Electronic Supplementary Information

for

Photoredox Diels–Alder Ladder Polymerization

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I. General Information

General Procedures. Unless otherwise noted, reactions were performed under N_2 atmosphere in oven-dried (150 ºC) glassware. Reaction progress was monitored by thin layer chromatography (Merck silica gel 60 F_{254} plates) or by either liquid chromatography-mass spectrometry using an Agilent 6120 Quadrupole LC/MS or gas-chromatography mass-spectrometry using an Agilent GCMSD-Headspace. TLC plates were visualized using mainly UV-light (254 nm) fluorescence quenching, potassium permanganate stain, ceric ammonium molybdate followed by heat. Automated column chromatography was performed using SiliCycle SiliaFlash F60 (40-63 μm, 60 Å) in SNAP cartridges on a Biotage Isolera One. Organic solvents were removed *in vacuo* using a rotary evaporator (Büchi Rotovapor R-100, ~20–300 torr) and residual solvent was removed under high vacuum (<200 mtorr).

Materials and Methods. Commercial reagents were purchased from Sigma-Aldrich, Acros, Alfa Aesar, TCI, or Oakwood and used as received. All solvents were purified and dried using a solvent-purification system that contained activated alumina. Additionally, THF used for glovebox experiments was degassed by 3 freeze-pump-thaw cycles before being stored in a nitrogen-filled glove box over activated 3Å sieves.

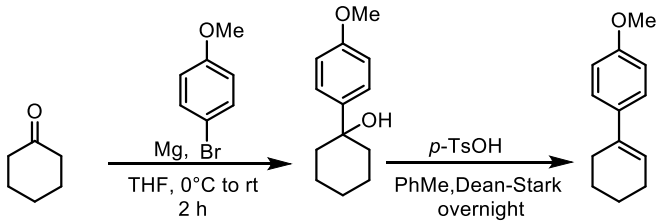
Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker AVANCE-500 spectrometers at 500 MHz and 125 MHz, and referenced to the solvent residual peaks. ^{19}F NMR spectra were recorded on Bruker AVANCE-500 spectrometers at 470 MHz. NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz) and integration. Blue LED strip lights (wavelength = 470 nm, power = 6.6 W) and green LED strip lights (wavelength = 525 nm, low power = 5.7 W, high power = 16 W) were purchased from superbrightleds.com. Gel permeation chromatography (GPC) measurements were performed in stabilized, HPLC-grade tetrahydrofuran using one of two instruments. For relative molecular weight determination, the GPC instrument is an Agilent 1260 Infinity II system with variable-wavelength diode array (254, 400, 480, 530, and 890 nm) and refractive index detectors, guard column (Agilent PLgel; 5μm; 50 x 7.5 mm), and three analytical columns (Agilent PLgel; 5μm; 300 x 7.5 mm; 105 , 104 , and 103 Å pore sizes). The instrument was calibrated with narrow dispersity polystyrene standards between 640 g/mol and 2300 kg/mol (Polymer Standards Service GmbH). All runs were performed at 1.0 mL/min flow rate and 40 ºC. Molecular weight values are calculated based on the refractive index signal. For absolute molecular weight determination, the GPC instrument used in this report was an Agilent Infinity II series system running tetrahydrofuran as the mobile phase and two PolyPore 300 × 7.5 mm columns (Varian p/n 5M-POLY-008-112). The instrument is equipped with 18-angle DAWN HELEOS II multiangle light scattering (MALS) detector, a ViscoStar II viscometer, and a Optilab T-rEX differential refractive index detector (Wyatt). All runs were performed at 1.0 mL/min flow rate and at 27 ºC. When the MALS detector was used, dn/dc values were determined experimentally using mass-recovery. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed on Bruker rapiflex MALDI-TOF Tissue typer in reflector positive mode. Samples were prepared by preparing solutions of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, 10 mg/mL) in THF, silver nitrate (5mg/mL) in deionized water, and sample (1 mg/mL) in THF. Approximately 2.5 μL of silver nitrate, polymer solution, and matrix were spotted on the MALDI chip and dried, respectively. The sample/additive/matrix ratios were varied to achieve good signal to noise. The glove box in which specified procedures were carried out was an MBraun Unilab Pro with N_2 atmosphere. N_2 and CO_2 isotherms were obtained at 77 K and 195 K on a micromeritics Tristar 3020 and ASAP 2020, respectively, after further activation at 100 ºC under vacuum. Differential scanning calorimetry was performed on a TA DSC 250 at 10 ºC/min with 50.0 mL/min flow of N_2.

Cyclic Voltammetry. All cyclic voltammetry experiments were conducted in a nitrogen-filled glovebox using acetonitrile with 0.1 M tetrabutylamonnium hexafluorophosphate electrolyte. Ferrocene was added as an internal standard following every run. Due to irreversibility of most of the measured redox events, potentials

are reported as half-peak potentials determined by finding the potential at which the measured current reaches the average of the maximum and pre-onset currents of a peak. These values were referenced to the half-wave potential of ferrocene.

II. Synthesis of initiator and monomers

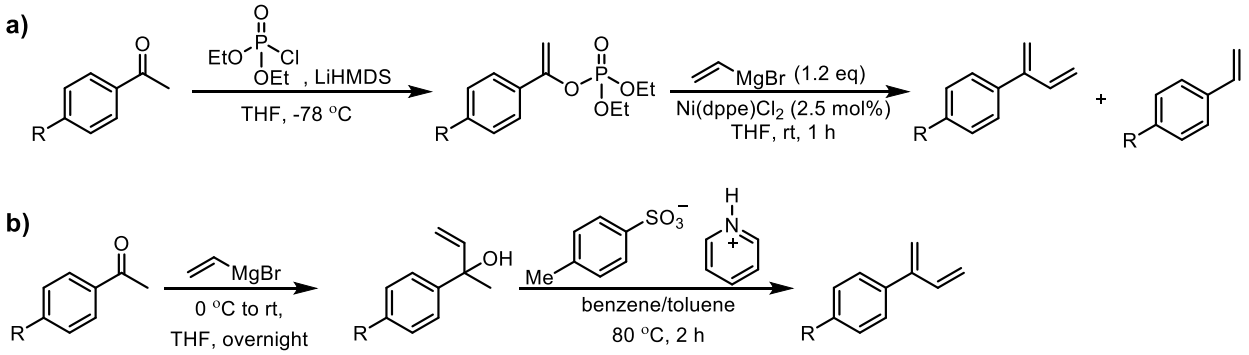
Scheme S1. Synthesis of cyclohexene initiator[1]



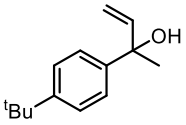
R=OMe. To a 100mL three-necked round bottom flask, magnesium (1.07 g, 1.1 equivalents, 44.0 mmol) was added followed by dry THF (10 mL) and 0.4 mL of 1-bromo-4-methoxybenzene was added. The solution was heated to reflux with a heat gun under nitrogen. The remaining 1-bromo-4-methoxybenzene (7.9 g, 5.3 mL total, 1.1 equivalents 42.0 mmol) was added in 30 mL of dry THF and heated to reflux with an oil bath. After one hour, the flask was cooled to 0 °C and cyclohexanone (3.9 g, 4.1 mL, 40 mmol) in 20 mL of dry THF was added dropwise via addition funnel. The solution was refluxed for one hour. After reflux, the solution was cooled to 0 °C and quenched by adding 6 M HCl dropwise (approximately 60 mL). The mixture was extracted with ethyl acetate (100 mL), washed with brine (40 mL) and dried with sodium sulfate. The organic layer was concentrated *in vacuo* and the crude product (dark amber oil) was immediately carried forward to the subsequent elimination step. The oil was dissolved in 40 mL of dry toluene in a 100-mL round-bottom flask. To this flask, *p*-toluenesulfonic acid monohydrate (0.76g, 4.0 mmol, 0.1 eq) was added and the solution was refluxed under a Dean-Stark trap under nitrogen overnight. The reaction was quenched at room temperature with 1 M NaOH (50 mL) and extracted with diethyl ether. The organic layer was dried over sodium sulfate and concentrated *in vacuo* with additional toluene removed via distillation. The crude oil was purified by column chromatography (100% pentane) to yield 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (1.2 g, 16%) as a clear oil. Characterization of this material matched literature reports.[1]
^{1}H NMR: (500 MHz, $CDCl_3$-d_3) δ 7.31 dd (J = 8.8, 2.1 Hz, 2H), 6.85 (dd, J = 8.8, 2.0 Hz, 2H), 6.04-6.02 (m, 1H), 3.81 (s, 3 H), 2.40-2.36 (m, 2 H), 2.21-2.17, (m, 2H), 1.79-1.75 (m, 2 H), 1.68-1.63 (m, 2H).
LRMS: m/z expected for $C_{13}H_{17}O$ $[M+H]^+$ 188.1, measured 188.2

We sought to synthesize aryl dienes through a synthetic route originally reported by Mazet and coworkers (**Scheme S2a**).[2] However, we found that while we synthesized the diene in moderate yields, we often also obtained the styrene product, most likely due to a hydrate addition that can happen during Grignard addition reactions.[3] This styrene product was very challenging to separate from the diene *via* column chromatography, so we chose to synthesize many dienes through a Grignard addition-elimination pathway (**Scheme S2b**).[4] In this way, any carbonyl reduction product could be more easily separated from the Grignard addition product via column chromatography before proceeding to the elimination step.

Scheme S2. Synthetic routes for diene monomers



2-(4-(tert-butyl)phenyl)but-3-en-2-ol

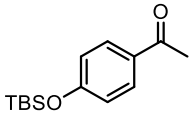


A solution of vinyl magnesium bromide (1.0 M in THF, 41 mL, 41 mmol, 1.8 equiv) was cooled to 0°C and a solution of 1-(4-(tert-butyl)phenyl)ethan-1-one (4.1 g, 4.2 mL, 23 mmol, 1 equiv) in 36 mL of diethyl ether was added dropwise under nitrogen. The reaction was stirred at room temperature overnight and quenched with saturated ammonium chloride (80 mL). The product was extracted with ether (50 mL), and washed with brine. The organic layer was dried with sodium sulfate and concentrated *in vacuo*. The crude oil was purified by column chromatography (10-30% ethyl acetate in hexanes) to yield 2-(4-(tert-butyl)phenyl)but-3-en-2-ol (1.3 g, 27%) as a yellow oil.

^{1}H NMR: (500 MHz, $CDCl_3$-d_3) δ 7.44 – 7.33 (m, 4H), 6.18 (dd, J = 17.3, 10.6 Hz, 1H), 5.31 (dd, J = 17.3, 1.1 Hz, 1H), 5.14 (dd, J = 10.6, 1.1 Hz, 1H), 1.86 (s, 1H), 1.66 (s, 3H), 1.32 (s, 10H).

^{13}C NMR: (126 MHz, CDCl3) δ 149.95, 145.09, 143.56, 125.25, 125.00, 112.11, 74.67, 34.52, 31.47, 29.49.

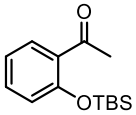
1-(4-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one



Under nitrogen atmosphere, to a solution of 4-hydroxyacetophenone (5.0 g, 36.7 mmol) and imidazole (5.0 g, 36.7 mmol) in anhydrous dimethyl formamide (50 mL) was added chloro tert-butyldimethylsilane (TBSCl, 6.64 g, 44.1 mmol). The resulting solution was stirred for 24 h at room temperature. The reaction mixture was diluted with hexane/Et2O = 1/1 (200 mL), and organic layer was washed three times with H2O (100 mL) and once with brine (100 mL), dried over Na_2SO_4, filtered, and the filtrate was concentrated to give a colorless liquid, which crystallized on standing to yield 1-(4-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one as a colorless solid (9.23g, quantitative).

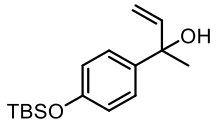
^{1}H NMR: (400 MHz, $CDCl_3$, δ): 7.86 (d, J = 6.9 Hz, Ar H-2, 6, 2H), 6.84 (d, J = 6.9 Hz, Ar H-3, 5, 2H), 2.53 (s, -$COCH_3$, 3H), 0.97 (s, -$SiC(CH_3)_3$, 9H), 0.22, (s, -$Si(CH_3)_2$, 6H)

1-(2-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one



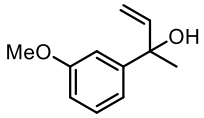
Under nitrogen atmosphere, to a solution of 1-(2-hydroxyphenyl)ethan-1-one (4.1 g, 3.6 mL, 30 mmol) and imidazole (4.9 g, 72 mmol, 2.4 equiv) in anhydrous dichloromethane (60 mL) was added chloro tert-butyldimethylsilane (TBSCl, 5.4 g, 36 mmol). The resulting solution was stirred for 24 h at room temperature. The organic layer was washed three times with H_2O (100 mL) and once with brine (100 mL), dried over Na_2SO_4, filtered, and the filtrate was concentrated to give a colorless liquid, which crystallized on standing to yield 1-(2-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one as a colorless solid (2.92 g, 39%).
^{1}H NMR: 1H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.33 (ddd, *J* = 8.2, 7.3, 1.9 Hz, 1H), 6.98 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.2, 1.0 Hz, 1H), 2.60 (s, 3H), 0.99 (s, 9H), 0.26 (s, 6H).

2-(4-((tert-butyldimethylsilyl)oxy)phenyl)but-3-en-2-ol



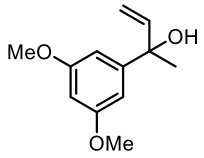
A solution of vinyl magnesium bromide (1.0 M in THF, 36 mL, 36 mmol, 1.8 equiv) was cooled to 0°C and a solution of 1-(4-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one (5.0 g, 20 mmol, 1 equiv) in 36 mL of diethyl ether was added dropwise under nitrogen. The reaction was stirred at room temperature overnight and quenched with saturated ammonium chloride (80 mL). The product was extracted with ether (50 mL) and washed with brine. The organic layer was dried with sodium sulfate and concentrated *in vacuo*. The crude oil was purified by column chromatography (10-30% ethyl acetate in hexanes) to yield 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)but-3-en-2-ol (2.1 g, 38%) as a pale yellow oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 6.83 – 6.77 (m, 2H), 6.15 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.20 (ddd, *J* = 78.7, 17.3, 1.0 Hz, 2H), 1.81 (s, 1H), 1.63 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H).

2-(3-methoxyphenyl)but-3-en-2-ol



A solution of vinyl magnesium bromide (1.0 M in THF, 39 mL, 39 mmol, 1.7 equiv) was cooled to 0°C and a solution of 1-(3-methoxyphenyl)ethan-1-one (3.5 g, 3.2 mL, 23 mmol, 1 equiv) in 36 mL of tetrahydrofuran was added dropwise under nitrogen. The reaction was stirred at room temperature overnight and quenched with saturated ammonium chloride (80 mL). The product was extracted with ether (50 mL) and washed with brine. The organic layer was dried with sodium sulfate and concentrated *in vacuo*. The crude oil was purified by column chromatography (10-30% ethyl acetate in hexanes) to yield 2-(3-methoxyphenyl)but-3-en-2-ol (1.6 g, 38%) as a yellow oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.30 – 7.22 (m, 2H), 7.09 – 6.99 (m, 1H), 6.80 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 6.16 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.31 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.15 (dd, *J* = 10.6, 1.1 Hz, 1H), 3.82 (s, 3H), 1.87 (s, 1H), 1.65 (s, 3H).

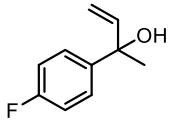
2-(3,5-dimethoxyphenyl)but-3-en-2-ol



A solution of vinyl magnesium bromide (1.0 M in THF, 17 mL, 15 mmol, 1.8 equiv) was cooled to 0°C and a solution of 1-(3,5-dimethoxyphenyl)ethan-1-one (1.5 g, 8.3 mmol, 1 equiv) in 17 mL of tetrahydrofuran was added dropwise under nitrogen. The reaction was stirred at room temperature overnight and quenched with

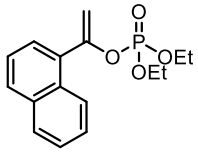
saturated ammonium chloride (80 mL). The product was extracted with ether (50 mL) and washed with brine. The organic layer was dried with sodium sulfate and concentrated *in vacuo*. The crude oil was purified by column chromatography (10-30% ethyl acetate in hexanes) to yield 2-(3,5-dimethoxyphenyl)but-3-en-2-ol (1.6 g, 92%) as a yellow oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 6.63 (d, *J* = 2.3 Hz, 2H), 6.36 (t, *J* = 2.3 Hz, 1H), 6.14 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.31 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.14 (dd, *J* = 10.6, 1.1 Hz, 1H), 3.80 (s, 6H), 1.87 (s, 1H), 1.63 (s, 3H).

2-(4-fluorophenyl)but-3-en-2-ol



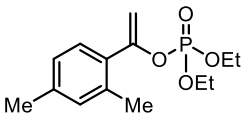
A solution of vinyl magnesium bromide (0.7 M in THF, 59 mL, 42 mmol, 1.8 equiv) was cooled to 0°C and a solution of 1-(4-fluorophenyl)ethan-1-one (3.2 g, 2.8 mL, 23 mmol, 1 equiv) in 36 mL of tetrahydrofuran was added dropwise under nitrogen. The reaction was stirred at room temperature overnight and quenched with saturated ammonium chloride (80 mL). The product was extracted with ether (50 mL) and washed with brine. The organic layer was dried with sodium sulfate and concentrated *in vacuo*. The crude oil was purified by column chromatography (10-30% ethyl acetate in hexanes) to yield 2-(4-fluorophenyl)but-3-en-2-ol (1.6 g, 43%) as a pale yellow oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.05 – 6.97 (m, 2H), 6.14 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.22 (ddd, *J* = 68.8, 17.4, 0.6 Hz, 2H), 1.89 (s, 1H), 1.64 (s, 3H).
^{19}F NMR: (470 MHz, $CDCl_3$-d_3) δ -116.24 (tt, *J* = 8.7, 5.5 Hz).

diethyl (1-(naphthalen-1-yl)vinyl) phosphate



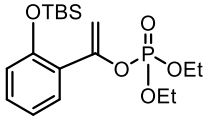
To a stirred solution of 1-(naphthalen-1-yl)ethan-1-one (2.47 g, 14.5 mmol, 1.0 equiv.) in anhydrous THF (45.0 mL, 0.2 M overall concentration) at –78 ºC and under an inert atmosphere of nitrogen, LiHMDS (18.9 mL of 1 M solution in THF/ethylbenzene, 18.9 mmol, 1.3 equiv.) was added dropwise. After 30 min, diethyl chlorophosphate (3.15 mL, 21.8 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred at –78 °C 2 hours. The reaction mixture was warmed up to room temperature for 10 hours, quenched with saturated ammonium chloride solution and then extracted with ethyl acetate (3 x 100 mL). The combined organics were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (20 – 50% ethyl acetate in hexanes) affording pure diethyl (1-(naphthalen-1-yl)vinyl) phosphate (4.18 g, 94%) as an orange oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.24 (dq, *J* = 8.7, 0.9 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.60 (dd, *J* = 7.1, 1.3 Hz, 1H), 7.51 (dddd, *J* = 18.0, 8.1, 6.8, 1.4 Hz, 2H), 7.45 (dd, *J* = 8.3, 7.0 Hz, 1H), 5.49 (t, *J* = 2.1 Hz, 1H), 5.06 (t, *J* = 2.1 Hz, 1H), 4.10 – 3.96 (m, 4H), 1.21 (td, *J* = 7.1, 1.1 Hz, 6H).
^{31}P NMR: (202 MHz, $CDCl_3$) δ -6.78 (p, *J* = 7.9 Hz).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 152.94, 152.87, 133.65, 133.60, 133.56, 130.97, 129.78, 128.39, 127.38, 126.68, 126.16, 125.73, 125.13, 103.20, 103.17, 64.48, 64.43, 16.07, 16.02.

1-(2,4-dimethylphenyl)vinyl diethyl phosphate



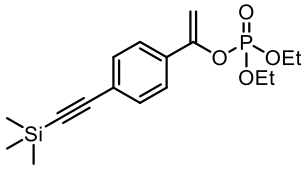
To a stirred solution 1-(2,4-dimethylphenyl)ethan-1-one (2.15 g, 2.16 mL, 14.5 mmol, 1.0 equiv.) in anhydrous THF (45.0 mL, 0.2 M overall concentration) at –78 ºC and under an inert atmosphere of nitrogen, LiHMDS (18.9 mL of 1 M solution in THF/ethylbenzene, 18.9 mmol, 1.3 equiv.) was added dropwise. After 30 min, diethyl chlorophosphate (3.15 mL, 21.8 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred at -78 °C 2 hours. The reaction mixture was warmed up to room temperature for 10 hours, quenched with saturated ammonium chloride solution and then extracted with ethyl acetate (3 x 100 mL). The combined organics were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (30 – 60% ethyl acetate in hexanes) affording pure 1-(2,4-dimethylphenyl)vinyl diethyl phosphate (4.04 g, 98%) as an amber oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 1H), 7.01 – 6.96 (m, 2H), 5.27 (t, *J* = 2.1 Hz, 1H), 4.80 (t, *J* = 2.1 Hz, 1H), 4.18 – 4.01 (m, 4H), 2.38 (s, 3H), 2.31 (s, 3H), 1.32 – 1.24 (m, 9H).
^{31}P NMR: (202 MHz, $CDCl_3$) δ -6.79 (p, *J* = 8.1 Hz).

1-(2-((tert-butyldimethylsilyl)oxy)phenyl)vinyl diethyl phosphate



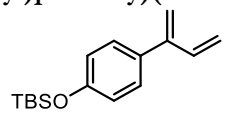
To a stirred solution 1-(2-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one (2.91 g, 11.6 mmol, 1.0 equiv.) in anhydrous THF (45.0 mL, 0.17 M overall concentration) at –78 ºC and under an inert atmosphere of nitrogen, LiHMDS (15.1 mL of 1 M solution in THF/ethylbenzene, 15.1 mmol, 1.3 equiv.) was added dropwise. After 30 min, diethyl chlorophosphate (3.01 g, 2.53 mL, 17.4 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred at -78 °C 2 hours. The reaction mixture was warmed up to room temperature for 10 hours, quenched with saturated ammonium chloride solution and then extracted with ethyl acetate (3 x 100 mL). The combined organics were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (30 – 60% ethyl acetate in hexanes) affording pure 1-(2,4-dimethylphenyl)vinyl diethyl phosphate (2.6 g, 58%) as an amber oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.18 (ddd, *J* = 8.1, 7.3, 1.8 Hz, 1H), 6.94 (td, *J* = 7.6, 1.2 Hz, 1H), 6.83 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.35 (dt, *J* = 12.8, 2.1 Hz, 2H), 4.19 – 4.07 (m, 4H), 1.29 (td, *J* = 7.1, 1.1 Hz, 6H), 0.99 (s, 9H), 0.22 (s, 6H).
^{31}P NMR: (202 MHz, $CDCl_3$) δ -6.53 (p, *J* = 8.1 Hz).

diethyl (1-(4-((trimethylsilyl)ethynyl)phenyl)vinyl) phosphate



To a stirred solution 1-(4-((trimethylsilyl)ethynyl)phenyl)ethan-1-one (2.0 g, 9.2 mmol, 1.0 equiv.) in anhydrous THF (34.0 mL, 0.2 M overall concentration) at –78 ºC and under an inert atmosphere of nitrogen, LiHMDS (12 mL of 1 M solution in THF/ethylbenzene, 12 mmol, 1.3 equiv.) was added dropwise. After 30 min, diethyl chlorophosphate (2.4 g, 2.0 mL, 14 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred at -78 °C 2 hours. The reaction mixture was warmed up to room temperature for 10 hours, quenched with saturated ammonium chloride solution and then extracted with ethyl acetate (3 x 25 mL). The combined organics were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (30 – 60% ethyl acetate in hexanes) affording pure 1-(2,4-dimethylphenyl)vinyl diethyl phosphate (2.53 g, 78%) as an orange oil.
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.54 – 7.42 (m, 4H), 5.33 – 5.24 (m, 2H), 4.20 (dqt, *J* = 8.2, 7.1, 3.5 Hz, 4H), 1.34 (td, *J* = 7.1, 1.1 Hz, 6H), 0.25 (s, 9H).
^{31}P NMR: (202 MHz, $CDCl_3$) δ 31P NMR (162 MHz, CDCl3) δ -6.28 (s).

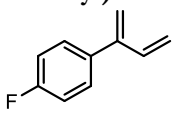
(4-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane



To a solution of 2 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)but-3-en-2-ol (1.6 g, 5.7 mmol, 1.0 equiv) in 40 mL of benzene, pyridinium p-toluenesulfonate (14 mg, 0.057 mmol, 0.01 equiv), dibutylhydroxytoluene (13 mg, 0.057 mmol, 0.01 equiv), and sodium sulfate (50 mg, 0.35 mmol, 0.061 equiv) were added. The reaction was stirred at reflux for overnight. After, the reaction was quenched with saturated sodium bicarbonate (60 mL), extracted with ethyl acetate (30 mL) and the organic layer was dried with sodium sulfate before being concentrated under reduced pressure. The crude product was redissolved in 60 mL of dichloromethane and imidazole (1.1 g, 16 mmol, 2.8 equiv) and stirred for 5 minutes. After, tert-butylchlorodimethylsilane (1.2 g, 8.0 mmol, 1.4 equiv) was added and the reaction was stirred at room temperature overnight under nitrogen. The resulting product was quenched with saturated ammonium chloride (60 mL) and washed with brine (75 mL) and water (75 mL). The organic layer was dried with sodium sulfate and concentrated *in vacuo*. The crude product was purified by flash column chromatography (100% hexanes) to afford (4-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane (1.07g, 72%) as a colorless oil which was stored at -20 ºC with 1 mol % BHT. The spectra of the compound match that of previous reports.[2]

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 6.86 – 6.78 (m, 2H), 6.61 (ddd, *J* = 17.4, 10.6, 0.8 Hz, 1H), 5.26 – 5.15 (m, 4H), 1.00 (s, 9H), 0.22 (s, 6H).

1-(buta-1,3-dien-2-yl)-4-fluorobenzene

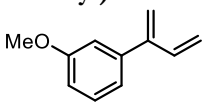


To a solution of 2-(4-fluorophenyl)but-3-en-2-ol (1.6 g, 9.6 mmol, 1.0 equiv) in 40 mL of benzene, pyridinium p-toluenesulfonate (24 mg, 0.096 mmol, 0.01 equiv), dibutylhydroxytoluene (21 mg, 0.096 mmol, 0.01 equiv), and sodium sulfate (50 mg, 0.32 mmol, 0.042) were added. The reaction was stirred at reflux for overnight. After, the reaction was quenched with saturated sodium bicarbonate (60 mL), extracted with ethyl acetate (30 mL) and the organic layer was dried with sodium sulfate before being concentrated under reduced pressure. The crude product was purified by flash column chromatography (100% hexanes) to afford 1-(buta-1,3-dien-2-yl)-4-fluorobenzene (617 mg, 43%) as a colorless oil which was stored at -20 ºC with 1 mol % BHT. The spectra of the compound match that of previous reports.[2]

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.07 – 7.00 (m, 2H), 6.61 (dd, *J* = 17.4, 10.7 Hz, 1H), 5.30 – 5.12 (m, 4H).

^{19}F NMR: (470 MHz, $CDCl_3$-d_3) δ -115.16 (ddd, *J* = 14.0, 9.7, 5.3 Hz).

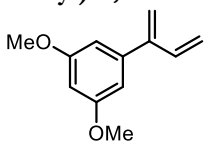
1-(buta-1,3-dien-2-yl)-3-methoxybenzene



To a solution of 2-(3-methoxyphenyl)but-3-en-2-ol (1.5 g, 8.4 mmol, 1.0 equiv) in 20 mL of benzene, pyridinium p-toluenesulfonate (21 mg, 0.084 mmol, 0.01 equiv) and sodium sulfate (50 mg, 0.32 mmol, 0.042) was added. The reaction was stirred at reflux for 2 hours. After, the reaction was quenched with saturated sodium bicarbonate (50 mL), extracted with ethyl acetate (20 mL) and the organic layer was dried with sodium sulfate before being concentrated under reduced pressure. The crude product was purified by flash column chromatography (100% hexanes) to afford 1-(buta-1,3-dien-2-yl)-3-methoxybenzene (120 mg, 9%) as a colorless oil. The spectra of the compound match that of previous reports.[2]

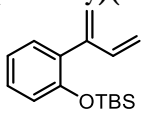
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (td, *J* = 7.7, 0.8 Hz, 1H), 6.95 – 6.83 (m, 3H), 6.65 – 6.55 (m, 1H), 5.34 – 5.19 (m, 4H), 3.82 (s, 3H).

1-(buta-1,3-dien-2-yl)-3,5-dimethoxybenzene



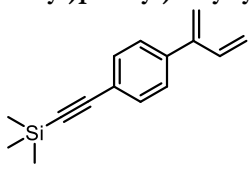
To a solution of 2-(3,5-dimethoxyphenyl)but-3-en-2-ol (1.6 g, 7.7 mmol, 1.0 equiv) in 20 mL of benzene, pyridinium p-toluenesulfonate (19 mg, 0.077 mmol, 0.01 equiv) and sodium sulfate (50 mg, 0.35 mmol, 0.046) was added. The reaction was stirred at reflux for 2 hours. After, the reaction was quenched with saturated sodium bicarbonate (50 mL), extracted with ethyl acetate (20 mL) and the organic layer was dried with sodium sulfate before being concentrated under reduced pressure. The crude product was purified by flash column chromatography (100% hexanes) to afford 1-(buta-1,3-dien-2-yl)-3,5-dimethoxybenzene (323 mg, 22%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 – 6.54 (m, 1H), 6.48 (d, *J* = 2.3 Hz, 2H), 6.43 (t, *J* = 2.3 Hz, 1H), 5.31 – 5.18 (m, 4H), 3.80 (s, 6H).

(2-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane



Under an argon atmosphere, [(dppe)NiCl2] (25.50 mg, 0.07093 mmol, 2.5 mol%) was weighted in a 25 mL Schlenk flask and suspended in 4.0 mL of anhydrous and degassed tetrahydrofuran. The flask was sealed and removed from argon atmosphere. The heterogeneous mixture was cooled to 0°C and 1-(2-((tert-butyldimethylsilyl)oxy)phenyl)vinyl diethyl phosphate (1.4 g, 3.65 mmol, 1.0 equiv.) was added to the mixture using a syringe. Vinylmagnesium bromide(5.5 mL of a 0.7 M solution in THF, 3.83 mmol, 1.05 equiv.) was added dropwise by syringe at 0°C (final volume: 14.56 mL, concentration: 0.25 M). The reaction mixture was stirred for 1 hour at room temperature. The reaction was then quenched by addition of 5.0mL of a saturated solution of ammonium chloride at 0°C and extracted with diethyl ether (3 x 25 mL). The organic layers were dried over sodium sulfate, filtered and the solvent removed under vacuum affording the crude residue that, after purification by silica gel flash chromatography (100% pentane), afforded (2-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane (498 mg, 52%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (ddd, *J* = 8.1, 7.3, 1.8 Hz, 1H), 7.11 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.94 (td, *J* = 7.4, 1.2 Hz, 1H), 6.83 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.55 (ddd, *J* = 17.2, 10.3, 0.7 Hz, 1H), 5.39 – 5.11 (m, 3H), 5.12 – 4.83 (m, 3H), 0.94 (s, 11H), 0.14 (s, 7H).
^{13}C NMR: (126 MHz, $CDCl_3$) δ 153.07, 146.43, 138.52, 131.60, 131.22, 128.50, 120.98, 119.42, 118.61, 116.45, 25.94, 25.82, 18.25, 0.15.

((4-(buta-1,3-dien-2-yl)phenyl)ethynyl)trimethylsilane

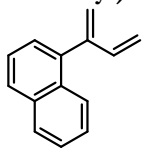


Under an argon atmosphere, [(dppe)NiCl2] (39.7 mg, 0.00141 mmol, 2.5 mol%) was weighted in a 25 mL Schlenk flask and suspended in 4.0 mL of anhydrous and degassed tetrahydrofuran. The flask was sealed and removed from argon atmosphere. The heterogeneous mixture was cooled to 0°C and diethyl (1-(4-

((trimethylsilyl)ethynyl)phenyl)vinyl) phosphate (1.00 g, 2.84 mmol, 1.0 equiv.) was added to the mixture using a syringe. Vinylmagnesium bromide(4.3 mL of a 0.7 M solution in THF, 2.98 mmol, 1.05 equiv.) was added dropwise by syringe at 0°C (final volume: 11.35 mL, concentration: 0.25 M). The reaction mixture was stirred for 1 hour at room temperature. The reaction was then quenched by addition of 5.0mL of a saturated solution of ammonium chloride at 0°C and extracted with diethyl ether (3 x 25 mL). The organic layers were dried over sodium sulfate, filtered and the solvent removed under vacuum affording the crude residue that, after purification by silica gel flash chromatography (pentane buffered with 0.1% triethylamine), afforded ((4-(buta-1,3-dien-2-yl)phenyl)ethynyl)trimethylsilane (465 mg, 72%) as a yellow oil. The spectra matched that of literature reports.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.26 (dt, *J* = 6.3, 1.8 Hz, 2H), 6.64 – 6.55 (m, 1H), 5.33 – 5.13 (m, 4H), 0.26 (s, 9H).

1-(buta-1,3-dien-2-yl)naphthalene

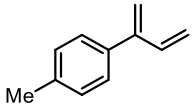


To a stirred 1.0 M solution of vinyl magnesium bromide in THF (3.7 g, 28 mmol, 28 mL, 1.2 equiv), a solution of 1-(p-tolyl)ethan-1-one in 36 mL of THF was added dropwise over thirty minutes at 0ºC under a nitrogen atmosphere. The reaction mixture was stirred at the same temperature for two hours and then quenched with saturated ammonium chloride (200 mL) and extracted with ethyl acetate (100 mL). The organic layer was dried with sodium sulfate and concentrated under reduced pressure. The crude product was dissolved in 60 mL of toluene with pyridinium p-toluenesulfonate (38 mg, 0.15 mmol, 0.005 equiv) and sodium sulfate (50 mg, 0.35 mmol, 0.012 equiv) and heated to 80ºC for three hours. The reaction was quenched with 75 mL of saturated sodium bicarbonate and washed with brine (80 mL). The organic layer was dried with sodium sulfate and concentrated *in vacuo* before being purified by column chromatography (100% hexanes) to yield 1-(buta-1,3-dien-2-yl)-4-methylbenzene (72 mg, 2% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.83 (m, 3H), 7.55 – 7.46 (m, 3H), 7.38 (dd, *J* = 7.0, 1.3 Hz, 1H), 6.83 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.65 (d, *J* = 2.0 Hz, 1H), 5.32 (t, *J* = 1.7 Hz, 1H), 5.19 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.77 (dd, *J* = 17.3, 1.2 Hz, 1H).

^{13}C NMR (126 MHz, CDCl3) δ 147.49, 139.21, 137.83, 133.58, 131.94, 128.16, 127.71, 126.70, 126.39, 125.79, 125.74, 125.40, 119.69, 117.81.

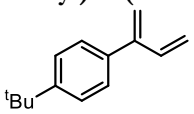
1-(buta-1,3-dien-2-yl)-4-methylbenzene



To a stirred 1.0 M solution of vinyl magnesium bromide in THF (3.7 g, 28 mmol, 28 mL, 1.2 equiv), a solution of 1-(p-tolyl)ethan-1-one in 36 mL of THF was added dropwise over thirty minutes at 0ºC under a nitrogen atmosphere. The reaction mixture was stirred at the same temperature for two hours and then quenched with saturated ammonium chloride (200 mL) and extracted with ethyl acetate (100 mL). The organic layer was dried with sodium sulfate and concentrated under reduced pressure. The crude product was dissolved in 60 mL of toluene with pyridinium p-toluenesulfonate (38 mg, 0.15 mmol, 0.005 equiv) and sodium sulfate (50 mg, 0.35 mmol, 0.012 equiv) and heated to 80ºC for three hours. The reaction was quenched with 75 mL of saturated sodium bicarbonate and washed with brine (80 mL). The organic layer was dried with sodium sulfate and concentrated *in vacuo* before being purified by column chromatography (100% hexanes) to yield 1-(buta-1,3-dien-2-yl)-4-methylbenzene (72 mg, 2% yield) as a colorless oil. The spectra matched that of previous literature reports.[5]

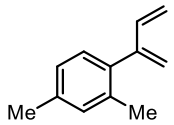
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.16 (dt, *J* = 7.8, 0.7 Hz, 2H), 6.65 – 6.57 (m, 1H), 5.28 – 5.17 (m, 4H), 2.37 (s, 3H).

1-(buta-1,3-dien-2-yl)-4-(tert-butyl)benzene



To a solution of 2-(4-(tert-butyl)phenyl)but-3-en-2-ol (2.8 g, 14 mmol, 1.0 equiv) in 40 mL of benzene, pyridinium p-toluenesulfonate (34 mg, 0.14 mmol, 0.01 equiv) and sodium sulfate (50 mg, 0.35 mmol, 0.026 equiv) was added. The reaction was stirred at reflux for 2 hours. After, the reaction was quenched with saturated sodium bicarbonate (80 mL), extracted with ethyl acetate (40 mL) and the organic layer was dried with sodium sulfate before being concentrated under reduced pressure. The crude product was purified by flash column chromatography (100% hexanes) to afford 1-(buta-1,3-dien-2-yl)-4-(tert-butyl)benzene (932 mg, 37%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.29 – 7.25 (m, 2H), 6.66 – 6.56 (m, 1H), 5.30 – 5.17 (m, 4H), 1.34 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.44, 147.97, 138.20, 136.72, 127.85, 125.04, 117.01, 116.35, 34.55, 31.38.

1-(buta-1,3-dien-2-yl)-2,4-dimethylbenzene



Under an argon atmosphere, [(dppe)NiCl2] (25.50 mg, 0.07093 mmol, 2.5 mol%) was weighted in a 25 mL Schlenk flask and suspended in 4.0 mL of anhydrous and degassed tetrahydrofuran. The flask was sealed and removed from argon atmosphere. The heterogeneous mixture was cooled to 0°C and 1-(2,4-dimethylphenyl)vinyl diethyl phosphate (1g, 3.65 mmol, 1.0 equiv.) was added to the mixture using a syringe. Vinylmagnesium bromide(5.5 mL of a 0.7 M solution in THF, 3.83 mmol, 1.05 equiv.) was added dropwise by syringe at 0°C (final volume: 14.56 mL, concentration: 0.25 M). The reaction mixture was stirred for 1 hour at room temperature. The reaction was then quenched by addition of 5.0mL of a saturated solution of ammonium chloride at 0°C and extracted with diethyl ether (3 x 25 mL). The organic layers were dried over sodium sulfate, filtered and the solvent removed under vacuum affording the crude residue that, after purification by silica gel flash chromatography (100% pentane), afforded 1-(buta-1,3-dien-2-yl)-2,4-dimethylbenzene (221 mg, 38%) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 – 6.94 (m, 3H), 6.59 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.36 (d, *J* = 2.0 Hz, 1H), 5.11 (dq, *J* = 10.3, 1.2 Hz, 1H), 5.04 (t, *J* = 1.8 Hz, 1H), 4.72 (dd, *J* = 17.2, 1.5 Hz, 1H), 2.33 (s, 3H), 2.17 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.54, 148.50, 138.75, 136.79, 136.50, 135.79, 135.73, 130.59, 129.47, 128.28, 126.11, 125.55, 118.19, 116.81, 34.25, 30.34, 21.21, 21.10, 19.53.

III. LED emission profiles

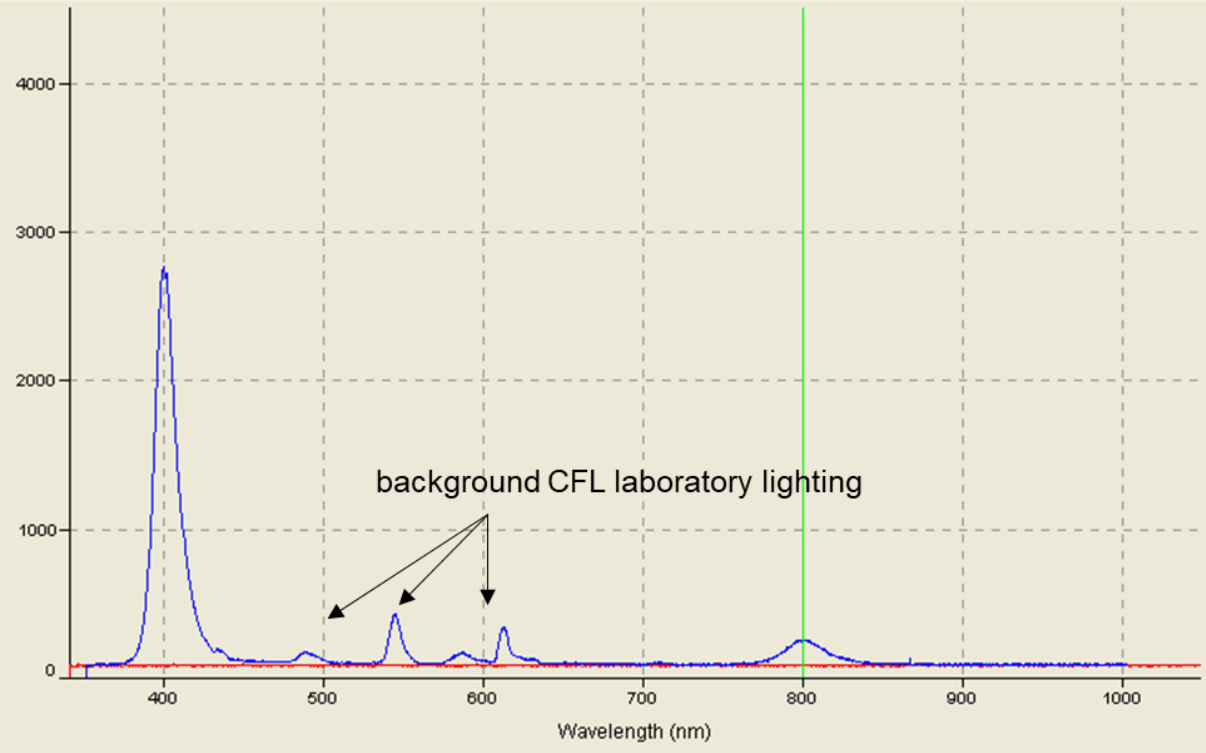


Figure S1 Measured emission spectra of "470 nm" LEDs used.

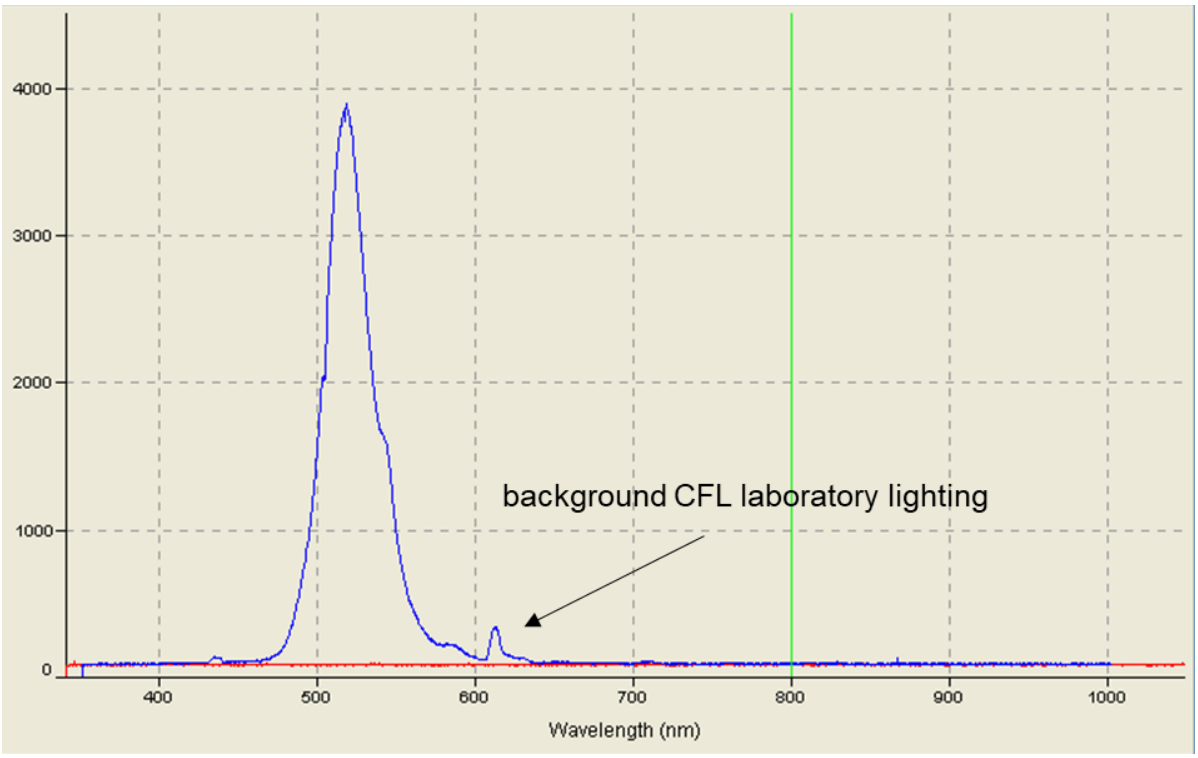
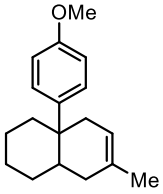


Figure S2 Measured emission spectra of "525 nm" LEDs used.

IV. Procedure for the small-molecule photoredox Diels–Alder

Procedure for identification of small-molecule Diels–Alder product: An oven-dried 1-dram vial was charged with a stir bar and sealed with a septa cap. In three separate, sealed, oven-dried 1-dram vials, solutions of cyclohexene **1** (50 mg/mL), photocatalyst (8μmol/mL), and isoprene (50 mg/mL) were prepared in dichloromethane or acetonitrile. To each 1-dram vial with a stir bar, 0.1 mL of each solution was added under nitrogen. The reactions were then stirred at 450 rpm either under a steady flow of nitrogen or with a 25 G needle to vent the reaction and introduce oxygen. The reaction was irradiated with blue LEDs (470 nm) and cooled with a fan for 16 hours. After which, the reactions were concentrated *in vacuo* and redissolved in solvent for GC-MS (dichloromethane) or LC-MS (10:1 acetonitrile:water with 0.1% formic acid) analysis. To isolate the cycloaddition product **2**, four reaction vials were combined and purified using preparatory thin-layer chromatography in 100% pentane.

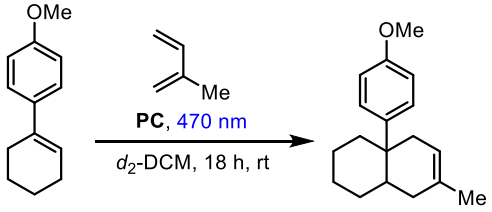
2



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 6.83 – 6.80 (m, 2H), 5.39 (s, 1H), 3.79 (s, 3H), 2.53 (d, *J* = 18.7 Hz, 1H), 2.19 (dd, *J* = 5.6, 2.7 Hz, 1H), 2.15 (d, *J* = 4.8 Hz, 1H), 1.98 – 1.92 (m, 1H), 1.84 (t, *J* = 9.3 Hz, 2H), 1.79 – 1.65 (m, 5H), 1.53 – 1.50 (m, 3H), 1.40 – 1.35 (m, 2H).
LRMS m/z expected for $C_{18}H_{25}O$ [M+H]+ 257.18, measured 257.1

Procedure for optimization and quantification of small-molecule Diels–Alder reaction: An oven-dried 1-dram vial was charged with a stir bar (and external oxidant if that was a variable for screening) and sealed with a septa cap. In three separate, sealed, oven-dried 1-dram vials, solutions of cyclohexene **1** (50 mg/mL, 0.3mmol/mL), photocatalyst (8μmol/mL), and isoprene (50 mg/mL) were prepared in deuterated dichloromethane (0.12 M concentration total). To each 1-dram vial with a stir bar, 0.1 mL of each solution was added under nitrogen. The reactions were then stirred at 450 rpm either under static nitrogen (if an external oxidant was added) or with a 25 G needle to vent the reaction and introduce oxygen. The reaction was irradiated with blue LEDs (470 nm) and cooled with a fan for 16 hours. The reactions were diluted with an additional 0.2 mL of deuterated DCM. A solution of benzaldehyde as an external standard was prepared (30mg/mL, 0.3mmol/mL) in deuterated dichloromethane and 0.1 mL of this solution was added to each reaction vile. The resulting solutions were analyzed via ^{1}H NMR to measure conversion of starting cyclohexene and product formation.

Table S1. Optimization of small-molecule reaction



Entry	Catalyst	Oxidant	Solvent	Conversion	Yield
1	MesAcr (1 mol%)	Air	DCM	68%	1%
2	TPT-OMe	Air	DCM	100%	1%

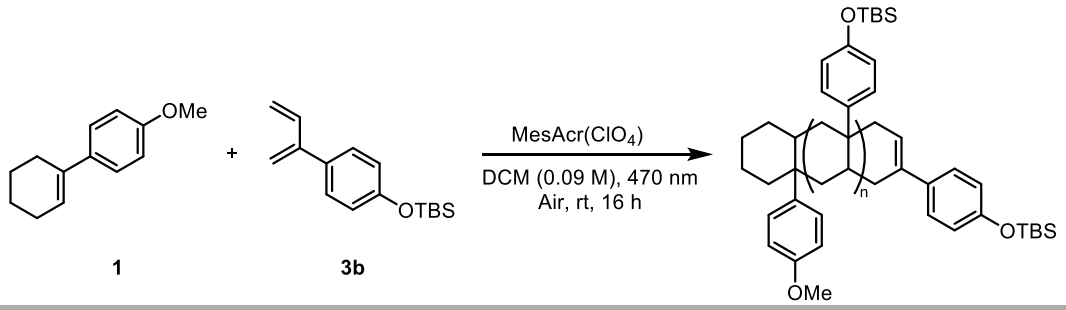
3	TPT	Air	DCM	64%	<1%
4	CzIPn	Air	DCM	90%	<1%
5	MesAcr	DDQ (0.2 eq)	DCM	96%	<1%
6	MesAcr	DDQ (1 eq)	DCM	74%	13%
7	MesAcr	CAN (0.2 eq)	DCM	77%	<1%
8	MesAcr	CAN (1 eq)	DCM	85%	n.d.

n.d.= not detected

V. Procedure for the optimization of photoredox Diels–Alder polymerization

General procedure for reaction optimization. An oven-dried 1-dram vial was charged with a stir bar (and external oxidant if that was a variable for screening) and sealed with a septa cap. In three separate, sealed, oven-dried 1-dram vials, solutions of cyclohexene **1** (50 mg/mL, 0.3mmol/mL), photocatalyst (8μmol/mL), and **3b** (1.10 g/mL) were prepared in solvent (0.09 M concentration total). To each 1-dram vial with a stir bar, 0.1 mL of each solution was added under nitrogen. For reactions without initiator, 0.1 mL of solvent was added. The reactions were then stirred at 450 rpm with a 25 G needle to vent the reaction and introduce oxygen. The reaction was irradiated with blue LEDs (470 nm) and cooled with a fan for 16 hours. The reaction solution in each vial was precipitated into a 7:1 methanol/water solution and centrifuged at 10,000 rpm at 0 ºC for 10 minutes.

Table S2. Optimization of standard reaction conditions



1 3b

Entry	Deviation from standard conditions	M_n	Đ	Yield
1	None	1300	1.5	71
2	No initiator	1300	1.2	38
3	F-Cyclohexene	1800	1.3	25
4	TPT-OMe	1200	1.2	33
5	TPT	860	1.1	7.2
6	^{t}BuMesAcr	1000	1.3	40
7	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	1300	1.4	15
8	No solvent	860	1.03	No precipitate
9	Chloroform	1600	1.2	12
10	DMSO	2700	1.6	11
11	Nitromethane	1100	1.1	59
12	DMF	n.d.	n.d.	n.d.
13	THF	1500	1.4	6
14	4 M	1500	1.3	46
15	2 M	1600	1.3	44

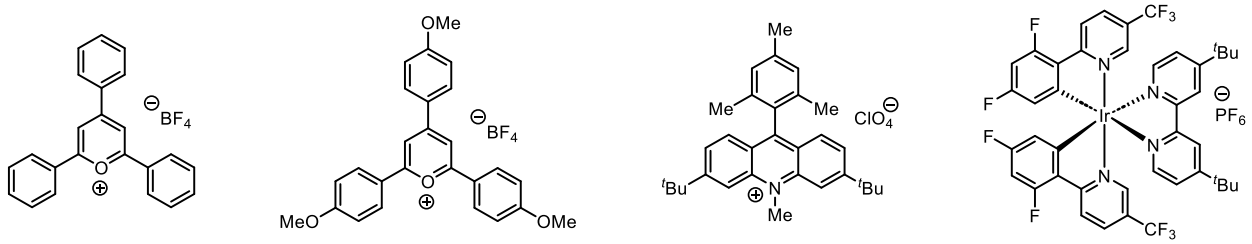
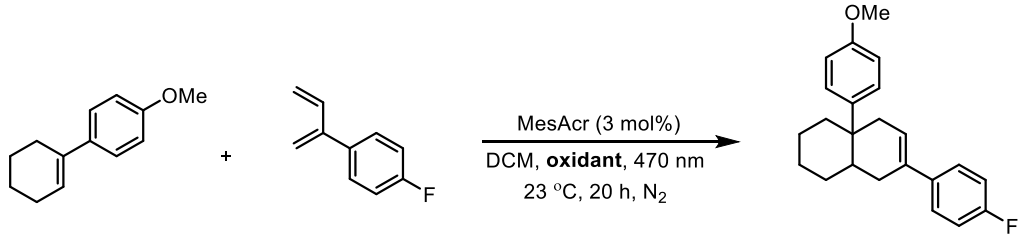


Chart S1. Photocatalysts used in Table S2

Procedure for external oxidant screens. In 6 separate 1 dram vials the following solutions were prepared: 15 mg of **1** was dissolved in 0.3 mL of DCM or THF (50 mg/mL), 59.1 mg of diene **3e** was dissolved in 0.3 mL of DCM or THF (197 mg/mL), and 2.0 mg of MesAcr was dissolved in 0.61 mL of DCM or THF (3.2 mg/mL, 3 mol%). Six 1-dram vials were charged with a stir bar and external oxidant (0.2 eq) was added and the vials were sealed with septa and kept under nitrogen. Two vials contained CAN (2.91 mg), two contained DDQ (1.12 mg), and two contained methyl viologen (1.37 mg). To three vials with different oxidants in each, 0.1mL of each solution (photocatalyst, **1**, and **3e**) were added via syringe under nitrogen. The reactions were run at room temperature with irradiation with blue light (470 nm) for 20 hours. Then, the samples were concentrated and prepared for GC-MS analysis by creating 0.5 mg/mL solutions of crude reaction mixture in HPLC DCM with toluene as an external standard. Toluene internal standard was made by dissolving 2.61 mg of toluene in 1.0 mL of HPLC DCM (0.0284 mmol). Samples were redissolved in 1.0 mL of HPLC DCM (0.0284 mmol) from which 0.1 mL of this solution was combined with toluene standard and 0.8 mL of HPLC DCM. Reactions were evaluated based on conversion of **3e** and formation of **1**+**3e** product according to MS (336.2 m/z). Note: diene **3e** was used due to the ability to detect the **1**+**3e** product using GC-MS.

