

Supplementary Information

Catalytic living ring-opening metathesis polymerization with Grubbs' second and third generation catalysts

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Materials

All reagents including Grubbs' second (**G2**) and third (**G3**) generation catalysts, dicyclopentadiene, 7-norbornadienyl benzoate and ethyl vinyl ether were purchased from Sigma-Aldrich and used without further purification. All reactions were performed in flame-dried glassware under an inert argon atmosphere employing standard Schlenk techniques unless otherwise noted. *Exo*-N-methylnorbornenecarboximide (**M1**)¹, *exo*-N-hexylnorbornenecarboximide (**M3**)¹, (*E*)-(3-bromoprop-1-en-1-yl)cyclohexane², **CTA1**³ and *exo*-N-hydroxyethyl-norbornenecarboximide (**S1**)⁴ were synthesized as reported previously. Deuterated solvents (CDCl₃, CD₂Cl₂) were purchased from Cambridge Isotope Laboratories. Deuterated dichloromethane was degassed by three successive freeze-vacuum-thaw cycles immediately before use. Analytical thin layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 F254 (Merck) and visualised using either UV light (254 nm or 366 nm) or staining with potassium permanganate. Flash chromatography was performed using silica gel (SiliCycle, 230-400 mesh, particle size 32-63 µm, 60 Å).

Instrumentation

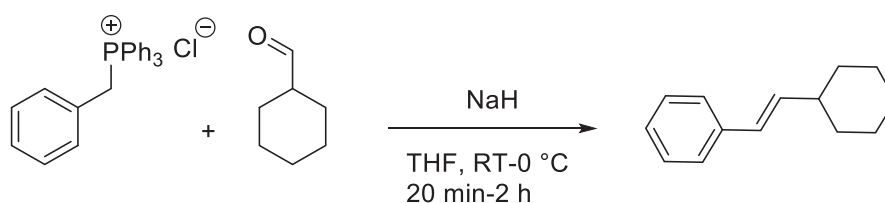
Injections of monomers into reaction mixtures were conducted using a syringe pump (World Precision Instruments, SP100iZ) equipped with a 20 mL BD syringe and a needle measuring 0.8 mm in diameter. High-resolution mass spectra (HR-MS) were obtained by electrospray ionization (ESI) on a Bruker BioApex II 4.7T mass spectrometer. Low-resolution mass spectra by electrospray ionization (ESI) were acquired on Bruker Daltonics Esquire HCT mass spectrometer. Electron impact ionization mass spectra (EI-MS) were run on a gas chromatography - mass spectrometry (GC-MS) instrument (Thermo Scientific DSQ II Series Single GC/MS with Trace GC Ultra gas chromatograph and Zebron capillary GC column (ZB-5MS, 0.25 µm, 30 x 0.25 mm)). MALDI-ToF (Matrix Assisted Laser Desorption Ionization Time of Flight) mass spectrometry was conducted on a Bruker ultrafleXtreme instrument using 2-[(2*E*)-3-(4-*tert*butylphenyl)-2-methylprop-2-enylidene] malononitrile (DCTB) as the matrix and silver trifluoroacetate as the ionizing salt. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC). For measurements in CHCl₃, the GPC was performed using an Agilent Technologies 1260 Infinity II GPC system, an refractive index (RI) detector, two MZ-Gel SDplus Linear columns (5 µm, 300 × 8.0 mm) and a MZ-Gel SDplus Linear precolumn (5 µm, 50 × 8.0 mm) at a flow rate of 1 mL/min. For measurements in THF, which were also conducted at a flow rate of 1 mL/min, the GPC instrument was equipped with a Viscotek GPCmax VE2001 GPC solvent/sample module, a Viscotek UV detector 2600, a Viscotek VE3580 RI detector and two Viscotek T6000 M columns (7.8 Å, 300 mm, 10³–10⁷ Da). All samples were filtered through a PTFE syringe membrane filter (0.45 µm pore size, VWR) prior to GPC measurements.

Polystyrene standards (Malvern Polycal PS standards, MW from 1×10^3 to 3×10^6) were used for calibration. ^1H and ^{13}C NMR spectra were recorded at 298 K on a Bruker Avance 300 NMR spectrometer (^1H NMR 300 MHz, ^{13}C NMR 75 MHz) and on a Bruker Avance 400 NMR spectrometer (^1H NMR 400 MHz, ^{13}C NMR 101 MHz). NMR signals were referenced to the residual undeuterated solvent proton signals, which were used as an internal reference. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane. NMR multiplicities are given by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), td (triplet of doublets) and dq (doublet of quartets).

Experimental procedures

Synthesis of (*E*)-(2-cyclohexylvinyl) benzene (CTA0)

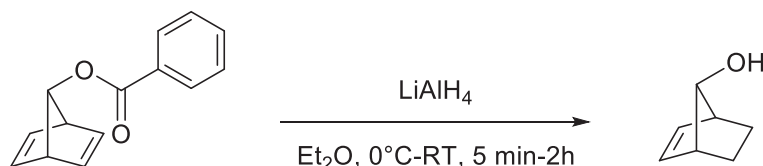
Phosphonium salt (3.46 g, 8.91 mmol, 2 eq) and NaH (60 % dispersion in oil, 0.318 g, 8.02 mmol, 1.8 eq) were dissolved in dry THF (18 mL). The reaction mixture was stirred at room temperature for 20 min and then allowed to cool to 0 °C. Cyclohexanecarboxaldehyde (0.5 g, 4.45 mmol, 1 eq) was added to the reaction mixture, which was stirred at 0 °C for 2 h. After removal of the solvent *in vacuo*, the crude product was purified by column chromatography with hexane as the eluent to give the product as colourless liquid (0.65 g, 78 % yield). ^1H NMR (300 MHz, CDCl_3): δ = 7.15-7.40 (m, 5H), 6.29-6.42 (m, 1H), 6.13-6.25 (m, 1H), 2.05-2.24 (m, 1H), 1.62-1.90 (m, 5H), 1.10-1.44 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3): δ = 139.0, 138.1, 136.8, 128.6, 128.4, 128.2, 127.2, 126.8, 126.7, 126.4, 125.9, 41.1, 36.9, 33.3, 33.0, 26.2, 26.0, 25.7. EI-MS m/z [M]: calculated 186.14, found 186.06.



Synthesis of bicyclo[2.2.1]hept-2-en-7-ol (S2)

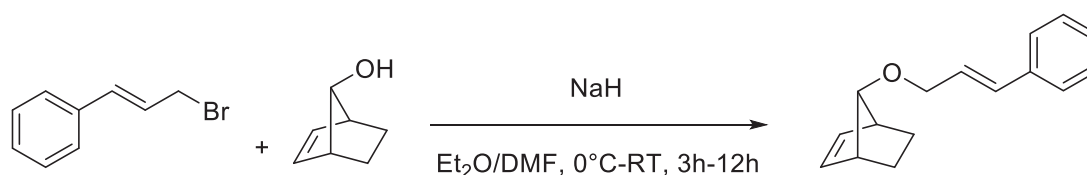
Lithium aluminum hydride (0.572 g, 15.07 mmol) was suspended in dry Et_2O (40 mL) at 0 °C, and a solution of 7-norbornadienyl benzoate (2 g, 9.42 mmol) in dry Et_2O (8 mL) was added slowly over 15 min. The mixture was stirred at 0 °C for further 5 min. It was then allowed to warm to room temperature and stirred for 2 hours. The suspension was then cooled to 0 °C and quenched carefully with saturated Na_2SO_4 . The crude mixture was dried over anhydrous MgSO_4 and filtered through a filter paper. The filtrate was carefully concentrated *in vacuo* and purified by column chromatography

(Et₂O:pentane 2:8) to yield the product as a white solid (0.98 g, 94 % yield). ¹H NMR (400 MHz, CDCl₃): δ = 5.98 (t, *J* = 2.1 Hz, 2H), 3.58 (s, 1H), 2.54 (dq, *J* = 3.8, 2.0 Hz, 2H), 1.78-1.85 (m, 2H), 1.61 (s, 1H), 1.01-1.06 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ = 134.5, 82.5, 45.6, 21.3.



Synthesis of 7-(cinnamyloxy)bicyclo[2.2.1]hept-2-ene (**S3**)

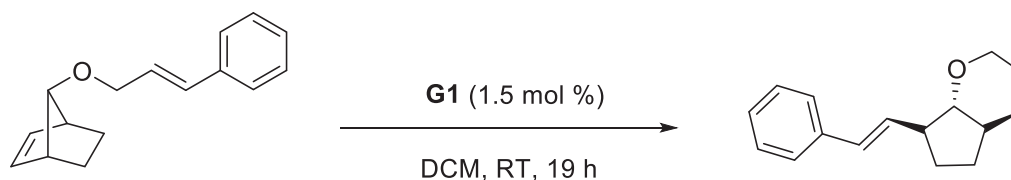
NaH (60 % dispersion in oil, 0.333 mg, 13.91 mmol, 1.5 eq) was suspended in dry Et₂O (70mL). After cooling to 0 °C, a solution of bicyclo[2.2.1]hept-2-en-7-ol (**S2**) (1.022 g, 9.27 mmol, 1 eq) in dry Et₂O (10 mL) was added over 15 min and the suspension stirred at 0 °C for 3 hours. Dry DMF (10 mL) was then added in one portion, followed by dropwise addition of cinnamyl bromide (2.19 g, 11.13 mmol, 1.2 eq) in dry Et₂O (12 mL) over a period of 30 min. The suspension was stirred until all the alcohol **S2** was consumed, the progress of which was followed by TLC. The reaction mixture was then quenched with water and extracted with ethyl acetate (3 x 50 mL). The organic layers were combined, dried over anhydrous MgSO₄ and concentrated *in vacuo*. The crude product was purified by column chromatography (Et₂O:pentane 1:24) to give the compound **S3** (1.7 g, 81 % yield) as a yellowish oil. ¹H NMR (300 MHz, CDCl₃): δ = 7.20-7.43 (m, 5H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.28 (dt, *J* = 16.0, 6.0 Hz, 1H), 5.95-6.03 (m, 2H), 4.09 (dd, *J* = 6.0, 1.5 Hz, 2H), 3.32 (s, 1H), 2.71 (dq, *J* = 3.8, 2.0 Hz, 2H), 1.77-1.89 (m, 2H), 0.96-1.04 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ = 136.8, 134.2, 131.8, 128.5, 127.6, 126.5, 126.5, 88.9, 68.9, 43.5, 21.8. HR-ESI-MS *m/z* [M + Na]⁺: calculated 249.12499, found 249.12523.



Synthesis of (*E*)-7-styryl-2,4a,5,6,7,7a-hexahydopenta[*b*]pyran (**CTA2**)

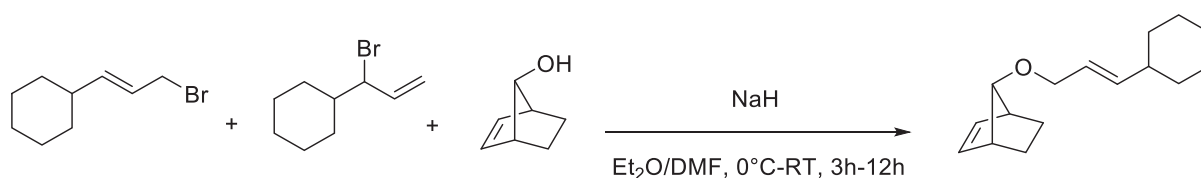
A solution of 7-(cinnamyloxy)bicyclo[2.2.1]hept-2-ene **S3** (2 g, 8.84 mmol) in dry, degassed DCM (37 mL) was added to a solution of **G1** (2 mol %) in dry, degassed DCM (13 mL). The reaction mixture was stirred at room temperature for 19 hours. It was then quenched with ethyl vinyl ether (0.2 mL). The solvent was removed *in vacuo* and residual solid purified by column chromatography (Et₂O:pentane

1:24) to give the product as a white solid (1 g, 50 % yield). ^1H NMR (300 MHz, CDCl_3): δ = 7.15-7.42 (m, 5H), 6.48 (d, J = 15.9 Hz, 1H), 6.20 (dd, J = 15.8, 8.0 Hz, 1H), 5.97 (dq, J = 10.0, 2.0 Hz, 1H), 5.63 (dq, J = 10.1, 2.6 Hz, 1H), 4.25-4.46 (m, 2H), 3.22 (t, J = 9.9 Hz, 1H), 2.58-2.74 (m, 1H), 2.25-2.42 (m, 1H), 2.13 (dtd, J = 13.6, 9.8, 7.6 Hz, 1H), 1.87 (dddd, J = 12.2, 9.6, 7.4, 2.6 Hz, 1H), 1.59-1.70 (m, 1H), 1.22-1.40 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ = 137.5, 132.6, 130.4, 128.6, 128.4, 126.9, 126.3, 126.1, 84.8, 68.3, 45.1, 41.1, 27.6, 23.6. HR-ESI-MS m/z $[\text{M} + \text{Na}]^+$: calculated 249.12499, found 249.12545.



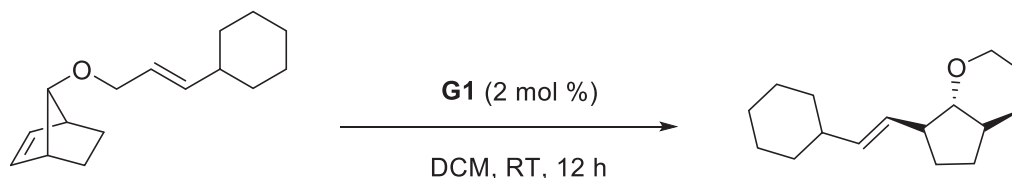
Synthesis of (*E*)-7-((3-cyclohexylallyl)oxy)bicyclo[2.2.1]-hept-2-ene (**S4**)

A suspension of NaH (60 % dispersion in oil, 0.145 mg, 6.04 mmol, 1.5 eq) in dry Et_2O (35 mL) was cooled to 0 °C. Bicyclo[2.2.1]hept-2-en-7-ol **S2** (0.444g, 4.03 mmol, 1eq) in dry Et_2O (5 mL) was then slowly added over a 15 min period. After stirring the suspension at 0 °C for 3 hours, dry DMF (5 mL) was added. A mixture of (1-bromoallyl)cyclohexane (9 %) and (*E*)-(3-bromoprop-1-en-1-yl)cyclohexane (91 %) (0.982 g, 4.83 mmol, 1.2 eq) in dry diethyl ether (6 mL) was then added dropwise over a period of 30 min. The reaction mixture was stirred until all the alcohol **S2** was consumed. The progress of the completion of the reaction was followed by TLC. The solution was quenched with water and extracted with ethyl acetate (3 x 50 mL). The organic layers were combined, dried over anhydrous MgSO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (Et_2O :pentane 1:99) to yield the product as a yellowish oil (0.8 g, 85 % yield). ^1H NMR (400 MHz, CDCl_3): δ = 5.94-6.00 (m, 2H), 5.57-5.66 (m, 1H), 5.43-5.53 (m, 1H), 3.85 (d, J = 6.0 Hz, 2H), 3.24 (s, 1H), 2.66 (dq, J = 3.7, 2.0 Hz, 2H), 1.90-2.02 (m, 1H), 1.62-1.82 (m, 7H), 1.02-1.33 (m, 5H), 0.93-0.99 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ = 139.7, 134.2, 124.1, 88.7, 69.3, 43.5, 40.3, 32.7, 26.2, 26.0, 21.8. HR-ESI-MS m/z $[\text{M} + \text{Na}]^+$: calculated 255.17194, found 255.17202.



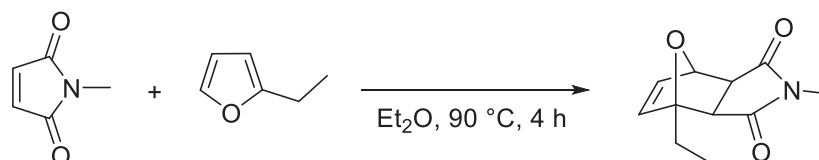
Synthesis of (*E*)-7-(2-cyclohexylvinyl)-2,4a,5,6,7,7a-hexahydrocyclopenta[*b*]pyran (**CTA3**)

A solution of (*E*)-7-((3-cyclohexylallyl)oxy)bicyclo[2.2.1]-hept-2-ene **S4** (0.7 g, 3.01 mmol) in dry, degassed DCM (16 mL) was added to a solution of **G1** (2 mol %) in dry, degassed DCM (4 mL). The reaction mixture was stirred at room temperature for 12 hours before being quenched by the addition of ethyl vinyl ether (0.2 mL). The solvent was removed *in vacuo* and residual solid purified by column chromatography (Et₂O:pentane 1:99) to give the product as a white solid (0.56 g, 80 % yield). ¹H NMR (400 MHz, CDCl₃): δ = 5.93 (dq, *J* = 10.0, 2.0 Hz, 1H), 5.56-5.63 (m, 1H), 5.43-5.51 (m, 1H), 5.29-5.38 (m, 1H), 4.28-4.42 (m, 2H), 3.03-3.12 (m, 1H), 2.41 (tt, *J* = 10.2, 7.9 Hz, 1H), 2.20-2.31 (m, 1H), 1.88-2.09 (m, 2H), 1.56-1.85 (m, 6H), 1.47 (dddd, *J* = 13.6, 10.9, 8.1, 2.7 Hz, 1H), 0.99-1.33 (m, 6H). ¹³C NMR (101 MHz, CDCl₃): δ = 137.1, 129.4, 128.7, 126.2, 84.8, 68.2, 44.6, 41.1, 40.5, 33.2, 33.0, 27.9, 26.3, 26.2, 26.1, 23.5. HR-ESI-MS *m/z* [M + Na]⁺: calculated 255.17194, found 255.17199.



Synthesis of *exo*-4-ethyl-*N*-methyl-7-oxanorbornenecarboximide (**M2**)

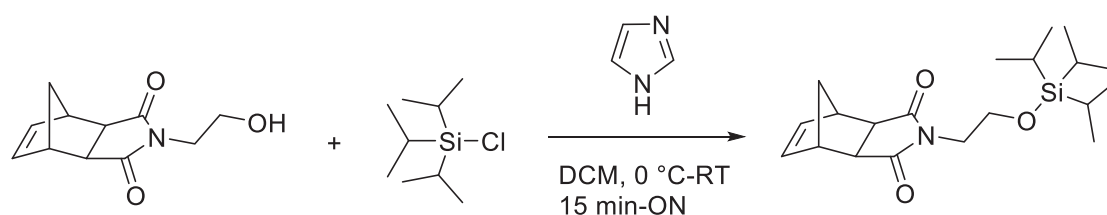
N-Methylmaleimide (2 g, 18 mmol, 1 eq) and 2-ethylfuran (3.79 mL, 36 mmol, 2 eq) were reacted in dry Et₂O (10 mL) in a sealed pressure tube under argon atmosphere. The reaction mixture was heated to 90 °C and stirred for 4 hours. Upon cooling the reaction mixture to -25 °C, white crystals formed. The crystals were washed four times with Et₂O to yield **M2** (1.75 g, 47 % yield). ¹H NMR (400 MHz, CDCl₃): δ = 6.52 (dt, *J* = 5.7, 0.8 Hz, 1H), 6.40 (d, *J* = 5.6 Hz, 1H), 5.21 (d, *J* = 1.7 Hz, 1H), 2.90-3.04 (m, 4H), 2.78 (d, *J* = 6.4 Hz, 1H), 1.97-2.17 (m, 2H), 1.14 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 176.3, 174.9, 138.5, 137.0, 92.4, 80.4, 50.6, 48.7, 24.8, 22.6, 9.4.



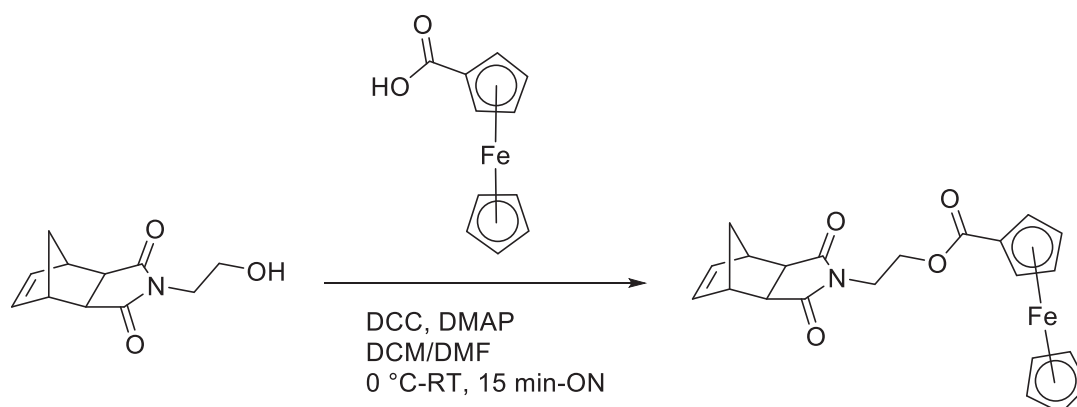
Synthesis of *exo*-*N*-triisopropylsilyloxyethyl-norbornenecarboximide (**M4**)

A solution of *exo*-*N*-hydroxyethyl-norbornenecarboximide **S1** (2 g, 9.65 mmol, 1 eq) and imidazole (1.31 g, 19.24 mmol, 2 eq) in dry DCM (30 mL) was cooled to 0 °C. Next, triisopropylsilyl chloride

(2.79 g, 14.47 mmol, 1.5 eq) dissolved in dry DCM (5 mL) was added dropwise over a period of 15 min. The reaction mixture was stirred overnight at room temperature. The suspension was then filtered, the filtrate concentrated *in vacuo* and the crude product purified by column chromatography (ethyl acetate:hexane 1:9) to yield the product as a colourless liquid (2.8 g, 80 % yield). ^1H NMR (300 MHz, CDCl_3): δ = 6.28 (t, J = 1.7 Hz, 2H), 3.81-3.89 (m, 2H), 3.62-3.70 (m, 2H), 3.23-3.31 (m, 2H), 2.67 (d, J = 1.1 Hz, 2H), 1.45-1.52 (m, 1H), 1.36-1.44 (m, 1H), 0.96-1.10 (m, 21H). ^{13}C NMR (75 MHz, CDCl_3): δ = 178.0, 137.8, 59.5, 47.8, 45.2, 42.9, 40.9, 17.9, 11.8. ESI-MS m/z [$\text{M} + \text{H}$] $^+$: calculated 364.2, found 364.1.



Synthesis of *exo*-N-ferrocenylcarbonyloxy-ethyl-norbornenecarboximide (**M5**)

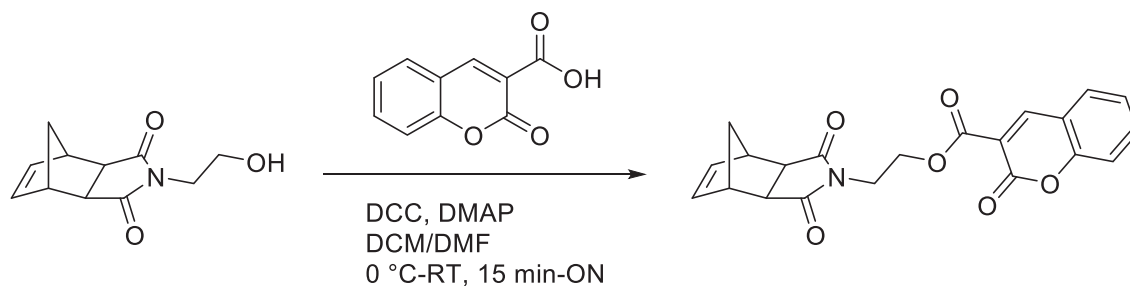


Dry DCM (50 mL) and dry DMF (5 mL) were added to a mixture of *exo*-N-hydroxyethyl-norbornenecarboximide **S1** (3 g, 14.47 mmol, 1 eq), ferrocenecarboxylic acid (3.66 g, 15.91 mmol, 1.1 eq) and 4-dimethylaminopyridine (DMAP, 0.176 g, 1.44 mmol, 0.1 eq). The reaction mixture was cooled to 0 °C and a solution of *N,N'*-dicyclohexylcarbodiimide (3.58 g, 17.35 mmol, 1.2 eq) in dry DCM (10 mL) was added dropwise over a period of 15 min. The reaction mixture was allowed to warm to room temperature, stirred overnight (ON) and filtered to remove dicyclohexylurea. The filtrate was concentrated *in vacuo* and purified by column chromatography (ethyl acetate:hexane 20:80) to give the product as an orange solid (3.18 g, 52 % yield). ^1H NMR (300 MHz, CDCl_3): δ = 6.30 (t, J = 1.8 Hz, 2H), 4.69-4.78 (m, 2H), 4.33-4.42 (m, 4H), 4.16-4.26 (m, 5H), 3.82-3.89 (m, 2H), 3.27-3.35 (m, 2H), 2.73 (d, J = 1.3 Hz, 2H), 1.53 (dt, J = 9.8, 1.5 Hz, 1H), 1.35 (d, J = 9.9 Hz, 1H). ^{13}C NMR (75

MHz, CDCl₃): δ = 177.7, 171.4, 137.8, 71.4, 70.5, 70.1, 69.8, 60.7, 47.8, 45.3, 42.7, 37.8. ESI-MS m/z [M + H]⁺: calculated 420.1, found 419.9.

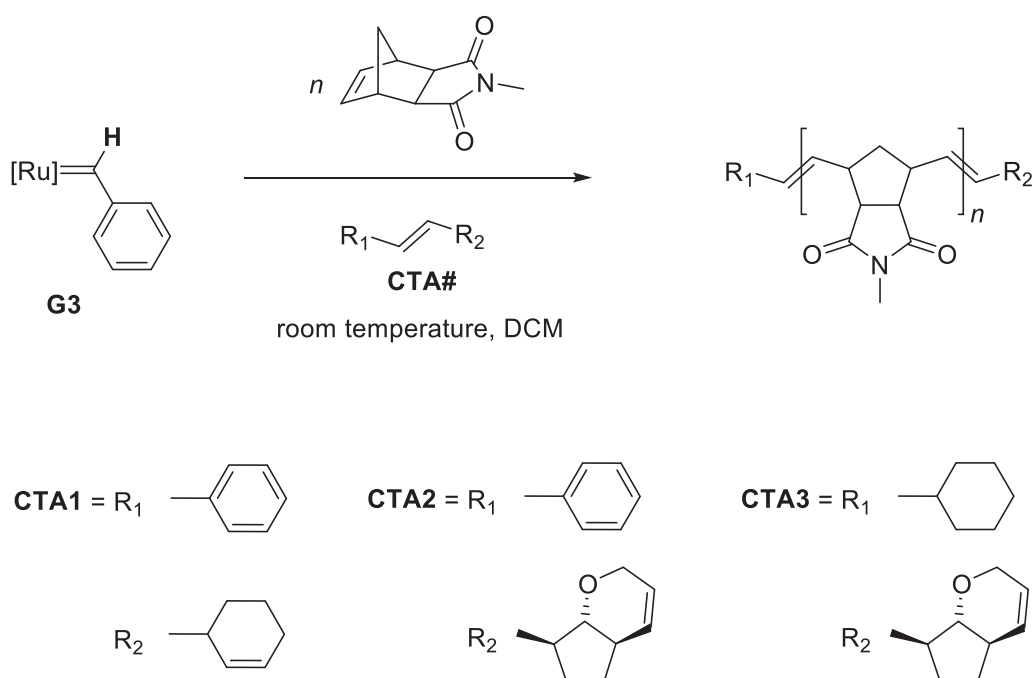
Synthesis of *exo*-N-coumarin-3-carboxyloxy-ethyl-norbornenecarboximide (**M6**)

Dry DCM (60 mL) was added to a mixture of *exo*-N-hydroxyethyl-norbornenecarboximide **S1** (3 g, 14.47 mmol, 1 eq), coumarin-3-carboxylic acid (2.75 g, 14.47 mmol, 1 eq) and dimethylaminopyridine (DMAP, 0.176 g, 1.44 mmol, 0.1 eq). The reaction mixture was cooled to 0 °C and a solution of N,N'-dicyclohexylcarbodiimide (3.28 g, 15.89 mmol, 1.1 eq) in dry DCM (10 mL) was added dropwise over a period of 15 min. The reaction mixture was allowed to warm to room temperature and stirred overnight (ON). The progress of the reaction was followed by TLC. Since a small amount of the **S1** starting material was still present in the reaction mixture, dry DMF (5 mL) was added and the suspension was stirred for further 7 hours. After removal of dicyclohexylurea by filtration, the filtrate was concentrated *in vacuo* and purified by column chromatography (ethyl acetate:hexane 1:1) to give **M6** (2.63 g, 48 % yield). ¹H NMR (300 MHz, CDCl₃): δ = 8.57 (s, 1H), 7.58-7.72 (m, 2H), 7.31-7.41 (m, 2H), 6.28 (t, J = 1.8 Hz, 2H), 4.45-4.57 (m, 2H), 3.87-3.95 (m, 2H), 3.22-3.32 (m, 2H), 2.76 (d, J = 1.2 Hz, 2H), 1.54 (dt, J = 10.0, 1.5 Hz, 1H), 1.35 (d, J = 9.9 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃): δ = 178.0, 162.7, 156.4, 155.3, 149.5, 137.8, 134.5, 129.7, 124.9, 117.9, 117.5, 116.8, 62.2, 48.0, 45.2, 42.9, 37.3. ESI-MS m/z [M + H]⁺: calculated 380.0, found 380.1.



Catalytic living ring-opening metathesis polymerization with **G3** catalyst

A typical procedure for the catalytic living ring-opening metathesis polymerization with **G3** catalyst is described as follows. A Schlenk flask containing monomer **M1** (0.45 g, 2.54 mmol, 561.84 eq) and another Schlenk flask containing a mixture of **G3** catalyst (4 mg, 4.52 μ mol, 1 eq) and chain-transfer agent **CTA#** (10-50 eq, see Table 1) were closed, evacuated and backfilled with argon three times. A solution of the deoxygenated monomer **M1** in dry, degassed DCM (4.5-18.0 mL, see Table 1) was added to a mixture of **G3** and **CTA#** in dry, degassed DCM (1 mL) at room temperature using a syringe pump (see Table 1). Immediately after the addition of the monomer, active metathesis species were quenched with ethyl vinyl ether (231 eq). The crude product was concentrated *in vacuo*, precipitated into methanol and dried under high vacuum. The polymerization led to nearly quantitative yields.

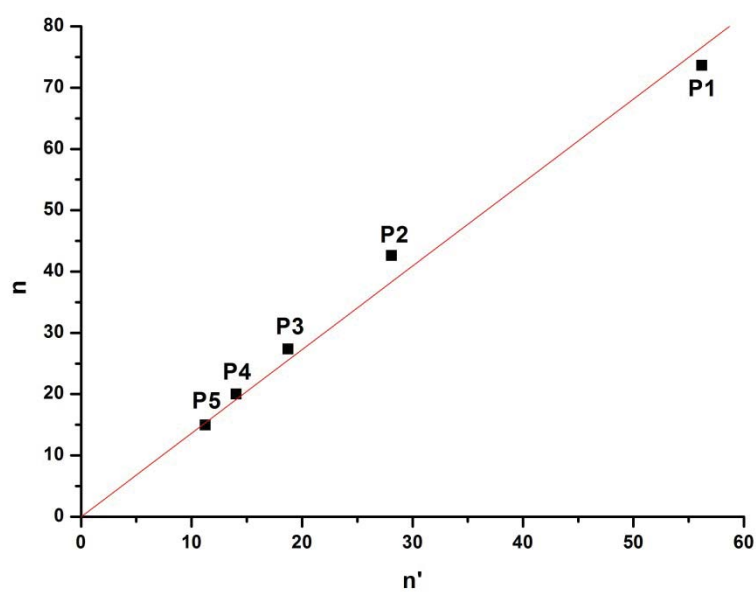


Scheme 1: Catalytic living ROMP with Grubbs' third generation catalyst and chain-transfer agents (CTA1-CTA3).

Table 1: The first part of the table shows detailed conditions for the catalytic living ROMP procedure with G3 catalyst (4 mg, 4.52 μ mol, 1 eq) and monomer M1 (0.45 g, 2.54 mmol, 561.84 eq) in dry, degassed DCM as described on page 8. Polymers prepared under preliminary reaction conditions are designated as OP1-OP7. Polymers prepared under optimized reaction conditions, on the other hand, are labelled as P1-P5. The second part of the table shows number average molecular weight (M_n) and polydispersity index ($\mathcal{D} = M_w/M_n$) values obtained by gel permeation chromatography, whereby polymers were dissolved either in CHCl_3 (GPC- CHCl_3) or in THF (GPC-THF). When the speed of monomer addition was increased to 10 mL/h (OP4), the broadening of \mathcal{D} was observed due to the accumulation of monomers, resulting in faster propagation rate compared to the reversible chain-transfer rate. At lower monomer concentration (0.025 g/mL), a better molecular weight control could be achieved since the viscosity of the solution was decreased thus increasing the reaction rates between propagating ruthenium carbene and macromolecular CTA.

Polymer	CTA	Flow rate monomer addition [mL/h]	Monomer conc. [g/mL]	CTA with respect to G3 [eq]	CTA [mmol]	Monomer: CTA ratio (n')	$M_{n\text{-theo}}$ [kDa]	M_n (GPC- CHCl_3) [kDa]	M_n (GPC-THF) [kDa]	Number of repeat units (n) (GPC- CHCl_3)	\mathcal{D} (GPC- CHCl_3)	\mathcal{D} (GPC-THF)
OP1	CTA2	0.3	0.100	10	0.0452	56.18	10	20.5	-	115.41	1.26	-
OP2	CTA2	0.5	0.100	10	0.0452	56.18	10	20.7	-	116.54	1.25	-
OP3	CTA2	2	0.100	10	0.0452	56.18	10	20.6	-	115.97	1.27	-
OP4	CTA2	10	0.100	10	0.0452	56.18	10	19.7	-	110.90	1.56	-
OP5	CTA3	2	0.100	10	0.0452	56.18	10	23.9	-	134.60	1.32	-
OP6	CTA2	4	0.025	10	0.0452	56.18	10	13.6	-	76.47	1.33	-
OP7	CTA1	2	0.025	10	0.0452	56.18	10	51	-	287.78	1.46	-
P1	CTA2	2	0.025	10	0.0452	56.18	10	13.1	-	73.65	1.24	-
P2	CTA2	2	0.025	20	0.0904	28.09	5	7.6	4.2	42.61	1.29	1.23
P3	CTA2	2	0.025	30	0.1356	18.73	3.3	4.9	3.4	27.37	1.42	1.22
P4	CTA2	2	0.025	40	0.1808	14.04	2.5	3.6	2.9	20.04	1.31	1.16
P5	CTA2	2	0.025	50	0.2261	11.24	2	2.7	2.3	14.96	1.37	1.20

a



b

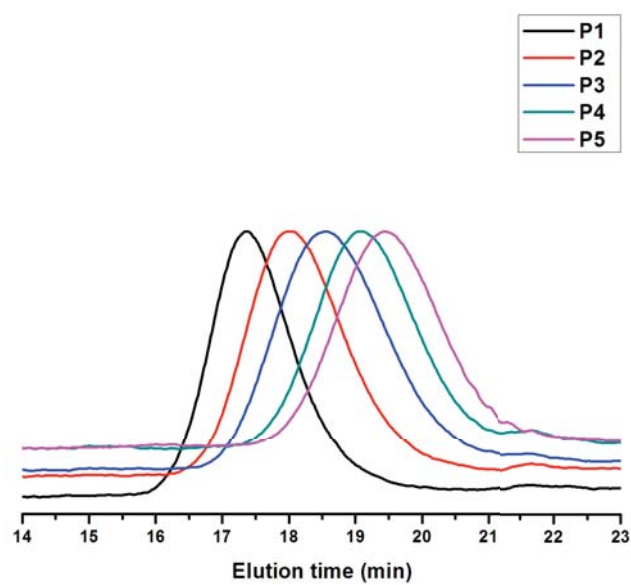
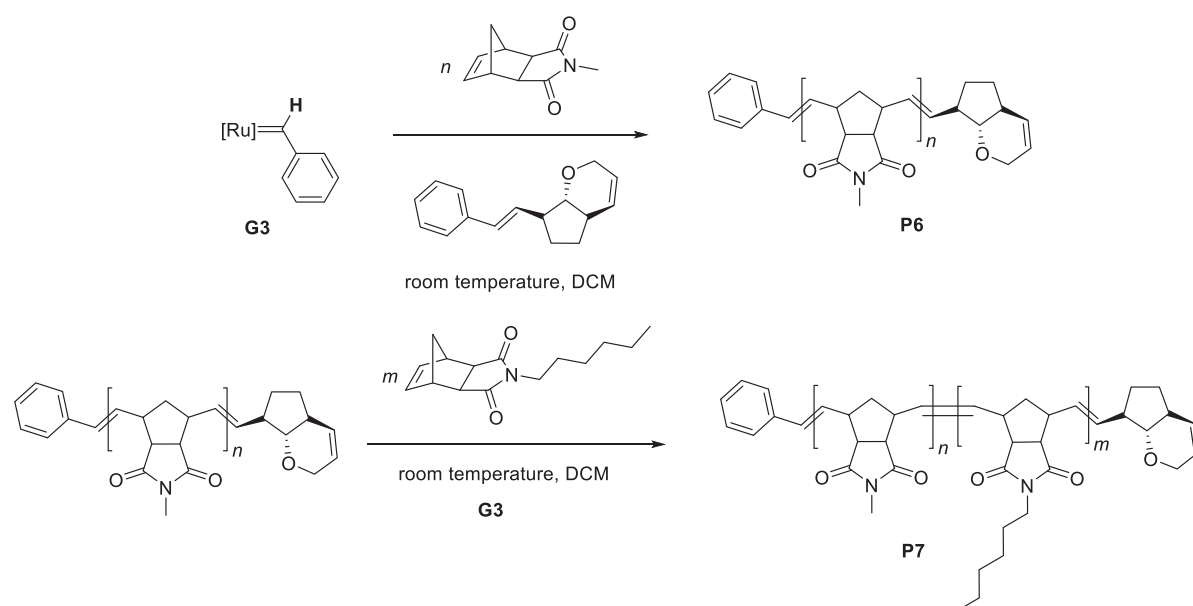


Figure 1: a, Plot showing linear dependency of the number of repeat units (n) on monomer:CTA2 (n') ratio in polymers P1-P5. b, GPC traces of polymers P1-P5 dissolved in CHCl_3 .

