Supporting Information for

Backbone Editing of Oxidized Polyethylene: Insertion of Oxygen and Nitrogen Atoms via Hydroxyalkyl Azide-Mediated Rearrangements

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Materials and Methods

Purchased Materials

5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, 3-bromo-propanol, 3-bromo-2,2-dimethyl-1-propanol, and tetraethylammonium bicarbonate were purchased from Combi-Blocks and used without further purification. 2,6-dichloropyridine *N*-oxide, 2-bromo-ethanol, sodium azide, triethylamine, chlorotrimethylsilane, 2-(chloromethyl)oxirane, (R)- 2-(chloromethyl)oxirane, (S)- 2-(chloromethyl)oxirane, tetrabutylammonium hydrogensulfate, ammonium chloride, allyl alcohol, propargyl alcohol, and polyethylene (M_n = 1.7 kg/mol) were purchased from Sigma-Aldrich and used without further purification. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and scandium(III) triflate were purchased from Oakwood Chemical and used without further purification. Ruthenium carbonyl ($Ru_3(CO)_{12}$) was purchased from Strem and used without further purification. Commercial LDPE was obtained from Boulder reclosable ziplock sandwich bags purchased from ALDI and used without any purification.

Silica gel for column chromatography (SiliaFlash® F60) (230–400 mesh, 40–63 micron particle size, 60 Å pore size) was purchased from Silicycle. Glass-backed silica 20 x 20 cm^2 "SiliaPlate™ TLC Plates Optimized for $KMnO_4$, 250 µm, F254" plates were purchased from Silicycle and utilized for analytical thin-layer chromatography (TLC). Neutral alumina with 60/325 mesh was purchased from Fisher Scientific and heated in an oven for >1 h prior to use.

Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and were used as received. All other chemicals and solvents were purchased from Sigma-Aldrich, Alfa-Aesar, Acros Organics, Fisher Scientific, Oakwood Chemical, or VWR and used as received. Dry solvents were either passed through solvent purification columns prior to use[1] or tried over 3 or 4 Å molecular sieves.

Instrumentation

Nuclear magnetic resonance (NMR) spectroscopy

^1H, $^{13}C\{^1H\}$, ^1H–$^{13}C\{^1H\}$ HSQC, ^1H–$^{13}C\{^1H\}$ HMBC and ^1H–^1H COSY NMR spectra were recorded on Bruker NMR spectrometers operating at 400, 500, and 600 MHz for ^1H, 101, 126, and 151 MHz for $^{13}C\{^1H\}$. These instrument models are listed here with their corresponding supporting federal grants (if applicable): Bruker AVANCE II3I Nanobay 400 MHz (NSF Grant No. CHE-0922858), Bruker AVANCE III 500 MHz (NSF Grant No. CHE-0922858), Bruker AVANCE III 600 MHz (NSF Grant No. CHE-0922858), Bruker AVANCE NEO 600 MHz (NSF Grant No. CHE-1828183), Bruker UNI400, AV3BIO500, UNI500, or NEO600. Chemical shifts are expressed in parts per million (ppm), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), oct (octet), m (multiplet), b (broad), and combinations thereof. Scalar coupling constants *J* are reported in Hertz (Hz). MestReNova v15.0.0-34764 software (Mestrelab Research S. L.) was used to analyze the NMR spectra. ^1H and ^{13}C NMR spectra were referenced to residual monoproteo-solvent peaks as reported in literature.[2]

Gel permeation chromatography (GPC)

Polymer molecular weights were analyzed using a high temperature (HT) Tosoh EcoSEC-HT GPC. Samples were dissolved at ~2 mg/mL in 1,2,4-trichlorobenzene with 200 ppm dibutylhydroxytoluene (BHT). Samples were run at 140 °C with a mobile phase of 1,2,4-trichlorobenzene with 200 ppm

dibutylhydroxytoluene at a flow rate of 1 mL/min. Calibration was performed using polystyrene standards, which ranged from 860 to 100,000 g/mol.

Thermo-gravimetric analysis

Thermo-gravimetric analysis was performed on a TA Instruments Q500-0154 thermogravimetric analyzer. Polymer samples (<10 mg) were loaded onto a tared platinum pan then heated from ambient temperatures to 600 °C at a rate of 10 °C/min.

Differential scanning calorimetry

Differential scanning calorimetry was performed on a TA Instruments Discovery DSC. Polymer samples were subjected to the following temperature segments: (1) heating to 170 °C (10 °C/min), (2) cooling to -50 °C (10 °C/min), and (3) heating to 170 °C (10 °C/min). The first segment was used to erase the thermal history of the material and the third segment was used to report melting transitions for the polymer samples.

FT-IR

Fourier Transform Infrared spectroscopy was performed using a Thermo Scientific NICOLET iS5 spectrometer with an iD7 ATR diamond attachment.

Melt pressing

Polymer films of materials sourced from commercial LDPE were prepared by melt-pressing using a PHI Manual Compression Press. On a pre-heated steel plate was placed a Kapton film (Kapton KN .01''). A steel shim (~0.2 mm thick) with rectangular stencil of 4.5 x 6.0 cm was placed on the Kapton film then polymer was added. Another Kapton film was placed on top followed by a second steel plate. The setup was transferred to the hot melt press (125 °C) then pressed to 6 tons for 30-60 seconds. Pressure was momentarily released, then pressed again to 6 tons for 30-60 seconds. After removal of the setup, the films were rapidly cooled to room temperature by transferring to an aluminum surface. **Note:** for functionalized polymer samples, the Kapton sheets were pre-treated with Frekote 770- NC.

Uniaxial tensile testing

Uniaxial tensile testing was conducted on an INSTRON® 34SC-1 instrument. Dogbones were cut from meltpressed films using an ISO 527 Type 5B cutting die, which produced dogbones with a 12 mm bridge length and 2 mm bridge width. For each sample, bridge width and thickness at the bridge was measured using calipers. Dogbones were loaded with a starting gap of ~18 mm to ensure consistent pulls then pulled at a rate of 0.09 mm/s. Averages and standard deviation of triplicate testing is reported.

Mass Spectrometry

HRMS data was collected with a Q Exactive HF-X mass spectrometer. Samples were introduced via a heated electrospray source (HESI) at a flow rate of 10 µL/min. HESI source conditions were set as: nebulizer temperature 400 deg C, sheath gas (nitrogen) 20 arb, auxillary gas (nitrogen) 0 arb, sweep gas (nitrogen) 0 arb, capillary temperature 320 degrees C, RF voltage 45 V. The mass range was set to 100-1000 m/z. All measurements were recorded at a resolution setting of 120,000. Solutions were analyzed at 0.1 mg/mL or less based on responsiveness to the ESI mechanism. Xcalibur was used to analyze the data. Molecular formula assignments were determined with Molecular Formula Calculator (v 1.3.0). All observed species were singly charged, as verified by unit m/z separation between mass spectral peaks corresponding to the ^{12}C and $^{13}C^{12}C_{c-1}$ isotope for each elemental composition. We thank the University of North Carolina's Department of Chemistry Mass Spectrometry Core Laboratory for their assistance

with mass spectrometry analysis. This instrument is supported by the National Science Foundation under Grant No. (CHE-1726291)

Polarimetry

Optical rotation was measured using a 2 mL cell with 2.0 dm path length as an average of duplicate measurements on an Autopol® IV automatic polarimeter. Concentrations are reported in g/100 mL.

Synthetic Procedures

General Synthetic Protocol

All air-sensitive reactions were carried out in flame- or oven-dried glassware in a nitrogen filled glove box or using standard Schlenk techniques. Inhomogeneous reaction mixtures were stirred with Teflon-coated magnetic stir bars. Hamilton gas-tight syringes were cleaned by multiple rinses of hexanes, methanol, acetone, and dichloromethane (or a subset of aforementioned solvents), then dried under a stream of air.

Reactions were monitored via NMR and TLC, and the TLC plates were visualized under UV irradiation or via standard staining procedures. Removal of solvents *in vacuo* was achieved using an IKA rotary evaporator and a Schlenk line (~20 mTorr, dynamic vacuum). Purification via flash chromatography was carried out following standard procedures or using a Biotage Isolera One automated flash chromatography system.

Materials prepared following reported or modified procedures:

3-azido-1-propanol (**1-OH**) was prepared according to the literature procedure[3] except 3.0 equiv of NaN_3 were used in the reaction. ^{1}H NMR matches the reported one.[3]

(3-azidopropoxy)trimethylsilane was prepared according to the literature procedure.[4]

2-azido-1-ethanol (**2-OH**) was prepared according to the literature procedure[5] except the reaction was run at 0.93 M in DI water and a silica gel column eluting with 1:1 Et_2O:pentanes was run on the crude product. ^{1}H NMR spectrum matched the reported one.[5]

3-azido-2,2-dimethyl-1-propanol (**5-OH**) was prepared according to the literature procedure[6] except 3-bromo-2,2-dimethyl-1-propanol was used as starting material and purification was performed using silica gel chromatography eluting with 1:1 Et_2O:pentanes (R_f: 0.38 visualized by PMA stain with heating) instead of distillation. ^{1}H NMR spectrum matched the reported one.[6]

2-((prop-2-yn-1-yloxy)methyl)oxirane was prepared according to the literature procedure[7] and ^{1}H NMR matches the reported one.

(R)-2-((allyloxy)methyl)oxirane was prepared according to the procedure used for 2-((prop-2-yn-1-yloxy)methyl)oxirane and (R)-2-((prop-2-yn-1-yloxy)methyl)oxirane,[7] and ^{1}H NMR and optical rotation ($[\alpha]^{25}_D$) matches what has been reported in the literature.[8]

(S)-2-((allyloxy)methyl)oxirane was prepared according to the procedure used for 2-((prop-2-yn-1-yloxy)methyl)oxirane and (R)-2-((prop-2-yn-1-yloxy)methyl)oxirane,[7] and ^{1}H NMR and optical rotation ($[\alpha]^{25}_D$) matches what has been reported in the literature.[8]

2-((allyloxy)methyl)oxirane was prepared according to the procedure used for 2-((prop-2-yn-1-yloxy)methyl)oxirane and (R)-2-((prop-2-yn-1-yloxy)methyl)oxirane,[7] and ^{1}H NMR matches what has been reported in the literature.

(R)-1-(allyloxy)-3-azidopropan-2-ol (**(*R*)-3-OH**) was prepared according to the literature procedure[9] and ^{1}H NMR matches what has been reported in the literature.

(S)-1-(allyloxy)-3-azidopropan-2-ol (**(S)-3-OH**) was prepared according to the literature procedure[9] and ^{1}H NMR matches what has been reported in the literature.

1-(allyloxy)-3-azidopropan-2-ol (***rac*-3-OH**) was prepared according to the literature procedure,[9] and ^{1}H NMR matches what has been reported in the literature.

1-azido-3-(prop-2-yn-1-yloxy)propan-2-ol (***rac*-4-OH**) was prepared according to the literature procedure,[9] and ^{1}H NMR matches what has been reported in the literature.

Ru(TPFPP)CO was prepared according to literature procedures[10] except an additional silica gel column eluting with toluene and preparatory TLC eluting with toluene were performed to isolate product. ^{1}H NMR spectrum matched the reported one.[10]

ox-PE was made according to the literature procedure[11] with 0.1 equiv 2,6-dichloropyridine *N*-oxide and 0.00005 equiv Ru(TPFPP)CO (from a 1 mM stock solution in either DCM or 1,2-dichloroethane). Solvent and temperature conditions are below:

M_n = 1.7 kg/mol polyethylene: 1.7 kg/mol polyethylene was dissolved at a concentration of 28 mg/mL in 1,2-dichloroethane at 120 °C then cooled for addition of 2,6-dichloropyridine *N*-oxide and the catalyst stock solution (1 mM in either DCM or 1,2-dichloroethane). After addition, the flask was heated again to 120 °C for 30 min before cooling and precipitating **ox-Pe** into MeOH. Oxidation was performed up to a 5 g scale of polyethylene starting material. ^{1}H NMR spectrum matched the reported one.[11]

Commercial LDPE: Commercial LDPE was dissolved at a concentration of 28 mg/mL in 1,1,2,2-tetrachloroethane at 160 °C then cooled to 120 °C for addition of 2,6-dichloropyridine *N*-oxide followed by the catalyst stock solution (1 mM in 1,2-dichloroethane). After addition, the solution was stirred at 120 °C for 30 min before cooling and precipitating **zip-ox-Pe** into MeOH. Oxidation was performed up to a 5 g scale of polyethylene starting material. ^{1}H NMR spectrum matched the reported one.[11]

Materials prepared using new procedures

((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (*rac*-3-OTMS): To a 250 mL round-bottom flask was added a magnetic stir bar, 1-(allyloxy)-3-azidopropan-2-ol (1.70 g, 10.8 mmol) and THF (54 mL). Triethylamine (4.52 mL, 32.4 mmol) was added dropwise, followed by trimethylsilyl chloride (4.12 mL, 32.4 mmol). Upon addition of trimethylsilyl chloride, a white precipitate immediately formed. The white slurry was left to stir for 4 h, or until gauged complete by TLC. The reaction was quenched by addition of 100 mL of DI water, and the mixture was then poured into a 250 mL separatory funnel. Organic material was extracted with diethyl ether (3x, 50 mL) and collected organic extracts were washed with brine (2x, 100 mL). The organic layers were dried with sodium sulfate, filtered into a 250 mL conical flask, and then concentrated under reduce pressure. The crude material was loaded neat onto an 80 G silica column, and eluted with 100% DCM. The pure fractions were collected and concentrated under

reduced pressure to reveal ((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (1.23 g, 5.36 mmol, 50% yield) as a clear, fragrant liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 17.3, 10.3, 5.6 Hz, 1H), 5.26 (ddt, *J* = 17.2, 1.7 Hz, 1H), 5.19 (ddt, *J* = 10.4, 1.4 Hz, 1H), 3.98 (c, 3H), 3.40 (d, *J* = 5.8 Hz, 2H), 3.35 – 3.21 (m, 2H), 0.16 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.58, 117.34, 72.51, 71.89, 71.02, 54.45, 0.21.

HRMS: Found m/z = 230.13190 (mass error = -0.14 ppm)

(S)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (*(S)*-3-OTMS): To a 250 mL round-bottom flask was added a magnetic stir bar, (S)-1-(allyloxy)-3-azidopropan-2-ol (1.01 g, 6.43 mmol) and THF (32 mL). Triethylamine (2.7 mL, 19.3 mmol) was added dropwise, followed by trimethylsilyl chloride (2.5 mL, 19.3 mmol). Upon addition of trimethylsilyl chloride, a white precipitate immediately formed. The white slurry was left to stir for 4 h, or until gauged complete by TLC. The reaction was quenched by addition of 100 mL of DI water, and the mixture was then poured into a 250 mL separatory funnel. Organic material was extracted with diethyl ether (3x, 50 mL) and collected organic extracts were washed with brine (2x, 100 mL). The organic layers were dried with sodium sulfate, filtered into a 250 mL conical flask, and then concentrated under reduce pressure. The crude material was loaded neat onto an 80 G silica column, and eluted with 100% DCM. The pure fractions were collected and concentrated under reduced pressure to reveal (S)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (750 mg, 6.4 mmol, 51% yield) as a clear, fragrant liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 17.3, 10.5, 5.6 Hz, 1H), 5.26 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.19 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.00 – 3.92 (c, 3H), 3.40 (d, *J* = 5.8 Hz, 2H), 3.35 – 3.19 (c, 2H), 0.16 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.57, 117.33, 72.50, 71.88, 71.02, 54.45, 0.20.

HRMS: Found m/z = 230.13173 (mass error = -0.88 ppm)

Specific rotation: $[\alpha]^{25}_{D}$ = -2.7°/[(g/mL)(dm)] (c. 6.0, MeOH).

(R)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (*(R)*-3-OTMS): To a 250 mL round-bottom flask was added a magnetic stir bar, (R)-1-(allyloxy)-3-azidopropan-2-ol (760 mg, 4.8 mmol) and THF (24 mL). Triethylamine (2.0 mL, 14.5 mmol) was added dropwise, followed by trimethylsilyl chloride (1.8 mL, 14.5 mmol). Upon addition of trimethylsilyl chloride, a white precipitate immediately formed. The white slurry was left to stir for 4 h, or until gauged complete by TLC. The reaction was quenched by addition of 100 mL of DI water, and the mixture was then poured into a 250 mL separatory funnel. Organic material was extracted with diethyl ether (3x, 50 mL) and collected organic extracts were washed with brine (2x, 100 mL). The organic layers were dried with sodium sulfate, filtered into a 250 mL conical flask, and then concentrated under reduce pressure. The crude material was loaded neat onto an 80 G silica column, and eluted with 100% DCM. The pure fractions were collected and concentrated under reduced pressure to reveal (R)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (800 mg, 4.8 mmol, 71% yield) as a clear, fragrant liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.26 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.19 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.00 – 3.92 (c, 3H), 3.40 (d, *J* = 5.8 Hz, 2H), 3.34 – 3.22 (c, 2H), 0.16 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.57, 117.33, 72.50, 71.88, 71.02, 54.45, 0.20.

HRMS: Found m/z = 230.13184 (mass error = -0.40 ppm)

Specific rotation: $[\alpha]^{25}_{D}$ = + 2.5°/[(g/mL)(dm)] (c. 6.0, MeOH)**((1-azido-3-(prop-2-yn-1-yloxy)propan-2-yl)oxy)trimethylsilane (*rac*-4-OTMS):** To a 250 mL round-bottom flask was added a magnetic stir bar, 1-azido-3-(prop-2-yn-1-yloxy)propan-2-ol (1.03 g, 6.64 mmol) and THF (33 mL). Triethylamine (2.78 mL, 19.9 mmol) was added dropwise, followed by trimethylsilyl chloride (2.53 mL,19.9 mmol). Upon addition of trimethylsilyl chloride, a white precipitate immediately formed. The white slurry was left to stir for 4 h, or until gauged complete by TLC. The reaction was quenched by addition of 100 mL of DI water, and the mixture was then poured into a 250 mL separatory funnel. Organic material was extracted with diethyl ether (3x, 50 mL) and collected organic extracts were washed with brine (2x, 100 mL). The organic layers were dried with sodium sulfate, filtered into a 250 mL conical flask, and then concentrated under reduce pressure. The crude material was loaded neat onto an 80 G silica column, and eluted with 100% DCM. The pure fractions were collected and concentrated under reduced pressure to reveal ((1-azido-3-(prop-2-yn-1-yloxy)propan-2-yl)oxy)trimethylsilane (802 mg, 3.52 mmol, 53% yield) as a clear, fragrant liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (d, *J* = 2.4 Hz, 2H), 3.96 (qd, *J* = 5.7, 4.0 Hz, 1H), 3.50 (d, *J* = 5.6 Hz, 2H), 3.35 – 3.22 (c, 2H), 2.44 (t, *J* = 2.4 Hz, 1H), 0.17 (s, 9H).

^{13}C NMR (100 MHz, CDCl3) δ 79.30, 74.71, 71.36, 70.71, 58.57, 54.15, 0.03.

HRMS: Found m/z = 228.11608 (mass error = -0.89 ppm)

General procedure for screening of acids with 5-nonanone

In an oven dried 1-dram vial with stir bar and septum cap was added the acid (60 µmol, 3.0 equiv) and 0.9 mL anhydrous DCE. The vial was heated to 120 °C then 0.1 mL of a 200 mM stock solution of 5-nonanone (20 µmol, 1.0 equiv) with **1-OH** (30 µmol, 1.5 equiv), and mesitylene in anhydrous DCE was added. The reactions were stirred for 2 h at 120 °C then cooled to RT. After cooling, a portion was diluted with $CDCl_3$ for analysis with ^{1}H NMR spectroscopy. **Note**: for TfOH, the acid was added directly to a vial with 1.0 mL of a 20 mM stock solution of 5-nonanone (20 µmol, 1.0 equiv) with **1-OH** (30 µmol, 1.5 equiv), and mesitylene in anhydrous DCE at 120 °C. The reaction was then stirred for 10 min before cooling for analysis.

General procedure for reactions with 3-pentanone in Table 1

To a 0.5-2 mL micorowave vial with stir bar was added varying amounts of $Sc(OTf)_3$ according to **Table 1**, 0.7 mL chlorobenzene, and 0.2 mL of HFIP. The vial was sealed and heated to the temperature indicated in **Table 1**, and left to stir for a few minutes to achieve thermal equilibrium. Then, 100 uL of a 900 mmolar (w.r.t. 3-pentanone) stock solution containing 1.5 equiv of azide reagent and 1.0 equiv of mesitylene internal standard dissolved in chlorobenzene was injected with a 250 uL Hamilton syringe (to achieve a final reaction concentration of 90 mmolar w.r.t. 3-pentanone), and the vial was further sealed with parafilm and left to stir for 24 h. After the reactions were allowed to stir for 24 h, they were removed from the heat and allowed several minutes to cool to room temperature. Because the solution was not homogenous—solids were suspended in the vial—200 uL of ACN-d_3 was added to dissolve the reaction mixture which dissolved all solids and produced a clear solution. A 400 uL aliquot of this solution was taken with a 1.0 mL syringe, which was added to another 100 uL of ACN-d_3 for subsequent analysis via ^{1}H-NMR spectroscopy. Yields were calculated based off integration relative to the internal standard as detailed below.

*Optimization of reaction of **1-OH** with **ox-PE** (sourced from 1.7 kg/mol PE)*

To a 1-dram vial with stir bar was added 20 mg **ox-PE** (2.8% ketone and average MW of repeat unit of 28.87 g/mol) and 0.8 mL chlorobenzene. The vial was heated to 80 °C to dissolve **ox-PE** then the solution was cooled to 50 °C and 0.2 mL HFIP was added to produce a 4:1 chlorobenzene:HFIP solution with a polymer concentration of 20 mg/mL). Varying amounts of **1-OH** and $Sc(OTf)_3$ were then added and the reactions were stirred for 24 h at 50 °C. The reaction mixtures were precipitated into 5 mL cold MeOH then centrifuged (4000 g, 8 °C, 5 min). The solution was decanted and the pellet was rinsed with 1 mL MeOH. The pellet was resuspended in MeOH, centrifuged (4000 g, 8 °C, 5 min), and the solution decanted. The resulting polymer pellet was dried *in vacuo* to yield **P1-1**.

*General procedure for Synthesis of **P1** with **1-OH**, **5-OH**, **2-OH**, and **1-OTMS** (**ox-PE** sourced from 1.7 kg/mol PE)*

In a 1-dram vial with stir bar, **ox-PE** (2.7% ketone and average MW of repeat unit of 28.84 g/mol) was dissolved in 1.6 mL of a 0.175 M solution of either **1-OH**, **5-OH**, **2-OH**, or **1-OTMS** (281 µmol, 1.5 equiv w.r.t ketones) in chlorobenzene at 80 °C. After dissolving **ox-PE**, the solution was slowly cooled to 50 °C and 0.4 mL HFIP was added during the cooling process (at ~75 °C) to produce a 4:1 chlorobenzene:HFIP solution with a polymer concentration of 100 mg/mL. After cooling to 50 °C, $Sc(OTf)_3$ (276 mg, 562 µmol, 3.0 equiv w.r.t ketone) was added then the mixture was stirred at 50 °C for 24 h. The mixture was then precipitated into 20 mL MeOH and centrifuged (4000 g, 20 °C, 6 min). The solution was decanted and the pellet was rinsed with 1 mL MeOH. The pellet was resuspended in 10 mL MeOH, centrifuged (4000 g, 20 °C, 6 min) and the solution decanted. This process was repeated one additional time, then the polymer pellet was dried *in vacuo* to yield **P1**. Isolated polymer masses are reported in **Table S2**.

*General procedure for Synthesis of **P1** with **OTMS variants** (**ox-PE** sourced from 1.7 kg/mol PE)*

In a 1-dram vial with stir bar, **ox-PE** (2.7% ketone and average MW of repeat unit of 28.84 g/mol) was dissolved in 1.6 mL chlorobenzene at 80 °C. After dissolving **ox-PE**, the solution was slowly cooled to 50 °C and 0.4 mL HFIP was added during the cooling process (at ~75 °C) to produce a 4:1 chlorobenzene:HFIP solution with a polymer concentration of 100 mg/mL. After cooling to 50 °C, **(*R*)-3-OTMS**, ***rac*-3-OTMS**, or ***rac*-4-OTMS** (281 µmol, 1.5 equiv w.r.t ketones) was added *via* Hamilton syringe and $Sc(OTf)_3$ (276 mg, 562 µmol, 3.0 equiv w.r.t ketones) was added immediately after. The reaction mixture was then stirred at 50 °C for 24 h. The mixture was precipitated into 20 mL MeOH then centrifuged (4000 g, 20 °C, 6 min). The solution was decanted, and the pellet was rinsed with 1 mL MeOH. The pellet was resuspended in 10 mL MeOH, centrifuged (4000 g, 20 °C, 6 min) and the solution decanted. This process was repeated one additional time, then the polymer pellet was dried *in vacuo* to yield **P1**. Isolated polymer masses are reported in **Table S2**.

*General procedure for Synthesis of **zip-P1** with **1-OH** and **2-OH** (**ox-PE** sourced from commercial LDPE)*

To a 40 mL vial with stir bar was added 2.00 g **zip-ox-PE** (2.0% ketone and average MW of repeat unit of 28.63 g/mol) and **1-OH** or **2-OH** (2.10 mmol, 1.5 equiv w.r.t ketones). 16 mL chlorobenzene was added then the vial was heated to 140 C to dissolve the polymer. After **zip-ox-PE** was dissolved, the solution was slowly cooled to 70 °C and 4.0 mL HFIP was added during the cooling process (at ~120 °C) to produce a 4:1 chlorobenzene:HFIP solution with a polymer concentration of 100 mg/mL. After cooling to 70 °C, $Sc(OTf)_3$ (2.06 g, 4.19 mmol, 3.0 equiv w.r.t ketones) was added then the vial was stirred at 70

°C for 24 h. The reaction mixture was then precipitated into 400 mL MeOH, filtered, washed with 3 x 25 mL MeOH, then dried *in vacuo* at 40 °C. Isolated polymer masses are reported in **Table S3.**

*General procedure for synthesis of **P2** (from **P1** sourced from 1.7 kg/mol PE)*
To a 1-dram vial with stir bar was added 80 mg **P1**, 57 mg tetraethylammonium bicarbonate (0.30 mmol, 4.0 equiv w.r.t ketones from original **ox-PE**), and 1.6 mL chlorobenzene. The solution was heated to 80 °C for 5 h with stirring, then precipitated into 8 mL MeOH, and centrifuged (4000 g at 20 °C for 6 min). After decanting the solution, the polymer pellet was resuspended in 5 mL MeOH, centrifuged (4000 g at 20 °C for 6 min), and the solution was decanted. This process was repeated one additional time, then the polymer pellet was dried *in vacuo* to yield **P2**. Isolated polymer masses are reported in **Table S2**.

*General procedure for synthesis of **zip-P2** (from **zip-P1** sourced from commercial LDPE)*
To a 40 mL vial with stir bar was added 1.00 g **zip-P1**, 535 mg tetraethylammonium bicarbonate (2.79 mmol, 4.0 equiv w.r.t ketones from original **zip-ox-PE**), and 20 mL chlorobenzene. The solution was headed to 120-130 °C for 15 min to dissolve the polymer then cooled to 100 °C and stirred for 5 h. The solution was then precipitated into 400 mL MeOH, filtered, washed with 3 x 25 mL MeOH, and dried *in vacuo* at 30 °C to yield **zip-P2**. Isolated polymer masses are reported in **Table S3**.

*Isomerization of **zip-P2-1*** from ester to amide
In solution:

To a 1-dram vial with stir bar was added 83 mg **zip-P2-1** (from melt-pressed film) and 0.83 mL chlorobenzene. The vial was heated to 120 °C while stirring for 23 h. Isomerized polymer was isolated *via* precipitation in methanol, decanting of the solvent, and drying *in vacuo*.

Solvent free:

To a 1-dram vial was added 102 mg **zip-P2-1** (from melt-pressed film) and the vial was heated to 140 °C for 8.25 h.

Relevant Calculations

Calculation of % Ketone and % Alcohol in ox-PE

From ^{1}H NMR, the integration of the range from 0.8 to 1.7 ppm (corresponding to the 4H of the –CH_2–CH_2– repeat units) was set to 100. Then the integration of the methine resonance at ~3.6 ppm (corresponding to 1H from alcohol unit) and the integration of the methylene resonance at ~2.4 ppm (corresponding to 4H of the ketone unit) were used to determine % alcohol and % ketone using the following formulas:

$$\%\ \text{alcohol} = \frac{[\text{alcohol}]}{[\text{–CH}_2\text{–CH}_2\text{–}] + [\text{ketone}] + [\text{alcohol}]}$$

$$\%\ \text{ketone} = \frac{[\text{ketone}]}{[\text{–CH}_2\text{–CH}_2\text{–}] + [\text{ketone}] + [\text{alcohol}]}$$

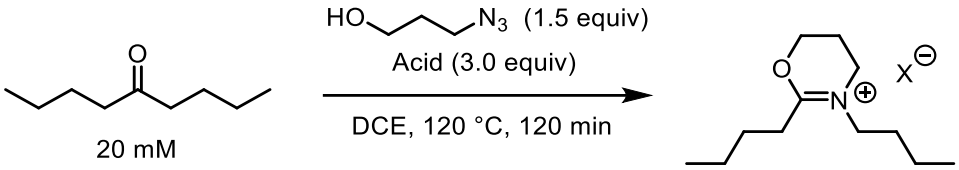
For example for **ox-PE** in Figure S29:

$$\% \text{ alcohol} = \frac{[0.32]}{[100/4] + [2.96/4] + [0.32]} = 1.2\%$$

$$\% \text{ ketone} = \frac{[2.96/4]}{[100/4] + [2.96/4] + [0.32]} = 2.8\%$$

Supplementary Figures and Tables

Table S1. Screening of acids for reaction of 5-nonanone and **1-OH**.



Acid	% Yield Iminium Ether[b]	% Consumption of 5-nonanone[c]	% Consumption of 1-OH[d]
TfOH[a]	47	59	100
BF_3OEt_2	21	20	100
$Zn(OTf)_2$	0	0	1
$SnCl_4$	26	27	100
TMSOTf	61	67	100
$Et_3Si(OTf)$	49[e]	71[f]	100
$^tBuMe_2Si(OTf)$	38[e]	66[f]	100
$LiBArF^{20}$	0	0	46
$Mg(ClO_4)_2$	0	1	34
$La(OTf)_3$	6	9	35
$Yb(OTf)_3$	0	7	36
BCF	0	2	100
BPh_3	0	3	40
Tropylium tetrafluoroborate	6	8	23
Tritylium tetrafluoroborate	0	12	100
$BiCl_3$	9	19	29[g]
$Al(O^iPr)_3$	0[h]	56[f]	100
$AlCl_3$	42	41	82[g]
$Bi(OTf)_3$	18	29	100
$Sc(OTf)_3$	25	24	35

[a] Reaction ran for 10 min.
[b] Yield determined by ^1H NMR spectroscopy of aliquot of reaction mixture using integration of methyl resonances at ~0.9 ppm from iminium ether formed from 5-nonanone.
[c] Consumption determined by ^1H NMR spectroscopy of aliquot of reaction mixture by integrating methyl resonance of 5-nonanone at ~0.8 ppm
[d] Consumption determined by ^1H NMR spectroscopy of aliquot of reaction mixture by integrating methylene resonance of **1-OH** at ~1.7-1.8 ppm.
[e] Yield determined by ^1H NMR spectroscopy of aliquot of reaction mixture using integration of methylene resonance at ~4.5 ppm from iminium ether formed from 5-nonanone.
[f] Consumption determined by ^1H NMR spectroscopy of aliquot of reaction mixture by integrating methylene resonance of 5-nonanone at ~2.3-2.4 ppm

[g] Consumption determined by ^{1}H NMR spectroscopy of aliquot of reaction mixture using integration of ½ of methylene resonance of **1-OH** at ~1.7-1.8 ppm due to overlapping peaks.
[h] Yield determined by ^{1}H NMR spectroscopy of aliquot of reaction mixture using integration of methylene resonance at ~2.6 ppm from iminium ether formed from 5-nonanone.

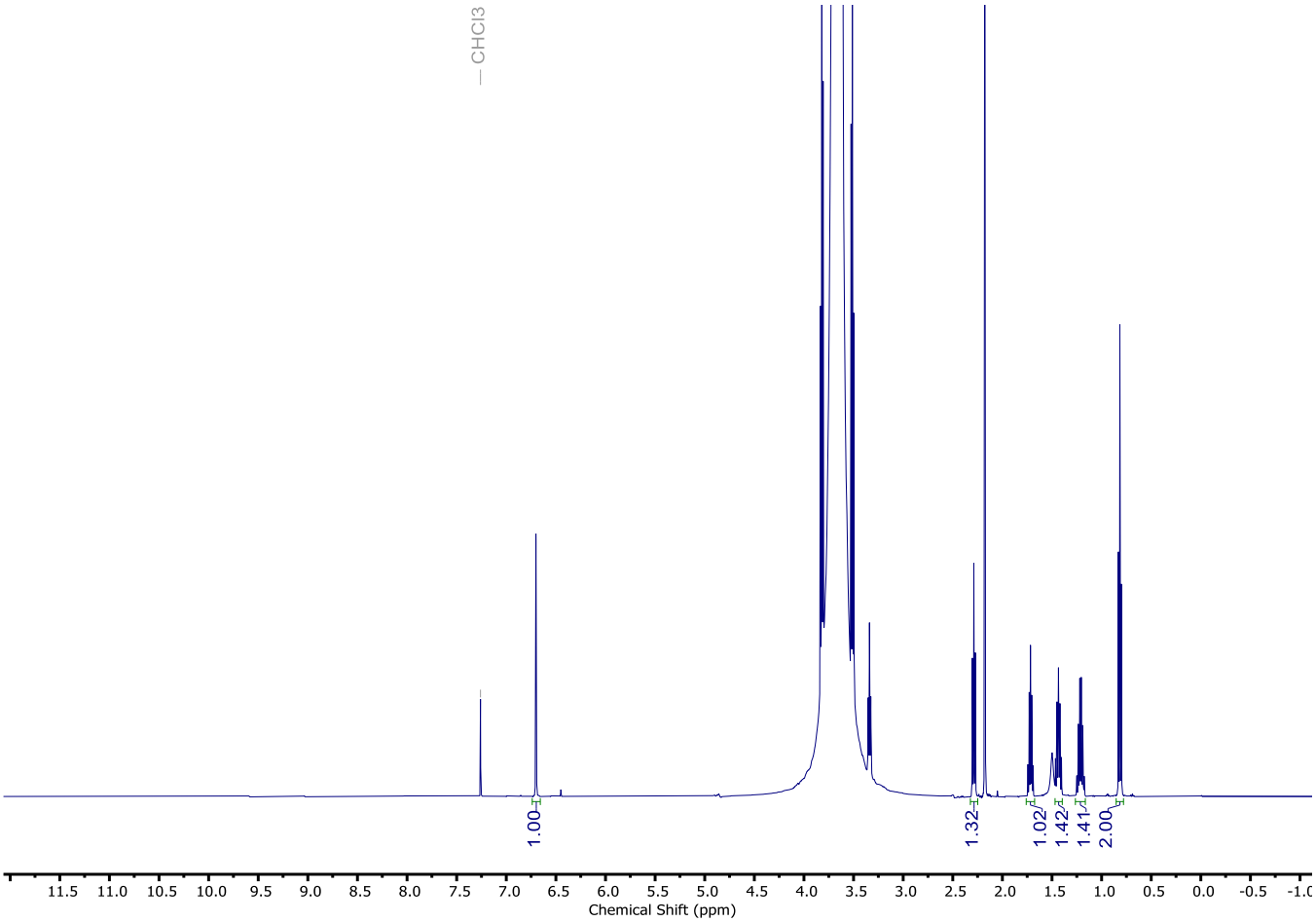


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of stock solution of 5-nonanone, **1-OH**, and mesitylene in DCE for reaction with TfOH

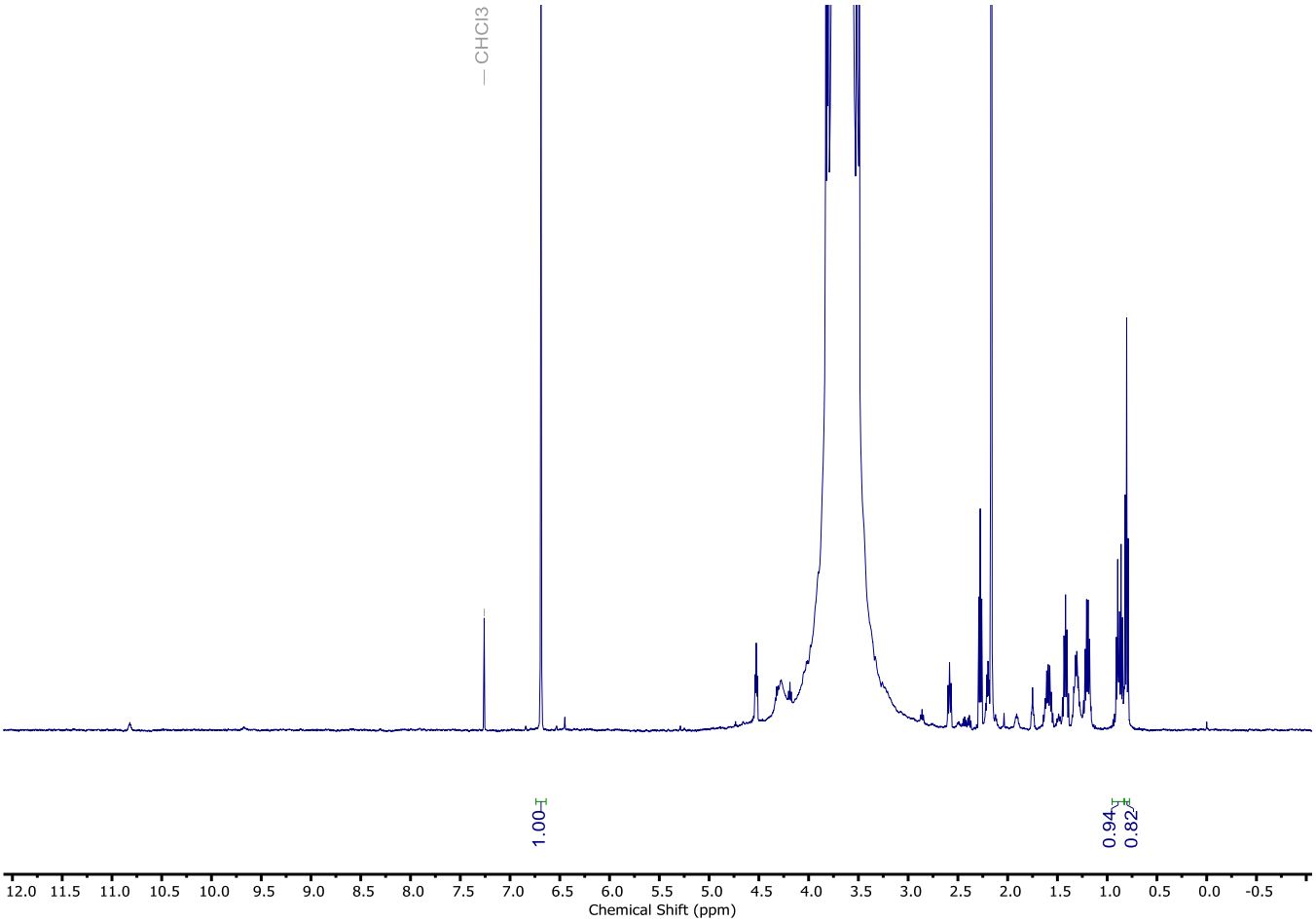


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and TfOH.

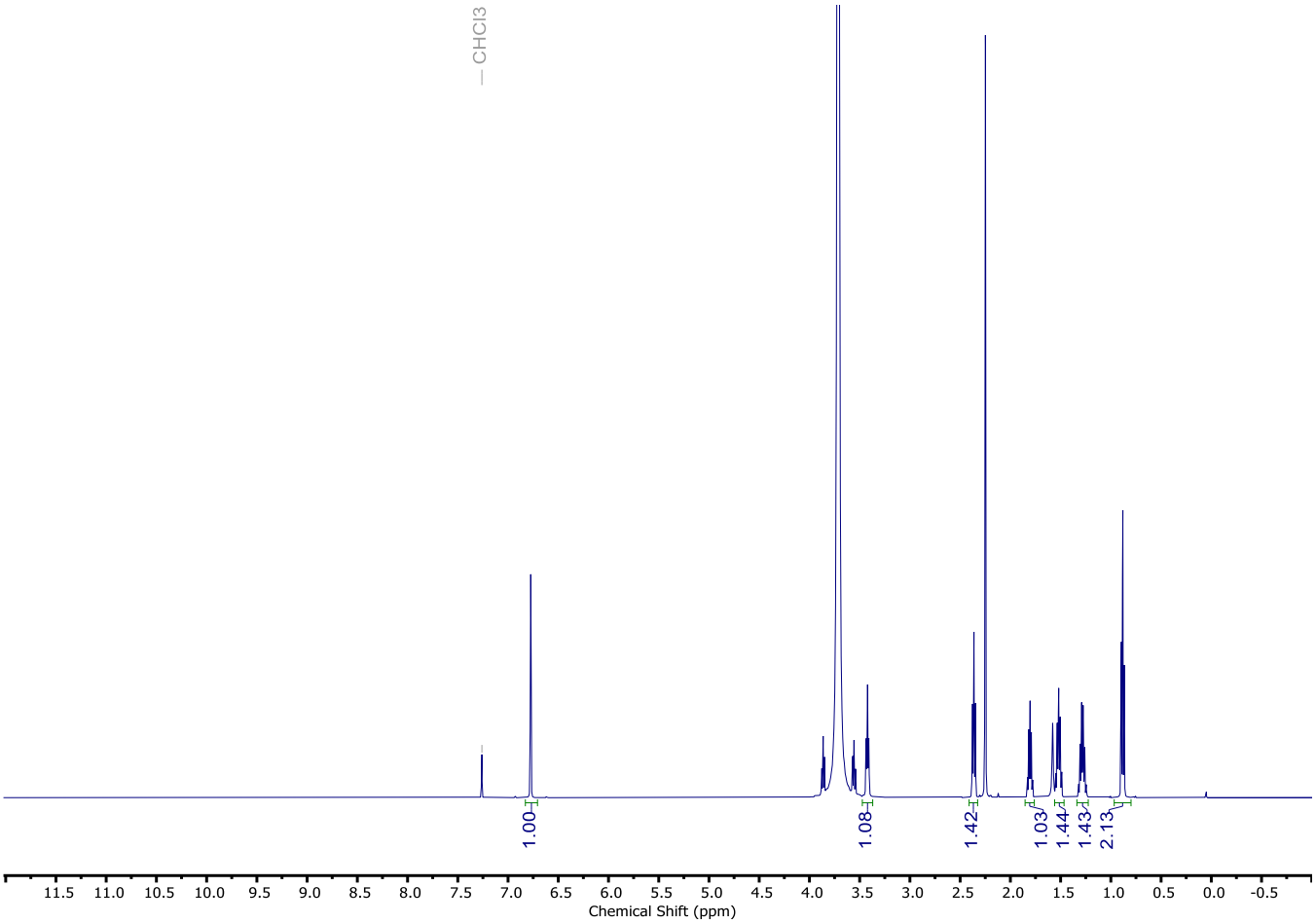


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of stock solution of 5-nonanone, **1-OH**, and mesitylene in DCE for reactions with BF_3•OEt_2, $Zn(OTf)_2$,$SnCl_4$, TMSOTf, $Et_3Si(OTf)$, $^{t}BuMe_2Si(OTf)$, $LiBArF^{20}$, $Mg(ClO_4)_2$, $La(OTf)_3$, $Yb(OTf)_3$, BCF, BPh_3, tropylium tetrafluoroborate, and tritylium tetrafluoroborate.

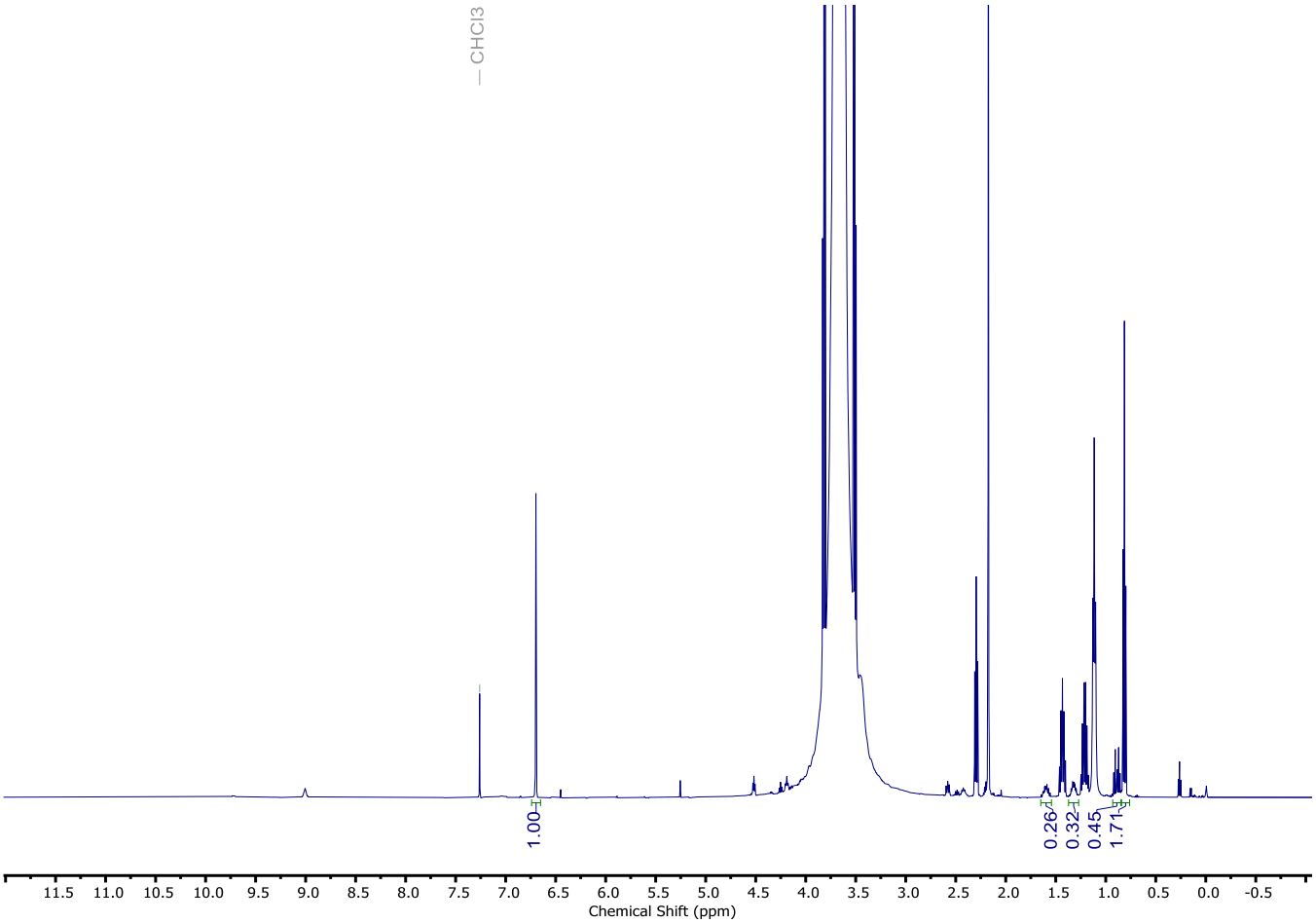


Figure S4. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and BF_3•OEt_2.

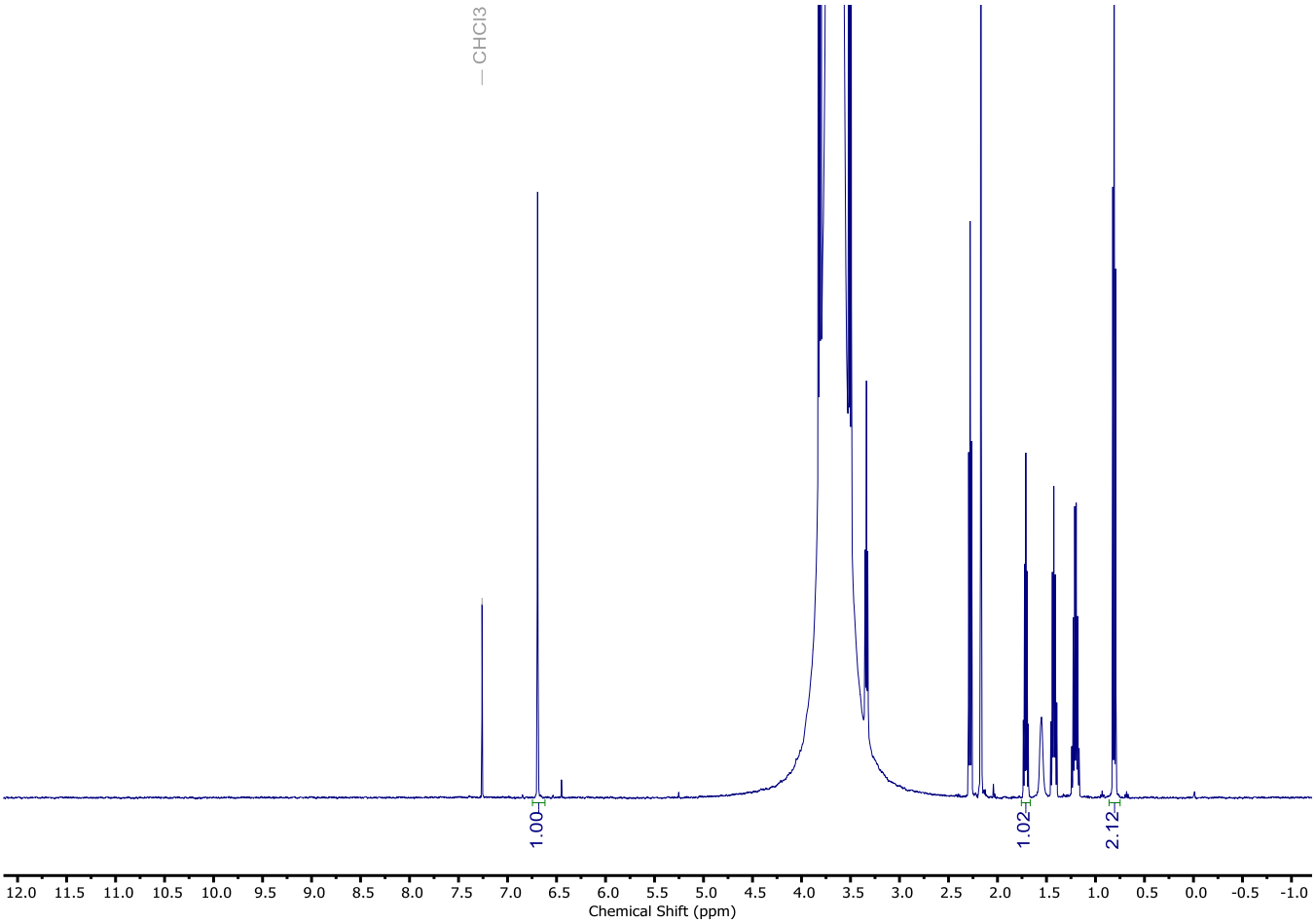


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $Zn(OTf)_2$.

