Supplementary Information

Supramolecular Templation of Entanglements in Organogels

Erin C. Krist, Benjamin J. Kruse, John C. Dickenson, and Aleksandr V. Zhukhovitskiy*

Department of Chemistry, University of North Carolina at Chapel Hill, 101 South Road, Chapel Hill, NC, 27514, US

*alexzhuk@email.unc.edu

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1. MATERIALS AND METHODS

1.1 Purchased materials

Unless otherwise noted, solvents were used as received from VWR International. Deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. Anhydrous and deoxygenated tetrahydrofuran (THF), dimethyl formamide (DMF), acetonitrile (MeCN), triethylamine (TEA), and dichloromethane (DCM) were purchased from Fisher Scientific and dried with a Pure Process Technologies solvent purification system. 3-bromopropanol, sodium azide, 4-toluenesulfonyl chloride (tosyl-cl), 4-bromoanisole, 1.7 M *tert*-butyllithium (*tert*-BuLi) in hexane, manganese(IV) oxide (MnO_2), pyridine hydrochloride (pyridine-HCl), tris(dibenzylidenacetone)-dipalladium(0) ($Pd_2(dba)_3$), bromobenzene, lithium aluminum hydride (LAH_4), bromine (Br_2), sodium bisulfate, N-hydroxysuccinimide, methanesulfonyl chloride (mesyl-Cl), N-methyl pyrrolidinone, potassium cyanide (KCN) and propylene carbonate were purchased from Sigma-Aldrich and used without further purification. Dibenzosuberenone, hydroxylammonium chloride, Eaton's reagent, potassium *tert*-butoxide (KOtBu), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC HCl), magnesium sulfate ($MgSO_4$), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), ammonium chloride (NH_4Cl), sodium bicarbonate ($NaHCO_3$), and hydrochloric acid (HCl) were purchased from Fisher Scientific and used as received. 1,10-phenanthroline, cesium carbonate (Cs_2CO_3), 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,2,3-dioxaborolane, and 4-dimethylaminopyridine (DMAP) were purchased from Oakwood Chemical and used as received. Tetrakis(acetonitrile) copper(I) tetrafluroborate ($Cu(MeCN)_4BF_4$) and tricyclohexylphosphine (PCy_3) were purchased and used as received from Tokyo Chemical Industry. 4,7-dichloro-1,10-phenanthroline was purchased from Ambeed and used as received. Potassium phosphate tribasic (K_3PO_4) was purchased from Alfa Aesar and used as received. 4-arm polyethylene glycol-OH (5k MW) was purchased from Jen Kem Technology and polyethylene glycol-OH (2K MW) was purchased from Sigma-Aldrich. Basic aluminum oxide and celite were purchased from Acros. Silica-gel was from SiliCycle, Inc.

1.2 Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H and ^{13}C NMR spectra were recorded on Bruker NMR spectrometers operating at 400, 500, and 600 MHz for ^1H (100, 125, and 150 MHz for ^{13}C, respectively). These instrument models are listed with the corresponding federal grant numbers: Bruker AVANCE III Nanobay 400 MHz (NSF Grant No. CHE-0922858), Bruker AVANCE III 500 MHZ (NSF Grant No. CHE-0922858), Bruker AVANCE III 600 MHz (NSF Grant No. CHE-0922858), and Bruker AVANCE NEO 500 MHz (NSF Grant No. CHE-1828183). Chemical shifts are reported in parts per million (ppm), and splitting patterns are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), sextet (sext), septet (sept), octet (oct), multiplet (m), broad (b), and combinations thereof. Scalar coupling constants *J* are reported in Hertz (Hz). Spectra were processed and analyzed using MestReNova v14.3.0-30573. The presented spectra are referenced to residual monoproteo-solvent peaks as reported in the literature.[1]

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

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR)
Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) spectra were acquired of solids, liquids, and oils with a Thermo Scientific Nicolet iS5 FTIR spectrometer with an ATR accessory over 32 scans. Thirty-two background scans were performed before each sample was analyzed. Data was collected and baseline-corrected using Thermo Scientific OMNIC software.

Analytical Gel Permeation Chromatography (GPC)
Analytical gel permeation chromatography (GPC) was conducted on an Agilent Technologies 1260 Infinity II instrument equipped with two PL-gel 10 μm mixed-B columns connected in series, with HPLC-grade THF stabilized with butylated hydroxytolune (BHT) as the mobile phase at 35 °C, a Wyatt Technologies DAWN multi-angle light scattering (MALS, 8 angles) detector (λ = 658 nm), a Wyatt Technologies ViscoStar differential viscometer, and a Wyatt Technologies Optilab T-rEX differential refractometer. Samples were prepared by dissolving the polymer at a concentration of 2 mg/mL for the 4-arm PEG and 3 mg/mL for the linear PEG in the same THF used in the mobile phase, followed by filtration through a 0.22 μm PTFE syringe filter. The *dn/dc* value of each PEG sample was calculated using a 100% mass recovery method.

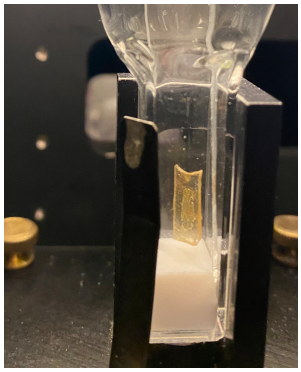
Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
Inductively coupled plasma mass spectrometry was operated in standard mode, and all operating parameters were optimized to meet requirements as defined by the manufacturer prior to method calibration and analysis. Calibration curves were constructed using a zero-point standard and a six-point calibration curve in a range 25 to 500 ppb. Quantification was performed by Ge as an internal standard. The samples were digested in 70% nitric acid at 70 °C overnight and diluted in 2% nitric acid solution. Dilution was adjusted so the samples' measured concentration was in the calibration curve.

Parallel-Plate Oscillatory Rheometry
Parallel-plate oscillatory rheometry measurements were performed with a TA Instruments Discovery HR equipped with 8 mm parallel plates. For measuring shear modulus of the

organogels, the materials were punched to make discs 8 mm in diameter. The axial force of the measurements was set to 0.75 N.

Steady-state Fluorimetry

Steady-state fluorescence spectra were recorded on a Horiba Fluorolog 3 fluorimeter and corrected by calibration with a standard tungsten-halogen lamp. The intensity was integrated for 0.1 s at 1 nm resolution and averaged over 3 scans. Excitation and emission slit widths were adjusted to obtain maximum signal without overloading the detector. For the emission spectra of organogel samples, a piece of organogel large enough to encompass the excitation beam was synthesized and placed on a glass microscope slide (pictured below). The slide was affixed within a 1 cm glass cuvette at a 45° angle using a Teflon block on the diagonal. The side of the slide with the organogel was arranged to face the excitation beam and detector to reduce excitation source scatter pictured below. The excitation wavelength used was 365 nm.



Dynamic Mechanical Analysis – Uniaxial Tensile Tests

Uniaxial tensile stress-strain tests were conducted using dynamic mechanical analysis (RSA-G2, TA Instruments). The organogels were cut into dog bone-shaped samples with a punch DIN 53504-S3, 2 mm in width with an initial length of 12 mm. The uniaxial deformation was carried out with a strain rate of 0.01 s^{-1} at room temperature. The engineering strain (ε) was calculated from the gap change divided by the initial length. The true stress (σ) was calculated from the stretching force divided by the cross-section area, equal to the cross-section area of the undeformed sample multiplied by 1+ ε. Young's modulus was determined by linear fitting of the stress-strain curves below 1% strain. Toughness was calculated by integrating the area under stress-strain curves.

1.3 General experimental information

All air sensitive reactions were carried out in flame- or oven-dried glassware in a nitrogen-filled glove box or using standard Schlenk techniques. Reaction mixtures were stirred via Teflon-coated magnetic stir bars. Reactions were monitored via NMR and thin layer chromatography (TLC), and the TLC plates were visualized either under UV irradiation or through standard staining procedures. Removal of solvents *in vacuo* was accomplished using an IKA rotary evaporator and a Schlenk line (~12–50 mTorr, dynamic vacuum). Purification via flash chromatography was carried out following standard procedures. Volumes smaller than 1 mL were transferred with Hamilton gas-tight syringes, which were washed after transfer with solvents appropriate for the reaction, then with acetone and dichloromethane.

1.4 Swelling ratio test

A piece of the organogels was weighed and then soaked in 15 mL of propylene carbonate in a 20-mL vial until the mass no longer changed (120 hours). The materials were then subjected to 15 mL of DCM in a 20 mL vial. The DCM solution was switched out two times for a total of 3 DCM washes in 4.5 hours. The materials were placed in clean 20 mL vials, after which they were dried under reduced pressure at room temperature until the mass no longer changed (66 hours) and the weight recorded. The swelling ratio (SR) is calculated by:

$$SR = \frac{W_t}{W_0}$$

Where W_t is the weight after swelling, and W_0 is the weight of the network after solvent removal.

1.5 Estimation of storage modulus using phantom network theory

The storage modulus (G') can be expressed from the phantom network theory:

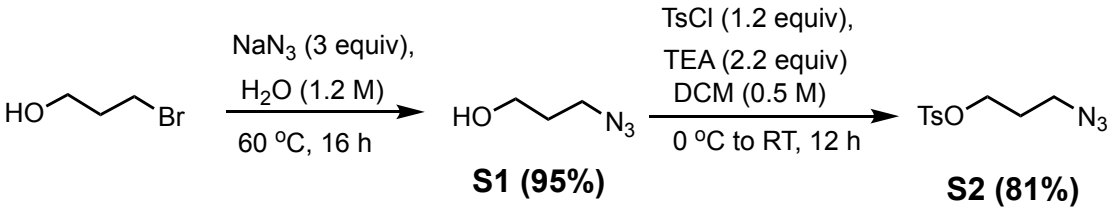
$$G' = \frac{\rho RT}{M_c}\frac{f-2}{f},$$

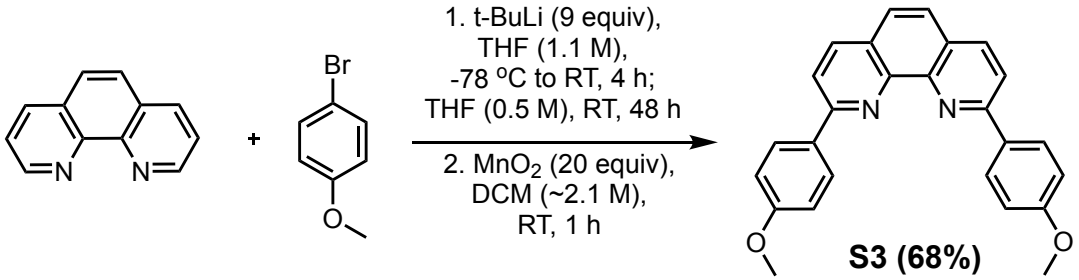
where ρ is the density of elastic chains, R is the ideal gas constant, T is temperature in Kelvin, M_c is the molecular weight between cross-links, and f is branch functionality. In an ideal network for our system swelled to a comparable amount, $\rho = 0.132\,\frac{g}{cm^3}$, $T = 298\ K$, $M_c = 1300\,\frac{g}{mol}$, and $f = 4$, resulting in $G' = 126\ kPa$.

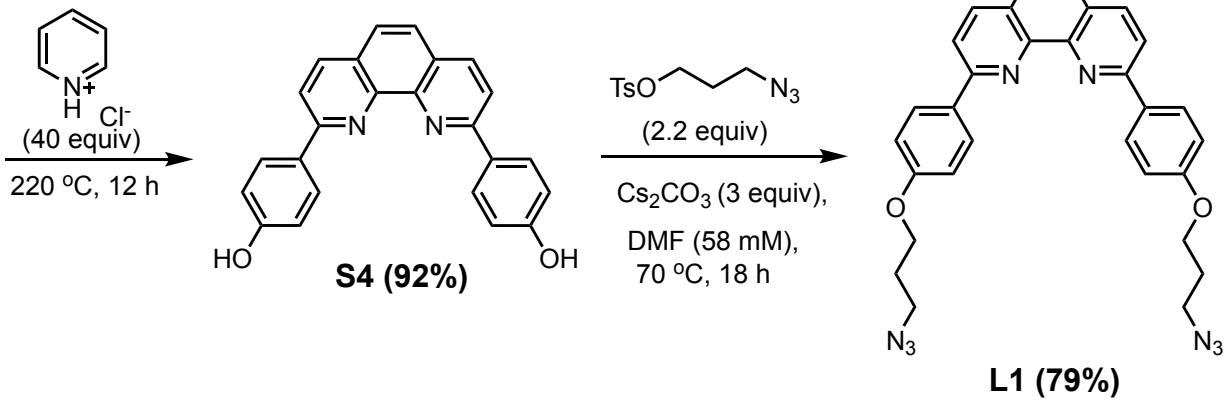
2. EXPERIMENTAL PROCEDURES

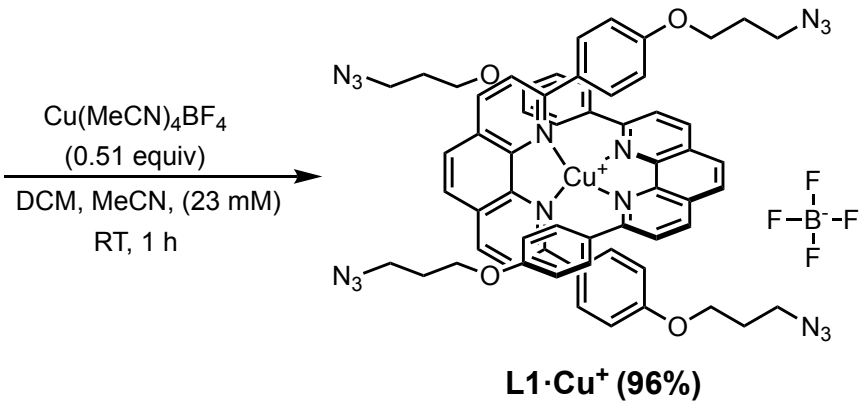
2.1 Synthesis of crosslinkers

2.1.1 Synthesis of L1·Cu$^+$









3-azidopropan-1-ol (**Compound S1)**: Compound **S1** was prepared following reported methods.[2] 3-bromopropanol (10.0 g, 6.51 mL, 1.00 equiv, 71.9 mmol), 55 mL DI water, and sodium azide (14.0 g, 3.00 equiv, 216 mmol) were added to a 200 mL RBF with stir bar under ambient conditions. The reaction was stirred at 60 °C for 16 hours. The reaction mixture was cooled to room temperature and extracted twice with diethyl ether. The organic layers were dried over $MgSO_4$ and the solvent was removed via rotary evaporation. The product was purified via silica gel chromatography (pentane:diethyl ether 1:1, R_f = 0.33), and the solvent was again removed via rotary evaporation, resulting in the product as a colorless oil (6.9 g, 95%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[2]

3-azidopropyl 4-methylbenzenesulfonate (Compound S2): Compound **S2** was prepared following reported methods.[3] In a flame-dried 250 mL three-neck round-bottom flask, 3-azidopropanol (6.00 g, 5.48 mL, 1.00 equiv, 59.3 mmol) and triethylamine (13.2 g, 18.2 mL, 2.20 equiv, 131 mmol) were added with 60 mL of dry DCM, and the flask was cooled in an ice water bath to 0 °C. Tosyl-Cl (13.6 g, 1.20 equiv, 71.2 mmol) was dissolved in 40 mL of DCM and added to the mixture dropwise over 15 minutes. The reaction was allowed to warm to room temperature and was stirred overnight. The reaction mixture was then washed with 1 M NH_4Cl (40 mL) twice and once with water (40 mL). The solvent was removed via rotary evaporator and purified by silica gel chromatography (hexane/ethyl acetate 3:1, R_f = 0.64). The solvent was removed via rotary evaporator and the liquid was sparged to remove solvent, resulting in the product as a yellow oil (12.3 g, 81%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[3]

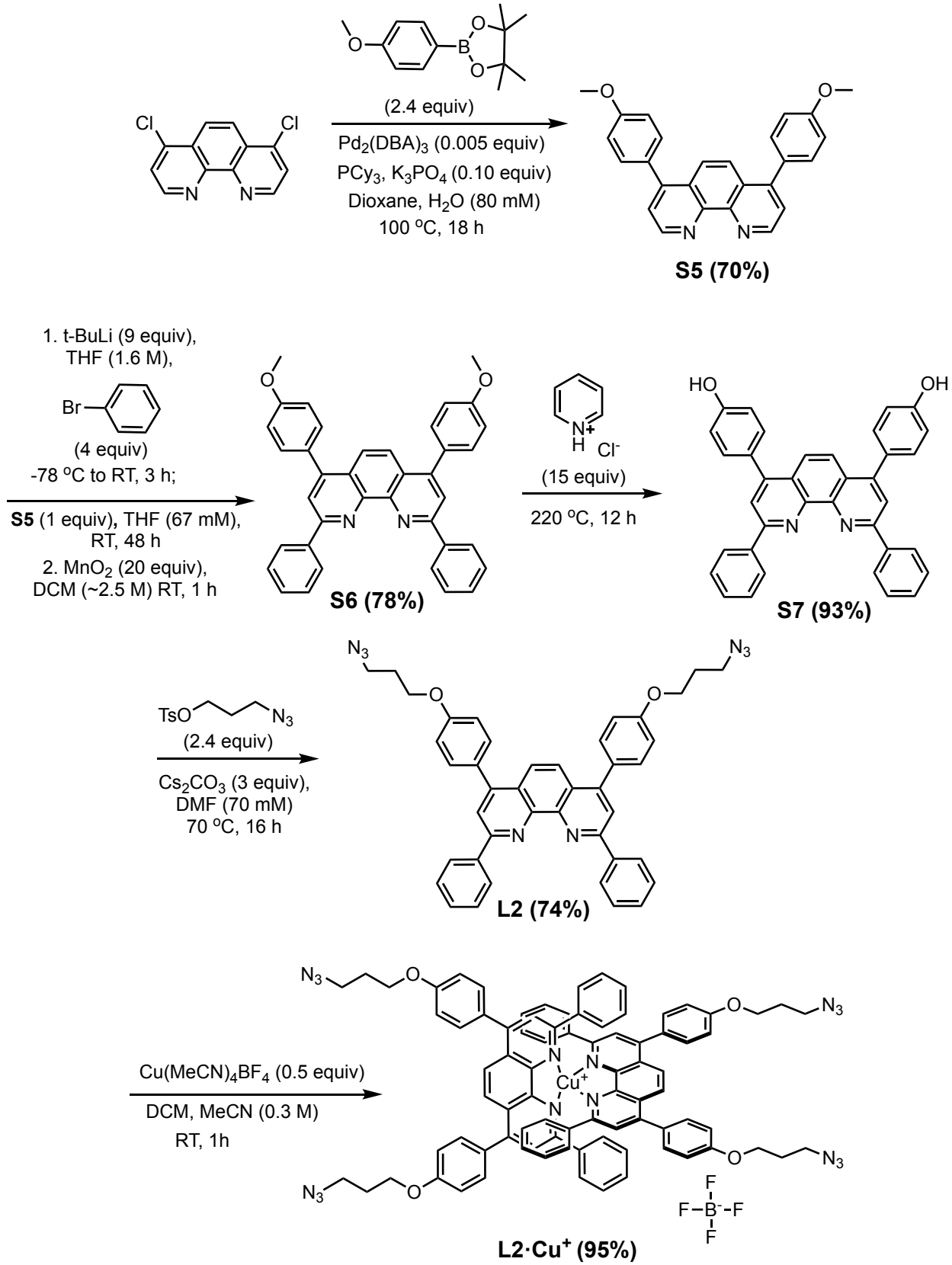
2,9-bis(4-methoxyphenyl)-1,10-phenanthroline (Compound S3): Compound **S3** was prepared following reported methods.[4] To a flame-dried 1 L round-bottom flask 1-bromo-4-methoxybenzene (40.0 g, 26.8 mL, 4.00 equiv, 214 mmol) and anhydrous THF (200 mL) were added. The solution was cooled in an acetone/dry ice bath, and tert-butyllithium (30.8 g, 300 mL, 1.6 molar, 9.00 equiv, 480 mmol) was added into the flask dropwise via addition funnel while stirring under nitrogen. The solution was stirred at -78 °C for two hours, transferred to an ice bath, and stirred for two hours. The ice bath was then removed, and the reaction was stirred for two hours, slowly warming to room temperature. The resulting solution was transferred via cannula to a flame-dried 1 L round-bottom flask containing a solution of (9.62 g, 1.00 equiv, 53.4 mmol) in anhydrous THF (100 mL) cooled in an ice bath. The resulting dark red solution was stirred in an ice bath for an hour and was then allowed to warm up to room temperature while stirring for 48 hours. The reaction was quenched by adding water (100 mL) that had been cooled in an ice bath, and the solvent was removed via rotary evaporator. The aqueous residue was extracted with DCM (3 x 250 mL). The organic layers were combined, dried over sodium sulfate, and filtered. The filtrate was evaporated *in vacuo*, and the residue was re-dissolved in DCM (500 mL). Manganese(IV) oxide (92.8 g, 20.0 equiv, 1.07 mol) was added to the solution. The suspension was stirred for one hour and the solution was filtered through a plug of celite. The filtrate was concentrated by rotary evaporation. The resulting solid was then recrystallized from hot toluene to afford the target product as yellow crystals (14.2 g, 68%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[4]

4,4'-(1,10-phenanthroline-2,9-diyl)diphenol (Compound S4): Compound **S4** was prepared following reported methods.[4] To a 250 mL round-bottom flask pyridine-HCl (92.8 g, 40.0 equiv, 803 mmol) was added. The solid was heated to 190 °C with a heating mantle under stirring to remove water. The liquid was cooled to 140 °C and 2,9-bis(4-methoxyphenyl)-1,10-phenanthroline (8.00 g, 1.00 Eq, 20.4 mmol) was added. The solution was heated to 220 °C for 12 hours. The solution was removed from heat, cooled to 100 °C, and hot water (90°C, 50 mL) was added. The solution was then poured into hot water (90 to 100°C, 100 mL). Then the solution was cooled to 4 °C. The precipitates were filtered out and washed with 600 mL water. The solids were suspended in 4:1 ethanol:water (400 mL:100 mL) and neutralized with 2M NaOH(aq) until a pH of 7.5. The solid was collected and washed with 500 mL water, then dried in an oven (ambient pressure, 120 °C) to get the target product as a red powder (6.84 g, 92%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[4]

2,9-bis(4-(3-azidopropoxy)phenyl)-1,10-phenanthroline (Compound L1): To a flame-dried 250 mL Schlenk flask, compound **S4** (2.00 g, 1.00 equiv, 5.49 mmol), **S2** (3.08 g, 2.20 equiv, 12.1 mmol) and cesium carbonate (5.37 g, 3.00 equiv, 16.5 mmol) were added under nitrogen, and dissolved in 150 mL of dry DMF. The solution was brought to 70 °C and stirred for 18 hours. DMF was removed via rotary evaporator and the mixture was redissolved in DCM (50 mL) and washed with 50 mL of water thrice. The organic layer was dried with $MgSO_4$ and the DCM was removed via rotary evaporator. The solid was redissolved in DCM and run on silica gel chromatography (DCM:MeOH 97:3, R_f = 0.18). The solvent was removed via rotary evaporator and the product was dried on high vac to produce the product as a tan powder (2.30 g, 79%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.76 (s, 1H), 7.11 (d, *J* = 8.8 Hz, 2H), 4.18 (t, *J* = 5.9 Hz, 2H), 3.58 (t, *J* = 6.6 Hz, 2H), 2.13 (p, *J* = 6.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.15, 156.44, 146.15, 136.98, 132.57, 129.20, 127.73, 125.81, 119.51, 114.91, 64.81, 48.47, 29.01. HRMS (HESI): calculated for $C_{30}H_{27}N_8O_2$: $[M+H]^+$, m/z = 531.22570; found, 531.22443.

Compound L1•Cu$^+$: In a nitrogen filled glovebox, $Cu(CH_3CN)_4BF_4$ (333 mg, 0.510 equiv, 1.06 mmol) was dissolved in 5 mL of dry acetonitrile and added to **L1** (1.10 g, 1.00 equiv, 2.07 mmol) dissolved in 10 mL of dry DCM. The solution immediately turned dark red and was stirred for 1 hour at room temperature. The solvent was removed via rotary evaporator and the crude product was redissolved in 5 mL of DCM precipitated in 300 mL of cold diethyl ether. The precipitate was filtered and dried on vacuum, producing the product as a burgundy powder (1.20 g, 96%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.50 (d, J = 8.3 Hz, 1H), 8.02 (s, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 8.6 Hz, 2H), 6.05 (d, J = 8.6 Hz, 2H), 3.67 (t, J = 5.9 Hz, 2H), 3.47 (t, J = 6.4 Hz, 2H), 1.98 – 1.91 (p, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.46, 156.48, 143.58, 137.34, 131.52, 129.39, 128.10, 126.30, 124.64, 113.18, 64.60, 48.27, 28.61. HRMS (HESI): calculated for $C_{60}H_{52}N_{16}O_4Cu$: $[M+H]^+$, m/z = 1123.36534; found, 1123.36340.

2.1.2 Synthesis of $L_2 \cdot Cu^+$



4,7-bis(4-methoxyphenyl)-1,10-phenanthroline (Compound S5): Compound **S5** was prepared following reported methods.[4] To a flame-dried 500 mL three-neck round-bottom flask equipped with a condenser, 4,7-dichloro-1,10-phenanthroline (5.00 g, 1.00 equiv, 20.1 mmol), 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11.3 g, 11.1 mL, 2.40 equiv, 48.2 mmol), $Pd_2(dba)_3$ (919 mg, 0.0500 equiv, 1.00 mmol), PCy_3 (563 mg, 0.100 equiv, 2.01 mmol), and K_3PO_4 (17.0 g, 4.00 equiv, 80.3 mmol) were added under nitrogen. A mixture of dioxane (180 mL) and water (60 mL) was added to the flask and the solution was sparged with nitrogen for 30 minutes. The solution was then heated at 100 °C and stirred for 18 hours under nitrogen. The solution was allowed to cool to room temperature and diluted with $CHCl_3$ (200 mL), washed with water (200 mL), saturated sodium bicarbonate (200 mL), brine (200 mL), and dried over sodium sulfate. The crude product was purified by passing it through a plug of basic aluminum oxide using 98:2 DCM:MeOH as the eluent and the solvent was removed by rotary evaporation. The resulting solids were then recrystallized from hot toluene to get the target product as a brown powder (5.50 g, 70%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[4]

4,7-bis(4-methoxyphenyl)-2,9-diphenyl-1,10-phenanthroline (Compound S6): Compound **S6** was prepared following reported methods.[4] To a flame-dried 500 mL round-bottom flask, bromobenzene (6.40 g, 4.27 mL, 4.00 equiv, 40.8 mmol) and anhydrous THF (50 mL) were added. The solution was cooled in an acetone/dry ice bath. *Tert*-BuLi (5.88 g, 57.3 mL, 1.6 molar, 9.00 equiv, 91.7 mmol) was cannulated into the flask while the solution was stirred at -78 °C. The solution was stirred at -78 °C for another hour, allowed to warm to room temperature, and stirred for another 2 hours. The resulting yellow solution was transferred via cannula to a flame-dried 500 mL round-bottom flask containing a suspension of compound **S5** (4.00 g, 1.00 equiv, 10.2 mmol) in anhydrous THF (40 mL) that had already been pre-cooled in an ice bath. The resulting dark red solution was stirred in an ice bath for an hour and was then allowed to warm up to room temperature. The solution was then stirred for an additional 48 hours. The reaction was then cooled in an ice bath and quenched by adding water (15 mL). The solvent was removed via rotary evaporation. The aqueous residue was extracted with DCM (3 x 40 mL). The organic layers were combined, dried over sodium sulfate, and filtered. The filtrate was concentrated via rotary evaporation and the residue was re-dissolved in DCM (80 mL). Manganese(IV) oxide (17.7 g, 20.0 equiv, 204 mmol) was then added, and the solution was stirred for an hour. The suspension was dried over sodium sulfate, and the solids were filtered through a plug of celite. The filtrate was concentrated by rotary evaporation. The resulting solid was then recrystallized from toluene to afford the product as yellow crystals (4.32 g, 78%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[4]

4,4'-(2,9-diphenyl-1,10-phenanthroline-4,7-diyl)diphenol (Compound S7): Compound **S7** was prepared following reported methods.[4] Pyridine-HCl (12.7 g, 15.0 equiv, 110 mmol) was heated in a 100 mL round-bottom flask to 190 °C under stirring to remove water. The melt was cooled to 140 °C. Compound **S6** (4.00 g, 1.00 equiv, 7.34 mmol) was added to the flask. The mixture was heated to 220 °C and stirred for 16 hours. The solution was cooled to 100 °C and hot water

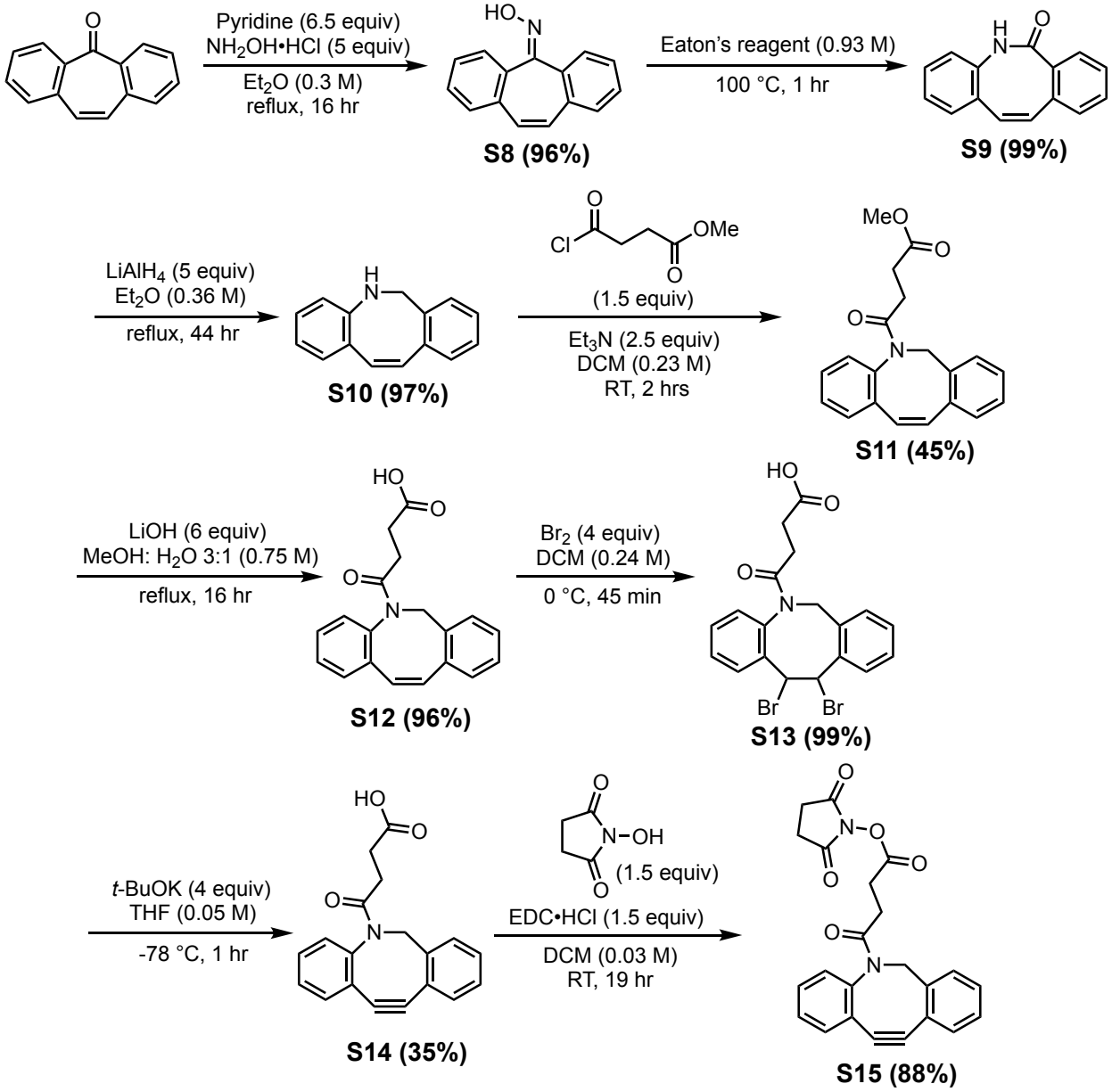
(80 mL, 100 °C) was added. The solution was poured into hot water (400 mL, 90 to 100 °C), cooled to 4 °C overnight, and then filtered. The solid was washed with water (500 mL) and resuspended with a mixture of 1:1: ethanol/water (400 mL:400 mL). The slurry was neutralized with 2M NaOH(aq) solution until pH of 7.5. The product was collected via filtration. The solid was dried in an oven (ambient pressure, 120 °C) to give the product as an orange powder (3.52 g, 93%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[4]

4,7-bis(4-(3-azidopropoxy)phenyl)-2,9-diphenyl-1,10-phenanthroline (Compound L2): To a flamed-dried 250 mL round bottom flask, **S7** (3.60 g, 1.00 equiv, 6.97 mmol), **S2,** and cesium carbonate (6.81 g, 3.00 equiv, 20.9 mmol) were added under nitrogen and dissolved in 100 mL of dry DMF. The flask was heated to 70 °C and stirred for 16 hours. The reaction was cooled to room temperature and the DMF was removed by rotary evaporation and the residue was dried on high vac. The residue was taken up in DCM (40 mL) and washed with water (40 mL) three times. The eluent was dried with $MgSO_4$ and the solvent was removed via rotary evaporator. The resulting residue was then recrystallized from hot ethyl acetate (30 mL) and filtered, to give the product as a tan powder (3.54 g, 74%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 7.5 Hz, 2H), 8.08 (s, 1H), 7.86 (s, 1H), 7.60 (t, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 4.17 (t, *J* = 5.9 Hz, 2H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.13 (p, *J* = 6.3 Hz, 2H). 13C NMR (151 MHz, $CDCl_3$) δ 159.12, 156.29, 149.00, 147.14, 139.82, 131.28, 131.20, 129.52, 128.96, 127.88, 126.09, 123.68, 120.68, 114.81, 64.86, 48.41, 28.98. HRMS (HESI): calculated for $C_{42}H_{35}N_8O_2$: $[M+H]^+$, m/z = 683.28830; found, 683.28699.

Compound L2•Cu$^+$: In a nitrogen filled glovebox, $Cu(CH_3CN)_4BF_4$ (705 mg, 0.510 equiv, 2.24 mmol) was dissolved in 15 mL of dry acetonitrile and added to **L2** (3.00 g, 1.00 equiv, 4.39 mmol) dissolved in 30 mL of dry DCM. The solution immediately turned dark purple and was stirred for 1 hour at room temperature. The solvent was removed via rotary evaporator and the crude product was redissolved in 20 mL of DCM precipitated in 400 mL of cold diethyl ether. The precipitate was filtered and dried on vacuum, producing the product as a purple solid (2.98 g, 95%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.81 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 2H), 4.22 (t, *J* = 5.9 Hz, 2H), 3.60 (t, *J* = 6.6 Hz, 2H), 2.16 (p, *J* = 6.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.97, 159.97, 156.14, 149.60, 144.64, 139.24, 131.17, 129.26, 128.83, 127.86, 127.36, 126.36, 125.15, 124.33, 115.40, 65.08, 48.41, 28.91. HRMS (HESI): calculated for $C_{84}H_{68}N_{16}O_4Cu$: $[M+H]^+$, m/z = 1427.49054; found, 1427.49060.

