Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Benzaldehyde-mediated Selective Aerobic Polyethylene Functionalisation with Isolated Backbone Ketones

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1. Experimental Procedures

1.1 Materials

All chemicals were used as received unless stated otherwise. Polyethylene (PE, M_n ~ 7.7 kDa, M_w ~ 35 kDa, PDI = 4.55) and 1,1,2,2-tetrachloroethane (TCE, ≥ 98%) were purchased from Sigma-Aldrich. The co-oxidant, benzaldehyde (> 98%), was sourced from Tokyo Chemical Industry (TCI). Anhydrous copper (II) chloride ($CuCl_2$) and dicyclohexyl-18-crown-6 (DCH18C6, >98.0%) were purchased from Alfa Aesar and TCI respectively. 1,1,2,2-tetrachloroethane-d_2 (99.5%) was supplied by Cambridge Isotope Laboratories.

All glassware and stirrer bars were soaked in aqua regia for 3 days, before being thoroughly rinsed with deionised water and acetone before they were used for any oxidation reactions, to eliminate the presence of any trace metals which could act as oxidation catalysts.

1.2 Characterisation

The presence of functional groups was identified by ^{1}H nuclear magnetic resonance (NMR) in TCE-d_2 at 80 °C using a JEOL 500 MHz spectrometer (Tokyo, Japan). These were further confirmed through Fourier-transform infrared (FTIR) spectroscopy, all performed on a Bruker VERTEX 80v spectrometer (Karlsruhe, Germany) in the attenuated total reflectance mode from 4000 to 400 cm^{-1}. Thermogravimetric analysis (TGA) was conducted using PerkinElmer Pyris 1 TGA (Waltham, USA) under nitrogen atmosphere with a flow rate of 20 mL/min. Each sample was heated from 35 to 800 °C at a rate of 20 °C/min. Differential scanning calorimetry (DSC) was performed using PDSC Q100 (TA Instruments) under nitrogen at a heating rate of 10 °C/min over a temperature range of 0 to 150 °C. The DSC data were collected from the second cycle of heating.

Gel-permeation chromatography (GPC) was performed at 160 °C in 1,2,4-trichlorobenzene (TCB) using an Agilent 1260 Infinity II High Temperature GPC system. The samples were first immersed in TCB containing 250 ppm butylated hydroxytoluene (BHT) at room temperature overnight without shaking. The samples were then heated to 160 °C and kept at 160 °C with gentle shaking on Agilent SP 260VS sample preparation system for about 1 hour, followed by filtering through an Agilent 1-μm glass fibre filter. For analysis, the GPC system was equipped with 2 columns of Agilent PLgel 5 μm Mixed B (7.5 mm x 300 mm) together with the corresponding Guard column, as well as both refractive index and viscometer detectors. The flow rate was set at 1.0 mL/min with a sample injection volume of 200 μL. The calibration standard in use is Agilent EasiVial PS-H polystyrene.

A Static Rame-Hart contact angle goniometer (Model 590-U1) was equipped with a high speed GigE camera and DROPimage Advanced program was used to image and measure the static contact angles directly. Unreacted PE and PE oxidised with benzaldehyde (Table 1 entry 1) were first melted on separate glass slides and smoothed to form a thin uniform film. Static contact angle was then measured using sessile drop method, where 3 μL of deionized water drops were carefully dispensed onto the surface of the SI samples. 3 measurements were performed for each PE sample.

1.3 Aerobic oxidation of PE with benzaldehyde

Polyethylene (300 mg) was added to benzaldehyde (3.3 mL, 3.0 eqv. w.r.t. ethylene repeating units) in a Schlenk flask and the mixture was thoroughly degassed before being refilled with O_2 from a balloon. The reaction mixture was stirred at 120 °C for 24 hours under ambient lighting conditions. After the reaction, the crude reaction mixture was poured into vigorously-stirred methanol or ethanol (~100 mL) to afford a white suspension, which was then filtered, rinsed with the same solvent, and dried in vacuo to obtain the oxidised PE as a powder (typical recovered yields > 90%). The filtrate was then collected and solvent removed under reduced pressure, and the benzoic acid was recovered by recrystallization from hot water as white

crystals. ^{1}H NMR of oxidised PE ($C_2D_2Cl_4$, 80 ^{o}C) δ/ ppm: 2.40 (t, C_{α}-H of ketones); 0.8-1.6 (m, PE methylene-CH_2s).

1.4 Aerobic Oxidation of PE by [$CuCl_2$·DCH18-crown-6] in Benzaldehyde

Anhydrous $CuCl_2$ (14.4 mg, 0.11 mmol) and dicyclohexyl-18-crown-6 (39.8 mg, 0.11 mmol) were first stirred in benzaldehyde (2 mL) at room temperature for 5 minutes in a Schlenk flask. Thereafter, PE (300 mg) was added, followed by the remainder of the benzaldehyde (total added = 3.3 mL, 3.0 eqv w.r.t. ethylene repeat units). The reaction was thoroughly degassed and refilled with O_2, and stirred at 120 °C for 24 hours. Thereafter, the crude reaction mixture was poured into vigorously-stirred methanol (~100 mL) to afford a suspension. The oxidised PE was isolated by filtration, and dried in vacuo to obtain the oxidised PE as a powder (typical recovered yields > 90%). The filtrate was then collected and solvent removed under reduced pressure, and the benzoic acid was recovered by recrystallization from hot water as white crystals.

2. Supporting Spectra for PE Oxidation

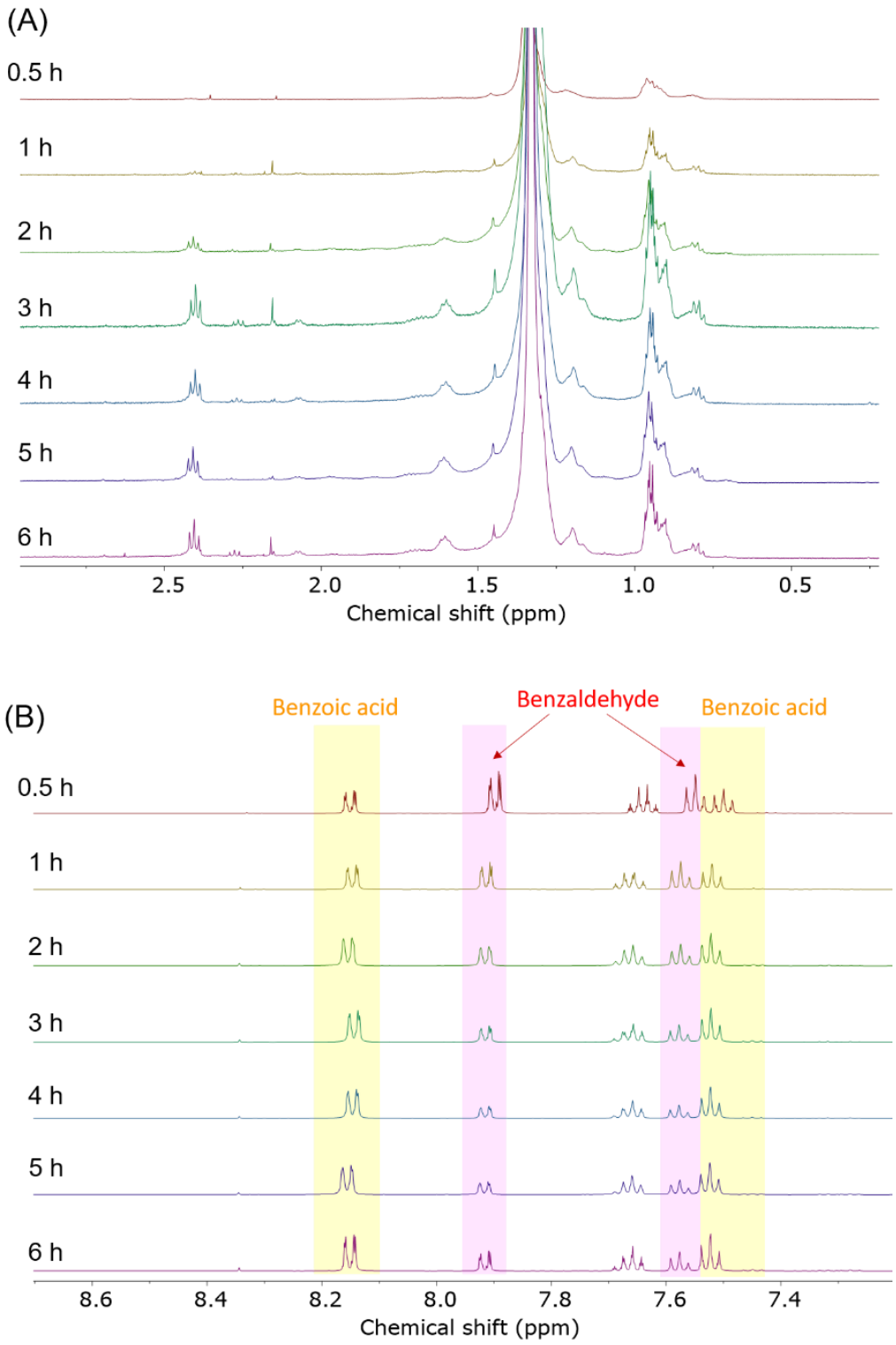


Figure S1. Stacked ^{1}H NMR spectra ($C_2D_2Cl_4$, 80 ^{o}C) showing appearance of (A) a peak at 2.40 ppm arising from the carbonyl α-H on PE and (B) the corresponding formation of benzoic acid from benzaldehyde as the reaction progresses.

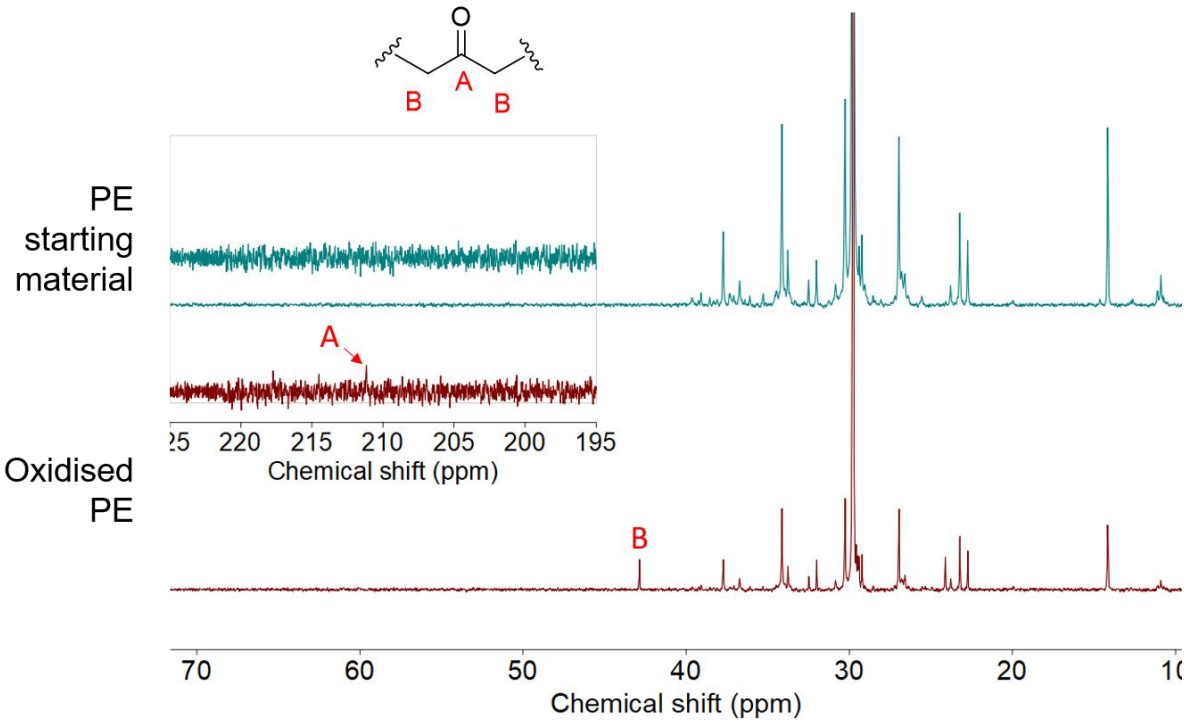


Figure S2. Stacked ^{13}C NMR spectra ($C_2D_2Cl_4$, 80 °C) of the PE starting material and the oxidised PE from Table 1 entry 1. Assignments are based on those reported by Nozaki and coworkers.[1]

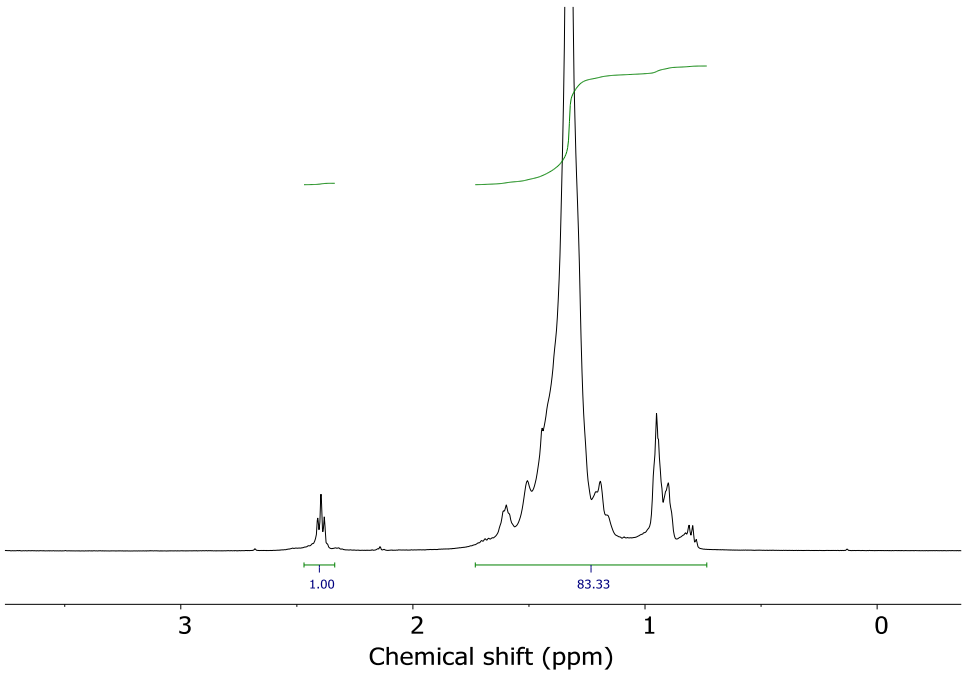


Figure S3. ^1H NMR spectrum ($C_2D_2Cl_4$, 80 °C) of the oxidised PE using benzaldehyde at 120 °C (Table 1, entry 1).

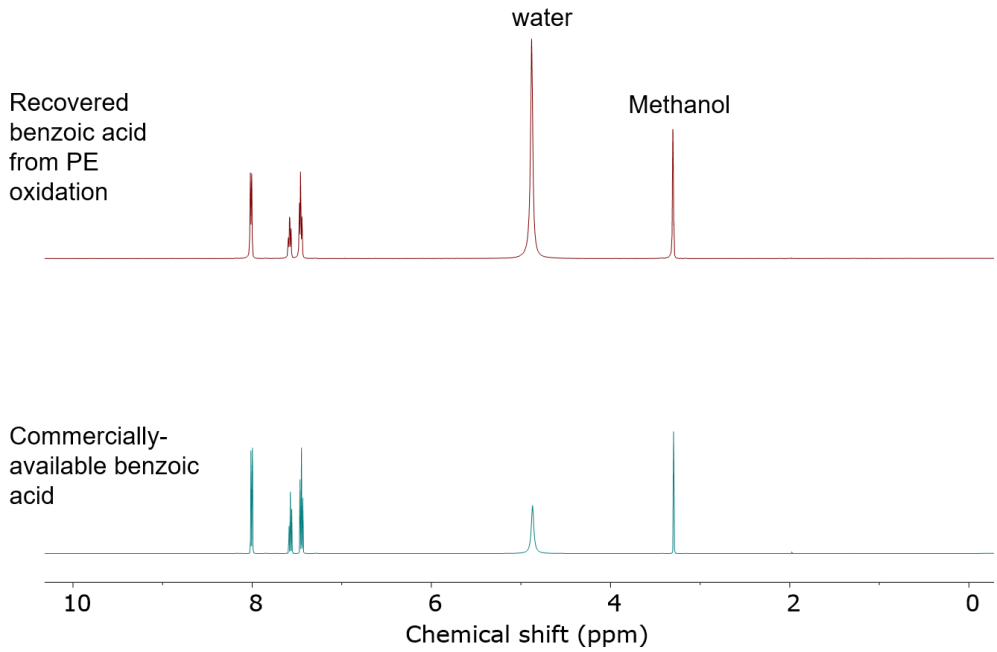


Figure S4. ^{1}H NMR spectra (d_4-MeOD, 25 ^{o}C) of (A) benzoic acid recovered from the reaction after recrystallization from hot water; and (B) pure commercially-available benzoic acid for comparison.

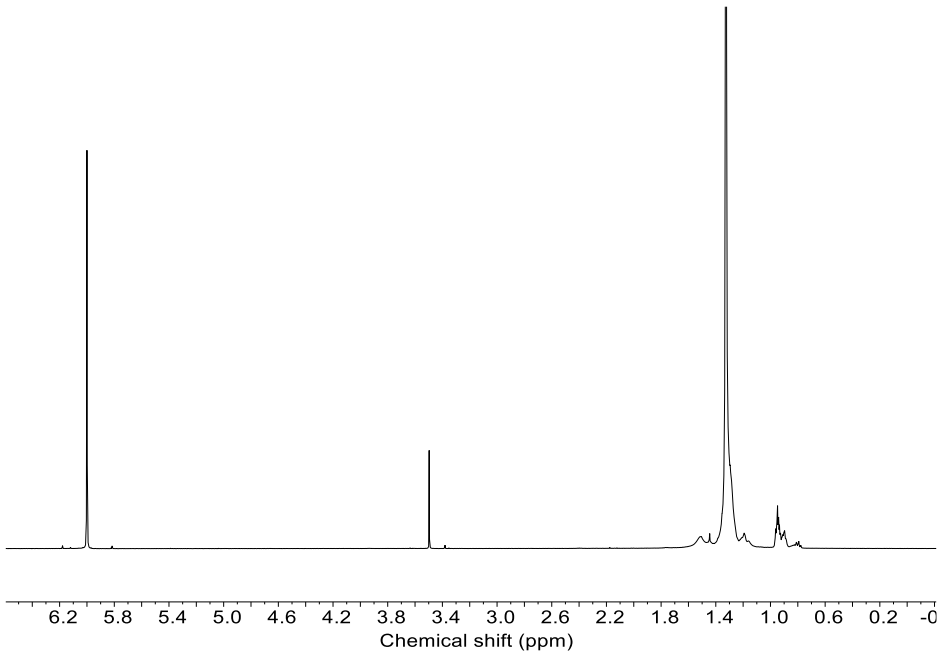


Figure S5. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the PE product after a 24 hour reaction in benzaldehyde at 120 ^{o}C under an inert Ar atmosphere (Table 1, entry 2).