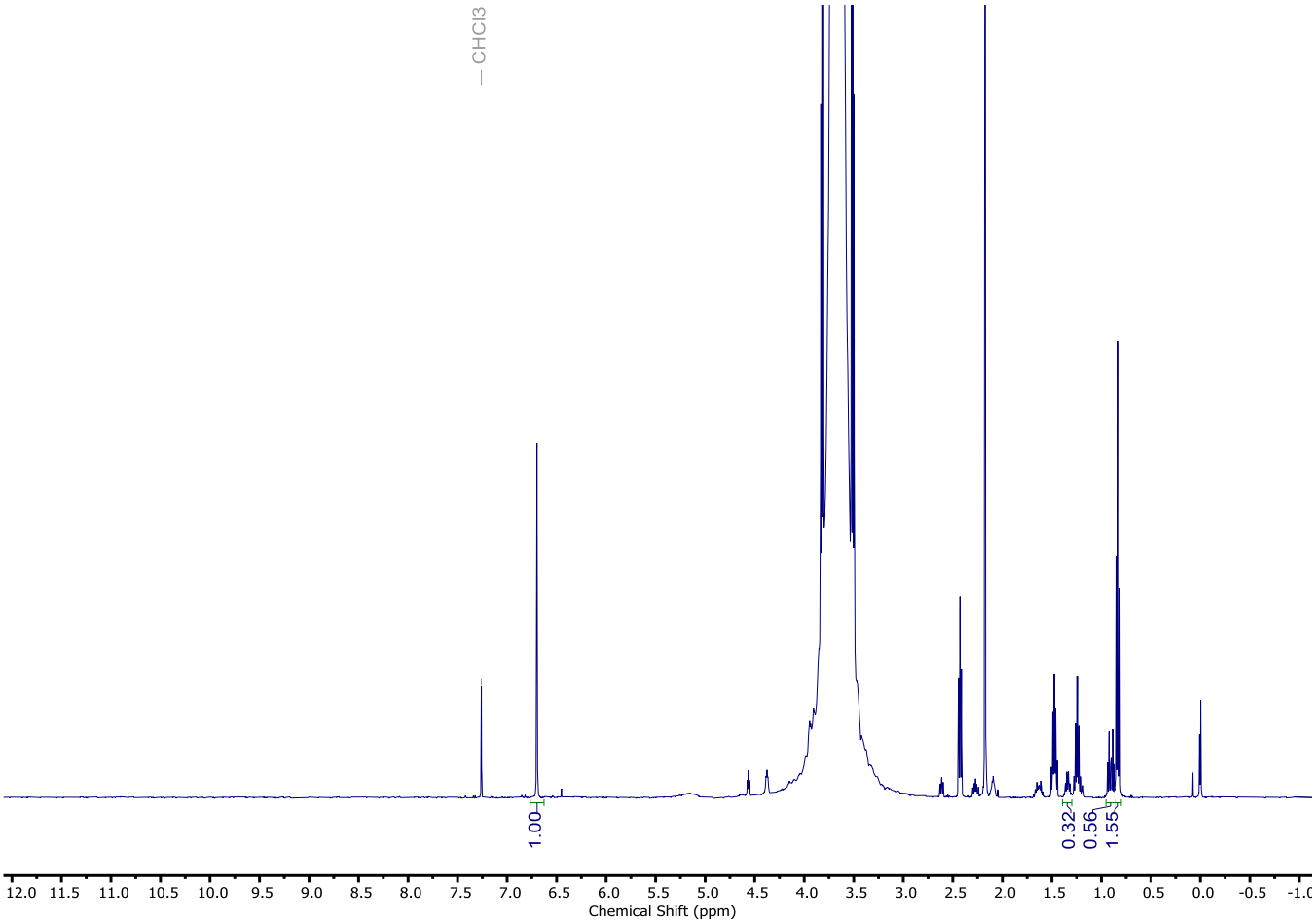


Figure S6. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $SnCl_4$.

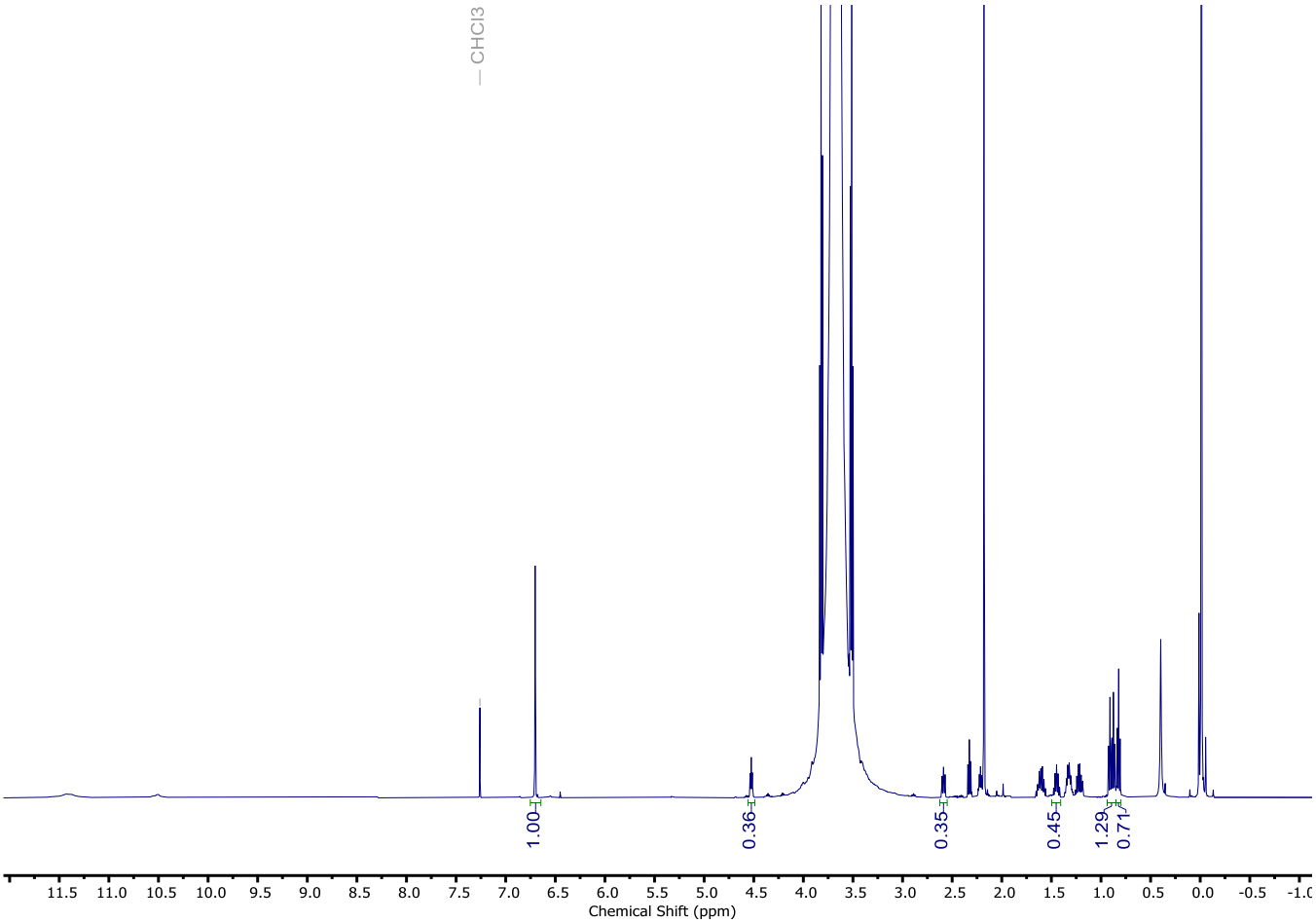


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and TMSOTf.

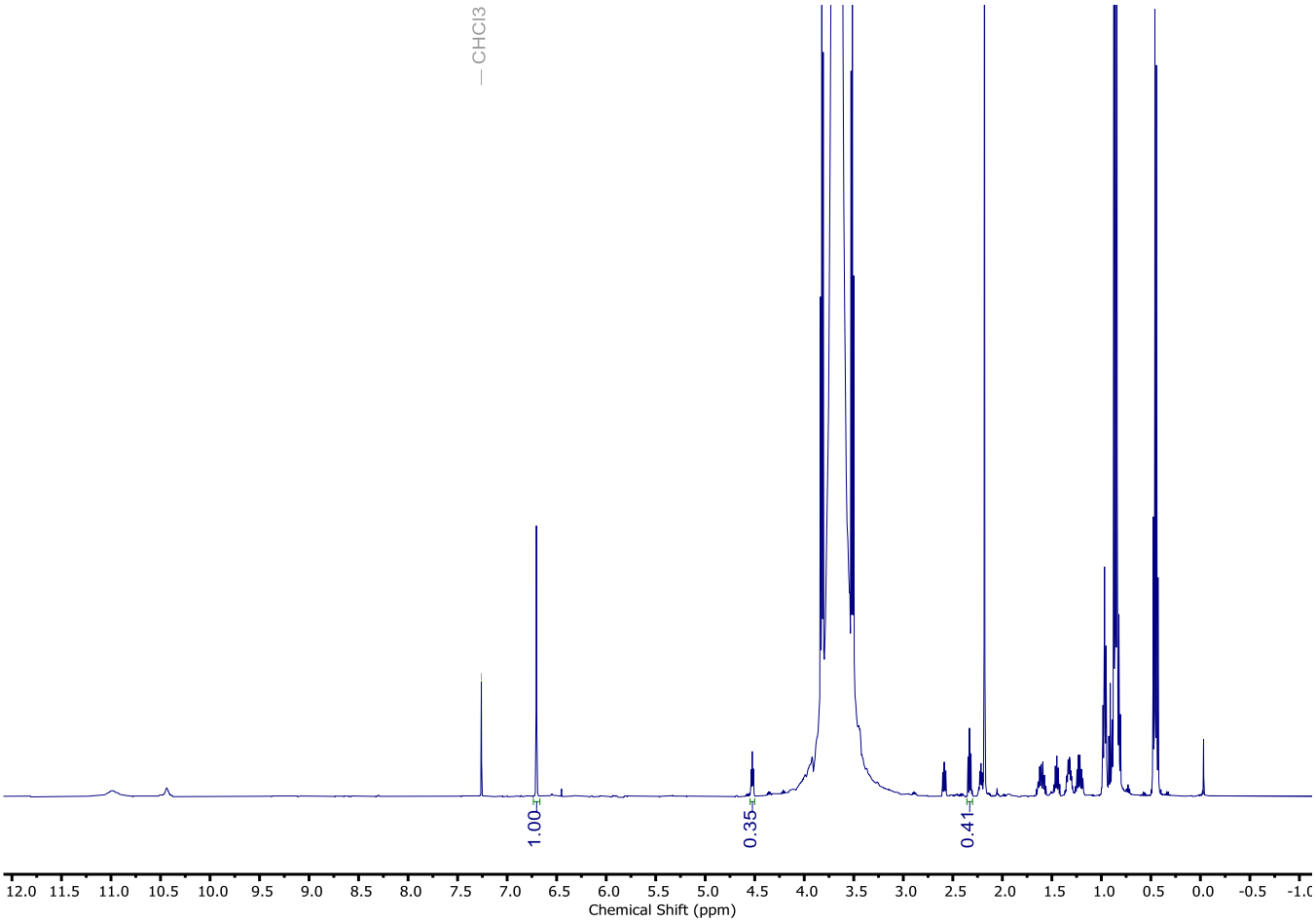


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $Et_3Si(OTf)$.

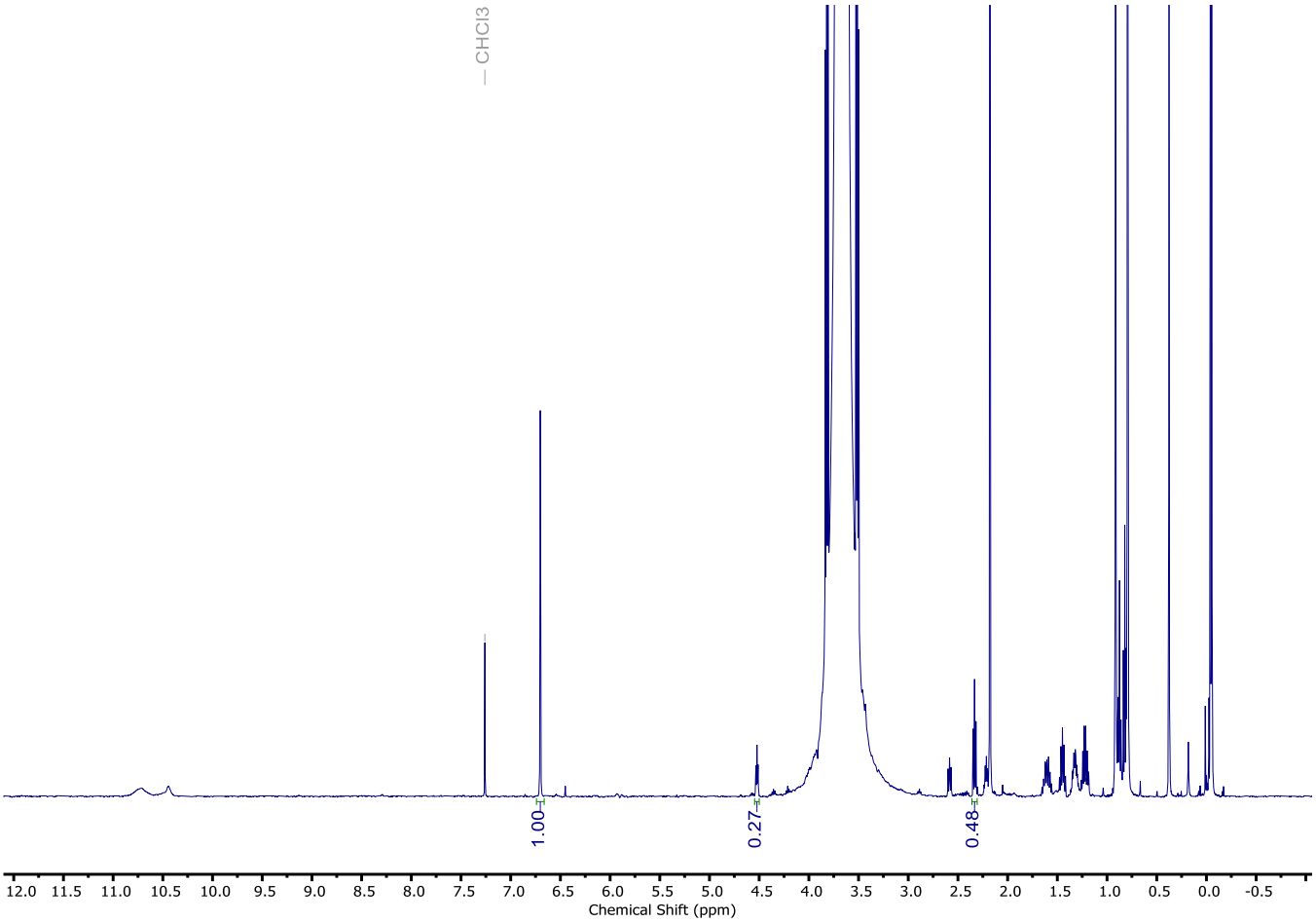


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $^{t}BuMe_2Si(OTf)$.

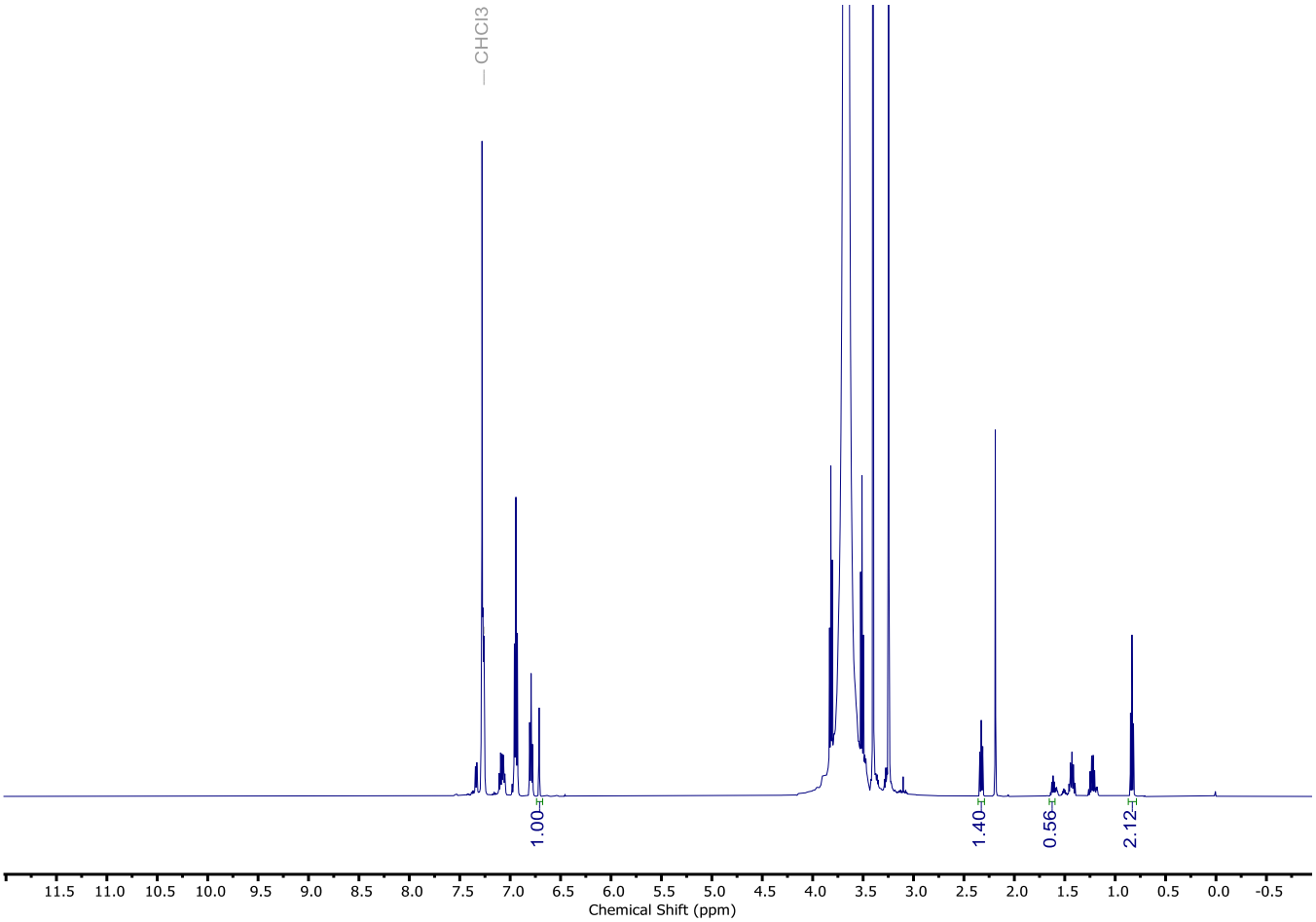


Figure S10. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and LiBArF[20].

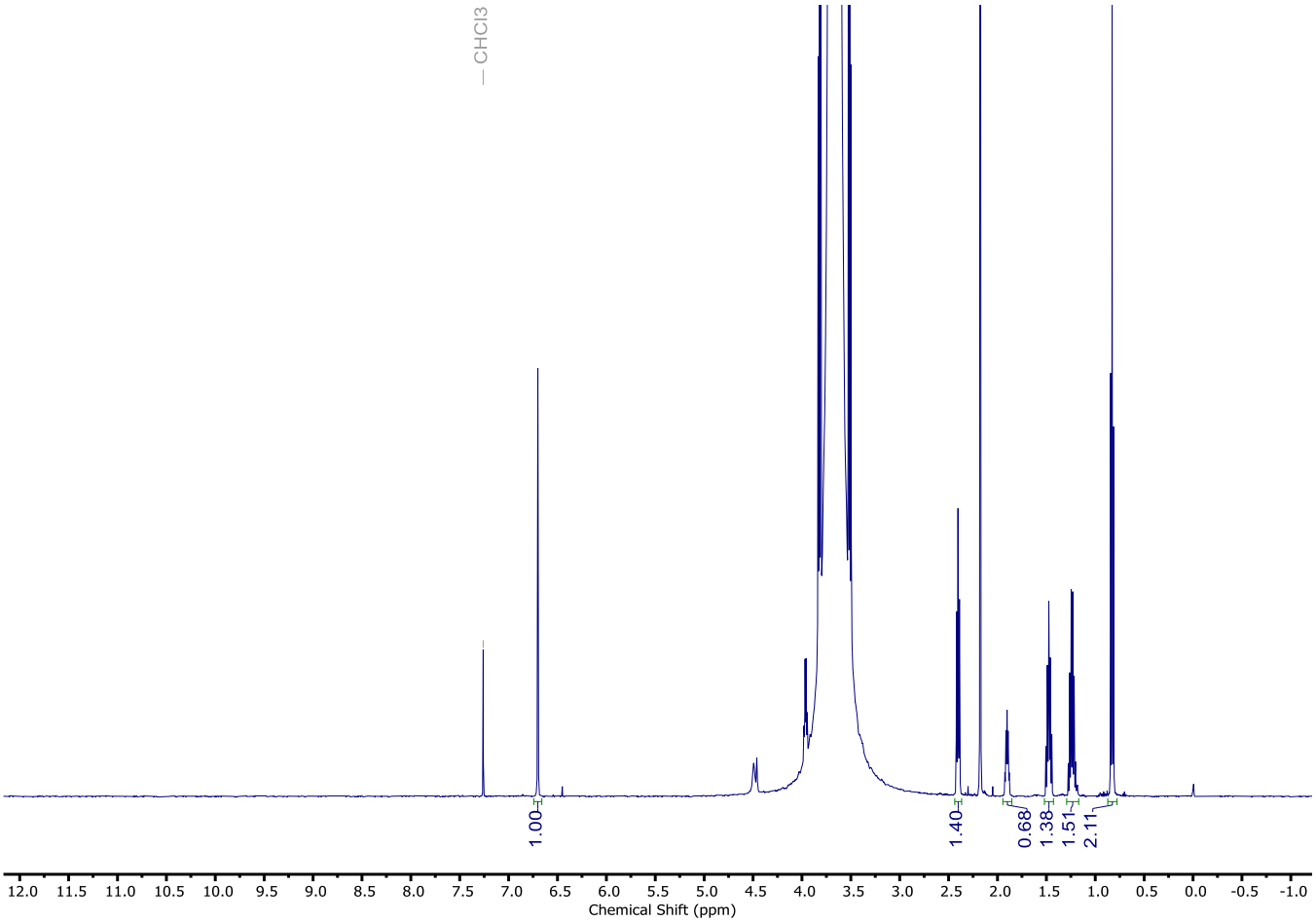


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $Mg(ClO_4)_2$

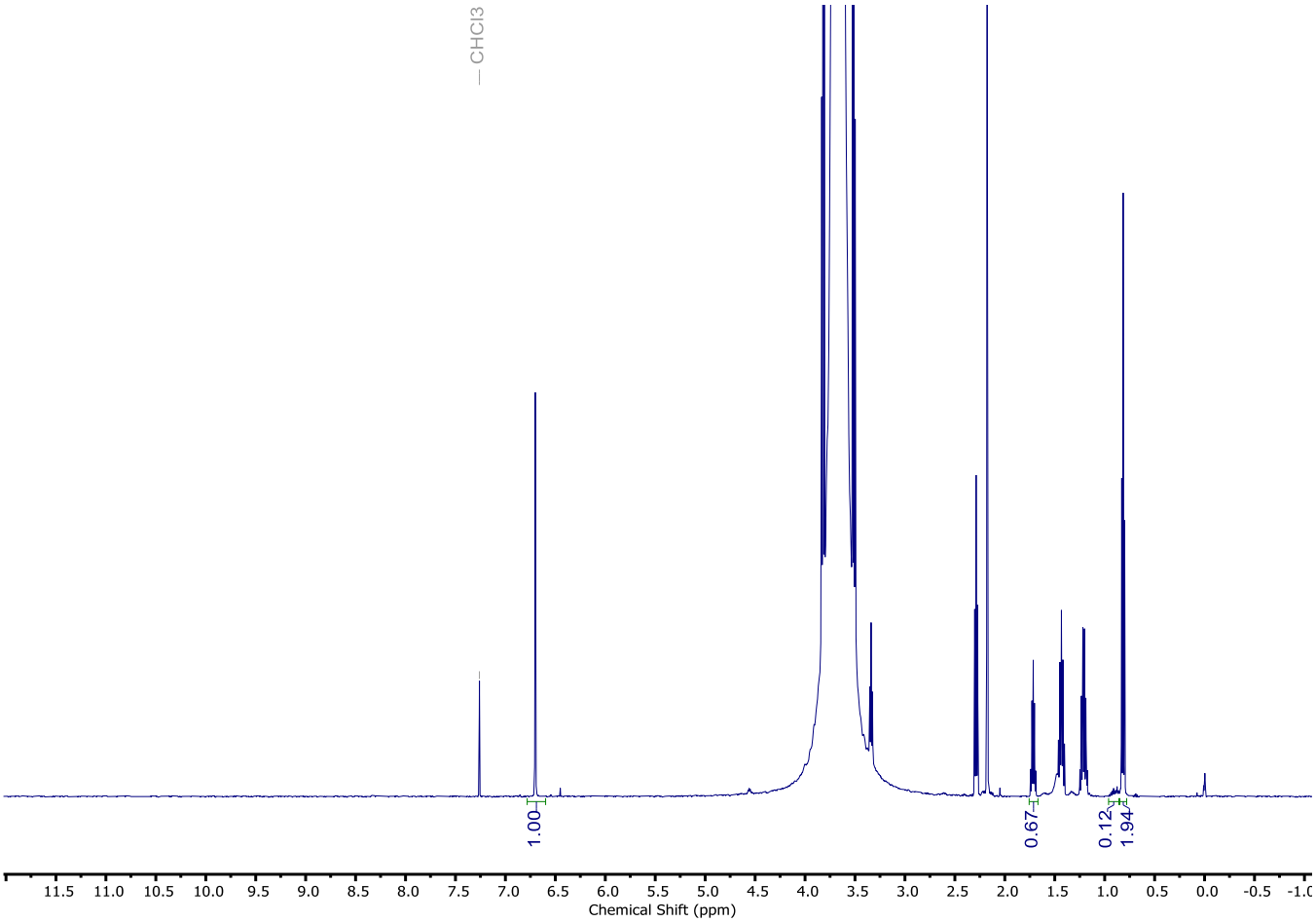


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $La(OTf)_3$

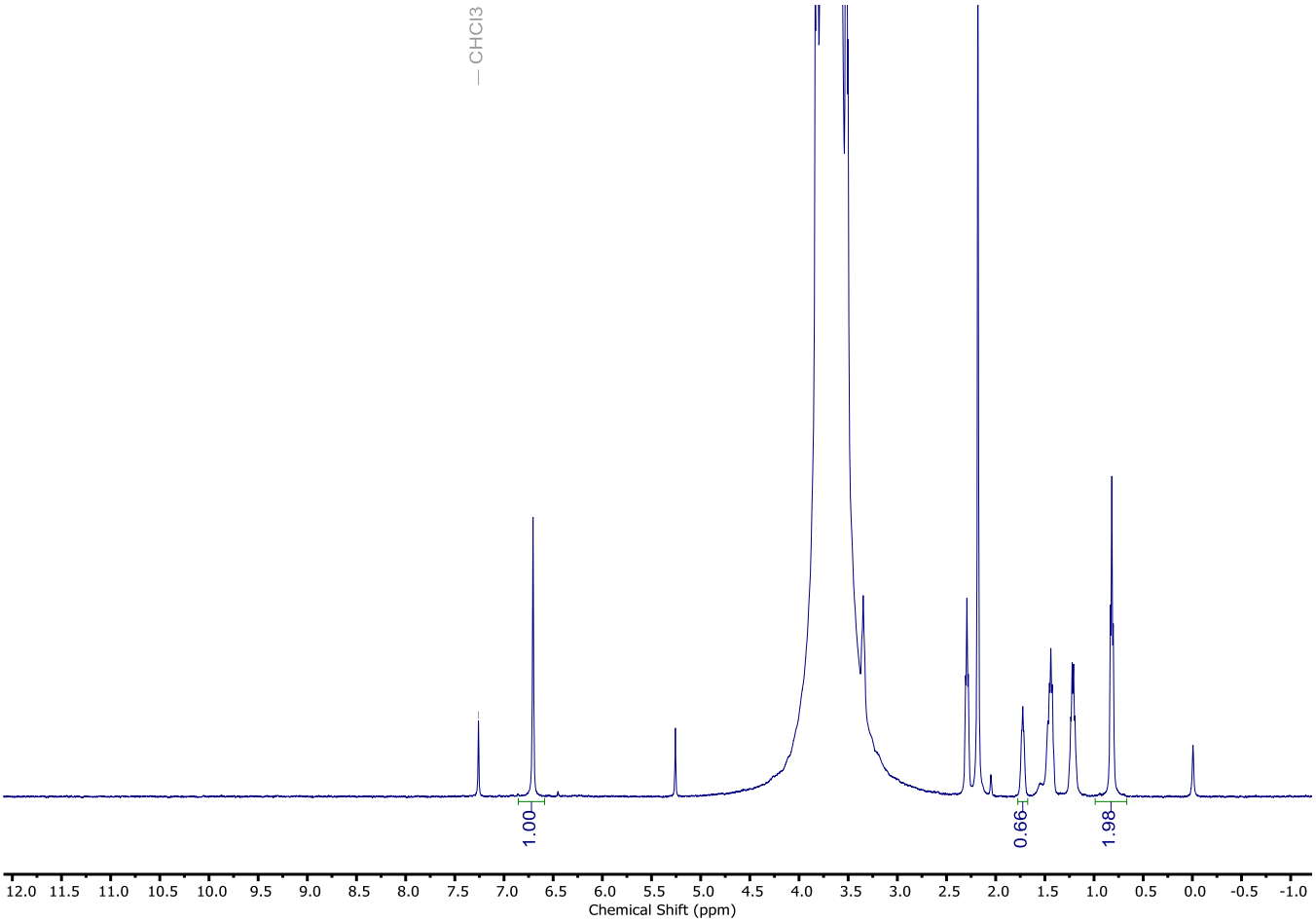


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $Yb(OTf)_3$

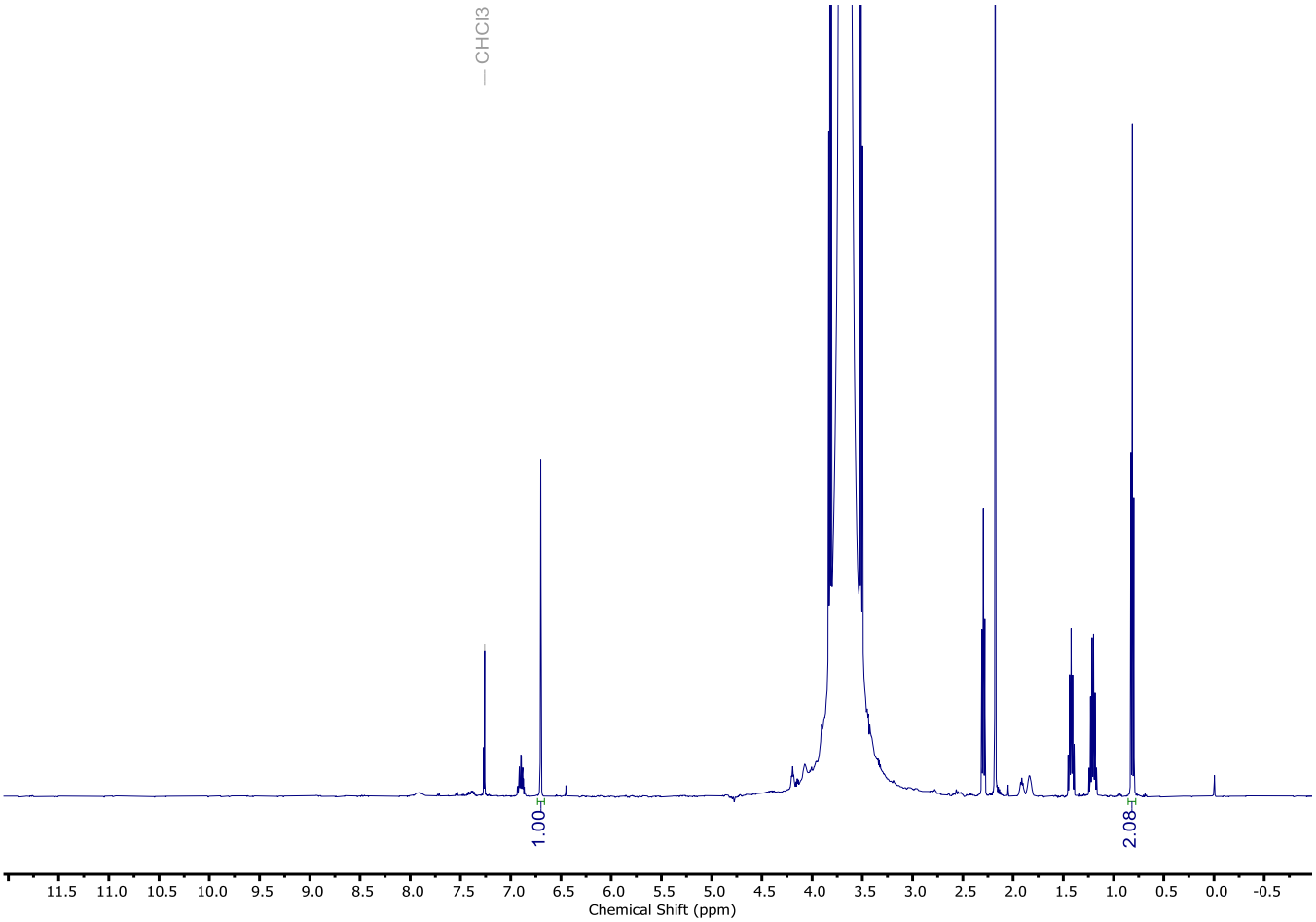


Figure S14. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and BCF

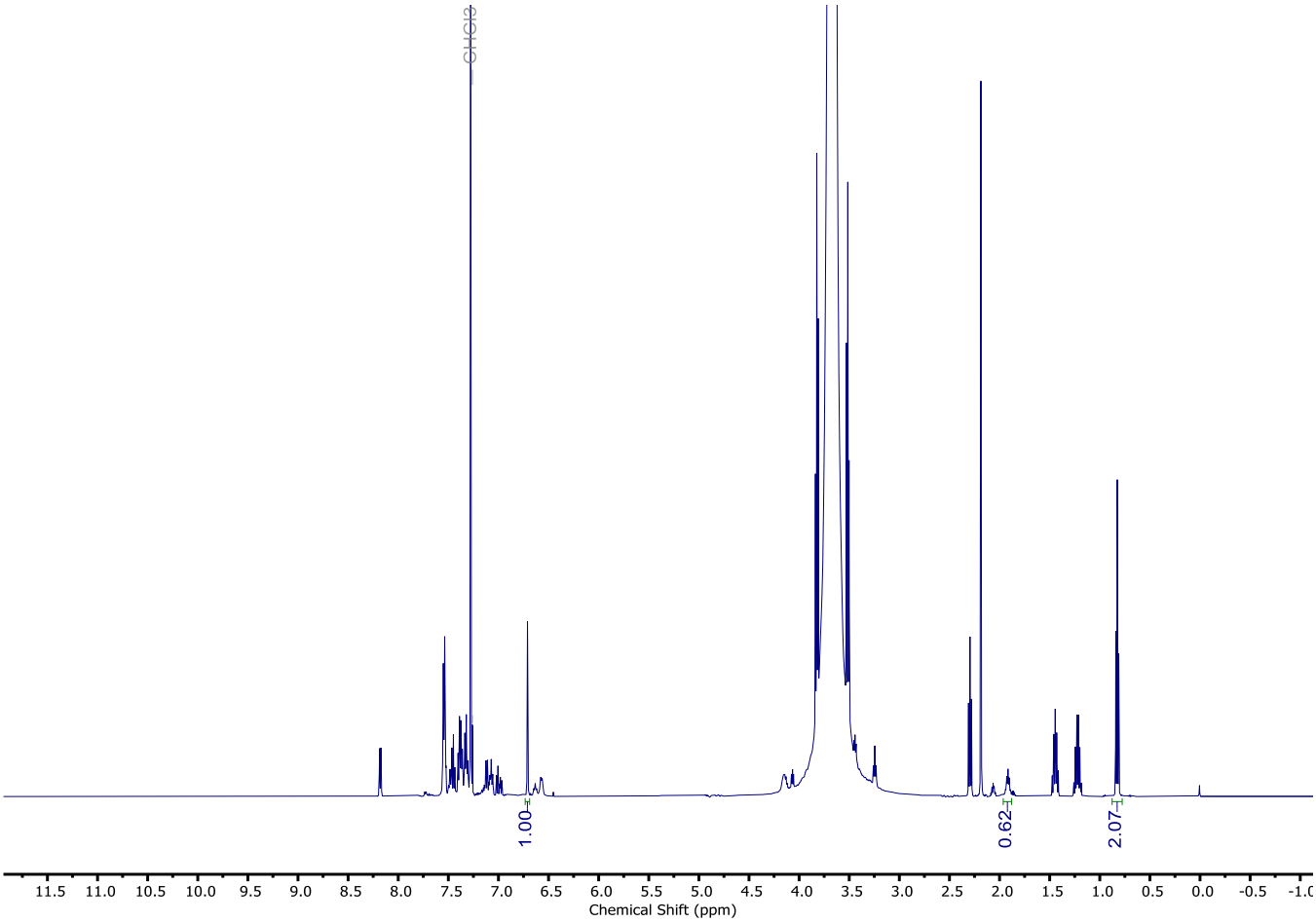


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and BPh_3

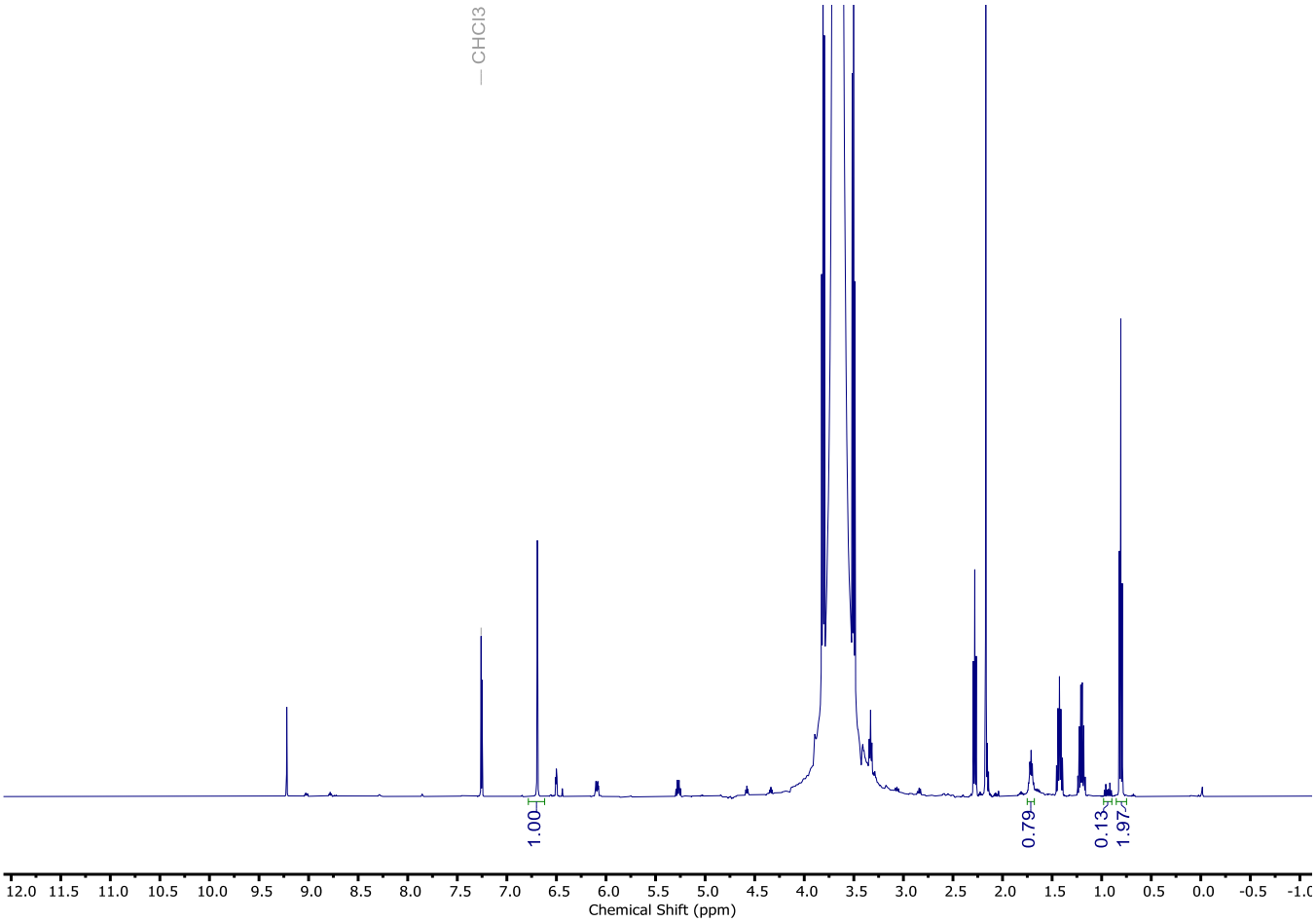


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and tropylium tetrafluoroborate

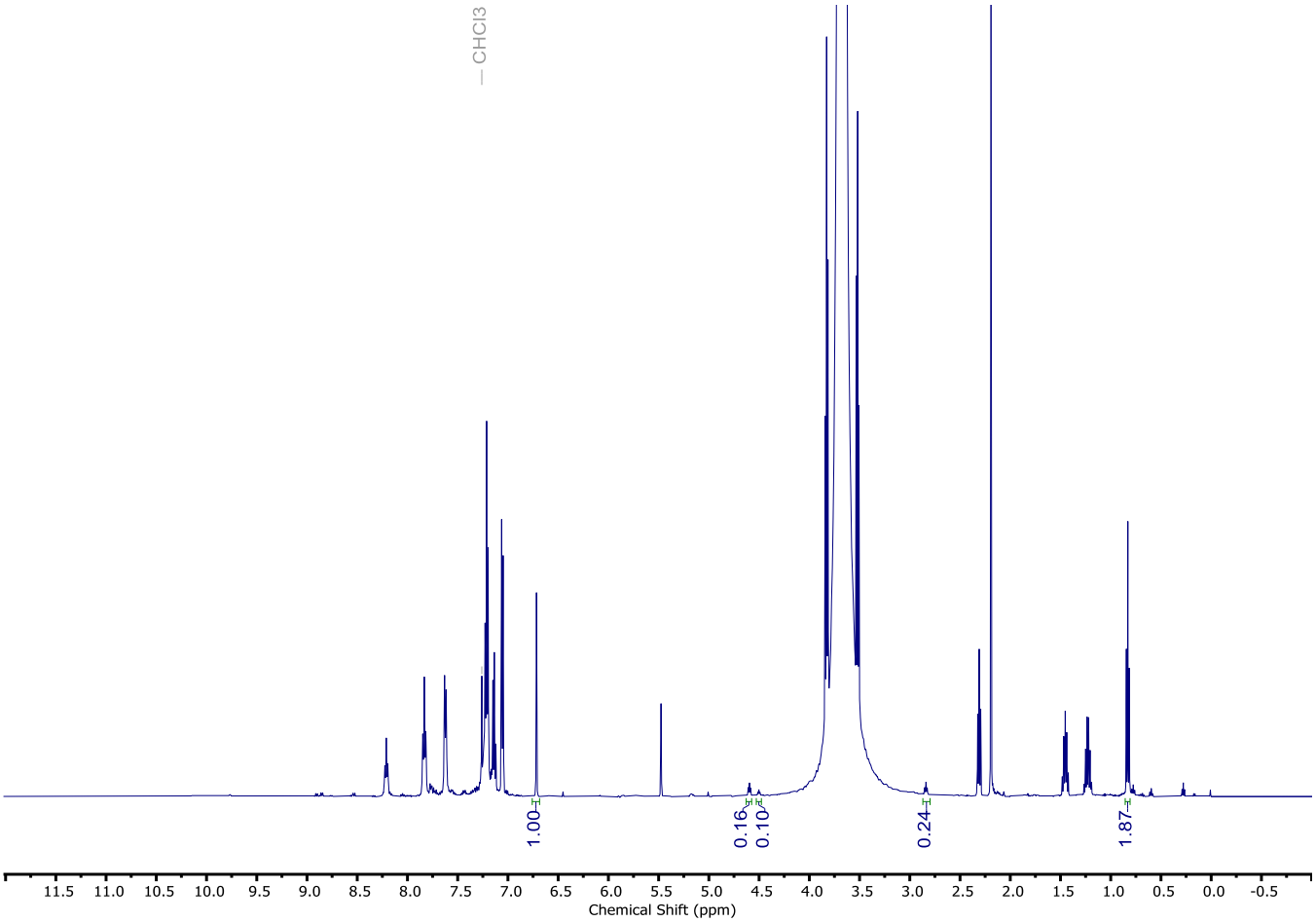


Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and tritylium tetrafluoroborate

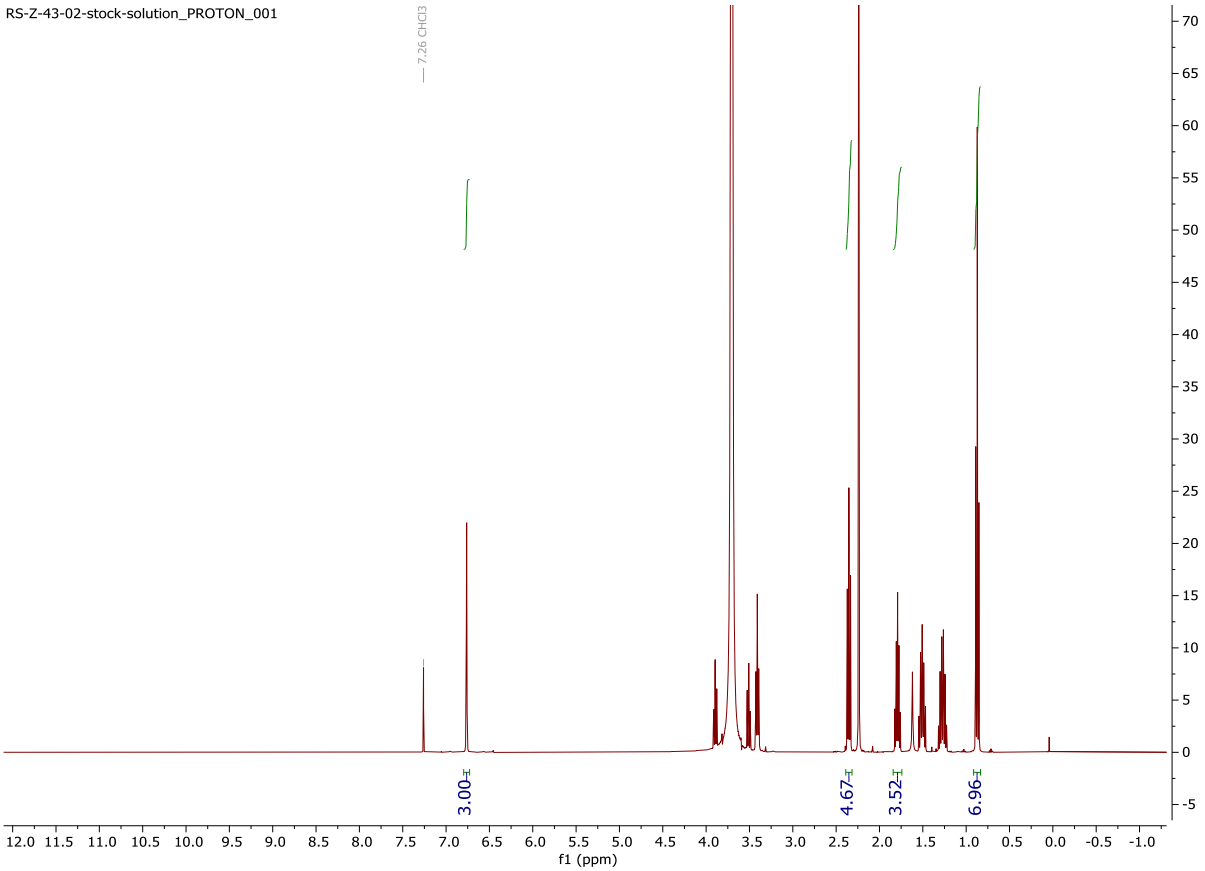


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of stock solution of 5-nonanone, **1-OH**, and mesitylene in DCE for reactions with $BiCl_3$, $Al(O^iPr)_3$, $AlCl_3$, $Bi(OTf)_3$, and $Sc(OTf)_3$.

