Supporting Information

Catalytic synthesis of functionalized (polar and non-polar) polyolefin block copolymers†

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I. General Methods and Materials

All reactions were carried out under an argon atmosphere using oven-dried glassware and utilized dried solvents (toluene, DCM, THF) unless otherwise noted. The following reagents were purchased and used as received unless specified: 2-hydroxyethyl acrylate (HEA, Aldrich, contains 200-650 ppm monomethyl ether hydroquinone as inhibitor), tert-butyl glycidyl ether (tBuGE, Aldrich), diethylene glycol dimethyl ether (Diglyme, TCI America), ethylene (Airgas, Research Plus), propylene (Airgas, electronic grade), copper(I) bromide (CuBr, Aldrich, 99.999% trace metals basis), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, Aldrich), Hoveyda-Grubbs catalyst 2nd generation (HG-catalyst, Umicore), potassium bis(trimethylsilyl)amide ($KN(TMS)_2$, Aldrich), 1-hexene (Aldrich) , dichloro[rac-ethylenebis(indenyl)]zirconium(IV) (Aldrich), 2-[di(2-methoxyphenyl)phosphino]benzenesulfonic acid (97%, Aldrich). A 7 wt% aluminum methylaluminoxane (MAO) solution was purchased from Aldrich and concentrated to yield a white solid prior to use (known as “Dried MAO”). 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA) was synthesized following literature procedure[1]. Rac-lactide was purchased from Aldrich and recrystallized 6 times from dry toluene and dried under reduced pressure (0.01 mm Hg) with P_2O_5 for 2 days prior to use. Stabilized styrene was purchased from Acros and passed over a neutral aluminum oxide plug prior to use. Stannous octoate ($Sn(Oct)_2$, Aldrich) was distilled under reduced pressure (0.01 mm Hg) and stored in a glovebox prior to use.

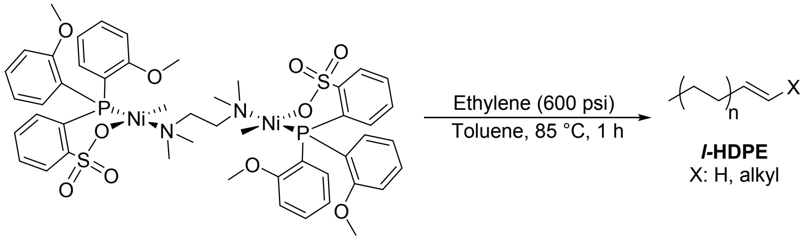
A dinickel methyl diamine phosphinesulfonate complex was synthesized according to literature and used for the synthesis of low molecular weight linear polyethylene (*l*-HDPE).[2] A palladium methyl phosphinesulfonate complex was synthesized according to literature and used for the synthesis of high molecular weight high density polyethylene (*h*-HDPE).[3] A methylaluminoxane-activated bis(phenoxyimine)titanium dichloride complex was synthesized according to literature and used for the synthesis of syndiotactic polypropylene (synPP) and linear low density polyethylene (LLDPE).[4] A palladium diimine complex was synthesized according to literature and used for the synthesis of hyperbranched polyethylene (HBPE).[5]

NMR spectra were recorded on a Varian Unity 500 MHz, Varian Unity Inova NMR 600 MHz or Bruker AVANCE III 500 MHz spectrometer and spectrum were referenced to the residual solvent peak: $CDCl_3$(^1H 7.26 ppm and ^{13}C 77.2 ppm), DCl_2CCCl_2D (d_2-TCE) (^1H 6.00 ppm and ^{13}C 73.78 ppm). When d_2-TCE was employed $Cr(acac)_2$ was added to aid in reducing relaxation times. The differential scanning calorimetry (DSC) measurement was performed using TA Instrument Q20. Tzero aluminum pans and lids were used as sample testing containers. Polymer crystallinities were calculated based on a melt enthalpy of 294 J/g for 100% crystalline polyethylene and a melt enthalpy of 207 J/g for 100% crystalline polypropylene.

Gel Permeation Chromatography (GPC) was performed using a Tosoh Ecosec HLC-8320GPC at 40 ºC fitted with a reference column (6.0 mm ID x 15 cm), a guard column (6.0 mm ID x 4.0 cm x 5 µm), and two analytical columns (7.8 mm ID x 30 cm x 5 µm). The reference flow rate is 0.5 mL/min while the analytical column is at 1.0 mL/min. THF (HPLC grade) was used as the eluent, and polystyrene standards (15 points ranging from 500 Mw to 8.42 million Mw) were used for calibration. High temperature gel permeation chromatography (GPC) was performed at 160 °C in 1,2,4-trichlorobenzene at a flow rate of 1.0 mL/min on a Malvern Viscotek HT-GPC equipped with triple detection. Absolute molecular weights were calculated from dn/dc values assuming 100% mass recovery.

II. Polyolefin Synthesis Procedure

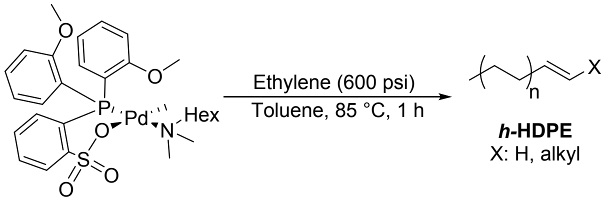
Procedure for the synthesis of *l*-HDPE



Procedure adopted from literature.[2]

The polymerization was carried out in a mechanically stirred (1000 rpm) high-pressure stainless steel reactor equipped with a heating and cooling jacket, thermocouple. To run a polymerization, the reactor was cleaned with detergent, rinsed with excess water, and heated under vacuum for ~1 h at 85 °C. The reactor was backfilled with argon. Three more quick cycles of vacuum-and-backfilling with argon were repeated before the transfer of degassed toluene (100 ml) at 60 °C. Dinickel methyl diamine phosphinesulfonate complex (10 mg, 7.8 µmol) was transferred into the reactor and pressurized to 600 psi with ethylene. The temperature was uncontrolled, rising significantly before returning back to 60 °C within 5 min. After 30 min. of polymerization, the ethylene was vented quickly and the polymer solution was poured hot into excess methanol. The resulting precipitates were collected by filtration. The solid polymer was dried under vacuum at 50 °C overnight to yield a white polymer. Yield = 68 g, fraction of terminal double bonds (NMR) = 0.43, M_n (NMR) = 800 g/mol, T_m (DSC) = 85 ^oC.

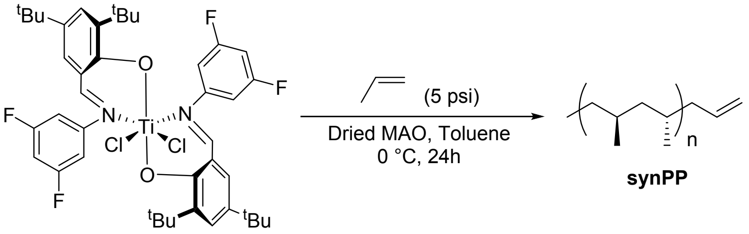
Procedure for the synthesis of *h*-HDPE



Procedure adopted from literature.[3]

The polymerization was carried out in a mechanically stirred (1000 rpm) high-pressure stainless steel reactor equipped with a heating and cooling jacket, thermocouple. The temperature was controlled within 5 °C of the polymerization via a thermocouple dipped into the polymerization mixture. To run polymerization, the reactor was cleaned with detergent, rinsed with excess water, and heated under vacuum for ~1 h at 85 °C. The reactor was backfilled with argon. Three more quick cycles of vacuum-and-backfilling with argon were repeated before the transfer of degassed toluene (100 ml) at 85 °C. Palladium methyl phosphinesulfonate complex (4 mg, 6.0 µmol) was transferred into the reactor and pressurized to 600 psi at 85 °C. The temperature was controlled using a thermocouple dipped into the reaction mixture. After one hour of polymerization, the ethylene was vented quickly and the polymer solution was poured hot into excess methanol. The resulting precipitates were collected by filtration. The solid polymer was dried under vacuum at 50 °C overnight to yield a white polymer. Yield = 5.5 g, fraction of terminal double bonds (NMR) = 0.83, M_n (NMR) = 16,000 g/mol, M_n (GPC) = 18,000 g/mol, M_w/M_n (GPC) = 1.6, T_m (DSC) = 132 °C, % crystallinity = 57 %.

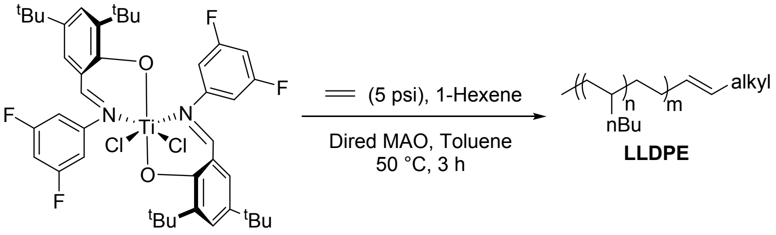
Procedure for the synthesis of synPP



Procedure adopted from literature.[4]

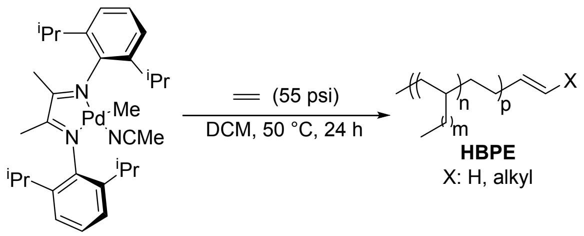
The polymerization was carried out in a mechanically stirred (1000 rpm) low-pressure glass reactor equipped with a heating and cooling jacket, thermocouple. To run a polymerization, the reactor was cleaned with detergent, rinsed with excess water, and heated under vacuum for ~6 h at 50 °C. The reactor was backfilled with argon. Three more quick cycles of vacuum-and-backfilling with argon were repeated before the transfer of a solution of degassed toluene (140 ml) and dried MAO (580 mg, 10 mmol) into the reactor. The solution is then cooled to 0 °C and pressured with propylene (5 psi) and vented 3 times, allowing for equilibration time (5 min) before venting. A solution of bis(phenoxyimine)titanium dichloride (40.4 mg, 0.05 mmol) in toluene (10ml) was transferred into the reactor and re-pressurized to 5 psi quickly. The temperature was maintained at 0 °C for 24 h at which time the propylene was quickly vented and the polymer solution was poured into excess acidic methanol, and the resulting precipitates were collected by filtration. The solid polymer was dried under vacuum at 50 °C overnight to yield a white polymer. Yield = 6.6 g, fraction of terminal double bonds (NMR) = 0.99, M_n (NMR) = 5,000 g/mol, M_n (GPC) = 5,800 g/mol, M_w/M_n (GPC) = 1.8, T_m (DSC) = 113 °C, T_g (DSC) = -13 °C.

Procedure for LLDPE



The polymerization was carried out in a mechanically stirred (1000 rpm) low-pressure glass reactor equipped with a heating and cooling jacket, thermocouple. To run a polymerization, the reactor was cleaned with detergent, rinsed with excess water, and heated under vacuum for ~6 h at 50 °C. The reactor was backfilled with argon. Three more quick cycles of vacuum-and-backfilling with argon were repeated before the transfer of a solution of degassed 1-hexene (100 ml) and dried MAO (290 mg, 5 mmol) into the reactor. The solution is then heated to 50 °C and pressured with ethylene (5 psi) and vented 3 times, allowing for equilibration time (5 min) before venting. A solution of bis(phenoxyimine)titanium dichloride (20.2 mg, 0.025 mmol) in toluene (10 ml) was transferred into the reactor and re-pressurized to 5 psi quickly. The temperature was maintained at 50 °C for 3 h at which time the ethylene was vented and the polymer solution was poured into excess acidic methanol, and the resulting precipitates were collected by filtration. The solid polymer was dried under vacuum at 50 °C overnight to yield a white polymer. Yield = 8.4 g, fraction of terminal double bonds (NMR) = >0.01, mole fraction of hexene: 0.15, M_n (NMR) = 14,000 g/mol, M_n (GPC) = 17,000 g/mol, M_w/M_n (GPC) = 1.6, T_m (DSC) = 35 °C.

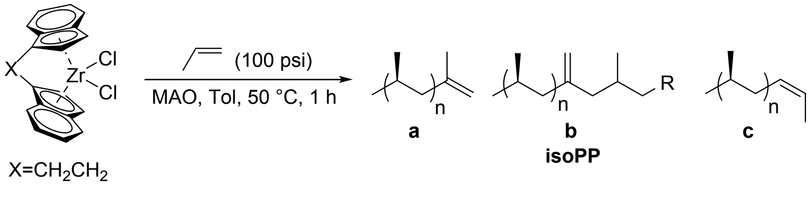
Procedure for the synthesis of HBPE



Procedure adopted from literature.[5]

The polymerization was carried out in a mechanically stirred (1000 rpm) low-pressure glass reactor equipped with a heating and cooling jacket, thermocouple. To run a polymerization, the reactor was cleaned with detergent, rinsed with excess water, and heated under vacuum for ~6 h at 50 °C. The reactor was backfilled with argon. Three quick more cycles of vacuum-and-backfilling with argon were repeated before the transfer of a solution of palladium diimine complex (77.1 mg, 0.05 mmol) in degassed DCM (50 ml). The solution is then allowed to equilibrate at 50 °C before being pressured with ethylene (55 psi). The temperature was maintained at 50 °C for 24 h at which time the ethylene was vented and the polymer solution was dried under vacuum at 50 °C overnight. The remaining residual was re-dissolved into pentane and passed through a silica plug. The resulting solution was dried under vacuum at 50 °C for 5 days to yield a colorless polymer. Yield = 27 g, fraction of terminal double bonds (NMR) = 0.19, M_n (NMR) = 83,000 g/mol, M_n (GPC) = 89,000 g/mol , M_w/M_n (GPC) = 1.8, T_g (DSC) = -68 °C.

Procedure for the synthesis of isoPP

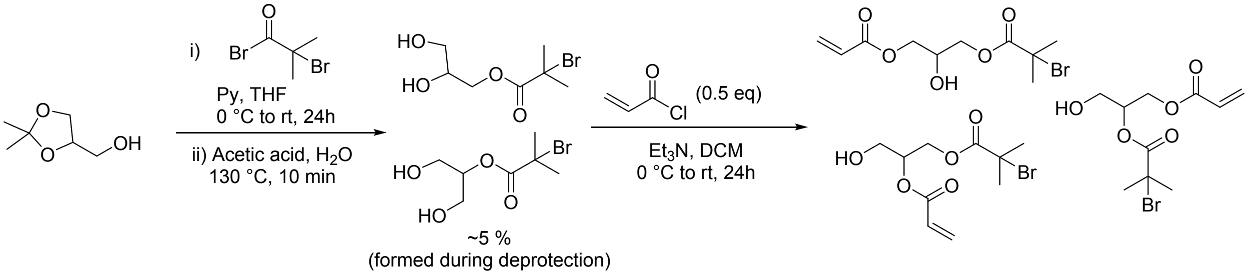


Procedure adopted from literature.[6]

The polymerization was carried out in a mechanically stirred (1000 rpm) glass reactor equipped with a heating and cooling jacket, thermocouple. To run a polymerization, the reactor was cleaned with detergent, rinsed with excess water, and heated under vacuum for ~6 h at 50 °C. The reactor was backfilled with argon. Three more quick cycles of vacuum-and-backfilling with argon were repeated before the transfer of a solution of degassed toluene (140 ml) and dried MAO (140 mg, 2.4 mmol) into the reactor. The solution is then heated to 50 °C and pressured with propylene (100 psi) and vented 3 times, allowing for equilibration time (15 min) before venting. A solution of dichloro[rac-ethylenebis(indenyl)]zirconium(IV) (0.25 mg, 0.6 μmol) in toluene (10ml) was generated and added to a vial with dried MAO (140 mg, 2.4 mmol). This mixture was allowed to react for 5 min. before injecting into the pressurized reactor. The temperature was maintained at 50 °C for 1 h at which time the propylene was vented and the polymer solution was poured into excess acidic methanol/diethyl ether (50% vol), and the resulting precipitates were collected by filtration. The collected solid was re-dissolved in boiling toluene and precipitated two more times. The solid polymer was then dried under vacuum at 50 °C overnight to yield a white polymer. Yield = 24.8 g, fraction of **a** (NMR) = 0.24, fraction of **b** (NMR) = 0.06, fraction of **c** (NMR) = 0.70, M_n (NMR) = 27,000 g/mol, M_n (GPC) = 26,000 g/mol, M_w/M_n (GPC) = 2.1, T_m (DSC) = 142 °C, % crystallinity = 40 %.

III. Cross Coupling Procedure

Synthesis of 3 arm star coupling partner

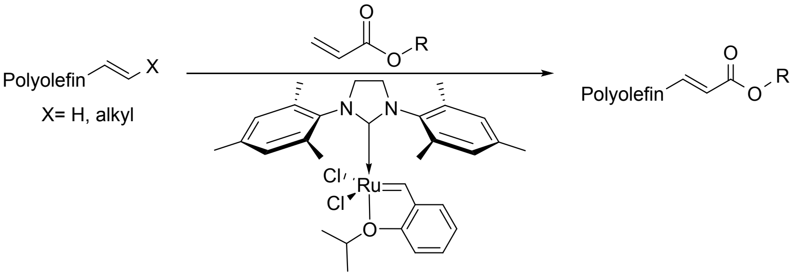


Procedure adopted from literature.[7–9]

A solution of solketal (8 g, 60 mmol), pyridine (9.7 ml, 120 mmol) and THF (120 ml) was generated and cooled to 0 °C. 2-bromoisobutylryl (11.2 ml, 90 mmol) was added dropwise over 1 h at 0 °C. Upon completion of the addition, the cooling bath was removed and the reaction was allowed to stir at room temperature for 12 h. The mixture was diluted with DCM and washed with a saturated solution of sodium bicarbonate. The organic layer was then concentrated. A solution of acetic acid (100 ml) and deionized water (13 ml) was added to the organic concentrate. The mixture was heated, open to air, at 130 °C for 10 minutes. The flask is then cooled quickly by placing the flask in a room temperature water bath. The solution is then concentrated in vacuo and diluted with toluene multiple times to aid in the removal of water and acetic acid. A colorless solid is obtained. 13.1 g, 54.6 mmol (91 % yield) A mixture of two regio-isomers (5 % of untargeted product) is observed and matches literature.[10]

A portion of the crude mixture (5 g, 20.8 mmol) above is dissolved in dried and degassed DCM (80 ml) and trimethylamine (2.32 ml, 16.7 mmol). The mixture is cooled to 0 °C and a solution of acryloyl chloride (0.84 ml, 10.4 mmol) and DCM (10 ml) is added dropwise over 1 h. (A sub-stoichiometric amount of acryloyl chloride is used to avoid the double substituted product.) After the addition of acryloyl chloride, the reaction mixture is stirred for 12 h at room temperature. Mequinol (MEHQ) was added at this point to avoid spontaneous polymerization during workup and storage. The mixture was diluted with DCM and washed with a saturated solution of sodium bicarbonate. The organic layer was dried over $MgSO_4$, filtered, and concentrated. A colorless oil is obtained, 5.1 g. The product is stored at 0 °C and used as is for cross coupling reactions.

General cross coupling procedure



In a round bottom flask, polymer and toluene are mixed and heated to 120 °C until a homogeneous mixture is formed. (Warning: Toluene's boiling point is 110 °C, so electrical tape was used to secure a rubber septum on-to the round bottom.) The solution was maintained at 120 °C and a syringe pump was utilized to simultaneously inject two different solutions over 30 mins. The first solution contained HG-catalyst dissolved in toluene. The second solution contained the coupling partner dissolved in toluene. After the addition, the mixture was heated at 120 °C for an additional 30min before precipitating the polymer in methanol.

***l*-HDPE-HEA**
Polymer: 200 mg *l*-HDPE and 10 ml of toluene
Catalyst solution: 1.6 mg of HG-catalyst and 0.5 ml of toluene
Coupling solution: 290 mg HEA and 2 ml toluene
Alteration: Precipitated in methanol/H_2O (80/20) mixture.
Conversion of *l*-HDPE to *l*-HDPE-HEA (NMR): Quantitative*
M_n (NMR) = 900 g/mol
Note: Both 95 % trans / 5 % cis was observed in ^1H NMR and identified based on literature.[11]

***h*-HDPE-HEA**
Polymer: 1.5 g *h*-HDPE and 150 ml of toluene
Catalyst solution: 0.5 mg of HG-catalyst and 0.5 ml of toluene
Coupling solution: 97 mg HEA and 2 ml toluene
Conversion of *h*-HDPE to *h*-HDPE-HEA (NMR): Quantitative*
M_n (NMR) = 18,000 g/mol, M_n (GPC) = 19,000 g/mol, M_w/M_n (GPC) = 1.5

synPP-HEA
Polymer: 1.5 g synPP and 15 ml of toluene
Catalyst solution: 1.6 mg of HG-catalyst and 0.5 ml of toluene
Coupling solution: 300 mg HEA and 2 ml toluene
Alteration: All of the HEA was fully added prior to beginning 30 min addition of the catalyst solution.
Conversion of synPP to synPP-HEA (NMR): Quantitative*
M_n (NMR) = 6,400 g/mol, M_n (GPC) = 5,500 g/mol, M_w/M_n (GPC) = 1.8

LLDPE-HEA
Polymer: 1.5 g synPP and 15 ml of toluene
Catalyst solution: 0.55 mg of HG-catalyst and 0.5 ml of toluene
Coupling solution: 102 mg HEA and 2 ml toluene
Conversion of LLDPE to LLDPE-HEA (NMR): Quantitative*
M_n (NMR) = 15,000 g/mol, M_n (GPC) = 17,000, M_w/M_n (GPC) = 1.5

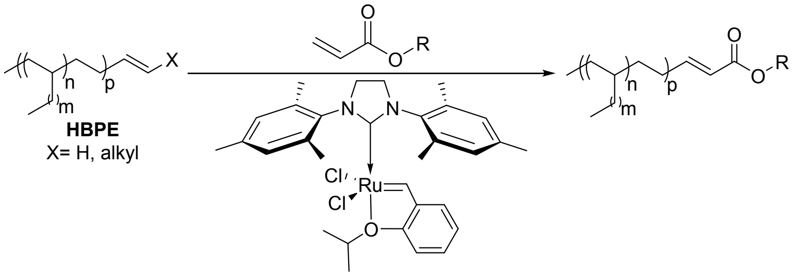
***l*-HDPE-BIEA**
Polymer: 800 mg *l*-HDPE and 25 ml of toluene
Catalyst solution: 6.3 mg of HG-catalyst and 0.5 ml of toluene
Coupling solution: 2.7 g BIEA and 3.2 ml toluene
Alteration: Precipitated in methanol/H_2O (80/20) mixture.
Conversion of *l*-HDPE to *l*-HDPE-BIEA (NMR): Quantitative*
M_n (NMR) = 1,100 g/mol

***l*-HDPE-3 arm linker**
Polymer: 380 mg *l*-HDPE and 20 ml of toluene
Catalyst solution: 3.0 mg of HG-catalyst and 0.5 ml of toluene
Coupling solution: 1.5 g 3 arm linker and 3.2 ml toluene
Alteration: Precipitated in methanol/H_2O (80/20) mixture.
Conversion of *l*-HDPE to *l*-HDPE-3 arm linker: Quantitative*
M_n (NMR) = 1,300 g/mol

isoPP-HEA
Polymer: 600 mg isoPP and 14 ml of toluene
Catalyst solution: 15 µg of HG-catalyst and 0.5 ml of toluene
Coupling solution: 5 mg HEA and 0.5 ml toluene
Conversion of isoPP to isoPP-HEA (NMR): 70%
M_n (NMR) = 30,000 g/mol, M_n (GPC) = 29,000 g/mol, M_w/M_n (GPC) = 2.0

* The meaning of quantitative conversion is discussed in section 9.

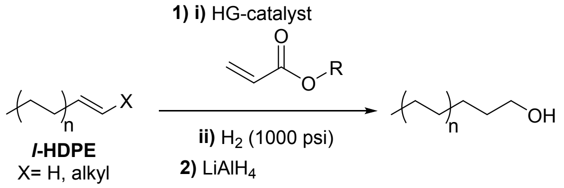
Procedure for cross coupling of HBPE



Procedure adopted from literature.[12]

In a vial, HBPE (2 g), HG-catalyst (0.14 mg), HEA (26 mg) and toluene (15 ml) are mixed and heated at 80 °C for 24 h. The mixture was then cooled to room temperature and passed through a plug of silica gel. The remaining solution was concentrated (80 °C, 0.1mm Hg, 5 days yielding a colorless oil. Conversion of HBPE to HBPE-HEA (NMR): Quantitative*, M_n (NMR) = 93,000 g/mol, M_n (GPC) = 95,000 g/mol, M_w/M_n (GPC) = 1.7

Procedure for cross coupling, hydrogenation and reduction of *l*-HDPE



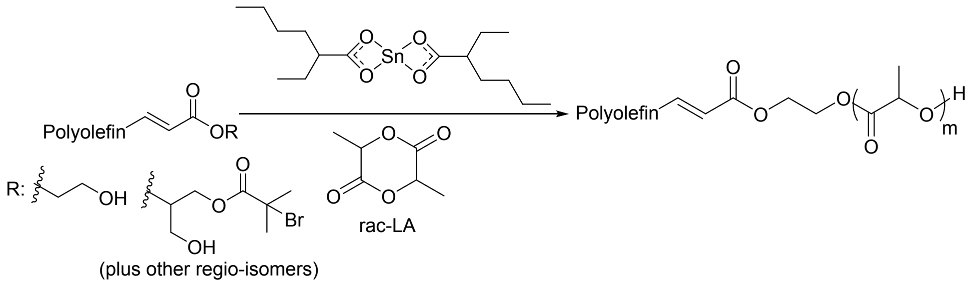
Procedure adopted from literature.[12]

In a mechanically stirred (1000 rpm) high-pressure stainless steel reactor, *l*-HDPE (4 g) and toluene (100 ml) are added and heated to 120 °C until a homogeneous mixture is formed. The solution was maintained at 120 °C and a syringe pump was utilized to simultaneously inject two different solutions over 30 mins. The first solution contained HG-catalyst (31 mg) dissolved in toluene (5 ml). The second solution contained the HEA (5.8 g) dissolved in toluene (20 ml). After the addition, the mixture was heated at 120 °C for an additional 30 min. The reactor was then pressurized to 1000 psi of hydrogen gas and stirred at 120 °C for 12 h. The hydrogen was quickly vented and the flask was cooled down. The polymer solution was poured into excess methanol, and the resulting precipitates were collected by filtration. The solid polymer was dried under vacuum at 50 °C overnight to yield a white polymer.

Polymer, lithium aluminum hydride (840 mg) and toluene (80 ml) were added into a flask and heated to 120 °C. After 6 hours, water was slowly added to quench the reaction. The mixture was filtered hot and the polymer was precipitated in acidic methanol. The resulting precipitates were collected by filtration and was dried under vacuum at 50 °C overnight to yield a white polymer. Conversion of *l*-HDPE to *l*-HDPE-OH (NMR): Quantitative*, M_n (NMR) = 1,000 g/mol

IV. Living Chain Growth Procedures

General procedure for coordinative ring opening polymerization of lactide



Procedure adopted from literature.[13]

In a glass screw cap pressure vessel polymer, $Sn(Oct)_2$, lactide and toluene were mixed. The mixture was heated in an oil bath to 120 ℃ for 3 hours. The blend was then allowed to air cool to 110 ℃ and poured hot into a large excess of methanol. The resulting precipitates were collected by filtration and were dried under vacuum at 50 ℃ overnight to yield a white polymer.

***l*-HDPE-PLA**
Reagents: 200 mg *l*-HDPE-HEA, 9.0 mg $Sn(Oct)_2$, 514 mg rac-lactide, 2 ml of toluene
Conversion of *l*-HDPE -HEA to *l*-HDPE -PLA (NMR): Quantitative*
Number fraction of polyolefin (NMR): 0.54
M_n (NMR) = 3,400 g/mol, M_N (GPC) = 4,200 g/mol, M_w/M_n (GPC) = 1.4

***h*-HDPE-PLA**
Reagents: 150 mg *h*-HDPE-HEA, 0.32 mg $Sn(Oct)_2$, 386 mg rac-lactide, 3 ml of toluene
Conversion of *h*-HDPE -HEA to *h*-HDPE -PLA (NMR): Quantitative*
Number fraction of polyolefin (NMR): 0.47
M_n (NMR) = 65,000 g/mol, M_n (GPC) = 69,000 g/mol, M_w/M_n (GPC) = 1.3

synPP-PLA
Reagents: 150 mg synPP-HEA, 1.1 mg $Sn(Oct)_2$, 257 mg rac-lactide, 1 ml of toluene
Conversion of synPP-HEA to synPP-PLA (NMR): Quantitative*
Number fraction of polyolefin (NMR): 0.58
M_n (NMR) = 14,000 g/mol, M_n (GPC) = 15,000 g/mol, M_w/M_n (GPC) = 1.6

LLDPE-PLA
Reagents: 150 mg LLDPE-HEA, 0.36 mg $Sn(Oct)_2$, 297 mg rac-lactide, 3 ml of toluene
Conversion of LLDPE-HEA to LLDPE-PLA (NMR): Quantitative*
Number fraction of polyolefin (NMR): 0.72
M_n (NMR) = 28,000 g/mol, M_n (GPC) = 29,000 g/mol, M_w/M_n (GPC) = 1.2

HBPE-PLA
Reagents: 200 mg HBPE-HEA, 0.1 mg $Sn(Oct)_2$, 515 mg rac-lactide, 1 ml of toluene
Conversion of HBPE-HEA to HBPE-PLA (NMR): Quantitative*
Number fraction of polyolefin (NMR):0.84
M_n (NMR) = 220,000 g/mol, M_n (GPC) = 170,000 g/mol, M_w/M_n (GPC) = 1.8

***l*-HDPE-PLA-Br**
Reagents: 150 mg *l*-HDPE-3 arm linker, 4.7 mg $Sn(Oct)_2$, 386 mg rac-lactide, 3 ml of toluene
Conversion of *l*-HDPE-3 arm linker to *l*-HDPE-PLA-Br (NMR): Unable to determine by NMR due to overlapping signals
Number fraction of polyolefin (NMR): 0.49
M_n (NMR) = 4,200 g/mol, M_n (GPC) = 4,300 g/mol; M_w/M_n (GPC) = 1.3

isoPP-PLA

Reagents: 200 mg isoPP-HEA, 6.2 µg $Sn(Oct)_2$, 344 mg rac-lactide, 12 ml of toluene, heated for 24 h

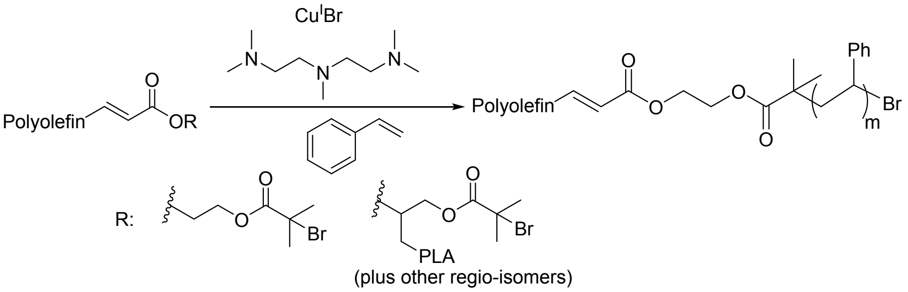
Conversion of isoPP-HEA to isoPP-PLA (NMR): Quantitative*

Number fraction of polyolefin (NMR): 0.51

M_n (NMR) = 56,000 g/mol, M_n (GPC) = 60,000 g/mol, M_w/M_n (GPC) = 1.4

* The meaning of quantitative conversion is discussed in section 9.

General procedure for ATRP of styrene



Procedure adopted from literature. [14]

In a round bottom flask, polymer and toluene are mixed and heated to 120 °C until a homogeneous mixture is formed. (Warning: Toluene's boiling point is 110 °C, so electrical tape was used to secure a rubber septum on to the round bottom.) The solution was maintained at 120 °C and a mixture of styrene, CuBr, and N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA) was injected rapidly. The mixture was allowed to stir at 120 °C for 20 min. The blend was then quickly cooled to 110 °C and poured hot into a large excess of methanol. The resulting precipitates were collected by filtration. The collected solid was re-dissolved into toluene and re-precipitated in excess methanol two more times. The final collected solid was dried under vacuum at 50 °C overnight to yield a white polymer.

