1	Co 2p	63.06	-	0.66
2	Si 2p	-	32.53	32.12
3	O 1s	36.94	67.47	67.22





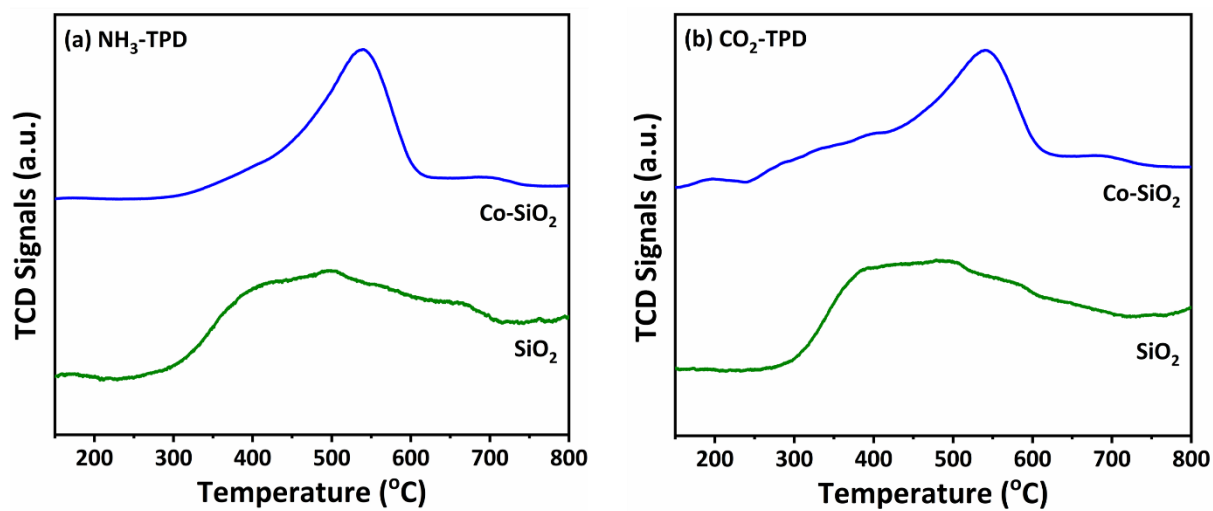
**Figure S6.** C 1s XPS spectrum of (a) Co NP, (b) SiO<sub>2</sub>, and (c) Co-SiO<sub>2</sub>.

**Table S2.** Peak table showing different peaks of Co 2p present in Co NP and Co-SiO<sub>2</sub> catalysts from XPS analysis.

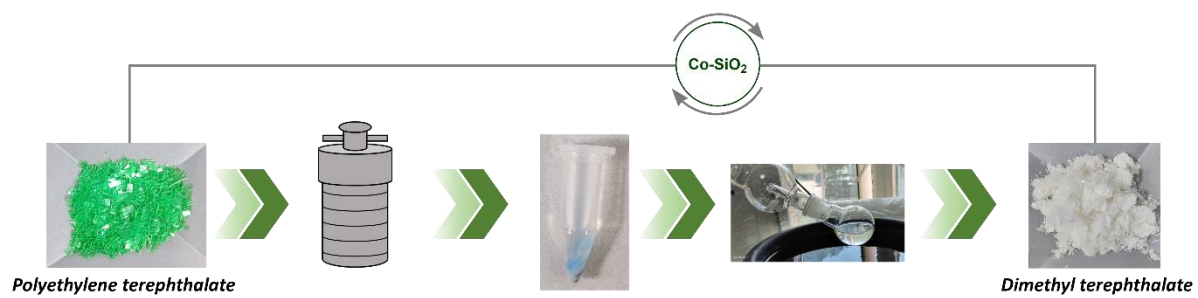
Element	Binding Energy (eV)		Peak assignment
	Co NP	Co-SiO <sub>2</sub>	
Co 2p	778.2	778.3	Co (0) 2p <sub>3/2</sub>
	779.4	781.2	Co (III) 2p <sub>3/2</sub>
	782.1	785.1	Co (II) 2p <sub>3/2</sub>
	786.5	788.6	Co 2p <sub>3/2</sub> satellite
	793.1	793.2	Co (0) 2p <sub>1/2</sub>
	794.2	796.7	Co (III) 2p <sub>1/2</sub>
	796.8	801.1	Co (II) 2p <sub>1/2</sub>
	802.6	804.2	Co 2p <sub>1/2</sub> satellite

