Supplementary Materials

A General Strategy for the Diversification of Aliphatic C–H Bonds Via Radical Chain Transfer

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General Methods and Materials

Proton, carbon, and fluorine magnetic resonance spectra (^{1}H NMR, ^{13}C NMR, and ^{19}F NMR) were recorded on a Bruker model DRX 400 MHz, Bruker 500 MHz, or Bruker AVANCE III 600 MHz CryoProbe spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, bs = broad singlet), coupling constants (Hz), and integration.

High temperature NMR (HT NMR) for polyolefin characterization was recorded on a Bruker 500 MHz spectrometer at 110 °C with solvent resonance as the internal standard (^{1}H NMR: $C_2D_2Cl_4$ at 6.00 ppm; ^{13}C NMR: $C_2D_2Cl_4$ at 73.78 ppm). In all experiments, an ethylene glycol standard confirmed the temperature of the NMR, roughly 116 °C in all cases, and the delay time was set to 5 sec (d1 = 5). 1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, tdd = triplet of doublet of doublets, qd = quartet of doublets, m = multiplet, bs = broad singlet), coupling constants (Hz), and integration.

GC spectra were obtained using a Shimadzu GC-2010 gas chromatograph with a Shimadzu AOC-20s Autosampler, and Shimadzu SHRXI-5MS GC column. Four different GC methods are used. Method 1: Initial temperature of 30.0 °C, ramping at 2.0 °C/min until 75.0 °C, holding for 1.0 min, then ramping at 30.0 °C/min until 250.0 °C, and holding for 2.0 min. Method 2: Initial temperature of 55.0 °C, ramping at 2.0 °C/min until 95.0 °C, then ramping at 30.0 °C/min until 250.0 °C, and holding for 2.0 min. Method 3: Initial temperature of 55.0 °C, ramping at 3.0 °C/min until 120.0 °C, then ramping at 30.0 °C/min until 250.0 °C, and holding for 2.0 min. Method 4: Initial temperature of 55.0 °C, ramping at 15.0 °C/min until 200.0 °C, then ramping at 3.0 °C/min until 250.0 °C, and holding for 2.0 min. The results of the kinetic isotope study were analyzed using an Agilent Gas Chromatograph-Mass Spectrometer with a 7820A series GC system and a 5977E Mass Selective Detector.

Infrared (IR) spectra were obtained using PerkinElmer Frontier FT-IR spectrometer. Thin layer chromatography (TLC) was performed on SiliaPlate 250μm thick silica gel plates provided by Silicycle. Visualization was accomplished with short wave UV light (254 nm), iodine, aqueous basic potassium permanganate solution, or aqueous acidic ceric ammonium molybdate solution followed by heating. Flash chromatography was performed using SiliaFlash P60 silica gel (40-63

μm) purchased from Silicycle, or using a Biotage™ Isolera auto-column with silica gel purchased from Biotage. Tetrahydrofuran, diethyl ether, and dichloromethane were dried by passage through a column of neutral alumina under nitrogen prior to use. Irradiation of reactions was performed using two Kessil KSH150B Blue 34W LED Grow Lights with fan cooling. UV light experiments were performed in a Luzchem LZC-ORG photoreactor containing UVA lamps. All other reagents were obtained from commercial sources and used without further purification unless otherwise noted. In addition, all reactions were carried out under an atmosphere of argon in flame or oven-dried glassware with magnetic stirring unless otherwise noted.

Mass spectra were obtained via one of 3 methods: with a Q Exactive HF-X (ThermoFisher, Bremen, Germany) mass spectrometer with samples introduced via a heated electrospray source (HESI) or via an atmospheric pressure chemical ionization (APCI) source at a flow rate of 20 μL/min, or with a ThermoFisher GC Exactive with an Electron Ionization (EI) source.

All post-polymerization modifications were performed under an inert atmosphere using standard glove box and Schlenk-line techniques. Commercial polyolefins were obtained from their respective companies and purified prior to use by dissolution in chlorobenzene and precipitation into methanol or acetone. The company and lot number are named in the individual procedures. Chlorobenzene was distilled over calcium hydride, degassed through three freeze-pump-thaw cycles, and stored in a glove box. Reagents, unless otherwise specified, were purchased and used without further purification.

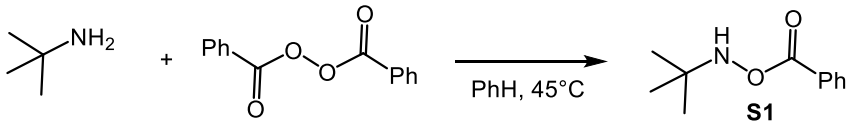
High temperature gel permeation chromatography (HT GPC) spectra were obtained using a Tosoh EcoSEC-HT GPC using TSKgel GMH$_{HR}$-M columns. 1,2,4-trichlorobenzene (TCB) was prepared with 200 ppm dibutylhydroxytoluene (BHT) by stirring overnight and was the mobile phase. The flow rate was set to 1 mL/min and samples were prepared at concentrations of 2 mg/mL in TCB with 200 ppm BHT. The instrument was calibrated using 17 polystyrene standards in the range of 580 to 5,480,000 Da. A calibration curve was created using refractive index detection against 2 mg/mL polystyrene standards in TCB with 200 ppm BHT at 140 °C. A tandem multi-angle light scattering (MALS) detector could also be employed on the HT GPC via a Wyatt DAWN 8 heated flow cell instrument.

Differential scanning calorimetry (DSC) was used to determine the thermal characteristics of the polyolefins and small molecules using a TA Instruments DSC (Discovery Series). For polymer samples, DSC measurements were performed on 1 – 10 mg of sample in Tzero pans. The samples underwent a heat, cool, heat cycle with a temperature ramp rate of 10 °C/min. Data

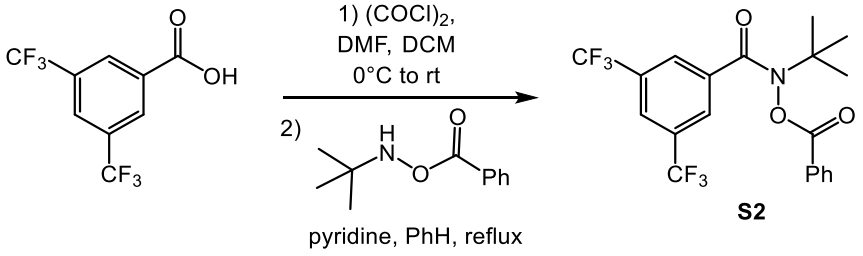
was taken from the second heating cycle. For small molecules, 1 – 10 mg of sample was prepared in TA Instruments high-volume pans rated for high pressures. The samples underwent a single heating cycle at a rate of 5 °C/min from 25 – 200 °C.

Thermal gravimetric analysis (TGA) was obtained using a TA Instruments TGA (Discovery Series) in the temperature range of 40 – 600 °C at a temperature ramp rate of 10 °C/min. The temperature of decomposition (T_d) was defined by the temperature at which 10% of total mass was lost.

Alkenylhydroxyamide Synthesis



N-(*tert*-butyl)-O-benzoylhydroxylamine (S1): Adapted from a previously reported procedure (*1*). To a flame dried round bottom flask with a stir bar was added benzoyl peroxide (20.0 g, 82.6 mmol), which was then dissolved in benzene (115 mL). The reaction was sealed and placed under N_2. Roughly 60% of total volume of *tert*-butylamine (21 mL) was added and the reaction heated at 45°C for 1 hour, and changed color from cloudy white color to cloudy Carolina blue. After 1 hour, the remaining amount of *tert*-butylamine (13.7 mL, to total of 34.7 mL, 330 mmol) was added through the septum and the reaction was let to stir overnight. Then, the reaction was let to cool to room temperature, diluted with diethyl ether, and solid ammonium salt was filtered off. To the filtrate was added acidic aqueous $FeSO_4$ in ~1M H_2SO_4 (50 mL); the mixture was stirred for 10 minutes. The mixture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with saturated sodium bicarbonate solution (3 X 50 mL), water (1 X 50 mL), dried over $MgSO_4$, filtered and concentrated to afford product **S1** as yellow oil (13.8 g, 87% yield) in accordance with reported spectral data; the compound was used directly without purification.



N-(*tert*-butyl)-O-benzoyl-(3,5-bis-trifluoromethyl)-hydryoxyamide (S2): To a flame dried round bottom flask with stir bar was added (3,5-bis-trifluoromethyl)-benzoic acid (16.8 g, 65.1 mmol), dissolved in dichloromethane (100 mL). Dimethylformamide was added (26 µL), and the reaction was sealed, and brought to 0°C. Oxalyl chloride was added dropwise via syringe (11.0 mL, 130 mmol), and the reaction stirred at 0°C for 15 minutes, then was let come to room temperature. The reaction was let stir until the cloudy white solution completely dissolved, forming a clear yellow solution, and continued to stir until bubbling subsided (~3 hours). Then, the reaction was carefully concentrated *in vacuo* to remove all volatiles; the resulting yellow oil was taken up

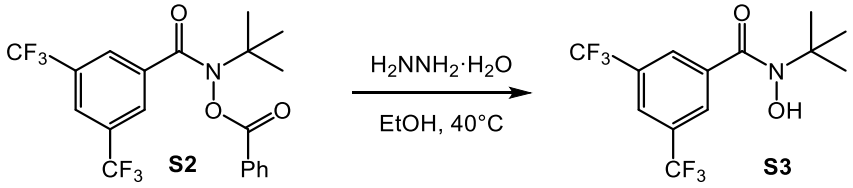
in benzene (100 mL), and benzoylhydroxylamine (**S1**) was added (13.8 g, 71.6 mmol) in minimal amount of benzene. Pyridine was added (11.1 mL, 137 mmol), the flask was equipped with a condenser, and brought to reflux overnight. At end of the reaction, the mixture allowed to cool to room temperature, diluted with diethyl ether, and pyridinium salt filtered off. Filtrate was transferred to separatory funnel, washed with 1 M hydrochloric acid (2 X 100 mL), water, dried over $MgSO_4$, filtered and concentrated to afford product **S2** as amber-colored solid (28.21 g, 99% yield). Used directly in next step.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.82 (d, 2H), 7.76 (s, 1H), 7.59 (t, 1H), 7.41 (t, 2H), 1.62 (s, 9H),

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.5, 165.2, 137.5, 134.6, 131.3 (q), 129.6, 128.8, 127.89, 125.7, 123.6, 121.9, 63.8, 27.5

^{19}F NMR (376 MHz, $CDCl_3$) δ –63.0

HRMS (HESI) Exact mass calcd for $C_{20}H_{17}F_6NO_3H$ $[M+H]^+$, 434.1191. Found 434.1180.



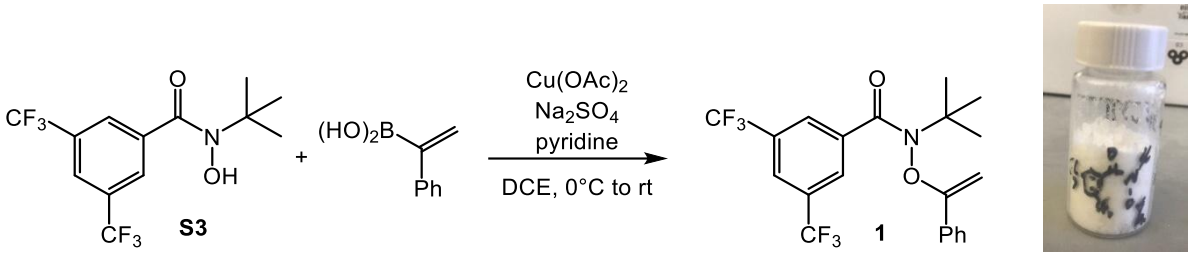
N-(*tert*-butyl)-(3,5-bis-trifluoromethyl)-hydryoxyamide (S3): To a large round bottom flask with magnetic stir bar was added O-benzoylhydroxyamide **S2** (28.21 g, 65.10 mmol), dissolved in ethanol (180 mL), reaction capped and sealed with Teflon tape, equipped with N_2 line. Hydrazine monohydrate (23.7 mL, 488 mmol) was added dropwise, and the reaction was heated to 40°C for 2 hours. At end of the reaction, mixture let cool to room temperature, then brought to 0°C. Ice water was added to mixture (~1.5 X volume of ethanol used), inducing precipitation of white solid from yellow solution. Reaction kept at 0°C for 5 minutes, then solid collected by filtration, washed with water then pentanes, and dried thoroughly on hi-vac overnight to afford hydroxyamide product **S3** (18.1, 85% yield). Used directly in next step.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.96 (s, 1H), 6.68 (br s, 1H), 1.49 (s, 9H),

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 138.5, 131.6, 131.3, 128.1, 123.8, 123.6, 122.0, 62.2, 27.8

^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9

HRMS (HESI) Exact mass calcd for $C_{13}H_{13}F_6NO_2H$ $[M+H]^+$, 330.0929. Found 330.0918.



N-(*tert*-butyl)-O-(1-phenylvinyl)-(3,5-bis-trifluoromethyl)-hydryoxyamide (1): Procedure adapted from report by Rovis and coworkers (*2*). To a large, dry round bottom flask with stir bar was added copper acetate (10.02 g, 55.2 mmol), sodium sulfate (31.3 g, 221 mmol), and hydroxamic acid **S3** (18.16 g, 55.2 mmol). Mixture left open to ambient atmosphere; 1,2-dichloroethane added (600 mL) to make a slurry, mixture cooled to 0°C. The flask was covered with aluminum foil, and hood lights turned off. Pyridine added (13.4 mL, 166 mmol), mixture let come to room temperature overnight. Next morning, 1,1-phenylvinylboronic acid (16.32 g, 110 mmol) was added, and the reaction was let stir at room temperature under ambient atmosphere, monitored by TLC until no more product being formed (~4 days). At end of reaction, the mixture was filtered through a pad of silica gel with dichloromethane to remove solid sodium sulfate and copper acetate. The filtrate was concentrated *in vacuo*, and further purified by silica gel column chromatography with 2% diethyl ether/hexanes (R_f ~ 0.5 in 5% Et_2O/hexanes) to give product **1** as yellow solid (15.05 g, 63% yield). Stored in freezer in the dark, but could be weighed out in the light on the benchtop for future use.

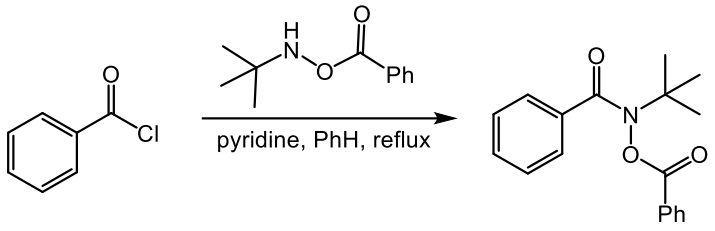
Note: when boronic acid added at beginning, reaction proceeded but a large amount of boronic-acid derived homodimer seen; pre-mixing and adding in boronic acid later reduced this byproduct and increased product yield

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.82 (s, 1H), 7.33 (m, 1H), 7.27 (m, 4H), 4.83 (d, 1H), 4.76 (d, 1H), 1.69 (s, 9H)

^{13}C NMR (151 MHz, $CDCl_3$) 169.4, 160.6, 138.2, 132.0, 131.3-130.6 (q, CF_3), 129.4, 128.3, 127.3 (d), 125.6-120.2 (q), 125.1, 123.3 (p), 87.3, 64.2, 27.5

^{19}F NMR (376 MHz, $CDCl_3$) δ –63.0

HRMS (HESI) Exact mass calcd for $C_{21}H_{19}F_6NO_2H$ $[M+H]^+$, 432.1398. Found 432.1387.



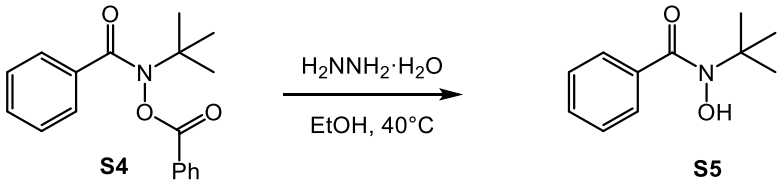
S4

N-(*tert*-butyl)-O-benzoyl-phenyl-hydryoxyamide (S4): To a flame dried round bottom flask with stir bar was added benzoyl chloride (0.82 mL, 7.1 mmol), benzene (20 mL), and benzoylhydroxylamine (**S1**) (1.5 g, 7.8 mmol). Pyridine was added (1.4 mL, 17 mmol), the flask was equipped with condenser, brought to reflux overnight. At end of the reaction, mixture was allowed to cool to room temperature, diluted with diethyl ether, pyridinium salt filtered off. Filtrate was transferred to separatory funnel, washed with 1 M hydrochloric acid (2 X 100 mL), water, dried over $MgSO_4$, filtered and concentrated to afford product **S4** as white solid (2.1 g, 99% yield). Used directly in next step.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (dm, 2H), 7.56 (m, 3H), 7.40 (m, 2H), 7.26 (m, 3H), 1.62 (s, 9H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 165.5, 136.1, 133.9, 129.9, 129.6, 128.6, 127.8, 127.1, 126.8, 63.0, 27.6

HRMS (HESI) Exact mass calcd for $C_{18}H_{19}NO_3H$ $[M+H]^+$, 298.1443. Found 298.1433.



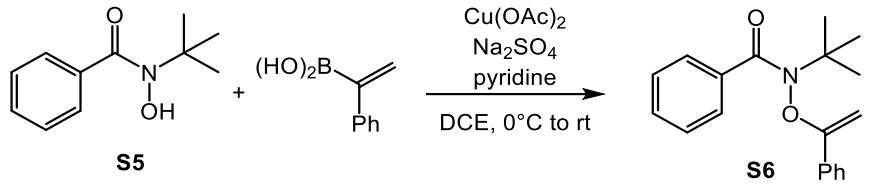
S4 **S5**

N-(*tert*-butyl)-phenyl-hydryoxyamide (S5): To a large round bottom flask with magnetic stir bar was added O-benzoylhydroxyamide **S4** (2.11 g, 7.10 mmol), dissolved in ethanol (18 mL), reaction capped and sealed with Teflon tape, equipped with N_2 line. Hydrazine monohydrate (2.58 mL, 53.2 mmol) was added dropwise, reaction heated to 40°C for 1.5 hours. At end of the reaction, mixture was let cool to room temp, reaction concentrated *in vacuo*, purified by silica gel column chromatography (15% EtOAc/hexanes, R_f = 0.10) to afford hydroxyamide product **S5** (0.90 g, 66% yield). Used directly in next step.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (br s, 1H), 7.38 (m, 3H), 7.28 (m, 2H), 1.37 (s, 9H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 136.3, 129.8, 127.8, 127.6, 61.6, 28.0

HRMS (HESI) Exact mass calcd for $C_{11}H_{15}NO_2H$ $[M+H]^+$, 194.1181. Found 194.1174.



S5 **S6**

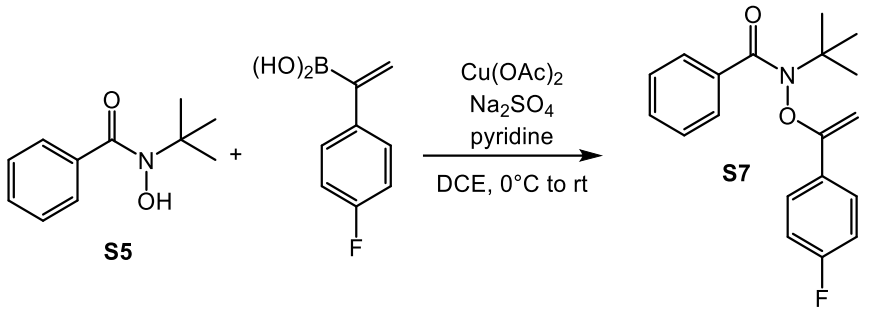
N-(*tert*-butyl)-O-(1-phenylvinyl)-phenyl- hydryoxyamide (S6): Procedure adapted from report by Rovis and coworkers (*2*). To a large, dry round bottom flask with stir bar was added copper acetate (848 mg, 4.67 mmol), sodium sulfate (2.65 g, 18.7 mmol), hydroxamic acid **S5** (0.902 g, 4.67 mmol). Mixture was left open to ambient atmosphere; 1,2-dichloroethane was added (80 mL) to make a slurry, mixture cooled to 0°C. Flask covered with aluminum foil, hood lights turned off. Pyridine added (1.10 mL, 14.0 mmol), mixture let come to room temperature overnight. Next morning, 1,1-phenylvinylboronic acid (1.38 g, 9.34 mmol) was added, reaction let stir at room temperature under ambient atmosphere, monitored by TLC until no more product being formed (~4 days). At end of the reaction, the mixture was filtered through a short pad of silica gel with dichloromethane to remove solid sodium sulfate and copper acetate. Filtrate concentrated i*n vacuo*, purified by silica gel column chromatography with 2% diethyl ether/hexanes (R_f 0.15 in 5% Et_2O/hexanes) to give product **S6** as yellow solid (0.70 g, 51% yield). Stored in freezer in the dark, but could be weighed out in the light on the benchtop for future use.

Note: when boronic acid added at beginning, reaction proceeded but a large amount of boronic-acid derived homodimer seen; pre-mixing and adding in boronic acid later reduced this byproduct and increased product yield

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, 2H), 7.28 (m, 8H), 4.78 (d, 1H), 4.74 (d, 1H), 1.66 (s, 9H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.4, 160.9, 136.8, 133.1, 129.5, 129.0, 128.1, 127.5, 126.6, 125.6, 87.1, 63.5, 27.8

HRMS (HESI) Exact mass calcd for $C_{19}H_{21}NO_2H$ $[M+H]^+$, 296.1651. Found 296.1651.



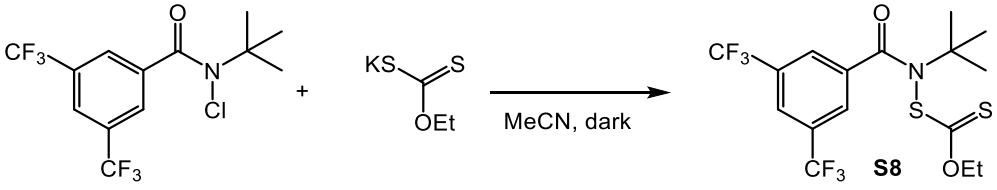
N-(*tert*-butyl)-O-(1-p-fluorophenylvinyl)-phenyl- hydryoxyamide (S7): Boronic acid synthesized by procedure described by Rovis and coworkers (*2*). To a large, dry round bottom flask with stir bar was added copper acetate (640 mg, 3.52 mmol), sodium sulfate (2.00 g, 14.1 mmol), hydroxamic acid **S5** (0.681 g, 3.52 mmol). Mixture was left open to ambient atmosphere; 1,2-dichloroethane added (35 mL) to make a slurry, mixture cooled to 0°C. Flask covered with aluminum foil, hood lights turned off. Pyridine was added (0.85 mL, 10.6 mmol), and the mixture was let come to room temperature overnight. Next morning, 1,1-p-fluorophenylvinylboronic acid (1.17 g, 7.05 mmol) was added, reaction let stir at room temperature under ambient atmosphere, monitored by TLC until no more product being formed (~4 days). At end of reaction, the mixture was filtered through a short pad of silica gel with dichloromethane to remove solid sodium sulfate and copper acetate. Filtrate concentrated i*n vacuo*, purified by silica gel column chromatography with 4% diethyl ether/hexanes to give product **S7** as yellow semisolid (0.28 g, 25% yield). Stored in freezer in the dark, but could be weighed out in the light on the benchtop for future use.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, 2H), 7.31 (m, 3H), 7.17 (dd, 2H), 6.94 (t, 2H), 4.77 (d, 1H), 4.68 (d, 1H), 1.65 (s, 9H)

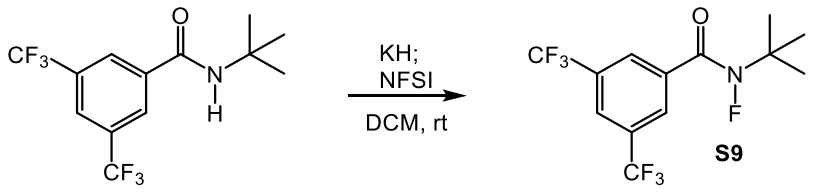
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.5, 163.9, 162.2, 160.1, 136.8, 129.5, 129.2, 129.2, 127.5 (q), 115.1 (d), 87.0 (d), 63.5, 27.7

^{19}F NMR (376 MHz, $CDCl_3$) δ –112.12

HRMS (HESI) Exact mass calcd for $C_{19}H_{21}FNO_2H$ $[M+H]^+$, 314.1556. Found 314.1548.



N-(*tert*-butyl)-N-((ethoxycarbonothioyl)thio)-3,5-bis(trifluoromethyl)benzamide (S8): Compound was prepared according to literature procedures (*3*).

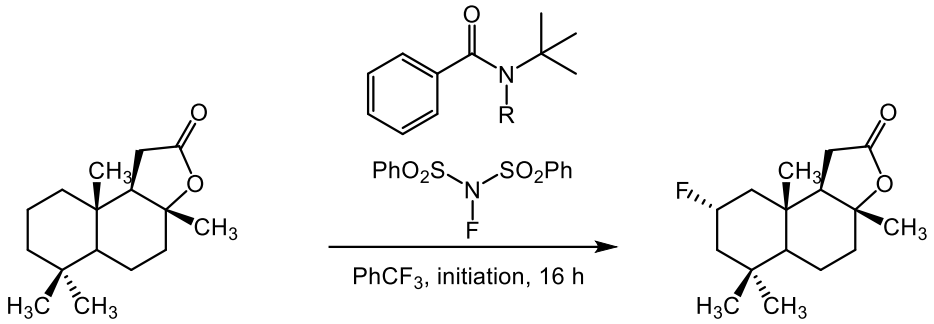


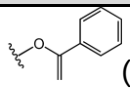
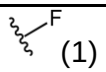
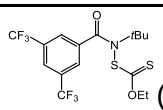
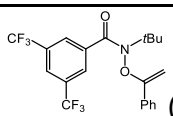
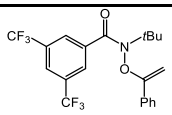
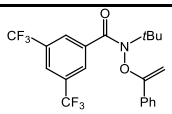
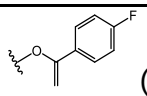
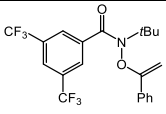
S9

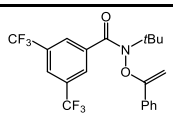
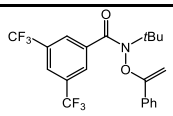
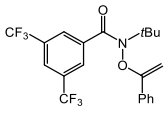
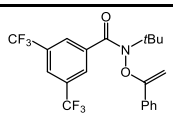
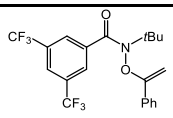
N-(*tert*-butyl)-N-fluoro-3,5-bis(trifluoromethyl)benzamide (S9): Compound was prepared according to literature procedures (*4*).

Reaction Optimization

Table S1. Optimization of C–H Fluorination Reaction



Entry	R group or reagent (equiv)	Equiv NFSI	Initiation	Conc. (M)	Yield (combined yield) (%)*
1	 (1)	2	440 nm BLED	1	22
2	 (1)	2	440 nm BLED	1	0
3	 (1)	2	440 nm BLED	1	0
4	 (1)	2	440 nm BLED	1	65
5	 (2)	2	440 nm BLED	1	64
6	 (2)	4	440 nm BLED	1	67
7	 (1)	2	440 nm BLED	1	22
8	 (2)	2	427 nm BLED	1	30

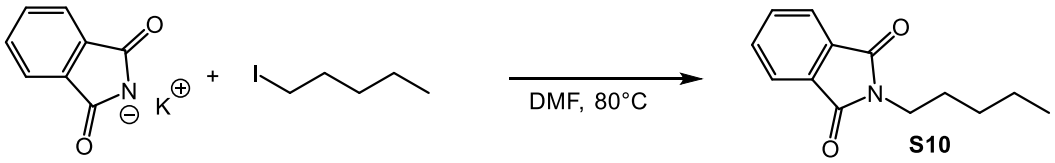
9	 (2)	2	60°C	1	67
10	 (2)	2	70°C	1	74
11	 (2)	2	80°C	1	58
12	 (2)	2	70°C	0.5	57
13[†]	 (2)	2	70°C	1	56

*NMR yield versus hexamethyldisiloxane (HMDS) ^{1}H NMR internal standard

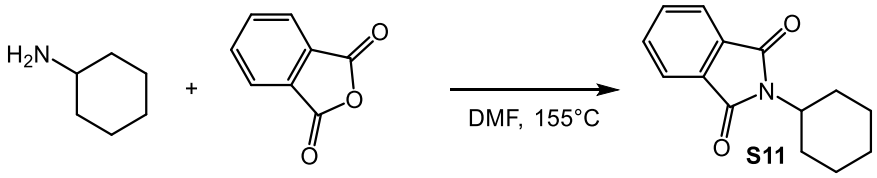
[†]1 mmol reaction scale

Substrate/Trap Synthesis

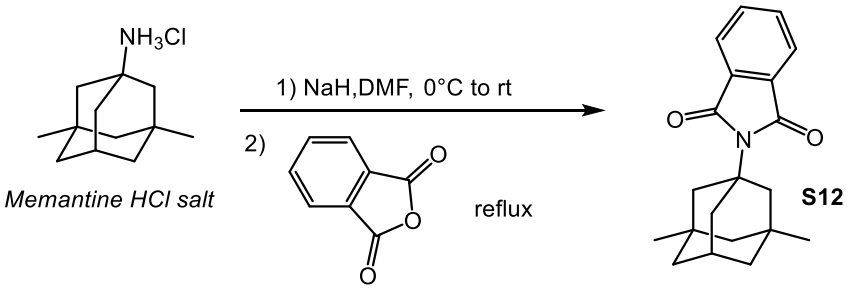
Substrates and traps were commercially available and used without further purification unless otherwise specified.



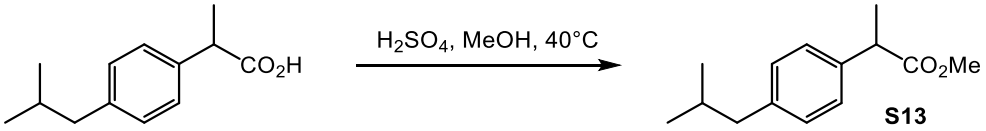
N-Pentyl Phthalimide (S10): Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*5*).



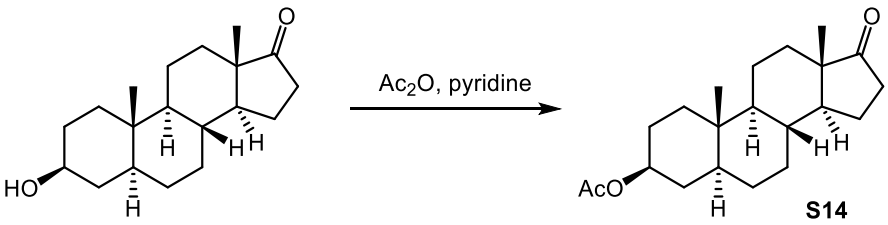
N-Cyclohexyl Phthalimide (S11): Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*5*).



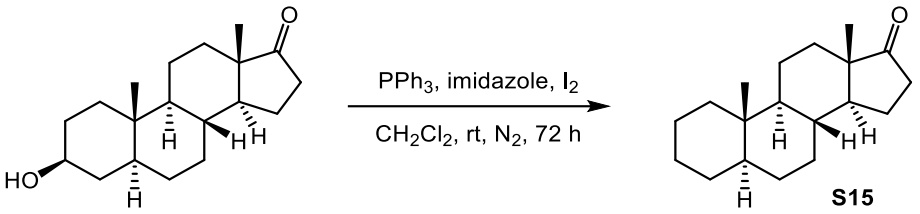
N-Phthalimidyl Memantine (S12): Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*5*).



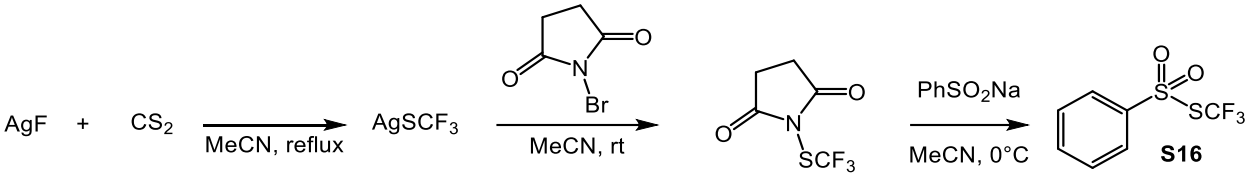
Ibuprofen Methyl Ester (S13): Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*6*).



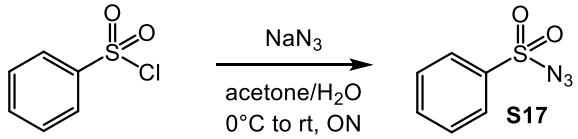
***Trans*-androsterone Acetate (S15):** Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*7*).



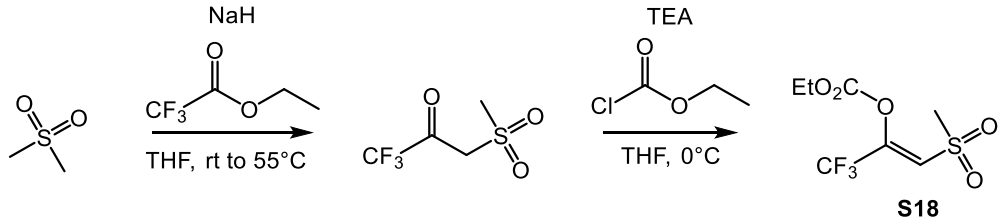
Androstan-17-one (S15): Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*8*).



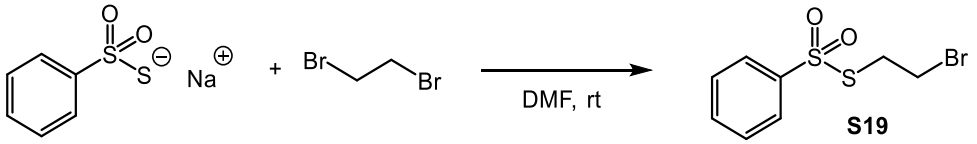
(S)-trifluoromethyl benzenesulfonothionate (S16): Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*9*).



Benzenesulfonyl azide (S17): Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*10*).



Ethyl (3,3,3-trifluoro-1-(methylsulfonyl)prop-1-en-2-yl) carbonate (S18): Compound was prepared in accordance to literature procedure, giving product in accordance with literature values (*11*).



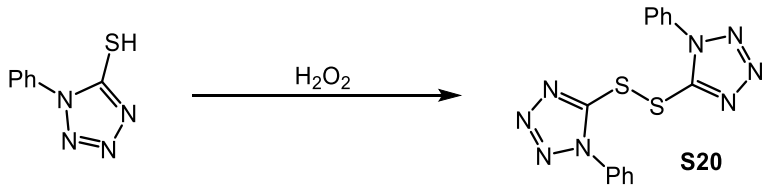
***S*-(2-bromoethyl) benzenesulfonothioate (S20):** To a flame-dried round bottom flask with a stir bar was added benzenethionosulfonic acid sodium salt (3.0 g, 15 mmol). Dry DMF (130 mL) was added, and the mixture was stirred until the salt was completely dissolved. Then, dibromoethane

was added (3.3 mL, 38 mmol). The reaction was stirred at room temperature and was monitored by TLC. After 24 hours, more dibromoethane was added to the reaction (3.3 mL). After 2 days, the reaction was quenched with deionized water. The aqueous mixture was extracted with diethyl ether three times. The organic layer was washed with aqueous sodium bicarbonate and dried with magnesium sulfate. The filtrate was concentrated in vacuo to yield product as a white, flaky solid (1.10 g, 26% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (m, 2H), 7.67 (m, 1H), 7.60 (m, 2H), 3.53 (m, 2H), 3.39 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.4, 134.1, 129.6, 127.0, 37.2, 28.8.

HRMS (APCI) Exact mass calcd for $C_8H_9BrO_2S_2H$ $[M+H]^+$ 280.9306. Found, 280.9300.



S20

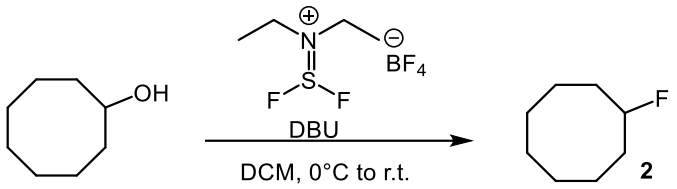
1,2-bis(1-phenyl-1*H*-tetrazol-5-yl)disulfane (S20): Compound was prepared according to a previously reported procedure (*12*). To a round bottom flask equipped with a stir bar was added 1-phenyl-1*H*-tetrazole-5-thiol (17.8 g, 100 mmol), which was dissolved in EtOH (500 mL). The reaction was sealed and placed under N_2 atmosphere. 30% aqueous H_2O_2 (37.0 g, 33.3 ml, 3.26 eq.) was added. After 1 h, the formation of a white precipitate was observed. The reaction was allowed to run overnight for 16 h. At end, reaction was cooled to 0°C, and the white precipitate was collected via filtration with washing by cold diethyl ether. The disulfide was purified via recrystallization from a $CHCl_3$/EtOH mixture (2:3, ~500 ml). The pure product was filtered and obtained as a crystalline white-yellow solid (12.5 g, 70% yield) in accordance with reported spectral data; compound used directly without purification.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (m, 6H), 7.57 (m, 4H)

^{13}C NMR (151 MHz, $CDCl_3$) 151.28, 132.99, 131.09, 130.11, 124.45

HRMS (APCI) Exact mass calcd for $C_{14}H_{10}N_8S_2$ $[M+H]^+$ 355.0548, Found, 355.0539

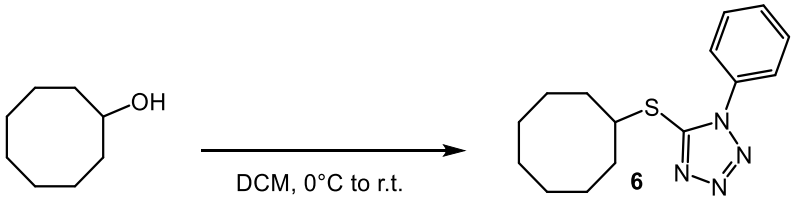
Independent Synthesis of Standards



Cyclooctyl fluoride (2): To a solution of cyclooctanol (0.658 mL, 5.0 mmol) and DBU (1.14 g, 7.5 mmol) in 15 mL DCM at 0°C was added XtalFluor-E (1.72 g, 7.5 mmol). The mixture was stirred 30 minutes at 0°C, then warmed to room temperature and let stir until the disappearance of cyclooctanol was seen by TLC (visualized with CAM stain; note extended reaction times resulted in elimination of fluoride to cyclooctene). At the end of the reaction, the mixture was quenched with 5% $NaHCO_3$ aqueous solution and let stir for 15 minutes. The resulting mixture was extracted 2X with DCM, organics were dried over $MgSO_4$, filtered over a pad of silica, and carefully concentrated (note high volatility of product). Reaction was then purified via column chromatography using a gradient of 0-10% Et_2O/pentanes to afford product **2** as a clear oil, in accordance with literature values (*13*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.75 (dm, 1H), 1.95 (m, 4H), 1.76 (m, 2H), 1.60 (m, 8H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 95.4, 94.3, 32.2, 32.1, 27.2, 25.1, 22.1, 22.0

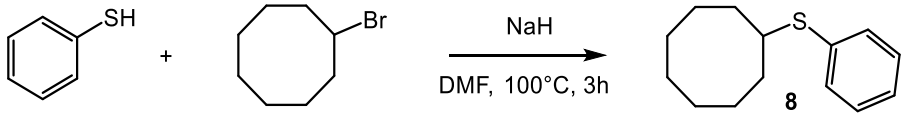


5-(cyclooctylthio)-1-phenyl-1H-tetrazole (6): To a flame dried round bottom flask with stir bar was added cyclooctanol (641 mg, 0.658 ml, 5.00 mmol), triphenylphosphine (1.44 g, 5.50 mmol, 1.1 eq), and 5-mercapto-1-phenyltetrazole (980 mg, 5.50 mmol, 1.1 eq). THF (25 ml) was added and the solution was cooled to 0°C. DIAD (1.11 g, 1.07 ml, 5.50 mmol, 1.1 eq) was added dropwise to the mixture and the reaction was allowed to warm to room temperature and stir for 12 hrs. Upon completion of the reaction, the reaction mixture was concentrated and dry loaded onto silica and purified by column chromatography (gradient of 2% to 5% ether/pentanes) to afford the pure thioether (531 mg, 1.84 mmol, 37% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (m, 5H), 4.22 (m, 1H), 2.16 (m, 2H), 1.87 (m, 2H), 1.75 (m, 2H), 1.63 (m, 5H), 1.53 (m, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 133.9, 130.1, 129.8, 124.0, 49.2, 32.3, 27.0, 25.7, 25.0

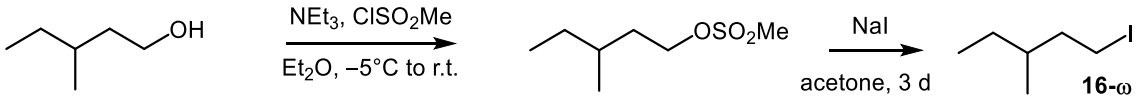
HRMS (APCI) Exact mass cacld for $C_{15}H_{20}N_4S$ $[M+H]^+$ 289.1487. Found, 289.1478



Cyclooctyl phenyl thioether (8): Compound was prepared according to literature procedure, and purified by silica gel chromatography with a gradient of 0% to 10% EtOAc in hexanes. Spectral data in accordance with literature values (*14*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, 2H), 7.31 (t, 2H), 7.22 (t, 1H), 3.42 (m, 1H), 1.99 (m, 2H), 1.78 (m, 2H), 1.70 (m, 2H), 1.56 (m, 8H)

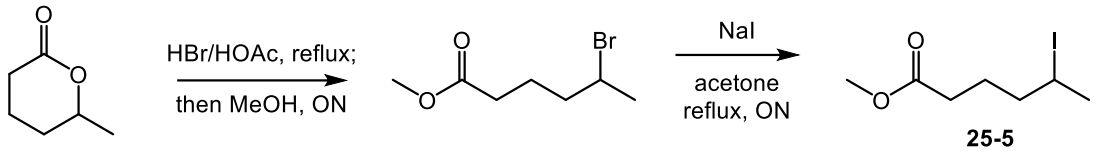
^{13}C NMR (151 MHz, $CDCl_3$) δ 136.1, 131.3, 128.8, 126.4, 47.6, 31.9, 27.1, 25.8, 25.1



3-methyl-1-iodo-pentane (16-ω): To a solution of 3-methyl-1-pentanol (0.704 mL, 5.68 mmol) and triethylamine (1.58 mL, 11.4 mmol) in 25 mL diethyl ether at –5°C was added mesyl chloride dropwise (0.531 mL, 6.81 mmol). The mixture was warmed to room temperature, let stir one hour. At the end of the reaction, the mixture was quenched with saturated $NaHCO_3$ solution and layers were separated. Aqueous layer was extracted 2X with diethyl ether. Combined organics were washed with 1M HCl, water, brine, and dried over $MgSO_4$, filtered and concentrated to afford product as a clear, colorless oil. Product (1.02 g, 5.68 mmol) was then dissolved in 20 mL acetone, sodium iodide added (2.95 g, 19.7 mmol), and let stir 3 days at room temperature. At the end of the reaction, solvent mostly removed *in vacuo*, residue was taken up in water and extracted 3X with pentanes. Organics were washed with dilute $Na_2S_2O_3$ aqueous solution, brine, dried over $MgSO_4$, filtered and concentrated. Product was purified by Kuglerohr distillation to afford product **16** as a clear, colorless oil with spectral data matching literature values (*15*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.28 (m, 1H), 3.19 (m, 1H), 1.90 (m, 1H), 1.67 (m, 1H), 1.50 (m, 1H), 1.39 (m, 1H), 1.20 (m, 1H), 0.90 (m, 6H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 40.5, 35.4, 28.7, 18.2, 11.1, 5.4

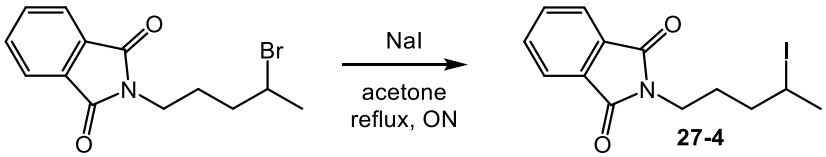


Methyl 5-Iodo-hexanoate (25-5): Adapted from literature precedent (*16*). To a round bottom flask equipped with a condenser was added delta-hexalactone (2.00 g, 17.5 mmol), hydrobromic acid (1.66 mL), acetic acid (3.33 mL). The mixture was heated to 70°C for 4 hours, then let come to room temperature, methanol added (8 mL), let stir at room temperature overnight. At the end of the reaction, the mixture was partially concentrated *in vacuo*, taken up in ethyl acetate, washed 3X with saturated aqueous sodium bicarbonate, brine, dried over $MgSO_4$, filtered and concentrated. Compound was further purified by column chromatography (5% EtOAc in hexanes), yielding alkyl bromide (0.86 g, 4.1 mmol). The bromide product (0.86 g, 4.1 mmol) was added to a flame dried round bottom flask with a stir bar, dissolved in 10 mL acetone, the vessel was charged with sodium iodide (2.16 g, 14.4 mmol), and heated to reflux overnight. At the end of this reaction, mixture was partially concentrated *in vacuo*, residue was taken up in ethyl acetate, washed with saturated aqueous $Na_2S_2O_3$ solution, brine, dried over $MgSO_4$, filtered and concentrated. Purified via silica gel chromatography with 5% EtOAc in hexanes to yield methyl 5-iodo-hexanoate **25-5** (0.470 g, 1.84 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.19 (m, 1H), 3.70 (s, 3H), 2.37 (td, 2H), 1.95 (d, 3H), 1.87 (m, 2H), 1.72 (m, 2H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 51.6, 42.0, 33.0, 29.1, 28.8, 25.1

HRMS (HESI) Exact mass calcd for $C_7H_{13}IO_2H$ $[M+H]^+$, 257.0038. Found 257.0029.



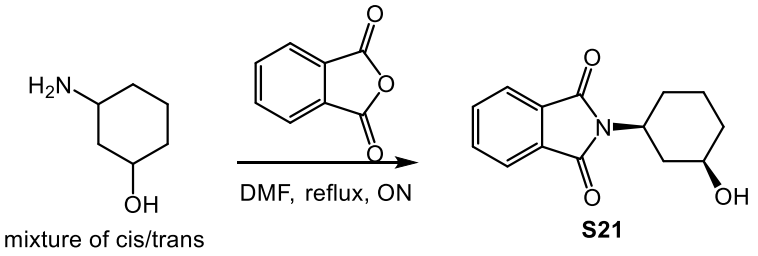
***N*-4-iodopentyl phthalimide (27-4):** Bromide prepared according to literature precedent (*5*). Iodide substitution adapted from literature precedent (*16*). To a flame dried round bottom flask with stir bar was added the alkyl bromide (0.500 g, 1.69 mmol), which was then dissolved in 7 mL acetone. The vessel was charged with sodium iodide (886 mg, 5.91 mmol), equipped with a condenser, and was brought to reflux overnight. At the end of this reaction, mixture was partially concentrated *in vacuo*, residue was taken up in ethyl acetate, washed with saturated aqueous $Na_2S_2O_3$ solution, brine, dried over $MgSO_4$, filtered and concentrated. Purified via column

chromatograph with a gradient of 5% to 20% EtOAc in hexanes to yield *N*-4-iodopentyl phthalimide **27-4** (0.340 g, 0.99 mmol, 59% yield).

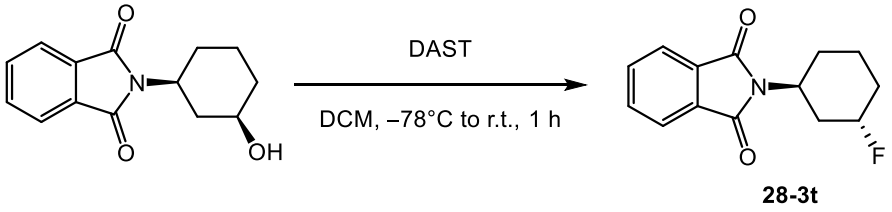
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (m, 2H), 7.74 (m, 2H), 4.22 (m, 1H), 3.74 (t, 2H), 1.93 (d, 3H), 1.95-1.85 (m, 2H), 1.81 (m, 1H), 1.68 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 134.0, 132.0, 123.3, 123.2, 39.7, 36.9, 28.9, 28.9, 28.7

HRMS (HESI) Exact mass calcd for $C_{13}H_{14}INO_2H$ $[M+H]^+$, 344.0147. Found 344.0137.



1,3-oxycyclohexyl phthalimide (S21): To a dried round bottom flask was added aminoalcohol, DMF, and phthalic anhydride. The vessel was equiiped with a condenser and heated to reflux overnight. At the end of the reaction, the mixture was cooled to room temp, diluted with ethyl acetate, and washed 2X with 1M HCl. The aqueous layer was extracted with ethyl acetate, combined organics were dried over $MgSO_4$, filtered and concentrated. The cis/trans isomers were separated by silica gel chromatography (3:1:1 hexanes/DCM/EtOAc). Separate isomers were recrystallized from ethyl acetate to provide product **S21** as a white solid, with spectral data in accordance to literature values (*17*).



1,3-*trans* fluorocyclohexyl phthalimide (28-3t): To a flame dried round bottom flask with stir bar was added aminoalcohol **S21**, DCM, cooled to –78°C. DAST (diethylaminosulfur trifluoride) was added dropwise, cooling bath removed and reaction let stir at room temperature for 1 hour (monitored by TLC for disappearance of alcohol). At end of reaction, quenched by addition of reaction mixture to a dilute, cold solution of aqueous potassium hydroxide. This was then diluted with diethyl ether, layers separated, aqueous layer extracted 1X with ether, organics dried over $MgSO_4$, filtered and concentrated. Reaction gave one fluoride product as major product, which

was assigned to be the *trans* product **28-3t**, formed by an invertive S_N2 mechanism (note: reaction of the *trans* alcohol under the same reaction conditions gave a mixture of *cis* and *trans* fluoride, likely by a competing S_N1 mechanism). The product was further purified by silica gel chromatography.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.73 (m, 2H), 5.07 (dm, 1H), 4.58 (tt, 1H), 2.55 (dtd, 1H), 2.23 (qd, 1H), 2.10 (m, 2H), 1.81 (m, 3H), 1.55 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 133.9, 131.9, 123.1, 89.5 (d), 45.3, 33.9 (d), 29.5 (d), 29.1, 19.7

^{19}F NMR (376 MHz, $CDCl_3$) δ –185.4

HRMS (HESI) Exact mass calcd for $C_{14}H_{14}FNO_2Na$ $[M+Na]^+$, 270.0906. Found 270.0896.

C–H Functionalized Products

General Procedure for Small Molecule C–H Diversification:

Procedure A: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol), alkenylhydroxamate reagent **1** (172.6 mg, 0.400 mmol), and NFSI (0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The reaction was heated to 70°C overnight. At the end of the reaction, mixture was passed through a short pad of silica, concentrated, and crude analyzed by NMR. Products were further purified by silica gel column chromatography.

Procedure B: To a dried 1-dram screw cap vial with stir bar was added benzenesulfonyl azide (0.800 mmol), substrate (0.200 mmol), and alkenylhydroxamate reagent **1** (172.6 mg, 0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial capped and sealed with Teflon tape. The reaction was heated to 70°C overnight. At the end of the reaction, the crude mixture was passed through a short pad of silica, concentrated, and analyzed by NMR. Products were further purified by silica gel column chromatography. *Note: in some cases reaction yields were observed to be higher when reaction was run in the absence of solvent.*

Procedure C: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol) and alkenylhydroxamate reagent **1** (172.6 mg, 0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The corresponding radical trap (0.800 mmol) was added through the septum outside of the glovebox. The reaction was heated to 70°C overnight. At the end of the reaction, mixture was passed through a short pad of silica, concentrated, and crude analyzed by NMR. Products were further purified by silica gel column chromatography.

Procedure D: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol), alkenylhydroxamate reagent **1** (172.6 mg, 0.400 mmol), and the corresponding radical trap (0.800 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The reaction was heated to 70°C overnight. At the end of the reaction, the crude mixture was passed through a short pad of silica, concentrated, and analyzed by NMR. Products were further purified by silica gel column chromatography.

Procedure E: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol), alkenylhydroxamate reagent **1** (172.6 mg, 0.200 mmol), and the corresponding radical trap (0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was

capped and sealed with Teflon tape. Reaction heated to 70°C overnight. At the end of the reaction, mixture was passed through a short pad of silica, concentrated, and crude analyzed by NMR. Products further purified by silica gel column chromatography.

Procedure F: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol), alkenylhydroxamate reagent **1** (172.6 mg, 0.200 mmol), and the corresponding radical trap (0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The reaction was heated to 70°C overnight. At the end of the reaction, crude mixture was passed through a short pad of silica, concentrated, and analyzed by NMR. Products were further purified by silica gel column chromatography.

Procedure G: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol), alkenylhydroxamate reagent **1** (172.6 mg, 0.200 mmol), and NFSI (0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The reaction was heated to 60°C overnight. At the end of the reaction, the crude mixture was passed through a short pad of silica, concentrated, and analyzed by NMR. Products were further purified by silica gel column chromatography.

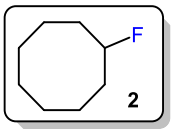
Procedure H: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol), alkenylhydroxamate reagent **1** (172.6 mg, 0.200 mmol), and NFSI (0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The reaction was heated to 60°C overnight. At the end of the reaction, the crude mixture was passed through a short pad of silica, concentrated, and analyzed by NMR. Products were further purified by silica gel column chromatography.

Procedure I: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol) and alkenylhydroxamate reagent **1** (172.6 mg, 0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The corresponding radical trap (0.800 mL) was added through the septum outside of the glovebox. The reaction was heated to 60°C overnight. At the end of the reaction, mixture was passed through a short pad of silica, concentrated, and analyzed by NMR. Products further purified by silica gel column chromatography.

Procedure J: To a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol), alkenylhydroxamate reagent **1** (172.6 mg, 0.200 mmol), and the corresponding radical trap (0.400 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The reaction was heated to 60°C overnight. At the end of

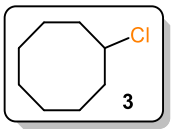
the reaction, the crude mixture was passed through a short pad of silica, concentrated, and analyzed by NMR. Products were further purified by silica gel column chromatography.

Characterization of C–H Diversification Products



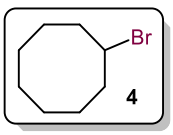
Cyclooctyl fluoride (2): Prepared according to General Procedure G on 0.200 mmol scale with NFSI trap giving 77% GC yield. GC data was obtained using Method 2, and supported by comparison with independently synthesized product.

Compound	Ret Time (min)	Percent area (%)
Fluorocyclooctane	5.975	81.648
Dodecane standard	15.595	18.352



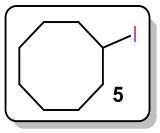
Cyclooctyl chloride (3): Prepared according to General Procedure C on 0.200 mmol scale with CCl_4 trap giving 63% GC yield. GC data was obtained using Method 2, and supported by comparison with work previously done in our lab (*18*).

Compound	Ret Time (min)	Percent area (%)
Chlorocyclooctane	12.513	80.855
Dodecane standard	15.595	19.145

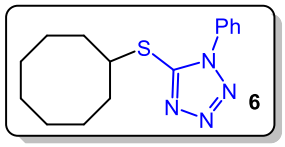


Cyclooctyl bromide (4): Prepared according to General Procedure F on 0.200 mmol scale with $BrCCl_3$ trap giving 62% GC yield. GC data was obtained using Method 3, and supported by comparison to commercially available product.

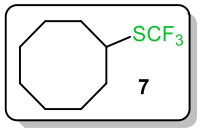
Compound	Ret Time (min)	Percent area (%)
Dodecane standard	12.707	22.359
Bromocyclooctane	13.893	77.641



Cyclooctyl iodide (5): Compound was prepared according to General Procedure C on 0.200 mmol scale with perfluorohexyl iodide trap giving 70% yield by ^1H NMR, with spectral data consistent with literature values (*19*).

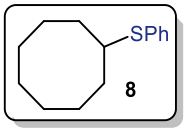


5-(cyclooctylthio)-1-phenyl-1*H*-tetrazole (6): Prepared via a modified general procedure: to a flame dried 1-dram screw cap vial equipped with a stir bar was reagent **1** (176 mg, 0.400 mmol), and disulfide **S21** (283 mg, 0.800 mmol). In an Argon-filled glovebox was added cyclooctane (26.9 µL, 0.200 mmol), chlorobenzene solvent (0.20 mL), and the vial was capped and taped. The reaction was heated to 80°C and stirred overnight. Reaction was passed through a silica plug and further analyzed, giving 78% NMR yield, in accordance with independently synthesized product. The crude residue was purified using flash column chromatography on silica (1–5% Et_2O in Hexanes) to afford pure **6** as a white solid, isolated with a minor inseparable impurity.



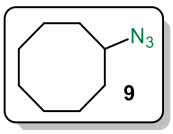
Cyclooctyl(trifluoromethyl)sulfane (7): Prepared via a modified procedure: to a dried 1-dram screw cap vial with stir bar was added substrate (0.200 mmol), vinylhydroxyamide reagent **1**

(172.6 mg, 0.200 mmol), and $PhSO_2SCF_3$ trap (0.200 mmol). In an Argon-filled glovebox was added trifluorotoluene solvent (0.20 mL), and the vial was capped and sealed with Teflon tape. The reaction was heated to 70°C overnight. At the end of the reaction, the crude mixture was purified away from byproducts overlapping in NMR via silica gel chromatography using 2% ethyl acetate in pentanes, and analyzed to give 76% yield by ^{1}H NMR. Spectral data is consistent literature values (*20*).

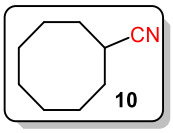


Cyclooctyl phenyl sulfide (8): Prepared according to General Procedure E on 0.200 mmol scale with $PhSO_2SPh$ trap giving 44% GC yield. GC data was obtained using Method 4, and supported by comparison to independently synthesized product.

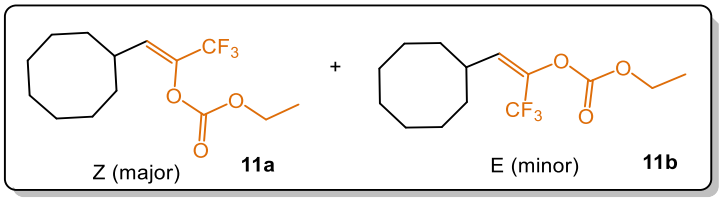
Compound	Ret Time (min)	Percent area (%)
Dodecane standard	5.024	15.704
Cyclooctyl Phenyl Thioether	10.629	85.296



Cyclooctyl azide (9): Compound was prepared according to General Procedure B on 0.200 mmol scale with $PhSO_2N_3$ trap giving 84% yield by ^{1}H NMR, with spectral data consistent with literature values (*21*).



Cyclooctanecarbonitrile (10): Compound was prepared according to General Procedure D on 0.200 mmol scale with p-toluenesulfonyl cyanide trap giving >95% yield by ^{1}H NMR, with spectral data consistent with literature values (*22*).



1-cyclooctyl-3,3,3-trifluoroprop-1-en-2-yl ethyl carbonate (11): Prepared according to General Procedure D on 0.200 mmol scale with vinyl trap giving 70% yield by ^{1}H NMR as 6:1 mixture of E:Z isomers. Isomers assigned based off of previous work done by Zard (*11*).

Major (E) isomer (**11a**):

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.99 (d, 1H), 4.33 (q, 2H), 2.50 (m, 1H), 1.75-1.45 (m, 14H), 1.39 (t, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.2, 131.9 (q), 120.0, 119.0, 65.6, 34.3, 30.8, 26.9, 26.1, 24.9, 14.1

^{19}F NMR (376 MHz, $CDCl_3$) δ –70.5

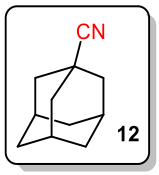
Minor (Z) isomer (**11b**):

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.96 (p, 1H), 4.28 (m, 2H), 2.44 (m, 2H), 2.22 (d, 1H), 2.00 (m, 2H), 1.75-1.45 (m, 9H), 1.36 (t, 3H)

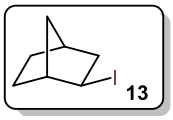
^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 132.7 (q), 122.7, 117.2, 65.0, 46.4, 40.3, 38.7, 35.0 (d), 31.8 (d), 24.8 (d)

^{19}F NMR (376 MHz, $CDCl_3$) δ –73.8

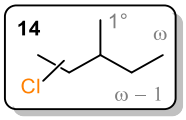
HRMS (HESI) Exact mass calcd for $C_{14}H_{21}F_3O_3Na$ $[M+Na]^+$, 317.1340. Found 317.1329.



1-adamantanecarbonitrile (12): Compound was prepared according to General Procedure D on 0.200 mmol scale with p-toluenesulfonyl cyanide trap giving 64% yield by ^{1}H NMR as an average of two experiments. Spectral data is consistent literature values (*22*).

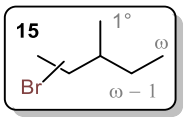


2-iodo-bicyclo[2.2.1]heptane (13): Compound was prepared according to General Procedure C on 0.200 mmol scale with perfluorohexyl iodide trap giving 56% yield by ^{1}H NMR, with spectral data consistent with literature values (*23*).



3-methyl-chloro-pentane (14): Prepared according to General Procedure I on 0.200 mmol scale with CCl_4 trap giving 64% GC yield. GC data was obtained using Method 1, and supported by comparison with independently synthesized product.

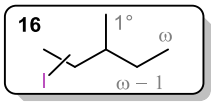
Product	Retention time (min)	Peak Area (%)
3°	3.697	6.2
ω-1	4.123	32.8
ω-1 (diastereomer)	4.209	31.8
1°	4.884	3.8
ω	4.987	25.5



3-methyl-bromo-pentane (15): Prepared according to General Procedure I on 0.200 mmol scale with $BrCCl_3$ trap giving 62% GC yield. GC data was obtained using Method 1, and supported by comparison with independently synthesized product.

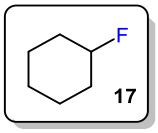
Product	Retention time (min)	Relative Area (%)
3°	6.063	1.0

ω-1	6.670	31.1
ω-1 (diastereomer)	6.846	30.1
1°	7.690	5.9
ω	7.926	31.9



3-methyl-iodo-pentane (16): Prepared according to General Procedure I on 0.200 mmol scale with perfluorohexyl iodide trap giving 54% GC yield. GC data was obtained using Method 2, and supported by comparison with previously published work and independently synthesized terminal product.

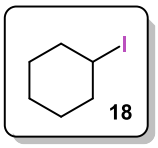
Product	Retention time (min)	Relative Area (%)
3°	3.958	1.7
ω-1	5.046	31.5
ω-1 (diastereomer)	5.185	31.4
1°	5.674	3.7
ω	5.885	31.7



Cyclohexyl fluoride (17): Prepared according to General Procedure A on 0.200 mmol scale with NFSI trap giving 50% GC yield. GC data was obtained using Method 1, and supported by comparison to commercially available product.

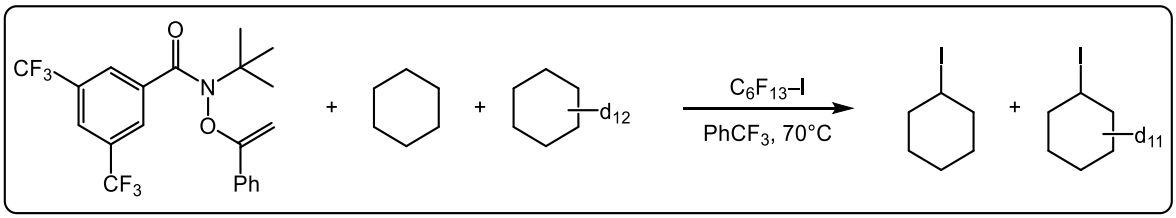
Compound	Ret Time (min)	Percent area (%)

Fluorocyclohexane	2.83	70.484
Dodecane standard	25.0	29.516

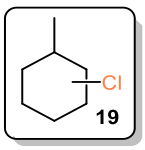


Cyclohexyl iodide (18): Prepared according to General Procedure C on 0.200 mmol scale with perfluorohexyl iodide trap giving 63% GC yield. GC data was obtained using Method 3, and supported by comparison to commercially available product.

Compound	Ret Time (min)	Percent area (%)
Iodocyclohexane	7.457	72.626
Dodecane standard	12.707	27.374

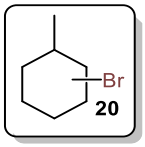


Competition Experiment: To a flame dried 1 dram vial with stir bar was added alkenylhydroxamate reagent **1** (172 mg, 0.400 mmol). In the glovebox, reagent was dissolved in $PhCF_3$ (0.20 mL), and cyclohexane (216 µL, 2.00 mmol) and cyclohexane-d12 (216 µL, 2.00 mmol) were added. The mixture was heated to 70°C for 15 minutes, and then diluted with CH_2Cl_2, passed through a short silica plug, and analyzed by GCMS using an Agilent 7820A GC System with an Agilent 5977E MSD to determine the ratio of non-deuterated to deuterated product (k_H/k_D=6.4).



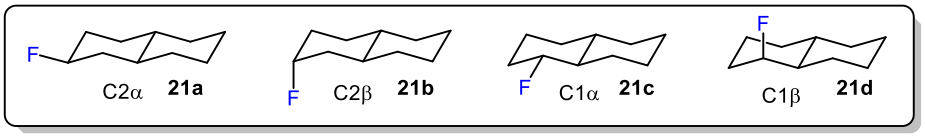
Methylcyclohexyl-chloride (19): Prepared according to General Procedure C on 0.200 mmol scale with CCl_4 trap giving 56% yield of secondary chloride products by NMR. Selectivity data was obtained by GC using Method 2, and supported by comparison with previously published worked from our laboratory (*18*).

Peak	Retention Time (min)	Rel % Area
3°	4.009	3.2
3-cis, 2-trans	4.58	46.1
4-trans	4.73	26.9
3-trans	4.82	12.2
4-cis	5.06	10.0
2-cis	5.95	1.6

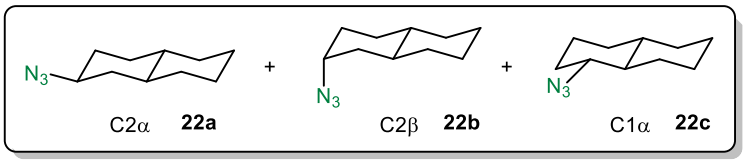


Methylcyclohexyl-bromide (20): Prepared according to General Procedure C on 0.200 mmol scale with $BrCCl_3$ trap giving 76% combined GC yield. GC data was obtained using Method 2, and supported by comparison with previously published worked from our laboratory (*5*).

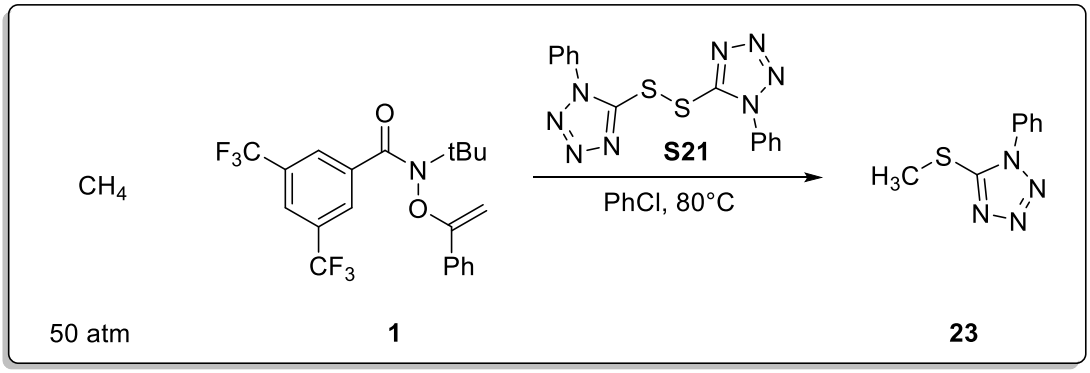
Peak	Retention Time (min)	Rel % Area
3°	6.185	0.8
3-cis, 4-trans	7.007	45.3
3-trans	7.243	29.1
4-cis	7.373	13.8
2-cis	7.766	11.0



Fluoro-*trans*-decalin (21): Compound was prepared according to General Procedure A on 0.200 mmol scale with NFSI trap giving 50% combined yield by ^{19}F NMR (1-bromo-4-fluorobenzene added as internal standard). Regioisomers were assigned by comparison to known literature values: 5% C2α **21a** (^{19}F NMR: –167.8 ppm), 17% C2β **21b** (–183.0 ppm), 16% C1α **21c** (–177.3 ppm), 12% C1β **21d** (–196.6), with spectral data consistent with literature values (*24*).



