Supporting Information for:

Block Co-PolyMOFs: Assembly of Polymer-PolyMOF Hybrids via Iterative Exponential Growth and "Click" Chemistry

Michelle J. MacLeod and Jeremiah A. Johnson*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA,
02139, United States

E-mail: jaj2109@mit.edu

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Supplementary Figures Cited in the Main Text.

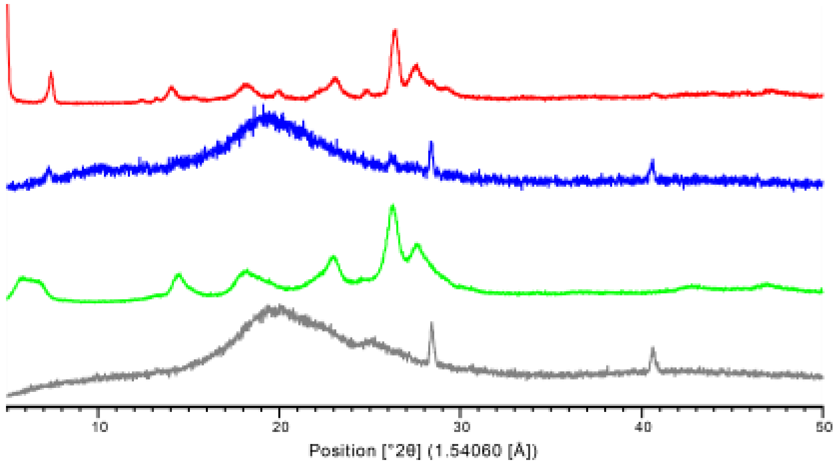


Figure S1. PXRD spectra for BDC-based polyMOF and BCPMOF ligands. Red is **L_2**, blue is **L_2PS**, green is **L_4** and gray is **L_4PS**. Note that **L_4** is highly hygroscopic.

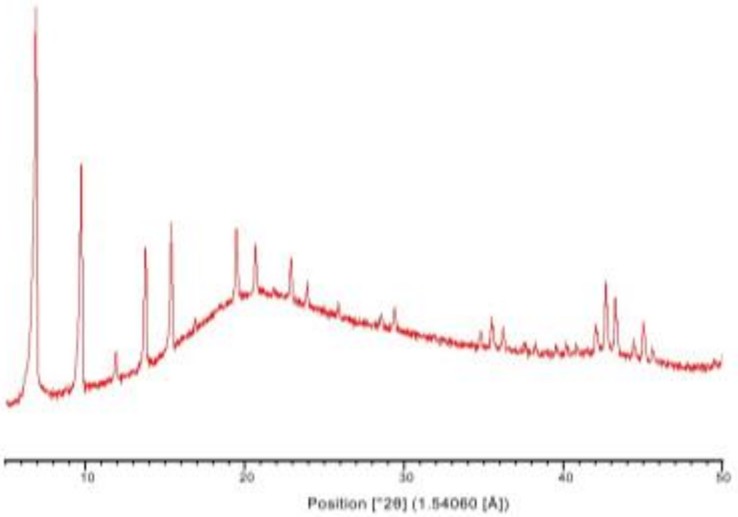


Figure S2. PXRD spectrum for **L_4Bn-Zn**.

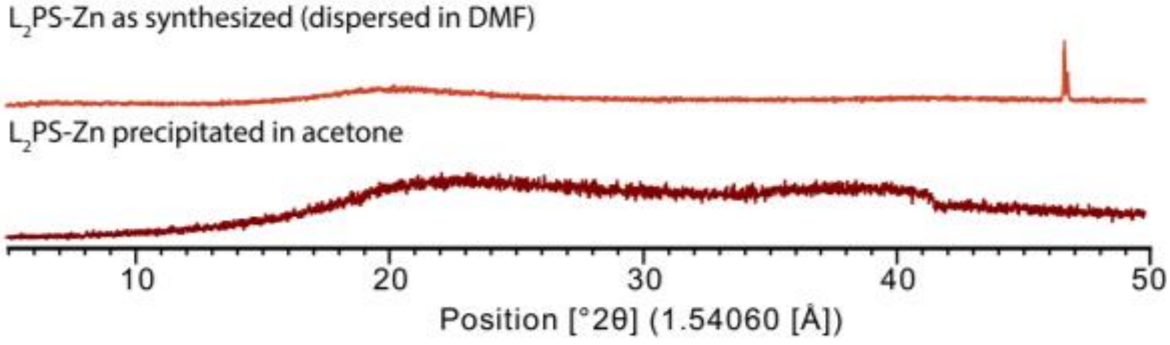


Figure S3. PXRD spectra for **L_2PS-Zn**.

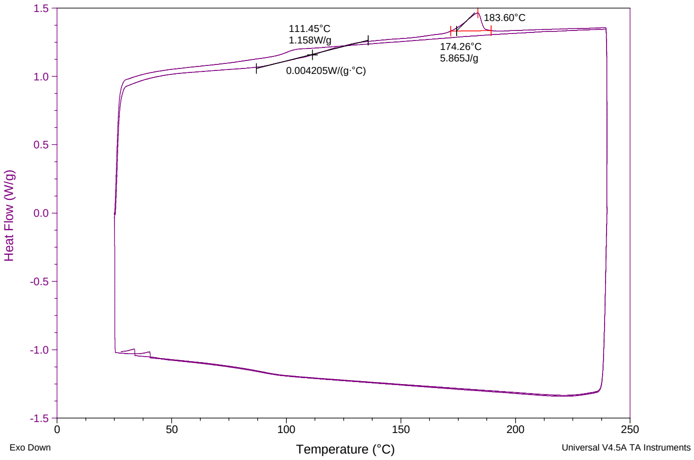


Figure S4. DSC data for **L$_4$PS**.

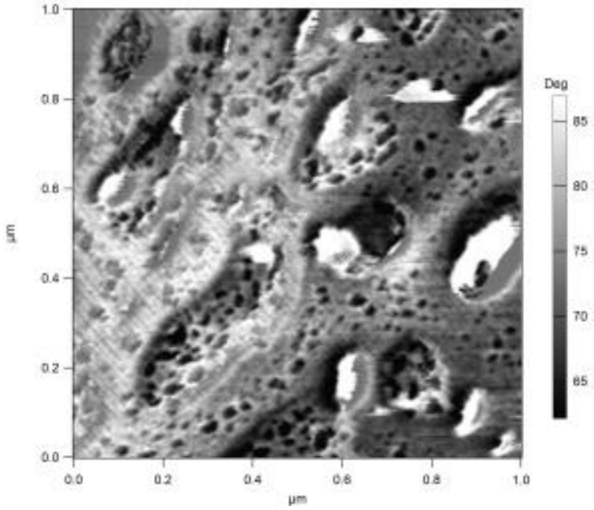


Figure S5. AFM image of **L$_4$PS-Zn** annealed at 120 °C for 12 hours.

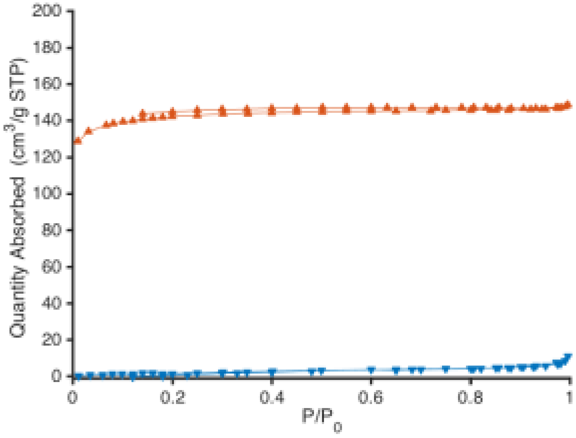


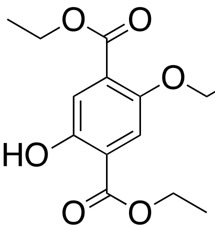
Figure S6. N_2 sorption isotherms for **L$_4$-Zn** (orange) and **L$_4$PS-Zn** (blue). Note: we obtained reasonable surface area not controlling water content which was found to be the optimal synthetic protocols for MOF-5's gas storage.[2] The low value for **L$_4$PS-Zn** is not unexpected due to the high content of nonporous polymer and high solubility in organic solvents which made solvent exchange difficult. The activation at 160°C, above the T_g of polystyrene, could also lead to incorporation of polymers in to the polyMOF pores.

Material/General methods/Instrumentation

All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Polystyrene azide was synthesized as previously reported using ethyl α-bromoisobutyrate initator.[1] Column chromatography was performed on a Biotage® Isolera One with Accelerated Chromatographic Isolation flash chromatography system, using Biotage® KP-Sil SNAP cartridges at the recommended flow rates. High-resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS) using an electrospray ionization (ESI) source (NSF Grant #CHE-0234877). X-ray diffraction was performed using a Rigaku Smartlab Multipurpose Diffracteter with an incident beam Ge (022) double bounce monochromator and a diffracted beam graphite monochromator using the variable-slit Bragg Brentano method (NSF Grant #DMR-1419807). No corrections were made. Samples were cast as powder or from residual DMF or acetone onto zero background plates. The samples were air dried for 10 minutes before measurements began. SAXS and WAXS were preformed using Rigaku H3r Source/Bruker Nanostar SAXS system with a two-dimensional CCD detector and a beam path length of 60.4 cm. Samples were prepared in Kapton tape. The Kapton tape scattering was subtracted. Nuclear magnetic resonance spectroscopy (NMR), ^{1}H NMR and ^{13}C NMR were recorded using a Bruker AVANCE-400 NMR spectrometer or a VARIAN Inova-500 NMR spectrometer. Chemical shifts are reported in parts per million (ppm), and are referenced to residual solvent peaks. The data were analyzed using MestReNova or Topspin software. Gel permeation chromatography (GPC) analyses were carried out in tetrahydrofuran (THF) at a flow rate of 1.0 mL/min using an Agilent 1260 Infinity system with a variable-wavelength diode array (254, 450, and 530 nm) and a refractive index detector for PS-N_3. Matrix-absorption laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded with a Bruker model MicroFlex MALDI-TOF at the Koch Institute for Integrative Cancer Research at MIT. Dithranol in THF was used as the matrix in negative ion mode. Thermogravimetric analysis (TGA) was performed using a TA Instruments Discovery TGA. Samples were run in platinum TGA pans at a ramp rate of 10 °C per minute from 30 to 600 °C. Differential scanning calorimetry (DSC) was performed on a TA Instruments Discovery DSC, where each sample was run with a Tzero aluminum pan sealed with a hermetic lid. Scanning electron microscopy (SEM) was performed in a Zeiss Merlin high-resolution SEM. Samples were prepared by drop casting a solution of the desired material on silicon wafers from dichloromethane suspensions. The samples were allowed to dry overnight. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai multipurpose scope (G2 Spirit TWIN). The samples were prepared by drop-casting a dilute dichloromethane suspension (0.1 mg/mL) of the BCPMOF onto a carbon coated copper grid. Consequently, uniform thin films were difficult to obtain. For positively stained samples, after casting the samples were dried for 30 minutes, the sample-coated grids were placed in a four mL vial which was placed in a sealed 20 mL vial containing 1 mL RuO_4. It was allowed to rest for 30 minutes. The sample was then removed and allowed to rest for 30 minutes. Gas adsorption measurements were measured with an ASAP 2020 surface area and pore size analyzer. ~50 mg of **L_4-Zn** was soaked in $CHCl_3$ for 2 days, decanting and refreshing $CHCl_3$ every 12 hours. ~100 mg of **L_4PS-Zn** was soaked in $CHCl_3$ for 12h and was centrifuged down to isolate ~20 mg of sample. The samples were dried on a vacuum line for ~10 min at room temperature, and transferred to pre-weighed sample tubes with a filler rods and degassed at 160 °C for 10 h. The sample tube was reweighed to obtain a consistent mass for the degassed sample. UHP grade (99.999%) N2 were used for all measurements and the sample temperature was maintained at 77 K.

Synthetic Procedures

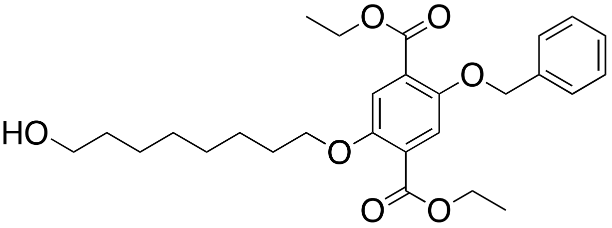
A



10 g (39.3 mmol, 1.0 eq.) of diethyl 2,5-dihydroxyterephthalate, 2.7 g (19.7 mmol, 0.50 eq.) K_2CO_3, 2.3 mL (19.7 mmol, 0.50 eq.) benzyl bromide and 39 mL acetone were added to a pressure vessel. The vessel was sealed and the reaction was stirred at 80 °C overnight. The reaction was cooled and water was added. The solution was neutralized with 1 M HCl and then extracted with dichloromethane three times. The extracts were dried with Na_2SO_4, filtered and concentrated under vacuum. The solid collected was loaded with minimal DCM and purified by silica gel chromatography using 0-5% ethyl acetate in hexanes. Unreacted starting material elutes at 1-2% ethyl acetate in hexanes and can be reisolated. The product elutes at 2-3% ethyl acetate in hexanes in 61% yield.

^{1}H ($CDCl_3$, 400 Hz): 1.32 (2H, t), 1.40 (2H, t), 4.35 (2H, q), 4.39 (2H, q), 5.07 (2H, s), 7.24-7.54 (7H, m), 10.41 (1H, s). ^{13}C ($CDCl_3$, 400 Hz): 14.33, 61.60, 62.07, 72.13, 115.00, 115.05, 120.20, 127.45, 128.07, 128.64, 129.45, 149.74, 155.62, 165.53, 169.31. HRMS: calcd. for $C_{19}H_{21}O_6$ $[M+H]^+$, most abundant m/z = 345.1333; found, 345.1338.

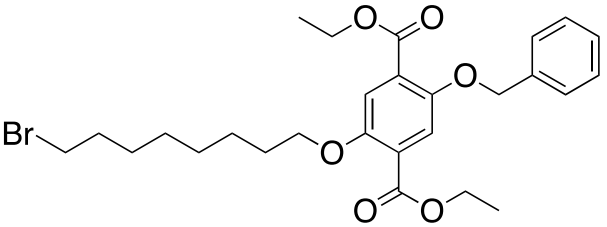
L$_1$Et



1.2 g (8.7 mmol, 1.5 eq.) of potassium carbonate, 0.15 g (0.58 mmol, 0.10 eq.) 18-crown-6, 2.0 g (5.8 mmol, 1.0 eq.) of **1** and 0.95 mL (6.3 mmol, 1.1 eq.) of 8-bromo-1-octanol were dissolved in a 18 mL of 50:50 DMF/ethanol mixture. The mixture was heated at 80 °C for 16 h in a sealed pressure vessel. The reaction was then cooled. 70 mL of DI water were added and the reaction was neutralized with 1 M HCl and then extracted with dichloromethane three times. The extracts were dried with Na_2SO_4, filtered and concentrated under vacuum. The oil collected was loaded with minimal DCM and columned using 0 to 40% ethyl acetate in hexanes on silica (eluting at 35%) in 86% yield.

^{1}H ($CDCl_3$, 400 Hz): 1.24-1.40 (12H, m), 1.40-1.58 (4H, m), 1.77 (2H, dt), 3.58 (2H,t), 3.98 (2H, t), 4.34 (4H, q), 5.09 (2H, s), 7.24-7.49 (7H, m). ^{13}C ($CDCl_3$, 400 Hz): 14.16, 14.22, 25.63, 25.68, 29.15, 29.21, 29.27, 32.66, 61.26, 61.39, 62.72, 69.67, 71.64, 76.83, 77.15, 77.47, 116.56, 117.38, 124.53, 125.10, 127.19, 127.82, 128.37, 136.57, 151.07, 152.13, 165.85, 165.90. HRMS: calcd. for $C_{27}H_{37}O_7$ $[M+H]^+$, most abundant m/z = 473.2534; found, 473.2549.

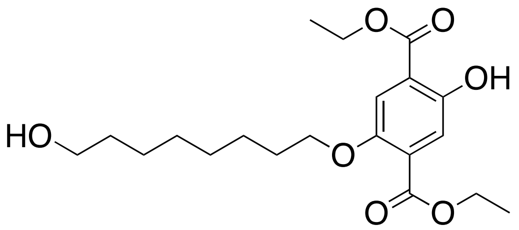
L$_1$EtBr



A solution of **L$_1$Et** 4.3 g (9.0 mmol, 1.0 eq.) and tetrabromomethane 3.3 g (9.9 mmol, 1.1 eq.) in 39 mL of DCM was cooled to 0 °C. 2.6 g (9.9 mmol, 1.1 eq.) of triphenyl phosphine was added in four portions every 5-10 minutes. The reaction was stirred at RT for 1 h. Then an additional 0.25 eq. of CBr_4 and PPh_3 were added and the reaction was stirred for an additional 2h. The reaction was concentrated and subjected to silica gel chromatography (0 to 20% ethyl acetate in hexanes, eluting at 10%) to provide the product in 89% yield.

^{1}H ($CDCl_3$, 400 Hz): 1.30-1.53 (14H, m), 1.75-1.90 (4H, m), 3.40 (2H, t), 4.01 (2H, t), 4.37 (4H, q), 5.12 (2H, s), 7.28-7.40 (4H, m), 7.43-7.50 (3H, m). ^{13}C ($CDCl_3$, 400 Hz): 14.32, 14.38, 25.95, 28.18, 28.78, 29.22, 29.30, 32.86, 34.02, 61.37, 61.51, 69.81, 71.85, 116.76, 117.59, 124.75, 125.32, 127.35, 127.98, 128.53, 136.74, 151.26, 152.29, 165.93, 166.01. HRMS: calcd. for $C_{27}H_{36}BrO_6$ $[M+H]^+$, most abundant m/z = 535.1690; found, 535.1684.

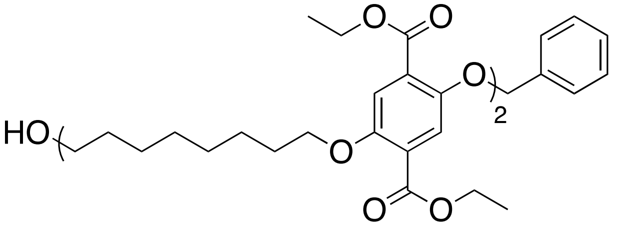
L$_1$EtOH



A solution of **L$_1$Et** 3.8 g (8.0 mmol, 1.0 eq.) and 10% palladium on carbon 0.85 g (8.0 mmol, 1.0 eq.) in 40 mL ethanol was sparged with nitrogen for 10 minutes. The solution was then sparged with hydrogen for 5 minutes and stirred under hydrogen atmosphere for 18 h at RT. The reaction was filtered to remove the palladium, concentrated, purified by silica gel chromatography (0 to 50% ethyl acetate in hexanes, eluting at 30%) and isolated in 99% yield.

^{1}H ($CDCl_3$, 400 Hz): 1.27-1.61 (16H,m), 1.79 (2H,tt), 3.60 (2H,t), 3.96 (2H, t), 4.35 (2H, q), 4.41 (2H, q), 7.27 (1H, s), 7.33 (1H, s), 10.36 (1H, s). ^{13}C ($CDCl_3$, 400 Hz): 14.32, 14.48, 25.95, 28.18, 28.78, 29.22, 29.30, 32.96, 34.02, 61.36, 61.50, 69.81, 71.85, 116.75, 117.58, 124.75, 125.32, 127.34, 127.97, 128.53, 136.74, 151.26,152.29, 165.93, 166.01. HRMS: calcd. for $C_{20}H_{31}O_7$ $[M+H]^+$, most abundant m/z = 383.2064; found, 383.2078.

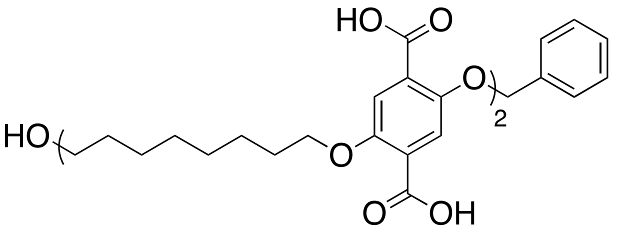
L$_2$Et



0.39 g (2.8 mmol, 1.5 eq.) of potassium carbonate, 0.47 g (0.18 mmol, 0.10 eq.) 18-crown-6, 0.68 g (1.8 mmol, 0.95 eq.) of **L$_1$EtOH** and 1.0 g (1.9 mmol, 1.0 eq.) of **L$_1$EtBr** were dissolved in a 22 mL of 50:50 DMF/ethanol mixture. The mixture was heated at 80 °C for 25 h in a sealed pressure vessel. The reaction was then cooled to RT. 50 mL of DI water were added and the reaction was neutralized with 1 M HCl and then extracted with dichloromethane three times. The extracts were dried with Na_2SO_4, filtered and concentrated under vacuum. The solid collected was loaded with minimal DCM and was purified by silica gel chromatography (0 to 60% Ethyl acetate in hexanes, eluting at 30%.). Note: if moisture content is high, a side product will form that elutes at 60% ethyl acetate. It can be treated with ethanol and a catalytic amount of HCl under reflux conditions to convert it back to the desired product. **L$_2$Et** isolated in 91% yield.