***l*-HDPE-PS**

Reagents: 100 mg *l*-HDPE-BIEA, 47.8 mg CuBr, 57.8 mg PMDETA, 4.8 ml styrene, and 2 ml of toluene

Conversion of *l*-HDPE - BIEA to *l*-HDPE -PS (NMR): Quantitative

Number fraction of polyolefin (NMR): 0.46

M_n (NMR) = 4,300 g/mol, M_n (GPC) = 5,000 g/mol; M_w/M_n (GPC) = 1.1

***l*-HDPE-PLA-PS**

Reagents: 200 mg *l*HDPE -PLA-Br, 23.0 mg CuBr, 27.7 mg PMDETA, 4.6 ml styrene, and 8 ml of toluene

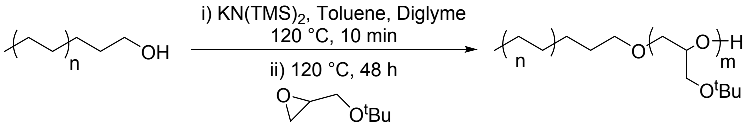
Conversion of *l*-HDPE -PLA-Br to *l*-HDPE -PLA-PS (NMR): Unable to determine by NMR due to overlapping signals

Number fraction of polyolefin (NMR): 0.44

Number fraction of polystyrene (NMR): 0.26

M_n (NMR) = 7,100 g/mol, M_n (GPC) = 7,700 g/mol; M_w/M_n (GPC) = 1.3

Procedure for anionic polymerization of tBuGE



Procedure adopted from literature.[15]

In a round bottom flask, polymer (200 mg), KN(TMS)$_2$ (20 mg), toluene (4 ml) and diglyme (4 ml) are mixed and heated at 120 °C for 10 min. (Warning: Toluene boiling point is 110 °C, so electrical tape was used to secure a rubber septum on to the round bottom.) The solution was maintained at 120 °C and tBuGE (2.8 ml) was injected rapidly. The mixture was allowed to stir at 120 ℃ for 48 h. The blend was then concentrated by distillation (80 °C, 0.1 mmHg). Conversion of *l*-HDPE-OH to *l*-HDPE-P(tBuGE) (NMR): Unable to determine by NMR due to overlapping signals, Number fraction of polyolefin (NMR): 0.29, M_n (NMR) = 9,000 g/mol, M_n (GPC) = 7,500 g/mol; M_w/M_n (GPC) = 1.2

V. NMR Spectra

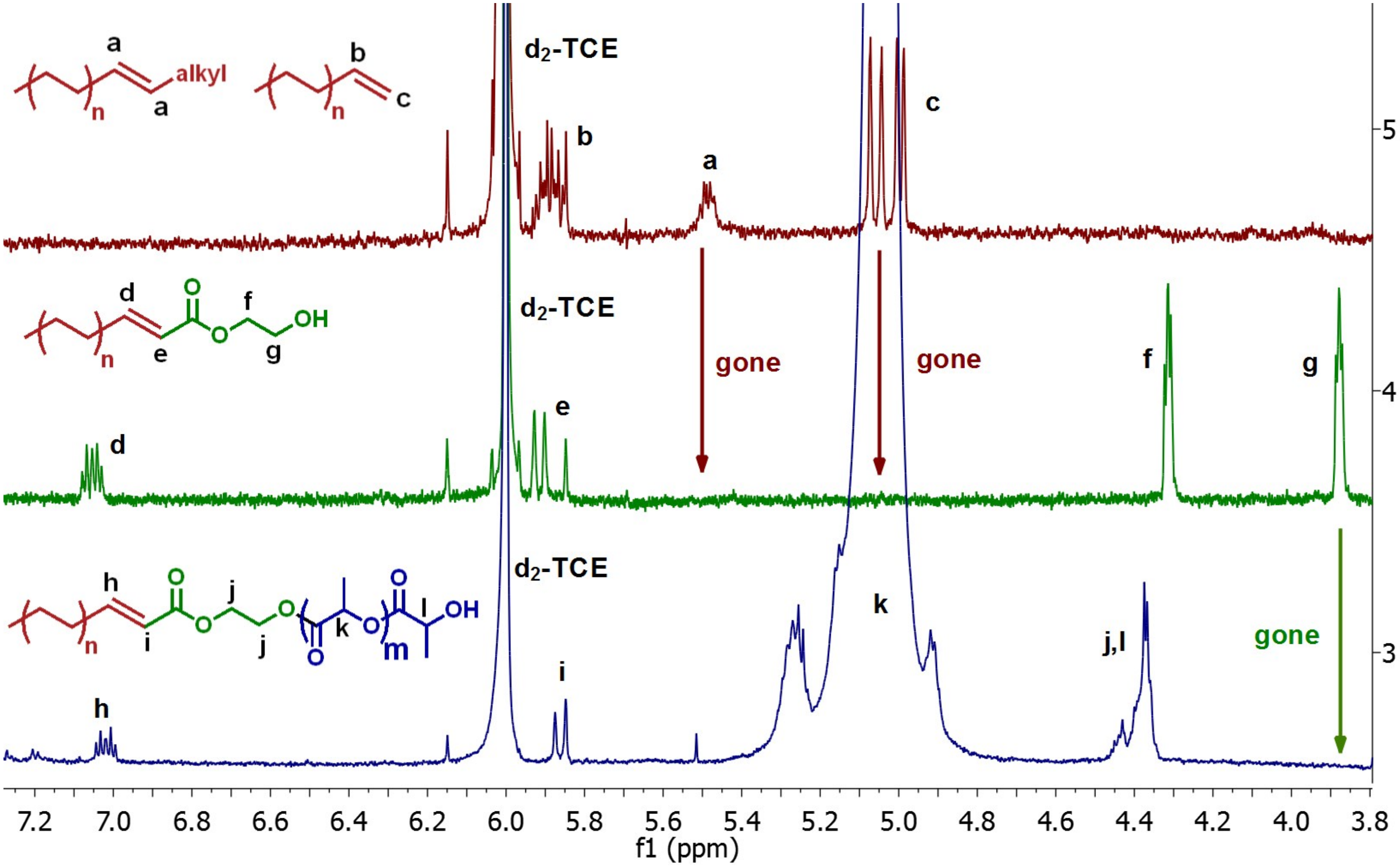


Figure S1: Stacked ^{1}H NMR for the synthesis of *h*-HDPE-PLA

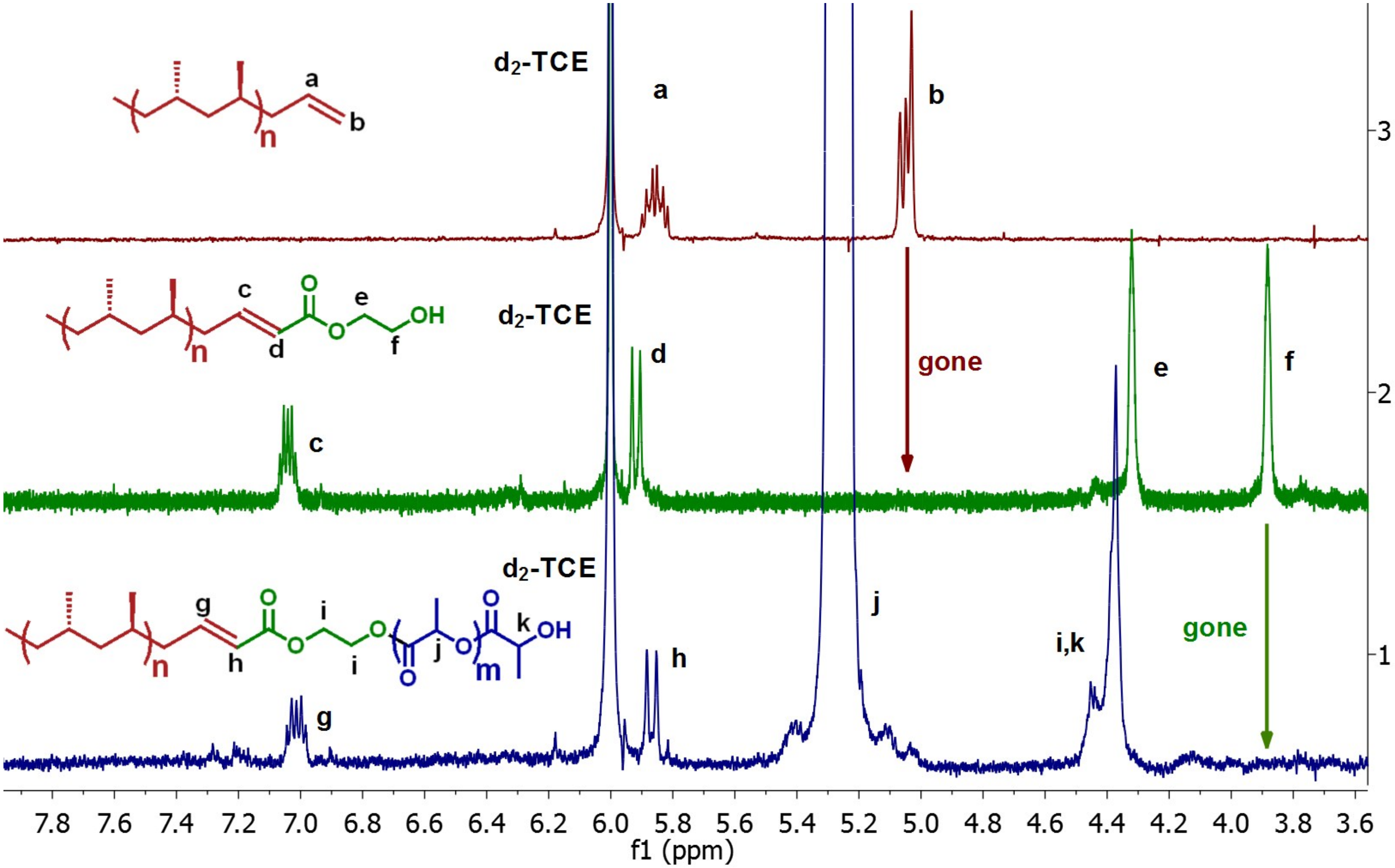


Figure S2: Stacked ^1H NMR for the synthesis of synPP-PLA

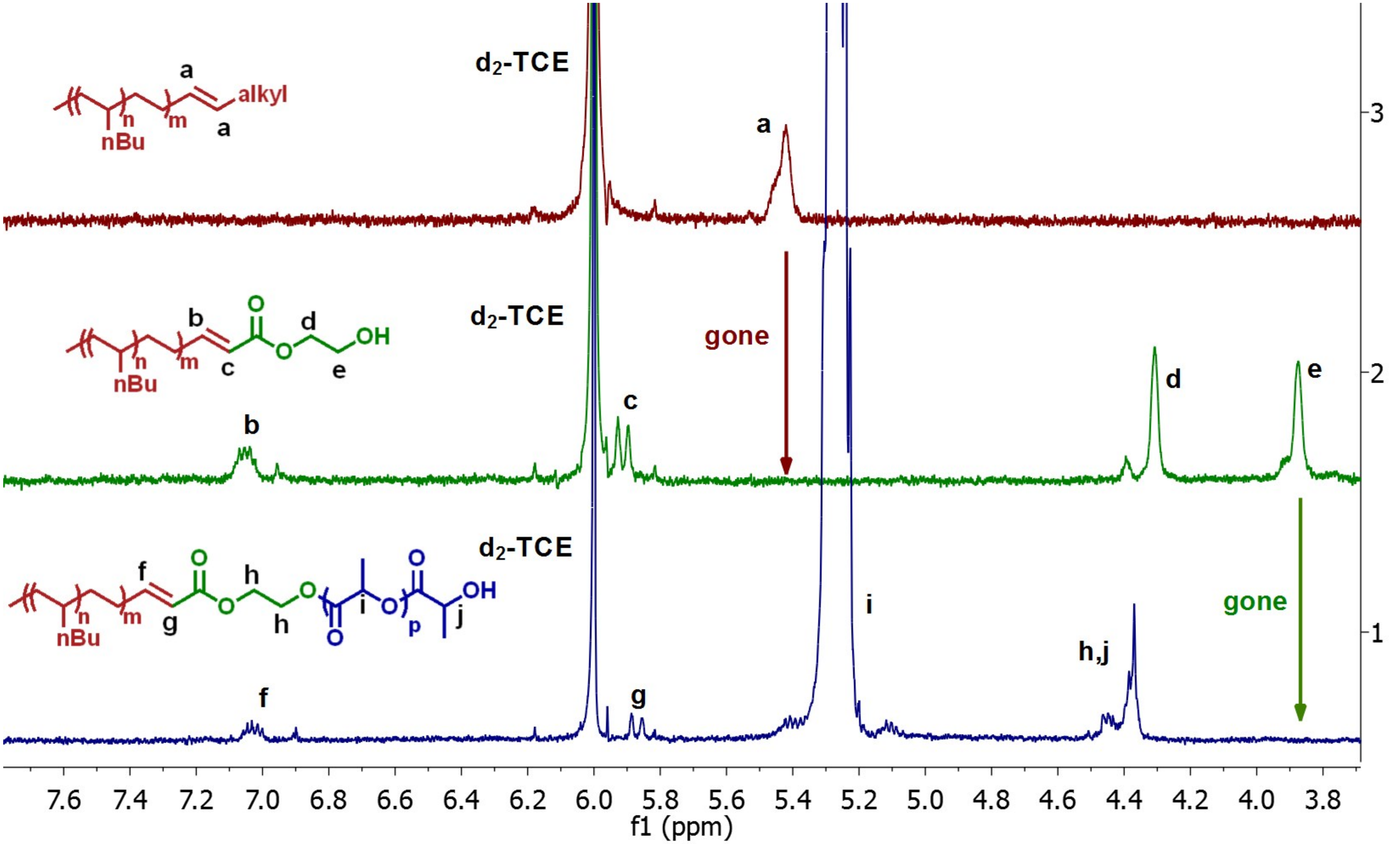


Figure S3: Stacked ^{1}H NMR for the synthesis of LLDPE-PLA

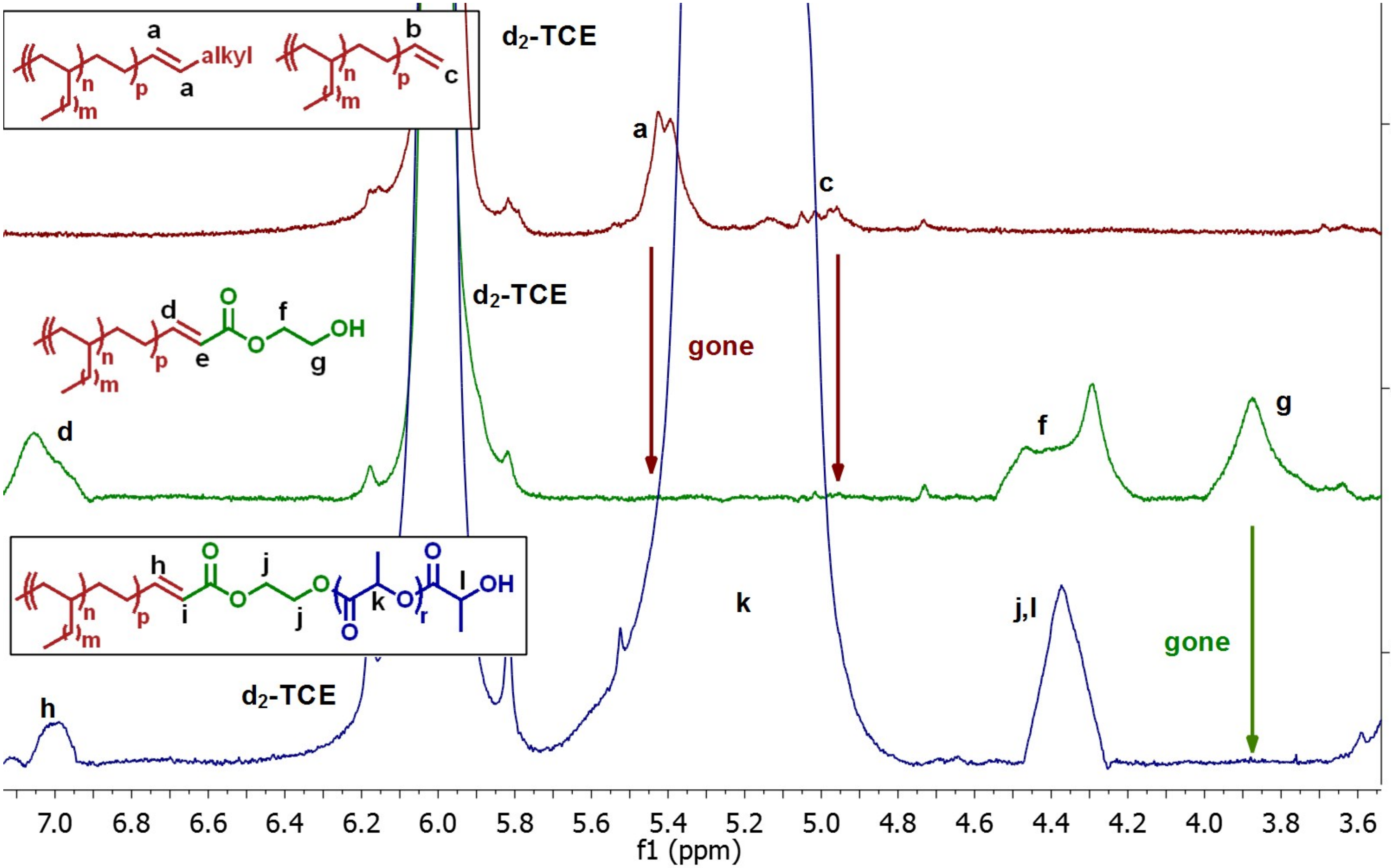


Figure S4: Stacked ^{1}H NMR for the synthesis of HBPE-PLA

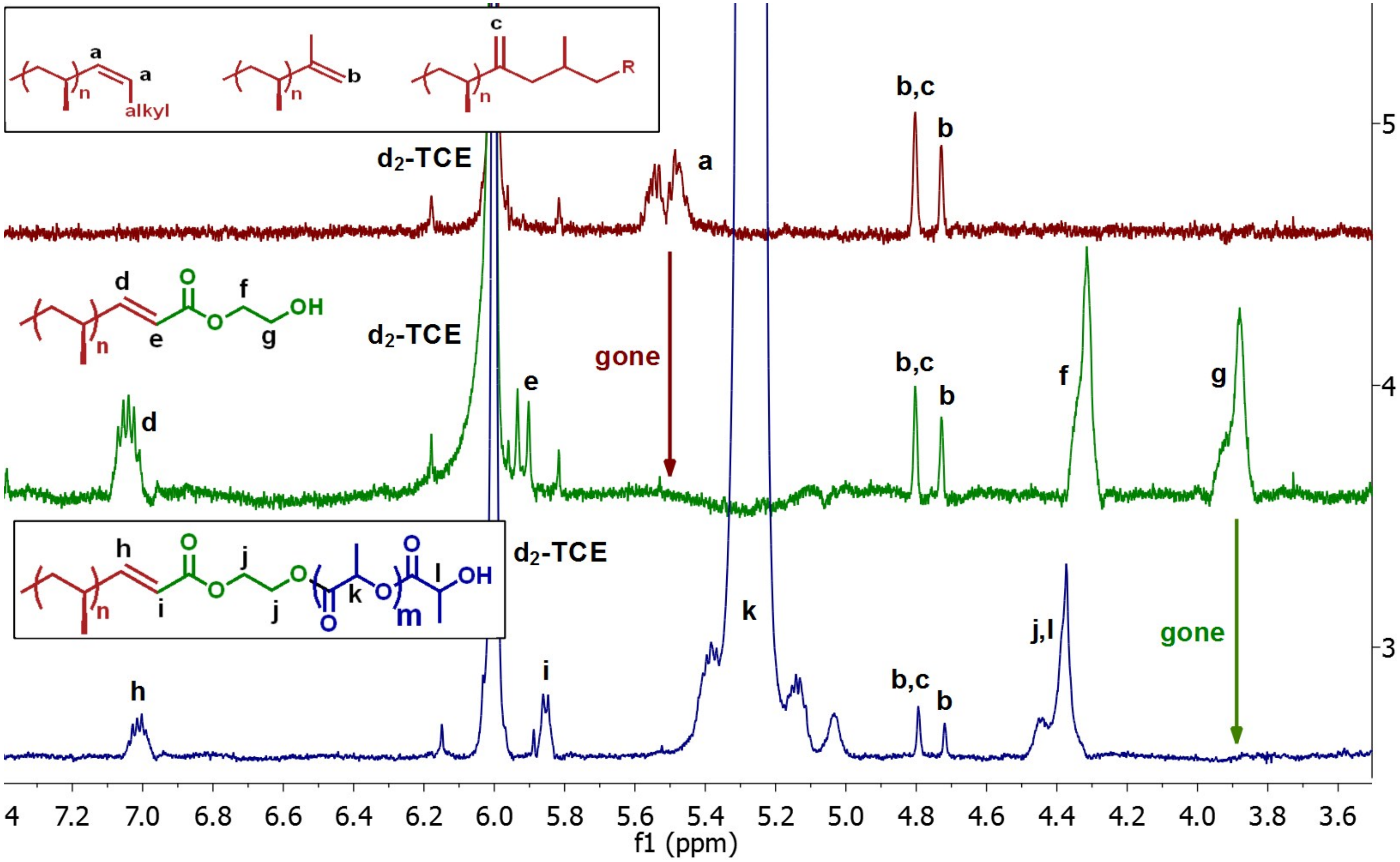


Figure S5: Stacked ^{1}H NMR for the synthesis of isoPP-PLA

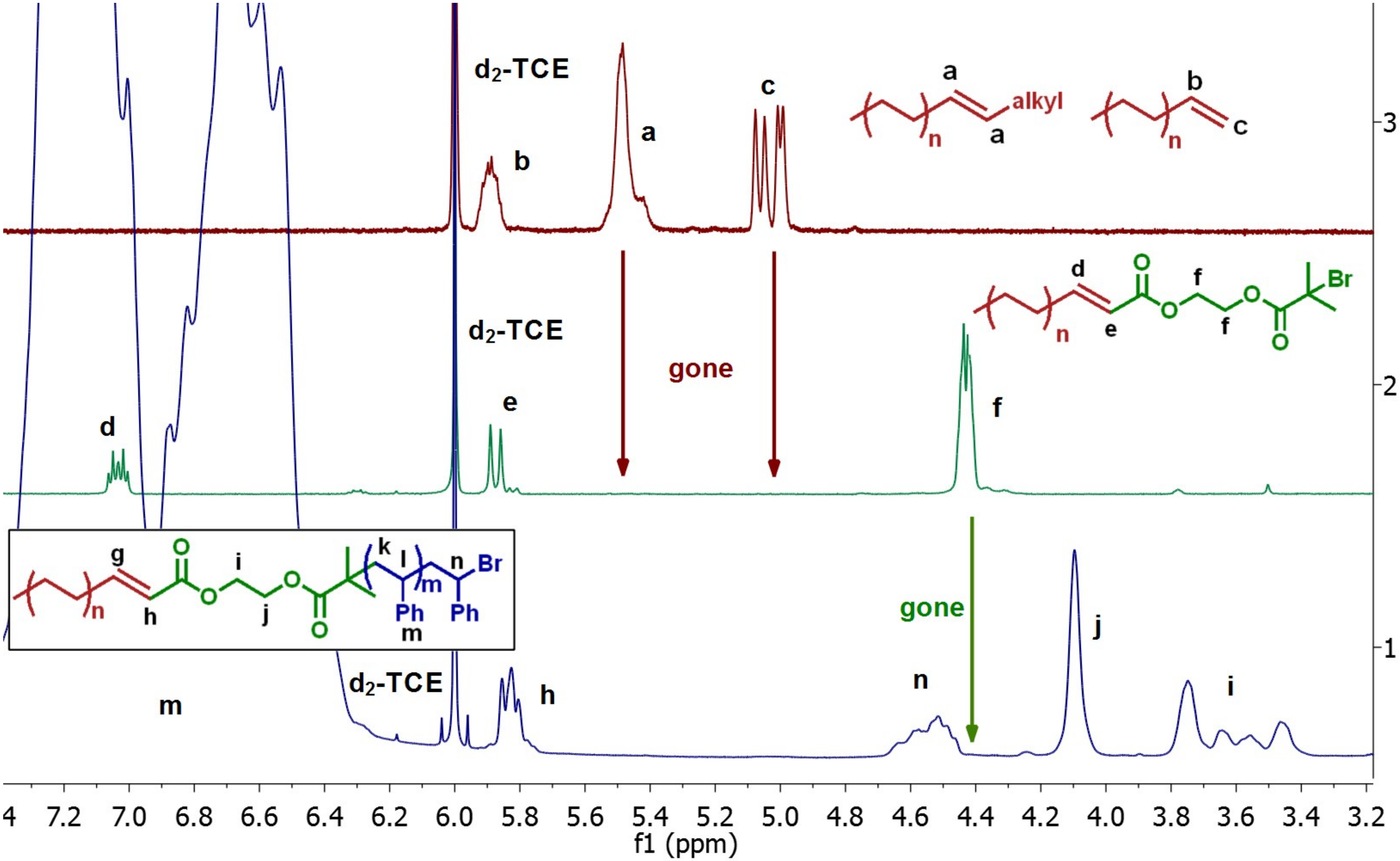


Figure S6: Stacked ^{1}H NMR for the synthesis of *l*-HDPE-PS

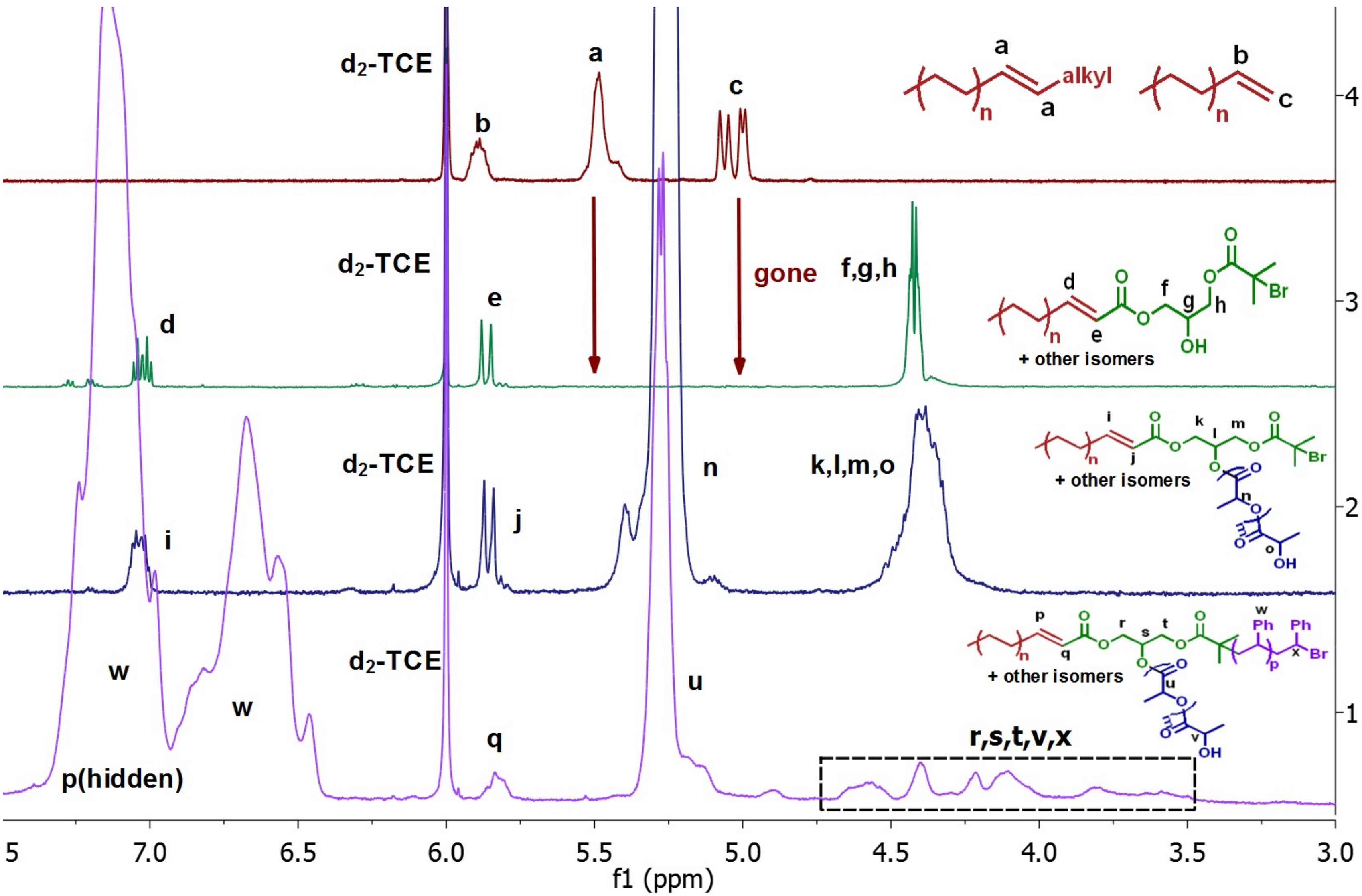


Figure S7: Stacked ^{1}H NMR for the synthesis of *l*-HDPE-PLA-PS

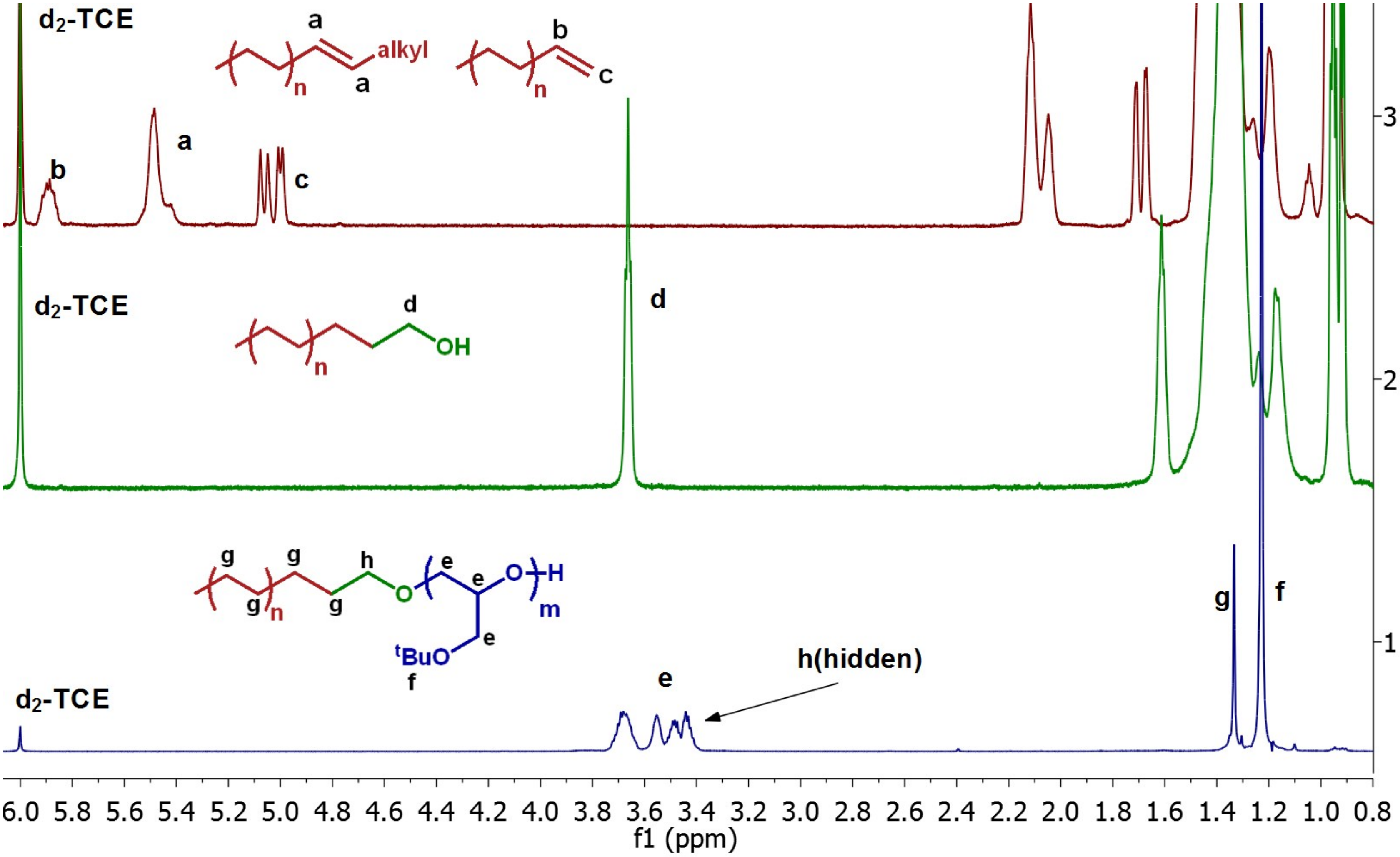


Figure S8: Stacked ^{1}H NMR for the synthesis of *l*-HDPE-P(tBuGE)

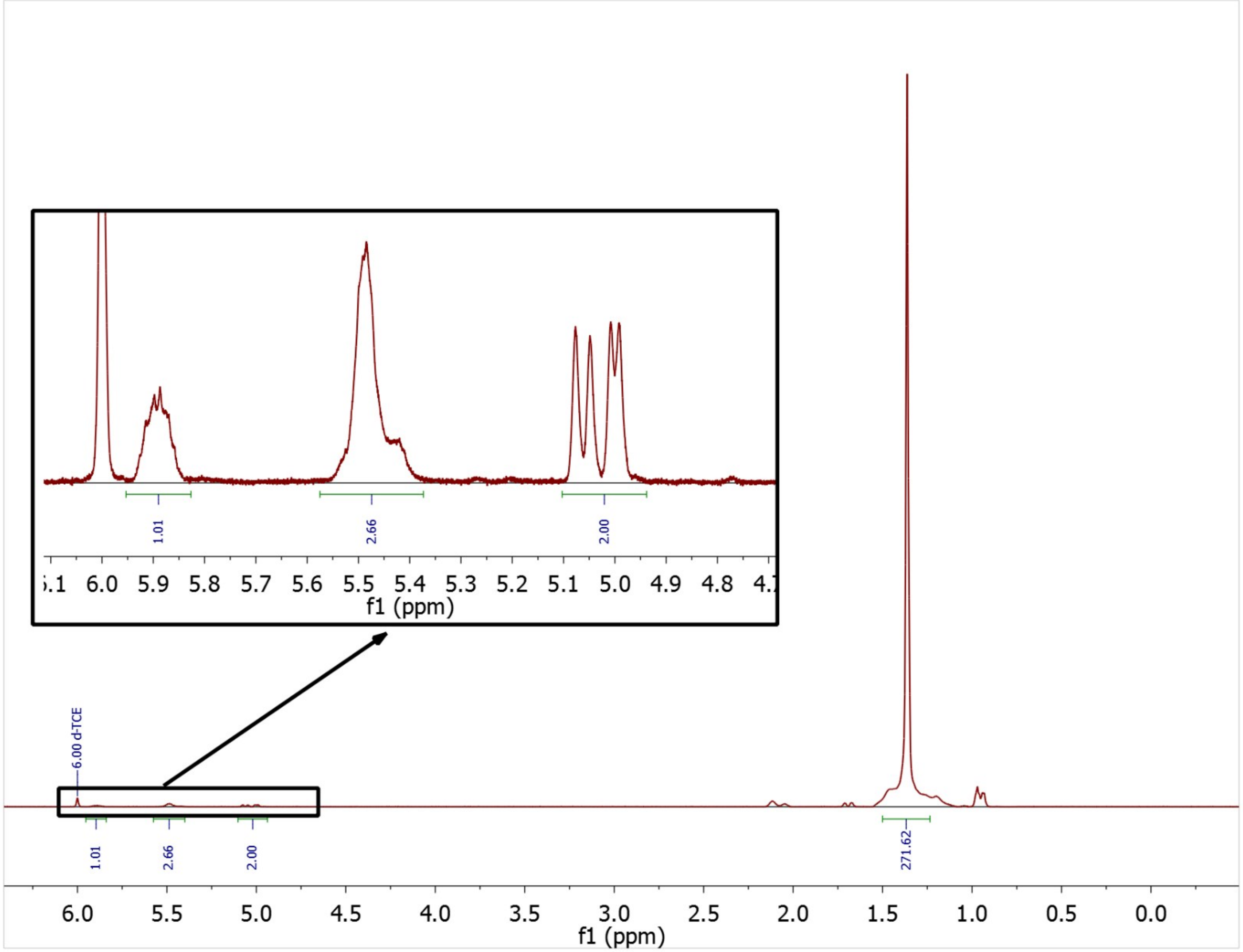


Figure S9: ^{1}H NMR of *l*-HDPE (d_2-TCE, 500 MHz, 95 ^{o}C)

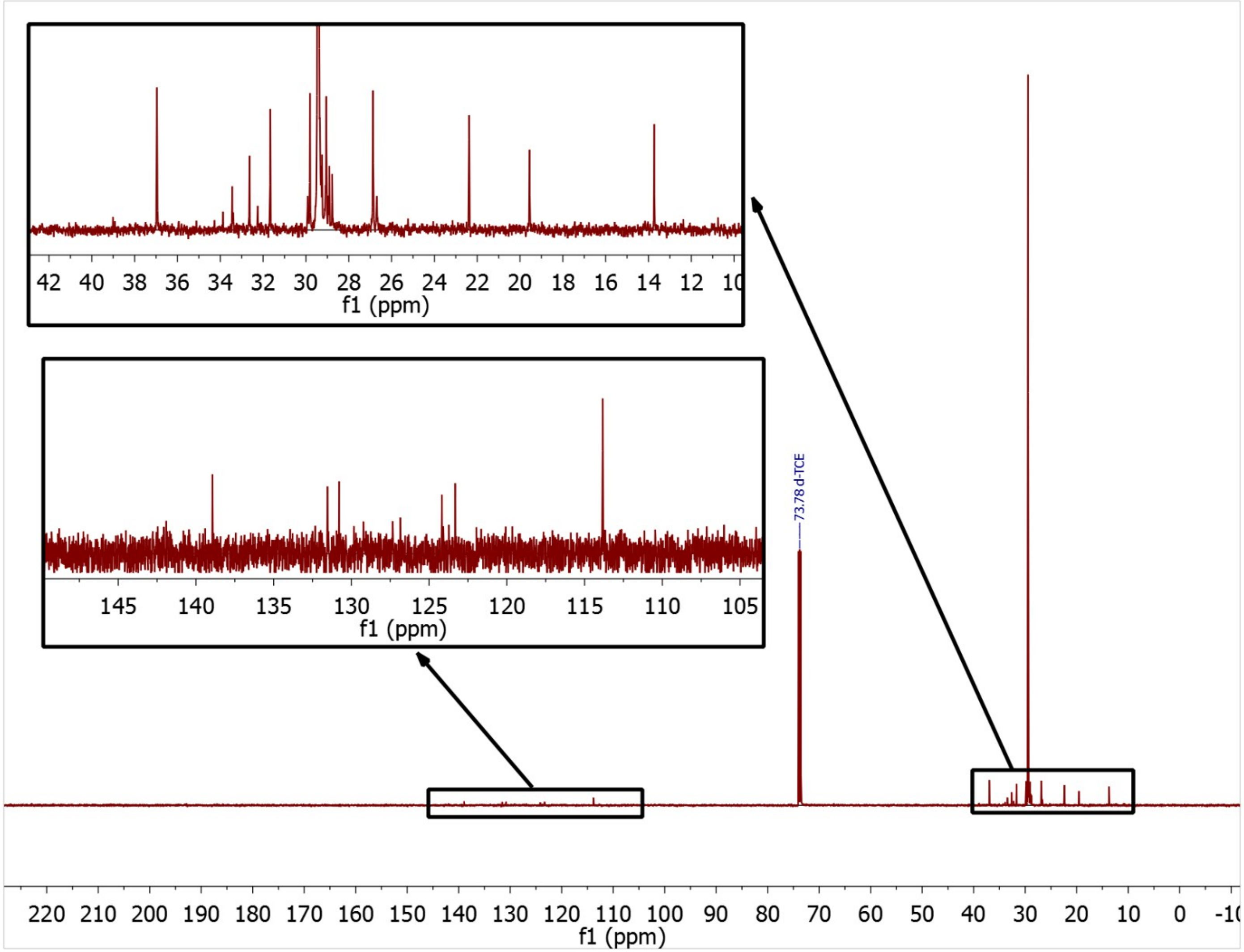


Figure S10: ^{13}C NMR of *l*-HDPE (d$_2$-TCE, 500 MHz, 95 ^{o}C)

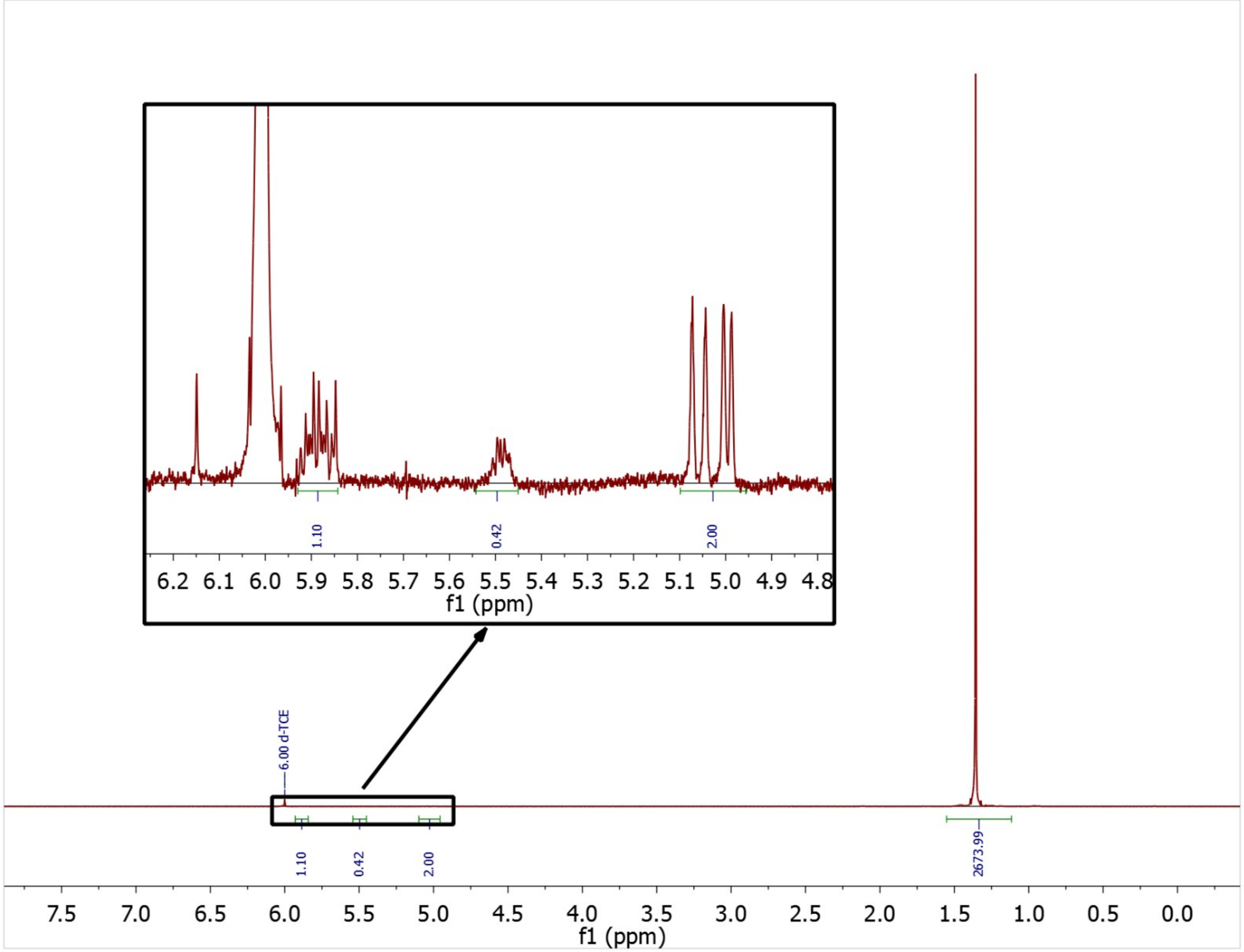


Figure S11: ^{1}H NMR of *h*-HDPE (d_2-TCE, 600 MHz, 120 ^{o}C)