Preparation of block-copolymers by catalytic living ring-opening metathesis polymerization with **G3** catalyst



Scheme 2: Block-copolymerization by the catalytic living ROMP with Grubbs' third generation catalyst and chain-transfer agent CTA2.

The typical procedure for the catalytic living ring-opening metathesis block-copolymerization with **G3** catalyst is described as follows. A Schlenk flask containing monomer **M1** (0.25 g, 1.41 mmol, 312.13 eq) and another Schlenk flask containing a mixture of **G3** catalyst (4 mg, 4.52 μ mol, 1 eq) and chain-transfer agent **CTA2** (10 eq) were closed, evacuated and backfilled with argon three times. A solution of the deoxygenated monomer **M1** in dry, degassed DCM (10 mL) was added to the mixture of **G3** and **CTA3** in dry, degassed DCM (1 mL) at room temperature using a syringe pump (flow rate 2 mL/h). After the addition of the monomer, the crude product was concentrated *in vacuo*, precipitated into methanol and dried under high vacuum. The polymer **P6** (M_n = 8 kDa and \bar{D} = 1.33) was obtained in nearly quantitative yields.

For the block-copolymerization, polymer **P6** (100 mg, 0.0164 mmol) and catalyst **G3** (4 mg, 4.52 μ mol) were stirred in dry, degassed DCM (5 mL) for 1 hour. A Schlenk flask containing *exo*-N-hexyl-norbornenecarboximide **M3** (0.15 g, 0.61 mmol) was closed, evacuated and backfilled with argon three times and dissolved in dry, degassed DCM (6 mL). The **M3** solution was added to the mixture of polymer **P6** and catalyst **G3** at room temperature using a syringe pump (flow rate 2 mL/h). After complete addition of the monomer **M3**, ethyl vinyl ether (231 eq) was added to quench active metathesis species. The crude product was concentrated *in vacuo*, precipitated into methanol and dried under high vacuum to yield polymer **P7** (M_n = 16 kDa and \bar{D} = 1.52).

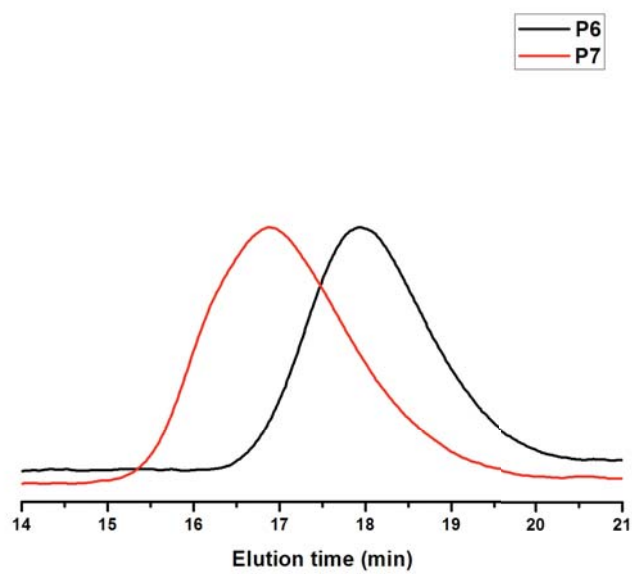
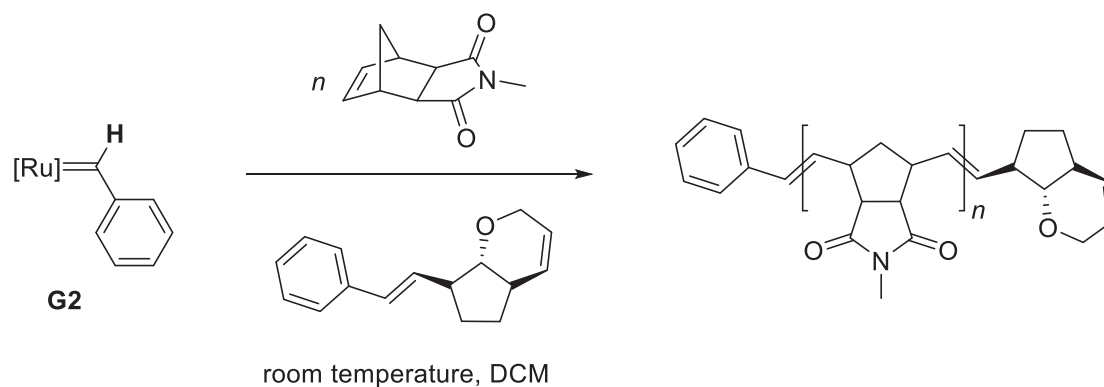


Figure 2: GPC traces of polymer P6 and block-copolymer P7 dissolved in CHCl_3 .

Catalytic living ring-opening metathesis polymerization with **G2** catalyst

A typical procedure for the catalytic living ring-opening metathesis polymerization with **G2** catalyst is described as follows. A Schlenk flask containing monomer **M1** (0.45 g, 2.54 mmol, 561.84 eq) and another Schlenk flask containing a mixture of **G2** catalyst (4 mg, 4.71 μ mol, 1 eq) and chain-transfer agent **CTA2** (10-40 eq, see Table 2) were closed, evacuated and backfilled with argon three times. A solution of the deoxygenated monomer **M1** in dry, degassed DCM (18 mL) was added to the mixture of **G2** and **CTA2** in dry, degassed DCM (1 mL) at room temperature using a syringe pump (flow rate 2 mL/h). Immediately after the addition of the monomer, active metathesis species were quenched with ethyl vinyl ether (222 eq). The resulting polymers were concentrated *in vacuo*, precipitated into methanol and dried under high vacuum. The polymerization led to nearly quantitative yields.

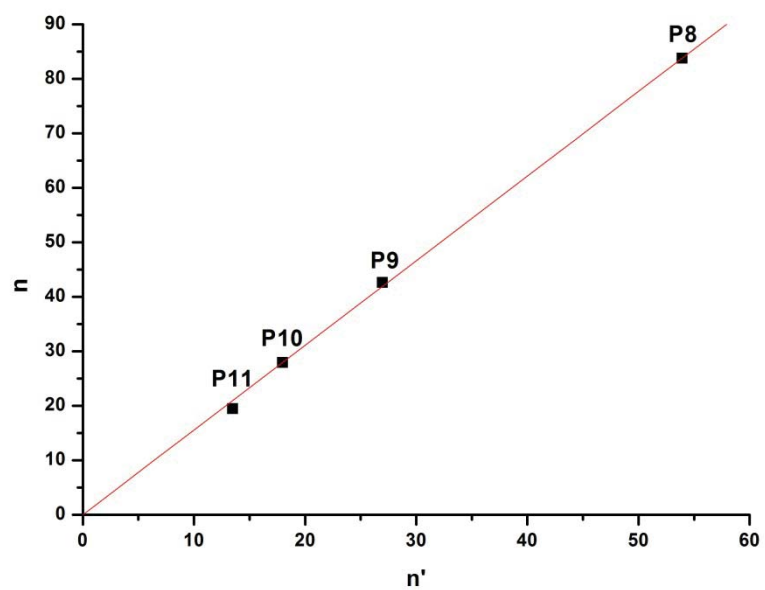


Scheme 3: Catalytic living ROMP with Grubbs' second generation catalyst and chain-transfer agent CTA2.

Table 2: The table shows the effects of varying the amount of CTA2 on the number average molecular weights (M_n) and polydispersity indices ($\mathcal{D} = M_w/M_n$). Catalytic living ROMP was conducted with **G2 (4 mg, 4.71 μ mol, 1 eq) and **M1** (0.45 g, 2.54 mmol, 539.17 eq).**

Polymer	CTA2 with respect to G2	CTA2 [mmol]	Monomer: CTA ratio (n')	M_{n-theo} [kDa]	M_n (GPC-CHCl ₃ /THF) [kDa]	Number of repeat units (n) (GPC-CHCl ₃)	\mathcal{D} (GPC-CHCl ₃ /THF)
P8	10 eq	0.0471	53.92	9.6	14.9/-	83.81	1.25/-
P9	20 eq	0.0942	26.96	4.8	7.6/4.4	42.61	1.39/1.25
P10	30 eq	0.1413	17.97	3.2	5.0/3.4	27.94	1.37/1.21
P11	40 eq	0.1884	13.48	2.4	3.5/2.9	19.47	1.40/1.18

a



b

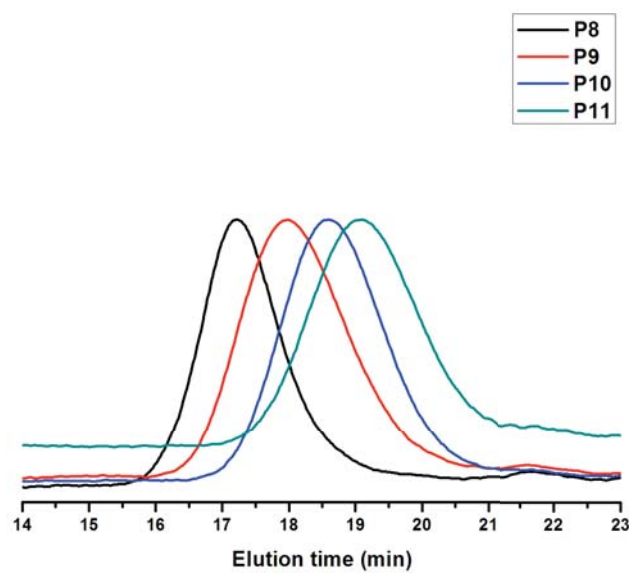
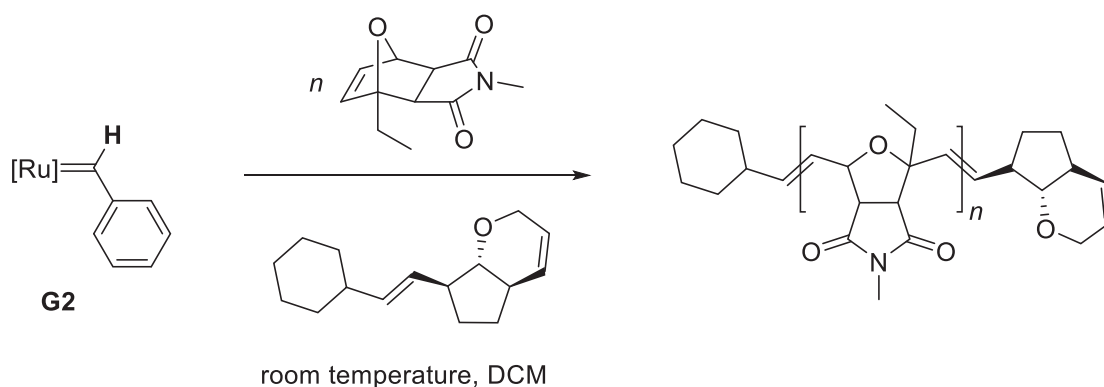


Figure 3: a, Plot showing linear dependency of the number of repeat units (n) on monomer:CTA2 ratio (n') in polymers P8-P11. b, GPC traces of polymers P8-P11 dissolved in CHCl_3 .

One shot catalytic living ring-opening metathesis polymerization

A typical procedure for the one shot catalytic living ring-opening metathesis polymerization with **G2** catalyst is described as follows. A Schlenk flask containing monomer **M2** (0.3 g, 1.45 mmol, 307.36 eq) was closed, evacuated and backfilled with argon three times. A solution of the deoxygenated monomer **M2** in dry, degassed DCM (18 mL) was added in one portion to the mixture of **G2** and **CTA2** in dry, degassed DCM (1 mL) and polymerized at room temperature for 24 h. Active metathesis species were then quenched with ethyl vinyl ether (222 eq). The resulting polymers were concentrated *in vacuo*, precipitated into methanol and dried under high vacuum.



Scheme 4: Catalytic living ROMP with Grubbs' second generation catalyst and chain transfer-agent CTA2.

Table 3: The table shows the effects of varying the amount of CTA2 on the number average molecular weights (M_n) and polydispersity indices ($\bar{D} = M_w/M_n$). One shot catalytic living ROMP was conducted with **G2 (4 mg, 4.71 μ mol, 1 eq) and **M2** (0.3 g, 1.45 mmol, 307.36 eq).**

Polymer	CTA2 with respect to G2	CTA2 [mmol]	Mono-mer: CTA ratio (n')	M_{n-theo} [kDa]	M_n (GPC-THF /CHCl ₃) [kDa]	Number of repeat units (n) (GPC-THF /CHCl ₃)	\bar{D} (GPC-THF /CHCl ₃)	Yield [%]
P12	20 eq	0.0942	15.37	3.2	2.7/2.6	12.91/12.43	1.19/1.44	86
P13	30 eq	0.1413	10.25	2.1	2.1/1.8	10.01/8.56	1.20/1.45	84
P14	40 eq	0.1884	7.68	1.6	1.8/1.4	8.56/6.63	1.17/1.40	85
P15	50 eq	0.2356	6.15	1.28	1.6/1.2	7.60/5.67	1.14/1.35	86

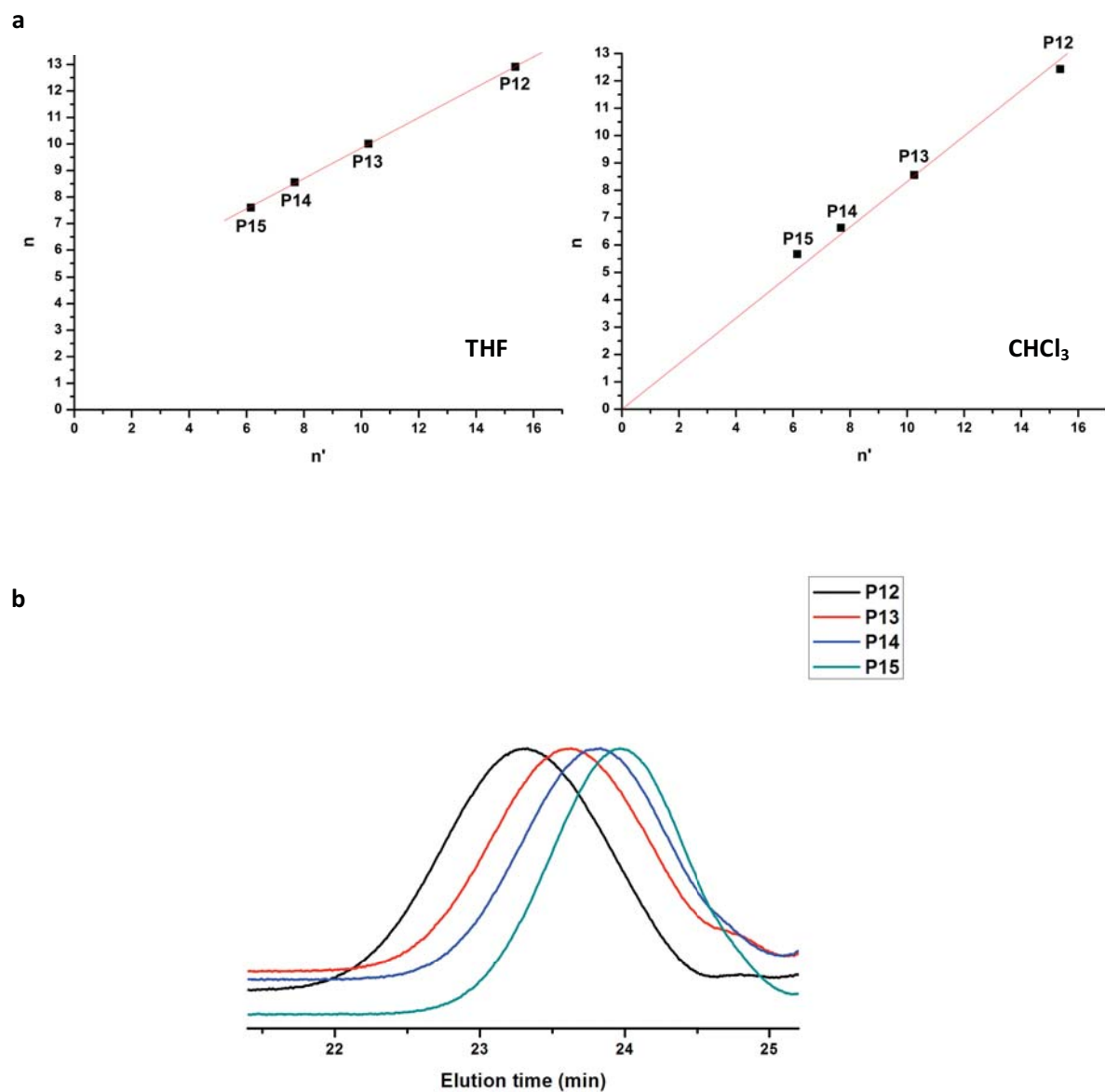
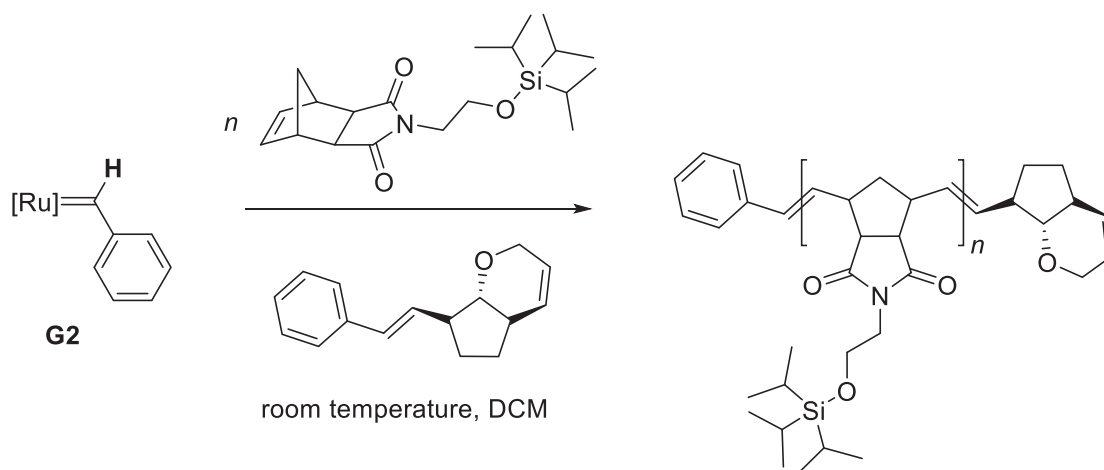


Figure 4: a, Plots showing linear dependency of the number of repeat units (n) on monomer:CTA₂ ratio (n') in polymers P12-P15. b, GPC traces of polymers P12-P15 dissolved in THF.

Catalytic living ring opening metathesis polymerization of bulky monomers with **G2** catalyst

A typical procedure for the catalytic living ring-opening metathesis polymerization of bulky monomers with **G2** catalyst is described as follows. A Schlenk flask containing monomer **M#** (see Tables 4-6) and another Schlenk flask containing a mixture of **G2** catalyst (4 mg, 4.71 μmol , 1 eq) and chain-transfer agent **CTA2** (10-20 eq, see Tables 4-6) were closed, evacuated and backfilled with argon three times. A solution of a deoxygenated monomer **M#** in dry, degassed DCM (18 mL) was added to the mixture of **G2** and **CTA2** in dry, degassed DCM (1 mL) at room temperature using a syringe pump (see Table 4-6). Immediately after the addition of the monomer, active metathesis species were quenched with ethyl vinyl ether (222 eq). The crude product was concentrated *in vacuo*, precipitated into methanol and dried under high vacuum.

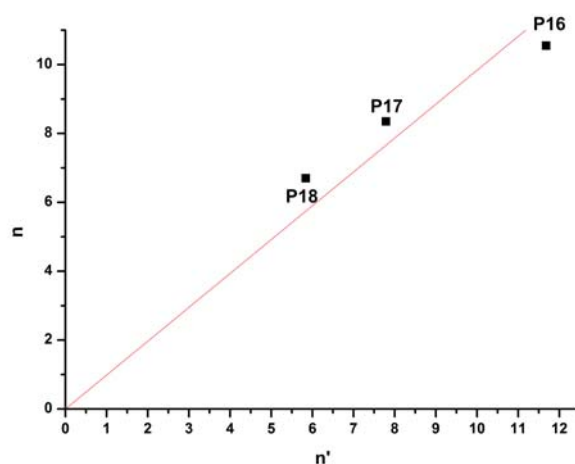


Scheme 5: Catalytic living ROMP of *exo*-N-triisopropylsilyloxyethyl-norbornenecarboximide **M4 with Grubbs' second generation catalyst and chain-transfer agent **CTA2**.**

Table 4: The table shows the effects of varying the amount of CTA2 and the flow rate of the syringe pump on the number average molecular weights (M_n) and polydispersity indices ($\mathcal{D} = M_w/M_n$). Catalytic living ROMP of M4 (0.2 g, 0.55 mmol, 116.79 eq) was conducted with G2 (4 mg, 4.71 μ mol, 1 eq) at room temperature. Polymerization of OP8 polymer, on the other hand, was carried out at -20 °C. Poor molecular weight control and broad molecular weight dispersity were observed due to low reactivity of propagating carbene at such low temperatures.

Polymer	Flow rate [mL/h]	CTA2 with respect to G2	CTA2 [mmol]	Monomer: CTA ratio (n')	M_{n-theo} [kDa]	M_n (GPC-CHCl ₃) [kDa]	Number of repeat units (n)	\mathcal{D}	Yield [%]
P16	2	10 eq	0.0471	11.68	4.2	3.7	10.55	1.25	87
OP8	2	10 eq	0.0471	11.68	4.2	32.8	90.59	1.66	80
OP9	4	10 eq	0.0471	11.68	4.2	4.1	11.65	1.30	90
P17	2	15 eq	0.0706	7.79	2.8	2.9	8.35	1.23	82
P18	2	20 eq	0.0942	5.84	2.1	2.3	6.70	1.39	78

a



b

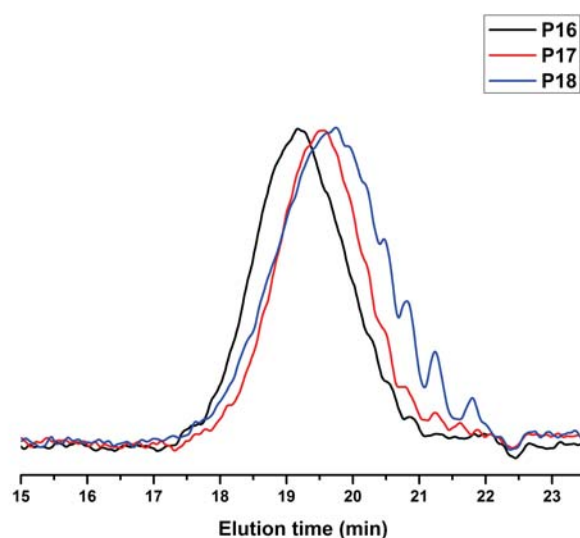
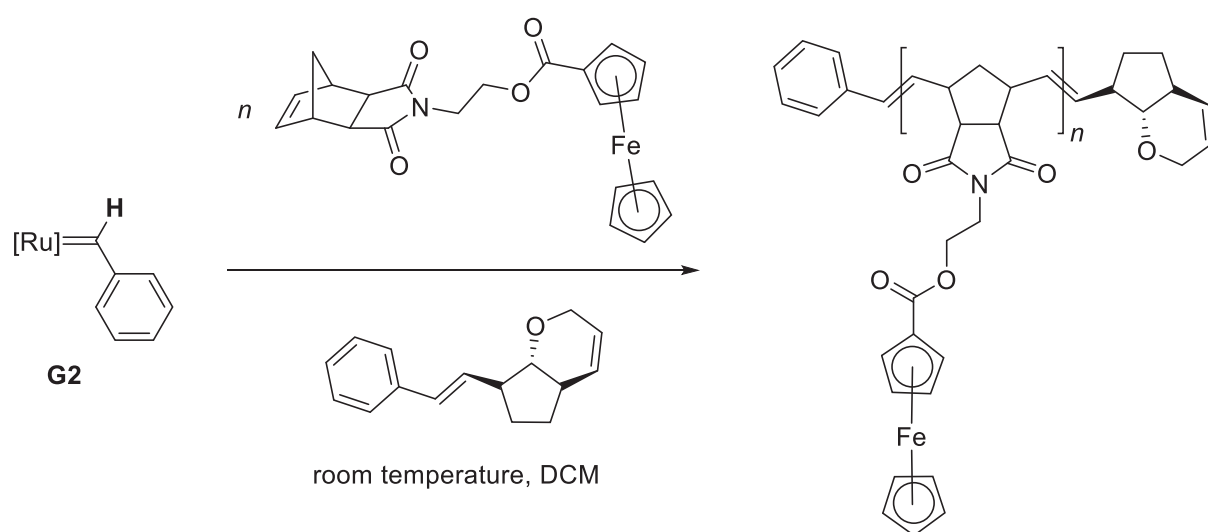


Figure 5: a, Plot showing linear dependency of the number of repeat units (n) on monomer:CTA2 ratio (n') in polymers P16-P18. b, GPC traces of polymers P16-P18 dissolved in CHCl₃.

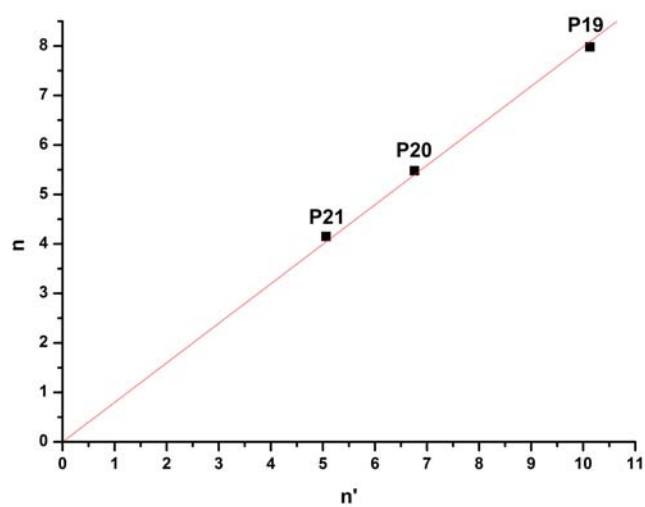


Scheme 6: Catalytic living ROMP of *exo*-N-ferrocenylcarbonyloxy-ethyl-norbornenecarboximide (M5) with Grubbs' second generation catalyst and chain transfer-agent CTA2.

Table 5: The table shows the effects of varying the amount of CTA2 and the flow rate of the syringe pump on the number average molecular weights (M_n) and polydispersity indices ($\mathfrak{D} = M_w/M_n$). Catalytic living ROMP of M5 (0.2 g, 0.477 mmol, 94.5 eq) was conducted with G2 (4 mg, 4.71 μ mol, 1 eq) at room temperature. The standard errors of the mean M_n values were obtained from triplicate GPC measurements of the respective polymeric samples dissolved in CHCl_3 .

Polymer	Flow rate [mL/h]	CTA2 with respect to G2	CTA2 [mmol]	Monomer: CTA ratio (n')	$M_{n\text{-theo}}$ [kDa]	M_n (GPC- CHCl_3) [kDa]	Number of repeat units (n)	\mathfrak{D}	Yield [%]
P19	2	10 eq	0.0471	10.13	4.2	3.152 ± 0.010	7.98 ± 0.02	1.29	95
OP10	4	10 eq	0.0471	10.13	4.2	3.345	8.44	1.39	95
P20	2	15 eq	0.0706	6.76	2.8	2.104 ± 0.008	5.48 ± 0.020	1.36	93
P21	2	20 eq	0.0942	5.06	2.1	1.548 ± 0.005	4.15 ± 0.01	1.25	92

a



b

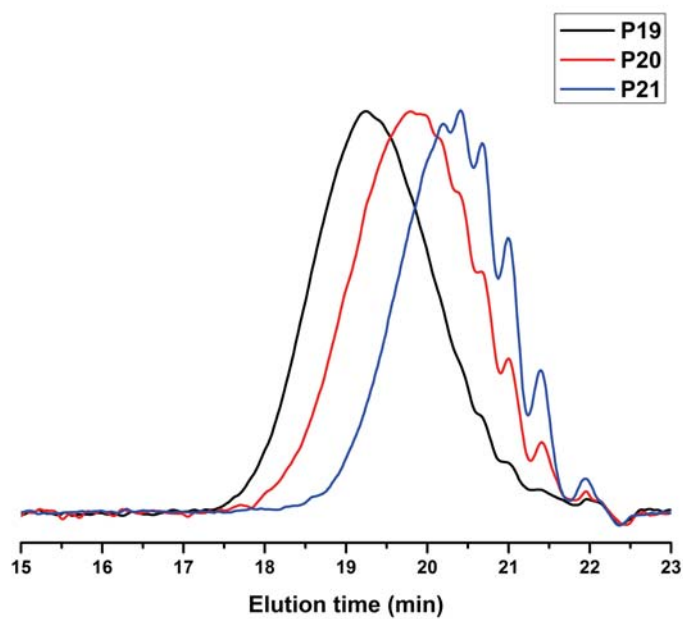
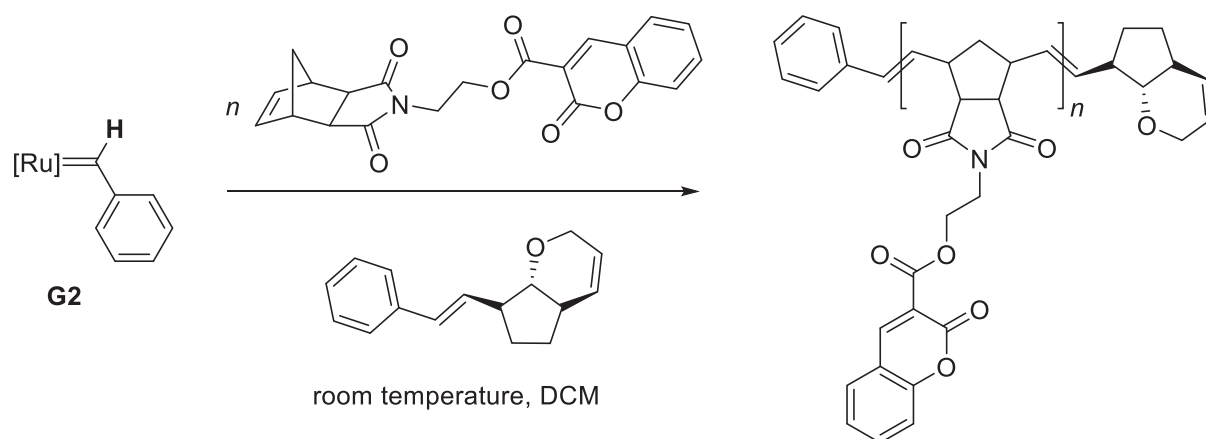


Figure 6: a, Plot showing linear dependency of the number of repeat units (n) on monomer:CTA2 ratio (n'), polymers P19-P21. b, GPC traces of polymers P19-P21 dissolved in CHCl_3 .

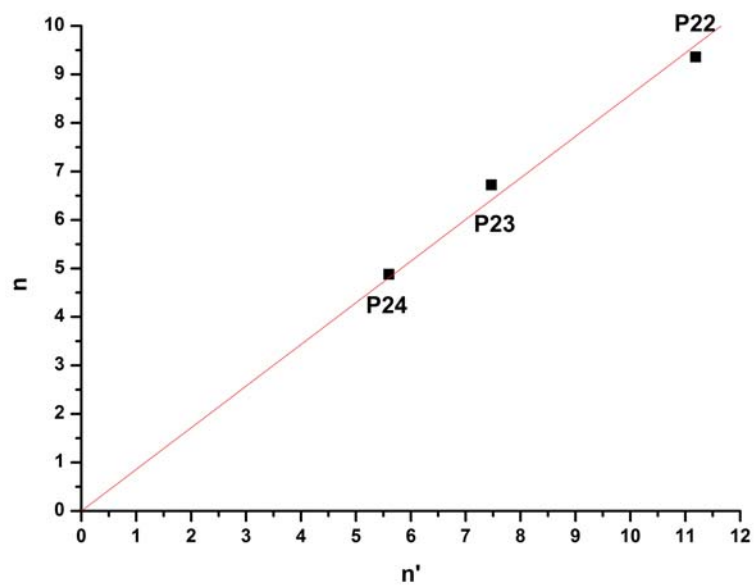


Scheme 7: Catalytic living ROMP of *exo*-N-coumarin-3-carboxyloxy-ethyl-norbornenecarboximide M6 with Grubbs' second generation catalyst and chain-transfer agent CTA2.

Table 6: The table shows the effects of varying the amount of CTA2 and the flow rate of the syringe pump on the number average molecular weights (M_n) and polydispersity indices ($\mathcal{D} = M_w/M_n$). Catalytic living ROMP of M6 (0.2 g, 0.527 mmol, 111.93 eq) was conducted with G2 (4 mg, 4.71 μ mol, 1 eq) at room temperature.

Polymer	Flow rate [mL/h]	CTA2 with respect to G2	CTA2 [mmol]	Monomer: CTA ratio (n')	M_{n-theo} [kDa]	M_n (GPC - $CHCl_3$) [kDa]	Number of repeat units (n)	\mathcal{D}	Yield [%]
P22	2	10 eq	0.0471	11.19	4.2	3.4	9.36	1.42	95
OP11	4	10 eq	0.0471	11.19	4.2	3.6	9.89	1.44	96
P23	2	15 eq	0.0706	7.47	2.8	2.4	6.72	1.40	94
P24	2	20 eq	0.0942	5.60	2.1	1.7	4.88	1.34	92

a



b

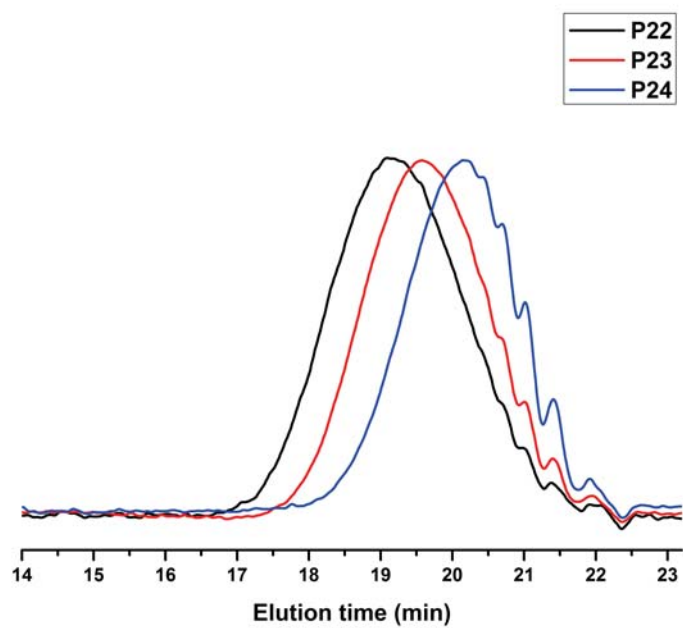


Figure 7: Plot showing linear dependency of the number of repeat units (n) on monomer:CTA2 ratio (n') in polymers P22-P24. b, GPC traces of polymers P22-P24 dissolved in CHCl_3 .

End-capping of the polymer chains with CTAs for the determination of reaction rate constants by ^1H NMR

A mixture of *exo*-N-methyl-norbornenecarboximide monomer **M1** (16 mg, 0.09 mmol, 20 eq) and 1,3,5-trimethoxybenzene (13 mg) was dissolved in dry, degassed CD_2Cl_2 (0.3 mL) and added in one portion to a solution of **G3** catalyst (4 mg, 4.52 μmol , 1 eq) in dry, degassed CD_2Cl_2 (0.2 mL). 1,3,5-trimethoxybenzene was employed as an NMR standard. **M1** and **G3** formed a ruthenium carbene complex (**POLY-G3**), which was transferred to an NMR tube under argon atmosphere. ^1H NMR spectra were recorded before and at various time intervals after the addition of a solution of **CTA#** in dry, degassed CD_2Cl_2 (0.3 mL).

