Supporting Information

Thermodynamically Leveraged Solventless Aerobic Deconstruction of Polyethylene-Terephthalate Plastics Over a Single-Site Molybdenum-Dioxo Catalyst

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1. Experimental

1.1 Materials and Methods

All manipulations of reagents were carried out in oven-dried reaction vessels unless otherwise noted. The reactions of all polyesters, 1,2-ethanediol dibenzoate (**4**), vinyl benzoate (**6**), were carried out in cylindrical 100 mL Schlenk vessels under air with heating supplied by a dry bath metal block (Figure S1). Schlenk vessels was purchased from Chemglass Life Sciences. Polyethylene terephthalate (PET) powder was purchased from Goodfellow Inc. with a specified particle size of 300 μm and containing 1 ppm of acetaldehyde. Polybutylene terephthalate (PBT) pellets, polyethylene naphthalate (PEN) pellets were purchased from Sigma-Aldrich. Reagents, $CDCl_3$, DMSO-d_6, mesitylene were purchased from Sigma-Aldrich and used without further purification. Vinyl benzoate and 1,2-ethanediol dibenzoate were purchased from Sigma-Aldrich. AC/MoO_2, CNH/MoO_2 and AlS/MoO_2 were prepared and characterized previously by this group from (dme)MoO_2Cl_2 (dme = 1,2-dimethoxyethane).[S1-S4] AC/WO_2 was prepared by reaction of AC + (dme)WO_2Cl_2 using earlier reported procedure.[S8] The loading of Mo (3.24 wt%) and W (2.8 wt%) on carbon was determined by ICP analysis.

1.2 Physical and Analytical Measurements.

NMR spectra were recorded on a Varian Bruker Avance III HD system equipped with a TXO Prodigy probe (500 MHz) spectrometer. Chemical shifts (δ) for ^1H are referenced to solvent resonances. Mesitylene was used as the internal standard. FTIR spectra of gaseous products were recorded on a Nicolet iS50 FTIR spectrometer equipped with a MCT detector and collected using a custom-built airtight gas cell (100 mm long, ca. 3 ml cell volume) with IR-transparent ZnSe windows. The detector was cooled with liquid N_2. A spectral resolution of 4 cm^{-1} was used, and the reported spectra are an average of 64 scans. For the FTIR measurements, the gas cell was first evacuated down to 100 mtorr, where a background spectrum was collected. In a typical experiment, a 5 ml charge of the sample was introduced to the cell via an injection port fitted with a silicon septum by using an airtight syringe. Sample spectra were collected against the background spectrum obtained under the vacuum. X-ray photoelectron spectroscopy spectra were recorded at

the Keck-II facility at Northwestern University with a Thermo Scientific ESCALAB 250 Xi spectrometer, equipped with an Al K alpha radiation source and electron flood-gun, at a pressure of 8×10^{-8} mbar with a pass energy of 50 eV. Typically, a 50 ms dwell time and 10 scans were used for each spectrum. All spectra were calibrated according to the asymmetric graphitic peak at 284.8 eV using the Thermo Avantage software. Inductively coupled plasma (ICP) analysis was performed at the Northwestern University Quantitative Bio-element Imaging Center.

2. General Procedure

General setup for polyester depolymerization. In a typical experiment, polyester, AC/MoO_2 (3.24 wt% Mo catalyst) and a PTFE-coated magnetic stir bar was loaded to a 100 mL J-Young reaction flask in open air (= lab condition). The reactor was then closed and heated in aluminum block heater while stirring at 450 rpm (Figure S1). During the reaction, the product sublimes from the reaction zone and crystallizes near the top of the reaction tube (Figure S1). The conversion and selectivity were calculated by ^{1}H-NMR spectroscopy by integration against the mesitylene internal standard.

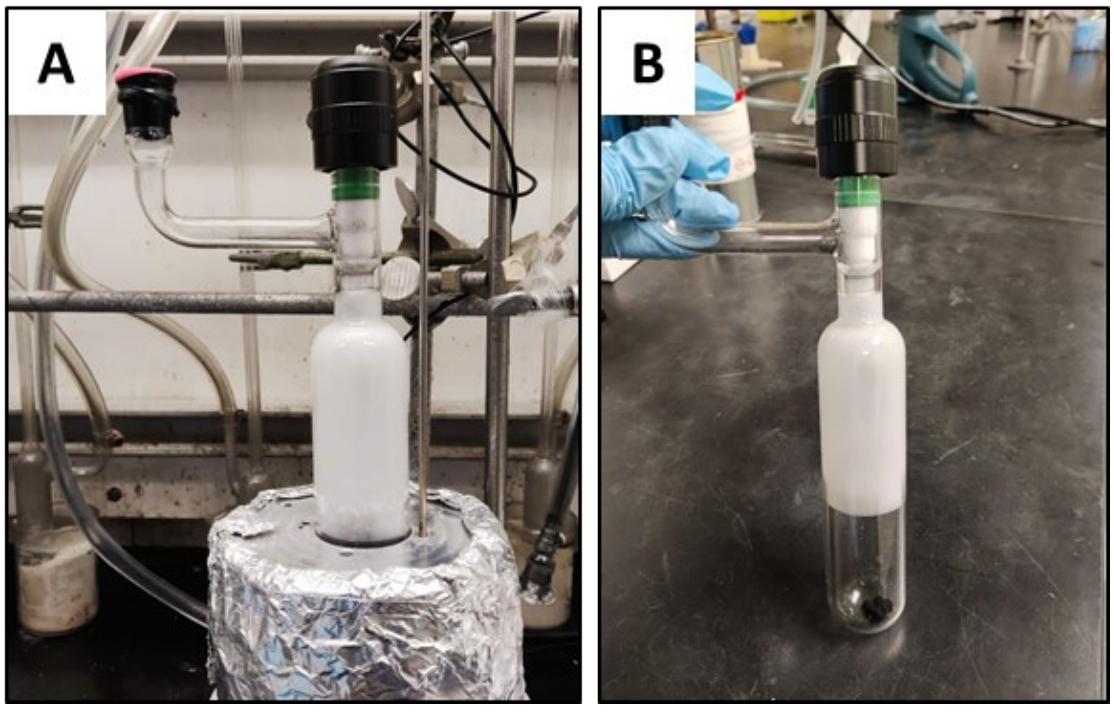
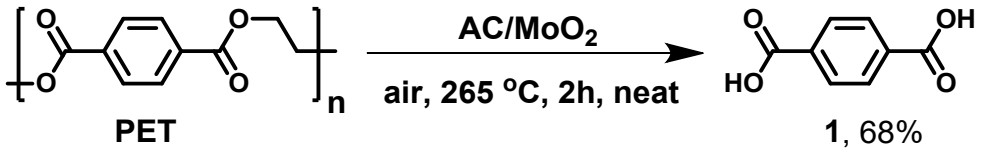


Figure S1. PET polymer depolymerization reactor setup. The terephthalic acid (TPA) sublimes to the colder region of the flask.

Table 1 Entry 1 (Reaction time screening): Heating of PET for 2 h under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 41 mg (1.37×10^{-5} mol, 26:1 ester group to Mo mole ratio) of MoO_2/AC was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 2 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 38.6 mg of mesitylene (= internal standard) was added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 68% yield.

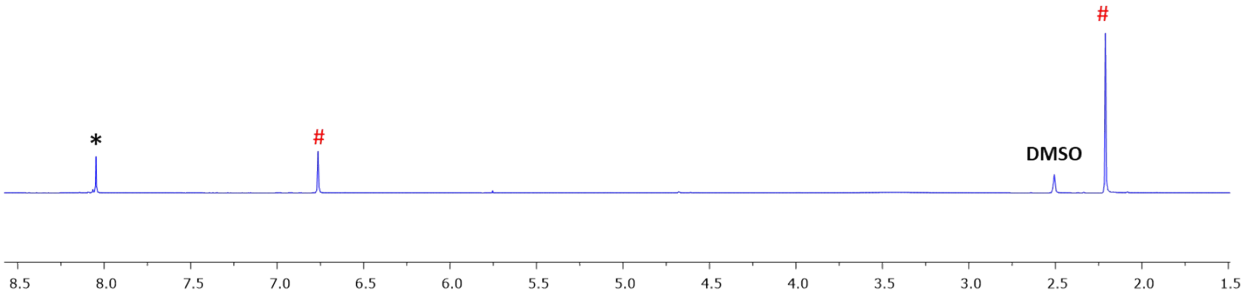
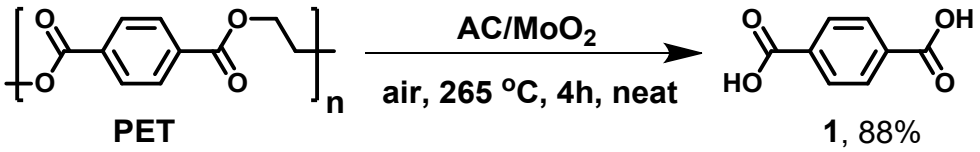


Figure S2. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 1. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 2 (Reaction time screening): Heating of PET for 4 h under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 41 mg (1.37×10^{-5} mol, 26:1 ester group to Mo mole ratio) of AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 38.6 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 88% yield.

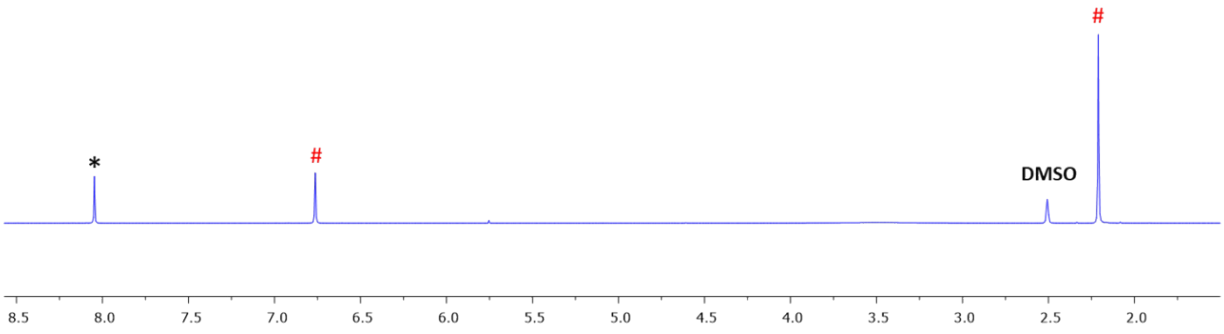
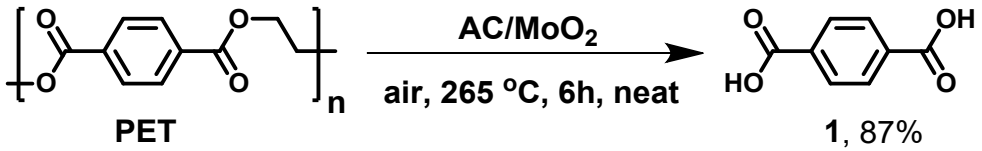


Figure S3. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 2. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 3 (Reaction time screening): Heating of PET for 6 h under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 41 mg (1.37×10^{-5} mol, 26:1 ester group to Mo mole ratio) of AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 6 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 38.0 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 87% yield.

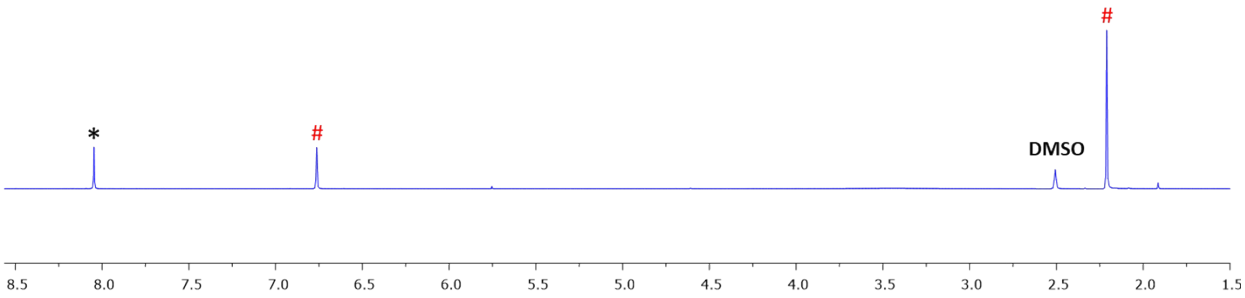
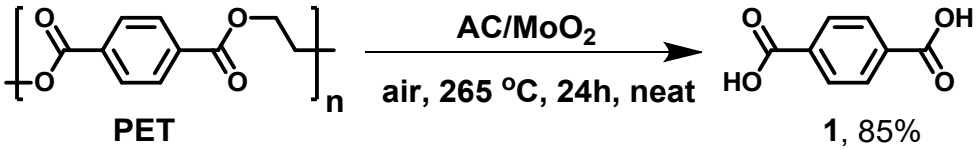


Figure S4. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 3. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 4 (Reaction time screening): Heating of PET for 24 h under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 41 mg (1.37×10^{-5} mol, 26:1 ester group to Mo mole ratio) of AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 24 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 37.4 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 85% yield.

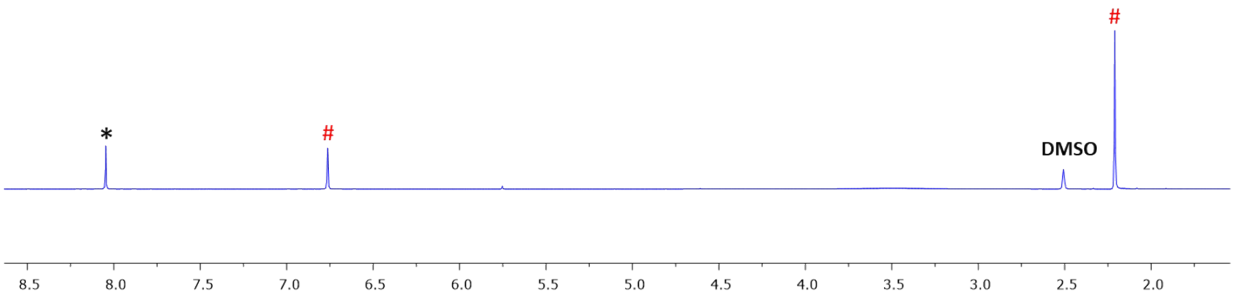
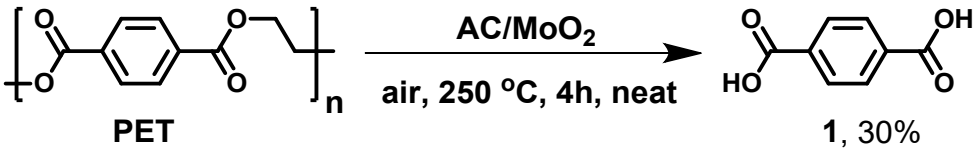


Figure S5. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 4. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 5 (Reaction temperature screening): Heating of PET at 250 °C under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 41 mg (1.37×10^{-5} mol, 26:1 ester group to Mo mole ratio) of AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 250 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 31.9 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 30% yield.

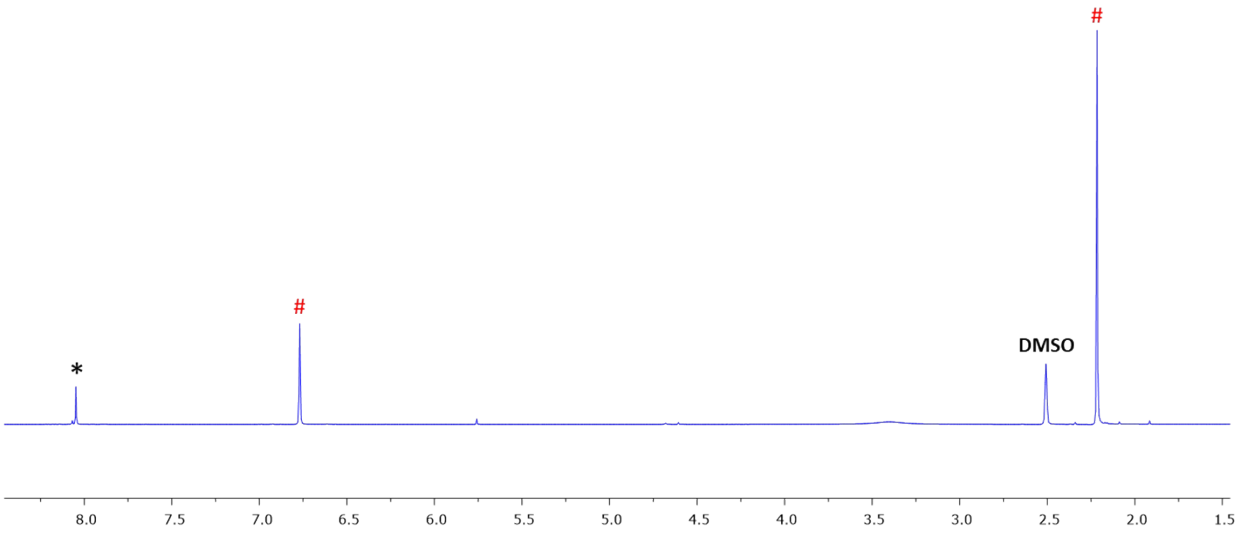
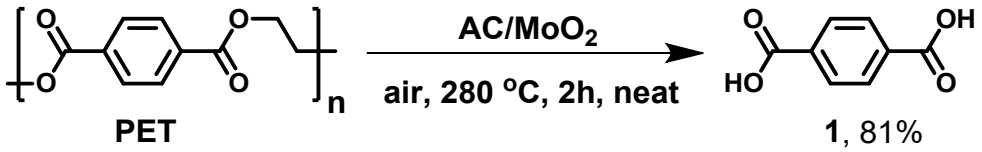


Figure S6. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 5. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 6 (Reaction temperature screening): Heating PET at 280 °C under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 41 mg (1.37×10^{-5} mol, 26:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 280 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 39.9 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 81% yield.

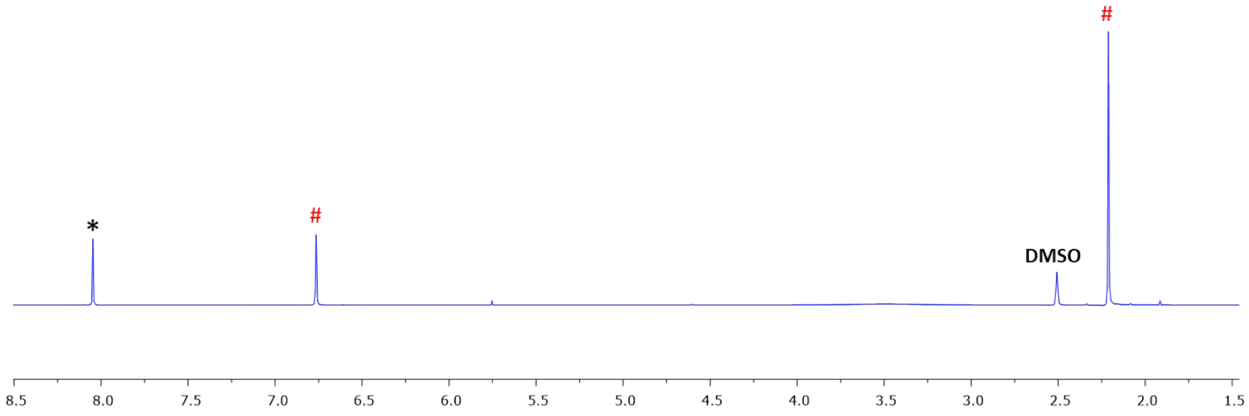
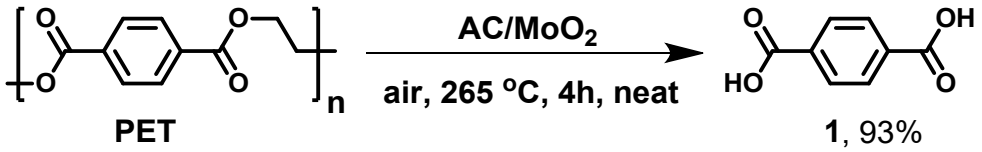
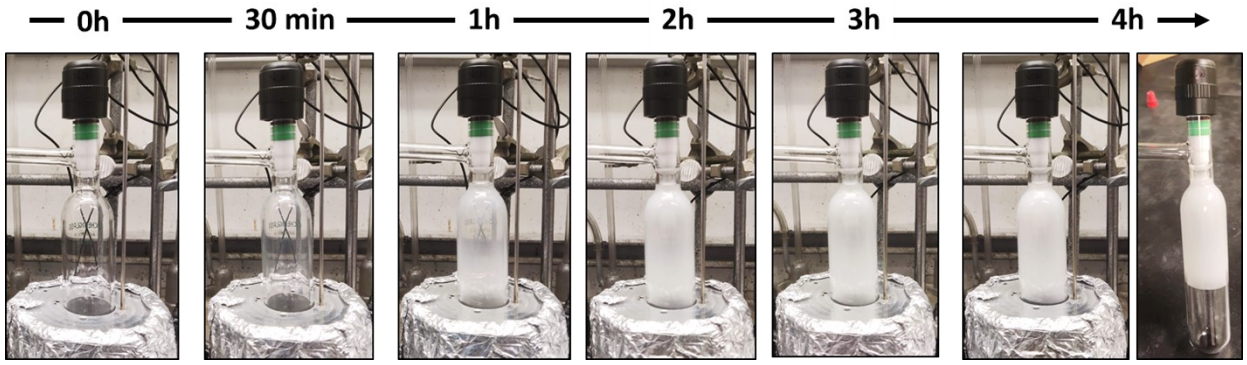


Figure S7. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 6. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 7 (Catalyst amount screening): 34:1 ester to Mo mole ratio under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 32 mg (1.07×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 42.4 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 93% yield. The photographs of terephthalic acid formation at different time intervals are shown below.



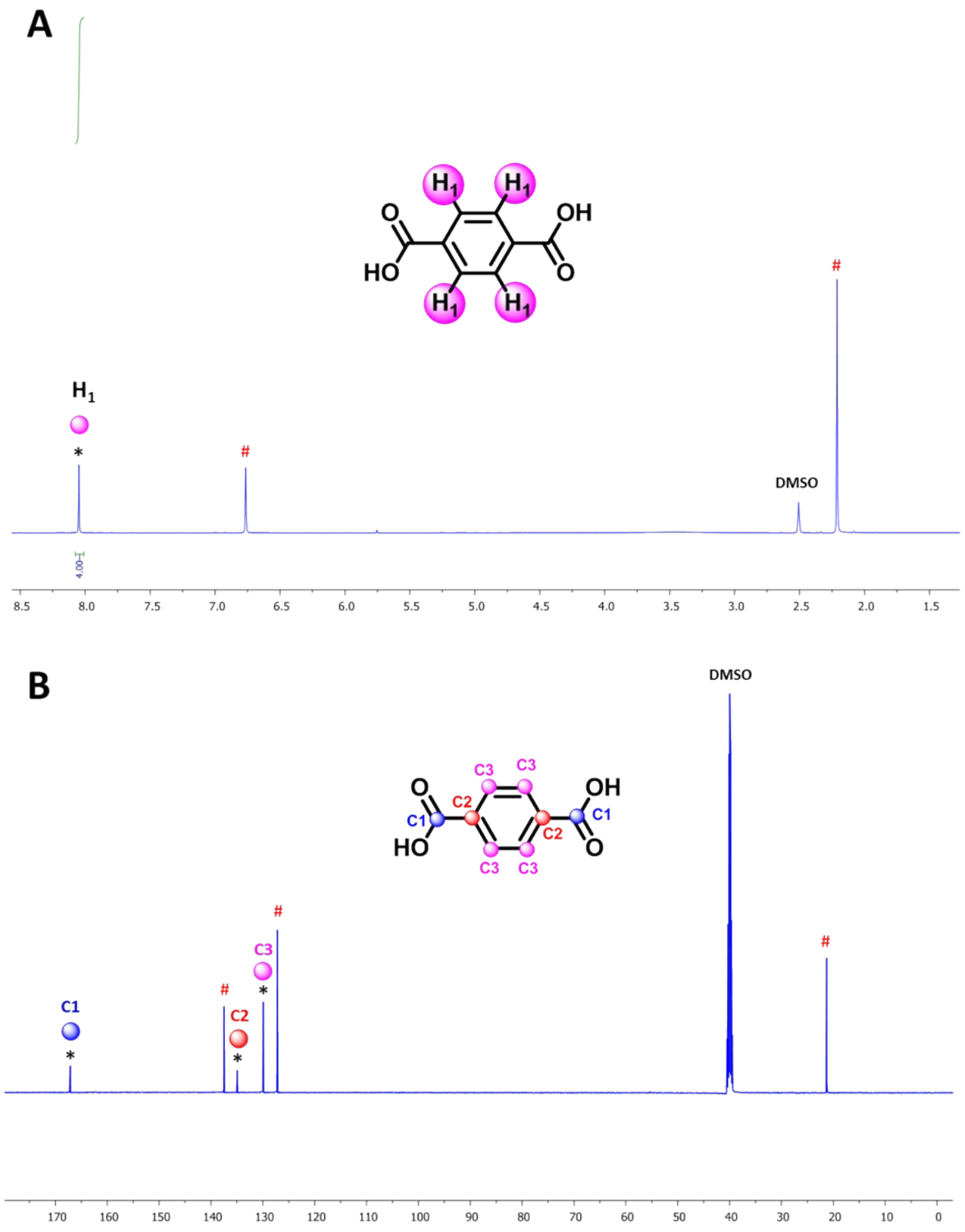
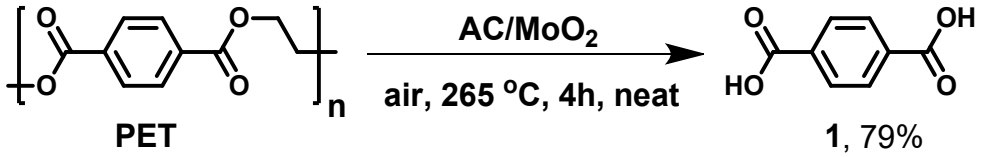


Figure S8. (A, B) ^{1}H and ^{13}C NMR spectra (500 MHz, DMSO-d_6) of the PTA produced in Table 1, entry 7. TPA signals are denoted by black asterisks, and mesitylene (= internal standard) signals are denoted by red # signs. By expanding the y-scale of the ^{1}H NMR spectrum and careful integrating, the purity of this TPA is determined to be ≥97%.

Table 1 Entry 8 (Catalyst amount screening): 45:1 ester to Mo mole ratio under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 24 mg (0.8×10^{-5} mol, 45:1 ester group to Mo mole ratio) of AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 40.7 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 79% yield.