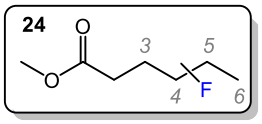
Azido-*trans*-decalin (22): Compound was prepared according to General Procedure B on 0.200 mmol scale with $PhSO_2N_3$ trap giving 50% combined yield by ^{1}H NMR (15% C2α **22a** by tt at 3.26 ppm, 17% C2β **22b** by p at 3.94 ppm, 18% C1α **22c** by m at 3.85 ppm), and spectral data consistent with literature values (*25*).



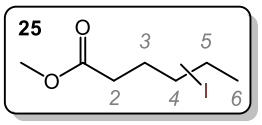
5-(methylthio)-1-phenyl-1H-tetrazole (23): To a Parr bomb under argon atmosphere, alkenylhydroxamate reagent **1** (433 mg, 0.500 mmol) and disulfide **S21** (708 mg, 1.00 mmol) were added and dissolved in PhCl (0.50 ml). The bomb was sealed prior to removal from the glovebox. The bomb was purged with methane twice carefully so as to not expose to air prior to pressurizing at 50 atm. The reaction was heated to 80°C and stirred overnight. Upon completion of the reaction, the bomb was allowed to cool to room temperature. The reaction mixture was filtered and concentrated under reduced pressure, giving the product in a 20% yield (^{1}H NMR, δ2.83, s, 3H) (*26*).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (m, 5H), 2.85 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 133.6, 130.0, 129.7, 123.6, 15.3

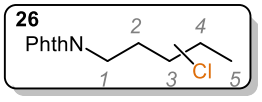


Fluoro-methyl-hexanoate (24): Compound was prepared according to General Procedure A on 0.200 mmol scale with NFSI trap giving 52% combined yield by ^{19}F NMR as an average of two experiments (1-bromo-4-fluorobenzene added as internal standard). Regioisomers were assigned by comparison to known literature values: 33% yield 5-fluoro (^{19}F NMR: –173.2 ppm) 13% 4-fluoro (–183.9 ppm), <1% 6-fluoro (–219.0 ppm), 6% 3-fluoro (–179.8 ppm, assigned by analogy to previously observed selectivity), with spectral data consistent with literature values (*27*, *28*).



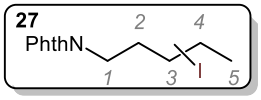
Iodo-methyl-hexanoate (25): Compound was prepared according to General Procedure C on 0.200 mmol scale with perfluorohexyl iodide trap giving 49% combined GC yield. GC data was obtained using Method 3, and supported by comparison with previously published work and independently synthesized 5-iodo product.

Product	Retention time (min)	Relative Area (%)
2	13.665	6.6
3	14.260	13.2
4	15.852	15.8
5	16.617	52.4
6	19.384	11.9



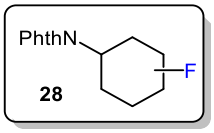
***N*-pentylphthalimidyl chloride (26):** Compound was prepared according to General Procedure C on 0.200 mmol scale with CCl_4 trap giving 66% combined yield by ^1H NMR. GC data was obtained using Method 2 and used to evaluate selectivity, and was supported by comparison with previously published work (*18*).

Product	Retention time (min)	Relative Area (%)
1	-	-
2	-	-
3	11.389	5.0
4	11.951	81.1
5	12.779	13.9

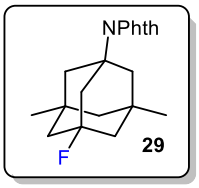


***N*-pentylphthalimidyl iodide (27):** Compound was prepared according to General Procedure C on 0.200 mmol scale with perfluorohexyl iodide trap giving 53% combined GC yield. GC data was obtained using Method 4, and supported by comparison with previously published work and independently synthesized 4-iodo product.

Product	Retention time (min)	Relative Area (%)
1	-	-
2	-	-
3	13.505	7.0
4	14.618	79.4
5	17.067	13.6



***N*-cyclohexylphthalimidyl fluoride (28):** Compound was prepared according to General Procedure H on 0.200 mmol scale with NFSI trap giving 70% combined yield by ^{19}F NMR (1-bromo-4-fluorobenzene added as internal standard). Regioisomers were assigned by comparison to literature values and independent synthesis: 4% 4-trans (^{19}F NMR: –172.2 ppm), 12% 4-cis (–185.7 ppm), 40% 3-trans (–185.5 ppm), 14% 3-cis (–169.3 ppm) (*29*).



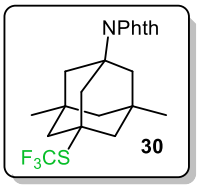
3-fluoro-*N*-phthalimidyl memantine (29): Compound was prepared according to General Procedure A on 0.200 mmol scale with NFSI trap giving 68% yield by ^{1}H NMR. Product further purified via silica gel column chromatography using ethyl acetate/hexanes (R_f = 0.5 in 15% ethyl acetate in hexanes, slightly UV active and stains with $KMnO_4$).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.71 (m, 2H), 2.61 (d, 2H), 2.14 (dd, 4H), 1.65 (dm, 4H), 1.22 (dm, 2H), 1.03 (s, 6H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 133.9, 131.7, 122.7, 49.0, 47.6 (d), 44.9, 43.7, 34.8, 34.7, 29.2

^{19}F NMR (376 MHz, $CDCl_3$) δ –135.70

HRMS (HESI) Exact mass calcd for $C_{20}H_{22}FNO_2Na$ $[M+Na]^+$, 350.1532. Found 350.1521.



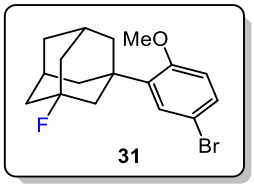
3-trifluoromethlthio-*N*-phthalimidyl memantine (30): Compound was prepared according to General Procedure D on 0.200 mmol scale with $PhSO_2SCF_3$ trap giving >95% yield by ^{1}H NMR as an average of 2 experiments. Compound further purified via silica gel column chromatography using 38:1:1 hexanes:ethyl acetate:DCM (R_f = 0.2 in solvent mixture).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.71 (m, 2H), 2.70 (br s, 2H), 2.20 (dd, 4H), 1.75 (dd, 4H), 1.28 (m, 2H), 1.01 (s, 6H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 133.9, 131.7, 122.7, 61.5, 51.3, 48.8, 48.3, 44.7, 44.1, 34.1, 29.6

^{19}F NMR (376 MHz, $CDCl_3$) δ –33.9

HRMS (HESI) Exact mass calcd for $C_{21}H_{22}F_3NO_2SNa$ $[M+Na]^+$, 432,1221. Found 432.1209.



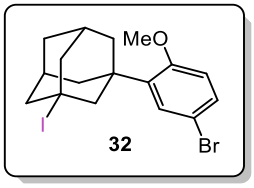
(5S)-1-(5-bromo-2-methoxyphenyl)-3-fluoroadamantane (31): Compound was prepared according to General Procedure A on 0.200 mmol scale with NFSI trap giving 72% yield by ^{1}H NMR. Compound was further purified by silica gel chromatography using 78/1/1 pentanes/DCM/Et_2O.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (dd, 1H), 7.29 (d, 1H), 6.77 (d, 1H), 3.84 (s, 3H), 2.40 (br s, 2H), 2.23 (d, 2H), 2.00 (br s, 4H), 1.95 (br s, 4H), 1.66 (m, 2H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 138.1, 129.9, 129.6, 113.3, 113.2, 93.9, 92.7, 55.2, 45.1 (d), 42.1 (d), 41.5 (d), 38.8 (d), 35.2 (d), 31.5 (d)

^{19}F NMR (376 MHz, $CDCl_3$) δ –129.6

HRMS (EI) Exact mass calcd for $C_{17}H_{20}BrFOH$ $[M+H]^+$, 339.0760. Found 338.0711.

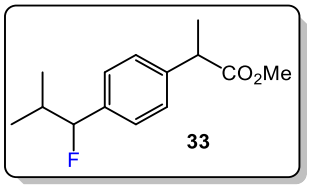


(5S)-1-(5-bromo-2-methoxyphenyl)-3-iodoadamantane (32): Compound was prepared according to General Procedure C on 0.200 mmol scale with perfluorohexyl iodide trap giving >95% yield by ^{1}H NMR. Compound was further purified by silica gel chromatography using 78/1/1 hexanes/DCM/EtOAc.

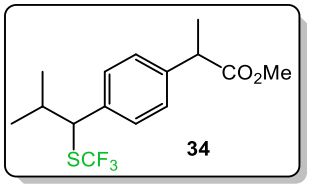
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (dd, 1H), 7.26 (d, 1H), 6.76 (d, 1H), 3.85 (s, 3H), 2.96 (s, 2H), 2.66 (d, 4H), 2.23 (d, 2H), 2.12 (br s, 2H), 2.05 (d, 2H), 1.83 (br s, 2H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 138.0, 129.9, 129.4, 113.3, 113.2, 55.3, 54.2, 51.7, 50.6, 41.9, 38.5, 35.0, 33.1

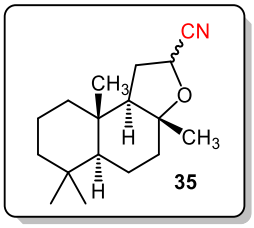
HRMS (APCI) Exact mass calcd for $C_{17}H_{20}BrIOH$ $[M+H]^+$, 446.9820. Found 446.9808.



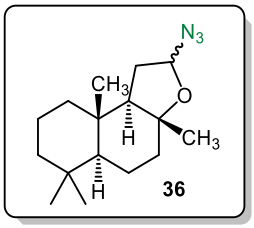
Methyl 2-(4-(1-fluoro-2-methylpropyl)phenyl)propanoate (33): Compound was prepared according to General Procedure H on 0.200 mmol scale with NFSI trap giving 67% yield (>20:1 rr) by ^{1}H NMR as an average of 2 experiments, with spectral data consistent with literature values (*30*).



Methyl 2-(4-(1-trifluoromethylthio-2-methylpropyl)phenyl)propanoate (34): Compound was prepared according to General Procedure J on 0.200 mmol scale with $PhSO_2SCF_3$ trap giving 48% yield by ^{1}H NMR, and with spectral data consistent with literature values (*31*).

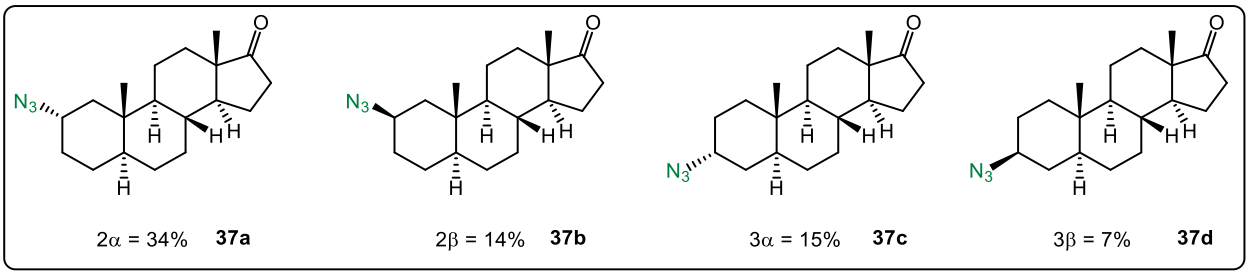


(3aR,9aS,9bR)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan-2-carbonitrile (35): Compound was prepared according to General Procedure D on 0.200 mmol scale with p-toluenesulfonyl cyanide trap giving 84% yield as a 1.3:1 mixture of diastereomers by ^{1}H NMR, and with spectral data consistent with literature values (*22*).



36

(3aR,9aS,9bR)-2-azido-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan (36): Compound was prepared according to General Procedure B on 0.200 mmol scale with $PhSO_2N_3$ trap giving 56% yield by ^1H NMR (1.5:1 mix of diastereomers), and with spectral data consistent with literature values (*21*).



(2S,5S,8R,9S,10S,13S,14S)-2-azido-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (37a): Compound was prepared according to General Procedure B on 0.200 mmol scale with $PhSO_2N_3$ trap giving 70% combined yield by ^1H NMR. Regioisomers were assigned by comparison to known literature values and by NMR analysis: 34% 2α **37a** (^1H NMR: 3.14 (dtd)), 14% 2β **37b** (3.41, m), 15% 3α **37c** (3.91, m)[68], 7% 3β **37d** (3.30, m)(*32*). Product isomers were slightly separable by silica gel chromatography (10% ethyl acetate in hexanes) yielding the major product as a slight mixture of 2α, 2β, and 3α regioisomers.

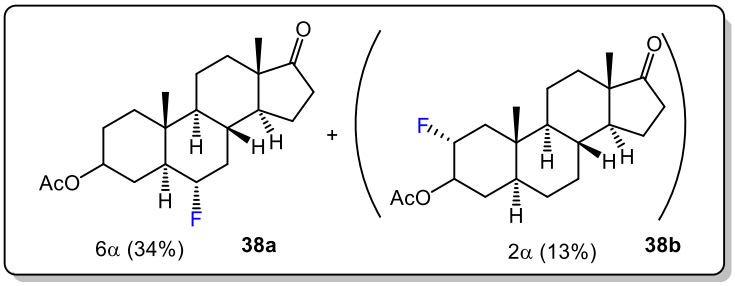
Structural assignment: the major product peak presents as a doublet of triplet of doublets (J = 20.1, 11.4, 4.4 Hz), suggesting it is coupled to 4 protons (2 presenting the same J value and 2 presenting different J values); assuming this does not arise from long range coupling (typified by J values of 1-3 Hz), this eliminates sites of functionalization α to tertiary and quaternary centers and limits possible sites of functionalization to the 2 and 3 positions. As spectrum does not match known literature values for either azidation product at the 3 position (seen separately in the crude NMR), the major product must be at the C2 position, and is assumed to be the 2α product by comparison to Groves' fluorination of deoxy-androsterone (*32*, *33*).

Major (2α) isomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.14 (dtd, 1H), 2.48 (dd, 1H), 2.20-0.90 (m, 21H), 0.86 (s, 3H), 0.84 (s, 3H)

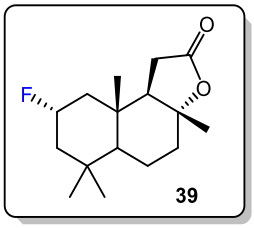
^{13}C NMR (151 MHz, $CDCl_3$) δ 221.1, 61.8, 54.5, 51.3, 47.8, 46.0, 37.5, 35.8, 34.7, 32.1, 31.5, 30.7, 30.3, 27.5, 23.6, 21.7, 20.4, 13.8, 13.1

HRMS (HESI) Exact mass calcd for $C_{19}H_{29}N_3OH$ $[M+H]^+$, 316.2389. Found 316.2380

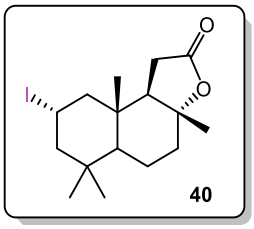


(3S,5S,6S,8R,9S,10R,13S,14S)-6-fluoro-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (38a): Compound was according to General Procedure H on 0.200 mmol scale with NFSI trap giving 47% combined yield by ^{19}F NMR (1-bromo-4-fluorobenzene added as internal standard).

Structural assignment: The major product (6α, **38a**, ^{19}F NMR: –180.6 ppm) was assigned in comparison to previous selectivity observed in our laboratory, along with comparison to literature values to previous characterization of said product.(*3*, *34*) Minor product assigned by comparison to previous selectivity observed in our lab (2α, **38b**, –193.1 ppm). Physical and spectral data is consistent literature values (*34*).



(3aR,8S,9aS,9bR)-8-fluoro-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (39): Compound was prepared according to General Procedure A on 0.200 mmol scale with NFSI trap giving 74% yield by ^{1}H NMR, and with spectral data consistent with literature values (*33*).

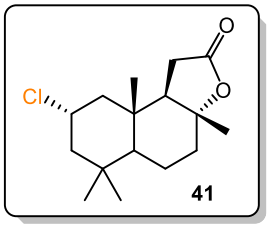


(3aR,8S,9aS,9bR)-8-iodo-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (40): Compound was prepared according to General Procedure C on 0.200 mmol scale with perfluorohexyl iodide trap giving >95% yield by ^{1}H NMR as an average of two experiments. Product further purified via silica gel column chromatography using 5% EtOAc in hexanes (R_f = 0.3 in 15% EtOAc/hexanes, stains with CAM). Noted that the product could be consistently obtained in 65-75% isolated yield upon scaling up to 2.00 mmol sclareolide starting material.

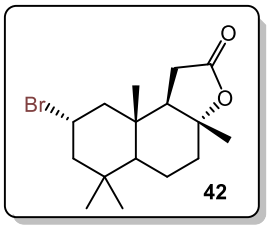
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.58 (tt, 1H), 2.43 (dd, 1H), 2.28 (m, 2H), 2.20 (dm, 1H), 2.12 (dt, 1H), 2.03 (dd, 1H), 1.92 (m, 2H), 1.74 (m, 2H), 1.33 (m, 4H), 1.20 (dd, 1H), 0.98 (s, 3H), 0.95 (s, 3H), 0.91 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.01, 85.7, 58.3, 55.6, 55.5, 52.9, 39.6, 38.4, 37.5, 32.6, 28.5, 22.8, 21.6, 21.0, 20.4, 15.3

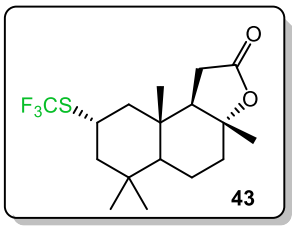
HRMS (HESI) Exact mass calcd for $C_{16}H_{25}IO_2Na$ $[M+Na]^+$, 399.0797. Found 399.0786.



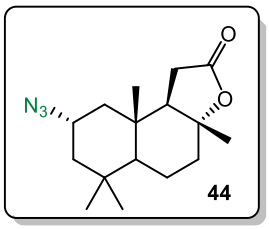
(3aR,8S,9aS,9bR)-8-chloro-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (41): Compound was prepared according to General Procedure C on 0.200 mmol scale with CCl_4 trap giving 71% yield by ^{1}H NMR. The same conditions but initiating using blue LED conditions (2 X Kessil H150 440 nm) and fan cooling showed >95% yield by ^{1}H NMR. Spectral data was consistent literature values (*18*).



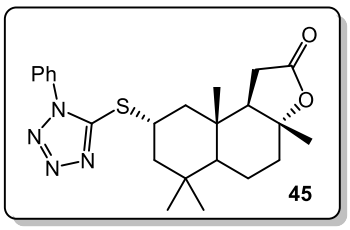
(3aR,8S,9aS,9bR)-8-bromo-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (42): Compound was prepared according to General Procedure C on 0.200 mmol scale with $BrCCl_3$ trap giving 90% yield by ^1H NMR and spectral data consistent with literature values (*5*).



(3aR,8S,9aS,9bR)-8-trifluoromethylthio-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (43): Compound was prepared according to General Procedure D on 0.200 mmol scale with $PhSO_2SCF_3$ trap giving 85% yield by ^1H NMR, and spectral data consistent with literature values (*3*).



(3aR,8S,9aS,9bR)-8-azido-3a,6,6,9a-tetramethyldecahydronaphtho[2,1-b]furan-2(1H)-one (44): Compound was prepared according to General Procedure D on 0.200 mmol scale with $PhSO_2N_3$ trap giving 76% yield by ^1H NMR, and spectral data consistent with literature values (*3*).



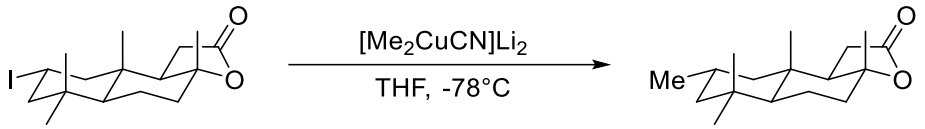
(3aR,8S,9aS,9bR)-3a,6,6,9a-tetramethyl-8-((1-phenyl-1H-tetrazol-5-yl)thio)decahydronaphtho[2,1-b]furan-2(1H)-one (45): Prepared via a modified general procedure: to a flame dried 1-dram screw cap vial equipped with a stir bar was added sclareolide (251 mg, 1.00 mmol), reagent **1** (863 mg, 2.00 mmol), and disulfide **S21** (1.42 g, 4.00 mmol). In an Argon-filled glovebox was added chlorobenzene solvent (1.00 mL), and the vial was capped and taped. The reaction was heated to 80°C and stirred overnight. Crude product was analyzed by ^{1}H NMR giving a 74% yield. The products were further purified by silica gel column chromatography. The crude residue was purified using flash column chromatography on silica (3 DCM: 3 Hexanes: 0.75 Et_2O) to afford pure **45** as a white-yellow solid (285 mg, 67% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (m, 5H), 4.33, (tt, *J*=12.8, 7.4 Hz, 1H), 2.46 (dd, *J*=15.5 Hz, 1H), 2.21 (dd, *J*=22.4, 6.7 Hz, 1H), 2.05 (m, 3H), 1.99 (dd, *J*=22.0, 7.4 Hz, 1H), 1.92 (m, 1H), 1.70 (td, 14.8, 4.2 Hz, 1H), 1.41 (m, 2H), 1.37 (s, 3H), 1.26 (m, *J*=12.4 Hz 2H), 1.14 (dd, 15.3, 3.5 H 1H), 1.10 (s, 3H), 1.01 (s, 3H), 0.98 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.13, 153.60, 133.66, 130.17, 129.80, 124.44, 123.92, 85.93, 58.73, 56.15, 48.19, 46.13, 40.83, 38.47, 37.81, 35.36, 32.88, 28.70, 21.65, 21.21, 20.29, 15.56

HRMS (APCI) Exact mass calcd for $C_{23}H_{30}N_4O_2S$ $[M+H]^+$ 427.2168. Found, 427.2159

Further Derivatization of Functionalized Products



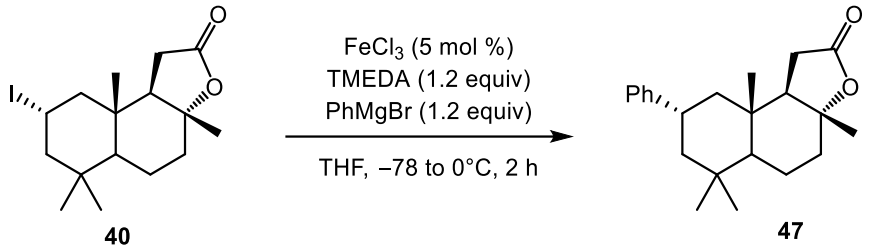
40 **46**

(3aR,9aS,9bR)-3a,6,6,8,9a-pentamethyldecahydronaphtho[2,1-b]furan-2(1H)-one (46): Method adapted from literature procedure (*35*). To a flame dried round bottom flask under argon atmosphere was added CuCN (179 mg, 1 equiv, 2.00 mmol) and THF (10.0 ml). The flask was capped and sealed with Teflon tape prior to removal from the glovebox. This solution was cooled to -78°C and methyllithium (2.50 ml, 1.6 M in Et_2O, 4.00 mmol) was added dropwise. This solution was stirred for 3 hours until it reached a homogenous, tan color. To a separate flame dried vial in the glovebox was added iodosclareolide **40** (37.6 mg, 0.100 mmol) and THF (0.125 ml), and the vial was capped and taped. This solution was cooled to -78°C and 1.00 ml of the $[Me_2CuCN]Li_2$ solution was added dropwise. The reaction was stirred for 3 h before slowly warming to room temperature. The reaction was quenched with saturated aqueous NH_4Cl before the addition of 25% aqueous NH_3, water, and diethyl ether. This solution was stirred for 30 minutes until the organic layer was separated. The aqueous layer was diluted with brine and extracted twice with diethyl ether. The combined organic layers were dried over $MgSO_4$ and concentrated to afford the crude product. The crude residue was purified via silica gel chromatography (10% EtOAc in Hexanes) affording product as a white solid (22.5 mg, 0.086 mmol, 86% isolated (66% isolated overall from sclareolide)).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.41 (dd, *J*=15.3 Hz, 1H), 2.25 (dd, *J*= 22.4, 6.6 Hz 1H), 2.08 (dt, *J*=12.6, 6.6 Hz, 1H), 1.95 (dd, *J*=21.3, 5.9, 1H), 1.88 (m, 1H), 1.81 (tdt, 1H), 1.69 (m, *J*=29.9 Hz, 1H), 1.41 (s, 3H), 1.33 (d, 3H), 1.25 (bs, 1H), 0.99 (dd, *J*=15.5, 2.7 Hz 1H), 0.92 (s, 3H), 0.89 (s, 3H), 0.87 (d, 6.1 Hz, 3H), 0.84 (s, 3H), 0.69 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$) 176.90, 86.43, 59.13, 51.44, 48.43, 38.69, 36.71, 33.75, 33.22, 29.72, 28.74, 23.75, 22.57, 21.63, 21.52, 20.47, 15.88

HRMS (HESI) Exact mass calculated for $C_{17}H_{29}O_2$ $[M+H]^+$ 265.2089. Found 265.2161.



40 47

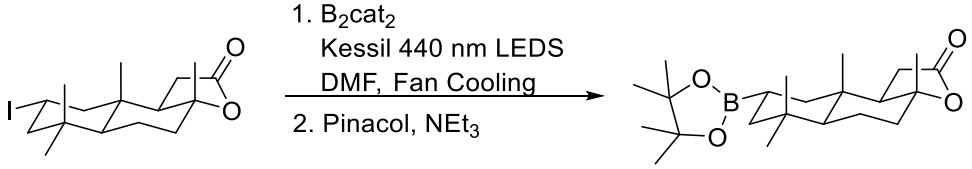
(3aR,8S,9aS,9bR)-3a,6,6,9a-tetramethyl-8-phenyldecahydronaphtho[2,1-b]furan-2(1H)-one (47): Method adapted from literature procedure (*36*). To a flame-dried round bottom flask with a stir bar was added iodosclareolide **40** (94.1 mg, 0.250 mmol), $FeCl_3$ (2.0 mg, 0.0125 mmol), and THF (0.125 mL). The mixture was cooled to –78°C. To this solution was added a mixture of tetramethylethylenediamine (TMEDA) (45.0 µL, 0.300 mmol) and phenylmagnesium bromide (1.0 M, 300 µL, 0.300 mmol) dropwise over 10 minutes. The resulting solution was immersed in an ice bath and let stir at 0°C for 3 hours. At the end of the reaction, the mixture was quenched with saturated aqueous NH_4Cl, the layers were separated, and the aqueous layer was extracted 2X with ether (25 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated. Product was further purified by silica gel column chromatography (10% EtOAc in hexanes) to obtain product as a white solid (47 mg, 58% yield (57% overall from sclareolide).

Structural assignment: coupling constants of benzylic C2 hydrogen peak (J = 12.7, 3.5 Hz) suggest a diaxial hydrogen relationship between C2 and neighboring protons, and allow us to assign the phenyl group as equatorial.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (t, 2H), 7.23 (m, 3H), 3.00 (tt, 1H), 2.44 (dd, 1H), 2.25 (dd, 1H), 2.15 (dt, 1H), 2.07 (dd, 1H), 1.98 (dm, 1H), 1.69 (td, 1H), 1.66 (ddm, 2H), 1.45 (t, 2H), 1.39 (s, 3H), 1.29 (m, 1H), 1.21 (m, 1H), 3.02 (s, 3H), 0.99 (s, 3H), 0.99 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.6, 146.2, 128.5, 127.0, 126.2, 86.2, 59.1, 56.4, 49.9, 47.2, 38.7, 36.9, 35.5, 34.1, 33.1, 28.7, 21.7, 21.3, 20.5, 15.8

HRMS (HESI) Exact mass calcd for $C_{22}H_{30}O_2H$ $[M+H]^+$, 327.2324. Found 327.2315.



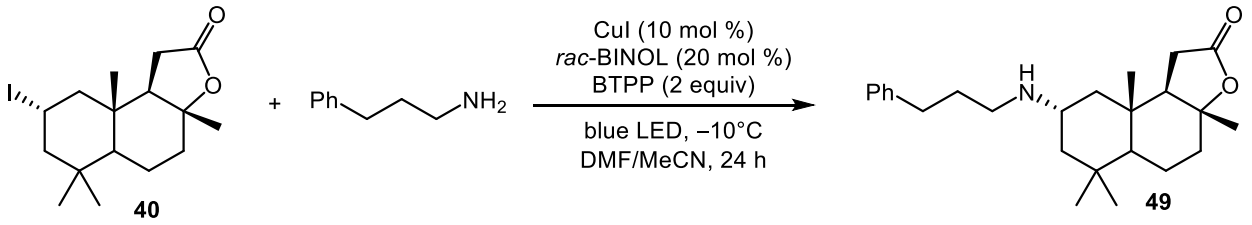
40 48

(3aR,9aS,9bR)-3a,6,6,9a-tetramethyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decahydronaphtho[2,1-b]furan-2(1H)-one (48): Compound prepared from an adapted literature procedure (*37*). To a flame dried vial was added iodosclareolide **40 (**37.6 mg, 0.100 mmol). The vial was brought into the glovebox, and B_2cat_2 (95.1 mg, 4.0 equiv, 0.400 mmol) was added. The mixture was then dissolved in DMF (0.30 mL), capped, and taped. The reaction mixture was irradiated from the side with a Kessil 440 nm BLED positioned 2 cm away from the vial under fan cooling for 24 h. Upon completion of the reaction, a mixture of NEt_3 (0.25 g, 0.350 ml, 25 equiv, 2.5 mmol) and pinacol (47.3 mg, 4.0 equiv, 0.400 mmol) was added. The mixture was stirred for 1 h at room temperature. The reaction solution was poured into water and extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *en vacuo* to afford the crude product. The crude residue was purified via flash column chromatography on silica (2–5% EtOAc in Hexanes) as a white solid (25.2 mg, 67% isolated yield (66% overall from sclareolide)).

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.38 (dd, *J*=15.8 Hz, 1H), 2.28 (dd, *J*=22.4, 5.7 Hz, 1H), 2.06 (dt, *J*=12.9, 6.8 Hz, 1H), 1.95 (dd, *J*=21.3, 6.6 Hz, 1H), 1.87 (m, 1H), 1.67 (td, *J*=29.8, 4.6 Hz, 1H), 1.47 (ddd, 1H), 1.43-1.33 (m, 3H), 1.32 (s, 3H), 1.25 (m, 1H), 1.23 (s, 12H), 1.18 (t, *J*=27.4, 13.7 Hz, 1H), 1.04 (m, 2H), 0.90 (s, 3H), 0.88 (s, 3H), 0.82 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 177.06, 86.53, 83.22, 59.13, 56.55, 43.38, 40.74, 38.86, 36.20, 33.26, 33.09, 28.88, 24.88, 21.72, 20.99, 20.68, 15.26

HRMS (HESI) Exact Mass calculated for $C_{22}H_{38}O_4B$ $[M+H]^+$ 377.2785. Found, 377.2853.



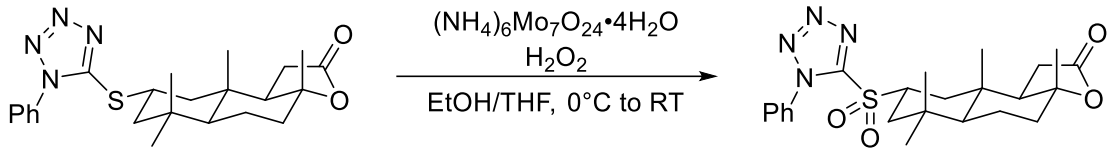
(3aR,8S,9aS,9bR)-3a,6,6,9a-tetramethyl-8-((3-phenylpropyl)amino)decahydronaphtho[2,1-b]furan-2(1H)-one (49): Prepared according to an adapted literature procedure (*38*). To a flame dried vial with a stir bar was added copper iodide (3.8 mg, 0.020 mmol) and *rac*-BINOL (11.4 mg, 0.0400 mmol). In the glovebox was added DMF (0.20 mL), acetonitrile (0.80 mL), and *tert*-butylimino-tri(pyrrolidino)phosphorane (BTPP) (122 µL, 0.400 mmol). The mixture was stirred in the glovebox for 5 minutes. Then, 3-phenyl-1-propylamine (28.4 µL, 0.200 mmol), iodo-sclareolide **40** (75.3 mg, 0.200 mmol) were added. Vial was capped and taped, and thoroughly sealed with

parafilm. The vial was immersed in a cryobath (isopropanol used as solvent) at –10°C and irradiated with 3 Kessil H150 440 nm blue LED lamps for 24 hours (see picture below). At end of the reaction, the mixture was concentrated in vacuo to remove acetonitrile. The resulting residue was taken up in dichloromethane and washed with 30 mL of an aqueous 5% lithium chloride solution. The layers were separated and the aqueous layer was extracted twice more with dichloromethane. The combined organic layers were dried over MgSO4, filtered, and concentrated. ^{1}H NMR analysis showed a 61% yield with reference to HMDS internal standard over an average of two experiments (59% yield overall from sclareolide). The resultant residue was further purified by silica gel chromatography with a solvent system of 20% EtOAc/ 20% MeOH in hexanes, doped with 1% triethylamine, to afford the product **47** as a yellow oil (32 mg, 42% isolated yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, 2H), 7.22 (m, 3H), 2.85 (m, 1H), 2.69 (m, 4H), 2.44 (m, 1H), 2.27 (dd, 1H), 2.11 (dm, 1H), 1.98 (dd, 1H), 1.92 (dm, 1H), 1.86 (m, 2H), 1.77 (dm, 1H), 1.73 (m, 2H), 1.40 (m, 1H), 1.35 (s, 3H), 1.09 (dm, 1H), 1.02 (m, 1H), 0.96 (s, 3H), 0.95 (s, 3H), 0.84 (m, 1H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 141.8, 128.4, 128.3, 125.9, 86.1, 59.0, 56.5, 49.4, 46.4, 38.5, 36.8, 34.1, 33.6, 33.2, 31.8, 29.7, 28.7, 21.7, 21.6, 20.3, 16.1

HRMS (HESI) Exact Mass calculated for $C_{25}H_{37}NO_2H$ $[M+X]^+$ 384.2903. Found, 384.2892.



45 **S22**

(3aR,9aS,9bR)-3a,6,6,9a-tetramethyl-8-((1-phenyl-1H-tetrazol-5-yl)sulfonyl)decahydronaphtho[2,1-b]furan-2(1H)-one (S22): Prepared according to a literature procedure (*39*). To a one-dram vial equipped with a stir bar was added sulfide **44** (85.2 mg, 0.200 mmol) and $(NH_4)_6Mo_7O_{24}•4H_2O$ (24.7 mg, 0.10 equiv). EtOH/THF (1:1, 1.00 ml) was added and the solution was cooled to 0°C. 30% aq. H_2O_2 (82.0 µl, 0.800 mmol, 4.0 equiv) was added and the reaction was allowed to warm to room temperature. The reaction was allowed to stir overnight. Upon completion as monitored by TLC analysis, the solution was cooled to 0°C and quenched with 10% aq. $Na_2S_2O_3$. The solution was diluted with brine and washed with DCM (3×1.00 ml). The combined organic layers were dried over $MgSO_4$, filtered through a short silica plug, and concentrated *en vacuo*. The product was purified via flash column chromatography on silica (3:3:0.75 DCM/hexanes/diethyl ether) (64.2 mg, 70% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (m, 5H), 4.23 (tt, *J*=26.3 Hz, 1H), 2.45 (dd, J=15.9 Hz, 1H), 2.24 (dd, *J*=25.2, 8.5 Hz, 1H), 2.12, dt, *J*=12.6 Hz, 1H), 2.02 (m, 3H), 1.94 (dq, 1H), 1.72, (td, *J*=15.3, 5.8 Hz, 1H), 1.57 (t, *J*=24.7, 12.6 Hz, 1H), 1.45-1.41 (m, 2H), 1.35 (s, 3H), 1.27 (m, 1H), 1.19 (m, 1H), 1.04 (s, 3H), 1.03 (s, 3H), 0.97 (s, 3H)

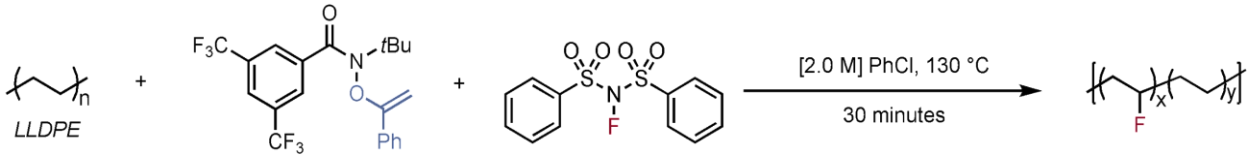
^{13}C NMR (151 MHz, $CDCl_3$) 175.71, 152.82, 133.16, 131.71, 129.86, 125.36, 85.71, 58.62, 58.52, 56.15, 39.01, 38.43, 37.25, 36.93, 34.50, 32.85, 32.88, 28.71, 21.79, 21.30, 20.37, 15.81, 14.2

HRMS (APCI) Exact mass cacld for $C_{23}H_{31}O_4N_4S$ $[M+H]^+$ 459.2066. Found, 459.2056

General Procedure for Functionalization of Polyolefins

General Polymer Procedure I (130 °C): The polyolefin (40 mg, 1.4 mmol) was pre-dissolved in 0.2 mL of chlorobenzene by heating the solution for 30 min at 130 °C under N_2 atmosphere with magnetic stirring. The pre-dissolved polyolefin, amide reagent **1**, and radical trap were then combined in a 1-dram reaction vial and diluted with 0.5 mL of chlorobenzene in a nitrogen-filled glovebox. The vial was equipped with a magnetic stir bar and sealed with electrical tape under an inert atmosphere. The reaction was heated and stirred on a magnetic stir plate at the desired temperature. After completion of the reaction, the solution was pipetted into stirring acetone to precipitate polymer and collected via Büchner filtration with nylon filter paper to yield the functionalized polyolefins. Collected polymer is placed on high vacuum overnight before characterization.

Characterization of Polymer Functionalization Products

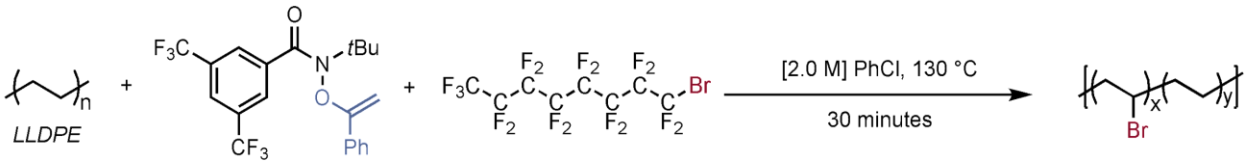


Fluorinated LLDPE (P1): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and *N*-fluorobenzenesulfonimide were reacted according to General Polymer Procedure I. LLDPE (RI M_n = 19 kg/mol, RI *Đ* = 4.76, MALS dn/dc = 0.105, M_n = 1.58 x 10^4 g/mol $\pm$ 3.74%, MALS *Đ* = 2.97 $\pm$ 3.77%, 19% branched, 40 mg, 1.4 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and *N*-fluorobenzenesulfonimide (90 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (26 mg) was 5 mol % fluorinated LLDPE. Collection of the filtrate revealed 85% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 5 mol % fluorinated LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 4.60 (bs), 4.50 (bs), 1.73 (bs), 1.56 (bs), 1.41 (bs), 1.02 (bs). **^{19}F NMR (400 MHz, $C_2D_2Cl_4$, 80 °C)** δ –179.53 (bs). **IR (neat, ATR, cm^{-1})** 2917, 2850, 1472, 1374, 1279, 1169, 1140, 1087, 1069, 1000, 864, 750, 719. **GPC (TCB, 140 °C):** RI M_n = 17 kg/mol, RI *Đ* = 4.76; MALS dn/dc = 0.105, M_n = 2.96 x 10^4 g/mol $\pm$ 3.38%, MALS *Đ* = 3.58 $\pm$ 3.42%. **TGA (°C)** parent T_d = 428, product T_d = 294**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 112 with 30% crystallinity (DH = 86 J/g).

Determination of percent fluorination of LLDPE: Upon purification, the percent fluorination of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated fluorine group that appear between 4.4–4.6 ppm are used to determine mol % fluorination per repeat unit.

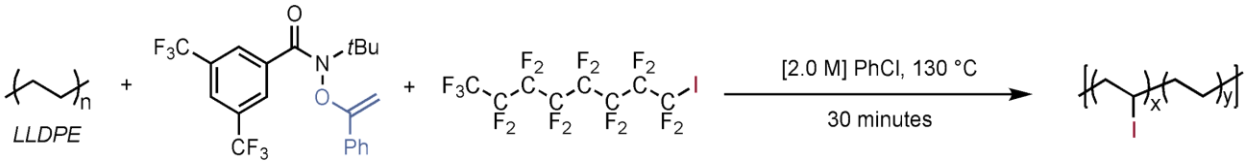


Brominated LLDPE (P2): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and 1-bromoheptadecafluorooctane were reacted according to General Polymer Procedure I. LLDPE (M_n = 19 kg/mol, $Đ$ = 4.76, 19% branched, 40 mg, 1.4 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and 1-bromoheptadecafluorooctane (.56 mL, 0.29 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (30 mg) was 4 mol % brominated LLDPE. Collection of the filtrate revealed 77% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 4 mol % brominated LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 4.11 (bs), 1.89 (bs), 1.61 (bs), 1.46 (bs), 1.35 (bs), 0.96 (bs). **IR (neat, ATR, cm^{-1}):** 2916, 2849, 1464, 1463, 1242, 1240, 1142, 813, 722, 719. **GPC (TCB, 140 °C)** M_n = 20 kg/mol, $Đ$ = 4.58. **TGA (°C)** parent T_d = 428, product T_d = 270**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 119 with 18% crystallinity (DH = 53.2 J/g).

Determination of percent bromination of LLDPE: Upon purification, the percent bromination of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated bromine group that appear at 4.1 ppm are used to determine mol % bromination per repeat unit.

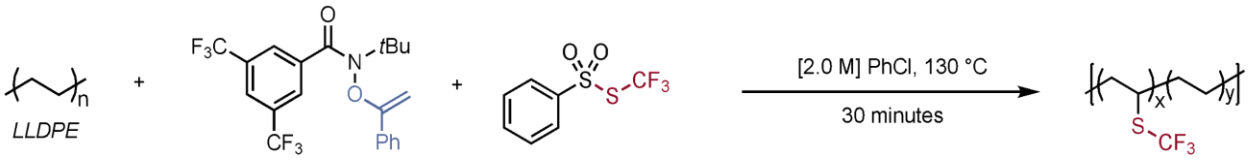


Iodinated LLDPE (P3): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and 1-iodoperfluorooctane were reacted according to General Polymer Procedure I. LLDPE (M_n = 19 kg/mol, *Đ* = 4.76, 19% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and 1-iodoperfluorooctane (81 µL, 0.29 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (39 mg) was 4 mol % iodinated LLDPE. Collection of the filtrate revealed 79% conversion of the functionalized amide to the parent amide by ^{19}F NMR.

The following was gathered using 4 mol % iodinated LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 4.21 (bs), 1.95 (bs), 1.79 (bs), 1.57 (bs), 1.44 (bs), 1.36 (bs), 0.98 (bs). **IR (neat, ATR, cm^{-1})** 2916, 2848, 1644, 1549, 1463, 1367, 1241, 1219, 1178, 1154, 1146, 907, 720. **GPC (TCB, 140 °C):** M_n = 22 kg/mol, *Đ* = 4.19. **TGA (°C)** parent T_d = 428, product T_d = 225 (T_{d1} = 194, T_{d2} = 318)**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 95 with 21% crystallinity (DH = 63 J/g).

Determination of percent iodination of LLDPE: Upon purification, the percent iodination of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated iodo group that appear between 4.15 – 4.3 ppm are used to determine mol % iodination per repeat unit.

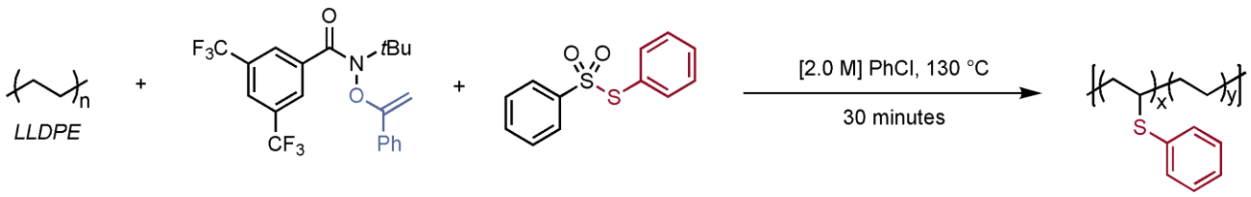


Trifluoromethylthiolated LLDPE (P4): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and *S*-(trifluoromethyl) benzenesulfonothioate were reacted according to General Polymer Procedure I. LLDPE (M_n = 19 kg/mol, *Đ* = 4.76, 19% branched, 15 mg, 0.54 mmol) reacted with (1-phenylvinyloxy)amide (23 mg, 0.05 mmol) and *S*-(trifluoromethyl) benzenesulfonothioate (26 mg, 0.11 mmol) in chlorobenzene (0.3 mL) upon heating at 130 °C for 30 min. The resultant material (10 mg) was 3 mol % trifluoromethylthiolated LLDPE. Collection of the filtrate revealed 91% conversion of the functionalized amide to the parent amide by ^{19}F NMR.

The following was gathered using 3 mol % trifluoromethylthiolated LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 3.25 (bs), 1.79 (bs), 1.61 (bs), 1.55 (bs), 1.49 (bs), 1.41 (bs), 1.02 (bs). **^{19}F NMR (400 MHz, $C_2D_2Cl_4$, 80 °C)** δ –41.00, –39.87, –39.85. **IR (neat, ATR, cm^{-1})** 2917, 2849, 1648, 1549, 1464, 1367, 1280, 1277, 1148, 1107, 907, 731, 720 . **GPC (TCB, 140 °C):** M_n = 22 kg/mol, *Đ* = 7.74. **TGA (°C)** parent T_d = 428, product T_d = 317**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 103 with 12% crystallinity (DH = 35.2 J/g).

Determination of percent trifluoromethylthiolation of LLDPE: Upon purification, the percent trifluoromethylation of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated trifluoromethylthiol group that appear between 3.2 – 3.3 ppm are used to determine mol % trifluoromethylthiolation per repeat unit.

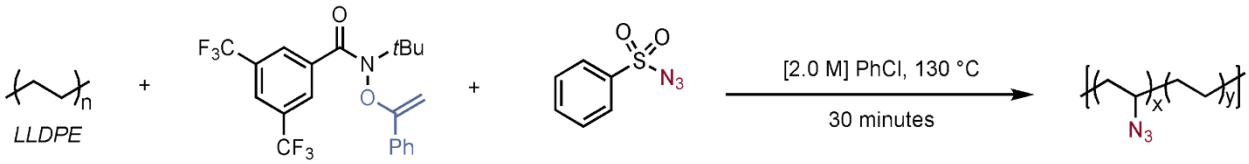


Thiophenolated LLDPE (P5): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and *S*-phenyl benzenesulfonothioate were reacted according to General Polymer Procedure I. LLDPE (M_n = 19 kg/mol, *Đ* = 4.76, 19% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and *S*-phenyl benzenesulfonothioate (72 mg, 0.29 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (42 mg) was 7 mol % functionalized LLDPE. Collection of the filtrate revealed 90% conversion amide reagent by ^{19}F NMR. Employing phenyl disulfide or 2-(phenyldisulfaneyl)pyridine instead of *S*-phenyl benzenesulfonothioate yielded products with similar NMR peaks and GPC traces of 3 mol % and 4 mol % materials, respectively.

The following was gathered using 7 mol % thiophenolated LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 7.52 (bs), 7.37 (bs), 7.30 (bs), 3.19 (bs), 1.74 (bs), 1.62 (bs), 1.61 (bs), 1.45 (bs), 1.37 (bs), 1.04 (bs). **IR (neat, ATR, cm^{-1}):** 2917, 2849, 1586, 1464, 1439, 1279, 1149, 1026, 721, 694, 691. **GPC (TCB, 140 °C):** M_n = 22 kg/mol, *Đ* = 4.34. **TGA (°C)** parent T_d = 428, product T_d = 317**. DSC (°C):** parent T_m = 125 with 42% crystallinity (DH = 122 J/g), product T_m = 55 with 10% crystallinity (DH = 28 J/g).

Determination of percent thiophenolation of LLDPE: Upon purification, the percent thiophenolation of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated thiophenol group that appear at 3.2 ppm are used to determine mol % thiophenolation per repeat unit. The aromatic region between 7.30 – 7.55 ppm was integrated and divided by 5 to confirm the percent incorporation concluded from the *alpha* protons.

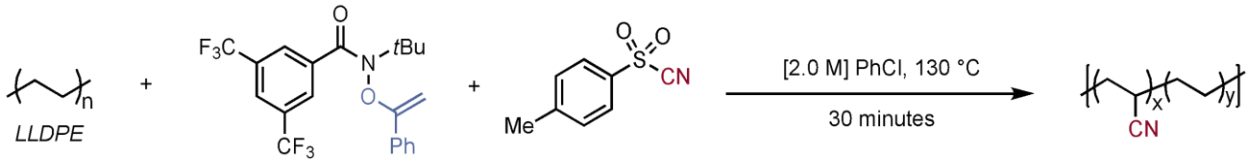


Azidated LLDPE (P6): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and benzenesulfonyl azide were reacted according to General Polymer Procedure I. LLDPE (M_n = 19 kg/mol, *Đ* = 4.76, 19% branched, 20 mg, 0.71 mmol) reacted with (1-phenylvinyloxy)amide (31 mg, 0.071 mmol) and benzenesulfonyl azide (26 mg, 0.14 mmol) in chlorobenzene (0.4 mL) upon heating at 130 °C for 30 min. The resultant material (14 mg) was 4 mol % azidated LLDPE. Collection of the filtrate revealed 86% conversion of the amide reagent by ^{19}F NMR. Increasing the stoichiometry of the reagents increased the percent incorporation of the azide group.

The following was gathered using 4 mol % azidated LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 3.34 (bs), 1.64 (bs), 1.49 (bs), 1.40 (bs), 1.02 (bs). **IR (neat, ATR, cm^{-1})** 2917, 2849, 2097, 1464, 1342, 1278, 1247, 1142, 720. **GPC (TCB, 140 °C)** M_n = 20 kg/mol, *Đ* = 3.78. **TGA (°C)** parent T_d = 428, product T_d = 377**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 98 with 10% crystallinity (DH = 31 J/g).

Determination of percent azidation of LLDPE: Upon purification, the percent azidation of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated azide group that appear at 3.3 ppm are used to determine mol % azidation per repeat unit.



Cyanated LLDPE (P7): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and tosyl cyanide were reacted according to General Polymer Procedure I. LLDPE (M_n = 19 kg/mol, *Đ* = 4.76, 19% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (120 mg, 0.29 mmol) and tosyl cyanide (100 mg, 0.57 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material was 7 mol % cyanated LLDPE (36mg). Similar characterization data was obtained using other stoichiometric ratios of (1-phenylvinyloxy)amide **1** and tosyl cyanide to polymer repeat unit (see Table S1 for exact conditions). See accompanying tables and figures for more information.

The following was gathered using 7 mol % cyanated LLDPE:

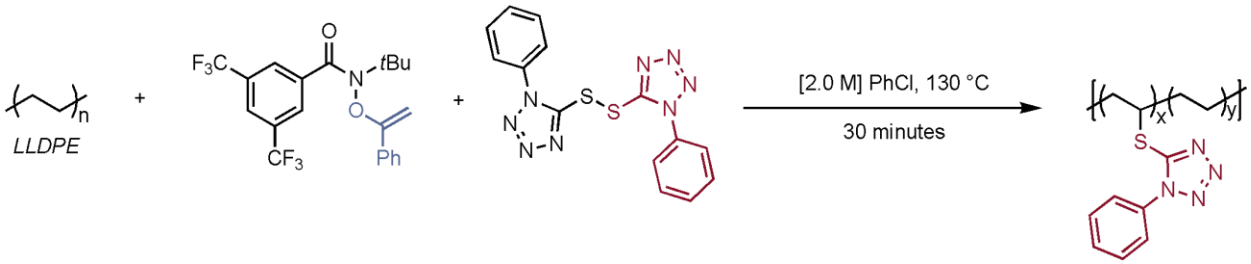
^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 2.58 (bs), 1.71 (bs), 1.64 (bs), 1.56 (bs), 1.41 (bs), 1.02 (bs). **^{13}C NMR (101 MHz, $C_2D_2Cl_4$, 80 °C)** δ 122.5, 74.3, 74.1, 73.8, 32.4, 32.2, 31.8, 31.6, 29.8, 29.6, 29.2, 27.3, 27.2, 26.9, 23.1, 14.2, 14.2. **IR (neat, ATR, cm^{-1})** 2918, 2850, 2237, 1467, 1378, 720. **GPC (TCB, 140 °C)** M_n = 21 kg/mol, *Đ* = 3.98. **TGA (°C)** parent T_d = 428, product T_d = 339**.** **DSC (°C):** parent T_m = 125 with 42% crystallinity (DH = 122 J/g), product T_m = 96 with 2% crystallinity (DH = 6 J/g).

Determination of percent cyanation of LLDPE: Upon purification, the percent cyanation of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated cyano group that appear at 2.6 ppm are used to determine mol % cyanation per repeat unit. Only secondary C–H cyanation was observed in all cases.

Reagent Loading (r.u.:amide: trap)	% conversion	% functionalization	M_n	*Đ*
10:1:2	90%	7 mol %	19	3.93
10:1:2	88%	6 mol %	20	4.78

5:1:2	85%	11 mol %	25	3.55
5:1:2	90%	7 mol %	21	3.85
5:1:2	--	7 mol %	21	3.98
2:1:2	87%	13 mol %	31	3.11
2:1:2	82%	16 mol %	42	2.63
1:1:2	82%	13 mol %	38	2.80

Table S2: Cyanation of LLDPE at various target functionalizations dictated by the stoichiometry of the reagents. r.u. = repeat unit of the polyolefin. Percent conversion was determined with respect to amide reagent by ^{19}F NMR. Percent functionalization was determined by ^{1}H NMR. Molecular weight (M_n) and dispersity ($Đ$) were determined by HT GPC.

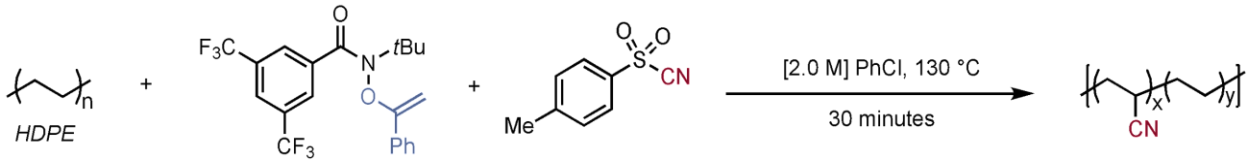


Phenyl tetrazole LLDPE (P8): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and phenyl tetrazole dimer were reacted according to General Polymer Procedure I. LLDPE (M_n = 19 kg/mol, $Đ$ = 4.76, 19% branched, 20 mg, 0.71 mmol) reacted with (1-phenylvinyloxy)amide (31 mg, 0.071 mmol) and phenyl tetrazole dimer (51 mg, 0.14 mmol) in chlorobenzene (0.4 mL) upon heating at 130 °C for 30 min. The resultant material (14 mg) was 2 mol % phenyl tetrazolated LLDPE. Collection of the filtrate revealed 82% conversion of the functionalized amide to the parent amide by ^{19}F NMR.

The following was gathered using 2 mol % phenyl tetrazolated LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 7.63 (bs), 3.96 (bs), 1.83 (bs), 1.46 (bs), 1.35 (bs), 0.96 (bs). **IR (neat, ATR, cm^{-1})** 2916, 2849, 1599, 1500, 1462, 1394, 1386, 1245, 1238, 1074, 1073, 1017, 1015, 979, 911, 758, 719, 694. **GPC (TCB, 140 °C):** M_n = 21 kg/mol, $Đ$ = 5.58. **TGA (°C)** parent T_d = 428, product T_d = 229 (T_{d1} = 141, T_{d2} = 373)**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 91 with 6% crystallinity (DH = 17 J/g).

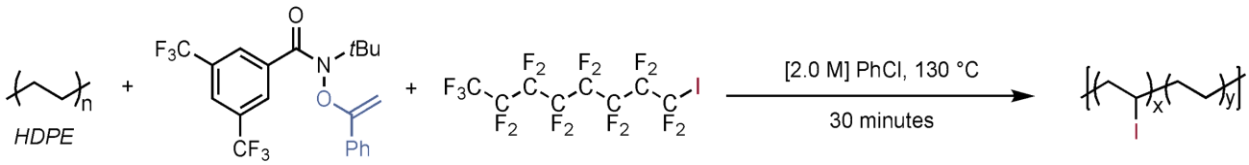
Determination of percent phenyl tetrazolation of LLDPE: Upon purification, the percent phenyl tetrazolation of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated thioether group that appear between 3.9 – 4.0 ppm are used to determine mol % phenyl tetrazole per repeat unit. These protons were in agreement with the aromatic protons observed around 7.6 ppm.



Cyanated HDPE (P9): ExxonMobil™ High Density Polyethylene, (1-phenylvinyloxy)amide, and tosyl cyanide were reacted according to General Polymer Procedure I. HDPE (M_n = 32 kg/mol, $Đ$ = 4.27, 0% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and tosyl cyanide (52 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (22 mg) was 5 mol % cyanated HDPE as whitish flakes. Collection of the filtrate revealed 84% conversion of the amide reagent by ^{19}F NMR. The following was gathered using 5 mol % cyanated HDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 2.58 (bs), 1.67 (bs), 1.40 (bs), 1.01 (bs). **IR (neat, ATR, cm^{-1})** 2916, 2849, 2240, 1473, 1463, 723. **GPC (TCB, 140 °C)** M_n = 28 kg/mol, $Đ$ = 5.24. **TGA (°C)** parent T_d = 433**,** product T_d = 320**. DSC (°C):** parent T_m = 129 with 62% crystallinity (DH = 183 J/g), product T_m = 105 with 20% crystallinity (DH = 59 J/g).

Determination of percent cyanation of HDPE: Upon purification, the percent cyanation of HDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated cyano group that appear at 2.6 ppm are used to determine mol % cyanation per repeat unit.



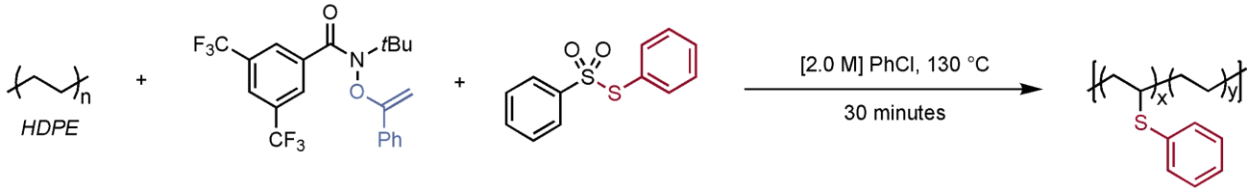
Iodinated HDPE (P10): ExxonMobil™ High Density Polyethylene, (1-phenylvinyloxy)amide, and perfluorooctyl iodide were reacted according to General Polymer Procedure I. HDPE (M_n = 38

kg/mol, *Đ* = 8.13, 0% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and perfluorooctyl iodide (81 µL, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (44 mg) was 2 mol % iodinated HDPE as whitish flakes. Collection of the filtrate reveleated 74% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 2 mol % iodinated HDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 4.21 (bs), 1,94 (bs), 1.78 (bs), 1.62 (bs), 1.46 (bs), 1.36 (bs), 0.97 (bs). **IR (neat, ATR, cm^{-1})** 2916, 2849, 1473, 1463, 1281, 1143, 1063, 801, 721, 719. **GPC (TCB, 140 °C)** M_n = 41 kg/mol, *Đ* = 7.38. **TGA (°C)** parent T_d = 433**,** product T_d = 251 (T_{d1} = 202, T_{d2} = 388)**. DSC (°C):** parent T_m = 129 with 62% crystallinity (DH = 183 J/g), product T_m = 111 with 26% crystallinity (DH = 75 J/g).

Determination of percent iodination of HDPE: Upon purification, the percent iodination of HDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated iodo group that appear at 4.3 ppm are used to determine mol % iodination per repeat unit.



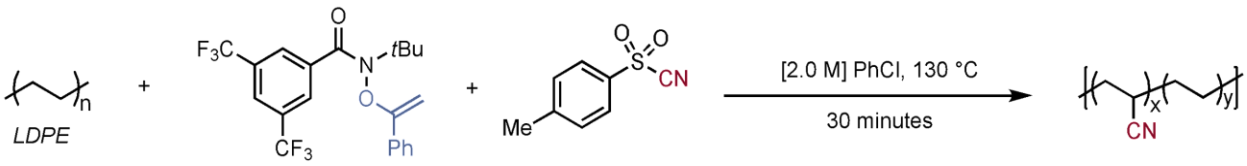
Thiophenolated HDPE (P11): ExxonMobil™ High Density Polyethylene, (1-phenylvinyloxy)amide, and phenyl benzenesulfonate were reacted according to General Polymer Procedure I. HDPE (M_n = 38 kg/mol, *Đ* = 8.13, 0% branched, 60 mg, 2.1 mmol) reacted with (1-phenylvinyloxy)amide (92 mg, 0.21 mmol) and phenyl benzenesulfonate (110 mg, 0.43 mmol) in chlorobenzene (0.9 mL) upon heating at 130 °C for 30 min. The resultant material (44 mg) was 8 mol % thiophenolated HDPE as whitish flakes. Collection of the filtrate revealed 85% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 8 mol % thiophenolated HDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 7.43 (bs, 2H), 7.30 (bs, 2H), 7.23 (bs, 1H), 3.10 (bs, 1H), 1.65 (bs), 1.51 (bs), 1.36 (bs), 0.97 (bs). **IR (neat, ATR, cm^{-1})** 2915, 2849, 1585, 1473, 1463, 1438, 1093, 1027, 1026, 734, 720, 718, 692. **GPC (TCB, 140 °C)** M_n = 43 kg/mol, *Đ* = 7.68. **TGA**

(°C) parent T_d = 433**,** product T_d = 398**. DSC (°C):** parent T_m = 129 with 62% crystallinity (DH = 183 J/g), product T_m = 124 with 20% crystallinity (DH = 57 J/g).

Determination of percent thiophenolation of HDPE: Upon purification, the percent thiophenolation of HDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated thiophenol group that appear at 3.1 ppm are used to determine mol % thiophenolation per repeat unit. The phenyl peaks were found to be in agreement with the *alpha* protons.

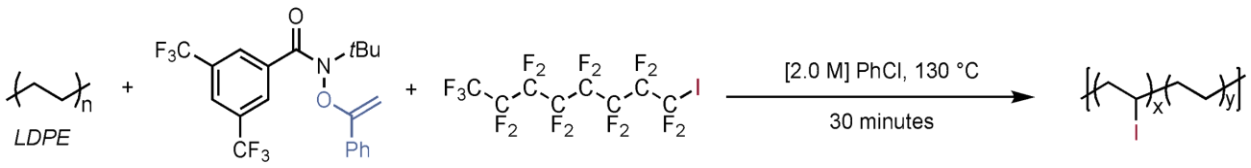


Cyanated LDPE (P12): Dow™ Polyethylene 4012 Low Density, (1-phenylvinyloxy)amide, and tosyl cyanide were reacted according to General Polymer Procedure I. LDPE (M_n = 34 kg/mol, *Đ* = 13.5, 49% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and tosyl cyanide (52 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (28 mg) was 5 mol % cyanated LDPE as whitish flakes. Collection of the filtrate revealed 89% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 5 mol % cyanated LDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 2.54 (bs), 1.66 (bs), 1.50 (bs), 1.44 (bs), 1.36 (bs), 0.97 (bs). **IR (neat, ATR, cm^{-1})** 2917, 2849, 2239, 1724, 1468, 1378, 1280, 1039, 720. **GPC (TCB, 140 °C)** M_n = 40 kg/mol, *Đ* = 13.56. **TGA (°C)** parent T_d = 416, product T_d = 341**. DSC (°C):** parent T_m = 105 with 36% crystallinity (DH = 105 J/g), product T_m = 82 with 10% crystallinity (DH = 28 J/g).

Determination of percent cyanation of LDPE: Upon purification, the percent cyanation of LDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated cyano group that appear at 2.6 ppm are used to determine mol % cyanation per repeat unit.

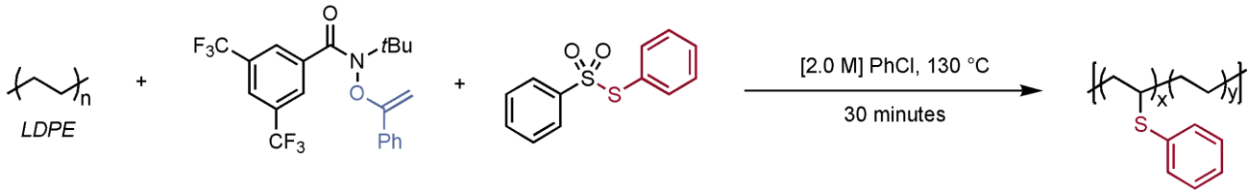


Iodinated LDPE (P13): Dow™ Polyethylene 4012 Low Density, (1-phenylvinyloxy)amide, and perfluorooctyl iodide were reacted according to General Polymer Procedure I. LDPE (M_n = 41 kg/mol, *Đ* = 17.10, 49% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and perfluorooctyl iodide (81 µL, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (46 mg) was 3 mol % iodinated LDPE as whitish flakes. Collection of the filtrate revealed 75% conversion of the amide reagent ^{19}F NMR.

The following was gathered using 3 mol % iodinated LDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 4.21 (bs), 1.97 (bs), 1.80 (bs), 1.57 (bs), 1.46 (bs), 1.36 (bs), 0.97 (bs). **IR (neat, ATR, cm^{-1})** 2916, 2849, 1465, 1463, 1368, 1281, 1217, 1214, 1145, 719. **GPC (TCB, 140 °C)** M_n = 49 kg/mol, *Đ* = 15.16. **TGA (°C)** parent T_d = 416, product T_d = 245 (T_{d1} = 189, T_{d2} = 383)**. DSC (°C):** parent T_m = 105 with 36% crystallinity (DH = 105 J/g), product T_m = 89 with 16% crystallinity (DH = 46 J/g).

Determination of percent iodination of LDPE: Upon purification, the percent iodination of LDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated iodo group that appear at 4.2 ppm are used to determine mol % iodination per repeat unit.

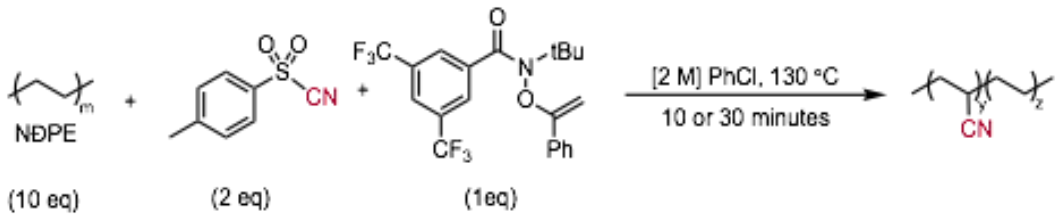


Thiophenolated LDPE (P14): Dow™ Polyethylene 4012 Low Density, (1-phenylvinyloxy)amide, and phenyl benzenesulfonate were reacted according to General Polymer Procedure I. LDPE (M_n = 34 kg/mol, *Đ* = 13.5, 49% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and phenyl benzenesulfonate (72 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (34 mg) was 6 mol % phenyl thioether LDPE as whitish flakes. Collection of the filtrate revealed 93% conversion of amide reagent by ^{19}F NMR.