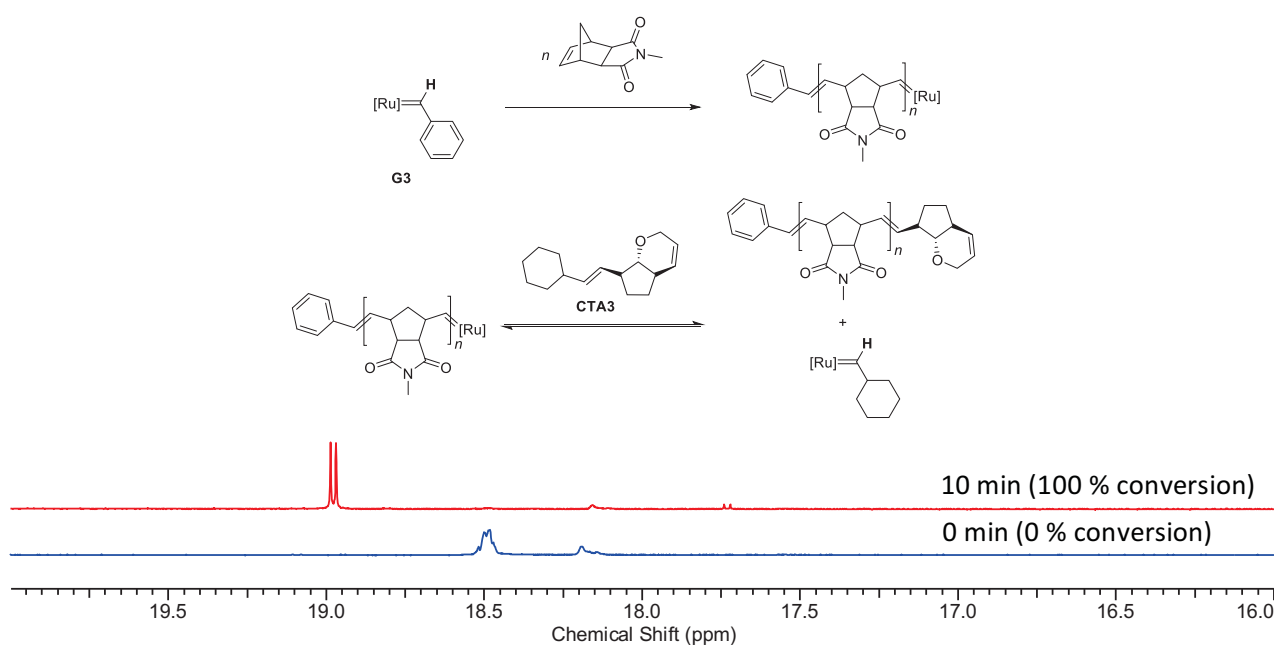


Figure 8: Stacked ^1H NMR spectra (CD_2Cl_2 , 400 MHz) showing the decreasing **POLY-G3** peak around 18.50 ppm and the doublet of the newly formed ruthenium cyclohexyl methyldene species at 18.98 ppm as a result of the reaction between **CTA3** (10 eq) and **POLY-G3**, which was completed within 10 min.

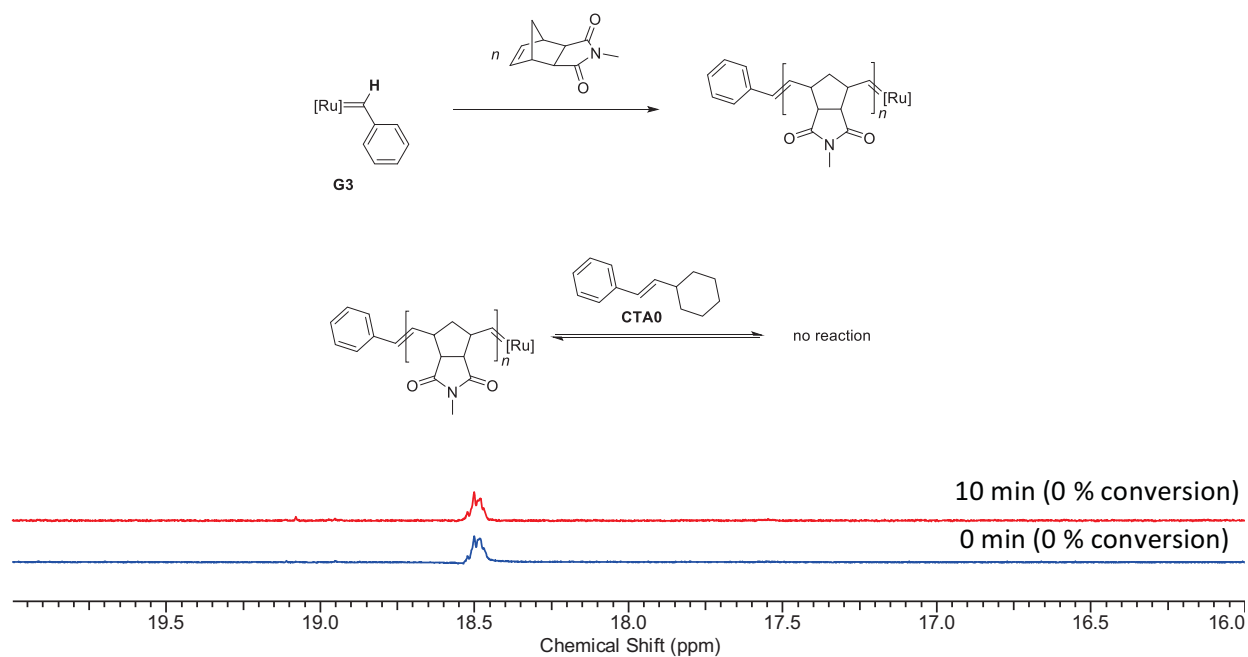


Figure 9: Stacked ^1H NMR spectra (CD_2Cl_2 , 300 MHz) show that within 10 min POLY-G3 did not react with *exo*-cyclic styrenic bond of CTA0 (10 eq). ^1H NMR spectra of the reactions of CTA1 and CTA2 with POLY-G3 are shown in Figure 2.

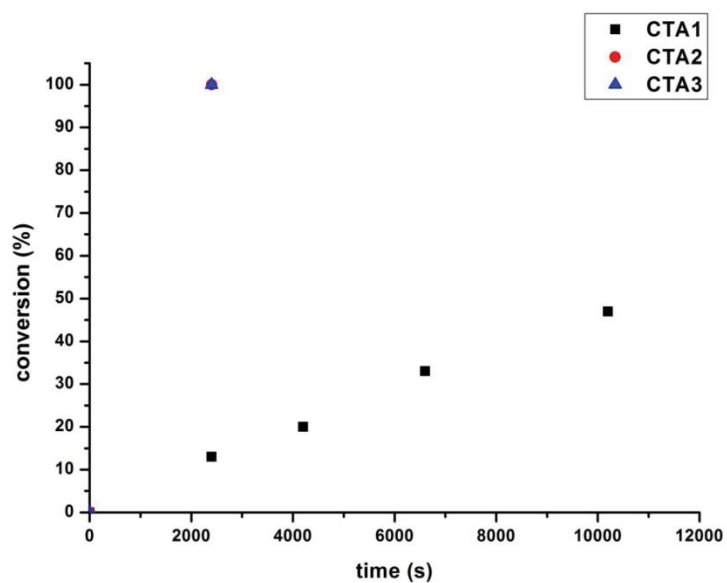


Figure 10: Graph showing reaction rates of CTA1-CTA3 (10 eq) with POLY-G3.

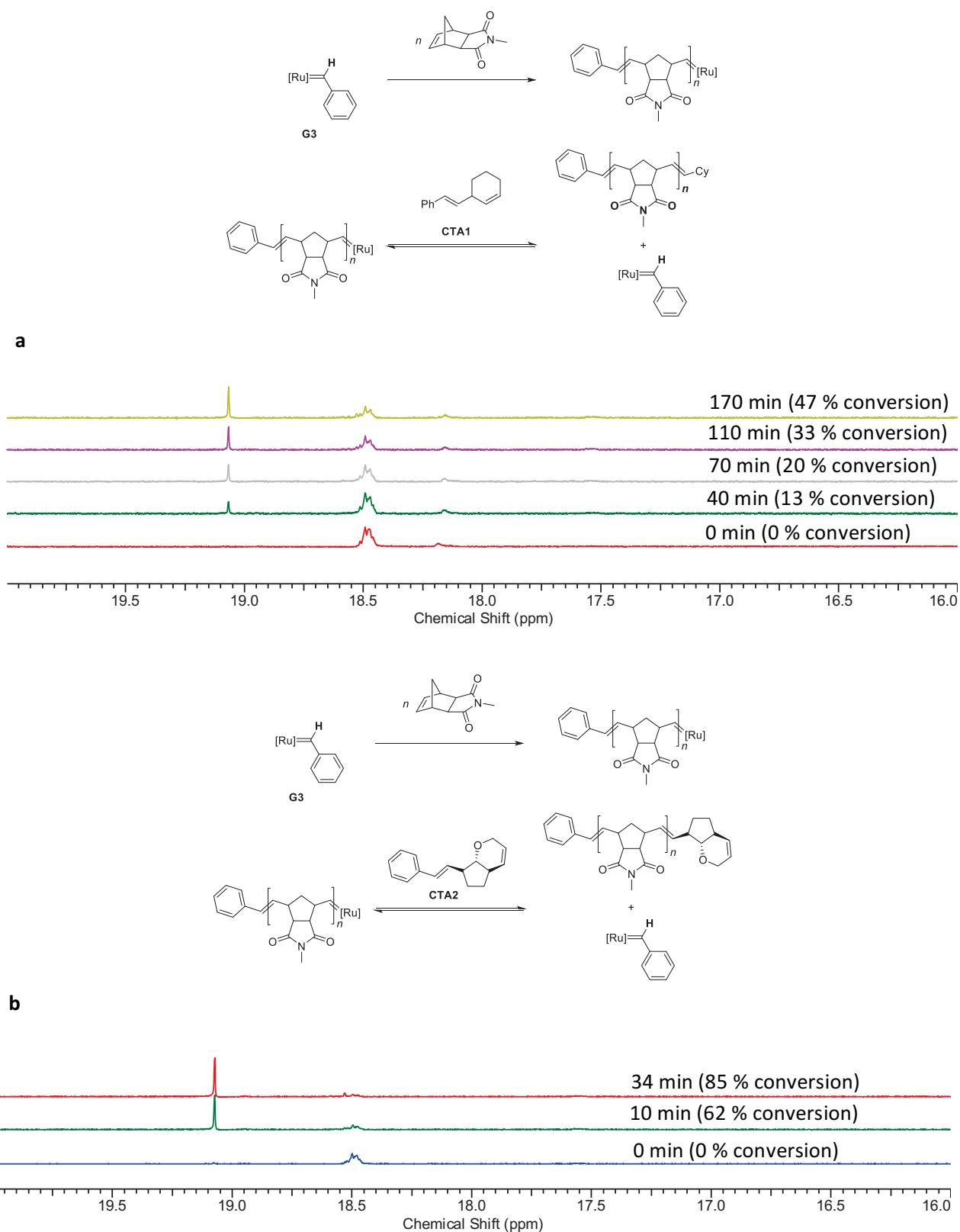


Figure 11: a, Stacked ^1H NMR spectra (CD_2Cl_2 , 300 MHz) showing the decreasing POLY-G3 peak around 18.50 ppm and the growing peak of G3 at 19.07 ppm during the reaction between CTA1 (10 eq) and POLY-G3. b, Stacked ^1H NMR spectra (CD_2Cl_2 , 300 MHz) also showing the growing G3 peak at 19.07 ppm during the reaction between CTA2 (1.1 eq) and POLY-G3.

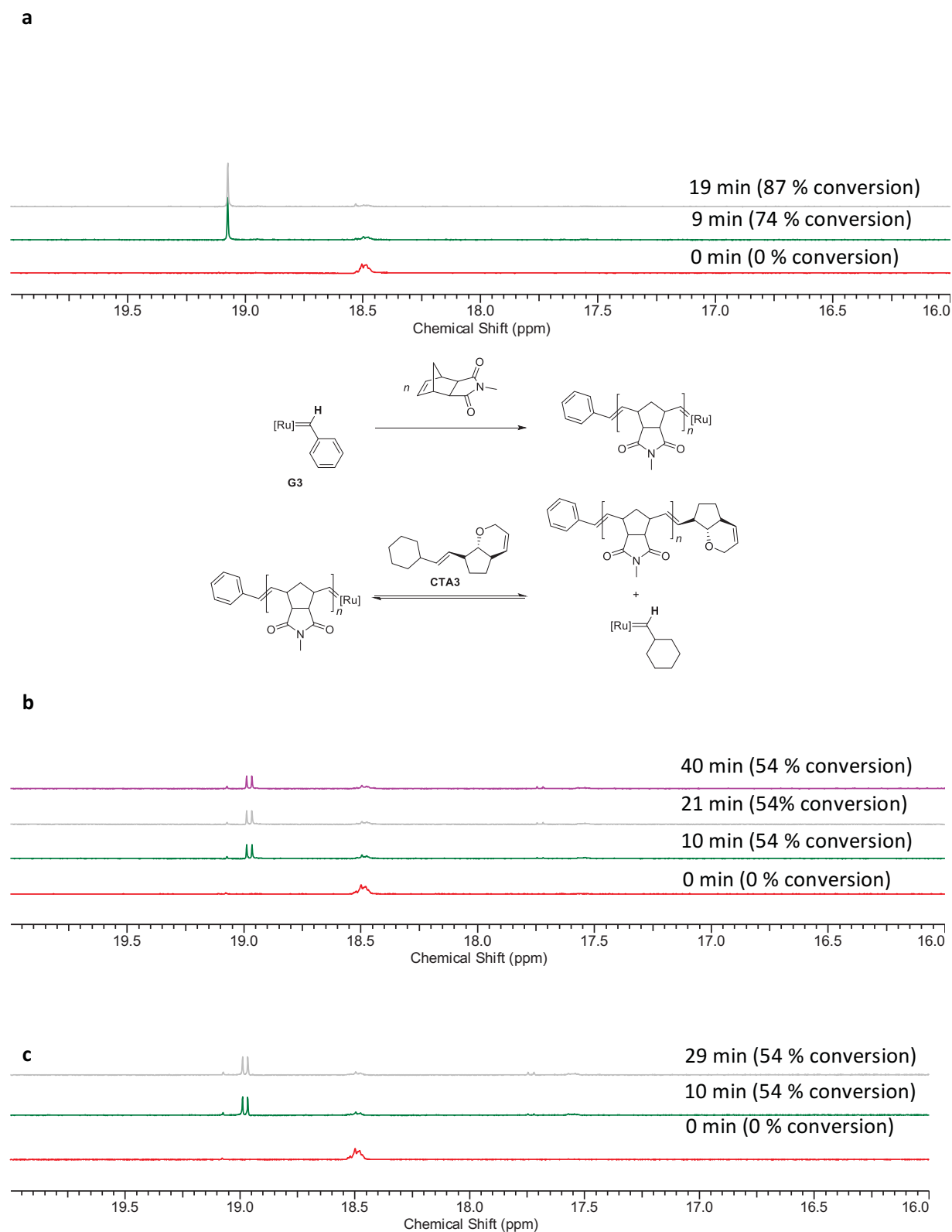


Figure 12: a, Stacked ^1H NMR spectra (CD_2Cl_2 , 300 MHz) showing the decreasing POLY-G3 peak around 18.50 ppm and the growing peak of G3 at 19.07 ppm during the reaction between CTA2 (1.5 eq) and POLY-G3. b-c, Stacked ^1H NMR spectra (CD_2Cl_2 , 300 MHz) showing the newly formed doublet peak of ruthenium cyclohexyl methyldene complex at 18.98 ppm during the reaction between either b, CTA3 (1.1 eq) or c, CTA3 (1.5 eq) and POLY-G3. The equilibrium was reached within 10 minutes as the newly formed ruthenium cyclohexyl methyldene was competing with the POLY-G3 to react with the remaining amount of CTA3.

$$A = \frac{1}{[CTA]_0 - [Ru]_0} \ln \frac{[Ru]_0([CTA]_0 - x)}{([Ru]_0 - x)[CTA]_0}$$

The above equation was used for the rate constant estimation of reactions that follow a second-order rate law as adapted from Atkins and others⁵. $[Ru]_0$ corresponds to the initial concentration of **POLY-G3**, $[CTA]_0$ refers to the initial concentration of **CTA#**, x represents the decrease in the concentration of **POLY-G3** at a given time and A is equal to $t \cdot k$, whereby t stands for time and k is the second-order rate constant. The backward reactions were not taken into the account.

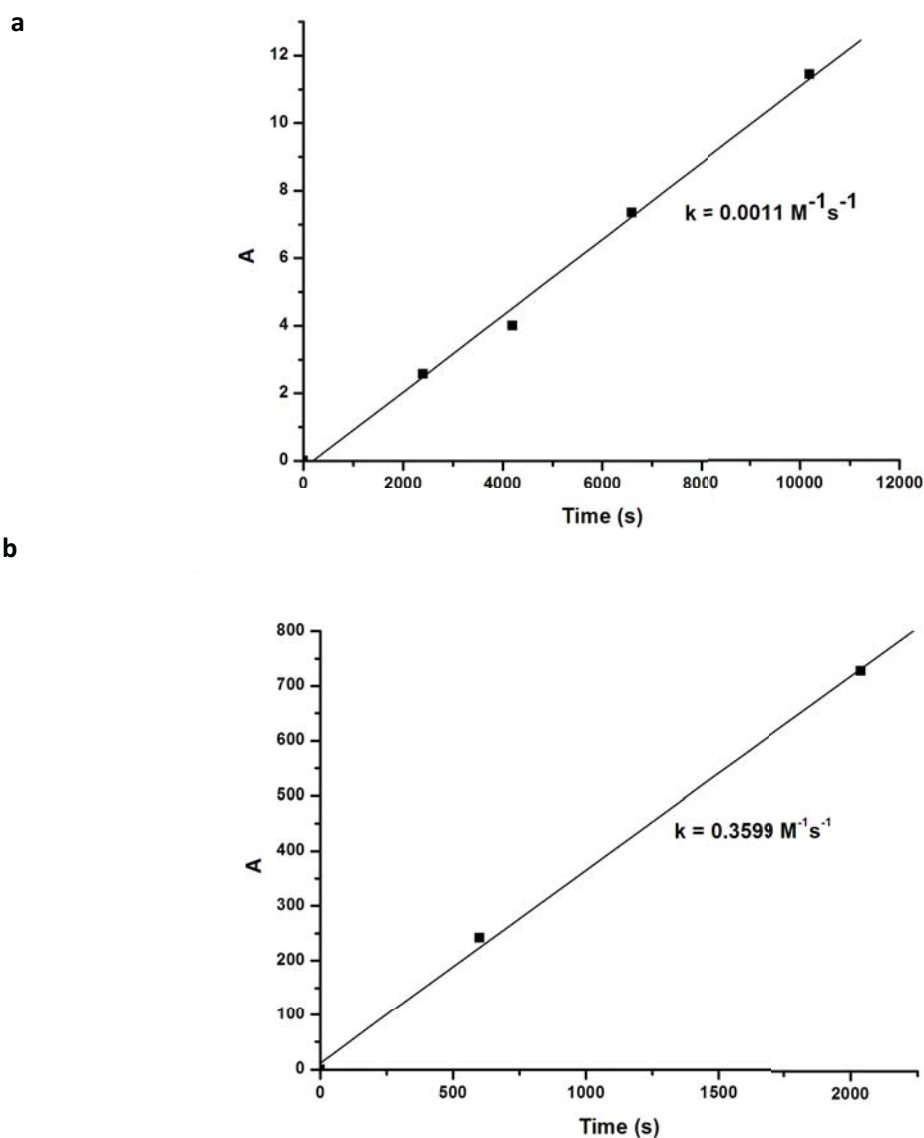


Figure 13: Rate constant estimation of a, the reaction of POLY-G3 with CTA1 (10 eq) (see Figure 11a) b, the reaction of POLY-G3 with CTA2 (1.1 eq) (see Figure 11b).

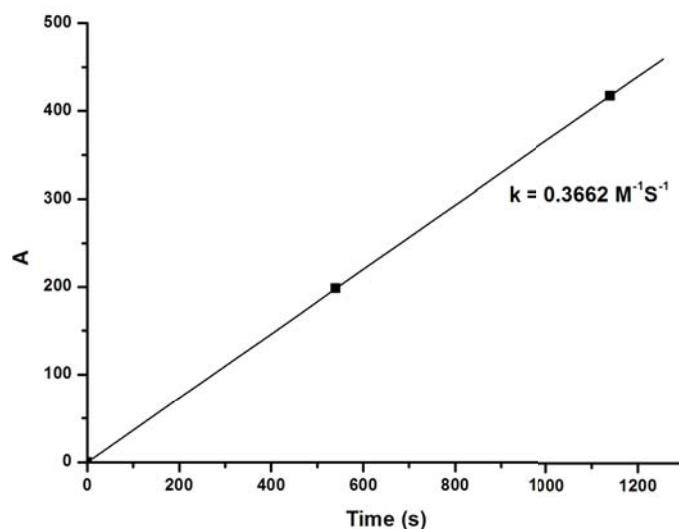


Figure 14: Rate constant estimation of the reaction of POLY-G3 with CTA2 (1.5 eq). For the reactions of CTA3 with POLY-G3, the equilibrium was already reached within 10 min and thus the rate constants were not calculated (see Figure 12b-c).

Reaction of G3 with CTA3

A solution of the **G3** catalyst (4 mg, 4.52 μmol , 1 eq) in dry, degassed CD_2Cl_2 (0.5 mL) was transferred to the NMR tube under argon. ^1H NMR spectra were recorded before and at various time intervals after the addition of a solution of **CTA3** (10 eq) in dry, degassed CD_2Cl_2 (0.3 mL).

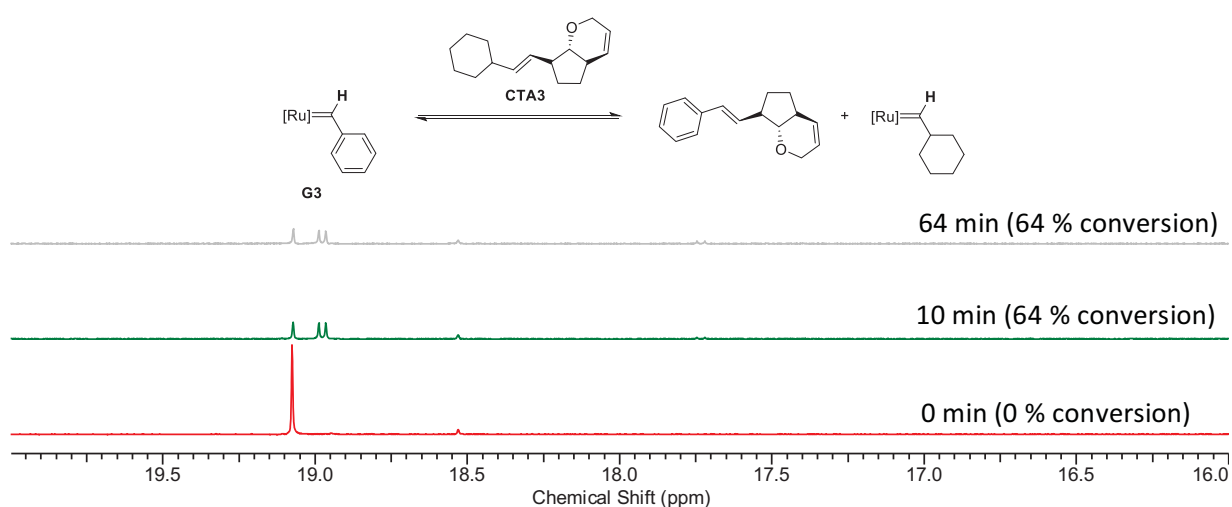


Figure 15: Stacked ^1H NMR spectra (CD_2Cl_2 , 300 MHz) showing the newly formed doublet of cyclohexyl methylidene at 18.98 ppm during the reaction between CTA3 (10 eq) and G3. The equilibrium was reached within 10 min since ruthenium cyclohexyl methylidene was competing with G3 to react with the remaining amount of CTA3.

MALDI-ToF MS data

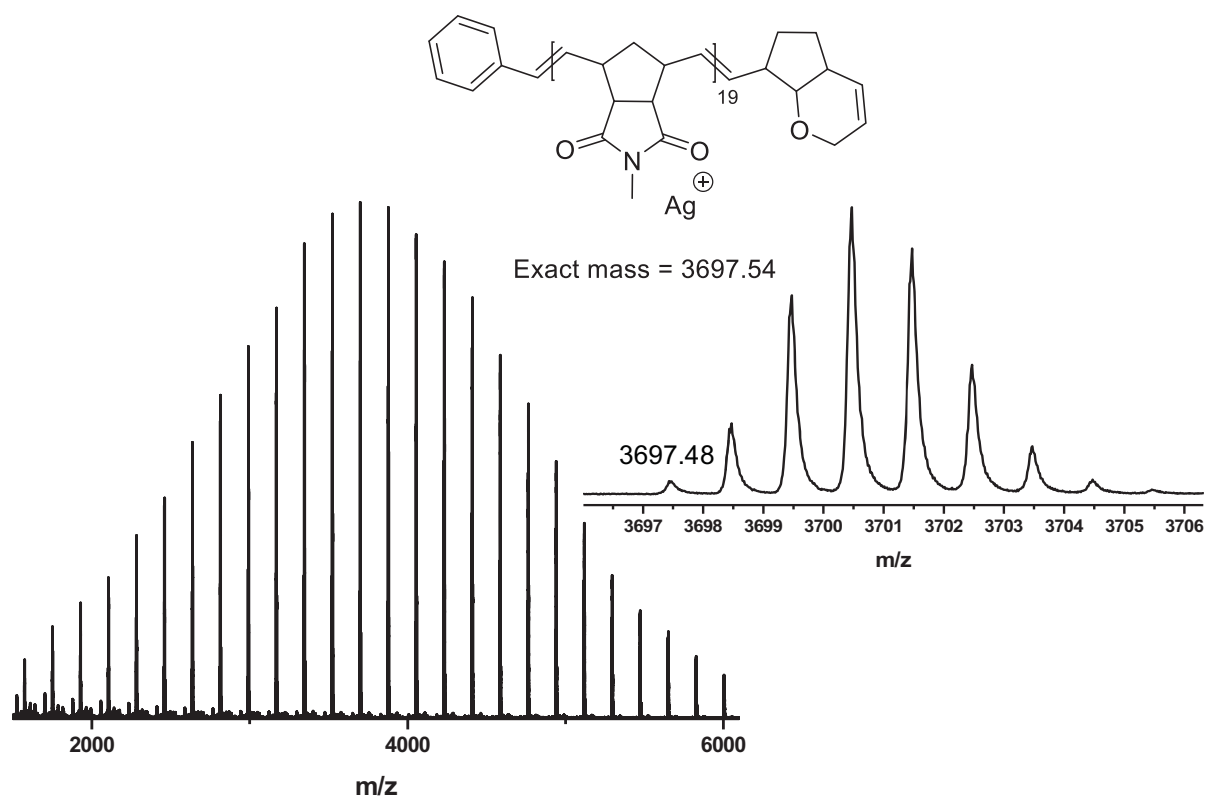


Figure 16: MALDI-ToF mass spectrum of P1.

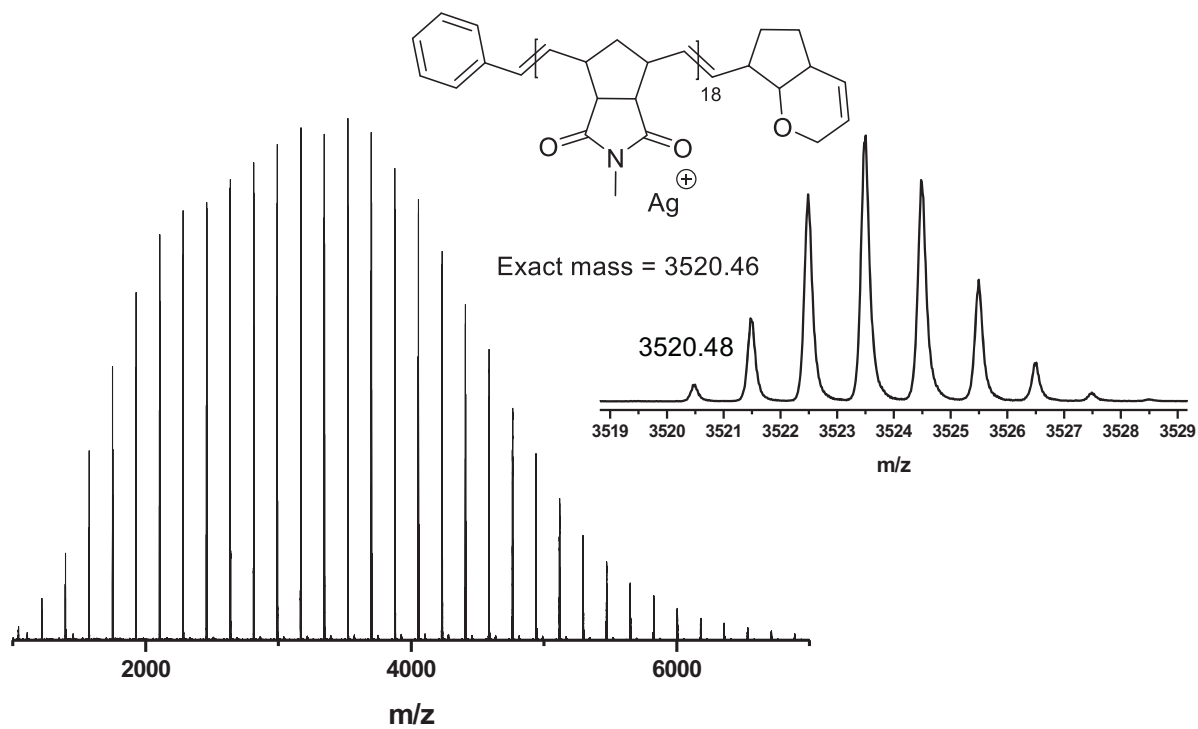


Figure 17: MALDI-ToF mass spectrum of P2.

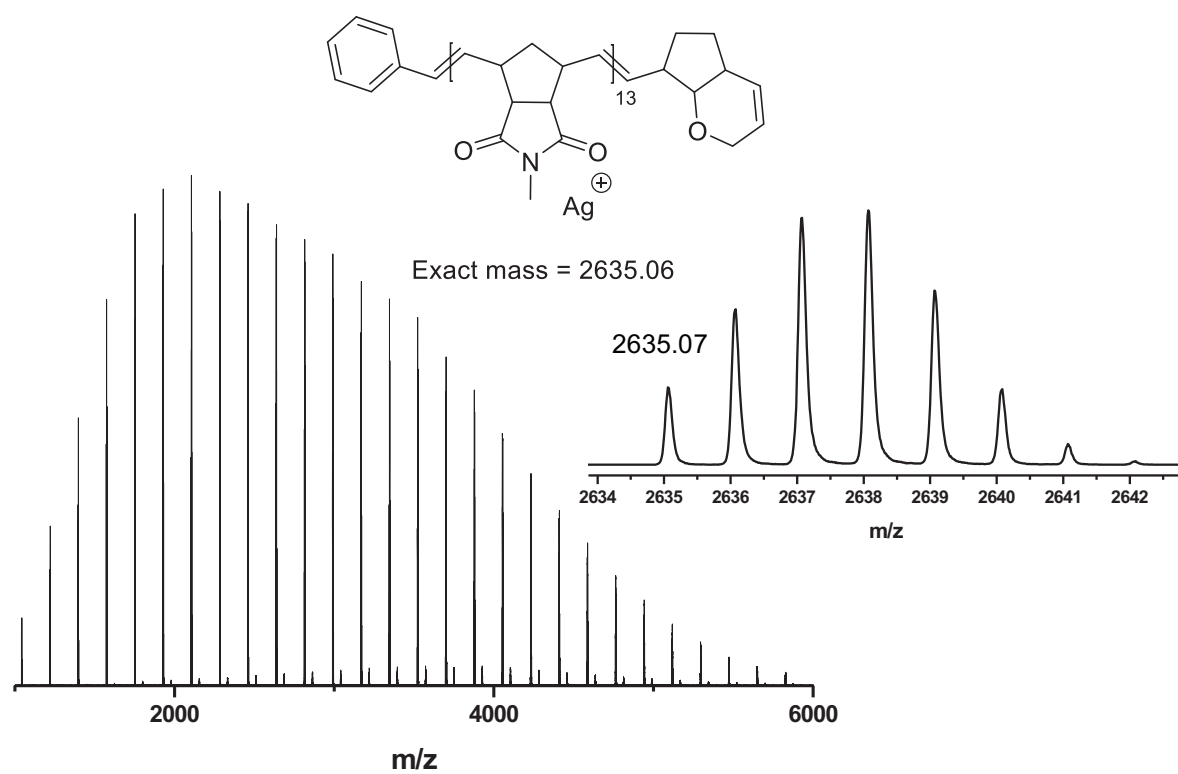


Figure 18: MALDI-ToF mass spectrum of P3.

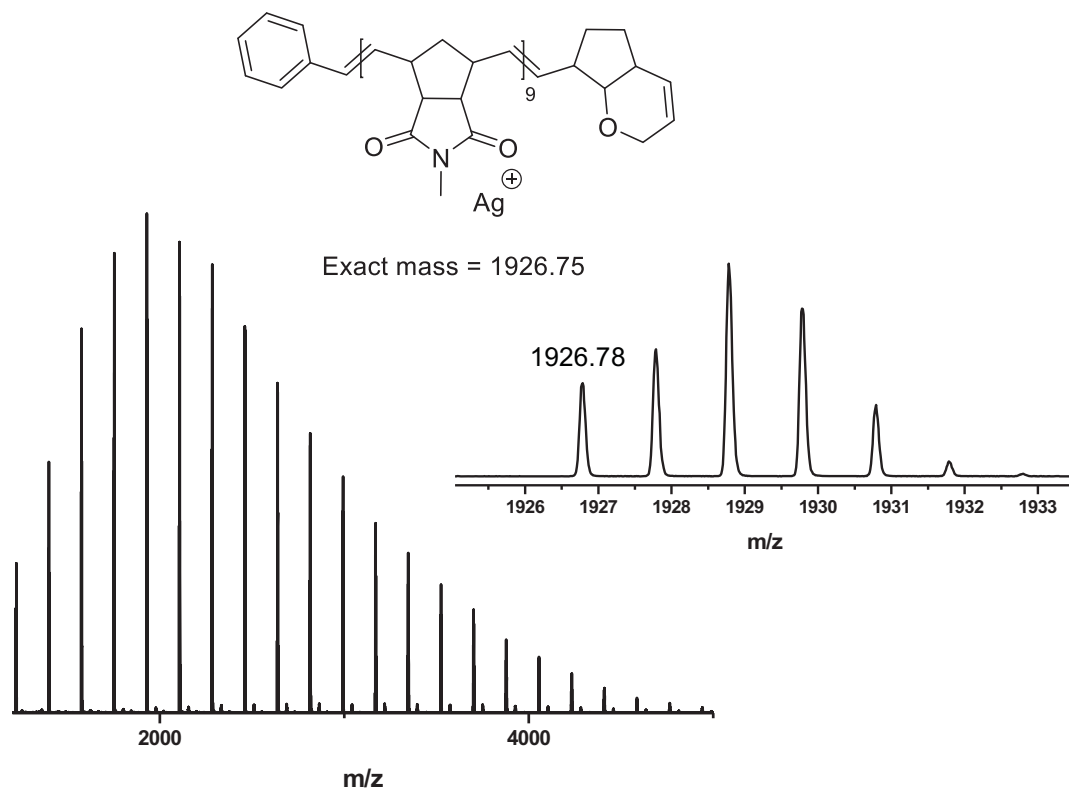


Figure 19: MALDI-ToF mass spectrum of P4.

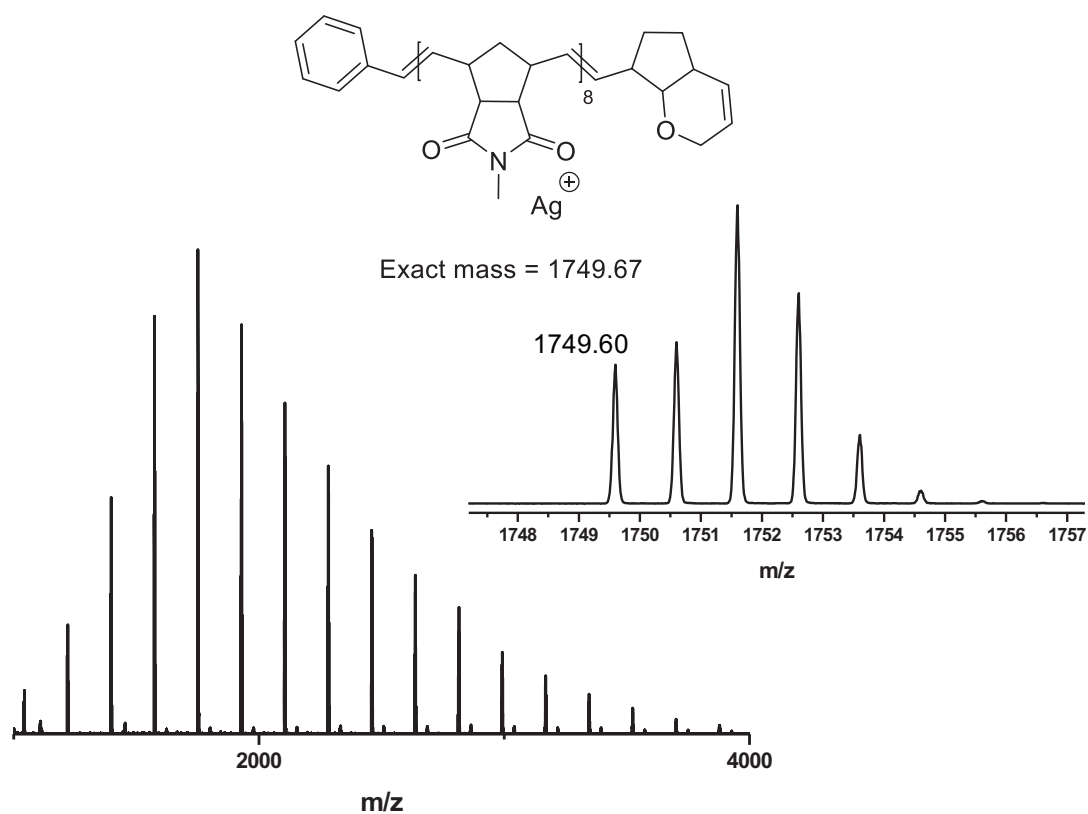


Figure 20: MALDI-ToF mass spectrum of P5.