2.2 Synthesis of PEG-DIBAC

2.2.1 Synthesis of Strained Alkyne



5*H*-Dibenzo[*a,d*]cyclohepten-5-one-oxime (S8) was prepared from dibenzosuberenone (60.6 g, 1.00 eq., 294 mmol), pyridine (181 g, 185 mL, 7.78 eq., 2.29 mol), hydroxlammoniumchloride (110.5 g, 5.41 eq., 1.59 mmol), and absolute ethanol (0.95 L, 16.0 mol) as reported by the cited reference[5], which yielded **S8** as a brown powder that was used without further purification (62.2 g, 96%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[5]

Dibenzo[*b,f*]azocin-6(5*H*)-one (S9) was prepared from **S8** (62.2 g, 1.00, 281 mmol) and Eaton's reagent (303 mL, 1.91 mol) as reported by the cited reference[5], which yielded **S9** as a brown

powder that was used without further purification (62.1 g, 99%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[5]

5,6-Dihydrodibenzo[b,f]azocine (S10) was prepared from a modified literature procedure.[5,6] To a flame-dried 1.0 L three-neck round bottom flask under inert atmosphere **S9** (20.0 g, 1.00 eq., 90.4 mmol) and diethyl ether (250 mL, 0.36 M) were added. Lithium aluminum hydride ($LiAlH_4$) (15.5 g, 5.01 eq., 407 mmol) was slowly added to the stirring mixture, which was then heated to reflux. After 20 hours, a further 1.70 g (45.1 mmol) of lithium aluminum hydride was added to the reaction mixture, and all starting material was consumed after 40 hours. The reaction mixture was cooled to room temperature, then placed in an ice bath. Caution: The original cited procedure called for the $LiAlH_4$ to be quenched with only water. This process is extremely exothermic and produces hydrogen gas (H_2), which is flammable when exposed to a spark or heat source. We adjusted the procedure by using fewer equivalents of lithium aluminum hydride, and used first isopropanol and then water to quench the excess LAH, which results in a more controlled quenching process. Isopropyl alcohol (207 mL) was added dropwise until the reaction no longer visibly emitted hydrogen. Water (120 mL) was added dropwise to quench remaining lithium aluminum hydride. Upon addition of the water the reaction mixture solidified and would no longer stir. To ensure that water did not rest on the surface of the reaction mixture, water was injected throughout the slurry via syringe. Caution: Do not allow water to pool on top of the reaction mixture, if the water accumulates and then falls through to unreacted lithium aluminum hydride, a runaway reaction can occur due to the exotherm and rapid generation of H_2. Dichloromethane (1.5L) was added, then the reaction mixture was filtered over celite. The remaining lithium aluminum hydride side product was washed with dichloromethane (3 x 200 mL) to remove residual product. Dichloromethane was removed under reduced pressure to yield **S10** as a yellow powder (18.3 g, 97%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[5]

Methyl 4-Dibenzo[*b,f*]azocin-5(6*H*)-yl-4-oxobutanoate (S11) was prepared from **S10** (32.8 g, 1.00 eq., 158 mmol), methyl-4-chloro-4-oxobutanoate (35.7 g, 29.1 mL, 1.50 eq., 237 mmol), and triethylamine (40.0 g, 55.1 mL, 2.5 eq., 395 mmol) in dichloromethane (700 mL, 0.26 M) as reported by the cited reference[5], and was further purified in accordance with methods from multiple cited references[5,6], wherein the product was initially purified using flash column chromatography (3:1 hexanes:ethyl acetate) followed by recrystallization with ethanol to yield **S11** as a white solid (23.1 g, 45%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[5,6]

4-Dibenzo[*b,f*]azoncin-5(6*H*)-yl-4-oxobutanoic Acid (S12) was prepared from **S11** (23.1 g, 1.00 eq., 71.8 mmol) and lithium hydroxide (10.32 g, 6.00 eq., 430.9 mmol) in methanol (700 mL) and water (250 mL) (0.076 M) as reported by the cited reference[5], and yielded **S12** as a white solid that was used without further purification (21.2 g, 96%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[5]

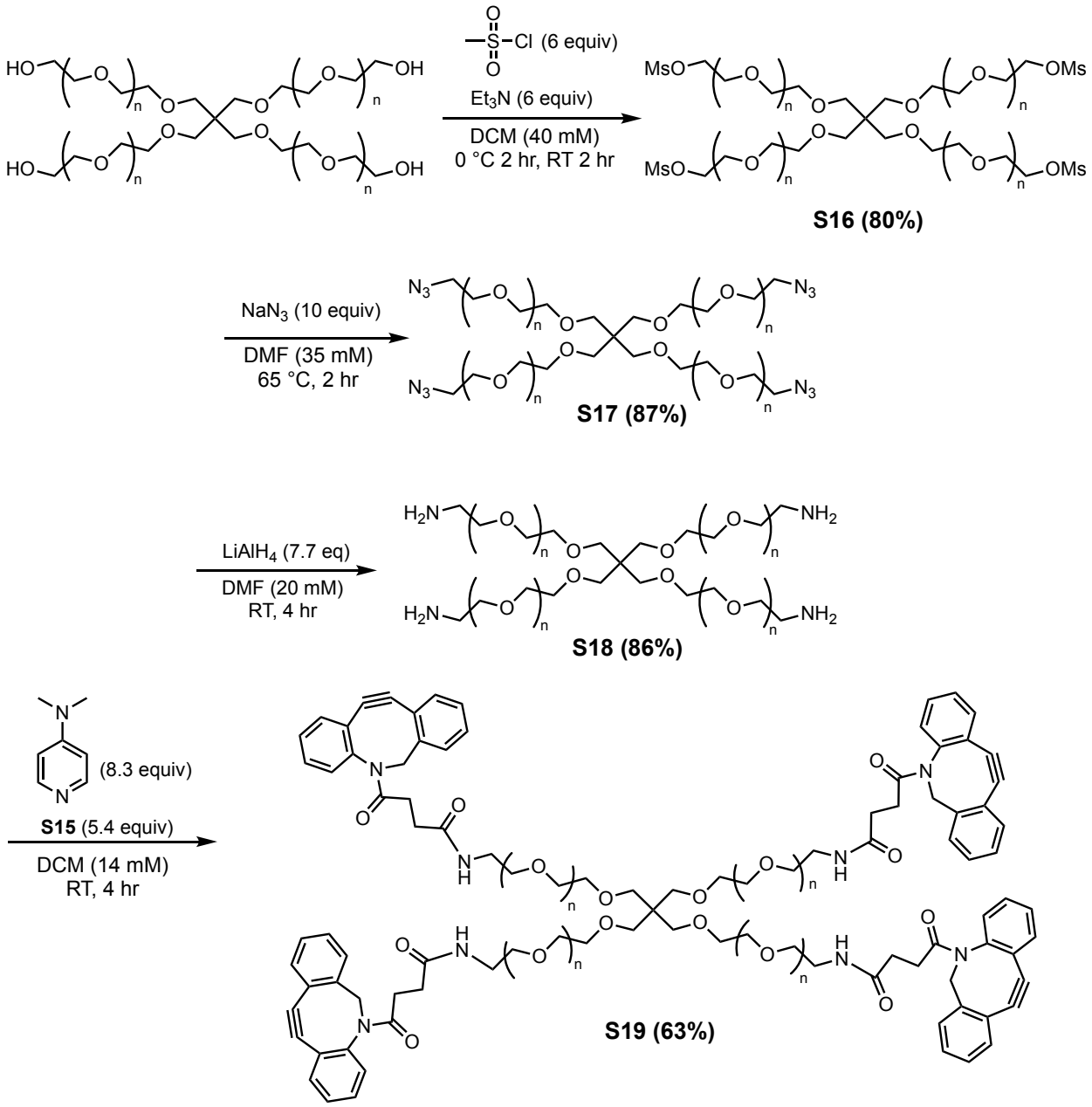
4-[11,12-Dibromo-11,12-dihydrodibenzo[*b,f*]azocin-5(6*H*)-yl]-4-oxobutanoic Acid (S13) was prepared from **S12** (6.71 g, 1.00 eq., 21.8 mmol) and bromine (10.0 g, 5.00 mL, 4.00 eq., 80.0

mmol) in dichloromethane (0.24 M) as reported by the cited reference[5], which yielded **S13** as a green-brown solid that was used without further purification (10.1 g, 99%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[5]

5-[11,12-Didehydrodibenzo[*b,f*]azocin-5(6*H*)-yl]-4-oxobutanoic Acid (S14, DIBAC) was prepared from a modified literature procedure[5,6]. **S13** was converted to **S14** on the same day as it was prepared. To a flame dried 1L Schlenk flask under inert atmosphere, **S13** (10.1 g, 1.00 eq., 21.6 mmol) was dissolved in anhydrous tetrahydrofuran (350 mL, 0.06 M). The reaction mixture was cooled to -78°C in a dry ice/acetone bath. A 1M solution of potassium tert butoxide (9.68 g, 4.00 eq., 86.2 mmol) was also cooled to -78°C before being cannulated into the reaction mixture. The reaction was complete by NMR after 1 hour, at which point the reaction mixture was cannulated into a 1M solution of sodium bisulfate (1.5 L). The reaction mixture was washed 3 times with dichloromethane (3 x 200 mL), the the organic layers were combined and washed with water (1 x 200 mL) and brine (1 x 200 mL). The organic layer was dried with sodium sulfate and solvent removed under reduced pressure, forming a yellow/orange solid. The solid was washed thoroughly with cold diethyl ether, filtered, and dried under reduced pressure, yielding **S14** as an off-white powder (2.3 g, 35%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited references.[5–7] Note: Upon quenching of the potassium tert-butoxide with sodium bisulfate, unreacted starting material was observed. Upon washing with diethyl ether, which separated **S13** from **S14**, we were able to resubject the liquor containing **S13** to reaction conditions to form more of **S14**. Completing this process effectively doubled the initial yields of **S14**.

2,5-Dioxopyrrolidin-1-yl 4-(didehydrodibenzo[*b,f*]azocin-5(6*H*)-yl)-4-oxobutanoate (S15) was prepared in inert atmosphere from **S14** (5.70 g, 1.00 eq., 18.6 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (5.40 g, 28.2 mmol), and *N*-hydroxysuccinimide (NHS) (3.20 g, 28.0 mmol) in dry dichloromethane (600 mL, 0.03 M) as reported by the cited reference[4], and was purified via column chromatography (1:1 ethyl acetate: hexanes) to yield **S15** as an off white solid (6.6 g, 88%). The ^{1}H NMR spectrum of this material matched the spectrum reported in the cited reference.[7]

2.2.2 Synthesis of 4-arm PEG-DIBAC (5k MW)



4-arm PEG-methanesulfonyl 5k MW (S16) was prepared in inert atmosphere by mixing 4-arm PEG-OH (5k MW) (10.1 g, 1.00 eq., 1.98 mmol) and triethylamine (1.20 g, 1.66 mL, 6.00 eq., 11.9 mmol) in DCM (50 mL, 40 mM) and lowering the temperature of the solution to 0°C in an ice water bath. Methanesulfonyl chloride (1.36 g, 0.92 mL, 6.00 eq., 11.9 mmol) was added dropwise to the solution over 30 minutes. The reaction then proceeded at 0 °C for 2 hours then at room temperature for 2 hours. The reaction mixture washed with 1M HCl (3 x 50 mL) and brine (3 x 50 mL). The organic layer was dried over sodium sulfate and then under reduced pressure to yield **S16** as an off-white solid (8.50 g, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.40 – 4.36

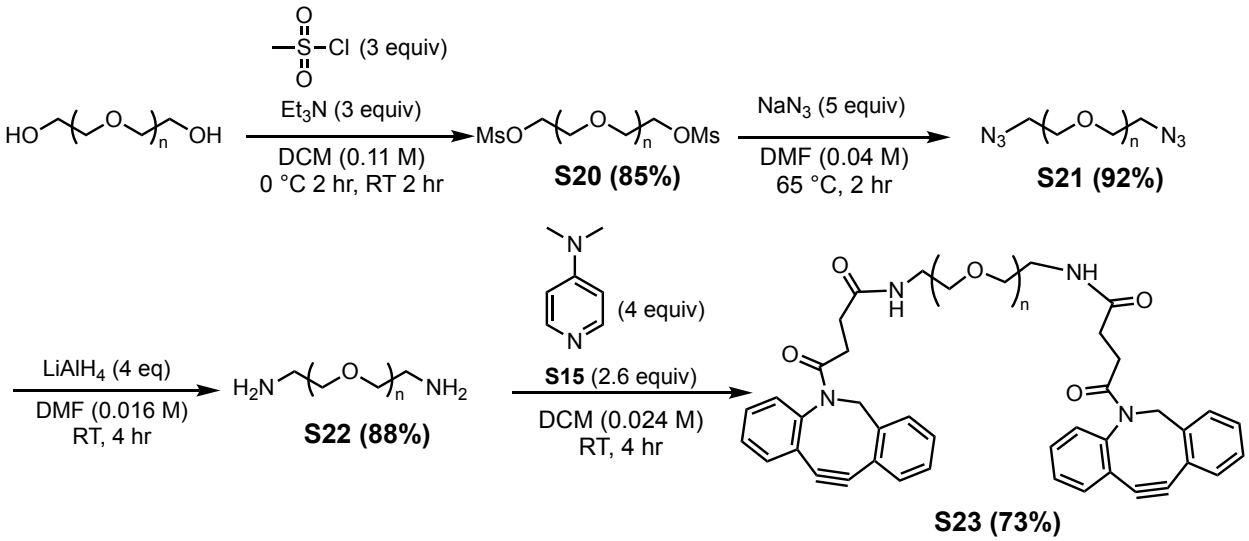
(m, 8H), 3.64 (s, 476H), 3.41 (s, 8H), 3.08 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.98, 70.65, 70.58, 70.54, 70.36, 70.04, 69.36, 69.04, 45.53, 37.77. M_n = 4.85 kg/mol, M_w = 5.18 kg/mol, $Đ$ = 1.07 (GPC). M_n = 5.38 kg/mol (^{1}H NMR).

4-arm PEG-azide 5k MW (S17) was prepared in inert atmosphere by adding **S16** (7.57 g, 1.00 eq., 1.40 mmol) and sodium azide (915 mg, 10.0 eq., 14.0 mmol) in dimethylformamide (DMF) (40 mL, 35 mM). The reaction proceeded at 65°C from 2 hours. DMF was removed under reduced pressure and excess sodium azide removed by dissolving the mixture in hot toluene and filtering. Excess toluene was removed under reduced pressure to yield **S17** as an off-white solid (6.54g, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.90 – 3.45 (m, 470H), 3.40 (s, 8H), 3.38 (t, J = 5.1 Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.96, 70.69, 70.66, 70.63, 70.56, 70.33, 70.04, 70.01, 50.66, 45.51. M_n = 4.88 kg/mol, M_w = 5.20 kg/mol, $Đ$ = 1.06 (GPC). M_n = 5.35 kg/mol (^{1}H NMR).

4-arm PEG-amine 5k MW (S18) was synthesized in inert atmosphere by mixing **S17** (6.54 g, 1.00 eq., 1.26 mmol) and lithium aluminum hydride (357 mg, 7.7 eq., 9.40 mmol) in dry tetrahydrofuran (60 mL, 20 mM) at 0°C under nitrogen. The reaction was stirred at room temperature for 4 hours, then cooled to 0°C and quenched with 3 mL of water added dropwise. The product was extracted with dichloromethane (3 x 50 mL), then washed with brine (2 x 50 mL). The organic layer was dried over sodium sulfate and solvent removed under reduced pressure to yield **S18** as an off-white solid (5.51 g, 86 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.78 – 3.48 (m, 462H), 3.41 (s, 8H), 2.86 (t, J = 5.2 Hz, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 73.48, 71.05, 70.71, 70.65, 70.44, 70.38, 70.11, 45.62, 41.86. M_n = 5.24 kg/mol (^{1}H NMR).

4-arm PEG-DIBAC 5k MW (S19) was synthesized in inert atmosphere by adding **S18** (5.30 g, 1.00 eq., 1.05 mmol), **S15** (2.20 g, 5.39 eq., 5.46 mmol), and 4-dimethylaminopyridine (DMAP) (1.02 g, 8.27 eq., 8.37 mmol) to a flame dried 200 mL Schlenk flask. Anhydrous dichloromethane (70 mL, 14 mM) was subsequently added, and the reaction stirred for 4 hours. The product was extracted with 1.0 M HCl (3 x 33 mL) and brine (2 x 50 mL) then dried with magnesium sulfate. Flash column chromatography was conducted with variated conditions – 7.5% methanol in DCM to remove excess **S15** followed by 10% methanol in DCM to flush remaining product off the column. Removal of solvent under reduced pressure yielded **S19** product as a yellow solid (4.18 g, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (dd, J = 7.6, 1.3 Hz, 4H), 7.53 – 7.49 (m, 4H), 7.40 – 7.32 (m, 16H), 7.28 (d, J = 1.3 Hz, 4H), 7.24 (dd, J = 7.5, 1.5 Hz, 4H), 6.11 (s, 4H), 5.14 (d, J = 13.9 Hz, 4H), 3.79 – 3.28 (m, 510H), 2.80 (ddd, J = 16.9, 8.4, 6.5 Hz, 4H), 2.45 (ddd, J = 15.0, 8.4, 6.4 Hz, 4H), 2.16 (dt, J = 15.3, 6.3 Hz, 4H), 1.93 (d, J = 16.9 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.17, 172.00, 151.41, 148.07, 132.20, 129.37, 128.61, 128.11, 128.05, 127.66, 126.97, 125.41, 123.15, 122.39, 114.64, 107.89, 70.92, 70.59, 70.52, 70.49, 70.43, 70.30, 70.18, 69.98, 69.68, 55.43, 45.48, 39.14, 31.10, 30.07. M_n = 6.74 kg/mol (^{1}H NMR).

2.2.3 Synthesis of Linear PEG-DIBAC (2k MW)



Linear PEG-methanesulfonyl 2k MW (S20) was prepared in inert atmosphere by mixing linear PEG-OH (2k MW) (60.0 g, 1.00 eq., 29.0 mmol) and triethylamine (8.70 g, 12.0 mL, 3.00 eq., 86.0 mmol) in DCM (260 ml, 0.11 M). The reaction was cooled to 0 °C and methylsulfonyl chloride (9.90 g, 6.70 mL, 3.00 eq., 86.0 mmol) was added dropwise to the mixture. The reaction proceeded at 0 °C for two hours then at room temperature for a further 2 hours. The reaction mixture was concentrated to dryness and washed first with 1M HCl (100 mL) and then brine (100 mL), extracting with DCM (100 mL). This procedure was repeated thrice and the organic layer dried over Na_2SO_4 followed by removal of the DCM via rotovap and then reduced pressure to unveil **S20** as a yellow solid (51.4 g, 85%) ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.39 – 4.36 (m, 4H), 3.78 – 3.74 (m, 4H), 3.64 (s, 184H), 3.08 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 70.79, 70.73, 70.72, 70.67, 69.43, 69.17, 37.89. M_n = 2.08 kg/mol, M_w = 2.26 kg/mol, $Đ$ = 1.08 (GPC). M_n = 2.16 kg/mol (^{1}H NMR).

Linear PEG-azide 2k MW (S21) was prepared in inert atmosphere by adding **S20** (51.4 g, 1.00 eq., 24.3 mmol), sodium azide (7.91 g, 5.00 eq., 122 mmol), and DMF (600 mL, 0.4 M) to a 2L round bottom flask. The reaction was stirred at 65°C for 2 hours, then DMF was removed under reduced pressure. Excess sodium azide was removed by dissolving the reaction mixture in hot toluene followed by filtering. Toluene was removed via rotovap followed by sparging with nitrogen at 50 °C, and remaining solvent removed under reduced pressure to unveil **S21** as a yellow solid (48.02 g, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.64 (s, 196H), 3.39 (t, J = 5.1 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 70.86, 70.83, 70.80, 70.73, 70.19, 50.84. M_n = 2.12 kg/mol, M_w = 2.17 kg/mol, $Đ$ = 1.03 (GPC). M_n = 2.27 kg/mol (^{1}H NMR).

Linear PEG-amine 2k MW (S22) was synthesized in inert atmosphere by mixing **S21** (11.5 g, 1.00 eq., 5.39 mmol) and lithium aluminum hydride (802 mg, 3.92 eq., 21.1 mmol) in tetrahydrofuran (500 mL, 0.1 M) in a 500 mL flame dried flask at 0°C. The reaction was stirred at room temperature for four hours, then cooled to 0°C and quenched with 5 mL of water added slowly. The product was extracted with dichloromethane (2 x 200 mL) and washed with

brine (2 x 100 mL). The organic layers were dried with sodium sulfate and solvent removed under reduced pressure to afford **S22** as a yellow solid (10.6 g, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.64 (d, *J* = 2.2 Hz, 192H), 3.52 (t, *J* = 5.2 Hz, 4H), 2.87 (t, *J* = 5.2 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 70.83, 70.80, 70.77, 70.69, 70.17, 50.81. M_n = 2.22 kg/mol (^{1}H NMR).

Linear PEG-DIBAC 2k MW (S23) was synthesized in inert atmosphere by adding **S22** (7.07 g, 1.00 eq., 3.18 mmol), **S15** (3.47 g, 2.71 eq., 8.63 mmol), and DMAP (1.65 g, 4.25 eq., 13.5 mmol) to a flame dried 200 mL Schlenk flask. Anhydrous dichloromethane (140 mL, 0.02 M) was subsequently added, and the reaction stirred for 4 hours. The reaction was diluted with additional dichloromethane (200 mL), then extracted with 0.5 M HCl (3 x 50 mL) and brine (3 x 50 mL) then dried with magnesium sulfate. Flash column chromatography was conducted with variated conditions – 5% methanol in DCM to remove excess **S15** followed by 7.5% methanol in DCM to remove product from the column, followed by 10% methanol in DCM to remove residual compound. Removal of solvent under reduced pressure followed by sparging with nitrogen at 50°C afford **S23** as a yellow solid (6.54 g, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.52 (m, 2H), 7.44 – 7.35 (m, 8H), 7.34 – 7.30 (m, 2H), 7.28 – 7.25 (m, 2H), 6.20 (s, 2H), 5.17 (d, *J* = 13.9 Hz, 2H), 3.81 – 3.31 (m, 200H), 2.88 – 2.78 (m, 2H), 2.53 – 2.43 (m, 2H), 2.19 (d, *J* = 15.4 Hz, 2H), 1.97 (dd, *J* = 14.9, 8.3 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.36, 172.17, 151.60, 148.25, 132.38, 129.54, 128.78, 128.31, 128.22, 127.84, 127.17, 125.61, 123.34, 122.61, 114.84, 108.05, 70.71, 70.69, 70.66, 70.63, 70.38, 69.88, 55.64, 39.33, 31.33, 30.27. M_n = 2.77 kg/mol (^{1}H NMR).

2.3 Synthesis of Gel-1, Gel-2, and Gel-1'

Gel-1, **Gel-2**, and **Gel-1'** were prepared using the ratios and masses listed in Table S1: A stock solution of the ligand (**L1•Cu^{+}**, **L2•Cu^{+}**, or **L1**) was made using 43% of the total amount of propylene carbonate (PC) used (unless otherwise noted). The volume change caused to the solution was measured via Hamilton syringe. A separate stock solution containing the 4-arm PEG-DIBAC (**S19**) and linear PEG-DIBAC (**S23**) was made in the remaining 57% of the total propylene carbonate added. When the stock solutions of the ligands and PEG-DIBAC were made, the amount of all reagents measured was typically a factor of 1.1 times the amount required for each individual gel (e.g. to make 4 gels the masses and volumes required for a single gel were multiplied by 4.4). For the 400 µL gels, four gels (two **Gel-1** and two **Gel-2**) were made at a time, whereas for the 2.3 mL gels two gels (one **Gel-1** and one **Gel-2**) were made. The PEG-DIBAC mixture was heated at 50 °C for 10 minutes to melt the PEG into the PC. The mixture was cooled to room temperature, and the volume difference from the PEG-DIBAC measured via Hamilton Syringe. The solution was vortexed vigorously to ensure complete homogenization of PEG. The respective amount of the PEG-DIBAC solution (accounting for volume increase) was measured out into a vial, and the respective amount of **L1•Cu^{+}**, **L2•Cu^{+}**, or **L1** (accounting for volume increase) was quickly added to the PEG-DIBAC solution and vortexed vigorously for ~2 seconds before being poured into a small Teflon mold (400 µL, Figure S1 or into a large Teflon mold (2.3 mL gels, Figure S1) to form metallated **Gel-1•Cu^{+}** and **Gel-2•Cu^{+}** as red solids and **Gel-1'** as a yellow solid. The metallated gels sat for ~18 hours before being subjected to a saturated

solution of potassium cyanide (KCN) in dimethyl sulfoxide (DMSO). Caution: KCN is potentially fatal upon exposure, and while DMSO on its own is not toxic, it easily absorbs through skin. Thus, the saturated KCN/DMSO solution presents a more significant dermal hazard than either component on its own. Safety precautions taken included 3 layers of gloves (nitrile, silver shield, nitrile), a lab coat, and a face shield. Additionally, the solution was pipetted with a 1 mL glass pipet to reduce the amount handled a time, and the tip of the pipet lowered to the bottom of the 20 mL vial when depositing the solution onto the gel to reduce splashback. The KCN/DMSO solution (20x gel volume) was exchanged every hour for a total of 3 washes. Complete removal of copper was determined by the visible color change of the gel from red and opaque to yellow and translucent. Remaining KCN was washed from the gel with 3 one hour washes in DMSO (50 x gel volume). Re-equilibration in propylene carbonate (50x gel volume) was accomplished in 3 one hour washes to afford **Gel-1** and **Gel-2**. To remove solvent to increase the wt% of the network to ~11%, the gels were placed on chemwipes until solvent had diffused out of the gel to give the desired weight (Table S2). The wt% of the network in the gel is calculated by the following formula:

$$Wt\% = \frac{Wt_n}{Wt_g} \times 100$$

Where Wt_n is the estimated mass of the network incorporated in the gel based on the initial weight of the metallated gel and Wt_g is the mass of the gel after copper removal, re-equilibration in propylene carbonate, and removal of excess solvent. In the case of calculations for metallated gels **Gel-1•Cu$^+$** and **Gel-2•Cu$^+$**, Wt_g is the mass of the metallated gel.

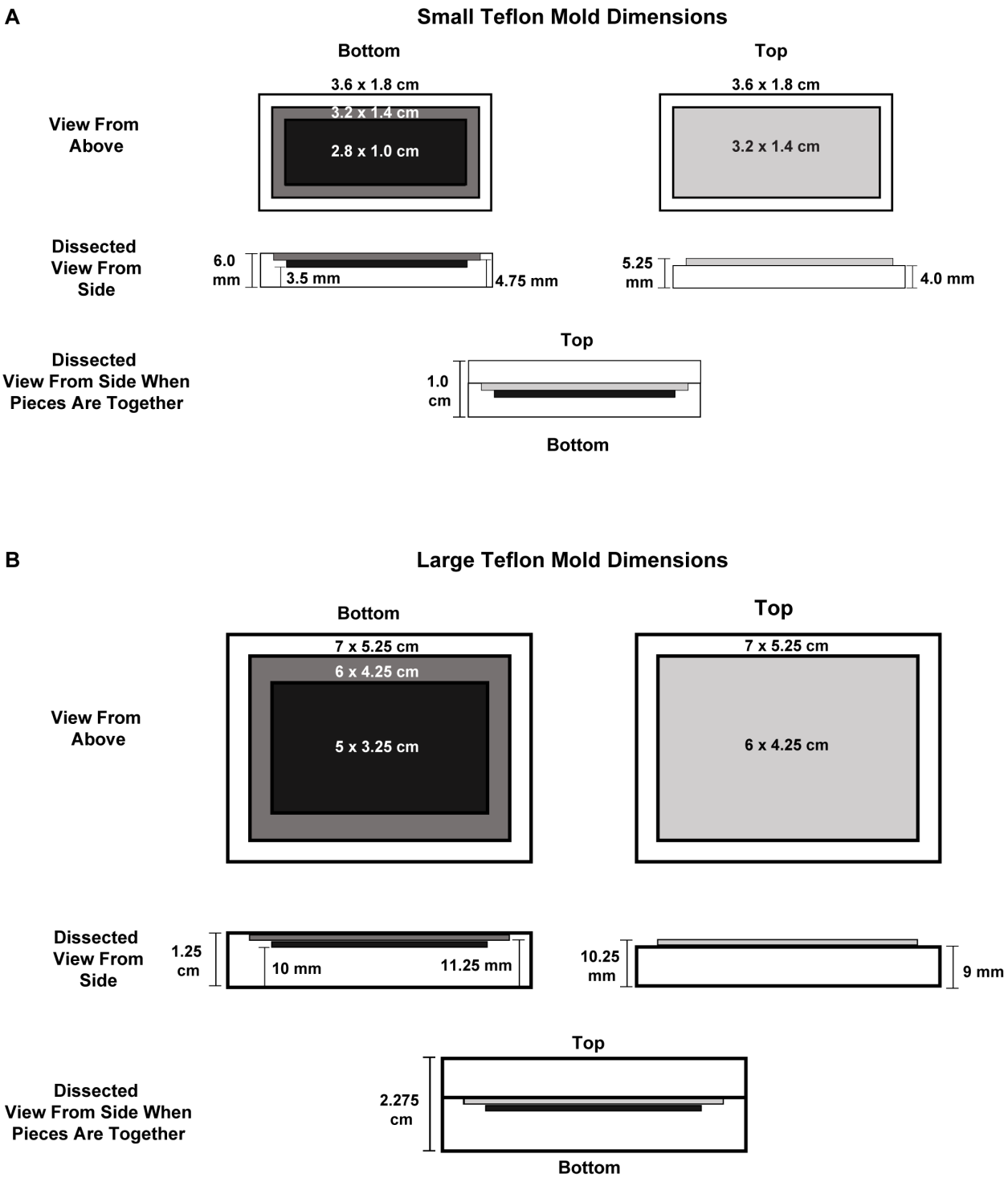


Figure S1. A. Small Teflon Mold Dimensions. B. Large Teflon Mold Dimensions.

Table S1. The equivalents and masses of the ligand, copper salt, and propylene carbonate for making the organogels. The type and total amount of solvent used is indicated with abbreviations for the following solvents: propylene carbonate (PC), N-methyl-2-pyrrolidone (NMP), and deuterated dimethyl sulfoxide (DMSO-*d*6). Large scale gels are labeled 100:0 (L). Amounts used for fluorimetry are labeled 100:0 (F)

Ratio of 4-arm to Linear PEG	Ligand	Equiv	Mass (mg)	4-arm PEG-DIBAC Equiv	4-arm PEG-DIBAC (mg)	Linear PEG-DIBAC Equiv	Linear PEG-DIBAC (mg)	Solvent (mg)
0:100	**L1•Cu$^+$**	1.00	4.9	0	0	1.95	22.1	238 (DMSO-*d*6)
0:100	**L1**	1.00	4.3	0	0	0.97	21.9	51 (NMP) 179 (DMSO-*d*6)
5:95	**L1•Cu$^+$**	1.00	48.0	0.081	25.0	1.8	210	749 (PC)
5:95	**L2•Cu$^+$**	1.00	65.9	0.081	25.0	1.8	210	749 (PC)
60:40	**L1•Cu$^+$**	1.00	9.0	0.75	37.8	0.50	10.4	480 (PC)
60:40	**L2•Cu$^+$**	1.00	11.3	0.75	37.8	0.50	10.4	480 (PC)
70:30	**L1•Cu$^+$**	1.00	9.1	0.82	41.4	0.35	7.3	480 (PC)
70:30	**L2•Cu$^+$**	1.00	11.3	0.82	41.4	0.35	7.3	480 (PC)
80:20	**L1•Cu$^+$**	1.00	9.1	0.89	44.7	0.22	4.6	480 (PC)
80:20	**L2•Cu$^+$**	1.00	11.3	0.89	44.7	0.22	4.6	480 (PC)
90:10	**L1•Cu$^+$**	1.00	9.0	0.95	47.6	0.11	2.2	480 (PC)
90:10	**L2•Cu$^+$**	1.00	11.3	0.95	47.6	0.11	2.2	480 (PC)
100:0	**L1•Cu$^+$**	1.00	9.0	1.00	50.3	0.00	0.00	480 (PC)
100:0	**L2•Cu$^+$**	1.00	11.3	1.00	50.3	0.00	0.00	480 (PC)
100:0 (L)	**L1•Cu$^+$**	1.00	52.9	1.00	289.2	0	0	2758 (PC)
100:0 (L)	**L2•Cu$^+$**	0.99	64.4	1.00	289.2	0	0	2758 (PC)
100:0 (F)	**L1•Cu$^+$**	1.00	9.0	1.00	50.5	0	0	480 (PC)
100:0 (F)	**L2•Cu$^+$**	1.00	11.3	1.00	50.5	0	0	480 (PC)
100:0 (F)	**L1**	2.00	7.9	1.00	50.5	0	0	179 (NMP) 271 (PC)

Adjustments Made for Specific Gel Syntheses

0:100 Gel-1 and Gel-1'

The purpose of the following experiments was to determine the effect of the KCN in DMSO washes on the material. Incorporating the 4-arm PEG-DIBAC cross-linked the material and formed a network that could not be re-dissolved. However, we found that upon conducting the gelation with linear PEG-DIBAC only, the material formed with **L1** (which does not crosslink the material) remained in solution. We therefore used **L1** to make **Gel-1'** by dissolving **L1** in 150 µL N-methyl-2-pyrrolidone (NMP) and adding 50 µL of the solution to linear PEG-DIBAC (**S23**) in 150 µL deuterated dimethyl sulfoxide (DMSO-*d*6) before combining, which was then evaluated by NMR, exposed to KCN in DMSO-*d*6, then evaluated again by NMR. **Gel-1** was made by dissolving **L1•Cu$^+$** in 150 µL DMSO-*d*6 and adding 50 µL of that solution to linear PEG-DIBAC **S23** in 150 µL DMSO-*d*6, which afforded the product as a red gel. Upon exposure to KCN in DMSO-*d*6, the gel dissoluted and the resulting solution evaluated by NMR.

5:95 Gel-1 and Gel-2

The purpose of the following experiments was to determine if slow addition was an effective method for forming **Gel-1** and **Gel-2** at low ratios of 4-arm to linear PEG-DIBAC. The gels were made by dissolving either **L1•Cu**$^{+}$ (62.04 mg) or **L2•Cu**$^{+}$ (78.2 mg) in 304.5 µL PC and dissolving **S19** (55.0 mg and **S23** (462 mg) in PC (728 µL). 510 µL of the PEG-DIBAC solution containing **S19** and **S23** was deposited into a 1 dram vial, and the respective ligand solution added dropwise with mild vortexing conducted between drops. When forming **Gel-1**, 180 µL of ligand was added before gelation initiated, and the remaining 180 µL was deposited, vortexed, and the gel allowed to sit for 18 hours. When forming **Gel-2**, 160 µL of ligand was added before gelation initiated, and the remaining 200 µL was deposited, vortexed, and the gel allowed to sit for 18 hours. Upon exposure to KCN in DMSO, **Gel-2** dissociated completely whereas a small portion of **Gel-1** remained intact.

100:0 Gel-1, Gel-2, and Gel-1' For Fluorimetry

The synthesis of the fluorimetry gels followed the general procedure with the exception of **Gel-1'**, as the ligand **L1** used to make **Gel-1'** had to be dissolved in a proportional volume of NMP rather than PC. After vortexing the solutions for **Gel-1**, **Gel-2**, and **Gel-1'**, the solutions were poured into the small Teflon mold (Figure S1). Upon removal from the mold after 18 hours, **Gel-1** and **Gel-2** underwent the demetallation protocol, then were equilibrated along with **Gel-1'** in DCM (soaked for 4.5 hours, DCM changed every 1.5 hours), and the solvent removed under reduced pressure for 48 hours before the 0 hour fluorimetry measurement was taken. The gels were exposed to atmosphere for a total of 8 hours, and further fluorimetry measurements were taken at 3.5 and 8 hours.

3. SUPPLEMENTARY FIGURES REFERENCED IN THE MAIN TEXT

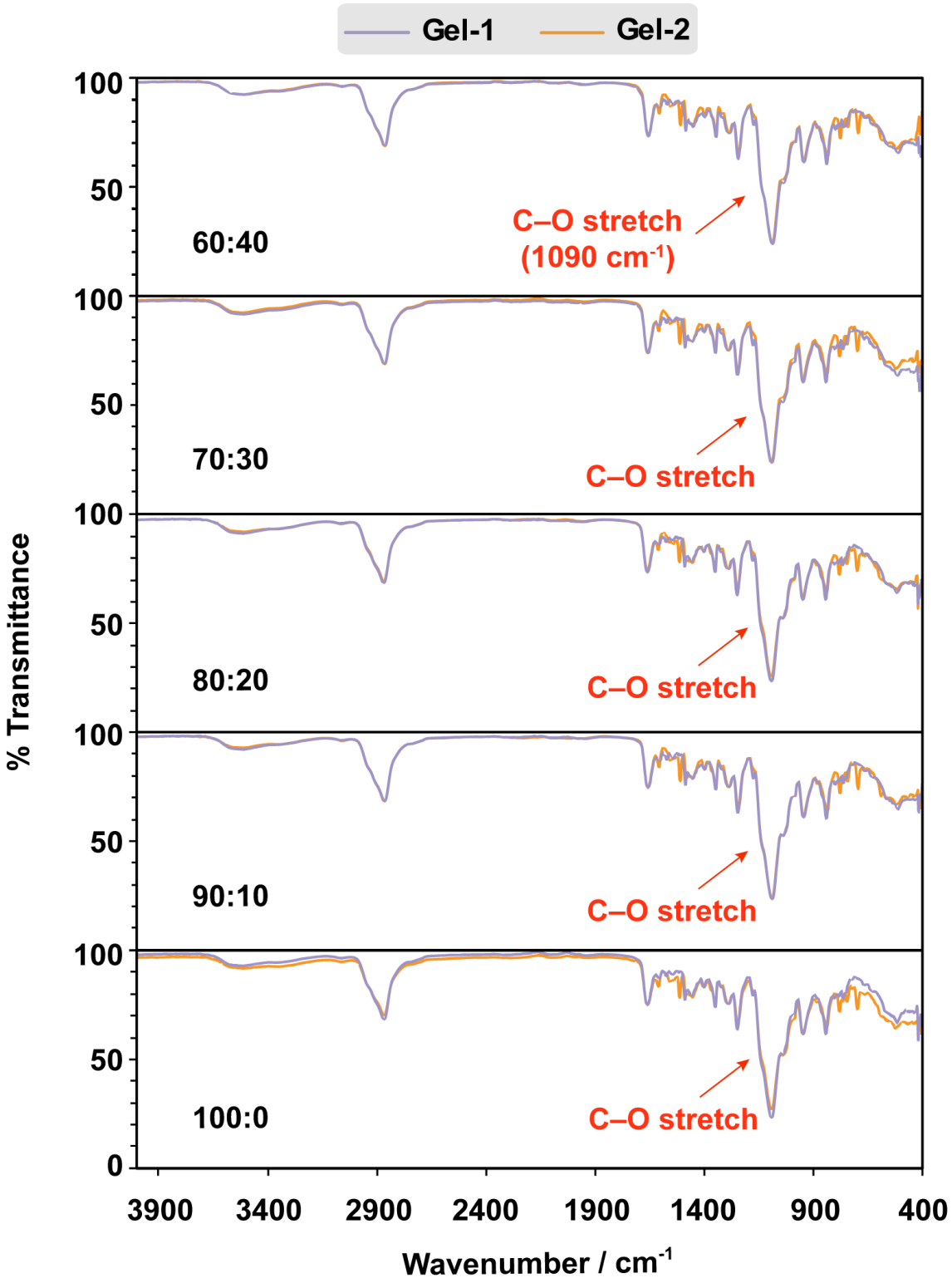


Figure S2. Representative IR spectra of **Gel-1** and **Gel-2** at all ratios of 4-arm to linear PEG-DIBAC.

Table S2. ICP-MS data collected for **Gel-1**, **Gel-2**, **Gel-1•Cu$^+$**, and **Gel-2 Cu$^+$**.

Sample	Weight (mg)	Cu^+ per sample (ng)	µg Cu^+/g network	% Cu^+ removed
Gel-1•Cu$^+$	26.8	2.07×10^5	7.72×10^3	0.0
Gel-2•Cu$^+$	27.4	2.20×10^5	8.02×10^3	0.0
Gel-1	9.6	192.3	20	99.7
Gel-2	9.3	148.7	16	99.8

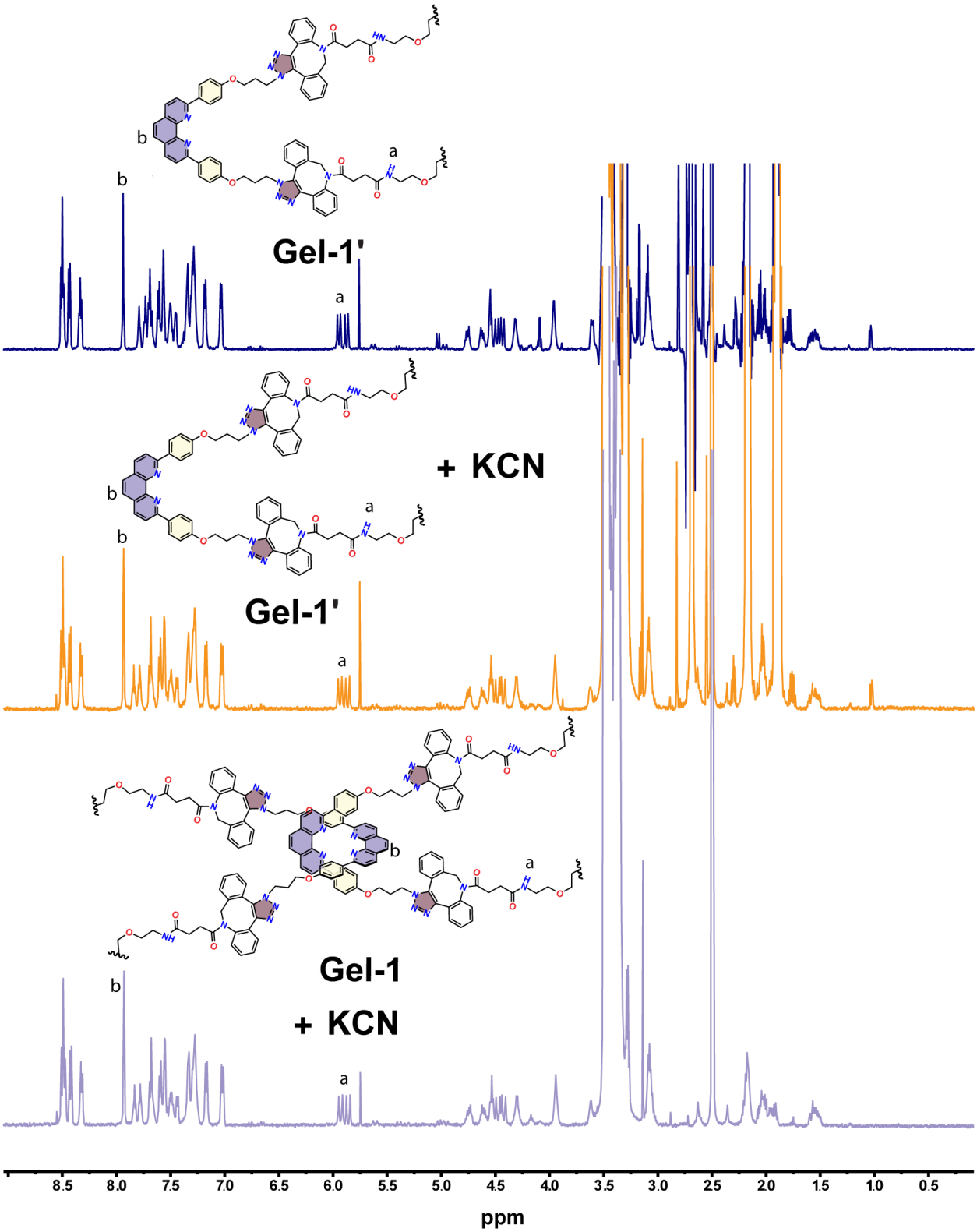


Figure S3.[1]H NMR (500 MHz, DMSO) of KCN tests conducted to determine if KCN was degrading the resulting gels.