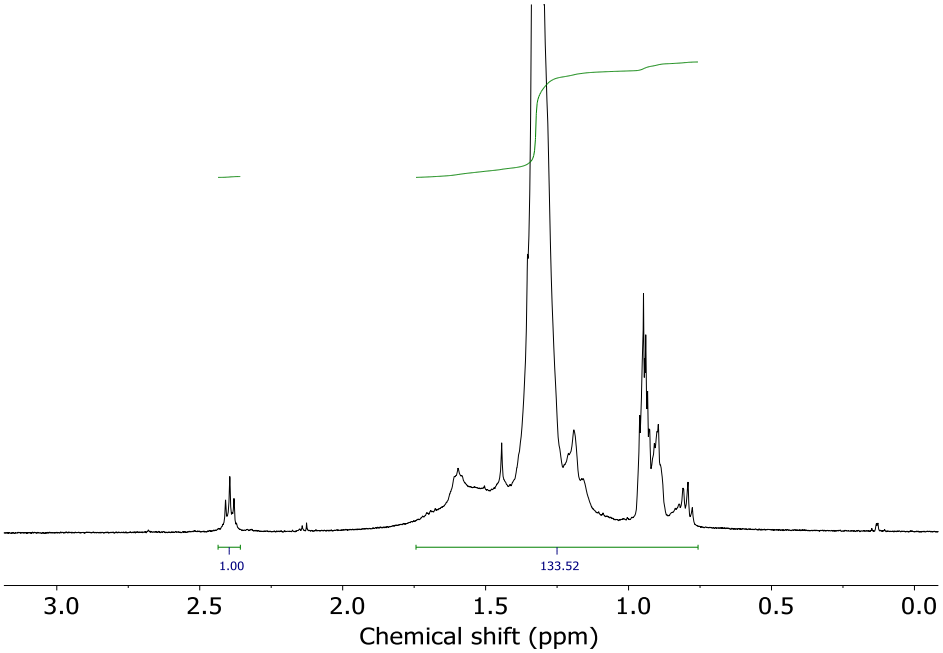


Figure S6. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the PE product after a 24 hour reaction in benzaldehyde at 120 ^{o}C in air (Table 1, entry 3).

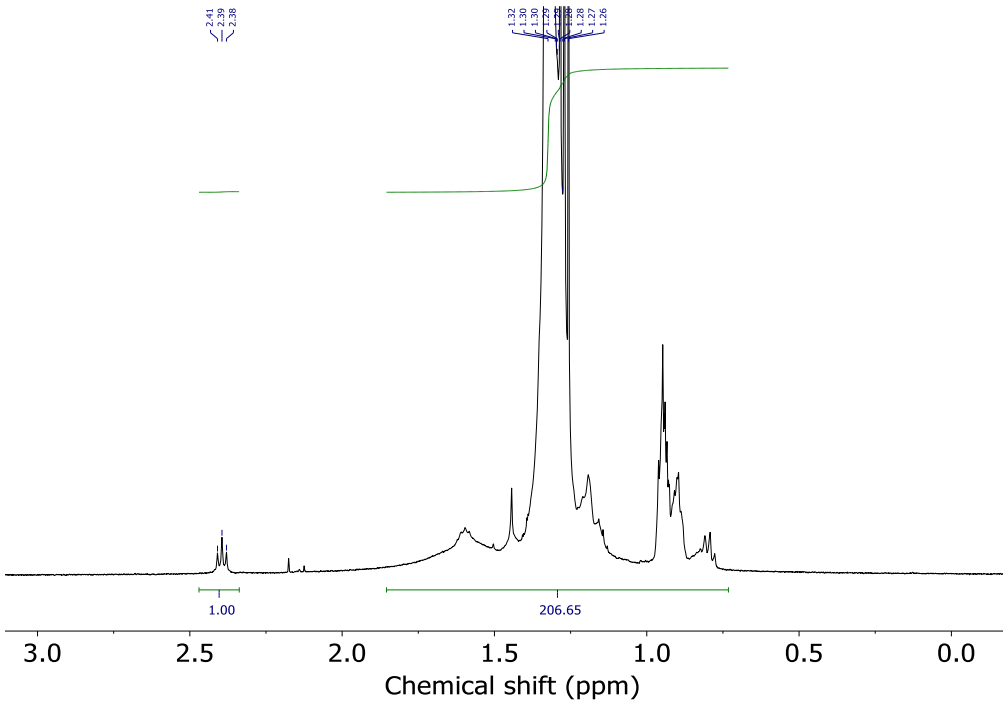


Figure S7. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the PE product after a 24 hour reaction in benzaldehyde at 100 ^{o}C under O_2 (Table 1, entry 4).

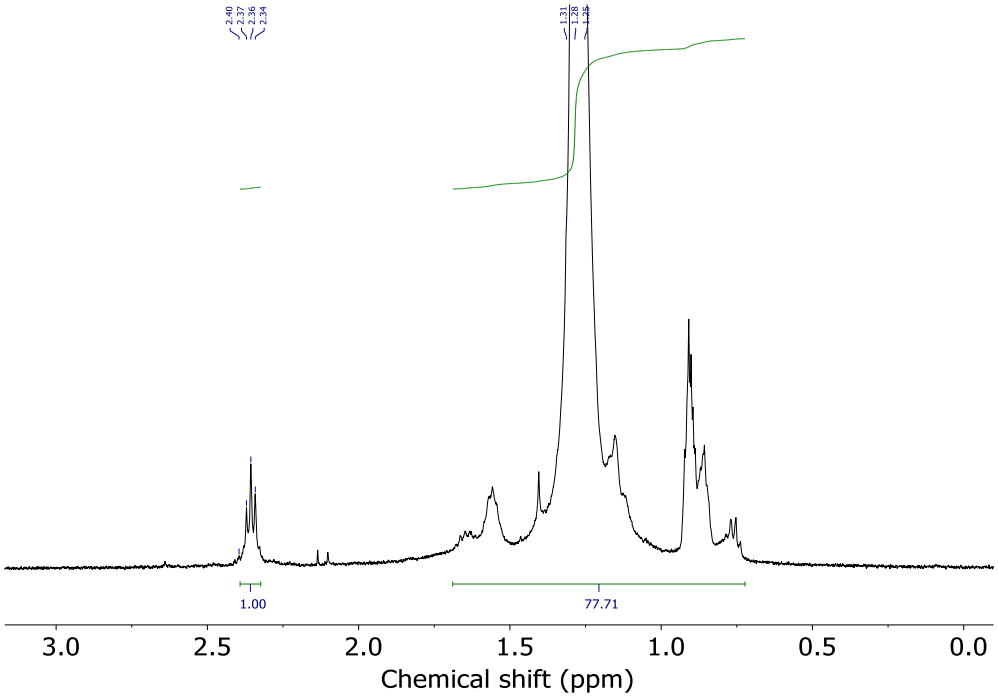


Figure S8. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the PE product after a 24 hour reaction in benzaldehyde at 140 ^{o}C under O_2 (Table 1, entry 5).

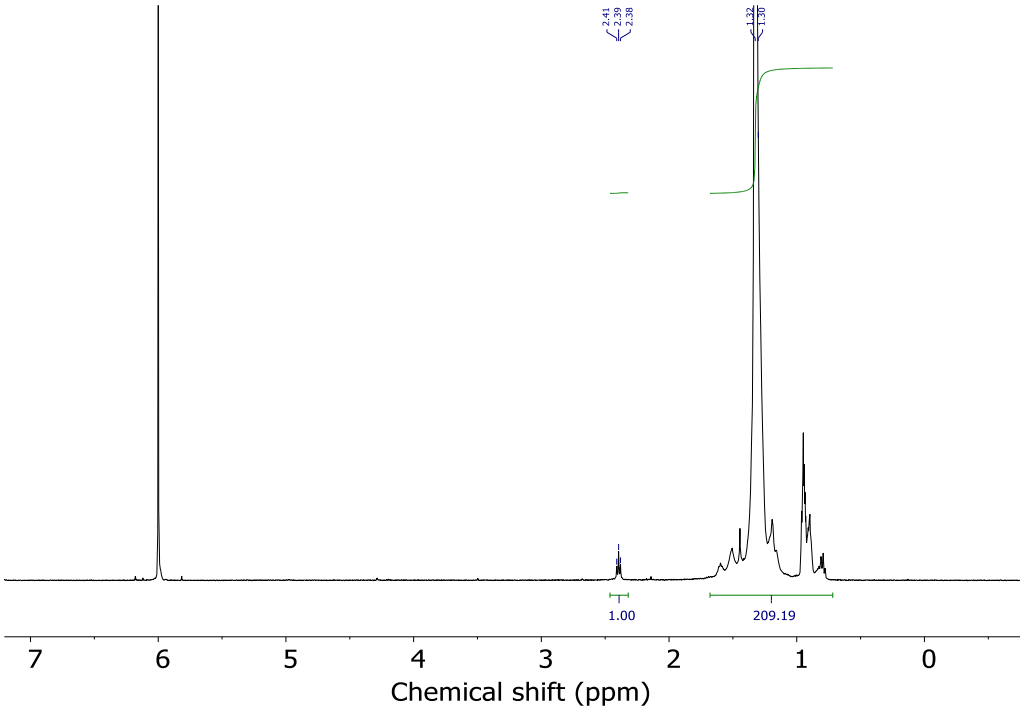


Figure S9. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the PE product after a 24 hour reaction in the presence of 1 equivalent of benzaldehyde at 120 ^{o}C under O_2 (Table 1, entry 6).

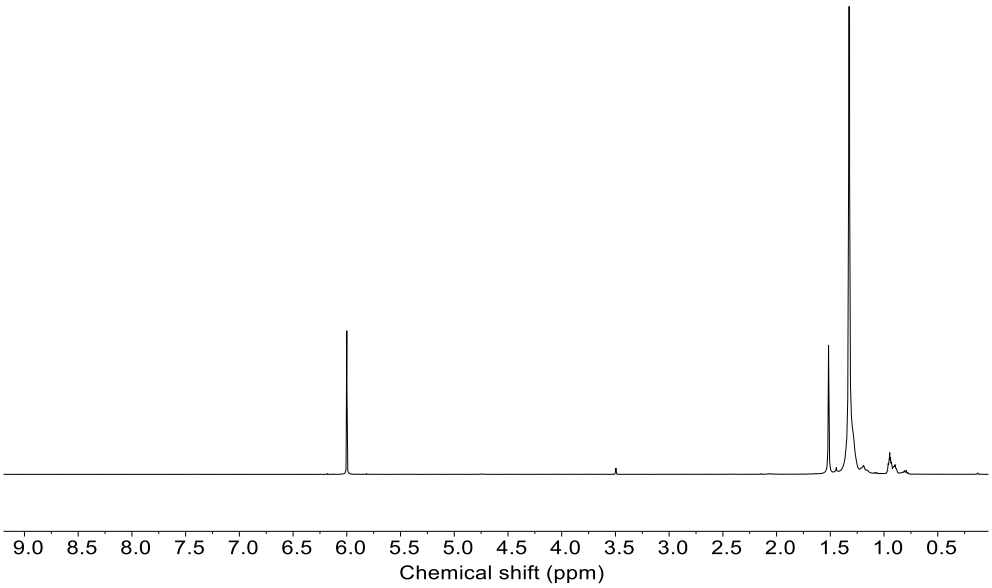


Figure S10. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the PE product after stirring for 24 hours in 1,2,4-TCB under O_2 without benzaldehyde at 120 ^{o}C (Table 1, entry 7).

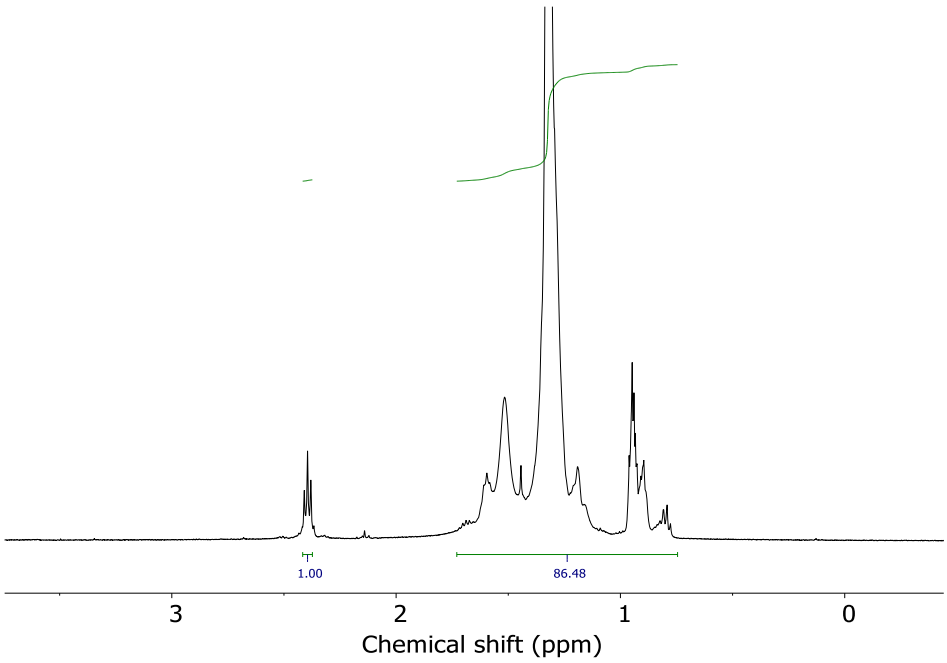


Figure S11. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the oxidised PE using benzaldehyde at 120 ^{o}C under O_2 in the dark (Table 1, entry 8).

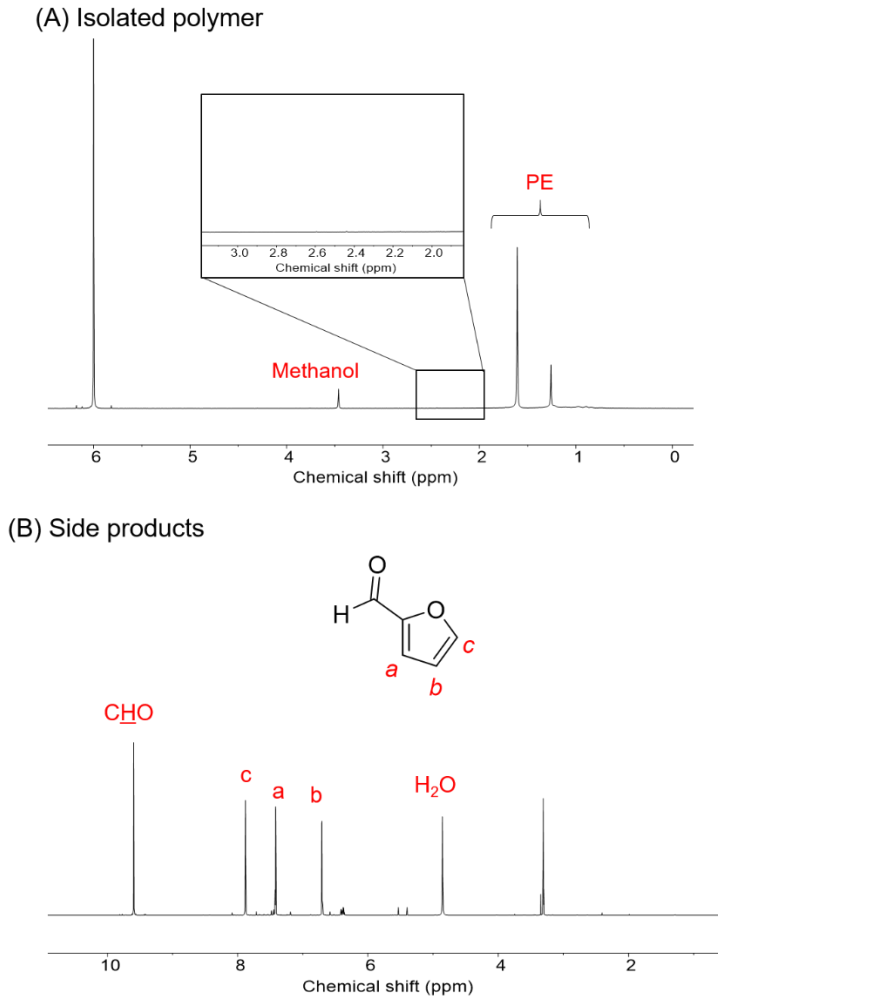


Figure S12. (A) ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the isolated PE product after a 24 hour reaction in furfural at 130 ^{o}C under O_2 (Table 1, entry 9); (B) ^{1}H NMR spectrum (d_4-MeOD) of the recovered bulk phase of the reaction showing the presence of mainly furfural; (C) Possible furfural auto-oxidation products.[2]

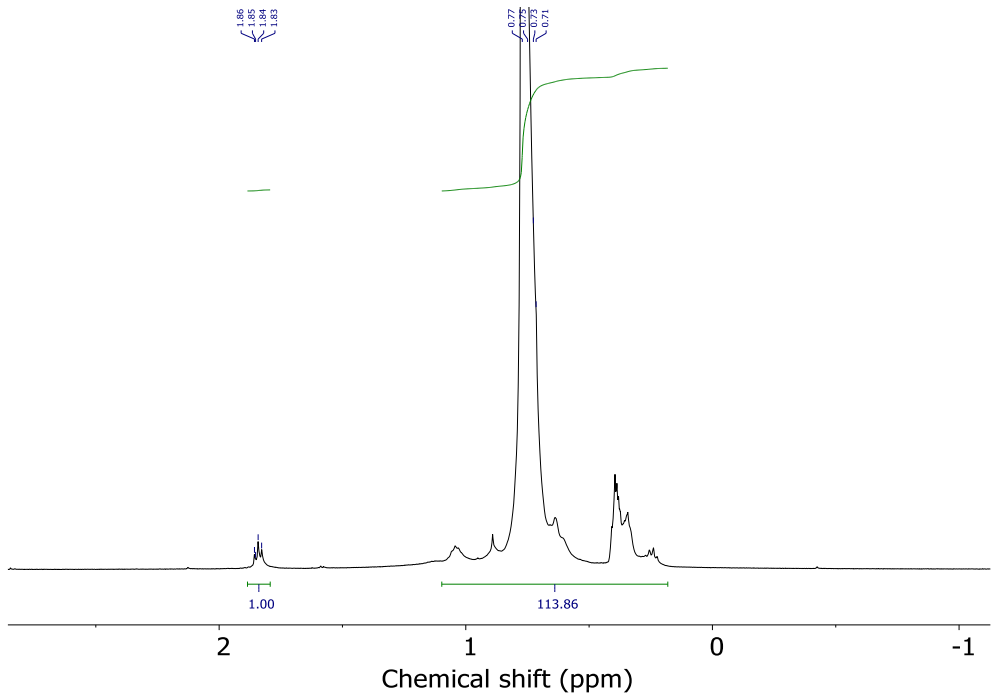


Figure S13. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the oxidised PE using benzaldehyde with 1 eqv of benzyl alcohol at 120 ^{o}C under O_2 (Table 1, entry 10).

