Electronic Supporting Information for
Nickel Catalyzed Hydrodechlorination and CO Functionalization of Polyvinyl Chloride

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1. General Considerations

All reactions were set up under anaerobic and anhydrous conditions in a Vacuum Atmospheres OMNI glovebox under a dinitrogen atmosphere. Tetrahydrofuran (THF), Toluene were sparged with UHP argon (Praxair) and dried by passage over Q-5 and molecular sieves using a JCMeyer solvent purification system. Poly (vinyl chloride) (PVC) (Aldrich, Mn = 67.6 kDa, Đ = 1.76 was dried under reduced pressure at 110 °C for 24 h prior to use. Ni precursors, phosphine ligands (except DCyPE and DPPE), sodium formate, potassium formate, anhydrous grade triethyl silane (Et_3SiH), 1,1,3,3 tetramethyl disiloxane (TMDS), Anhydrous cyclopentyl methyl ether (CPME), 1,4 dioxane and cyclohexanone, para-xylene, dimethyl formamide (DMF), 2-chlorohexane, silver nitrate, potassium chromate were purchased from Aldrich. 2-chlorohexane was dried over mol sieves and potassium formate was dried under reduced pressure at 80 °C for 48 h prior to use. Dicyclohexyl phophino ethane (DCyPE) and Diphenyl phosphinoethane (DPPE) were bought from Acros Organics and TCI. $CDCl_3$ was purchased from Cambridge Isotope Laboratories and tetrachloroethane-d2 was purchased from Fischer Chemical. Toy PVC lizards were purchased from amazon.

2. Methods

^1H nuclear magnetic resonance (NMR) and ^{31}P NMR spectra were recorded on a Varian VNMRS-600 3-Channel NMR spectrometer at room temperature or 90 °C and referenced against residual solvent resonances. Attenuated Total Reflectance Fourier Transform Infrared (FT-IR) spectra were recorded on an Agilent Cary 630 FTIR spectrometer equipped with a single reflection diamond (Di) attenuated total reflectance (ATR) module. Thermogravimetric analysis (TGA) data were collected using a Mettler-Toledo TGA/DSC3+ instrument and T_d was determined at 5% mass loss. Differential scanning calorimetry (DSC) traces were recorded using a TA Instruments Discovery DSC 250 Auto, equipped with a Discovery LN Pump, and processed with TRIOS software. The thermal measurements were made at a heating rate of 5-10 °C/min and a dinitrogen flow rate of 20 mL/min. Energy-dispersive X-ray spectroscopy (EDX) measurements were made on a Thermo Scientific Helios G4 PFIB UXe instrument equipped with an Oxford UltimMax 170 Silicon Drift Detector and processed with a Aztec software. EDX measurements were collected in different locations of a sample and average values thereof are tabulated herein.

FT-IR spectroscopy was used as it is a quick and easy method to identify general characteristics of the final polymer product to identify promising reaction conditions. The FT-IR spectra of polyethylene (PE) and PVC are very different, with polyethylene showing three distinct peaks, most prominent thereof appears in the 2800-3000 cm^{-1} region. The FT-IR spectrum of PVC has a distinct C-Cl stretch between 600-650 cm^{-1} that does not overlap with any PE peaks, allowing us to track reaction progress by monitoring its intensity relative to those of polyethylene. While not quantitative, this method enables quick identification of conditions that yield PE-like polymers, as well as those that do not convert PVC very well. Once optimal conditions were identified, further characterization of the polymer product was carried out for holistic analysis of reaction outcomes. The area of the C-Cl peak at 611 cm^{-1} in the infrared spectra of PVC and DPVC (dechlorinated PVC) was analyzed to evaluate the degree of dechlorination of DPVC under different reaction condition. The maximum intensity of PE peaks at 2800-3000 cm^{-1} and C-Cl peak at 611 cm^{-1} were used to calculate the conversion. In a few cases, the mother liquor was evaporated to dryness, and the residues were weighed and characterized by FT-IR to confirm no PVC was remaining in solution.

^{1}H NMR spectroscopy was used to identify H-C-Cl, CH_2-CH_2, and any side products present in soluble portions of polymer products. While these products cannot give a full picture of the final products, they can give an insight into partial structure. NMR products were stirred in tetrachloroethane-d_2 (TCE-d_2) (Cambridge Isotope Labs Inc) at 100 °C overnight to ensure all soluble polymer product was dissolved. The products were then cooled to 90 °C and filtered hot through a pipet filter to filter out insoluble products still present. ^{1}H NMR spectroscopy was then performed at 90 °C. If any product crashed out during transport to the instrument, products were allowed to heat again to 90 °C in the NMR product chamber before analyzed to ensure homogeneity.

%Cl loss from FTIR calculated using Equation 1:

$$\%\ \text{Cl loss} = \frac{Peak\ Area\ of\ C{-}Cl\ bond\ in\ PVC - Peak\ area\ of\ C{-}Cl\ bond\ in\ DPVC}{Peak\ \ area\ of\ C{-}Cl\ bond\ in\ PVC} \times\ 100\% \tag{1}$$

Conversion of polyethylene products were calculated as follows in Equation 2:

% Conversion to polyethylene =

$$\frac{Maximum\ intensity\ of\ CH_2\ stretching\ \ peak\ of\ PE\ in\ product}{Maximum\ intensity\ of\ \ CH_2\ stretching\ \ peak\ of\ PE\ in\ product + \ intensity\ of\ C{-}Cl\ stretching\ peak\ in\ product} \tag{2}$$

Branching calculated using Equation 3:

$$\text{Branches per 1000 C} = \frac{\frac{Integration\ of\ CH_3}{3}}{\frac{Integration\ of\ CH_3}{3} \times 2 + \frac{Integration\ of\ CH_2}{2}} \times\ 1000 \tag{3}$$

%Cl loss from EDX calculated using Equation 4:

$$\%\ \text{Cl loss} = \frac{Amount\ of\ Cl\ present\ in\ PVC - Amount\ of\ Cl\ presentin\ DPVC}{Amount\ of\ Cl\ present\ in\ PVC} \times\ 100\% \tag{4}$$

The amount of chloride ions present in the mother liquor (in mmol) was calculated using Equation 5:

Amount of chloride present (in mmol) = Amount of Ag+ needed (in mmol)

$$= Concentration\ of\ silver\ nitrate\ solution\ \times Volume\ of\ AgNO3\ needed\ for\ titration \tag{5}$$

Amount of NaCl formed as a byproduct calculated using Equation 6:

$$\text{Amount of NaCl} = mmol\ of\ chloride\ ion\ \times molecular\ weight\ of\ NaCl \tag{6}$$

%Cl loss from titration using Equation 7:

$$\%\ \text{Cl loss} = \frac{mmol\ of\ PVC\ used\ for\ reaction - mmol\ of\ NaCl\ produced}{mmol\ of\ PVC\ used\ for\ reaction} \times 100\% \tag{7}$$

3. General Procedures for Reactions with PVC and 2-Chlorohexane

Standard PVC reactions. In a glovebox, Ni precursor (0.016-0.08 mmol, 1-5 mol%) and ligand (0.032-0.16 mmol, 2-10 mol%), poly (vinyl chloride) (PVC) (99 mg, 1.6 mmol, 1 equiv.), $NaHCO_2$ (1.6-4.8 mmol, 1-3 equiv.), and solvent (5 mL THF) were charged into a vial equipped with a Teflon-coated cap. The vial was sealed, secured with electrical tape, brought out of the glovebox, and placed inside a preheated oil bath for the desired time. The vial was then cooled to room temperature and the mixture quenched with excess isopropanol, followed by excess water, which resulted in precipitation of a light yellow solid. The solid was allowed to settle, and the supernatant was gravity filtered away. The isolated polymer was then dried under reduced pressure at 100 °C overnight.

500 mg scale PVC reactions. In a glovebox, Ni precursor (0.2 mmol, 2.5 mol%) and ligand (0.4 mmol, 5 mol%), poly (vinyl chloride) (PVC) (495 mg, 8 mmol, 1 equiv.), $NaHCO_2$ (1.08 g, 16 mmol, 2 equiv.), and solvent (25 mL THF) were charged into a 100 ml Schlenk flask with Teflon stopcock. The flask was brought out of the glovebox and placed inside a preheated oil bath for 72 hours. The flask was then cooled to room temperature and the mixture quenched with excess isopropanol, followed by excess water, which resulted in precipitation of a light yellow solid. The solid was allowed to settle, and the supernatant was gravity filtered away. The isolated polymer was then dried under reduced pressure at 100 °C overnight.

Reaction Conditions with 2-Chlorohexane. In a glovebox, $NiCl_2$ (2.5 mol%) and DCyPE (5 mol%), 2-chlorohexane (0.5 mL, 3.6 mmol), $NaHCO_2$ (7.2 mmol) and 5 mL Toluene were charged into a 35 mL bomb flask. The flask is then brought out of the glovebox, and placed inside a preheated oil bath for 96 hours at 120 °C. The flask was then cooled to room temperature and the mixture was distilled under reduced pressure to separate the liquid product from the solid residue. The isolated product was then characterized by ^1H NMR spectroscopy.

Reaction Conditions with PVC Toy Lizard. PVC toy lizard was ground in a coffee grinder and dried in a vacuum oven before use. Reaction conditions are made with the assumption that the PVC toy is 100 % PVC. While we know this isn't true, the exact PVC content is unknown, so the reaction conditions are meant to match the conditions of clean PVC in weight% instead.

In a glovebox, 2.5 mol% $NiBr_2$·diglyme and 5 mol% DCyPE, PVC toy lizard (100 mg,), $NaHCO_2$ (217 mg, 3.2 mmol) and 5 mL Toluene were charged into a vial equipped with a Teflon-coated cap. The vial was sealed, secured with electrical tape, brought out of the glovebox, and placed inside a preheated oil bath for 48 hours. The vial was then cooled to room temperature and the mixture quenched with excess isopropanol, followed by excess water, which resulted in deposition of a light yellow precipitation. The solid was allowed to settle, and the supernatant was gravity filtered away. The isolated polymer was then dried under reduced pressure at 100 °C overnight.

4. Determination of amount of Sodium Chloride by titration

The concentration of chloride ions in the mother liquor was determined using Mohr's titration method, which involves titration with a standardized 0.1 M aqueous silver nitrate ($AgNO_3$) solution and potassium chromate as an indicator. For titration mother liquor of the reaction from

Table S1 entry 3 was considered. Literature reports indicate that this method yields accurate results when the pH of the sample lies between 6.5 and 10.[1,2]

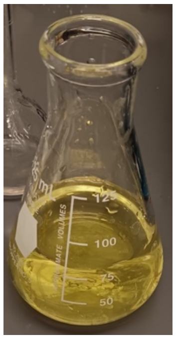
The pH of a water wash from the toluene-based mother liquor was measured and confirmed to be within the range of 7–8, ensuring the reliability of the data obtained.

To prepare the titrant, 0.85 g of solid $AgNO_3$ was accurately weighed and dissolved in 50 mL of distilled water in a volumetric flask to make a 0.1 M solution. The sample (mother liquor) was transferred to a conical flask, and 2–3 drops of potassium chromate indicator were added. During the titration, the initially lemon-yellow solution gradually changed color as silver ions reacted with chloride ions to form a white silver chloride (AgCl) precipitate. The endpoint was detected by the first appearance of a red-brown color due to the formation of silver chromate (Ag_2CrO_4), indicating all chloride had reacted.

The amount of chloride ions present (in mmol) was calculated using Equation 5 and subsequently with equation 6 and 7 amount of NaCl and % dechlorination were determined:

Concentration of $AgNO_3$ (M)	Amount of $AgNO_3$ needed (ml)	Cl^- present in solution (mmol)	Amount of NaCl	% dechlorination
0.1	12	1.2 mmol	71 mg	75

This data aligns well with the FTIR results obtained for this reaction (Table S1 entry 3).

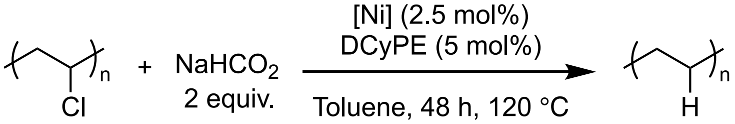


Initial point

End point

5. Reaction Data Tables

Table S1 Effect of different Ni precursors on the PVC hydrodechlorination with DCyPE ligand



Entry	[Ni]	Characterization	$T_{d,5\%}$ (°C), (Char left in %)
1.	$NiCl_2$	FT-IR (Fig. S4), NMR (Fig. S55), TGA (Fig. S82), DSC (Fig. S114)	281 (13)
2.	$NiCl_2$[a]	FT-IR (Fig. S5), NMR (Fig. S56), TGA (Fig. S83)	258 (10)
3.	$Ni(COD)_2$	FT-IR (Fig. S6), NMR (Fig. S57), TGA (Fig. S84), DSC (Fig. S115)	290 (6)
4.	$Ni(acac)_2$	FT-IR (Fig. S7), NMR (Fig. S58), TGA (Fig. S85)	262 (7)
5.	$NiBr_2$. glyme	FT-IR (Fig. S8), NMR (Fig. S59), TGA (Fig. S86), DSC (Fig. S116)	262 (8)
6.	$NiBr_2$. diglyme	FT-IR (Fig. S9), NMR (Fig. S60), TGA (Fig. S87)	272 (7)
7	No Ni	FT-IR (Fig. S10)	-

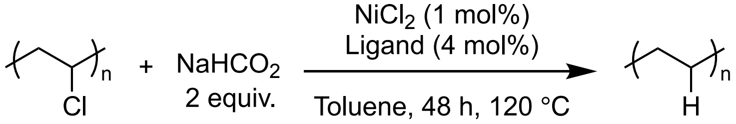
[a]DCyPE (10 mol%)

Table S1a Effect of different Ni precursors on the PVC hydrodechlorination with DCyPE ligand

Entry	[Ni]	% dechlorination[b]	Yield (in %)[c]	Branches per 1000C[d]
1	$NiCl_2$	74	66	140
2	$NiCl_2$[a]	75	65	112
3	$Ni(COD)_2$	77	66	128
4	$Ni(acac)_2$	69	59	129
5	$NiBr_2$. glyme	83	74	91
6	$NiBr_2$. diglyme	83	74	191
7	No Ni	-	-	-

[a]DCyPE (10 mol%), [b] % dechlorination was calculated from FT-IR spectra using equation 1, [c]Yield was calculated from FT-IR spectra using equation 2, [d] Branching number was calculated from FT-IR spectra using equation 3

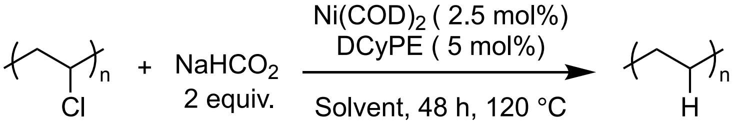
Table S2 Effect of different phosphine ligands on the hydrodechlorination with $NiCl_2$



Entry	Ligand	% dechlorination[a]	Characterization	$T_{d,5\%}$ (°C), (Char left in %)
1	Xantphos	No Reaction	FT-IR (Fig. S11)	-
2	DPPM	No Reaction	FT-IR (Fig. S12)	-
3	DPPE	No Reaction	FT-IR (Fig. S13)	-
4	DPPP	No Reaction	FT-IR (Fig. S14)	-
5	DPPF	Low	FT-IR (Fig. S15)	-
6	DCyPE	75	FT-IR (Fig. S16), NMR (Fig. S61), TGA (Fig. S88)	258 (8)
7	PCy_3	No Reaction	FT-IR (Fig. S17)	-
8	No ligand	No Reaction	FT-IR (Fig. S18)	

[a] % dechlorination was calculated from FT-IR spectra using equation 1

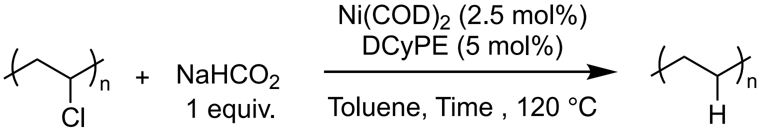
Table S3 PVC hydrodechlorination with Ni(COD)$_2$ and DCyPE in various solvents



Entry	Solvent	% dechlorination[a]	Characterization	$T_{d,5\%}$ (°C), (Char left in %)
1	THF[b]	69	FT-IR (Fig. S19), NMR (Fig. S62), TGA (Fig. S89)	327 (5)
2	Toluene	77	FT-IR (Fig. S6), NMR (Fig. S57), TGA (Fig. S84), DSC (Fig. S115)	290 (6)
3	Cyclo Pentyl Methyl Ether (CPME)[b]	52	FT-IR (Fig. S20), TGA (Fig. S90)	224 (17)
4	Dimethyl Formamide (DMF)[c]	Low	FT-IR (Fig. S21),	-
5	Cyclohexanone[d]	78	FT-IR (Fig. S22), TGA (Fig. S91)	263 (23)
6	Para Xylene	63	FT-IR (Fig. S23)	-
7	1,4 Dioxane	87	FT-IR (Fig. S24), NMR (Fig. S63), TGA (Fig. S92)	292 (38)

[a] % dechlorination was calculated from FT-IR spectra using equation 1
[b] 110 °C, [c] 80 °C (low temperature was chosen to avoid dehydrochlorination), [d] 150 °C

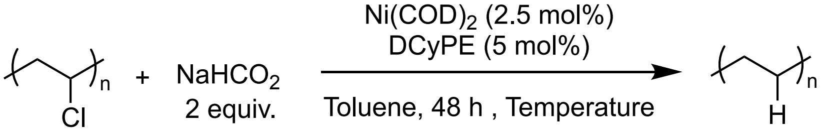
Table S4 PVC hydrodechlorination with Ni(COD)$_2$ and DCyPE, following the reaction over time



Entry	Reaction time (h)	% dechlorination[a]	Characterization	$T_{d,5\%}$ (°C), (Char left in %)
1	4	60	FT-IR (Fig. S25), NMR (Fig. S64), TGA (Fig. S93)	246 (18)
2	8	74	FT-IR (Fig. S26), NMR (Fig. S65), TGA (Fig. S94)	255 (10)
3	12	70	FT-IR (Fig. S27), NMR (Fig. S66), TGA (Fig. S95)	256 (8)
4	16	72	FT-IR (Fig. S28), NMR (Fig. S67), TGA (Fig. S96)	262 (20)
5	24	74	FT-IR (Fig. S29), NMR (Fig. S68), TGA (Fig. S97)	249 (7)
6	48	76	FT-IR(Fig. S30), NMR (Fig. S69), TGA (Fig. S98)	280 (7)

[a] % dechlorination was calculated from FT-IR spectra using equation 1

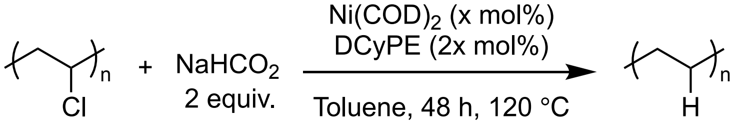
Table S5 Identifying the impact of temperature on rate and selectivity for PVC hydrodechlorination with Ni(COD)$_2$ and DCyPE



Entry	Reaction Temperature (°C)	% dechlorination[a]	Characterization	$T_{d,5\%}$ (°C), (Char left in %)
1	80	42	FT-IR (Fig. S31), NMR (Fig. S70)	-
2	100	71	FT-IR (Fig. S32), NMR (Fig. S71), TGA (Fig. S99)	237 (13)
3	120	77	FT-IR (Fig. S6), NMR (Fig. S57), TGA (Fig. S84), DSC (Fig. S115)	290 (6)
4	150	84	FT-IR (Fig. S33), NMR (Fig. S72), TGA (Fig. S100)	315 (40)

[a] % dechlorination was calculated from FT-IR spectra using equation 1

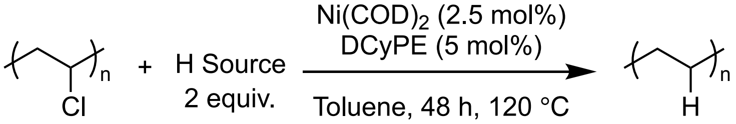
Table S6 PVC hydrodechlorination with Ni(COD)$_2$ and DCyPE, following the reaction with changes in metal salt and ligand loading



Entry	catalyst loading (mol%)	DCyPE Loading	% dechlorination[a]	Characterization	$T_{d,5\%}$ (°C) (Char left in %)
1	1	2	66	FT-IR (Fig. S34), NMR (Fig. S73), TGA (Fig. S101)	258 (6)
2	2.5	5	77	FT-IR (Fig. S6), NMR (Fig. S57), TGA (Fig. S84), DSC (Fig. S115)	290 (6)
3	2.5	2.5	82	FT-IR (Fig. S35), NMR (Fig. S74), TGA (Fig. S102) DSC (Fig. S117)	317 (6)
4	5	10	71	FT-IR (Fig. S36), NMR (Fig. S75), TGA (Fig. S103)	259 (18)

[a] % dechlorination was calculated from FT-IR spectra using equation 1

Table S7 PVC hydrodechlorination with Ni(COD)$_2$ and DCyPE, following the reaction over various hydrogen sources

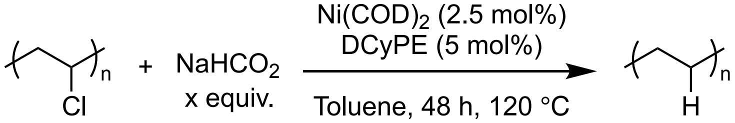


Entry	H Source	% dechlorination[a]	Characterization	$T_{d,5\%}$ (°C) (Char left in %)
1	NaCOOH	77	FT-IR (Fig. S6), NMR ((Fig. S57), TGA (Fig. S84), DSC (Fig. S115)	290 (6)
2	KCOOH[b]	85	FT-IR (Fig. S37), NMR (Fig. S76), TGA (Fig. S104)	262 (20)
3	NaH[b]	Low	FT-IR (Fig. S38)	-
4	$HSiEt_3$	Minimal	FT-IR (Fig. S39)	-
5	TMDS	Minimal	FT-IR (Fig. S40)	-

[a] % dechlorination was calculated from FT-IR spectra using equation 1

[b] Solvent (THF)

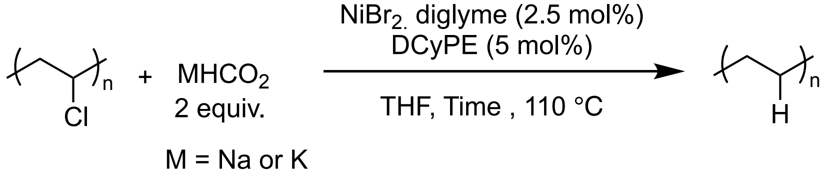
Table S8 PVC hydrodechlorination with Ni(COD)$_2$ and DCyPE, following the reaction with changes in NaHCO$_2$ equivalents.



Entry	Formate equivalent	% dechlorination[a]	Characterization	$T_{d,5\%}$ (°C) (Char left in %)
1	1	76	FT-IR (Fig. S30), NMR (Fig. S69), TGA (Fig. S98)	280 (7)
2	2	77	FT-IR (Fig. S6), NMR (Fig. S57) TGA (Fig. S84), DSC (Fig. S115)	290 (6)
3	3	71	FT-IR (Fig. S41), NMR (Fig. S77), TGA (Fig. S105)	280 (6)
4	No NaHCO$_2$	-	FT-IR (Fig 42)	-

[a] % dechlorination was calculated from FT-IR spectra using equation 1

Table S9 Optimized conditions for PVC hydrodechlorination



Entry	[Ni]	DCyPE loading	H source	Time (h)	% dechlorination[a]	Characterization	$T_{d,5\%}$ (°C) (Char left in %)
1	2.5	5	NaCOOH	24	80	FT-IR(Fig. S43), TGA (Fig. S106)	282 (12)
2	2.5	5	NaCOOH	48	81	FT-IR(Fig. S44), TGA (Fig. S107) SEM (Fig. S118, S119)	292 (9)
3	1	2	NaCOOH	24	77	FT-IR(Fig. S45), TGA (Fig. S108)	287 (11)
4	1	2	NaCOOH	48	84	FT-IR(Fig. S46), NMR (Fig. S78) TGA (Fig. S109)	281 (11)
5	2.5	5	KCOOH	24	83	FT-IR(Fig. S47), TGA (Fig. S110)	292 (14)
6	1	2	KCOOH	48	75	FT-IR(Fig. S48), TGA (Fig. S111) SEM (Fig. S125)	278 (11)
7	1	4	NaCOOH	24	81	FT-IR(Fig. S49), TGA (Fig. S112)	281 (11)
8	1	4	NaCOOH	48	81	FT-IR(Fig. S50), TGA (Fig. S113)	254 (11)
9[b]	2.5	5	NaCOOH	72	74	FT-IR(Fig. S147), NMR (Fig. S148) TGA (Fig. S149)	279 (23)

[a] % dechlorination was calculated from FT-IR spectra using equation 1

[b] PVC scale is increased to 500 mg

6. FT-IR

Note: noise present around 1950 cm^{-1} is instrument noise and is present in all products.

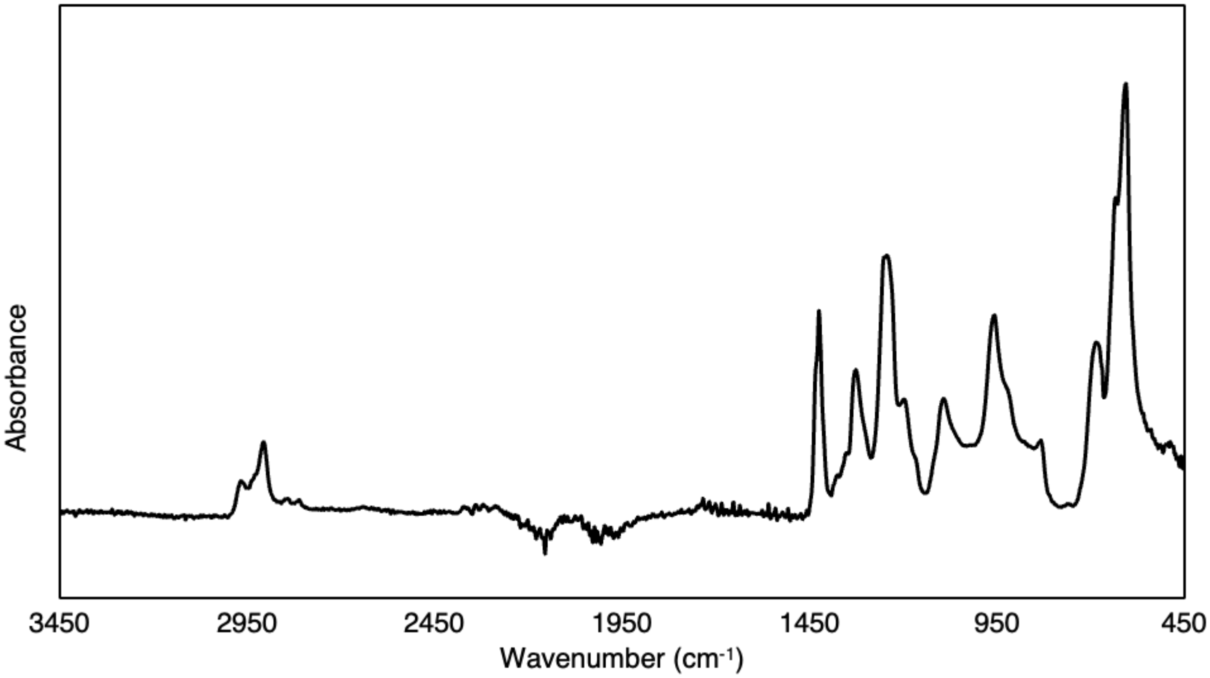


Fig. S1 FT-IR spectrum of low molecular weight PVC (CAS: 9002-86-2, Product #: 81388, Sigma Aldrich).

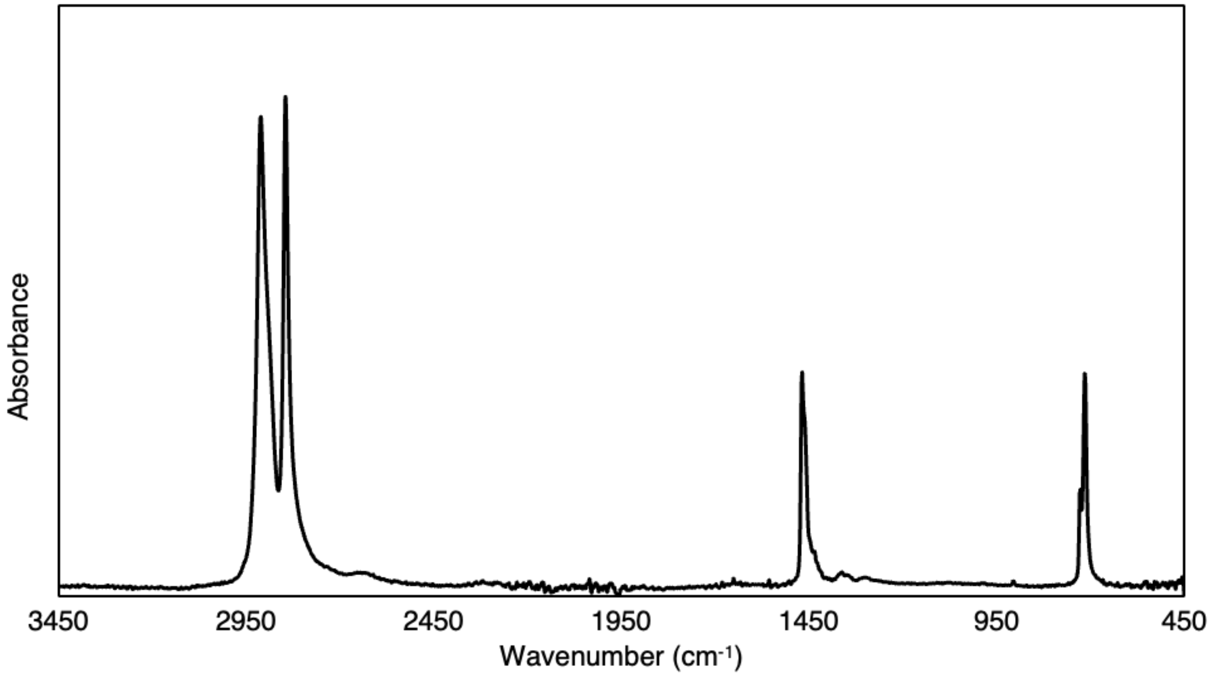


Fig. S2 FT-IR spectrum of HDPE pellets (CAS: 9002-88-4, Sigma Aldrich).

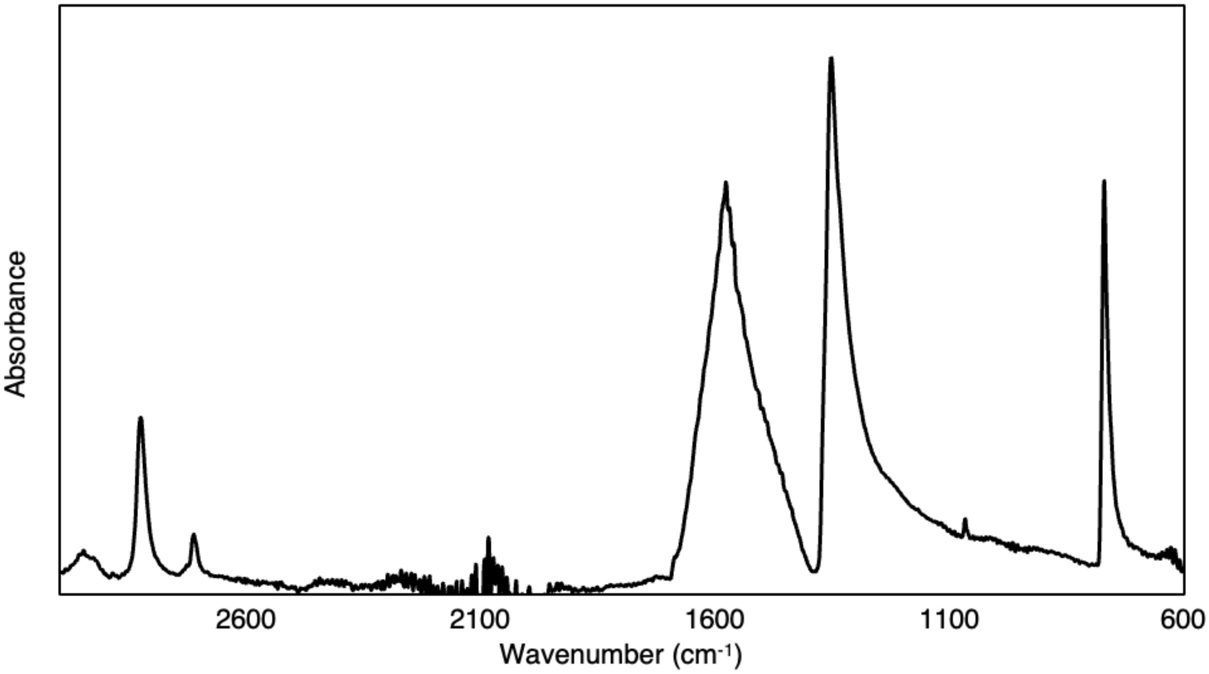


Fig. S3 FT-IR spectrum of NaCOOH (CAS: 141-53-7, Sigma Aldrich).

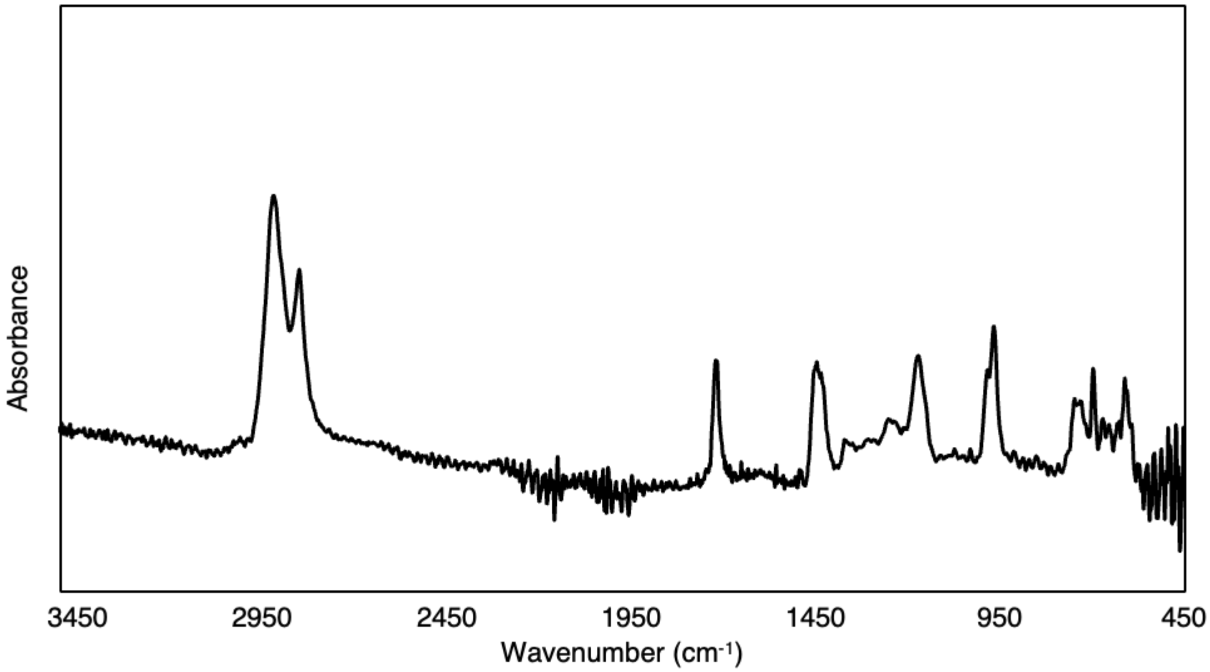


Fig. S4 FT-IR spectra Table S1, Entry 1 for PVC hydrodechlorination product with $NiCl_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

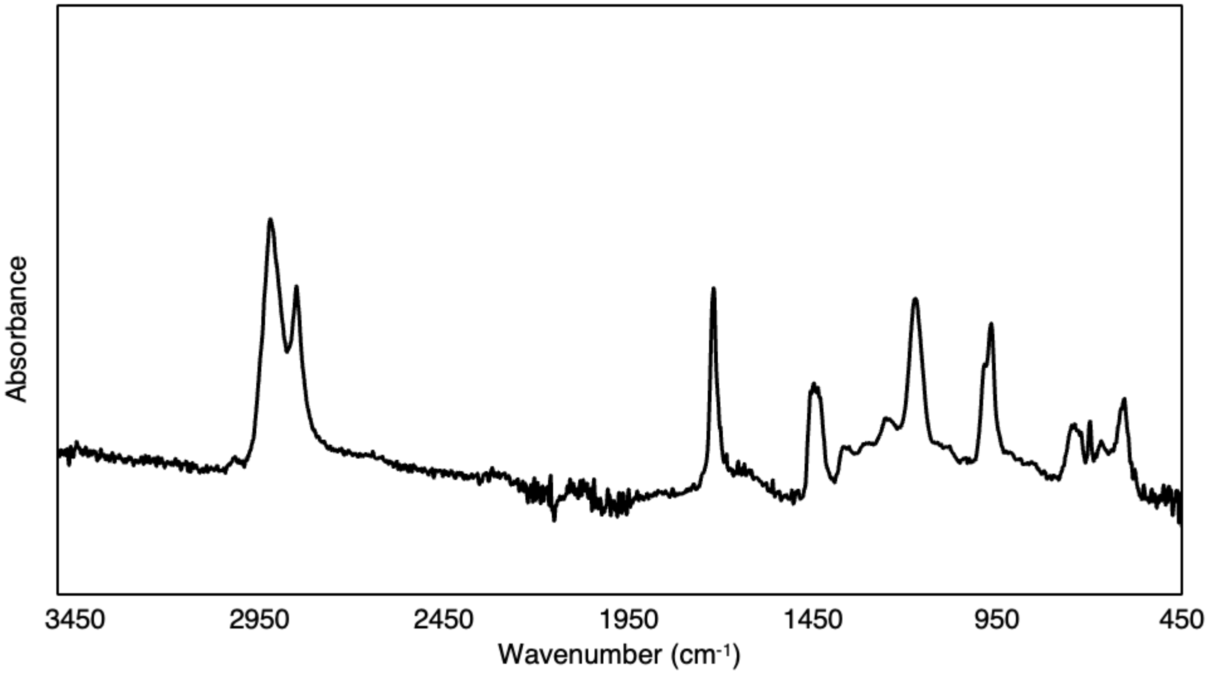


Fig. S5 FT-IR spectra Table S1, Entry 2 for PVC hydrodechlorination product with $NiCl_2$ (2.5 mol%), DCyPE (10 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

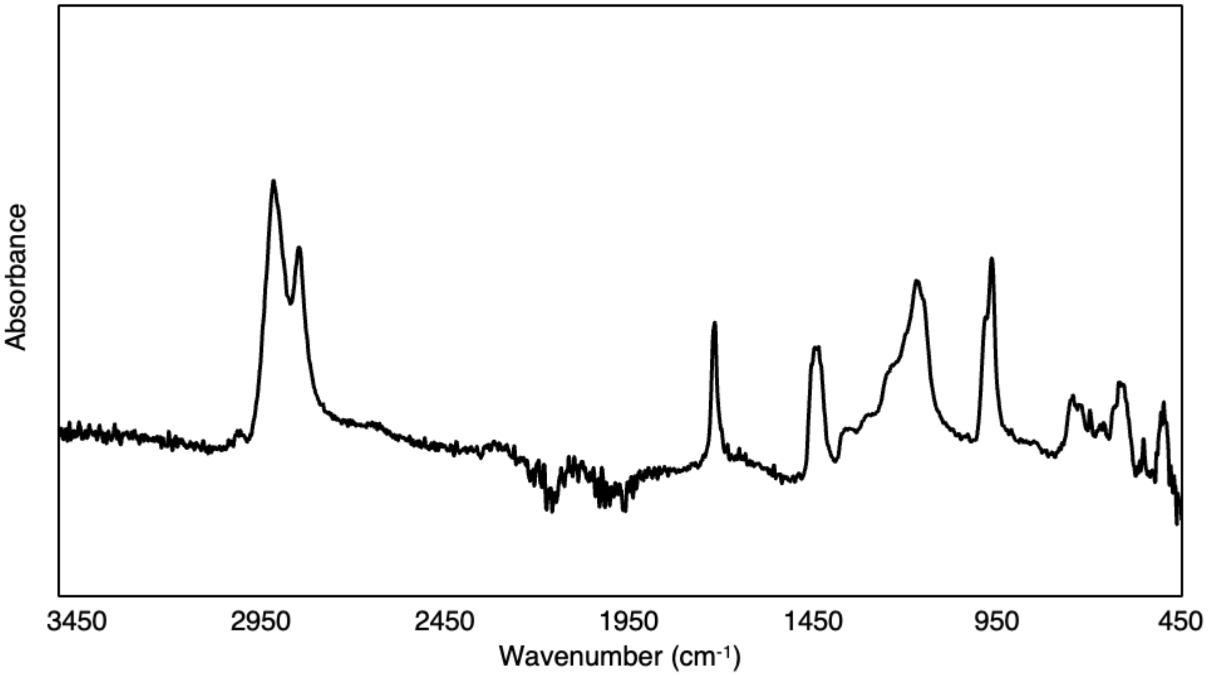


Fig. S6 FT-IR spectra Table S1, Entry 3 for PVC hydrodechlorination product with $Ni(COD)_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

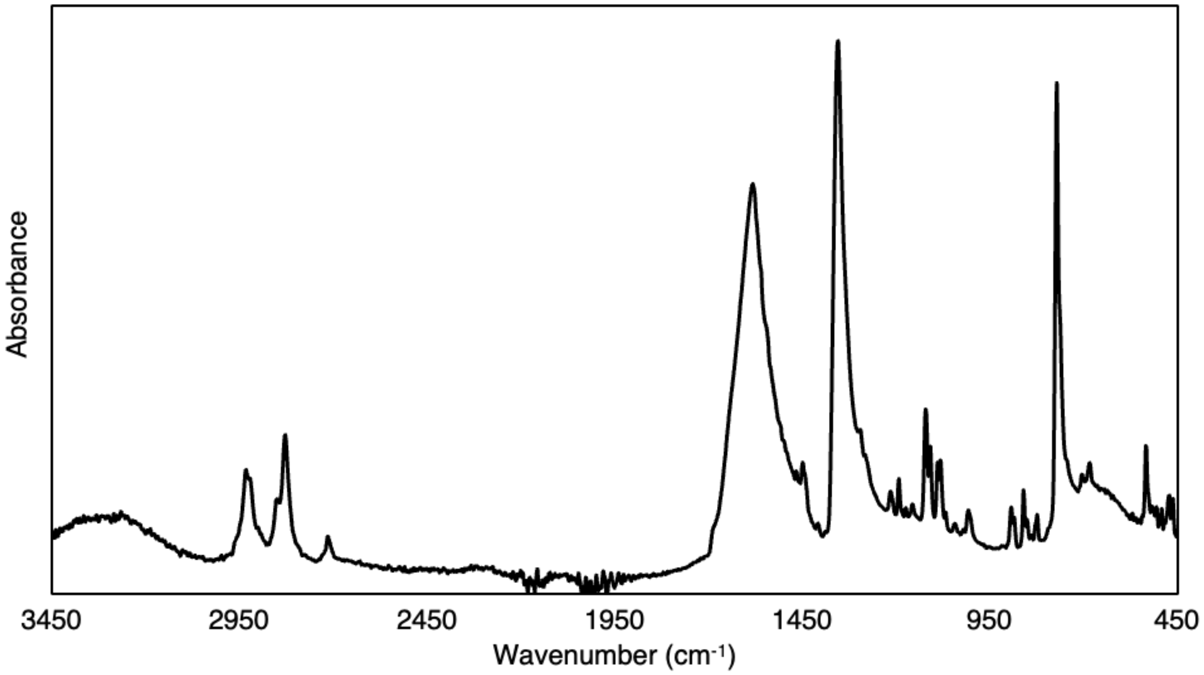


Fig. S6a FT-IR spectra of solids from mother liquor Table S1, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