Table S3. Estimated weight % of network incorporated in each gel at time of testing.

	60:40	70:30	80:20	90:10	100:0
Gel-1•Cu (400 µL)	10.5 ± 0.0	10.6 ± 0.0	10.7 ± 0.0	10.8 ± 0.0	10.9 ± 0.0
Gel-2•Cu^{+} (400 µL)	10.9 ± 0.0	11.0 ± 0.0	11.1 ± 0.0	11.2 ± 0.0	11.3 ± 0.0
Gel-1 (400 uL)	10.8 ± 0.4	11.7 ± 0.3	11.3 ± 0.4	12.4 ± 0.2	11.7 ± 0.3
Gel-2 (400 uL)	10.9 ± 0.3	11.7 ± 0.2	11.6 ± 0.4	12.4 ± 0.1	11.9 ± 0.5
Gel-1 (2.3 mL)	-	-	-	-	12.1 ± 0.1
Gel-2 (2.3 mL)	-	-	-	-	12.5 ± 0.0

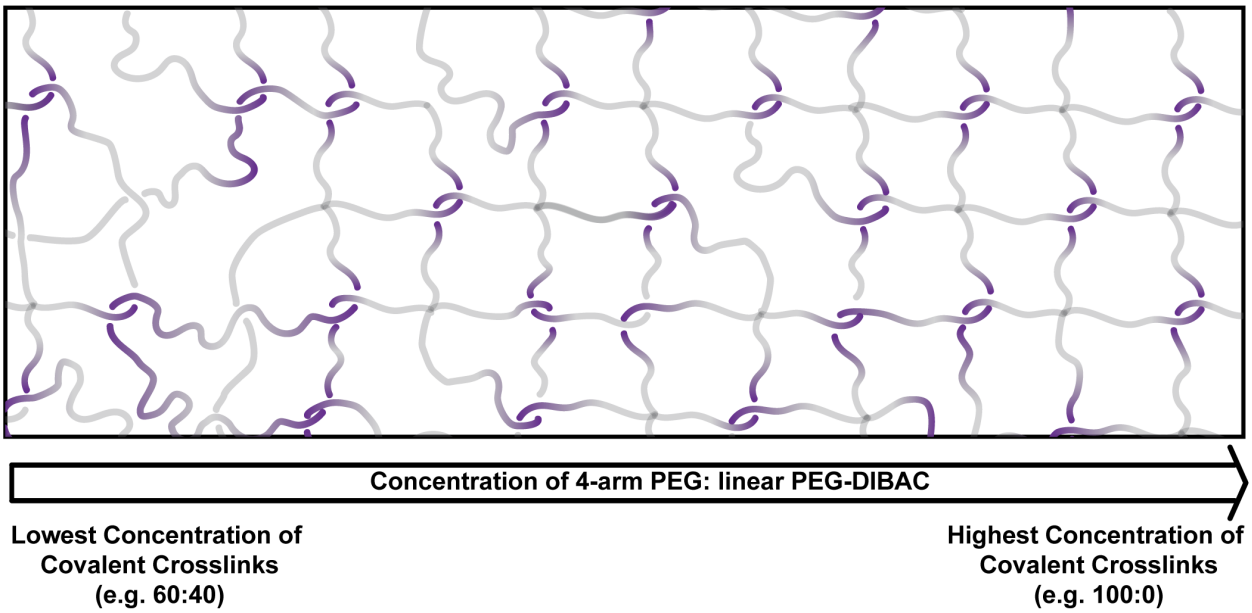


Figure S4. Visual representation of general network structure from low to high ratios of 4-arm to linear PEG-DIBAC. Increasing concentration of 4-arm PEG-DIBAC leads to increasing concentration of covalent cross-links.

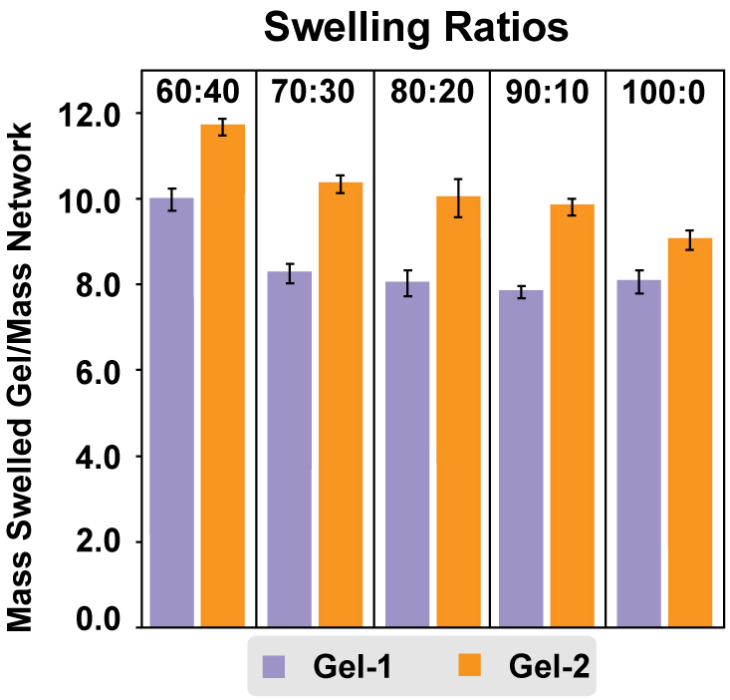


Figure S5. Equilibrium swelling tests of **Gel-1** and **Gel-2** at different ratios of 4-arm to linear PEG-DIBAC. The swelling and subsequent dried network masses were recorded for a minimum of four samples of each ratio.

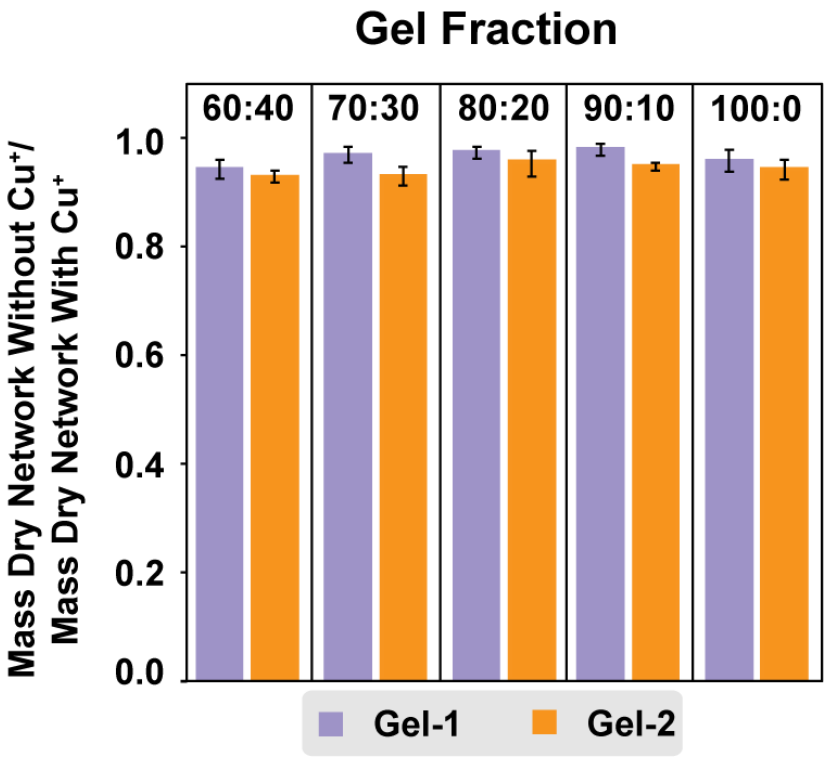


Figure S6. Gel fractions of **Gel-1** and **Gel-2** at different ratios of 4-arm to linear PEG-DIBAC were calculated by dividing the mass of the dry network without Cu^+ by the calculated mass of dry network with Cu^+ for a minimum of four samples for each ratio.

Table S4. Swelling ratio (SR) and gel fraction (GF) calculated for all ratios of 4-arm to linear PEG-DIBAC.

	60:40	70:30	80:20	90:10	100:0
Gel-1 (SR)	10.0 ± 0.3	8.3 ± 0.2	8.0 ± 0.3	7.8 ± 0.2	8.1 ± 0.3
Gel-2 (SR)	11.7 ± 0.2	10.3 ± 0.2	10.0 ± 0.5	9.8 ± 0.2	9.0 ± 0.2
Gel-1 (GF)	0.94 ± 0.02	0.97 ± 0.02	0.97 ± 0.01	0.98 ± 0.01	0.96 ± 0.02
Gel-2 (GF)	0.93 ± 0.01	0.93 ± 0.02	0.95 ± 0.02	0.95 ± 0.02	0.94 ± 0.02

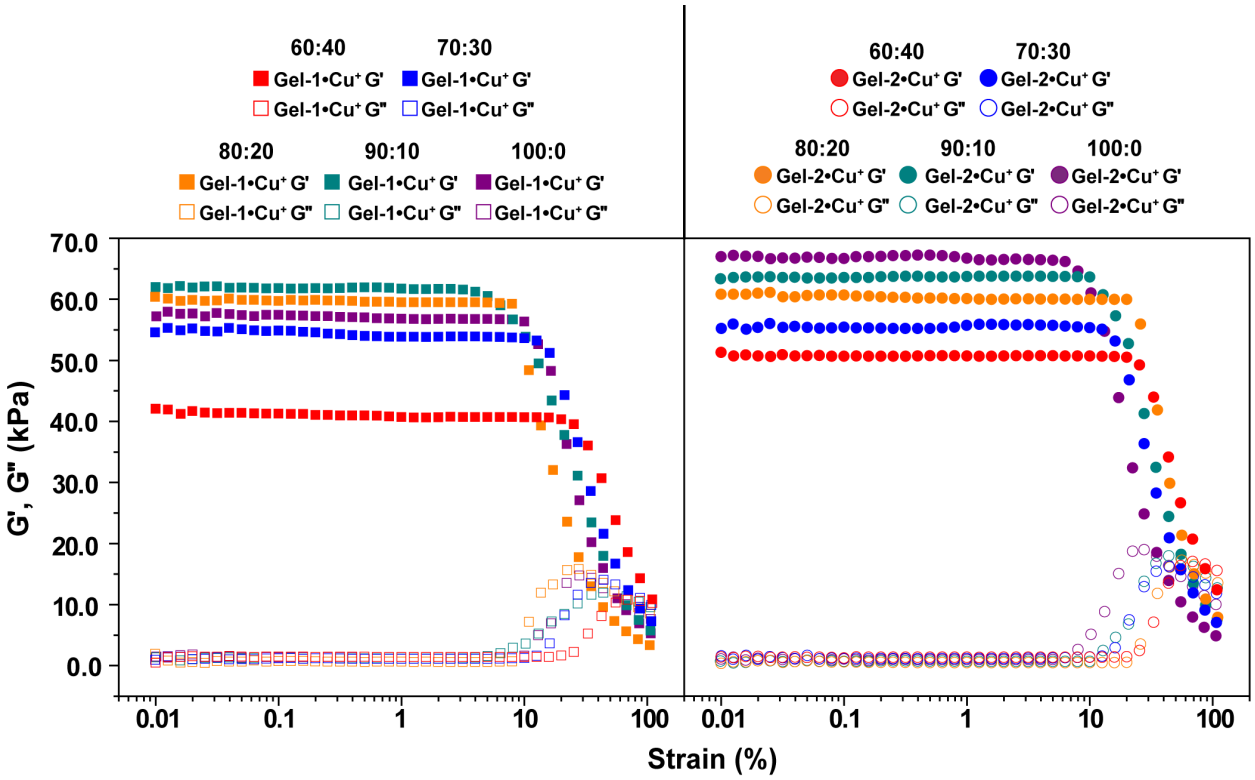


Figure S7. Strain sweeps from 0.01 to 100% strain on **Gel-1•Cu⁺** and **Gel-2•Cu⁺** for all ratios of 4-arm to linear PEG-DIBAC.

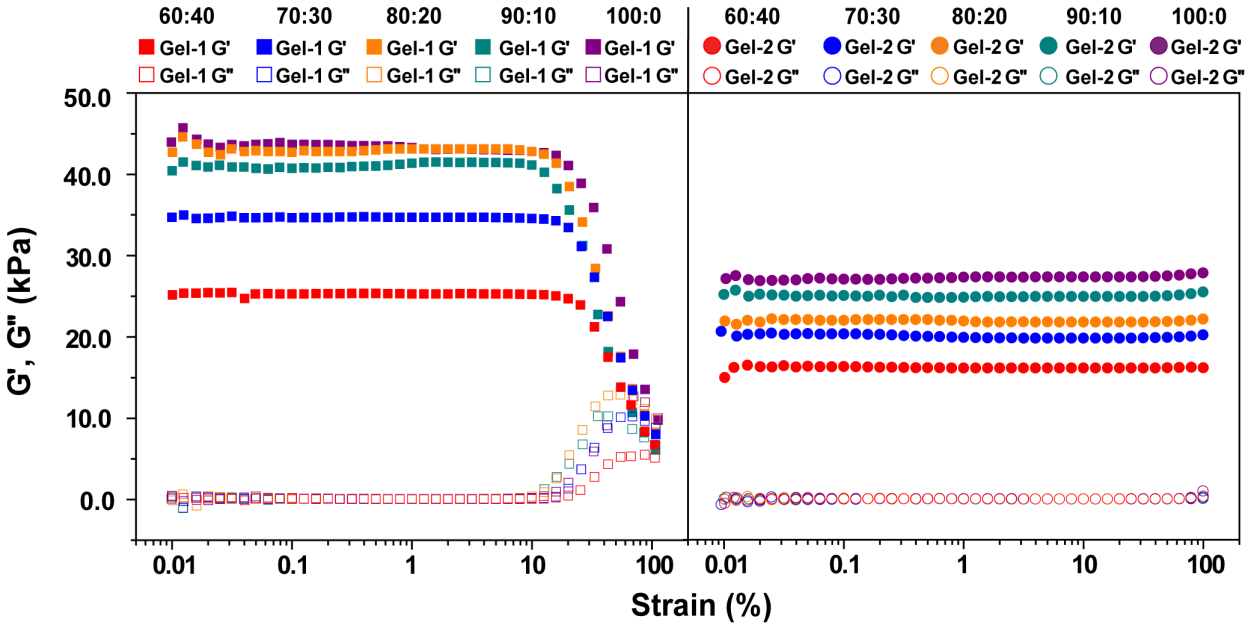


Figure S8. Strain sweeps from 0.01 to 100% strain on **Gel-1** and **Gel-2** for all ratios of 4-arm to linear PEG-DIBAC.

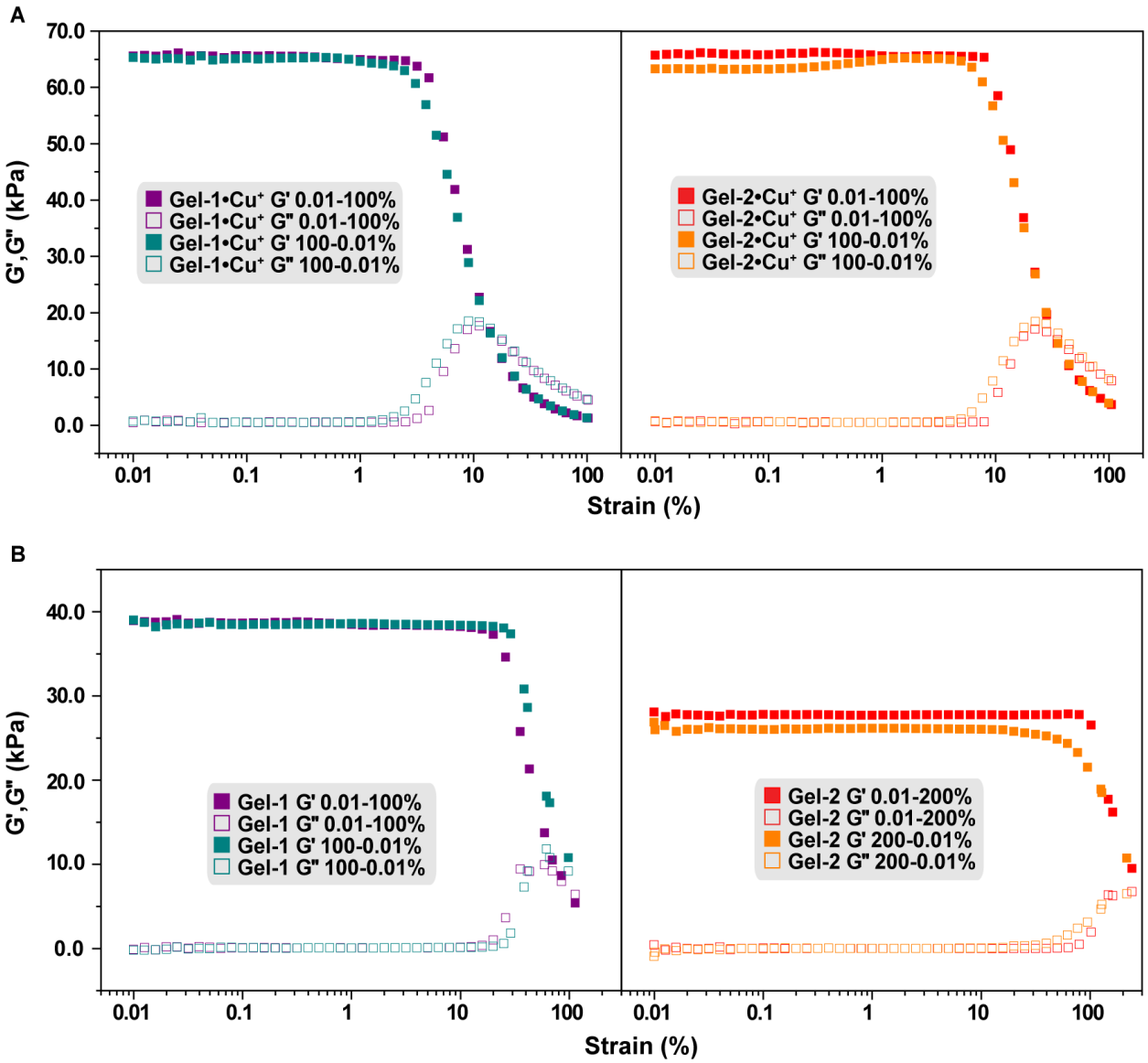


Figure S9. A. Strain sweeps from 0.01-100 rad/s and 100-0.01 rad/s of **Gel-1•Cu⁺** and **Gel-2•Cu⁺**. B. Strain sweeps from 0.01-100 rad/s and 100-0.01 rad/s for **Gel-1** and from 0.01-200 rad/s and 200-0.01 rad/s for **Gel-2**.

Table S5. Rheological analysis of **Gel-1** and **Gel-2** at different ratios of 4-arm PEG-DIBAC to linear PEG-DIBAC. Frequency sweeps were conducted at 1% strain with initial axial forces of 0.75 N upon each gel. Data was collected for the gels while still coordinated with copper (Cu^+) and after copper removal (Free). The storage moduli (G') at 1 rad/s are reported in kPa.

	60:40		**70:30**		**80:20**		**90:10**		**100:0**	
	Cu^+	Free	Cu^+	Free	Cu^+	Free	Cu^+	Free	Cu^+	Free
GEL-1	40 ± 1.0	24 ± 1.3	54 ± 2.1	35 ± 1.7	57 ± 1.8	42 ± 1.3	60 ± 1.9	40 ± 1.5	56 ± 1.6	41 ± 1.6
GEL-2	50 ± 0.7	16 ± 0.2	55 ± 0.7	19 ± 0.7	59 ± 1.8	22 ± 1.1	63 ± 2.0	24 ± 1.4	65 ± 1.9	27 ± 1.6

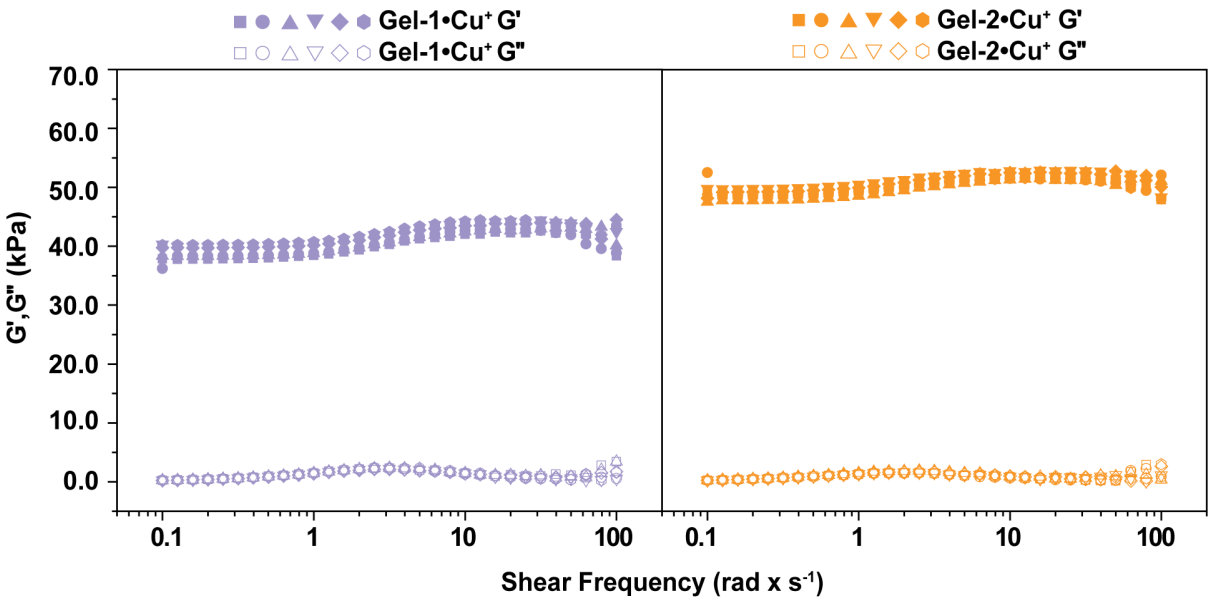


Figure S10. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1•Cu^{+}** and **Gel-2•Cu^{+}** for the 60:40 ratio of 4-arm to linear PEG-DIBAC.

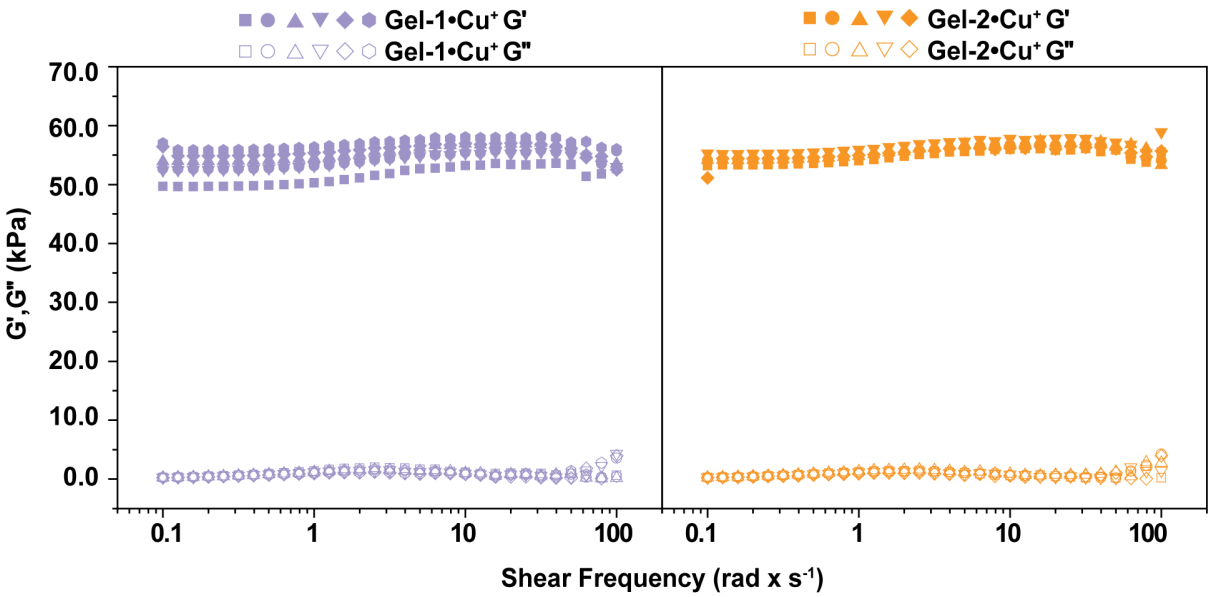


Figure S11. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1•Cu^{+}** and **Gel-2•Cu^{+}** for the 70:30 ratio of 4-arm to linear PEG-DIBAC.

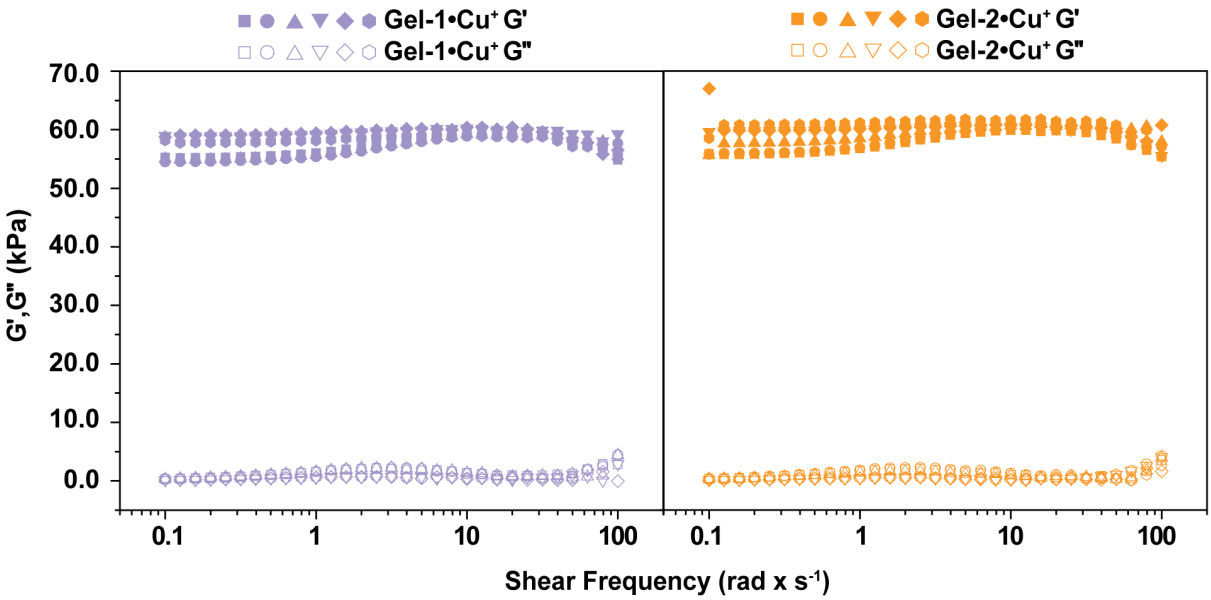


Figure S12. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1•Cu^{+}** and **Gel-2•Cu^{+}** for the 80:20 ratio of 4-arm to linear PEG-DIBAC.

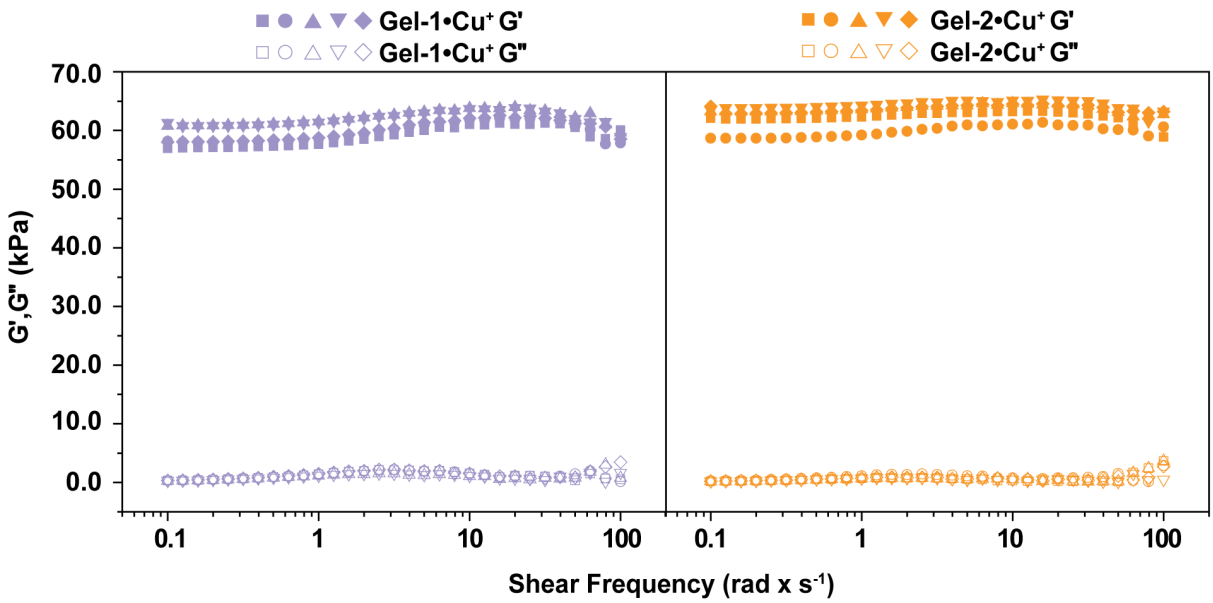


Figure S13. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1•Cu^{+}** and **Gel-2•Cu^{+}** for the 90:10 ratio of 4-arm to linear PEG-DIBAC.

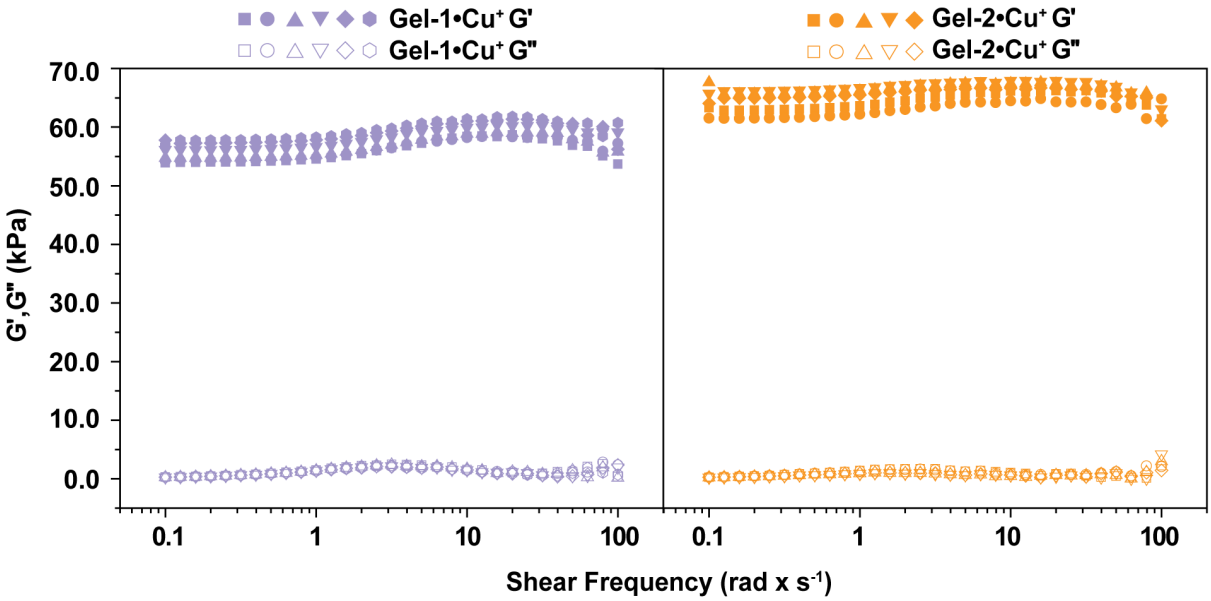


Figure S14. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1•Cu⁺** and **Gel-2•Cu⁺** for the 100:0 ratio of 4-arm to linear PEG-DIBAC.

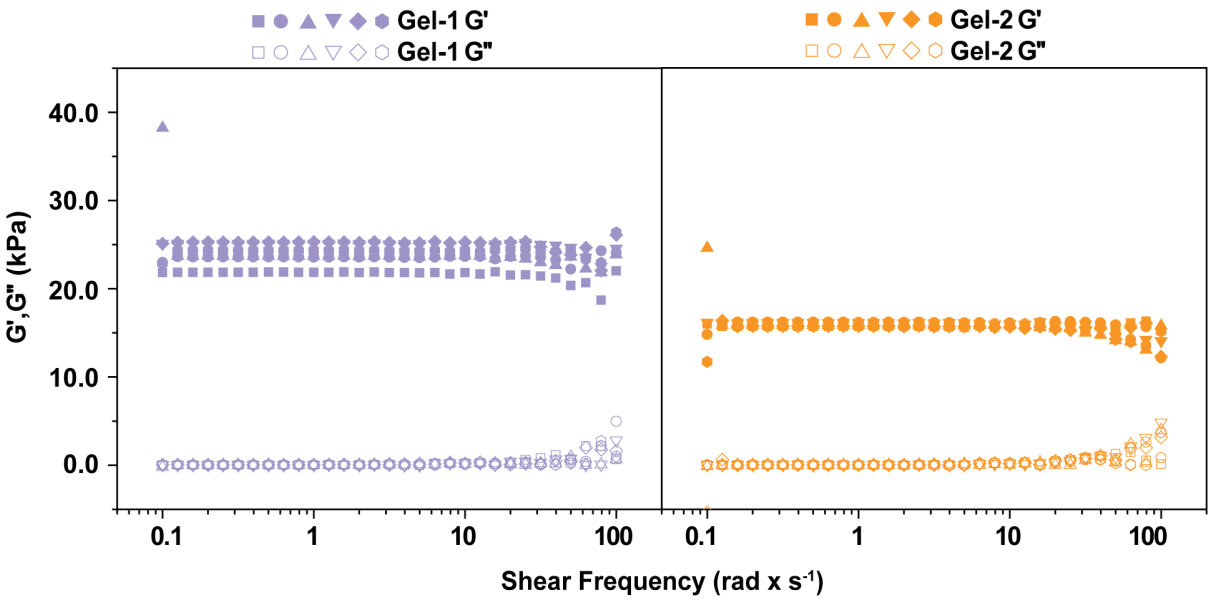


Figure S15. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1** and **Gel-2** for the 60:40 ratio of 4-arm to linear PEG-DIBAC.

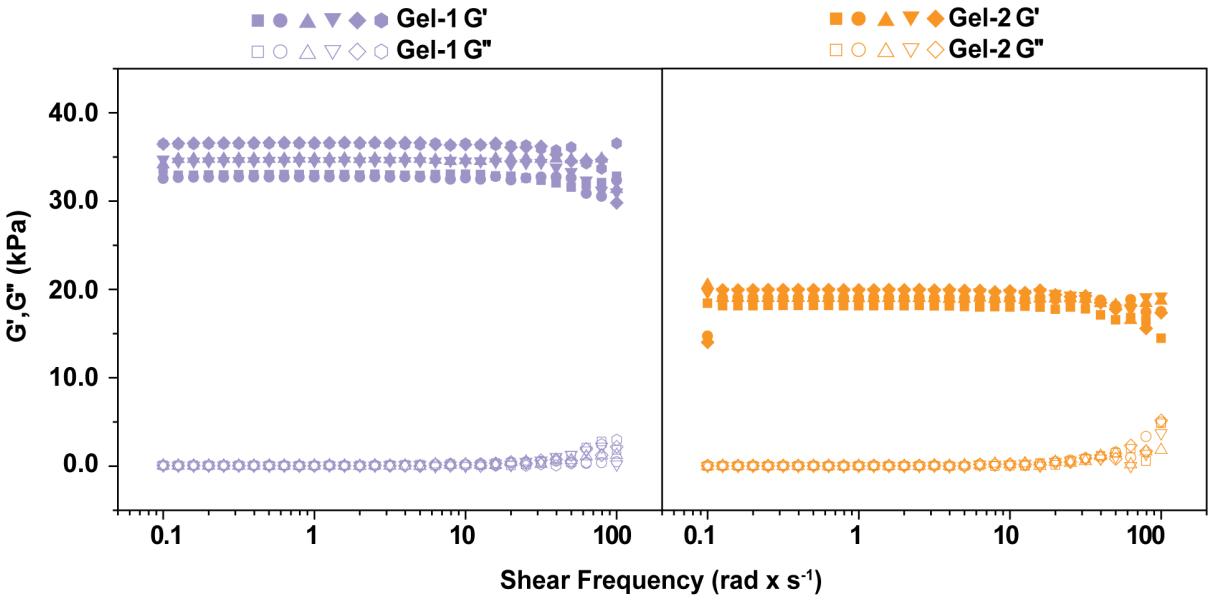


Figure S16. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1** and **Gel-2** for the 70:30 ratio of 4-arm to linear PEG-DIBAC.