Table S3. Optimization of terminal oxidant

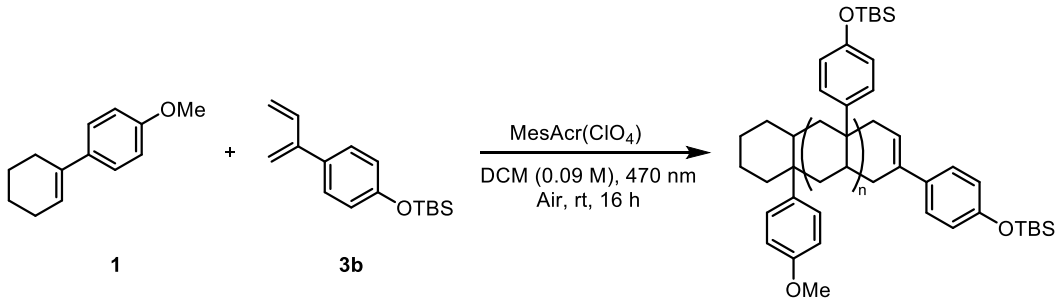


Oxidant	Solvent	% 3e conversion	% mono
CAN	THF	47	14
DDQ	THF	40	4
Methyl violegen	THF	37	0
Air	THF	62	48
CAN	DCM	55	16
DDQ	DCM	63	2
Methyl violegen	DCM	38	1.1
Air	DCM	82	43

Procedure for elimination experiments. Solutions of photocatalyst, diene **3b**, and **1** were made by dissolving MesAcr (1.5 mg) in 0.5 mL of DCM, 440 mg **3b** 0.4 mL of DCM, and 25 mg of **1** in 0.5 mL of DCM. Reactions were set up where in two 1-dram vials charged with stir bars, 0.1 mL of each solution was added. One of these vials was the control, while the other was prepared in the dark and the vial was wrapped in electrical tape. In the three remaining vials, only two of the three solutions were added to each vial, and 0.1 mL of DCM was added to replace the omitted solution (0.3 mL total volume). The reactions were vented with 25 G needles,

irradiated with blue light (470 nm), and stirred at 450 rpm for 16 hours. The solvent was removed in vacuo and the reaction solution was re-dissolved in 1 mL of dichloromethane. An external standard of toluene in dichloromethane (2.5 mg/mL) and 0.1 mL of each of these solutions was added to 0.8 mL of dichloromethane and analyzed using GC-MS.

Table S4. Control experiments[a]



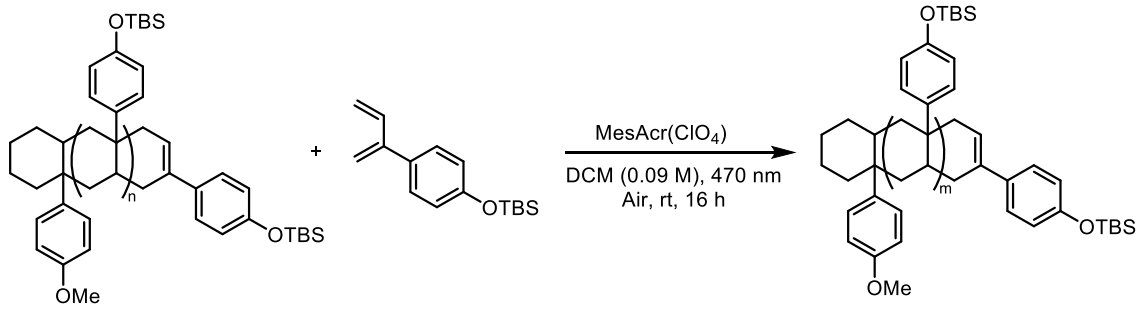
1 3b

Entry	Eliminated component	M_n (Đ)
1	None	1500 (1.6)
2	MesAcr	n.d.
3	**1**	1200 (1.3)
4	**3e**	n.d.
5	Light (run in dark)	n.d.

[a]M_n was determined using GPC with MALS detector.

Procedure for extension experiment. An oven-dried 2-dram vial was charged with a stir bar and sealed with a septa cap. In three separate, sealed, oven dried 1-dram vials, solutions of **LP-3b** (42 mg/mL), photocatalyst (8 μmol/mL), and **3b** (4.0 mmol/mL) were prepared in dry dichloromethane. In the 2-dram vial with stir bar, 0.24 mL of the polymer solution was added with 0.1 mL of the photocatalyst solution and 0.1 mL diene solution under nitrogen. The reactions were then stirred at 450 rpm with a 25 G needle and irradiation with blue LEDs (470 nm) and cooled with a fan for 20 hours. The reaction solution was precipitated into 7:1 methanol-water solution and centrifuged at 7500 rpm at 0 ºC for 10 minutes. The precipitate was isolated and analyzed on GPC.

Table S5. Extension experiment[a]

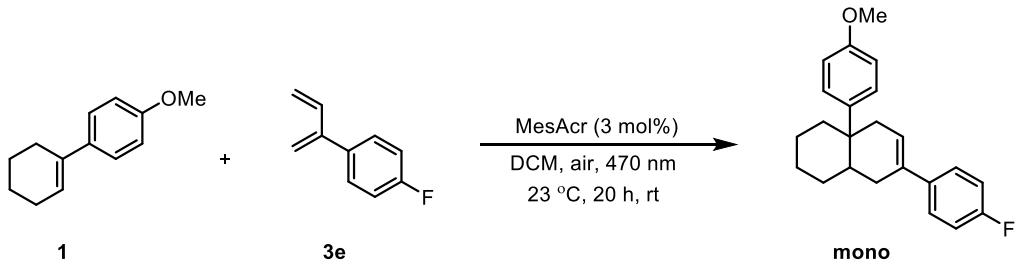


LP-3b 3b LP-3b"

Entry	Polymer	M_n (g/mol)	M_p (g/mol)	Đ
1	**LP-3b**	1300	1207	1.1
2	**LP-3b"**	1600	1534	1.2

[a]M_n was determined using GPC with RI detector

Table S6. Diene conversion experiments. 3e composition was determined as a % yield of all products observed in GC-MS.



1 3e mono

Entry	Equiv. of 3e	% of 1 conversion	% 3e composition	% mono composition
1	5	100	26	34
2	15	100	53	22

Procedure for diene conversion experiments. An oven-dried 1-dram vial was charged with a stir bar and sealed with a septa cap. In three separate, sealed, oven-dried 1-dram vials, solutions of cyclohexene **1** (50 mg/mL, 0.3mmol/mL), photocatalyst (8μmol/mL), and diene **3e** (4.0 mmol/mL) were prepared in dichloromethane (0.09 M concentration total). To each 1-dram vial with a stir bar, 0.1 mL of each solution was added under nitrogen. The reactions were then stirred at 450 rpm with a 25 G needle to vent the reaction and introduce oxygen. The reaction was irradiated with blue LEDs (470 nm) and cooled with a fan for 16 hours. The solvent was removed in vacuo and the reaction solution was re-dissolved in 1 mL of dichloromethane. An external standard of toluene in dichloromethane (2.5 mg/mL) and 0.1 mL of each of these solutions was added to 0.8 mL of dichloromethane and analyzed using GC-MS.

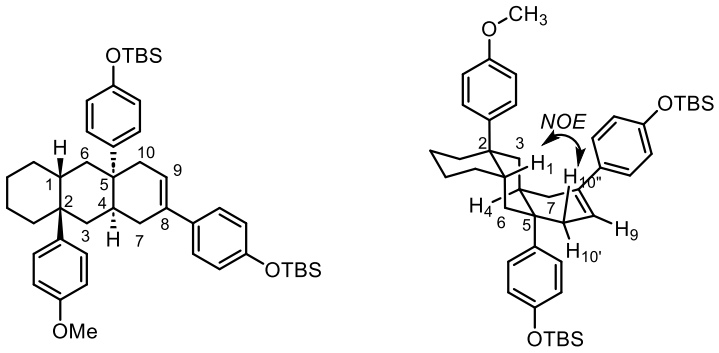
Procedure for substrate scope experiments. An oven-dried 1-dram vial was charged with a stir bar and sealed with a septa cap. In three separate, sealed, oven-dried 1-dram vials, solutions of cyclohexene **1** (50 mg/mL, 0.3mmol/mL), photocatalyst (8μmol/mL), and diene (4.0 mmol/mL) were prepared in dichloromethane (0.09 M concentration total). To each 1-dram vial with a stir bar, 0.1 mL of each solution was added under nitrogen. The reactions were then stirred at 450 rpm with a 25 G needle to vent the reaction and introduce oxygen. The reaction was irradiated with blue LEDs (470 nm) and cooled with a fan for 16 hours. The reaction solution in each vial was precipitated into a 7:1 methanol–water solution and centrifuged at 10,000 rpm at 0 ºC for 10 minutes.

Procedure for cationic polymer extension experiments. In a 1 dram vial with stir bar, 10 mg of polymer sample was dissolved in 0.15 mL of DCM under nitrogen. Stock solutions of *tert*-butyl chloride were prepared (115 μL in 0.5 mL, 2.0 mmol/mL) and 0.1 mL of this solution was added to the vial with dissolved polymer under nitrogen. This reaction was stirred as titanium tetrachloride (18 μL, 18 μmol, 1.0 M in DCM) was added and the reaction was stirred for 30 minutes before precipitation into 8mL of a 7:1 methanol–water solution and centrifuged at 10,000 rpm at 0 ºC for 10 minutes. The precipitate was isolated and analyzed via GPC using MALS detection.

Procedure for probing polymerization initiation and characterization of oligomers. Supernatant from polymerizations with **1** and **3b** with MesAcr was concentrated in vacuo and redissolved in ~1 mL of DCM to deposit at the baseline of a preparatory TLC plate. The plate was developed in a solution of 2% ether in pentane with 0.1% triethylamine. The top six lines which were isolated and purified using ^{1}H NMR and various 2D NMR experiments including COSY, HSQC, HMBC, TOCSY, and NOESY.

Polymerization initiated via addition to 1. HRMS results indicated **LP-3b-2** had a mass corresponding to $C_{45}H_{65}O_3Si_2$ ($[M+H]^+$ 709.447 calculated, 709.4474 measured). Due to the appearance of only one peak in the alkene region, but several silyl-protected groups according to HRMS and NMR, the structure of **LP-3b-2** is

likely due to multiple cycloadditions of monomer **3b**. After using COSY, TOCSY, HSCQ, and HMBC to assign the majority of the carbons in the ladder backbone, we identified a NOE cross peak to determine the isolated diastereomer. Key correlations and tentative assignments are shown below.



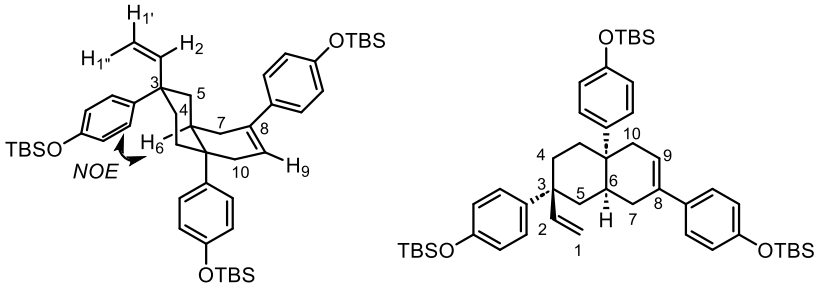
LP3b-2

#	^{1}H δ (ppm)	^{13}C δ (ppm)	COSY and TOCSY* cross peaks	HSQC cross peaks	HMBC cross peaks
9, 10”/10’	6.03 (1 H) 2.95 (1 H) 2.51 (1 H)	120.06 28.72	(6.03, 2.52)	(6.03, 120.04) (2.94, 28.72) (2.49, 28.72)	(2.94, 119.99) (2.50, 119.99)
10’, 8	2.51 (1 H)	28.72 134.04			(2.50, 134.04)
9, 7’/7”	6.03 (1 H) 1.77 (1 H) 2.08 (1 H)	120.06 30.99	(6.03, 1.77)* (6.03, 2.08)*	(1.77, 30.99) (2.08, 30.99)	(1.77, 119.75)
3, 7’/7”	1.77 (1 H) 2.08 (1 H) 1.31 (1 H) 1.66 (1 H)	30.99 46.88	(2.07, 1.30)* (2.07, 1.65)*	(1.31, 46.88) (1.66, 46.88)	(1.31, 31.02)
3, 4	1.31 (1 H) 1.66 (1 H) 2.45 (1 H)	46.88 35.53	(2.45, 1.66) (2.45, 1.31)	(2.45, 35.53)	
4, 7’/7”	1.77 (1 H) 2.08 (1 H) 2.45 (1 H)	30.99 35.53	(2.07, 2.45)		
4, 6’/6”	2.45 (1 H) 2.44 (1 H) 1.37 (1 H)	40.66		(1.37, 40.66) (2.44, 40.66)	(2.45, 40.66)
1, 6’/6”	2.44 (1 H) 1.37 (1 H) 2.73 (1 H)	32.89	(2.74, 1.35) (2.74, 2.44)	(2.74, 32.89)	(2.74, 40.66)

We first began structure confirmation by assigning **9** as the proton at 6.03 ppm. From there, COSY allowed us to identify a cross-peak with **10’** and **10”** and HMBC allowed us to identify carbon **8**. TOCSY and HMBC allowed us to identify **7** relative to C-**8** and **9**, respectively. HMBC allowed for the identification of **3** from **7**, and the cross-peaks in COSY from both **3** and **7** enabled the identification of **4**. The COSY cross peaks of **4** with both **3** and **7** confirmed the regioselectivity of the cycloaddition; if both dienes had added to the propagating alkene with the aromatic group on the same side, 4 would have only had a cross peak with one of

the two CH_2 groups. TOCSY and HMBC cross-peaks helped identify **6** (which has a very similar chemical shift to **4**, but with different signals on HSQC to distinguish it), and from there we were able to identify **1**. We were then able to confirm the diastereomer because of an NOE cross-peak between **1** and **10"**.

Polymerization initiated via addition to diene 3b. HRMS results indicated **LP-3b'-2** had a mass corresponding to $C_{48}H_{72}NaO_3Si_3$ ([M+Na]$^+$ 803.470 calculated, 803.4704 measured), or three additions of the diene **3b** without the initiator. While the appearance of a peak at 6.11 ppm corresponds to that of the alkene in **LP-3b-2**, we noticed three additional distinct peaks in the alkene region suggesting an additional vinyl group. After using COSY, TOCSY, HSCQ, and HMBC we identified a NOE cross peak to determine the isolated diastereomer. Key correlations and tentative assignments are shown below.



LP-3b'-2

#	^{1}H δ (ppm)	^{13}C δ (ppm)	COSY and TOCSY* cross peaks	HSQC cross peaks	HMBC cross peaks
9, 10'/10"	6.11 (1 H) 2.83 (1 H) 2.45 (1 H)	120.23 28.74	(6.12, 2.86) (6.12, 2.46)	(6.12, 120.24) (2.83, 28.73) (2.45, 28.69)	(2.85, 120.24)
9/8	6.11 (1 H)	120.23 135.25			(6.11, 135.23)
9, 7	6.11 (1 H) 1.93 (2 H)	120.23 31.69	(6.11, 1.92)*	(1.93, 31.69)	(1.92, 120.24)
7, 6	1.93 (2 H) 2.08 (1 H)	31.69 35.85	(1.93, 2.08)	(2.08, 35.85)	(1.93, 35.85) (2.08, 31.70)
6, 5'	2.08 (1 H) 2.28 (1 H)	35.85 31.01	(2.08, 2.28)	(2.28, 31.01)	(2.08, 31.01)
2, 3	5.91 (1 H)	45.11			(5.91, 45.11)

We were able to identify **1'**, **1"**, **2**, and **9** using ^{1}H NMR. We were able to identify **10'** and **10"** using COSY and HMBC. TOCSY and HMBC also allowed for the identification of **7**. Additional COSY cross peaks with 6 allowed for the identification of 5' and confirm regioselectivity. We used HMBC to identify multiple aromatic peaks (using **H-10** and **C-8**) and determine aromatic rings, which was useful in identifying the aromatic ring with a cross peak with **6** in the NOESY spectrum. Through process of elimination, we determined that the aromatic group with the adjacent vinyl group had a cross peak with **6**, which confirmed the diastereomer.

VI. Gas sorption experiments

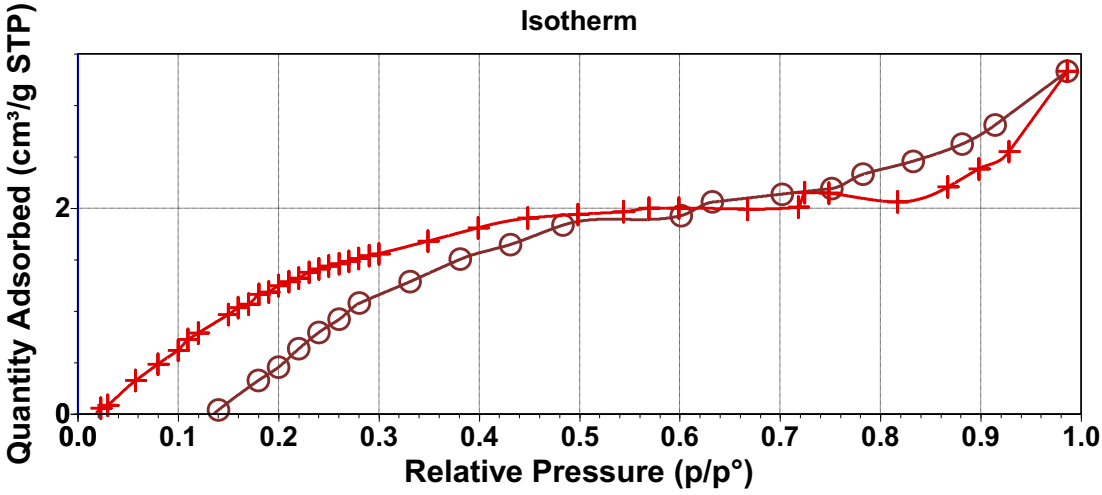


Figure S3. N_2 isotherms of LP-3b (5.7 m^2/g)

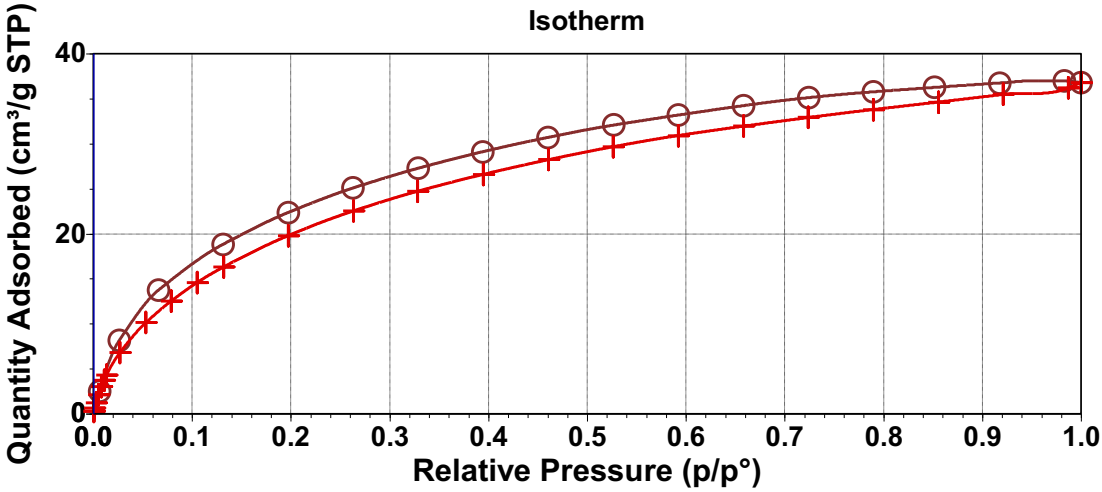


Figure S4. CO_2 isotherms of LP-3b (110 m^2/g)

VII. GPC Traces

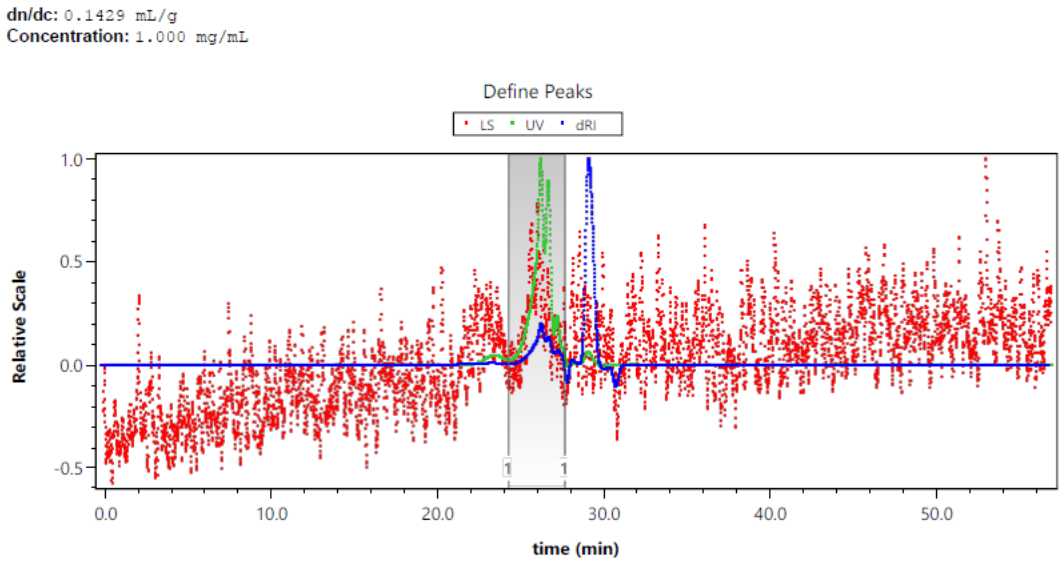


Figure S5. GPC traces of reaction in Table S2, entry 1 using MALS detection.

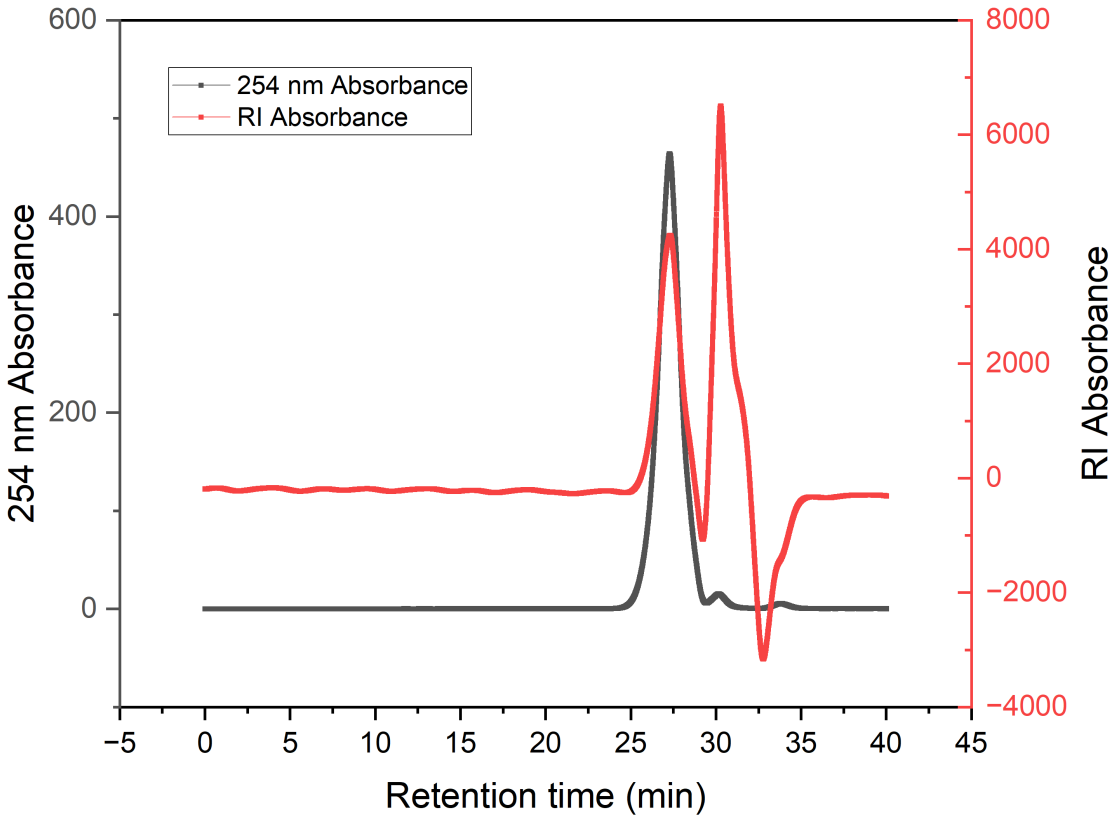


Figure S6. GPC traces of reaction from Table S2, entry 2 using RID detection.

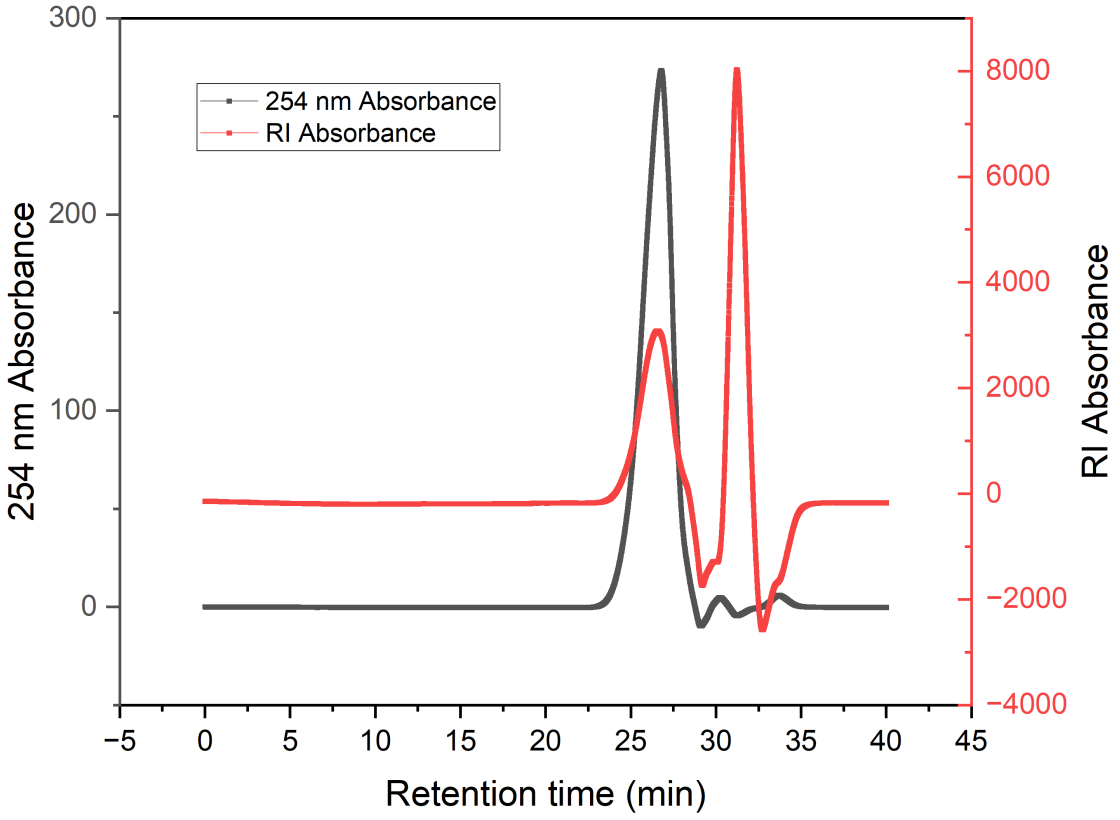


Figure S7. GPC traces of reaction in Table S2, entry 3 using RID detection.

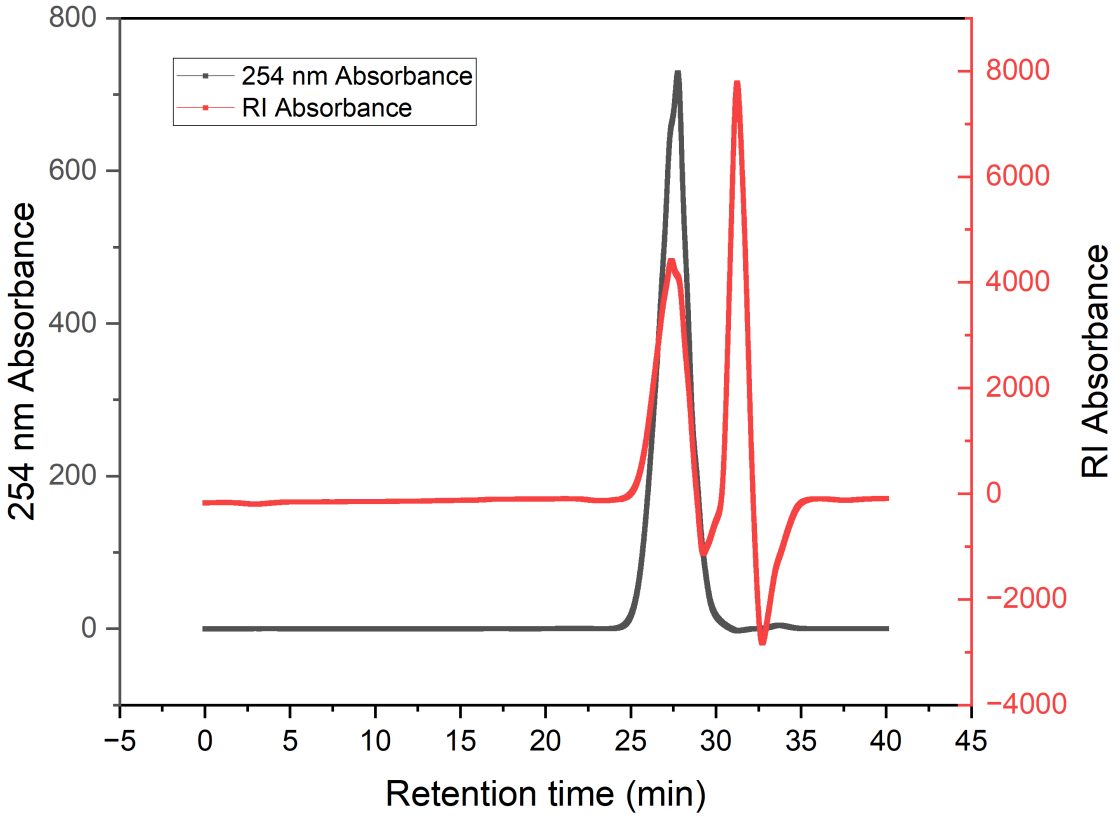


Figure S8. GPC of reaction from Table S2, entry 4 using RID detection.

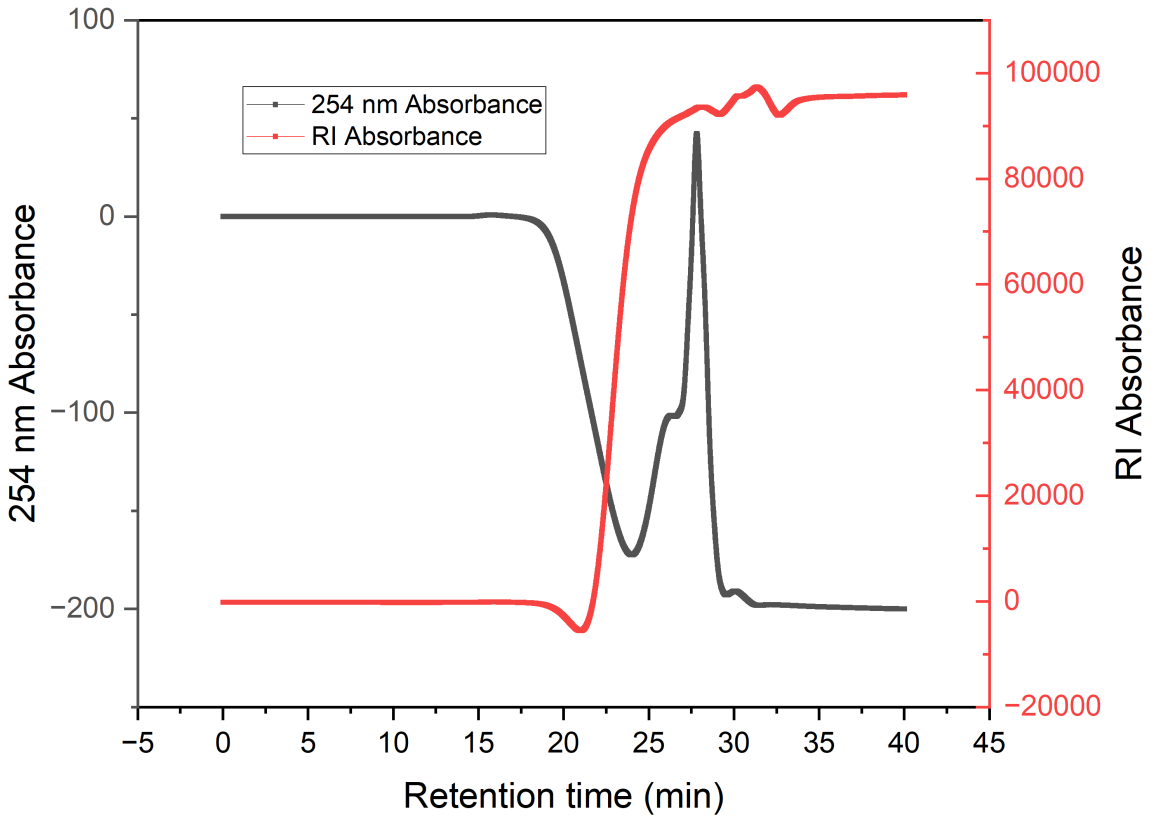


Figure S9. GPC of reaction from Table S2, entry 5 using RID detection.

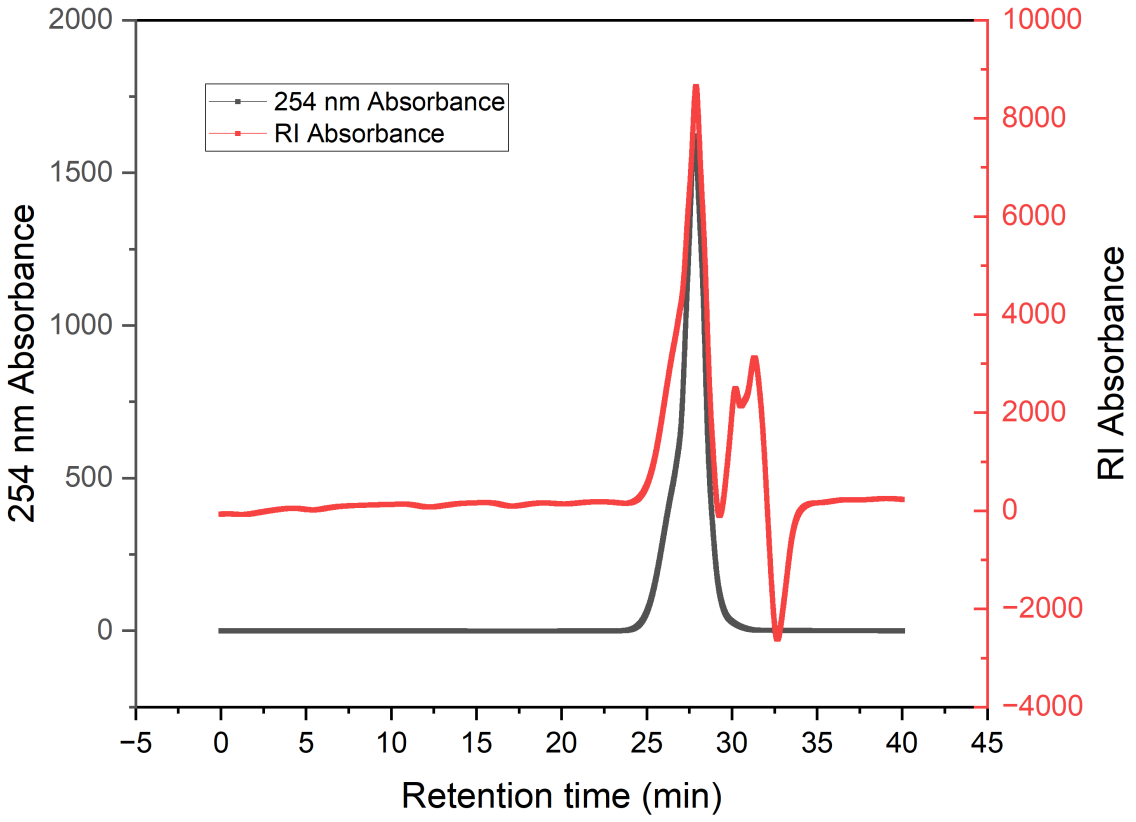


Figure S10. GPC traces of reaction from Table S2, entry 6 using RID detection.

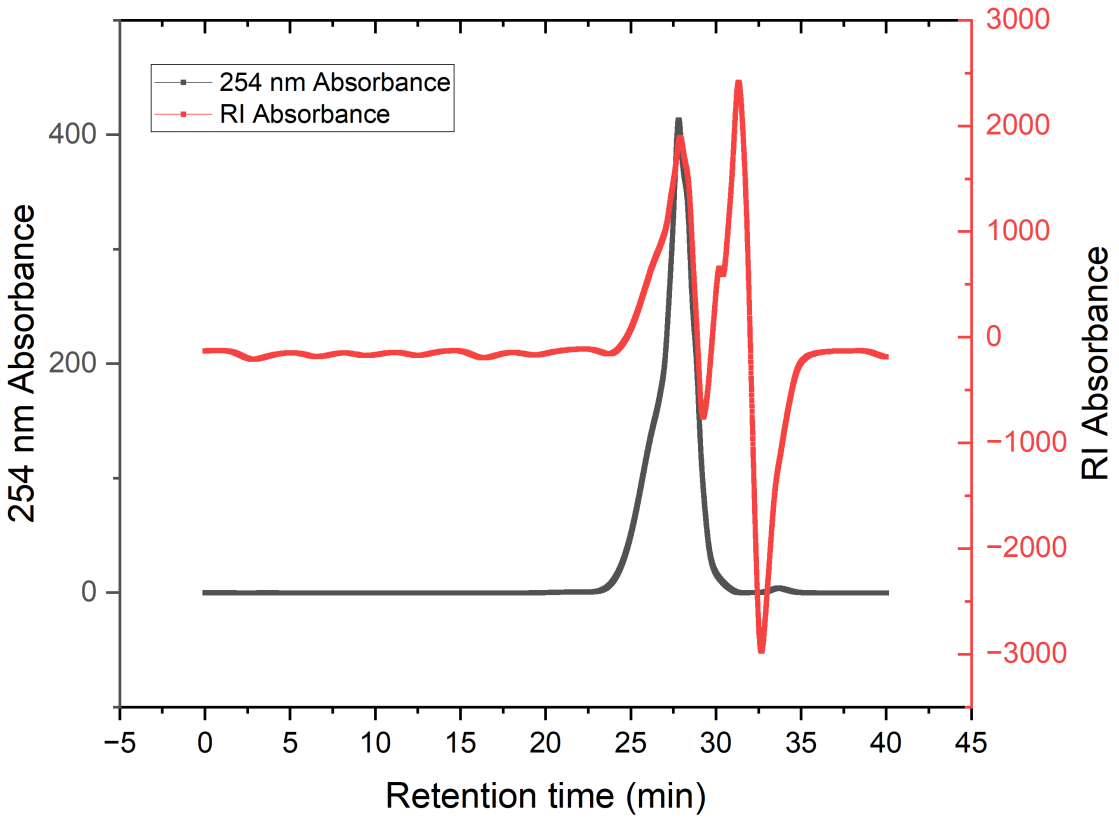


Figure S11. GPC traces of reaction in Table S2, entry 7 using RID detection.

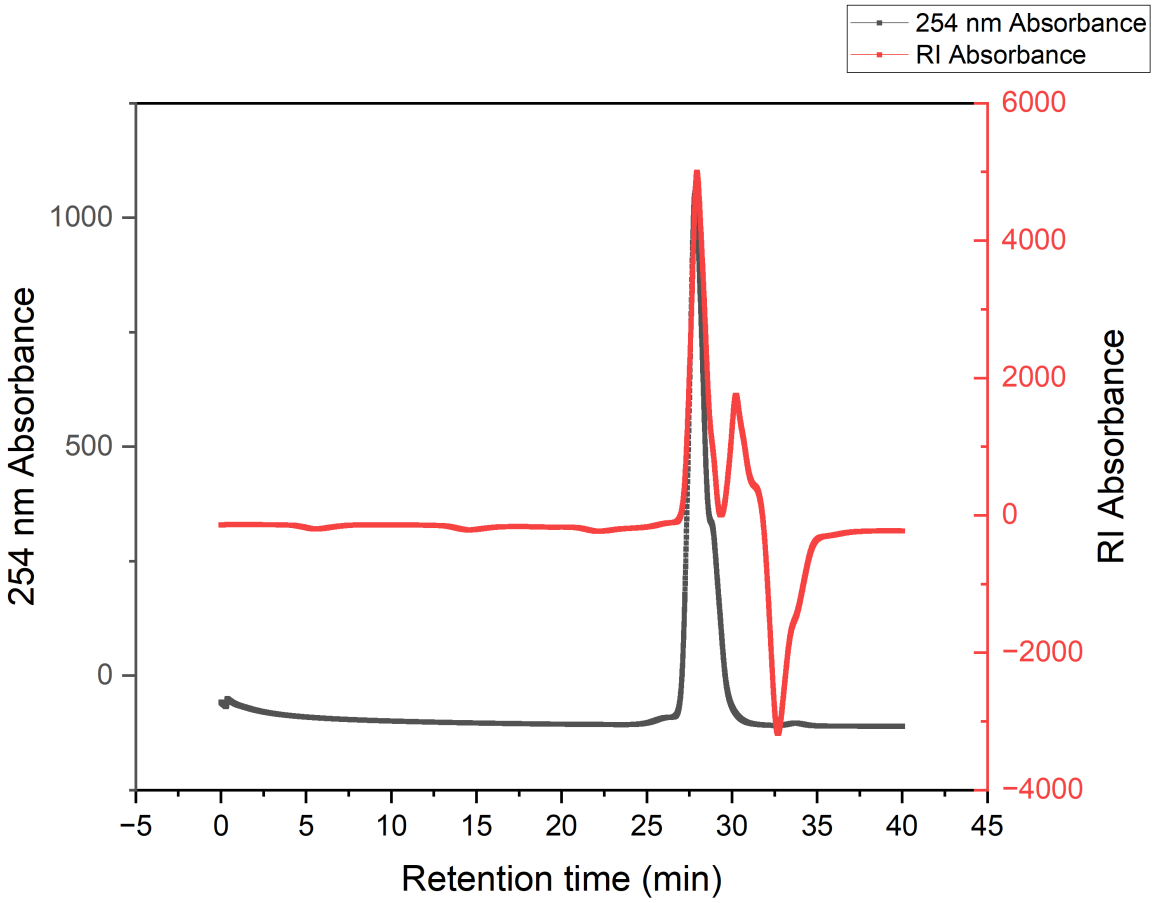


Figure S12. GPC traces of reaction in Table S2, entry 8 using RID detection.

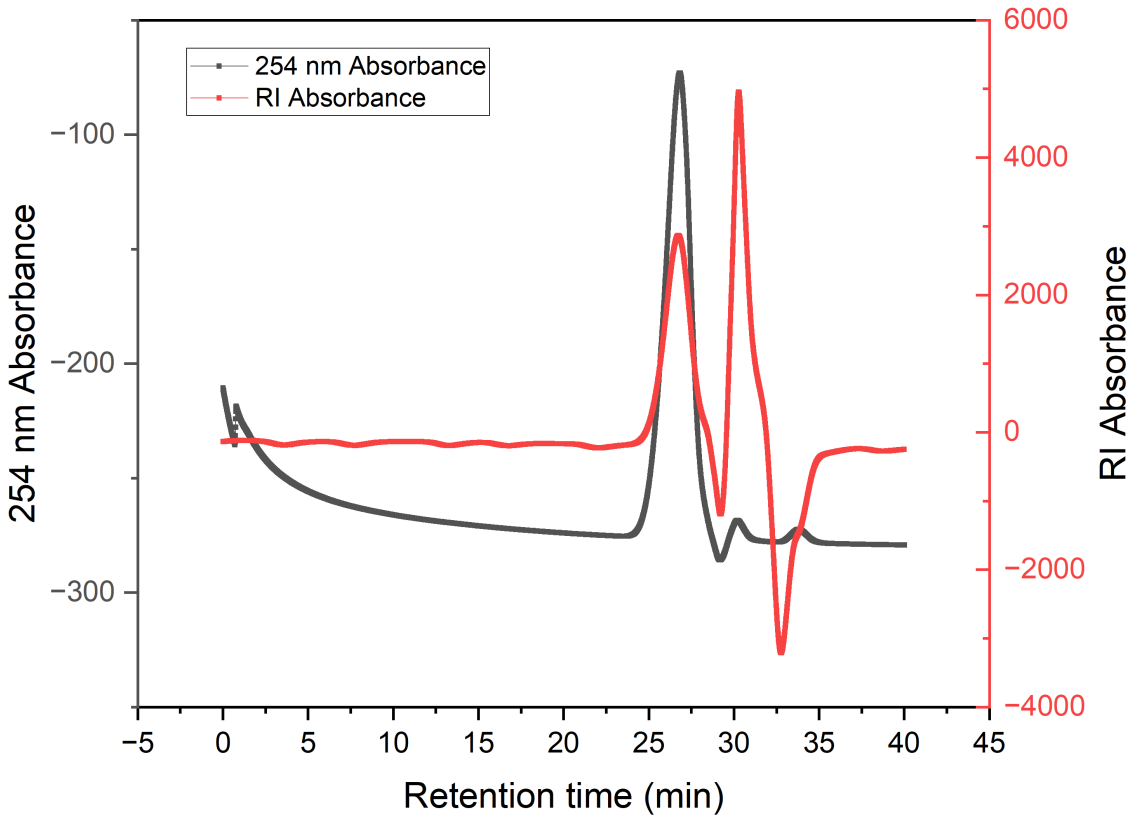


Figure S13. GPC traces of Table S2, entry 9 using RID detection.

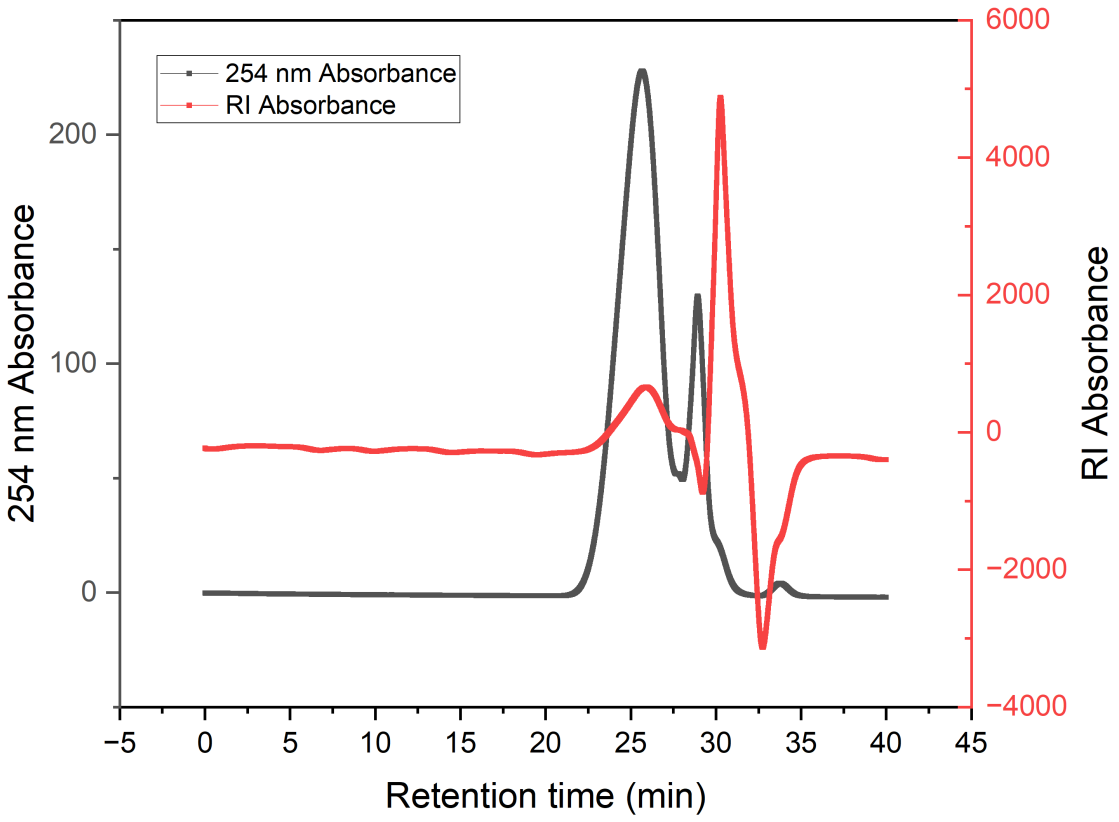


Figure S14. GPC traces of Table S2, entry 10 using RID detection.

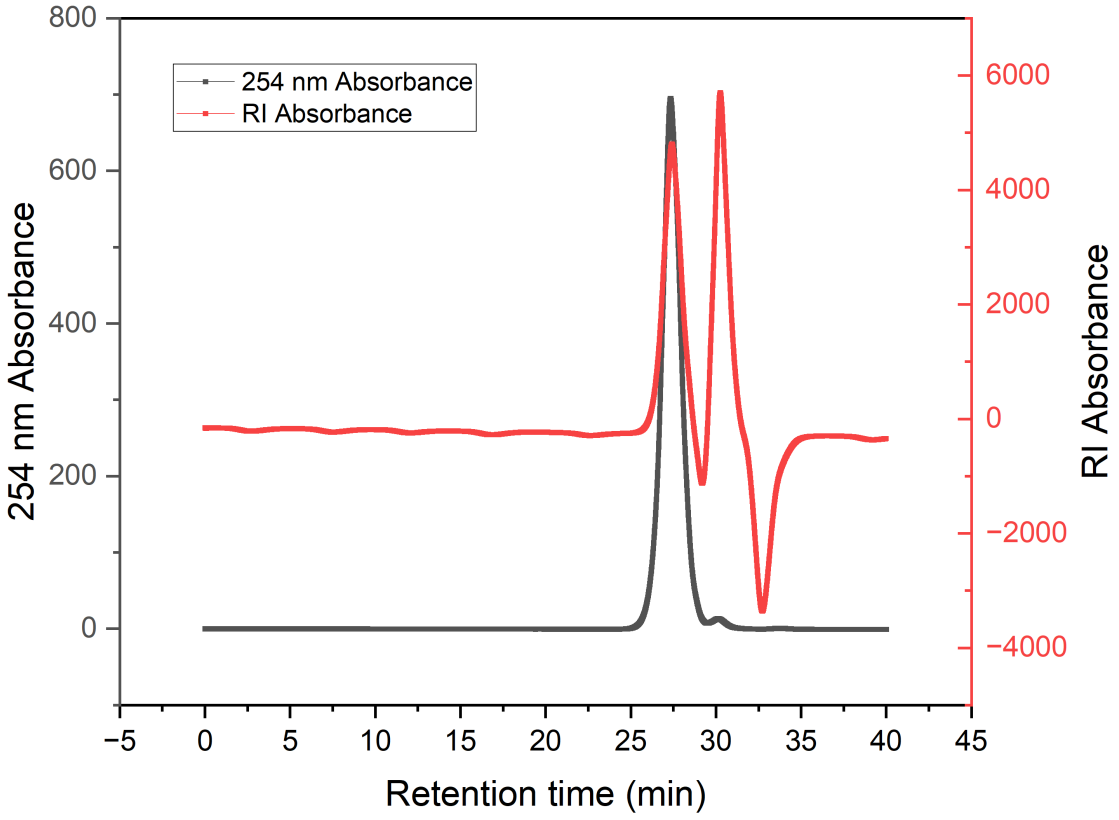


Figure S15. GPC traces of Table S2, entry 11 using RID detection.

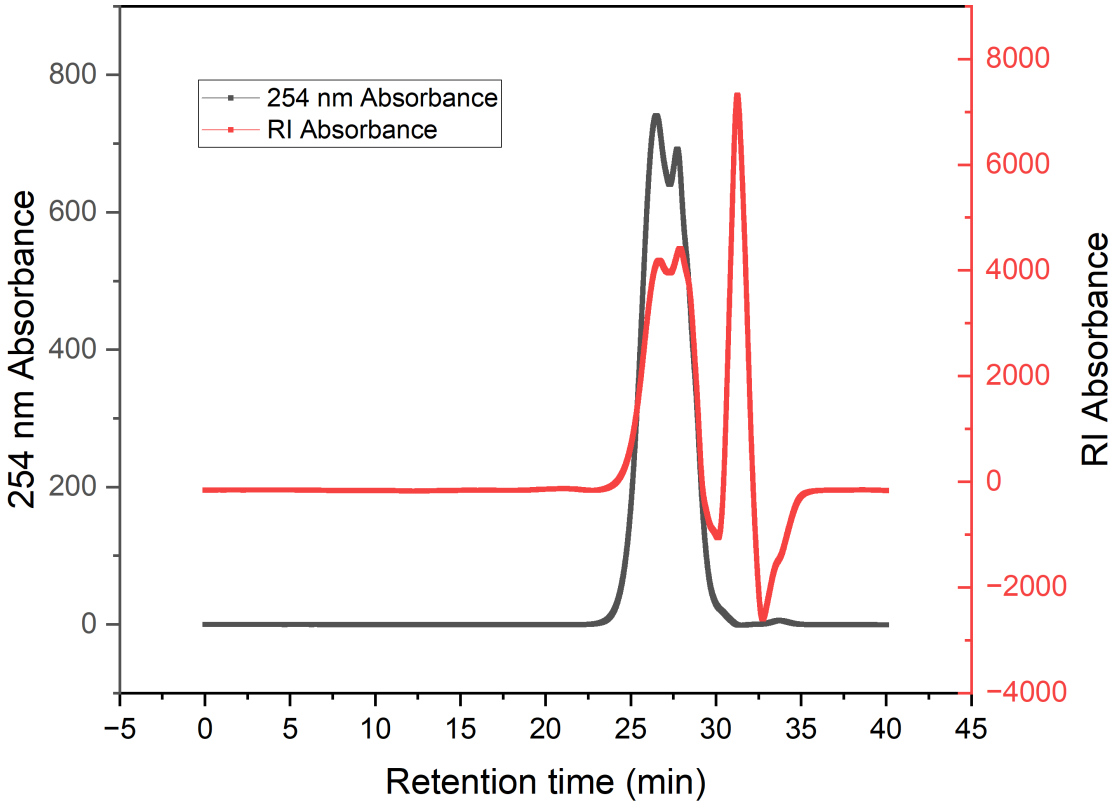


Figure S16. GPC traces of reaction in Table S2, entry 13 using RID detection.

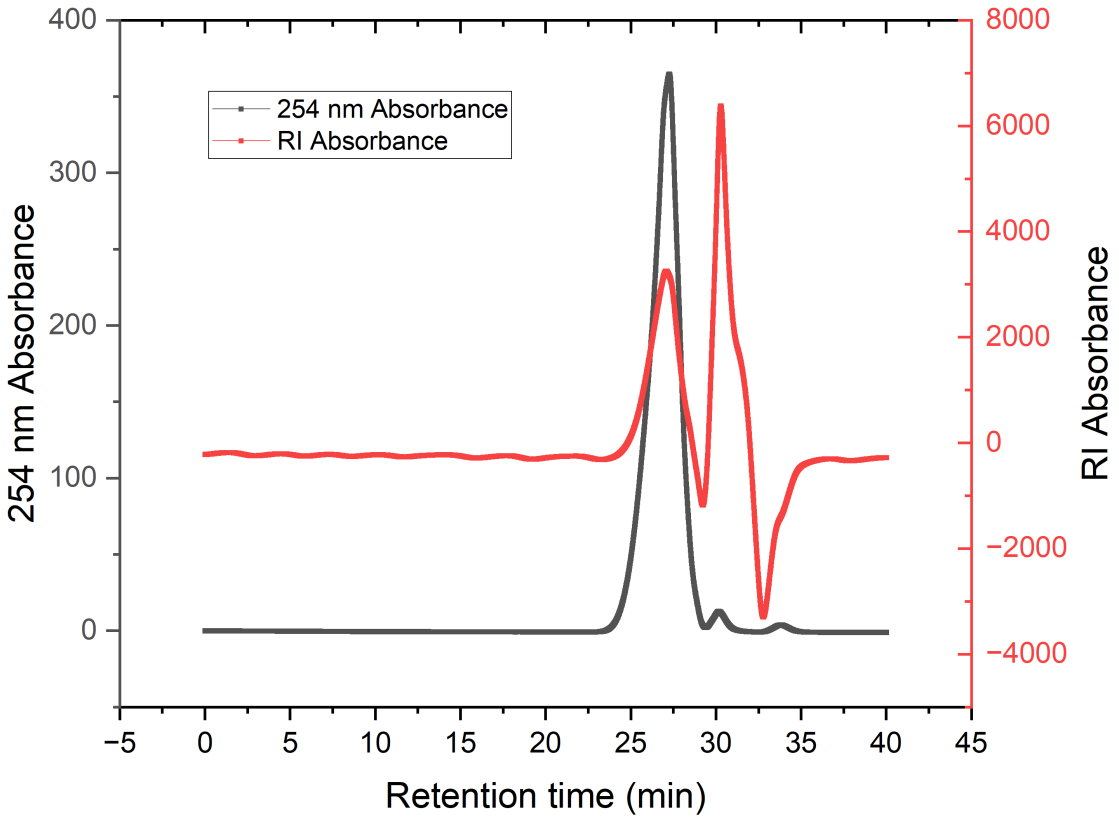


Figure 17. GPC traces of the reaction in Table S2, entry 14 using RID detection.