The following was gathered using 6 mol % thiophenolated LDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 7.44 (bs, 2H), 7.31 (bs, 2H), 7.23 (bs, 1H), 3.11 (bs, 1H), 1.66 (bs), 1.53 (bs), 1.36 (bs), 0.98 (bs). **IR (neat, ATR, cm^{-1})** 2917, 2850, 1585, 1464, 1438, 1366, 1280, 1141, 1092, 1068, 1025, 746, 720, 691. **GPC (TCB, 140 °C)** M_n = 65 kg/mol, *Đ* = 13.76. **TGA (°C)** parent T_d = 416, product T_d = 391**. DSC (°C):** parent T_m = 105 with 36% crystallinity (DH = 105 J/g), product T_m = 74 with 11% crystallinity (DH = 32 J/g).

Determination of percent thiophenolation of LDPE: Upon purification, the percent thiophenolation of LDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated thiophenol group that appear at 3.1 ppm are used to determine mol % thiophenol per repeat unit. The integration of the phenyl peaks were found to be in agreement with the *alpha* protons.



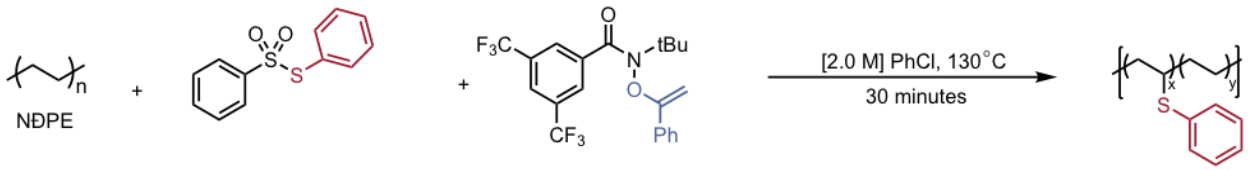
Cyanated NĐPE (P15): Narrow Đ polyethylene (NĐPE), (1-phenylvinyloxy)amide, and tosyl cyanide were reacted according to General Polymer Procedure I. NĐPE (M_n = 30 kg/mol, *Đ* = 1.23, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and tosyl cyanide (52 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 10 (P15) or 30 (P15b) min. The resultant P15a (20 mg) was 3 mol % cyanated NĐPE as whitish flakes. Collection of the filtrate revealed 90% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 3 mol % cyanated NĐPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 2.58 (bs, 1H), 1.51(bs), 1.43 (bs), 1.41 (bs) 0.98 (bs). **IR (neat, ATR cm^{-1})** 3500, 3407, 2917, 2850, 2180, 1638, 1468, 1226, 1200, 1011, 816, 718, 687. **GPC (TCB, 140 °C)** M_n = 28 kg/mol, *Đ* = 1.34 **TGA (°C)** parent T_d= 218.16**,** product T_d= 329 **DSC (°C):** parent T_m= 108 °C with 41% crystallinity (DH= 124 J/g) , product T_m= 83 °C with 11% crystallinity (DH= 34 J/g).

Determination of percent cyanation of NĐPE: Upon purification, the percent cyanation of NĐPE can be determined through integration of the ^{1}H NMR. Considering the composition of the

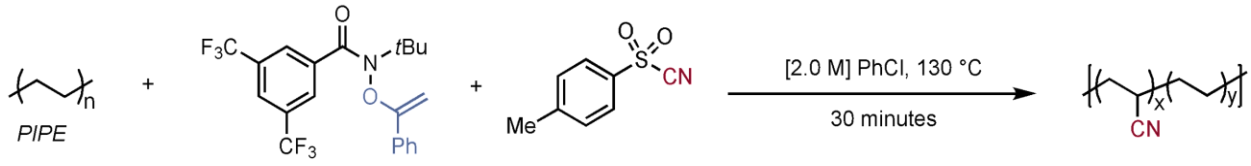
polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated cyano group that appear at 2.5 ppm are used to determine mol % cyanation per repeat unit. Only secondary C–H cyanation was observed.



Thiophenolated NĐPE (P16): Narrow Đ polyethylene (NĐPE), (1-phenylvinyloxy)amide, and phenyl benzenesulfonate were reacted according to General Polymer Procedure I. NĐPE (M_n = 30 kg/mol, *Đ* = 1.23, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and phenyl benzenesulfonate (72 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (25 mg) was 3 mol % thiophenolated NĐPE as whitish flakes. Collection of the filtrate revealed 90% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 3 mol % thiophenolated NĐPE:
^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 7.48 (d, 2H), 7.34 (t, 2H), 7.27 (bs, 1H), 3.14 (bs, 1H), 1.69 (bs), 1.51 (bs), 1.38 (bs), 0.96 (bs). **IR (neat, ATR, cm^{-1})** 3500, 3408, 2916, 2849, 1633, 1473, 1278, 1201, 1143, 1088, 1027, 827, 718, 692. **GPC (TCB, 140 °C)** M_n = 32 kg/mol, *Đ* = 1.35. **TGA (°C)** parent T_d = 218, product T_d = 297. **DSC (°C):** parent T_m = 108 with 41% crystallinity (DH= 124 J/g), product T_m = 85 with 15% crystallinity (DH= 45 J/g).

Determination of percent thiophenolation of NĐPE: Upon purification, the percent thiophenolation of NĐPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated thiophenol group that appear at 3.1 ppm are used to determine mol % thiophenolation per repeat unit. The phenyl protons were in agreement with the *alpha* protons.



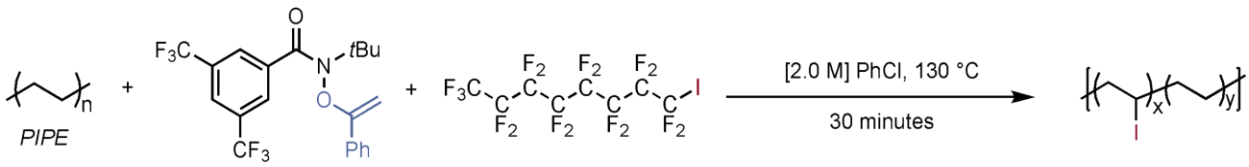
Cyanated PIPE (P17): Post-industrial PE (PIPE) gathered from remnants of packaging forms, (1-phenylvinyloxy)amide, and tosyl cyanide were reacted according to General Polymer Procedure

I. PIPE (M_n = 45 kg/mol, *Đ* = 8.65, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and tosyl cyanide (52 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (30 mg) was 5 mol % cyanated PIPE as whitish flakes. Collection of the filtrate revealed 90% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 5 mol % cyanated PIPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 2.53 (bs), 1.66 (bs), 1.62 (bs), 1.52 (bs), 1.44 (bs), 1.36 (bs), 1.25 (bs), 0.98 (bs). **IR (neat, ATR, cm^{-1})** 2917, 2850, 2240, 1468, 1378, 1000, 720. **GPC (TCB, 140 °C)** M_n = 48 kg/mol, *Đ* = 8.44. **TGA (°C)** parent T_d = 412, product T_d = 393. **DSC (°C):** parent T_m = 109 with 24% crystallinity (DH = 72 J/g), product T_m = 87 with 21% crystallinity (DH = 60 J/g).

Determination of percent cyanation of PIPE: Upon purification, the percent cyanation of PIPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated cyano group that appear at 2.6 ppm are used to determine mol % cyanation per repeat unit.



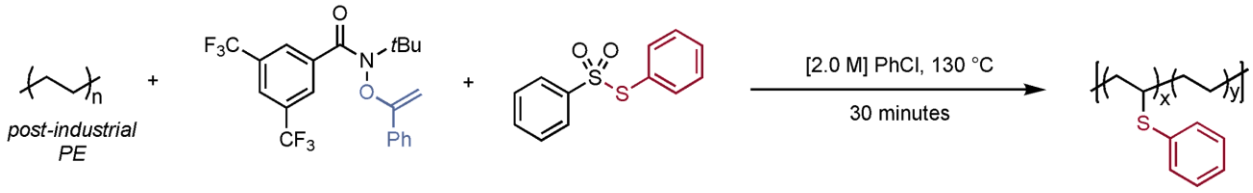
Iodinated PIPE (P18): Post-industrial PE (PIPE) gathered from remnants of packaging forms, (1-phenylvinyloxy)amide, and perfluorooctyl iodide were reacted according to General Polymer Procedure I. PIPE (M_n = 48 kg/mol, *Đ* = 14.07, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and perfluorooctyl iodide (81 µL, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (47 mg) was 4 mol % iodinated PIPE as whitish flakes. Collection of the filtrate revealed 75% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 4 mol % iodinated PIPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ . **IR (neat, ATR, cm^{-1})** 2916, 2849, 1473, 1464, 1366, 1281, 1241, 1216, 1146, 730, 719. **GPC (TCB, 140 °C)** M_n = 57 kg/mol, *Đ* = 12.60. **TGA (°C)**

parent T_d = 412, product T_d = 234 (T_{d1} = 197, T_{d2} = 383). **DSC (°C):** parent T_m = 109 with 24% crystallinity (DH = 72 J/g), product T_m = 88 with 13% crystallinity (DH = 37 J/g).

Determination of percent iodination of PIPE: Upon purification, the percent iodination of PIPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated iodo group that appear at 4.2 ppm are used to determine mol % iodination per repeat unit.

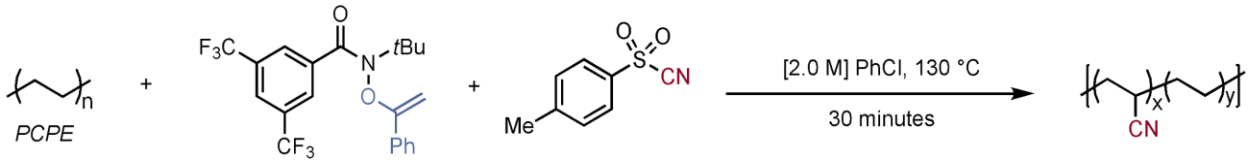


Thiophenolated PIPE (P19): Post-industrial PE (PIPE) gathered from remnants of packaging forms, (1-phenylvinyloxy)amide, and phenyl benzenesulfonate were reacted according to General Polymer Procedure I. PIPE (M_n = 48 kg/mol, *Đ* = 14.07, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and phenyl benzenesulfonate (72 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (37 mg) was 6 mol % thiophenolated PIPE as whitish flakes. Collection of the filtrate revealed 91% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 6 mol % thiophenolated PIPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 7.44 (bs, 2H), 7.30 (bs, 2H), 7.23 (bs, 1H), 3.11 (bs, 1H), 1.66 (bs), 1.52 (bs), 1.44 (bs), 1.36 (bs), 0.97 (bs). **IR (neat, ATR, cm^{-1})** 2917, 2849, 1739, 1586, 1467, 1438, 1370, 1279, 1242, 1090, 1068, 1026, 746, 694, 692. **GPC (TCB, 140 °C)** M_n = 66 kg/mol, *Đ* = 11.73. **TGA (°C)** parent T_d = 412, product T_d = 391. **DSC (°C):** parent T_m = 109 with 24% crystallinity (DH = 72 J/g), product T_m = 76 with 8% crystallinity (DH = 24 J/g).

Determination of percent thiophenolation of PIPE: Upon purification, the percent thiophenolation of PIPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated thiophenol group that appear at 3.1 ppm are used to determine mol % thiophenolation per repeat unit. The phenyl protons were in agreement with the *alpha* protons.

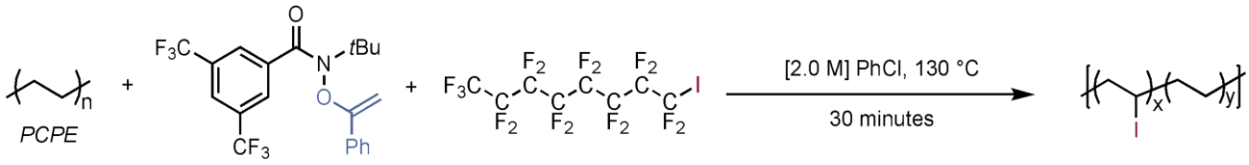


Cyanated PCPE (P20): Post-consumer PE (PCPE) gathered from PE foam television packaging, (1-phenylvinyloxy)amide, and tosyl cyanide were reacted according to General Polymer Procedure I. PCPE (M_n = 34 kg/mol, $Đ$ = 7.80, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (60 mg, 0.14 mmol) and tosyl cyanide (52 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (36 mg) was 6 mol % cyanated PCPE as whitish flakes. Collection of the precipitate confirmed 90% conversion of the amide ^{19}F NMR.

The following was gathered using 7 mol % cyanated PCPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 2.60 (bs), 1.67 (bs), 1.44 (bs), 1.37 (bs), 0.99 (bs). **IR (neat, ATR, cm^{-1}):** 2916, 2849, 2239, 1681, 1468, 1379, 1305, 1278, 1152, 1146, 1129, 1038, 1012, 812, 719. **GPC (TCB, 140 °C)** M_n = 33 kg/mol, $Đ$ = 7.34. **TGA (°C)** parent T_d = 414, product T_d = 370**. DSC (°C):** parent T_m = 111 °C with 37% crystallinity (DH = 111 J/g), product T_m = 89 °C with 16% crystallinity (DH = 48 J/g).

Determination of percent cyanation of PCPE: Upon purification, the percent cyanation of PCPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated cyano group that appear at 2.6 ppm are used to determine mol % cyanation per repeat unit.



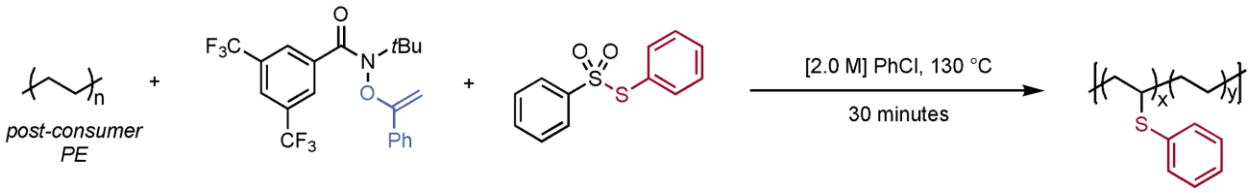
Iodinated PCPE (P21): Post-consumer PE (PCPE) gathered from PE foam television packaging, (1-phenylvinyloxy)amide, and perfluorooctyl iodide were reacted according to General Polymer Procedure I. PCPE (M_n = 40 kg/mol, $Đ$ = 12.08, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (60 mg, 0.14 mmol) and perfluorooctyl iodide (81 µL, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (47 mg) was 3

mol % iodinated PCPE as whitish flakes. Collection of the precipitate confirmed 74% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 3 mol % iodinated PCPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 4.21 (bs), 1.94 (bs), 1.80 (bs), 1.61 (bs), 1.57 (bs), 1.45 (bs), 1.36 (bs), 0.97 (bs). **IR (neat, ATR, cm^{-1})** 2916, 2849, 1473, 1462, 1367, 1281, 1238, 1216, 1146, 722, 719. **GPC (TCB, 140 °C)** M_n = 44 kg/mol, $Đ$ = 11.36. **TGA (°C)** parent T_d = 414, product T_d = 231 (T_{d1} = 190, T_{d2} = 385)**. DSC (°C):** parent T_m = 111 °C with 37% crystallinity (DH = 111 J/g), product T_m = 95 °C with 18% crystallinity (DH = 52 J/g).

Determination of percent iodination of PCPE: Upon purification, the percent iodination of PCPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated iodo group that appear at 4.2 ppm are used to determine mol % iodination per repeat unit.

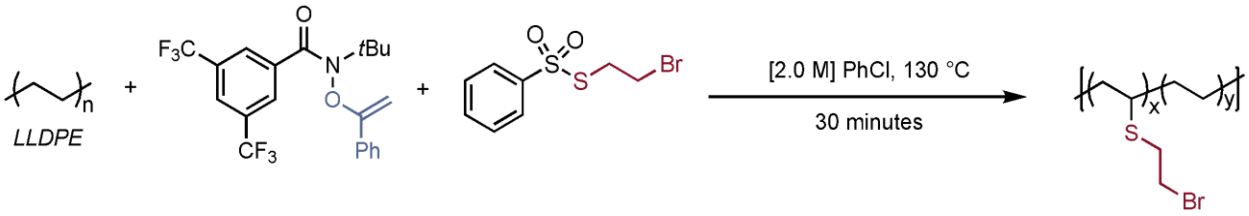


Thiophenolated PCPE (P22): Post-consumer PE (PCPE) gathered from PE foam television packaging, (1-phenylvinyloxy)amide, and phenyl benzenesulfonate were reacted according to General Polymer Procedure I. PCPE (M_n = 40 kg/mol, $Đ$ = 12.08, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (60 mg, 0.14 mmol) and phenyl benzenesulfonate (72 mg, 0.28 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (35 mg) was 6 mol % thiophenolated PCPE as whitish flakes. Collection of the precipitate confirmed 91% conversion of the amidyl reagent to the parent amide by ^{19}F NMR.

The following was gathered using 6 mol % thiophenolated PCPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 7.50 (bs, 2H), 7.36 (bs, 2H), 7.29 (bs, 1H), 3.16 (bs, 1H), 1.71 (bs), 1.58 (bs), 1.50 (bs), 1.41 (bs), 1.03 (bs). **IR (neat, ATR, cm^{-1})** 2916, 2848, 1584, 1467, 1439, 1369, 1304, 1093, 1027, 1025, 718, 694, 692. **GPC (TCB, 140 °C)** M_n = 55 kg/mol, $Đ$ = 10.25. **TGA (°C)** parent T_d = 414, product T_d = 392**. DSC (°C):** parent T_m = 111 °C with 37% crystallinity (DH = 111 J/g), product T_m = 79 °C with 9% crystallinity (DH = 26 J/g).

Determination of percent thiophenolation of PCPE: Upon purification, the percent thiophenolation of PCPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated thiophenol group that appear at 3.1 ppm are used to determine mol % thiophenol per repeat unit. The phenyl protons were in agreement with the alpha protons.

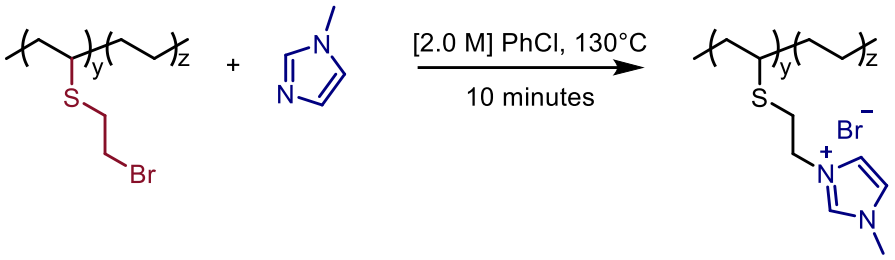


Bromoethylthiolated LLDPE (P23): DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin, (1-phenylvinyloxy)amide, and *S*-(2-bromoethyl) benzenesulfonothioate were reacted according to General Polymer Procedure I. LLDPE (M_n = 18 kg/mol, *Đ* = 9.31, 19% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and *S*-(2-bromoethyl) benzenesulfonothioate (80 mg, 0.29 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (44 mg) was 5 mol % bromoethylthiolated LLDPE. Collection of the filtrate revealed 86% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 5 mol % bromoethylthiolated LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 3.53 (bs, 2H), 3.00 (bs, 2H), 2.68 (bs, 1H), 1.63 (bs), 1.49 (bs), 1.36 (bs), 0.98 (bs). **IR (neat, ATR, cm^{-1})** 2917, 2849, 1577, 1541, 1473, 1463, 1369, 1279, 1250, 1188, 1140, 722, 720. **GPC (TCB, 140 °C):** M_n = 25 kg/mol, *Đ* = 9.32. **TGA (°C)** parent T_d = 428, product T_d = 235 (T_{d1} = 159, T_{d2} = 380)**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 100 with 11% crystallinity (DH = 32 J/g).

Determination of percent bromoethylthiolation of LLDPE: Upon purification, the percent bromoethylthiolation of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated bromo group that appear around 3.5 ppm are used to determine mol % bromoethylthiolation per repeat unit. The protons *alpha* the bromide atom were in agreement with the protons *alpha* the sulfur atom.

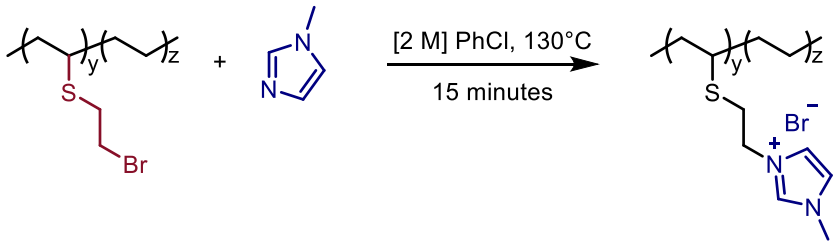


Imidazolium functionalized LLDPE (4 mol %) (P24): Bromoethylthiolated LLDPE (5 mol % funct, 590 mg, 21 mmol polyolefin, 1.1 mmol bromoethylthiol) reacted with methyl imidazole (1.7 mL, 21 mmol) in chlorobenzene (10.5 mL) upon heating at 130 °C for 10 min. The resultant material (582 mg) was 4 mol % imidazolium-functional LLDPE.

The following was gathered using 4 mol % imidazolium-functional LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 10.55 (bs, 1H), 7.30 (bs, 2H), 4.62 (bs, 2H), 4.14 (bs, 3H), 3.13 (bs, 2H), 2.73 (bs, 1H), 1.63 (bs), 1.46 (bs), 1.36 (bs), 0.98 (bs). **IR (neat, ATR, cm^{-1})** 3409, 3105, 3046, 2917, 2850, 1573, 1468, 1279, 1172, 732, 719. Not soluble for GPC characterization. **TGA (°C)** parent T_d = 428, product T_d = 257 (T_{d1} = 200, T_{d2} = 343)**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 97 with 5% crystallinity (DH = 14 J/g).

Determination of percent imidazolium functionalization of LLDPE: Upon purification, the percent imidazolium functionalization of LLDPE can be determined through integration of the ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated imidazolium group that appear around 4.6 ppm are used to determine mol % functionalization per repeat unit. The protons *alpha* the imidazolium moiety were in agreement with the other protons located along on the side chain.



Imidazolium functionalized LLDPE (2 mol %) (P24): Bromoethylthiolated LLDPE (4 mol % functionalized, 3x 500 mg, 3x 18 mmol polyolefin) reacted with methyl imidazole (3x 1.4 mL, 3x

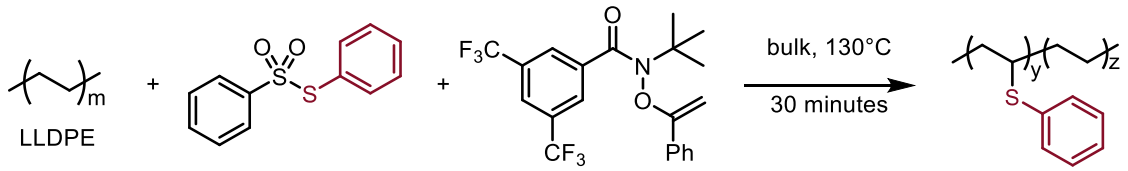
18 mmol) in chlorobenzene (3x 9 mL) upon heating at 130 °C for 15 min. The resultant material (1.69 g) was 2 mol % imidazolium-functional LLDPE.

The following was gathered using 2 mol % imidazolium-functional LLDPE:

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 10.55 (bs, 1H), 7.50 (bs, 2H), 4.67 (bs, 2H), 4.18 (bs, 3H), 3.17 (bs, 2H), 2.73 (bs, 1H), 1.70 (bs), 1.51 (bs), 1.41 (bs), 1.03 (bs). **IR (neat, ATR, cm^{-1})** 3409, 3105, 3046, 2917, 2850, 1573, 1468, 1279, 1172, 732, 719. Not soluble for GPC characterization. **TGA (°C)** parent T_d = 428, product T_d = 231**. DSC (°C):** parent T_m = 125 with 41% crystallinity (DH = 122 J/g), product T_m = 100 with 8% crystallinity (DH = 23 J/g).

Determination of percent imidazolium functionalization of LLDPE: Upon purification, the percent imidazolium functionalization of LLDPE can be determined through integration of ^{1}H NMR. Considering the composition of the polymer, the peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated imidazolium group that appear around 4.6 ppm are used to determine mol % functionalization per repeat unit.

The protons *alpha* the imidazolium moiety were in agreement with the other protons located along on the side chain.

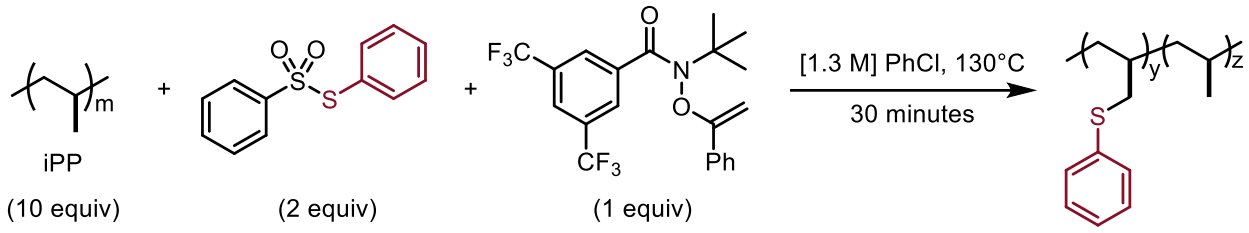


Thiophenolated LLDPE (P26) in bulk: Linear Low Density Polyethylene (LLDPE), (1-phenylvinyloxy)amide, and phenyl benzenesulfonate were reacted according to General Polymer Procedure I. LLDPE (M_n =19 kg/mol, $Đ$ = 4.76, 19% branched, 40 mg, 1.43 mmol) reacted with (1-phenylvinyloxy)amide (62 mg, 0.14 mmol) and phenyl benzenesulfonate (72 mg, 0.28 mmol) upon heating in the absence of solvent at 130 °C for 30 min. The resultant material 25 mg) was 2 mol % thiophenolated LLDPE as whitish flakes. Collection of the filtrate revealed 57% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using 2 mol % thiophenolated LLDPE: **^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C)** δ 7.50 (bs), 7.35 (bs), 7.28 (bs), 3.14 (bs), 1.74 (bs), 1.62 (bs), 1.61 (bs), 1.45 (bs), 1.37 (bs), 1.04 (bs). **IR (neat, ATR, cm^{-1}):** 2917, 2849, 1586, 1464, 1439, 1279, 1149, 1026, 721, 694, 691. **GPC (TCB, 140 °C):** M_n = 24 kg/mol, $Đ$ = 3.5. **TGA (°C)** parent T_d = 428, product T_d = 352.

DSC (°C): parent Tm = 125 with 42% crystallinity (DH = 122 J/g), product Tm = 114.7 with 27% crystallinity (DH = 74.7 J/g).

Determination of percent thiophenolation of LLDPE: Upon purification, the percent thiophenolation of LLDPE can be determined through integration of the ^{1}H NMR. Peaks between 0.8 – 2.0 ppm were integrated to a total of 400 protons. The protons *alpha* the incorporated thiophenol group that appear at 3.2 ppm are used to determine mol % thiophenolation per repeat unit. The aromatic region between 7.30 – 7.55 ppm was integrated and divided by 5 to confirm the percent incorporation concluded from the *alpha* protons.



Thiophenolated iPP (P27): Isotactic Polypropylene (iPP), (1-phenylvinyloxy)amide, and phenyl benzenesulfonate were reacted according to General Polymer Procedure I. iPP (M_n = 27 kg/mol, $Đ$ = 14, 40 mg, .95 mmol) reacted with (1-phenylvinyloxy)amide (41 mg, 0.096 mmol) and phenyl benzenesulfonate (72 mg, 0.19 mmol) in chlorobenzene (0.7 mL) upon heating at 130 °C for 30 min. The resultant material (15 mg) was <1 mol % thiophenolated LLDPE as whitish flakes. Collection of the filtrate revealed 67% conversion of the amide reagent by ^{19}F NMR.

The following was gathered using <1 mol % thiophenolated iPP: **^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C)** δ 7.45 (bs), 7.35 (bs), 7.24 (bs), 3.01 (bs), 1.67 (m), 1.50 (bs),1.37 (m), 1.20 (bs),1.01 (bs). **IR (neat, ATR, cm^{-1}):** 2924, 2918, 2868, 2838, 1457, 1377, 1359, 1168, 976, 975, 842. **GPC (TCB, 140 °C):** M_n = 60 kg/mol, $Đ$ = 6.7. **TGA (°C)** parent T_d = 241, product T_d = 239. **DSC (°C):**parent T_m = 143 (DH =77 J/g), product T_m = 143 (DH = 77 J/g).

Determination of percent thiophenolation of iPP: Upon purification, the percent thiophenolation of iPP can be determined through integration of the ^{1}H NMR. Peaks between 0.8 – 2.0 ppm were integrated to a total of 600 protons. The protons *alpha* the incorporated thiophenol group that appear at 3.2 ppm are divided by 2 to determine mol % thiophenolation per repeat unit. The aromatic region between 7.30 – 7.55 ppm was integrated and divided by 5 to confirm the percent incorporation concluded from the *alpha* protons.

Gel Permeation Chromatographs

Polyolefin gel permeation chromatographs (GPC) were obtained using a Tosoh EcoSEC-HT (high temperature) GPC with refractive index detection against polystyrene standards in 2 mg/mL solutions of trichlorobenzene (TCB) with 200 ppm BHT at 140 °C.

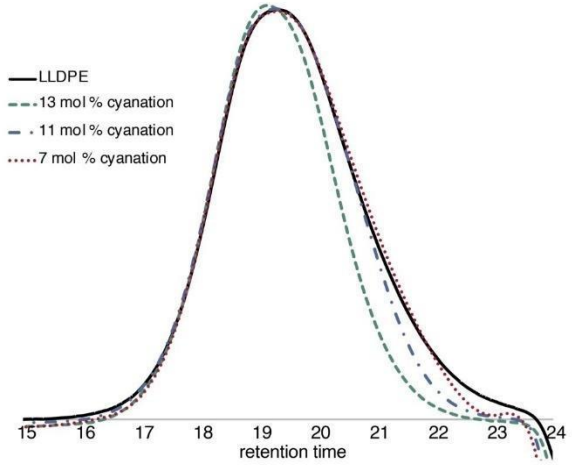


Figure S1. C–H cyanation using reagent **1** and tosyl cyanide successfully incorporated cyano groups into the polymer scaffold of LLDPE without significantly altering the molecular weight distribution according to GPC.

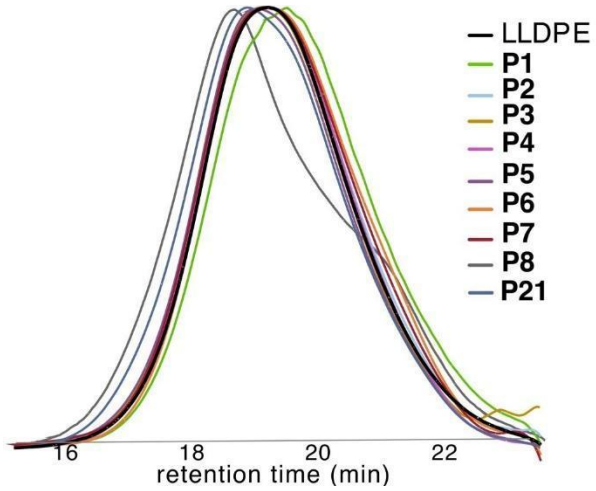


Figure S2. A multitude of functionalities were installed into the LLDPE microstructure using this general method. The GPC here demonstrates that the polyolefin C–H functionalization was successful without concurrent chain scission or chain coupling events. Two outliers exist: **P1** (5 mol % fluorination) and **P8** (2 mol % phenyl tetrazolation). The fluorinated LLDPE was observed in increase in molecular weight by MALS, contrary to what is observed by RI.

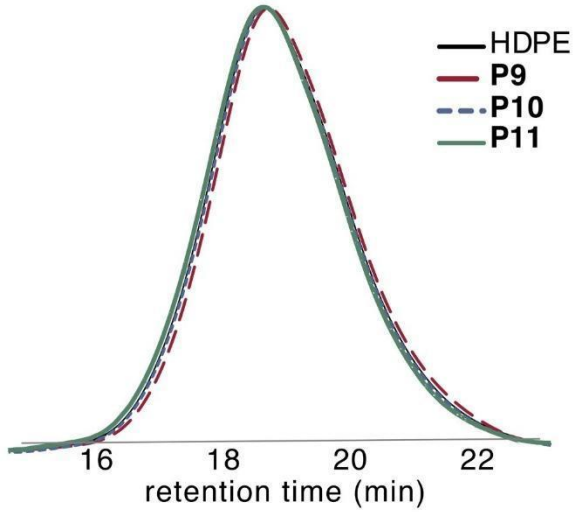


Figure S3. Cyanation (red trace), thiophenolation (green trace), and iodination (blue trace) successfully C–H functionalized high-density polyethylene (HDPE) without altering the molecular weight distribution. The molecular weight and dispersity are almost identical pre- and post-functionalization.

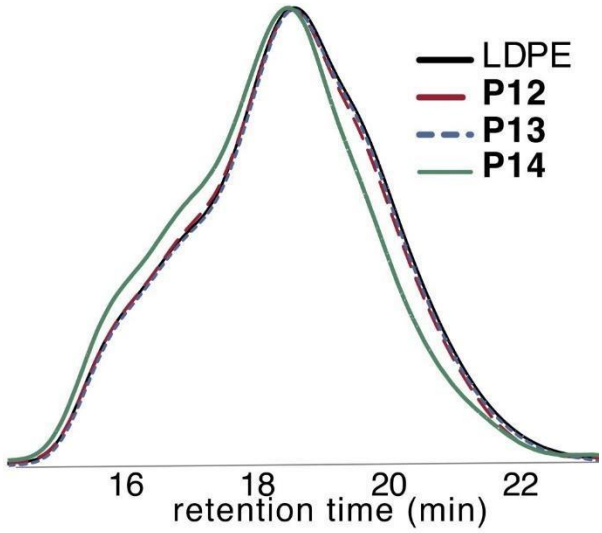
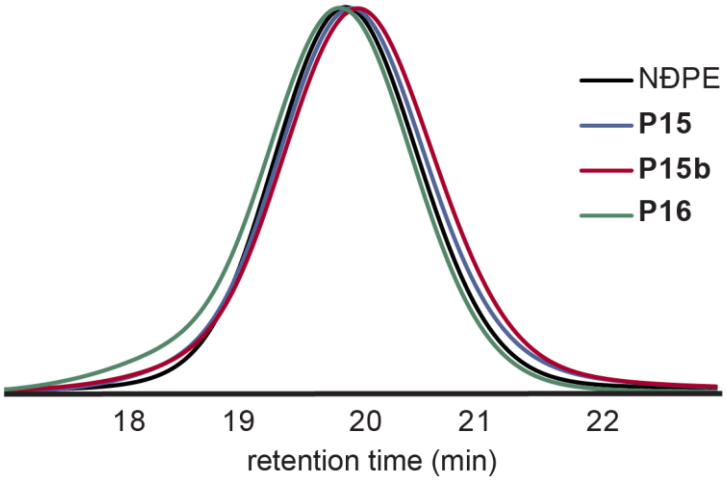


Figure S4. Low-density polyethylene (LDPE) was functionalized with nitrile (red trace), iodo (blue trace), and thiophenol (green trace) moieties. According to the HT GPC, there was minimal change to the molecular weight distribution.



Polymer	Mn	Đ
NĐPE	29,500	1.22
P15a	27,500	1.30
P15b	25,900	1.35
P16	32,000	1.35

Figure S5. Narrow dispersity polyethylene (NĐPE) was functionalized with cyanide (blue and red traces) and thiophenol (green trace) moieties. Functionalization of this narrow dispersity material demonstrates little increase in Đ.

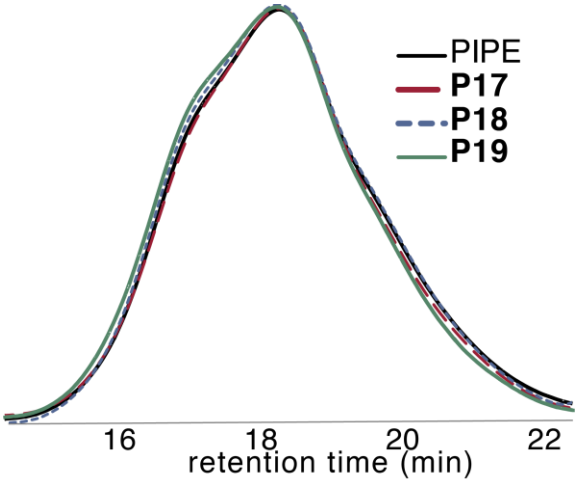


Figure S6. Cyanated (red trace), iodinated (blue trace), and thiophenolated (green trace) post-industrial polyethylene (PIPE) mimicked the molecular weight distribution of the virgin polymer. This demonstrates that the chemistry is robust to post-industrial waste streams.

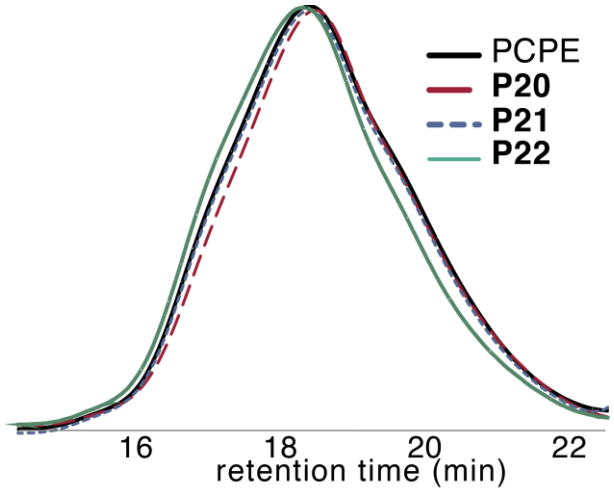


Figure S7. Cyanated (red trace), iodinated (blue trace), and thiophenolated (green trace) post-consumer polyethylene (PCPE) of the PCPE starting material. Upon functionalization, the molecular weight distribution did not change according to high temperature GPC.

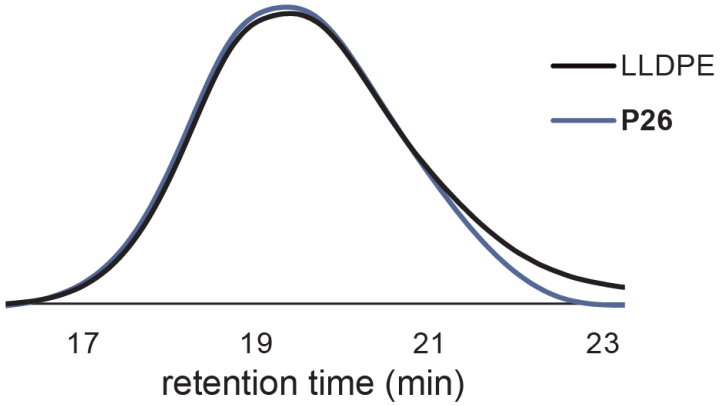


Figure S8. Linear low density polyethylene (LLDPE) was functionalized with thiophenol (blue trace) in the bulk. Functionalization demonstrates minimal impact on Đ.

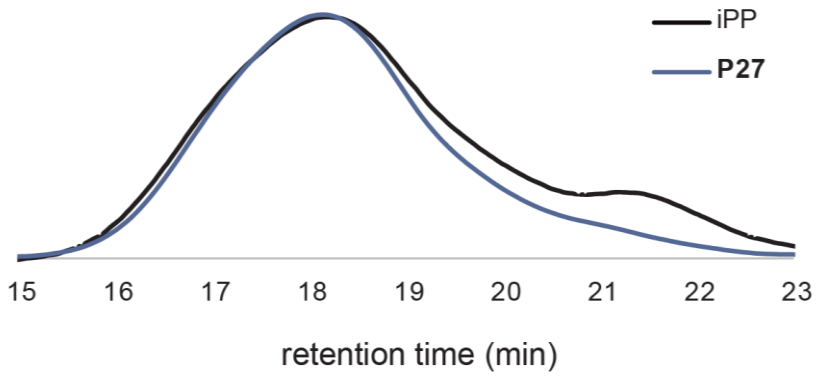


Figure S9. Isotactic polypropylene (iPP) was functionalized with thiophenol (blue trace).

Differential Scanning Calorimetry (DSC) Spectra

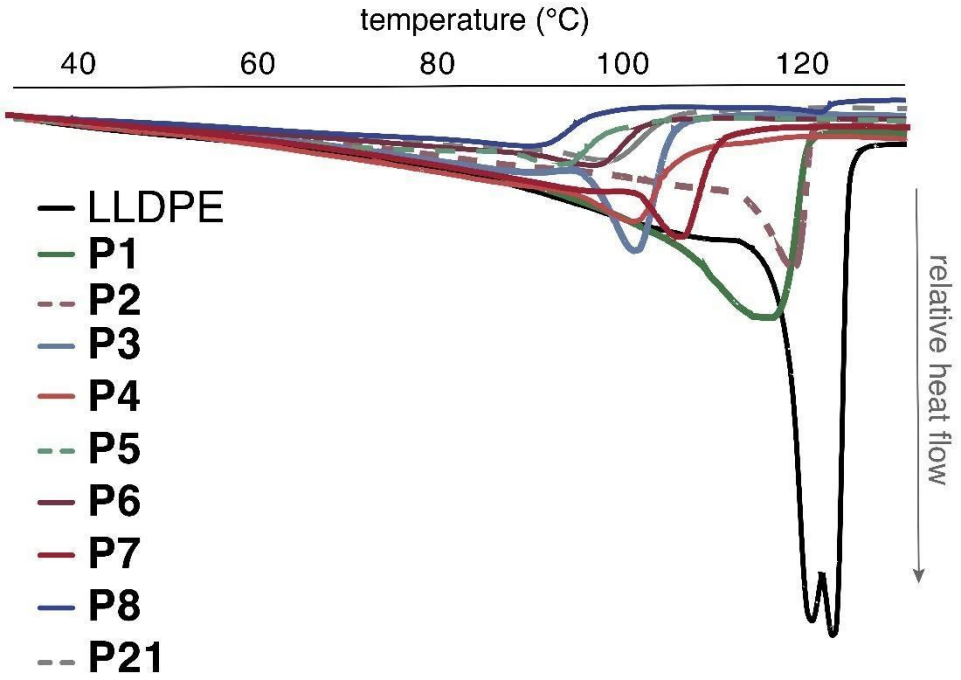


Figure S10. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of LLDPE and functionalized LLDPEs were analyzed. In all functionalizations, the semicrystallinity decreased, so observed through a decrease in enthalpy. The relative heat flow is normalized with respect to the sample mass.

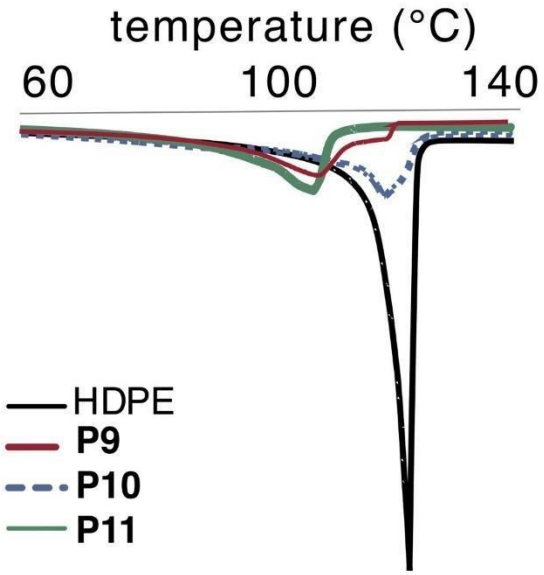


Figure S11. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of HDPE and functionalized HDPEs were analyzed. In all functionalizations, the semicrystallinity decreased, so observed through a decrease in enthalpy. The melting temperature of iodo-functional HDPE was most similar to the virgin polymer, but all functionalized HDPEs exhibited melting temperatures above 100 °C.

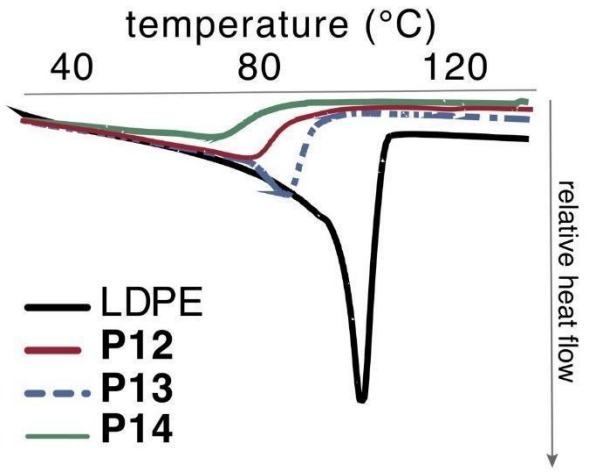


Figure S12. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of LDPE and functionalized LDPEs were analyzed. In all functionalizations, the semicrystallinity decreased as observed through a decrease in enthalpy. The melting temperature of iodo-functional LDPE was most similar to the virgin polymer, but all functionalized HDPEs exhibited melting temperatures above 60 °C.

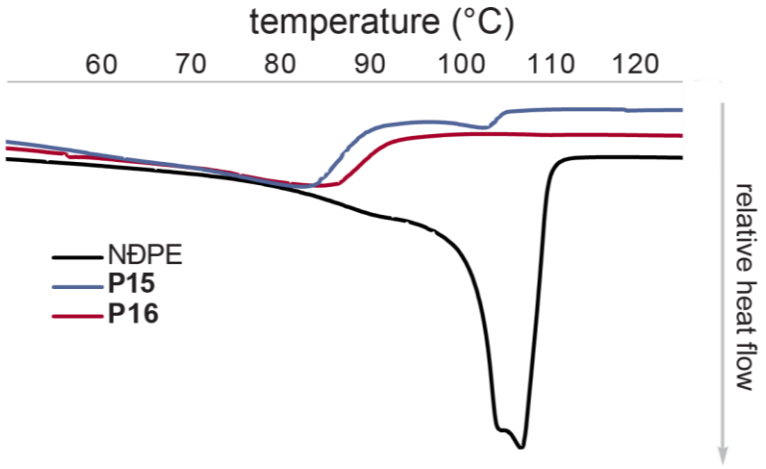


Figure S13. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of NĐPE and functionalized NĐPEs were analyzed. In both functionalizations, the semicrystallinity decreased as observed through a decrease in heat flow into the polymer sample. All functionalized NĐPEs exhibited melting temperatures above 80°C.

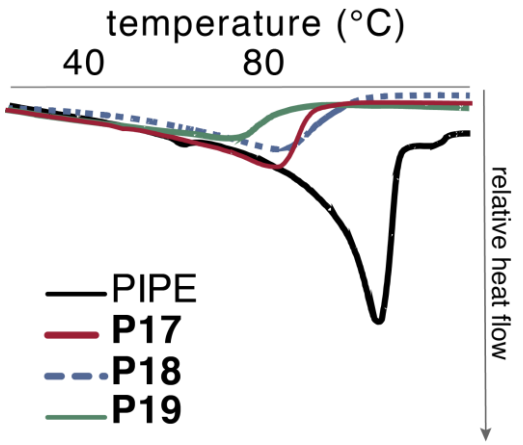


Figure S14. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of PIPE and functionalized PIPE were analyzed. In all functionalizations, the semicrystallinity decreased, so observed through a decrease in heat flow into the polymer sample. All functionalized PIPEs exhibited melting temperatures above 60 °C, with a decrease in semicrystallinity with higher degrees of functionalization.

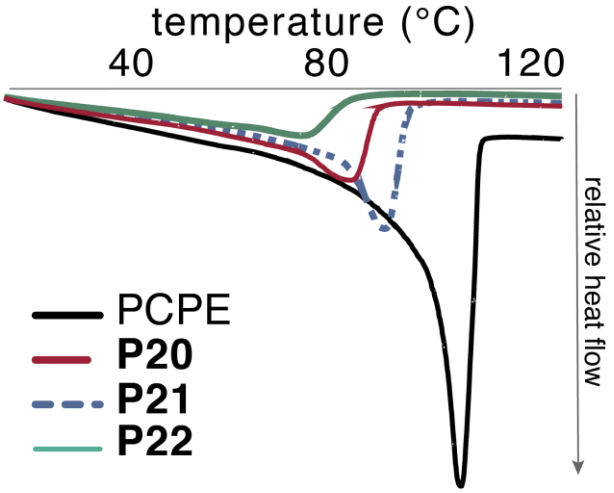


Figure S15. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of PCPE and functionalized PCPEs were analyzed. In all functionalizations, the semicrystallinity decreased as observed through a decrease in heat flow into the polymer sample. The iodo-functional PCPE most resembles the virgin PCPE melting temperature. All functionalized PCPEs exhibited melting temperatures above 60 °C, with reduced semicrystallinity with higher degrees of functionalization.

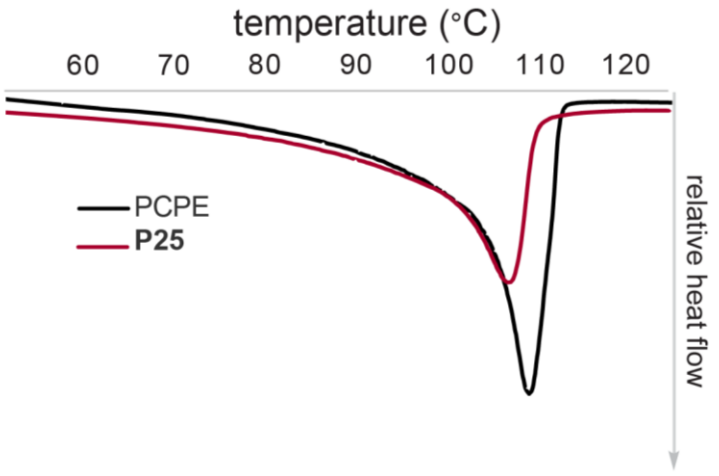


Figure S16. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of PCPE and bromoethylthiolated PCPE functionalized via extrusion (P25) were analyzed. The semicrystallinity decreased as observed through a decrease in heat flow into the polymer sample. Functionalized PCPE exhibited a melting temperature of 108 °C.

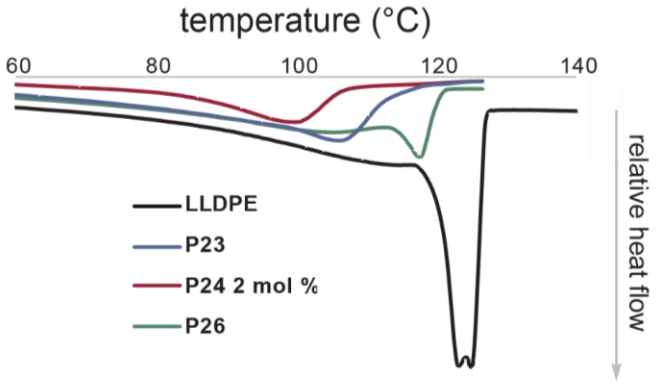


Figure S17. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of LLDPE and functionalized LLDPEs were analyzed. The semicrystallinity decreased as observed through a decrease in heat flow into the polymer sample.

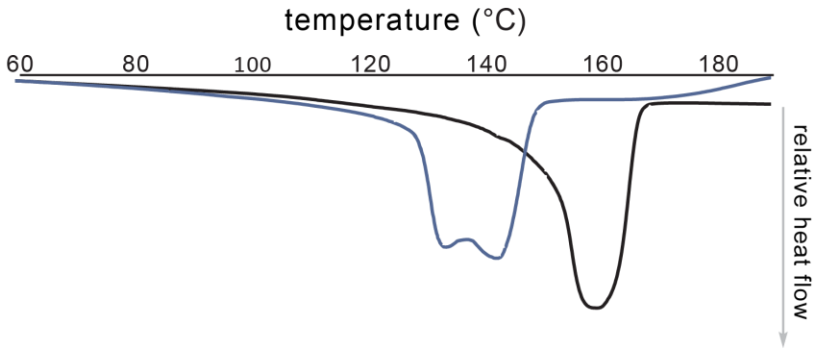


Figure S19. Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min; the melting temperature and enthalpy of iPP and thiophenolated iPP (P27) was analyzed. The semicrystallinity decreased as observed through a decrease in heat flow into the polymer sample.

DSC Spectra of Reagent 1 and Yoshida's Correlation

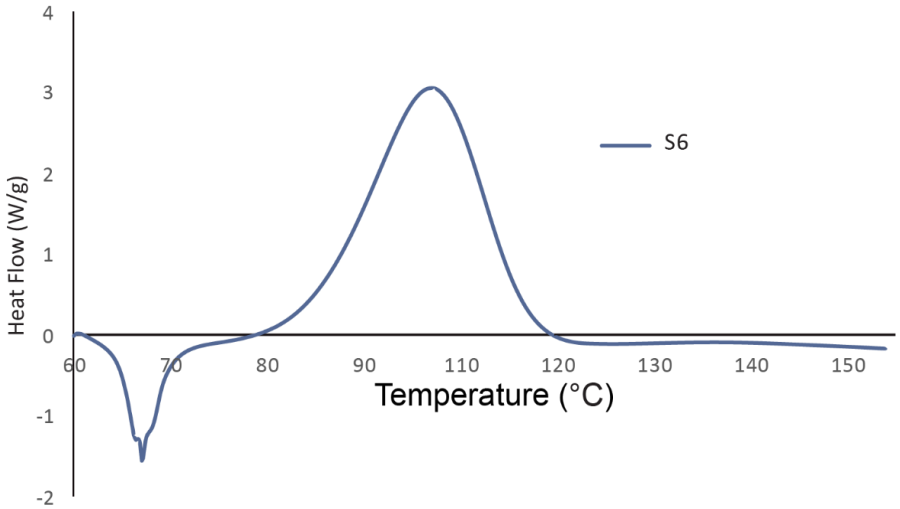


Figure S20. DSC of reagent **1**; Data plotted from the 2nd heating cycle at a heating rate of 5 °C/min, the enthalpic flow of the (1-phenylvinyloxy)amide reagent (**1**) was analyzed. An exotherm was observed with T_{onset} (°C) = 73.5 and Q (cal/g) = 125.5.

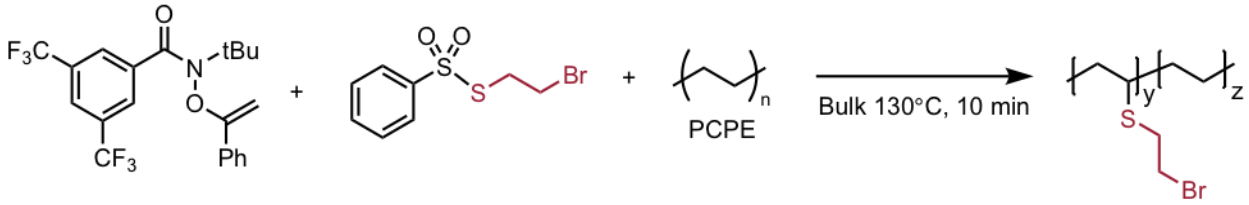
Yoshida correlation determines shock sensitivity and explosive propagation via differential scanning calorimetry (DSC) and is given as:

impact sensitivity (IS) = $\log_{10}(Q) - 0.72[\log_{10}(T_{onset} - 25)] - 0.98$
explosive propagation (EP) = $\log_{10}(Q) - 0.38[\log_{10}(T_{onset} - 25)] - 1.67$

Where Q = Δ*H* (cal/g) of enthalpic flow by DSC and T_{onset} (°C) = extrapolated temperature of onset by DSC software. A value greater than 0 predicts impact sensitivity and/or explosive propagation. Temperature is scanned by DSC at a rate of 5 °C/min.

For the (1-phenylvinyloxy)amide reagent (S6), T_{onset} (°C) = 73.5 and Q (cal/g) = 125.5 resulting in values less than 0 for both IS and EP where IS = –0.095 and EP = –0.21.

Reactive Extrusion Experiments



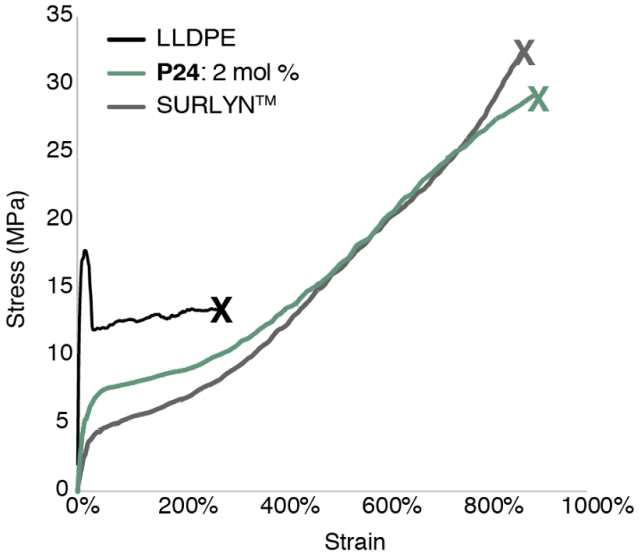
Extruded bromoethylthiolated PCPE (P25): Small pellets of post-consumer PE (PCPE) (M_n = 23 kg/mol, *Đ* = 19.79, 6.0g, 213 mmol) were mixed with (1-phenylvinyloxy)amide (4.60g, 10.7 mmol) and *S*-(2-bromoethyl) benzenesulfonothioate (6.00 g, 21.3 mmol) in a weigh-boat for extrusion. An Xplore twin-screw extruder was purged with N_2, the heat profile was set to 133 °C with a melt temperature of 130 °C, and the screws were turned at 75 rpm. The mixture of powders (15g) were loaded into the extruder for 150 seconds. Material was mixed for 10 minutes before extruding into a filament. The crude material was dissolved and precipitated from chlorobenzene at 130 °C into acetone at room temperature, resulting in a 1 mol % functionalized white flakey solid.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 110 °C) δ 3.55 (bs, 2H), 3.05 (bs, 2H), 2.70 (bs, 1H), 1.68 (bs), 1.43 (bs), 1.01 (bs). **IR (neat, ATR, cm^{-1})** 3500, 3405, 2916, 2849, 1635, 1473, 1368, 1284, 1201, 1087, 1027, 827, 720. **GPC (TCB, 140 °C)** M_n = 28 kg/mol, Đ = 26.94. **TGA (°C)** parent T_d = 414 °C, product T_d= 323 °C. **DSC (°C)** parent T_m= 111 °C, 37% crystallinity (DH=111 J/g), product T_m= 108 °C, 32% crystallinity (DH=89 J/g).

Tensile Testing Experiments

Polymer films (0.2 mm) suitable for dynamic mechanical analysis (DMA) were prepared by melt-pressing using a PHI Manual Compression Press. DOW™ DNDA-1081 NT 7 Linear Low Density Polyethylene Resin (LLDPE), 2 mol % imidazolium bromide LLDPE, and 4 mol % imidazolium bromide LLDPE samples were placed between two Kapton films (pre-treated with Frekote 770-NC) and placed between steel plates to be heated at 150 °C for 2 minutes, pressed at 1000 psi for 5 minutes, and at 5000 psi for 1 minute. Brass shim cutouts were used to control ultimate film thickness. Films were removed from the melt press and cooled to room temperature by rapid heat transfer to an aluminum surface. Ionomers are known to be hygroscopic and demonstrate slow crystallization kinetics; therefore, the films were aged for four days in a desiccator before tensile testing.

Specimens for analysis were cut into dog-bones using an ISO 527 Type 5B cutting die to standard dimensions. Sample thickness at the bridge was measured using calipers. Test specimens were affixed to hand-tightened rubber grips on an Instron 5566 Universal Testing Machine. Tensile stress and strain were measured at room temperature using an extension rate of 1.0 mm/s. Measurements were repeated for at least 3 specimens and average values are reported. (Table S3)



	LLDPE	Polyolefin Ionomer **P24** (2 mol%)	Polyolefin Ionomer SURLYN™
σ_B *(MPa)*	13 ± 1	31 ± 2	32 ± 2
ε_B	250 ± 51%	1003 ± 104%	878 ± 10%
E (MPa)	27 ± 2	4.2 ± 0.1	1.8 ± 0.1
U_T *(MPa)*	387 ± 74	2160 ± 380	1536 ± 78

Table S3. DMA results from thin film tensile axial pull of 0.2 mm thick LLDPE, polyolefin ionomers, and SURLYN™ at a rate of 1.0 mm/s.

Additional Polymer Data

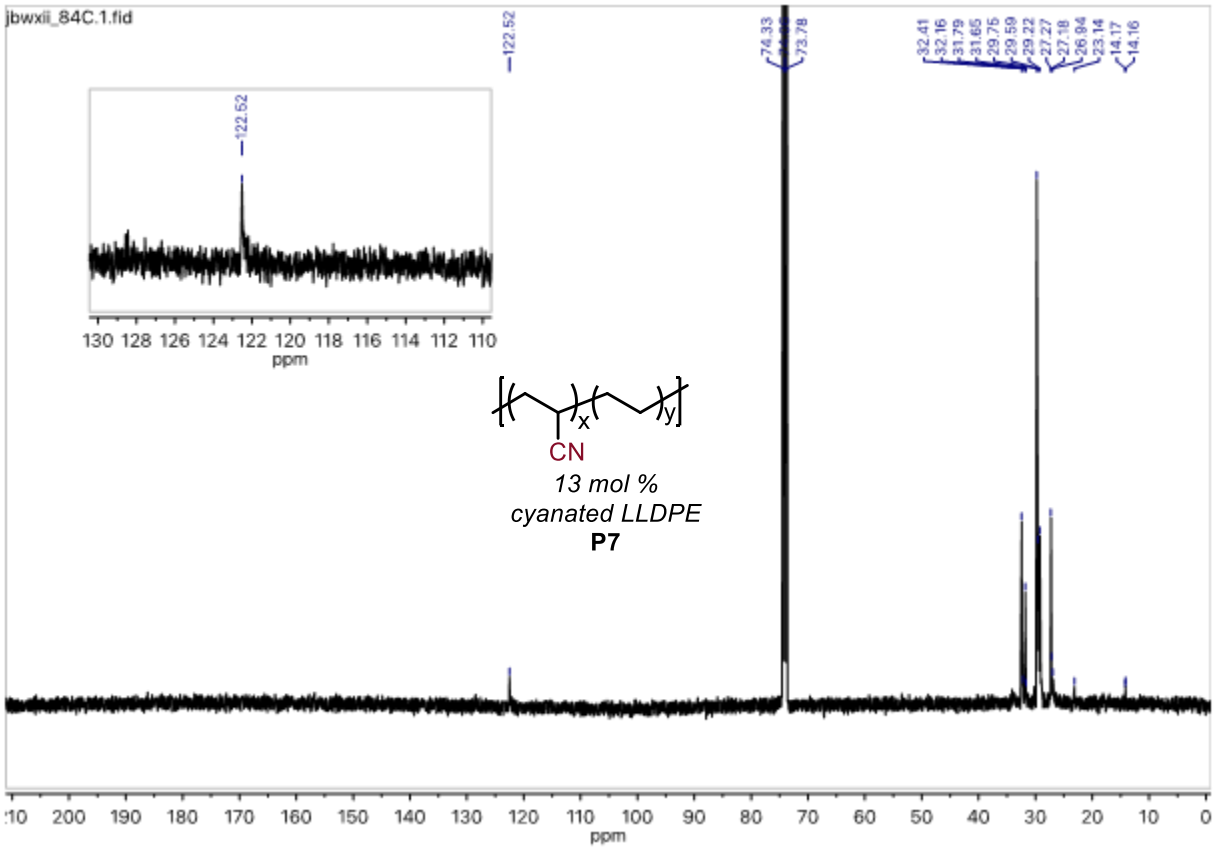


Figure S21: We analyzed the cyanated LLDPE via ^{13}C NMR spectroscopy at 80 °C with a 400 MHz NMR. Analyzed with 13 mol % cyanated LLDPE, the nitrile carbon is apparent at δ +122 ppm when referenced against $C_2D_2Cl_4$ at δ 73.78 ppm.

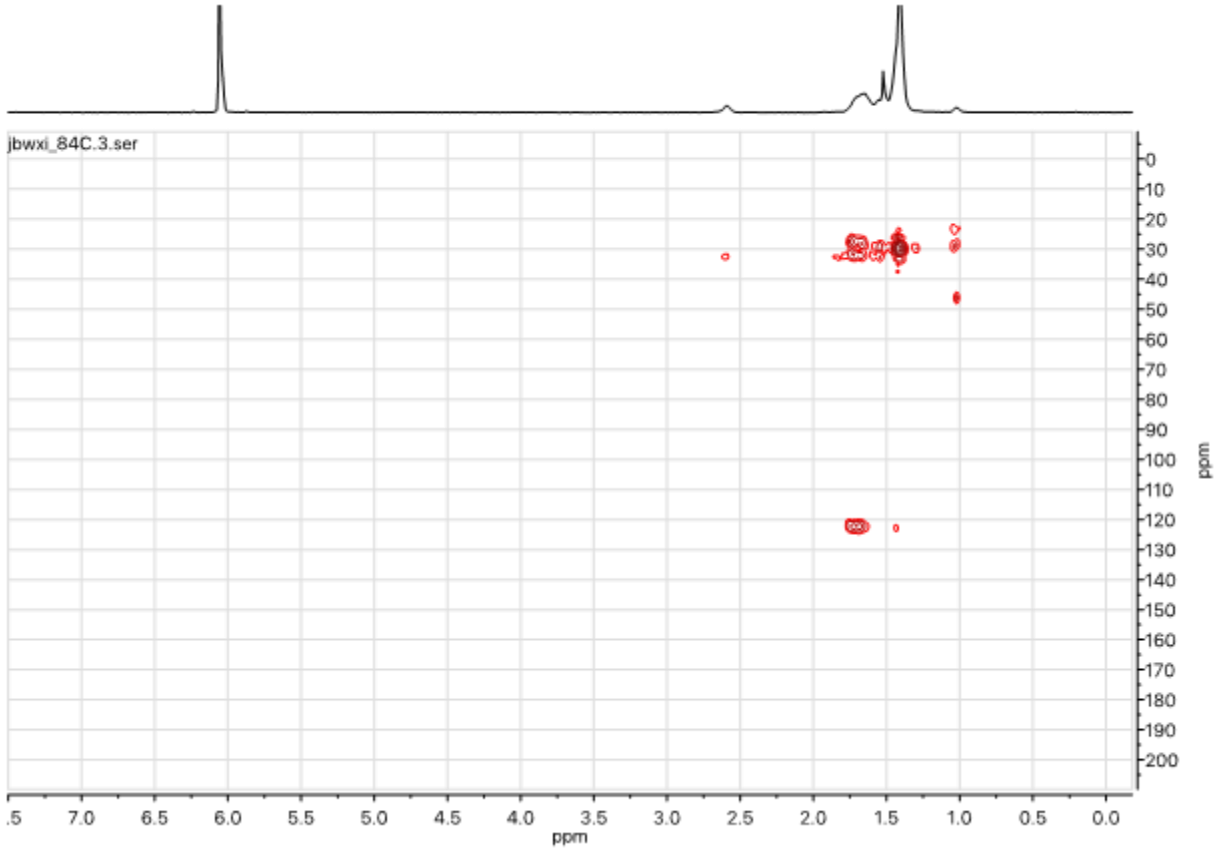


Figure S22: We evaluated the incorporation of a nitrile onto LLDPE by Heteronuclear Multiple Bond Correlation (HMBC) spectroscopy at 110 °C with a 500 MHz NMR. Analyzed with 13 mol % cyanated LLDPE, the y-axis shows carbons correlated in J- or W-coupling with the associated protons on the x-axis. The peaks at δ 121 ppm clearly indicate that a cyano group is present in the compound and is coupled to the polyolefin protons, likely through a W-coupling.