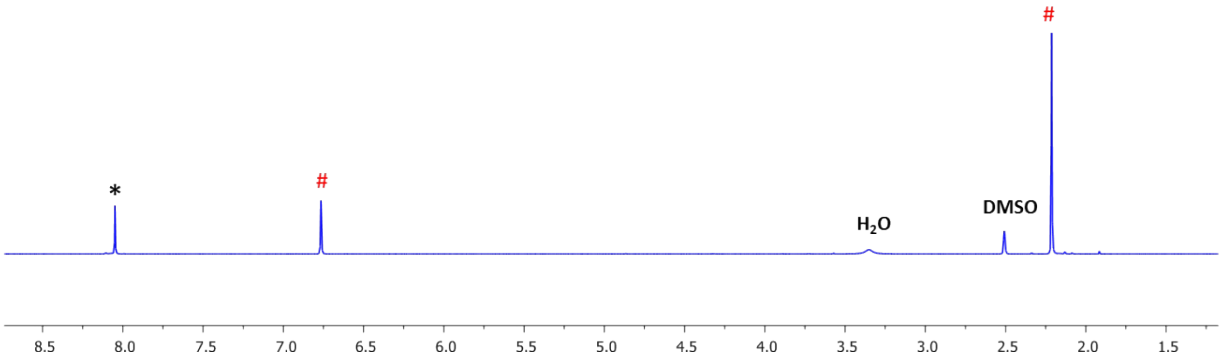
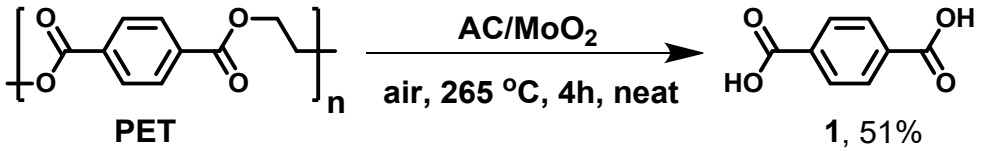


Figure S9. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 8. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 9 (Catalyst amount screening): 54:1 ester to Mo mole ratio under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 20 mg (0.67×10^{-5} mol, 54:1 ester group to Mo mole ratio) of AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 43.2 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 51% yield.

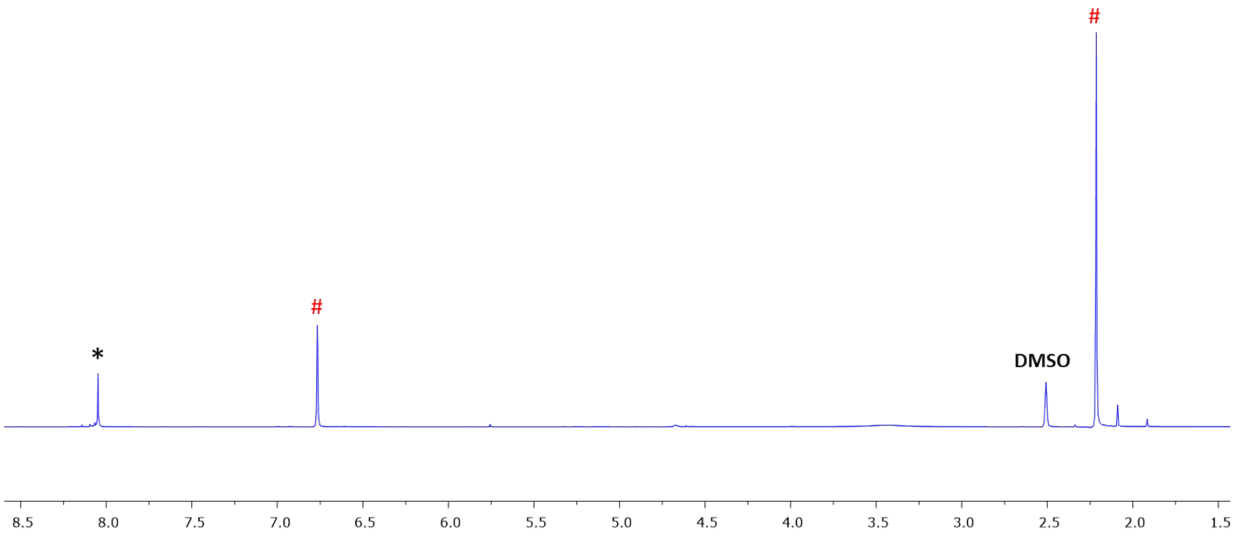
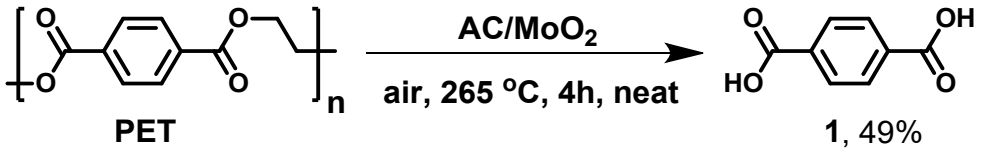


Figure S10. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 9. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 10 (Catalyst amount screening): 110:1 ester to Mo mole ratio under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 10 mg (0.33×10^{-5} mol, 110:1 ester group to Mo mole ratio) of AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 40.4 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 49% yield.

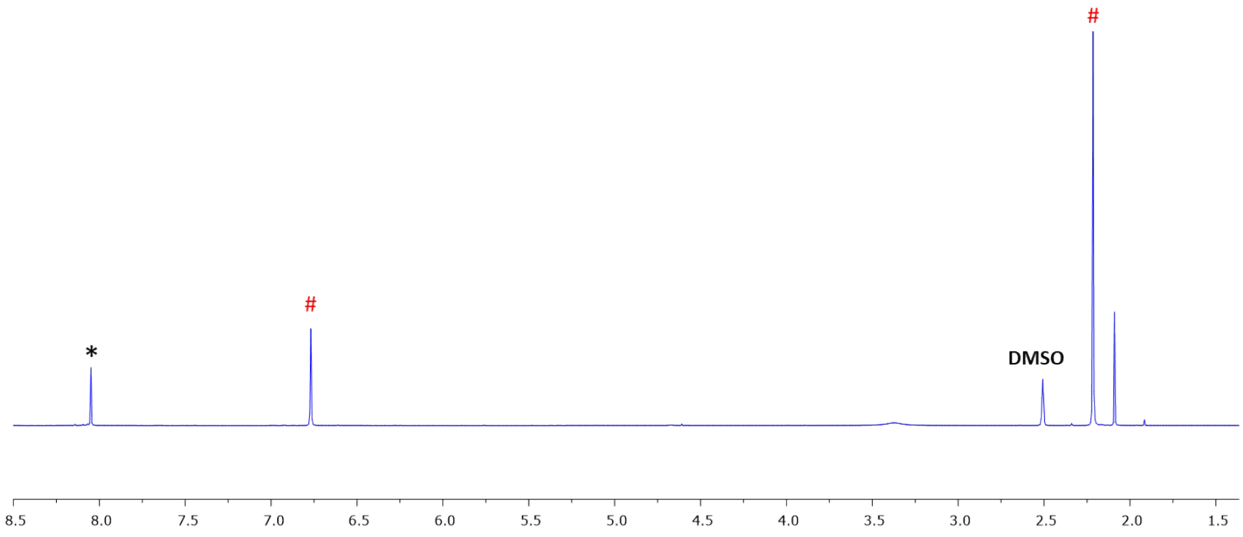
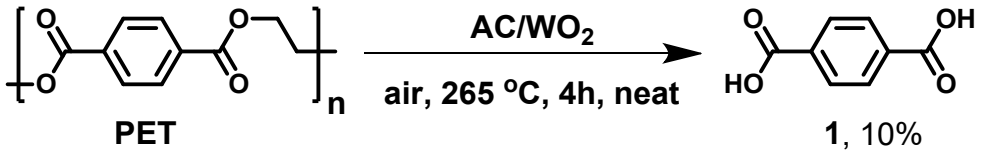


Figure S11. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 10. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 11: Heating of PET with AC/WO_2 under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 µm) and 70.6 mg (1.07×10^{-5} mol, 34:1 ester group to W mole ratio) of AC/WO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 32.1 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 10% yield.

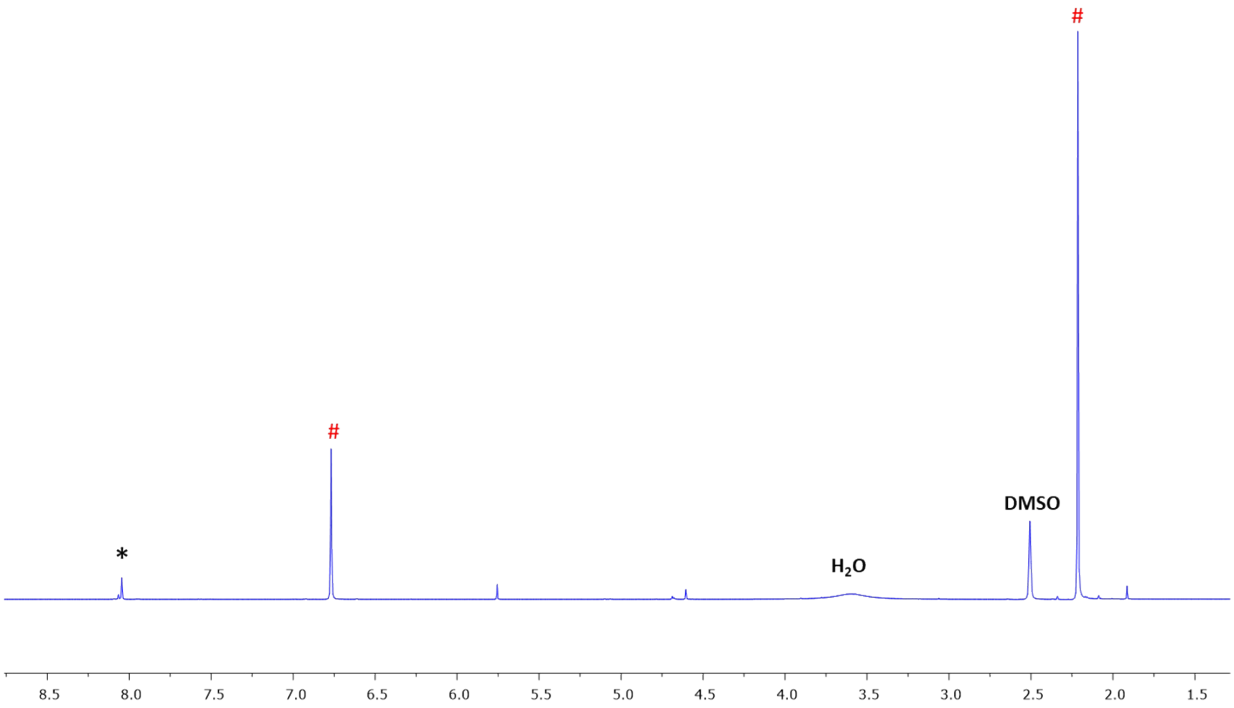
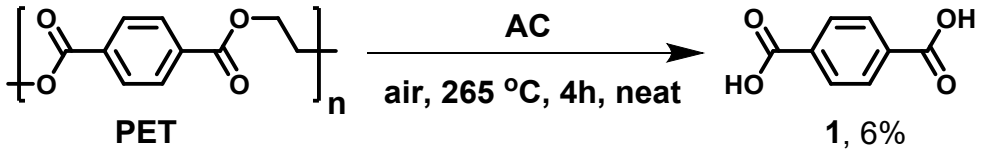


Figure S12. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 11. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 12: Heating of PET without catalyst under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 32 mg of activated carbon (AC) was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 32.1 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 6% yield.

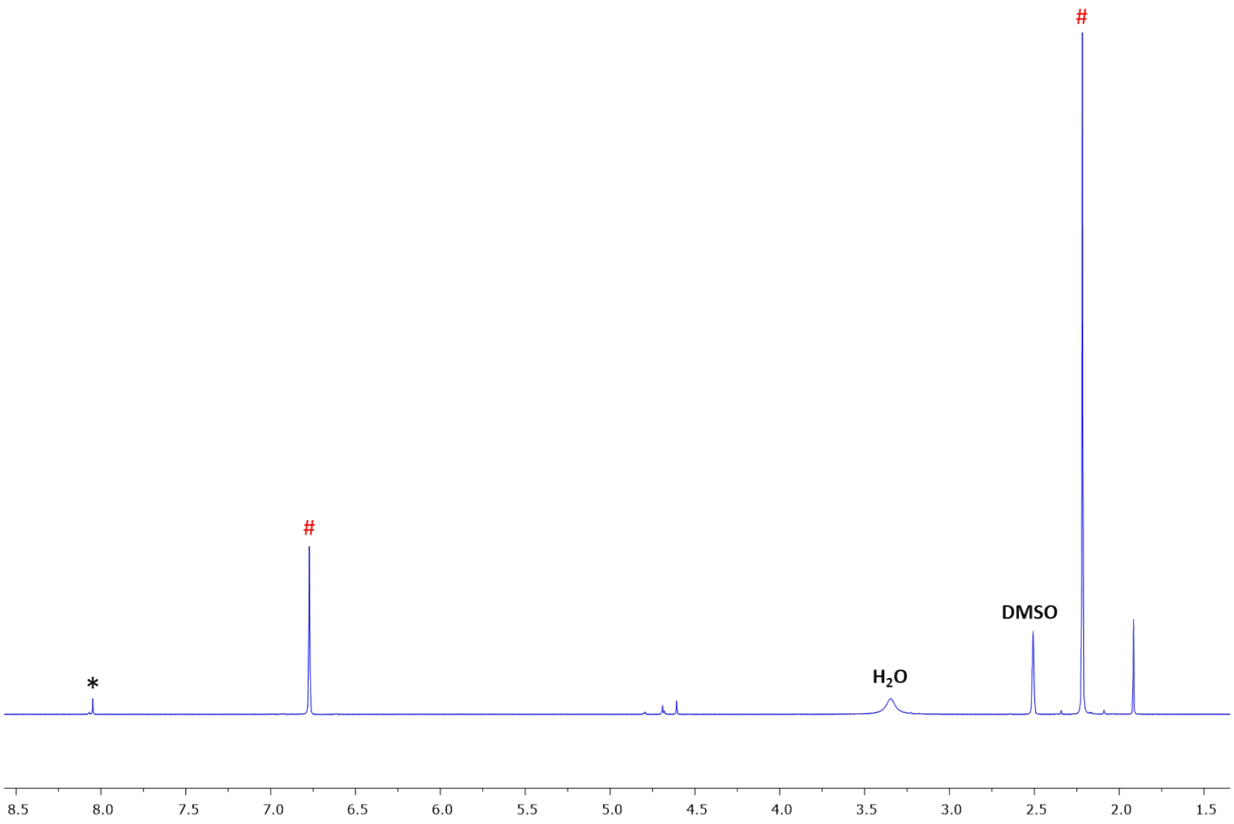
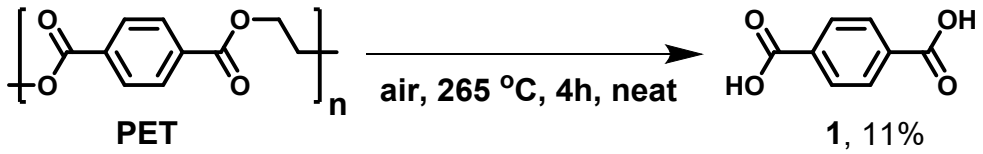


Figure S13. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 12. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 13: Heating of PET without AC/MoO_2 under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 31.6 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 11% yield.

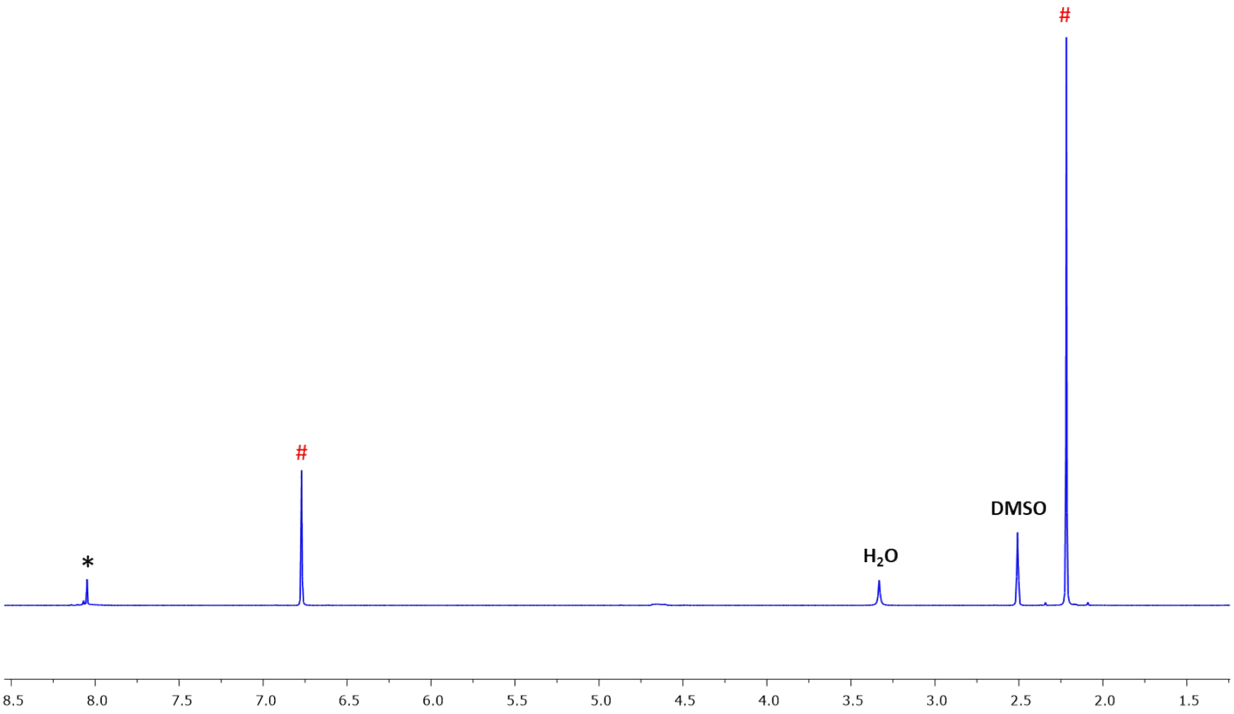
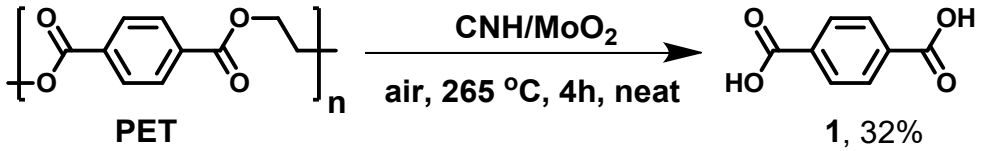


Figure S14. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 13. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 14: Heating of PET with CNH/MoO_2 under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 69 mg (1.07×10^{-5} mol, 34:1 ester group to Mo mole ratio) of CNH/MoO_2 (1.5 wt% Mo) was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 40.0 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 32% yield.

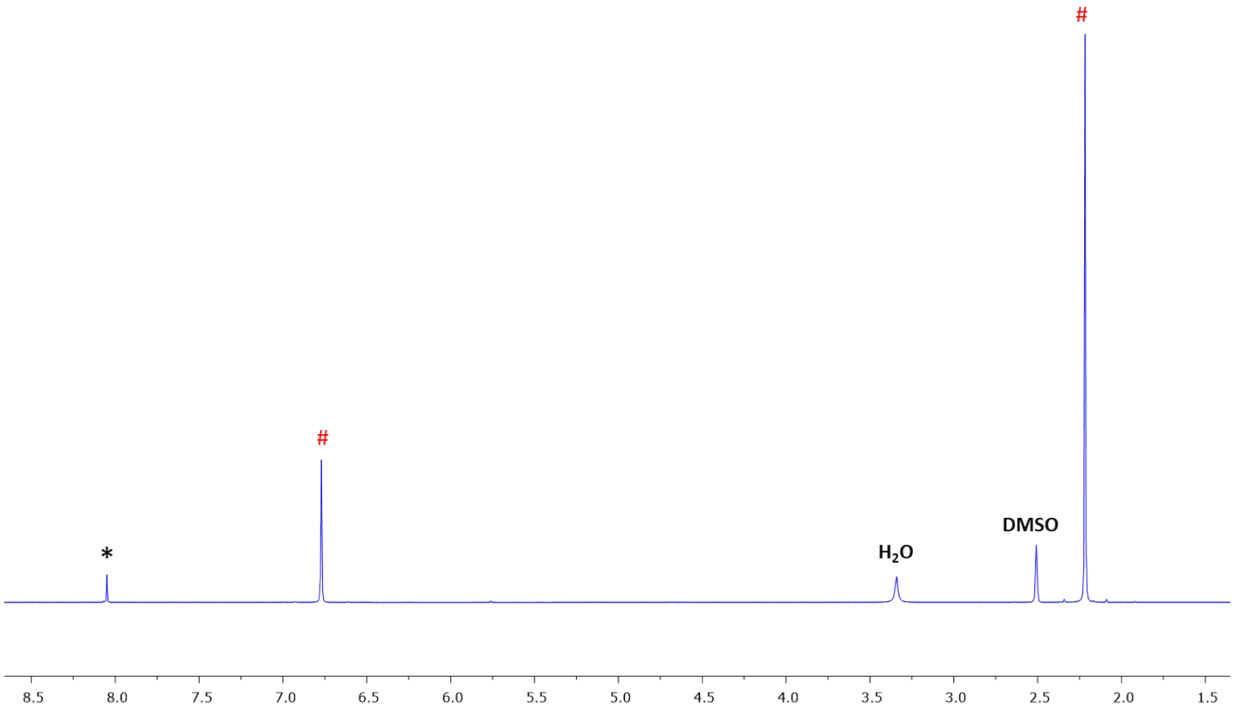
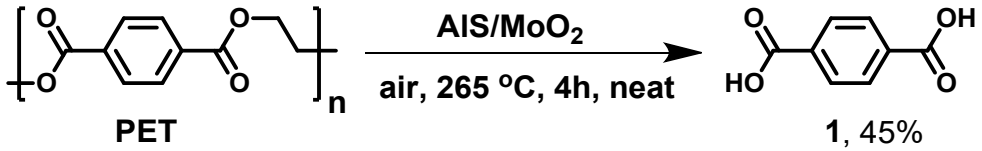


Figure S15. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 14. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 15: Heating of PET with AlS/MoO_2 under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 65 mg (1.07×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AlS/MoO_2 (1.6 wt% Mo) was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 43.7 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 45% yield.

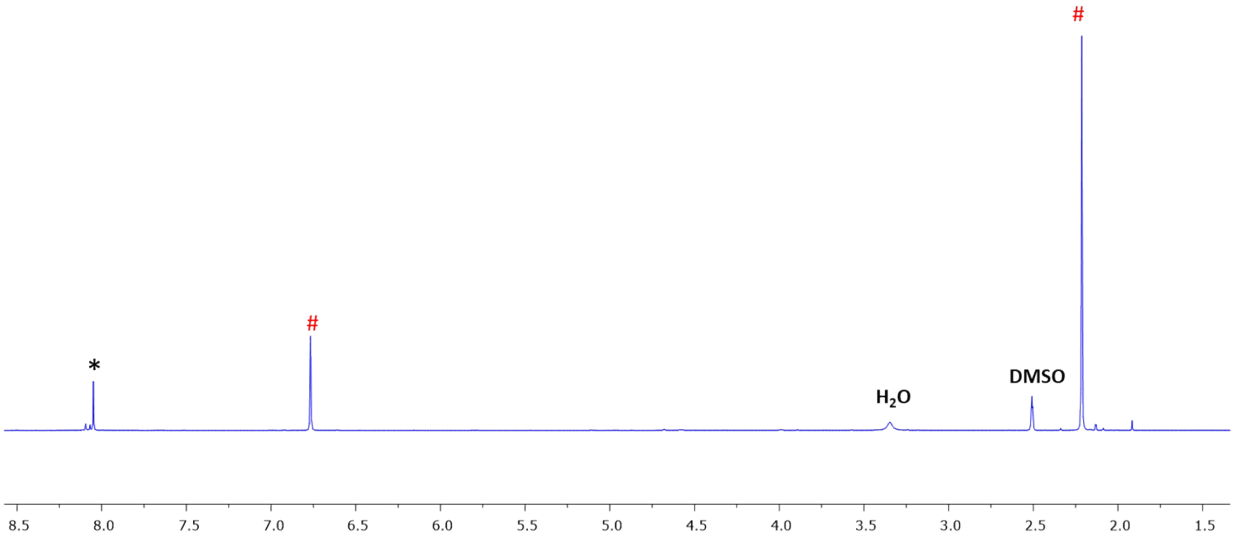
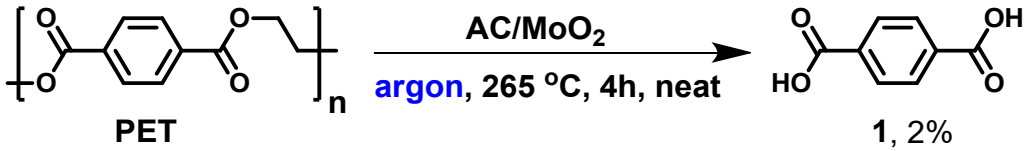


Figure S16. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 15. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 16: Heating of PET under argon



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 32 mg (1.07×10^{-5} mol, 34:1 ester group to Mo mole ratio) of MoO_2/AC was charged in a 100 mL Schlenk vessel in argon gas filled glove box. The reactor was then closed and heated at 265 °C in the presence of argon gas while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 25 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 2% yield.