^{1}H ($CDCl_3$, 400 Hz): 1.27-1.61 (30H, m), 1.75-1.85 (6H, m), 3.63 (2H, t), 4.00 (6H, m), 4.36 (8H, q), 5.12 (2H, s), 7.27-7.51 (9H, m). ^{13}C ($CDCl_3$, 400 Hz): 14.31, 14.37, 25.73, 25.94, 26.03, 29.31, 29.34, 29.36, 29.40, 32.83, 61.38, 61.52, 63.06, 69.83, 69.89, 71.82, 116.67, 116. 71, 117.56, 124.70, 124.78, 125.27, 127.34, 127.98, 128.54, 136.72, 151.23, 151.80, 152.29, 165.98, 166.02, 166.19. HRMS: calcd. for $C_{47}H_{64}NaO_{13}$ $[M+Na]^+$, most abundant m/z = 859.4239; found, 859.4255.

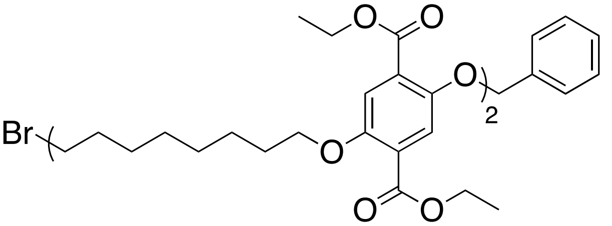
L$_2$



670 mg (0.80 mmol, 1.0 eq.) **L$_2$Et** and 100 eq. of potassium hydroxide were dissolved in 29.0 mL of DMF. 15 mL of water were added and the mixture was heated at 80 °C for 8 hrs. The reaction was acidified with 1 M HCl to a pH of 2. The product precipitated from solution as a white solid and was centrifuged at 6000 rpm. The solvent was decanted. The sample was washed with water three times and dried under vacuum overnight to give 68% yield.

^{1}H (d$_6$-DMSO, 400 Hz): 1.21-1.47 (23H, m), 1.62-1.72 (6H, m), 3.37 (2H, t), 3.98 (6H, m), 5.15 (2H, s), 7.24-7.41 (7H, m), 7.45-7.50 (2H, m), 12.93 (4H,s). ^{13}C (d$_6$-DMSO, 400 Hz): 25.28, 25.30, 25.44, 60.70, 69.15, 70.48, 115.50, 115.57, 115.99, 125.45, 125.63, 127.16, 127.64, 128.30, 137.02, 149.97, 150.43, 150.71, 166.76, 166.82. HRMS: calcd. for $C_{39}H_{48}NaO_{13}$ $[M+Na]^+$, most abundant m/z = 747.2987; found, 747.2975.

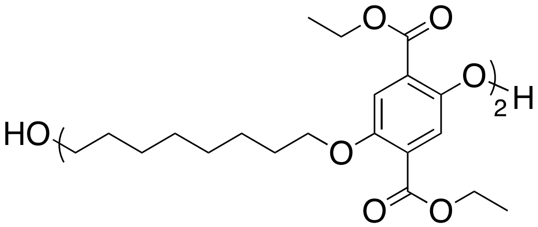
L$_2$EtBr



A solution of **L$_2$Et** 2.4 g (2.9 mmol, 1.0 eq.) and tetrabromomethane 1.1 g (3.2 mmol, 1.1 eq) in 24 mL of DCM was cooled to 0 °C. 0.84 g (3.2 mmol, 1.1 eq.) of triphenyl phosphine was added in four portions every 5-10 minutes. The reaction was stirred at RT for 1 hr. Then an additional 0.25 eq of CBr_4 and PPh_3 were added and the reaction was stirred for an additional 2 h. The reaction was concentrated and the product was purified by silica gel chromatography (0 to 60% ethyl acetate in hexanes, eluting at 17%) and isolated in 88% yield.

^{1}H (CDCl$_3$, 400 Hz): 1.31-1.55 (28H, m), 1.72-1.92 (8H, m), 3.41 (2H, t), 4.00 (6H, m), 4.37 (8H, q), 5.12 (2H, s), 7.28-7.41 (6H, m), 7.42-7.51 (3H, m). ^{13}C (CDCl$_3$, 400 Hz): 14.35, 14.41, 25.99, 26.07, 28.22, 28.82, 29.28, 29. 36, 29.39, 29.41, 29.44, 32.90, 34.07, 61.40, 61.54, 69.92, 69.97, 71.90, 77.34, 116.73, 116.78, 117.63, 124.78, 124.86, 125.36, 127.39, 128.01, 128.57, 137.68, 151.29, 151.84, 152.35, 166.01, 166.06, 166.19, 166.22. HRMS: calcd. for $C_{47}H_{63}BrNaO_{12}$ $[M+Na]^+$, most abundant m/z = 923.3406; found, 923.3416.

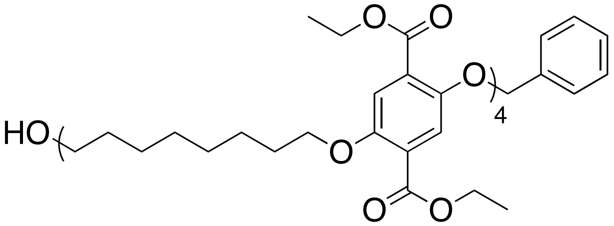
L$_2$EtOH



A solution of **L$_2$Et** 2.1 g (2.5 mmol, 1.0 eq.) and palladium on carbon 0.27 g (2.5 mmol, 1.0 eq.) in 38 mL of a 50:50 mixture of ethyl acetate:ethanol was sparged with nitrogen for 10 minutes. The solution was then sparged with hydrogen for 5 minutes and then stirred under hydrogen atmosphere for 18 h at 50 °C. The reaction was filtered to remove the catalyst, concentrated, and subjected to silica gel chromatography (0 to 60% ethyl acetate in hexanes, eluting at 40%) to yield the product in 98% yield.

^{1}H (CDCl$_3$, 400 Hz): 1.28-1.57 (30H, m), 1.71-1.83 (6H, m), 3.59 (2H, t), 3.96 (6H, m), 4.29-4.37 (6H, m), 4.40 (2H, q), 7.26 (1H, s), 7.31 (1H, s), 7.32 (1H, s), 10.33 (1H, s). ^{13}C (CDCl$_3$, 400 Hz): 14.25, 14.32, 25.70, 25.90, 25.97, 29.28, 29.29, 29.31, 29.35, 32.77, 61.31, 61.33, 61.36, 61.94, 62.94, 69.87, 69.97, 113.78, 114.82, 116.64, 119.78, 124.77, 128.96, 150.14, 151.76, 155.08, 165.61, 166.12, 166.15, 169.30. HRMS: calcd. for $C_{40}H_{58}NaO_{13}$ $[M+Na]^+$, most abundant m/z = 769.3770; found, 769.3768.

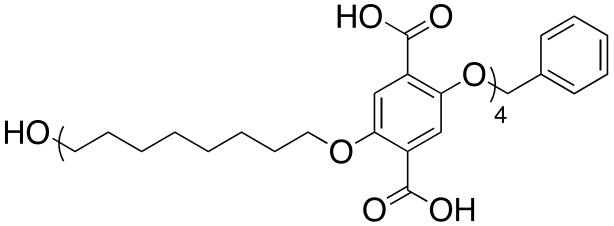
L_4Et



0.35 g (2.5 mmol, 1.5 eq.) of potassium carbonate, 21 mg (0.08, 0.05 eq.) 18-crown-6, 1.2 g (1.6 mmol, 0.95 eq.) of **L_2EtOH** and 1.5 g (1.7 mmol, 1.0 eq.) of **L_2EtBr** were dissolved in a 12.5 mL of 50:50 DMF/ethanol mixture. The mixture was heated at 80 °C for 29 h in a sealed pressure vessel. The reaction was then cooled. The solvent was removed under vacuum. The solid was dissolved in a 100 mL of a 50:50 mixture of DCM:DI water, neutralized with 1 M HCl and then extracted with dichloromethane three times. The extracts were dried with Na_2SO_4, filtered and concentrated under vacuum. The solid collected was dissolved with minimal DCM and purified by silica gel chromatography (0 to 8% methanol in DCM, eluting at 5%) and isolated in 90% yield.

^1H ($CDCl_3$, 400 Hz): 1.30-1.58 (58H, m), 1.79(14H, m), 3.61 (2H,t), 3.98 (14H,t), 4.35 (16H,q), 5.11 (2H,s), 7.27-7.50 (13H, m). ^{13}C ($CDCl_3$, 400 Hz): 14.28, 14.34, 25.72, 25.91, 26.00, 29.34, 29.37, 32.80, 61.34, 61.48, 63.00, 69.82, 69.89, 71.81, 116.65, 117.55, 124.70, 124.78, 125.27, 127.32, 127.95, 128.50, 136.70, 151.21, 151.79,152.26, 165.94, 165.99, 166.15. HRMS: calcd. for $C_{87}H_{124}NO_{25}$ $[M+NH_4]^+$, most abundant m/z = 1582.8457; found, 1582.8489.

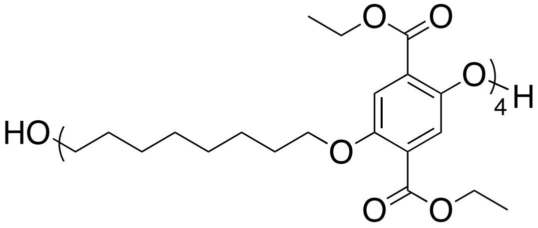
L_4



360 mg (0.23 mmol, 1 eq.) **L_4Et** and 150 eq. of potassium hydroxide were dissolved in 8 mL DMF. 3 mL of water were added and the mixture was heated at 80 °C for 8 hrs. The reaction was acidified with 1 M HCl to a pH of 2. The product crashed out of solution as a white solid and was centrifuged at 6000 rpm. The solvent was decanted. The sample was washed with water three times and dried under vacuum overnight to give 69% yield.

^1H (d_6-DMSO, 400 Hz): 1.23-1.45 (34H, m), 1.61-1.73 (14H, m), 3.37 (2H, t), 3.93-4.02 (14H, m), 5.15 (2H, s), 7.24-7.34 (8H, m), 7.35-7.41 (3H, m), 7.45-7.49 (2H, m), 12.90 (8H,s). ^{13}C (d_6-DMSO, 400 Hz): 25.28, 25.44, 28.69, 28.76, 28.92, 32.52, 60.70, 69.15, 70.48, 115.50, 116.03, 125.46, 125.64, 127.16, 127.64, 128.30, 137.02, 149.96, 150.43, 150.72, 166.77, 166.83. HRMS: calcd. for $C_{71}H_{88}NaO_{25}$ $[M+Na]^+$, most abundant m/z = 1363.5507; found, 1363.5522.

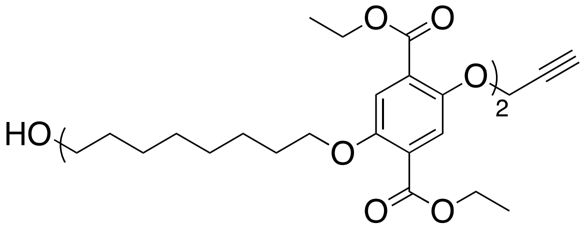
L_4EtOH



A solution of **L_4Et** 3.1 g (2.0 mmol, 1.0 eq.) and palladium on carbon 0.21 g (2.0 mmol, 1.0 eq.) in 240 mL of 50:50 mixture of toluene and ethanol was sparged with nitrogen for 10 minutes. The solution was then sparged with hydrogen for 5 minutes and then stirred under hydrogen atmosphere for 18 h at 60 °C. The reaction was filtered to remove the catalyst, concentrated, and subject to silica gel chromatography (0 to 8% methanol in DCM, eluting at 6%). **L_4EtOH** was isolated in 96% yield.

^{1}H ($CDCl_3$, 400 Hz): 1.32-1.58 (58H, m), 1.74-1.84 (14H, m), 3.63 (2H, t), 3.94-4.04 (14H, m), 4.31-4.39 (14H, m), 4.42 (2H, q), 7.29 (1H, s), 7.33 (6H, s), 7.34 (1H, s), 10.36 (1H, s). ^{13}C ($CDCl_3$, 400 Hz): 14.32, 14.38, 25.73, 25.94, 26.03, 29.33, 29.37, 29.42, 32.83. 61.37, 61.42, 61.99, 63.08, 69.90, 70.00, 77.33, 113.78, 114.86, 116.66, 119.86, 124.77, 128.98, 150.28, 151.80, 155.13, 165.63, 166.15, 116.28, 116.20, 269.36. HRMS: calcd. for $C_{80}H_{114}NaO_{25}$ $[M+Na]^+$, most abundant m/z = 1497.7541; found, 1497.7594.

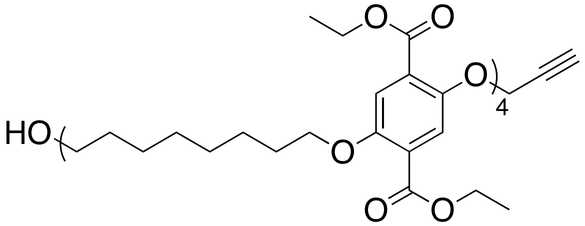
L_2Et-alkyne



0.11 g (0.83 mmol, 1.5 eq.) of potassium carbonate, 0.41 g (0.55 mmol, 1.0 eq.) of **L_2EtOH** and 0.077 mL (0.72 mmol, 1.3 eq.) of propargyl bromide were dissolved in 5.5 mL of acetone and 2.75 mL ethanol. The mixture was heated at 80 °C for 14 h in a sealed pressure vessel. The reaction was then cooled. 50 mL of DI water were added and the reaction was neutralized with 1 M HCl and then extracted with dichloromethane three times. The extracts were dried with Na_2SO_4, filtered, and concentrated under vacuum. The solid collected was dissolved in a minimal amount of DCM and purified by silica gel chromatography (0 to 80% ethyl acetate in hexanes, eluting at 25%). The product was obtained in 89% yield.

^{1}H ($CDCl_3$, 400 Hz): 1.29-1.59 (30H, m), 1.74-1.85 (6H, m), 2.52 (1H, t), 3.62 (2H, t), 3.95-4.03 (6H, mt), 4.31-4.40 (8H, m), 4.72 (2H, d), 7.32 (2H, s), 7.34 (1H, s), 7.52 (1H, s). ^{13}C ($CDCl_3$, 400 Hz): 14.35, 14.49, 25.74, 25.95, 26.02, 29.34, 29.40, 32.84, 58.60, 61.39, 61.41, 61.59, 63.07, 69.78, 69.91, 76.15, 78.32, 116.36, 116.69, 119.44, 124.71, 124.81, 126.10, 150.13, 151.82, 153.08, 165.55, 165.77, 166.20. HRMS: calcd. for $C_{43}H_{60}NaO_{13}$ $[M+Na]^+$, most abundant m/z = 807.3926; found, 807.3906.

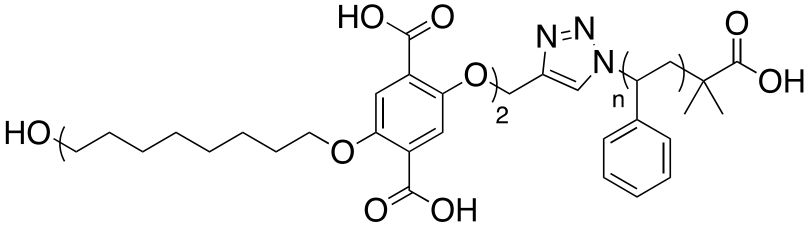
L_4Et-alkyne



75 mg (0.54 mmol, 1.5 eq.) of potassium carbonate, 0.53 g (0.36 mmol, 1.0 eq.) of **L_4EtOH** and 0.050 mL (0.47 mmol, 1.3 eq.) of propargyl bromide were dissolved in 3.6 mL of acetone and 1.2 mL of ethanol. The mixture was heated at 80 °C for 14 h in a sealed pressure vessel. The reaction was then cooled. 30 mL of DI water were added and the reaction was neutralized with 1 M HCl and then extracted with dichloromethane three times. The extracts were dried with Na_2SO_4, filtered and concentrated under vacuum. The solid collected was dissolved in a minimal amount of DCM and purified by silica gel chromatography (0 to 6% methanol in DCM, 3%) to provide the product in 86% yield.

^{1}H ($CDCl_3$, 400 Hz): 1.37-1.44 (40H, m), 1.47-1.55 (16H, m), 1.78-1.88 (16H, m), 2.55 (1H, t), 3.67 (2H, dt), 4.03 (14H, t), 3.36-3.44 (16H, m), 4.76 (2H, d), 7.36 (1H, s), 7.39 (1H, s), 7.57 (1H, s). ^{13}C ($CDCl_3$, 400 Hz): 14.37, 14.40, 25.76, 25.97, 26.06, 29.36, 29.41, 29.45, 29.81, 32.87, 58.62, 61.39, 61.59, 63.11, 69.80, 69.96, 76.15, 116.39, 116.72, 119.47, 124.74, 124.84, 126.12, 150.15, 121.84, 161.56, 165.57, 165.57, 165.78, 166.20. HRMS: calcd. for $C_{83}H_{116}NaO_{25}$ $[M+Na]^+$, most abundant m/z = 1535.7698; found, 1535.7708.

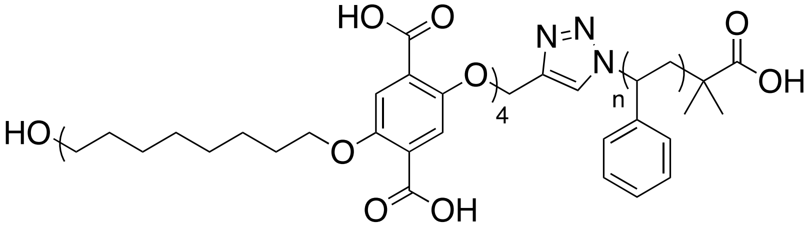
L_2PS



This reaction was set up in a nitrogen atmosphere glovebox. 0.13 g (0.17 mmol, 1 eq.) of **L_2Etyne** and 0.61 mg of polystyrene azide (0.16 mmol, 0.95 eq) were dissolved in 5 mL of THF. 0.005 mL (0.019 mmol, 0.11 eq) of Me_6Tren was added to 2.4 mg (0.017 mmol, 0.1 eq.) of CuBr dissolved in 1 mL of THF (prepared through iterative dilution) and added to the polystyrene mixture. The reaction was stirred at RT for 12 hrs and then concentrated. The mixture was purified by column chromatography (0-10% Methanol in DCM, eluting at 8%). The concentrated material was dissolved in 11 mL of DMSO and 100 eq. KOH were added. A few drops of water were added (the material precipitates if too much water is added) and was heated at 80 °C for 8 hours. The reaction was acidified with 1 M HCl to a pH of 2. The product precipitated from solution as a white solid and was centrifuged at 6000 rpm. The solvent was decanted. The sample was washed, centrifuged after each wash, with water three times and with acetone one time, and dried under vacuum overnight.

^{1}H ($CDCl_3$, 500 Hz): 0.82-0.90 (4H, m), 0.91-1.03 (11H, m), 1.18-1.97 (356H, m, *H_2O present), 2.00-2.11 (b), 3.6-3.70 (2H, t), 4.20-4.33 (6H, m), 5.24-5.35 (2H, b), 6.24-7.24 (161H, m, *overlap with $CDCl_3$), 7.61 (1H, s), 7.72-7.77 (m, 1H), 7.81-7.87 (3H, s). Note peaks shift and broaden significantly depending on solvent used and solvent contamination. Carboxylic acid protons only visible in DMF.

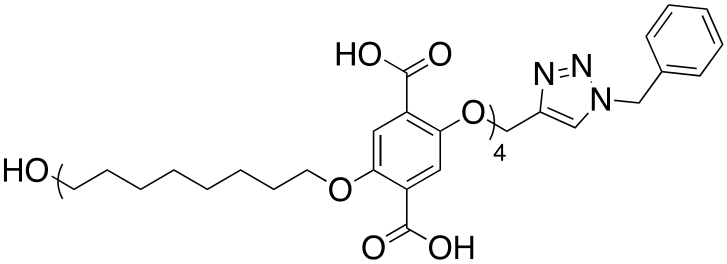
L_4PS



This reaction was set up in a nitrogen atmosphere glovebox. 0.20 g (0.14 mmol, 1 eq.) of **L_4Etyne** and 0.49 mg of polystyrene azide (0.13 mmol, 0.95 eq) were dissolved in 5 mL of THF. 0.004 mL (0.015 mmol, 0.11 eq) of Me_6Tren was added to 1.9 mg (0.014 mmol, 0.1 eq.) of CuBr dissolved in 1 mL of THF (prepared via iterative dilution) and added to the polystyrene mixture. The reaction was stirred at RT for 12 hrs and then concentrated. The mixture was purified by silica gel chromatography (0-10% Methanol in DCM, eluting at 8%). The concentrated material was dissolved in 4.0 mL of DMF and 100 eq. KOH were added. A few drops of water were added (the material precipitates if too much water is added) and was heated at 80°C for 8 hours. The reaction was acidified with 1 M HCl to a pH of 2. The product precipitated as a white solid and was centrifuged at 6000 rpm. The solvent was decanted. The sample was washed, centrifuging after each wash, with water three times and with acetone one time, and dried under vacuum overnight.