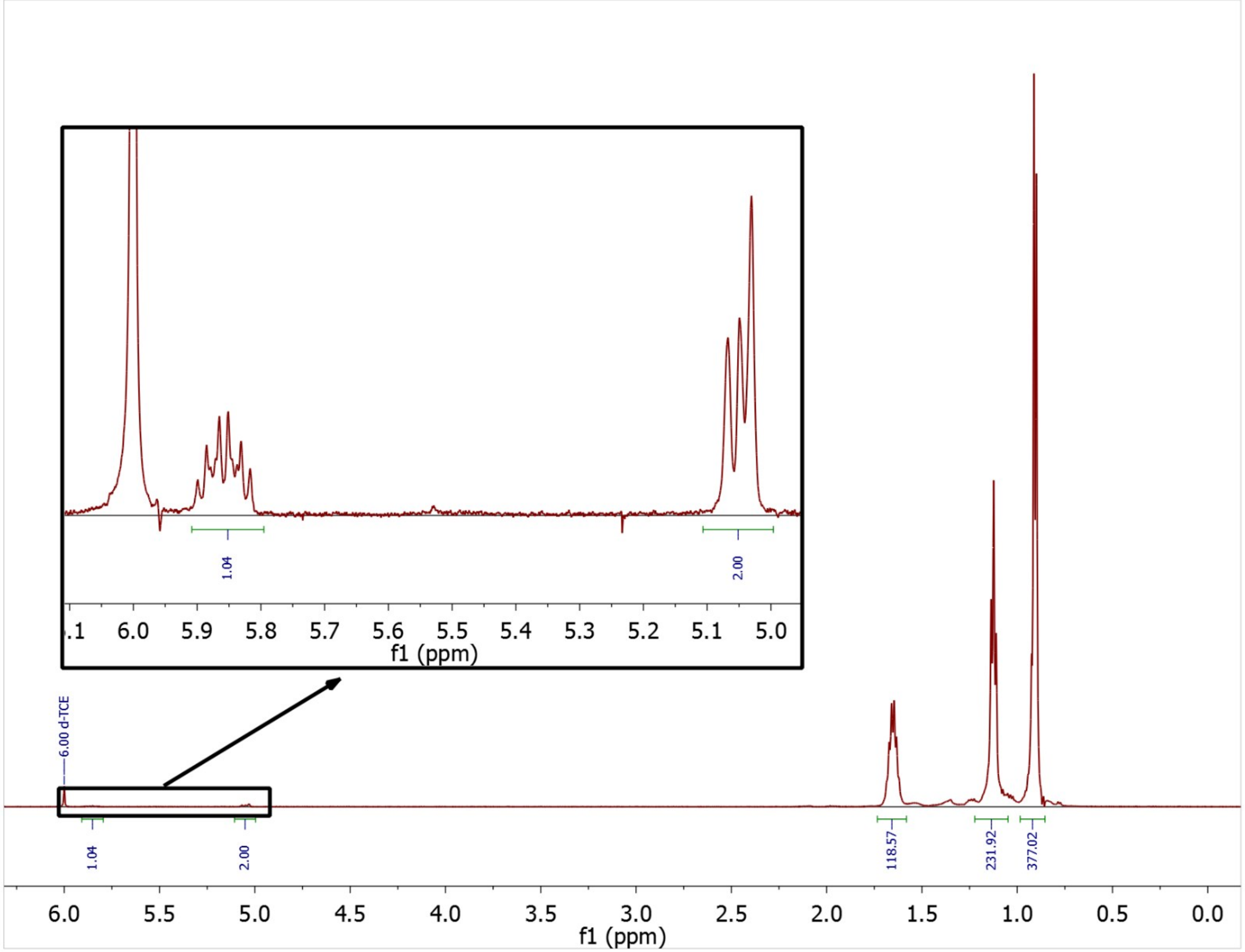


Figure S12: ^{1}H NMR of synPP (d_2-TCE, 500 MHz, 95 ^{o}C)

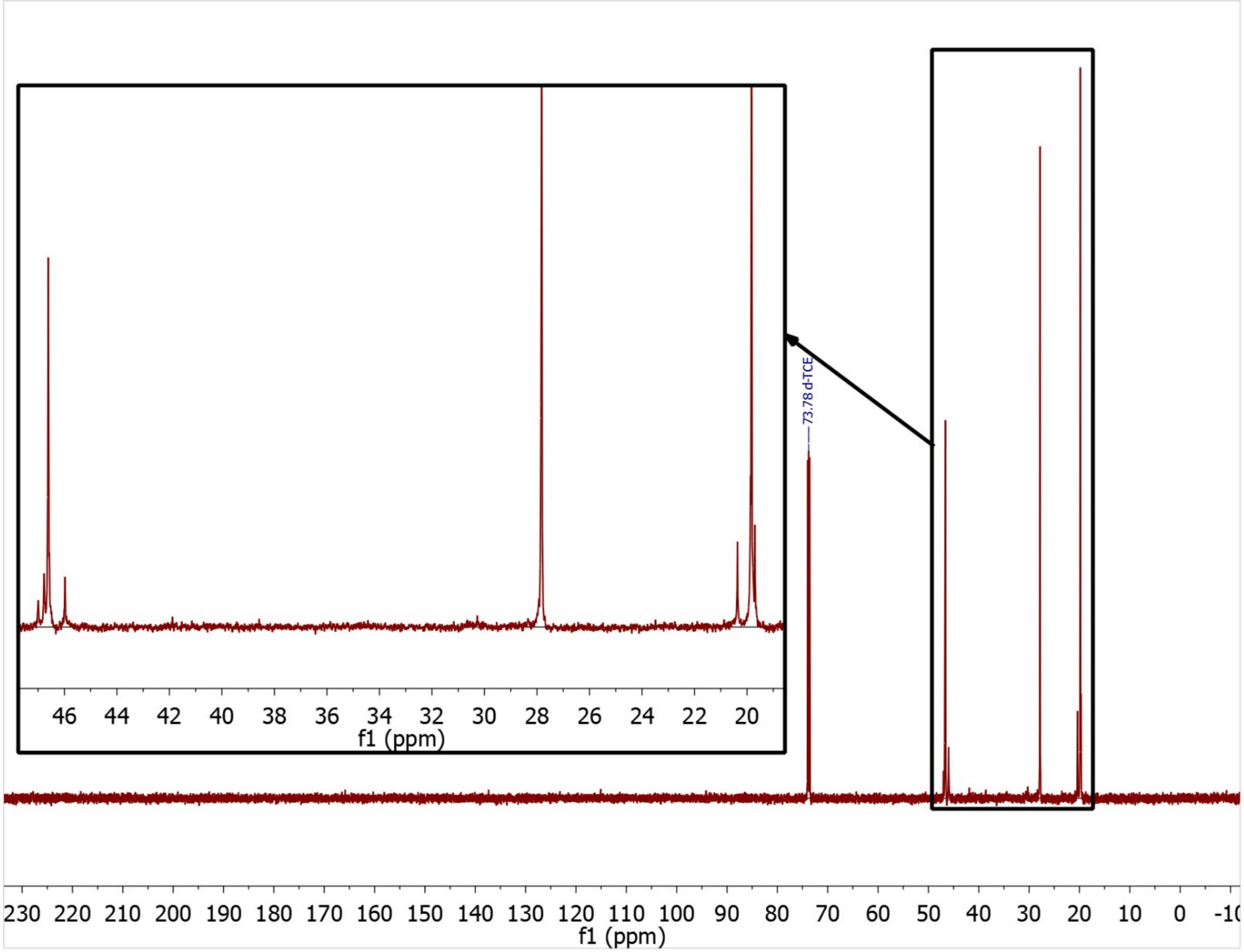


Figure S13 ^{13}C NMR of synPP (d$_2$-TCE, 500 MHz, 95 ^{o}C)

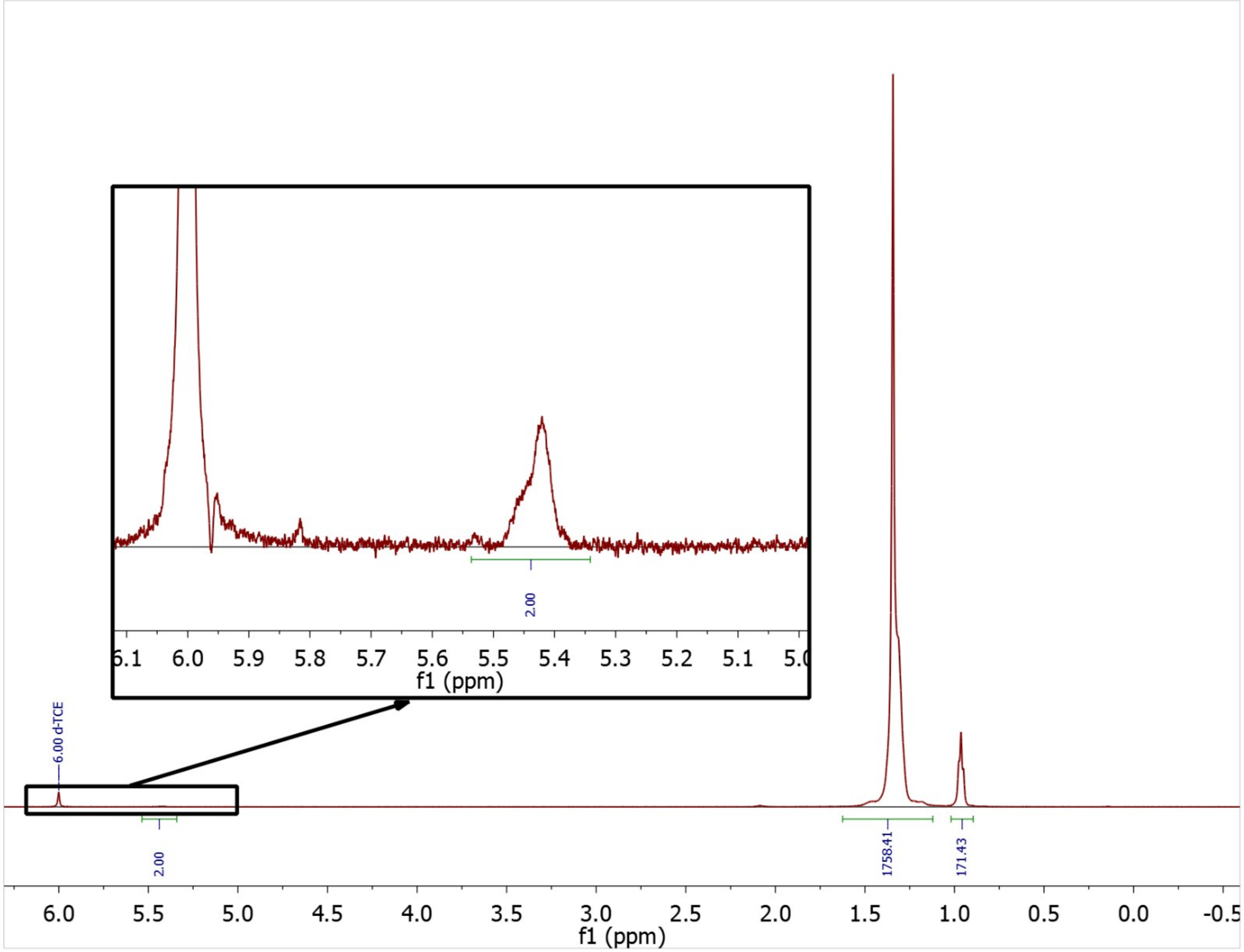


Figure S14: ^{1}H NMR of LLDPE (d_2-TCE, 500 MHz, 95 ^{o}C)

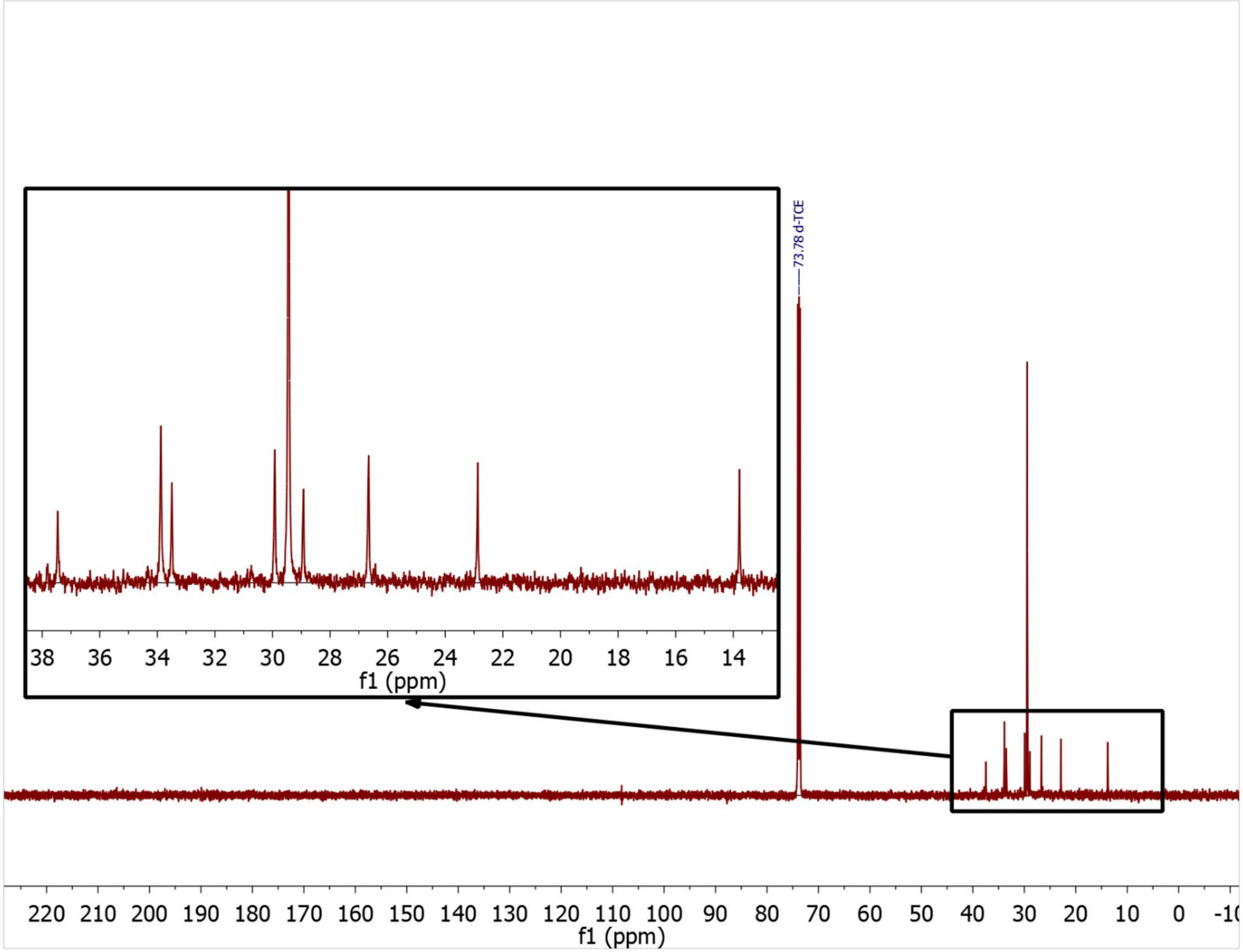


Figure S15: ^{13}C NMR of LLDPE (d_2-TCE, 500 MHz, 95 ^{o}C)

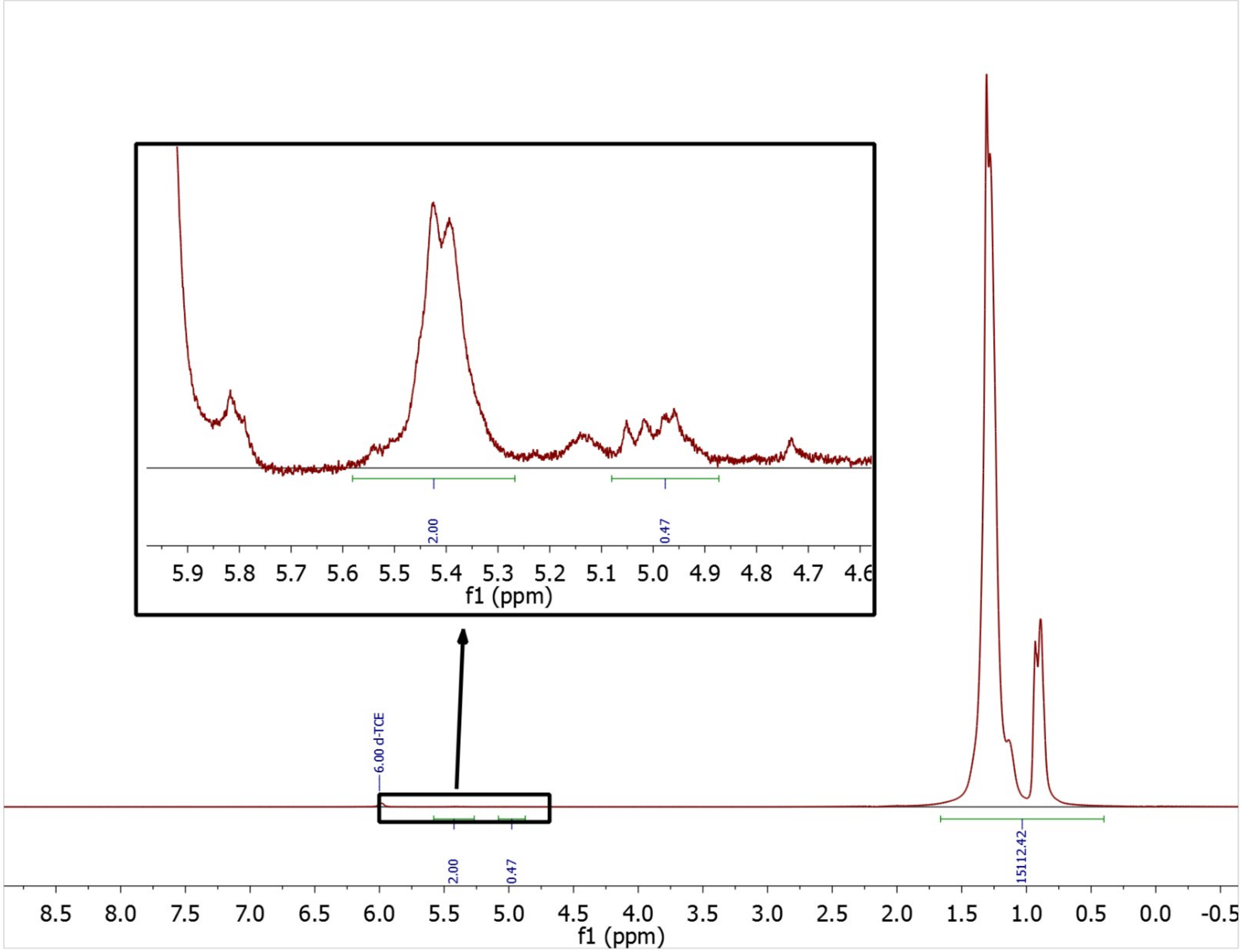


Figure S16: ^{1}H NMR of HBPE (d_2-TCE, 500 MHz, 25 ^{o}C)

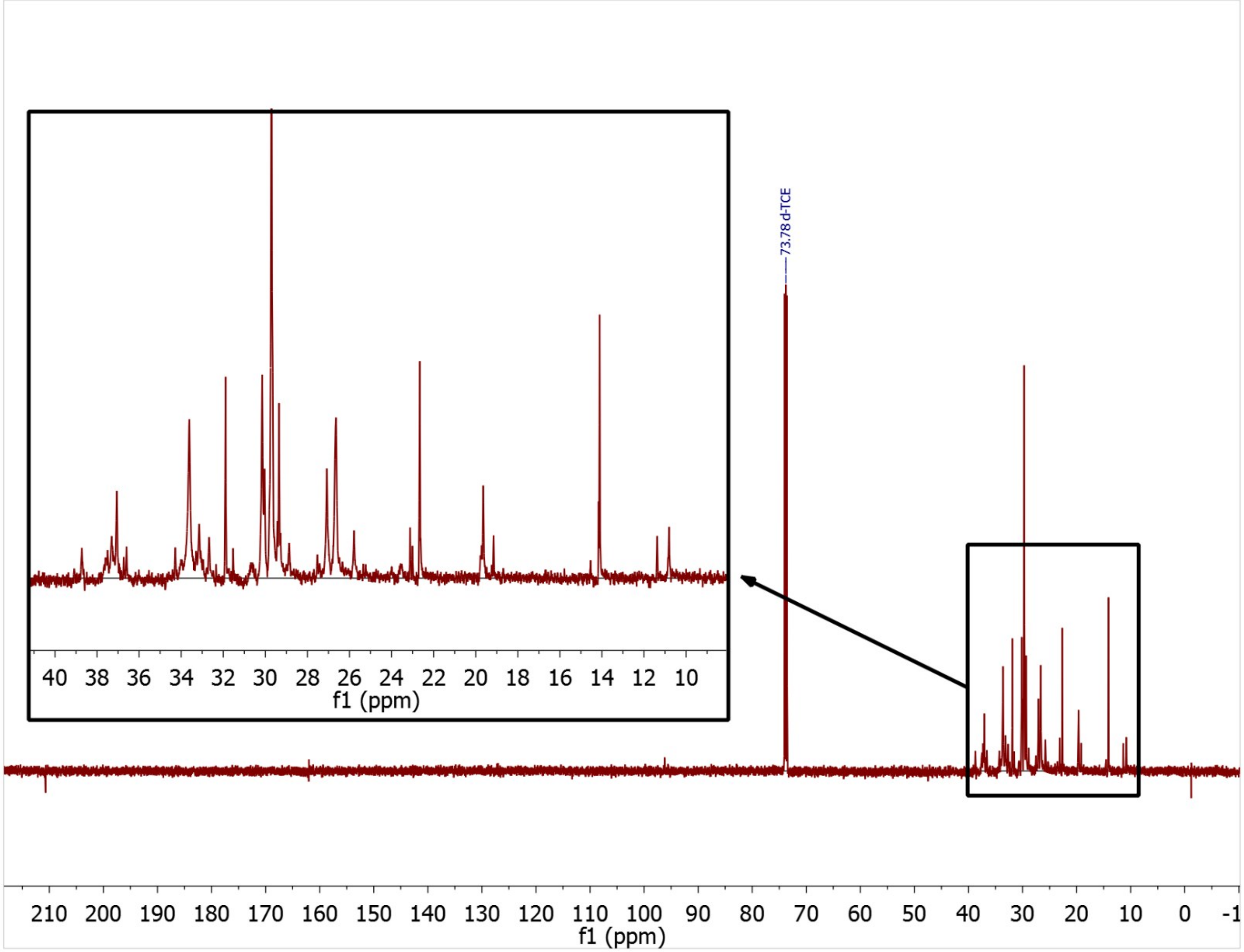


Figure S17: ^{13}C NMR of HBPE (d$_2$-TCE, 500 MHz, 25 ^{o}C)

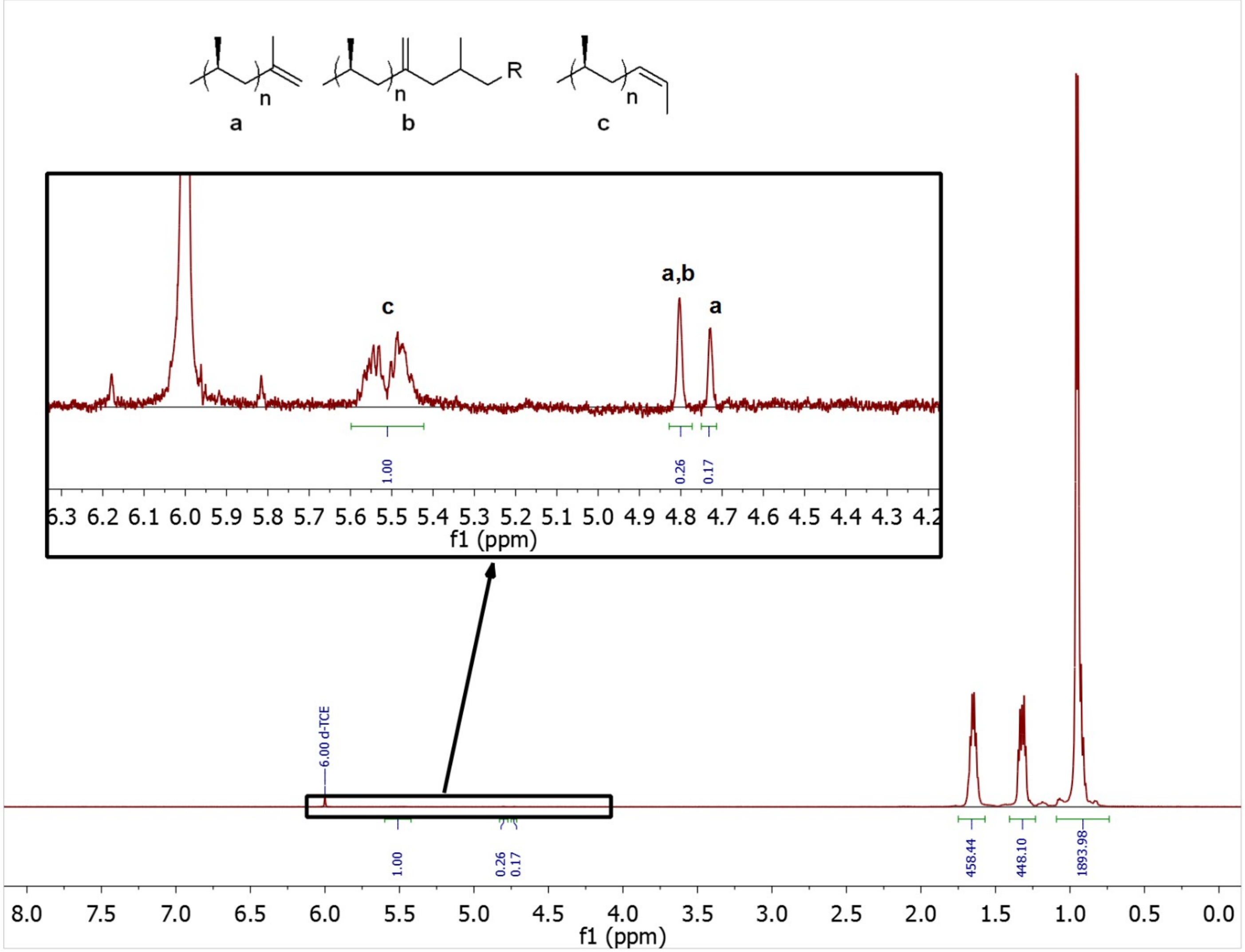


Figure S18: ^{1}H NMR for the synthesis of isoPP (d$_2$-TCE, 500 MHz, 95 ^{o}C)

Assignment made based on literature.[6]

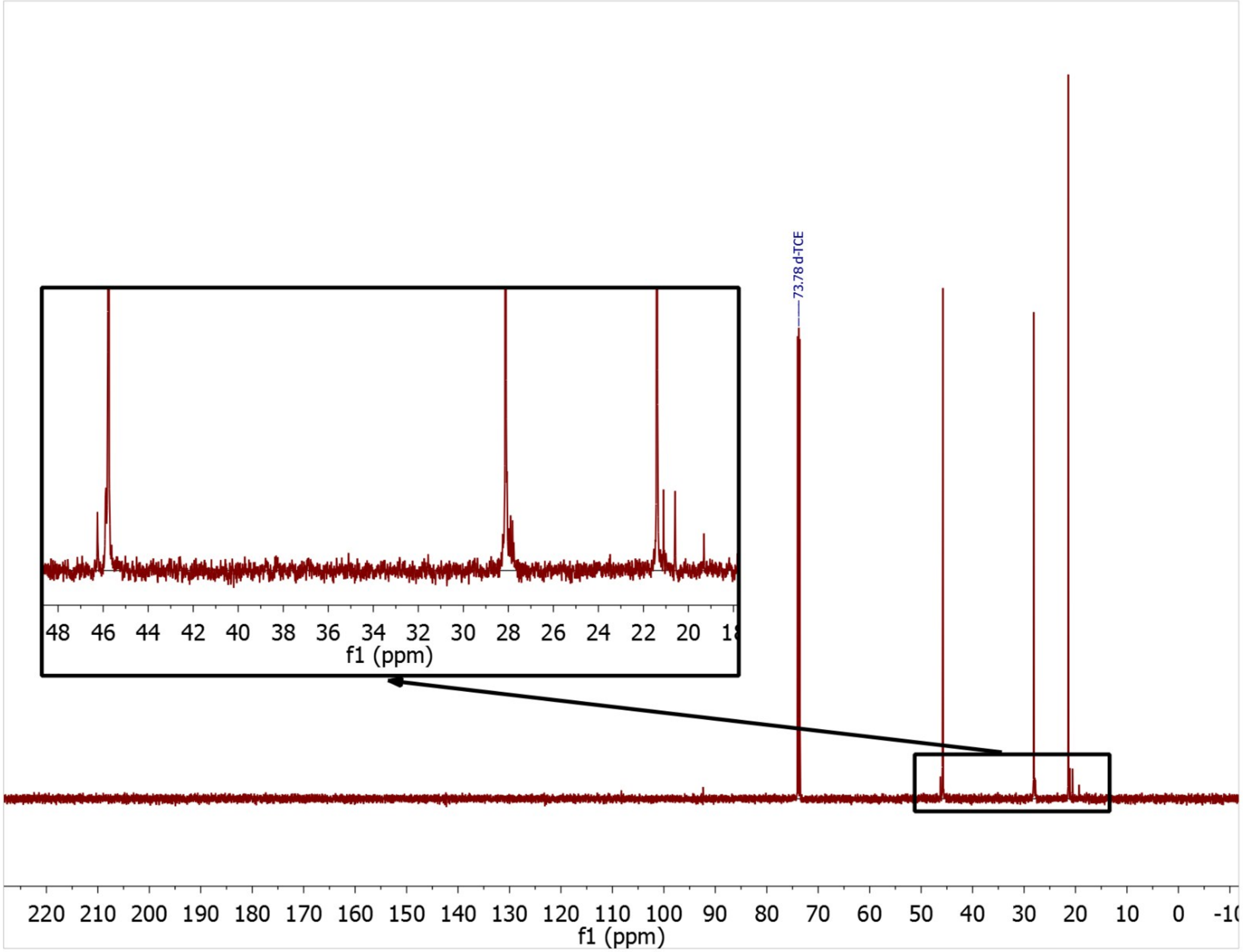


Figure S19: ^{13}C NMR for the synthesis of isoPP (d_2-TCE, 500 MHz, 95 °C)

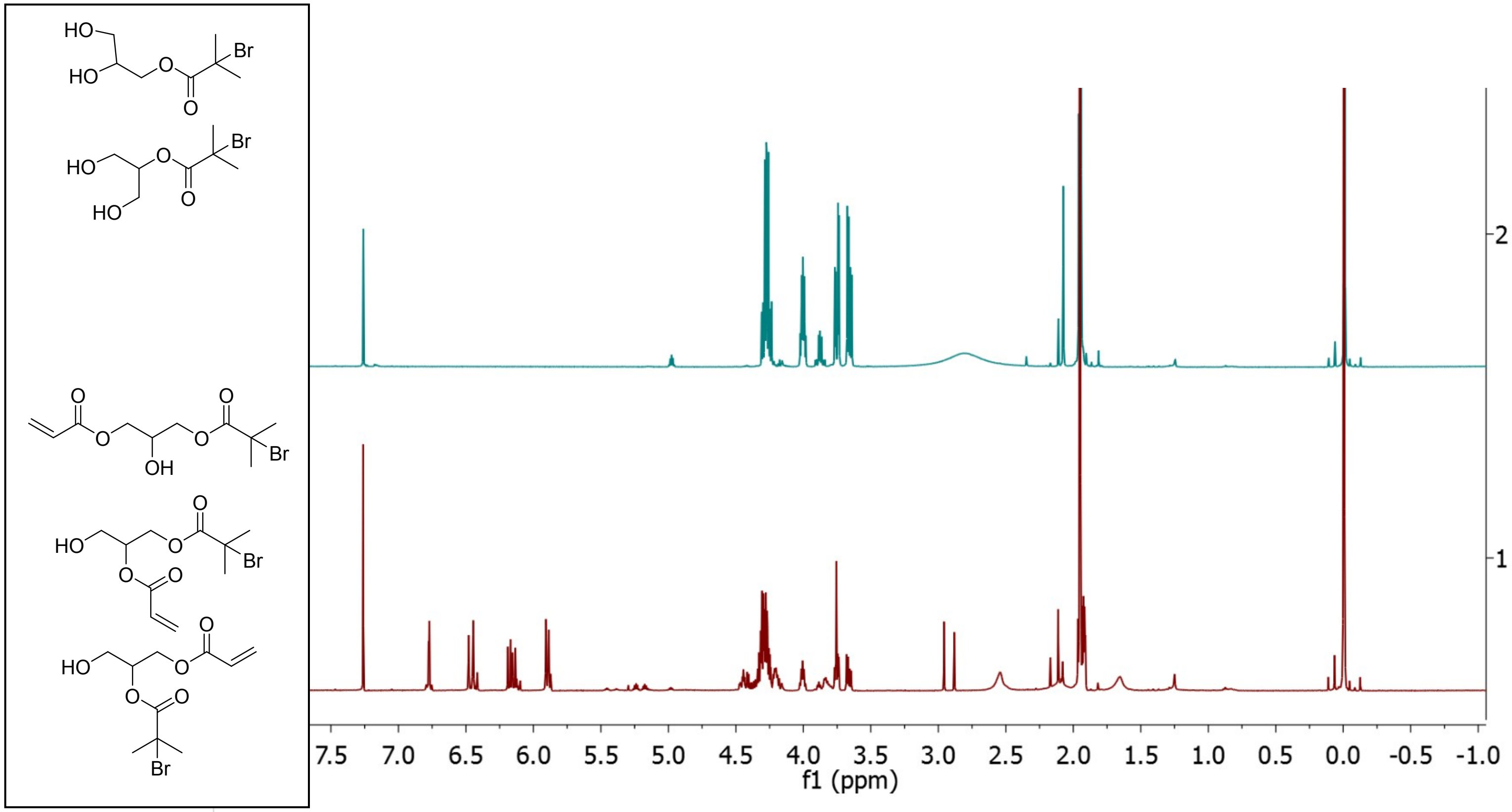


Figure S20: ^{1}H NMR of 3 arm star coupling partner ($CDCl_3$, 500 MHz, 25 ^{o}C)

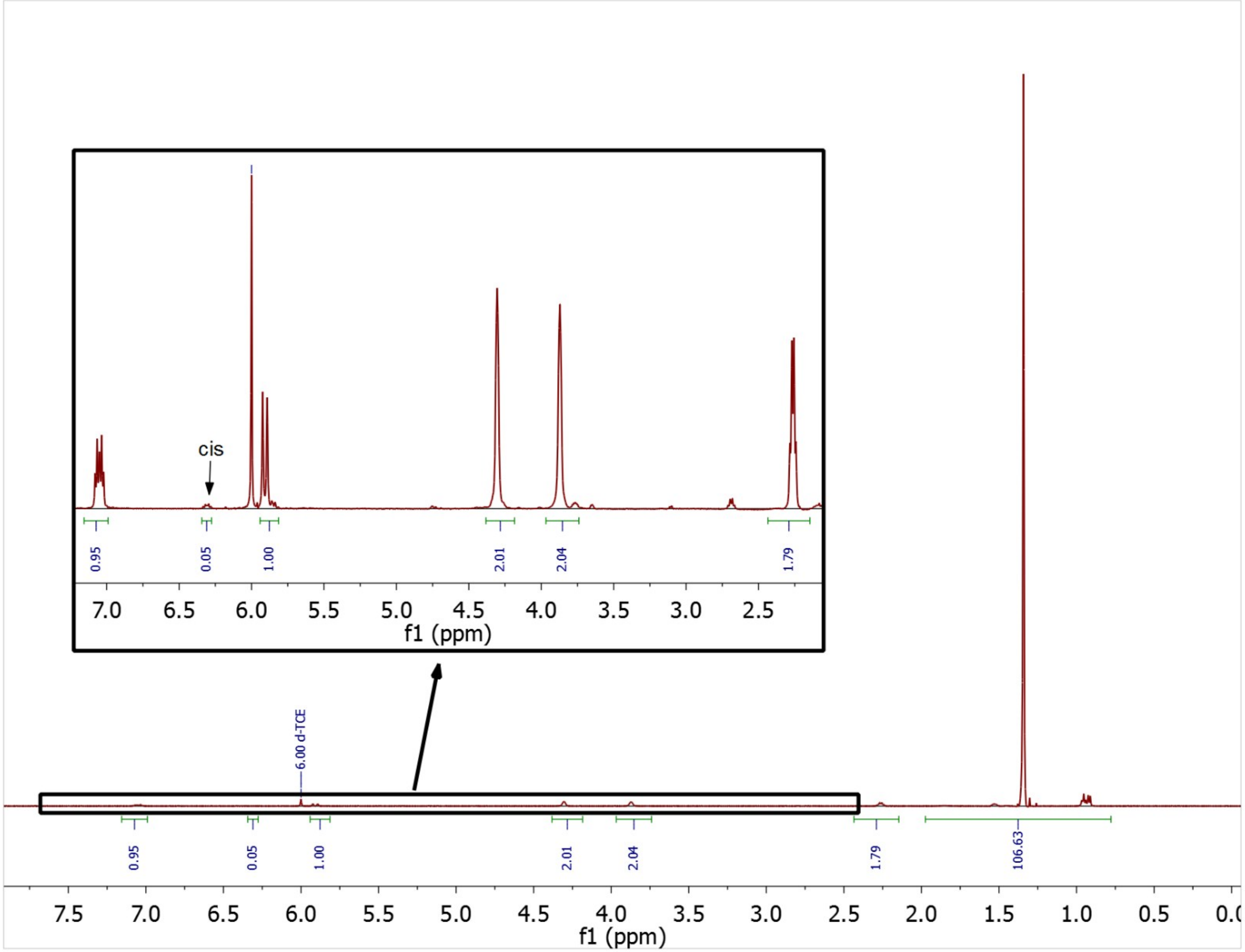


Figure S21: ^{1}H NMR of *l*-HDPE-HEA (d$_2$-TCE, 500 MHz, 95 ^{o}C)