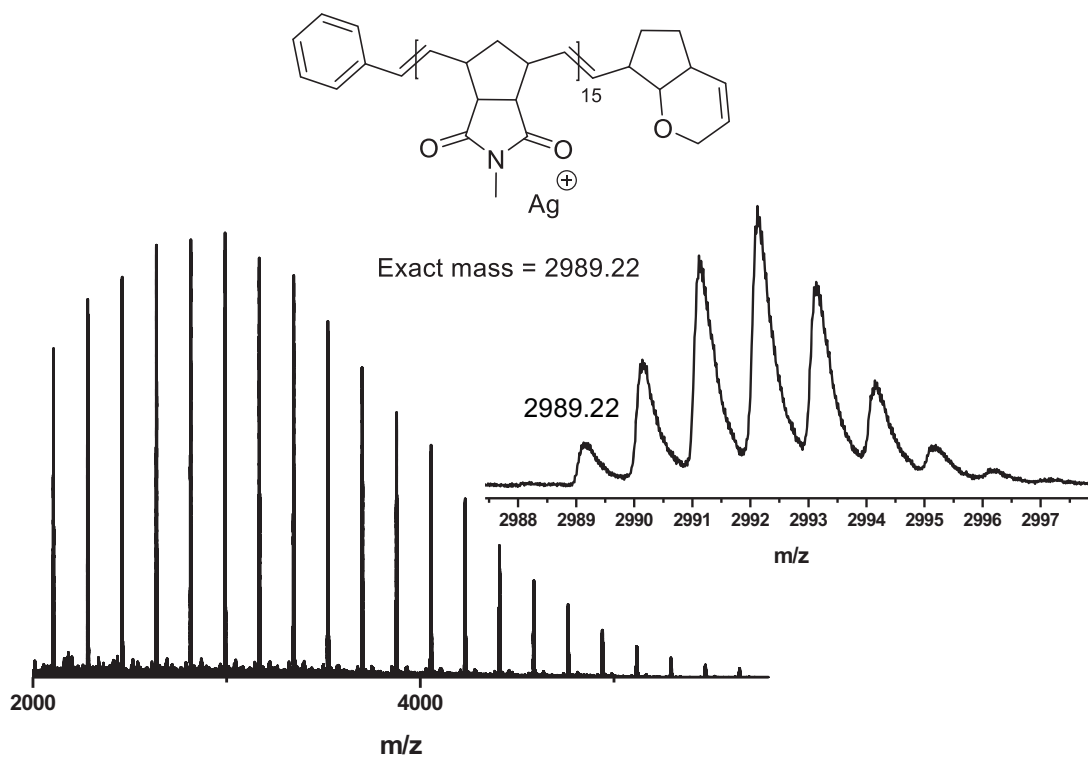


Figure 21: MALDI-ToF mass spectrum of P6.

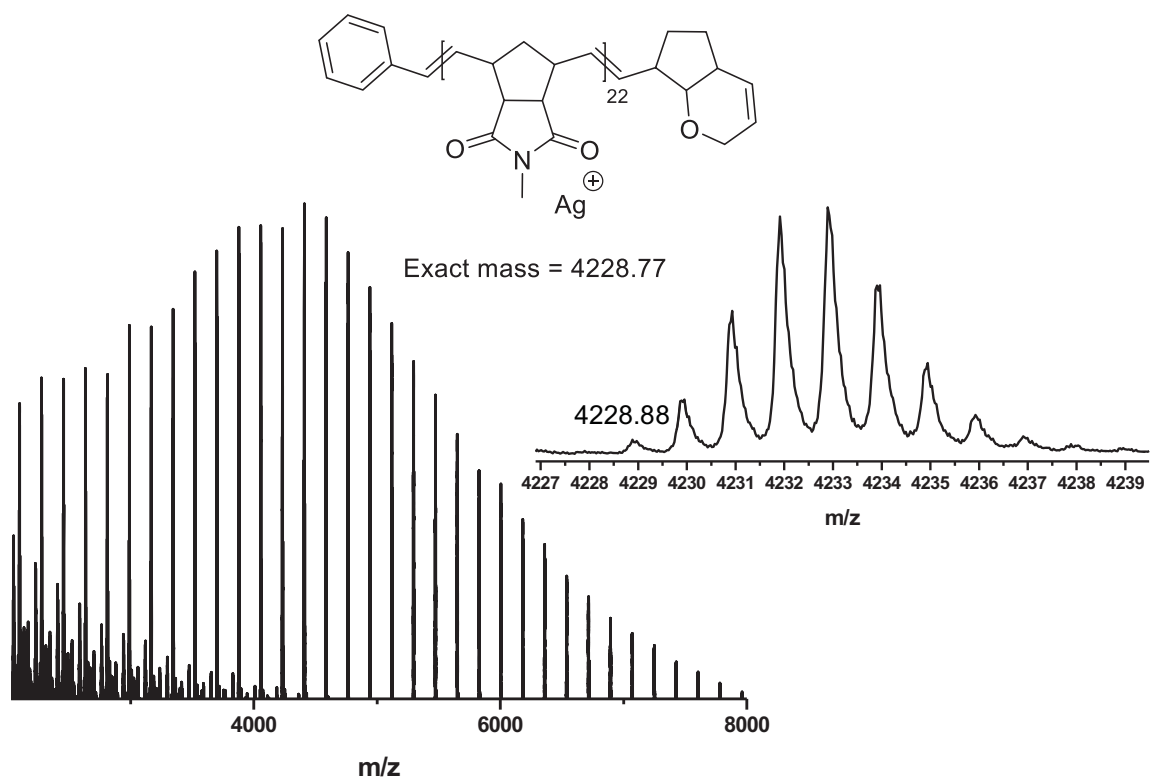


Figure 22: MALDI-ToF mass spectrum of P8.

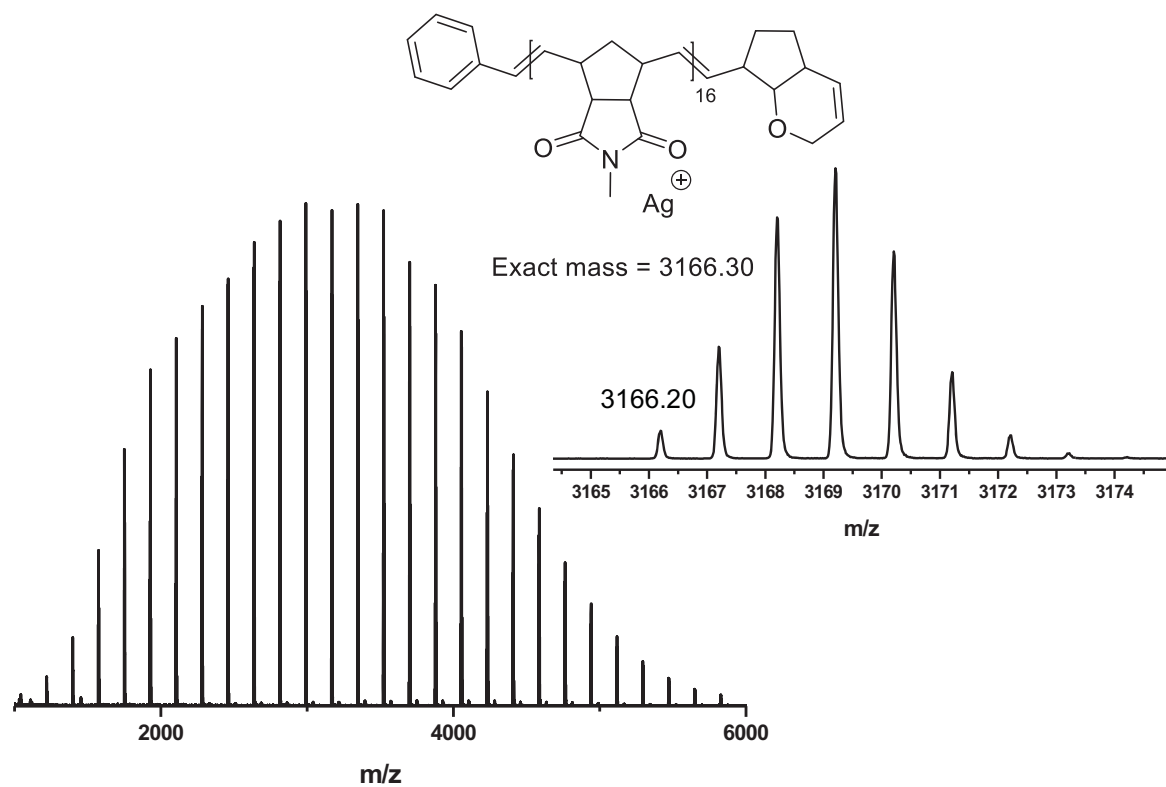


Figure 23: MALDI-ToF mass spectrum of P9.

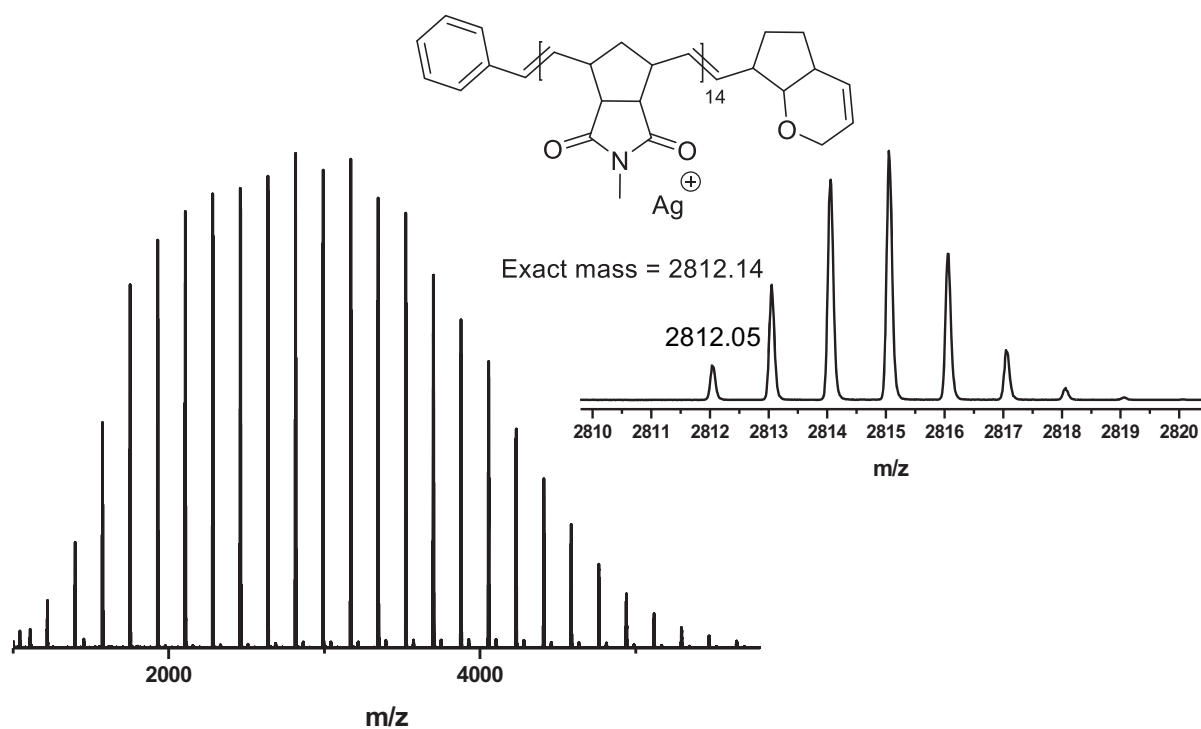


Figure 24: MALDI-ToF mass spectrum of P10.

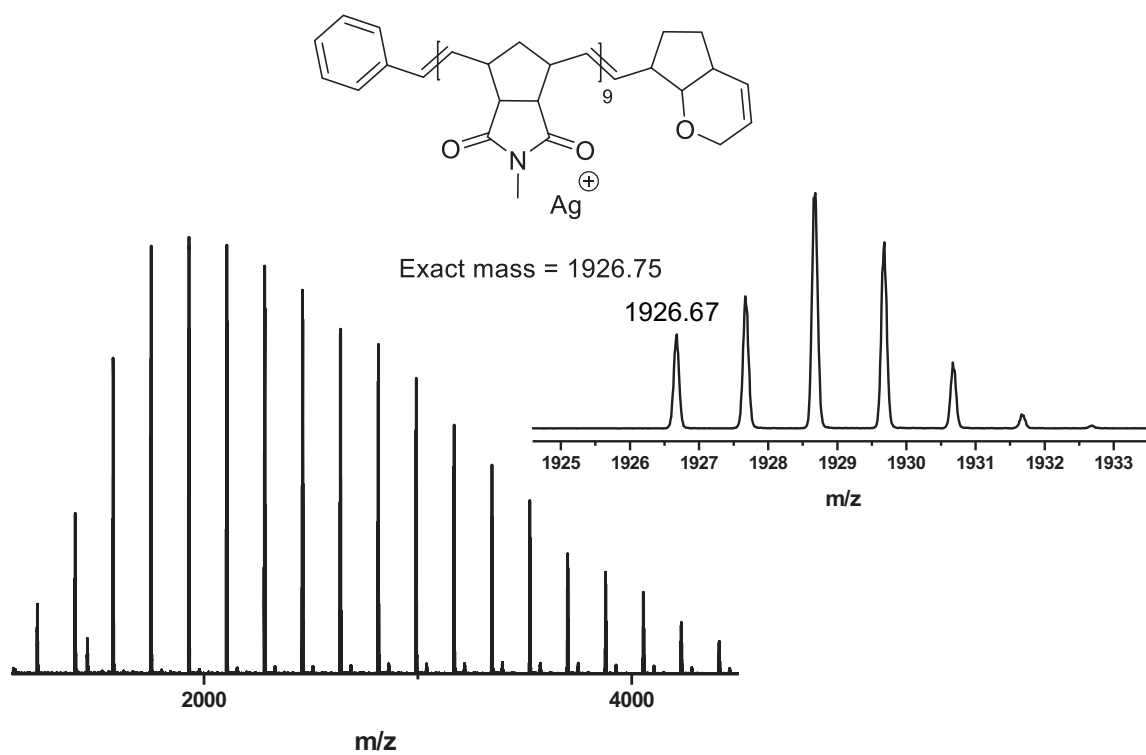


Figure 25: MALDI-ToF mass spectrum of P11.

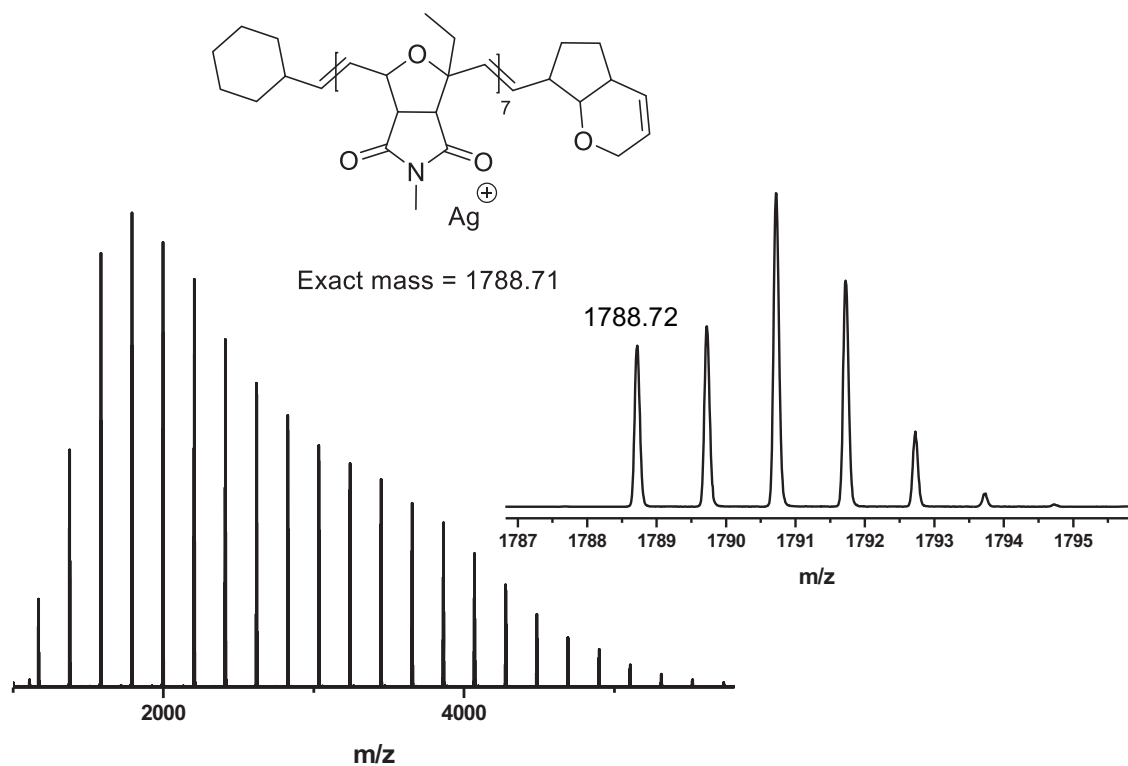


Figure 26: MALDI-ToF mass spectrum of P12.

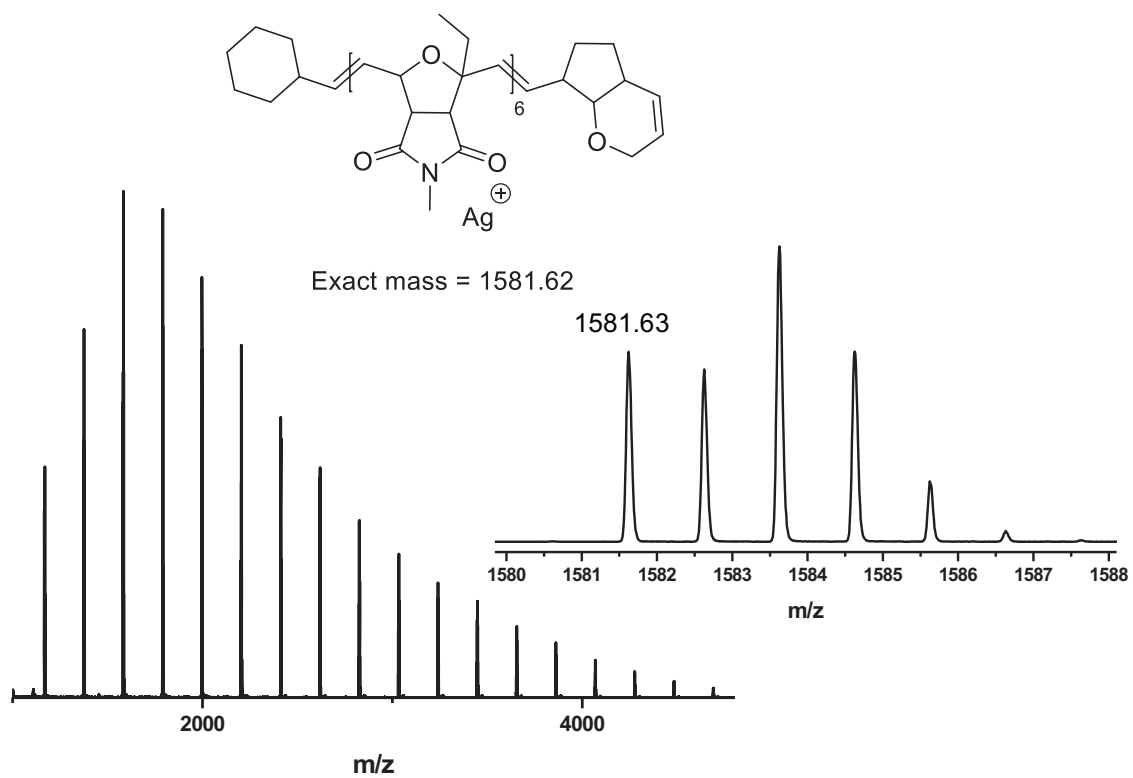


Figure 27: MALDI-ToF mass spectrum of P13.

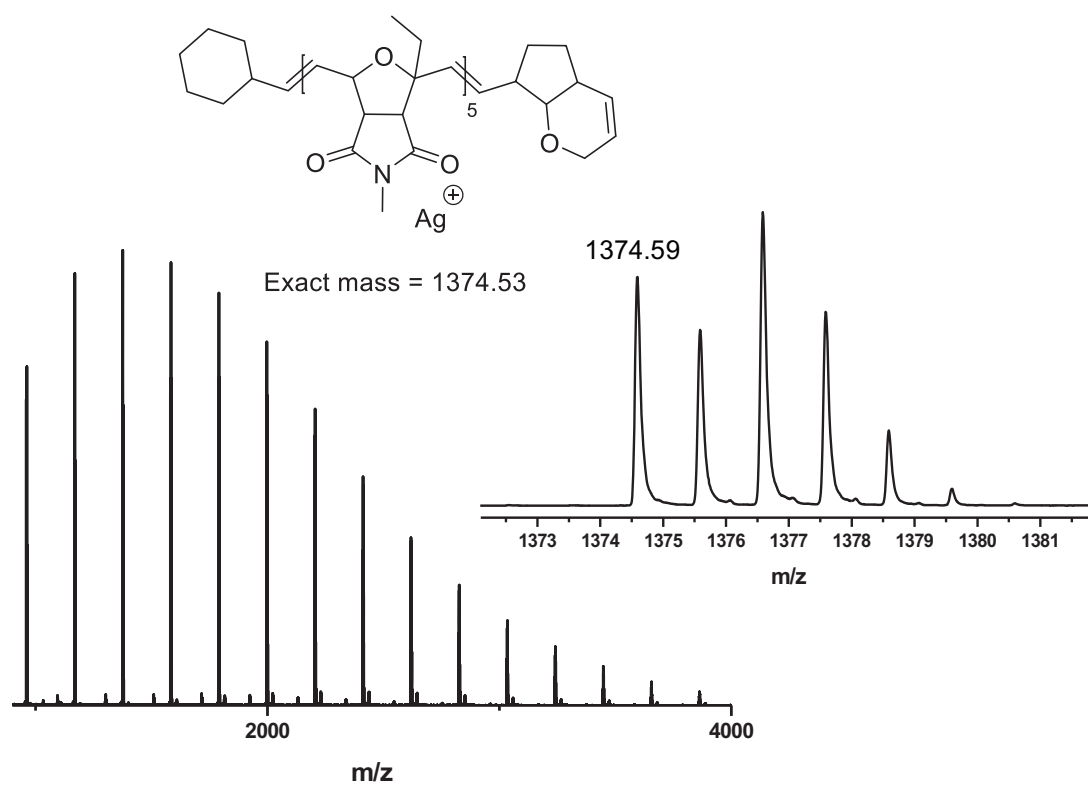


Figure 28: MALDI-ToF mass spectrum of P14.

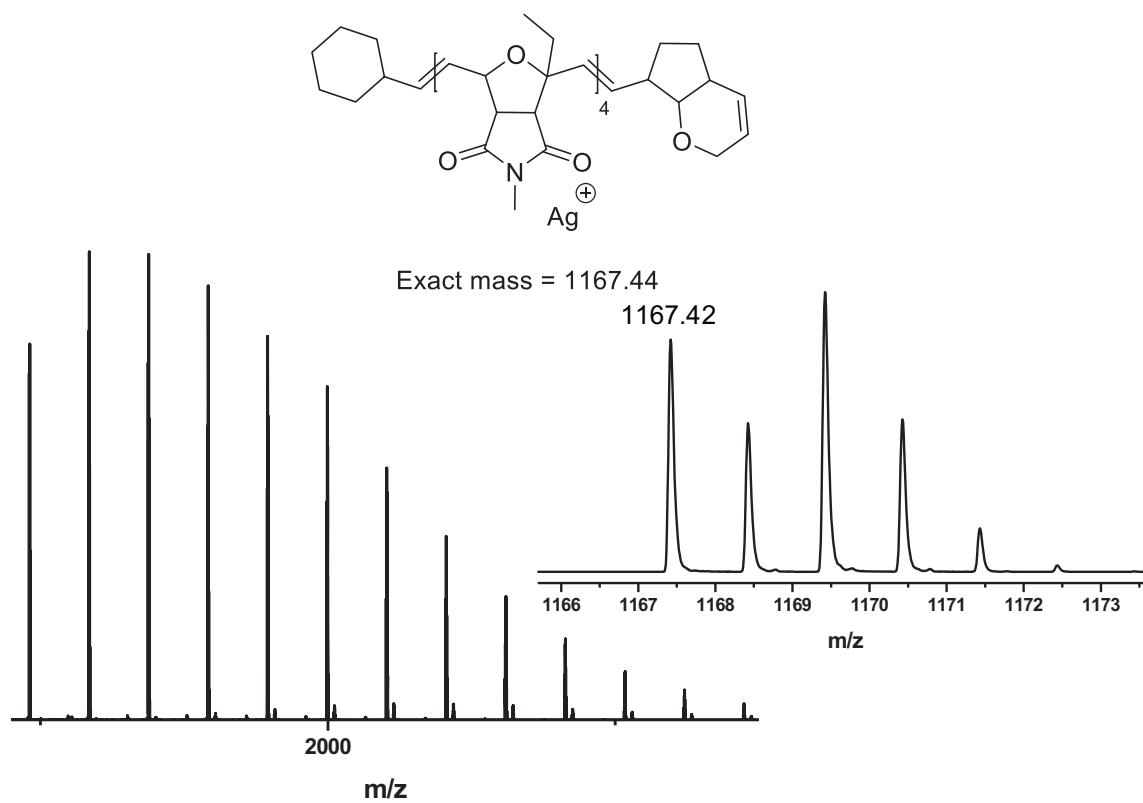


Figure 29: MALDI-ToF mass spectrum of P15.

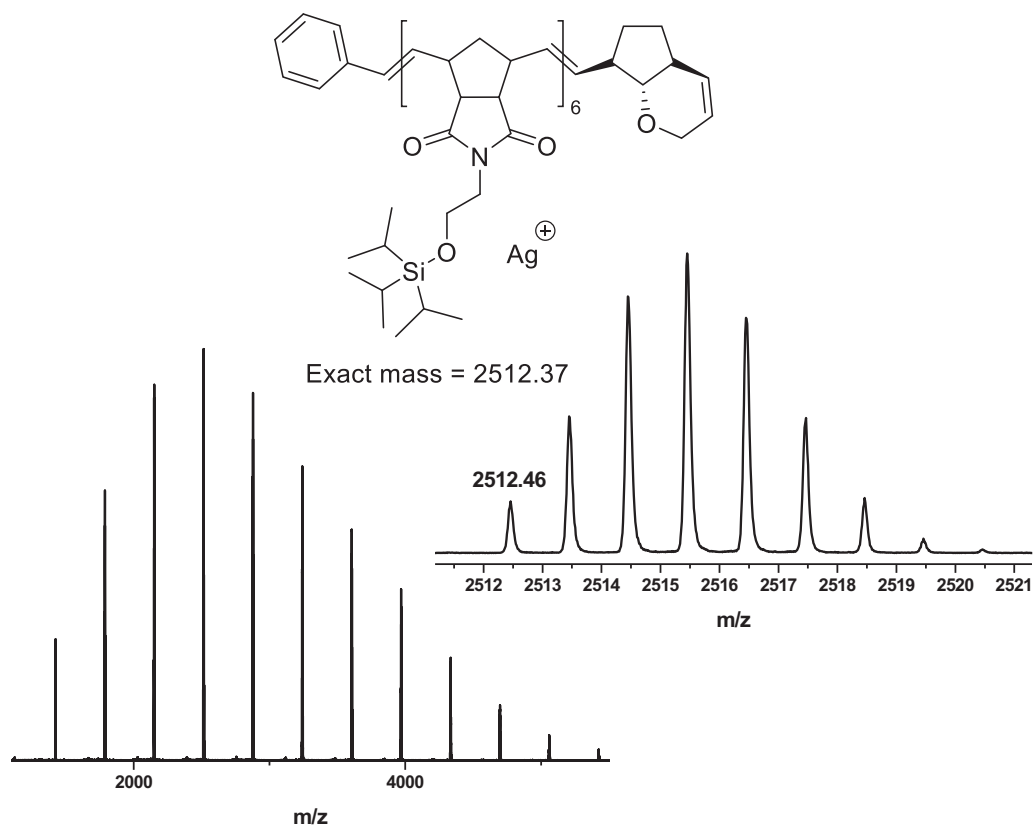


Figure 30: MALDI-ToF mass spectrum of P16.

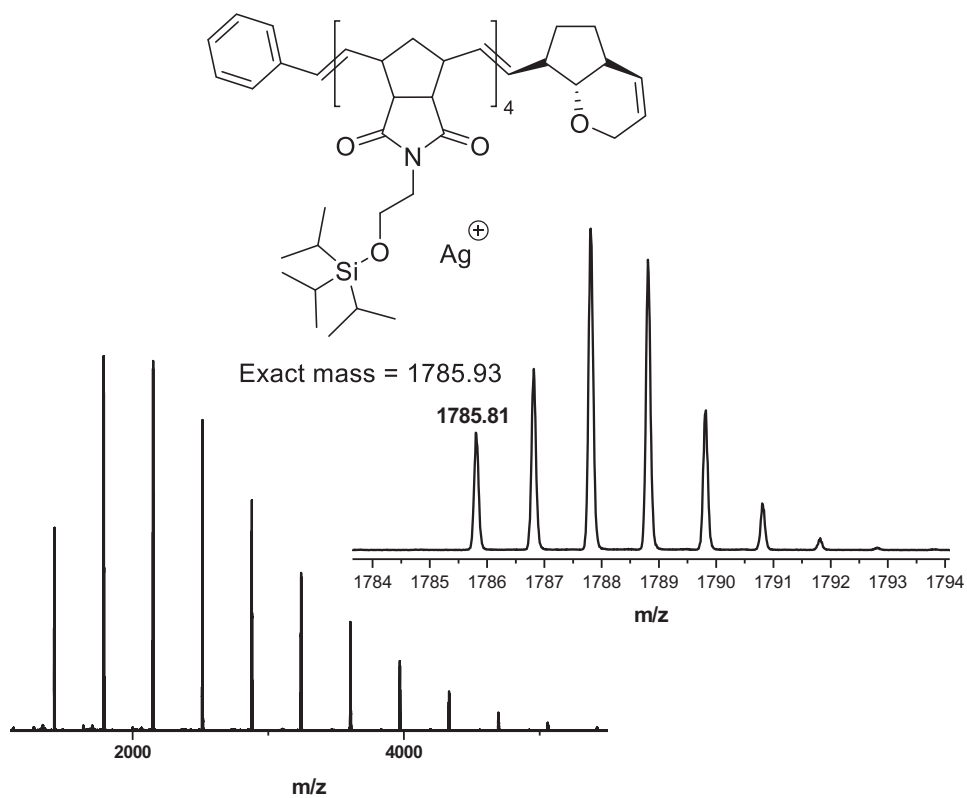


Figure 31: MALDI-ToF mass spectrum of P17.

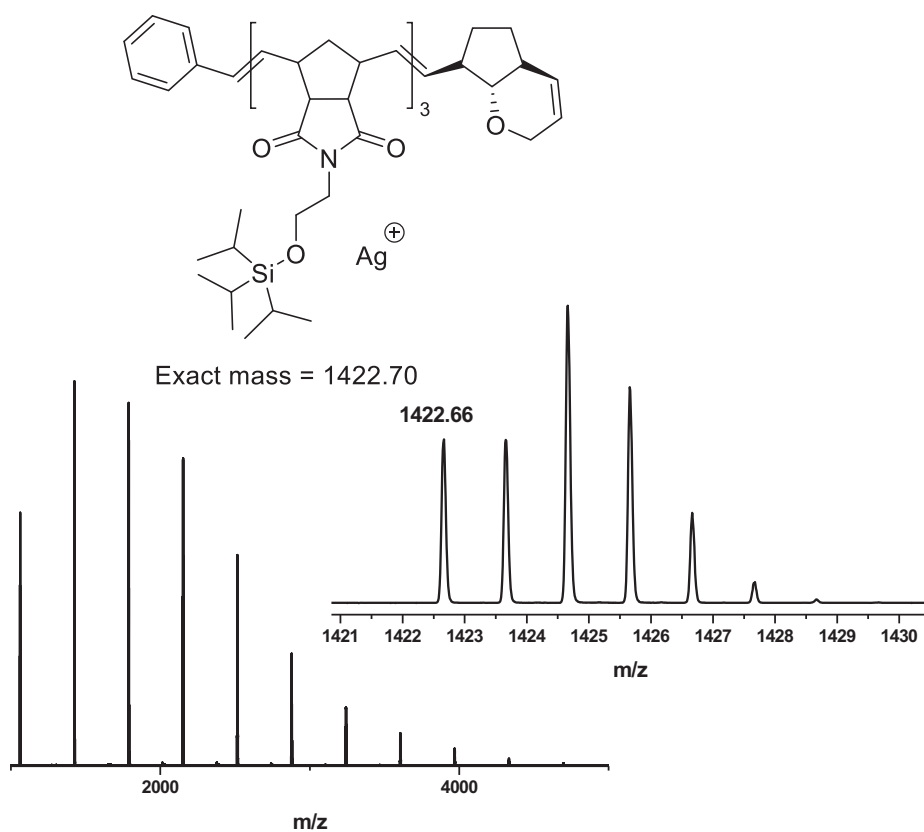


Figure 32: MALDI-ToF mass spectrum of P18.

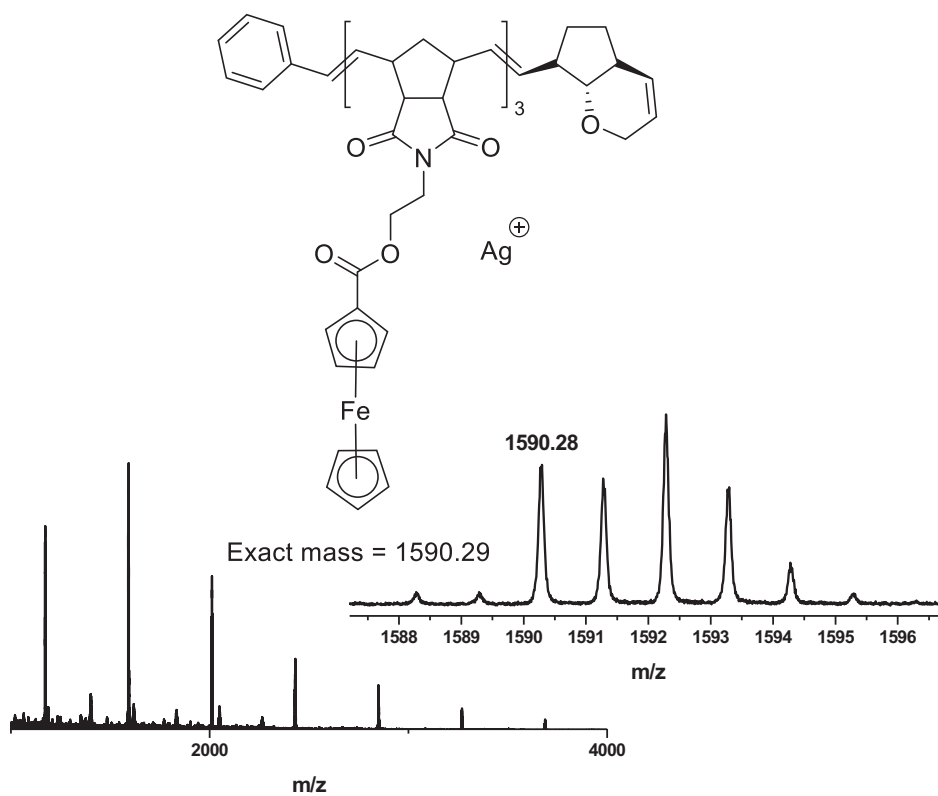


Figure 33: MALDI-ToF mass spectrum of P19.