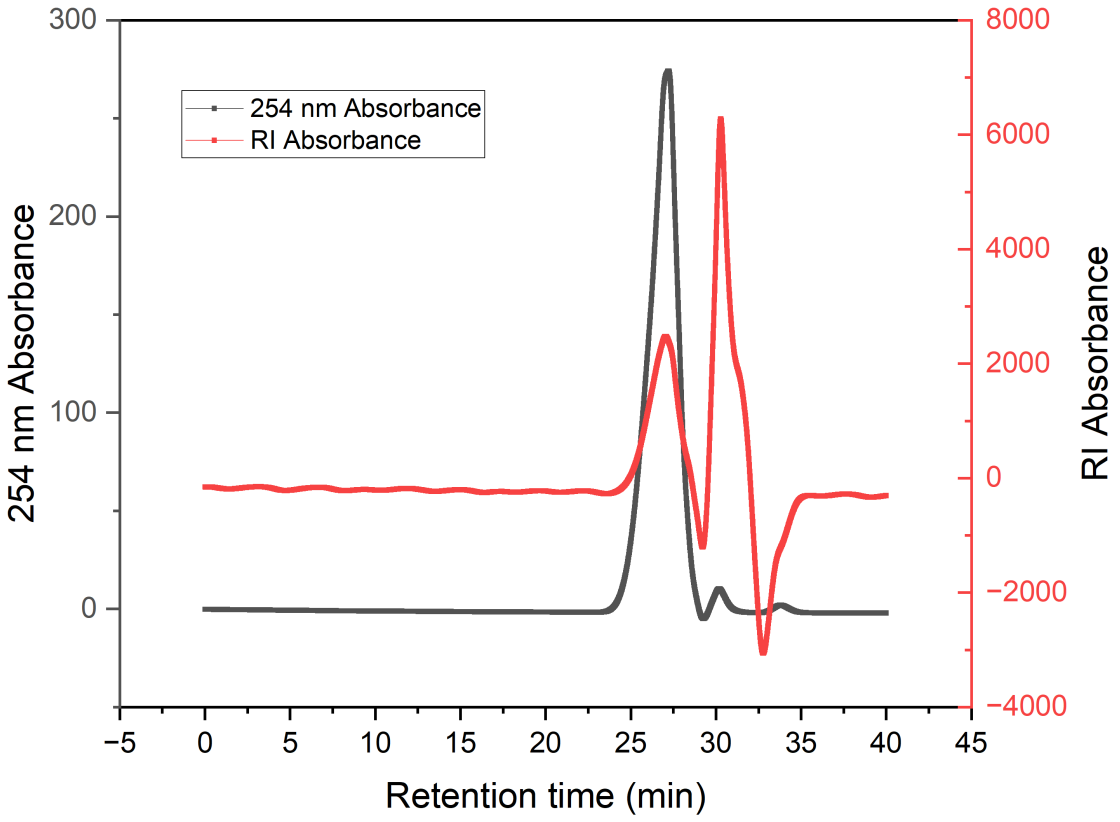
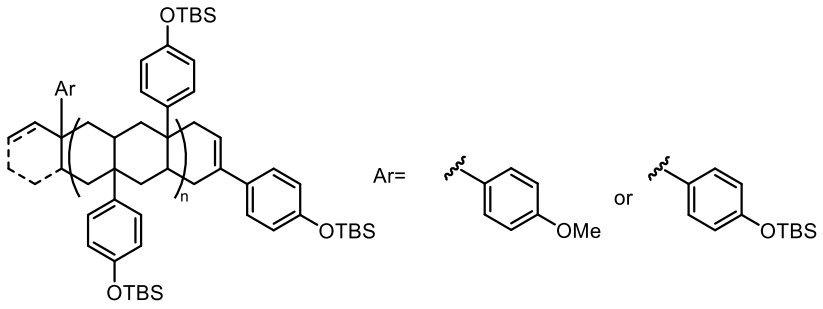


Figure S18. GPC traces of reaction in Table S2, entry 15.



dn/dc: 0.1429 mL/g
Concentration: 1.000 mg/mL

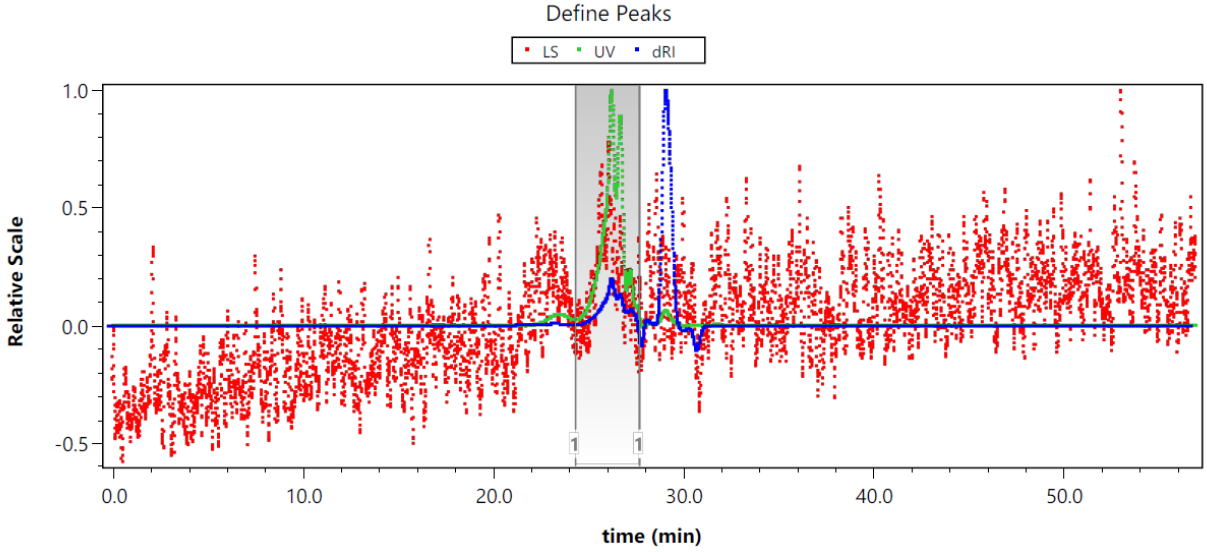
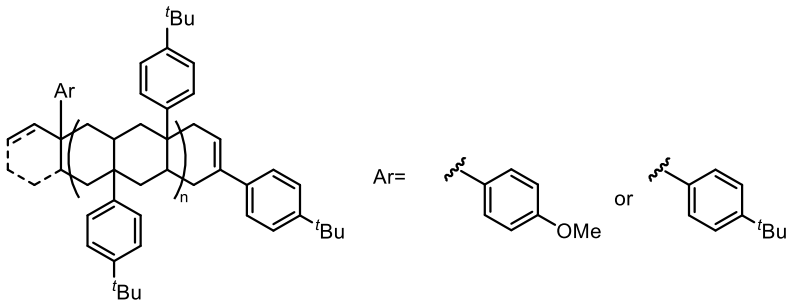


Figure S19. GPC traces of LP-3b measured with a MALS detector.



dn/dc: 0.1450 mL/g
Concentration: 1.000 mg/mL

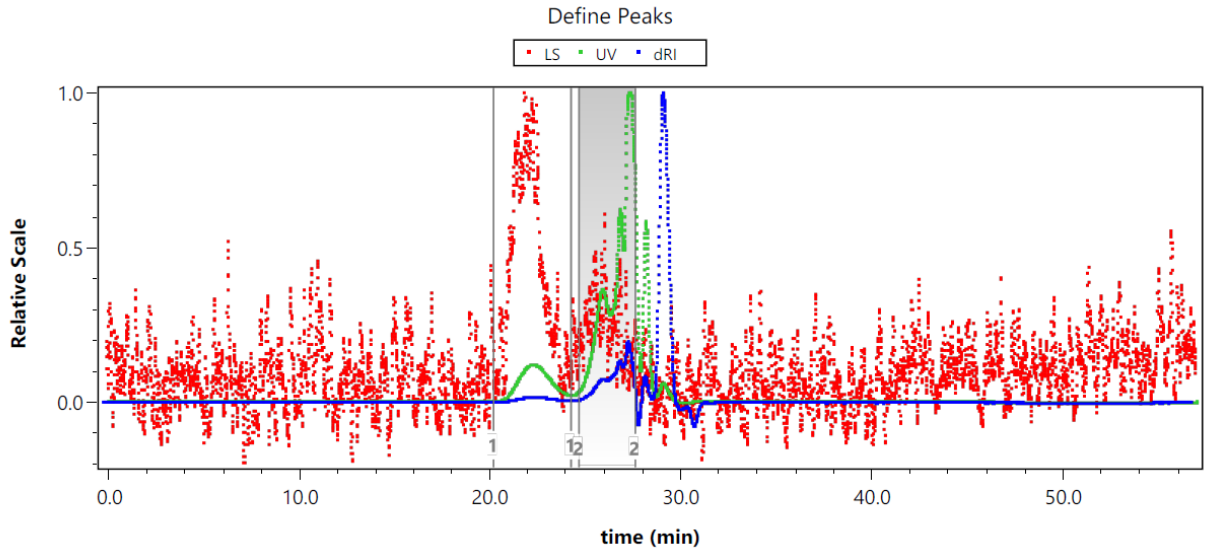
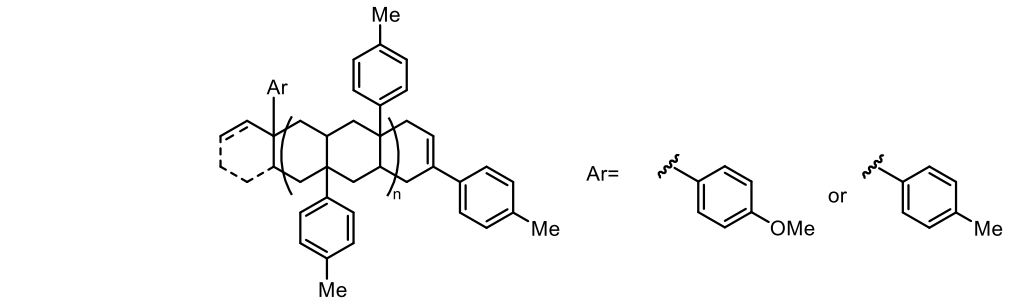


Figure S20. GPC traces of LP-3c measured with a MALS detector.



dn/dc: 0.3967 mL/g
Concentration: 1.000 mg/mL

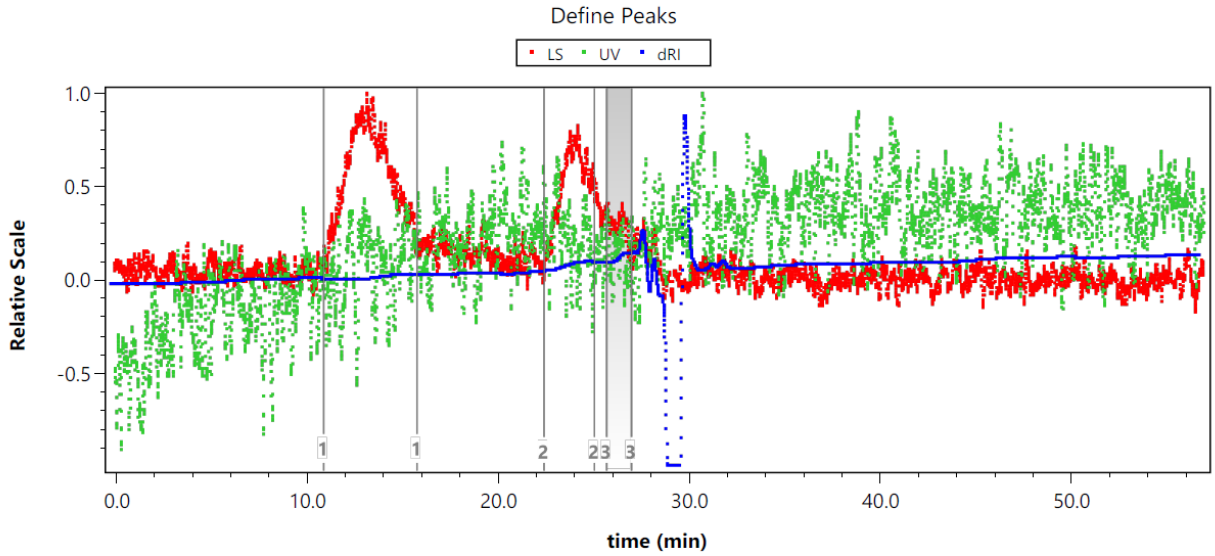
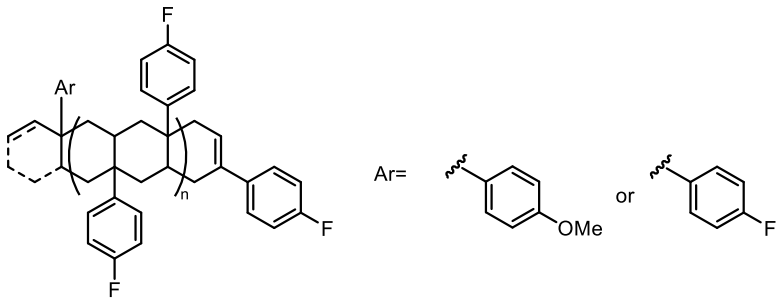


Figure S21. GPC traces of LP-3d using a MALS detector. M_n, M_w, and Đ were determined based on region 2.



dn/dc: 0.2666 mL/g
Concentration: 1.000 mg/mL

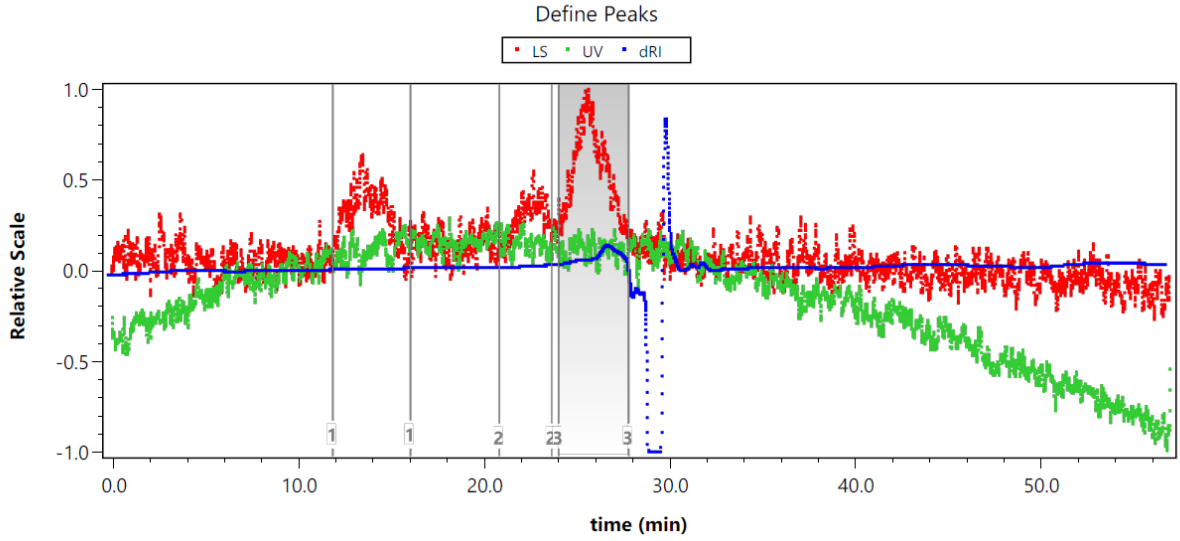


Figure S22. GPC traces of LP-3e using a MALS detector.

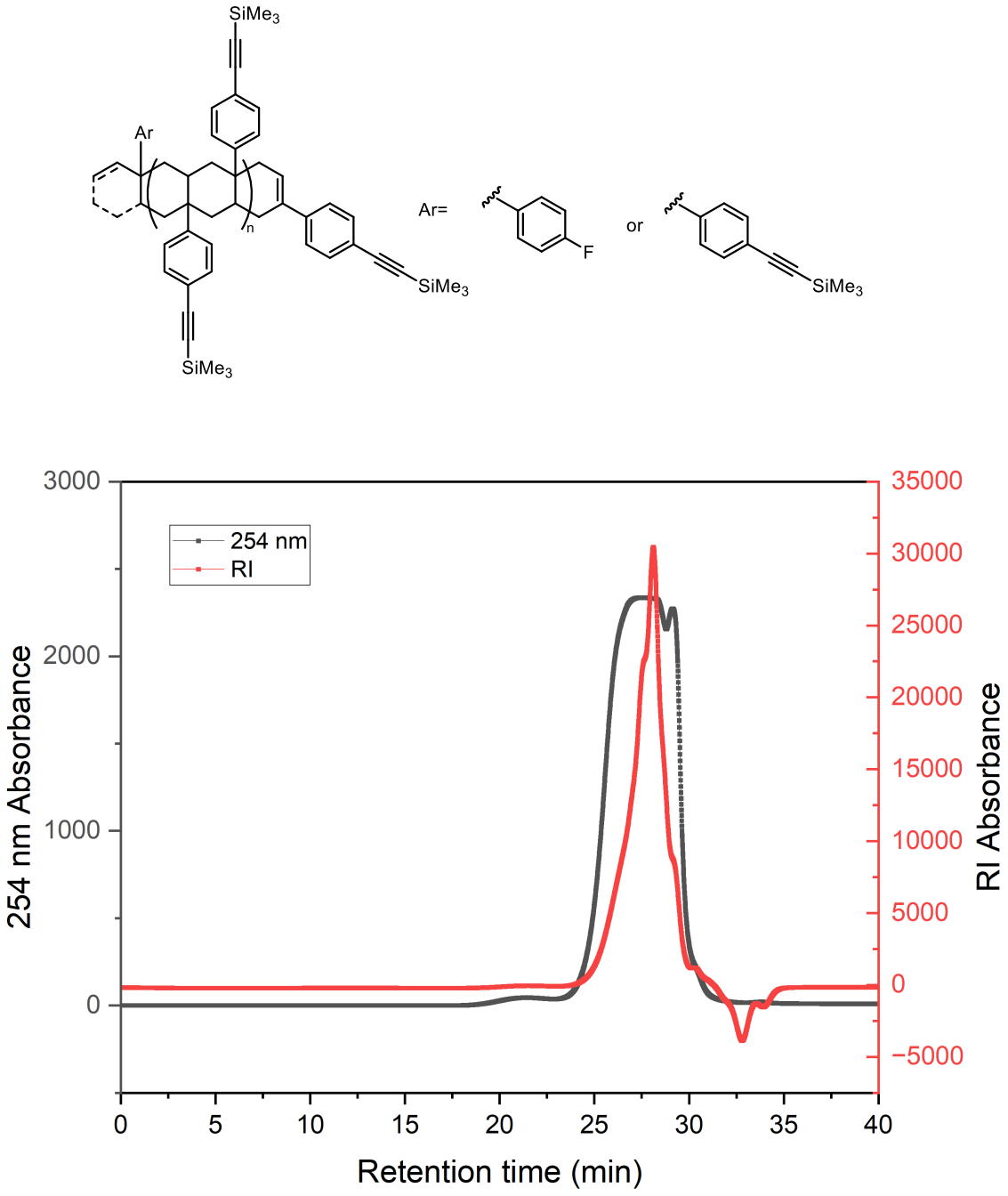


Figure S23. GPC of LP-3f using RI detection.

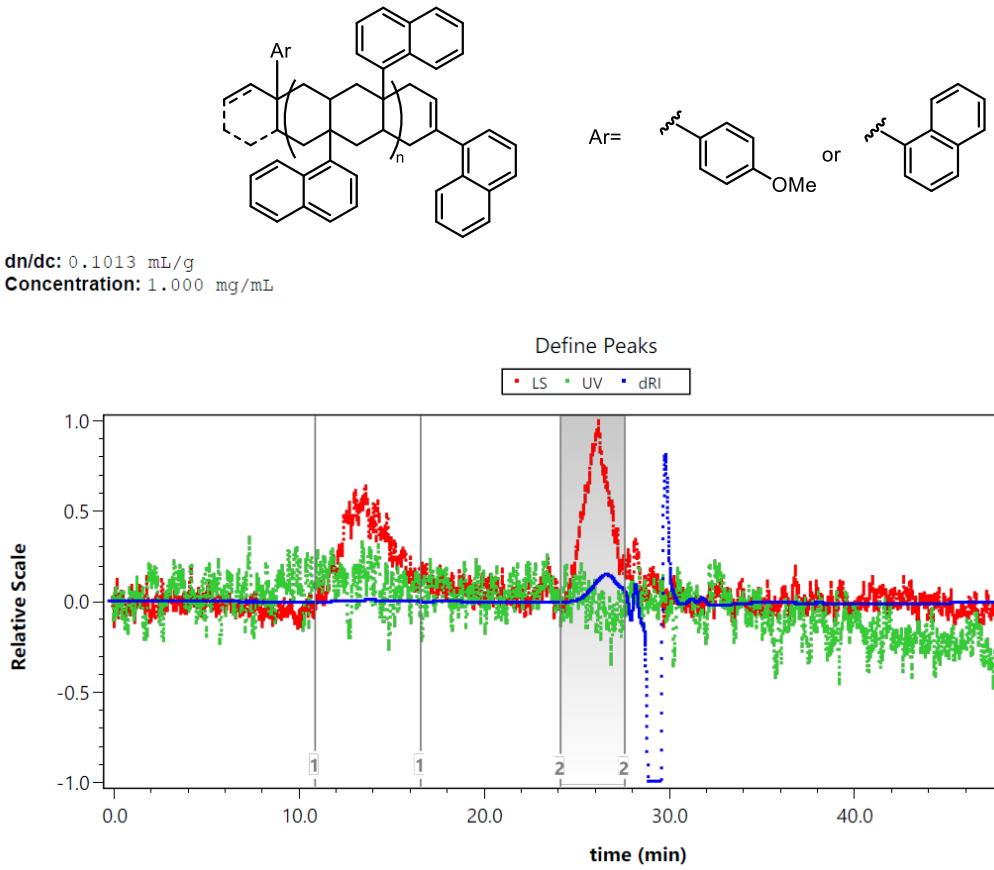


Figure S24. GPC traces of LP-3g using a MALS detector.

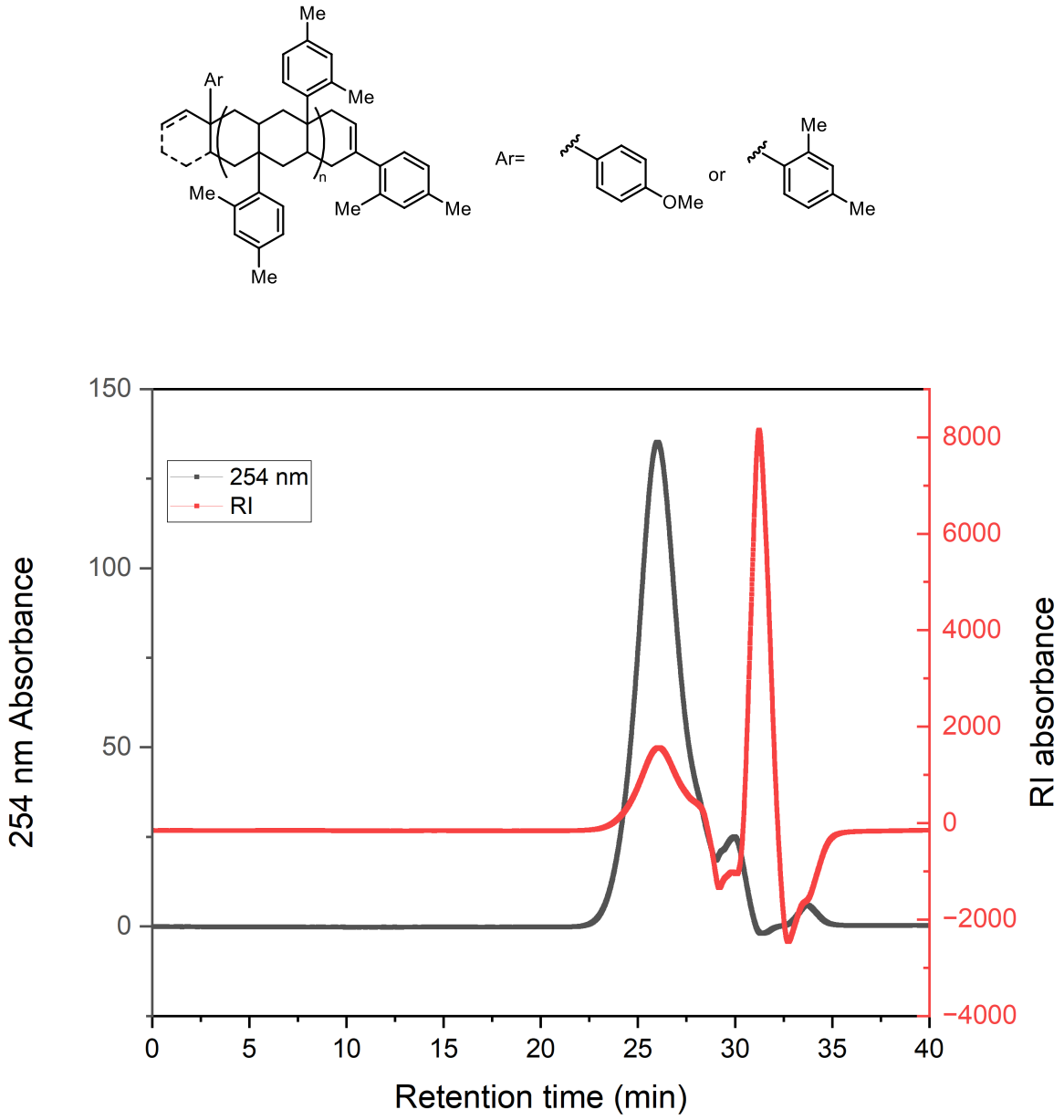


Figure S25. GPC of LP-3h using RID detection.

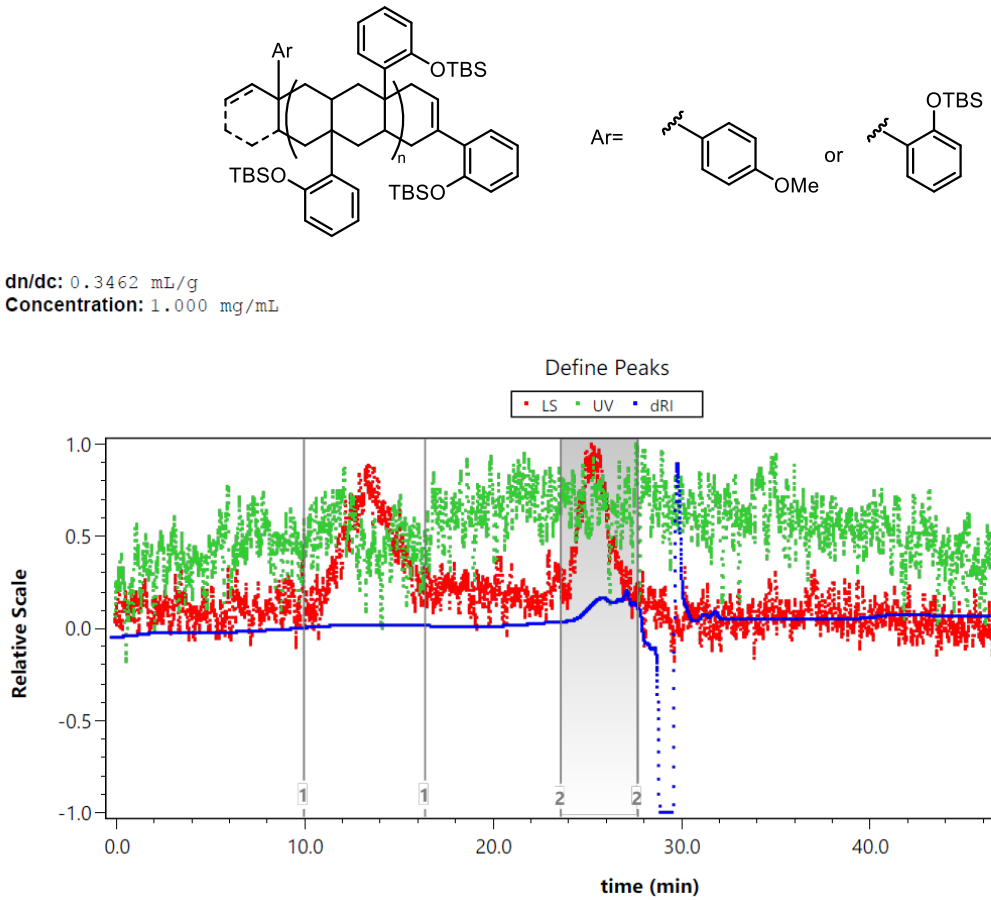


Figure S26. GPC traces of LP-3i using a MALS detector.

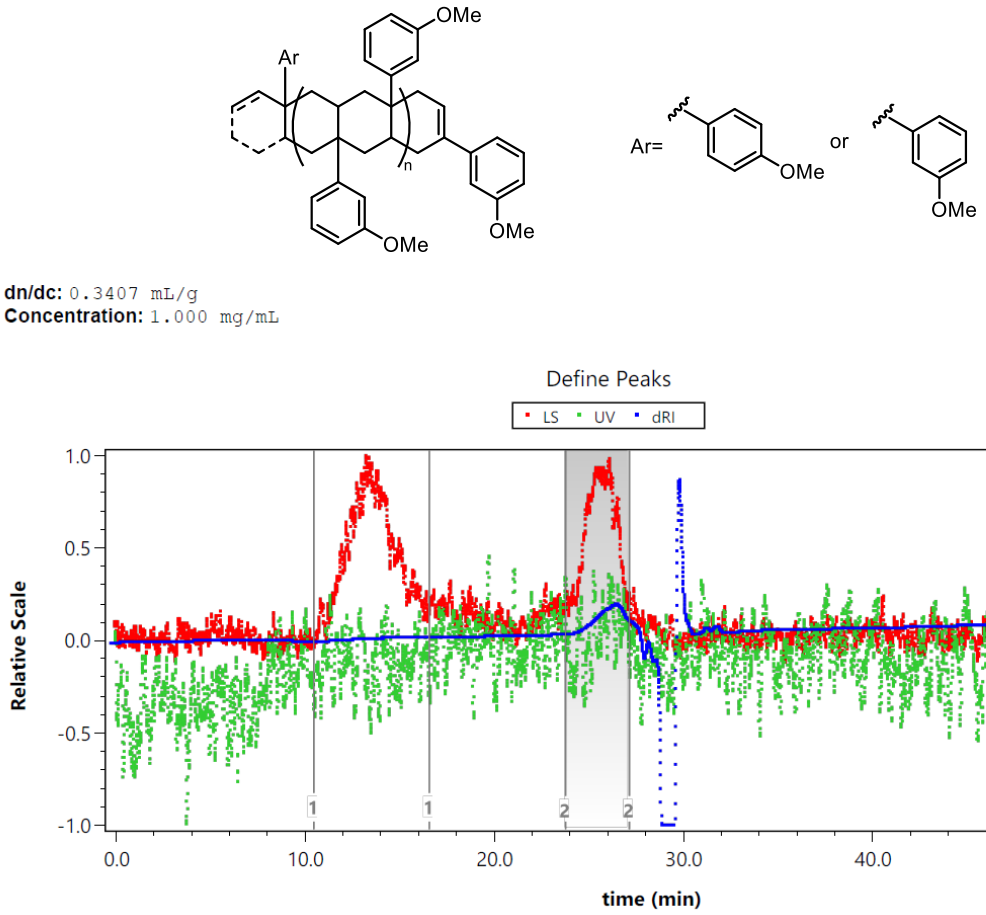
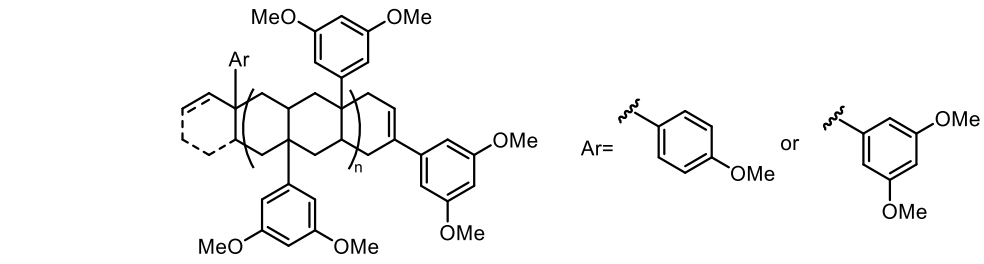


Figure S27. GPC traces of LP-3J using a MALS detector.



dn/dc: 0.2230 mL/g
Concentration: 1.000 mg/mL

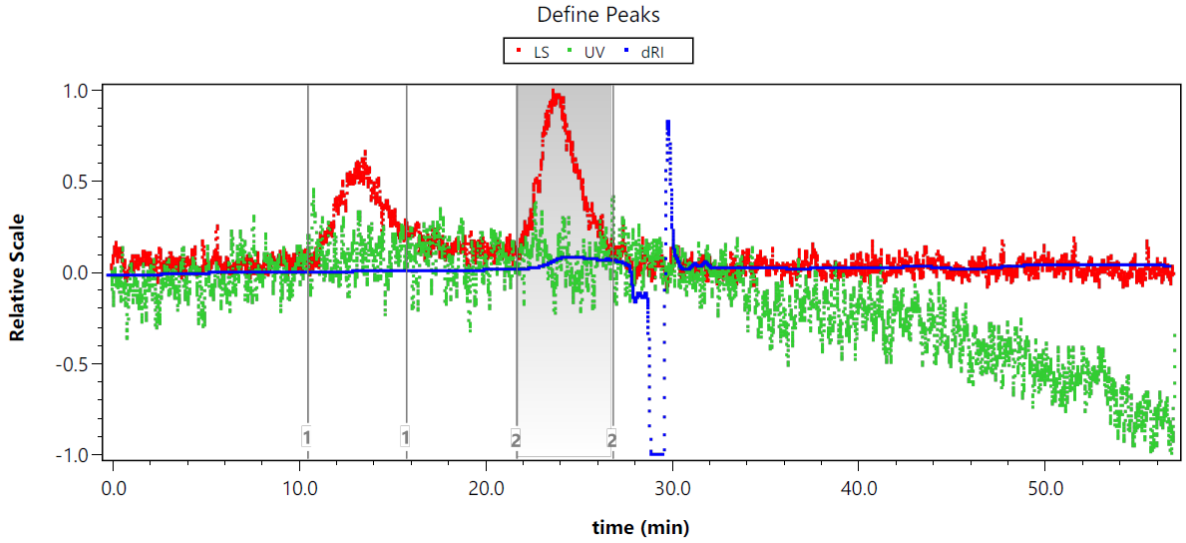


Figure S28. GPC traces of LP-3k using a MALS detector.

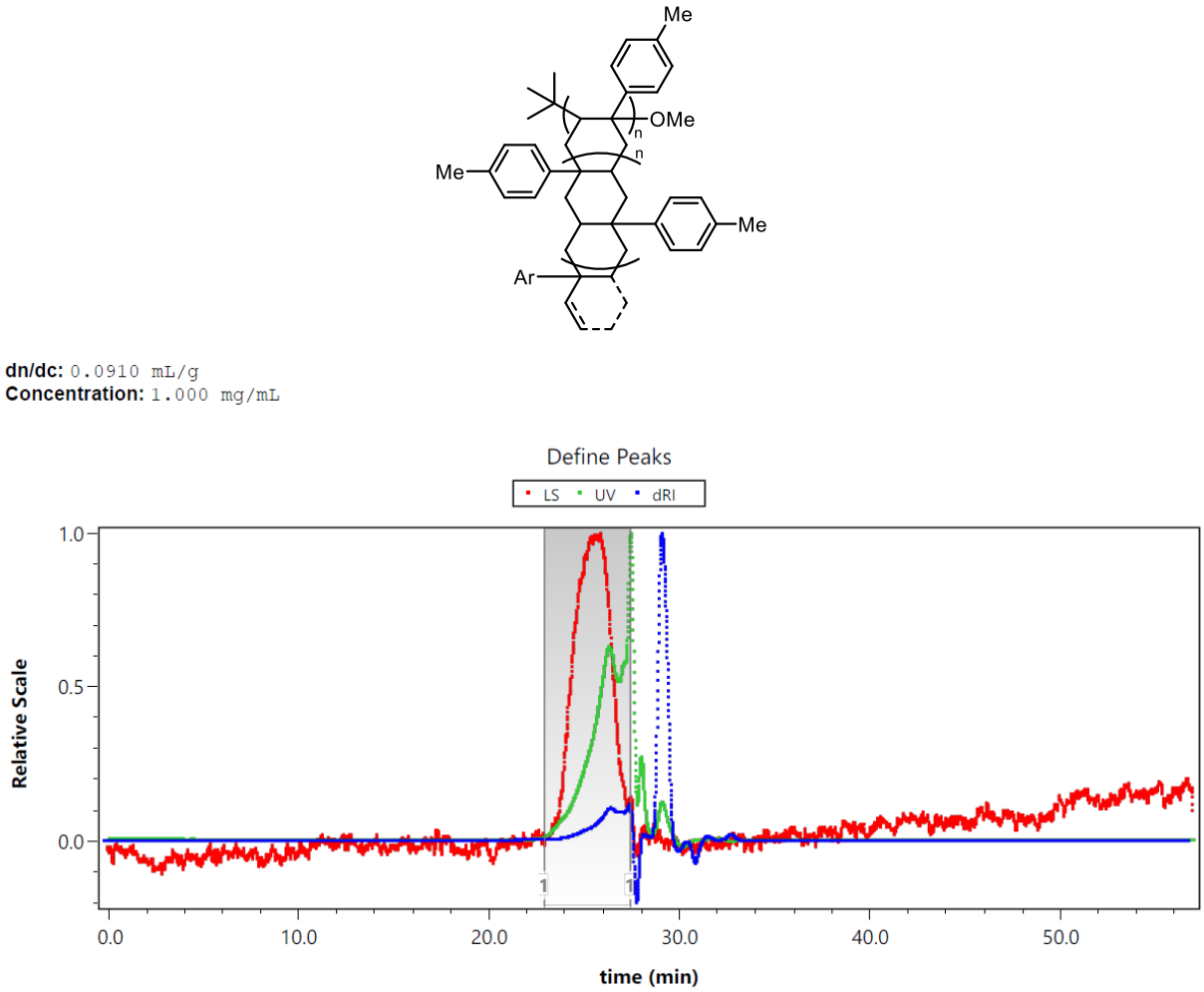


Figure 29. GPC traces of LP-3d-ext using a MALS detector.

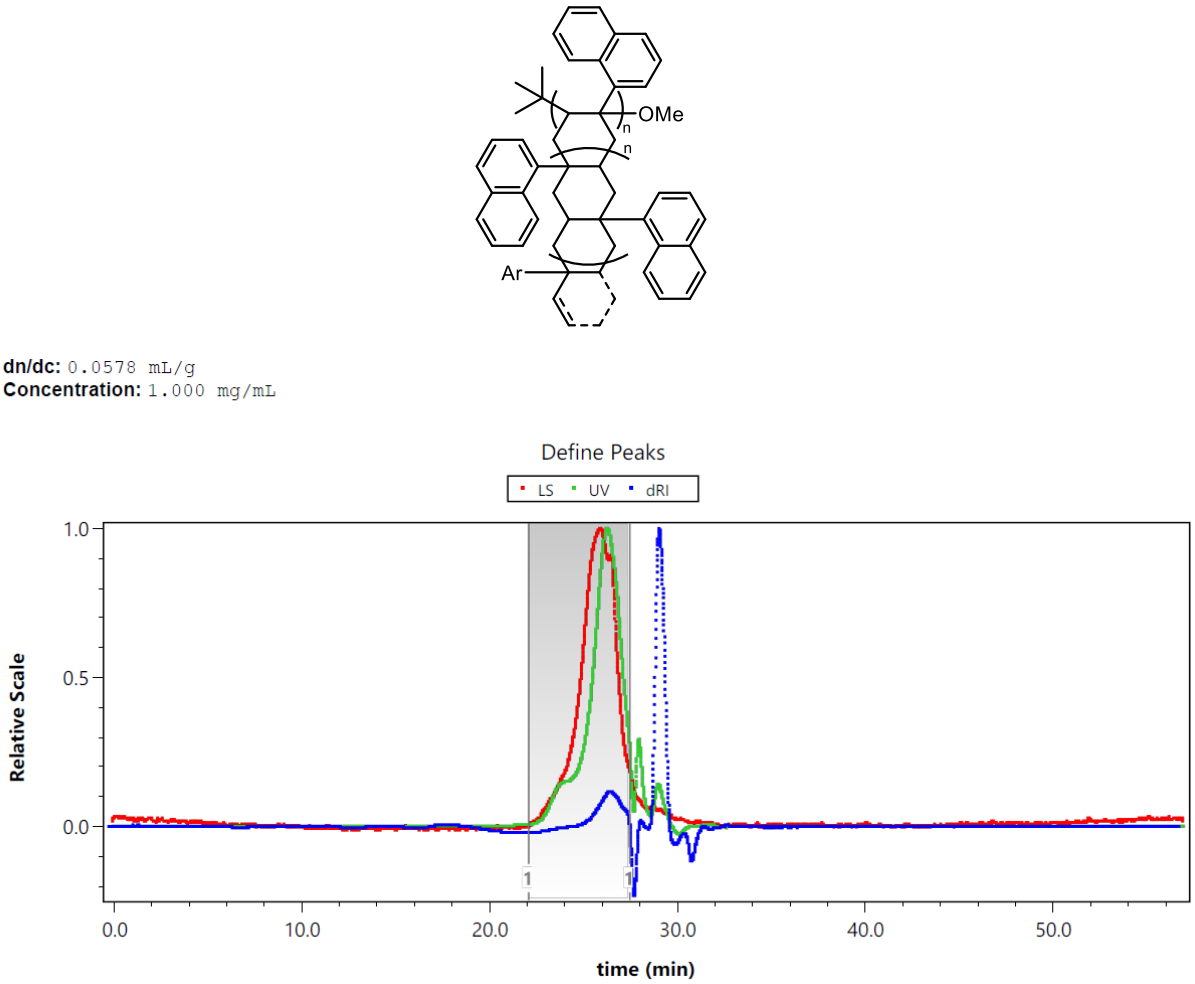
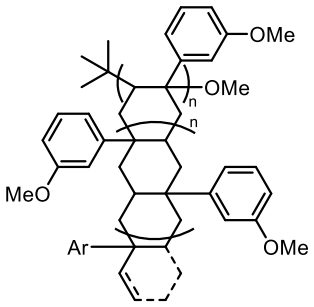


Figure S30. GPC traces of LP-3g-ext using a MALS detector.



dn/dc: 0.1423 mL/g
Concentration: 1.000 mg/mL

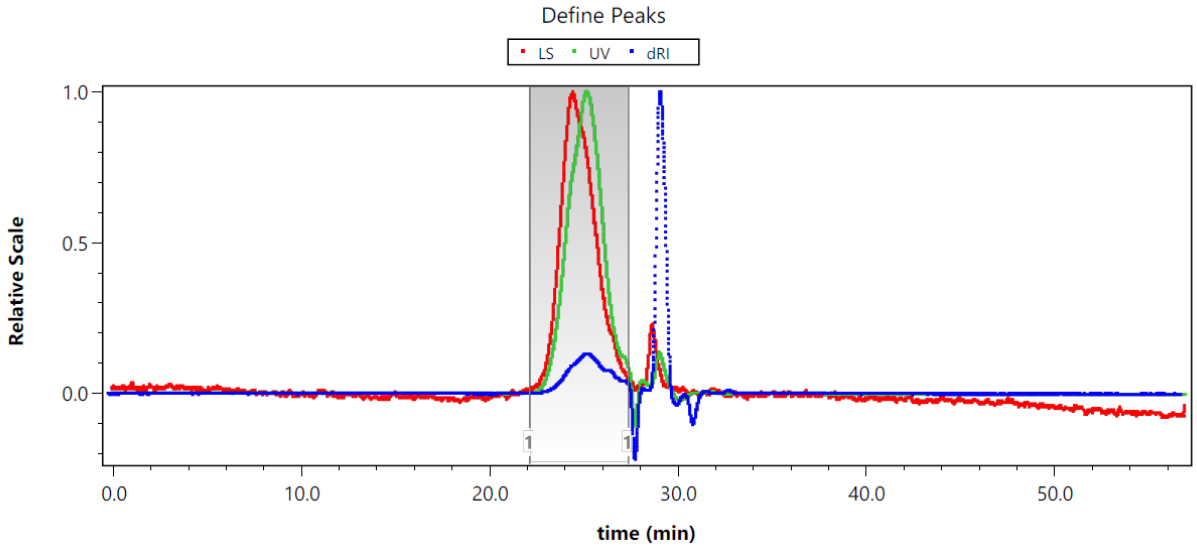
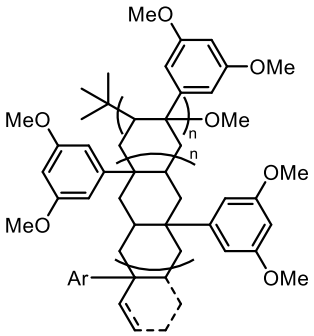


Figure S31. GPC trace of LP-3J-ext using a MALS detector.



dn/dc: 0.0771 mL/g
Concentration: 1.000 mg/mL

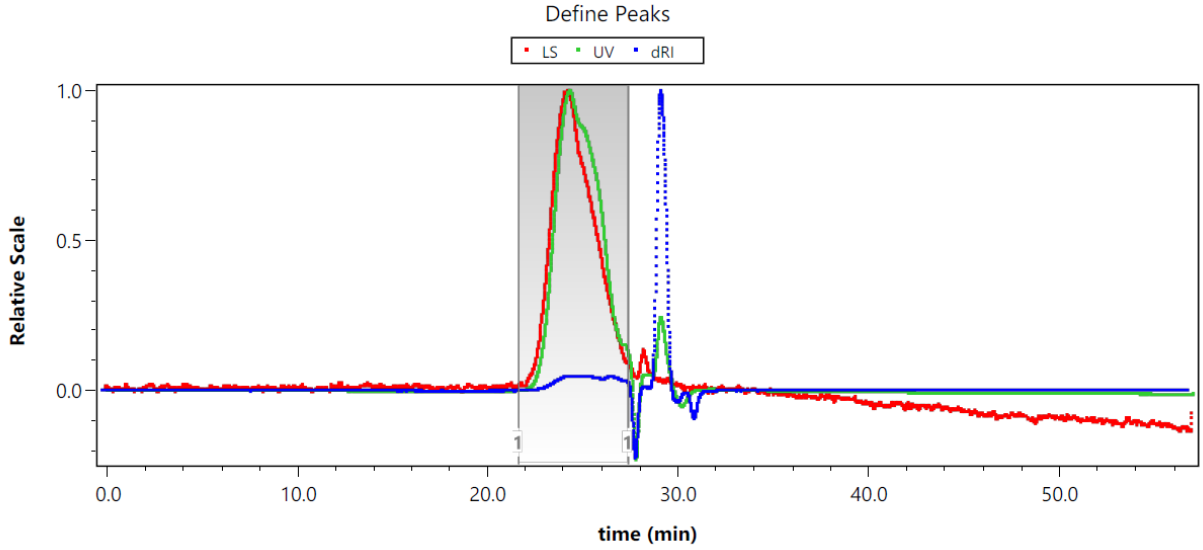


Figure S32. GPC trace of LP-3k-ext using a MALS detector.

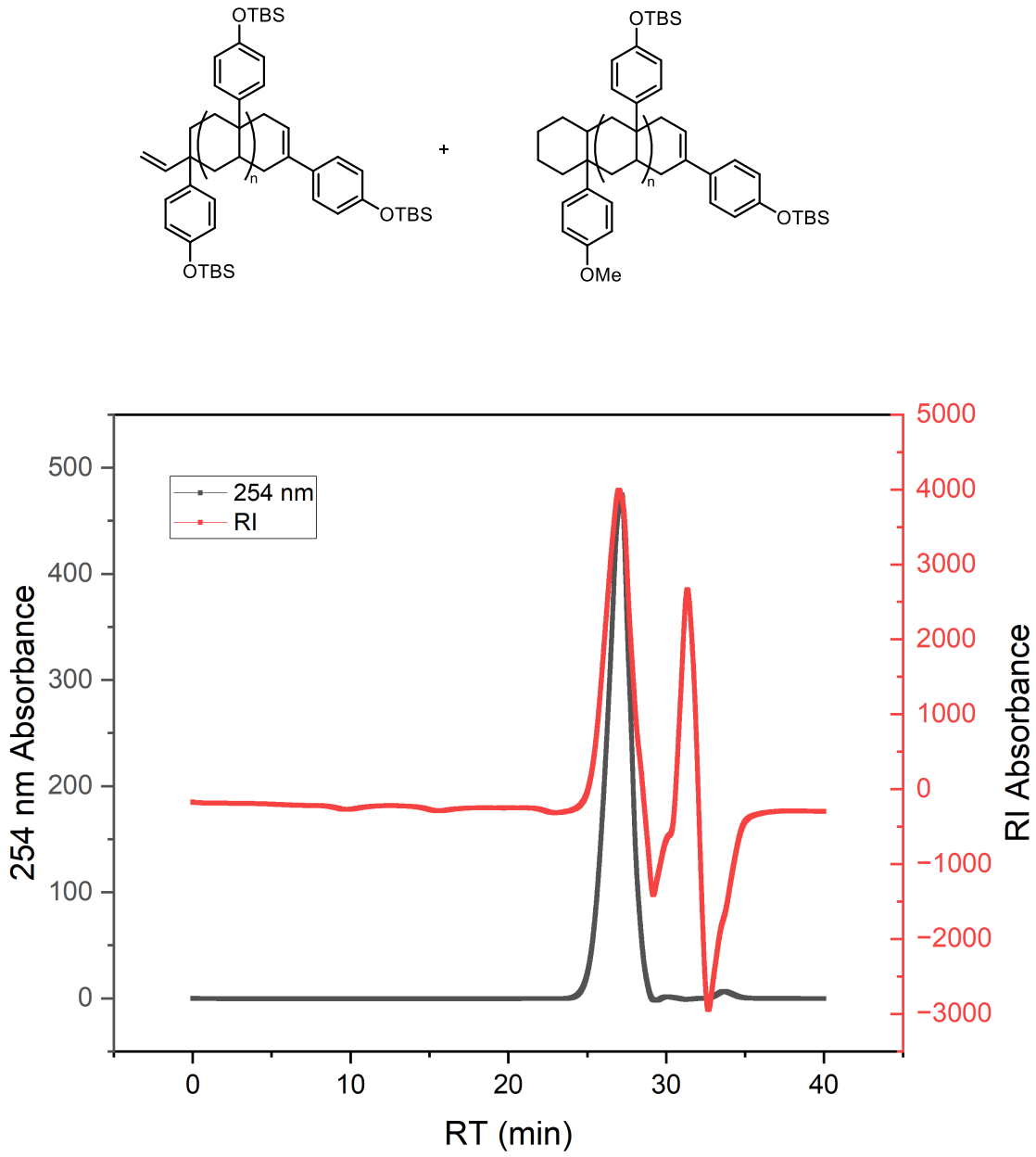
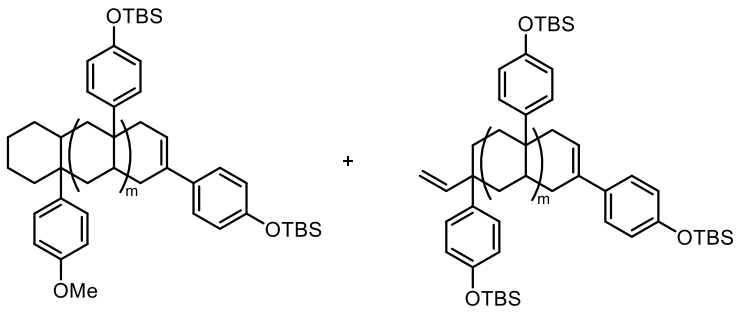


Figure S33 GPC trace of entry 1 in Table S5 (LP-3b before extension experiment)



LP-3b"

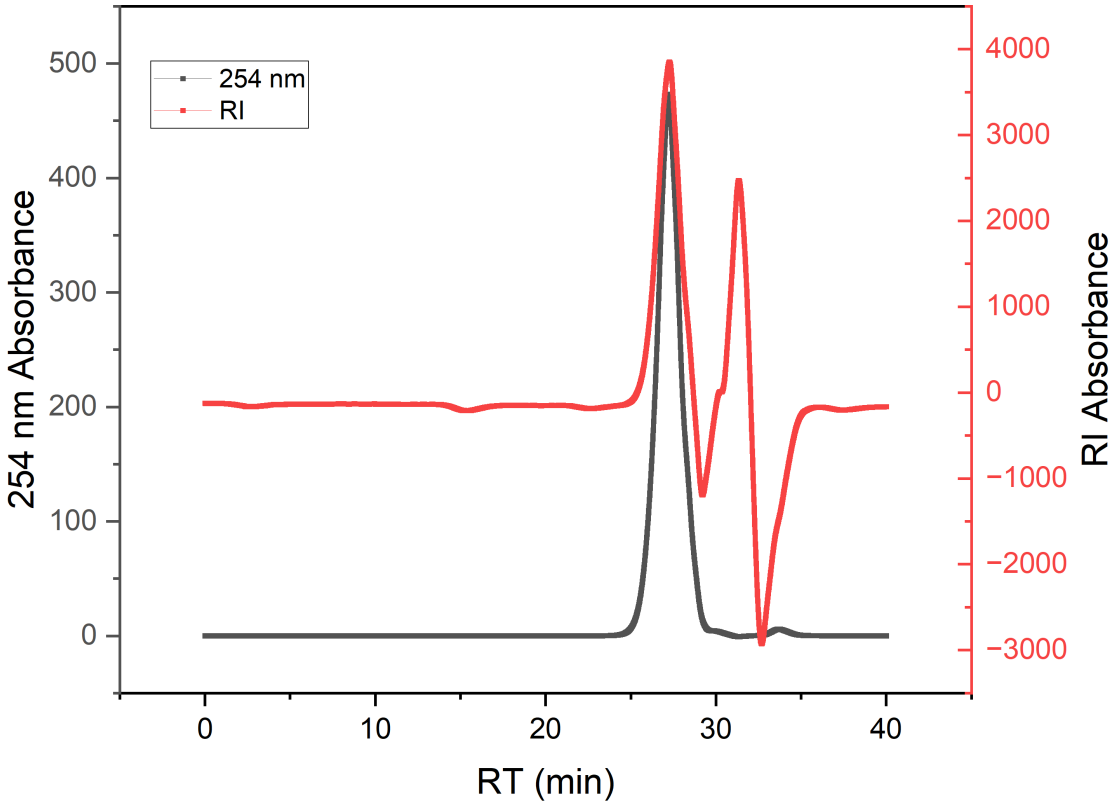


Figure S34. GPC trace of LP-3b" (entry 2 in Table S5. Extension experimenta

VIII. NMR Spectra

4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (1)

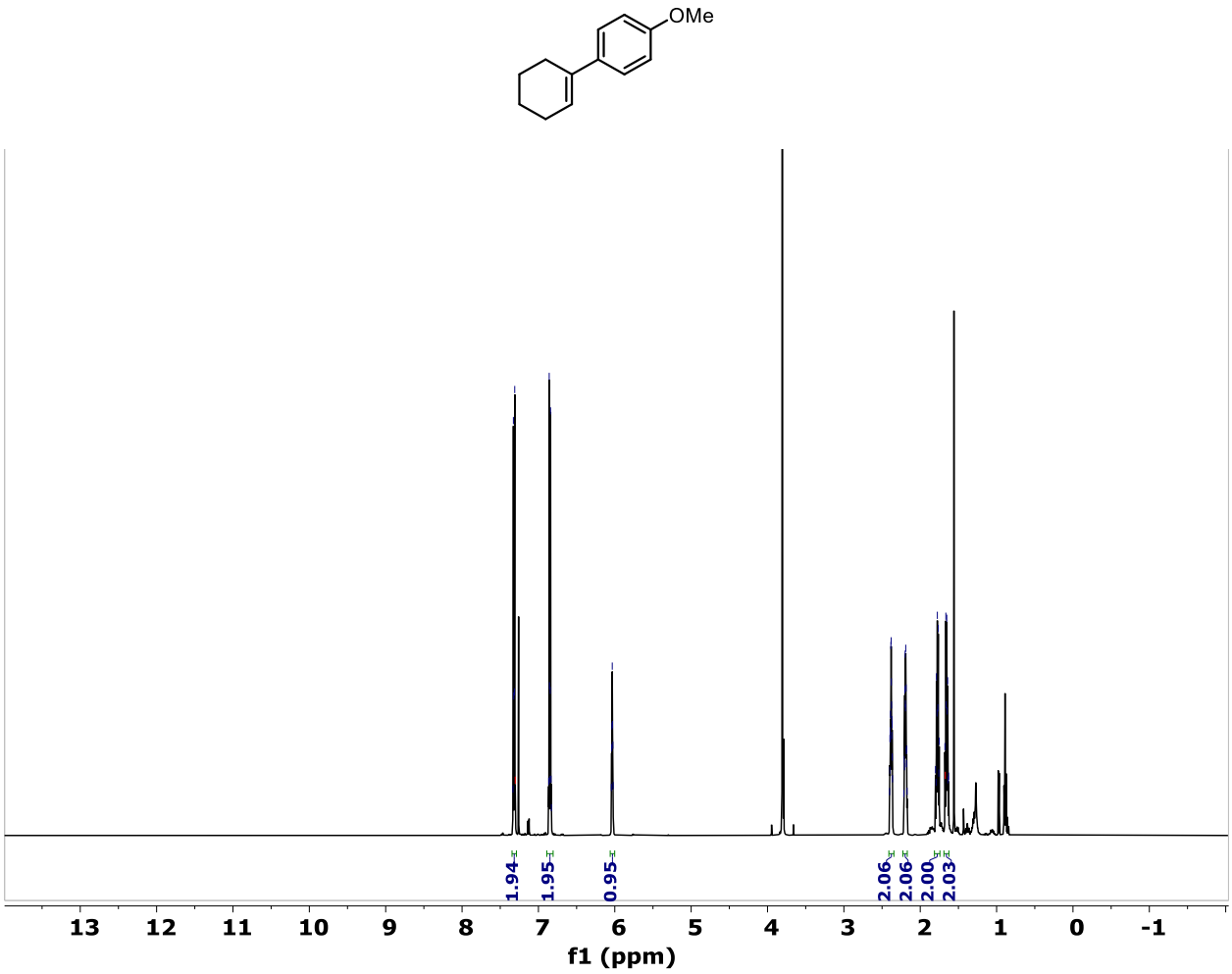


Figure S35 ^{1}H NMR, $CDCl_3$-*d* of 4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (**1**)

2 (4a-(4-methoxyphenyl)-7-methyl-1,2,3,4,4a,5,8,8a-octahydronaphthalene)

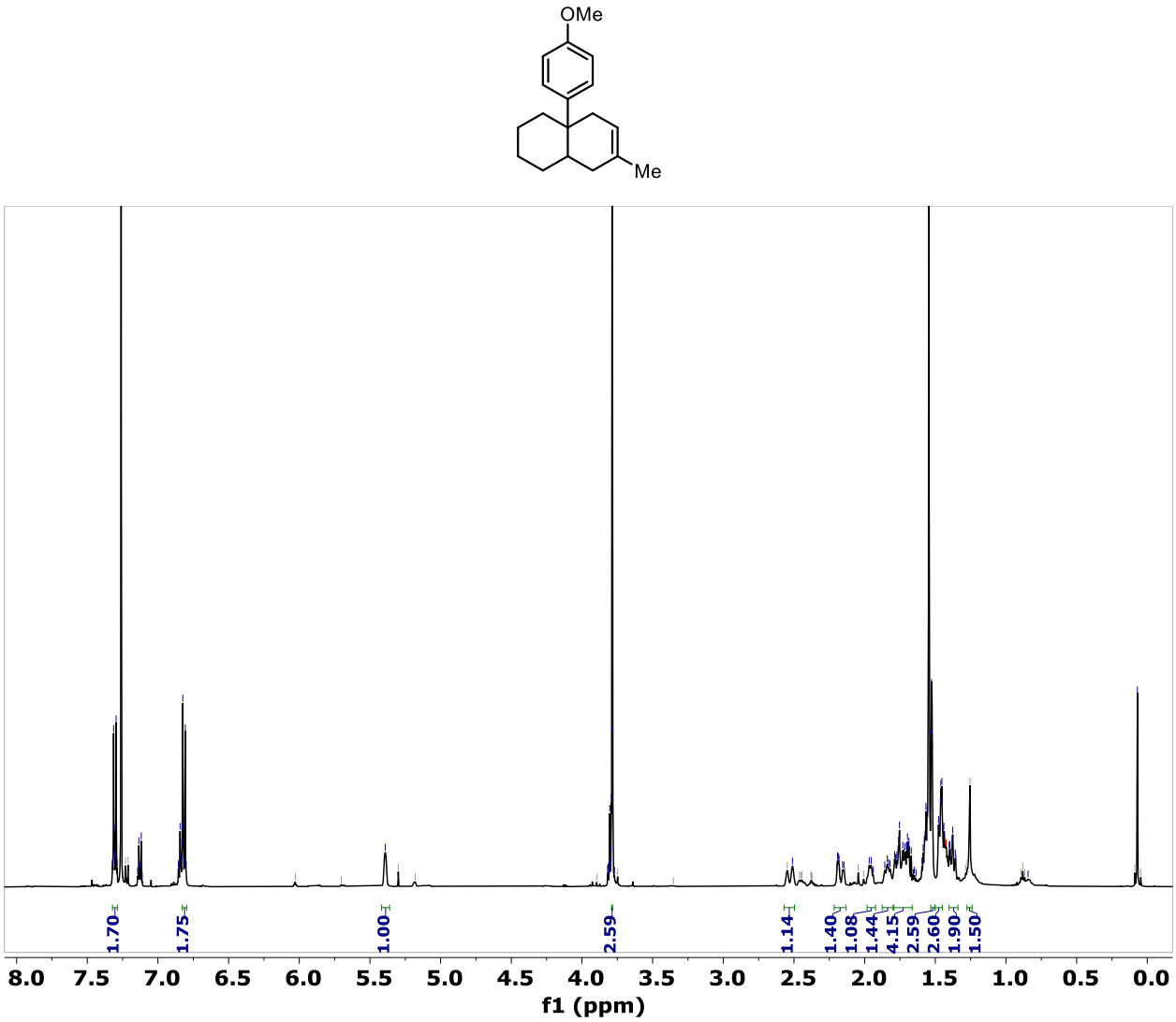


Figure S36 ^{1}H NMR, $CDCl_3$-*d* of **2** (with some unreacted starting material as an impurity).