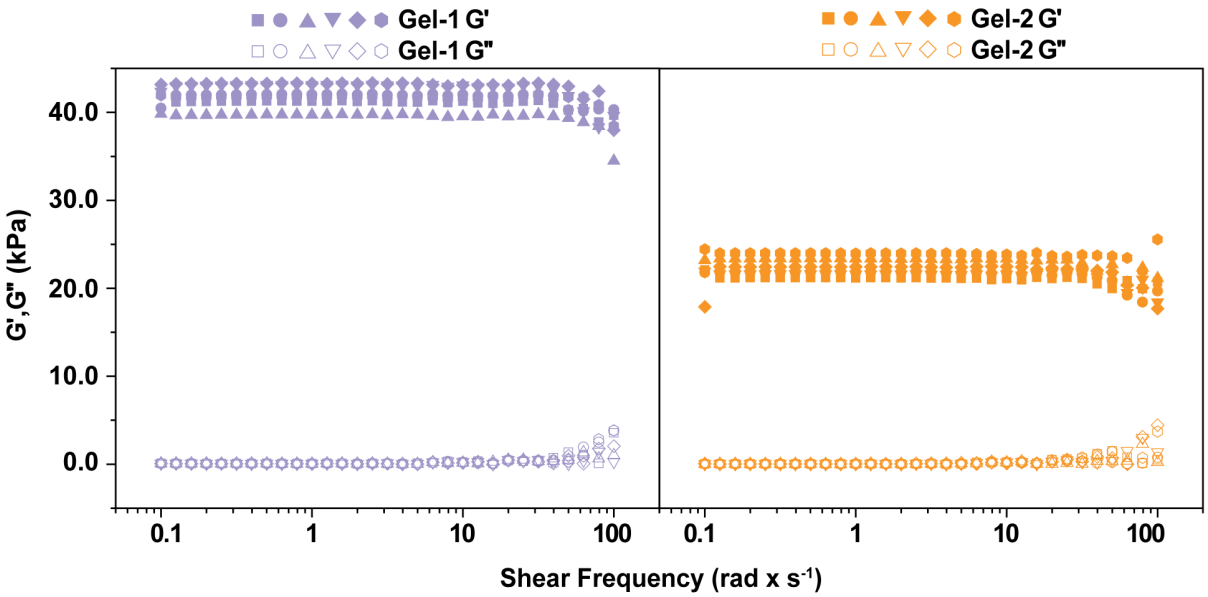


Figure S17. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1** and **Gel-2** for the 80:20 ratio of 4-arm to linear PEG-DIBAC.

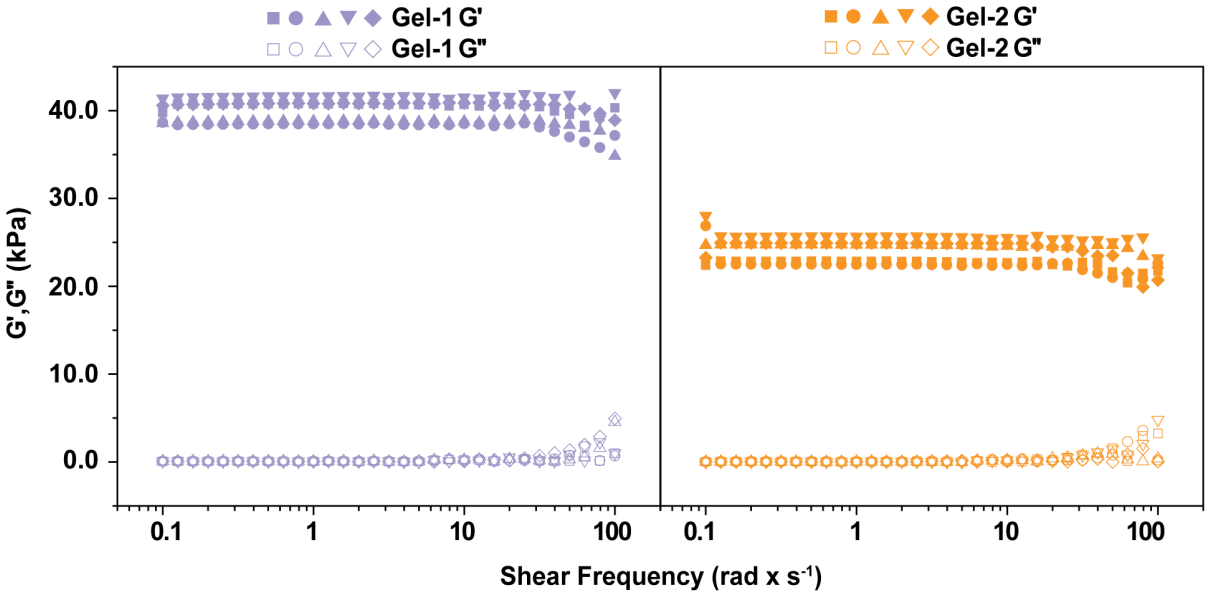


Figure S18. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1** and **Gel-2** for the 90:10 ratio of 4-arm to linear PEG-DIBAC.

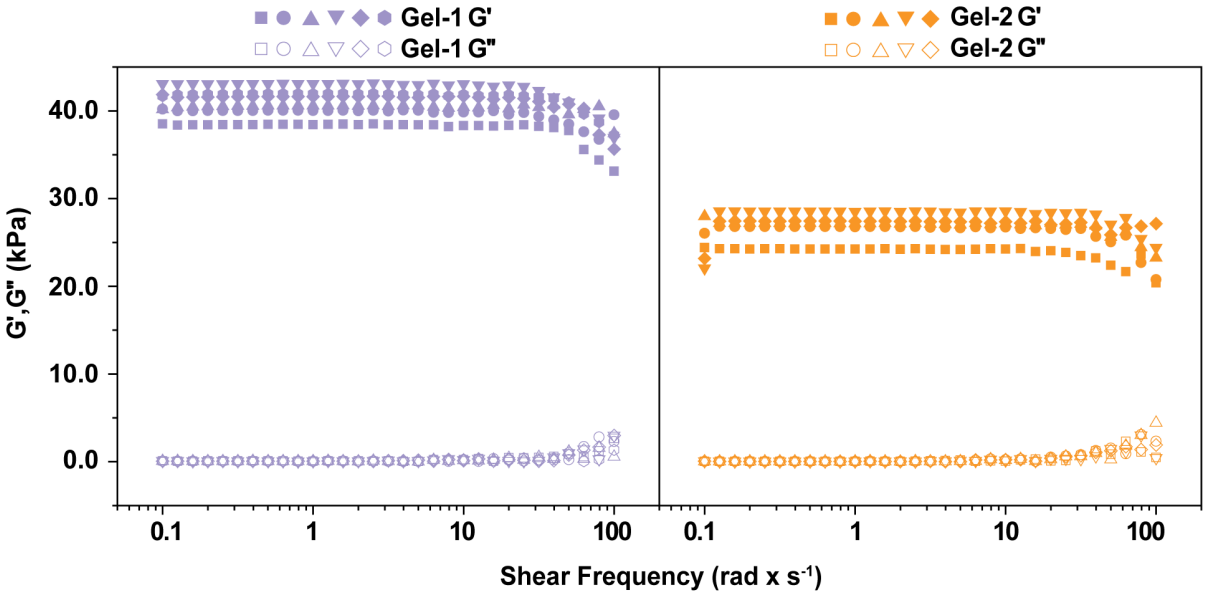


Figure S19. Frequency sweeps from 0.01 to 100 rad/s^{-1} on **Gel-1** and **Gel-2** for the small-scale 100:0 ratio of 4-arm to linear PEG-DIBAC.

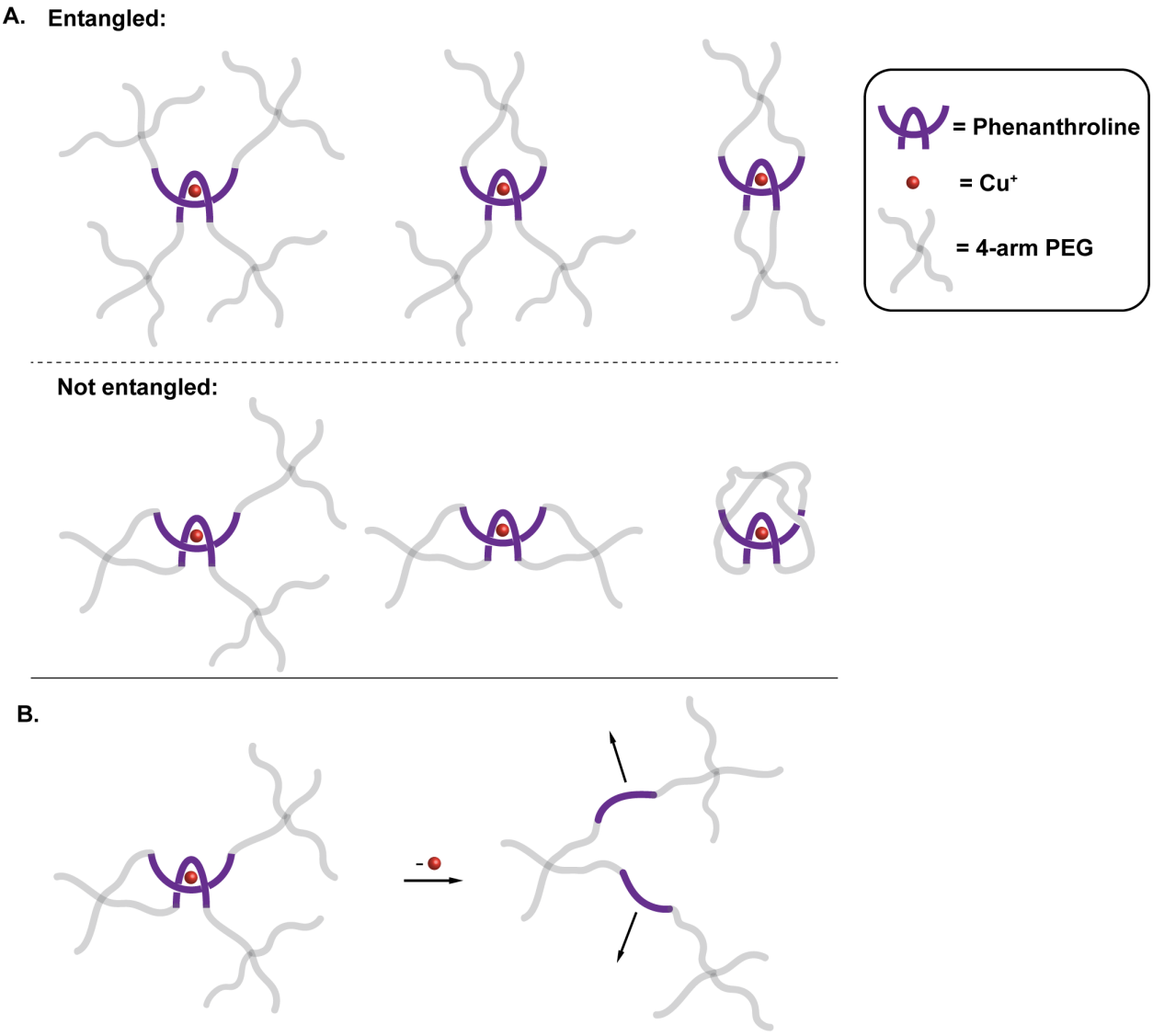


Figure S20. A. Possible network formations starting from phenanthroline building blocks that lead to entanglement and disentanglement. We assume all azide functional groups on the phenanthroline copper coordination complexes react with 4-arm PEG-DIBAC. B. Schematic of disentanglement upon demetallation.

Table S6. Efficiency of the transformation to a trapped entanglement (x) from a supramolecular template.

4-arm:linear	G'_{Cu}	G'_1	G'_2	x
60:40	39.6	24.0	15.9	0.341
70:30	53.8	34.7	19.1	0.448
80:20	57.3	41.9	22.4	0.558
90:10	59.8	39.9	24.1	0.443
100:0	56.2	40.9	26.8	0.454

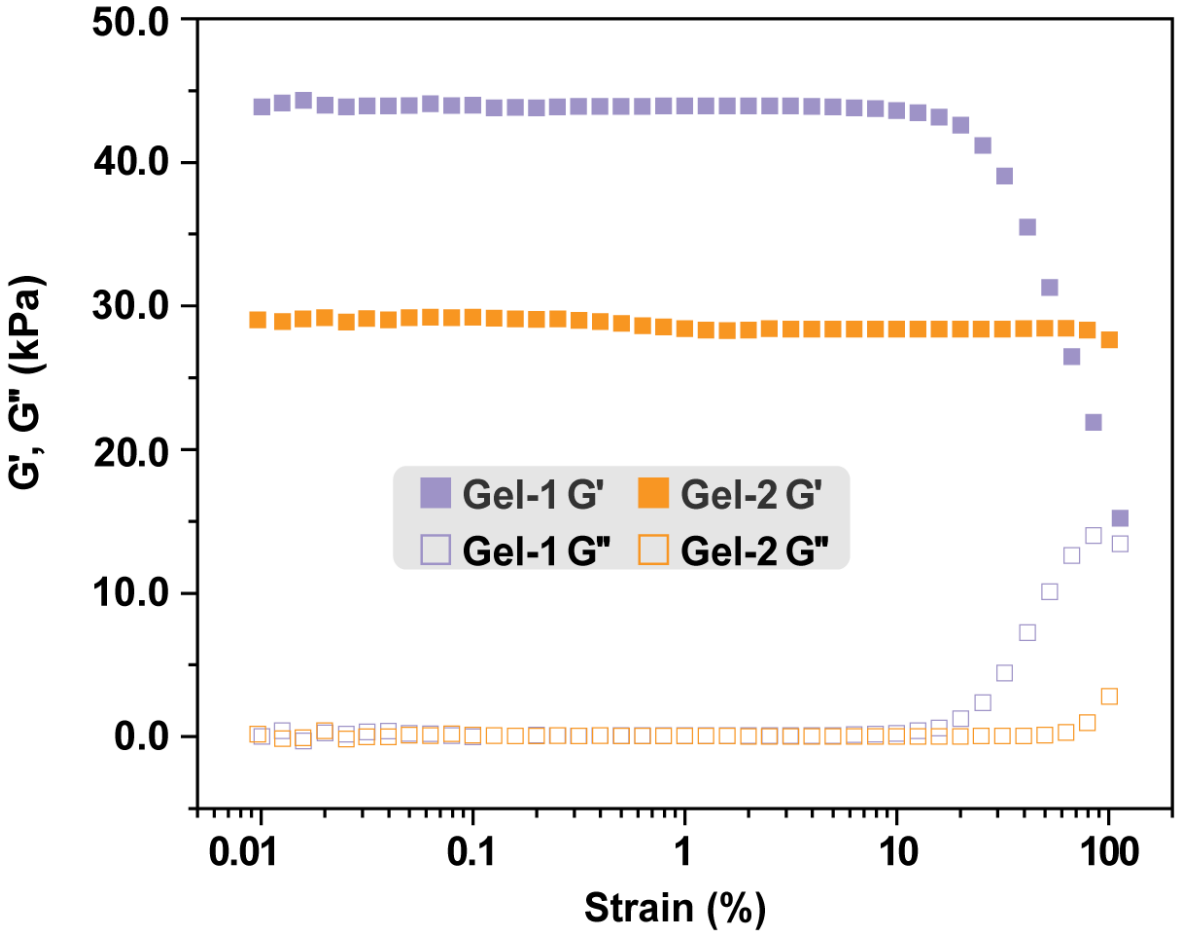


Figure S21. Strain sweeps from 0.01 to 100% strain on **Gel-1** and **Gel-2** for the large scale 100:0 4-arm to linear PEG-DIBAC.

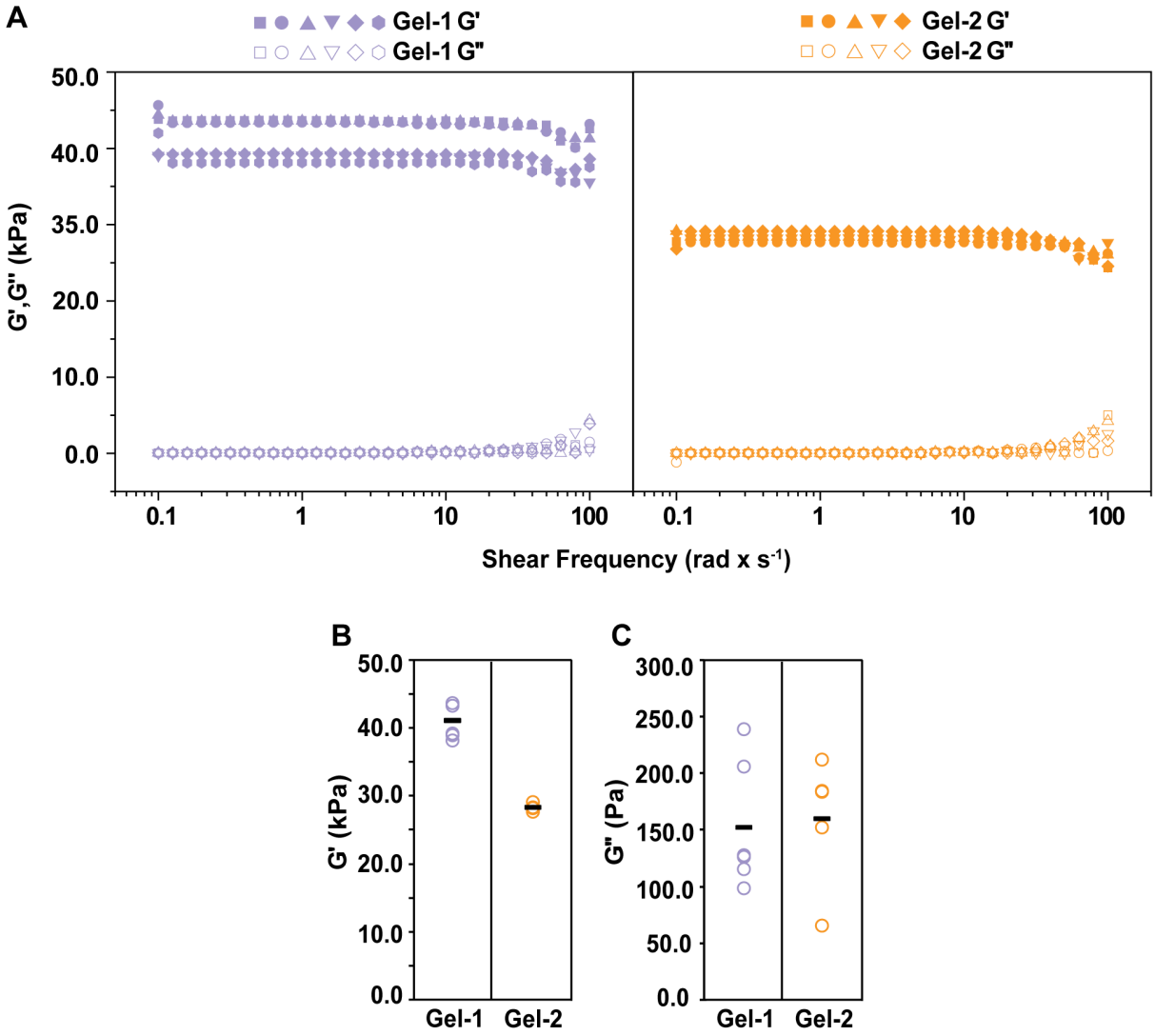


Figure S22. A. Frequency sweeps from 0.01 to 100 rad/s on Gel-1 and Gel-2 of the large-scale 100:0 ratio of 4-arm to linear PEG-DIBAC. B. Storage modulus (G') at 10 rad/s. The average of all trials is denoted by the solid black line. C. Loss modulus (G'') at 10 rad/s. The average of all trials is denoted by the solid black line.

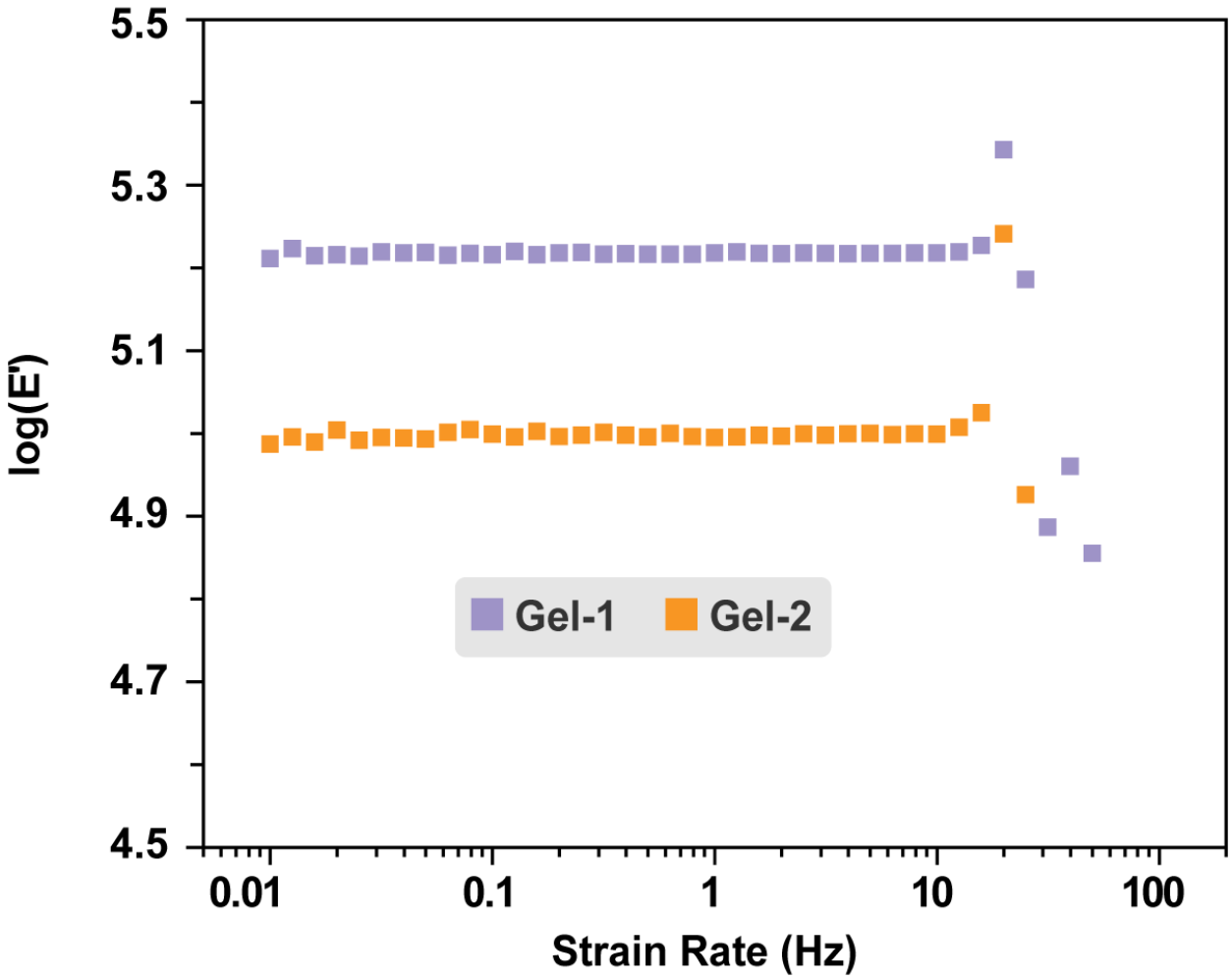


Figure S23. Strain rate scan (strain is 1%) for the tensile test of the large scale 100:0 4-arm to linear PEG-DIBAC gels.

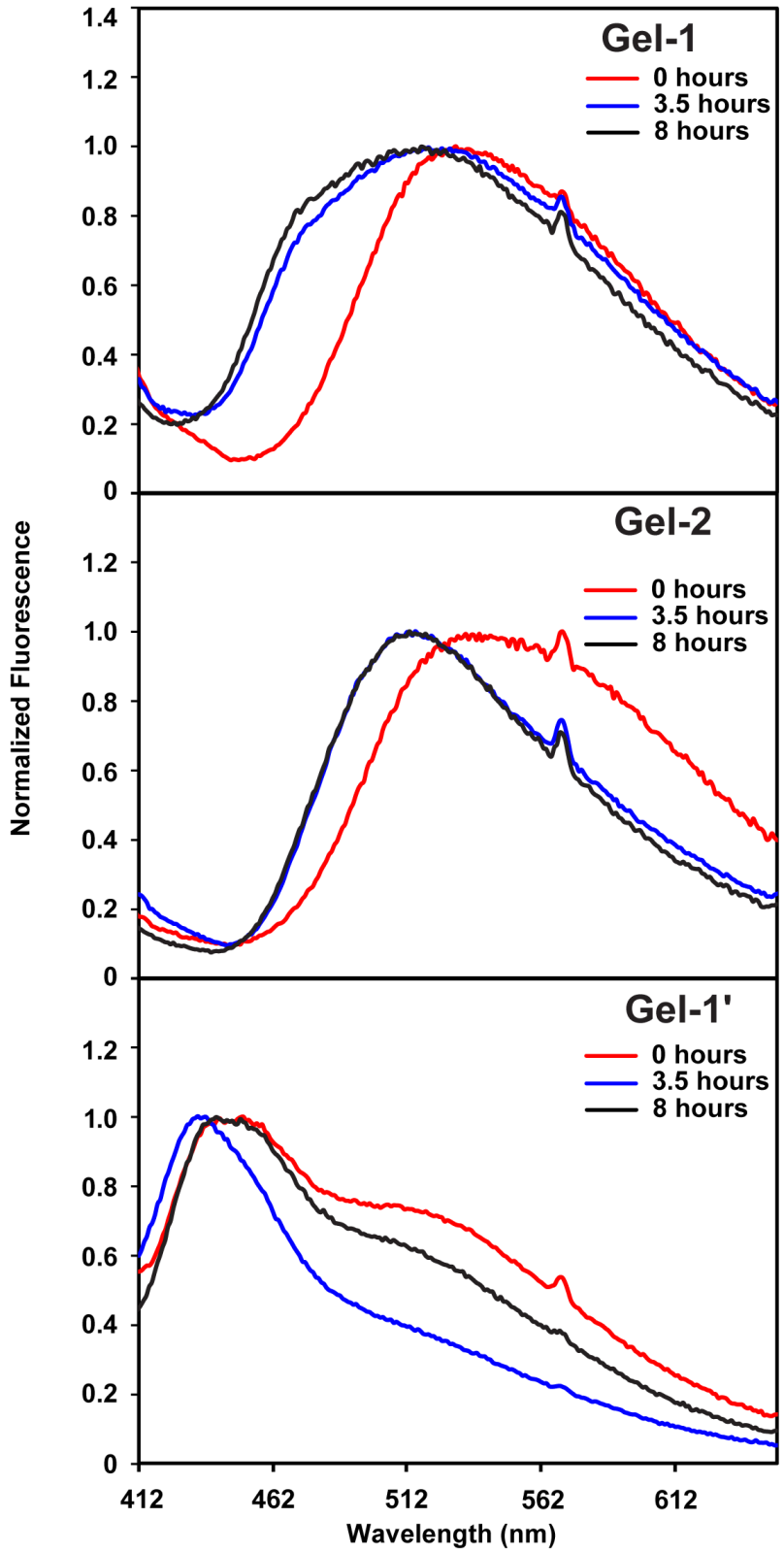


Figure S24. Fluorescence at 365 nm normalized to the highest peak of **Gel-1**, **Gel-2**, and **Gel-1'** at 0, 3.5, and 8 hours after being removed from negative pressure.

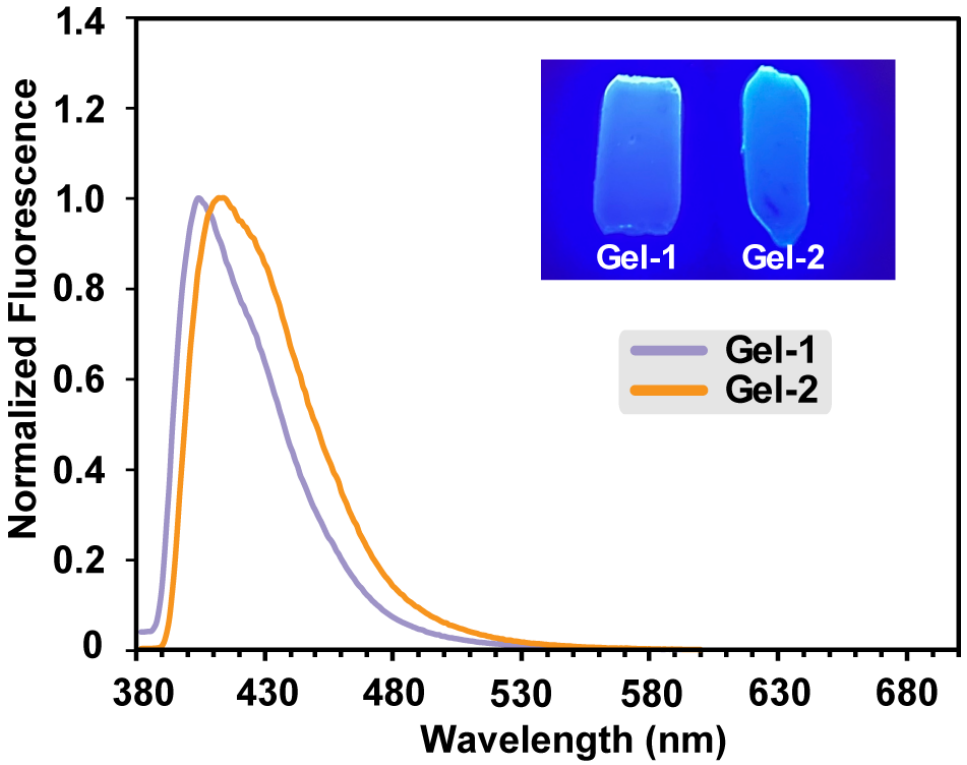


Figure S25. Fluorescence spectra at 365 nm of **Gel-1** and **Gel-2** normalized to the highest peak while solvated with propylene carbonate. The inset image is of both gels under 365 nm UV light.

4. SPECTRAL DATA

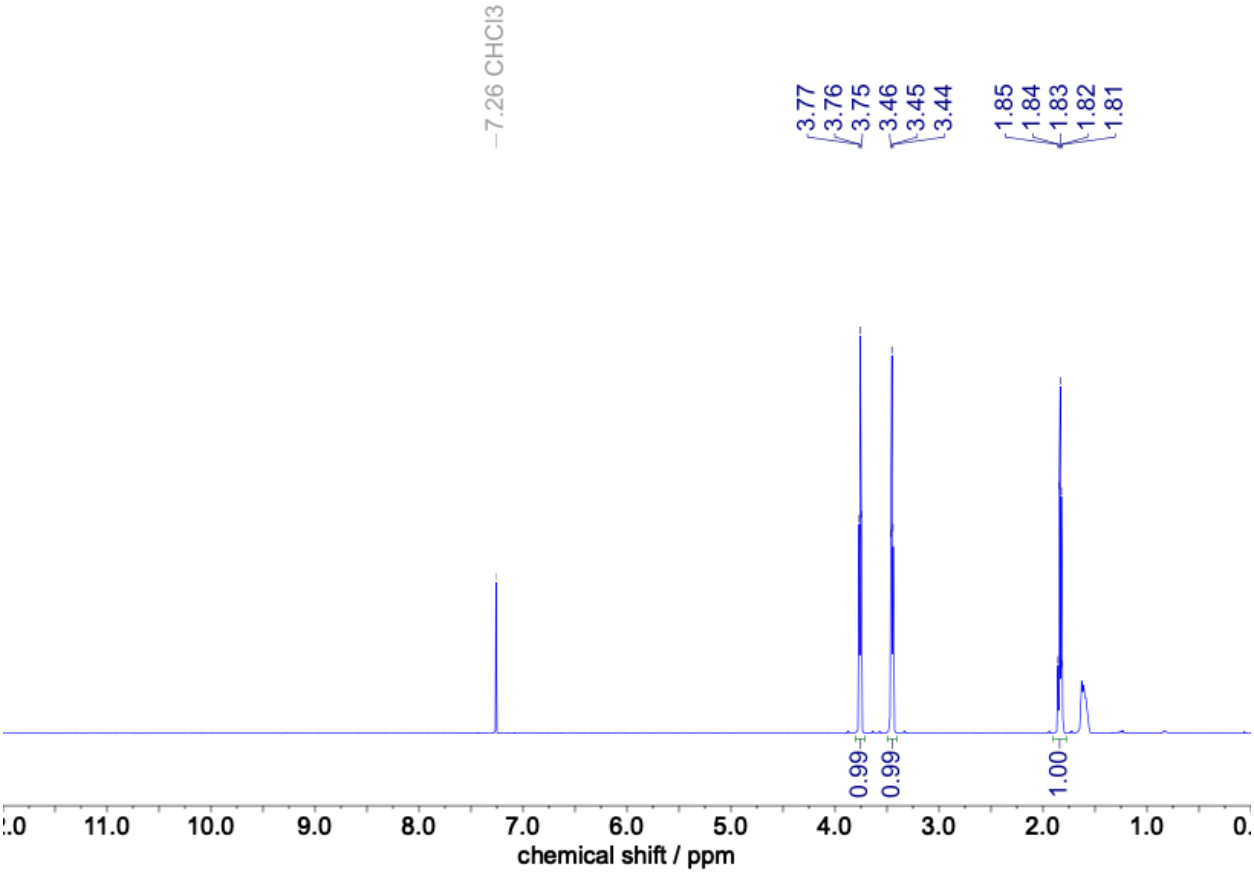


Figure S26. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **S1**.

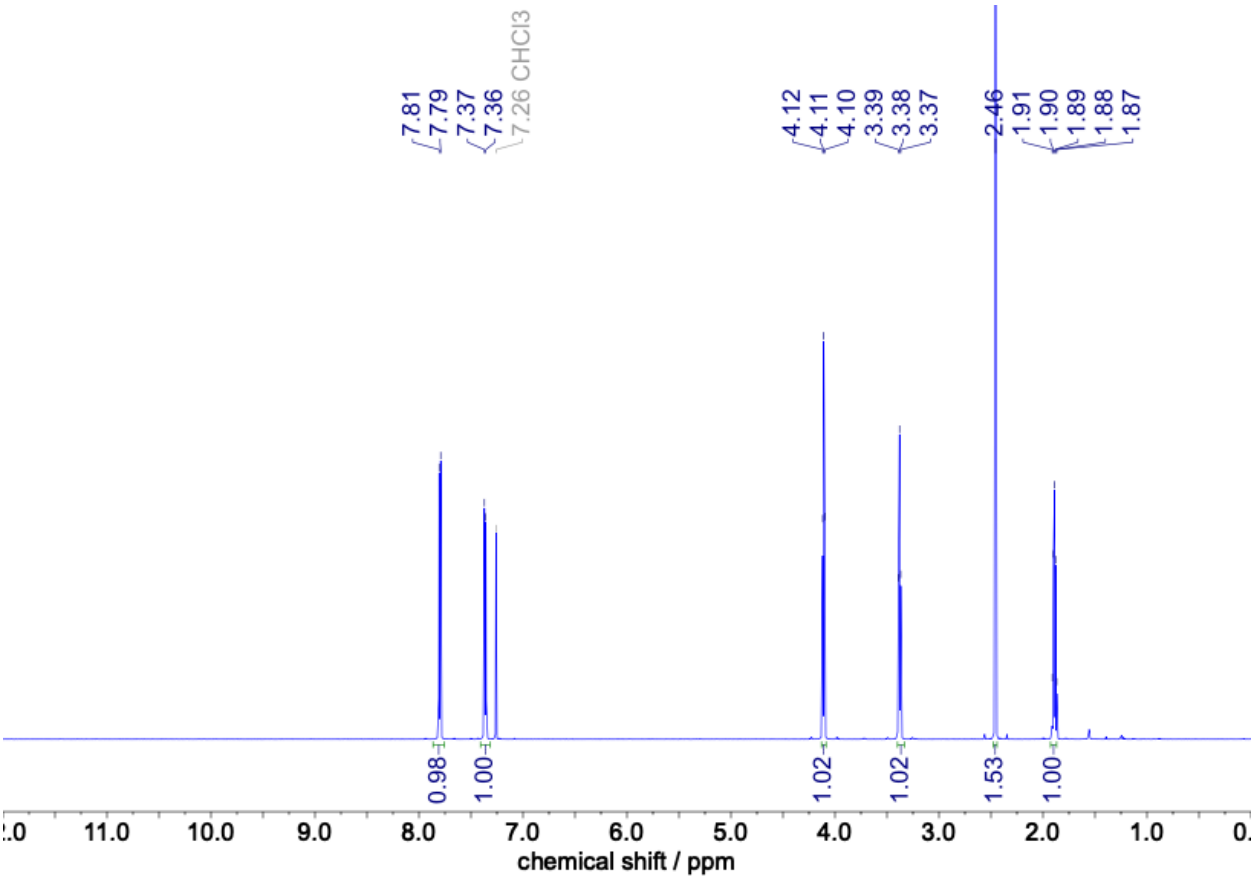


Figure S27. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **S2**.

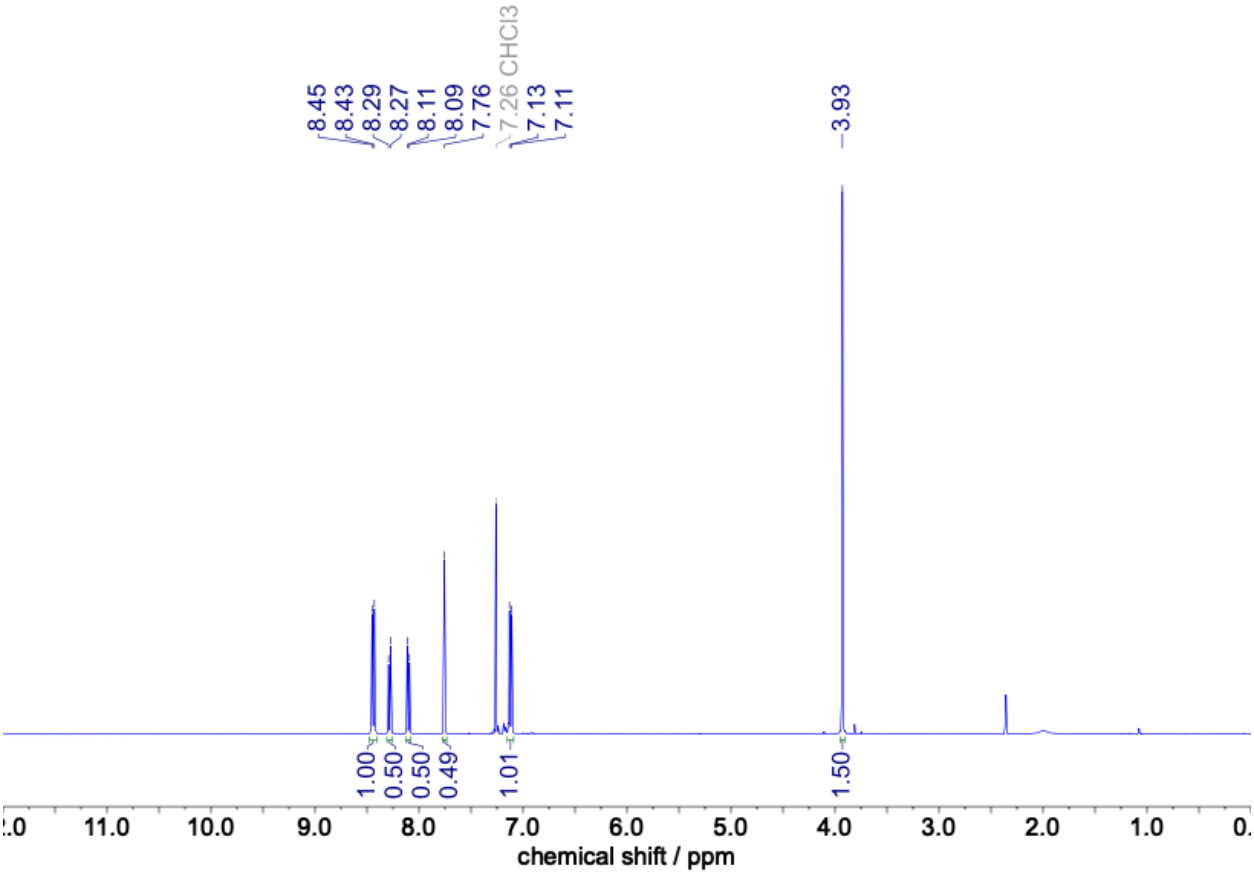


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **S3**.