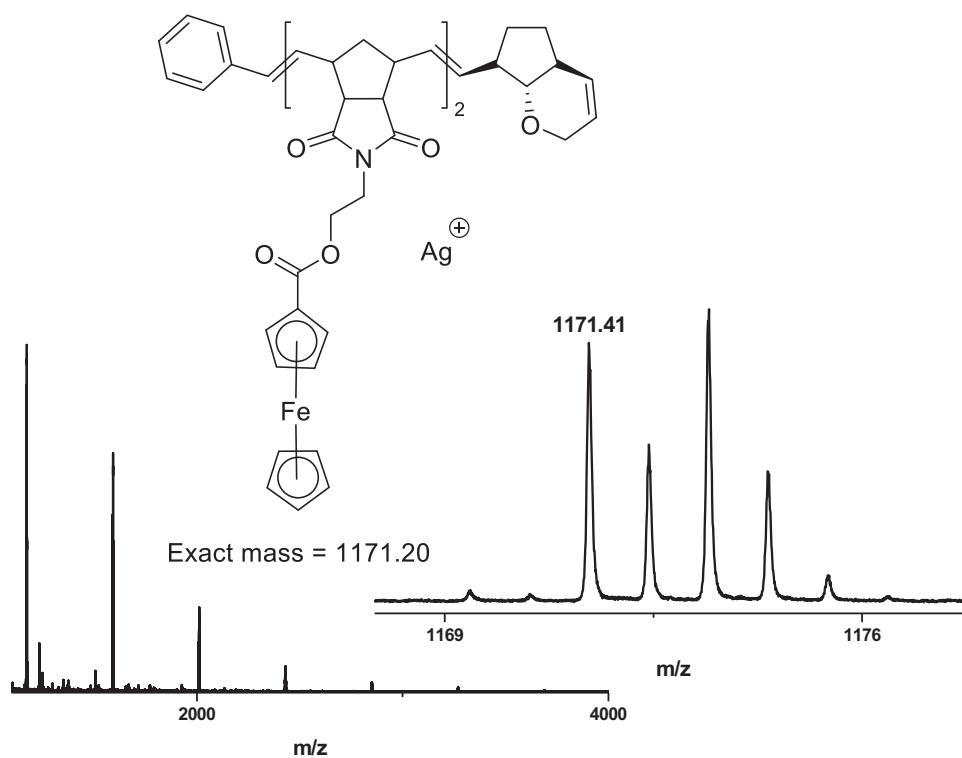


Figure 34: MALDI-ToF mass spectrum of P20.

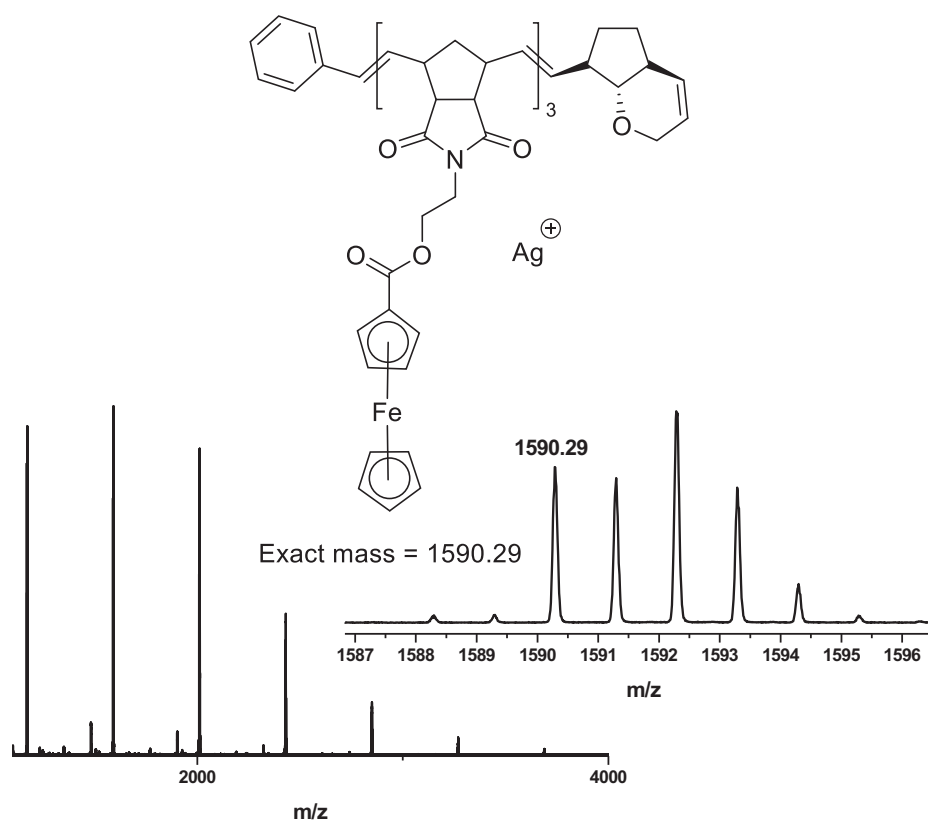


Figure 35: MALDI-ToF mass spectrum of P21.

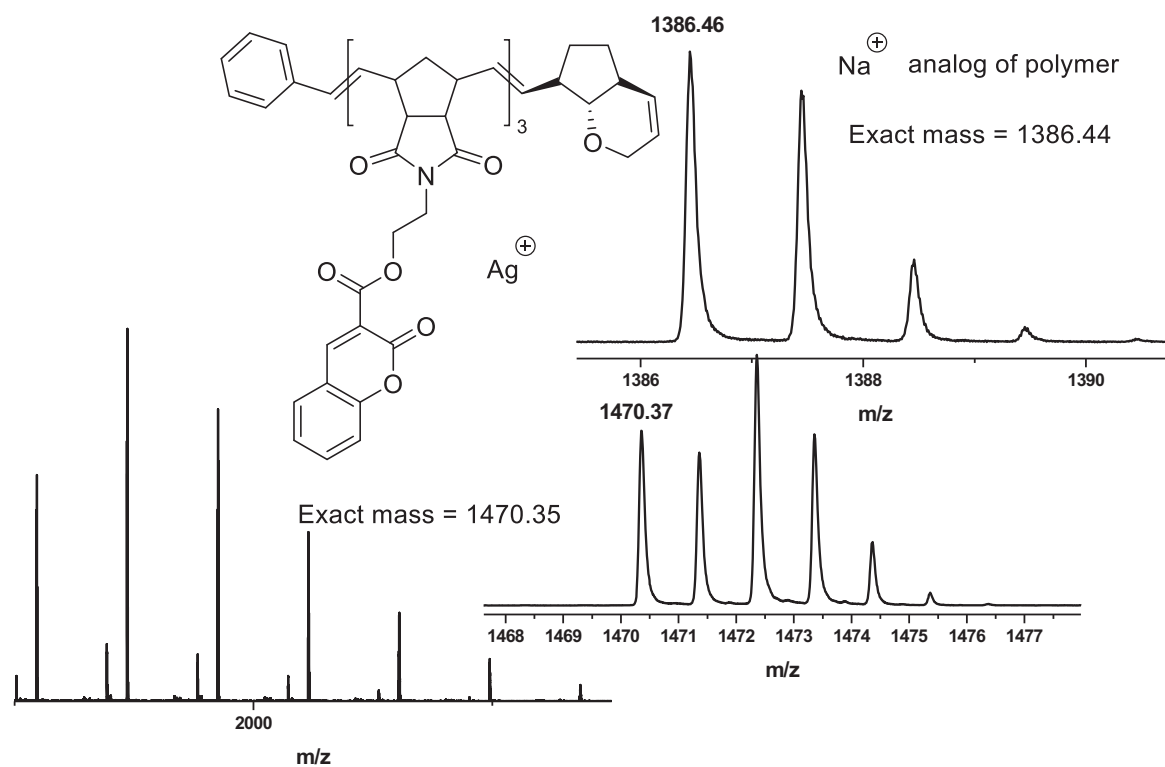


Figure 36: MALDI-ToF mass spectrum of P22.

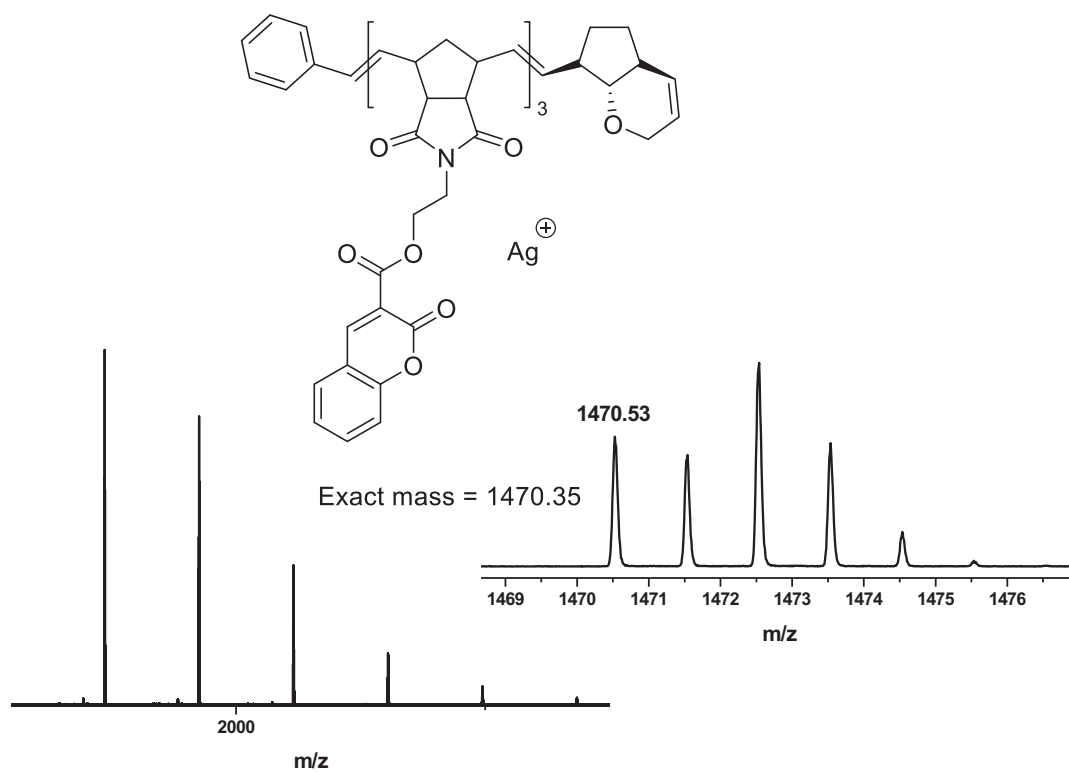


Figure 37: MALDI-ToF mass spectrum of P23.

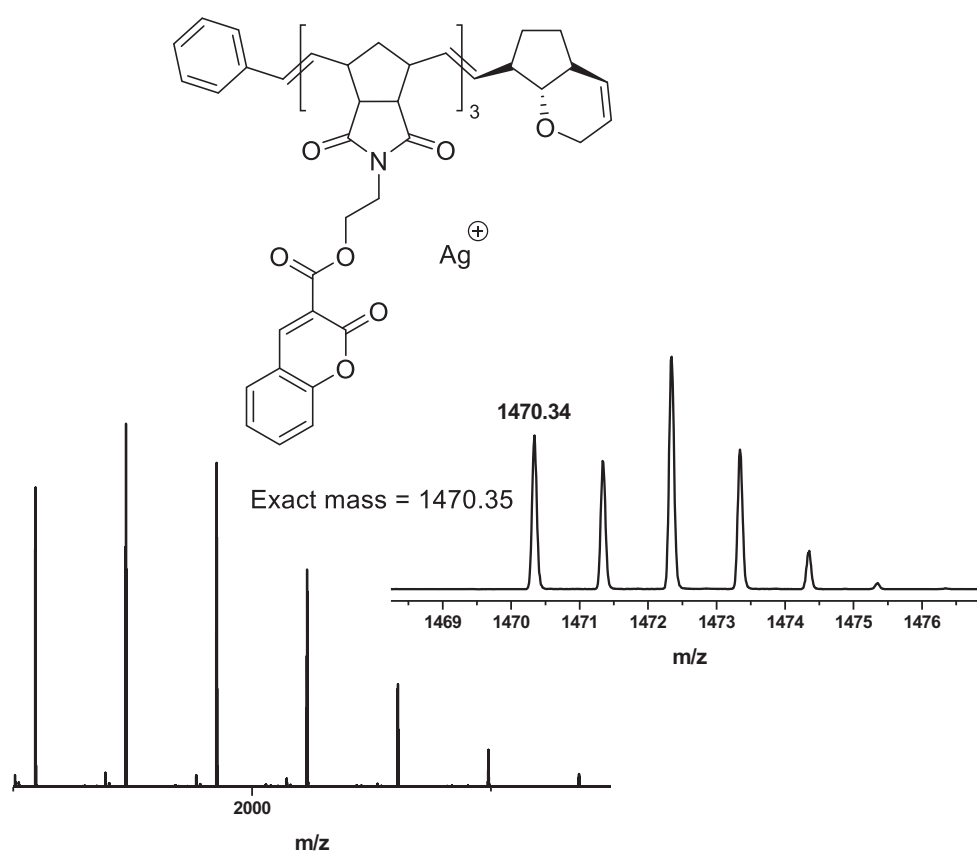


Figure 38: MALDI-ToF mass spectrum of P24.

^1H NMR and ^{13}C NMR spectra

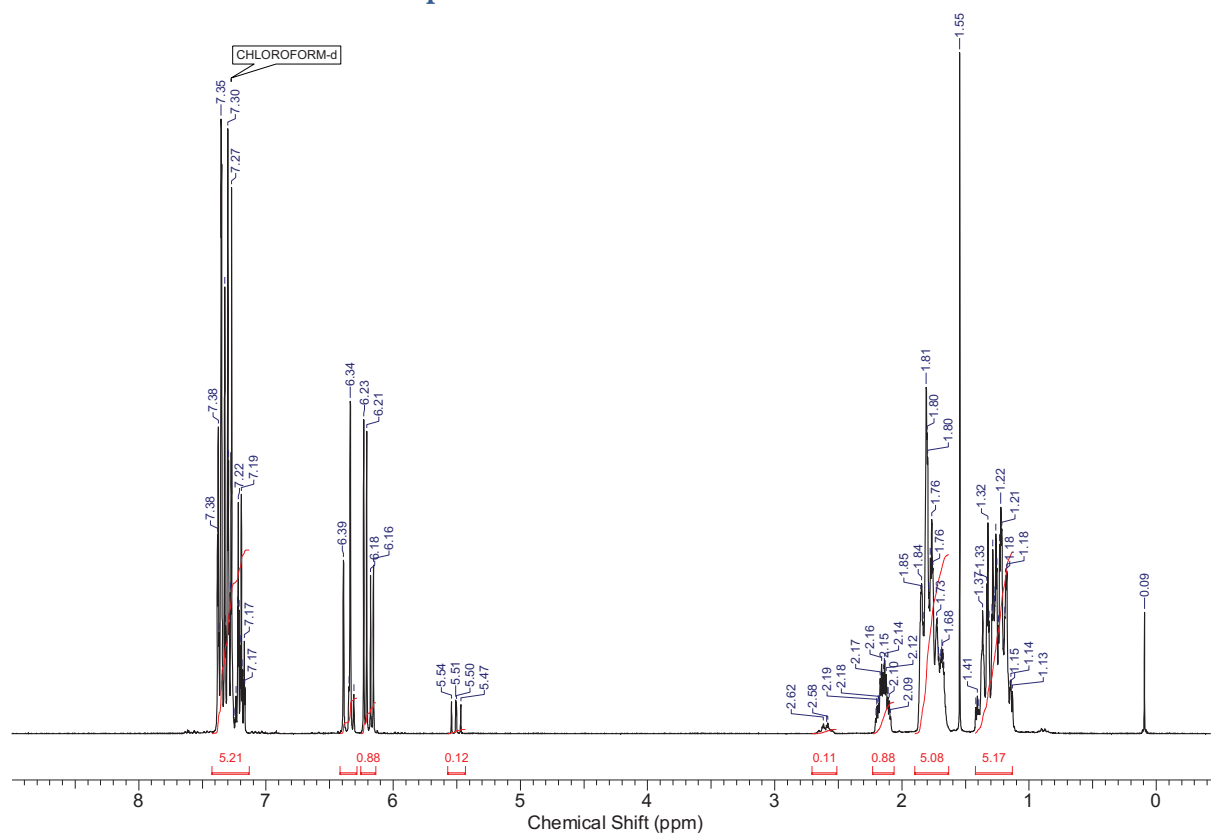


Figure 39: ^1H NMR spectrum (CDCl₃, 300 MHz) of CTA0.

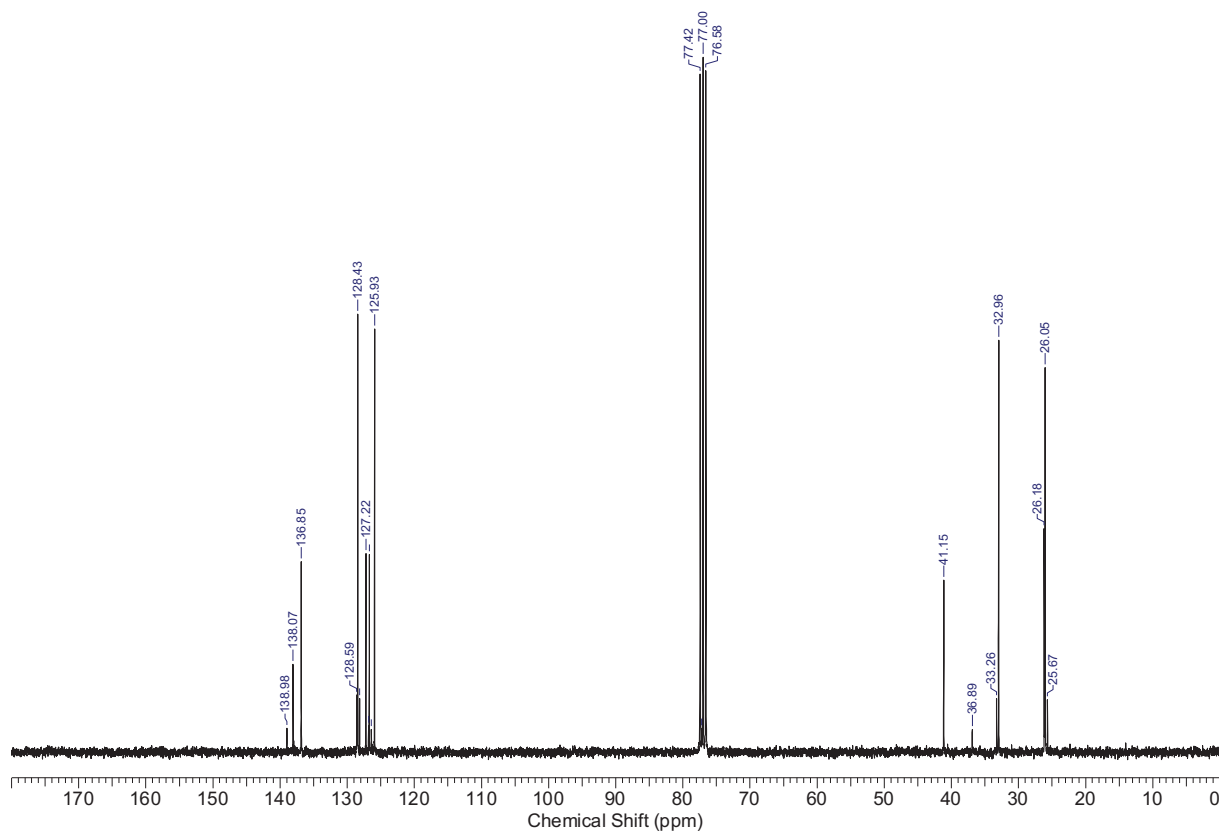


Figure 40: ^{13}C NMR spectrum (CDCl₃, 75 MHz) of CTA0.

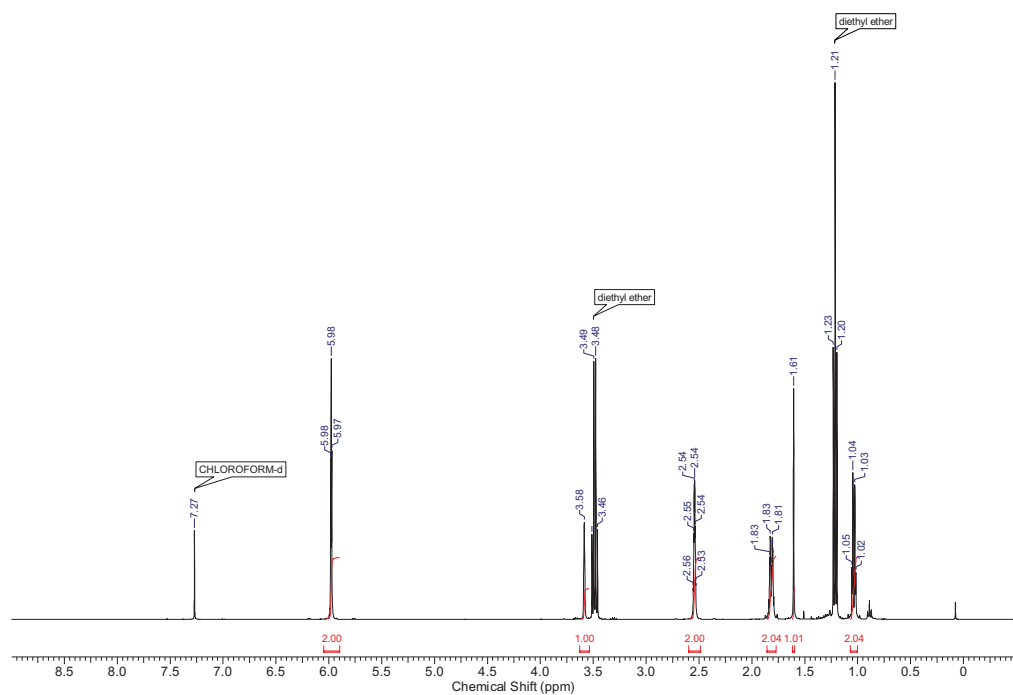


Figure 41: ¹H NMR spectrum (CDCl₃, 400 MHz) of S2.

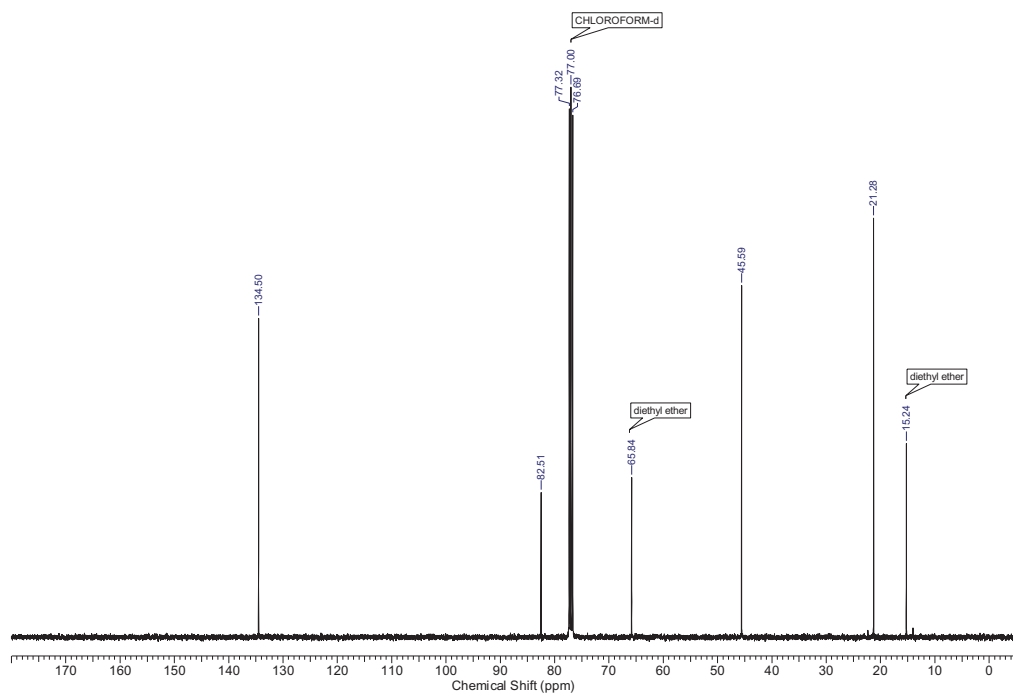


Figure 42: ¹³C NMR spectrum (CDCl₃, 101 MHz) of S2.

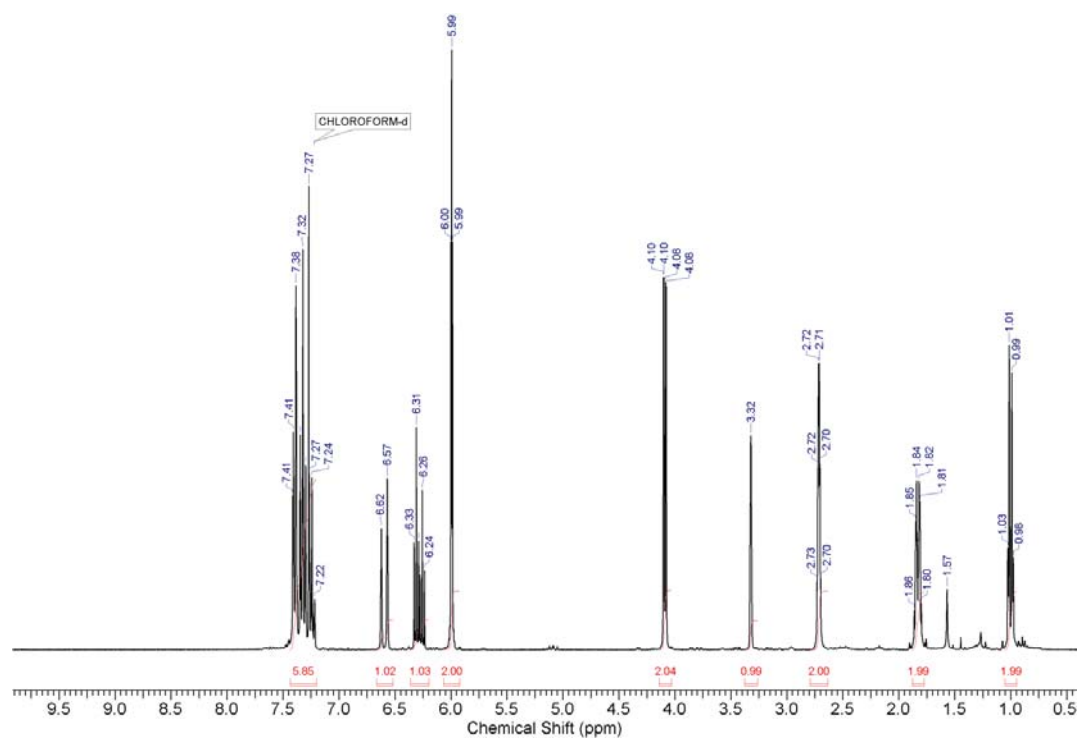


Figure 43: ¹H NMR spectrum (CDCl₃, 300 MHz) of S3.

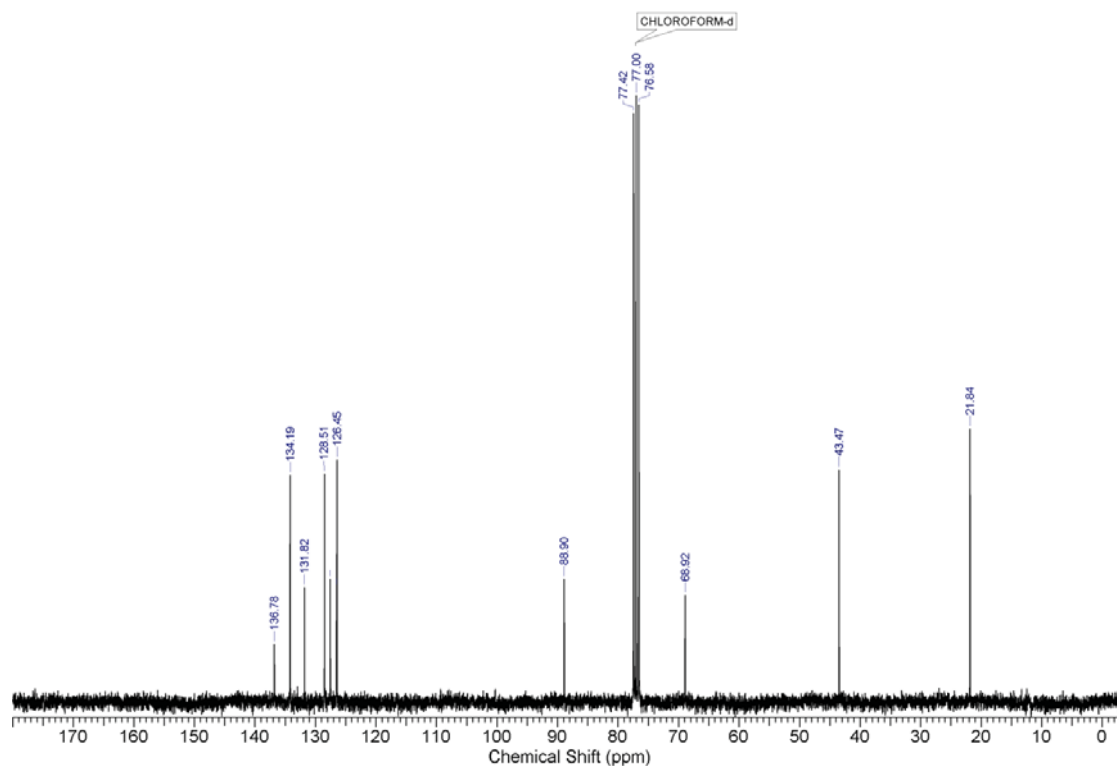


Figure 44: ¹³C NMR spectrum (CDCl₃, 75 MHz) of S3.

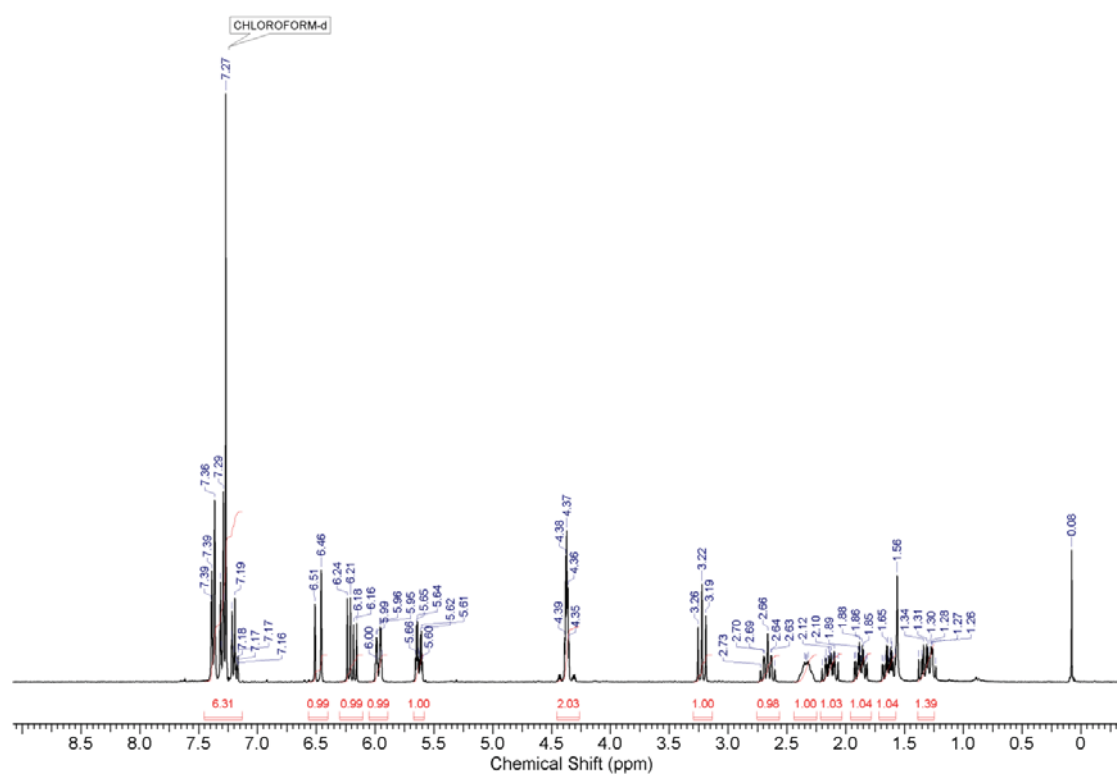


Figure 45: ¹H NMR spectrum (CDCl₃, 300 MHz) of CTA2.

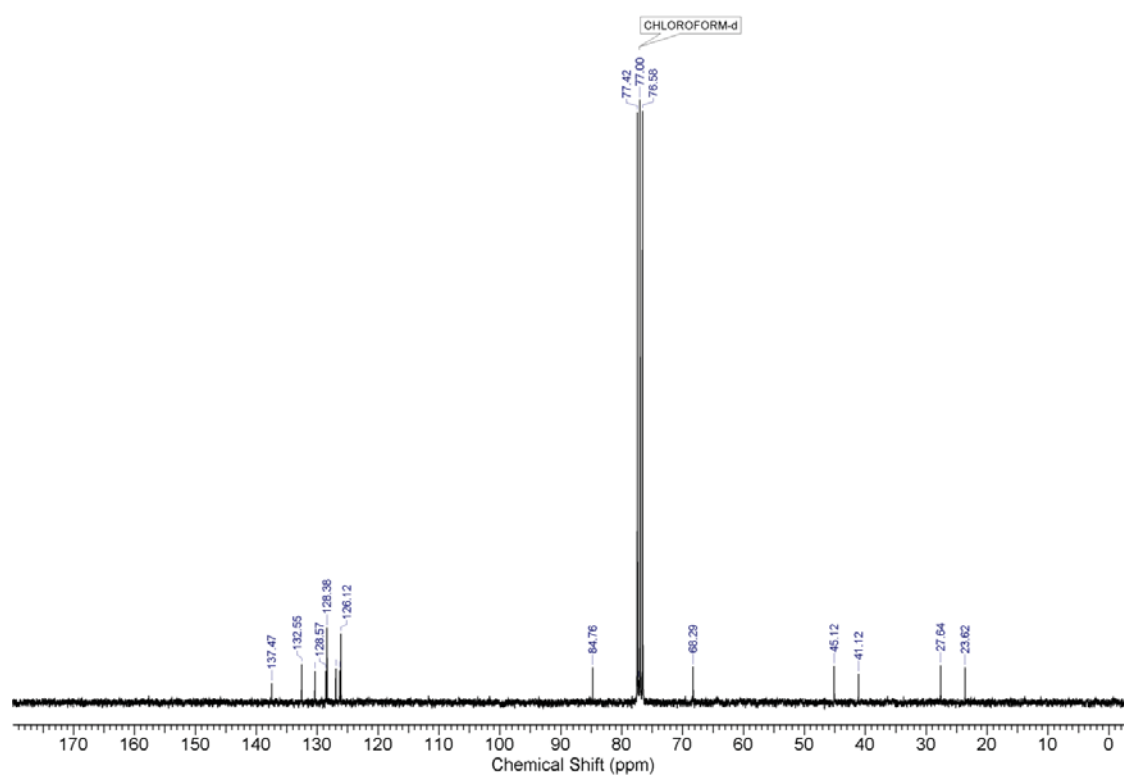


Figure 46: ¹³C NMR spectrum (CDCl₃, 75 MHz) of CTA2.

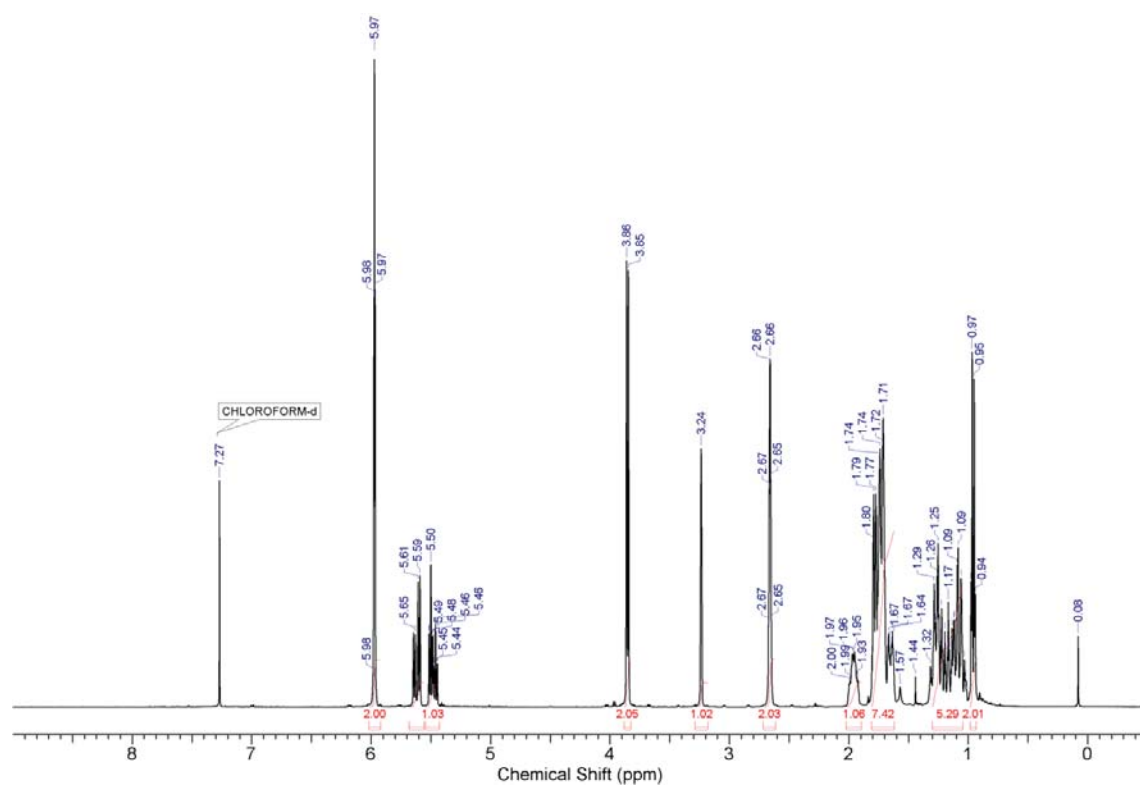


Figure 47: ^1H NMR spectrum (CDCl_3 , 400 MHz) of S4.

