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General information

Materials

Celite, DIBAL-H, ethyl vinyl ether, Grubbs 1st generation catalyst, Grubbs 3rd generation catalyst, Cinnamyl alcohol, Cinnamaldehyde, Cinnamic acid, Cinnamyl bromide, Cinnamyl chloride, chlorotriisopropylsilane, Imidazole, triethyl amine, 4-hydroxybenzaldehyde, 4′-Bromoacetophenone, Rhodamine B, 7-Methoxycoumarin-3-carboxylic Acid, Methyl crotonate, 1,3,5-trimethoxybenzene and Boc_2O were purchased from Sigma-Aldrich and used without further purification. Acetic anhydride methylamine in cyclohexane were purchased from Acros Organics and used without further purification. 4-Dimethylaminopyridine, Crotonic acid and *N,N′*-dicyclohexylcarbodiimide were purchased from TCI. 3-(4-hydroxyphenyl)acrylic acid, 3-(4-methoxyphenyl)acrylic acid, ethyl 3-(4-aminophenyl)acrylate, ethyl 3-(4-bromophenyl)acrylate and ethyl 3-(4-nitrophenyl)acrylate were purchased from Alfa-Aesar. Solvents of analytical grade were purchased from Honeywell, Acros Organics, Sigma Aldrich, Fischer Scientific and were used without further purification. Solvents of technical grade were purified by distillation. Deuterated solvents (CD_2Cl_2, $CDCl_3$) were purchased from Cambridge Isotope Laboratories. C_6D_6 and toluene-d_8 were purchased from Sigma-Aldrich. *Exo*-N-methyl norbornene imide (**MNI**)[1], *Exo*-N-hexyl norbornene imide (**HNI**)[1], *Exo*-N-cyclohexyl norbornene imide (**CHNI**) [1] and *Exo*-N-methyl oxanorbornene imide (**OMNI**)[2] were synthesized according to the described procedure. Exo-5-Norbornenecarboxylic acid was purchased from Sigma-Aldrich and reflux with ethanol under catalytic amount of con. H_2SO_4 to give *Exo*-Ethyl 5-norbornene-2-carboxylate (**ENC**). 5-Norbornene-2,3-dimethanol (mixture of endo- and exo-) was purchased from TCI and follow the method to synthesize **CTA 2** to give *Exo/Endo*-5-Norbornene-2,3-ditriisopropylsilylmethanol (**NDSM**). Coumarin 343 was purchased from Sigma-Aldrich.

Instrumentation

ESI-MS analysis for synthesized compounds was carried out on a Bruker 4.7T BioAPEX II. MALDI-ToF MS analysis of the polymers was carried out on a Bruker ultrafleXtreme™ using 2-(*2E*)-3-(4-tertbutylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix and silver trifluoroacetate or sodium trifluoroacetate as the added salt. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) 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) at a flow rate of 1mL/min for samples measured in THF and with a system consisting of a Duratec vacuum degasser, a JASCO PU-2087 plus pump, an Applied Biosystems UV absorbance detector 759A (set to 254 nm wavelength). Calibrations were carried out using Malvern Polycal™ UCS-PS polystyrene standards. UV absorbance were carried out using Perkin Elmer Lambda 900. NMR spectra were recorded on a Bruker Avance III 300 MHz NMR spectrometer (^{1}H NMR 300 MHz, ^{13}C-NMR 75 MHz) and Bruker Avance III 400 MHz NMR spectrometer (^{1}H NMR 400 MHz, ^{13}C-NMR 101 MHz). Fluorescence spectra were measured on an Endinburg FS 5 fluorimeter. UV-Vis absorption spectra were measured on a Perkin Elmer Lambda 35 spectrometer. All spectroscopic measurements were performed in spectroscopic grade $CHCl_3$ (Sigma Aldrich).

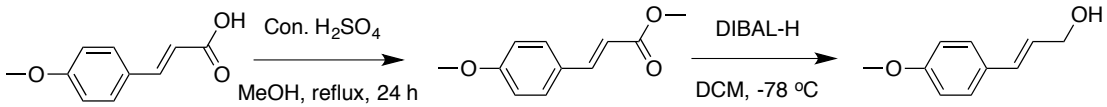
Table S1 Optimum reaction conditions[a,b]

Entry	CTA/Solvent	Name %	RT	40 °C	50 °C	55 °C	60 °C	65 °C	70 °C
	5eq	G1-OMe	0.93	2.38	12.24	22.91	29.07	35.75	17.51
1	**C_6D_6**	New:G1	1:99	3:97	12:88	26:74	49:51	78:22	85:15
	10eq	G1-OMe	0.89	3.14	11.09	23.78	32.68	41.04	29.06
2	**C_6D_6**	New:G1	1:99	3:97	15:85	38:62	67:33	90:10	93:7
	15eq	G1-OMe	0.81	4.15	20.73	30.24	38.05	34.07	14.15
3	**C_6D_6**	New:G1	1:99	5:95	28:72	59:41	81:19	91:9	92:8
	20eq	G1-OMe	2.38	4.44	24.76	34.37	49.95	52.80	44.56
4	**C_6D_6**	New:G1	2:98	5:95	29:71	69:31	93:7	96:4	96:4
	25eq	G1-OMe	2.91	3.91	25.52	42.64	57.57	46.91	27.65
5	**C_6D_6**	New:G1	3:97	4:96	32:68	76:24	95:5	96:4	>99:1
	30eq	G1-OMe	5.42	6.99	29.67	60.36	67.90	59.81	27.34
6	**C_6D_6**	New:G1	5:95	8:92	33:67	74:26	92:8	94:6	97:3
	35eq	G1-OMe	5.27	6.04	36.83	69.41	66.71	49.16	30.33
7[c]	**C_6D_6**		(2.49)	(6.75)	(37.12)	(65.72)	(67.14)	(51.87)	(31.08)
		New:G1	5:95	6:94	46:54	93:7	93:7	96:4	>99:1
			(3:97)	(7:93)	(40:60)	(90:10)	(96:4)	(96:4)	(>99:1)
	40eq	G1-OMe	1.77	9.97	43.31	68.83	66.67	51.18	32.87
8	**C_6D_6**	New:G1	2:98	10:90	44:56	92:8	95:5	92:8	>99:1
	45eq	G1-OMe	2.79	9.54	52.12	69.58	67.44	45.76	22.93
9	**C_6D_6**	New:G1	3:97	12:88	64:33	93:7	96:4	>99:1	>99:1
	35eq	G1-OMe	3.76	28.55	57.09	51.45	-	-	-
10	**$CDCl_3$**	New:G1	4:96	29:71	68:32	97:3	-	-	-
	35eq	Time	1h	2h	3h	4h	5h	7h	9h
11	**CD_2Cl_2**	G1-OMe	37.10	64.55	63.63	62.72	56.38	53.61	45.84
	RT	New:G1	57:43	75:25	87:13	95:5	97:3	99:1	>99:1

[a] All the reactions were carried out with **G1** (8.22 mg, 0.01mmol, 1.0 equiv) in 0.75 ml degassed solvent in NMR tube and heated in NMR machine 24 min from 40 °C to 55 °C. [b] 1,3,5-trimethoxybenzene was used as internal standard. [c] Brackets denote repeated experiments under identical conditions.

Synthesis of CTAs

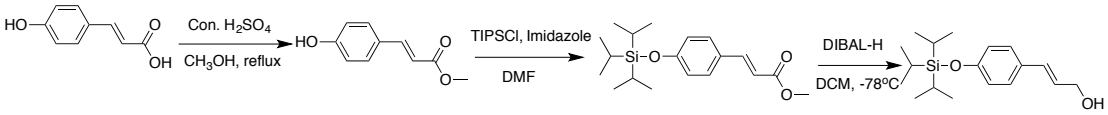
Synthesis of (E)-3-(4-methoxyphenyl)prop-2-en-1-ol (CTA1)



To a solution of (*E*)-3-(4-methoxyphenyl)acrylic acid (10.05g, 56mmol , 1.0 equiv) in 50ml MeOH was added concentrated H_2SO_4 (500mg, 2.8mmol, 5% equiv) and the mixture was stirred at reflux temperature for 24 h. The reaction mixture was concentrated under vacuum and the residue was dissolved in ethyl acetate. The organic layer was washed with water, saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. Filtration and concentration under vacuum gave 10.22g of methyl (*E*)-3-(4-methoxyphenyl)acrylate. The crude product was used for next step without purification. 10.22g of methyl (*E*)-3-(4-methoxyphenyl)acrylate was dissolved in 150 ml dry DCM and 140ml DIBAL-H (1M in cyclohexane, 140mmol, 2.5 equiv) was added over 40 min under -78^{o}C. The stirring was continued for 3 h. Water was slowly added to quench the reaction. The stirring was continued for 15 min then the reaction was allowed to warm up to 0^{o}C. $MgSO_4$ and NaCl were added and the reaction mixture was decanted. The decanted solution was washed with brine. The aqueous layer was then extracted with DCM. The organic layer was collected and concentrated under reduced pressure. The crude reaction mixture was purified by chromatography (hexane : EtOAc = 3 : 1) to afford (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol **CTA1** (7.54 g, 82%)as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.24 (d, *J* = 15.8 Hz, 1H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.33, 130.99, 129.42, 127.67, 126.25, 114.02, 63.96, 55.30. HR-MS (ESI) calcd. For $C_{10}H_{12}O_2Na^+$ $[M+Na]^+$: 187.0730; Found: 187.0731.

Synthesis of (E)-3-(4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol (CTA2)



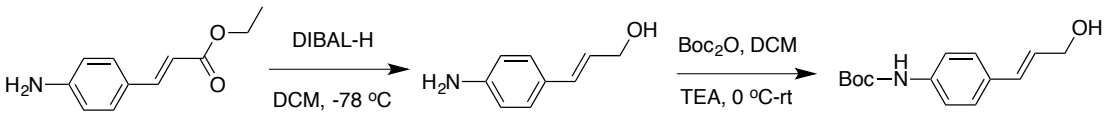
To a solution of (*E*)-3-(4-hydroxyphenyl)acrylic acid (8.2, 50mmol , 1.0 equiv) in 40ml MeOH was added concentrated H_2SO_4 (280mg, 2.5mmol, 5% equiv) and the mixture was stirred at reflux temperature for 24 h. The reaction mixture was concentrated under vacuum and the residue was dissolved in ethyl acetate. The organic layer was washed with water, saturated $NaHCO_3$ and brine, and dried over Na_2SO_4. Filtration and concentration under vacuum gave methyl (*E*)-3-(4-hydroxyphenyl)acrylate. The crude product was used for next step without purification.

(*E*)-3-(4-hydroxyphenyl)acrylate (50 mmol, 1.15 equiv) and tri-iso-propylchlorosilane (8.50 g, 44 mmol, 1 equiv) were added in sequence to a stirred solution of imidazole (6.01 g, 88 mmol, 2.00 equiv) in N,N-dimethylformamide (25 mL) at 24 °C. The homogenous mixture gradually became biphasic, and the biphasic mixture was vigorously stirred for 20 h at 24 °C. The product mixture was poured into a separatingfunnel that had been charged with 50% ether–hexanes and 1 N aqueous sulfuric acid solution. The layers that formed were separated and the organic layer was washed sequentially with 1 N aqueous sodium hydroxide solution and saturated aqueous sodium chloride solution. The washed organic layer was dried over sodium sulfate, and the dried solution was filtered. The filtrate was concentrated to afford the silylether as a light yellow liquid. The silyl ether was used without further purification. Methyl (*E*)-3-(4-((triisopropylsilyl)oxy)phenyl)acrylate (44mmol, 1.0 equiv) was dissolved in 100 ml dry DCM and 100ml DIBAL-H (1M in cyclohexane, 100mmol, 2.2 equiv) was added over 1h under -78^{o}C. The stirring was continued for 3 h. Water was slowly added to quench the reaction. The stirring was continued for 15 min then the reaction was allowed to warm up to 0^{o}C. $MgSO_4$ and NaCl were added and the reaction mixture was decanted. The decanted solution was washed with brine. The aqueous layer was then extracted with DCM. The organic layer was collected and concentrated under reduced pressure. The crude reaction mixture was purified by

chromatography (hexane : EtOAc = 5 : 1) to afford (*E*)-3-(4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol **CTA2** (8.5g, 63% for three steps)as colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.27 (m, 2H), 6.80-6.85 (m, 2H), 6.56 (dt, *J* = 15.8, 1.5 Hz, 1H), 6.23 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.29 (dd, *J* = 6.0, 1.5 Hz, 2H), 1.18-1.33 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.93, 131.16, 129.63, 127.59, 126.19, 120.03, 63.96, 17.91, 12.68. HR-MS (ESI) calcd. For $C_{18}H_{30}O_2SiNa^+$ $[M+Na]^+$: 329.1907; Found: 329.1902.