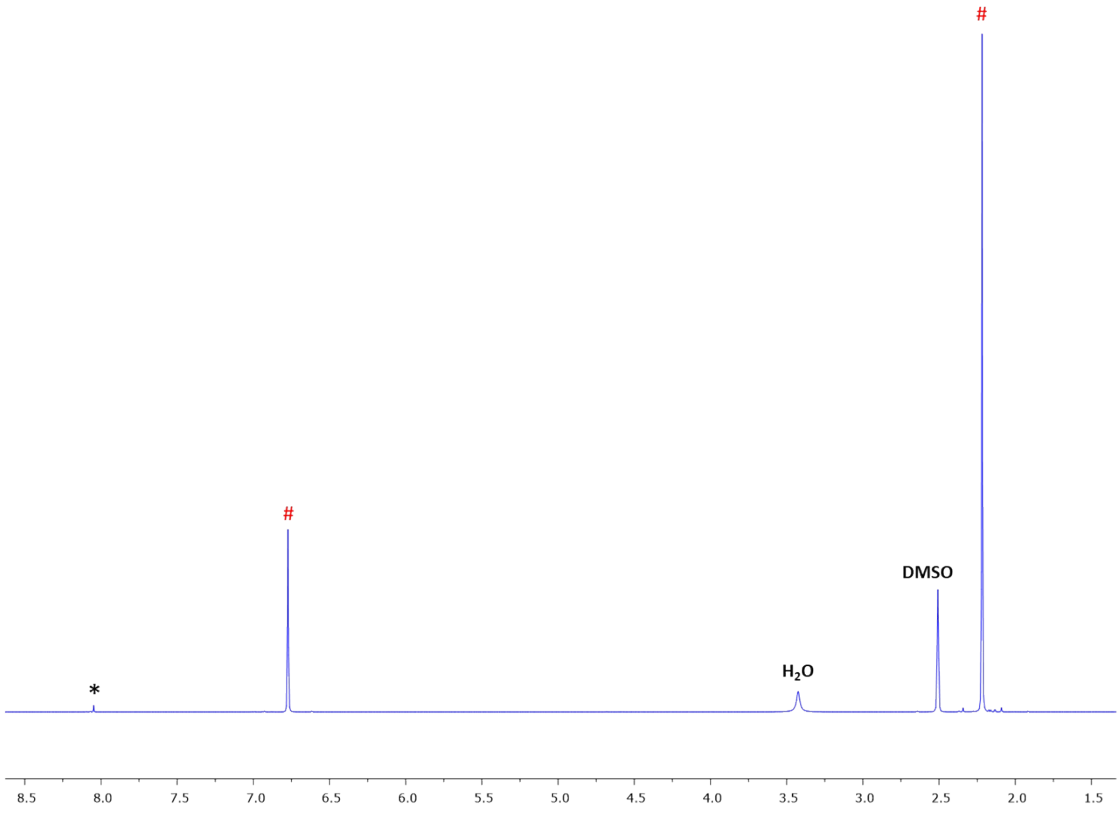
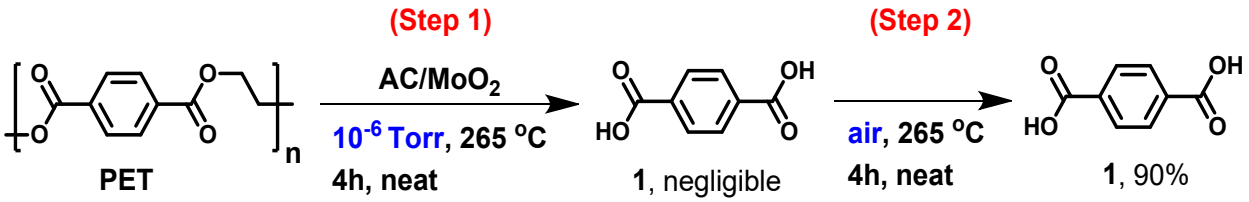


Figure S17. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 16. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 17: Heating of PET under vacuum followed by heating in the presence of air



Exactly 32 mg (1.66×10^{-4} mol) of air stored commercial PET powder (300 µm) and 29.3 mg (0.97×10^{-5} mol, 34:1 ester group to Mo mole ratio) of MoO_2/AC were charged in a 100 mL Schlenk vessel. The reactor was then closed under a static vacuum of 10^{-6} Torr and heated at 265 °C while stirring for 4 h. Terephthalic acid (**1**) was obtained in negligible amount (Figure S12, step 1). NMR was not measured for this step. Next, the flask was allowed to cool and then the cap was opened for 8 min to admit air and the reaction was continued for another 4 h and at 265 °C (Figure S12, step 2). After the reaction was completed, 2.5 mL of DMSO-d_6 containing 41.9 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 90% yield.

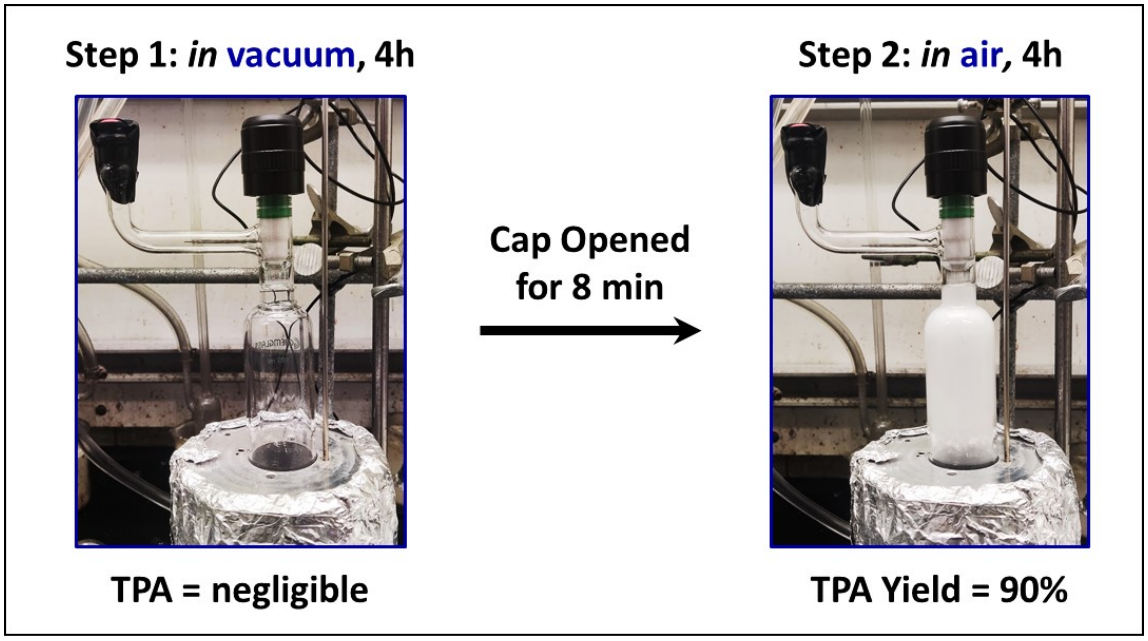


Figure S18. Photograph of the reaction vessel after 4 h reaction under vacuum environment of 10^{-6} Torr (step 1). Photograph of the reaction vessel after 4 h reaction under an ambient air environment (step 2).

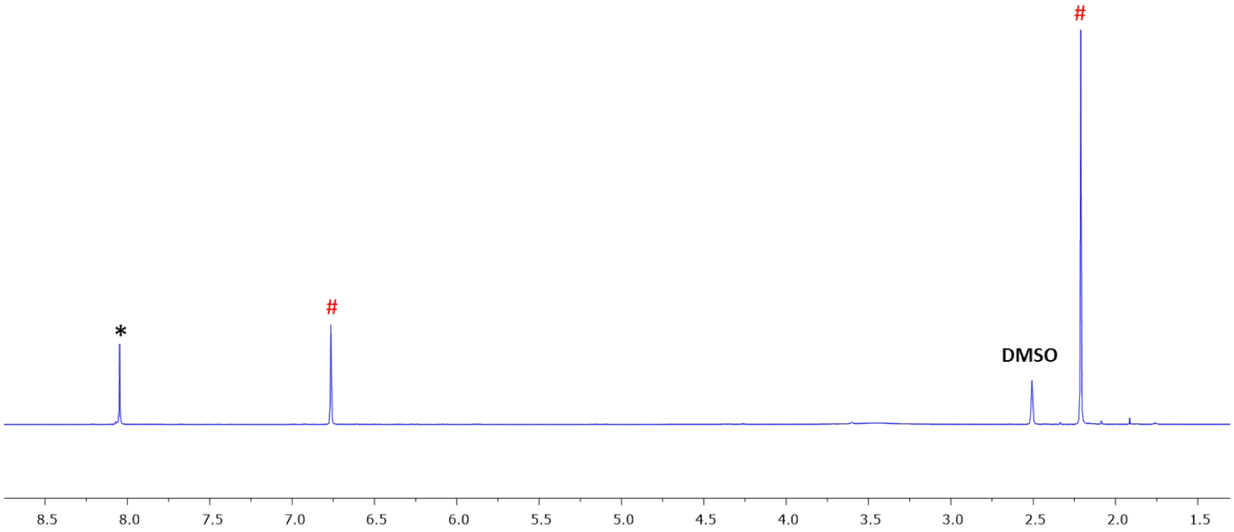
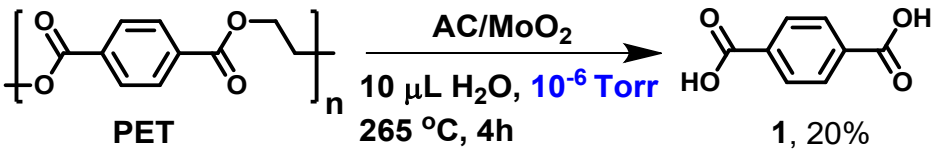


Figure S19. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 17 for step 2. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 18: Heating PET in the presence of water



Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm), 32 mg (1.07×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 and 10 μL (5.5×10^{-4} mol) of H_2O was charged in a 100 mL Schlenk vessel. The reactor was then closed and dipped in liquid nitrogen. After the water was frozen, the reaction flask was evacuated to 10^{-6} Torr, sealed, and heated at 265 °C while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 29.4 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 20% yield.

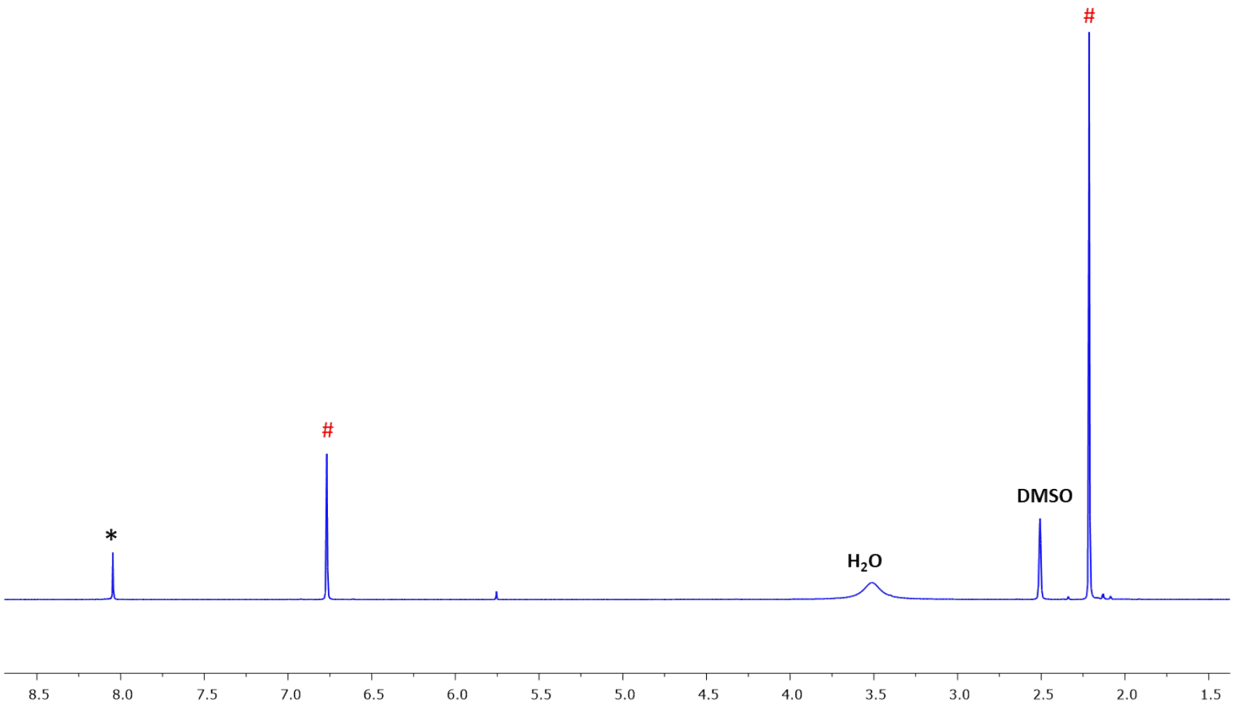


Figure S20. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 18. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 1 Entry 19: Catalyst recycling experiment

During the course of the PET depolymerization, terephthalic acid (**1**) sublimes to the top of the reaction vessel and the AC/MoO_2 free flowing black powder catalyst remains at the bottom. After every 4 h of heating fresh PET was added to the reaction vessel. The process was repeated four times. The catalyst recycling experiments show that the catalyst can be used at least five times without any deactivation or loss of product yield.

Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 32 mg (1.07×10^{-5} mol, 34:1 ester group to Mo mole ratio) of MoO_2/AC were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After every 4 h of reaction, fresh PET powder 35 mg, 35 mg, 33 mg, and 33 mg, respectively, were added to the reaction flask. After the reaction was completed (20 h, 5 run), 3.5 mL of DMSO-d_6 containing 46.6 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. The overall yield of terephthalic acid (**1**) after five run was 94%. Note that overall, a 170:1 ester group to Mo mole ratio was used during this process.

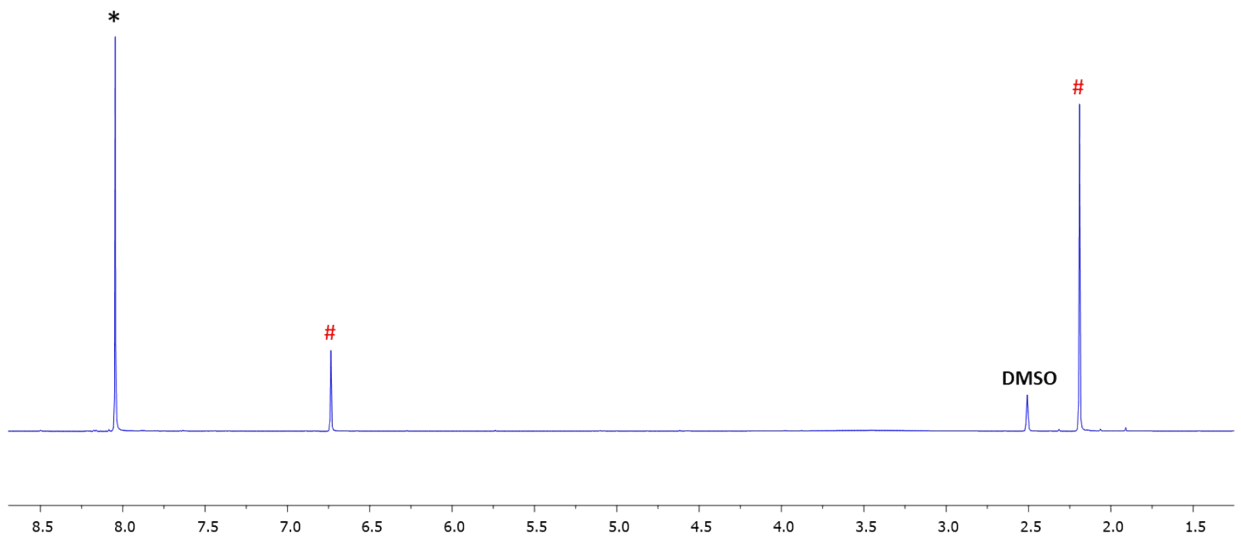


Figure S21. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 1, entry 19. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

XPS spectra Sample preparation of catalyst used for XPS. After completing five reaction cycles, the catalyst was retrieved from the reaction flask using a spatula, washed with acetone (3 × 10 mL), and then air-dried.

XPS results: The surface Mo of the fresh and spent catalysts were characterized by XPS (Figures S22). The Mo $3d_{5/2}$ orbital peak is found to be 232.7 eV for the spent and fresh catalysts. No variation in the Mo binding energy between the spent and fresh catalysts, indicating that the nature of the surface bound Mo species remains unchanged. These results are in good agreement with previously reported XPS data[S2] and supporting our hypothesis of the existence of single-site Mo(VI) dioxo species.

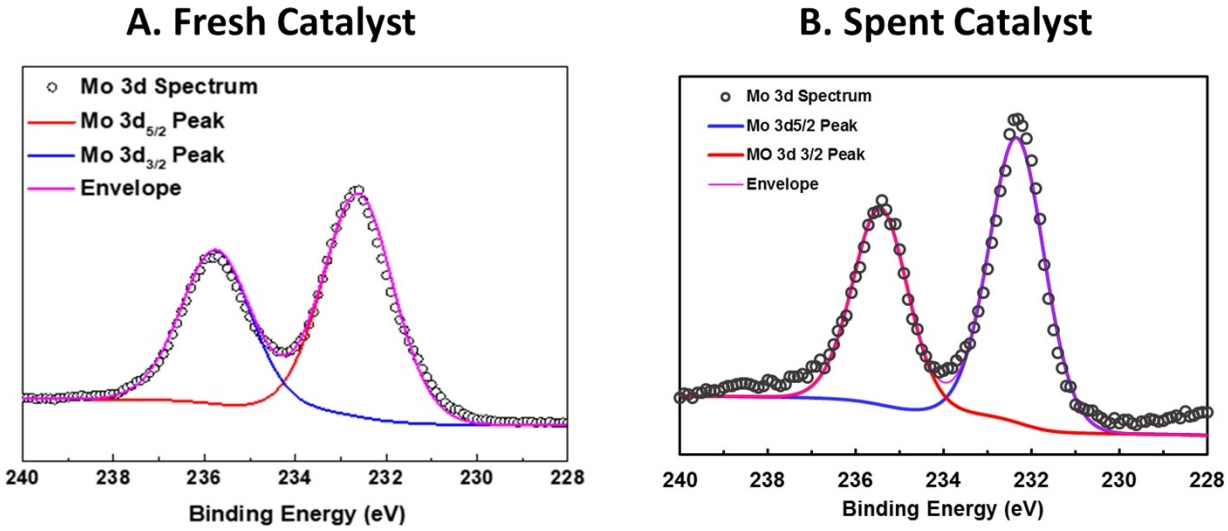


Figure S22. Mo(3d) XPS spectrum of AC/MoO_2 catalyst sample with fitting results. Spectrum of fresh (A) and used (B) catalysts.

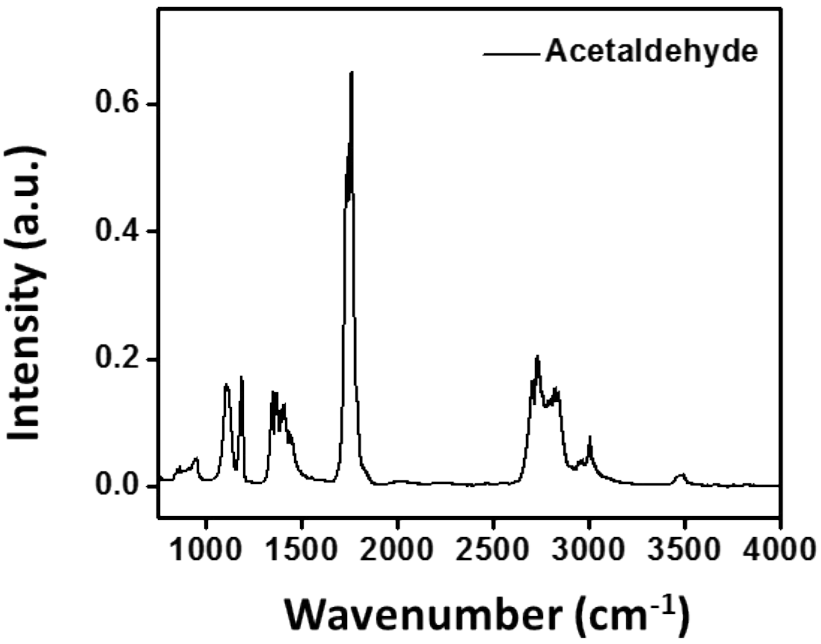


Figure S23. Fourier transform infrared (FTIR) spectrum of gaseous acetaldehyde.

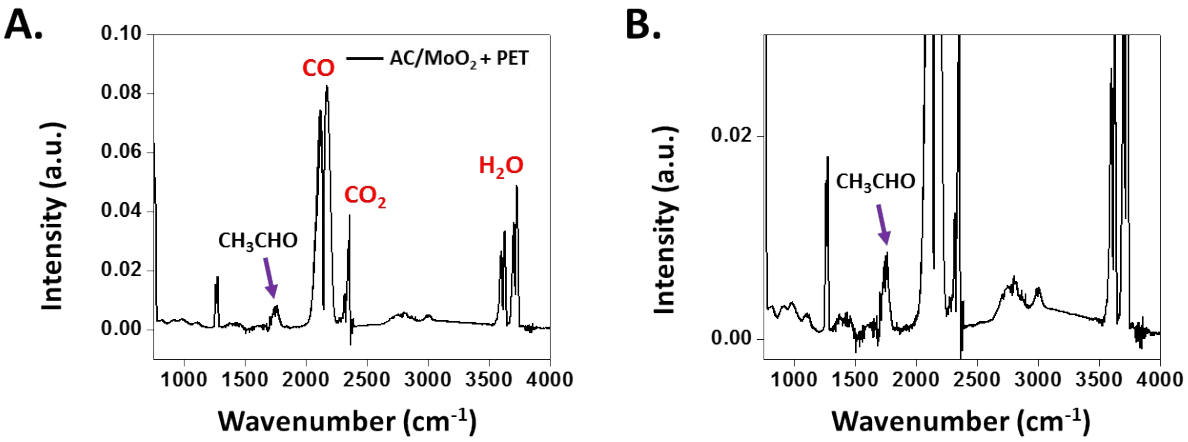


Figure S24. Fourier transform infrared (FTIR) spectra of headspace gases after AC/MoO_2 + PET reaction. Reaction condition: Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) and 32 mg (1.07 × 10-5 mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. (A) Full spectrum. (B) Zoom in spectrum to visualize the acetaldehyde peak with the purple arrow. In addition to the acetaldehyde peak, we observed signals for CO_2, CO, and H_2O. The spectra from the control experiment (heating AC/MoO_2 or PET) also have peaks for CO_2, CO, and H_2O, indicating the release of these gaseous products upon heating the AC/MoO_2 or PET.

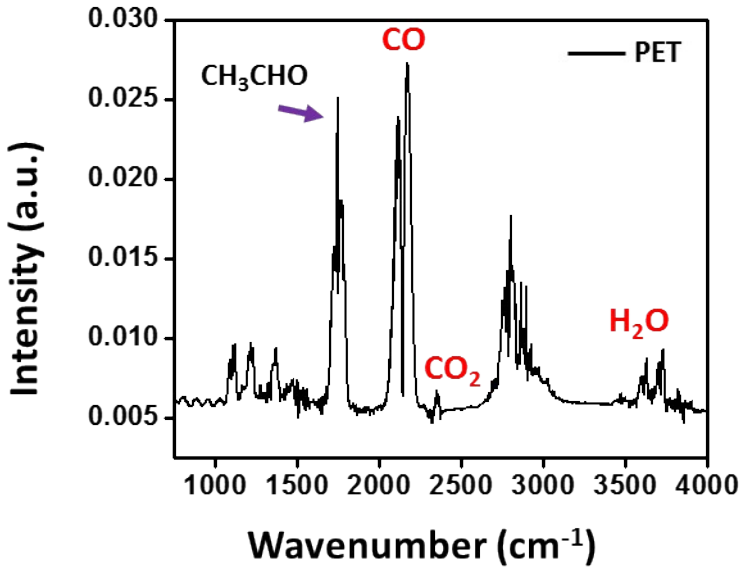


Figure S25. Fourier transform infrared (FTIR) spectra of headspace gases after PET heating. Reaction condition: Exactly 35 mg (1.82×10^{-4} mol) of air stored commercial PET powder (300 μm) was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. This experiment indicating the release of CO_2, CO, and H_2O gaseous products upon heating the PET. It is noteworthy that a significantly sharper peak for acetaldehyde was observed here as compared to Figure S24, despite a TPA yield of only 11%. This further confirms that, under this condition (heating PET in the absence of AC/MoO_2) acetaldehyde does not undergo oligomerization or form the cyclic trimer, as depicted in Figure S27.

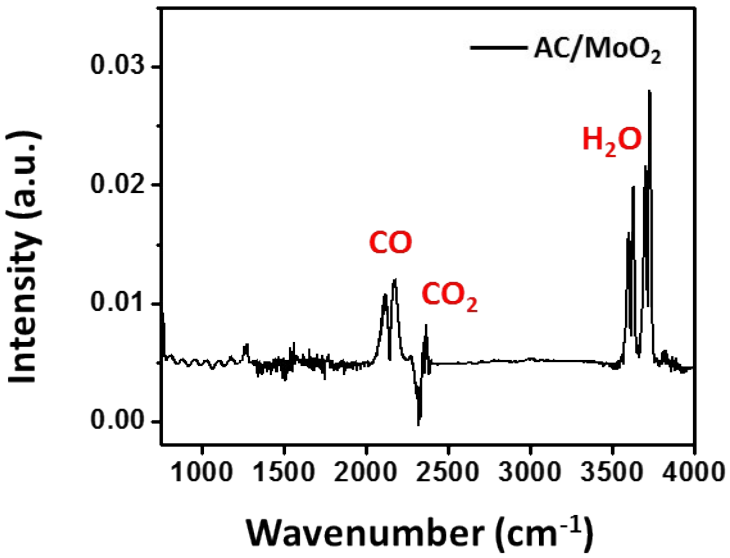


Figure S26. Fourier transform infrared (FTIR) spectra of headspace gases after AC/MoO_2 heating. Reaction condition: Exactly 32 mg (1.07×10^{-5} mol of air stored AC/MoO_2 was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. This experiment indicating the release of CO_2, CO, and H_2O gaseous products upon heating the AC/MoO_2.

Gas phase composition determination by NMR. Exactly 105 mg (5.46×10^{-4} mol) of air stored PET and 96 mg (3.21×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, the reaction vessel was connected to 100 mL glass flask containing D_2O (4 mL) under vacuum. Acetaldehyde and its cyclic oligomer 1,3,5-trioxane, 2,4,6-trimethyl are observed in the NMR spectrum. The acetone peak appearing in NMR might be due to adsorption of acetone on AC/MoO_2.

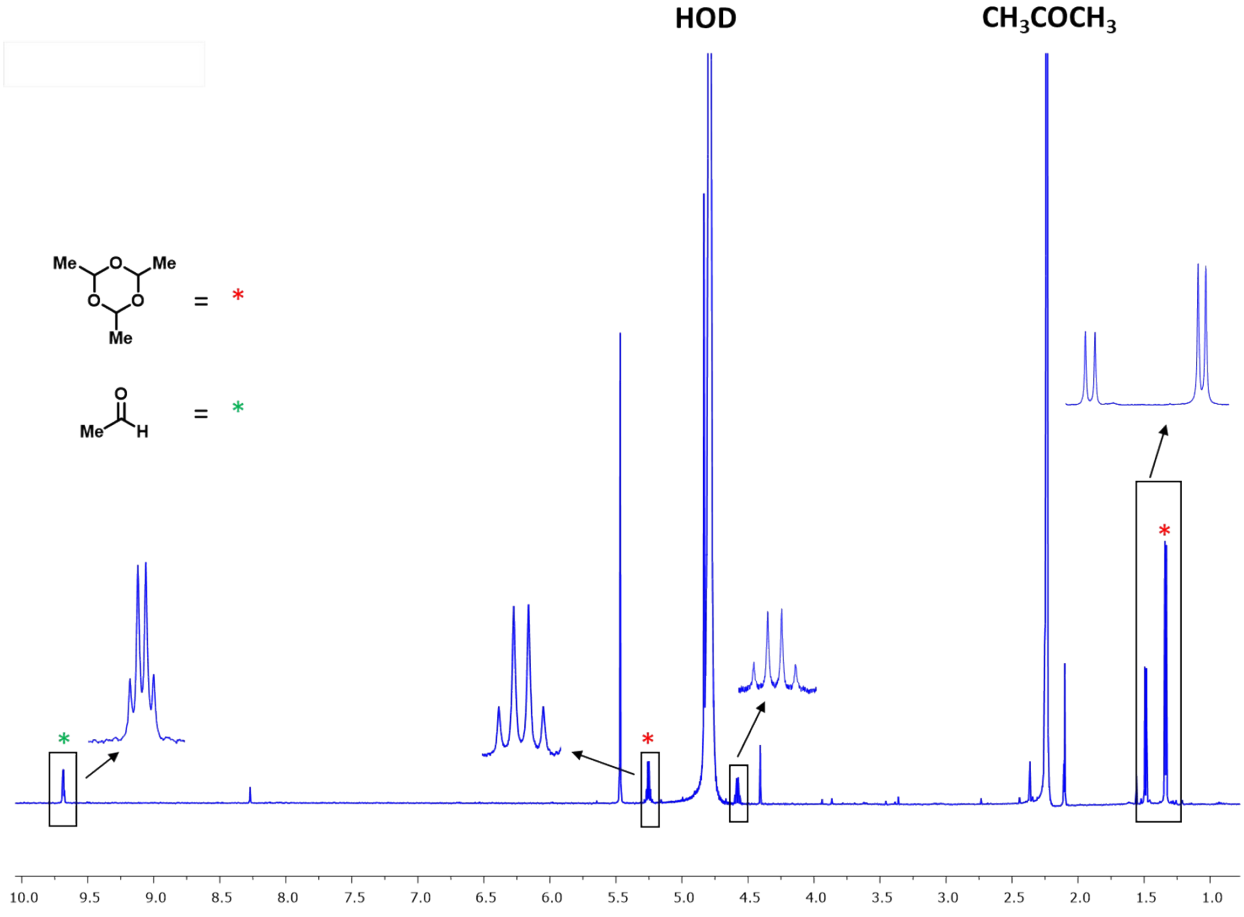


Figure S27. ^1H NMR spectrum (500 MHz, D_2O) of PET deconstruction, gas phase composition.