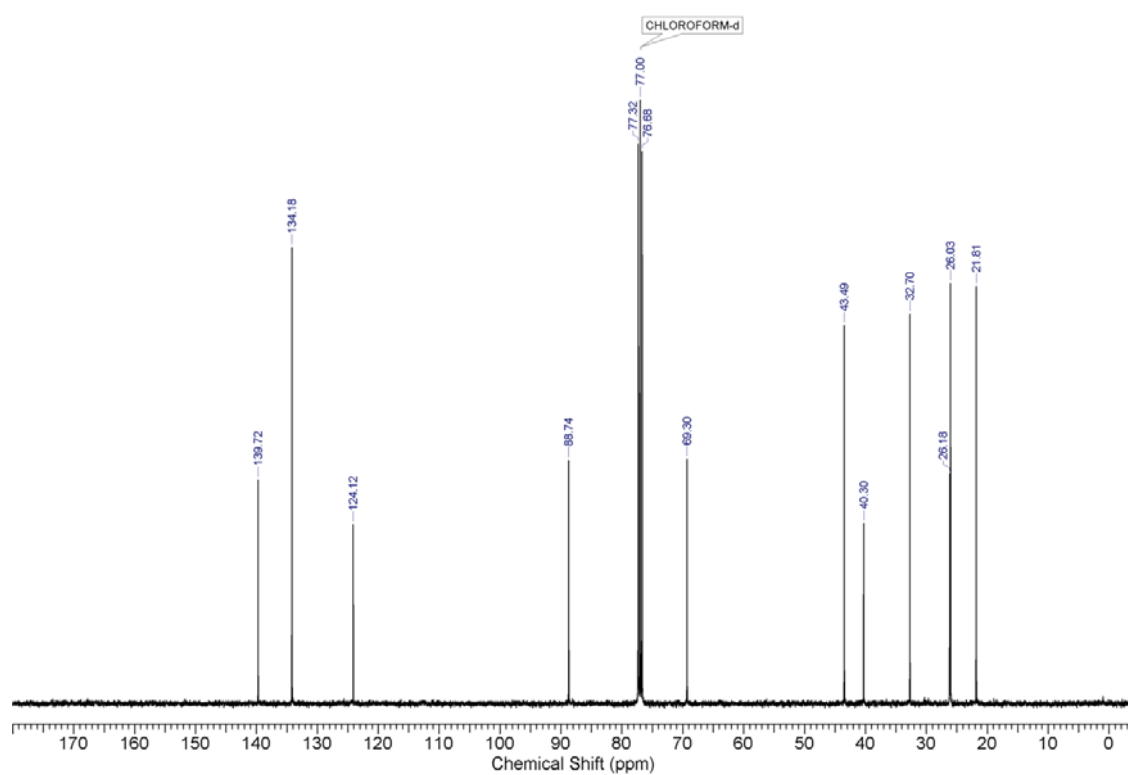


Figure 48: ^{13}C NMR spectrum (CDCl_3 , 101 MHz) of S4.

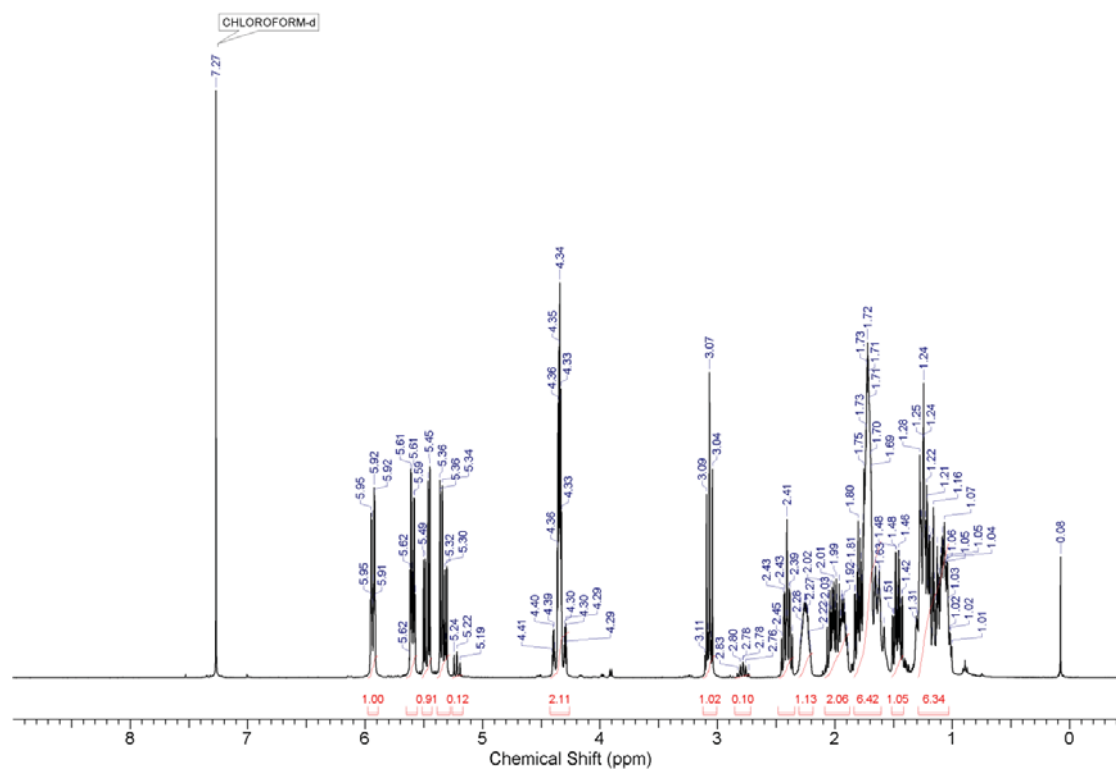


Figure 49: ¹H NMR spectrum (CDCl₃, 400 MHz) of CTA3.

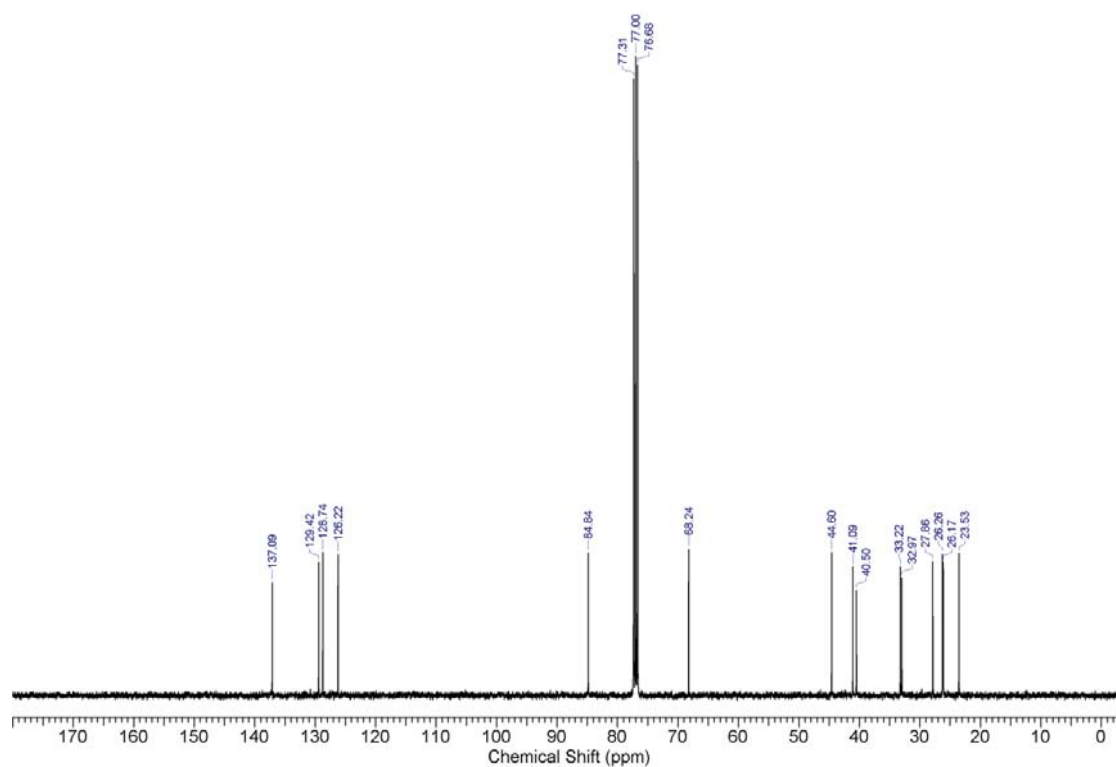


Figure 50: ¹³C NMR spectrum (CDCl₃, 101 MHz) of CTA3.

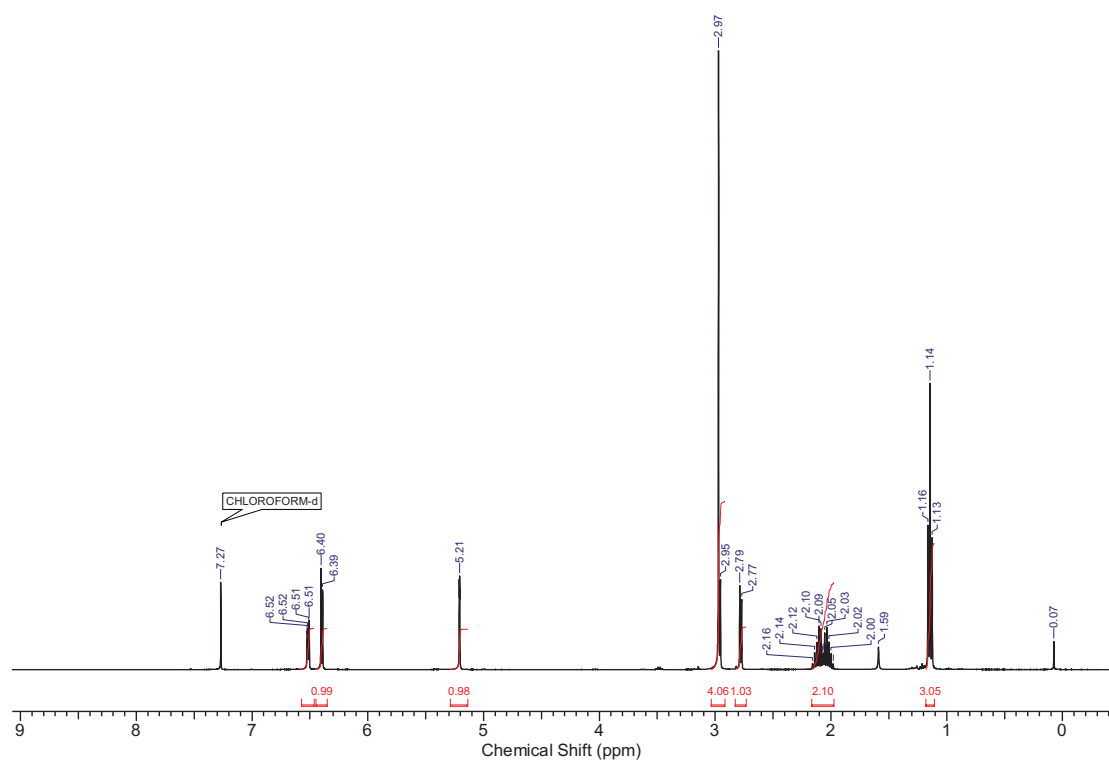


Figure 51: ¹H NMR spectrum (CDCl₃, 400 MHz) of M2.

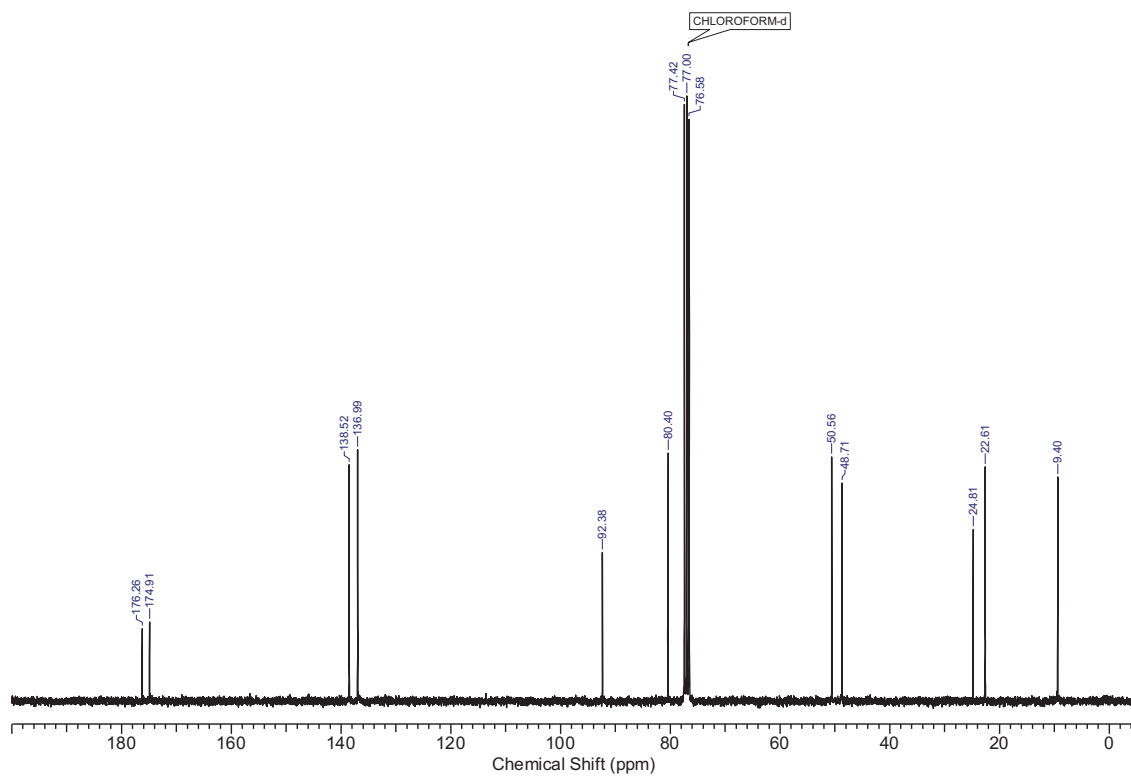


Figure 52: ¹³C NMR spectrum (CDCl₃, 75 MHz) of M2.

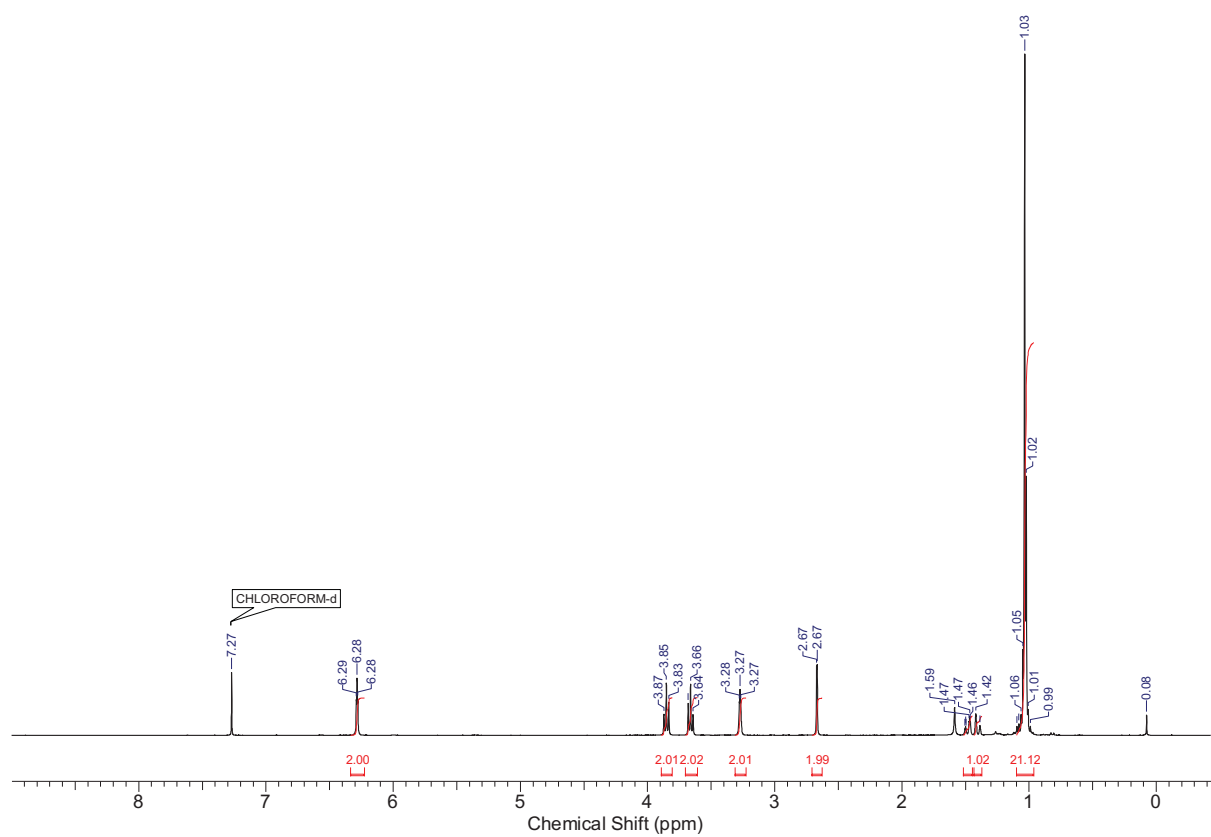


Figure 53: ¹H NMR spectrum (CDCl₃, 300 MHz) of M4.

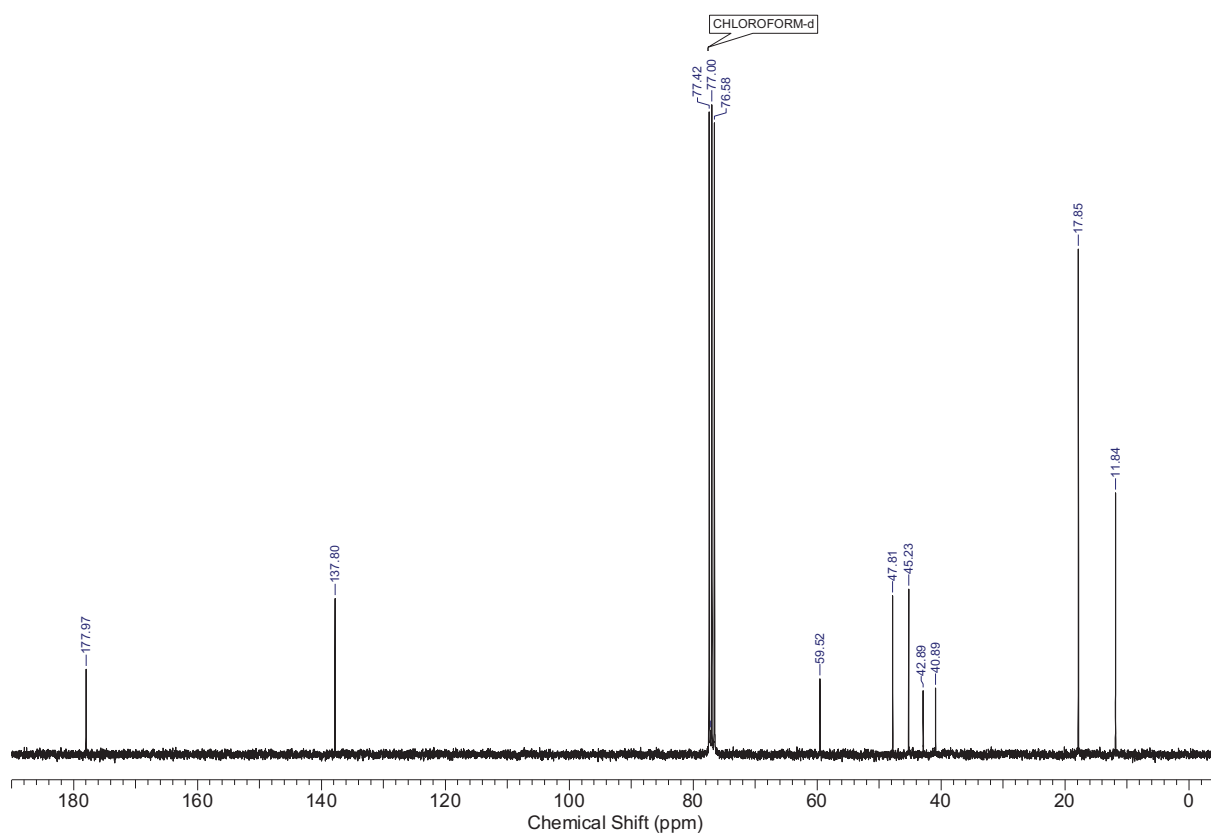


Figure 54: ¹³C NMR spectrum (CDCl₃, 75 MHz) of M4.

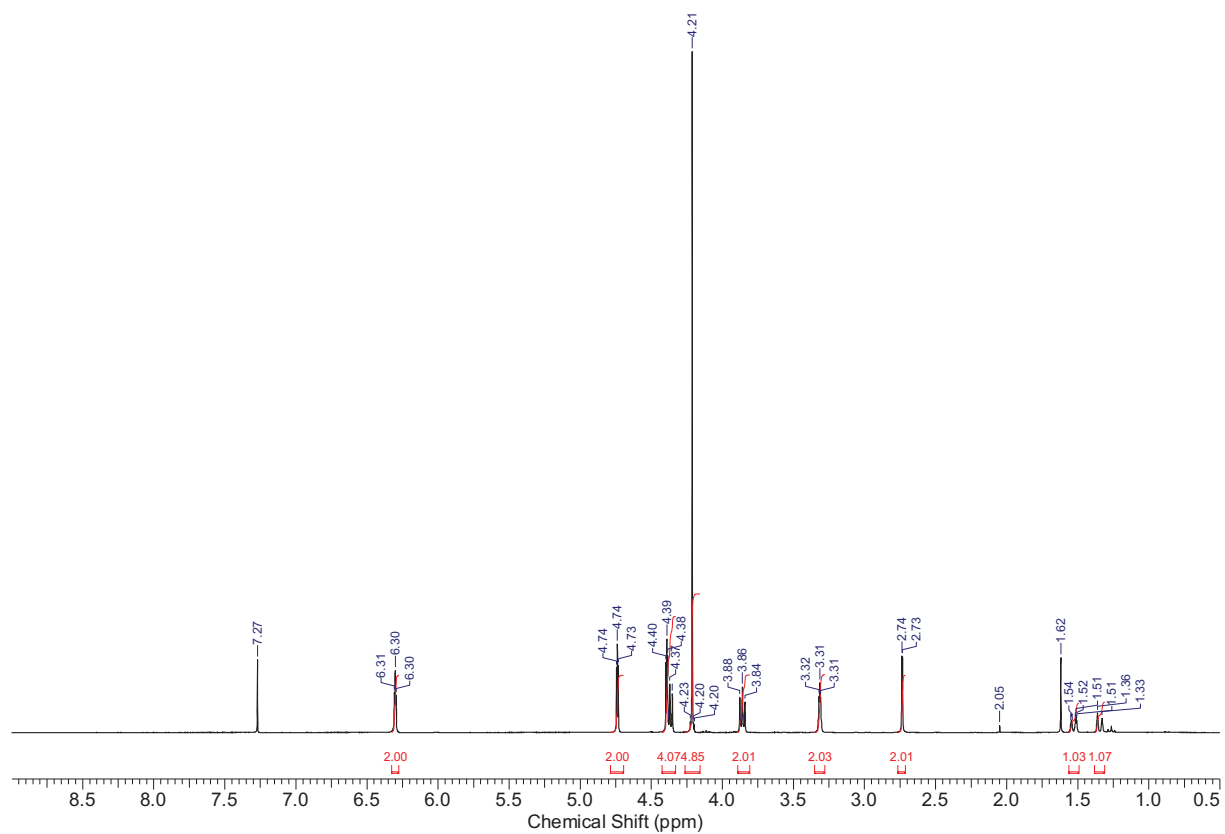


Figure 55: ¹H NMR spectrum (CDCl₃, 400 MHz) of M5.

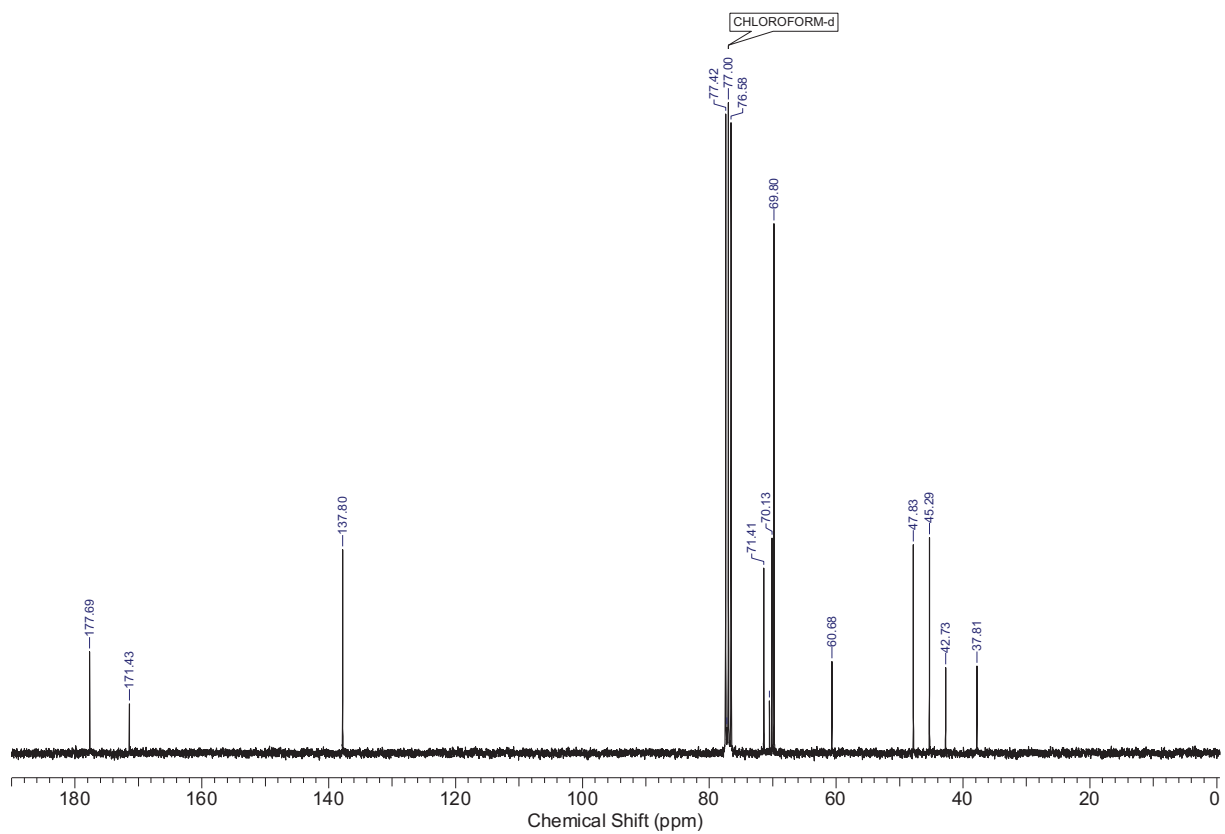


Figure 56: ¹³C NMR spectrum (CDCl₃, 400 MHz) of M5.

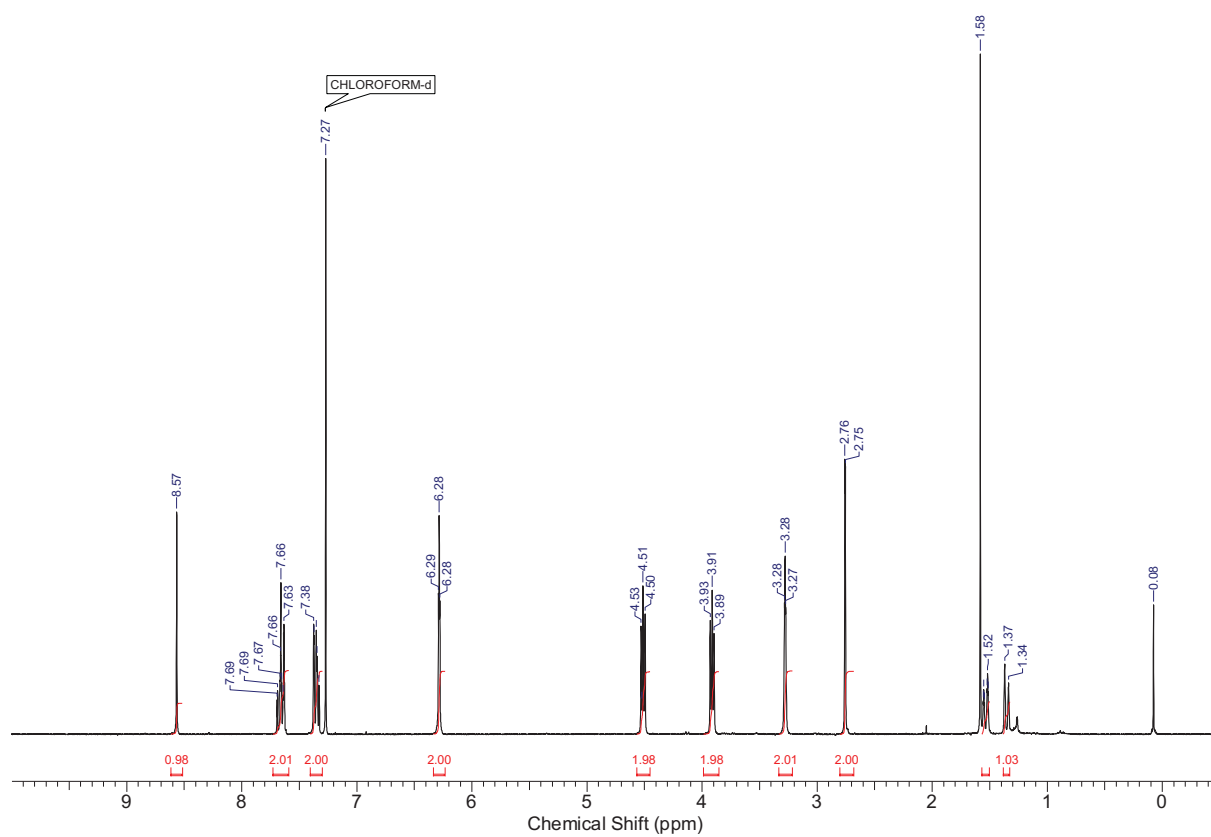


Figure 57: ¹H NMR spectrum (CDCl₃, 300 MHz) of M6.

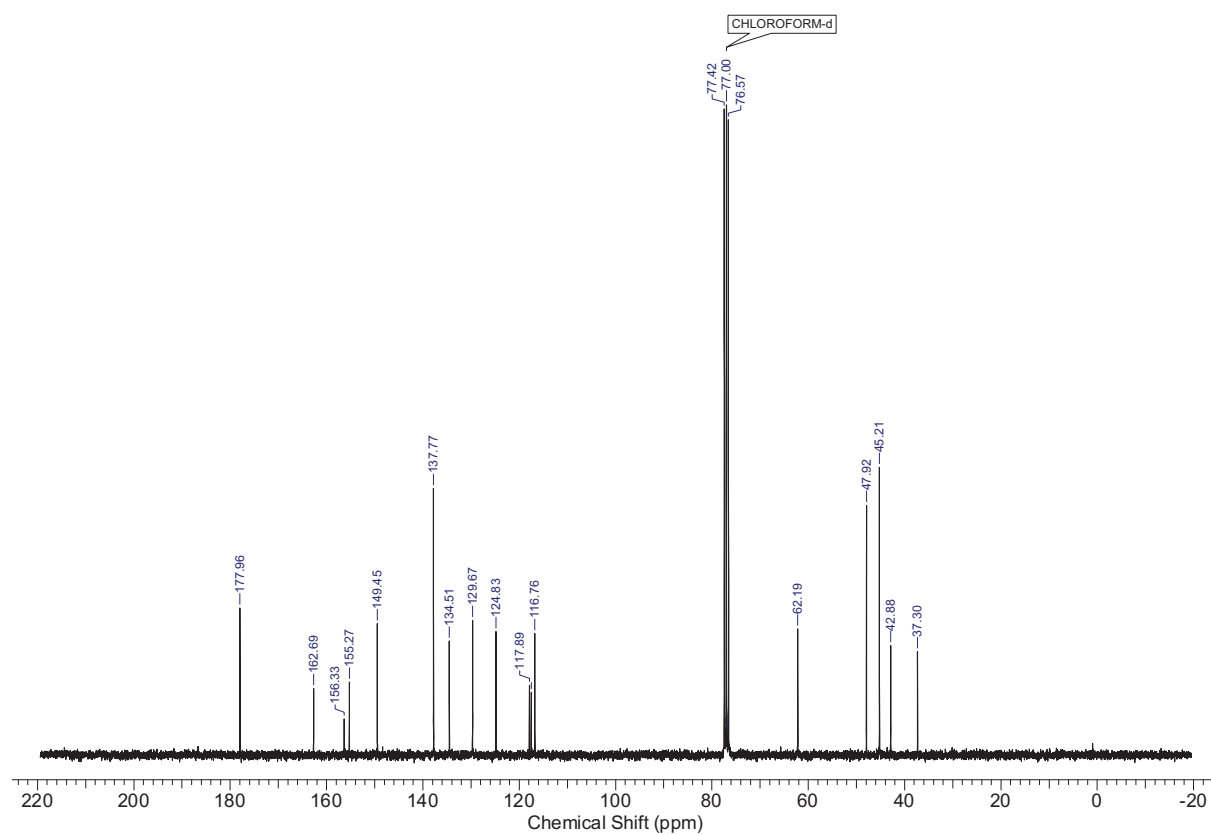


Figure 58: ¹³C NMR spectrum (CDCl₃, 75 MHz) of M6.

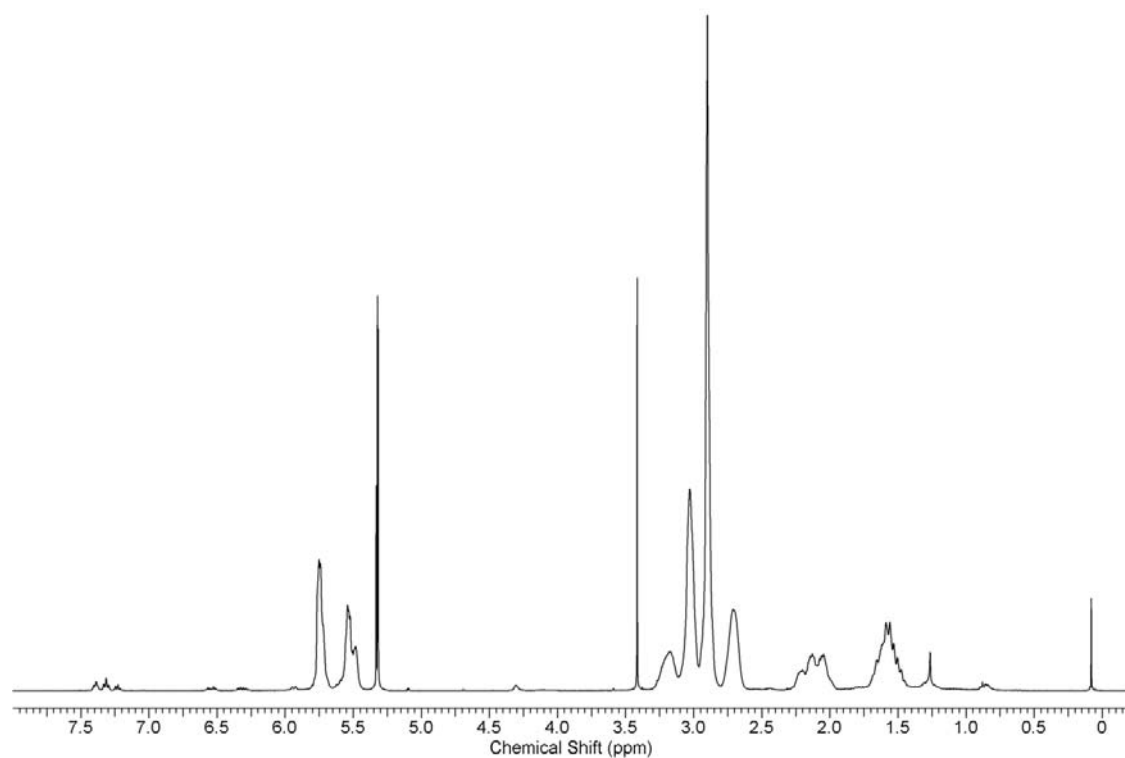


Figure 59: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P1.

