Supplementary Information

Cumene-mediated Aerobic Oxidation of Polyethylene

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1. Materials and Methods

Materials. Low-density polyethylene (LDPE, melting index = 20–30 g/10 min), high-density polyethylene (HDPE, melting index = 6–9 g/10 min), linear low-density polyethylene (LLDPE, melting index = 2 g/10 min), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 99%), manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 99%), ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, 99%), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99%), 1,2-dichlorobenzene (>99%), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 97%), ammonia aqua (>28%) and *p*-benzoquinone (98%) were purchased from MACKLIN. Nickel phthalocyanine (97+%) and cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%) was purchased from Adamas Reagent. Low M_w polyethylene (average M_w ~ 4,000 by GPC, M_n ~ 1,700 by GPC) and 1,3-diaminopropane (99%) were purchased from Sigma Aldrich. 2,6-Diformyl-4-methylphenol (95%) was purchased from Bidepharm. Cumene (99%) and phenol (99%) was purchased from TCI. 1,2-Dichlorobenzene-d_4 (99%), cumene hydroperoxide (80%), acetophenone (98%) and 2-phenyl-propan-2-ol (97%) were purchased from J&K. Methanol (AR, >99.5%), hydrochloric acid (GR, 36%), nitric acid (GR, 65%) and isoproponal (AR, >99.5%) were purchased from Greagents. Acetonitrile (HPLC, >99.95%) was purchased from Fisher. Al plates were purchased from Zhongyashiyanyiqi. PE bag was purchased from MyJae. PE pipette was purchased from Fanmi Kebang Laboratory Technology. All chemicals were used as received without further purification.

Methods. Binuclear complexes were prepared according to procedures reported previously by our group[1, 2]. Their structures are characterized by powder XRD and IR.

Synthesis of binuclear nickel complexes (Ni_2L): The synthesis of binuclear nickel complexes was conducted following the procedure in literature[2]. $NiCl_2 \cdot 6H_2O$ (0.84 g) was dispersed in boiling isopropanol (20 mL) to obtain solution A. 1,3-Diaminopropane (0.442 mL) in isopropanol (5 mL) was added dropwise into solution A to obtain blue solution B. 2,6-Diformyl-4-methylphenol (0.58 g) was dissolved in boiling isopropanol (25 mL) and added into solution B. The mixture was kept under reflux. After refluxing for 18 hours, the resulting brown solid was filtered and thoroughly washed in boiling methanol (40 mL) for 8 hours. The methanol-insoluble remnant was filtered to obtain light green flaky solid. IR (ATR, cm^{-1}): 2919 (m), 2853 (w), 1638 (s), 1553 (s), 1460 (m), 1438 (m), 1415 (s), 1343 (s), 1281(m), 1240 (m), 1118 (s), 1087 (m), 1004 (w), 974 (w), 932 (w), 868 (w), 827 (s), 771 (m).

Catalytic oxidation of PE with different catalysts: LDPE (200.0 mg) and catalyst (0.25 mol% of PE monomers) were added to cumene (6.0 mL) in a Schlenk flask. The flask was thoroughly degassed and refilled with O_2 for three times. The reaction is carried out at 120 ℃ with a stirring rate of 300 rpm. After 24 hours, the reaction solution was poured into methanol (50 mL) under stirring and the Ox-PE immediately precipitated from the mixture as a white solid. The oxidized PE was obtained by filtration, washing with methanol (10 mL×3), and vacuum drying. Oxidized PE (around 10 mg) was dissolved in 1,2-dichlorobenzene-d_4 (0.4 mL) and 1,2-dichlorobenzene (0.1 mL) in an NMR tube at 140 ℃. NMR spectra was performed at 100 ℃.

Catalytic oxidation of PE at different temperatures: LDPE (200.0 mg) and Ni_2L (0.25 mol% of PE monomers) were added to cumene (6.0 mL) in a Schlenk flask. The flask was thoroughly degassed and refilled with O_2 for three times. The reaction is carried out at a given temperature with a stirring rate of 300 rpm. After 24 hours, the reaction solution was poured into methanol (50 mL) under stirring and the Ox-PE immediately precipitated from the mixture as a white solid. The oxidized PE was obtained by filtration, washing with methanol (10 mL×3), and vacuum drying. Oxidized PE (around 10 mg) was dissolved in 1,2-dichlorobenzene-d_4 (0.4 mL) and 1,2-dichlorobenzene (0.1 mL) in an NMR tube at 140 ℃. NMR spectra was performed at 100 ℃. The collected solution from oxidation system was diluted to 1000 mL with methanol and filtered for HPLC analysis.

Catalytic oxidation of PE under different atmosphere: LDPE (200.0 mg) and Ni_2L (0.25 mol% of PE monomers) were added to cumene (6.0 mL) in a Schlenk flask. The flask was thoroughly degassed and refilled with different gas for three times. The reaction is carried out at 120 ℃ with a stirring rate of 300 rpm. After 24 hours, the reaction solution was poured into methanol (50 mL) under stirring and the Ox-PE immediately precipitated from the mixture as a white solid. The oxidized PE was obtained by filtration, washing with methanol (10 mL×3), and vacuum drying. Oxidized PE (around 10 mg) was dissolved in 1,2-dichlorobenzene-d_4 (0.4 mL) and 1,2-dichlorobenzene (0.1 mL) in an NMR tube at 140 ℃. NMR spectra was performed at 100 ℃.

Catalytic oxidation of various kinds of PE using an air flow: PE (200.0 mg) and Ni_2L (0.25 mol% of PE monomers) were added to cumene (6.0 mL) in a flask. Air was pumped into the system below the liquid surface, with a flow rate of 30 mL/min. The reaction is carried out at 120 ℃ with a stirring rate of 300 rpm. After 24 hours, the reaction solution was poured into methanol (50 mL) under stirring and the Ox-PE immediately precipitated from the mixture as a white solid. The oxidized PE was obtained by filtration, washing with methanol (10 mL×3), and vacuum drying. Oxidized PE (around 10 mg) was

dissolved in 1,2-dichlorobenzene-d_4 (0.4 mL) and 1,2-dichlorobenzene (0.1 mL) in an NMR tube at 140 ℃. NMR spectra was performed at 100 ℃.

Catalytic oxidation of PE in different solvents: LDPE (200.0 mg) and Ni_2L (0.25 mol% of PE monomers) were added to a given solvent (6.0 mL) in a Schlenk flask. The flask was thoroughly degassed and refilled with O_2 for three times. The reaction is carried out at 120 ℃ with a stirring rate of 300 rpm. After 24 hours, the reaction solution was poured into methanol (50 mL) under stirring and the Ox-PE immediately precipitated from the mixture as a white solid. The oxidized PE was obtained by filtration, washing with methanol (10 mL×3), and vacuum drying. Oxidized PE (around 10 mg) was dissolved in 1,2-dichlorobenzene-d_4 (0.4 mL) and 1,2-dichlorobenzene (0.1 mL) in an NMR tube at 140 ℃. NMR spectra was performed at 100 ℃.

Gram-scale catalytic oxidation of PE: PE (20.0 g) and Ni_2L (1.12 g, 0.06 mol% of PE monomers) were added to cumene (300 mL) in a 1 L round-bottom flask. Air was pumped into the system below the liquid surface, with a flow rate of 300 mL/min. The reaction was carried out under reflux at 120 °C for 32 hours. After reaction, the mixture was cooled to room temperature to make oxidized PE precipate, followed by filtration. The resulting solid was dispersed in vigorously-stirred methanol of 200 mL. The mixture was filtered and the solid was collected. This washing procedure was repeated twice. The final solid was dried overnight in a vacuum oven at 60 °C. Oxidized PE (around 10 mg) was dissolved in 1,2-dichlorobenzene-d_4 (0.4 mL) and 1,2-dichlorobenzene (0.1 mL) in an NMR tube at 140 ℃. NMR spectra was performed at 100 ℃.

Catalytic and non-catalytic oxidation of cumene: Cumene (6.0 mL) and Ni_2L (0.04 mol%) were added in a Schlenk flask, while Ni_2L was not added in the blank control system. The flask was thoroughly degassed and refilled with O_2 for three times. The reaction was carried out at 120 °C with a stirring rate of 300 rpm. 10 μL liquid was moved out every two hours and diluted to 10 mL by methnol for quantitative analysis by HPLC with a varible wavelength dector. Injection volume was 2 μL. Chromatography column was InfinityLab Poroshell 120 EC-C18 (4.6×100 mm) and its temperature was set as 30 ℃. Mobile phases were mixture of water and acetonitrile. The gradient for separation was shown in Table S1. Detecting wavelength was set to 220 nm. A chromatogram of cumene and its oxidation products were shown in Fig. S33. Analytes were quantified using external curves (r^2 coefficient > 0.999).

Catalytic and non-catalytic decomposition of CHP: A CHP solution of 40 wt% was developed first by diluting 80 wt% CHP by cumene. Then, 40 wt% CHP (6.0 mL) and Ni_2L (0.04 mol%) were added in a

Schlenk flask, while Ni_2L was not added in the blank control system. The flask was thoroughly degassed and refilled with O_2 for three times. The reaction was carried out at 120 °C with a stirring rate of 300 rpm. 10 μL liquid was moved out every two hours and diluted to 10 mL by methnol for quantitative analysis by HPLC with a varible wavelength dector. Injection volume was 2 μL. Chromatography column was InfinityLab Poroshell 120 EC-C18 (4.6×100 mm) and its temperature was set as 30 ℃. Mobile phases were mixture of water and acetonitrile. The gradient for separation was shown in Table S1. Detecting wavelength was set to 220 nm. Analytes were quantified using external curves (r^2 coefficient > 0.999).

PE purification and sample preparation for ICP-OES: To remove residual Ni, Ox-PE was purified by precipitation in methanol (within *ca*. 5% NH_3). Specifically, 100 mg Ox-PE was dissolved in 1,2-dichlorobenzene (1 mL) at 120 ℃. The hot solution was poured into 50 mL methanol (within *ca*. 5% NH_3) and PE precipitated immediately. The mixture was filtered to obtain purified Ox-PE and filtrate. A part of purified Ox-PE was heated to 600 ℃ at a rate of 10 ℃/min in a muffle furnace. After heating for 10 hours, aqua regia (*ca*. 500 μL) was added into solid residue to dissolve and diluted by water to a constant volume of 10 mL for ICP-OES. The filtrate was diluted by methanol to a constant volume of 250 mL for HPLC analysis.

Table S1 Gradient for separating products from cumene oxidation

Time (min)	Water (%)	Acetonitrile (%)	Flow rate (mL min^{-1})
0.00	55.0	45.0	1.000
5.00	55.0	45.0	1.000
6.00	35.0	65.0	1.000
12.00	35.0	65.0	1.000
13.00	55.0	45.0	1.000
15.00	55.0	45.0	1.000

2. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex600 diffractometer using a Cu-Kα radiation source (λ = 1.5405 Å). Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) experiments were performed on a Bruker Fourier transform infrared spectrometer (Horiba, Germany). The presence of functional groups was identified by ^{1}H nuclear magnetic resonance (NMR) spectra in 1,2-dichlorobenzene-d_4 at 100 ℃ using JEOL 400 MHz spectrometer (Tokyo, Japan). ^{13}C-NMR spectra was performed in 1,2-dichlorobenzene-d_4 at 100 ℃ on a JEOL 600 MHz spectrometer (Tokyo, Japan). Differential scanning calorimetry (DSC) was performed on a Q5000 IR of TA Inst. at a heating rate of 10 ℃/min ranged from -50 to 150 ℃. The DSC data were analyzed using the second cycle of heating. High-temperature gel permeation chromatography (HT-GPC) was performed at 150 ℃ using an Agilent 1260 Infinity II High Temperature GPC system equipped with two GPC columns (PLgel MIXED-B LS 300×7.5mm). The eluent was 1,2,4-trichlorobenzene (1,2,4-TCB) stabilized with 0.0125% butylated hydroxytoluene (BHT) at 1.0 mL/min and the injection volume was 200 μL. The amount of residual Ni in the Ox-PE was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 7400, Thermo, Waltham, USA). Muffle furnace (Hefei Kejing) was used to completely oxidize PE into CO_2. Contact angles were measured on an OCAH20 instrument (Dataphysics Ltd., Germany). High-performance liquid chromatography (HPLC) was performed on Agilent 1260 Infinity II system. Matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF-MS) was carried out with an AXIMA-Performance mass spectrometer (Shimadzu). Electron spin resonance spectra were recorded on a JEOL FA-200 EPR spectrometer using DMPO to capture radicals in reaction solution. Compression molding was conducted on a vacuum plate vulcanizing press from Suzhou Jieheshiye Co., Ltd. Tensile specimens were molded into dogbone-shaped samples at 200 ℃ for 5 min under vacuum. Tensile tests were conducted using an Instron universal materials tester (crosshead velocity=16 mm/min). Lap shear adhesion testing was conducted using an Instron universal materials tester with a crosshead velocity of 1.5 mm/min according to GB/T 7124-2008. Adhesion strength was calculated by the maximum load divided by the overlapped area, which was measured using digital calipers priorly, and the apparent failure mode was assessed visually. To evaluate adhesion strength of PE and Ox-PE to aluminum, single lap shear tests were performed on Al 6061 substrates, each measuring 0.16 cm in thickness, 1 cm in width, and 10 cm in length.

The functionalized degree was determined using the method described in the literature[3]. In the ^{1}H-NMR spectrum, the integration of peaks between 1.9 and 0.7 ppm were set to total 4 protons (per monomer unit). The integration of the peak at 3.5 ppm, corresponding to –C***H***(OH)–, was used to determine the

functionalization degree of hydroxyl groups (1 proton per alcohol unit). The integration of the peaks at 2.2 ppm, corresponding to –C***H*****2**C(O)C***H*****2**–, was used to determine the functionalization degree of carbonyl groups (4 protons per ketone unit). Functionalization degree was calculated using the equation provided below, where A represents the peak area obtained from integration:

$$\text{Functionalization degree} = \frac{A(CH\text{-}OH) + A\left[CH_2\text{-}C(O)\text{-}CH_2\right]/4 + A\left[CH_2\text{-}COOH\right]/2}{A(CH_2\text{-}CH_2)/4}$$

3. Scheme S1 and Figures S1-S41

Initiation

$RH + O_2 \rightarrow R\cdot + \cdot OOH$

$ROOH \rightarrow RO\cdot + \cdot OH$

Propagation

$R\cdot + O_2 \rightarrow ROO\cdot$

$ROO\cdot + RH \rightarrow ROOH + R\cdot$

$RO\cdot + RH \rightarrow ROH + R\cdot$

$\cdot OH + RH \rightarrow R\cdot + H_2O$

Termination

$2ROO\cdot \rightarrow ROOR + O_2$

$2R\cdot \rightarrow R–R$

$R\cdot + \cdot OOH \rightarrow ROOH$

$R\cdot + ROO\cdot \rightarrow ROOR$

***β*-scission**

$RO\cdot \rightarrow PhC(O)CH_3 + \cdot CH_3$

R = cumyl

Scheme S1. Mechanism of oxidation of cumene in liquid phase.

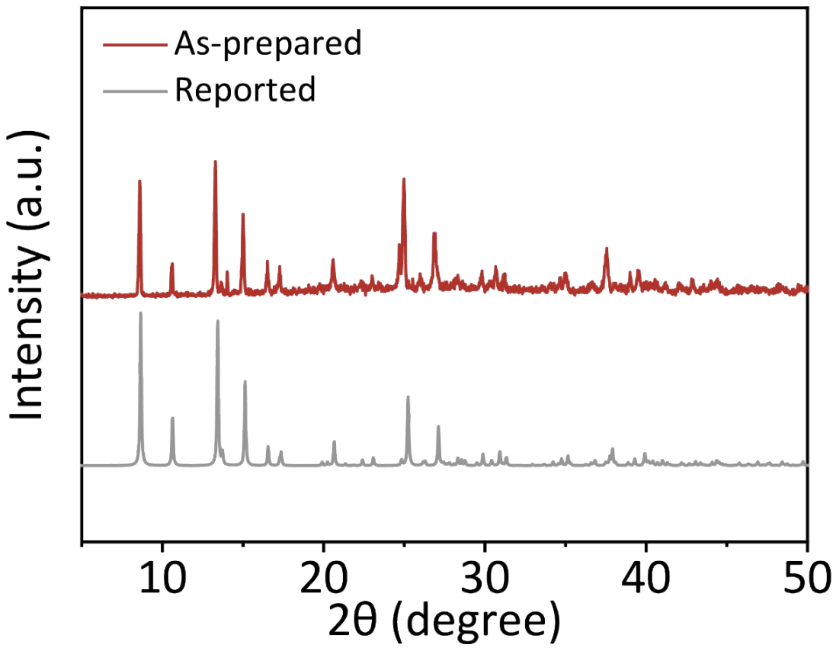


Fig. S1 Experimental and reported XRD patterns of Ni_2L^2.