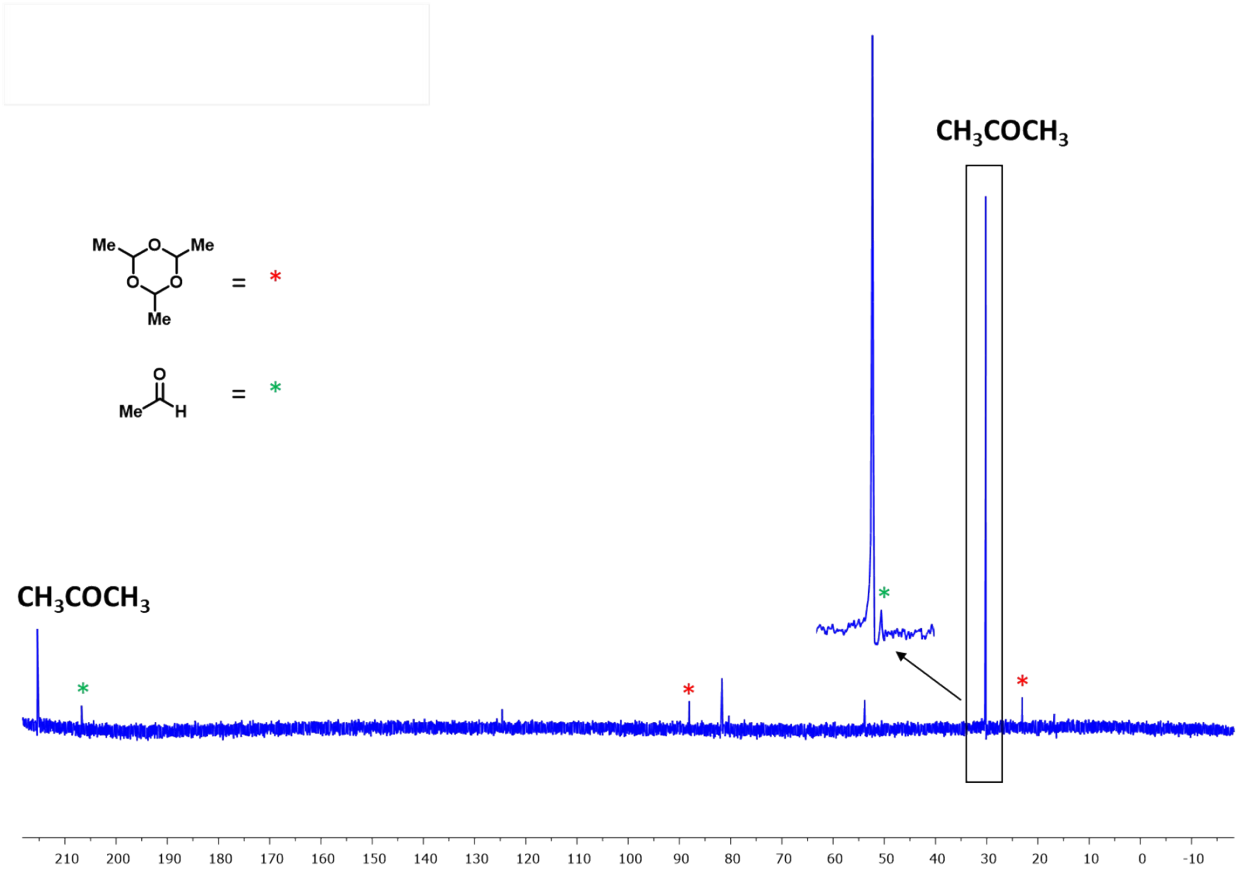
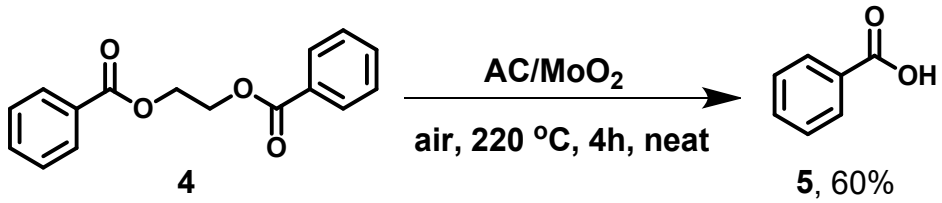


Figure S27 (Cont.). ^{13}C NMR spectrum (500 MHz, D_2O) of PET deconstruction, gas phase composition.

Figure 2B. Reaction of 2-ethanediol dibenzoate under optimized conditions



Exactly 50 mg (1.85×10^{-4} mol) of air stored 1,2-ethanediol dibenzoate (**4**) and 32.5 mg (1.09×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2.5 mL of CD_2Cl_2 containing 35.6 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Benzoic acid (**5**) was obtained in 60% yield.

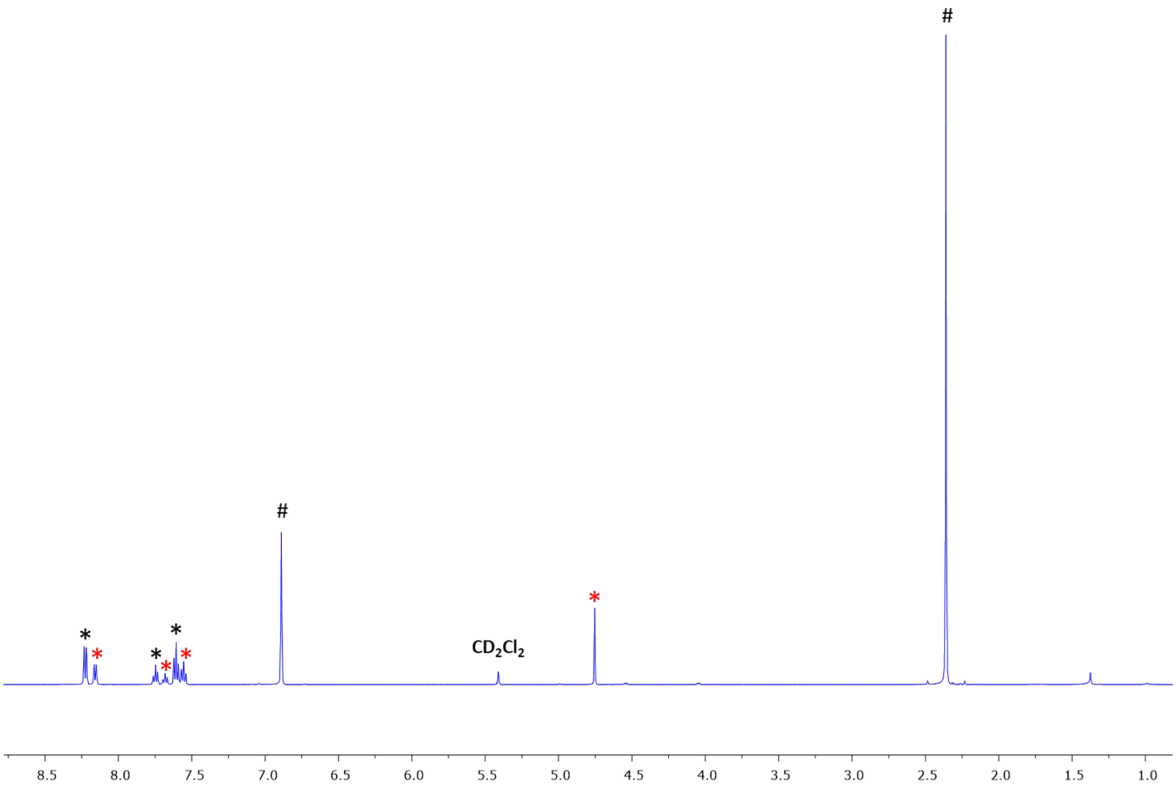
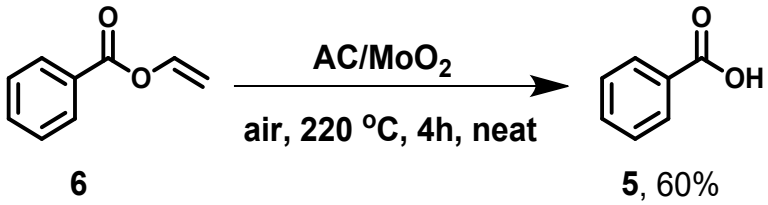


Figure S28. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of the reaction of Figure 2B. Signals of **4** are denoted by black asterisks, signals of **5** are denoted by red asterisks, mesitylene (= internal standard) signals denoted by # signs.

Figure 2C. Control experiments: Reaction of vinyl benzoate under optimized conditions



Exactly 43 mg (2.9×10^{-4} mol) of air stored vinyl benzoate (**6**) and 25.4 mg (0.84×10^{-5} mol) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was completed, 2.5 mL of $CDCl_3$ containing 23.3 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Benzoic acid (**5**) was obtained in 60% yield.

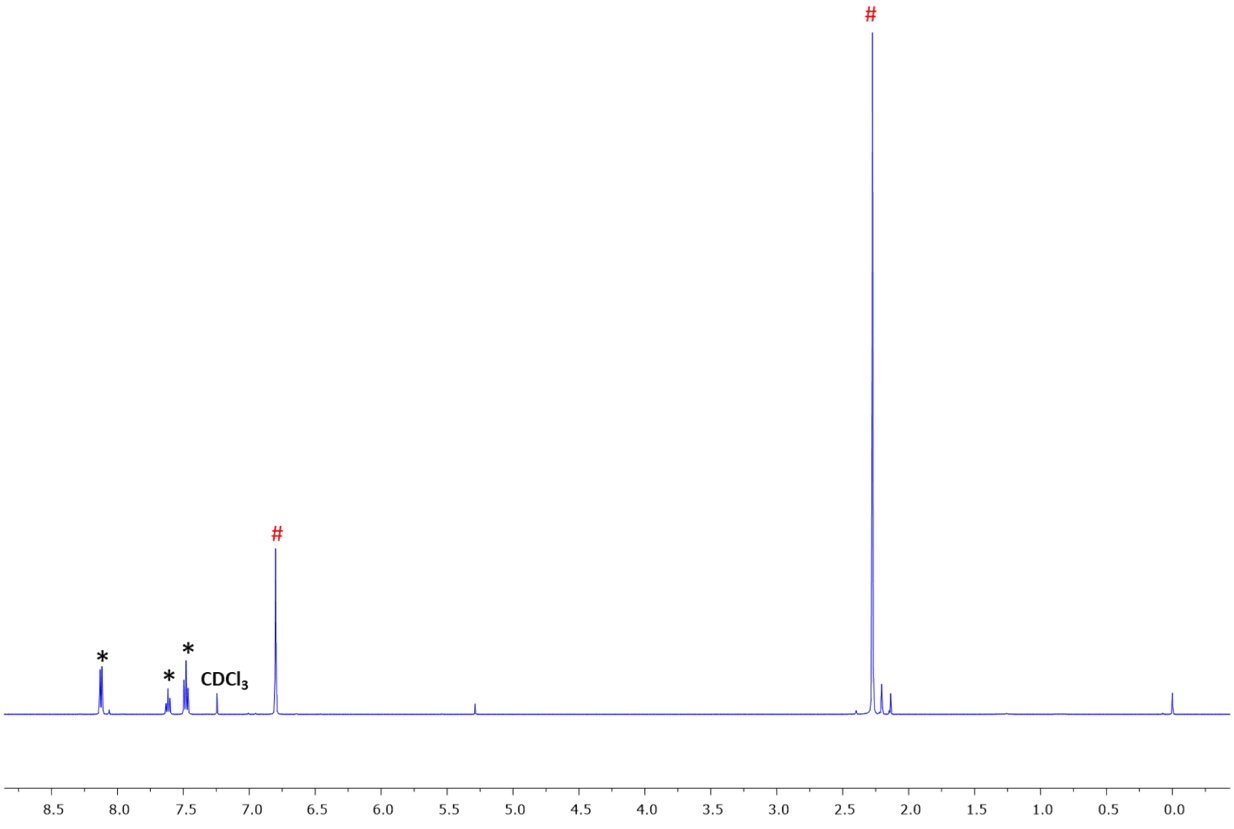
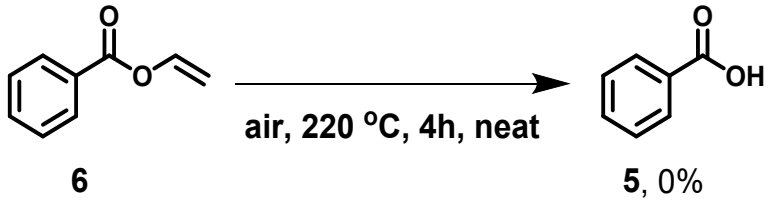


Figure S29. ^1H NMR spectrum (500 MHz, CD_2Cl_2) of the reaction of Figure 2C. Signals of **5** are denoted by black asterisks and mesitylene (= internal standard) signals denoted by # signs.

Figure 2C. Control experiments: Reaction of vinyl benzoate without catalyst under optimized conditions



6 **5**, 0%

Exactly 120 mg (8.1×10^{-4} mol) of air stored vinyl benzoate (**6**) was charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2.5 mL of $CDCl_3$ containing 46.1 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Benzoic acid (**5**) was obtained in 0% yield.

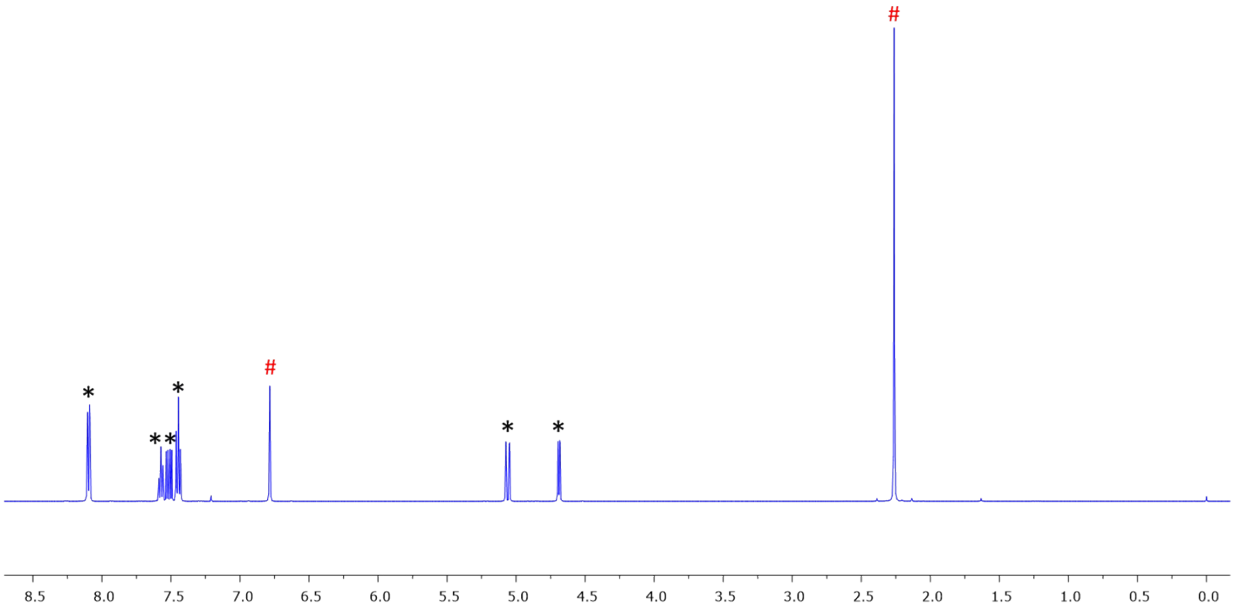


Figure S30. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the reaction of Figure 2C. Signals of **6** are denoted by black asterisks and mesitylene (= internal standard) signals denoted by # signs.

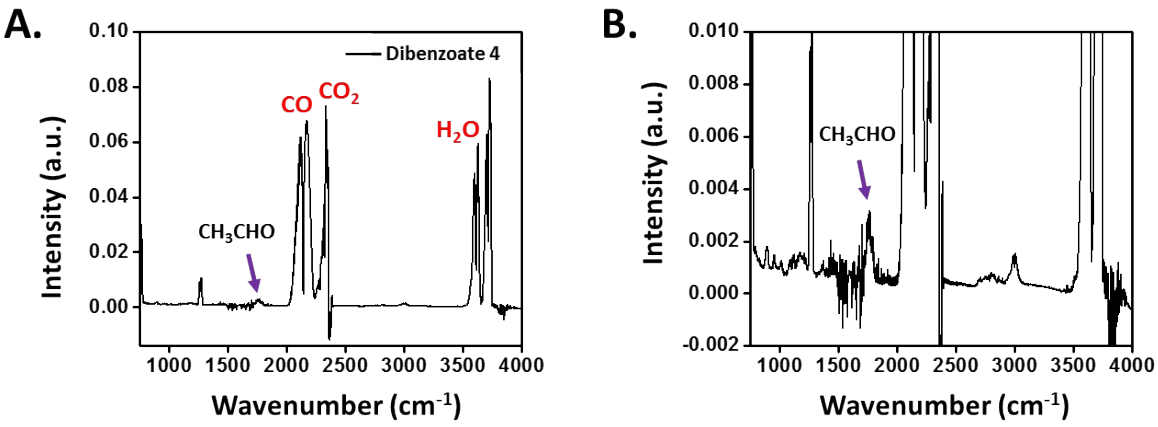
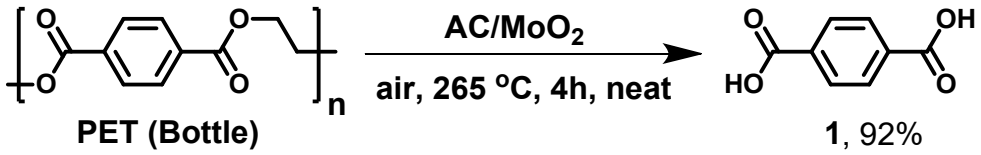


Figure S31. Fourier transfer infrared (FTIR) spectra of headspace gases after AC/MoO_2 + dibenzoate (**4**) reaction. Reaction condition: Exactly 50 mg (1.85×10^{-4} mol) of air stored 1,2-ethanediol dibenzoate (**4**) and 32.5 mg (1.09 × 10-5 mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. (A) Full spectrum. (B) Zoom in spectrum to visualize the acetaldehyde peak with purple arrow.

Table 2 Entry 2: Deconstruction of PET bottle under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored small pieces of PET bottle and 32 mg (1.07×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged into a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2.5 mL of DMSO-d_6 containing 43.5 mg of mesitylene (= internal standard) was added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 92% yield.

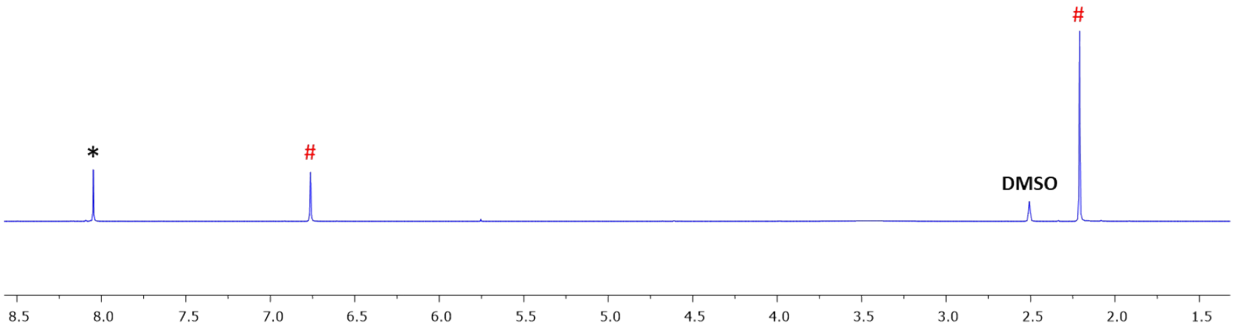
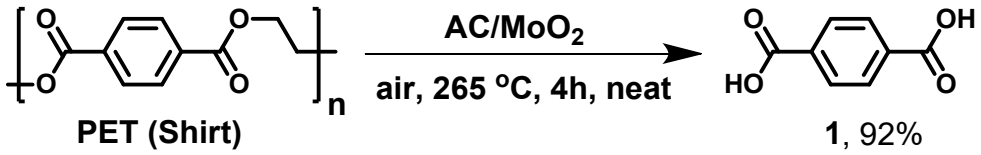


Figure S32. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 2. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 3: Deconstruction of PET shirt under air



Exactly 35 mg (1.82×10^{-4} mol) of air stored small pieces of PET shirt and 32 mg (1.07×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged into a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 39.3 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 92% yield.

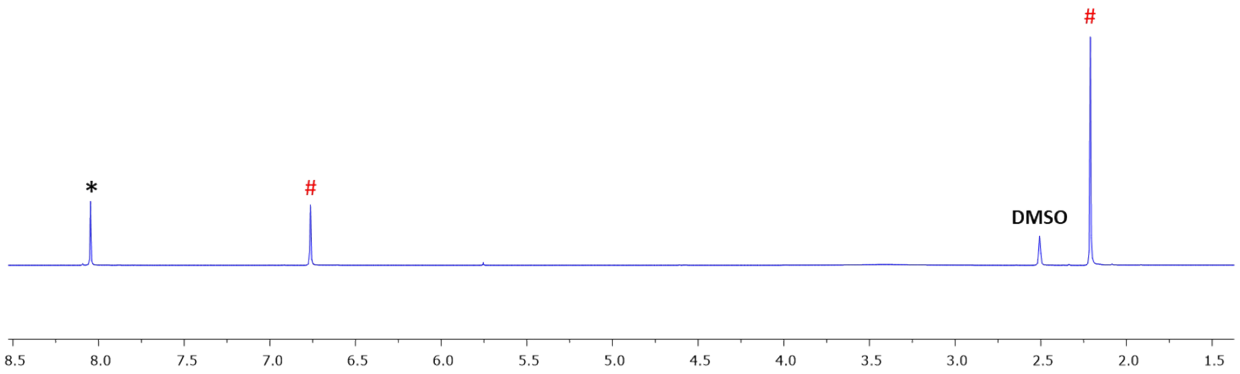
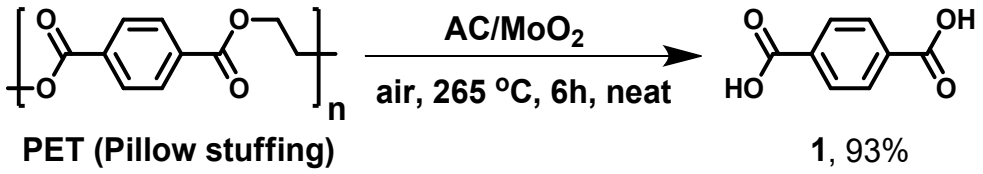


Figure S33. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 3. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 4: Deconstruction of PET pillow stuffing under air



PET (Pillow stuffing) **1**, 93%

Exactly 36 mg (1.87×10^{-4} mol) of air stored PET pillow stuffing and 33 mg (1.1×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged into a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 6 h. After the reaction was complete, 2.5 mL of DMSO-d_6 containing 42.2 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 93% yield.

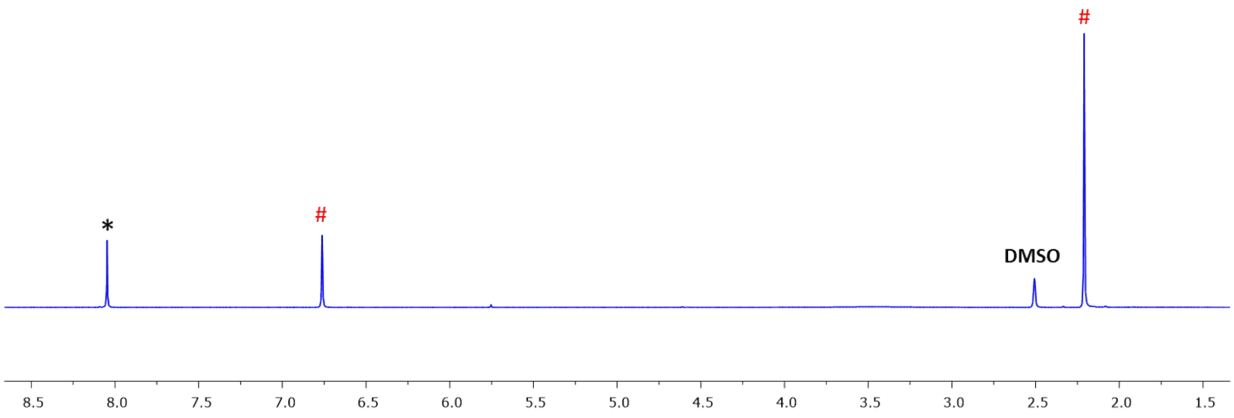
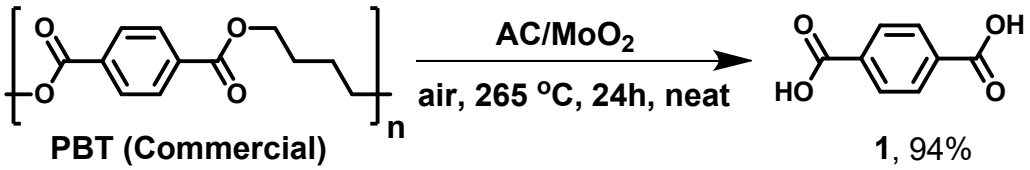


Figure S34. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 4. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 5: Deconstruction of commercial PBT under air



Exactly 35 mg (1.58×10^{-4} mol) of air stored commercial PBT pellets and 27.8 mg (0.93×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged into a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 4 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 40.6 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was then charged into an NMR tube. Terephthalic acid (**1**) was obtained in 94% yield.