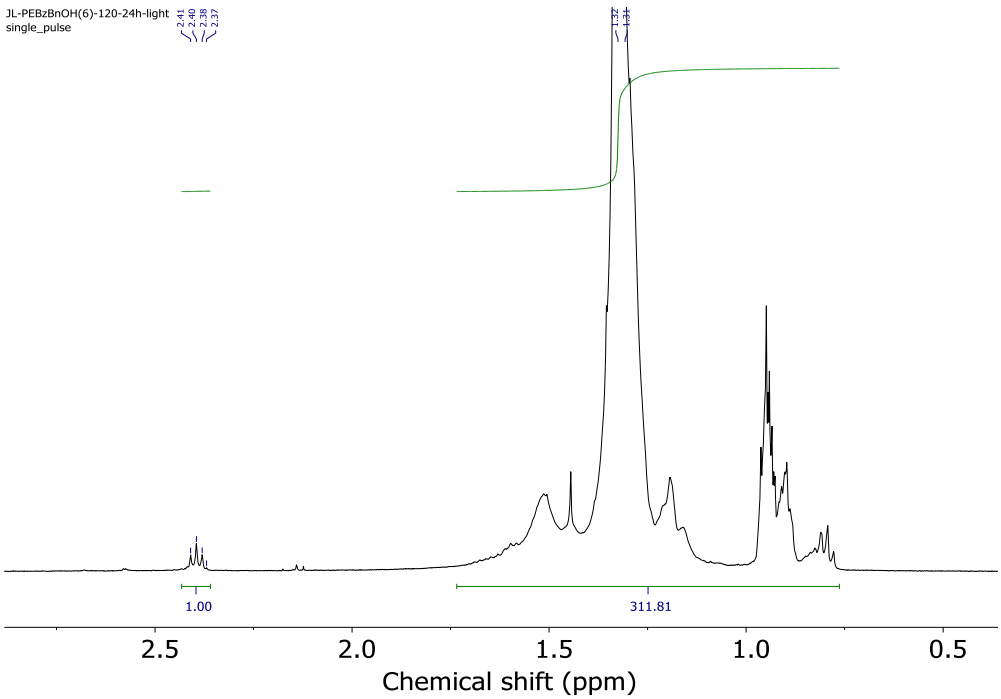


Figure S14. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the oxidised PE using benzaldehyde with 6 eqv of benzyl alcohol at 120 ^{o}C under O_2 (Table 1, entry 11).

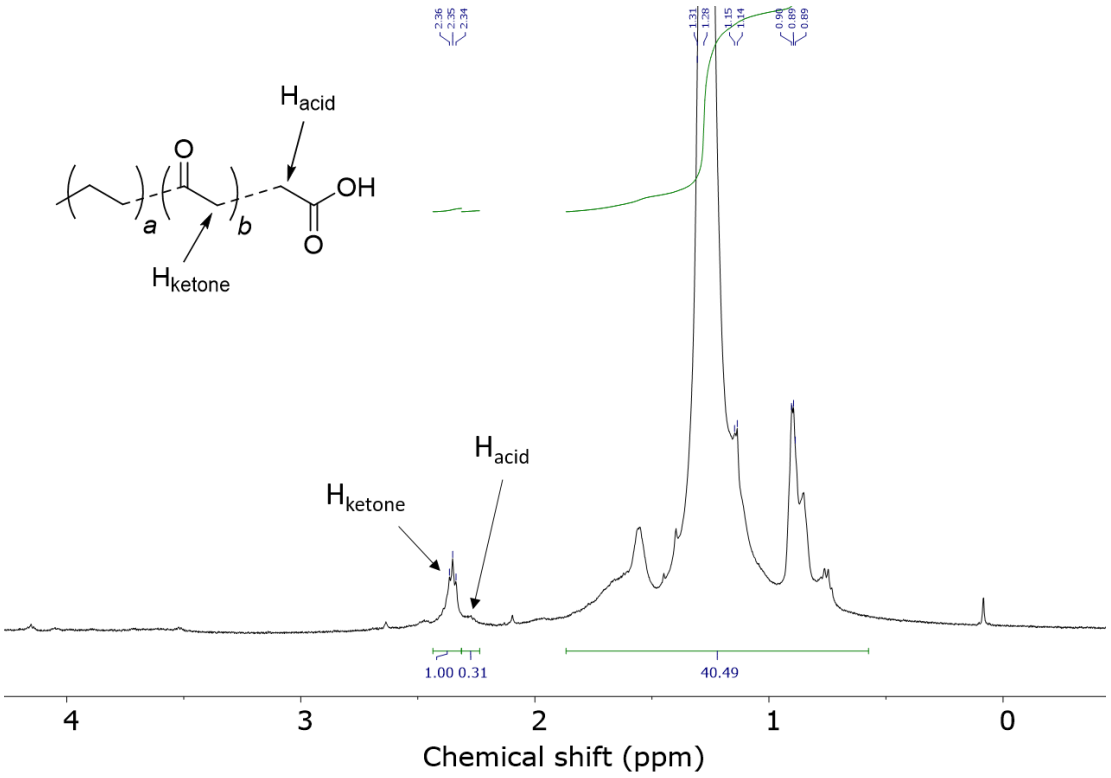


Figure S15. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the oxidised PE using benzaldehyde with [$CuCl_2$·DCH18-crown-6] (1 mol%) at 120 ^{o}C under O_2 (Table 1, entry 12).

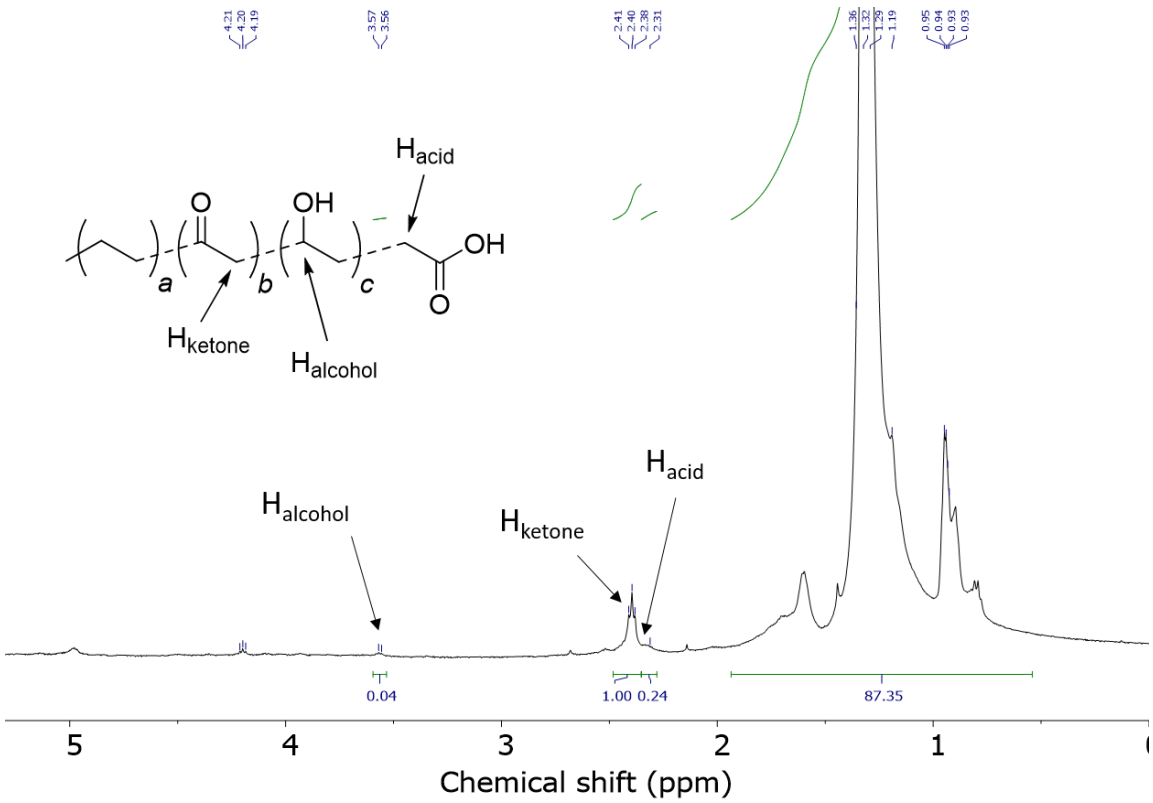


Figure S16. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the oxidised PE using benzaldehyde with anhydrous $CuCl_2$ (1 mol%) at 120 ^{o}C under O_2 (Table 1, entry 13).

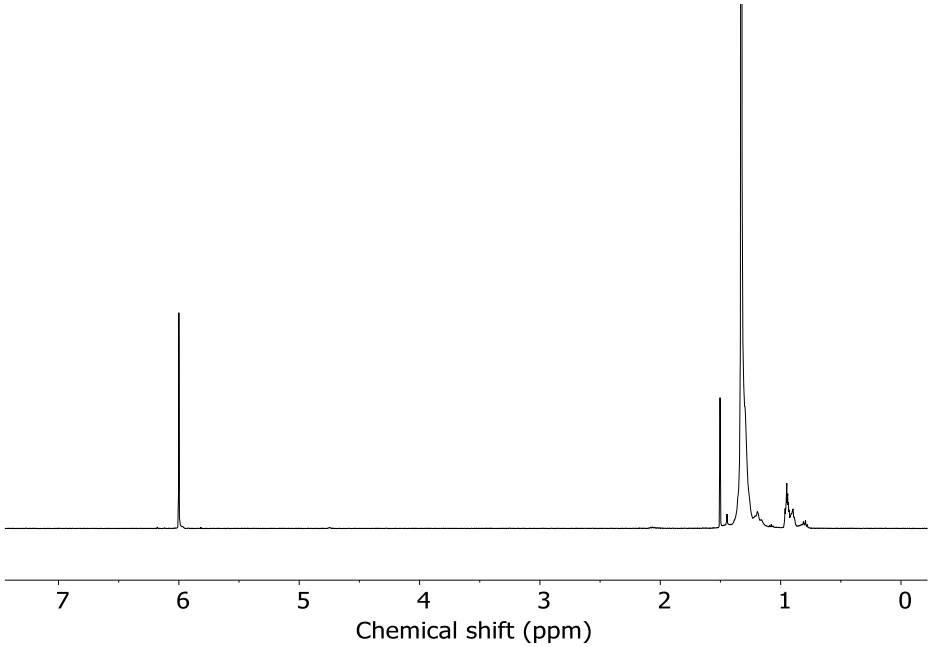


Figure S17. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the PE material after a 24 hour reaction at 120 ^{o}C under O_2 in the absence of benzaldehyde. The reaction was conducted neat without any solvents.

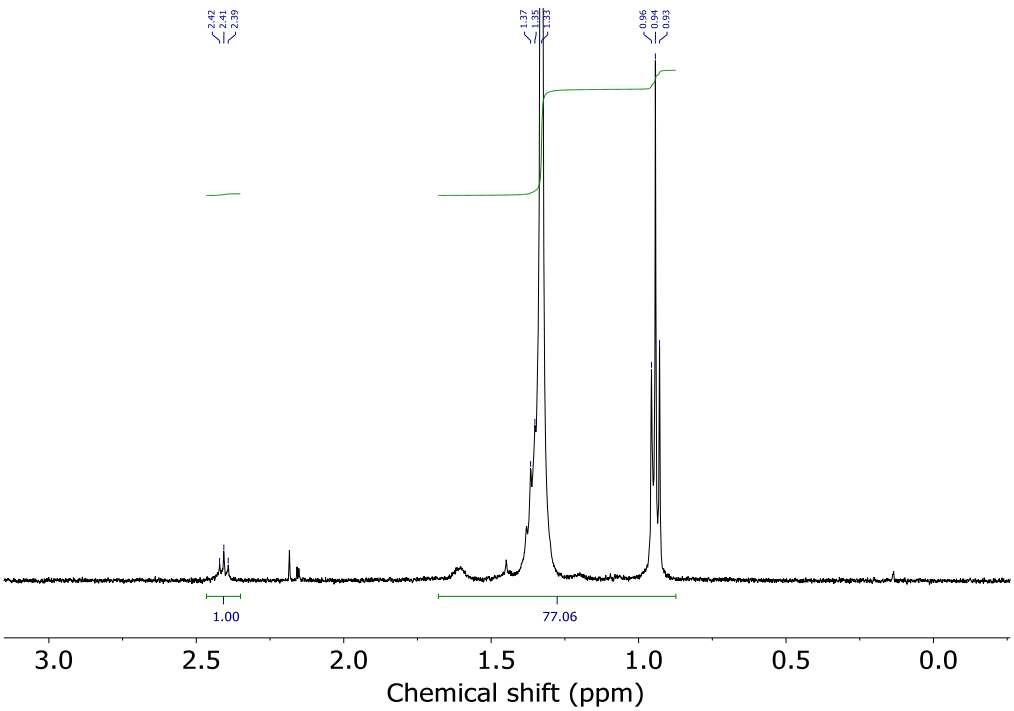


Figure S18. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the oxidised icosane ($C_{20}H_{42}$) using benzaldehyde at 120 ^{o}C under O_2.

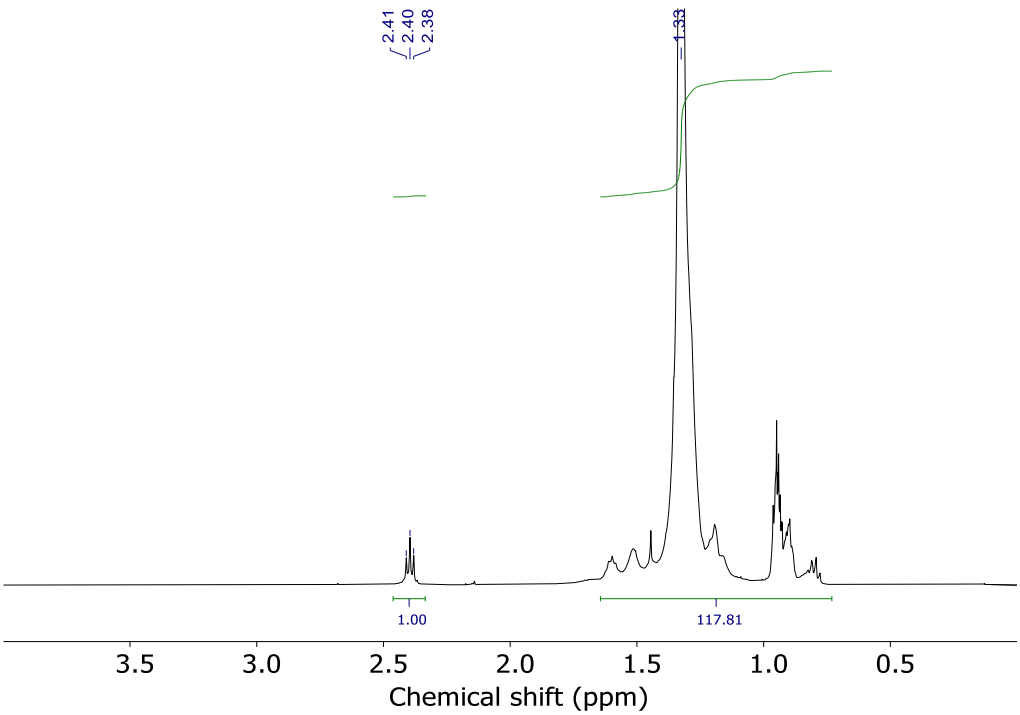


Figure S19. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the PE product after a 24 hour reaction at 120 ^{o}C under O_2 on a larger scale with 2.5 g PE starting material. A brand-new, unused stirrer bar was used for this reaction, which was soaked for 24 hours in aqua regia with the glassware used, to exclude the possibility of trace metal contamination being responsible for the PE oxidation observed.

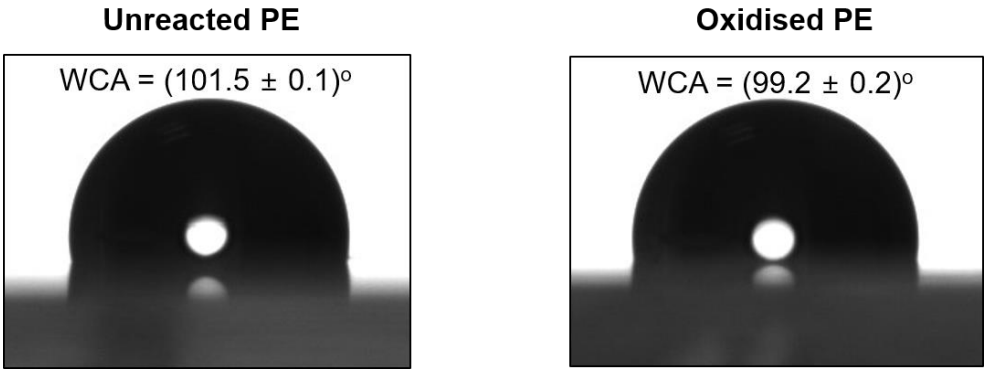


Figure S20. Contact angle images of water droplets on a film of unreacted PE and oxidised PE.

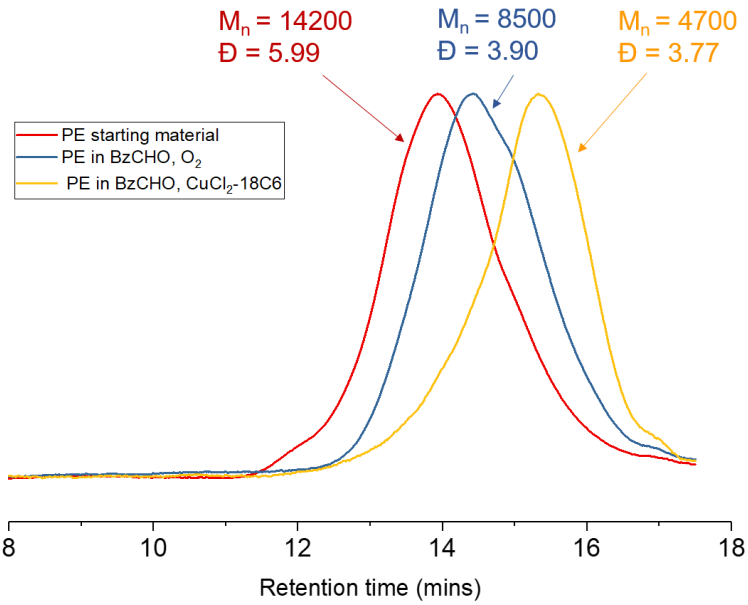


Figure S21. Stacked normalised GPC spectra showing changes in molecular weight distribution of PE before and after oxidation using benzaldehyde at 120 °C under O_2, and after oxidation using benzaldehyde at 120 °C under O_2 in the presence of [$CuCl_2$·DCH18-crown-6] (1 mol%).