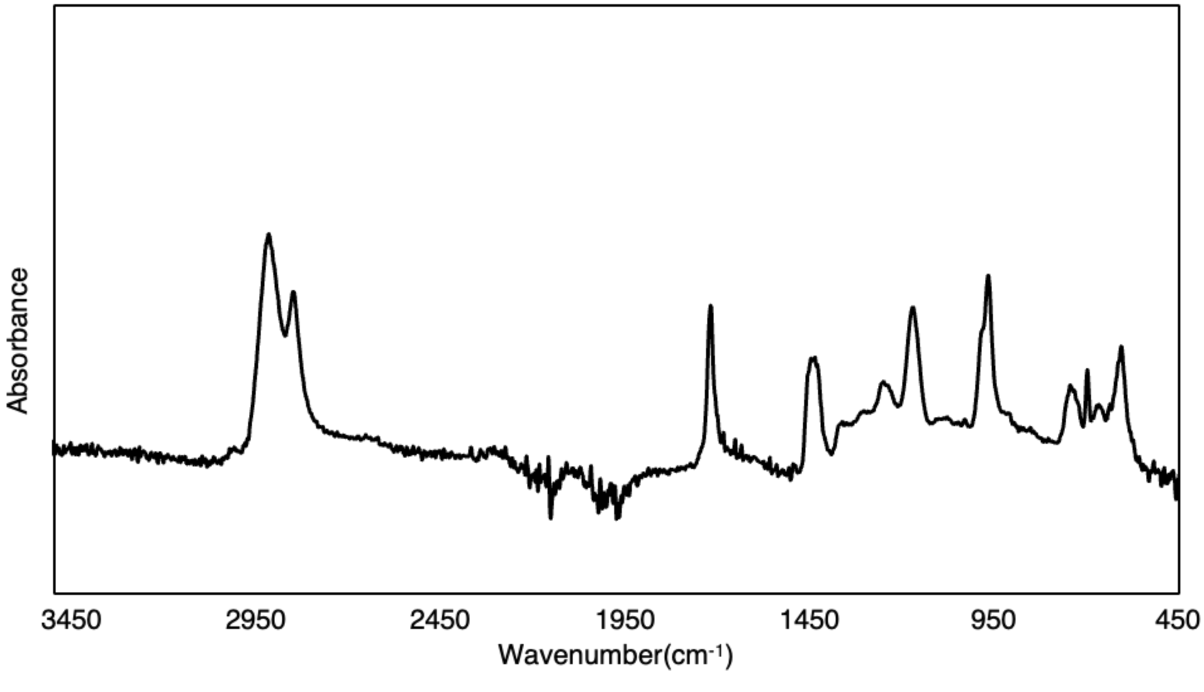


Fig. S7 FT-IR spectra Table S1, Entry 4 for PVC hydrodechlorination product with Ni(acac)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

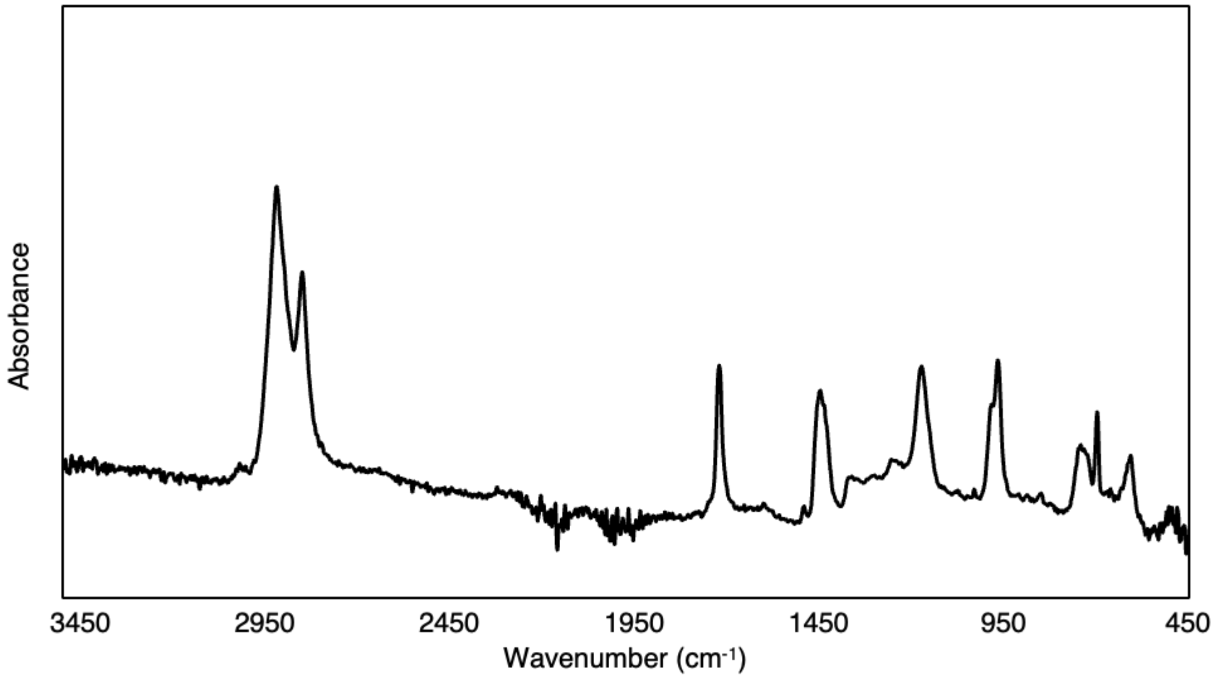


Fig. S8 FT-IR spectra Table S1, Entry 5 for PVC hydrodechlorination product with $NiBr_2$.glyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

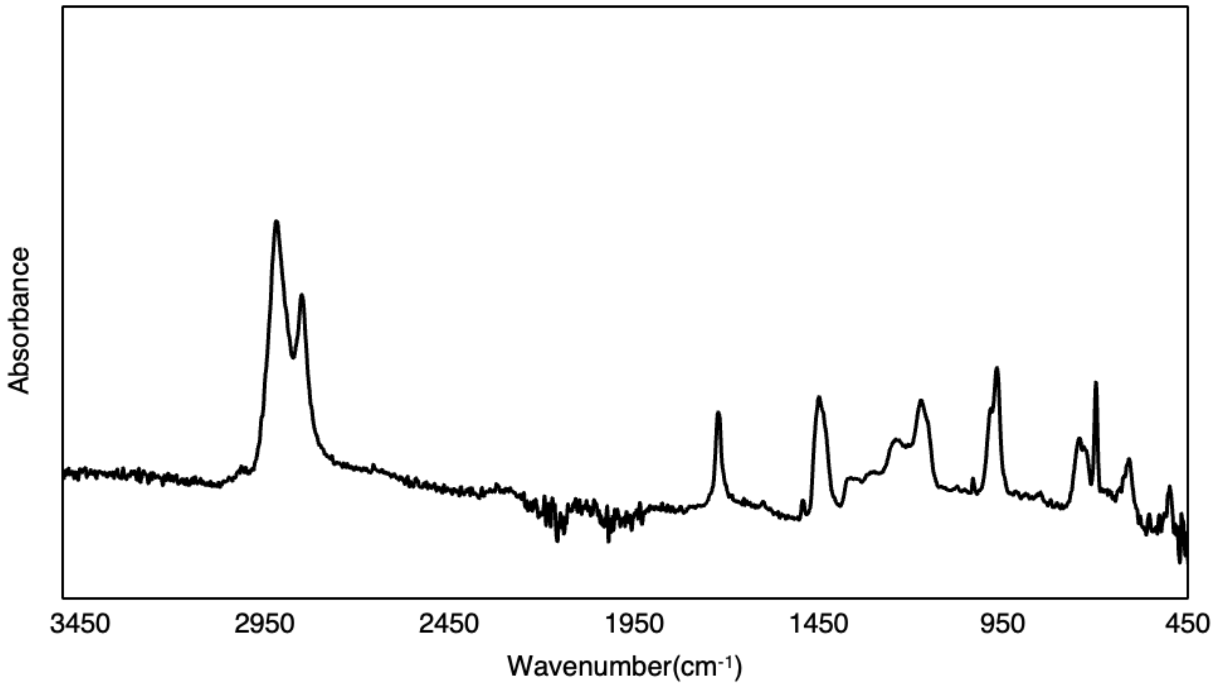


Fig. S9 FT-IR spectra Table S1, Entry 6 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

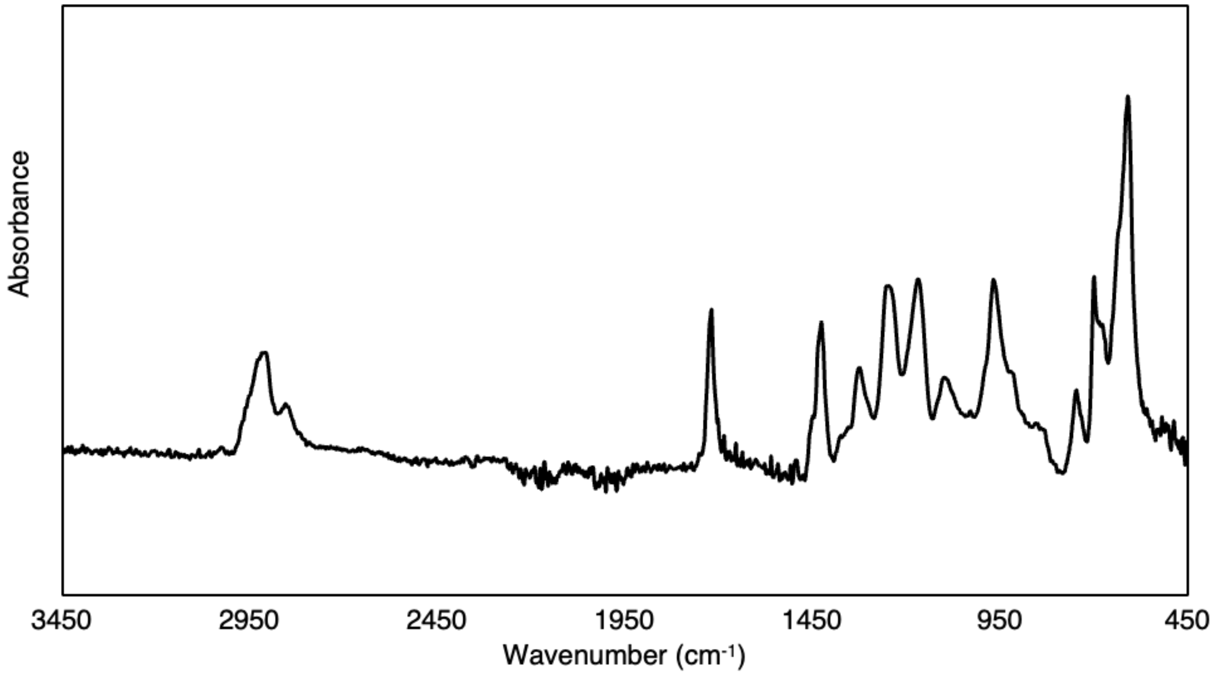


Fig. S10 FT-IR spectra Table S1, Entry 7 for PVC hydrodechlorination product with DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C without any Ni precursor.

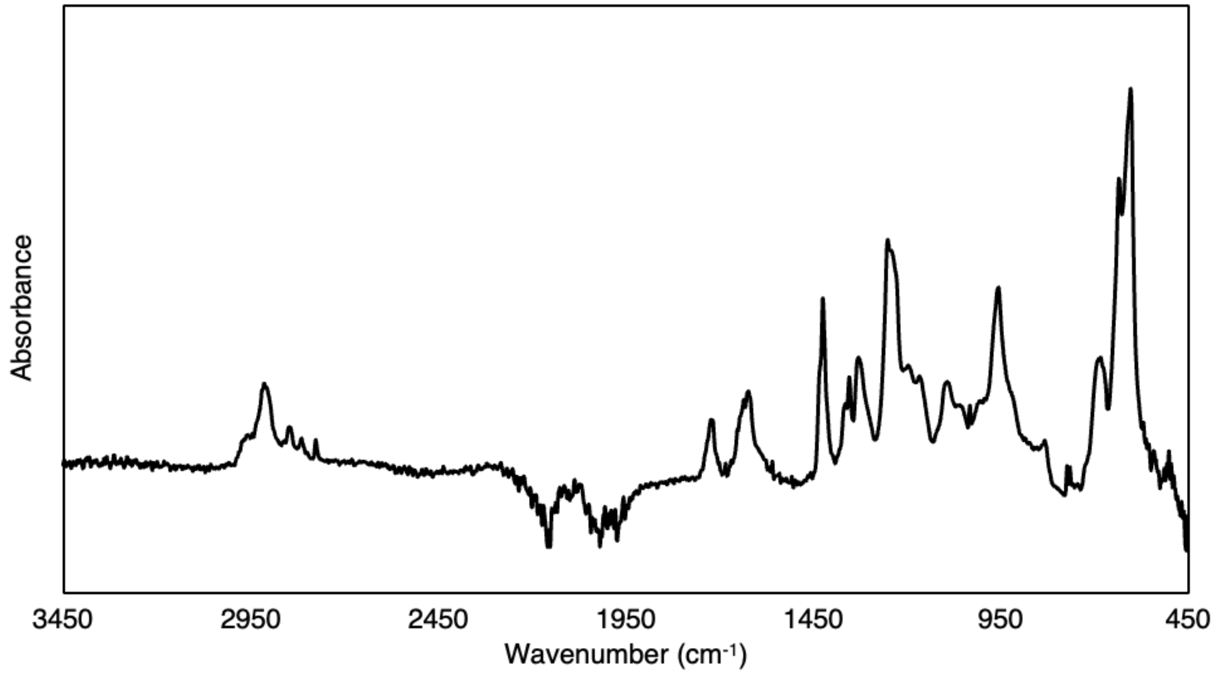


Fig. S11 FT-IR spectra Table S2, Entry 1 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), Xantphos (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

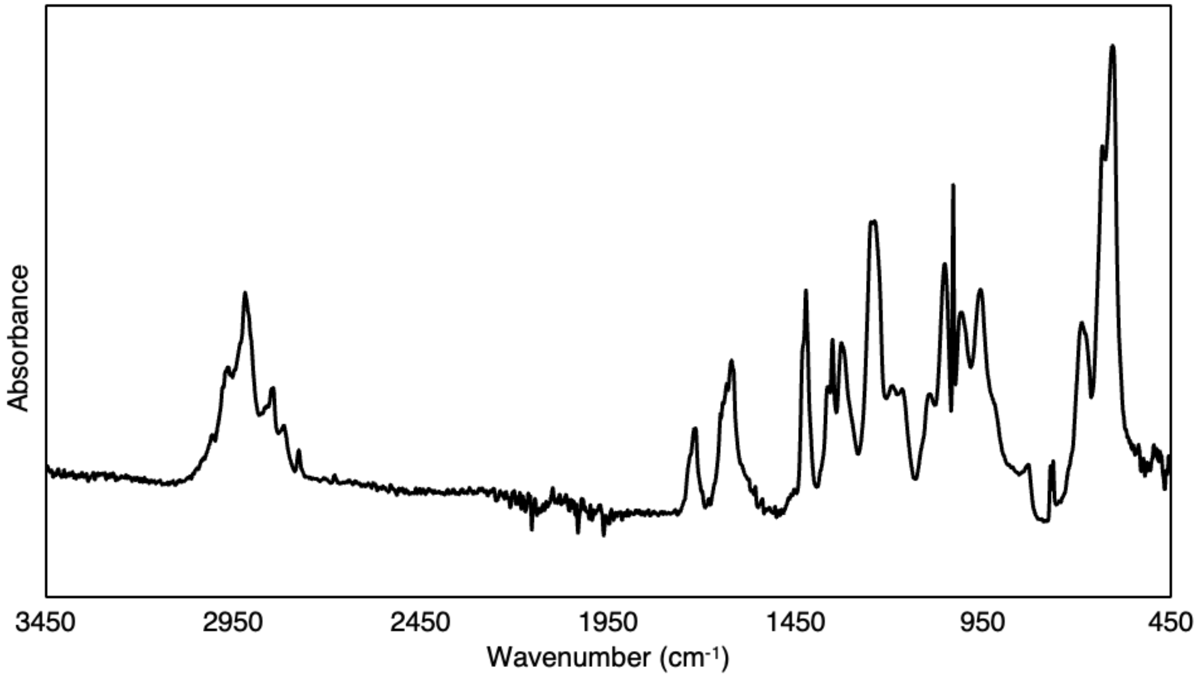


Fig. S12 FT-IR spectra Table S2, Entry 2 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DPPM (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

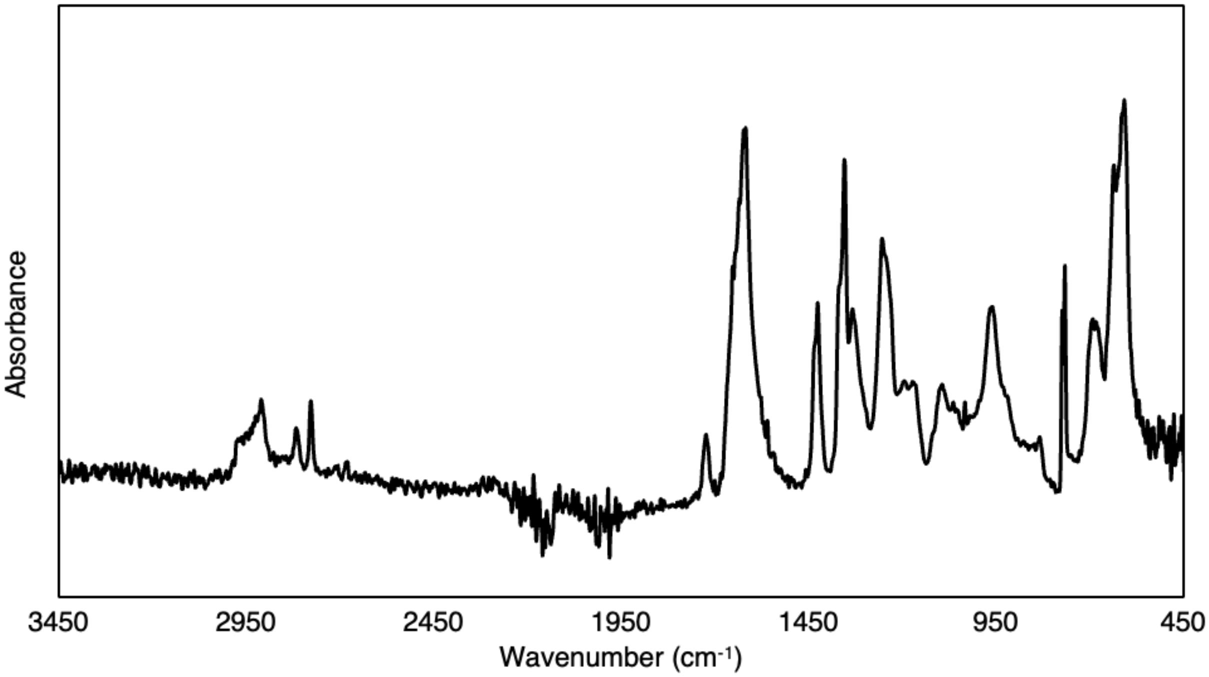


Fig. S13 FT-IR spectra Table S2, Entry 3 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DPPE (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

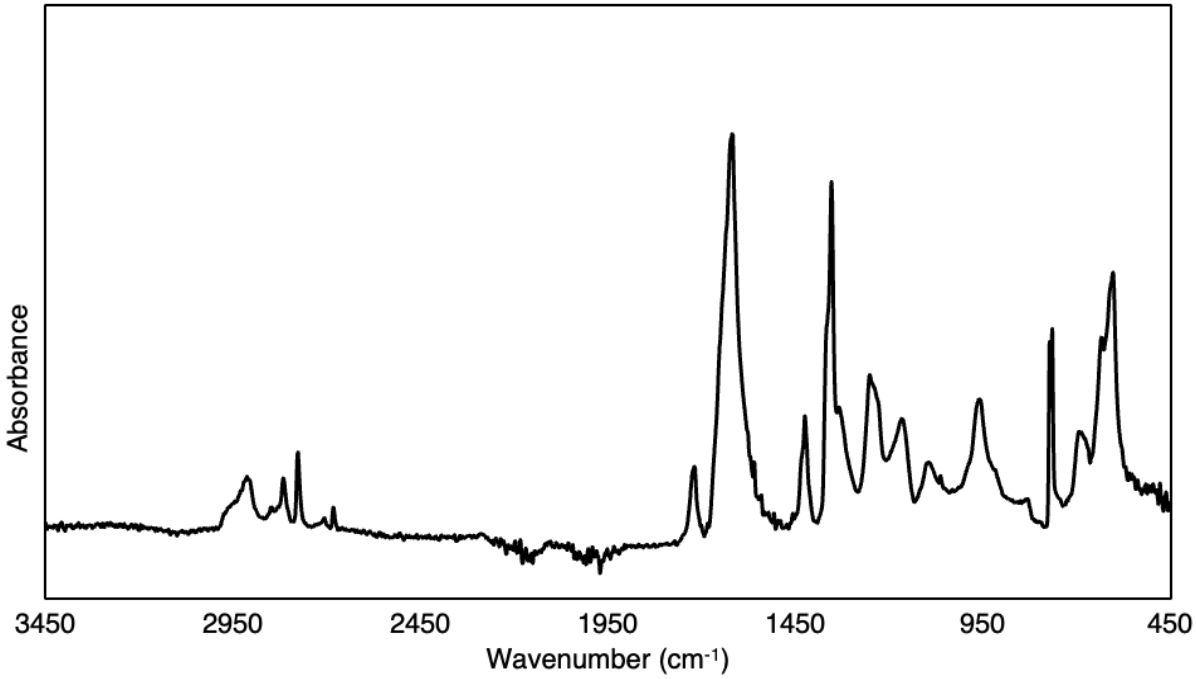


Fig. S14 FT-IR spectra Table S2, Entry 4 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DPPP (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

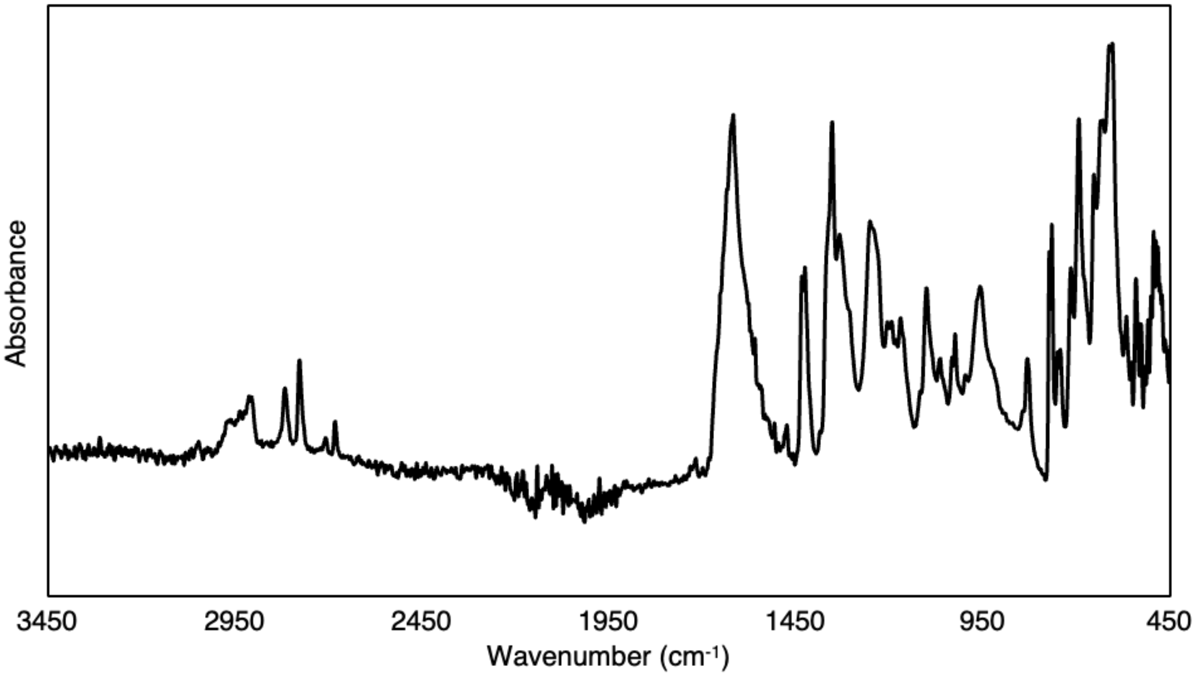


Fig. S15 FT-IR spectra Table S2, Entry 5 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DPPF (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

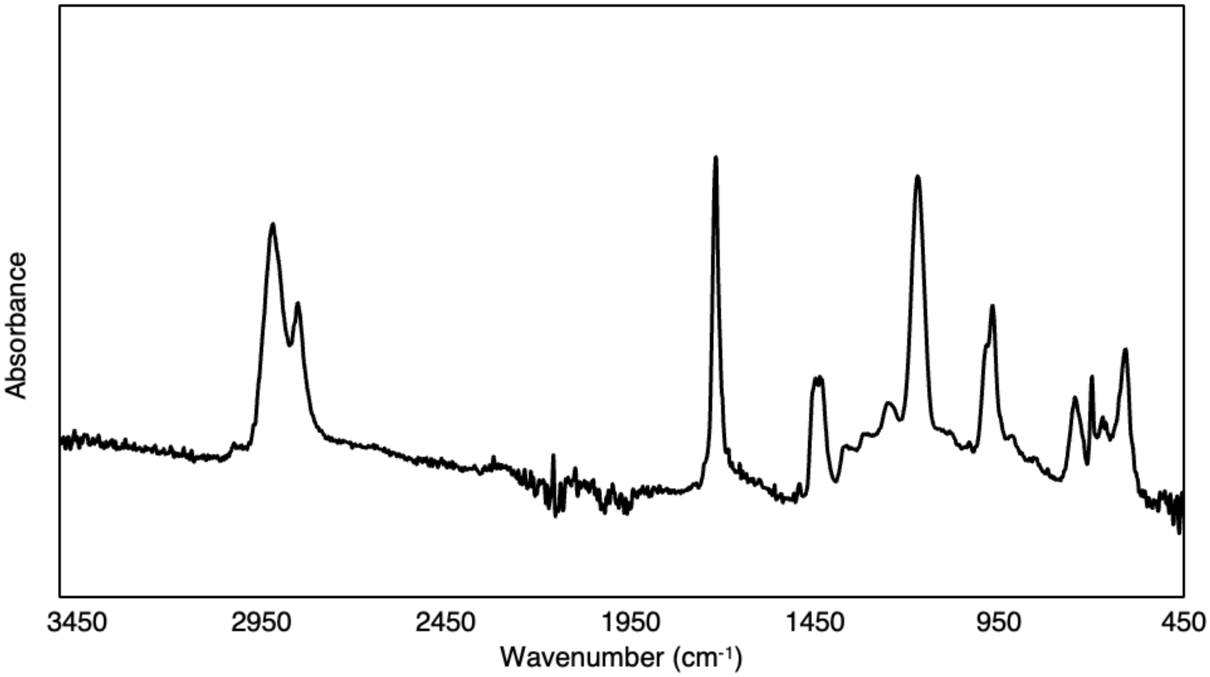


Fig. S16 FT-IR spectra Table S2, Entry 6 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DCyPE (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

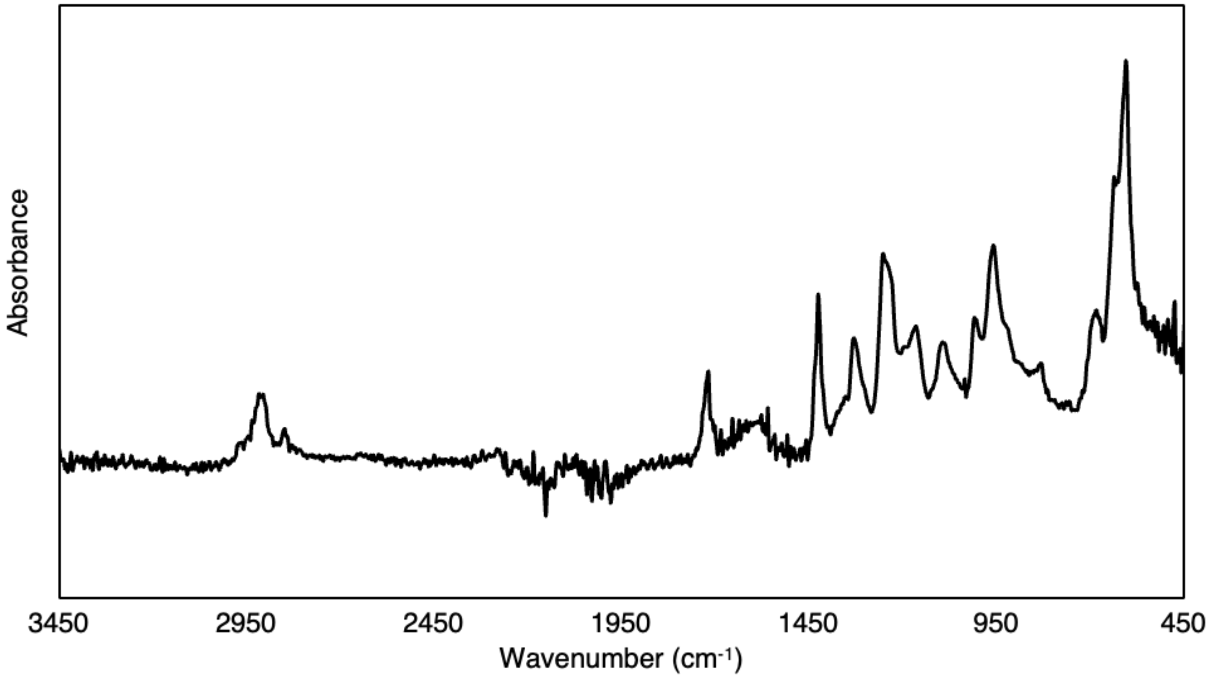


Fig. S17 FT-IR spectra Table S2, Entry 7 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), PCy_3 (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

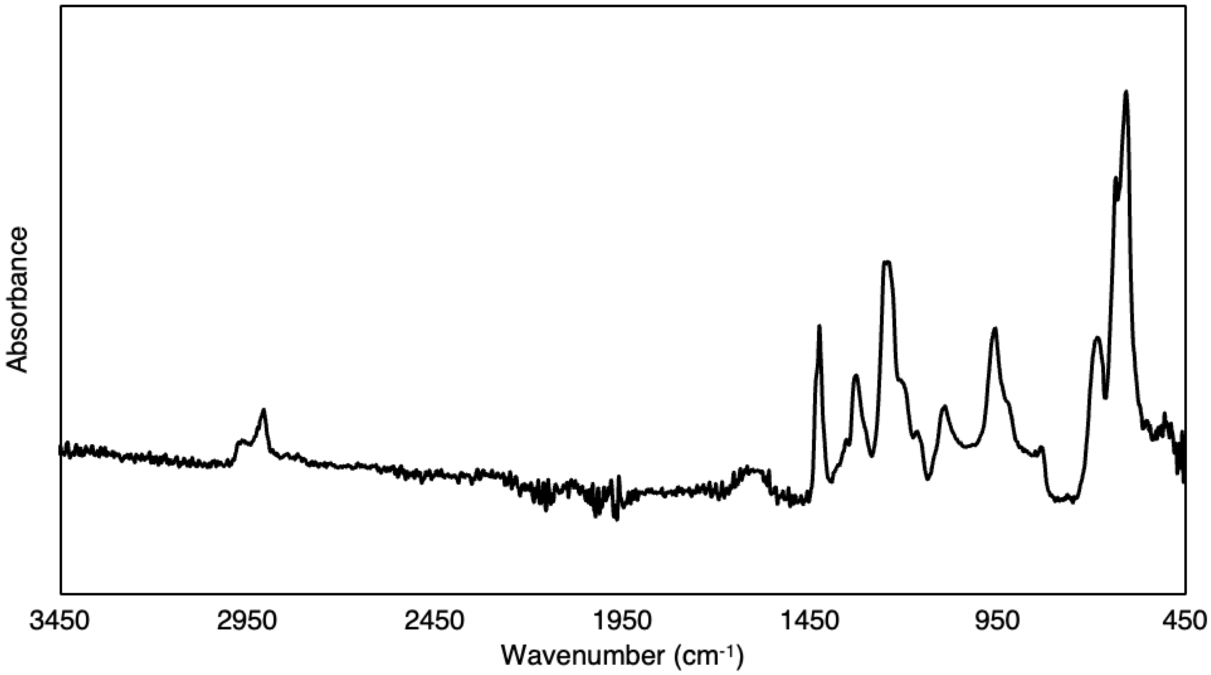


Fig. S18 FT-IR spectra Table S2, Entry 8 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%) and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C without any phosphorus ligand.

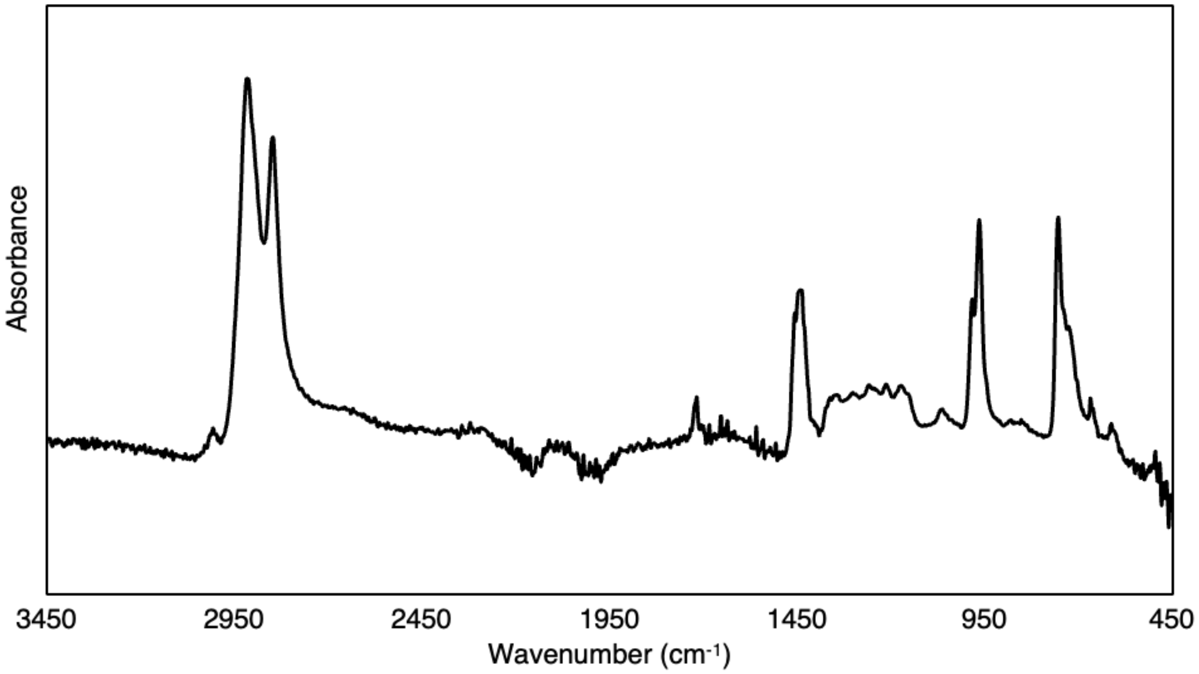


Fig. S19 FT-IR spectra Table S3, Entry 1 for PVC hydrodechlorination product with $Ni(COD)_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

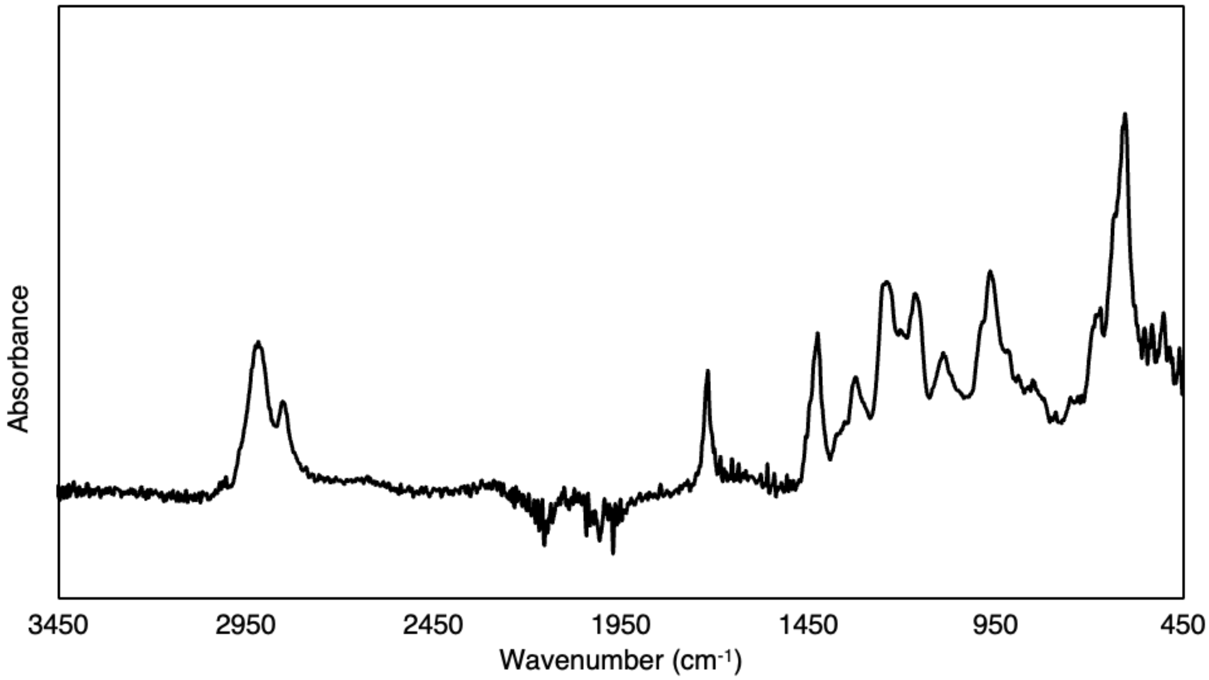


Fig. S20 FT-IR spectra Table S3, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Cyclo Pentyl methyl ether at 110 °C.

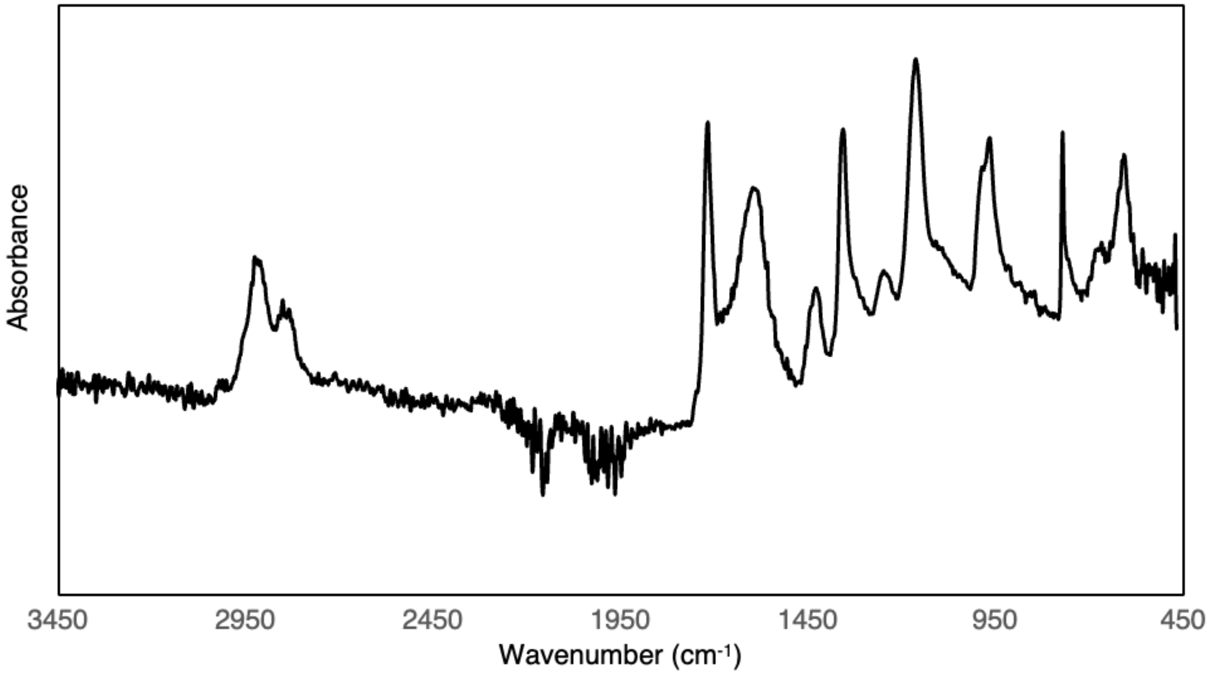


Fig. S21 FT-IR spectra Table S3, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Dimethyl Formide at 80 °C.

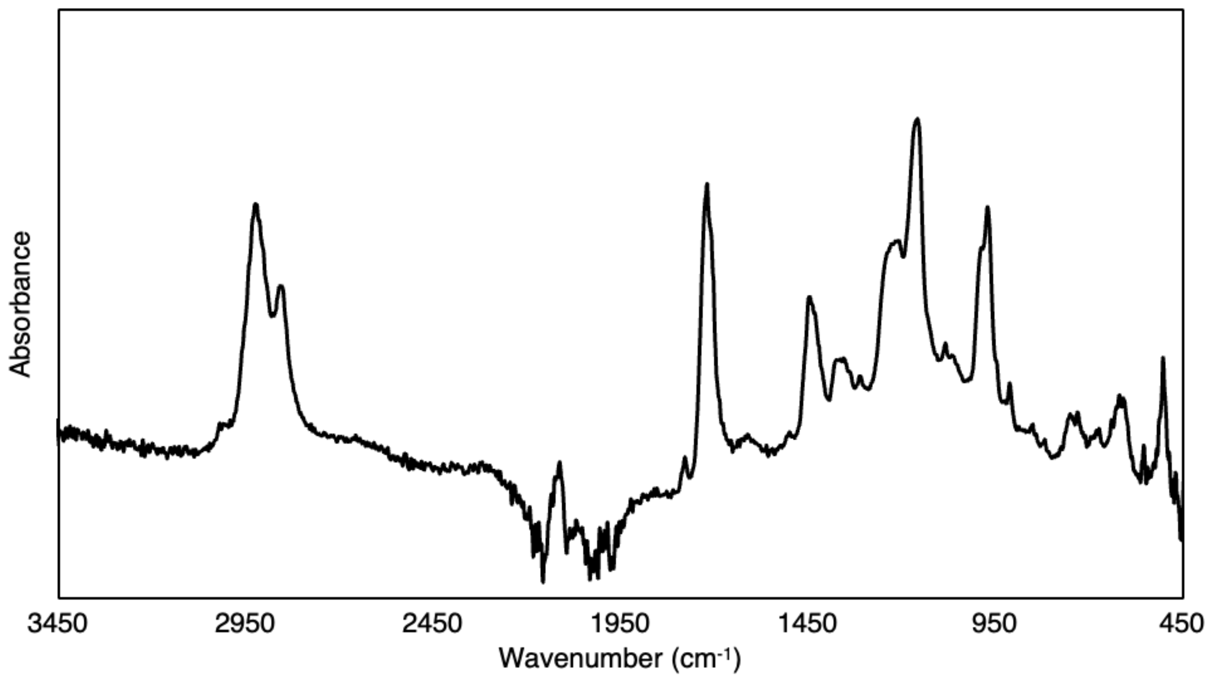


Fig. S22 FT-IR spectra Table S3, Entry 5 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Cyclohexanone at 150 °C.

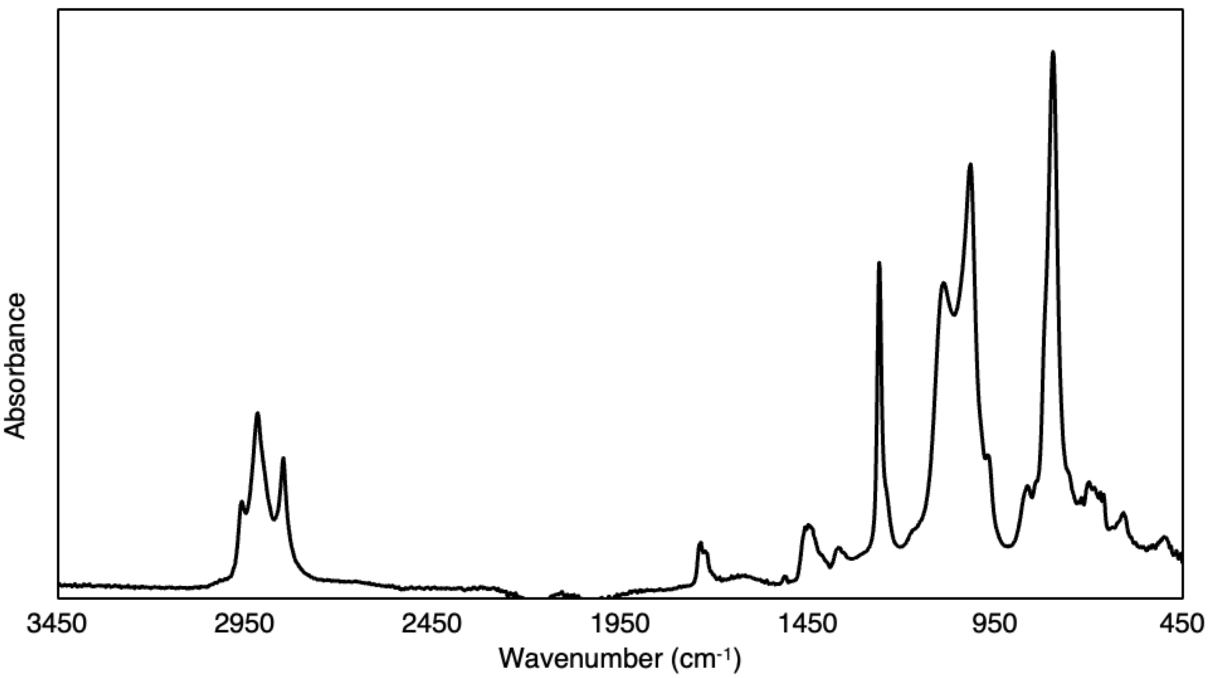


Fig. S23 FT-IR spectra Table S3, Entry 6 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Para-xylene at 120 °C.