Note: Both 95 % trans / 5 % cis was observed in ^{1}H NMR and identified based on literature.[11]

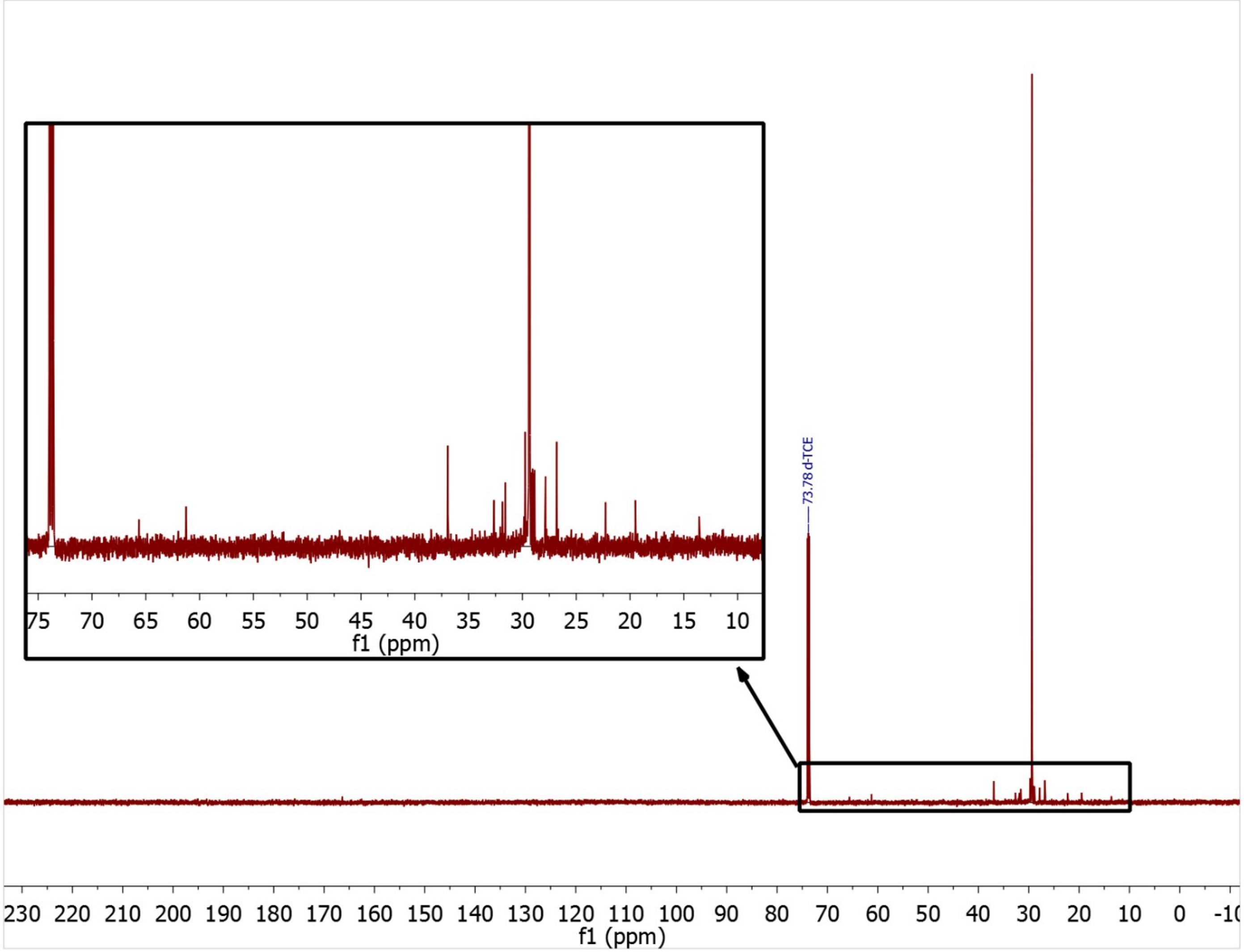


Figure S22: ^{13}C NMR of *l*-HDPE-HEA (d$_2$-TCE, 500 MHz, 95 ^{o}C)

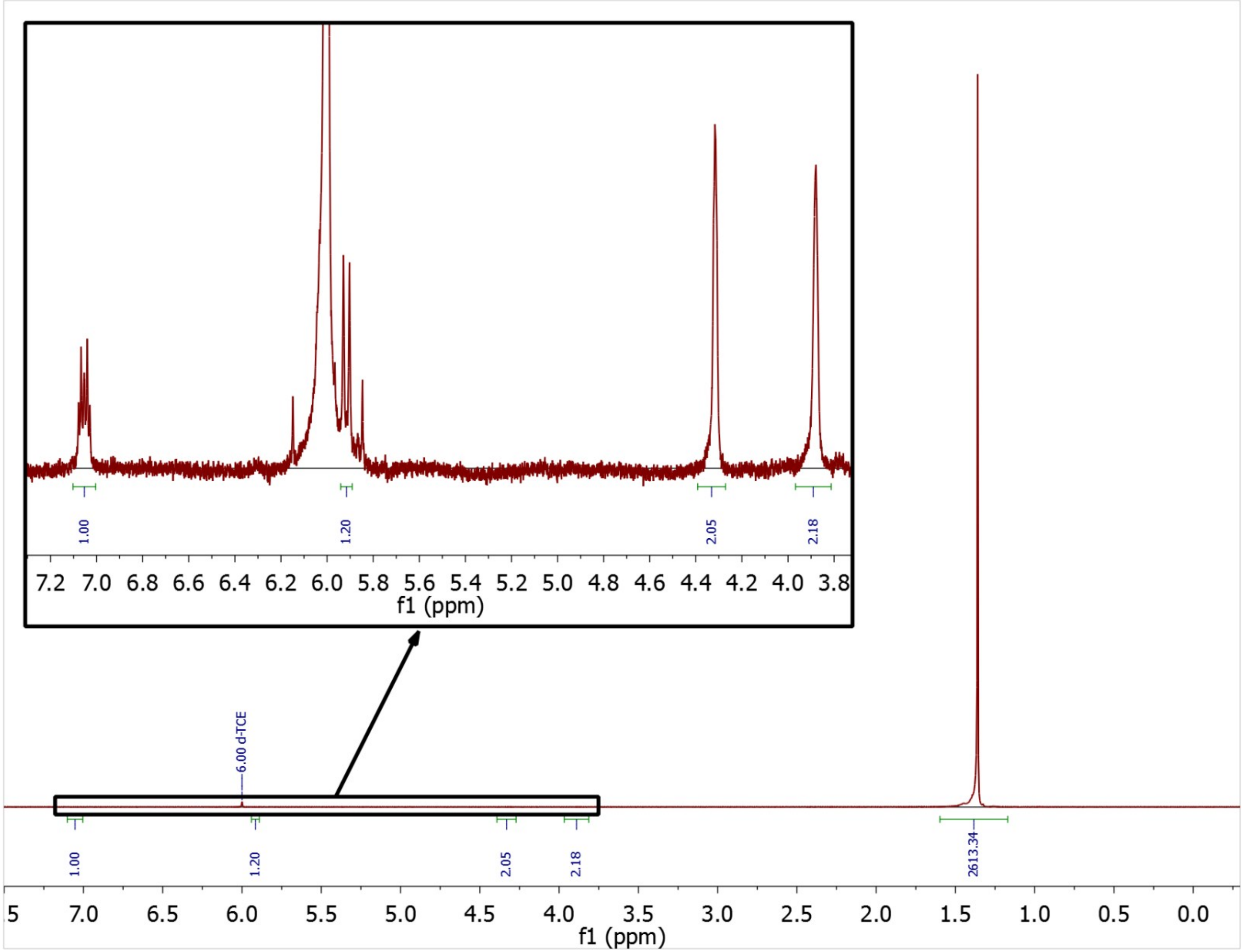


Figure S23: ^{1}H NMR of *h*-HDPE-HEA (d$_2$-TCE, 600 MHz,120 ^{o}C)

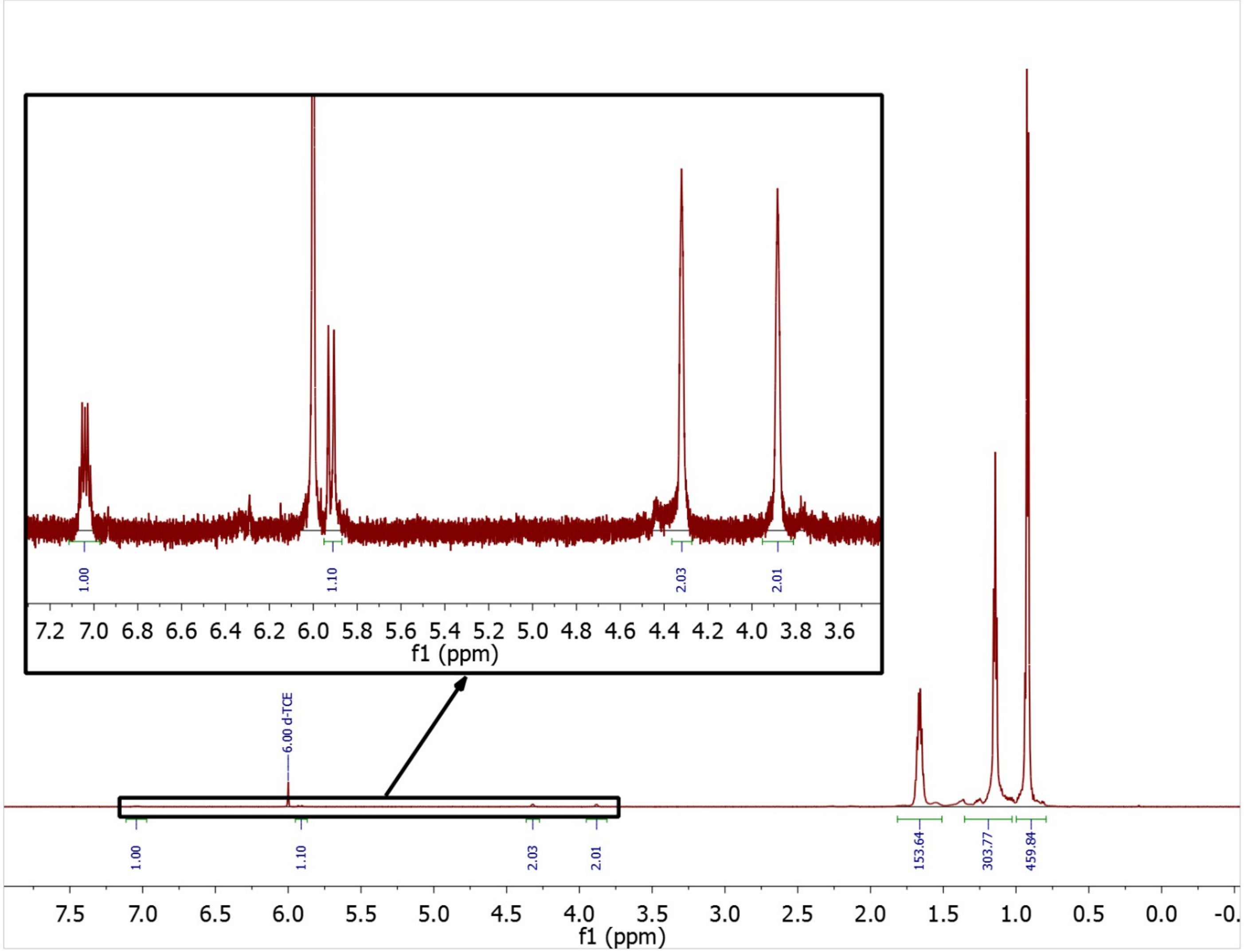


Figure S24: ^{1}H NMR of synPP-HEA (d$_2$-TCE, 500 MHz, 95 ^{o}C)

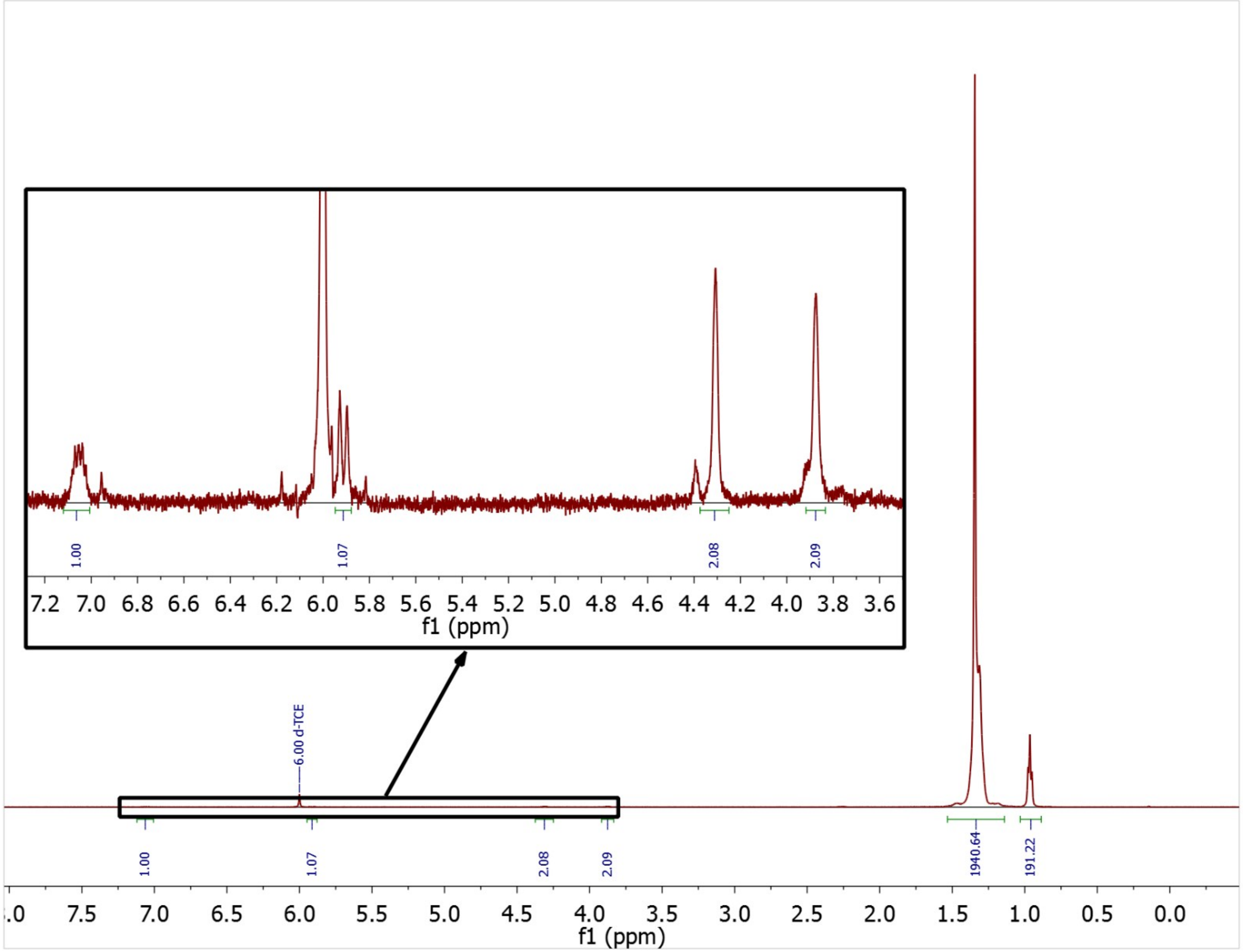


Figure S25: ^{1}H NMR of LLDPE-HEA (d_2-TCE, 500 MHz, 95 ^{o}C)

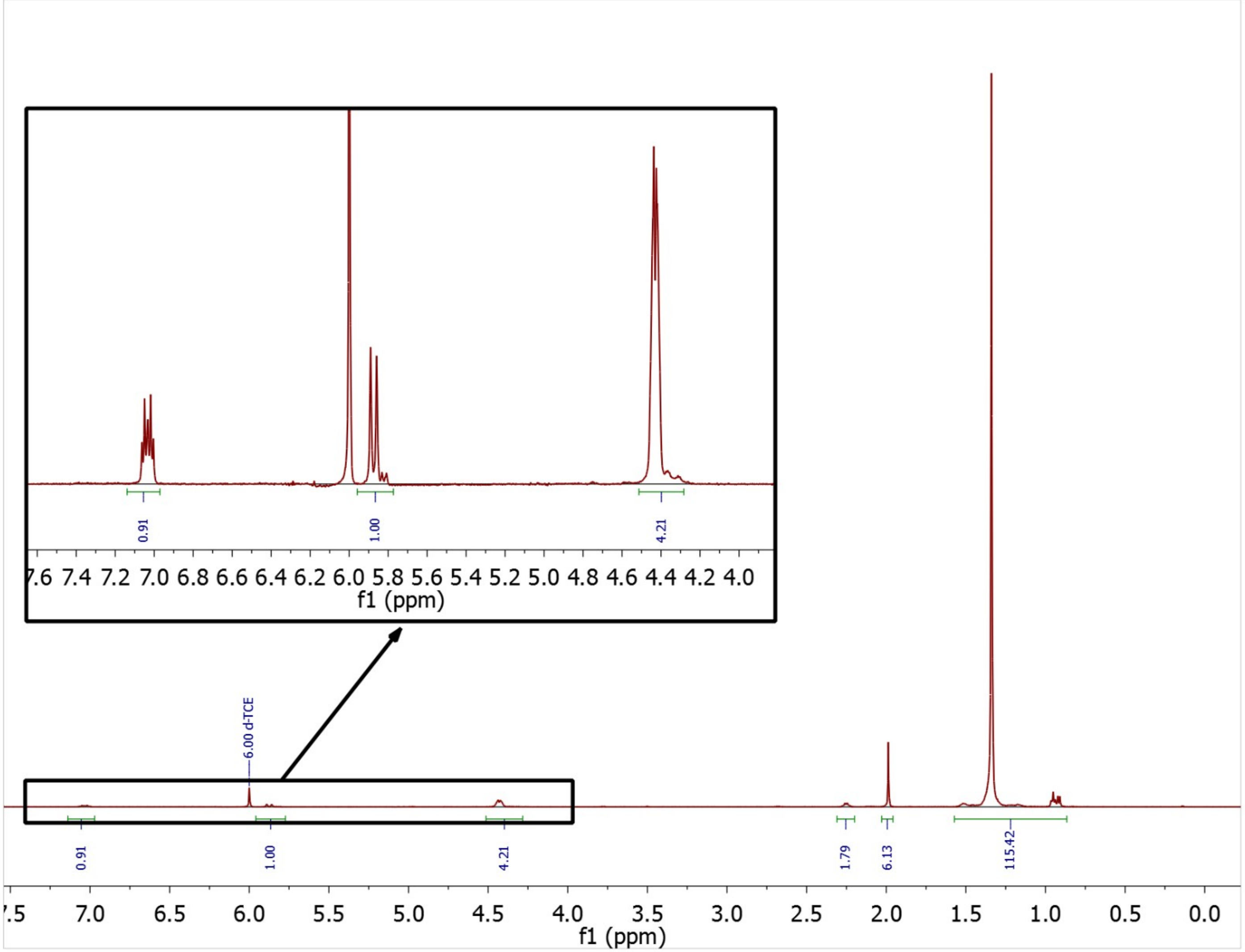


Figure S26: ^{1}H NMR of *l*-HDPE-BIEA (d_2-TCE, 500 MHz, 95 ^{o}C)

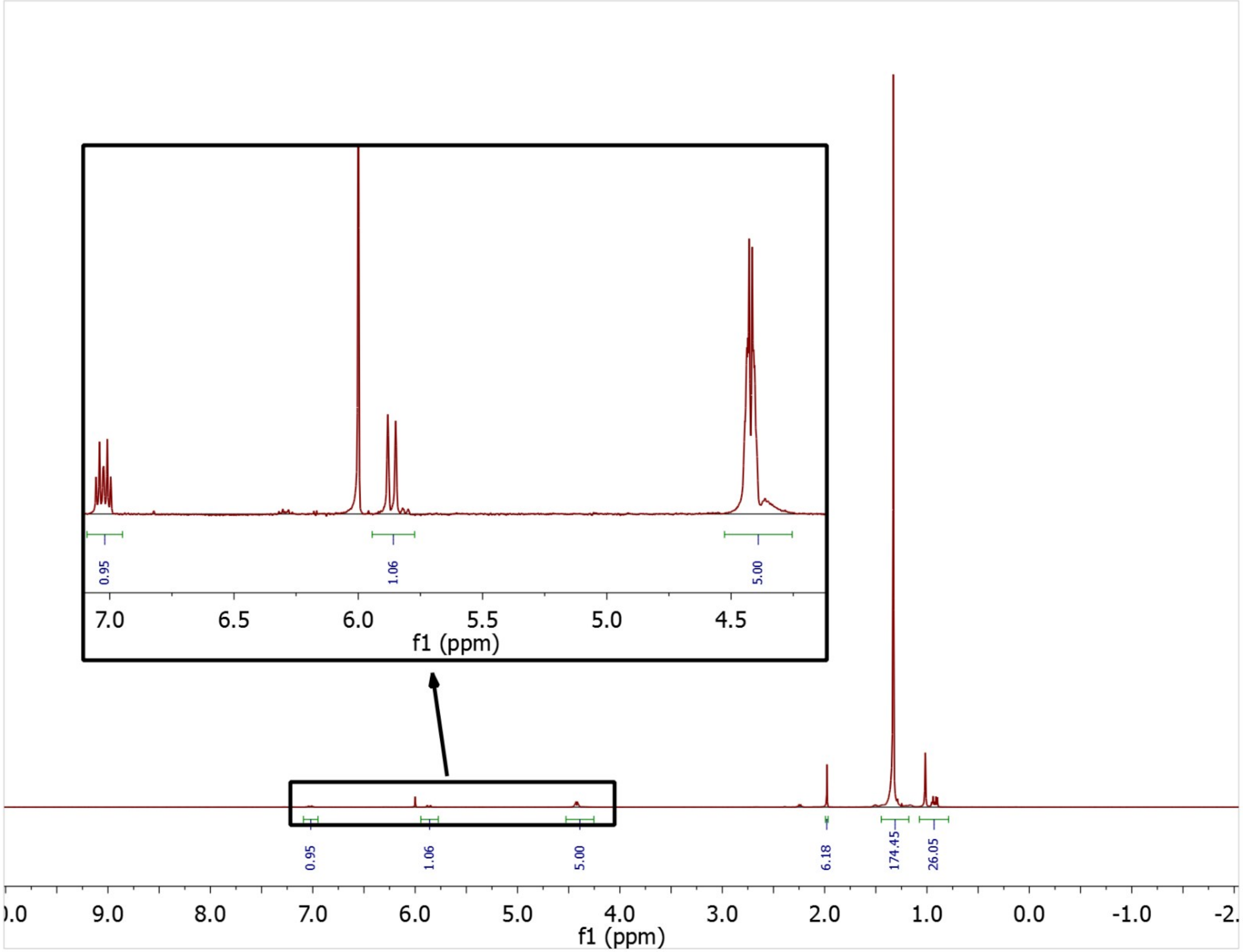


Figure S27: ^{1}H NMR of *l*-HDPE-3 arm star (d$_2$-TCE, 500 MHz, 95 ^{o}C)

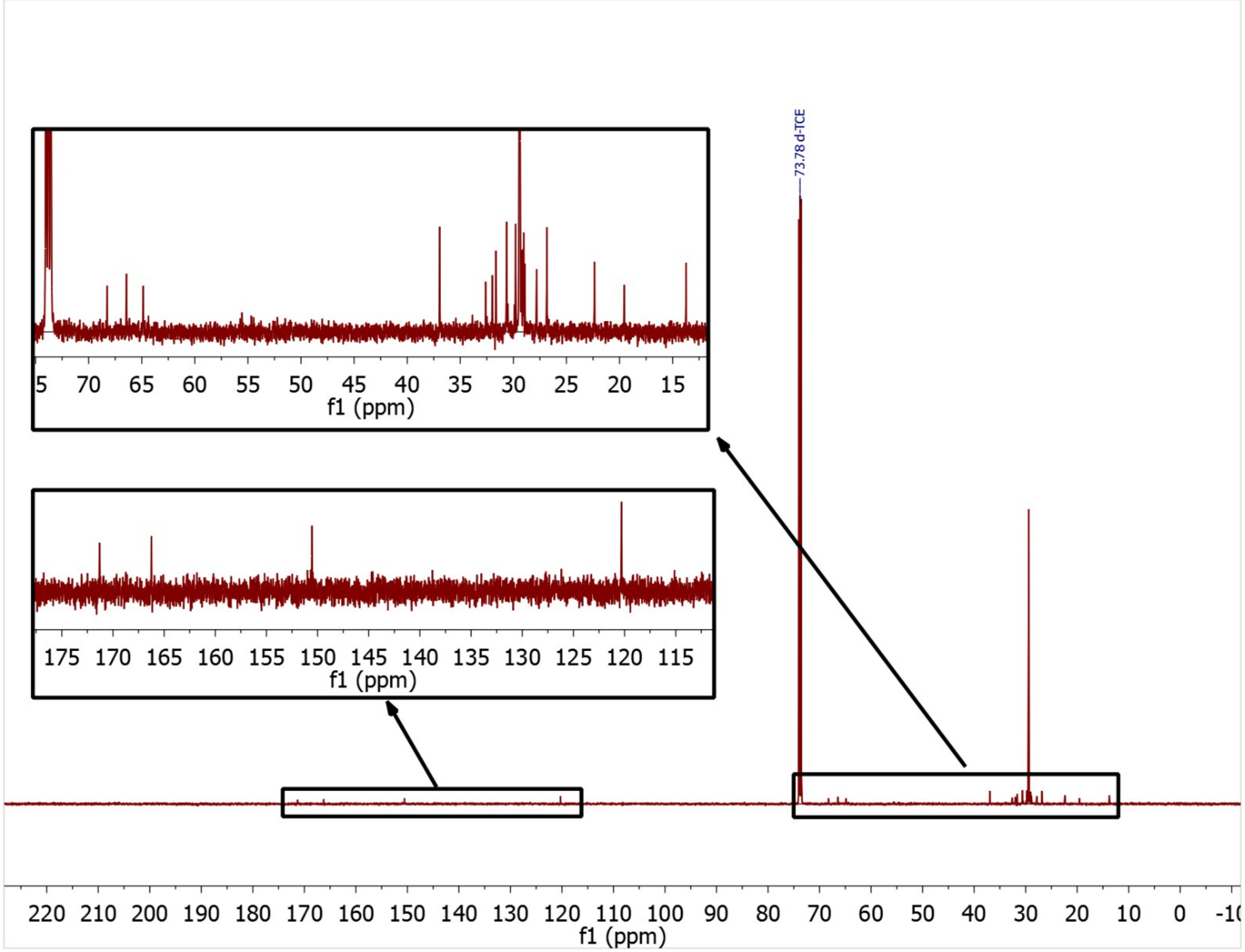


Figure S28: ^{13}C NMR of *l*-HDPE-3 arm star (d$_2$-TCE, 500 MHz, 95 ^{o}C)

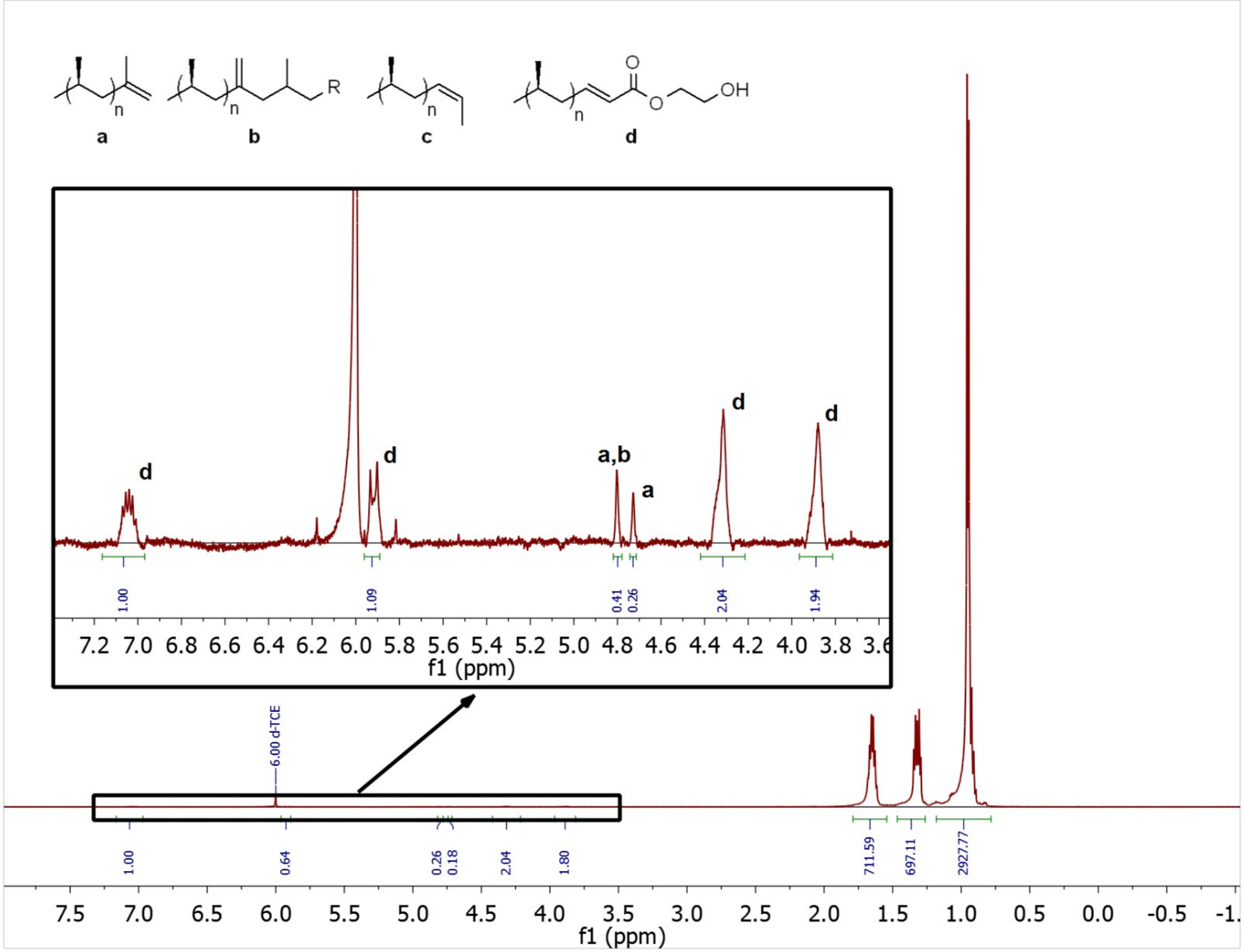


Figure S29: ^{1}H NMR of isoPP-HEA (d_2-TCE, 500 MHz, 95 ^{o}C)

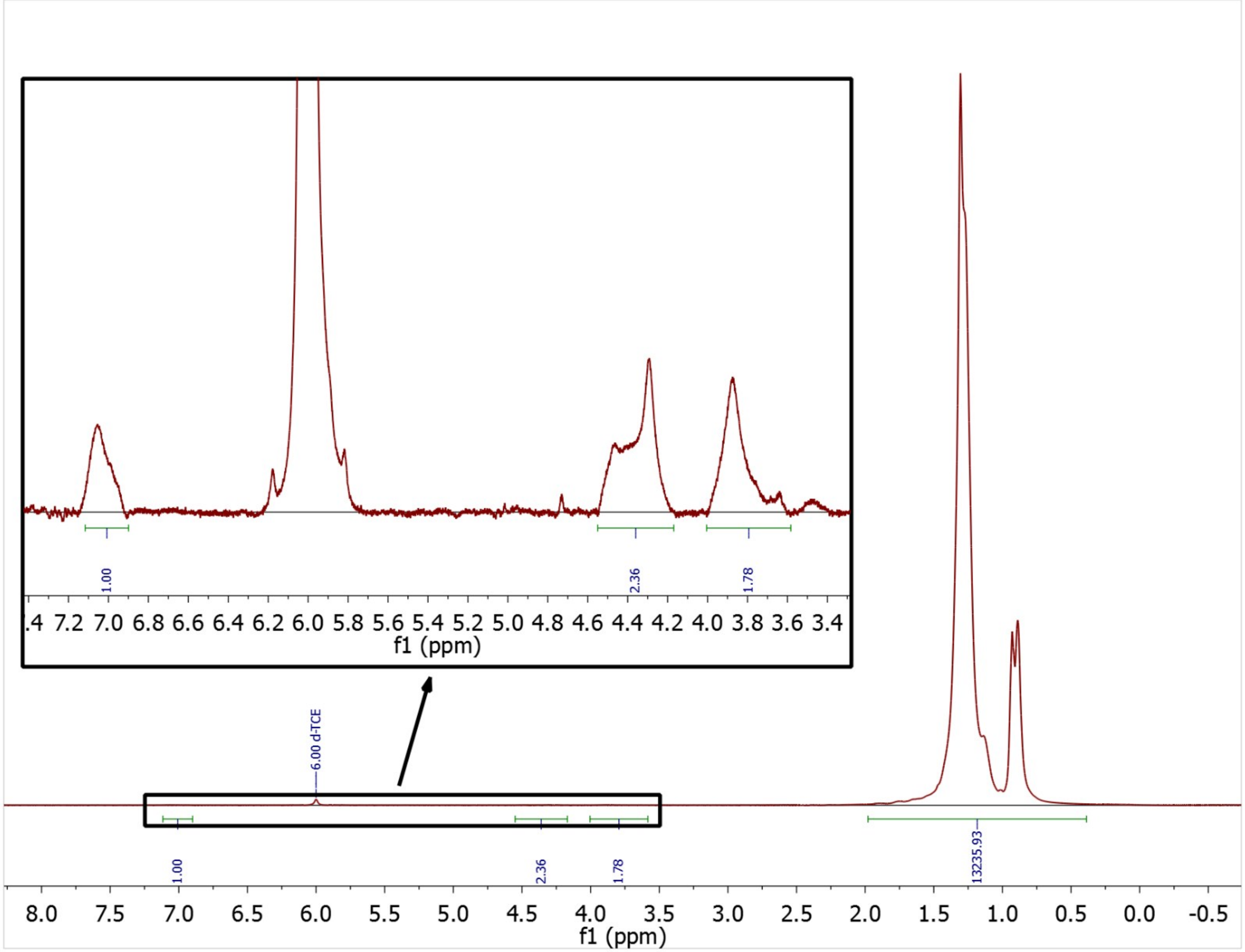


Figure S30: ^{1}H NMR of HBPE-HEA (d_2-TCE, 500 MHz, 25 ^{o}C)

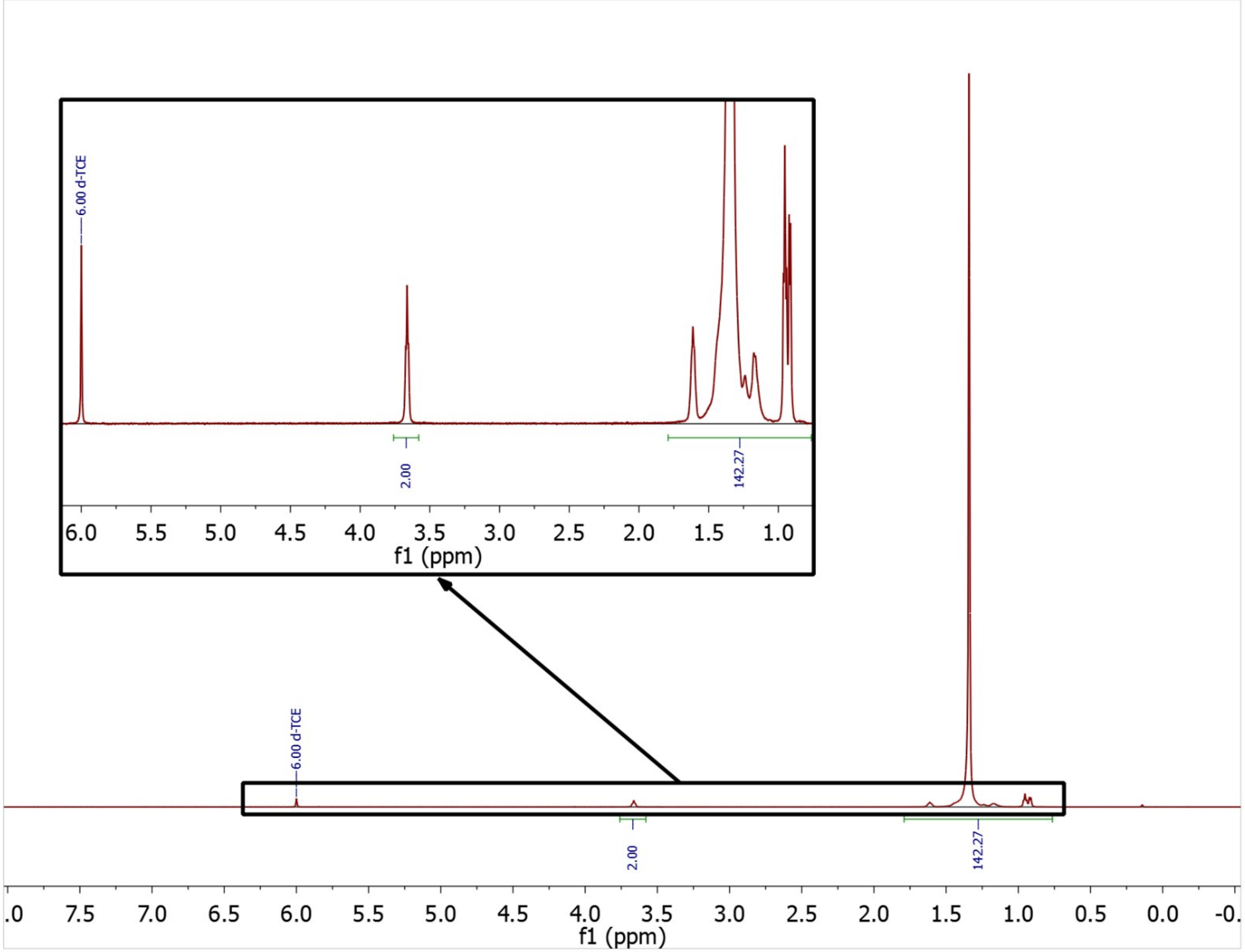


Figure S31: ^{1}H NMR of *l*-HDPE-OH (d_2-TCE, 500 MHz, 95 ^{o}C)