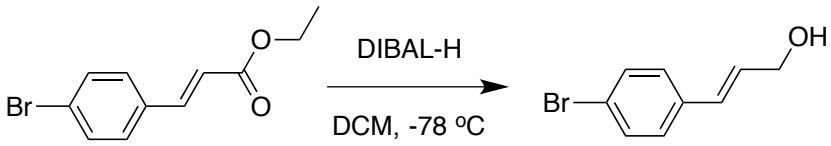
Synthesis of tert-butyl (E)-(4-(3-hydroxyprop-1-en-1-yl)phenyl)carbamate (CTA3)



1.02g(5.3mmol, 1.0 equiv) of ethyl (*E*)-3-(4-aminophenyl)acrylate was dissolved in 10 ml dry DCM and 13ml DIBAL-H (1M in cyclohexane, 14mmol, 2.5 equiv) was added over 40 min under -78°C. The stirring was continued for 3 h. Water was slowly added to quench the reaction. The stirring was continued for 15 min then the reaction was allowed to warm up to 0°C. $MgSO_4$ and NaCl were added and the reaction mixture was decanted. The decanted solution was washed with brine. The aqueous layer was then extracted with DCM. The organic layer was collected and concentrated under reduced pressure. The crude reaction mixture was purified by chromatography (hexane : EtOAc = 1 : 1) to afford (*E*)-3-(4-aminophenyl)prop-2-en-1-ol (0.7g, 89%)as pale yellow solid. (*E*)-3-(4-aminophenyl)prop-2-en-1-ol (0.7g, 4.7mmol)was dissolved in 20ml DCM. Then triethylamine (520mg, 5.1mmol, 1.1 equiv) and Boc_2O (1.11g, 5.1mmol, 1.1 equiv) were added at 0°C. After 1h, the reaction was warmed to room temperature and stirred overnight. The crude reaction mixture was purified by chromatography (hexane : EtOAc = 1 : 1) to afford *tert*-butyl (*E*)-(4-(3-hydroxyprop-1-en-1-yl)phenyl)carbamate **CTA3** (0.96g, 82%)as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 4H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.49 (s, 1H), 6.28 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.30 (t, *J* = 5.1 Hz, 2H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.60, 137.88, 131.56, 130.80, 127.13, 127.09, 118.50, 80.66, 63.86, 28.34. HR-MS (ESI) calcd. For $C_{14}H_{19}NO_3Na^+$ $[M+Na]^+$: 272.1257; Found: 272.1253.

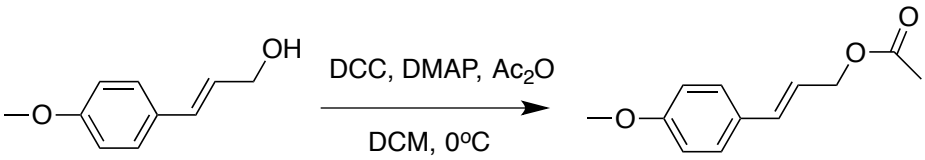
Synthesis of (E)-3-(4-bromophenyl)prop-2-en-1-ol (CTA4)



1.1g (4.3mmol, 1.0 equiv) of ethyl (*E*)-3-(4-bromophenyl)acrylate was dissolved in 10 ml dry DCM and 11ml DIBAL-H (1M in cyclohexane, 11mmol, 2.5 equiv) was added over 40 min under -78^{o}C. The stirring was continued for 3 h. Water was slowly added to quench the reaction. The stirring was continued for 15 min then the reaction was allowed to warm up to 0^{o}C. $MgSO_4$ and NaCl were added and the reaction mixture was decanted. The decanted solution was washed with brine. The aqueous layer was then extracted with DCM. The organic layer was collected and concentrated under reduced pressure. The crude reaction mixture was purified by chromatography (hexane : EtOAc = 2 : 1) to afford (*E*)-3-(4-bromophenyl)prop-2-en-1-ol **CTA4** (0.83g, 90%)as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.49 (m, 2H), 7.19-7.30 (m, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.32 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.64, 131.71, 129.79, 129.33, 127.98, 121.45, 63.52. GC-MS: 213.

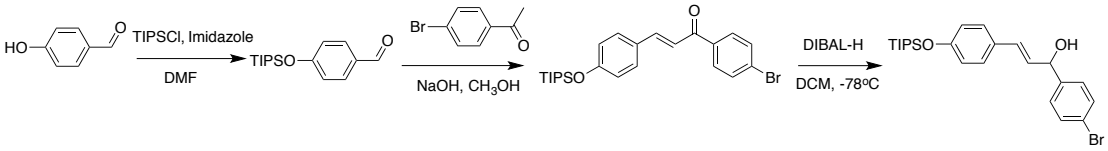
Synthesis of (E)-3-(4-methoxyphenyl)allyl acetate (CTA5)



DCC (1.13g, 5.5mmol, 1.1 equiv) which was dissolved in 1ml dry DCM was added to a solution of (*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol (0.82g, 5mmol, 1.0 equiv), DMAP (0.06g, 0.5mmol, 0.1 equiv) and Ac_2O (0.56g, 5.5mmol,1.1 equiv) in 8ml dry DCM under Ar at 0°C. Then the mixture was warmed to room temperature and stirred for 3h. Filtration and concentration under reduced pressure. The crude reaction mixture was purified by chromatography (hexane : EtOAc = 5 : 1) to afford (*E*)-3-(4-methoxyphenyl)allyl acetate **CTA5** (0.96g, 93%)as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.58 (s, 1H), 6.17 (s, 1H), 4.70 (d, *J* = 7.9 Hz, 2H), 3.81 (s, 2H), 2.09 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 170.88, 159.60, 134.04, 128.97, 127.86, 120.86, 114.02, 65.35, 55.29, 21.04. HR-MS (ESI) calcd. For $C_{12}H_{14}O_3Na^+$ $[M+Na]^+$: 229.0835; Found: 229.0836.

Synthesis of (E)-1-(4-bromophenyl)-3-(4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol (CTA6)



4-hydroxybenzaldehyde (50 mmol, 1.15 equiv) and tri-iso-propylchlorosilane (8.50 g, 44 mmol, 1 equiv) were added in sequence to a stirred solution of imidazole (6.01 g, 88 mmol, 2.00 equiv) in N,N-dimethylformamide (25 mL) at 24 °C. The homogenous mixture gradually became biphasic, and the biphasic mixture was vigorously stirred for 20 h at 24 °C. The product mixture was poured into a separating funnel that had been charged with 50% ether–hexanes and 1 N aqueous sulfuric acid solution The layers that formed were separated and the organic layer was washed sequentially with 1 N aqueous

sodium hydroxide solution and saturated aqueous sodium chloride solution. The washed organic layer was dried over sodium sulfate, and the dried solution was filtered. The filtrate was concentrated to afford the silylether as a light yellow liquid. The silyl ether was used without further purification.

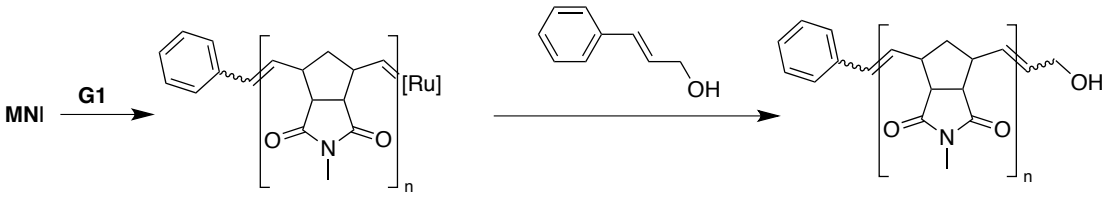
Sodium hydroxide (1.88 g, 47 mmol) and 4-bromoacetophenone (8.56g, 43 mmol) were dissolved in water (15 mL) and methanol (50 mL). 4-((triisopropylsilyl)oxy)benzaldehyde (11.92 g, 43 mmol) dissolved in methanol (20 mL) was added dropwise to the acetophenone solution. A slurry quickly formed, which was allowed to stir overnight. The slurry was filtered, washed with methanol water until the filtrate was neutral to pH paper, and dried at 100°C. for 12 hours. (*E*)-1-(4-bromophenyl)-3-(4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-one was obtained and used without further purification.

2.3 g (5.0 mmol, 1.0 equiv) of (*E*)-1-(4-bromophenyl)-3-(4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-one was dissolved in 10 ml dry DCM and 12.5ml DIBAL-H (1M in cyclohexane, 12.5mmol, 2.5 equiv) was added over 40 min under -78^{o}C. The stirring was continued for 3 h. Water was slowly added to quench the reaction. The stirring was continued for 15 min then the reaction was allowed to warm up to 0^{o}C. $MgSO_4$ and NaCl were added and the reaction mixture was decanted. The decanted solution was washed with brine. The aqueous layer was then extracted with DCM. The organic layer was collected and concentrated under reduced pressure. The crude reaction mixture was purified by chromatography (hexane : EtOAc = 5 : 1) to afford (*E*)-1-(4-bromophenyl)-3-(4-((triisopropylsilyl)oxy)phenyl)prop-2-en-1-ol **CTA 6** (2.05g, 90%)as colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.52 (m, 2H), 7.28-7.34 (m, 2H), 7.21-7.27 (m, 2H), 6.74-6.88 (m, 2H), 6.60 (dd, *J* = 15.8, 1.0 Hz, 1H), 6.18 (dd, *J* = 15.8, 6.9 Hz, 1H), 5.24-5.37 (m, 1H), 1.16-1.32 (m, 3H), 1.10 (d, *J* = 7.3 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.19, 141.94, 131.61, 131.02, 129.18, 128.77, 128.00, 127.80, 121.47, 120.06, 74.76, 17.90, 12.67. HR-MS (ESI) calcd. For $C_{24}H_{33}O_2SiBrNa^+$ $[M+Na]^+$: 483.1331; Found: 483.1331.

Polymerizations

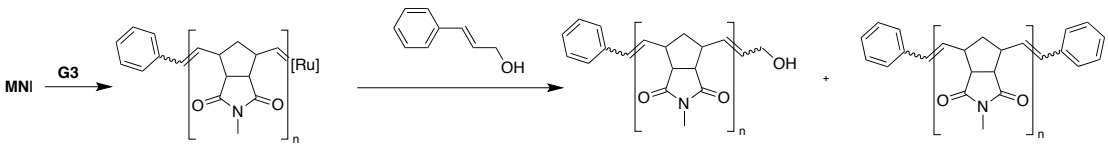
Polymer 1



G1 (1eq, 8.22 mg, 0.01mmol) was dissolved in CD_2Cl_2 (0.75 ml) in a NMR tube, then **MNI** (30eq, 53mg, 0.3mmol) was added quickly. After 1h, Cinnamyl alcohol (67mg, 0.5mmol, 50 equiv) was added. After another 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (51 mg, 94% yield, $Mn_{(GPC,\ Chloroform)}$ = 10000 g/mol, PDI: 1.35).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.30-7.40 (m), 7.21-7.25 (m), 6.53-6.63 (m), 6.29-6.41 (m), 5.72-5.80 (m), 5.54-5.56 (m), 4.29 (s), 4.11 (s), 2.91-3.23 (m), 2.70 (s), 2.03-2.17 (m), 1.53-1.70(m). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.27, 178.23, 136.87, 133.27, 132.05, 131.90, 131.87, 131.80, 130.37, 129.04, 128.53, 127.53, 126.33, 126.16, 63.39, 52.53, 51.30, 51.21, 51.12, 51.05, 46.17, 45.97, 45.80, 45.65, 42.94, 42.43, 42.36, 41.04, 24.52, 24.46. MALDI-ToF MS calcd. For $C_{289}H_{318}N_{28}O_{57}Ag^+$ [M+Ag^+]: 5199.190; Found: 5199.495