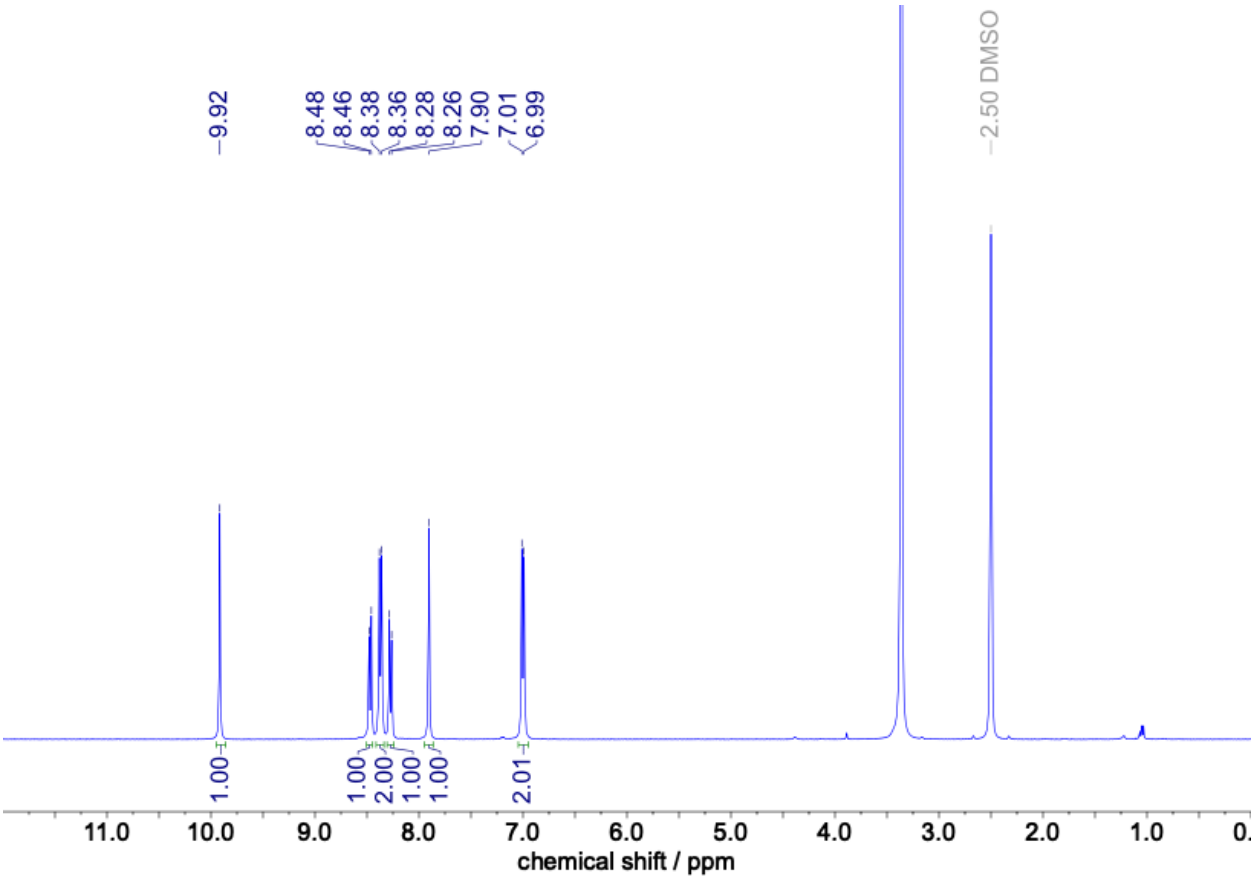


Figure S29. ^{1}H NMR (400 MHz, DMSO-*d*6) spectrum of compound **S4**.

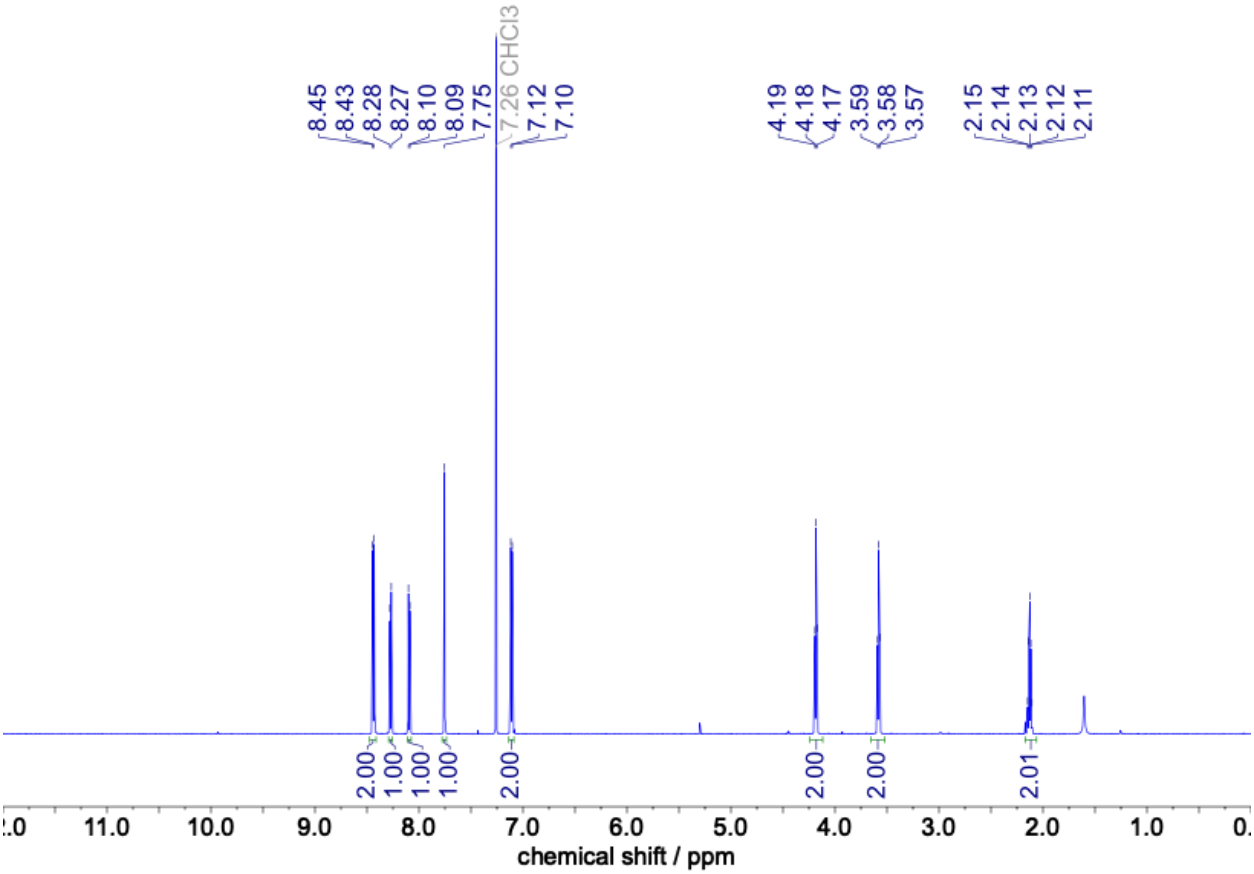


Figure S30. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **L1**.

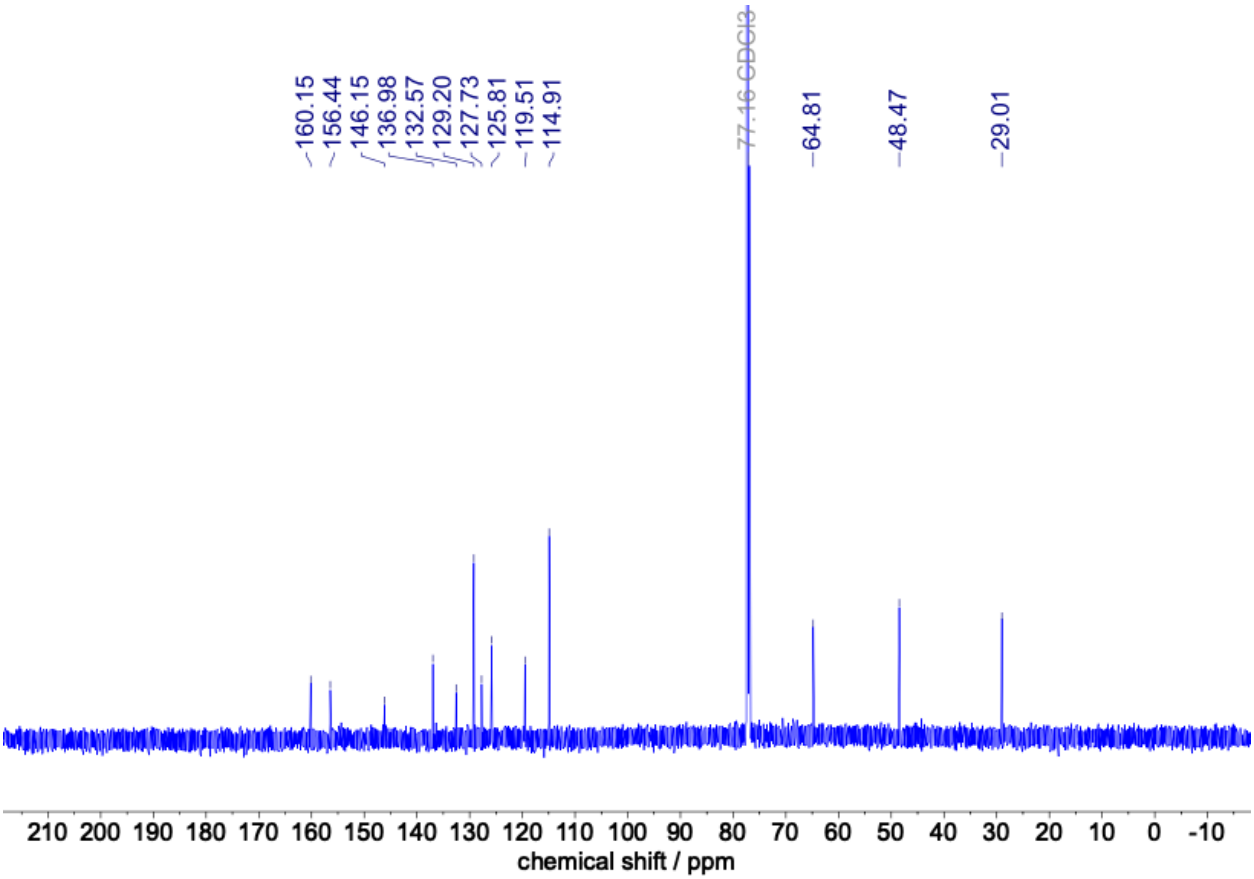


Figure S31. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound **L1**.

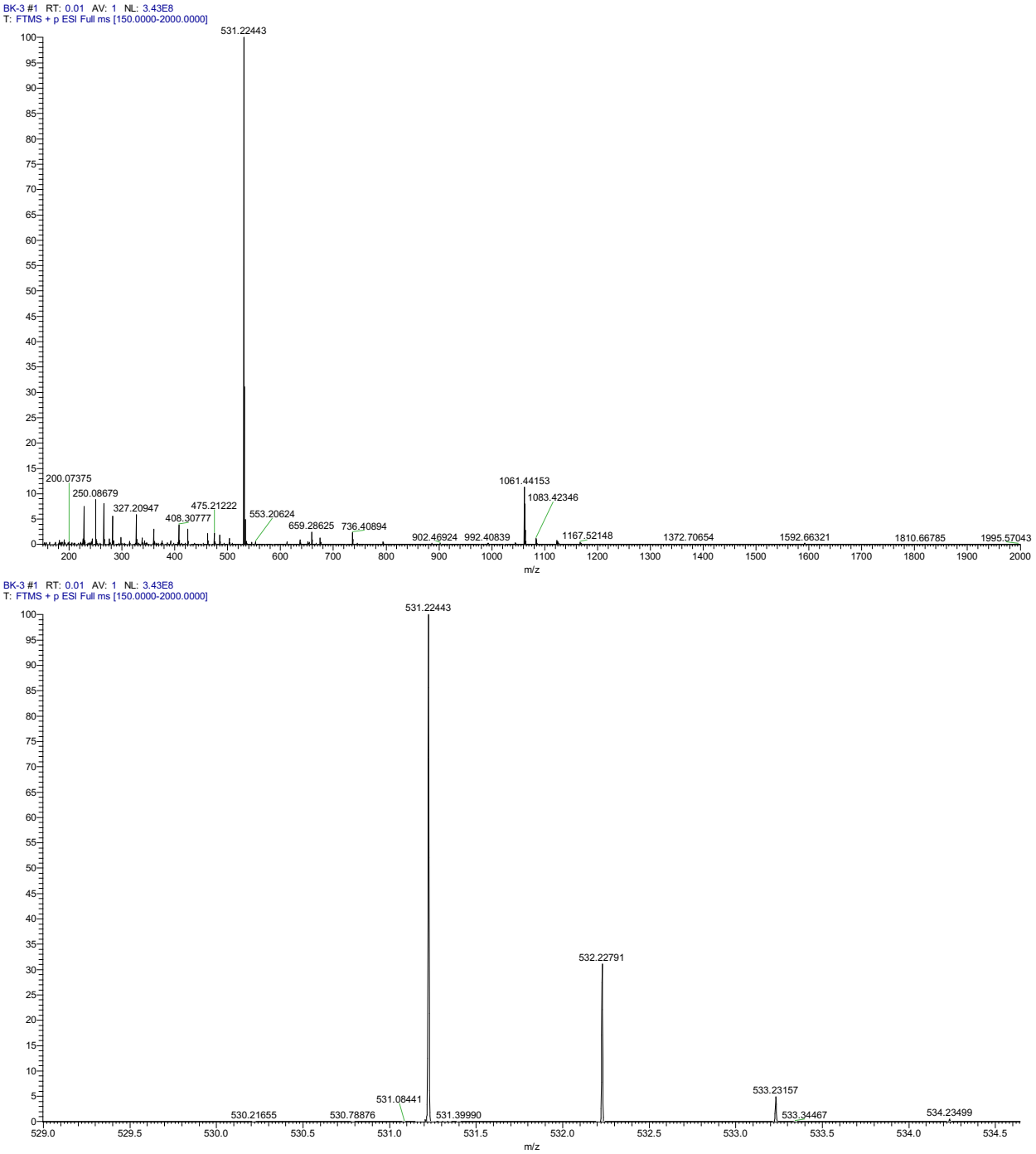


Figure S32. HRMS (ESI, positive mode) spectrum of compound **L1**.

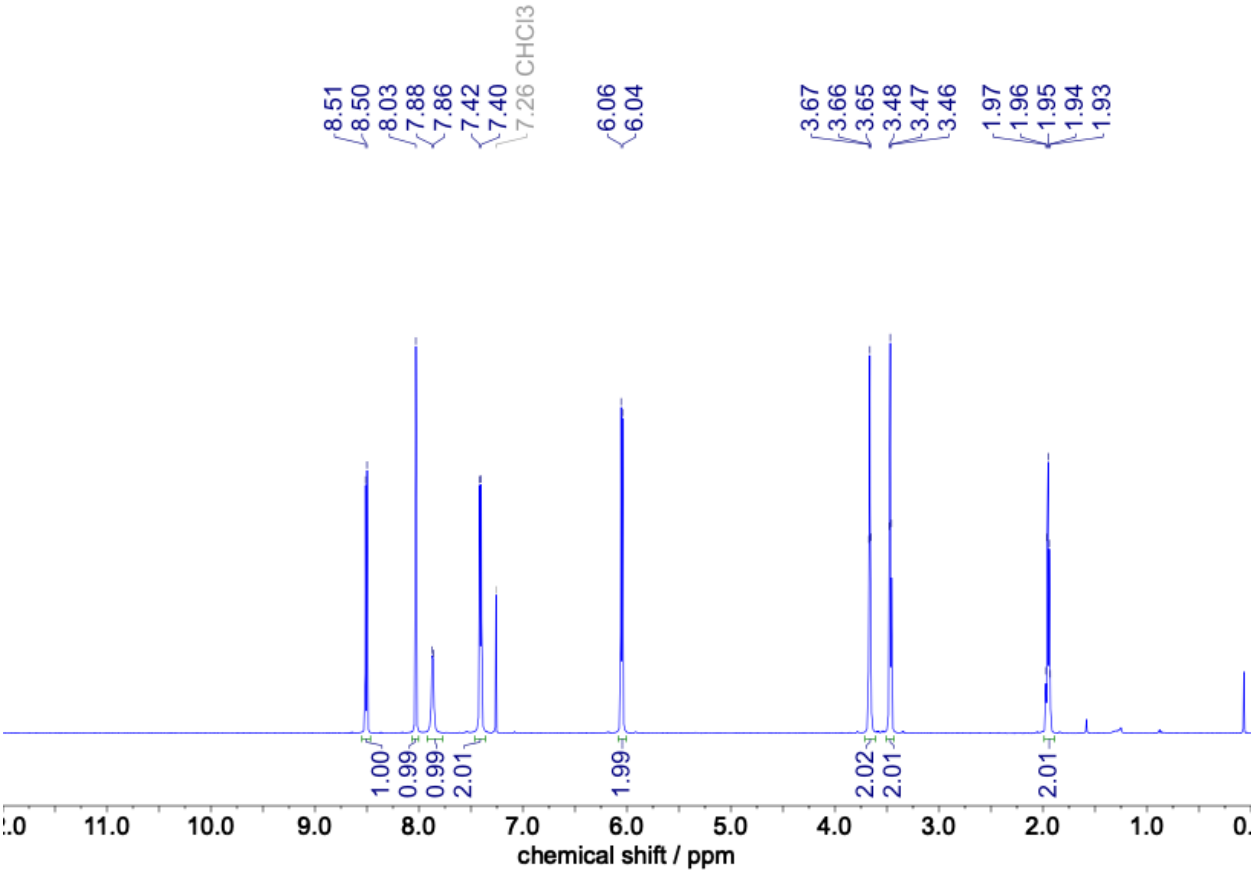


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **L1•Cu**$^{+}$.

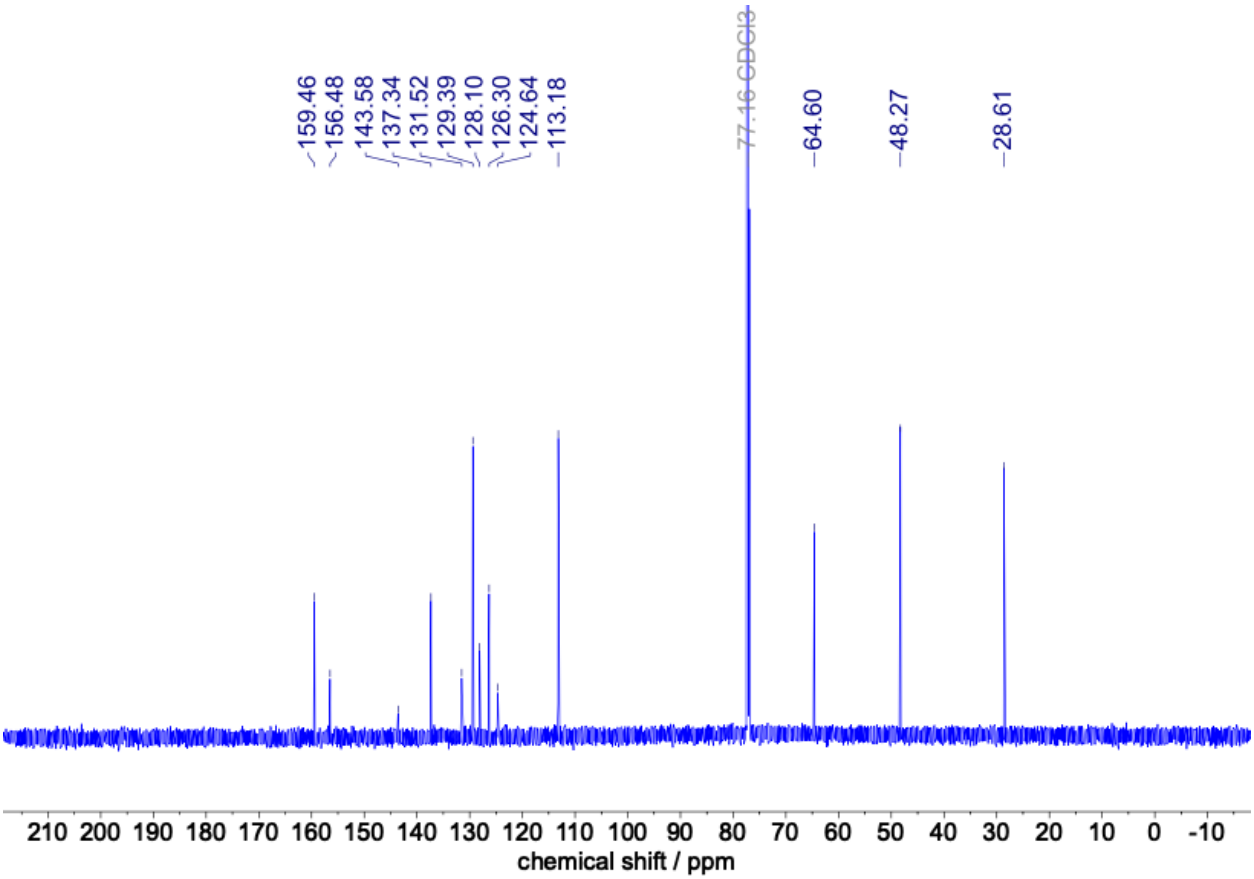


Figure S34. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound **L1•Cu**$^{+}$.

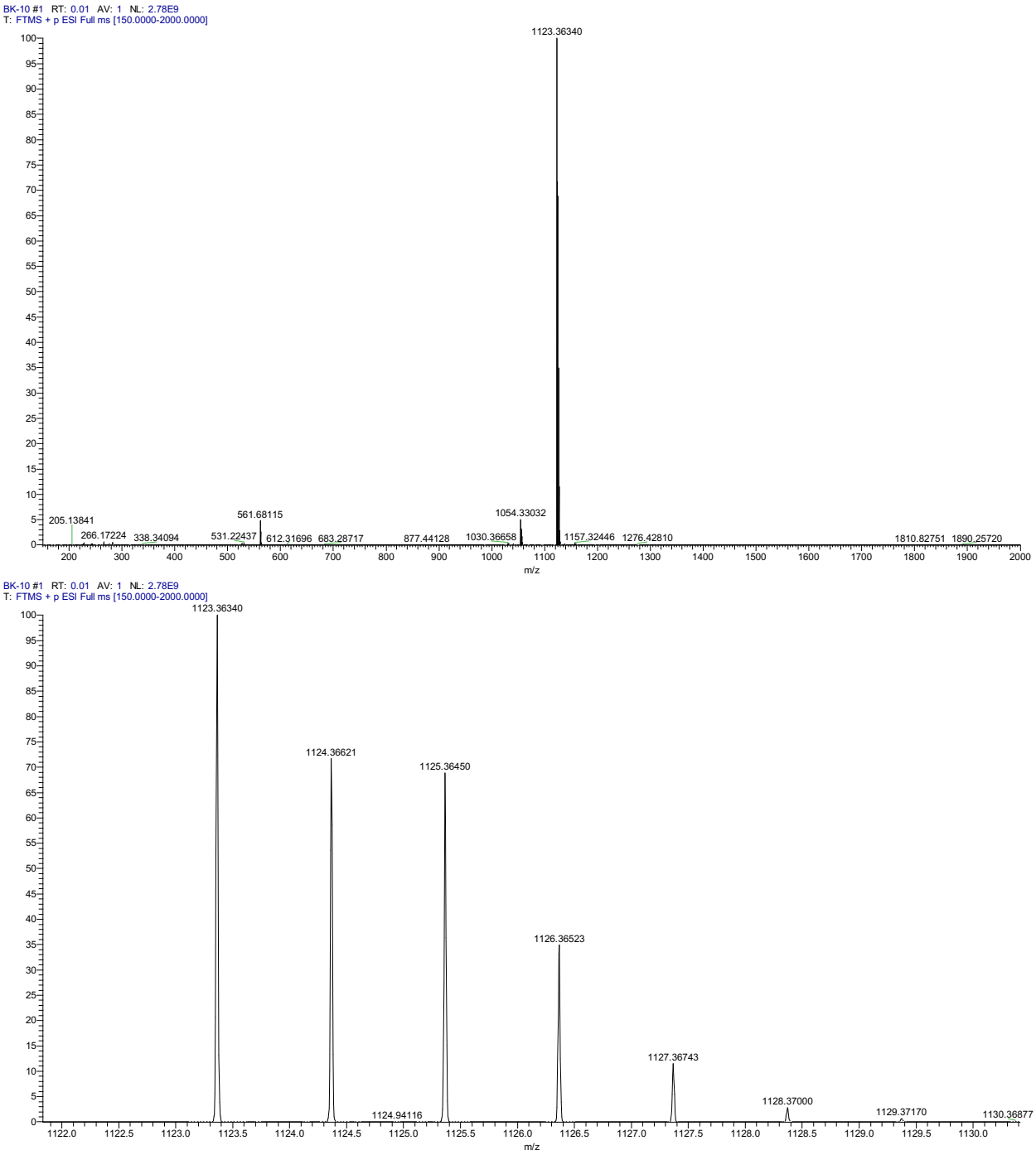


Figure S35. HRMS (ESI, positive mode) spectrum of compound **L1•Cu**$^{+}$.

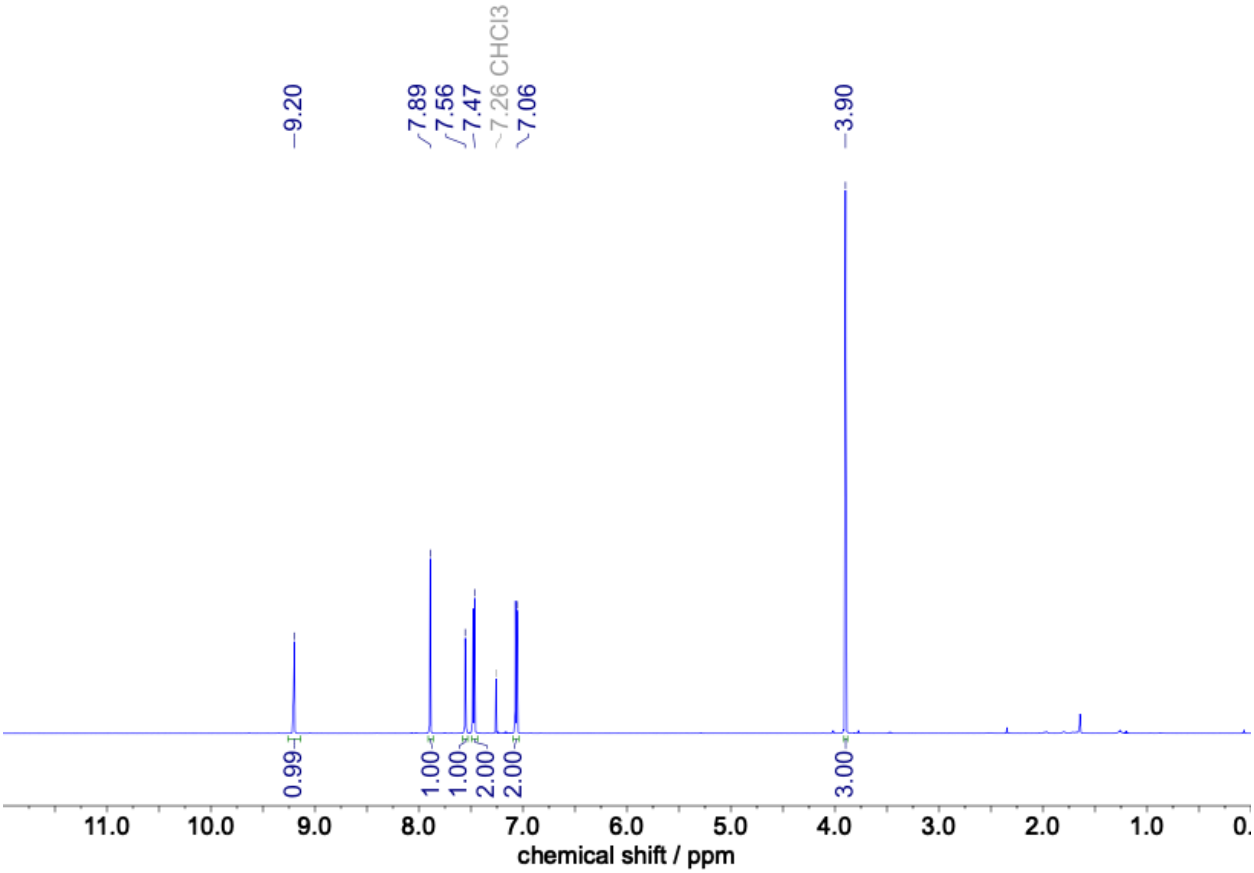


Figure S36. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **S5**.

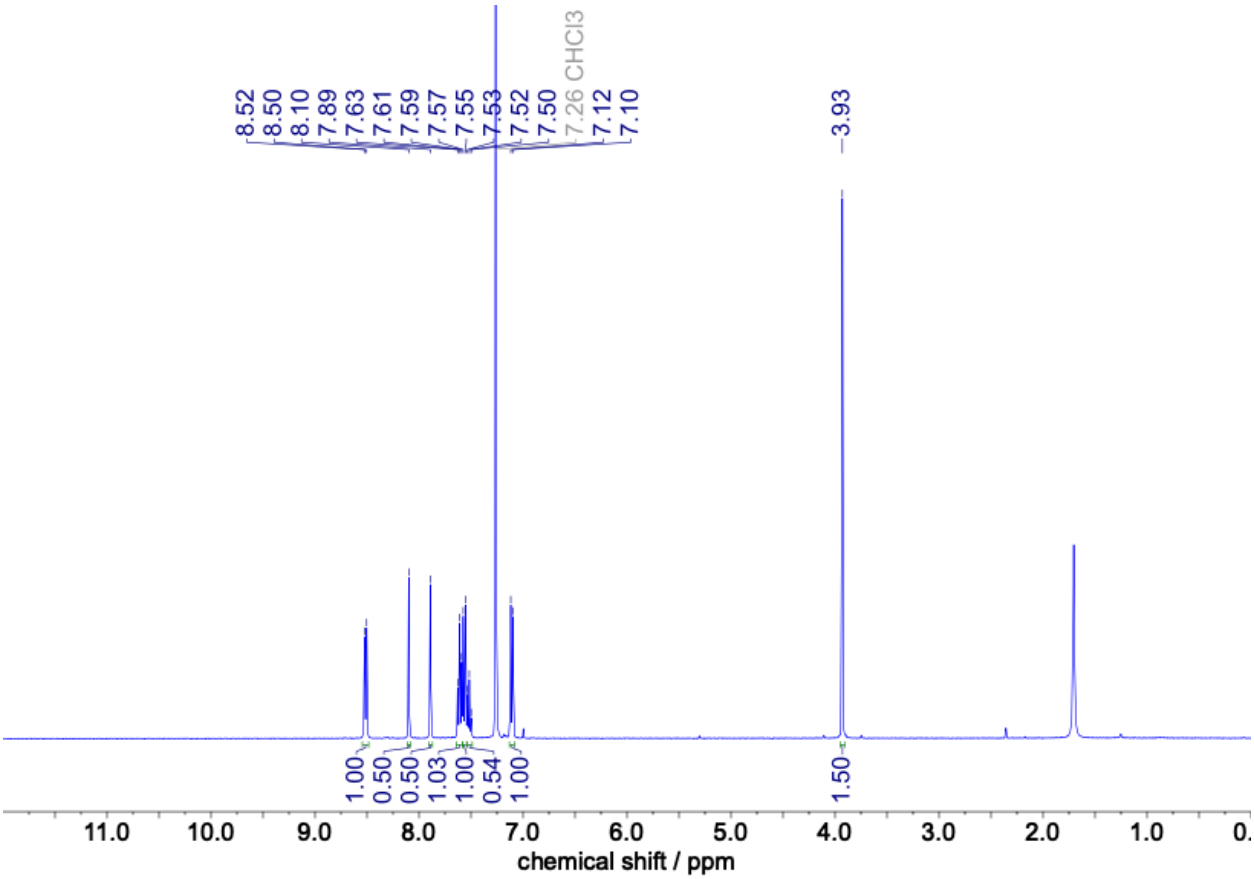


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **S6**.

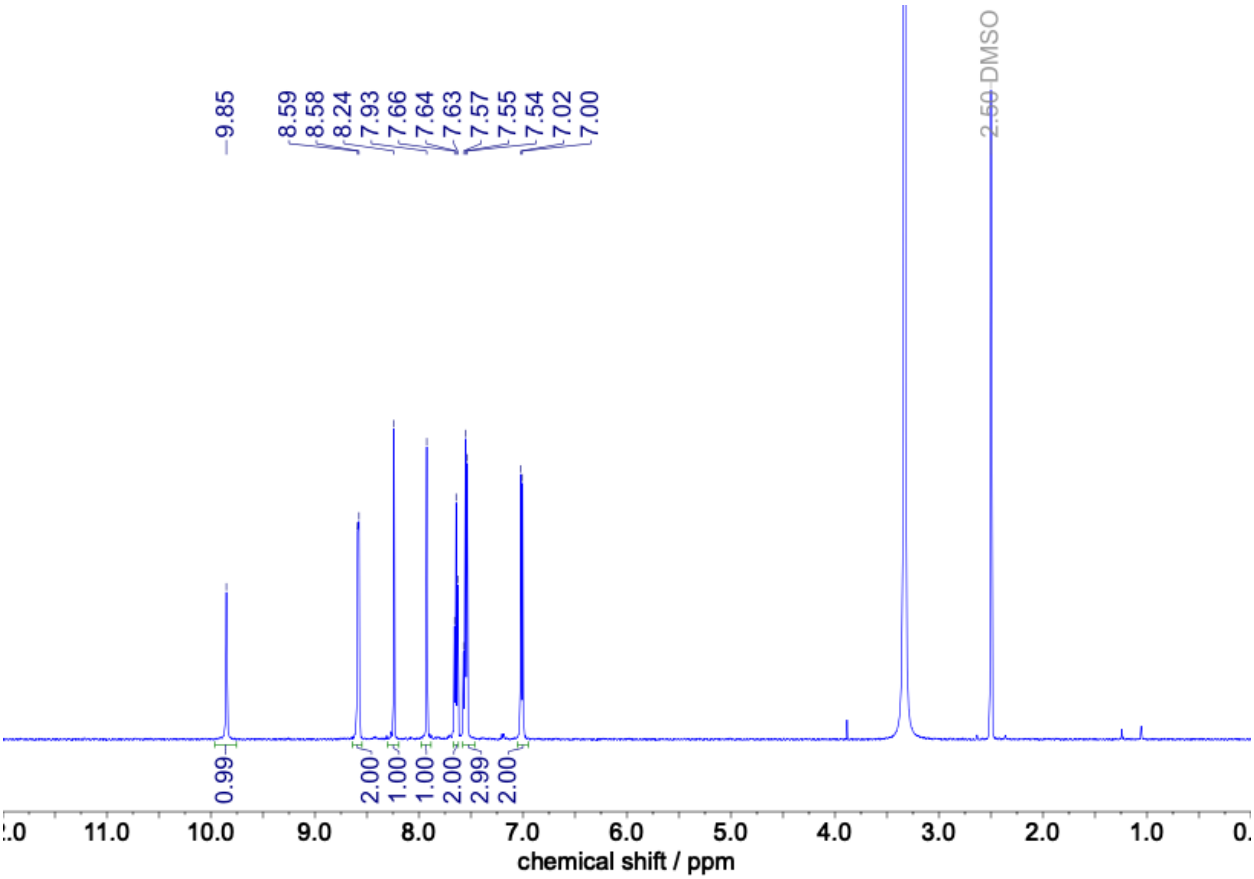


Figure S38. ^{1}H NMR (500 MHz, DMSO-*d*6) spectrum of compound **S7**.

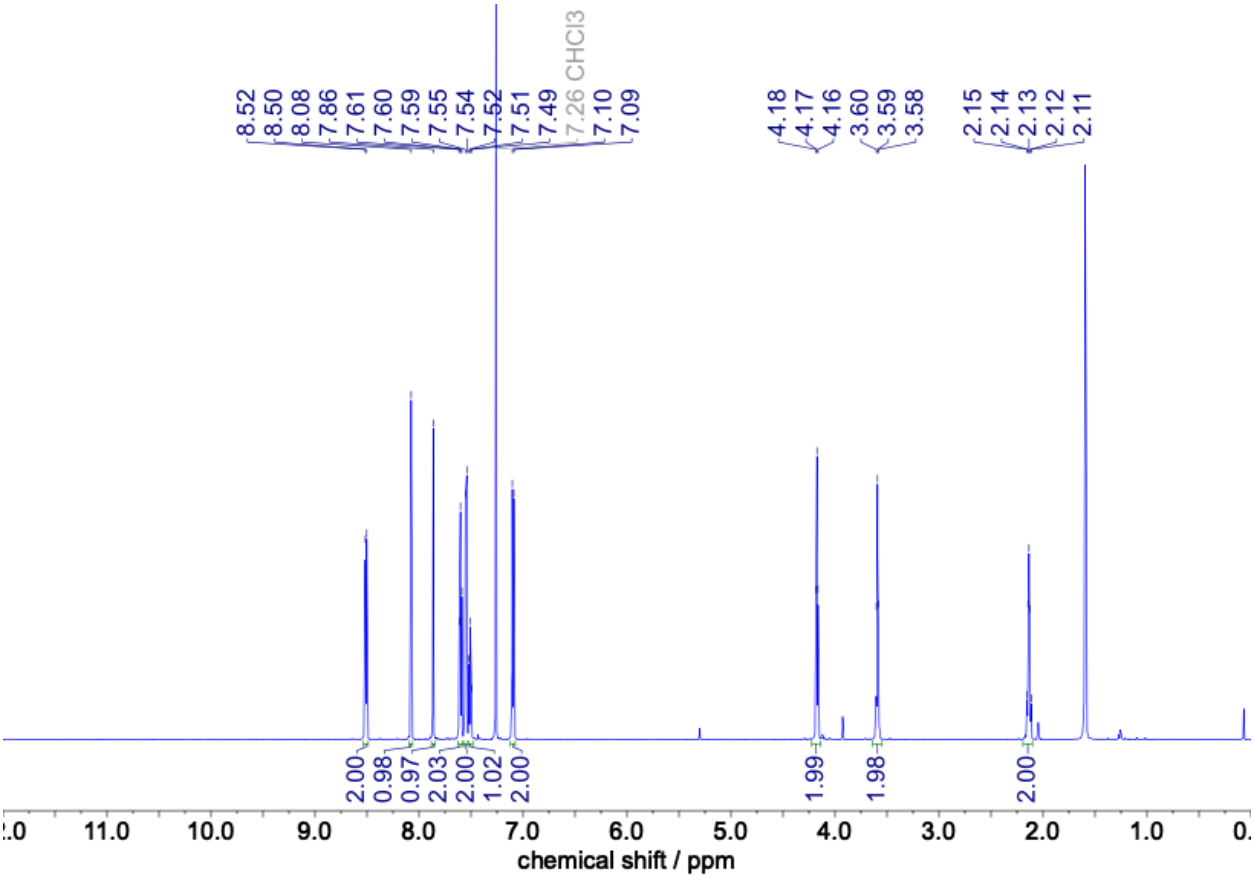


Figure S39. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **L2**.