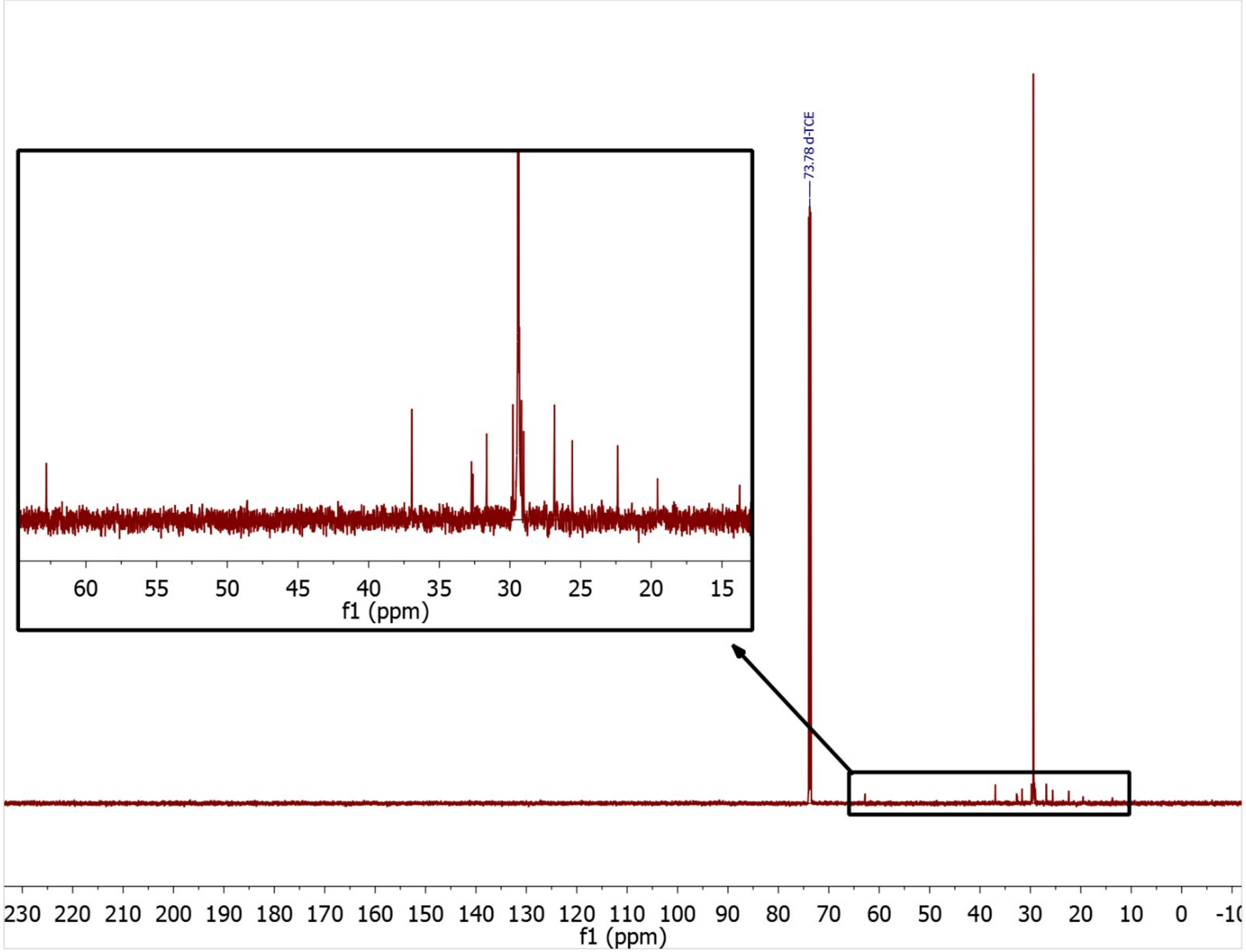


Figure S32: ^{13}C NMR of *l*-HDPE-OH (d$_2$-TCE, 500 MHz, 95 ^{o}C)

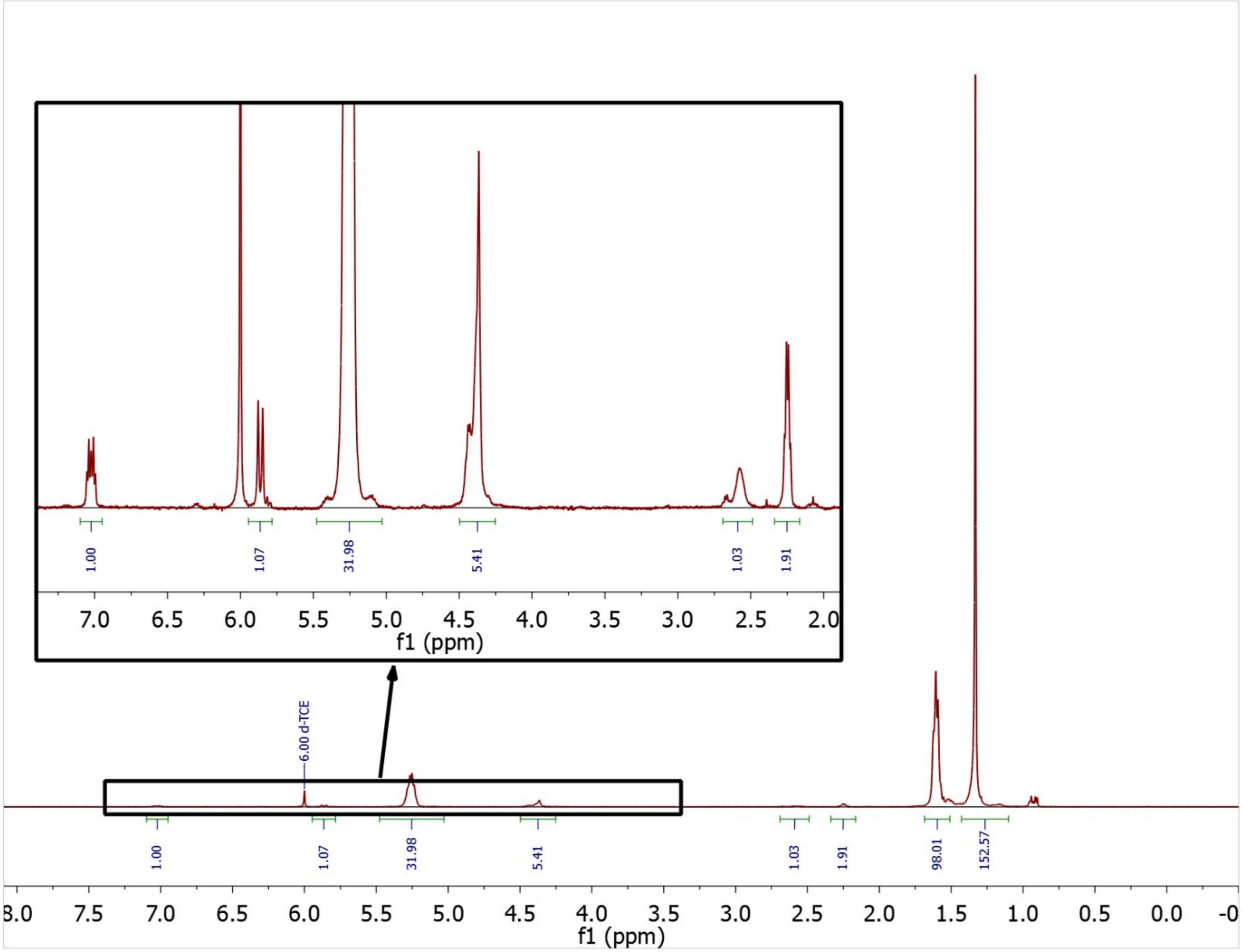


Figure S33: ^{1}H NMR of *l*-HDPE-PLA (d$_2$-TCE, 500 MHz, 95 ^{o}C)

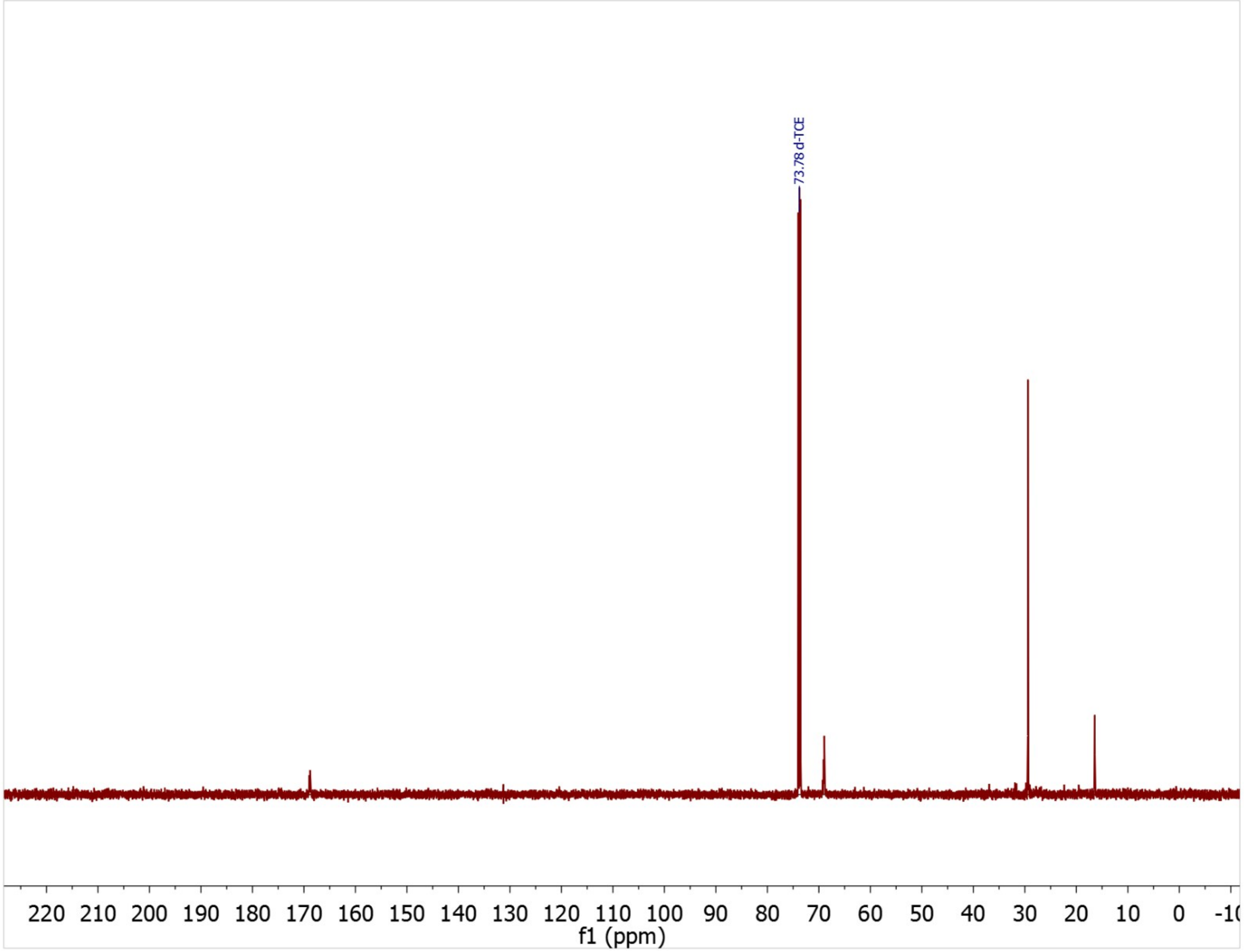


Figure S34: ^{13}C NMR of *l*-HDPE-PLA (d_2-TCE, 500 MHz, 95 °C)

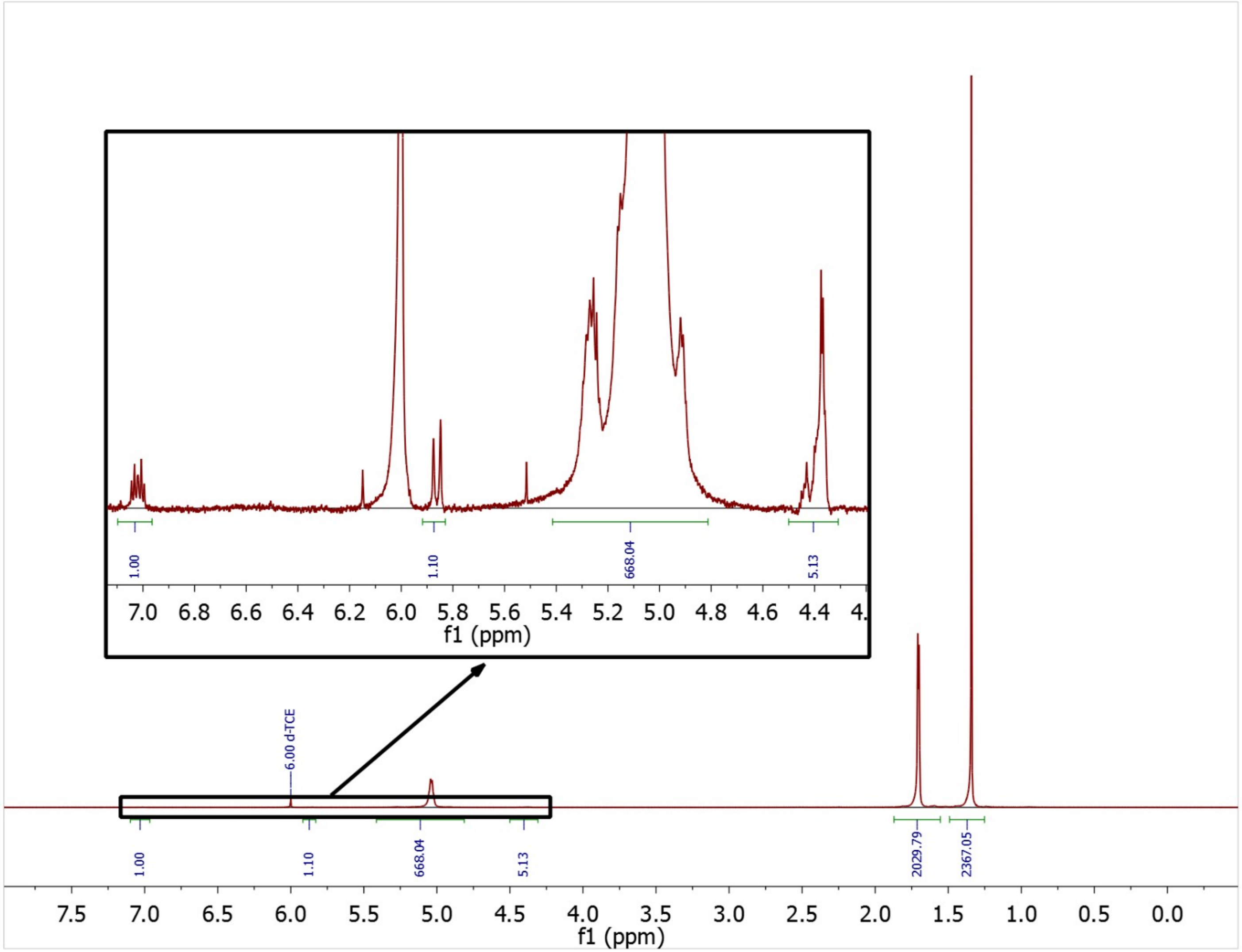


Figure S35: ^{1}H NMR of *h*-HDPE-PLA (d$_2$-TCE, 500 MHz, 95 ^{o}C)

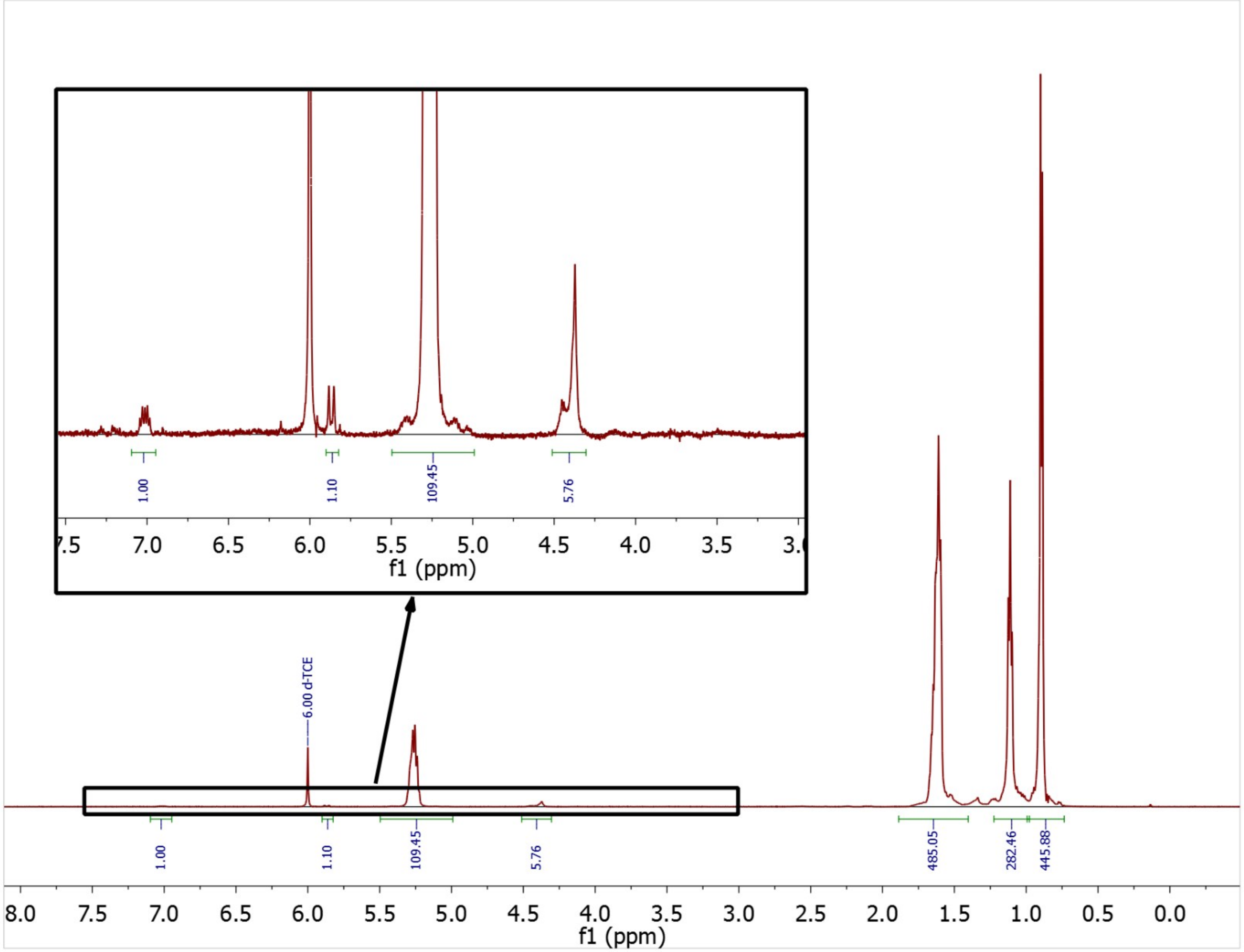


Figure S36: ^{1}H NMR of synPP-PLA (d_2-TCE, 500 MHz, 95 ^{o}C)

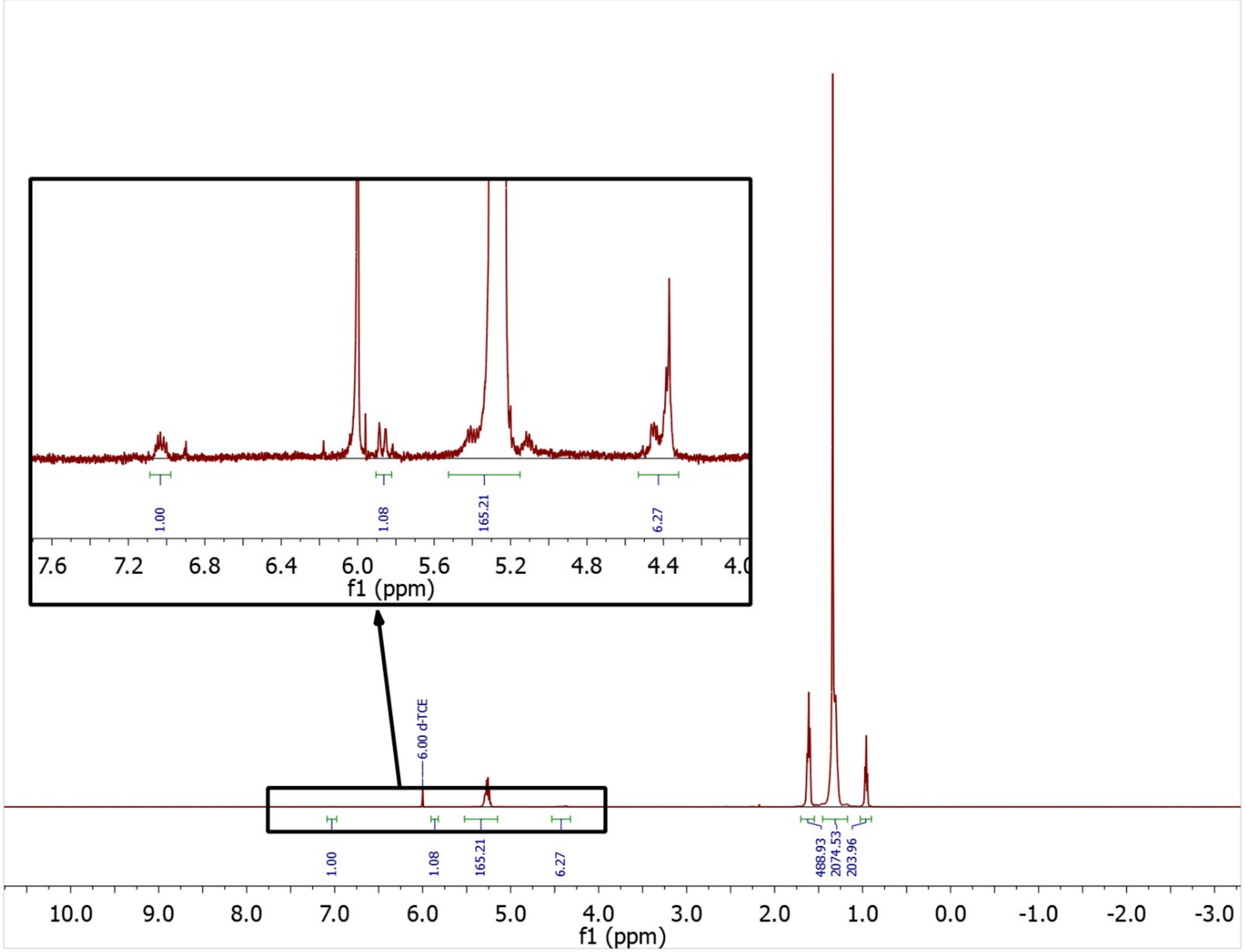


Figure S37: ^{1}H NMR of LLDPE-PLA (d_2-TCE, 500 MHz, 95 ^{o}C)

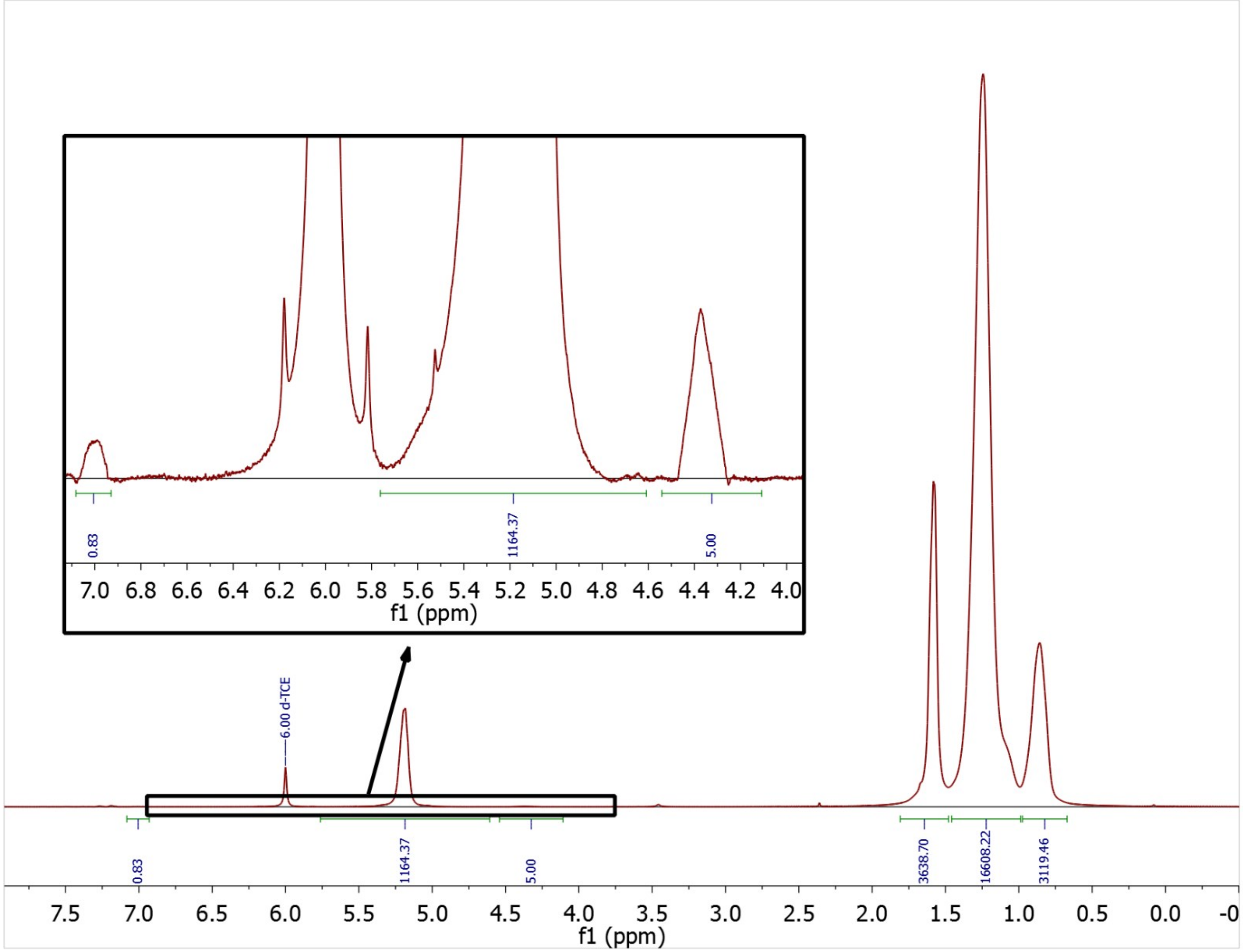


Figure S38: ^{1}H NMR of HBPE-PLA (d_2-TCE, 500 MHz, 25 ^{o}C)

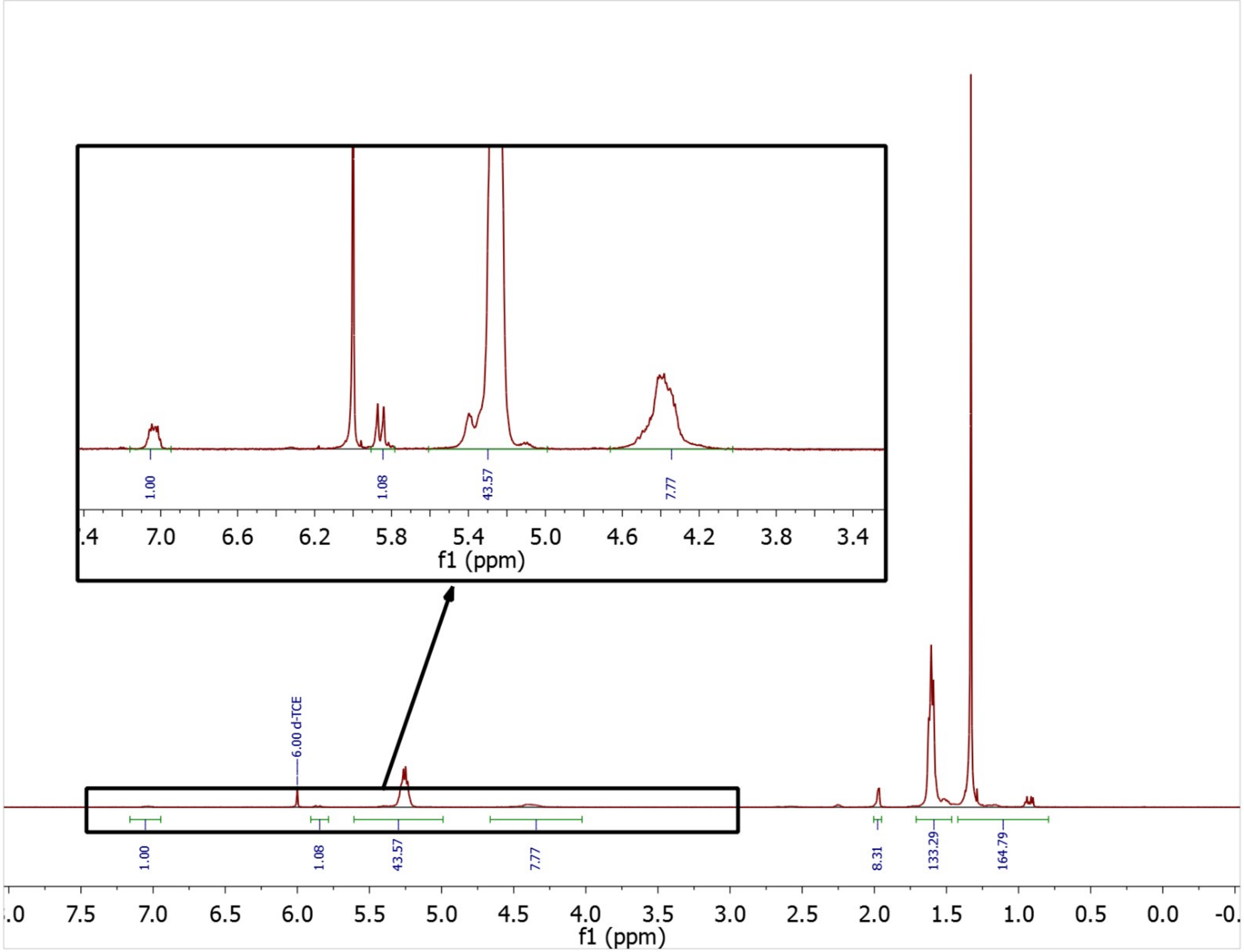


Figure S39: ^{1}H NMR of *l*-HDPE-PLA-Br (d_2-TCE, 500 MHz, 95 ^{o}C)

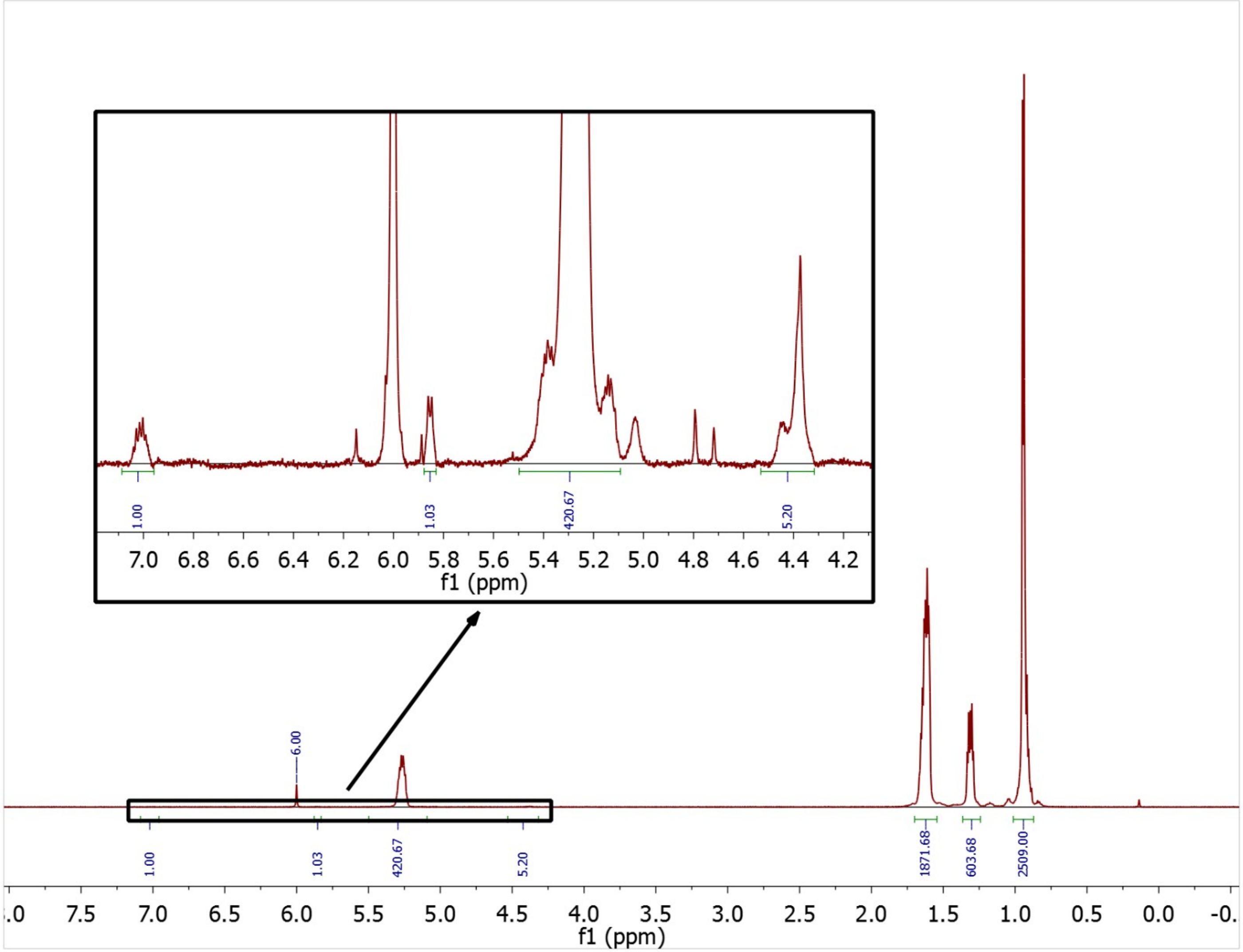


Figure S40: ^{1}H NMR of isoPP-PLA (d$_2$-TCE, 500 MHz, 95 ^{o}C)