Polymer 2

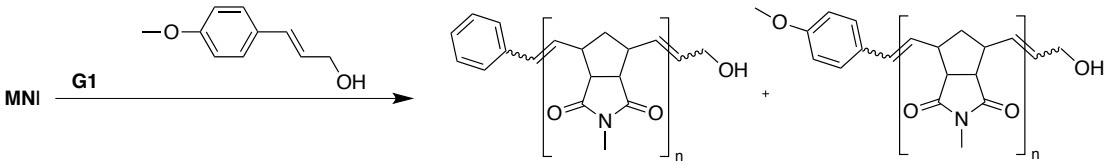


G3 (1eq, 8.84 mg, 0.01mmol) was dissolved in CD_2Cl_2 (0.75 ml) in a NMR tube. Then **MNI** (30eq, 53mg, 0.3mmol) was added quickly. After 30min, Cinnamyl alcohol (67mg, 0.5mmol, 50 equiv) was added. After another 1h, 0.5 ml ethyl vinyl ether was

added, then the reaction mixture was poured into 8 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (50 mg, 92% yield, $Mn_{(GPC,\ Chloroform)}$ = 4600 g/mol, PDI: 1.29).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.23-7.41 (m), 6.51-6.63 (m), 6.27-6.41 (m), 5.67-5.78 (m), 5.48-5.54 (m), 4.28-4.30 (m), 4.12 (s), 2.90-3.21 (m), 2.71 (s), 2.04-2.23 (m), 1.43-1.65 (m). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.21, 178.12, 133.25, 132.04, 131.89, 131.71, 128.59, 128.53, 128.26, 126.34, 126.16, 52.54, 51.85, 51.19, 51.05, 46.20, 46.07, 45.98, 45.79, 45.64, 43.12, 42.94, 42.35, 41.50, 41.04, 40.95, 24.56, 24.52, 24.47. MALDI-ToF MS calcd. For $C_{189}H_{208}N_{18}O_{37}Ag^+$ [M+Ag^+]: 3428.400; Found: 3428.435. MALDI-ToF MS calcd. For $C_{194}H_{210}N_{18}O_{36}Ag^+$ [M+Ag^+]: 3474.421; Found: 3474.434.

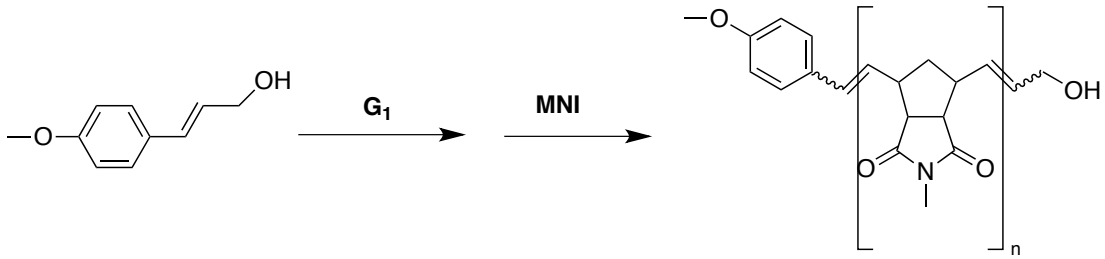
Polymer 3



G1 (1 eq, 8.22 mg, 0.01 mmol) **CTA 1**(33mg, 0.20mmol, 20 equiv) and **MNI** (25 eq, 45 mg, 0.25 mmol) were dissolved in CD_2Cl_2 (0.75 ml) in a NMR tube. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (41mg, 89% yield, $Mn_{(GPC,\ Chloroform)}$ = 5100 g/mol, PDI: 1.99).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.54 (m), 7.20-7.39 (m), 6.79-6.87 (m), 6.45-6.59 (m), 6.11-6.33 (m), 5.52-5.83 (m), 4.29 (s), 4.16 (s), 3.77-3.82 (m), 2.71-3.27 (m), 2.06-2.19 (m), 1.55-1.70 (m). ^{13}C NMR (400 MHz, $CDCl_3$) δ 178.32, 132.07, 131.87, 131.81, 128.55, 127.70, 127.45, 126.30, 113.97, 55.30, 52.69, 51.13, 51.02, 45.82, 45.61, 42.11, 41.92, 40.87, 24.83, 24.76. MALDI-ToF MS calcd. For $C_{109}H_{120}N_{10}O_{21}Ag^+$ [M+Ag^+]: 2011.768; Found: 2011.924. MALDI-ToF MS calcd. For $C_{110}H_{122}N_{10}O_{22}Ag^+$ [M+Ag^+]: 2041.779; Found: 2041.972.

Polymer 4



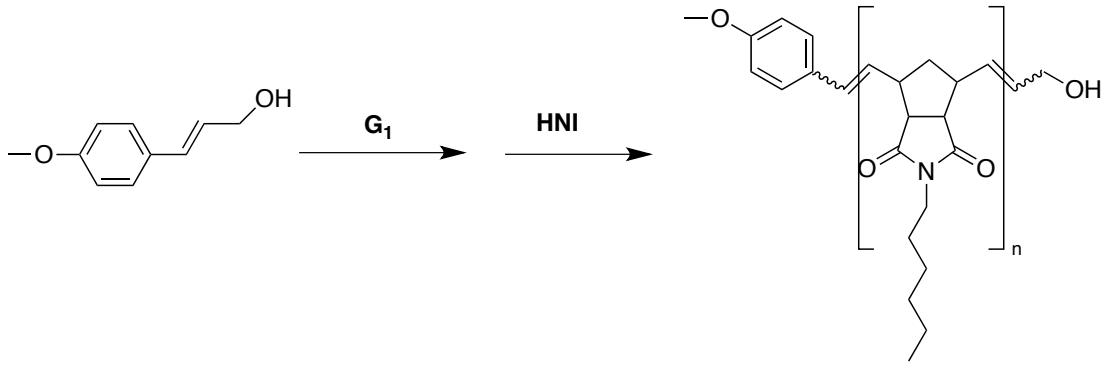
Procedure A: G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 1** (57.5mg, 0.35mmol, 35 equiv) were dissolved in benzene-d_6 (0.75ml) in a NMR tube. Then the NMR tube was heated in the NMR machine from 40°C to 55°C continuously. After heating, the NMR tube was cooled down to room temperature, **MNI** (50 equiv, 89mg, 0.50mmol) was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (83 mg, 92% yield, $Mn_{(GPC,\ Chloroform)}$ = 4000 g/mol, PDI: 2.42).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.33 (m), 6.83-6.88 (m), 6.46-6.58 (m), 6.08-6.27 (m), 5.52-5.83 (m), 4.28-4.31 (m), 4.16 (s), 3.80-3.81 (m), 2.71-3.27 (m), 2.06-2.19 (m), 1.55-1.72(m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.32, 132.08, 131.86, 131.82, 127.66, 127.45, 126.28, 114.02, 55.30, 52.69, 51.13, 51.02, 45.82, 45.62, 42.12, 41.93,41.88, 40.87, 24.83, 24.76. MALDI-ToF MS calcd. For $C_{130}H_{144}N_{12}O_{26}Ag^+$ [M+Ag^+]: 2395.937; Found: 2396.123.

Procedure B: G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA1** (57.5mg, 0.35mmol, 35 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 5h, then **MNI** (50 equiv, 89mg, 0.50mmol) was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (86 mg, 95% yield, $Mn_{(GPC,\ Chloroform)}$ = 4900 g/mol, PDI: 2.34).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.33 (m), 6.83-6.88 (m), 6.46-6.58 (m), 6.18-6.27 (m), 5.70-5.83 (m), 5.46-5.57 (m), 5.31 (s), 4.28-4.31 (m), 4.16 (s), 3.80-3.81 (m), 2.71-3.27 (m), 2.06-2.19 (m), 1.52-1.72 (m). ^{13}C NMR (400 MHz, $CDCl_3$) δ 178.31, 133.49, 132.08, 131.86, 131.81, 131.78, 127.66, 127.45, 114.02, 113.97, 77.34, 55.30, 52.69, 51.13, 51.02, 45.82, 45.61, 42.12, 41.92, 40.87, 24.83, 24.76. MALDI-ToF MS calcd. For $C_{110}H_{122}N_{10}O_{22}Ag^+$ [M+Ag^+]: 2041.779; Found: 2041.749.

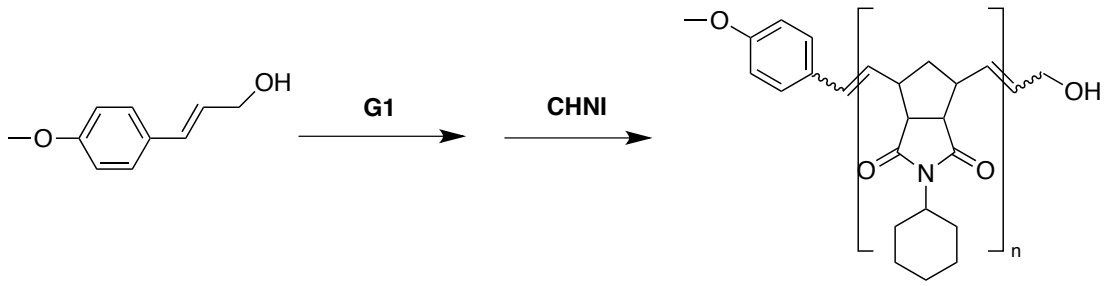
Polymer 5



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 1** (57.5mg, 0.35mmol, 35 equiv) were dissolved in benzene-d_6 (0.75ml) in a NMR tube. Then the NMR tube was heated in the NMR machine from 40^{o}C to 55^{o}C continuously. After heating, the NMR tube was cooled down to room temperature, **HNI** (25 equiv, 62mg, 0.5mmol) was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (57mg, 90% yield, $Mn_{(GPC,\ Chloroform)}$ = 4100g/mol, PDI: 1.73).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.33 (d, J = 9.6 Hz), 6.85 (d, J = 8.7 Hz), 6.44-6.58 (m), 6.07-6.27 (m), 5.33-5.81 (m), 4.25 (s), 4.12 (s), 3.75 (s), 3.79 (s), 3.40-3.43 (m), 2.98-3.20 (m), 2.68 (s), 2.04-2.21 (m), 1.52-1.70 (m), 1.29 (s), 0.87-0.90 (m).^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.16, 177.99, 159.20, 133.35, 132.04, 131.88, 131.85, 130.24, 129.71, 128.61, 127.53, 126.69, 113.90, 92.75, 63.60, 55.21, 51.19, 50.99, 50.92, 45.99, 45.88, 42.44, 41.14, 38.53, 38.40, 31.38, 31.32, 27.59, 26.54, 26.45, 22.49, 13.76. MALDI-ToF MS calcd. For $C_{145}H_{201}N_9O_{20}Ag^+$ [M+Ag^+]: 2495.404; Found: 2495.506.

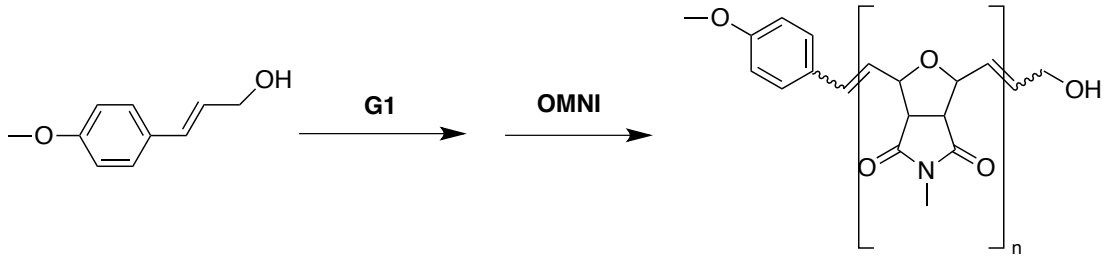
Polymer 6



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 1** (57.5mg, 0.35mmol, 35 equiv) were dissolved in benzene-d_6 (0.75ml) in a NMR tube. Then the NMR tube was heated in the NMR machine from 40°C to 55°C continuously. After heating, the NMR tube was cooled down to room temperature, **CHNI** (25 equiv, 61mg, 0.25mmol) was added. After 1h, the 0.5 ml ethyl vinyl ether was added, then reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (55 mg, 88% yield, $Mn_{(GPC,\ Chloroform)}$ = 2700 g/mol, PDI: 1.93).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.32-7.34 (m), 6.84-6.86 (m), 6.45-6.56 (m), 6.07-6.27 (m), 5.46-5.79 (m), 4.24-4.26 (m), 4.11 (s), 3.75-3.90 (m), 2.64-3.17 (m), 1.55-2.12 (m), 1.15-1.36 (m). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.31, 178.08, 159.17, 133.39, 132.06, 131.96, 131.86, 130.18, 129.81, 129.53, 128.78, 127.52, 127.29, 126.75, 113.90, 63.56, 55.21, 52.21, 51.22, 50.90, 50.71, 50.63, 46.81, 46.39, 46.10, 46.02, 42.42, 42.14, 41.21, 28.75, 25.90, 25.17. MALDI-ToF MS calcd. For $C_{130}H_{164}N_8O_{18}Ag^+$ [M+Ag^+]: 2232.122; Found: 2232.230.