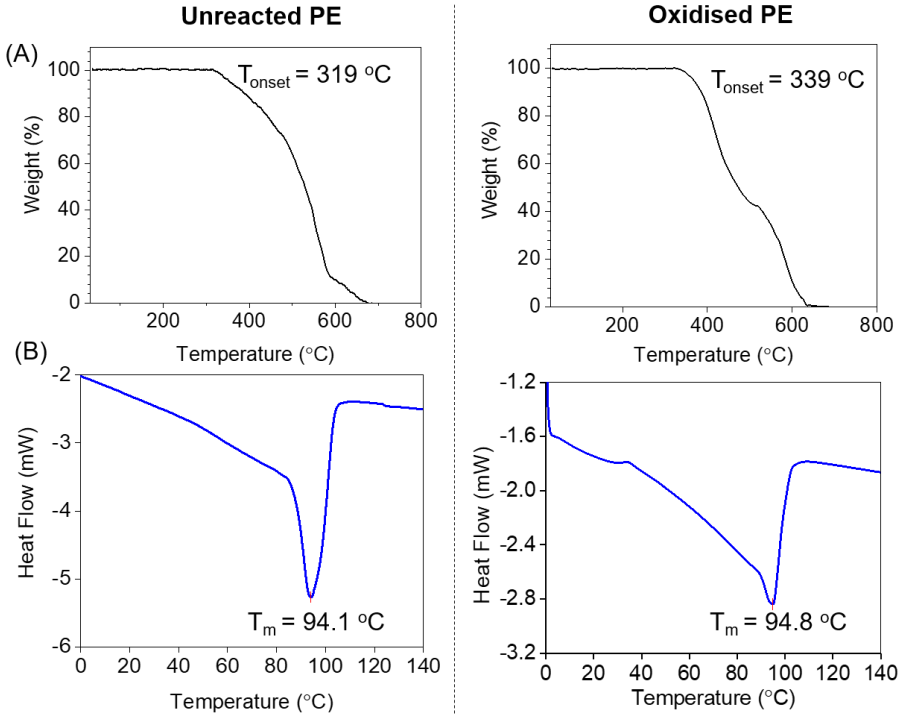


Figure S22. Comparisons of the properties of the (left panel) unreacted PE with the (right panel) carbonyl-containing oxidised PE (from Table 1, entry 1): (A) TGA curves, with the onset temperature of weight loss indicated; (B) DSC traces.

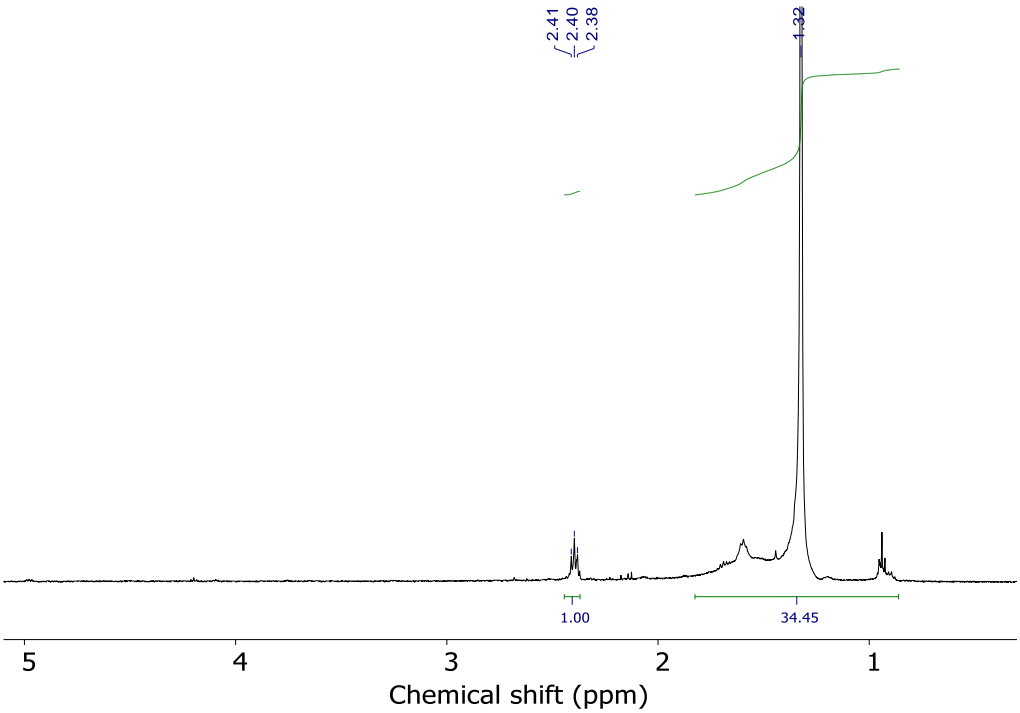


Figure S23. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the oxidised LDPE plastic bag after a 24 hour reaction in benzaldehyde at 120 ^{o}C under O_2.

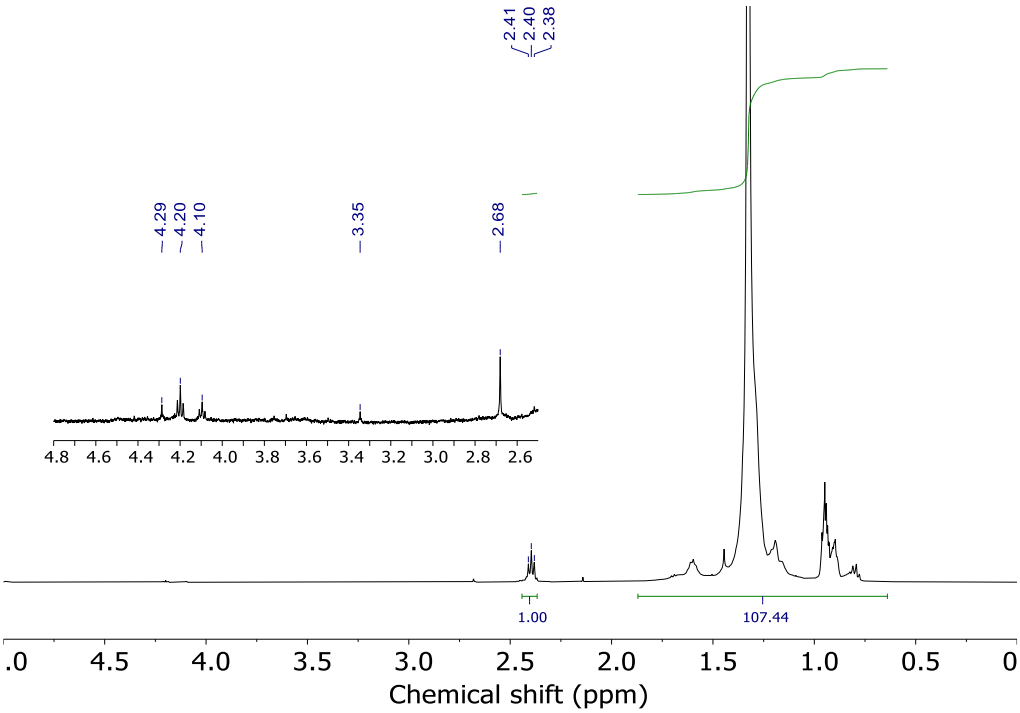


Figure S24. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 80 ^{o}C) of the oxidised PE using benzaldehyde with 6.7 mL of 1,2,4-TCB (equivalent volume to 6 eqv of benzyl alcohol) at 120 ^{o}C under O_2.

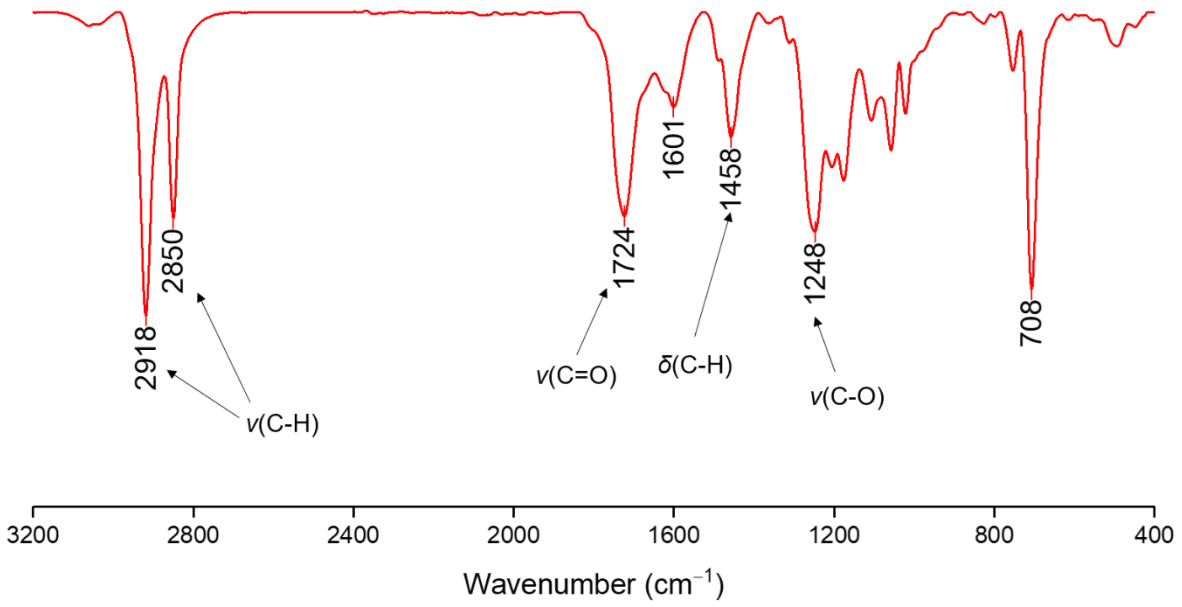


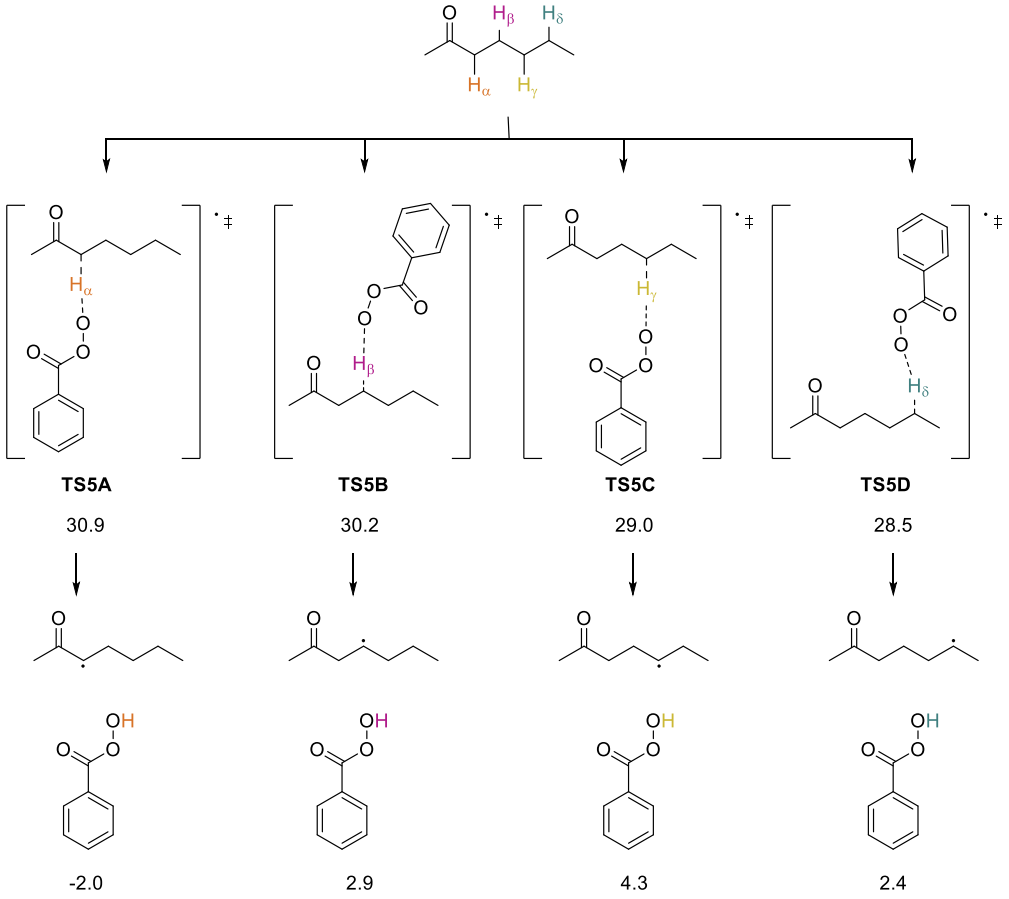
Figure S25. FTIR spectrum of PE after oxidation using benzaldehyde at 120 °C under O_2 in the presence of [$CuCl_2$·DCH18-crown-6] (1 mol%).

3. Computational Studies

3.1 Computational Details

All calculations were done using ORCA 5.0.3. Geometry optimizations and frequency calculations were done at the unrestricted B3LYP level of theory,[3-5] with an atom pairwise dispersion correction with Becke-Johnson damping (D3BJ),[6, 7] together with the def2-TZVP basis set.[8] These calculations were done using the RIJCOSX approximation with the def2/J Coulomb fitting basis set.[9] Enthalpy and entropy were calculated at 393 K using the rigid-rotor harmonic oscillator (RRHO) approximation, as implemented in ORCA. Solvation energies were calculated for both hexane (to simulate melted polyethylene) and benzaldehyde using the SMD solvation model[10] at the B3LYP-D3BJ/def2-TZVP level. Comparison of relative free energies with either solvation model were within 1 kcal/mol of each other, implying that the polarity of the medium had little effect on the reaction rates, which is to be expected for radical reactions. Single point electronic energies were recalculated at the DLPNO-CCSD(T)/def2-TZVP level[11, 12] with NormalPNO settings. We note that the translational and rotational entropies calculated for our model system (*n*-pentane in benzaldehyde or hexane) will be higher than those in our experimental system (melted polyethylene) and hence, the free energies calculated for the model system should only be interpreted qualitatively. In addition, solvation model inadequately describes the experimental system (mix of melted PE, benzaldehyde and benzoic acid). Kinetic modelling of the real system would require molecular dynamics simulations which are outside the scope of this study and will be conducted in a future project.

3.2 Hydrogen atom transfer between 2-heptone and benzoylperoxyl radical



Scheme S1: Reaction free energies of hydrogen atom transfer reactions between 2-heptone and benzoylperxoy radical, at various positions along the 2-heptone chain.

3.3 Activation of alcohols by benzoylperoxy radical

The mechanism discussed in the manuscript goes via the benzoyloxy radical reacting with alcohols without a barrier in the alpha hydrogen atom transfer. However, it is possible that the benzoyloxy radical generated is consumed by benzaldehyde, leaving the alcohol unreacted. We thus studied the reaction of alcohols with benzoylperoxy radical. We found that oxidation of pentanol to the gem-diol proceeds through a similar oxygen rebound mechanism that was found for the alkane. Elimination of water from the gem-diol to the give ketone is expected to occur during workup.

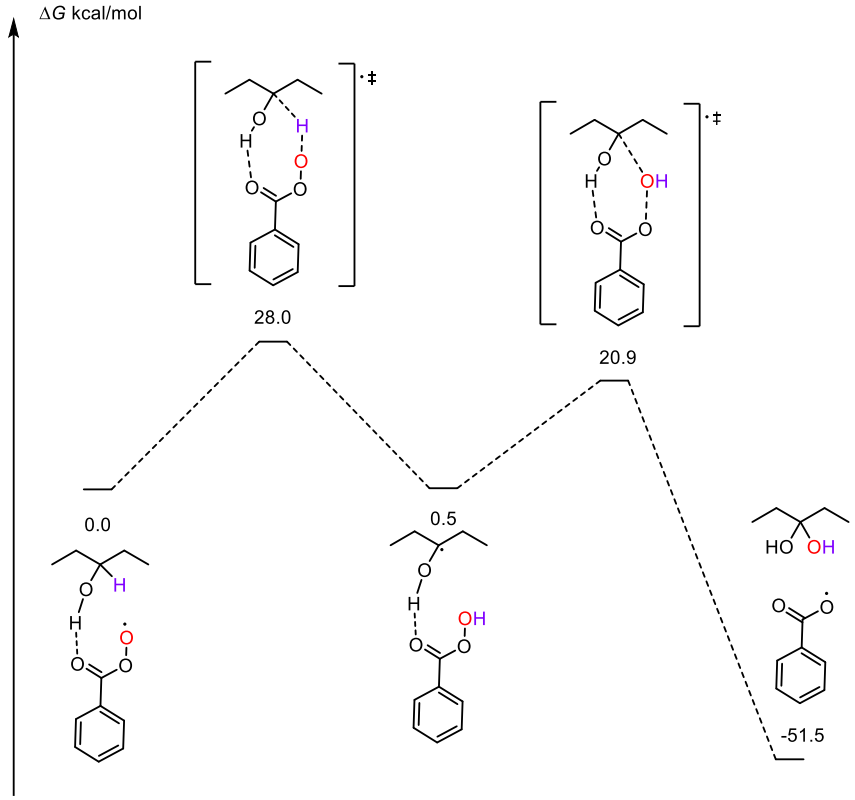


Figure S26. Reaction of benzoylperoxy radical with 3-pentanol via an oxygen rebound mechanism.

3.4 Analysis of hydroxyl transfer transition state (TS2B)

A key step in the profile outlined in Figure 3 is the transfer of a hydroxyl group from peroxybenzoic acid to the C-centered radical on the alkane. While a saddle point can be found (**TS2B**) at the unrestricted B3LYP-D3BJ/def2-TZVP level, intrinsic reaction coordinates (Figure S27) show that the electronic energy barrier is only 1.3 kcal/mol.