^{1}H ($CDCl_3$, 400 Hz): 0.82-0.93 (12H, m), 0.93-1.00 (10H, m), 1.16-1.99 (257H, m, *H_2O present), 2.00-2.11 (5H, m), 2.11-2.26 (2H, m), 3.62-3.70 (2H, t), 4.20-4.33 (14H, m), 5.23-5.34 (2H, m), 6.27-7.21 (285H, m, *overlap with $CDCl_3$), 7.44 (1H, s), 7.71-7.79 (m, 2H), 7.81-7.86 (6H, s). Note peaks shift and broaden significantly depending on solvent used. Carboxylic acid protons only visible in DMF.

L_4Bn



L_4Bn was synthesized using the same conditions as those for **L_4PS** except benzyl azide was used instead of polystyrene azide.

^{1}H (d$_6$-DMSO $_3$, 400 Hz): 1.23-147 (34H, m), 1.63-1.72 (14H, m), 3.37 (2H, t), 3.97 (14H, t), 5.16 (2H, s), 5.61 (2H, s), 7.24-7.40 (12H, m), 7.44 (1H, s), 8.18 (1H, s), 12.89 (8H, s). ^{13}C (d$_6$-DMSO, 400 Hz): 25.29, 25.45, 28.70, 28.78, 28.93, 32.53, 52.79, 60.71, 69.16, 115.52, 125.46, 125.53, 127.84, 128.11, 128.76, 150.43, 166.84. HRMS: calcd. for $C_{74}H_{91}N_3NaO_{25}$ $[M+Na]^+$, most abundant m/z = 1444.5834; found, 1444.5811.

MALDI-TOF data for BCPMOF precursors

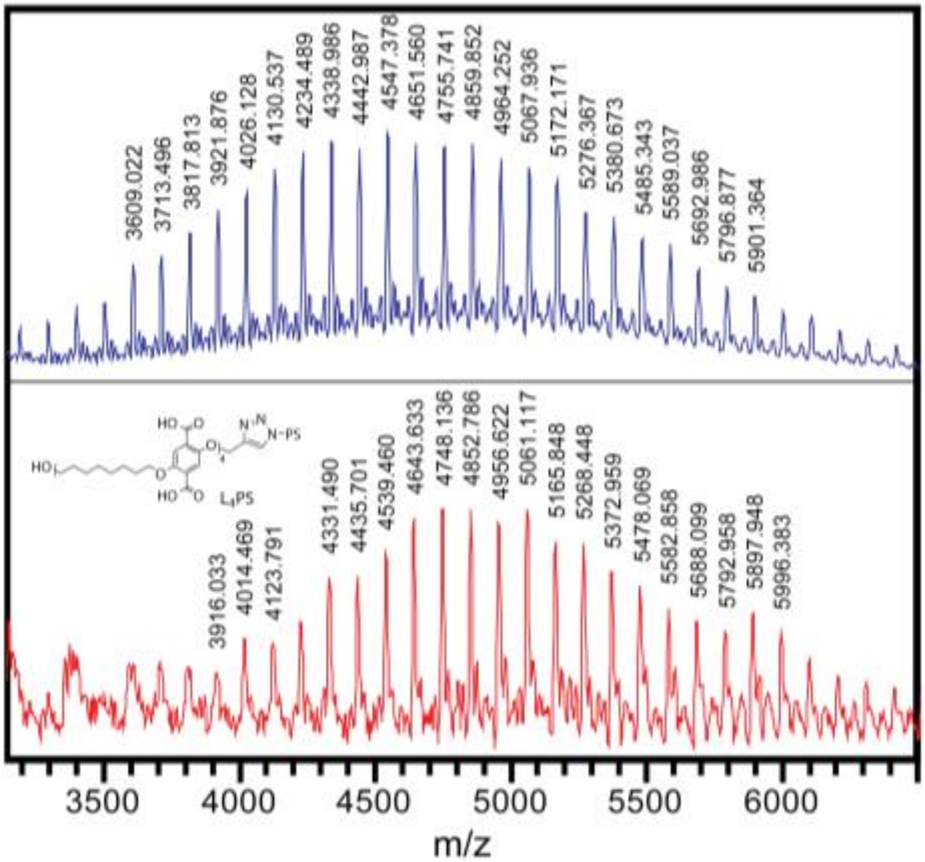


Figure S7. MALDI-TOF spectra in negative ion mode. Blue is **L$_2$PS** and red is **L$_4$PS**. Within a 0.1% margin of error, calculated m/z is 4445.53 for **L$_2$PS** and 5063.79 for **L$_4$PS** (35 units of styrene).

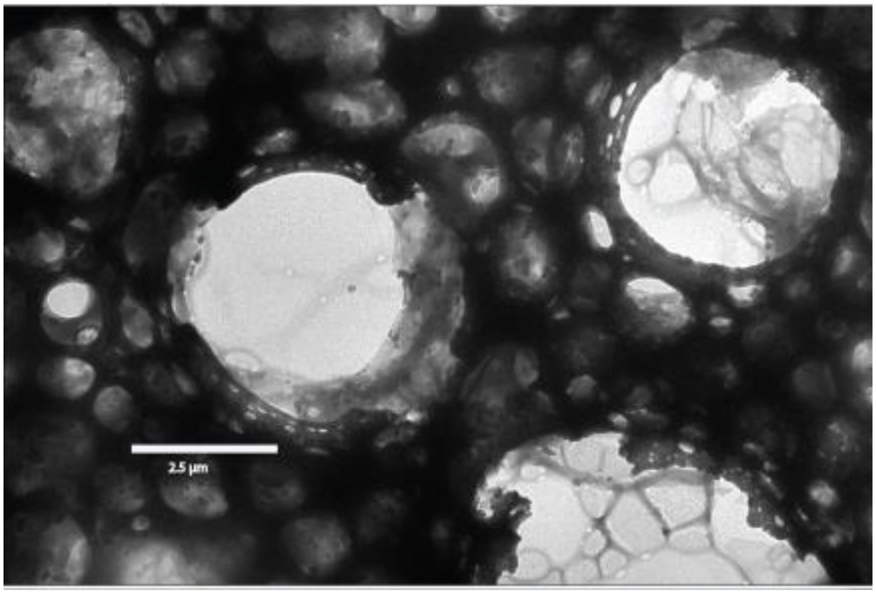


Figure S8. TEM image of **L$_4$PS-Zn** annealed at 120 °C for 12 hours.

NMR spectra

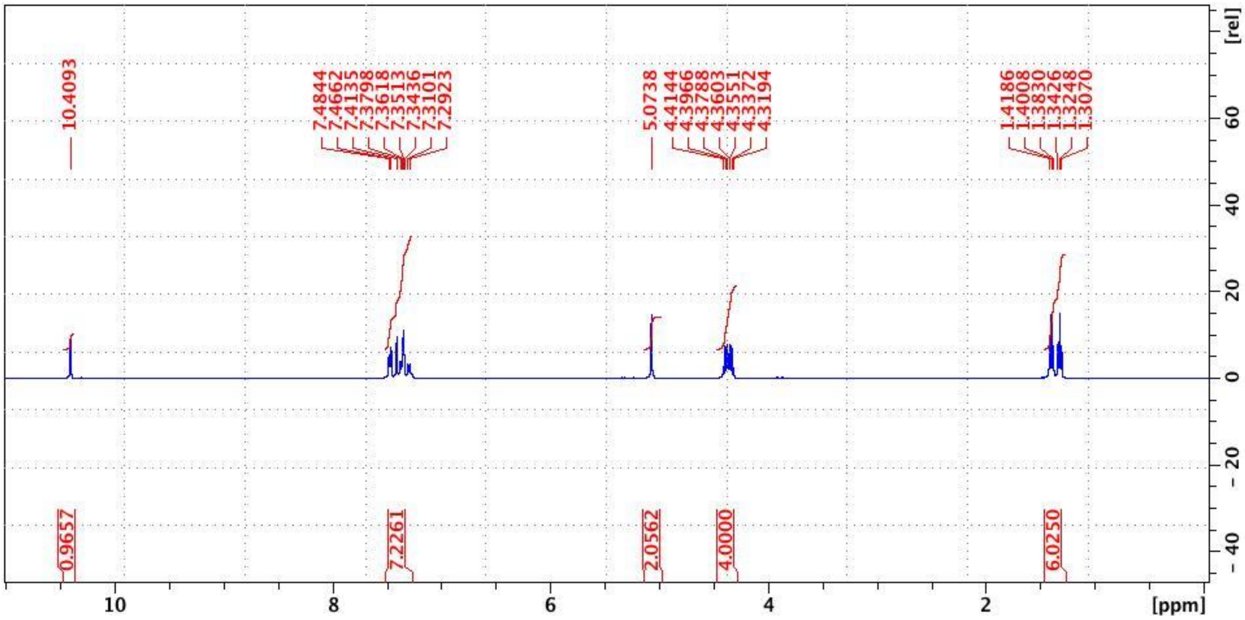


Figure S9. ^{1}H NMR of A.

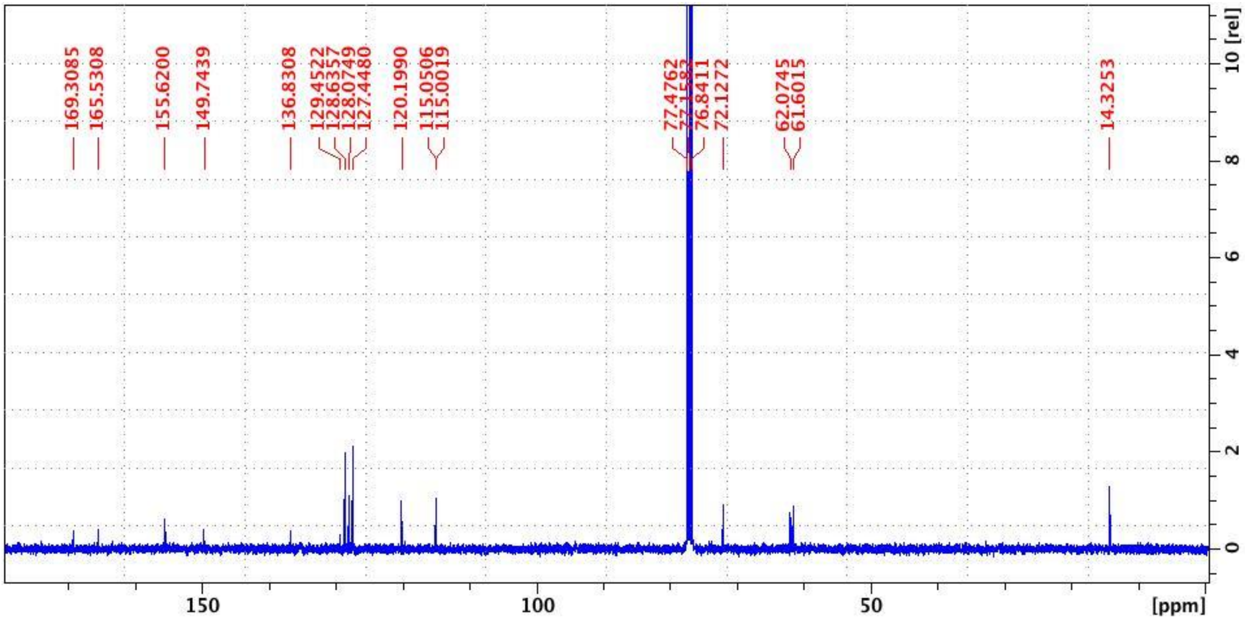


Figure S10. ^{13}C NMR of A.

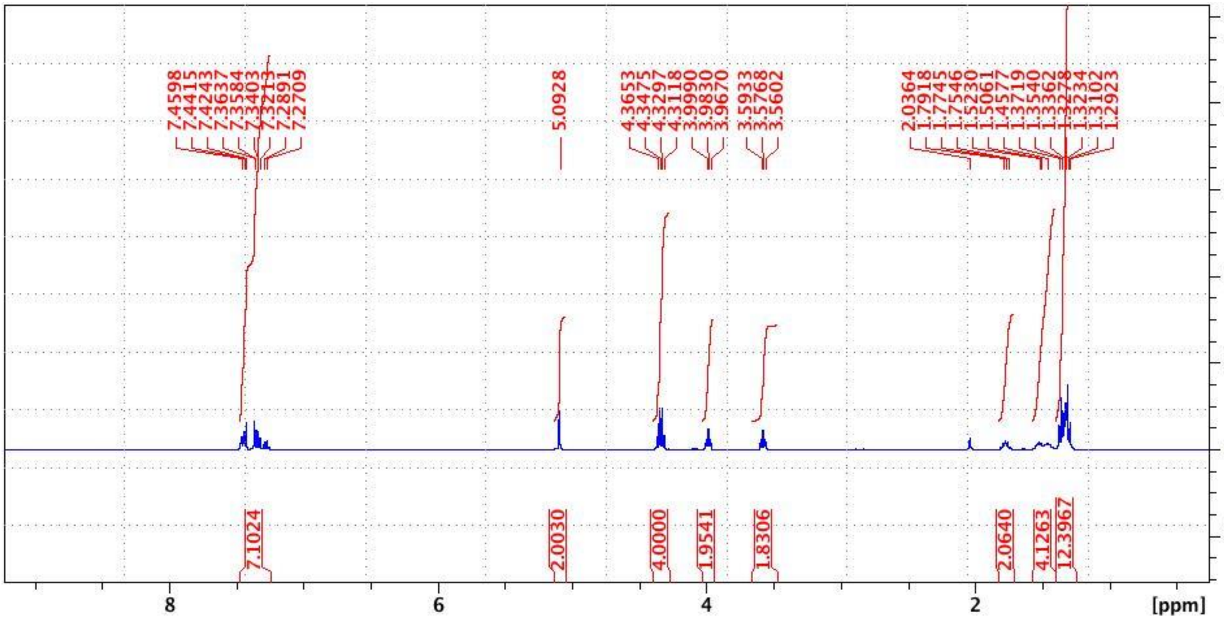


Figure S11. ^1H NMR of **L_1Et**.

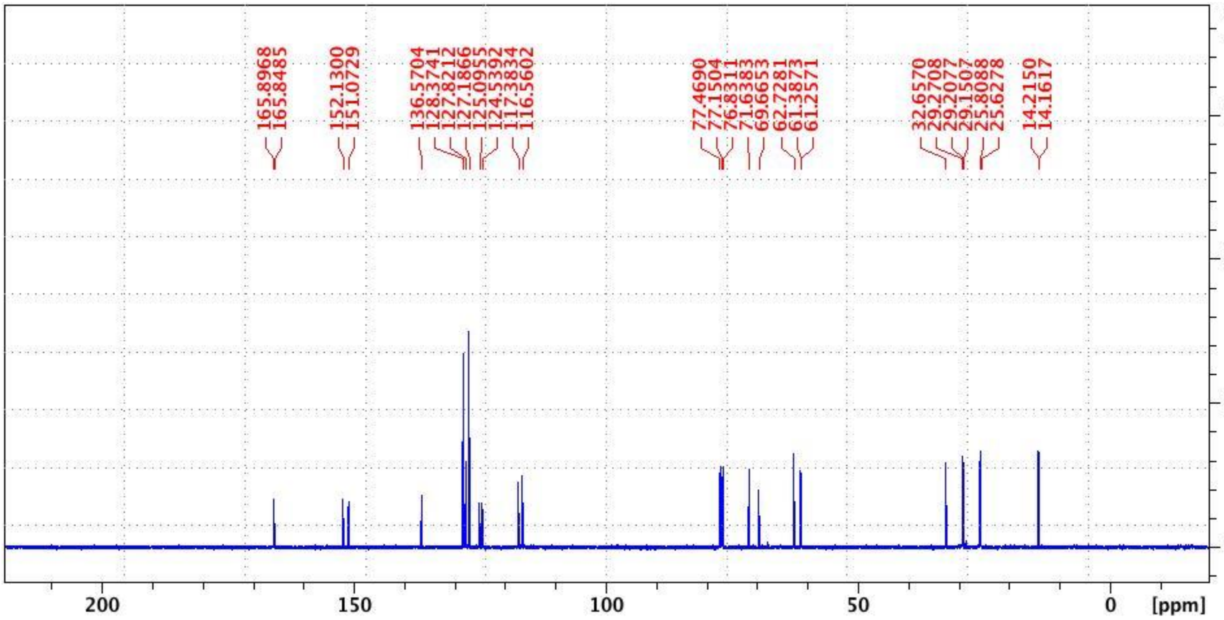


Figure S12. ^{13}C NMR of **L_1Et**.

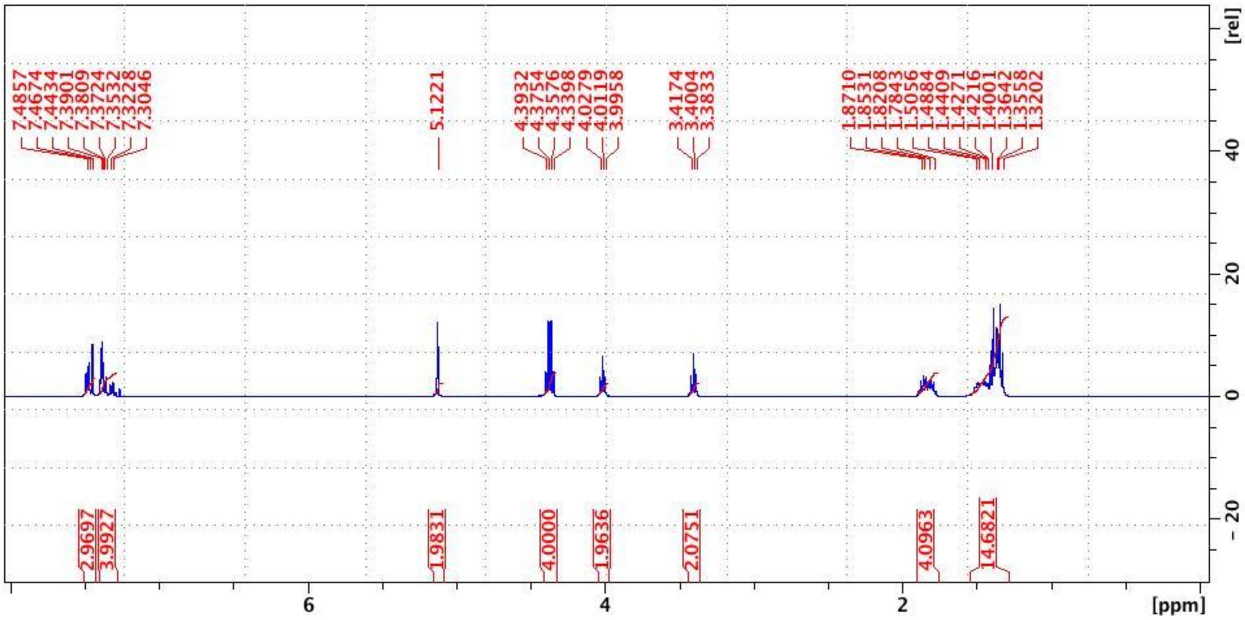


Figure S13. ^{1}H NMR of **L$_1$EtBr**.

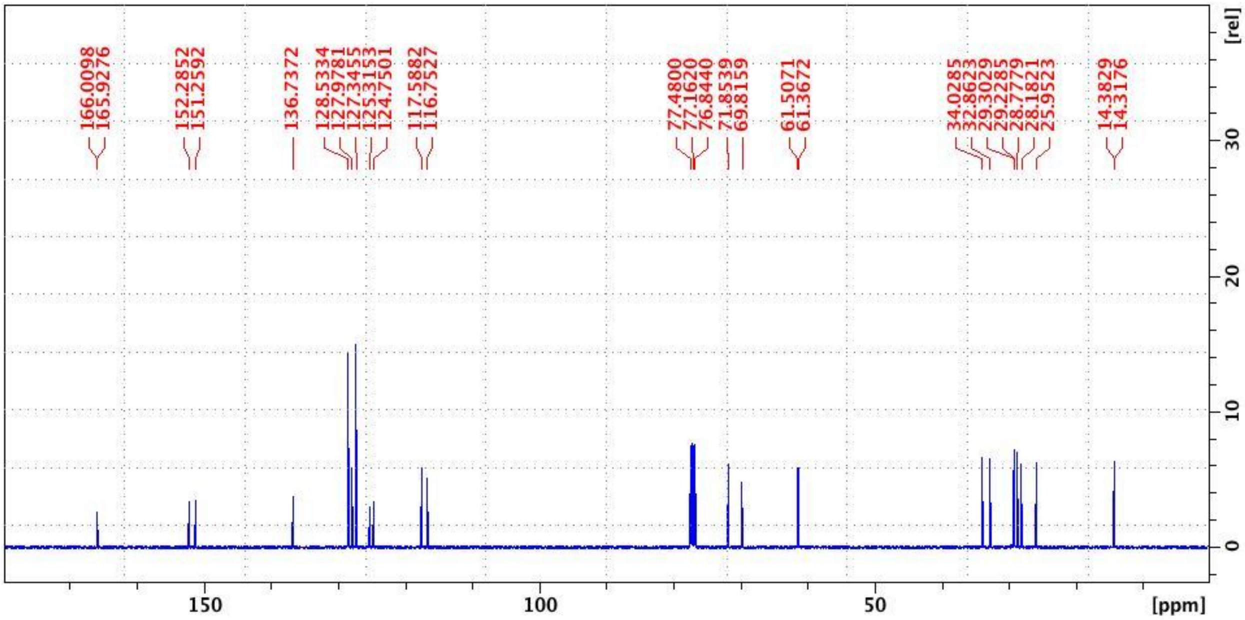


Figure S14. ^{13}C NMR of **L$_1$EtBr**.