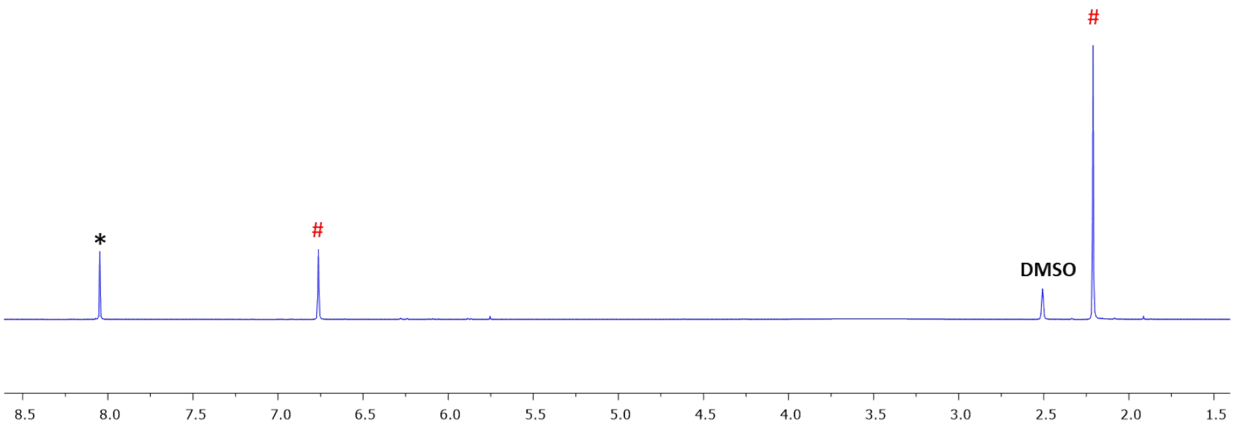
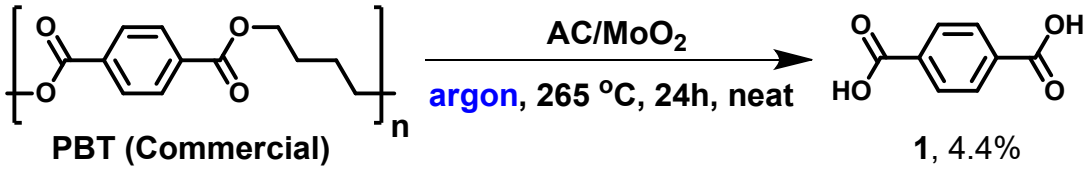


Figure S35. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 5. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 5: Attempted deconstruction of PBT under argon



Exactly 42 mg (1.91×10^{-4} mol) of air stored commercial PBT pellets and 33.5 mg (1.12×10^{-5} mol, 34:1 ester group to Mo mole ratio) of Ac/MoO_2 were charged into a 100 mL Schlenk vessel in glove box filled with argon gas. The reactor was then closed and heated at 265 °C under argon while stirring for 24 h. After the reaction was complete, 2.5 mL of DMSO-d_6 containing 28.0 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 4.4% yield.

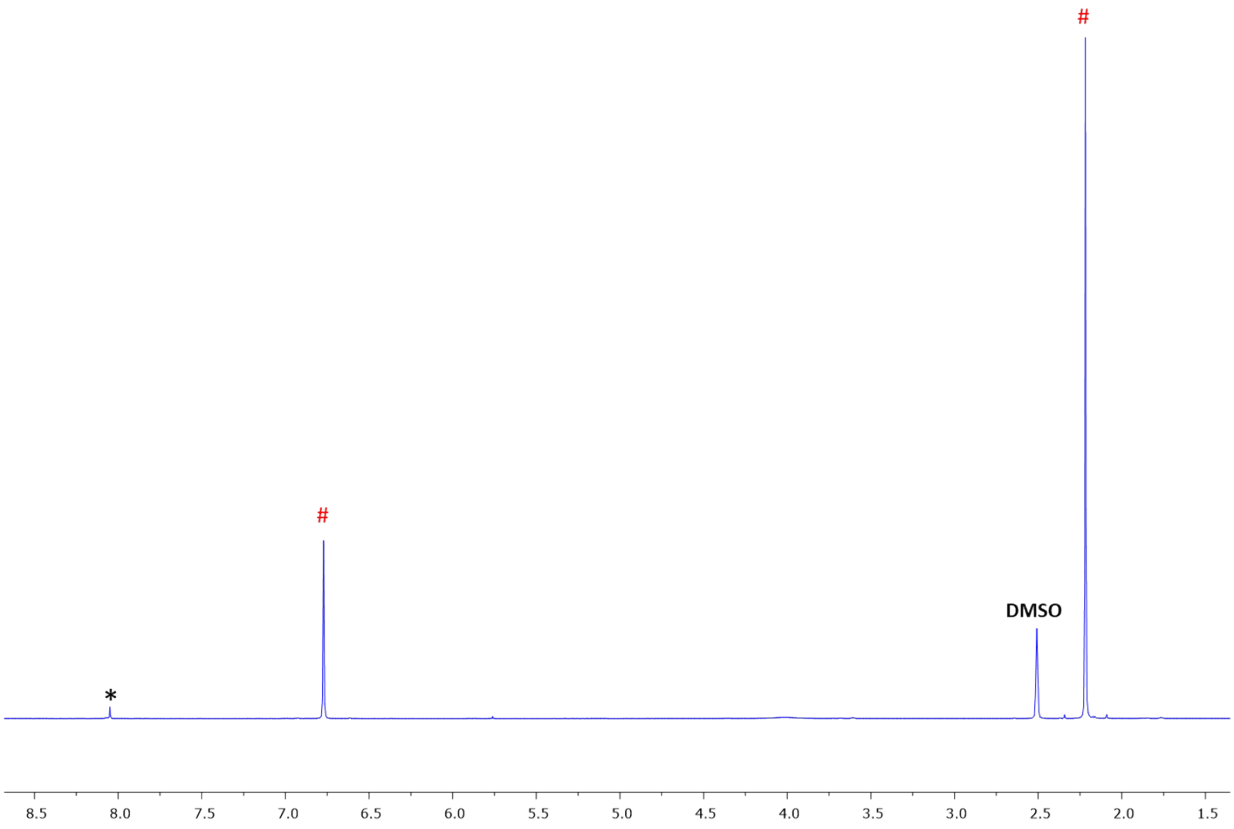
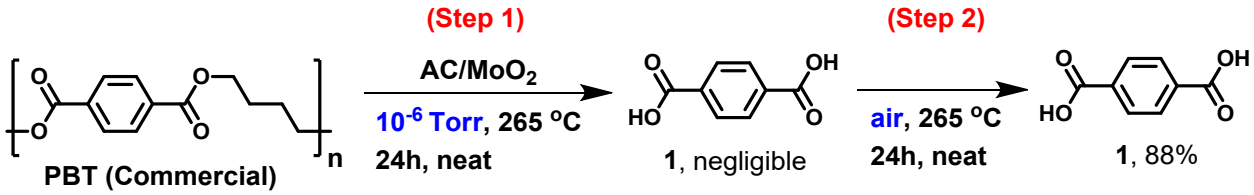


Figure S36. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 5. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 5: Deconstructing PBT under vacuum followed by deconstruction under air



Exactly 31 mg (1.4×10^{-4} mol) of air stored commercial PBT pellets and 24.6 mg (0.82×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed under a static vacuum of 10^{-6} Torr and heated at 265 °C while stirring for 24 h. Terephthalic acid (**1**) was obtained in negligible amount (Figure S25, step 1). NMR was not measured for this step. Next, we cooled down the flask and opened the cap for 10 min to allow filling with air and continued the reaction for another 24 h and at 265 °C (Figure S25, step 2). After the reaction was complete, 2.5 mL of DMSO-d_6 containing 41.7 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 88% yield.

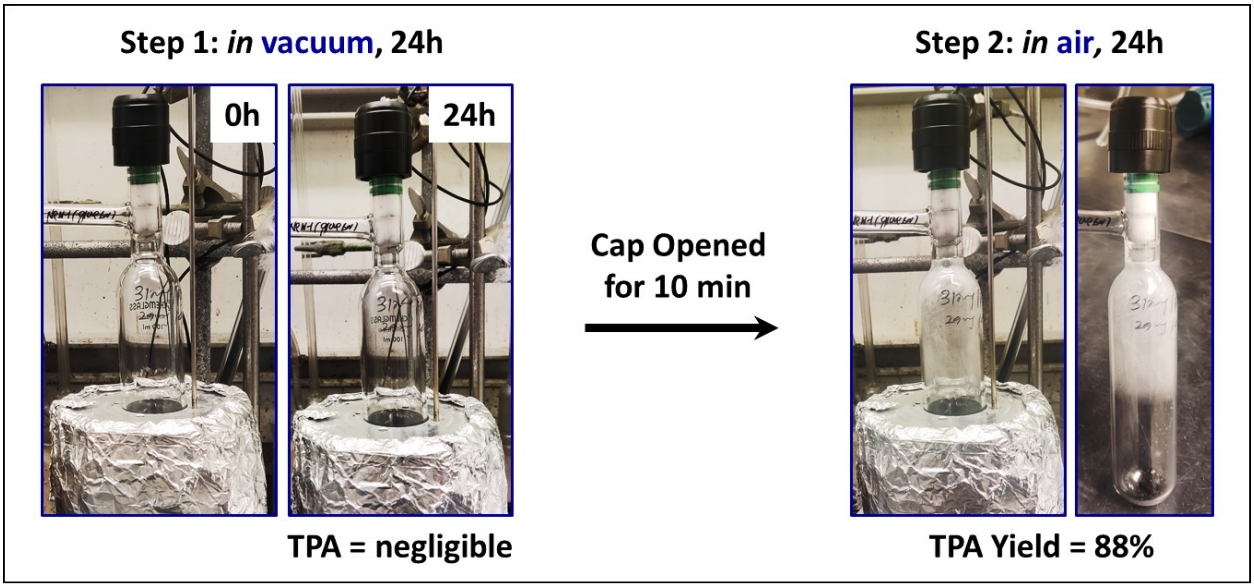


Figure S37. Photograph of the reaction vessel after 0 h and 24 h of heating under vacuum of 10^{-6} Torr (step 1). Photograph of the same reaction vessel after 24 h of heating under air environment (step 2).

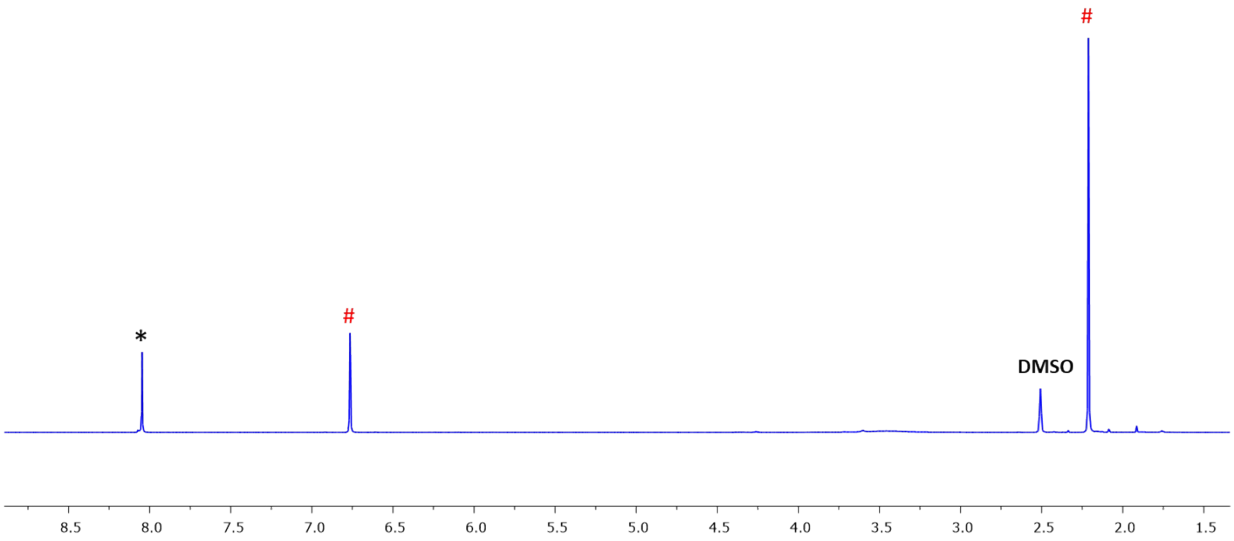
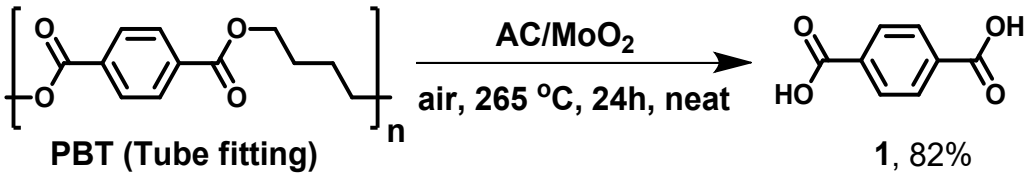


Figure S38. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 5. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 6: Deconstruction of PBT tube fitting under air



Exactly 36 mg (1.63×10^{-4} mol) of air stored commercial PET powder and 28.6 mg (0.95×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2.5 mL of DMSO-d_6 containing 42.0 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 82% yield.

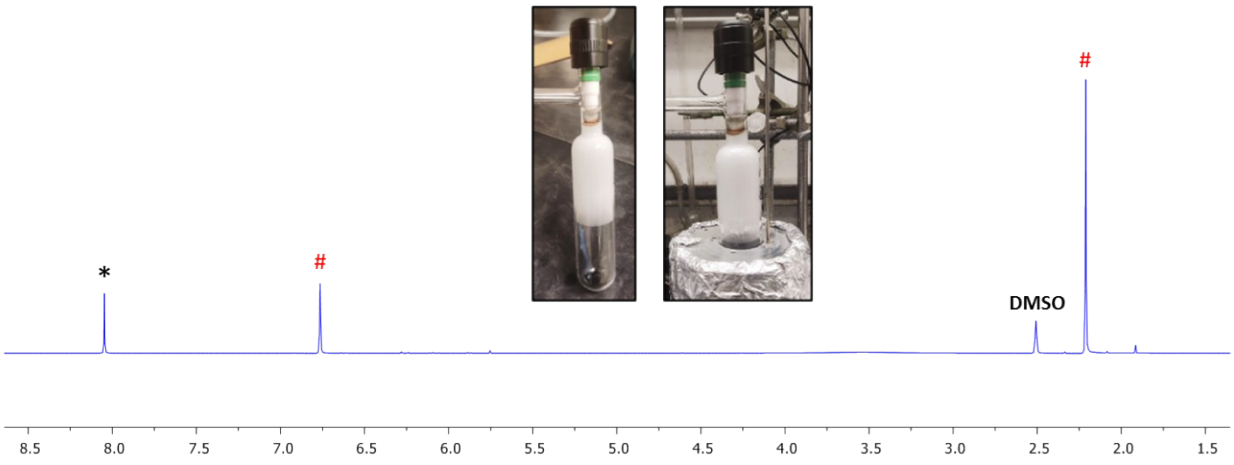
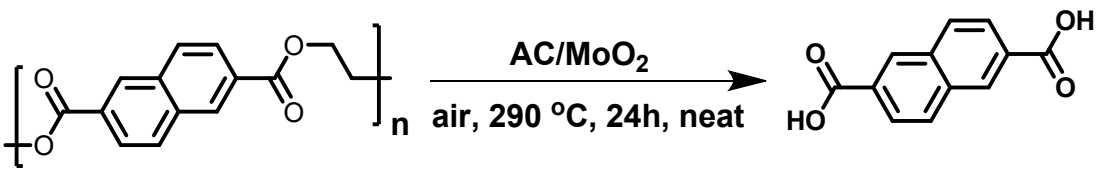


Figure S39. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 6. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 7: Deconstruction of commercial PEN under air



PEN (Commercial) **2**, 50%

Exactly 36 mg (1.49×10^{-4} mol) of air stored commercial PEN pellets and 26.2 mg (0.88×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed under an air atmosphere and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2.5 mL of DMSO-d_6 containing 43.5 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Naphthalene-2,6-dicarboxylic (**2**) was obtained in 50% yield.

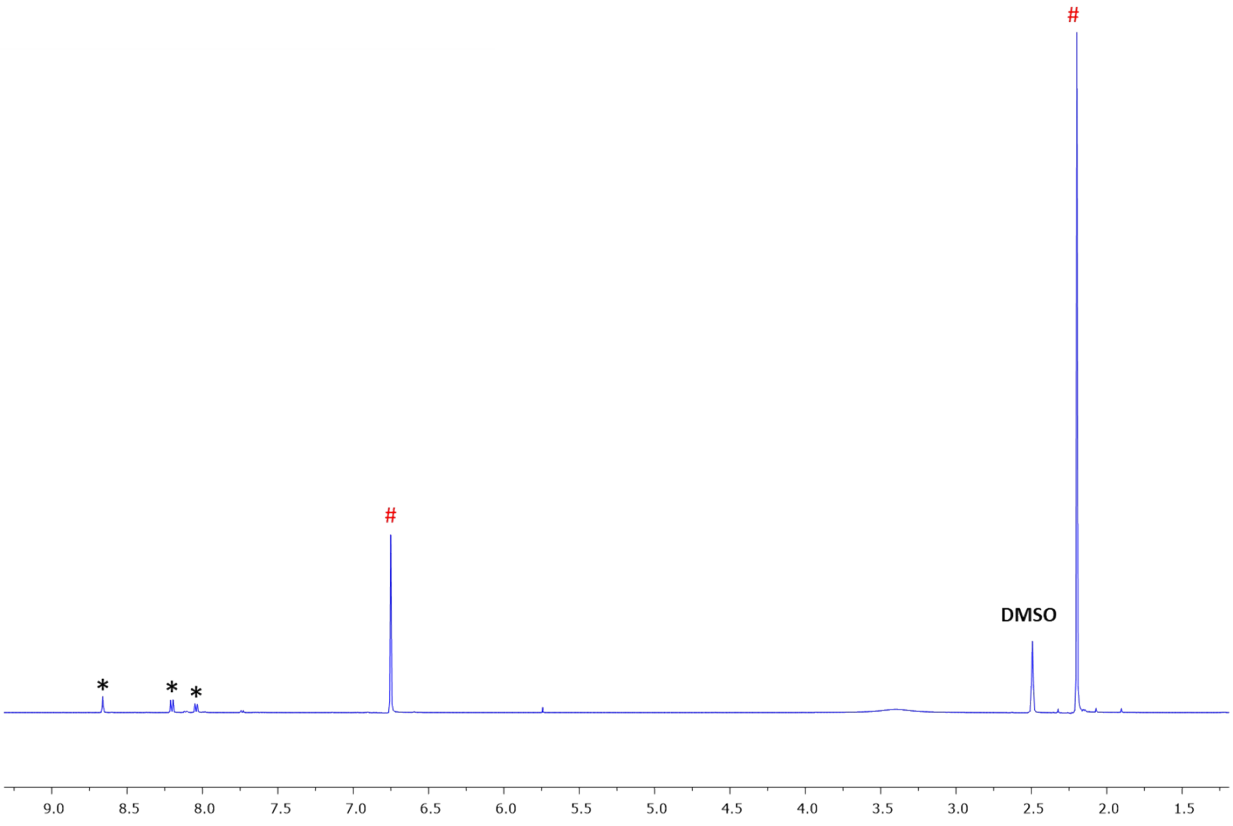
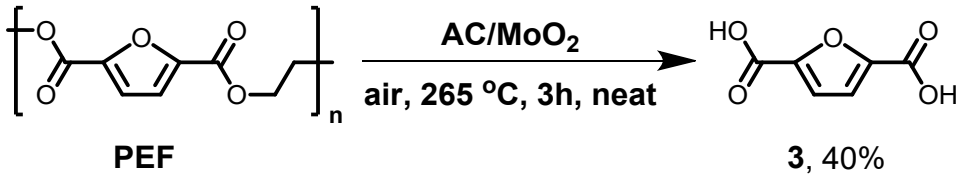


Figure S40. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 7. Naphthalene-2,6-dicarboxylic signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 8: Deconstruction of PEF under air



PEF **3**, 40%

Exactly 30 mg (1.64×10^{-4} mol) of air stored commercial PEF powder and 29 mg (0.97×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 3 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 40.6 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. 2,5 Furandicarboxylic acid (**3**) was obtained in 40% yield.

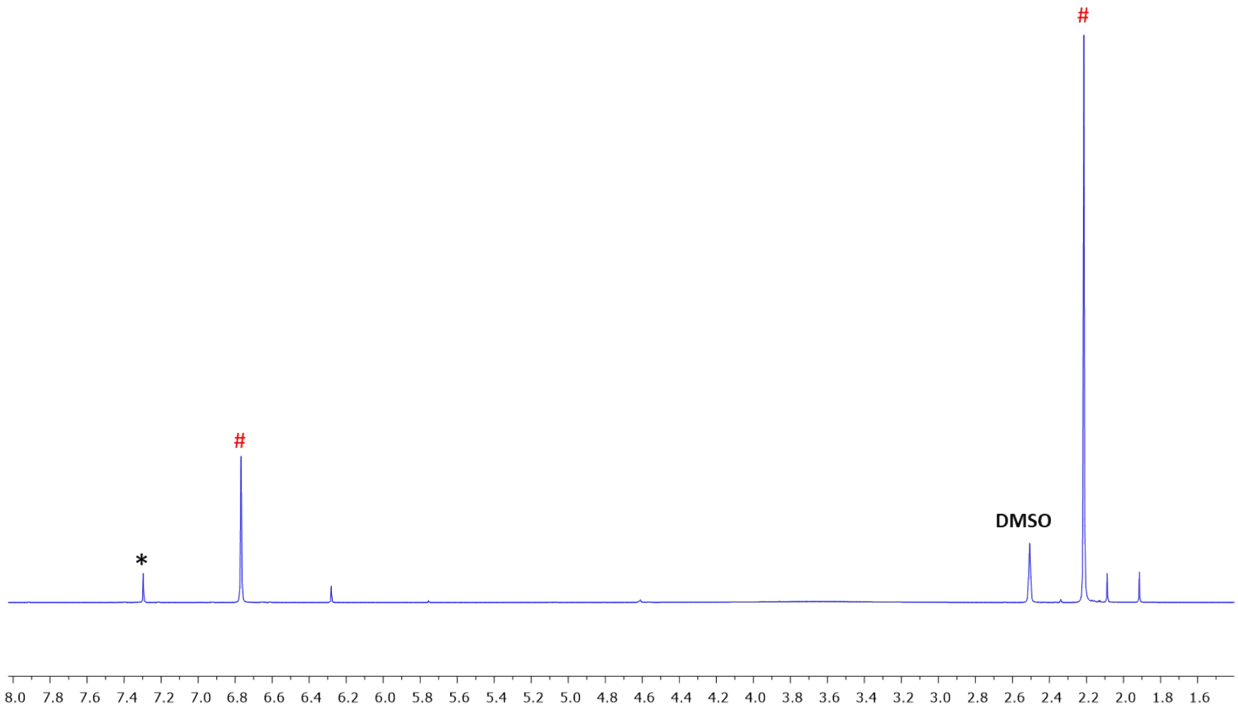
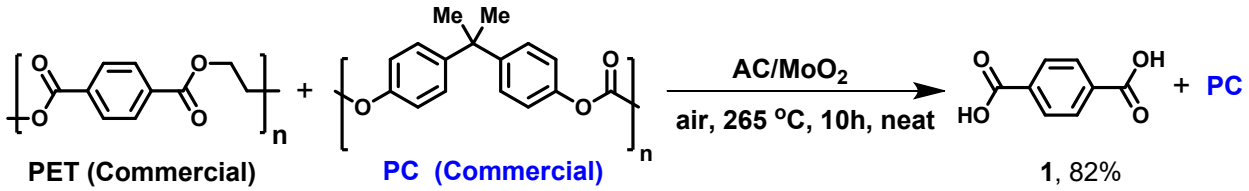


Figure S41. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 8. 2,5 Furandicarboxylic acid signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 9: Mixed plastics deconstruction



Exactly 18 mg (0.93×10^{-4} mol) of air stored commercial PET powder, 23 mg (0.9×10^{-4} mol) commercial PC pellets, and 32 mg (1.07×10^{-5} mol) of AC/MoO_2 were charged into a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 10 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 40.3 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 82% yield.

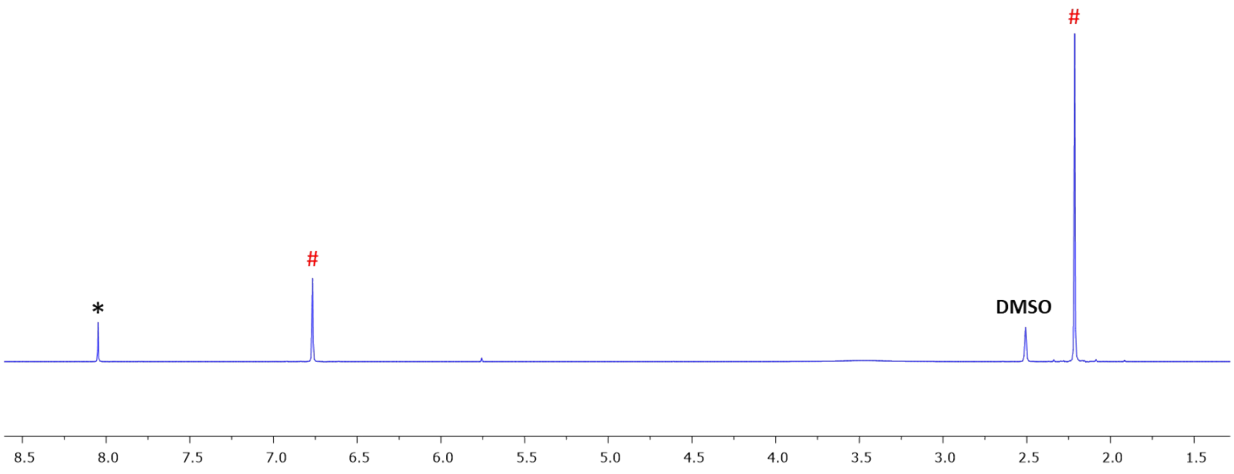
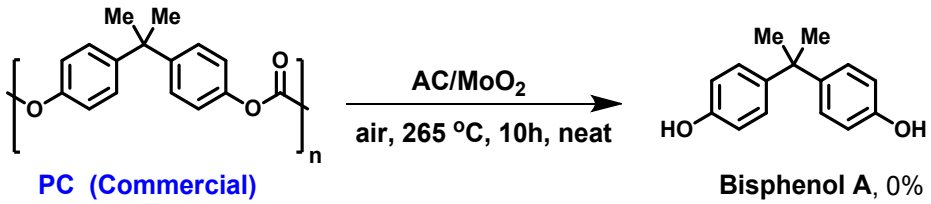


Figure S42. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 9. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Control experiment: Deconstruction of PC



PC (Commercial) Bisphenol A, 0%

Exactly 46 mg of air stored commercial PC pellets (1.8×10^{-4} mol) and 32 mg (1.07×10^{-5} mol) of AC/MoO_2 were charged into a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C in the presence of air while stirring for 10 h. After the reaction was completed, 2.5 mL of DMSO-d_6 containing 28.2 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Bisphenol A and other possible degradation product were obtained in 0% yield.