2-(4-(tert-butyl)phenyl)but-3-en-2-ol

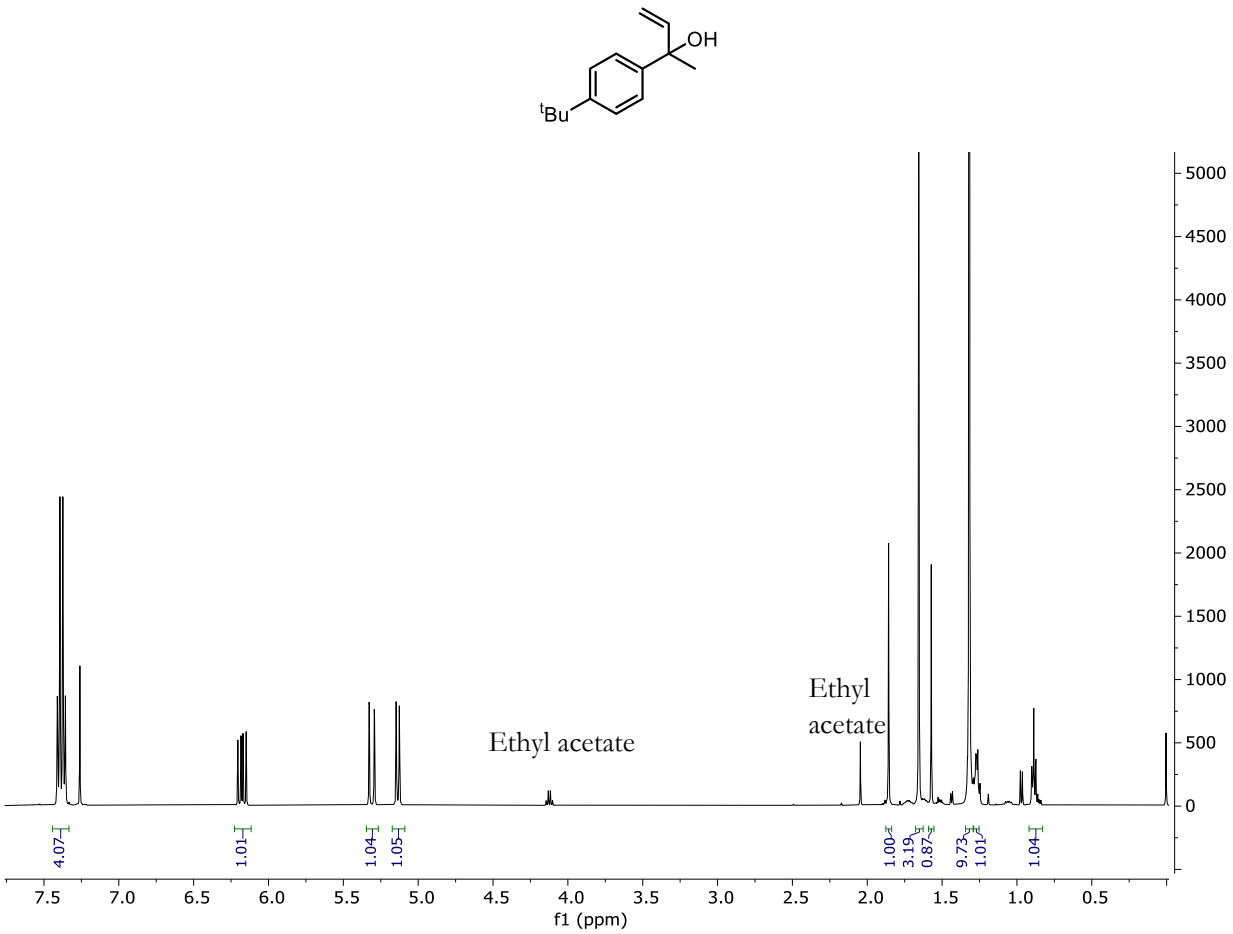


Figure S37 ^{1}H NMR, $CDCl_3$-*d* of 2-(4-(tert-butyl)phenyl)but-3-en-2-ol

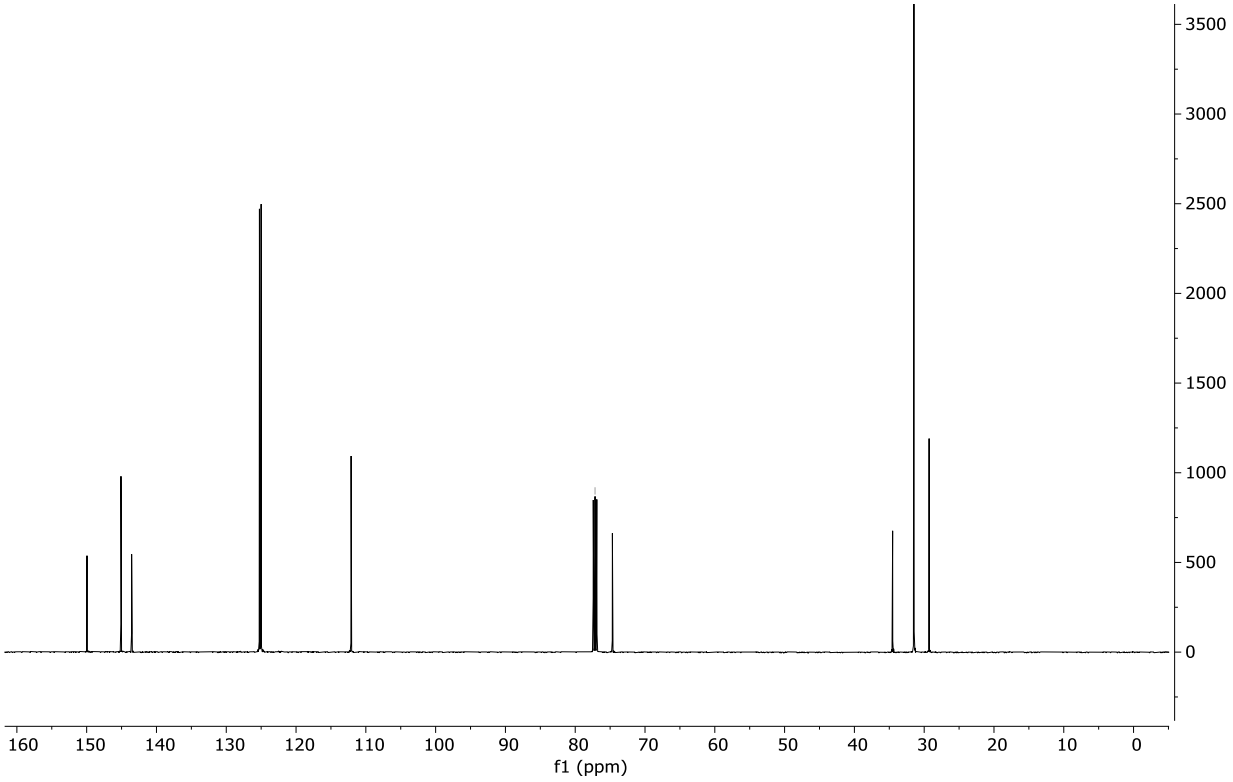


Figure S38 ^{13}C NMR, $CDCl_3$-*d* of 2-(4-(tert-butyl)phenyl)but-3-en-2-ol

1-(4-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one

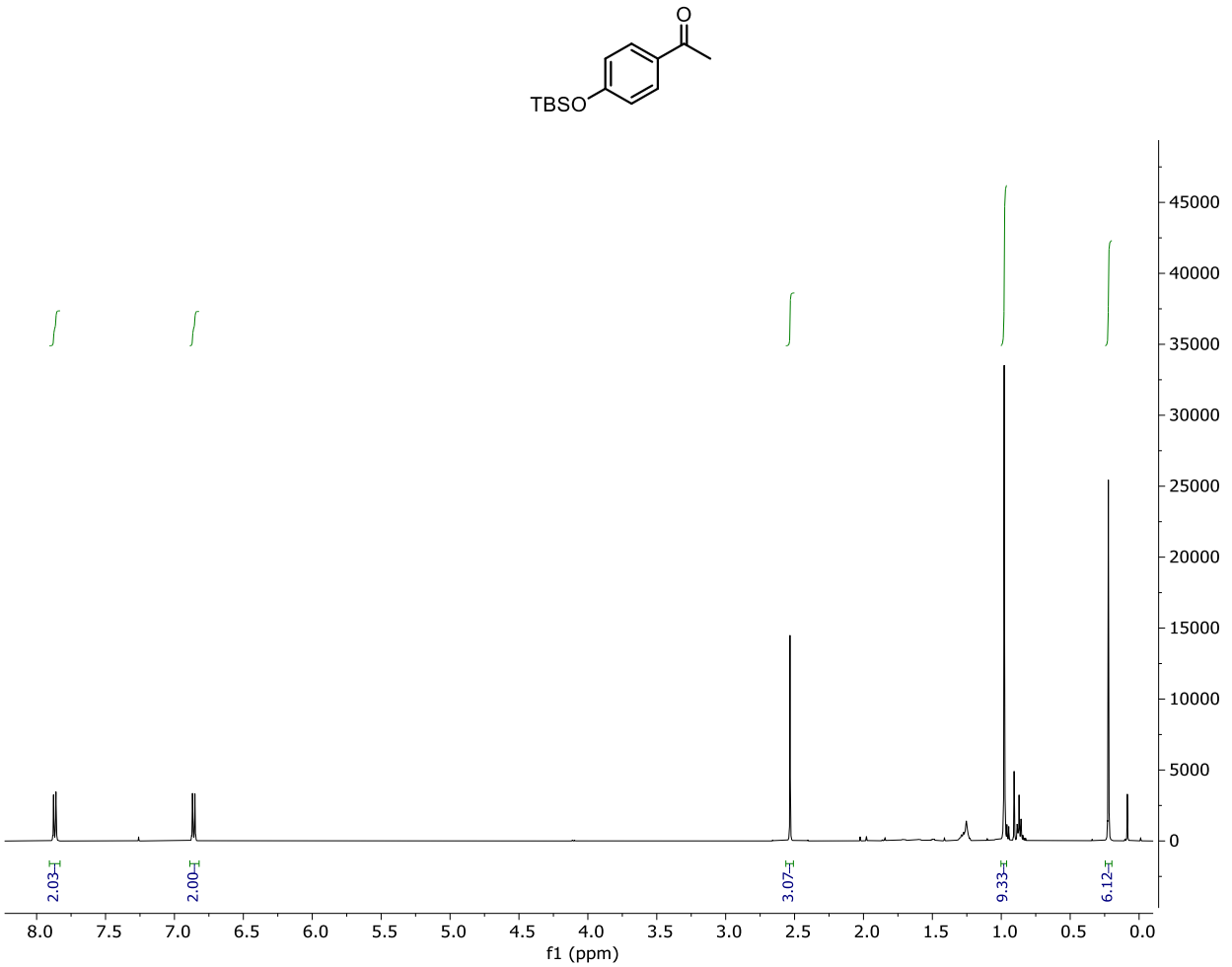


Figure S39 ^{1}H NMR, $CDCl_3$-*d* of 1-(4-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one

1-(2-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one

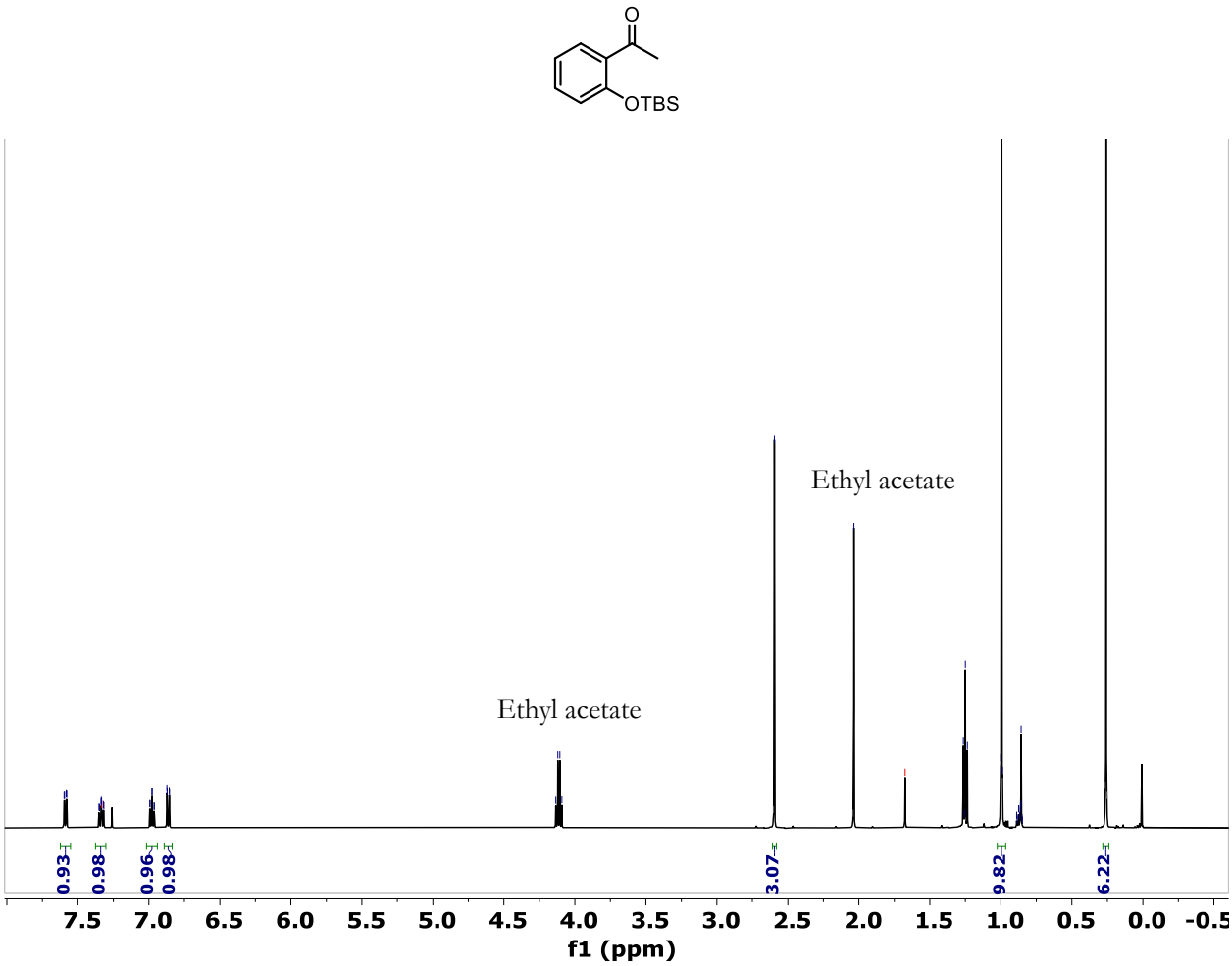


Figure S40 ^{1}H NMR, $CDCl_3$-*d* of 1-(2-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one

2-(4-((tert-butyldimethylsilyl)oxy)phenyl)but-3-en-2-ol

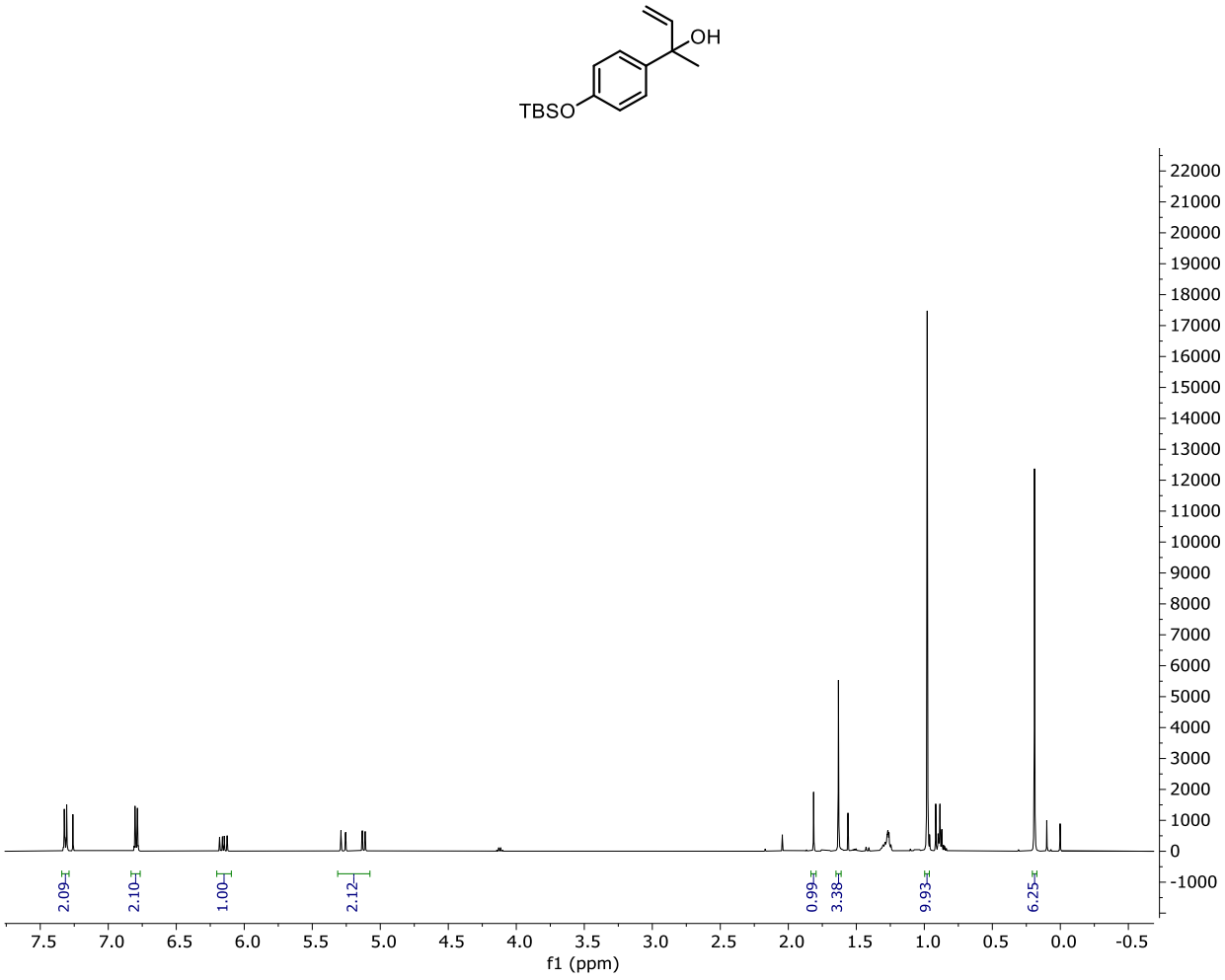


Figure S41 ^{1}H NMR, $CDCl_3$-*d* of 2-(4-((tert-butyldimethylsilyl)oxy)phenyl)but-3-en-2-ol

2-(3-methoxyphenyl)but-3-en-2-ol

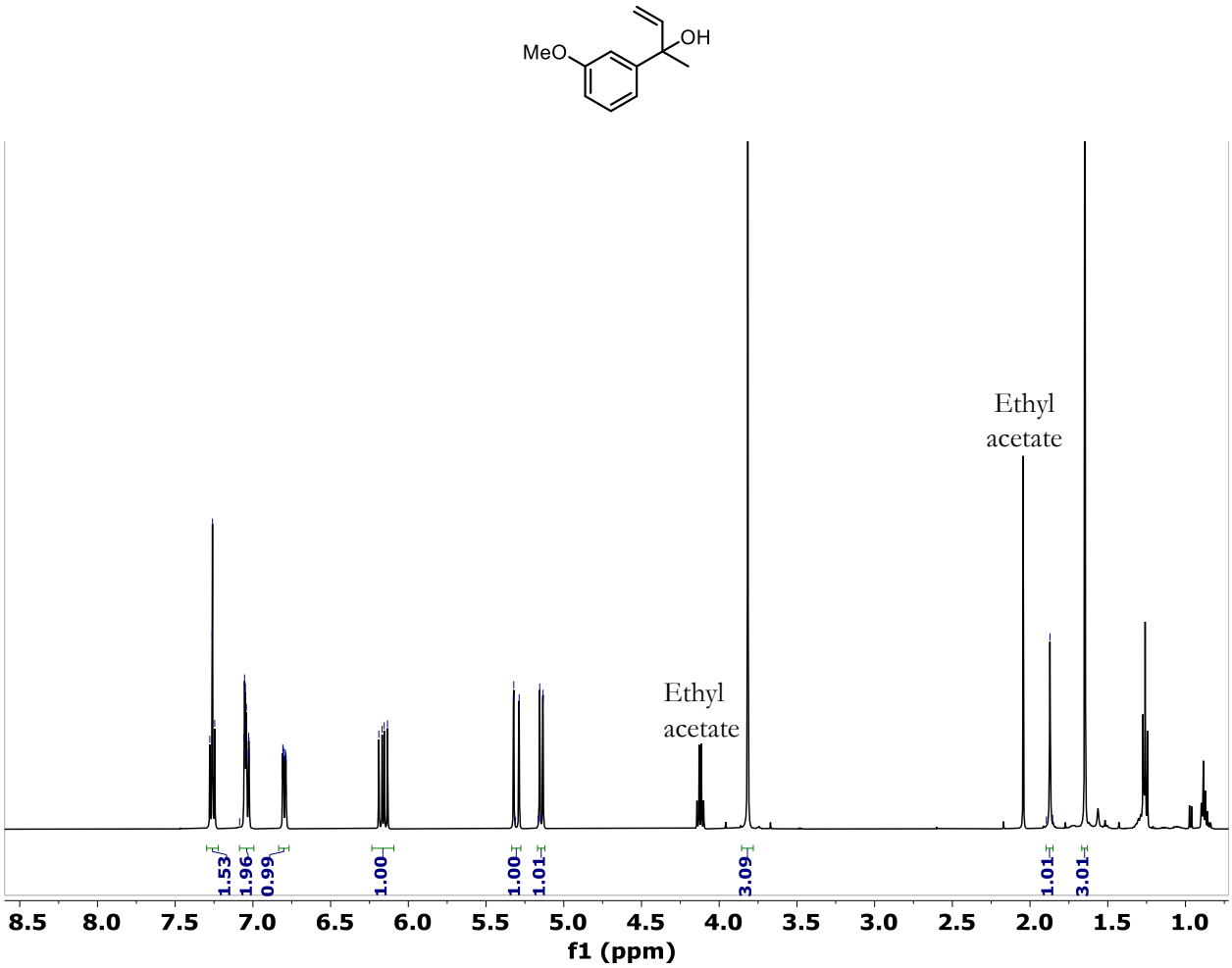


Figure S42 ^{1}H NMR, $CDCl_3$-*d* of 2-(3-methoxyphenyl)but-3-en-2-ol

2-(3,5-dimethoxyphenyl)but-3-en-2-ol

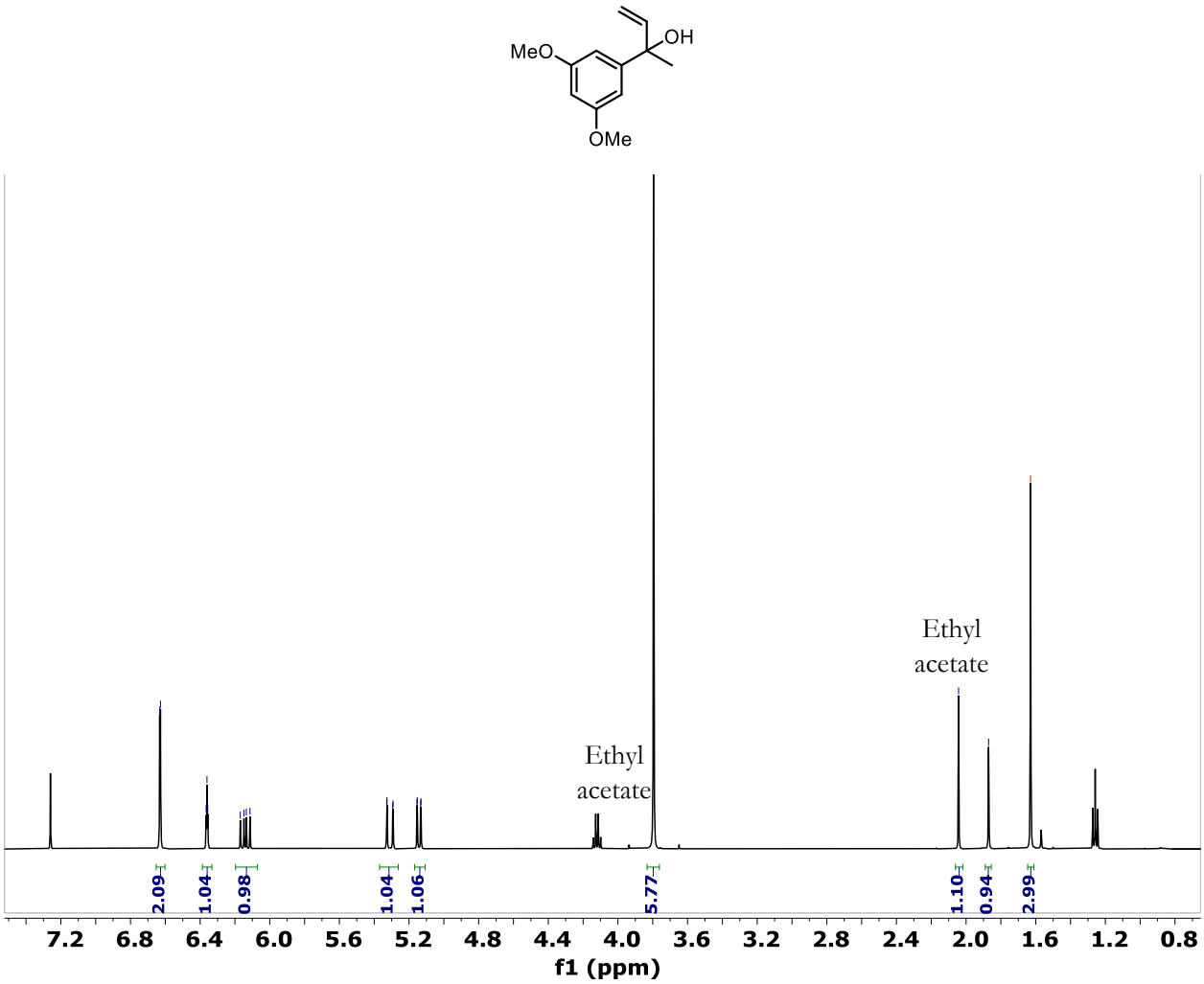


Figure S43 ^{1}H NMR, $CDCl_3$-*d* of 2-(3,5-dimethoxyphenyl)but-3-en-2-ol

2-(4-fluorophenyl)but-3-en-2-ol

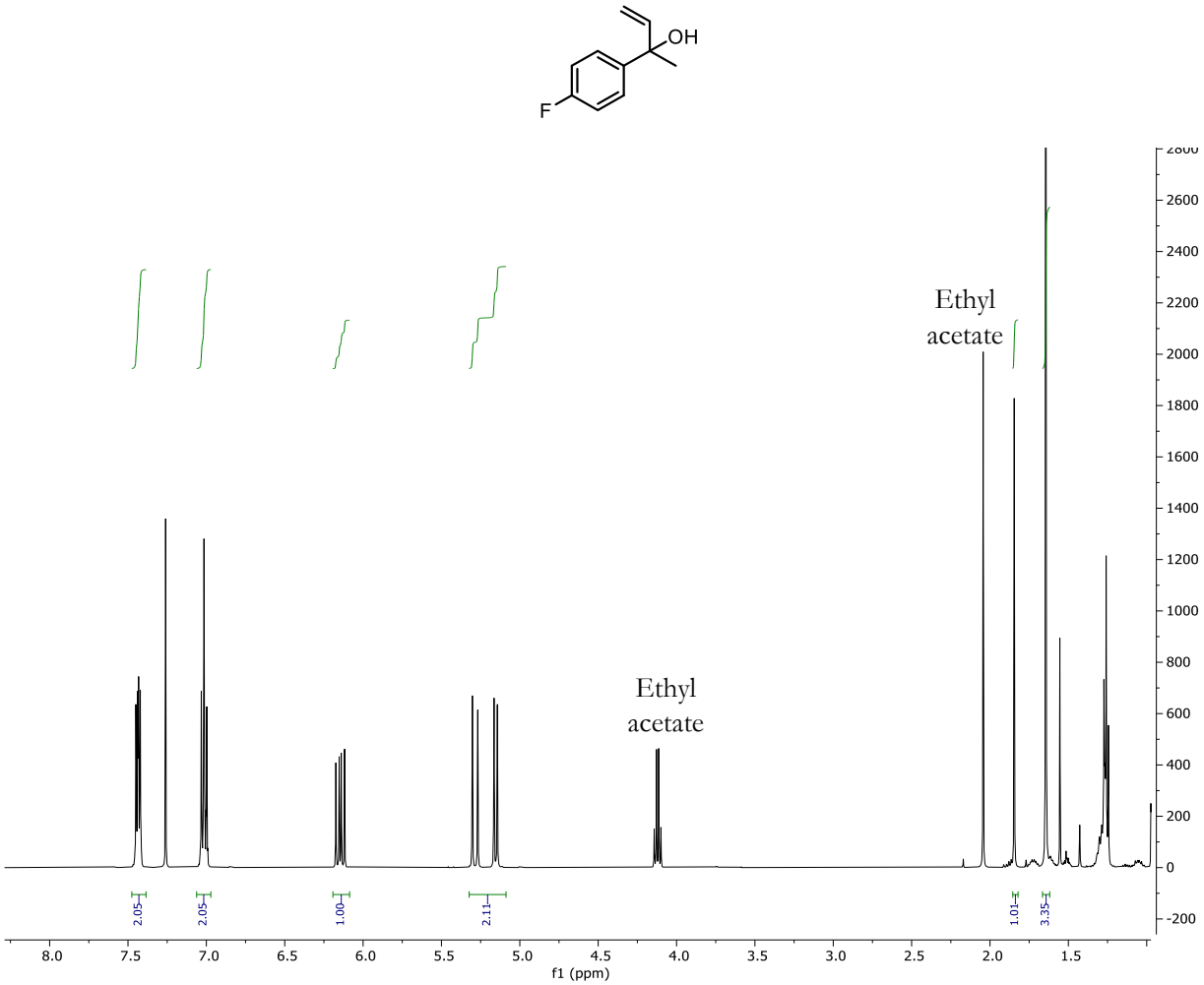


Figure S44 ^{1}H NMR, $CDCl_3$-*d* 2-(4-fluorophenyl)but-3-en-2-ol

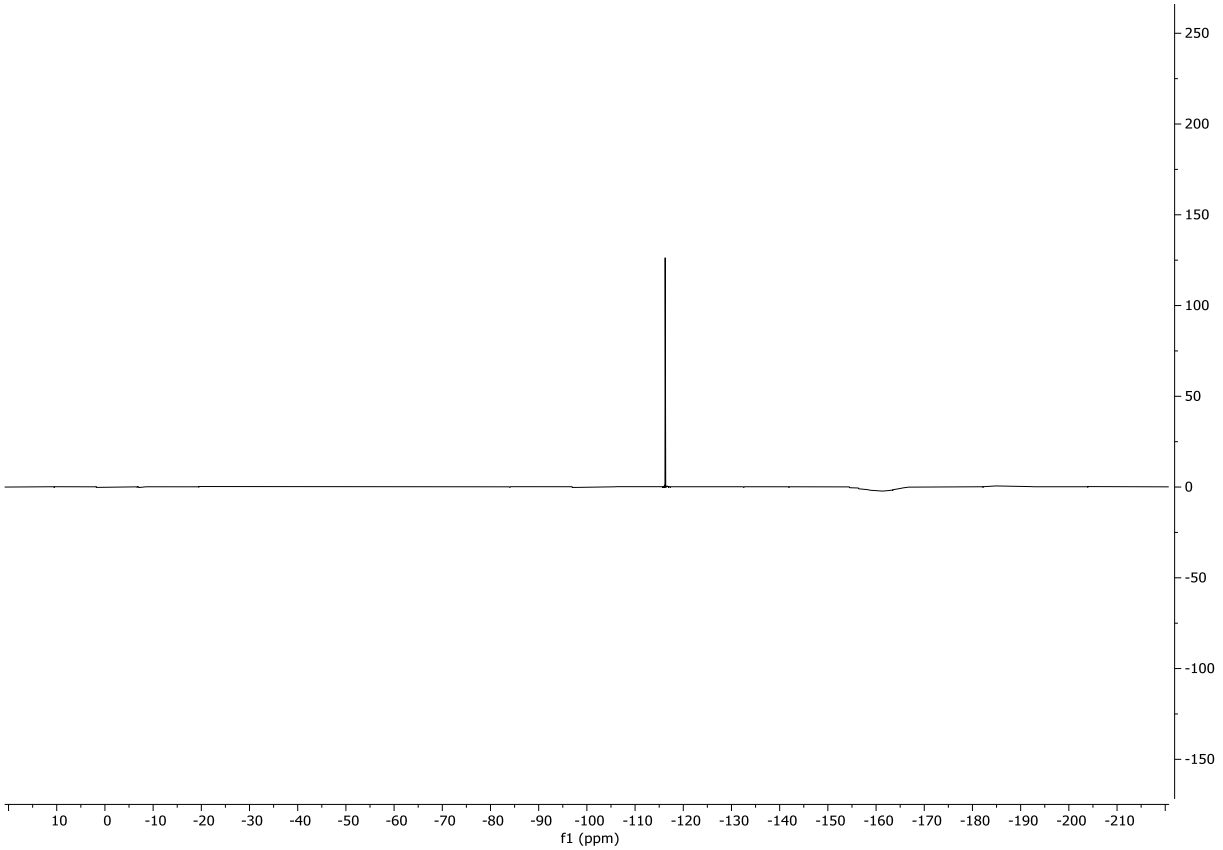


Figure S45 ^{19}F NMR, $CDCl_3$-*d* of 2-(4-fluorophenyl)but-3-en-2-ol

diethyl (1-(naphthalen-1-yl)vinyl) phosphate

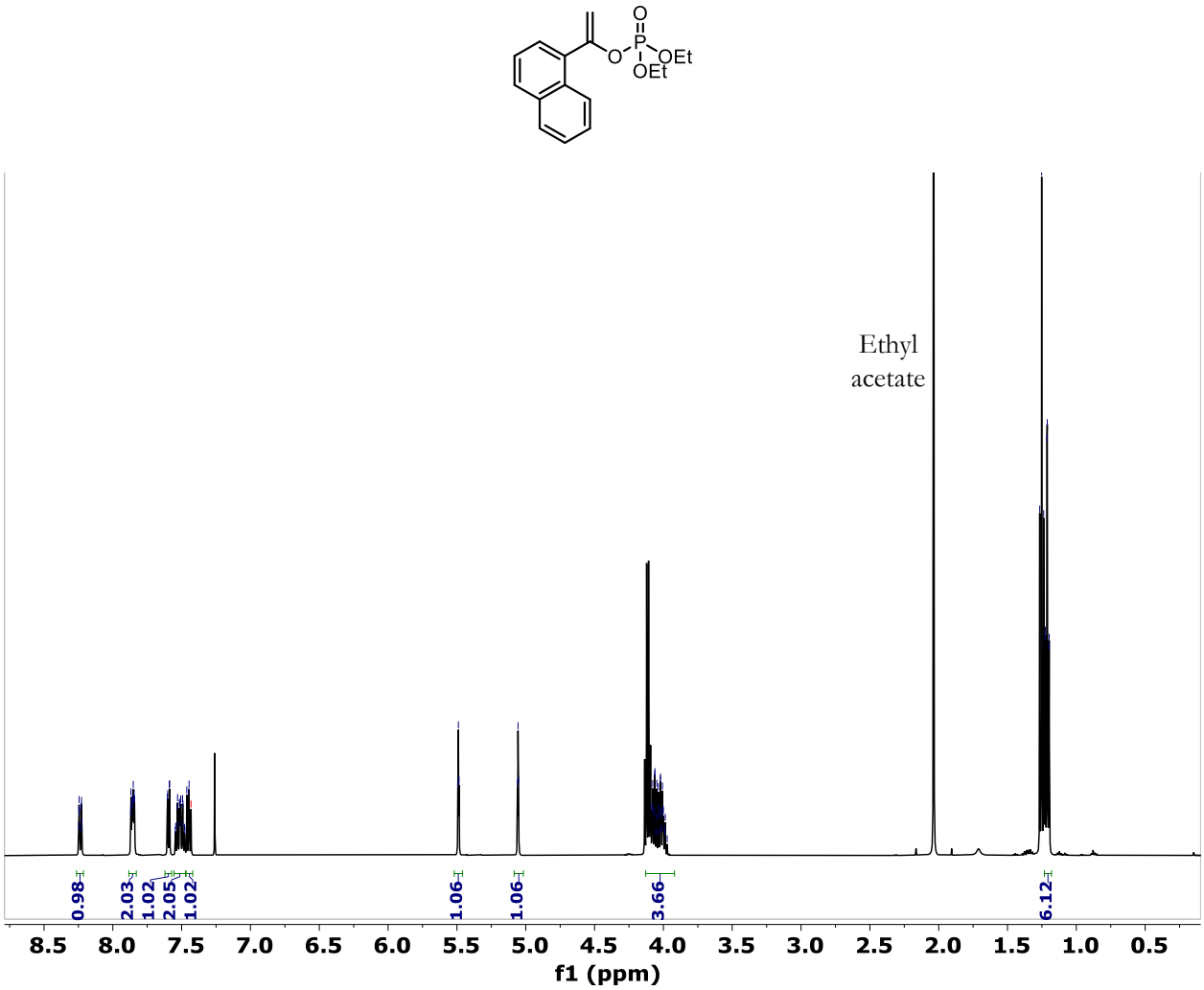


Figure S46 ^{1}H NMR, $CDCl_3$-*d* of diethyl (1-(naphthalen-1-yl)vinyl) phosphate

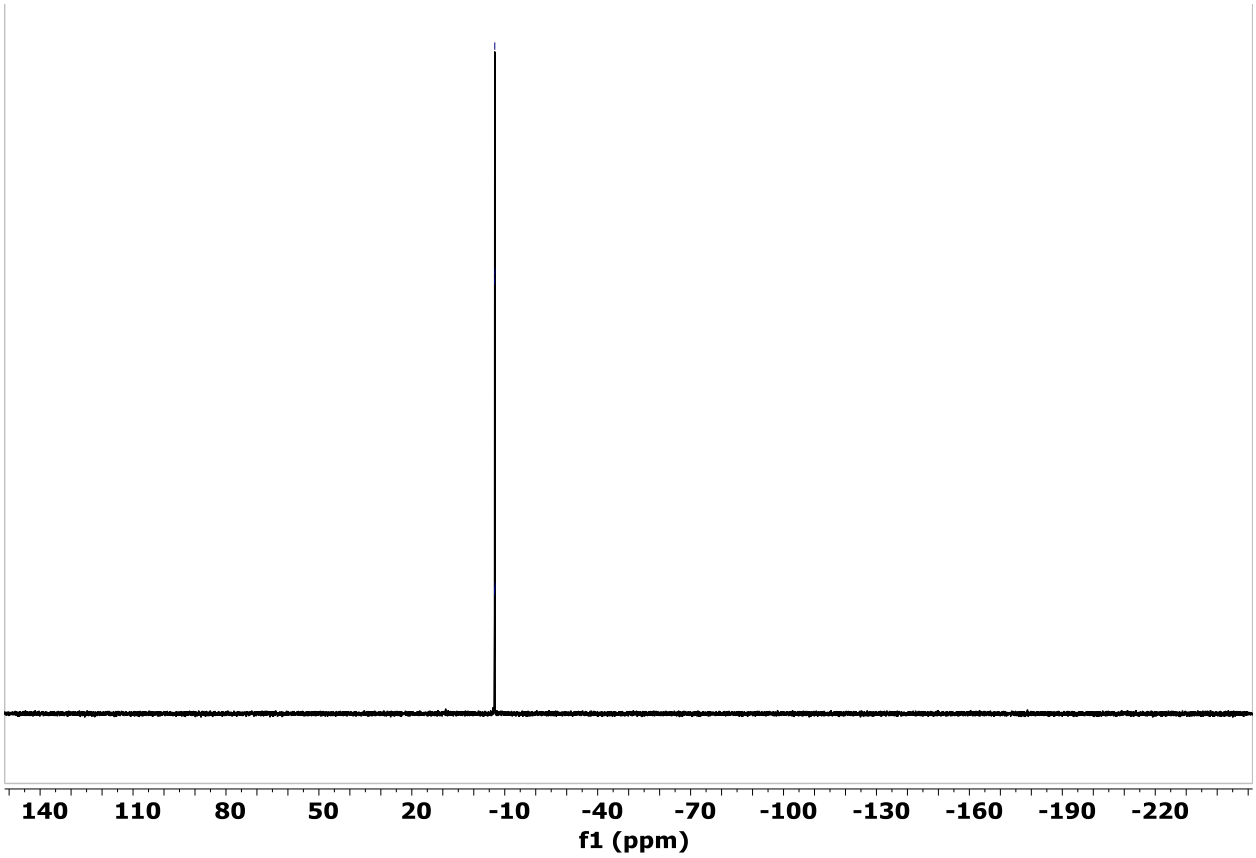


Figure S47 ^{31}P NMR, $CDCl_3$-*d* of diethyl (1-(naphthalen-1-yl)vinyl) phosphate

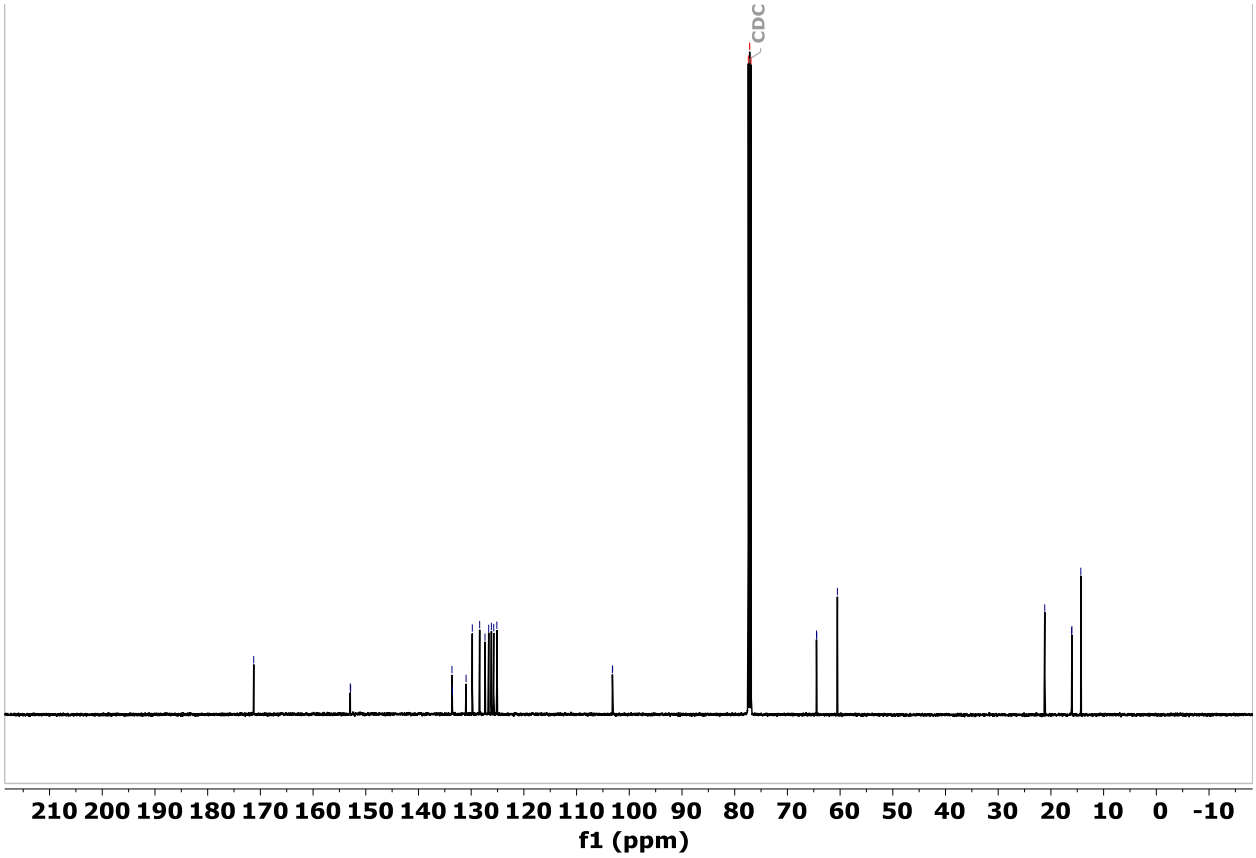


Figure S48 ^{13}C NMR, $CDCl_3$-*d* of diethyl (1-(naphthalen-1-yl)vinyl) phosphate

1-(2,4-dimethylphenyl)vinyl diethyl phosphate

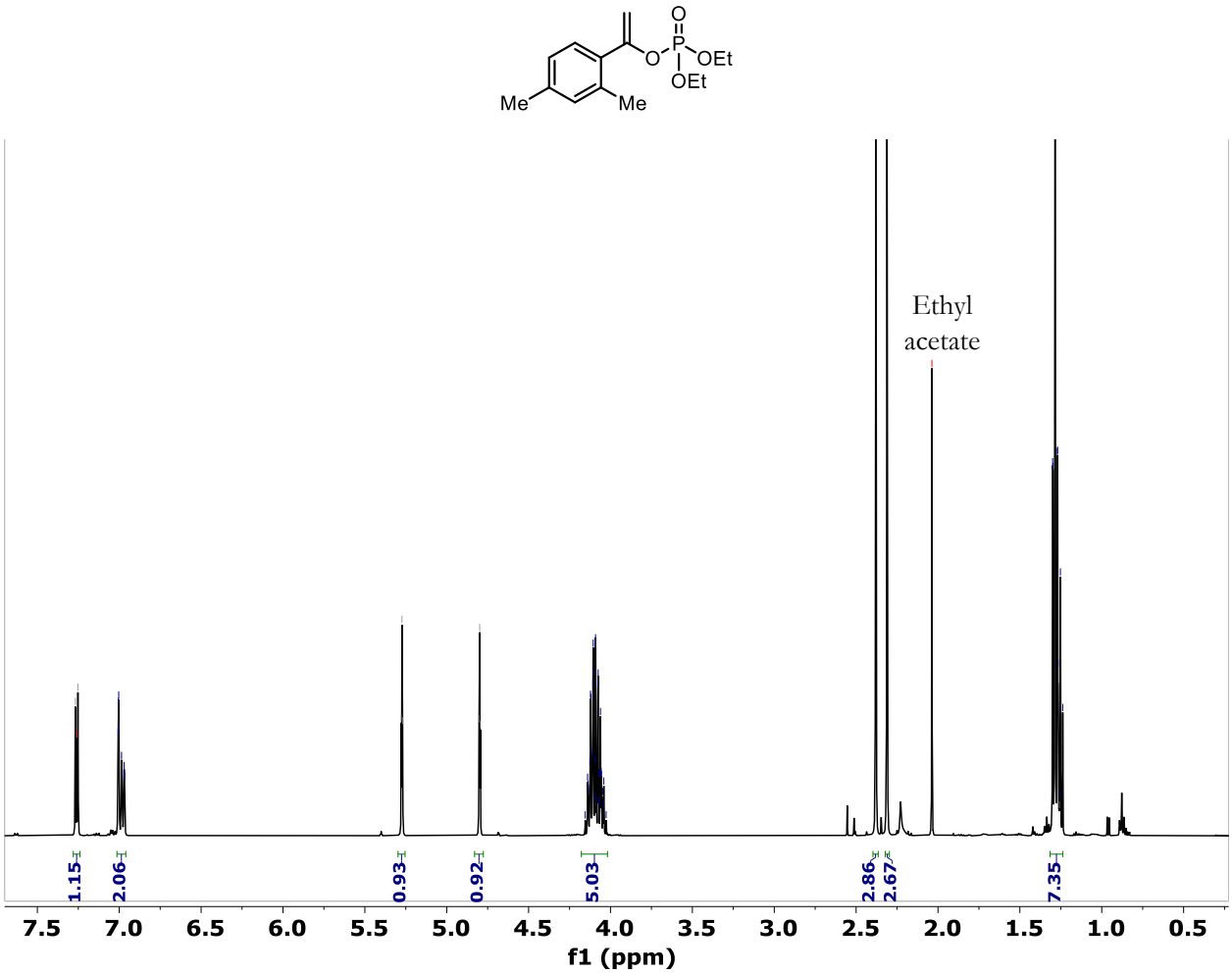


Figure S49 ^{1}H NMR, $CDCl_3$-*d* of 1-(2,4-dimethylphenyl)vinyl diethyl phosphate