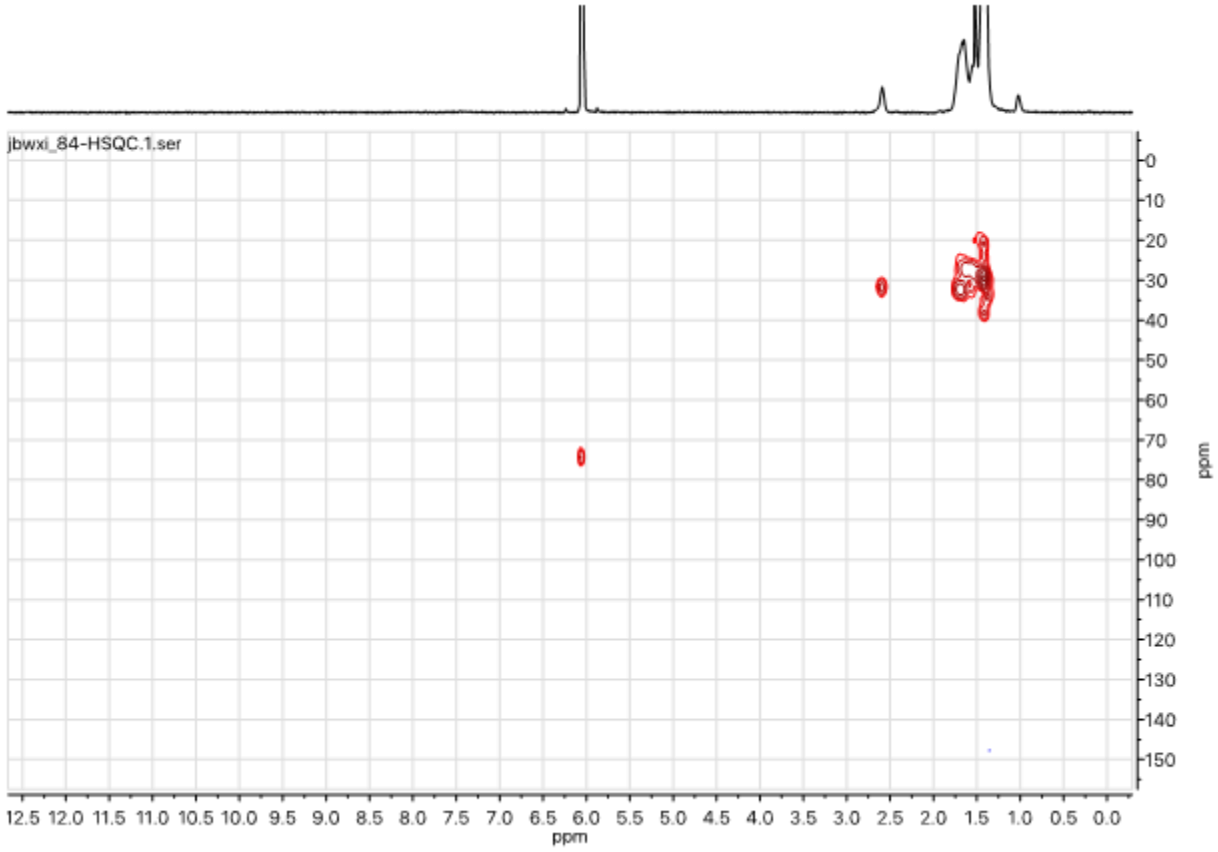


Figure S23: Heteronuclear Single Quantum Coherence (HSQC) spectroscopy at 110 °C with a 500 MHz NMR was performed on 13 mol % cyanated LLDPE showing the proton peak at δ 2.54 ppm correlates to carbon at 32.82 ppm.

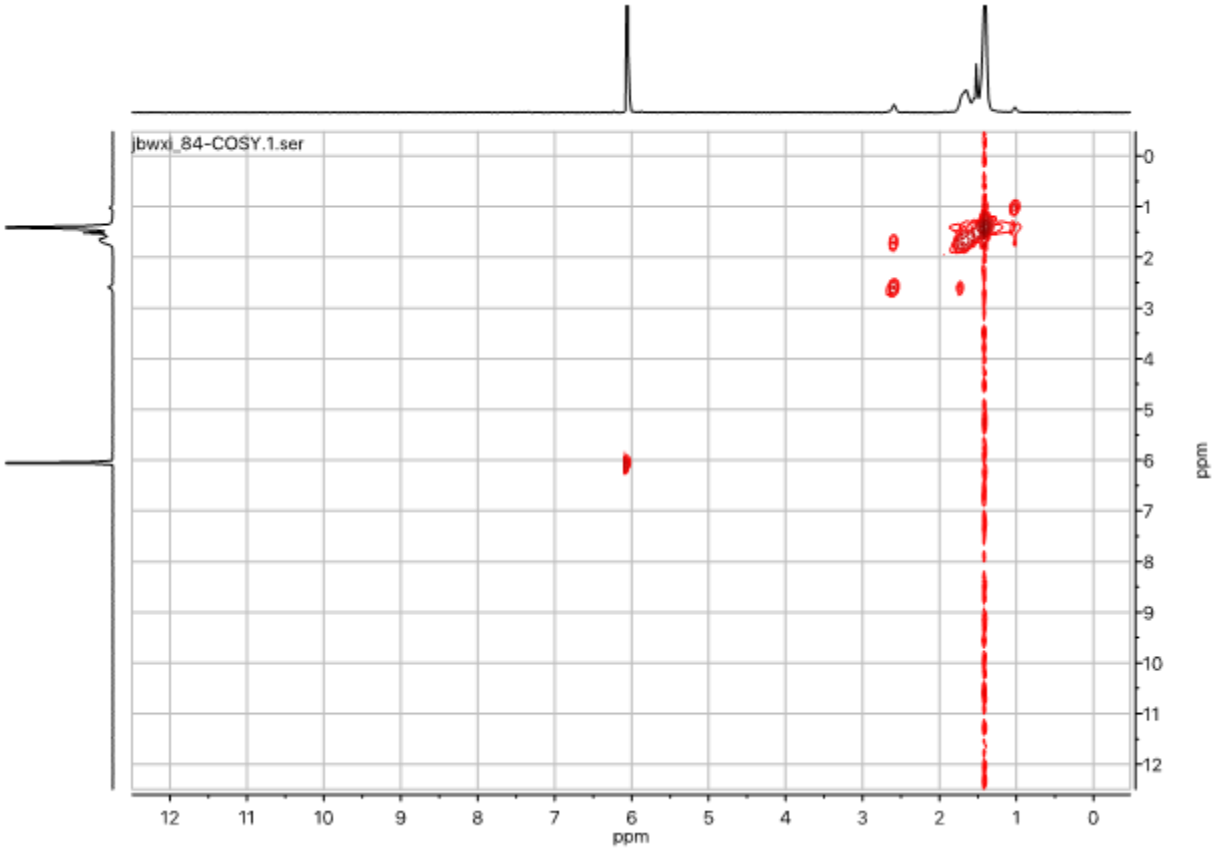


Figure S24: ^{1}H–^{1}H Correlated Spectroscopy (COSY) was performed on 13 mol % cyanated LLDPE at 110 °C on a 500 MHz NMR. The cross peaks between the polyolefin signal at δ 1.4 ppm and the proton alpha the nitrile at δ 2.54 ppm are evident, concluding that these protons are in the same spin system.

Figure S25. Top: Imidazolium bromide-functionalized LLDPE appears to be semi-crystalline with a slightly yellower tint than the parent LLDPE. Bottom: When trying to view an image, the film of LLDPE (left) remains translucent while the ionomer-LLDPE film (right) is more transparent.

IR of Post-Consumer and Post-Industrial PE

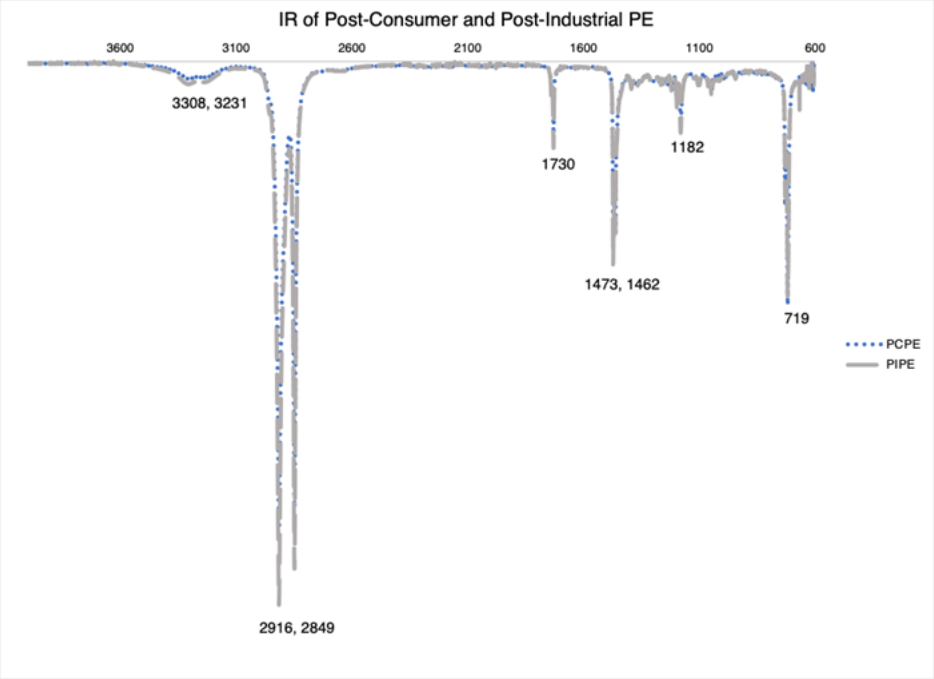
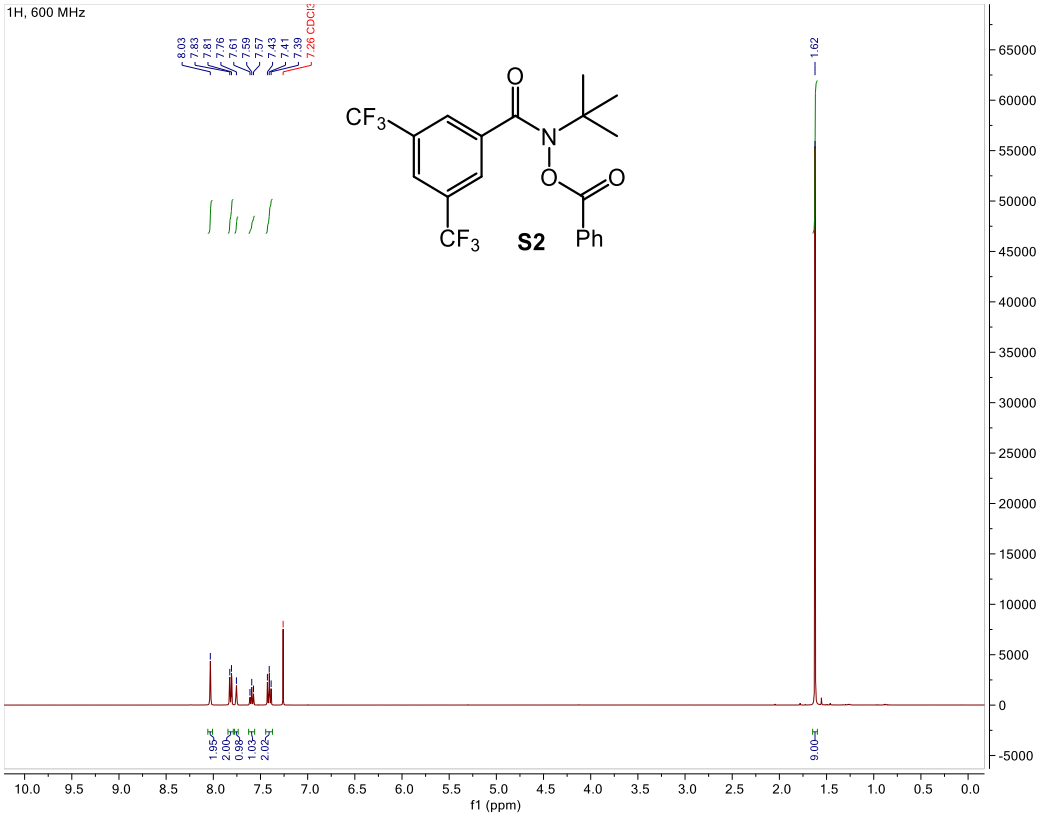
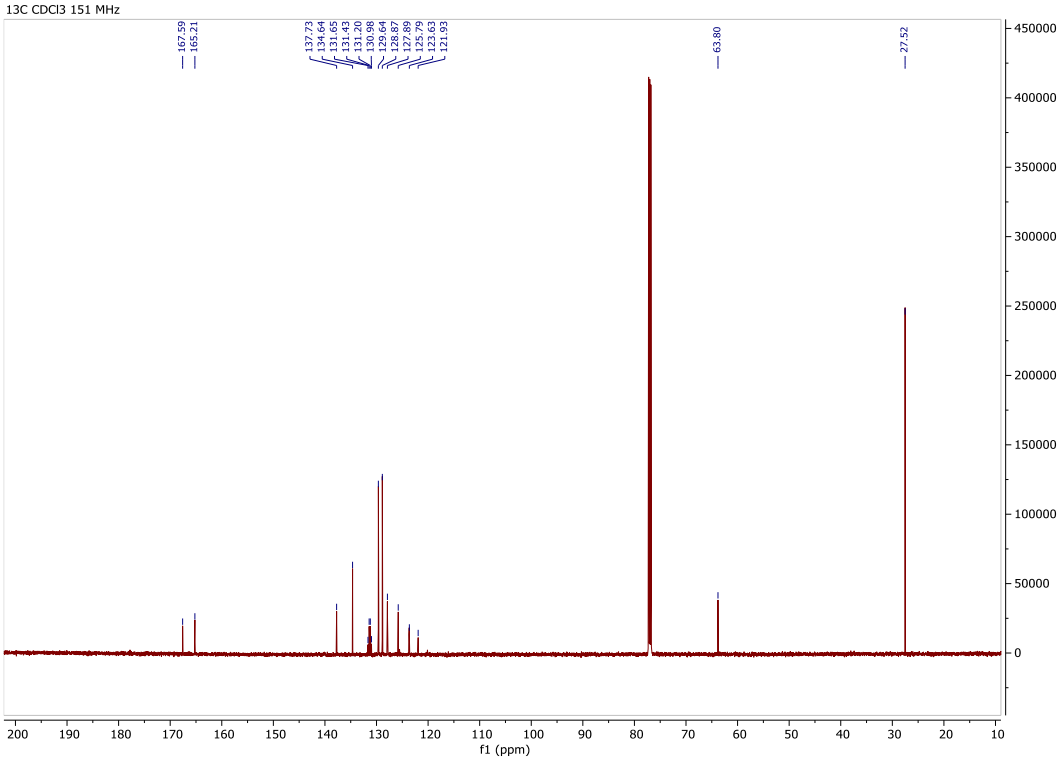


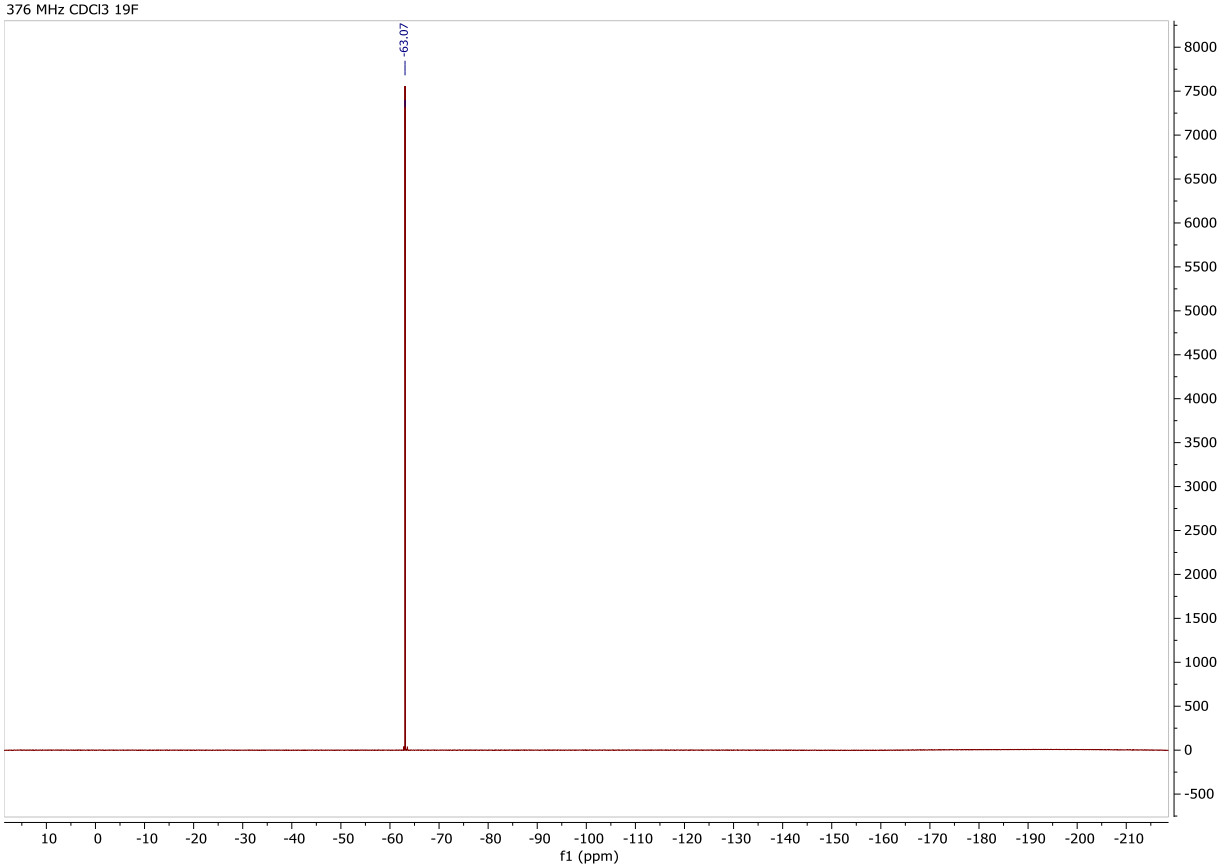
Figure S26: Infrared spectrum overlay of post-consumer PE (PCPE) and post-industrial PE (PIPE).

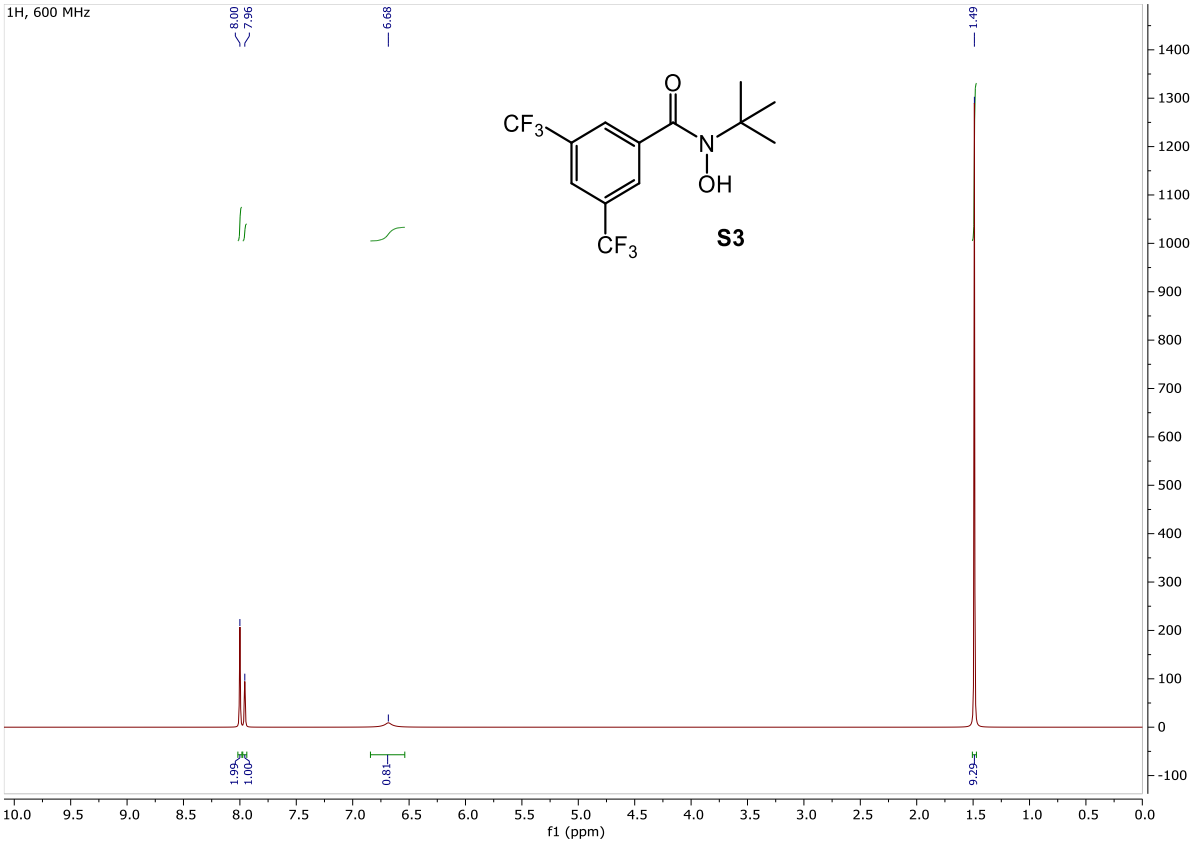
NMR Spectra for New Compounds





376 MHz CDCl3 19F

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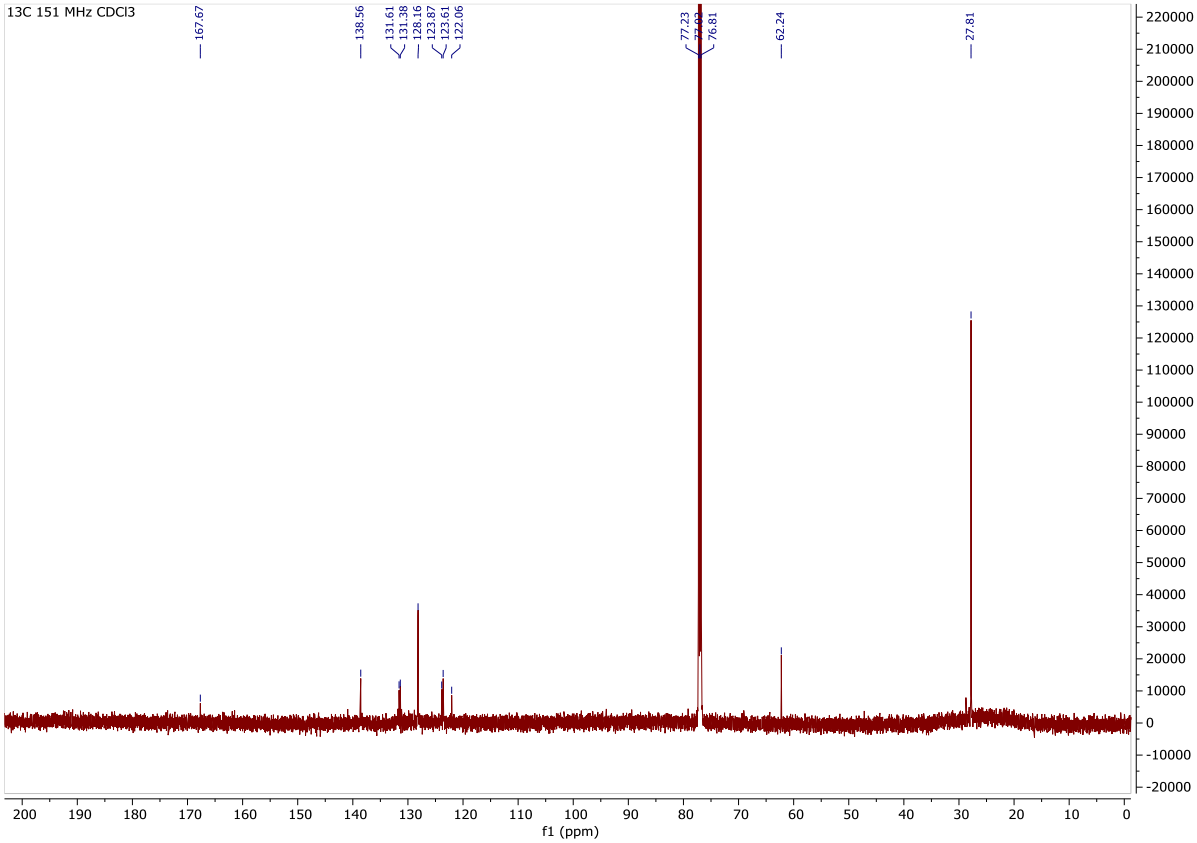
8.00
7.96
6.68
1.49
CF3
CF3
O
N
OH
S3
1.99
1.00
0.81
9.29
f1 (ppm)


13C 151 MHz CDCl3
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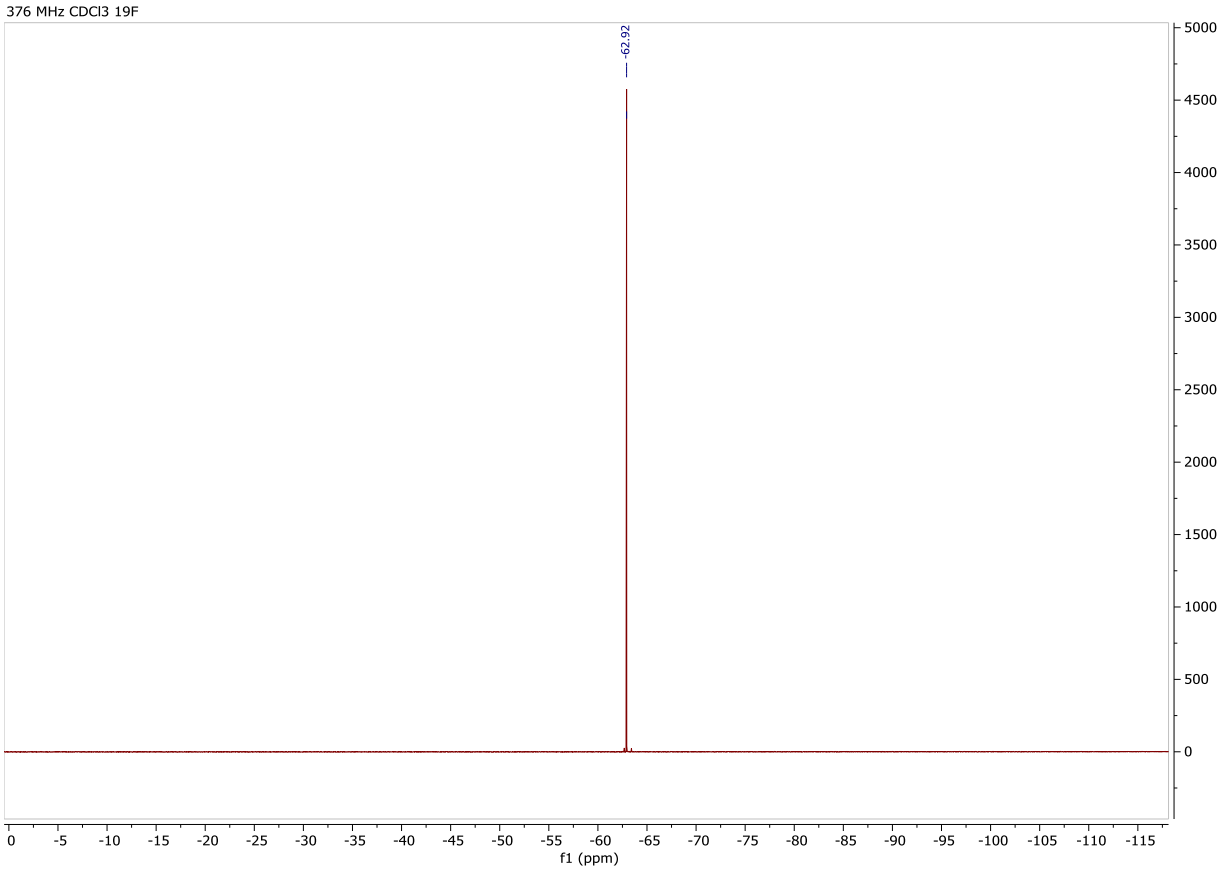
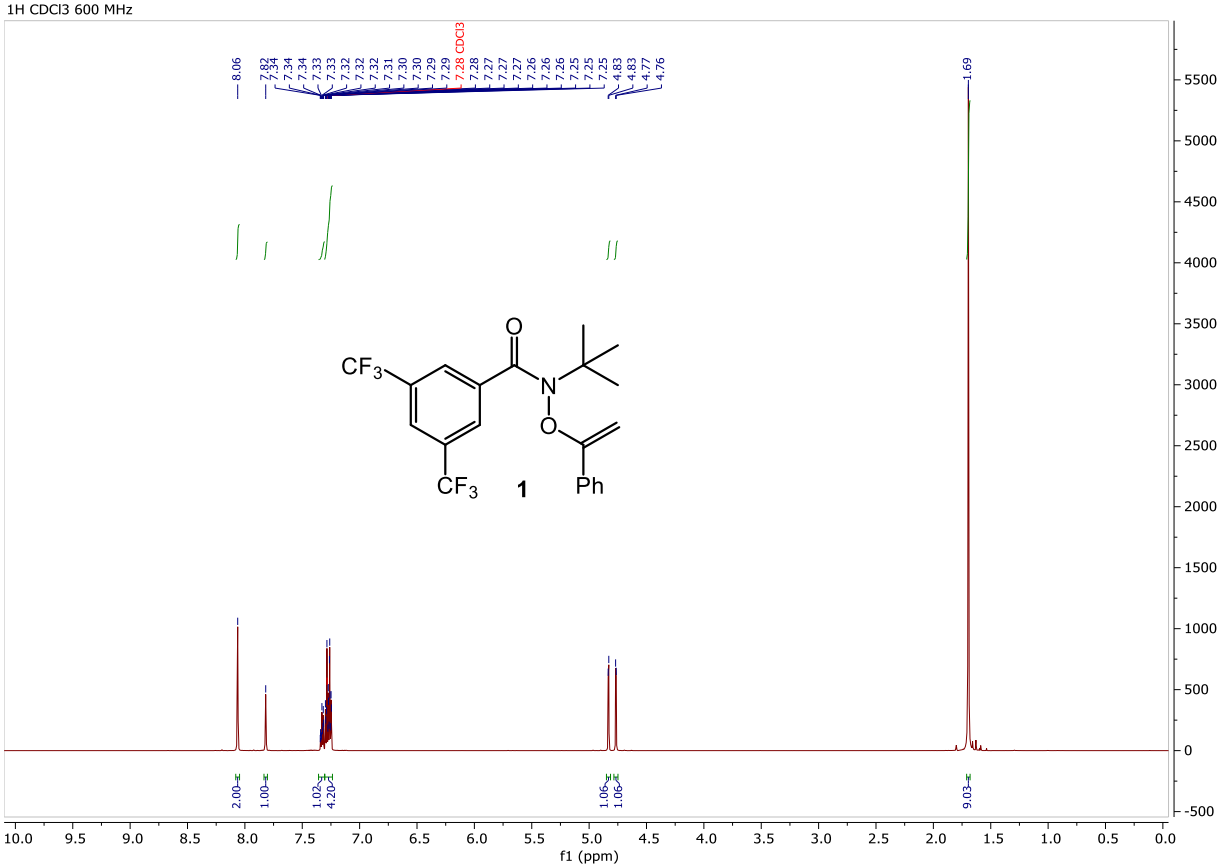
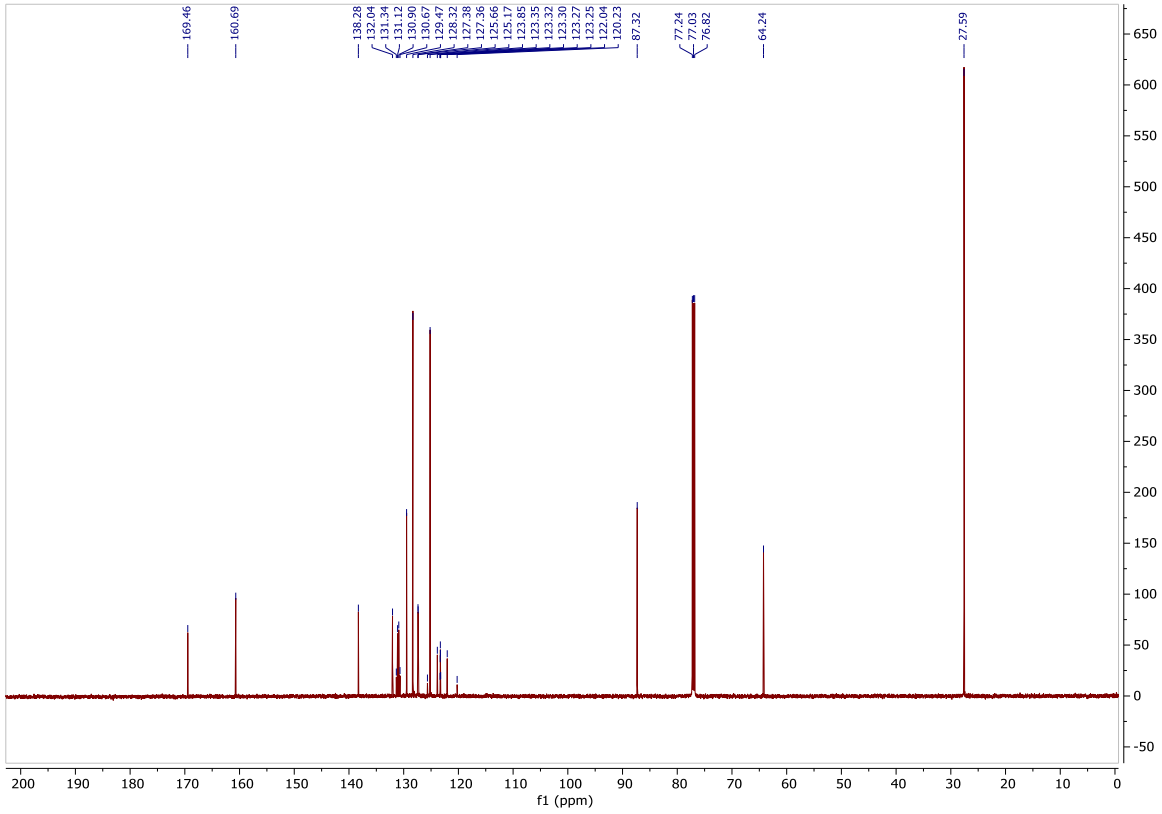
138.56
131.61
131.38
128.16
123.87
123.61
122.06
77.23
77.02
76.81
62.24
27.81
f1 (ppm)

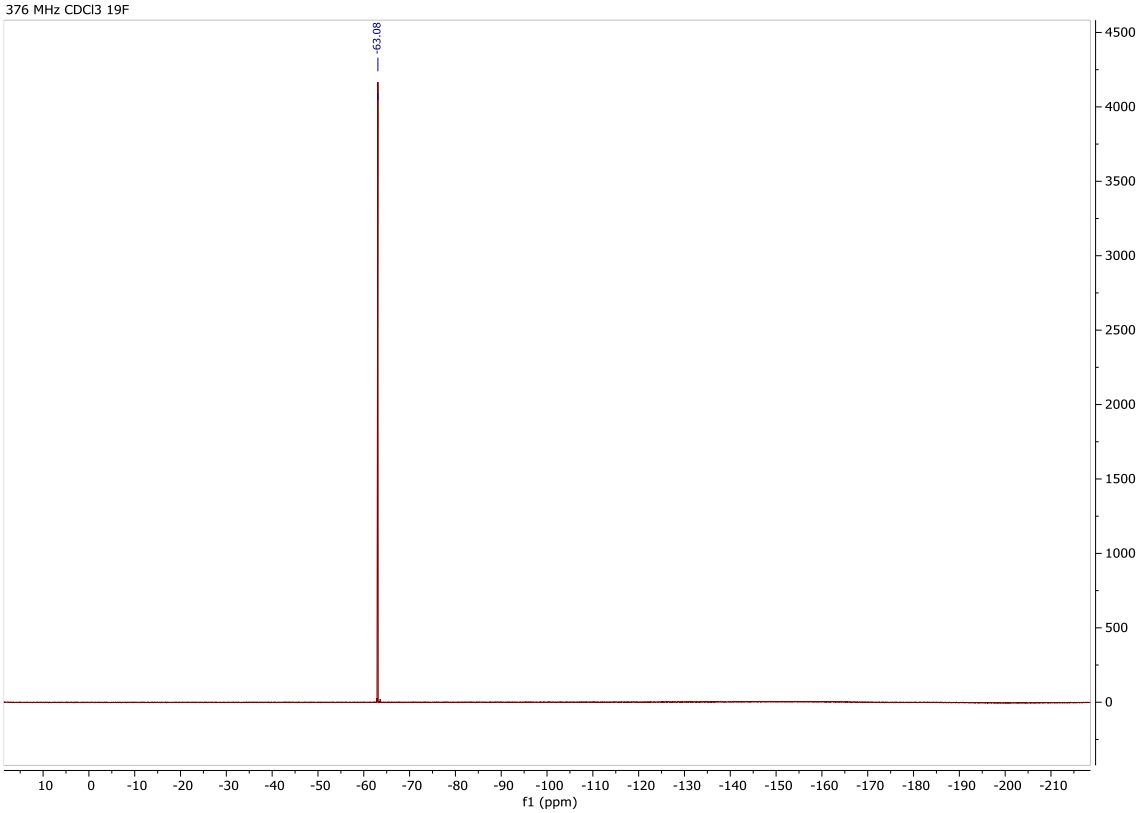

376 MHz CDCl3 19F
-62.92
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115
f1 (ppm)

1H CDCl3 600 MHz



13C CDCl3 151 MHz




376 MHz CDCl3 19F
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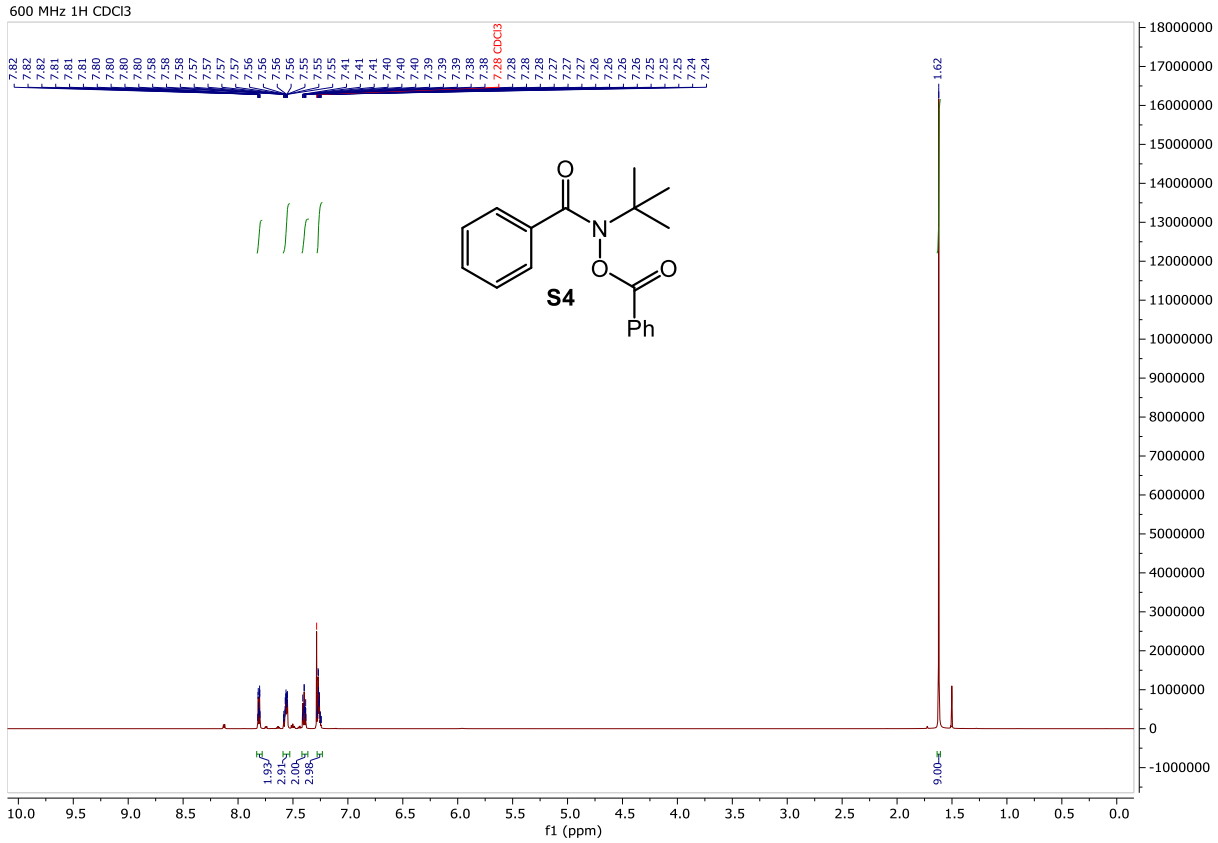
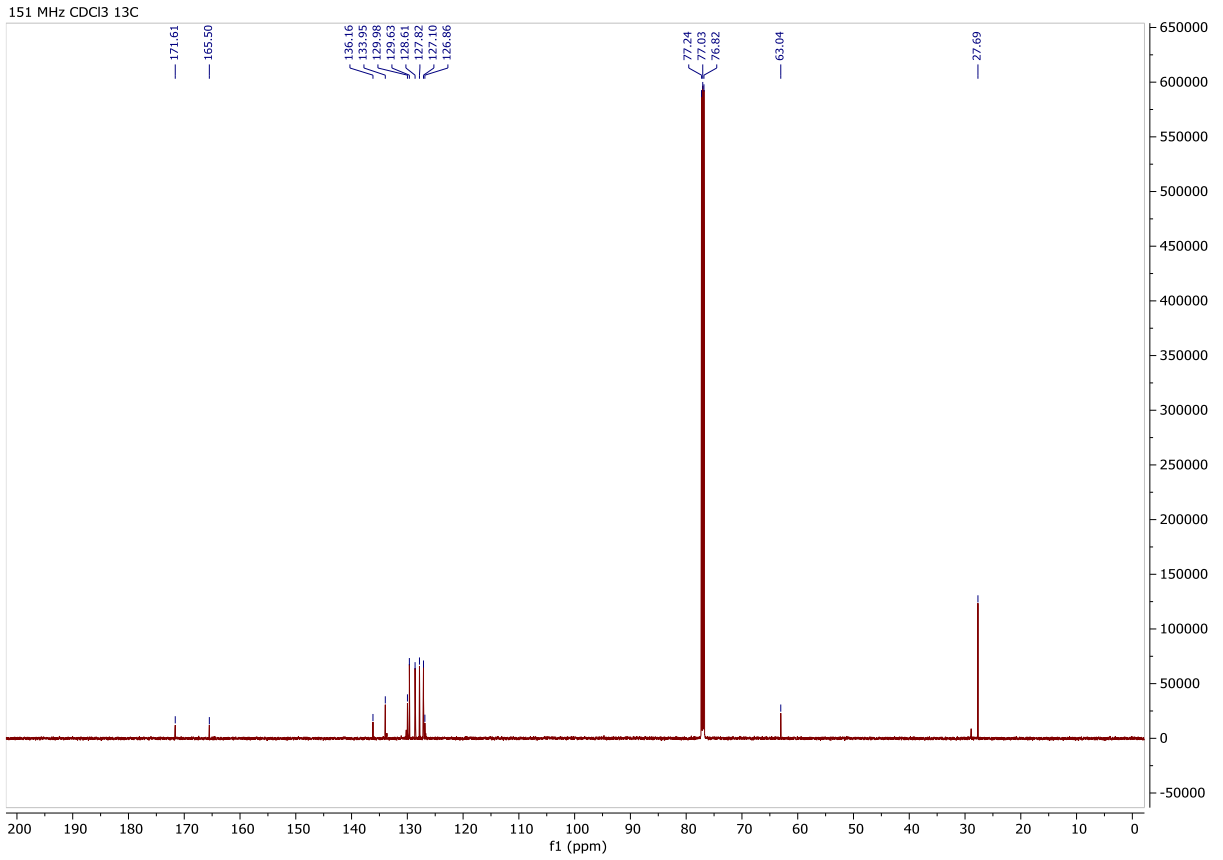
4000
3500
3000
2500
2000
1500
1000
500
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


600 MHz 1H CDCl3
S4
Ph
f1 (ppm)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165.50
136.16
133.95
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129.63
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127.82
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126.86
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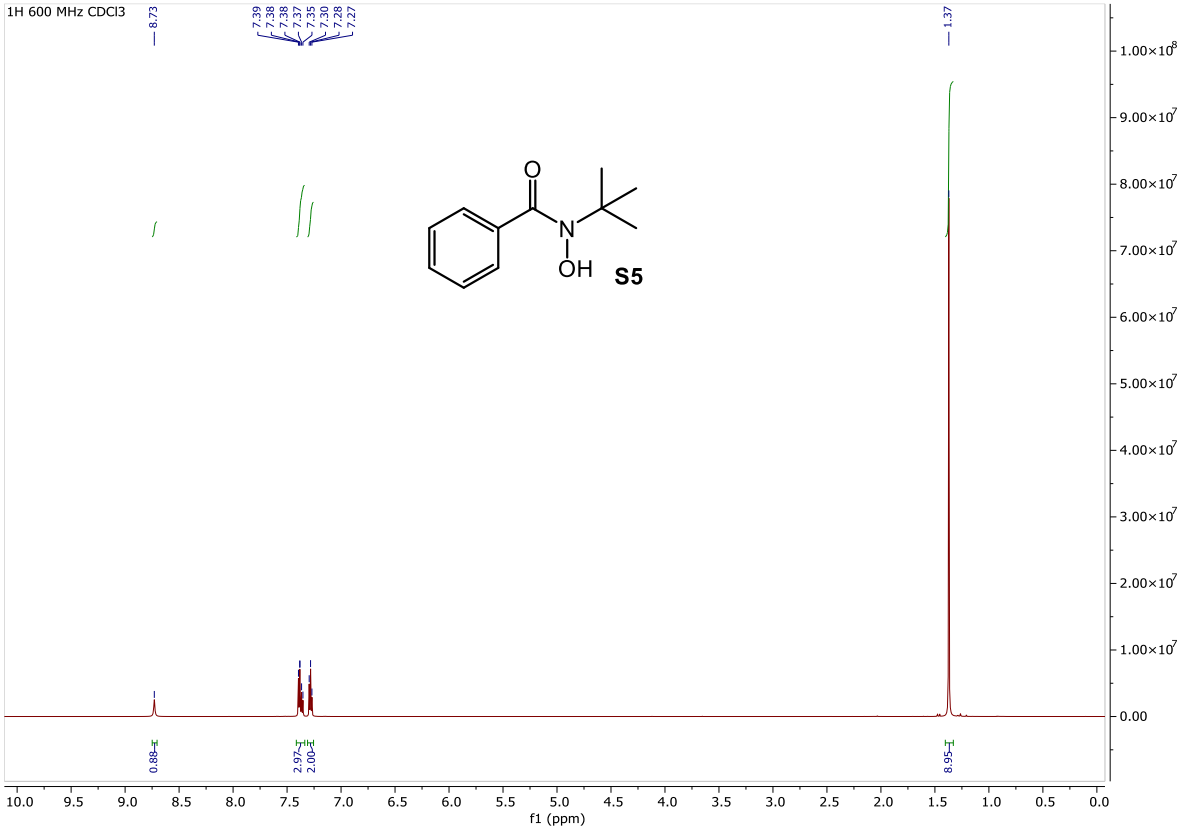
77.03
76.82
63.04
27.69
f1 (ppm)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7.37
7.35
7.30
7.28
7.27
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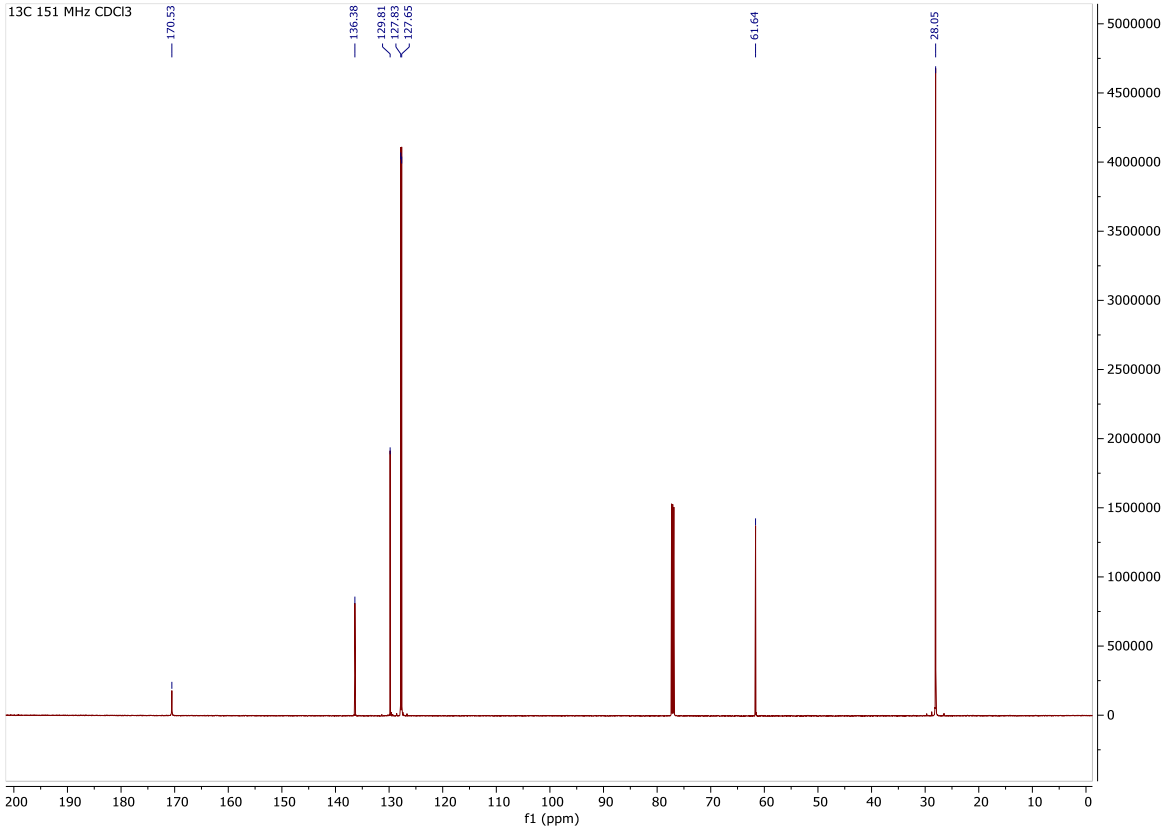
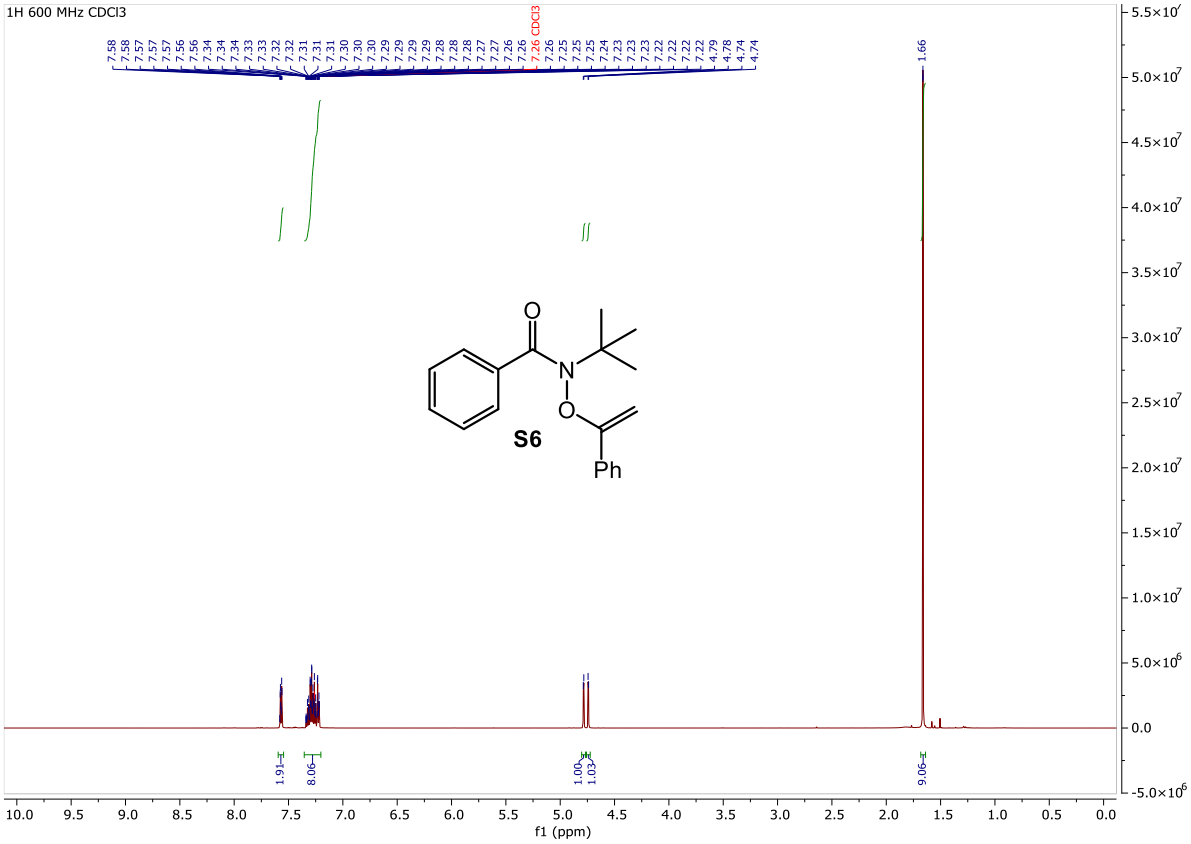
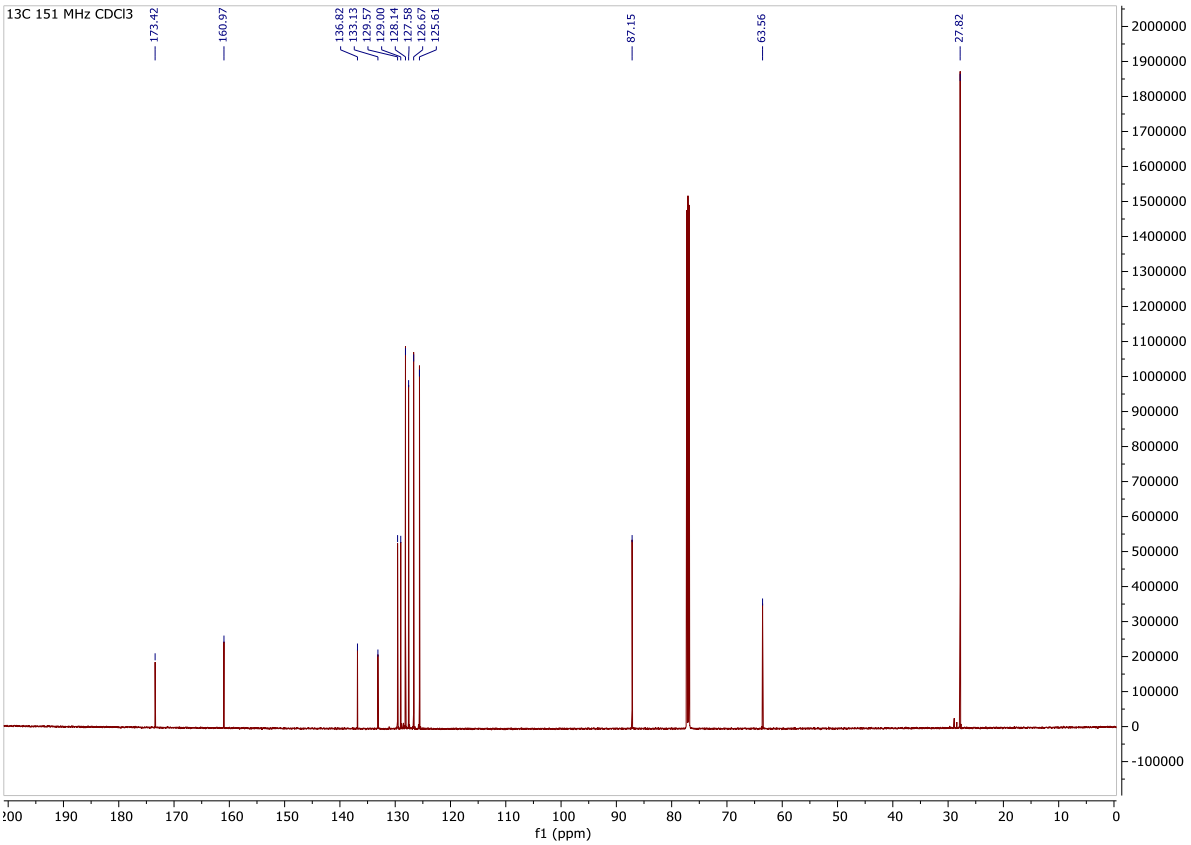
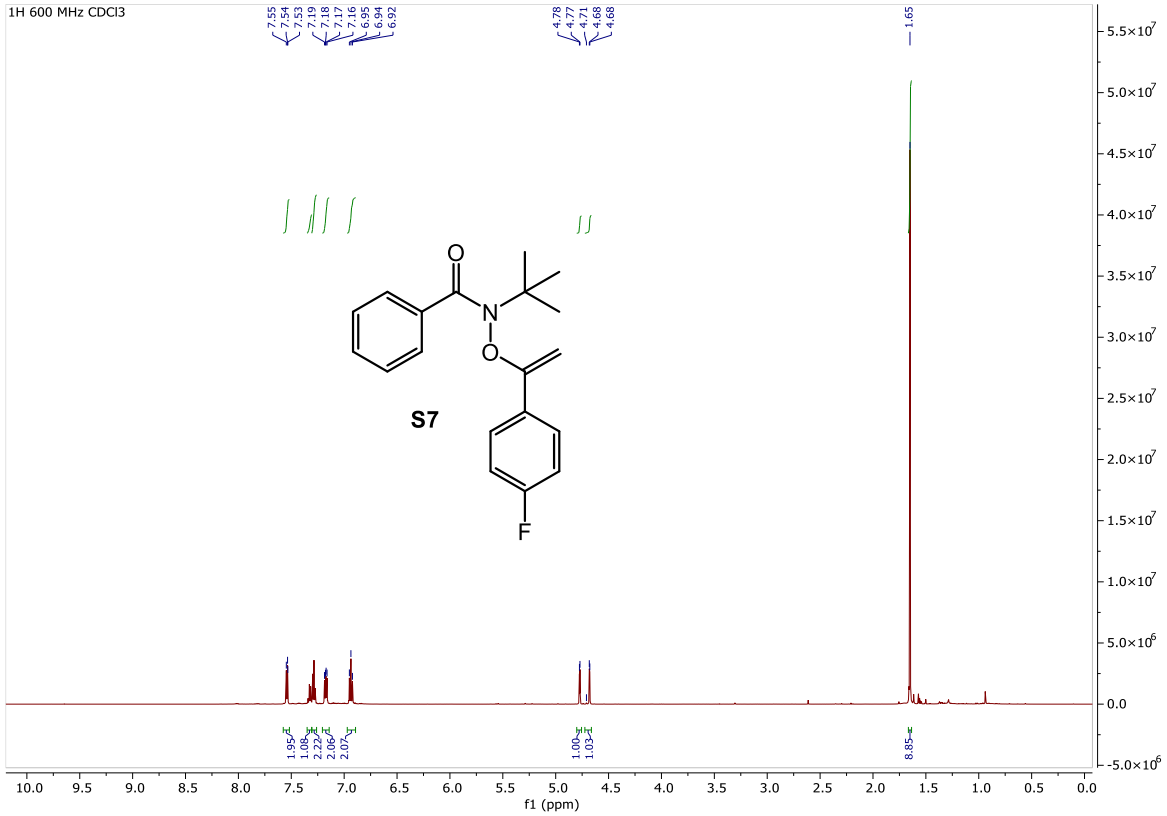
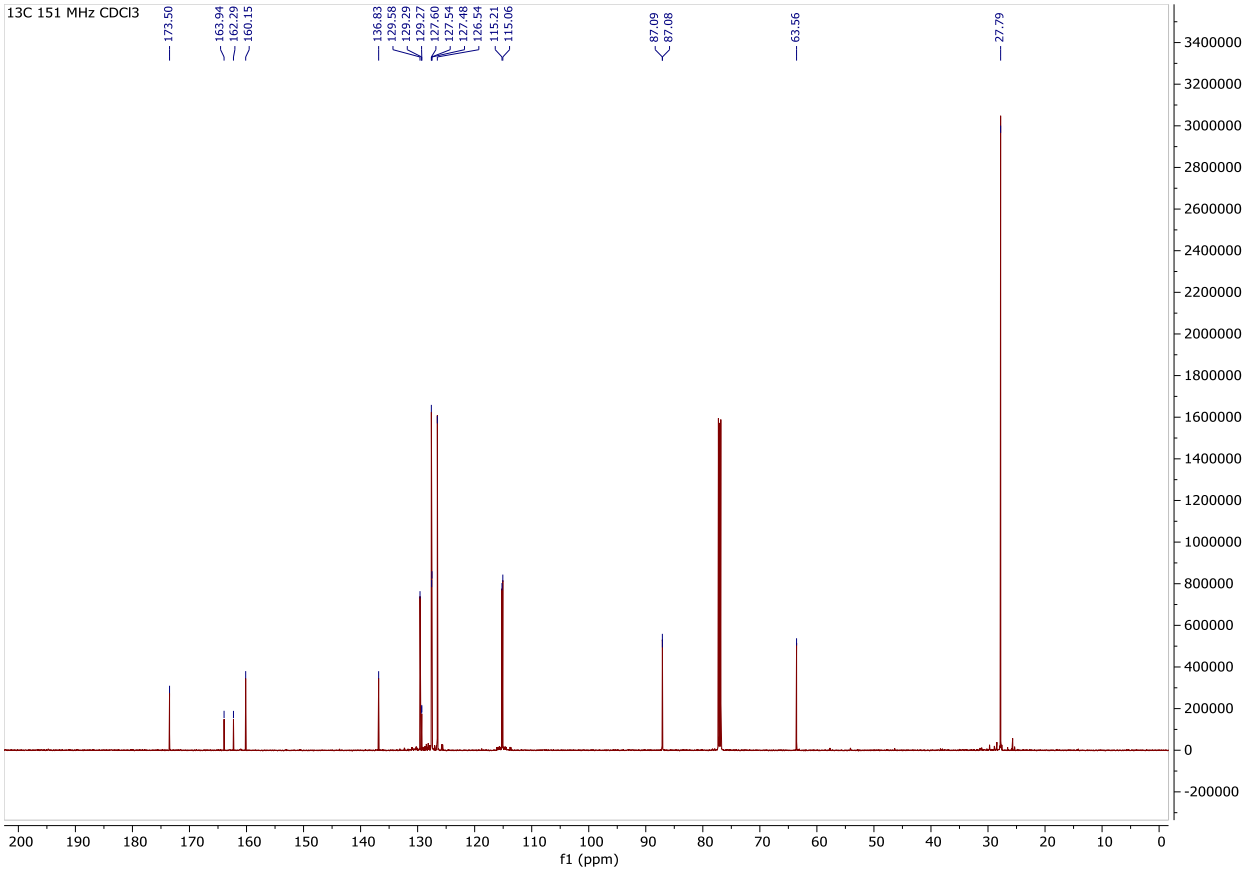
O
N
OH
S5
0.88
2.97
2.00
8.95
f1 (ppm)

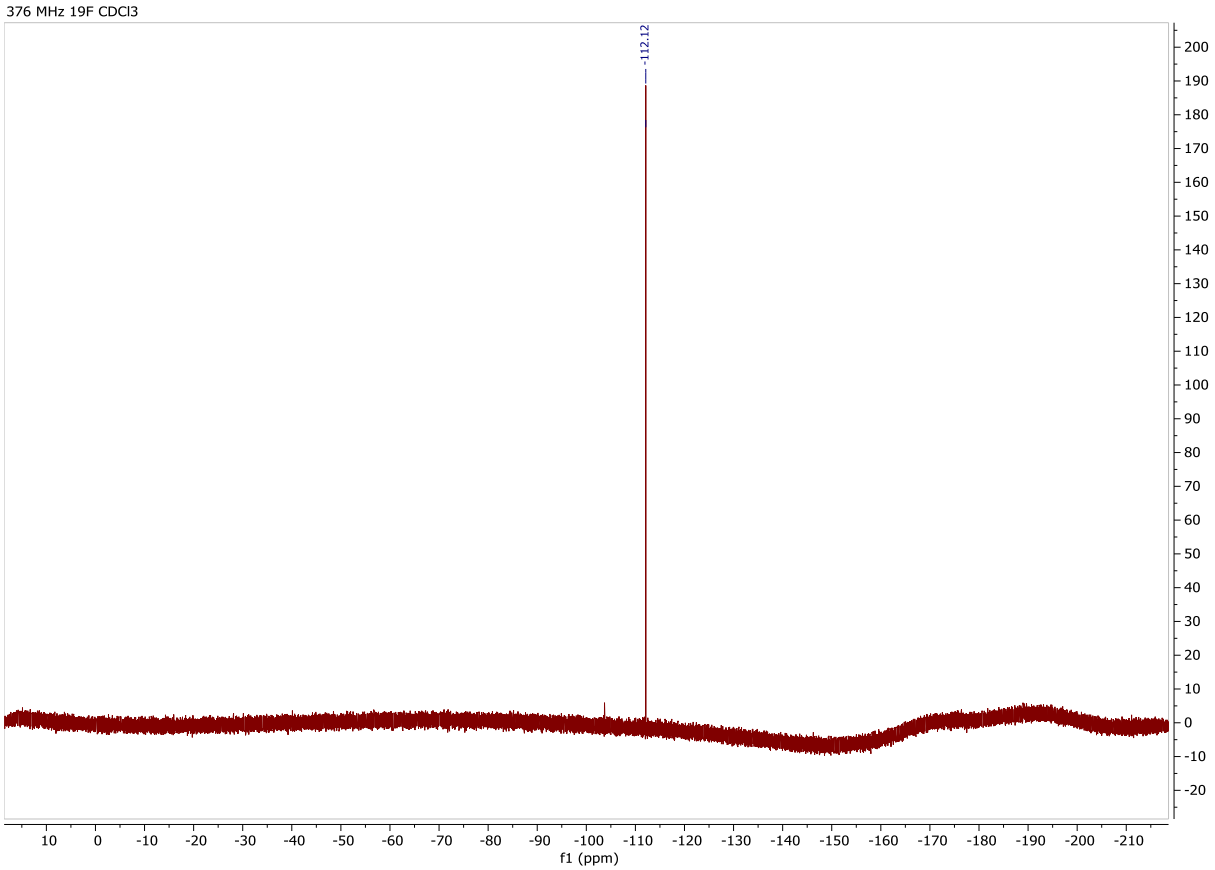

13C 151 MHz CDCl3
170.53
136.38
129.81
127.83
127.65
61.64
28.05
f1 (ppm)