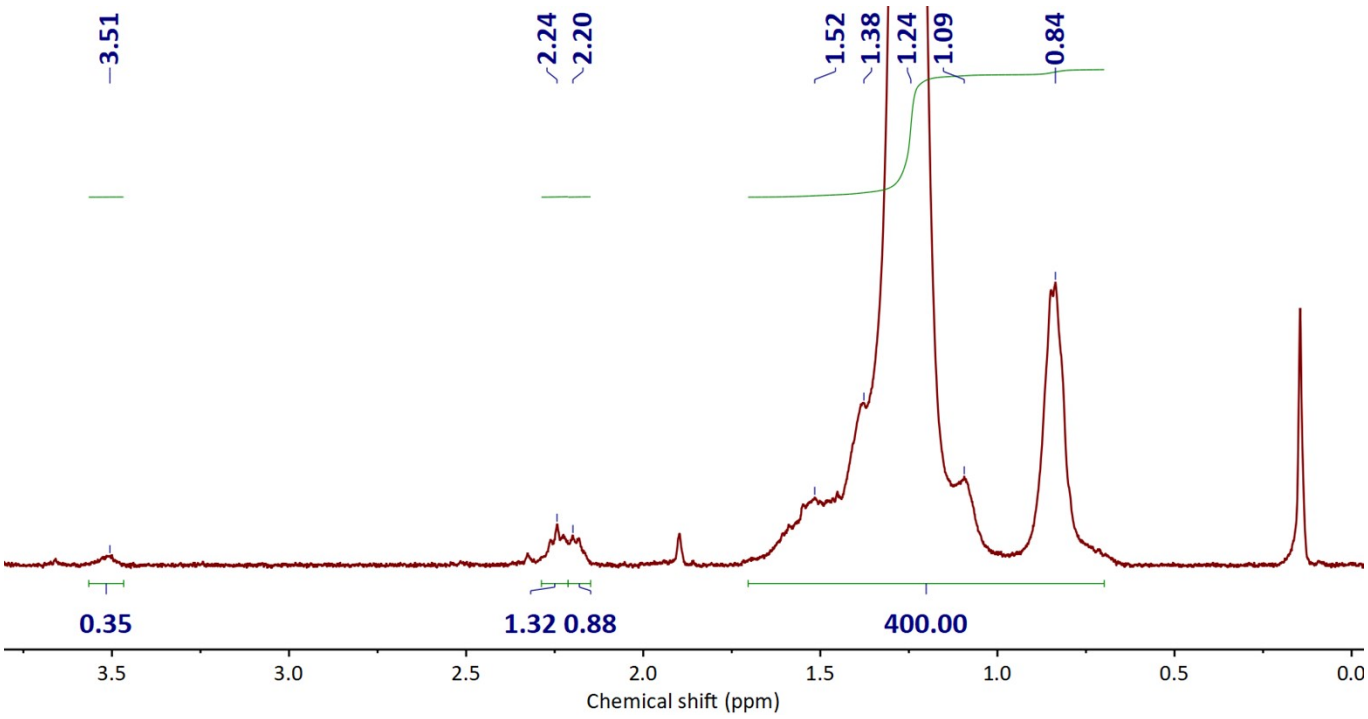


Fig. S2 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of oxidized PE without any catalyst at 120 °C.

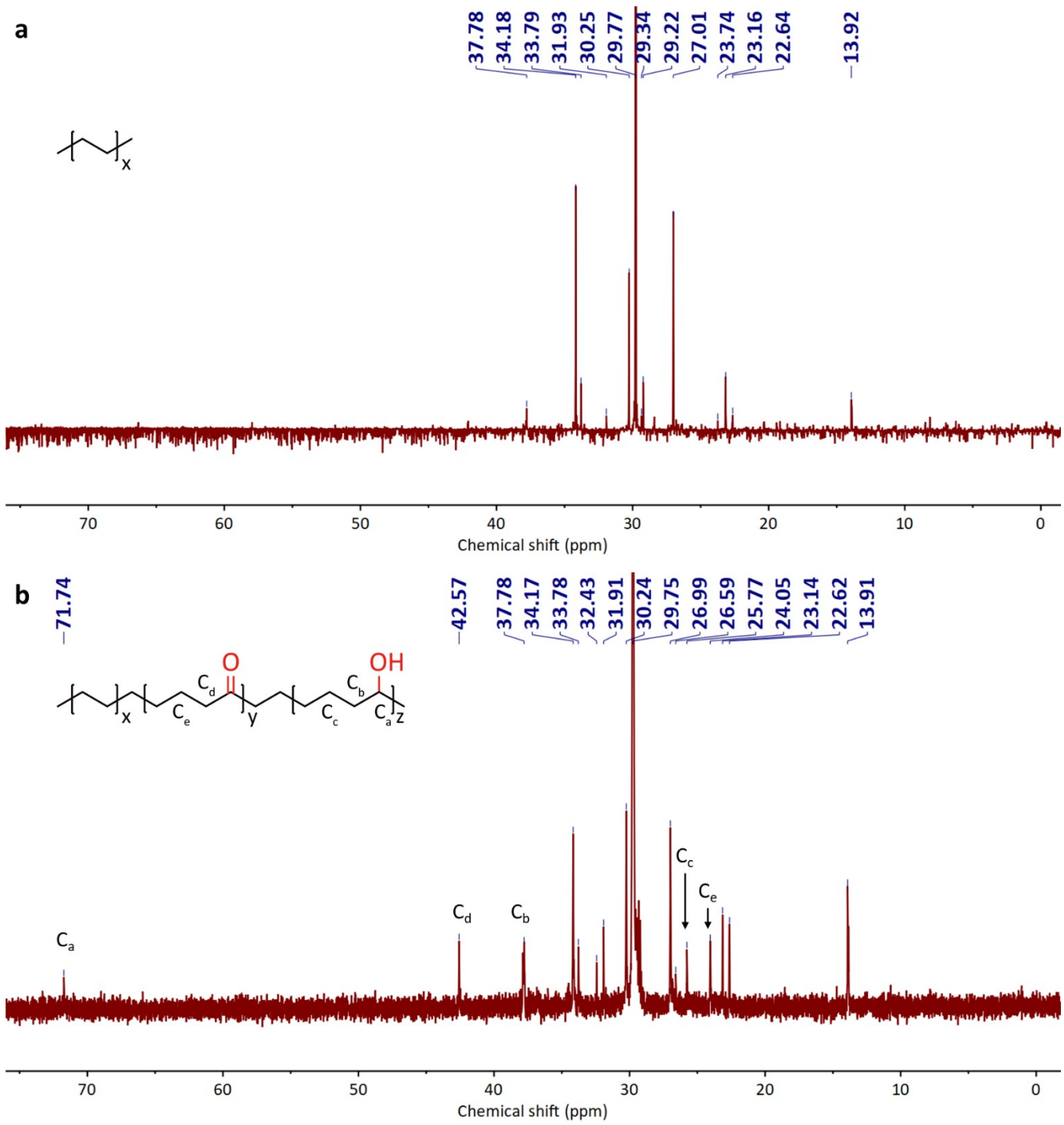


Fig. S3 ^{13}C-NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of virgin LDPE (a) and Ox-PE (b).

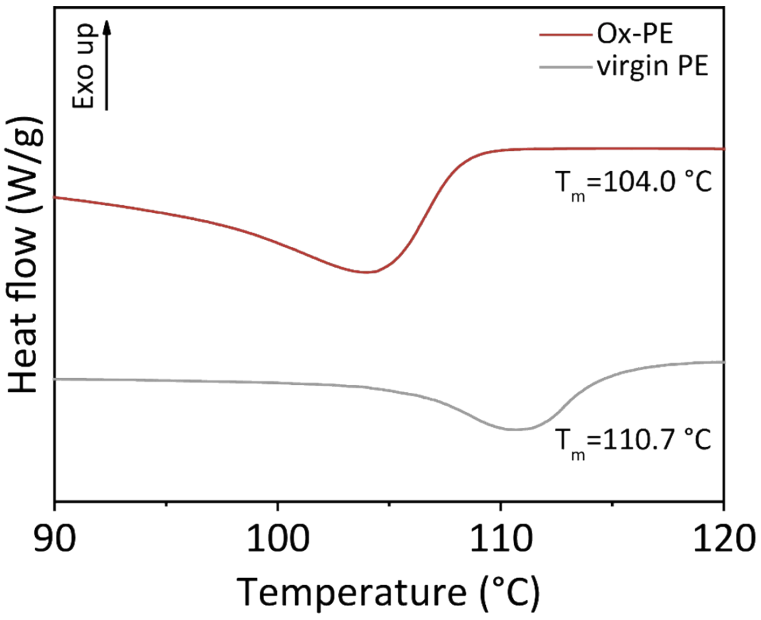
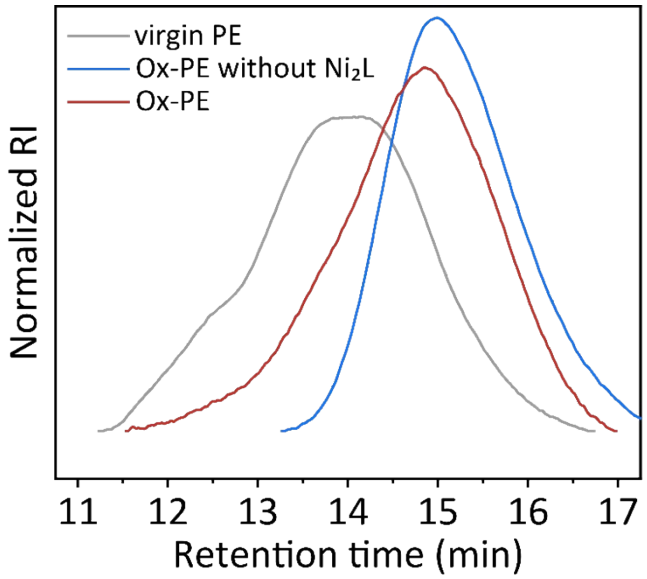


Fig. S4 Differential scanning calorimetry curves of Ox-PE and virgin PE.



Polymer	M_w/(kg/mol)	PDI
virgin PE	102.2	5.5
Ox-PE	34.8	4.8
Ox-PE without Ni_2L	10.9	3.0

Fig. S5 High-temperature gel permeation chromatography curves of virgin PE, Ox-PE without Ni_2L and Ox-PE.

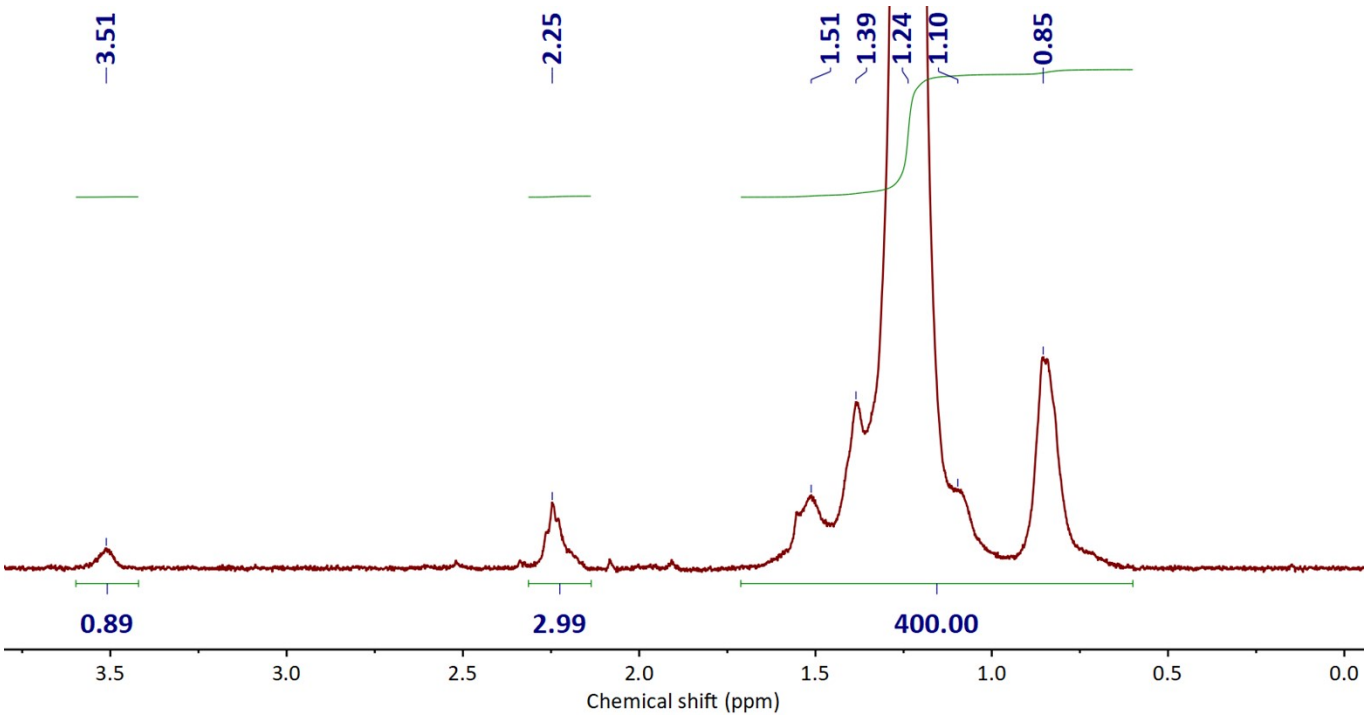


Fig. S6 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE catalyzed by Ni_2L at 120 °C.

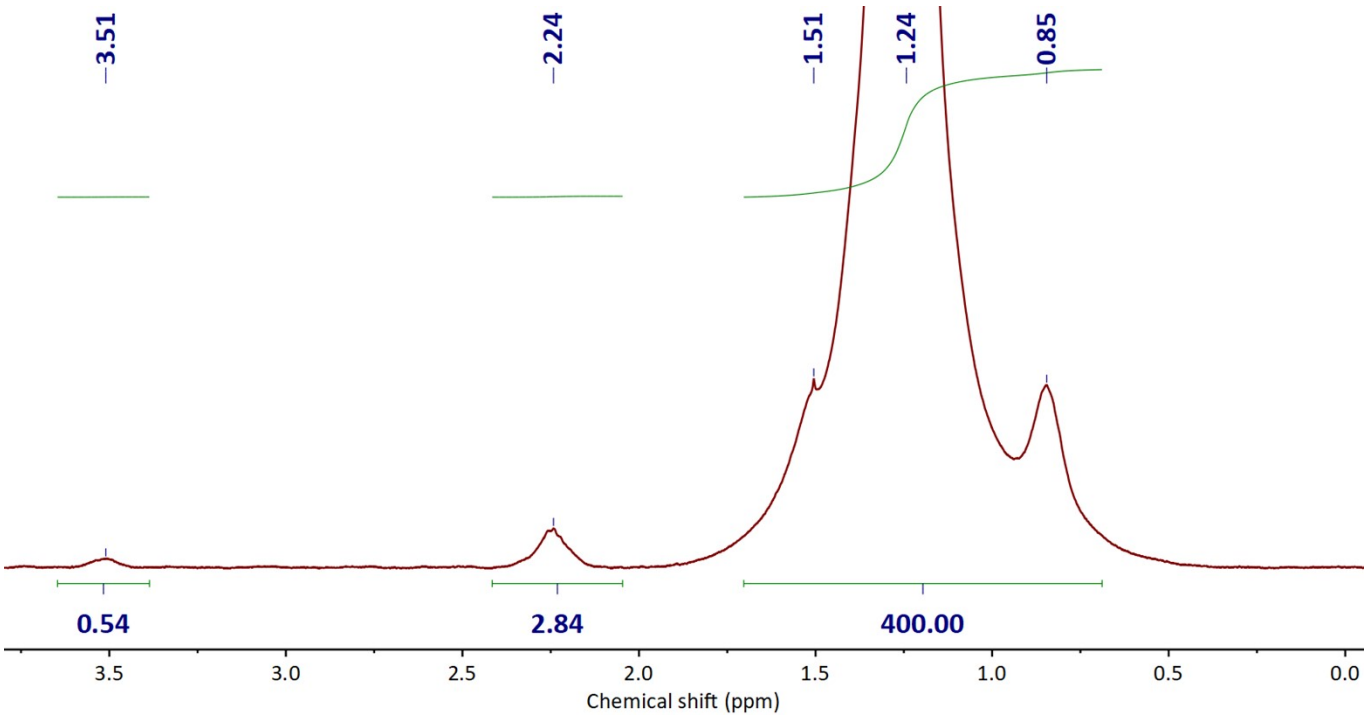


Fig. S7 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE catalyzed by Mn_2L at 120 °C.

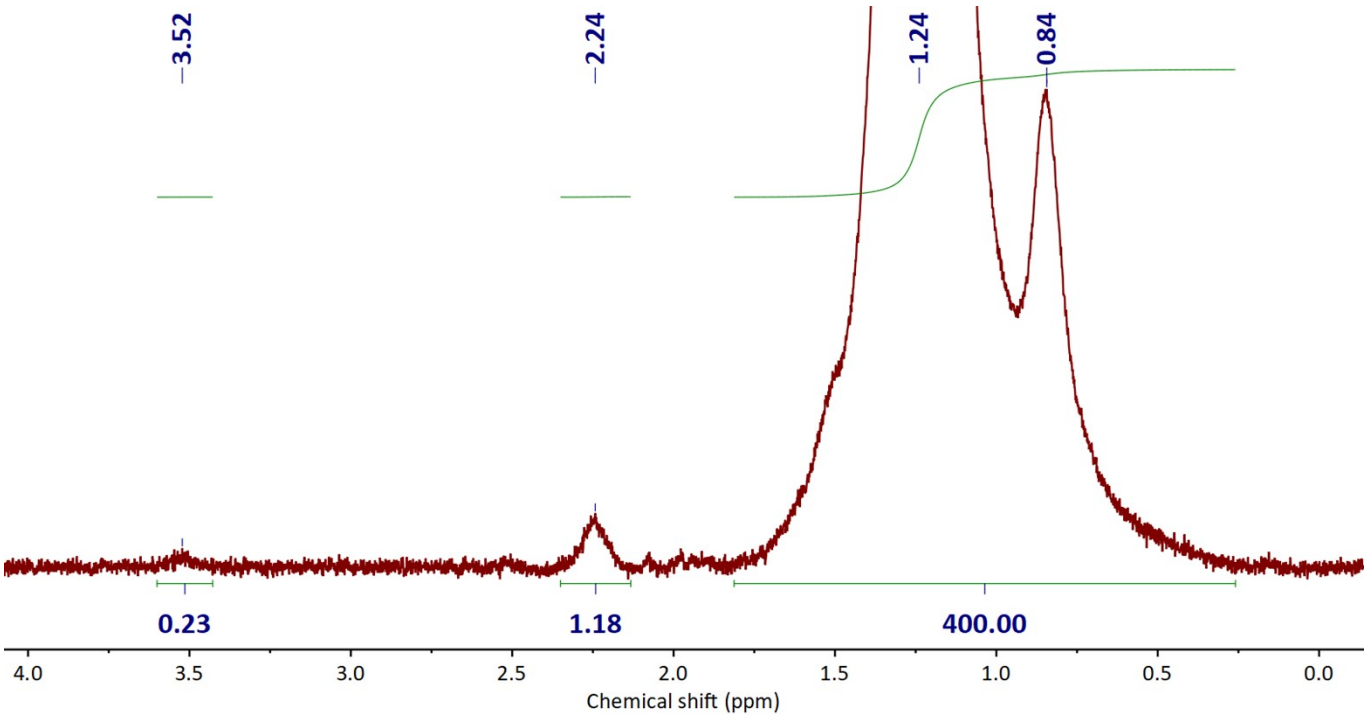


Fig. S8 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE catalyzed by Fe_2L at 120 °C.