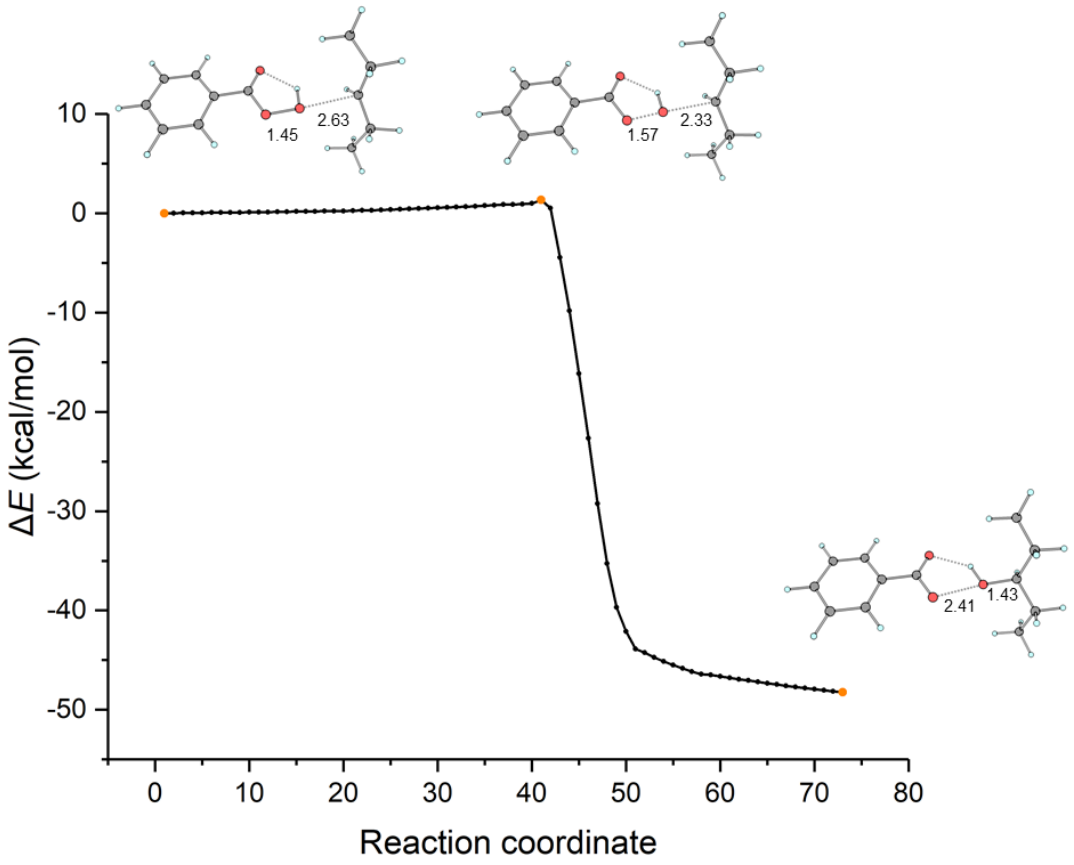


Figure S27. Intrinsic reaction coordinate for hydroxyl transfer from peroxybenzoic acid to the C-centered radical, calculated at B3LYP-D3BJ/def-TZVP level of theory.

Electronic energies of **TS2B** and the reactants calculated at the DLPNO-CCSD(T)/def-TZVP level gave a similar electronic barrier height of 1.91 kcal/mol. Distortion interaction analysis of **TS2B** (Figure S28) revealed a very low distortion energy for both reactants (0.2 kcal/mol for the C-centered radical and 3.7 kcal/mol for the peracid). Given the very low energy barrier found, the rate of hydroxyl transfer from the peracid to the C-centered radical can be considered diffusion controlled. The addition of O_2 to the C-centered radical is also diffusion controlled, and thus the rate of the two reactants would be determined by the strength of the solvent cage and the solubility of O_2 in the molten PE/benzaldehyde mixture.

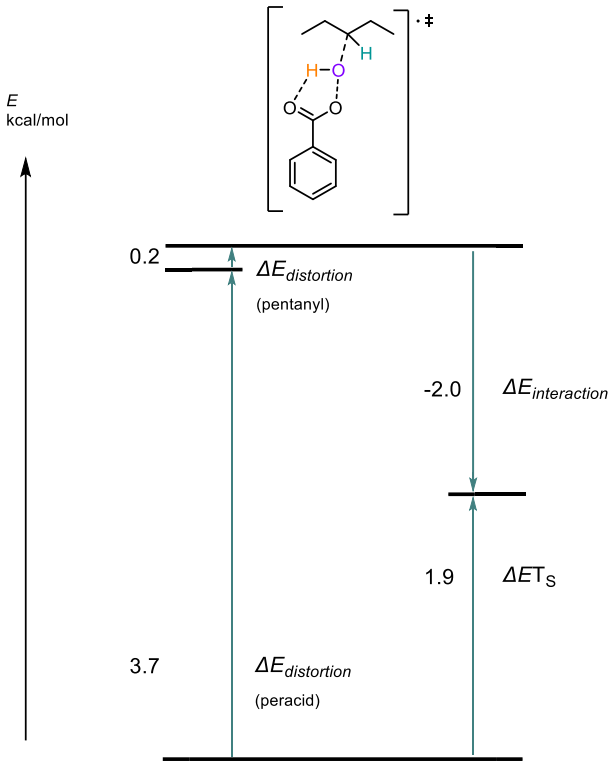
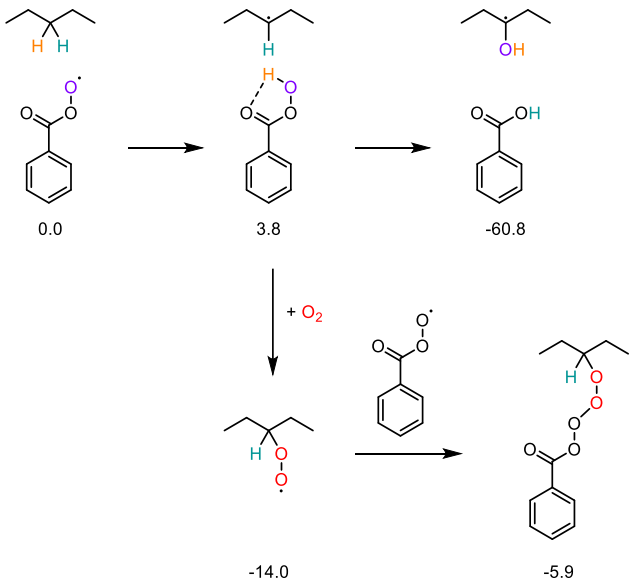


Figure S28. Distortion-interaction energy of **TS2B**.



Scheme S2: Alternate reactivity of C-centered radical.

Scheme S2 shows the alternate pathway from the C-centered radical, where addition of O_2 would yield a 3-pentylperoxy radical. The propagation steps from the alkyl peroxyl radical have already been studied,[13] and we also propose a Russell-type termination step which will also yield ketones.[14]

The products of the hydroxyl transfer reaction are an alcohol and a benzoyloxy radical. Hydrogen atom transfer of the alpha hydrogen atom to the benzoyloxy radical is barrierless (Figure S29).

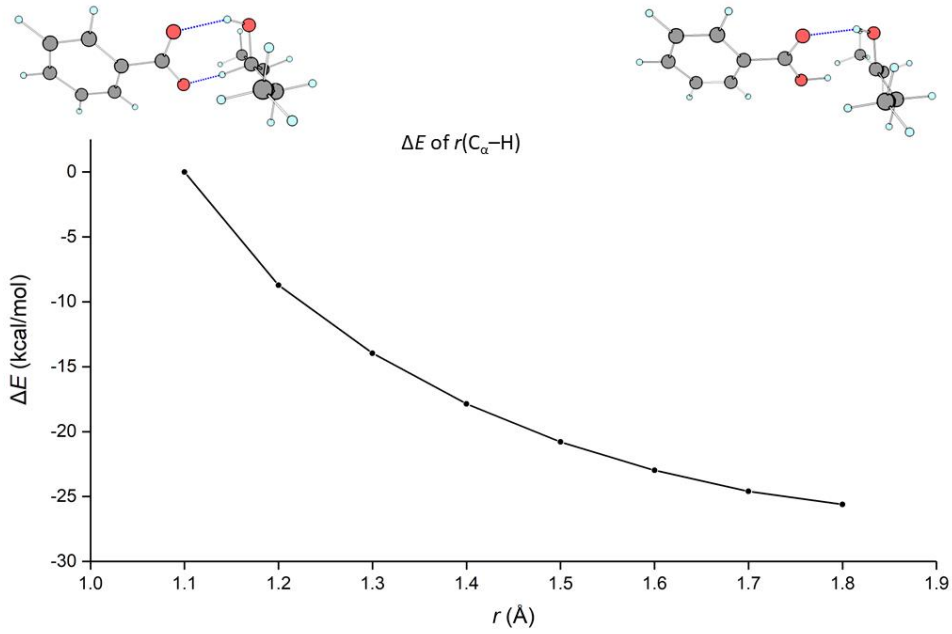
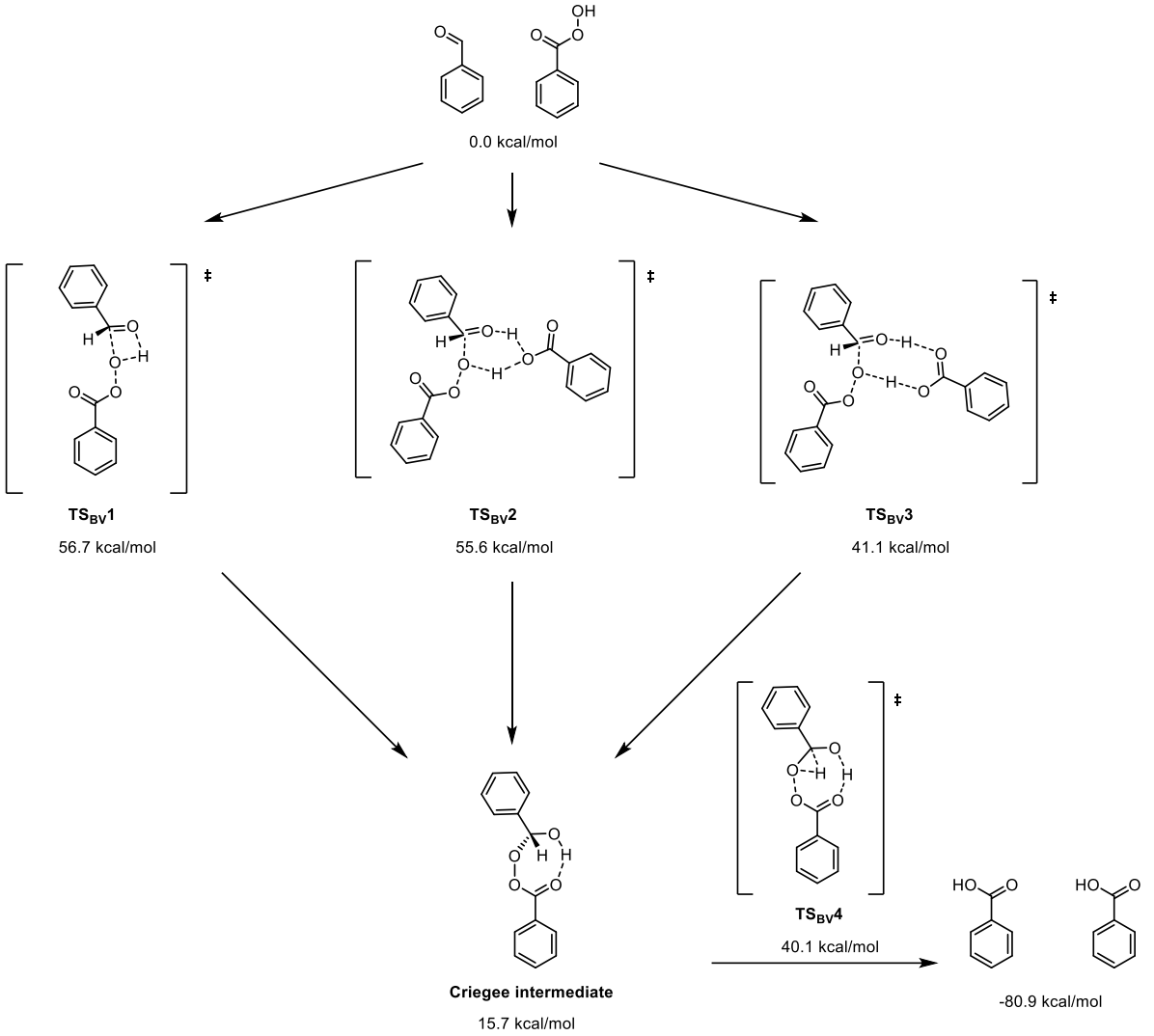


Figure S29. Relative single point electronic energies (DLPNO-CCSD(T)/def-TZVP) of B3LYP-D3BJ/def-TZVP geometries optimized with constrained C_α–H lengths, ranging from 1.1 Å to 1.8 Å.

3.5 Baeyer–Villiger reaction between benzaldehyde and peroxybenzoic acid

Given that a large excess of benzaldehyde was present in these reactions, it was possible that peroxybenzoic acid would be consumed by benzaldehyde in a Baeyer-Villiger type reaction. We thus modelled the reaction computationally to see if such a pathway was viable.

Scheme S3 details the possible transition states and the Criegee intermediate formed between peroxybenzoic acid and benzaldehyde.



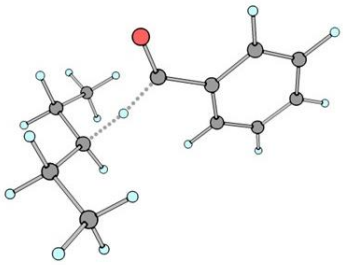
Scheme S3: Transition states of Baeyer–Villiger reaction between benzaldehyde and peroxybenzoic acid

The uncatalyzed reaction between peroxybenzoic acid and benzaldehyde proceeds over a very high reaction barrier ($\Delta G^{\ddagger}$ = 56.7 kcal/mol), and the tetrahedral Criegee intermediate is 15.7 kcal/mol uphill of the starting material.

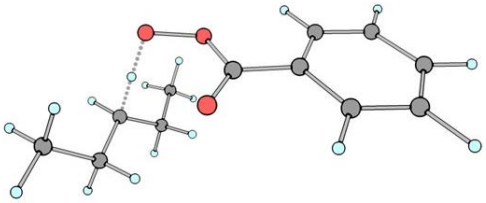
Baeyer–Villiger reaction can be catalysed by acids, and benzoic acid is present in the reaction.[15] We hence also investigated the benzoic acid catalysed reaction between peroxybenzoic acid and benzaldehyde. Two saddle points were found, with energy barriers of 55.6 and 41.1 kcal/mol. Considering the high barriers and the uphill energetics of the intermediate, we conclude that spontaneous reaction between benzaldehyde and peroxybenzoic acid is insignificant under our reported reaction conditions.

3.6 Structures of all transition states calculated

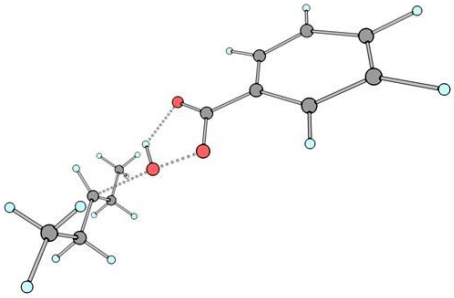
DFT-optimized molecular structures (B3LYP-D3BJ/def2-TZVP) of all transition states discussed.



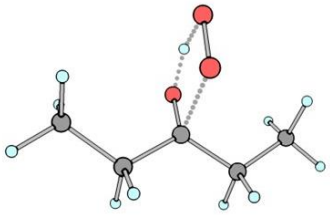
TS1



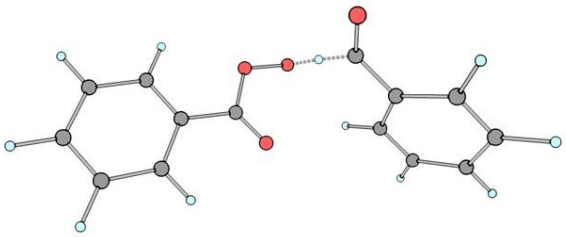
TS2A



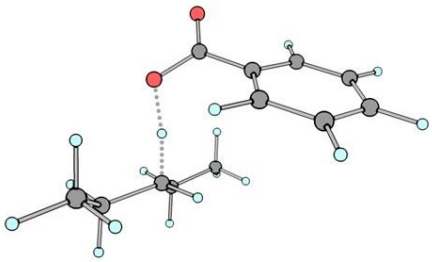
TS2B



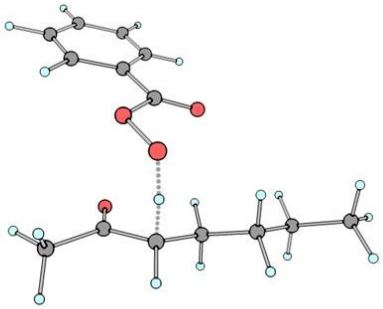
TS2C



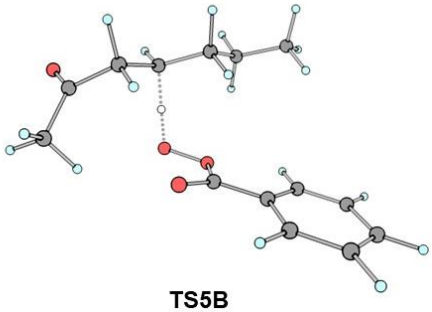
TS3



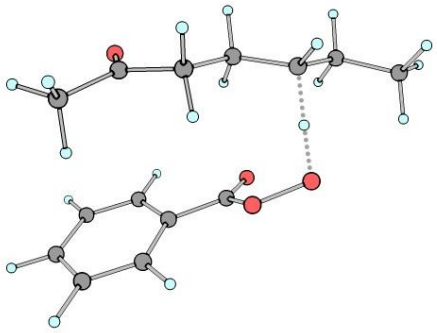
TS4



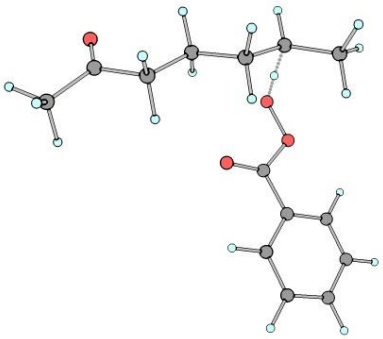
TS5A



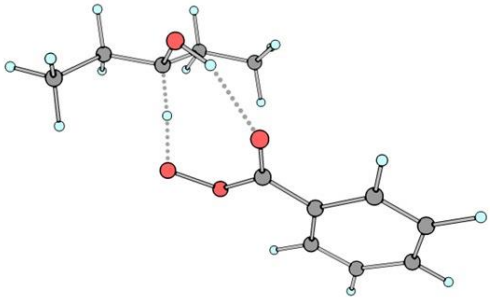
TS5B



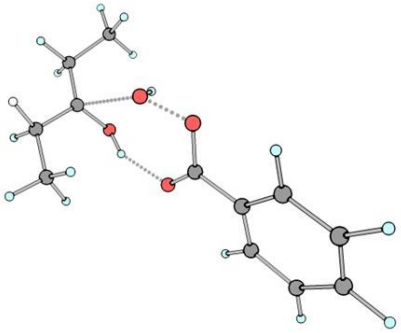
TS5C



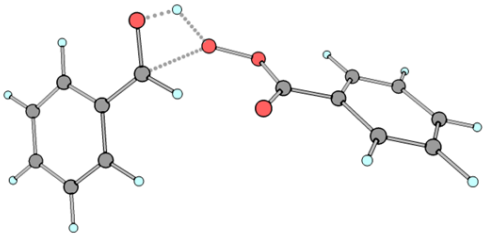
TS5D



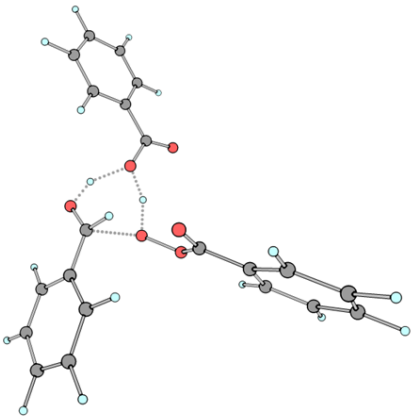
TS6A



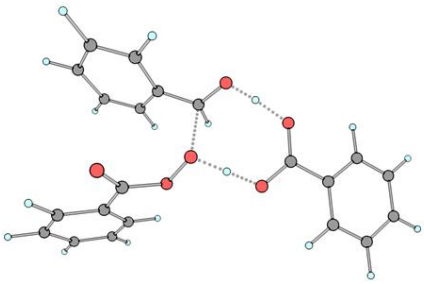
TS6B



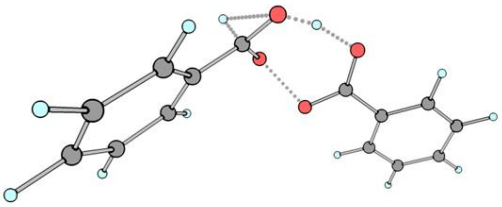
$TS_{BV}1$



$TS_{BV}2$



$TS_{BV}3$



$TS_{BV}2$

3.7 Computed Energies of all structures

Table S1. DFT-calculated gas phase electronic energies and Gibbs free energies, and SMD solvation corrected electronic energies calculated at the B3LYP-D3(BJ)/def2/TZVP level.