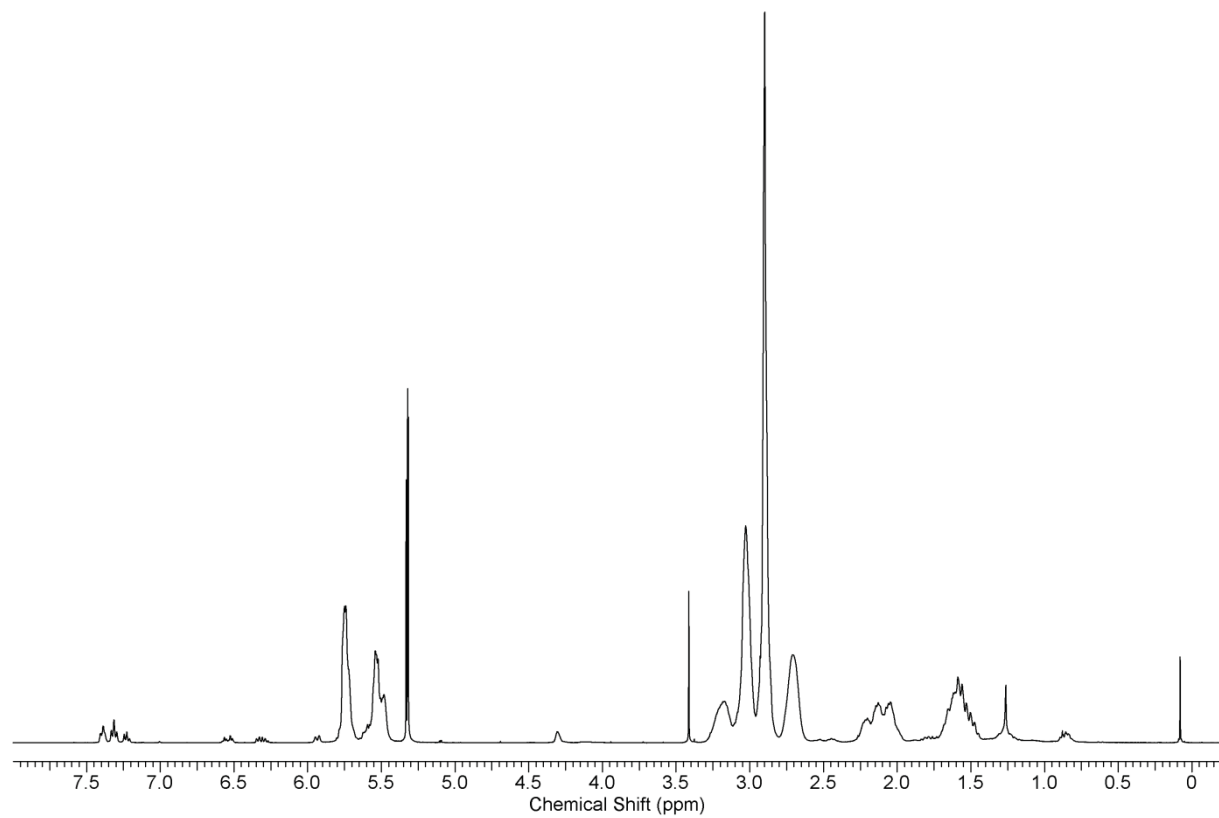


Figure 60: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P2.

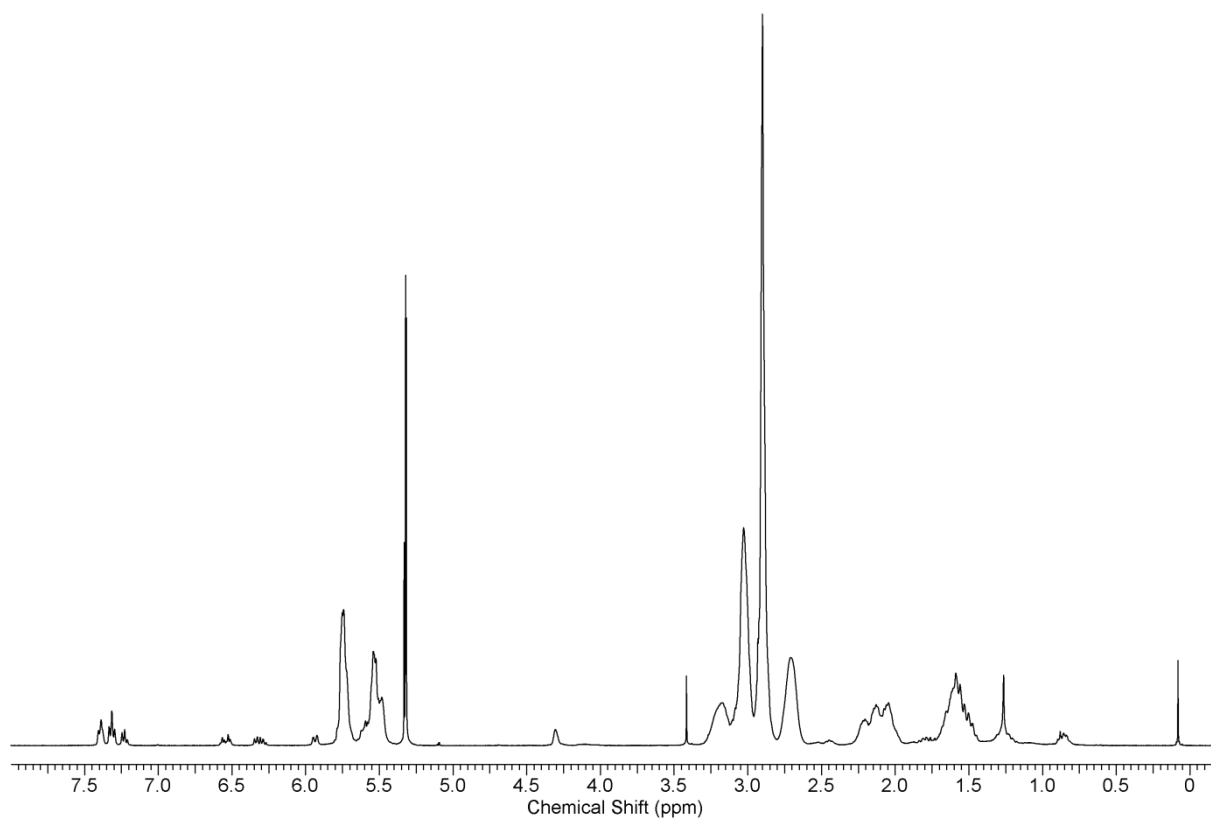


Figure 61: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P3.

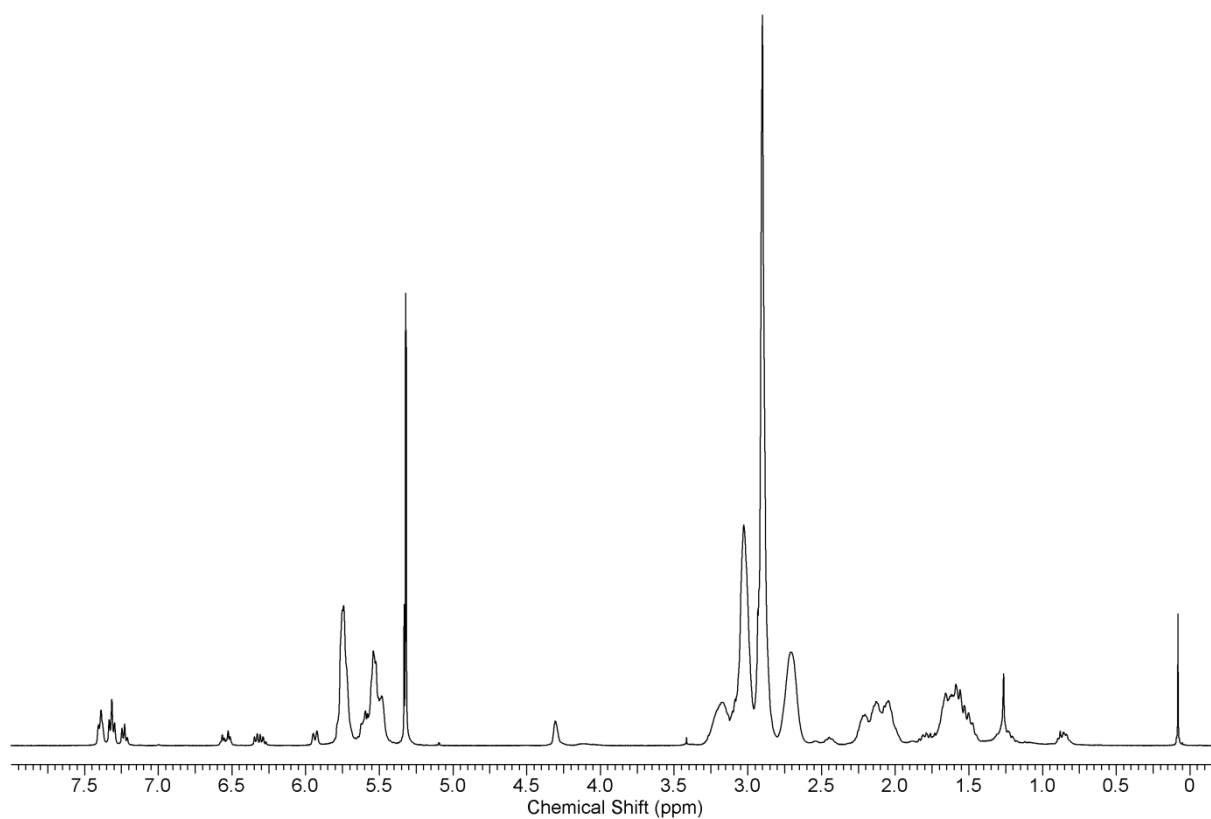


Figure 62: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P4.

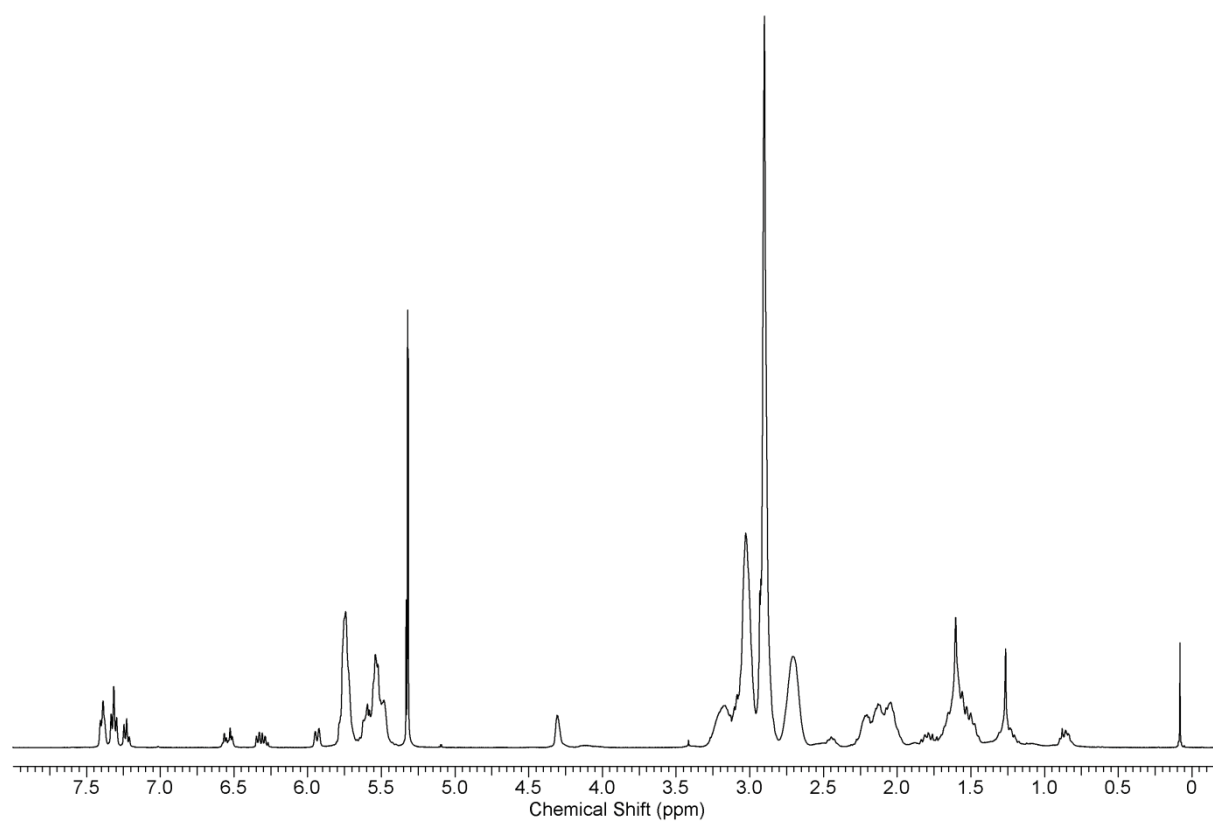


Figure 63: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P5.

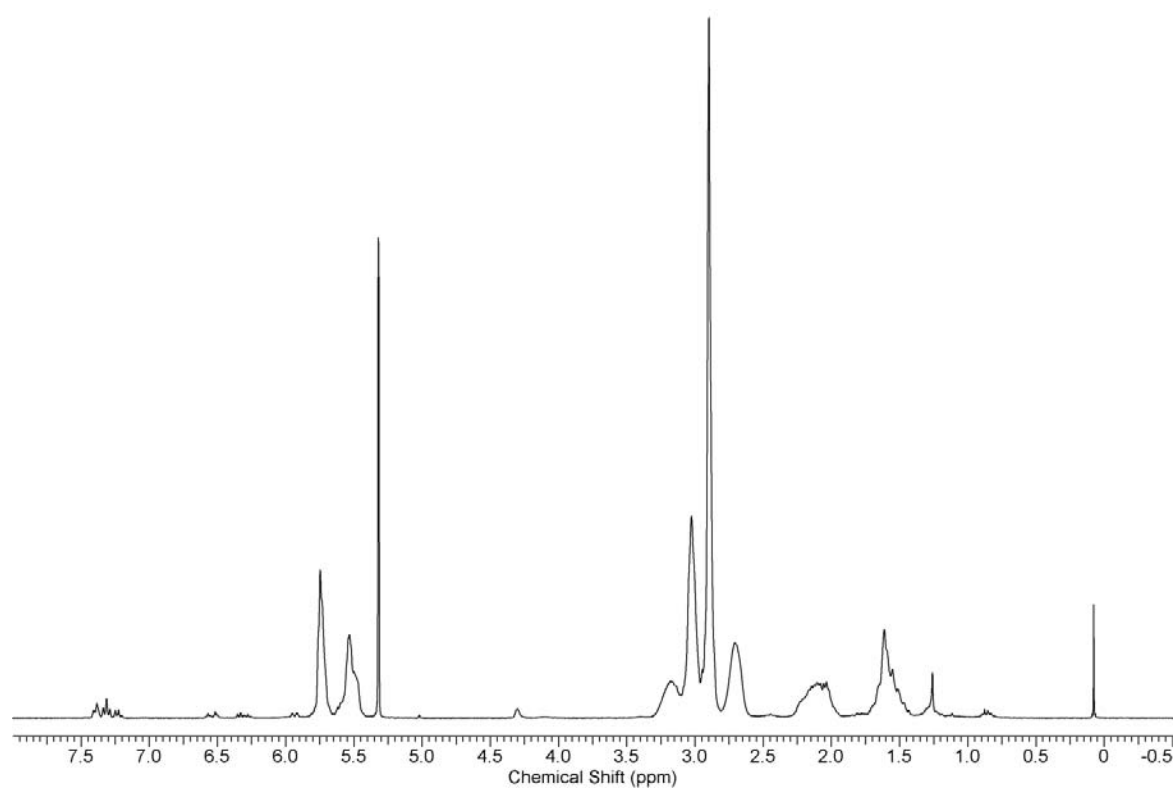


Figure 64: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P6.

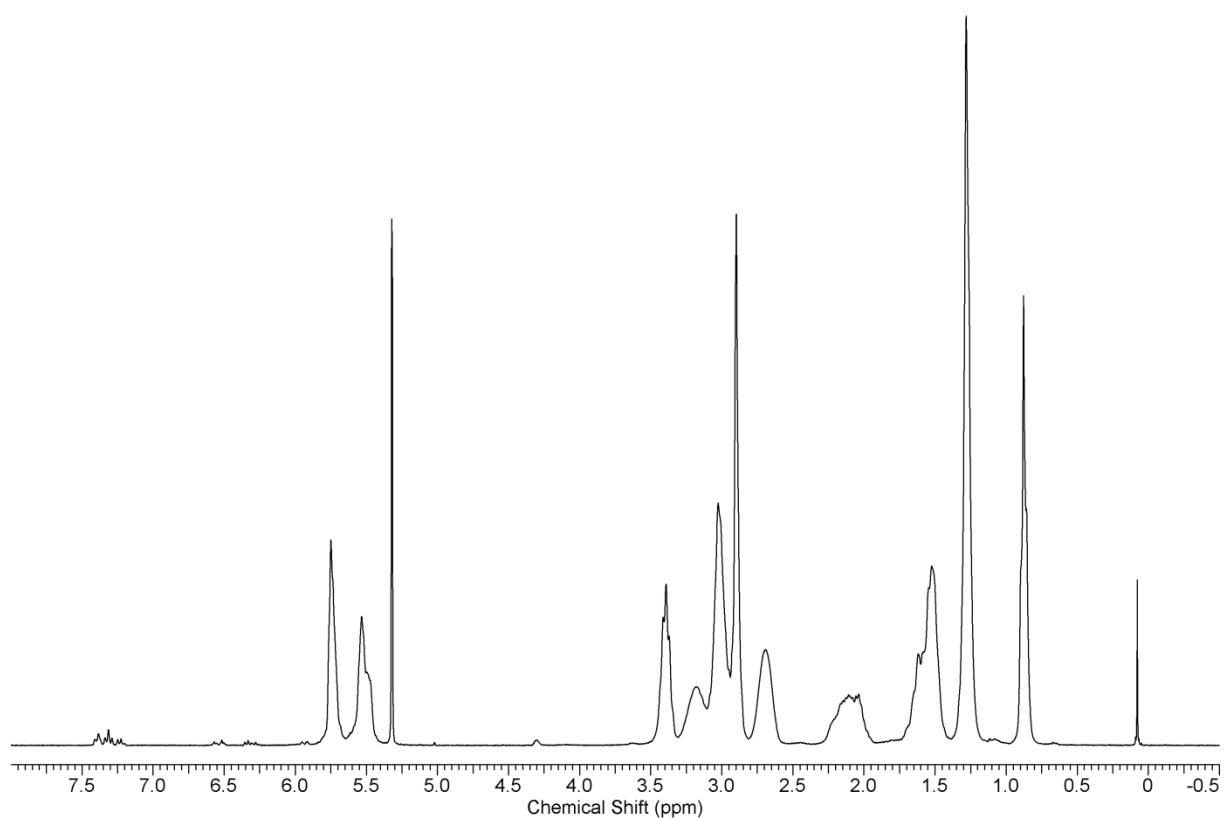


Figure 65: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P7.

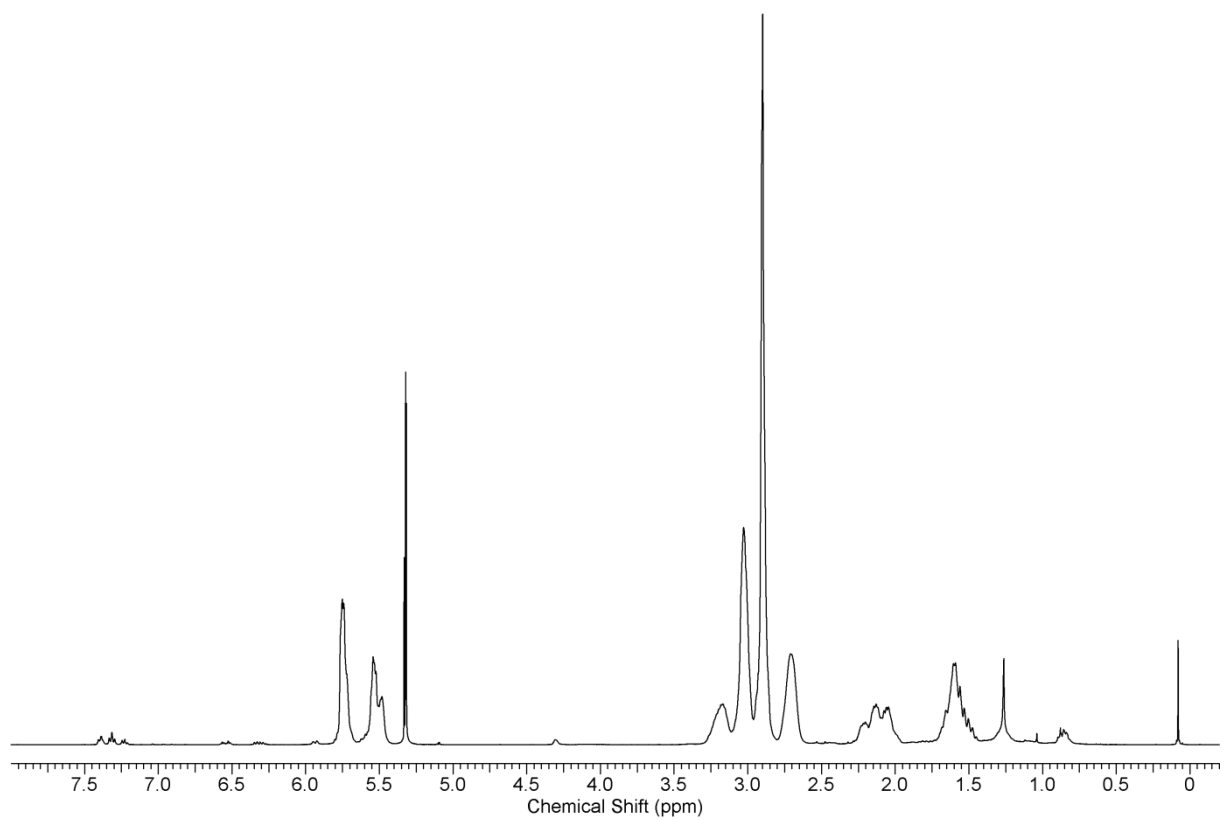


Figure 66: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P8.

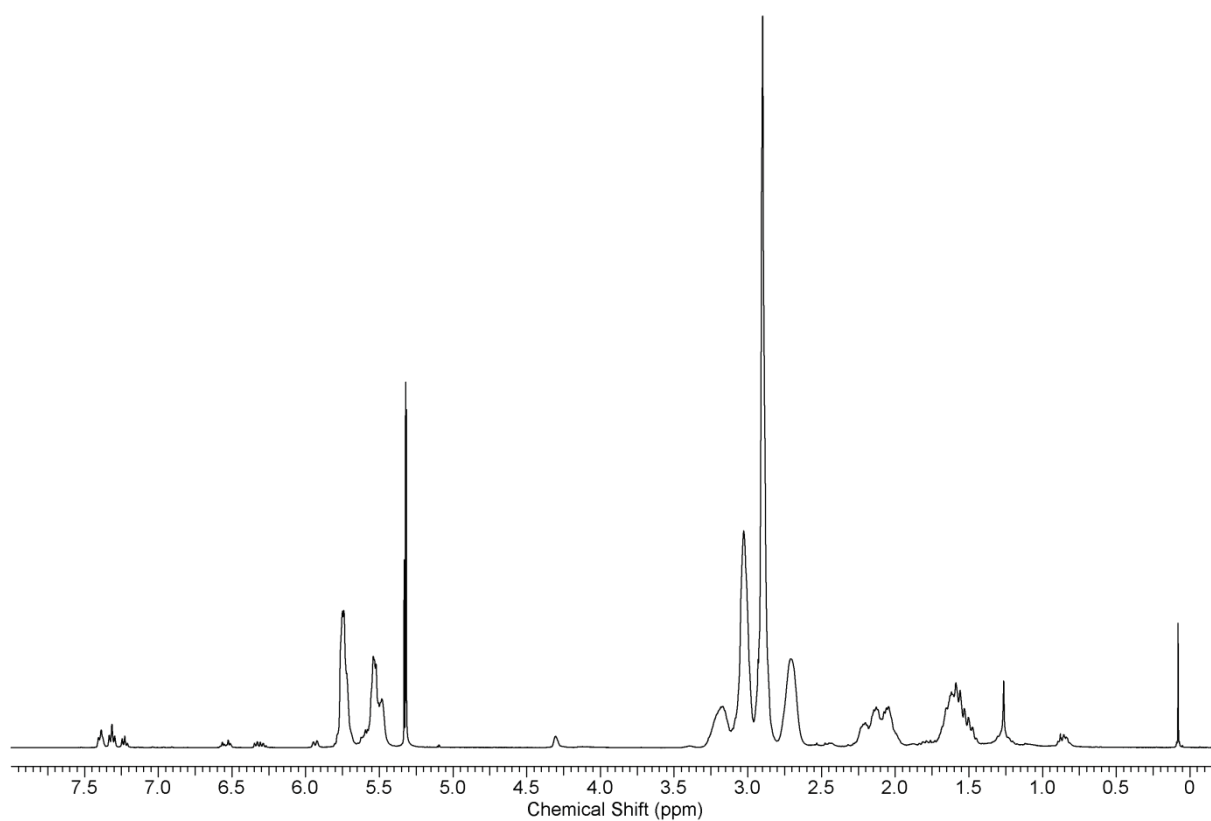


Figure 67: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P9.

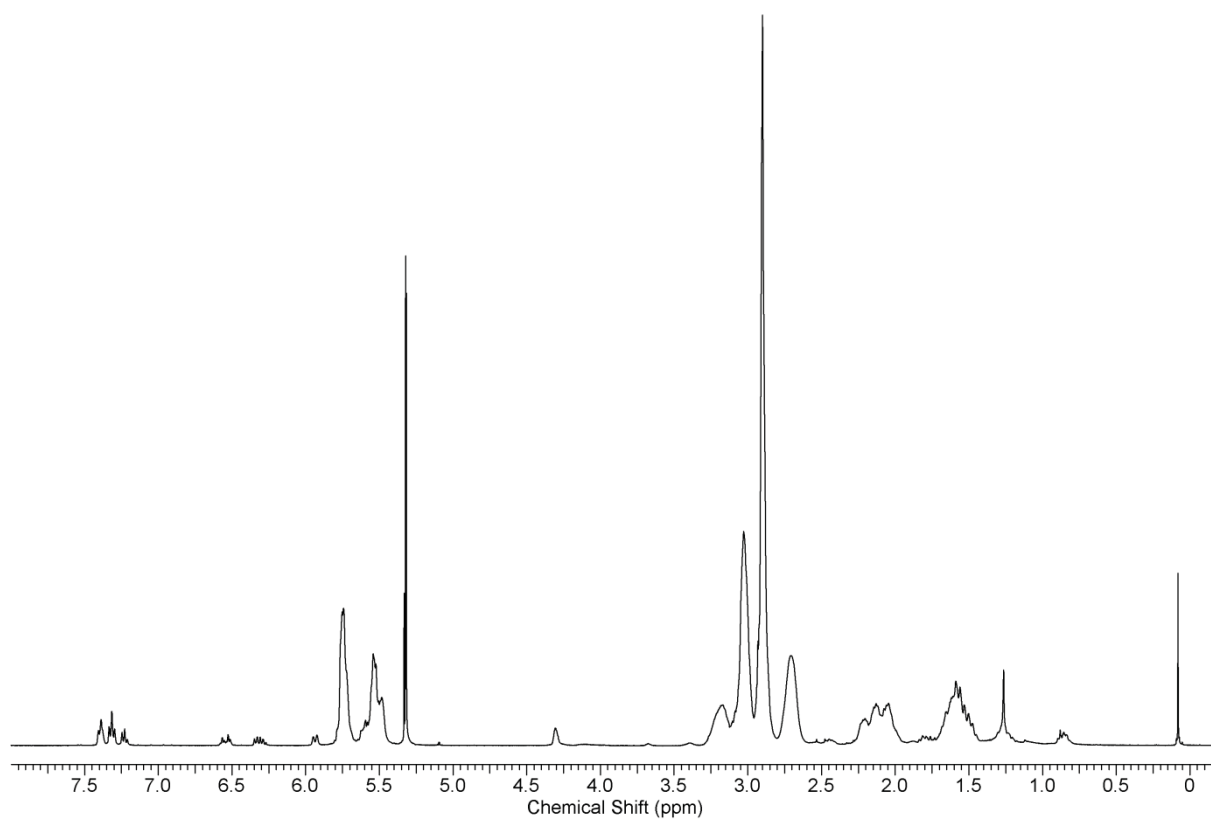


Figure 68: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P10.

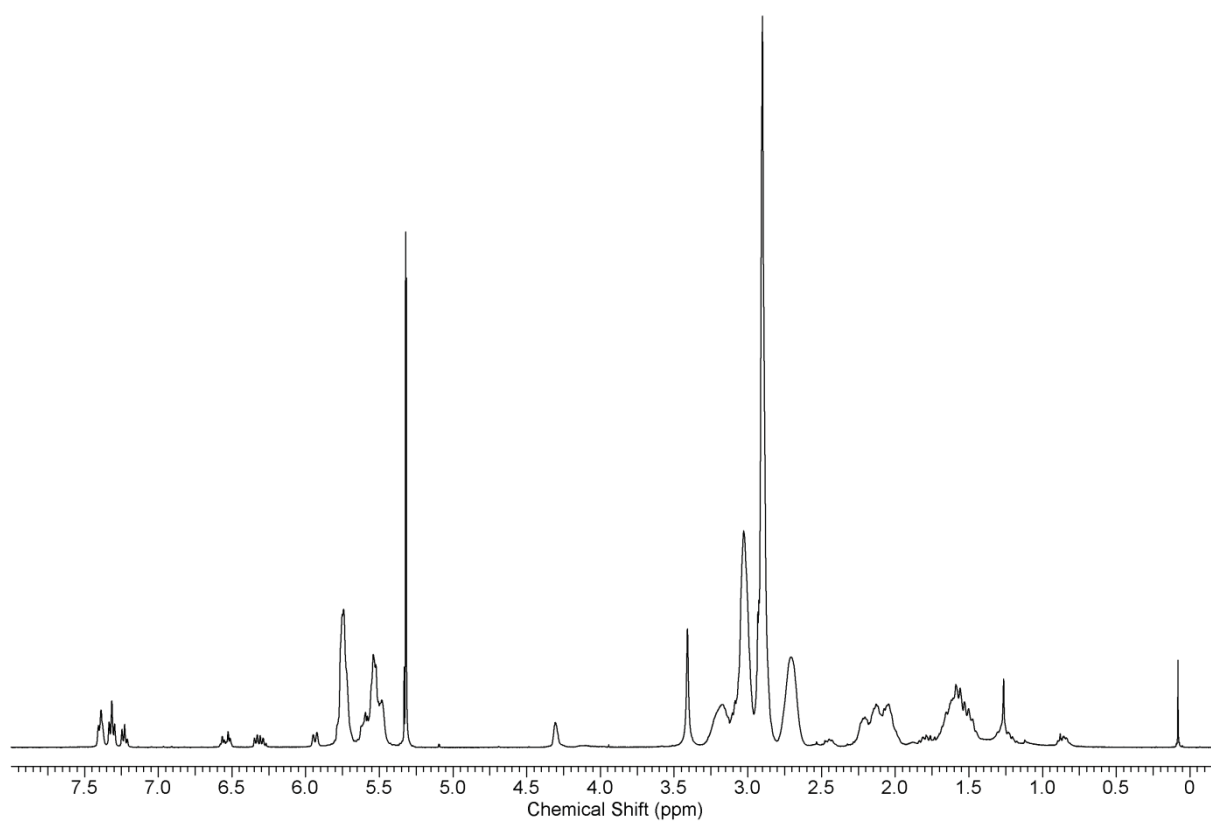


Figure 69: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P11.

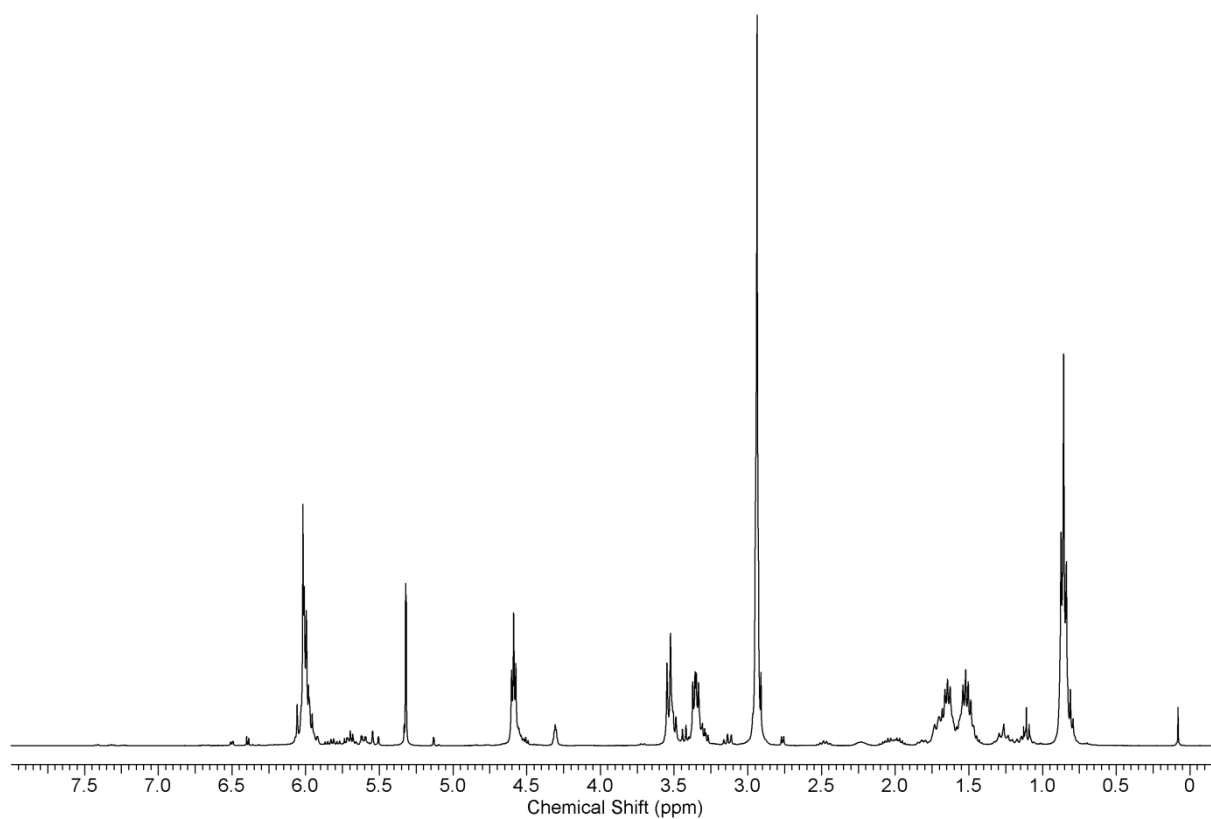


Figure 70: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P12.

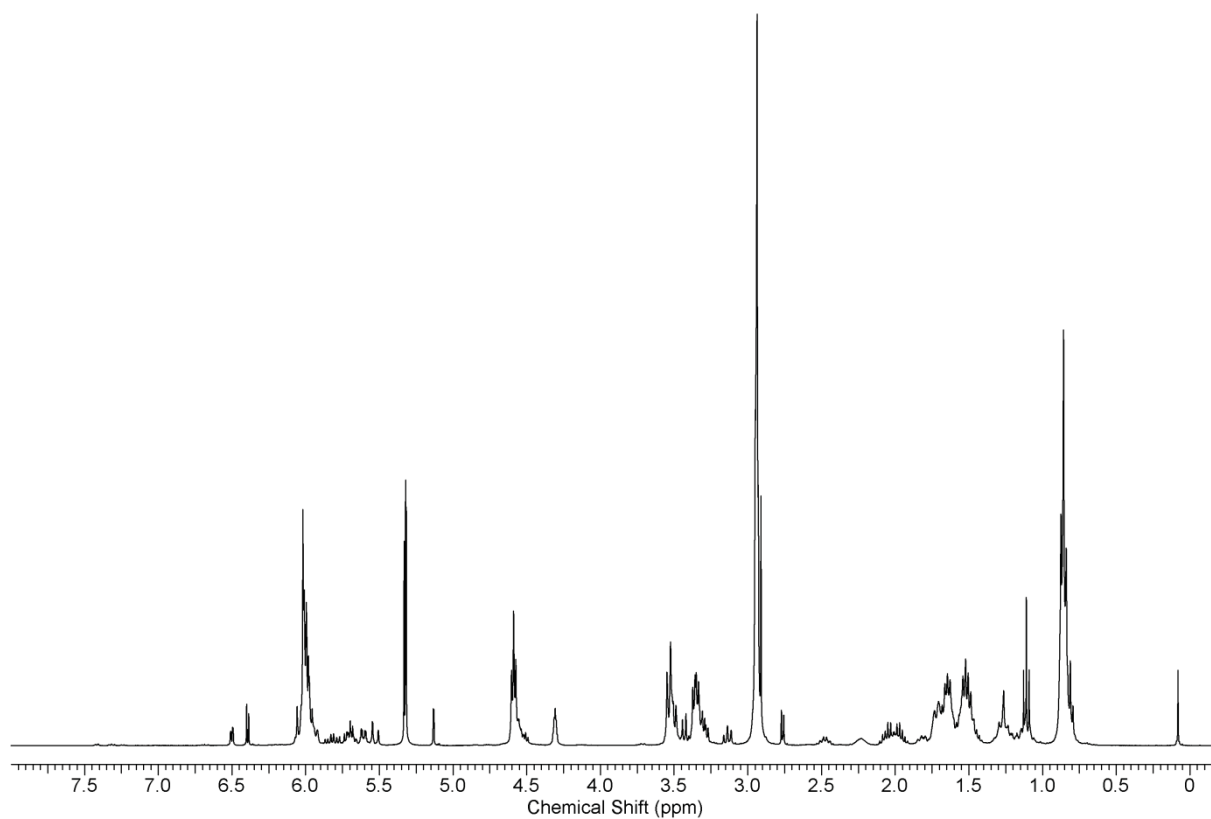


Figure 71: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P13.