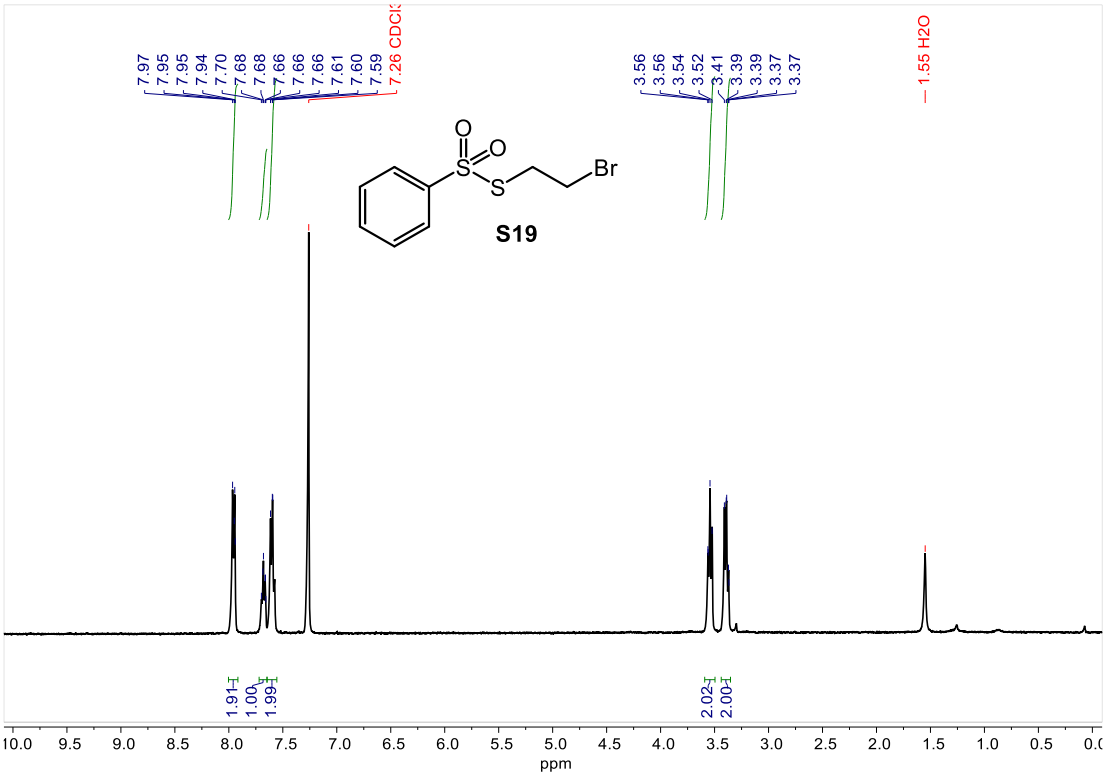

1H 600 MHz CDCl3
S6
Ph
f1 (ppm)

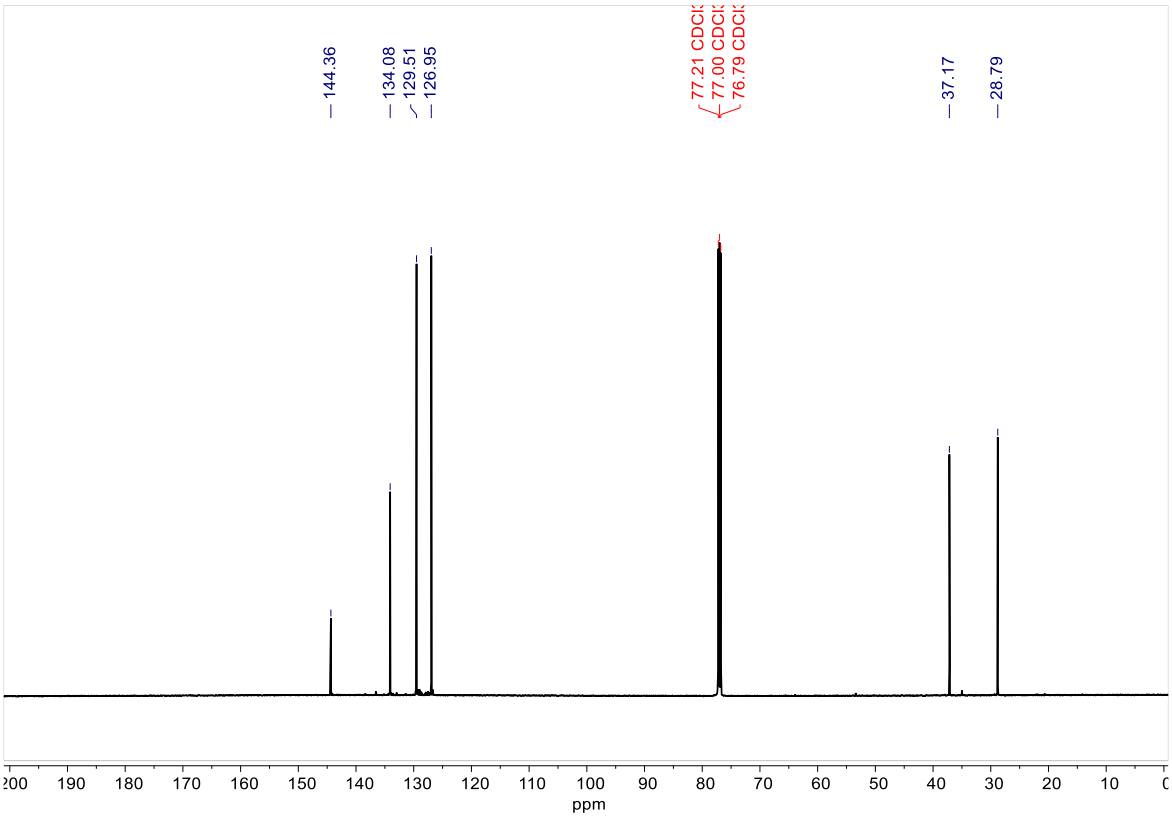

13C 151 MHz CDCl3
f1 (ppm)


1H 600 MHz CDCl3
7.55
7.54
7.53
7.19
7.18
7.17
7.16
6.95
6.94
6.92
4.78
4.77
4.71
4.68
4.68
1.65
O
N
O
F
S7
1.95
1.98
2.02
2.06
2.07
1.00
1.03
8.85
f1 (ppm)

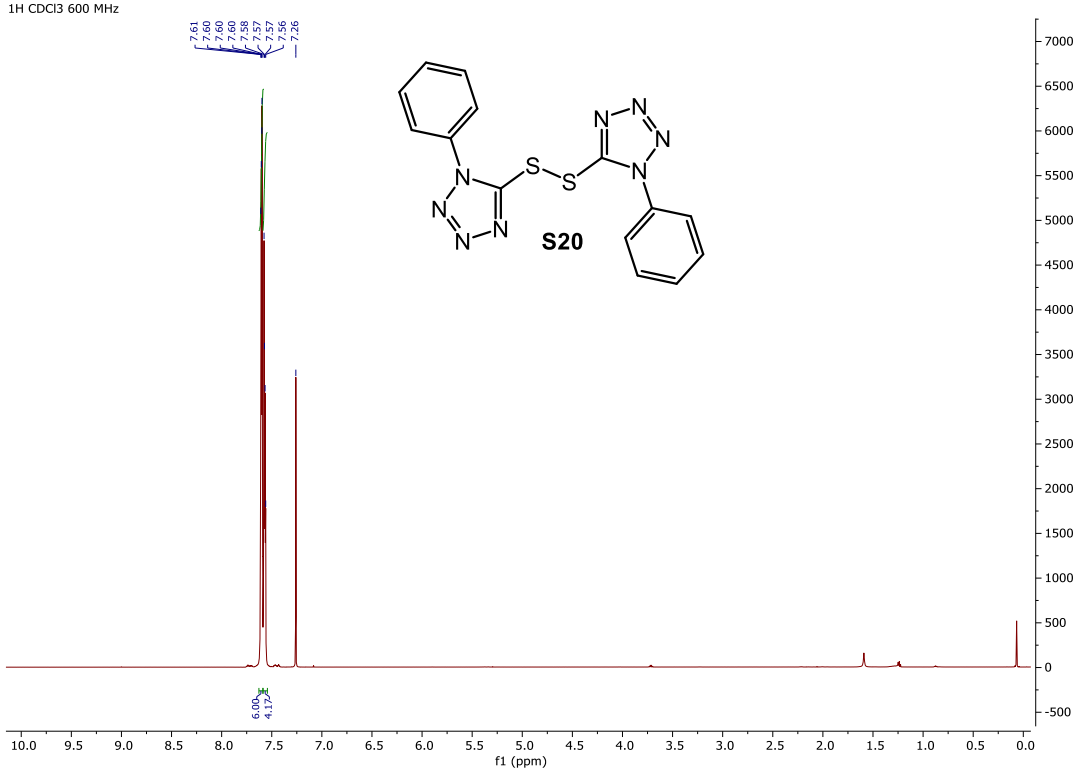

13C 151 MHz CDCl3
173.50
163.94
162.29
160.15
136.83
129.58
129.29
129.27
127.60
127.54
127.48
126.54
115.21
115.06
87.09
87.08
63.56
27.79
f1 (ppm)


376 MHz 19F CDCl3
-112.12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

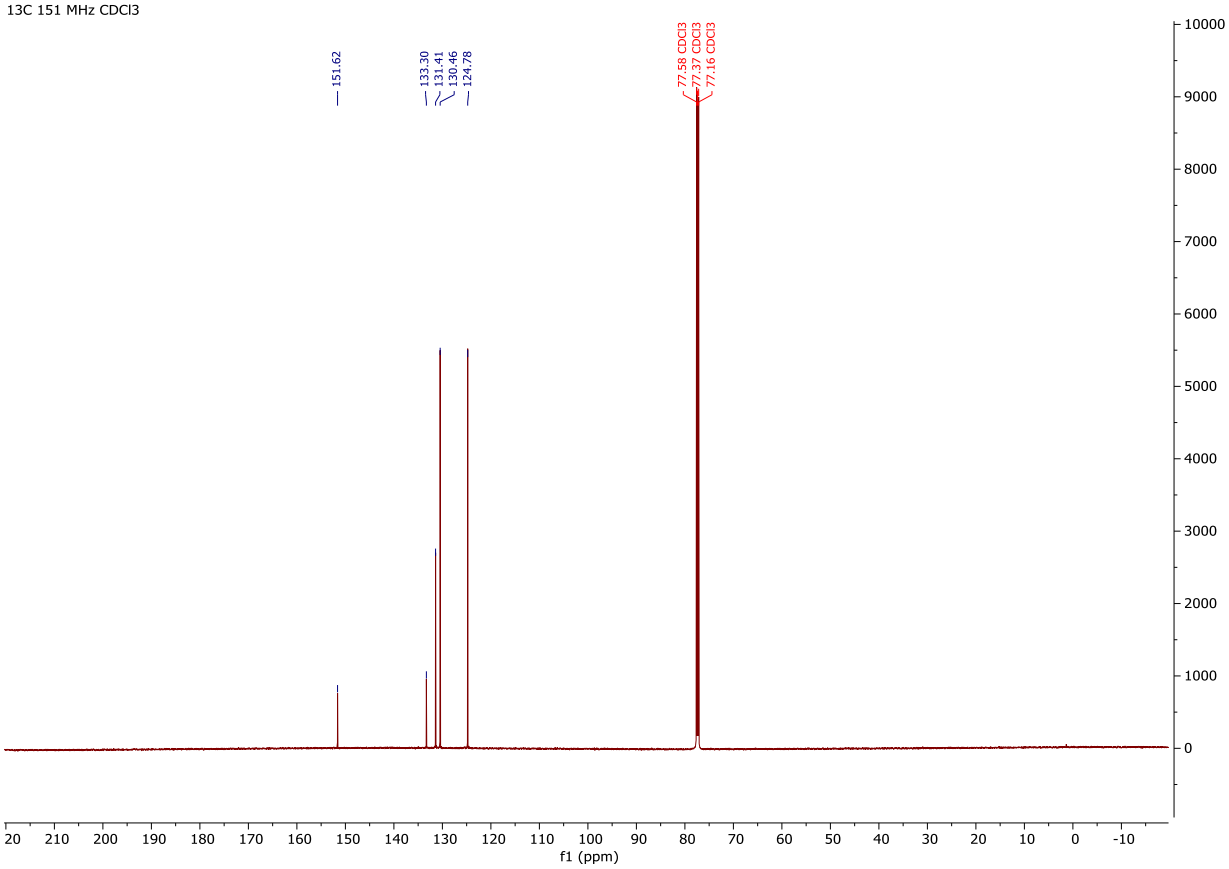

7.97
7.95
7.95
7.94
7.70
7.68
7.68
7.66
7.66
7.66
7.61
7.60
7.59
7.26 CDCl3
3.56
3.56
3.54
3.52
3.41
3.39
3.39
3.37
3.37
1.55 H2O
O
O
S
S
Br
S19
1.91
1.00
1.99
2.02
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


144.36
134.08
129.51
126.95
77.21 CDCl3
77.00 CDCl3
76.79 CDCl3
37.17
28.79
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

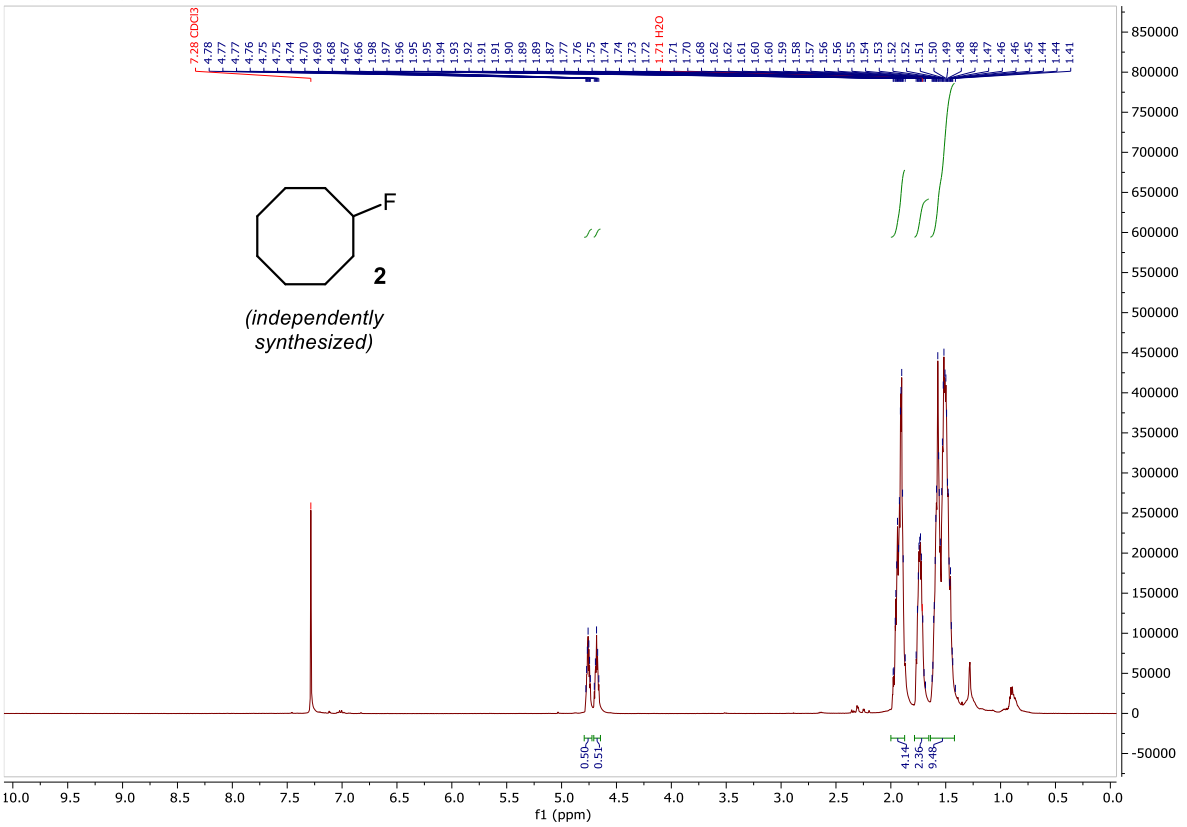
1H CDCl3 600 MHz



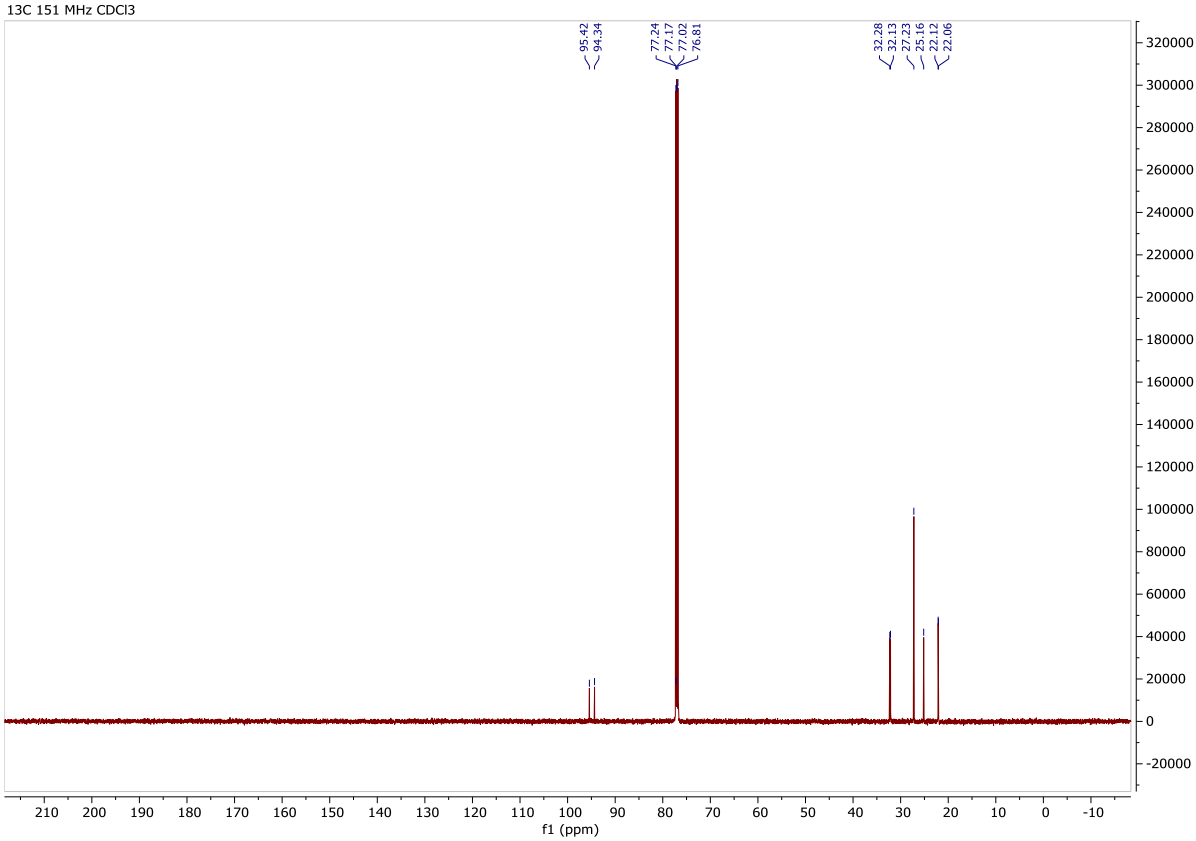
13C 151 MHz CDCl3

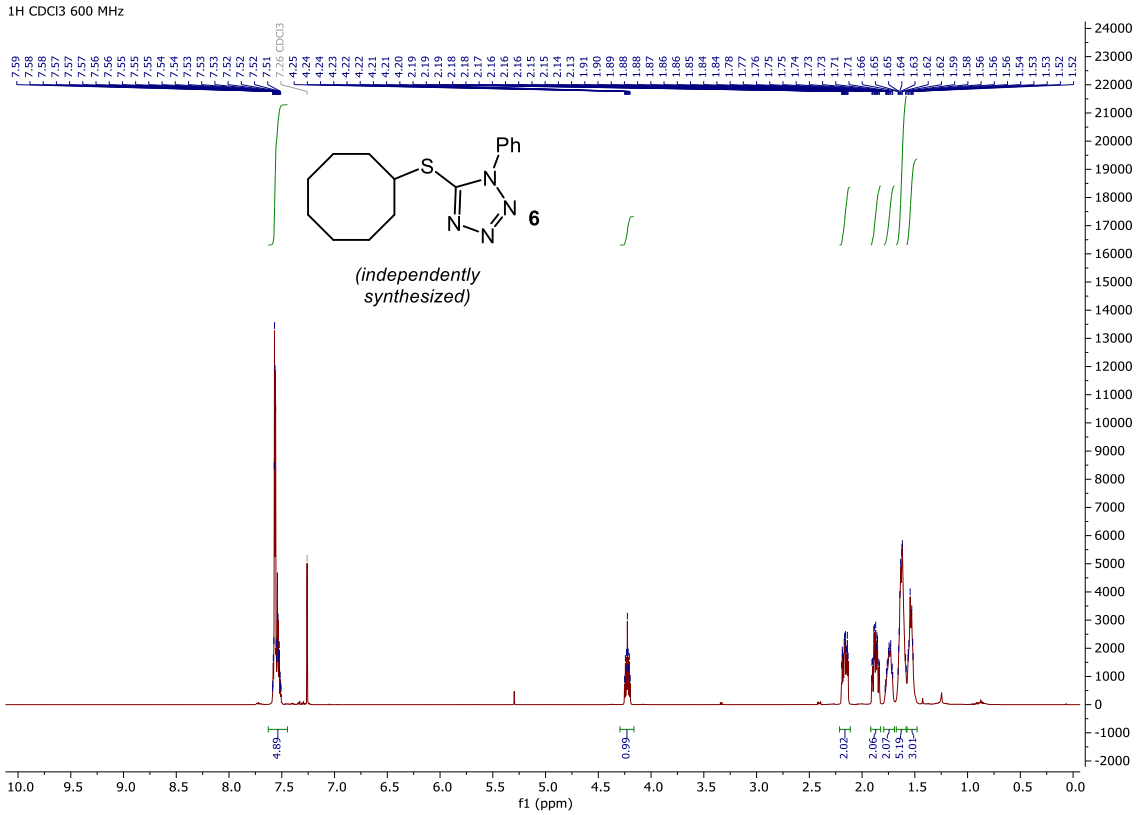


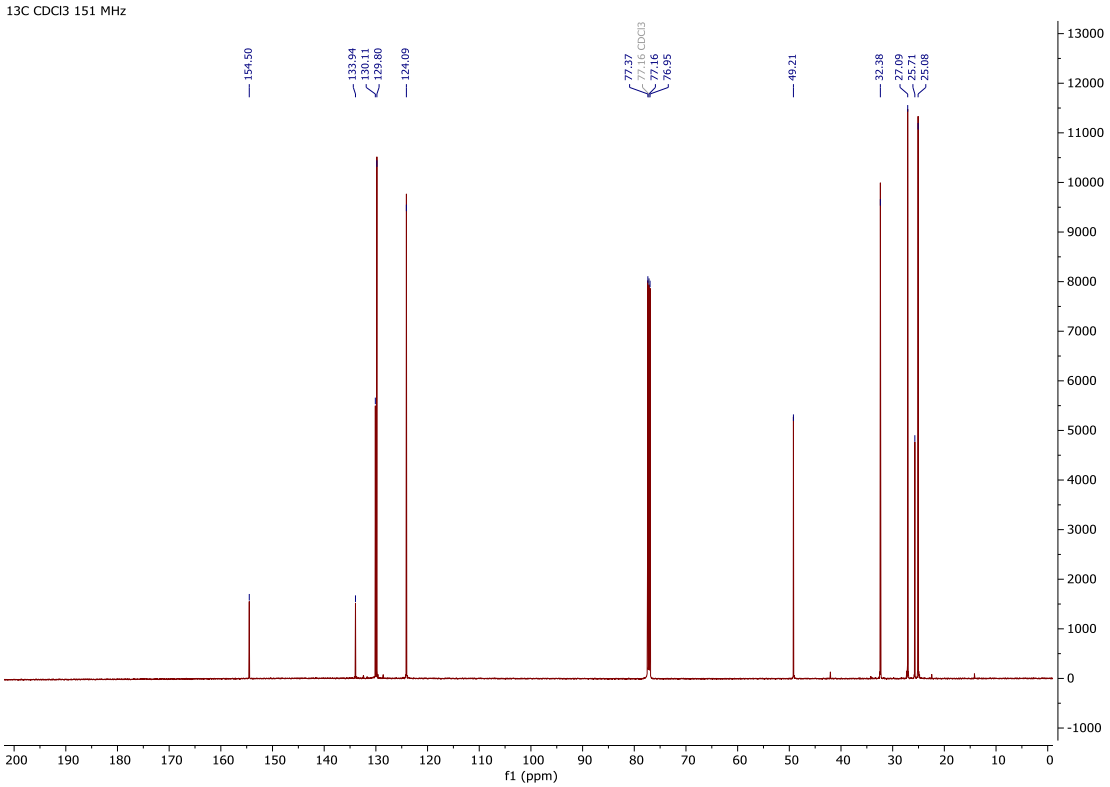
1H 600 MHz CDCl3

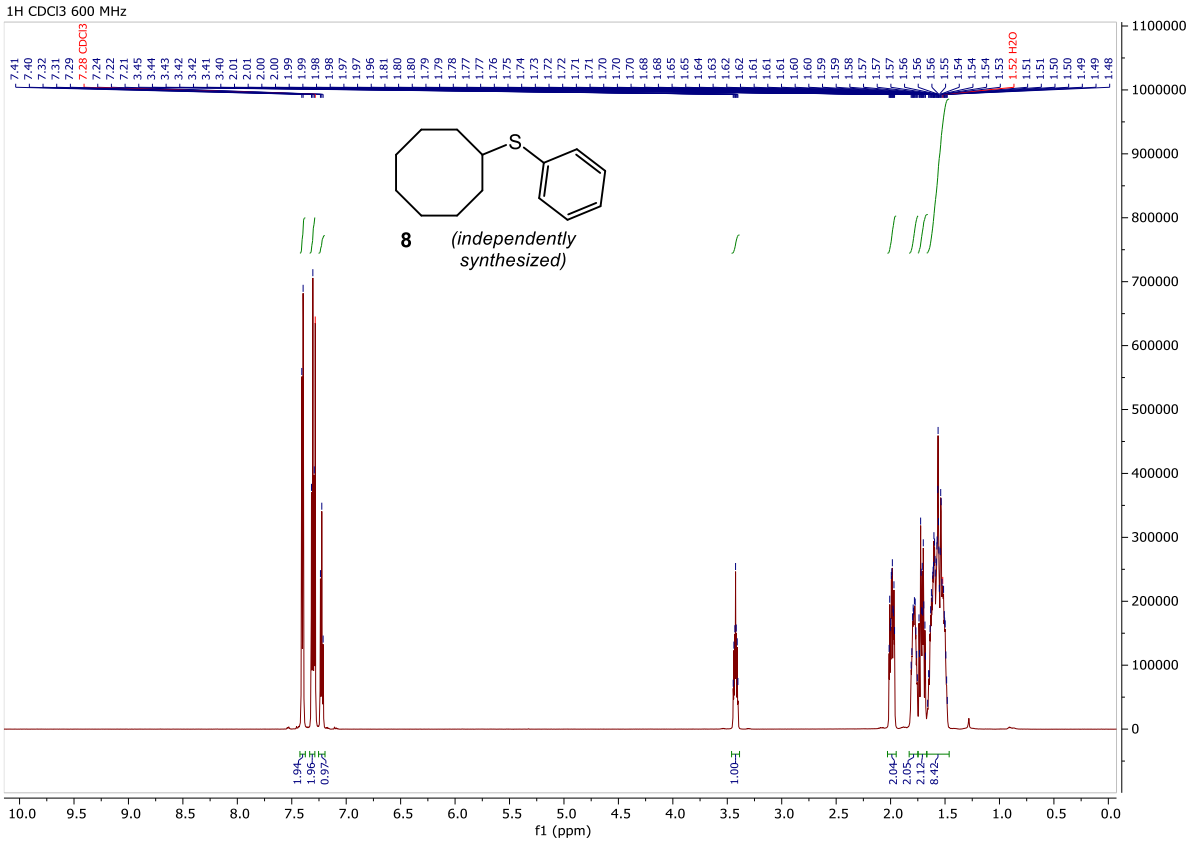


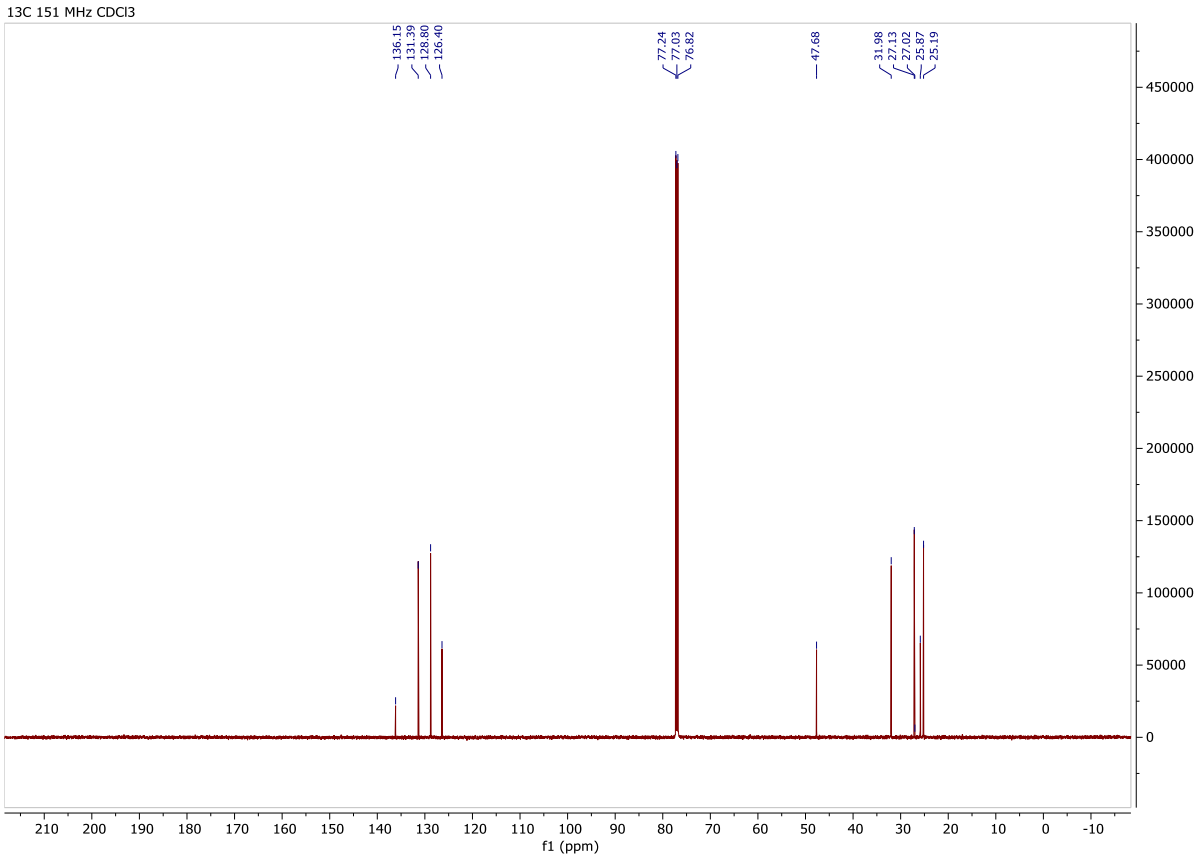
13C 151 MHz CDCl3

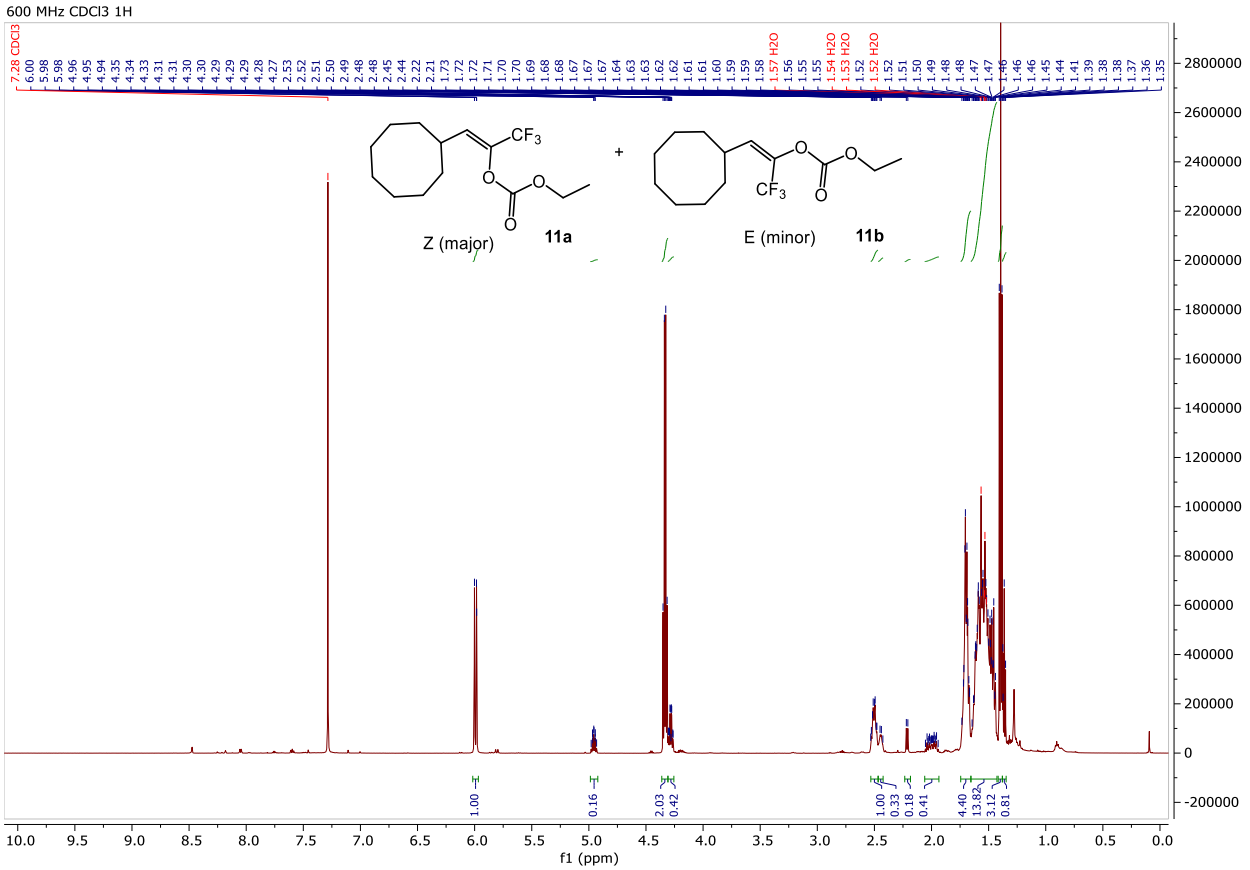


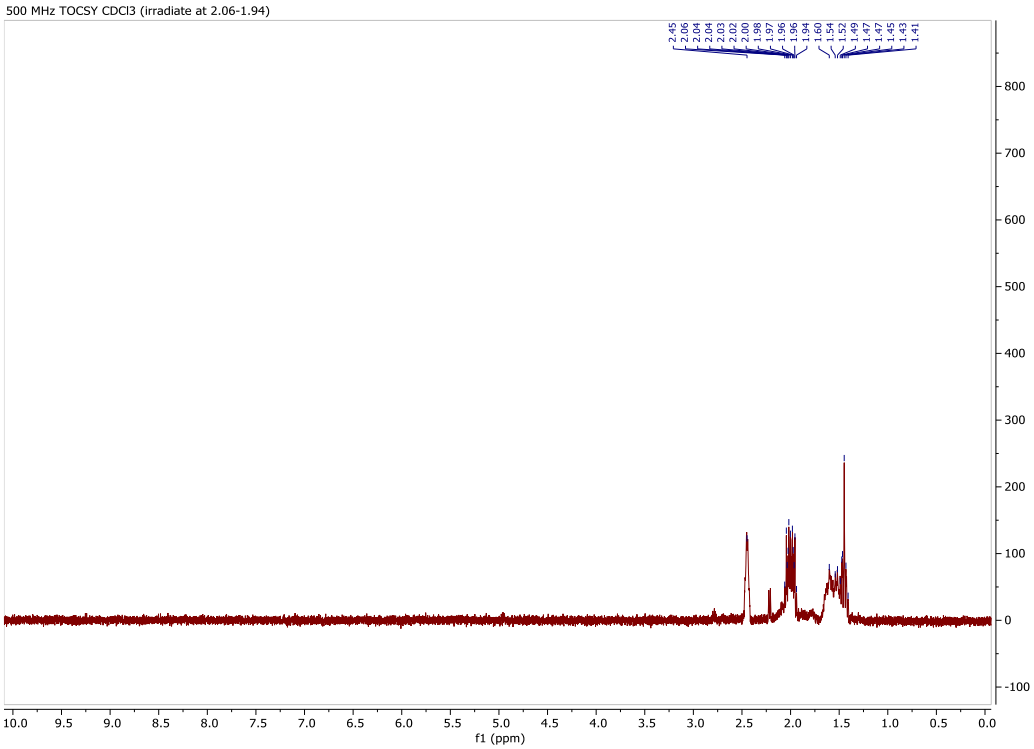

1H CDCl3 600 MHz
Ph
S
N
N
N
N
6
(independently
synthesized)
4.89
0.99
2.02
2.06
2.07
5.19
3.01
f1 (ppm)


13C CDCl3 151 MHz
154.50
133.94
130.11
129.80
124.09
77.37
77.16 CDCl3
77.16
76.95
49.21
32.38
27.09
25.71
25.08
f1 (ppm)

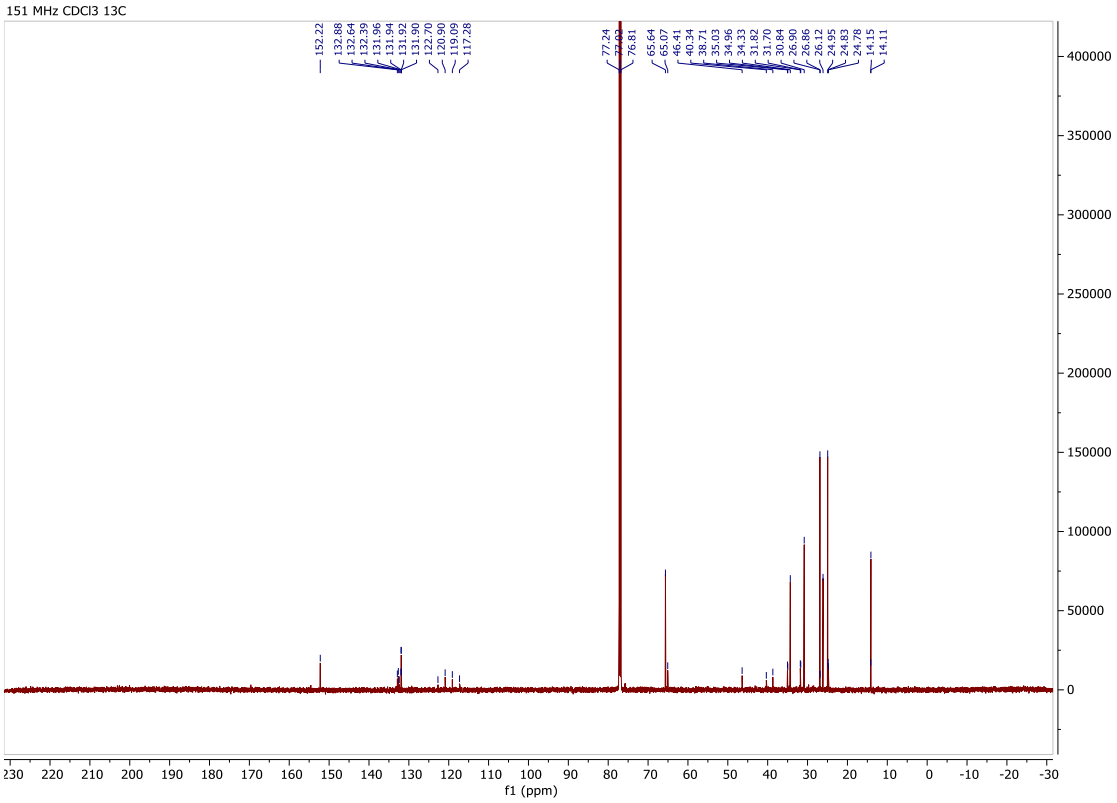

1H CDCl3 600 MHz
S
8 (independently synthesized)
f1 (ppm)

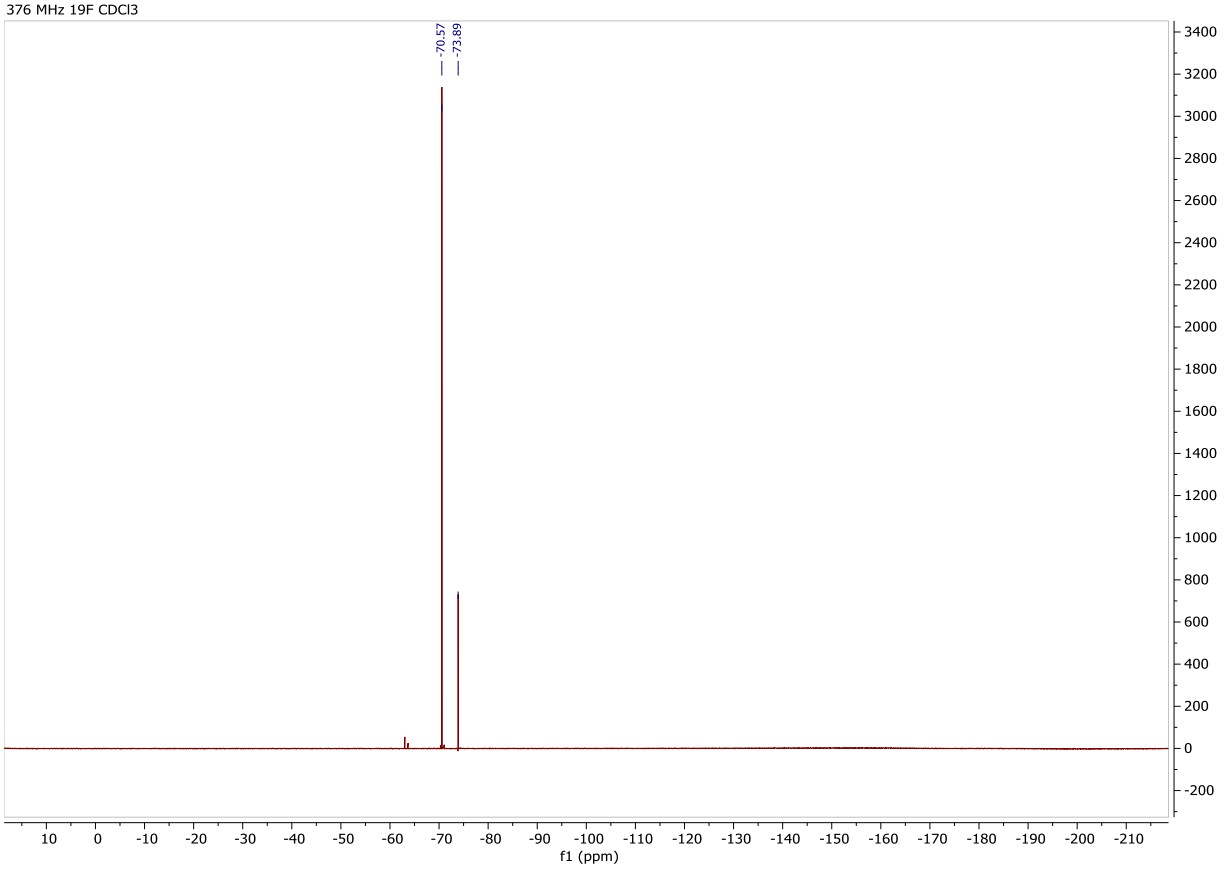

13C 151 MHz CDCl3
f1 (ppm)

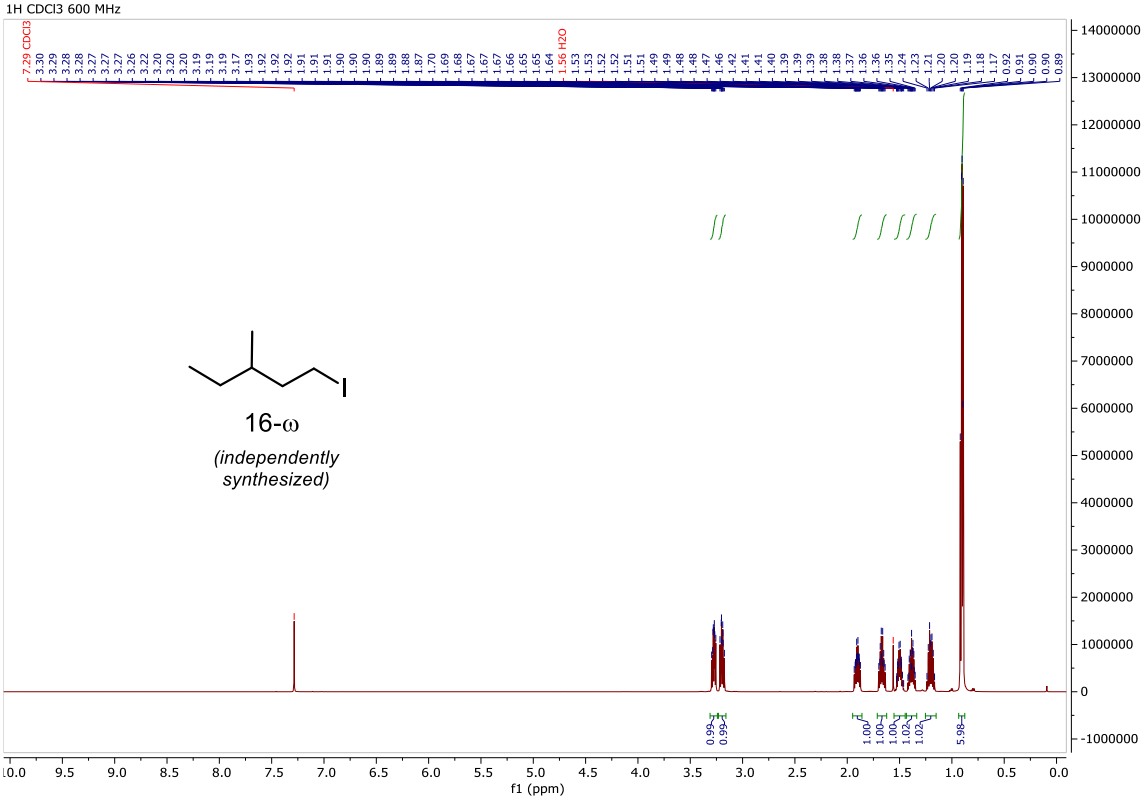


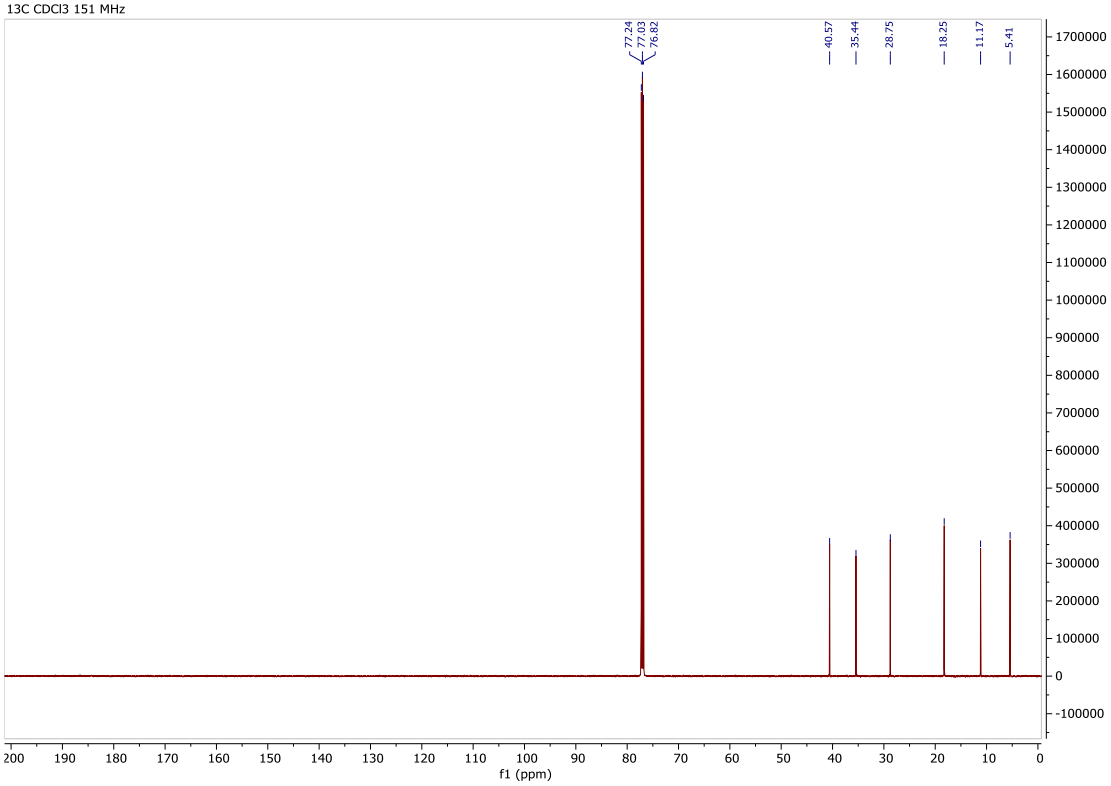


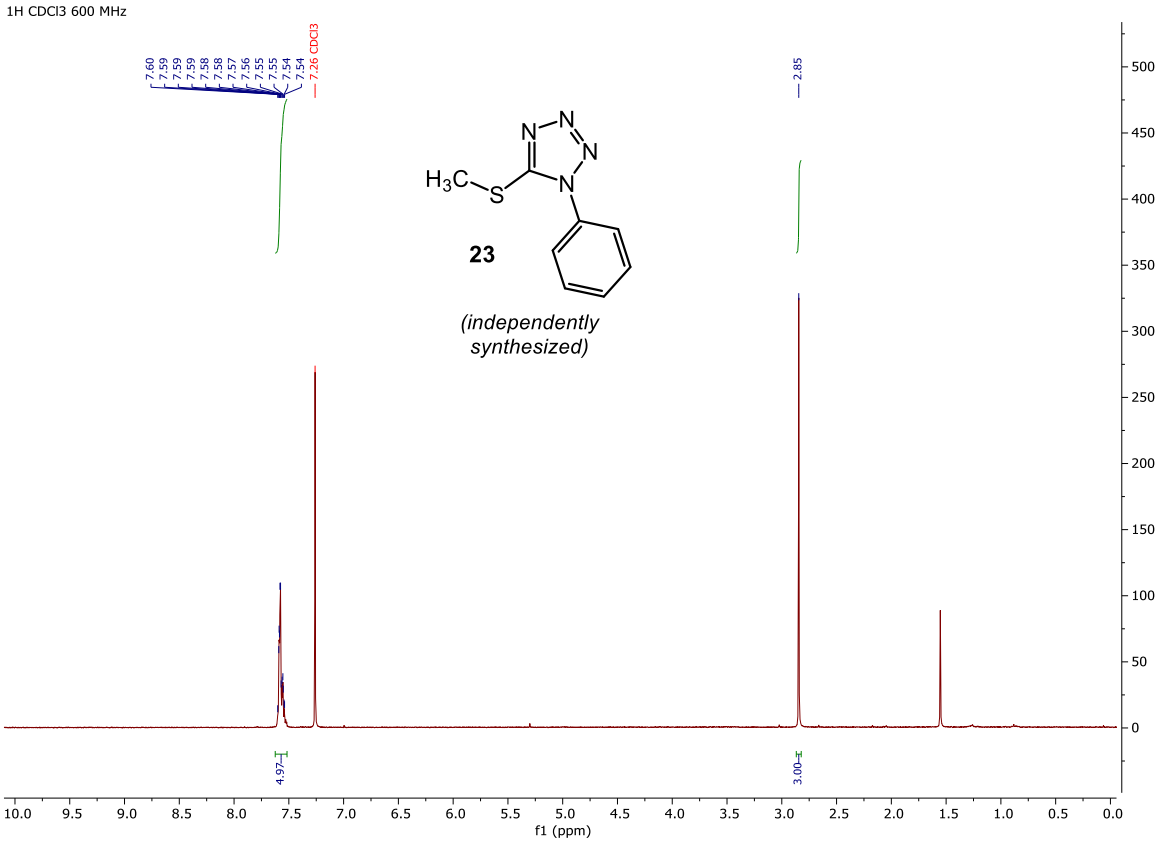
TOCSY irradiating at 2.0 ppm, showing multiplet at 2.0 ppm correlate to minor isomer, corresponding to the diastereotopic cyclooctyl protons alpha to the allylic site

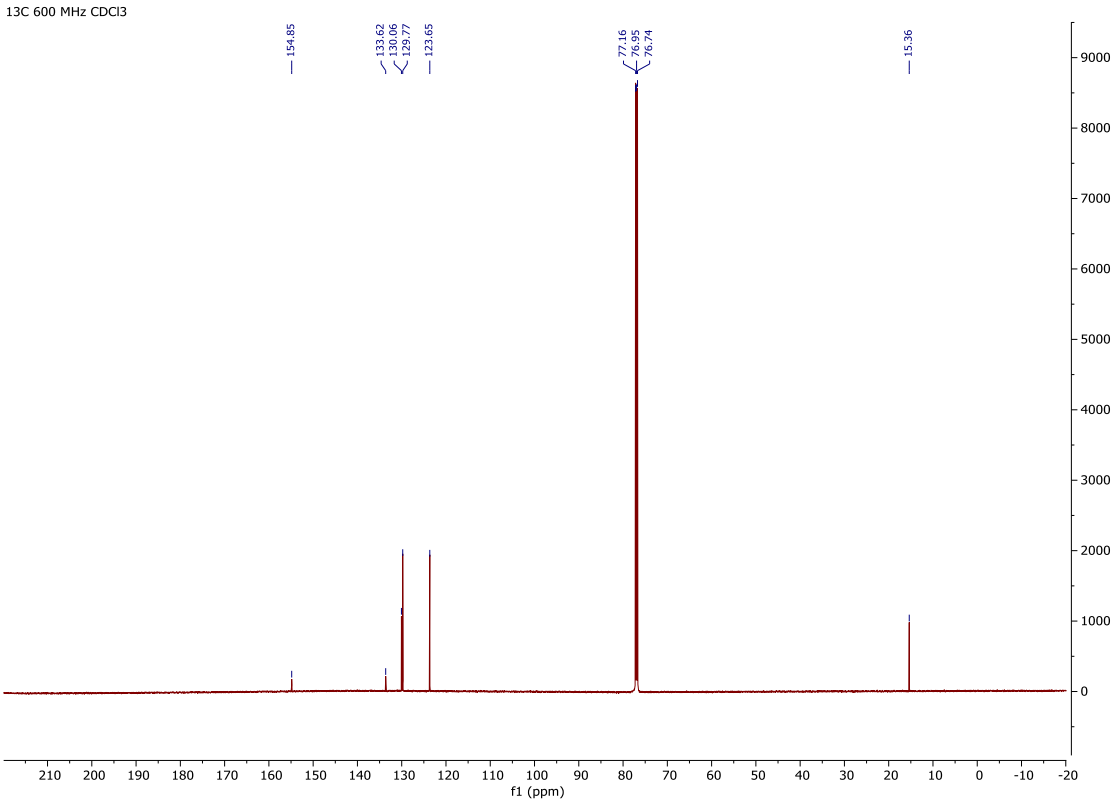

151 MHz CDCl3 13C
152.22
132.88
132.64
132.39
131.96
131.94
131.92
131.90
122.70
120.90
119.09
117.28
77.24
77.01
76.81
65.64
65.07
46.41
40.34
38.71
33.03
32.66
34.35
31.82
31.70
30.84
26.90
26.86
26.12
24.95
24.83
24.78
14.15
14.11
400000
350000
300000
250000
200000
150000
100000
50000
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)


376 MHz 19F CDCl3
-70.57
-73.89
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

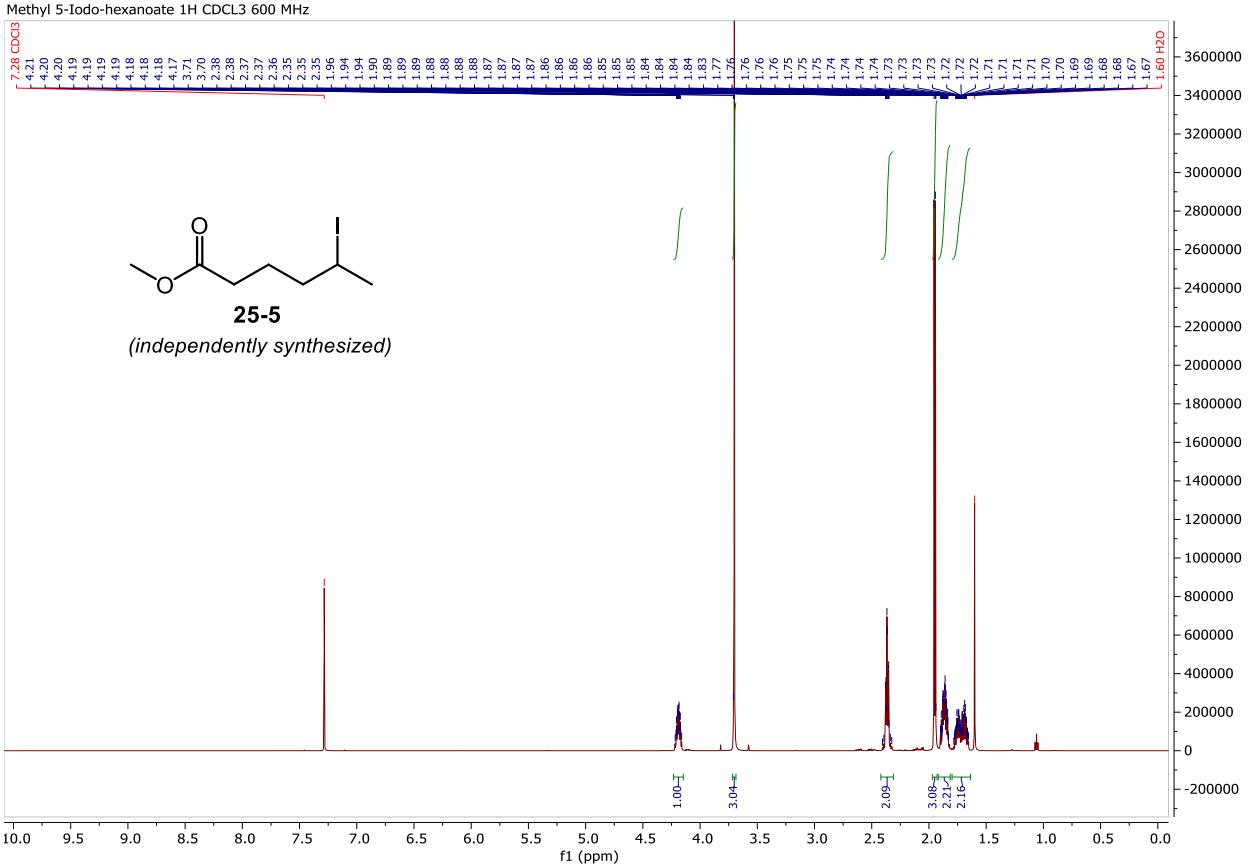

1H CDCl3 600 MHz
16-ω
(independently
synthesized)
f1 (ppm)


13C CDCl3 151 MHz
f1 (ppm)


1H CDCl3 600 MHz
7.60
7.59
7.59
7.59
7.58
7.58
7.57
7.56
7.55
7.55
7.54
7.54
7.26 CDCl3
2.85
N
N
N
N
H3C
S
23
(independently
synthesized)
4.97
3.00
f1 (ppm)


13C 600 MHz CDCl3
154.85
133.62
130.06
129.77
123.65
77.16
76.95
76.74
15.36
f1 (ppm)

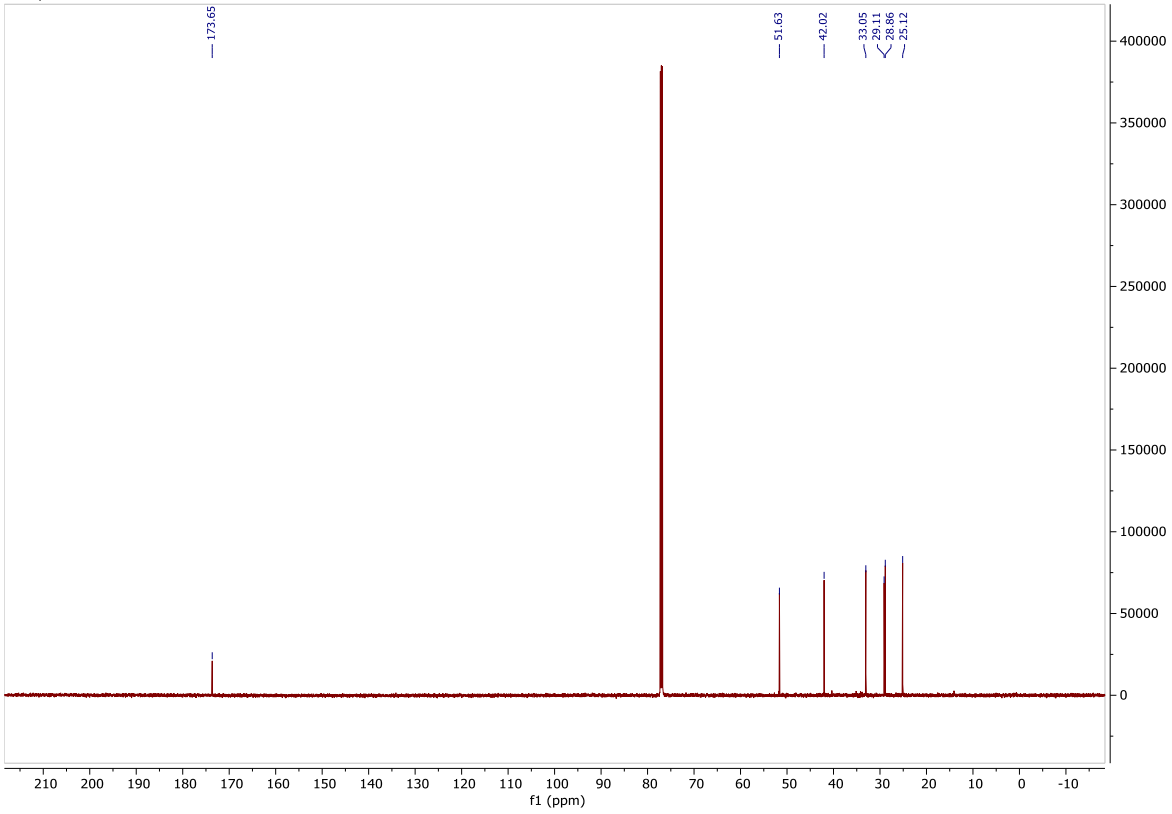
Methyl 5-Iodo-hexanoate 1H CDCL3 600 MHz



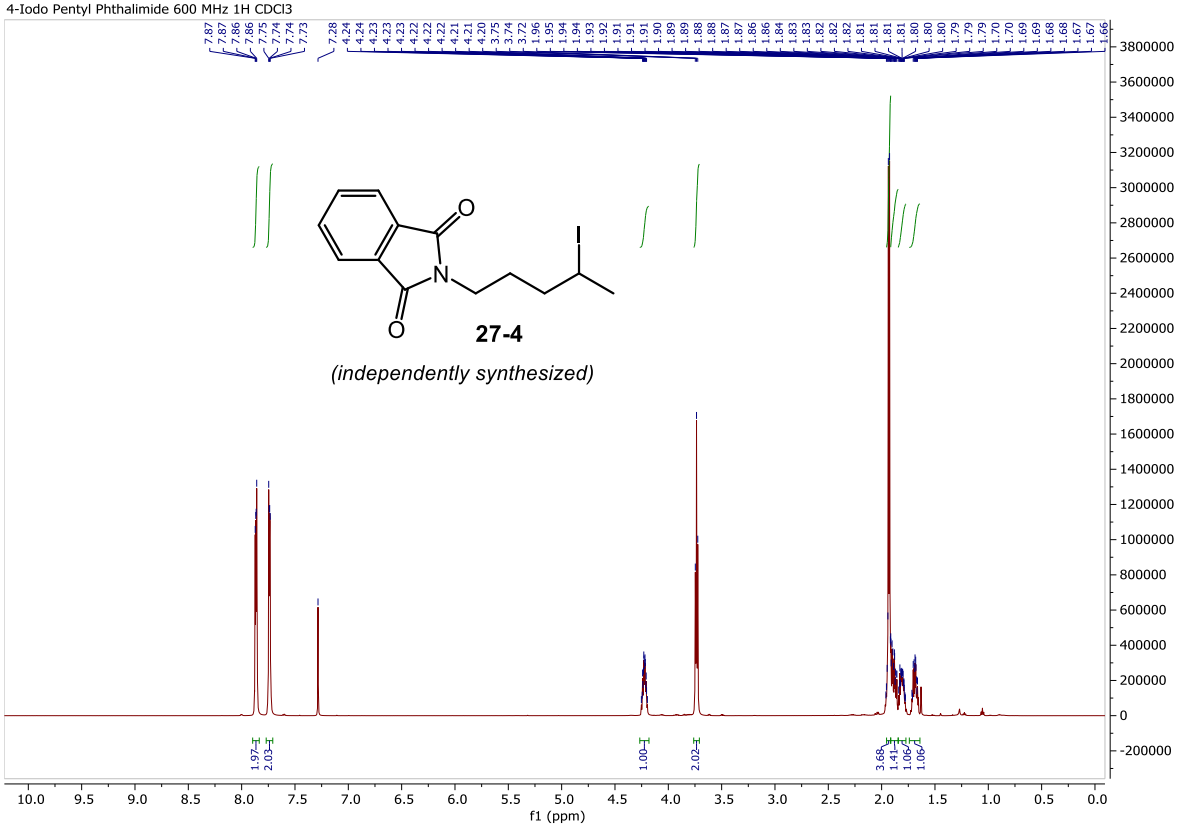
25-5

(independently synthesized)

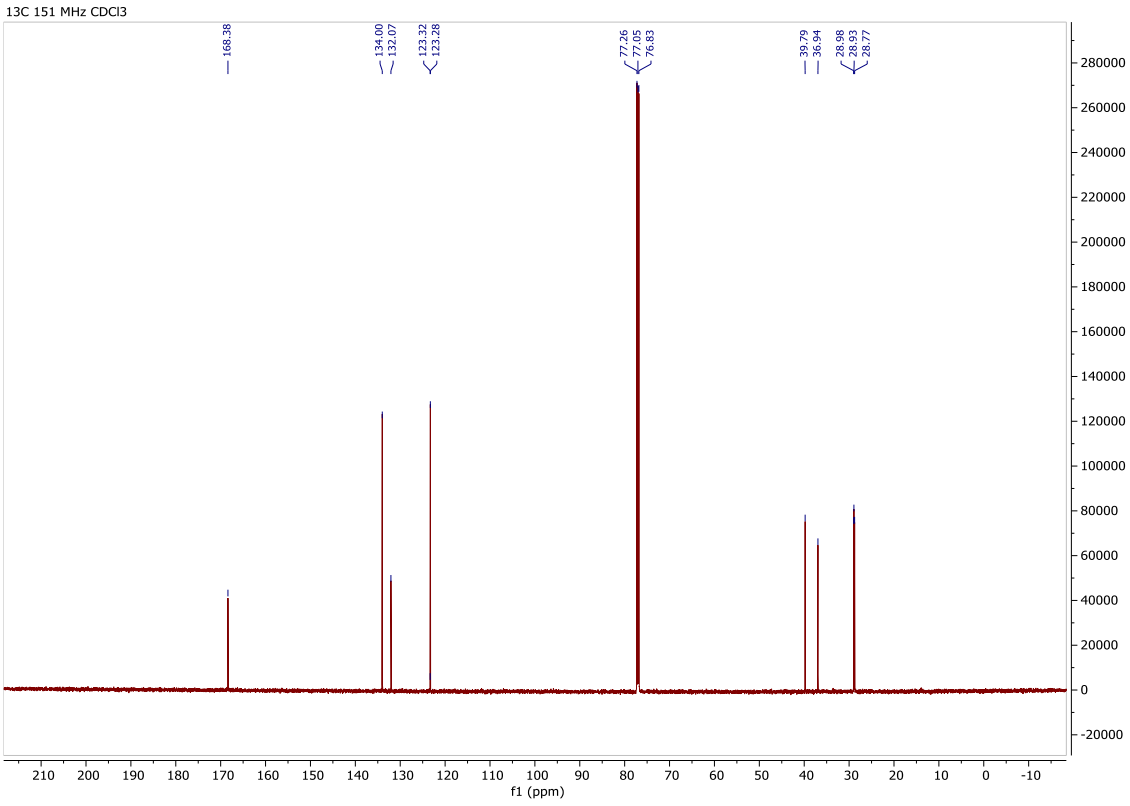
Methyl 5-Iodo-Hexanoate 151 MHz 13C CDCl3