Polymer 7

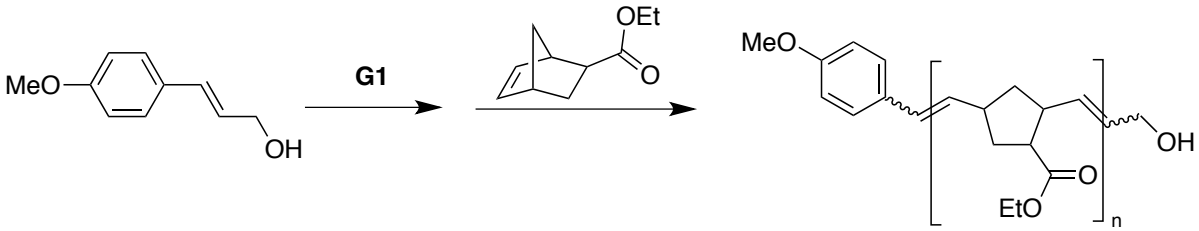


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 1** (57.5mg, 0.35mmol, 35 equiv) were dissolved in benzene-d_6 (0.75ml) in a NMR tube. Then the NMR tube was heated in

the NMR machine from 40°C to 55°C continuously. After heating, the NMR tube was cooled down to room temperature, **OMNI** (25 equiv, 45 mg, 0.25mmol) was added. After 1h, the 0.5 ml ethyl vinyl ether was added, then reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (43 mg, 92% yield, $Mn_{(GPC,\ Chloroform)}$ = 2400 g/mol, PDI: 1.73).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.31-7.39 (m), 6.84-6.88 (m). 6.52-6.70 (m), 6.20-6.27 (m), 5.77-6.10 (m), 4.94 (s), 4.49 (s), 4.16-4.26 (m), 3.75-3.85 (m), 3.35 (s), 2.95-2.97 (m), 1.61 (s). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 175.70, 159.34, 131.09, 130.23, 129.51, 127.99, 127.53, 126.70, 114.47, 113.92, 92.75, 80.86, 80.77, 77.33, 63.59, 55.25, 55.21, 52.47, 22.84. MALDI-ToF MS calcd. For $C_{91}H_{93}N_9O_{29}Ag^+$ [M+Ag^+]: 1882.513; Found: 1882.654.

Polymer 8

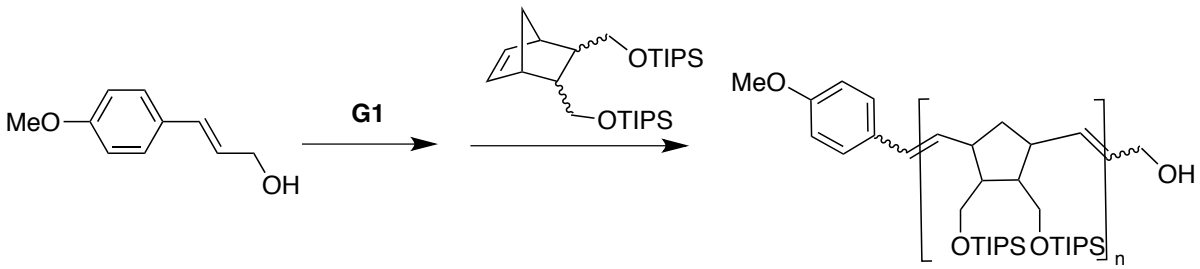


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 1** (328mg, 2.0mmol, 200 equiv) were dissolved in degassed CH_2Cl_2 (2.0ml) in a flask under Ar. Then ***Exo*-Ethyl 5-norbornene-2-carboxylate** (50 equiv, 83mg, 0.5mmol) in 1 ml degassed CH_2Cl_2 was added. After 1h, the reaction mixture was poured into 50 ml cool hexane to precipitate the formed polymer, then washed with methanol. The mixture was filtered to afford the respective polymer (75mg, 90% yield, $Mn_{(GPC,\ Chloroform)}$ = 6600 g/mol, PDI: 1.25).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.31 (m), 6.79-6.84 (m), 6.53 (d, J = 15.9 Hz), 6.17-6.27 (m), 5.93-6.01 (m), 5.16-5.38 (m), 4.06-4.10 (m), 3.78 (d, J = 4.8 Hz), 3.44 (s), 2.99 (d, J = 48.5 Hz), 2.46-2.68 (m), 1.93-2.07 (m), 1.56-1.64 (m), 1.21 (t, J = 7.1 Hz), 0.95-0.80 (m).^{13}C NMR (101 MHz, $CDCl_3$) δ 133.71, 132.62, 132.10, 131.09, 127.62,

113.99, 63.78, 60.27, 55.27, 50.69, 49.56, 49.43, 47.66, 47.32, 41.79, 40.96, 36.12, 31.56, 22.62, 14.33. MALDI-ToF MS calcd. For $C_{340}H_{474}O_{68}Ag^+$ [M+Ag^+]: 5752.27; Found: 5752.30.

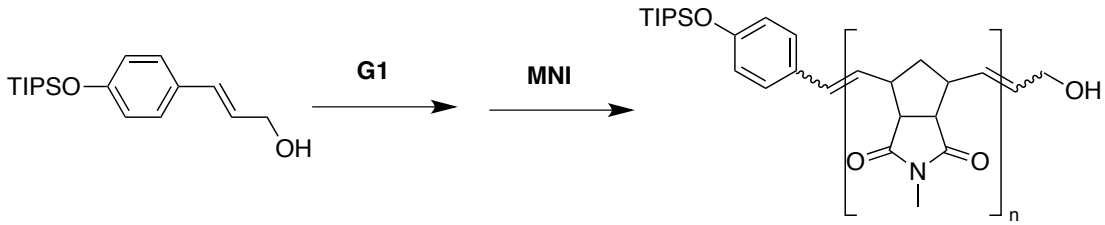
Polymer 9



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 1** (328mg, 2.0mmol, 200 equiv) were dissolved in degassed CH_2Cl_2 (2.0ml) in a flask under Ar. Then ***Exo/Endo*-5-Norbornene-2,3-di triisopropylsilylmethanol** (50 equiv, 233mg, 0.5mmol) in 2 ml degassed CH_2Cl_2 was added. After 1h, the reaction mixture was poured into 50 ml cool hexane to precipitate the formed polymer, then washed with methanol. The mixture was filtered to afford the respective polymer (222mg, 95% yield, $Mn_{(GPC,\ Chloroform)}$ = 4400 g/mol, PDI: 1.90).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.34 (m), 6.80 -6.83 (m), 6.19-6.35 (m), 5.87-5.93 (m), 5.30-5.63 (m), 4.07 (s), 3.76-3.80 (m), 2.98 (s), 2.64 (s), 2.19 (s), 1.89 (s), 1.54 (s), 1.05 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.34, 158.43, 132.55, 132.03, 131.00, 129.42, 127.67, 127.03, 126.25, 114.02, 113.71, 63.96, 61.83, 55.29, 48.84, 48.73, 48.22, 44.31, 44.08, 38.77, 18.18, 12.08. MALDI-ToF MS calcd. For $C_{145}H_{282}O_{12}Si_{10}Ag^+$ [M+Ag^+]: 2602.82; Found: 2603.11.

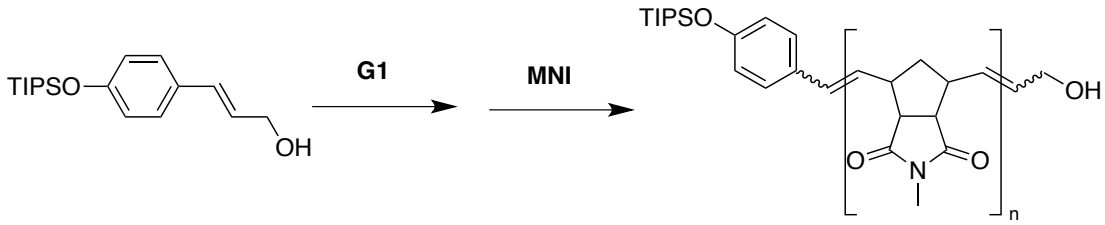
Polymer 10



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (108mg, 0.35mmol, 35 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 5h, then **MNI** (10 equiv, 18mg, 0.10mmol) was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (15mg, 70% yield, $Mn_{(GPC,\ Cholorform)}$ = 3300 g/mol, PDI: 1.21).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.33 (m), 6.81-6.84 (m), 6.46-6.56 (m), 6.12-6.26 (m), 5.50-5.83 (m), 4.17-4.30 (m), 2.72-3.29 (m), 2.08-2.19 (m), 1.57-1.70 (m), 1.09-1.29 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.32, 132.08, 131.87, 127.59, 120.02, 90.65, 63.99, 51.13, 51.03, 45.82, 45.62, 24.76, 17.91, 12.67. MALDI-ToF MS calcd. For $C_{158}H_{184}N_{14}O_{30}SiAg^+$ [M+Ag^+]: 2892.212; Found: 2892.083.

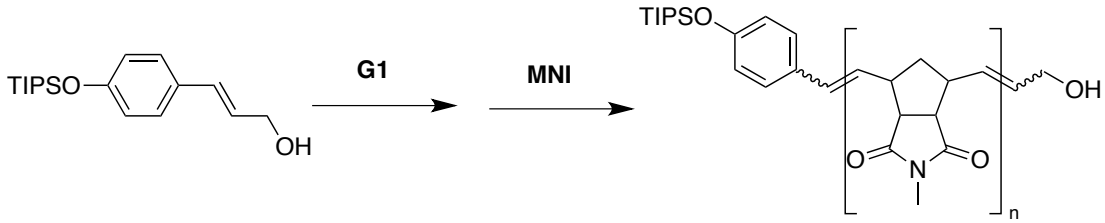
Polymer 11



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (108mg, 0.35mmol, 35 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 5h, then **MNI** (25 equiv, 45mg, 0.25mmol) was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (40mg, 83% yield, $Mn_{(GPC,\ THF)}$ = 3500 g/mol, PDI: 1.78).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.30 (m), 6.80-6.82 (m), 6.44-6.56 (m), 6.12-6.26 (m), 5.48-5.83 (m), 4.16-4.30 (m), 2.93-3.27 (m), 2.71 (s), 2.06-2.17 (m), 1.55-1.70 (m), 1.04-1.28 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.32, 132.07, 131.86, 131.81, 127.39, 119.98, 52.68, 51.02, 45.82, 45.61, 42.12, 40.86, 24.76, 17.92, 12.67. MALDI-ToF MS calcd. For $C_{148}H_{173}N_{13}O_{28}SiAg^{+}$ [M+Ag^{+}]: 2715.133; Found: 2715.181.

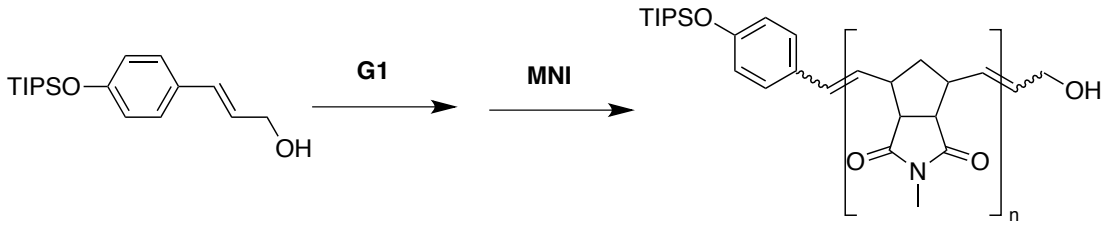
Polymer 12



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (108mg, 0.35mmol, 35 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 5h, then **MNI** (35 equiv, 62mg, 0.35mmol) was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (52 mg, 80% yield, $Mn_{(GPC,\ Chloroform)}$ = 5300 g/mol, PDI: 1.94).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26-7.28 (m), 6.82-6.85 (m), 6.44-6.55 (m), 6.06-6.26 (m), 5.75-5.80 (m), 5.47-5.58 (m), 4.12-4.26 (m), 2.71-3.19 (m), 2.05-2.16 (m), 1.53-1.70 (m), 1.21-1.30 (m), 1.10 (d, J = 7.4 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.25,178.22, 133.28, 132.05, 131.87, 130.10, 127.47, 127.25, 120.02, 52.54, 51.31, 51.12, 51.06, 45.80, 45.64, 42.41, 42.33, 41.04, 24.52, 24.46, 17.66, 12.65. MALDI-ToF MS calcd. For $C_{148}H_{173}N_{13}O_{28}SiAg^{+}$ [M+Ag^{+}]: 2715.133; Found: 2715.135.