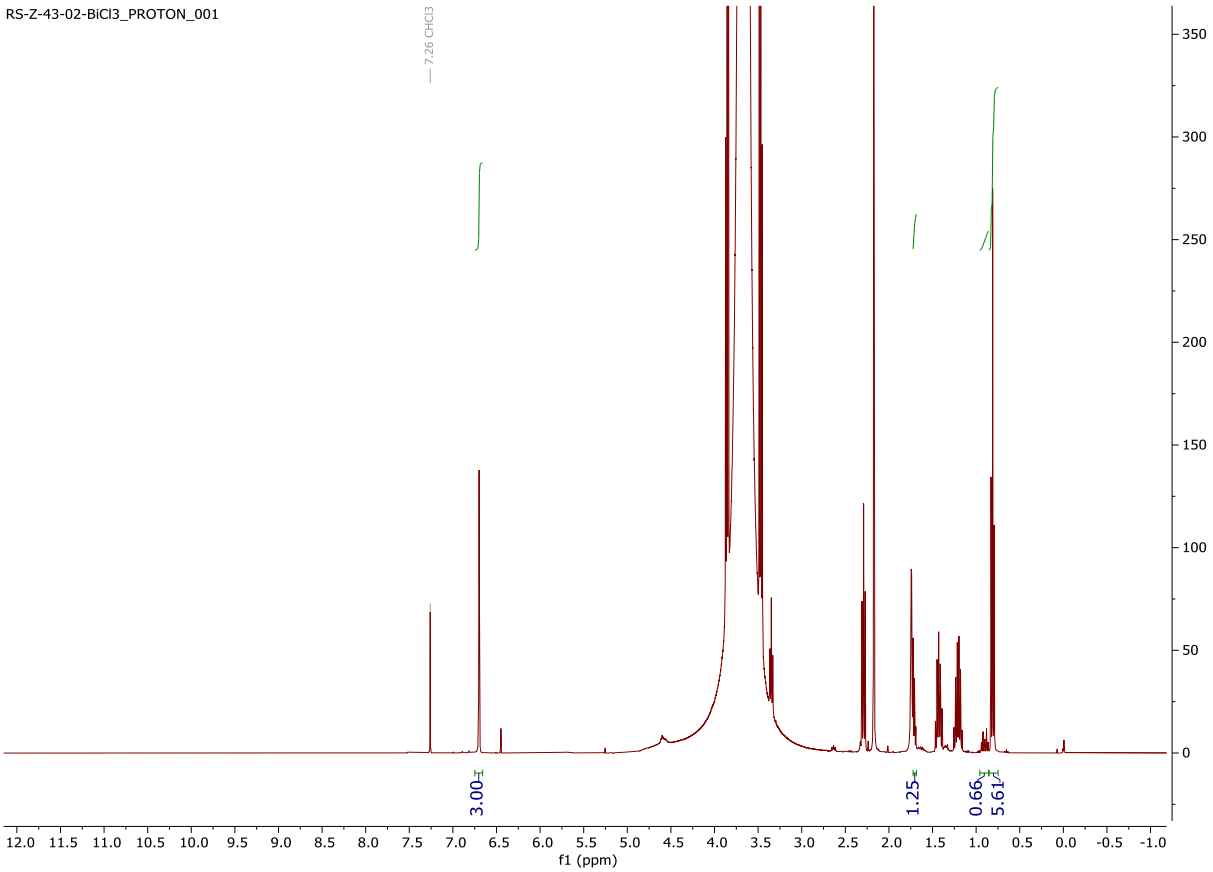


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $BiCl_3$

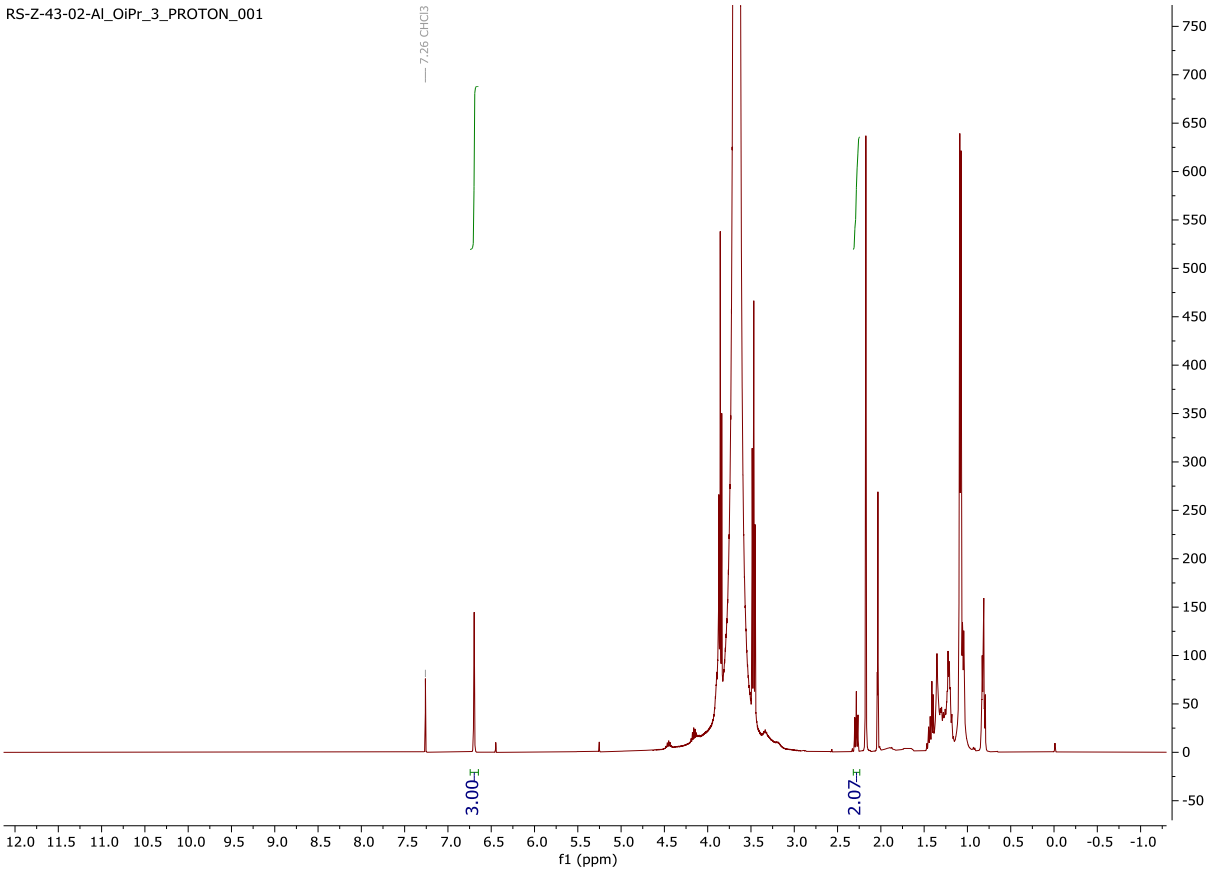


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $Al(O^iPr)_3$

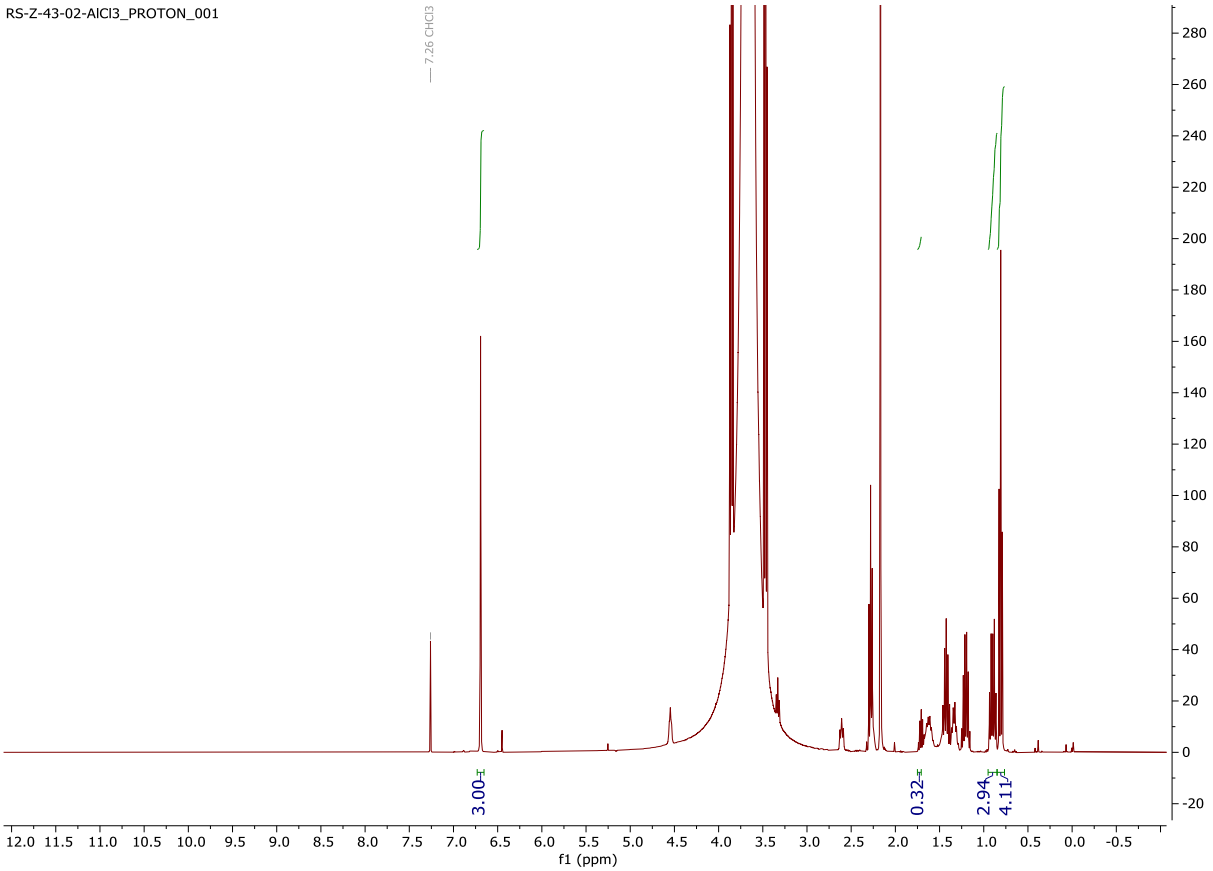


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $AlCl_3$

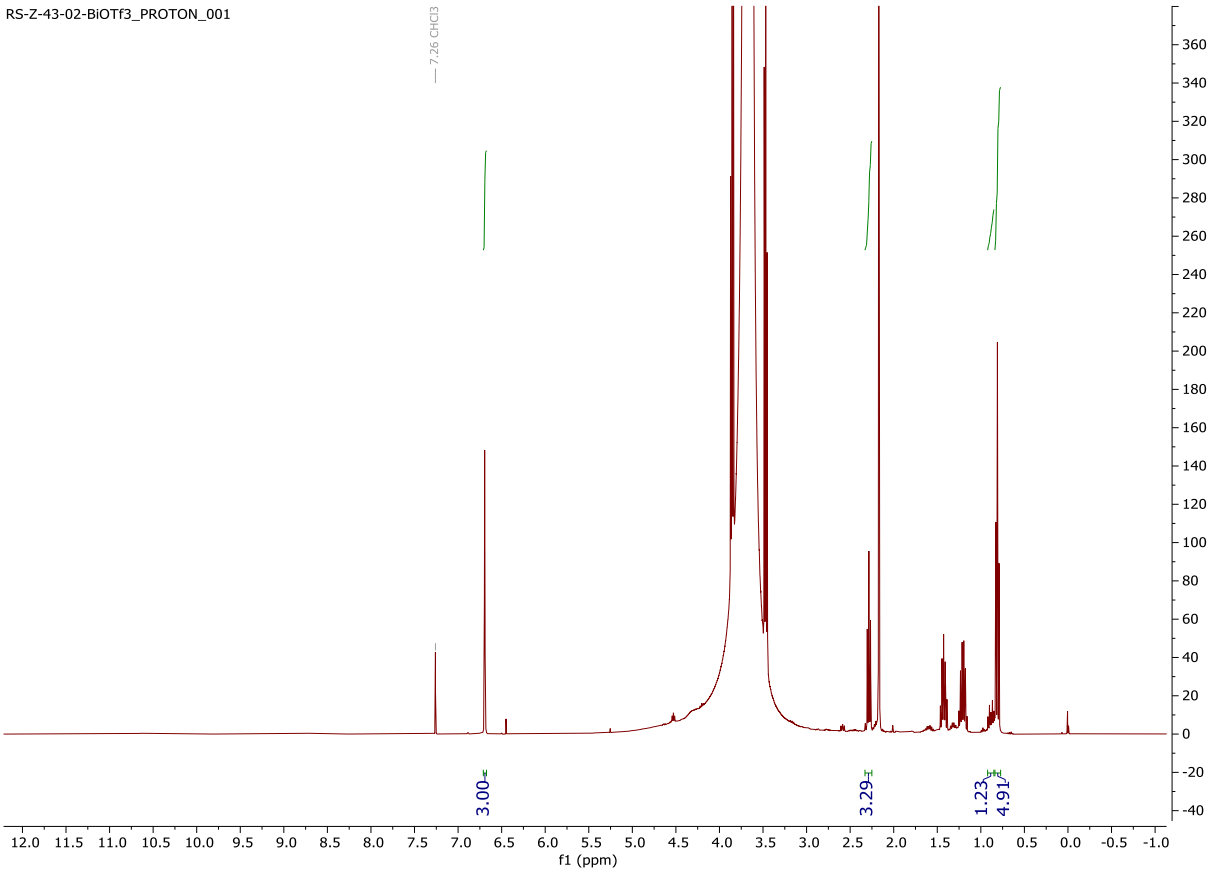


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $Bi(OTf)_3$

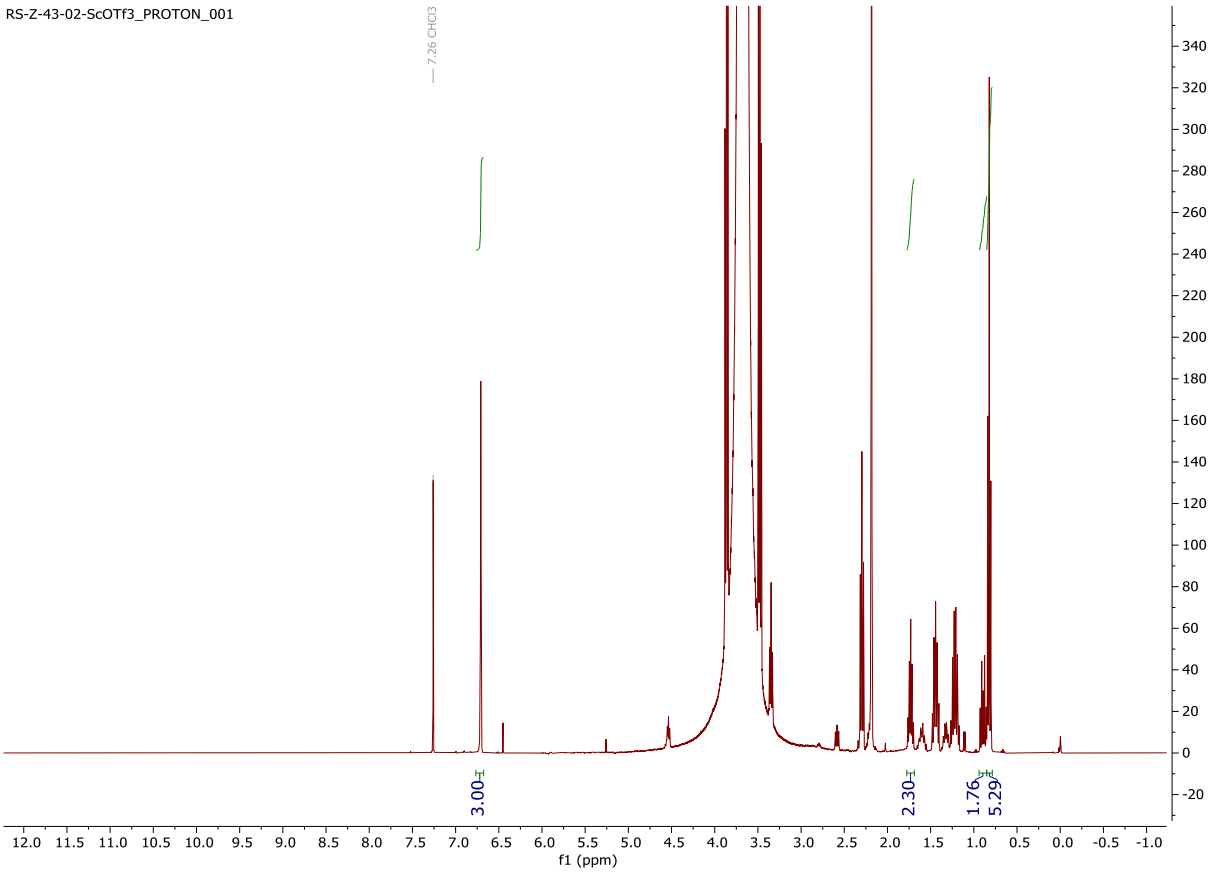


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of aliquot of reaction of 5-nonanone with **1-OH** and $Sc(OTf)_3$

Table S2. Reaction optimization results with small molecule model 3-pentanone. "Average of Triplicates" is reported in **Table 1** as the final reaction yield.

Reaction Conditions (Table 1 entry #)	Replicate 1 Yield	Replicate 2 Yield	Replicate 3 Yield	Average of Triplicates
1	30%	44%	34%	**36%**
2	100%	100%	100%	**100%**
3	89%	90%	88%	**89%**
4	77%	65%	79%	**74%**
11	100%	100%	100%	**100%**
12	81%	79%	79%	**80%**
13	49%	53%	47%	**50%**
14	53%	52%	48%	**51%**

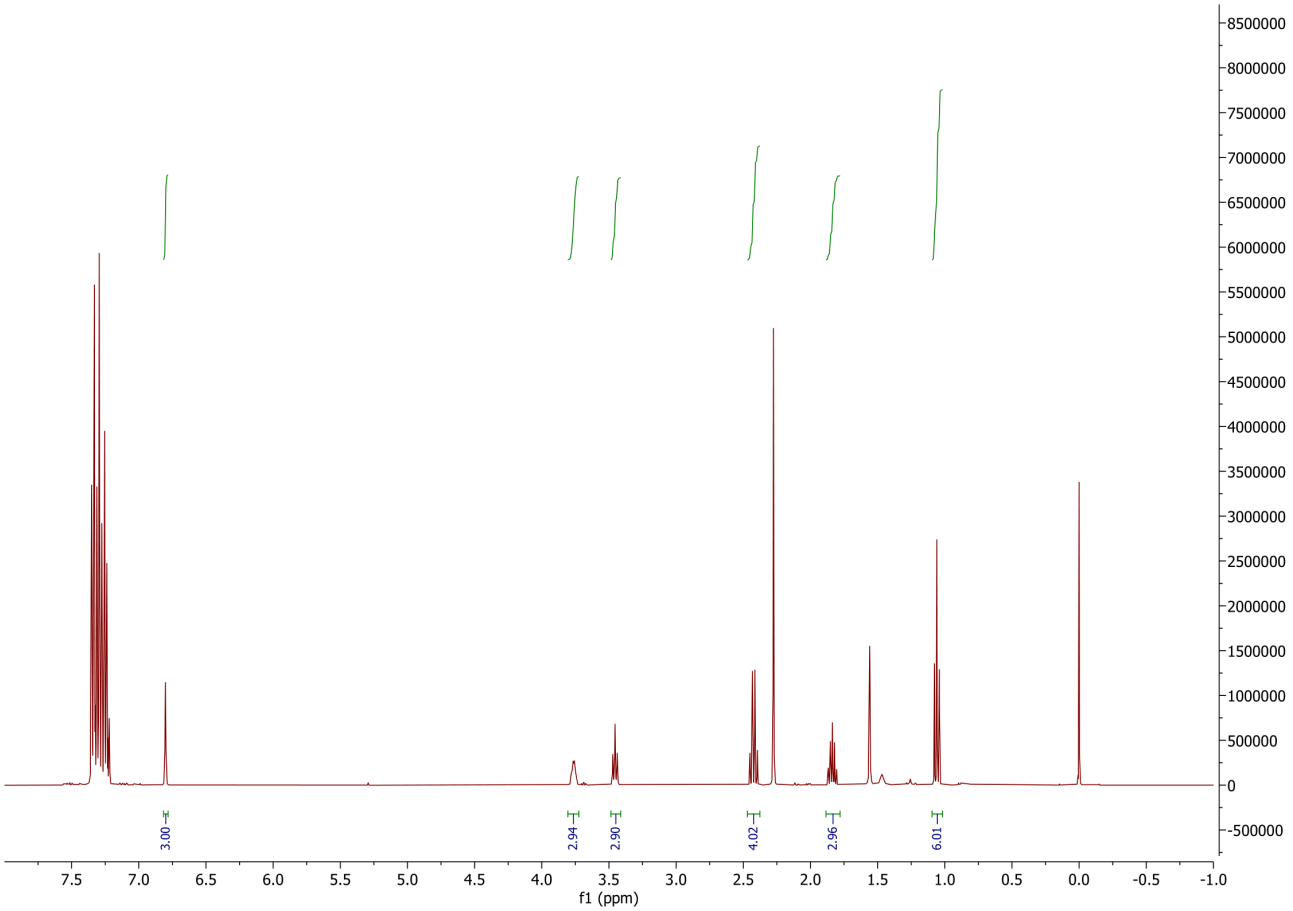
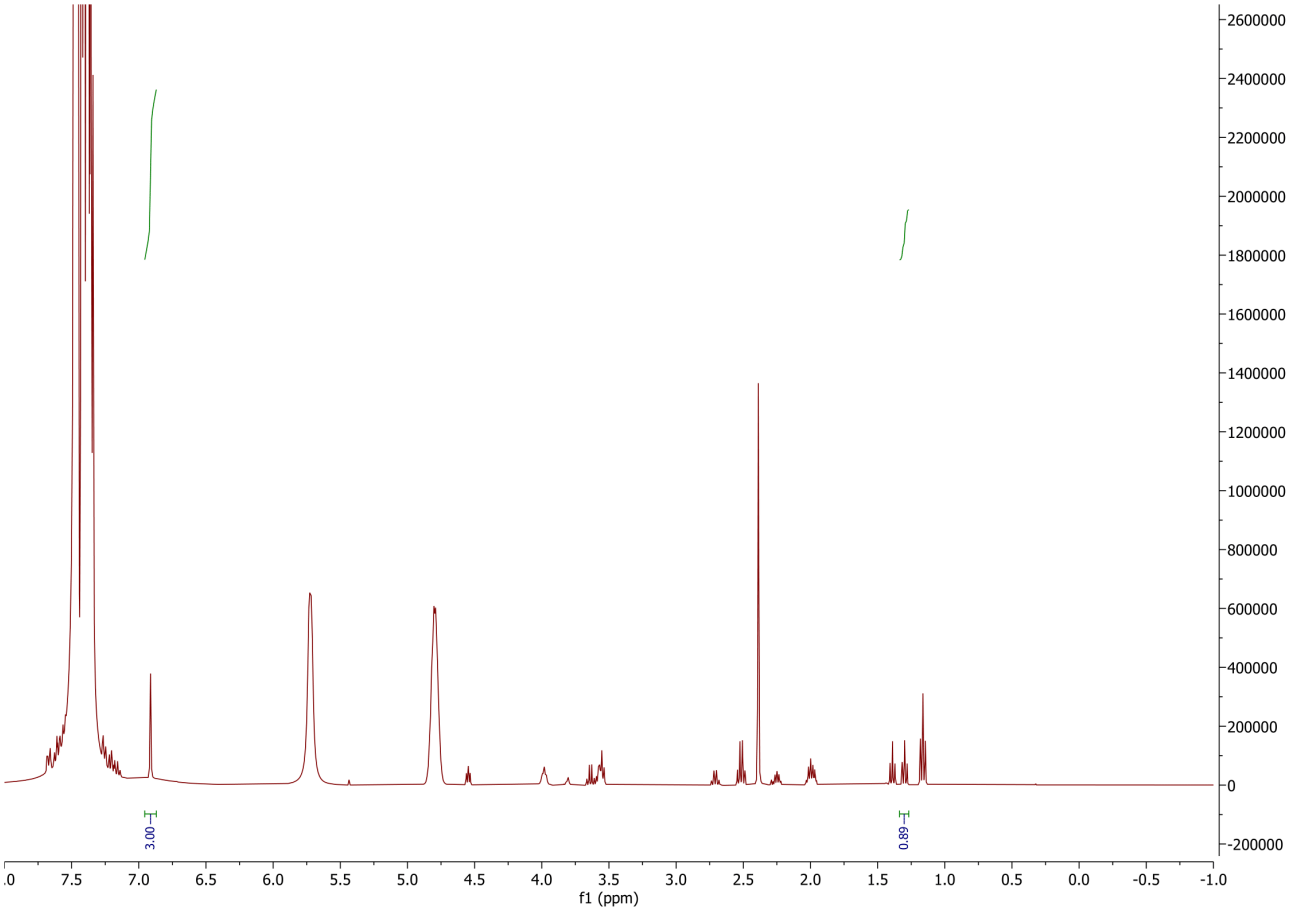


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of stock solution of 3-pentanone, **1-OH**, and mesitylene in chlorobenezene (900 mmolar w.r.t. 3-pentanone) used for **Table 1 entries 1–4**.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.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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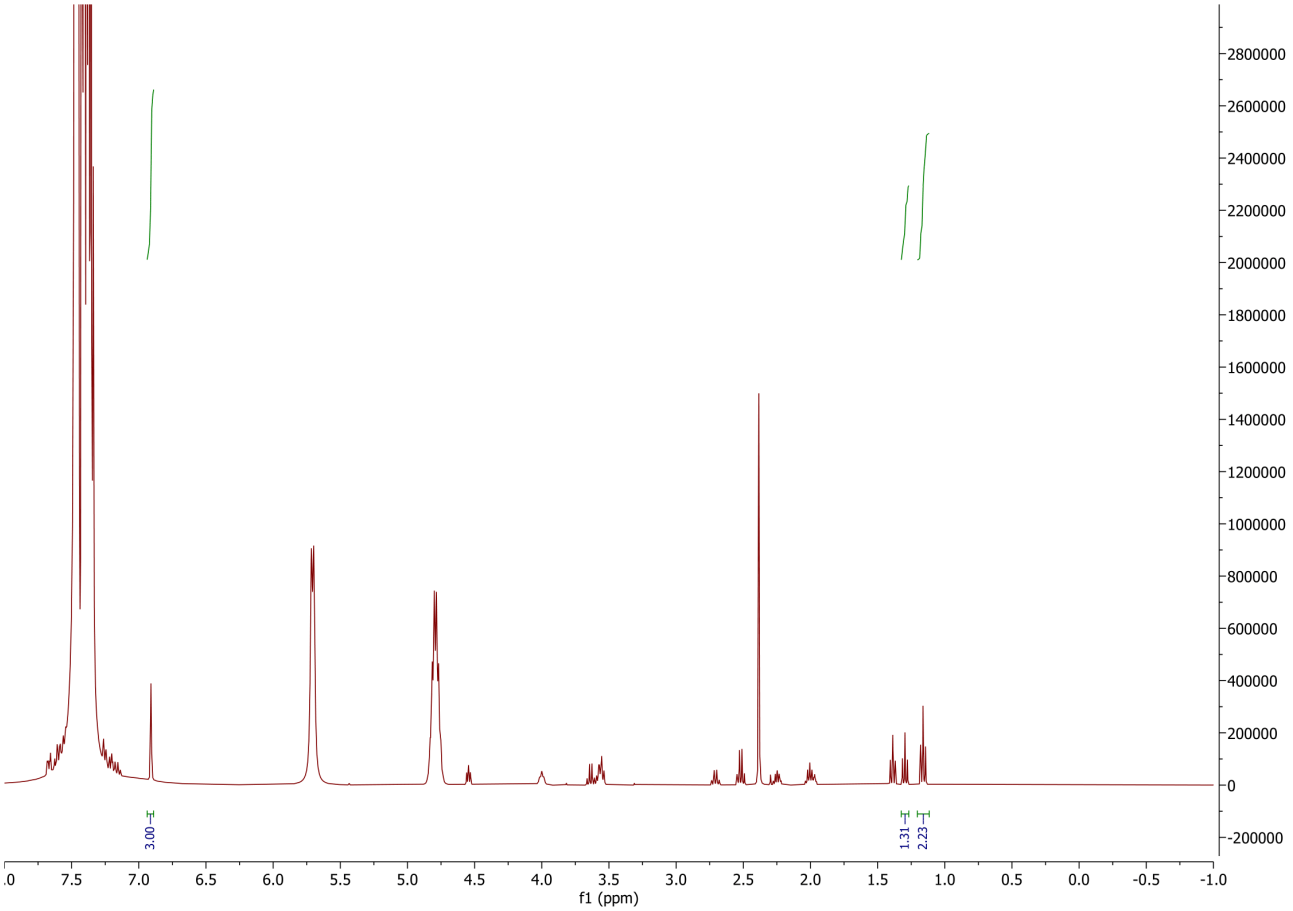
0.0
-0.5
-1.0
f1 (ppm)

Replicate 1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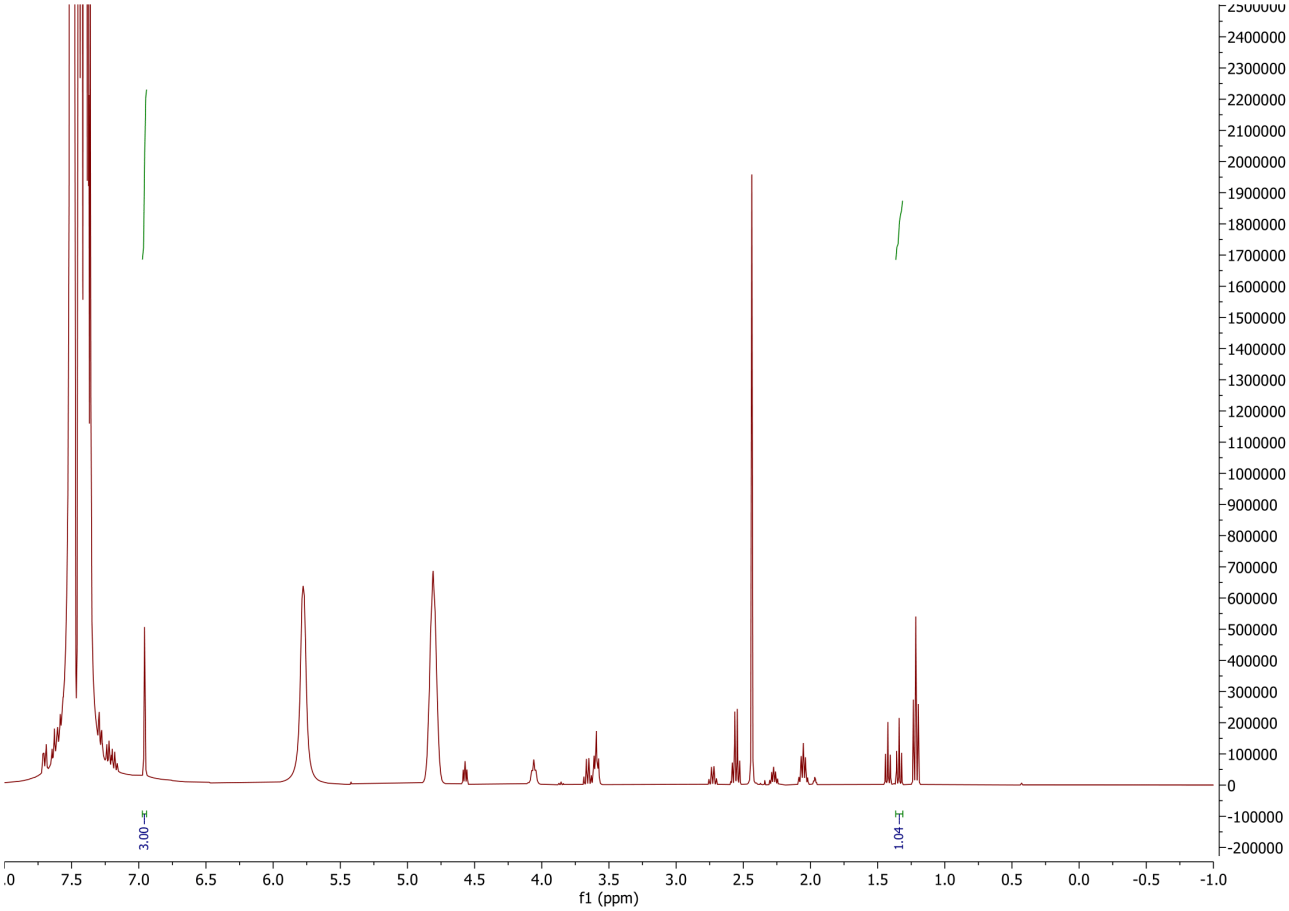
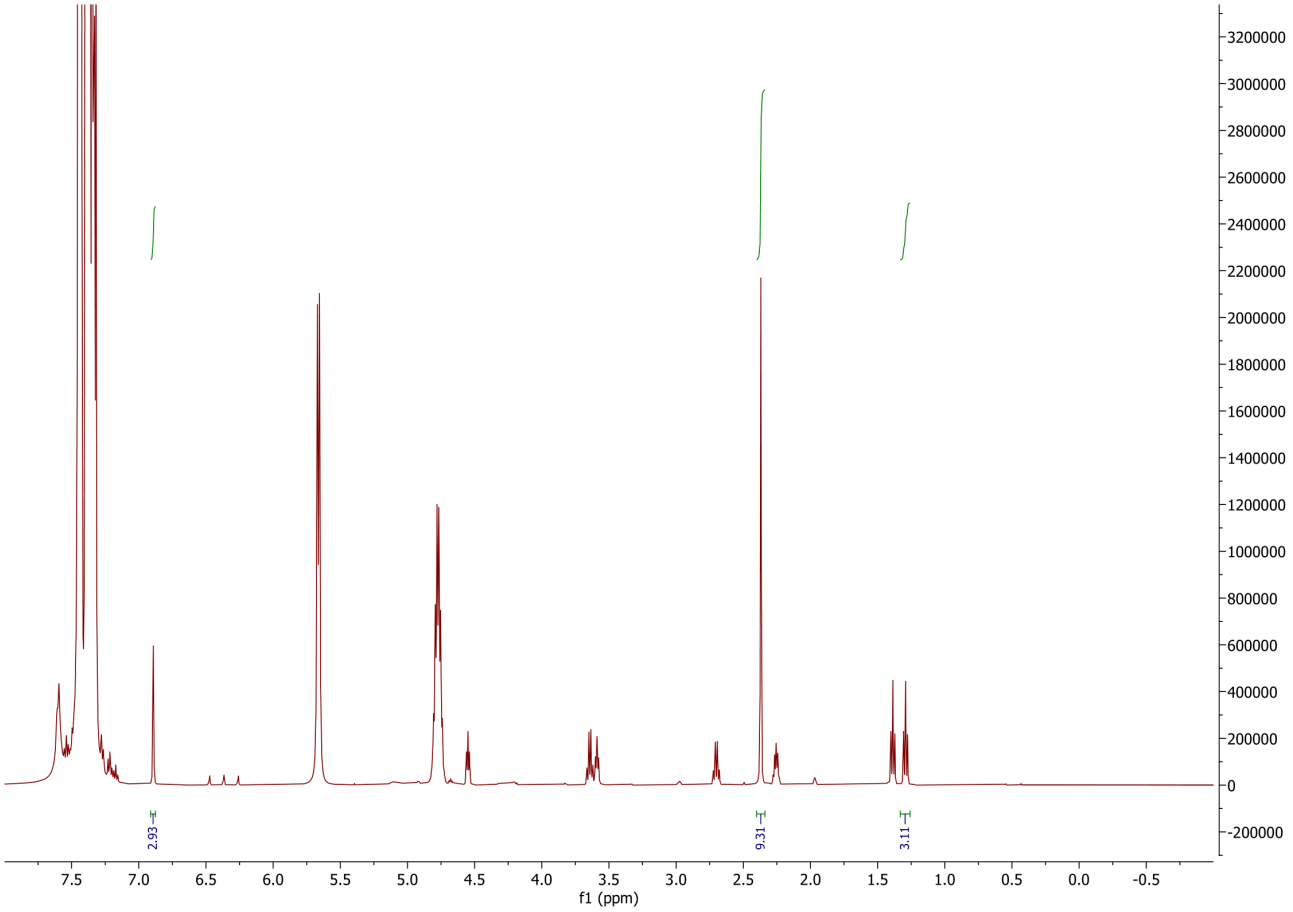
f1 (ppm)

Replicate 2



Replicate 3

Figure S25. ^{1}H NMR (400 MHz, ACN-d_3, 23 °C) spectra for triplicate results described in **Table 1 entry 1.** Yield is calculated from integration of methyl resonance of product iminium ether at ~1.3 ppm. Yield from each replicate (tabulated in **Table S2**) is averaged. The average is tabulated in **Table 1**.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9.31
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7.0
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4.5
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2.0
1.5
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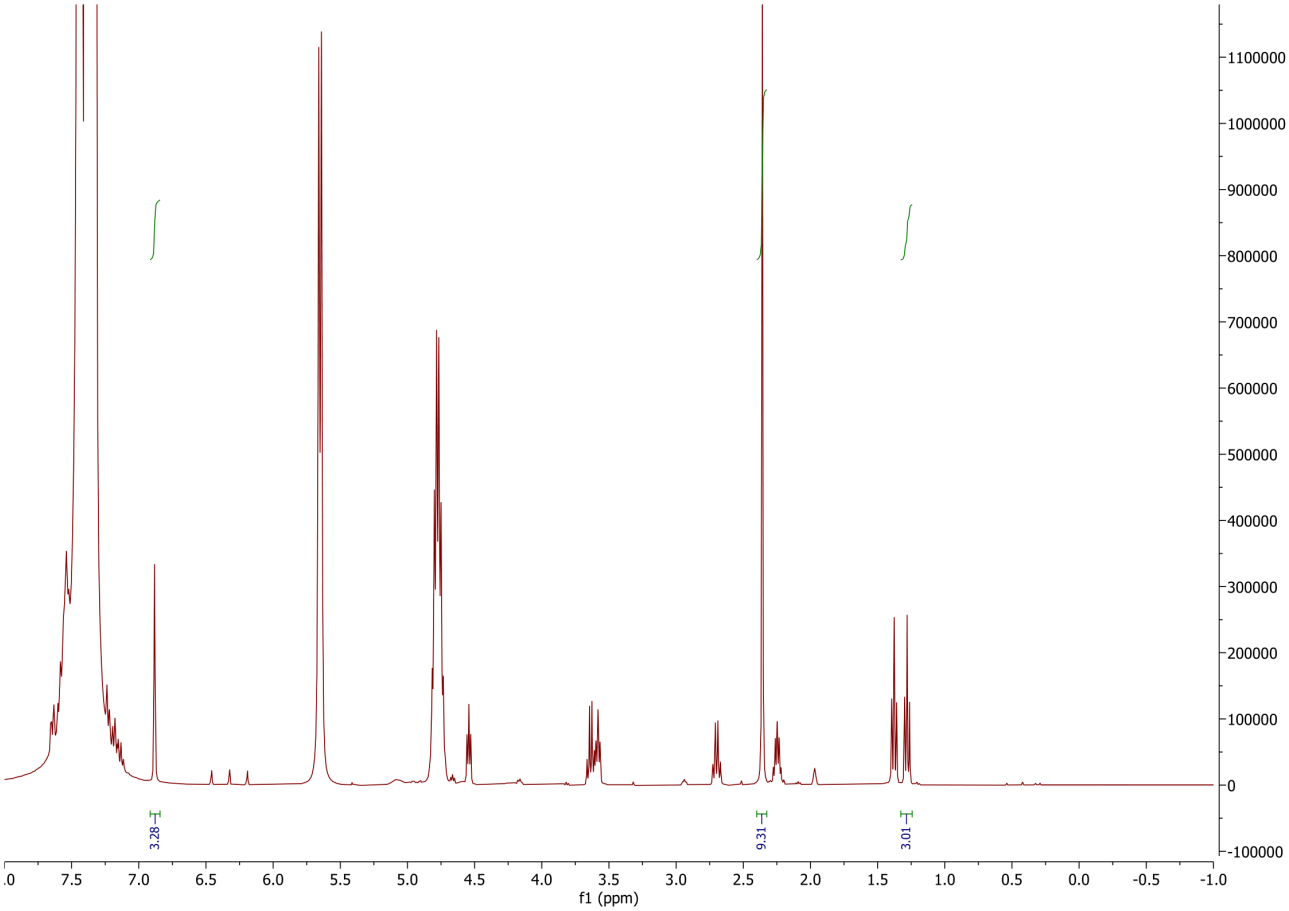
0.0
-0.5
f1 (ppm)

Replicate 1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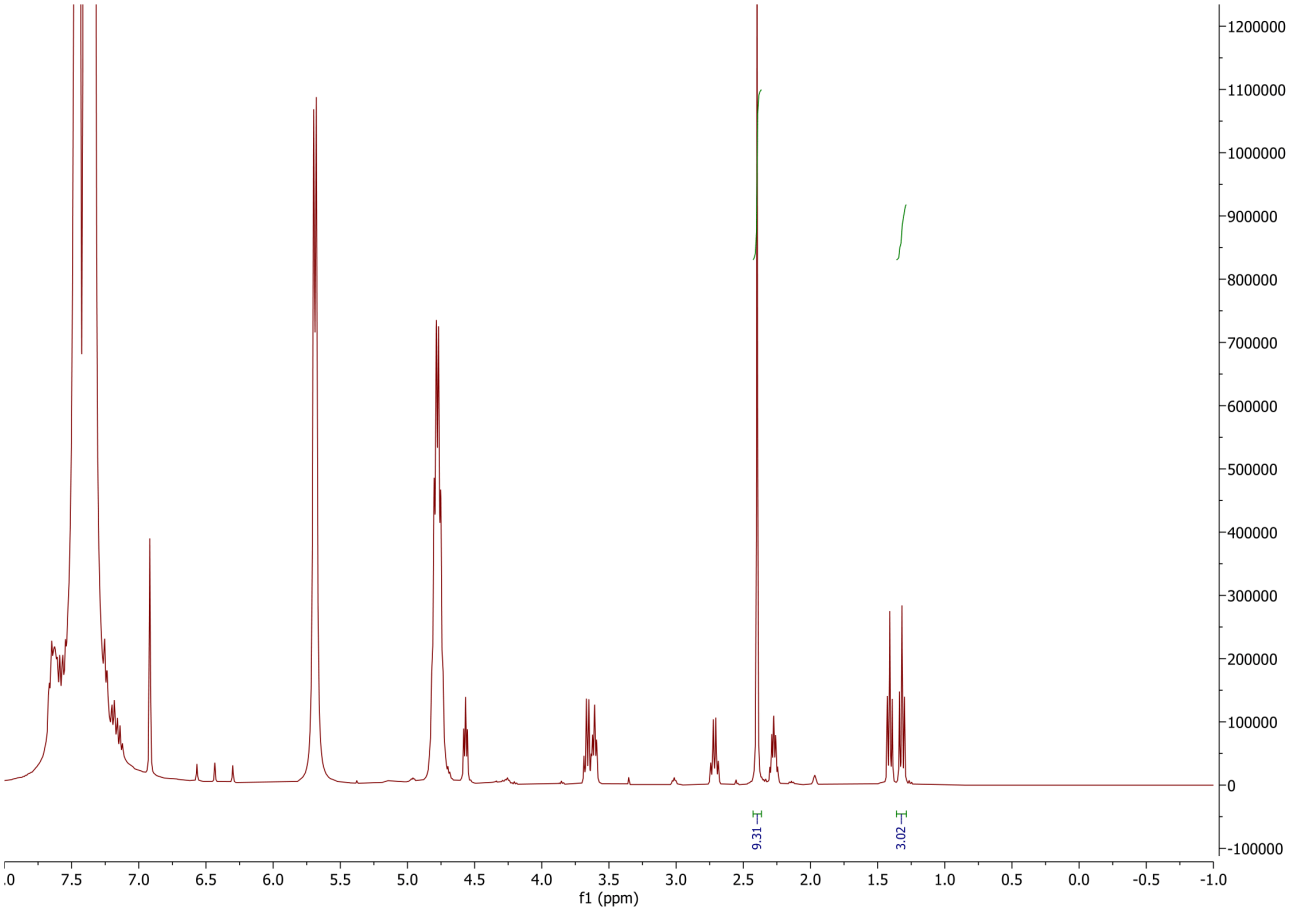
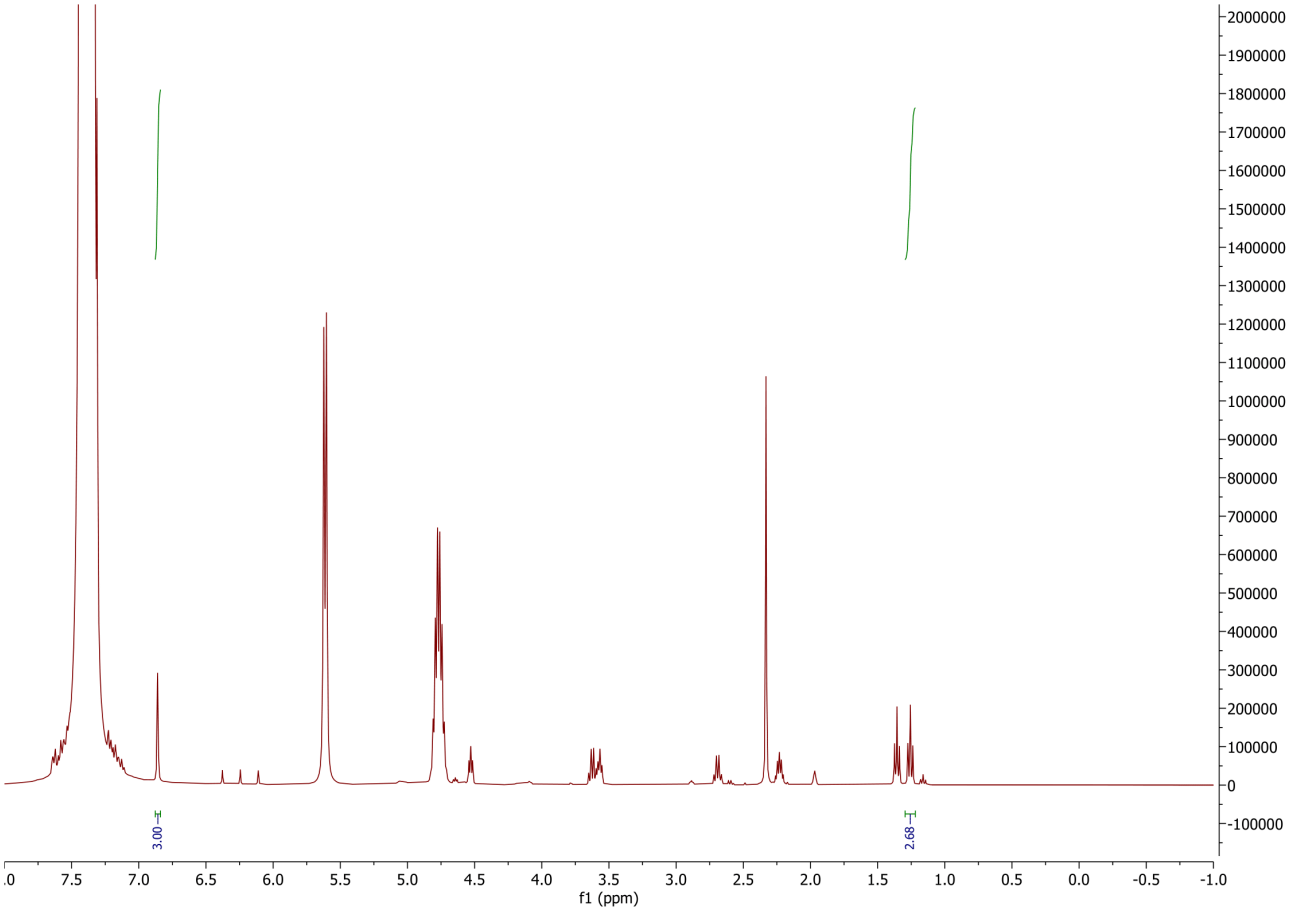
f1 (ppm)

Replicate 2



Replicate 3

Figure S26. ^{1}H NMR (400 MHz, ACN-d_3, 23 °C) spectra for triplicate results described in **Table 1 entry 2**. Yield is calculated from integration of methyl resonance of product iminium ether at ~1.3 ppm. Yield from each replicate (tabulated in **Table S2**) is averaged. The average is tabulated in **Table 1**.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4.0
3.5
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1.5
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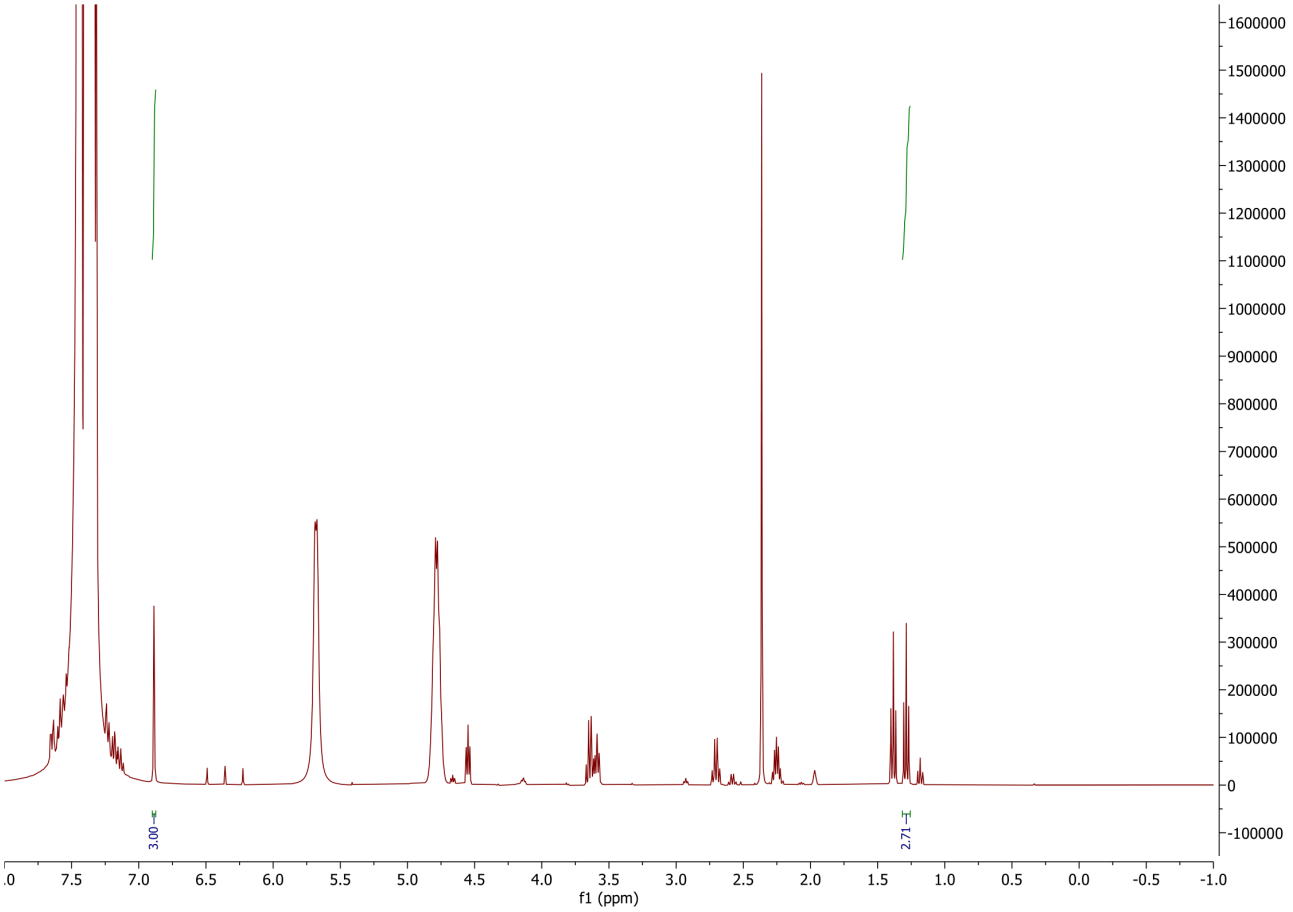
-0.5
-1.0
f1 (ppm)