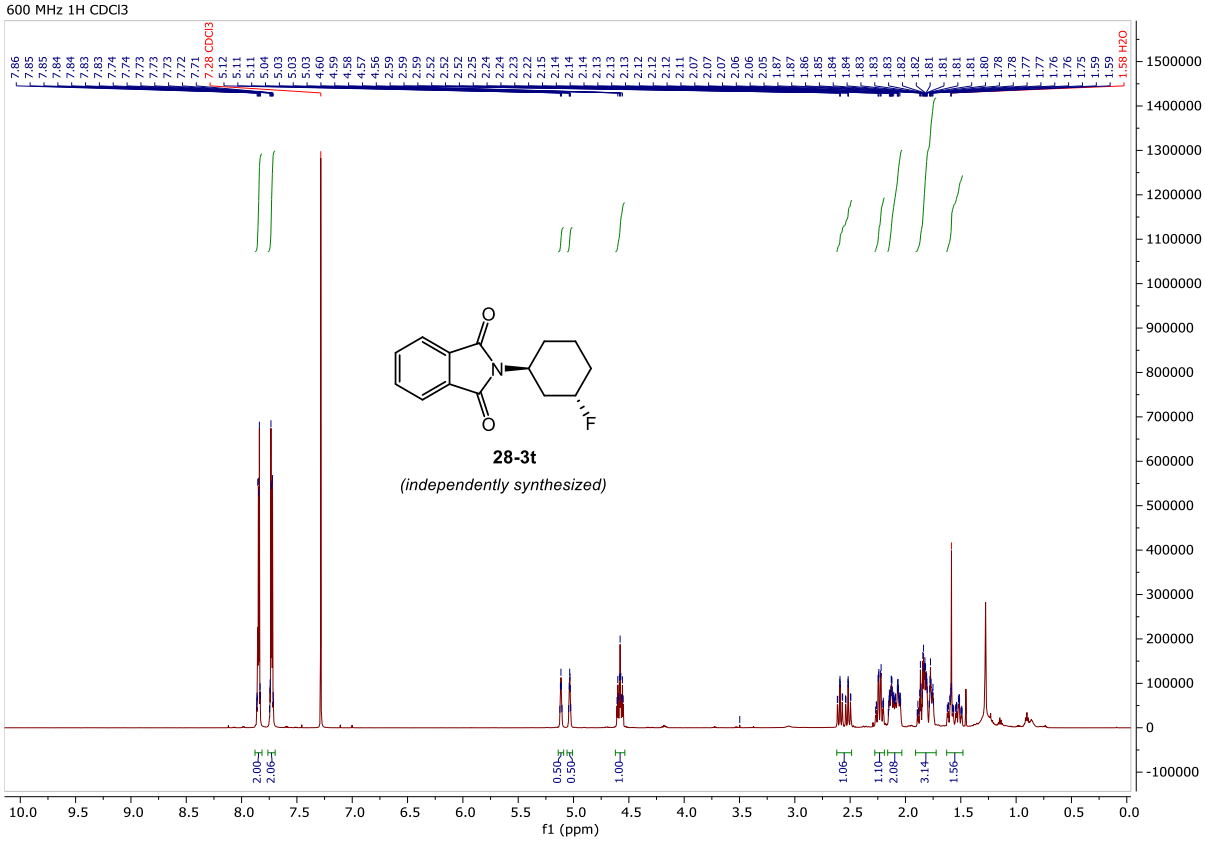


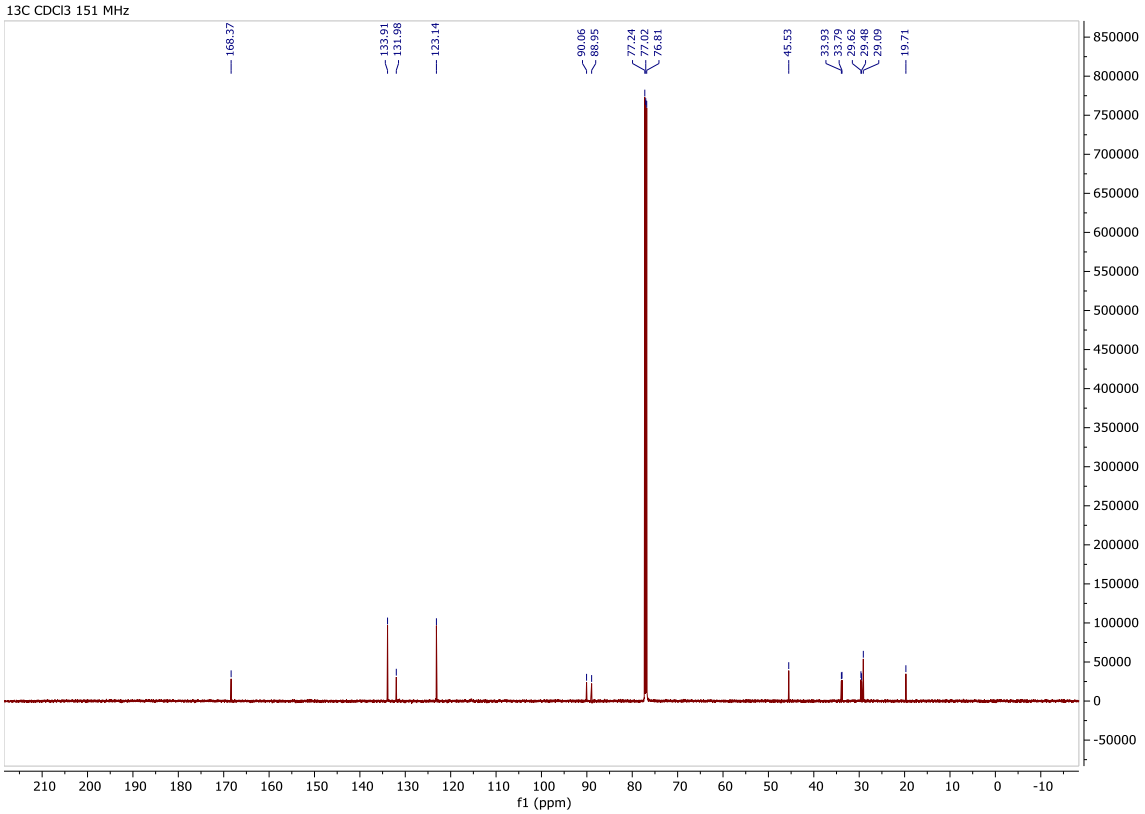
4-Iodo Pentyl Phthalimide 600 MHz 1H CDCl3

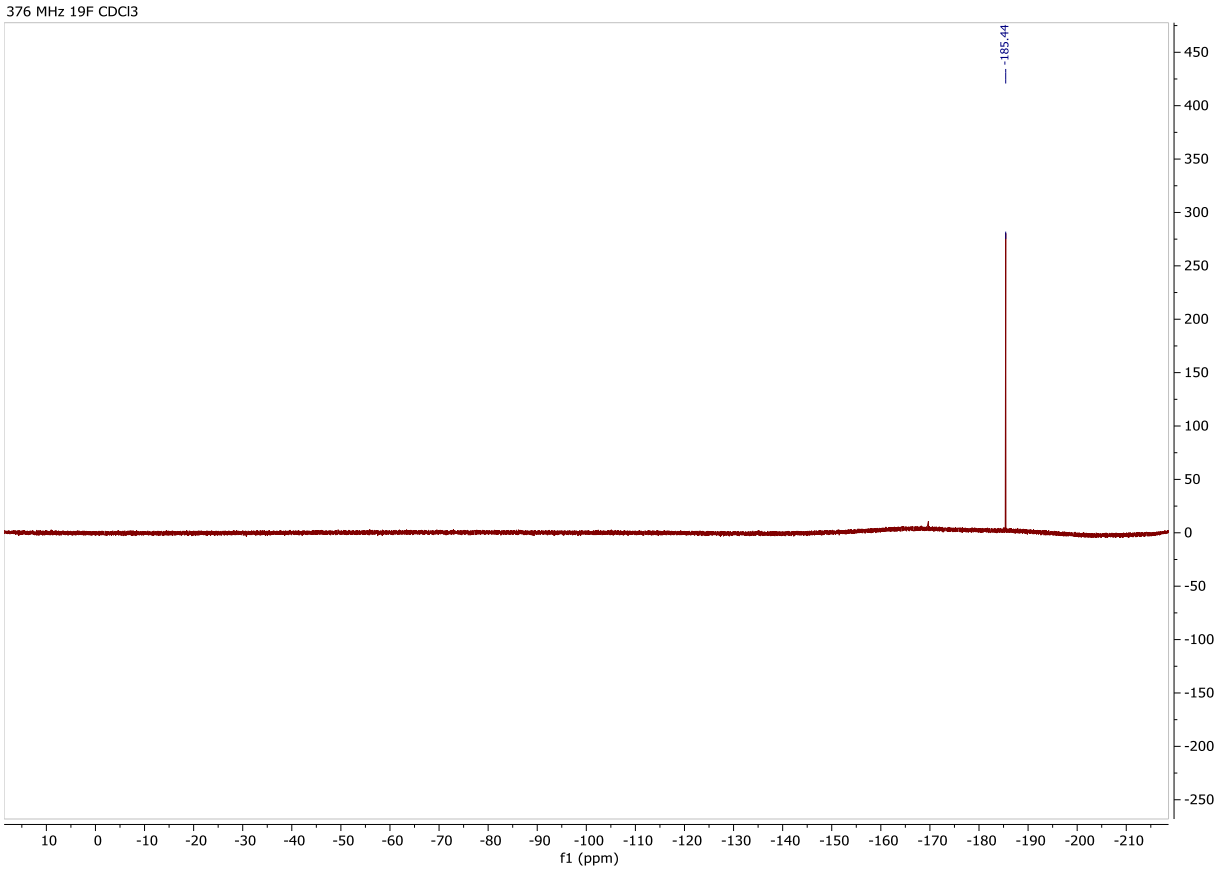


13C 151 MHz CDCl3

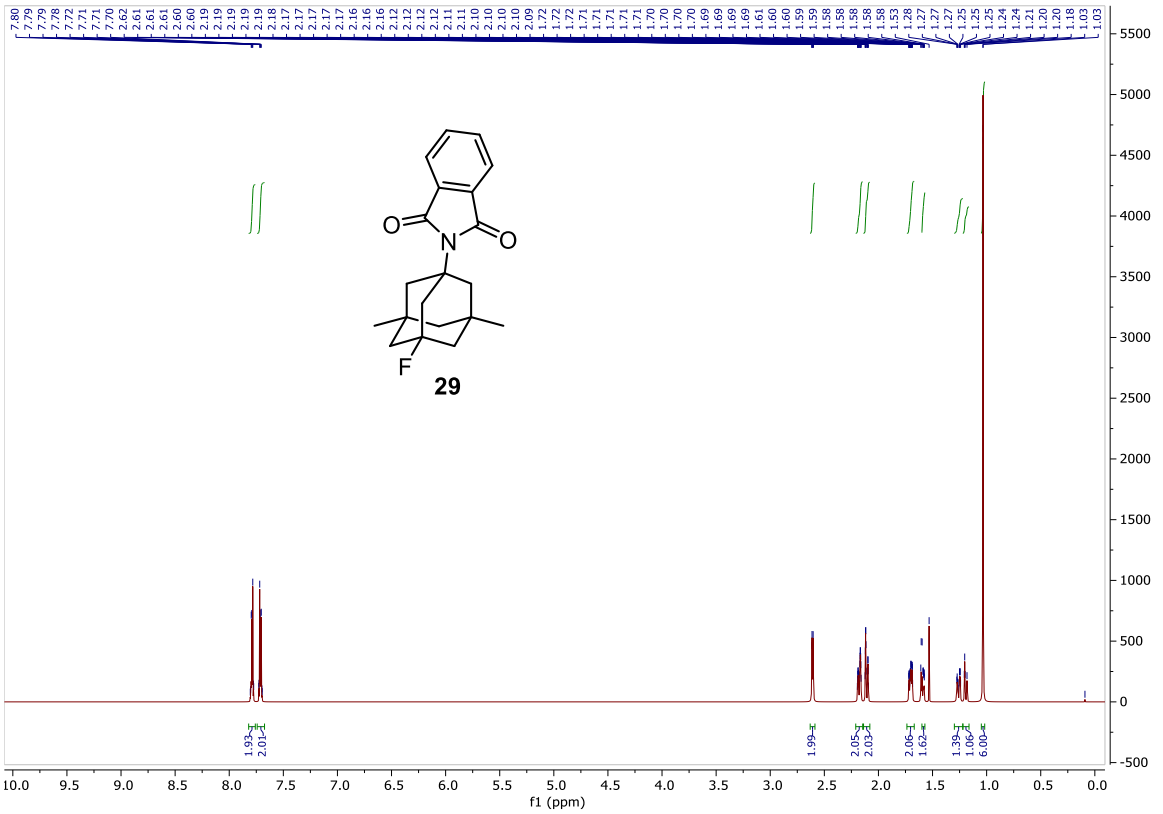



600 MHz 1H CDCl3
7.28 CDCl3
1.58 H2O
28-3t
(independently synthesized)
f1 (ppm)

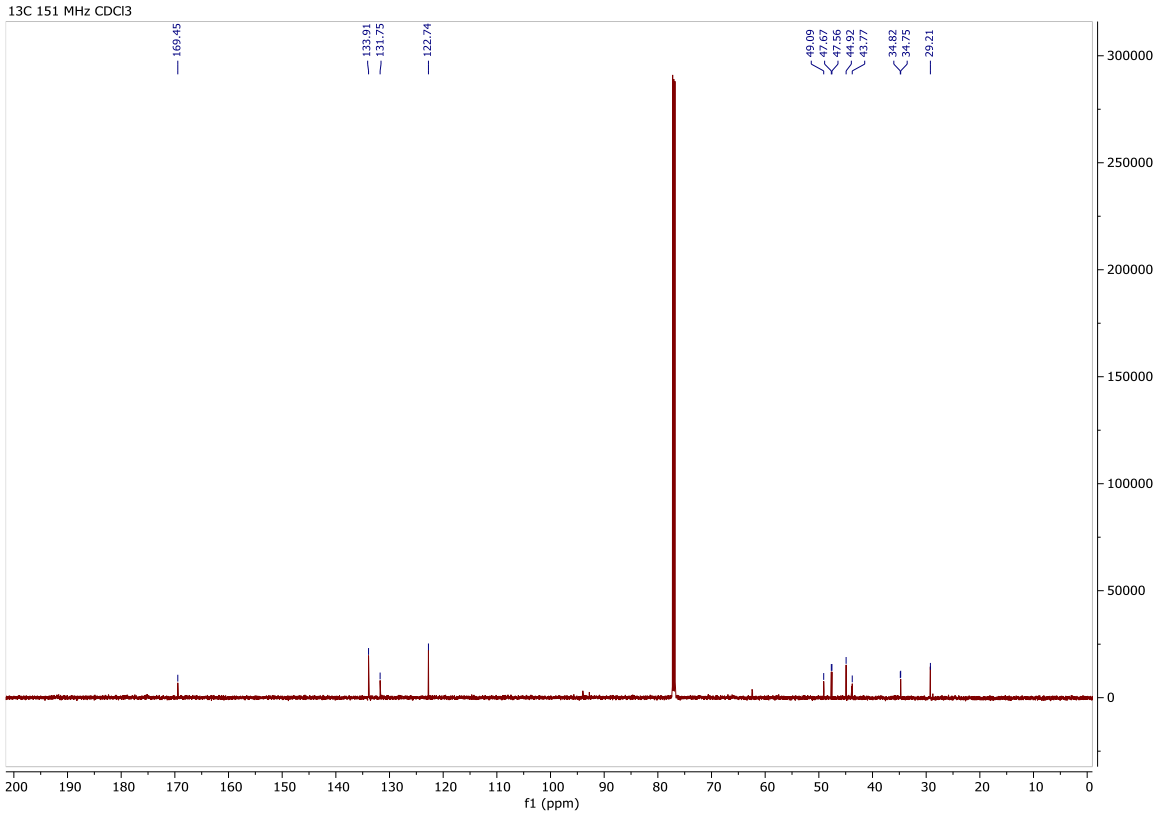

13C CDCl3 151 MHz
168.37
133.91
131.98
123.14
90.06
88.95
77.24
77.02
76.81
45.53
33.93
33.79
29.62
29.48
29.09
19.71
f1 (ppm)

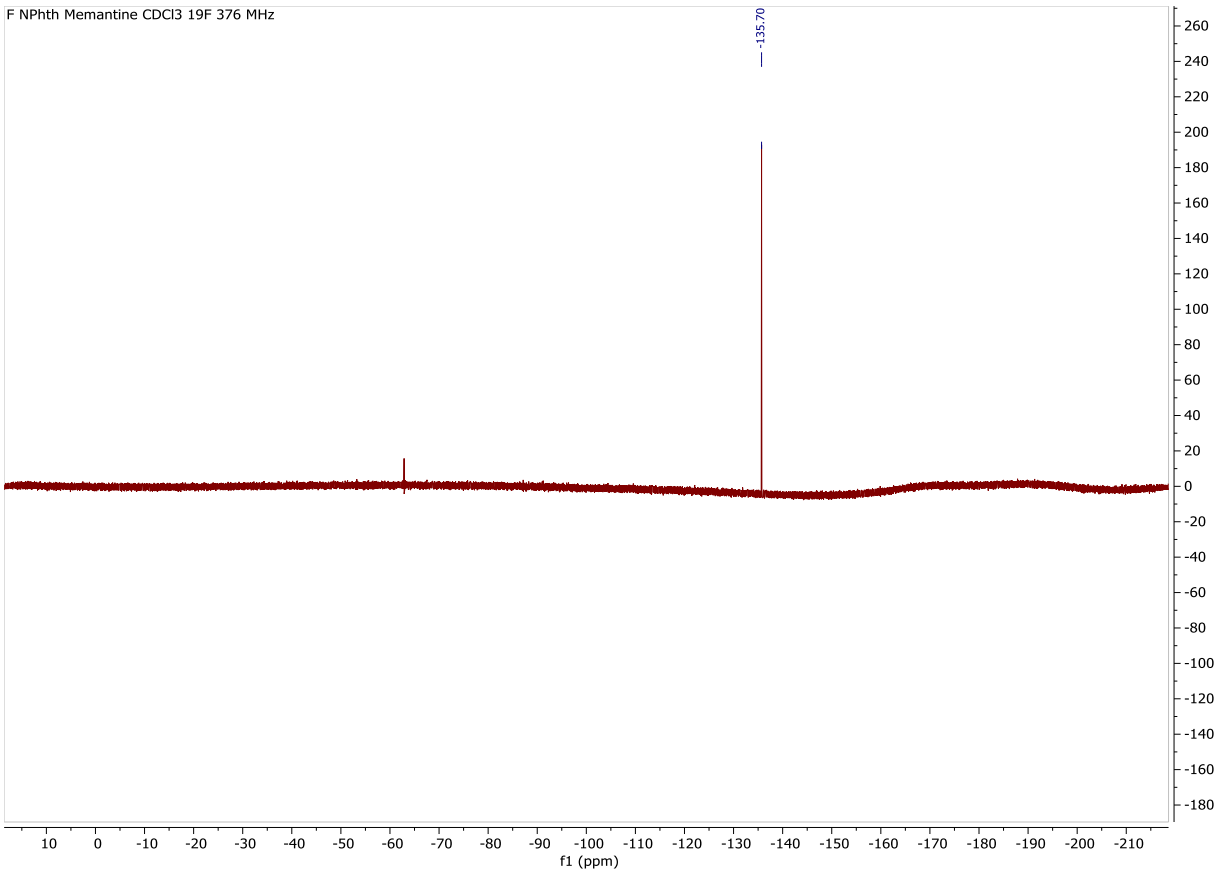

376 MHz 19F CDCl3
-185.44
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

F-NPhth memantine 1H 600 MHz

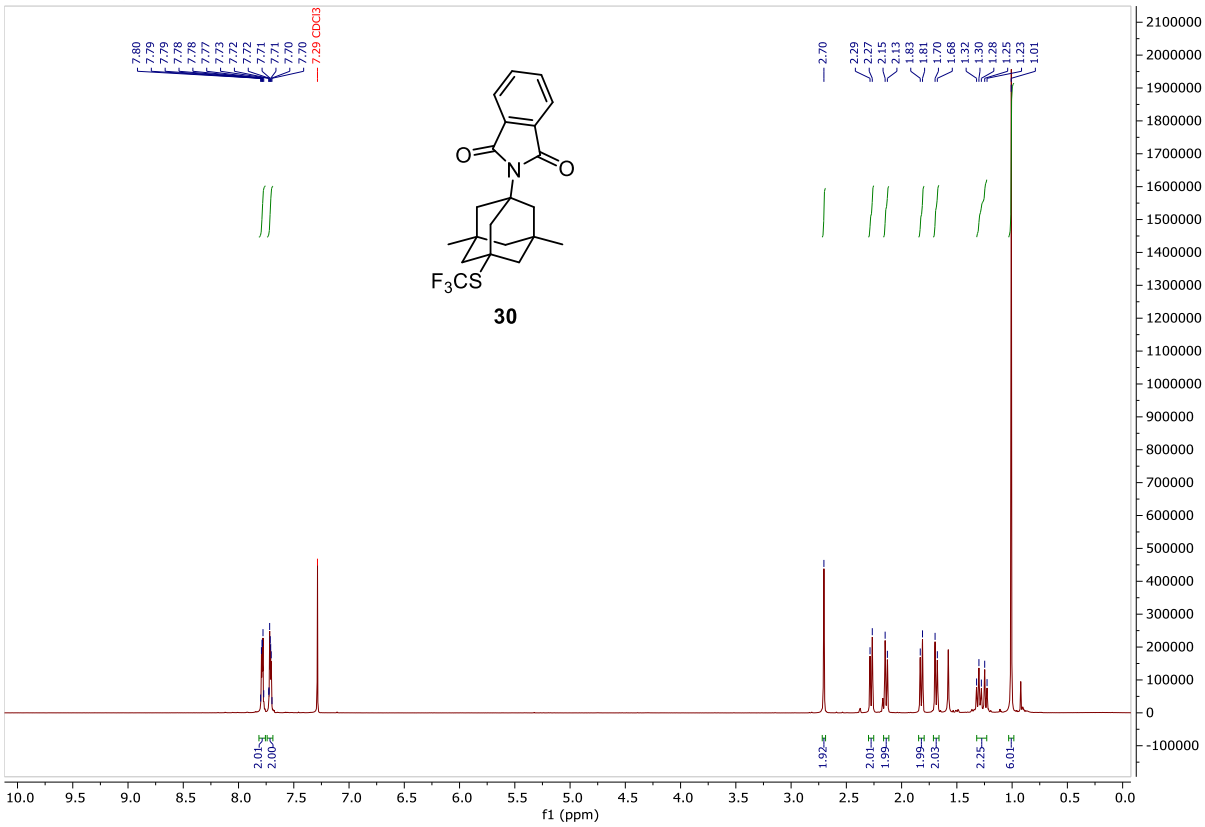


13C 151 MHz CDCl3

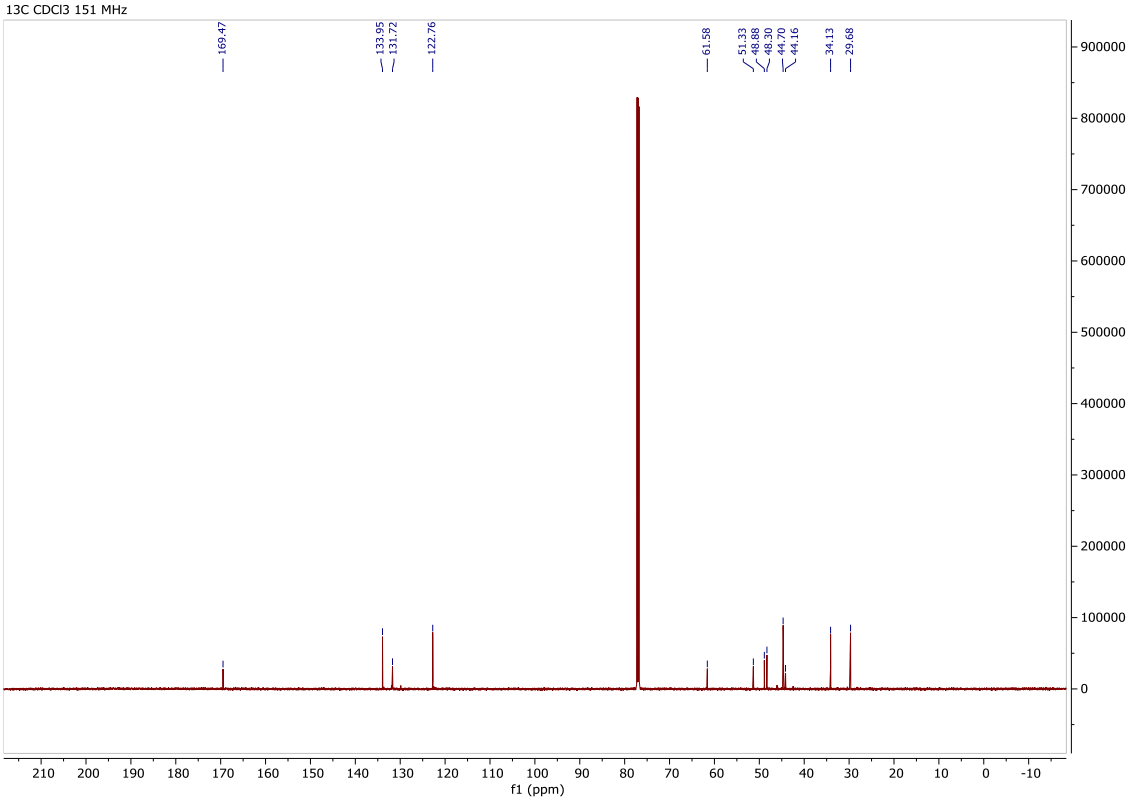


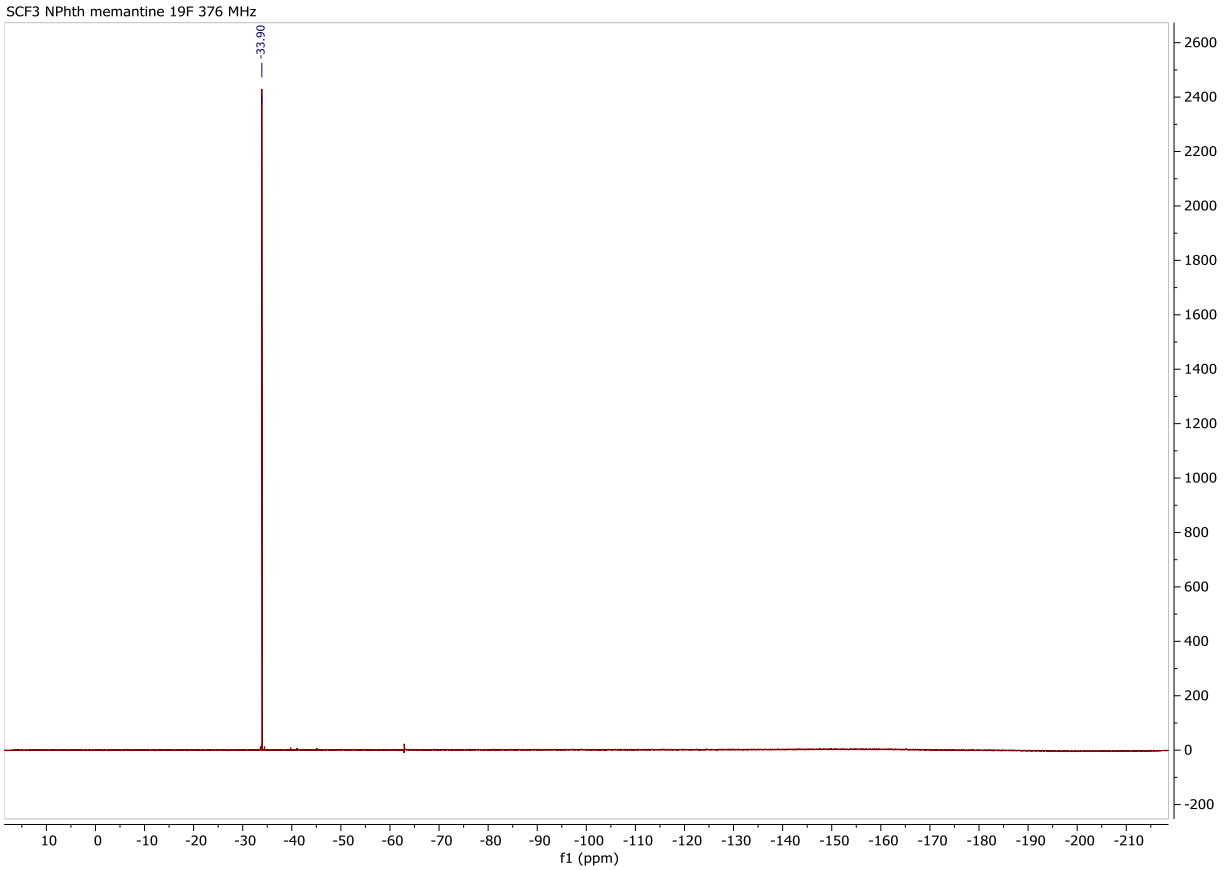

F NPhth Memantine CDCl3 19F 376 MHz
-135.70
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

600 MHz 1H CDCl3

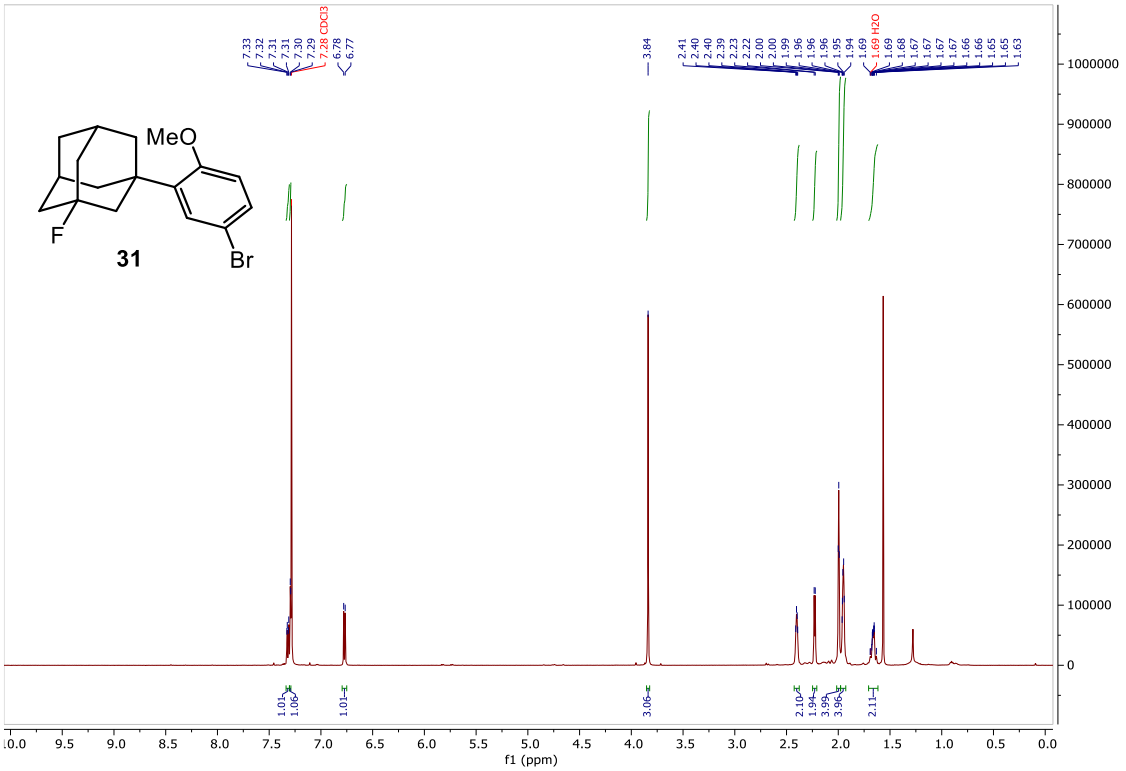


13C CDCl3 151 MHz

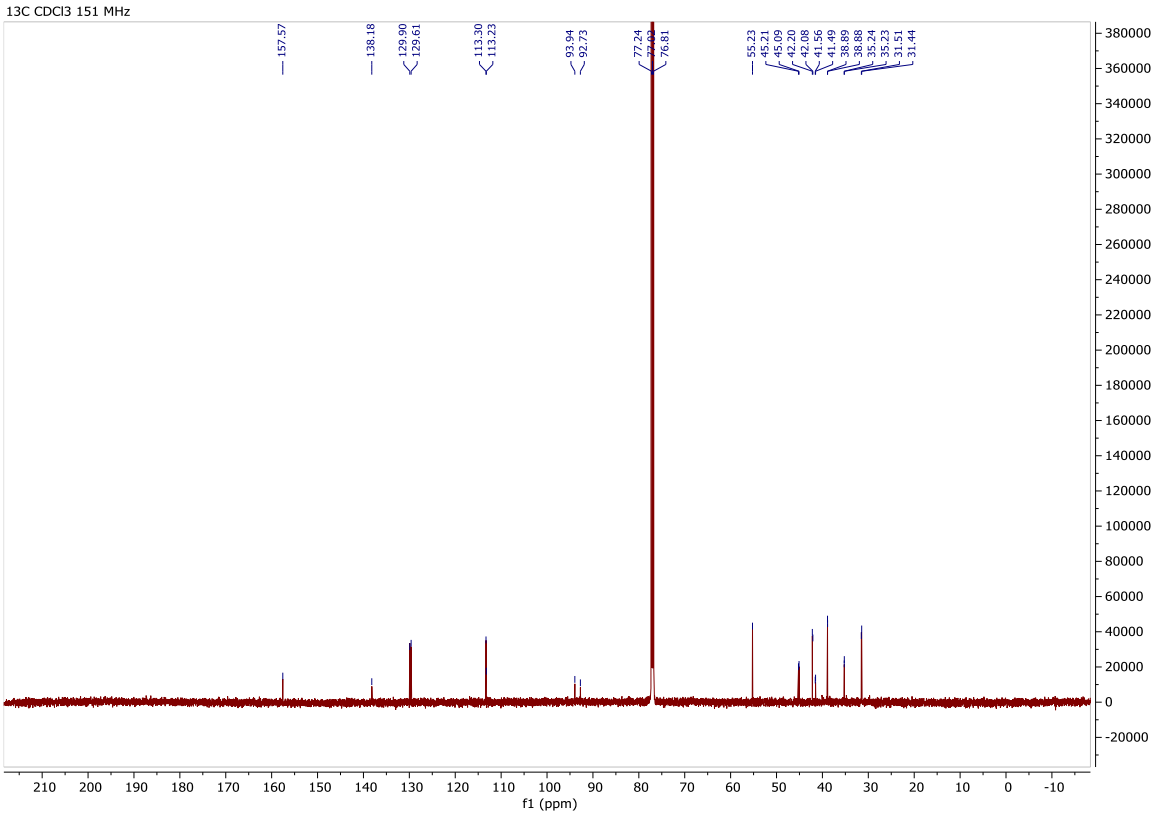


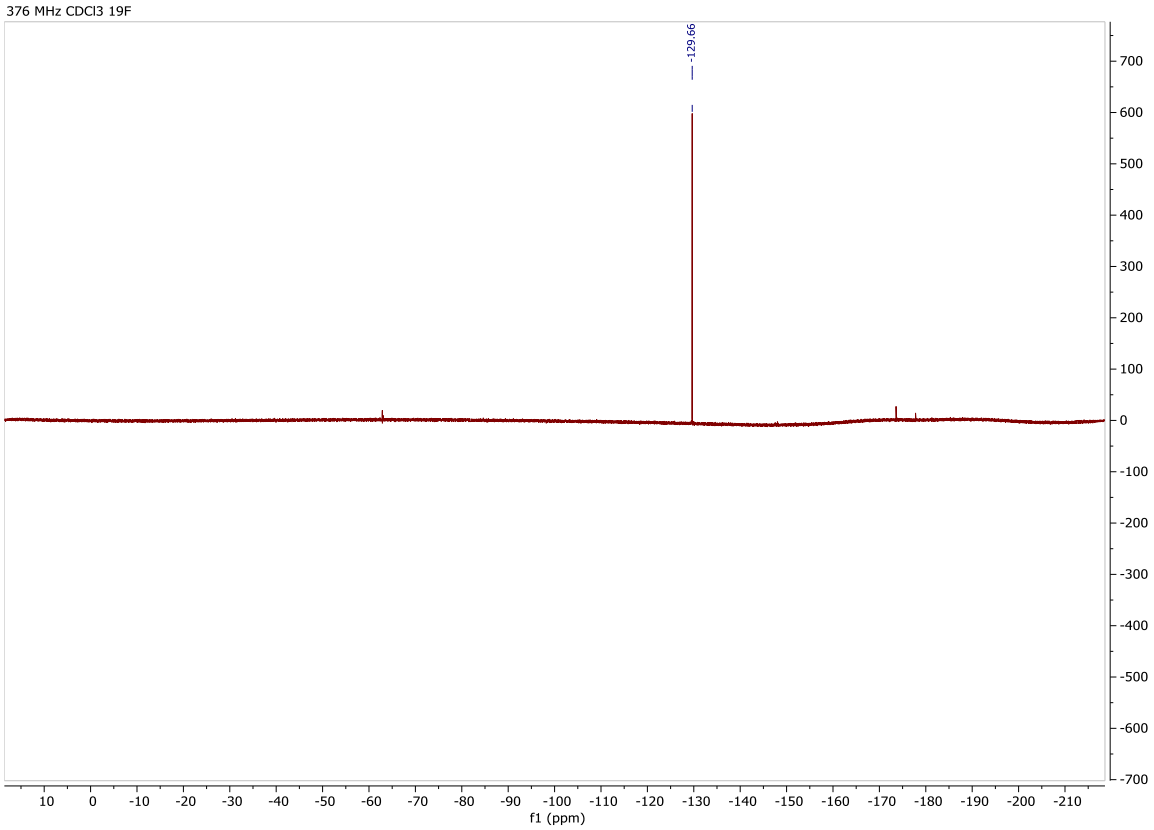

SCF3 NPhth memantine 19F 376 MHz
-33.90
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

600 MHz CDCl3 1H

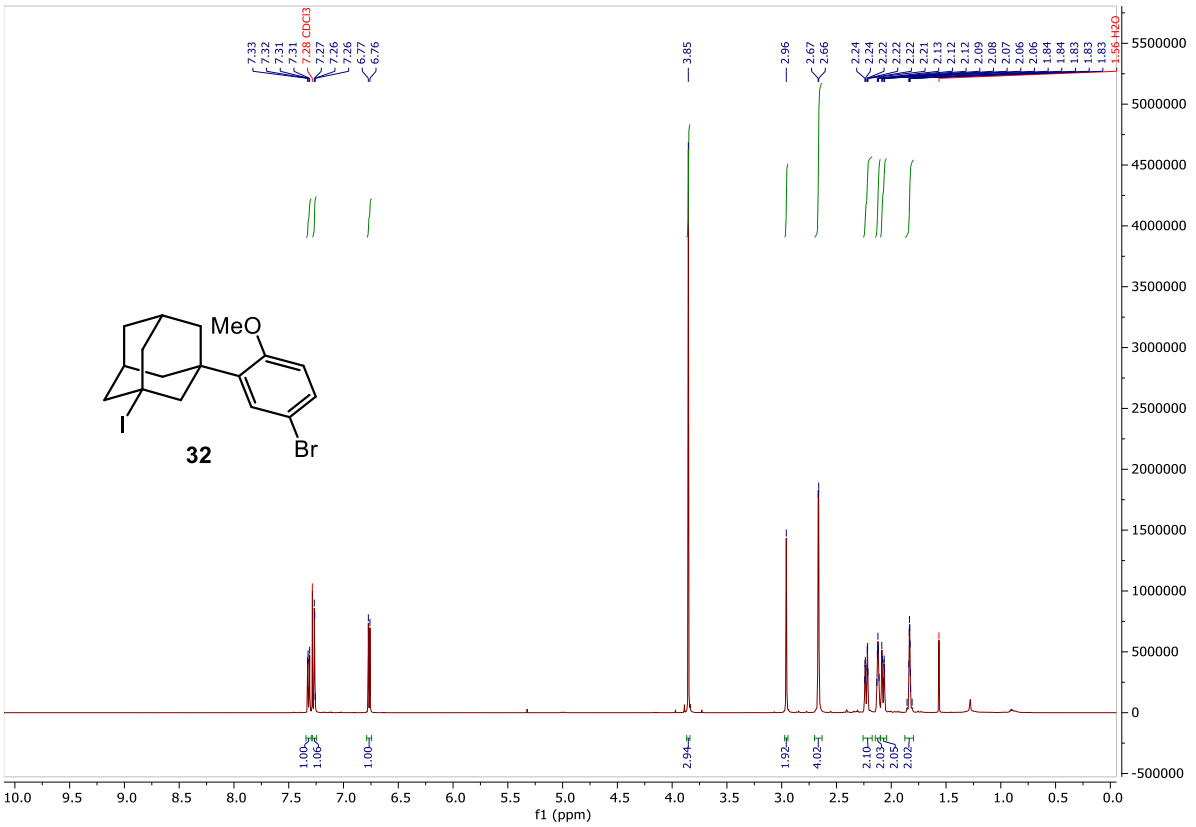


13C CDCl3 151 MHz

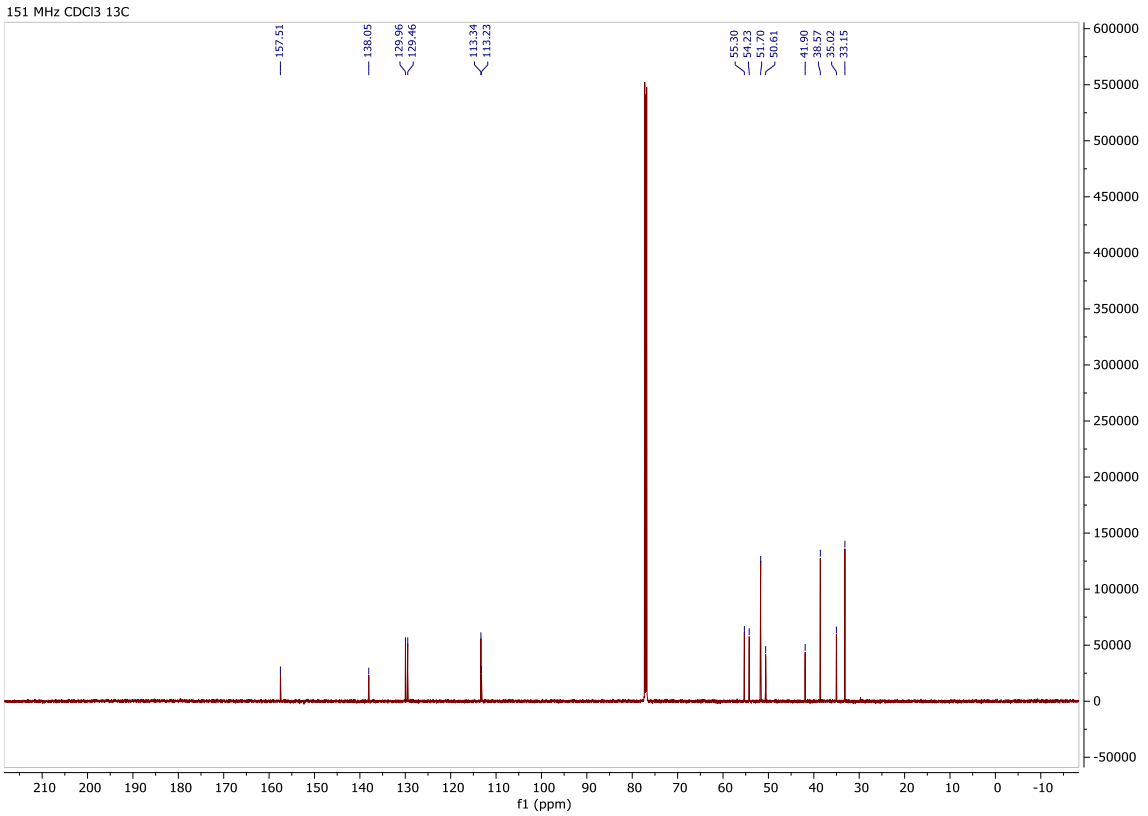


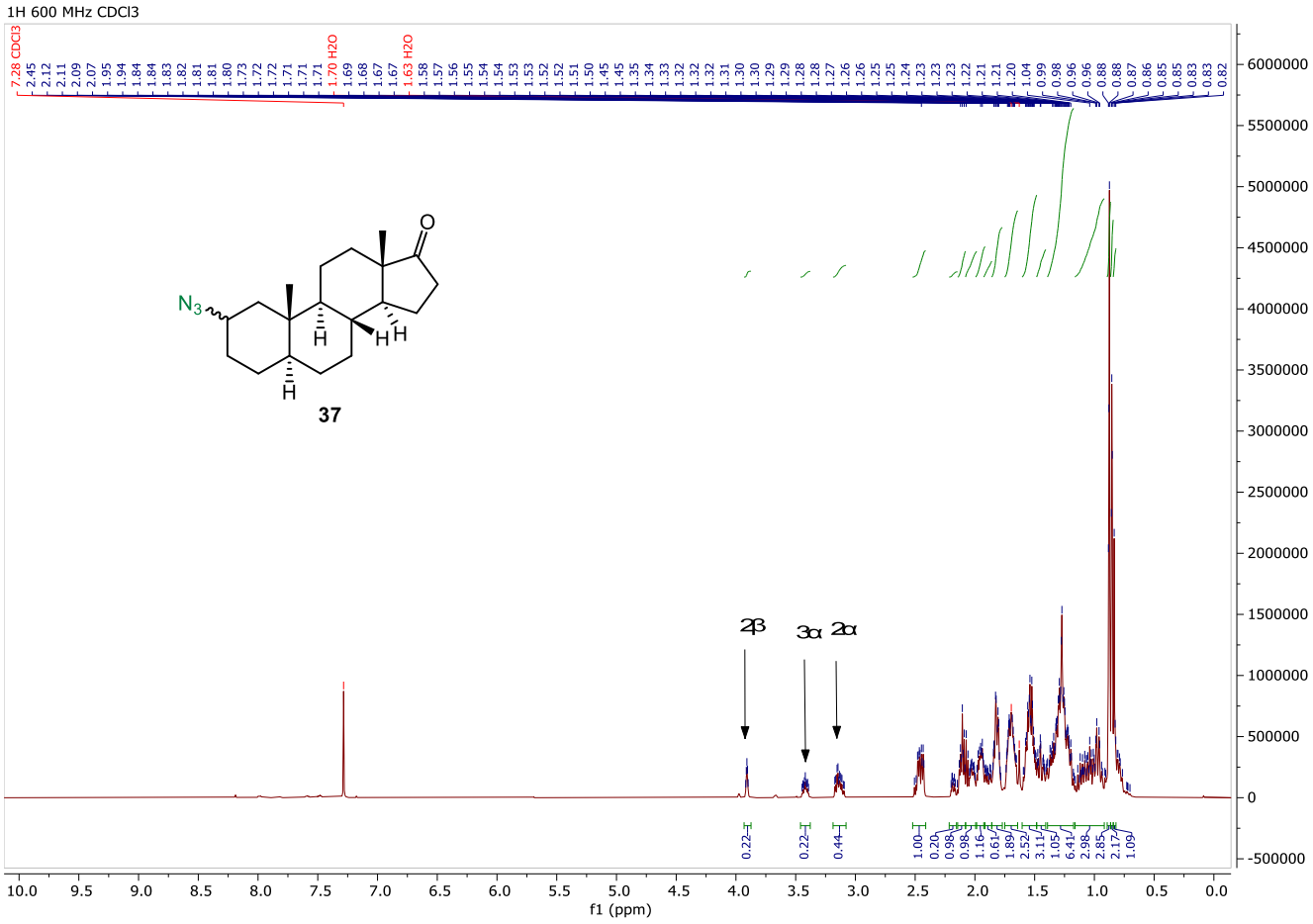

376 MHz CDCl3 19F
-129.66
700
600
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

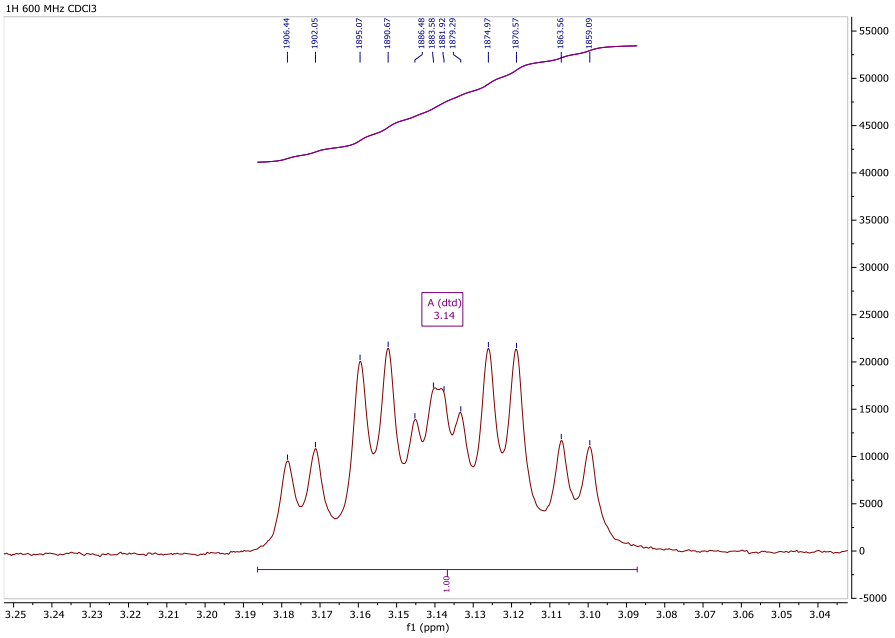
600 MHz CDCl3 1H



151 MHz CDCl3 13C

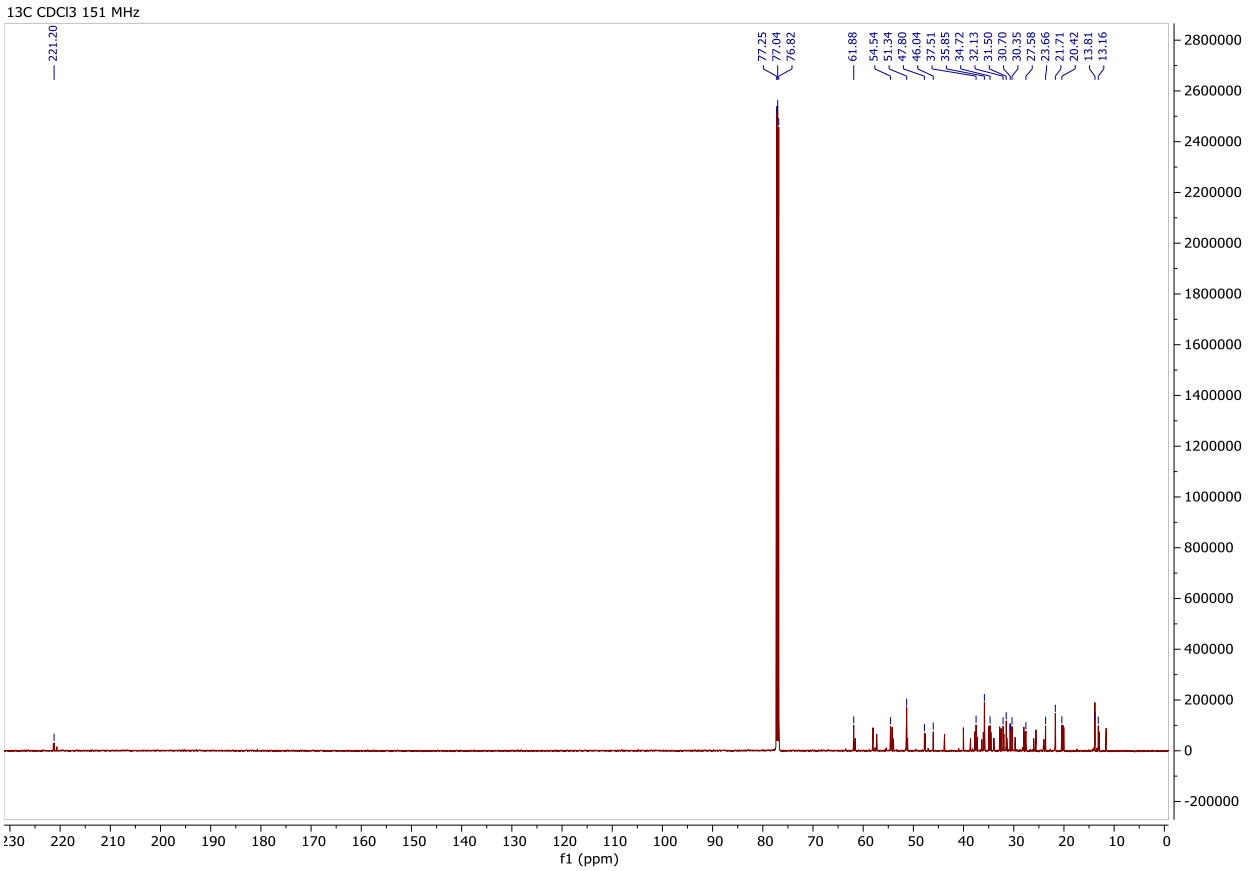




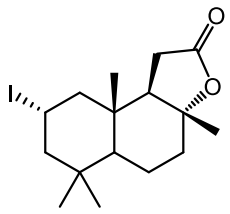


Major product peak presents as a doublet of triplet of doublets (J = 20.1, 11.4, 4.4 Hz), suggesting it is coupled to 4 protons (2 presenting the same J value and 2 presenting different J values); assuming this does not arise from long range coupling (J values generally 1-3 Hz), this

eliminates sites of functionalization α to tertiary and quaternary centers and limits possible sites of functionalization to the 2 and 3 positions. As both azidation products at the 3 position are known, major product must be at the 2 position, and is assumed to be the 2α product by comparison to Groves' fluorination of deoxy-androsterone (in our hands gave >4 fluorination products, but 2α as major product).[69]

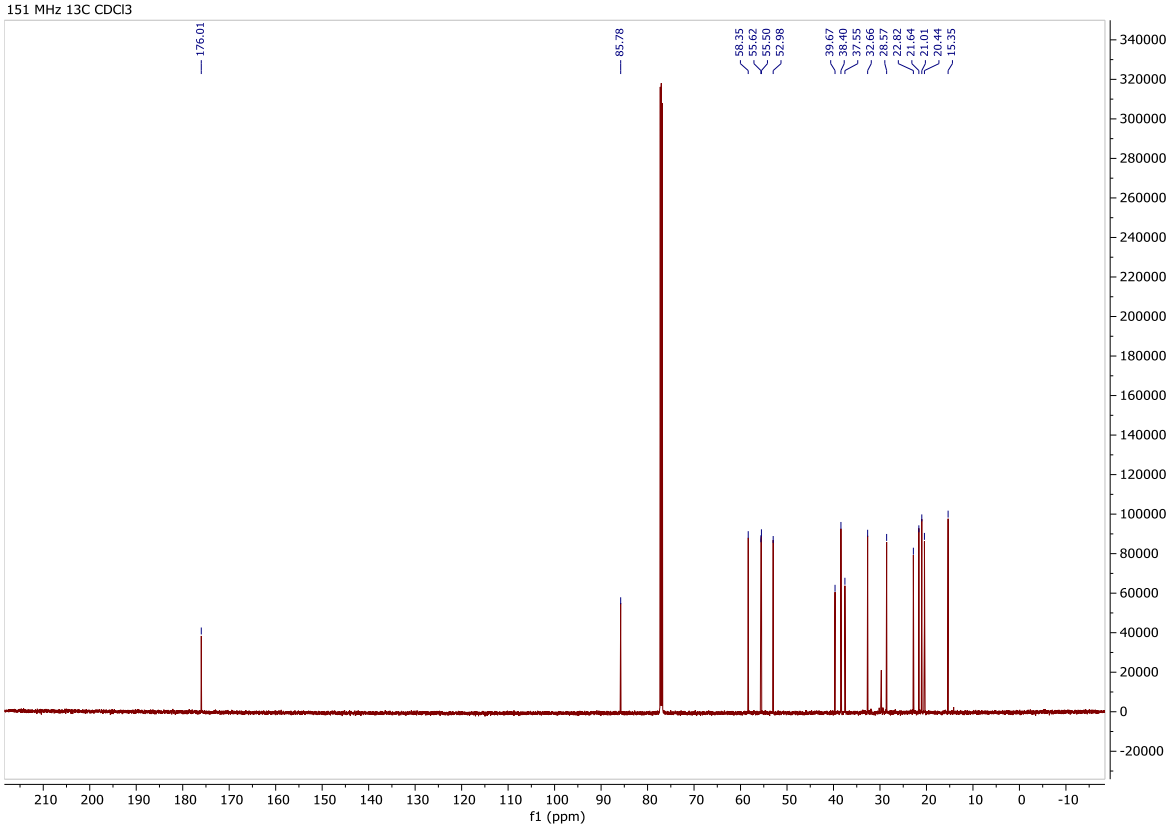


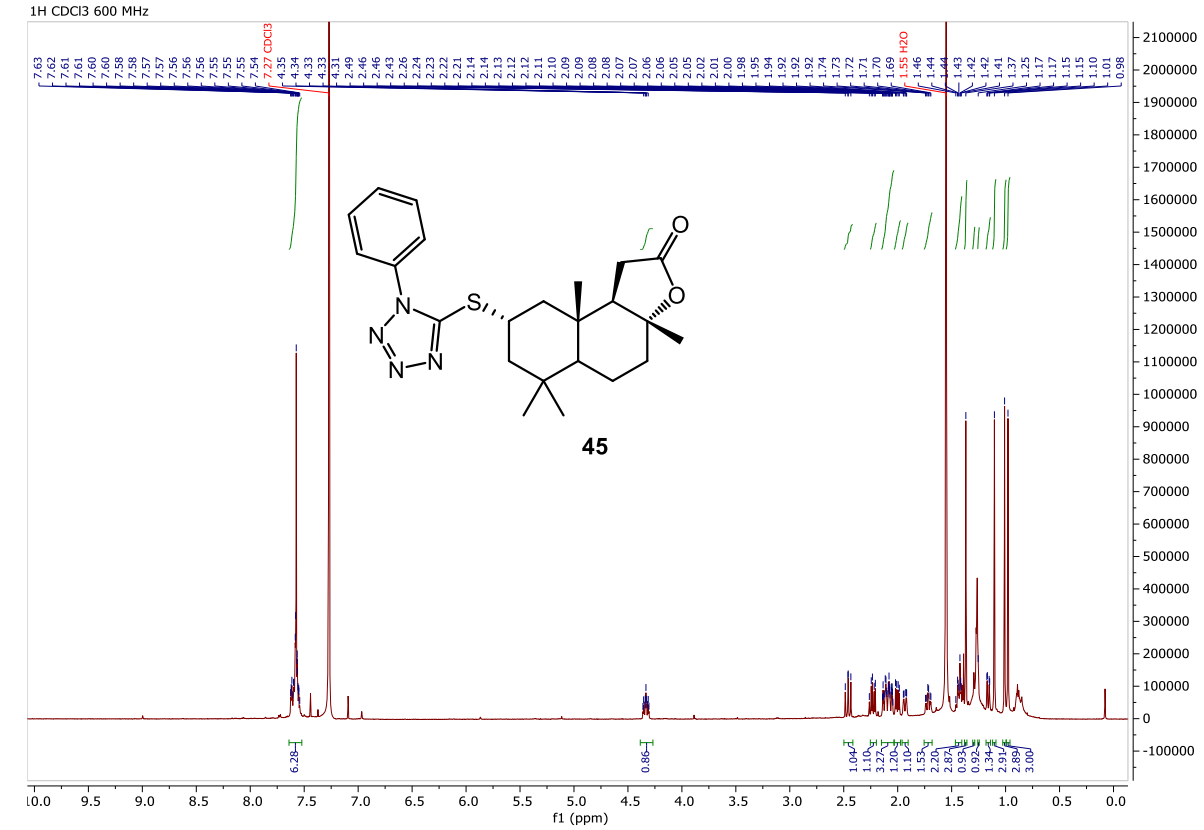
600 MHz 1H CDCl3

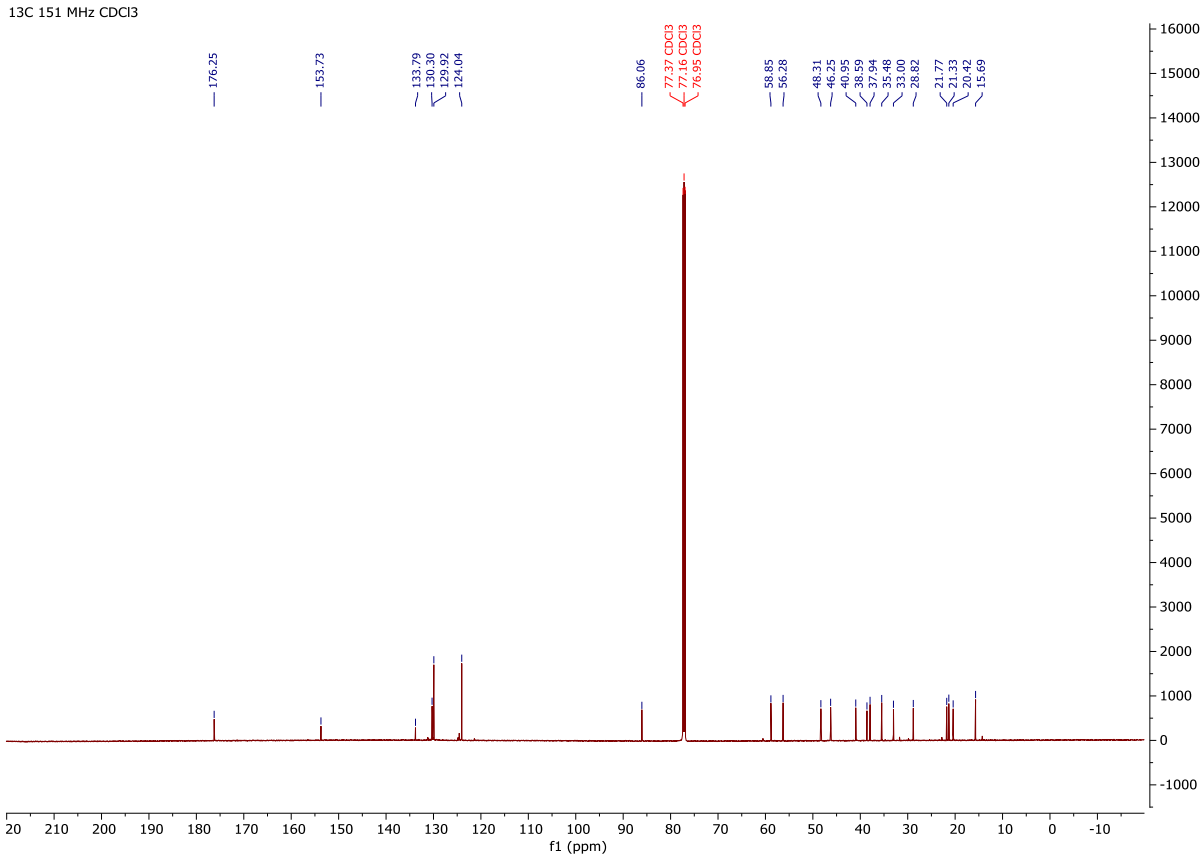


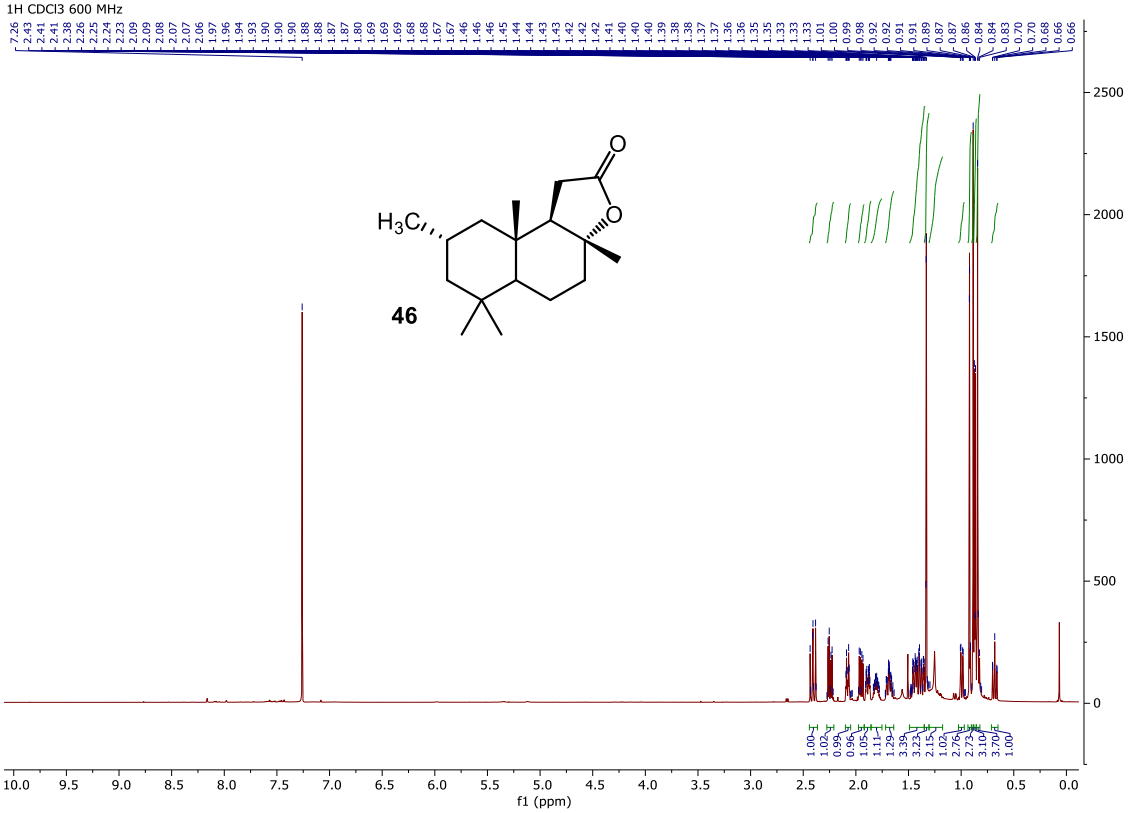
40

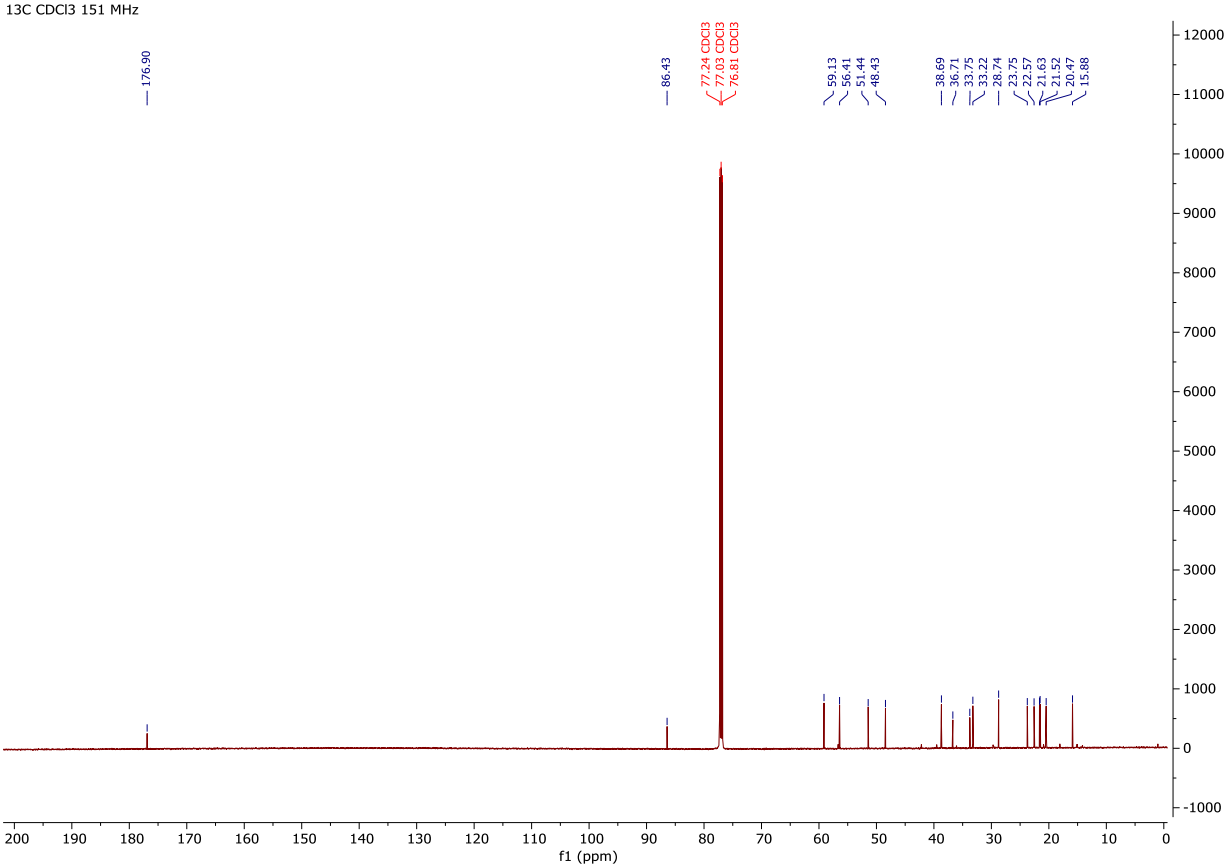
151 MHz 13C CDCl3

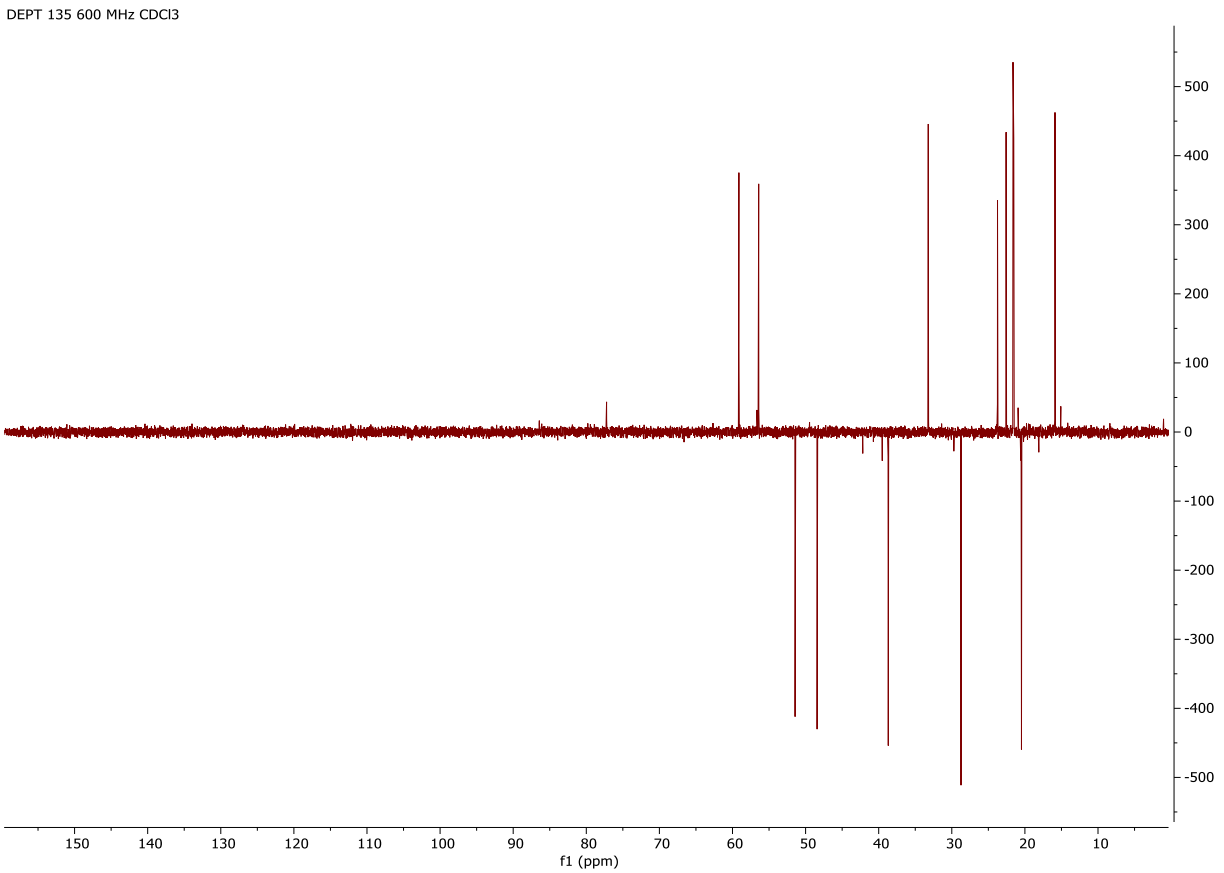


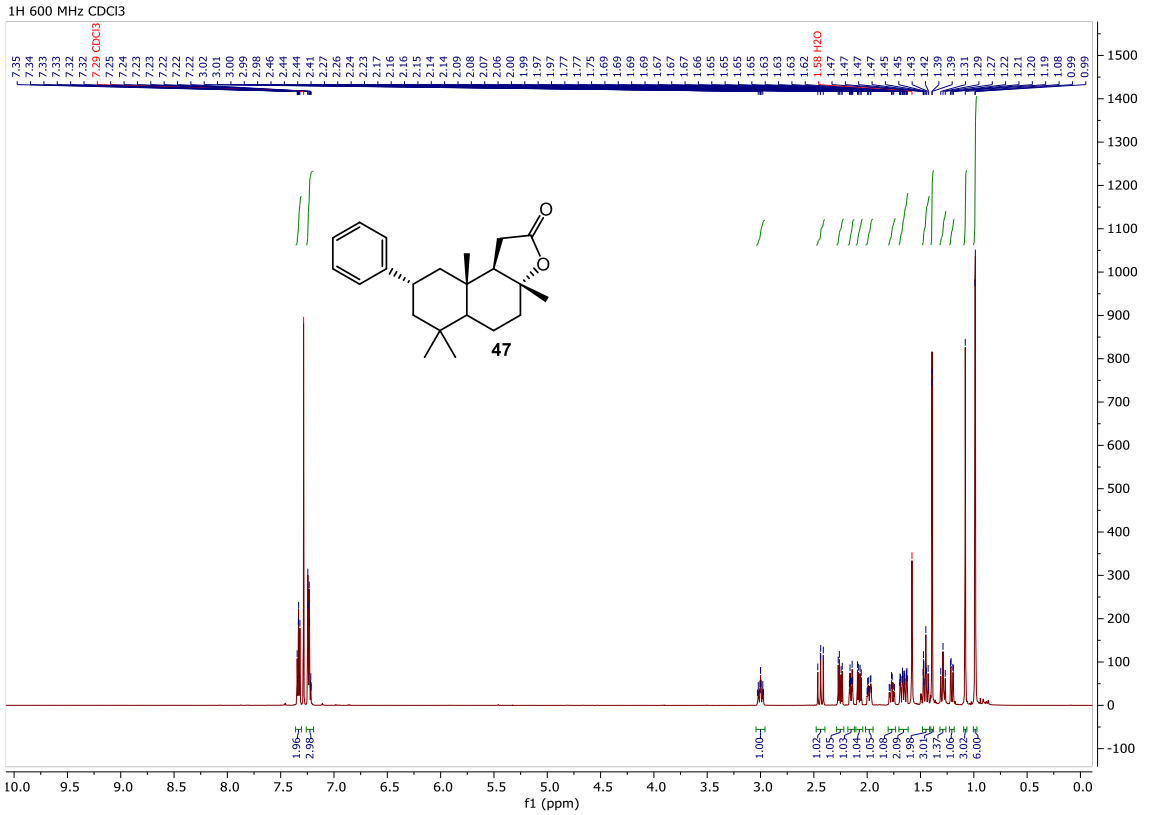

1H CDCl3 600 MHz
7.27 CDCl3
1.55 H2O
45
f1 (ppm)