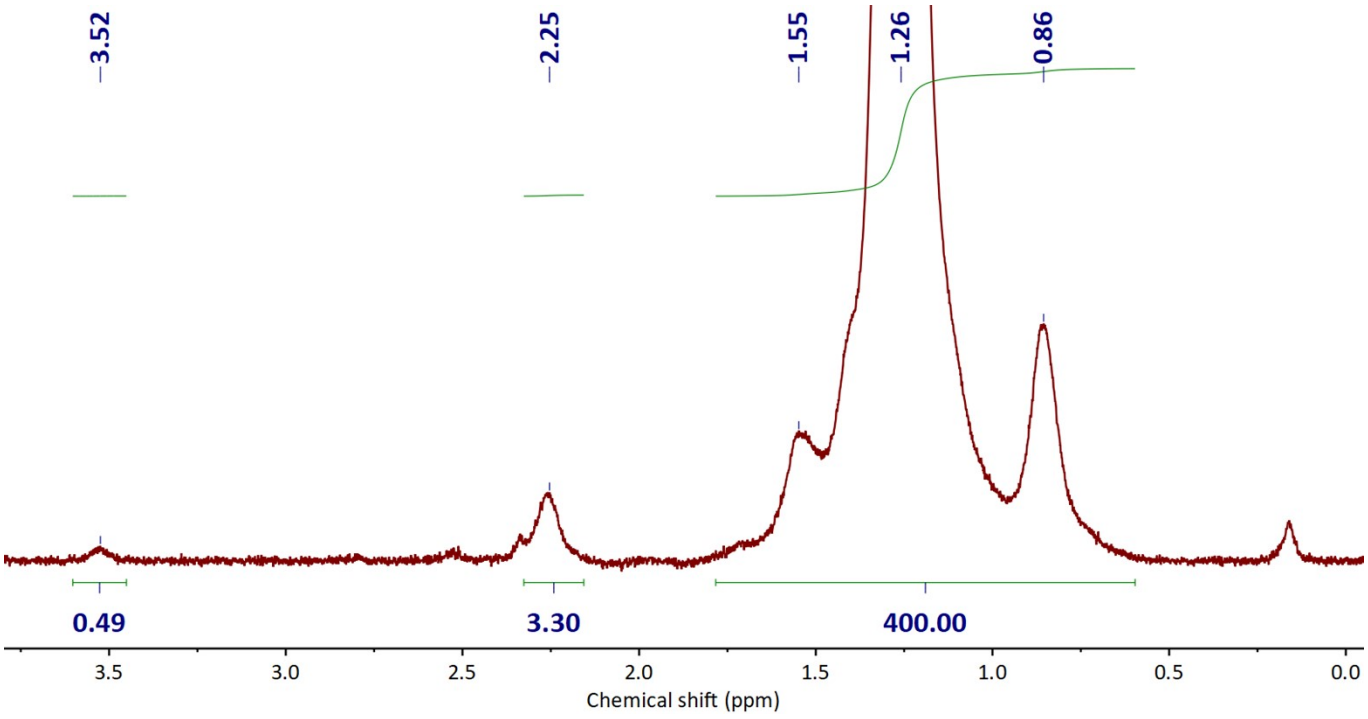


Fig. S9 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE catalyzed by Co_2L at 120 °C.

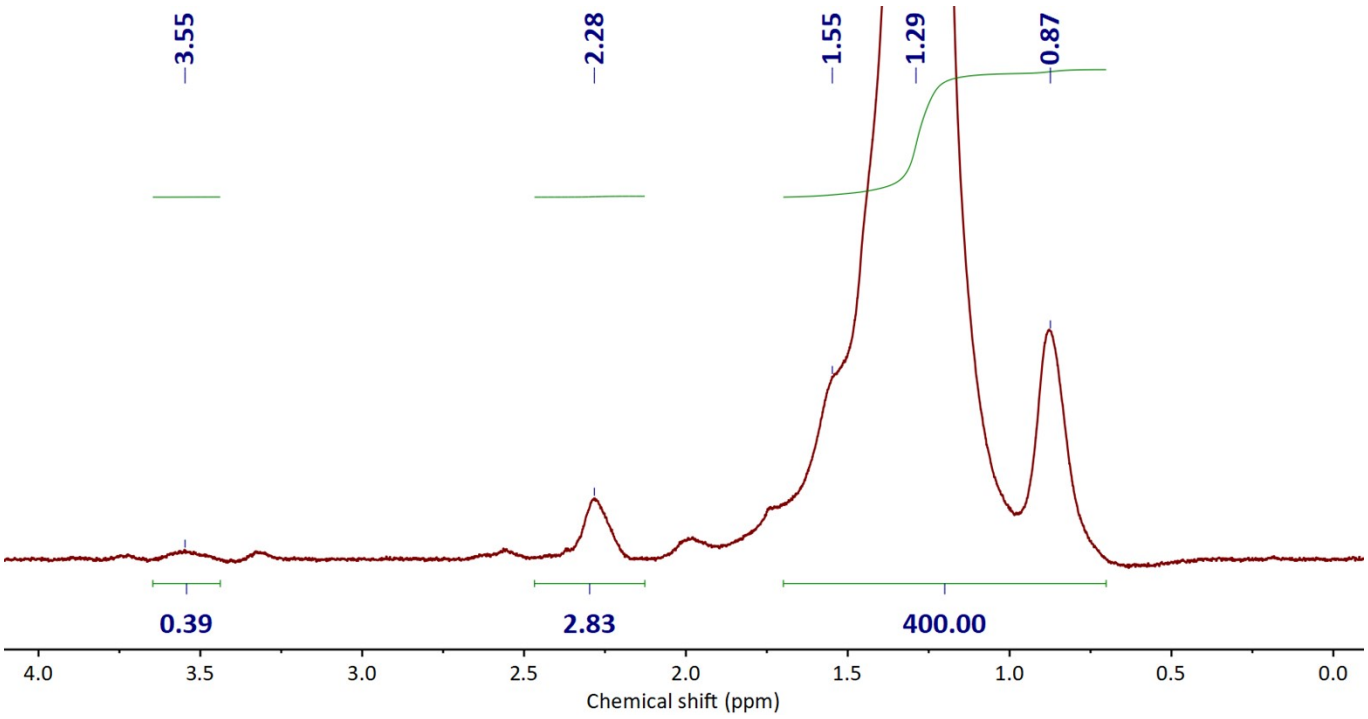


Fig. S10 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of oxidized PE catalyzed by Cu_2L at 120 °C.

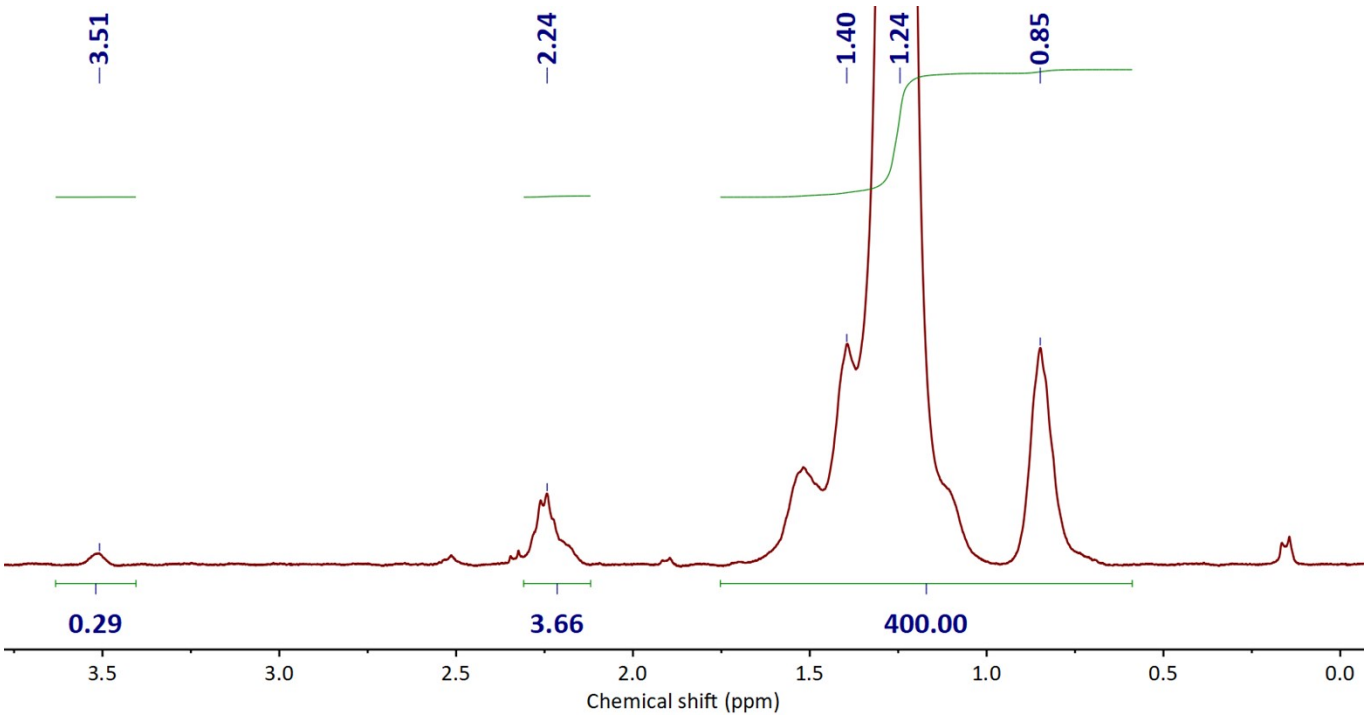


Fig. S11 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of oxidized PE catalyzed by NiPc at 120 °C.

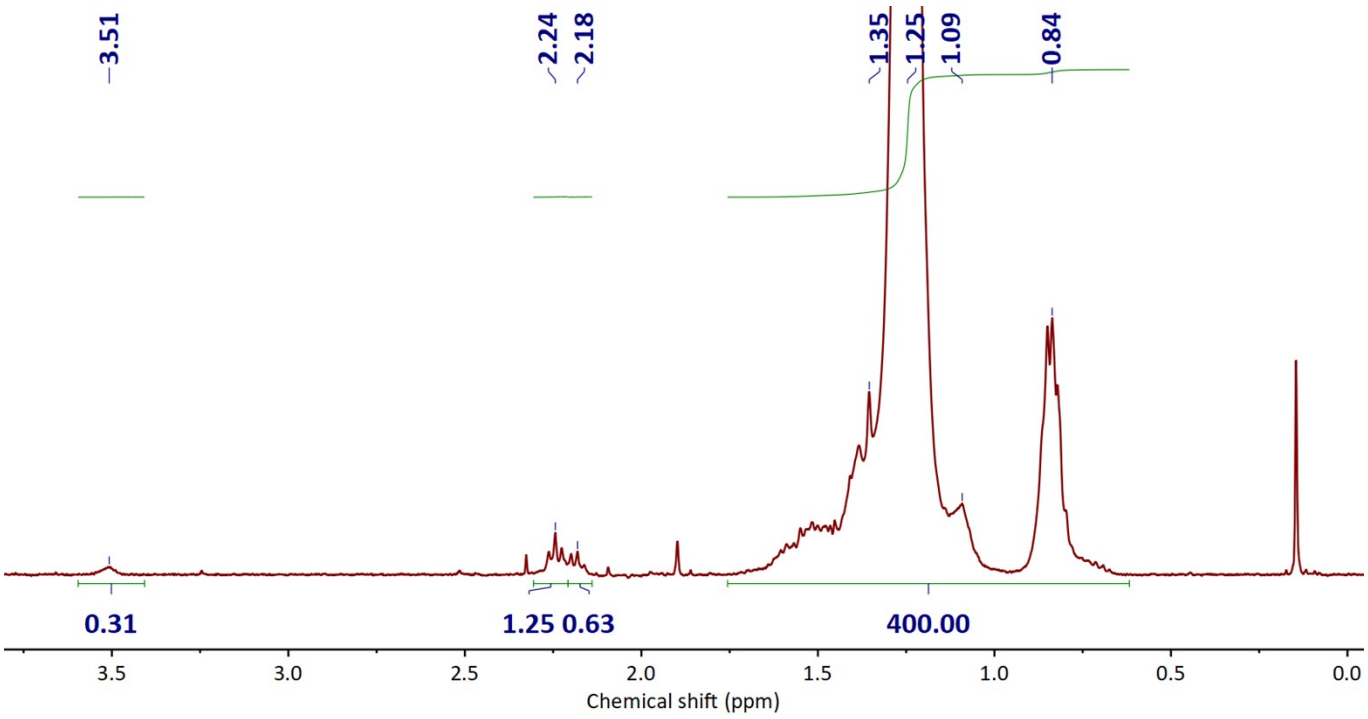


Fig. S12 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE catalyzed by $NiCl_2 \cdot 6H_2O$ at 120 °C.

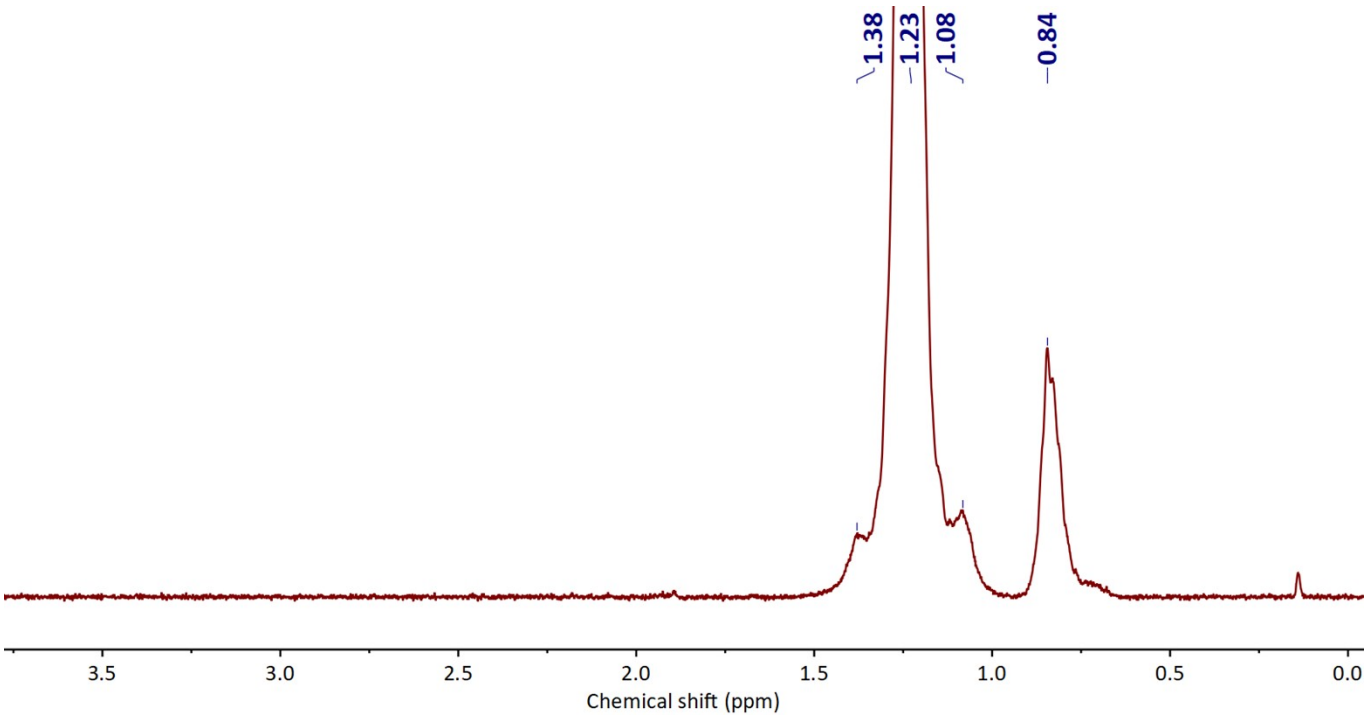


Fig. S13 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE at 100 ℃.