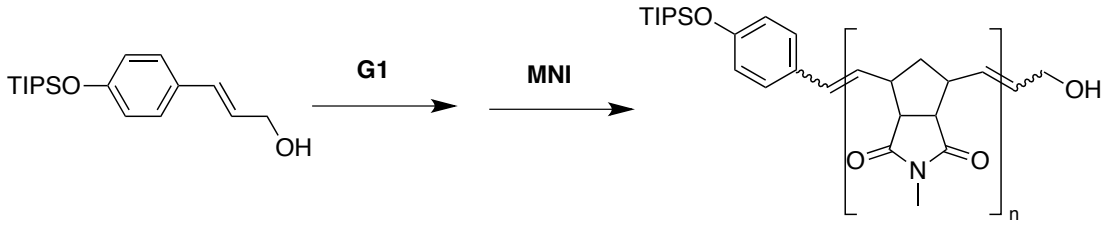
Polymer 13



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (215mg, 0.7mmol, 70 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 2h, then **MNI** (70 equiv, 124 mg, 0.7mmol) was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (108 mg, 85% yield, $Mn_{(GPC,\ Chloroform)}$ = 5300 g/mol, PDI: 2.14).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.31 (m), 6.80-6.82 (m) 6.45-6.56 (m), 6.12-6.26 (m), 5.46-5.83 (m), 4.16-4.30 (m), 2.71-3.27 (m), 2.09-2.19 (m), 1.455-1.71 (m), 1.19-1.29 (m), 1.09 (d, J = 7.3 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.31, 133.50, 132.08, 131.86, 131.81, 127.38, 119.98, 52.68, 51.13, 51.02, 45.98, 45.82, 45.61, 42.11, 41.93, 40.86, 24.83, 24.76, 17.92, 12.67. MALDI-ToF MS calcd. For $C_{128}H_{151}N_{11}O_{24}SiAg^+$ [M+Ag^+]: 2360.975; Found: 2360.976.

Polymer 14

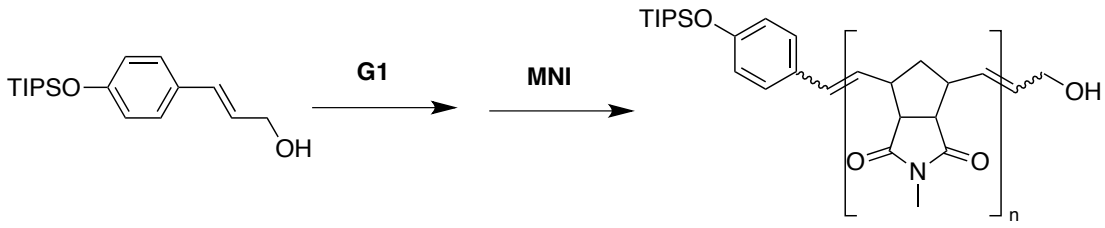


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (307mg, 1.0mmol, 100 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 1h, then **MNI** (100 equiv, 177 mg, 1.0mmol) was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the

respective polymer (160 mg, 89% yield, $Mn_{(GPC,\ Chloroform)}$ = 5600 g/mol, PDI: 2.43).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26-7.28 (m), 6.82-6.84 (m) 6.45-6.55 (m), 6.11-6.26 (m), 5.48-5.81 (m), 4.11-4.26 (m), 2.70-3.17 (m), 2.05-2.16 (m), 1.51-1.71 (m), 1.21-1.30 (m), 1.10 (d, *J* = 7.3 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.25, 178.22, 178.13, 133.27, 132.06, 131.87, 127.25, 120.02, 52.54, 51.31, 51.19, 50.12, 51.05, 46.18, 45.97, 45.80, 45.64, 43.15, 42.94, 42.42, 42.34 41.04, 24.52, 24.46, 17.65, 12.65. MALDI-ToF MS calcd. For $C_{128}H_{151}N_{11}O_{24}SiAg^+$ [M+Ag^+]: 2360.975; Found: 2361.970.

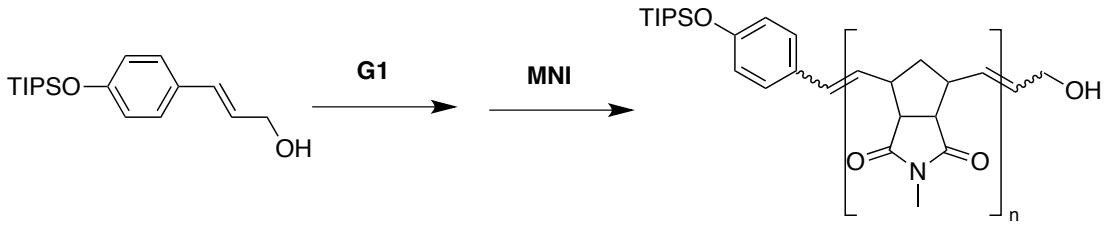
Polymer 15



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (108mg, 0.35mmol, 35 equiv) were dissolved in degassed CH_2Cl_2 (0.75ml) in a flask under Ar. Keep stirring at room temperature for 5h, **MNI** (175 equiv, 310 mg, 1.75mmol) in 2.8 ml degassed CH_2Cl_2 was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 30 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (290 mg, 93% yield, $Mn_{(GPC,\ Chloroform)}$ = 10300 g/mol, PDI: 3.07).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.30-7.32 (m), 6.86-6.89 (m), 6.49-6.59 (m), 6.17-6.29 (m), 5.52-5.88 (m), 4.16-4.30 (m), 2.74-3.24 (m), 2.09-2.20 (m), 1.57-1.72 (m), 1.25-1.34 (m), 1.14 (d, *J* = 7.3 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.25, 178.22, 178.13, 133.27, 132.06, 131.87, 127.25, 120.02, 52.54, 51.31, 51.19, 51.12, 51.05, 46.18, 45.97, 45.80, 45.64, 43.15, 42.94, 42.42, 42.34, 41.04, 24.52, 24.46, 17.65, 12.65. MALDI-ToF MS calcd. For $C_{178}H_{206}N_{16}O_{34}SiAg^+$ [M+Ag^+]: 3246.370; Found: 3246.369.

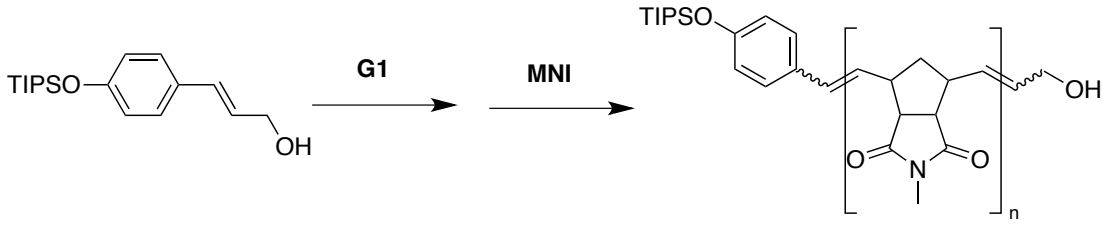
Polymer 16



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (108mg, 0.35mmol, 35 equiv) were dissolved in degassed CH_2Cl_2 (0.75ml) in a flask under Ar. Keep stirring at room temperature for 5h, **MNI** (350 equiv, 620 mg, 3.5mmol) in 6.5 ml degassed CH_2Cl_2 was added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 70 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (610 mg, 98% yield, $Mn_{(GPC,\ Chloroform)}$ = 28500 g/mol, PDI: 2.24).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26-7.28 (m), 6.82-6.85 (m) 6.45-6.55 (m), 6.13-6.26 (m), 4.11-4.26 (m), 2.70-3.20 (m), 2.03-2.17 (m), 1.54-1.71 (m), 1.21-1.30 (m), 1.10 (d, J = 7.3 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.21, 178.13, 133.38, 133.27, 132.06, 131.87, 131.14, 52.54, 51.13, 51.05, 45.96, 45.80, 45.64, 42.43, 42.35, 41.04, 24.52, 24.46, 17.65, 12.65. MALDI-ToF MS calcd. For $C_{178}H_{206}N_{16}O_{34}SiAg^+$ [M+Ag^+]: 3246.370; Found: 3246.477.

Polymer 17

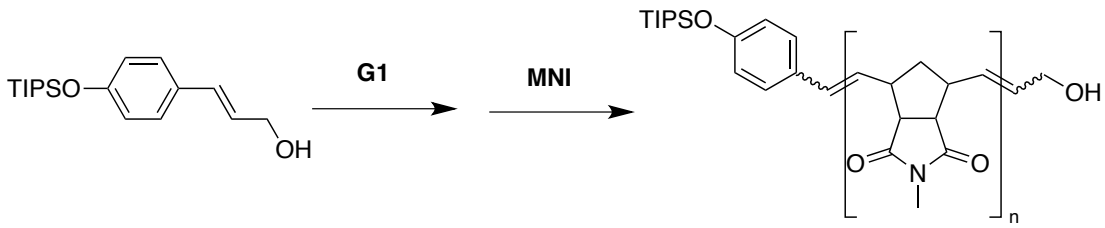


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (108mg, 0.35mmol, 35 equiv) were dissolved in degassed CH_2Cl_2 (0.75ml) in a flask under Ar. Keep stirring at room temperature for 5h, **MNI** (700 equiv, 1.24 g, 7.0mmol) in 14 ml degassed CH_2Cl_2 was

added. After 1h, 0.5 ml ethyl vinyl ether was added, then the reaction mixture was poured into 140 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (1.2g, 97% yield, $Mn_{(GPC,\ Chloroform)}$ = 40700 g/mol, PDI: 2.72).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.26-7.28 (m), 6.55-6.84 (m), 6.45-6.55 (m), 6.13-6.26 (m), 5.48-5.80 (m), 4.12-4.26 (m), 2.70-3.43 (m), 2.05-2.16 (m), 1.53-1.70 (m), 1.21-1.30 (m), 1.10 (d, *J* = 7.3 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.26, 178.22, 178.13, 133.27, 133.23, 132.06, 131.87, 131.79, 127.25, 52.54, 51.31, 51.20, 51.12, 51.05, 46.18, 45.96, 45.80, 45.64, 43.15, 42.94, 42.43, 42.35, 41.04, 24.52, 24.46, 17.65, 12.65. MALDI-ToF MS calcd. For $C_{178}H_{206}N_{16}O_{34}SiAg^{+}$ [M+Ag^{+}]: 3246.370; Found: 3246.515.