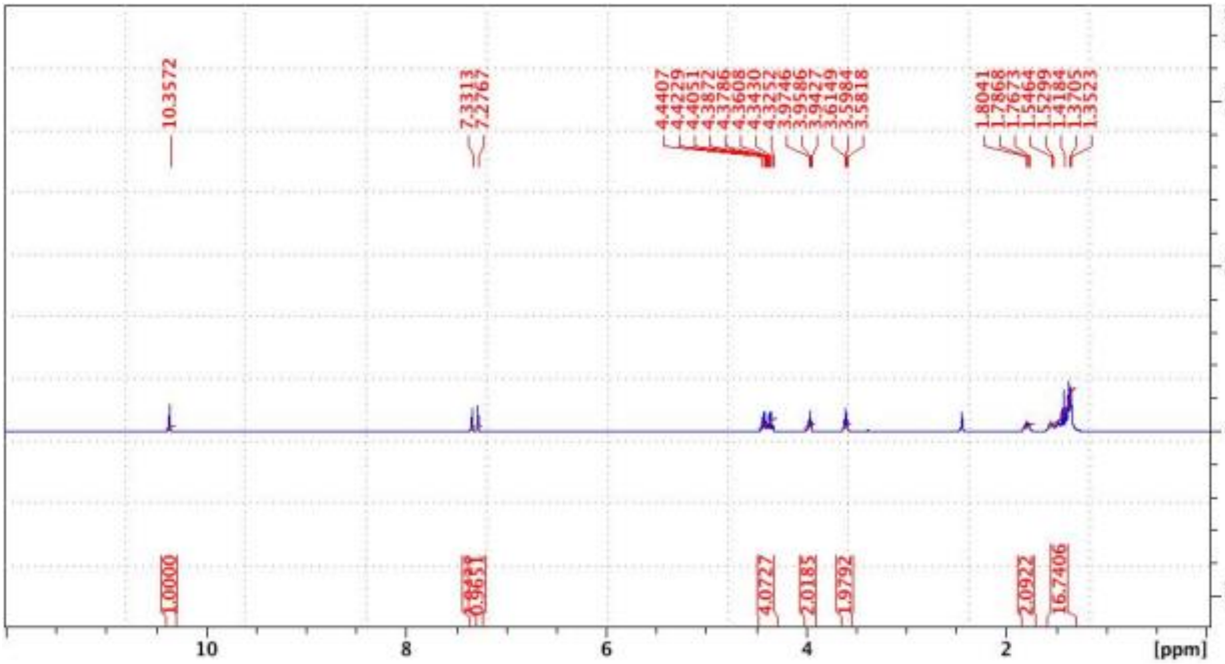


Figure S15. ^{1}H NMR of **L$_1$EtOH**.

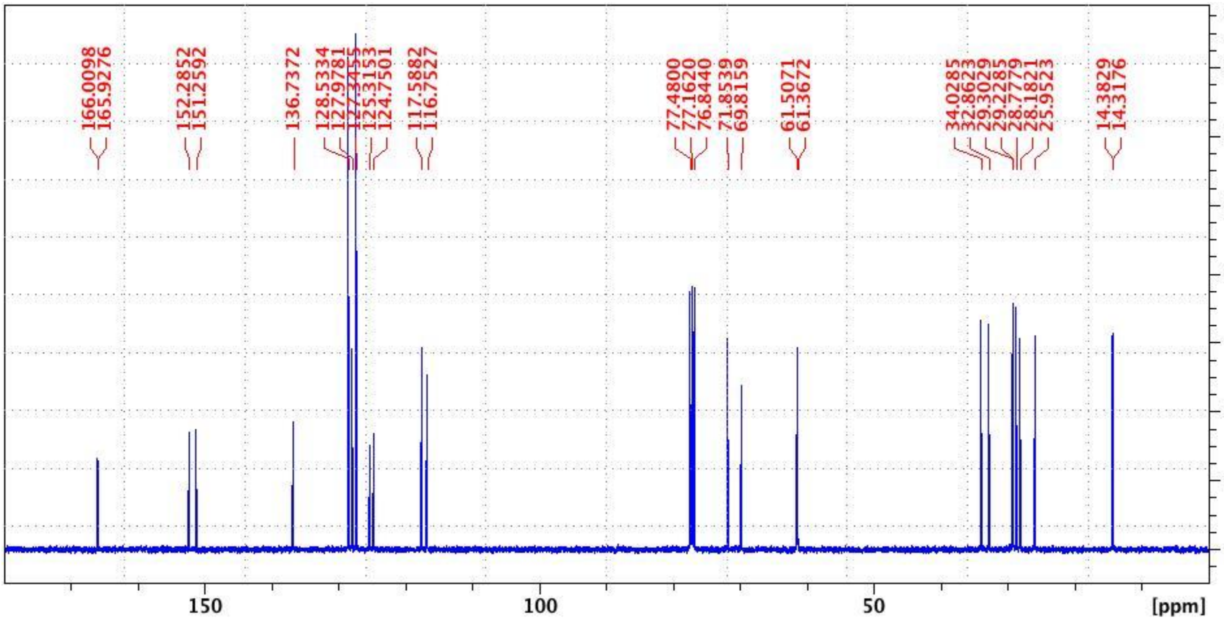


Figure S16. ^{13}C NMR of **L$_1$EtOH**.

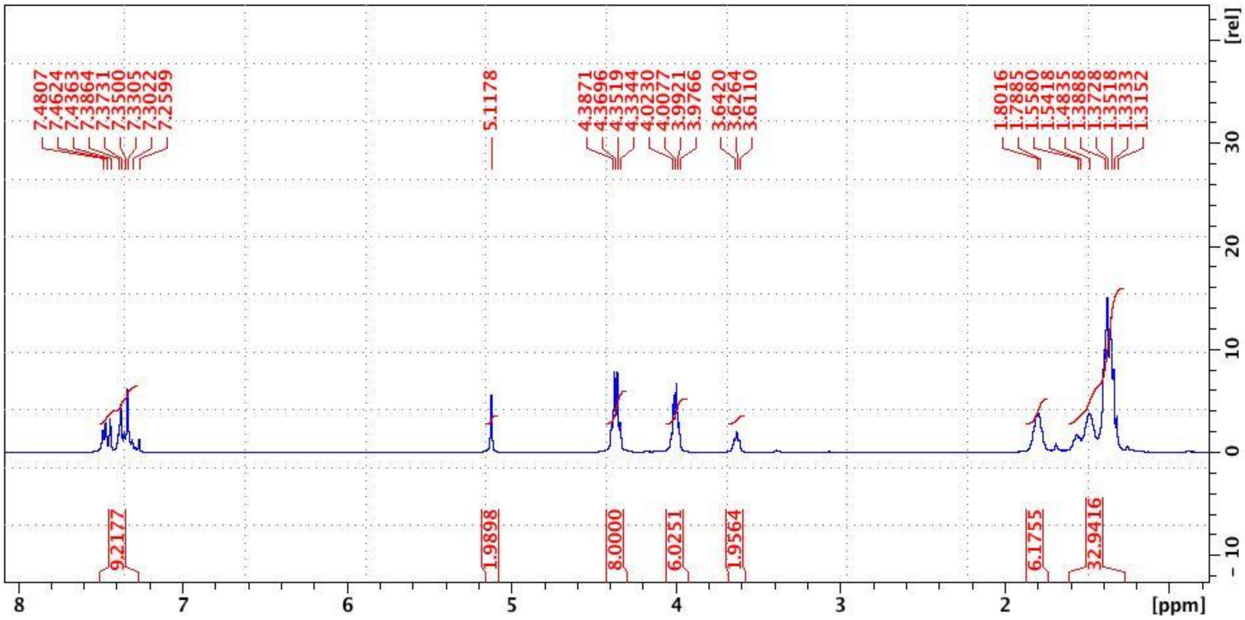


Figure S17. ^{1}H NMR of **L$_2$Et**.

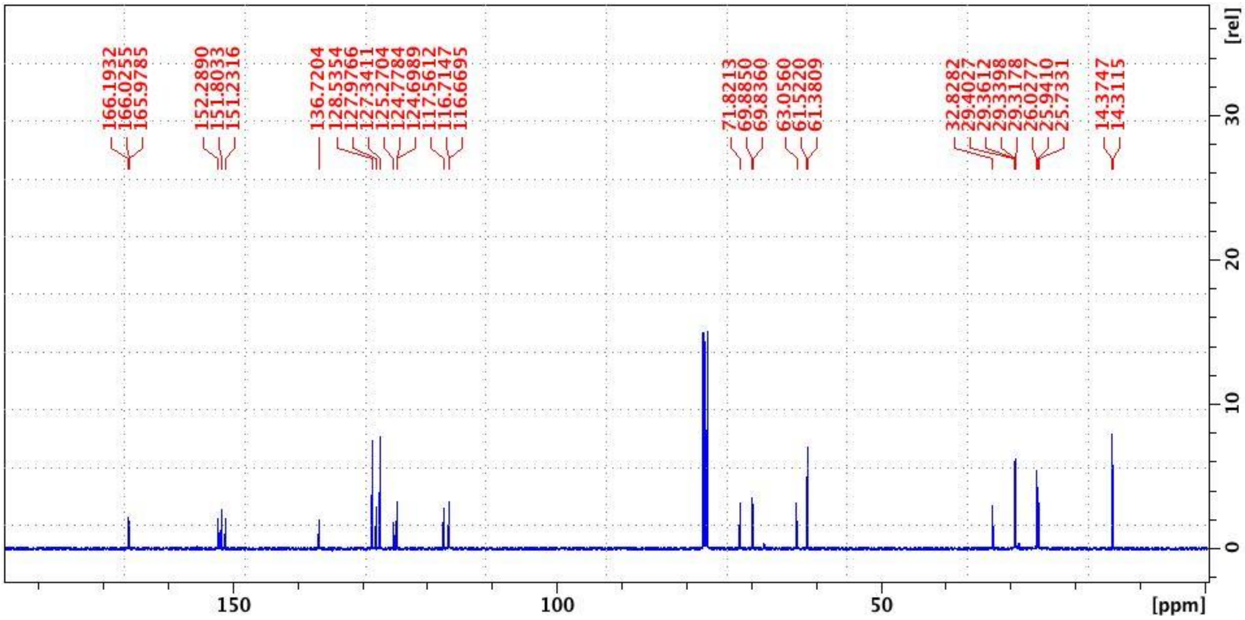


Figure S18. ^{13}C NMR of **L$_2$Et**.

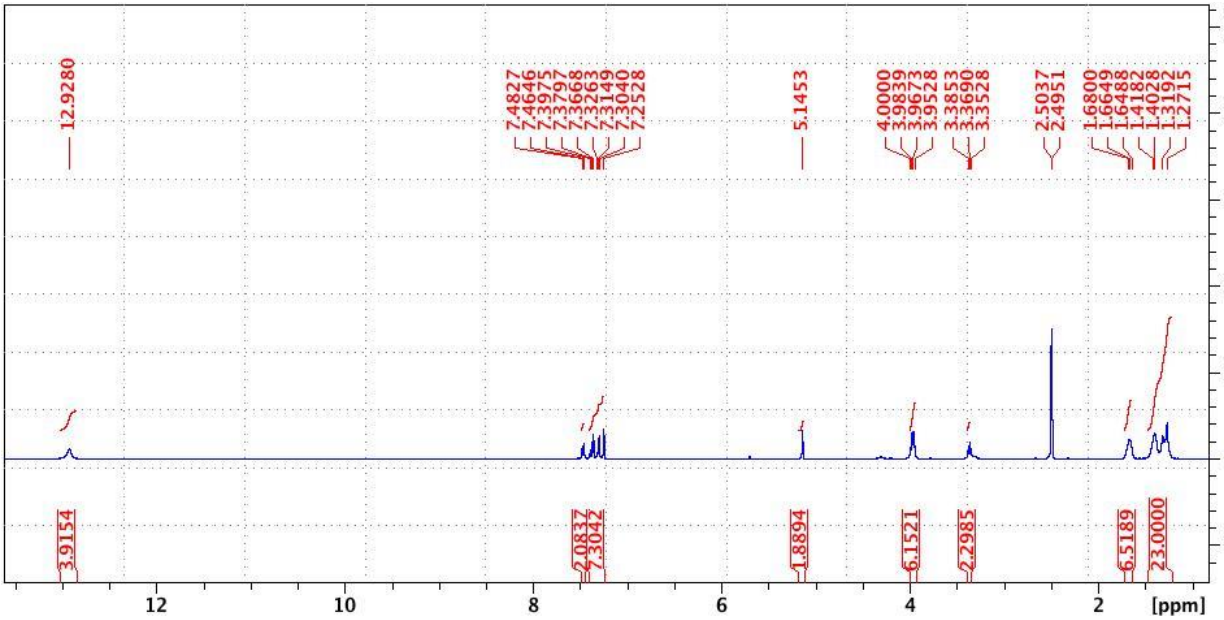


Figure S19. ^{1}H NMR of **L$_2$**.

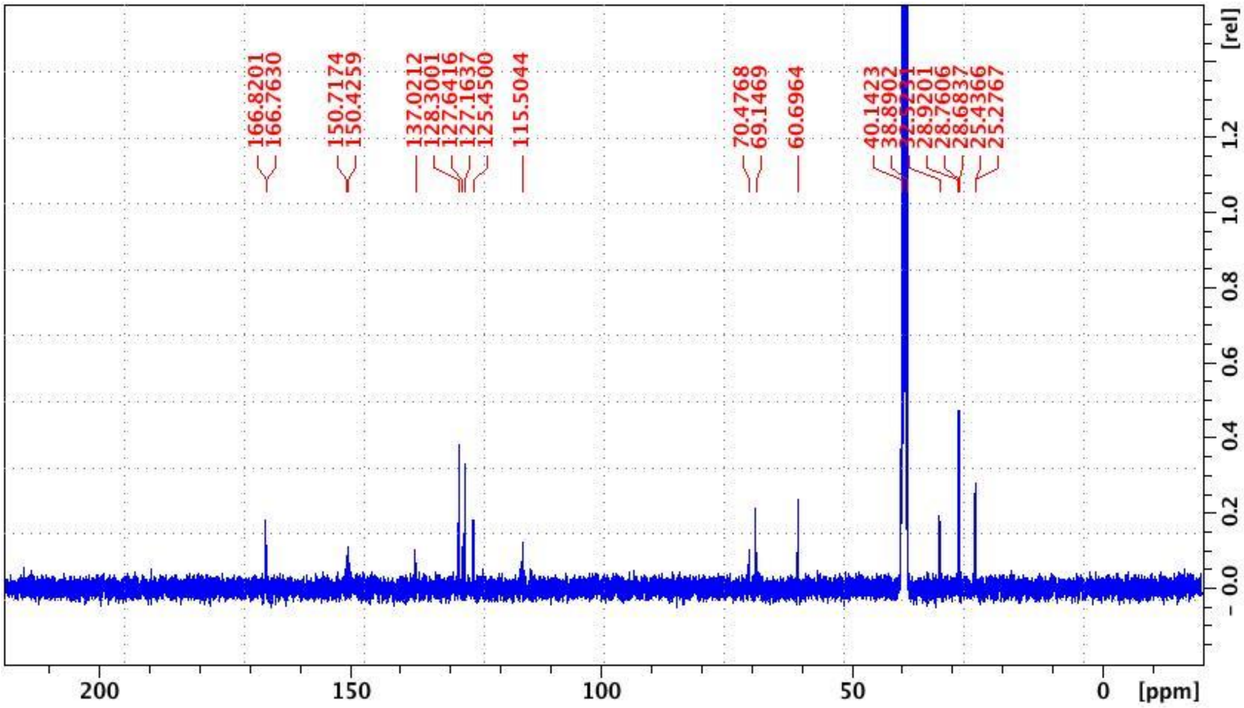


Figure S20. ^{13}C NMR of **L$_2$**.

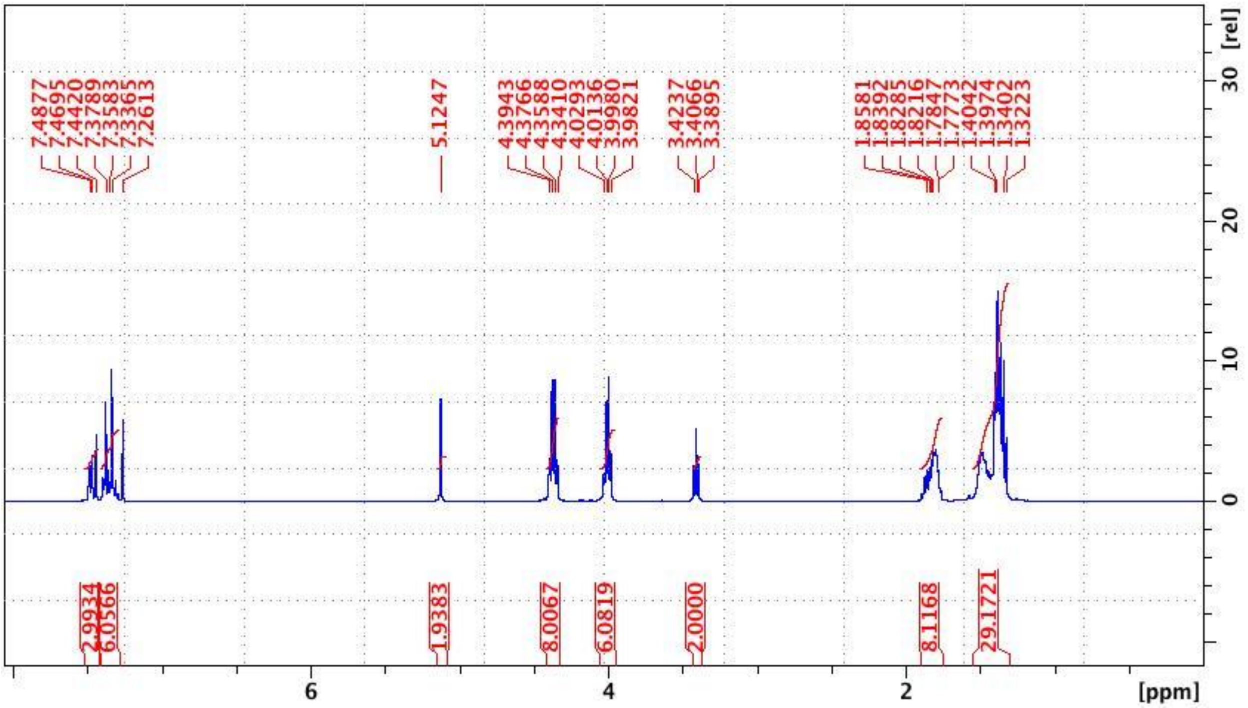


Figure S21. ^{1}H NMR of **L_2EtBr**.

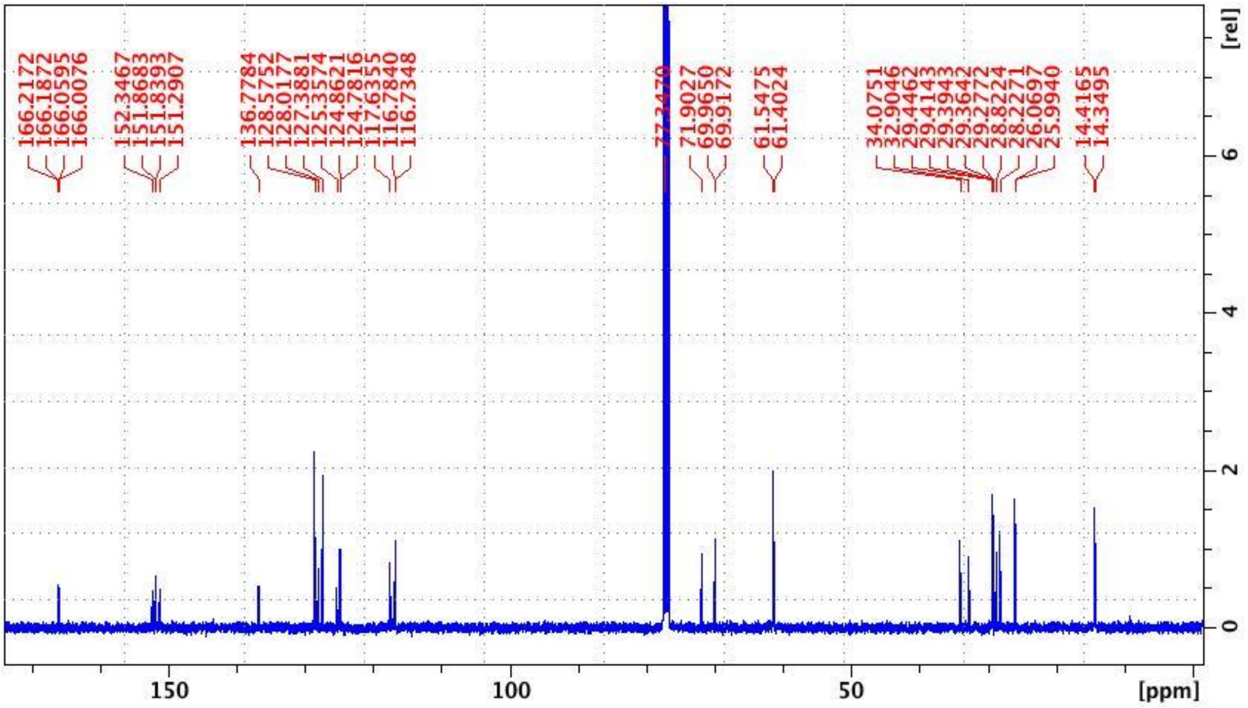


Figure S22. ^{13}C NMR of **L_2EtBr**.