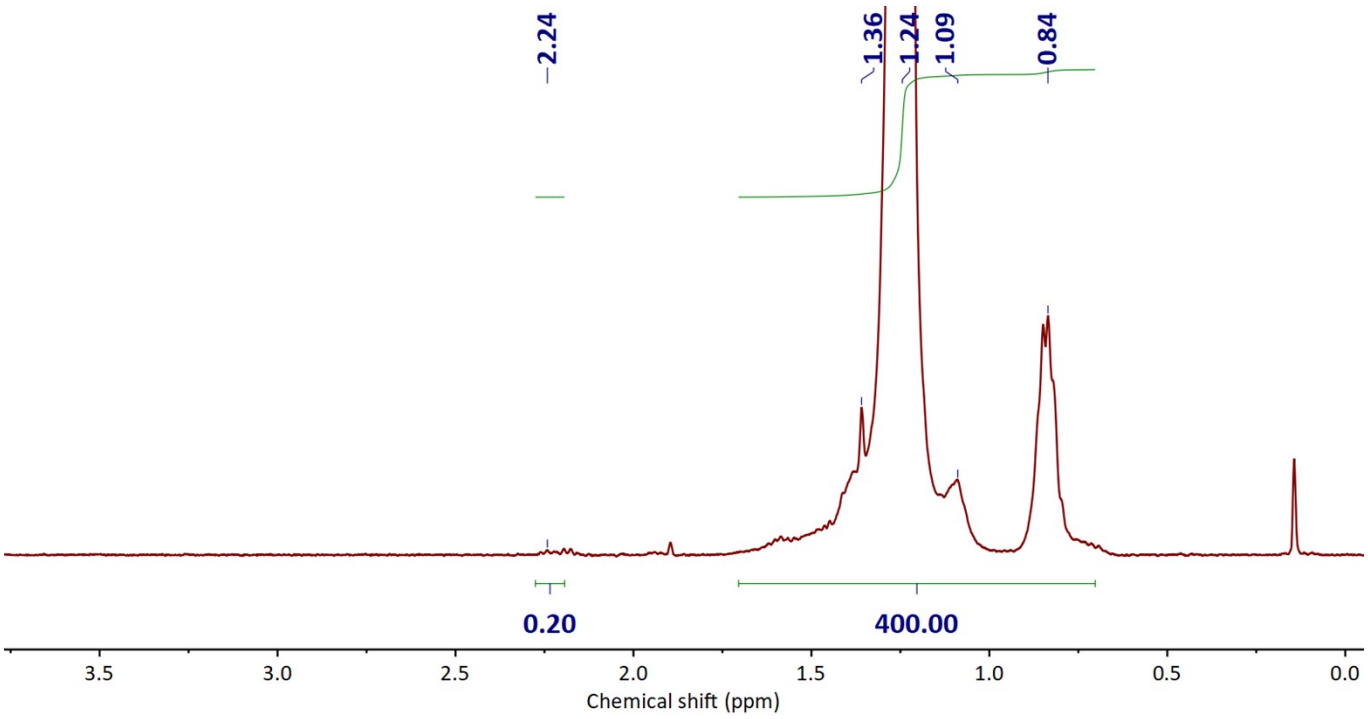


Fig. S14 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE at 110 ℃.

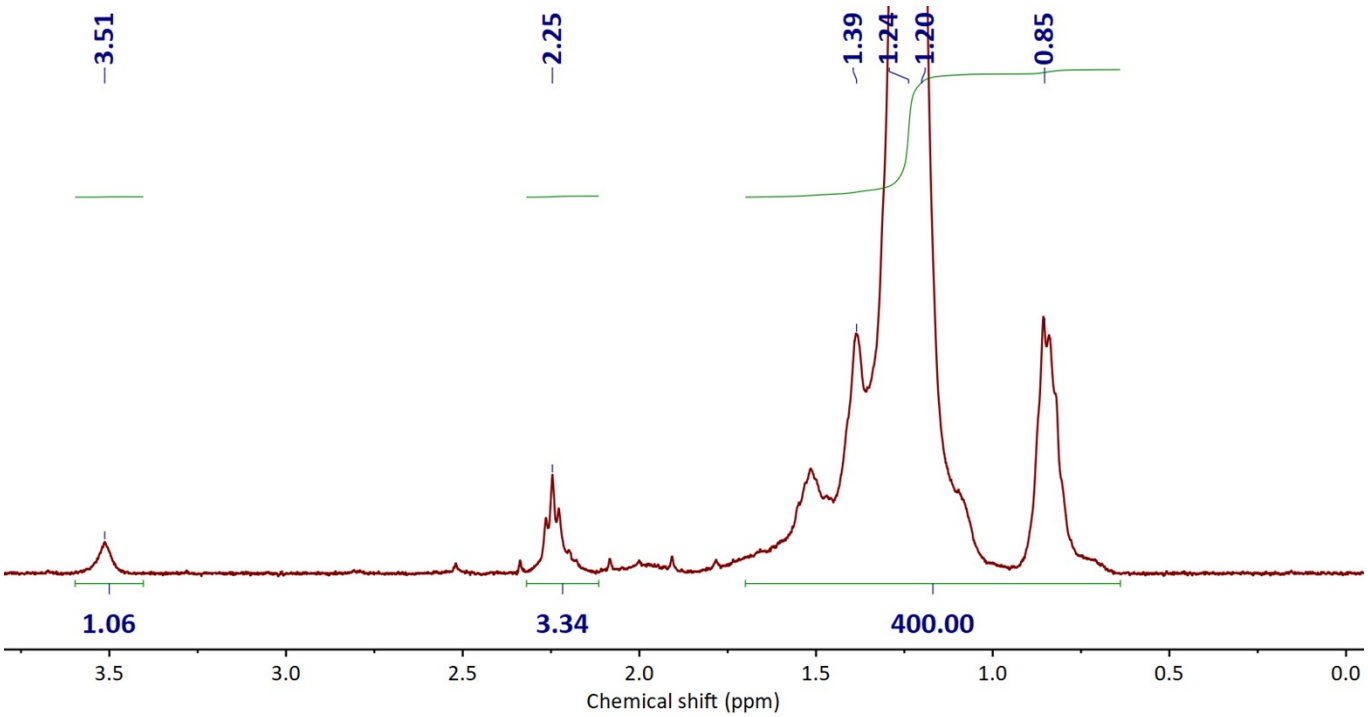


Fig. S15 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE at 130 ℃.

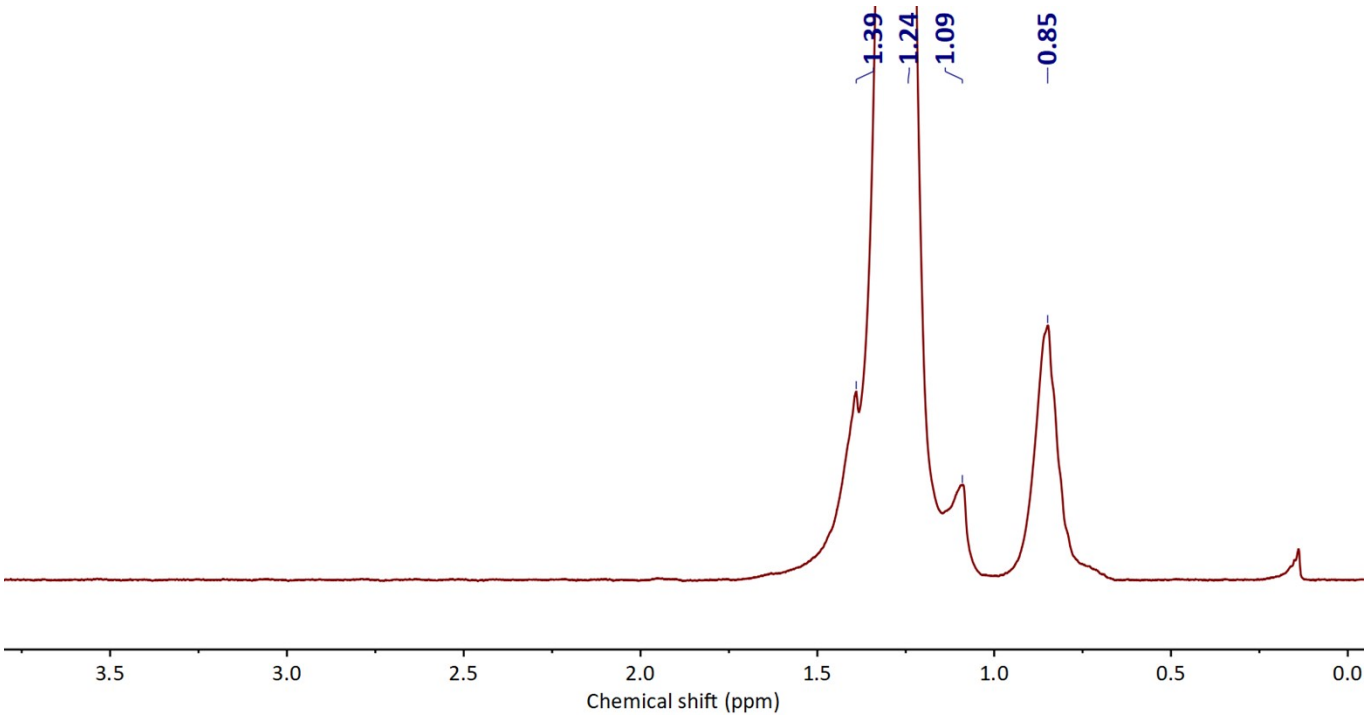


Fig. S16 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of PE product under N_2 at 120 °C.

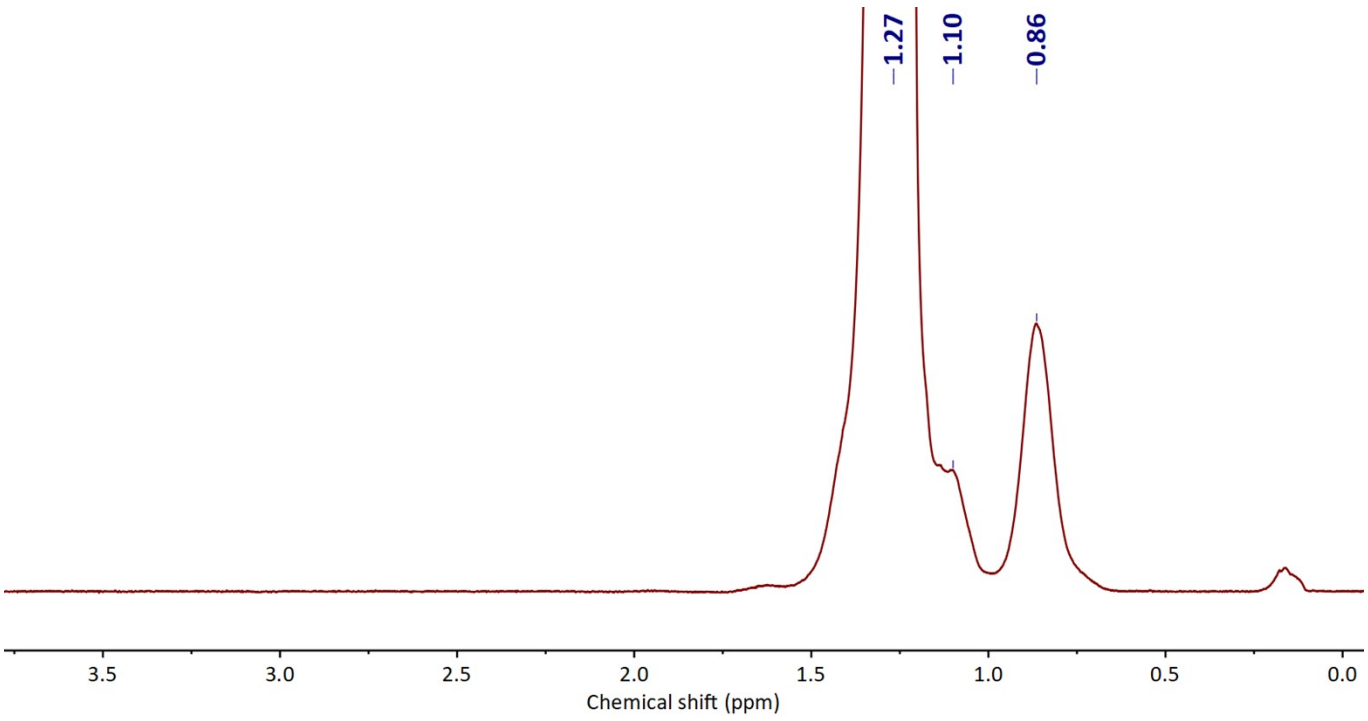


Fig. S17 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of PE product under air at 120 °C.

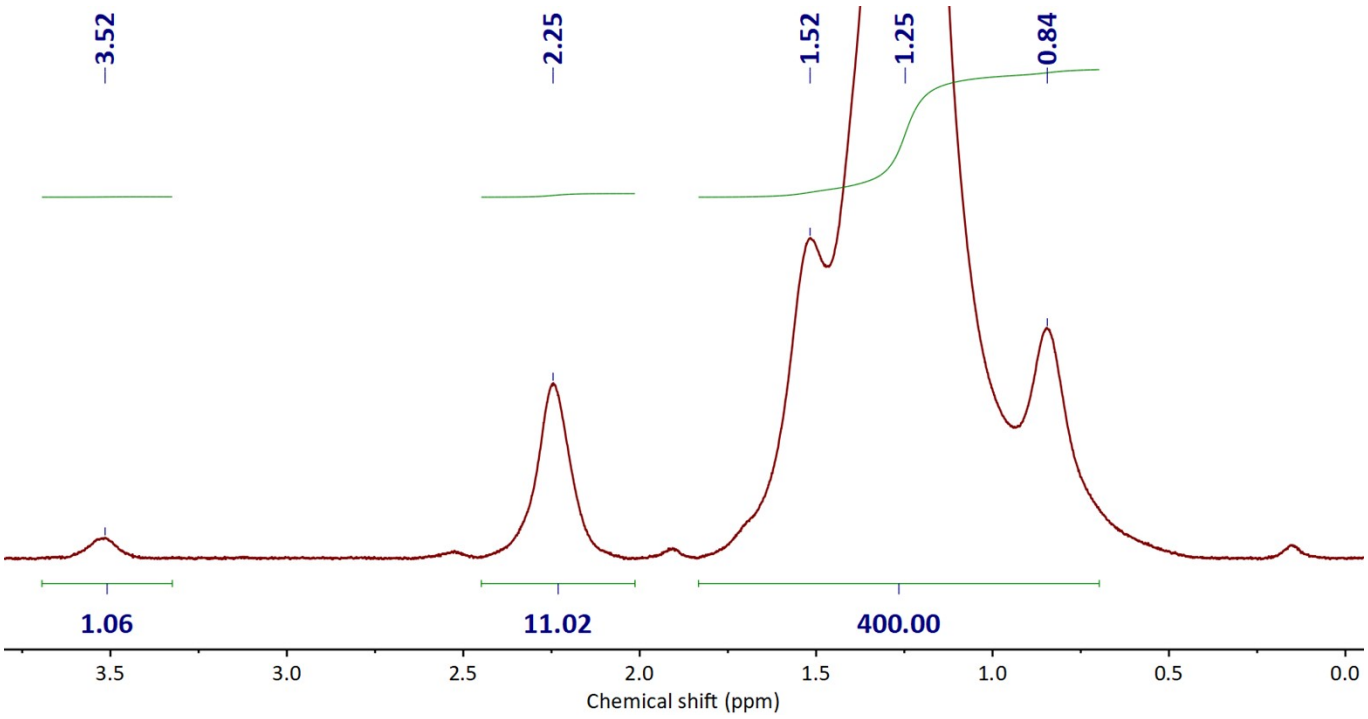


Fig. S18 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of oxidized PE using air flow of 30 mL/min at 120 °C.

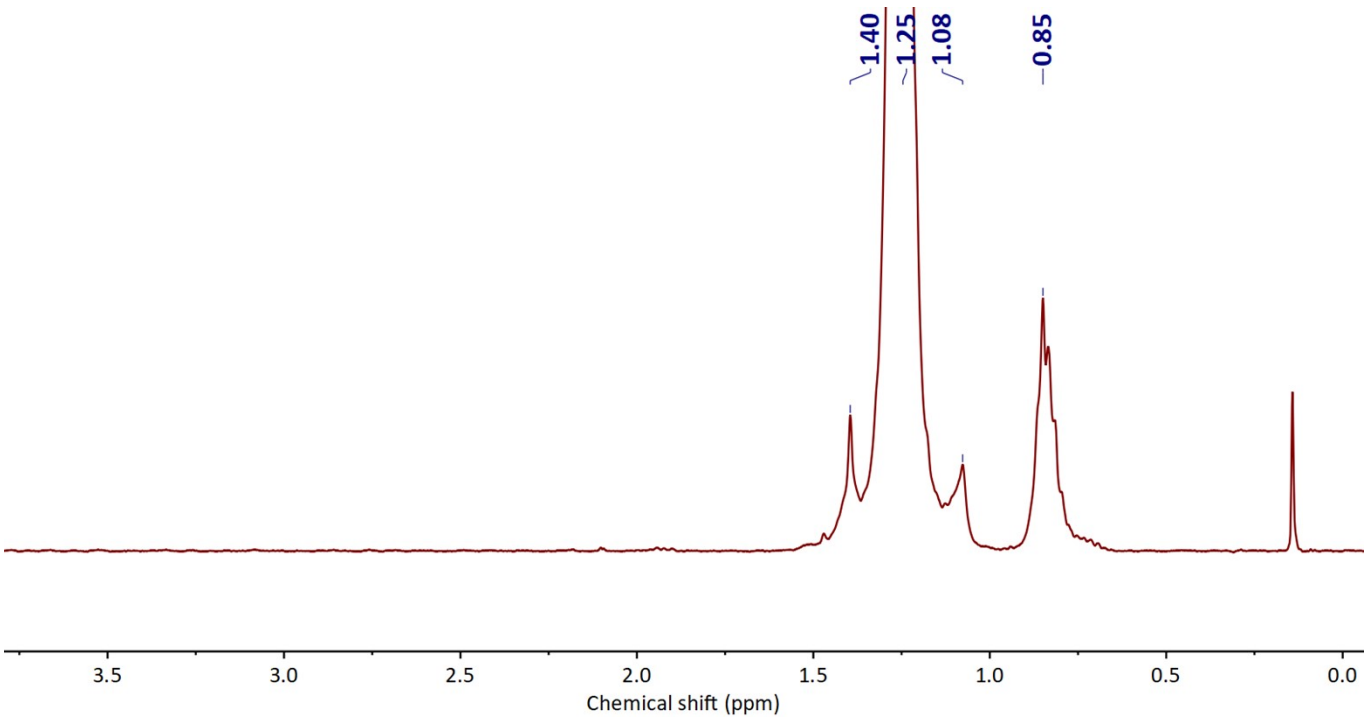


Fig. S19 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of PE product in 1,2-dichlorobenzene at 120 °C.