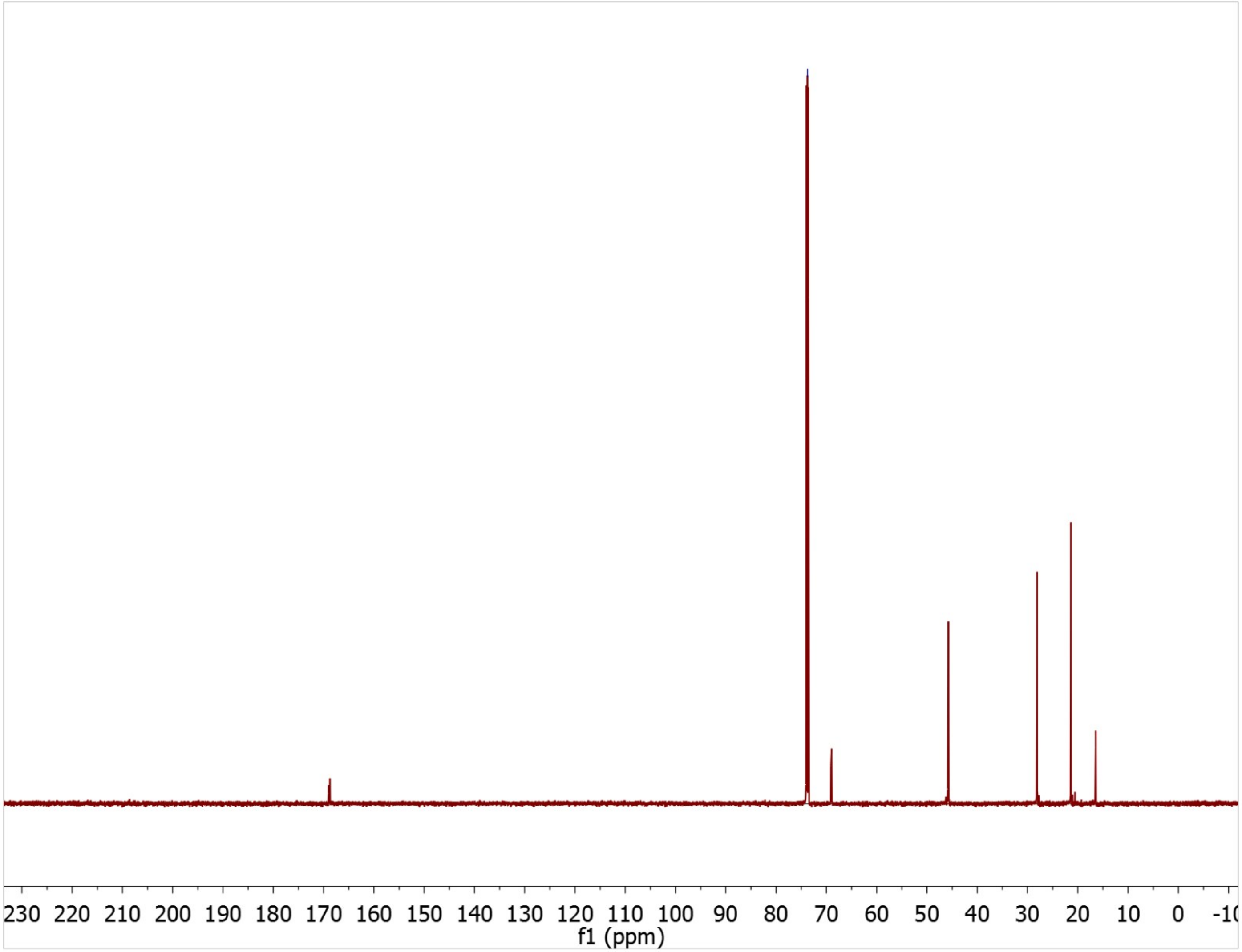


Figure S41: ^{13}C NMR of isoPP-PLA (d$_2$-TCE, 500 MHz, 95 ^{o}C)

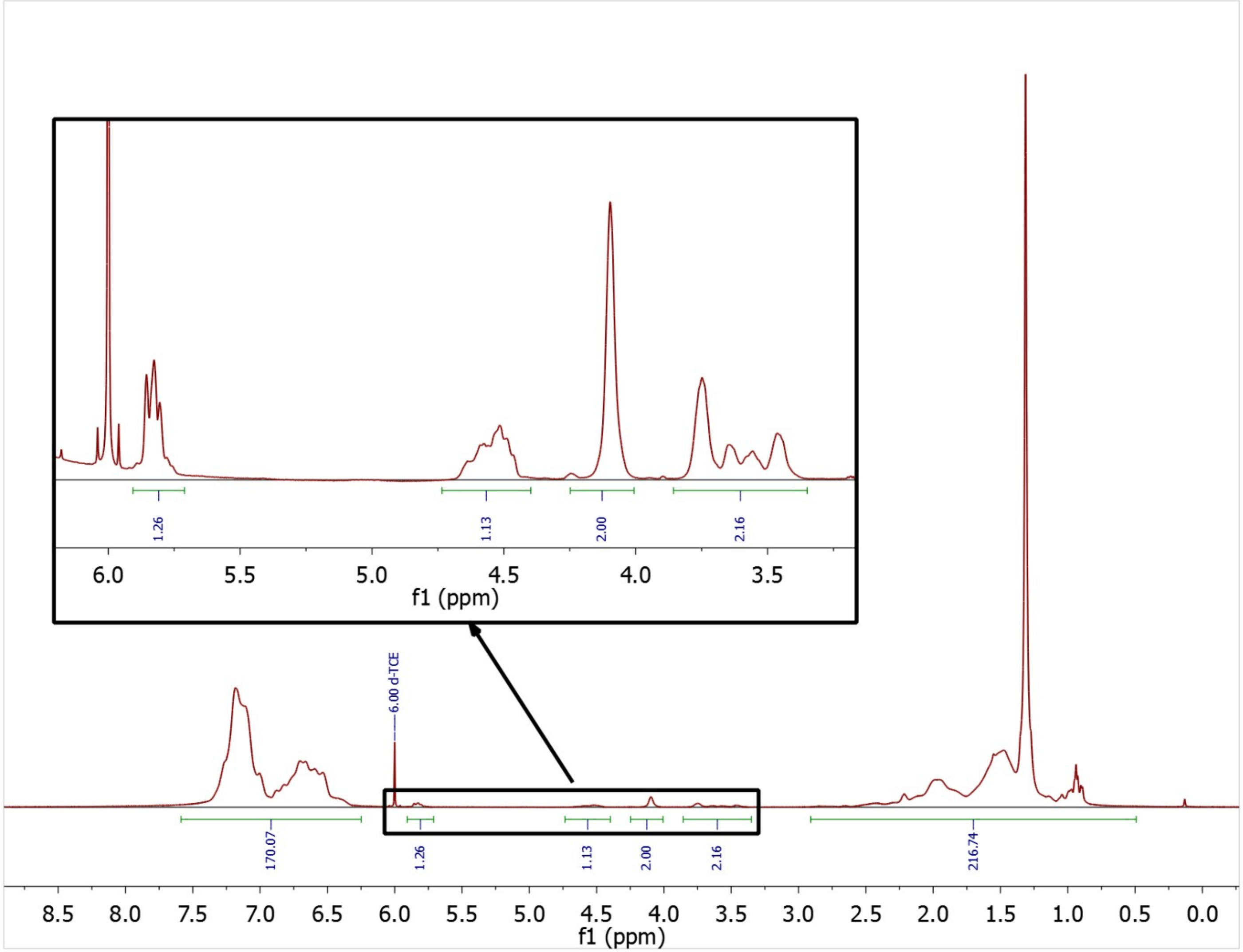


Figure S42: ^{1}H NMR of *l*-HDPE-PS (d_2-TCE, 500 MHz, 95 ^{o}C)

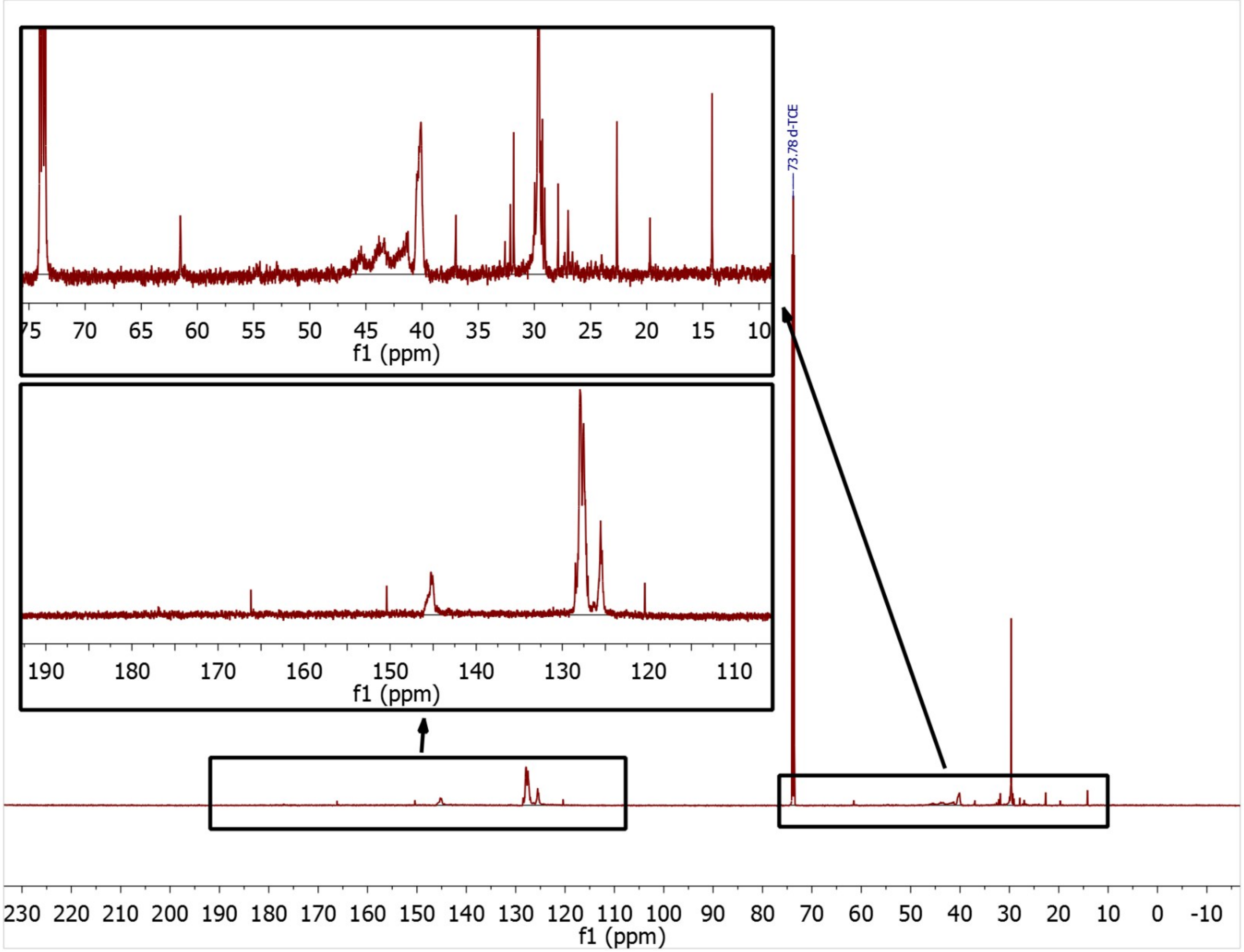


Figure S43: ^{13}C NMR of *l*-HDPE-PS (d$_2$-TCE, 500 MHz, 95 ^{o}C)

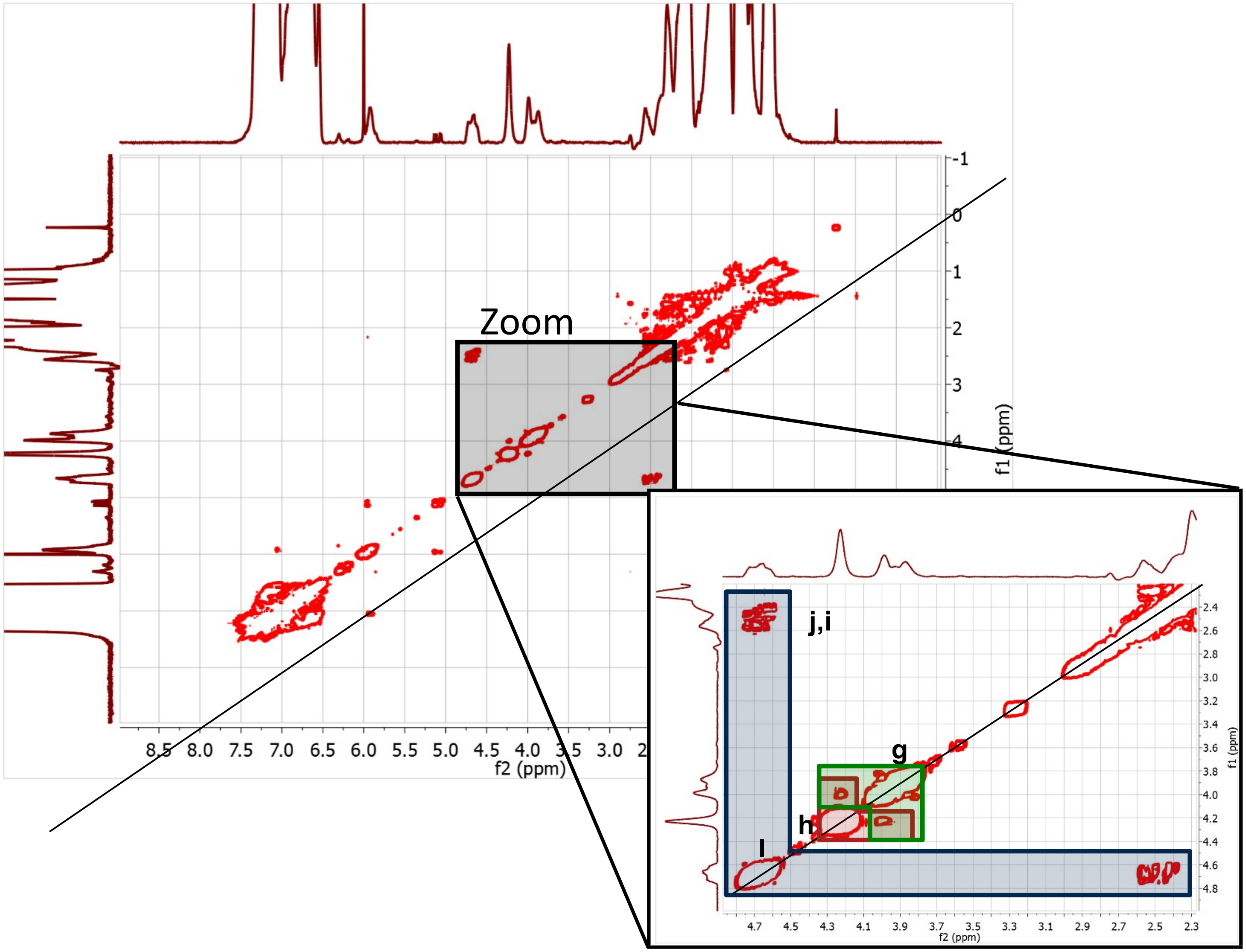


Figure S44: {^{1}H, ^{1}H} gCOSY of *l*-HDPE-PS* (d$_2$-TCE, 500 MHz, 95 ^{o}C)

*2D data taken on a batch of *l*-HDPE-PS early in the optimization process, thus a small amount of *l*-HDPE is present

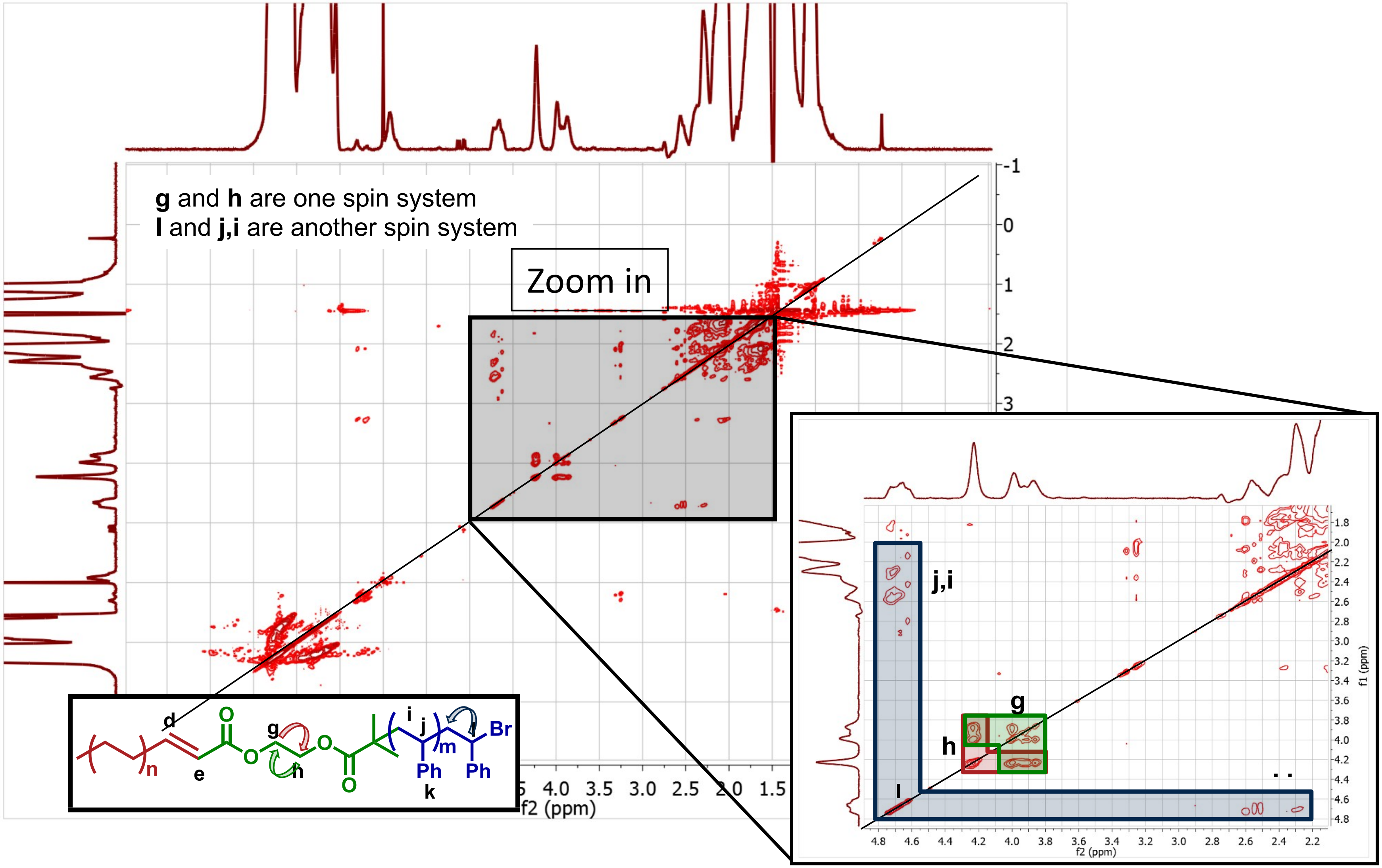


Figure S45: {^{1}H, ^{1}H} TOCSY of *l*-HDPE-PS* (d$_2$-TCE, 500 MHz, 95 °C)

*2D data taken on a batch of *l*-HDPE-PS early in the optimization process, thus a small amount of *l*-HDPE is present

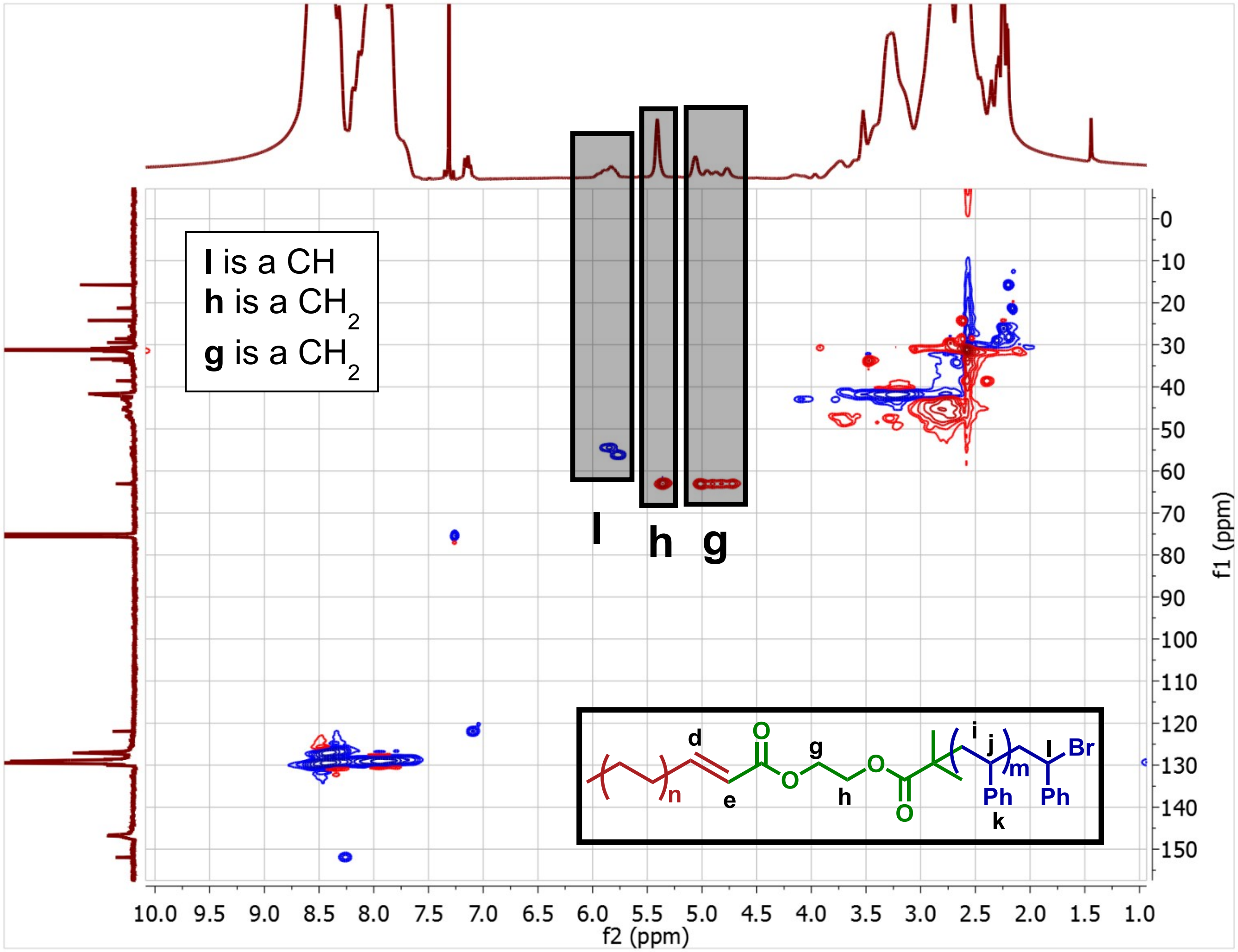


Figure S46: {^{1}H, ^{13}C} gHSQC of *l*-HDPE-PS* (d_2-TCE, 500 MHz, 95 ^{o}C)

*2D data taken on a batch of *l*-HDPE-PS early in the optimization process, thus a small amount of *l*-HDPE is present

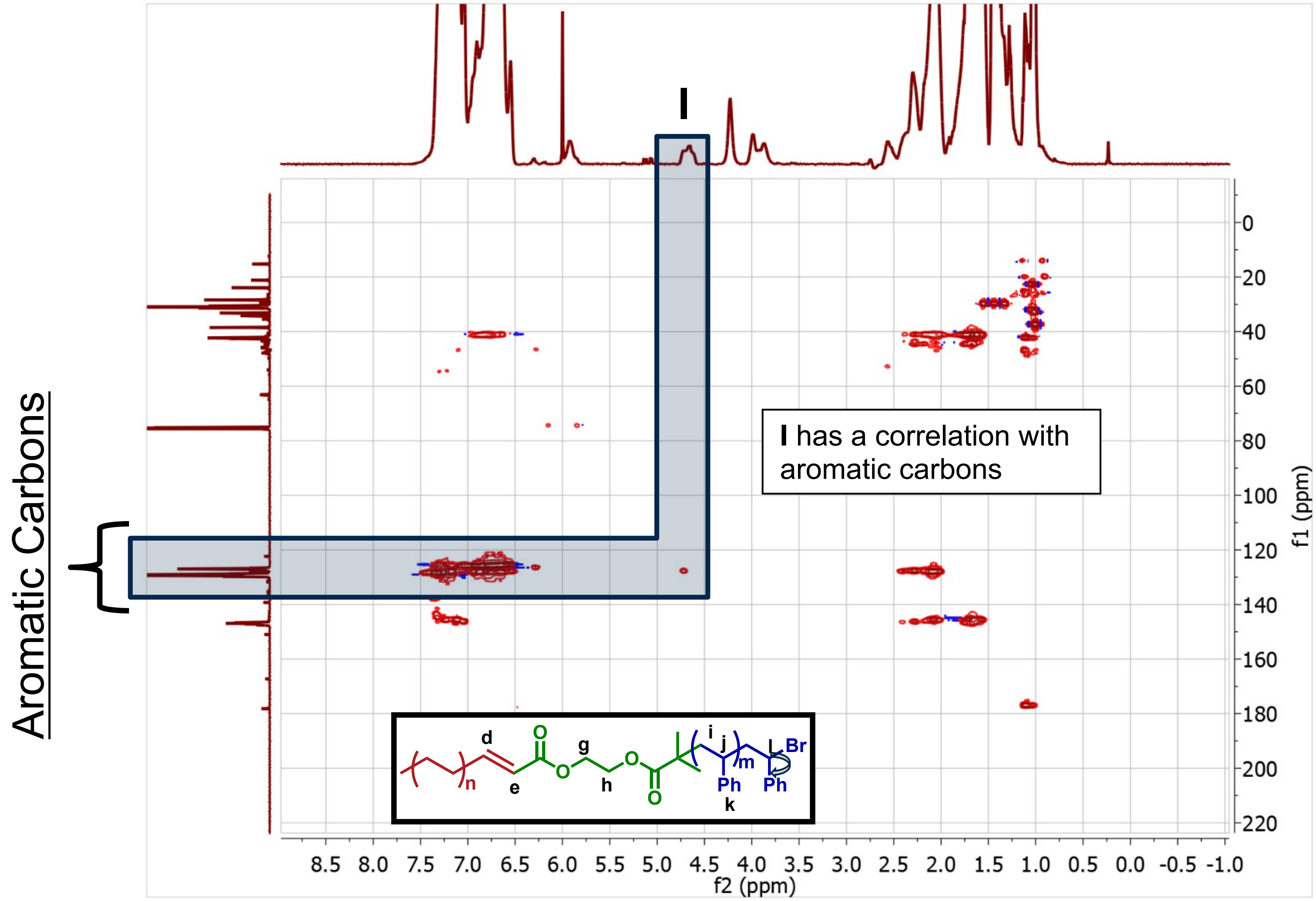


Figure S47: {^{1}H, ^{13}C} HMBC of *l*-HDPE-PS* (d_2-TCE, 500 MHz, 95 ^{o}C)

*2D data taken on a batch of *l*-HDPE-PS early in the optimization process, thus a small amount of *l*-HDPE is present

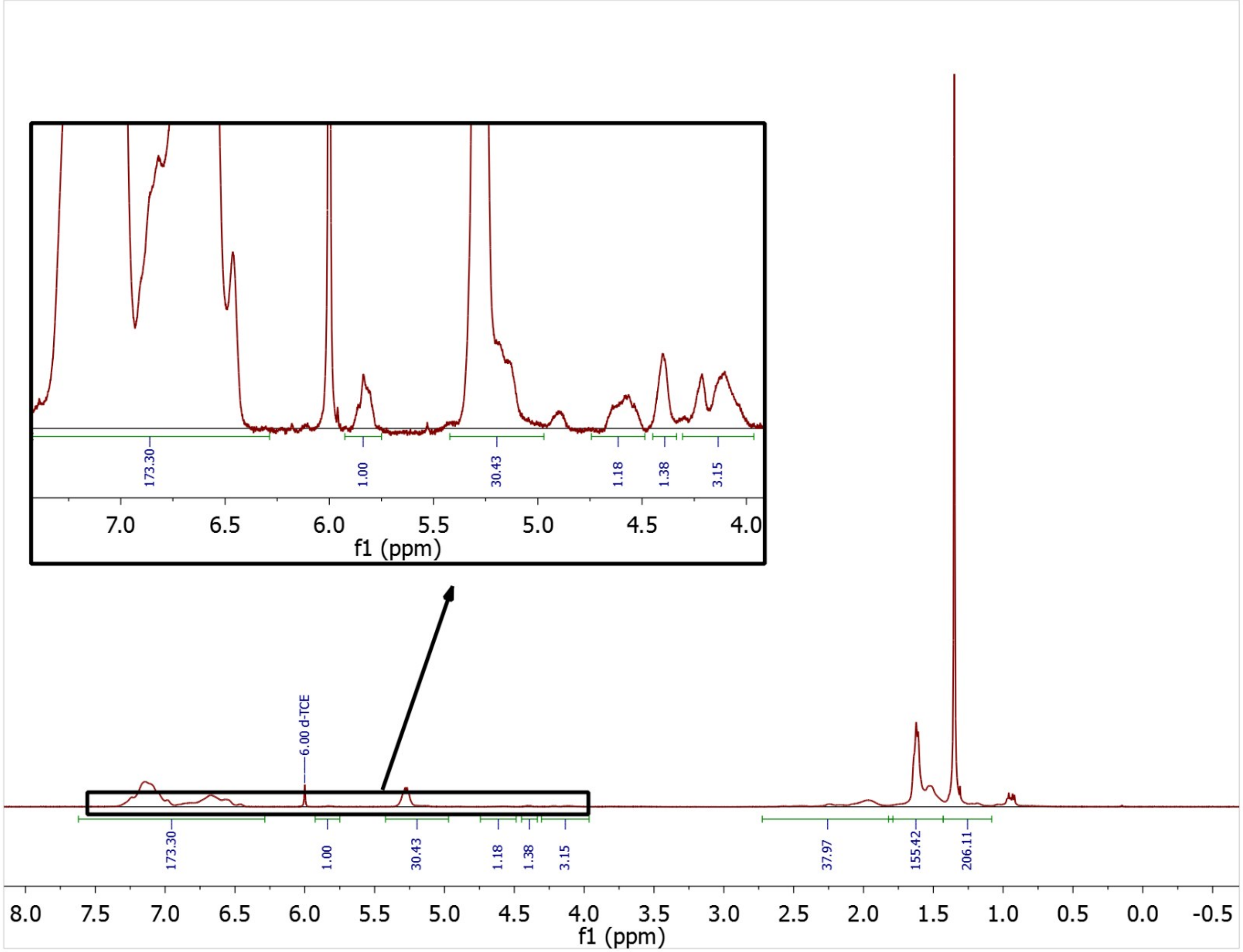


Figure S48: ^{1}H NMR of *l*-HDPE-PLA-PS (d$_2$-TCE, 500 MHz, 95 ^{o}C)

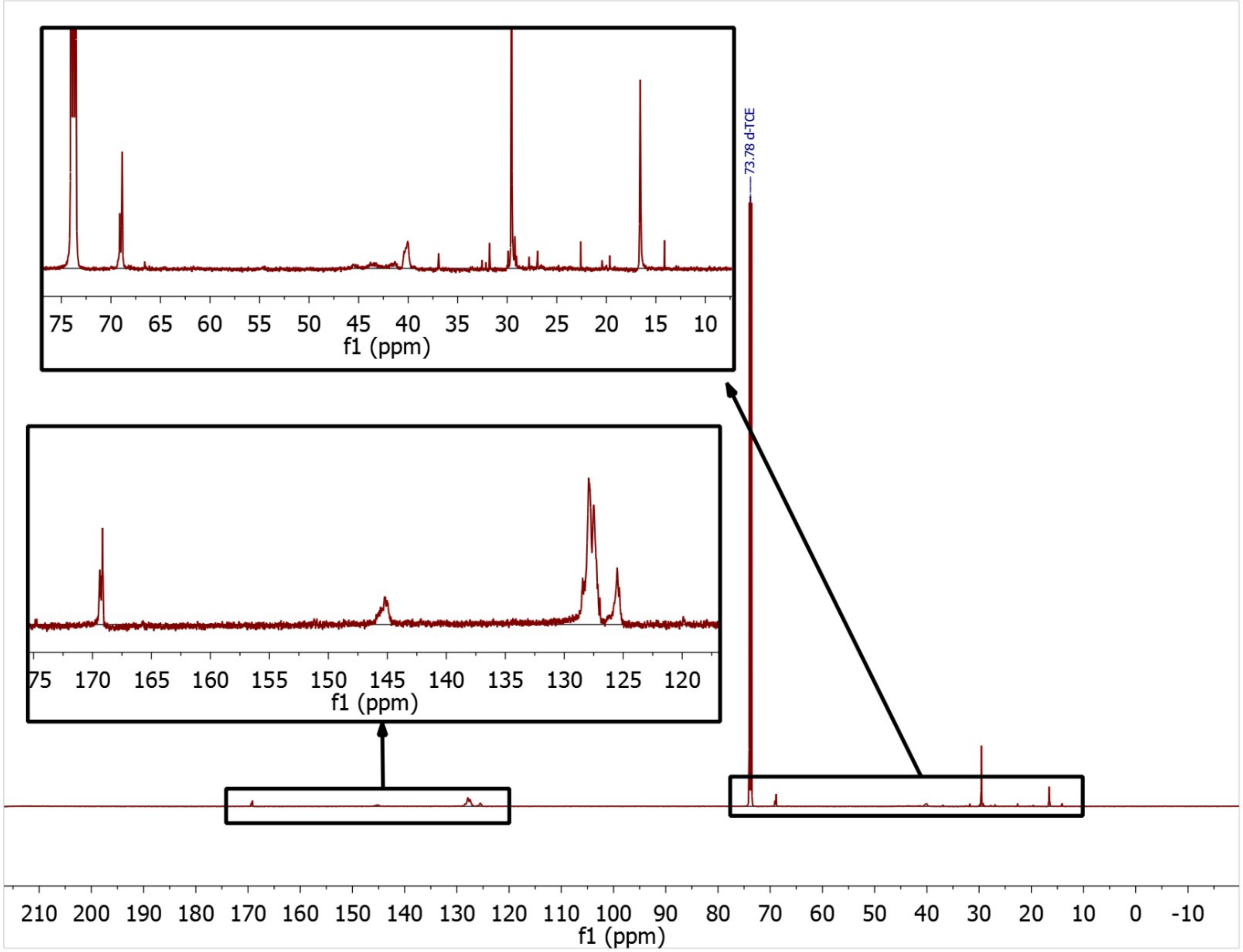


Figure S49: ^{13}C NMR of *l*-HDPE-PLA-PS (d$_2$-TCE, 500 MHz, 95 ^{o}C)

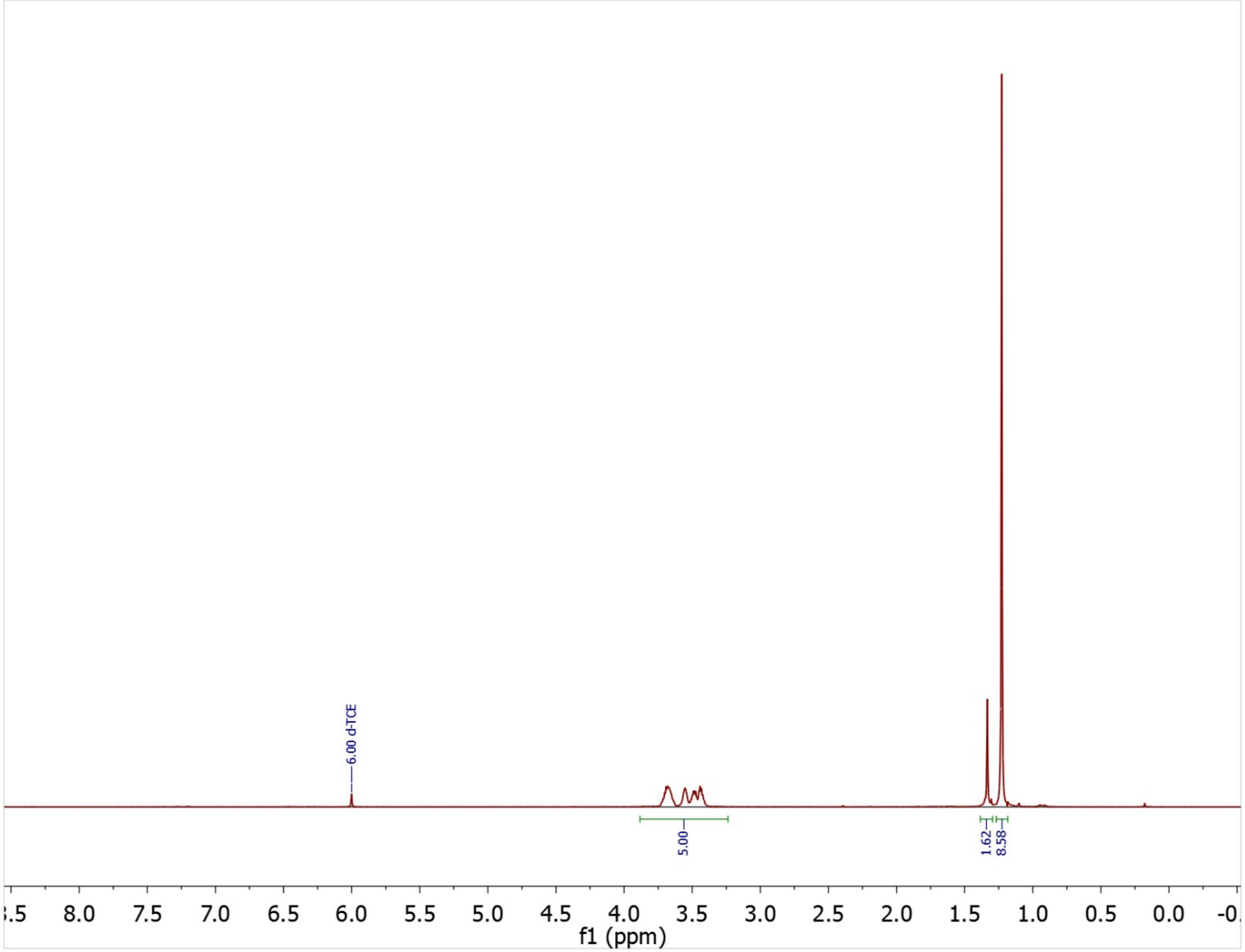


Figure S50: ^{1}H NMR of *l*-HDPE-P(tBuGE) (d_2-TCE, 500 MHz, 95 °C)