Replicate 1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400000
300000
200000
100000
0
-100000
3.00
2.71
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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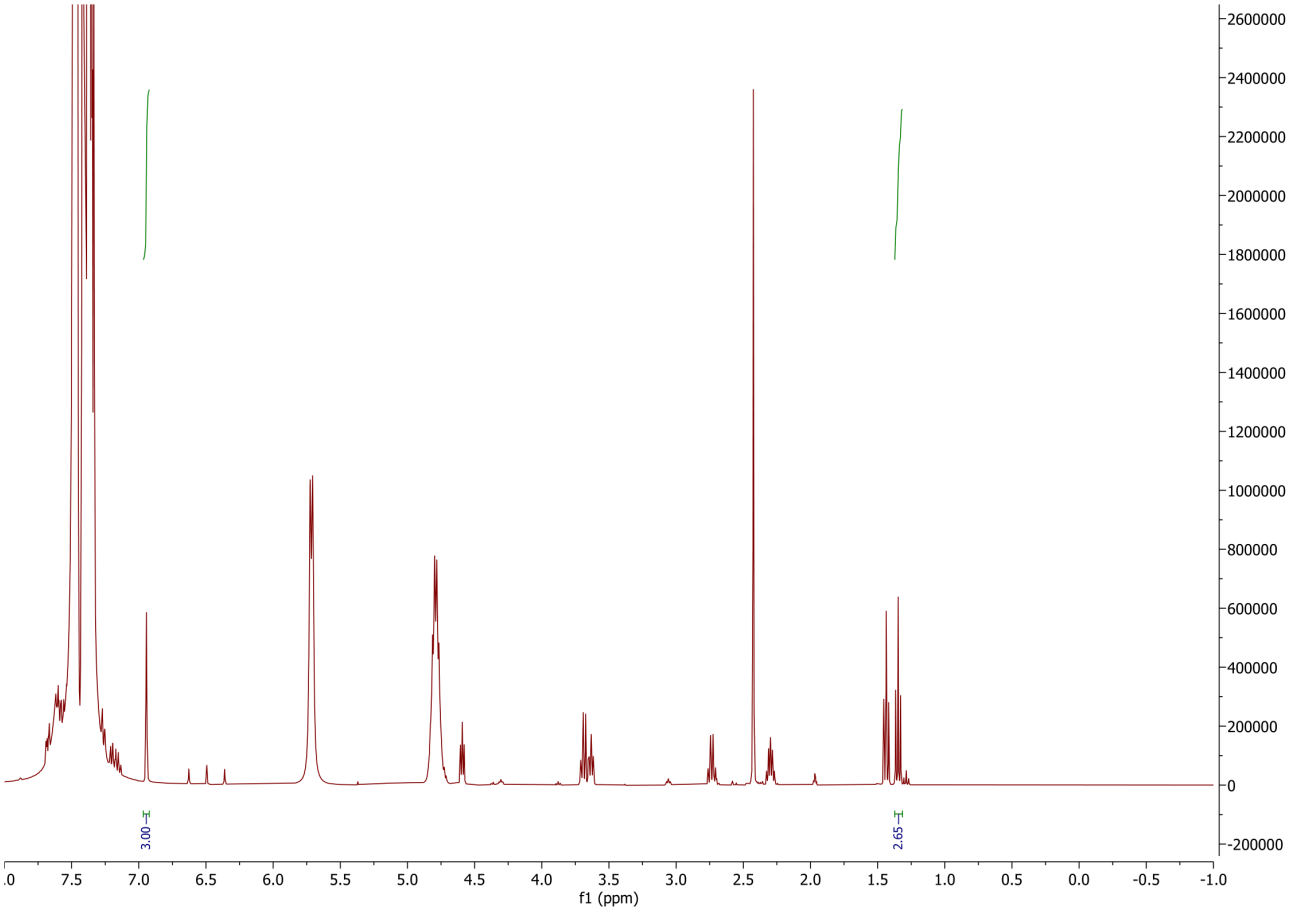
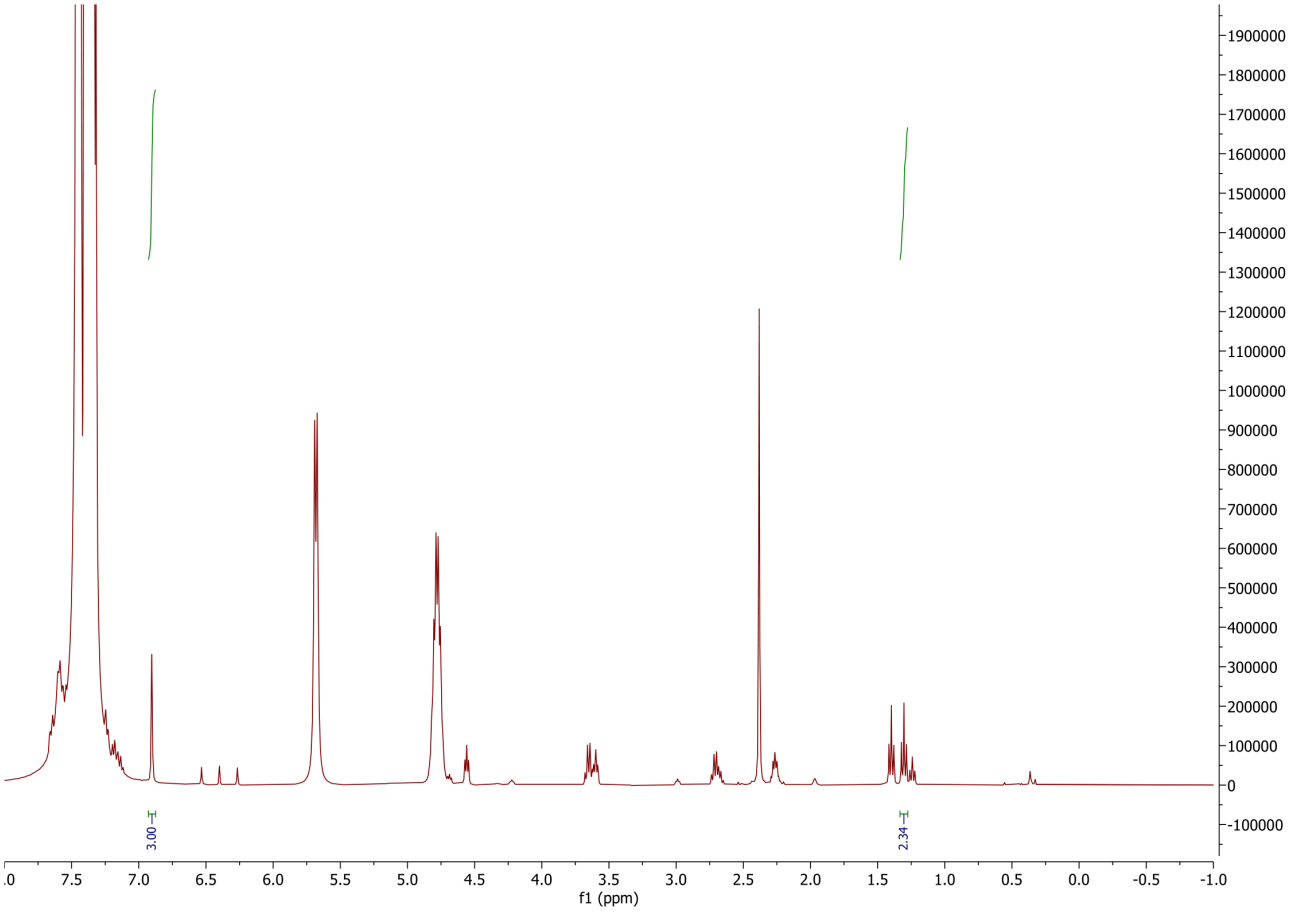
-0.5
-1.0
f1 (ppm)

Replicate 2



Replicate 3

Figure S27. ^{1}H NMR (400 MHz, ACN-d_3, 23 °C) spectra for triplicate results described in **Table 1 entry 3**. Yield is calculated from integration of methyl resonance of product iminium ether at ~1.3 ppm. Yield from each replicate (tabulated in **Table S2**) is averaged. The average is tabulated in **Table 1**.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300000
200000
100000
0
-100000
3.00
2.34
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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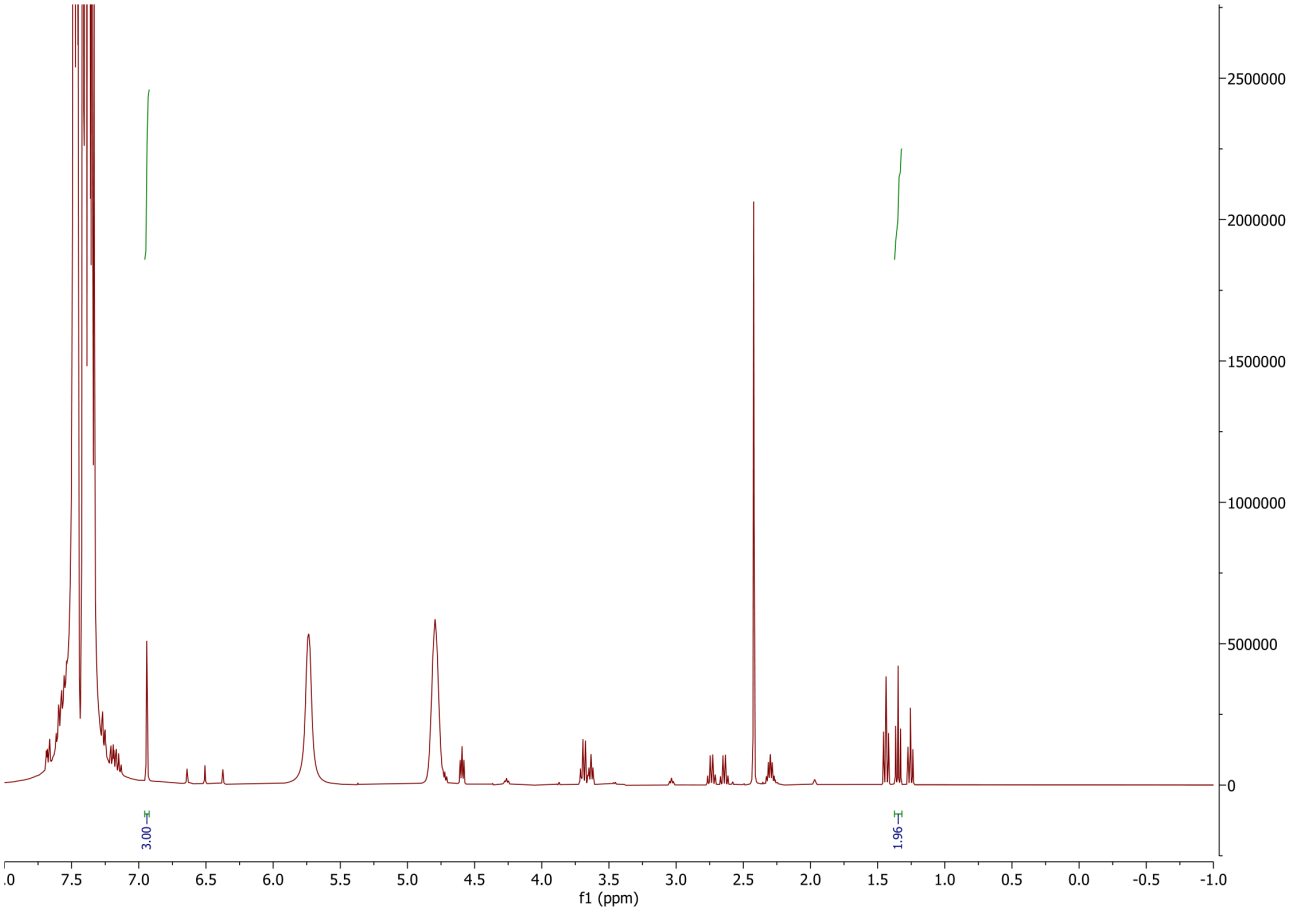
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

Replicate 1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5.0
4.5
4.0
3.5
3.0
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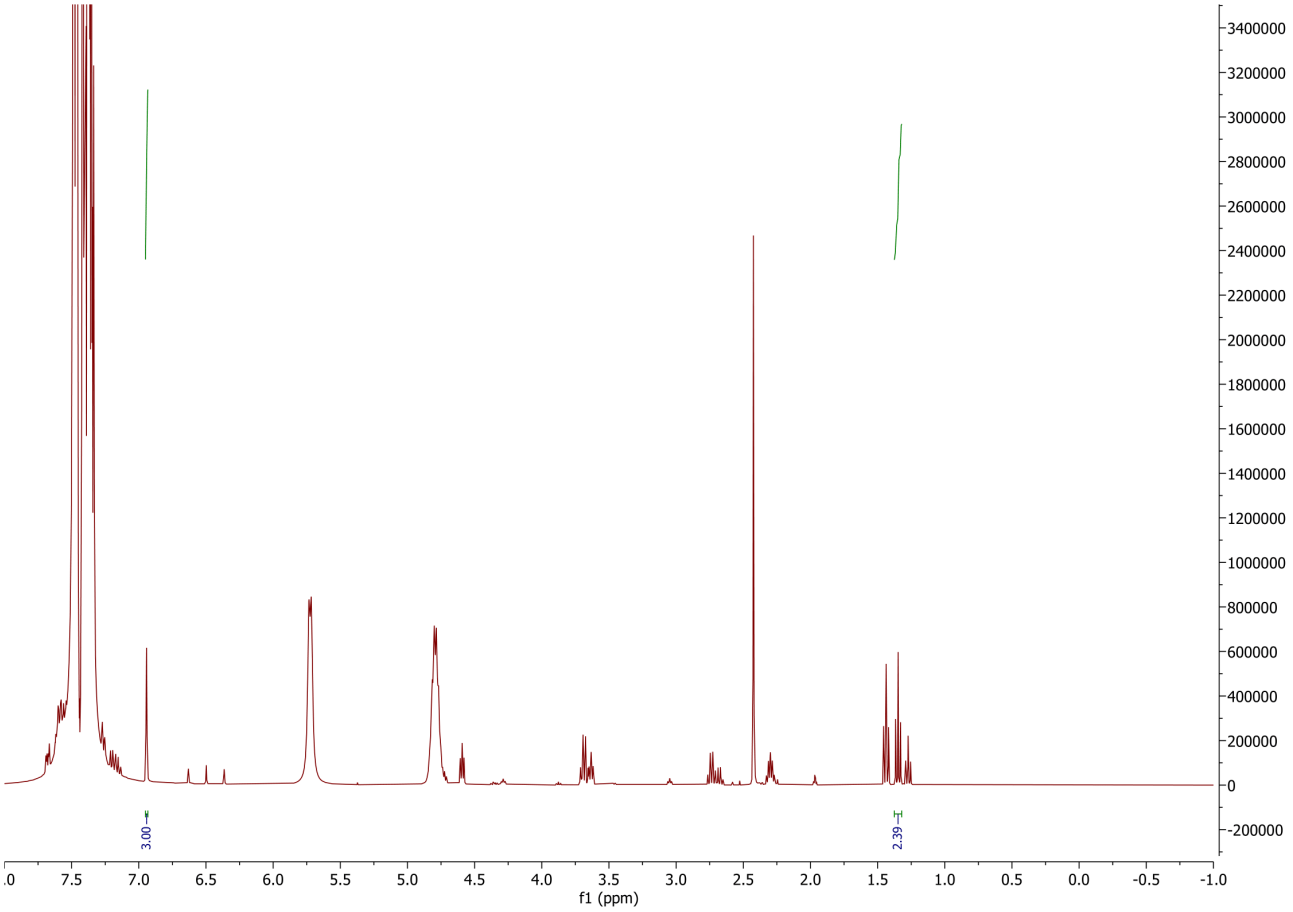
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

Replicate 2



Replicate 3

Figure S28. ^{1}H NMR (400 MHz, ACN-d_3, 23 °C) spectra for triplicate results described in **Table 1 entry 4**. Yield is calculated from integration of methyl resonance of product iminium ether at ~1.3 ppm. Yield from each replicate (tabulated in **Table S2**) is averaged. The average is tabulated in **Table 1**.

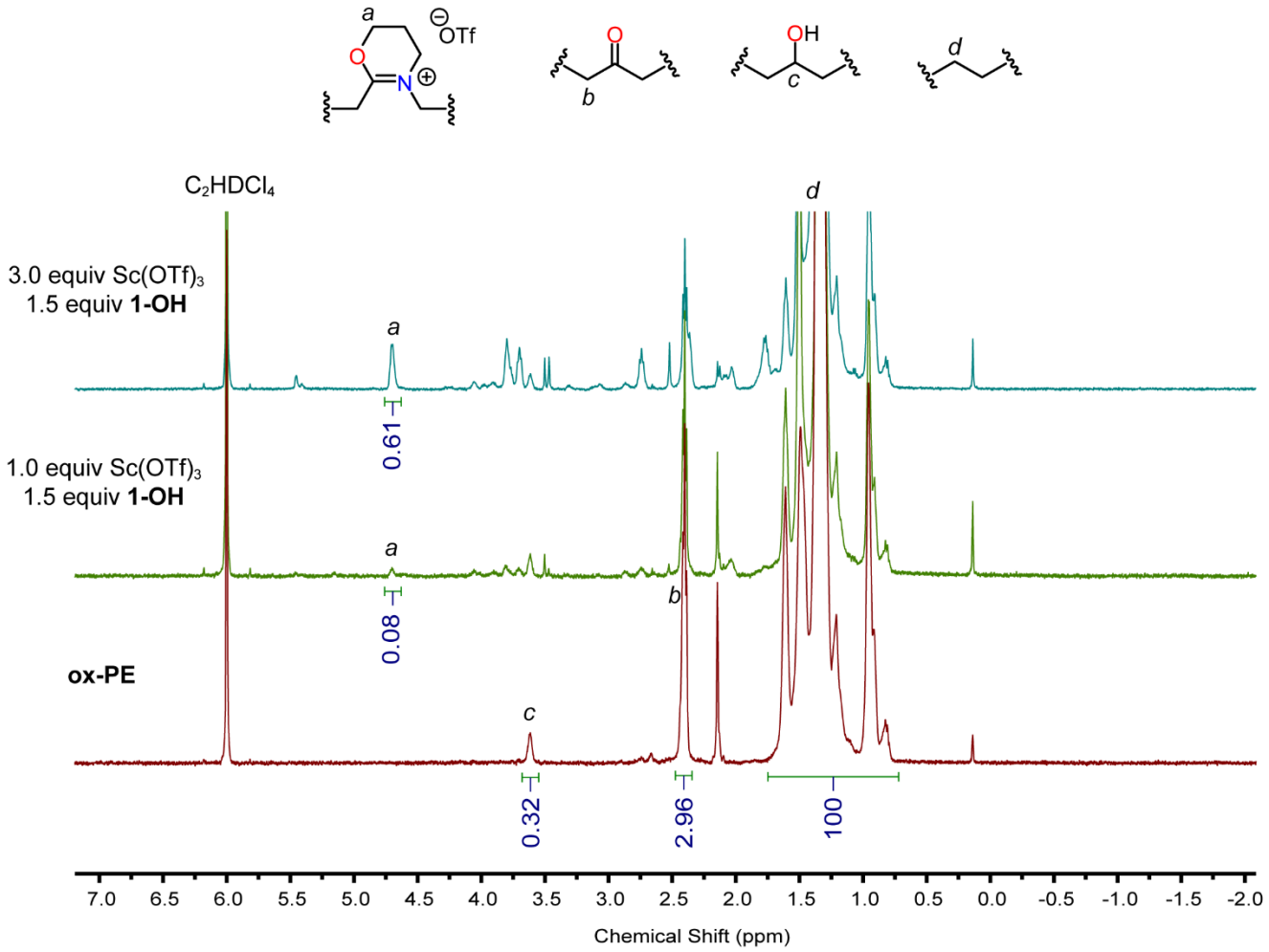


Figure S29. ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 92-94 °C) of **ox-PE** and products of reactions of **ox-PE** with 1.5 equiv **1-OH** and varying equivalents of $Sc(OTf)_3$ (**Table 1, entries 5–6**). The integral of the resonance from –CH_2–CH_2– repeat units (~0.7–1.7 ppm) was set to 100 for all spectra.

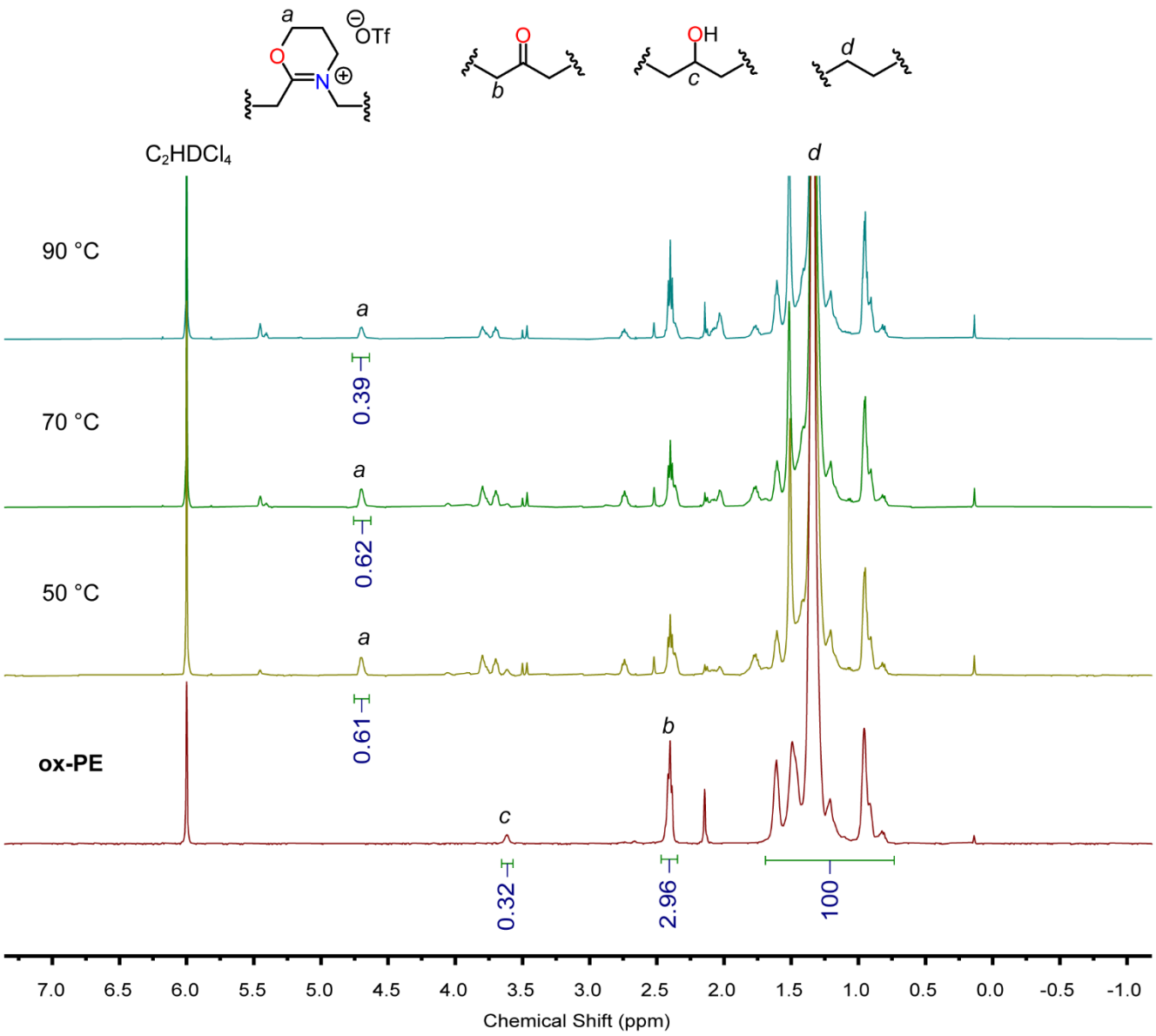


Figure S30. ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 93-94 °C) of **ox-PE** and products of reactions of **ox-PE** with 1.5 equiv **1-OH** and 3 equiv $Sc(OTf)_3$ at various temperatures (**Table 1**, **entries 6–8**). The integral of the resonance from –CH_2–CH_2– repeat units (~0.7–1.7 ppm) was set to 100 for all spectra.

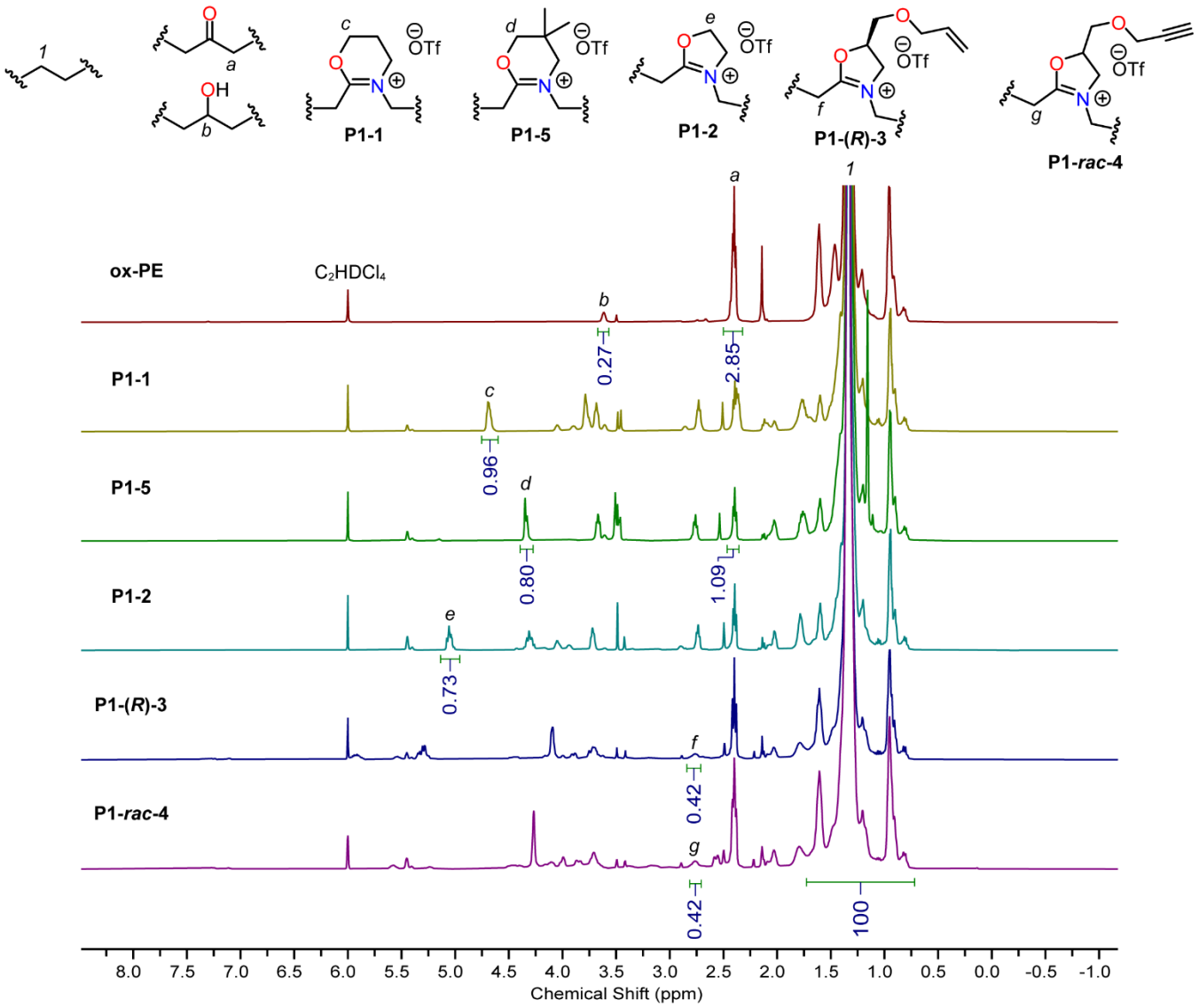


Figure S31. ^{1}H NMR (400 or 500 MHz, 1,1,2,2-tetrachloroethane-d_2, 90-94 °C) of **ox-PE** and **P1** series (**Table 1**, **entries 9**, **14**–**17**). The integral of the resonance from –CH_2–CH_2– repeat units (~0.7–1.7 ppm) was set to 100 for all spectra.

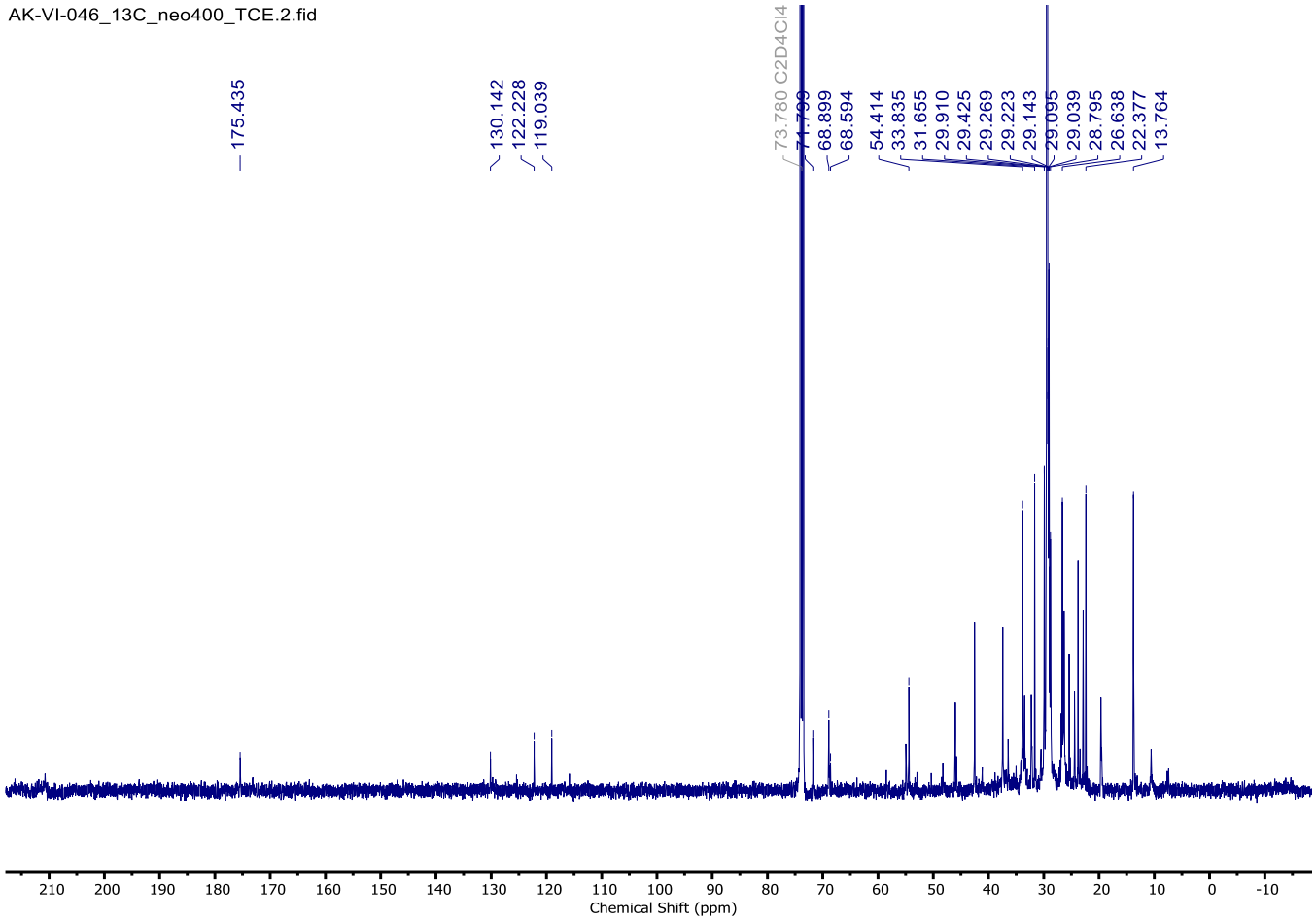


Figure S32. ^{13}C NMR (101 MHz, 1,1,2,2-tetrachloroethane-d_2, ~90 °C) of **P1-1**

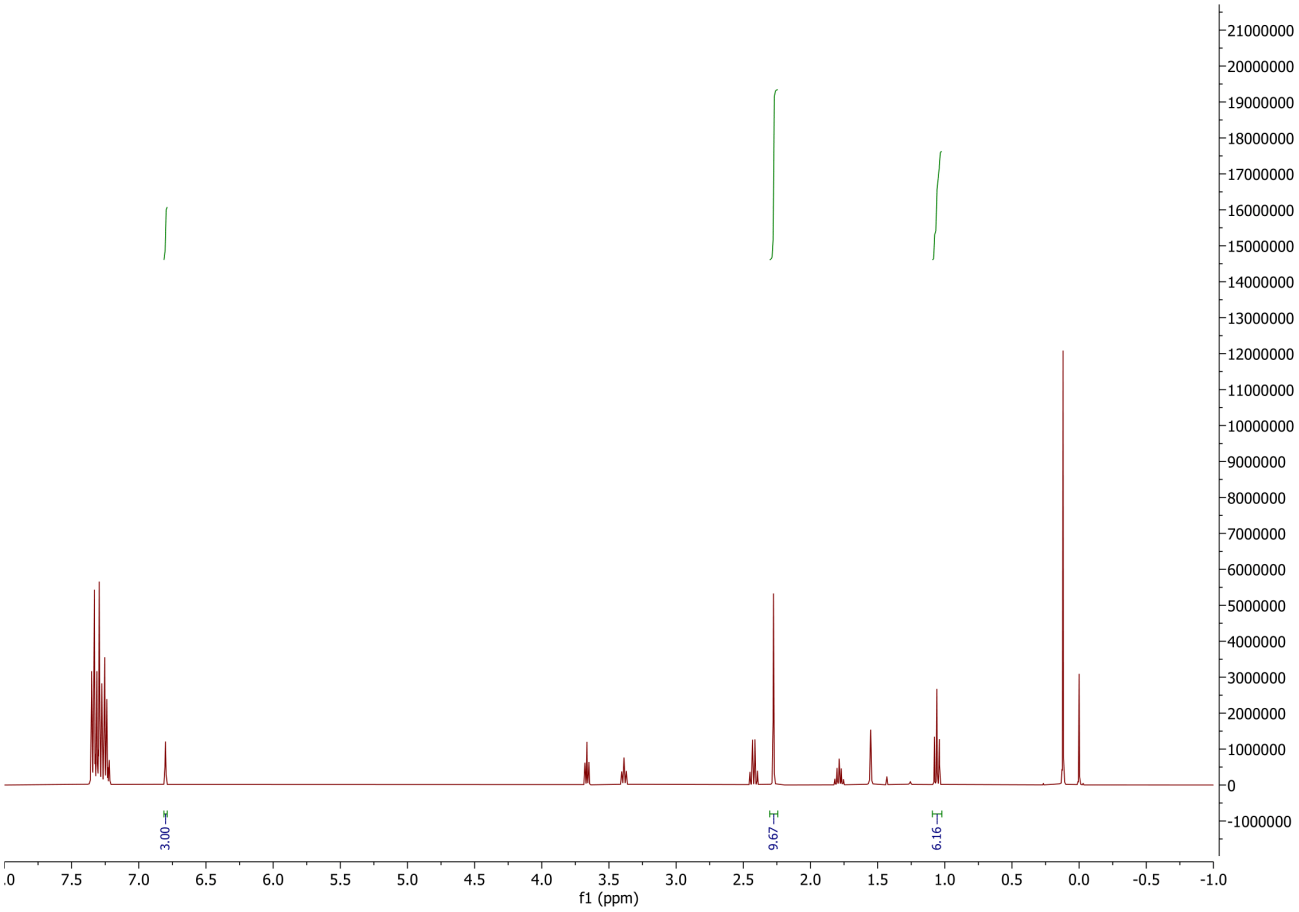
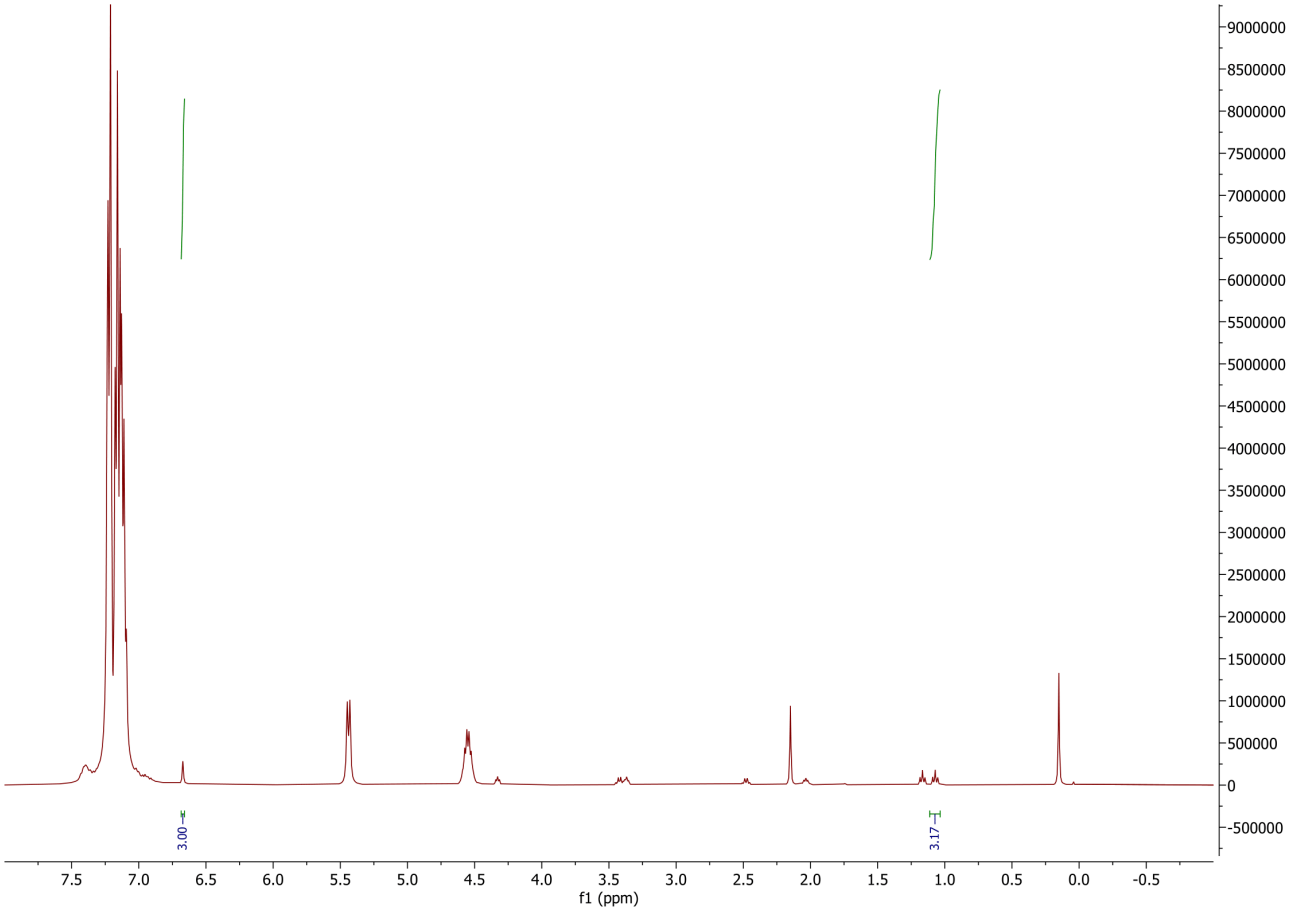


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of stock solution of 3-pentanone, **1-OTMS**, and mesitylene in chlorobenezene (900 mmolar w.r.t. 3-pentanone) used for **Table 1 entry 10**.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7.5
7.0
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5.0
4.5
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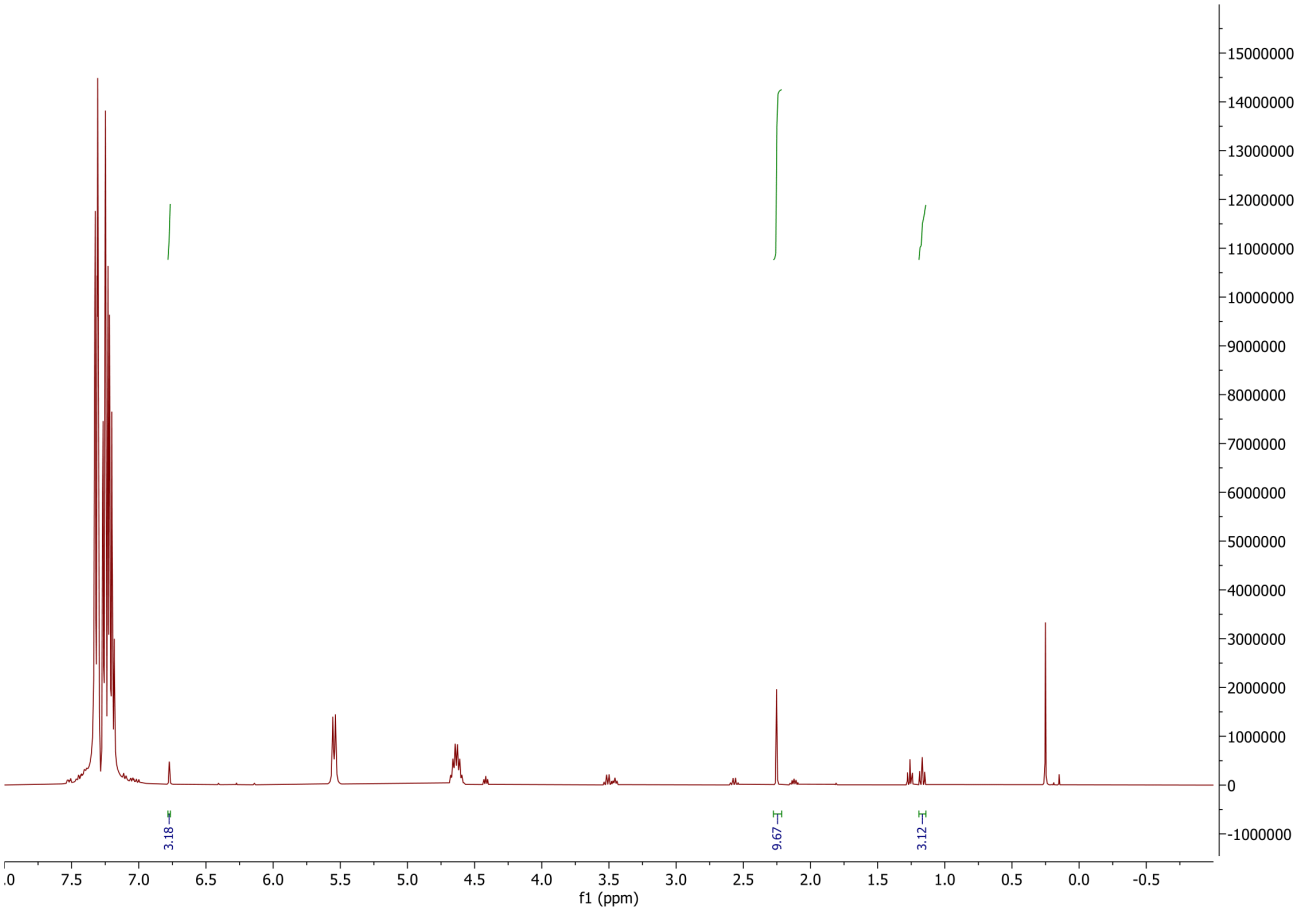
0.5
0.0
-0.5
f1 (ppm)

Replicate 1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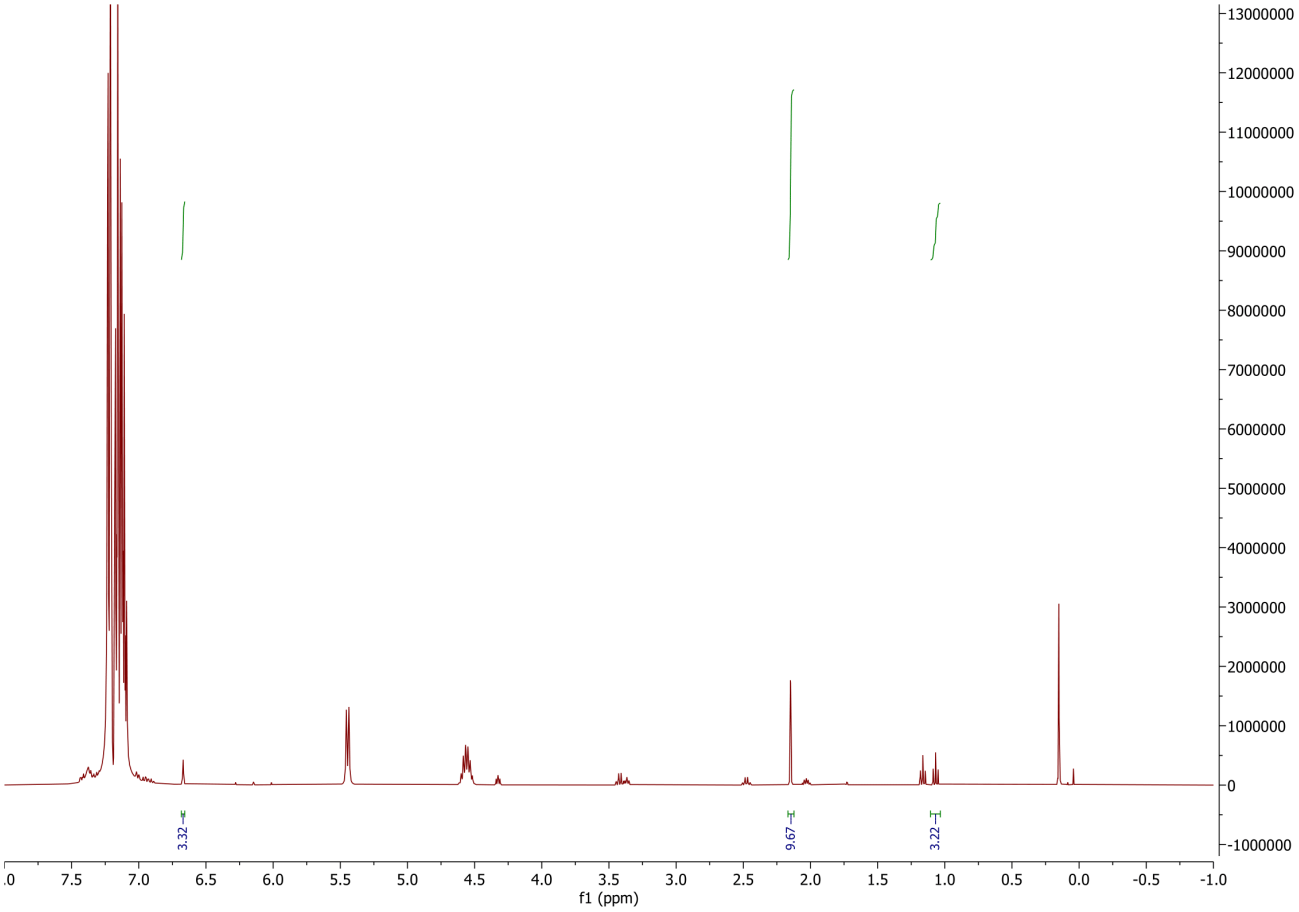
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

Replicate 2



Replicate 3

Figure S34. ^{1}H NMR (400 MHz, ACN-d_3, 23 °C) spectra for triplicate results described in **Table 1 entry 10**. Yield is calculated from integration of methyl resonance of product iminium ether at ~1.3 ppm. Yield from each replicate (tabulated in **Table S2**) is averaged. The average is tabulated in **Table 1**.