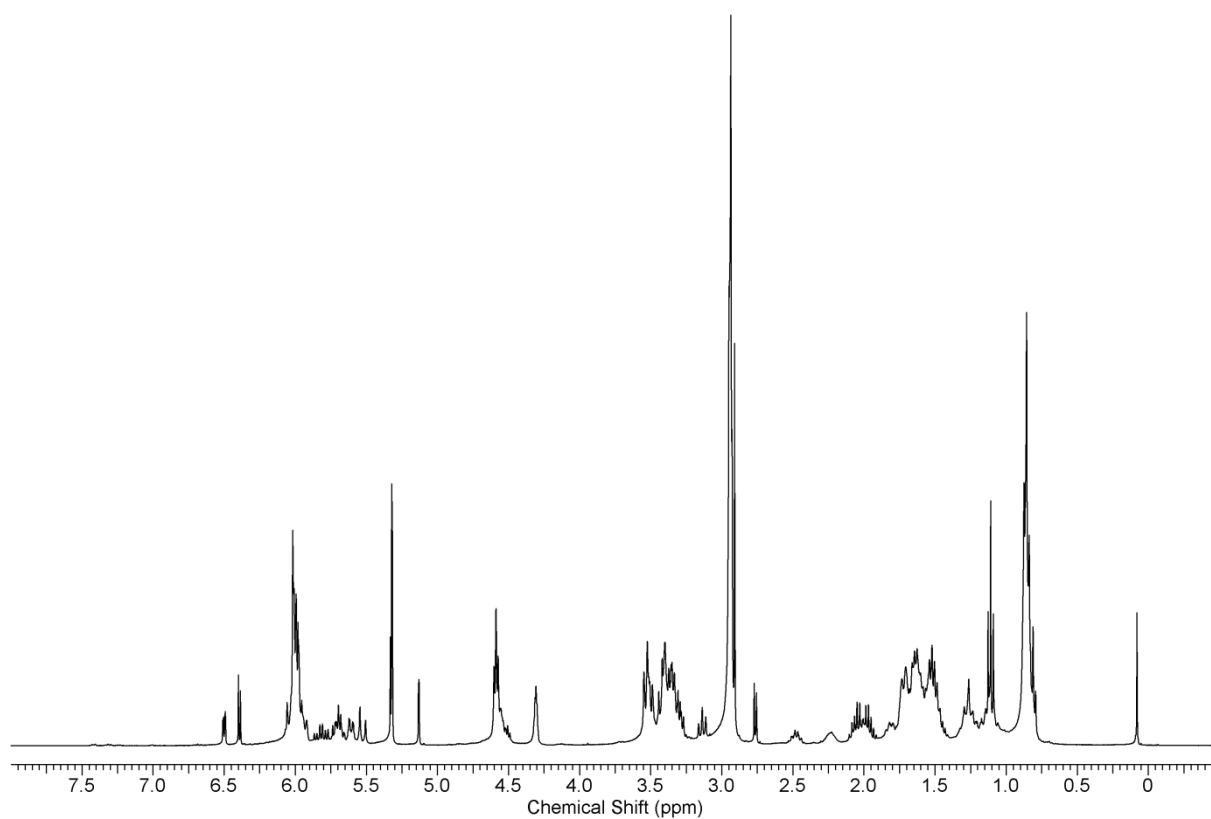


Figure 72: ^1H NMR spectrum (CDCl_3 , 400 MHz) of P14.

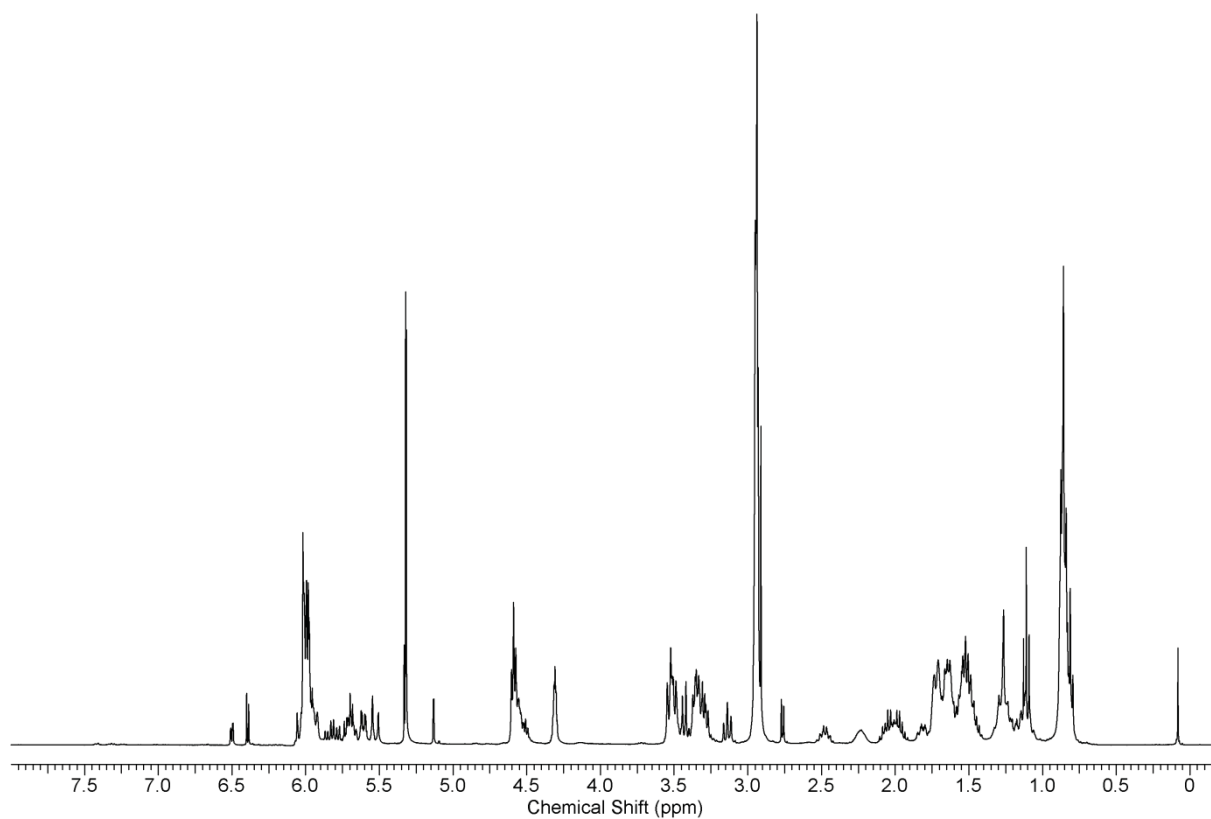


Figure 73: ¹H NMR spectrum (CDCl₃, 400 MHz) of P15.

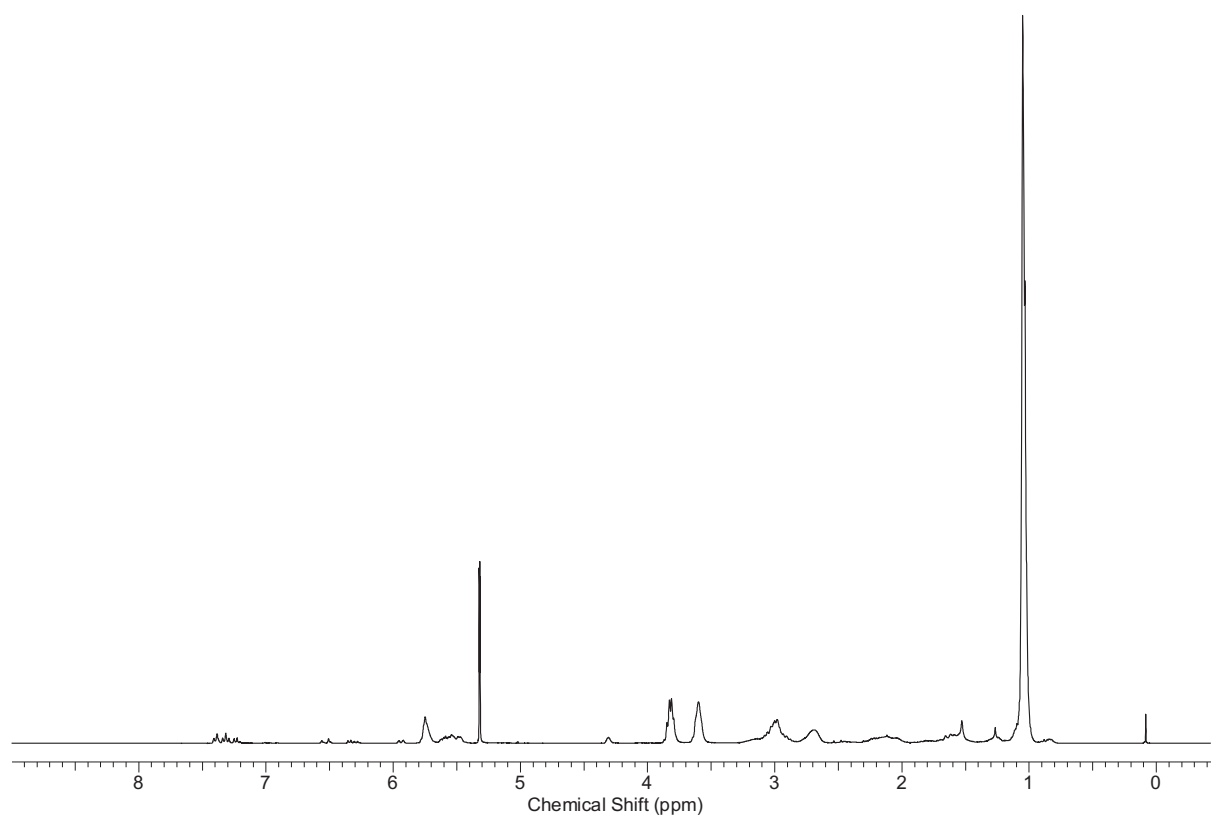


Figure 74: ¹H NMR spectrum (CDCl₃, 300 MHz) of P16.

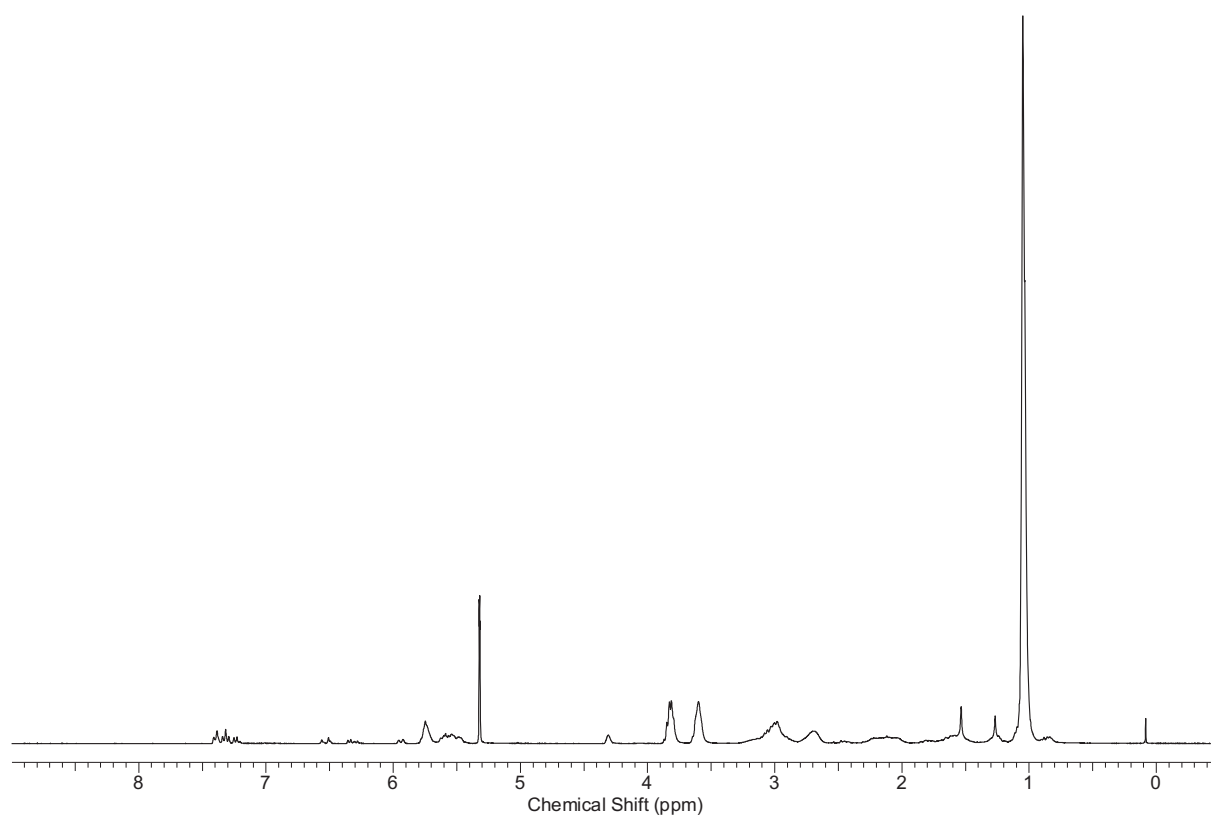


Figure 75: ^1H NMR spectrum (CDCl_3 , 300 MHz) of P17.

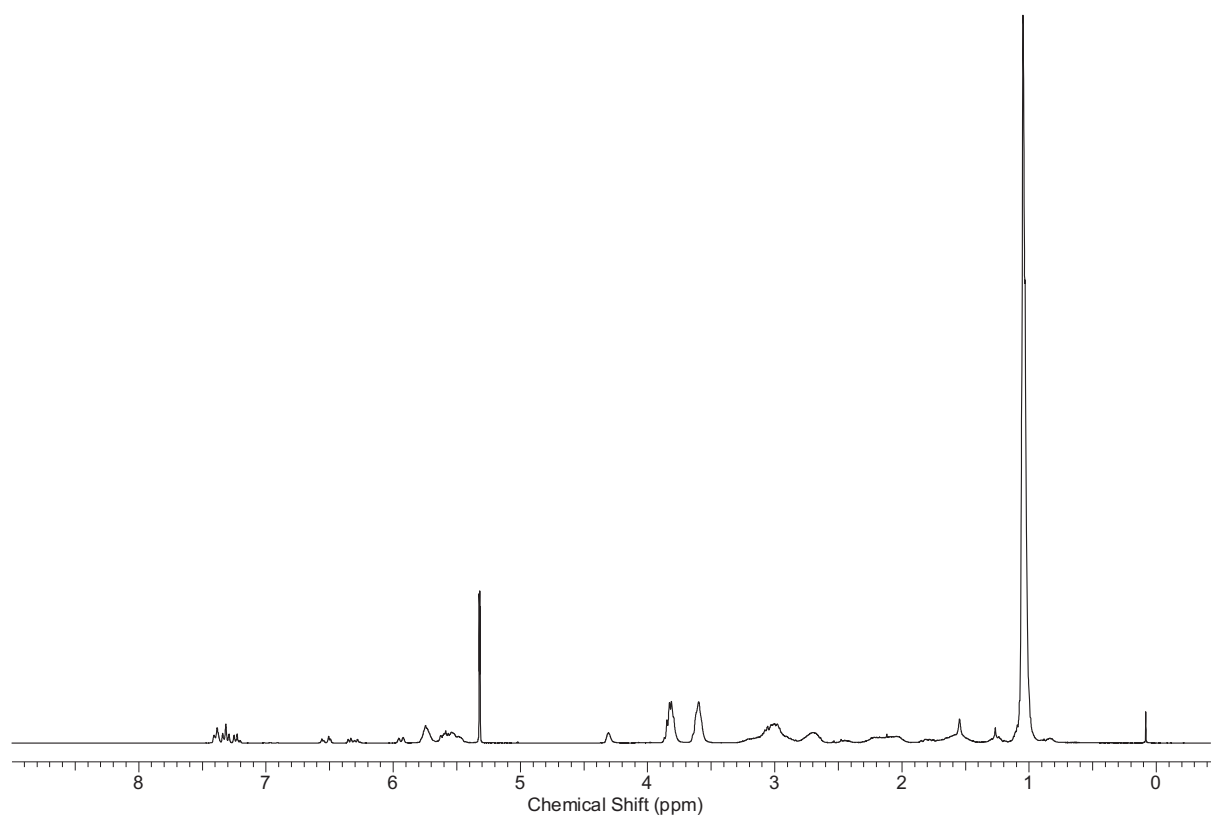


Figure 76: ^1H NMR spectrum (CDCl_3 , 300 MHz) of P18.

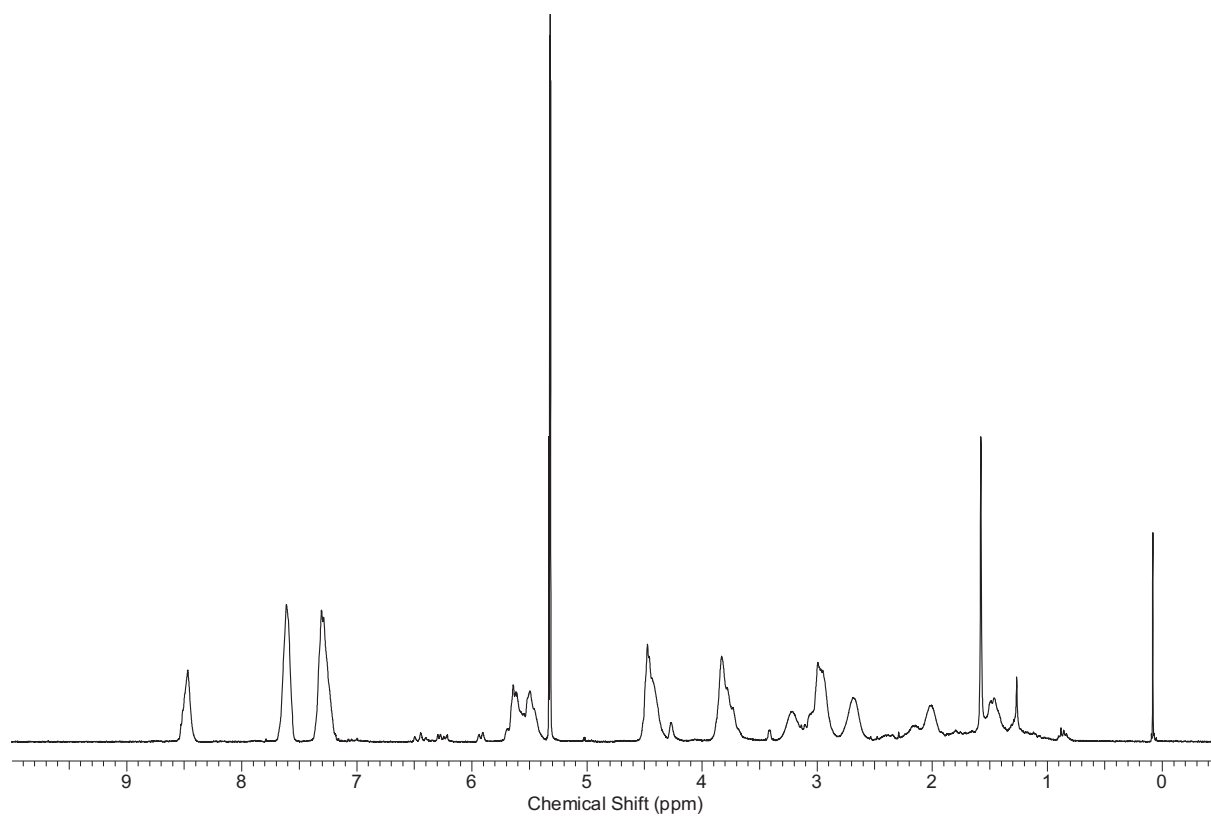


Figure 77: ^1H NMR spectrum (CDCl_3 , 300 MHz) of P19.

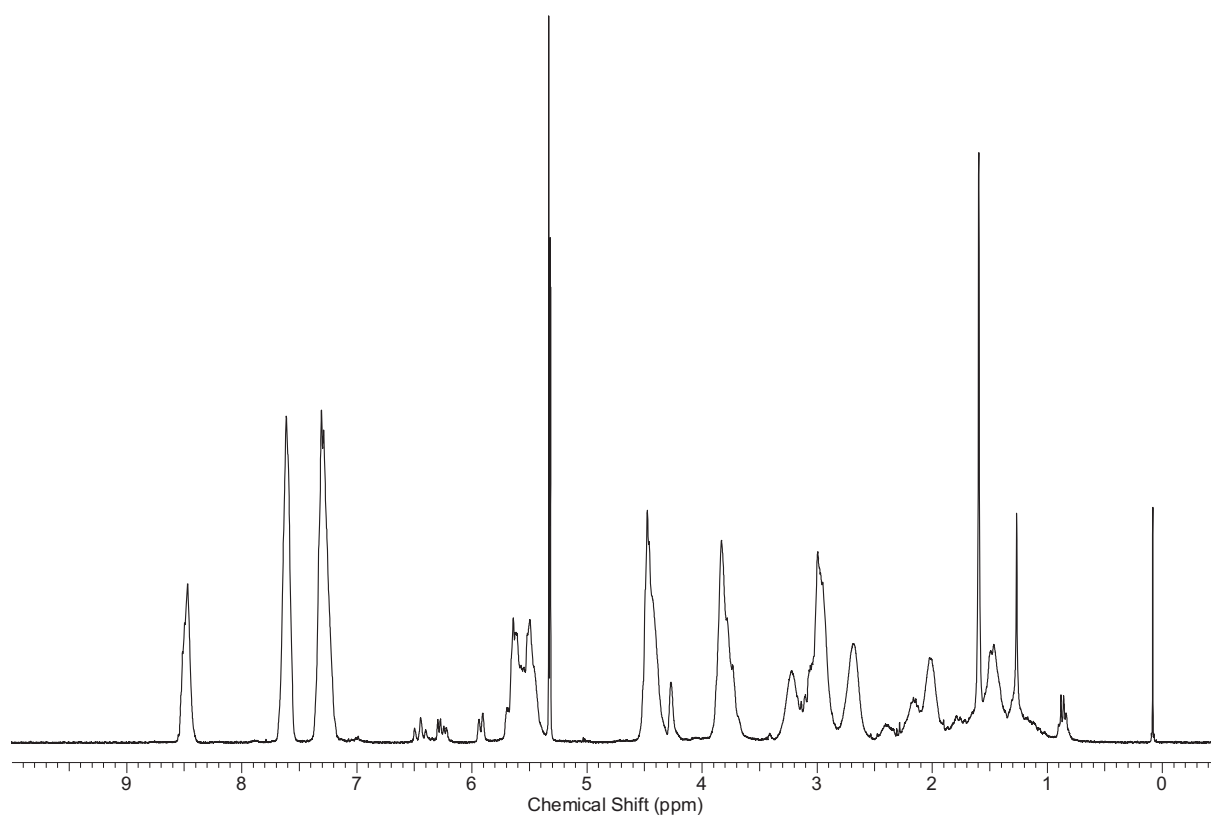


Figure 78: ^1H NMR spectrum (CDCl_3 , 300 MHz) of P20.

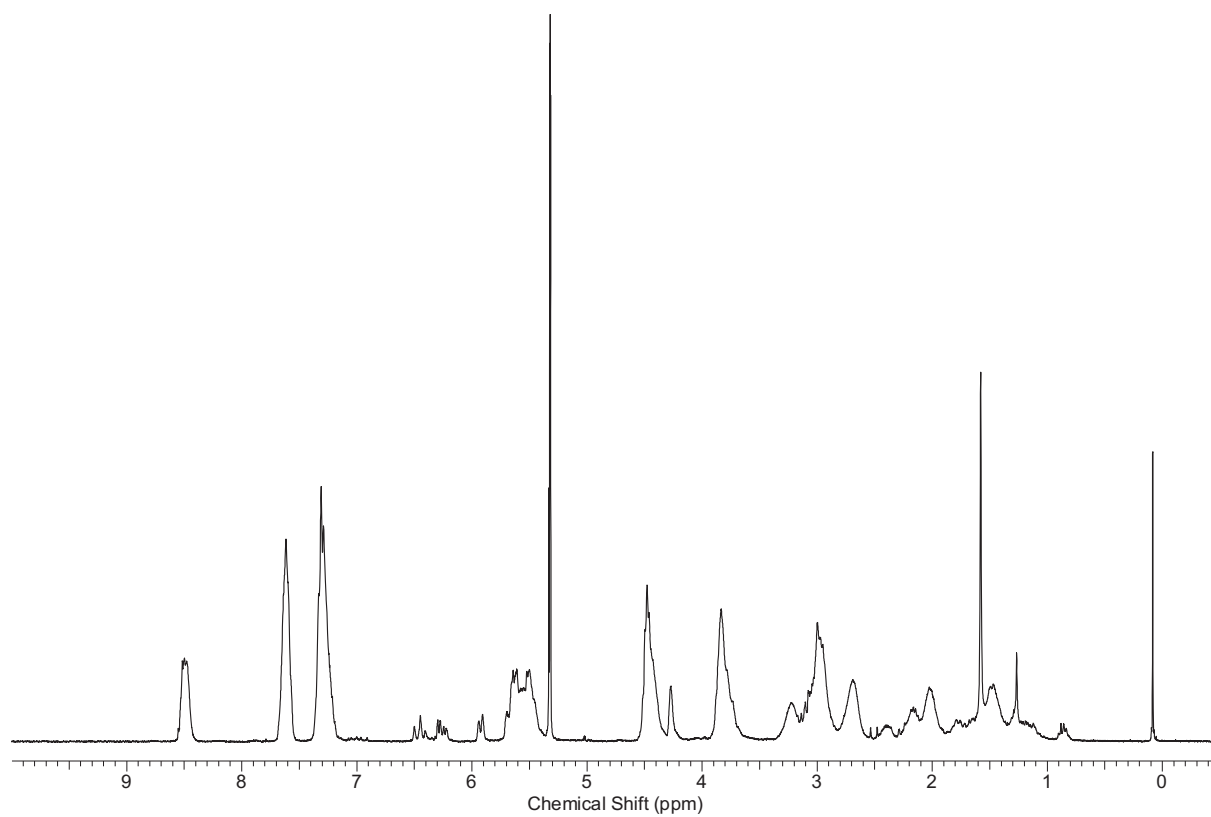


Figure 79: ^1H NMR spectrum (CDCl_3 , 300 MHz) of P21.

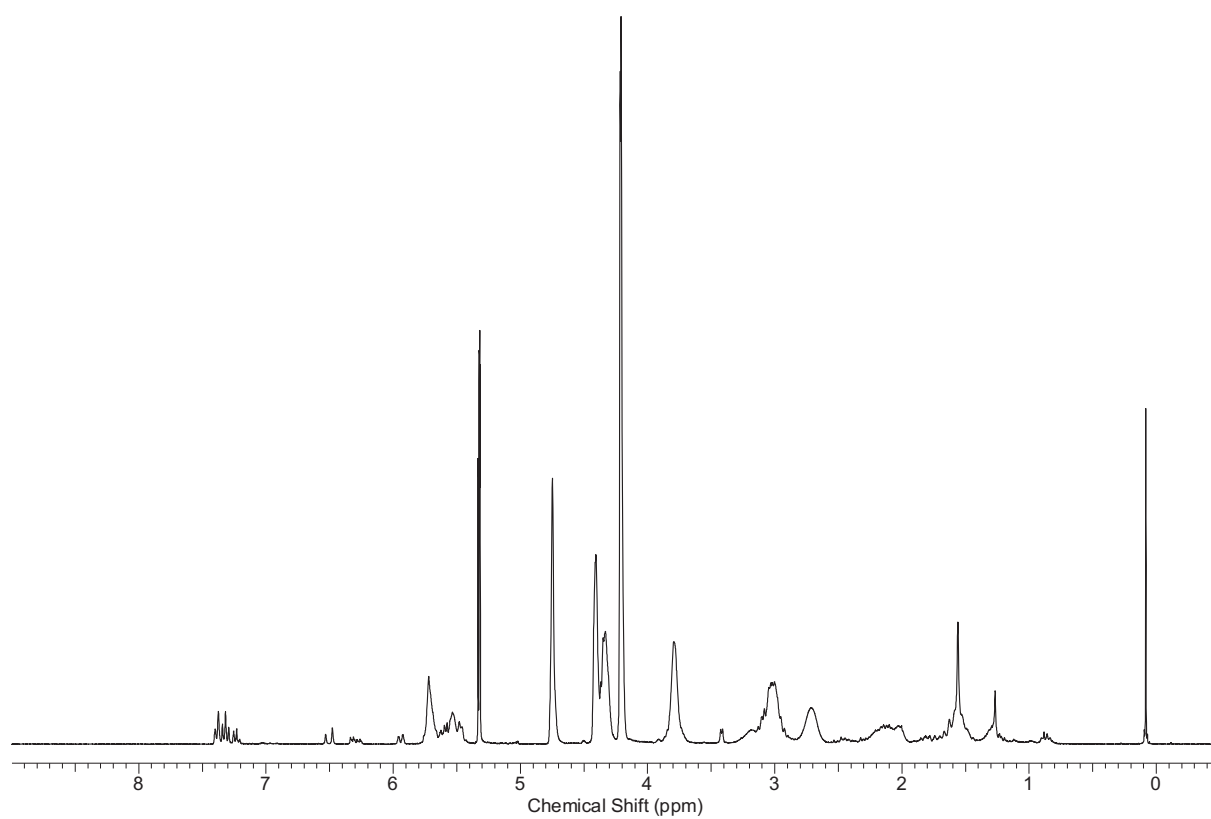


Figure 80: ^1H NMR spectrum (CDCl_3 , 300 MHz) of P22.

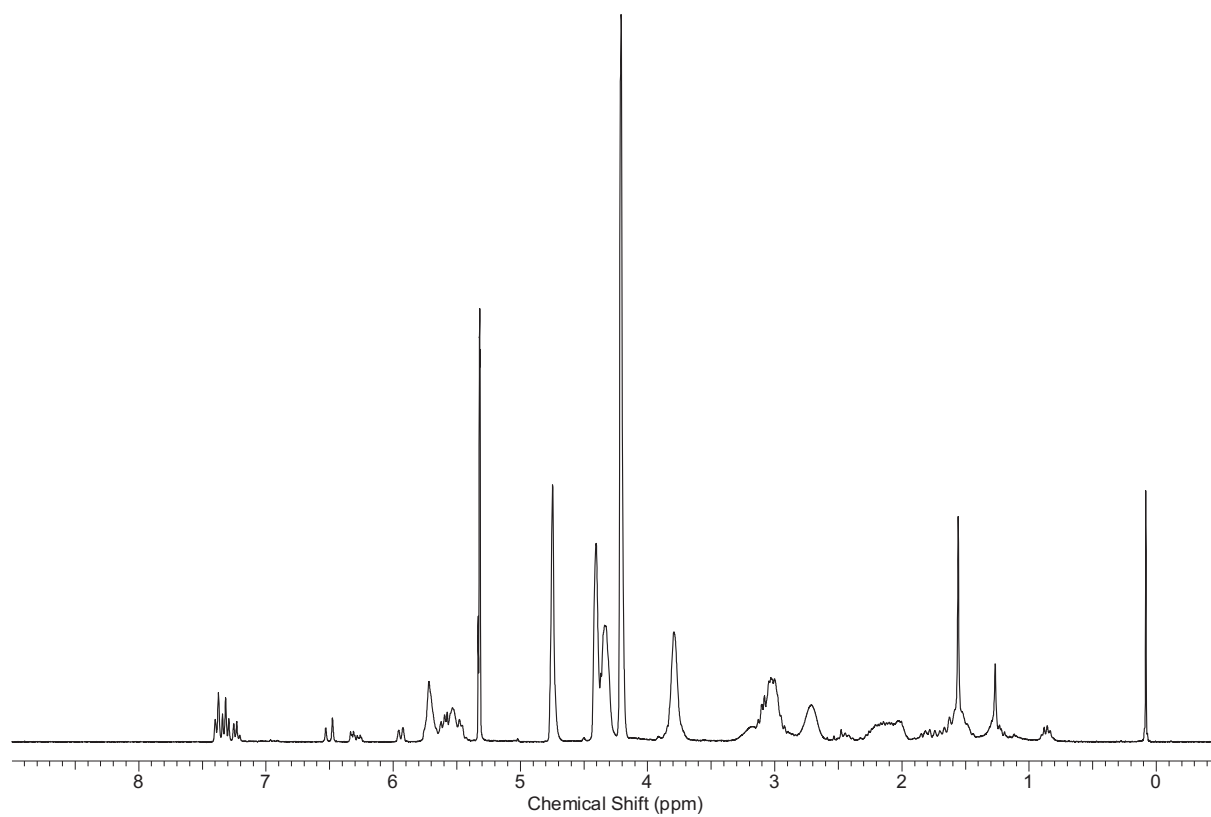


Figure 81: ^1H NMR spectrum (CDCl_3 , 300 MHz) of P23.

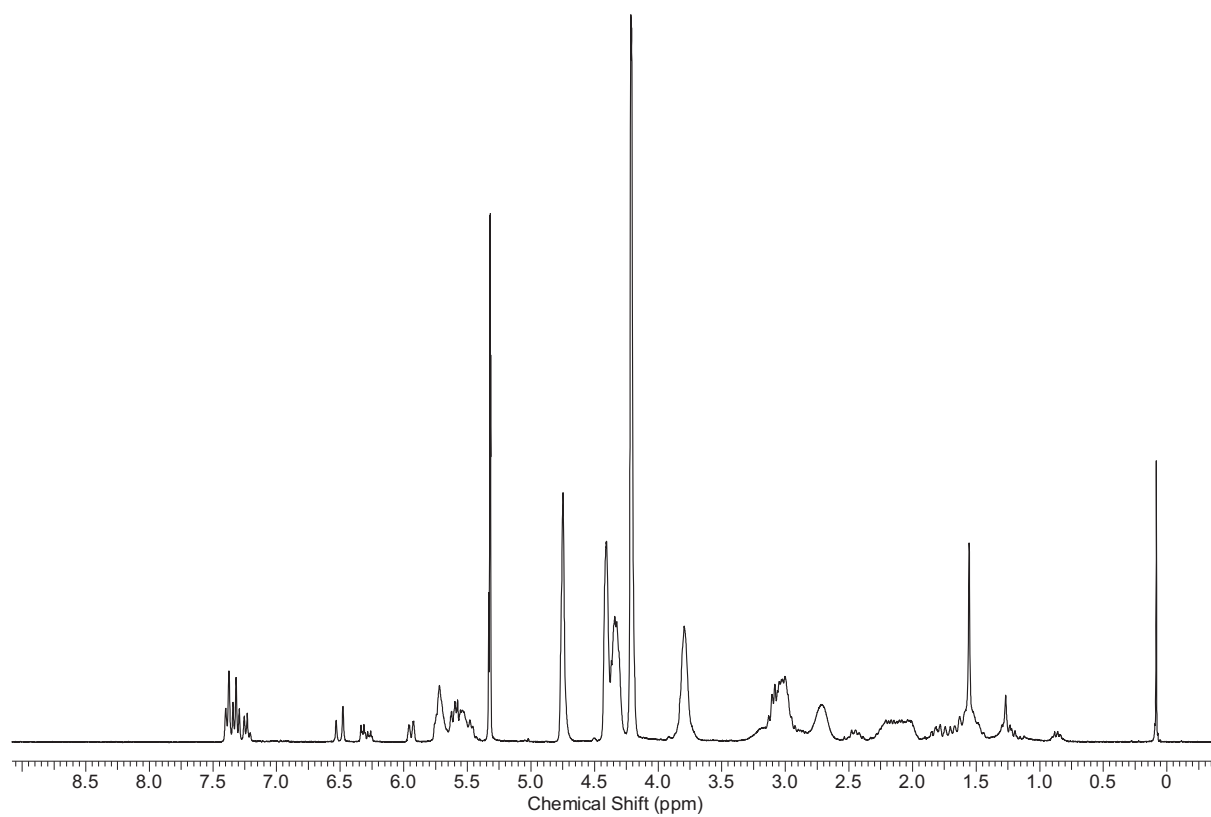


Figure 82: ^1H NMR spectrum (CDCl_3 , 300 MHz) of P24.



Figure 83: Photograph of P1 polymer.

References

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