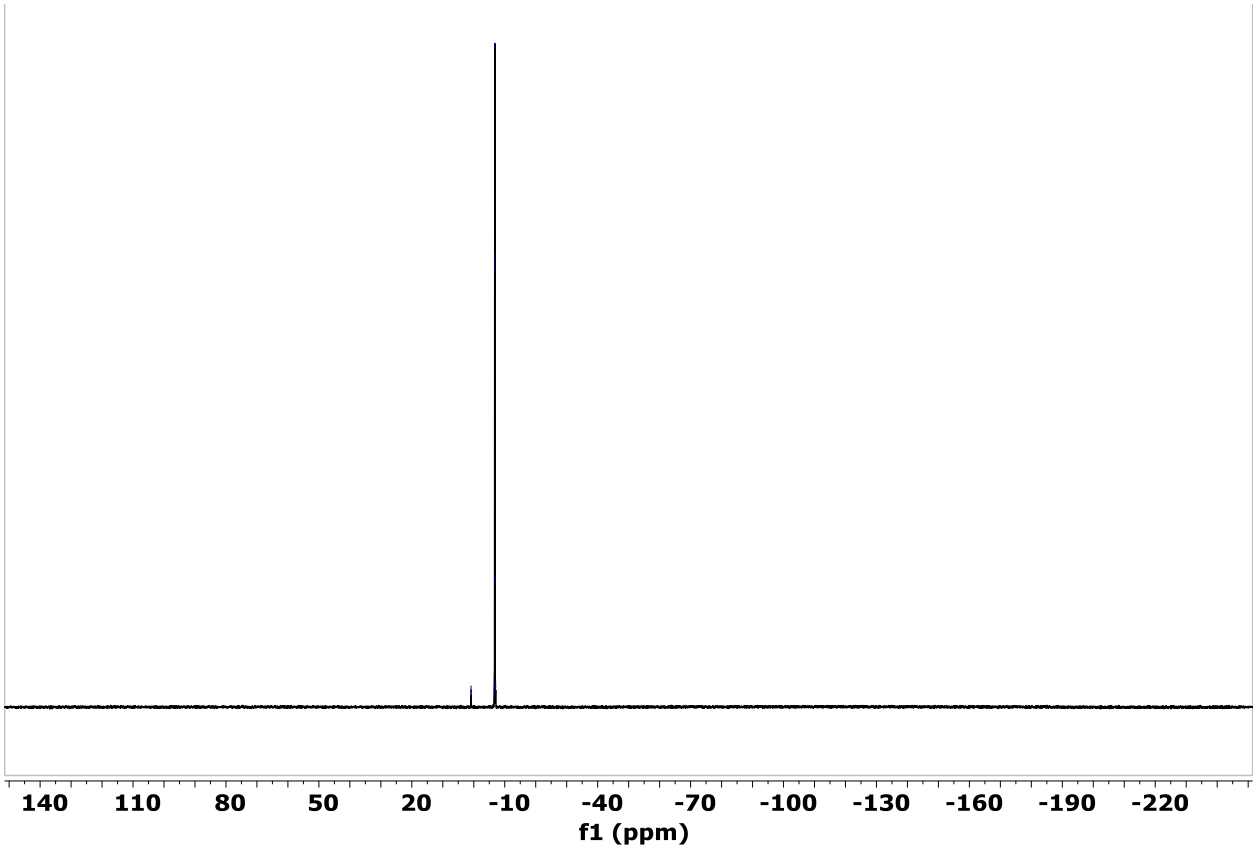


Figure S50 ^{31}P NMR, $CDCl_3$-*d* of 1-(2,4-dimethylphenyl)vinyl diethyl phosphate

1-(2-((tert-butyldimethylsilyl)oxy)phenyl)vinyl diethyl phosphate

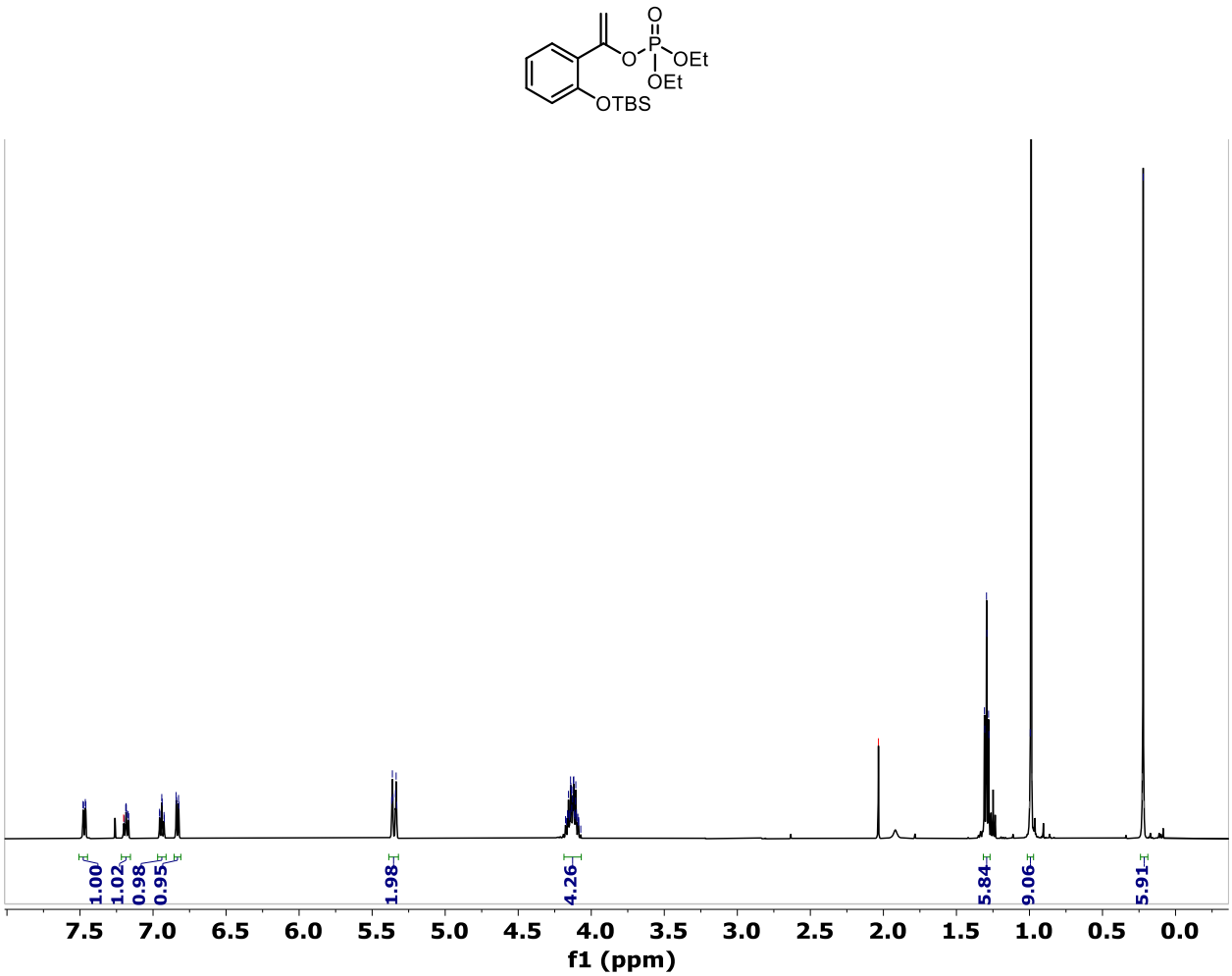


Figure S51 ^{1}H NMR, $CDCl_3$-*d* of 1-(2-((tert-butyldimethylsilyl)oxy)phenyl)vinyl diethyl phosphate

diethyl (1-(4-((trimethylsilyl)ethynyl)phenyl)vinyl) phosphate

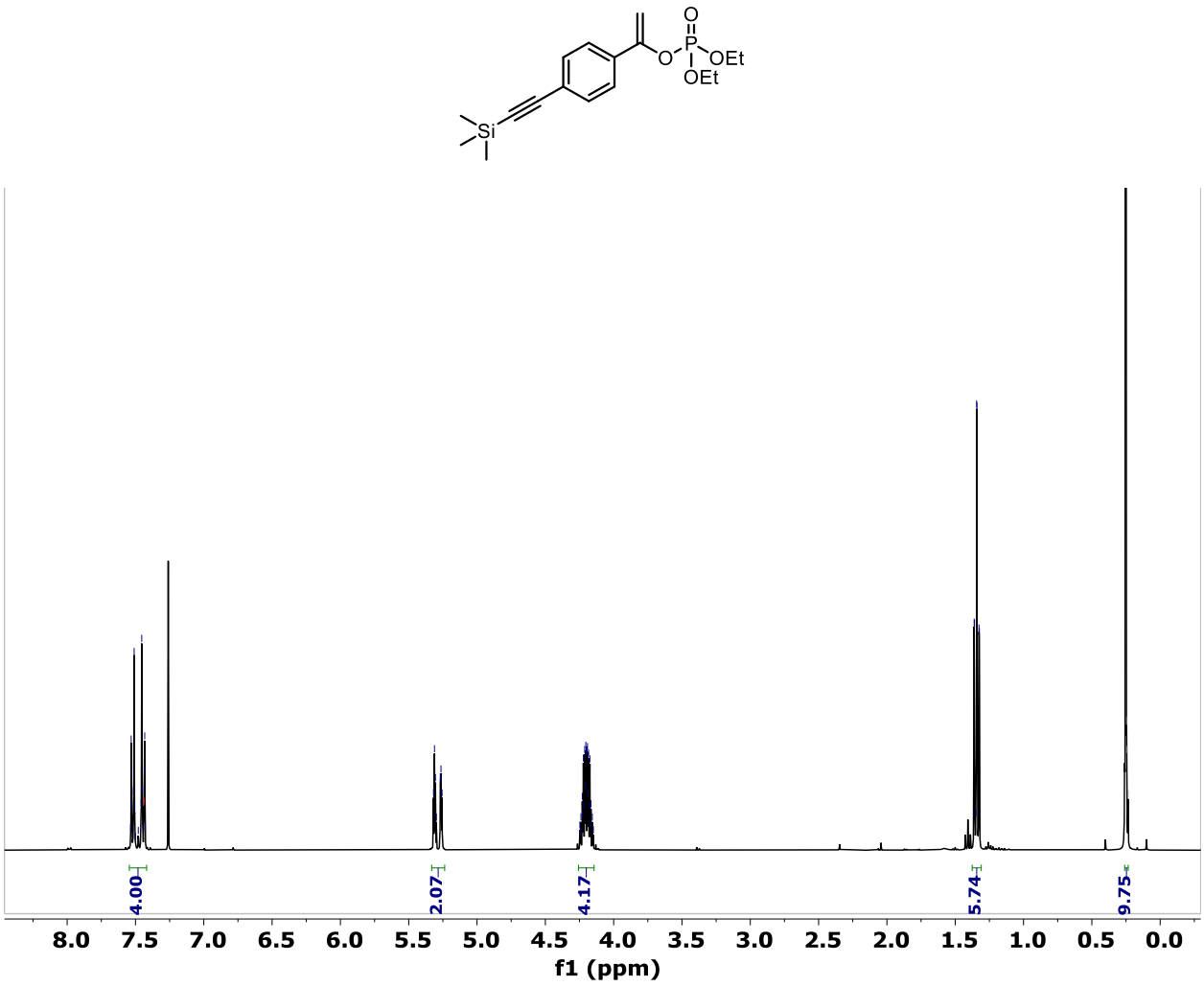


Figure S52 ^{1}H NMR, $CDCl_3$-*d* of diethyl (1-(4-((trimethylsilyl)ethynyl)phenyl)vinyl) phosphate

(4-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane

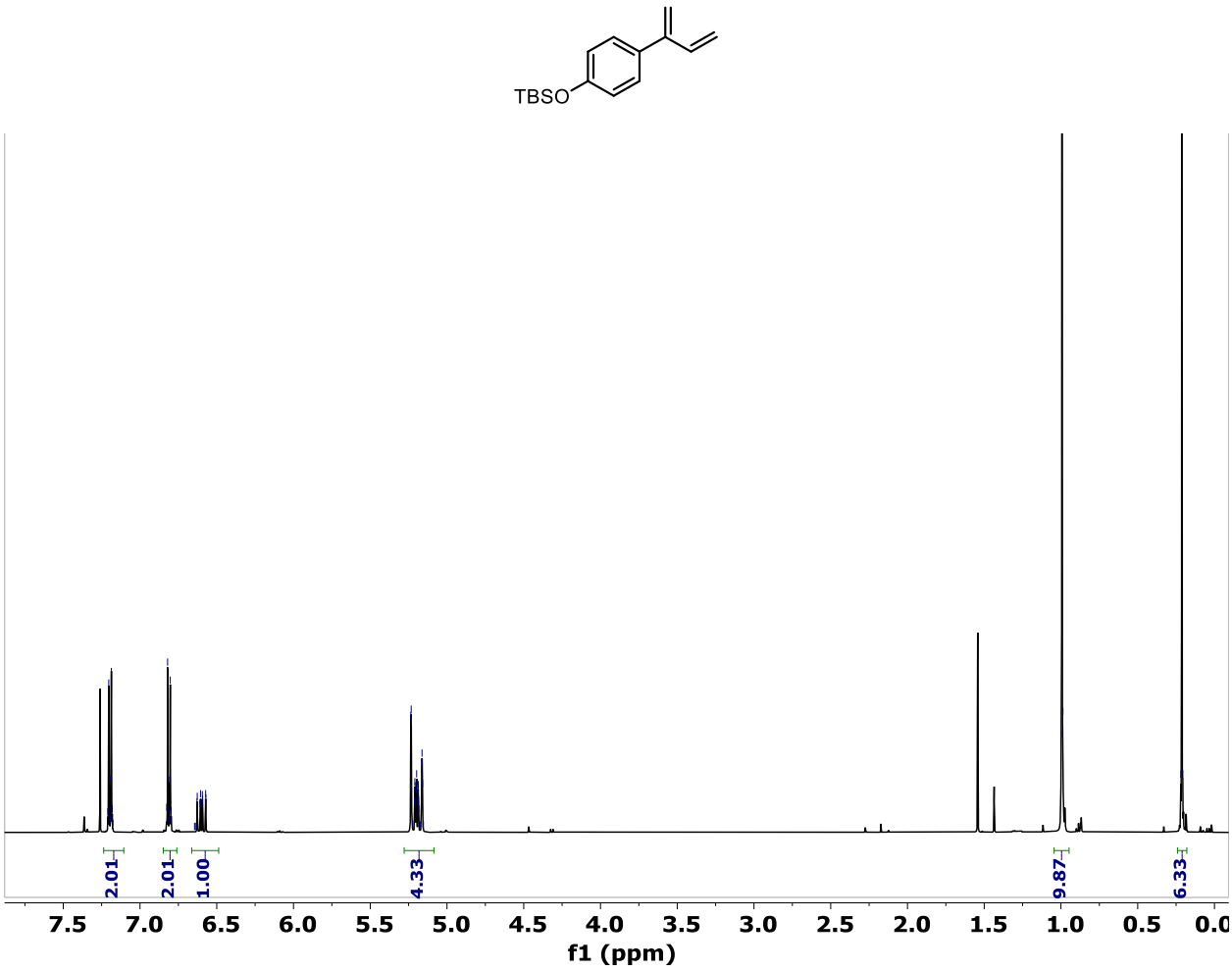


Figure S53 ^{1}H NMR, $CDCl_3$-*d* to (4-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane

1-(buta-1,3-dien-2-yl)-4-fluorobenzene

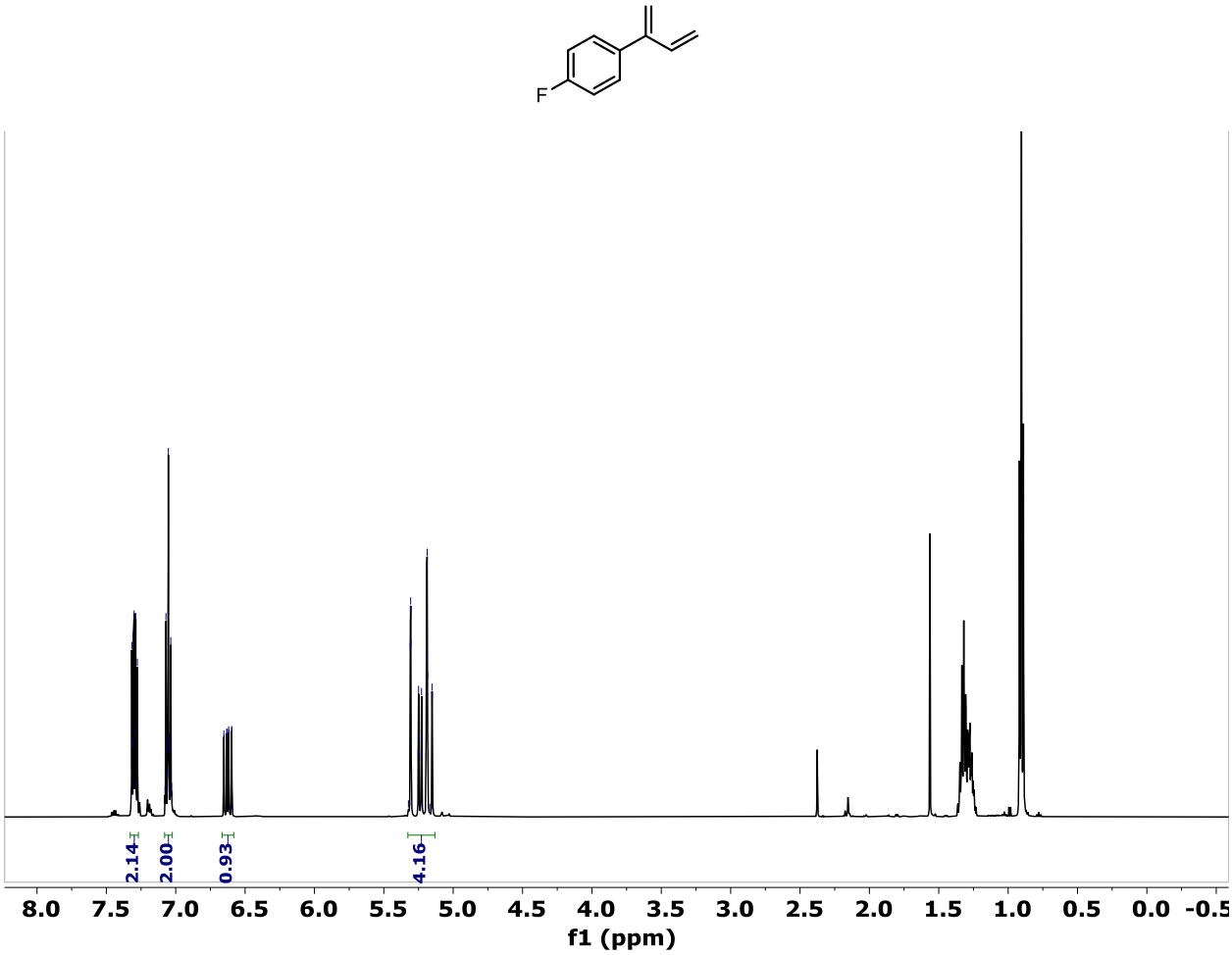


Figure S54 ^{1}H NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-4-fluorobenzene

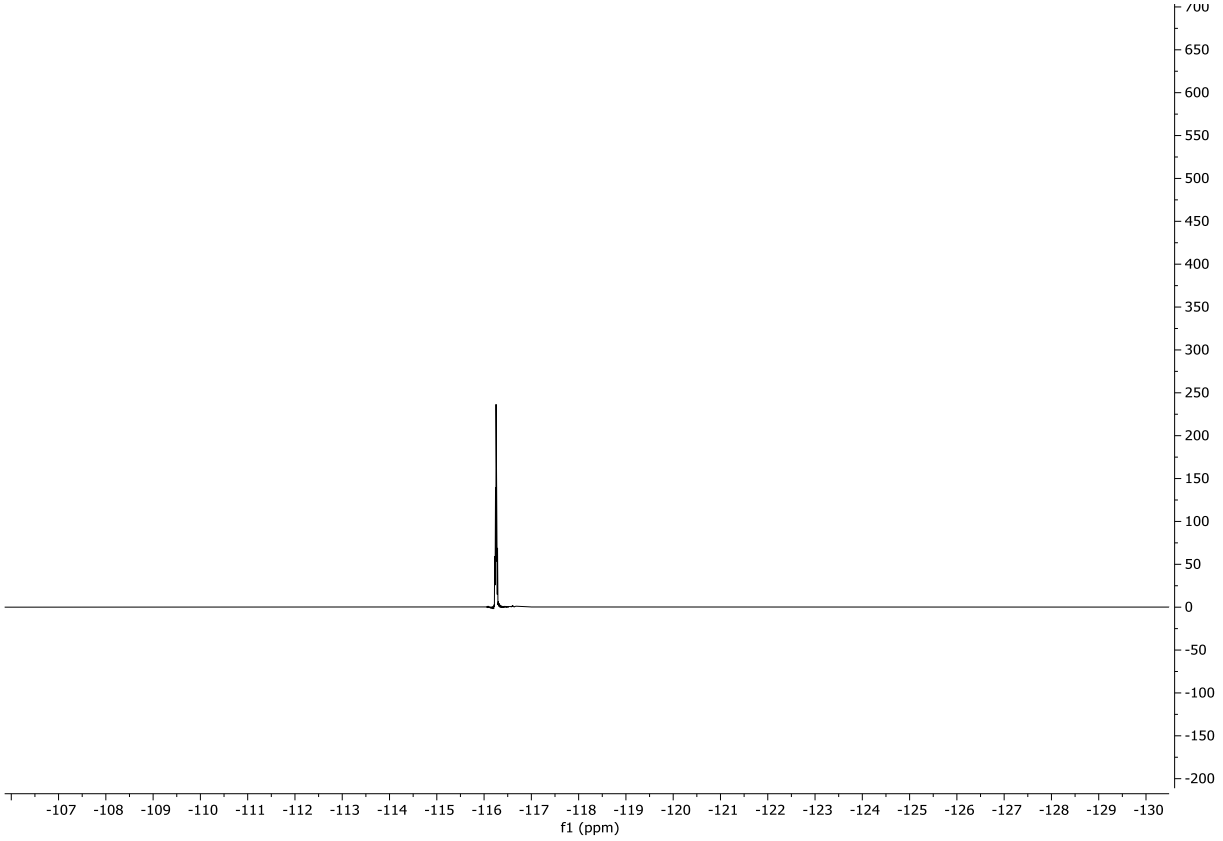


Figure S55 ^{19}F NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-4-fluorobenzene

1-(buta-1,3-dien-2-yl)-3-methoxybenzene

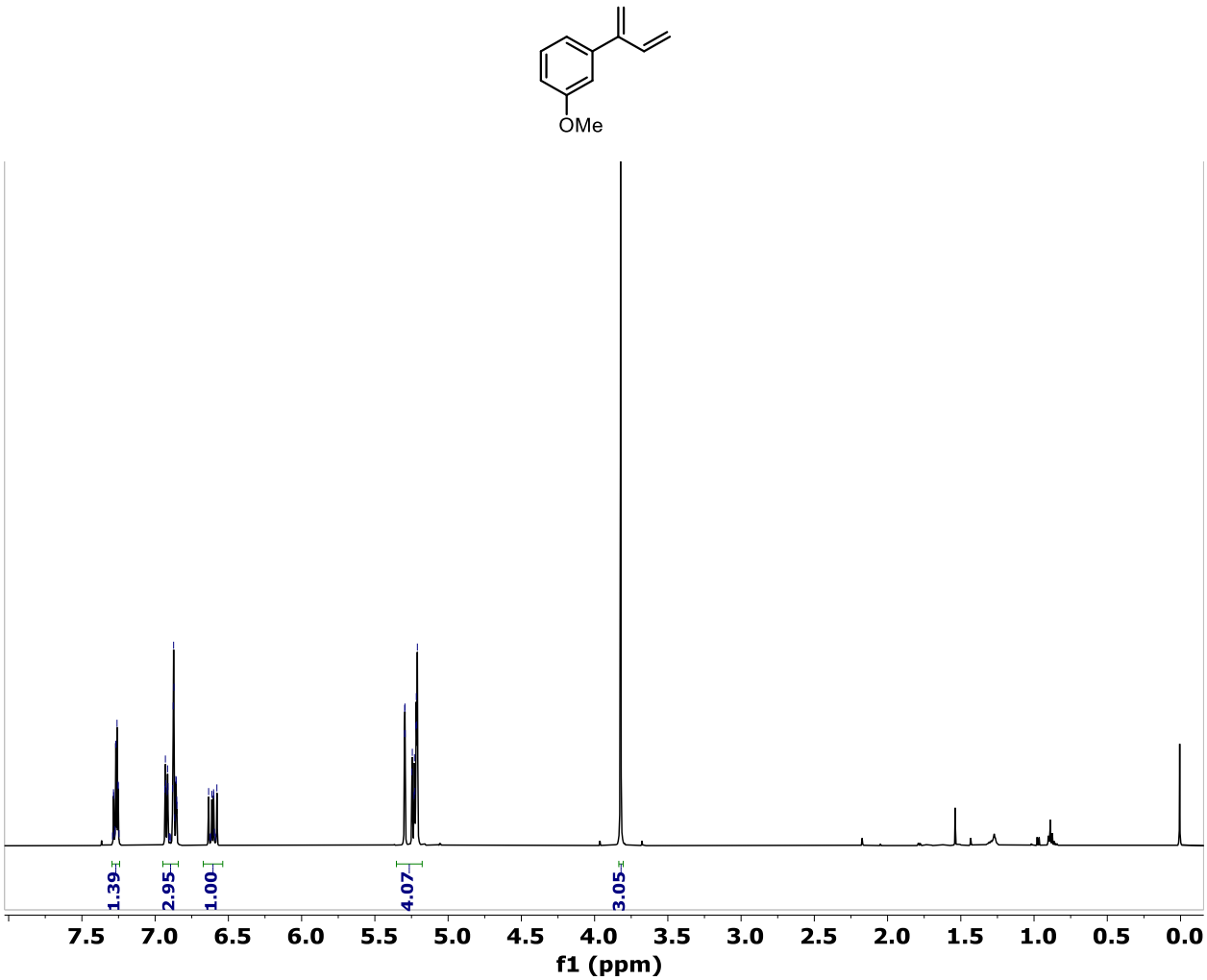


Figure S56 ^{1}H NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-3-methoxybenzene

1-(buta-1,3-dien-2-yl)-3,5-dimethoxybenzene

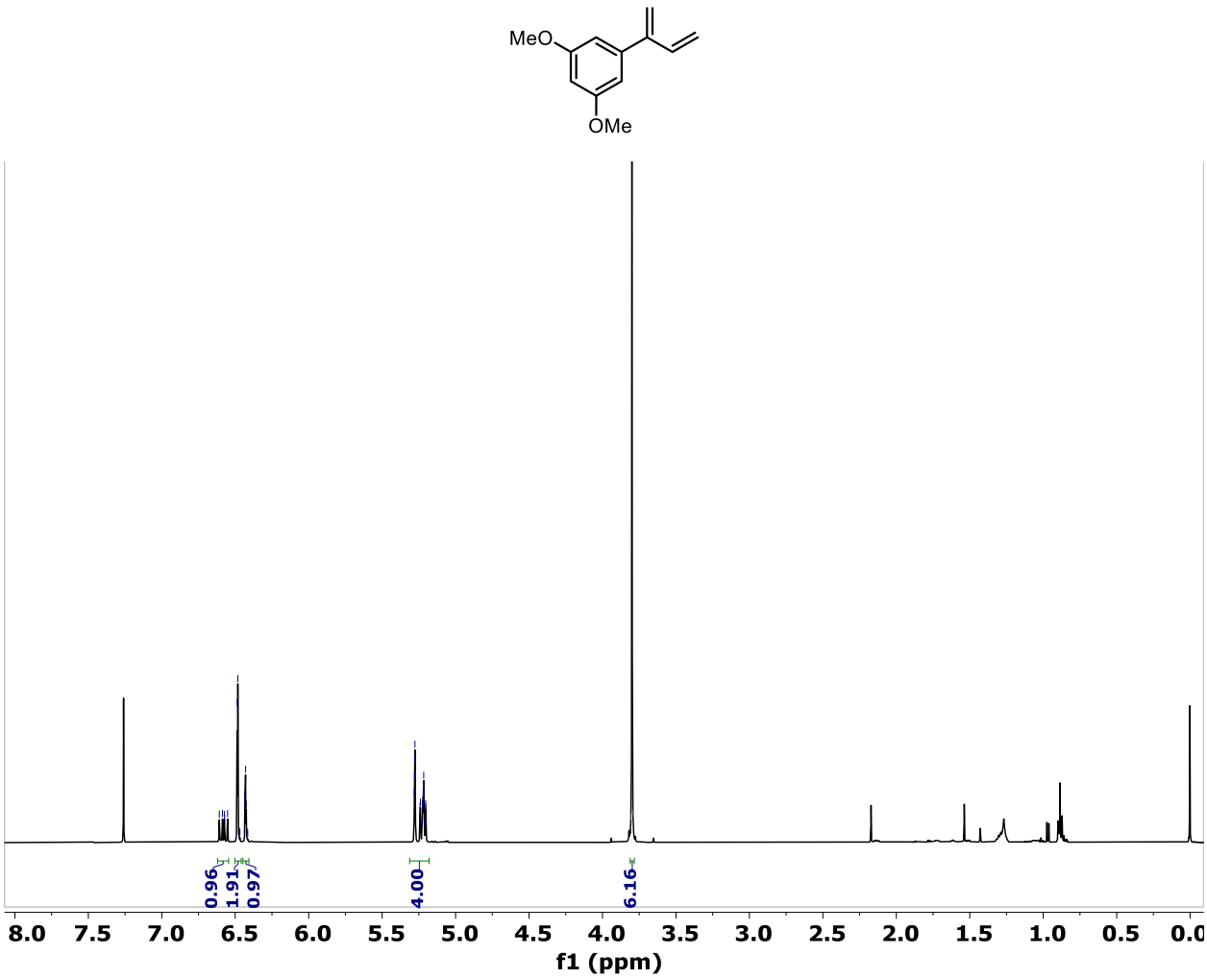


Figure S57 ^{1}H NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-3,5-dimethoxybenzene

(2-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane

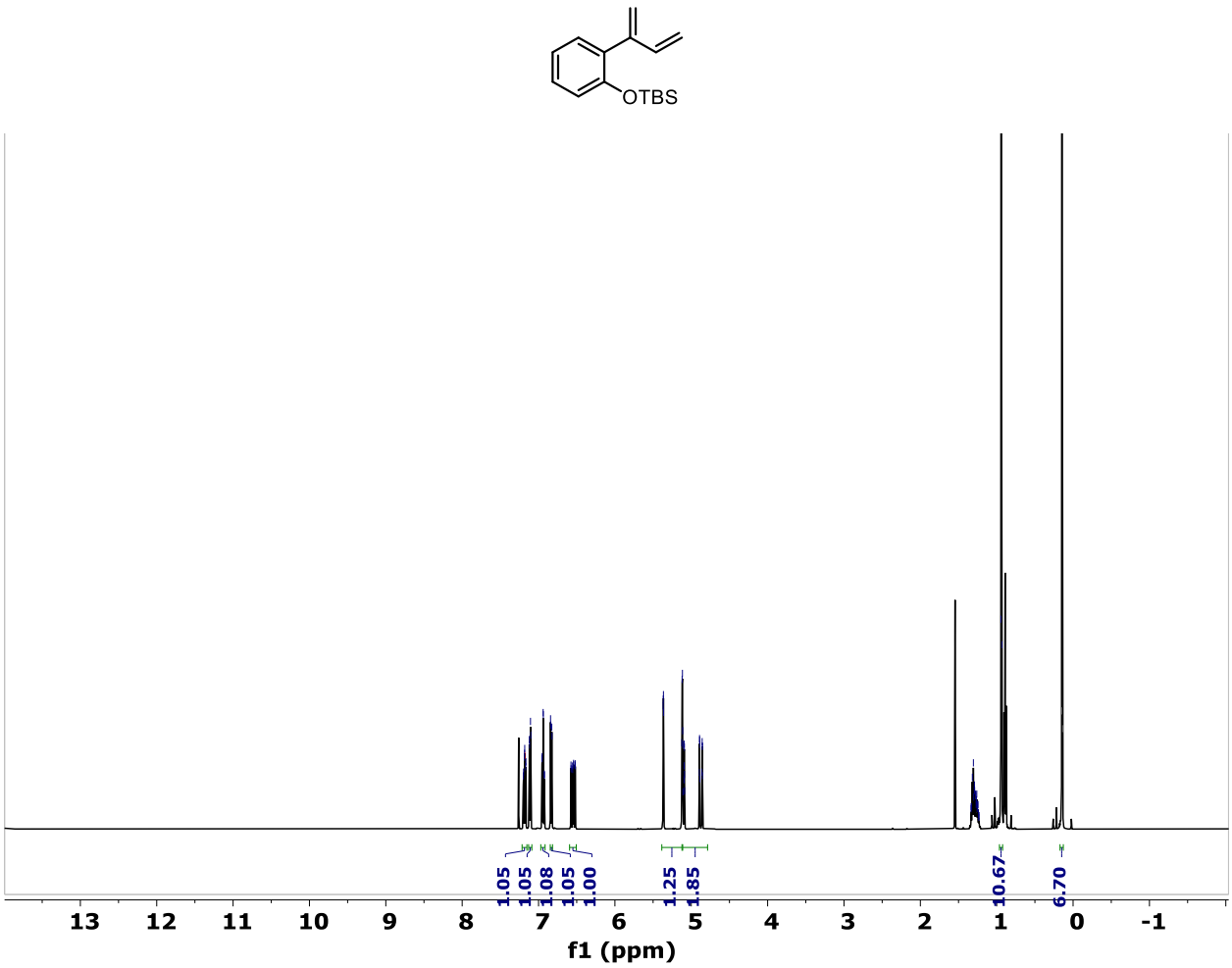


Figure S58 ^{1}H NMR, $CDCl_3$-*d* of (2-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane

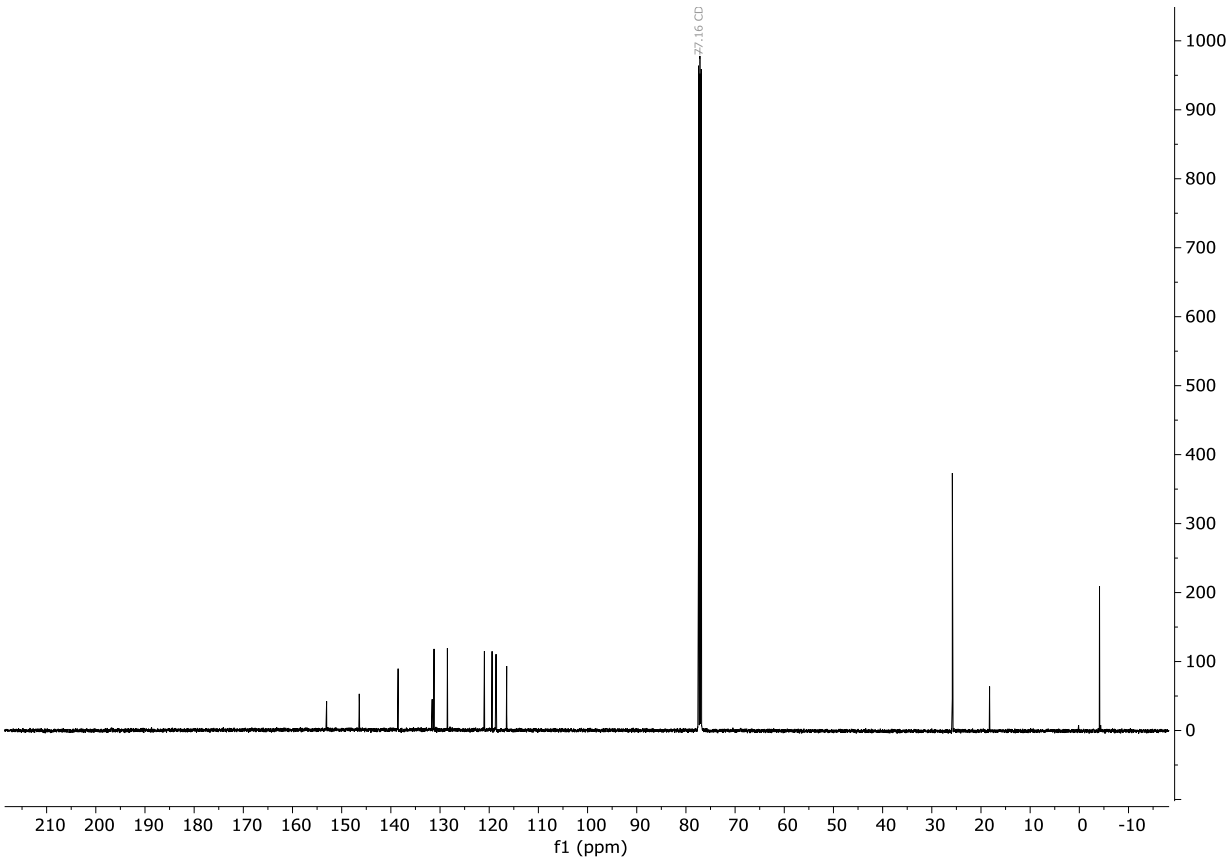


Figure S59 ^{13}C NMR, $CDCl_3$-*d* of (2-(buta-1,3-dien-2-yl)phenoxy)(tert-butyl)dimethylsilane

((4-(buta-1,3-dien-2-yl)phenyl)ethynyl)trimethylsilane

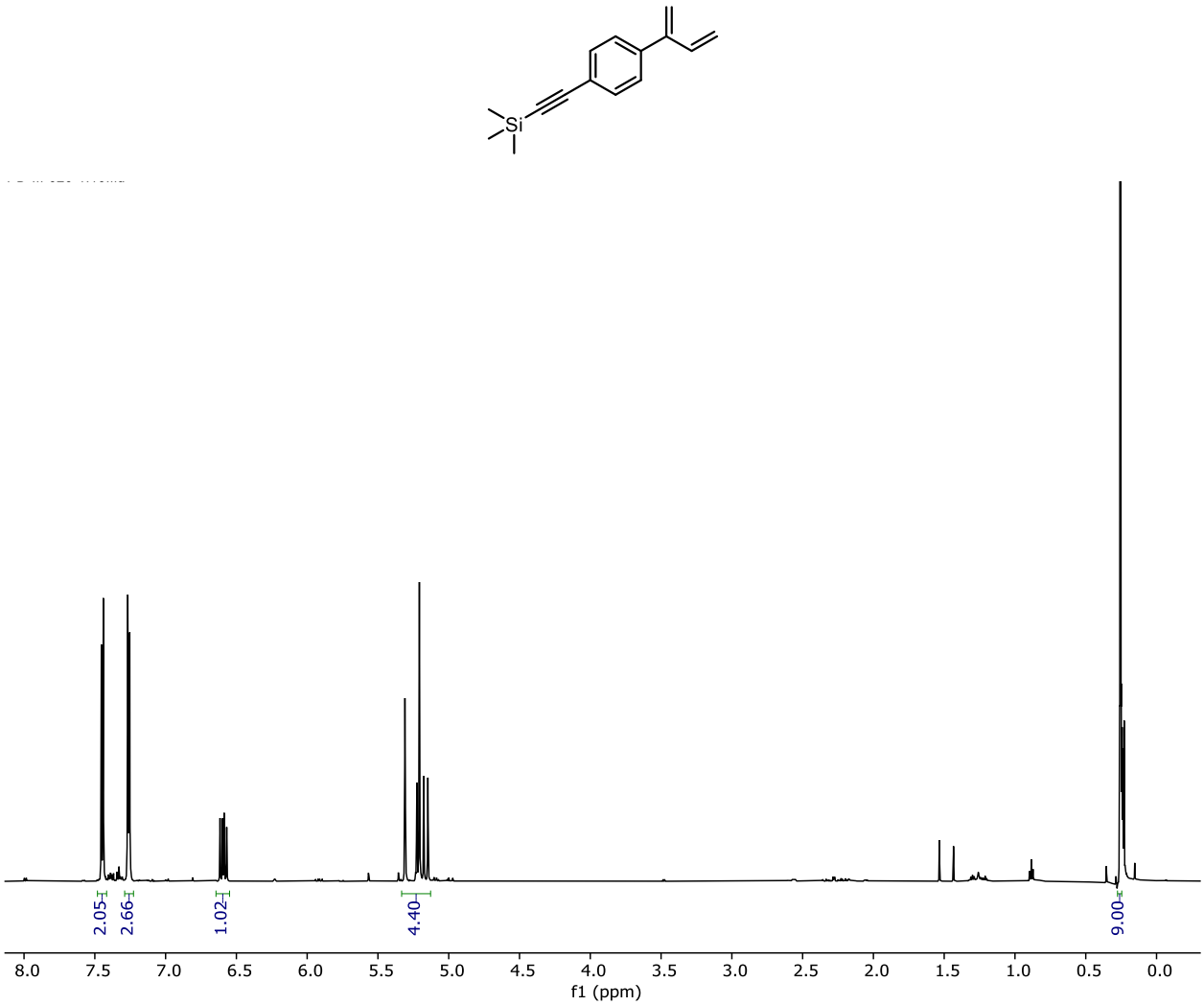


Figure S60 ^{1}H NMR, $CDCl_3$-*d* of ((4-(buta-1,3-dien-2-yl)phenyl)ethynyl)trimethylsilane

1-(buta-1,3-dien-2-yl)naphthalene

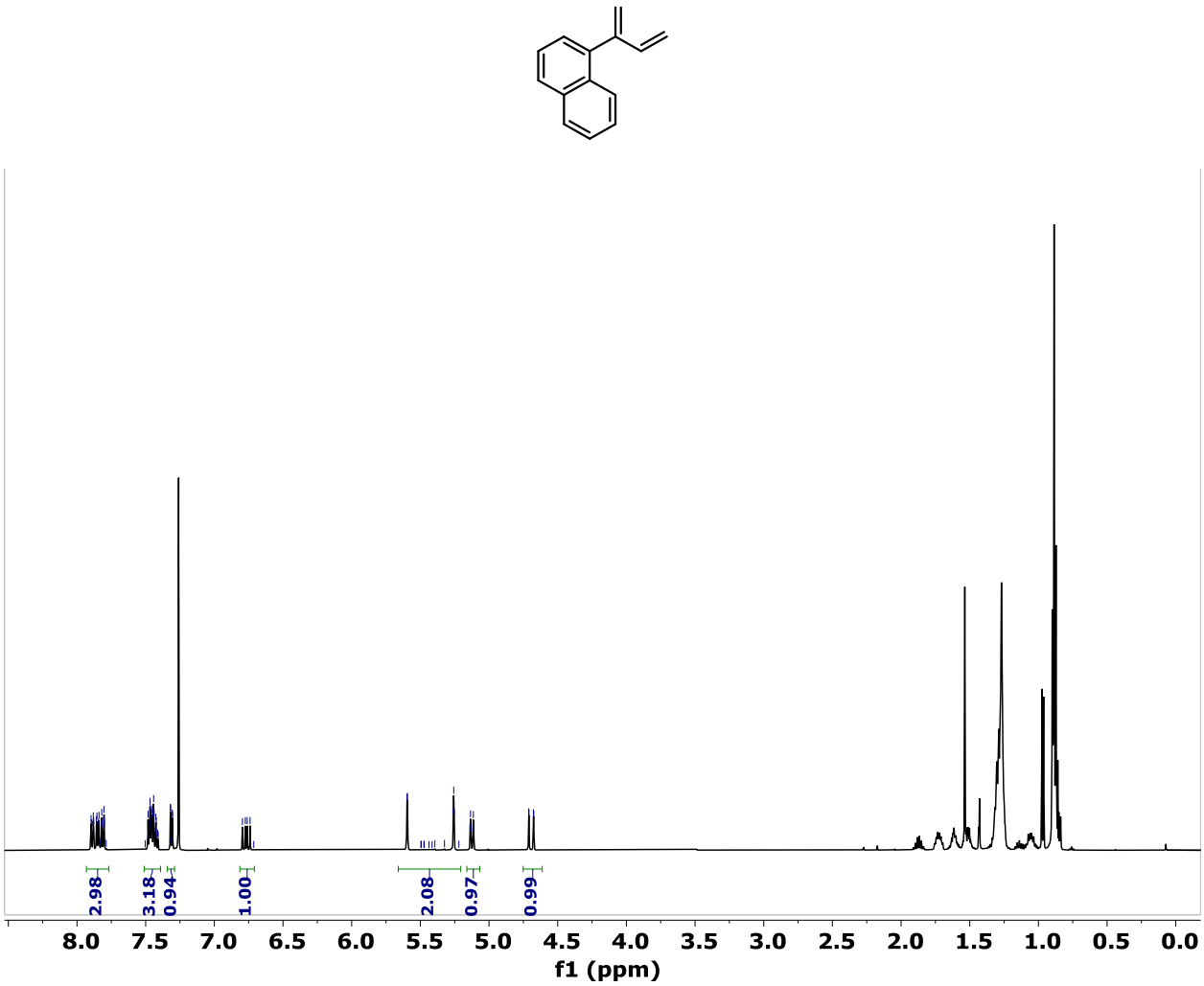


Figure S61 ^{1}H NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)naphthalene

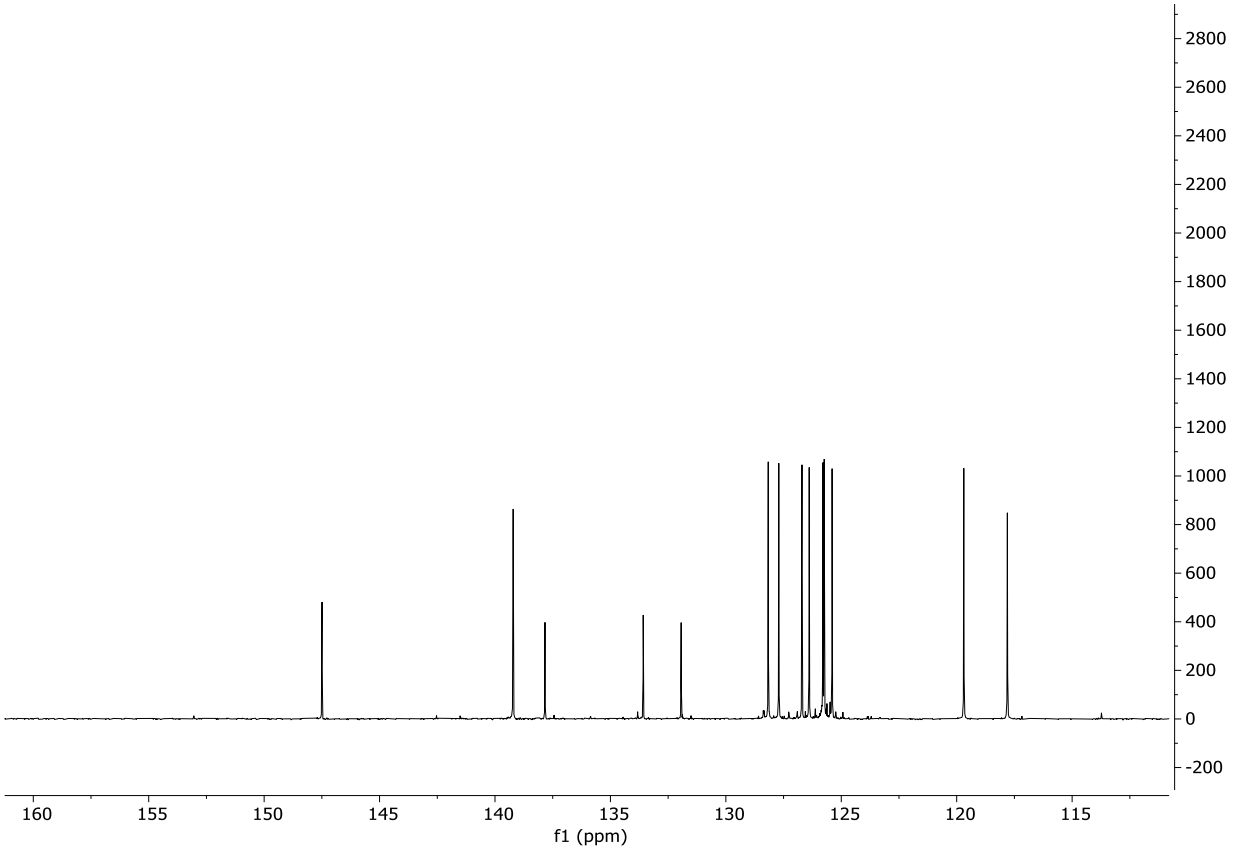


Figure S62 ^{13}C NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)naphthalene

1-(buta-1,3-dien-2-yl)-4-methylbenzene

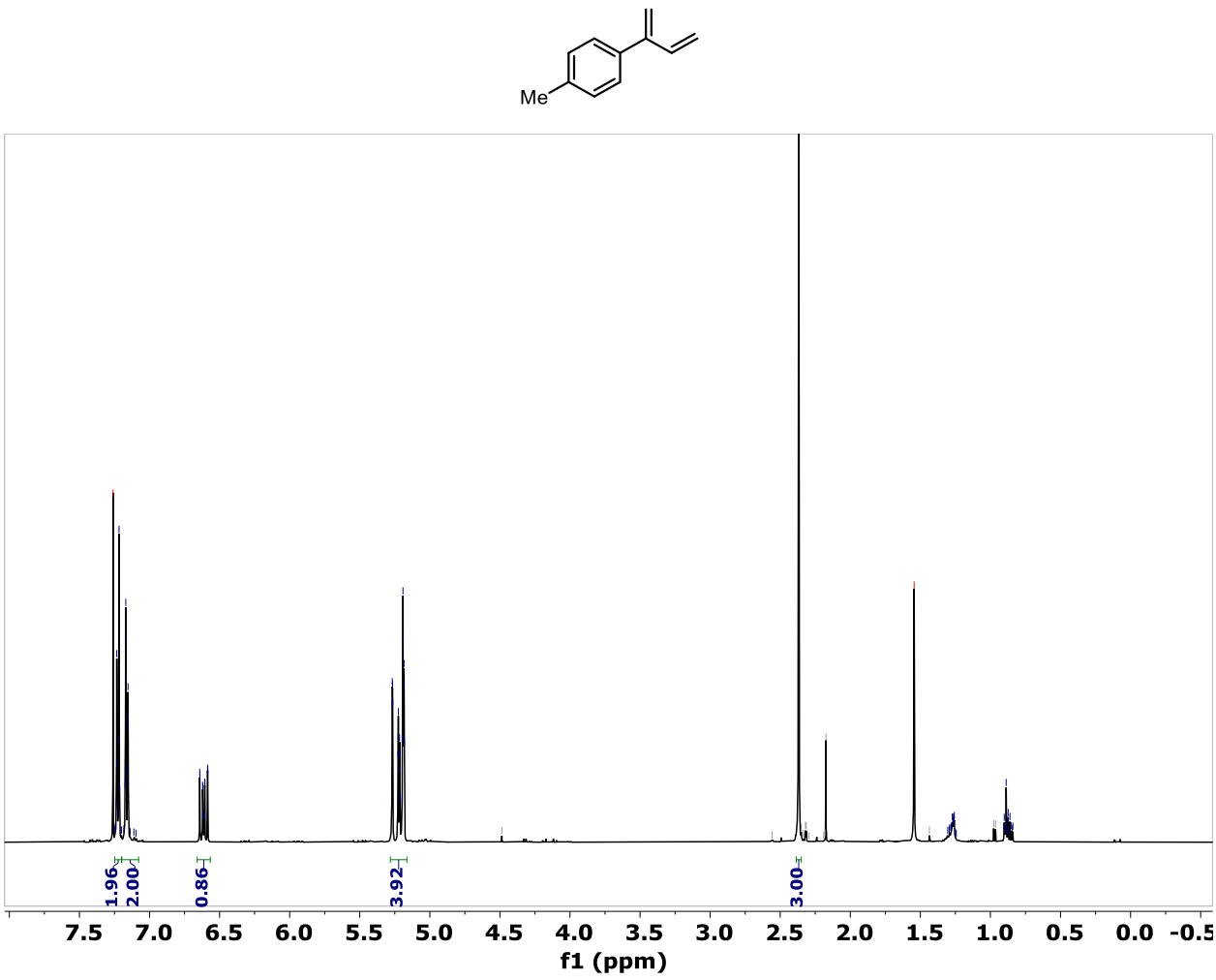


Figure S63 ^{1}H NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-4-methylbenzene

1-(buta-1,3-dien-2-yl)-4-(tert-butyl)benzene

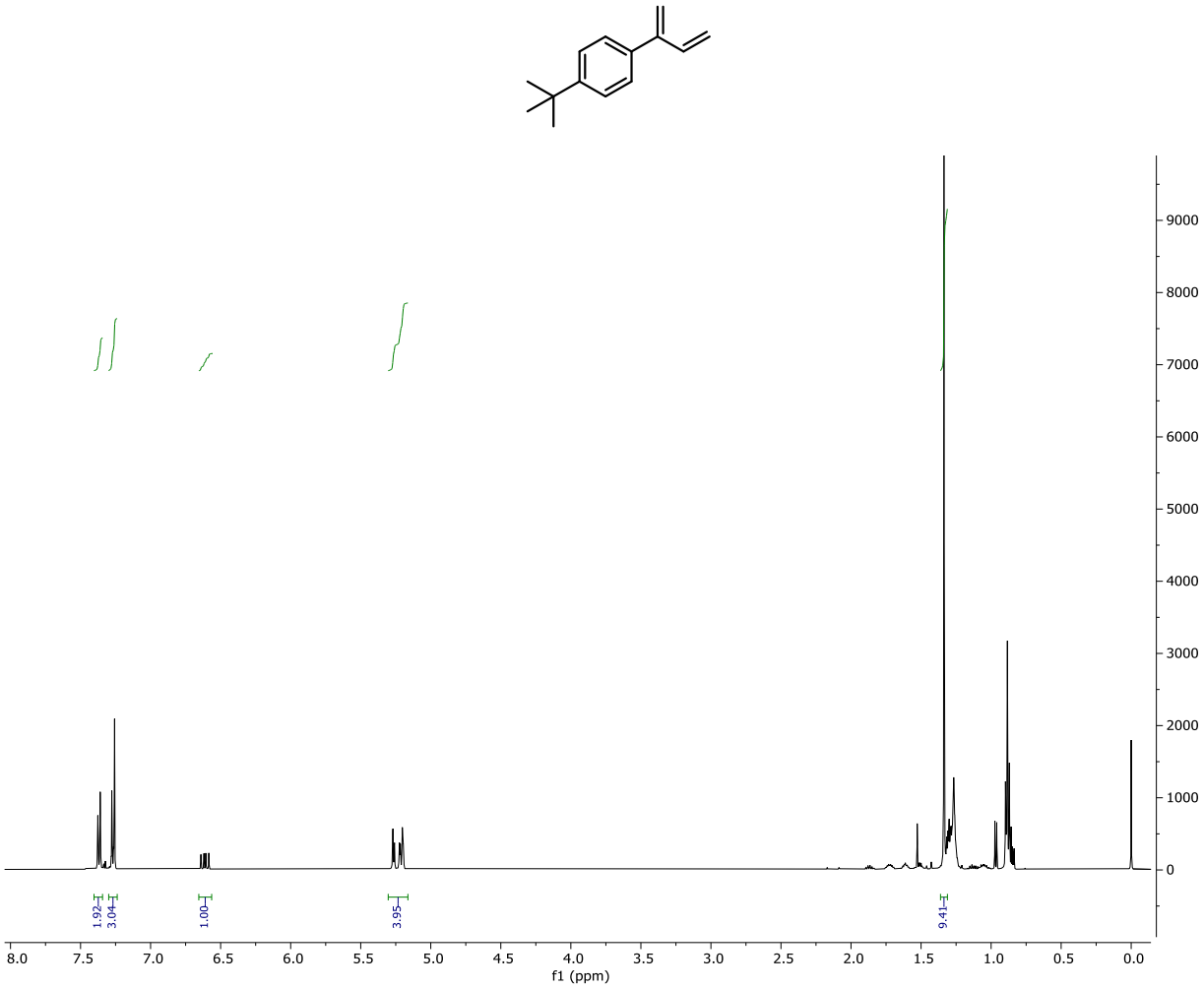


Figure S64 ^{1}H NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-4-(tert-butyl)benzene