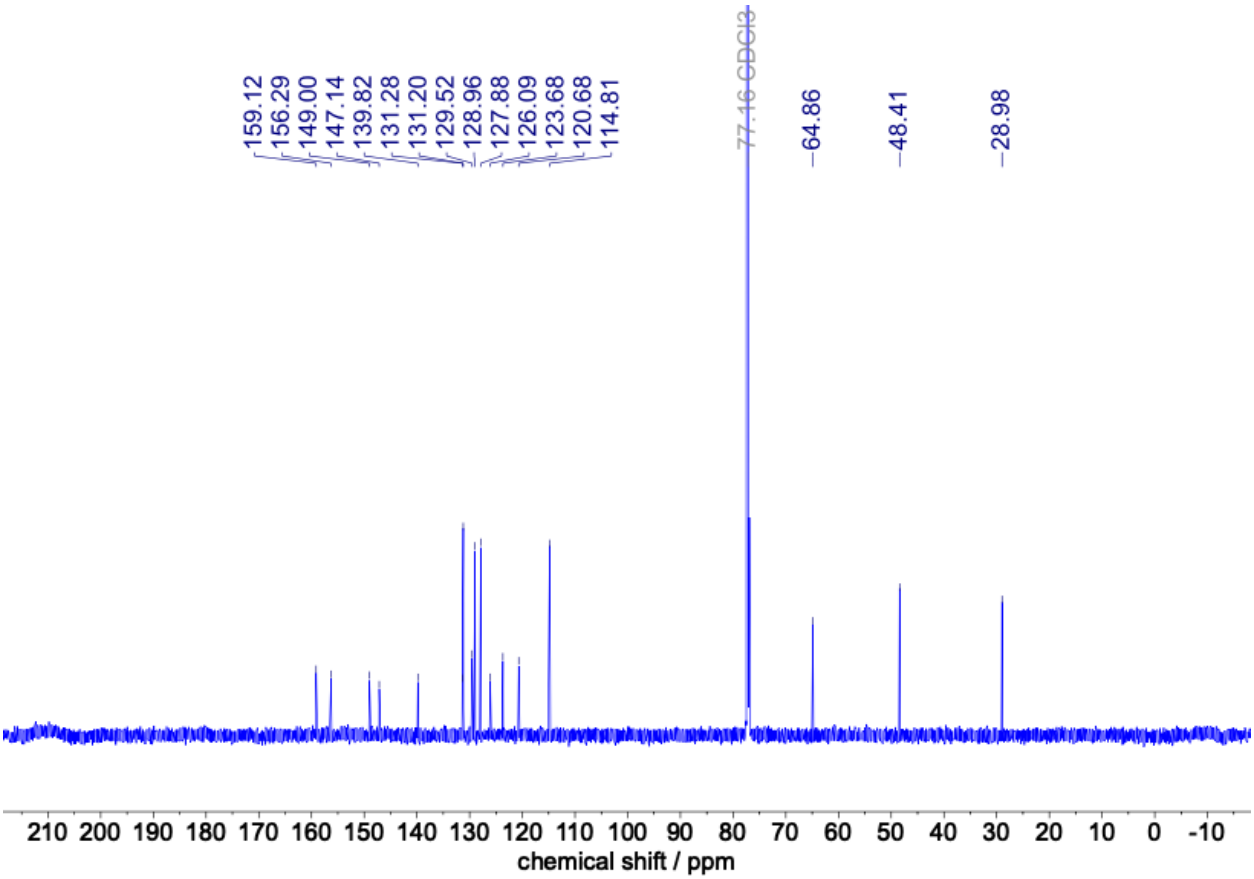


Figure S40. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound **L2**.

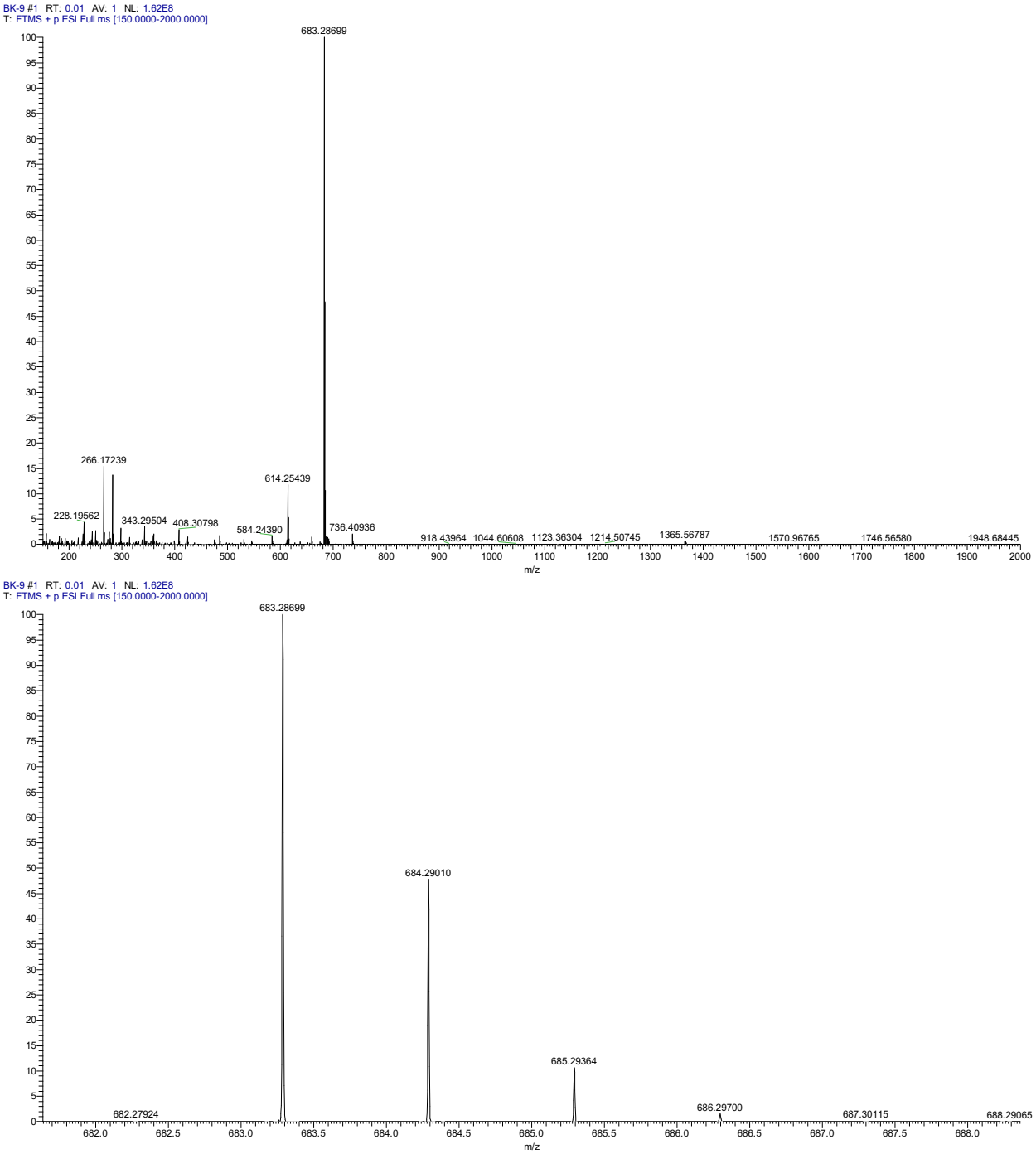


Figure S41. HRMS (ESI, positive mode) spectrum of compound **L2**.

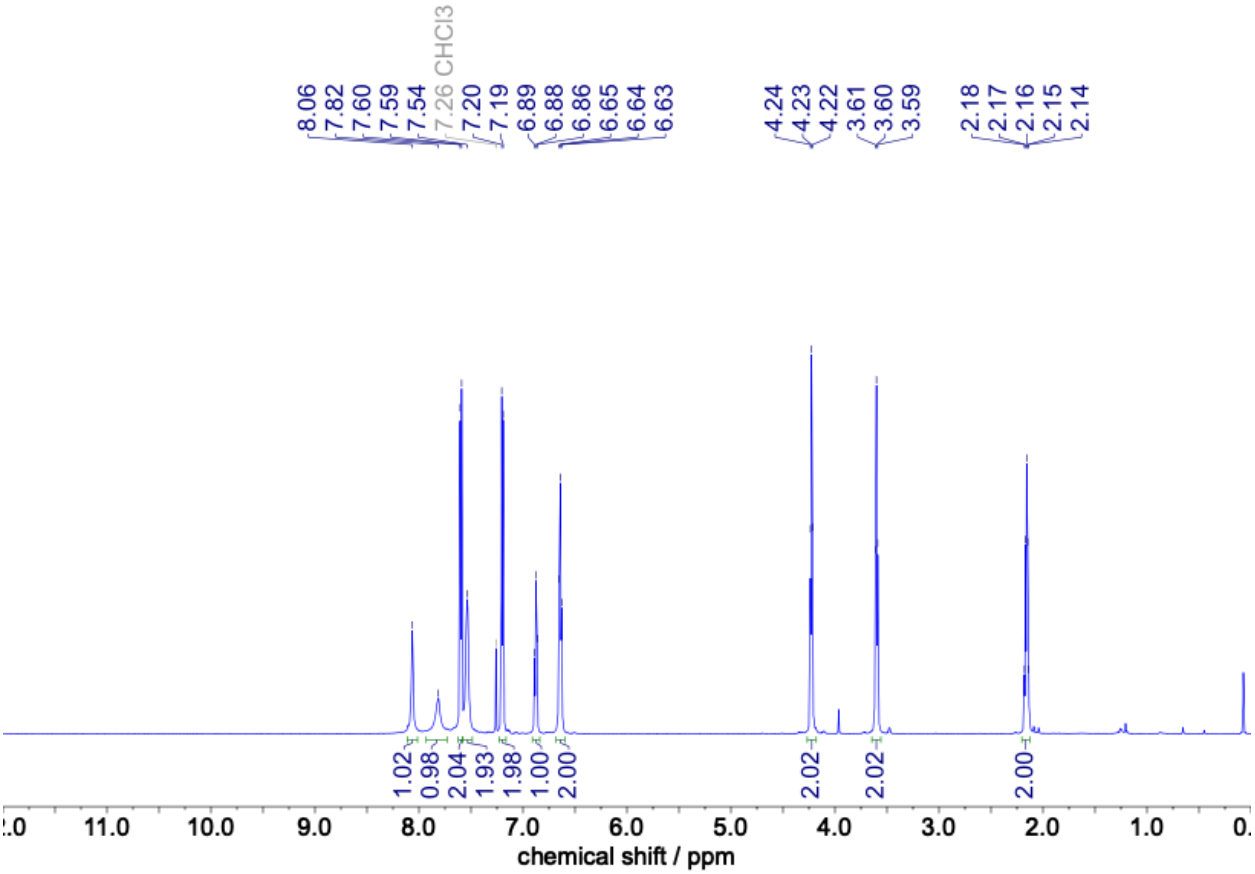


Figure S42. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of compound **L2•Cu**$^{+}$.

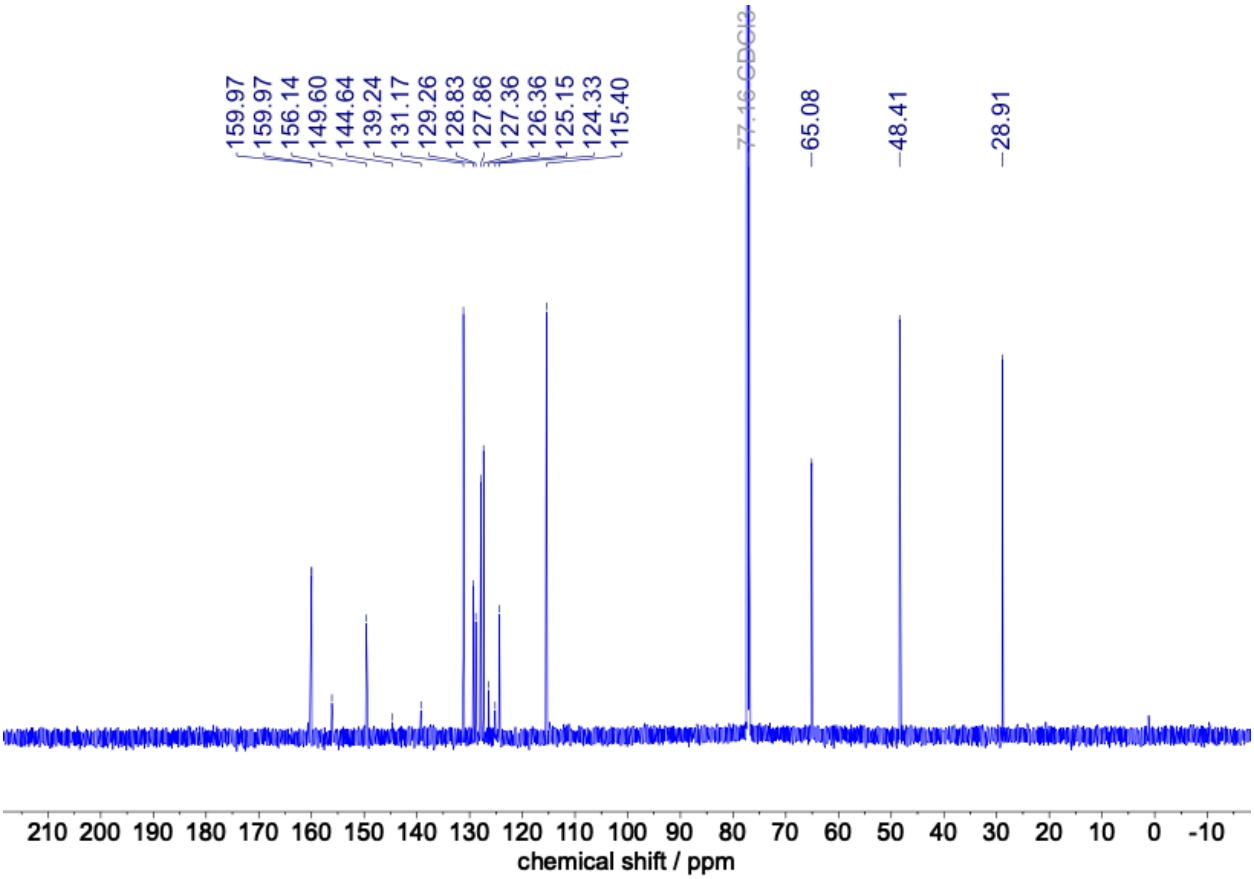


Figure S43. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of compound **L2•Cu**$^{+}$.

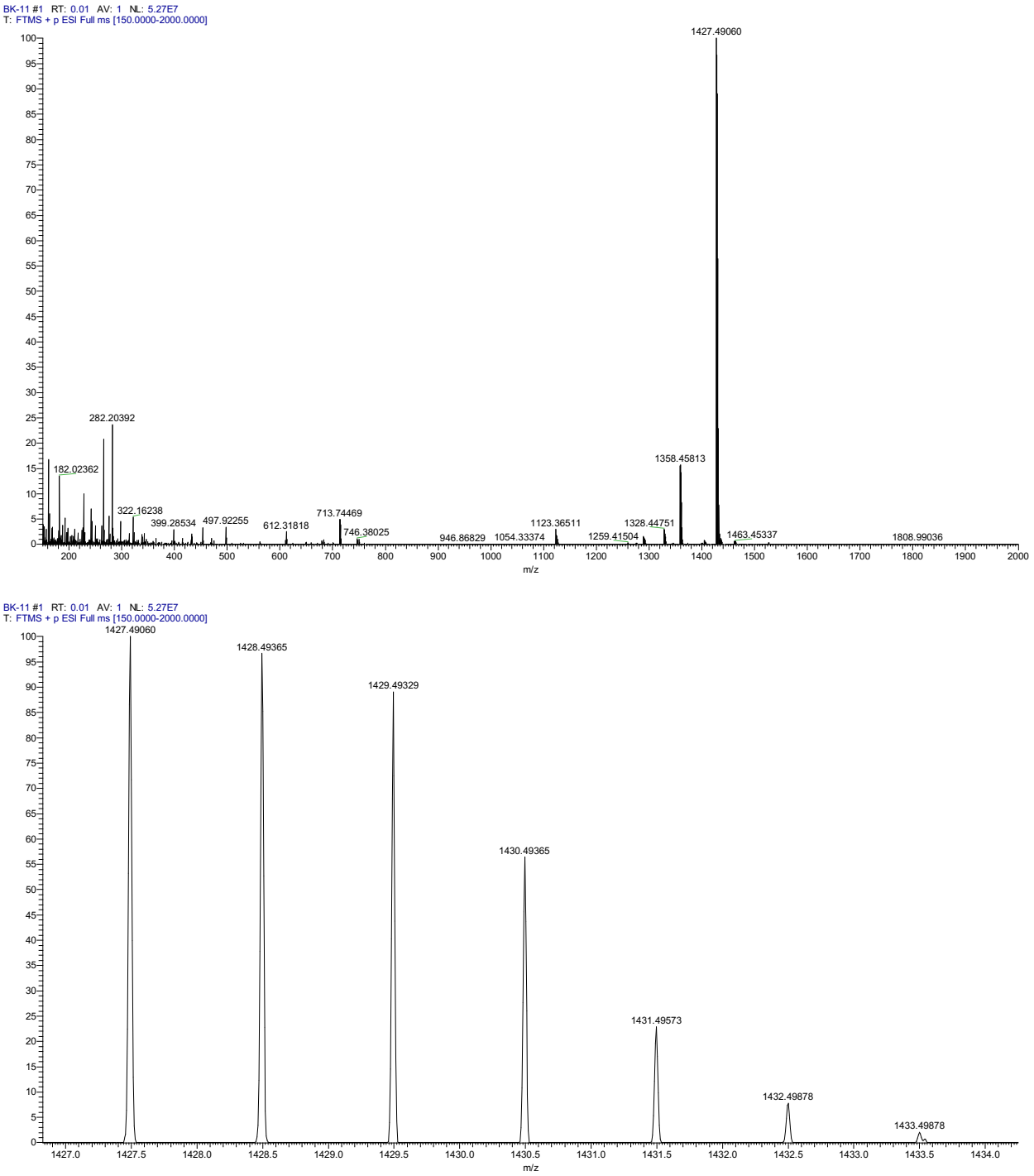


Figure S44. HRMS (ESI, positive mode) spectrum of compound **L2•Cu**$^{+}$.

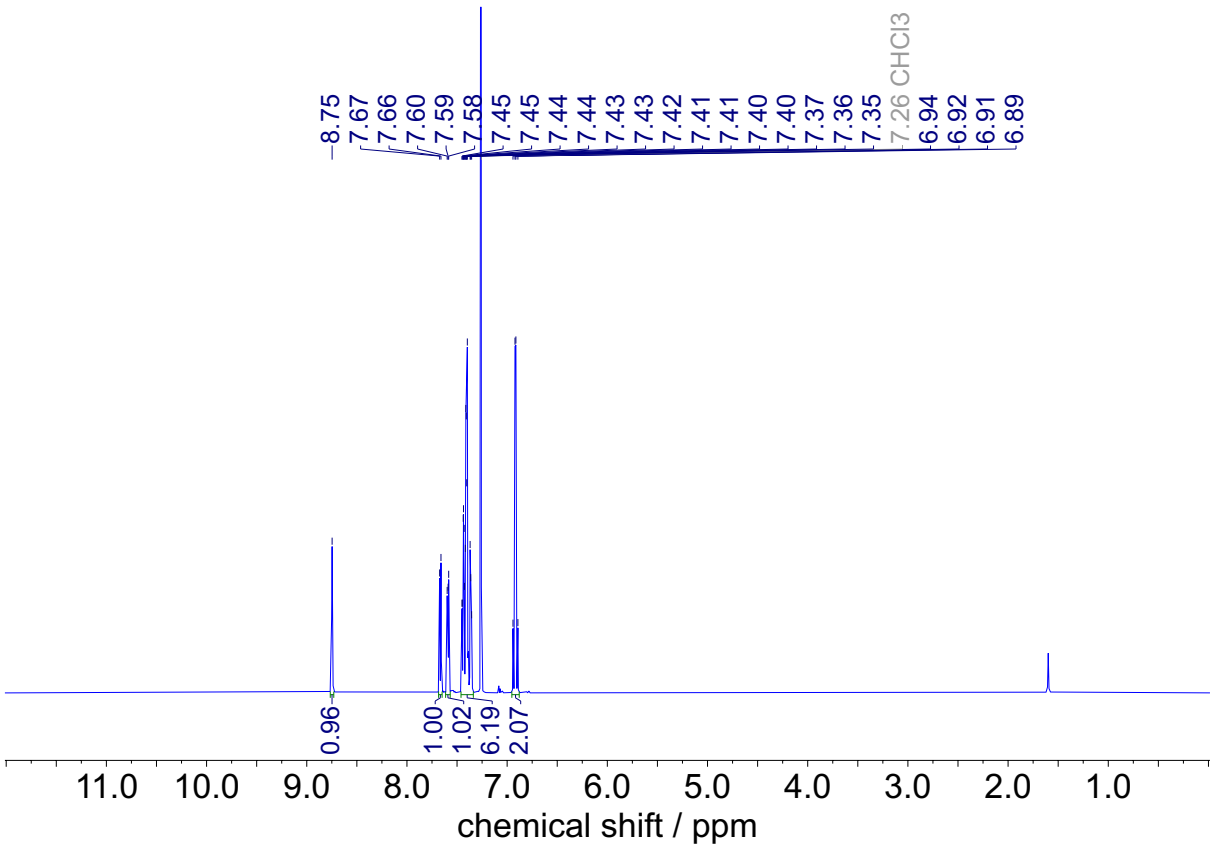


Figure S45. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S8**.

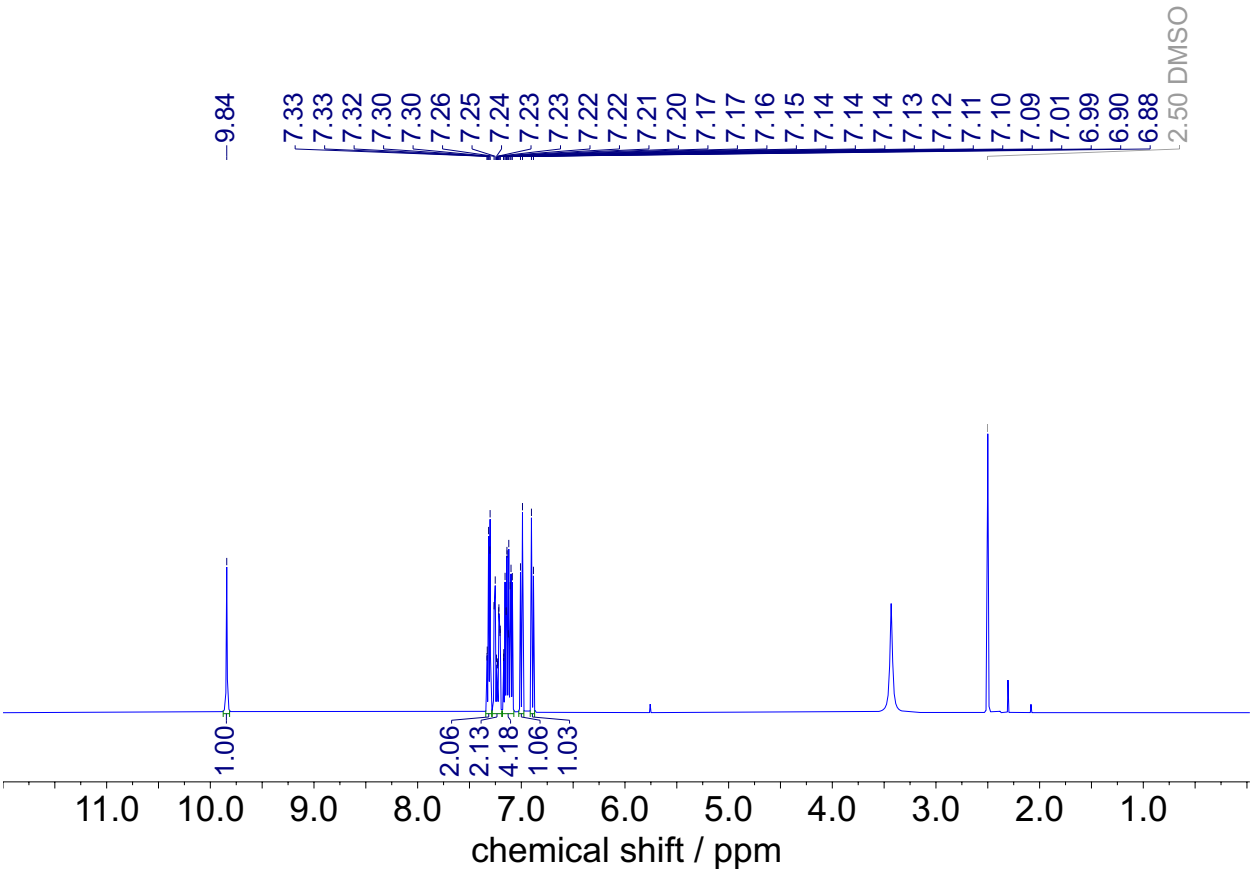


Figure S46. ^{1}H NMR (600 MHz, DMSO-*d*6) spectrum of **S9**.

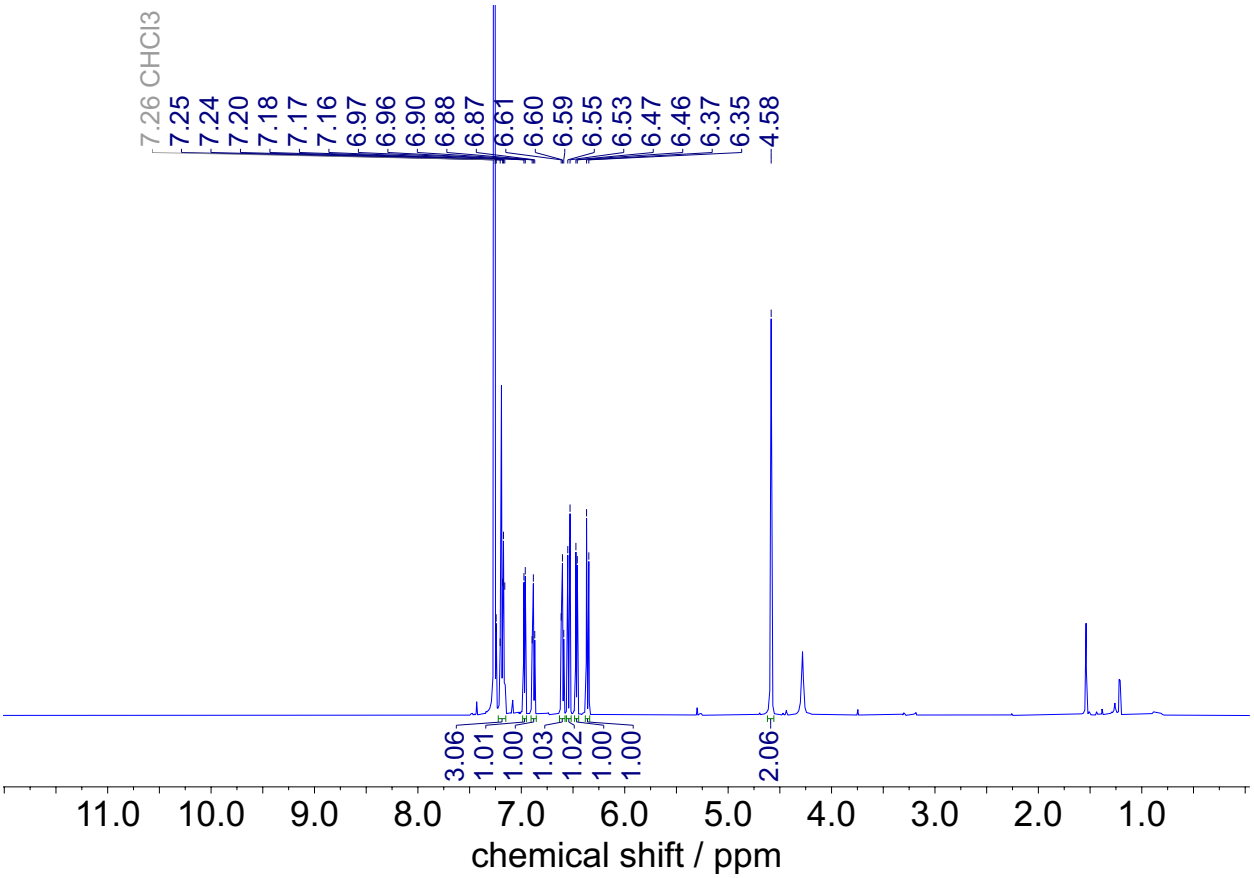


Figure S47. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S10.**

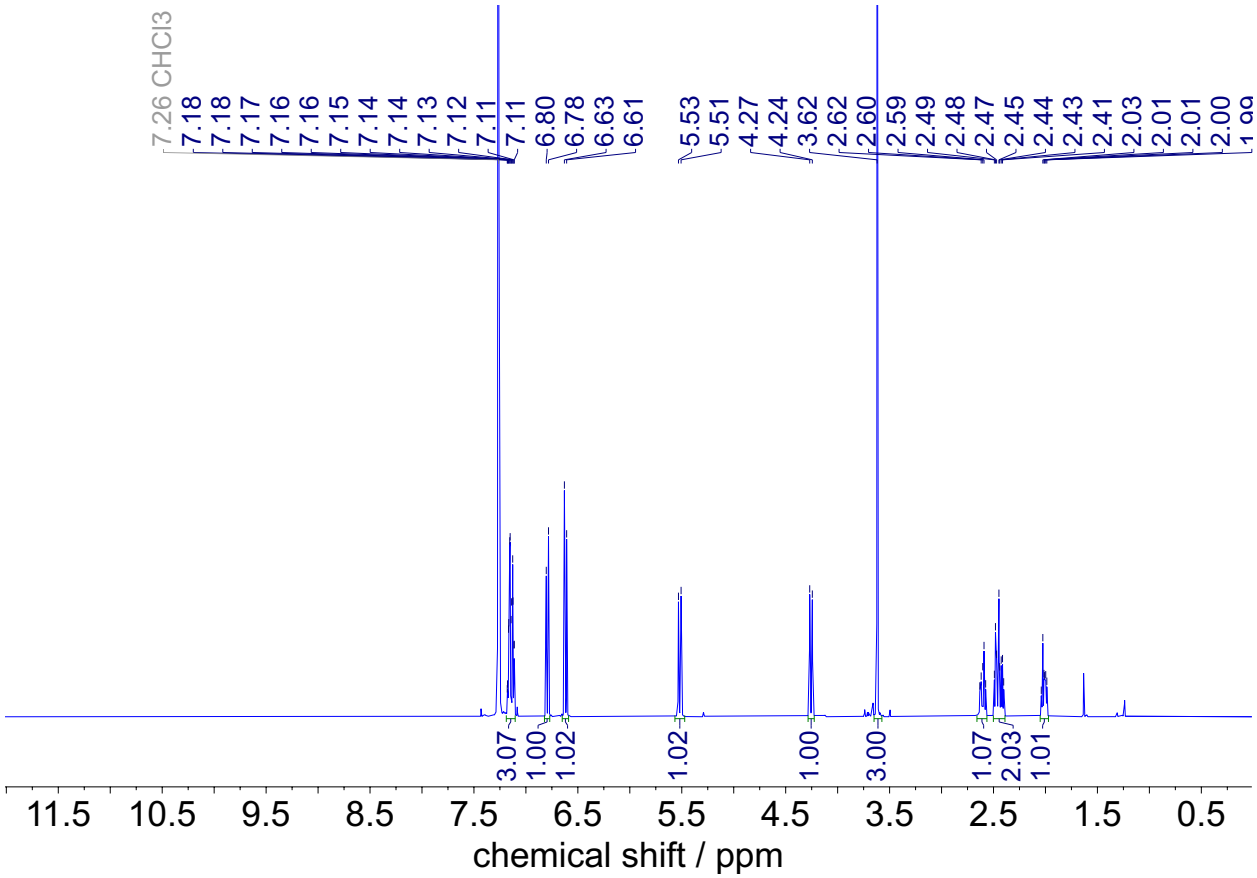


Figure S48. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S11**.

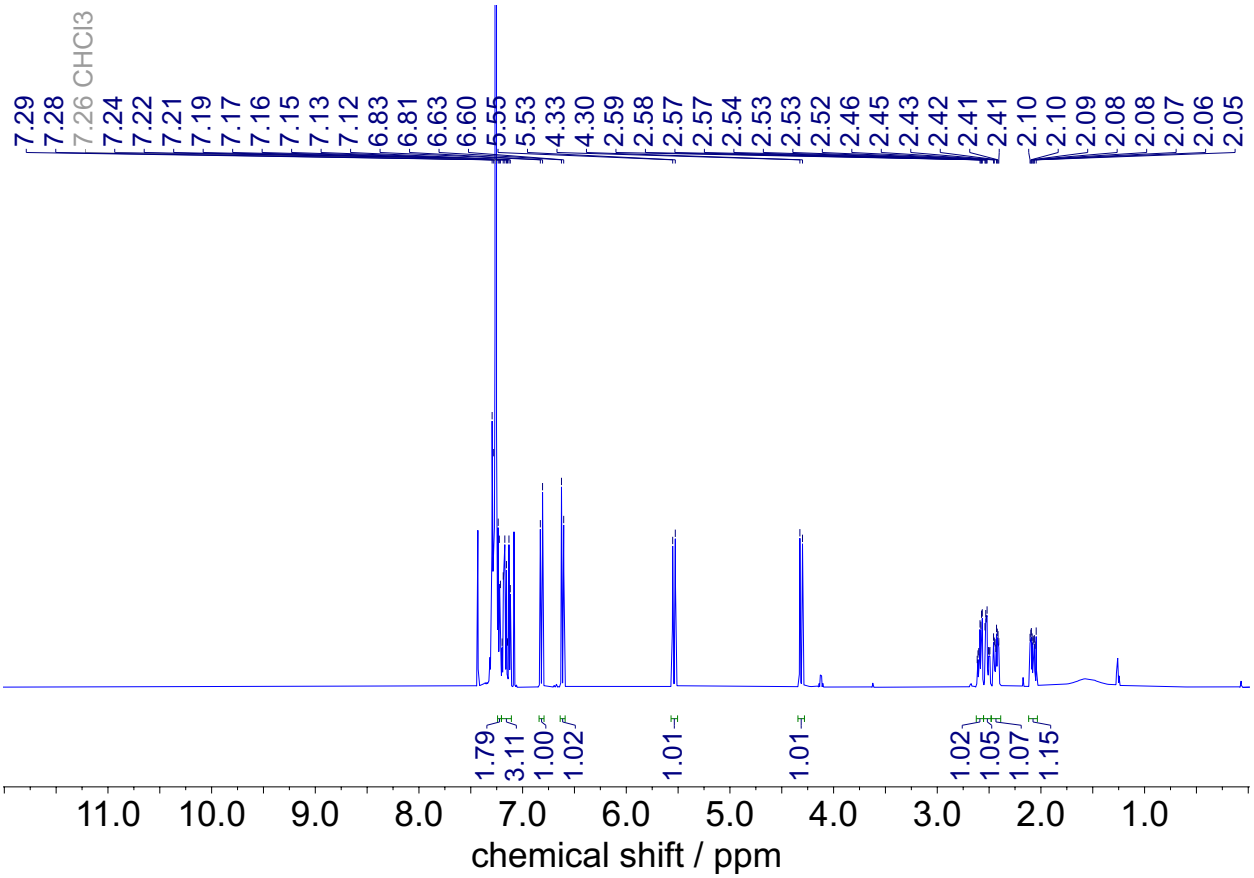


Figure S49. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **S12.**

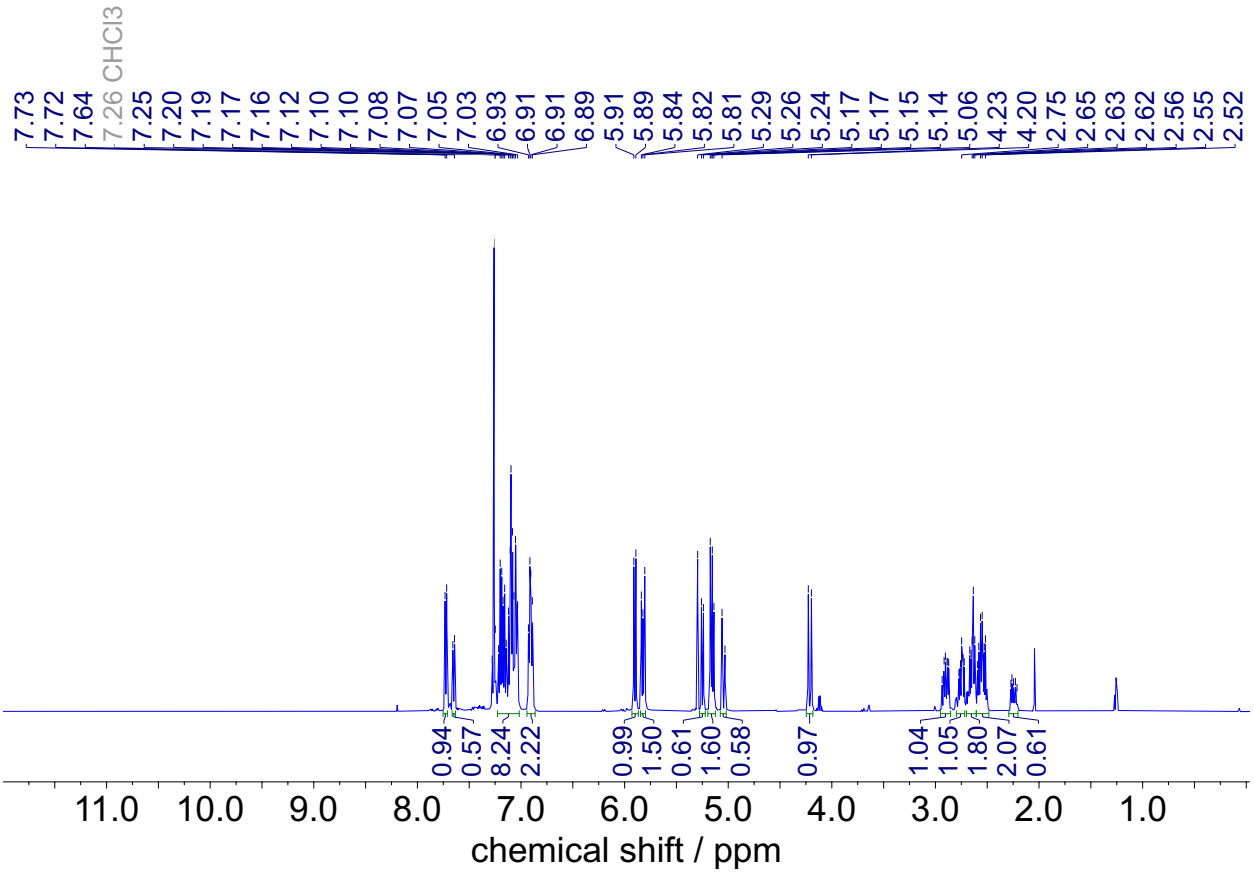


Figure S50. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum for **S13**.