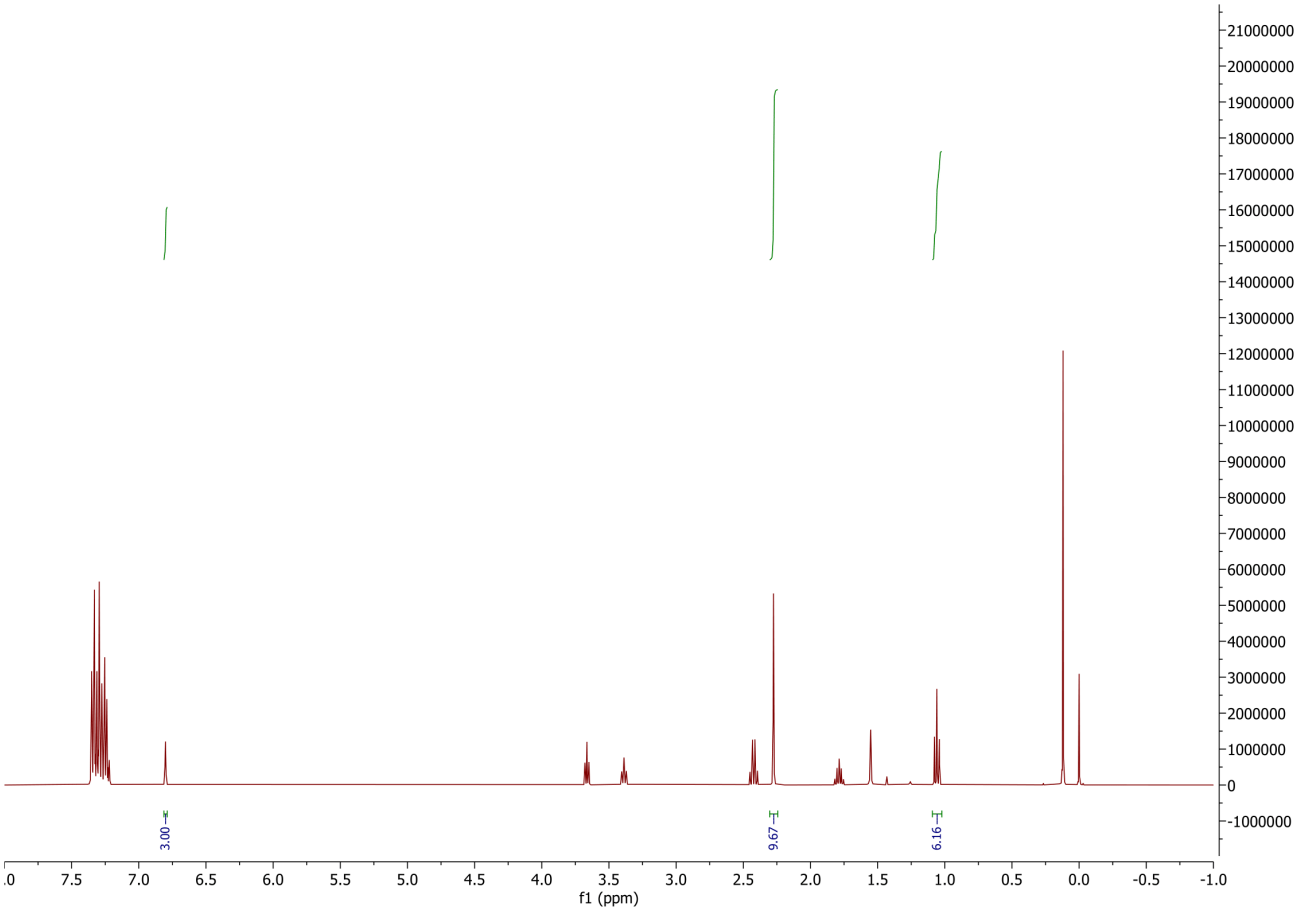
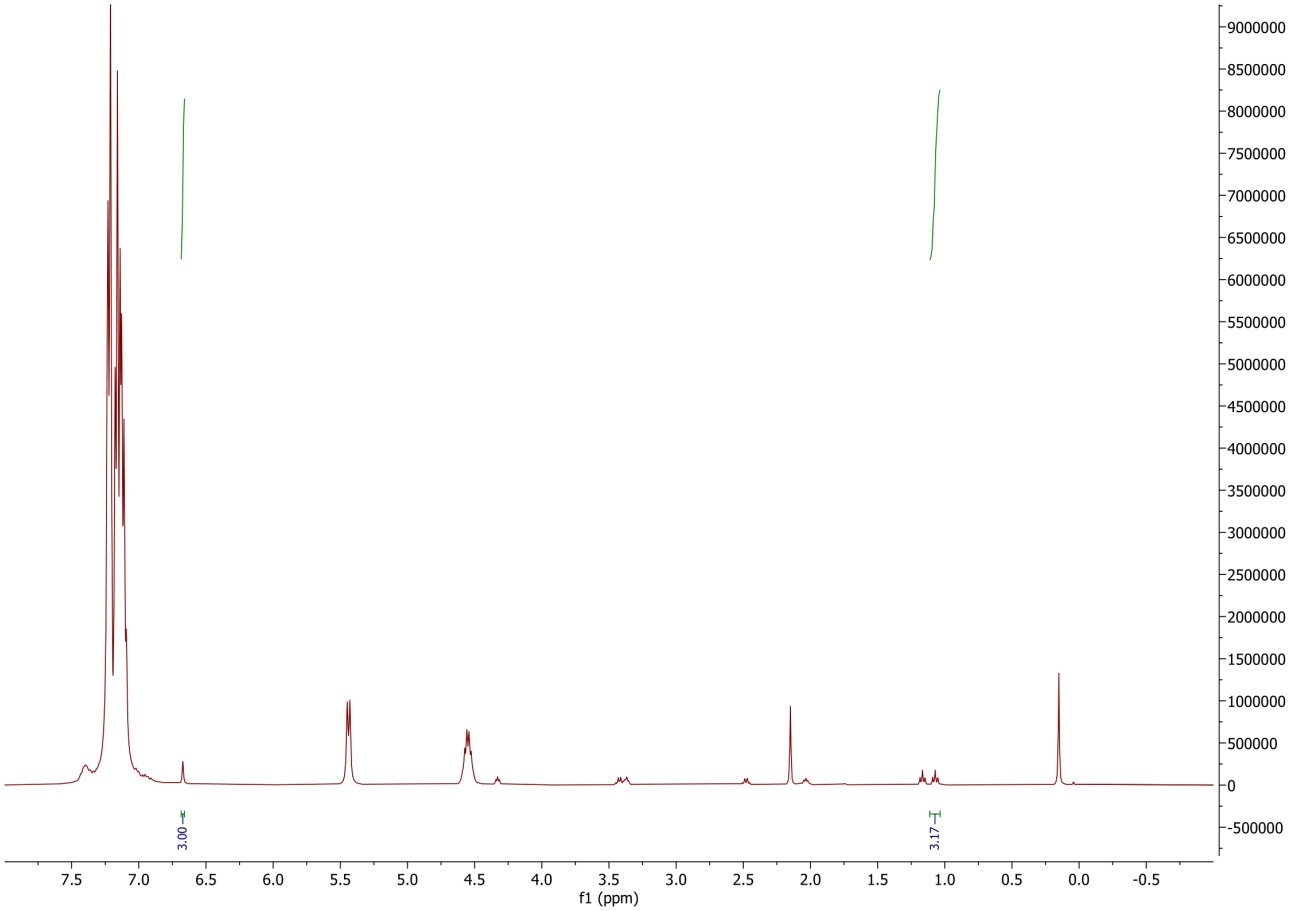


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of stock solution of 3-pentanone, **2-OH**, and mesitylene in chlorobenzene (900 mmolar w.r.t. 3-pentanone) used for **Table 1 entry 11**.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5.5
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4.5
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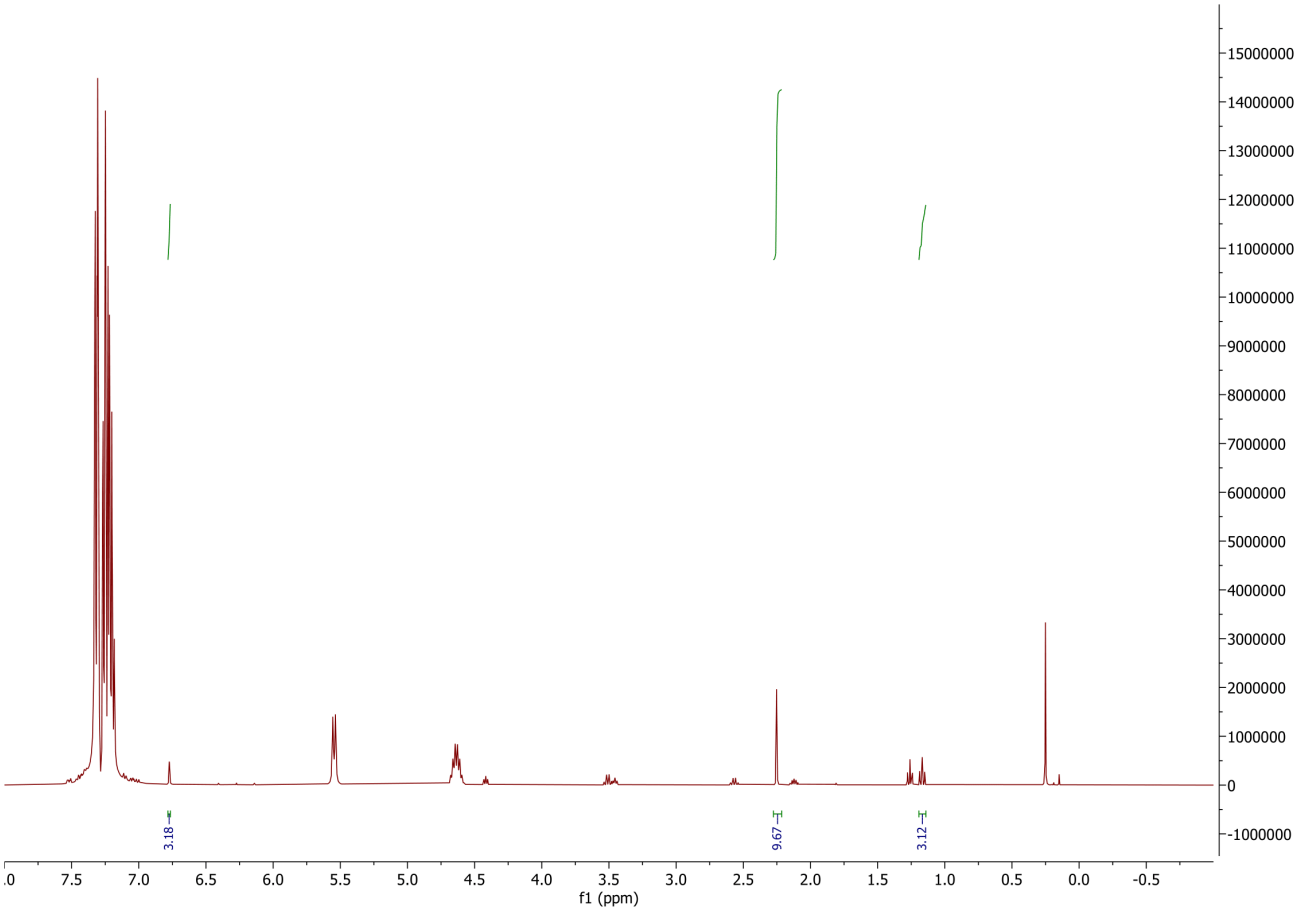
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

Replicate 1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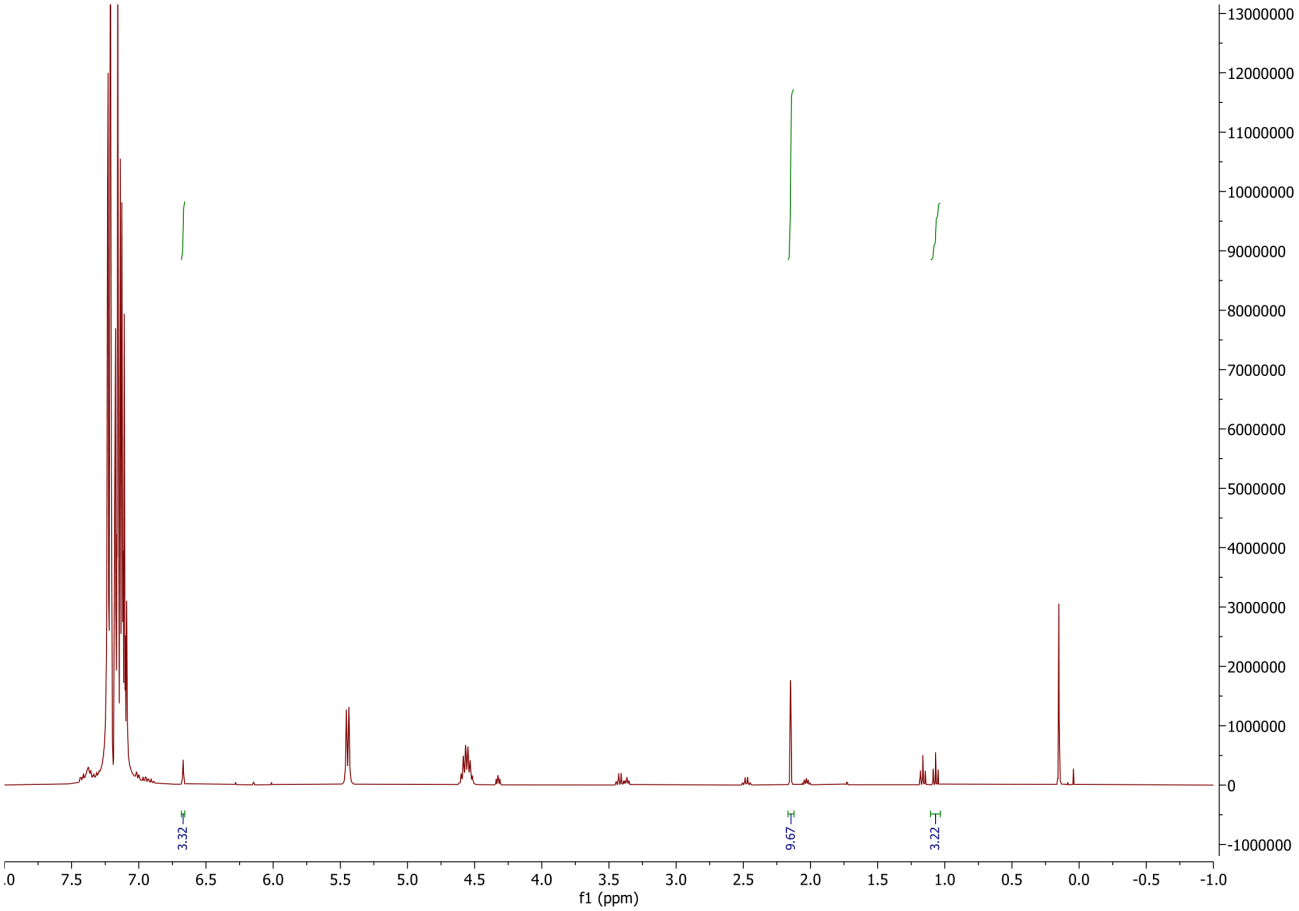
-0.5
f1 (ppm)

Replicate 2



Replicate 3

Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectra for triplicate results described in **Table 1 entry 11**. Yield is calculated from integration of methyl resonance of product iminium ether at ~1.3 ppm. Yield from each replicate (tabulated in **Table S2**) is averaged. The average is tabulated in **Table 1**.

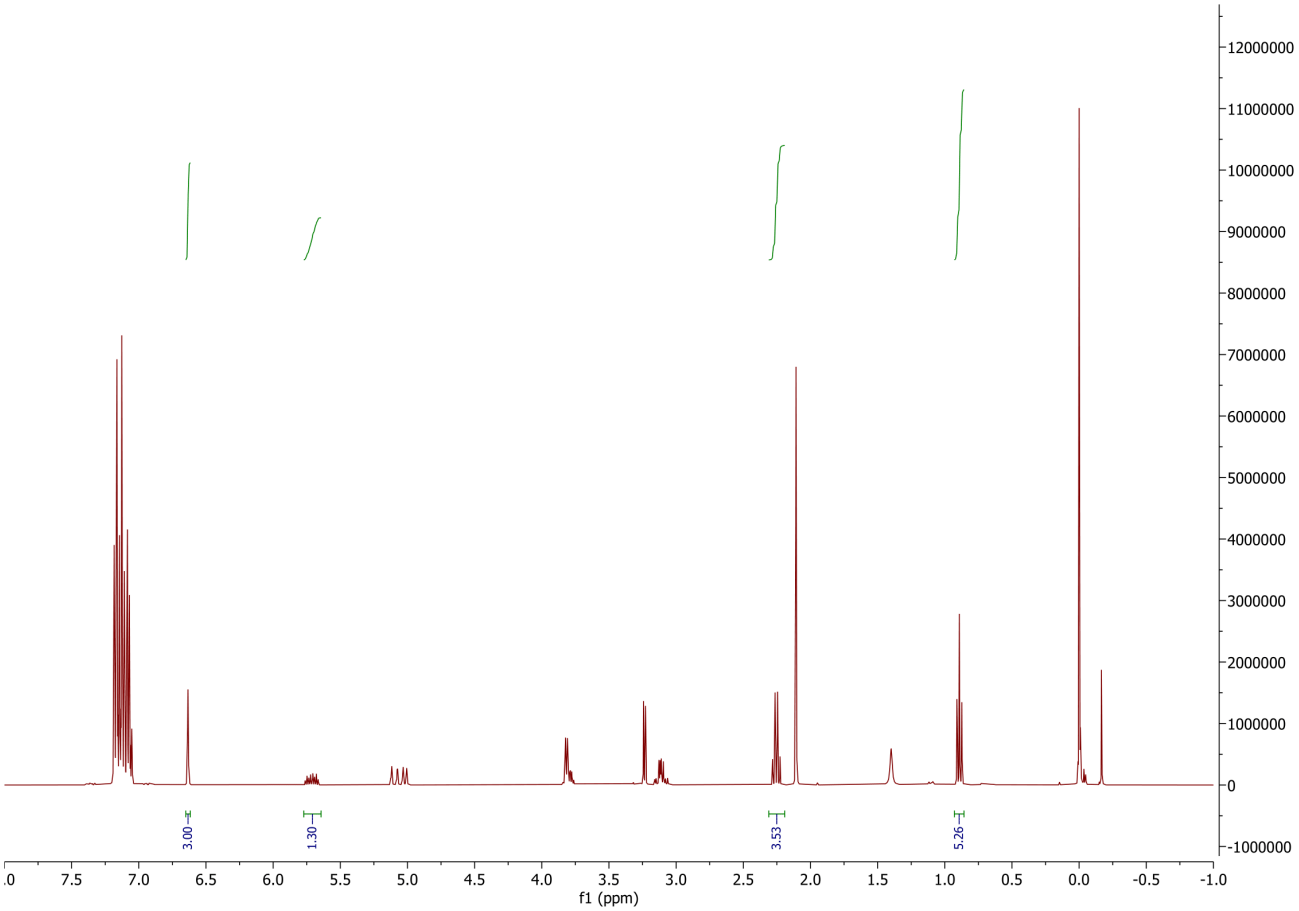
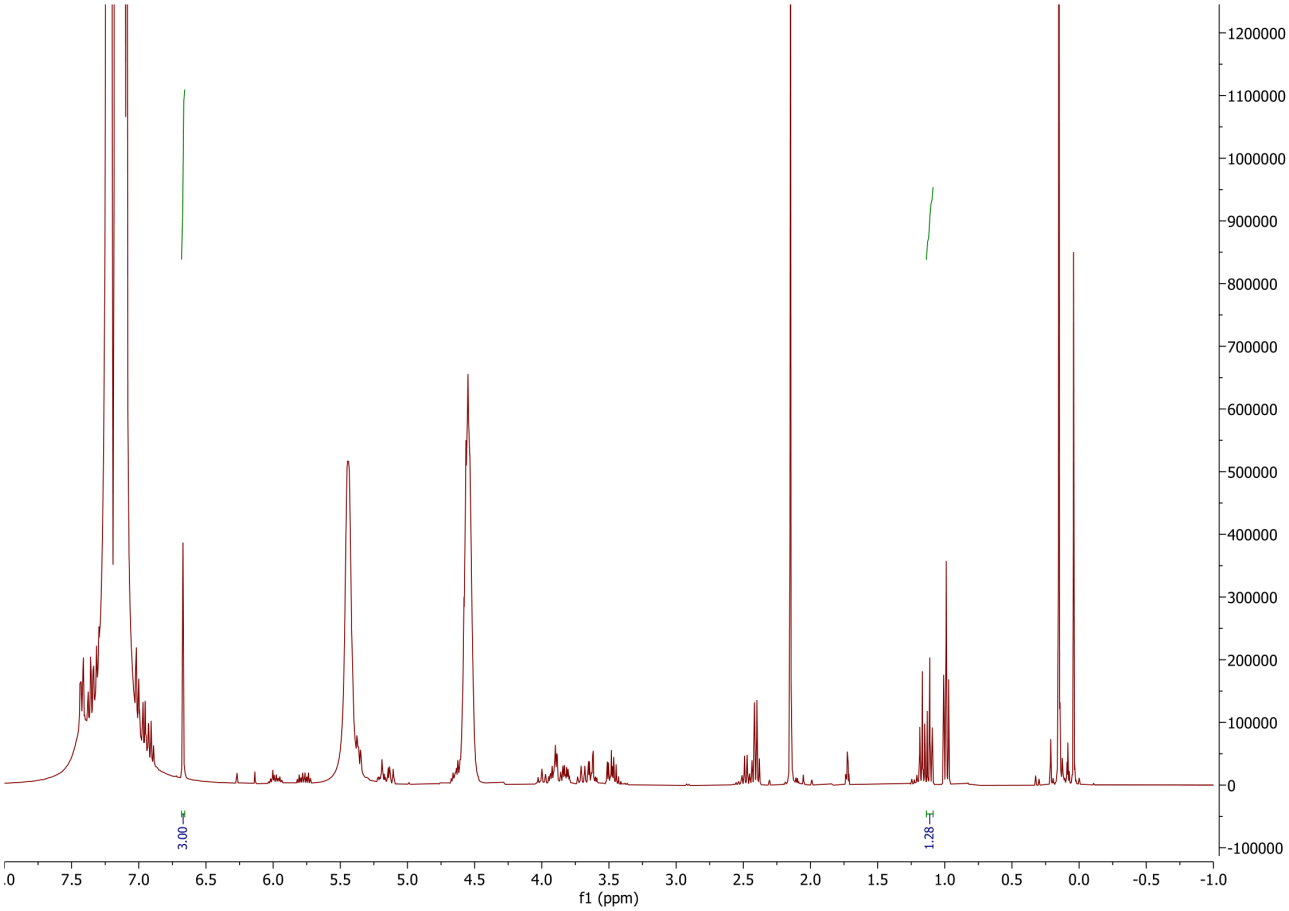


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of stock solution of 3-pentanone, ***rac*-3-OTMS**, and mesitylene in chlorobenzene (900 mmolar w.r.t. 3-pentanone) used for **Table 1 entry 12**.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4.5
4.0
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1.5
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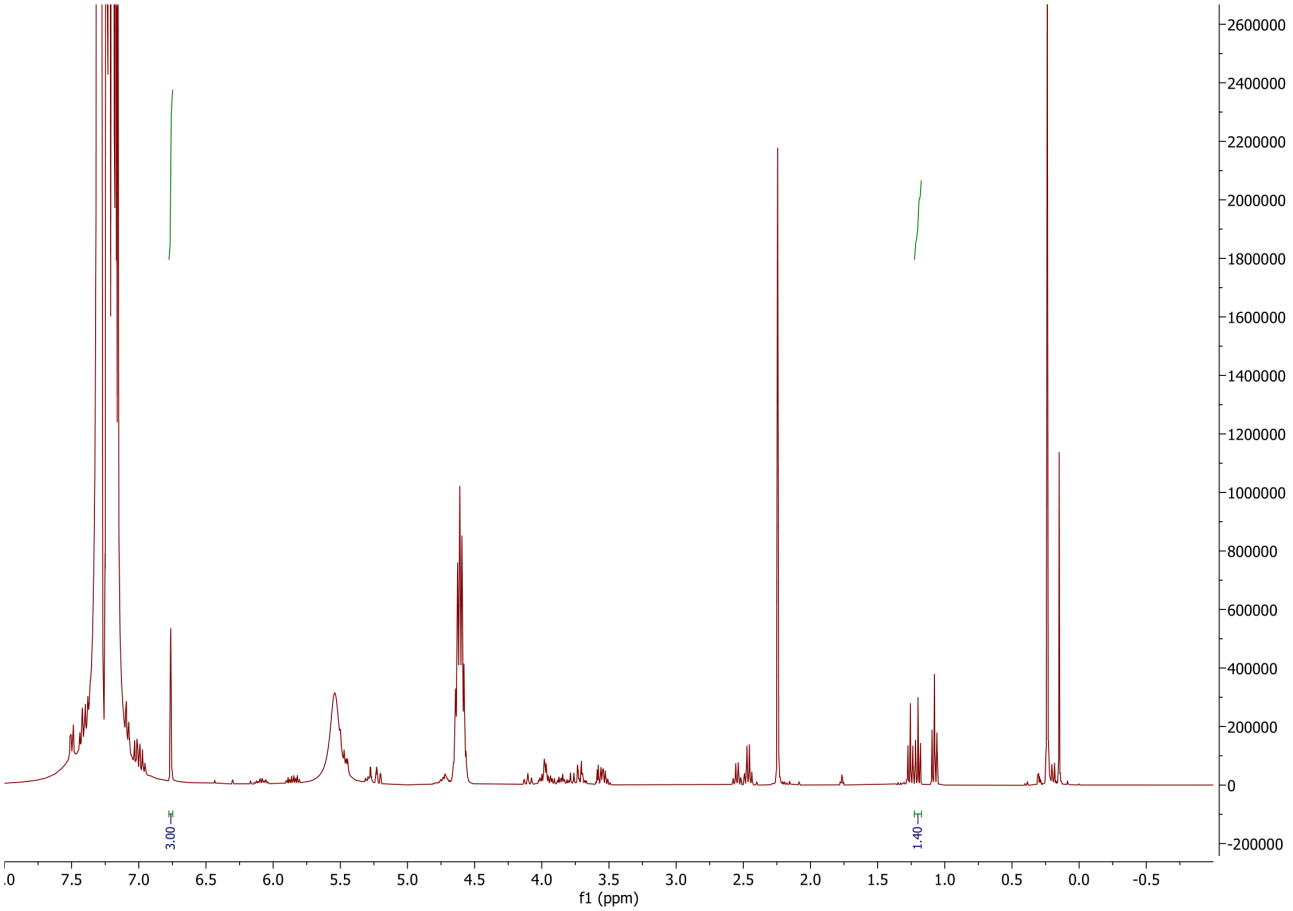
-0.5
-1.0
f1 (ppm)

Replicate 1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7.0
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6.0
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5.0
4.5
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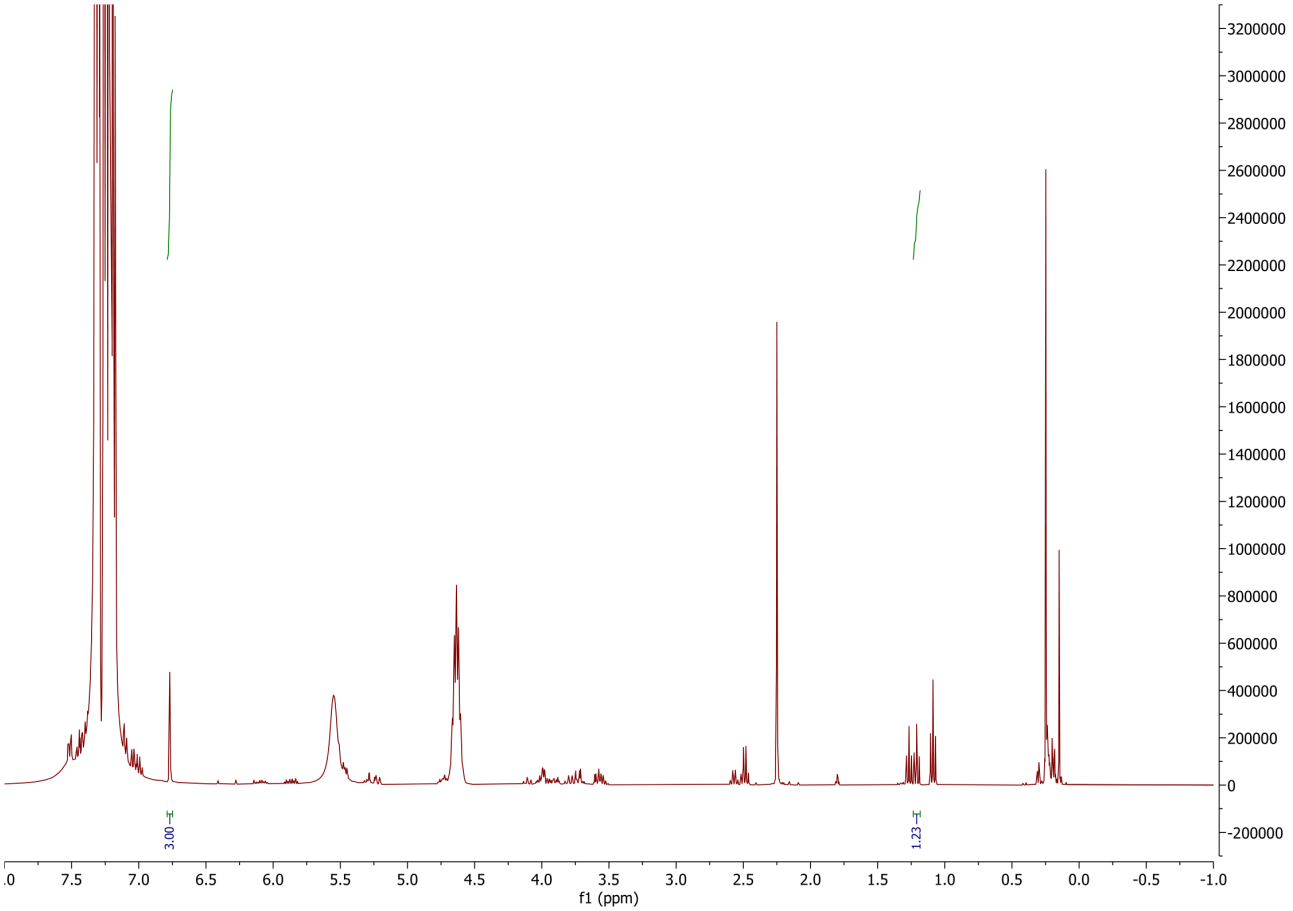
0.0
-0.5
f1 (ppm)

Replicate 2



Replicate 3

Figure S38. ^{1}H NMR (400 MHz, ACN-d_3, 23 °C) spectra for triplicate results described in **Table 1 entry 12**. Yield is calculated from integration of methyl resonance of product iminium ether at ~1.3 ppm. Yield from each replicate (tabulated in **Table S2**) is averaged. The average is tabulated in **Table 1**.

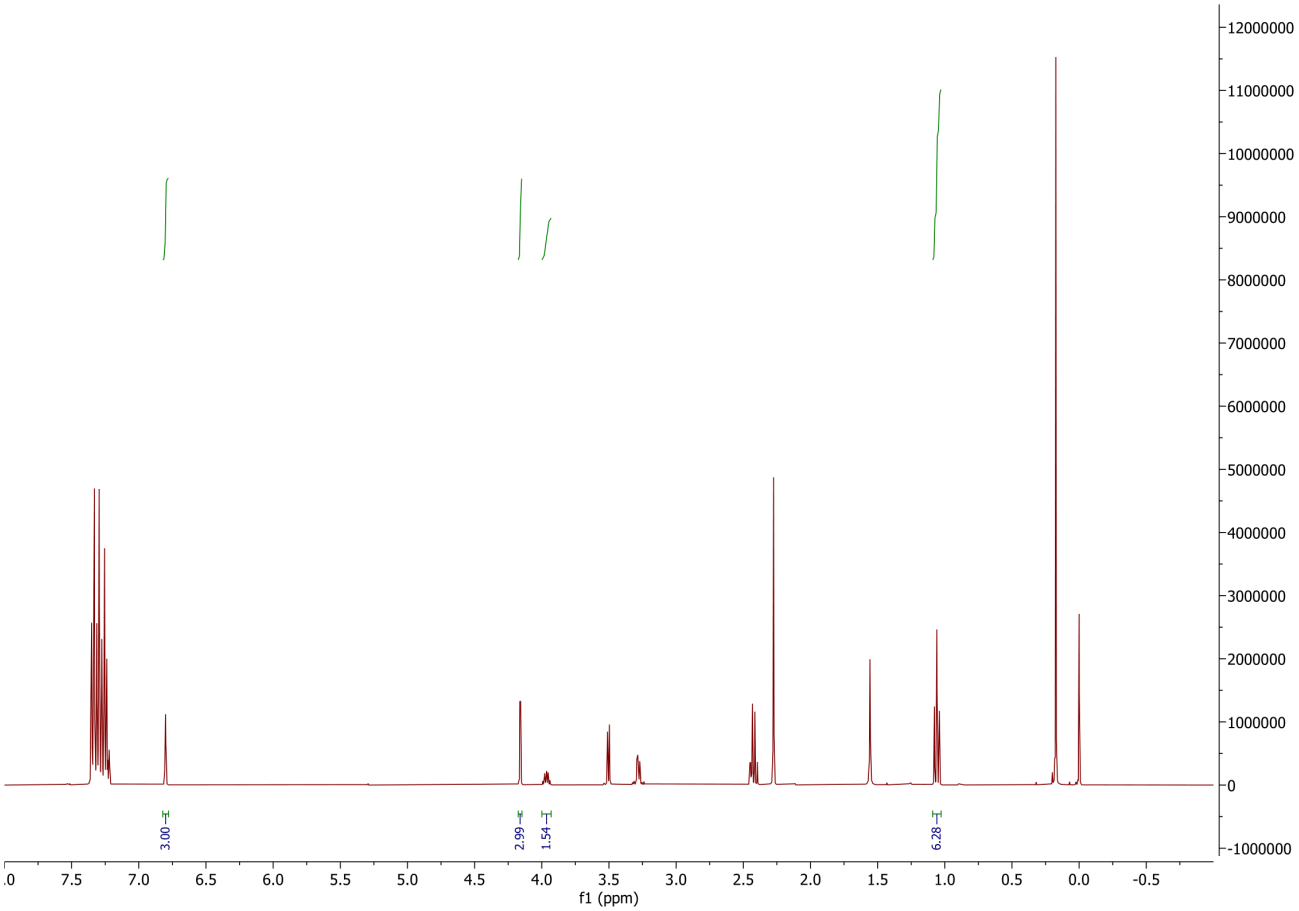
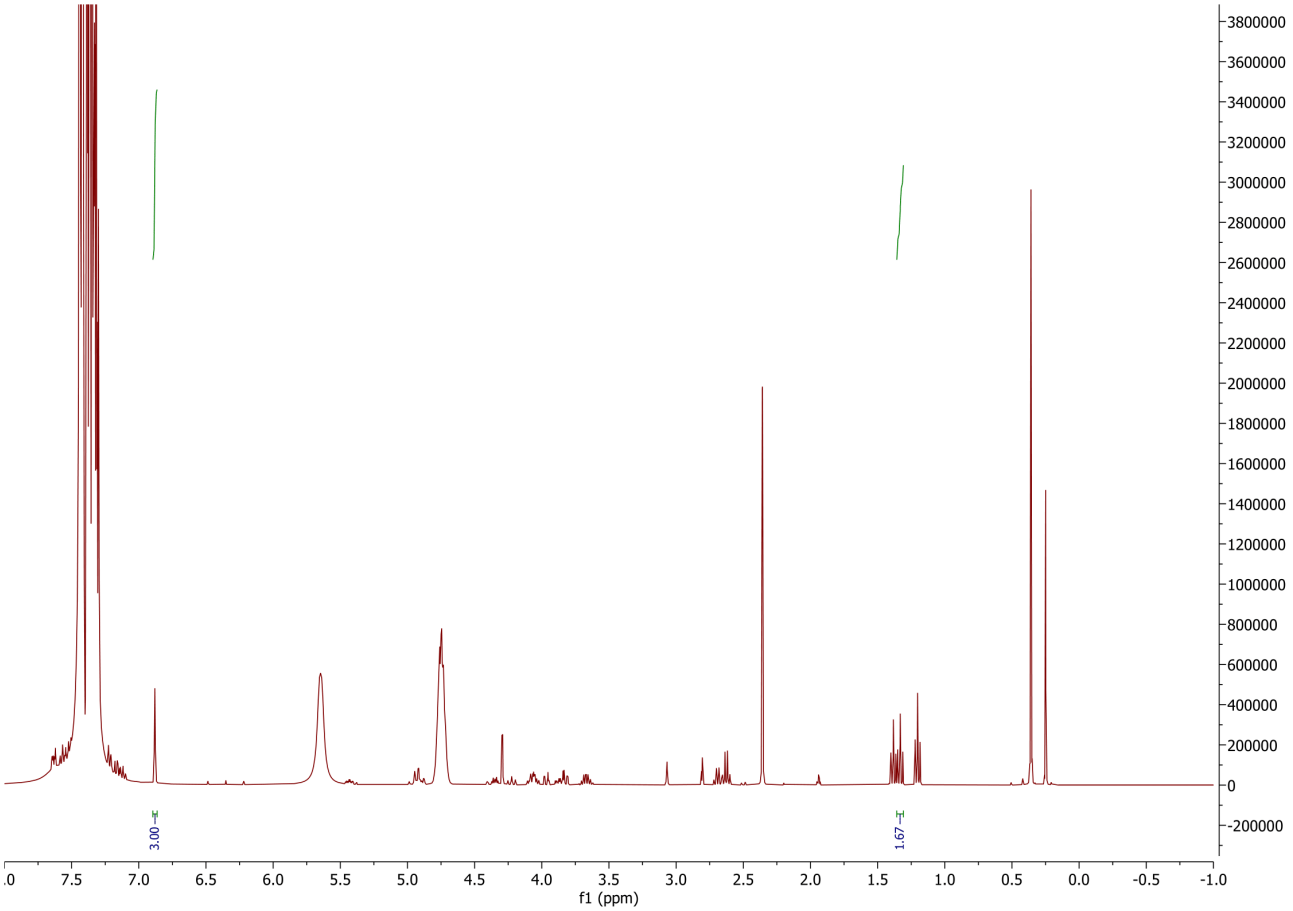


Figure S39. ^{1}H NMR (400 MHz, ACN-d_3, 23 °C) spectrum of stock solution of 3-pentanone, ***rac*-4-OTMS**, and mesitylene in chlorobenzene (900 mmolar w.r.t. 3-pentanone) used for **Table 1 entry 13**.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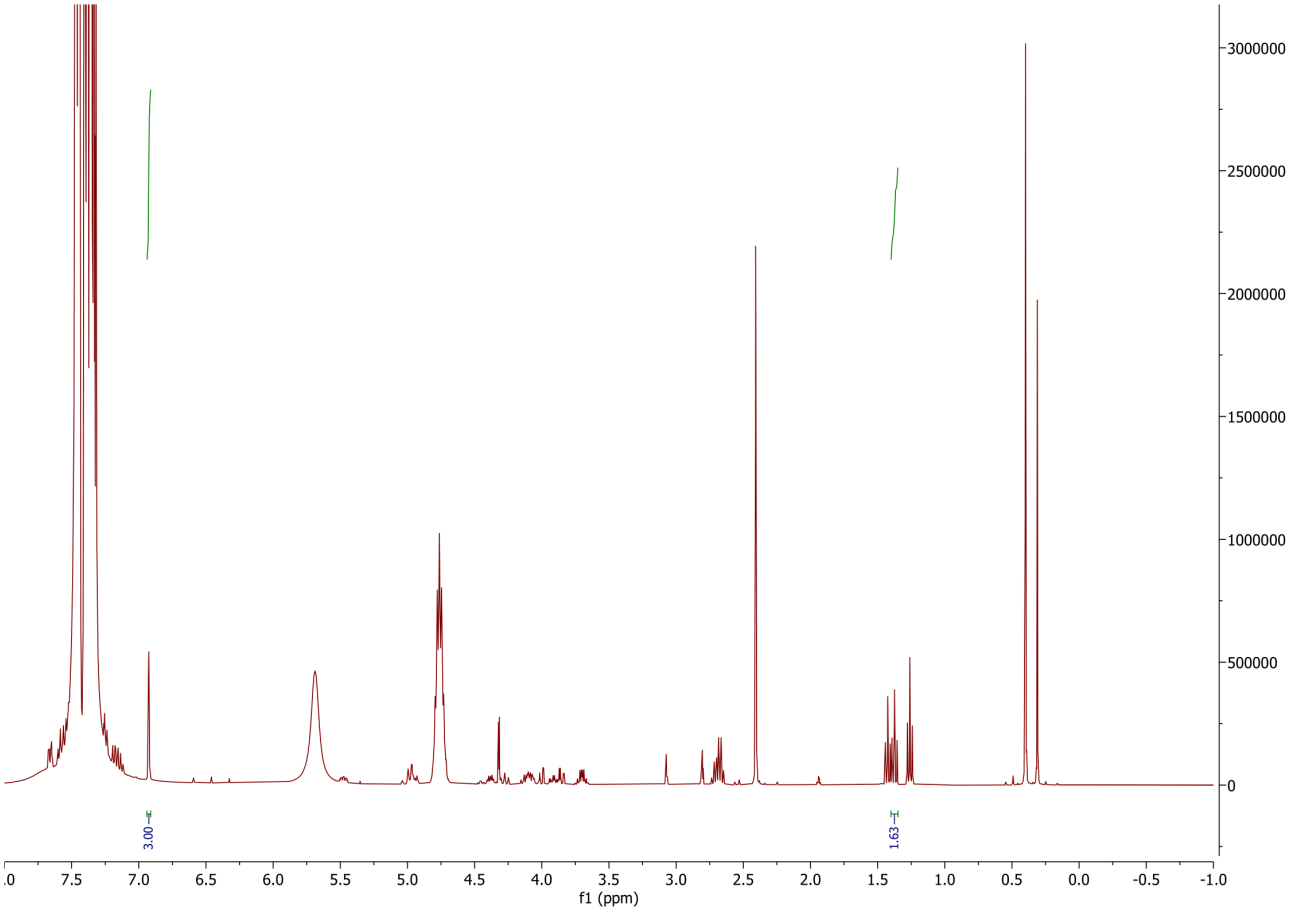
-0.5
-1.0
f1 (ppm)

Replicate 1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4.0
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1.5
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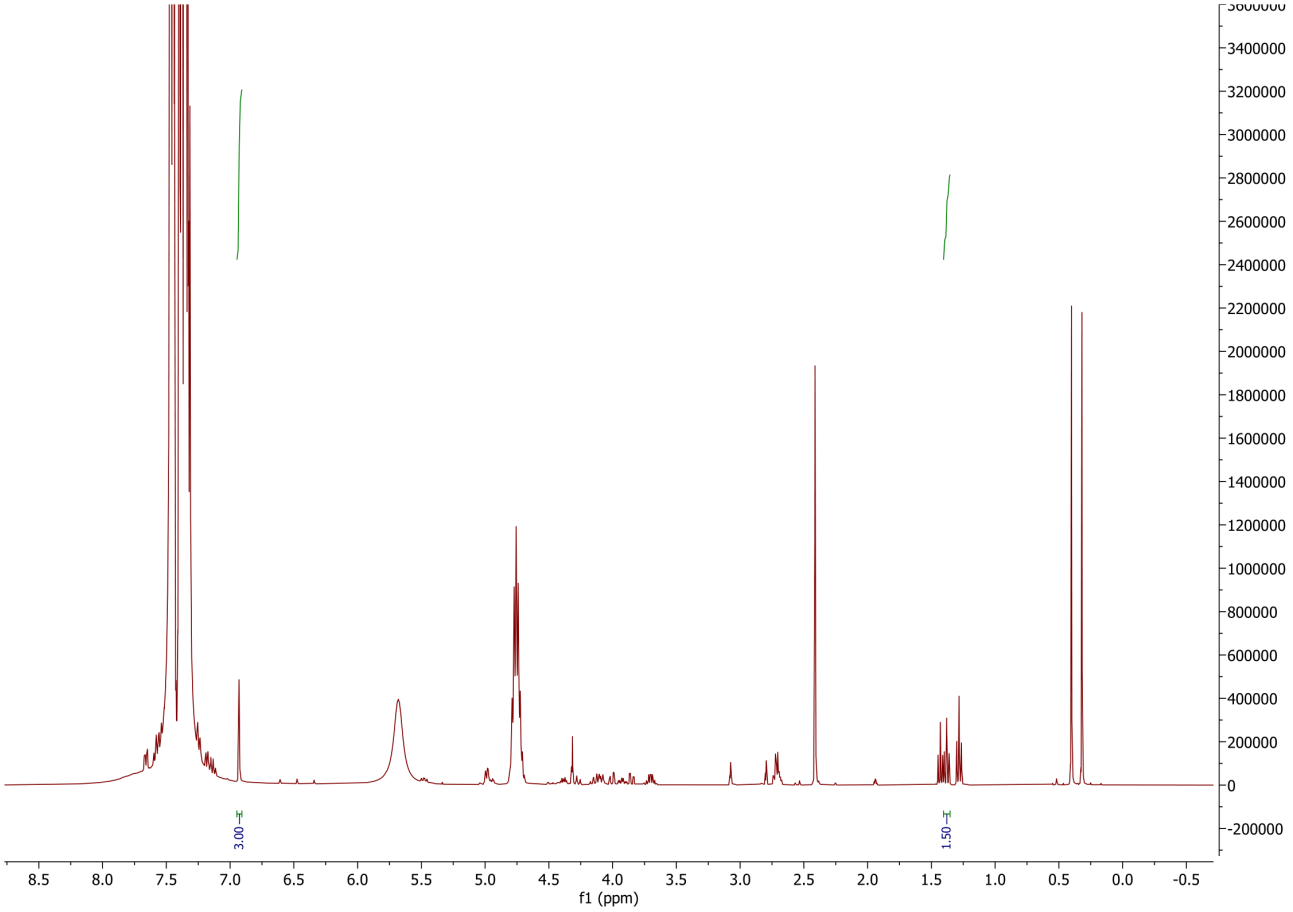
-0.5
-1.0
f1 (ppm)

Replicate 2



*Replicate 3***Figure S40.** ^{1}H NMR (400 MHz, ACN-d_3, 23 °C) spectra for triplicate results described in **Table 1 entry 13**. Yield is calculated from integration of methyl resonance of product iminium ether at ~1.3 ppm. Yield from each replicate (tabulated in **Table S2**) is averaged. The average is tabulated in **Table 1**.

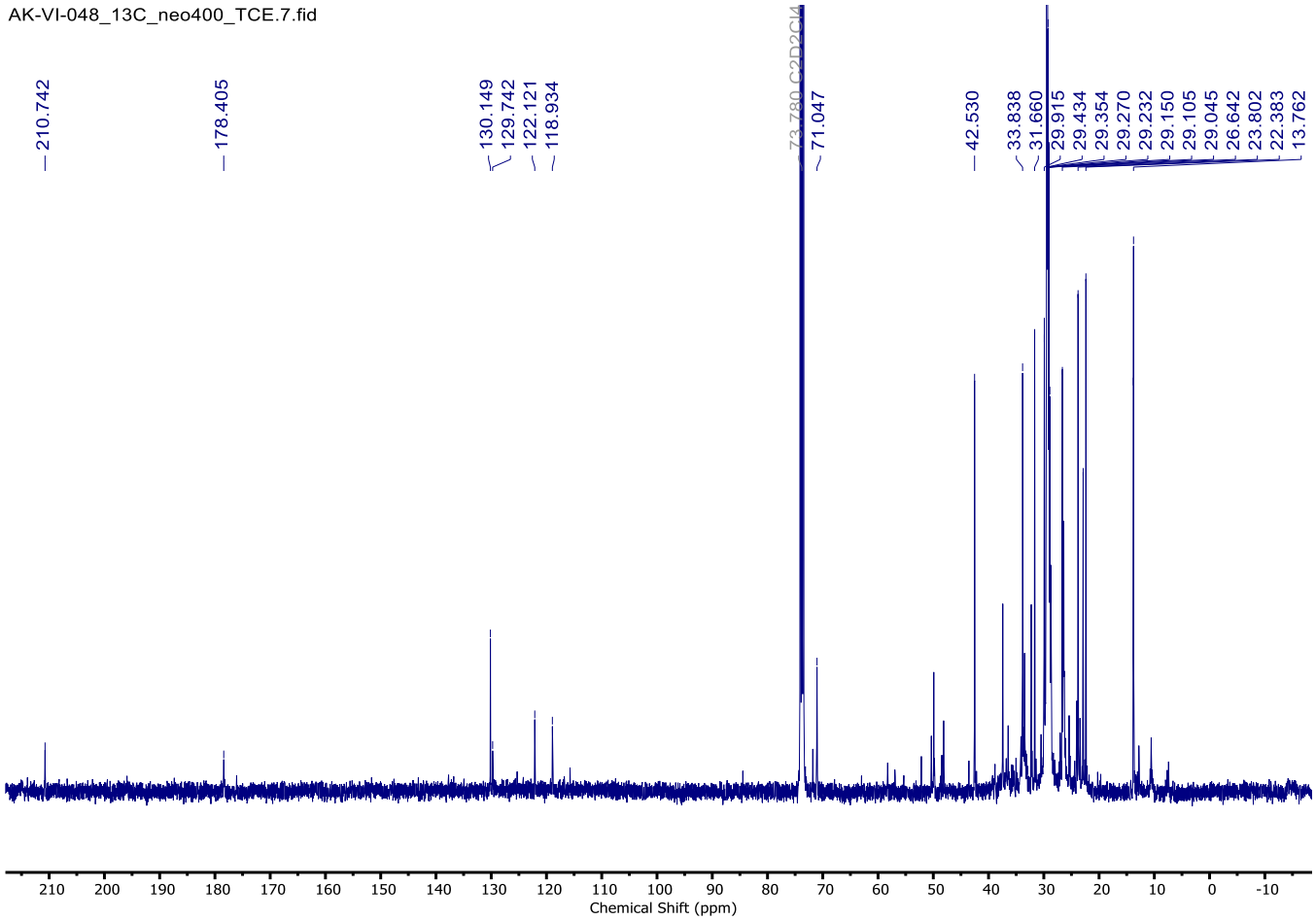


Figure S41. ^{13}C NMR (101 MHz, 1,1,2,2-tetrachloroethane-d_2, ~90 °C) of **P1-2**

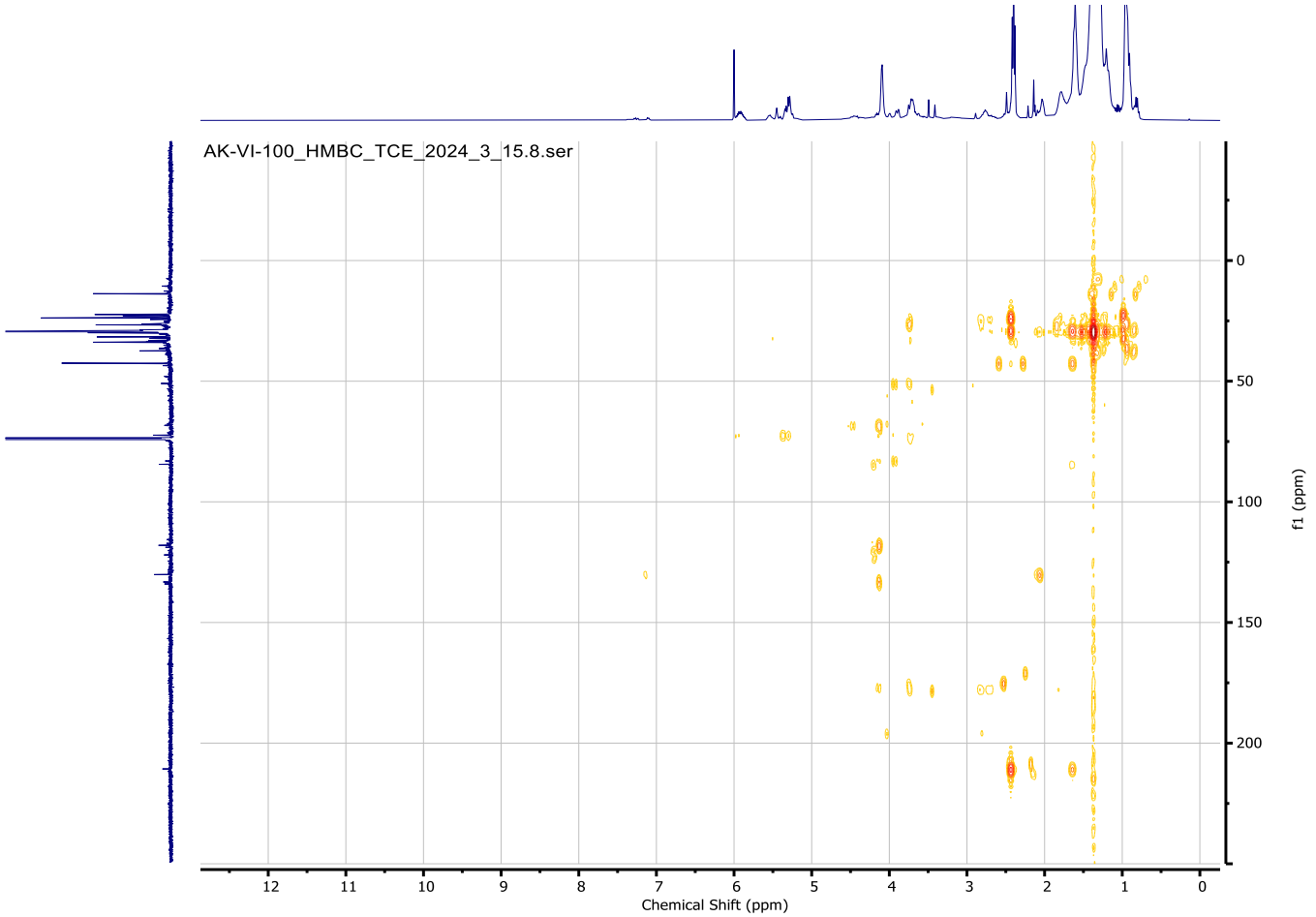


Figure S42. $^{1}H–^{13}C\{^{1}H\}$ HMBC NMR (1,1,2,2-tetrachloroethane-d_2, 94 °C) spectrum of **P1-(*R*)-3**