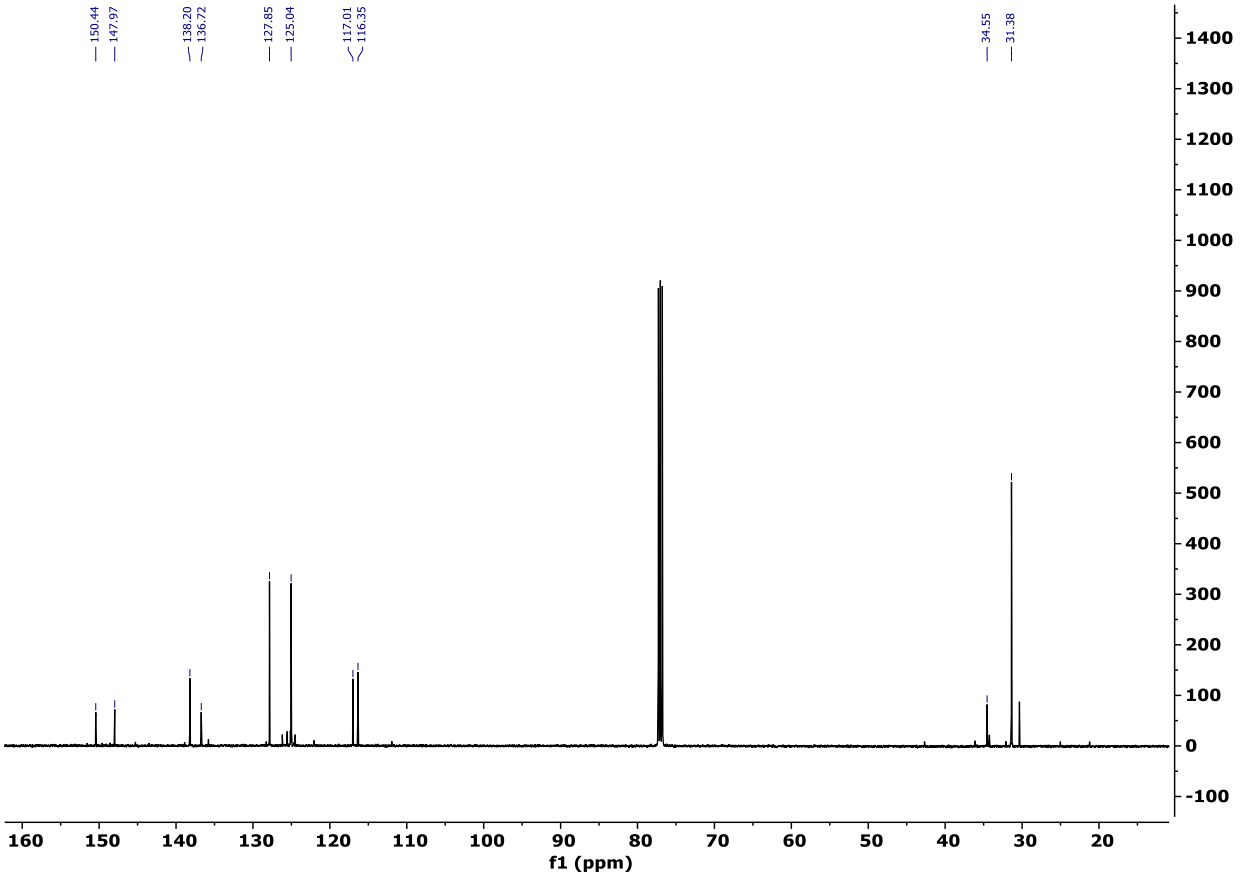
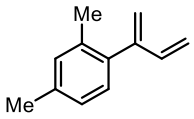


Figure S65 ^{13}C NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-4-(tert-butyl)benzene

1-(buta-1,3-dien-2-yl)-2,4-dimethylbenzene



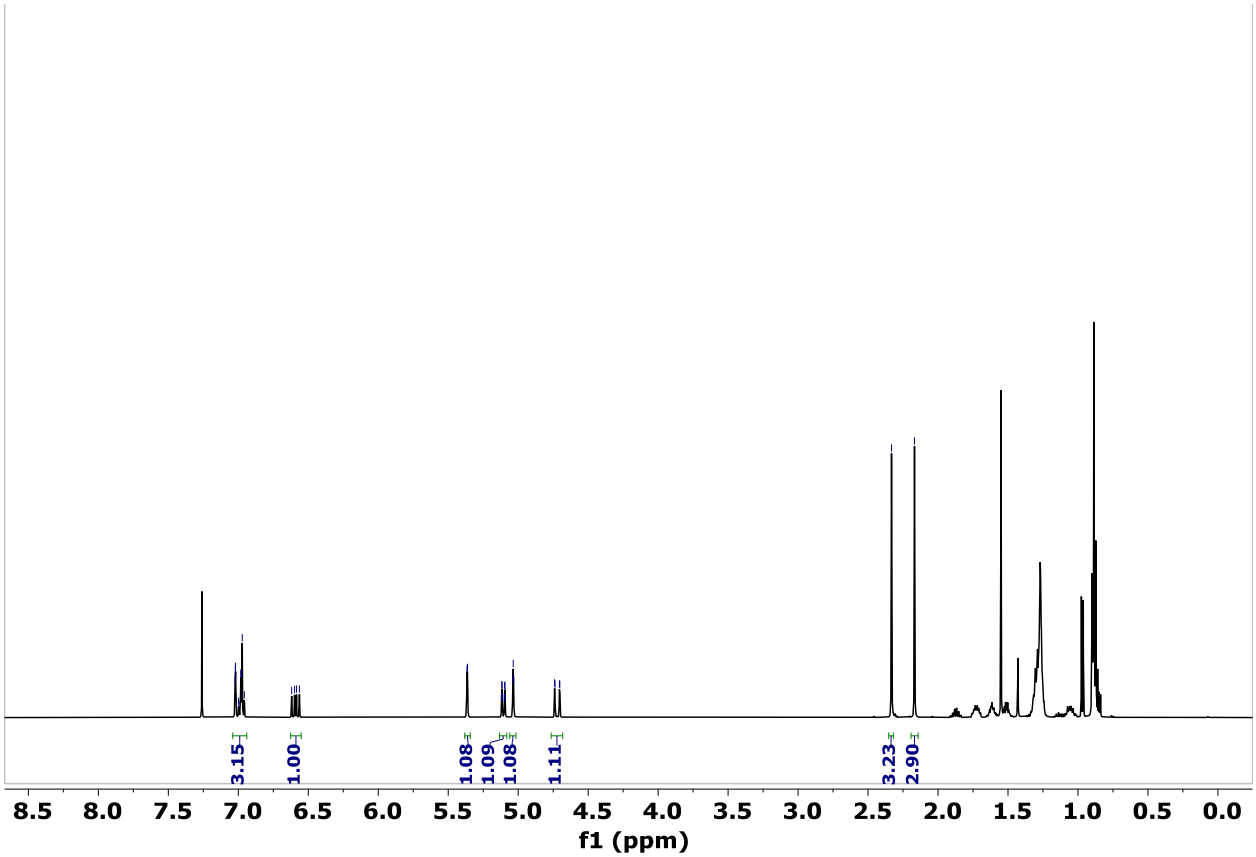


Figure S66 ^{1}H NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-2,4-dimethylbenzene

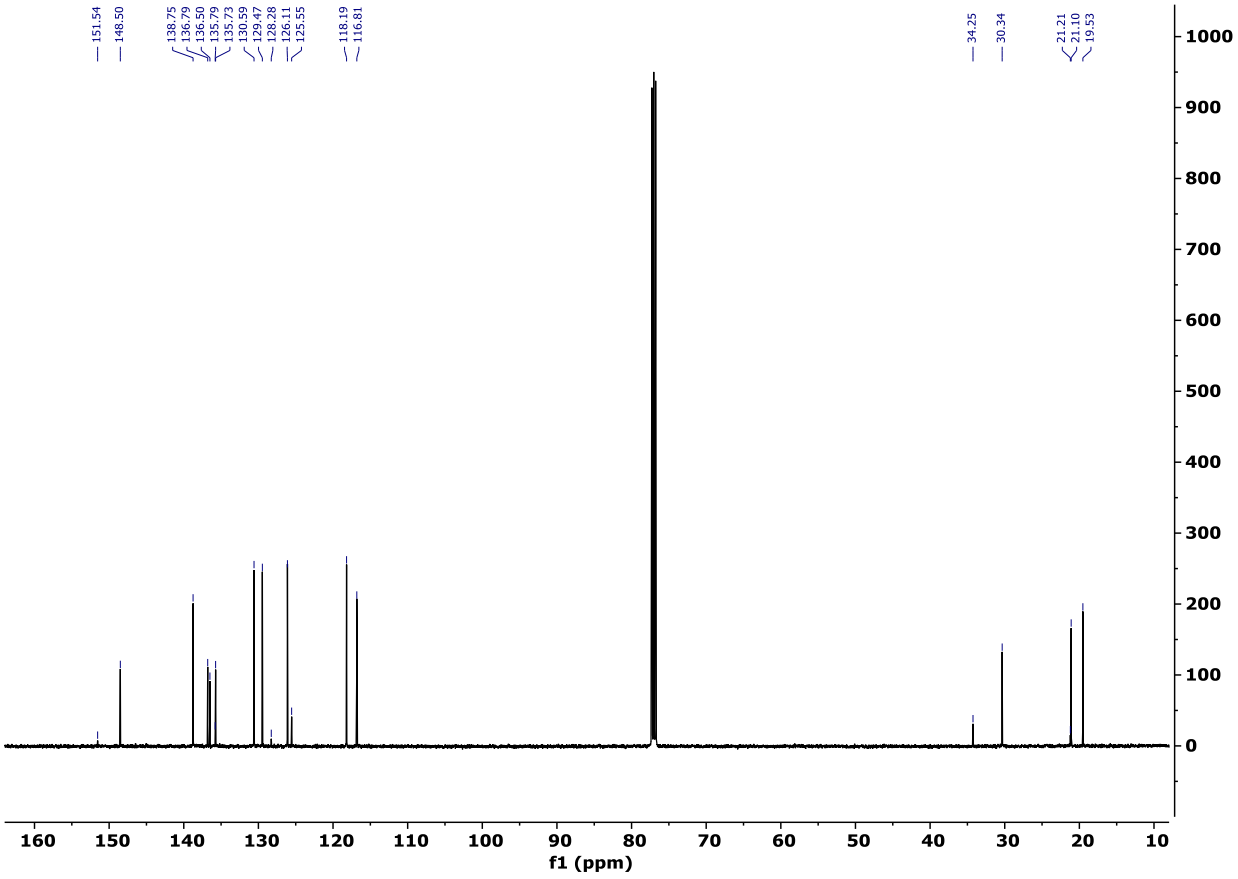


Figure S67 ^{13}C NMR, $CDCl_3$-*d* of 1-(buta-1,3-dien-2-yl)-2,4-dimethylbenzene

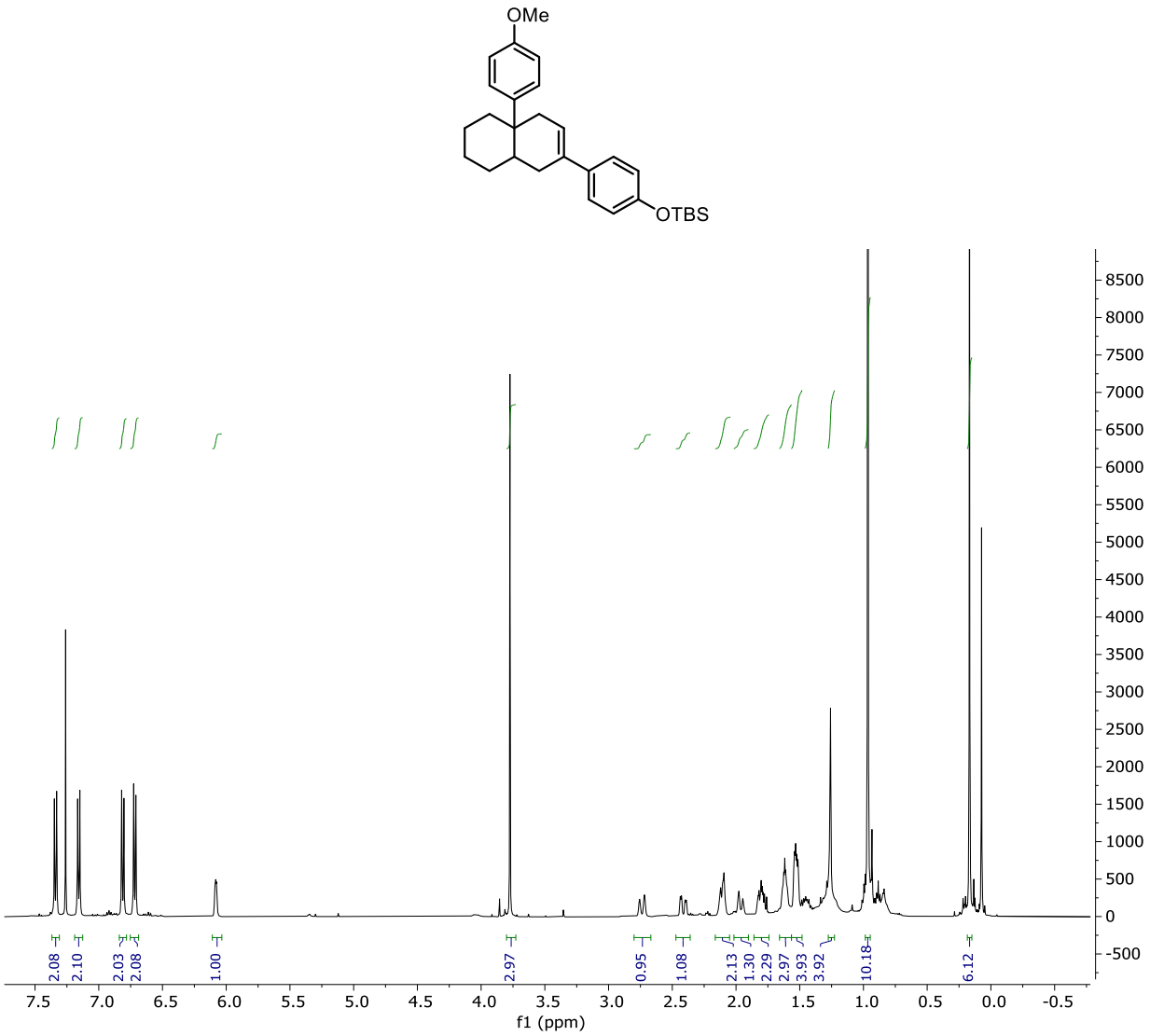


Figure S68 ^{1}H NMR, $CDCl_3$-*d* of LP-3b-1 (mono addition)

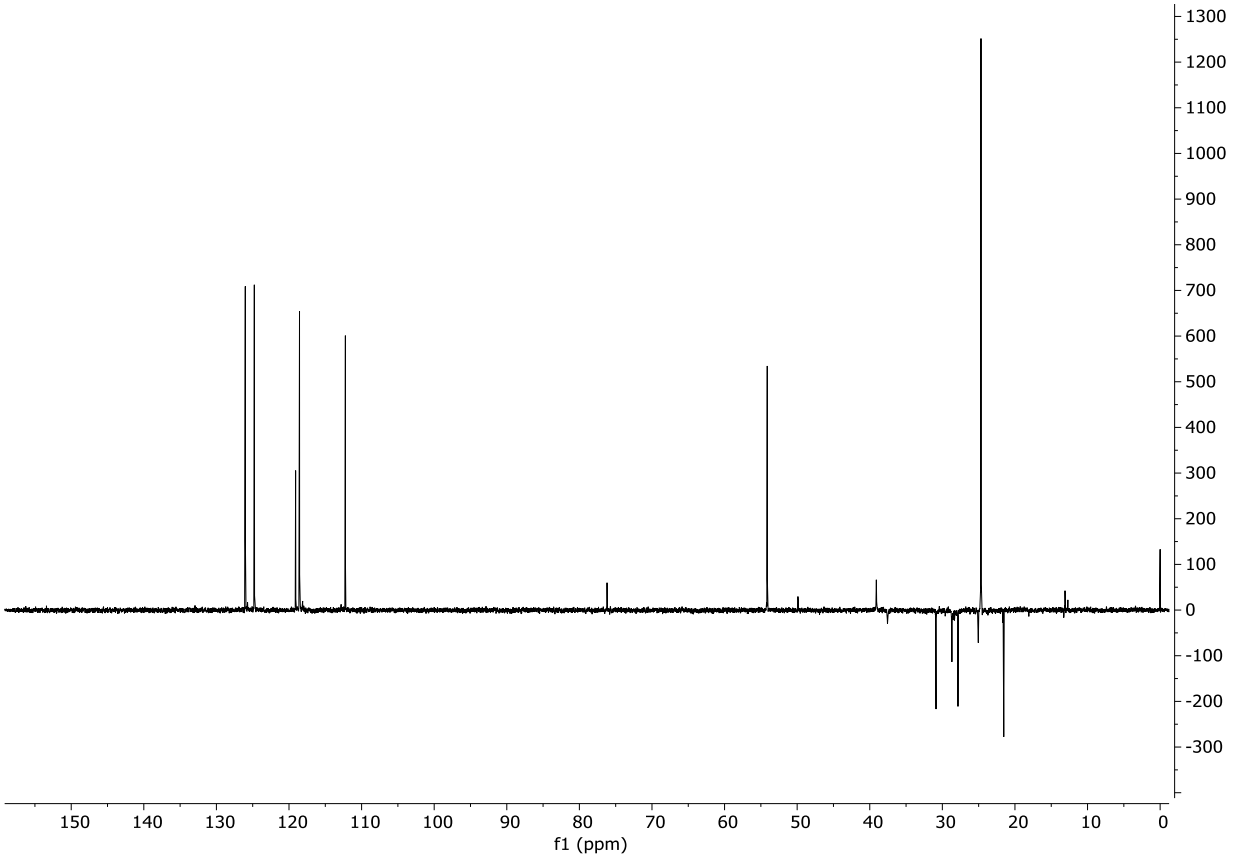


Figure S69 ^{13}C DEPT NMR, $CDCl_3$-*d* of LP-3b-1 (mono addition)

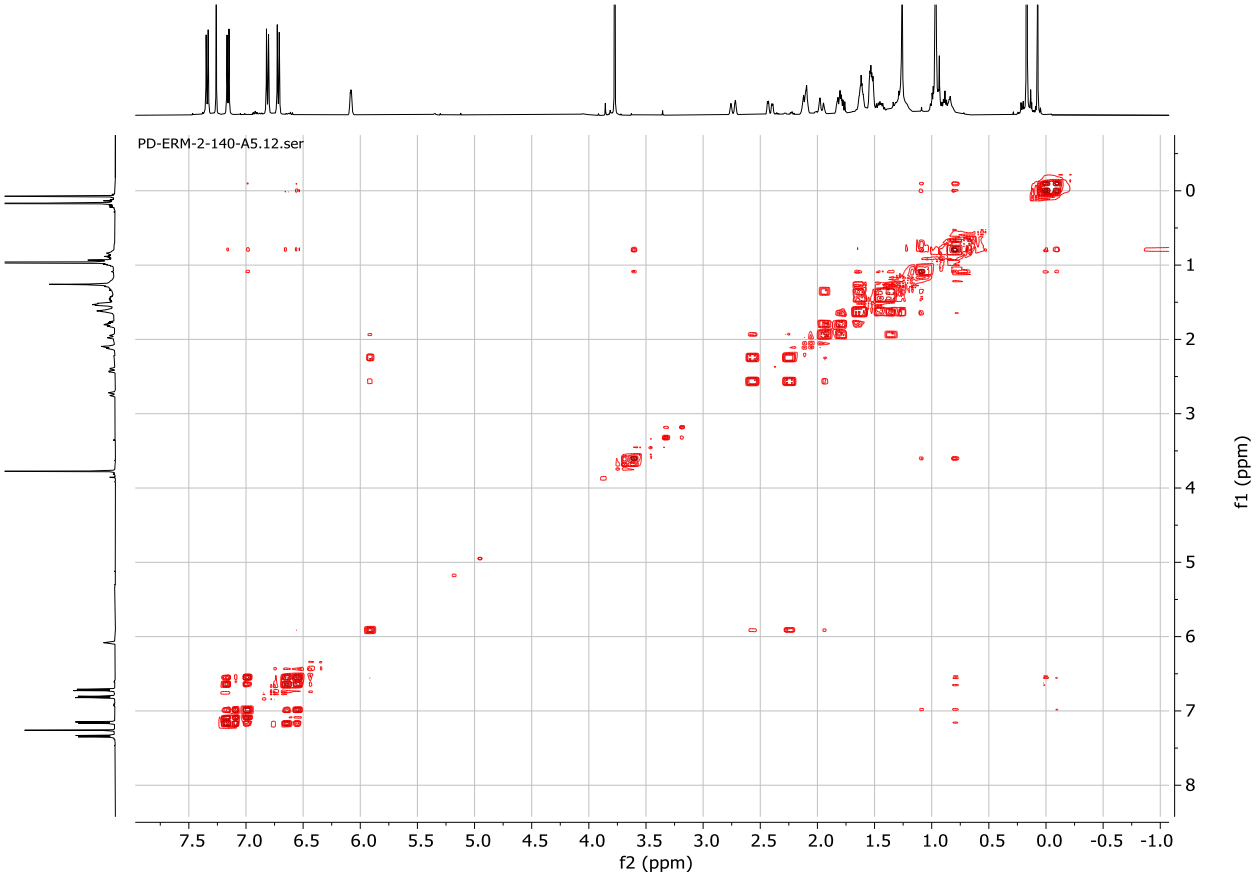


Figure S70 2D COSY NMR, $CDCl_3$-*d* of LP-3b-1 (mono addition)

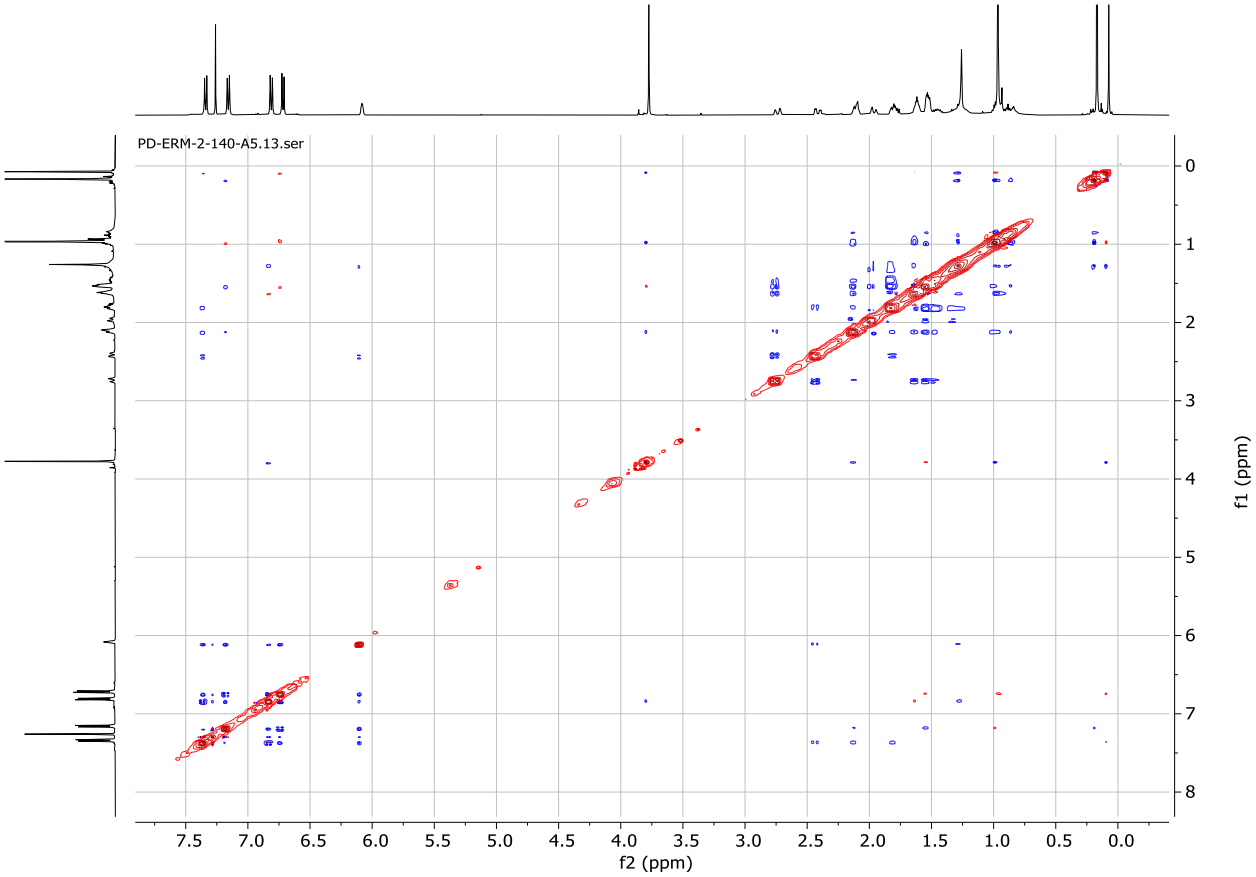


Figure S71 2D NOESY NMR, $CDCl_3$-*d* of of LP-3b-1 (mono addition)

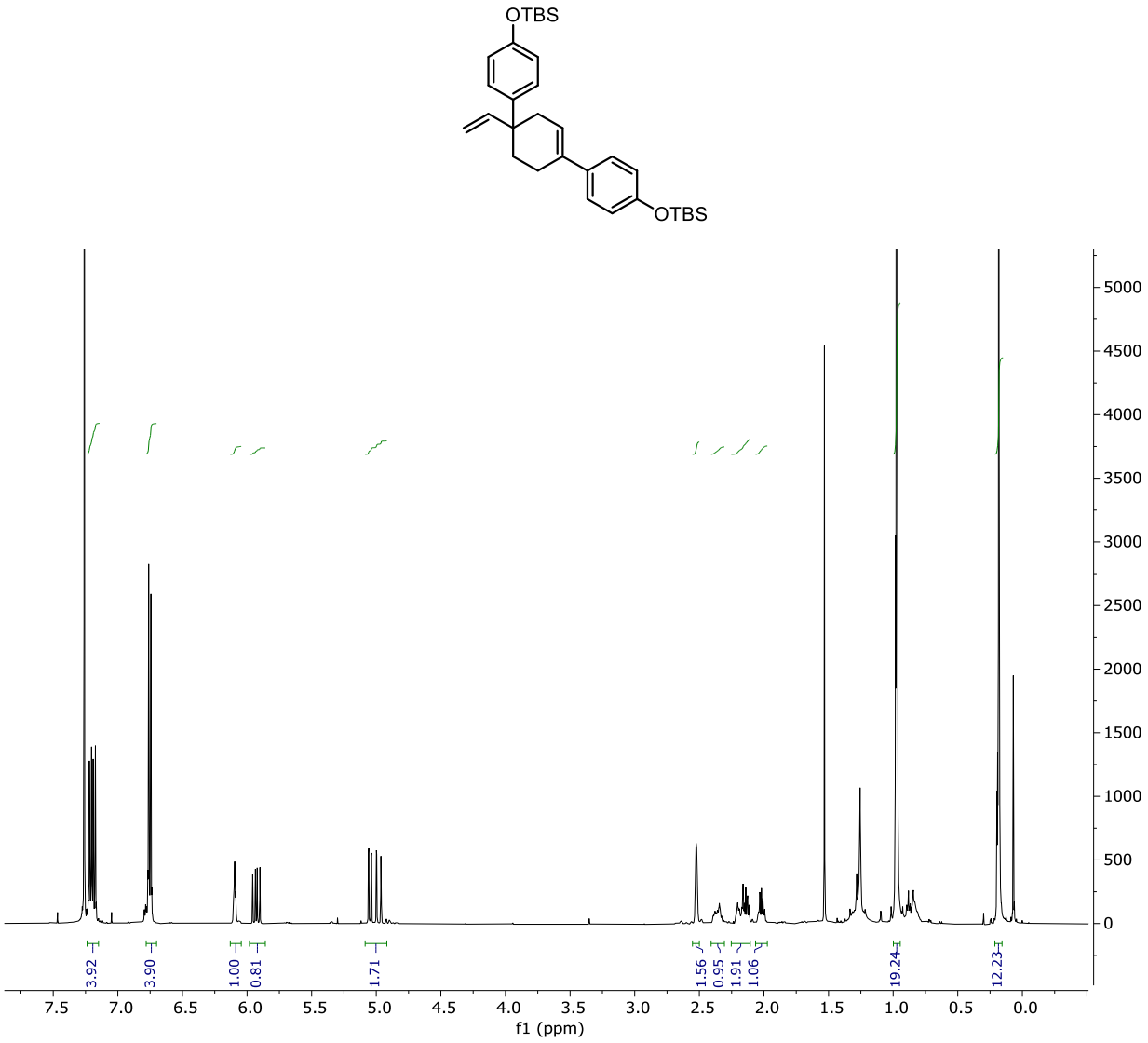


Figure S72 ^{1}H NMR, $CDCl_3$-*d* of LP-3b'-1 (mono addition)

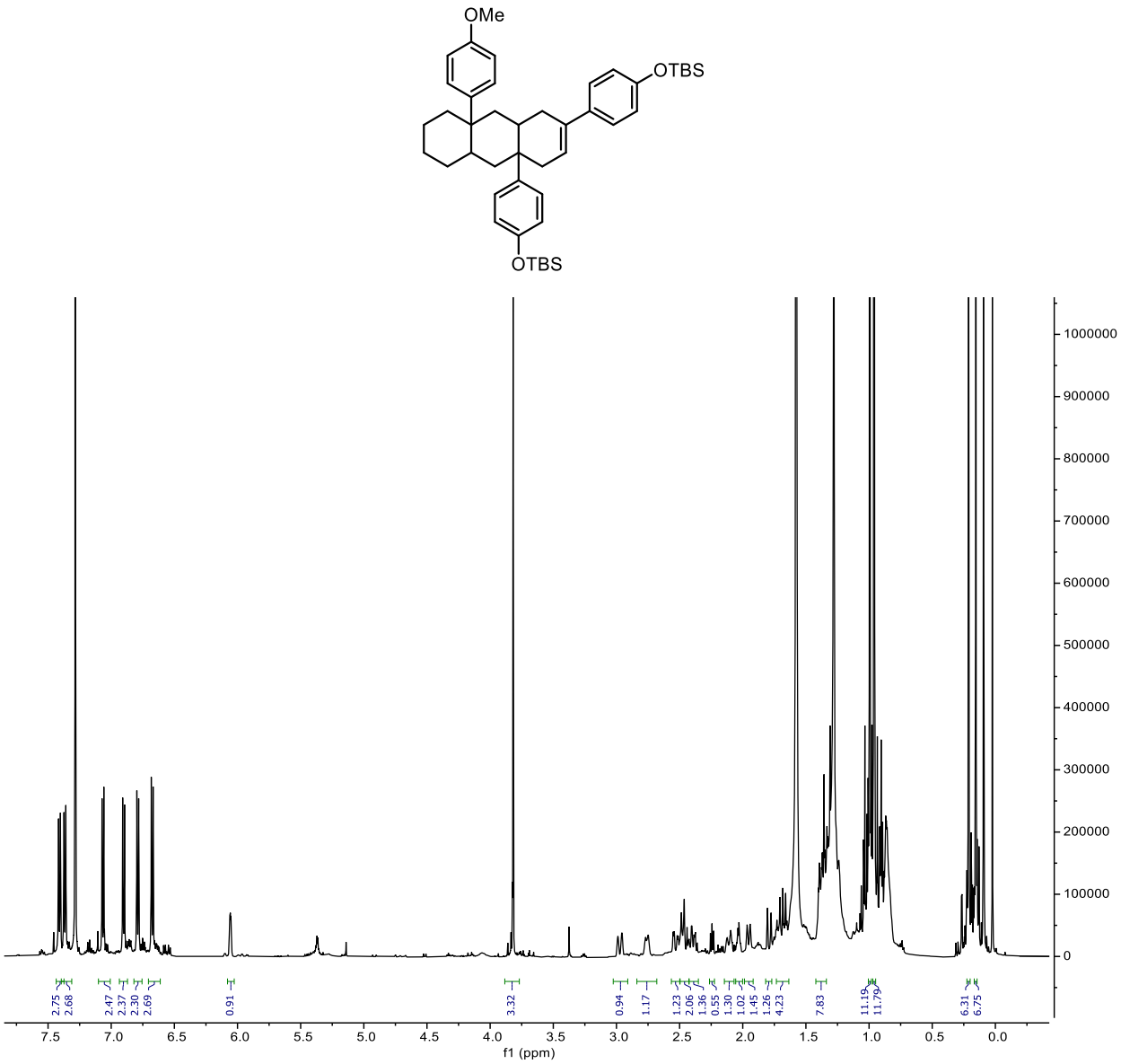


Figure S73 ^{1}H NMR, $CDCl_3$-*d* of LP-3b-2 (bis addition)

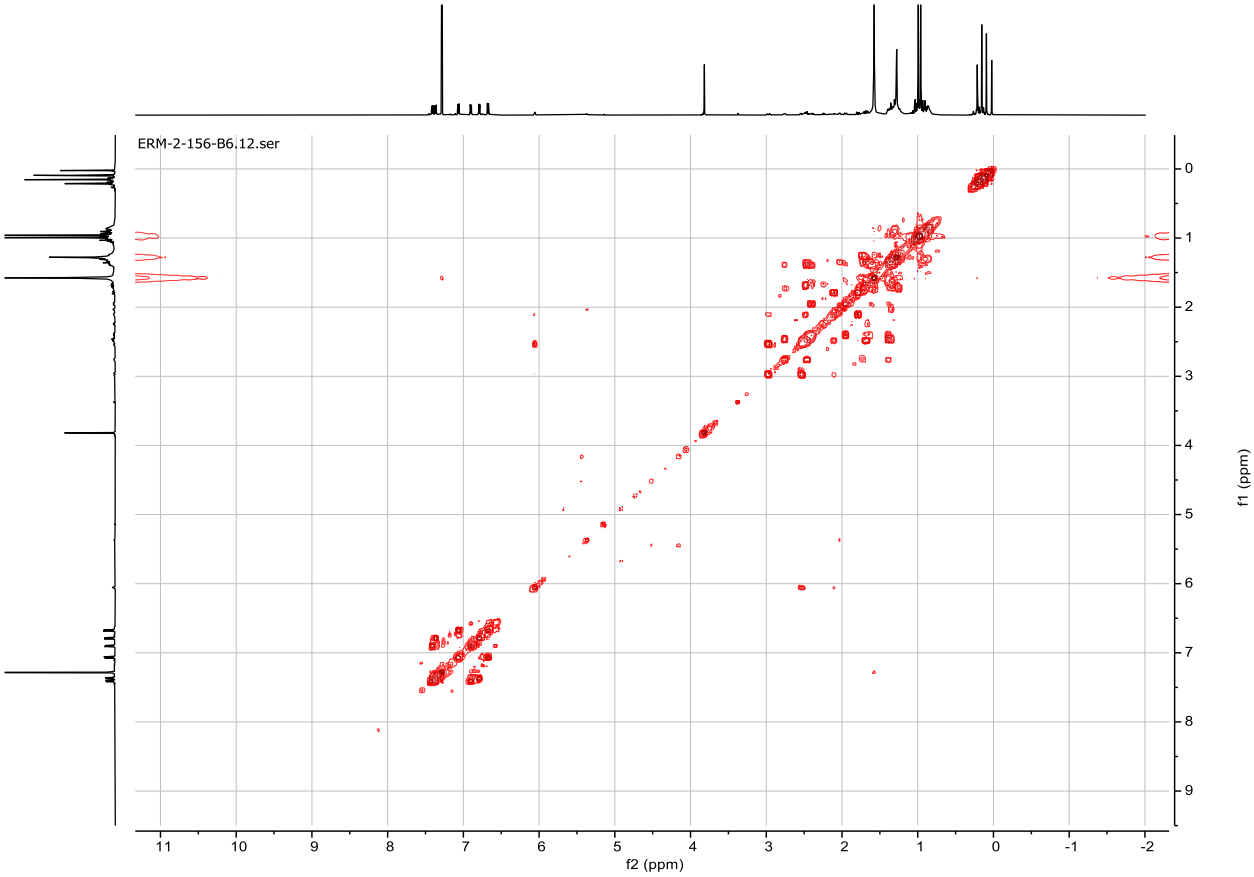


Figure S74 2D COSY NMR, $CDCl_3$-*d* of of LP-3b-2 (bis addition)

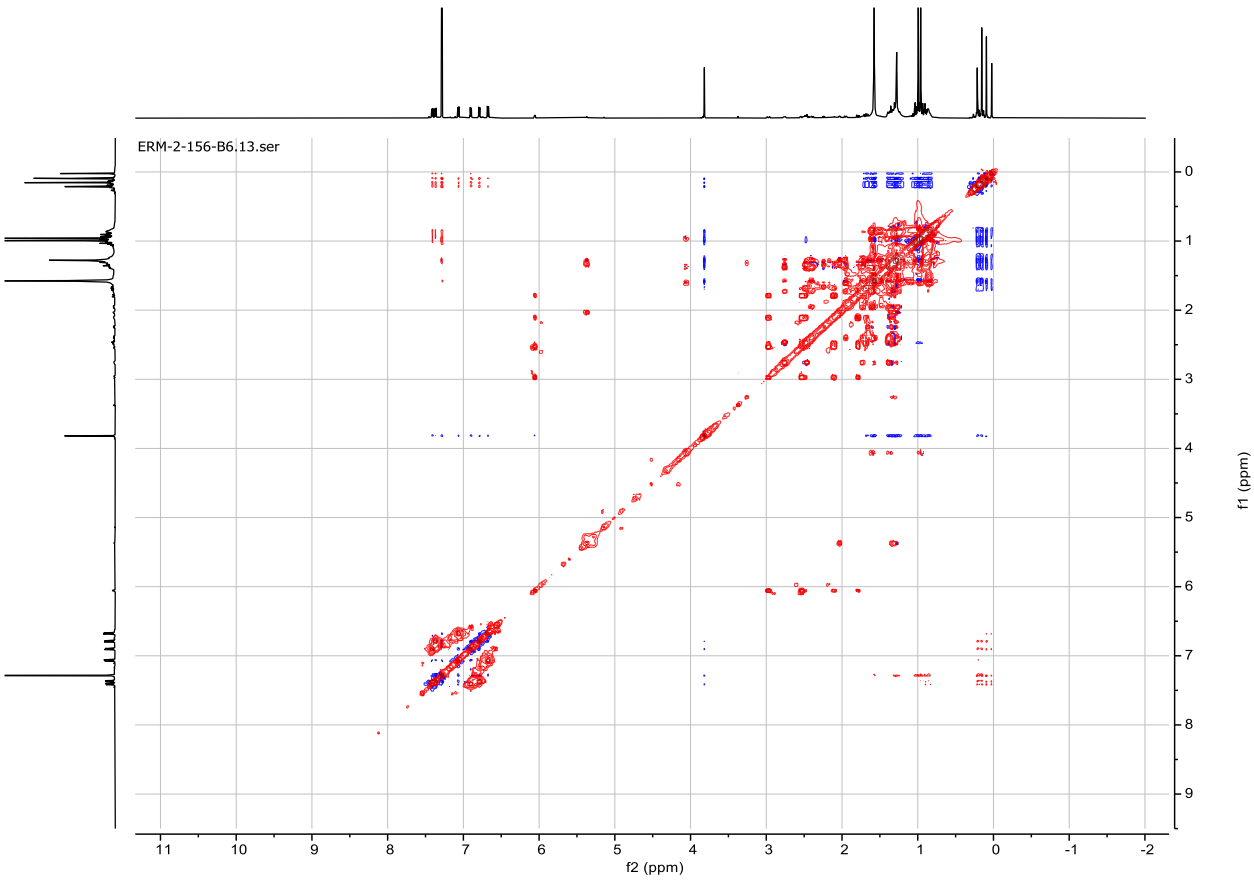


Figure S75 2D TOCSY NMR, $CDCl_3$-*d* of of LP-3b-2 (bis addition)

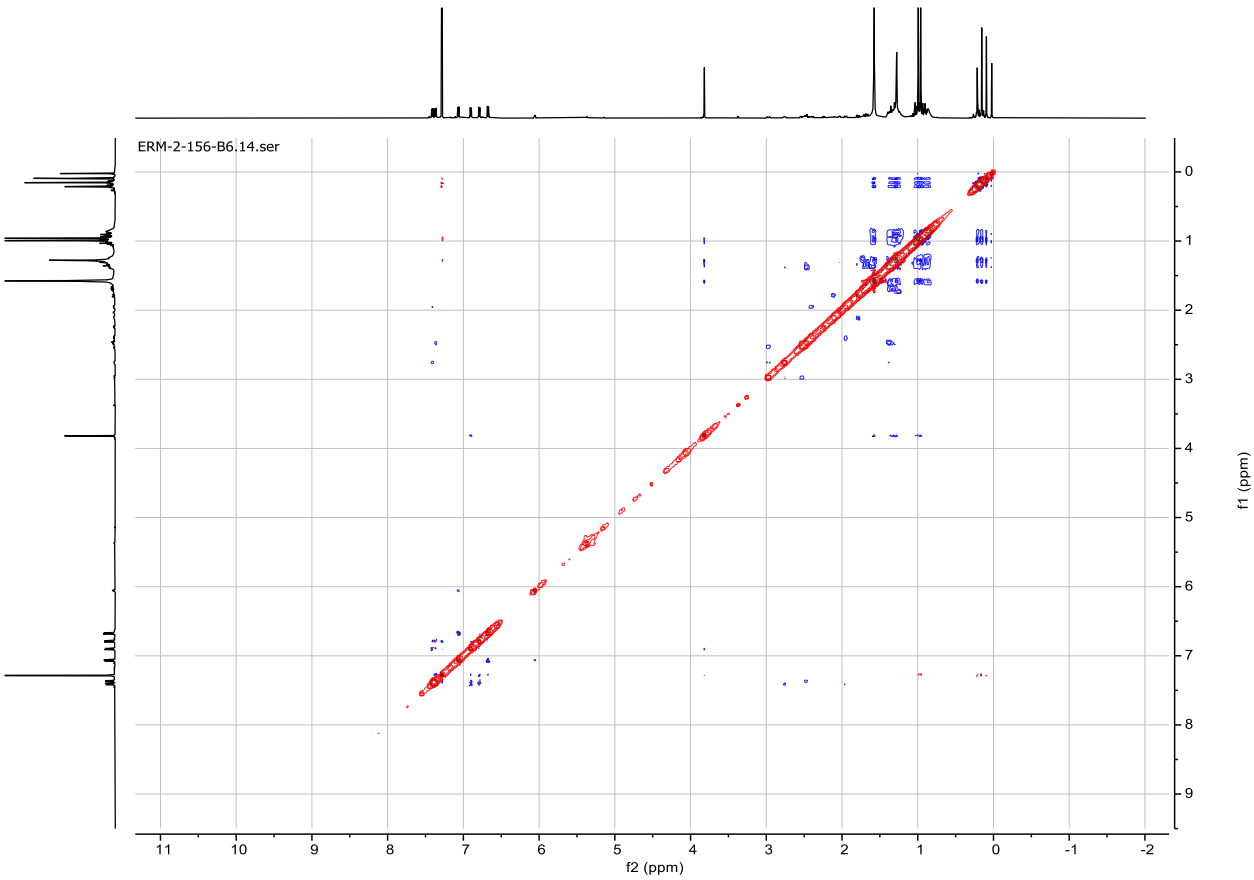


Figure S76 2D NOESY NMR, $CDCl_3$-*d* of LP-3b-2 (bis addition)

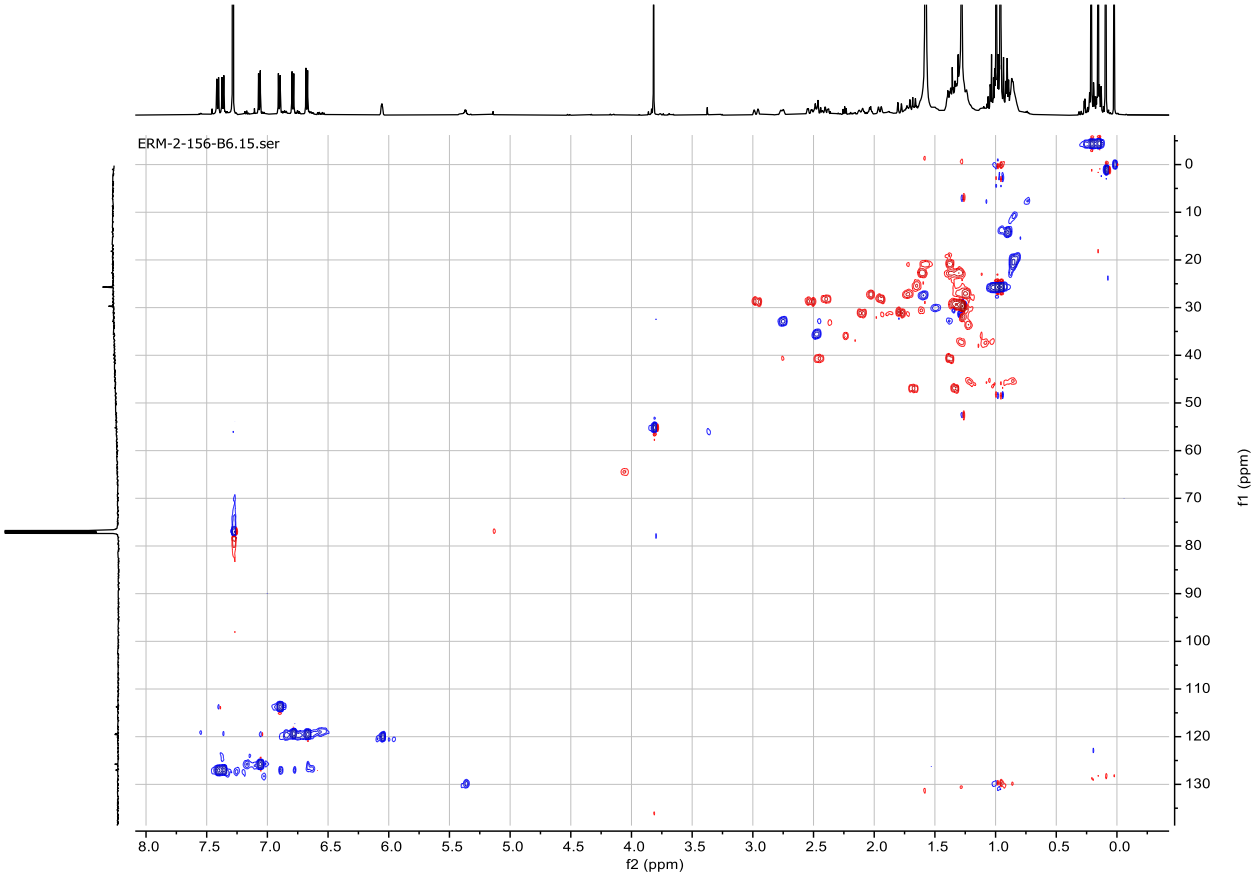


Figure S77 2D HSQC NMR, $CDCl_3$-*d* of of LP-3b-2 (bis addition)

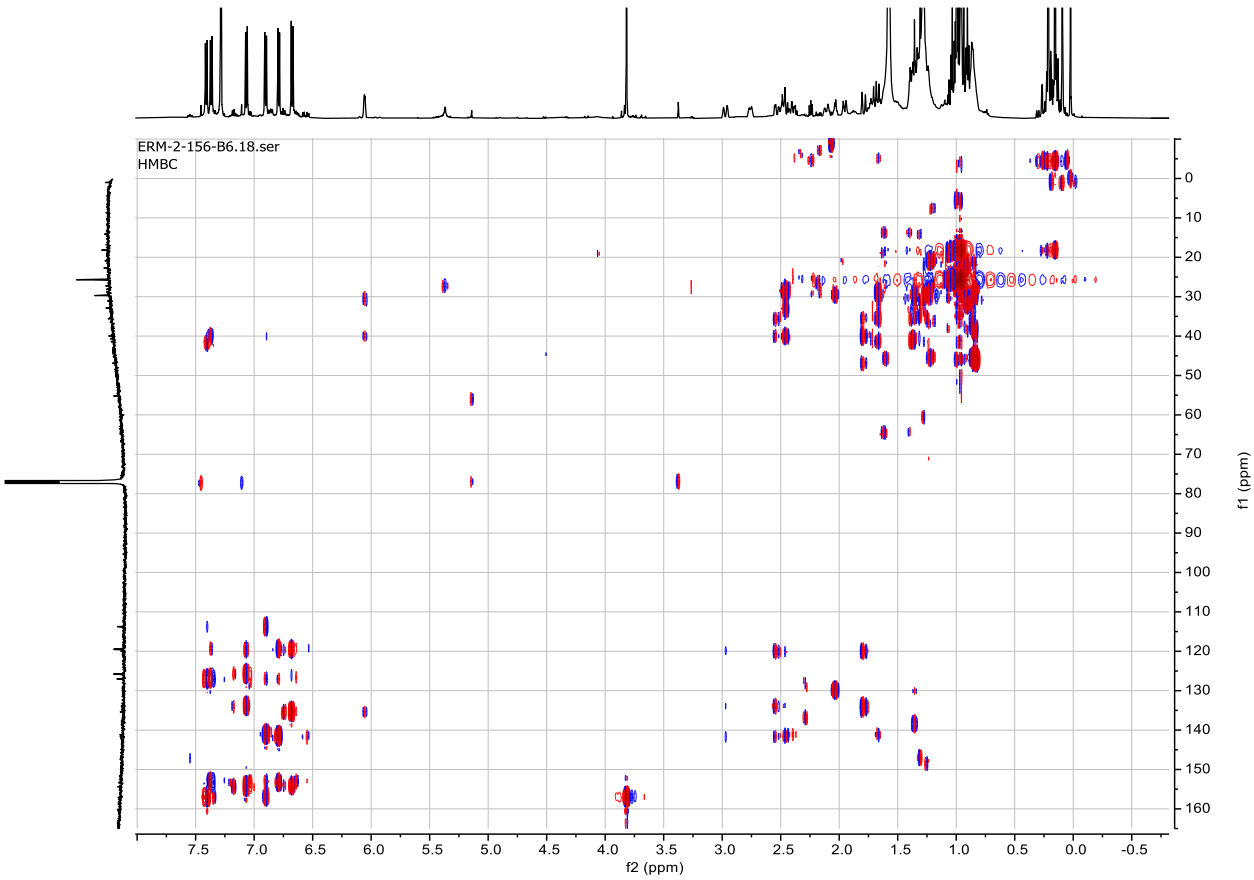


Figure S78 2D HMBC NMR, $CDCl_3$-*d* of of LP-3b-2 (bis addition)

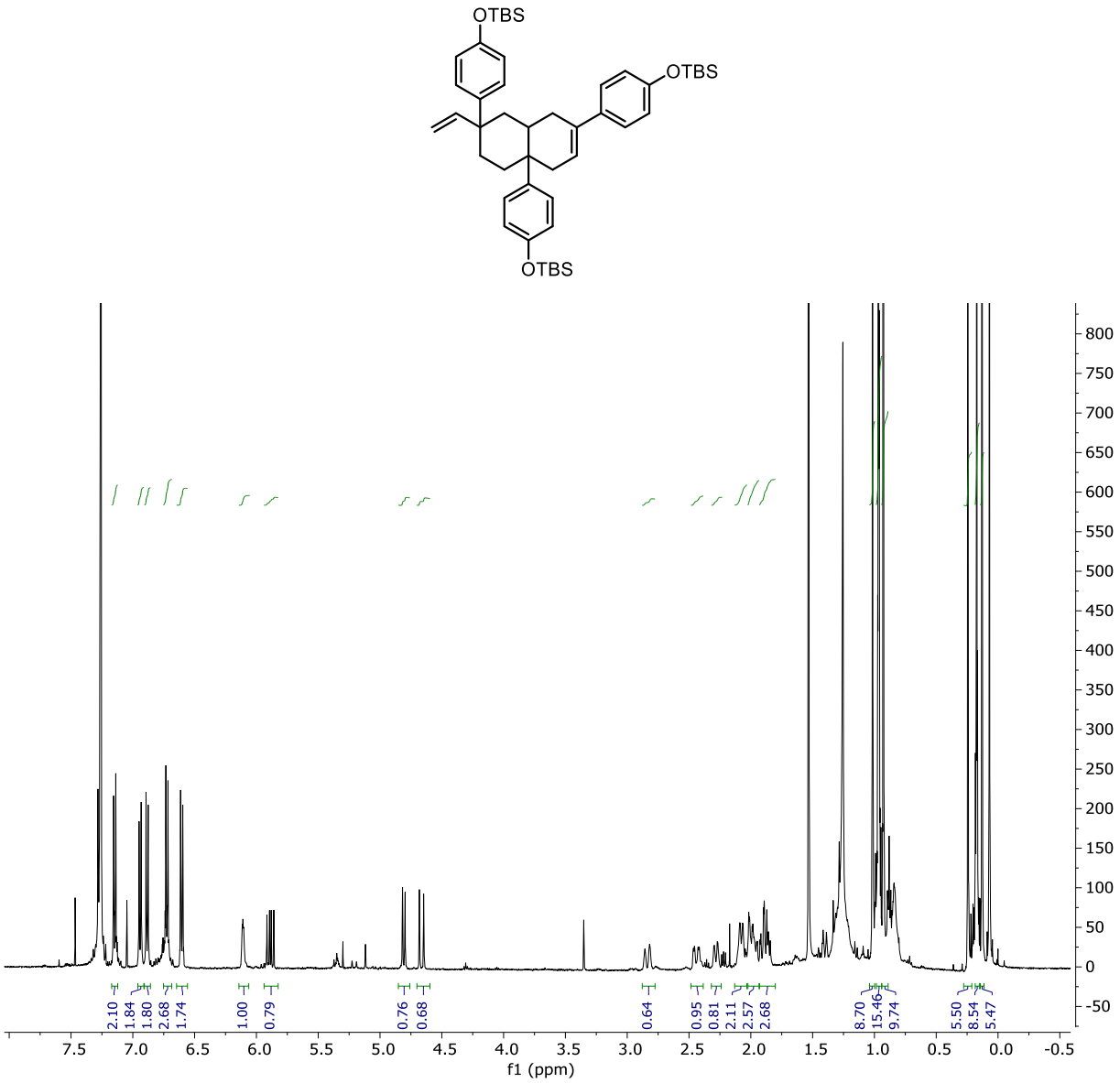


Figure S79 ^{1}H NMR, $CDCl_3$-*d* of LP-3b'-2 (bis addition)

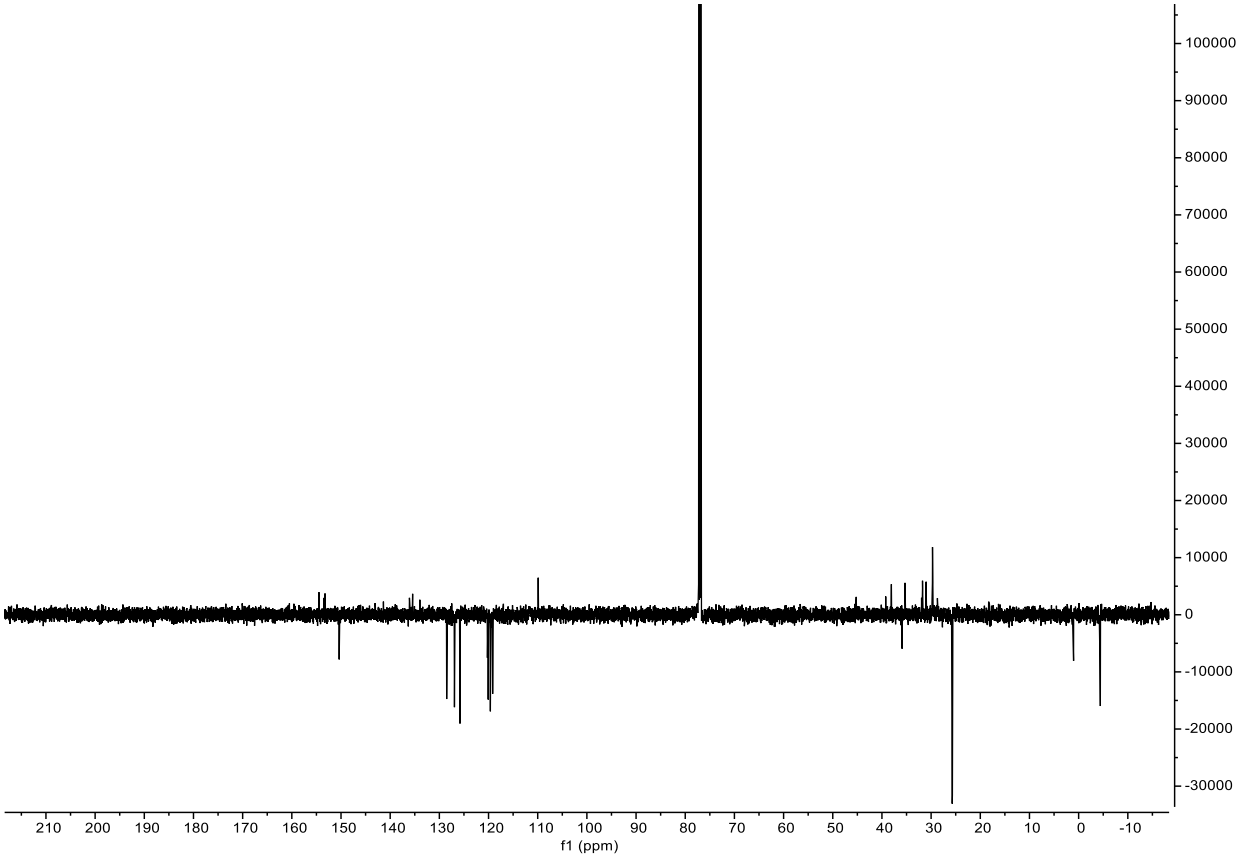


Figure S80 ^{13}C DEPT NMR, $CDCl_3$-*d* of LP-3b'-2 (bis addition)