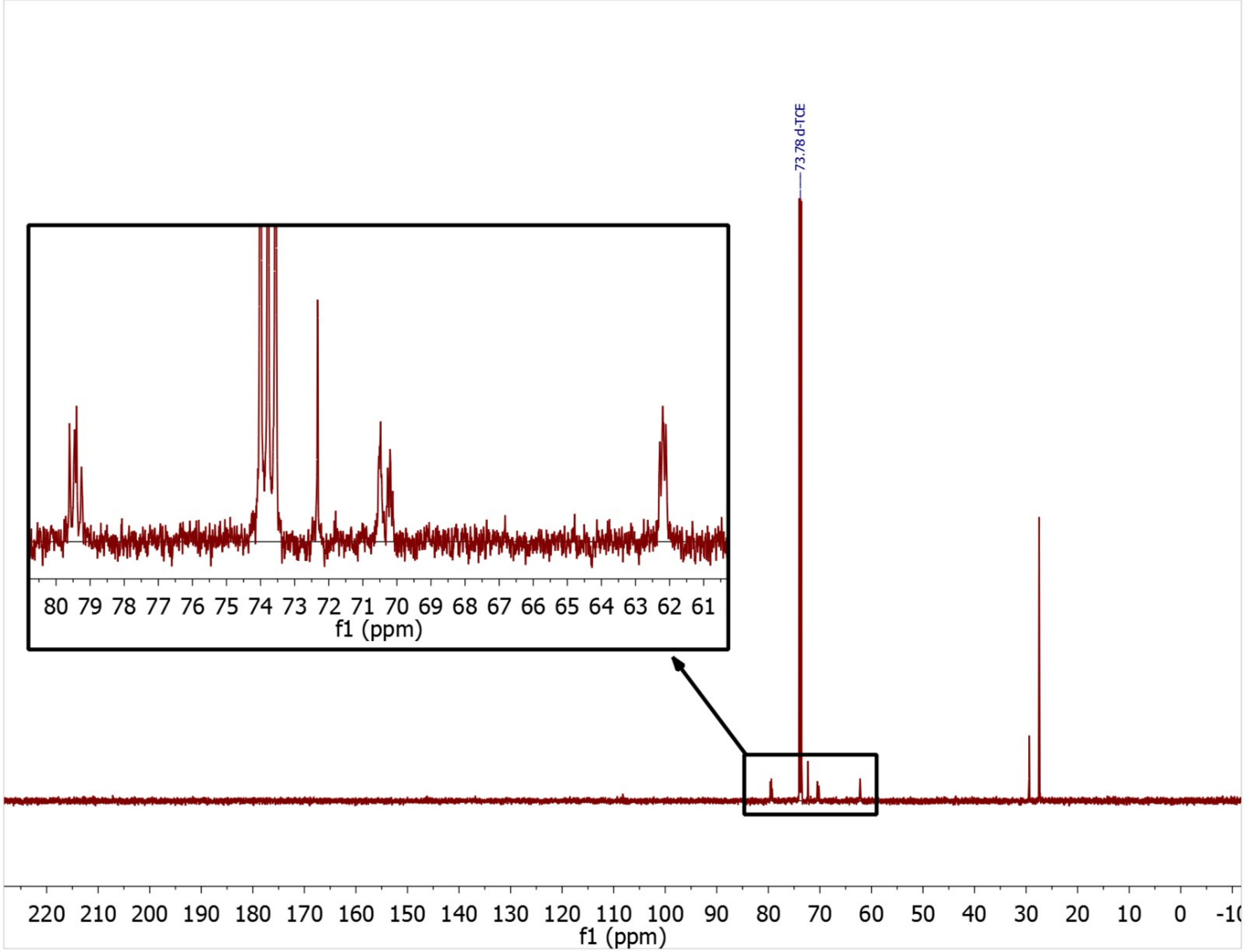
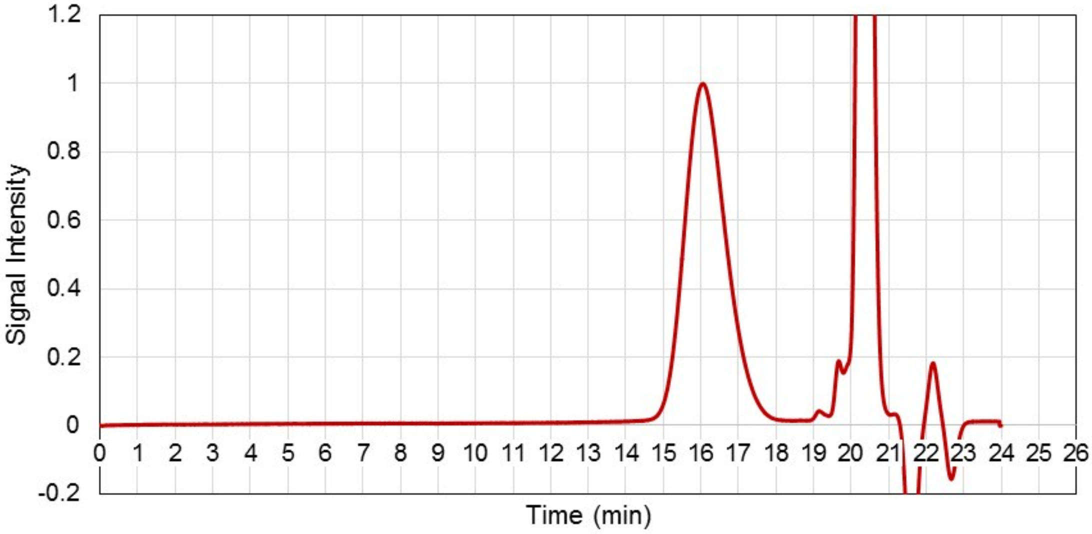


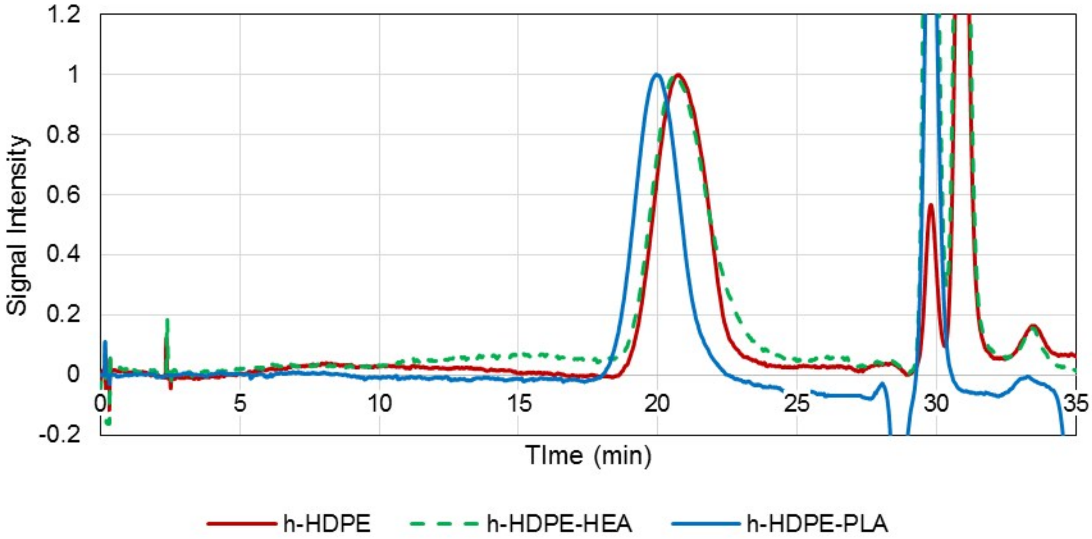
Figure S51: ^{13}C NMR of *l*-HDPE-P(tBuGE) (d_2-TCE, 500 MHz, 95 °C)

VI. GPC Traces



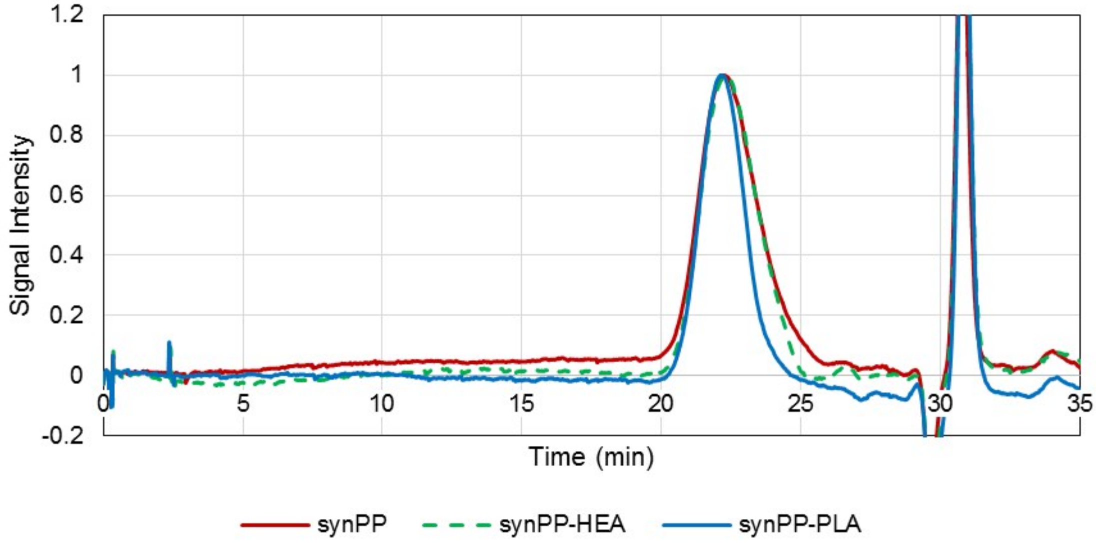
l-HDPE-PLA: M_n: 4,200 g/mol Đ: 1.4

Figure S52: RI trace for the synthesis of *l*-HDPE-PLA (40 °C, THF)



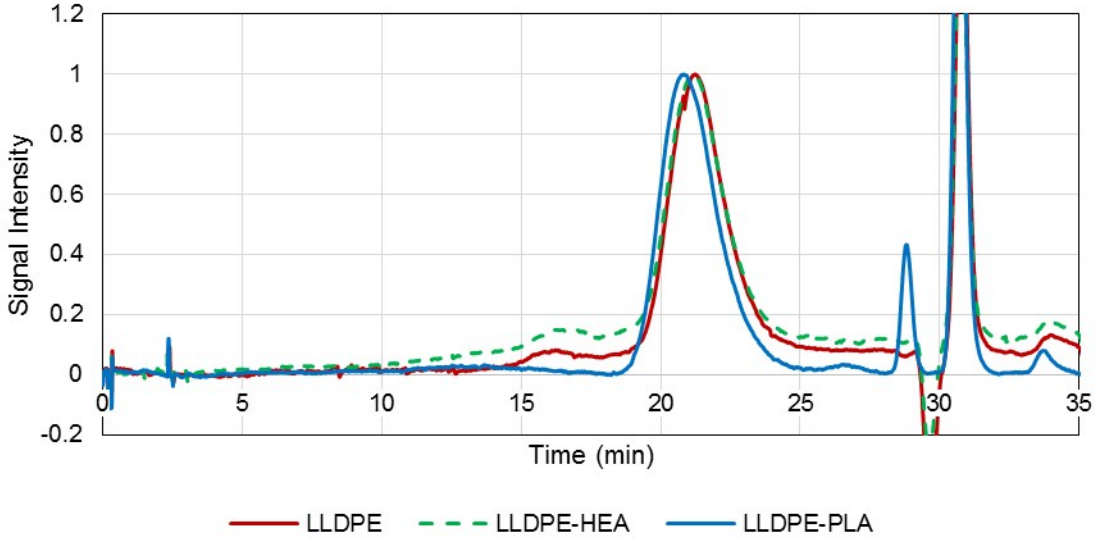
h-HDPE: M_n: 18,000 g/mol Đ:1.6
h-HDPE-HEA: M_n: 19,000 g/mol Đ:1.5
h-HDPE-PLA: M_n: 69,000 g/mol Đ: 1.3

Figure S53: RI trace from triple detection GPC for the synthesis of *h*-HDPE-PLA (160 °C, TCB)



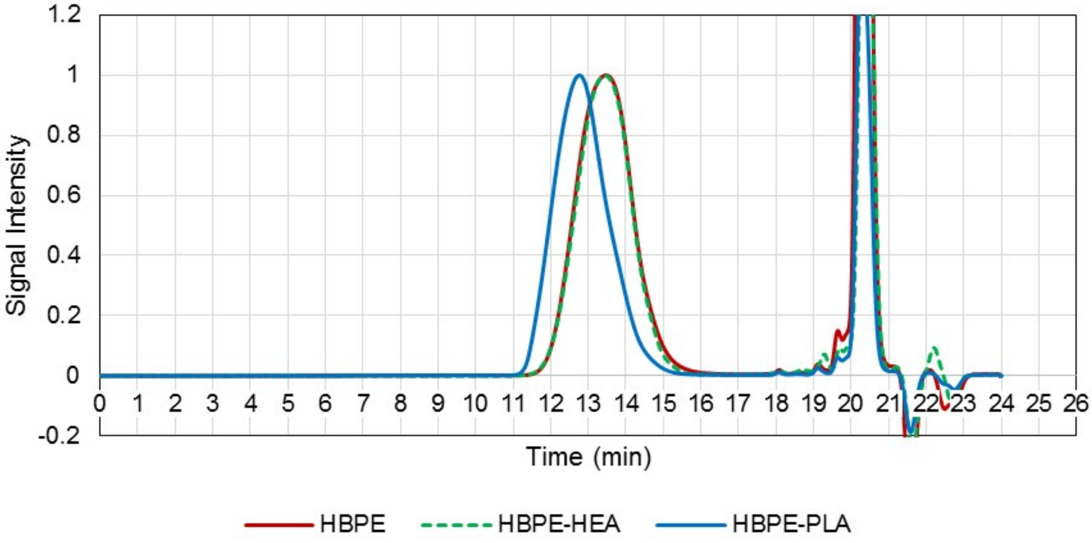
synPP: M_n: 5,800 g/mol Đ: 1.8
synPP-HEA: M_n: 5,500 g/mol Đ: 1.8
synPP-PLA: M_n: 15,000 g/mol Đ: 1.6

Figure S54: RI trace from triple detection GPC for the synthesis of synPP-PLA (160 ^{o}C, TCB)



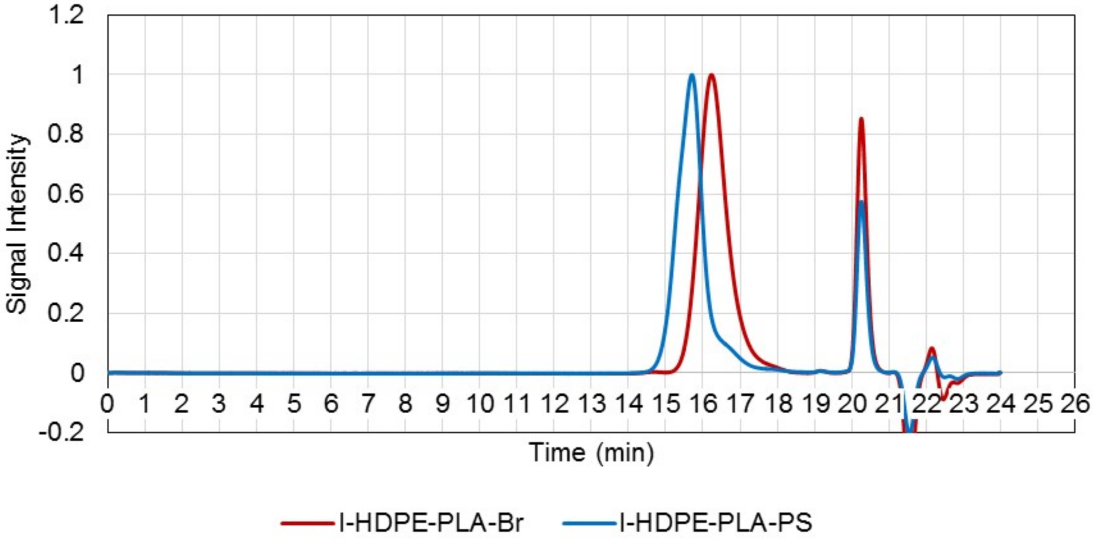
LLDPE: M_n: 17,000 g/mol Đ:1.6
LLDPE-HEA: M_n: 17,000 g/mol Đ:1.5
LLDPE -PLA: M_n: 29,000 g/mol Đ: 1.2

Figure S55: RI trace from triple detection GPC for the synthesis of LLDPE-PLA (160 ^{o}C, TCB)



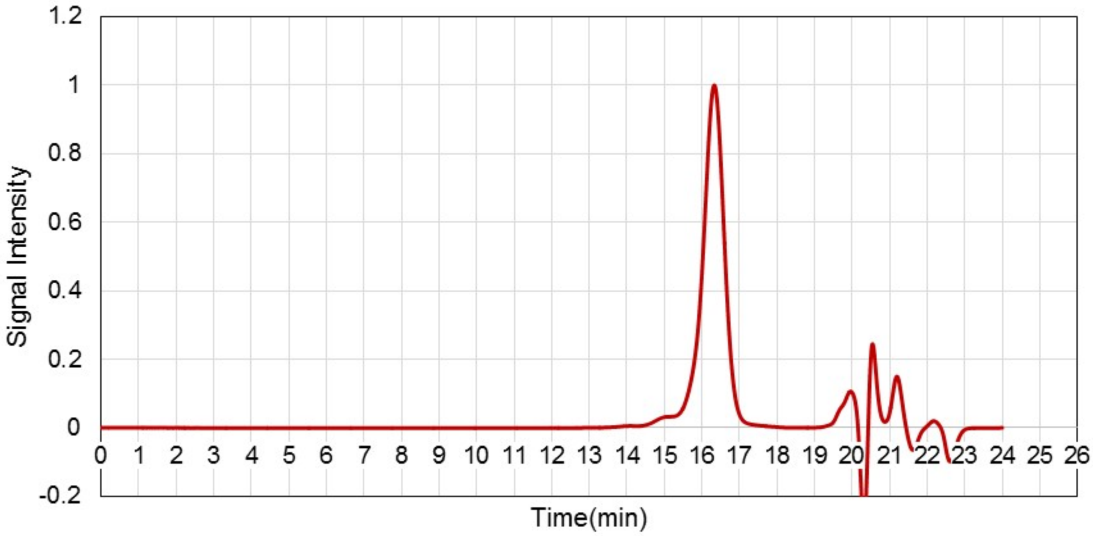
HBPE: M_n: 89,000 g/mol Đ: 1.8
HBPE-HEA: M_n: 95,000 g/mol Đ: 1.7
HBPE-PLA: M_n: 170,000 g/mol Đ: 1.8

Figure S56: RI trace for the synthesis of HBPE-PLA (40 ^{o}C, THF)



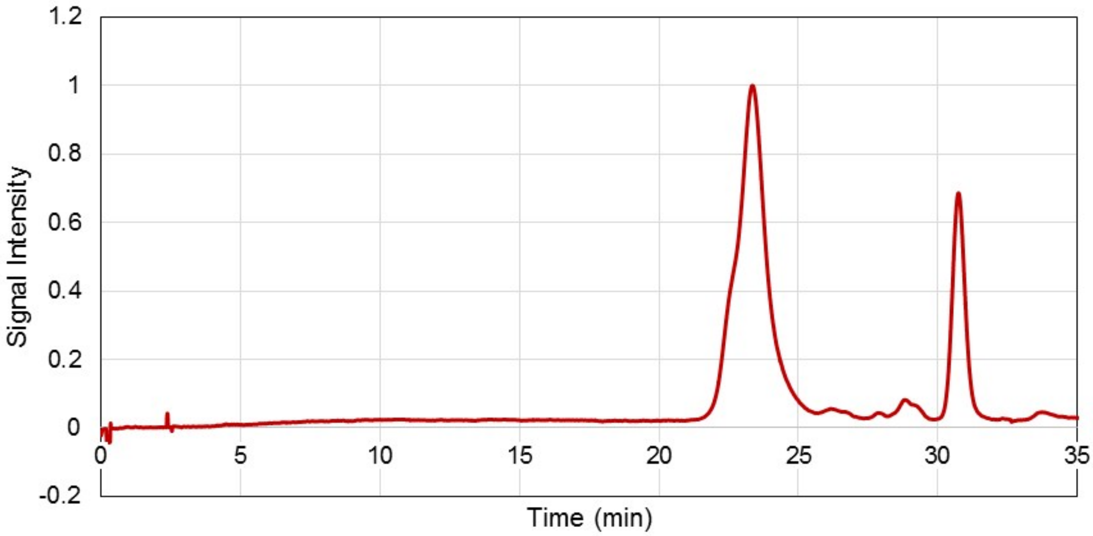
l-HDPE-PLA-Br: M_n: 4,300 g/mol Đ: 1.3
l-HDPE-PLA-PS: M_n: 7,700 g/mol Đ: 1.3

Figure S57: RI trace for the synthesis of *l*-HDPE-PLA-PS (40 ^{o}C, THF)



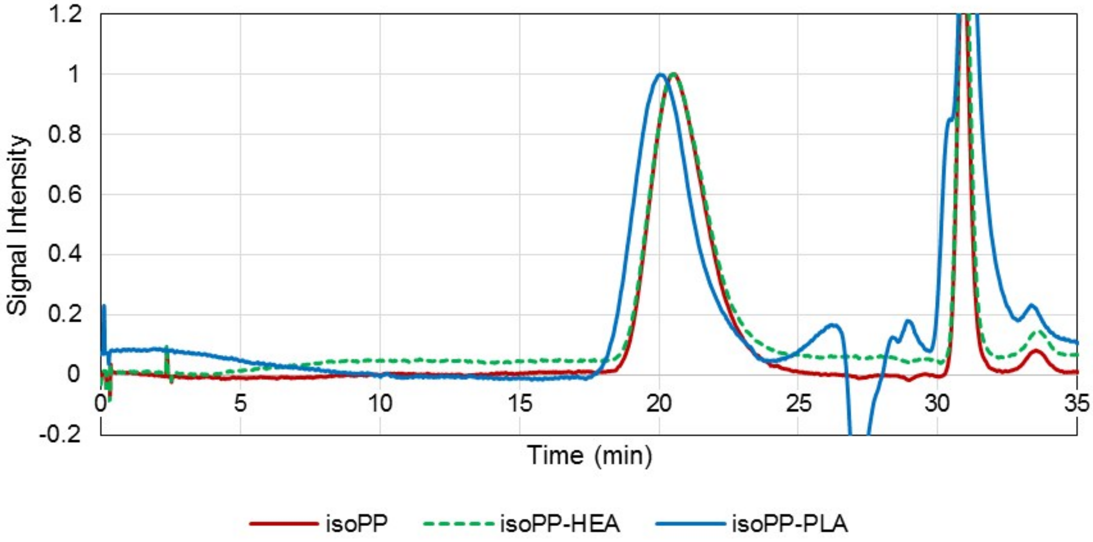
l-HDPE-PS: M_n: 5,000 g/mol Đ:1.1

Figure S58: RI trace of *l*-HDPE-PS (40 °C, THF)



l-HDPE-P(tBuGE): M_n: 7,500 g/mol Đ:1.2

Figure S59: RI trace from triple detection GPC of *l*-HDPE-P(tBuGE) (160 °C, TCB)



isoPP: M$_n$: 26,000 g/mol Đ: 2.1
isoPP-HEA: M$_n$: 29,000 g/mol Đ: 2.0
isoPP-PLA: M$_n$: 60,000 g/mol Đ: 1.4

Figure S60: RI trace from triple detection GPC for the synthesis of isoPP-PLA (160 ^{o}C, TCB)

VII. DSC Traces

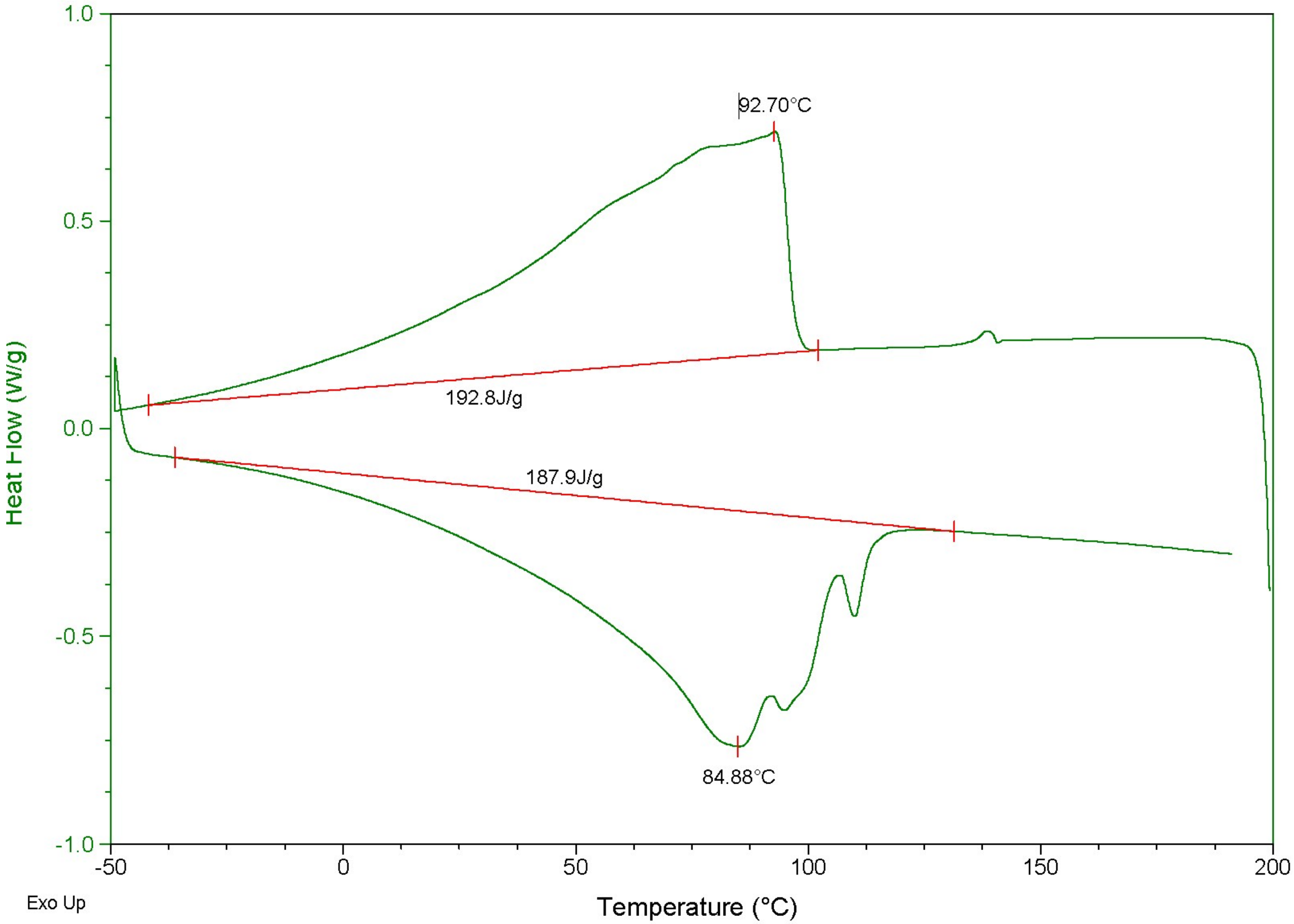


Figure S61: DSC trace for *l*-HDPE (heat/cool/heat, 10 ^{o}C/min, -50 ^{o}C – 200 ^{o}C)

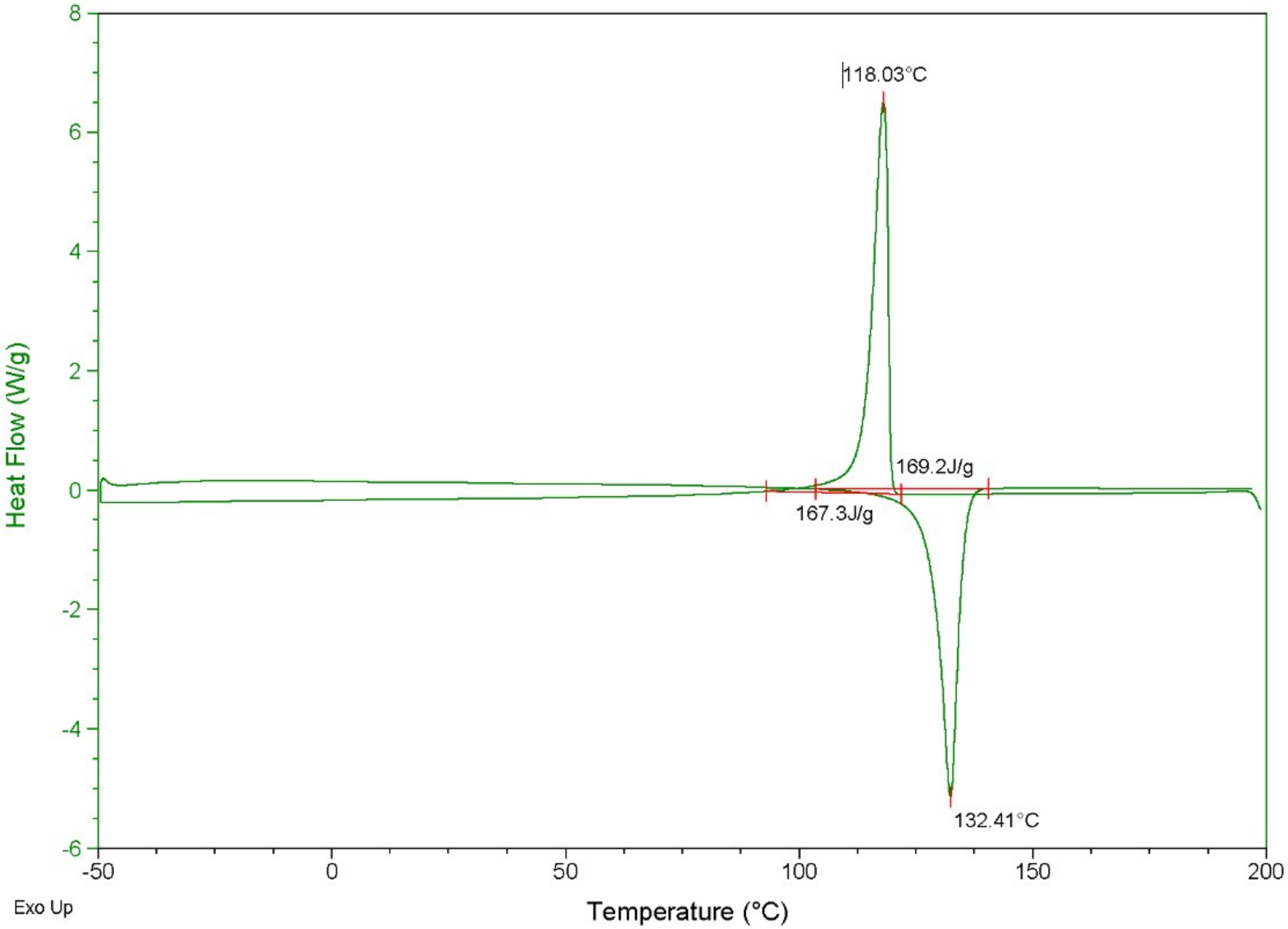


Figure S62: DSC trace for *h*-HDPE (heat/cool/heat, 10 ^{o}C/min, -50 ^{o}C – 200 ^{o}C)

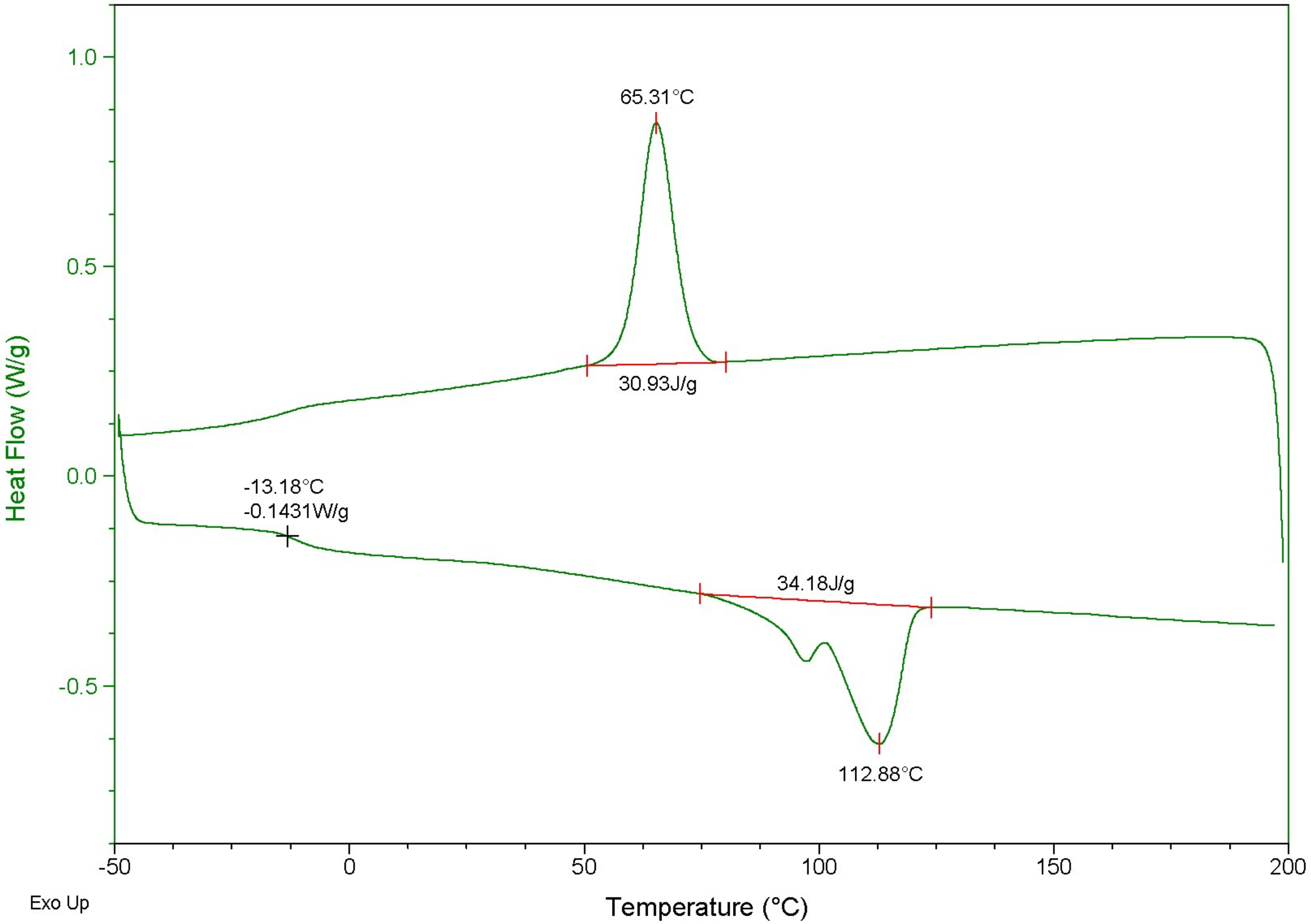


Figure S63: DSC trace for synPP (heat/cool/heat, 10 °C/min, -50 °C – 200 °C)

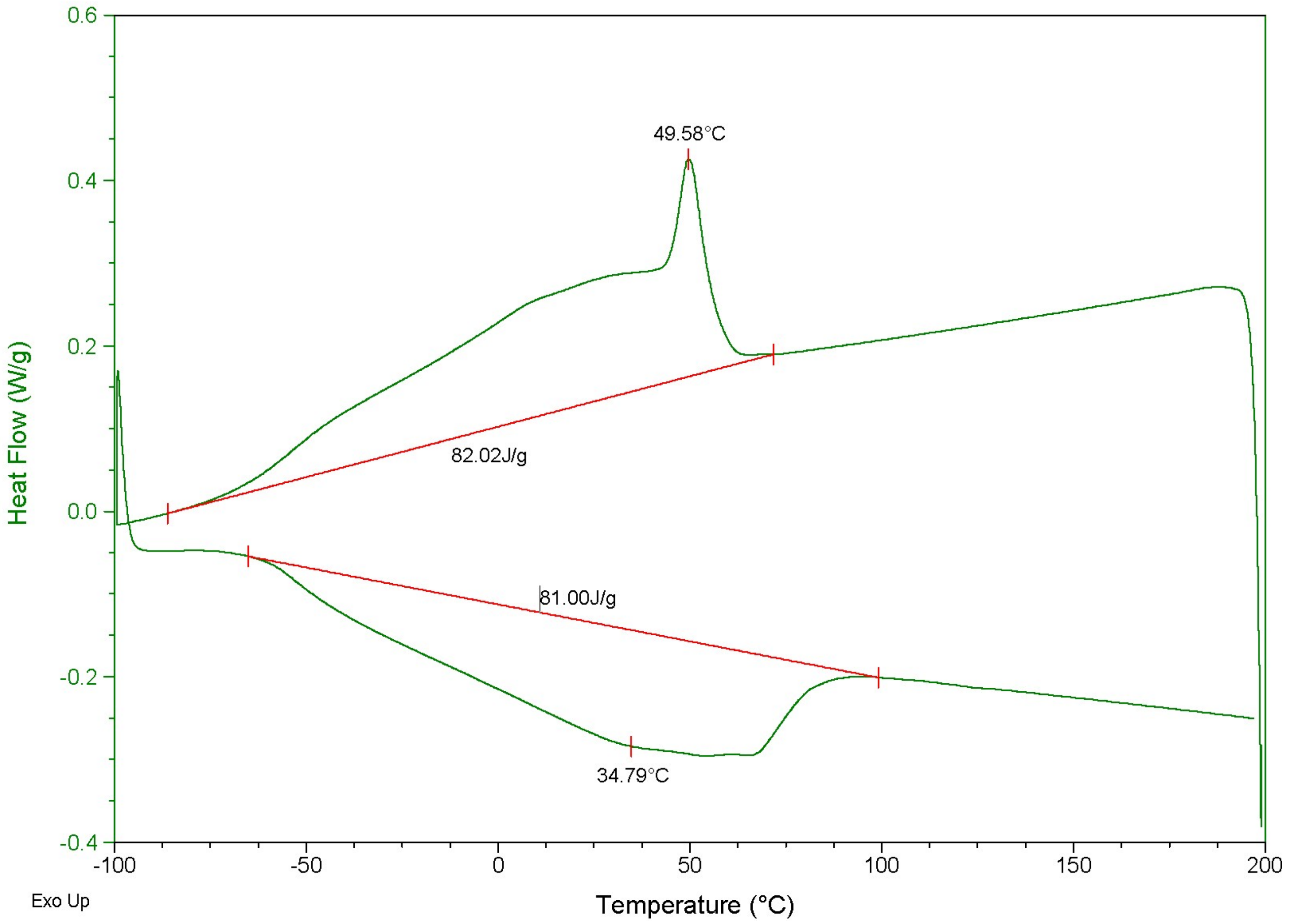


Figure S64: DSC trace for LLDPE (heat/cool/heat, 10 °C/min, -100 °C – 200 °C)