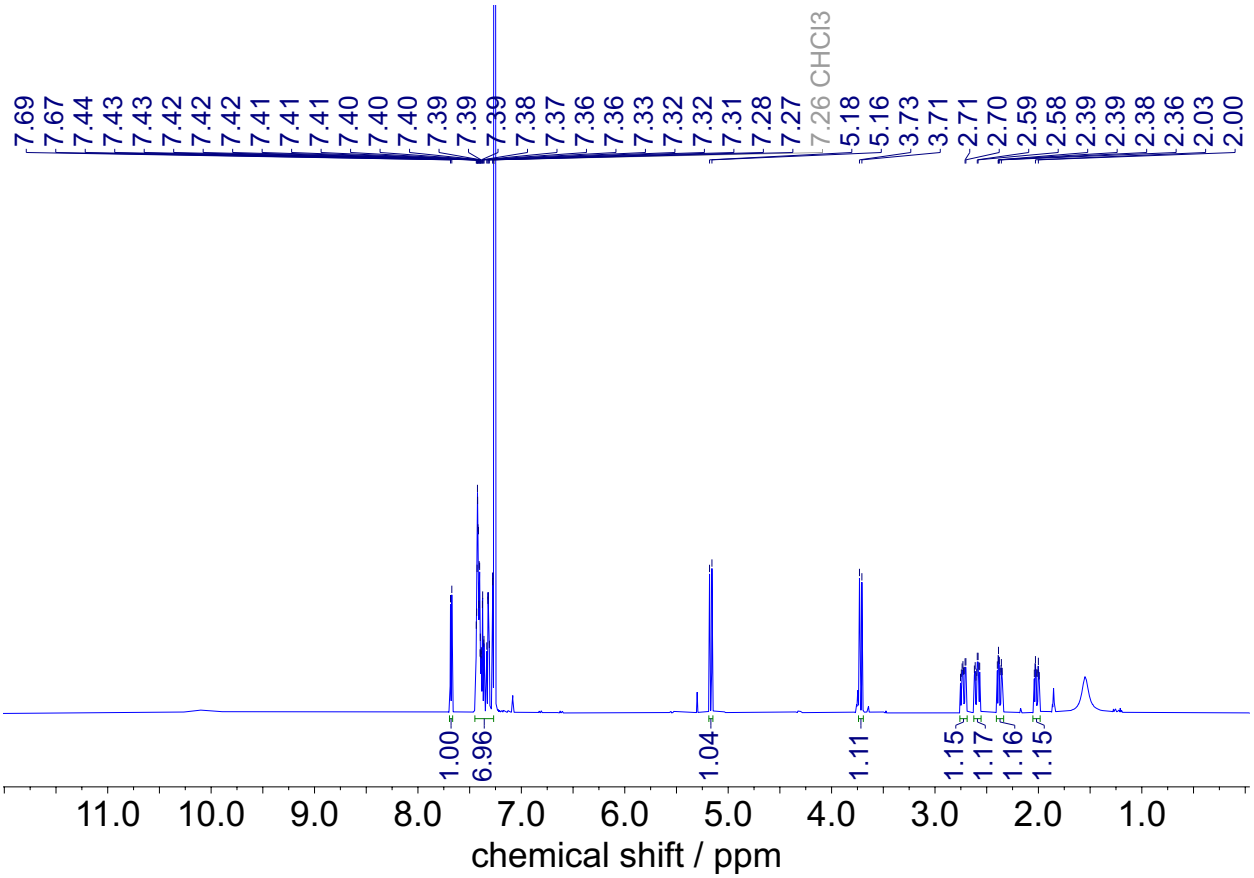


Figure S 51. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **S14**.

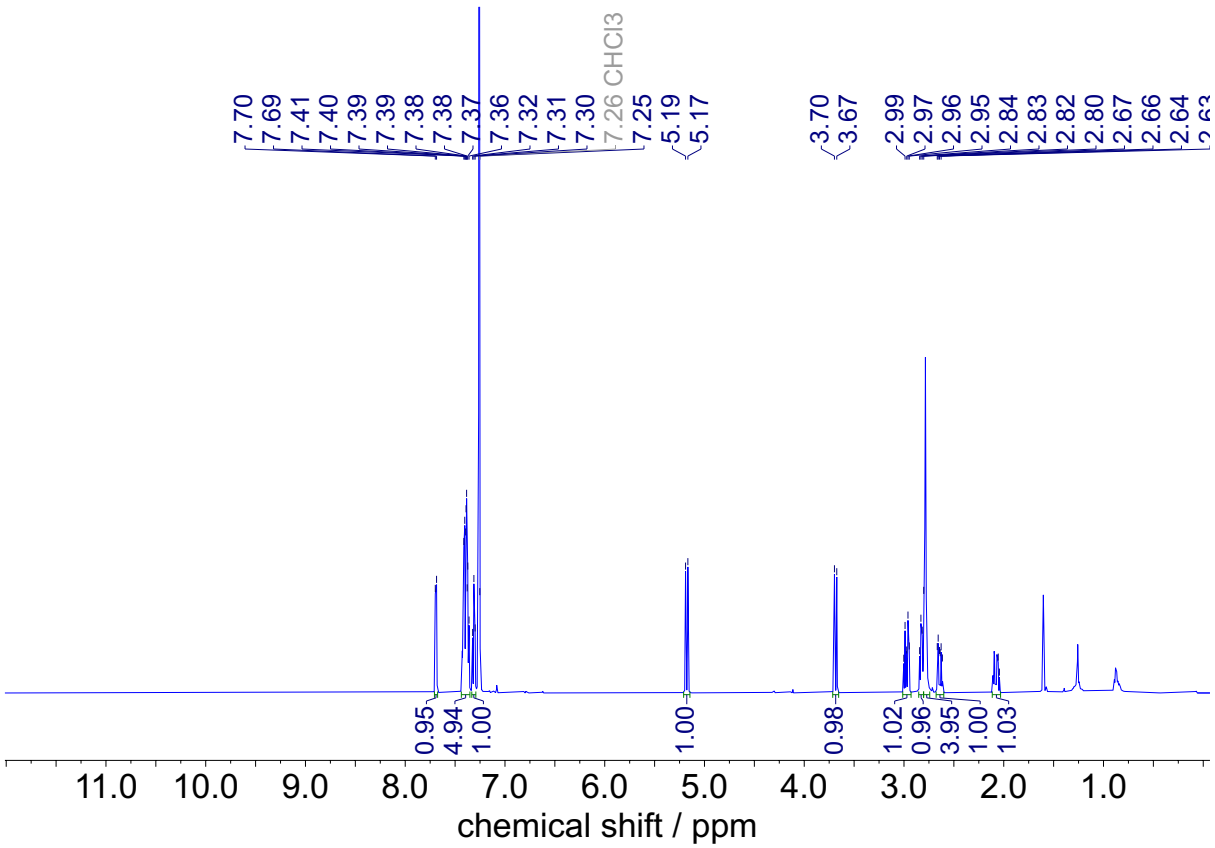


Figure S52. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum for **S15**.

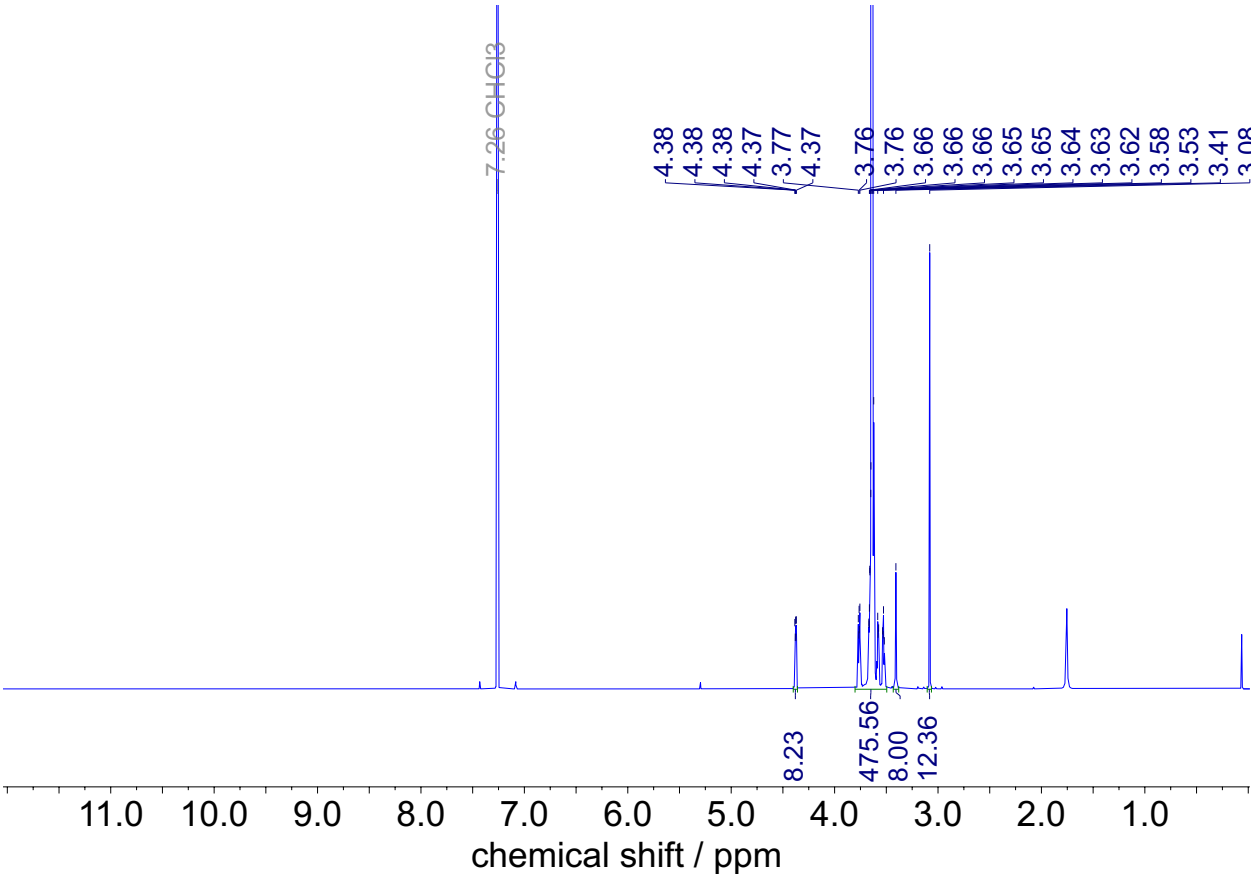


Figure S53. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S16**.

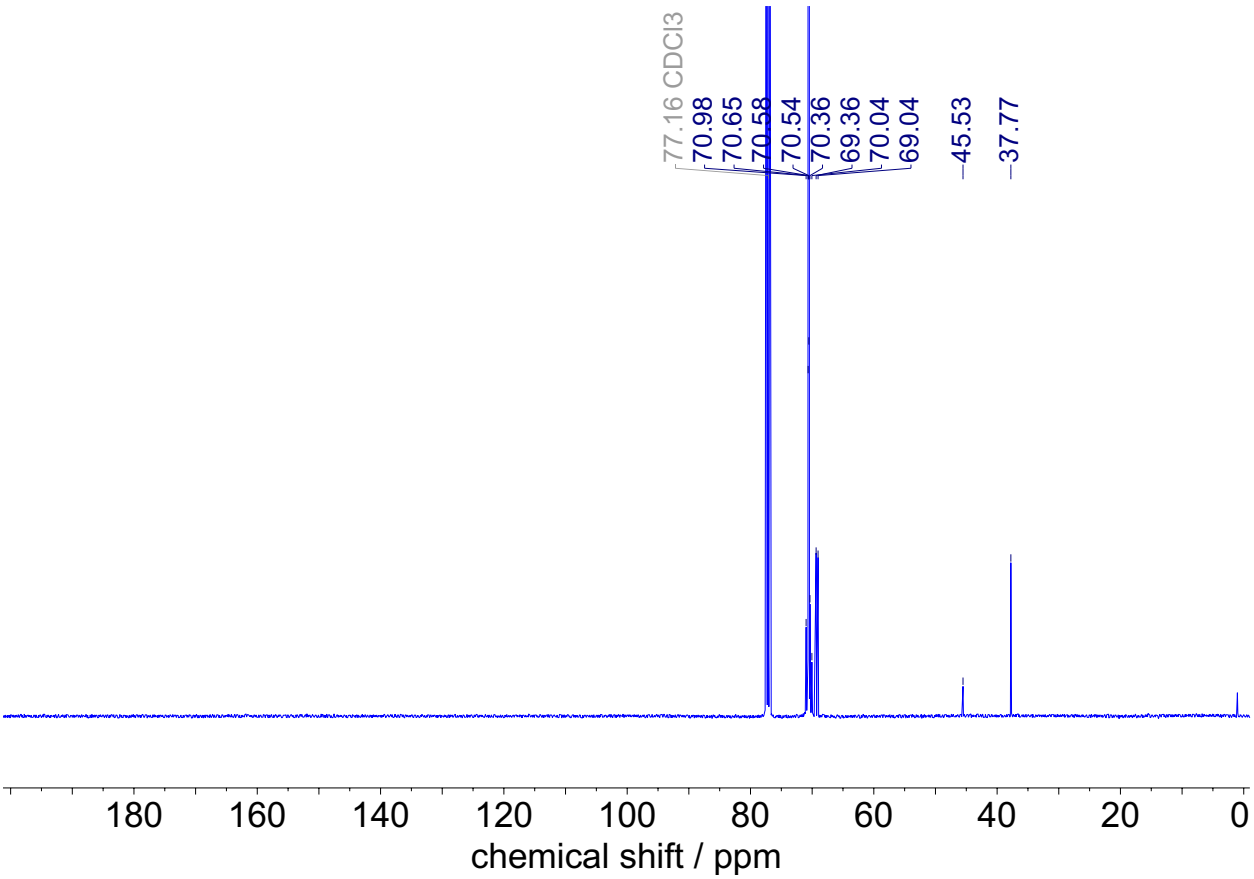


Figure S54. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **S16**.

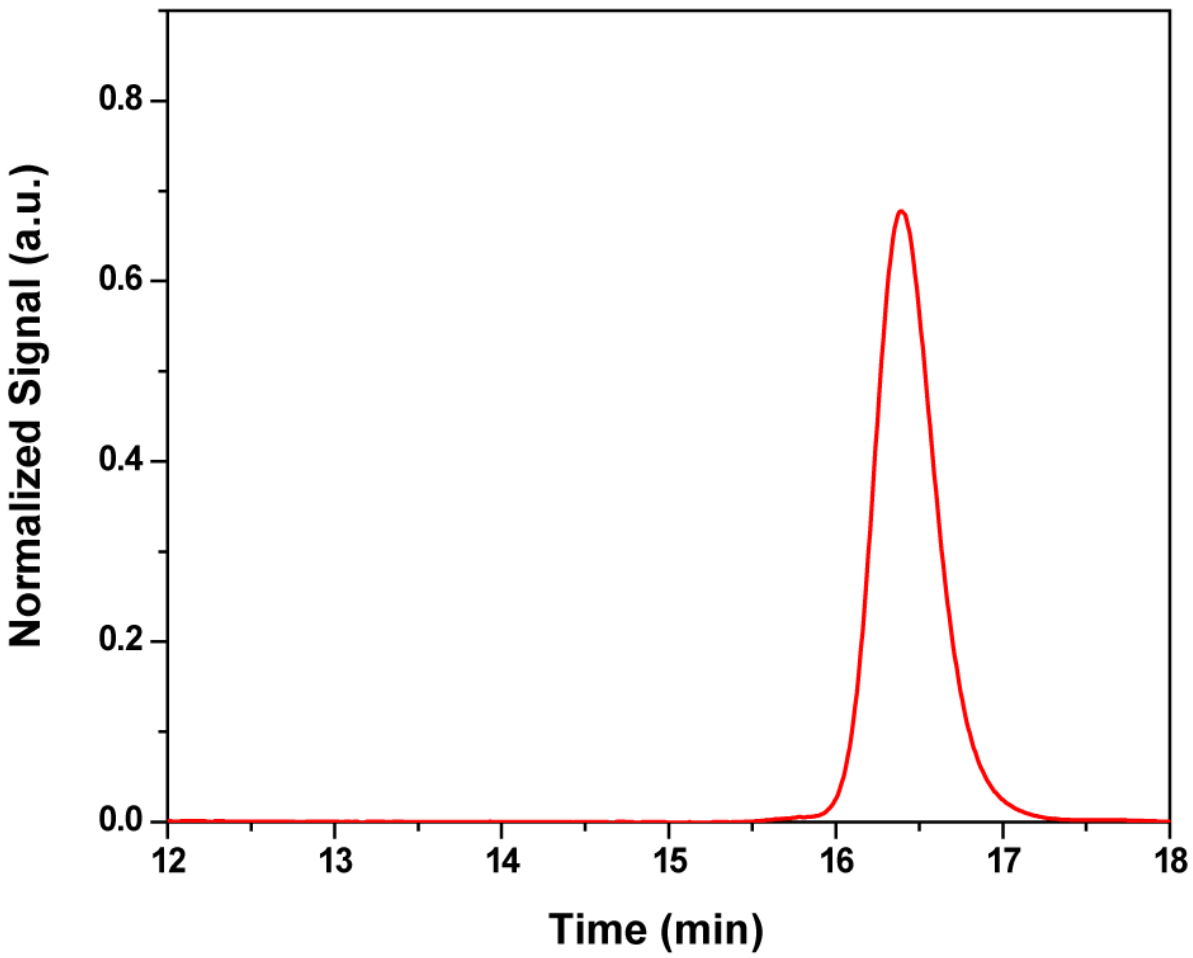


Figure S55. Normalized GPC-MALS differential refractive index (dRI) trace of **S16**. The molecular weight of the sample was measured at 5.18 kg/mol and the dispersity was recorded as $Đ$ = 1.07.

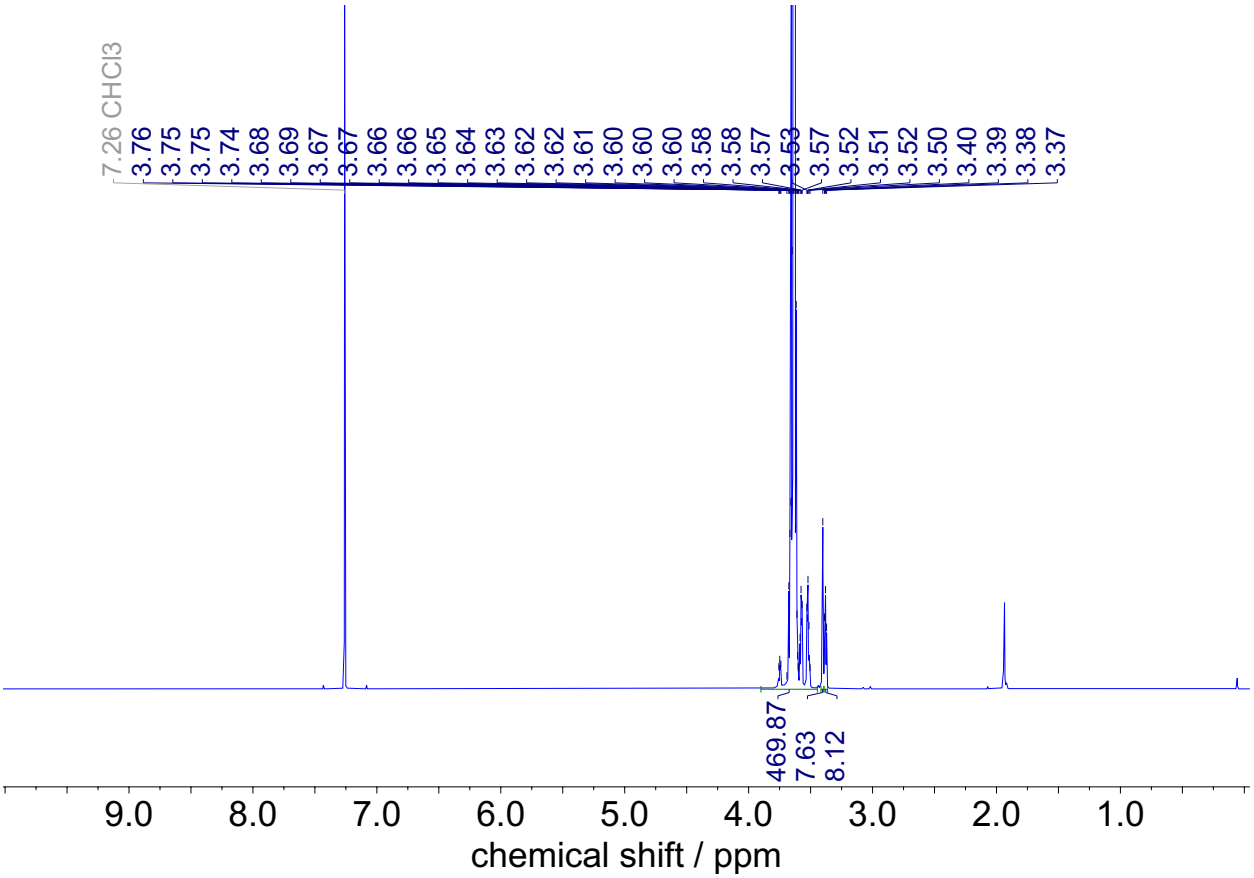


Figure S56. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S17**.

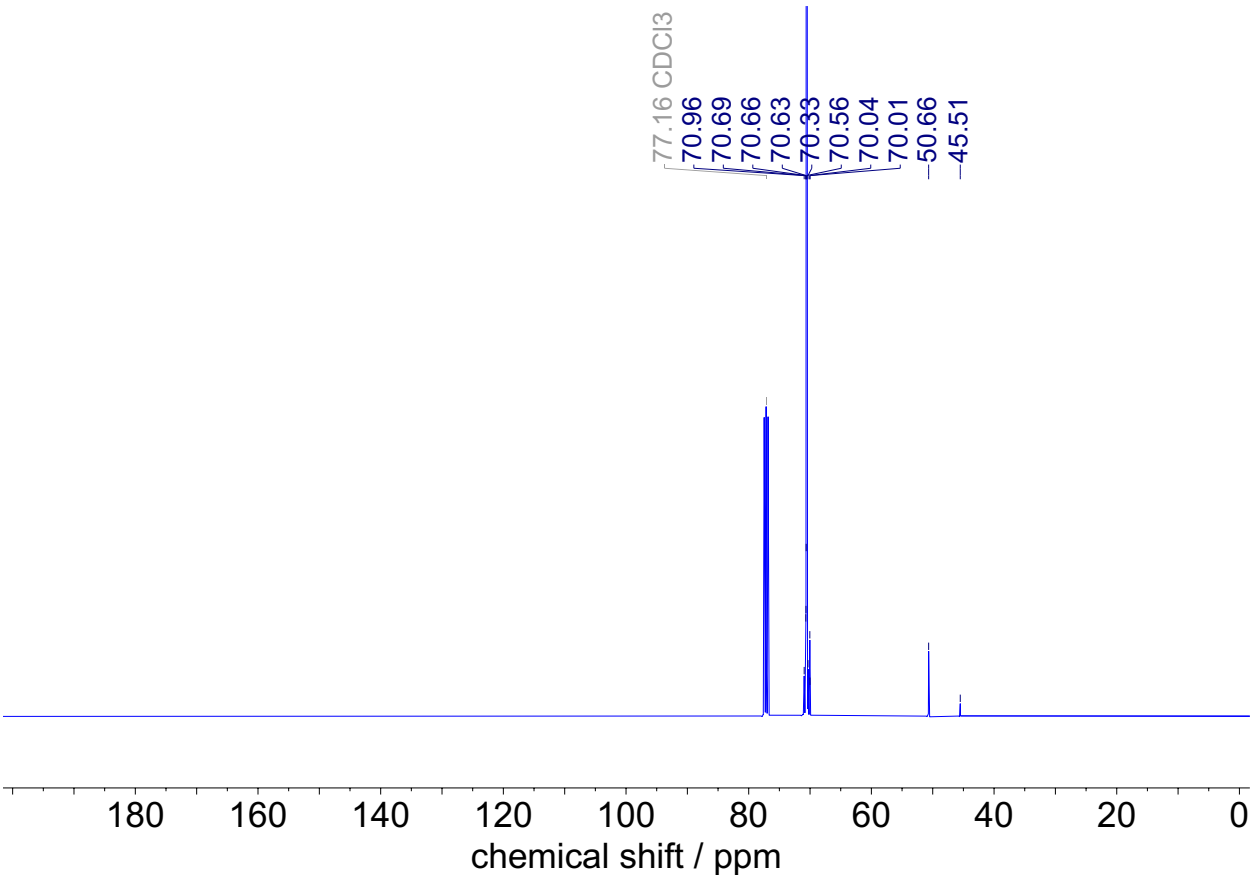


Figure S57. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **S17**.

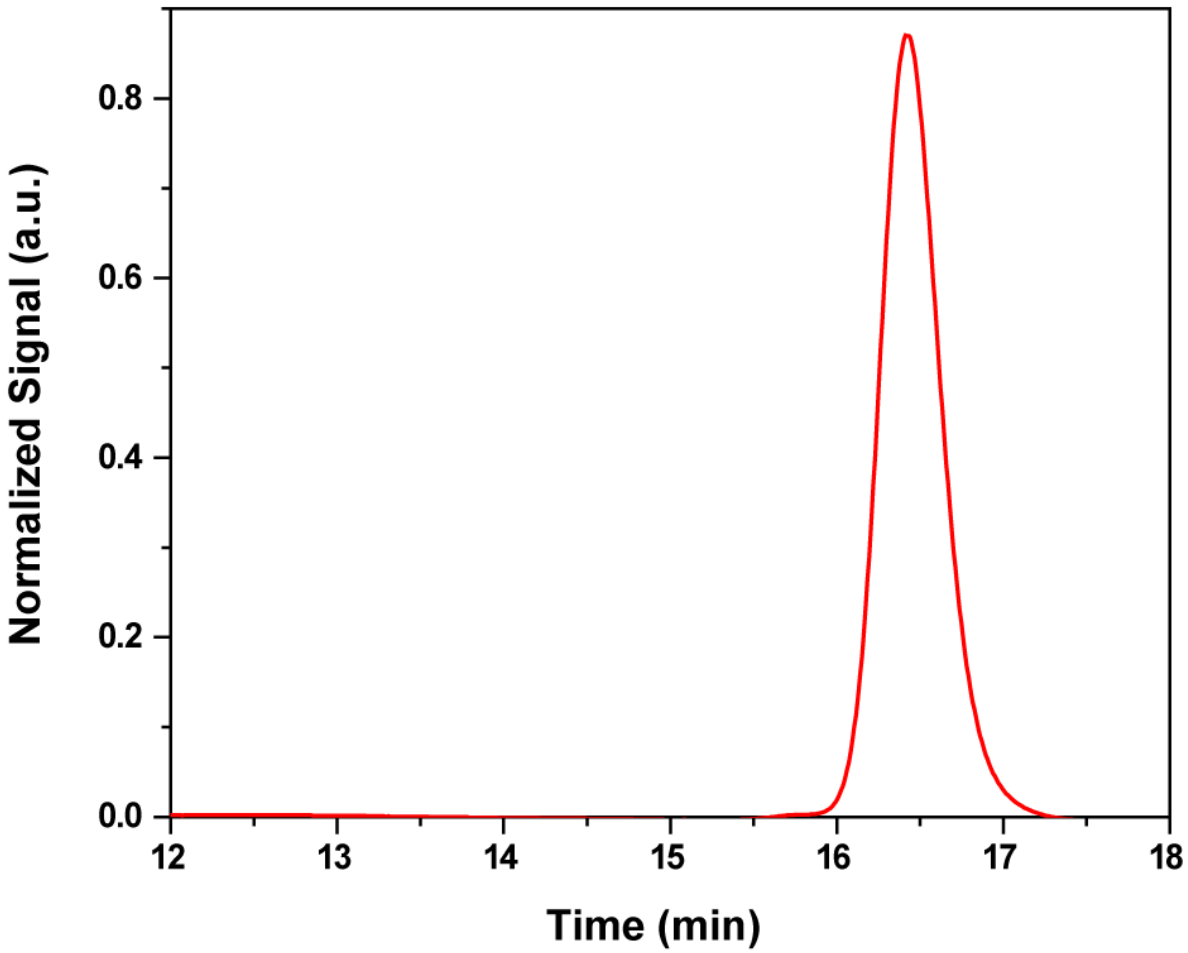


Figure S58. Normalized GPC-MALS differential refractive index (dRI) trace of **S17**. The molecular weight of the sample was measured at 5.20 kg/mol and the dispersity was recorded as $Đ$ = 1.06.

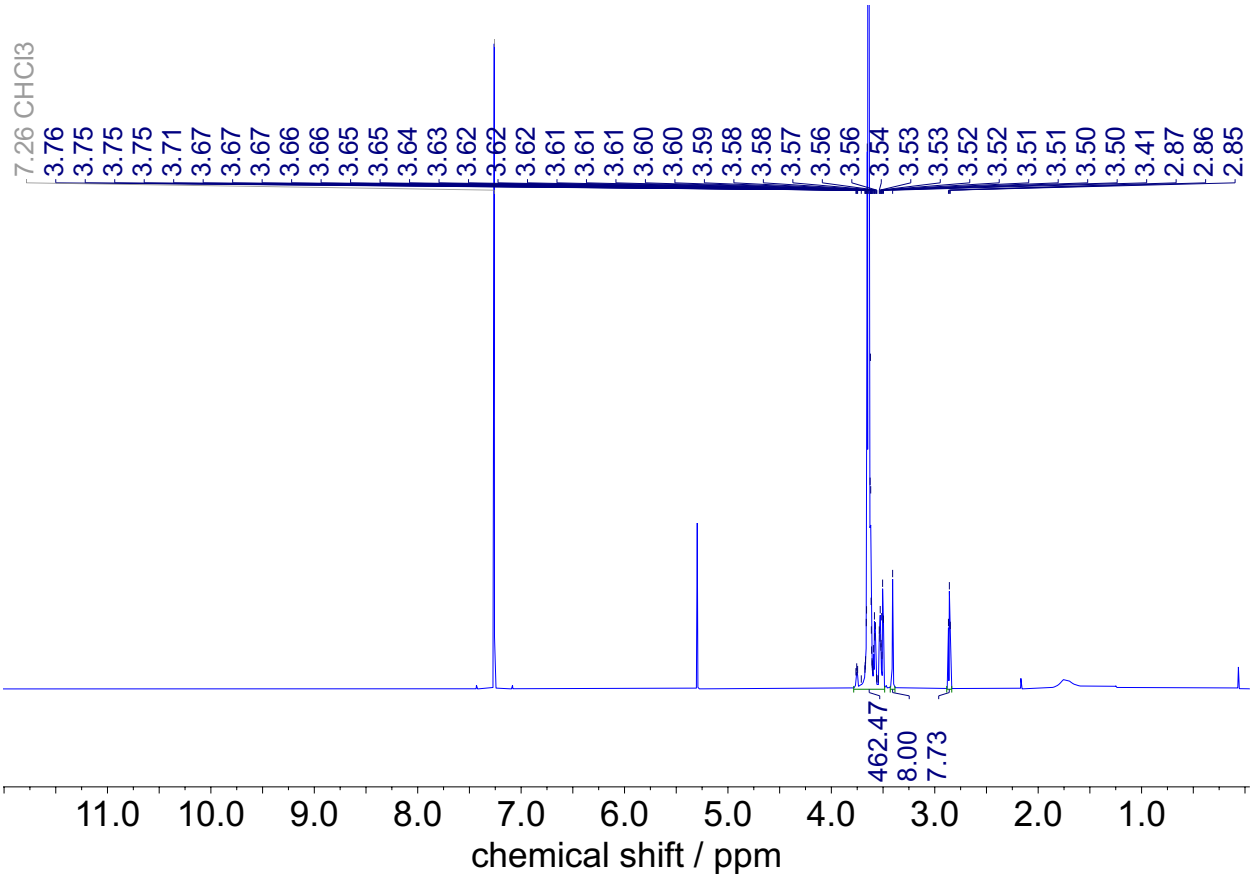


Figure S59. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S18**.

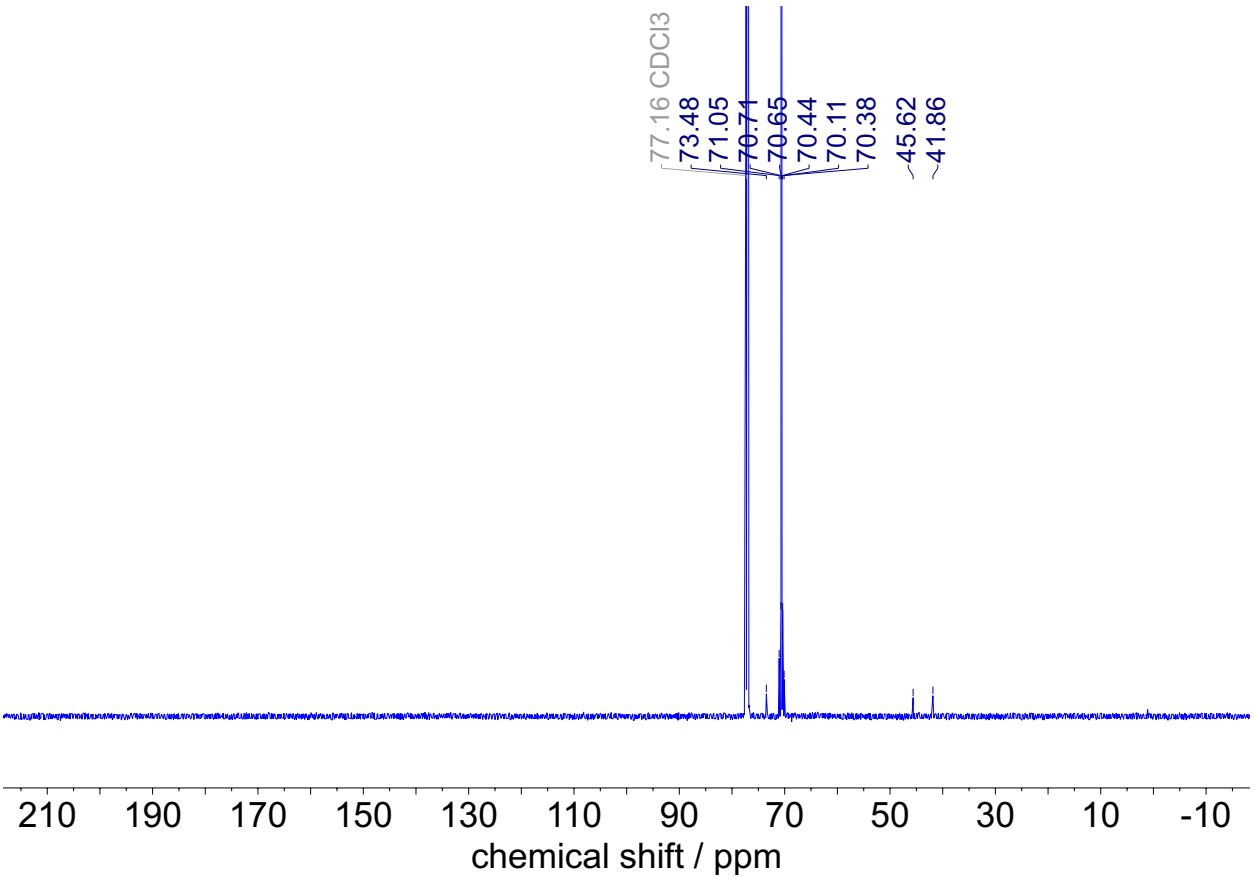


Figure S60. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **S18**.

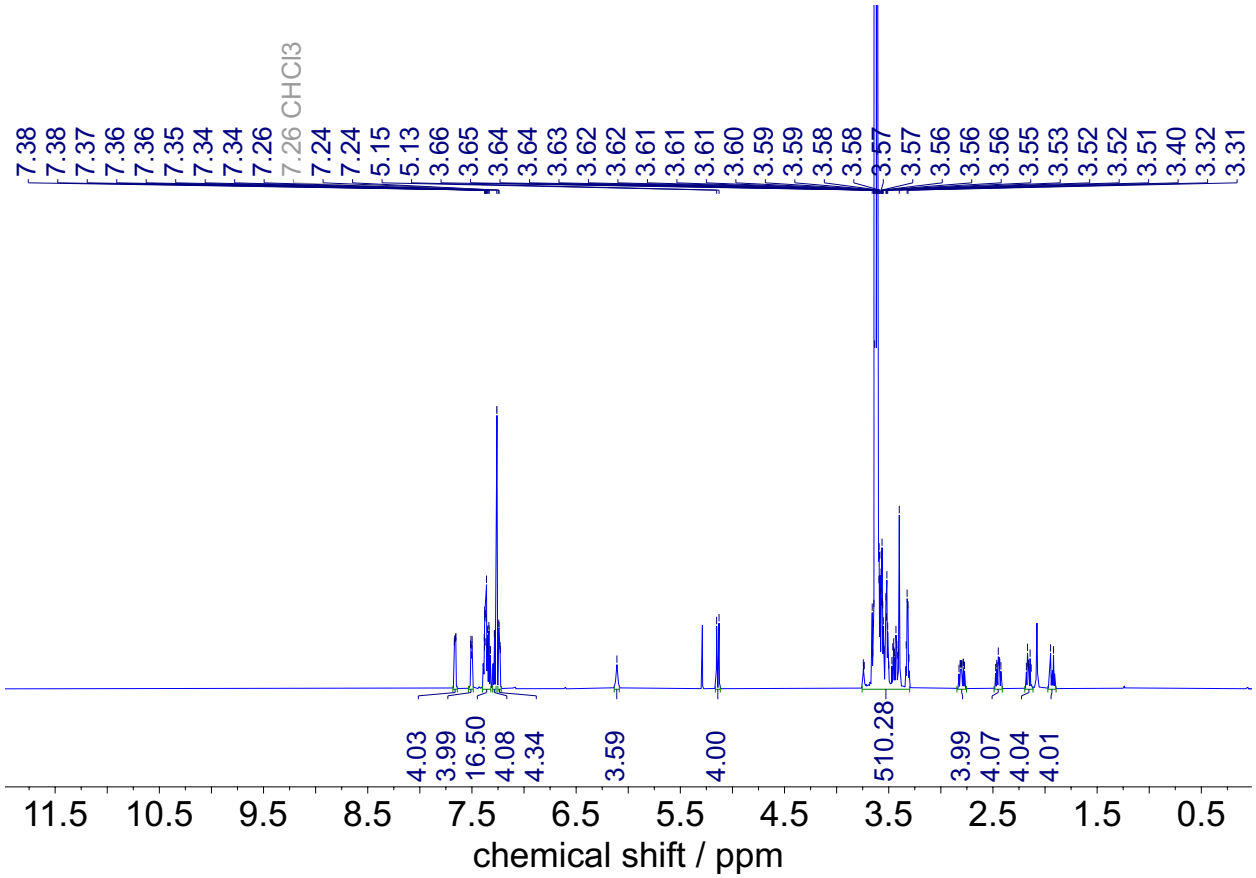


Figure S61. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S19**.