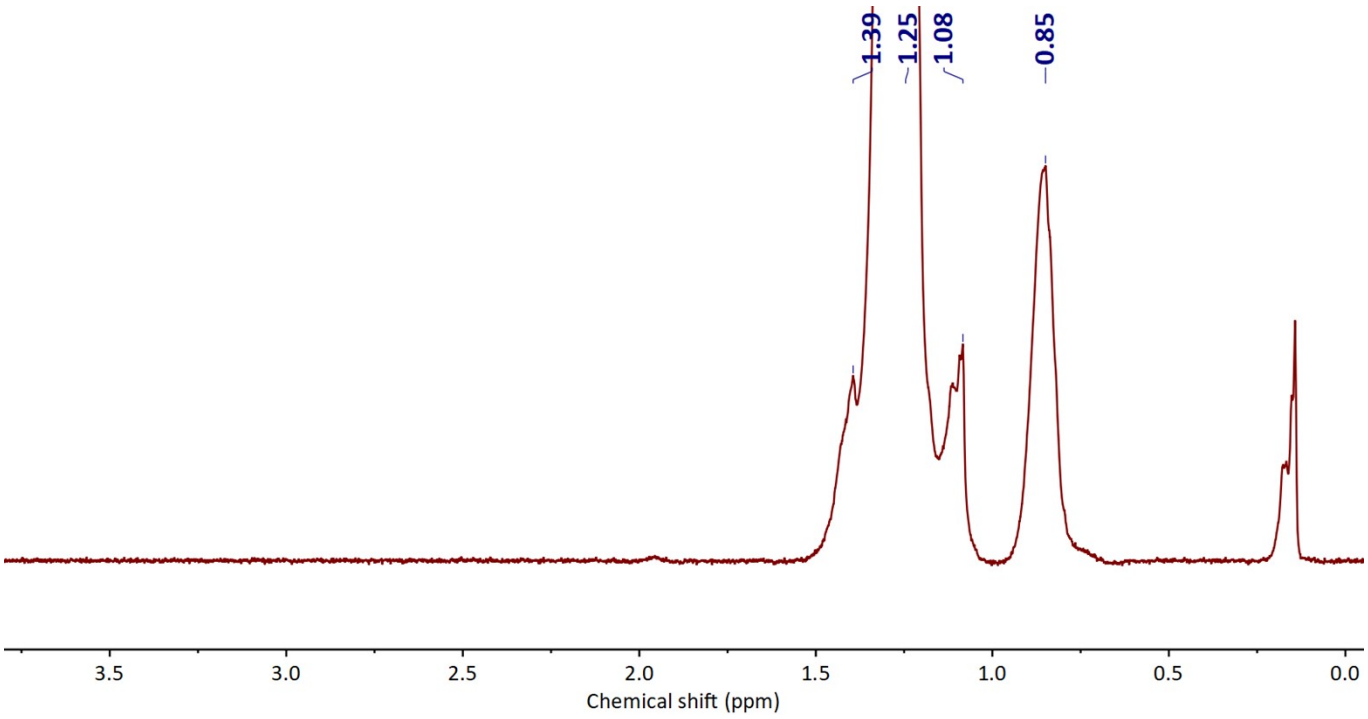


Fig. S20 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of PE product in *t*-butylbenzene at 120 °C.

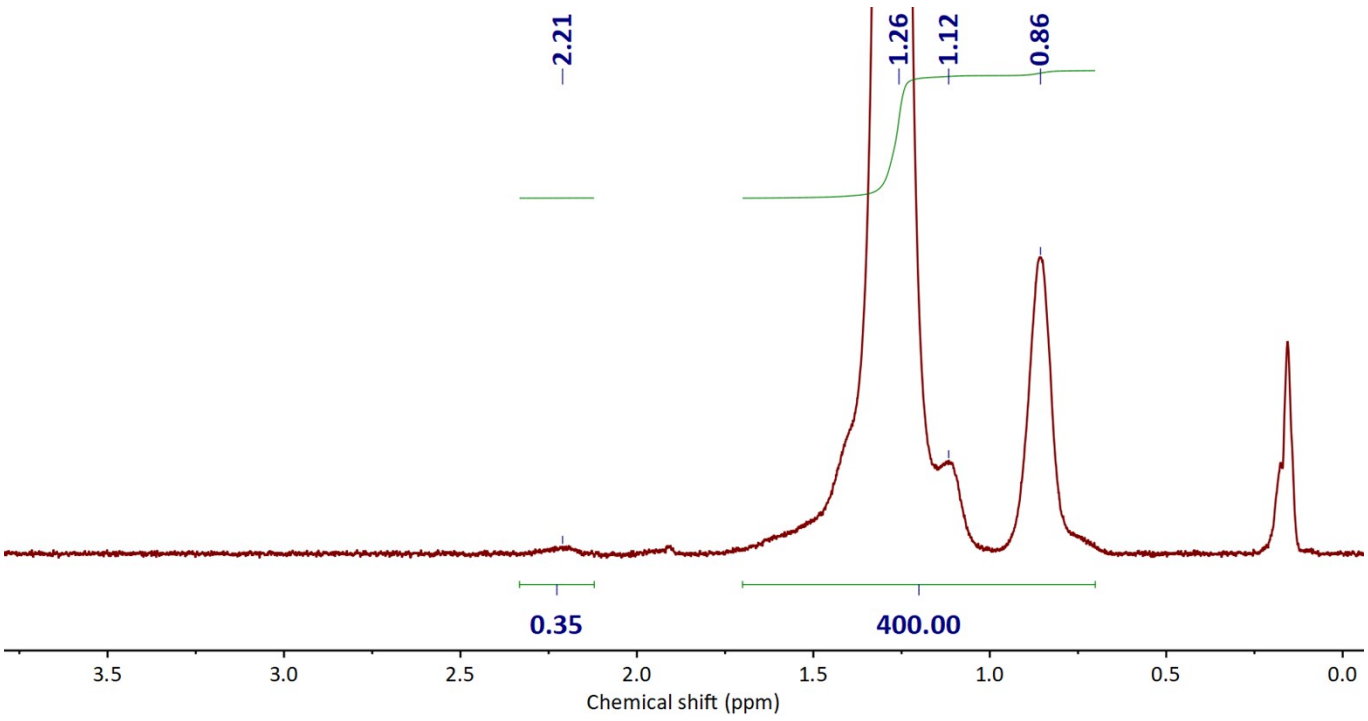


Fig. S21 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 ℃) of oxidized PE product in *p*-xylene at 120 °C.

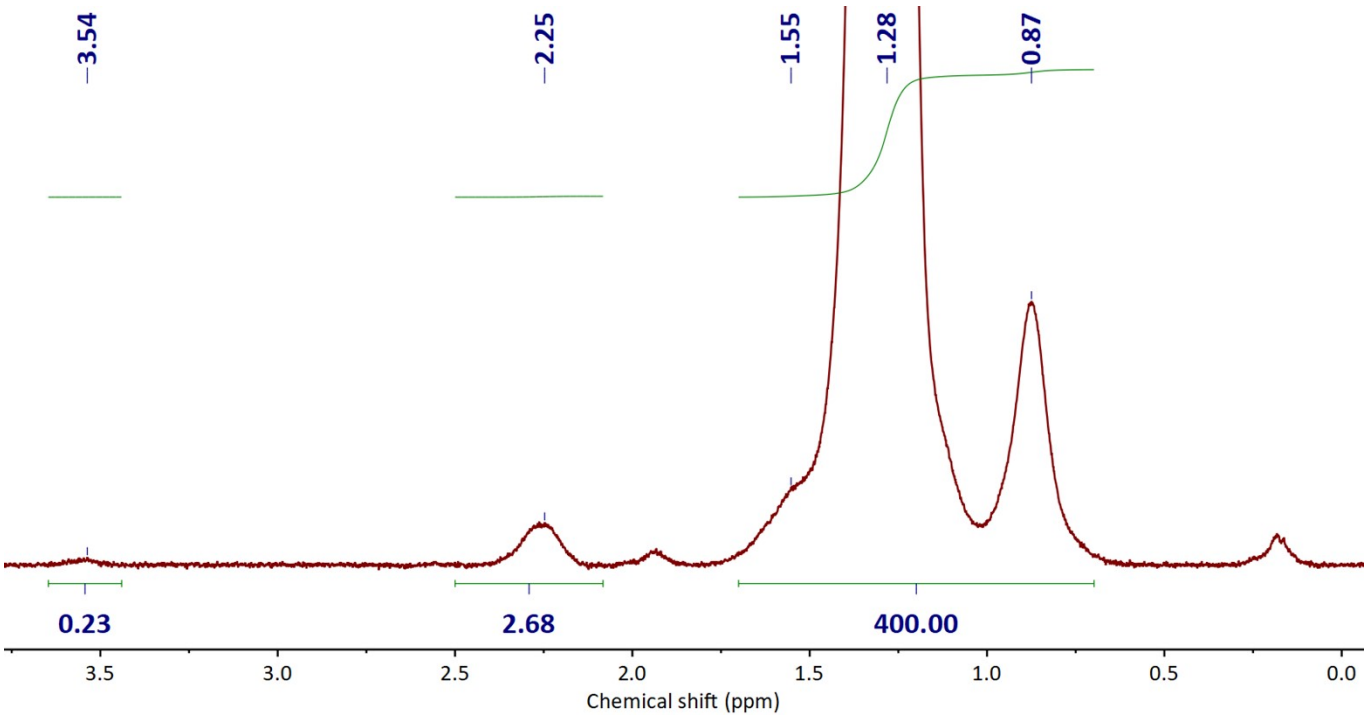


Fig. S22 ^{1}H-NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of PE product in *o*-xylene at 120 °C.

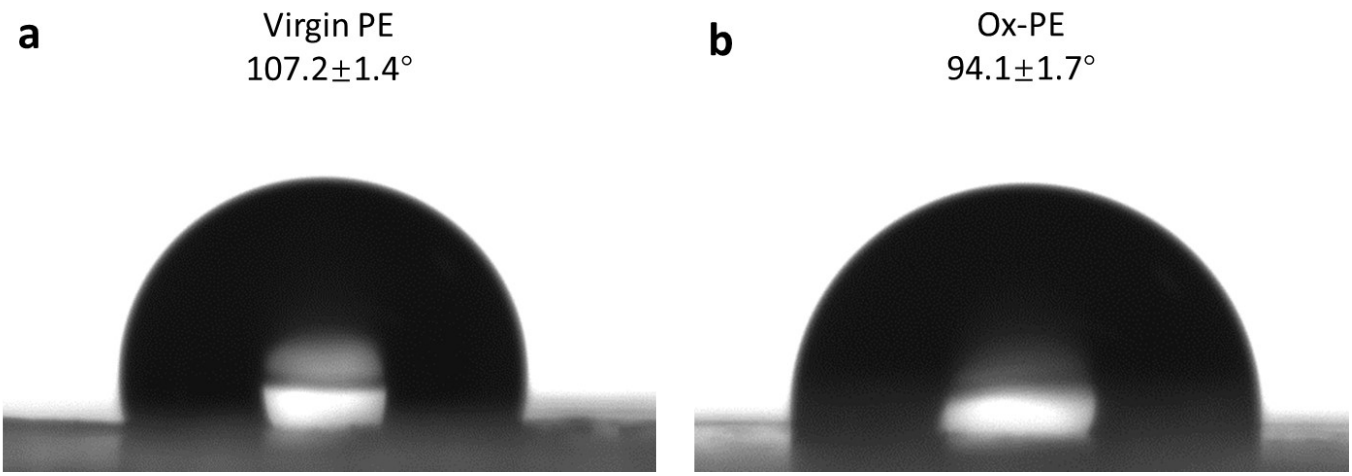


Fig. S23 Water contact angles of virgin PE (a) and Ox-PE (b). Three measurements were performed for each sample.

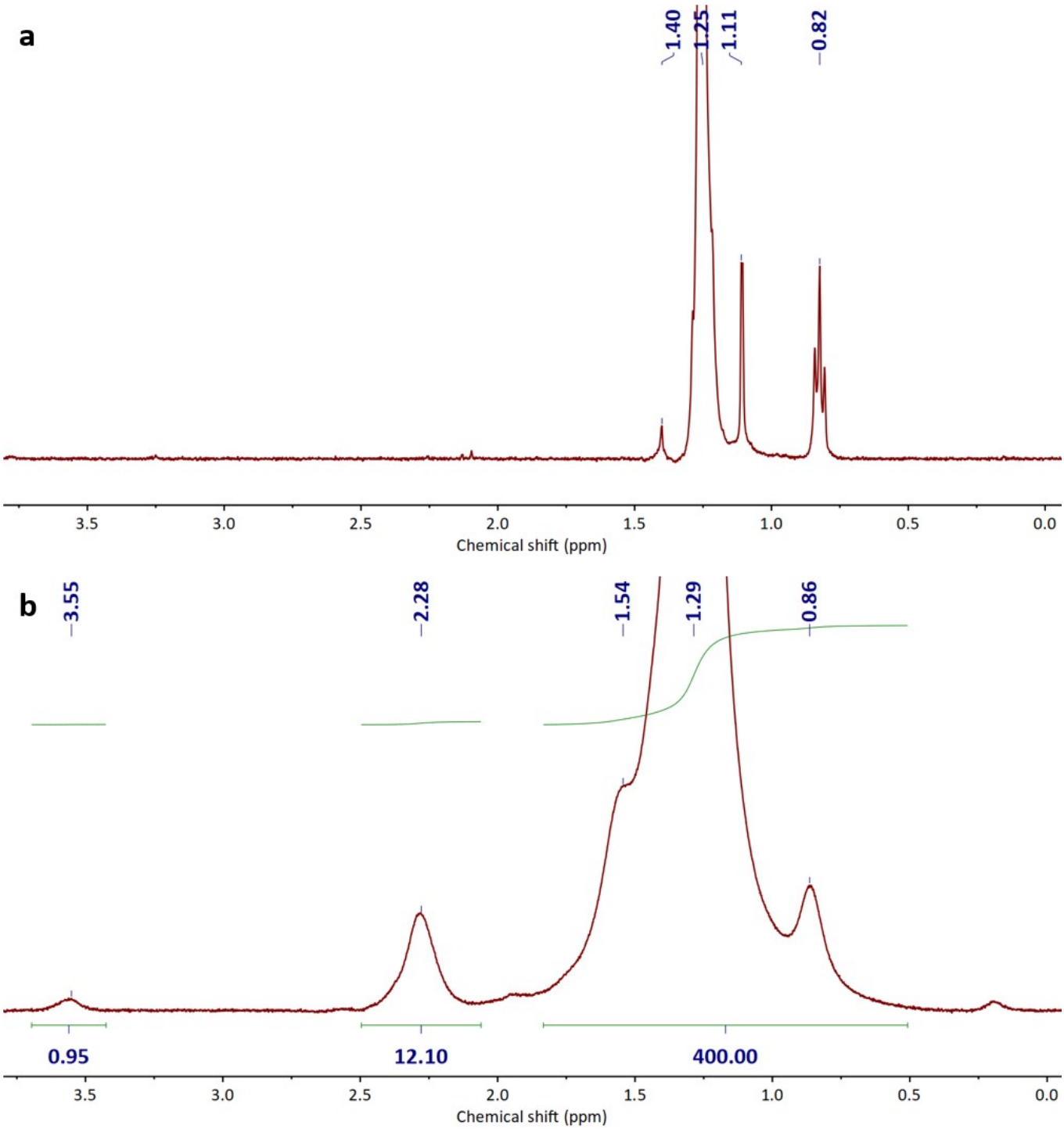


Fig. S24 ^{1}H-NMR spectra (1,2-dichlorobenzene-d_4, 100 ℃) of virgin LLDPE (a) and oxidized LLDPE (b).