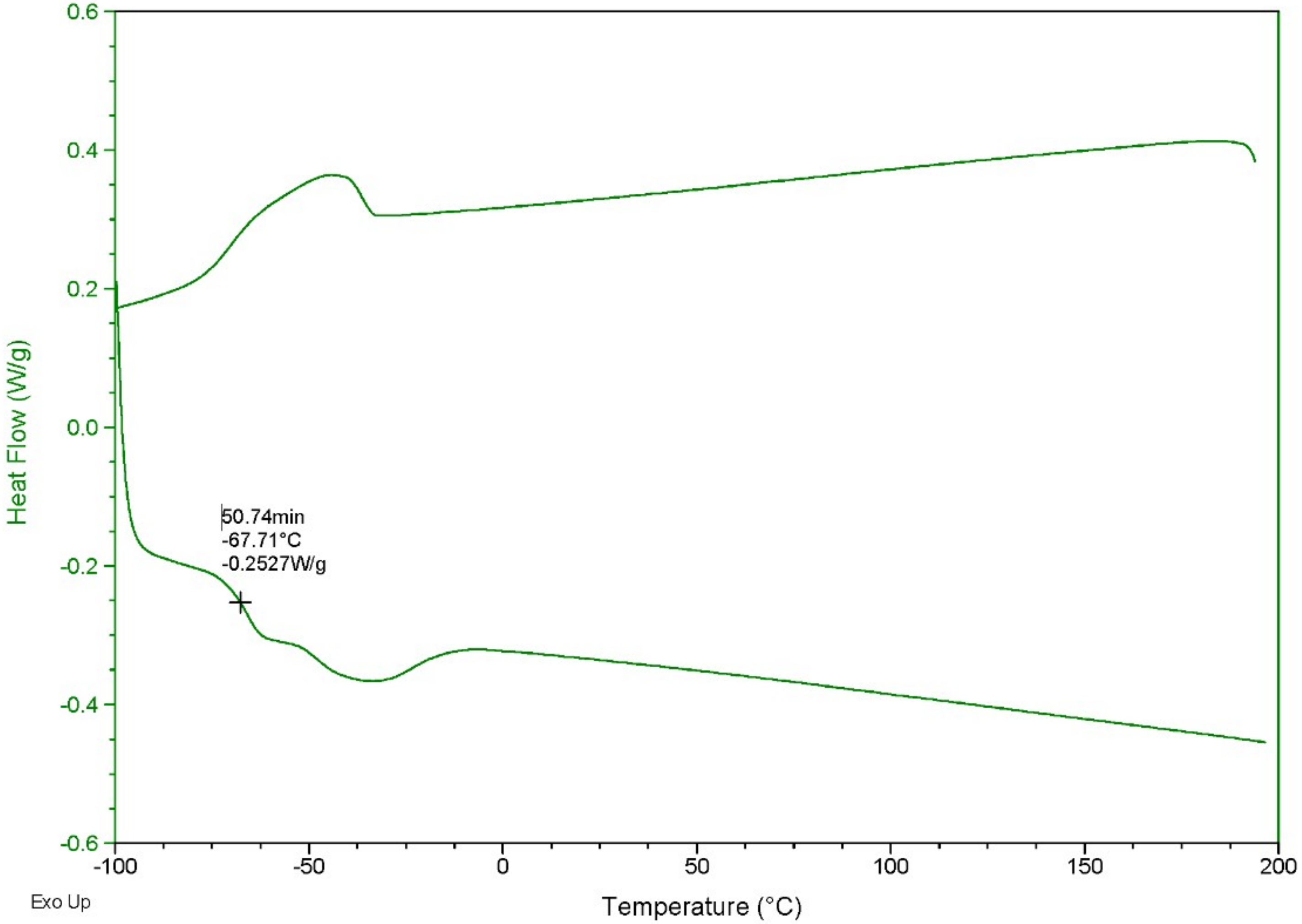


Figure S65: DSC trace for HBPE (heat/cool/heat, 10 °C/min, -100 °C – 200 °C)

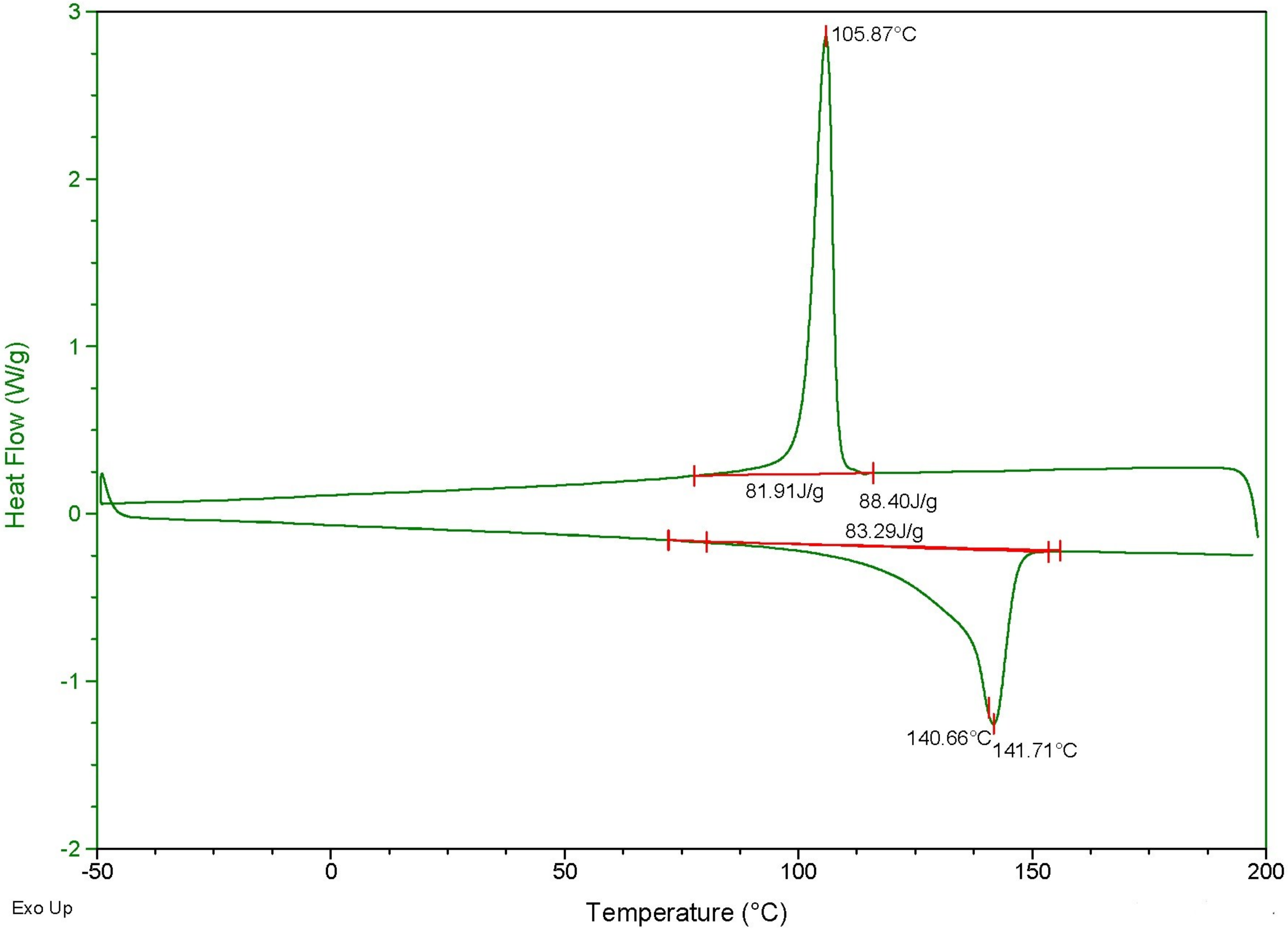
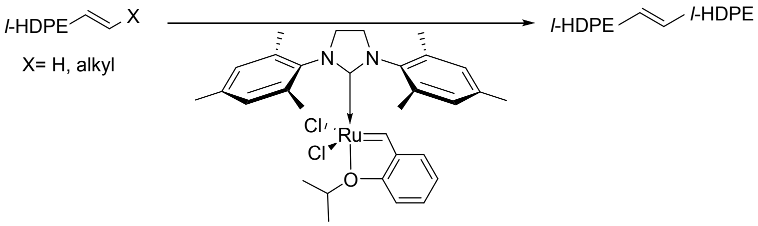


Figure S66: DSC trace for isoPP (heat/cool/heat, 10 °C/min, -50 °C – 200 °C)

VIII. Homo-coupling Experiments

Procedure for the synthesis of (*l*-HDPE)-(*l*-HDPE)



In a round bottom flask, *l*-HDPE (400 mg, M_n(NMR)=800 g/mol) and toluene (8 ml) are mixed and heated to 120 °C until a homogeneous mixture is formed. (Warning: Toluene boiling point is 110 °C, so electrical tape was used to secure a rubber septum on to the round bottom.) The solution was maintained at 120 °C and a syringe pump was utilized to inject HG-catalyst (6 mg, 0.0096 mmol) dissolved in toluene (2 ml) over 30 mins. After the addition, the mixture was heated at 120 °C for an additional 30 mins before precipitating the polymer in a methanol. Conversion of *l*-HDPE to (*l*-HDPE)-(*l*-HDPE) (NMR): Quantitative, M_n (NMR) = 1,200 g/mol.

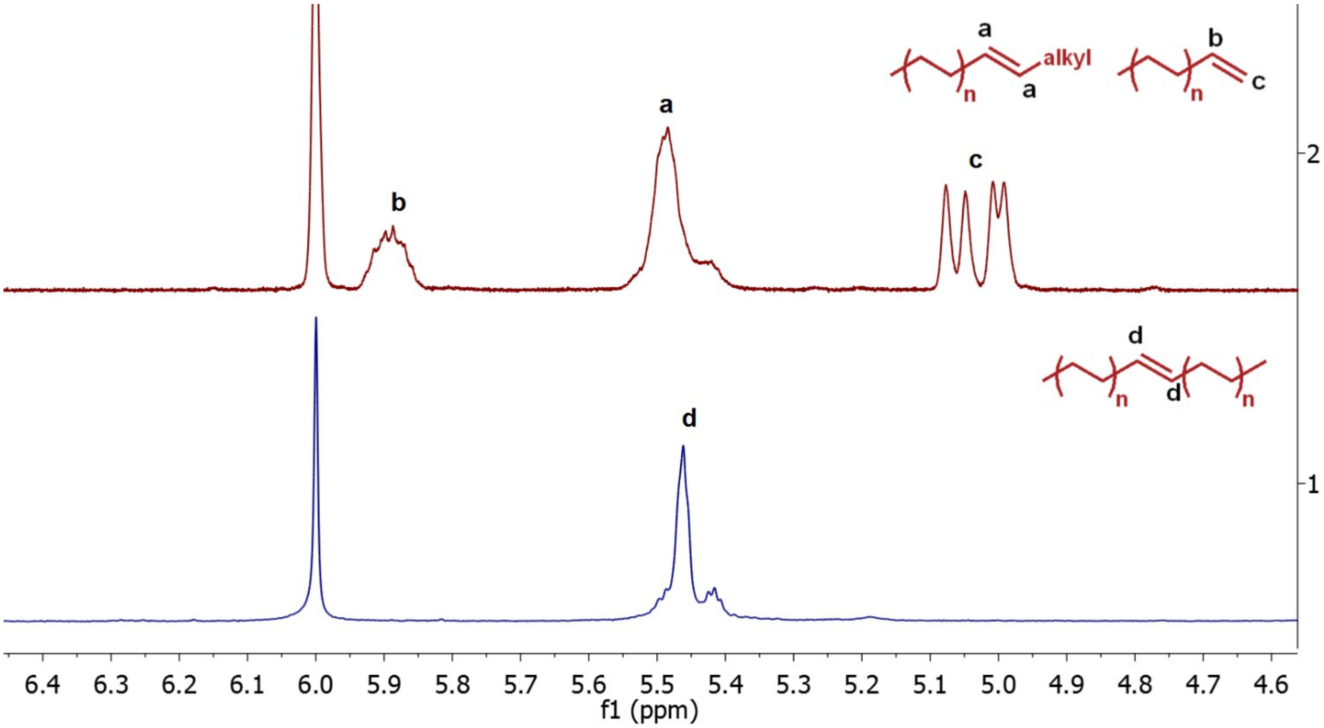


Figure S67: Stacked ^{1}H NMR of *l*-HDPE and (*l*-HDPE)-(*l*-HDPE) (d_2-TCE, 95 °C)

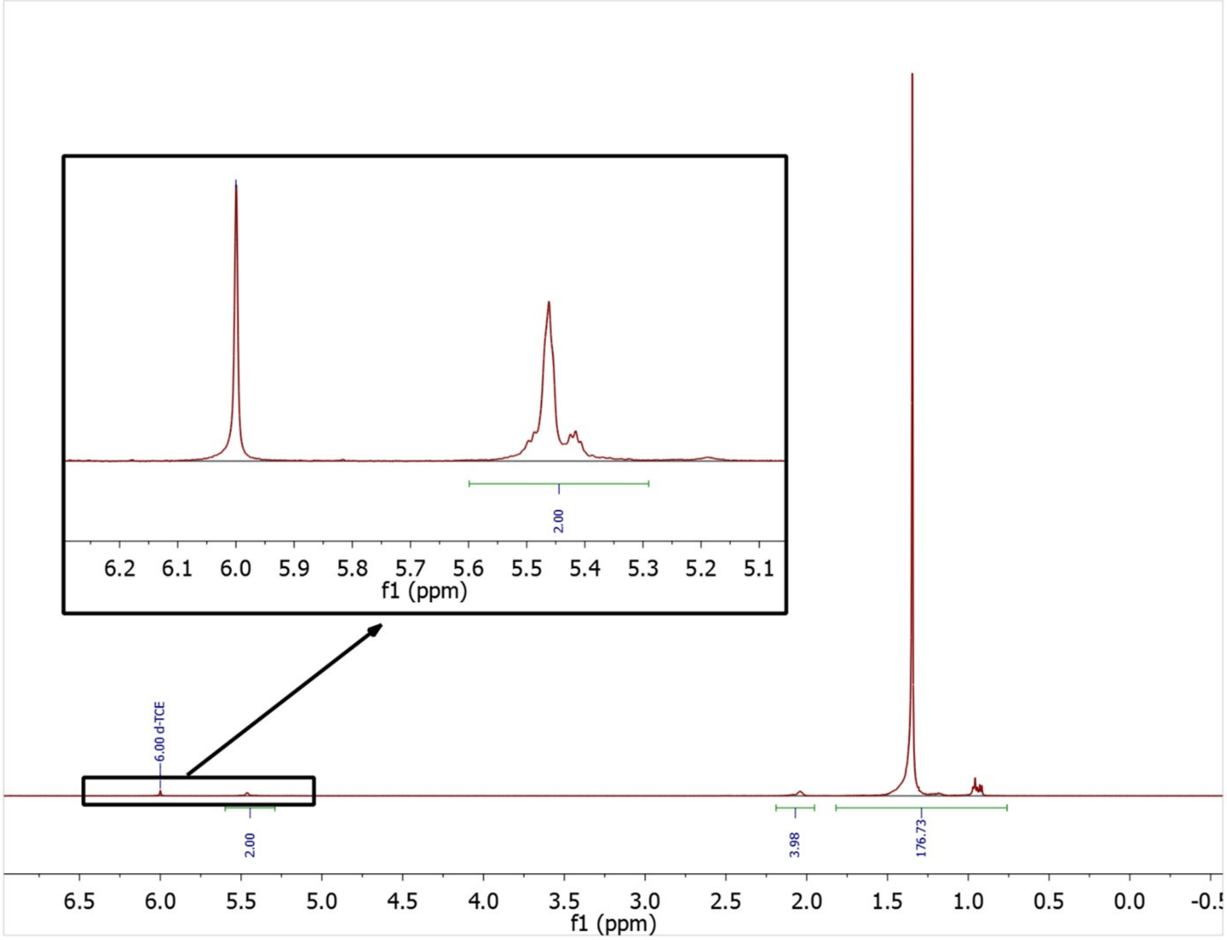
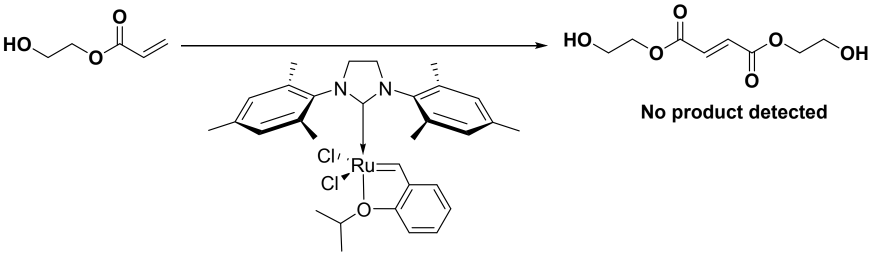


Figure S68: ^{1}H NMR of (*l*-HDPE)-(*l*-HDPE) (d_2-TCE, 95 ^{o}C)

Procedure for the synthesis of (HEA)-(HEA)



In a round bottom flask, HEA (200 mg, 1.72 mmol) and toluene (4 ml) are mixed and heated to 120 ^{o}C until a homogeneous mixture is formed. (Warning: Toluene boiling point is 110 ^{o}C, so electrical tape was used to secure a rubber septum on to the round bottom.) The solution was maintained at 120 ^{o}C and a syringe pump was utilized to inject HG-catalyst (108 mg, 0.17 mmol) dissolved in toluene (1 ml) over 30 mins. After the addition, the mixture was heated at 120 ^{o}C for an additional 30 mins before removing the solvent via evaporation and analyzed by NMR. Conversion of HEA to (HEA)-(HEA): 0%*, only unreacted HEA observed.

*NMR signals for targeted product reported in literature.[16]

IX. NMR Conversion Sensitivity Experiments

Since NMR is used as the primary form of characterization to determine the conversion of macromonomers into block copolymers, we believed it necessary to ascertain the limits of sensitivity. These experiments seek to give a specific meaning to the term 'quantitative' conversion for the range of polymers produced in this work. It is logical to consider that looking at the end groups of polymers will be more difficult for polymers of increasing molecular weights. Thus, we characterized the sensitivity of NMR for 3 different polymer molecular weights, *l*-HDPE (700 g/mol), *h*-HDPE (18,000 g/mol) and HBPE (89,000 g/mol).

Procedure for determining the sensitivity of ^{1}H NMR for the synthesis of *l*-HDPE

In a glass beaker *l*-HDPE-HEA (1 g) and *l*-HDPE (1 mg) were dissolved in 10 ml of boiling toluene. The mixture was then precipitated in methanol and dried. The collected solid was re-dissolved in boiling toluene and precipitated 2 more times to ensure thorough mixing of samples. The solid mixture was analyzed by ^{1}H NMR with a conc. 80 mg/ml in d_2-TCE (the same concentration used for all *l*-HDPE containing samples). The ^{1}H NMR parameters used for all data collection was: Varian Unity 500 MHz, 16 scans, relaxation time 8 sec. As seen in **Figure 69**, we can identify 0.1% contamination in our *l*-HDPE and thus we will set quantitative conversion for these types of materials at 99.9%.

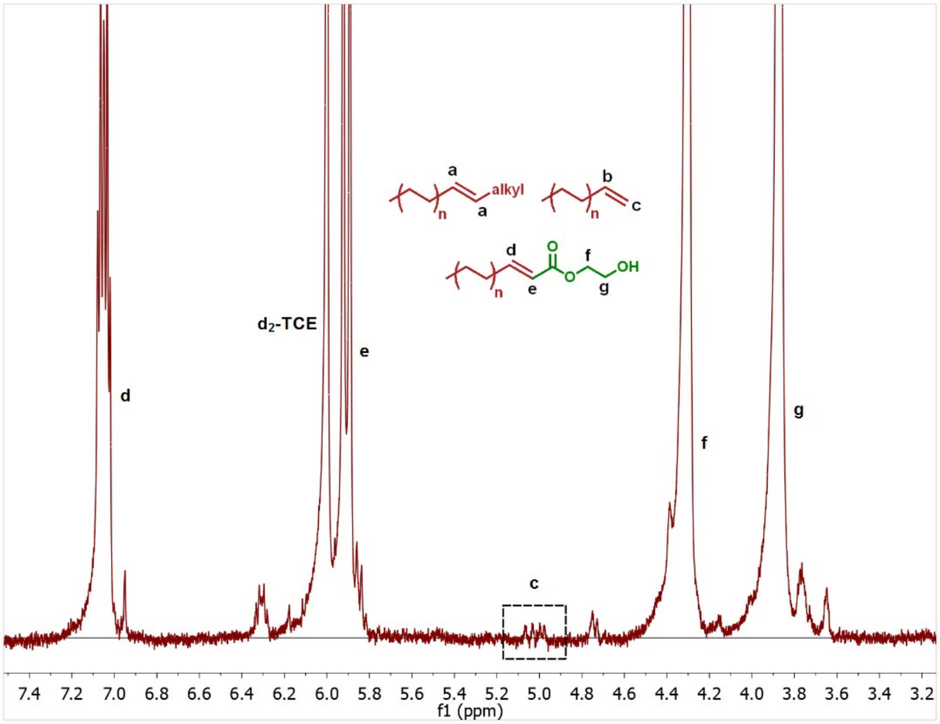


Figure S69: ^{1}H NMR of *l*-HDPE with enriched with 0.1% of *l*-HDPE-HEA (d_2-TCE, 95 ^{o}C)

Procedure for determining the sensitivity of ^{1}H NMR for the synthesis of *h*-HDPE

In a glass beaker *h*-HDPE-HEA (1 g) and *h*-HDPE (10 mg) were dissolved in 10 ml of boiling toluene. The mixture was then precipitated in methanol and dried. The collected solid was re-dissolved in boiling toluene and precipitated 2 more times to ensure thorough mixing of samples. The solid mixture was analyzed by ^{1}H NMR with a conc. 80 mg/ml in d_2-TCE (the same concentration used for all *h*-HDPE, synPP, isoPP, and LLDPE containing samples). The ^{1}H NMR parameters used for all data collection was: Varian Unity Inova NMR 600 MHz, 16 scans, relaxation time 8 sec. As seen in **Figure 70**, we can identify 1% contamination in our *h*-HDPE and thus we will set quantitative conversion for these types of materials at 99%.

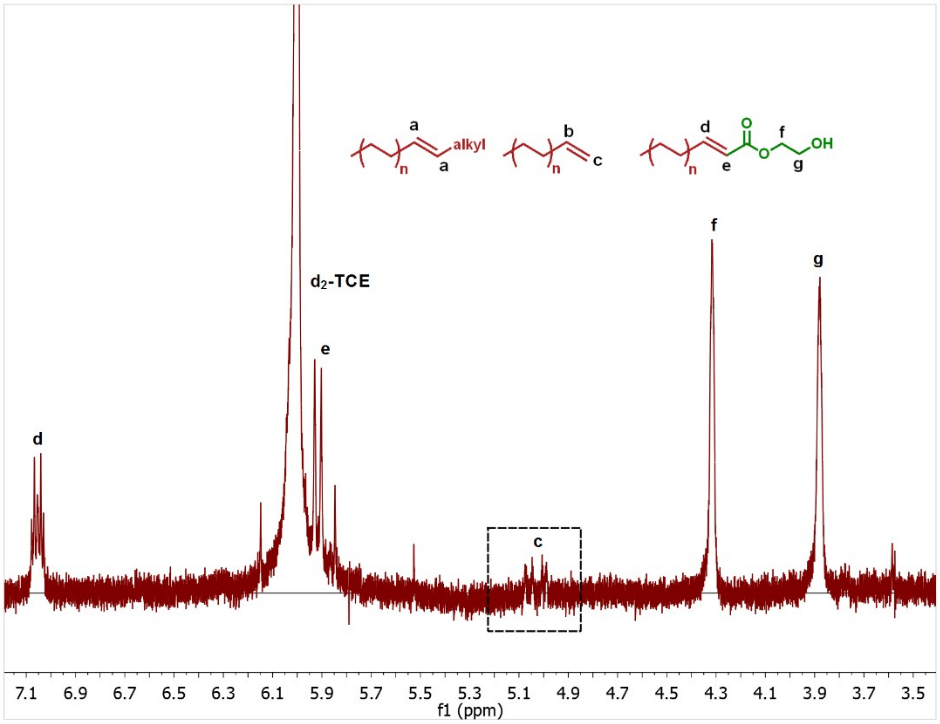


Figure S70 ^{1}H NMR of *h*-HDPE enriched with 1% of *h* -HDPE-HEA (d_2-TCE, 120 ^{o}C)

Procedure for determining the sensitivity of ^{1}H NMR for the synthesis of HBPE

In a glass beaker HBPE-HEA (1 g) and HBPE (50 mg) were dissolved in 10 ml of toluene. The mixture was stirred for 12 hours and toluene was removed. The residual mixture was analyzed by ^{1}H NMR with a conc. 120 mg/ml in d_2-TCE (the same concentration used for all HBPE, containing samples). The ^{1}H NMR parameters used for all data collection was: Bruker AVANCE III 500 MHz spectrometer, 32 scans, relaxation time 8 sec. As seen in **Figure 71**, we can identify 5% contamination in our HDPE and thus we will set quantitative conversion for these types of materials at 95%.

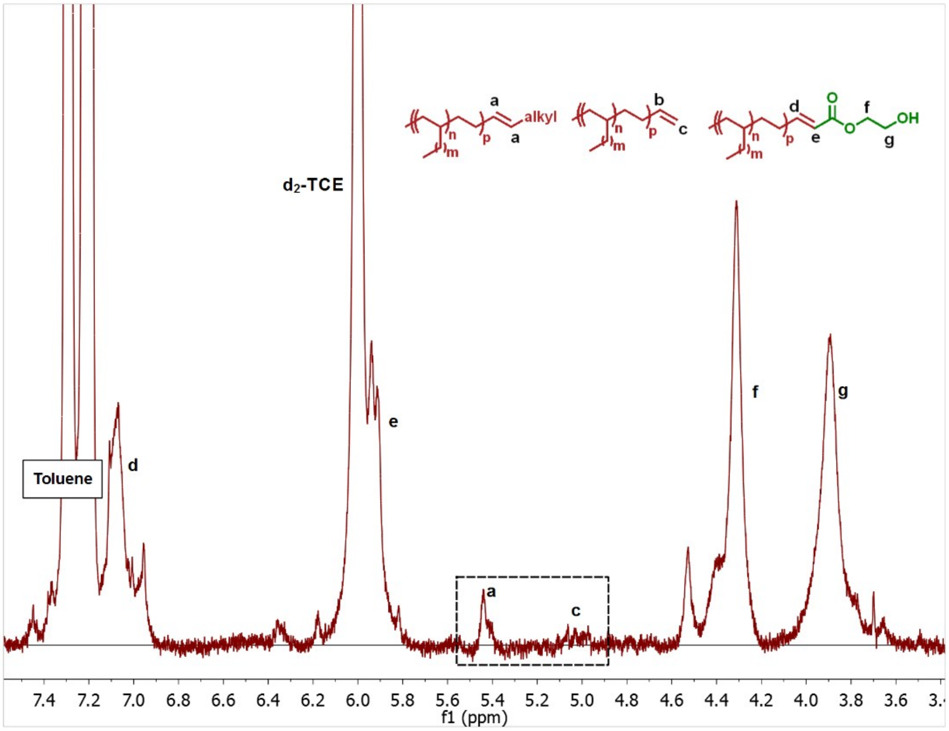


Figure S71: ^{1}H NMR of HBPE enriched with 5% of HBPE-HEA (d_2-TCE, 25 ^{o}C)

X. Productivity Calculations

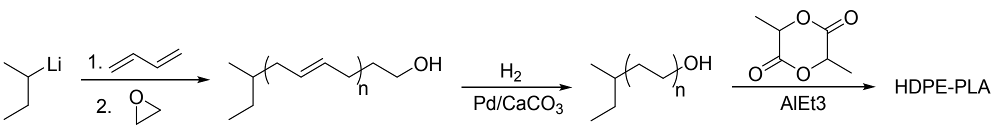
In order to compare the productivity of different synthetic routes, the procedures reported in literature were adjusted so that they produce the same block copolymer with the same molecular weight and same block sizes.

The values in Table 3 are calculated in the subsequent manner:

h-HDPE-PLA

For *h*-HDPE-PLA the target block copolymer was: M_n=64,000 g/mol with a f_{HDPE}=0.5 which corresponds to a HDPE block with a M_n =18,000 g/mol (which is our *h*-HDPE) and PLA block with a M_n=46,000 g/mol. The M_n = 64,000 g/mol was selected due to the fact our palladium catalyst for h-HPDE produces the correct molecular weight for the polyolefin block.

Anionic/Pd/AlEt$_3$[17]



Hillmyer et al. reported the synthesis of HDPE-PLA by means of anionic polymerization of butadiene, followed by hydrogenation with a palladium catalyst and ring opening polymerization of lactide by triethyl aluminum. [17] They produce a block copolymer with a M_n=61,000 g/mol with a f_{HDPE}= 0.72 (HDPE M_n=30,000 g/mol, PLA M_n=30,000 g/mol).

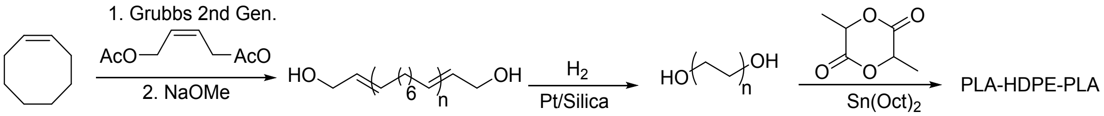
To apply this synthetic strategy to synthesize a HDPE-PLA block copolymer with an M_n=64,000 g/mol and f_{HDPE}=0.5, we will reduce the butadiene used in the anionic polymerization, reduce the $Pd/CaCO_3$ loading to keep the ratio of Pd to double bonds constant and add more lactide while assuming that the ring opening polymerization of lactide will remain living up to M_n=46,000 g/mol.

Using these assumptions to make 64 grams of block copolymer, these would be the chemical requirements:

	Catalyst	Metal	g of cat.	g of metal
Anionic	sBuLi	Li	0.0651	0.00694
Hydrogenation	$Pd/CaCO_3$	Pd	18.0	0.900
ROP	$AlEt_3$	Al	0.114	0.0134
Total			18.2	0.920

Thus, the performance of this system is 4 grams of polymer/ gram of catalyst or 70 g of polymer per gram of metal.

ROMP/Pt/Sn(Oct)$_2$[13]



Hillmyer et al. reported the synthesis of PLA-HDPE-PLA by means of ring opening metathesis of cyclooctene, followed by hydrogenation with a supported platinum catalyst and ring opening polymerization of lactide with tin octoate. They produce a tri-block copolymer with a M_n=55,700 g/mol with a f_{HDPE}=0.72 (HDPE M_n=28,200 g/mol, PLA M_n=27,500 g/mol).

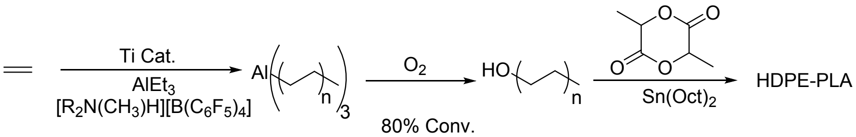
To apply this synthetic strategy to synthesize a HDPE-PLA block copolymer with an M_n=64,000 g/mol and f_{HDPE}=0.5, we will assume that the chain transfer agent will only have one acetate group so a di-block copolymer is formed. We maintain a ratio of 80 chain transfer agents per unit of Grubbs catalyst. Additionally, the ratio of cyclooctene to chain transfer agent will be reduced to get the desired molecular weight. The amount of platinum on silica will be reduced to keep the ratio of Pt to double bonds constant and more lactide to alcohol will be used, while assuming that the ring opening polymerization of lactide will remain living up to M_n=46,000 g/mol and we will maintain the ratio of 8 -OH groups for every one $Sn(Oct)_2$.

Using these assumptions to make 64 grams of block copolymer, these would be the chemical requirements:

	Catalyst	Metal	g of cat.	g of metal
ROMP	Grubbs 2nd	Ru	0.0106	0.00126
Hydrogenation	Pt/silica	Pt	1.80	0.0180
ROP	$Sn(Oct)_2$	Sn	0.0506	0.0148
Total			1.86	0.0341

Thus, the performance of this system is 34 grams of polymer/ gram of catalyst or 1,900 g of polymer per gram of metal.

$CTA/O_2/Sn(Oct)_2$[18]



Kempe and Co-works report the synthesis of HDPE-PLA by means of titanium-based catalyst system with triethyl aluminum as chain transfer agent, followed by an oxidation with O_2 and hydrolytic work-up. The end functionalized polymer than underwent ring opening polymerization of lactide with tin octoate. They produce a di-block copolymer with a M_n=5,500 g/mol with a f_{HDPE}=0.56 (HDPE M_n=3,300 g/mol, PLA M_n=2,200 g/mol). One important note to add here is, only 80% of the polymer chains contain a hydroxyl group after the oxidation step resulting in significant homo-HDPE contaimination in the final product.

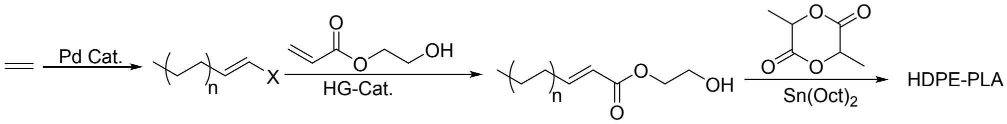
To apply this synthetic strategy to synthesize a HDPE-PLA block copolymer with an M_n=64,000 g/mol and f_{HDPE}=0.5, we will assume that a different titanium catalyst can be used that produces higher molecular weight HDPE with a similar activity. Additionally, we will assume that the oxidation step can be made quantitative and increase the lactide to alcohol ratio, while assuming that the ring opening polymerization of lactide will remain living up to M_n=46,000 g/mol.

Using these assumptions to make 64 grams of block copolymer, these would be the chemical requirements:

	Catalyst	Metal	g of cat.	g of metal
CTA Insertion	$Ti/AlEt_3$	Ti,Al	1.285	0.1519
ROP	$Sn(Oct)_2$	Sn	0.006	0.0017
Total			1.291	0.1536

Thus, the performance of this system is 50 grams of polymer/ gram of catalyst or 420 g of polymer per gram of metal. Note, that this does overestimate the block copolymer produced due to the presence of 20% homo-polymer.

Our Methodology Insertion/X-Metathesis/ Sn(Oct)$_2$



To apply our methodology to synthesize a HDPE-PLA block copolymer with an M_n=64,000 g/mol and f_{HDPE}=0.5, we did a quick optimization to examine the minimal amount of catalyst and HEA needed to quantitatively produce *h*-HDPE-PLA. We found that quantitative conversion of h-HDPE to h-HDPE-HEA can be achieved with a 1 mol% loading of HG-cat. and with 2 eq. of HEA to olefin end group, and ring opening polymerization of lactide will remain living down to loadings as low as 0.2 mol% (500 –OH to Sn(Oct)$_2$) of tin octoate.

To make 64 grams of block copolymer these would be the following requirements:

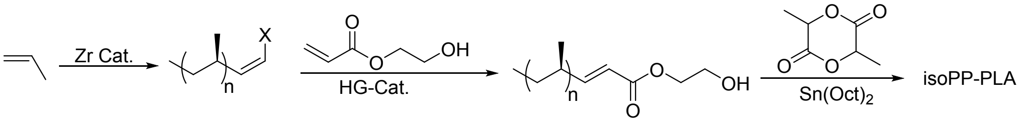
	Catalyst	Metal	g of cat.	g of metal
Insertion	Pd	Pd	0.0130	0.0021
X-Metathesis	HG-catalyst	Ru	0.0063	0.0010
ROP	Sn(Oct)$_2$	Sn	0.0008	0.0002
Total			0.0201	0.0033

Thus, the performance of this system is 3,200 grams of polymer/ gram of catalyst or 20,000 g of polymer per gram of metal.

isoPP-PLA

For isoPP-PLA block copolymer (M_n=71,000 g/mol, f_{PP}=0.5). That translates to an isoPP M_n =26,000 g/mol (which is our isoPP) and PLA M_n = 45,000 g/mol. The M_n = 71,000 g/mol was selected due to the fact our zirconium catalyst for isoPP produces the correct molecular weight for the polyolefin block.

Our Methodology Insertion/X-Metathesis/ Sn(Oct)$_2$



To apply our methodology to synthesize an isoPP-PLA block copolymer with an M_n=71,000 g/mol and f_{PP}=0.5, we did a quick optimization to examine the minimal amount of catalyst and HEA needed to quantitatively produce isoPP-PLA. We found that quantitative conversion of isoPP to isoPP-HEA can be achieved with a 0.1 mol% loading and with 2 eq. of HEA to olefin end group, and ring opening polymerization of lactide will remain living down to loadings as low as 0.2 mol% (500 –OH to Sn(Oct)$_2$) of tin octoate. One important note about this synthesis is the cross metathesis only functionalizes 70% of polymer chains since vinylidene double bonds are not reactive under our reaction conditions.

To make 71 grams of block copolymer these would be the following requirements:

	Catalyst	Metal	g of cat.	g of metal
Insertion	Zr	Zr	0.0003	0.00006
X-Metathesis	HG-catalyst	Ru	0.0006	0.00010
ROP	$Sn(Oct)_2$	Sn	0.0008	0.00024
Total			0.0017	0.00040

Thus, the performance of this system is 29,000 grams of polymer/ gram of catalyst or 125,000 g of polymer per gram of metal. Homopolymer is accounted for and not considered not the target material. Thus, it was subtracted out of final block copolymer produced.

XI. References

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