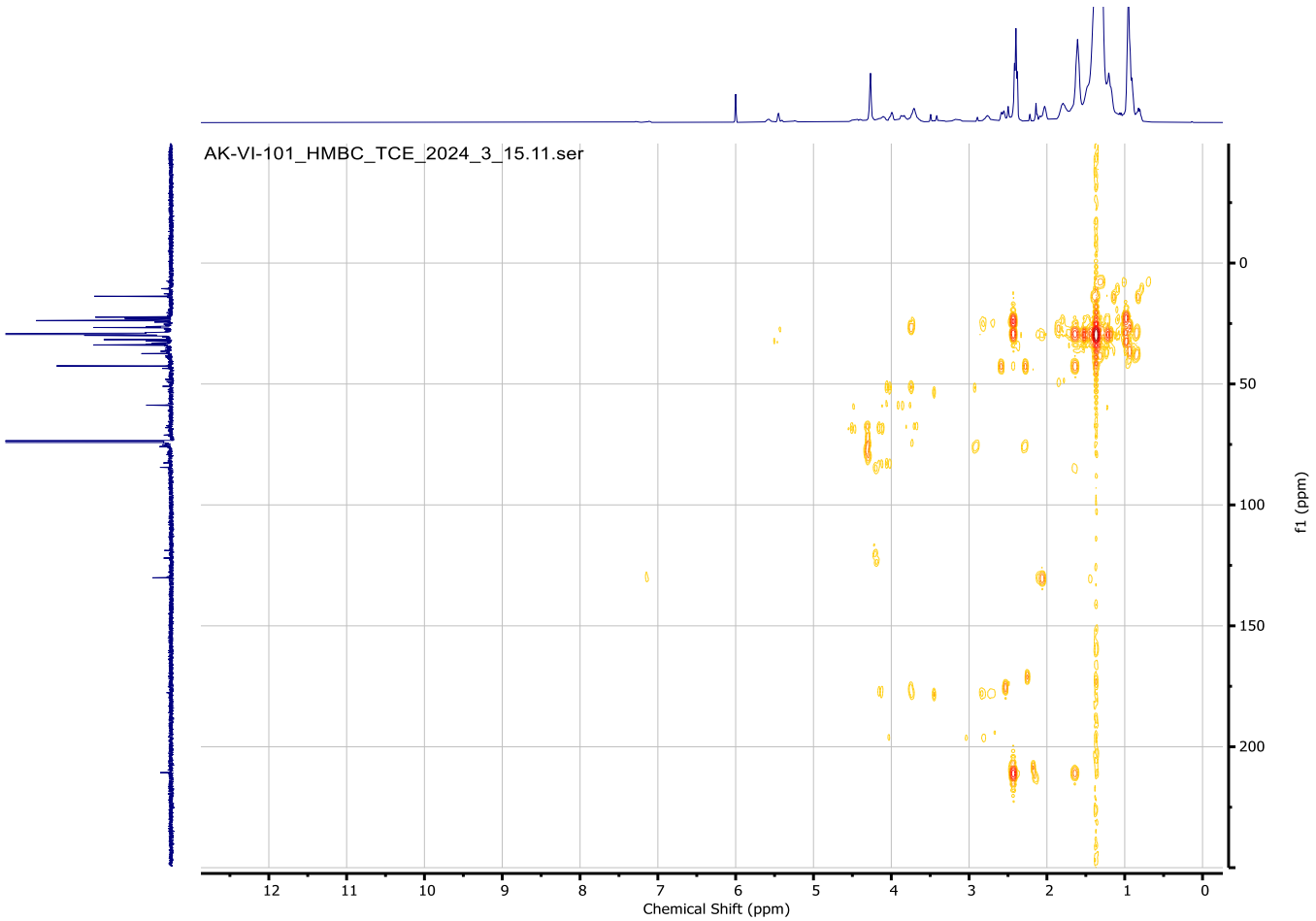


Figure S43. $^{1}H–^{13}C\{^{1}H\}$ HMBC NMR (1,1,2,2-tetrachloroethane-d_2, 94 °C) spectrum of **P1-*rac*-4**

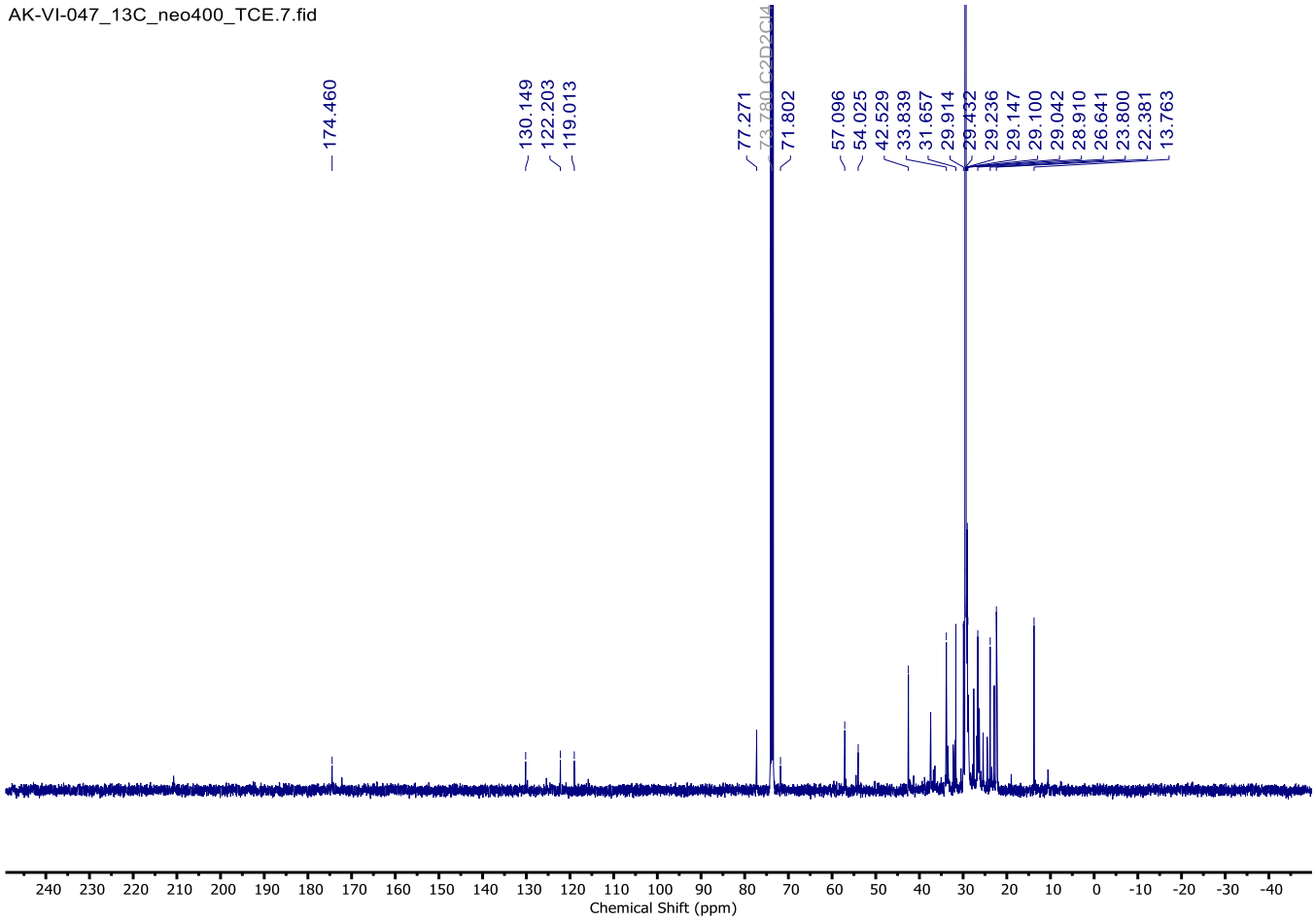


Figure S44. ^{13}C NMR (101 MHz, 1,1,2,2-tetrachloroethane-d_2, ~90 °C) of **P1-5**

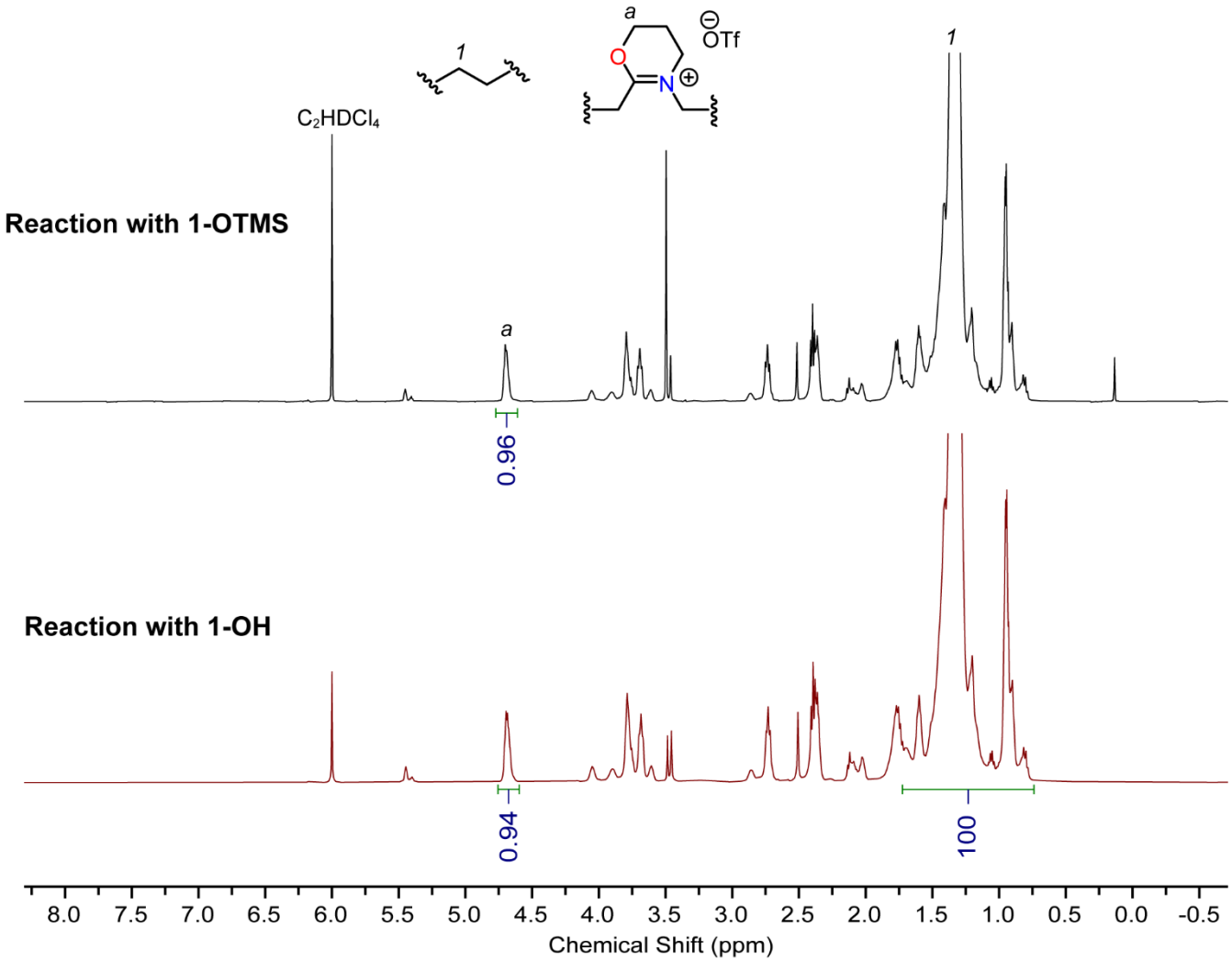


Figure S45. ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 90-94°C) of **P1-1** formed from reaction with **1-OH** and **1-OTMS**. The integral of the resonance from –CH_2–CH_2– repeat units (~0.7–1.7 ppm) was set to 100 for all spectra.

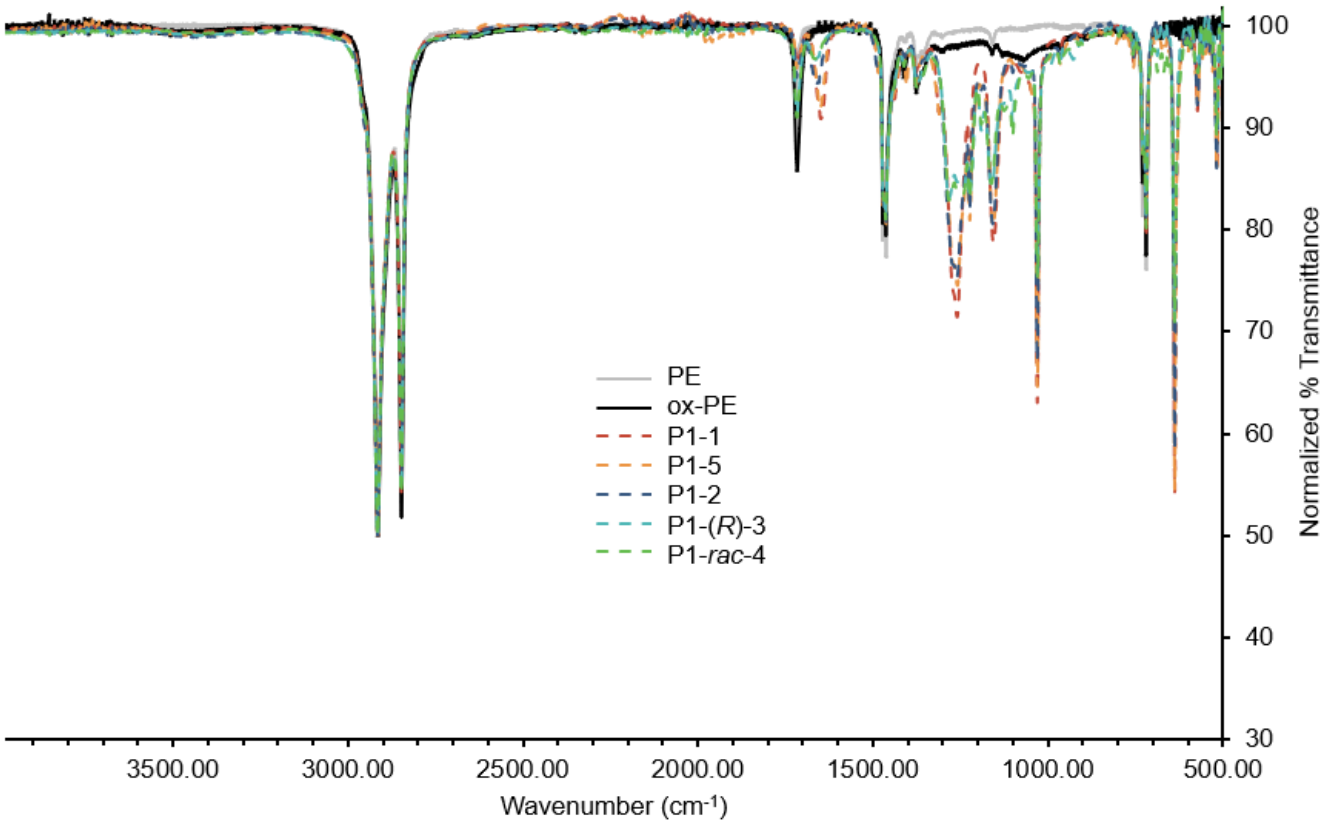


Figure S46. Full FTIR spectra for **PE**, **ox-PE**, and the **P1** series sourced from PE with M_n = 1.7 kg/mol.

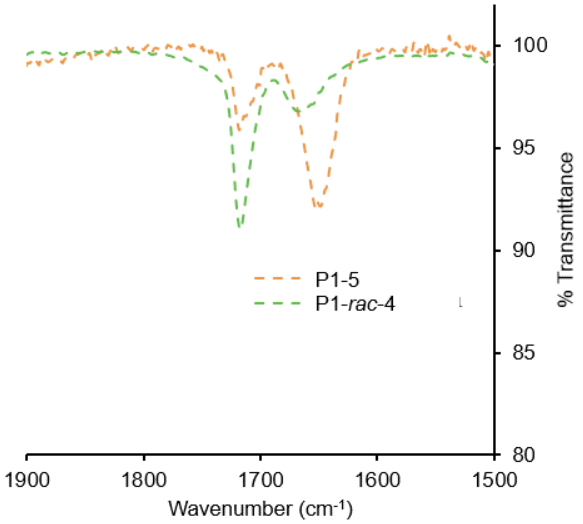


Figure S47. Zoomed FTIR spectra of **P1-5** and **P1-*rac*-4.**

Table S3. Isolated polymer masses (starting polymer mass in parentheses), temperature at 5% mass loss (determined by TGA), melting temperatures, and enthalpy of melting (determined by DSC) for all polymers sourced from PE with M_n = 1.7 kg/mol.

Sample	Isolated Polymer Mass (Starting Polymer Mass in Parentheses)	Temperature at 5% Mass Loss (T_d) (°C)	Melting Temperature (T_m) (°C)	Enthalpy of Melting (J/g)
PE	---	334.5	106	153
ox-PE	4.443 g (5 g)	395.6	103	140
P1-1	166 mg (200 mg)	318.5	93	102
P1-5	174 mg (200 mg)	309.3	90	101
P1-2	175 mg (200 mg)	327.6	93	105
P1-(*R*)-3	183 mg (200 mg)	264.8	92	106
P1-*rac*-4	179 mg (200 mg)	287.6	93	108
P2-1	66 mg (80 mg)	327.3	92	132
P2-5	68 mg (80 mg)	352.9	86	118
P2-2	60 mg (80 mg)	371.5	100	132
P2-*rac*-3	63 (60 mg)	331.4	91	120
P2-(*R*)-3	68 (80 mg)	338.9	90	124
P2-*rac*-4	66 (80 mg)	336.7	91	130

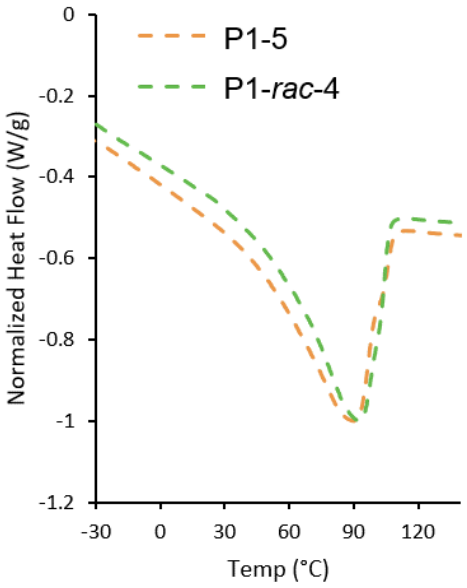


Figure S48. DSC traces for **P1-5** and **P1-*rac*-4.**

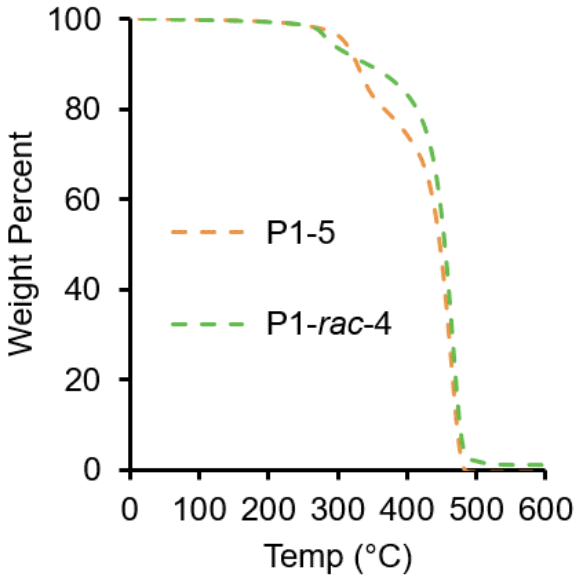


Figure S49. TGA traces for **P1-5** and **P1-*rac*-4.**

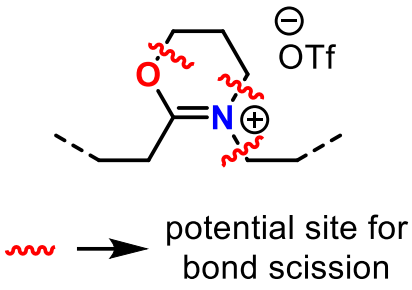


Figure S50. Hypothesized sites for thermal chain-cleavage in iminium ether containing polymers during TGA analysis. Structure shown is from **P1-1**

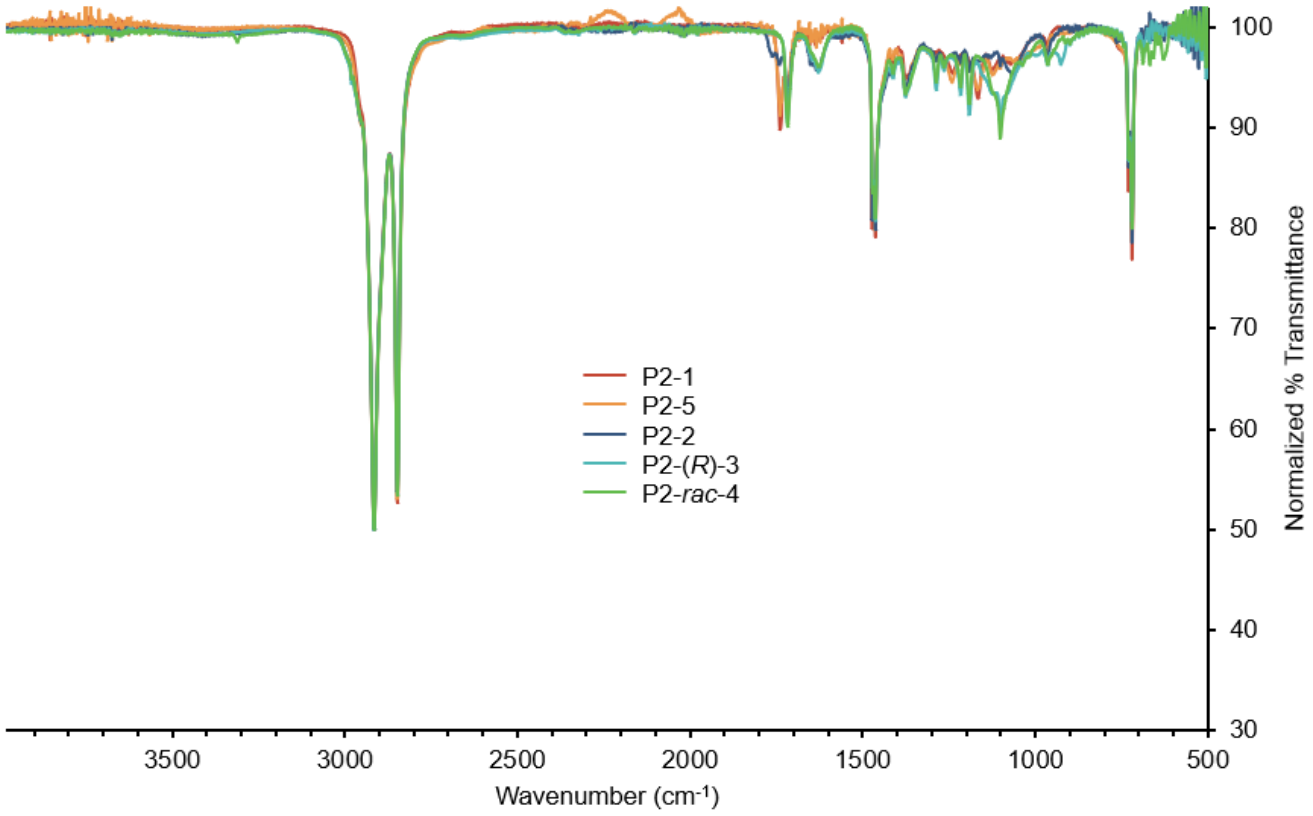


Figure S51. Full FTIR spectra for the **P2** series sourced from PE with M_n = 1.7 kg/mol.

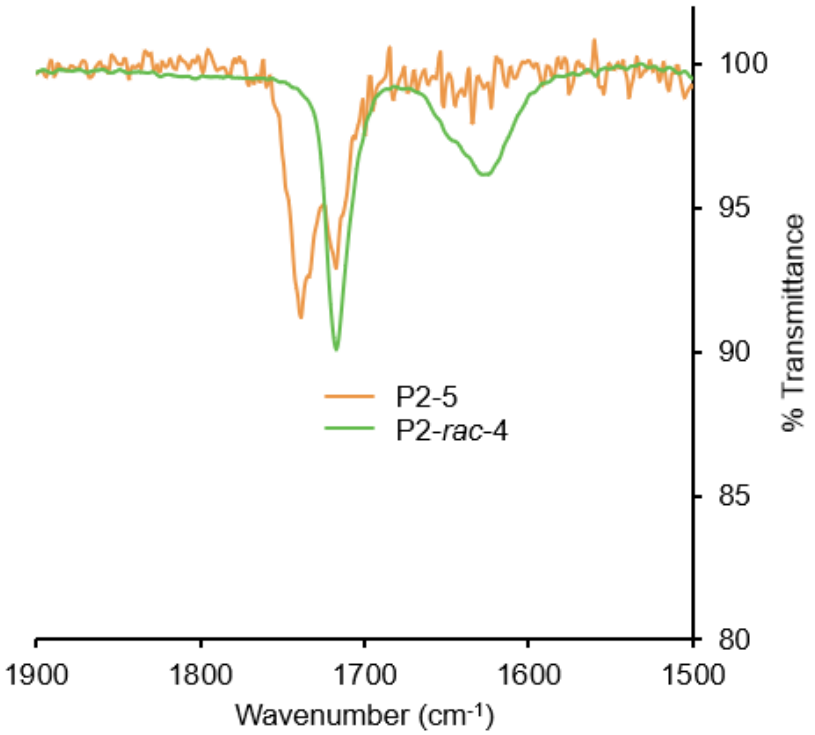


Figure S52. Zoomed FTIR spectra of **P2-5** and **P2-*rac*-4.**

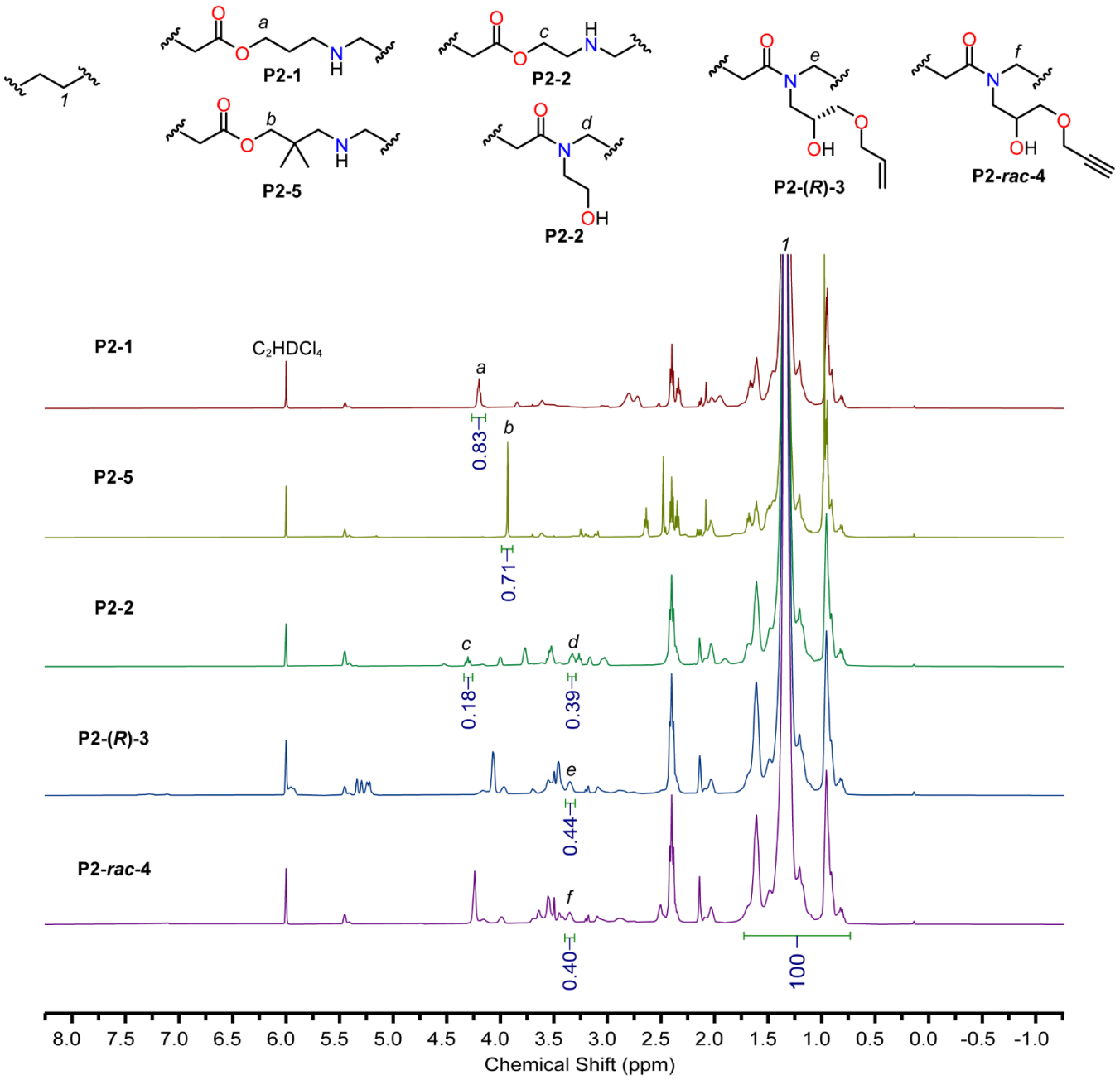


Figure S53. ^{1}H NMR (400 or 500 MHz, 1,1,2,2-tetrachloroethane-d_2, 90-94 °C) of **ox-PE** and **P2** series. The integral of the resonance from –CH_2–CH_2– repeat units (~0.7–1.7 ppm) was set to 100 for all spectra.

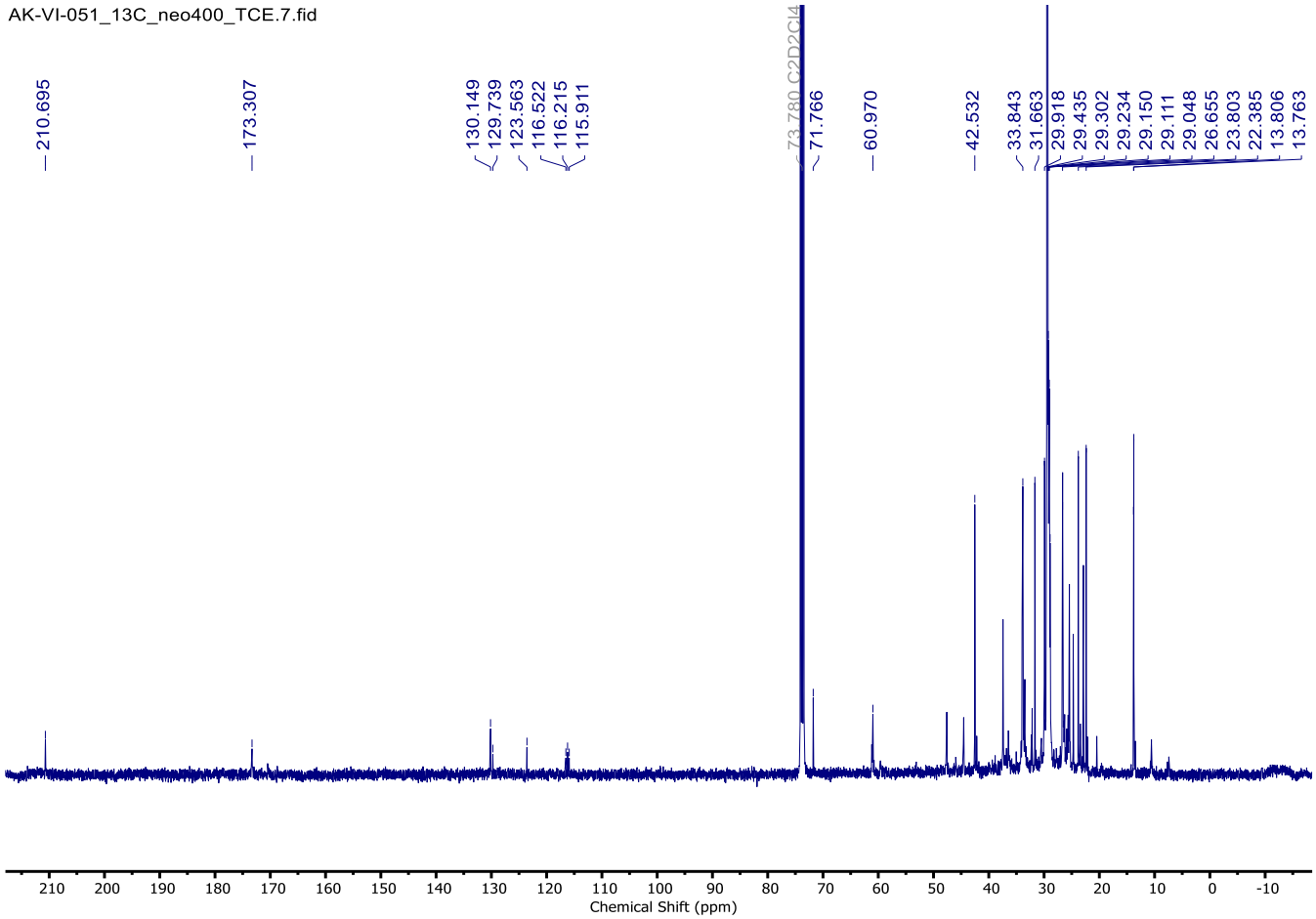


Figure S54. ^{13}C NMR (101 MHz, 1,1,2,2-tetrachloroethane-d_2, ~90 °C) of **P2-1**

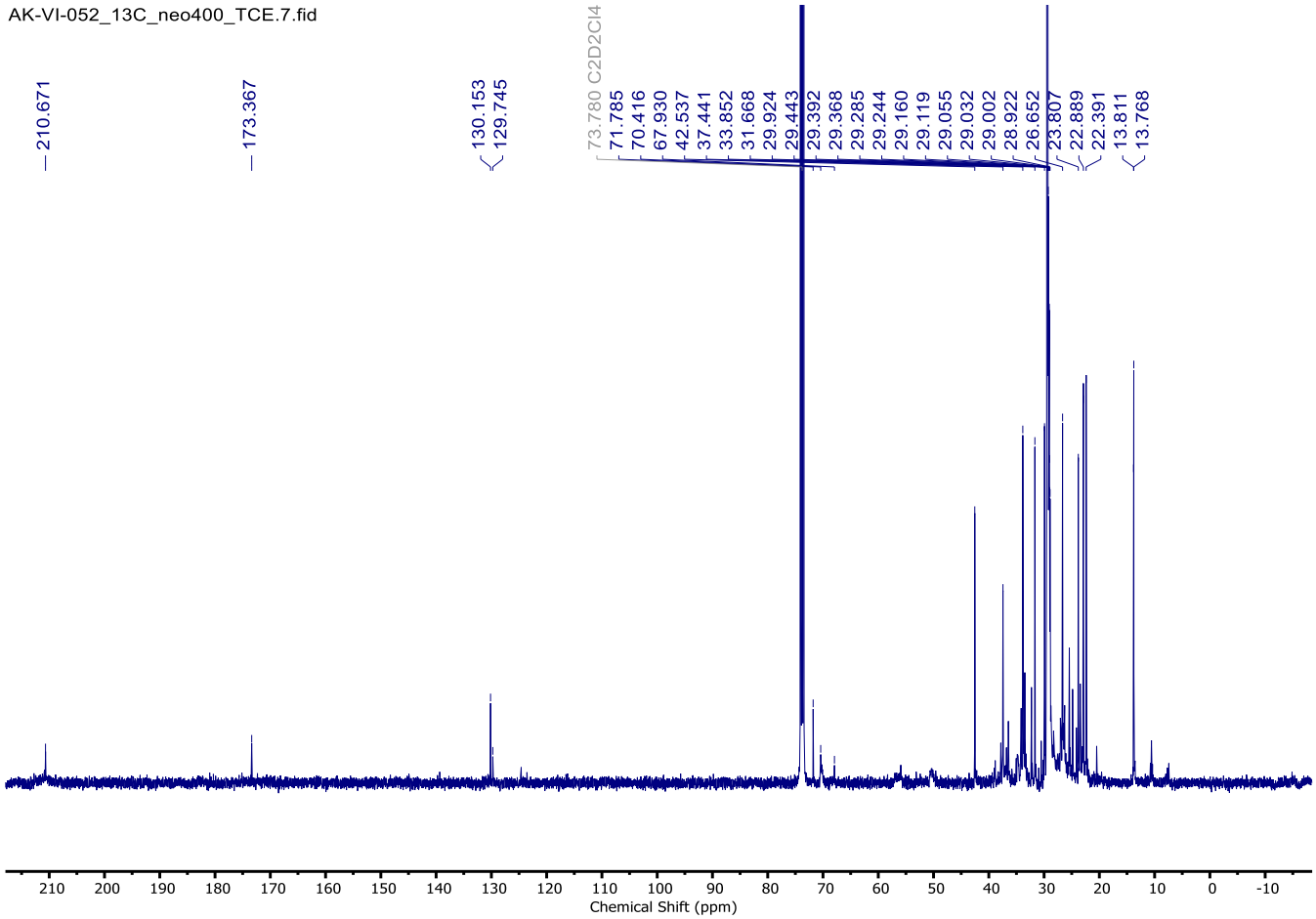


Figure S55. ^{13}C NMR (101 MHz, 1,1,2,2-tetrachloroethane-d_2, ~90 °C) of **P2-5**

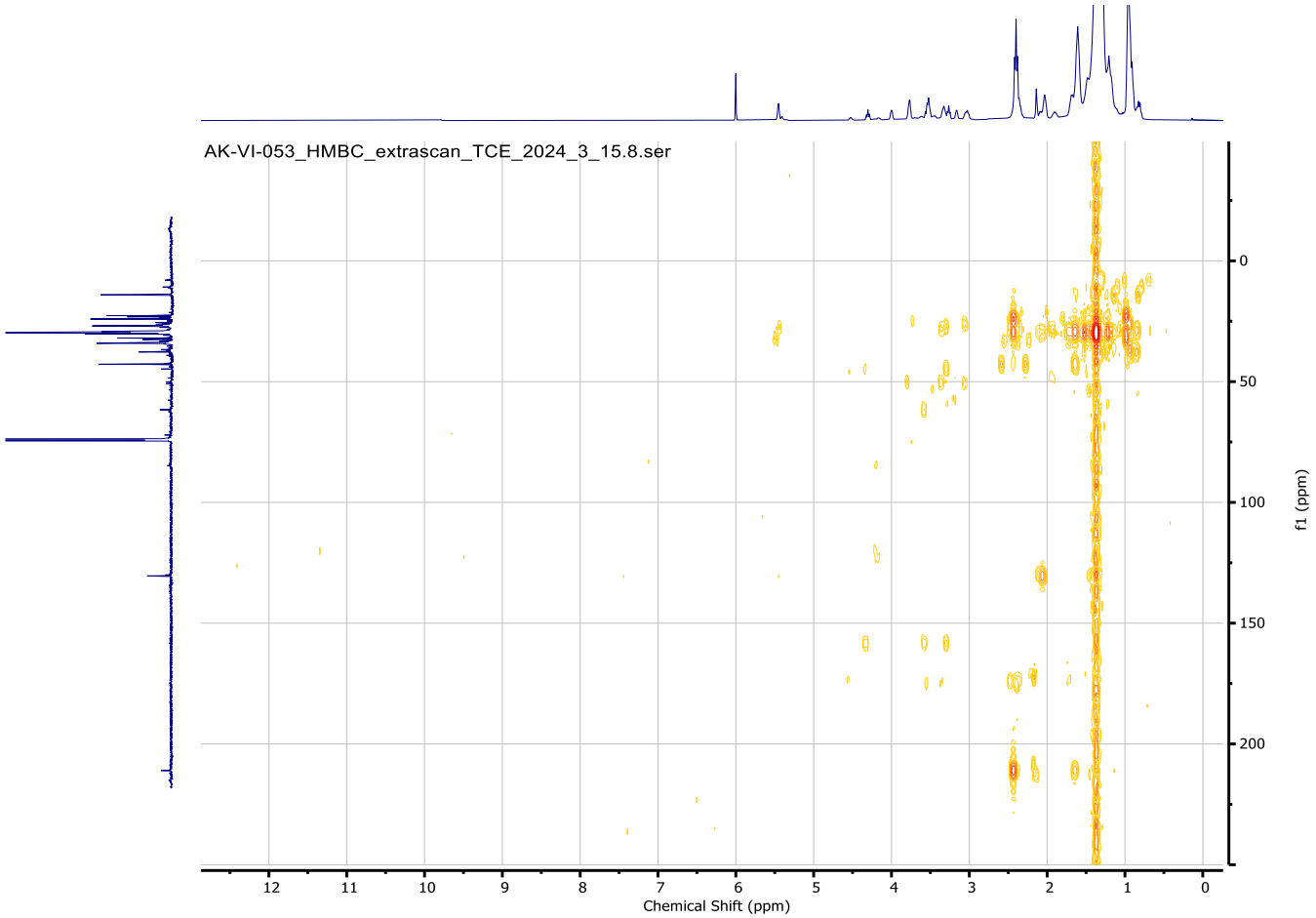


Figure S56. ^{1}H–$^{13}C\{^{1}H\}$ HMBC NMR (1,1,2,2-tetrachloroethane-d_2, 94 °C) spectrum of **P2-2**.

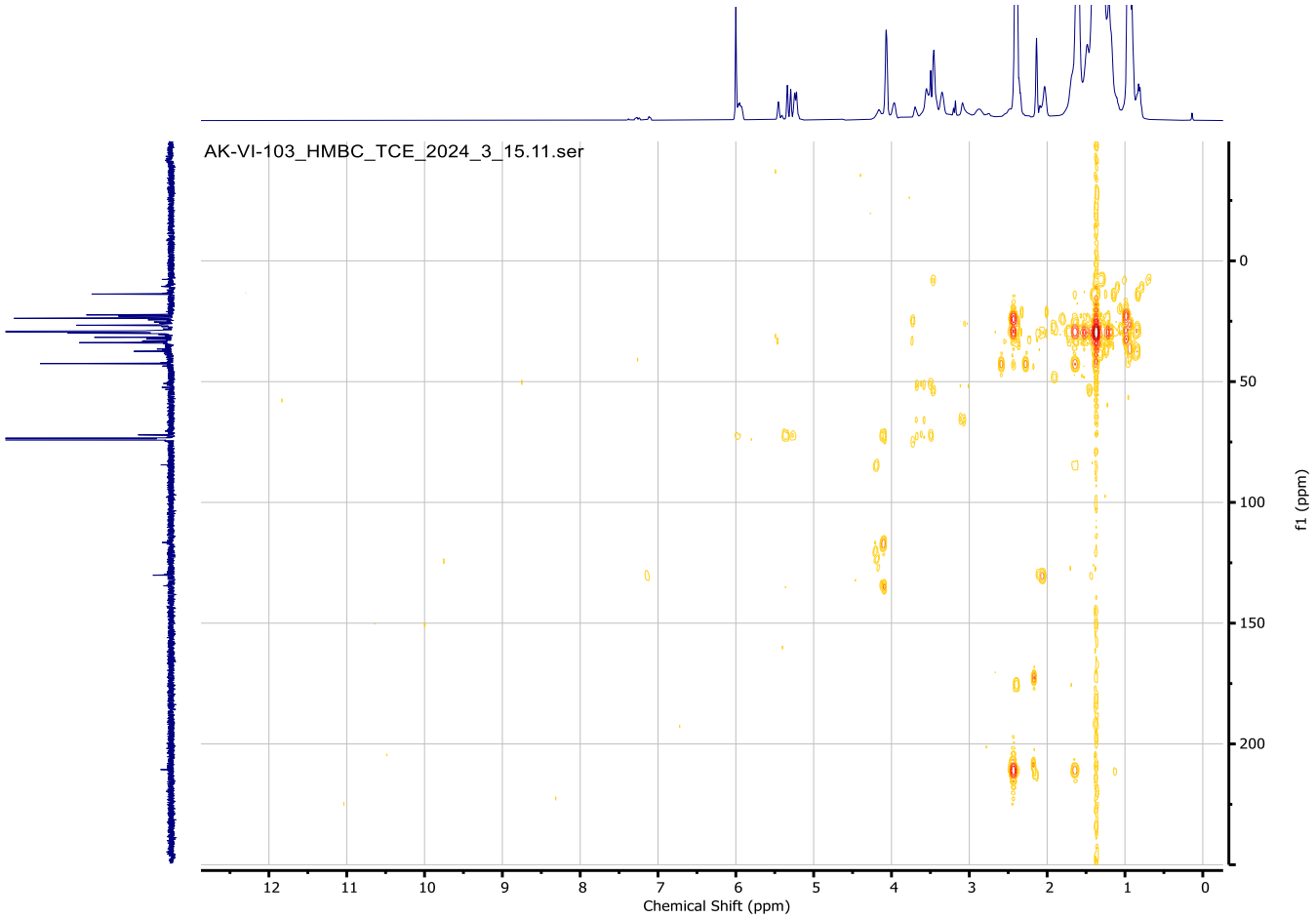


Figure S57. ^{1}H–$^{13}C\{^{1}H\}$ HMBC NMR (1,1,2,2-tetrachloroethane-d_2, 94 °C) spectrum of **P2-(*R*)-3**

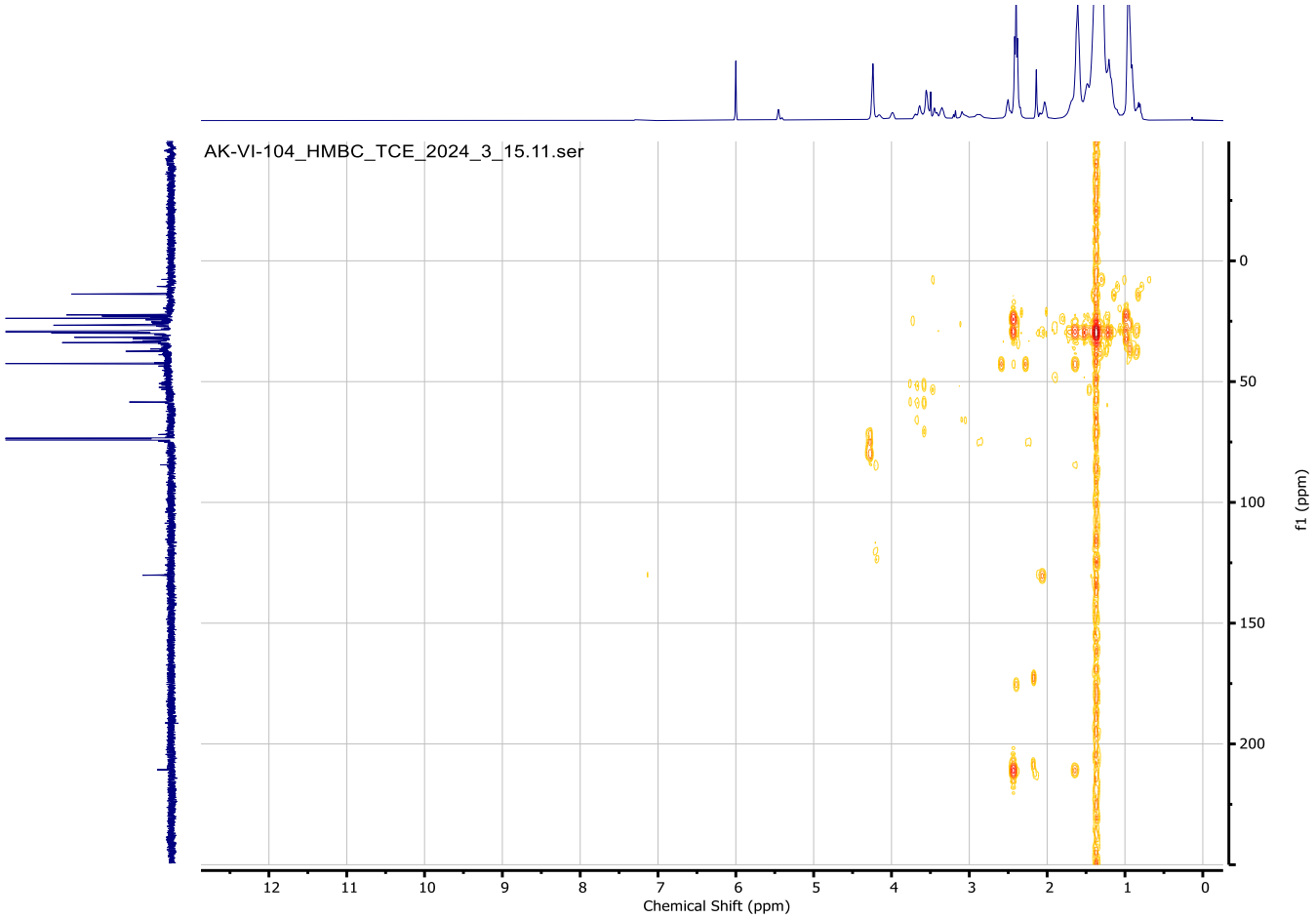


Figure S58. ^{1}H–$^{13}C\{^{1}H\}$ HMBC NMR (1,1,2,2-tetrachloroethane-d_2, 94 °C) spectrum of **P2-(*rac*)-4**

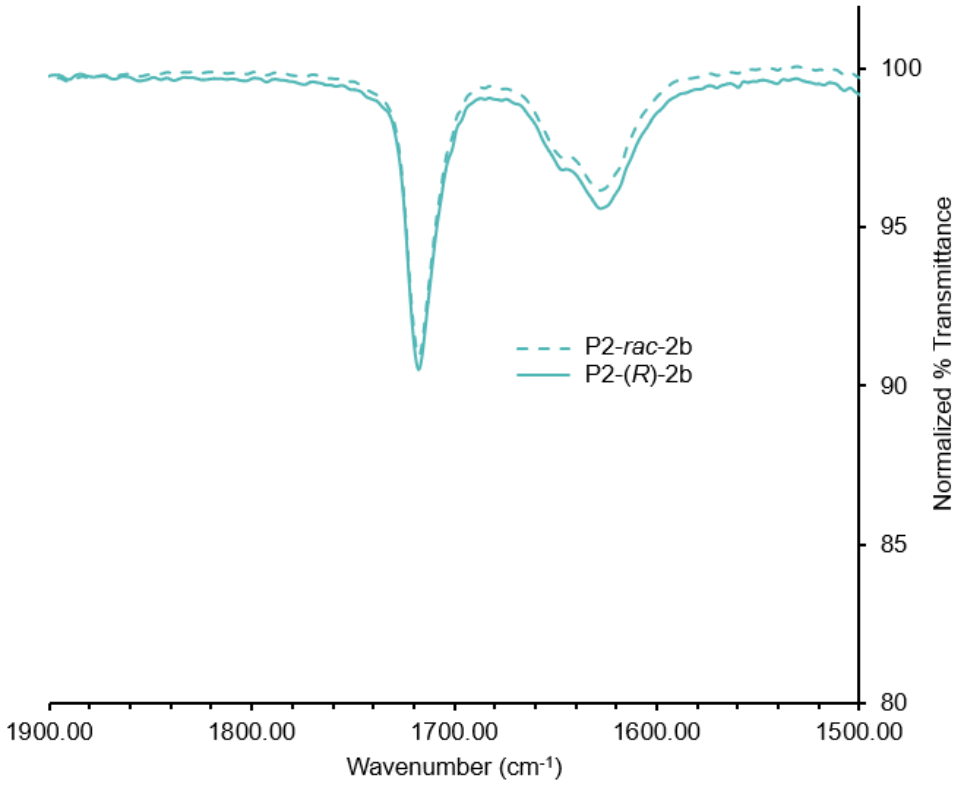


Figure S59. FTIR spectra for **P2-*rac*-3** and **P2-(*R*)-3**.