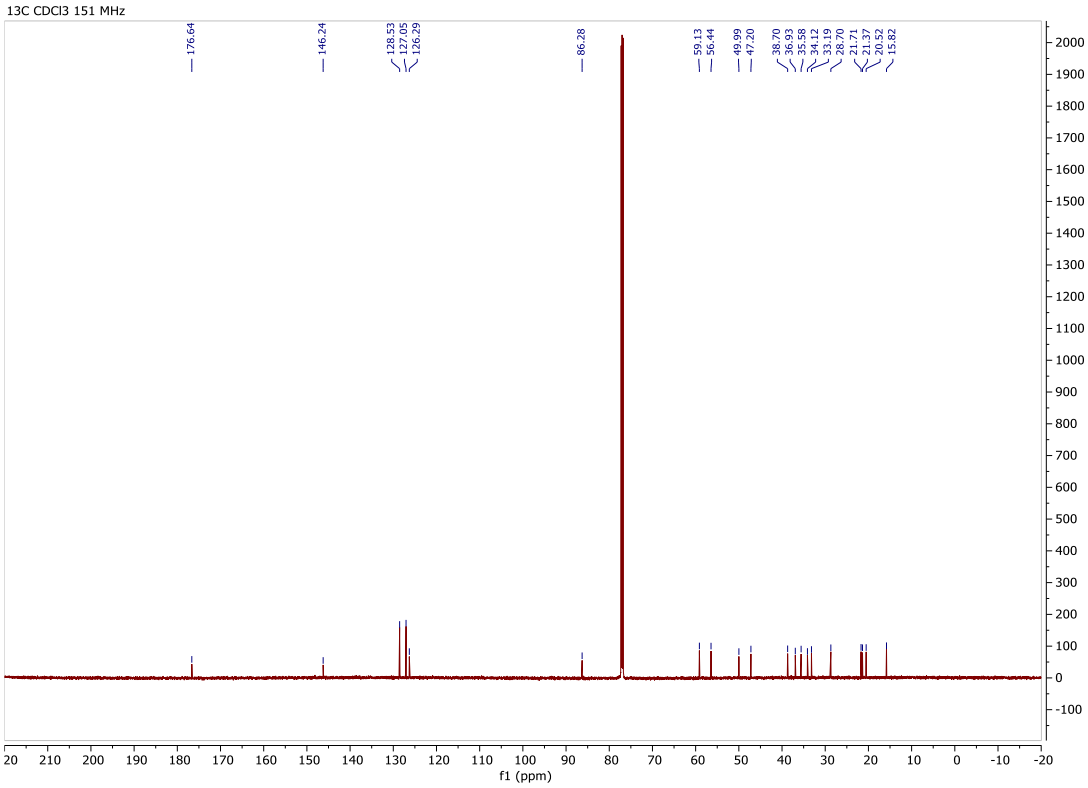

13C 151 MHz CDCl3
176.25
153.73
133.79
130.30
129.92
124.04
86.06
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
58.85
56.28
48.31
46.25
40.95
38.59
37.94
35.48
33.00
28.82
21.77
21.33
20.42
15.69
f1 (ppm)


1H CDCl3 600 MHz
46
f1 (ppm)

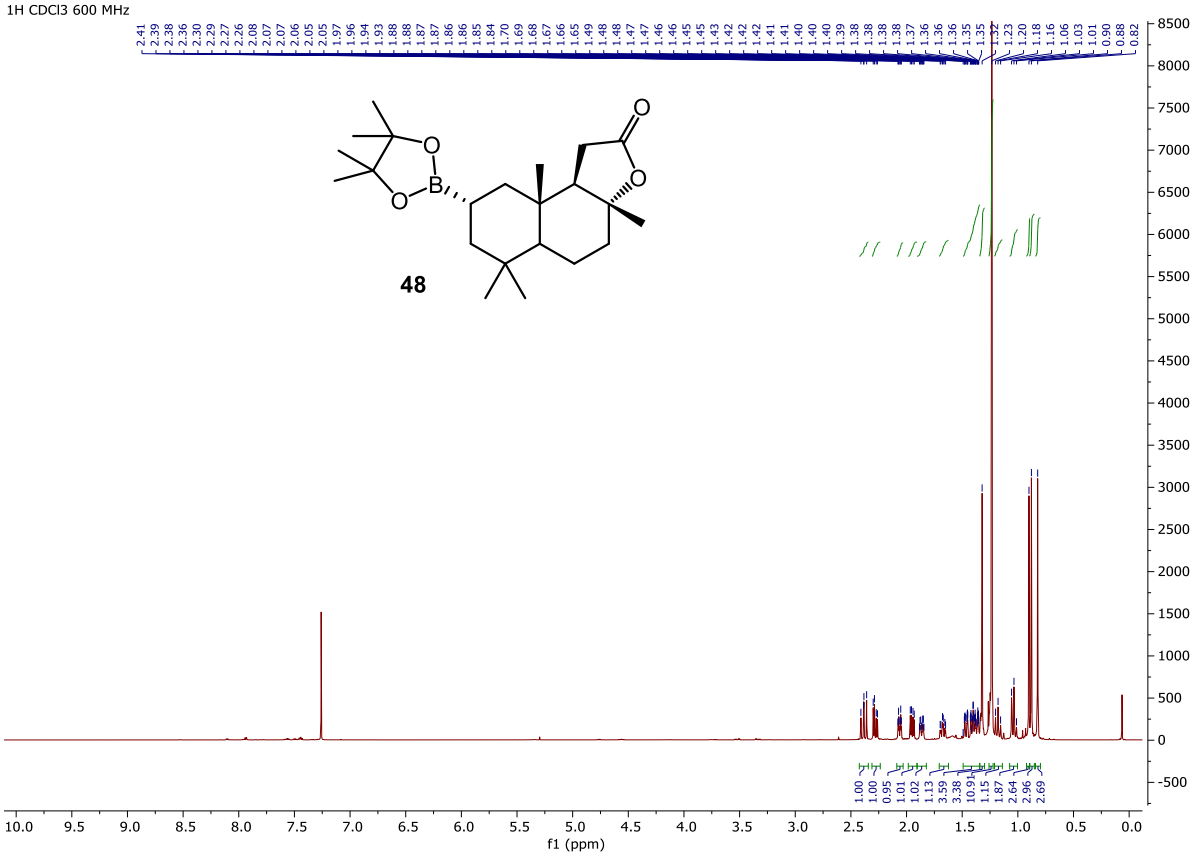

13C CDCl3 151 MHz
176.90
86.43
77.24 CDCl3
77.03 CDCl3
76.81 CDCl3
59.13
56.41
51.44
48.43
38.69
36.71
33.75
33.22
28.74
23.75
22.57
21.63
21.52
20.47
15.88
f1 (ppm)


DEPT 135 600 MHz CDCl3
500
400
300
200
100
0
-100
-200
-300
-400
-500
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

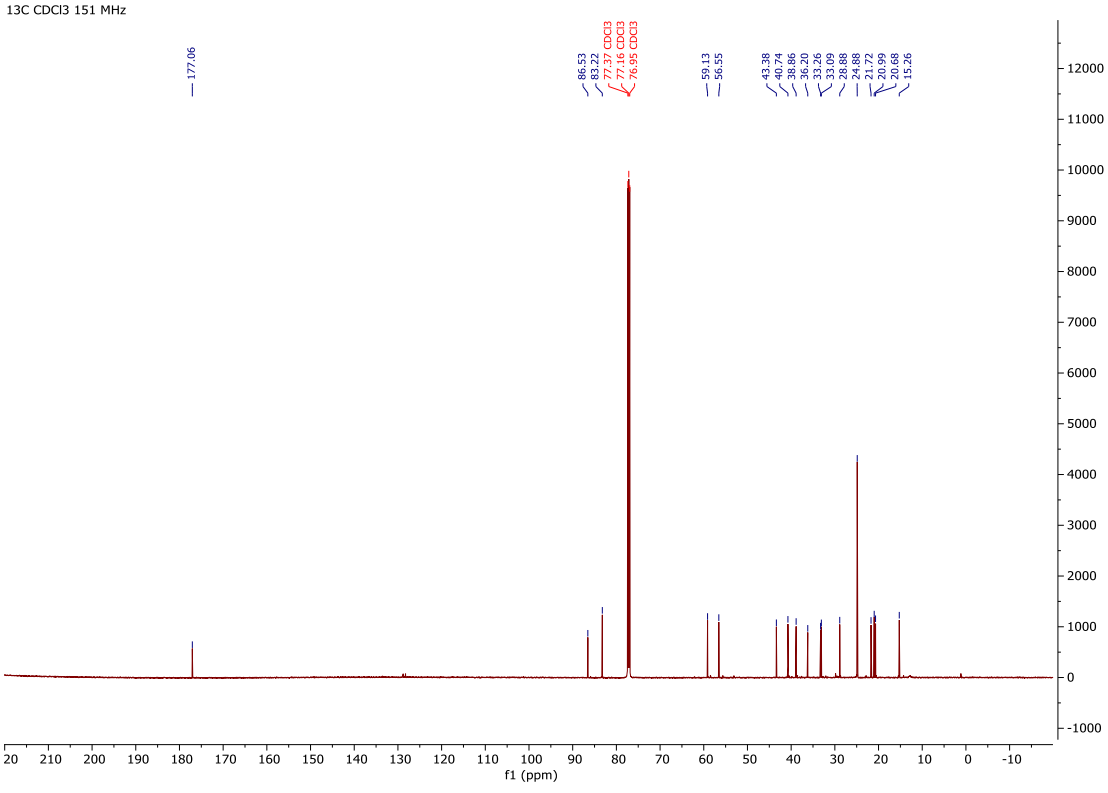

1H 600 MHz CDCl3
47
f1 (ppm)

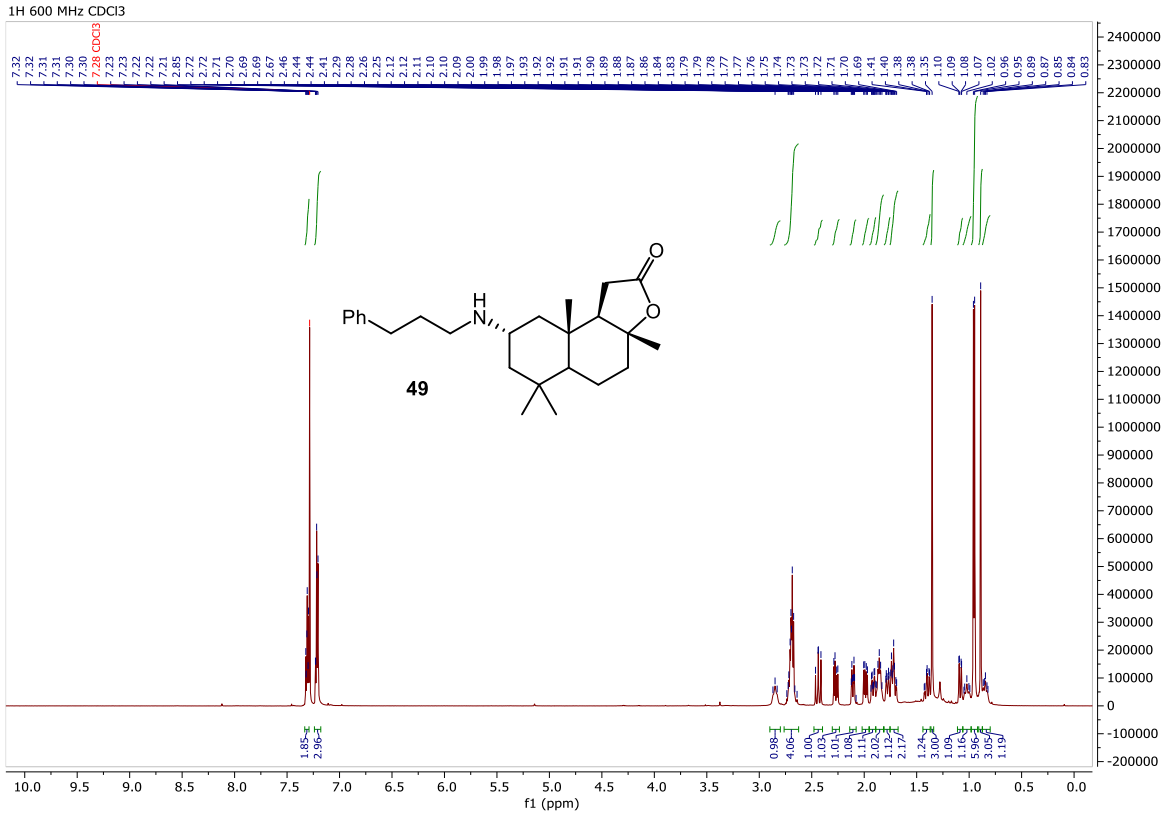

13C CDCl3 151 MHz
f1 (ppm)

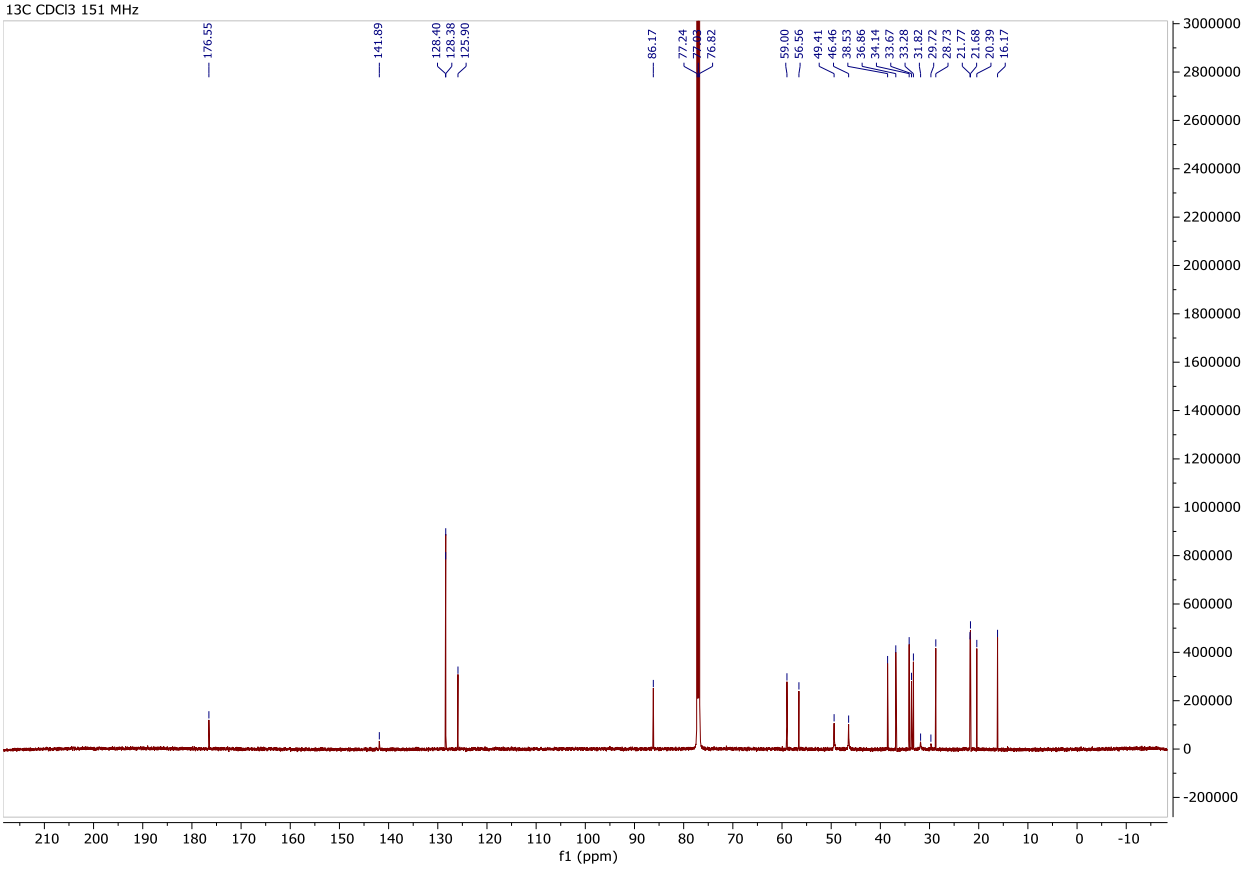
1H CDCl3 600 MHz

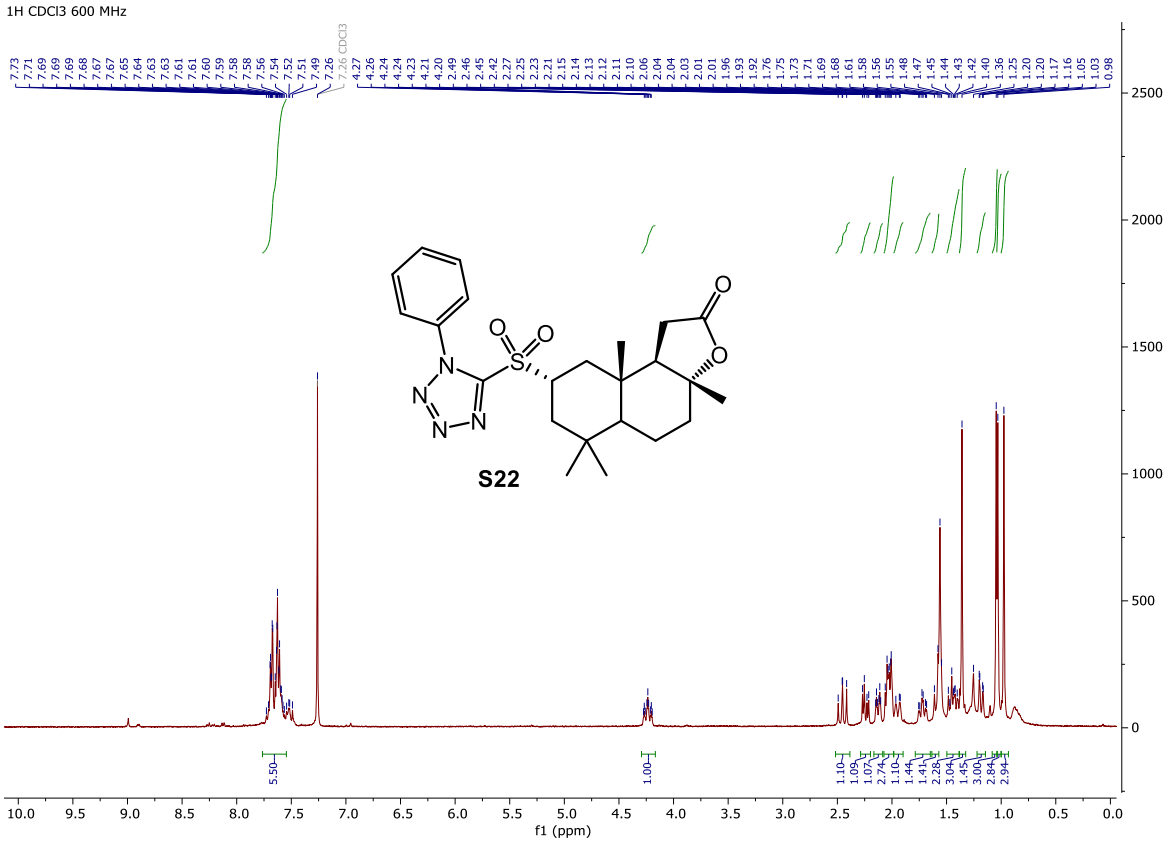


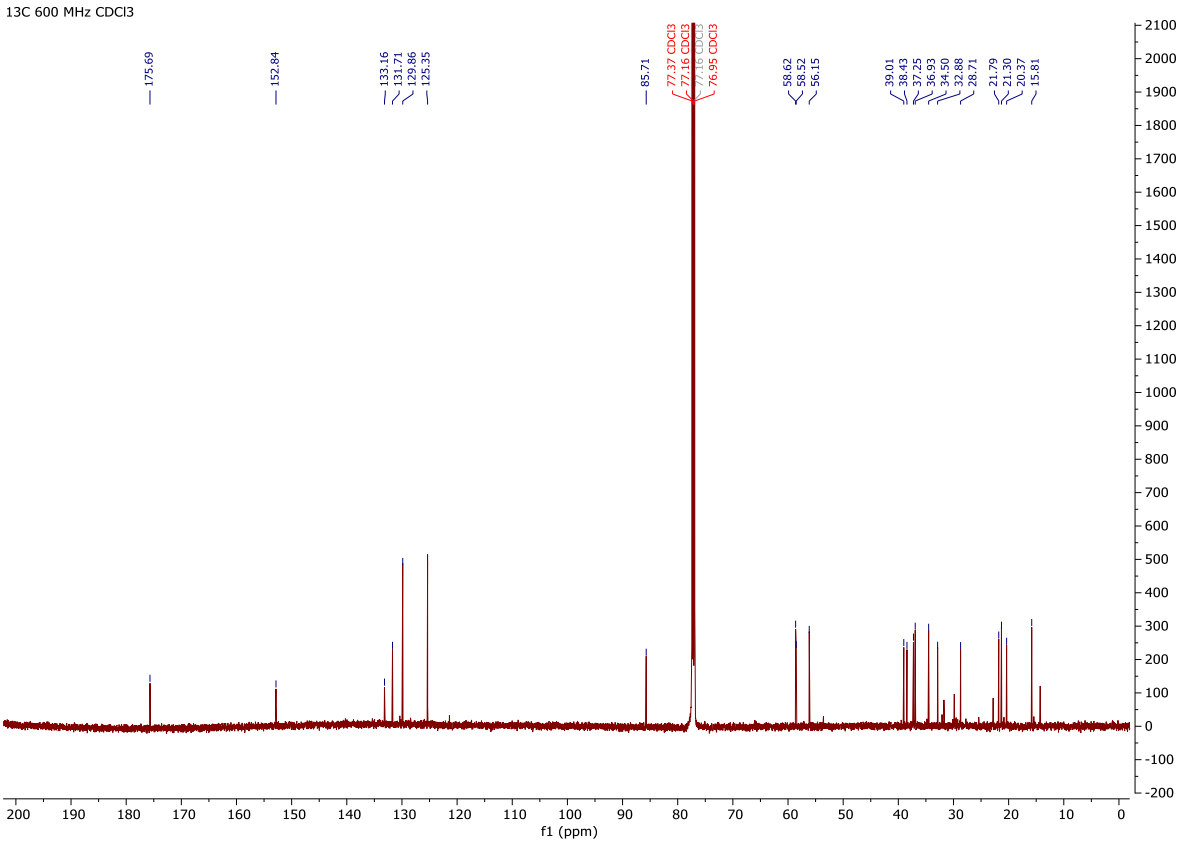
13C CDCl3 151 MHz

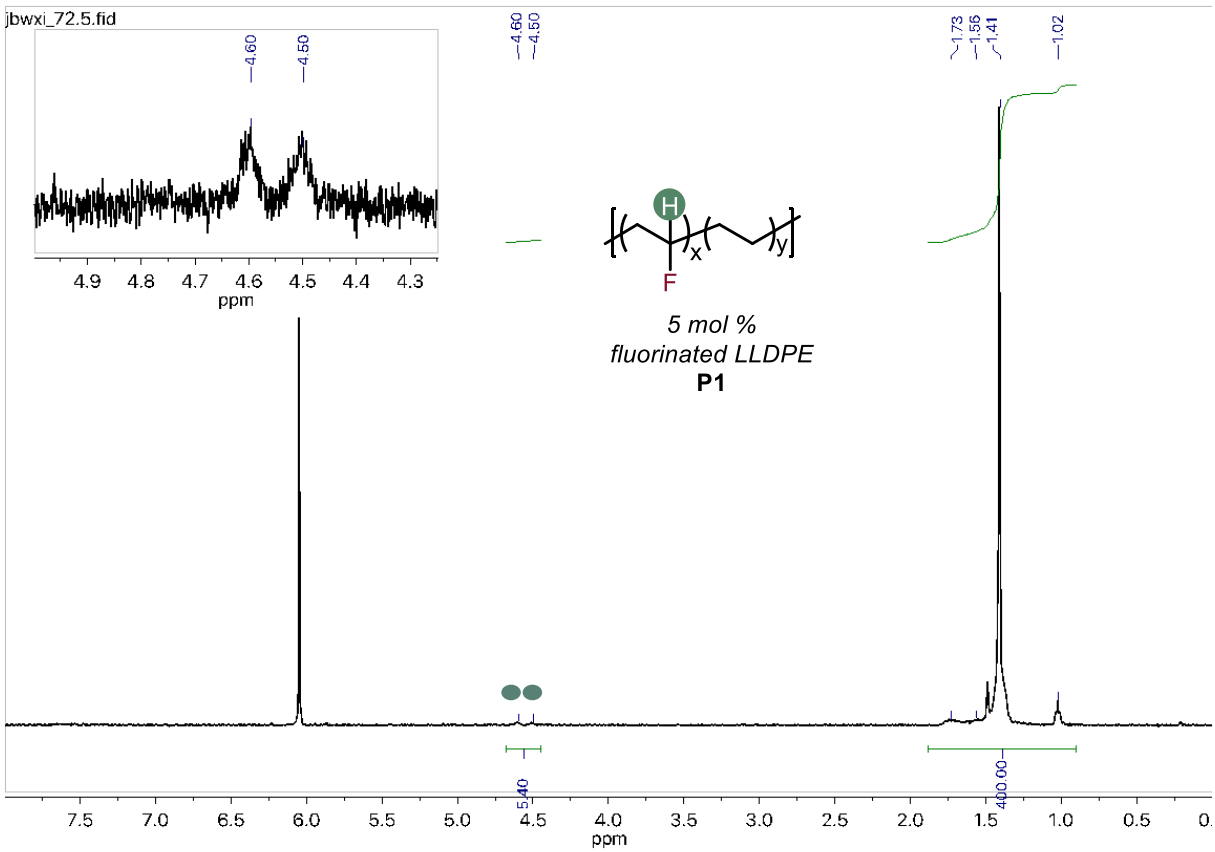



1H 600 MHz CDCl3
Ph
N
H
O
O
49
f1 (ppm)

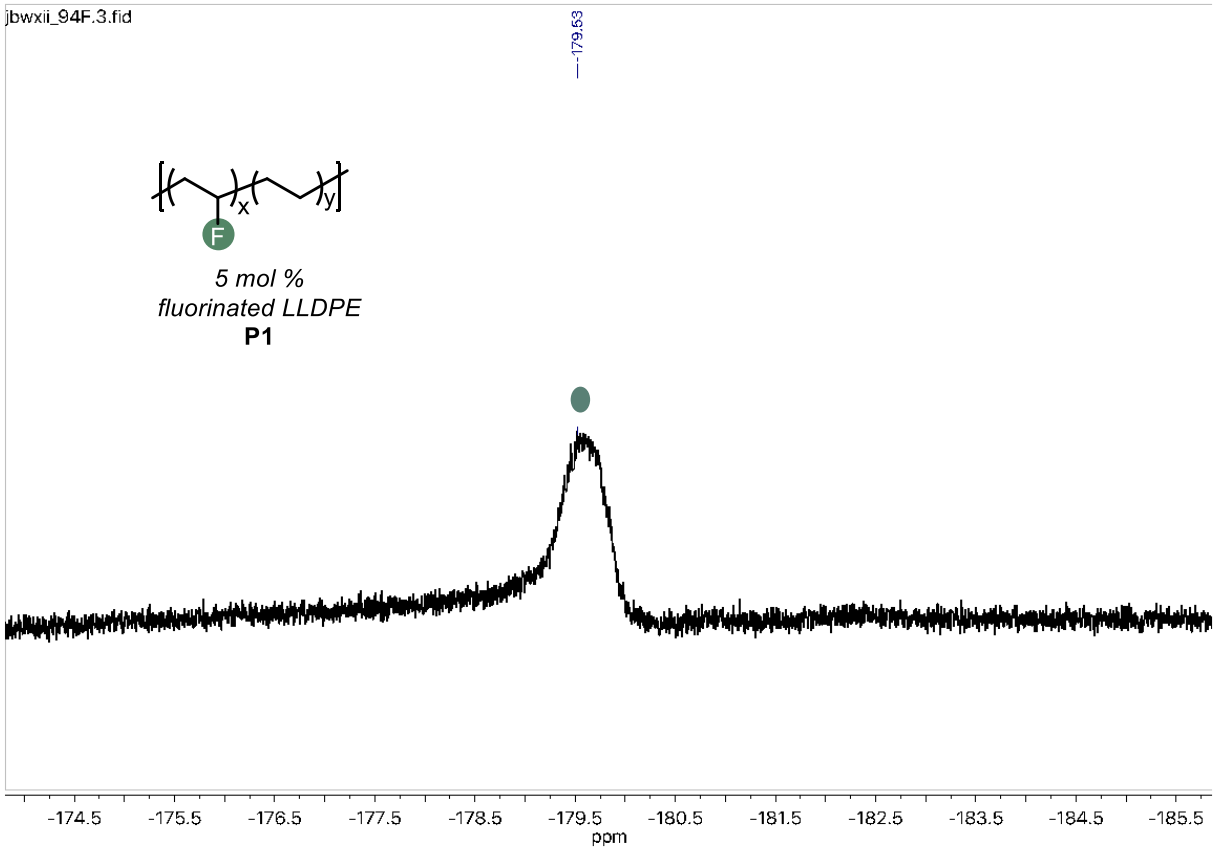

13C CDCl3 151 MHz
f1 (ppm)


1H CDCl3 600 MHz
S22
f1 (ppm)

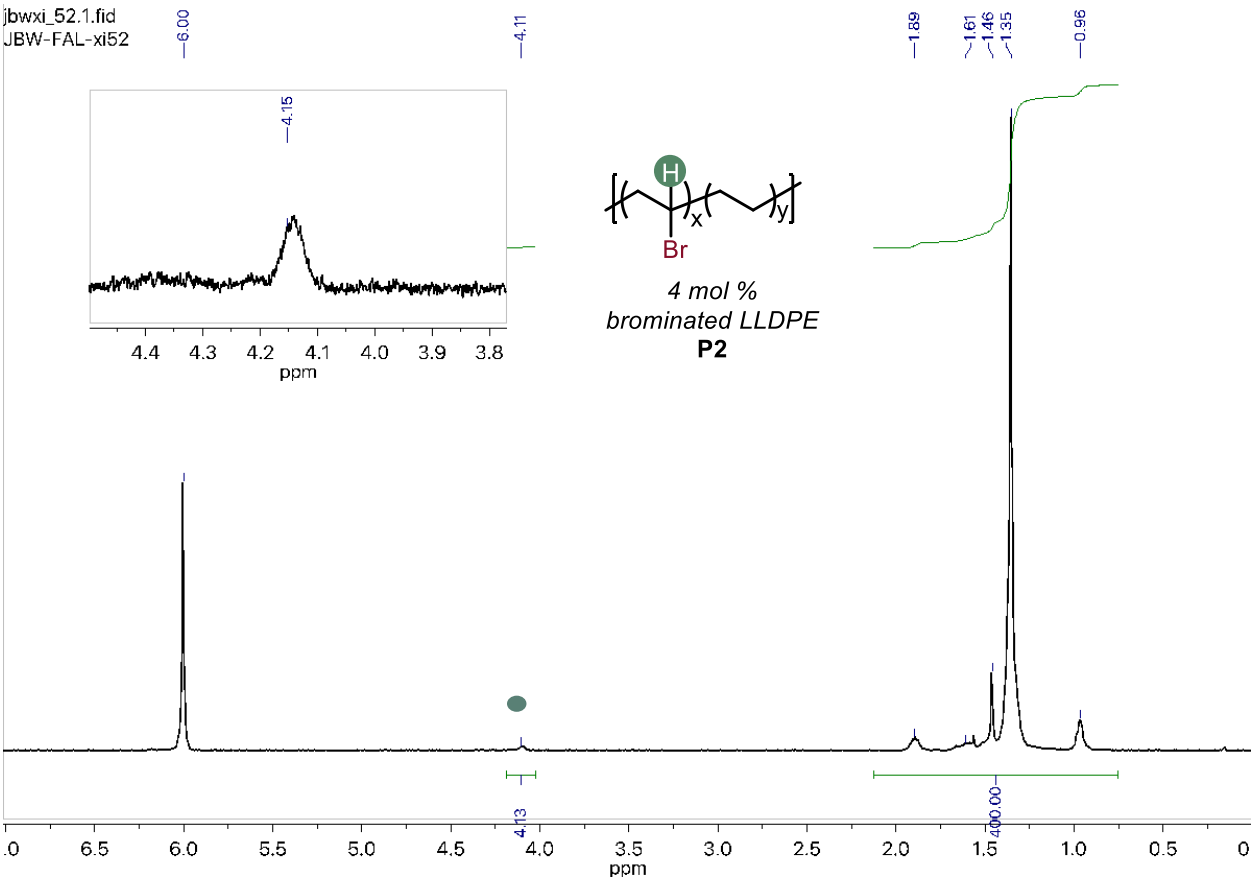

13C 600 MHz CDCl3
175.69
152.84
133.16
131.71
129.86
125.35
85.71
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
58.62
58.52
56.15
39.01
38.43
37.25
36.93
34.50
32.88
28.71
21.79
21.30
20.37
15.81
f1 (ppm)



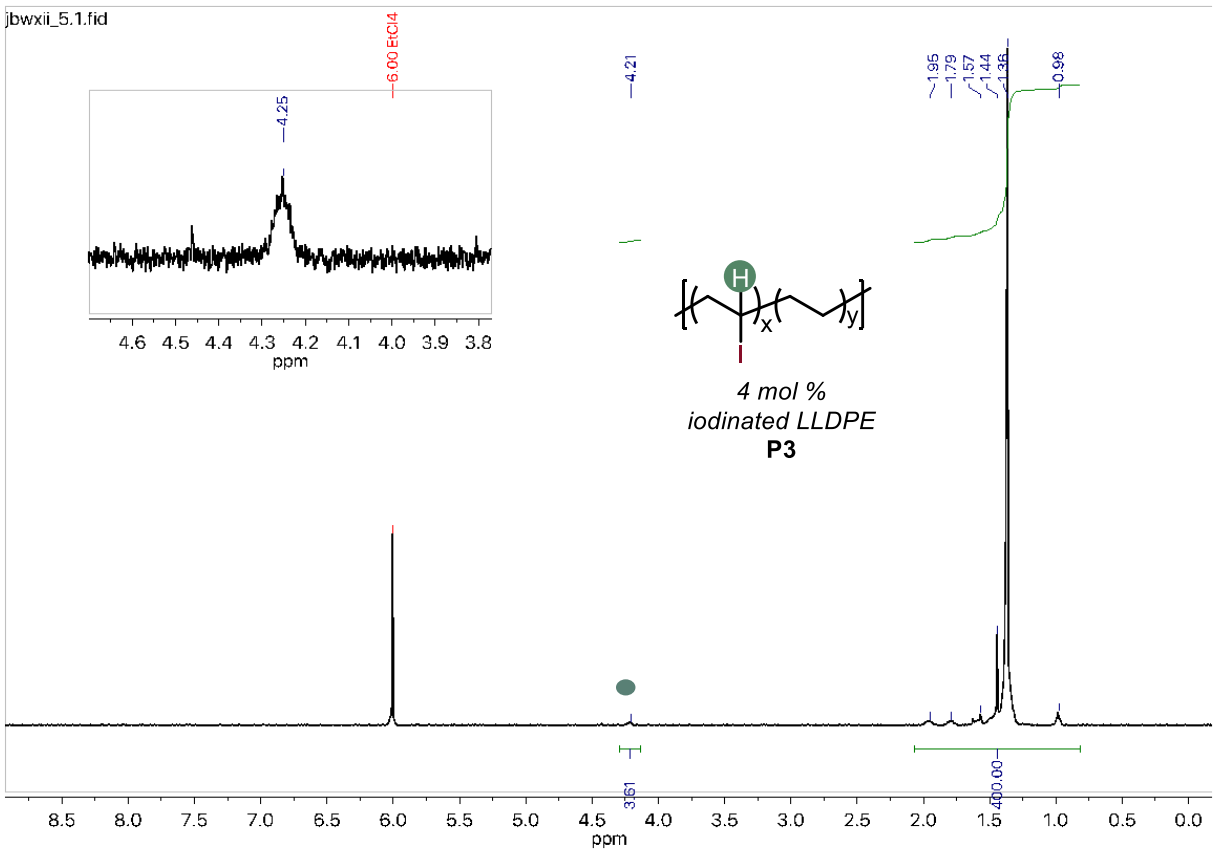
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



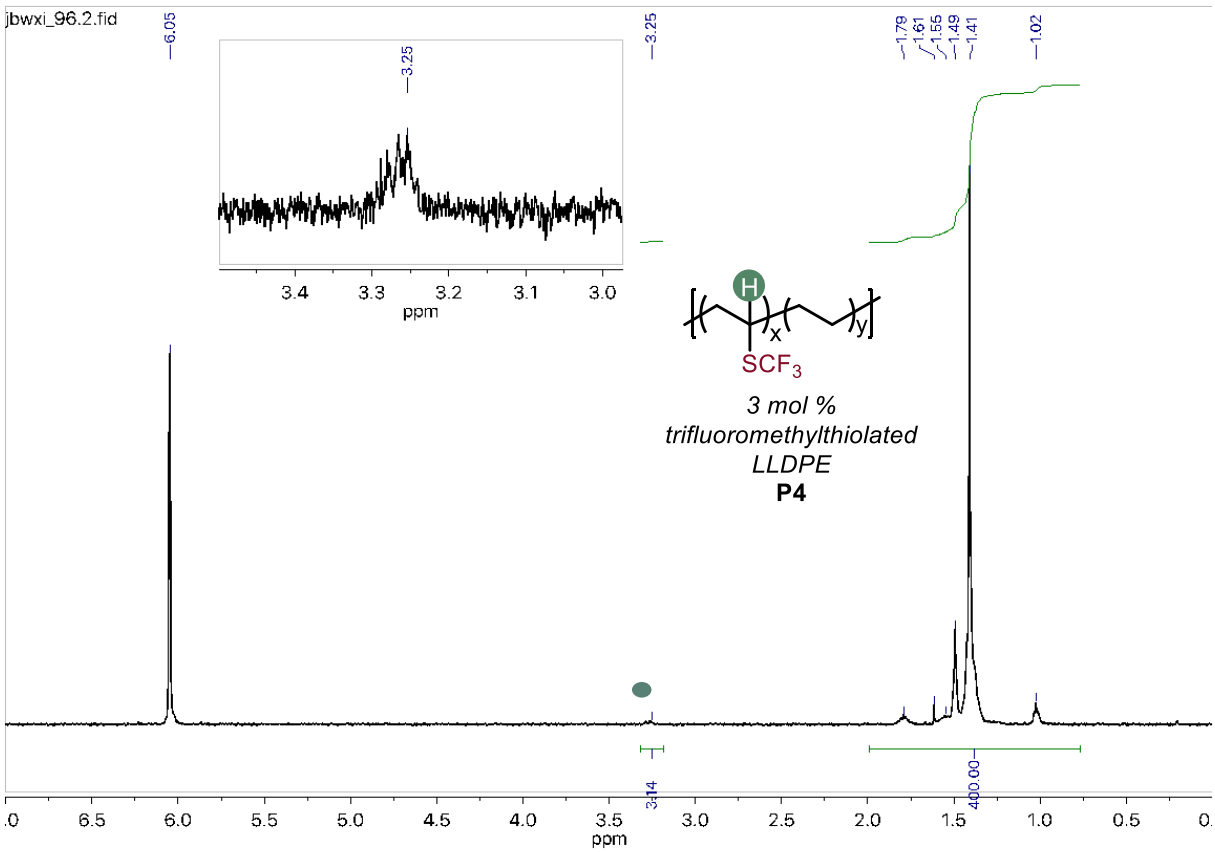
Referenced to trifluorotoluene at -63.72 ppm



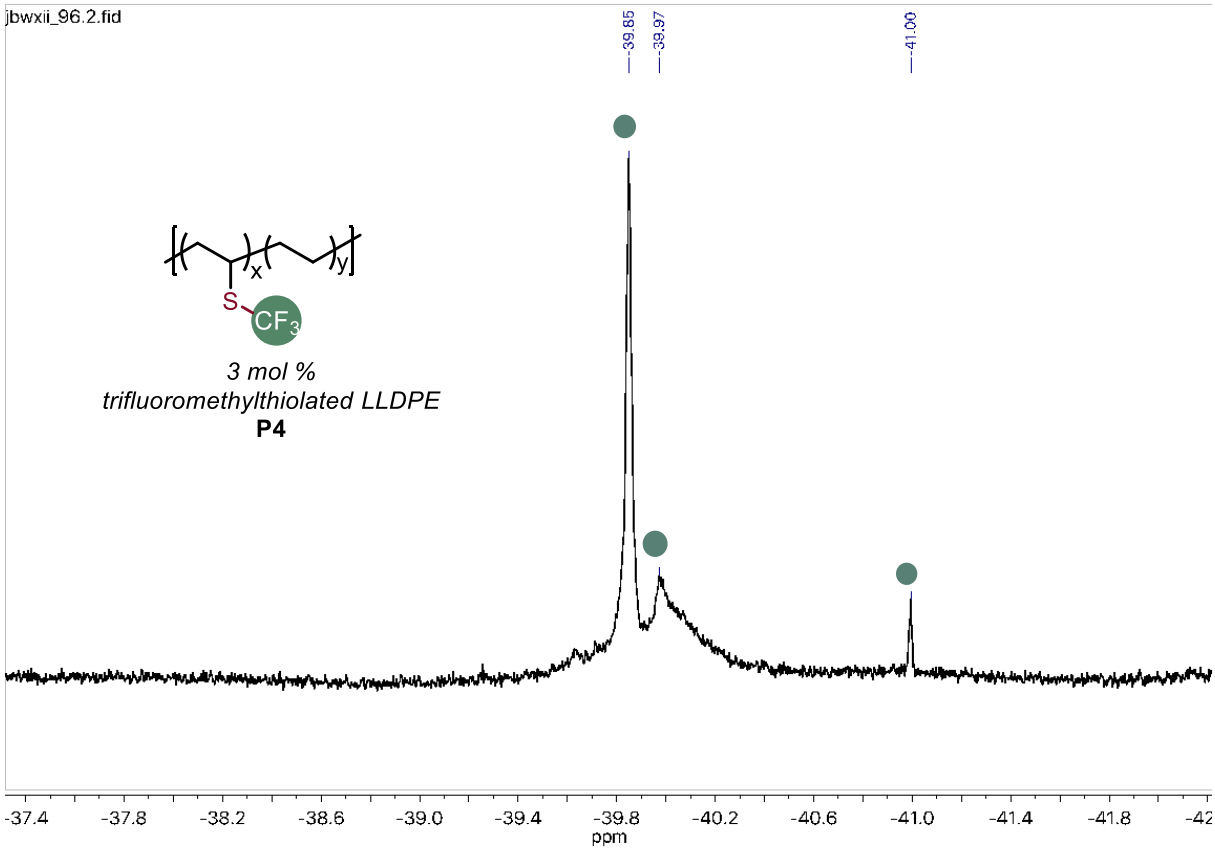
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



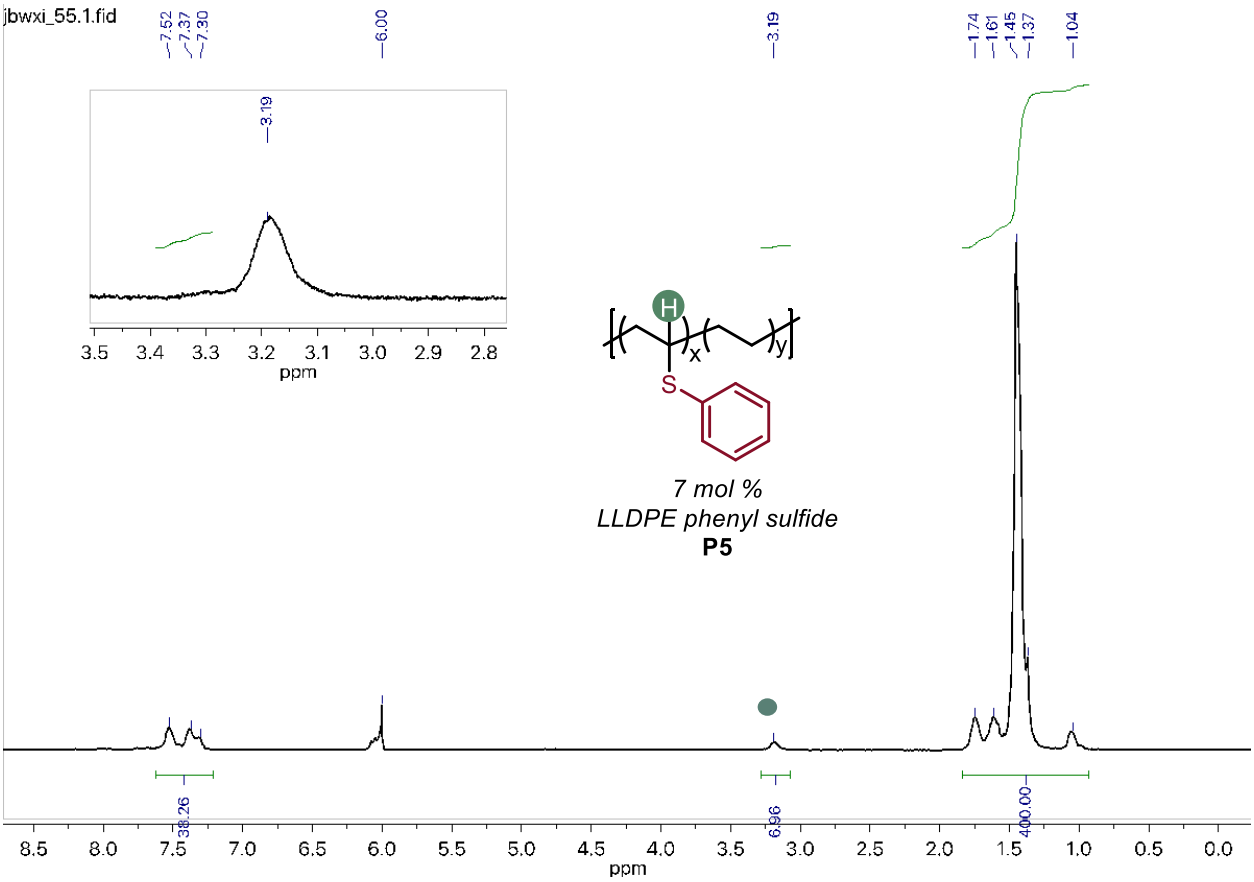
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



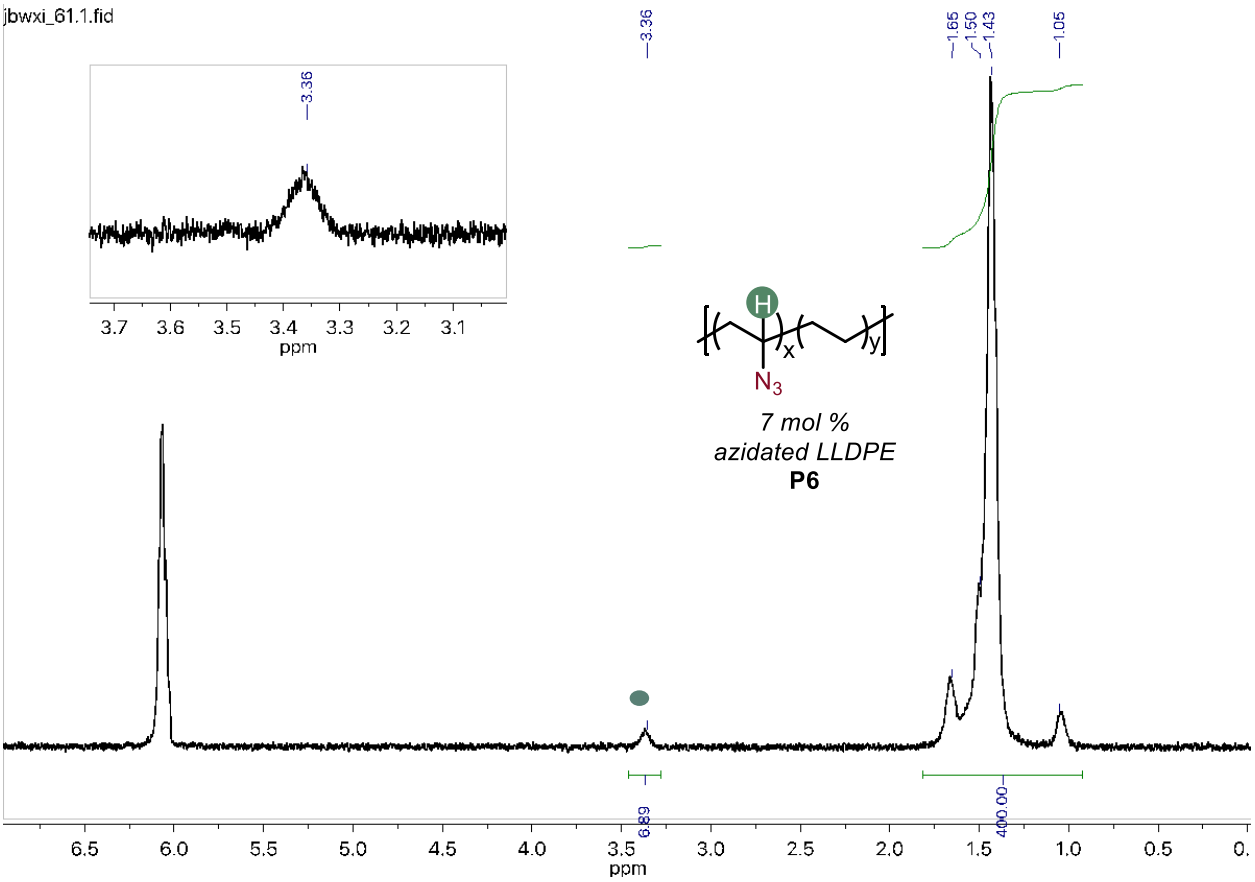
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



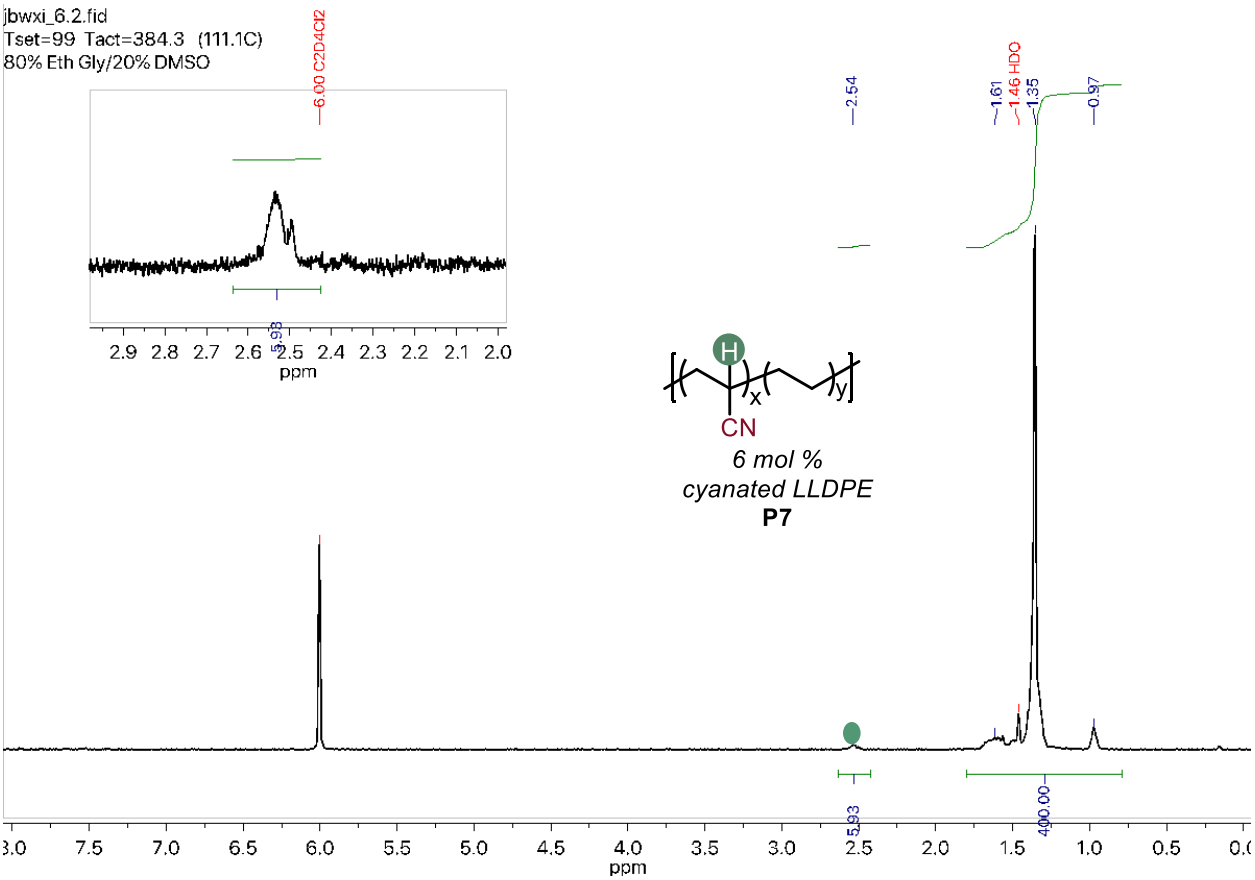
Referenced to trifluorotoluene at -63.72 ppm



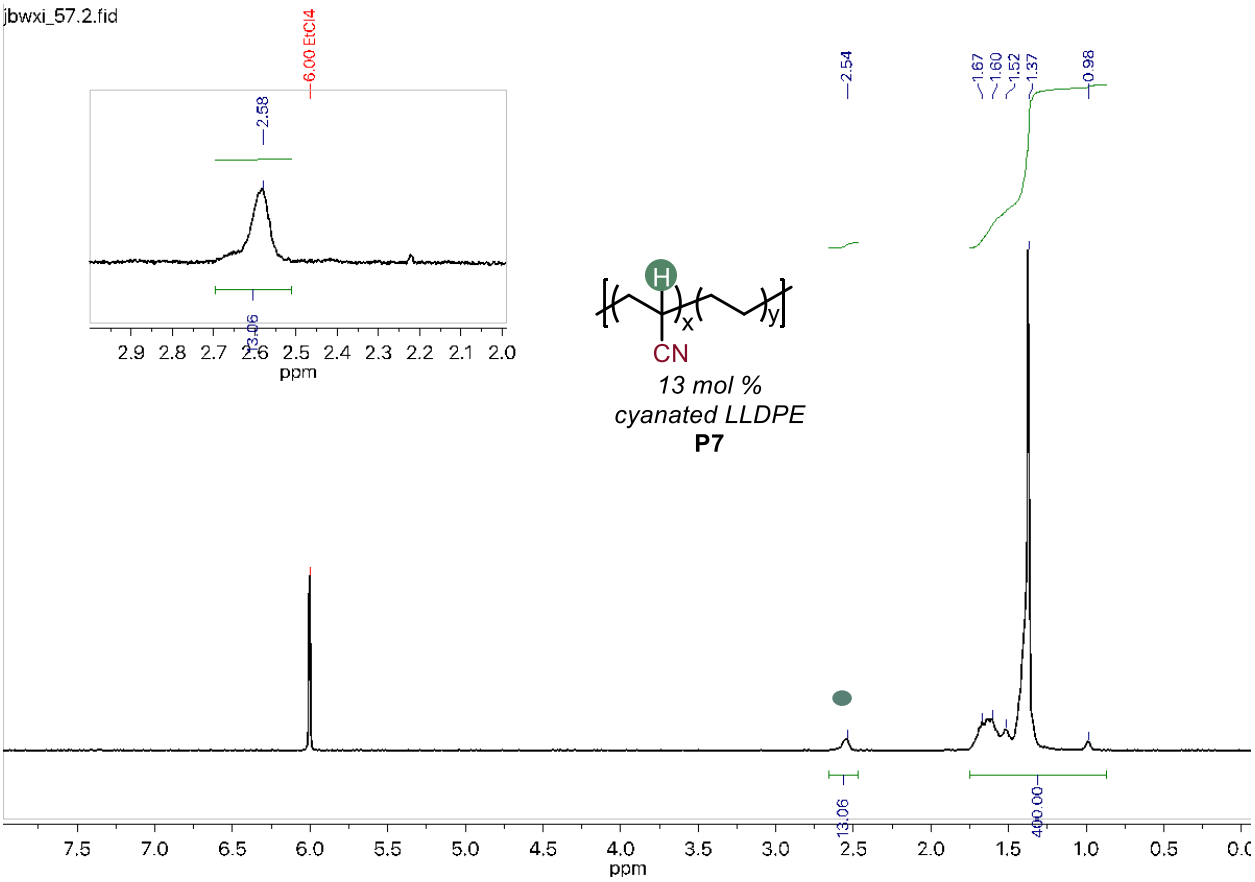
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



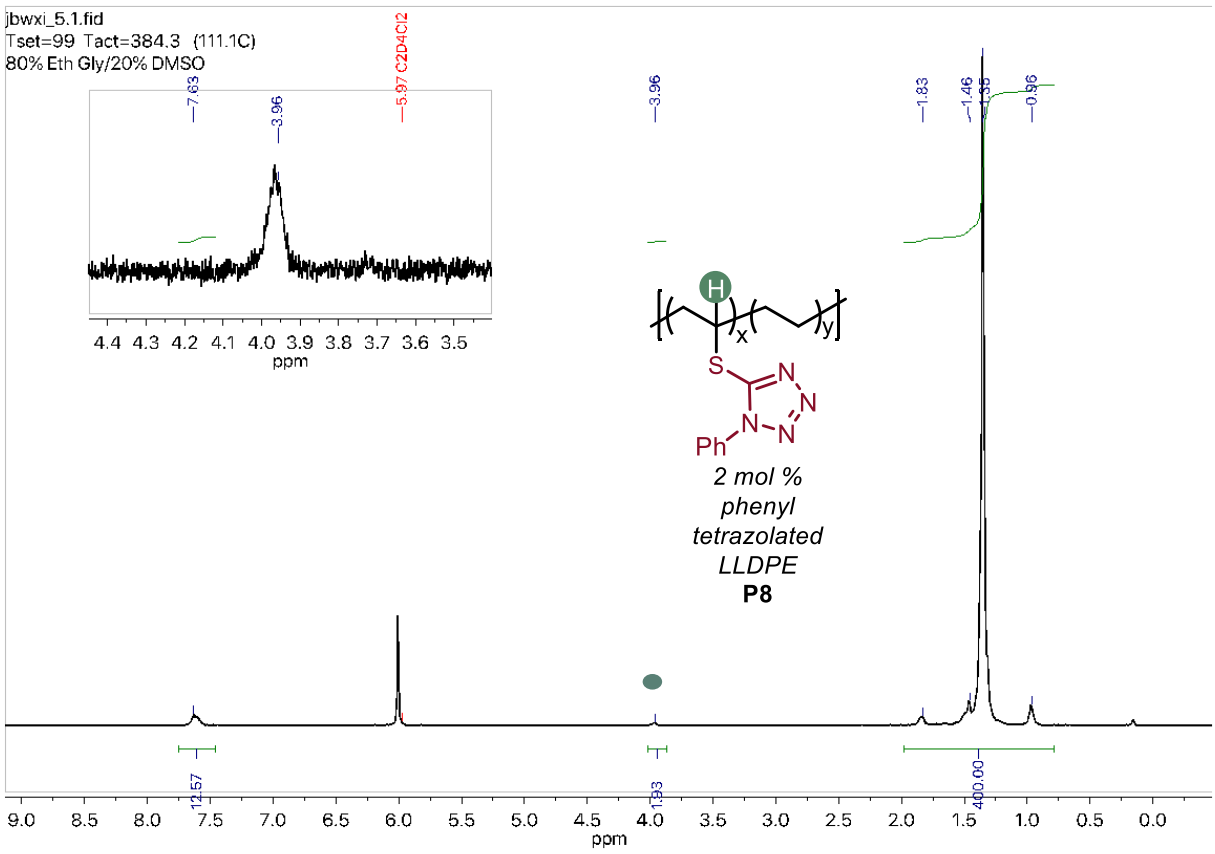
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