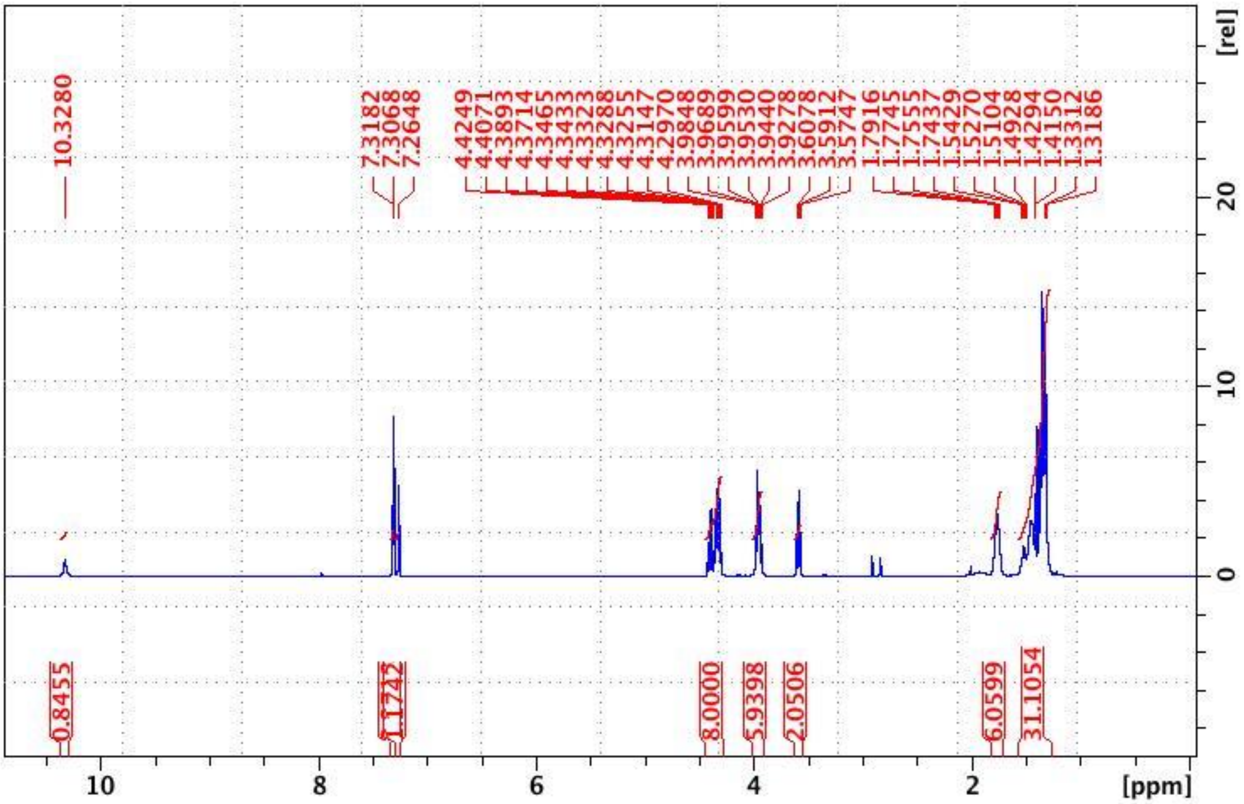


Figure S23. ^{1}H NMR of **L_2EtOH**.

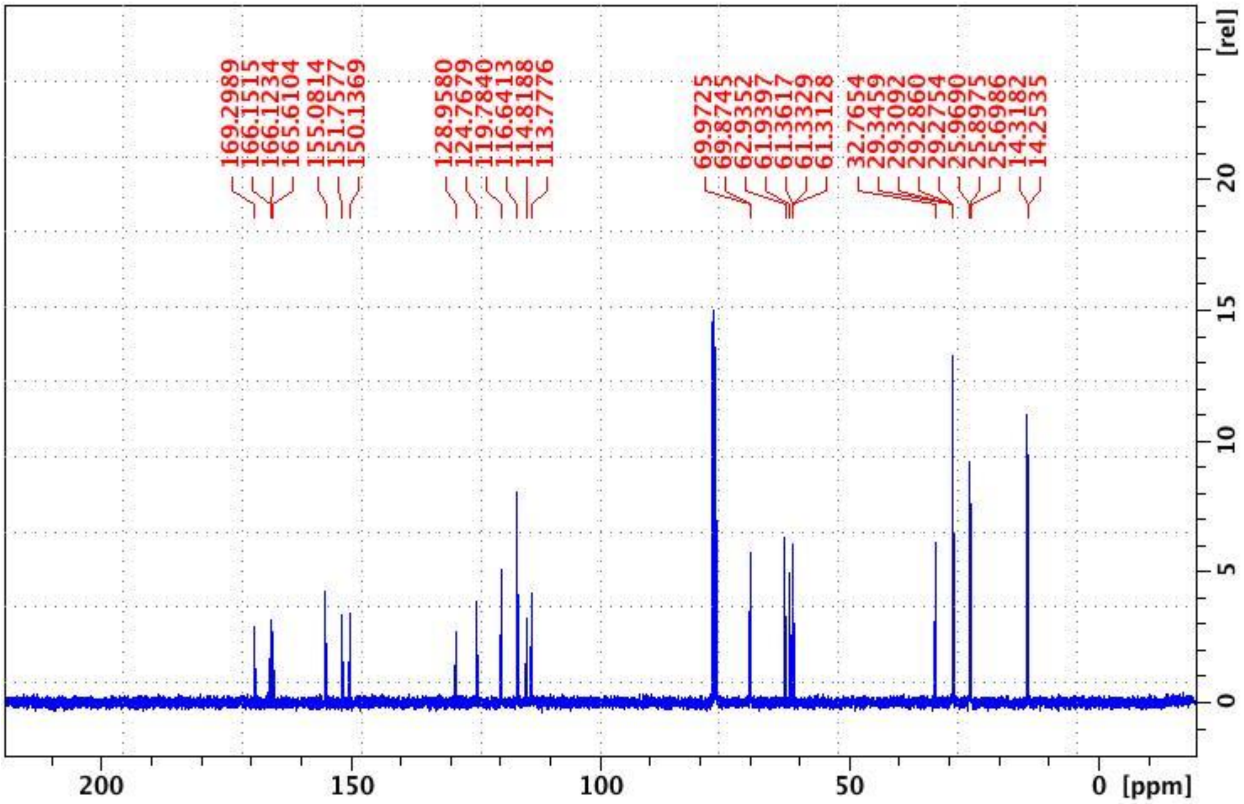


Figure S24. ^{13}C NMR of **L_2EtOH**.

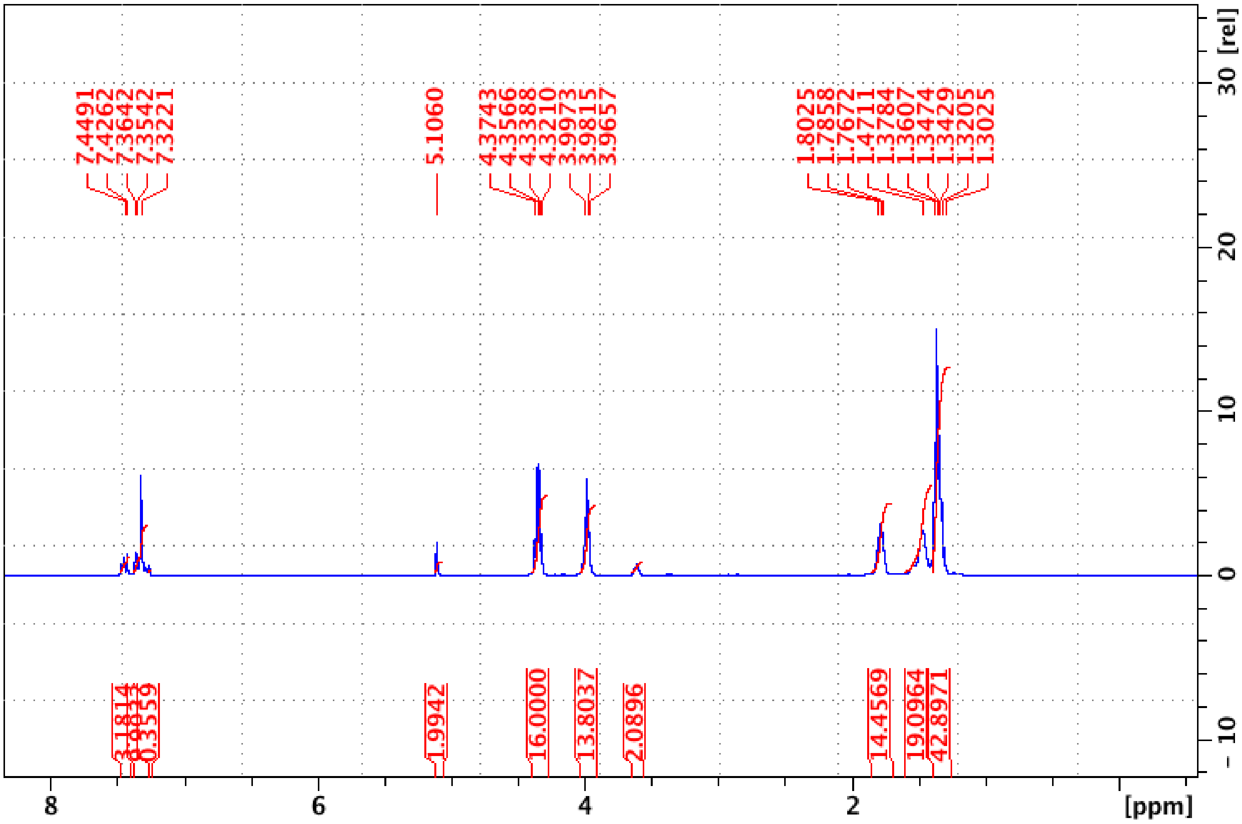


Figure S25. ^{1}H NMR of **L_4Et**.

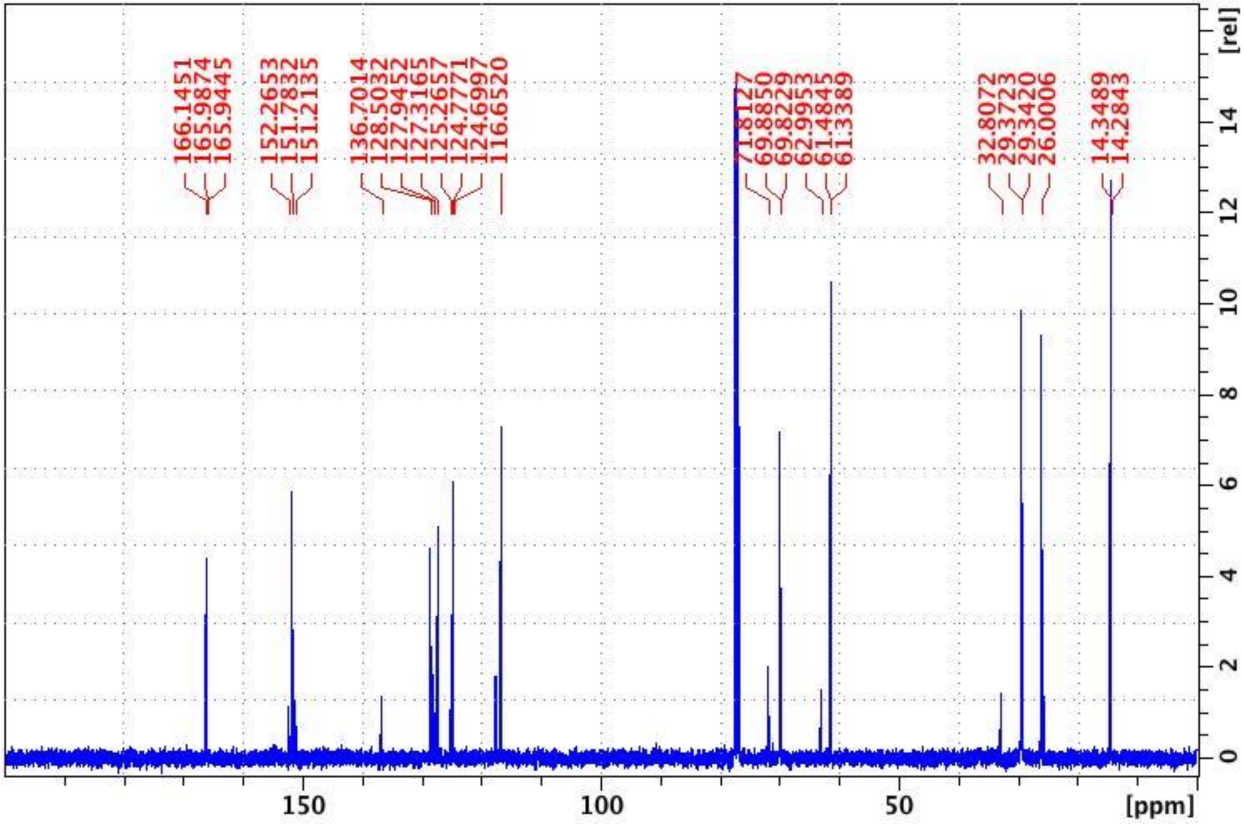


Figure S26. ^{13}C NMR of **L_4Et**.

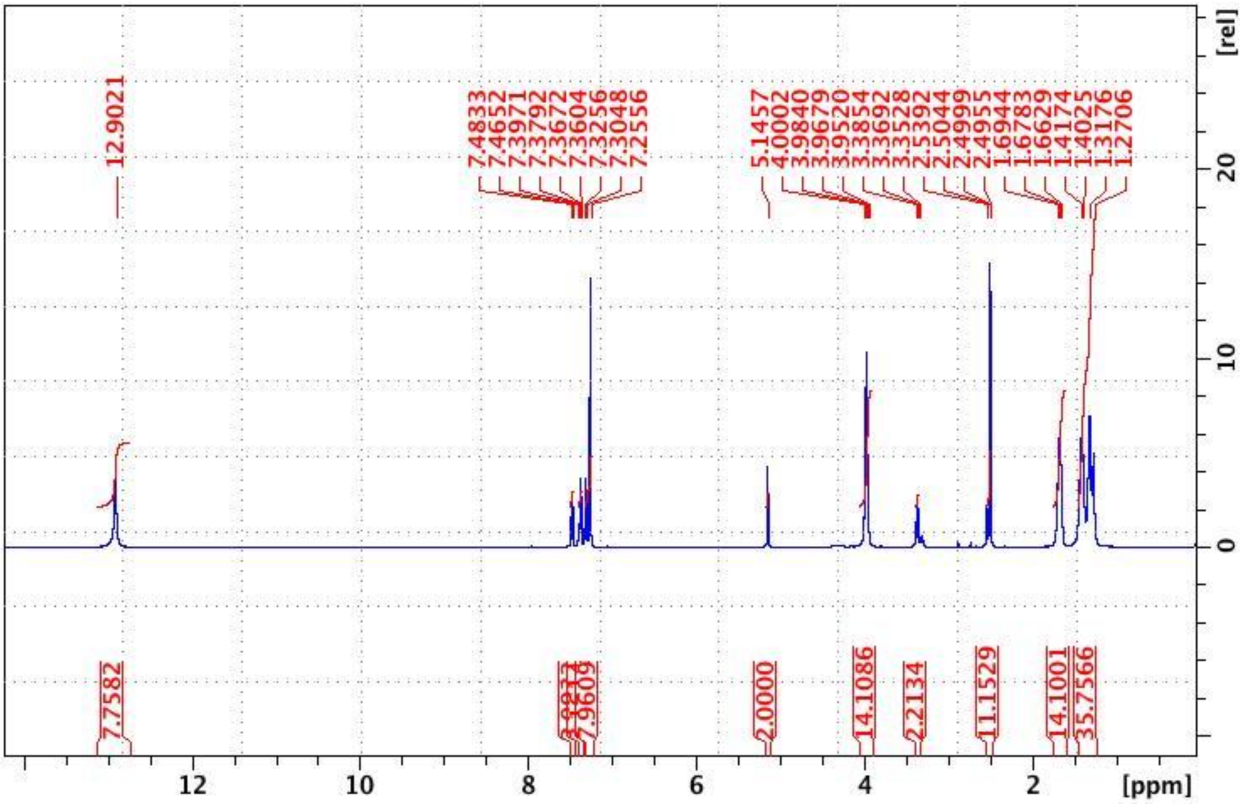


Figure S27. ^{1}H NMR of **L$_4$**.

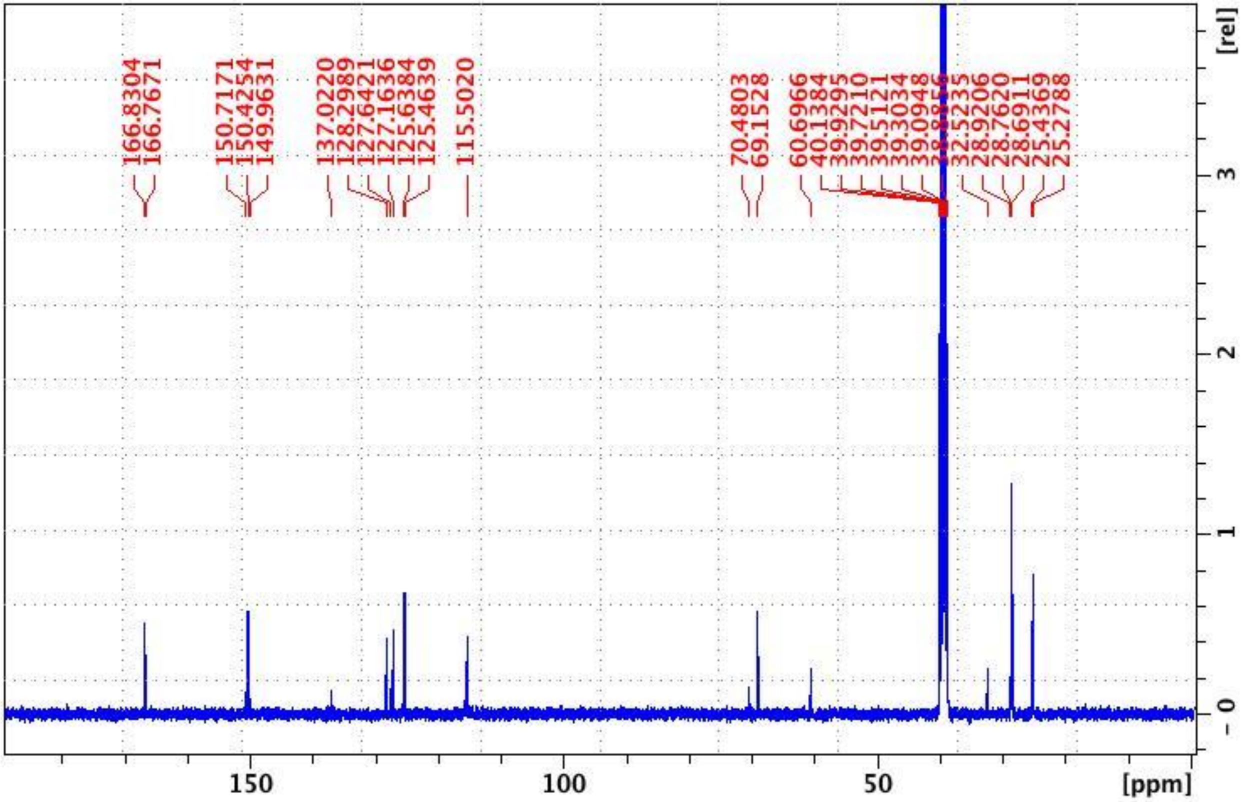


Figure S28. ^{13}C NMR of **L$_4$**.