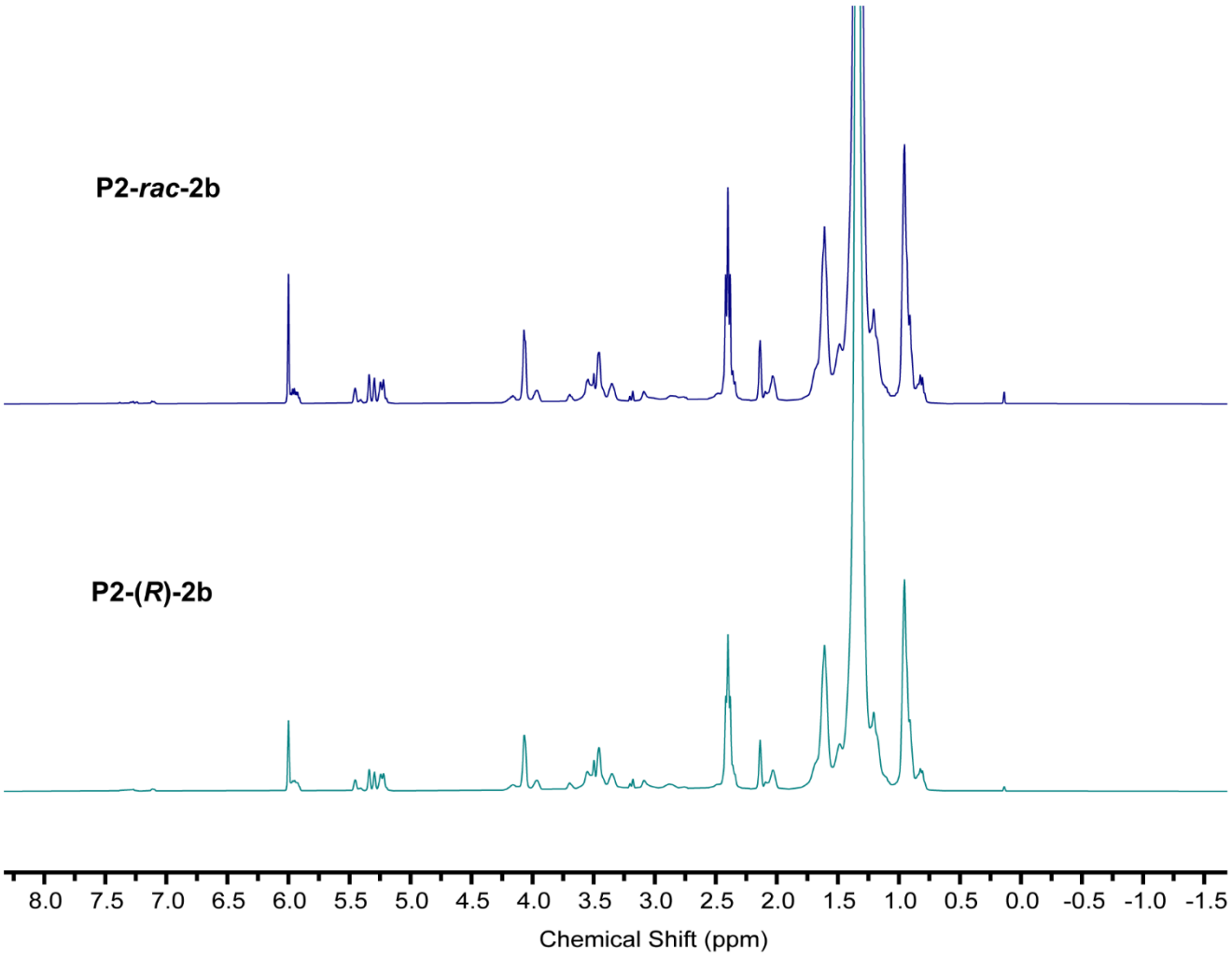


Figure S60. ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 94°C) of **P2-*rac*-3** and **P2-(*R*)-3.**

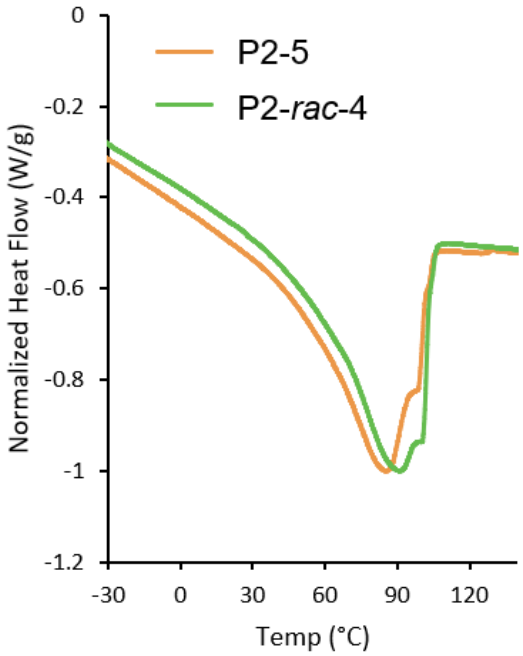


Figure S61. DSC traces for **P2-5** and **P2-*rac*-4.**

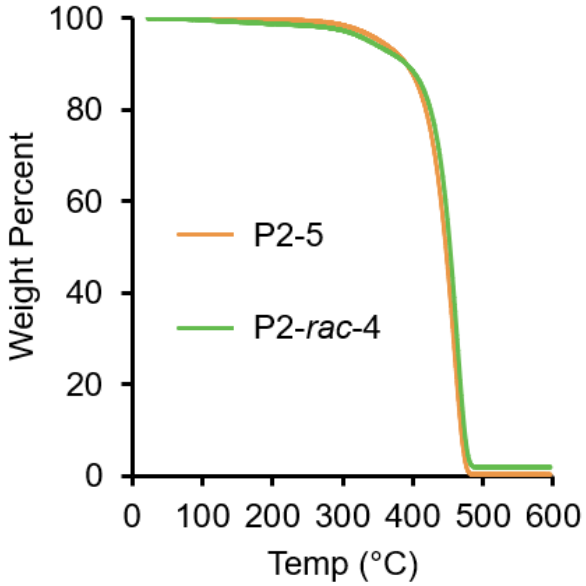


Figure S62. TGA traces for **P2-5** and **P2-*rac*-4.**

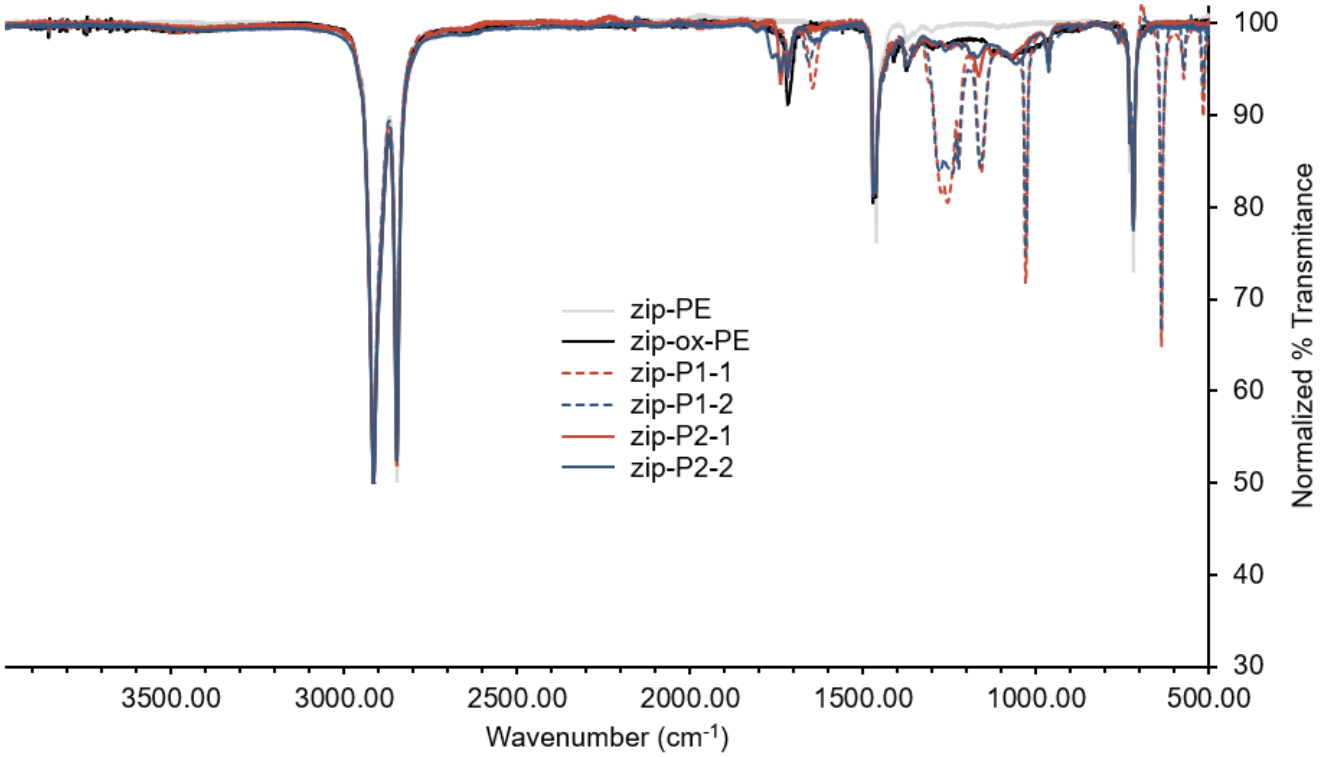


Figure S63. Full FTIR spectra for commercial **zip-PE**, **zip-ox-PE**, and **zip-P1** and **zip-P2** polymers sourced from commercial LDPE.

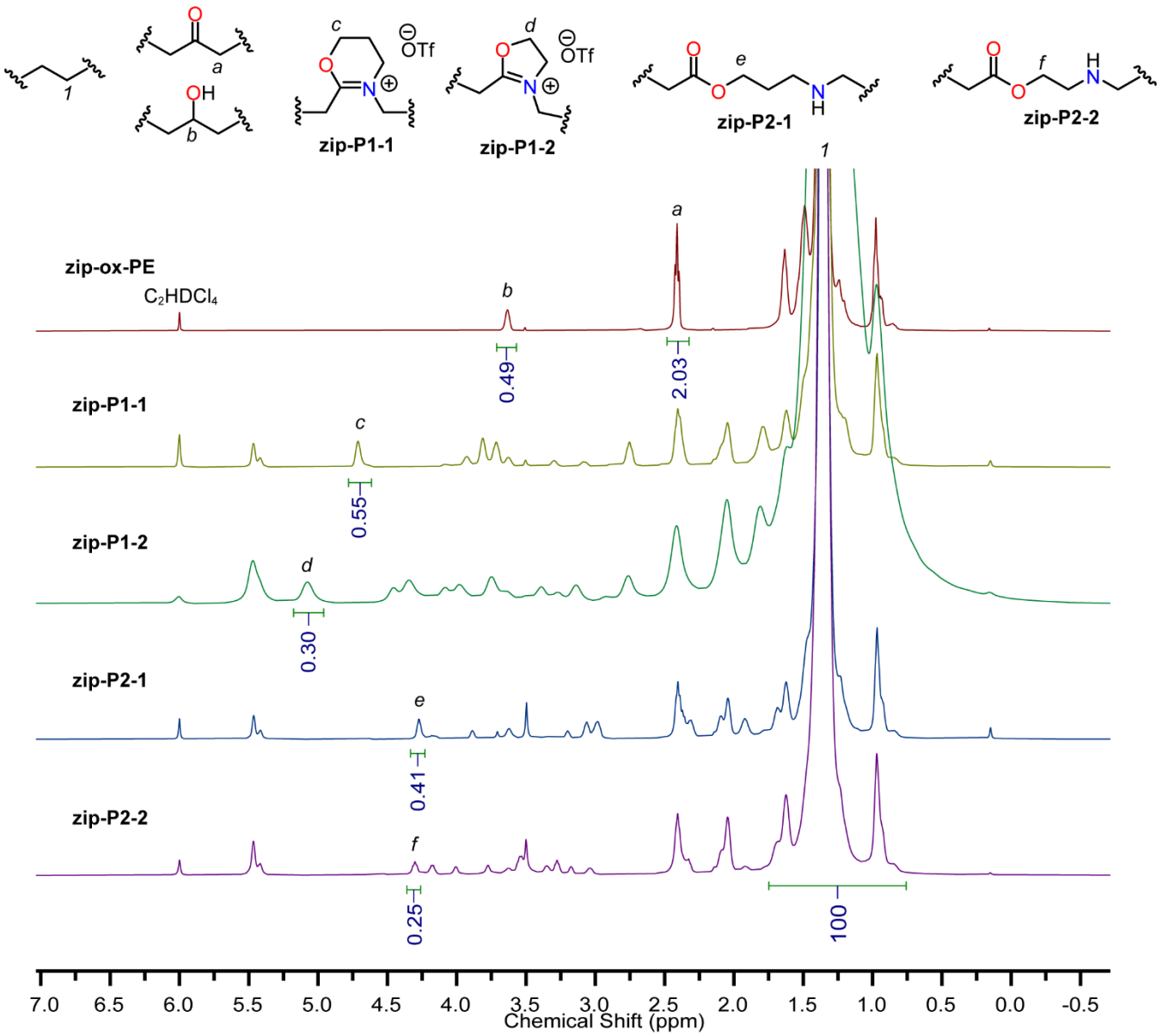


Figure S64. ^{1}H NMR (400 or 500 MHz, 1,1,2,2-tetrachloroethane-d_2, 111-118 °C) of **zip-ox-PE**, **zip-P1-1**, **zip-P1-2**, **zip-P2-1**, and **zip-P2-2** (sourced from LDPE). The integral of the resonance from –CH_2–CH_2– repeat units (~0.7–1.7 ppm) was set to 100 for all spectra.

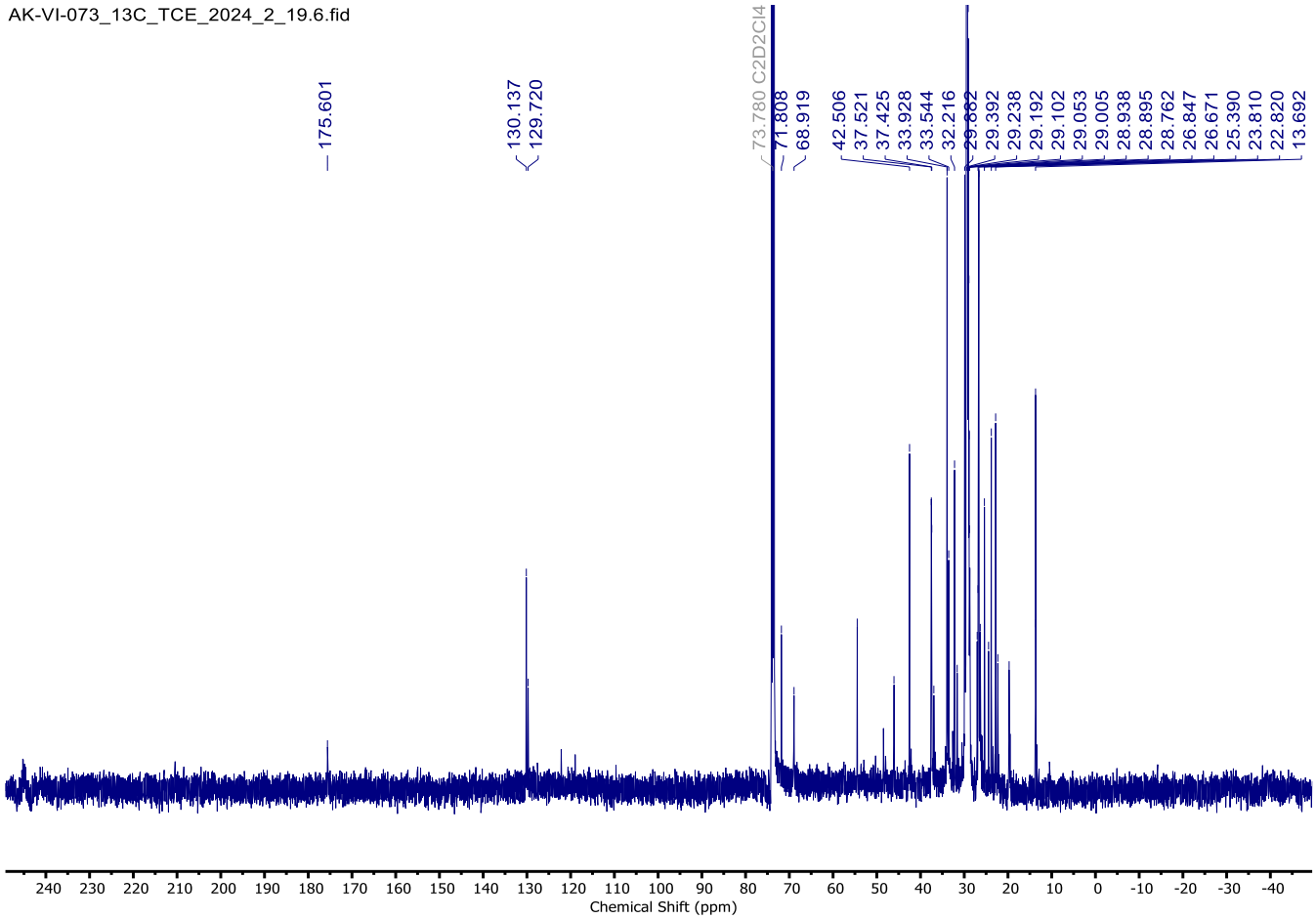


Figure S65. ^{13}C NMR (101 MHz, 1,1,2,2-tetrachloroethane-d_2, 111 °C) of **zip-P1-1** sourced from LDPE.

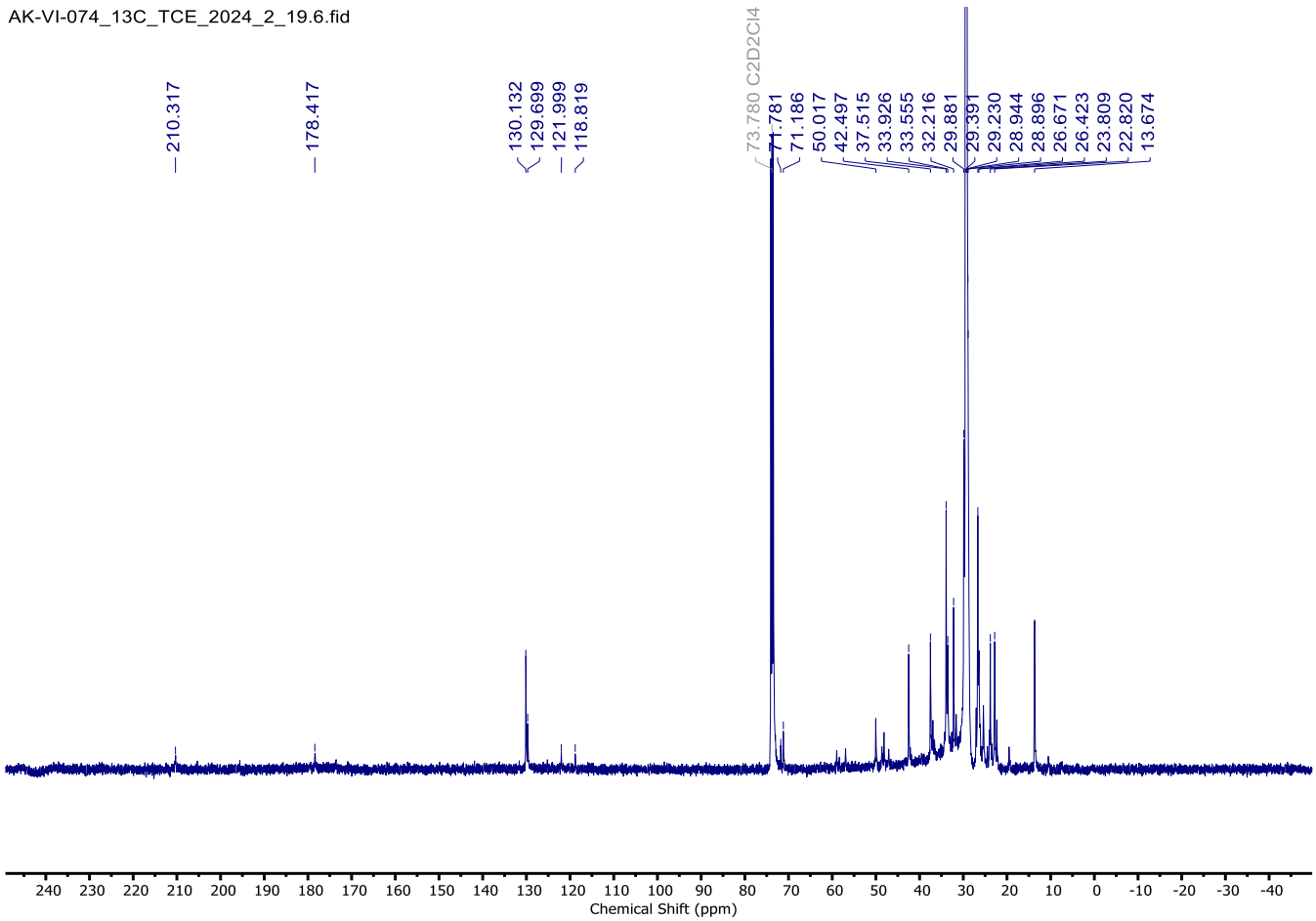


Figure S66. ^{13}C NMR (101 MHz, 1,1,2,2-tetrachloroethane-d_2, 111 °C) of **zip-P1-2** sourced from LDPE.

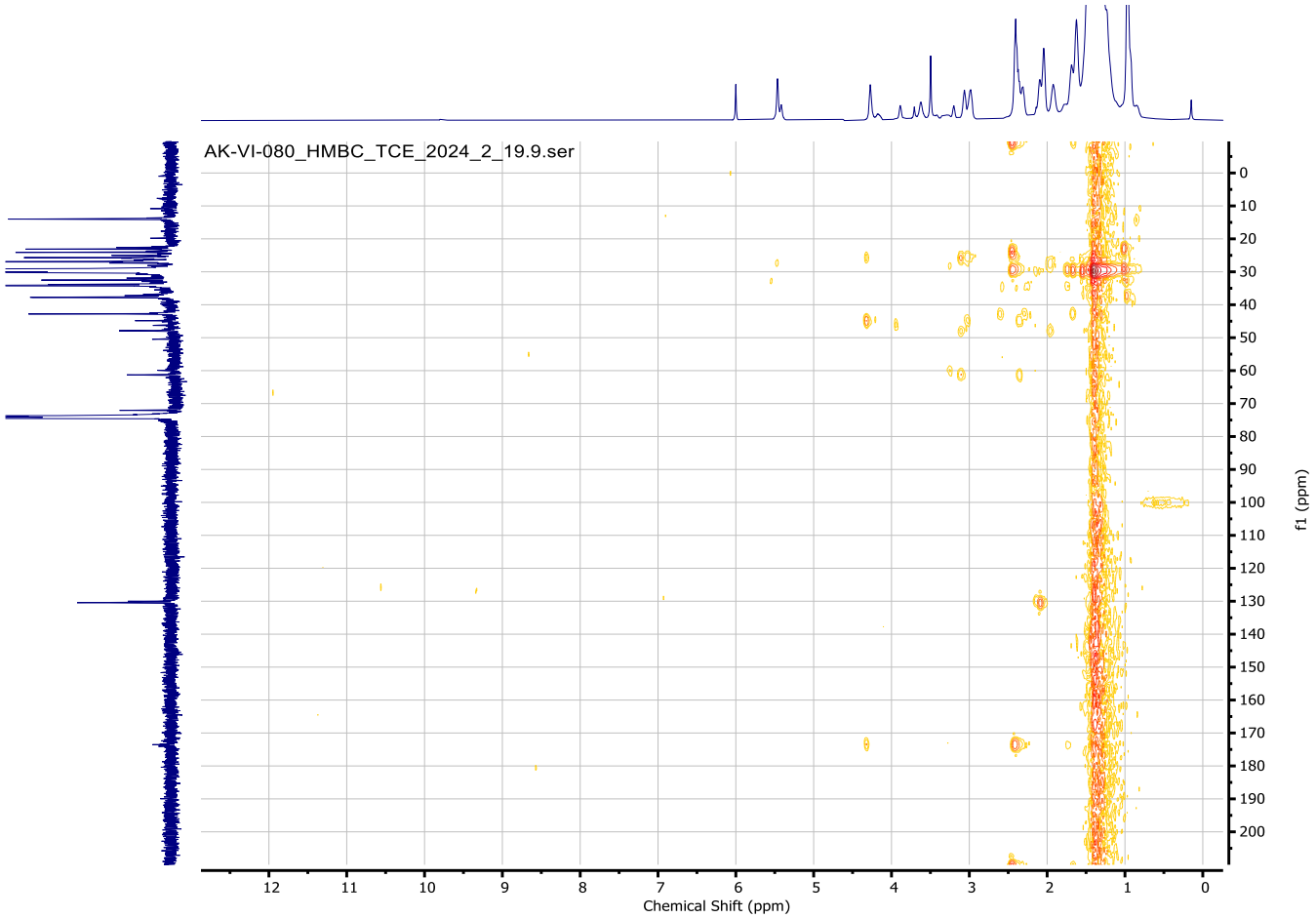


Figure S67. ^{1}H–$^{13}C\{^{1}H\}$ HMBC NMR (1,1,2,2-tetrachloroethane-d_2, 111 °C) spectrum of **zip-P2-1** sourced from LDPE

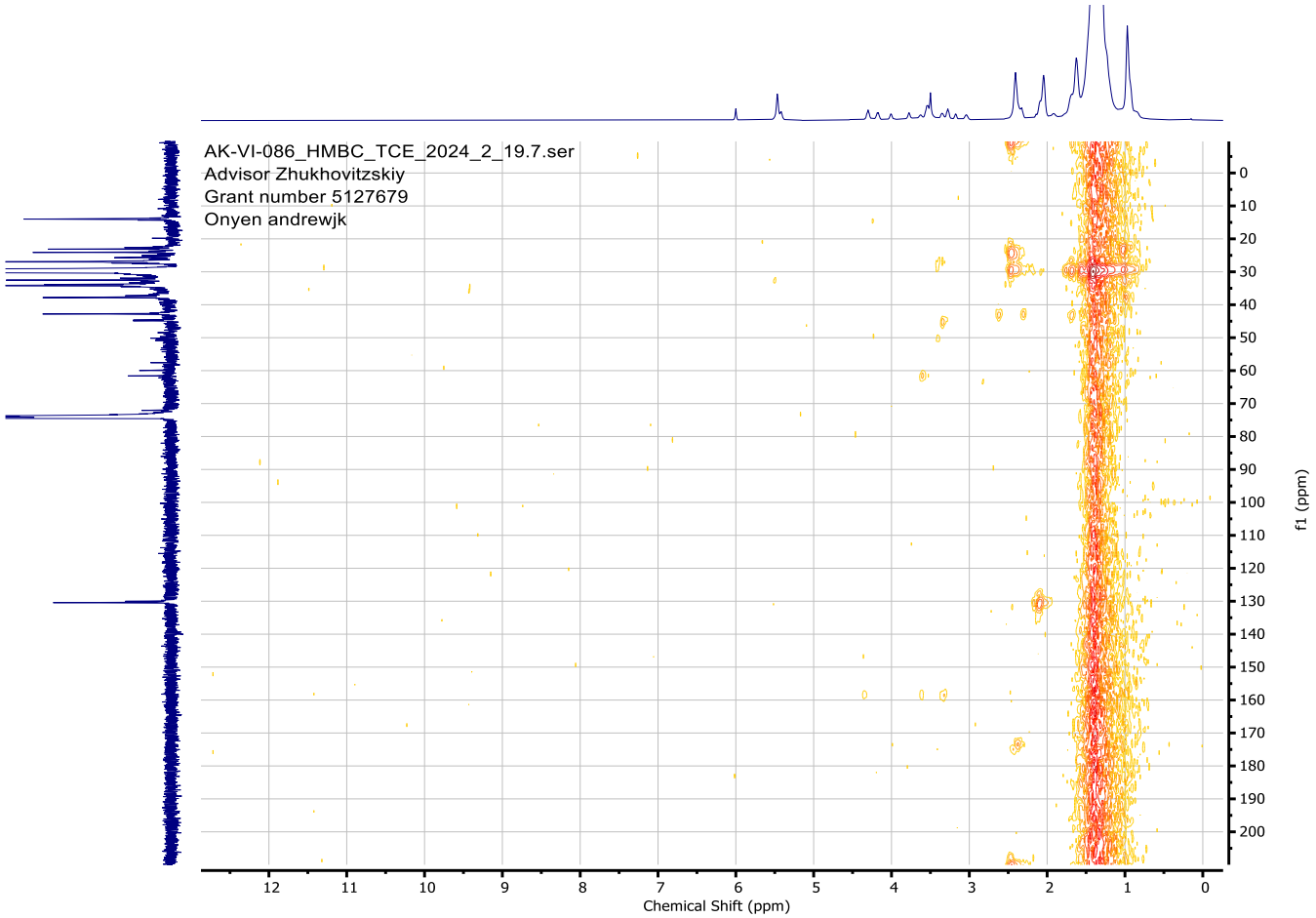


Figure S68. ^{1}H–$^{13}C\{^{1}H\}$ HMBC NMR (1,1,2,2-tetrachloroethane-d_2, 111 °C) spectrum of **zip-P2-2** sourced from LDPE

Table S4. Isolated polymer masses (starting polymer mass in parentheses), temperature at 5% mass loss (determined by TGA), melting temperatures, and enthalpy of melting (determined by DSC) for all polymers sourced from commercial LDPE.

Sample	Isolated Polymer Mass (Starting Polymer Mass in Parentheses)	Temperature at 5% Mass Loss (T_d) (°C)	Melting Temperature (T_m) (°C)	Enthalpy of Melting (J/g)
zip-PE	---	426.8	109.3	141.6
zip-ox-PE	4.822 g (5 g)	388.6	104.8	128.3
zip-P1-1	2.081 g (2 g)	328.0	100.7	98.5
zip-P1-2	2.025 g (2 g)	343.5	97.8	98.2
zip-P2-1	0.895 g (1 g)	385.0	101.0	132.8
zip-P2-2	0.800 g (1 g)	391.4	100.2	130.4

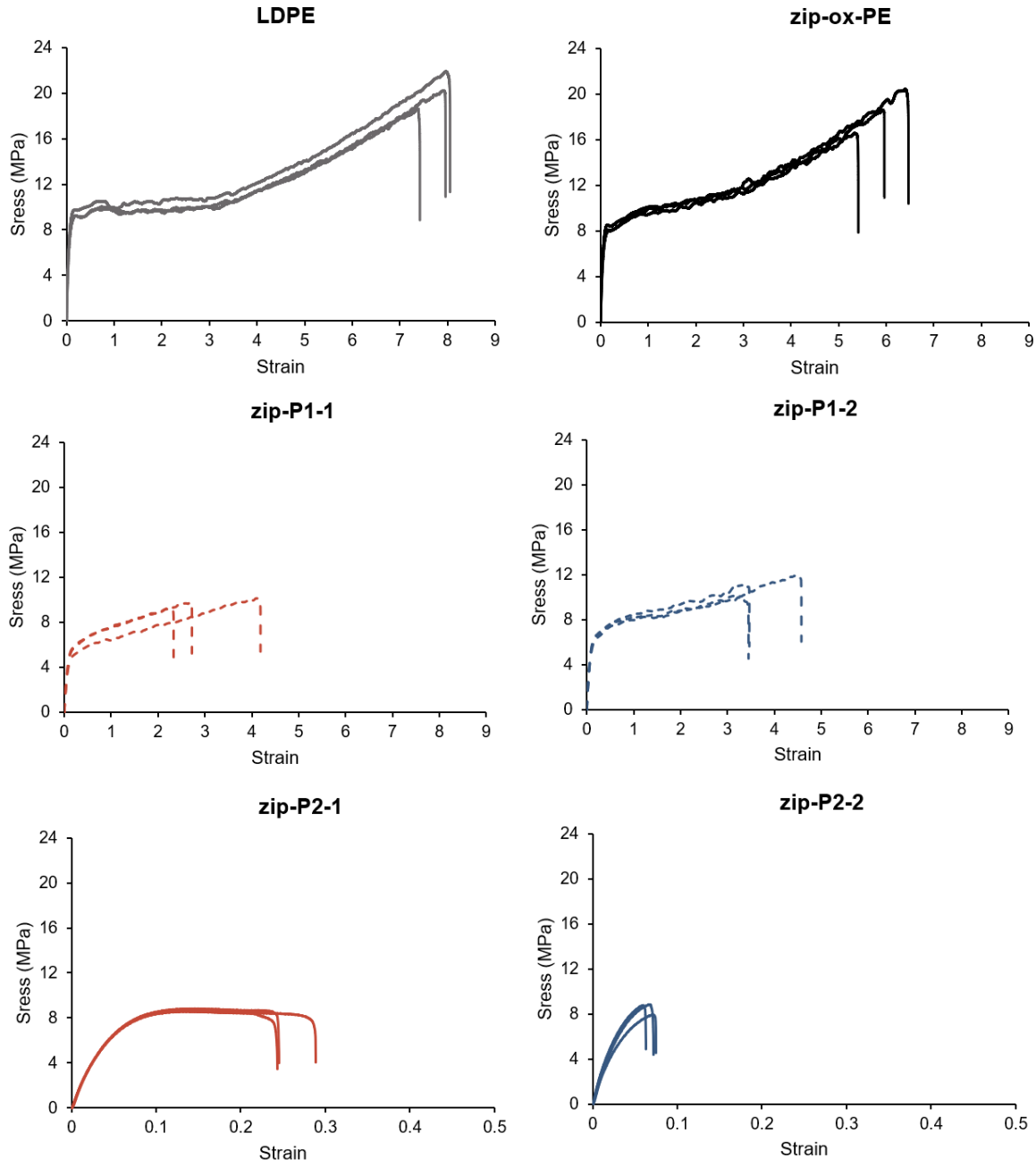


Figure S69. Triplicate uniaxial tensile tests for materials sourced from commercial **LDPE** (**Note**: strain axis has different scale for **zip-P2-1** and **zip-P2-2** to allow for better visualization of the data).

Table S5. Averages and standard deviation of triplicate measurements for stress at break (MPa), strain at break, and Young's modulus (MPa) for materials sourced from commercial **LDPE**.

Sample	Stress at Break (MPa)	Strain at Break	Young's Modulus (MPa)
zip-PE	20.3 ± 1.3	7.81 ± 0.28	195.8 ± 7.8
zip-ox-PE	18.3 ± 1.6	5.95 ± 0.43	149.9 ± 17.5
zip-P1-1	9.7 ± 0.4	3.08 ± 0.80	68.8 ± 4.7
zip-P1-2	10.8 ± 0.9	3.83 ± 0.53	83.4 ± 2.0
zip-P2-1	8.4 ± 0.2	0.26 ± 0.02	211.5 ± 1.2
zip-P2-2	8.5 ± 0.4	0.067 ± 0.005	287.3 ± 31.1

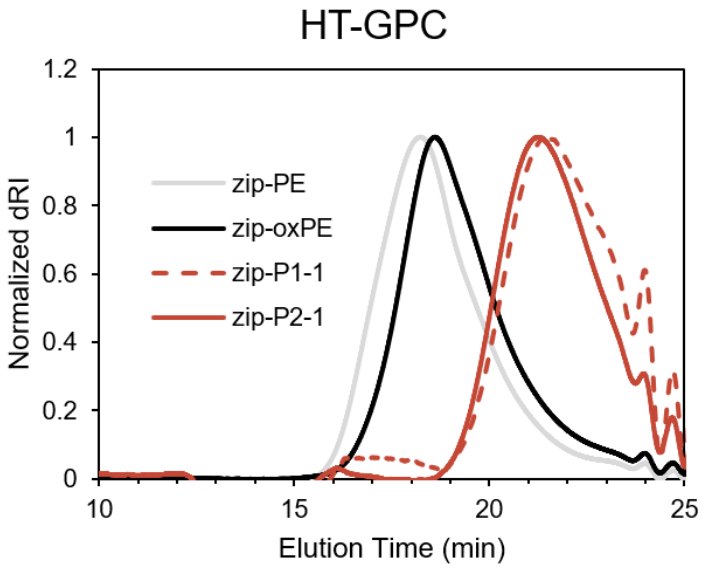


Figure S70. HT-GPC (140 °C, 1,2,4-trichlorobenzene) traces for **zip-PE**, **zip-ox-PE**, **zip-P1-1**, and **zip-P2-1**.

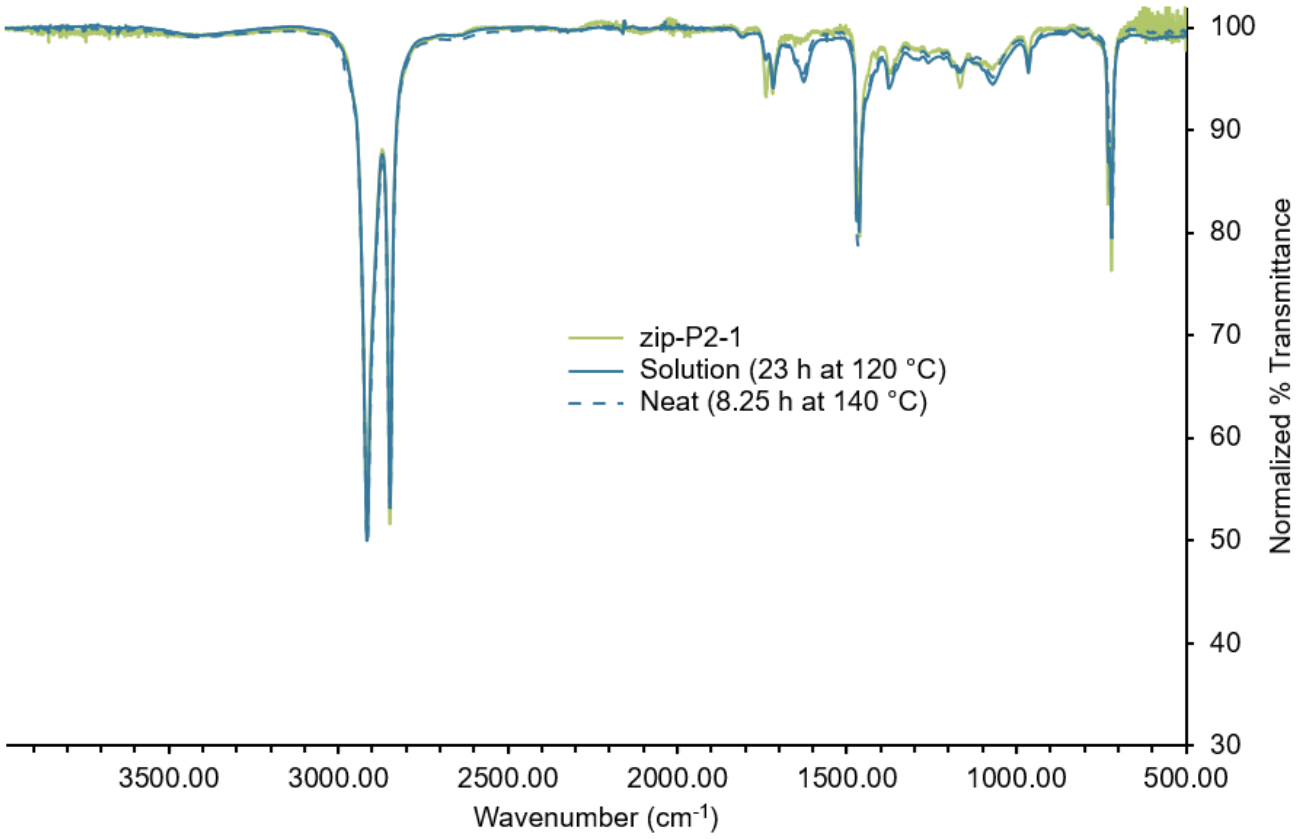


Figure S71. Full FTIR spectra for **zip-P2-1** and products of isomerization.

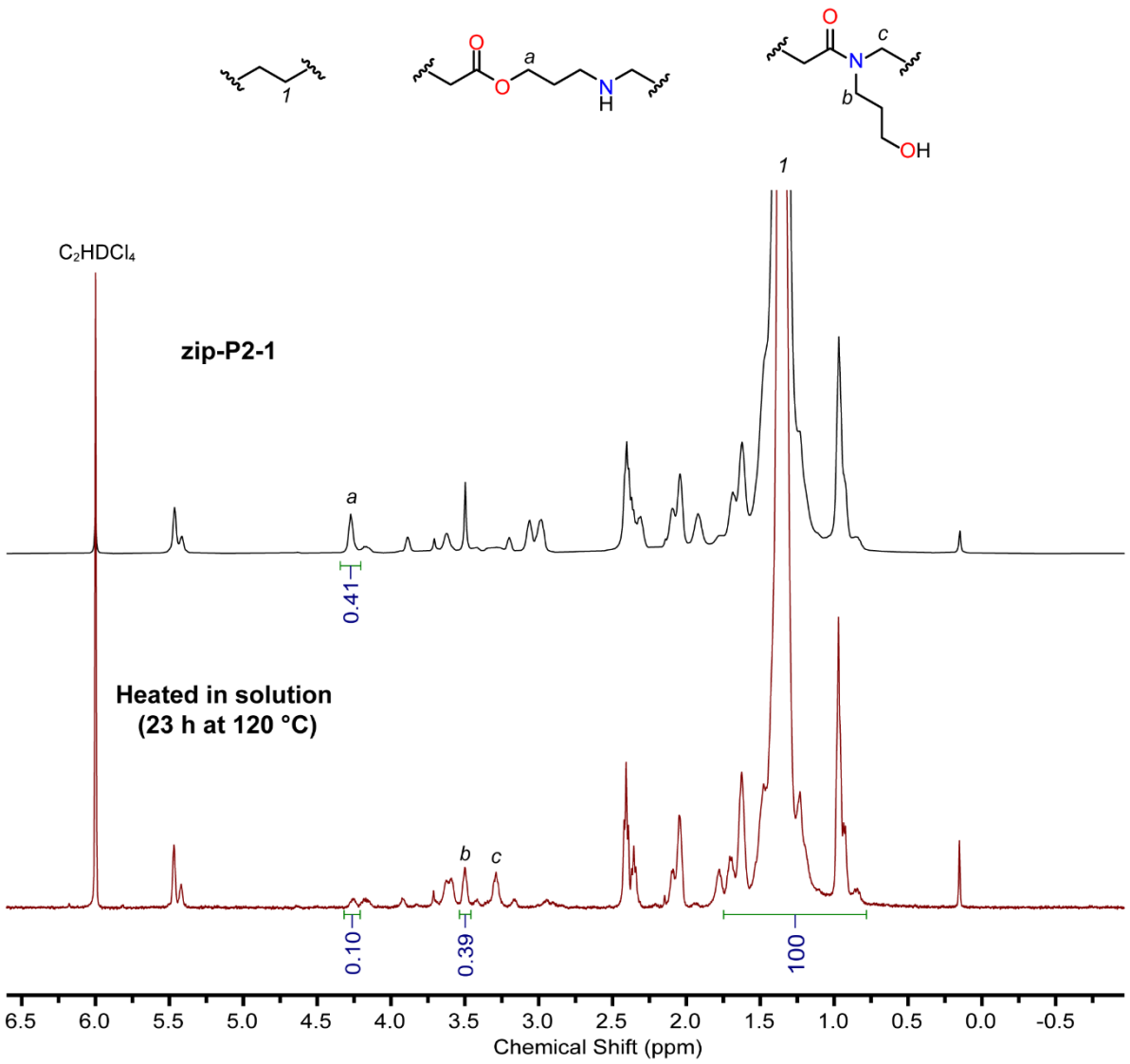


Figure S72. ^{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 112 °C) of **zip-P2-1** (sourced from LDPE) and isomerized **zip-P2-1**. The integral of the resonance from –CH_2–CH_2– repeat units (~0.7–1.7 ppm) was set to 100 for all spectra.

Spectral Data

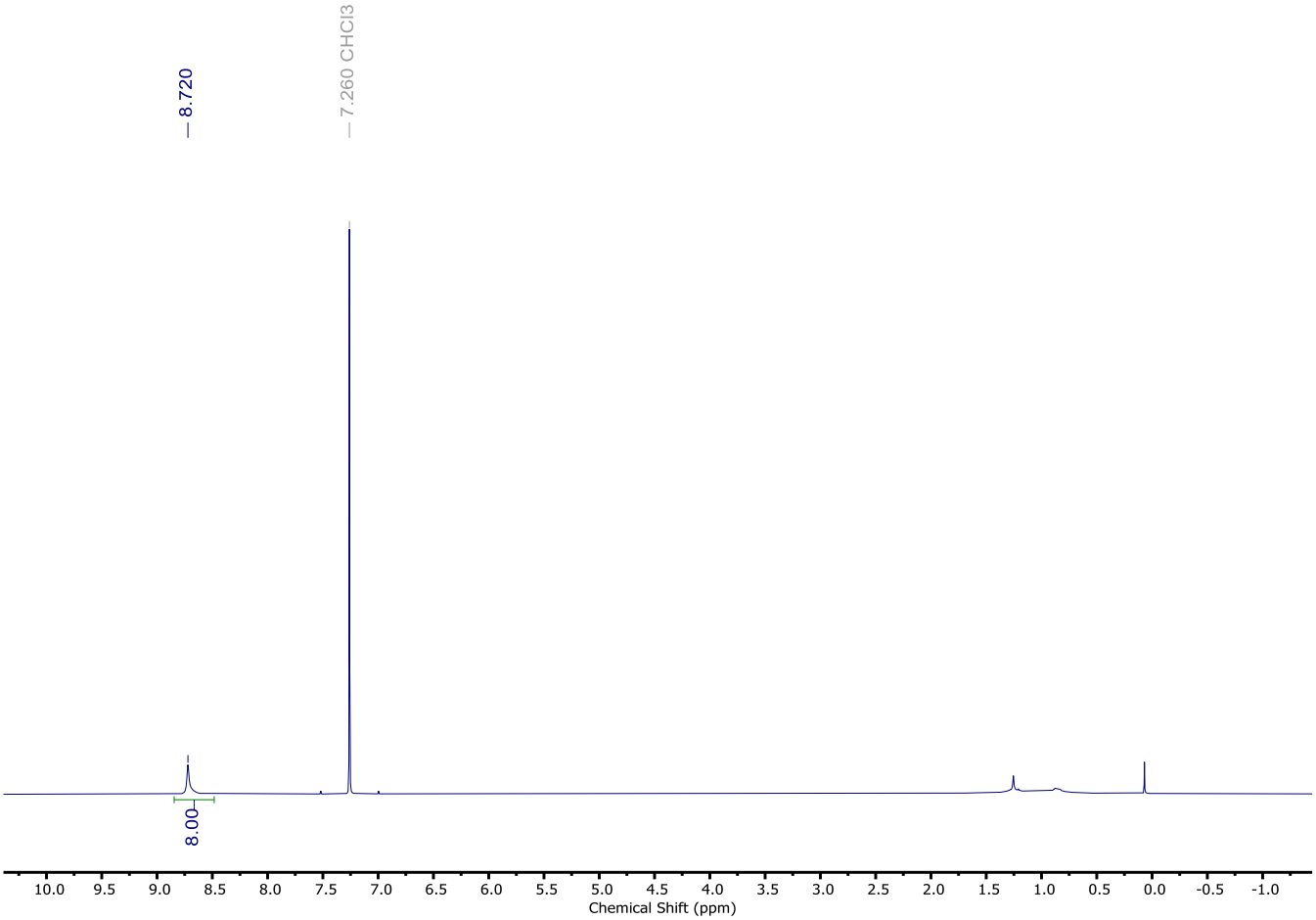


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of Ru(TPFPP)(CO).

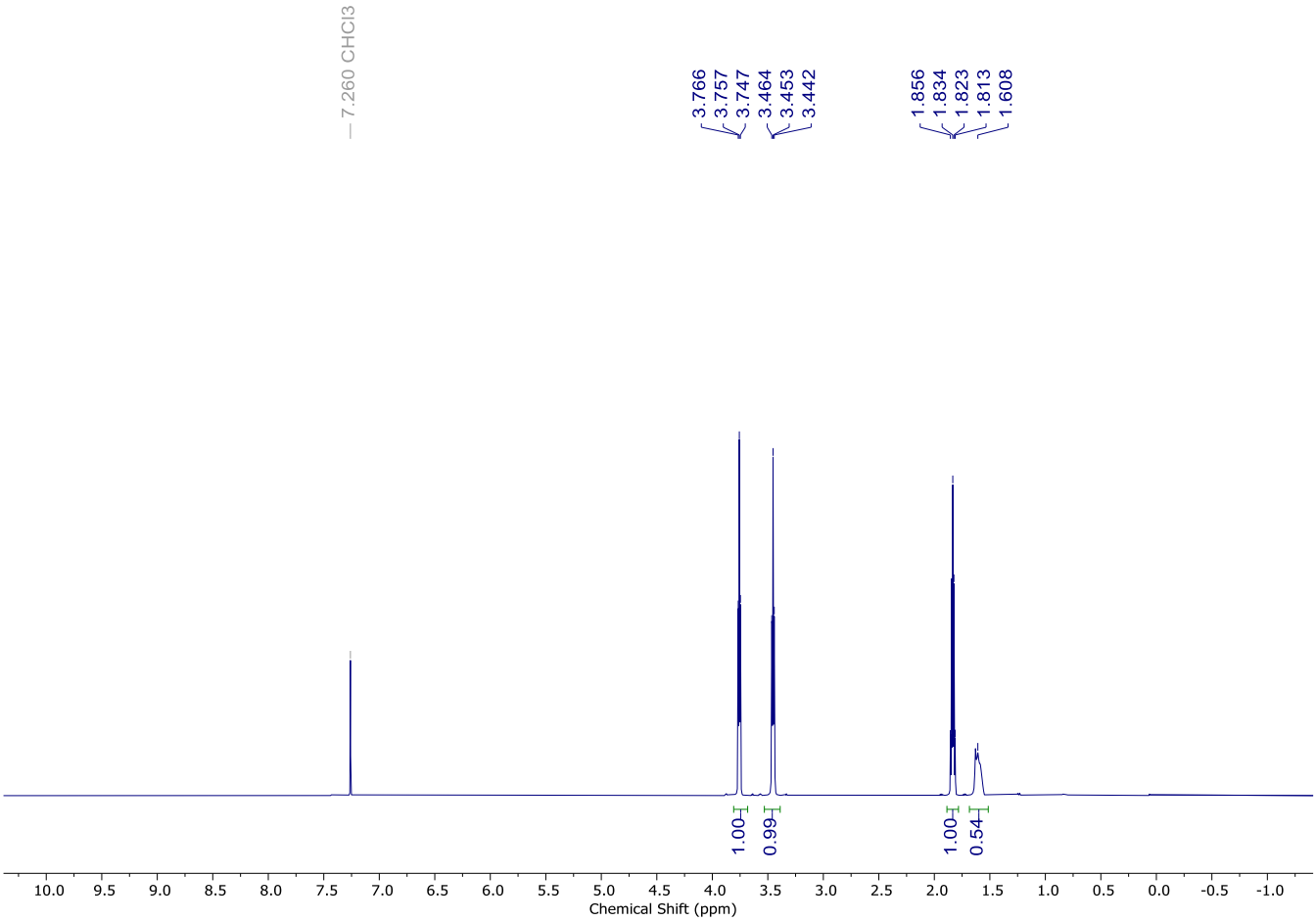


Figure S74. ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C) spectrum of 3-azido-1-propanol (**1-OH**).