**Table S3.** Atomic percentage of constituent elements in fresh and recovered Co-SiO<sub>2</sub> catalysts from XPS analysis.

Sl. No.	Elements	Atomic percentage of constituent elements (%)	
		Fresh Co-SiO <sub>2</sub>	Recovered Co-SiO <sub>2</sub>
1	Co 2p	0.66	0.59
2	Si 2p	32.12	31.46
3	O 1s	67.22	67.94



**Figure S7.** (a) NH<sub>3</sub>-TPD, (b) CO<sub>2</sub>-TPD of SiO<sub>2</sub> and Co-SiO<sub>2</sub> catalysts.



**Figure S8.** Reaction scheme showing conversion of colored PET bottles to DMT catalyzed by  $\text{Co-SiO}_2$  catalyst.

## S2. Conversion and Yield Calculations

The PET conversion and DMT yield was calculated by using the formula given below:

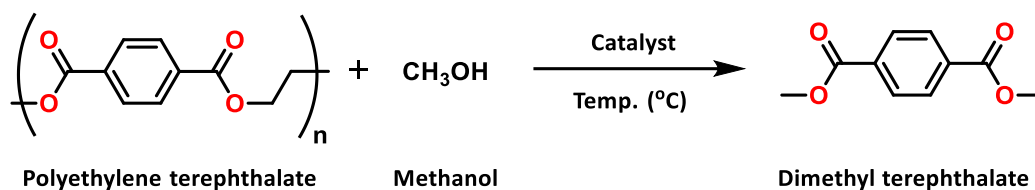
$$\text{PET conversion (\%)} = \frac{W_{\text{initial}} - W_{\text{final}}}{W_{\text{initial}}} \times 100$$

where “W initial” refers to the initial weight of PET and “W final” refers to the weight of PET that was not depolymerized.

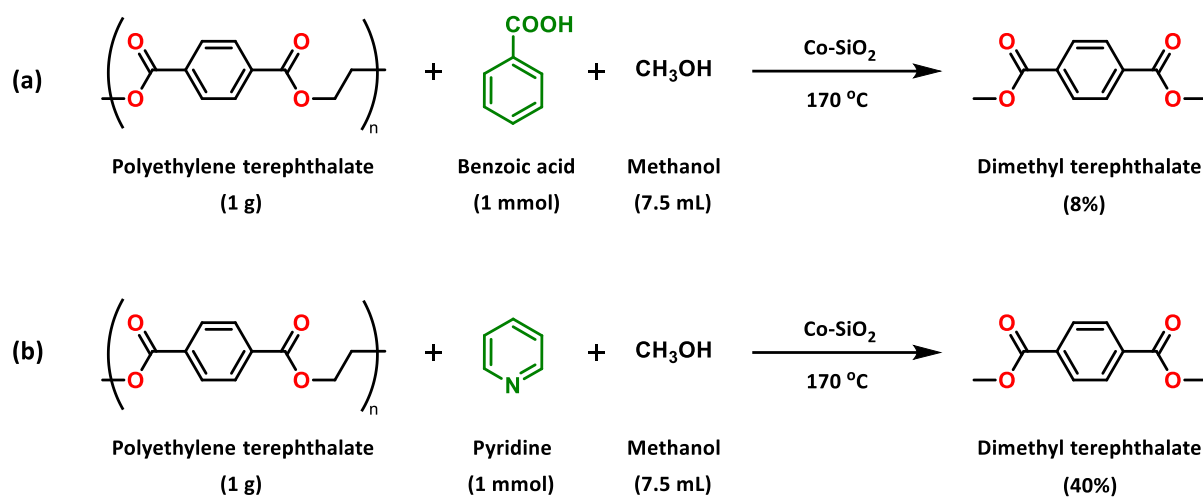
$$\text{DMT yield (\%)} = \frac{\frac{\text{Weight of DMT (obtained)}}{\text{Molar mass of DMT}}}{\frac{\text{Weight of PET (initial)}}{\text{Molar mass of PET repeating unit}}} \times 100$$