Polymer 18

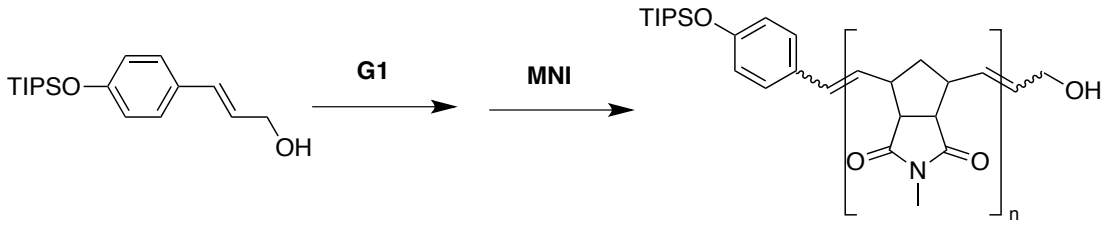


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (613mg, 2.0mmol, 200 equiv) were dissolved in degassed CH_2Cl_2 (1.0ml) in a flask under Ar. Then **MNI** (200 equiv, 354 mg, 2.0mmol) in 4 ml degassed CH_2Cl_2 was added. After 1h, 0.5ml ethyl vinyl ether was added, then the reaction mixture was poured into 50 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (350 mg, 98% yield, $Mn_{(GPC,\ Chloroform)}$ = 5000 g/mol, PDI: 1.90).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz), 6.79 (d, *J* = 8.6 Hz), 6.40 - 6.59 (m), 6.05 - 6.32 (m), 5.62 - 5.84 (m), 5.39 - 5.57 (m), 4.13 (s, 1H), 2.59 - 3.13 (m), 1.83 -2.24 (m), 1.47 - 1.74 (m), 1.14 - 1.31 (m), 1.07 (d, *J* = 7.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.36, 155.70, 133.46, 131.73, 130.54, 130.44, 129.85, 128.54, 127.97,

127.55, 127.37, 126.28, 119.97, 63.02, 52.64, 51.32, 51.09, 51.00, 46.22, 45.98, 45.80, 45.62, 42.49, 42.16, 42.02, 24.83, 24.76, 17.90, 12.65. MALDI-ToF MS calcd. For $C_{178}H_{206}N_{16}O_{34}SiAg^+$ [M+Ag^+]: 3246.370; Found: 3246.351.

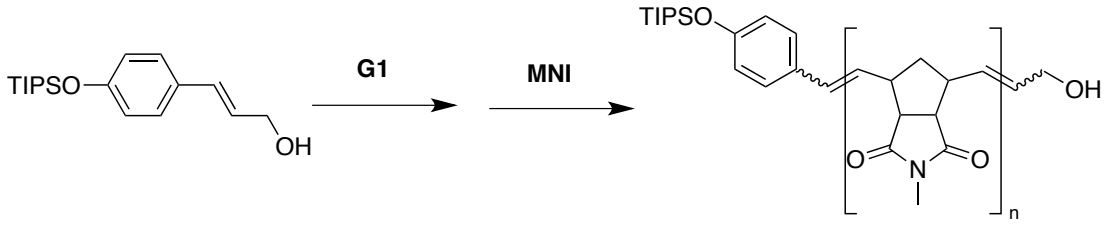
Polymer 19



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (613mg, 2.0mmol, 200 equiv) were dissolved in degassed CH_2Cl_2 (1.0ml) in a flask under Ar. Then **MNI** (1000 equiv, 1.77 g, 10.0mmol) in 4 ml degassed CH_2Cl_2 was added. After 1h, 0.5ml ethyl vinyl ether was added, then the reaction mixture was poured into 50 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (1.77 g, 99% yield, $Mn_{(GPC,\ Chloroform)}$ = 13300 g/mol, PDI: 3.02).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m), 6.79 (m), 6.48 (m), 6.06 - 6.26 (m), 5.73 (m), 5.42 - 5.58 (m), 4.26 (m), 4.12 (m), 2.50 - 3.32 (m), 1.83 - 2.34 (m), 1.42 - 1.77 (m), 1.13 -1.29 (m), 1.07 (d, J = 7.2 Hz, 8H).13C NMR (101 MHz, $CDCl_3$) δ 178.39, 155.88, 133.52, 133.46, 133.39, 132.03, 131.87, 131.84, 131.73, 130.98, 129.65, 127.55, 127.37, 126.29, 120.00, 119.97, 63.86, 52.64, 51.32, 51.09, 50.99, 46.22, 45.99, 45.80, 45.63, 42.76, 42.50, 42.17, 42.03, 40.86, 24.83, 24.76, 17.90, 12.64. MALDI-ToF MS calcd. For $C_{178}H_{206}N_{16}O_{34}SiAg^+$ [M+Ag^+]: 3246.370; Found: 3246.391.

Polymer 20

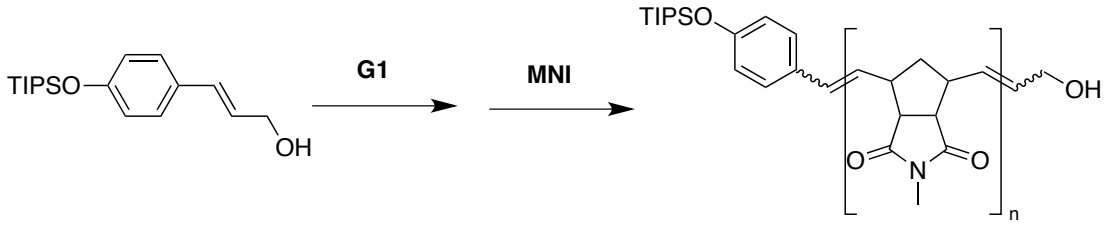


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (613mg, 2.0mmol, 200 equiv) were

dissolved in degassed CH_2Cl_2 (1.0ml) in a flask under Ar. Then **MNI** (200 equiv, 354 mg, 2.0mmol) in 4 ml degassed CH_2Cl_2 was added at -20°C. After 12h, 0.5ml ethyl vinyl ether was added, then the reaction mixture was poured into 50 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (192 mg, 54% yield, $Mn_{(GPC,\ Chloroform)}$ = 8100 g/mol, PDI: 1.81).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (m), 6.79 - 6.85 (m), 6.50 (m), 6.07 - 6.34 (m), 5.75 (m), 5.42 - 5.59 (m), 4.28 (m), 4.15 (s), 2.59 - 3.34 (m), 2.14 (m), 1.66 (m), 1.16 - 1.31 (m,), 1.09 (d, *J* = 7.2 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.35, 155.93, 137.75, 133.51, 132.06, 131.87, 131.83, 131.14, 129.62, 127.58, 126.20, 120.02, 63.96, 52.67, 51.12, 51.02, 47.97, 45.82, 45.63, 45.15, 42.92, 42.06, 40.86, 24.83, 24.76, 17.90, 12.66. MALDI-ToF MS calcd. For $C_{178}H_{206}N_{16}O_{34}SiAg^+$ [M+Ag^+]: 3246.370; Found: 3246.417.

Polymer 21

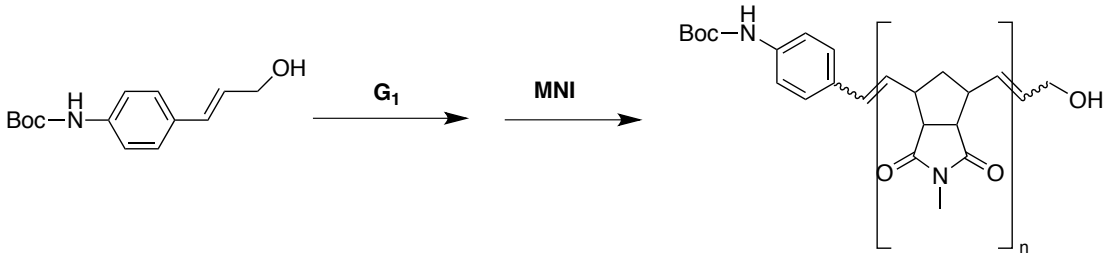


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 2** (613mg, 2.0mmol, 200 equiv) were dissolved in degassed CH_2Cl_2 (1.0ml) in a flask under Ar. Then **MNI** (1000 equiv, 1.77 g, 10.0mmol) in 4 ml degassed CH_2Cl_2 was added at -20 °C. After 12h, 0.5ml ethyl vinyl ether was added, then the reaction mixture was poured into 50 ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (1.39 g, 77% yield, $Mn_{(GPC,\ Chloroform)}$ = 17300 g/mol, PDI: 1.90).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6 Hz), 6.79 (d, *J* = 8.6 Hz), 6.51 (d, *J* = 15.9 Hz), 6.14 - 6.29 (m), 5.35 - 5.82 (m), 4.25 (d, *J* = 5.9 Hz), 4.12 (s), 2.42 - 3.34 (m), 1.86 - 2.21 (m), 1.43 - 1.73 (m), 1.19 (m), 1.06 (d, *J* = 7.2 Hz). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 178.35, 155.86, 137.73, 133.46, 132.03, 131.86, 130.94, 129.66, 127.54, 126.32, 120.00, 63.84, 52.65, 51.09, 51.00, 47.94, 45.80, 45.61, 45.12, 42.90, 42.14, 41.98, 40.85, 24.82, 24.75, 17.89, 12.64. MALDI-ToF MS calcd. For $C_{178}H_{206}N_{16}O_{34}SiAg^+$ [M+Ag^+]: 3246.370; Found: 3246.435.

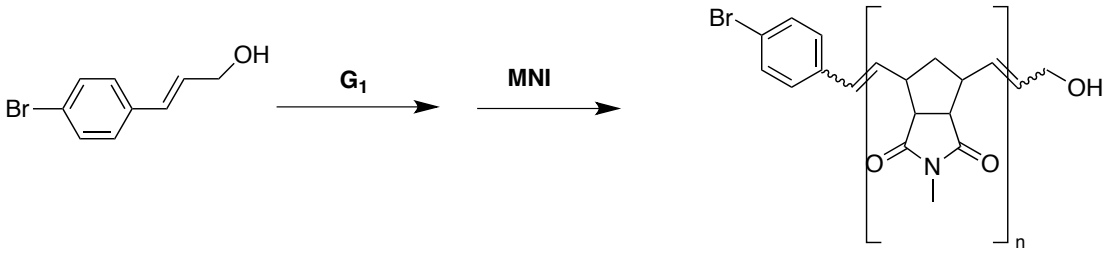
Polymer 22



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 3** (87.3mg, 0.35mmol, 35 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 5h, then **MNI** (50 equiv, 45 mg, 0.25mmol) was added. After 1h, 0.5ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (80 mg, 88% yield, $Mn_{(GPC,\ Chloroform)}$ = 4900 g/mol, PDI: 1.82).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.33 (m), 6.45-6.57 (m), 6.17-6.31 (m), 5.71-5.83 (m), 5.47-5.57 (m), 4.16-4.31 (m), 2.71-3.27 (m), 2.05-2.17 (m), 1.61-1.70(m), 1.51 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.32, 132.07, 131.87, 131.81, 126.91, 51.13, 51.02, 45.82, 45.62, 42.11, 41.95, 40.86, 28.36, 24.83, 24.76. MALDI-ToF MS calcd. For $C_{209}H_{231}N_{21}O_{41}Ag^+$ [M-Boc+Ag^+]: 3797.569; Found: 3797.813.

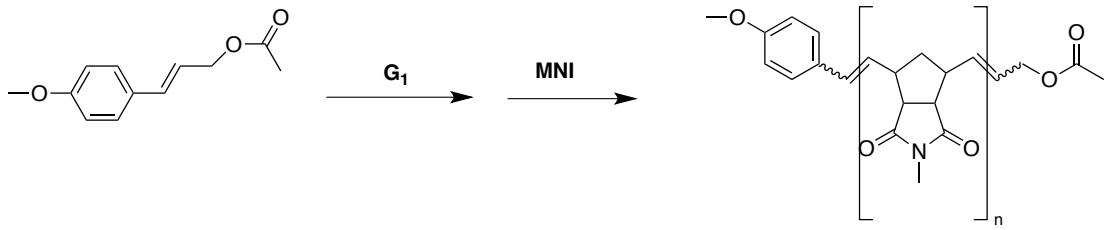
Polymer 23



G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 4** (107mg, 0.50mmol, 50 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR. Then the NMR tube was kept at room temperature for 5h, then **MNI** (50 equiv, 89 mg, 0.50mmol) was added. After 1h, 0.5ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (81 mg, 89% yield, $Mn_{(GPC,\ THF)}$ = 3900 g/mol, PDI: 1.98).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.43-7.45 (m), 7.26-7.28 (m), 6.48-6.58 (m), 6.30-6.40 (m), 5.47-5.80 (m), 4.11-4.28 (m), 2.70-3.21 (m), 2.04-2.21 (m), 1.48-1.81(m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.23, 178.13, 135.98, 133.27, 132.05, 131.89, 131.61, 130.08, 128.91, 127.95, 127.81, 121.08, 92.75, 63.16, 55.26, 52.53, 51.12, 51.05, 45.78, 45.63, 42.40, 41.04, 24.53, 24.47. MALDI-ToF MS calcd. For $C_{129}H_{141}N_{12}O_{25}BrAg^+$ [M+Ag^+]: 2443.837; Found: 2443.782.