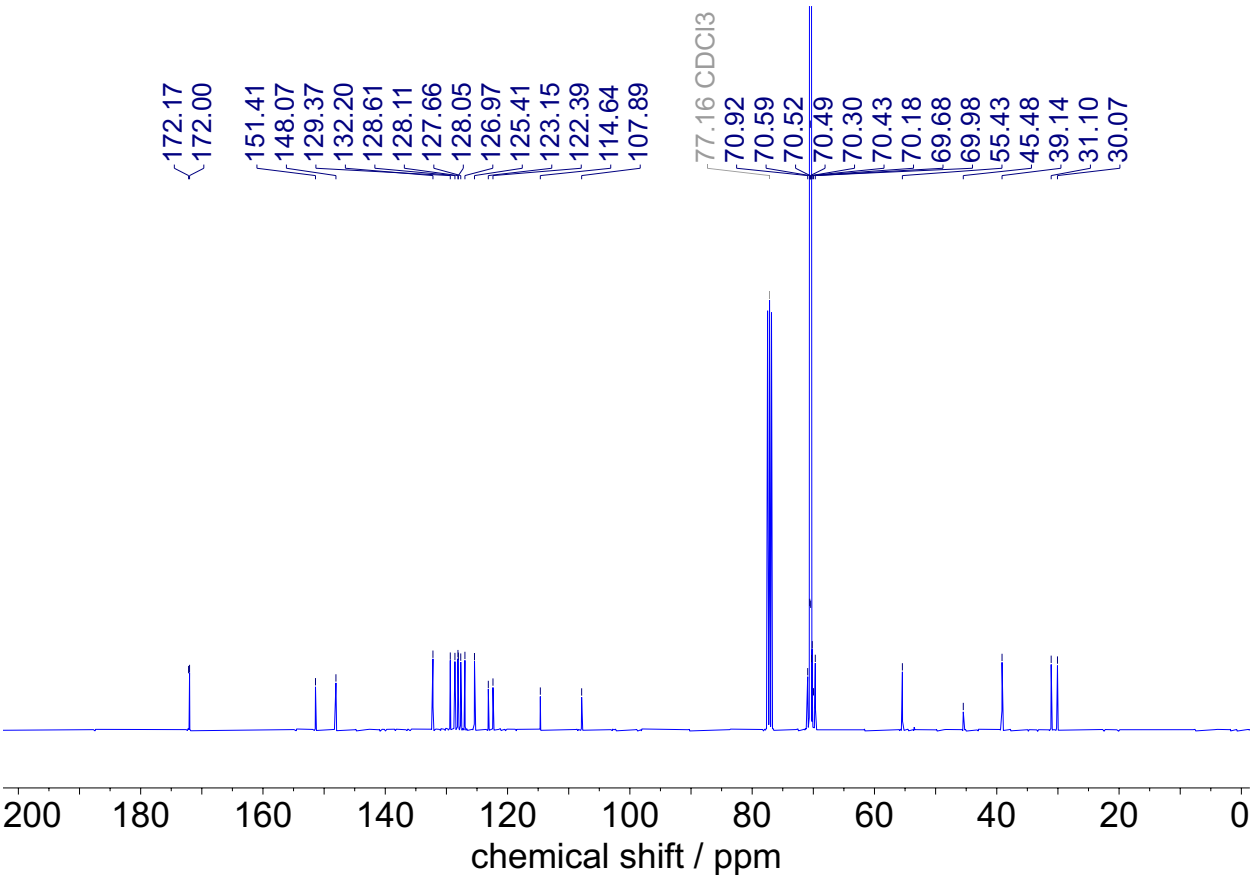


Figure S62. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **S19**.

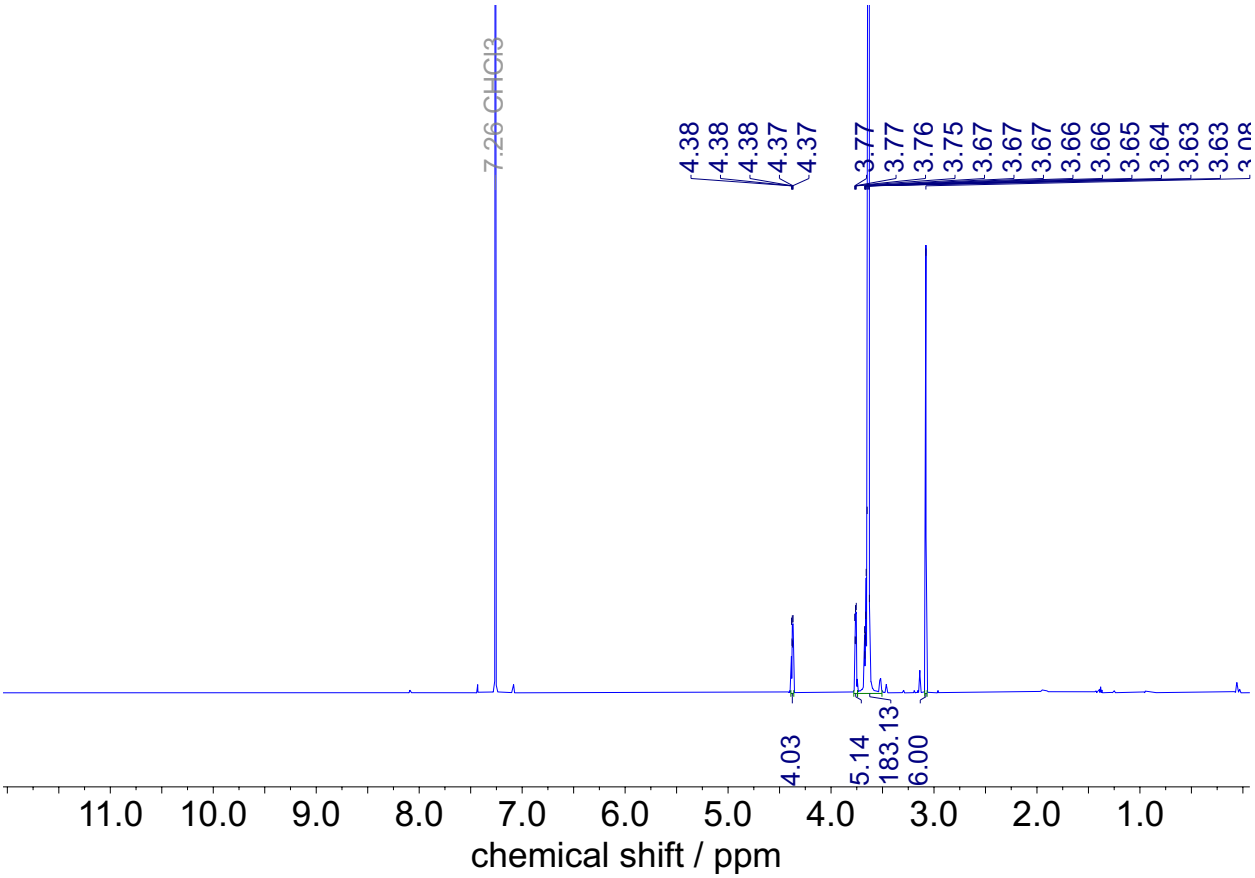


Figure S63. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S20**.

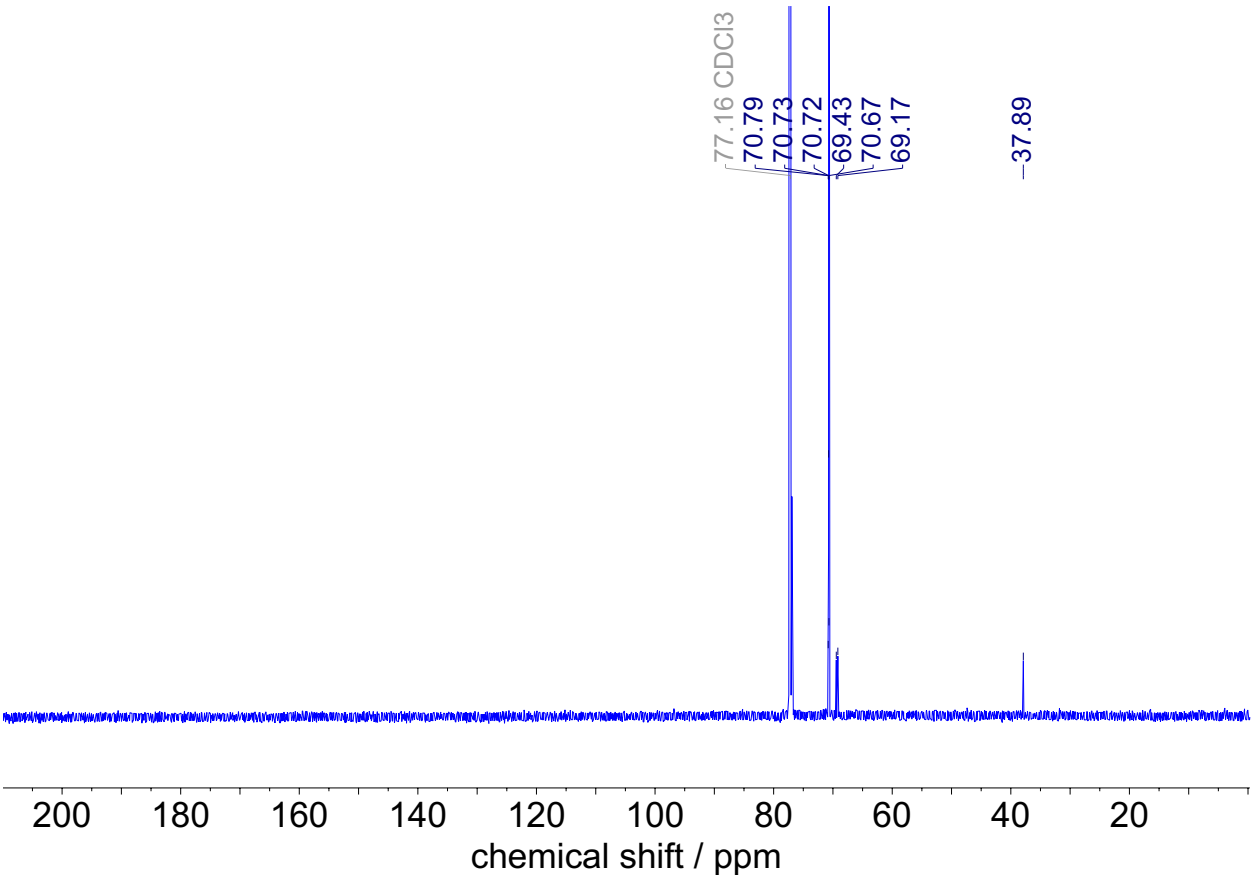


Figure S64. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **S20**.

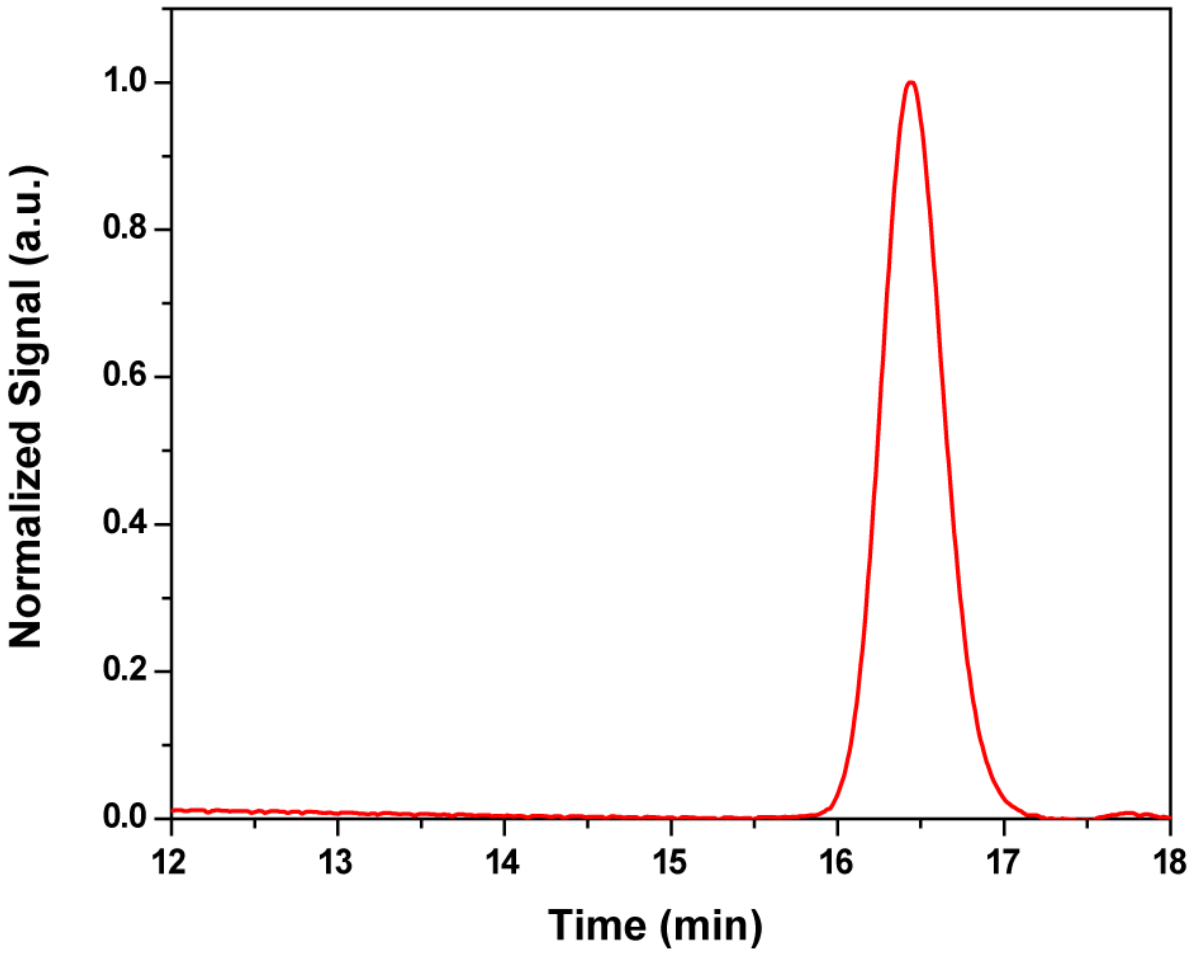


Figure S65. Normalized GPC-MALS differential refractive index (dRI) trace of **S20**. The molecular weight of the sample was measured at 2.08 kg/mol and the dispersity was recorded as $Đ$ = 1.08.

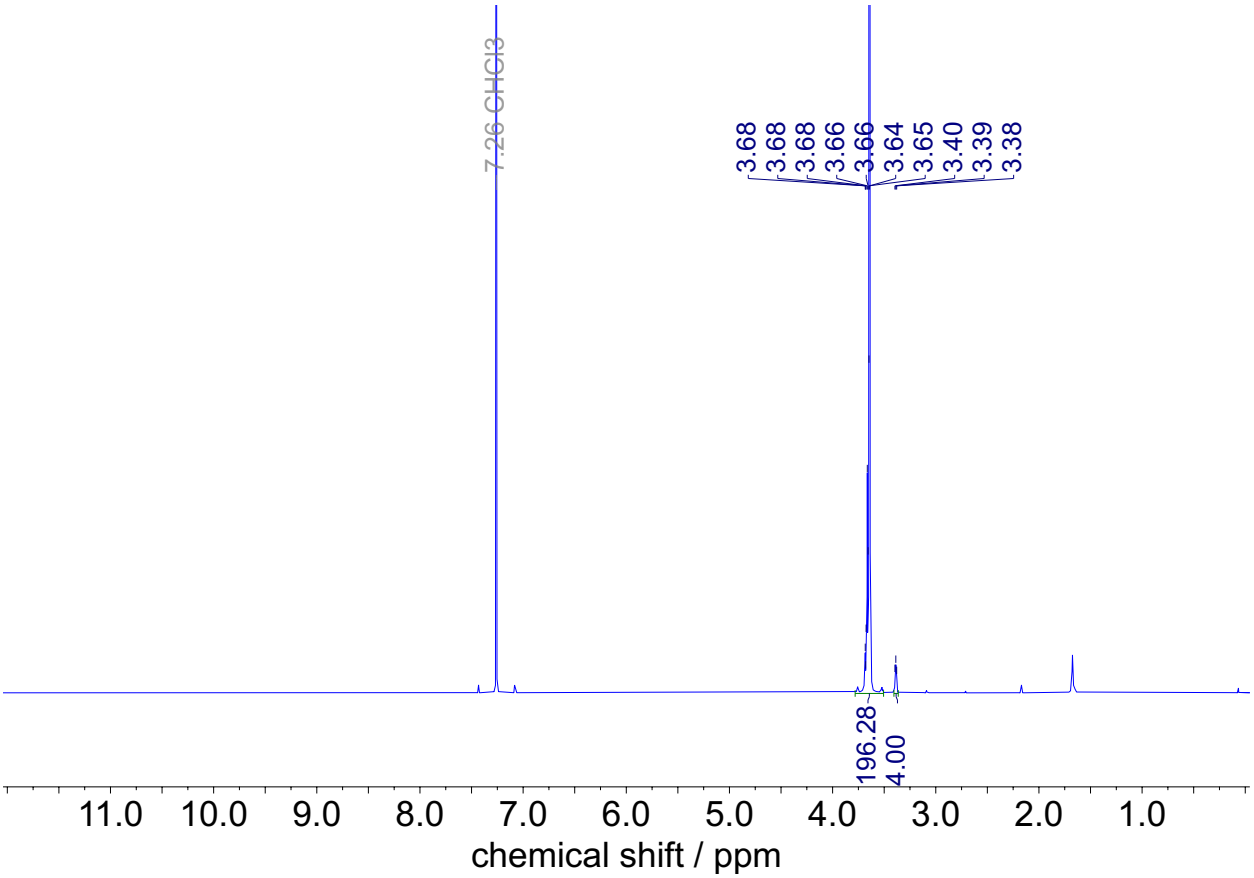


Figure S66. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S21**.

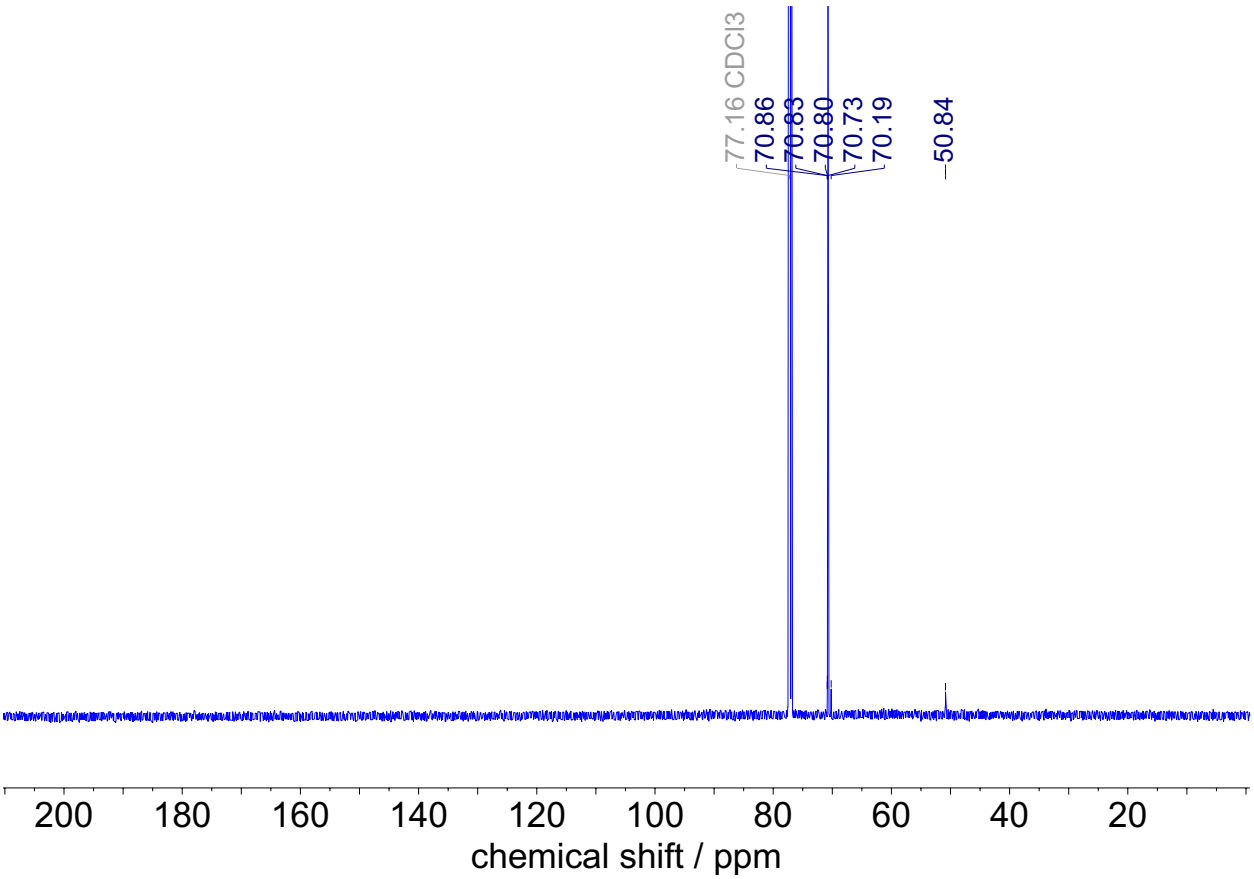


Figure S 67 ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **S21**.

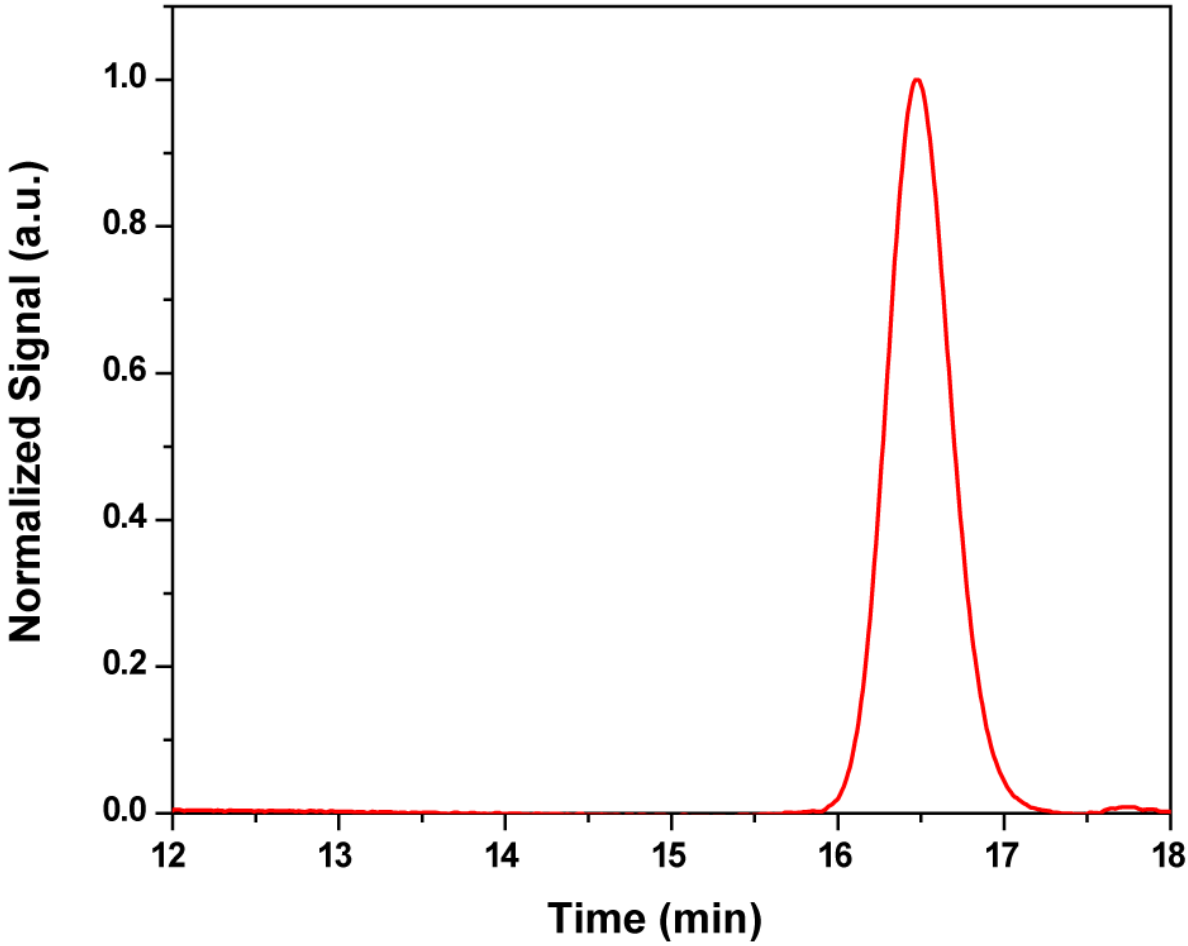


Figure S68. Normalized GPC-MALS differential refractive index (dRI) trace of **S21**. The molecular weight of the sample was measured at 2.12 kg/mol and the dispersity was recorded as $Đ$ = 1.08.

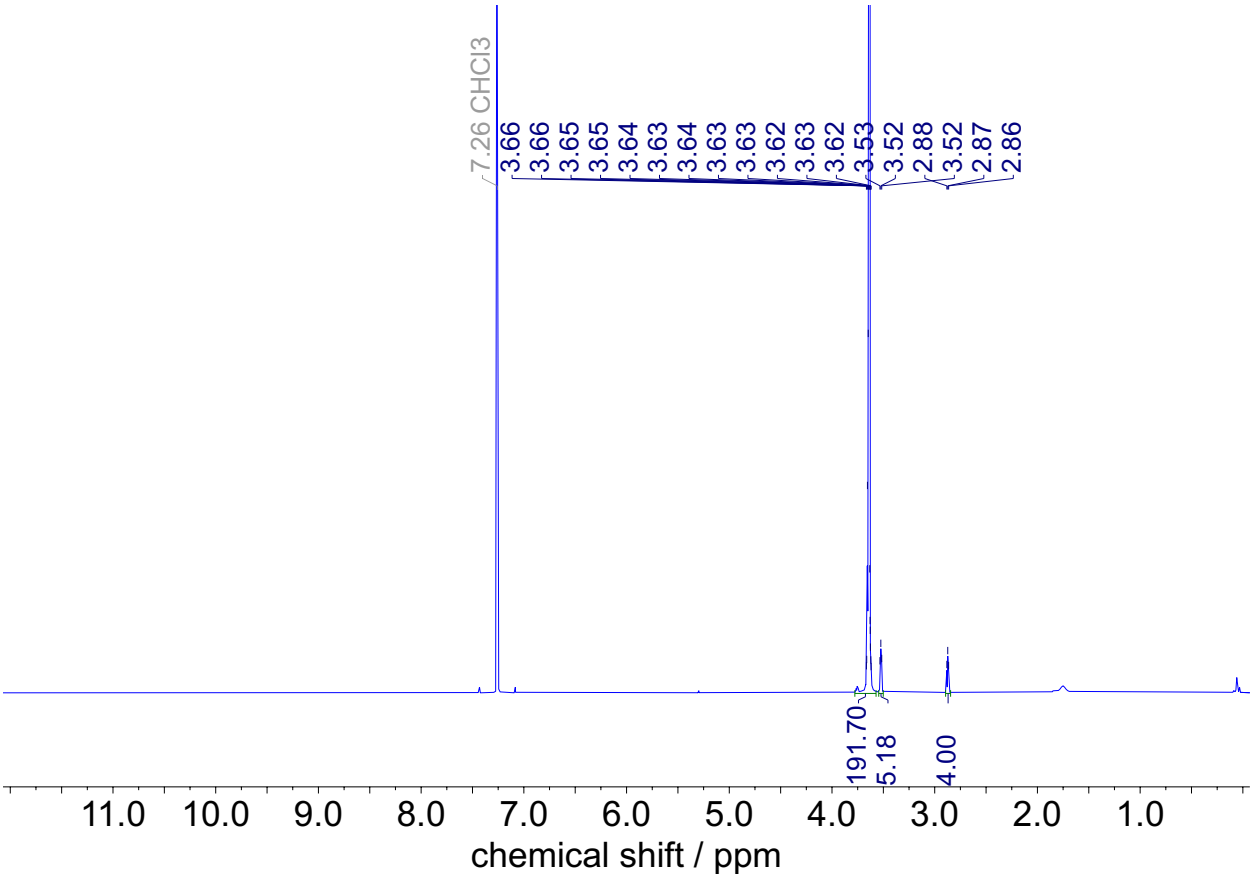


Figure S69. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S22**.

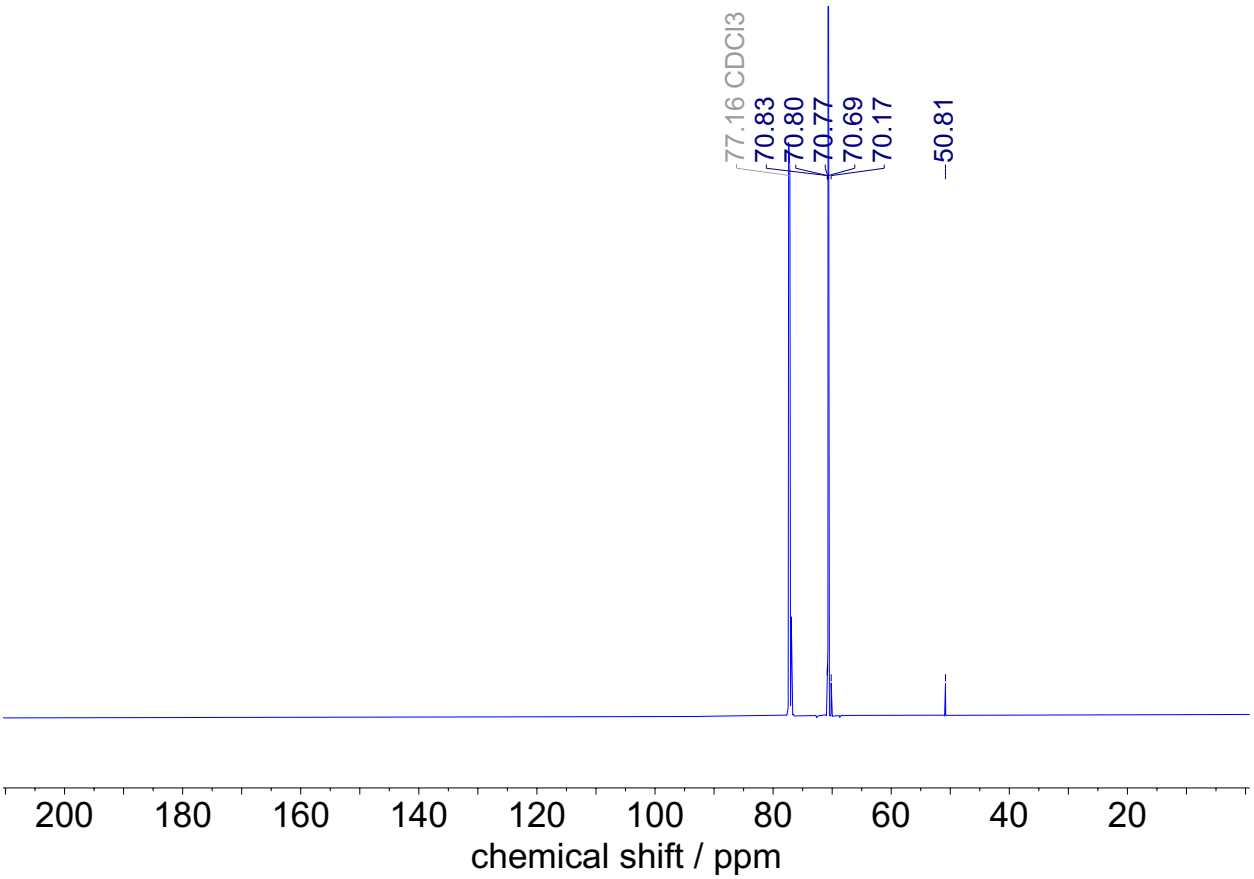


Figure S70. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **S22**.

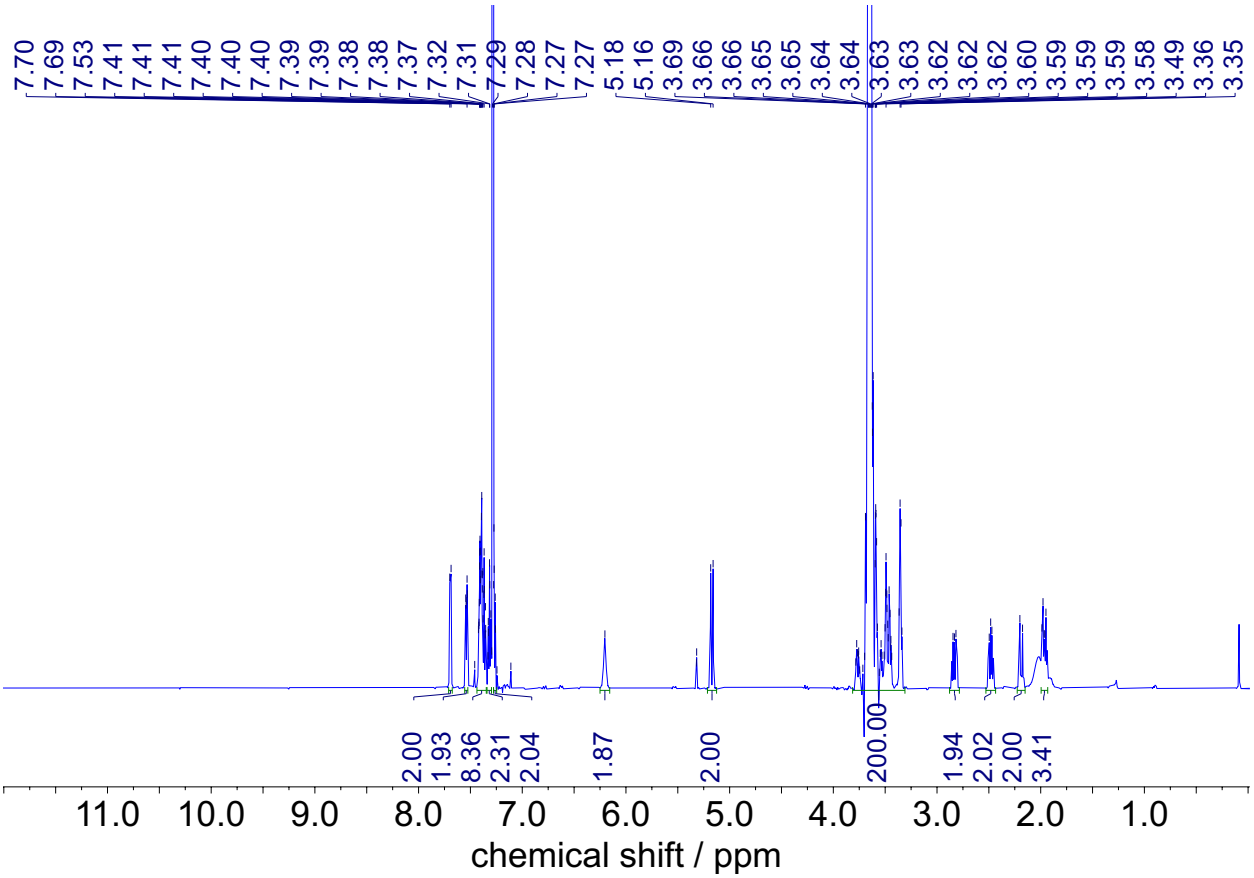


Figure S71. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **S23**.

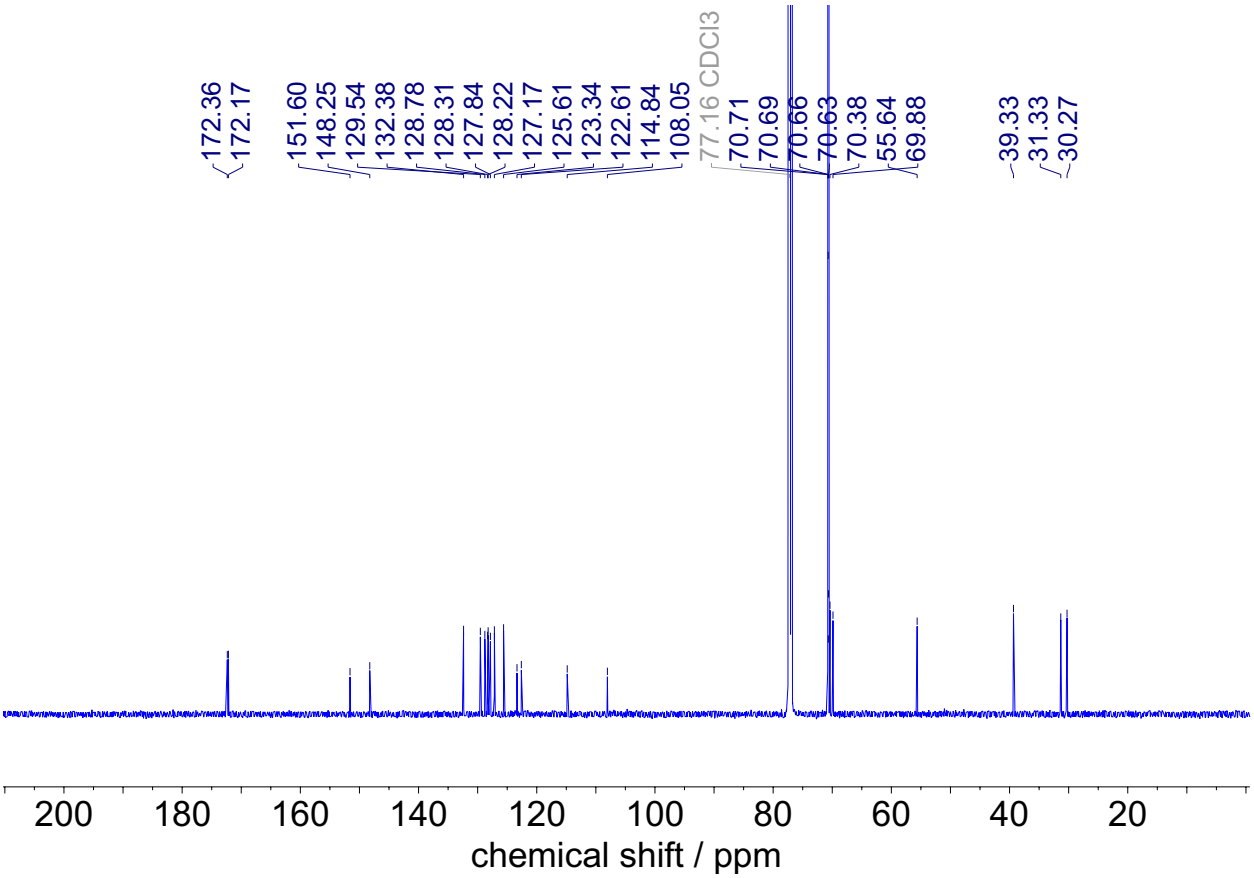


Figure S72. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **S23**.

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