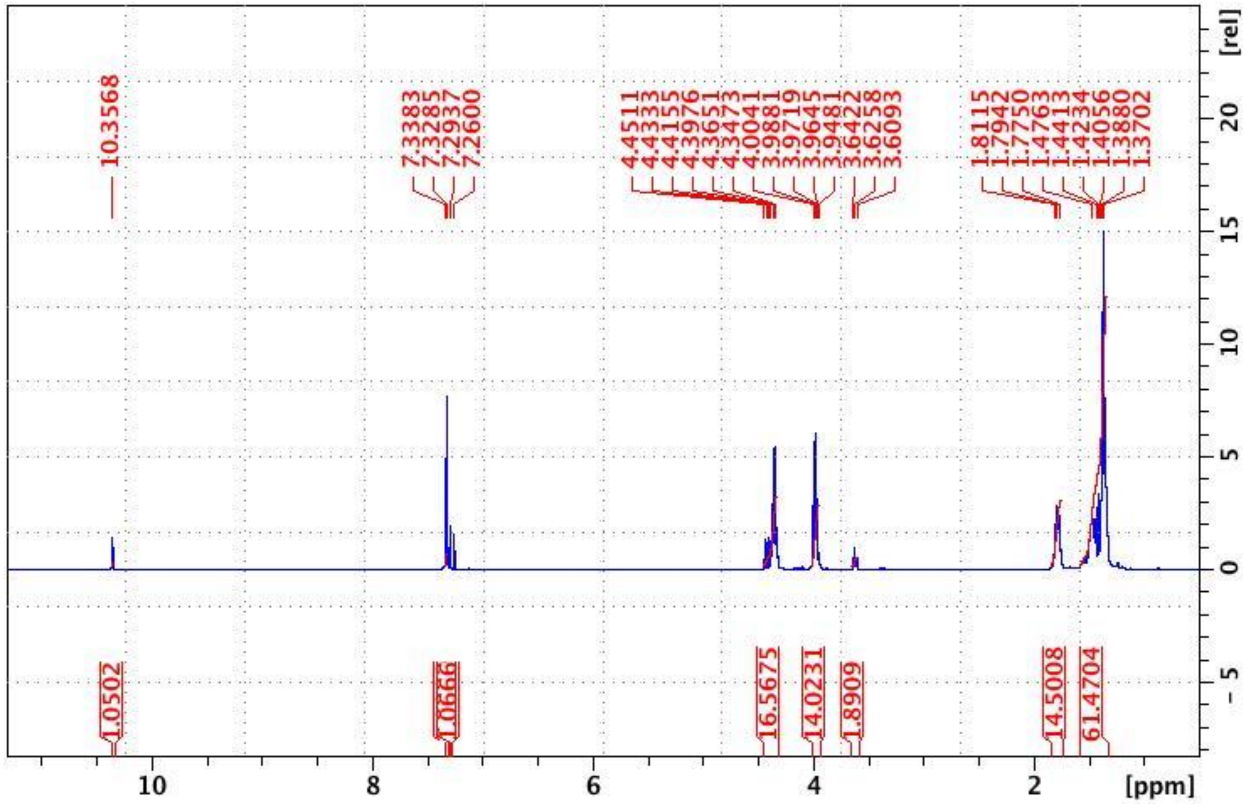


Figure S29. ^{1}H NMR of **L$_4$EtOH**.

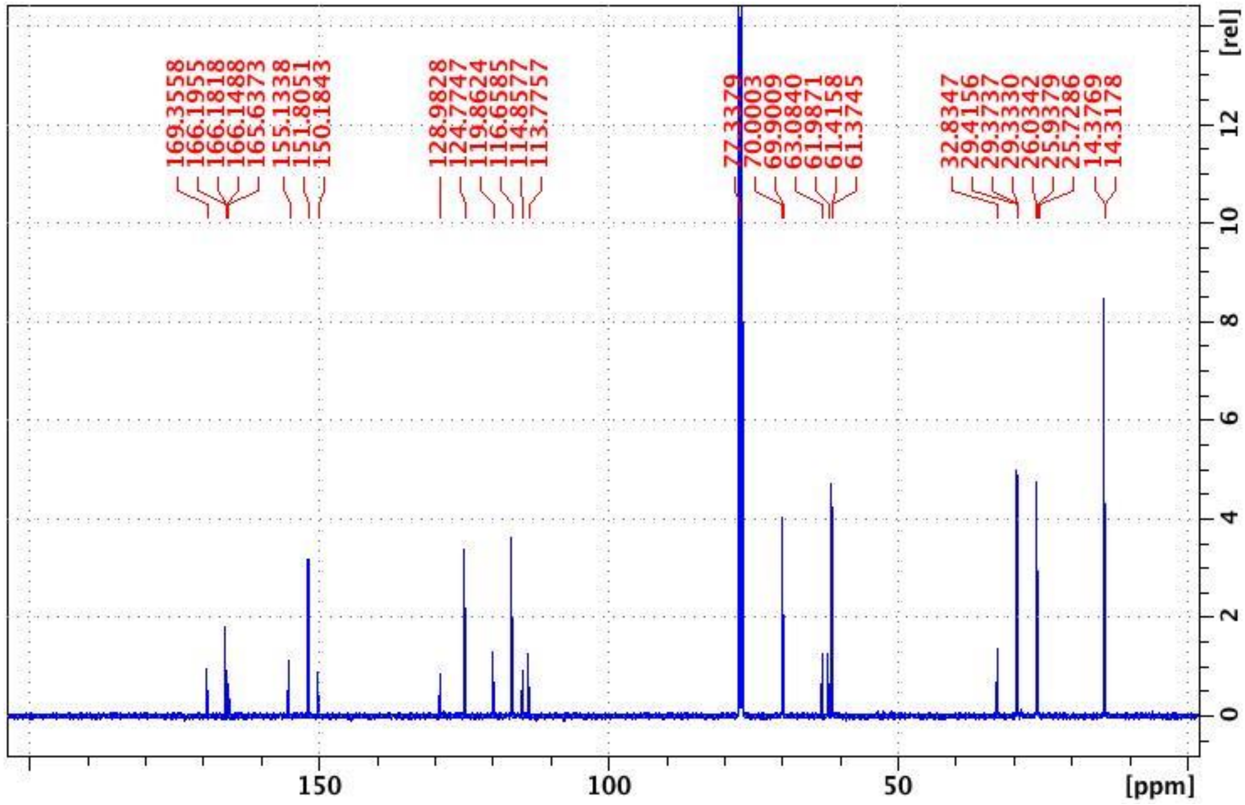


Figure S30. ^{13}C NMR of **L$_4$EtOH**.

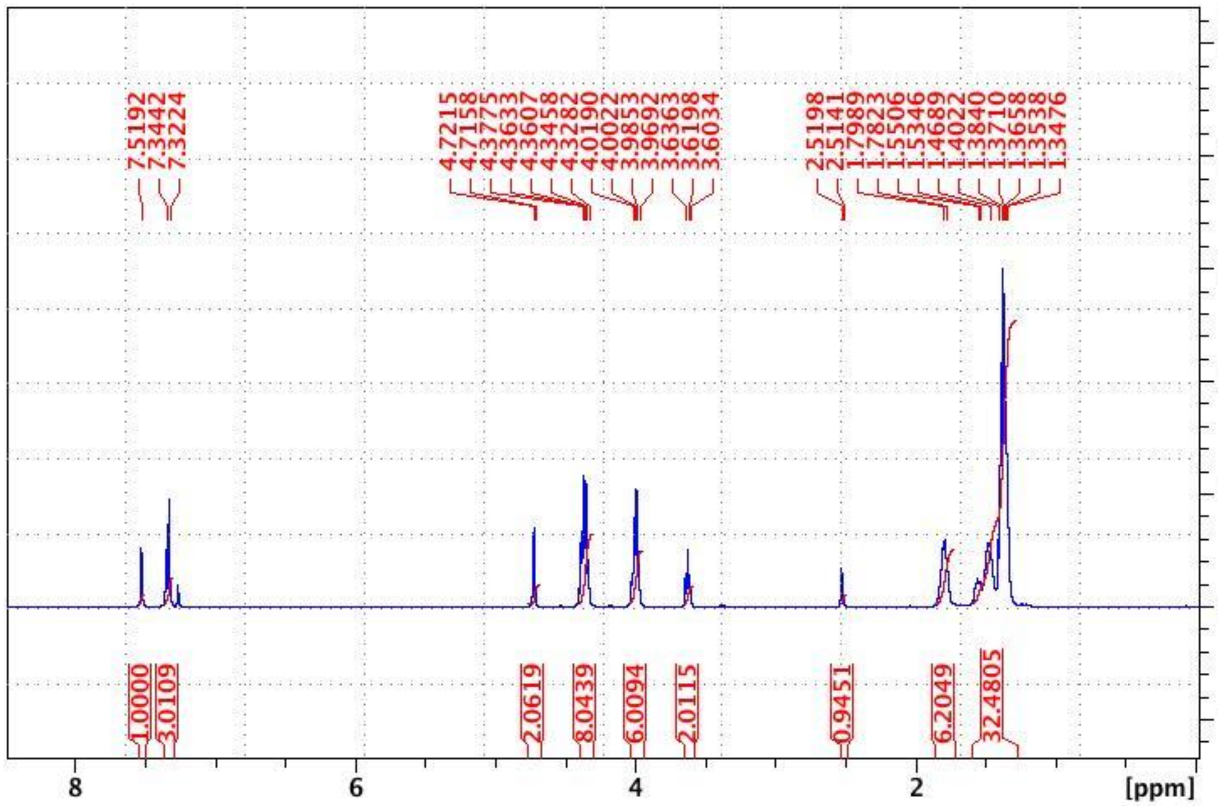


Figure S31. ^{1}H NMR of **L$_2$Et-alkyne**.

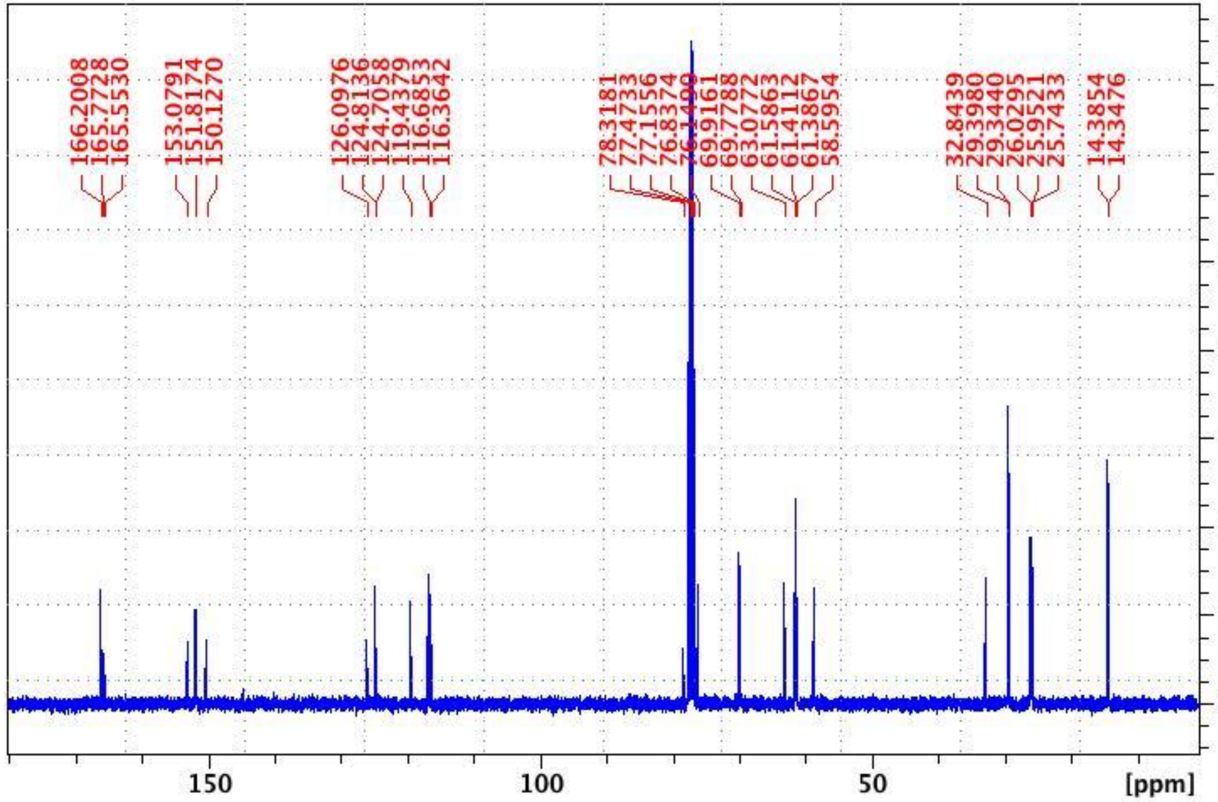


Figure S32. ^{13}C NMR of **L$_2$Et-alkyne**.

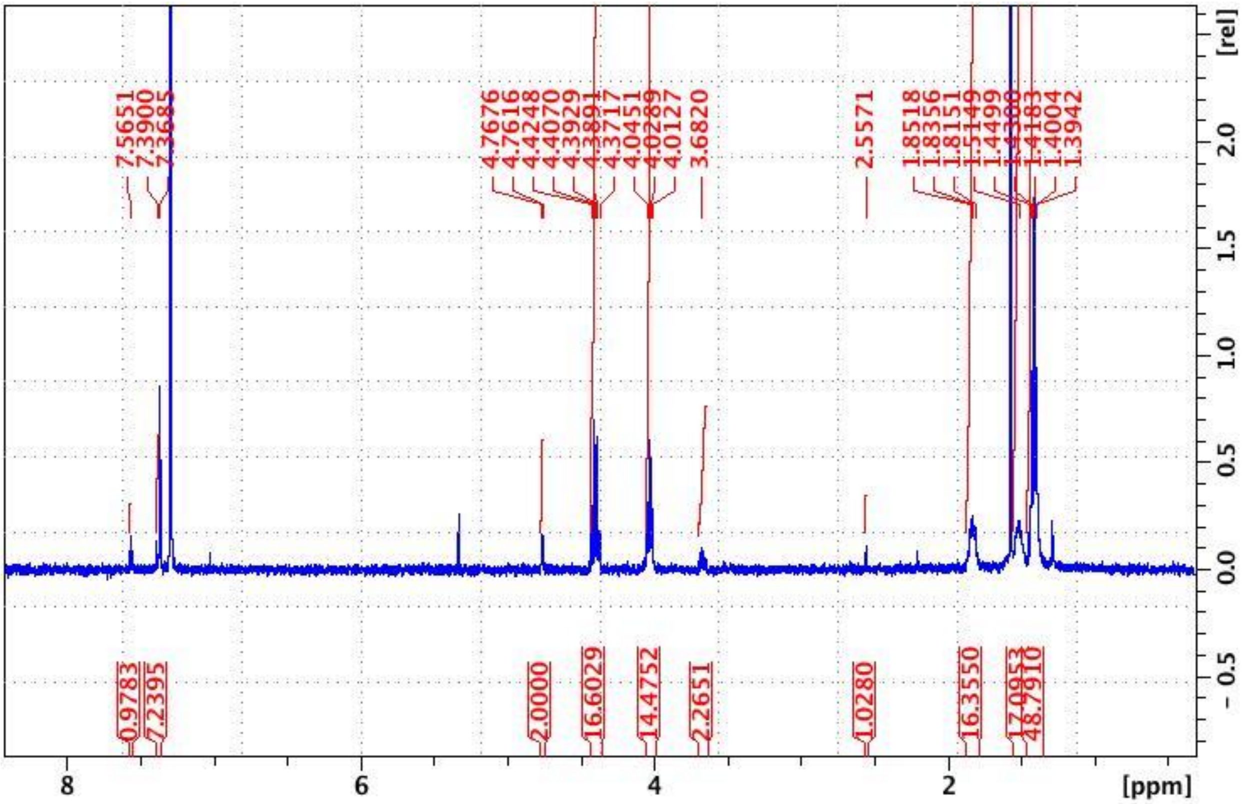


Figure S33. ^{1}H NMR of **L$_4$Et-alkyne**.

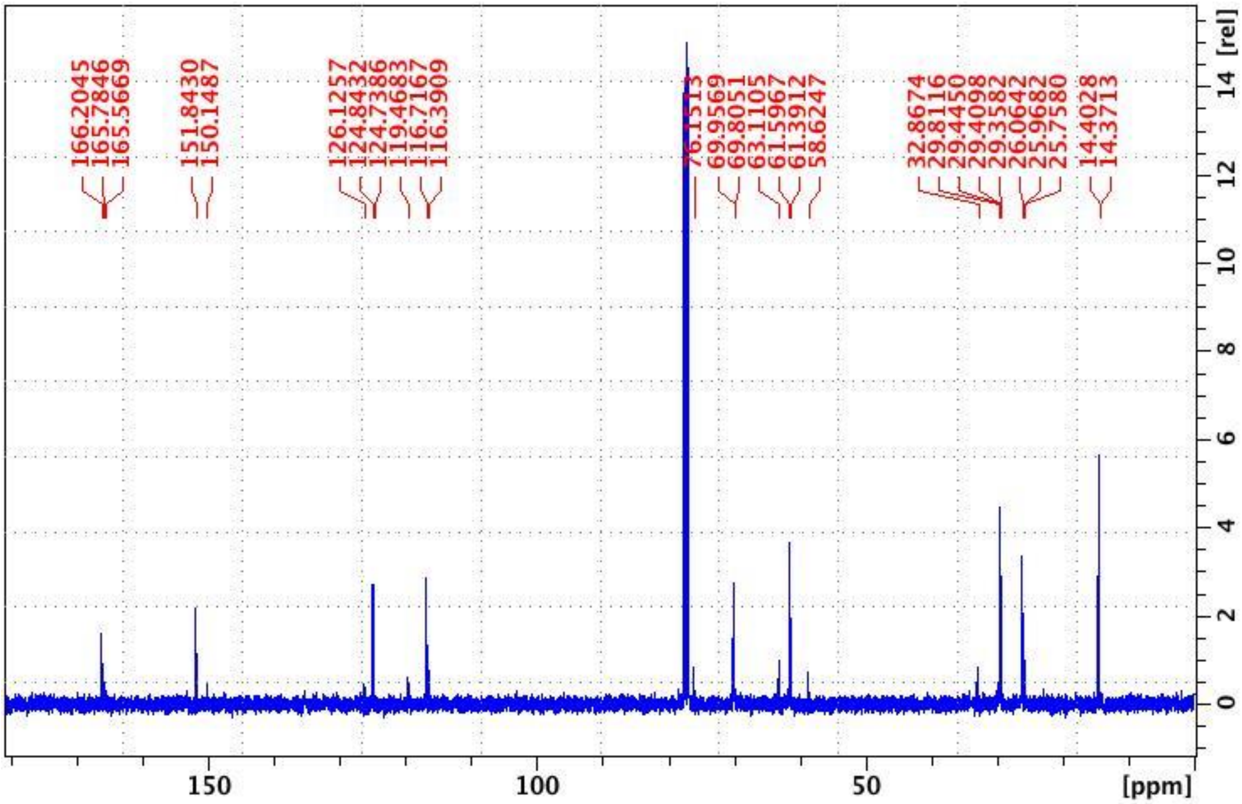


Figure S34. ^{13}C NMR of **L$_4$Et-alkyne**.

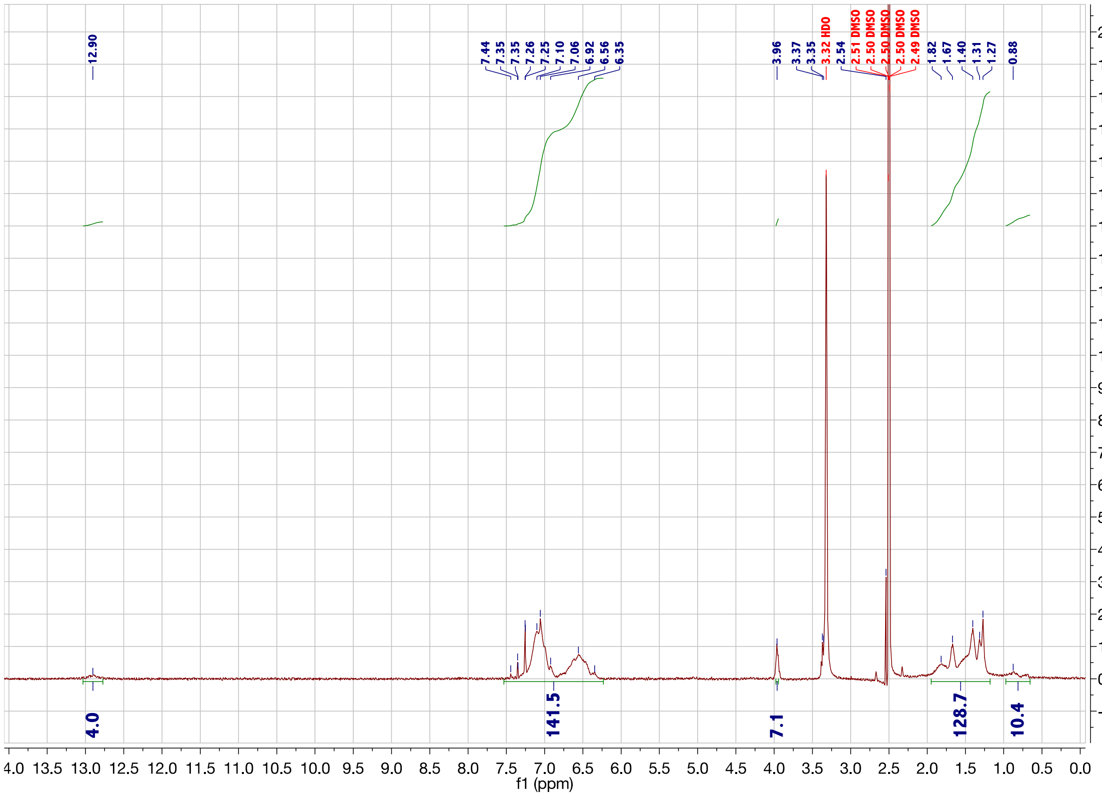


Figure S35. ^{1}H NMR of **L$_2$PS** in d$_6$-DMSO.