Structure	$E(el)_{Gas}$ E_h	G_{Gas} E_h	$E(el)_{Hexane}$ E_h	$E(el)_{Benzaldehyde}$ E_h
3-Hydroxy-3-pentanyl radical	-272.28345042	-272.17810538	-272.2905870	-272.2921034
3-Pentanol	-272.93762918	-272.81826342	-272.9446866	-272.9461482
3-Pentanone	-271.73903150	-271.64169578	-271.7472928	-271.7501097
Benzaldehyde	-345.52597279	-345.45952068	-345.5361584	-345.5393157
Benzoic acid	-420.78494263	-420.71446171	-420.7953975	-420.7986409
Benzoyl radical	-344.87562603	-344.82228182	-344.8843899	-344.8865338
Benzoyloxy radical	-420.10981797	-420.05400860	-420.1206334	-420.1243537
Benzoylperoxy radical	-495.25878145	-495.20116856	-495.2695867	-495.2758858
Hepta-2-one-3-yl radical	-349.69680823	-349.56261840	-349.7070212	-349.7097913
Hepta-2-one-4-yl radical	-349.68208021	-349.55276266	-349.6925275	-349.6955605
Hepta-2-one-5-yl radical	-349.68179358	-349.55078976	-349.6923032	-349.6952081
Hepta-2-one-6-yl radical	-349.68247197	-349.55324512	-349.6930193	-349.6961560
Hydroperoxide radical	-150.91321657	-150.92981330	-150.9172380	-150.9239192
Hydroxyl radical	-75.73517125	-75.75032119	-75.7382370	-75.7410351
$^3O_2$	-150.33036944	-150.35416510	-150.3318581	-150.3366113
Pentan-3-hydroxy-3-peroxyl radical	-422.67081840	-422.55950868	-422.6783276	-422.6826747
Pentan-3-yl radical	-197.05187445	-196.95117012	-197.0575458	-197.0568604
Pentan-3,3-diol	-348.17406620	-348.05172855	-348.1817424	-348.1842282
Pentane	-197.71533230	-197.59816740	-197.7208734	-197.7200520
Peroxybenzoic acid	-495.91446988	-495.84332143	-495.9247472	-495.9297087
Phenyl radical	-231.51596156	-231.46796554	-231.524	-231.525
Water	-76.42662869	-76.43011656	-76.4305868	-76.4340257
TS1	-542.56728599	-542.37420112	-542.5812666	-542.5831581
TS2A	-692.96108117	-692.76366588	-692.9758524	-692.9802292
TS2B	-692.96808652	-692.76949919	-692.9828454	-692.9862882
TS2C	-422.65829725	-422.55295347	-422.6663088	-422.6711702
TS3	-840.78346140	-840.63556714	-840.8015865	-840.8079049
TS4	-617.81855486	-617.62195971	-617.8346961	-617.8402650
TS5A	-845.59323991	-845.36486700	-845.6118865	-845.6187698
TS5B	-845.59311537	-845.36360548	-845.6115501	-845.6184953
TS5C	-845.59345082	-845.36371142	-845.6119948	-845.6202501
TS5D	-845.59119956	-845.36400596	-845.6108169	-845.6188857
TS6A	-768.19548133	-767.99260508	-768.2106956	-768.2158758
TS6B	-768.20291910	-767.99944483	-768.2178410	-768.2219152
$TS_{BV}1$	-841.3955188	-841.2280373	-841.4226015	-841.4151362
$TS_{BV}2$	-1262.2113064	-1261.9468184	-1262.2490252	-1262.2394081
$TS_{BV}3$	-1262.2349350	-1261.9695681	-1262.2698527	-1262.2617117
$TS_{BV}4$	-841.4182176	-841.2535329	-841.4431775	-841.4373976

Criegee Intermedate	-841.4493325	-841.2785065	-841.4730561	-841.4674003

Table S2. DLPNO-CCSD(T) calculated gas phase electronic energies, thermal corrections from DFT calculations and free energies calculated from DLPNO-CCSD(T) electronic energies and DFT thermal and solvation corrections.

Structure	E_{gas}	G_{Hexane}	$G_{Benzaldehyde}$
	E_h	kcal/mol	kcal/mol
3-Hydroxy-3-pentanyl radical	-271.83210466	-170515.631	-170516.582
3-Pentanol	-272.48981212	-170919.501	-170920.418
3-Pentanone	-271.29321557	-170183.204	-170184.972
Benzaldehyde	-344.95097007	-216424.740	-216426.721
Benzoic acid	-420.11539501	-263588.780	-263590.815
Benzoyl radical	-344.30057778	-216023.946	-216025.291
Benzoyloxy radical	-419.42909866	-263167.555	-263169.890
Benzoylperoxy radical	-494.48816917	-310266.705	-310270.658
Hepta-2-one-3-yl radical	-349.10836279	-218991.055	-218992.793
Hepta-2-one-4-yl radical	-349.09524586	-218986.029	-218987.932
Hepta-2-one-5-yl radical	-349.09484569	-218984.758	-218986.581
Hepta-2-one-6-yl radical	-349.09583617	-218986.519	-218988.487
Hydroperoxide radical	-150.71323104	-94586.939	-94591.131
Hydroxyl radical	-75.63684544	-47474.278	-47476.034
$^3O_2$	-150.13430963	-94226.588	-94229.571
Pentan-3-hydroxy-3-peroxyl radical	-422.02715770	-264760.961	-264763.688
Pentan-3-yl radical	-196.69634273	-123369.211	-123368.781
Pentan-3,3-diol	-347.63307759	-218071.145	-218072.705
Pentane	-197.36193781	-123776.467	-123775.952
Peroxybenzoic acid	-495.14636954	-310670.907	-310674.020
Phenyl radical	-231.10434095	-144995.128	-144995.621
Water	-76.32671865	-47900.422	-47902.580
TS1	-541.63159635	-339766.641	-339767.828
TS2A	-691.82997654	-434015.346	-434018.093
TS2B	-691.83967051	-434020.686	-434022.847
TS2C	-422.00655949	-264752.094	-264755.144
TS3	-839.42414429	-526665.284	-526669.249
TS4	-616.78155828	-386923.117	-386926.612
TS5A	-844.22961128	-529630.587	-529634.906
TS5B	-844.23051695	-529630.309	-529634.667
TS5C	-844.23130633	-529630.729	-529635.909
TS5D	-844.22852843	-529631.257	-529636.320
TS6A	-766.96445047	-481159.802	-481163.053
TS6B	-766.97773056	-481167.577	-481170.133
$TS_{BV}1$	-840.0383766	-527890.986	-527895.6706
$TS_{BV}2$	-1260.1851114	-791901.387	-791907.422
$TS_{BV}3$	-1260.2118821	-790645.346	-790650.455
$TS_{BV}4$	-840.0641285	-527057.006	-527060.6332
Criegee Intermedate	-840.1103961	-527081.488	-527085.037

3.8 Cartesian Coordinates of all structures

3-Hydroxy-3-pentanyl radical

C	1.364007027	0.289799745	-0.134803009
C	0.456768394	0.789212444	-1.262671961
H	-0.588620357	0.776132898	-0.951128500
H	0.680255494	1.822942141	-1.545130656
H	0.557169840	0.165814481	-2.153319031
C	2.815939606	0.212935100	-0.484882123
H	1.225819318	0.944493573	0.745055981
H	1.039148286	-0.704922975	0.178503137
C	3.765105481	-0.534105826	0.387606101
C	5.093412897	-0.883871688	-0.287103889
H	3.974136972	0.059596077	1.295177525
H	3.267649817	-1.444542858	0.731281558
H	5.746335396	-1.421838426	0.402841942
H	5.611338800	0.017615598	-0.613728864
H	4.929151845	-1.512643171	-1.164445685
O	3.390537470	1.330836868	-1.053511267
H	2.728007294	1.806930161	-1.566198386

3-Pentanol

C	-5.412812614	-0.785747262	-0.137815833
C	-3.995382557	-0.261105827	0.078709421
H	-5.515369472	-1.253492529	-1.121099992
H	-6.144990897	0.021020843	-0.078157057
H	-5.689439651	-1.522854425	0.620036792
C	-2.913651399	-1.327802834	-0.081551563
H	-3.906680304	0.173219236	1.079078092
H	-3.791651343	0.541060284	-0.637395135
C	-1.514292315	-0.766811670	0.126091364
C	-0.406511938	-1.782852499	-0.135866030
H	-1.447510745	-0.396301076	1.153767448
H	-1.392998233	0.098778403	-0.531608882
H	-0.516283250	-2.648689727	0.516641855
H	0.577506928	-1.344019590	0.039346652
H	-0.434867864	-2.135466250	-1.170310010
O	-3.078232624	-2.390028273	0.865544523
H	-2.978654030	-1.742452563	-1.099769109
H	-3.904087692	-2.847714241	0.679997462

3-Pentanone

C	-2.522728517	0.403923825	0.001962344
C	-1.408086775	-0.628504095	-0.080257849
H	-3.499237073	-0.079178335	-0.055511413

H	-2.445402374	1.126103698	-0.810919471
H	-2.467888542	0.962537205	0.936502575
C	-0.011587381	-0.034064827	-0.015835121
H	-1.476953665	-1.210038013	-1.006837103
H	-1.492912264	-1.367195407	0.724770127
C	1.139991248	-1.023713167	-0.054619971
C	2.514834010	-0.373495961	-0.006981169
H	1.022955727	-1.635334056	-0.956443546
H	1.004817281	-1.721157738	0.780007269
H	2.657113996	0.299292771	-0.852840856
H	3.299405510	-1.131172855	-0.031467696
H	2.633917874	0.218766155	0.900350034
O	0.172830945	1.158849798	0.061192847

Benzaldehyde

C	-1.934520666	1.786042955	0.000105030
C	-0.540264545	1.886057720	0.000173773
C	-2.536287234	0.538680635	-0.000010842
H	-2.521418775	2.695105103	0.000157272
C	-1.752479353	-0.614869297	-0.000067624
H	-3.615669507	0.457550919	-0.000057609
C	-0.365277963	-0.521308319	-0.000004825
H	-2.226903419	-1.588107417	-0.000160436
C	0.238742599	0.729111928	0.000110068
H	1.319449146	0.815061981	0.000160211
H	0.240114433	-1.418337600	-0.000047929
C	0.122900330	3.205896343	0.000332047
O	-0.447628354	4.270938495	-0.000334894
H	1.232323308	3.159436554	-0.000354240

Benzoic acid

C	-1.887048292	1.797186152	0.000050469
C	-0.493487911	1.875871304	0.000110471
C	-2.512509794	0.559840016	-0.000026625
H	-2.459390307	2.714552774	0.000071808
C	-1.750391165	-0.604801058	-0.000050546
H	-3.593178130	0.501258995	-0.000069415
C	-0.361562311	-0.530199276	0.000005063
H	-2.239577237	-1.570696485	-0.000112951
C	0.268840328	0.706437895	0.000083044
H	1.347206795	0.771653744	0.000126912
H	0.230245502	-1.436355628	-0.000013346
C	0.128595046	3.222943667	0.000202708
O	-0.478197868	4.266322790	-0.000044930
O	1.483914148	3.182734776	-0.000086526

H	1.784498734	4.104260621	-0.000246135

Benzoyl radical

C	-1.945726744	1.778661584	-0.000000566
C	-0.548994241	1.877132312	-0.000000503
C	-2.544304975	0.529514095	-0.000000182
H	-2.538551161	2.683897203	-0.000000874
C	-1.756570624	-0.620580015	0.000000261
H	-3.623615857	0.446010444	0.000000123
C	-0.369301517	-0.524812177	0.000000059
H	-2.228995568	-1.594779840	0.000000814
C	0.235731576	0.724661528	-0.000000401
H	1.313544125	0.823139685	-0.000000487
H	0.236809294	-1.421207758	0.000000200
C	0.109975809	3.198542458	-0.000000132
O	-0.381090116	4.275890483	0.000001688

Benzoyloxy radical

C	-1.891800401	1.792469093	0.001055657
C	-0.498619928	1.858898974	-0.000178614
C	-2.518469712	0.555261607	0.001289085
H	-2.469350516	2.707668833	0.001907063
C	-1.756103249	-0.609402188	0.000223267
H	-3.598836642	0.496034842	0.002359613
C	-0.365716133	-0.541924385	-0.001058325
H	-2.247702635	-1.573950660	0.000397964
C	0.266235544	0.692422821	-0.001228374
H	1.346107169	0.763323055	-0.002209460
H	0.221540828	-1.450631328	-0.001951886
C	0.170230087	3.166428062	-0.000286000
O	-0.424960865	4.276515295	-0.003894047
O	1.419320453	3.329907979	0.003574056

Benzoylperoxy radical

C	-1.918629072	1.797044469	0.000030797
C	-0.523925735	1.903363057	0.000052957
C	-2.517815535	0.548733822	-0.000000289
H	-2.511166634	2.701520039	0.000054768
C	-1.730941386	-0.600153174	-0.000025307
H	-3.596801295	0.467912819	-0.000003047
C	-0.344127549	-0.498979393	-0.000015564
H	-2.200618111	-1.575519020	-0.000051604
C	0.264363604	0.748007853	0.000024431
H	1.341159247	0.825858092	0.000036618
H	0.264943692	-1.393221355	-0.000037293

C	0.047113447	3.261162618	0.000111319
O	-0.519242377	4.302593634	-0.000166383
O	1.496582148	3.187733305	0.000092080
O	2.073777264	4.370701990	-0.000107116

Carbon dioxide

C	0.000000014	0.000000014	0.000000006
O	-0.000000007	-0.000000007	1.159944404
O	-0.000000007	-0.000000007	-1.159944410

Hepta-2-one-3-yl radical

C	-4.096985615	0.453320723	-0.578845056
C	-5.464281814	-0.187107448	-0.713391975
H	-5.589630295	-0.727236286	-1.651606441
H	-6.229925660	0.587181362	-0.640885516
H	-5.620640057	-0.876031731	0.118882059
C	-3.130088153	0.259969332	-1.623421636
C	-1.764147702	0.823636202	-1.547439220
H	-3.390343610	-0.377623684	-2.461597098
C	-0.737455798	-0.212001759	-1.038028698
H	-1.766225095	1.678516146	-0.869377543
H	-1.448460378	1.166340554	-2.538440878
C	0.679794500	0.352683183	-0.979197198
H	-0.754807373	-1.095413502	-1.684862755
H	-1.043747491	-0.545412044	-0.042699320
C	1.696983734	-0.660127309	-0.460517972
H	1.735026538	-1.544750765	-1.101222522
H	1.440060062	-0.993102637	0.547974499
H	2.700761529	-0.232432412	-0.423927135
H	0.684425346	1.240267247	-0.338897903
H	0.974289629	0.693337158	-1.977355615
O	-3.822998530	1.122858581	0.422830058

Hepta-2-one-4-yl radical

C	-4.330585561	0.668131075	-0.678411506
C	-5.693496797	0.074419556	-0.960176849
H	-5.811827695	-0.894919785	-0.471465822
H	-5.796291870	-0.092921780	-2.036344852
H	-6.472961755	0.759180499	-0.633141461
C	-3.153042576	-0.288636568	-0.795663700
C	-1.815813810	0.338695574	-0.693564001
H	-3.266946934	-0.854701926	-1.733473248
H	-3.298493650	-1.058203664	-0.016409923
C	-0.579361830	-0.467573832	-0.854525461
H	-1.763717781	1.387346784	-0.433827922

C	0.710308736	0.351641587	-0.800870553
H	-0.615974082	-1.025825070	-1.803460035
H	-0.537559044	-1.252538444	-0.080079128
C	1.964405586	-0.499604571	-0.972761897
H	1.958728446	-1.019811479	-1.934129711
H	2.036843236	-1.257431777	-0.188295620
H	2.869059479	0.109752284	-0.930352072
H	0.752607456	0.884021884	0.154267466
H	0.674974663	1.120560982	-1.578388555
O	-4.192740455	1.832059582	-0.384683020

Hepta-2-one-5-yl radical

C	-4.355259884	0.677577954	-0.906912846
C	-5.670067365	-0.077352033	-0.972531876
H	-5.542630161	-1.158290722	-0.921985936
H	-6.179720271	0.182147593	-1.902342559
H	-6.308317589	0.251166456	-0.150477859
C	-3.095472994	-0.156618959	-0.812252643
C	-1.805392702	0.650041116	-0.761909950
H	-3.091453412	-0.849994801	-1.662332272
H	-3.191535732	-0.798839559	0.072425427
C	-0.584051408	-0.191219712	-0.658659922
H	-1.864887937	1.354988532	0.082210629
H	-1.746944801	1.297350380	-1.644504511
C	0.773142843	0.399344145	-0.802063962
H	-0.669391306	-1.195746249	-0.255296841
C	1.884632575	-0.638067211	-0.959247297
H	1.729215121	-1.243183708	-1.854798326
H	1.910383493	-1.314033062	-0.101183882
H	2.863472143	-0.161859648	-1.038261103
H	0.996978403	1.034284019	0.072348889
H	0.782346149	1.090086876	-1.654866754
O	-4.332031404	1.886559505	-0.932714273

Hepta-2-one-6-yl radical

C	-4.346562943	0.704032977	-0.830724825
C	-5.693777472	0.041659653	-1.024847159
H	-5.820072972	-0.792194369	-0.330207432
H	-5.756532025	-0.373171284	-2.034756386
H	-6.490638528	0.768515607	-0.883669717
C	-3.139744764	-0.216401065	-0.836826791
C	-1.799560078	0.502347024	-0.791819480
H	-3.209362997	-0.864611660	-1.718584928
H	-3.245088153	-0.894352929	0.020035380
C	-0.614878787	-0.463355332	-0.768360671