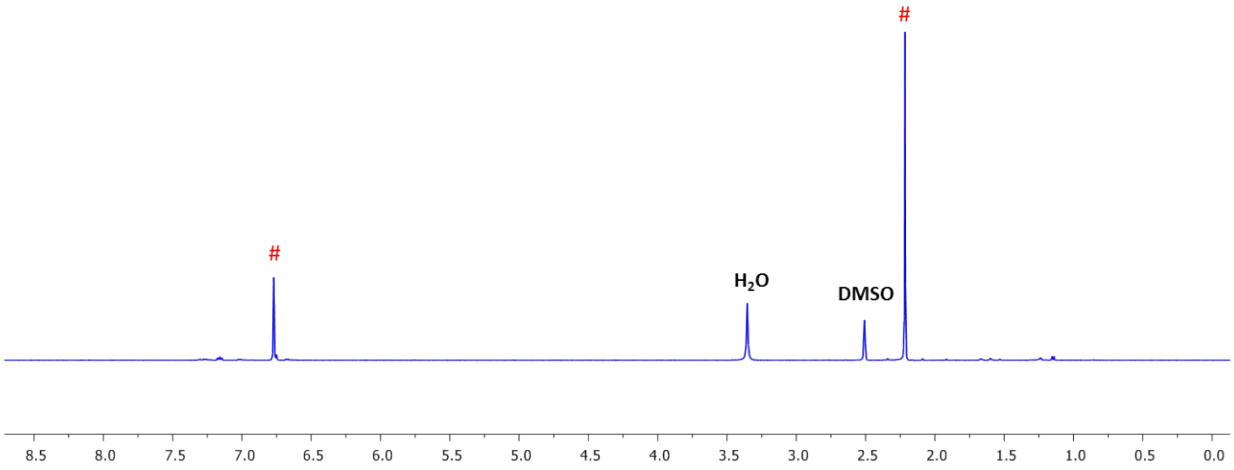
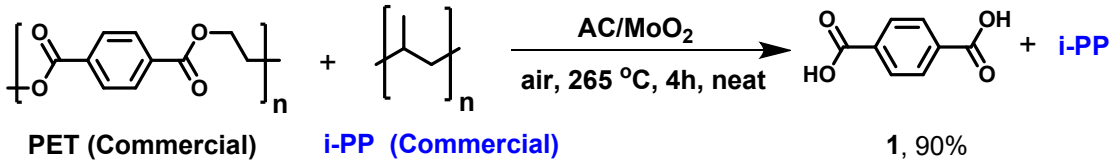


Figure S43. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of deconstruction of PC. Mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 10: Mixed plastics deconstruction



Exactly 19.3 mg (1×10^{-4} mol) of air stored commercial PET powder, 4.6 mg (1×10^{-4} mol) commercial PP pellets, and 32 mg (1.07×10^{-5} mol) of MoO_2/AC were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2.5 mL of DMSO-d_6 containing 40.2 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged in an NMR tube. Terephthalic acid (**1**) was obtained in 90% yield.

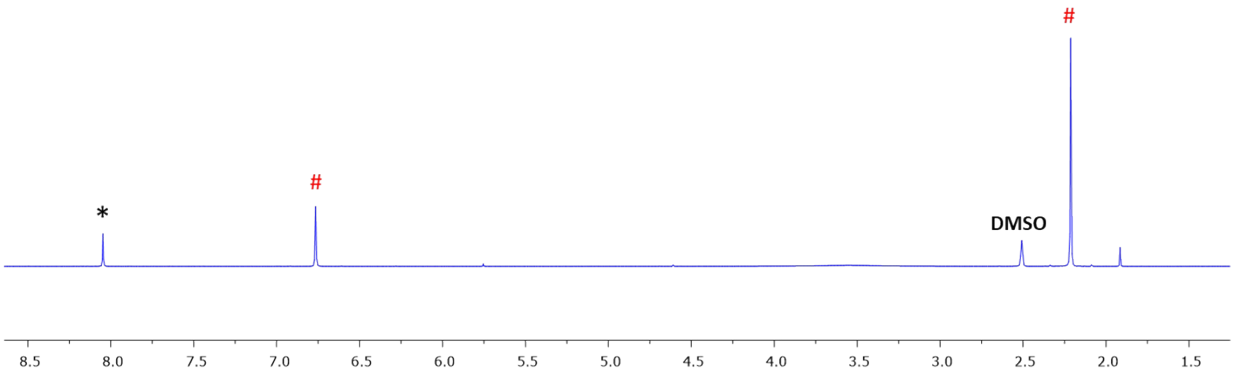
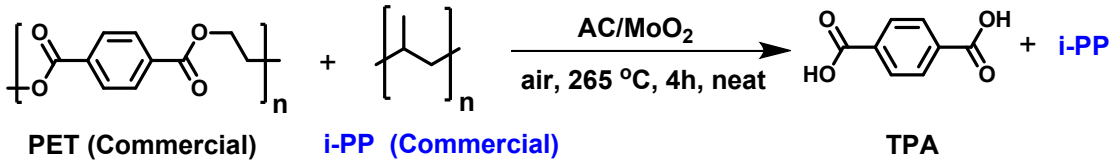


Figure S44. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 10. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 10: Control experiment for the characterization of i-PP residual polymer left unreacted in reaction flask



Exactly 20 mg (1×10^{-4} mol) of air stored commercial PET powder, 4.4 mg (0.9×10^{-4} mol) commercial PP pellets, and 32 mg (1.07×10^{-5} mol) of MoO_2/AC were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2 mL of C_2D2Cl_4 (TCE) were then added to the solid residual and heated at 150°C until most of the PP dissolved and 0.7 mL of the reaction mixture was charged in an NMR tube.

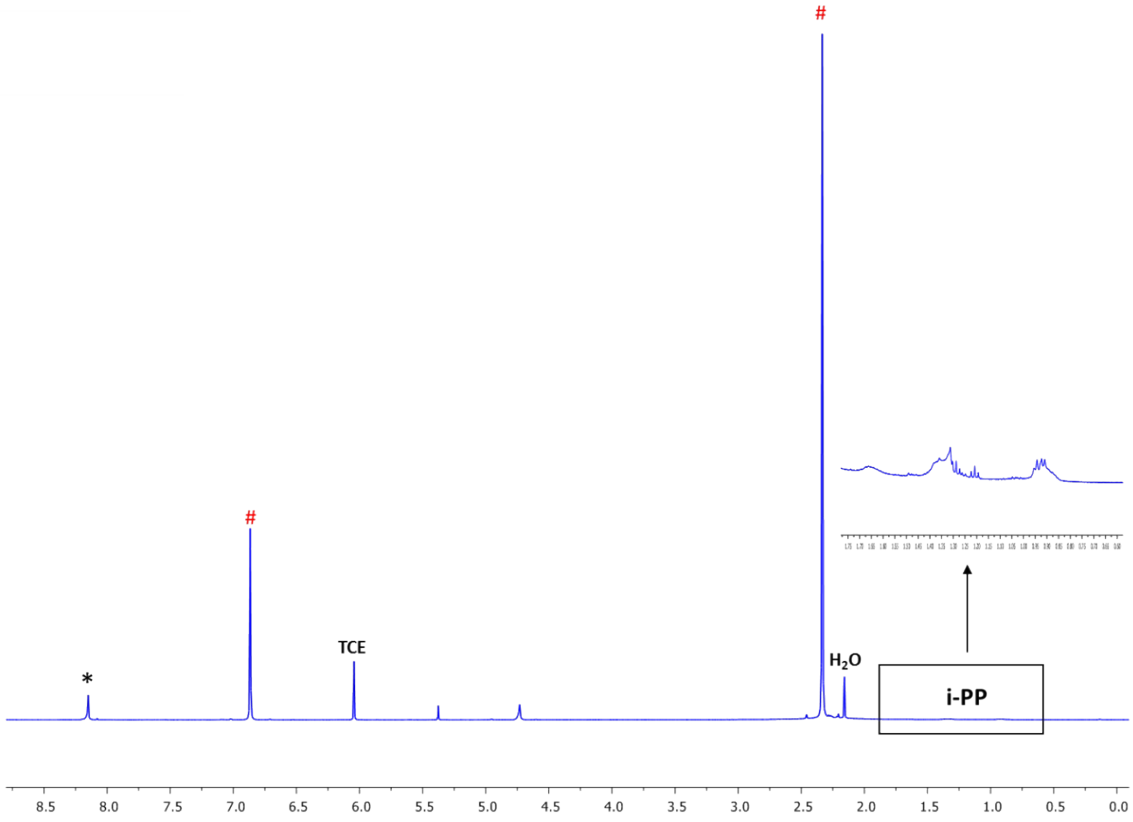
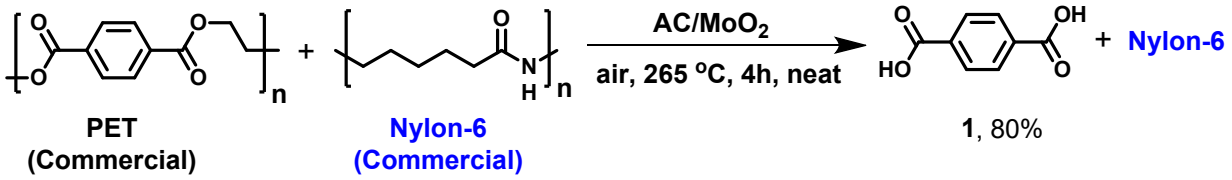


Figure S45. ^{1}H NMR spectrum (500 MHz, TCE-d_2) of the reaction of Table 2, entry 10. TPA signal denoted by black asterisks (signal appear due to partial solubility of TPA in TCE) and mesitylene (= internal standard) signals denoted by red # signs. PP signals denoted by zoom in aliphatic region (0.5-1.8 ppm).

Table 2 Entry 11: Mixed plastics deconstruction



Exactly 21.2 mg (1.1×10^{-4} mol) of air stored commercial PET powder, 5.5 mg (0.5×10^{-4} mol) commercial nylon-6 powder, and 32 mg (1.07×10^{-5} mol) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2.5 mL of DMSO-d_6 containing 41.7 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 80% yield.

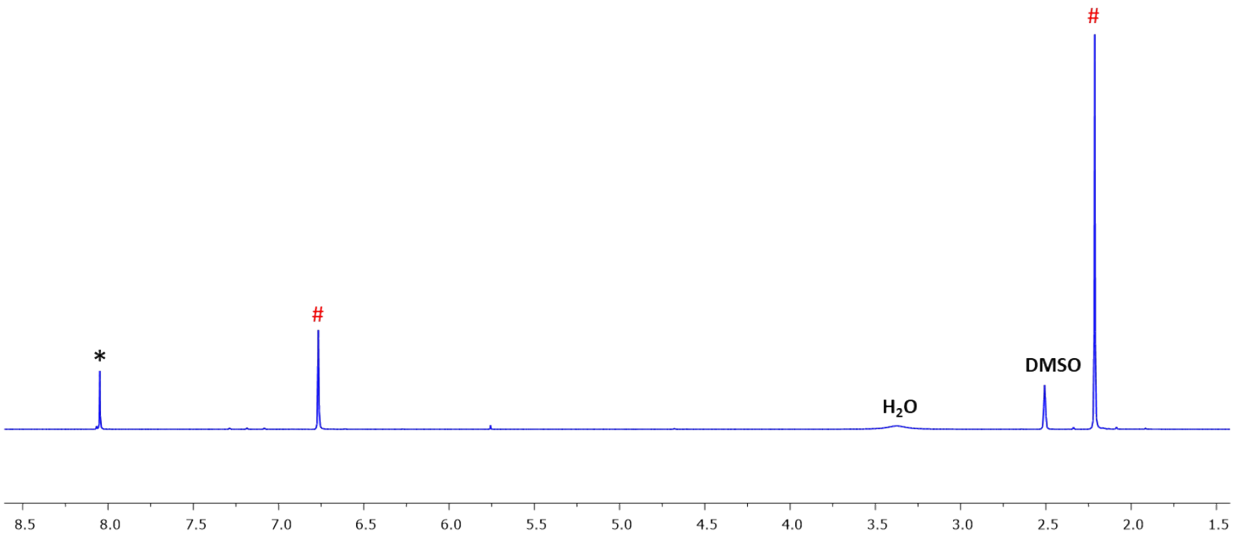
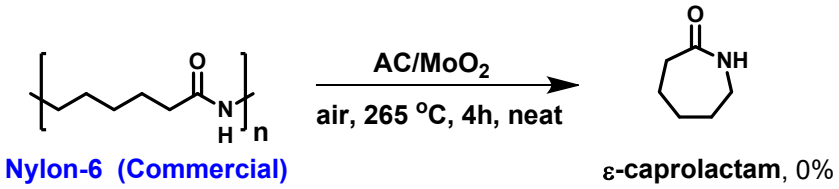


Figure S46. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 11. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

Control experiment: Deconstruction of Nylon-6



Exactly 18 mg (1.6×10^{-4} mol) of air stored commercial nylon-6 powder and 32 mg (1.07×10^{-5} mol) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 4 h. After the reaction was complete, 2.5 mL of CDCl-d_3 containing 22.8 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. ε-Caprolactam and other degradation products were obtained in 0% yield.

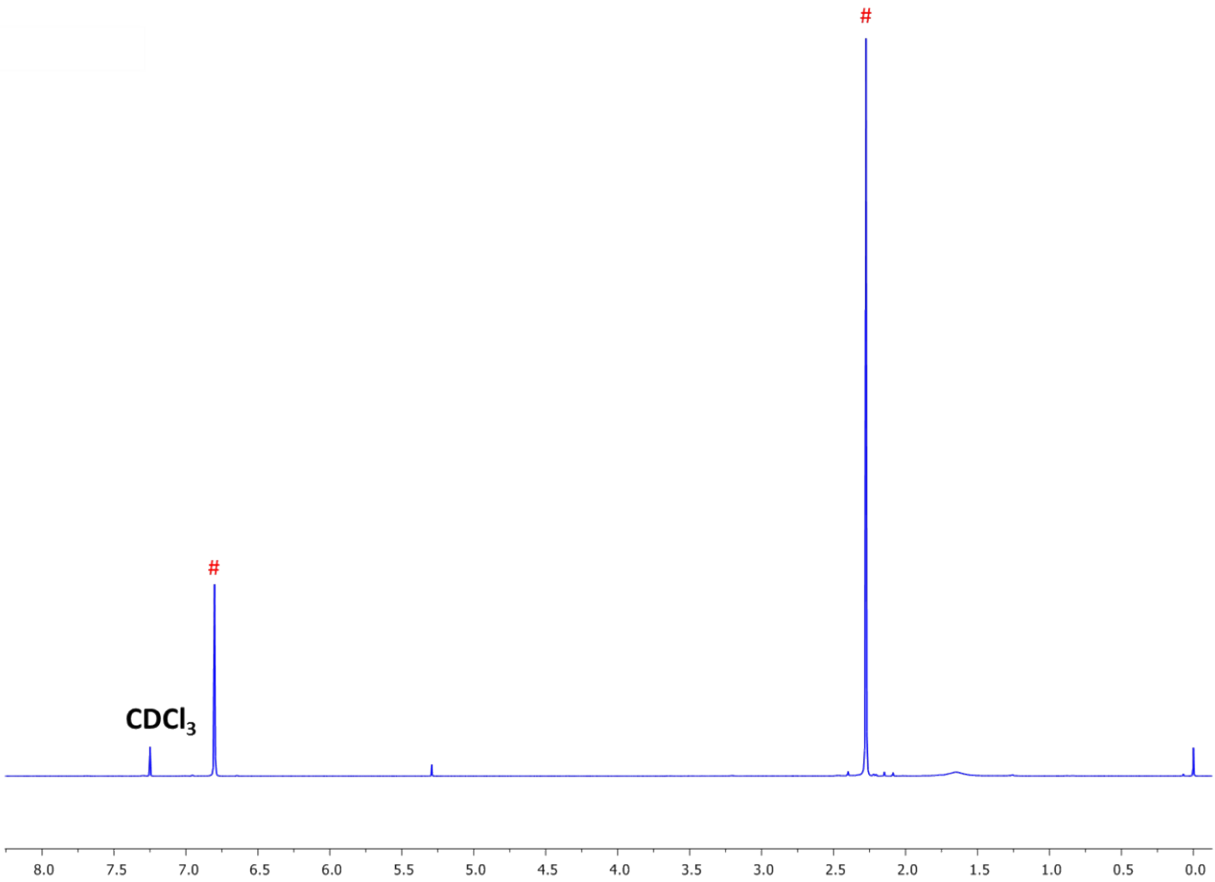
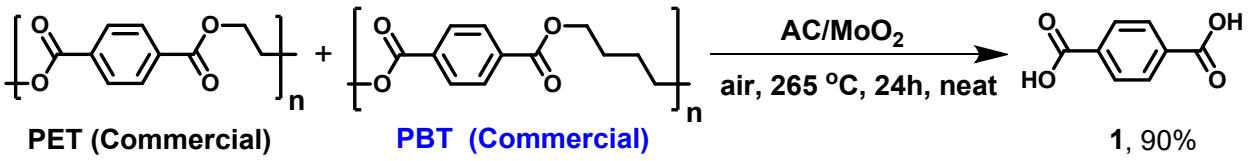


Figure S47. ^{1}H NMR spectrum (500 MHz, CDCl-d_3) of the reaction of Nylon-6. Mesitylene (= internal standard) signals denoted by red # signs.

Table 2 Entry 12: Mixed plastics deconstruction



Exactly 18 mg (0.93×10^{-4} mol) of air stored commercial PET powder, 20 mg (0.92×10^{-4} mol) commercial PBT pellets, and 32.5 mg (1.09×10^{-5} mol, 34:1 ester group to Mo mole ratio) of AC/MoO_2 were charged in a 100 mL Schlenk vessel. The reactor was then closed and heated at 265 °C under air while stirring for 24 h. After the reaction was complete, 2.5 mL of DMSO-d_6 containing 40.3 mg of mesitylene (= internal standard) were added, and 0.7 mL of the reaction mixture was charged into an NMR tube. Terephthalic acid (**1**) was obtained in 90% yield.

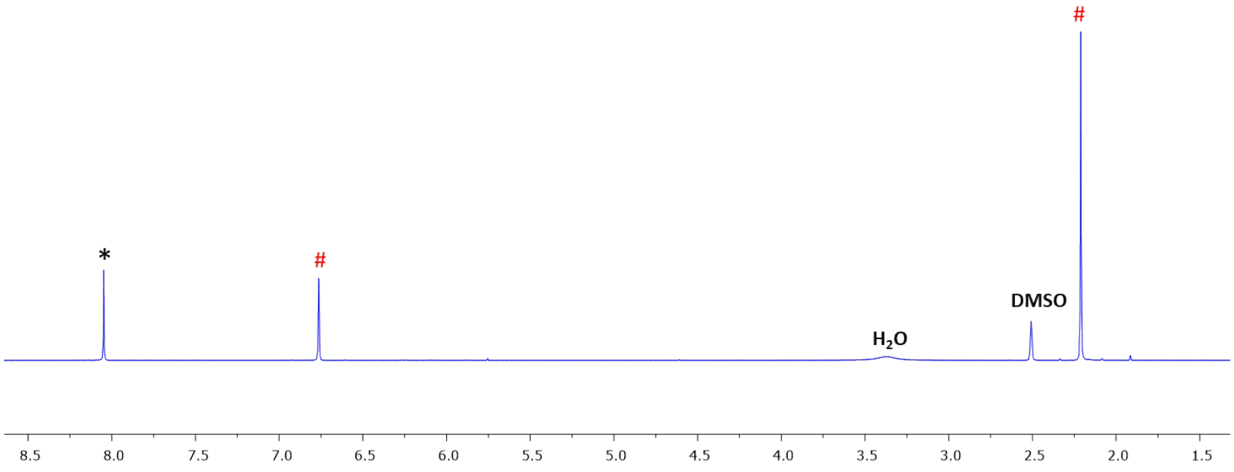
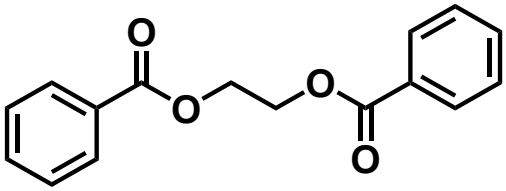


Figure S48. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of the reaction of Table 2, entry 12. TPA signal denoted by black asterisks and mesitylene (= internal standard) signals denoted by red # signs.

DFT calculations

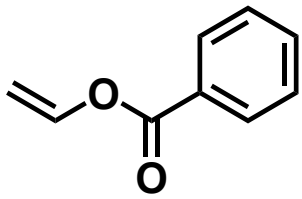
All quantum chemical calculations were performed using the ORCA software package.[S5] Geometry optimizations of all molecules shown in Scheme 2 were carried out at the b3lyp[S6]/6-31+G* level of theory with DFT integration Grid7. The calculations were carried out under the standard conditions of 298.15 K and 1 atm. Geometry optimizations of all molecules and complexes shown in Figure 3 were carried out at the CAM-B3LYP/Def2-SVP//CAM-B3LYP-D3/Def2-TZVP level of theory. Frequency calculations at the same level were performed to validate each structure as a minimum. Molecular graphics were produced by the CHEMCRAFT graphical package.[S7]

DFT-optimized Cartesian coordinates for Scheme 2



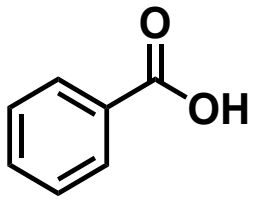
C	3.917838205	4.516012785	11.194897428
C	4.142615985	5.088853749	12.455949340
C	3.988890585	4.315484649	13.607236360
C	3.611287374	2.972503416	13.505541530
C	3.386582605	2.400315091	12.248523132
C	3.539314552	3.168935972	11.095482133
C	4.067304937	5.291862291	9.934183440
C	4.598444244	7.394773737	8.982785126
C	5.691704957	11.643592895	7.278830552
C	5.467336110	11.070779457	6.017672610
C	5.622761673	11.843674238	4.866336959
C	6.001003881	13.186475644	4.968194536
C	6.225075821	13.758714931	6.225308956
C	6.071339564	12.990309093	7.378375179
C	5.540947566	10.867922709	8.539515825
C	5.004767590	8.766270150	9.490864687

H	4.434731261	6.130586924	12.528469194
H	4.163537981	4.759837534	14.583407649
H	3.492630586	2.373172742	14.404604094
H	3.092868610	1.357197048	12.168556820
H	3.370428477	2.744718500	10.110854388
H	5.366625786	6.960759194	8.335730979
H	3.658419190	7.434333128	8.423953539
H	5.174008056	10.029350540	5.945612011
H	5.449284951	11.399115115	3.890066646
H	6.120603144	13.785789232	4.069235660
H	6.518934994	14.801838506	6.304975697
H	6.240654557	13.414742585	8.362839641
H	5.944654099	8.726789149	10.049837110
H	4.236293745	9.200152763	10.137904650
O	3.888143574	4.843343500	8.816853642
O	4.432381970	6.579123156	10.155319794
O	5.725756115	11.314714302	9.656609488
O	5.170154395	9.582251575	8.318497507

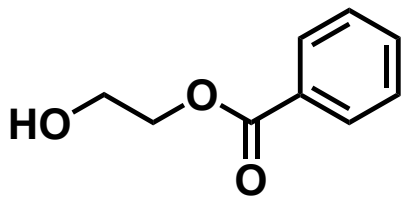


C	-3.337624398	0.053416184	1.350649125
C	-1.972953454	0.313110853	1.220866773
C	-1.409461928	1.424412291	1.866976708
C	-2.219705260	2.269490894	2.640825126
C	-3.582357150	2.005566823	2.767163300
C	-4.143019347	0.897359011	2.122273766
H	-3.773037595	-0.807136658	0.850034492
H	-1.343845861	-0.337573321	0.624128946
H	-1.765532216	3.123643826	3.132795357
H	-4.207264156	2.661751748	3.366784299
H	-5.205821691	0.691912118	2.221059003
C	0.034569292	1.753207196	1.766266237

O	0.575704333	2.695445772	2.309144877
O	0.710634200	0.849115975	0.990376578
C	2.070587995	1.027424265	0.812044469
H	2.481884343	1.891825764	1.320584923
C	2.758421084	0.167883410	0.063443703
H	2.283581142	-0.680962190	-0.419406696
H	3.824420666	0.311174039	-0.074473986

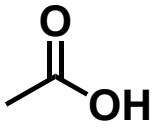


C	-3.522655188	-0.098957389	2.344907742
C	-2.133658611	-0.156632222	2.244255661
C	-1.407388242	0.995523198	1.907916197
C	-2.078499081	2.205247869	1.672996280
C	-3.469148352	2.257567696	1.775133056
C	-4.191574775	1.107797649	2.110571014
H	-4.084351638	-0.991884584	2.605386997
H	-1.594549928	-1.081687542	2.421812112
H	-1.511469175	3.092376721	1.413299205
H	-3.989266405	3.194115324	1.593173931
H	-5.274816709	1.151876917	2.189457934
C	0.070416393	0.886556668	1.812360502
O	0.711691552	-0.130020275	2.005589887
O	0.673394148	2.059886452	1.480376151
H	1.630942012	1.878743519	1.445026331

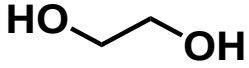


C	3.919534167	4.519461452	11.189825791
C	4.148198132	5.096898592	12.447834360

C	3.991999864	4.330342117	13.603484018
C	3.608225507	2.988622268	13.509219482
C	3.379878679	2.411531361	12.255172717
C	3.534780649	3.173837817	11.098064766
C	4.070783558	5.288993286	9.923688364
C	4.614005572	7.386431426	8.960725652
C	5.032846493	8.761789192	9.451726764
H	4.445489399	6.137603383	12.513786887
H	4.169440299	4.778953040	14.577296442
H	3.487336688	2.393957492	14.411108710
H	3.081686835	1.369228260	12.180730203
H	3.362614264	2.745635630	10.115737202
H	5.377176352	6.945441763	8.312812327
H	3.673085708	7.434012409	8.404635399
H	5.976107800	8.684775081	10.011984956
H	4.260841589	9.166071394	10.122659217
O	3.883778361	4.831919546	8.811018137
O	4.444750147	6.572509378	10.137314450
O	5.184905753	9.570082956	8.287215468
H	5.455469519	10.462256492	8.550481604