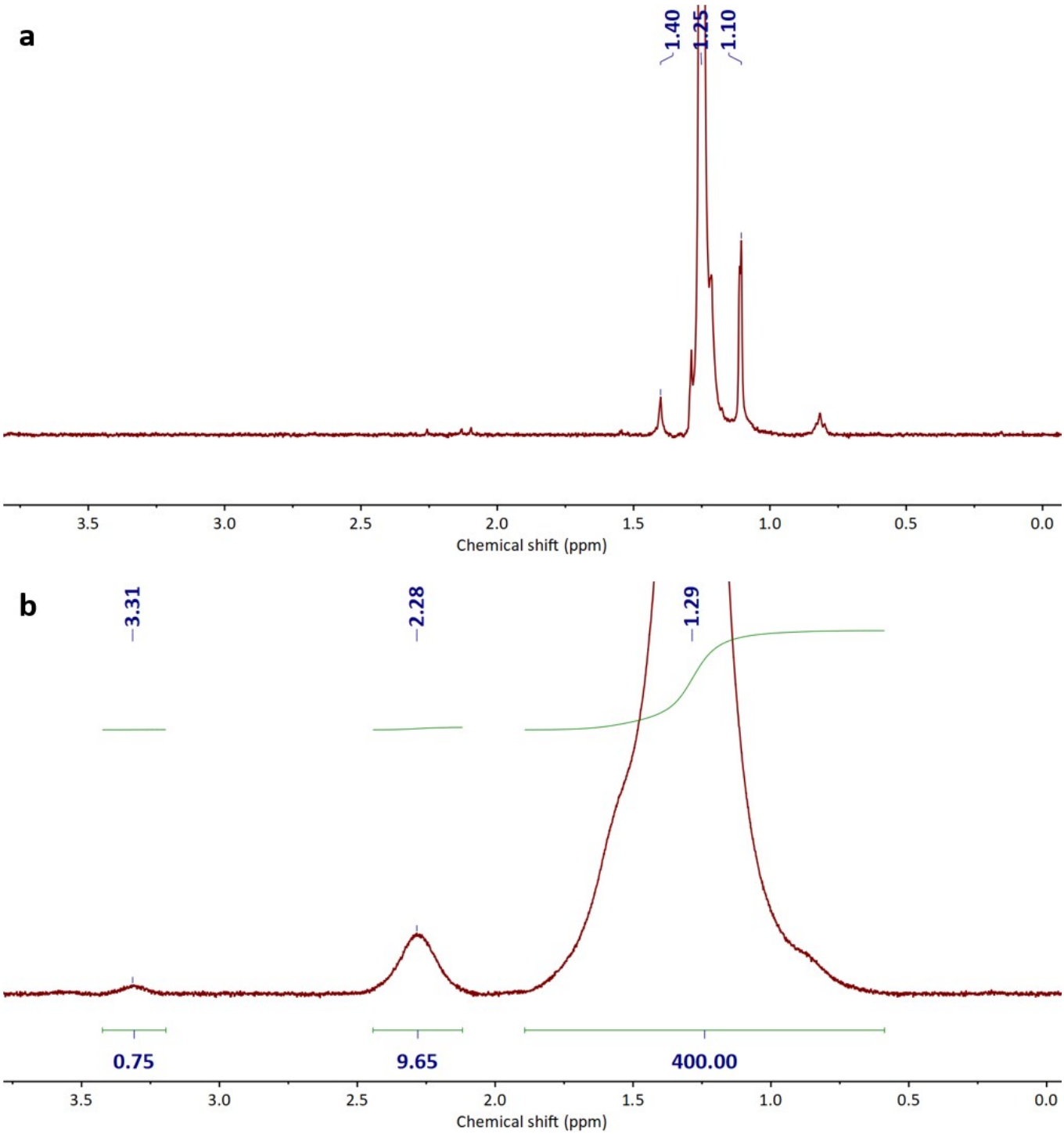


Fig. S25 ^{1}H-NMR spectra (1,2-dichlorobenzene-d_4, 100 °C) of virgin HDPE (a) and oxidized HDPE (b).

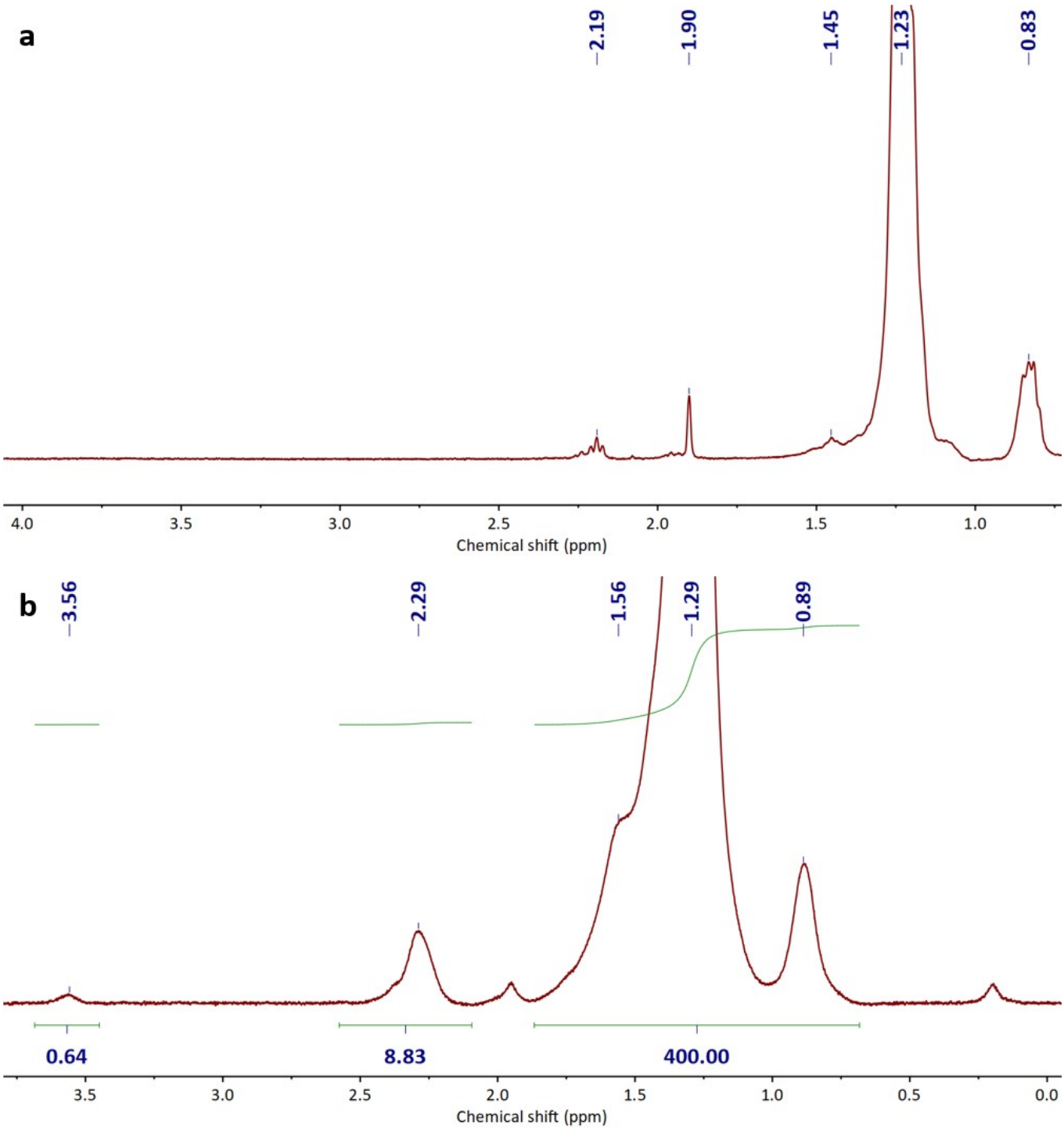


Fig. S26 ^{1}H-NMR spectra (1,2-dichlorobenzene-d_4, 100 °C) of virgin low M_w PE (a) and oxidized low M_w PE (b).

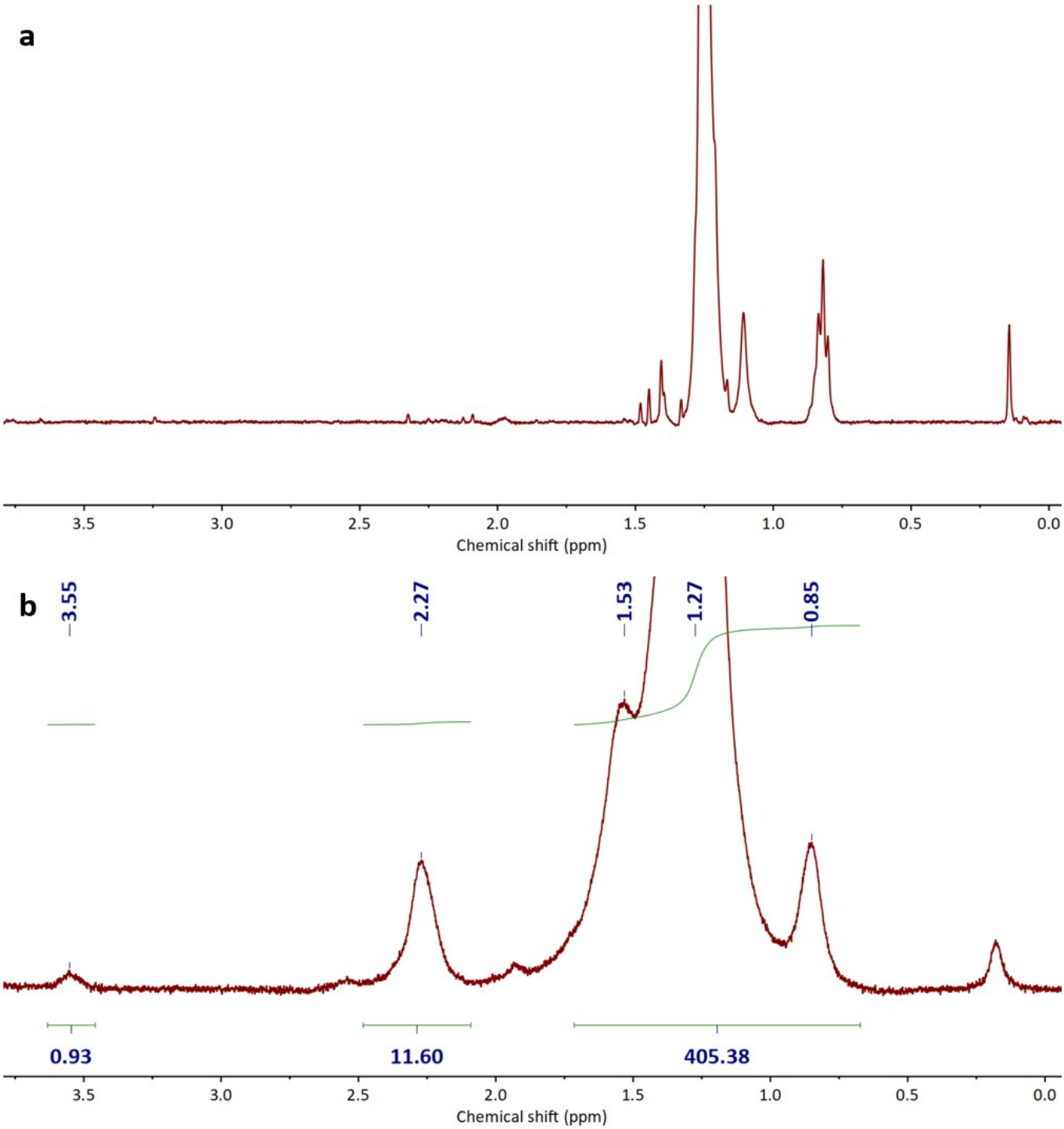


Fig. S27 ^{1}H-NMR spectra (1,2-dichlorobenzene-d_4, 100 °C) of virgin PE bag (a) and oxidized PE bag (b).

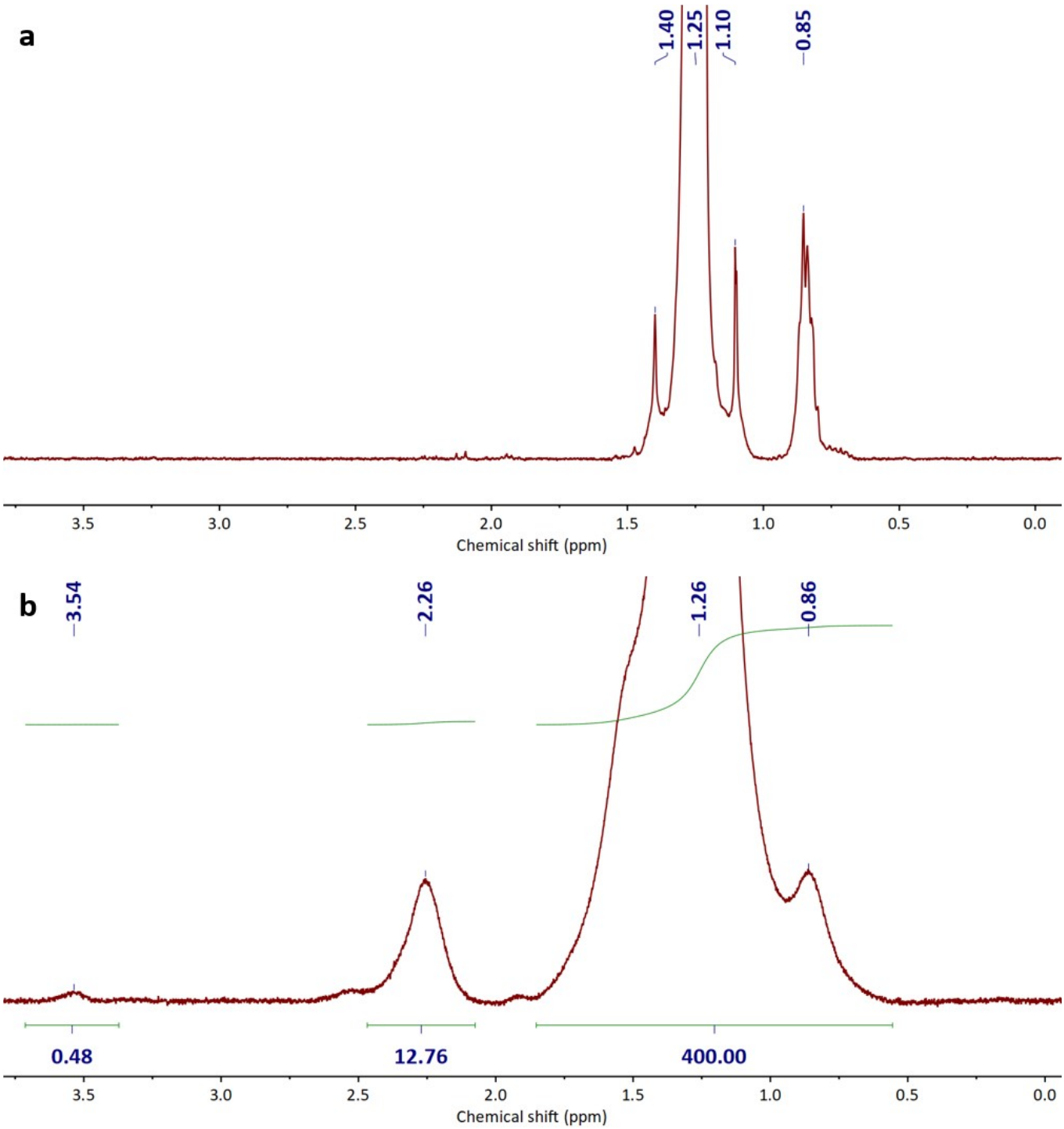
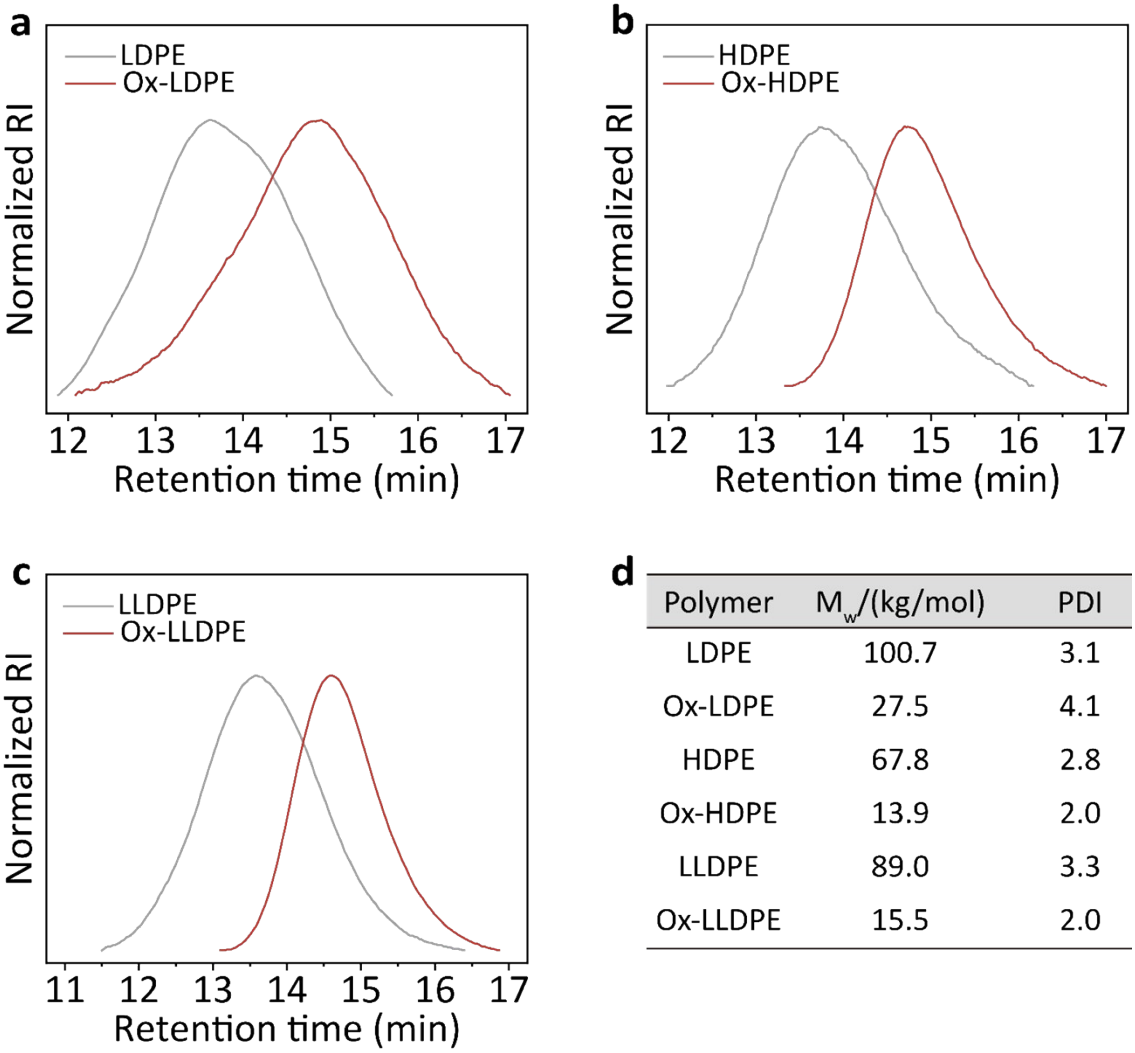


Fig. S28 ^{1}H-NMR spectra (1,2-dichlorobenzene-d_4, 100 °C) of virgin PE pipette (a) and oxidized PE pipette (b).



d

Polymer	M_w/(kg/mol)	PDI
LDPE	100.7	3.1
Ox-LDPE	27.5	4.1
HDPE	67.8	2.8
Ox-HDPE	13.9	2.0
LLDPE	89.0	3.3
Ox-LLDPE	15.5	2.0

Fig. S29 High-temperature gel permeation chromatography curves of LDPE (a), HDPE (b) and LLDPE (c) before and after oxidation. Molecular weight and polydispersity are shown in (d).