H	-1.767494242	1.149313784	0.087619336
H	-1.715585019	1.167210485	-1.654578708
C	0.710246389	0.208855676	-0.714482769
H	-0.654208985	-1.124436880	-1.645803822
H	-0.725747107	-1.143744145	0.095500360
C	1.966301730	-0.552879791	-0.933579560
H	1.897774862	-1.193185842	-1.820294935
H	2.190636278	-1.226227726	-0.090600307
H	2.828466187	0.104523774	-1.054596533
H	0.763738228	1.213360961	-0.310582539
O	-4.242823113	1.899733661	-0.683753137

$^{3}O_{2}$

O	0.000000000	0.000000000	0.602277073
O	0.000000000	0.000000000	-0.602277073

Hydroxyl radical

O	0.000000000	0.000000000	0.011513796
H	0.000000000	0.000000000	0.988486204

Hydroperoxyl radical

O	-0.008530197	0.003609797	-0.002533275
O	0.847294143	0.776875107	-0.657039590
H	-0.897273946	0.340005096	-0.234697135

Penta-3,3-diol

C	0.892621986	-0.948359444	-0.065131124
C	-0.428727977	-1.711996253	-0.059752647
H	-1.267680134	-1.022195926	-0.162868507
H	-0.580447482	-2.254336980	0.877426899
H	-0.472583504	-2.425345449	-0.882794899
C	2.136964404	-1.837390398	0.004733558
H	0.931449662	-0.258284417	0.780544725
H	0.967414233	-0.350257104	-0.975993195
C	3.414532187	-0.997942850	0.089165942
C	4.705206955	-1.812215799	0.070860695
H	3.362449824	-0.412172666	1.009567300
H	3.402177771	-0.293591068	-0.745412788
H	4.720659338	-2.540393493	0.881880726
H	5.570438907	-1.157642181	0.185612851
H	4.836122483	-2.344324168	-0.875257248
O	2.133158768	-2.665477759	1.158883496
H	1.345014432	-3.220162338	1.118588865
O	2.109666230	-2.644650312	-1.163939840
H	2.874511917	-3.231591397	-1.132174810

Pentan-3-hydroxy-3-peroxyl radical

C	-2.576774601	0.108480703	0.064566218
C	-1.365613211	-0.815165236	0.005000755
H	-2.590976763	0.783017287	-0.790926927
H	-2.572143751	0.711184829	0.973631162
H	-3.497991699	-0.475517111	0.054638312
C	-0.028278349	-0.087109526	-0.034637776
H	-1.406521181	-1.434586907	-0.895013665
H	-1.354504751	-1.498108986	0.857906532
C	1.171757045	-1.031692824	-0.043626580
C	2.523271025	-0.327854959	-0.079759033
H	1.055600710	-1.667055285	-0.925929742
H	1.099392861	-1.684579208	0.829492921
H	2.611687275	0.300391195	-0.966041296
H	3.329418174	-1.062182759	-0.104926947
H	2.671654252	0.299064986	0.800530185
O	0.059178725	0.635650410	1.319412392
O	0.332070163	1.904731639	1.205667927
O	0.019388562	0.855579238	-1.032418133
H	0.275401199	1.695987256	-0.598430439

Pentan-3-yl radical

C	-2.495493348	0.216916317	0.031443626
C	-1.383366971	-0.825465689	-0.087525527
H	-2.500999369	0.880915071	-0.836260253
H	-2.356493208	0.834361556	0.921192434
H	-3.477443822	-0.255357650	0.096524325
C	-0.022429142	-0.239775835	-0.214791363
H	-1.594038319	-1.473964450	-0.955643918
H	-1.411393386	-1.501167108	0.776945783
C	1.201316815	-1.062595669	-0.022763251
H	0.077613168	0.746316746	-0.658099400
C	2.496933287	-0.252400629	-0.011058634
H	1.263869625	-1.829115813	-0.814429342
H	1.112736391	-1.637173625	0.909149997
H	2.622273024	0.294736214	-0.948359809
H	3.368035770	-0.897095703	0.118475942
H	2.492377484	0.477208268	0.801473389

***n*-Pentane**

C	-2.540254182	0.190685020	0.003327605
C	-1.356450494	-0.772963763	0.002526540
H	-2.522699441	0.834987593	-0.879453309
H	-2.518758154	0.838570858	0.883409040

H	-3.492591328	-0.343302830	0.006567681
C	-0.005077953	-0.061535389	0.000562641
H	-1.418275755	-1.429153859	-0.872215794
H	-1.416205018	-1.428213104	0.878104066
C	1.188049708	-1.014109972	-0.006149507
H	0.059514182	0.593029240	0.877826316
H	0.054091518	0.598421088	-0.873047429
C	2.532993679	-0.291811494	-0.004933630
H	1.123117689	-1.665465330	-0.884294543
H	1.126248295	-1.674236707	0.865667693
H	2.634328858	0.351219950	-0.882945885
H	3.366430072	-0.997190904	-0.011225529
H	2.638548326	0.340439603	0.880374044

Peroxybenzoic acid

C	0.658441138	1.226547173	0.083035008
C	0.039718498	2.376733656	-0.382070152
C	-1.236045369	2.306192034	-0.932369444
C	-1.894416829	1.083548768	-1.016953411
C	-1.282253533	-0.070944741	-0.552157525
C	-0.001203108	-0.000702906	0.000207315
H	1.649733919	1.259155431	0.513343538
H	0.551173229	3.328035583	-0.316105036
H	-1.718028017	3.204718941	-1.296055650
H	-2.886331335	1.030031147	-1.446009716
H	-1.790936932	-1.022002475	-0.616787243
C	0.705170858	-1.193564031	0.512046561
O	1.825498731	-1.220061466	0.972510410
O	-0.043752243	-2.318016038	0.418727549
O	0.671274235	-3.456695360	0.915242945
H	1.518726828	-3.028269720	1.183979176

Water

O	-6.568557924	3.326062307	-0.014582476
H	-5.606279273	3.347137270	-0.042849258
H	-6.856052803	3.875360423	-0.751328266

TS1

C	-0.304437938	-0.142863848	-0.099402335
C	-1.612363877	-0.577232596	0.035772186
C	-1.881522337	-1.934491009	0.208513244
C	-0.843249554	-2.858360785	0.245787332
C	0.469359594	-2.425707768	0.110267554
C	0.743213549	-1.068958914	-0.062002895
H	-0.069970151	0.904995679	-0.234268588

H	-2.426738365	0.135496946	0.007625886
H	-2.905410678	-2.270461084	0.313932256
H	-1.057449669	-3.910673737	0.379796566
H	1.288229805	-3.132337204	0.137628700
C	2.146869634	-0.625287142	-0.200255672
O	2.519986447	0.503859394	-0.350281577
H	3.062430035	-1.619866548	-0.171470362
C	4.189000906	-2.460355058	-0.182637417
H	3.772254435	-3.470953157	-0.149601294
C	4.918063337	-2.070865779	1.077963129
H	5.898457908	-2.568373554	1.105088000
H	5.131820284	-0.996717327	1.049666062
C	4.849651080	-2.128141951	-1.496117286
H	5.828708692	-2.626163833	-1.551575309
H	5.060868155	-1.053757558	-1.528218235
C	4.010617121	-2.524008624	-2.709639945
H	4.519138048	-2.278643313	-3.643607124
H	3.807051065	-3.597957422	-2.711457229
H	3.049381244	-2.004899561	-2.708921291
C	4.143395180	-2.408219961	2.350687949
H	3.944547709	-3.481131474	2.415132597
H	4.697770586	-2.117353521	3.244655019
H	3.181208755	-1.891291290	2.373428079

TS2A

C	-0.149560724	2.416671538	-0.134109386
C	-0.677447716	3.598690555	-0.630012605
C	-1.655659923	3.562268874	-1.618931107
C	-2.105720478	2.341317780	-2.110142042
C	-1.581255751	1.154794789	-1.617050075
C	-0.598307505	1.189144839	-0.625006113
H	0.609649024	2.421675288	0.635717484
H	-0.328461392	4.548450435	-0.246137139
H	-2.068068244	4.485508150	-2.005664125
H	-2.867874424	2.313443951	-2.877943956
H	-1.931884098	0.205889178	-1.995341817
C	0.008422803	-0.038973951	-0.049115886
O	0.840222793	-0.071493342	0.813734816
O	-0.493128837	-1.157900659	-0.672194620
O	-0.049335951	-2.355201061	-0.092516116
H	1.115078151	-2.503822544	-0.497484222
C	2.328174070	-2.651857316	-0.969252611
H	2.317713466	-3.736329374	-1.115333498
C	3.250648861	-2.199494841	0.132290240
H	4.282022400	-2.390687873	-0.200244038

H	3.159879998	-1.119108995	0.260275223
C	2.336551393	-1.872639749	-2.258457404
H	3.362486835	-1.890468414	-2.655084999
H	2.127255679	-0.818911514	-2.048431446
C	1.370656821	-2.405308182	-3.313850420
H	1.430248844	-1.817561912	-4.231329221
H	1.601385598	-3.443005611	-3.565692868
H	0.341696929	-2.369022470	-2.954532828
C	3.003079313	-2.898449632	1.466791795
H	3.081802212	-3.984001263	1.365833917
H	3.729491001	-2.578423025	2.215336943
H	2.006472865	-2.659277168	1.838883010

TS2B

C	1.193938597	2.880726071	-2.753861829
C	2.066398517	3.858852601	-3.207451158
C	3.222316393	4.147958269	-2.489126067
C	3.506249882	3.456392134	-1.315978716
C	2.637213109	2.476769364	-0.857496683
C	1.476865945	2.185998087	-1.577388954
H	0.289916462	2.640912134	-3.296220037
H	1.845616293	4.397074772	-4.120107079
H	3.902309398	4.912257691	-2.843544124
H	4.405540251	3.681420558	-0.757487231
H	2.852699240	1.936960645	0.053505720
C	0.509742919	1.147522474	-1.133092168
O	-0.514660716	0.861387160	-1.727432509
O	0.875314974	0.549350558	-0.000536121
O	-0.193438210	-0.533261583	0.381111115
H	-0.808599572	-0.345384929	-0.364309083
C	-1.655322640	-2.240713144	1.005504967
H	-2.531609843	-1.622043114	0.829919139
C	-1.167157931	-2.363828288	2.402969436
H	-1.598638536	-3.278330012	2.843796954
H	-0.085297358	-2.536149058	2.387861576
C	-1.313874931	-3.268135860	-0.012686957
H	-1.755423912	-4.228764109	0.302419155
H	-0.231128676	-3.435177743	-0.002990840
C	-1.786275873	-2.942395921	-1.428275387
H	-1.560665238	-3.760662641	-2.113884882
H	-2.865821192	-2.776103160	-1.452049850
H	-1.300039076	-2.044198758	-1.812704488
C	-1.497599319	-1.167434280	3.291676547
H	-2.577030786	-1.004755168	3.342823173
H	-1.135878971	-1.323720963	4.309362429

H	-1.036527547	-0.262523779	2.896381879

TS2C

C	-2.656640687	0.043017171	-0.123520215
C	-1.470738691	-0.909987380	-0.053251443
H	-2.680263929	0.565124551	-1.079421778
H	-2.607607655	0.790581530	0.668726893
H	-3.591047795	-0.507657660	-0.009020060
C	-0.126171926	-0.266711415	-0.294207250
H	-1.570952096	-1.689474974	-0.819922509
H	-1.439089007	-1.435325686	0.903966366
C	1.086002009	-1.150609711	-0.122836283
C	2.423306675	-0.432077750	-0.245359874
H	1.003447567	-1.922408087	-0.899270201
H	1.002474078	-1.676066538	0.831136280
H	2.496770024	0.092644711	-1.197330880
H	3.243932578	-1.147647511	-0.182525585
H	2.551247336	0.298625314	0.553705764
O	0.019077282	0.795250140	1.414109440
O	0.118923791	1.981387493	0.925488606
O	-0.048896098	0.766748697	-1.048645286
H	0.056018545	1.648784101	-0.272483988

TS3

C	-2.934608684	1.087819770	-3.516143273
C	-3.443446601	-0.195156965	-3.338082348
C	-2.688047715	-1.160137744	-2.680215995
C	-1.423785870	-0.848705472	-2.200093243
C	-0.911085483	0.438662918	-2.378487851
C	-1.672329429	1.404751209	-3.039068552
H	-1.257609006	2.395000608	-3.167187610
H	-3.522265392	1.838980535	-4.027650017
H	-4.428776589	-0.442799028	-3.712167541
H	-3.084156325	-2.157645053	-2.541506801
H	-0.835269537	-1.596967884	-1.689773699
C	0.430790145	0.843713063	-1.890406749
O	0.918197146	1.935907838	-2.000480338
O	1.078681254	-0.220549626	-1.309000531
O	2.292922565	0.136612059	-0.723064794
C	6.092522896	3.506728406	-3.441110110
C	5.674718152	4.400430356	-2.455192723
C	4.671614062	4.047133609	-1.559683777
C	4.079734413	2.794468734	-1.640480653
C	4.497544199	1.902177052	-2.628846981
C	5.504703164	2.257900609	-3.534566070

H	5.809633431	1.549252066	-4.292859476
H	6.873771957	3.790564080	-4.134176731
H	6.135635437	5.377936441	-2.388686602
H	4.348189347	4.748585840	-0.802157503
H	3.280121972	2.507165498	-0.971712222
C	3.866456769	0.578596978	-2.718085448
O	4.000392758	-0.249956841	-3.564778546
H	3.107586960	0.334357945	-1.741213817

TS4

C	-0.354747935	0.320642643	0.848926481
C	-1.426705345	-0.472159623	1.232434682
C	-1.667918713	-1.679107307	0.583343082
C	-0.832361337	-2.092742982	-0.448379452
C	0.255062729	-1.312056280	-0.817197106
C	0.501212218	-0.103705368	-0.166978777
H	-0.165695598	1.271178429	1.329461054
H	-2.079115360	-0.147116005	2.032561030
H	-2.509737759	-2.293181730	0.877079418
H	-1.029448693	-3.021946120	-0.967542402
H	0.900941575	-1.628638783	-1.623989266
C	1.631745479	0.786463196	-0.558887931
O	1.551984953	1.999203525	-0.528674786
C	3.453173666	-2.060351733	-0.077069113
H	2.546890055	-2.656951121	0.057317457
C	4.116657435	-1.706985157	1.231536179
H	4.578764094	-2.623054800	1.626429786
H	4.940542630	-1.011630657	1.046345954
C	4.341325215	-2.576746853	-1.183605957
H	4.804538467	-3.510421413	-0.834518542
H	5.164317440	-1.874465710	-1.344636830
C	3.602464041	-2.828936142	-2.495144337
H	4.272405771	-3.238419277	-3.252424615
H	2.783837767	-3.539278816	-2.354924476
H	3.182722118	-1.900540432	-2.886609583
C	3.162636957	-1.128028324	2.273586050
H	2.314878711	-1.794786778	2.445629869
H	3.671029657	-0.975667839	3.226679679
H	2.767198211	-0.16425099	1.951249786
O	2.762699554	0.244491016	-0.982438356
H	3.003968002	-0.998362568	-0.517963978

TS5A

C	-1.929175235	-1.345510456	1.919570016
C	-3.418877396	-1.214254745	1.713724397

H	-3.808082169	-2.108357562	1.221281648
H	-3.631881977	-0.364663346	1.059592216
H	-3.914242352	-1.068289744	2.670751311
C	-1.118596946	-1.726378819	0.724911273
C	0.374233646	-1.590226076	0.792006769
H	-1.574130501	-1.446354367	-0.226958759
H	-1.387308028	-3.000696712	0.719410255
C	1.110905671	-2.390763571	-0.281230070
H	0.714410320	-1.884359381	1.785073897
H	0.621286674	-0.523852029	0.686646076
C	2.626196633	-2.232226932	-0.193105785
H	0.767917664	-2.082799352	-1.276040194
H	0.851229450	-3.446512534	-0.168081909
C	3.370332033	-3.053545109	-1.241995272
H	3.081835775	-2.755720861	-2.253470300
H	3.147391289	-4.117727982	-1.134047867
H	4.451355473	-2.928456506	-1.153824604
H	2.954238899	-2.531848825	0.807041188
H	2.889220300	-1.174017713	-0.299038235
O	-1.408987007	-1.183729851	3.005724994
C	0.036471156	-5.106565795	5.151502236
C	-0.177515378	-5.355462706	6.497791676
C	-1.045406038	-4.845153846	4.308276099
H	1.033505698	-5.108635732	4.733542907
C	-1.471186895	-5.340309634	7.010485089
H	0.662442971	-5.559038146	7.149012571
C	-2.550864773	-5.077335857	6.174071794
H	-1.637827759	-5.531724104	8.062953499
C	-2.343286297	-4.830480726	4.824707773
H	-3.556085660	-5.061951627	6.574481632
H	-3.180439984	-4.621888915	4.175316670
C	-0.744245925	-4.582361215	2.882544020
O	0.339808848	-4.514273395	2.383259605
O	-1.924458351	-4.402458997	2.164062014
O	-1.700293828	-4.210027832	0.806624369

TS5B

C	-2.158613149	-0.832983273	-2.015257633
C	-1.232960964	-1.954438966	-2.490153532
C	0.215116401	-1.551293005	-2.380300921
H	-1.469463081	-2.255982744	-3.510045747
H	-1.414944883	-2.811241455	-1.827119845
C	1.238542155	-2.472253474	-2.987000296
H	0.985922247	-2.667393634	-4.034833937
H	1.158835914	-3.449339666	-2.486243971

H	0.474609086	-1.156833354	-1.396620011
H	0.299633007	-0.447701450	-3.085022302
C	0.350518083	-1.743888304	-8.019723229
C	1.043416929	-2.205741827	-9.128039956
C	1.029002766	-1.074233665	-6.999735088
H	-0.716411479	-1.891522486	-7.925103156
C	2.417581849	-2.007131995	-9.221432651
H	0.514209106	-2.721560807	-9.918588115
C	3.097536161	-1.343609658	-8.205518405
H	2.958689370	-2.370115979	-10.085977260
C	2.408765100	-0.875032882	-7.095816946
H	4.166484909	-1.191368721	-8.277770500
H	2.935662328	-0.360530775	-6.305921674
C	0.233208748	-0.621299603	-5.830717542
O	-0.926913847	-0.860896145	-5.636318282
O	1.024982295	0.093637316	-4.965741362
O	0.336545607	0.543522023	-3.829798237
O	-2.041390039	-0.381325948	-0.899773208
C	-3.169693392	-0.328290051	-3.005705210
H	-2.643524688	0.018435856	-3.899005339
H	-3.817988220	-1.149534695	-3.325062862
H	-3.764383752	0.471075892	-2.569552723
C	2.678254374	-1.968609409	-2.882364655
H	2.949156429	-1.876576938	-1.826176717
H	2.737973501	-0.963089463	-3.304347240
C	3.668547021	-2.884058760	-3.596081643
H	3.639860041	-3.896907398	-3.186286239
H	3.437779644	-2.951970861	-4.662361713
H	4.690973422	-2.514677695	-3.499160848