O	-0.884998713	-0.286536472	-4.081343636
C	-0.884998445	0.169067791	-2.956231897
C	-0.884998582	-0.657097343	-1.696766496
H	-1.766756263	-0.405118921	-1.091331457
H	-0.884998609	-1.724924519	-1.930899022
H	-0.003240972	-0.405118993	-1.091331324
H	-0.884998693	1.271517670	-2.804414830



C	-0.249604154	-0.029729222	-1.041458932
H	-1.112517492	0.376815321	-1.587437419
H	0.676990628	0.264182564	-1.557600299

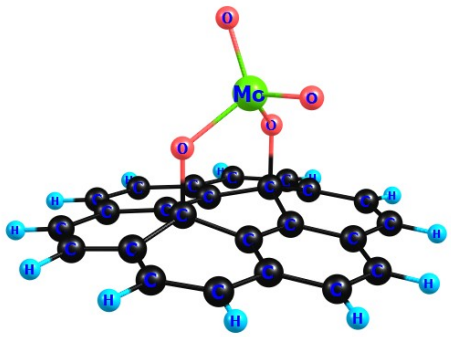
C	-0.246968820	0.502657699	0.381687829
H	-0.185862559	1.595593865	0.371810057
H	0.632973060	0.109882321	0.914793399
O	-0.344844423	-1.456897682	-0.938961398
H	-0.546363448	-1.835197709	-1.807564987
O	-1.445042233	0.167354736	1.069412579
H	-1.563561025	-0.793189703	0.976128544

H_2O

O	-2.101227932	0.000000000	-3.556736142
H	-2.101227932	0.771679703	-2.970267902
H	-2.101227932	-0.771679703	-2.970267902

DFT-optimized Cartesian coordinates for Figure 3

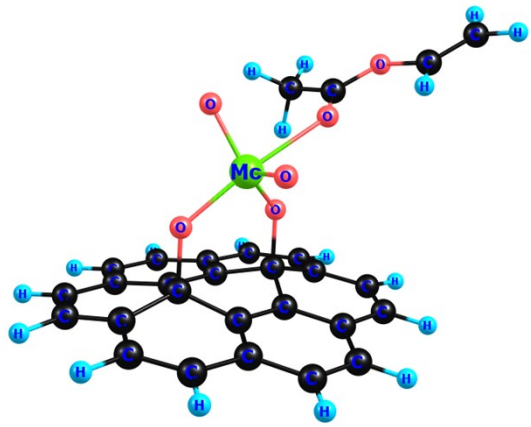
Intermediate A



C	1.159579000	0.691922000	-0.283160000
C	-0.086128000	1.429770000	0.162327000
C	-1.356412000	0.684514000	-0.176513000
C	-1.356825000	-0.683715000	-0.176506000
C	-0.086993000	-1.429735000	0.162350000
C	1.159160000	-0.692646000	-0.283147000
C	-2.582971000	-1.421424000	-0.328085000
C	-2.537513000	-2.806217000	-0.379204000

C	-1.319117000	-3.515098000	-0.368167000
C	-0.105021000	-2.885382000	-0.233758000
C	1.142719000	-3.542500000	-0.402741000
C	2.312164000	-2.848949000	-0.522962000
C	2.350094000	-1.416098000	-0.520406000
C	3.532757000	-0.689595000	-0.766235000
C	3.533174000	0.687430000	-0.766245000
C	2.350949000	1.414651000	-0.520428000
C	2.313884000	2.847525000	-0.522996000
C	1.144858000	3.541785000	-0.402784000
C	-0.103281000	2.885423000	-0.233799000
C	-1.316995000	3.515872000	-0.368219000
C	-2.535819000	2.807726000	-0.379246000
C	-2.582112000	1.422962000	-0.328103000
C	-3.801588000	0.680317000	-0.457756000
C	-3.801999000	-0.678044000	-0.457747000
Mo	0.543512000	-0.000154000	2.682649000
O	-0.069007000	1.435114000	1.643972000
O	-0.069892000	-1.435065000	1.643996000
O	2.215997000	-0.000668000	2.829051000
O	-0.123736000	0.000096000	4.217329000
H	-3.469653000	3.361039000	-0.500961000
H	-1.332061000	4.596369000	-0.532007000
H	-4.736686000	1.234342000	-0.565330000
H	-4.737431000	-1.231506000	-0.565315000
H	-3.471679000	-3.358972000	-0.500910000
H	-1.334841000	-4.595590000	-0.531937000
H	1.142349000	-4.631039000	-0.498993000
H	3.248767000	-3.386460000	-0.686356000
H	4.459577000	-1.236711000	-0.952096000
H	4.460323000	1.233984000	-0.952113000
H	3.250810000	3.384472000	-0.686392000
H	1.145151000	4.630323000	-0.499041000

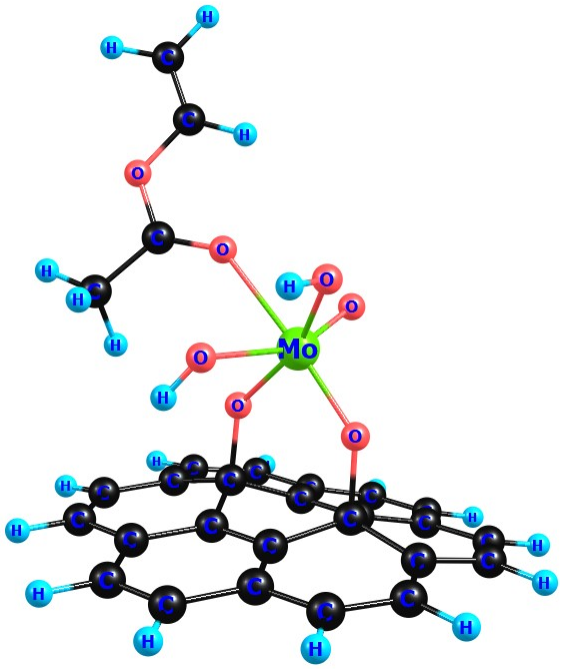
Intermediate B



C	0.260477000	1.287591000	-1.968882000
C	-0.706608000	2.441652000	-1.816228000
C	-2.094995000	1.987537000	-1.413780000
C	-2.212804000	0.900357000	-0.570768000
C	-0.948113000	0.221893000	-0.082203000
C	0.146010000	0.218263000	-1.128286000
C	-3.465551000	0.546138000	-0.017884000
C	-3.549331000	-0.584924000	0.854039000
C	-2.473223000	-1.392394000	1.099013000
C	-1.201666000	-1.143216000	0.522817000
C	-0.183704000	-2.070421000	0.512729000
C	0.986929000	-1.894237000	-0.250170000
C	1.154553000	-0.805168000	-1.095908000
C	2.281410000	-0.663463000	-1.969860000
C	2.394874000	0.403241000	-2.805511000
C	1.392212000	1.425869000	-2.842581000
C	1.461248000	2.521425000	-3.692537000
C	0.416875000	3.461155000	-3.785750000
C	-0.706719000	3.391411000	-2.994682000
C	-1.861212000	4.185568000	-3.210383000
C	-3.055597000	3.903567000	-2.607838000

C	-3.220684000	2.777422000	-1.741062000
C	-4.472030000	2.409679000	-1.202174000
C	-4.591244000	1.323693000	-0.364984000
Mo	-0.359480000	2.964931000	1.161885000
O	-0.170957000	3.196876000	-0.696584000
O	-0.434519000	1.042165000	1.000923000
O	-1.727763000	3.855531000	1.554181000
H	3.259348000	0.499062000	-3.466747000
H	3.052870000	-1.437197000	-1.952131000
H	1.753424000	-2.673203000	-0.235503000
H	-0.321312000	-3.007225000	1.059430000
H	-2.600196000	-2.299633000	1.695473000
H	-4.522900000	-0.832388000	1.283368000
H	-5.565231000	1.056710000	0.051168000
H	-5.350473000	3.009009000	-1.451614000
H	-3.933215000	4.515097000	-2.829541000
H	-1.797490000	5.001565000	-3.934753000
H	0.469021000	4.234124000	-4.557144000
H	2.324001000	2.619424000	-4.356008000
O	1.031917000	3.694926000	1.768374000
O	-0.093190000	1.194562000	5.255053000
C	-1.286254000	1.619798000	5.813776000
H	-1.913878000	2.214471000	5.149407000
C	-1.570976000	1.290239000	7.063558000
H	-0.882672000	0.691586000	7.663199000
H	-2.509165000	1.622856000	7.507128000
C	0.212385000	1.527729000	4.006584000
O	-0.543652000	2.205838000	3.333205000
C	1.523666000	0.994174000	3.545759000
H	2.039556000	0.456938000	4.347920000
H	2.127767000	1.836236000	3.178492000
H	1.332894000	0.334956000	2.686140000

Intermediate C

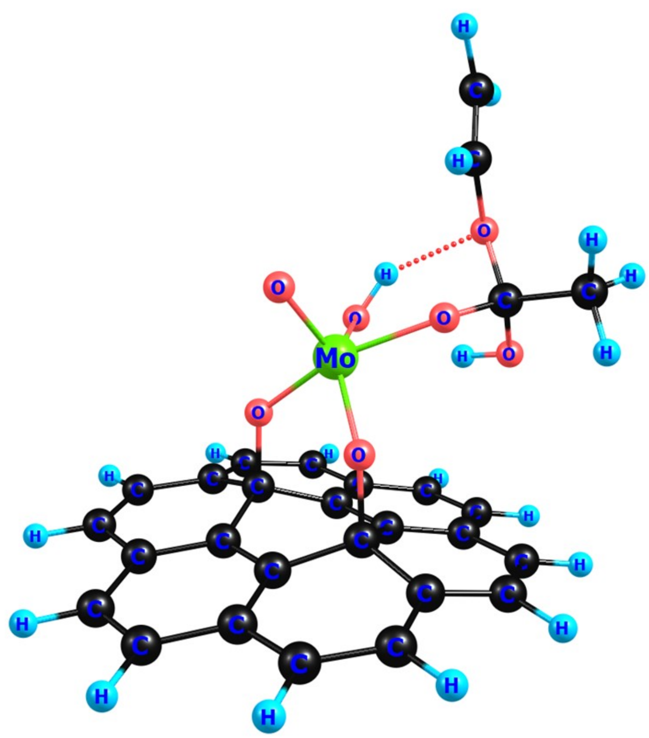


C	0.226493000	1.480999000	-1.845221000
C	-0.869736000	2.520245000	-1.791769000
C	-2.245086000	1.919201000	-1.618668000
C	-2.370708000	0.785492000	-0.845428000
C	-1.127335000	0.211751000	-0.200516000
C	0.098479000	0.356776000	-1.078776000
C	-3.648877000	0.286609000	-0.496057000
C	-3.738665000	-0.883742000	0.311745000
C	-2.628387000	-1.596623000	0.687963000
C	-1.324768000	-1.198766000	0.317840000
C	-0.222193000	-2.024635000	0.429768000
C	1.014301000	-1.703739000	-0.150190000
C	1.189640000	-0.562045000	-0.933098000
C	2.408846000	-0.267613000	-1.622332000
C	2.534018000	0.854200000	-2.383978000
C	1.452037000	1.778484000	-2.524081000

C	1.536732000	2.934294000	-3.297943000
C	0.431042000	3.771709000	-3.504269000
C	-0.791663000	3.540803000	-2.905139000
C	-1.974169000	4.225017000	-3.263272000
C	-3.213345000	3.795544000	-2.861608000
C	-3.387448000	2.617692000	-2.078547000
C	-4.661667000	2.103392000	-1.746358000
C	-4.788376000	0.970533000	-0.977952000
Mo	-0.411461000	2.898676000	1.238871000
O	-0.638854000	3.268191000	-0.557579000
O	-0.893239000	1.042028000	0.956600000
O	-1.832265000	3.455469000	1.925104000
H	3.472241000	1.069394000	-2.900145000
H	3.244826000	-0.964131000	-1.522904000
H	1.847400000	-2.404036000	-0.050059000
H	-0.339444000	-2.992170000	0.924993000
H	-2.748280000	-2.540882000	1.225090000
H	-4.732025000	-1.246963000	0.585027000
H	-5.779238000	0.589620000	-0.720665000
H	-5.550848000	2.627822000	-2.103020000
H	-4.105313000	4.332078000	-3.192589000
H	-1.890067000	5.080610000	-3.938051000
H	0.517080000	4.597714000	-4.215077000
H	2.475084000	3.154912000	-3.811946000
O	0.604111000	4.398348000	1.732010000
O	0.203174000	1.273429000	5.431998000
C	-0.392514000	2.320293000	6.111741000
H	-0.821043000	3.092796000	5.472083000
C	-0.405874000	2.313482000	7.435570000
H	0.047920000	1.499047000	8.003326000
H	-0.877862000	3.135864000	7.973022000
C	0.256178000	1.293332000	4.100109000
O	-0.209626000	2.221004000	3.469781000
C	0.939636000	0.103234000	3.523012000

H	1.114615000	-0.660832000	4.287350000
H	1.890216000	0.450088000	3.094150000
H	0.332276000	-0.280017000	2.692393000
O	1.471478000	2.173159000	1.277170000
H	1.546994000	4.210300000	1.585910000
H	1.552866000	1.270319000	0.948371000

Intermediate D

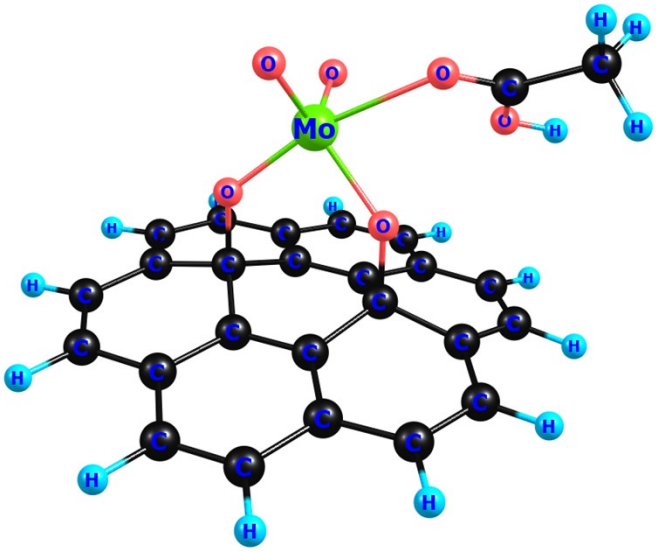


C	-0.063292000	1.737321000	-1.639336000
C	-1.250774000	2.677920000	-1.627775000
C	-2.576106000	1.950562000	-1.648064000
C	-2.677090000	0.758030000	-0.962127000
C	-1.457587000	0.242426000	-0.234966000
C	-0.163980000	0.553503000	-0.962149000
C	-3.932501000	0.131399000	-0.776576000
C	-3.996881000	-1.091378000	-0.042869000

C	-2.871003000	-1.727683000	0.409423000
C	-1.574786000	-1.202256000	0.195508000
C	-0.419935000	-1.936908000	0.367966000
C	0.834658000	-1.481561000	-0.070006000
C	0.982499000	-0.284972000	-0.764495000
C	2.230093000	0.156688000	-1.308151000
C	2.329787000	1.335285000	-1.982687000
C	1.190935000	2.181175000	-2.174011000
C	1.244826000	3.392746000	-2.856220000
C	0.094243000	4.157531000	-3.108481000
C	-1.152512000	3.789211000	-2.648511000
C	-2.353063000	4.401086000	-3.080180000
C	-3.579567000	3.834159000	-2.853222000
C	-3.724193000	2.583190000	-2.180679000
C	-4.970986000	1.938847000	-2.021436000
C	-5.072053000	0.747504000	-1.339328000
Mo	-0.673492000	2.716837000	1.374181000
O	-1.249876000	3.306469000	-0.315803000
O	-1.423660000	1.034767000	0.991334000
O	-1.667079000	3.558489000	2.396047000
H	3.291136000	1.660540000	-2.386215000
H	3.111409000	-0.470002000	-1.157517000
H	1.712829000	-2.113720000	0.078687000
H	-0.497968000	-2.938986000	0.797135000
H	-2.956655000	-2.707247000	0.885800000
H	-4.976014000	-1.551994000	0.106269000
H	-6.045674000	0.267934000	-1.215673000
H	-5.864197000	2.408100000	-2.439803000
H	-4.479072000	4.317935000	-3.240466000
H	-2.280161000	5.315249000	-3.674403000
H	0.176011000	5.039550000	-3.748699000
H	2.203147000	3.724814000	-3.261585000
O	0.909280000	3.723333000	0.988334000
O	2.338943000	3.003018000	3.279124000

C	1.832689000	3.548732000	4.423313000
H	0.845772000	3.178939000	4.718488000
C	2.478332000	4.500786000	5.086831000
H	3.457491000	4.852840000	4.756981000
H	2.023905000	4.948887000	5.970135000
C	1.825821000	1.727657000	2.855158000
O	0.458132000	1.872279000	2.673785000
C	2.104849000	0.642890000	3.870047000
H	3.187207000	0.568483000	4.034362000
H	1.725969000	-0.308781000	3.477640000
H	1.600865000	0.861948000	4.819066000
O	2.486003000	1.425955000	1.693306000
H	1.487479000	3.919148000	1.749371000
H	2.313125000	2.135332000	1.051978000

Intermediate E



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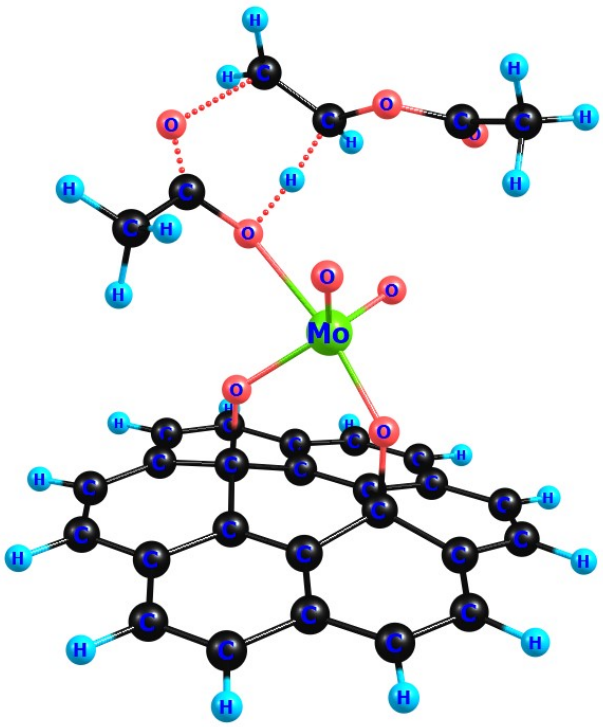
C	-1.401692000	2.958584000	-1.588282000
C	-2.527468000	1.950686000	-1.680546000
C	-2.409777000	0.769563000	-0.980351000

C	-1.158077000	0.534653000	-0.159572000
C	0.077648000	1.119359000	-0.818426000
C	-3.507829000	-0.118819000	-0.872090000
C	-3.350289000	-1.332124000	-0.140060000
C	-2.140468000	-1.714805000	0.379694000
C	-0.981628000	-0.916273000	0.245463000
C	0.293777000	-1.397124000	0.472006000
C	1.442929000	-0.679179000	0.104717000
C	1.366193000	0.542960000	-0.560790000
C	2.518873000	1.245799000	-1.032647000
C	2.401274000	2.426404000	-1.700257000
C	1.119532000	3.002371000	-1.964254000
C	0.954977000	4.193180000	-2.668315000
C	-0.312118000	4.680415000	-3.022024000
C	-1.476081000	4.042207000	-2.644453000
C	-2.745219000	4.367224000	-3.172903000
C	-3.831918000	3.547817000	-3.005074000
C	-3.746903000	2.308651000	-2.304786000
C	-4.833665000	1.410301000	-2.211660000
C	-4.717184000	0.230199000	-1.515031000
Mo	-1.184519000	3.164692000	1.448301000
O	-1.628481000	3.629219000	-0.327337000
O	-1.360350000	1.270048000	1.066060000
O	-2.336826000	4.002643000	2.332337000
H	3.290685000	2.955777000	-2.048951000
H	3.504757000	0.815293000	-0.842311000
H	2.427884000	-1.123245000	0.271568000
H	0.405687000	-2.408927000	0.872451000
H	-2.039224000	-2.700176000	0.842520000
H	-4.211895000	-1.998674000	-0.053618000
H	-5.567725000	-0.452151000	-1.444982000
H	-5.777066000	1.671461000	-2.696443000
H	-4.786282000	3.815561000	-3.464621000
H	-2.833217000	5.264433000	-3.790749000

H	-0.381035000	5.553578000	-3.675915000
H	1.844529000	4.725201000	-3.013186000
O	0.334165000	3.850772000	1.674752000
C	-0.000149000	1.266797000	3.705671000
O	-0.848482000	2.099373000	3.456826000
C	-0.053306000	0.415867000	4.939200000
H	0.911800000	0.428140000	5.466926000
H	-0.278459000	-0.621944000	4.647194000
H	-0.846694000	0.781132000	5.599326000
O	1.000610000	1.079965000	2.868400000
H	1.572885000	0.345790000	3.128207000

Transition state TS1



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C	-1.330164000	-0.743066000	-0.233652000

C	0.018284000	-1.234199000	0.245496000
C	1.171656000	-0.513850000	-0.422819000
C	-2.465957000	-1.620796000	-0.169619000
C	-2.268370000	-2.963048000	0.123426000
C	-0.979854000	-3.510675000	0.279536000
C	0.158552000	-2.740729000	0.218159000
C	1.466153000	-3.286719000	0.156735000
C	2.549769000	-2.530694000	-0.193341000
C	2.429206000	-1.147945000	-0.541599000
C	3.518453000	-0.383676000	-1.011473000
C	3.366558000	0.947774000	-1.326138000
C	2.117866000	1.590467000	-1.185248000
C	1.923849000	2.975090000	-1.490565000
C	0.689302000	3.560608000	-1.446500000
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C	-3.907839000	0.255710000	-0.734536000
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O	-0.224029000	1.802563000	1.038845000
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H	-1.882632000	4.313029000	-1.676731000
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H	-4.628129000	-1.722043000	-0.390549000
H	-3.136077000	-3.625351000	0.168601000
H	-0.875275000	-4.593524000	0.387565000
H	1.585582000	-4.359231000	0.330393000
H	3.535210000	-2.996296000	-0.267966000
H	4.494599000	-0.863062000	-1.113151000
H	4.221766000	1.527944000	-1.680229000
H	2.788398000	3.554552000	-1.822836000
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C	3.638662000	0.962934000	5.484507000
O	4.703984000	1.088890000	4.951326000
O	2.728605000	1.968805000	5.548847000
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C	2.505902000	4.304666000	5.178616000
H	2.041755000	4.420093000	6.158270000
H	2.816175000	5.211280000	4.661683000
O	0.586742000	4.664943000	4.459970000
C	0.088532000	3.768452000	3.763448000
O	0.853651000	2.905231000	3.175282000
C	-1.392115000	3.650846000	3.587850000
H	-1.623247000	3.500870000	2.524280000
H	-1.734744000	2.755849000	4.128324000
H	-1.887437000	4.544632000	3.983401000
C	3.111880000	-0.274722000	6.139994000
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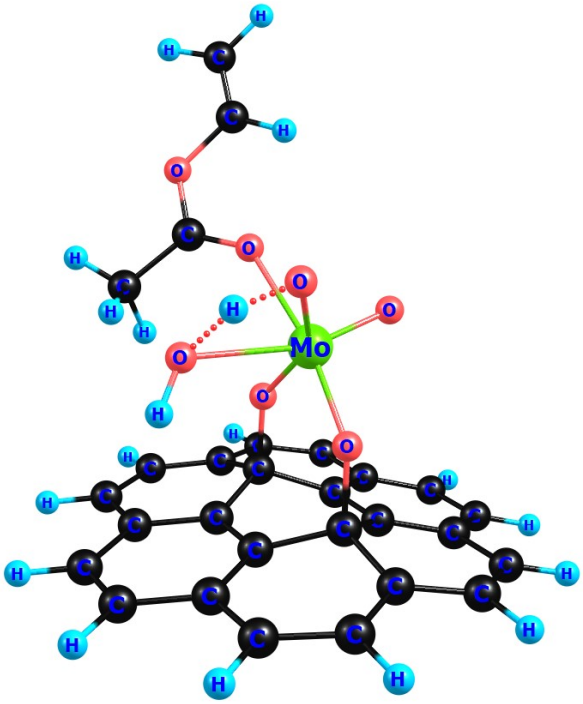
Mo	0.474782000	0.766102000	2.502417000
O	2.129221000	0.628649000	2.807197000
O	-0.398339000	0.646638000	3.937896000

Transition state TS2



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C	0.090951000	0.350776000	-1.001666000
C	-3.656351000	0.336848000	-0.411632000
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C	-2.658993000	-1.538377000	0.803839000
C	-1.349772000	-1.165463000	0.418113000
C	-0.263550000	-2.009332000	0.529287000
C	0.978795000	-1.712652000	-0.056024000
C	1.170197000	-0.580882000	-0.843068000
C	2.396154000	-0.307513000	-1.529717000
C	2.535586000	0.799683000	-2.310567000
C	1.459316000	1.729284000	-2.477198000
C	1.554360000	2.864454000	-3.276947000
C	0.453700000	3.706630000	-3.503455000
C	-0.767860000	3.503359000	-2.896080000
C	-1.944425000	4.195373000	-3.266776000

C	-3.185912000	3.790757000	-2.852673000
C	-3.371724000	2.630988000	-2.041869000
C	-4.650557000	2.139983000	-1.695793000
C	-4.788508000	1.024384000	-0.903396000
Mo	-0.521542000	2.956844000	1.282791000
O	-0.581452000	3.273906000	-0.546240000
O	-0.874361000	1.072276000	1.026595000
O	-1.985784000	3.547537000	1.813211000
H	3.477900000	0.997047000	-2.826619000
H	3.225515000	-1.009259000	-1.413481000
H	1.801072000	-2.424593000	0.050324000
H	-0.396111000	-2.971893000	1.030462000
H	-2.788535000	-2.471015000	1.358785000
H	-4.756835000	-1.161457000	0.704508000
H	-5.783175000	0.661265000	-0.635258000
H	-5.534478000	2.667690000	-2.060619000
H	-4.072769000	4.330326000	-3.192289000
H	-1.850810000	5.035589000	-3.959406000
H	0.546532000	4.513513000	-4.235076000
H	2.494431000	3.065416000	-3.795895000
O	0.617703000	4.270596000	1.789619000
O	0.218750000	1.225016000	5.281677000
C	-0.499361000	2.166219000	5.999999000
H	-0.957735000	2.949676000	5.396138000
C	-0.575720000	2.055359000	7.316652000
H	-0.084791000	1.236976000	7.846396000
H	-1.138132000	2.794568000	7.886918000
C	0.301433000	1.309644000	3.960243000
O	-0.259441000	2.221294000	3.368043000
C	1.104499000	0.236221000	3.331124000
H	1.633448000	-0.354560000	4.085726000
H	1.768991000	0.726969000	2.602198000
H	0.424017000	-0.393237000	2.739301000
O	1.647217000	2.317418000	1.218134000