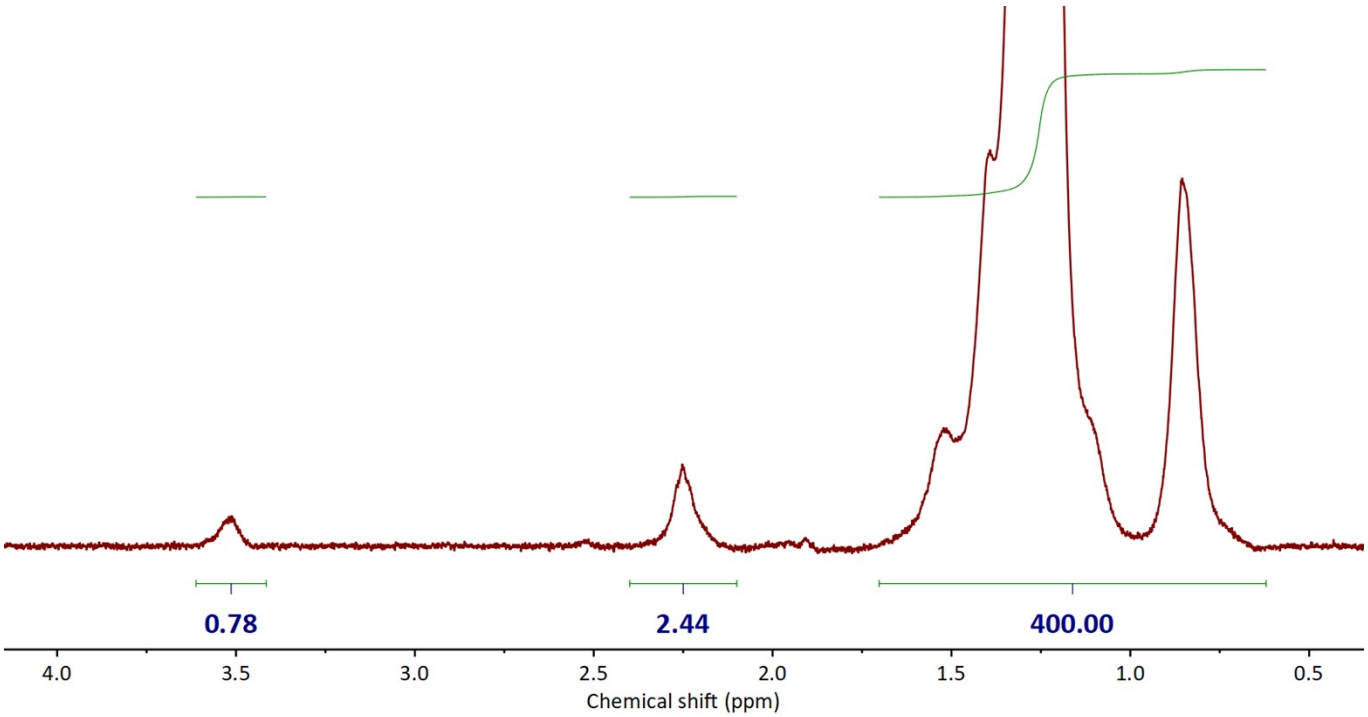


Fig. S30 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of oxidized PE from scaling experiment at 120 °C.

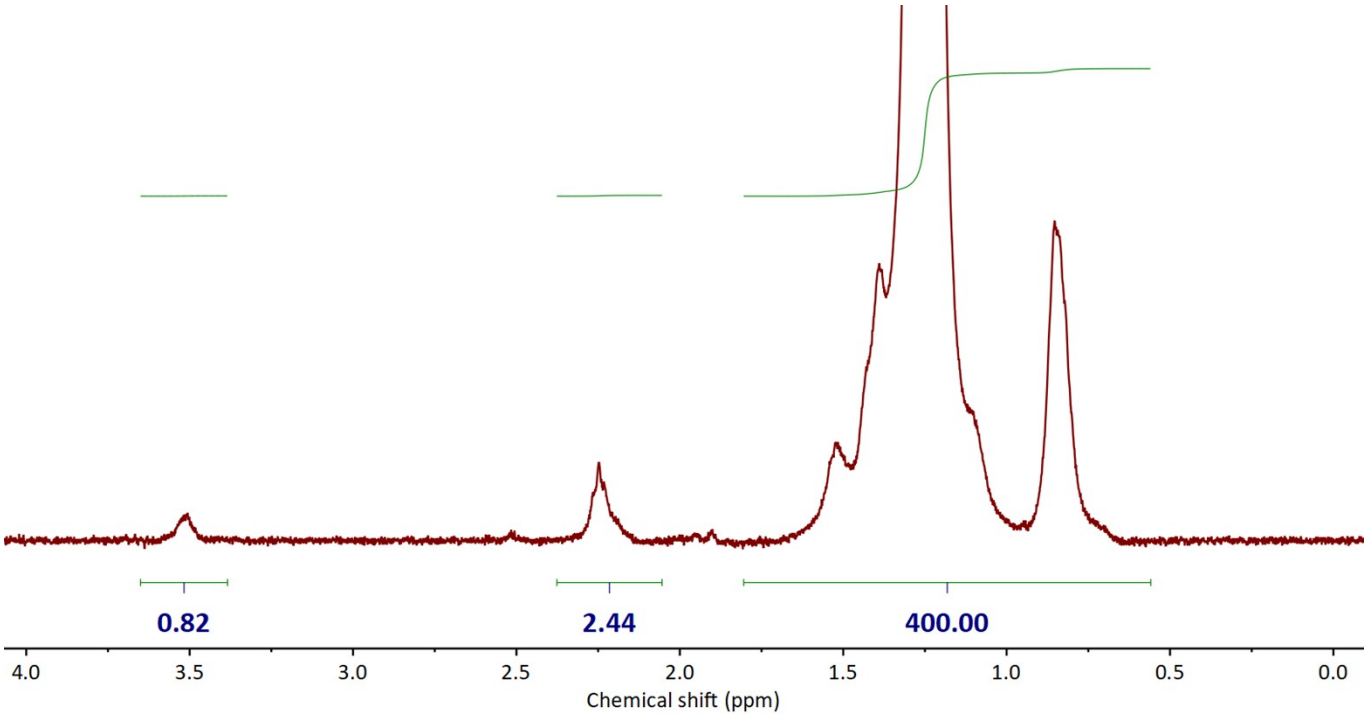


Fig. S31 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of oxidized PE after hot pressing.

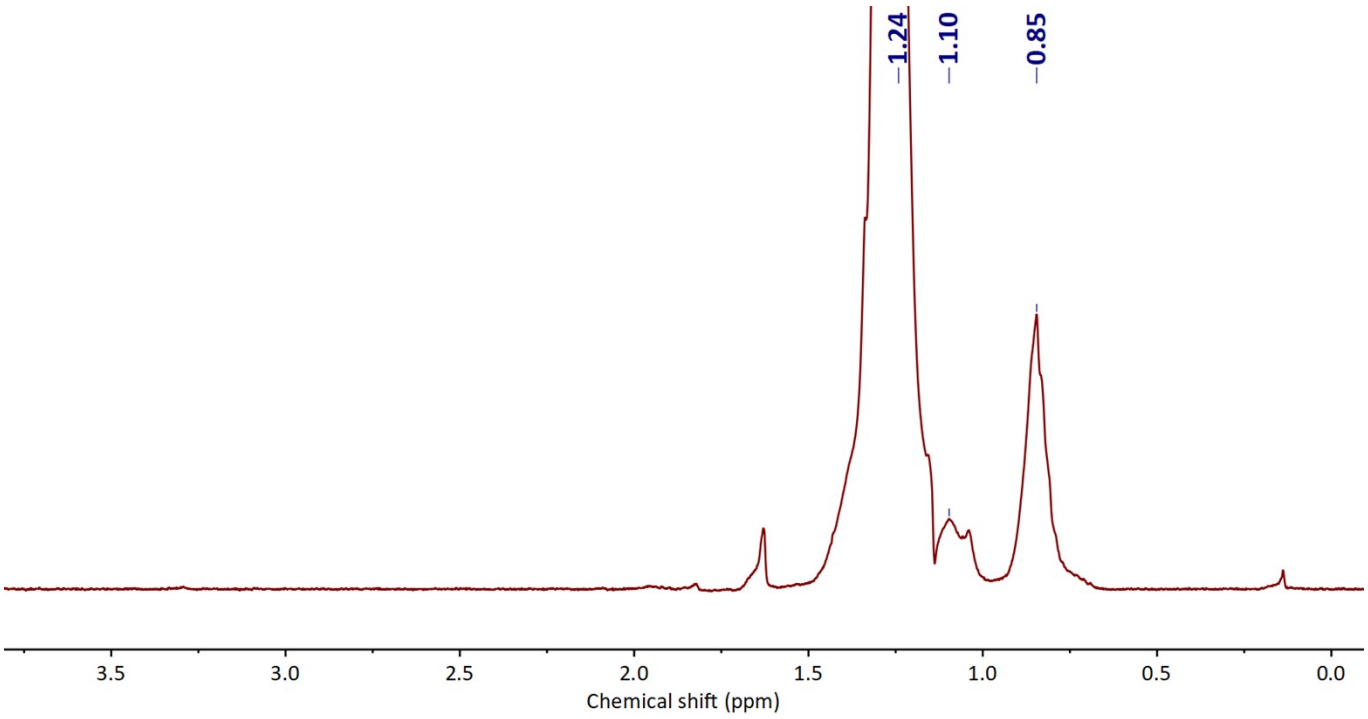


Fig. S32 ^{1}H NMR spectrum (1,2-dichlorobenzene-d_4, 100 °C) of PE product in cumene with *p*-benzoquinone at 120 °C.

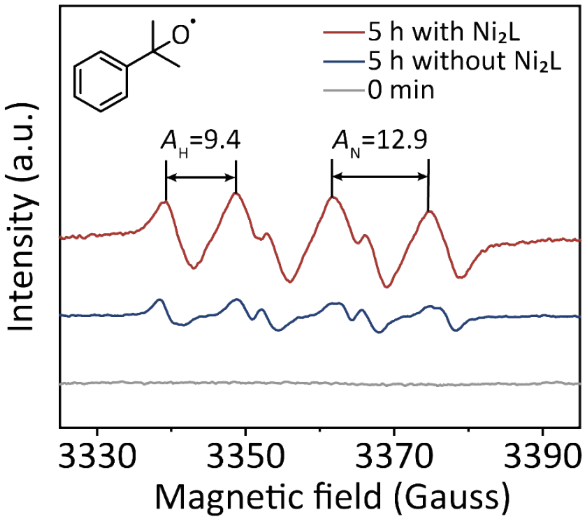


Fig. S33 ESR spectra of cumene-mediated system solutions with PE at five hours with and without Ni_2L. These spectra were calibrated by a Mn internal standard.

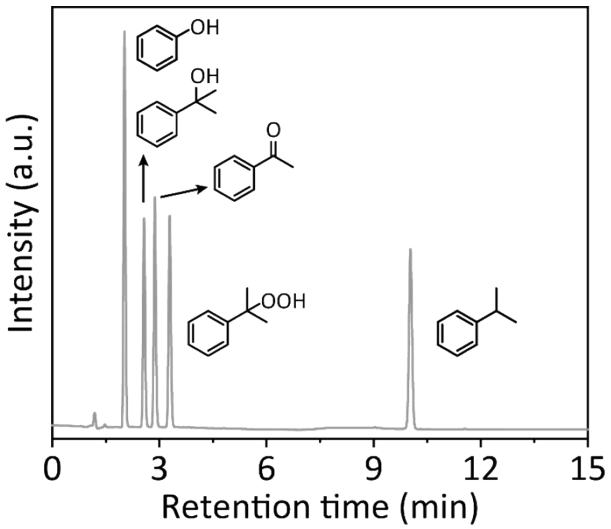


Fig. S34 HPLC chromatogram of cumene, cumene hydroperoxide, acetophenone, 2-phenyl-propan-2-ol and phenol.

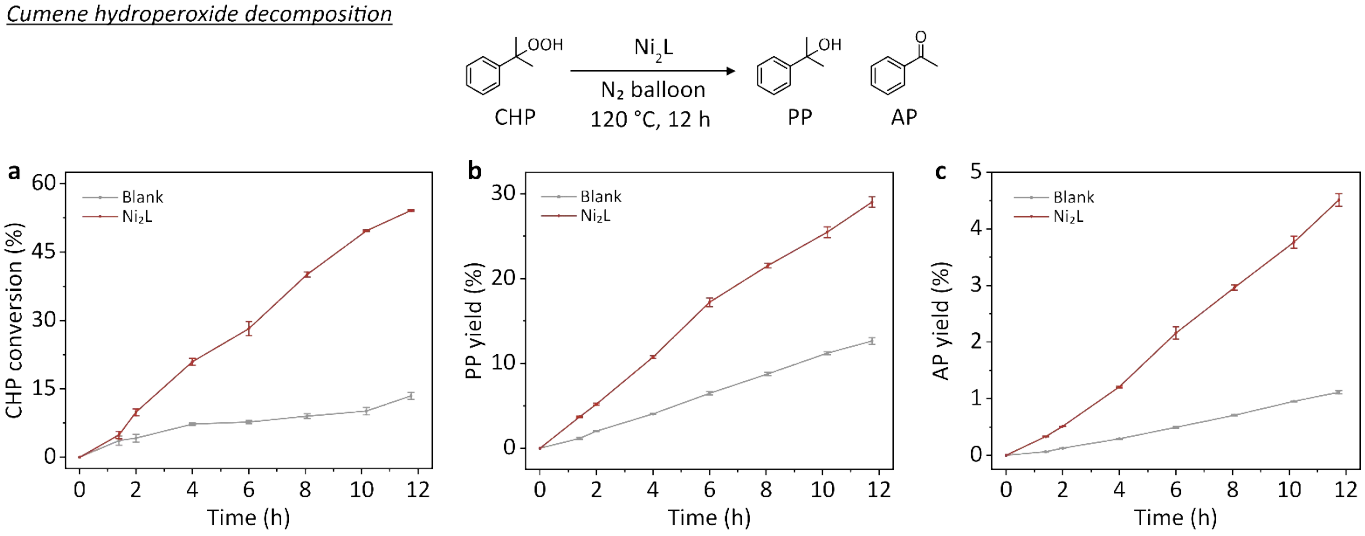


Fig. S35 CHP conversion (a), PP (b) and AP yield (c) from CHP decomposition experiments with and without Ni_2L. Reaction conditions: 6 mL *ca.* 40 wt% CHP dissolved in cumene, 0.04 mol% Ni_2L and N_2 balloon at 120 °C. 10 μL liquid was moved out every two hours and diluted to 10 mL using methanol for HPLC analysis.

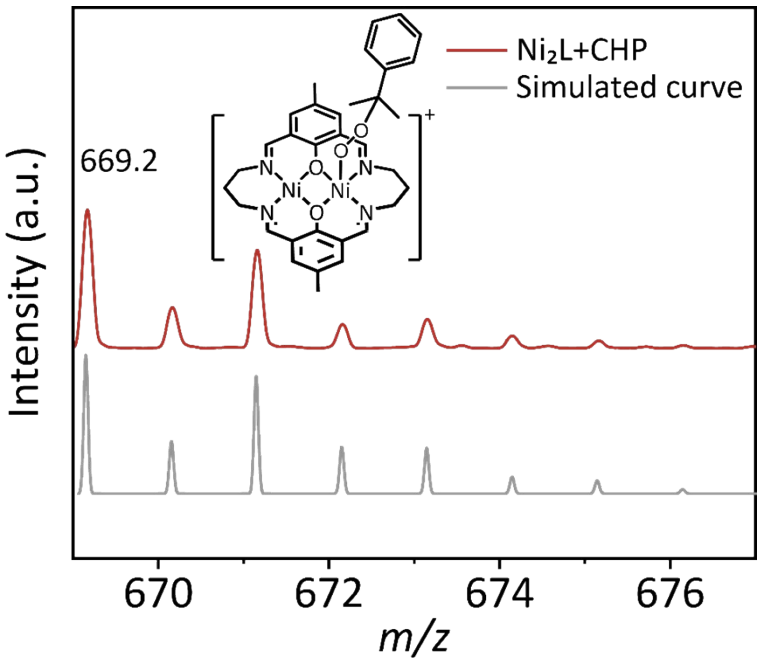


Fig. S36 MALDI-TOF-MS of Ni_2L dissolved in CHP and simulated result of $[C_{33}H_{41}O_4N_4Ni_2]^+$

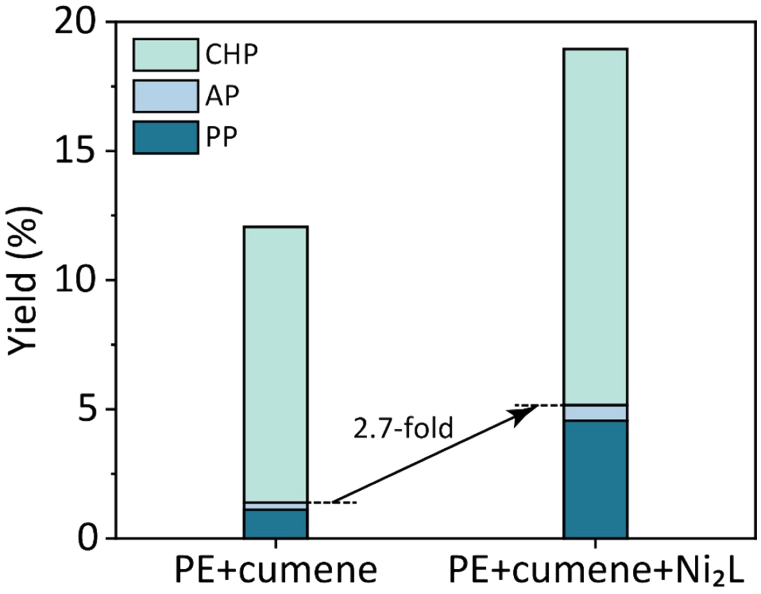


Fig. S37 CHP, AP and PP yield after cumene-mediated experiments with and without Ni_2L. Reaction conditions: 200 mg PE, 6 mL cumene, 0.25 mol% Ni_2L and O_2 balloon at 120 °C for 24 hours.