Polymer 24

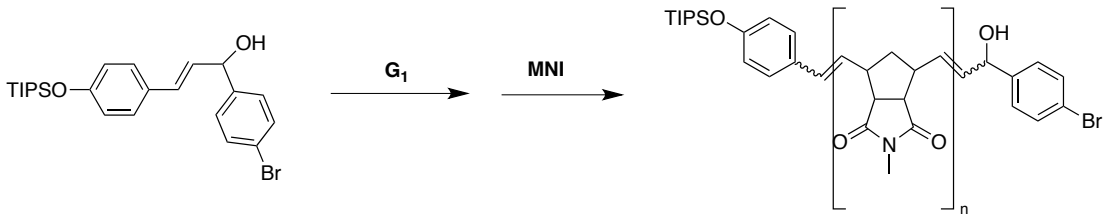


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 5** (73mg, 0.35mmol, 35 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 5h, then **MNI** (50 equiv, 89 mg, 0.5mmol) was added. After 1h, 0.5ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool

methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (83 mg, 91% yield, $Mn_{(GPC,\ THF)}$ = 5200 g/mol, PDI: 1.40).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.39 (m), 6.83-6.89 (m), 6.47-6.62 (m), 6.11-6.33 (m), 5.50-5.81 (m), 4.56-4.71 (m), 3.81 (s), 3.49 (s), 2.71-3.27 (m), 2.07-2.19 (m), 1.55-1.71(m), 0.95 (s). ^{13}C NMR (101MHz, $CDCl_3$) δ 178.32, 132.08, 131.87, 131.81, 127.86, 114.02, 107.82, 65.35, 52.69, 51.13, 51.02, 50.89, 45.83, 45.62, 42.13, 41.94, 40.86, 24.83, 24.76. MALDI-ToF MS calcd. For $C_{102}H_{113}N_9O_{21}Ag^+$ [M+Ag^+]: 1906.710; Found: 1906.657.

Polymer 25

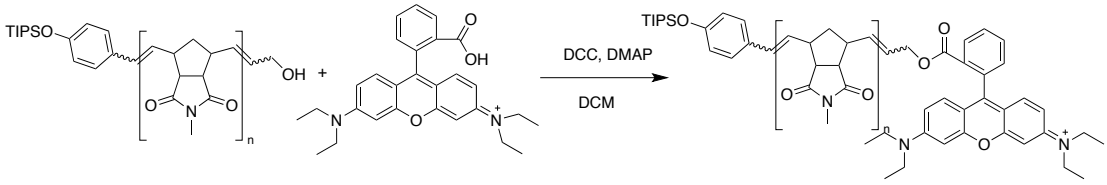


G1 (8.22mg, 0.01mmol, 1 equiv) and **CTA 6** (231mg, 0.50mmol, 50 equiv) were dissolved in CD_2Cl_2 (0.75ml) in a NMR tube. Then the NMR tube was kept at room temperature for 5h, then **MNI** (50 equiv, 89 mg, 0.50mmol) was added. After 1h, 0.5ml ethyl vinyl ether was added, then the reaction mixture was poured into 8ml cool methanol to precipitate the formed polymer. The mixture was filtered to afford the respective polymer (83mg mg, 89% yield, $Mn_{(GPC,\ THF)}$ = 5600 g/mol, PDI: 1.51).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.49 (m), 6.70-6.89 (m), 6.02-6.49 (m), 5.49-5.82 (m), 4.89-5.05 (m), 4.65-4.73 (m), 3.60-3.80 (m), 3.49 (s), 2.72-3.36 (m), 2.08-2.18 (m), 1.56-1.71 (m), 1.06-1.29 (m). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.33, 156.14, 155.79, 140.53, 135.71, 132.10, 131.88, 131.61, 131.39, 129.79, 129.24, 129.04, 128.67, 128.36, 128.10, 127.79, 127.76, 127.63, 121.44, 119.97, 119.74, 119.65, 119.11, 91.60, 78.66, 55.86, 51.04, 50.89, 45.83, 45.62, 42.14, 40.86, 24.77, 17.92, 12.68. MALDI-ToF MS calcd. For $C_{204}H_{231}BrN_{18}O_{38}SiAg^+$ [M+Ag^+]: 3754.470; Found: 3754.728.

Labelling Experiments

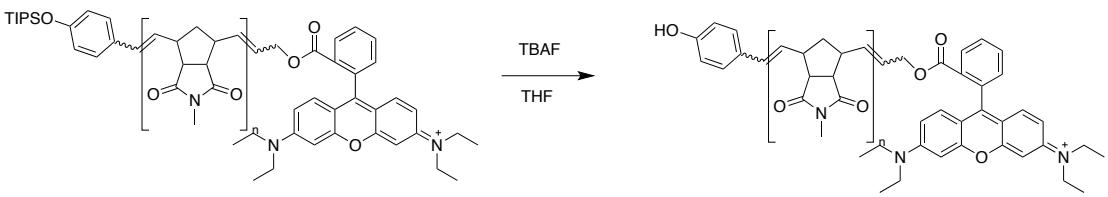
Polymer 26



Polymer 13 (100mg, 0.019mmol), Rhodamine B (100mg. 0.2mmol), DMAP (5mg, 0.04mmol), DCC (46mg, 0.22mmol) were dissolved in 2ml dry DCM under Ar at room temperature and stirring overnight. The reaction mixture was filtered to remove solid and the solvent was removed by rotary evaporator. Then the residue was dissolved in 1ml DCM and poured into cold CH_3OH to precipitate the **polymer 26** (93 mg, 85%，$Mn_{(GPC,\ Cholorform)}$ = 5800 g/mol, PDI: 1.81).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.33-8.36 (m), 7.76-7.86 (m), 7.09-7.33 (m), 6.80-6.88 (m), 6.13-6.49 (m), 5.48-5.84 (m), 5.10 (s), 3.58-3.64 (m), 2.70-3.22 (m), 2.04-2.16 (m), 1.54-1.70 (m), 1.22-1.33 (m), 1.10 (d, J = 7.3 Hz). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.25, 178.22, 133.23, 132.09, 131.89, 131.87, 131.79, 131.29, 120.02, 113.56, 99.99, 96.1152.54, 51.06, 46.05, 45.80, 45.65, 42.93, 42.42, 41.05, 24.52, 24.46, 17.65, 12.65, 12.35. MALDI-ToF MS calcd. For $C_{196}H_{224}N_{17}O_{34}Si$ [M]: 3387.609; Found: 3387.624.

Polymer 27

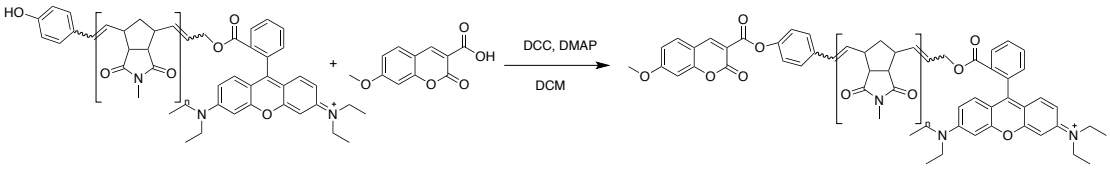


Polymer 26 (80mg) was dissolved 1ml dry DCM under Ar at room temperature. Then 1ml TBAF (1 M in THF) was added, keep stirring overnight. The solvent was removed by rotary evaporator. Then the residue was dissolved in 1ml DCM and poured into cold

CH_3OH to precipitate the **polymer 27** (72mg, 90%，$Mn_{(GPC,\ Cholorform)}$ = 5600 g/mol, PDI: 1.79).

^1H NMR (400 MHz, CD_2Cl_2) δ 8.14-8.16 (m), 7.94-7.96 (m), 7.58-7.67 (m), 7.17-7.22 (m), 6.33-6.84 (m), 6.05-6.11 (m), 5.48-5.80 (m), 5.09 (s), 4.64-4.66 (m), 4.11 (s), 2.70-3.42 (m), 2.00-2.16 (m), 1.57-1.70 (m), 1.40-1.43 (m), 1.15-1.26 (m), 0.98-1.02 (m), 0.84-0.90 (m). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.24, 131.87, 99.99, 82.06, 58.88, 51.06, 46.01, 45.80, 45.64, 42.35, 41.04, 24.46, 24.01, 19.72, 13.40, 12.26. MALDI-ToF MS calcd. For $C_{137}H_{149}N_{12}O_{24}$ [M]: 2346.081; Found: 2346.475.

Polymer 28

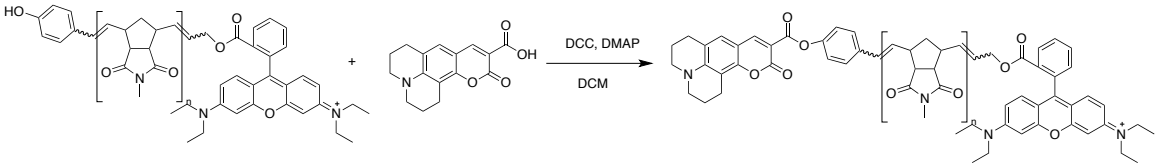


Polymer 27 (70mg), 7-Methoxycoumarin-3-carboxylic Acid (44mg. 0.2mmol), DMAP (5mg, 0.04mmol) and DCC (46mg, 0.22mmol) were dissolved in 2ml dry DCM under Ar at room temperature and stirring overnight. The reaction mixture was filtered to remove solid and the solvent was removed by rotary evaporator. Then the residue was dissolved in 1ml DCM and poured into cold CH_3OH to precipitate the **polymer 28** (58mg, 80%，$Mn_{(GPC,\ Cholorform)}$ = 5900 g/mol, PDI: 1.85).

^1H NMR (400 MHz, CD_2Cl_2) δ 8.71-8.72 (m), 8.53 (s), 8.20 (s), 7.39-7.74 (m), 7.33 (s), 7.17-7.19 (m), 6.75-6.99 (m), 6.54-6.60 (m), 6.30-6.36 (m), 5.99-6.05 (m), 5.48-5.90 (m), 4.80-4.81 (m), 3.90-3.93 (m), 2.70-3.16 (m), 2.04-2.20(m), 1.53-1.71 (m), 0.83-1.35 (m). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.27,178.23, 178.14, 178.11, 165.76, 165.29, 157.96, 157.64, 150.17, 149.12, 133.27, 132.05, 131.80, 131.17, 130.88, 129.52, 127.19, 124.80, 121.80, 114.24, 113.72, 113.46, 111.63, 100.58, 100.31, 77.56, 65.44, 56.19, 52.53, 51.12, 51.05, 46.17, 45.97, 45.79, 45.64, 43.15, 42.95, 42.42, 41.04, 24.52, 24.46. MALDI-ToF MS calcd. For $C_{186}H_{199}N_{16}O_{36}$ [M]: 3256.423; Found:

3256.614.

Polymer 29



Polymer 27 (65mg, 0.065mmol), Coumarin 343 (186mg 0.65mmol), DMAP (8mg, 0.065mmol) and DCC (134mg, 0.65mmol) were dissolved in 2ml dry DCM under Ar at room temperature and stirring overnight. The reaction mixture was filtered to remove solid and the solvent was removed by rotary evaporator. Then the residue was dissolved in 1ml DCM and poured into cold CH_3OH to precipitate the **polymer 26** (50mg, 77%, $Mn_{(GPC,\ Chloroform)}$ = 5700 g/mol, PDI: 1.91).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.53 (m), 7.78 (dd, *J* = 31.0, 8.9 Hz), 6.83-7.57 (m), 6.54 (d, *J* = 15.7 Hz), 6.27 (dd, *J* = 15.8, 6.9 Hz), 5.29-6.05 (m), 4.79 (d, *J* = 5.3 Hz), 4.51 (d, *J* = 5.6 Hz), 2.71-3.48 (m), 1.54-2.17 (m), 1.31 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.32, 132.07, 131.86, 127.12, 122.01, 105.81, 99.99, 52.69, 51.12, 51.02, 45.81, 45.61, 42.11, 41.94, 40.86, 27.43, 24.82, 24.76, 21.14, 20.08, 12.67. MALDI-ToF MS calcd. For $C_{193}H_{206}N_{17}O_{35}$ [M]: 3321.49; Found: 3321.12.