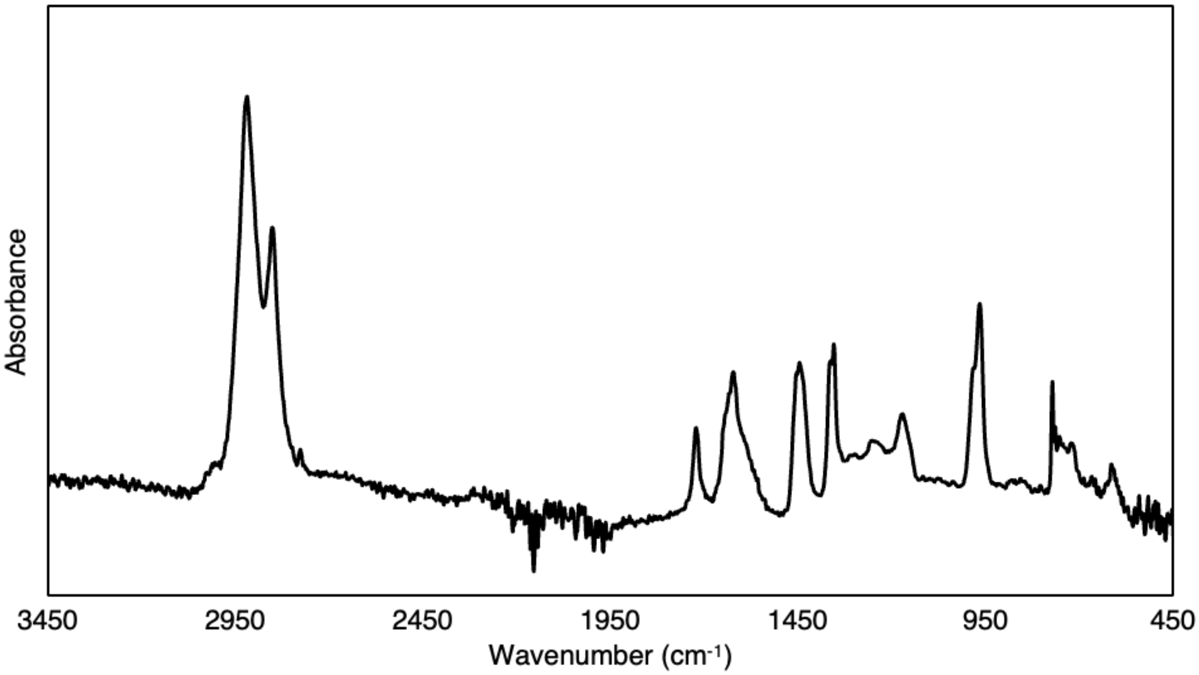


Fig. S24 FT-IR spectra Table S3, Entry 7 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in 1,4-dioxane at 120 °C.

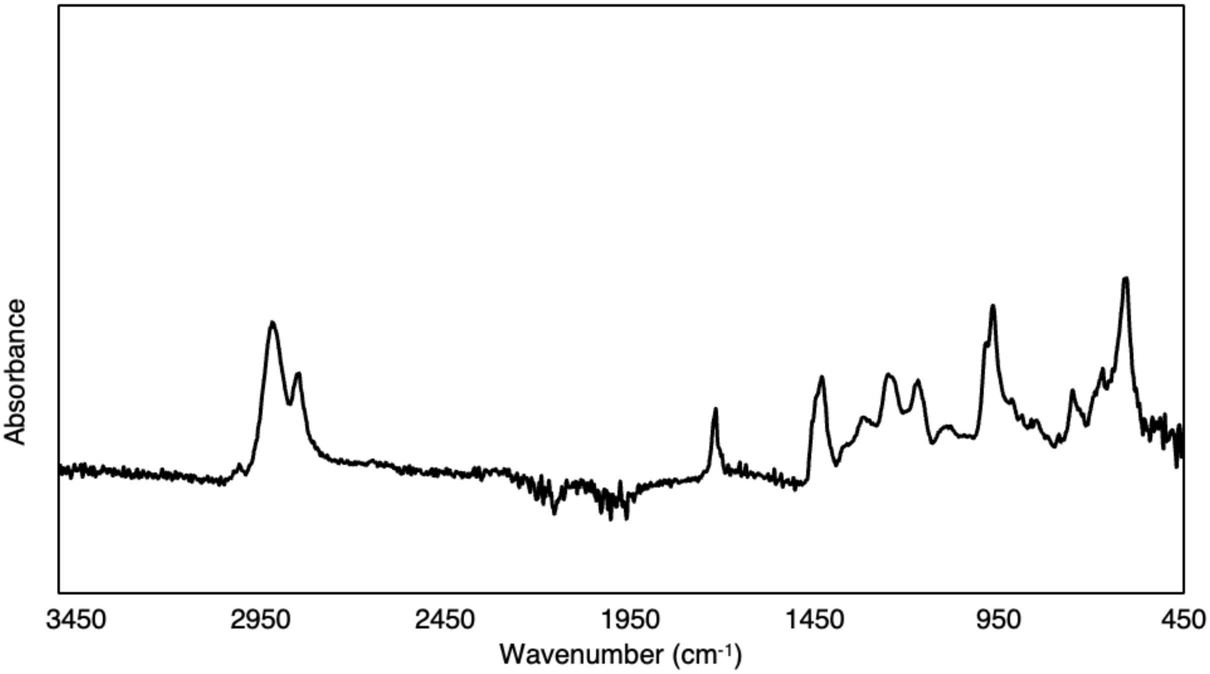


Fig. S25 FT-IR spectra Table S4, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 4 hours in Toluene at 120 °C.

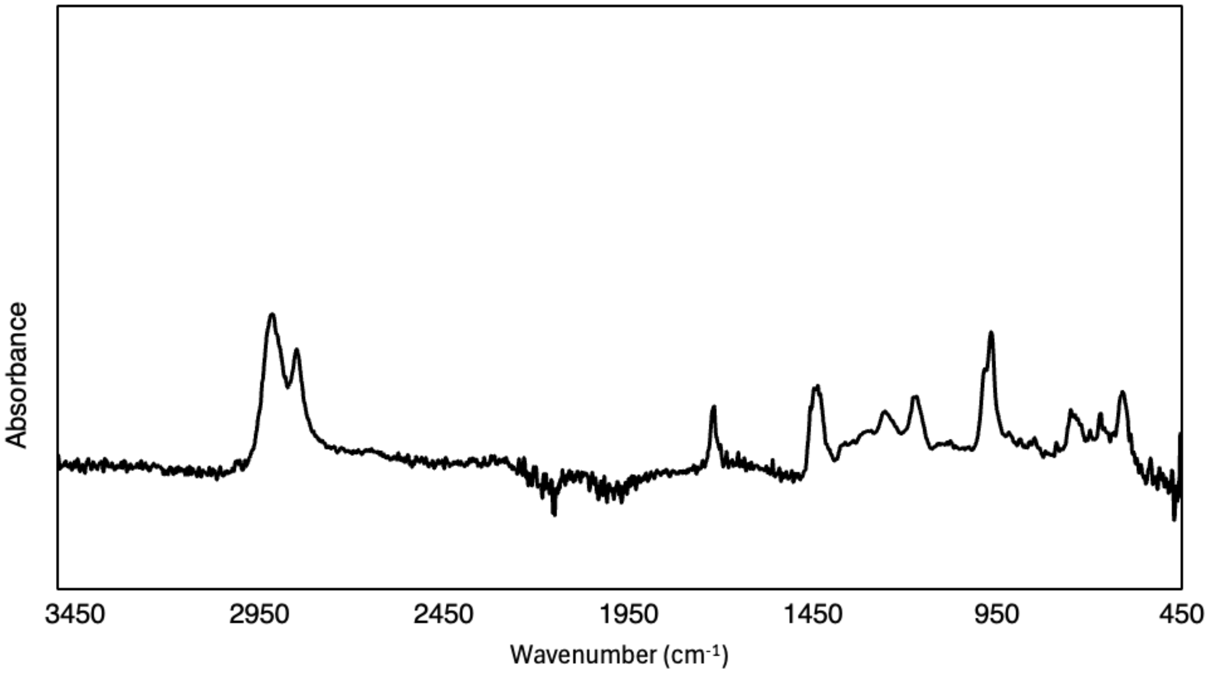


Fig. S26 FT-IR spectra Table S4, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 8 hours in Toluene at 120 °C.

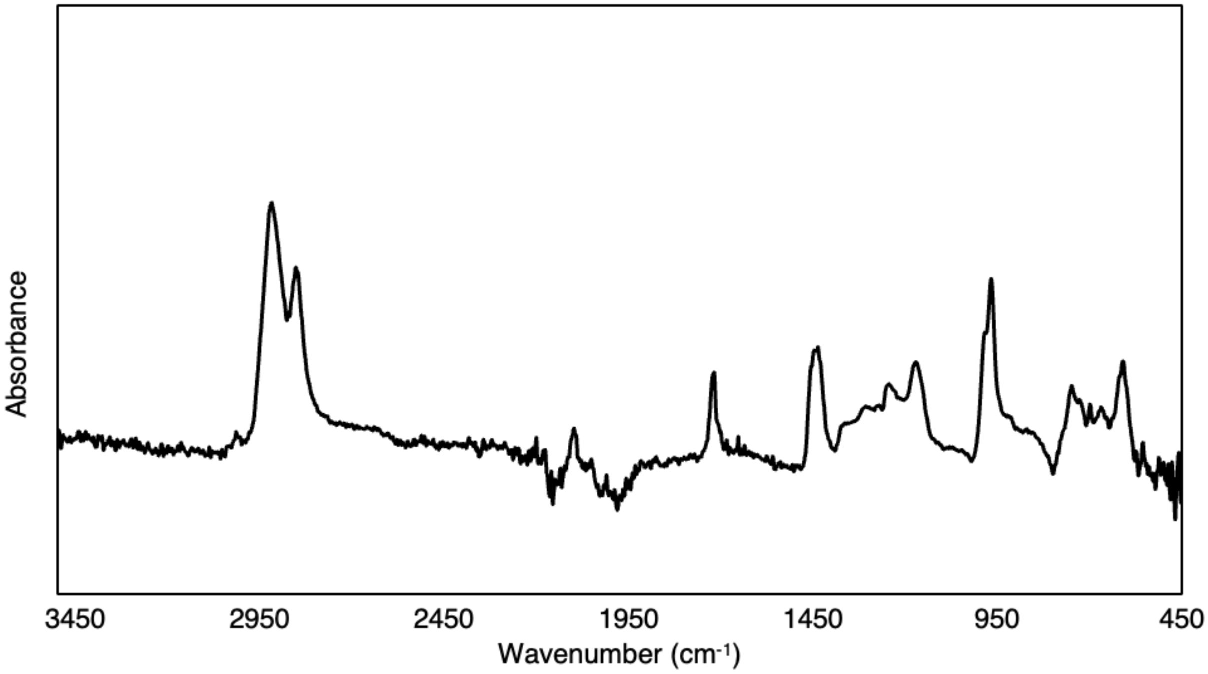


Fig. S27 FT-IR spectra Table S4, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 12 hours in Toluene at 120 °C.

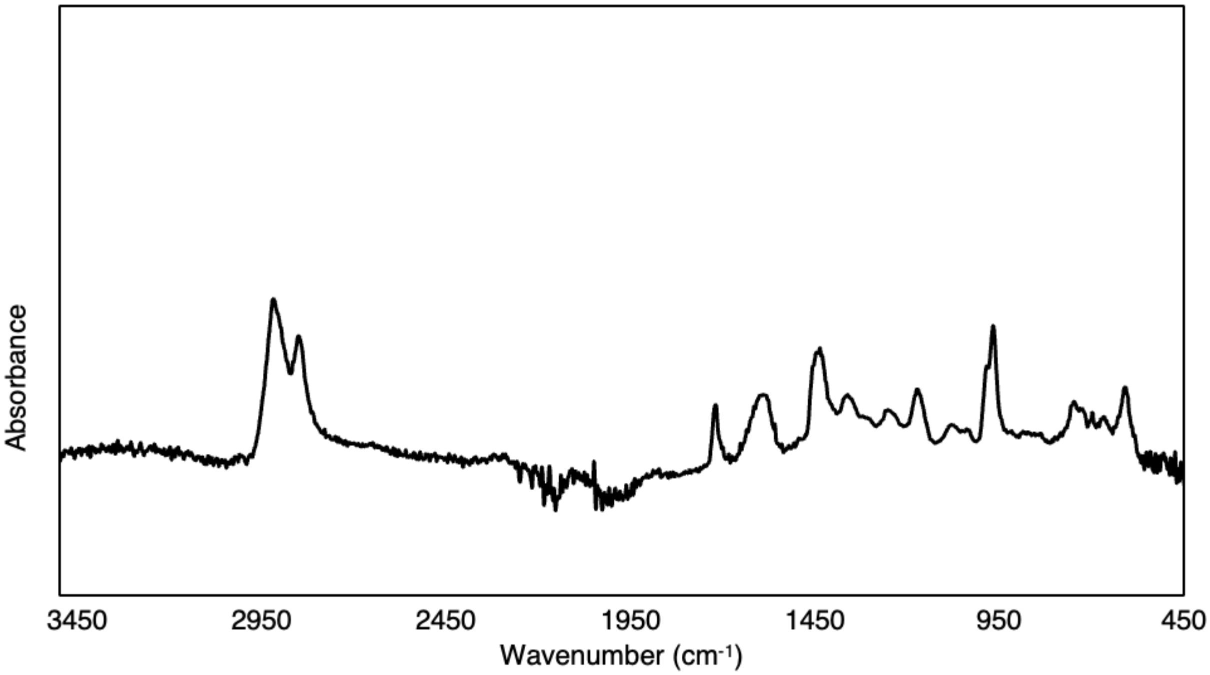


Fig. S28 FT-IR spectra Table S4, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 16 hours in Toluene at 120 °C

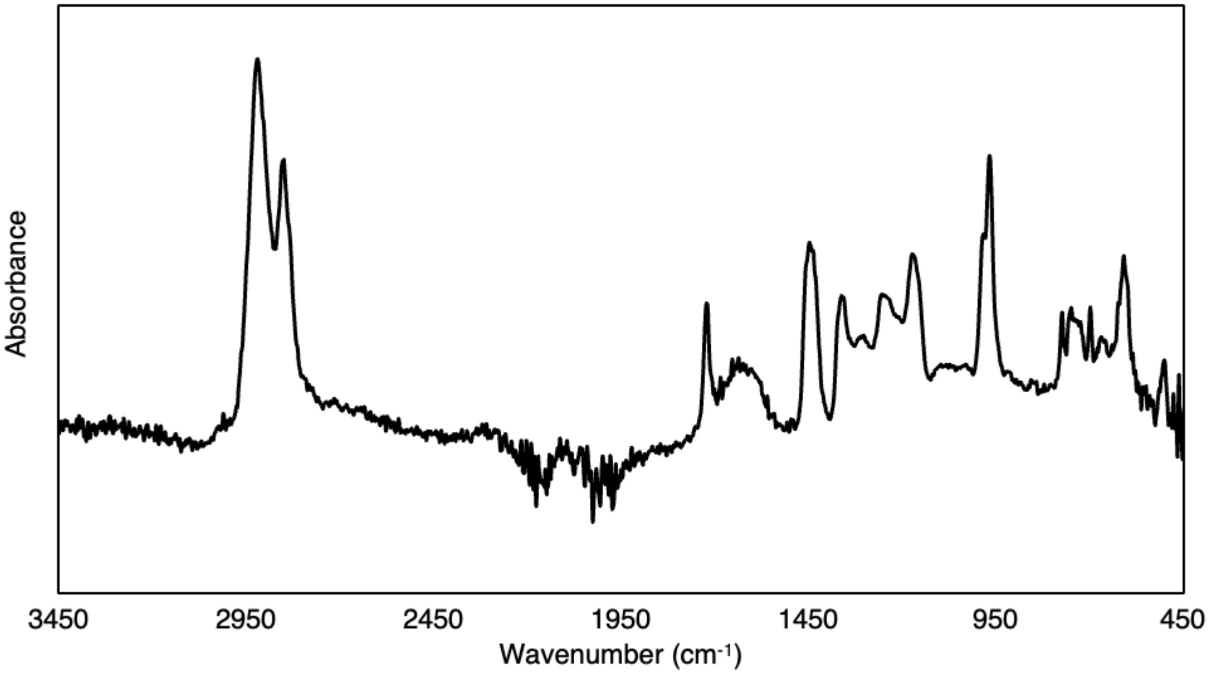


Fig. S29 FT-IR spectra Table S4, Entry 5 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 24 hours in Toluene at 120 ^{o}C.

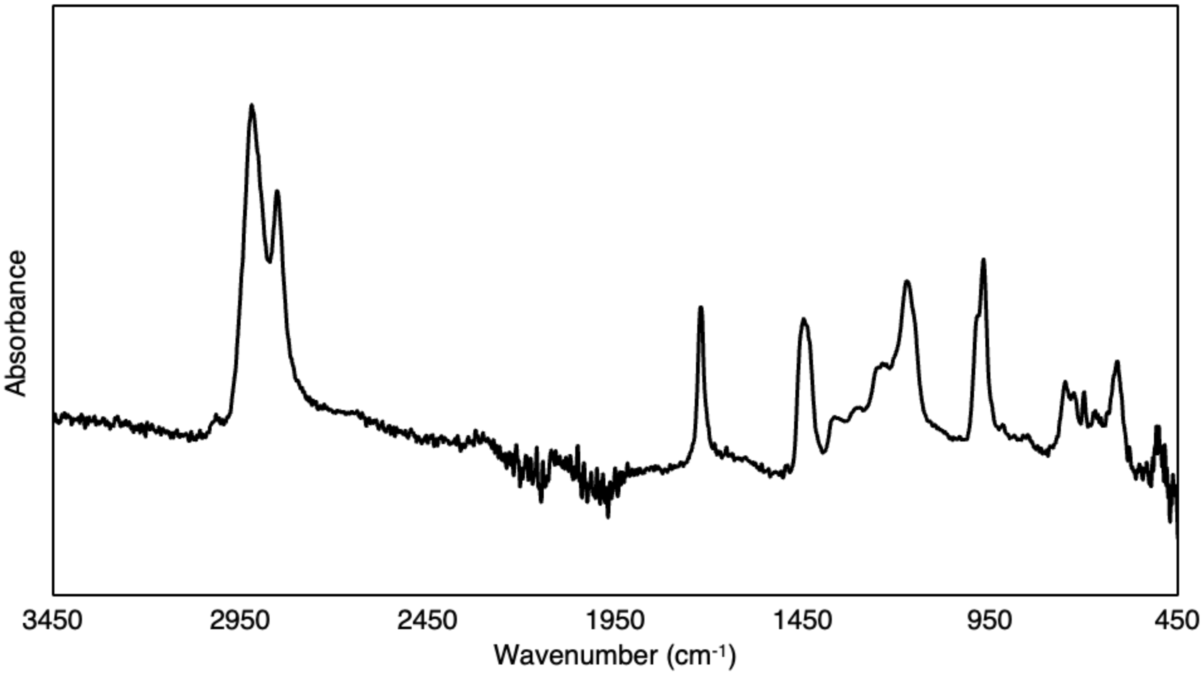


Fig. S30 FT-IR spectra Table S4, Entry 6 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C

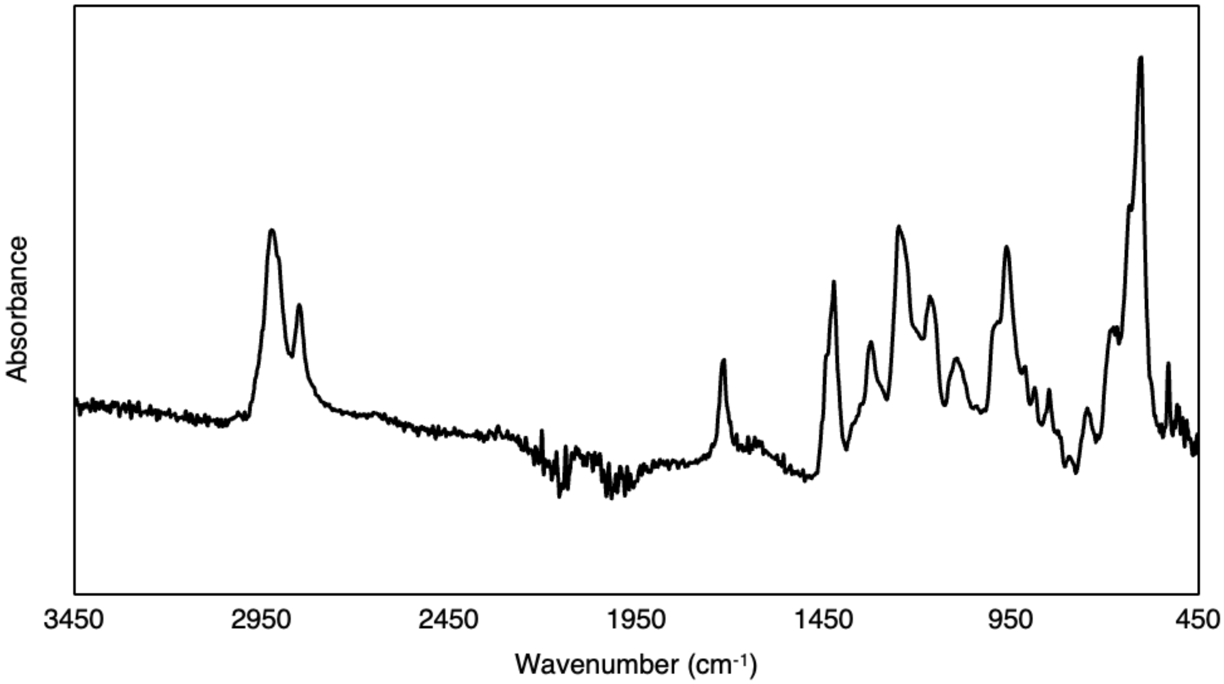


Fig. S31 FT-IR spectra Table S5, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 80 °C.

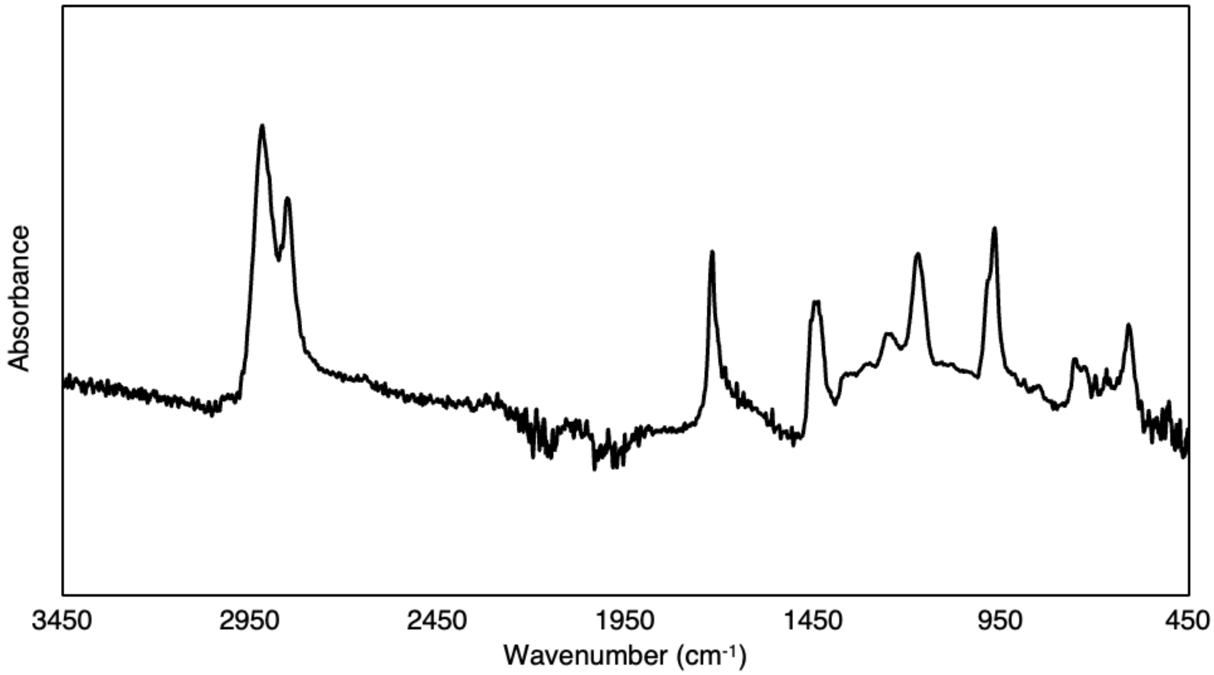


Fig. S32 FT-IR spectra Table S5, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 100 °C.

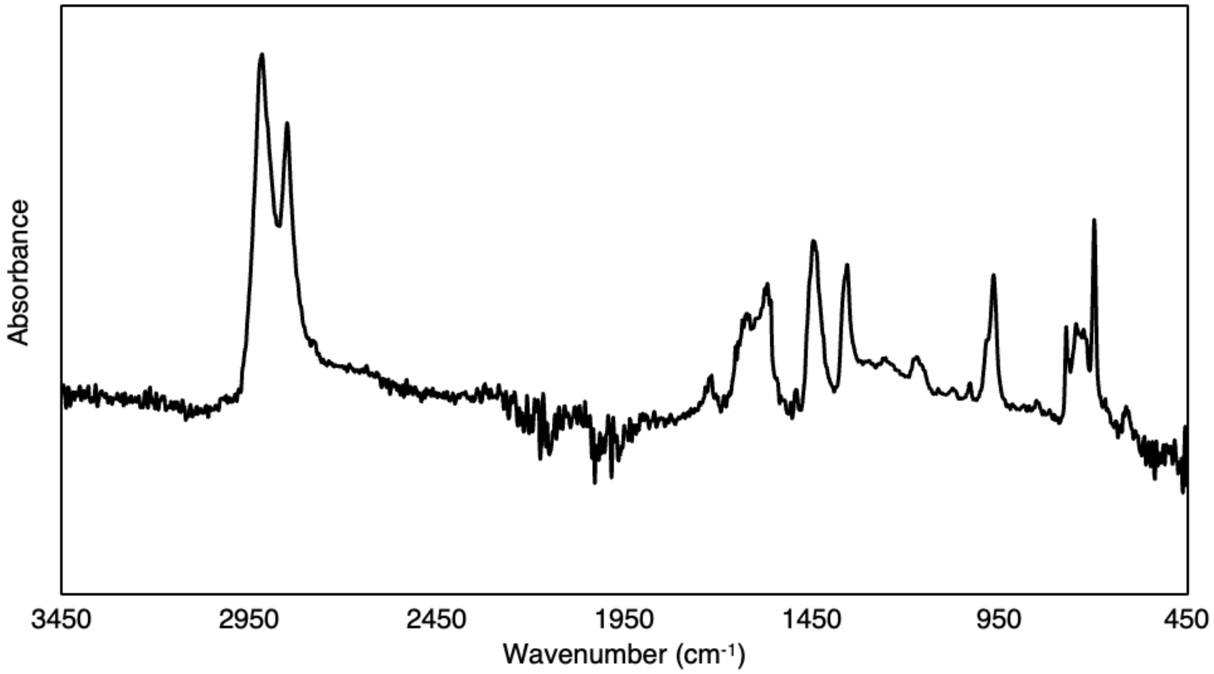


Fig. S33 FT-IR spectra Table S5, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 150 °C.

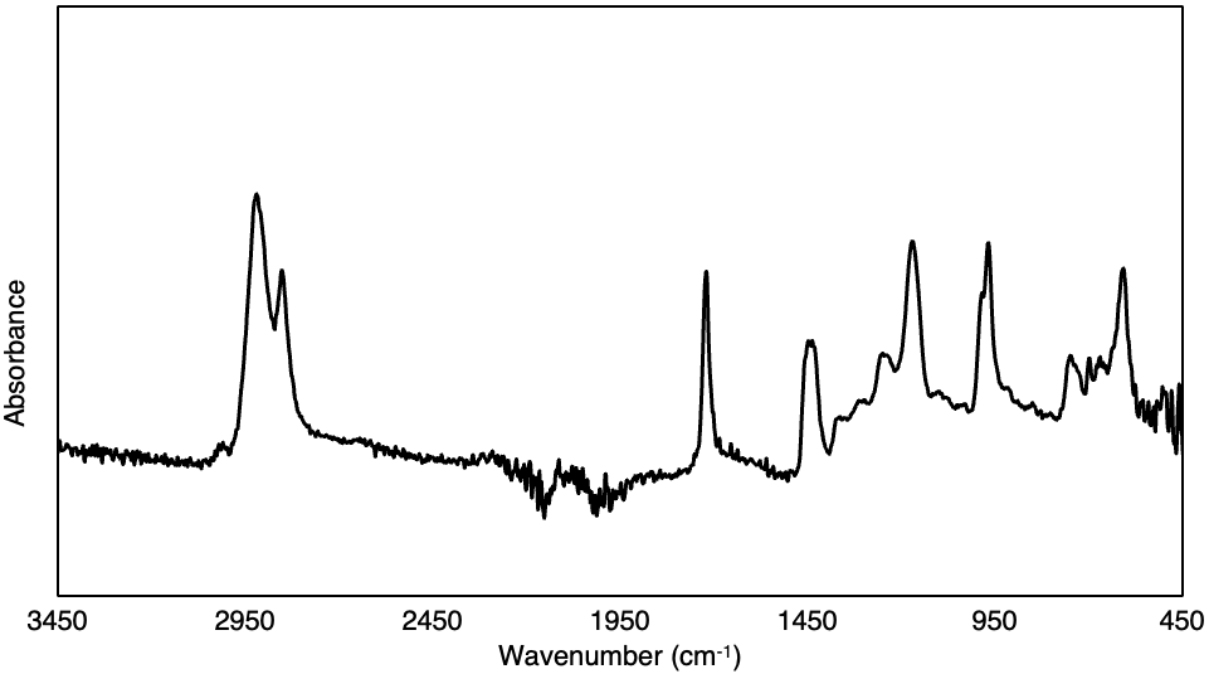


Fig. S34 FT-IR spectra Table S6, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (1 mol%), DCyPE (2 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

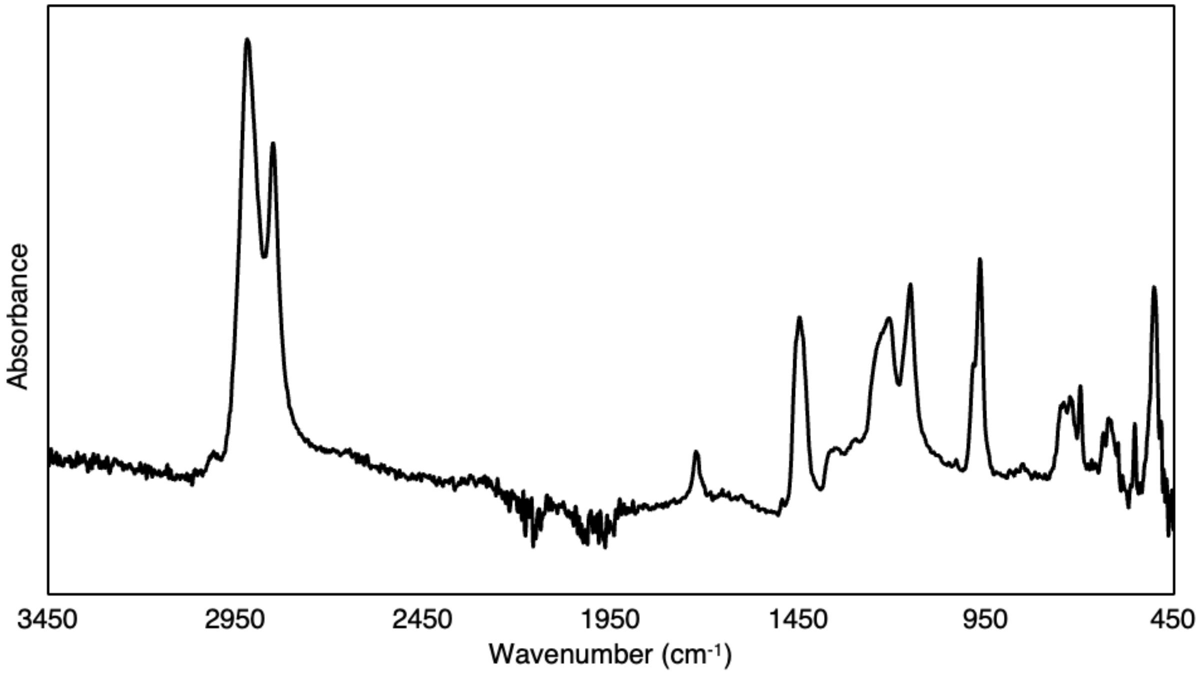


Fig. S35 FT-IR spectra Table S6, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (2.5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

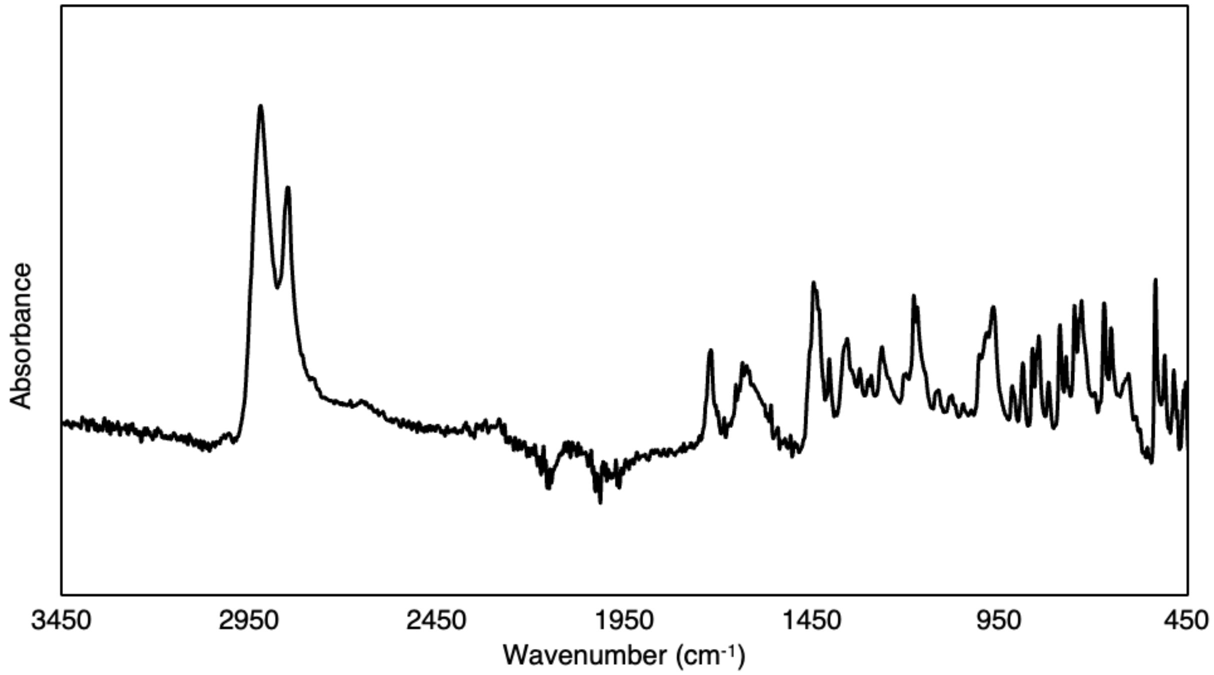


Fig. S36 FT-IR spectra Table S6, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (5 mol%), DCyPE (10 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

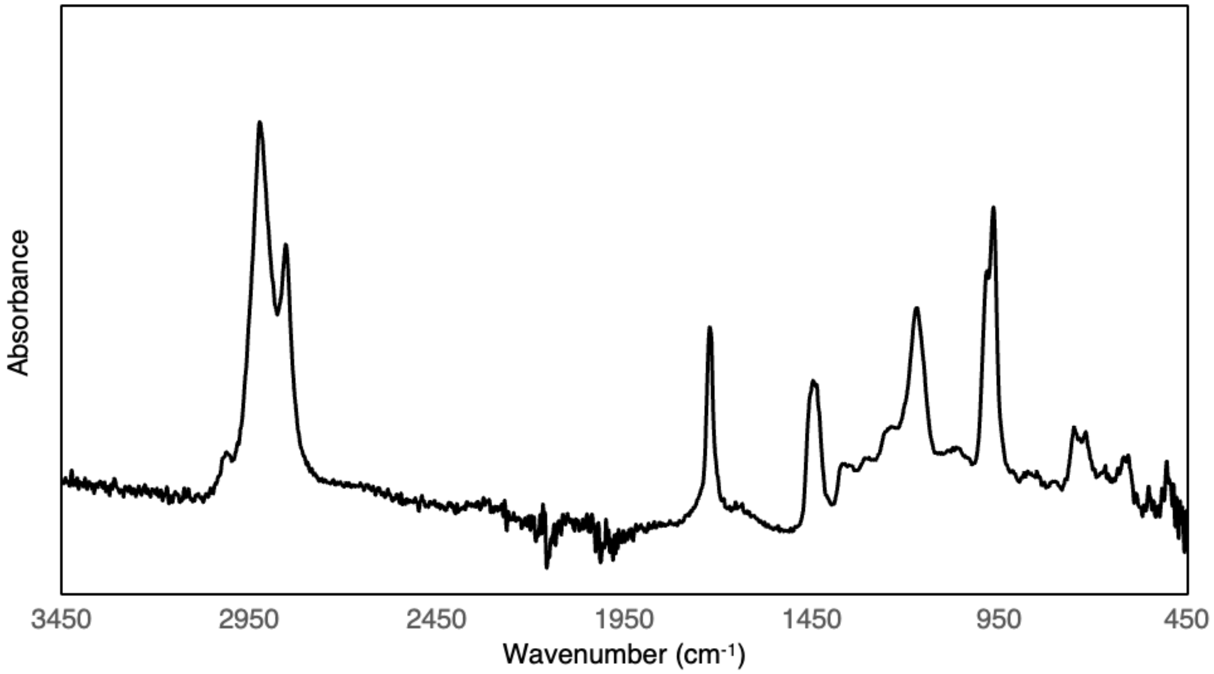


Fig. S37 FT-IR spectra Table S7, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. KHCO$_2$ for 48 hours in THF at 110 °C.

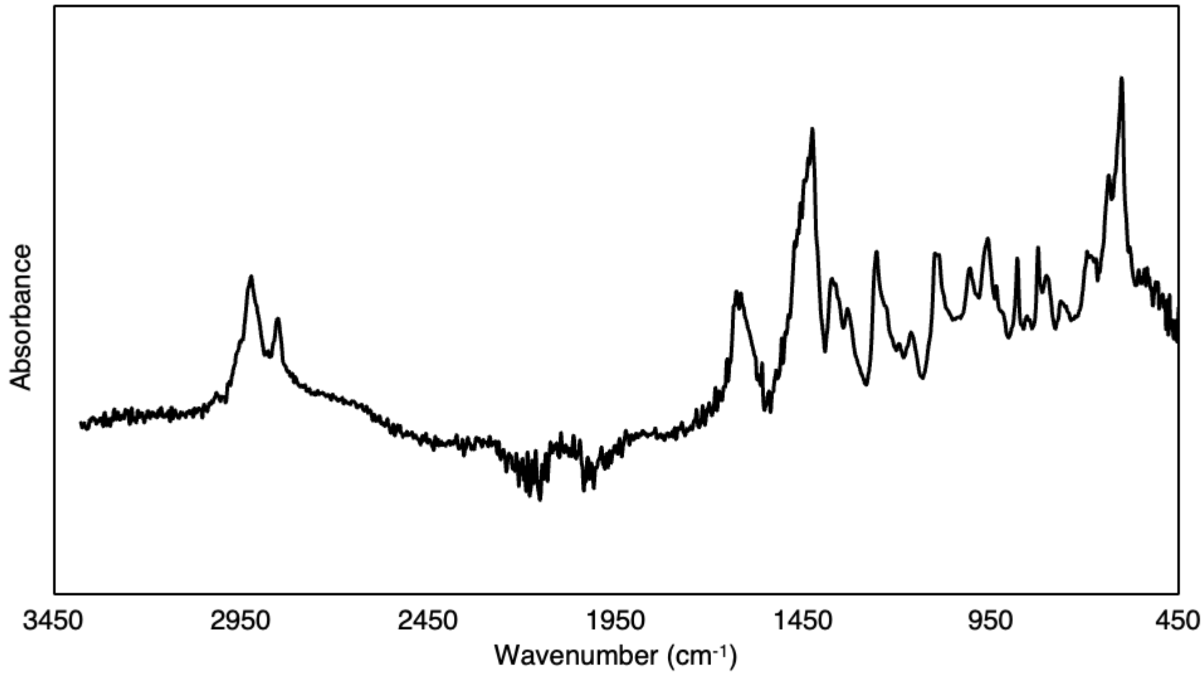


Fig. S38 FT-IR spectra Table S7, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaH for 48 hours in THF at 110 °C.

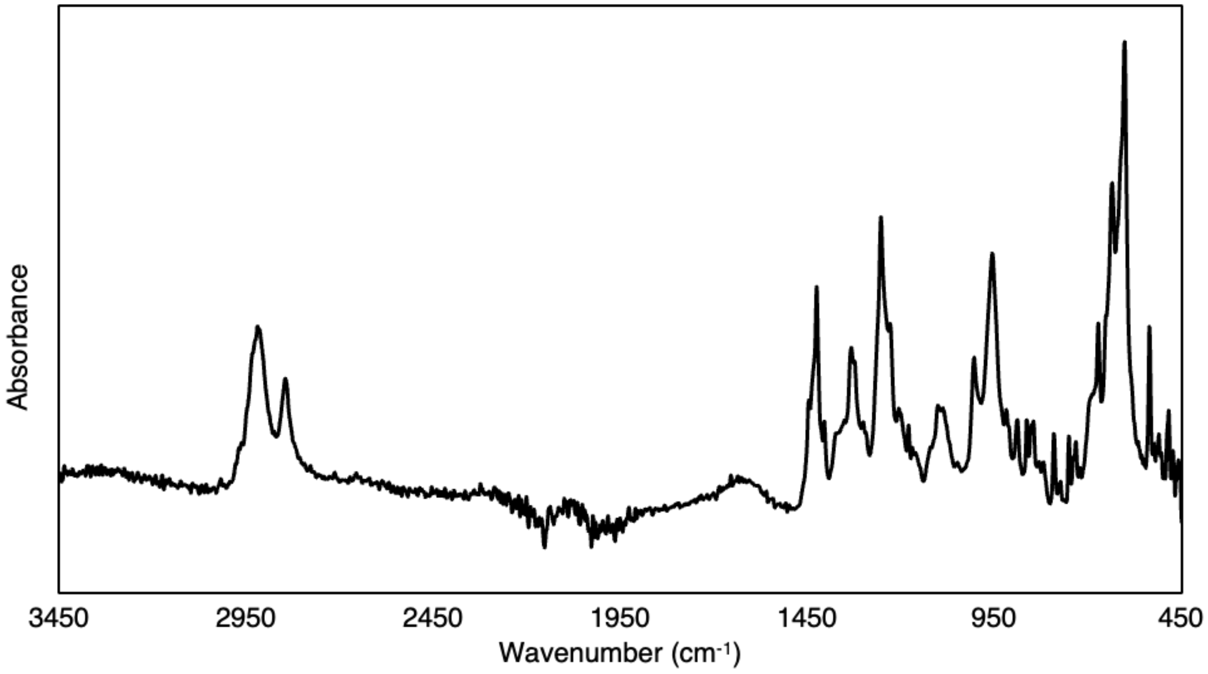


Fig. S39 FT-IR spectra Table S7, Entry 4 for PVC hydrodechlorination product with NiCl$_2$ (2.5 mol%), DCyPE (10 mol%), and 2 equiv. HSiEt$_3$ for 48 hours in Toluene at 120 °C.