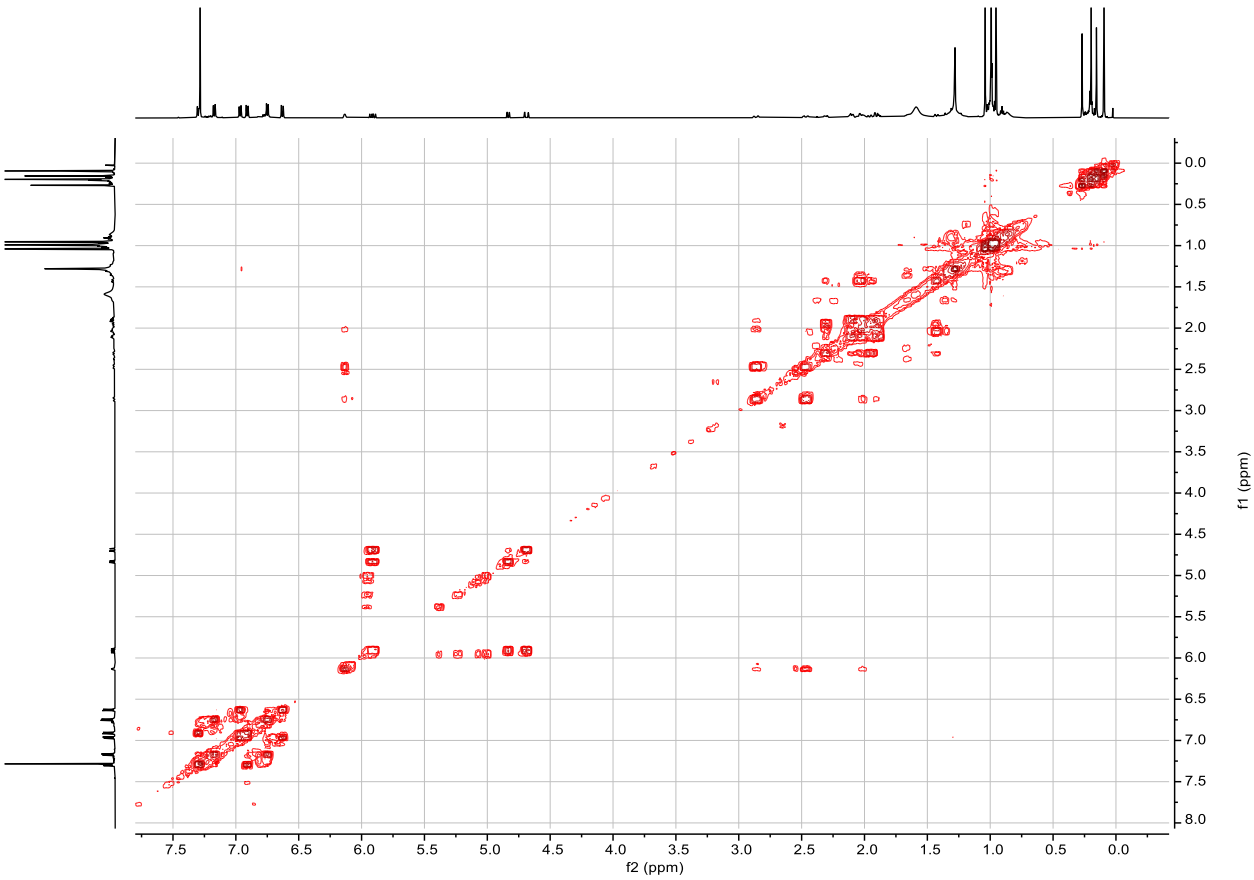


Figure S81 2D COSY NMR, $CDCl_3$-*d* of LP-3b'-2 (bis addition)

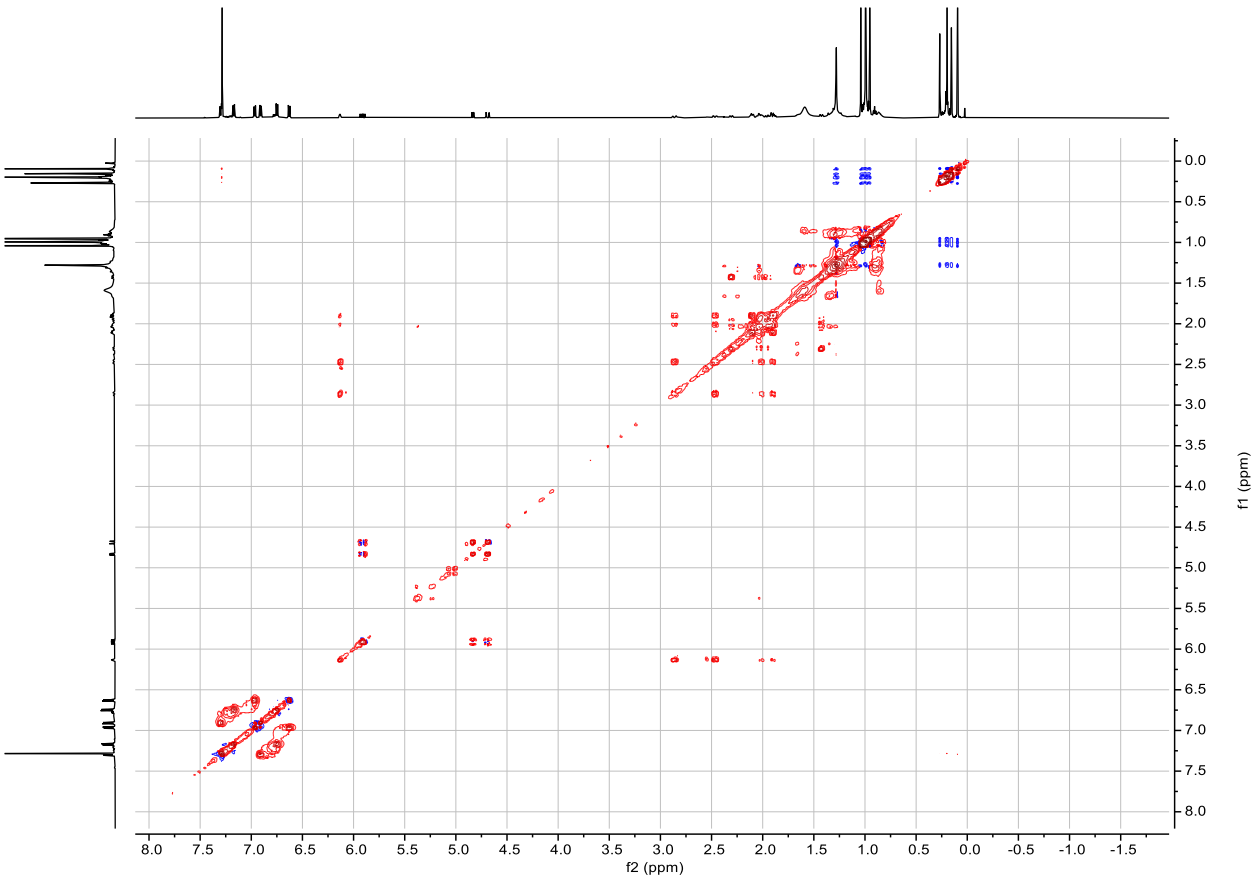


Figure S82 2D TOCSY NMR, $CDCl_3$-*d* of LP-3b'-2 (bis addition)

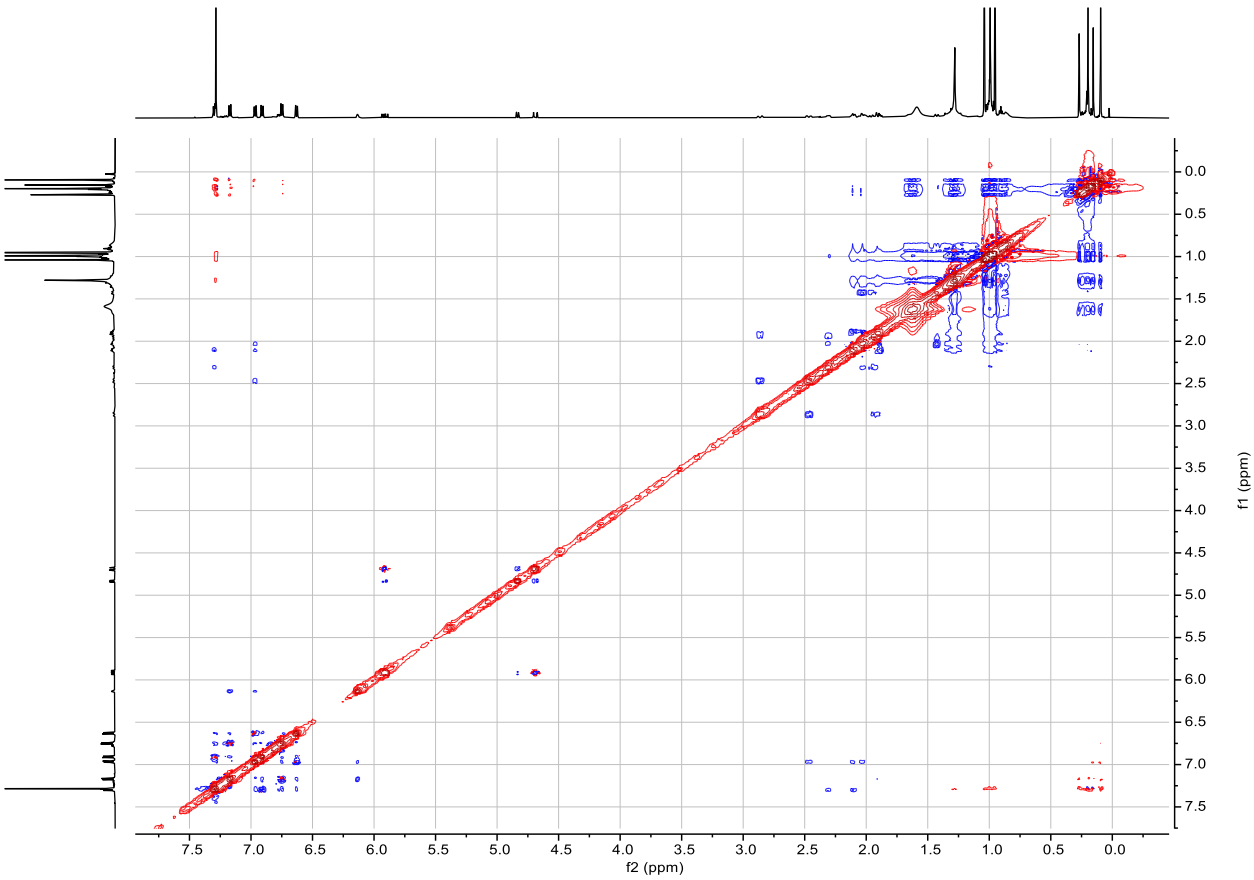


Figure S83 2D NOESY NMR, $CDCl_3$-*d* of LP-3b'-2 (bis addition)

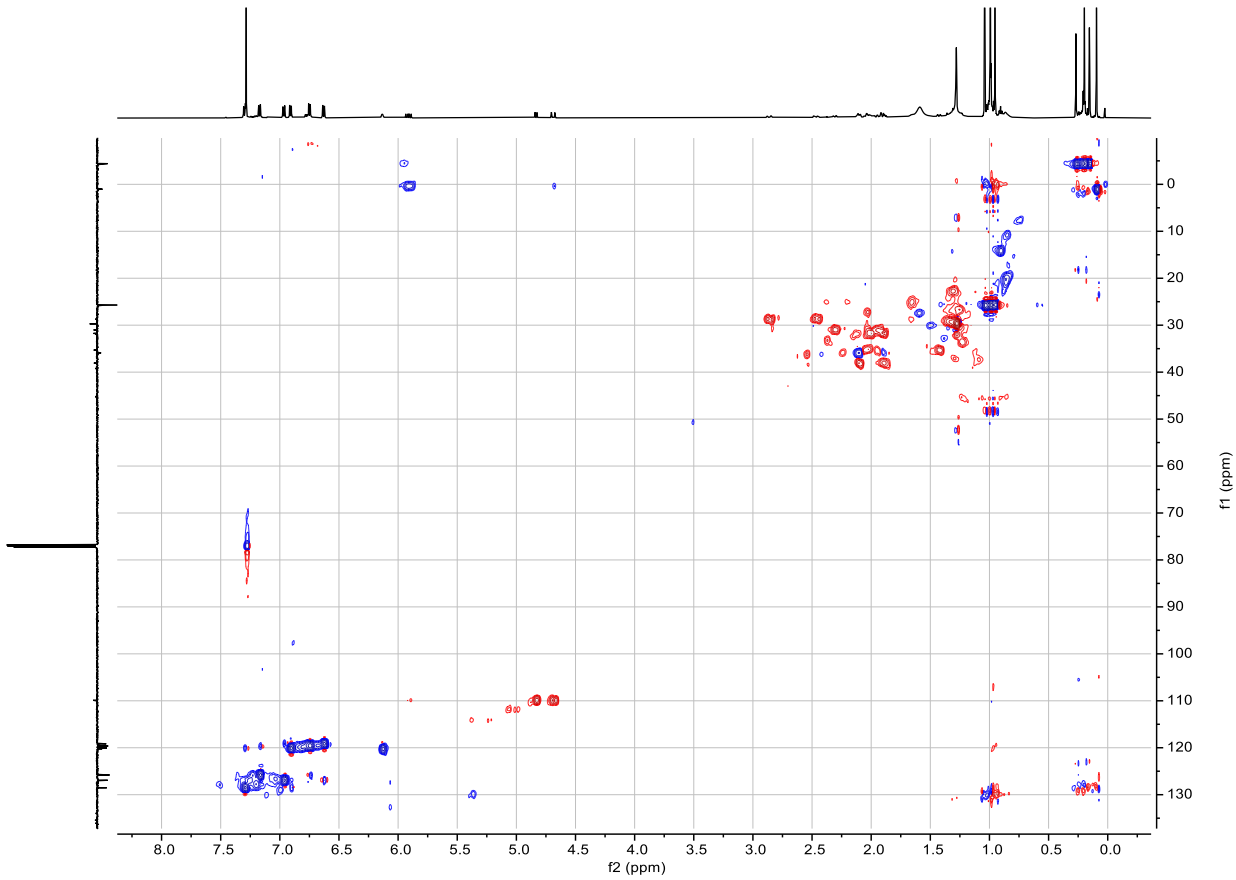


Figure S84 2D HSQC NMR, $CDCl_3$-*d* of LP-3b'-2 (bis addition)

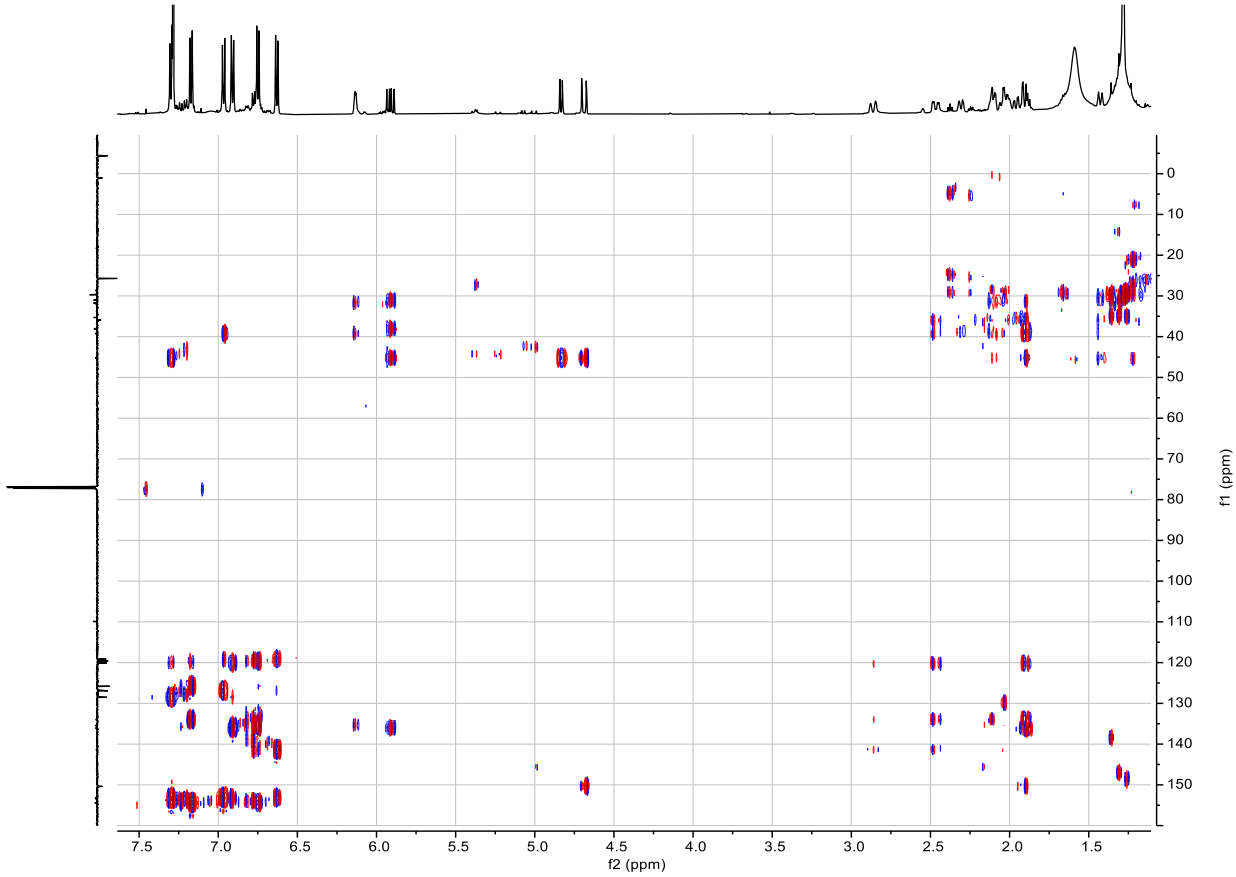


Figure S85 2D HMBC NMR, $CDCl_3$-*d* of LP-3b'-2 (bis addition)

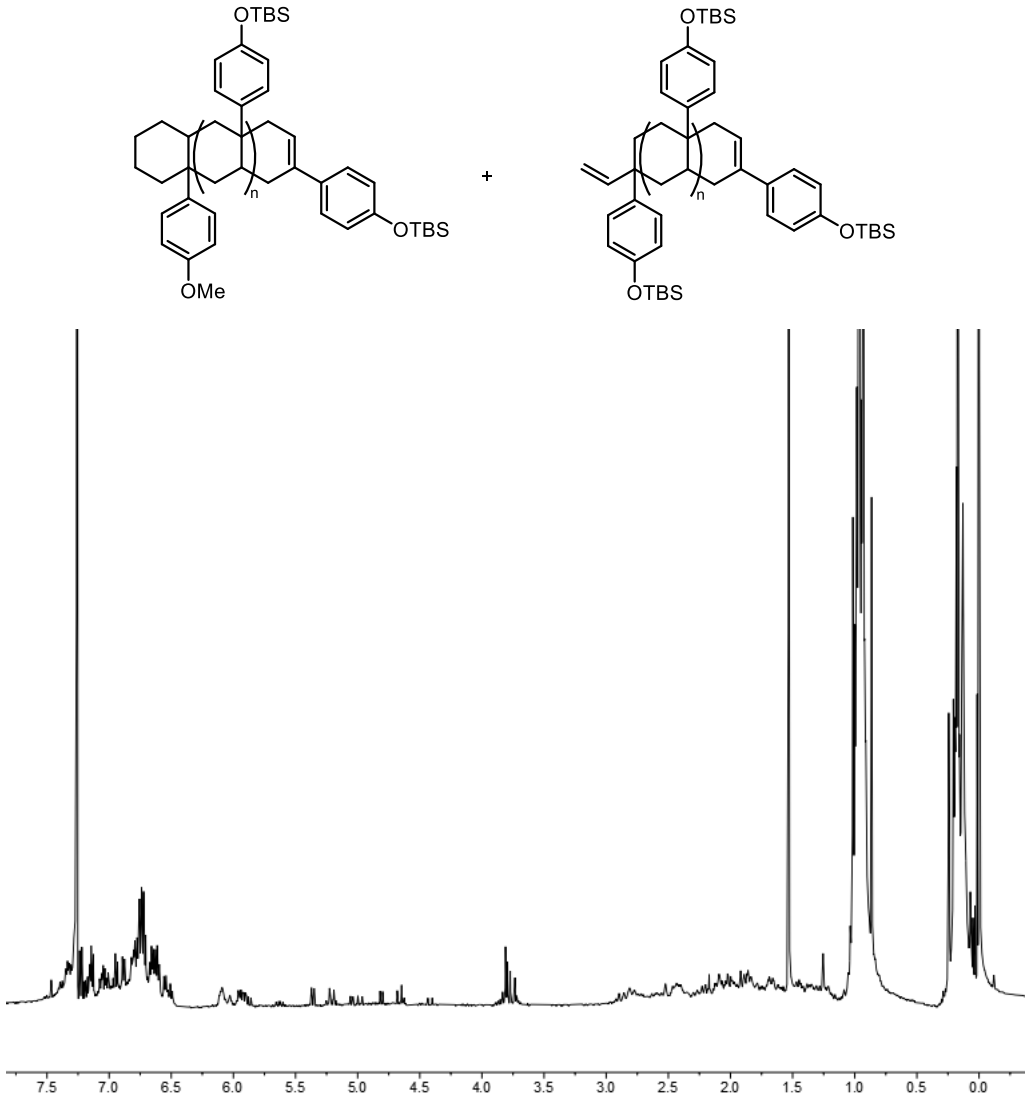


Figure S86 ^{1}H NMR, $CDCl_3$-*d* of LP-3b and LP-3b'

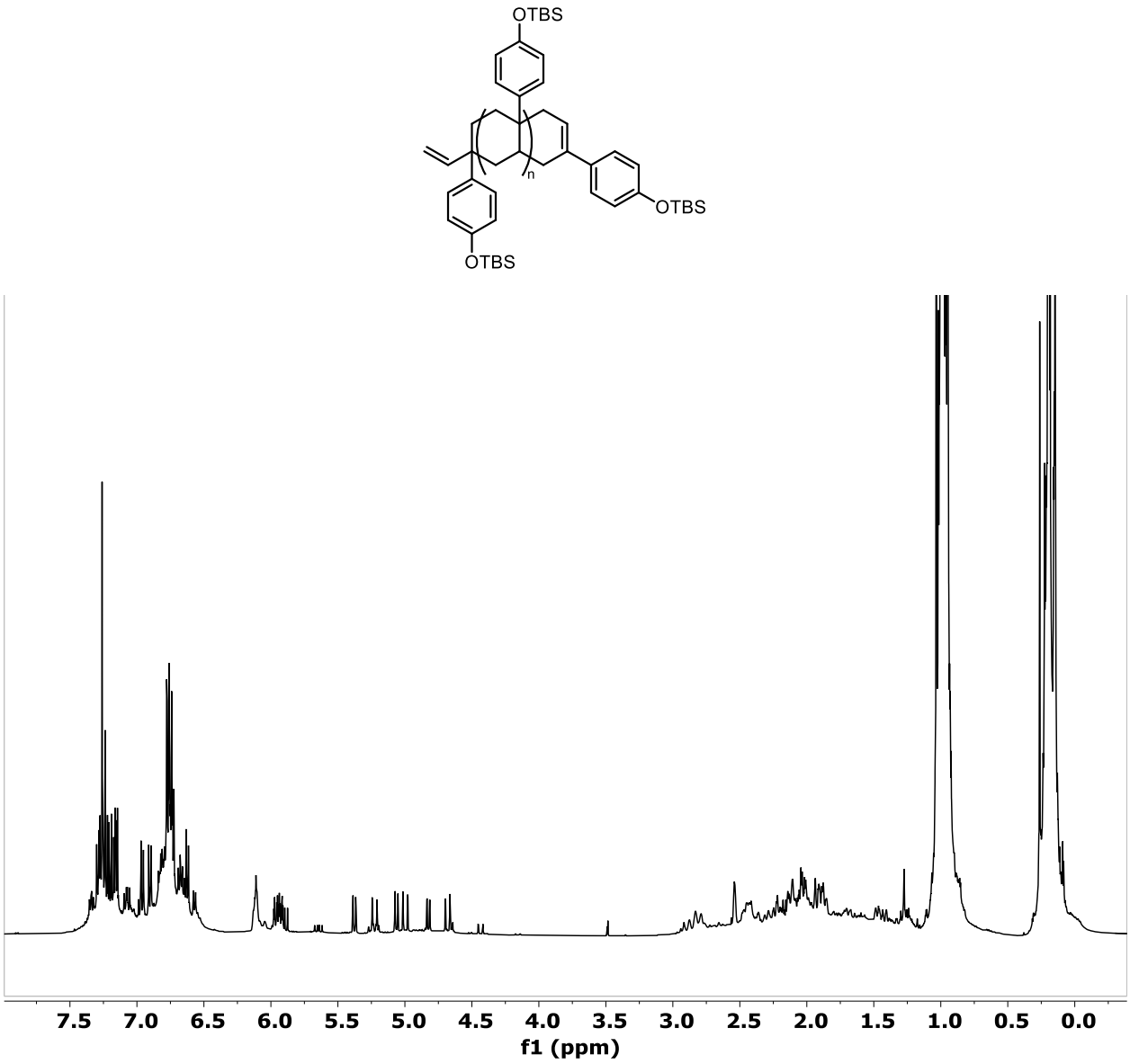


Figure S87 ^{1}H NMR, $CDCl_3$-*d* of LP-3b'

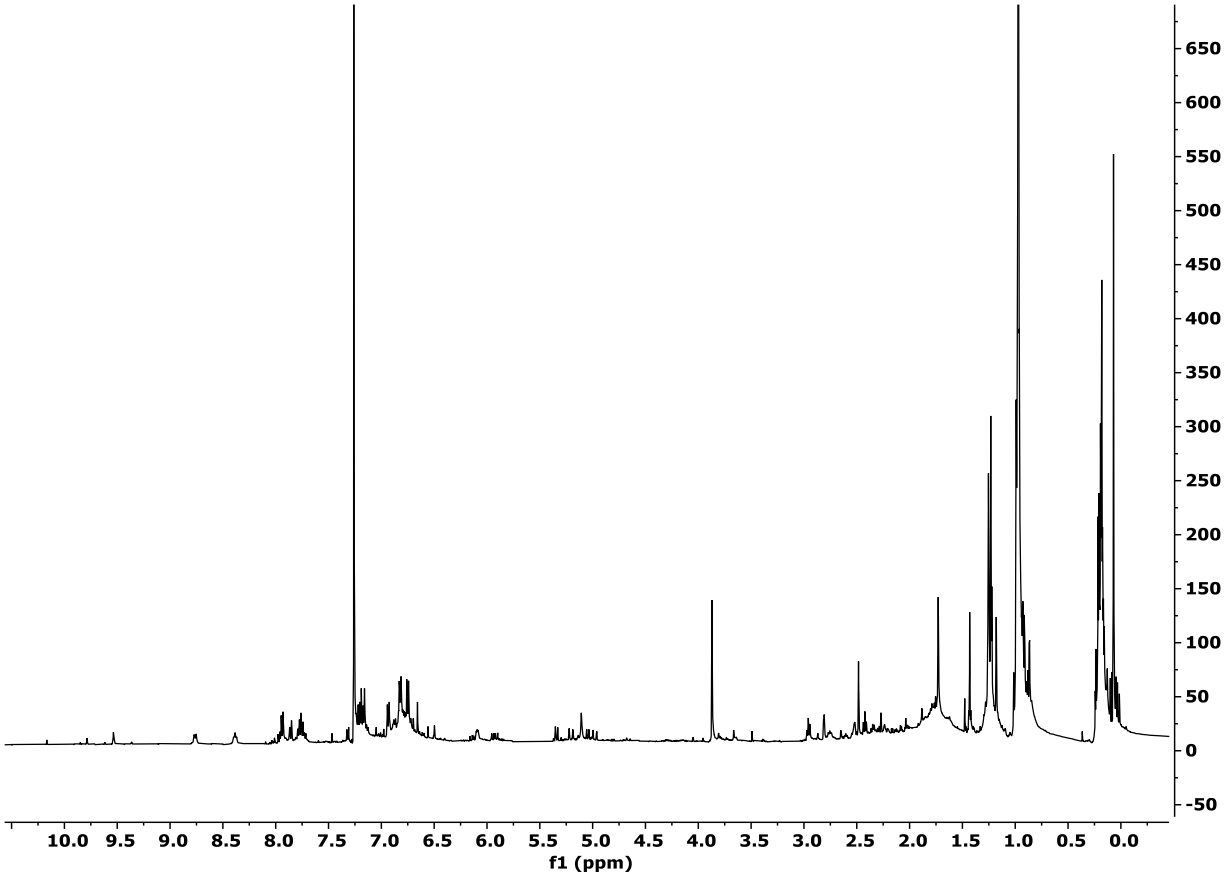


Figure S88 ^{1}H NMR, $CDCl_3$-*d* of LP-3b' supernatant

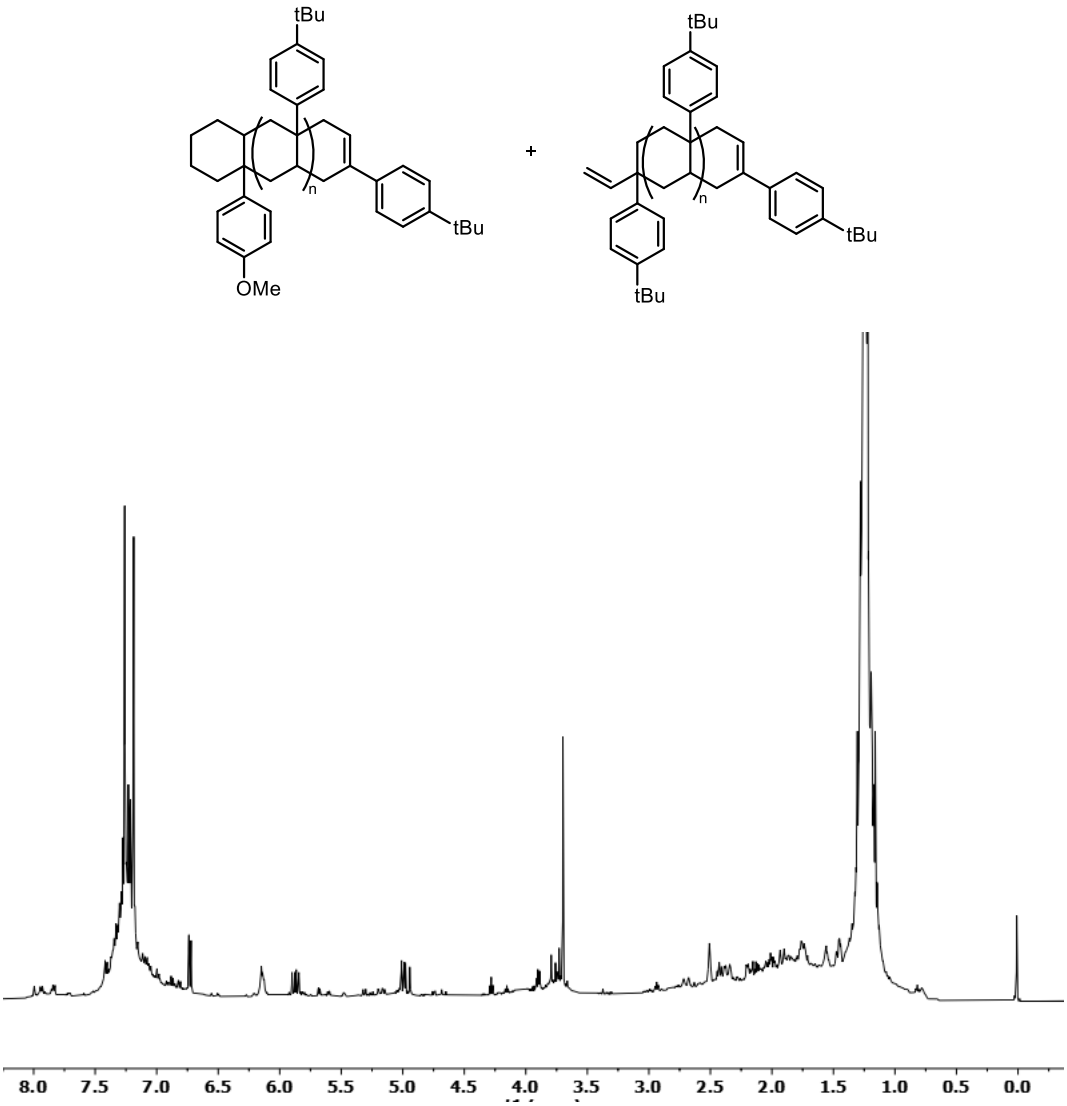


Figure S89 ^{1}H NMR, $CDCl_3$-*d* of LP-3c and 3c'

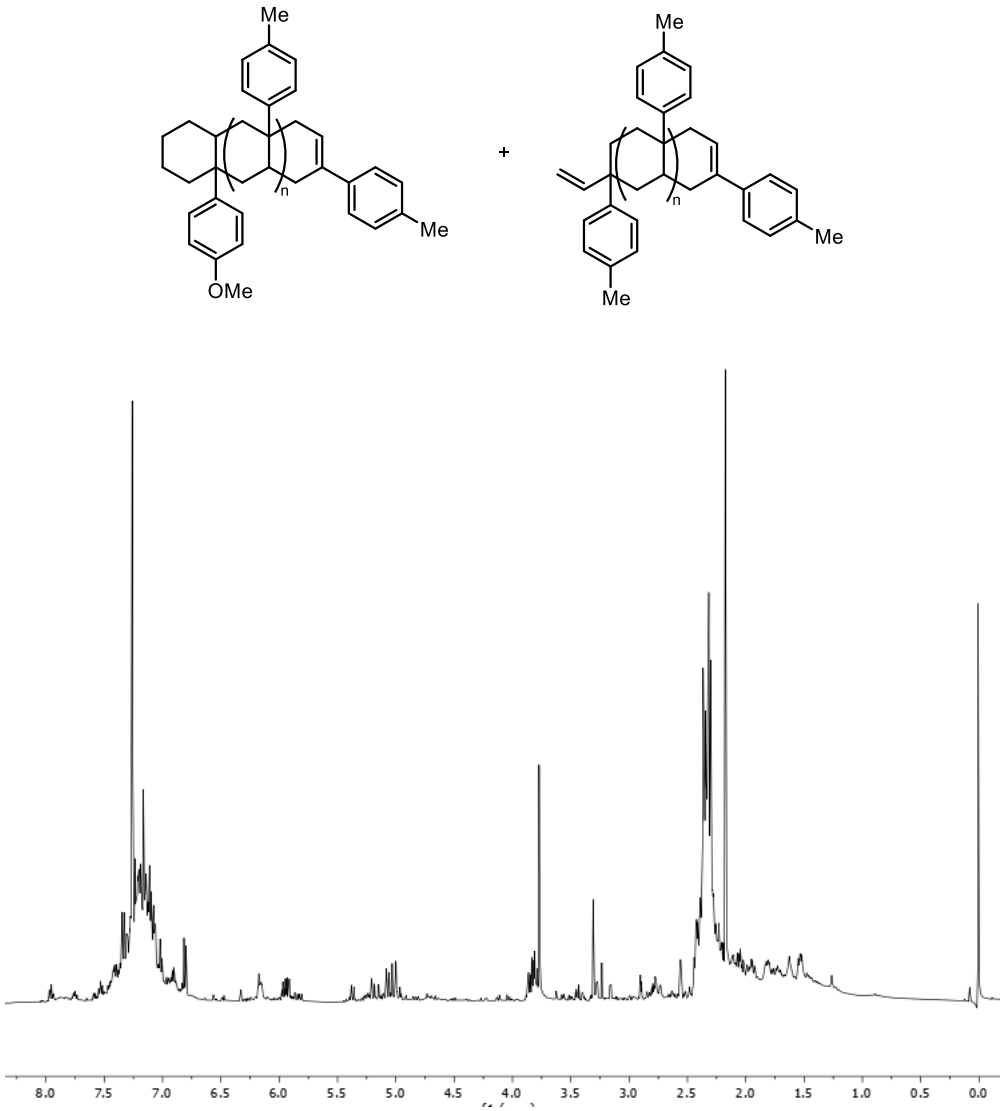


Figure S90 ^{1}H NMR, $CDCl_3$-*d* of LP-3d and 3d'

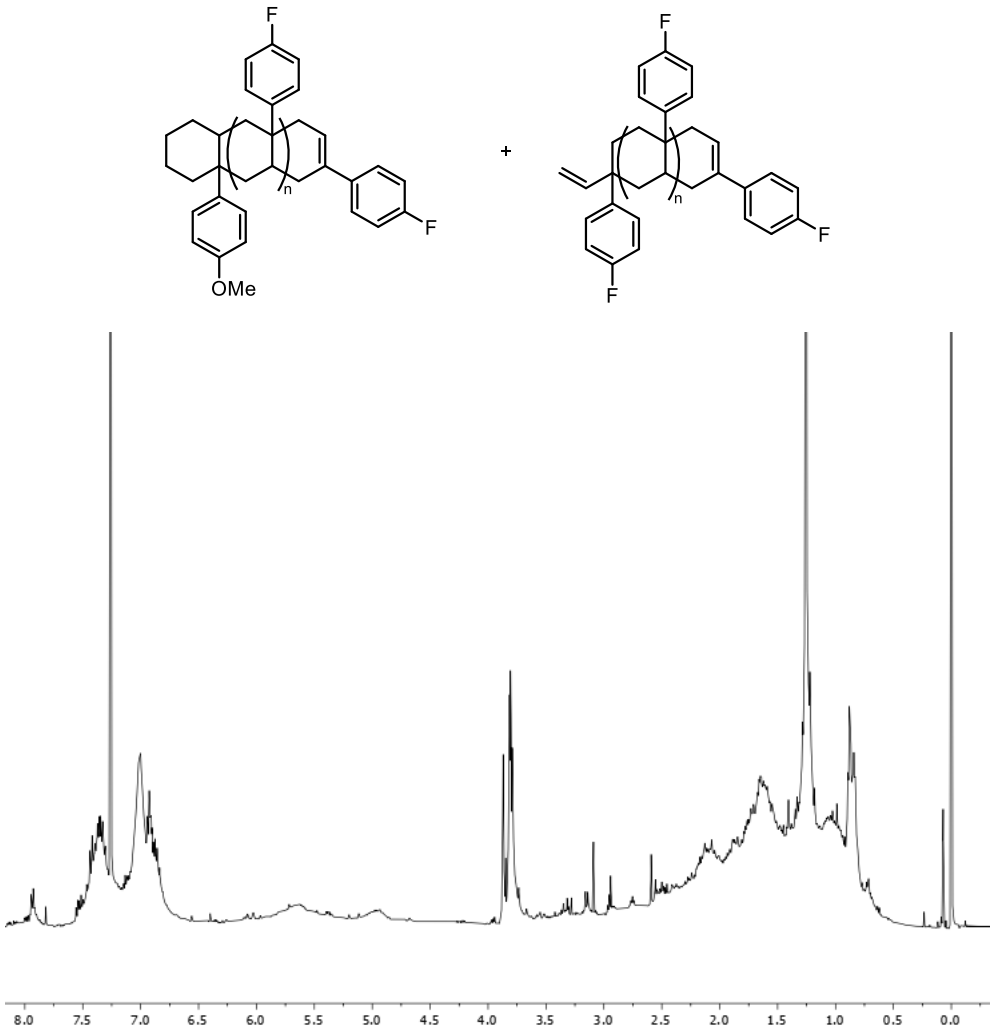


Figure S91 ^{1}H NMR, $CDCl_3$-*d* of LP-3e and 3e'

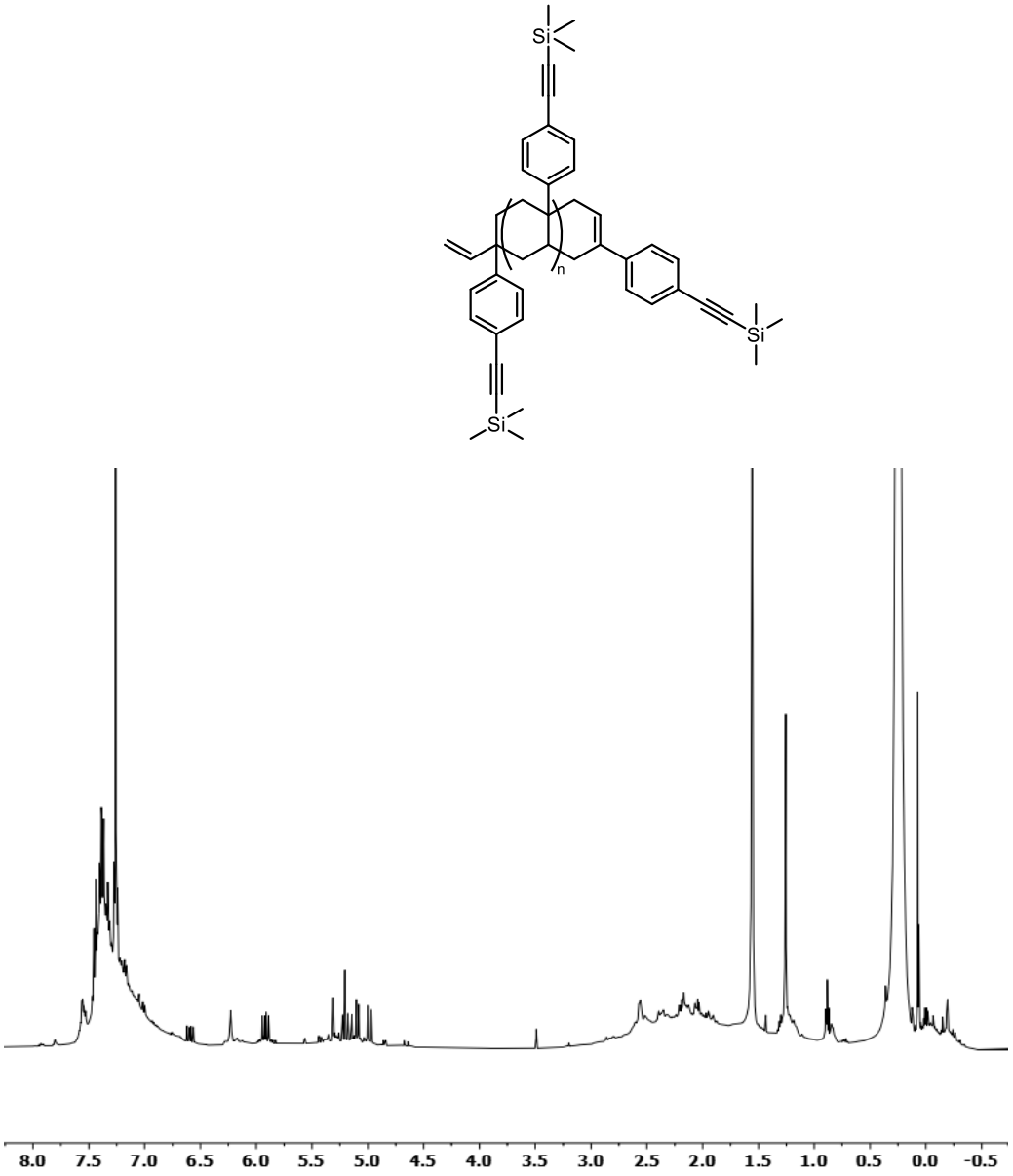


Figure S92 ^{1}H NMR, $CDCl_3$-*d* of LP-3f

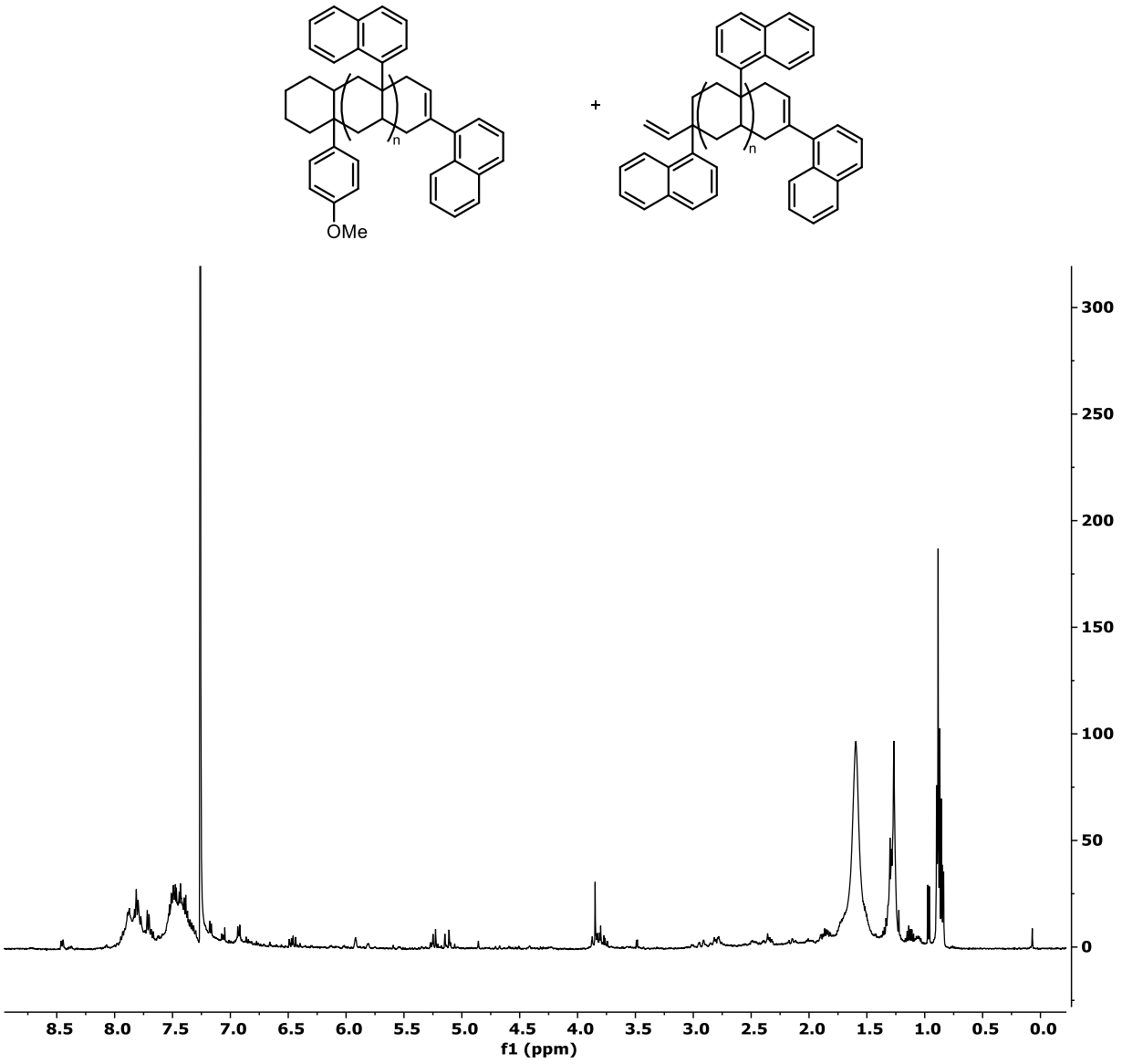


Figure S93 ^{1}H NMR, $CDCl_3$-*d* of LP-3g and 3g'

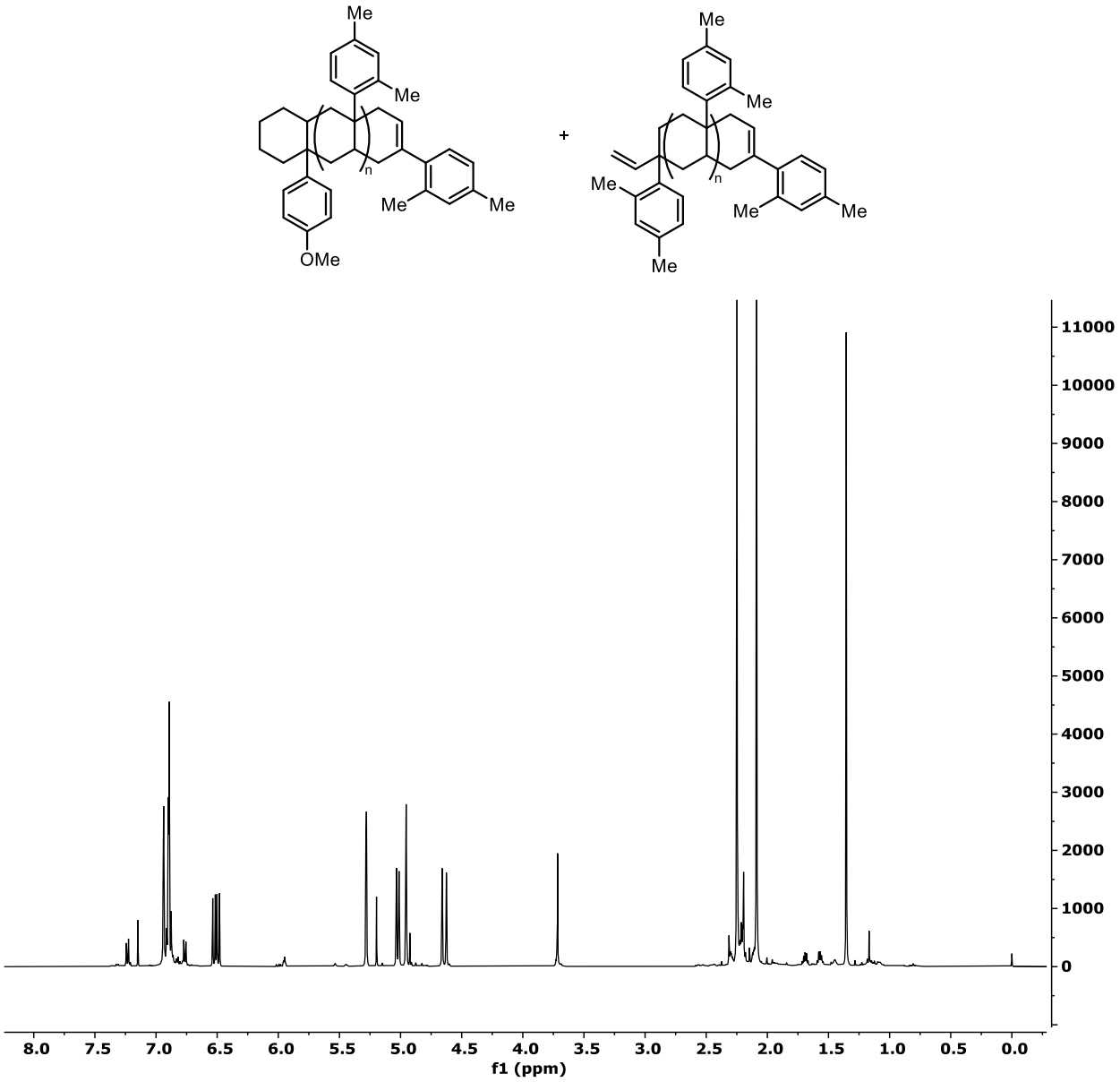


Figure S94 ^{1}H NMR, $CDCl_3$-*d* of LP-3h and 3h' *Note: the yield of the polymer precipitate was too low to obtain NMR spectra; therefore, this NMR is of the crude reaction mixture and shows mainly monomer*

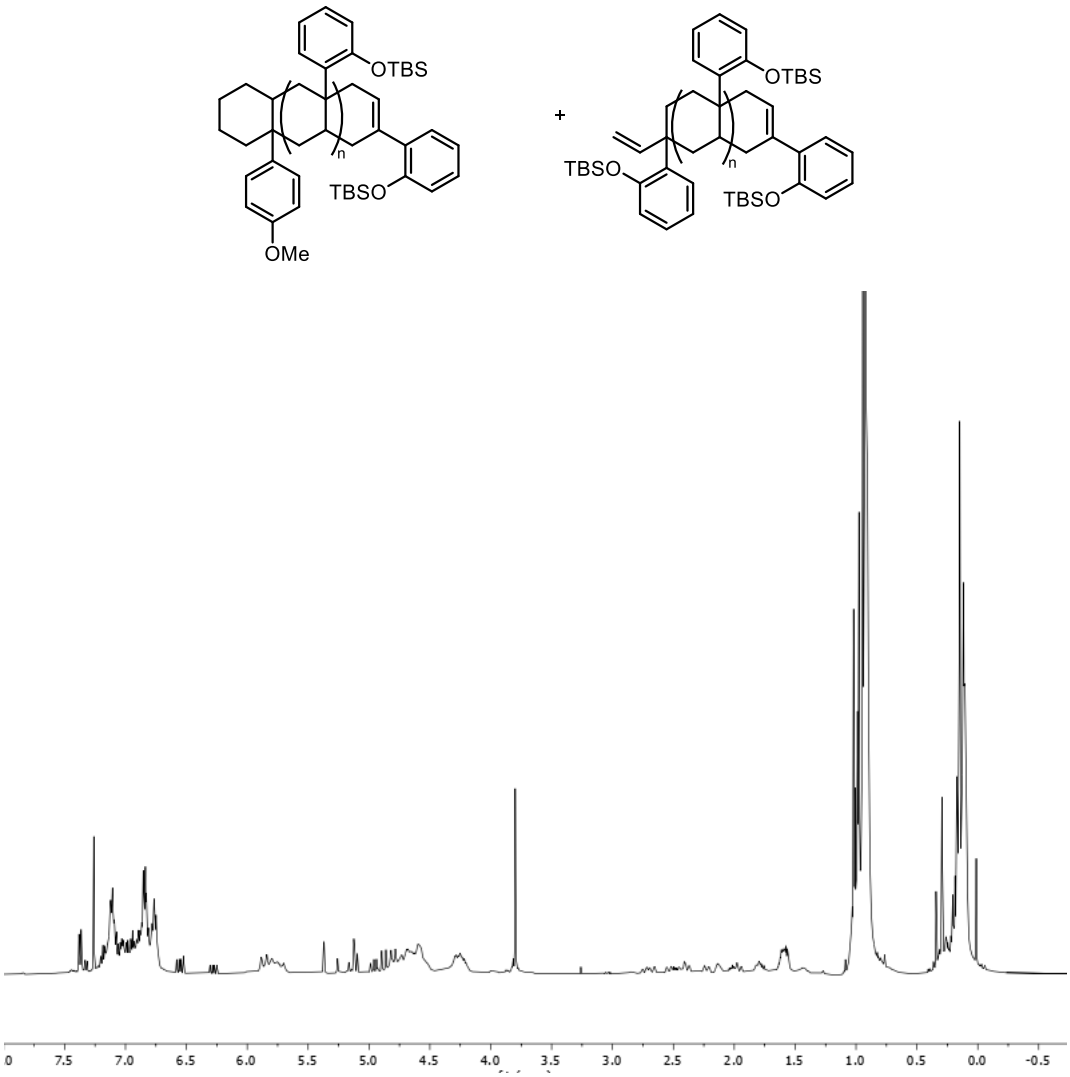


Figure S95 ^{1}H NMR, $CDCl_3$-*d* of LP-3i and 3i'