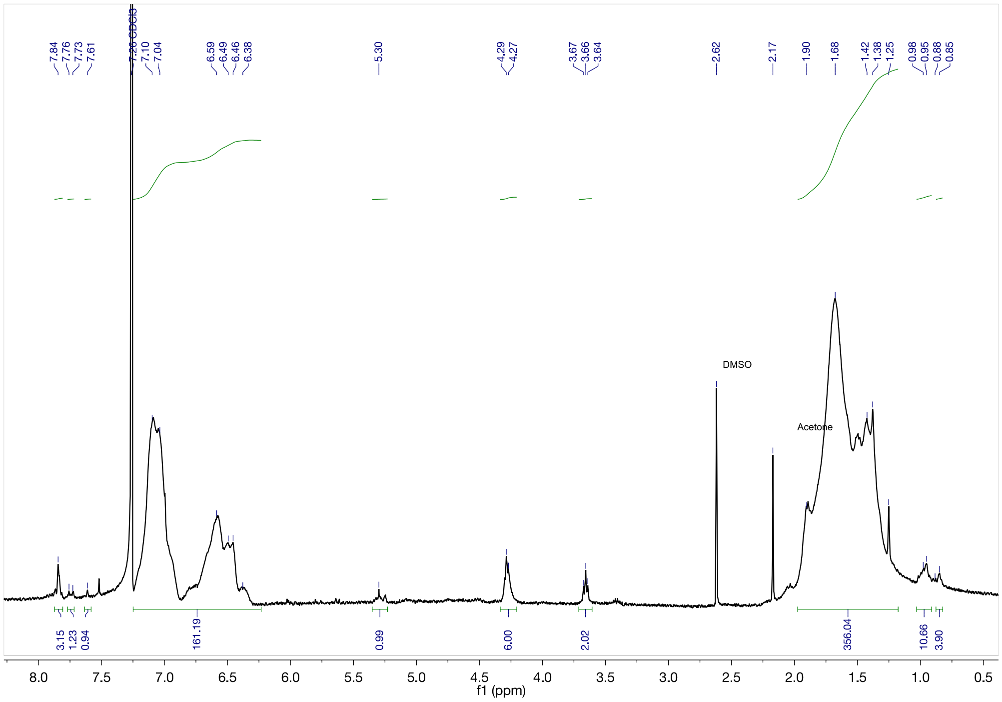


Figure S36. ^{1}H NMR of **L$_2$PS** in CDCl$_3$.

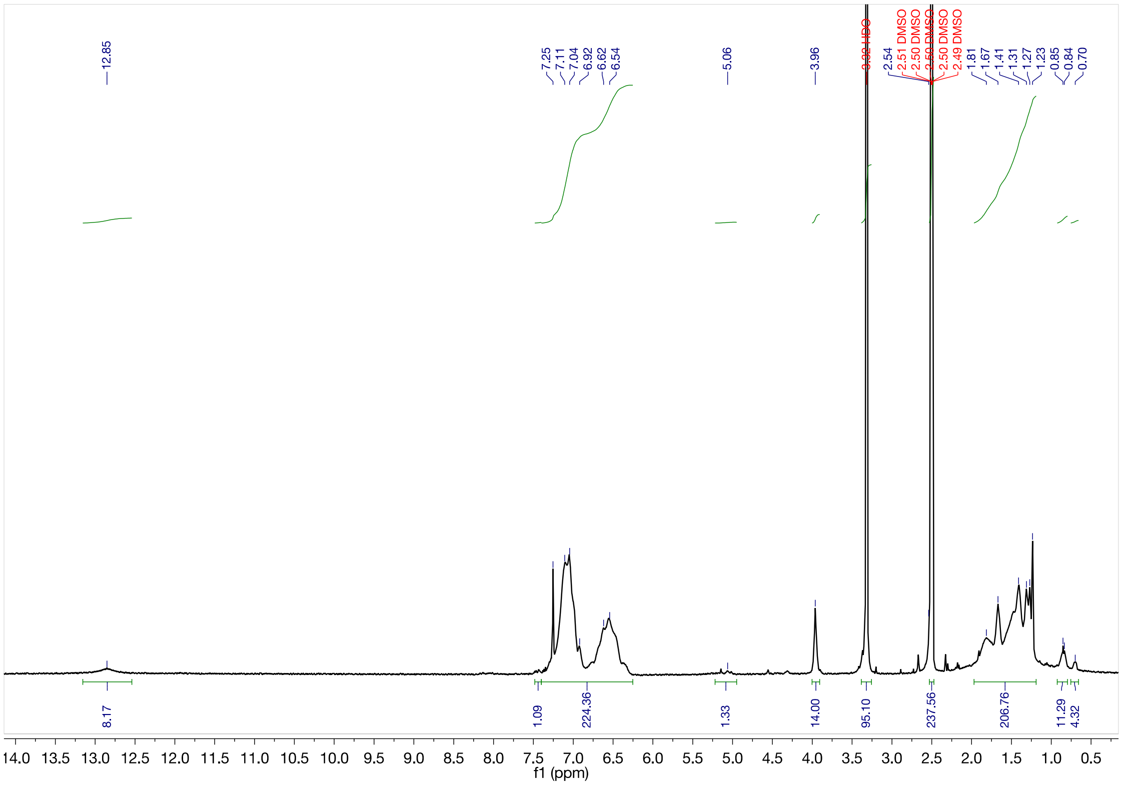


Figure S37. ^{1}H NMR of **L$_4$PS** in d$_6$-DMSO

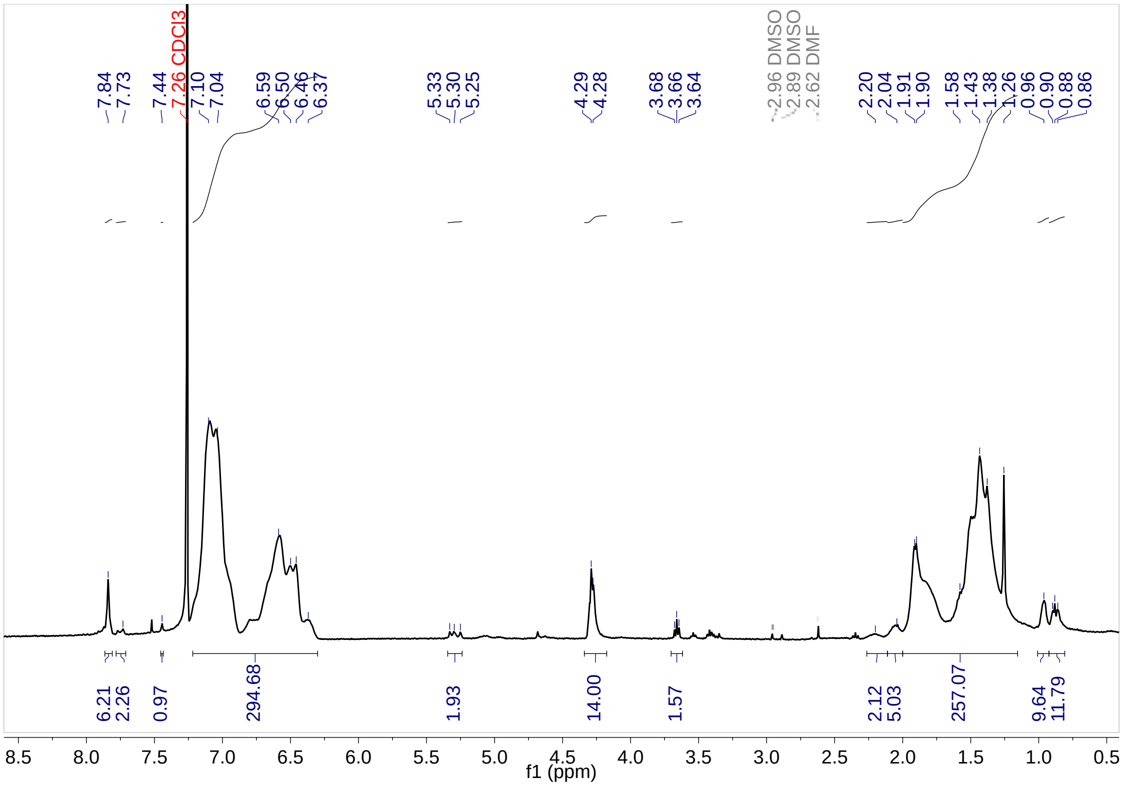


Figure S38. ^{1}H NMR of **L$_4$PS** in CDCl$_3$.

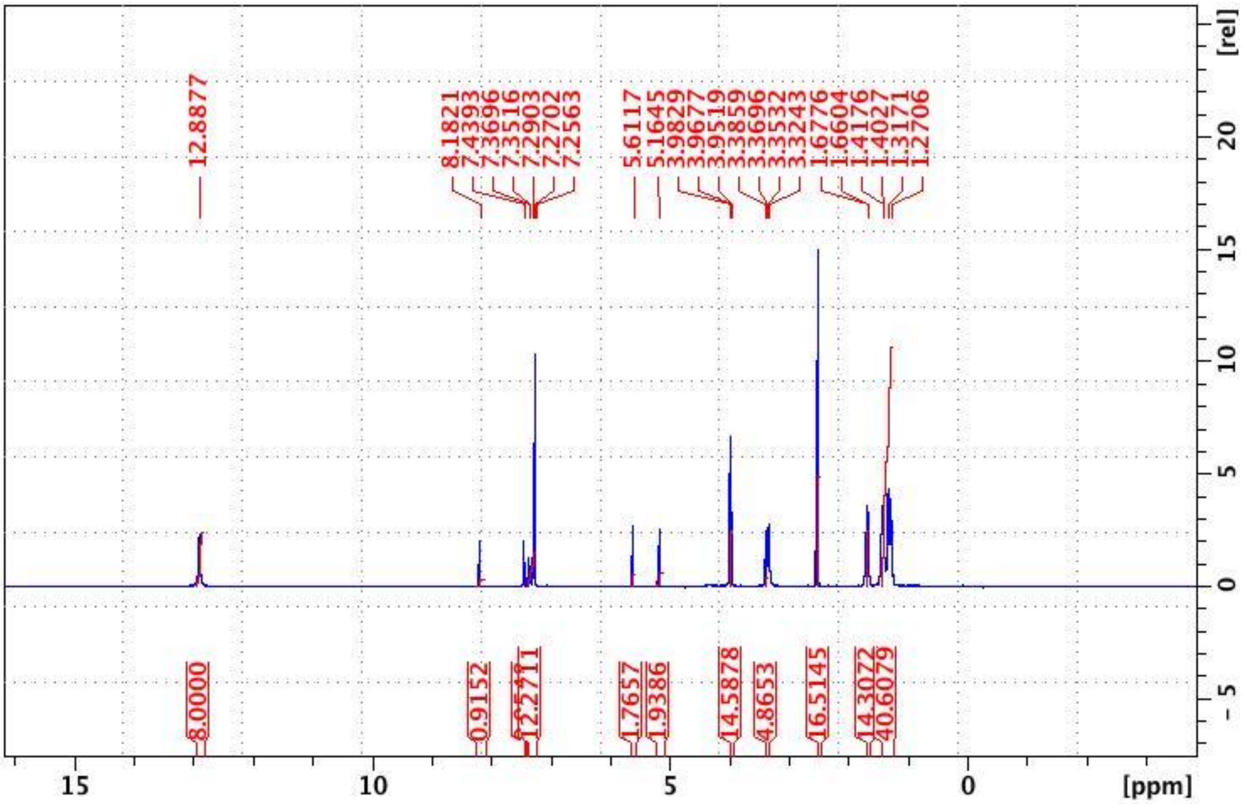


Figure S39. ^{1}H NMR of **L$_4$Bn**.

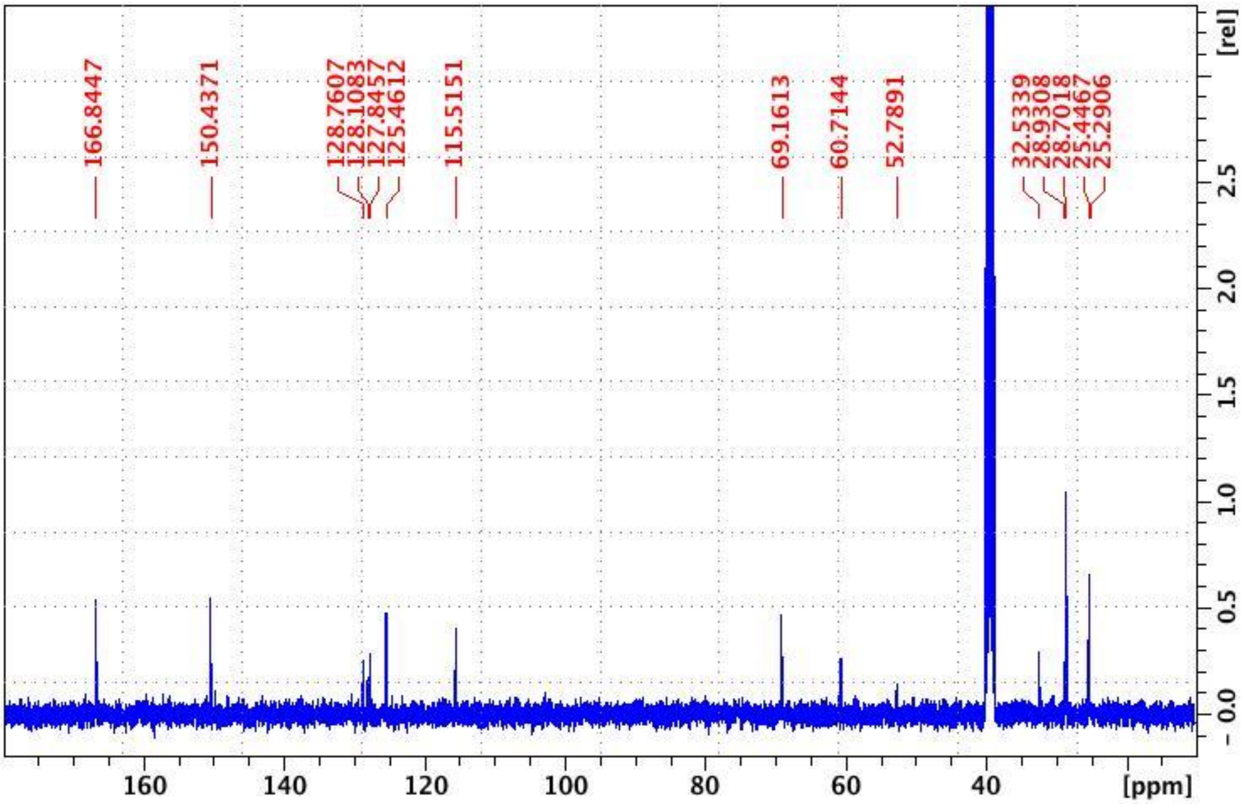


Figure S40. ^{13}C NMR of **L$_4$Bn**.

TGA and DSC data (Note: for DSC trace of **L$_4$PS** see Fig. S4 above)

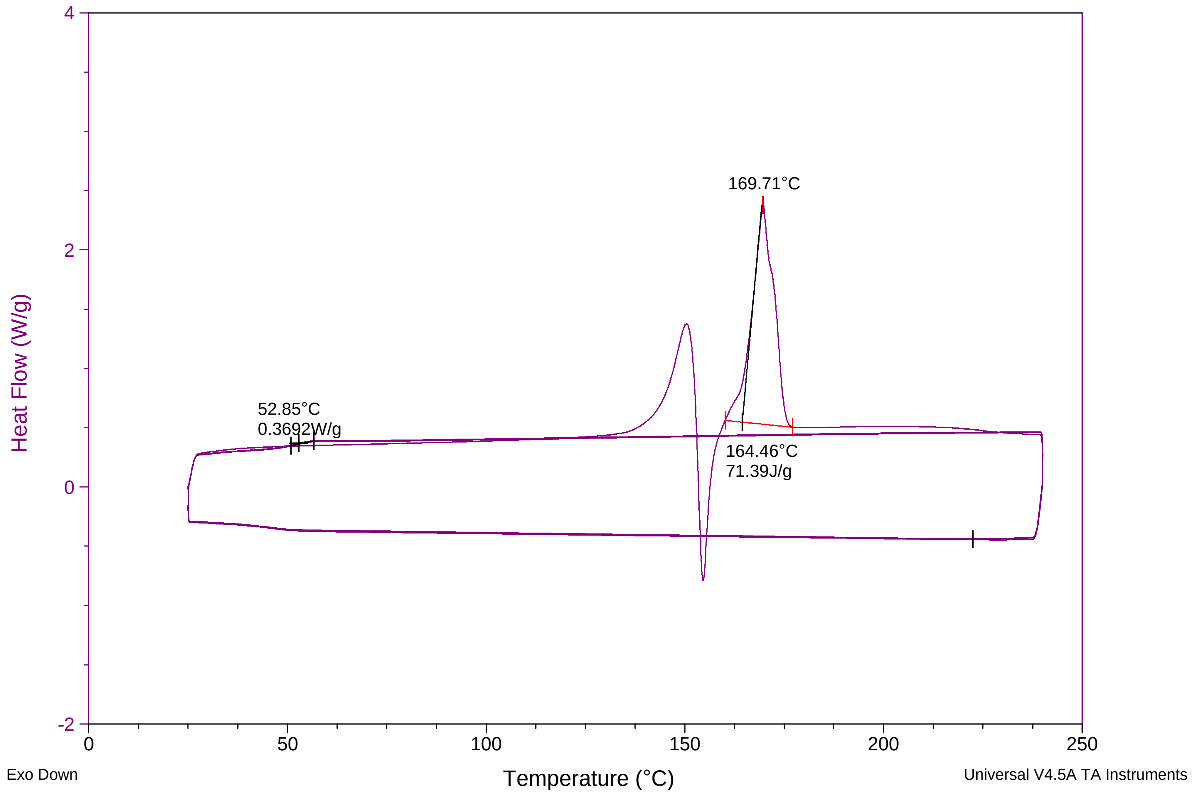


Figure S41. DSC trace of **L$_2$**.

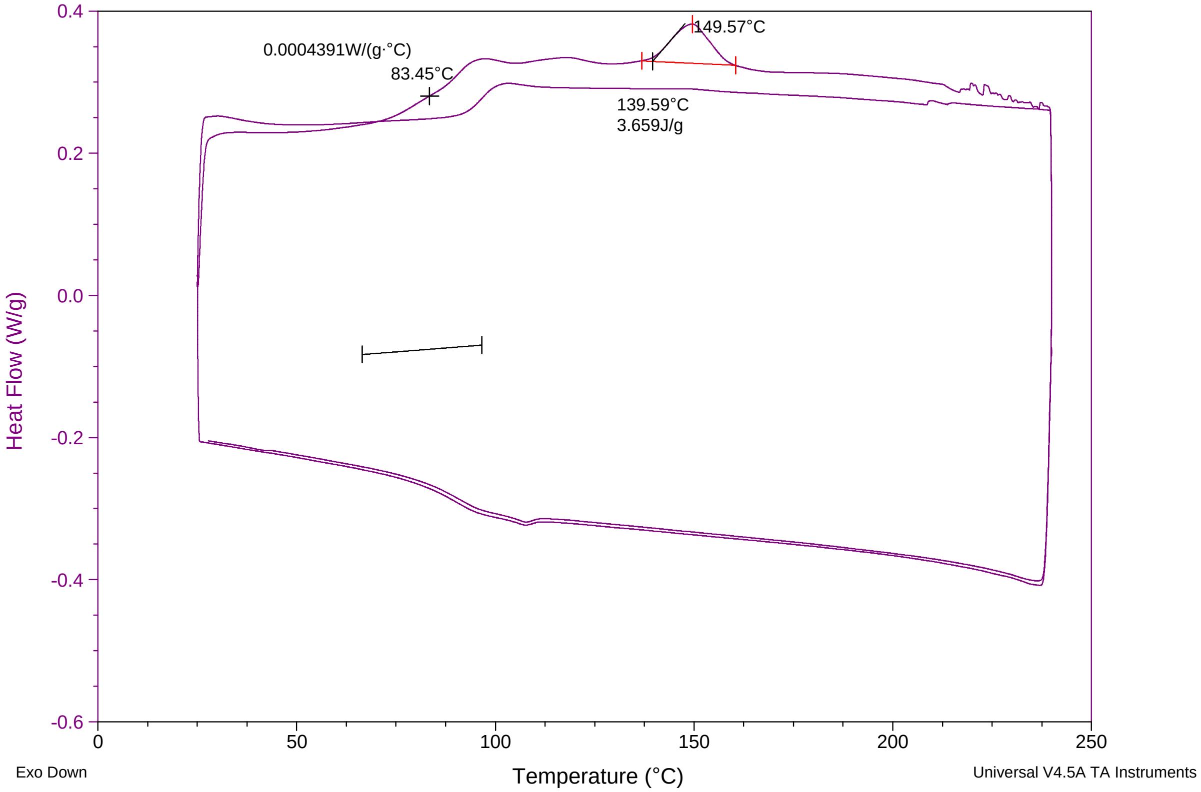


Figure S42. DSC trace of **L$_2$PS**.