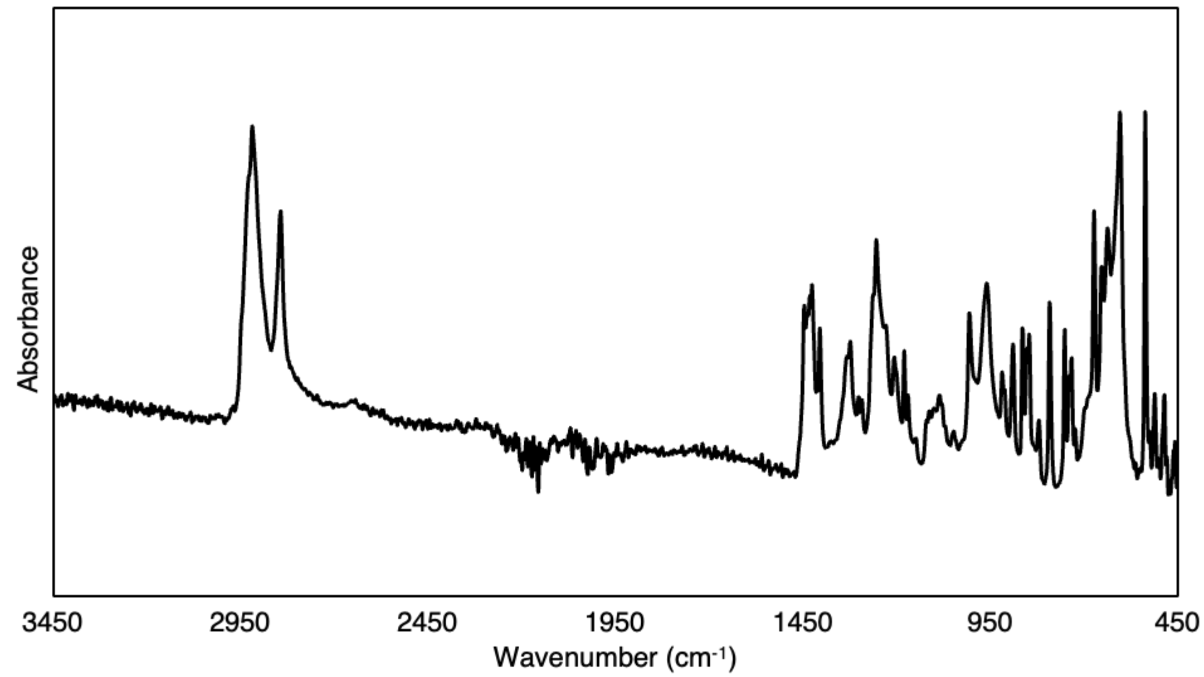


Fig. S40 FT-IR spectra Table S7, Entry 5 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. TMDS for 48 hours in Toluene at 120 °C.

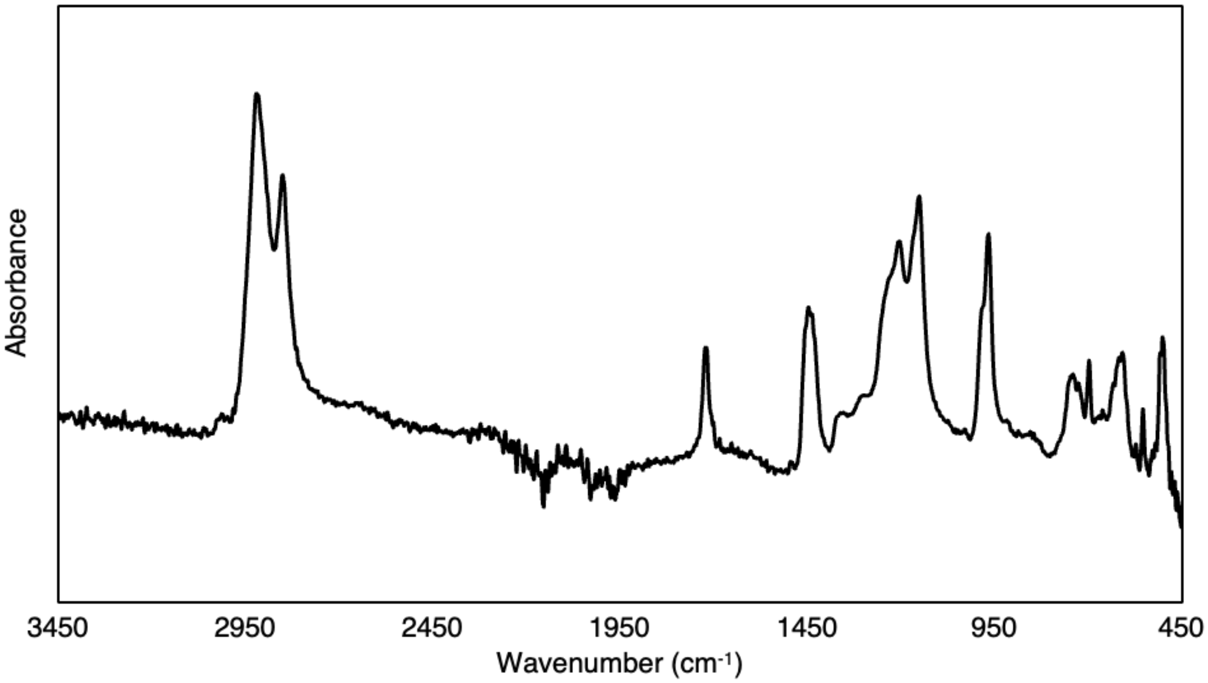


Fig. S41 FT-IR spectra Table S8, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 3 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

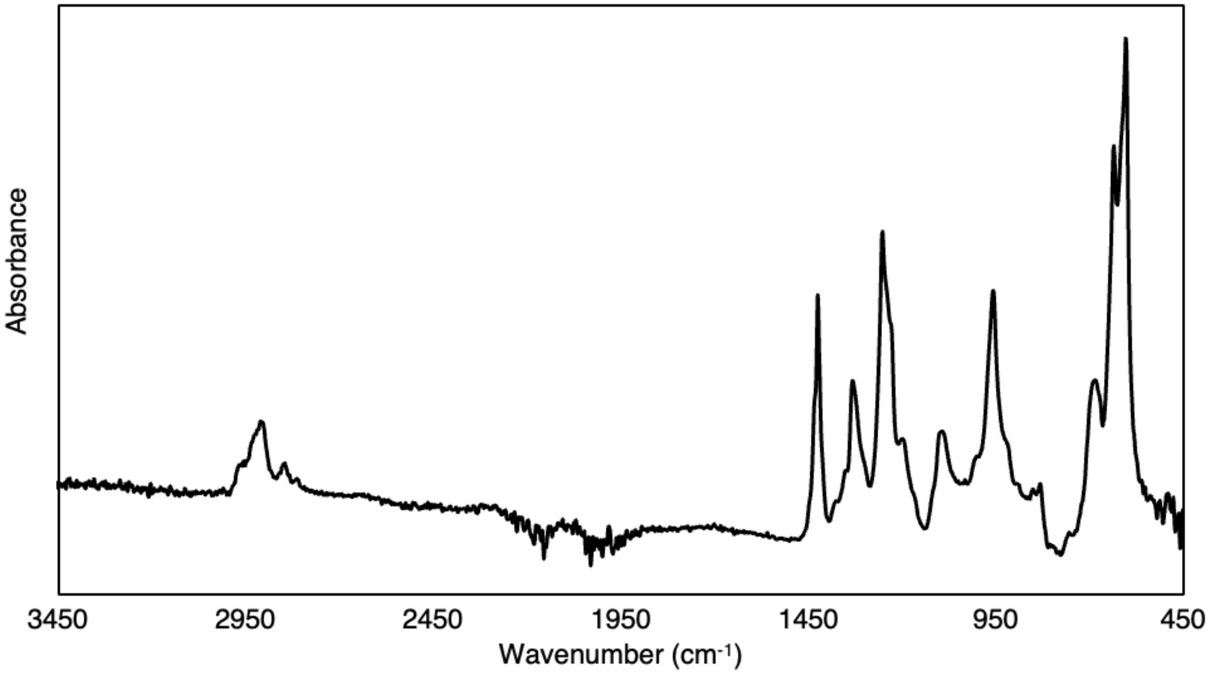


Fig. S42 FT-IR spectra Table S8, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), for 48 hours in Toluene at 120 °C without NaHCO$_2$.

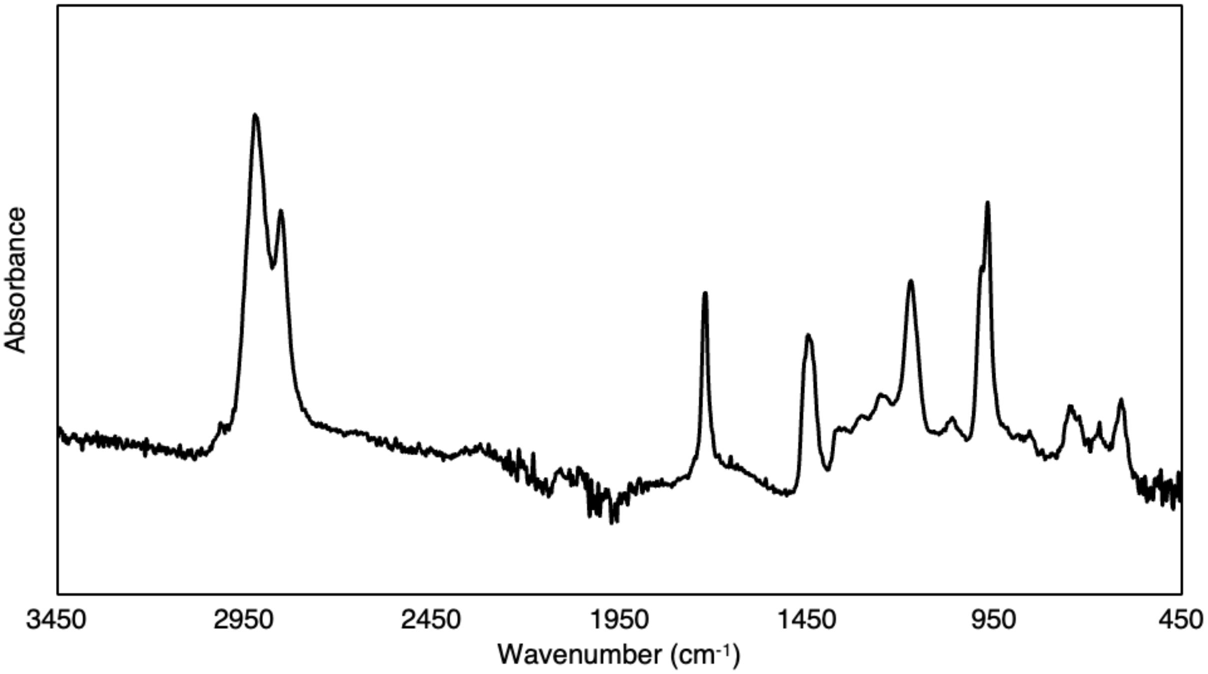


Fig. S43 FT-IR spectra Table S9, Entry 1 for PVC hydrodechlorination product with NiBr$_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 24 hours in THF at 110 °C.

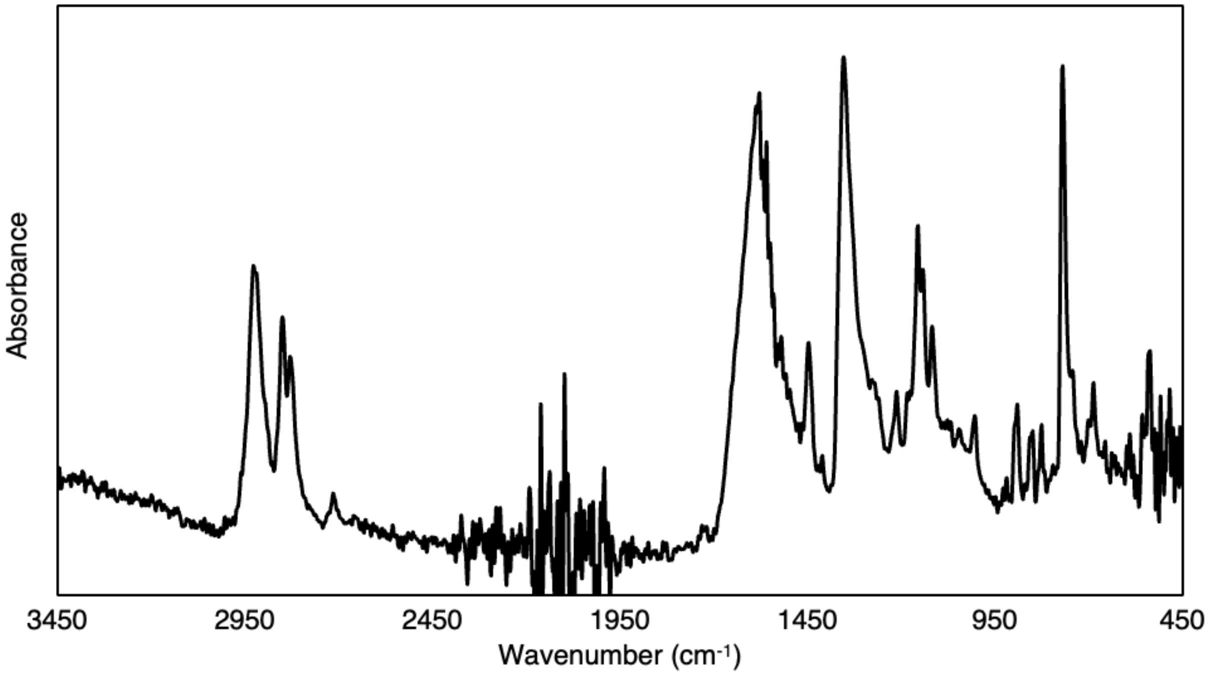


Fig. S43a FT-IR spectra of solids from mother liquor Table S9, Entry 1 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 24 hours in THF at 110 °C.

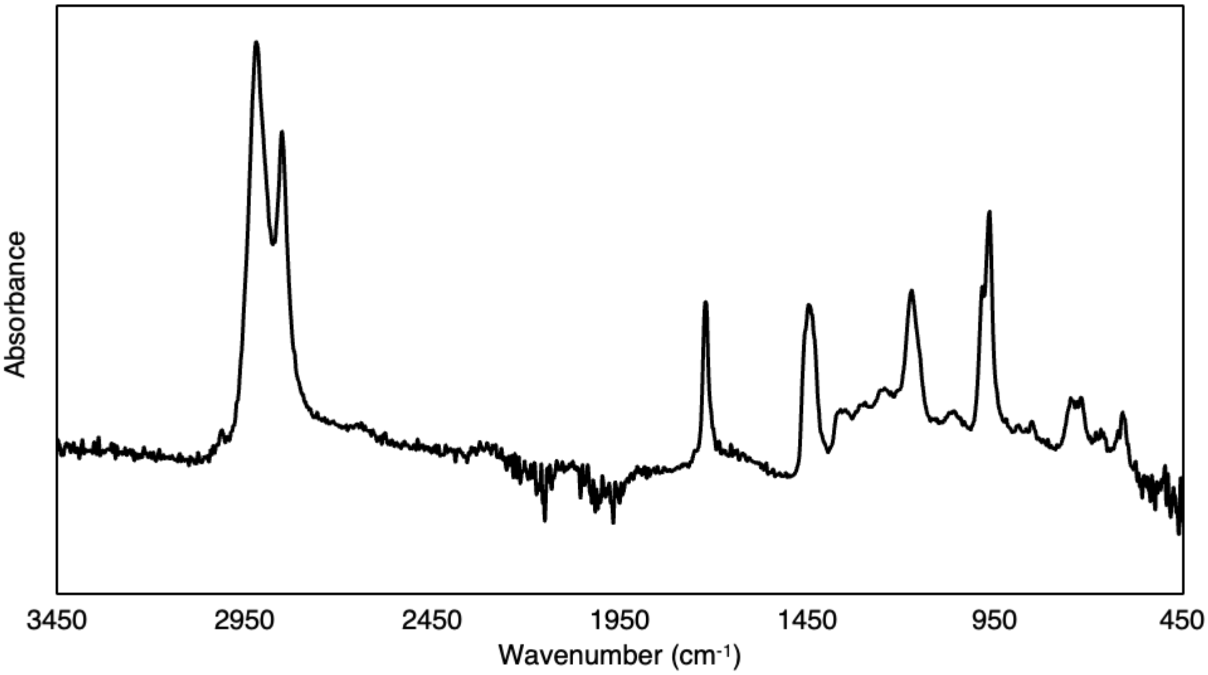


Fig. S44 FT-IR spectra Table S9, Entry 2 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

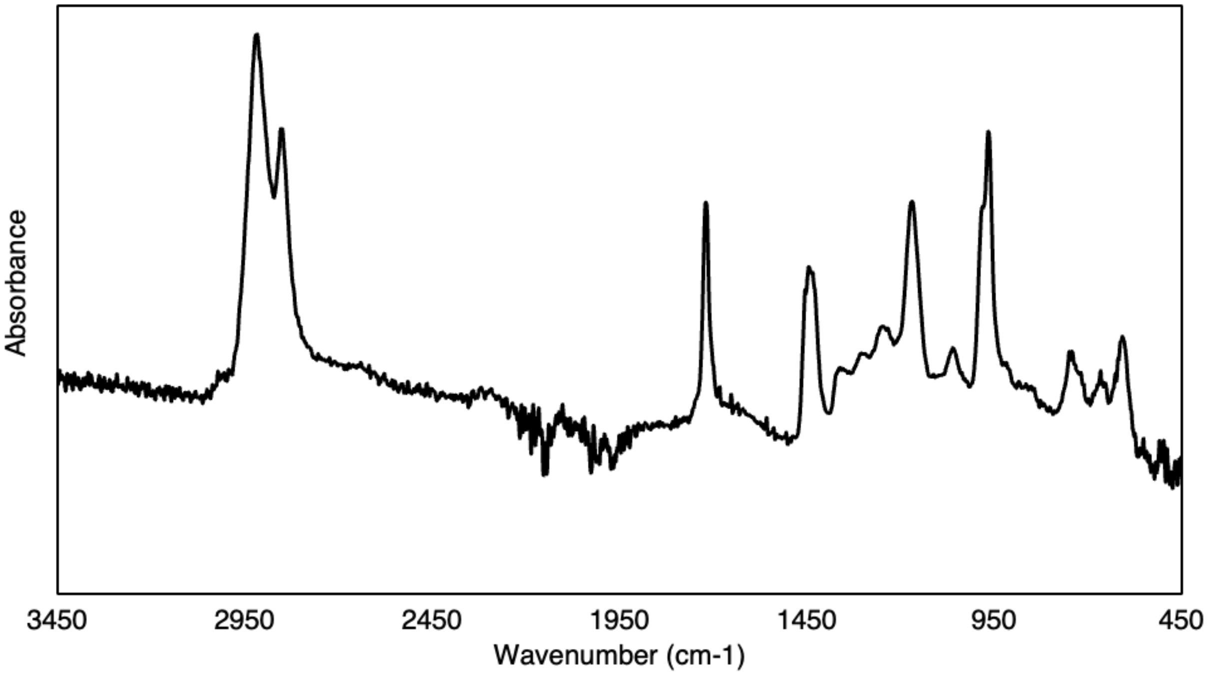


Fig. S45 FT-IR spectra Table S9, Entry 3 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (2 mol%), and 2 equiv. $NaHCO_2$ for 24 hours in THF at 110 °C.

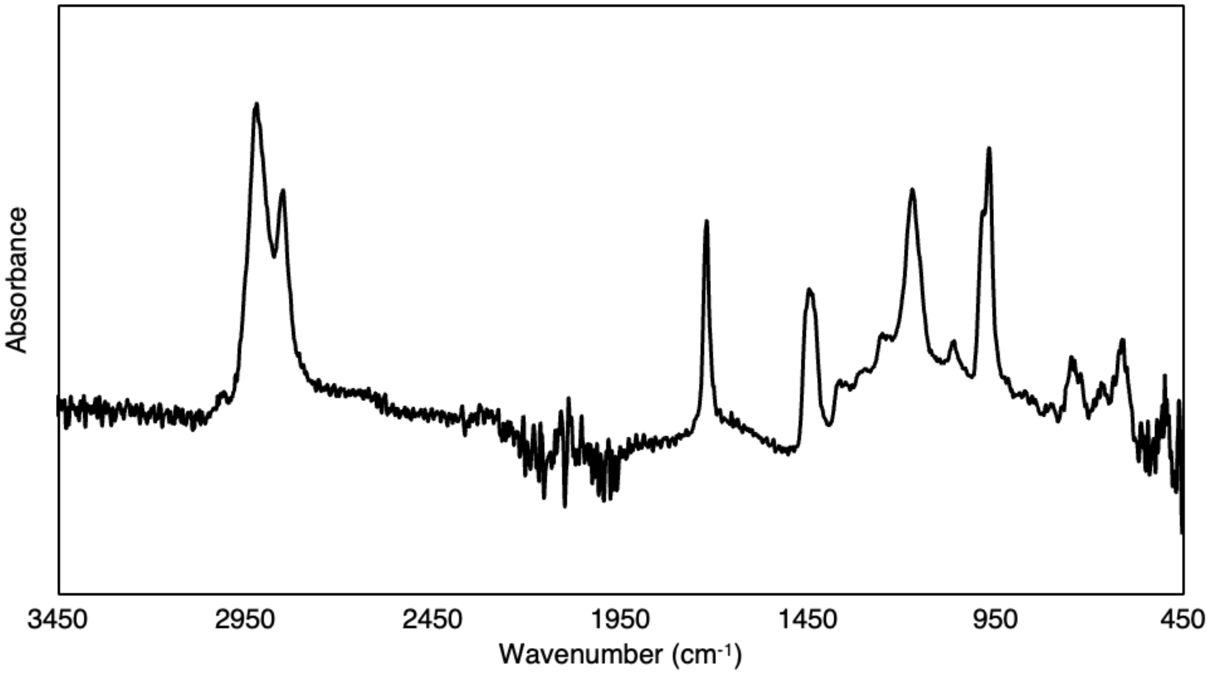


Fig. S46 FT-IR spectra Table S9, Entry 4 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (2 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

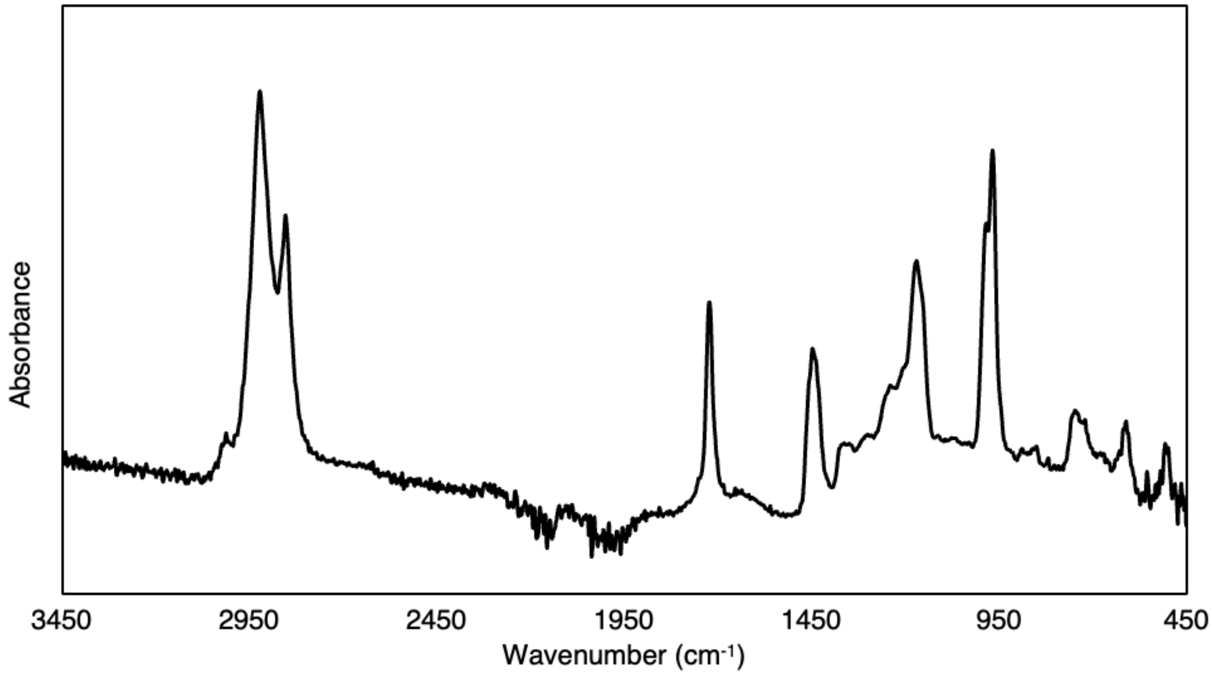


Fig. S47 FT-IR spectra Table S9, Entry 5 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $KHCO_2$ for 24 hours in THF at 110 °C.

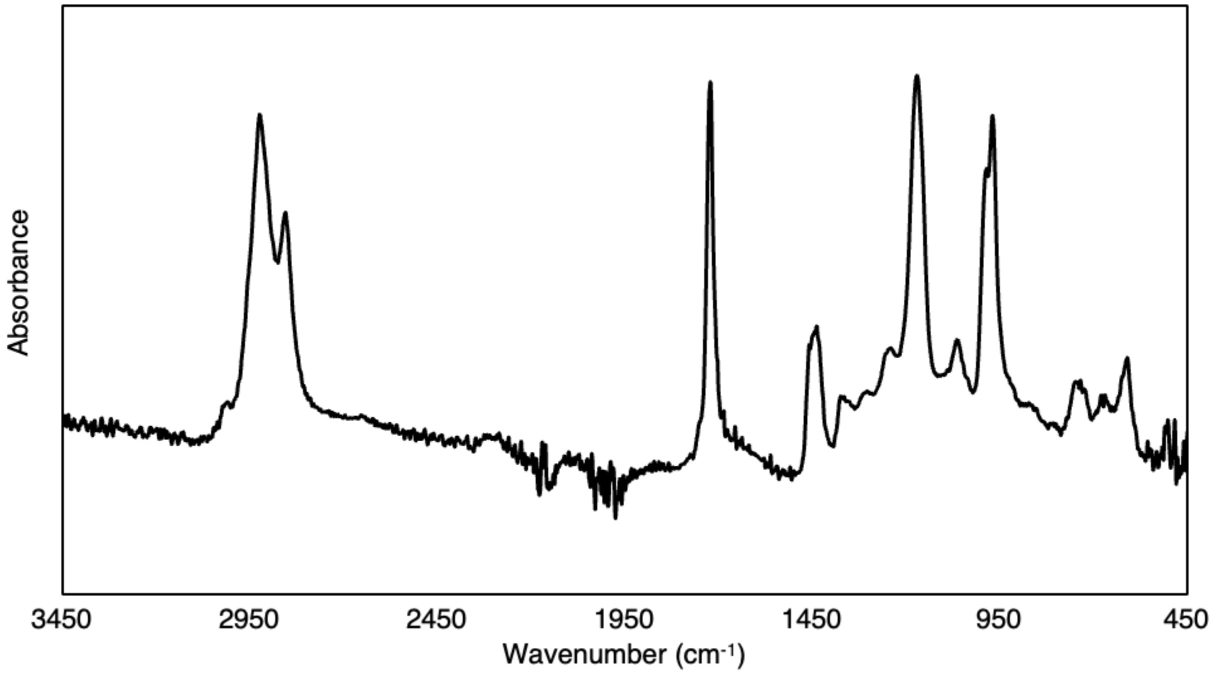


Fig. S48 FT-IR spectra Table S9, Entry 6 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (2 mol%), and 2 equiv. $KHCO_2$ for 48 hours in THF at 110 °C.

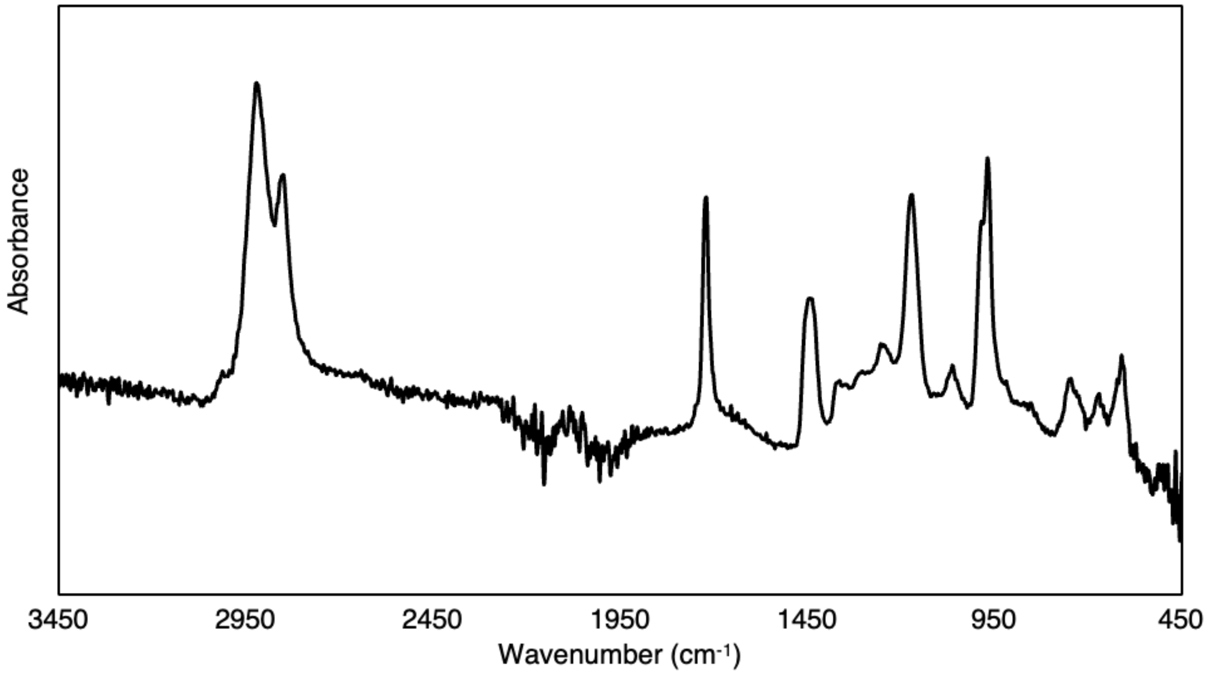


Fig. S49 FT-IR spectra Table S9, Entry 7 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C

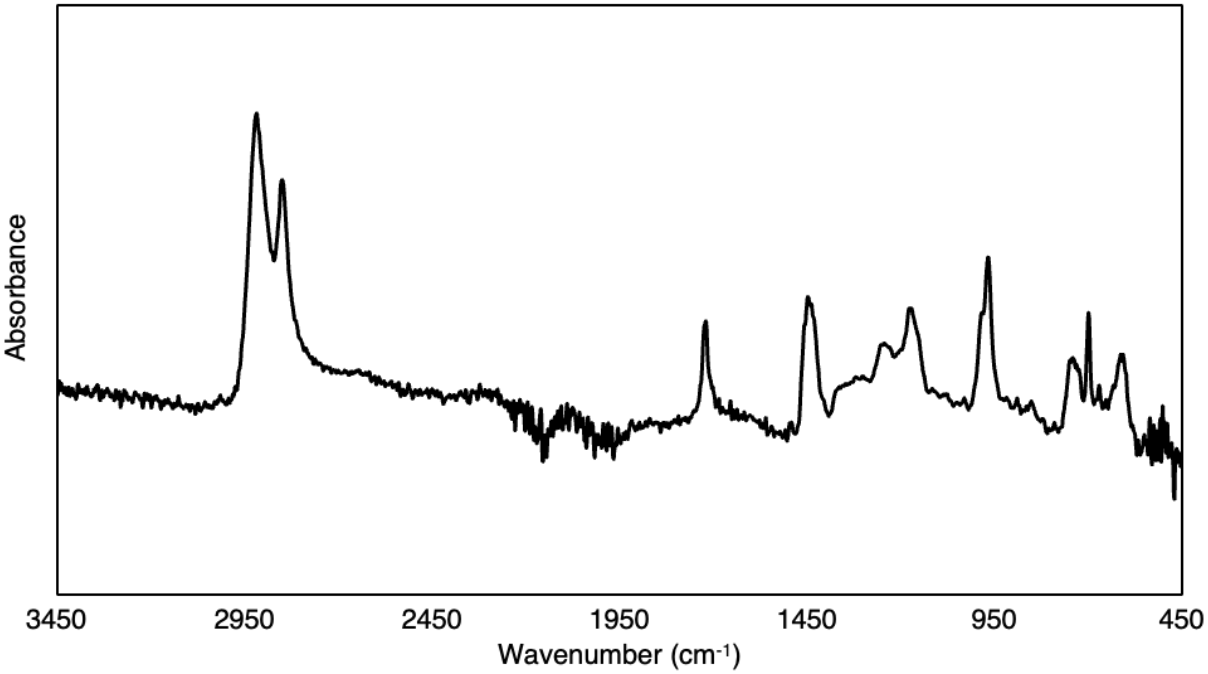


Fig. S50 FT-IR spectra Table S9, Entry 8 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 24 hours in Toluene at 120 °C.

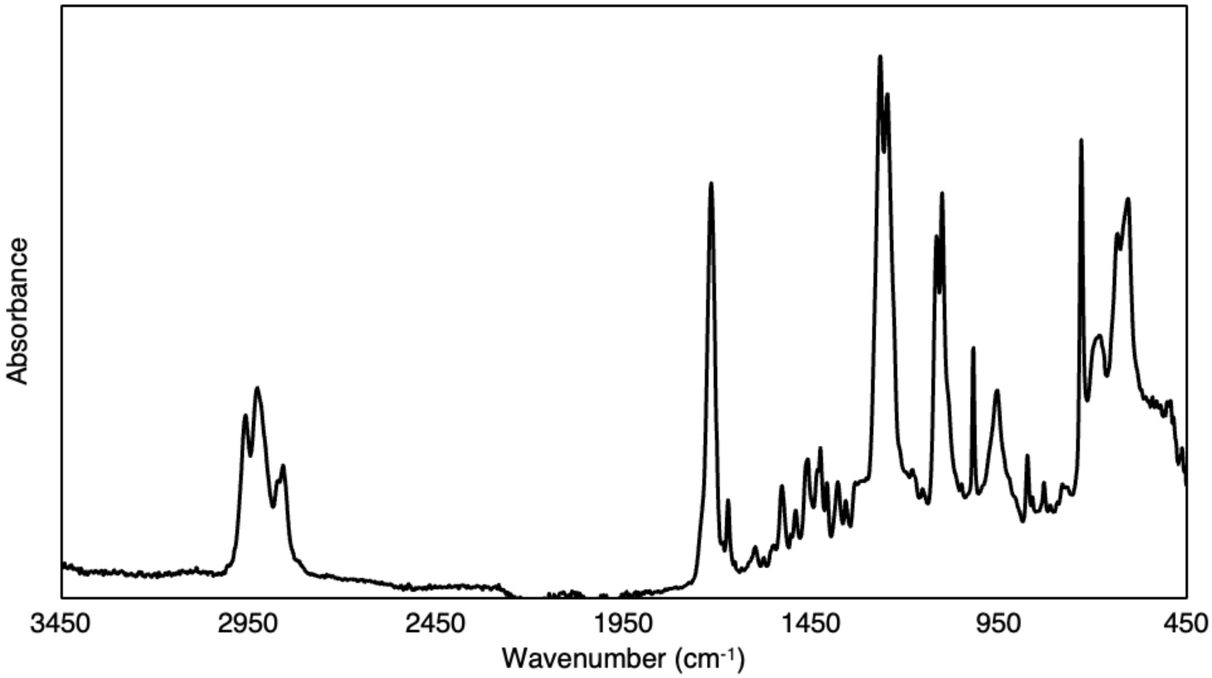


Fig. S51 FT-IR spectra for PVC toy lizard (before reaction).

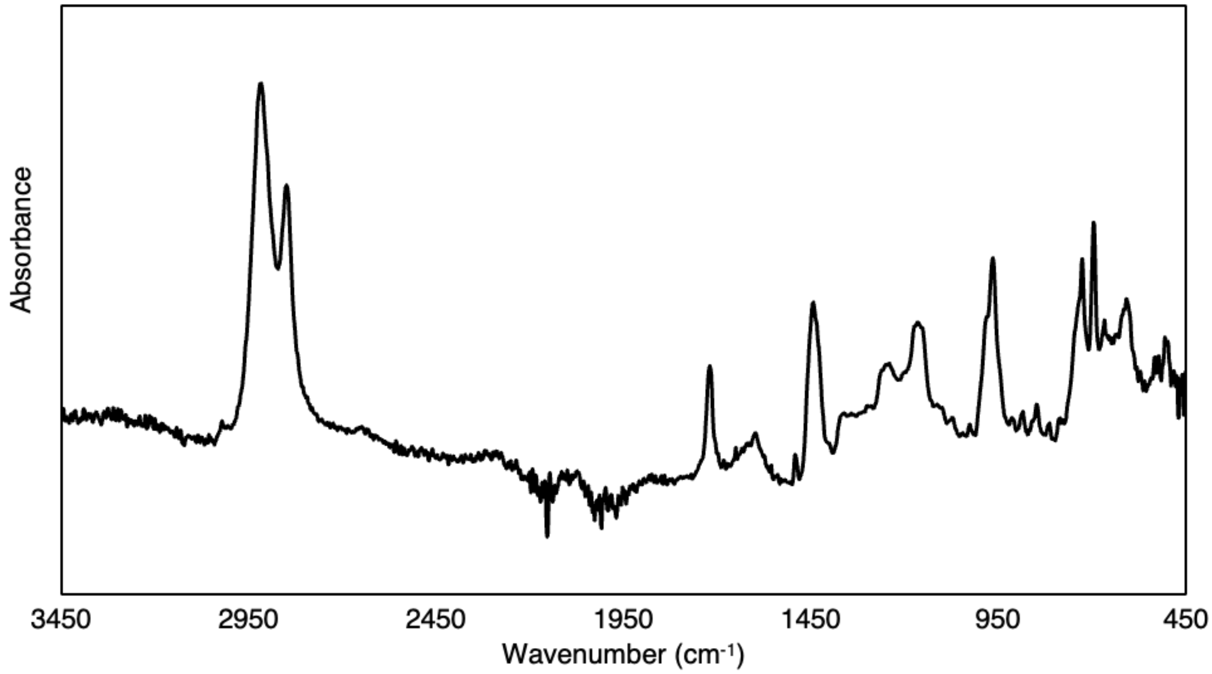


Fig. S52 FT-IR spectra for PVC toy lizard hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 24 hours in Toluene at 120 °C.

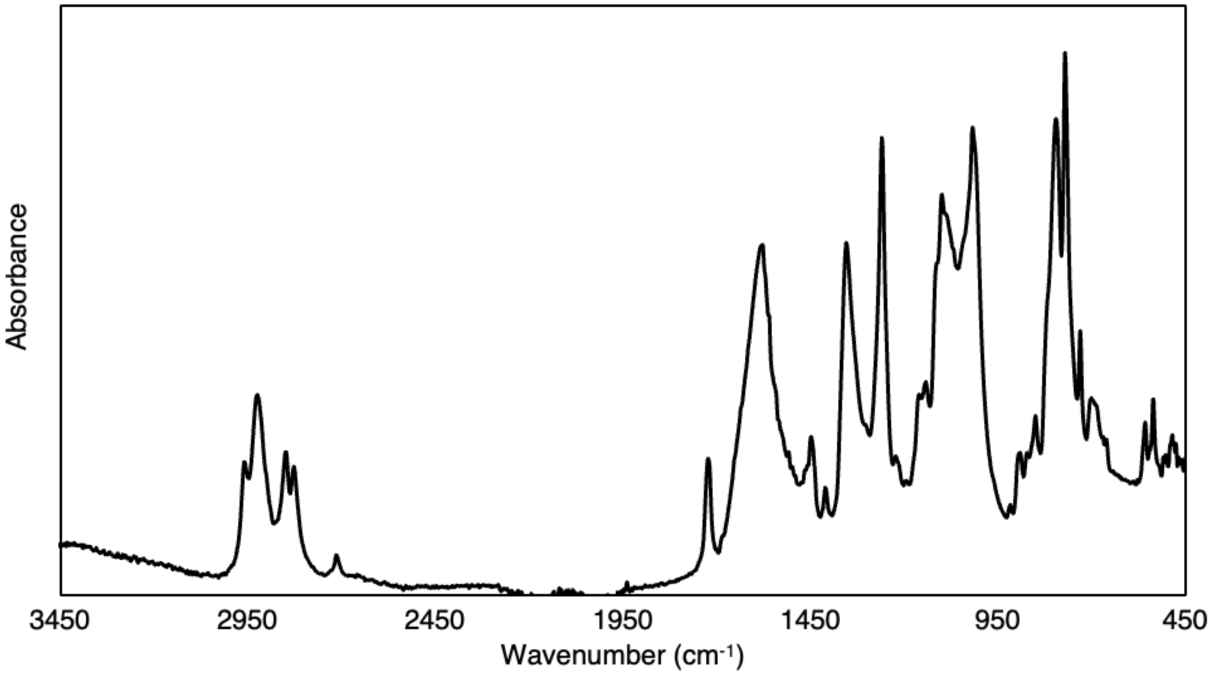


Fig. S52a FT-IR spectra of solids from mother liquor of PVC toy lizard hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 24 hours in Toluene at 120 °C.

7. NMR Spectra

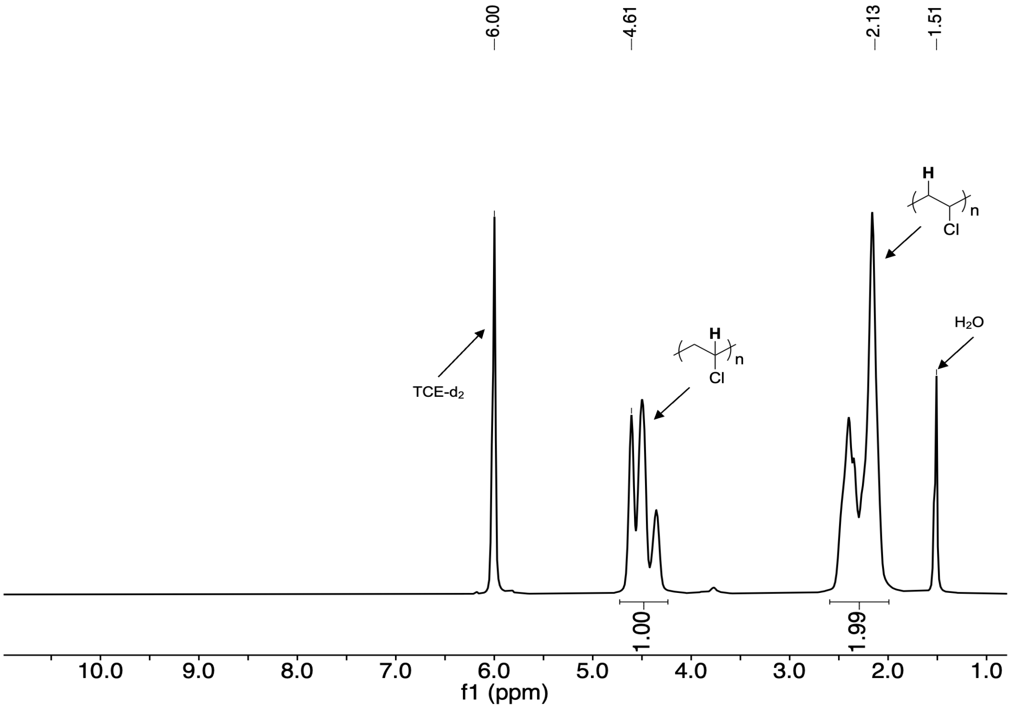


Fig. S53 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (80 °C) of low molecular weight PVC (CAS: 9002-86-2, Product #: 81388, Sigma Aldrich).

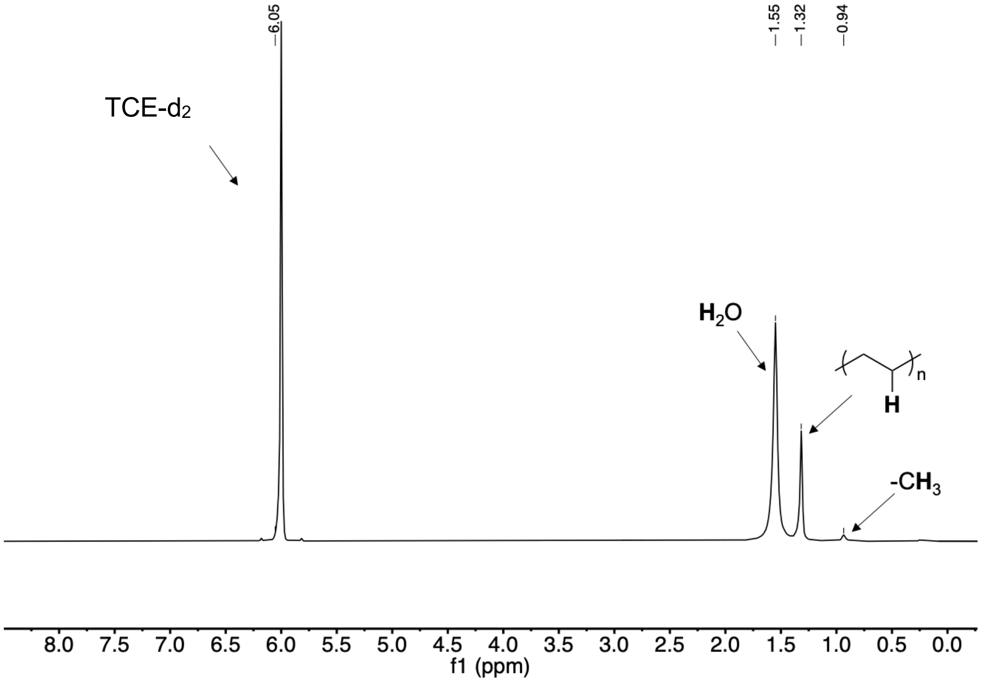


Fig. S54 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (80 °C) of HDPE pellets (CAS: 9002-88-4, Sigma Aldrich).