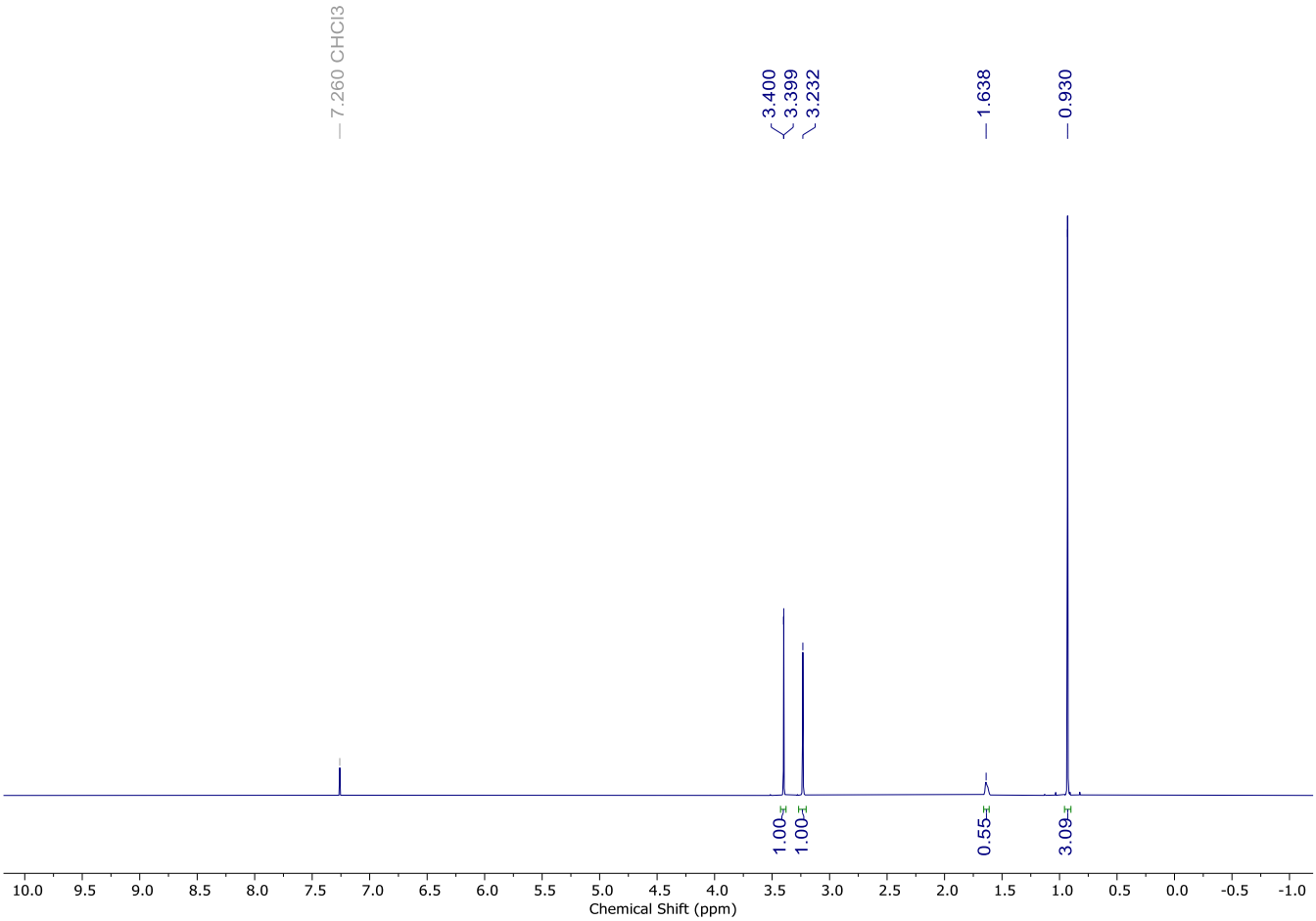


Figure S75. ^{1}H NMR (600 MHz, $CDCl_3$, 23 °C) spectrum of 3-azido-2,2-dimethyl-1-propanol (**5-OH**).

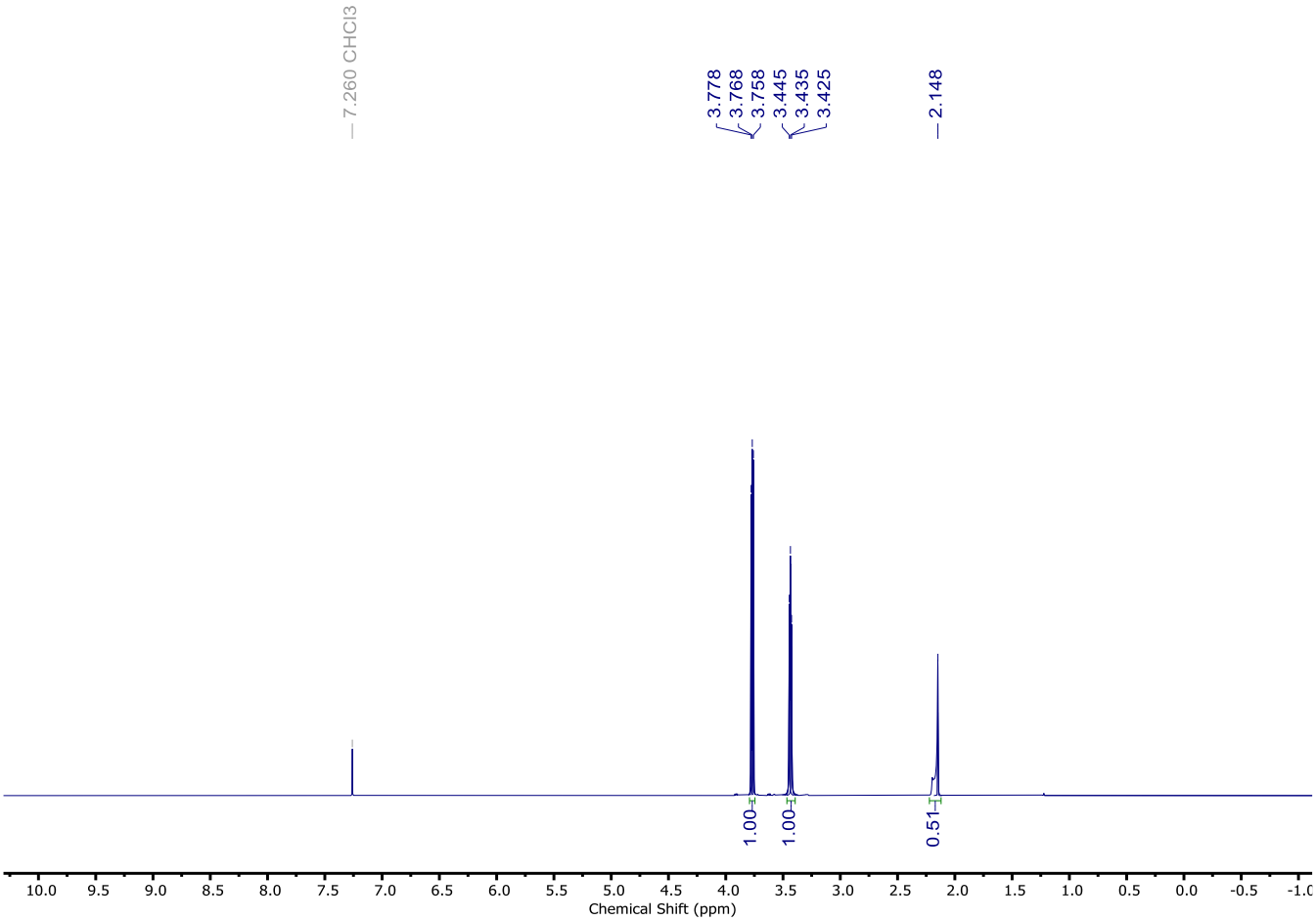


Figure S76. ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of 2-azido-1-propanol (**2-OH**).

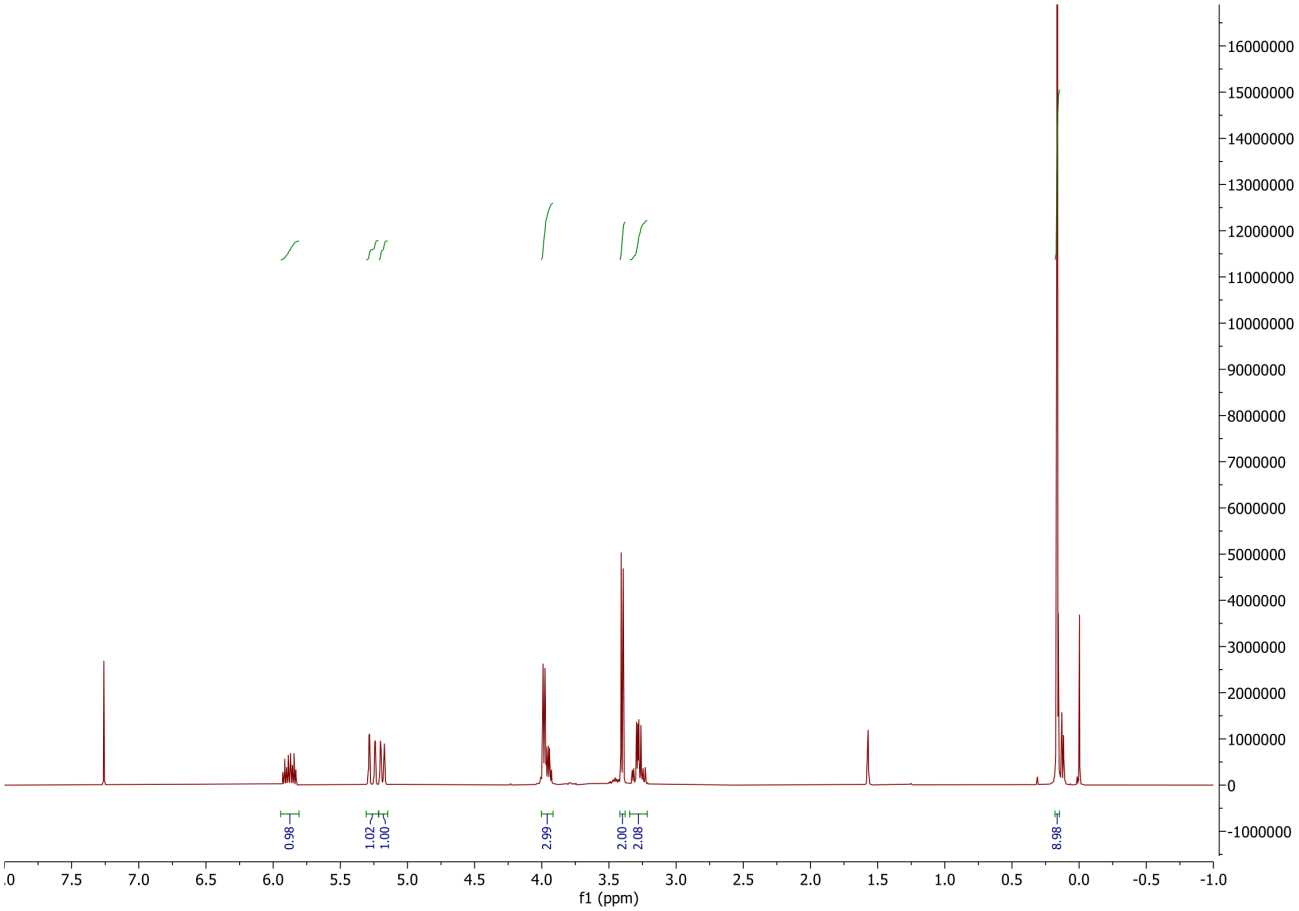


Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of (S)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(S)*-3-OTMS**)

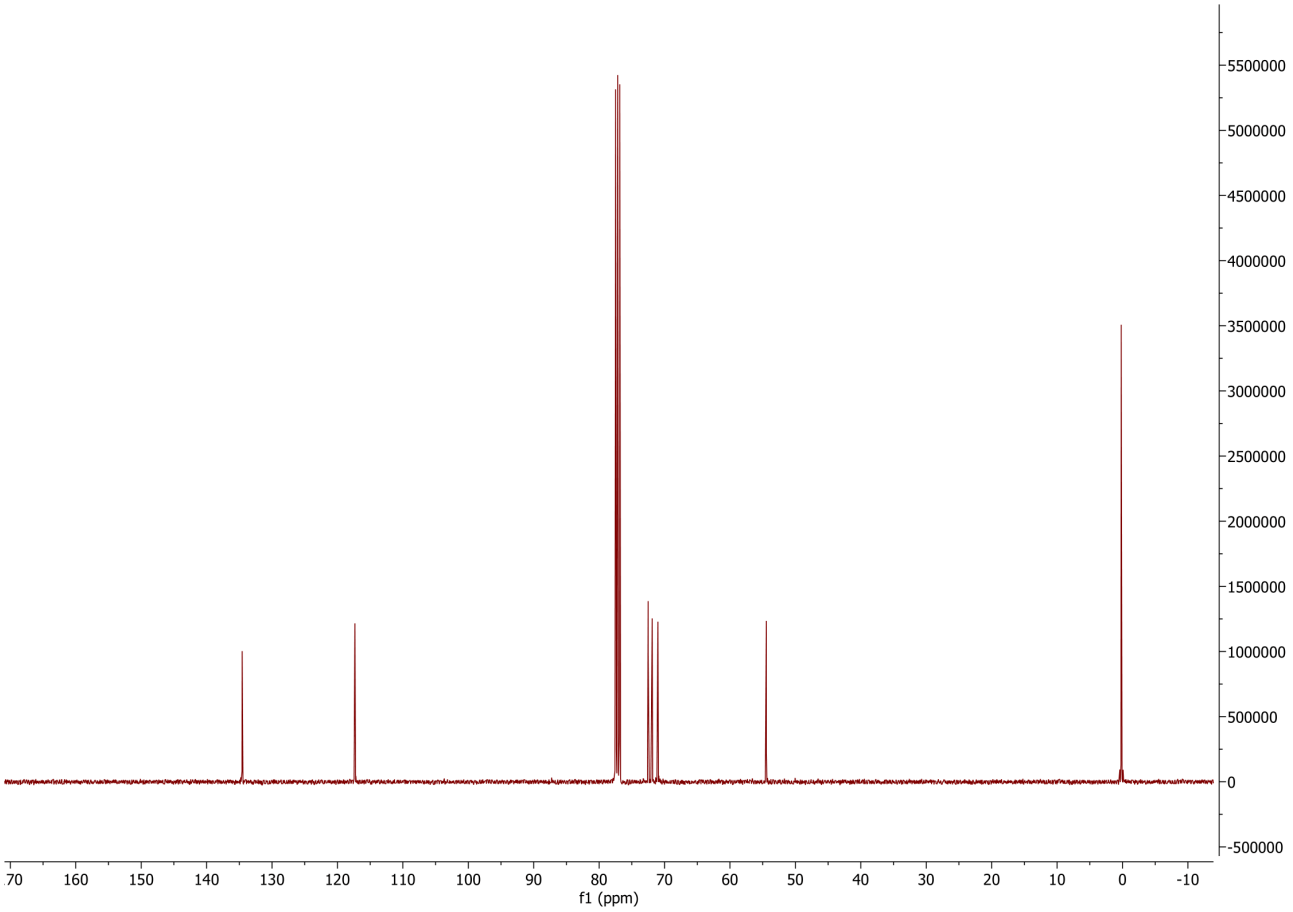
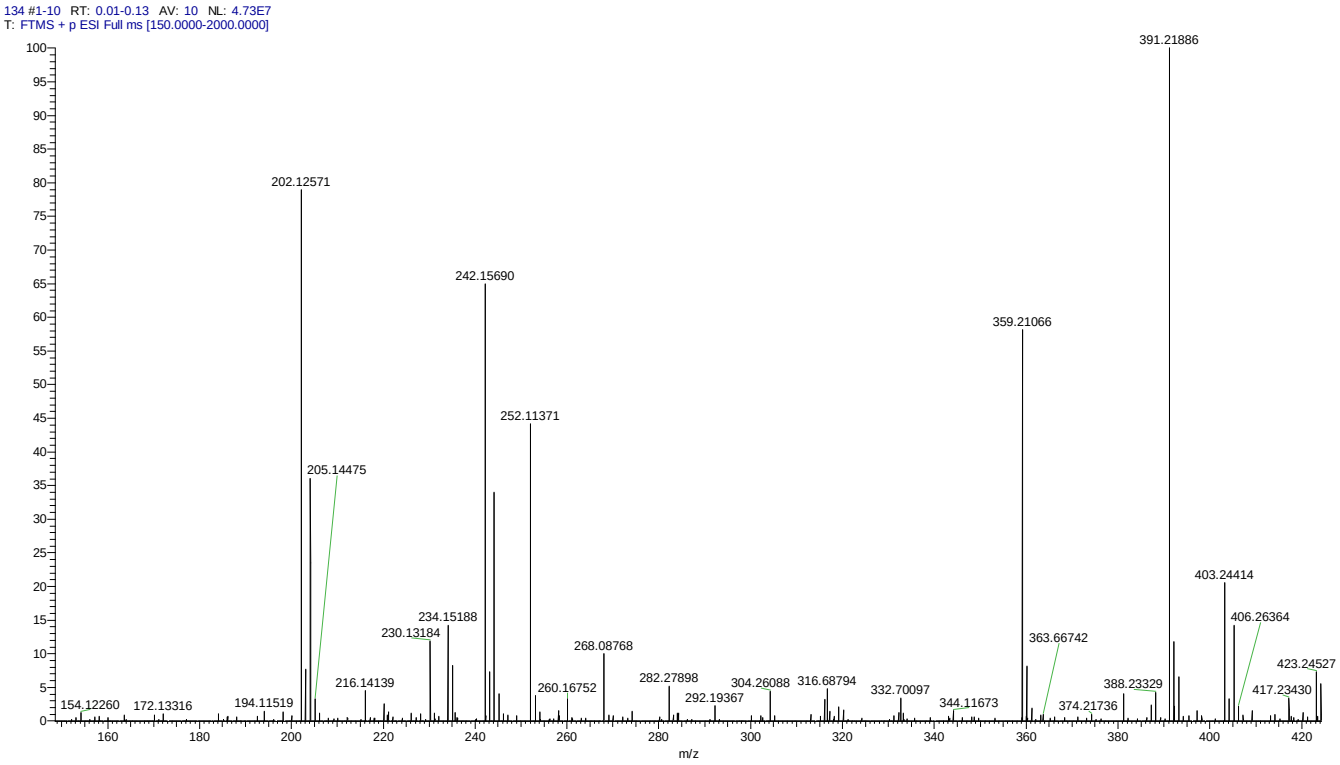


Figure S78. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (S)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(S)*-3-OTMS**)



<u>Figure S79.</u> HRMS spectrum of (S)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(S)*-3-OTMS**)

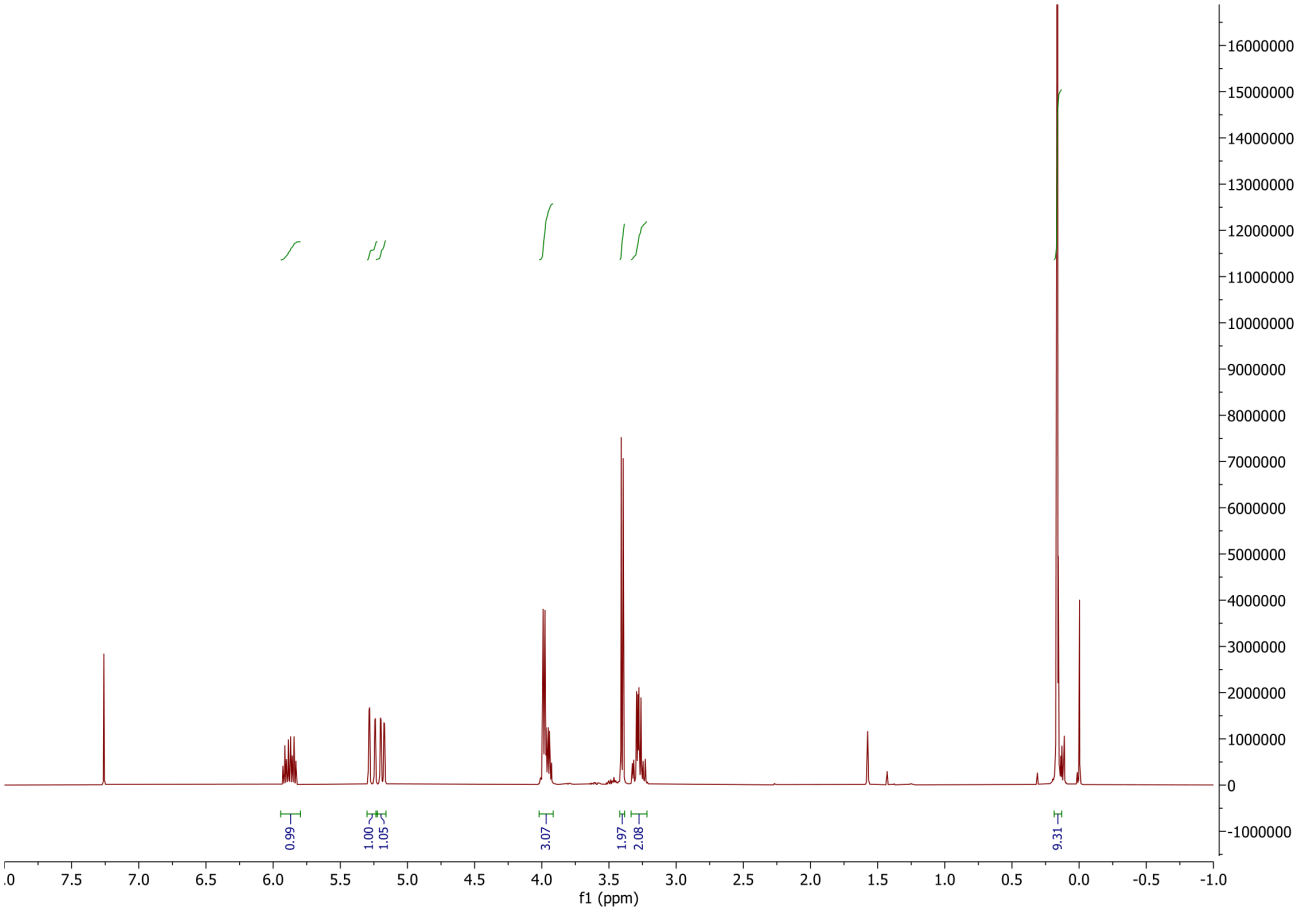


Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of (R)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(R)*-3-OTMS**)

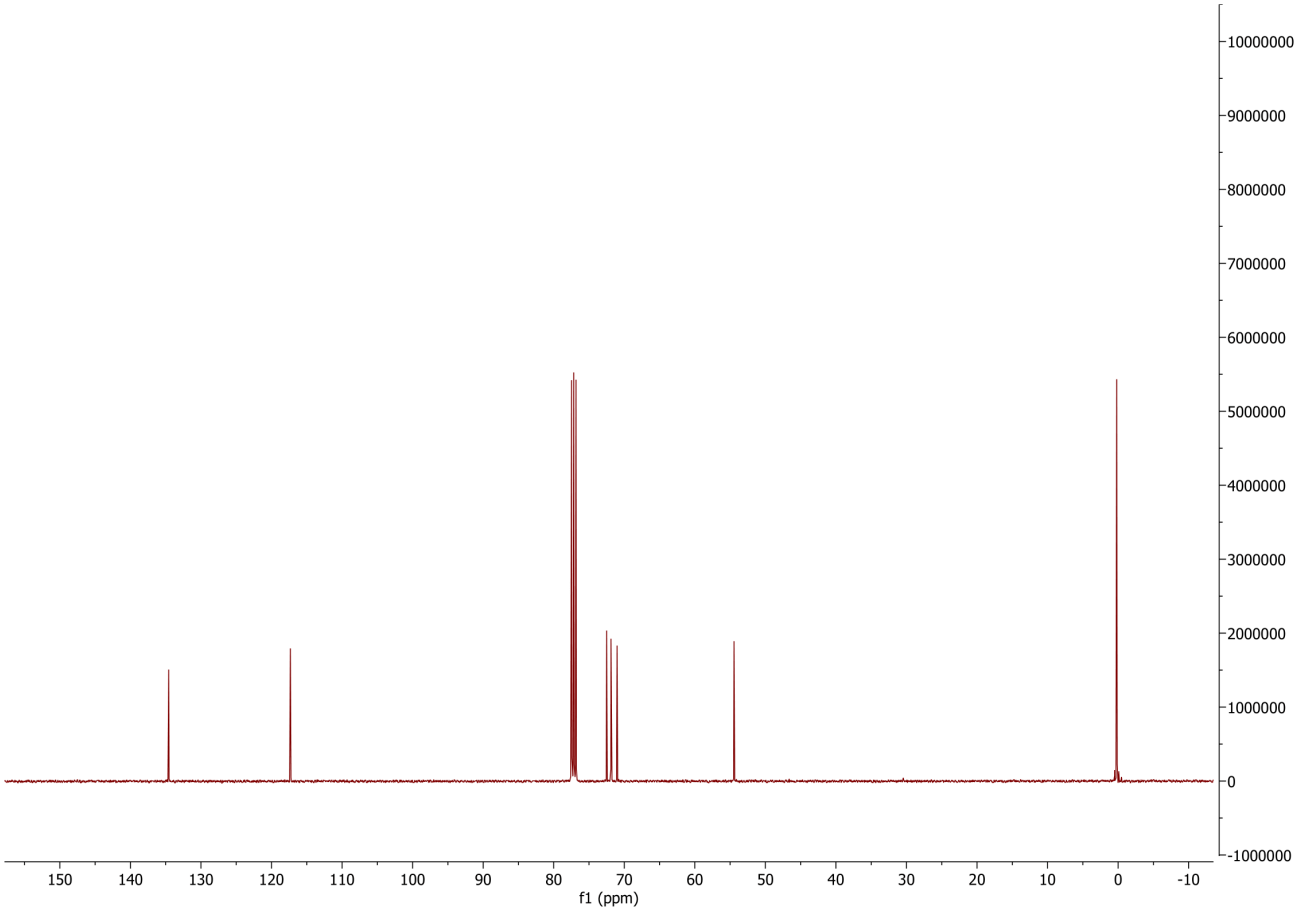


Figure S81. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (R)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(R)*-3-OTMS**)

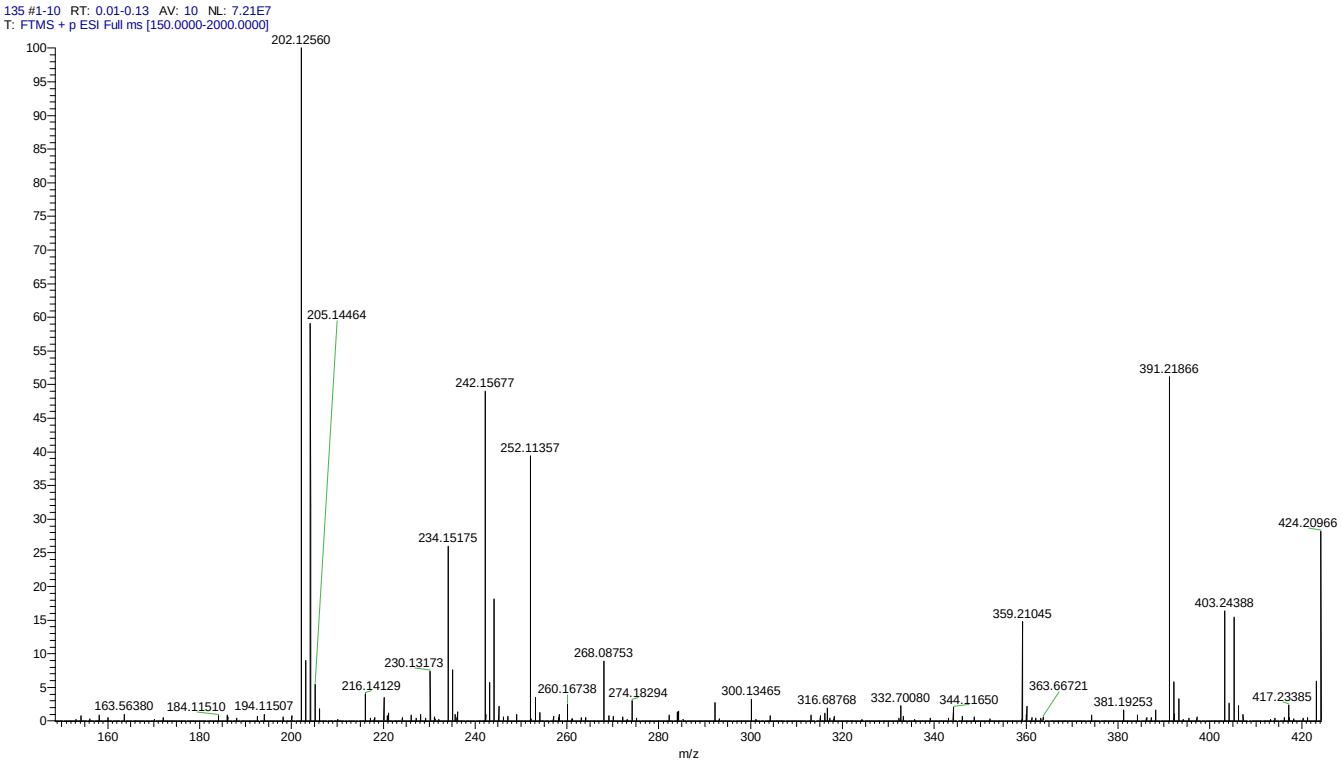


Figure S82. HRMS spectrum of (R)-((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(R)*-3-OTMS**)

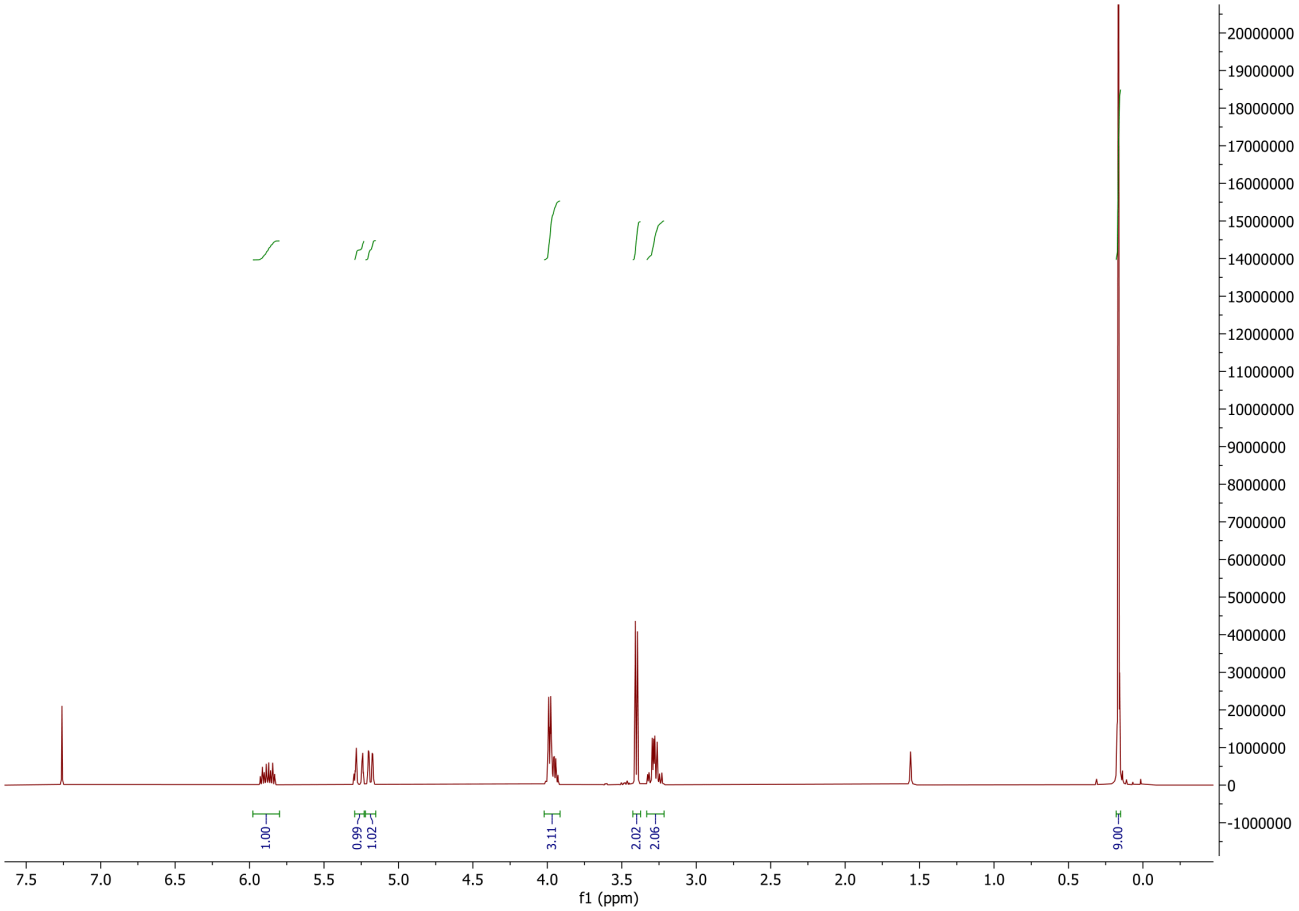


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of ((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(rac)*-3-OTMS**)

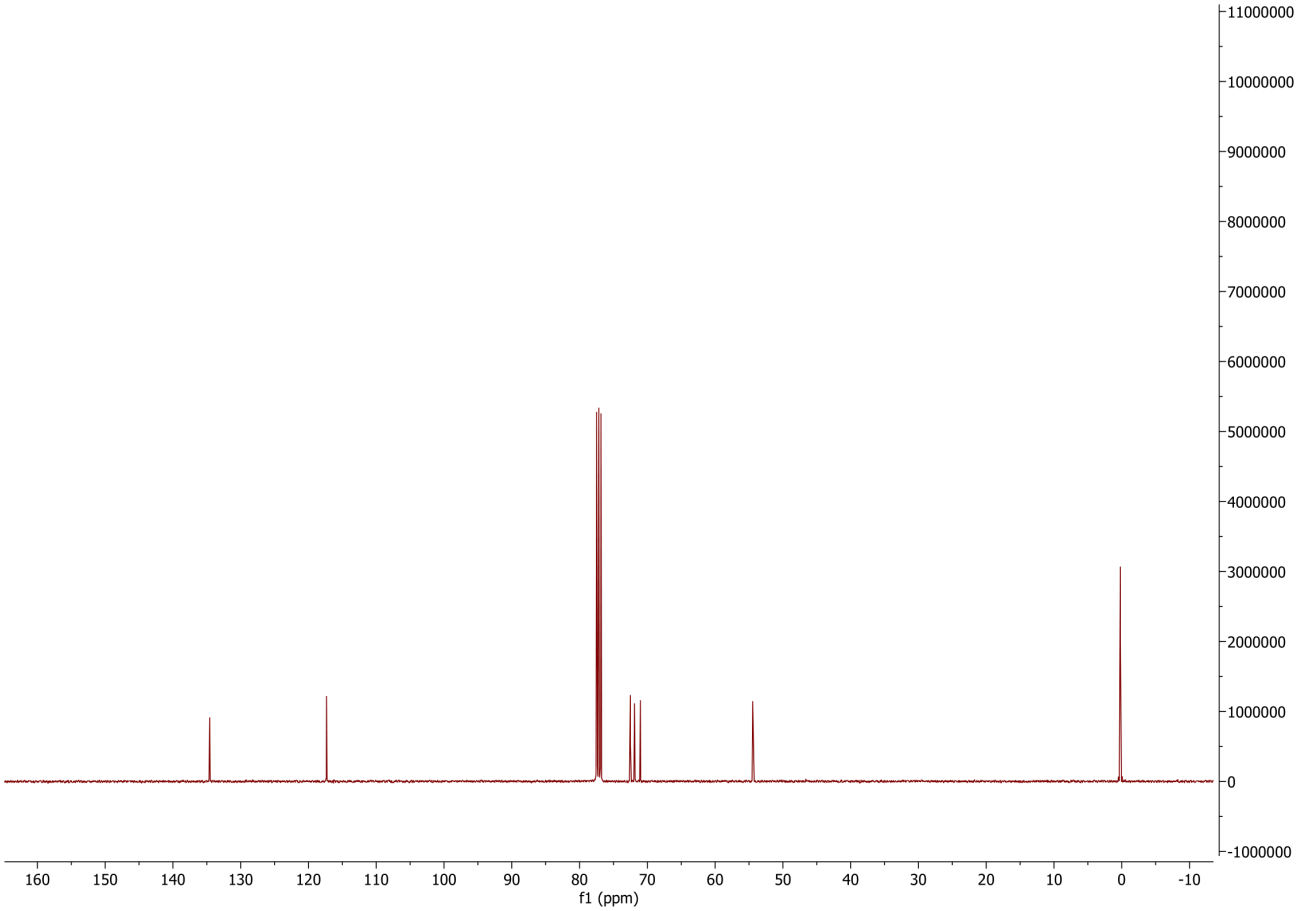


Figure S84. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(rac)*-3-OTMS**)

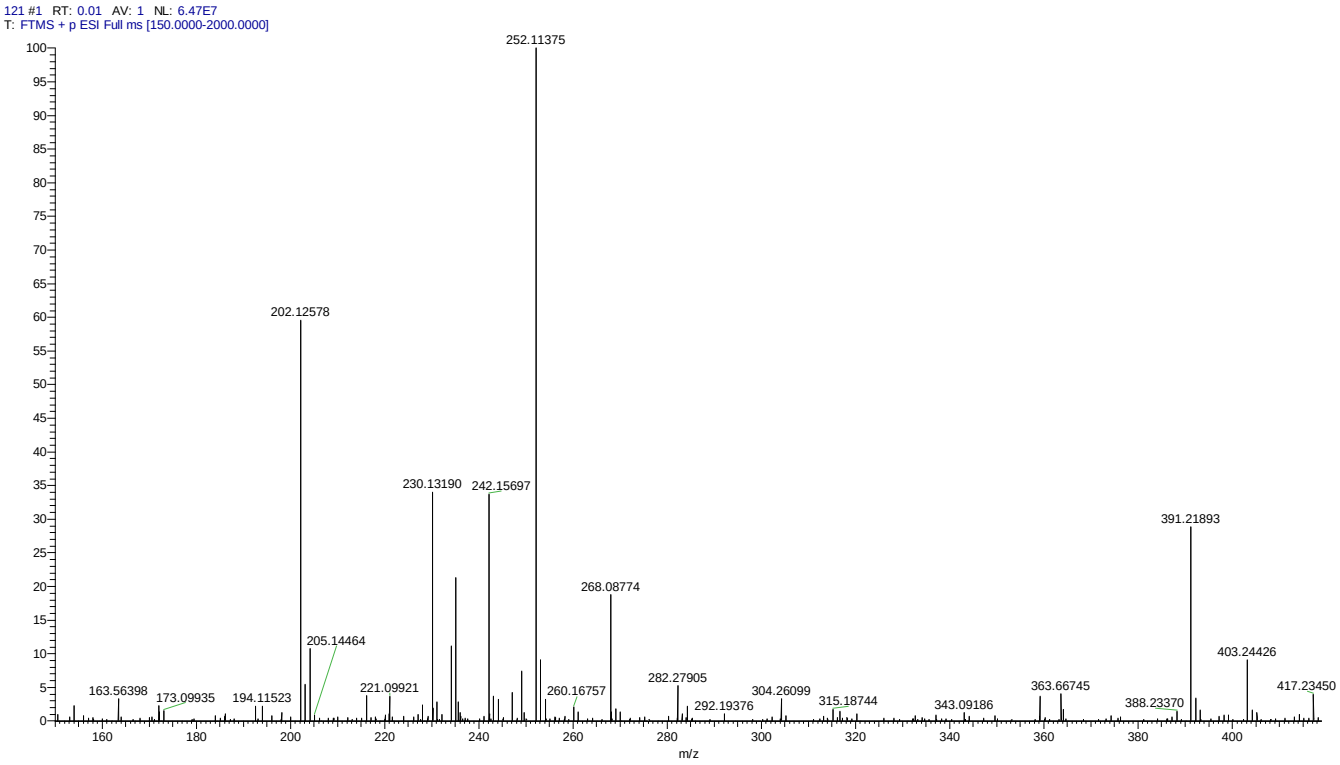


Figure S85. HRMS spectrum of ((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(rac)*-3-OTMS**)

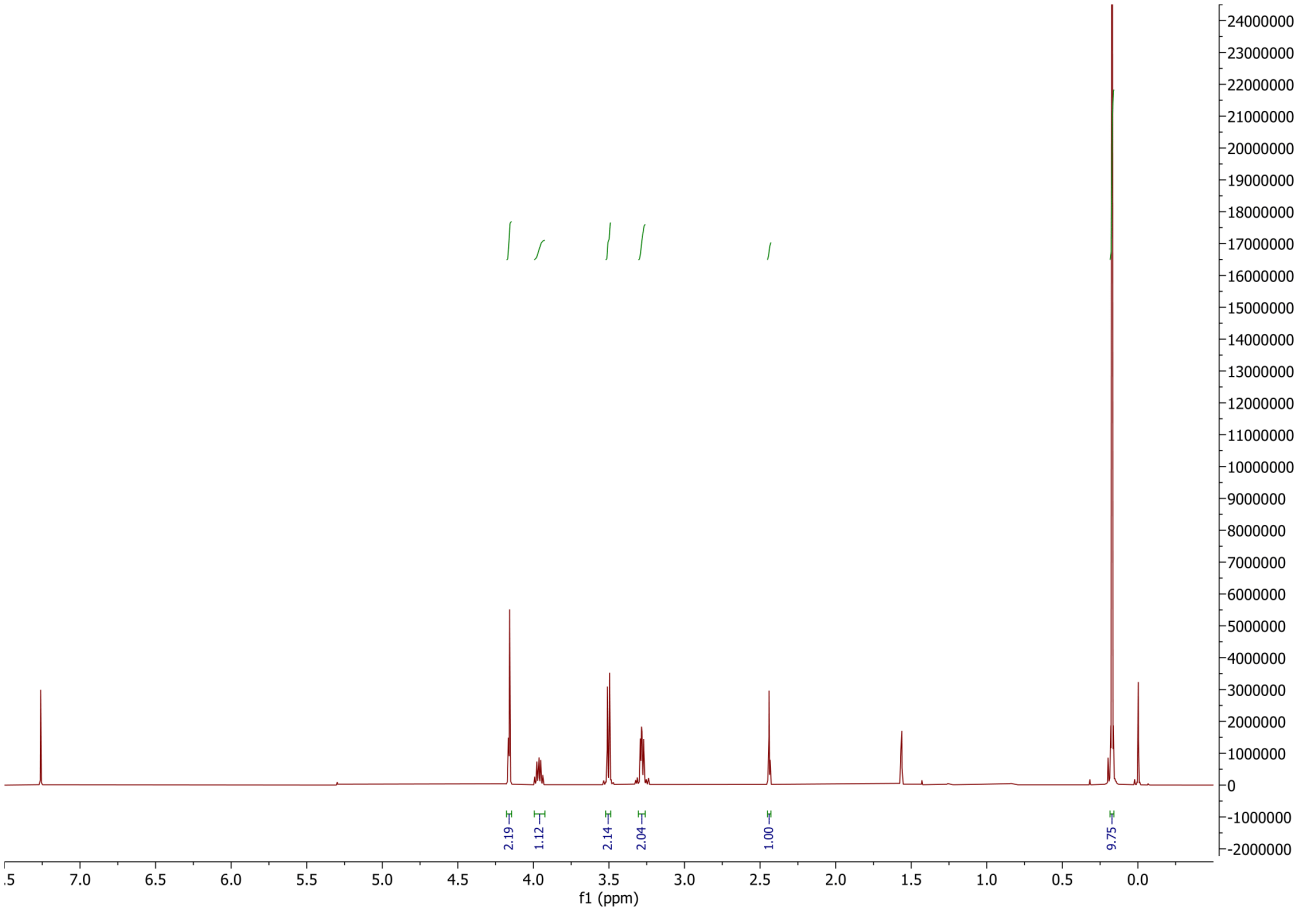


Figure S86. ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C) spectrum of ((1-azido-3-(prop-2-yn-1-yloxy)propan-2-yl)oxy)trimethylsilane (***(rac)*-4-OTMS**)

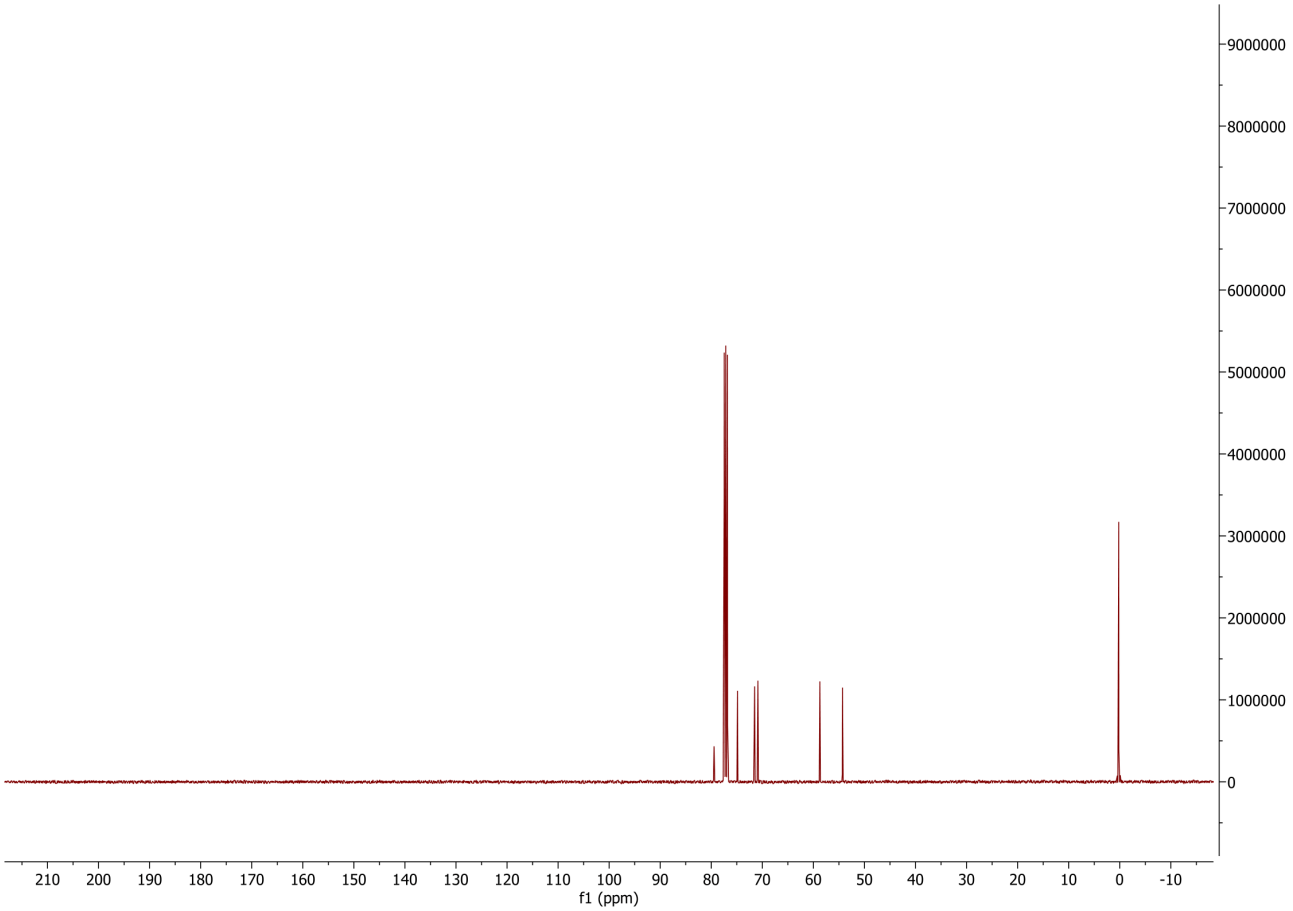
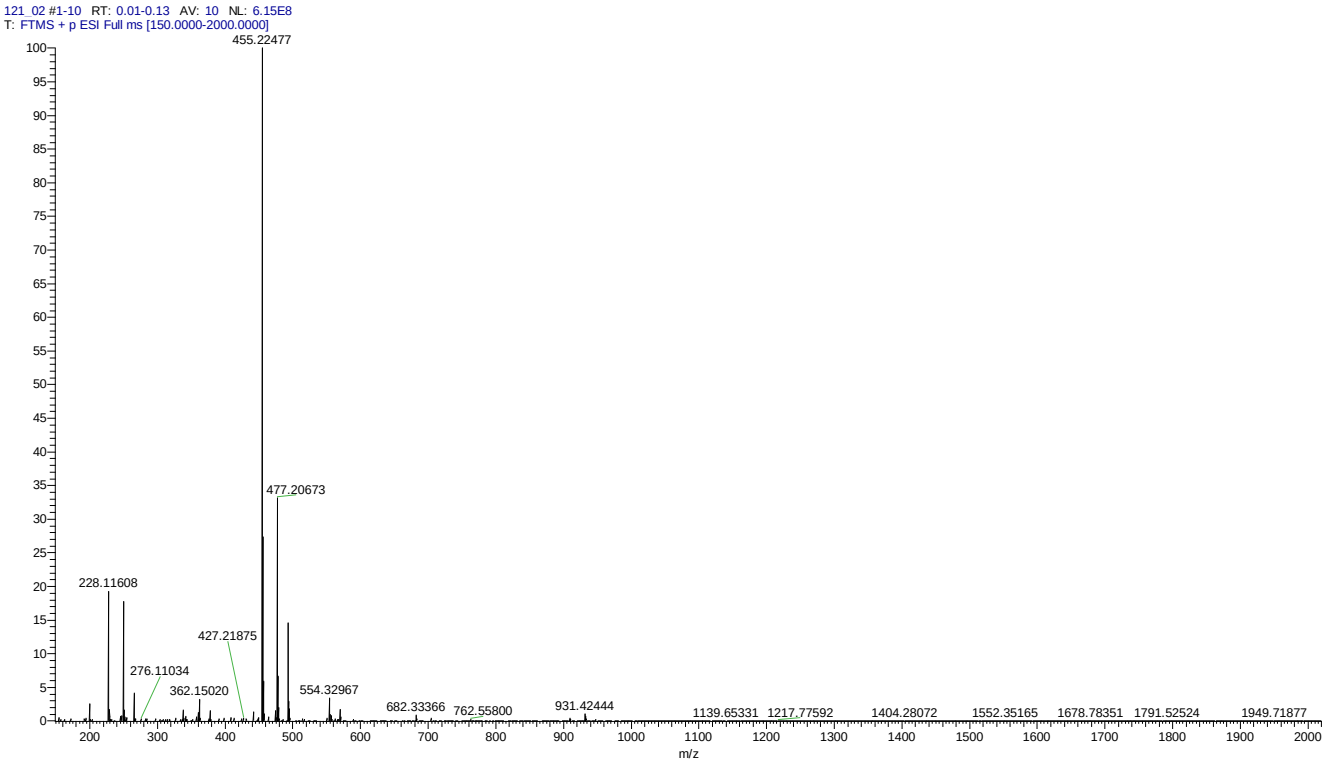


Figure S87. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of ((1-azido-3-(prop-2-yn-1-yloxy)propan-2-yl)oxy)trimethylsilane (***(rac)*-4-OTMS**)



<u>Figure S88.</u> HRMS spectrum of ((1-(allyloxy)-3-azidopropan-2-yl)oxy)trimethylsilane (***(rac)*-4-OTMS**)

References

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