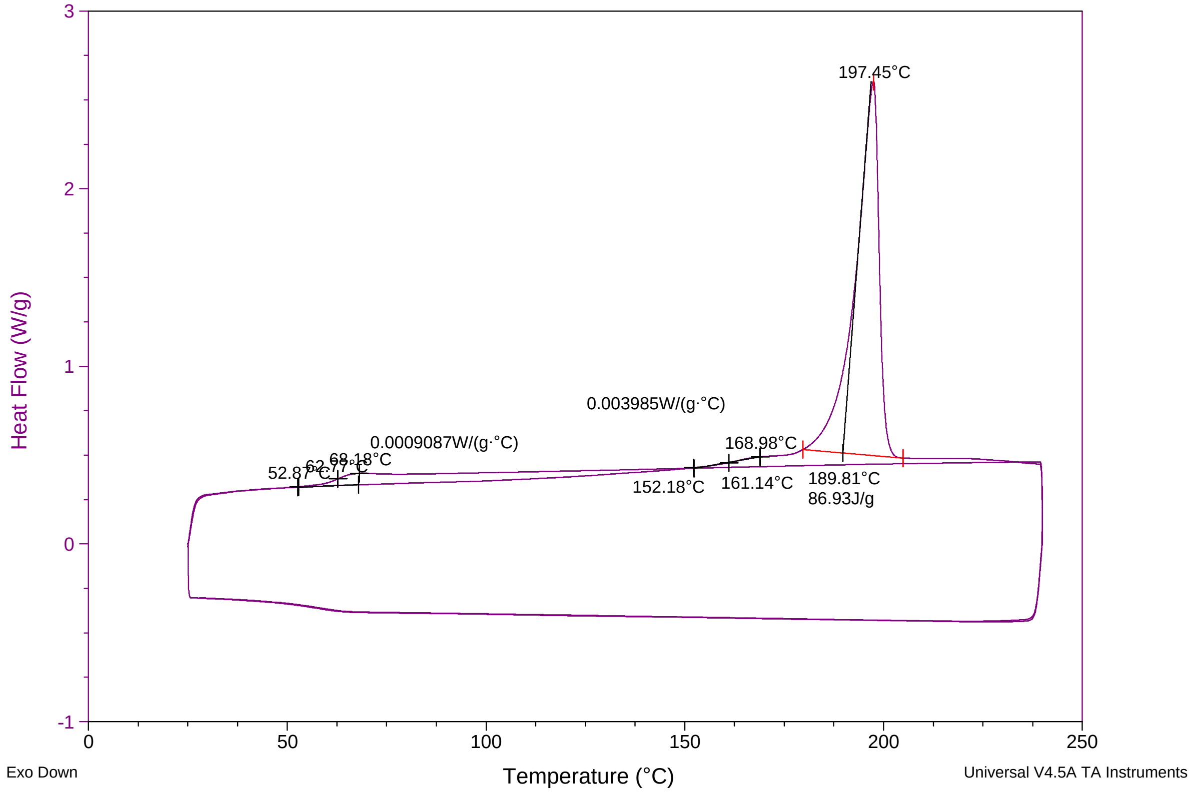


Figure S43. DSC trace of **L$_4$**.

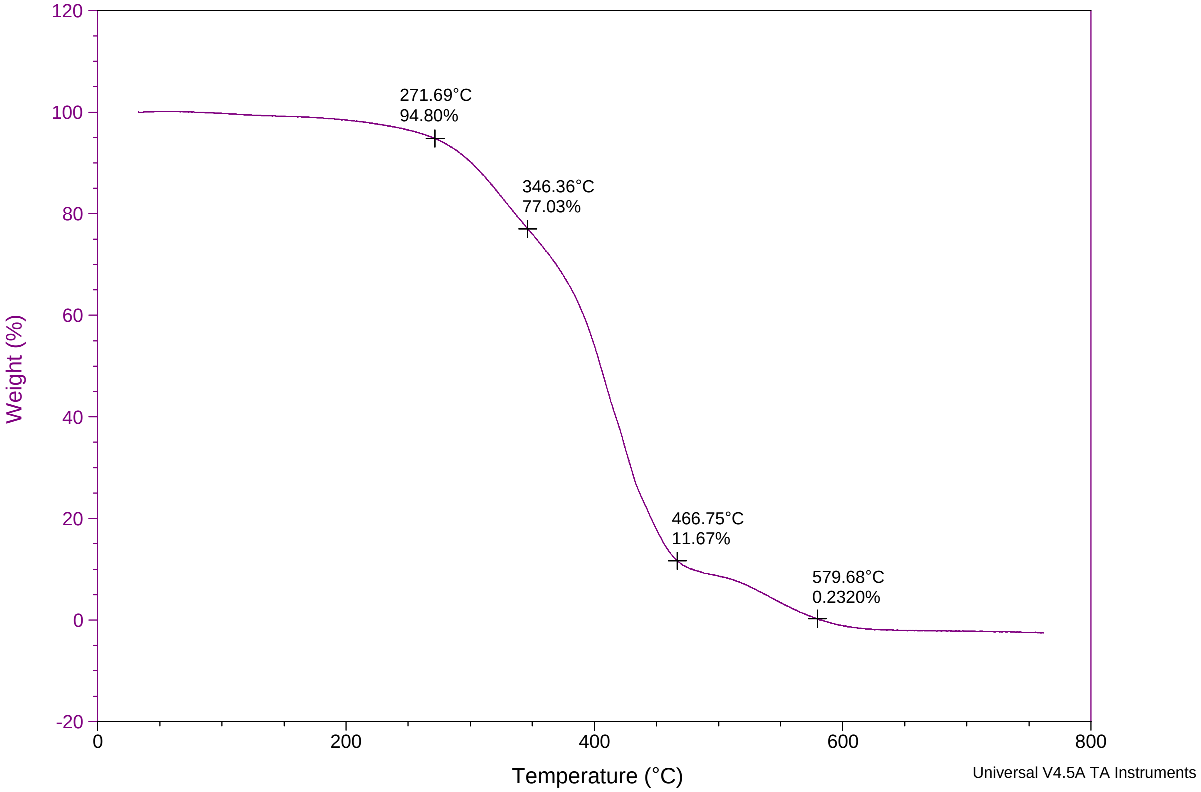


Figure S44. TGA data for **L$_2$**.

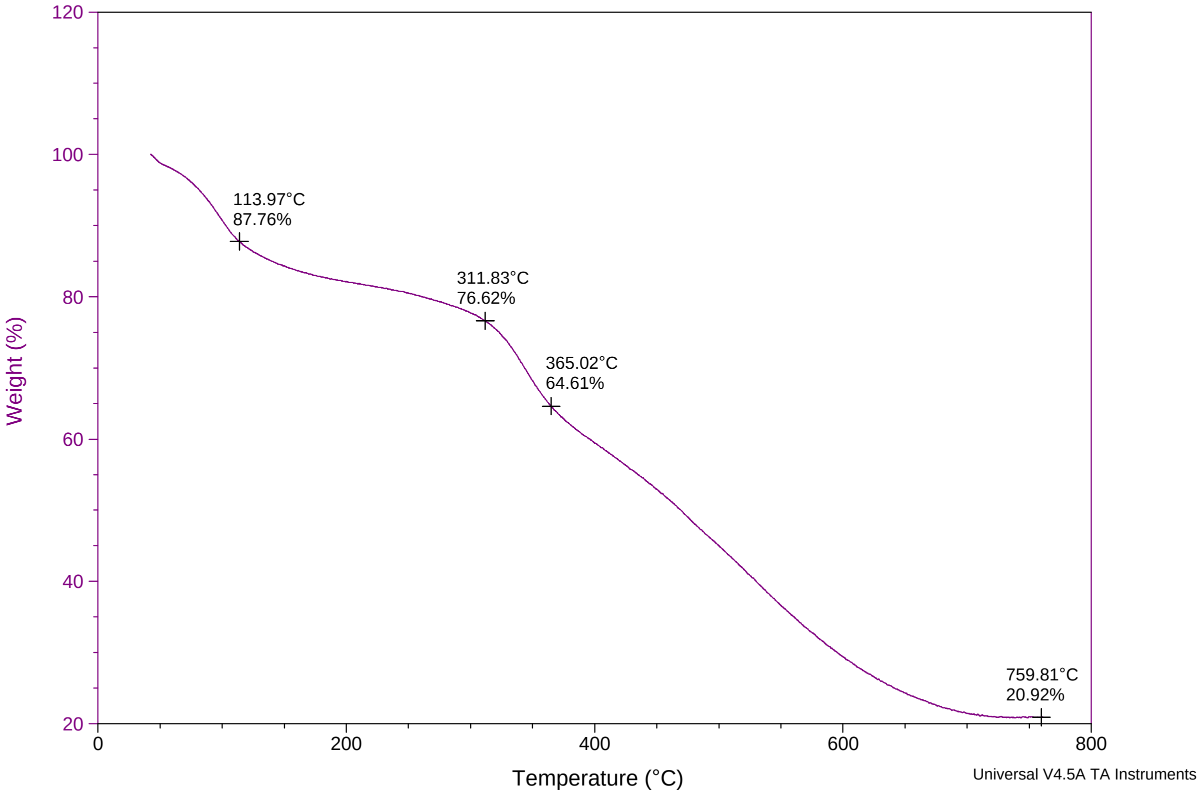


Figure S45. TGA data for **L_2-Zn**.

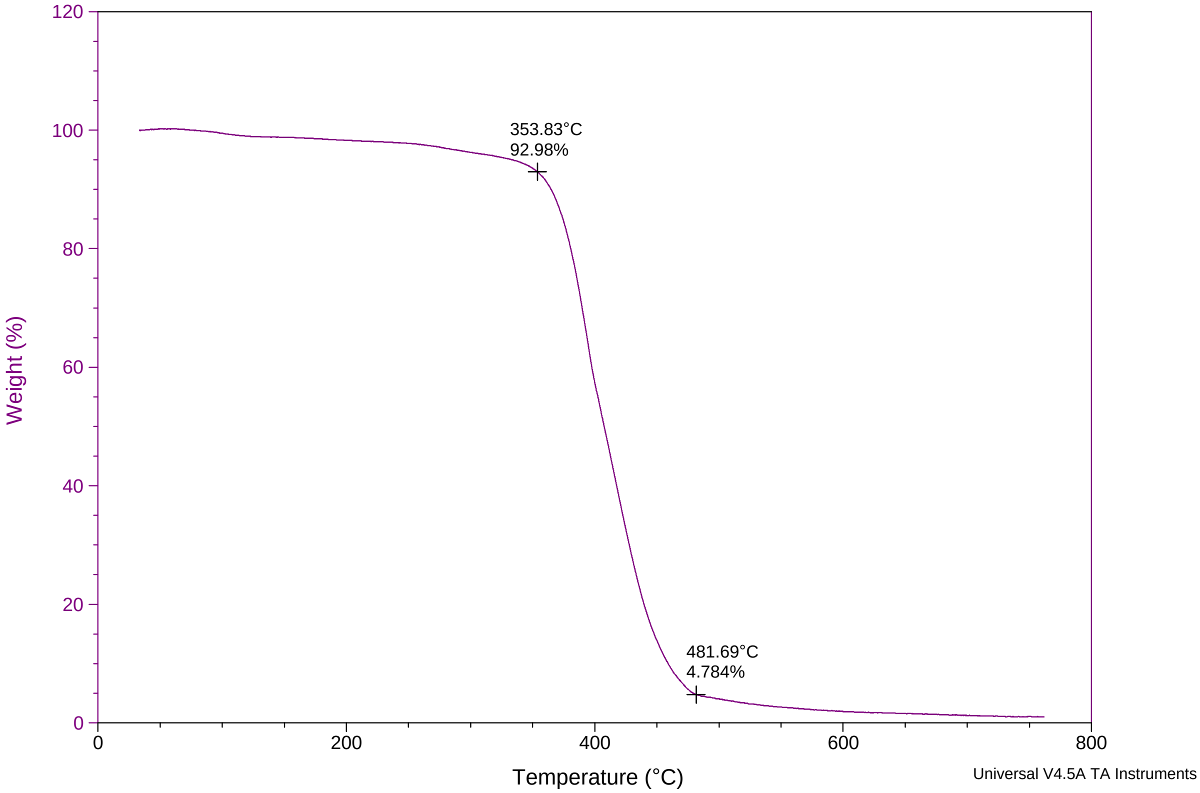


Figure S46. TGA data for **L_2PS**.

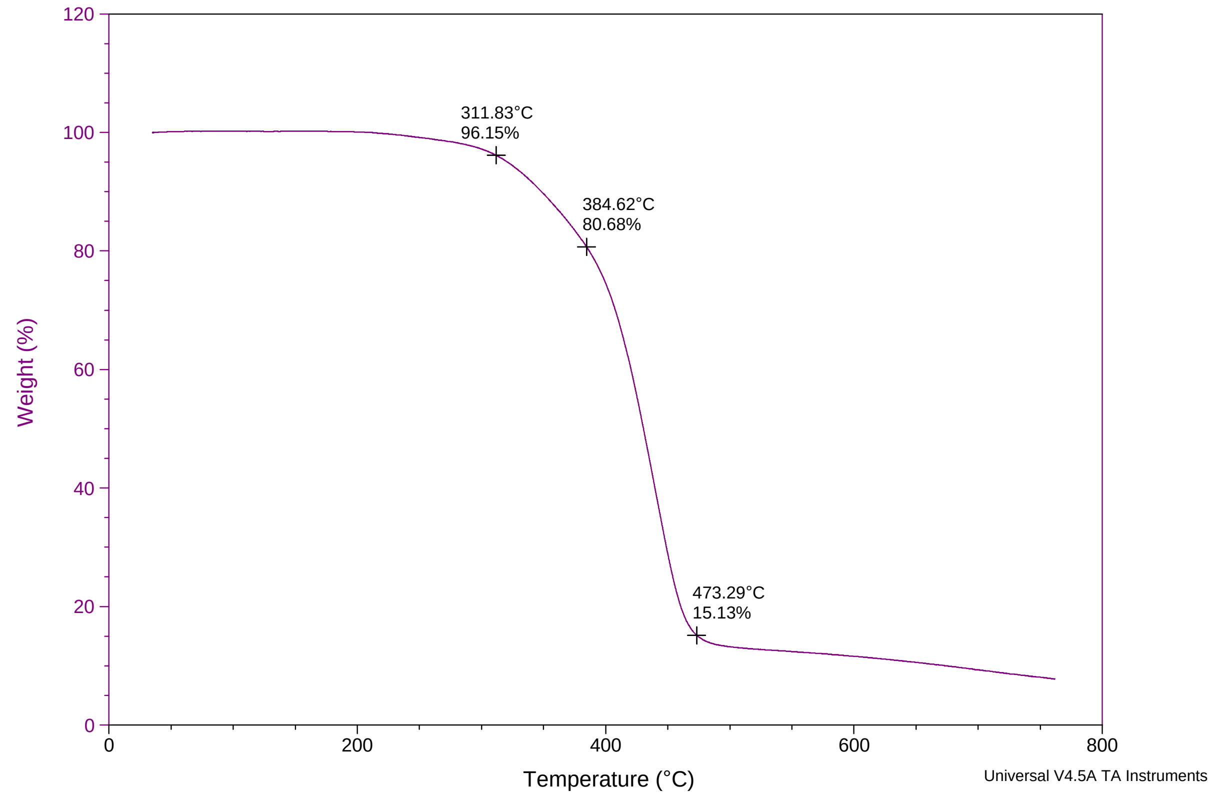


Figure S47. TGA data for **L$_4$**.

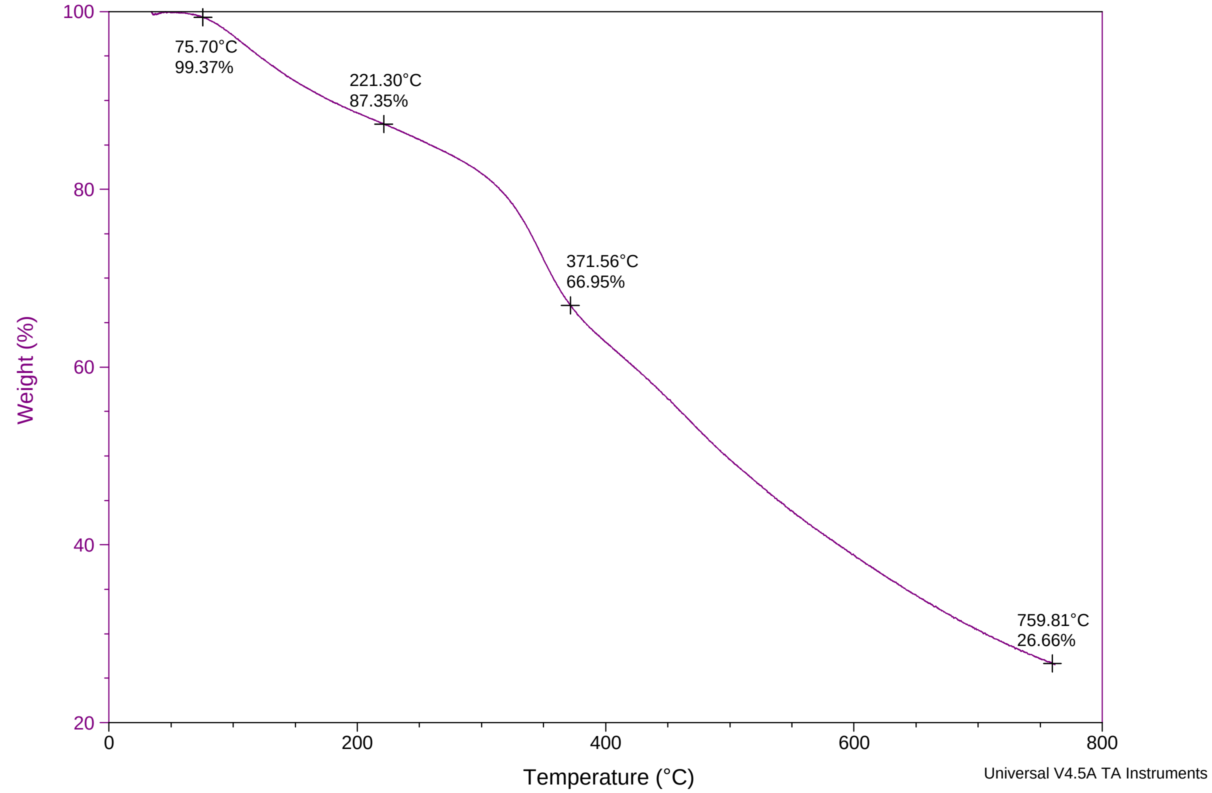


Figure S48. TGA data for **L$_4$-Zn**.

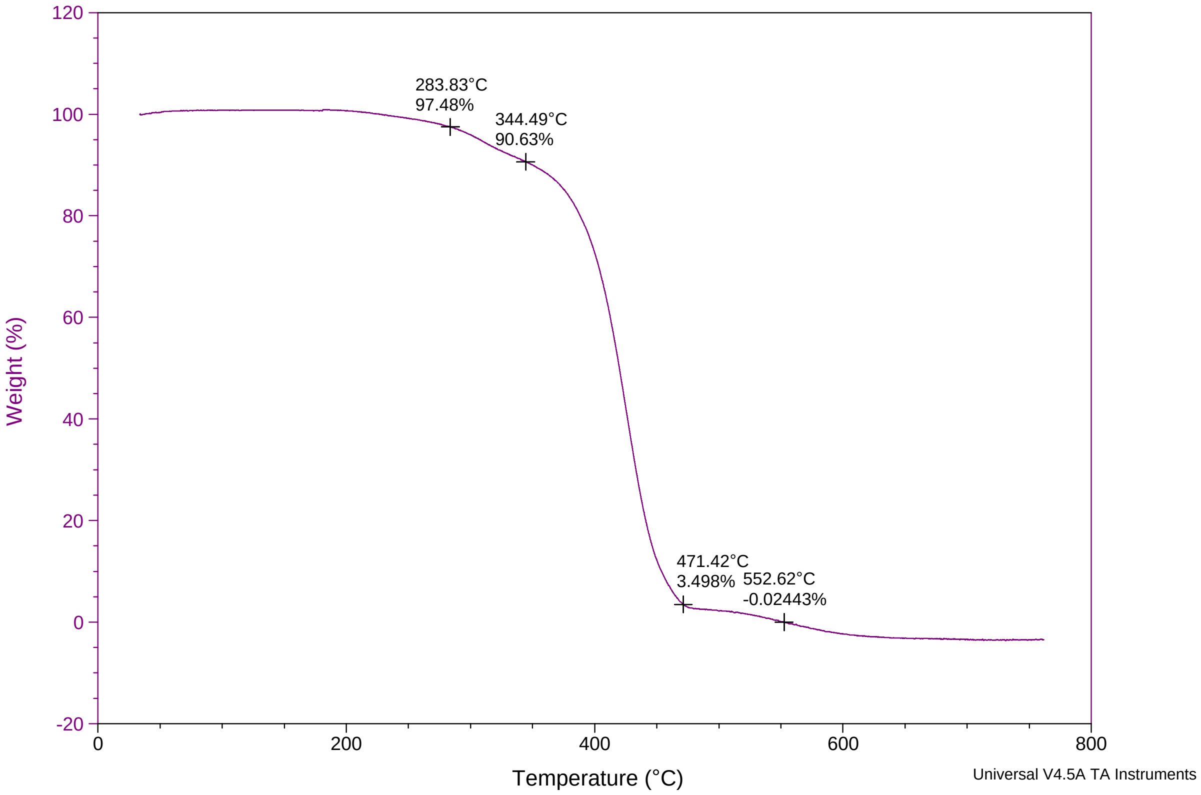


Figure S49. TGA data for **L_4PS**.

Supplemental Reference.

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