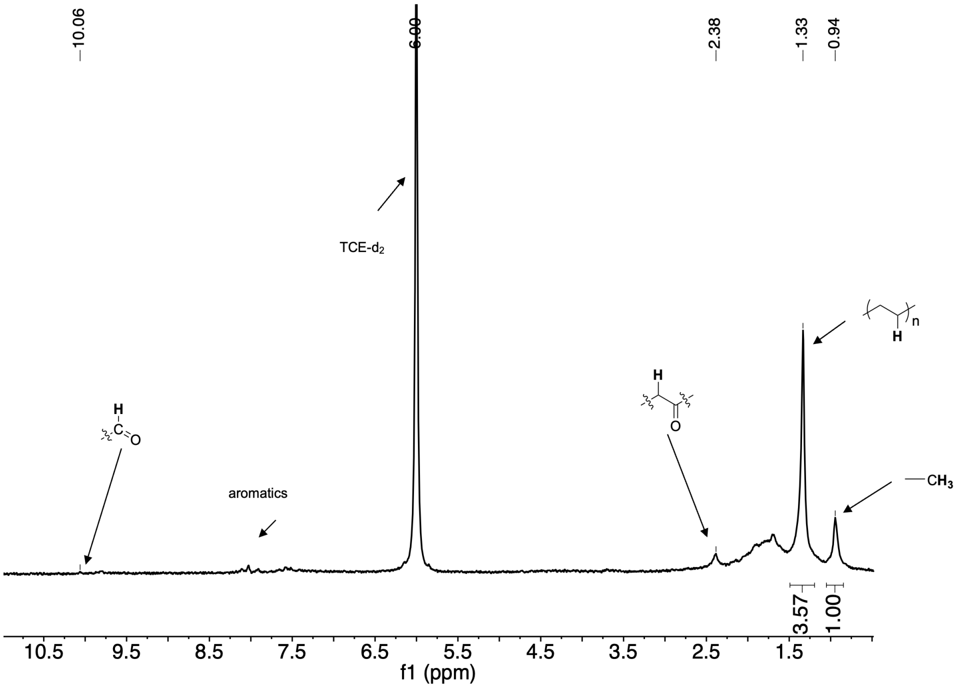


Fig. S55 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S1, Entry 1 for PVC hydrodechlorination product with $NiCl_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

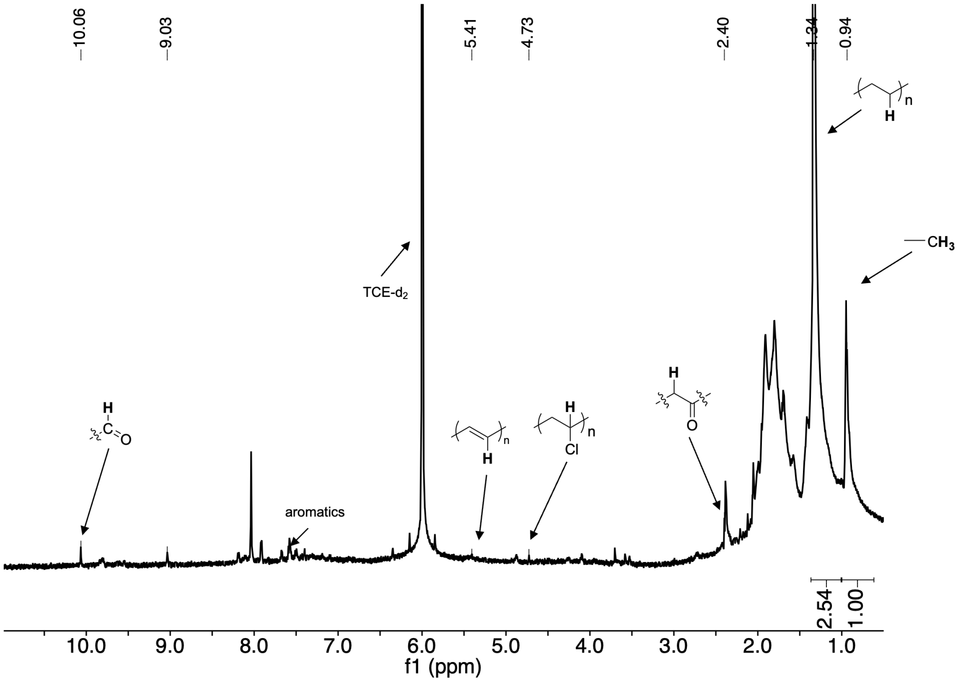


Fig. S56 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S1, Entry 2 for PVC hydrodechlorination product with $NiCl_2$ (2.5 mol%), DCyPE (10 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

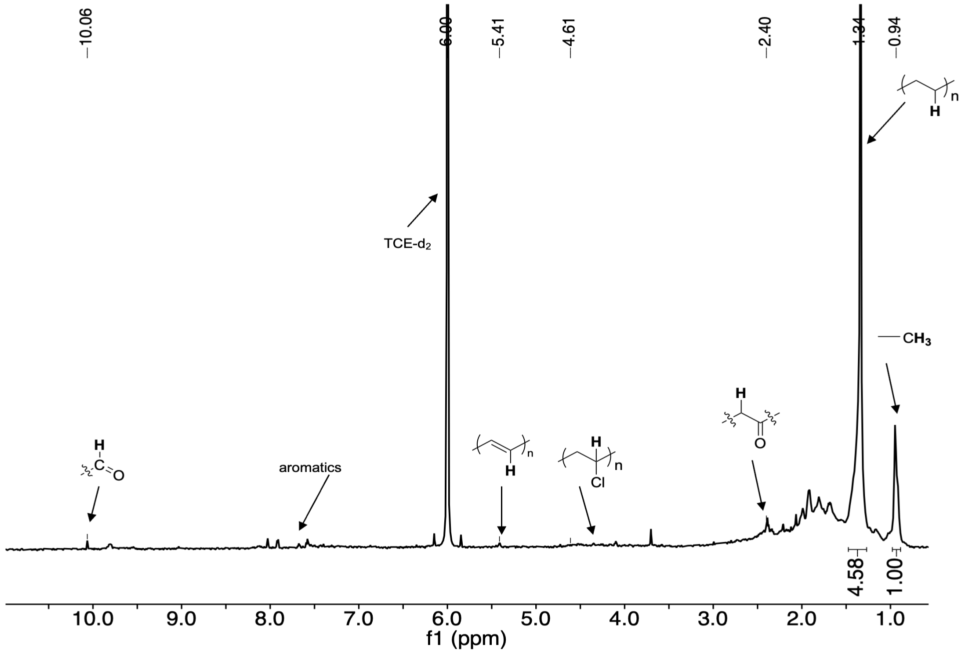


Fig. S57 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S1, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

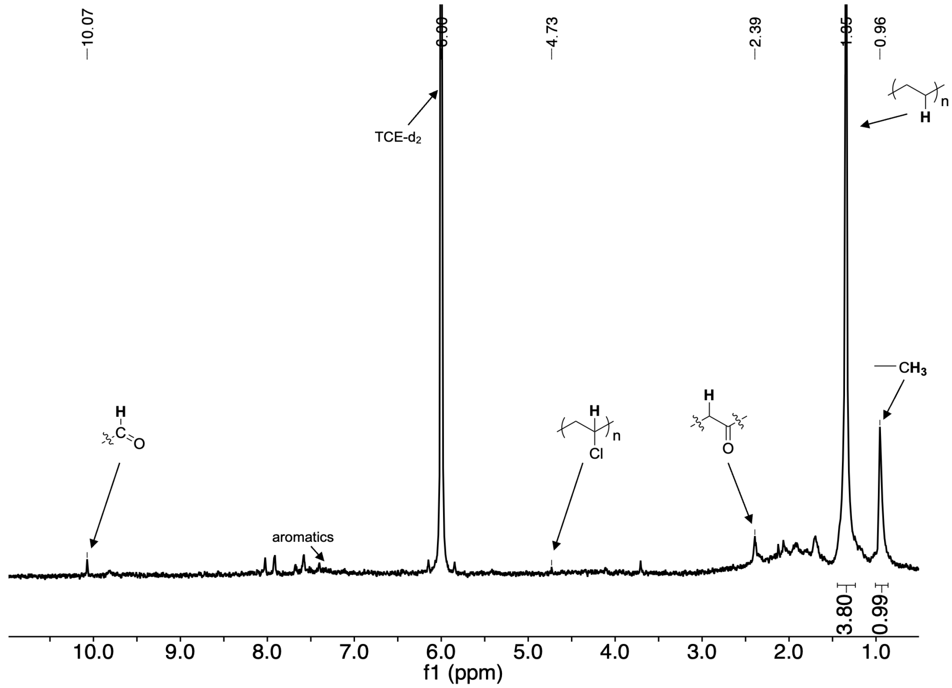


Fig. S58 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S1, Entry 4 for PVC hydrodechlorination product with Ni(acac)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

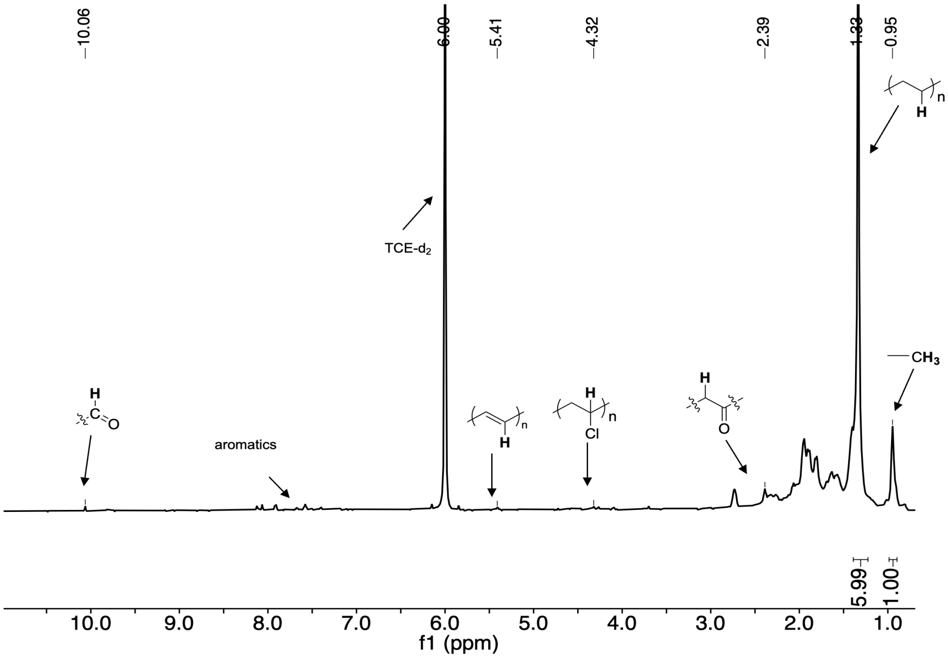


Fig. S59 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S1, Entry 6 for PVC hydrodechlorination product with $NiBr_2$.glyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

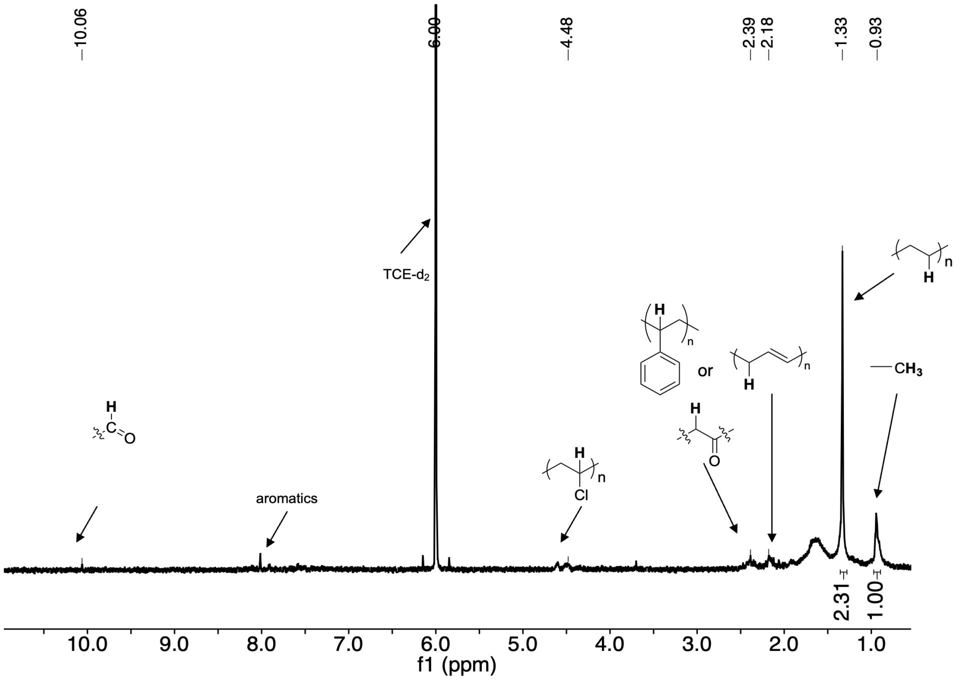


Fig. S60 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S1, Entry 6 for PVC hydrodechlorination product with $NiBr_2$.diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

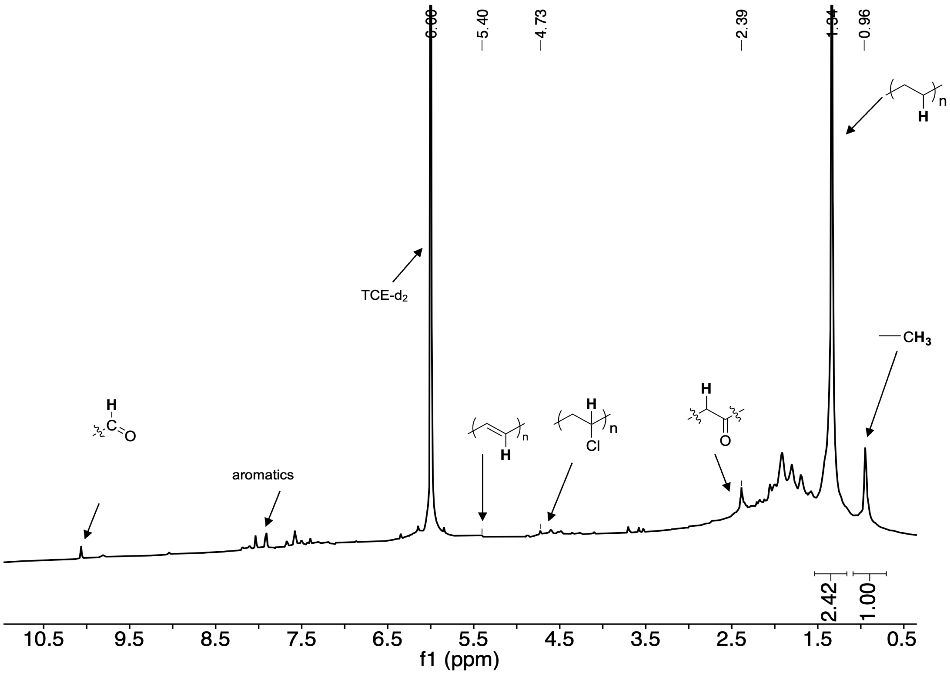


Fig. S61 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S2, Entry 6 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DCyPE (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

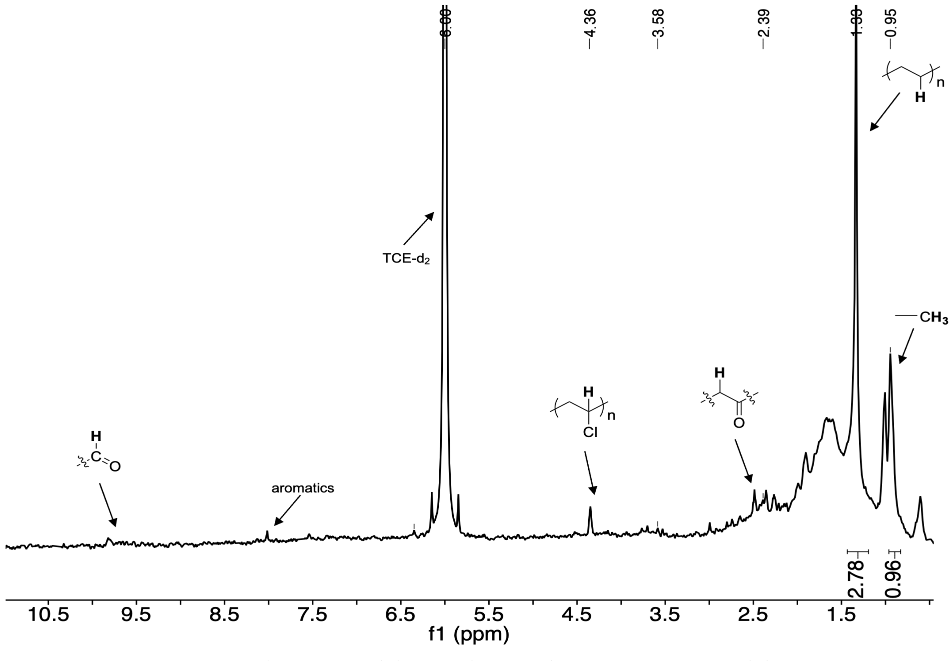


Fig. S62 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S3, Entry 1 for PVC hydrodechlorination product with $Ni(COD)_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 120 °C.

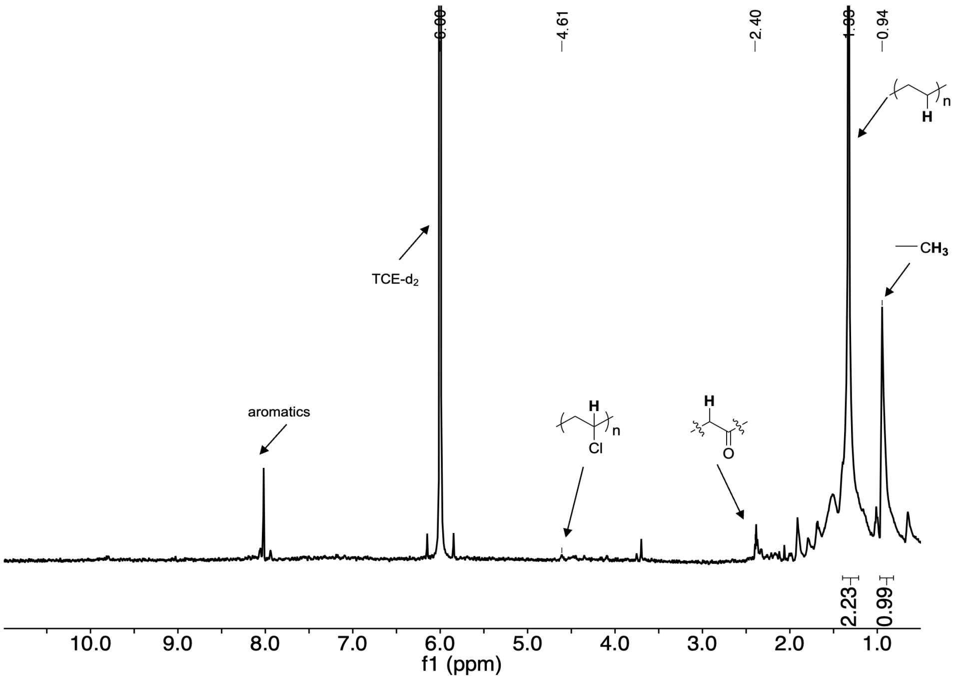


Fig. S63 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S3, Entry 8 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in 1,4-dioxane at 120 °C.

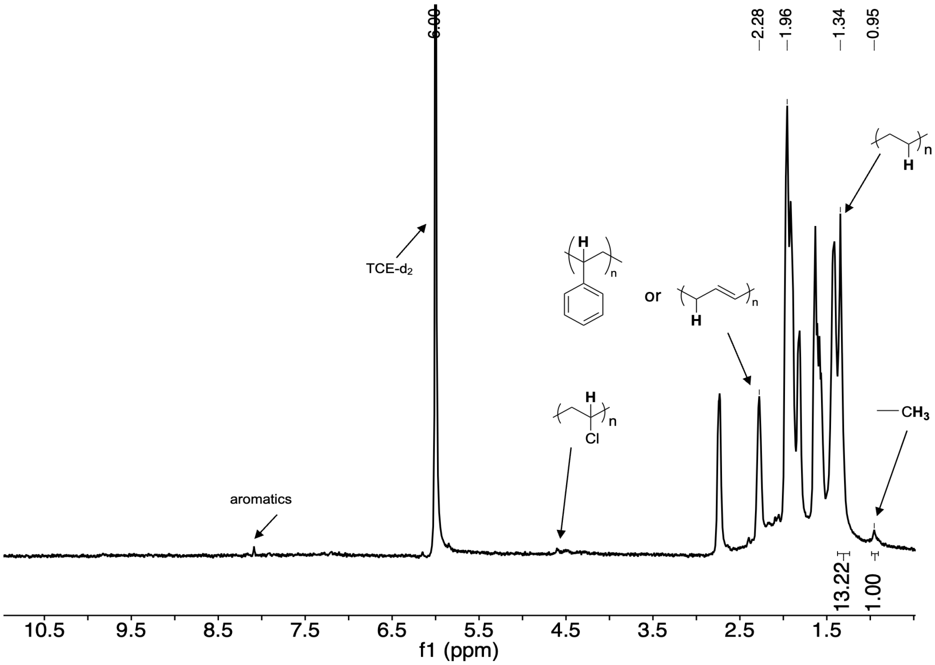


Fig. S64 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S4, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 4 hours in Toluene at 120 °C

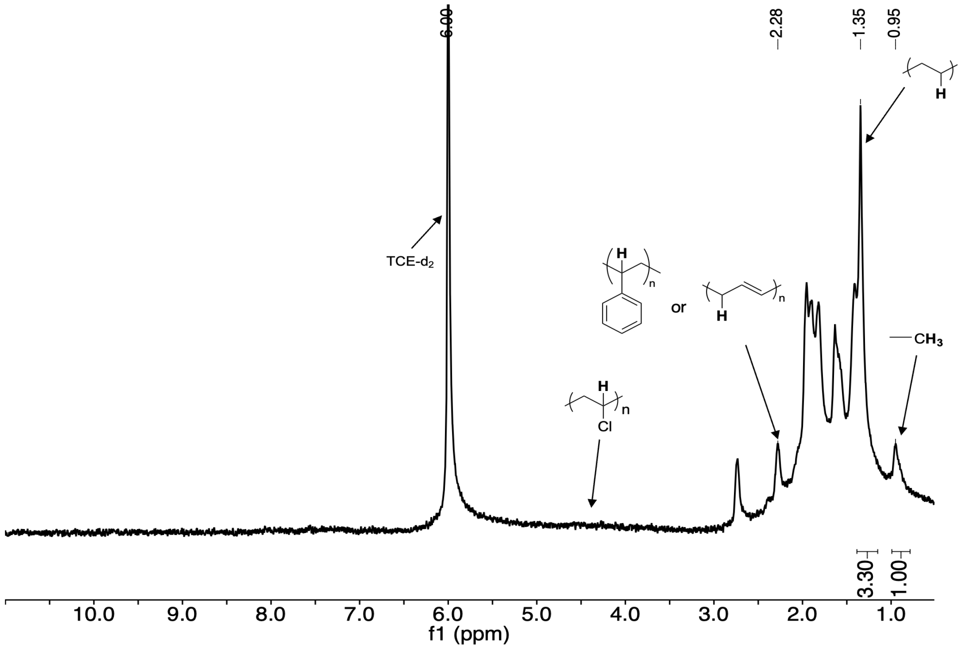


Fig. S65 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S4, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 8 hours in Toluene at 120 °C.

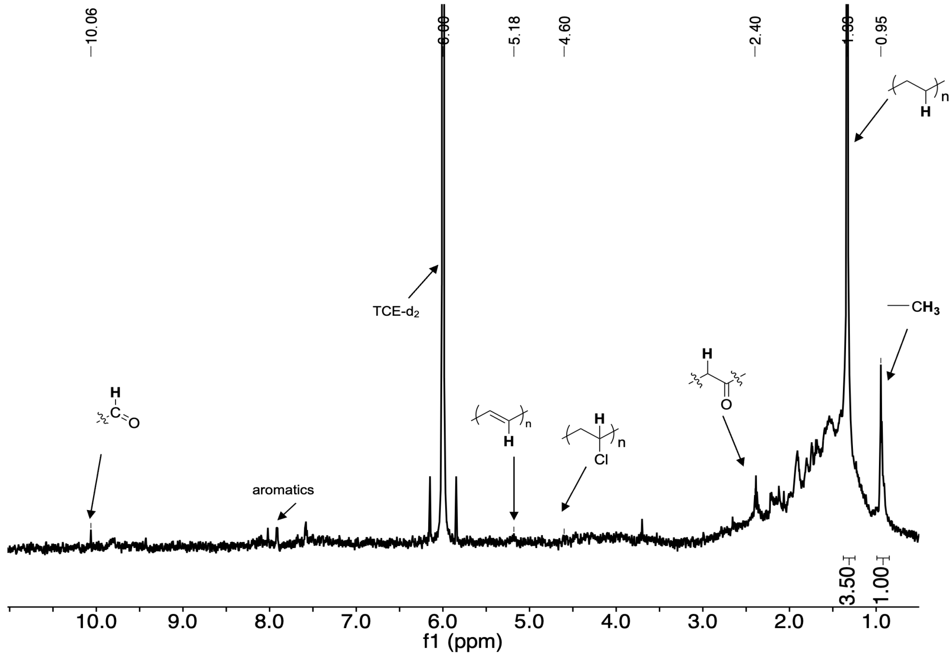


Fig. S66 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S4, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 12 hours in Toluene at 120 °C.

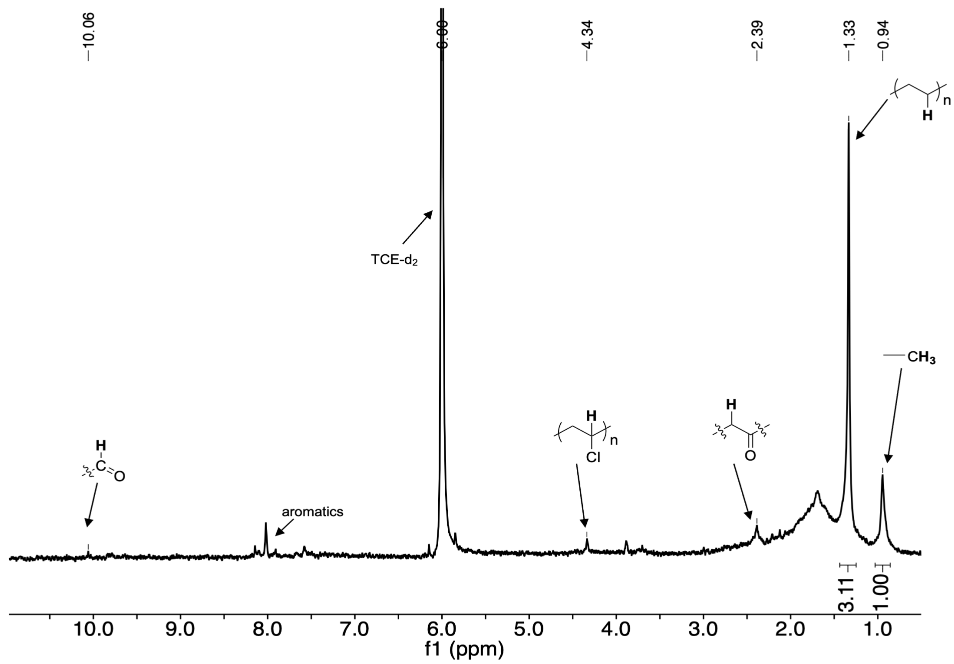


Fig. S67 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S4, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 16 hours in Toluene at 120 °C.

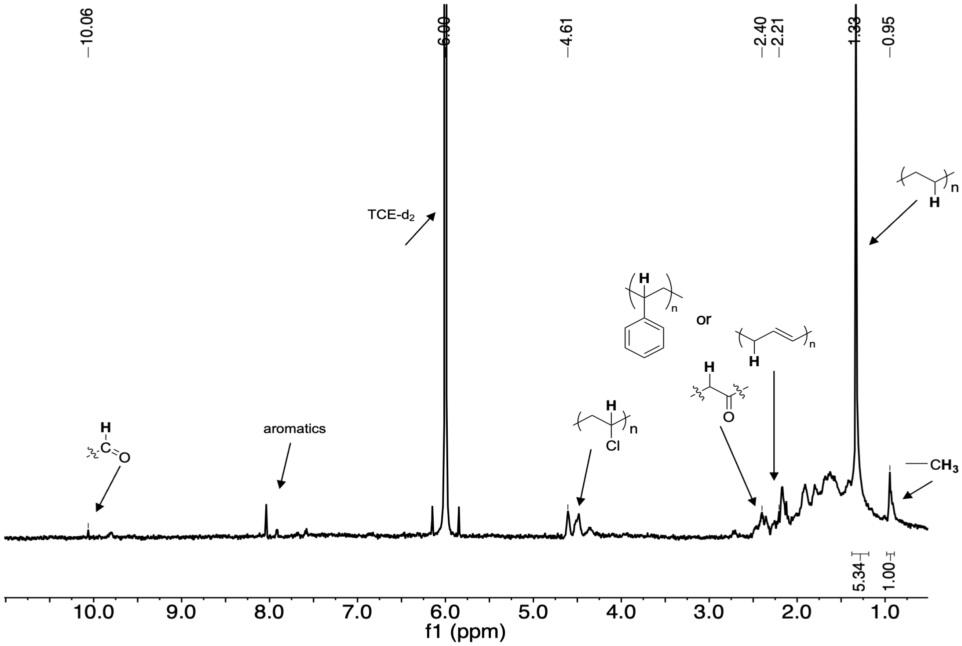


Fig. S68 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S4, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 16 hours in Toluene at 120 °C.

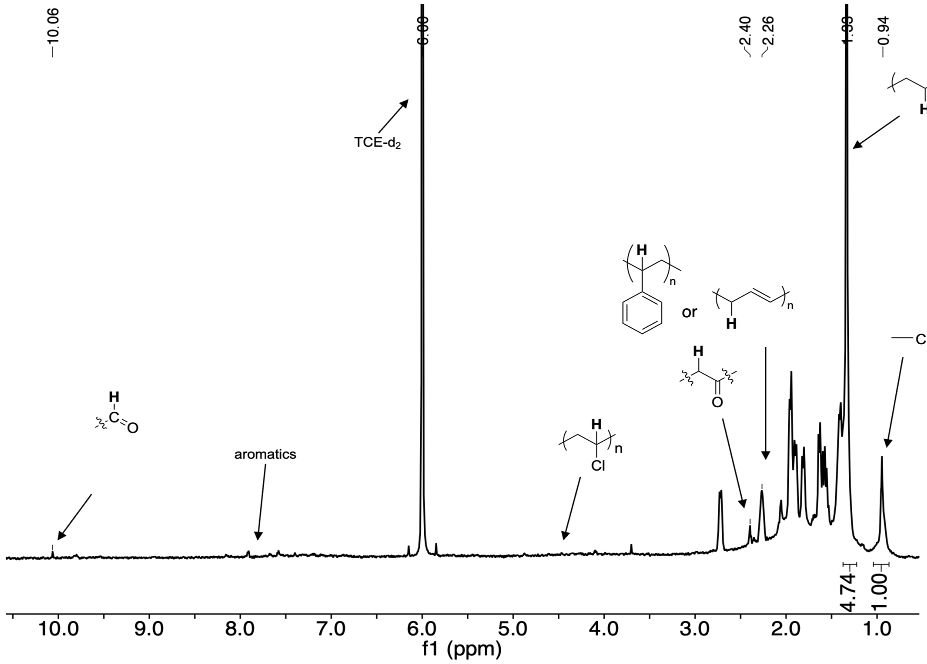


Fig. S69 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S4, Entry 6 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

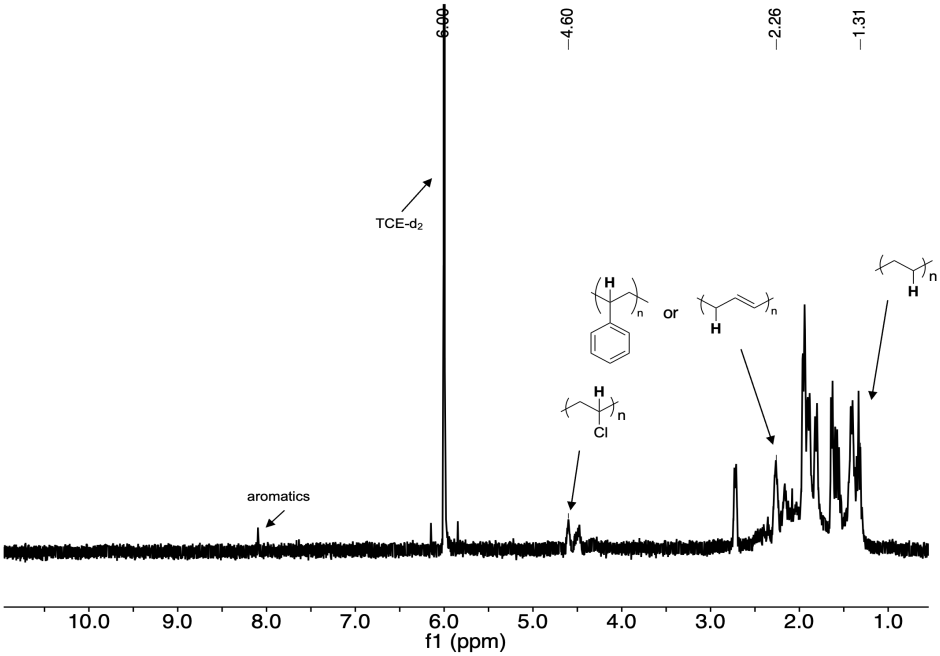


Fig. S70 ^{1}H NMR spectrum in tetrachloroethane-d_2 (90 °C), Table S5, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 80 °C.

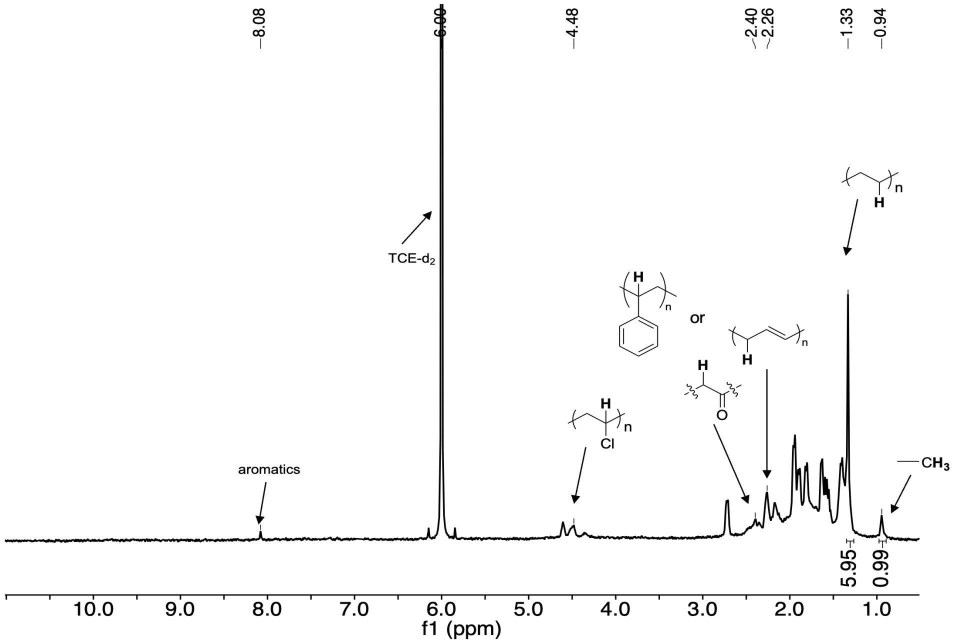


Fig. S71 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S5, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 100 °C.

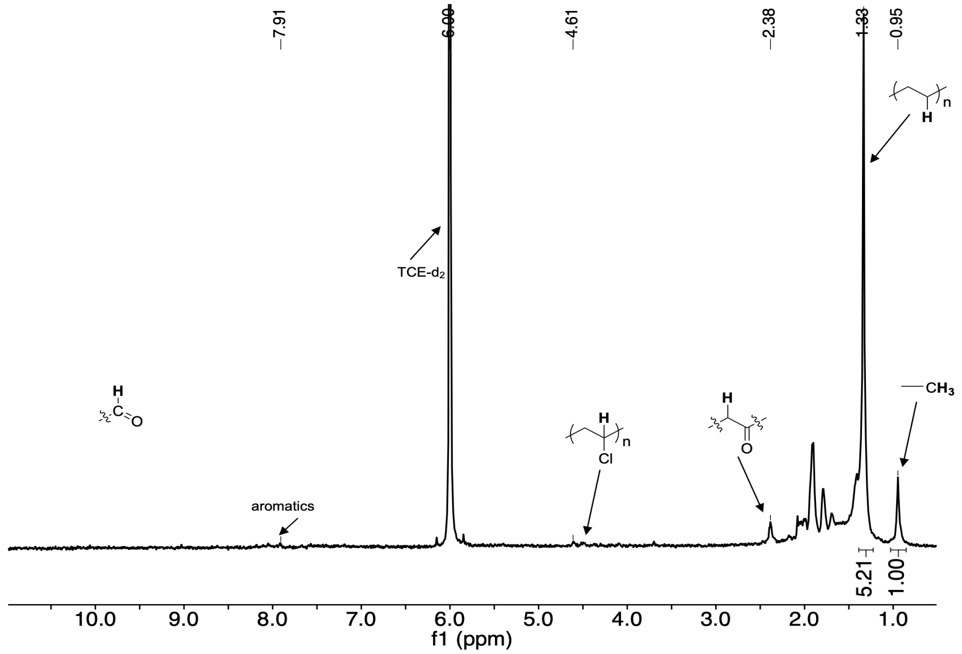


Fig. S72 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S5, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 150 °C.

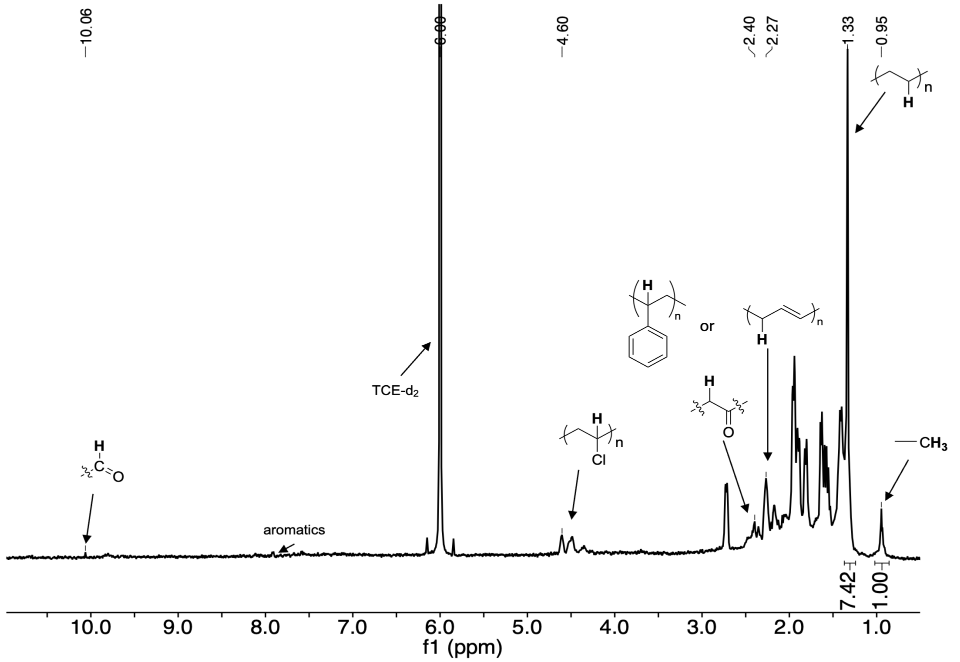


Fig. S73 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S6, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (1 mol%), DCyPE (2 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

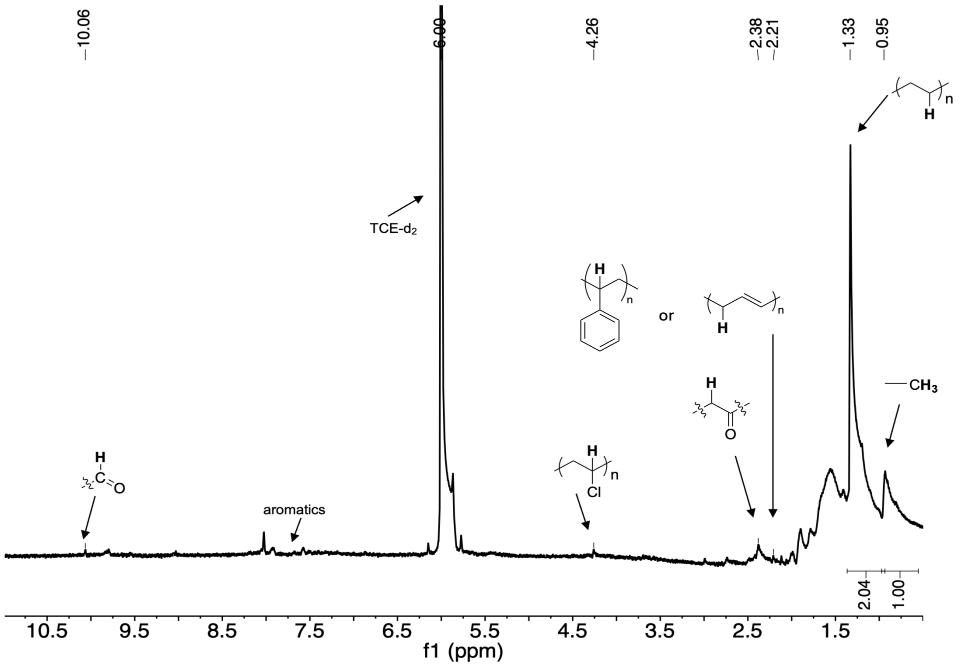


Fig. S74 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S6, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (2.5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

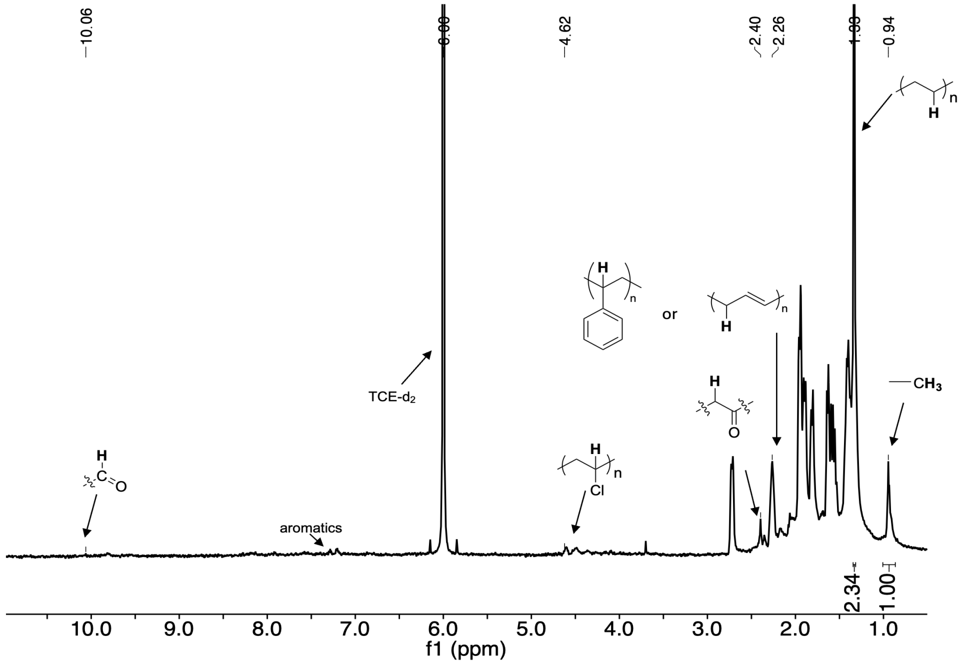


Fig. S75 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S6, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (5 mol%), DCyPE (10 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

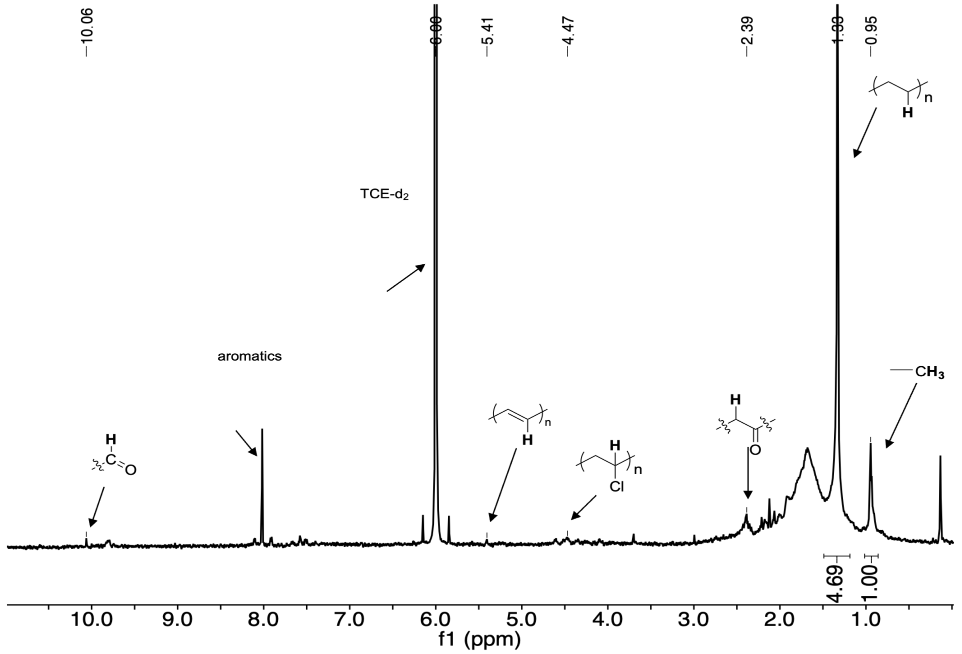


Fig. S76 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S7, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. KHCO$_2$ for 48 hours in THF at 110 °C.