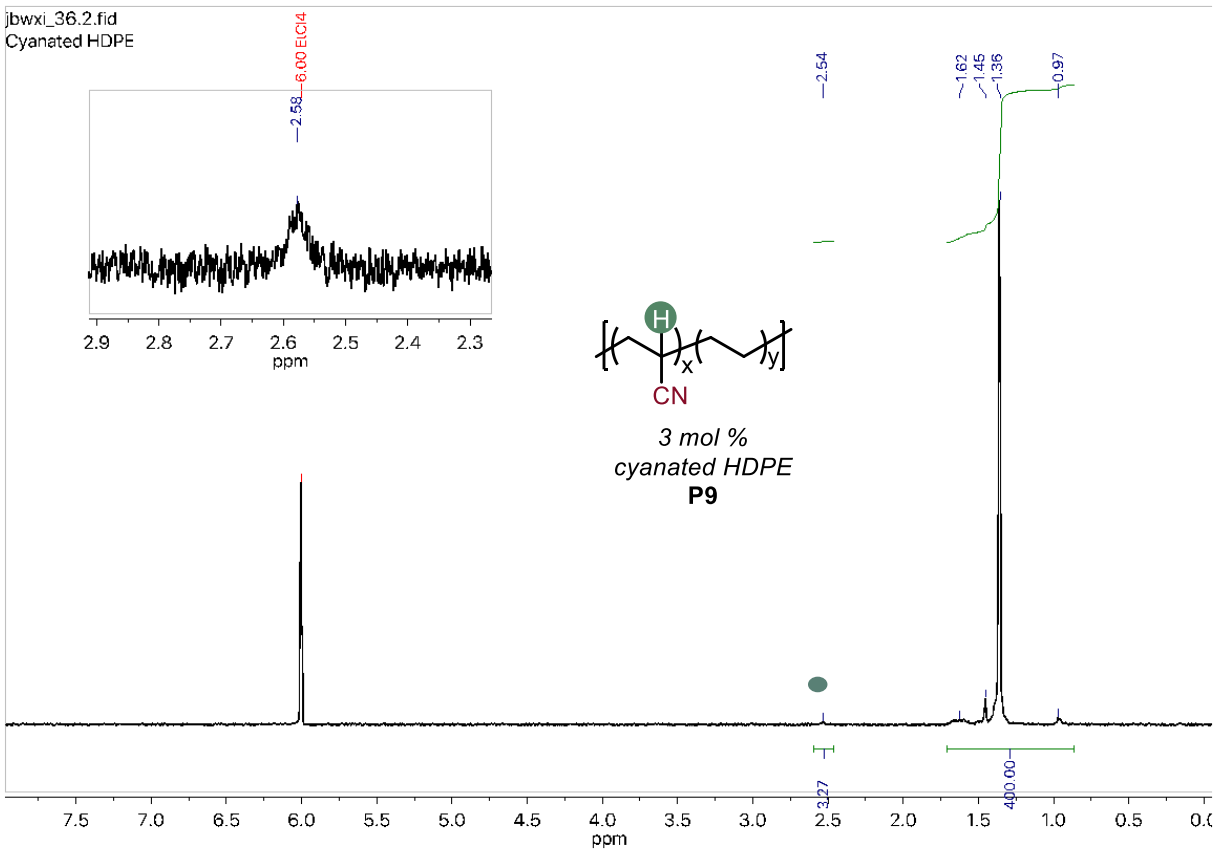
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



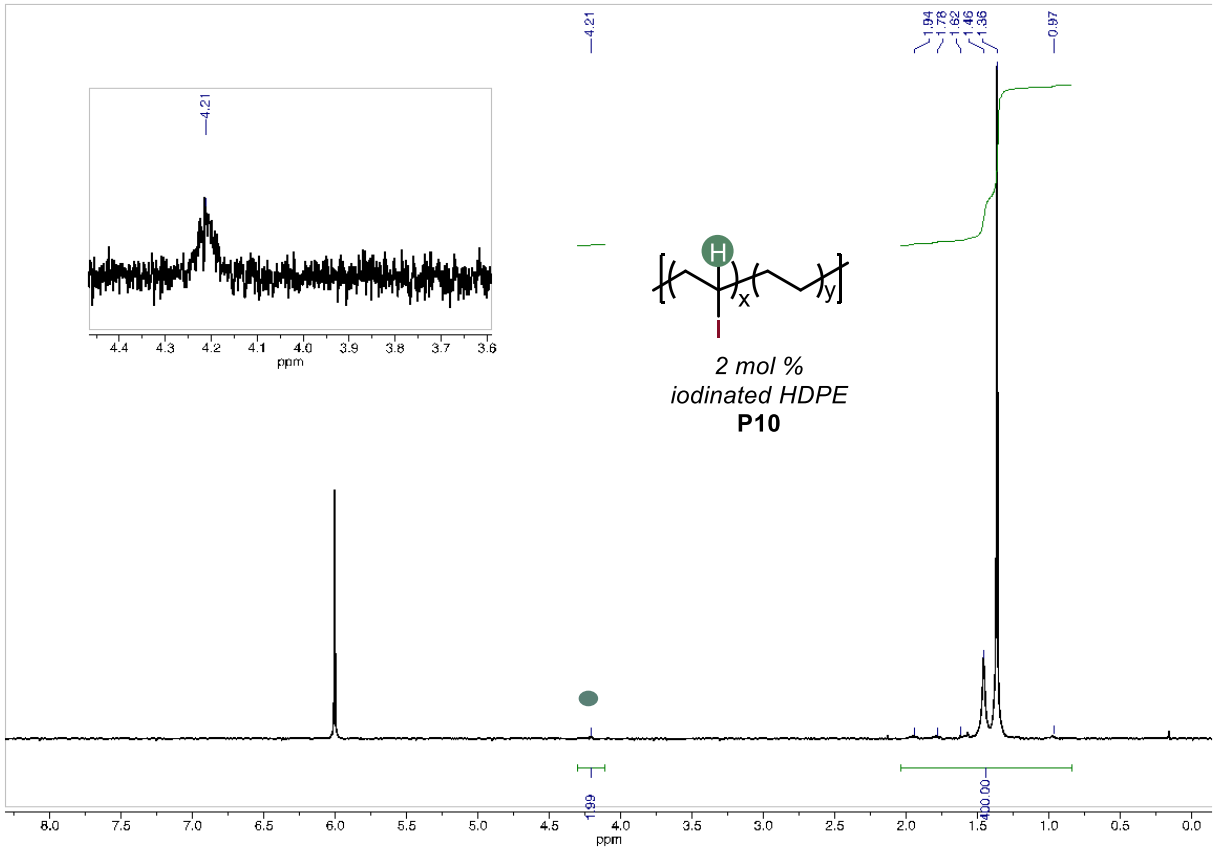
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



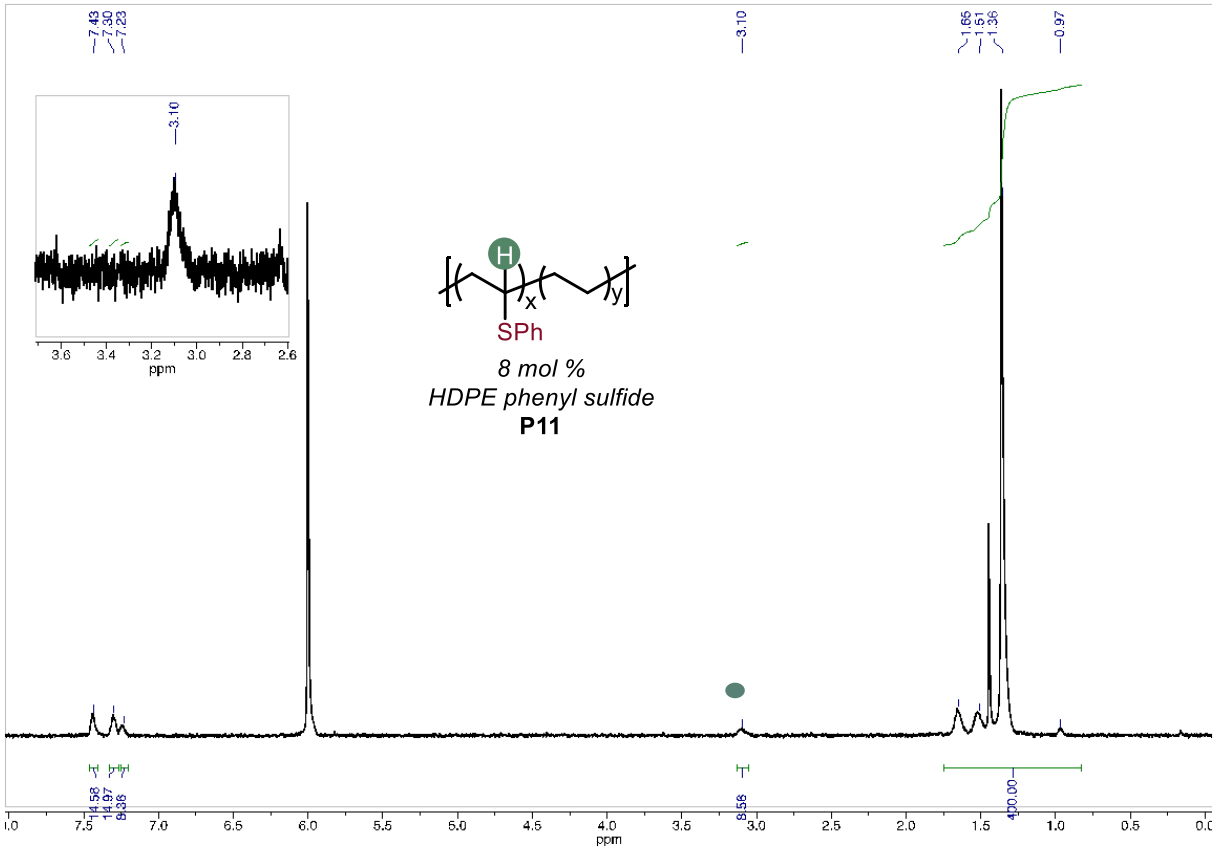
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



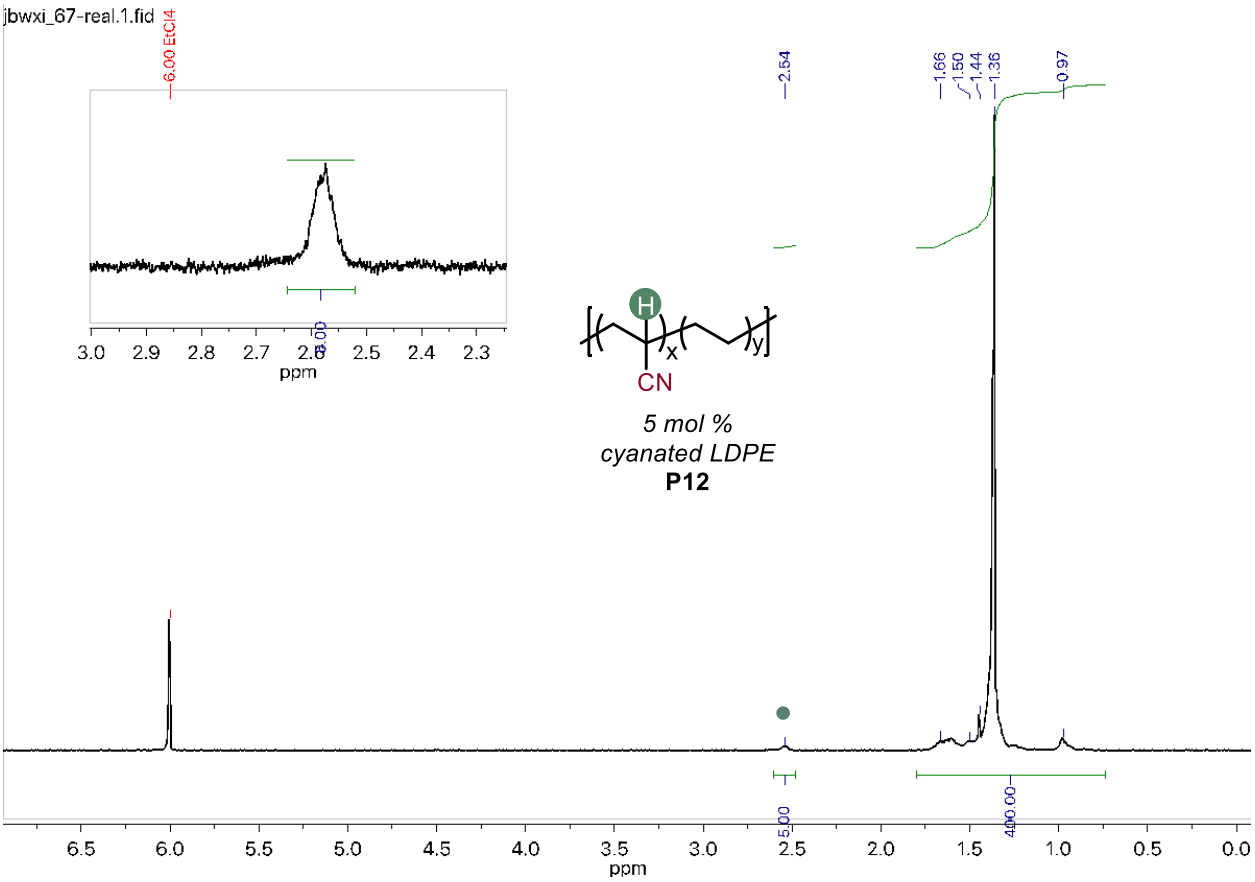
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



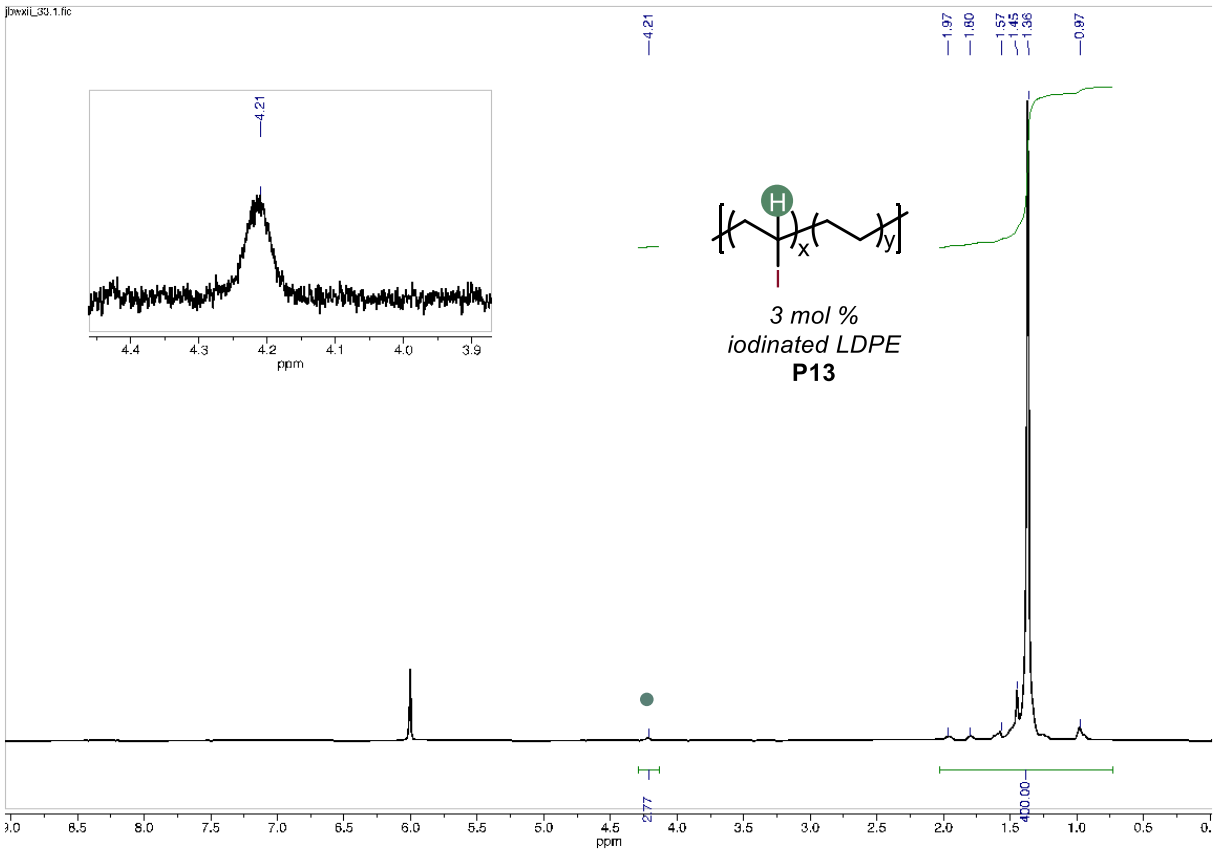
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



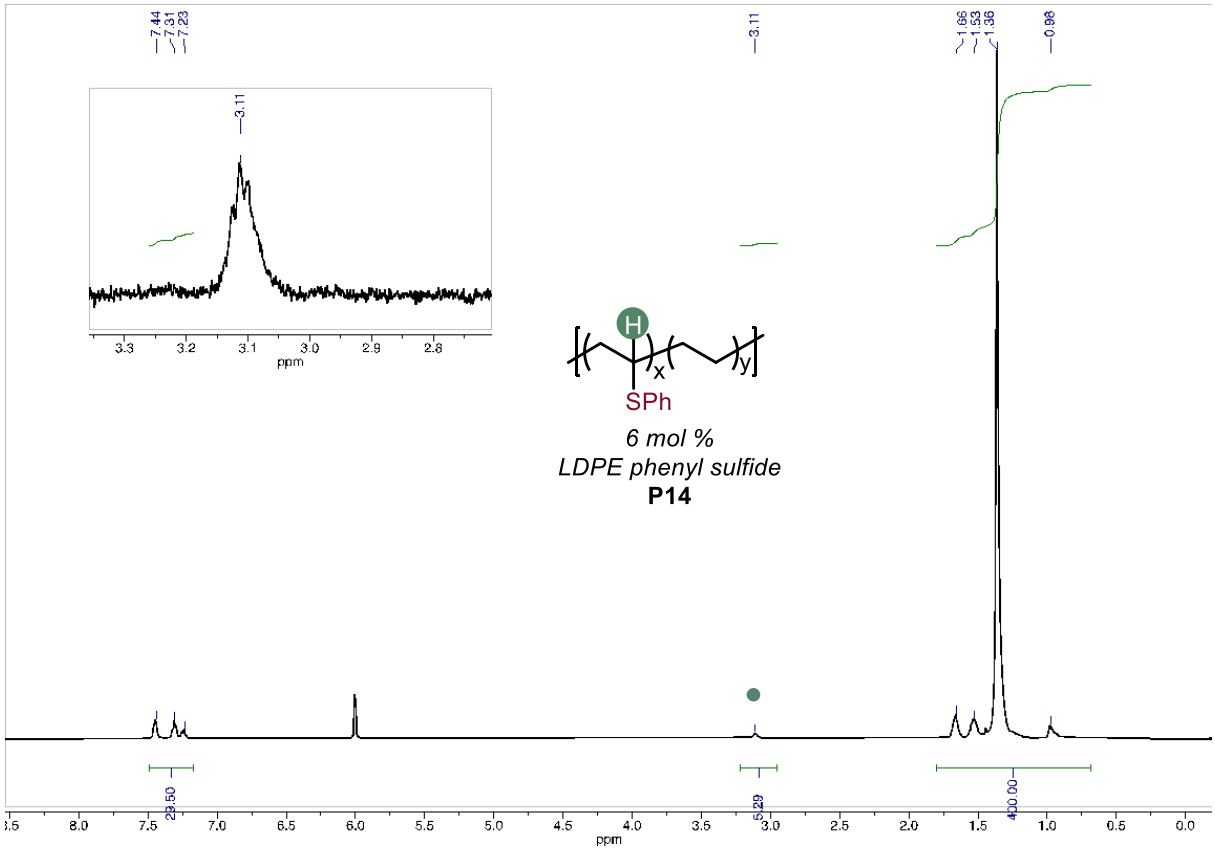
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



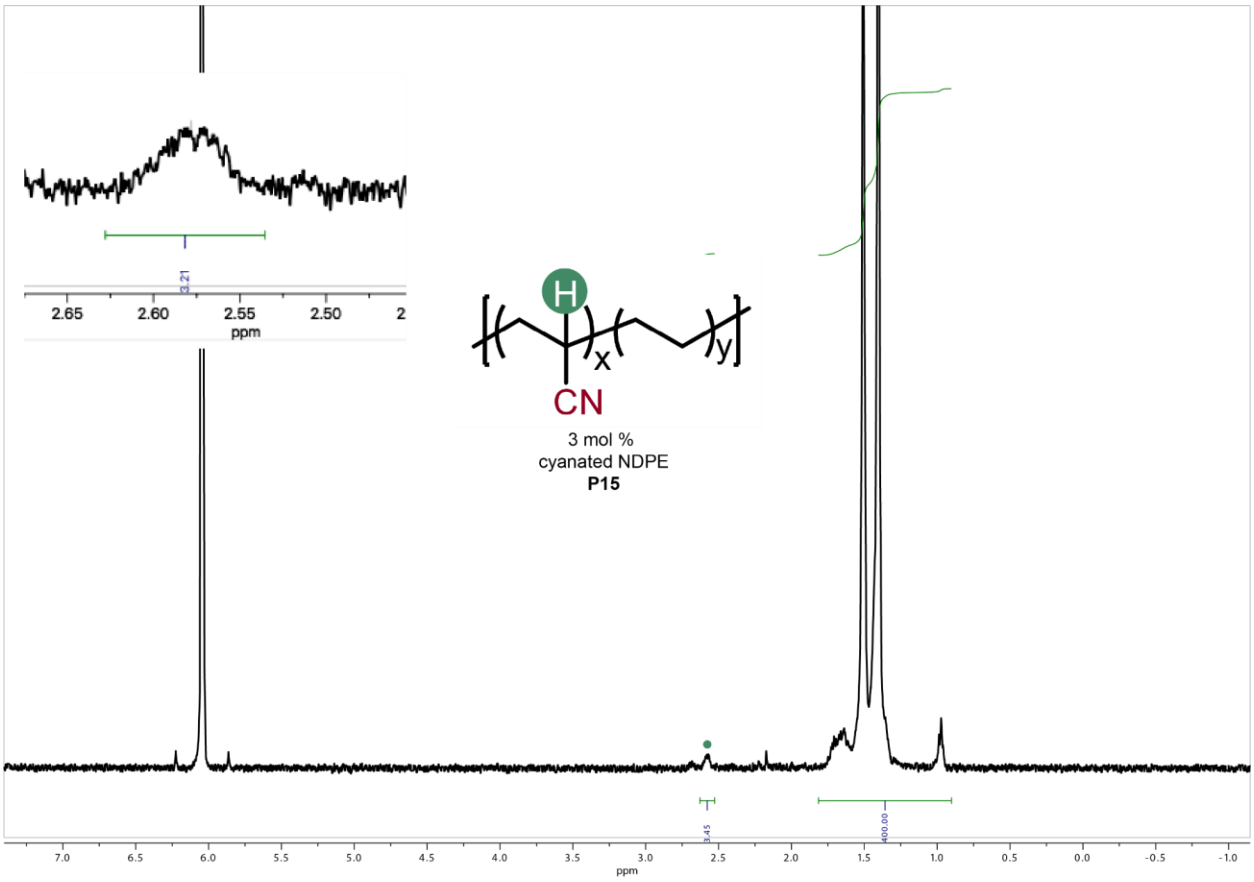
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



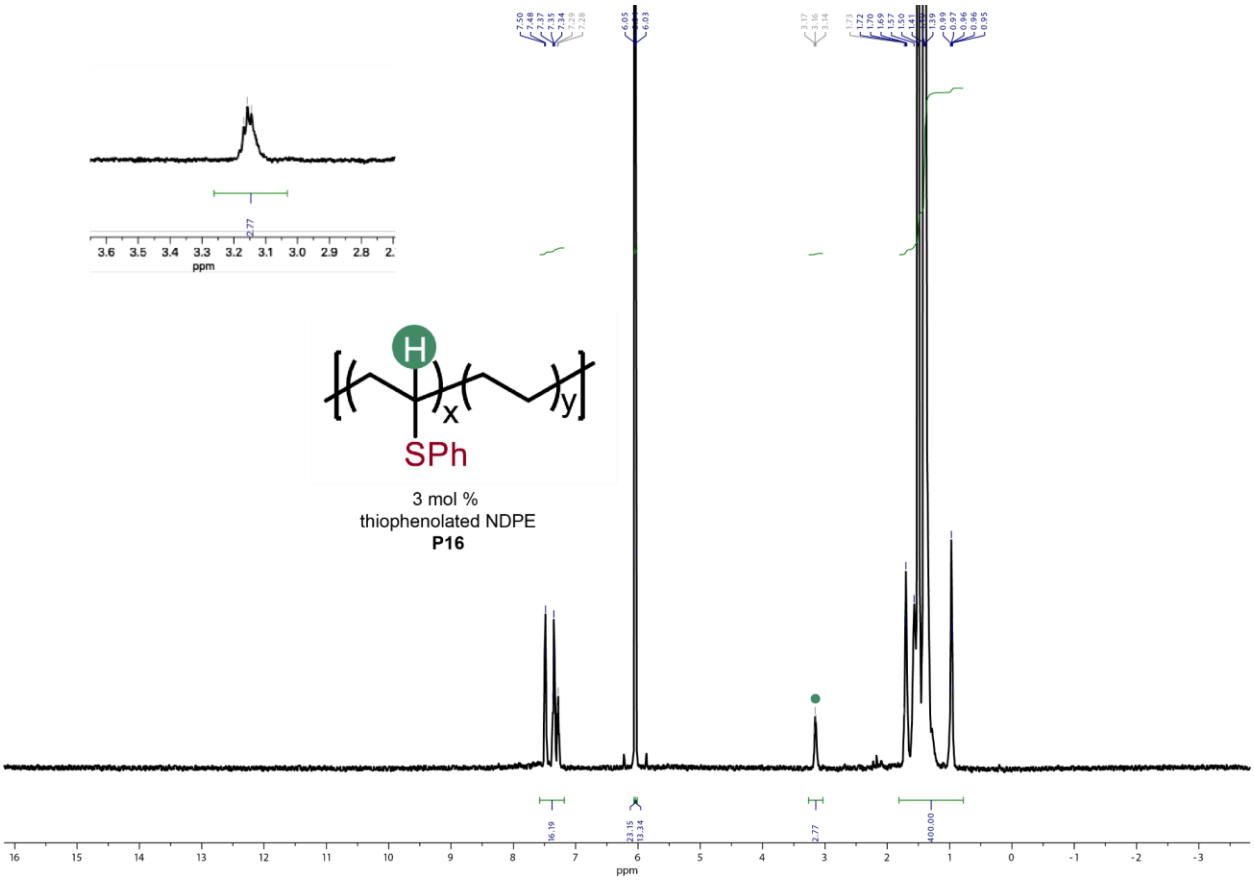
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



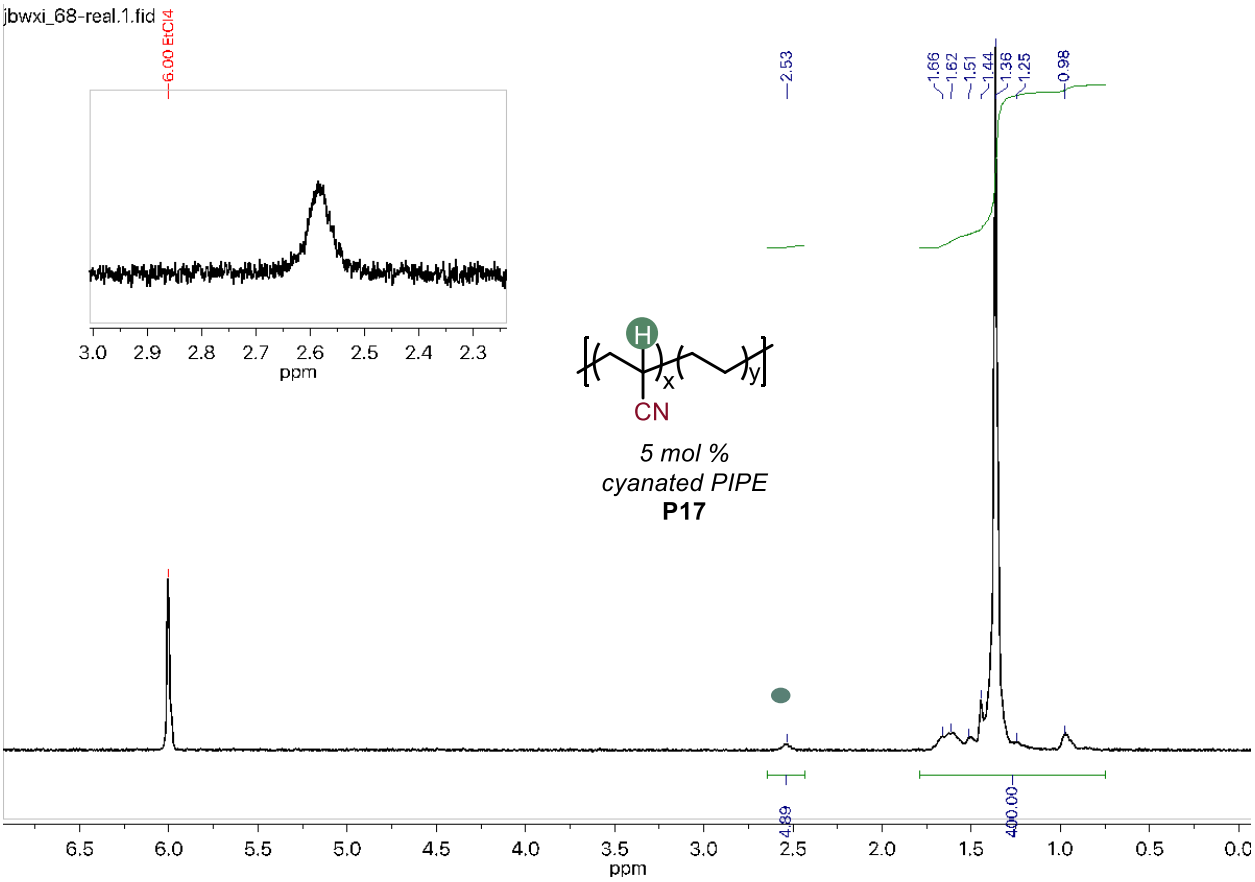
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



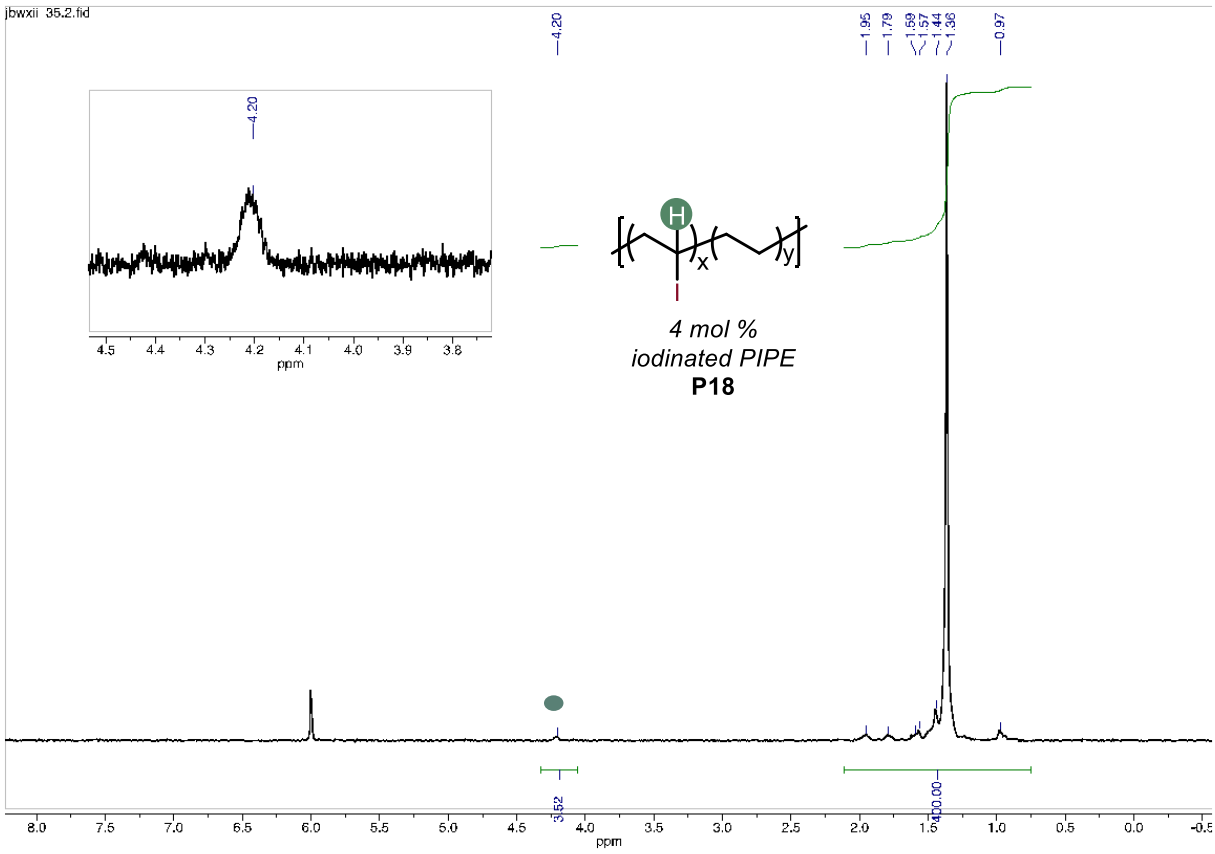
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



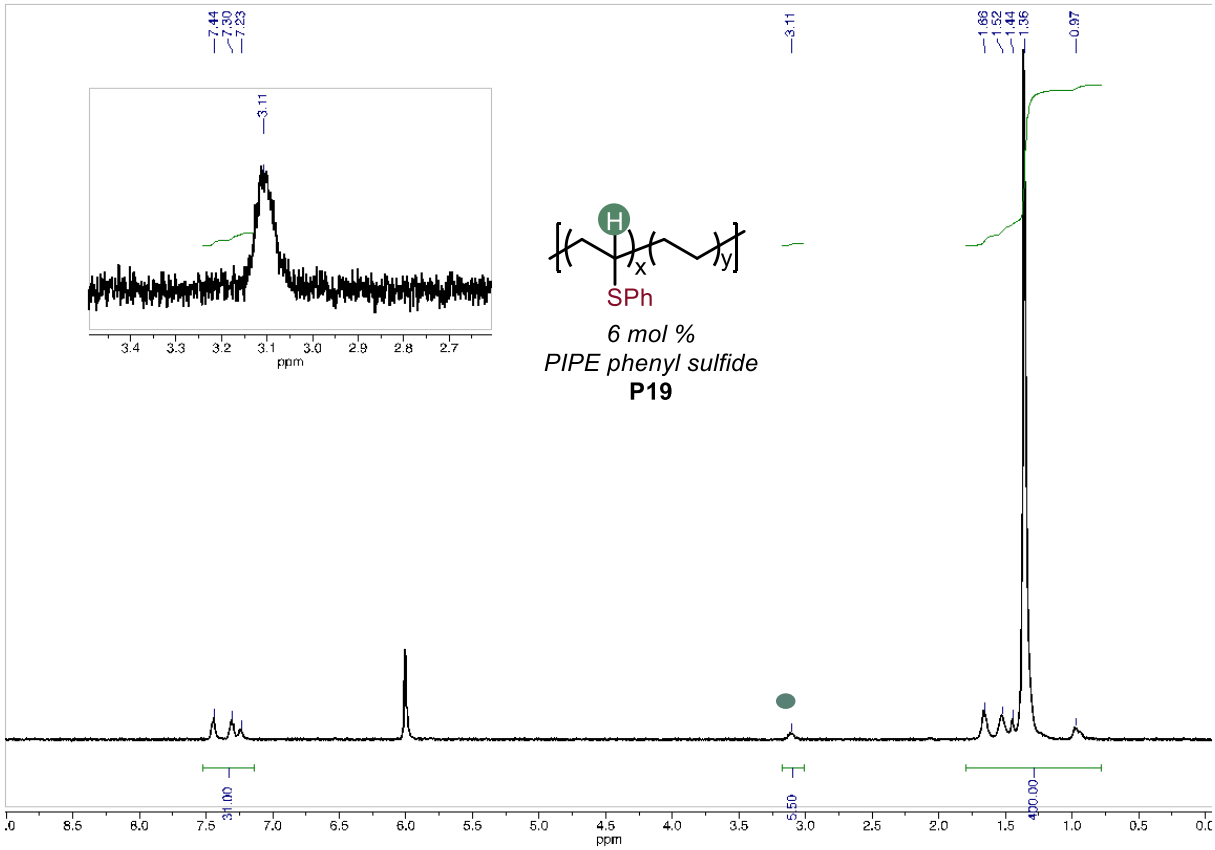
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



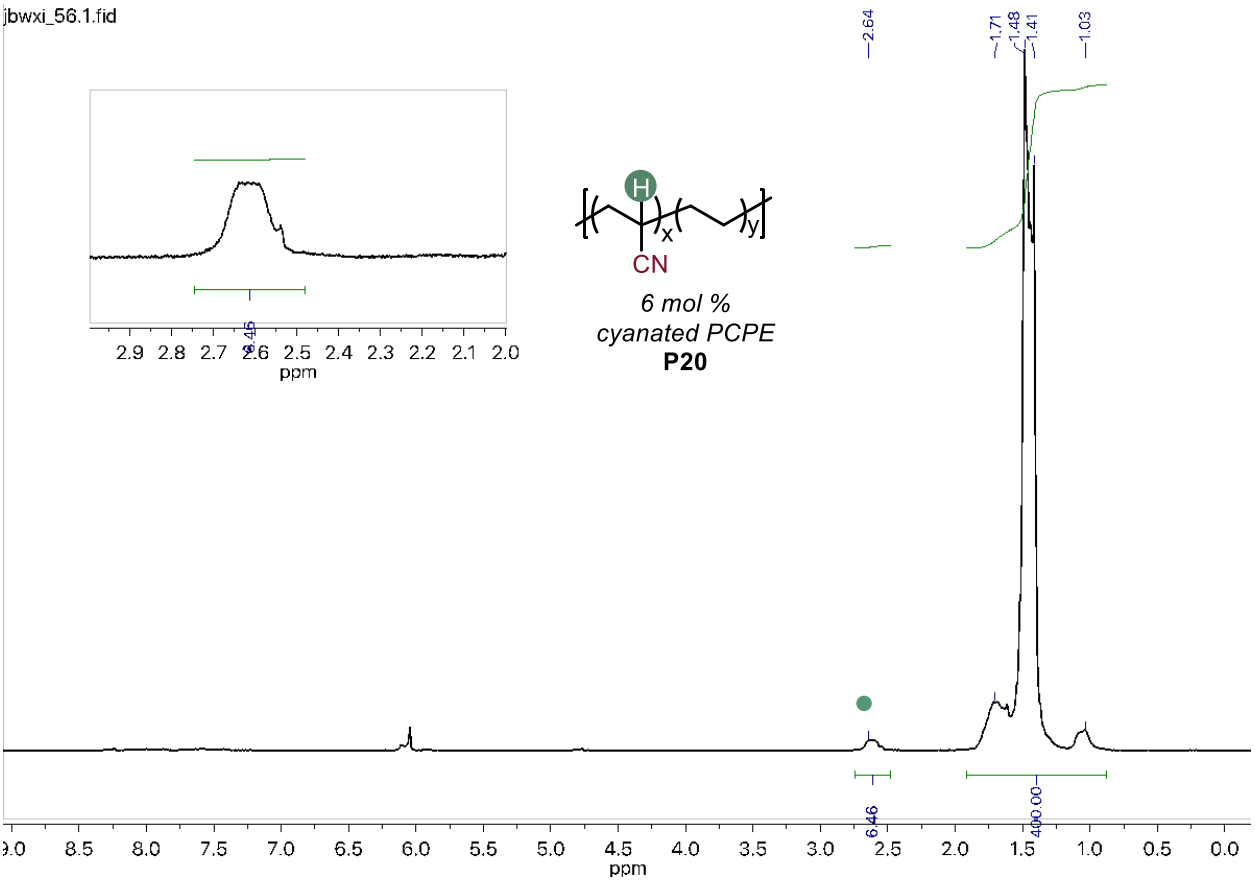
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



Referenced to $C_2D_2Cl_4$ at 6.00 ppm

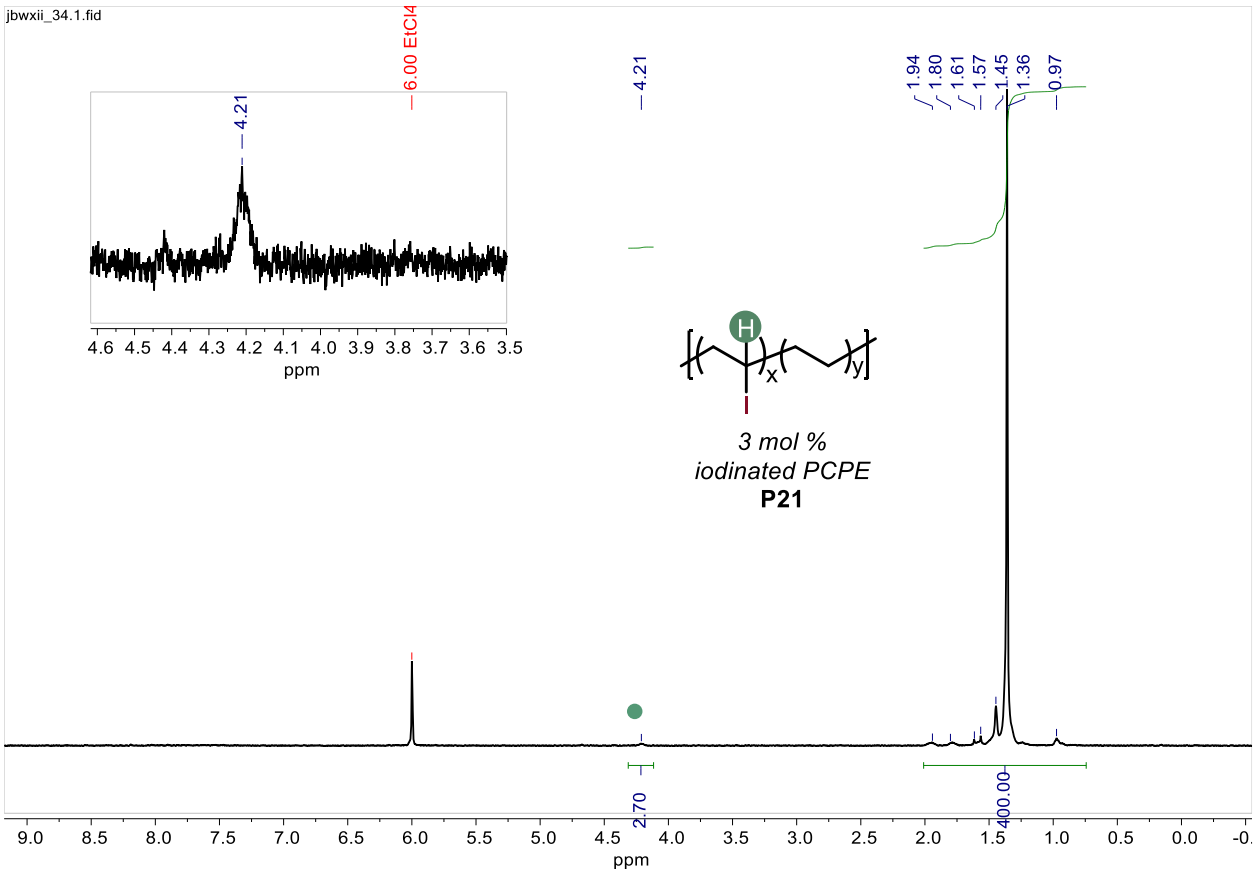


Referenced to $C_2D_2Cl_4$ at 6.00 ppm

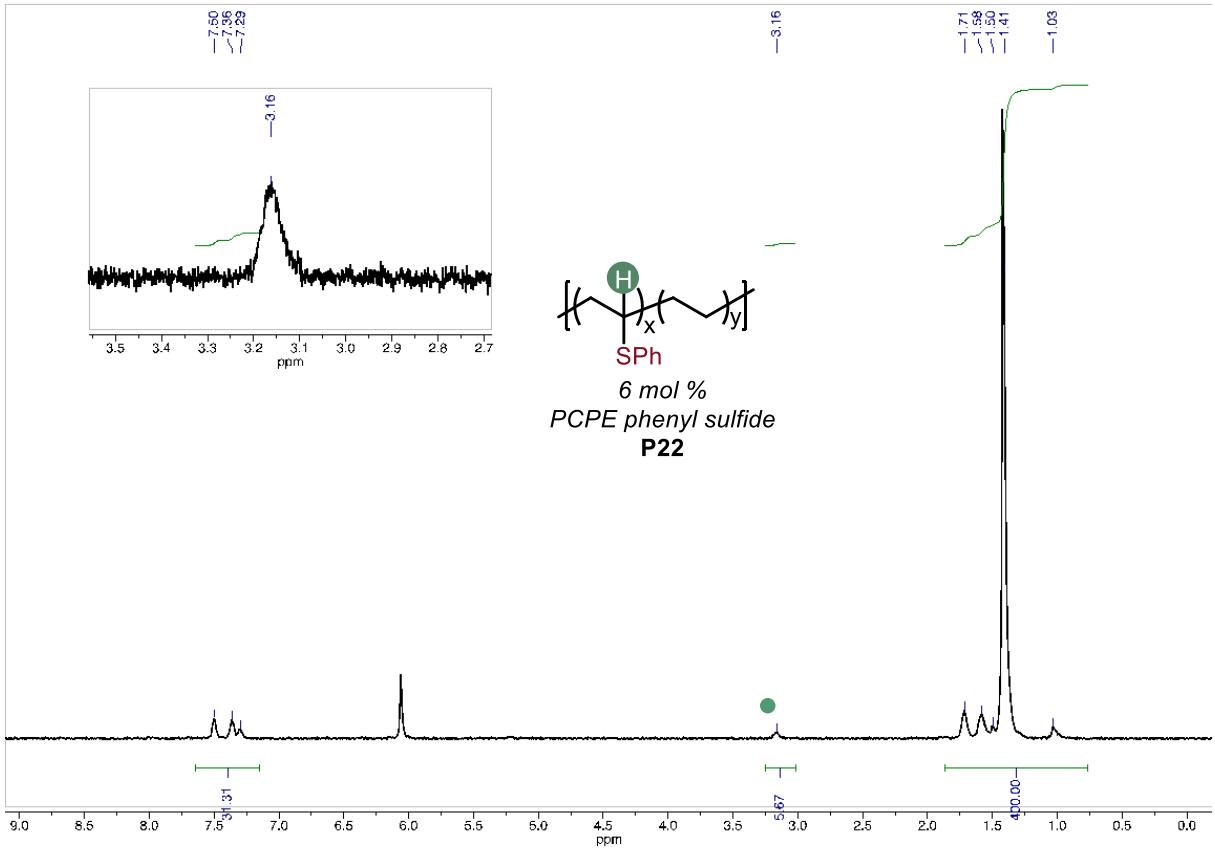


Note: post-consumer native impurities present (peaks in aromatic region, 6.2 ppm)

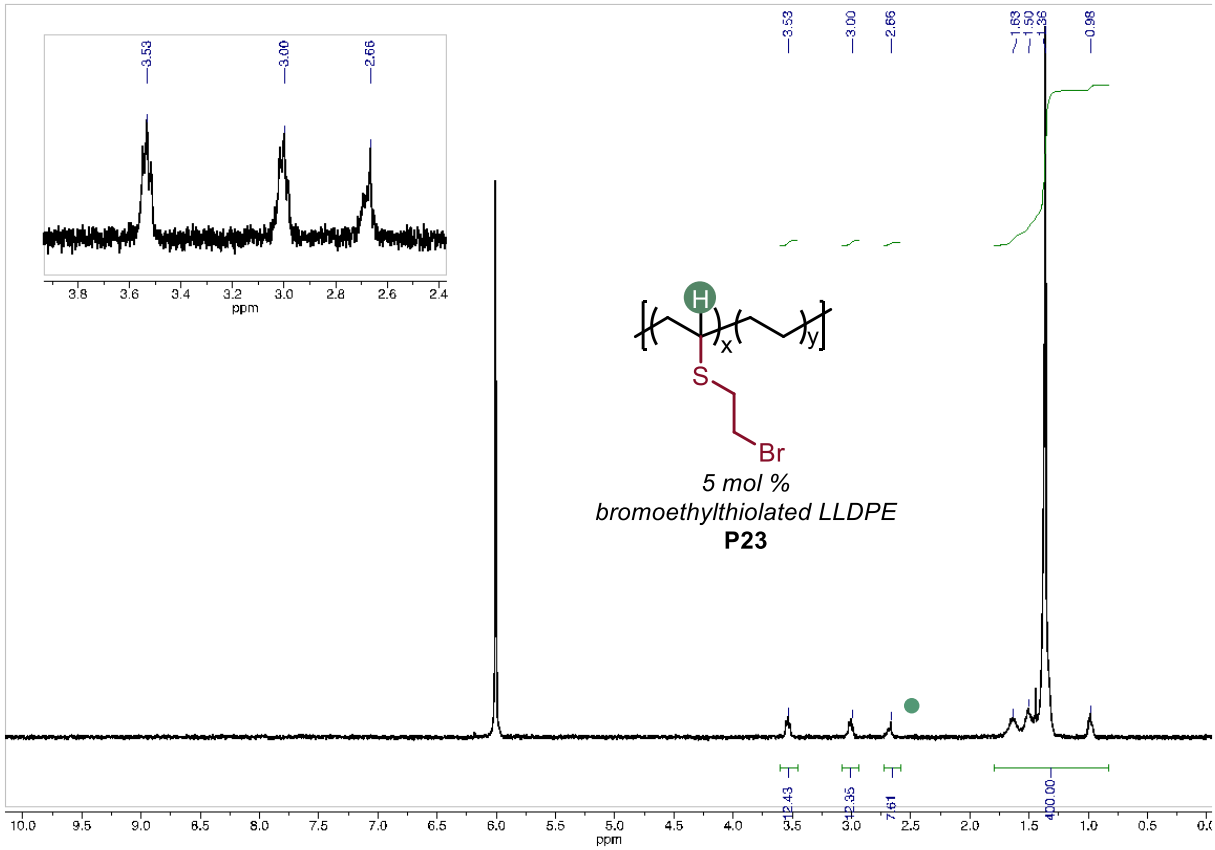
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



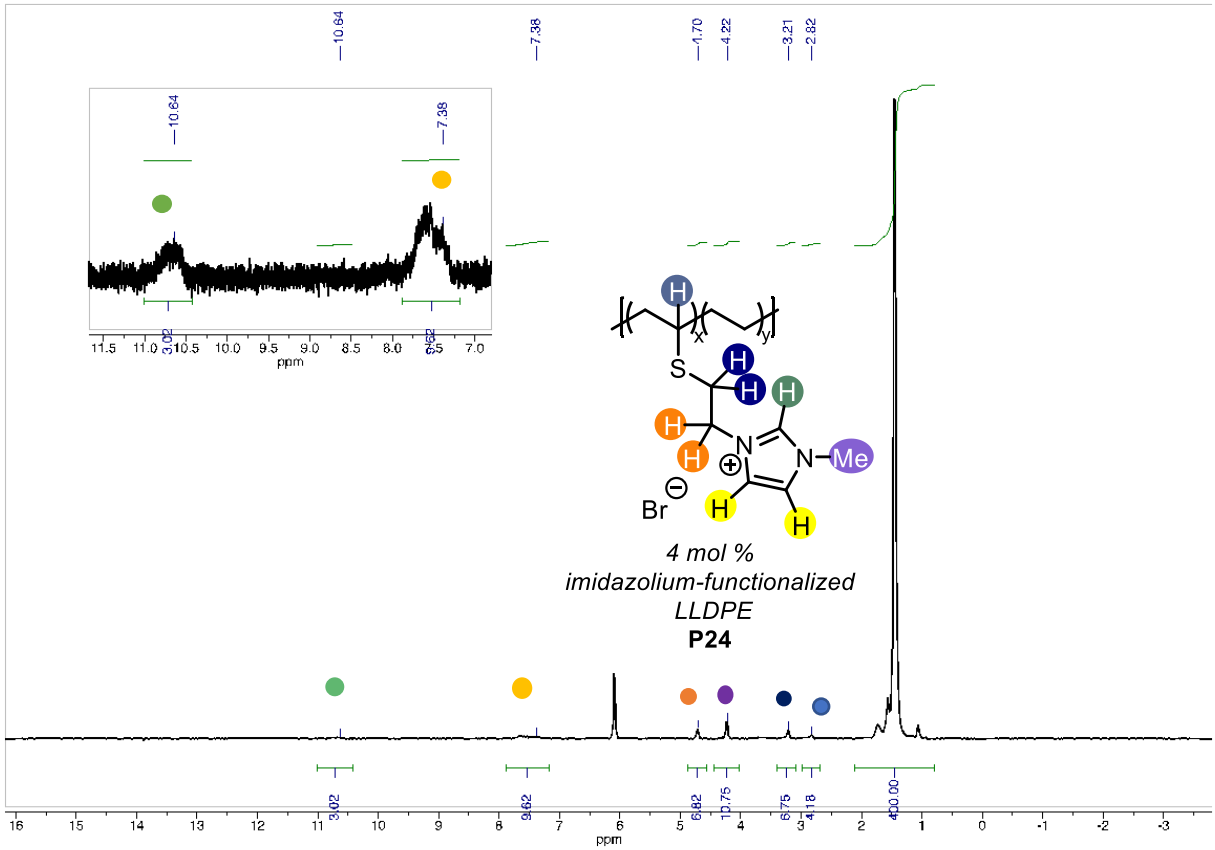
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



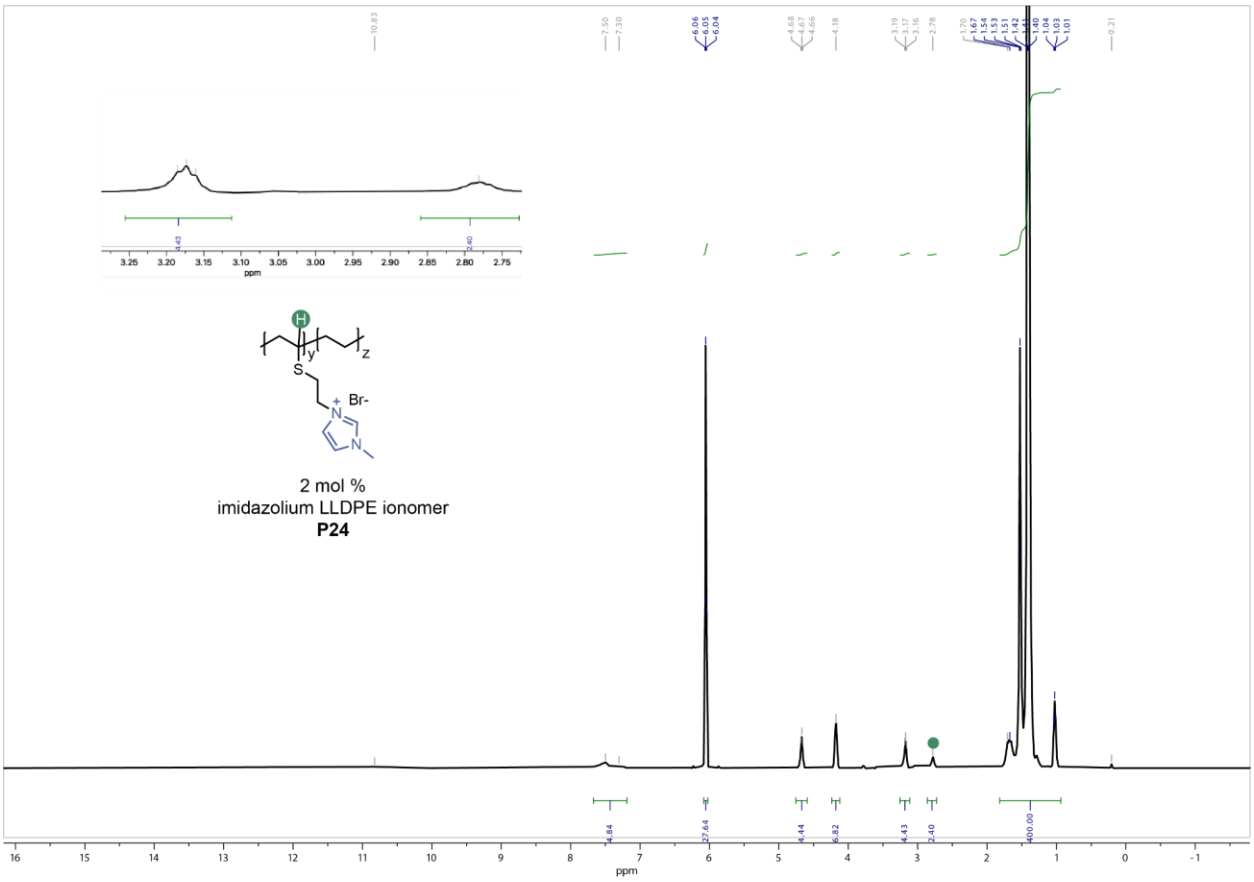
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



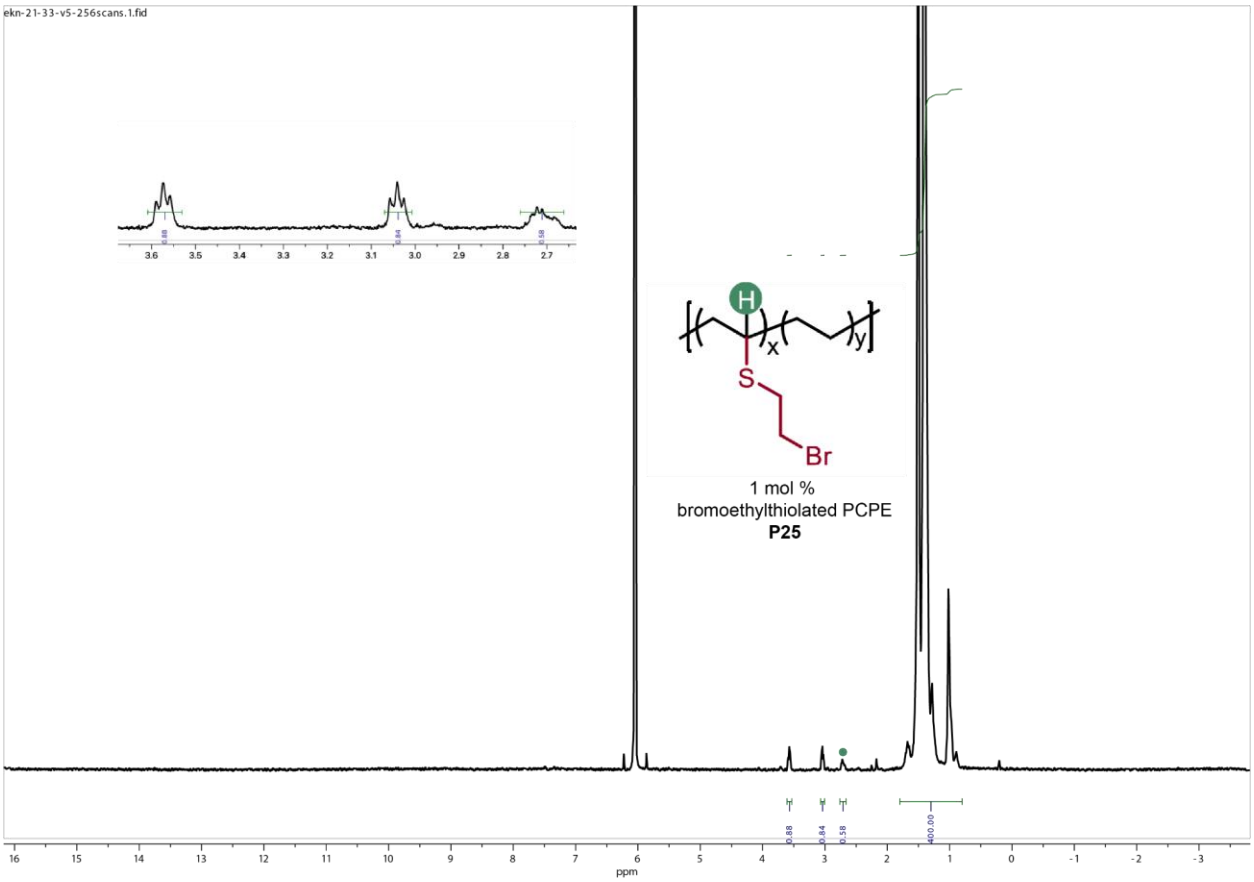
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



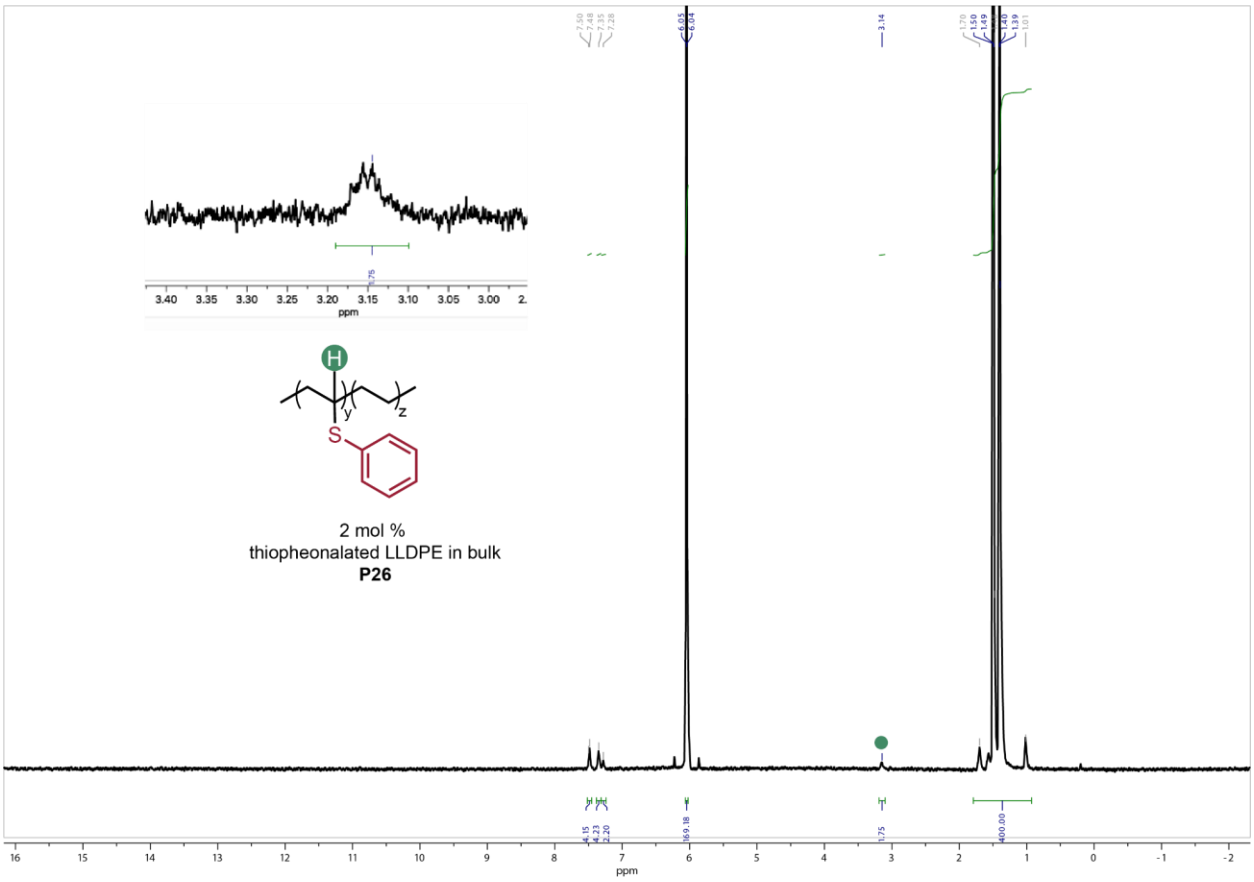
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



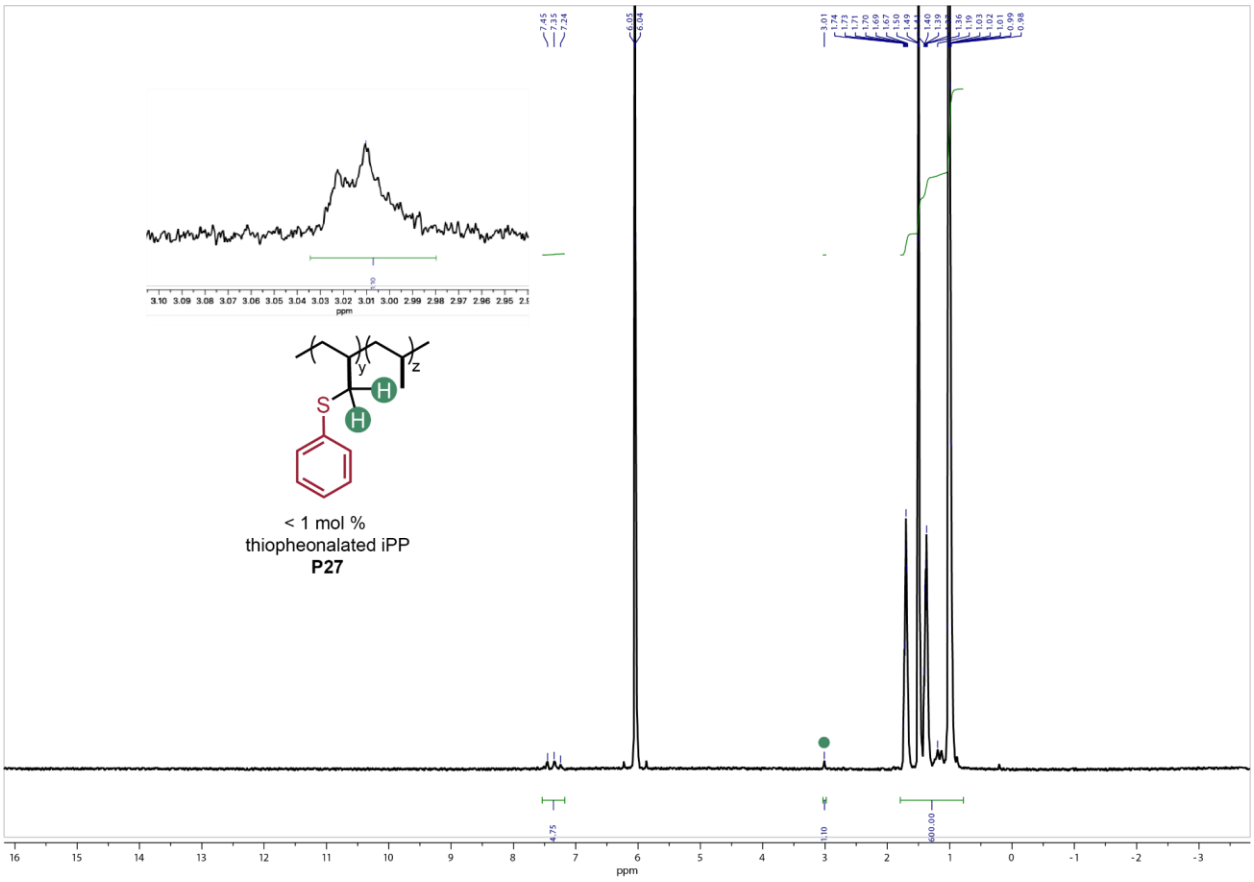
Referenced to $C_2D_2Cl_4$ at 6.00 ppm



Referenced to $C_2D_2Cl_4$ at 6.00 ppm



Referenced to $C_2D_2Cl_4$ at 6.00 ppm



Referenced to $C_2D_2Cl_4$ at 6.00 ppm

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