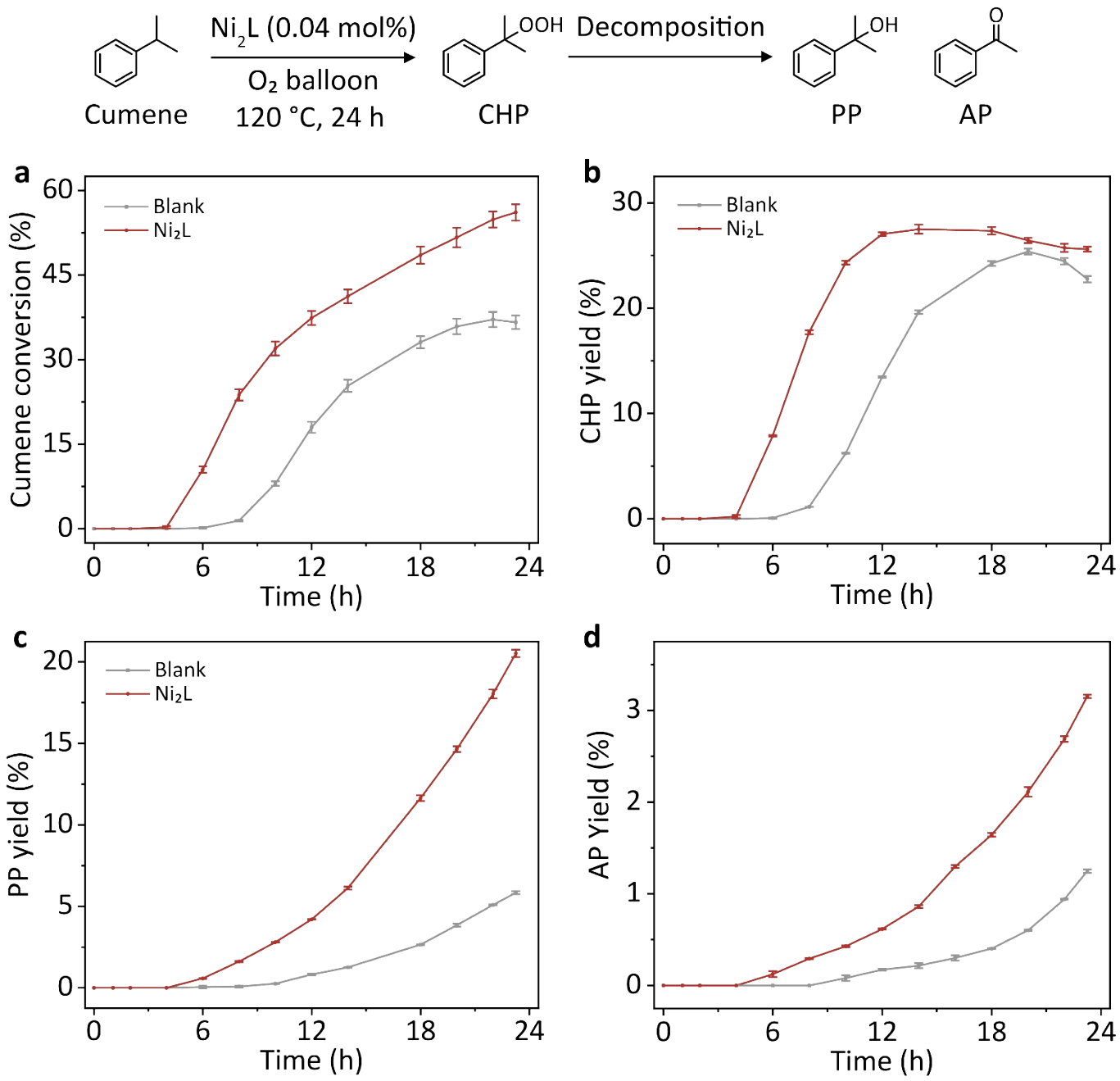
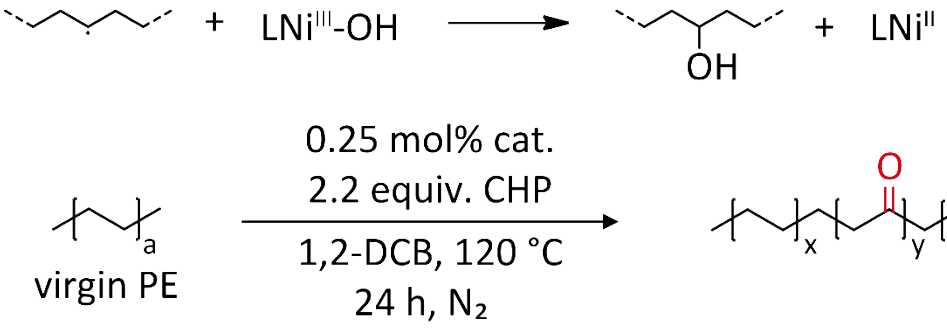


Fig. S38 Cumene conversion (a), CHP (b) and PP yield (c) from cumene autooxidation experiments with and without Ni_2L. Reaction conditions: 6 mL cumene, 0.04 mol% Ni_2L and O_2 balloon at 120 °C. 10 μL liquid was moved out every two hours and diluted to 10 mL using methanol for HPLC analysis.

Possible pathway I:



Entry	cat.	Functionalization degree (mol%)		A/C
		Hydroxyl	Carbonyl	
1	$NiCl_2·6H_2O$	0.43	0.21	2.05
2	NiPc	0.39	1.25	0.31
3	Ni_2L	0.58	1.04	0.56

Fig. S39 Oxidation of PE in the presence of different Ni-based catalysts. Reaction conditions: 200 mg LDPE, 6 mL 40 wt% CHP in 1,2-dichlorobenzene, 0.25 mol% catalyst, 120 °C under 1 atm N_2.

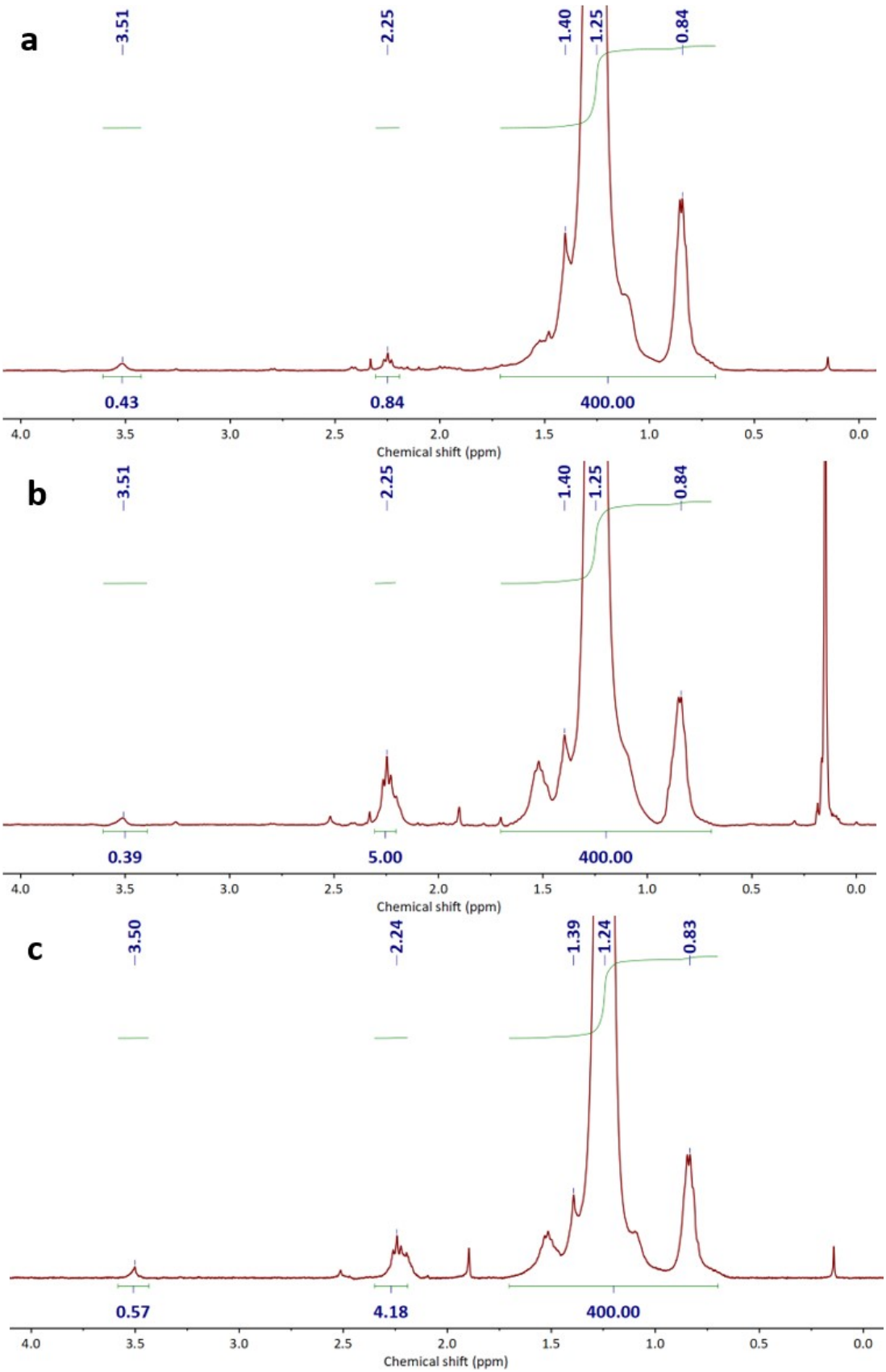
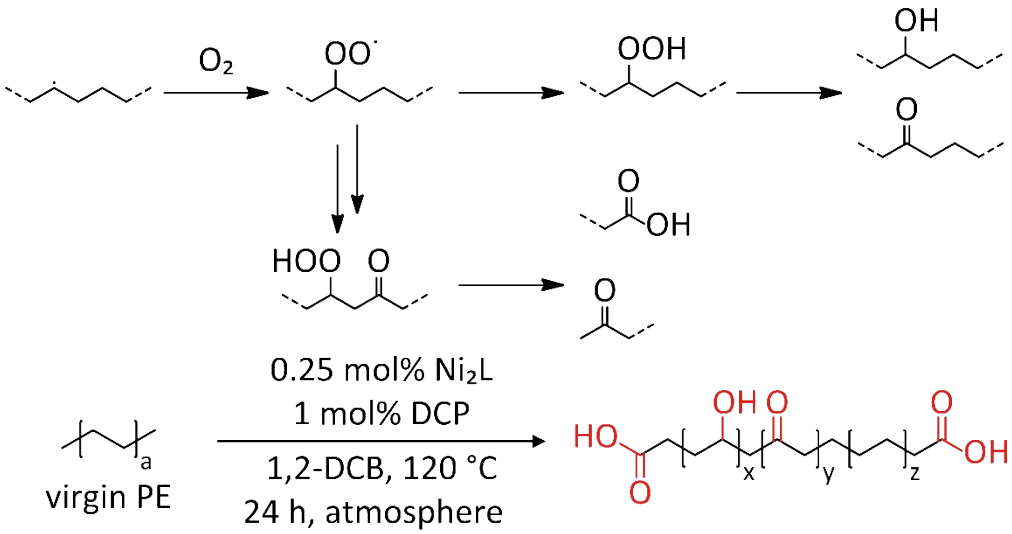


Fig. S40 ^{1}H-NMR spectra (1,2-dichlorobenzene-d_4, 100 °C) of PE products in Fig. S39. Spectra of products from Entry 1–3 were shown as (a–c), respectively.

Possible pathway II:



Entry	Atmosphere	Functionalization degree (mol%)			
		Hydroxyl	Carbonyl	Carboxyl	Total
1	1 atm air	0.17	0.25	0.61	1.03
2	1 atm O_2	0.39	0.40	1.04	1.83

Fig. S41 Oxidation of PE under different atmosphere. Reaction conditions: 200 mg LDPE, 0.25 mol% Ni_2L, 1 mol% dicumyl peroxide (DCP), 6 mL 1,2-dichlorobenzene, 120 °C under different atmosphere.

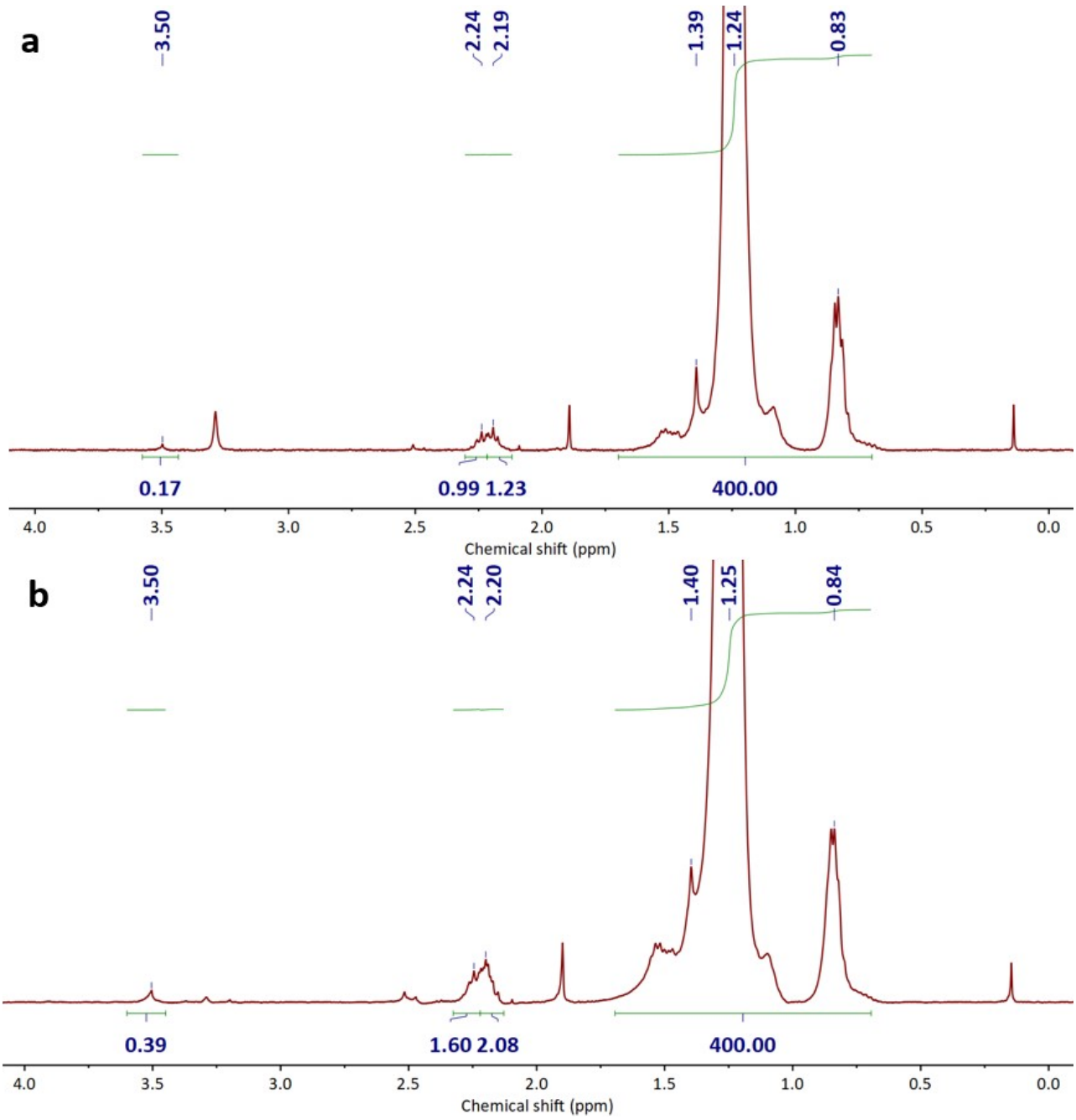


Fig. S42 ^{1}H-NMR spectra (1,2-dichlorobenzene-d_4, 100 °C) of PE products in Fig. S41. Spectra of products from Entry 1–2 were shown as (a–b), respectively.

4. References

1 H. Huang, M. Sun, S. Li, S. Zhang, Y. Lee, Z. Li, J. Fang, C. Chen, Y.-X. Zhang, Y. Wu, Y. Che, S. Qian, W. Zhu, C. Tang, Z. Zhuang, L. Zhang and Z. Niu, *J. Am. Chem. Soc.*, 2024, **146**, 9434-9443.

2 Y.-X. Zhang, S. Zhang, H. Huang, X. Liu, B. Li, Y. Lee, X. Wang, Y. Bai, M. Sun, Y. Wu, S. Gong, X. Liu, Z. Zhuang, T. Tan and Z. Niu, *J. Am. Chem. Soc.*, 2023, **145**, 4819-4827.

3 L. Chen, K. G. Malollari, A. Uliana, D. Sanchez, P. B. Messersmith and J. F. Hartwig, *Chem*, 2021, **7**, 137-145.