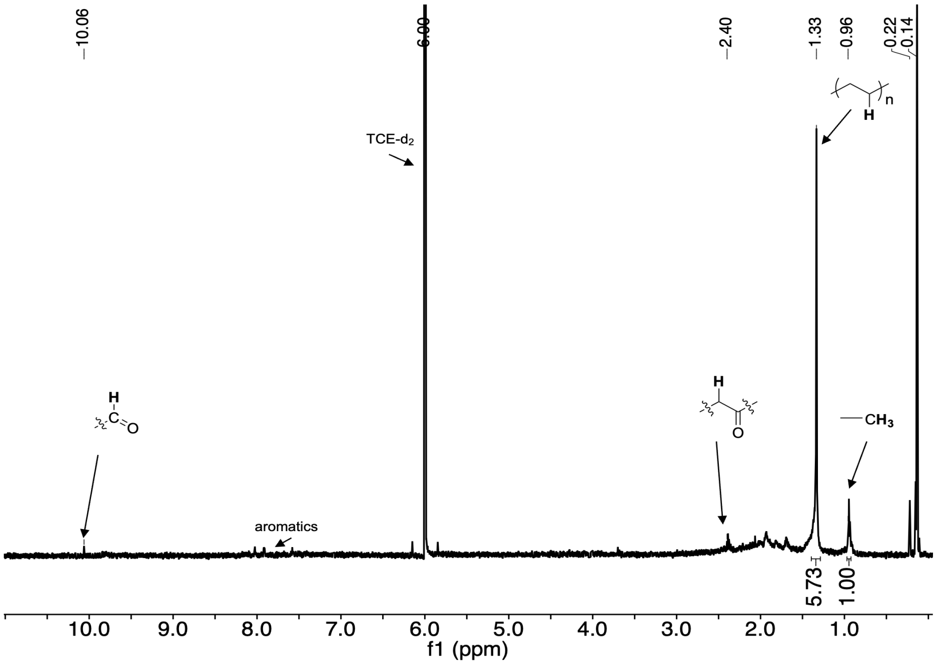


Fig. S77 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S8, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 3 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

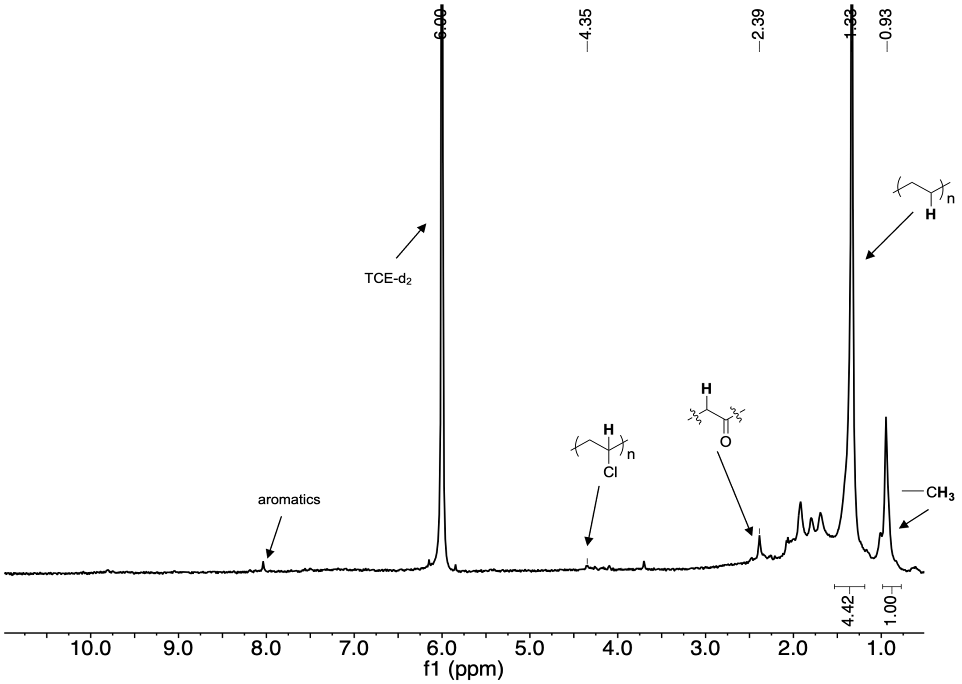


Fig. S78 ^{1}H NMR spectrum in tetrachloroethane-d$_2$ (90 °C), Table S9, Entry 4 for PVC hydrodechlorination product with NiBr$_2$. diglyme (1 mol%), DCyPE (2 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in THF at 110 °C.

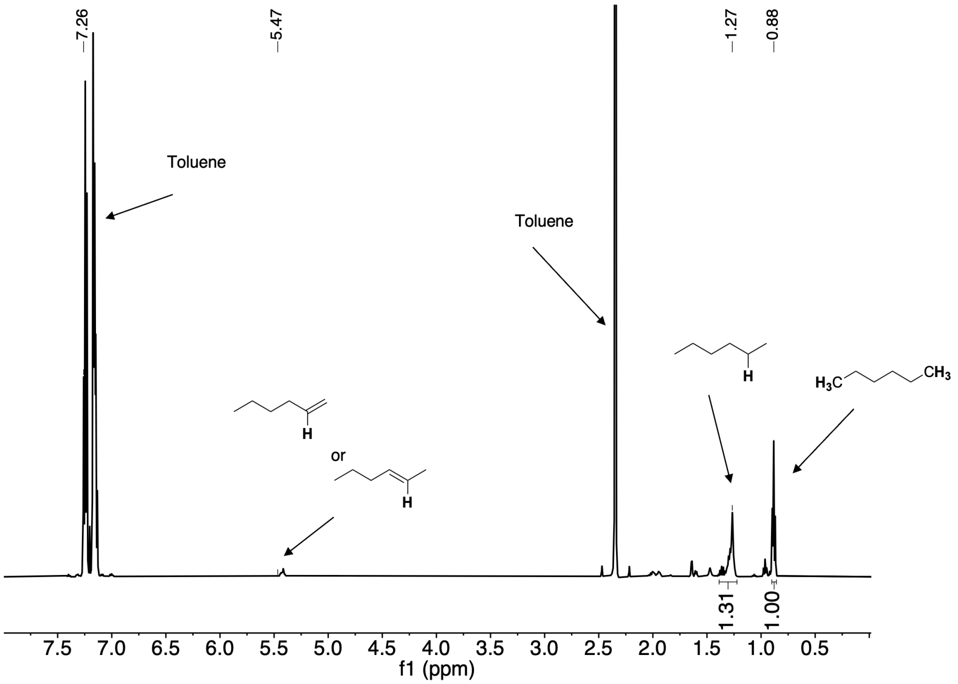


Fig. S79 ^{1}H NMR spectrum in $CDCl_3$ (25 °C) of 2-Chlorohexane hydrodechlorination products with $NiCl_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 96 hours in Toluene at 120 °C.

8. Thermogravimetric Analysis (TGA)

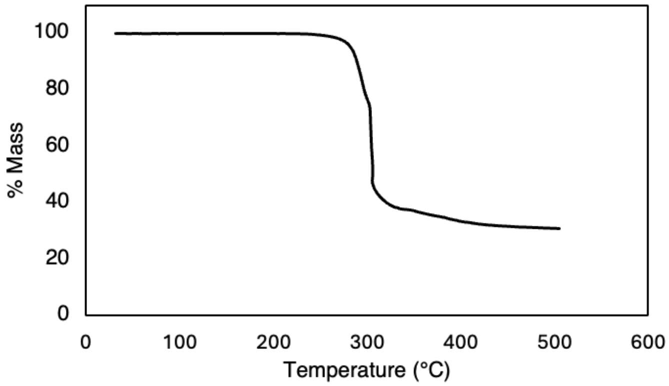


Fig. S80 TGA curve of low molecular weight PVC (CAS: 9002-86-2, Product #: 81388, Sigma Aldrich).

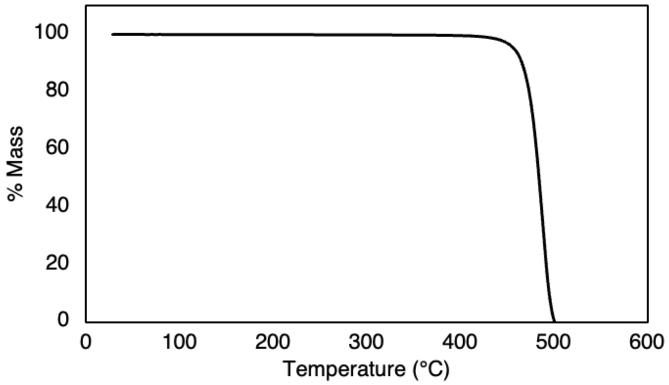


Fig. S81 FT-IR spectrum of HDPE pellets (CAS: 9002-88-4, Sigma Aldrich).

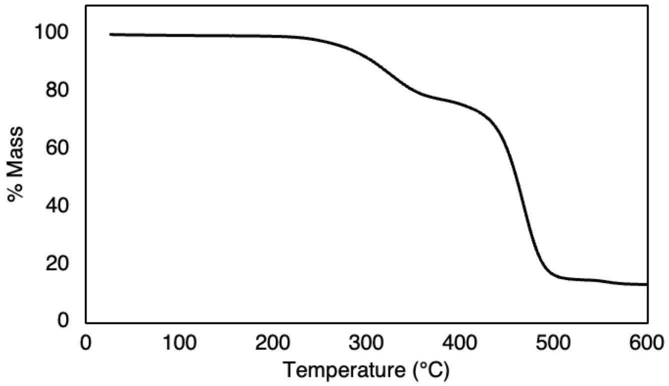


Fig. S82 TGA curve Table S1, Entry 1 for PVC hydrodechlorination product with $NiCl_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

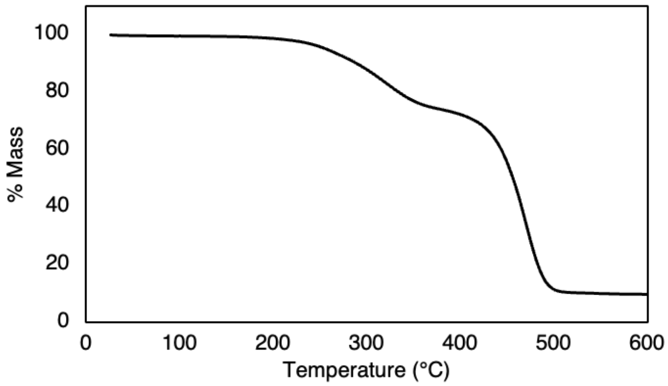


Fig. S83 TGA curve Table S1, Entry 2 for PVC hydrodechlorination product with $NiCl_2$ (2.5 mol%), DCyPE (10 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

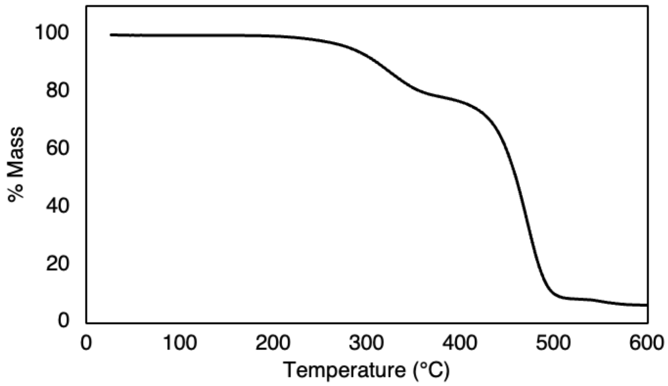


Fig. S84 TGA curve Table S1, Entry 2 for PVC hydrodechlorination product with $Ni(COD)_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

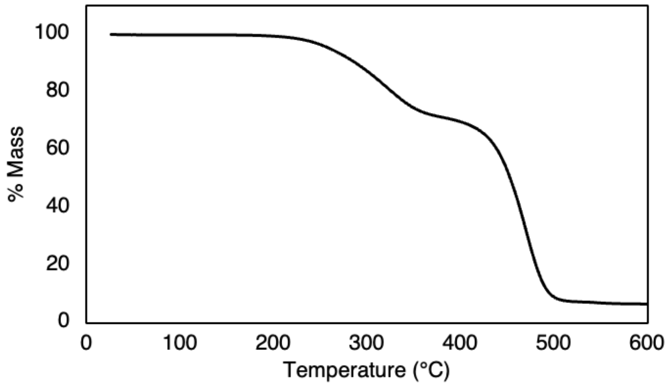


Fig. S85 TGA curve Table S1, Entry 4 for PVC hydrodechlorination product with $Ni(acac)_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

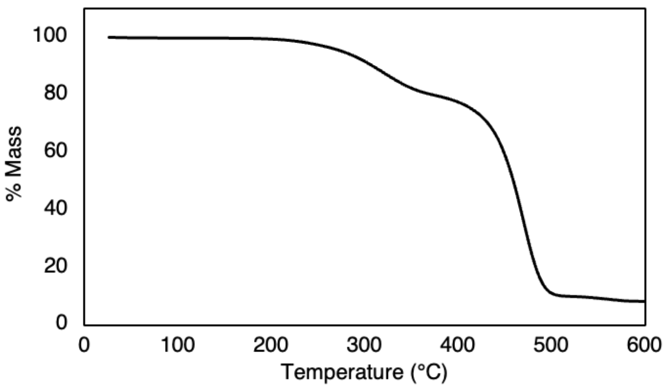


Fig. S86 TGA curve Table S1, Entry 5 for PVC hydrodechlorination product with $NiBr_2$.glyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

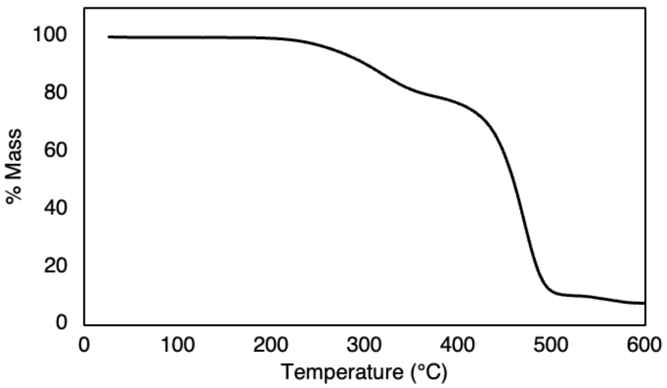


Fig. S87 TGA curve Table S1, Entry 6 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

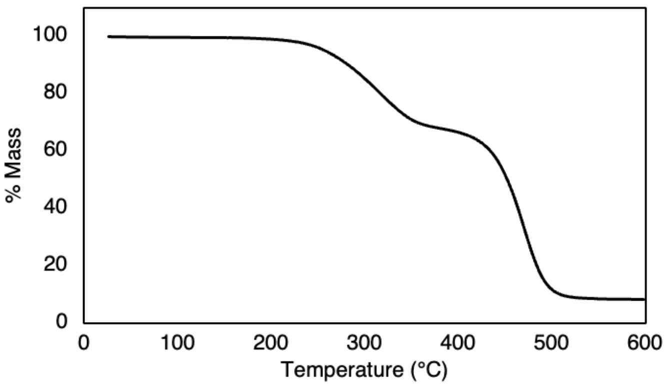


Fig. S88 TGA curve Table S2, Entry 6 for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DCyPE (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

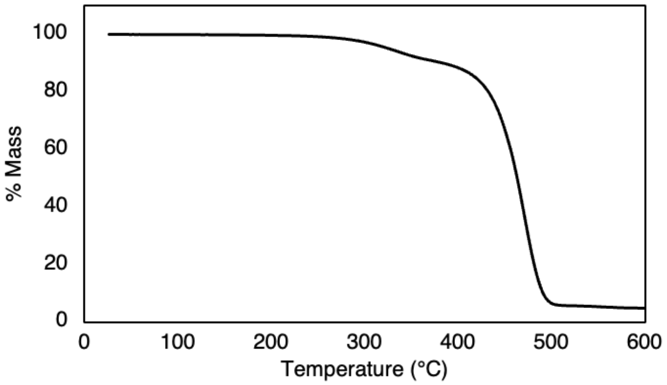


Fig. S89 TGA curve Table S3, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in THF at 110 °C.

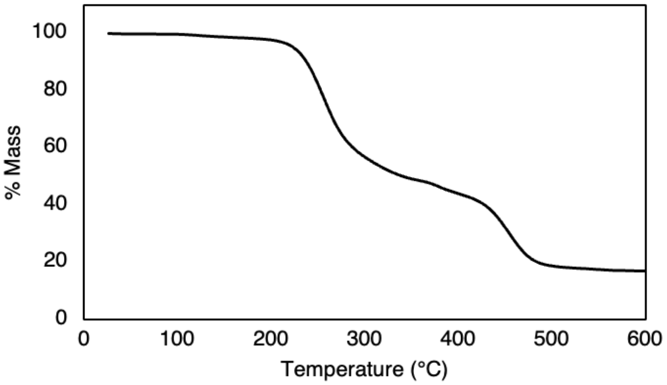


Fig. S90 TGA curve Table S3, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Cylclo pentyl methyl ether at 110 °C.

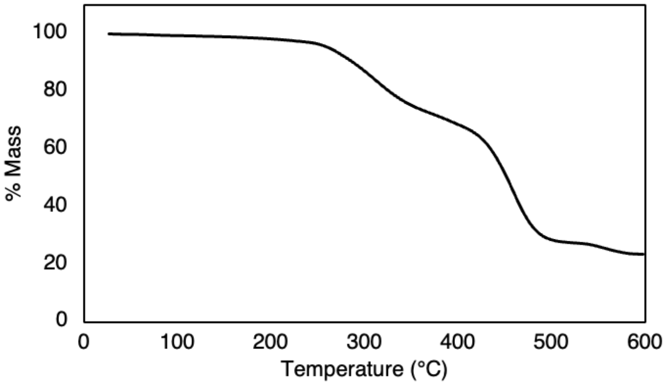


Fig. S91 TGA curve Table S3, Entry 5 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Cyclohexanone at 150 °C.

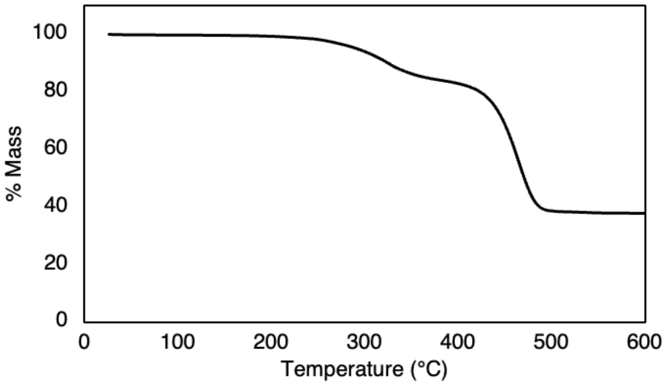


Fig. S92 TGA curve Table S3, Entry 7 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in 1,4-dioxane at 120 °C.

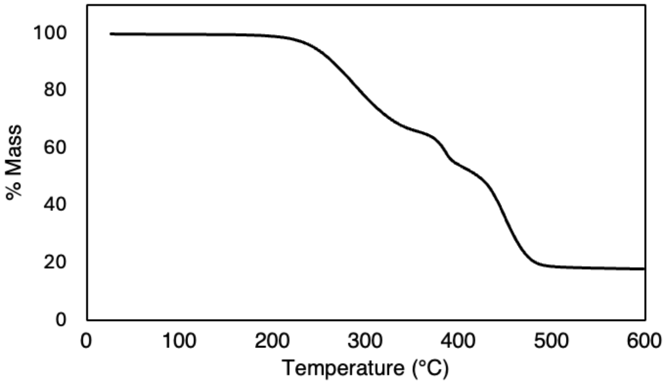


Fig. S93 TGA curve Table S4, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 4 hours in Toluene at 120 °C.

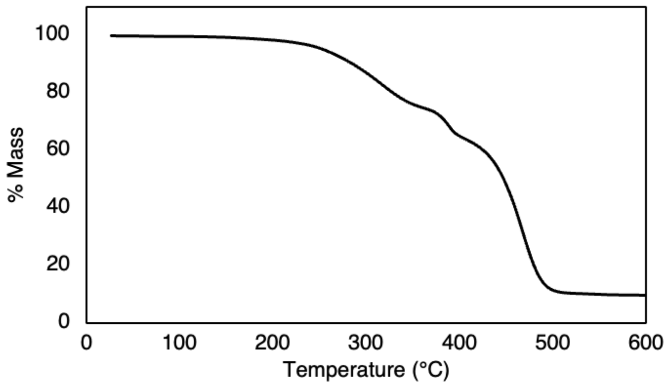


Fig. S94 TGA curve Table S4, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 8 hours in Toluene at 120 °C.

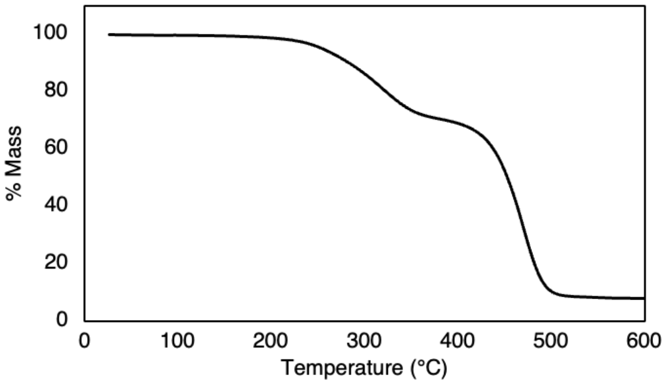


Fig. S95 TGA curve Table S4, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 12 hours in Toluene at 120 °C.

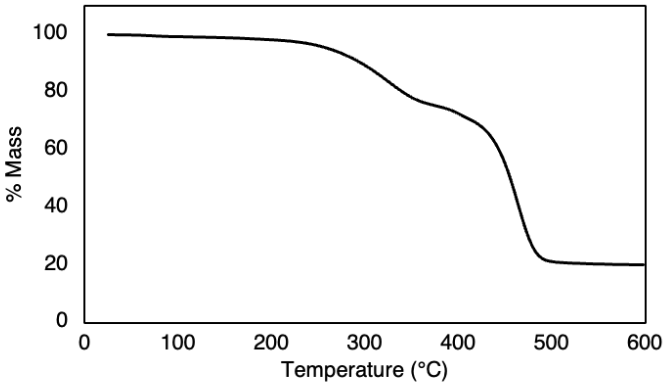


Fig. S96 TGA curve Table S4, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 16 hours in Toluene at 120 °C.

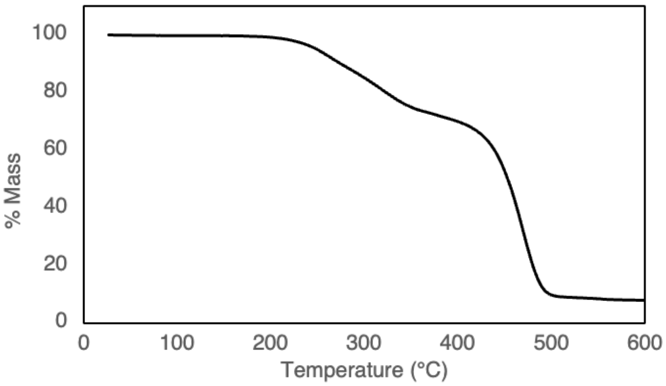


Fig. S97 TGA curve Table S4, Entry 5 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 24 hours in Toluene at 120 °C.

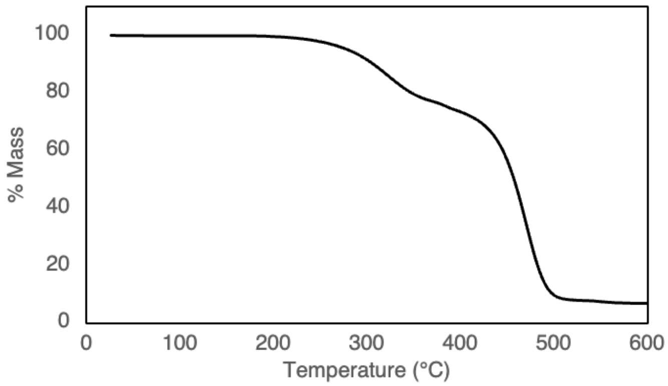


Fig. S98 TGA curve Table S4, Entry 6 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 1 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

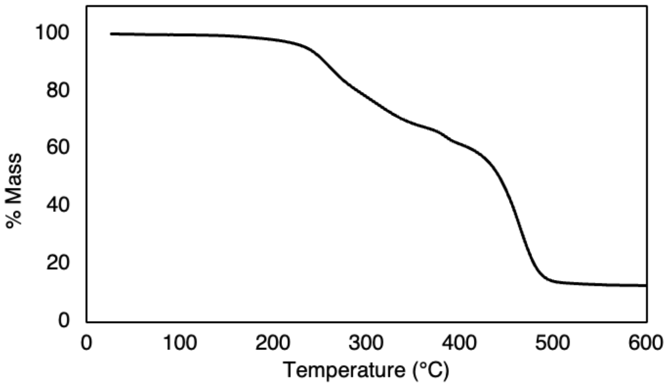


Fig. S99 TGA curve Table S5, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 100 °C.

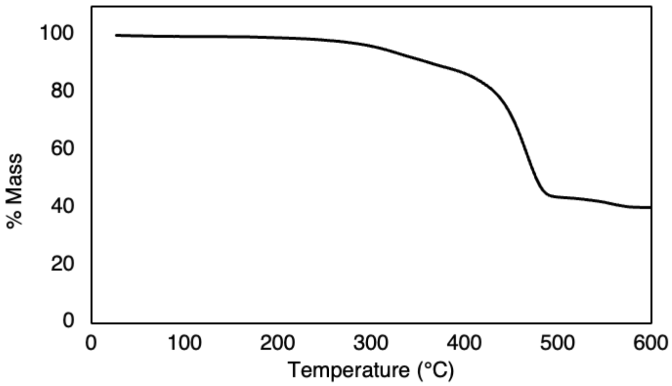


Fig. S100 TGA curve Table S5, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 150 °C.

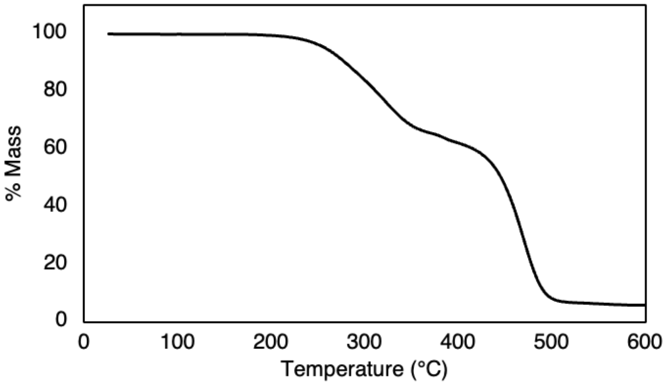


Fig. S101 TGA curve Table S6, Entry 1 for PVC hydrodechlorination product with Ni(COD)$_2$ (1 mol%), DCyPE (2 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

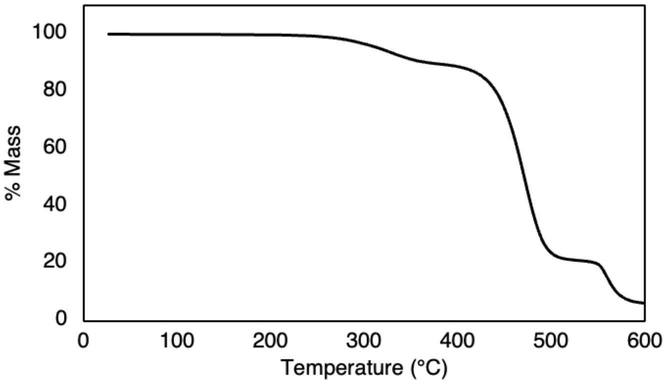


Fig. S102 TGA curve Table S6, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (2.5 mol%), DCyPE (2.5 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

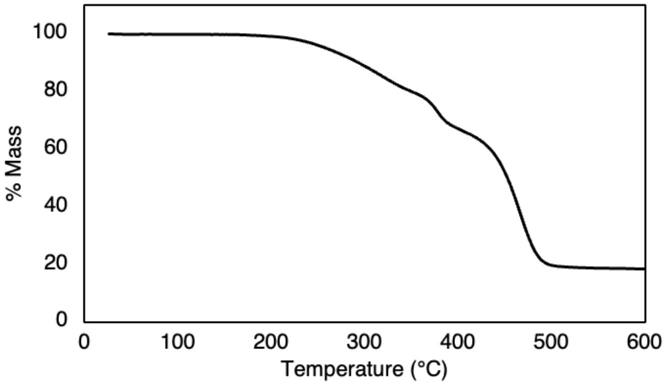


Fig. S103 TGA curve Table S6, Entry 4 for PVC hydrodechlorination product with Ni(COD)$_2$ (5 mol%), DCyPE (10 mol%), and 2 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

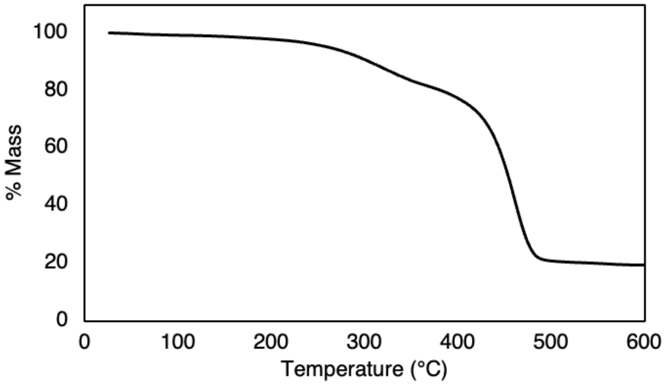


Fig. S104 TGA curve Table S7, Entry 2 for PVC hydrodechlorination product with Ni(COD)$_2$ (5 mol%), DCyPE (10 mol%), and 2 equiv. KHCO$_2$ for 48 hours in THF at 110 °C.

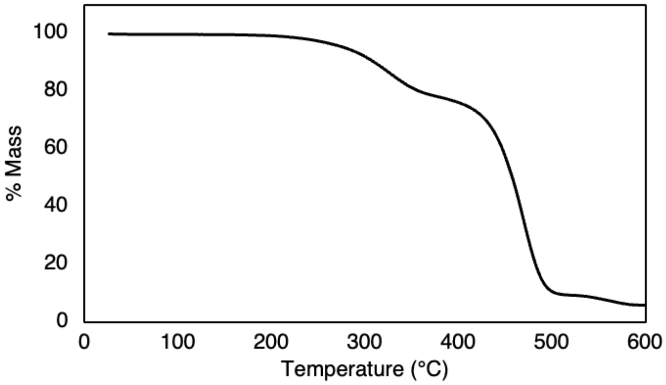


Fig. S105 TGA curve Table S8, Entry 3 for PVC hydrodechlorination product with Ni(COD)$_2$ (5 mol%), DCyPE (10 mol%), and 3 equiv. NaHCO$_2$ for 48 hours in Toluene at 120 °C.

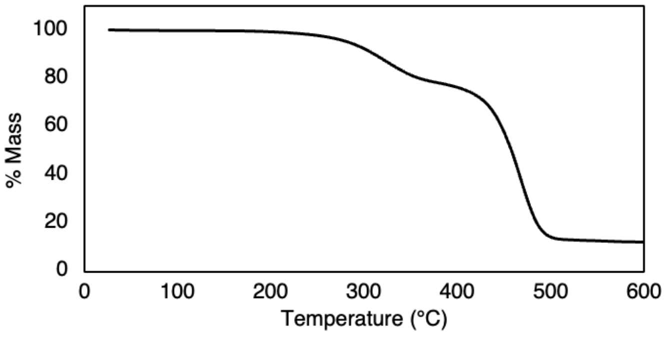


Fig. S106 TGA curve Table S9, Entry 1 for PVC hydrodechlorination product with NiBr$_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. NaHCO$_2$ for 24 hours in THF at 110 °C.

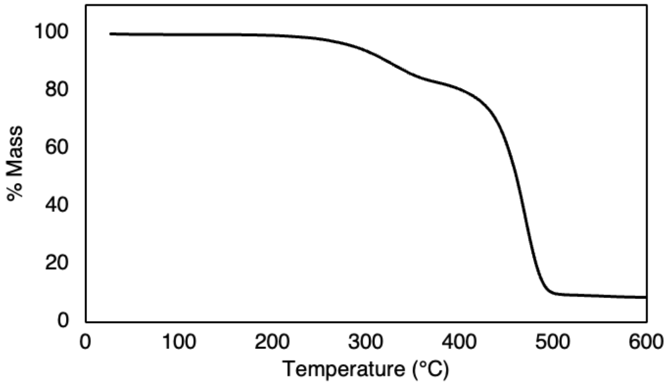


Fig. S107 TGA curve Table S9, Entry 2 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

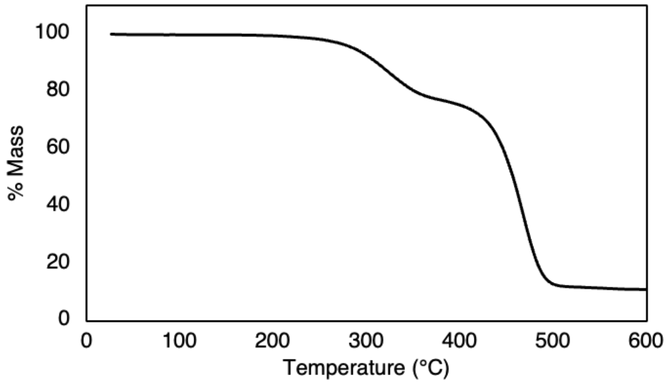


Fig. S108 TGA curve Table S9, Entry 3 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (2 mol%), and 2 equiv. $NaHCO_2$ for 24 hours in THF at 110 °C.

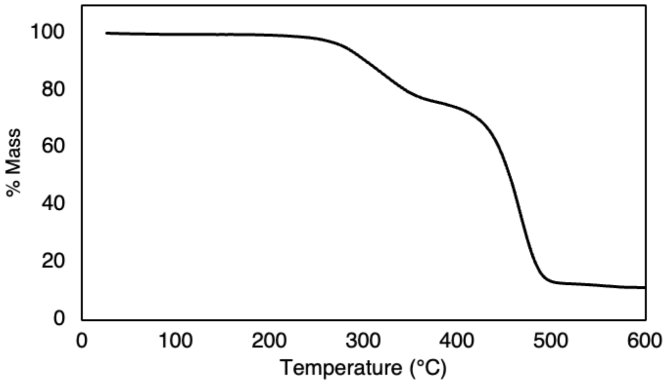


Fig. S109 TGA curve Table S9, Entry 4 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (2 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

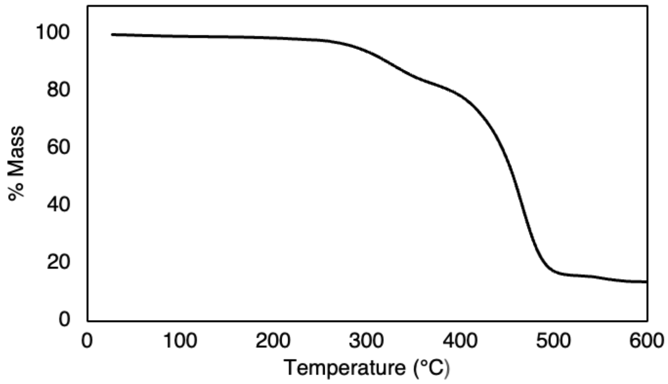


Fig. S110 TGA curve Table S9, Entry 5 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $KHCO_2$ for 24 hours in THF at 110 °C.

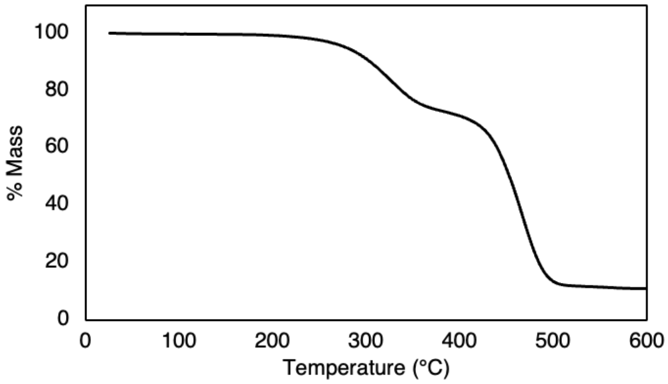


Fig. S111 TGA curve Table S9, Entry 6 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (2 mol%), and 2 equiv. $KHCO_2$ for 48 hours in THF at 110 °C.

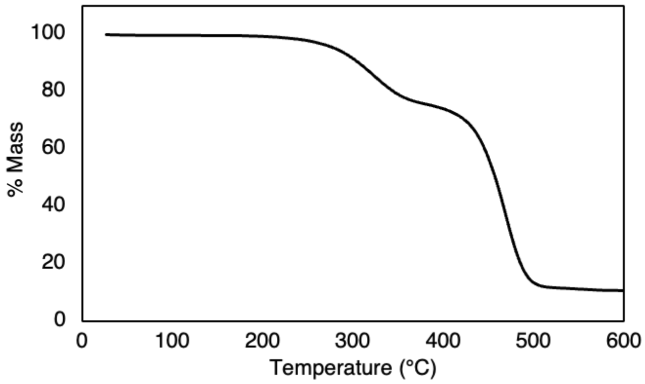


Fig. S112 TGA curve Table S9, Entry 7 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (4 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

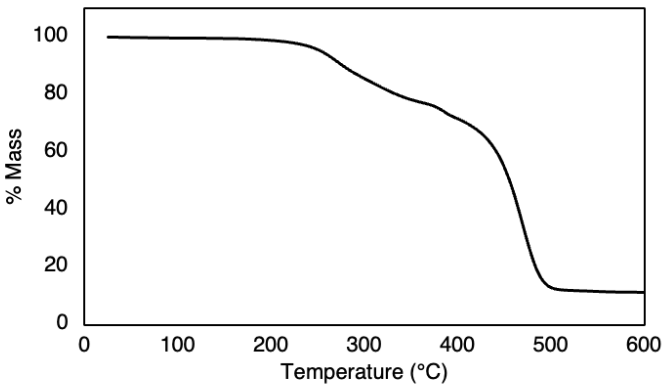


Fig. S113 TGA curve Table S9, Entry 8 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 24 hours in Toluene at 120 °C.

9. DSC

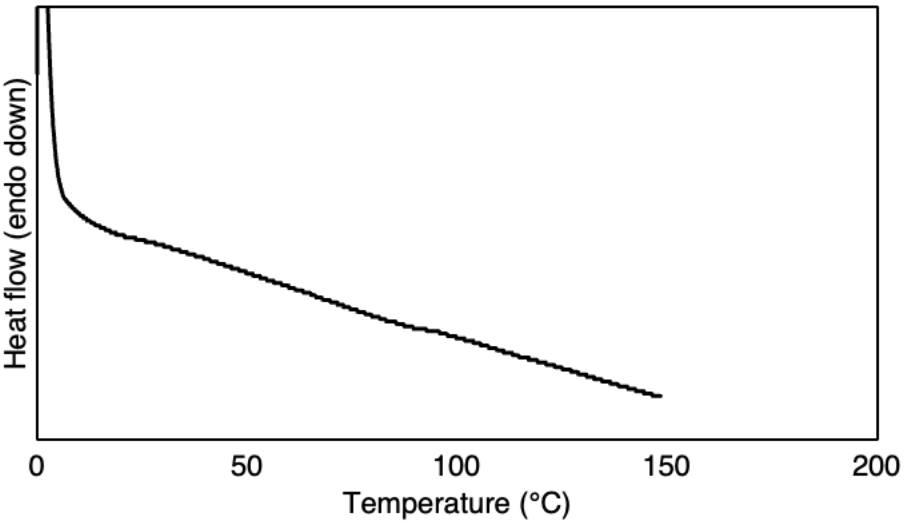


Fig. S114 DSC (2nd heating curve) Table S1, Entry 1 for PVC hydrodechlorination product with $NiCl_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

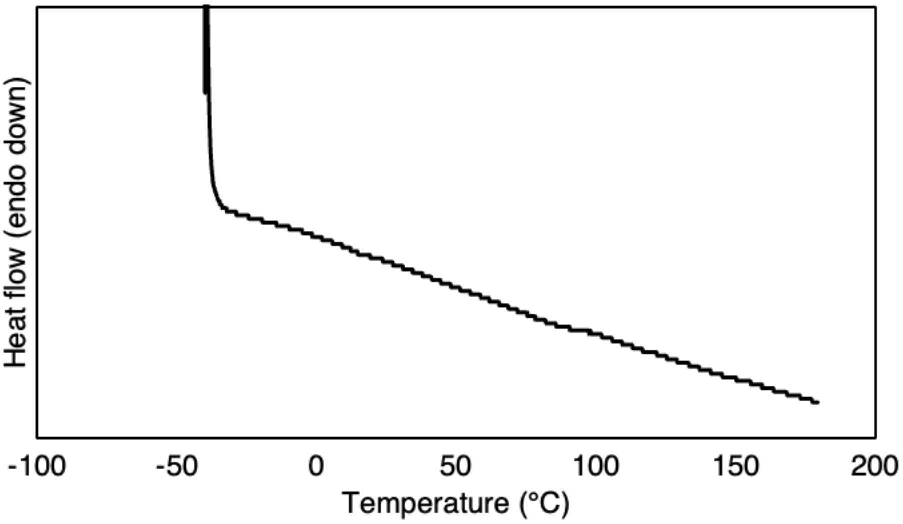


Fig. S115 DSC (2nd heating curve) Table S1, Entry 3 for PVC hydrodechlorination product with Ni(COD_2 (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

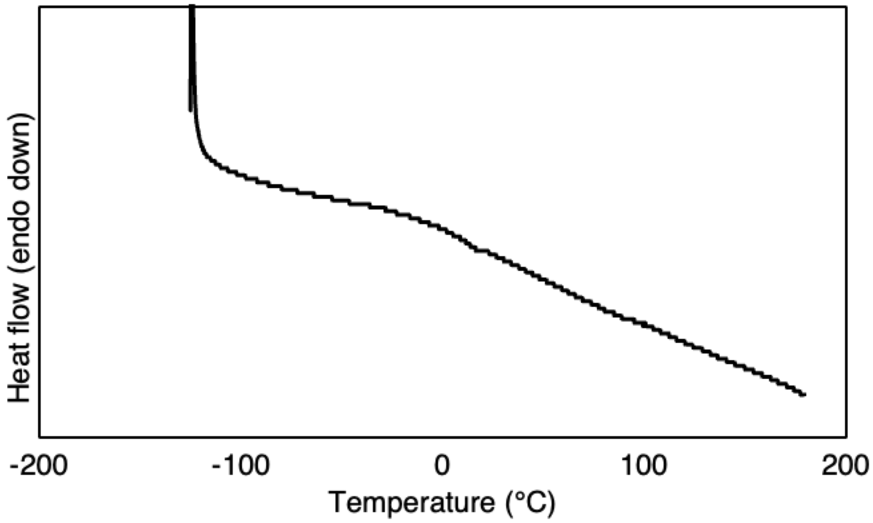


Fig. S116 DSC (2nd heating curve) Table S1, Entry 5 for PVC hydrodechlorination product with $NiBr_2$. glyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

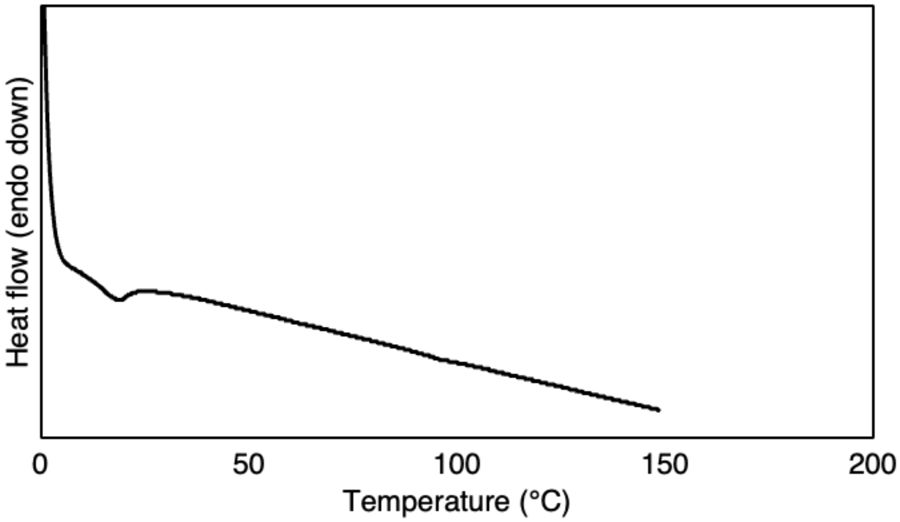


Fig. S117 DSC (2nd heating curve) Table S6, Entry 3 for PVC hydrodechlorination product with $Ni(COD)_2$ (2.5 mol%), DCyPE (2.5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in Toluene at 120 °C.

10. Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

Table S10 EDX data of sample Table S9, Entry 2 for PVC hydrodechlorination product with $NiBr_2$. diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

Sample #	Spot1	Spot 2	Spot 3	Spot 4	Spot 5	Average
C	90.2	91.3	92.4	93.5	91.2	91.7
Cl	4.2	4.5	5.3	2.9	6.0	4.6
O	5.6	4.1	2.3	3.6	2.7	3.7

Table S11 EDX data of sample Table S9, Entry 6 for PVC hydrodechlorination product with $NiBr_2$. diglyme (1 mol%), DCyPE (2 mol%), and 2 equiv. $KHCO_2$ for 48 hours in THF at 110 °C.

Sample #	Spot 1	Spot 2	Spot 3	Spot 4	Average
C	87.3	89.2	87.5	86.4	87.6
Cl	5.5	5.0	4.4	5.3	5.05
O	7.1	5.7	8.1	8.4	7.32

Table S12 EDX data of Pure PVC

Sample #	Spot 1	Spot 2	Spot 3	Average
C	83.6	76.0	78.5	79.36
Cl	16.4	24.0	21.5	20.6

Table S13 % Dechlorination based on EDX data

Sample	% Cl loss[a]
Table S9, Entry 2	78
Table S9, Entry 6	75

[a] %Cl loss from EDX calculated using Equation 4.

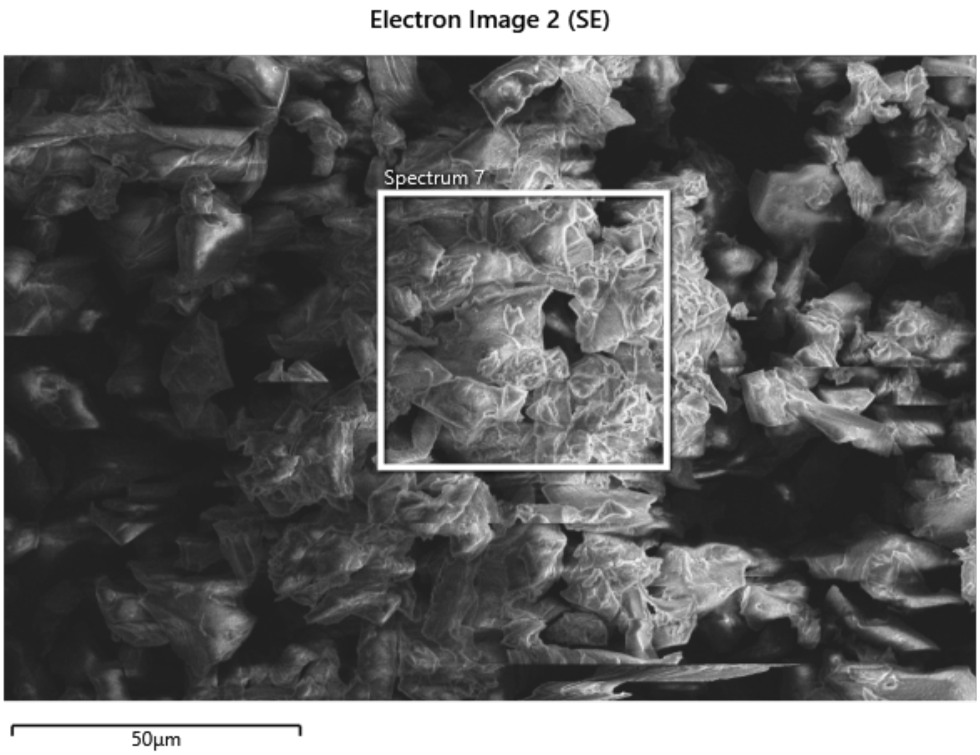


Fig. S118 SEM image of the polymer product from the optimized reaction Table S9, Entry 2 at spot 1

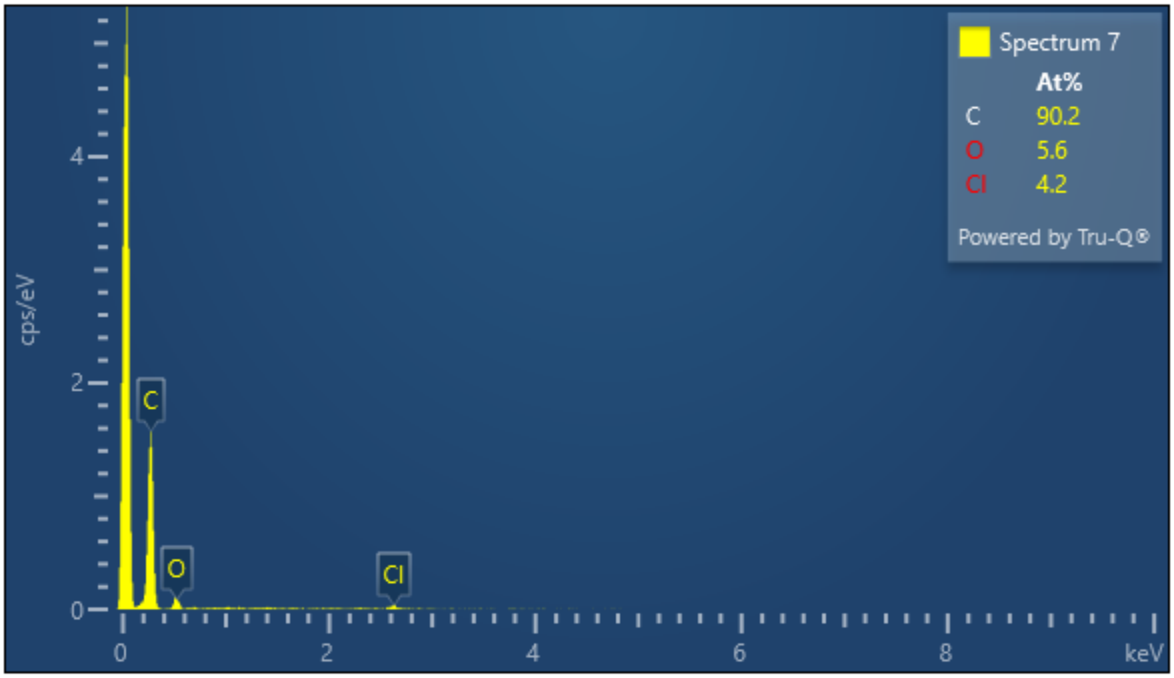


Fig. S119 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 2 at spot 1

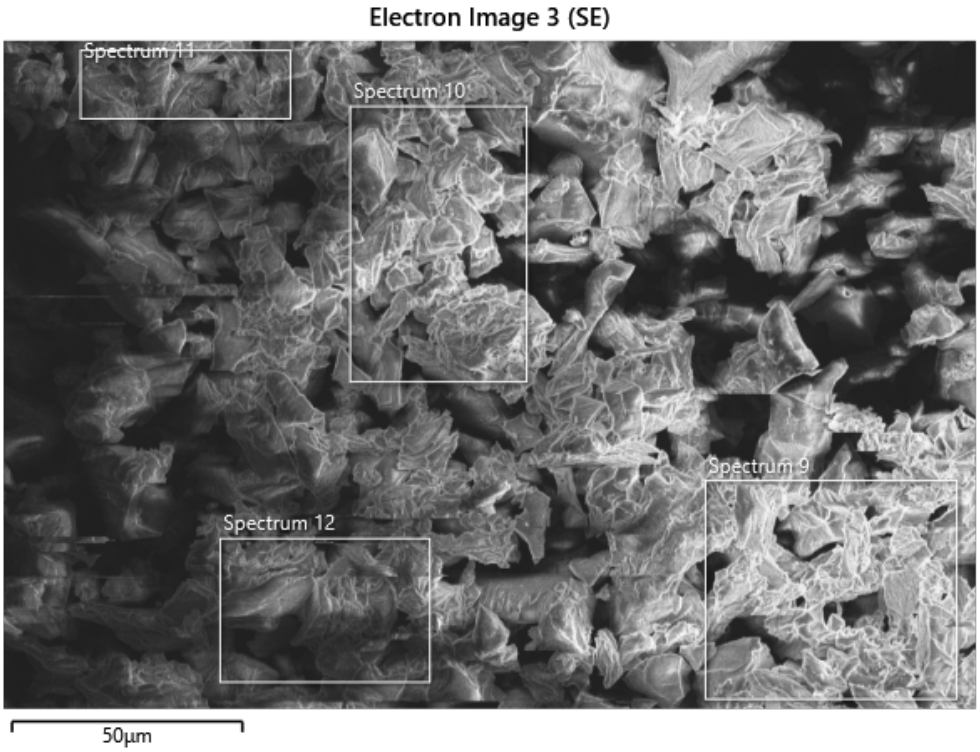


Fig. S120 SEM image of the polymer product from the optimized reaction Table S9, Entry 2 at spot 2, 3, 4, 5

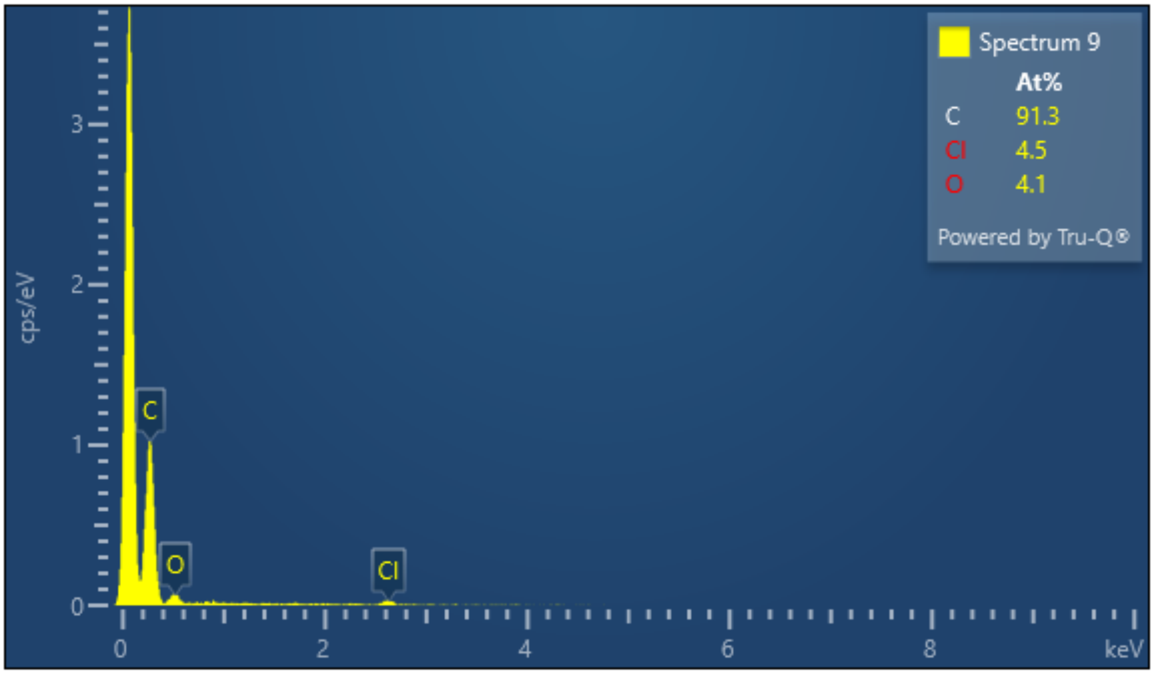


Fig. S121 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 2 at spot 2

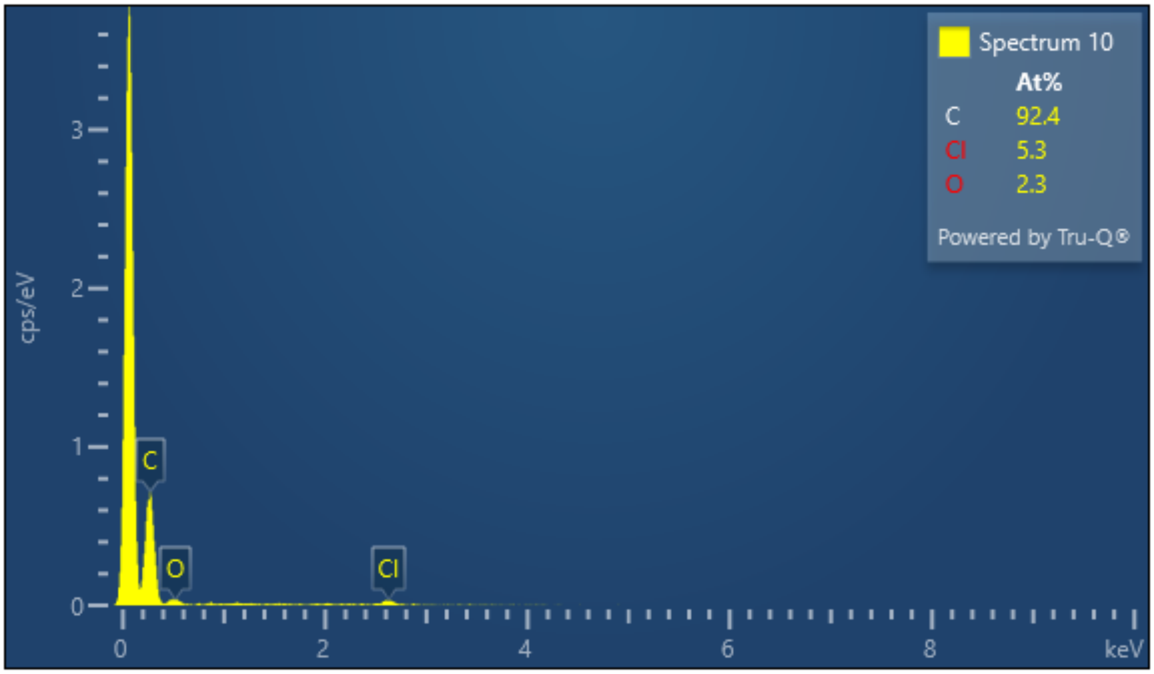


Fig. S122 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 2 at spot 3

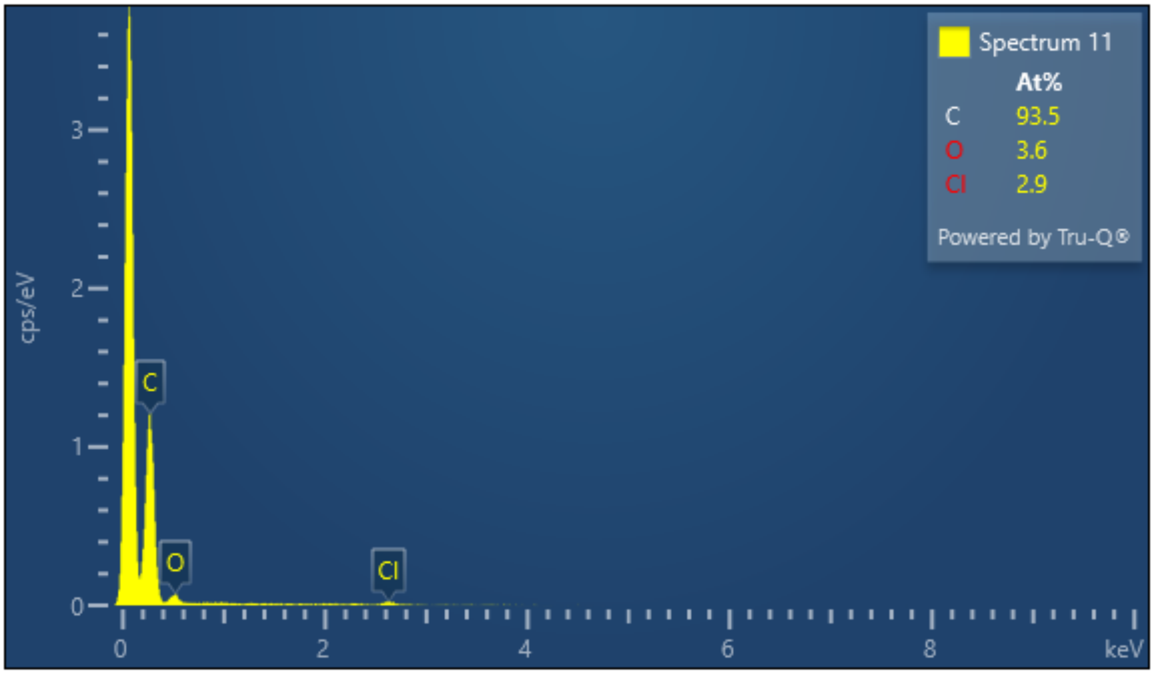


Fig. S123 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 2 at spot 4

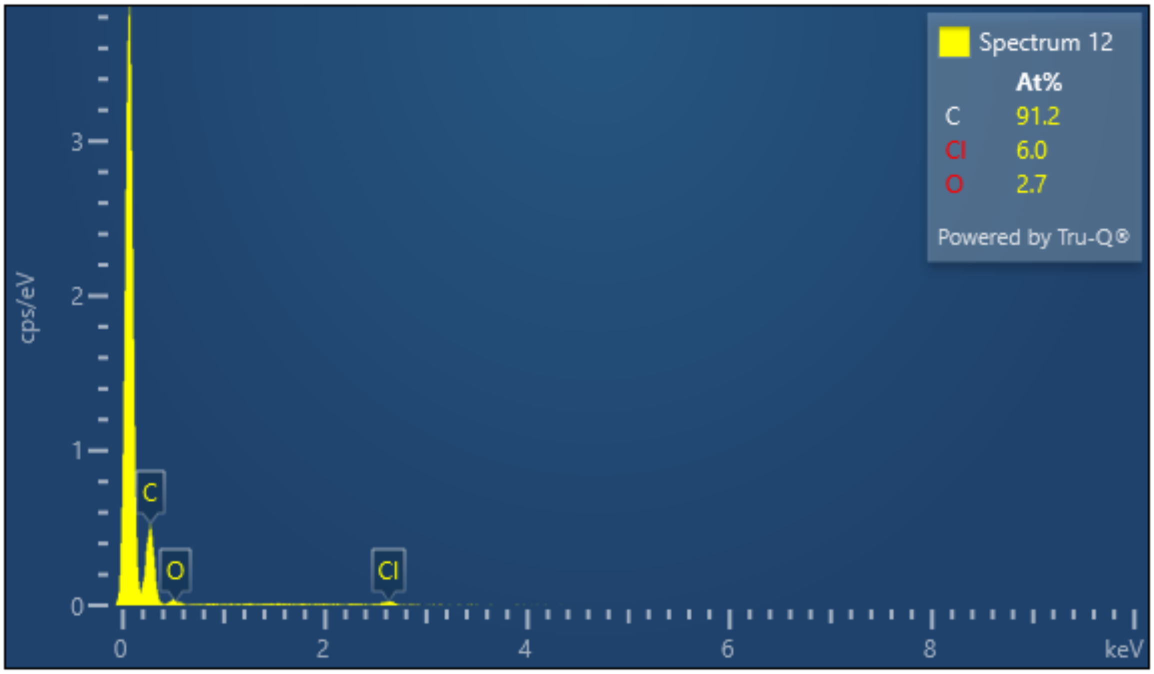


Fig. S124 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 2 at spot 5

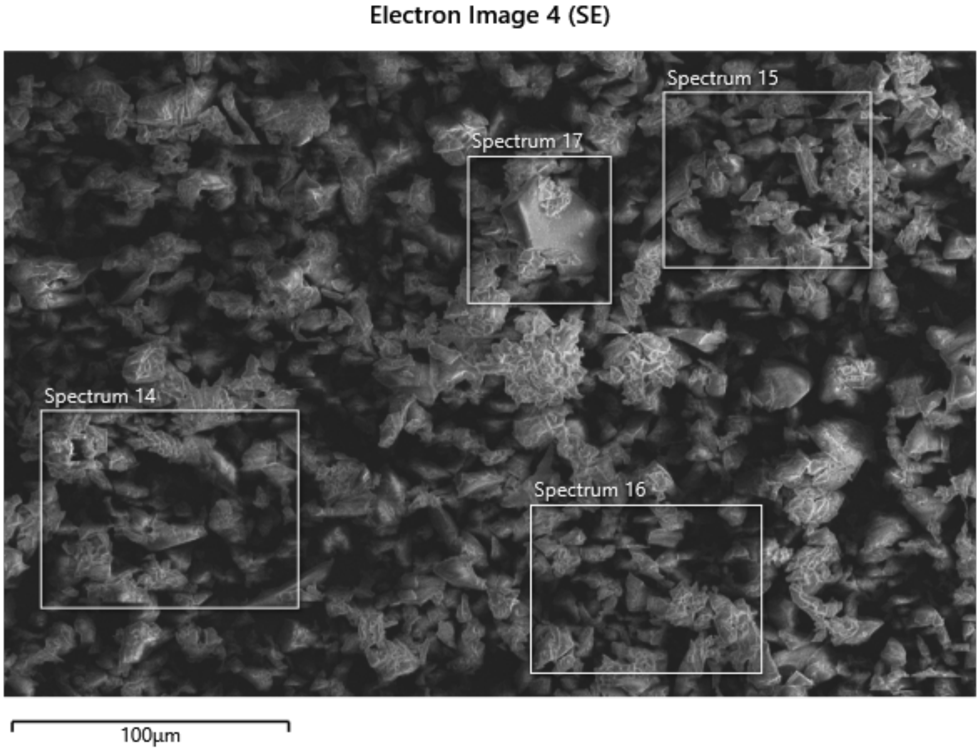


Fig. S125 SEM image of the polymer product from the optimized reaction Table S9, Entry 6 at spot 1, 2, 3, 4

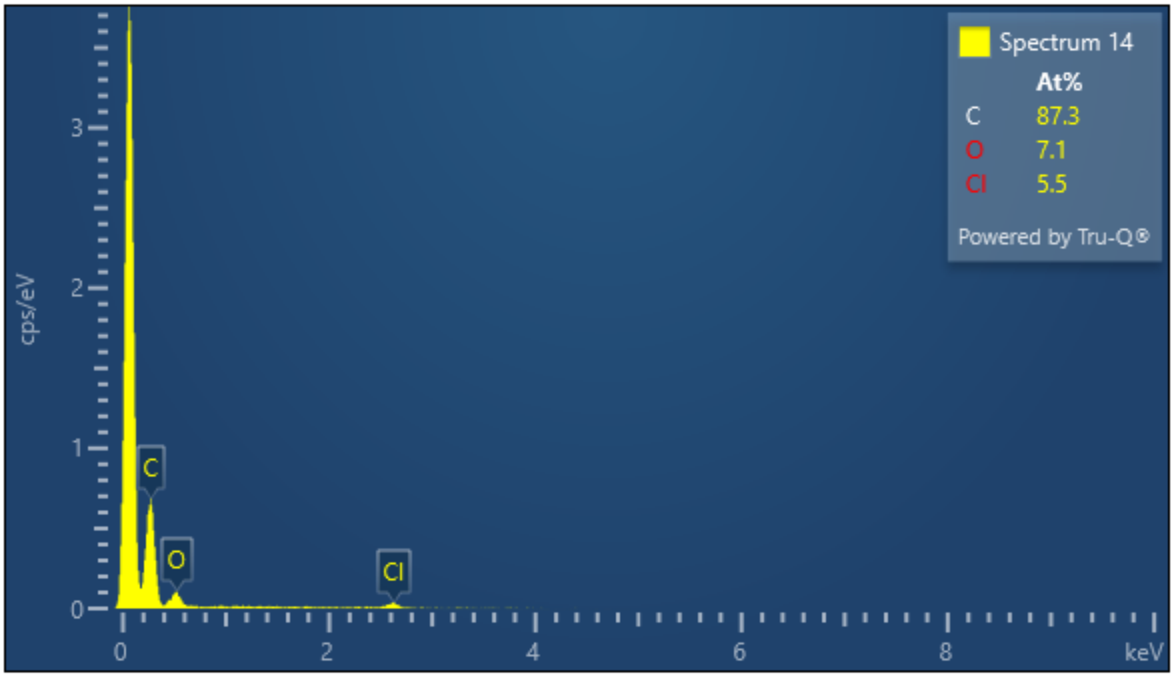


Fig. S126 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 6 at spot 1

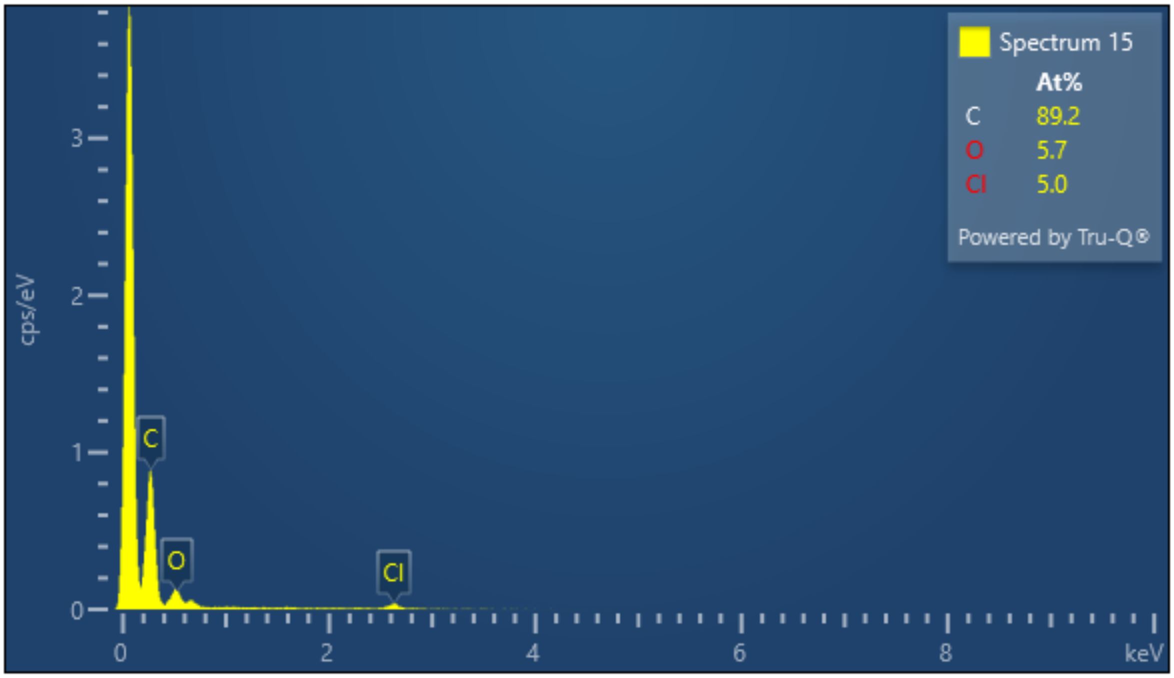


Fig. S127 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 6 at spot 2

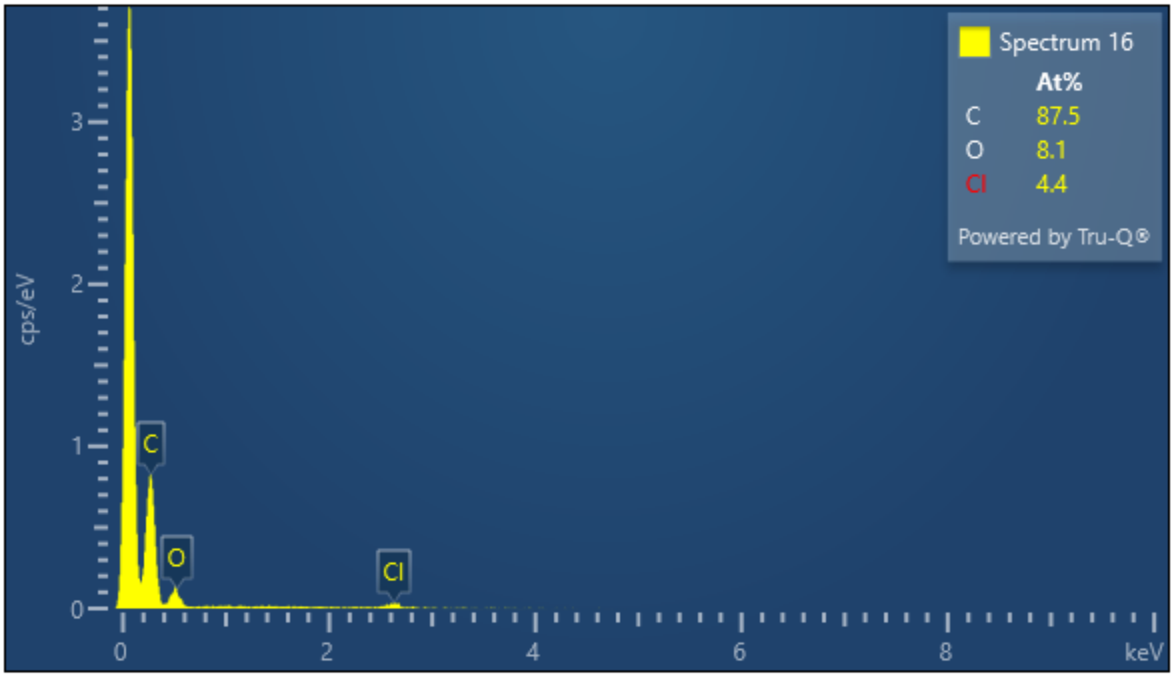


Fig. S128 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 6 at spot 3

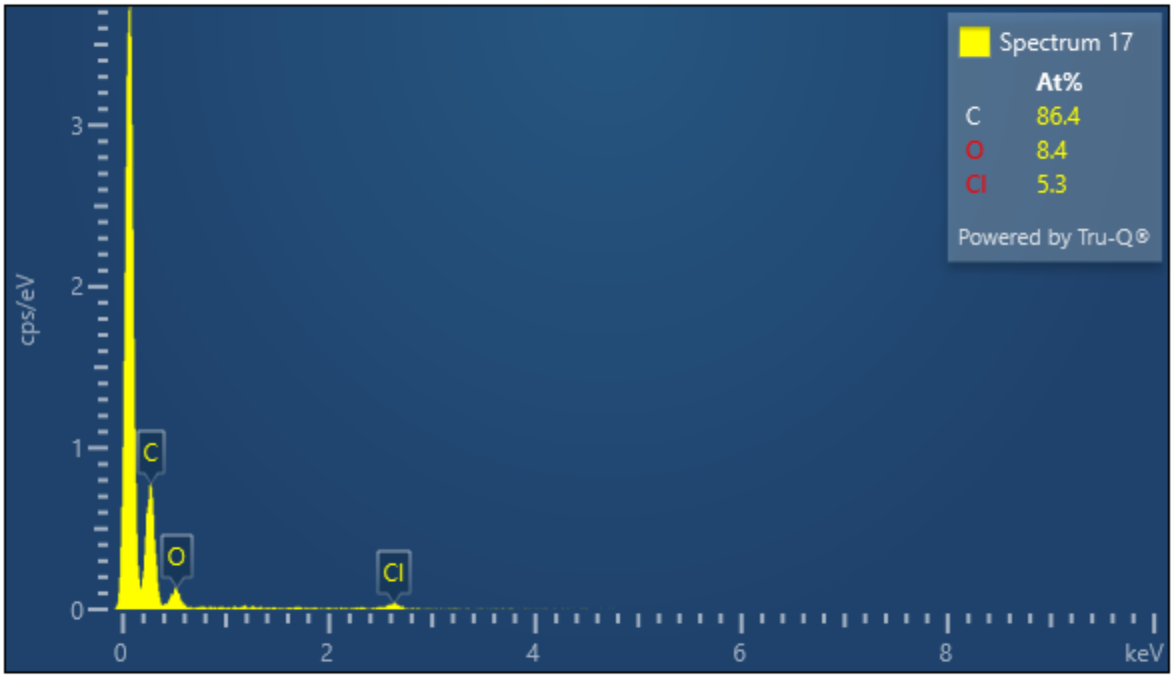


Fig. S129 EDX spectrum of the polymer product from the optimized reaction Table S9, Entry 6 at spot 1

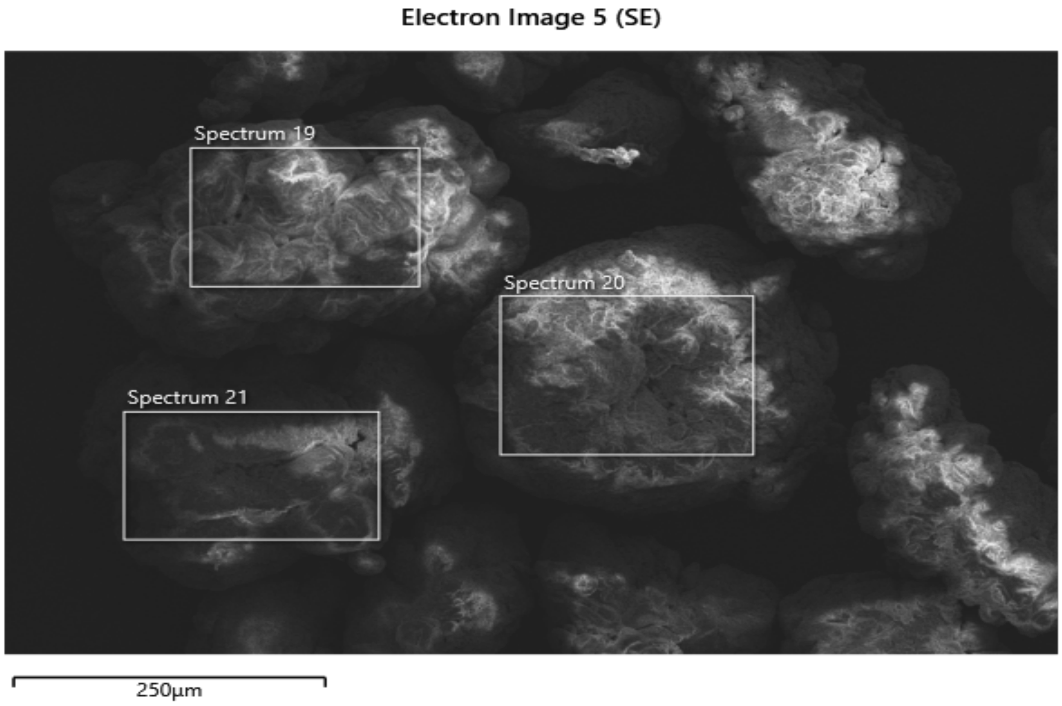


Fig. S130 SEM image of the pure PVC at spot 1, 2, 3

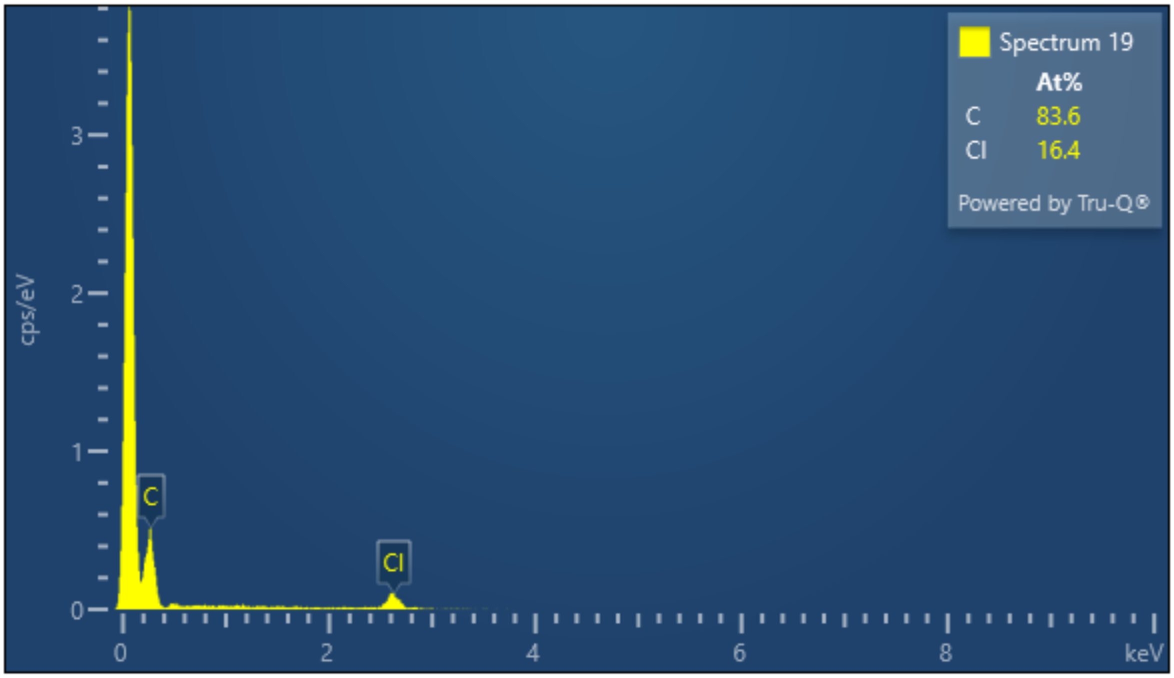


Fig. S131 EDX spectrum of the pure PVC at spot 1

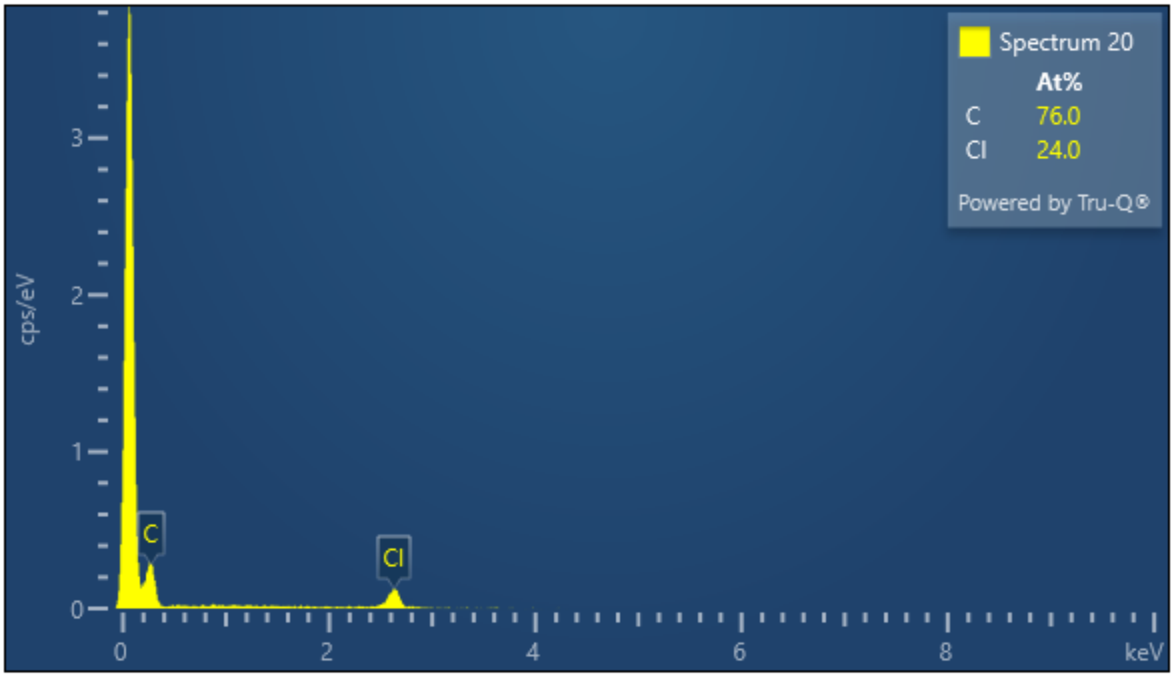


Fig. S132 EDX spectrum of the pure PVC at spot 2

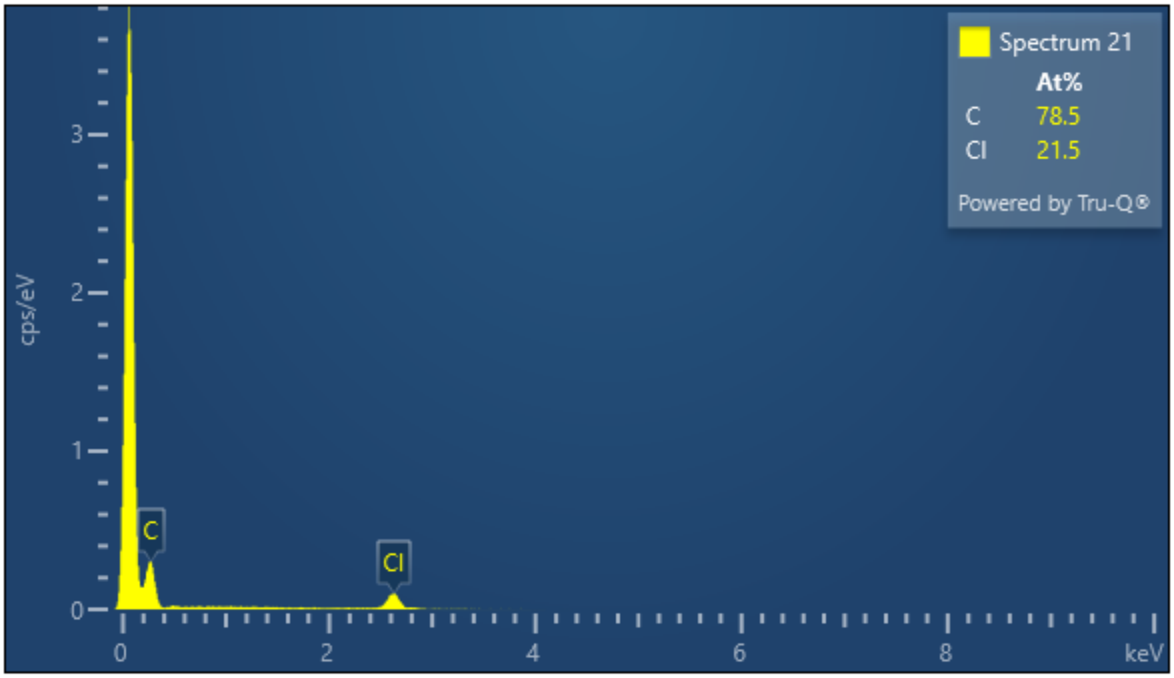


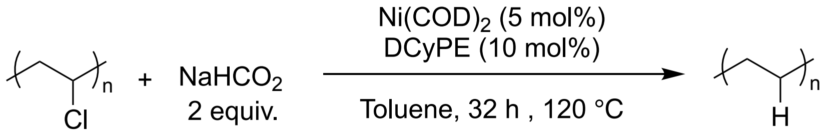
Fig. S133 EDX spectrum of the pure PVC at spot 3

11. Mechanistic Investigation

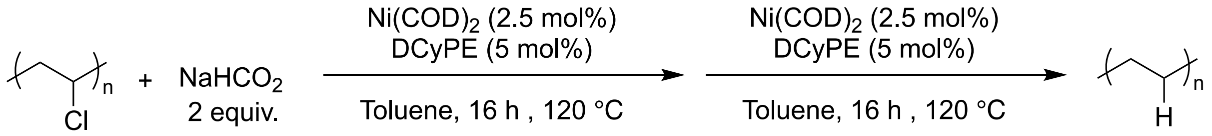
A standard reaction with Ni(COD)$_2$ (5 mol%), DCyPE (10 mol%), 2 equivalent NaHCO$_2$ was conducted for 32 hours at 120 °C (Condition I). Another reaction was run with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), 2 equivalent NaHCO$_2$ for 16 hours, whereupon additional 2.5 mol% Ni(COD)$_2$, 5 mol% DCyPE were added to the mixture, and the reaction run for a further 16 hours (Condition II). One more reaction was conducted with Ni(COD)$_2$ (2.5 mol%), DCyPE (5 mol%), 2 equivalent NaHCO$_2$ for 16 hours,whereupon only additional 2.5 mol% Ni(COD)$_2$, was added to the mixture and for 16 hours,whereupon additional 2.5 mol% Ni(COD)$_2$, 5 mol% DCyPE were added to the mixture (Condition III).