TS5C

C	-3.778041679	-2.439342162	-5.106801464
C	-4.690273732	-3.543856321	-5.585543615
H	-5.211473715	-4.021593315	-4.753520943
H	-4.079372204	-4.311316704	-6.069191212
H	-5.403661026	-3.154217466	-6.308486379
C	-2.980317887	-2.728960732	-3.848861109
C	-1.864431601	-1.721360843	-3.586515804
H	-2.589894584	-3.746934614	-3.920199365
H	-3.690570529	-2.752971905	-3.013173760
C	-0.905190347	-2.127654799	-2.498244262
H	-2.309480115	-0.755009187	-3.316780548
H	-1.313210931	-1.531041454	-4.507919903
C	0.254337787	-1.201503829	-2.233485925
H	-0.308472623	-3.226661669	-2.901310173

H	-1.387369895	-2.501063207	-1.589999241
C	1.243449925	-1.731948740	-1.198185726
H	1.701178658	-2.661973894	-1.539028956
H	0.748863845	-1.929118711	-0.243893391
H	2.043182582	-1.012158000	-1.017838599
H	-0.156248392	-0.239321743	-1.893951827
H	0.767391860	-0.998004924	-3.176993238
O	-3.674204493	-1.393356940	-5.706067211
C	-1.306394889	-3.516932166	-7.685405804
C	-2.136208566	-3.903721500	-8.726958856
C	-1.027951523	-4.407512741	-6.648122187
H	-0.881466281	-2.523618390	-7.649796414
C	-2.675601298	-5.185739936	-8.747543984
H	-2.365723582	-3.204177794	-9.519753848
C	-2.389836425	-6.080256886	-7.720515782
H	-3.321046776	-5.487728982	-9.562486522
C	-1.575554449	-5.692607119	-6.665778717
H	-2.806179066	-7.078991491	-7.739292671
H	-1.360085083	-6.380733189	-5.861103632
C	-0.175262545	-3.915248943	-5.535783290
O	0.544313215	-2.959199613	-5.566784472
O	-0.400970585	-4.678389048	-4.409738285
O	0.316808949	-4.232715045	-3.290223883

TS5D

C	-4.833388363	-1.102594393	-2.922574368
C	-6.031595546	-1.412172636	-3.793559774
H	-6.165611021	-2.489787690	-3.911962518
H	-5.860109101	-0.999160822	-4.791863321
H	-6.928444969	-0.964108792	-3.371116574
C	-3.571244347	-1.888049632	-3.223566438
C	-2.319787724	-1.342204838	-2.554269863
H	-3.436060728	-1.924847303	-4.309537533
H	-3.763547751	-2.925189837	-2.916507559
C	-1.097231925	-2.218160048	-2.821661583
H	-2.488308122	-1.244467329	-1.479782590
H	-2.131183301	-0.338461973	-2.936832581
C	0.202598388	-1.594891421	-2.386727717
H	-1.039429561	-2.460474645	-3.886528162
H	-1.208227720	-3.180956378	-2.298787611
C	1.472144613	-2.326056581	-2.726550899
H	1.519486327	-2.567873106	-3.790589305
H	1.522163081	-3.273592534	-2.175395477
H	2.356952620	-1.744552812	-2.465787830
H	0.180593973	-1.188578347	-1.372593730

H	0.276412537	-0.473950248	-3.056824673
O	-4.885803001	-0.274154369	-2.042943992
C	-0.335734844	-1.086797899	-8.152141524
C	0.161888196	-1.399763910	-9.407479676
C	0.517951150	-0.596576474	-7.162096254
H	-1.383916375	-1.212018297	-7.918623776
C	1.514895992	-1.225548923	-9.682014434
H	-0.503264938	-1.777912362	-10.172828130
C	2.368609021	-0.736349094	-8.699025206
H	1.903443776	-1.469263078	-10.662662980
C	1.875779007	-0.420980501	-7.440519313
H	3.420325234	-0.598532439	-8.913652433
H	2.537187000	-0.038118240	-6.677360416
C	-0.081742750	-0.282473923	-5.838933059
O	-1.239985306	-0.399465046	-5.551066029
O	0.891898660	0.142750557	-4.963803950
O	0.378278820	0.561761362	-3.729094724

TS6A

C	-5.145950525	-3.400701725	-3.377050315
C	-6.285864060	-3.966101879	-3.926235608
C	-7.490352457	-3.269597014	-3.896940740
C	-7.553378222	-2.007212814	-3.316010268
C	-6.416050253	-1.436243114	-2.763547241
C	-5.205128188	-2.133052909	-2.793914170
H	-4.200915356	-3.925524453	-3.386850092
H	-6.237443961	-4.948963851	-4.376399178
H	-8.380694625	-3.711579848	-4.325855410
H	-8.491286329	-1.468023555	-3.291037788
H	-6.462703404	-0.458219778	-2.307546022
C	-3.954253334	-1.584761529	-2.218796974
O	-2.906820405	-2.181542410	-2.153975961
O	-4.124128467	-0.293392825	-1.817707947
C	-0.858331211	0.356031592	-2.368163345
C	-0.013019539	1.341013669	-1.586316786
H	0.995956766	1.319043369	-2.017811793
H	-0.405771467	2.345681999	-1.759918174
C	-1.096716743	0.758068298	-3.822382579
H	-0.103041754	0.806892266	-4.285896335
H	-1.497473242	1.774384089	-3.830608213
C	-1.993132049	-0.162411443	-4.643237158
H	-1.981254885	0.139035148	-5.691750621
H	-1.657897943	-1.198876006	-4.594153138
H	-3.027824170	-0.119174242	-4.302978677
C	0.056553163	1.045102457	-0.090388396

H	0.448701065	0.044166885	0.085883090
H	0.705522536	1.763463559	0.413185187
H	-0.932581866	1.104022668	0.367381008
O	-0.395955298	-0.933836522	-2.180584374
H	-1.138163487	-1.555329556	-2.291269089
H	-1.978316461	0.372378893	-1.823244501
O	-3.069489830	0.206718581	-1.044104392

TS6B

C	-2.313477872	-2.766007376	-0.690448129
C	-3.480806944	-3.465855308	-0.955545110
C	-4.716837873	-2.864321811	-0.739858523
C	-4.784268035	-1.561814200	-0.256593899
C	-3.619372339	-0.857273313	0.012387998
C	-2.378254028	-1.458994009	-0.205428309
H	-1.342979272	-3.212832280	-0.854998849
H	-3.428278191	-4.479528227	-1.331002655
H	-5.627817968	-3.410453036	-0.949650140
H	-5.745868320	-1.093439424	-0.091609615
H	-3.666256002	0.156398096	0.383140011
C	-1.092699896	-0.747753522	0.049490162
O	-0.008685051	-1.192730371	-0.269430775
O	-1.293517480	0.413049069	0.683228798
C	2.535904021	1.267615283	0.259880592
C	3.328580844	2.000075237	1.290655700
H	4.376007676	1.660751872	1.228225018
H	3.335748198	3.060741351	1.032187872
C	2.549096629	1.760631032	-1.153162317
H	3.587161667	1.674600746	-1.521386199
H	2.330550064	2.830975256	-1.137192214
C	1.619628105	1.054909063	-2.136844426
H	1.750021072	1.473483545	-3.135851381
H	1.831054540	-0.013671086	-2.201782294
H	0.578488650	1.175064955	-1.843465028
C	2.833584324	1.808962717	2.725998486
H	2.814472338	0.751766890	2.992207948
H	3.487987746	2.322836341	3.432056367
H	1.826568934	2.215093390	2.846093824
O	2.447820937	-0.065859649	0.503471678
H	1.728509599	-0.474049557	-0.018871298
H	0.522615026	0.773603417	1.360413367
O	0.015319901	1.264024908	0.693680341

Criegee intermediate

C	-4.1444	3.275527	-3.19014

C	-4.54671	2.133295	-2.50056
C	-4.75234	0.941462	-3.17976
C	-4.55412	0.883731	-4.55625
C	-4.15167	2.021041	-5.24522
C	-3.94501	3.216044	-4.56482
C	-3.91723	4.55414	-2.42248
H	-3.63646	4.107873	-5.09025
H	-4.6928	2.179103	-1.42798
H	-5.06643	0.058168	-2.63852
H	-3.99703	1.979656	-6.31591
H	-4.71518	-0.04534	-5.08828
O	-3.79307	5.629928	-3.2814
H	-4.70148	4.705381	-1.67173
C	-2.21337	6.780588	1.0133
C	-2.08698	5.918632	2.10535
C	-1.87272	6.440647	3.372925
C	-1.7865	7.816691	3.556297
C	-1.91085	8.676338	2.469059
C	-2.12213	8.161559	1.199752
C	-2.43293	6.291197	-0.36999
H	-2.21645	8.81187	0.341333
H	-2.14773	4.850335	1.958114
H	-1.76985	5.773116	4.218305
H	-1.84158	9.746672	2.612088
H	-1.61956	8.219726	4.547049
O	-2.36377	6.977284	-1.36095
O	-2.76437	4.972568	-0.36533
O	-2.69069	4.336868	-1.66629
H	-3.32387	6.332247	-2.79489

$TS_{BV}1$

C	0.207971	1.091335	0.347287
O	0.146257	1.827102	-0.71625
O	-1.55452	0.293311	-0.76512
C	-3.23567	0.274032	0.825292
O	-2.86155	-0.11313	-0.39728
O	-2.53052	0.873819	1.612458
H	-0.84468	1.728815	-0.95715
C	1.398988	0.34887	0.644512
C	1.481498	-0.29989	1.88477
C	2.457641	0.250838	-0.27097
C	2.612453	-1.02943	2.209911
C	3.583768	-0.47934	0.060806
C	3.661478	-1.1176	1.298849
H	0.649695	-0.22834	2.574249

H	2.372616	0.744789	-1.22884
H	2.679267	-1.53216	3.165428
H	4.403502	-0.56068	-0.64068
H	4.544511	-1.69084	1.551466
C	-4.63961	-0.13566	1.118313
C	-6.74679	-1.136	0.508878
C	-5.44408	-0.78731	0.18084
H	-5.0468	-1.01549	-0.79748
C	-6.45558	-0.19154	2.705648
C	-5.15319	0.159457	2.381558
H	-4.51654	0.666509	3.093303
C	-7.25466	-0.84004	1.769757
H	-7.36782	-1.63928	-0.22102
H	-6.84864	0.040917	3.68714
H	-8.27152	-1.11376	2.021645
H	-0.59426	1.151672	1.074817

$TS_{BV}2$

C	-3.66936	3.37067	-3.79795
C	-4.85182	3.816645	-3.19398
C	-5.98809	3.025849	-3.24053
C	-5.94527	1.791428	-3.8821
C	-4.76848	1.342308	-4.48069
C	-3.62994	2.126304	-4.44073
C	-2.50884	4.217966	-3.72968
H	-2.70672	1.791418	-4.89258
H	-4.85576	4.770316	-2.68272
H	-6.90358	3.364451	-2.77426
H	-4.74583	0.378938	-4.97251
H	-6.8324	1.171627	-3.91336
O	-1.45464	3.921665	-4.40044
H	-2.5934	5.194719	-3.26834
C	-3.06073	5.535599	1.01284
C	-2.65714	4.7271	2.077859
C	-3.03991	5.049236	3.37204
C	-3.82174	6.174636	3.611231
C	-4.22212	6.98287	2.552065
C	-3.84301	6.665202	1.25644
C	-2.6885	5.246588	-0.39899
H	-4.13955	7.282494	0.419808
H	-2.04491	3.857275	1.890108
H	-2.72456	4.422798	4.196304
H	-4.82703	7.861091	2.737178
H	-4.116	6.423134	4.623065
O	-3.01169	5.930474	-1.3449

O	-1.96287	4.117142	-0.47845
O	-1.53557	3.768023	-1.79248
H	-0.68681	4.514565	-4.06962
C	2.202417	5.954726	-3.57081
C	3.577034	6.012888	-3.33925
C	4.423322	6.575584	-4.28334
C	3.902716	7.092997	-5.46577
C	2.532838	7.046705	-5.69913
C	1.685962	6.479128	-4.75567
C	1.329864	5.331124	-2.52451
O	1.753692	4.997596	-1.43975
O	0.057703	5.182955	-2.88089
H	-0.63085	4.53554	-2.14048
H	3.958766	5.609304	-2.41153
H	5.489372	6.613266	-4.09854
H	4.563097	7.533317	-6.2023
H	2.124448	7.455084	-6.61485
H	0.619534	6.455793	-4.93043

$TS_{BV}3$

C	-0.83614	2.084156	0.280099
O	-1.74252	2.160826	-0.61254
O	0.238651	0.550193	-0.47271
H	-2.40241	1.296153	-0.51962
C	2.465564	0.653246	0.128974
O	1.232668	0.161391	0.469298
O	2.697597	1.285117	-0.86074
C	-2.63973	-0.96893	-0.24742
O	-3.14785	0.18064	-0.32792
O	-1.39218	-1.22361	-0.25784
H	-0.5698	-0.32066	-0.37319
C	0.207461	3.091733	0.388118
C	0.984822	3.133558	1.547253
C	0.478456	3.961824	-0.67044
C	2.035921	4.032954	1.645764
H	0.773859	2.449167	2.359121
C	1.525447	4.859811	-0.56633
H	-0.12162	3.904293	-1.56765
C	2.306998	4.891926	0.587279
H	2.646399	4.057288	2.538506
H	1.747814	5.52783	-1.38785
H	3.132966	5.588206	0.657463
H	-1.0328	1.482218	1.167263
C	3.458162	0.301908	1.182878
C	4.118185	-0.75409	3.246162

C	3.143107	-0.47821	2.297388
H	2.143337	-0.8697	2.416034
C	5.722331	0.523638	1.980331
C	4.752272	0.800092	1.028682
H	4.974588	1.401133	0.157877
C	5.406477	-0.25321	3.090642
H	3.872928	-1.36232	4.107224
H	6.725168	0.911575	1.856748
H	6.164106	-0.47021	3.832979
C	-3.55983	-2.13593	-0.11887
C	-3.90809	-4.51221	0.09606
C	-3.04741	-3.43069	-0.02652
H	-1.97651	-3.57287	-0.05357
C	-5.79866	-3.01767	0.035072
C	-4.94022	-1.93452	-0.08802
H	-5.32244	-0.92629	-0.16222
C	-5.28387	-4.30706	0.127589
H	-3.50757	-5.5154	0.1663
H	-6.86907	-2.85821	0.05829
H	-5.9546	-5.15175	0.223188

$TS_{BV}4$

C	-5.89772	4.891681	-1.98886
C	-6.79018	5.737721	-2.66085
C	-8.16376	5.554126	-2.50709
C	-8.64719	4.529251	-1.68737
C	-7.75465	3.68452	-1.01934
C	-6.38062	3.85693	-1.17594
C	-4.4159	5.091836	-2.14183
H	-5.67225	3.213893	-0.65349
H	-6.39296	6.538111	-3.28367
H	-8.86025	6.215101	-3.02428
H	-8.13193	2.891817	-0.37242
H	-9.72237	4.389733	-1.56703
O	-4.01839	6.21635	-2.71483
H	-3.99121	4.065353	-2.6723
C	-1.93732	7.11968	1.260334
C	-1.93379	6.446983	2.490942
C	-1.30543	7.020674	3.595627
C	-0.68675	8.269222	3.479857
C	-0.6931	8.942528	2.25429
C	-1.31473	8.370902	1.145049
C	-2.60275	6.519222	0.055817
H	-1.32365	8.877283	0.180455
H	-2.42175	5.476056	2.564313

H	-1.29769	6.493068	4.550267
H	-0.20817	9.91527	2.16301
H	-0.19772	8.717931	4.345781
O	-2.38621	7.042634	-1.07436
O	-3.36724	5.515342	0.304838
O	-3.56431	4.472249	-1.29499
H	-3.19681	6.583627	-2.0752

4. PE Oxidation by Substituted Benzaldehydes

The influence of benzaldehyde substituents on the PE oxidation was investigated. As the melting points of the corresponding substituted benzoic acids were often much higher than the reaction temperatures, performing these reactions in the absence of TCE solvent resulted in the reaction solidifying after some time if no solvent was used, and preventing stirring for mixing with O_2. A control experiment where PE was stirred in TCE at 100 ^oC without any benzaldehydes under an O_2 atmosphere showed no discernable PE oxidative functionalization.

Procedure for PE oxidation by substituted benzaldehydes:

In a typical experiment, the following reagents were loaded into a Schlenk flask: PE (300 mg, 1 equiv), TCE (1.9 mL) and substituted benzaldehyde (1 equiv w.r.t. ethylene repeating units). After degassing and thoroughly-refilling the flask with O_2, the reaction was allowed to proceed at 100 ^oC for 20 h with vigorous stirring. O_2 gas was continuously supplied by a balloon (1 atm) throughout the reaction. Thereafter, the reaction mixture was allowed to cool at room temperature and precipitated in methanol (40 mL). The functionalised PE was subsequently recovered by centrifugation and further washings (sonication and centrifugation twice each) were conducted to remove all unreacted reagents and side products. The product was dried in a vacuum oven at 80 ^oC for at least 16 h before further analysis.

Table S3. Effects of benzaldehyde substituents on the oxidation of PE[a]

S/N	Substituted benzaldehyde	Relative molar percentage/ % [b]					TF/ % [c]
		C=O	OH	Cl	acid	ester	
1	Benzaldehyde (substituents = H)	84.4	0	15.6	0	0	1.03
2	4-anisaldehyde	100	0	0	0	0	0.02
3	4-fluorobenzaldehyde	82.1	0	17.9	0	0	1.38
4	4-bromobenzaldehyde	59.4	0	18.8	11.5	10.4	1.51
5	3-chlorobenzaldehyde	76.9	0.15	0	10.8	6.15	2.44
6	3-(trifluoromethyl)benzaldehyde	76.9	0	0	23.1	0	3.33
7	4-(trifluoromethyl)benzaldehyde	60.2	0	0	22.9	16.9	4.15
8	2-bromobenzaldehyde	100	0	0	0	0	0.44

[a] Reactions were performed under ambient lighting conditions for 20 hours under constant stirring, with 1 molar equivalents of benzaldehyde w.r.t the number of PE repeating units present, O_2 (1 atmospheric pressure) was delivered using a balloon.

[b] Determined from the ^1H NMR spectra of the oxidised PE polymers ($C_2D_2Cl_4$, 80 ^oC) by relative integration of the peaks arising from C***H***$_2$C(O)C***H***$_2$ (2.4 ppm), C***H***-OH (3.6 ppm), C***H***-Cl (3.9 ppm), C***H***$_2$COOH (2.3 ppm), C***H***$_2$OC(O) (4.1 ppm).

[c] Molar percentage of all the CH_2s present that have been functionalised with different functional groups, by comparing the relative integrals of the peaks in [b] with the unreacted CH_2s (0.8-1.6 ppm).

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