where the molar mass of DMT is 194 g mol<sup>-1</sup> and the molar mass of PET repeating unit is 192 g mol<sup>-1</sup>.

### S3. Control Studies



Entry	Catalyst (mg)	Temperature (°C)	Time (h)	PET conversion (%)	DMT yield (%)
1	Co NP (100 mg)	170	6	100	92
2	Co NP (20 mg)	170	6	95	89
3	SiO <sub>2</sub> (100 mg)	170	6	26	15
4	SiO <sub>2</sub> (80 mg)	170	6	25	13
5	Without catalyst	170	6	Trace	Trace

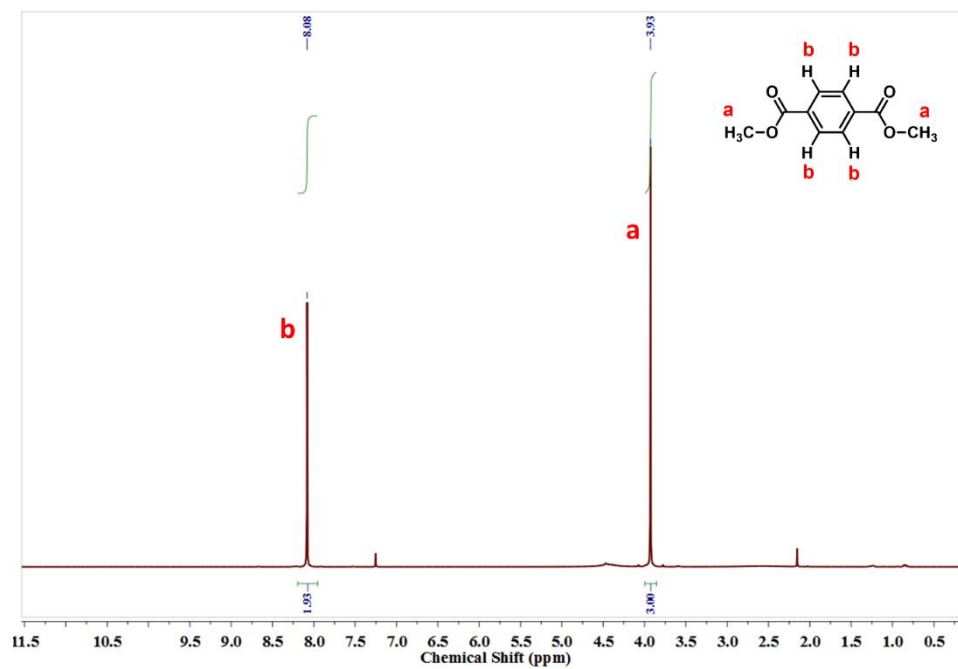


**Figure S9.** Control reactions for the determination of the role of acidic and basic sites (methanolysis of PET with (a) benzoic acid and (b) pyridine).



### S3. NMR Spectra

$^1\text{H-NMR}$  spectrum of DMT [500 MHz,  $\text{CDCl}_3$ ]



$^{13}\text{C-NMR}$  spectrum of DMT [125 MHz,  $\text{CDCl}_3$ ]