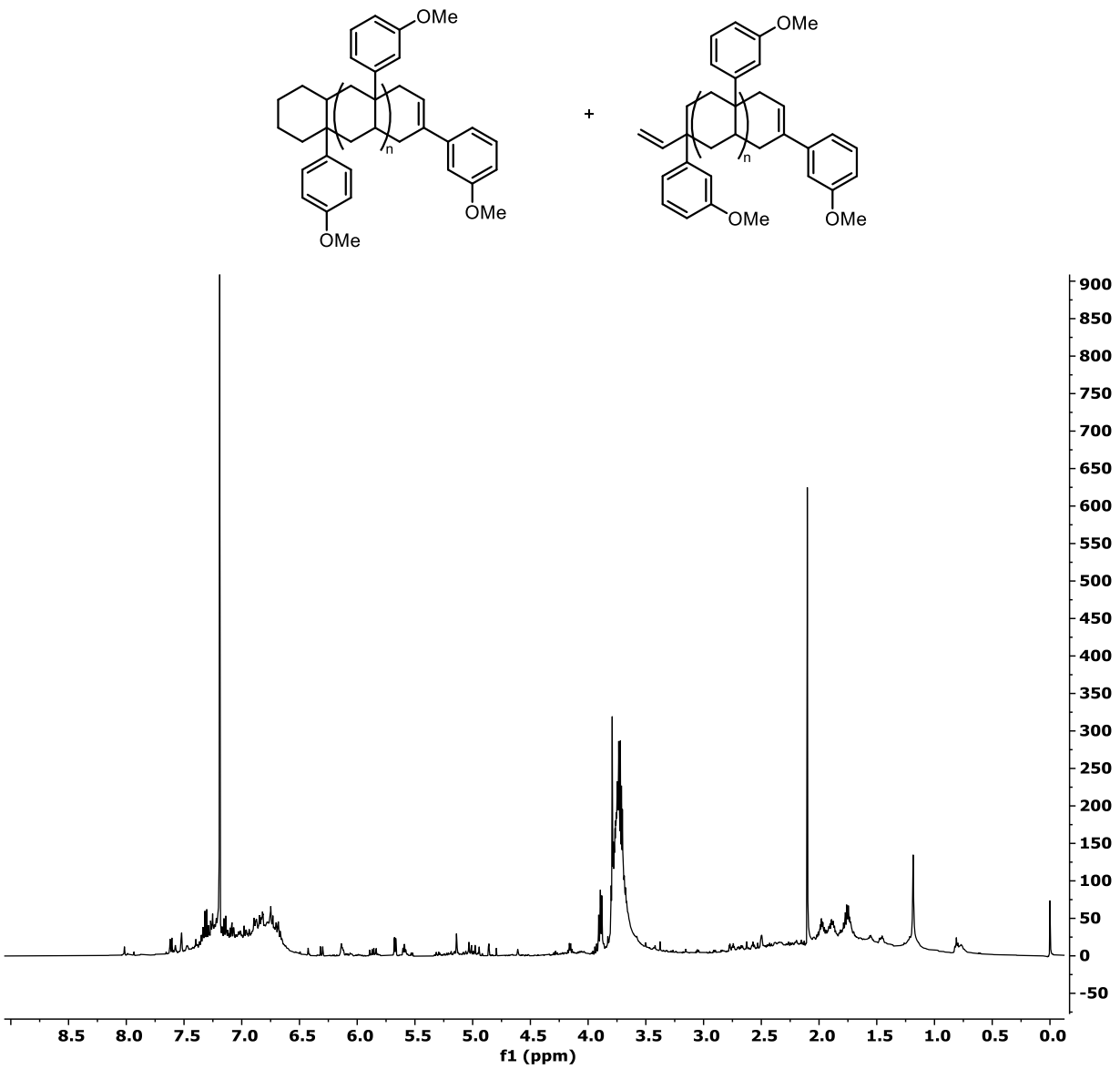


Figure S96 ^{1}H NMR, $CDCl_3$-*d* of LP-3j and 3j'

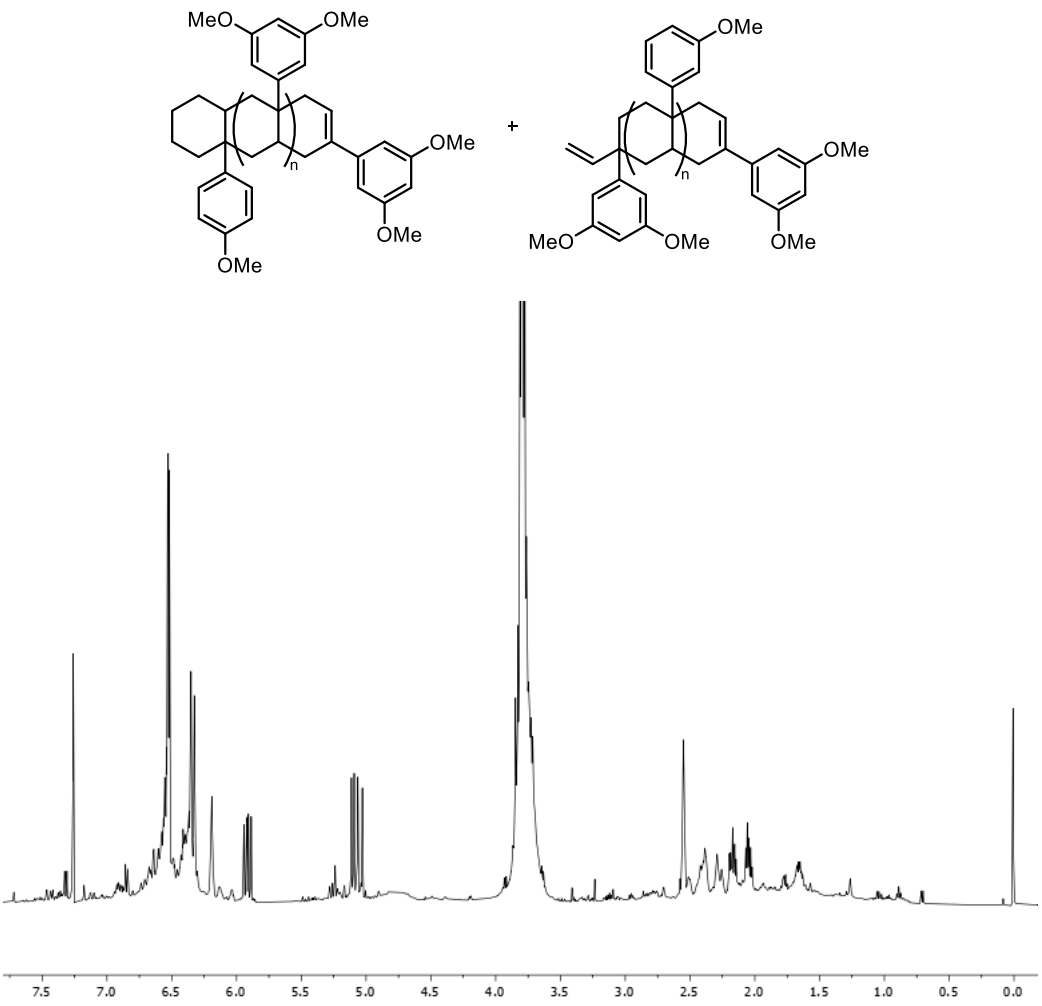


Figure S97 ^{1}H NMR, $CDCl_3$-*d* of LP-3k and 3k'

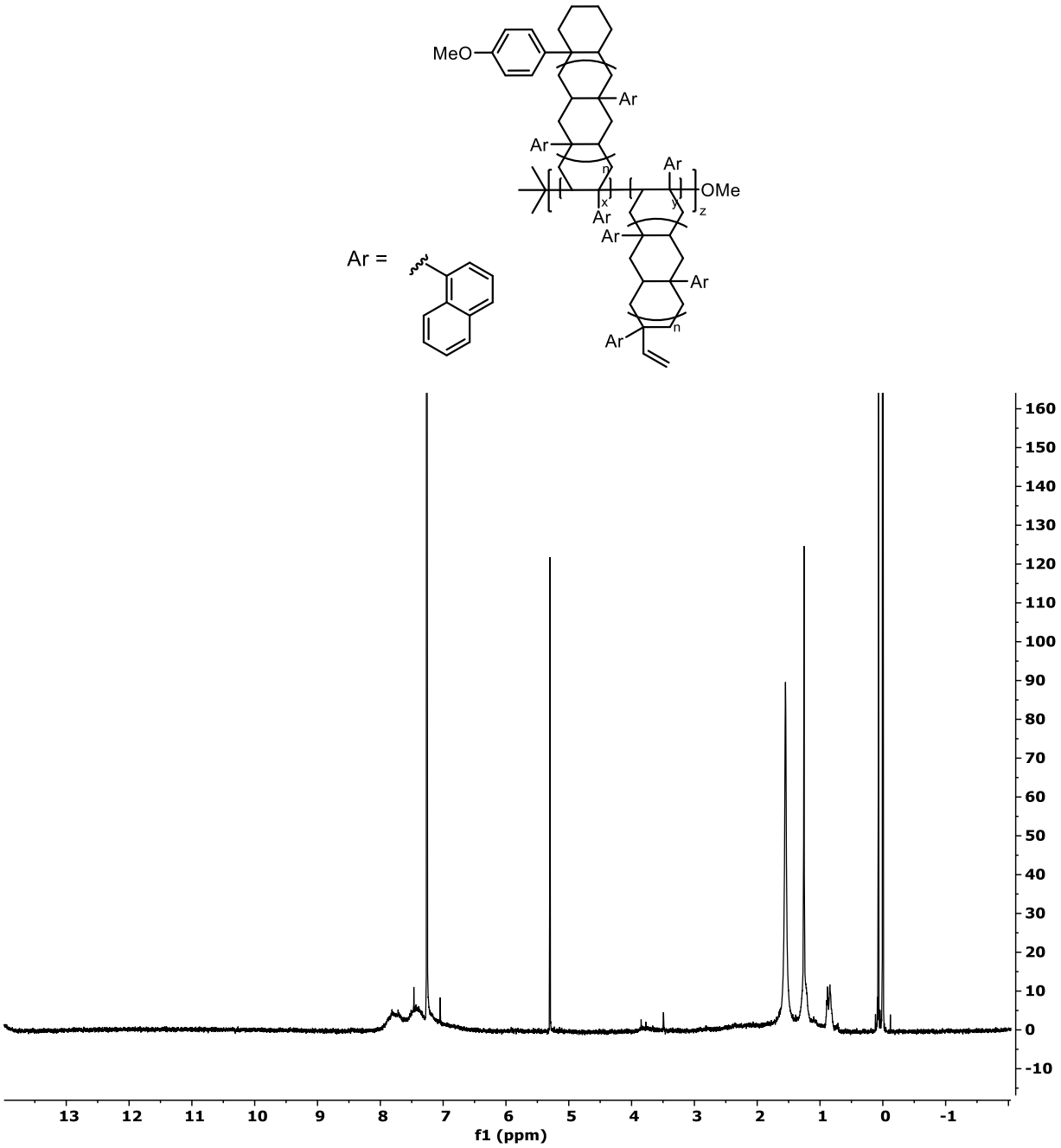


Figure S98 ^{1}H NMR, $CDCl_3$-*d* of LP-3g-ext

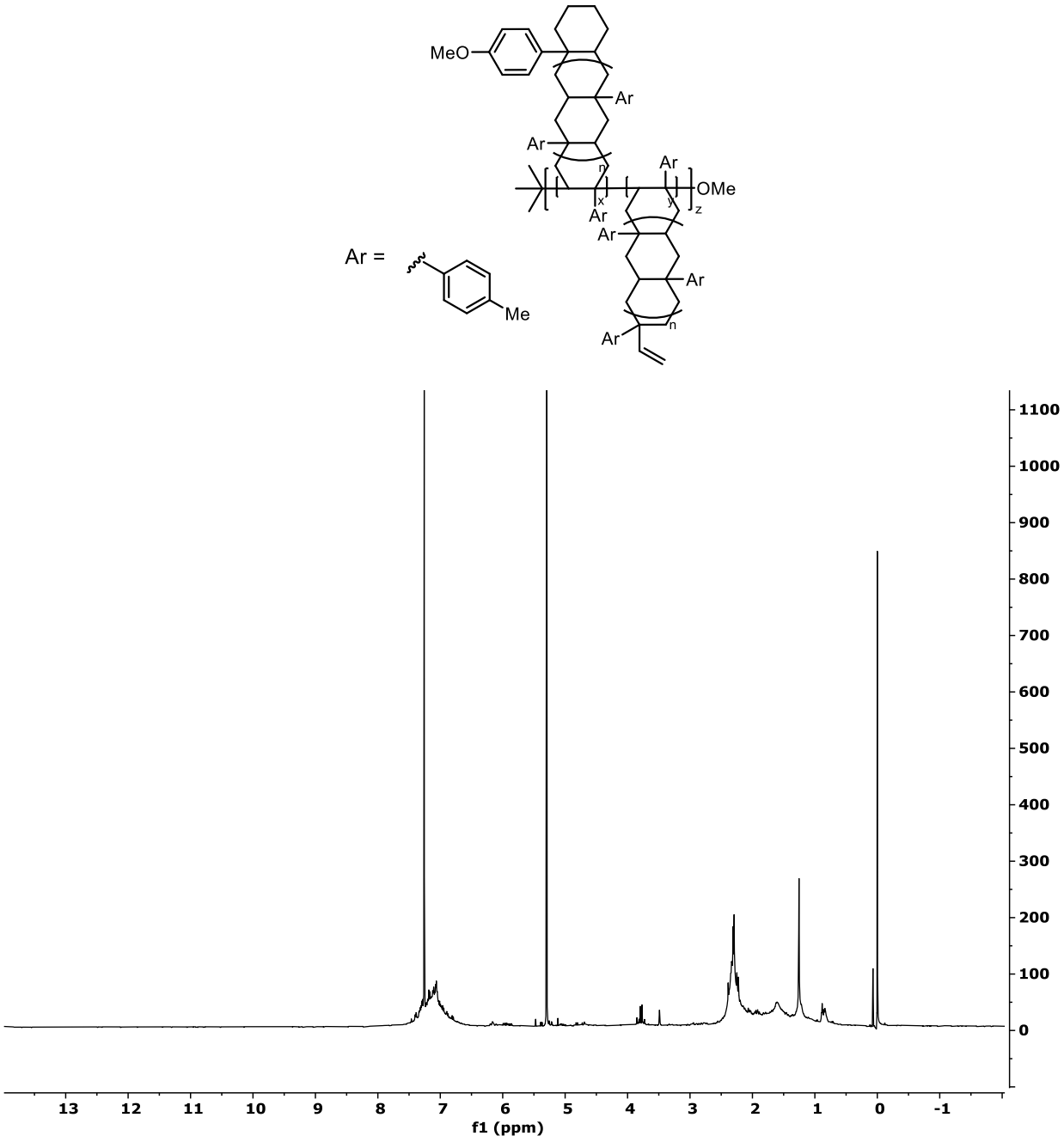


Figure S99 ^{1}H NMR, $CDCl_3$-*d* of LP-3d-ext

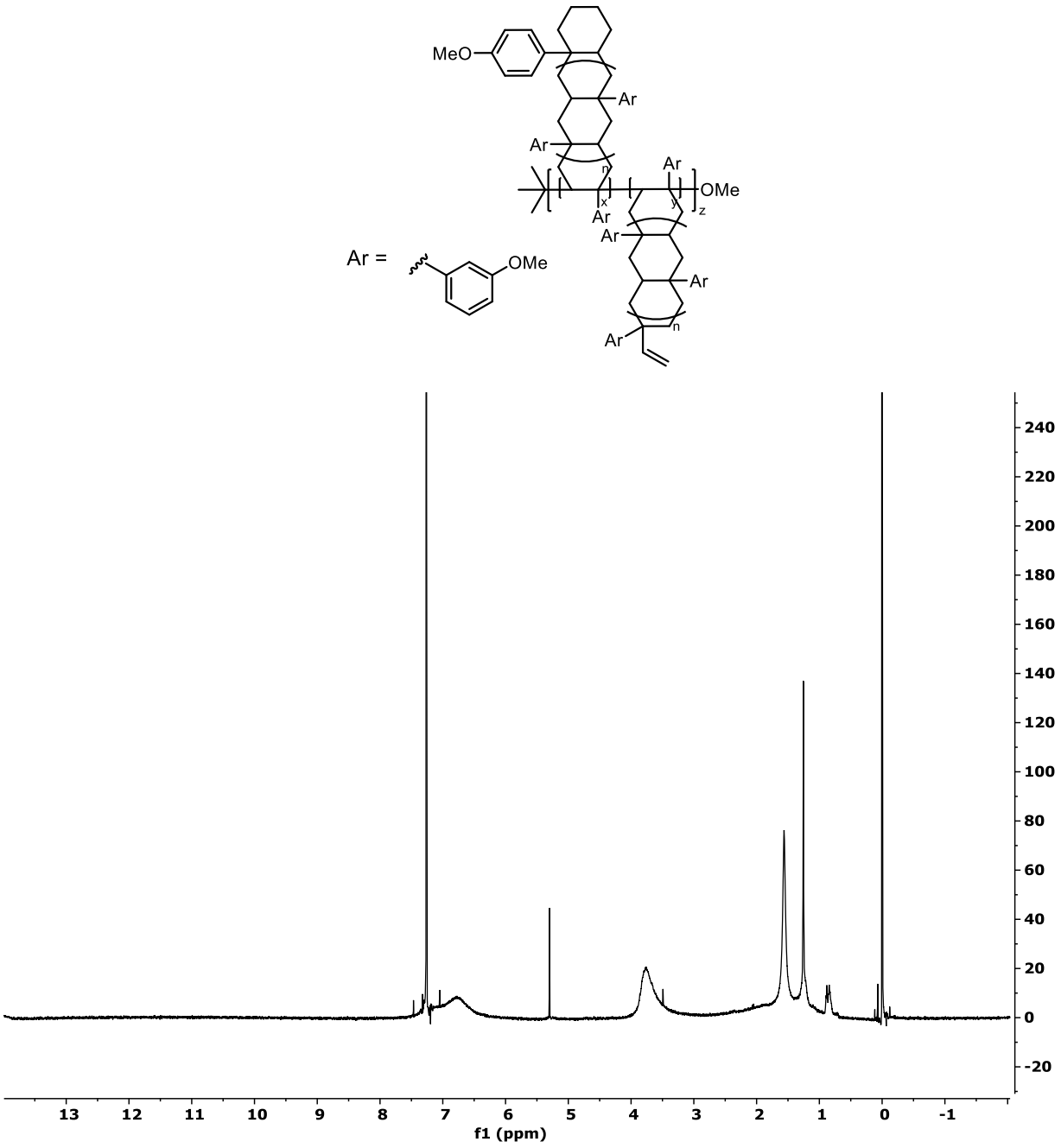


Figure S100 ^{1}H NMR, $CDCl_3$-*d* of LP-3j-ext

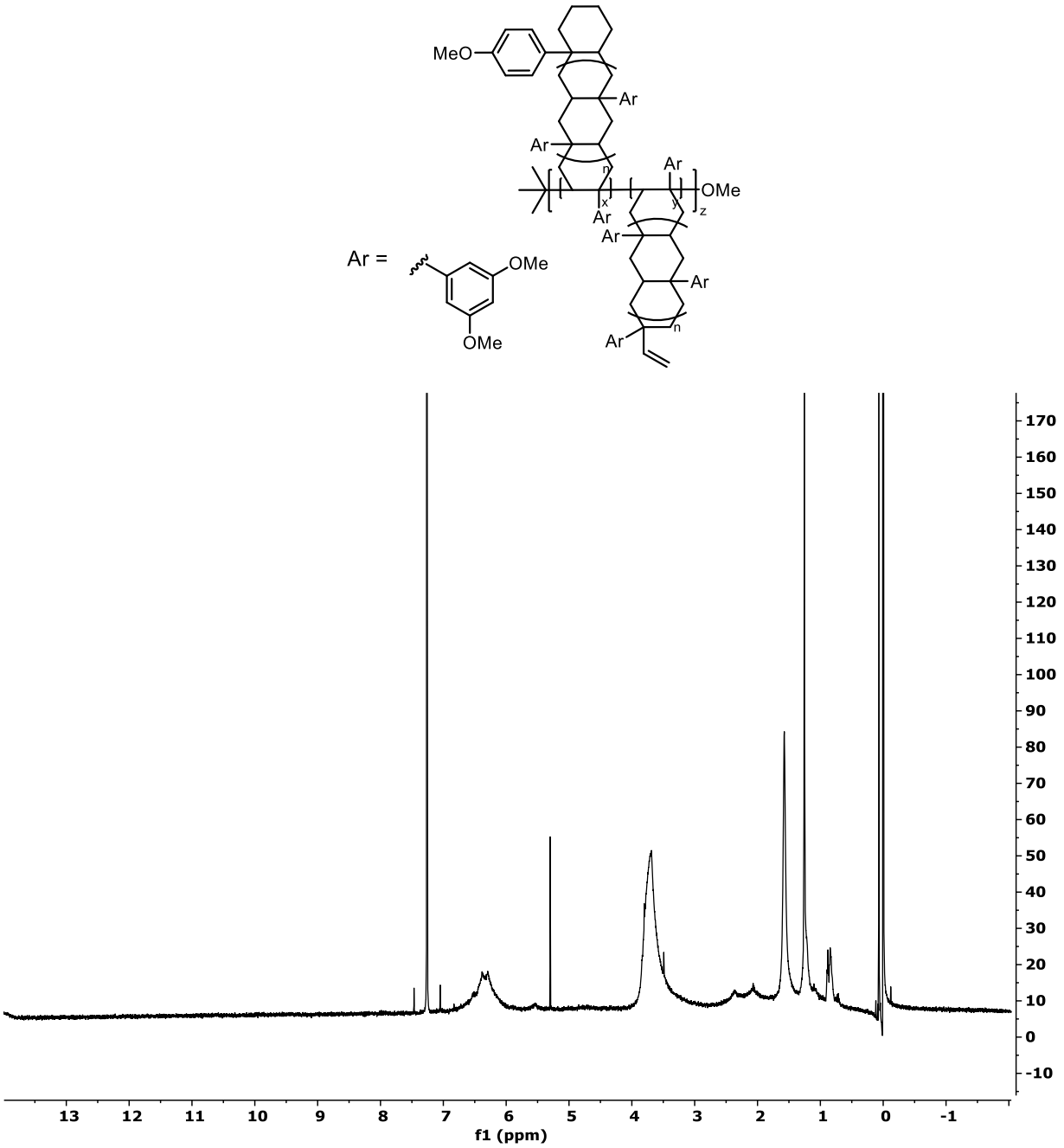


Figure S101 ^{1}H NMR, $CDCl_3$-*d* of LP-3k-ext

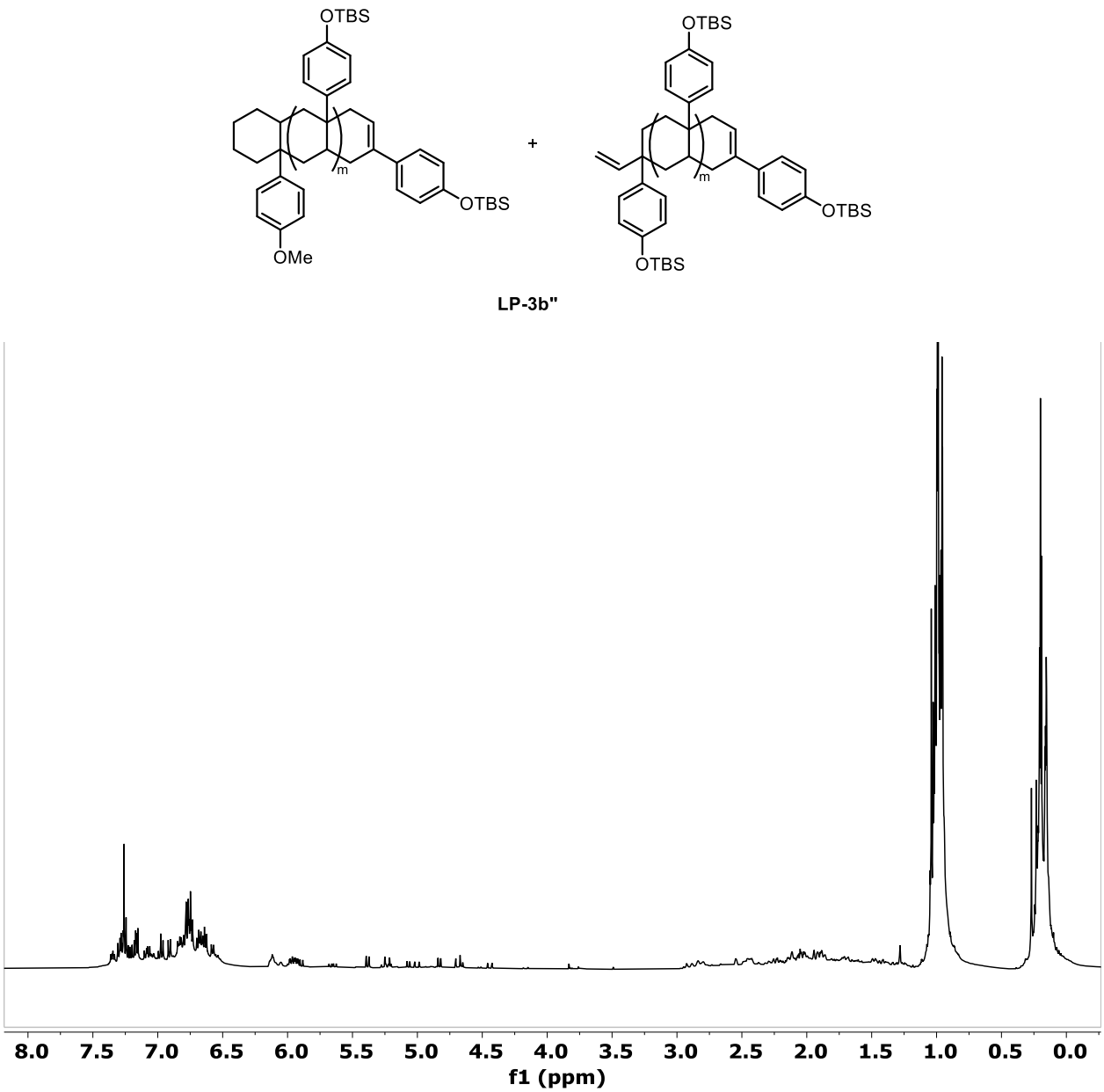


Figure S102 ^{1}H NMR, $CDCl_3$-*d* of LP-3b" (entry 2 in **Table S5. Extension experimenta**

IX. MALDI Spectra

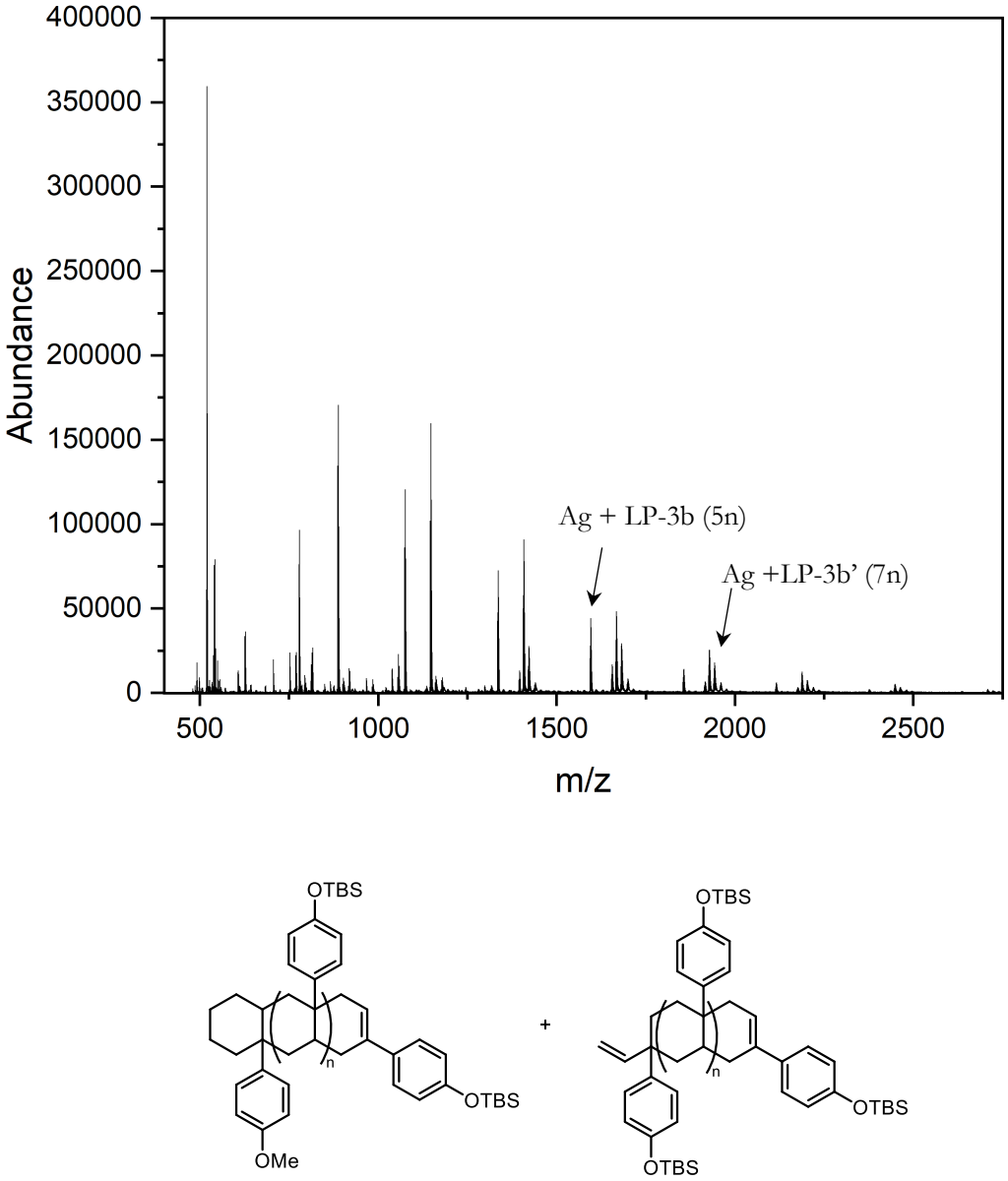


Figure S103. MALDI-TOF of LP-3b and LP-3b' (polymerization with initiator).

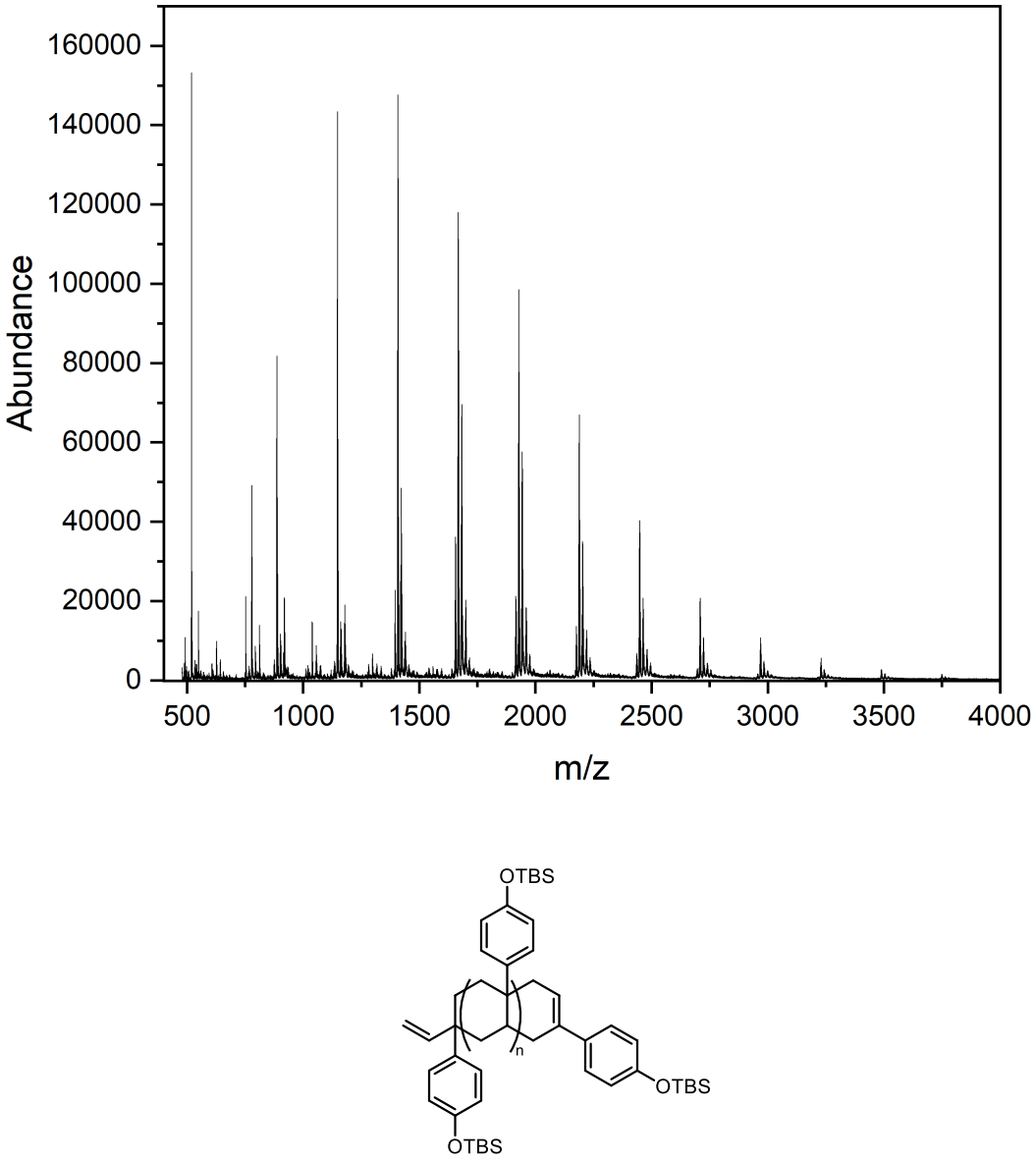


Figure S104. MALDI-TOF of LP-3b' (polymerization without initiator).

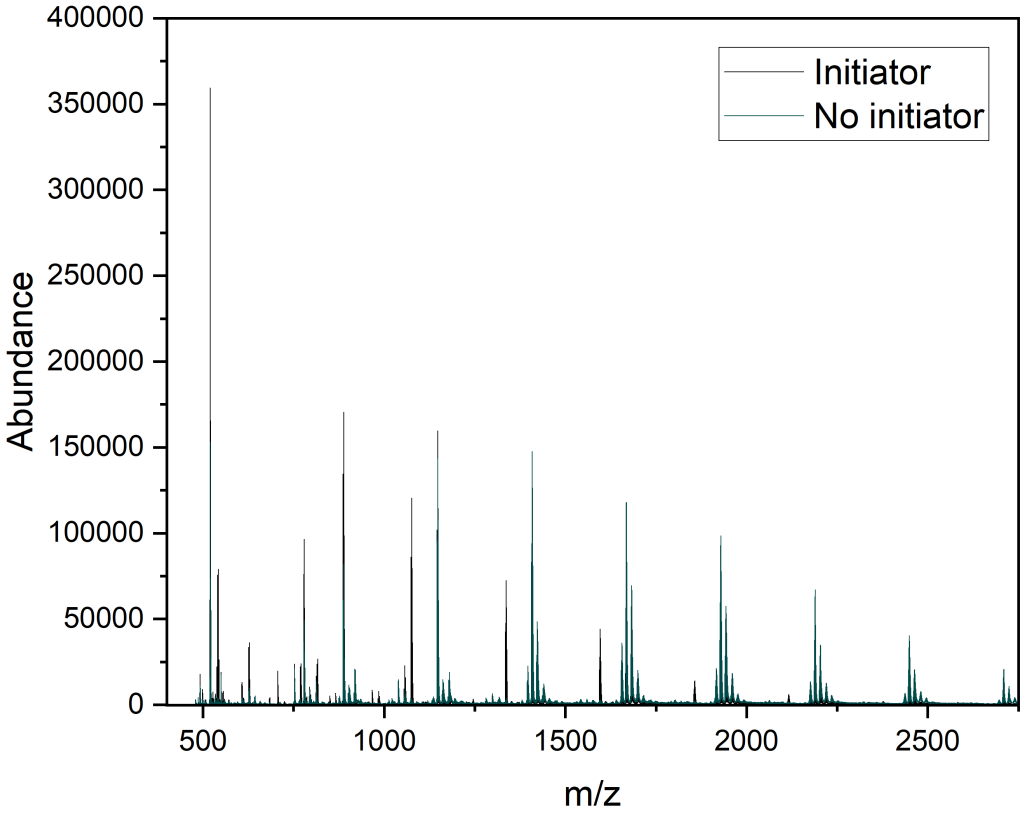


Figure S105. MALDI-TOF MS of LP-3b and LP-3b' (overlay).

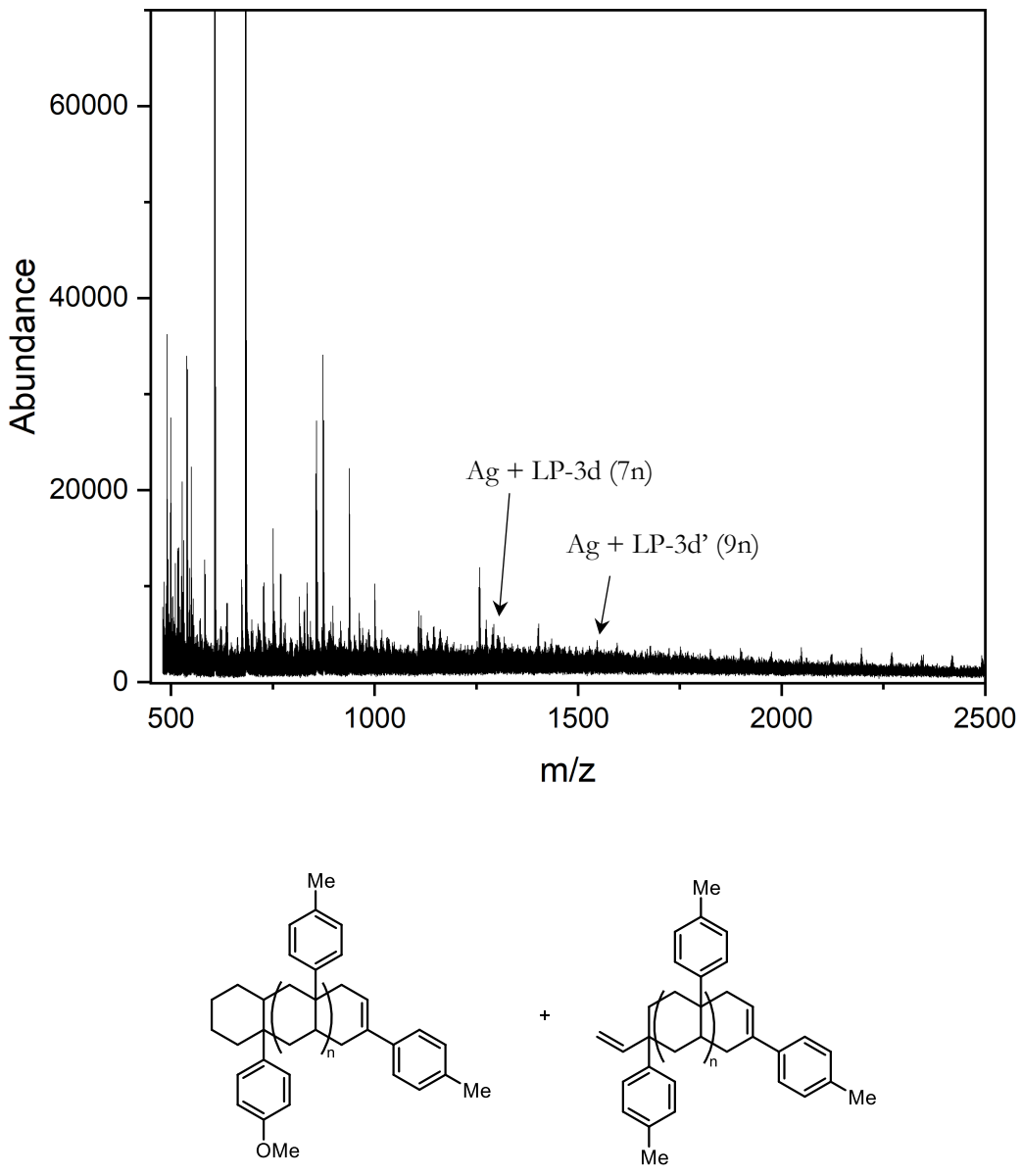


Figure S106. MALDI-TOF MS of LP-3d and LP-3d'.

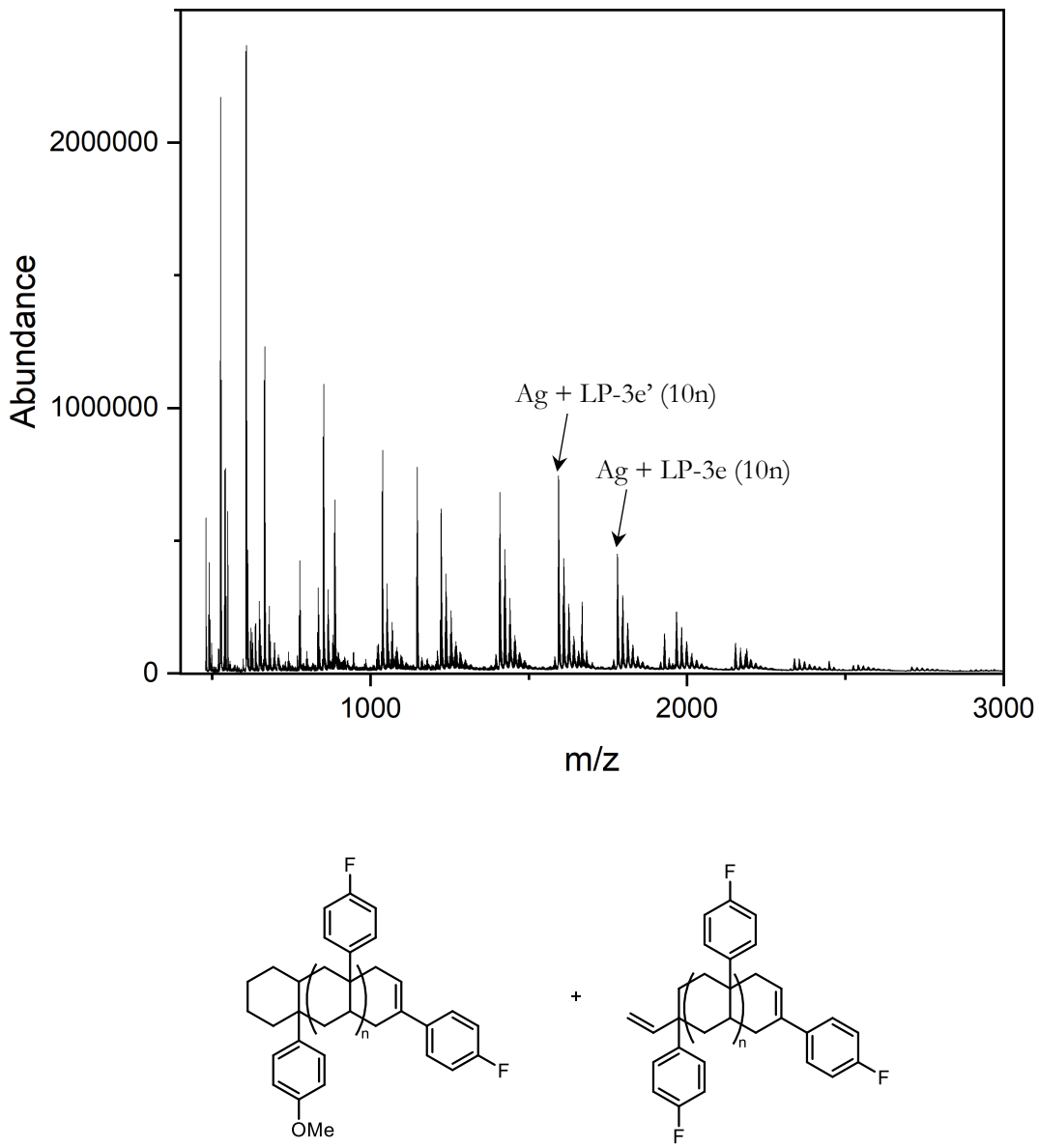


Figure S107. MALDI-TOF MS of LP-3e and PF-3e'.

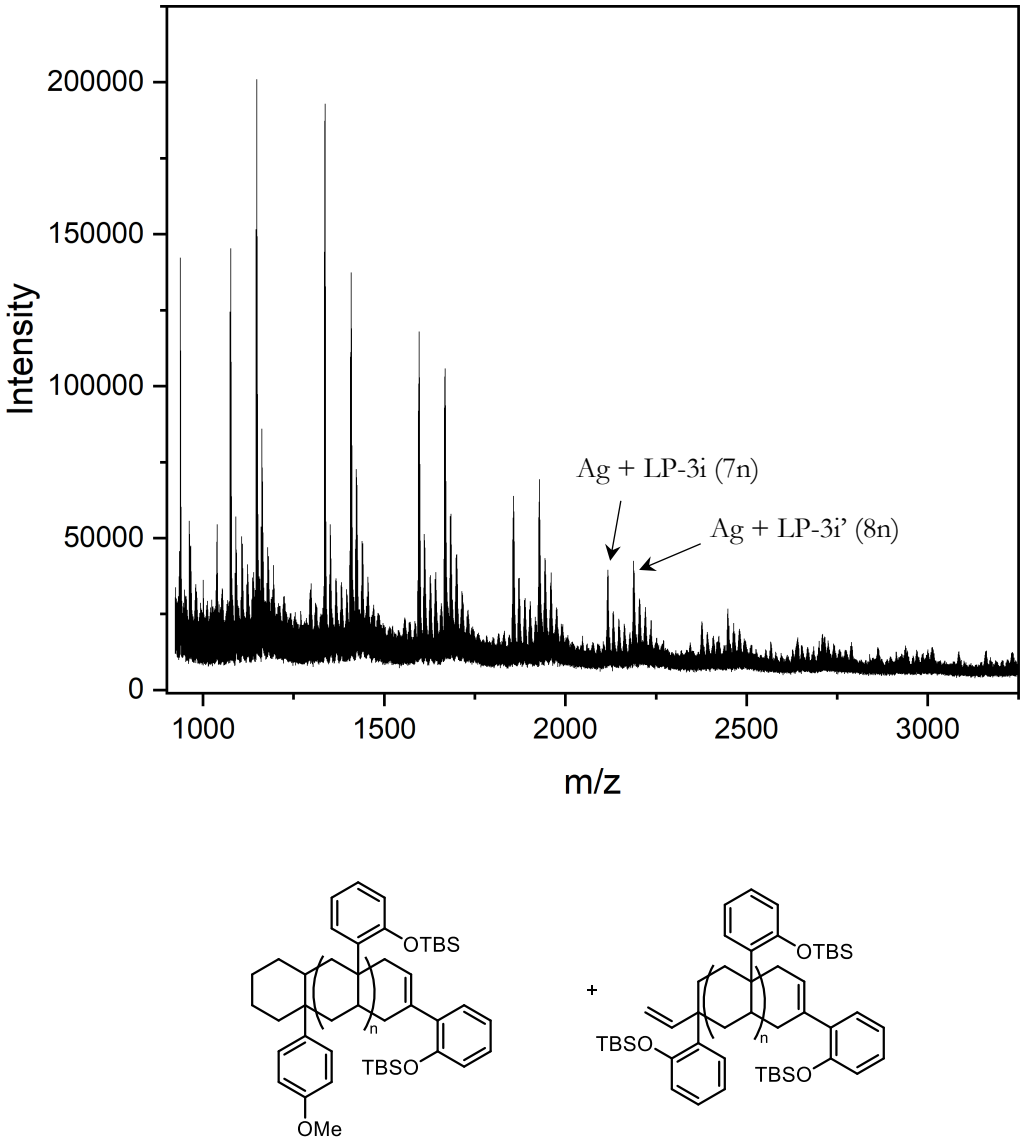


Figure S108. MALDI-TOF MS of LP-3i and 3i'.

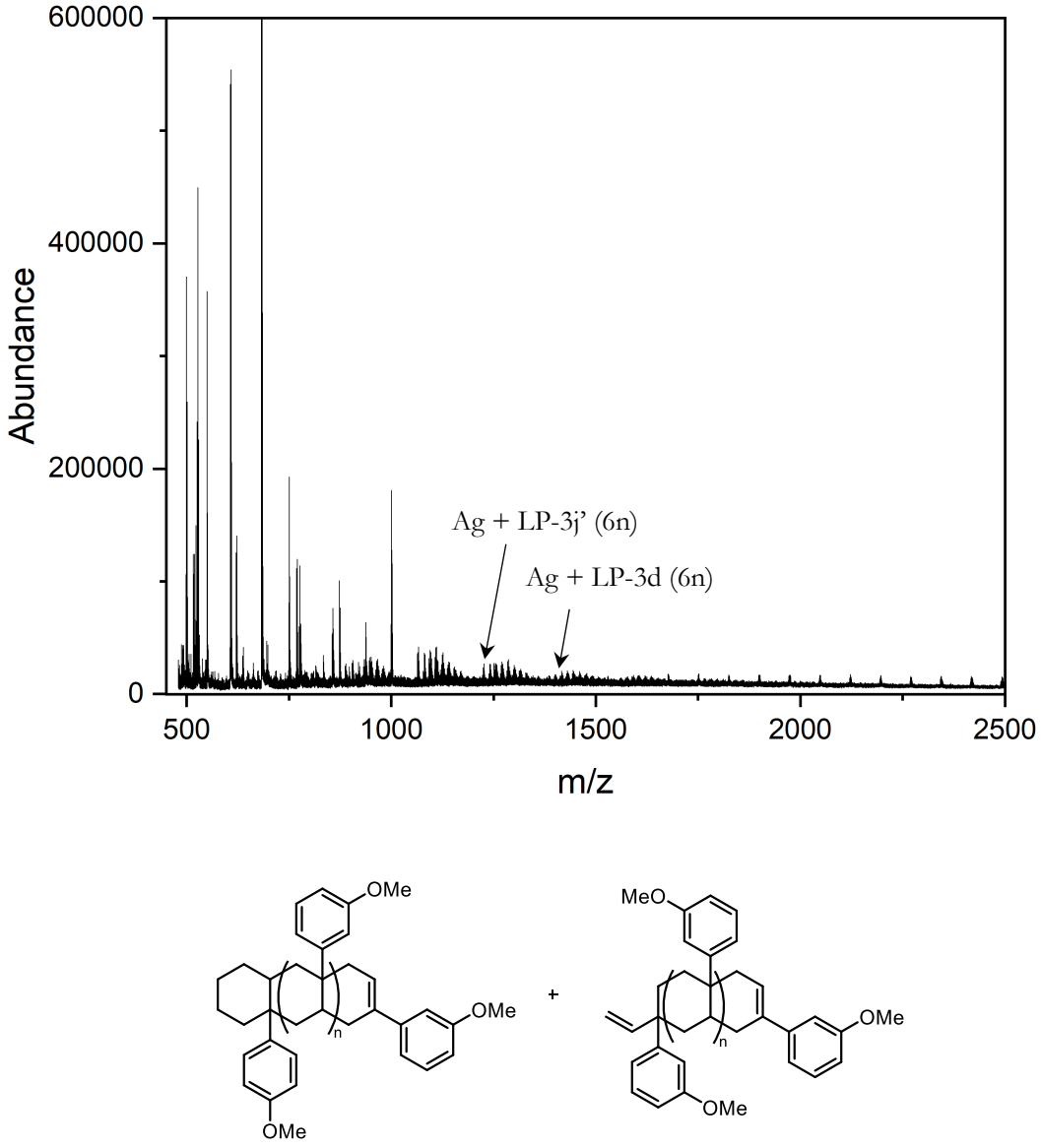


Figure S109. MALDI-TOF MS of LP-3j and LP-3j'.

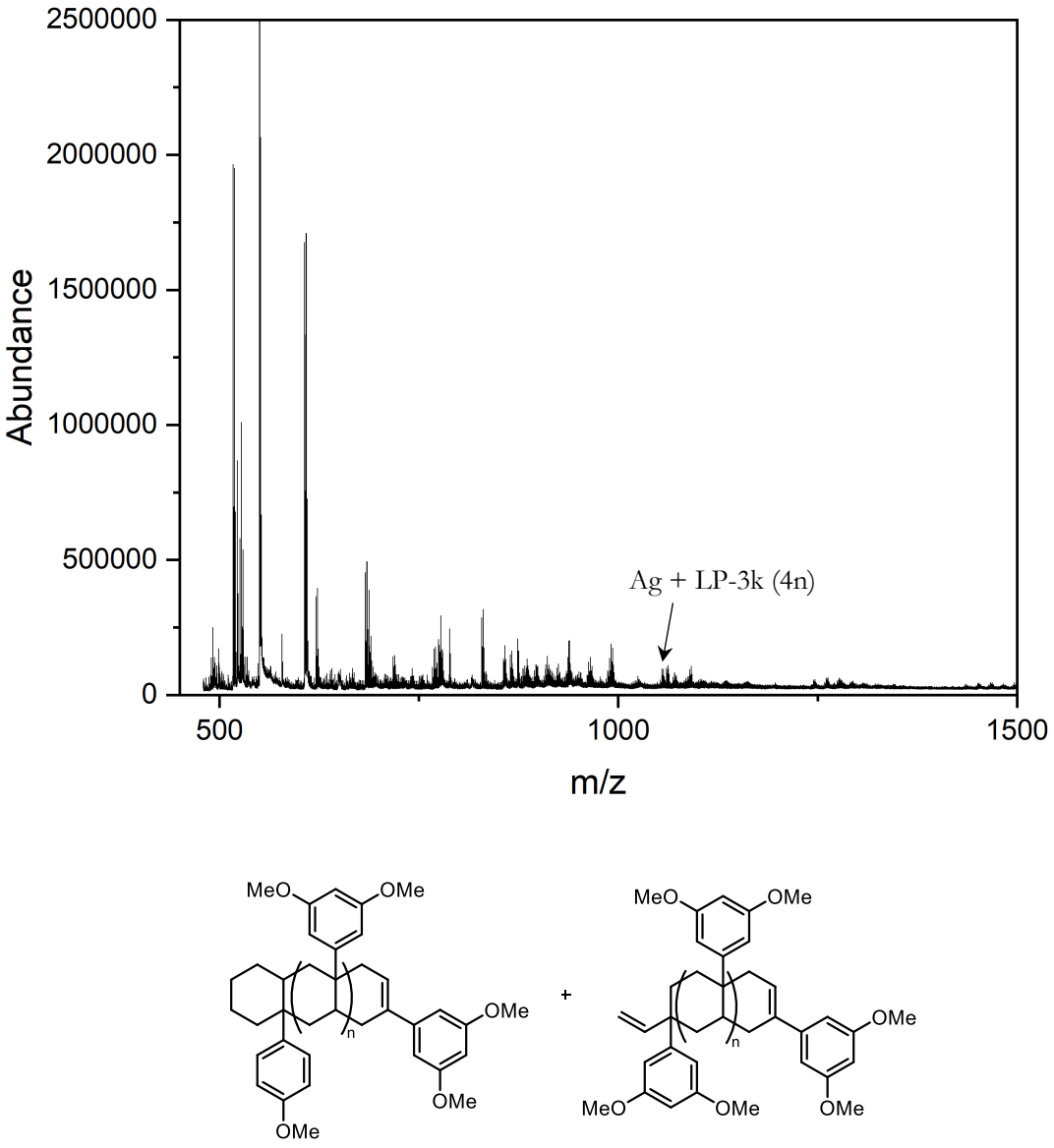


Figure S110. MALDI-TOF MS of LP-3k and LP-3k'.

X. References

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