Table S14 Effect of addition of Ni(COD)$_2$ and DCyPE in different equivalent at different time on the PVC hydrodechlorination

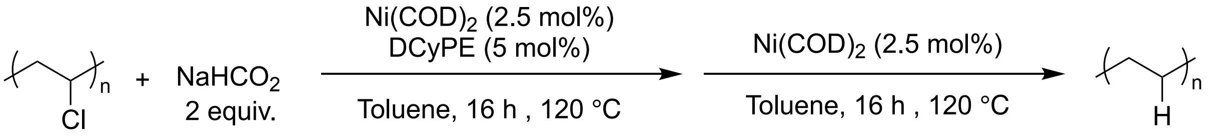
Condition I



Condition II



Condition III



Entry	Condition	% dechlorination[a]
1	Condition I	72
2	Condition II	75
3	Condition III	76

[a] % dechlorination was calculated from FT-IR spectra using equation 1

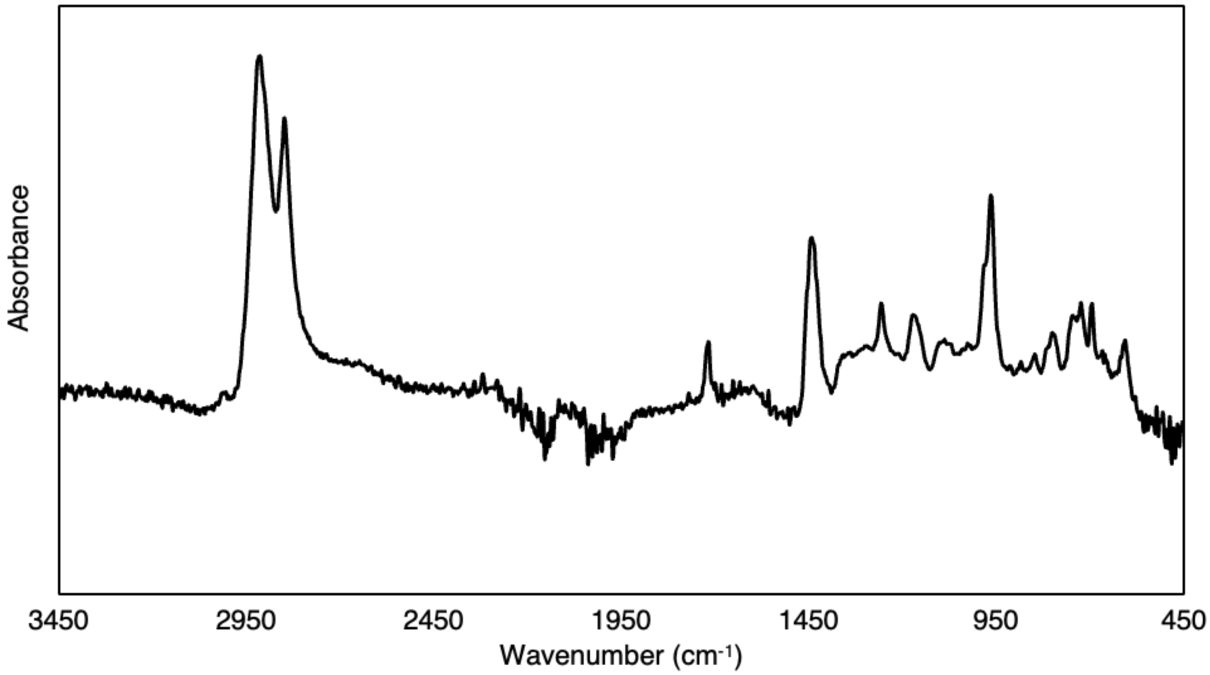


Fig. S134 FT-IR Table S10, Entry 1 for PVC hydrodechlorination product from condition I

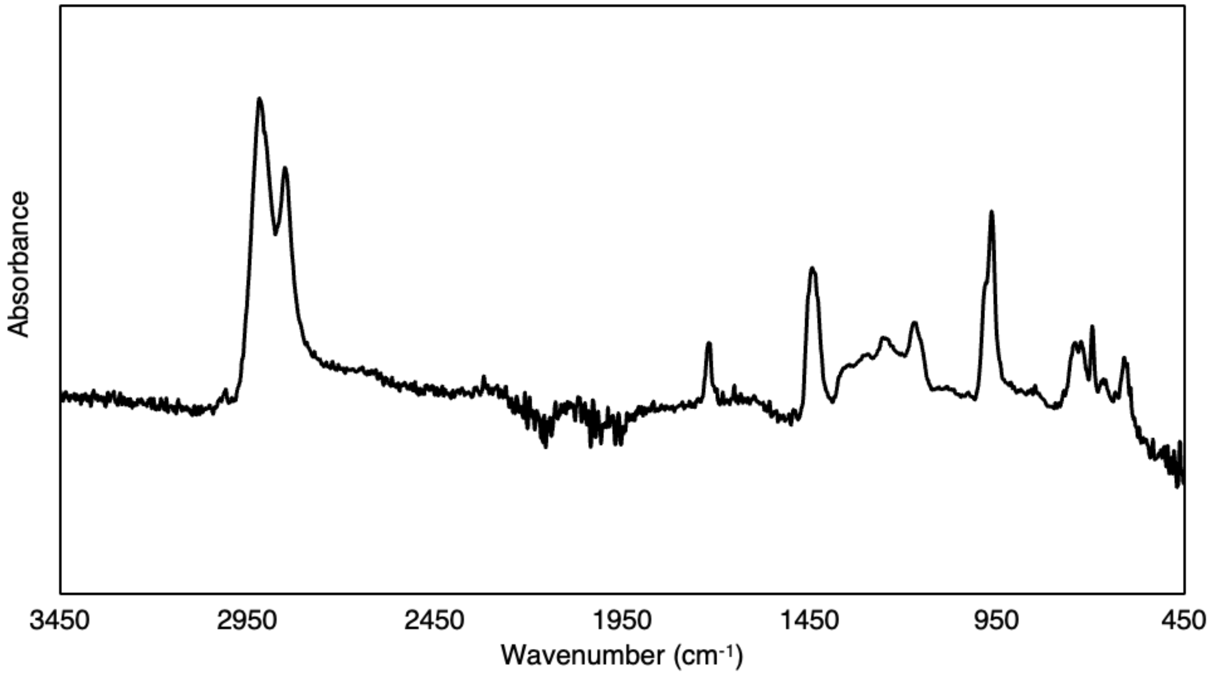


Fig. S135 FT-IR Table S10, Entry 2 for PVC hydrodechlorination product from condition II

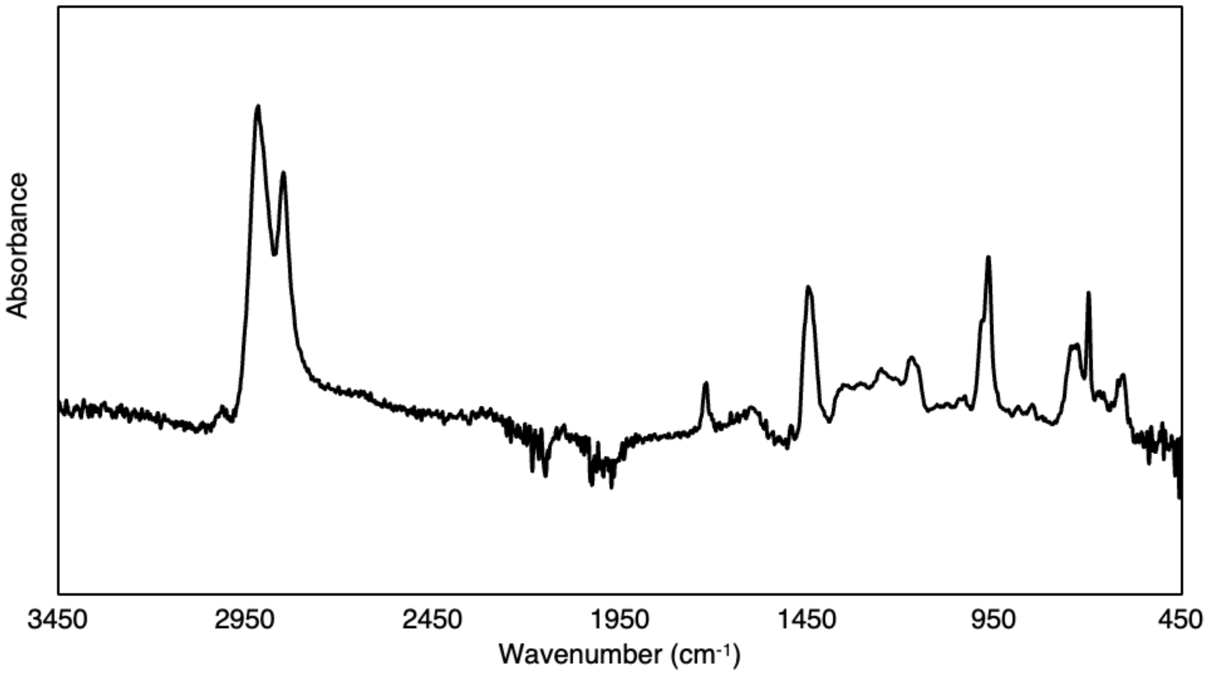


Fig. S136 FT-IR Table S10, Entry 3 for PVC hydrodechlorination product from condition

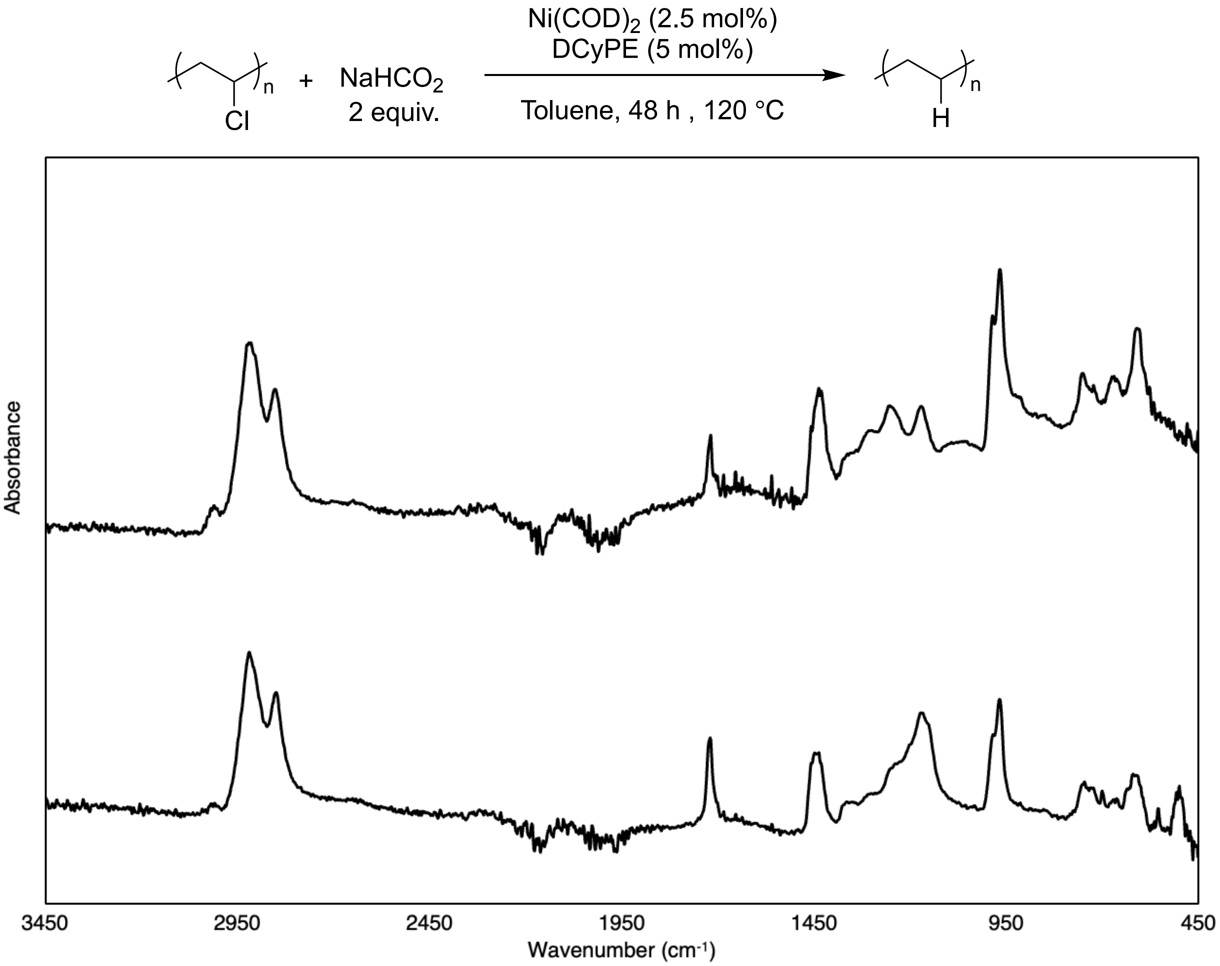


Fig. S137 Comparison of FT-IR spectra of products from Table S1, Entry 3 **(bottom)** and a reaction conducted under nitrogen pressure with a reflux condenser with same loading of all chemicals **(top)**

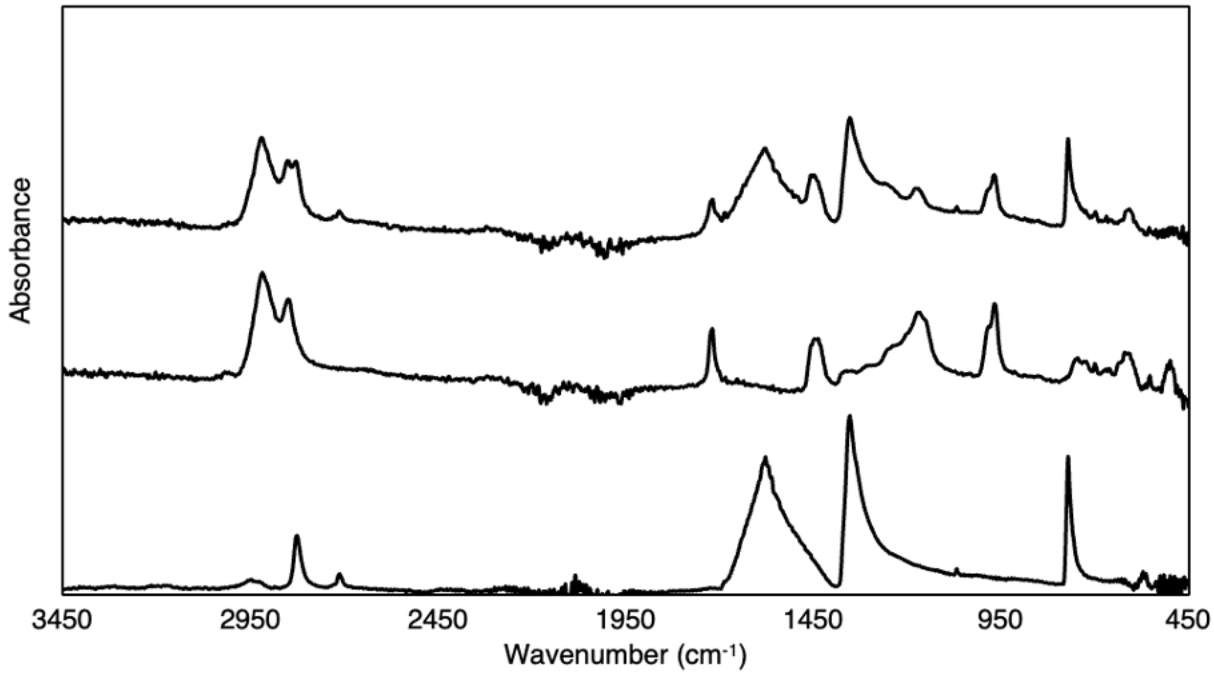


Fig. S138 Comparison of FT-IR spectra of Pure NaCOOH **(bottom)**, products from Table S1, Entry 3 **(middle)** externally added sodium formate to the product of Table S1, Entry 3 **(top)**

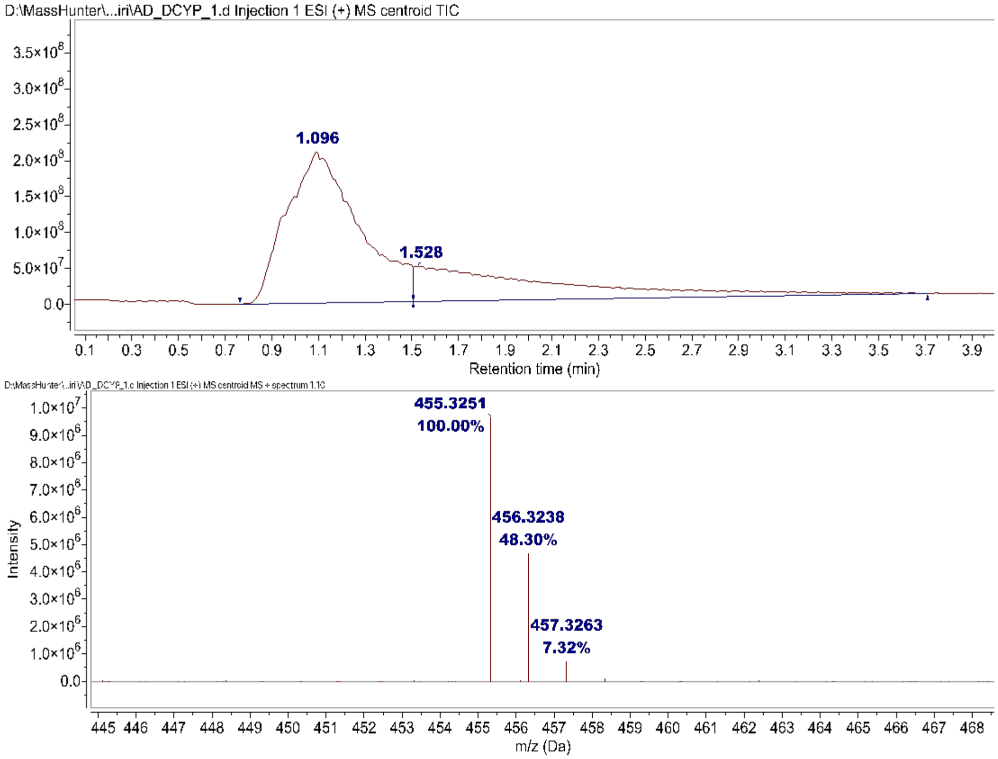


Fig. S139 QTOF Mass spectra of oxidized DCyPE ($C_{26}H_{48}O_2P_2$, Molecular Weight 454.62).

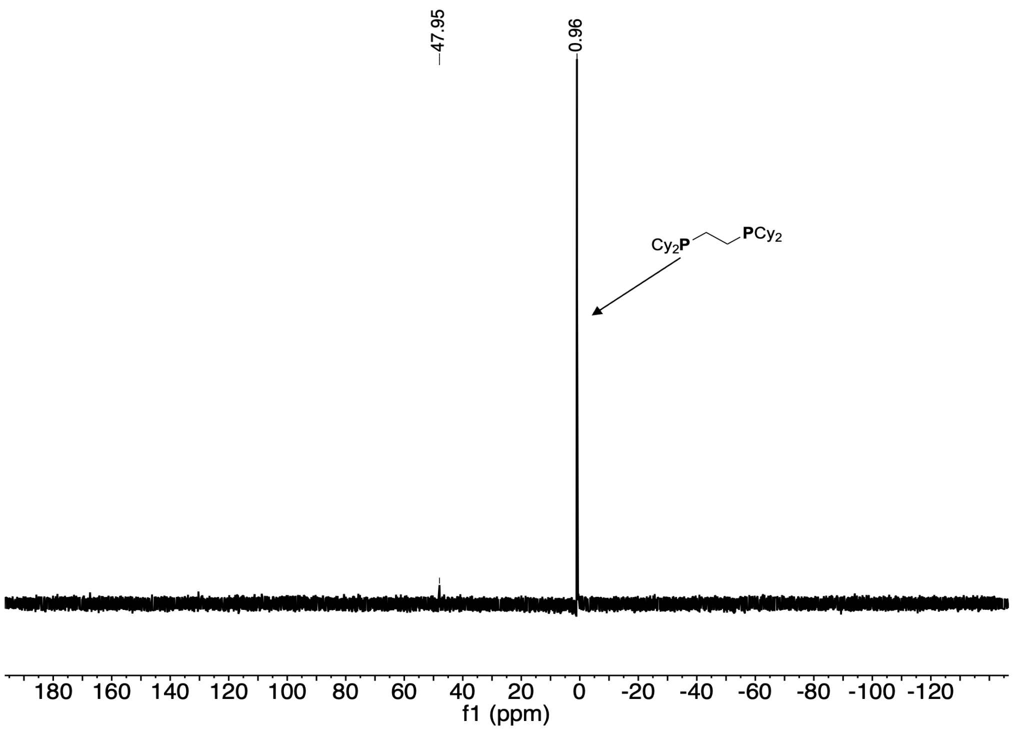


Fig. S140 ^{31}P NMR spectra of Pure DCyPE in $CDCl_3$.

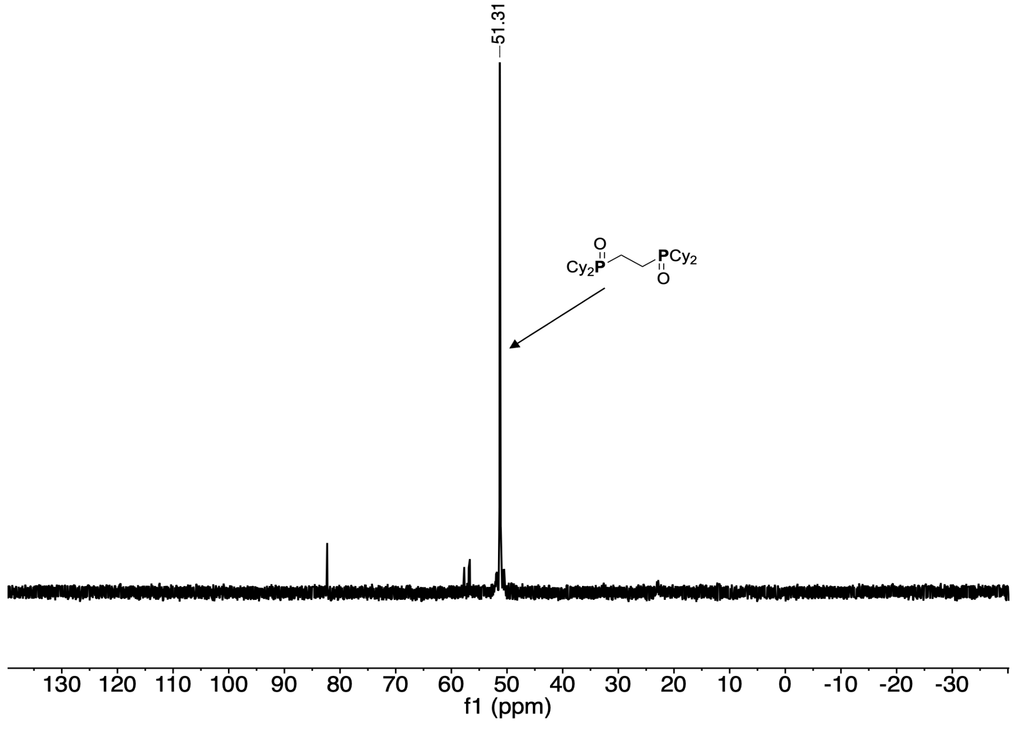


Fig. S141 ^{31}P NMR spectra of oxidized DCyPE in $CDCl_3$.

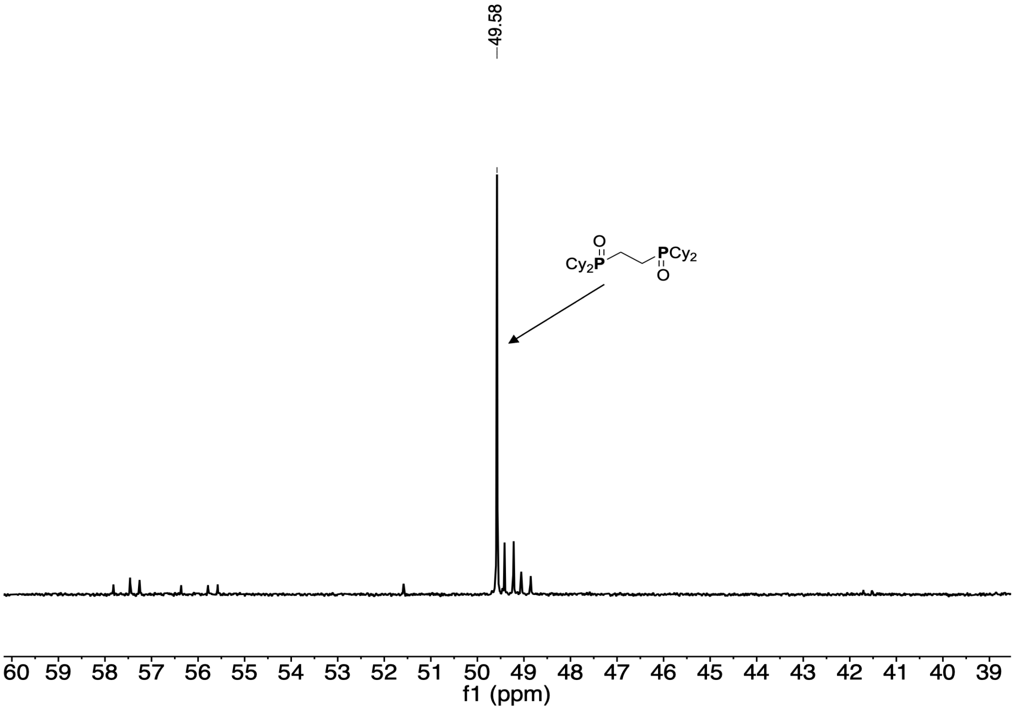


Fig. S142 ^{31}P NMR spectra of oxidized DCyPE in the mixture of THF and $CDCl_3$

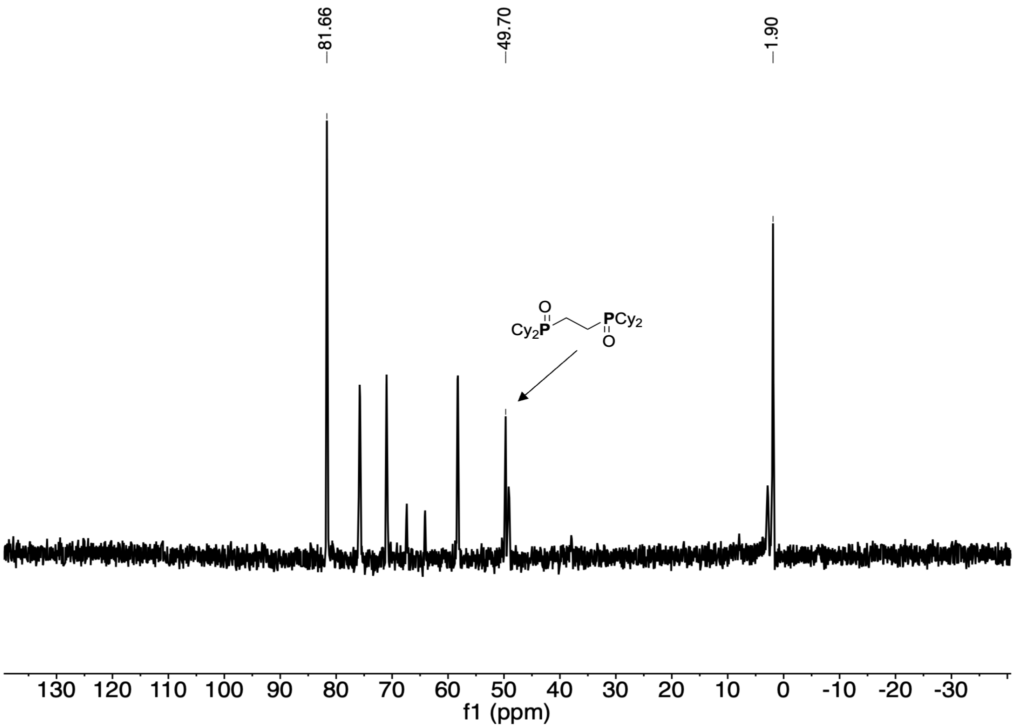
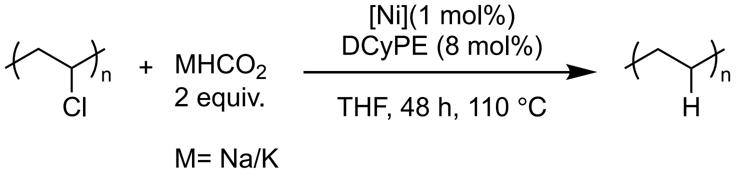


Fig. S143 ^{31}P NMR spectrum in $CDCl_3$ of Table S1, Entry 3 for PVC hydrodechlorination product with $Ni(COD)_2$ (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 120 °C.

Confirmation of involving of DCyPE in generation of carbonyl



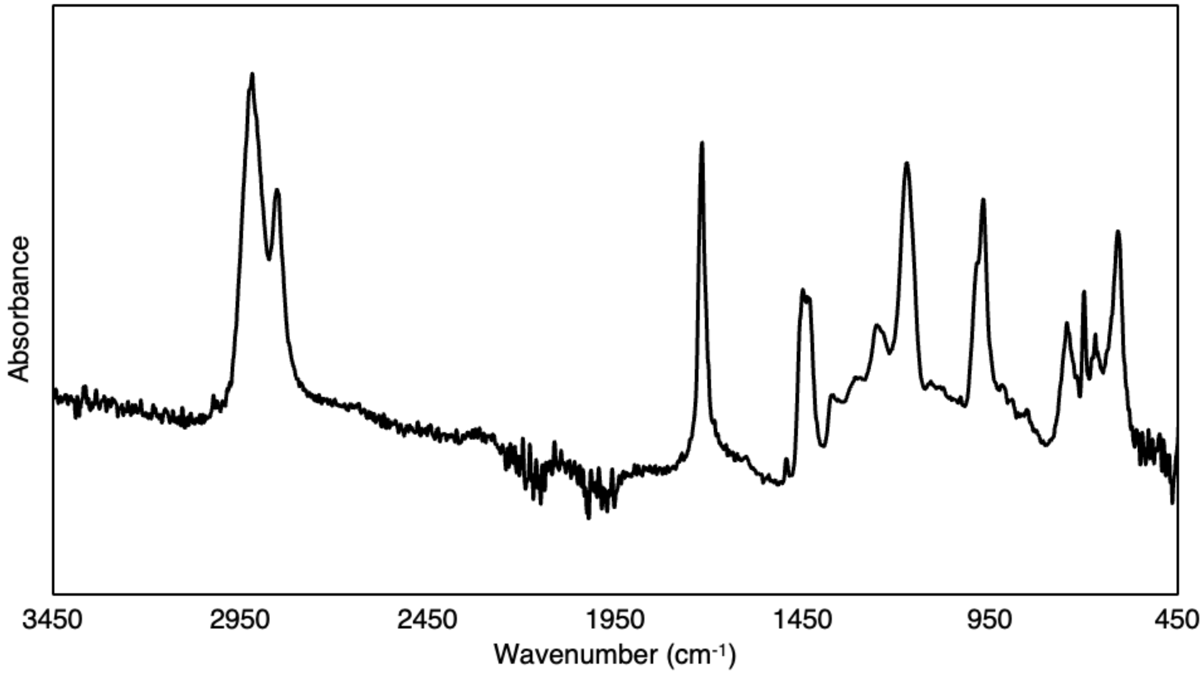


Fig. S144 FT-IR spectra for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DCyPE (8 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

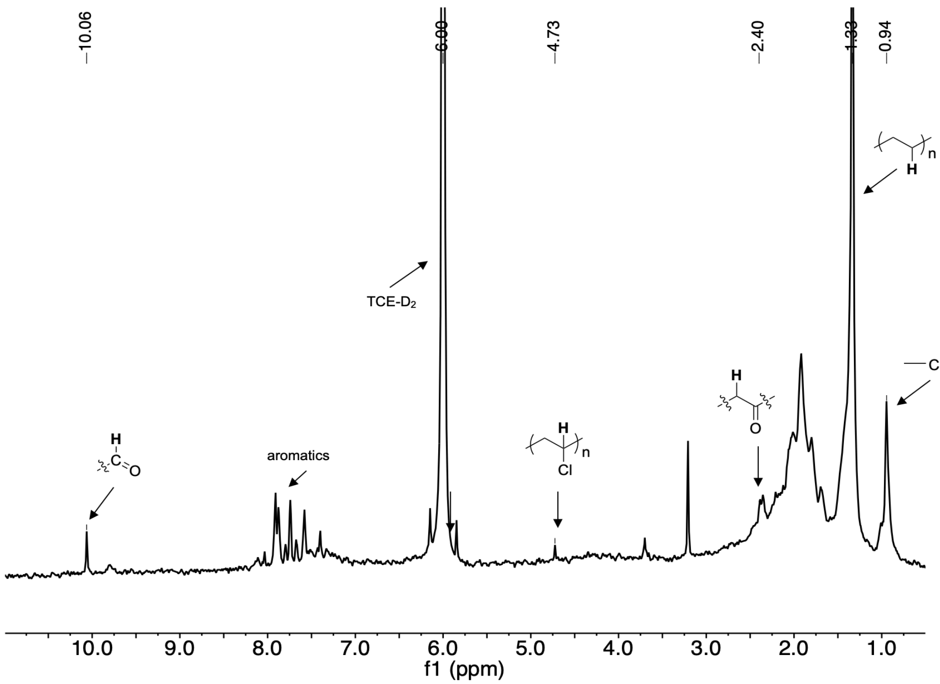


Fig. S145 NMR spectra for PVC hydrodechlorination product with $NiCl_2$ (1 mol%), DCyPE (8 mol%), and 2 equiv. $NaHCO_2$ for 48 hours in THF at 110 °C.

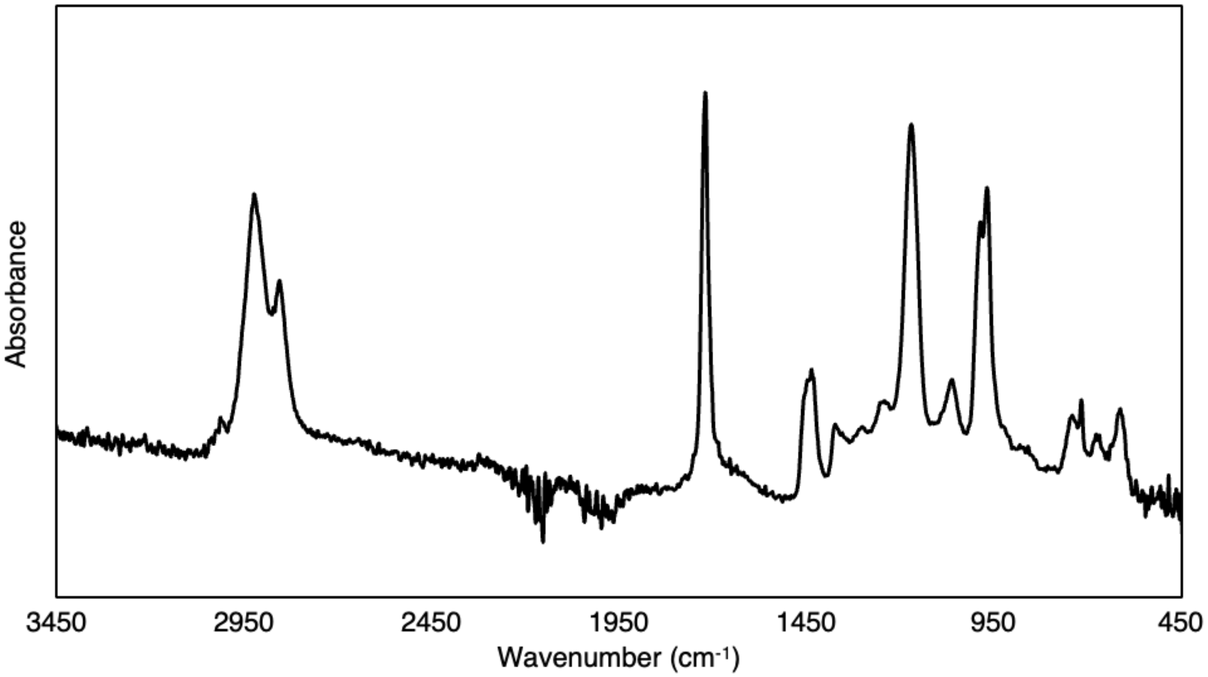


Fig. S146 FT-IR spectra for PVC hydrodechlorination product with $NiBr_2{\cdot}$Diglyme (1 mol%), DCyPE (8 mol%), and 2 equiv. $KHCO_2$ for 48 hours in THF at 110 °C.

500 mg scale reaction

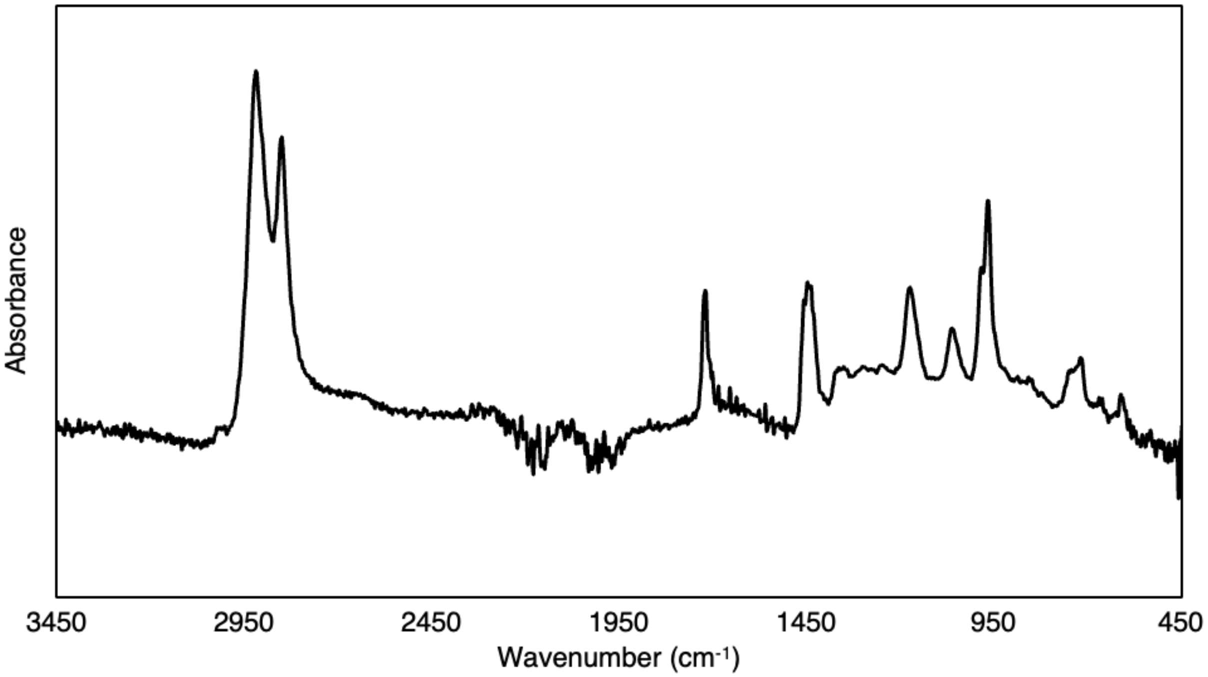


Fig. S147 FT-IR for PVC hydrodechlorination product on 500 mg scale reaction with $NiBr_2{\cdot}$Diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 72 hours in THF at 110 °C.

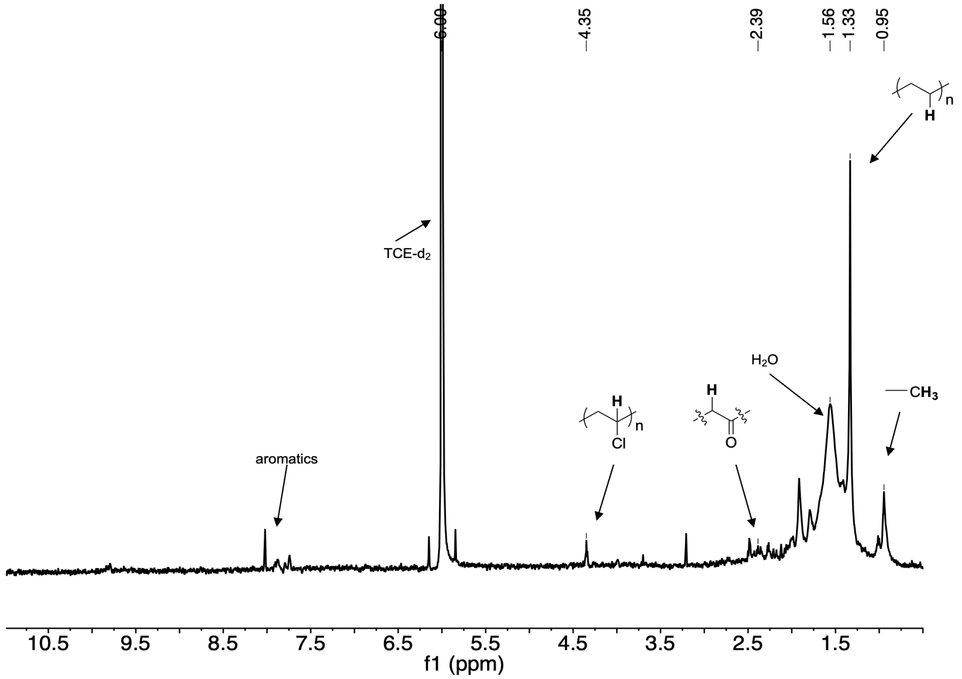


Fig. S148 ^{1}HNMR spectra for PVC hydrodechlorination product on 500 mg scale reaction with $NiBr_2{\cdot}$Diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 72 hours in THF at 110 °C.

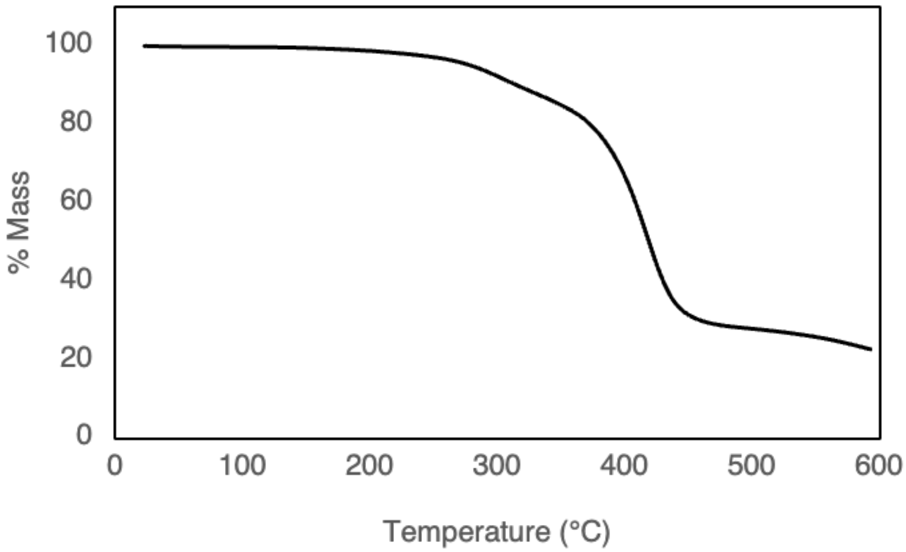


Fig. S149 TGA curve for PVC hydrodechlorination product on 500 mg scale reaction with $NiBr_2$·Diglyme (2.5 mol%), DCyPE (5 mol%), and 2 equiv. $NaHCO_2$ for 72 hours in THF at 110 °C.

References

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[1] A. I. Vogel and G. H. Jeffery, *Vogel's Textbook of Quantitative Chemical Analysis*, Longman Scientific & Technical, New York, 1989.

[2] 1D. A. Skoog, D. M. West, F. J. Holler and S. R. Crouch, *Fundamentals of Analytical Chemistry*, Brooks/Cole, Cengage Learning, Belmont, CA, 2014.