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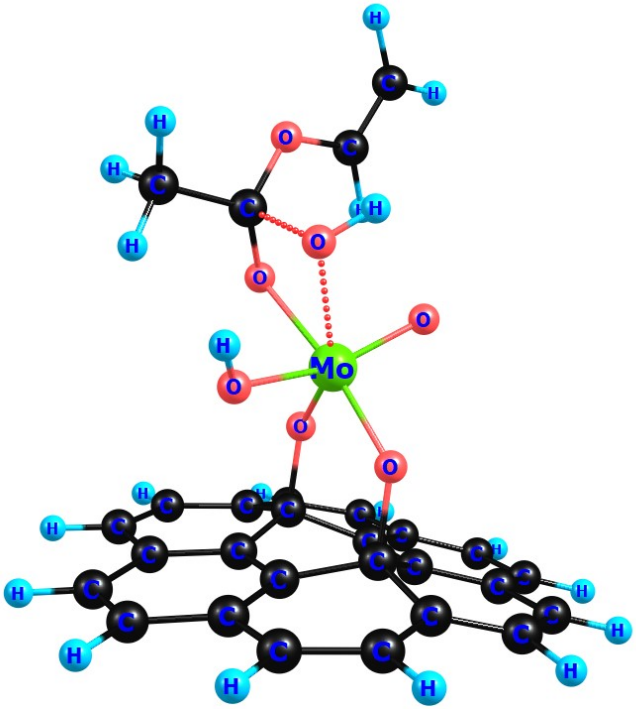
Transition state TS3



C	-0.132203000	1.359383000	-1.594594000
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C	-2.808437000	0.936422000	-0.649087000
C	-1.655273000	0.209422000	-0.003287000
C	-0.398683000	0.234081000	-0.842183000
C	-4.156490000	0.575122000	-0.310104000
C	-4.379385000	-0.572740000	0.438085000
C	-3.330121000	-1.437156000	0.804251000
C	-2.014303000	-1.166984000	0.504211000
C	-0.969948000	-2.113409000	0.663241000
C	0.260728000	-1.933799000	0.096605000
C	0.564740000	-0.790341000	-0.707974000
C	1.792360000	-0.643651000	-1.388462000
C	2.056158000	0.478331000	-2.140558000

C	1.107370000	1.516496000	-2.251179000
C	1.354642000	2.712019000	-2.997631000
C	0.393256000	3.667256000	-3.177578000
C	-0.904596000	3.539612000	-2.619405000
C	-1.975985000	4.308513000	-3.010200000
C	-3.297437000	4.019200000	-2.614401000
C	-3.610070000	2.896728000	-1.861223000
C	-4.953962000	2.524928000	-1.529416000
C	-5.214688000	1.415586000	-0.788059000
Mo	-0.516878000	2.642059000	1.486478000
O	-0.900373000	3.195743000	-0.262534000
O	-1.365631000	1.008123000	1.200243000
O	-1.640459000	3.694054000	2.164283000
H	3.016229000	0.583054000	-2.651310000
H	2.541567000	-1.434227000	-1.300850000
H	1.026893000	-2.704944000	0.207480000
H	-1.192450000	-3.039965000	1.198118000
H	-3.573048000	-2.388899000	1.283449000
H	-5.406290000	-0.846203000	0.690883000
H	-6.243175000	1.145582000	-0.538341000
H	-5.769641000	3.159527000	-1.882979000
H	-4.109047000	4.659925000	-2.966610000
H	-1.802827000	5.131062000	-3.709088000
H	0.591891000	4.523919000	-3.826625000
H	2.328700000	2.826234000	-3.479103000
O	0.760516000	3.819478000	2.745076000
O	0.272585000	3.002407000	5.129425000
C	-1.074630000	3.172379000	5.363369000
H	-1.731941000	2.681069000	4.645717000
C	-1.475006000	3.885885000	6.405524000
H	-0.756992000	4.349259000	7.084622000
H	-2.540709000	4.012836000	6.594384000
C	0.685912000	2.386373000	4.010158000
O	-0.129497000	1.669415000	3.349811000

C	2.139823000	2.043906000	4.073923000
H	2.720508000	2.881019000	4.476756000
H	2.487243000	1.763666000	3.074807000
H	2.242075000	1.175001000	4.742135000
O	1.286594000	2.305487000	0.918546000
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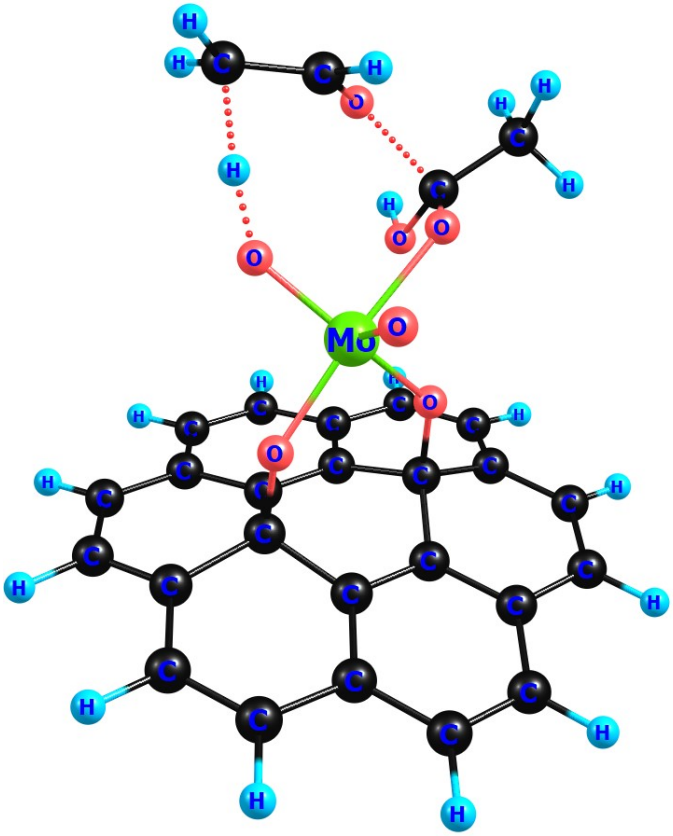
H	1.978007000	2.930388000	1.170331000

Transition state TS4



C	0.071565000	1.880253000	-1.786232000
C	-1.131886000	2.788759000	-1.643984000
C	-2.436775000	2.026329000	-1.575490000
C	-2.446919000	0.816980000	-0.913656000
C	-1.154054000	0.328759000	-0.296658000

C	0.059293000	0.681848000	-1.133285000
C	-3.664328000	0.152683000	-0.638275000
C	-3.634869000	-1.086044000	0.073668000
C	-2.459606000	-1.698295000	0.415832000
C	-1.199676000	-1.133185000	0.099175000
C	-0.023539000	-1.849555000	0.138431000
C	1.175531000	-1.356767000	-0.406038000
C	1.236187000	-0.136606000	-1.068630000
C	2.418999000	0.345724000	-1.716354000
C	2.433443000	1.544927000	-2.359181000
C	1.263525000	2.369108000	-2.418419000
C	1.230419000	3.597811000	-3.067845000
C	0.040865000	4.336535000	-3.200807000
C	-1.150765000	3.923568000	-2.646031000
C	-2.399952000	4.512610000	-2.960373000
C	-3.587173000	3.908139000	-2.645901000
C	-3.641048000	2.637616000	-1.994217000
C	-4.852992000	1.955957000	-1.746492000
C	-4.864017000	0.747741000	-1.087021000
Mo	-0.595459000	2.871447000	1.414366000
O	-1.006717000	3.402031000	-0.336019000
O	-1.020196000	1.074029000	0.934570000
O	-1.778489000	3.664084000	2.272935000
H	3.345210000	1.902957000	-2.842320000
H	3.319506000	-0.271997000	-1.679923000
H	2.072400000	-1.980256000	-0.369617000
H	-0.044293000	-2.866508000	0.538665000
H	-2.478796000	-2.689179000	0.876433000
H	-4.585888000	-1.575449000	0.296077000
H	-5.810626000	0.239196000	-0.890434000
H	-5.790354000	2.409916000	-2.075655000
H	-4.528570000	4.375122000	-2.944015000
H	-2.400373000	5.441481000	-3.536125000
H	0.043529000	5.233339000	-3.825863000

H	2.141124000	3.965495000	-3.546095000
O	0.935628000	3.743751000	1.542824000
O	2.299039000	2.288643000	3.853545000
C	1.918124000	3.480882000	4.063108000
H	0.943070000	3.616916000	4.567974000
C	2.508279000	4.599696000	3.494751000
H	3.506067000	4.499137000	3.057845000
H	2.200311000	5.585599000	3.849840000
C	0.987883000	1.174908000	3.437940000
O	-0.047246000	1.880360000	3.193690000
C	0.948378000	0.313036000	4.672138000
H	1.939831000	-0.094676000	4.907673000
H	0.245399000	-0.511917000	4.486723000
H	0.585331000	0.899308000	5.524463000
O	1.570117000	0.631990000	2.344802000
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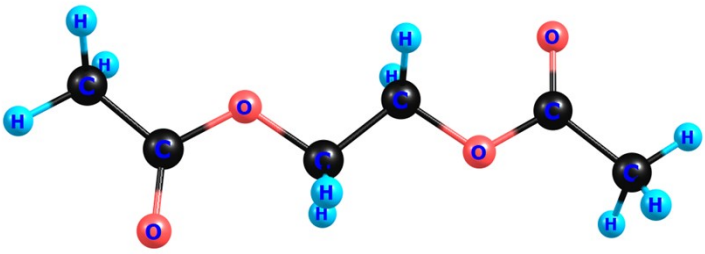
H	2.449857000	0.304861000	2.573979000

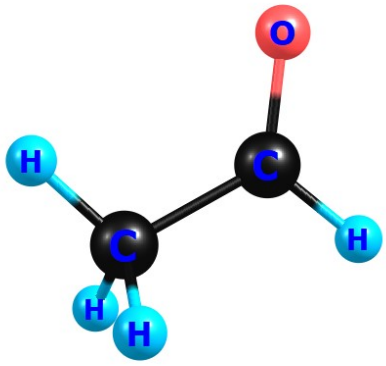
Ethylene glycol diacetate



C	4.212264000	5.252481000	9.837083000
C	4.712584000	7.379279000	8.971631000
C	5.395615000	10.907519000	8.636864000
C	4.896809000	8.780445000	9.502511000
H	5.623515000	7.021633000	8.468076000
H	3.894696000	7.336804000	8.236147000
H	5.714358000	8.822667000	10.238395000
H	3.985764000	9.138433000	10.005601000

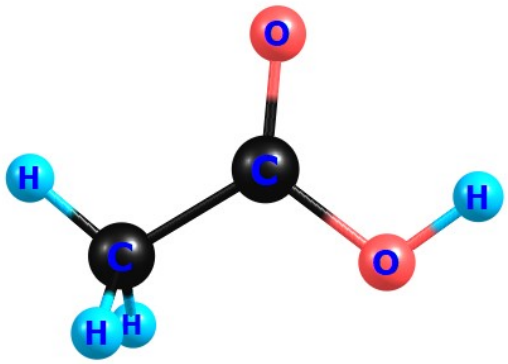
O	4.277852000	4.789358000	8.731983000
O	4.412943000	6.557578000	10.090763000
O	5.328374000	11.370937000	9.741742000
O	5.197329000	9.601995000	8.383501000
C	3.905689000	4.493145000	11.096091000
H	3.010799000	4.914032000	11.575956000
H	3.744395000	3.436776000	10.856699000
H	4.737650000	4.598930000	11.807213000
C	5.699116000	11.667446000	7.377467000
H	6.577159000	11.231699000	6.880374000
H	4.853278000	11.582629000	6.679798000
H	5.883420000	12.719366000	7.619746000

Acetaldehyde



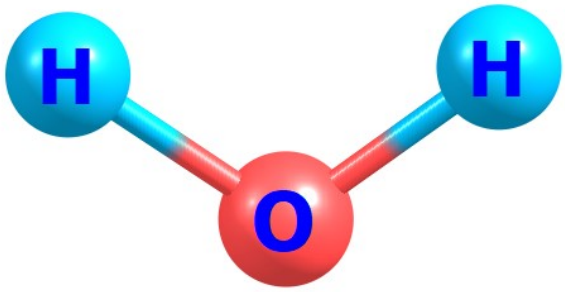
O	-2.170805000	-0.000849000	-1.770025000
C	-2.170805000	0.454056000	-0.659567000
C	-2.170805000	-0.362967000	0.599085000
H	-3.055472000	-0.110678000	1.206084000
H	-2.170805000	-1.433785000	0.357614000
H	-1.286138000	-0.110678000	1.206083000
H	-2.170805000	1.564902000	-0.500938000

Acetic acid



H	-0.090450000	0.001293000	-3.754204000
O	-0.090450000	-0.498956000	-2.921895000
O	-0.090450000	1.589054000	-2.141738000
C	-0.090450000	0.407436000	-1.930064000
C	-0.090450000	-0.245004000	-0.578323000
H	0.794801000	-0.889075000	-0.476552000
H	-0.090450000	0.524327000	0.200747000
H	-0.975701000	-0.889075000	-0.476552000

Water



O	-0.507846000	1.104883000	-1.909853000
H	-0.507846000	1.863074000	-1.313278000
H	-0.507846000	0.346692000	-1.313278000

Alternative mechanism to Figure 3.

An alternative mechanism for the conversion of the vinyl ester intermediate to acetaldehyde and the carboxylic acid product was also investigated. In this pathway, the vinyl ester undergoes a substitution reaction with an OH group in an exothermic step (-6.9 kcal/mol), producing a vinyl alkoxy intermediate **D'** and the corresponding carboxylic acid product. This reaction proceeds via a four-membered concerted transition state with an energy barrier of 25.6 kcal/mol, which is 6.5 kcal/mol higher than **TS3** shown in Fig. 3. In the final step, a hydrogen migration occurs, leading to the formation of vinyl alcohol, which rapidly tautomerizes to stable acetaldehyde. This step is exothermic (-2.1 kcal/mol) and has a transition state barrier of 16.7 kcal/mol.

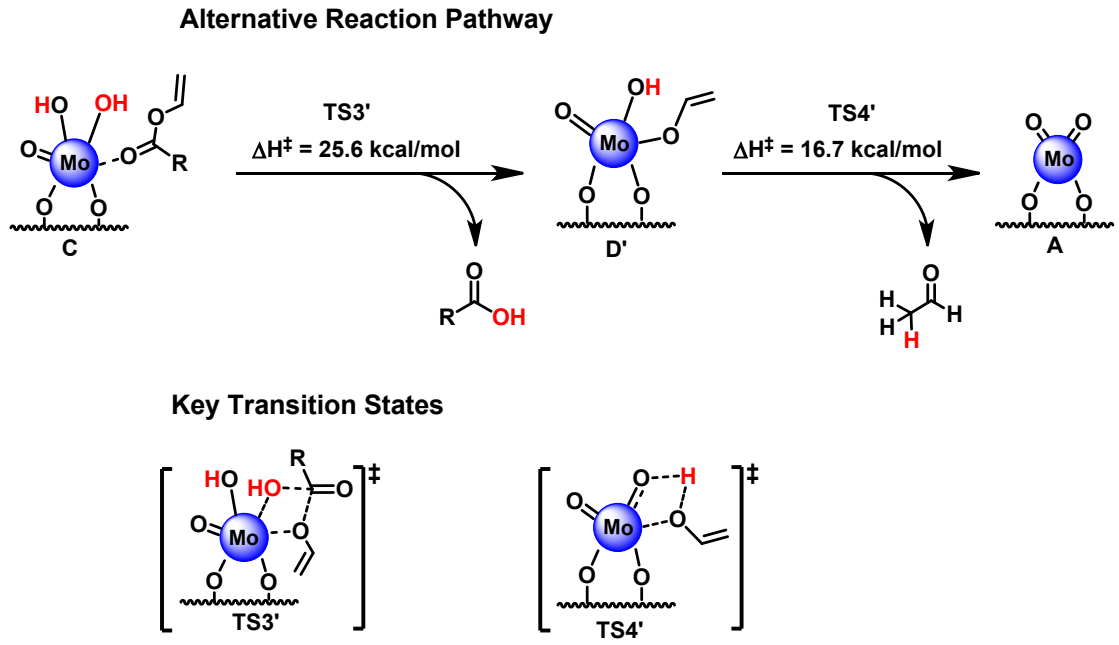
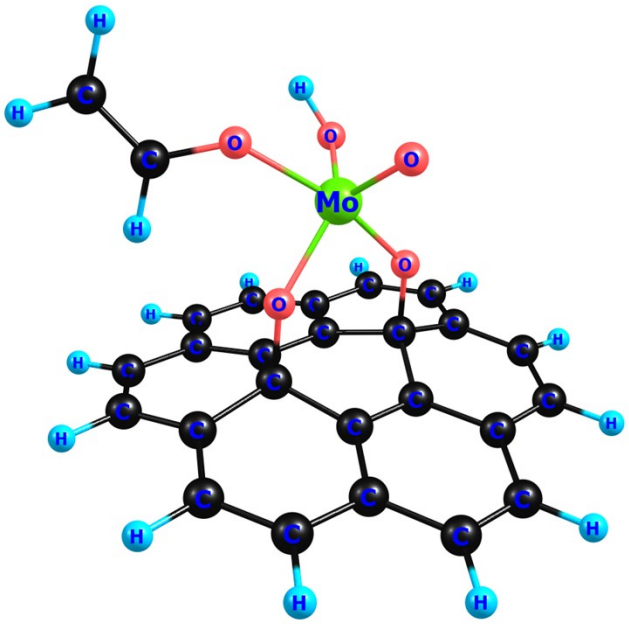


Figure S49. Alternative calculated reaction pathway.

DFT-optimized Cartesian coordinates for alternative mechanism.

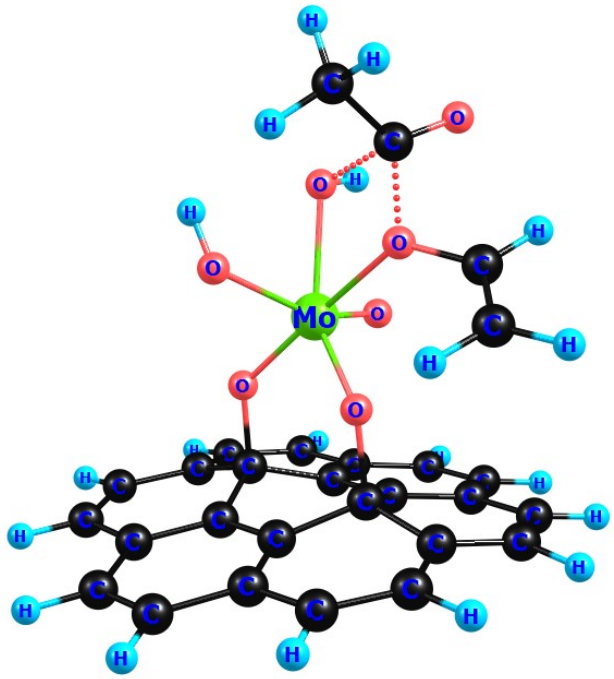
Alternative Intermediate D'



Mo	1.908224000	-0.953069000	-2.240071000
O	2.280103000	-2.684283000	-2.910864000
O	2.800756000	-0.598689000	-0.887922000
H	3.108866000	-2.795153000	-3.396917000
O	3.167663000	-0.312326000	-3.521761000
C	3.101244000	0.176966000	-4.768341000
H	2.133765000	0.633651000	-5.018228000
C	4.120497000	0.134272000	-5.626906000
H	5.074967000	-0.317276000	-5.349597000
H	4.008835000	0.563975000	-6.622525000
C	-1.020620000	-0.528164000	-3.890434000
C	-0.573400000	0.699210000	-3.123458000
C	-1.221401000	0.806490000	-1.761714000
C	-1.468313000	-0.337894000	-1.062348000
C	-1.061615000	-1.656913000	-1.682256000
C	-1.256701000	-1.689586000	-3.182728000
C	-1.885627000	-0.295980000	0.311731000

C	-2.108157000	-1.487705000	0.986096000
C	-2.016086000	-2.738404000	0.341522000
C	-1.637811000	-2.864308000	-0.974560000
C	-1.764733000	-4.071963000	-1.709275000
C	-1.684324000	-4.102397000	-3.072825000
C	-1.479345000	-2.915605000	-3.847159000
C	-1.489920000	-2.911845000	-5.258696000
C	-1.260835000	-1.752873000	-5.966795000
C	-1.005667000	-0.532465000	-5.304007000
C	-0.743462000	0.689180000	-6.003712000
C	-0.592919000	1.879228000	-5.347810000
C	-0.672476000	1.974710000	-3.933491000
C	-0.825528000	3.169815000	-3.269824000
C	-1.140558000	3.236223000	-1.897822000
C	-1.384357000	2.095313000	-1.147201000
C	-1.819184000	2.134622000	0.218491000
C	-2.060081000	0.992439000	0.915487000
O	0.845419000	0.507309000	-2.859964000
O	0.370335000	-1.676941000	-1.461918000
H	-1.266828000	4.214266000	-1.428059000
H	-0.772272000	4.098607000	-3.843722000
H	-1.950905000	3.109987000	0.691970000
H	-2.386623000	1.036923000	1.956701000
H	-2.427064000	-1.451036000	2.030117000
H	-2.325227000	-3.634874000	0.884885000
H	-2.007730000	-4.984521000	-1.159504000
H	-1.831452000	-5.045351000	-3.604177000
H	-1.671473000	-3.850234000	-5.787444000
H	-1.262587000	-1.769308000	-7.059339000
H	-0.721133000	0.663363000	-7.095870000
H	-0.481143000	2.804145000	-5.919138000

Alternative transition state TS3'



C	0.984920000	0.965666000	-0.377201000
C	-0.305413000	1.566102000	0.121022000
C	-1.523636000	0.768324000	-0.278010000
C	-1.424045000	-0.593531000	-0.341284000
C	-0.097638000	-1.237706000	-0.007277000
C	1.085589000	-0.408347000	-0.451348000
C	-2.586321000	-1.410472000	-0.521494000
C	-2.438395000	-2.793562000	-0.581900000
C	-1.176782000	-3.409702000	-0.561388000
C	-0.008538000	-2.690529000	-0.416588000
C	1.276150000	-3.242939000	-0.625815000
C	2.390538000	-2.457322000	-0.765613000
C	2.324455000	-1.032587000	-0.729277000
C	3.447315000	-0.207954000	-0.963890000
C	3.347347000	1.162252000	-0.892406000
C	2.118901000	1.787900000	-0.582803000
C	1.976791000	3.204454000	-0.488293000
C	0.756414000	3.798302000	-0.299026000

C	-0.431923000	3.043864000	-0.156641000
C	-1.693599000	3.595200000	-0.254769000
C	-2.852423000	2.809781000	-0.338075000
C	-2.794480000	1.419580000	-0.394655000
C	-3.950995000	0.599615000	-0.586380000
C	-3.851694000	-0.755768000	-0.646619000
O	-0.183637000	1.440920000	1.598608000
O	0.043719000	-1.211405000	1.448441000
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H	-4.923666000	1.087780000	-0.678240000
H	-4.743651000	-1.370438000	-0.786296000
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H	1.357384000	-4.325428000	-0.752832000
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H	4.226884000	1.786039000	-1.067430000
H	2.864728000	3.823401000	-0.635955000
H	0.672832000	4.887778000	-0.330251000
C	-1.143917000	1.070527000	5.535831000
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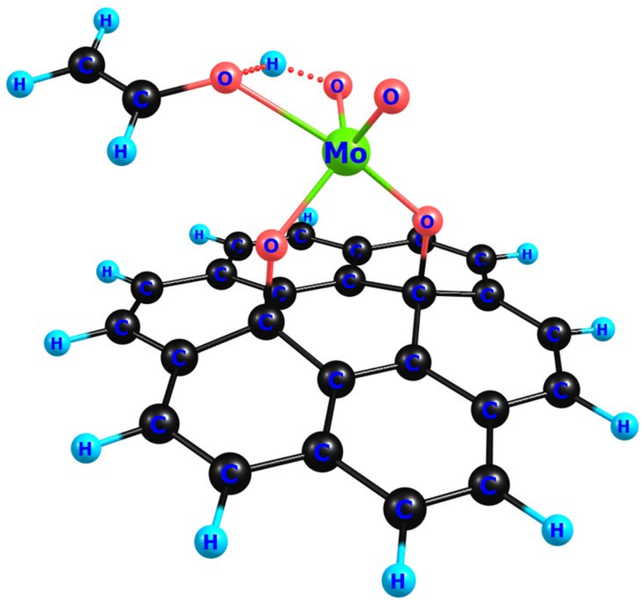
C	-1.196540000	2.989590000	3.943930000
H	-2.191172000	3.140923000	4.373280000
C	-0.506383000	3.926269000	3.306695000
H	0.481912000	3.725484000	2.893084000
H	-0.948812000	4.913797000	3.168757000
C	0.083290000	1.105080000	6.398369000
H	-0.074057000	0.436633000	7.254807000
H	0.978612000	0.814171000	5.841268000
H	0.204107000	2.132605000	6.770183000
Mo	-0.490533000	0.023493000	2.758759000
O	-2.121404000	-0.320357000	2.553130000

O	1.151831000	-0.399271000	3.633391000
O	-1.023703000	-0.515773000	4.755343000
H	-1.963373000	-0.760775000	4.762497000
H	1.170735000	-0.951522000	4.425144000

Alternative transition state TS4’



Mo	1.812680000	-1.111898000	-2.174590000
O	2.293936000	-2.515165000	-3.171201000
O	2.923735000	-0.807142000	-0.978232000
H	2.937239000	-1.786522000	-3.863241000
O	3.175652000	-0.570097000	-3.810341000
C	3.175284000	0.403888000	-4.737206000
H	2.773500000	1.355233000	-4.370563000
C	3.627529000	0.260585000	-5.982966000
H	4.034482000	-0.689320000	-6.336582000
H	3.610537000	1.109817000	-6.666448000
C	-0.903467000	-0.588091000	-3.828166000
C	-0.495728000	0.654314000	-3.064155000
C	-1.195379000	0.779138000	-1.731216000
C	-1.491291000	-0.353684000	-1.027557000

C	-1.107034000	-1.693872000	-1.607752000
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C	-2.205210000	-2.717249000	0.366989000
C	-1.762383000	-2.870556000	-0.925588000
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C	-1.394658000	-2.969887000	-3.777485000
C	-1.302828000	-2.990837000	-5.185164000
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C	-0.795601000	-0.617247000	-5.237295000
C	-0.487078000	0.591377000	-5.940466000
C	-0.383065000	1.793739000	-5.301196000
C	-0.545496000	1.914561000	-3.896238000
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O	0.919187000	0.465473000	-2.710115000
O	0.329143000	-1.784622000	-1.291819000
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H	-1.805198000	-5.088394000	-3.530875000
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H	-0.385359000	0.542416000	-7.026860000
H	-0.232694000	2.707083000	-5.881792000

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