Copies of NMR Spectra

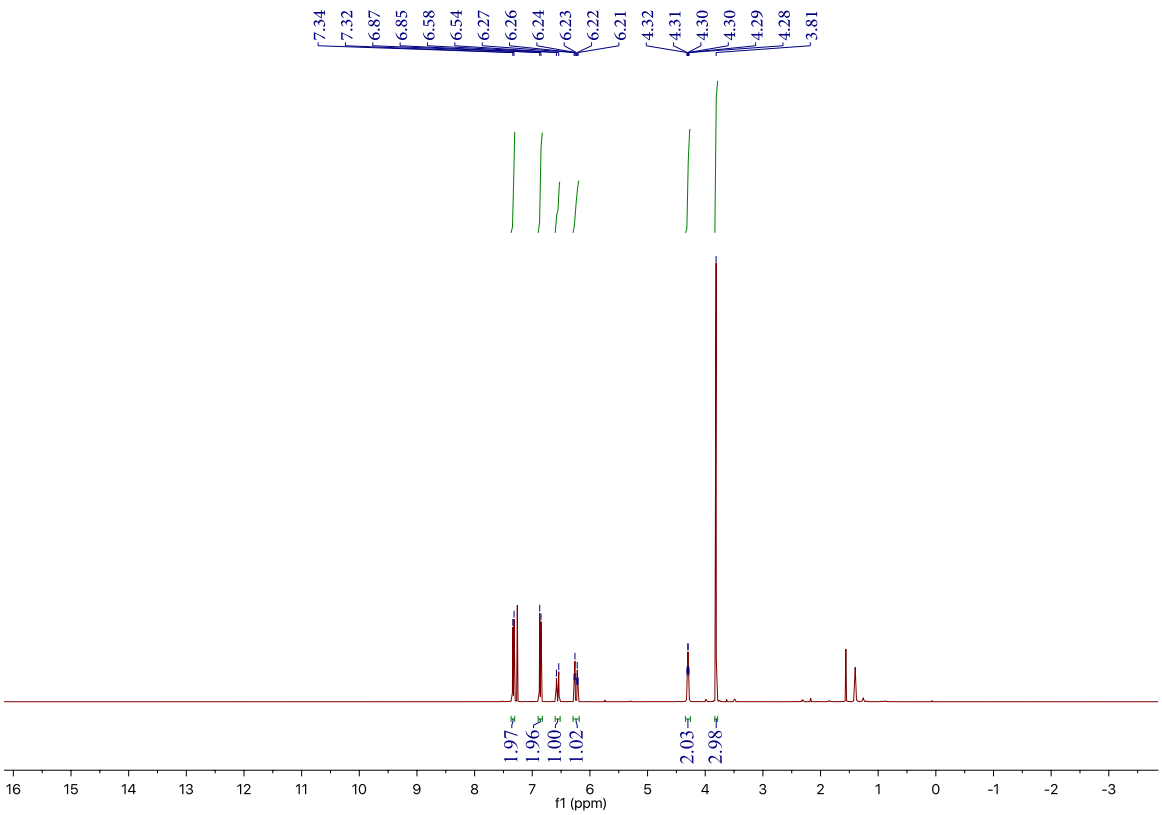


Figure S1 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA 1**

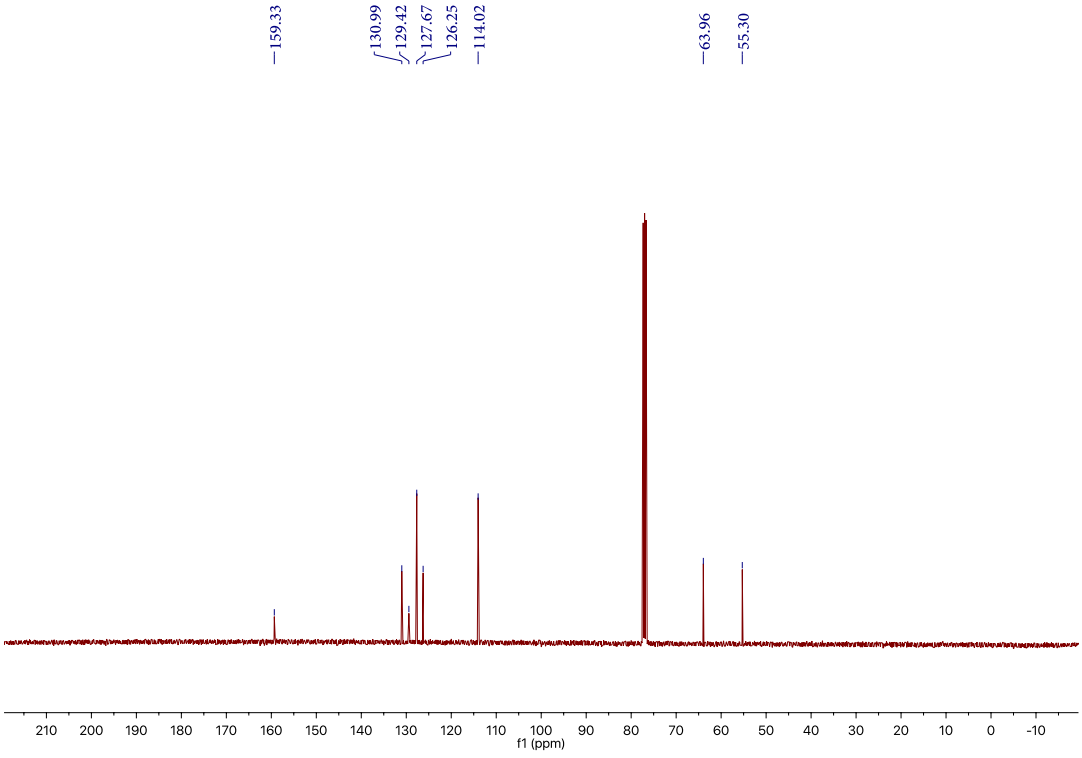


Figure S2 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA 1**

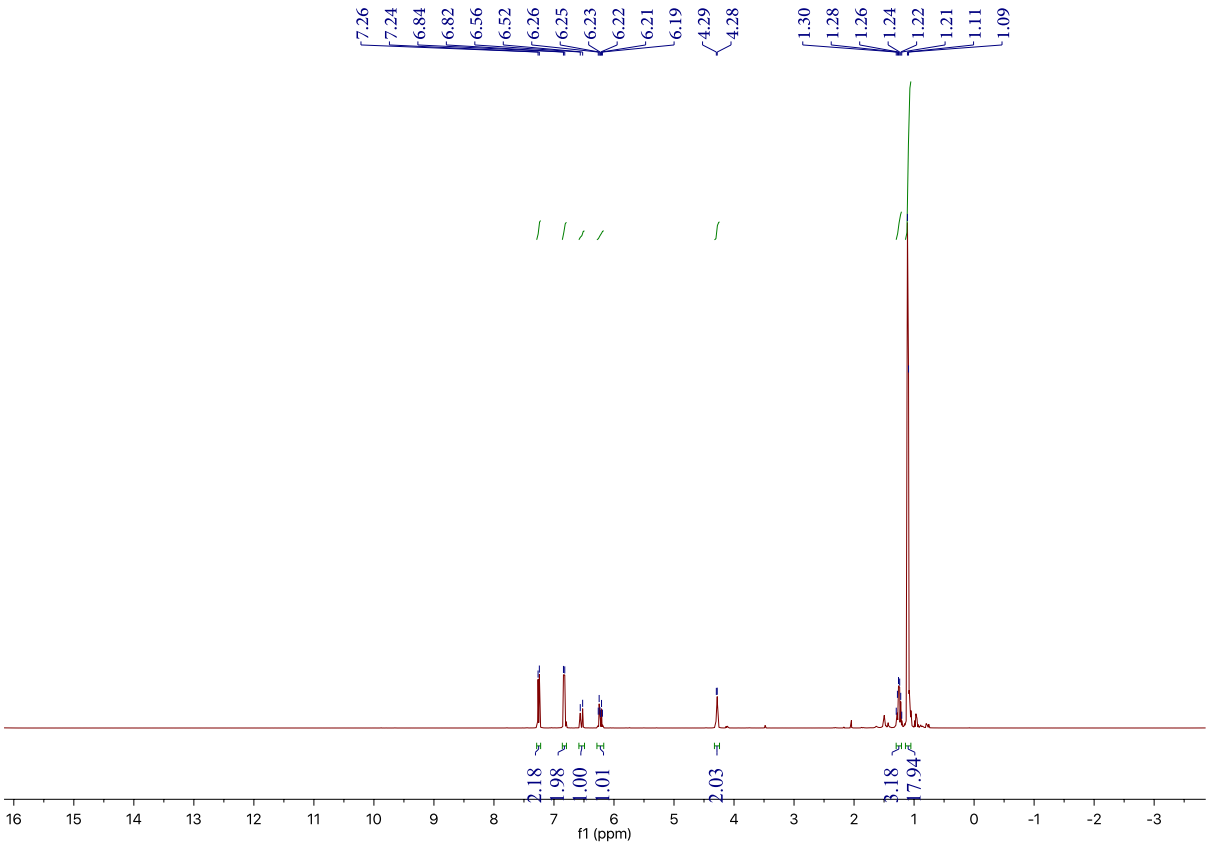


Figure S3 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA 2**

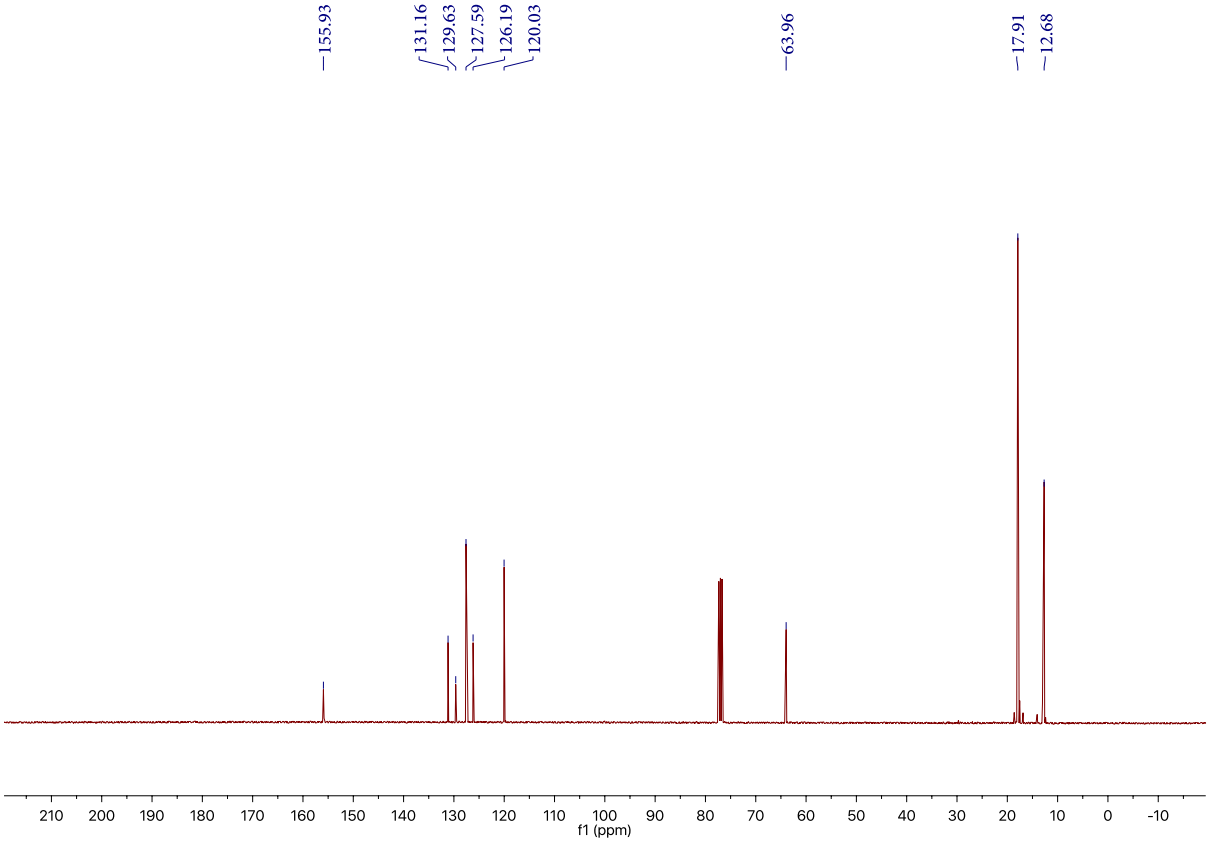


Figure S4 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA 2**

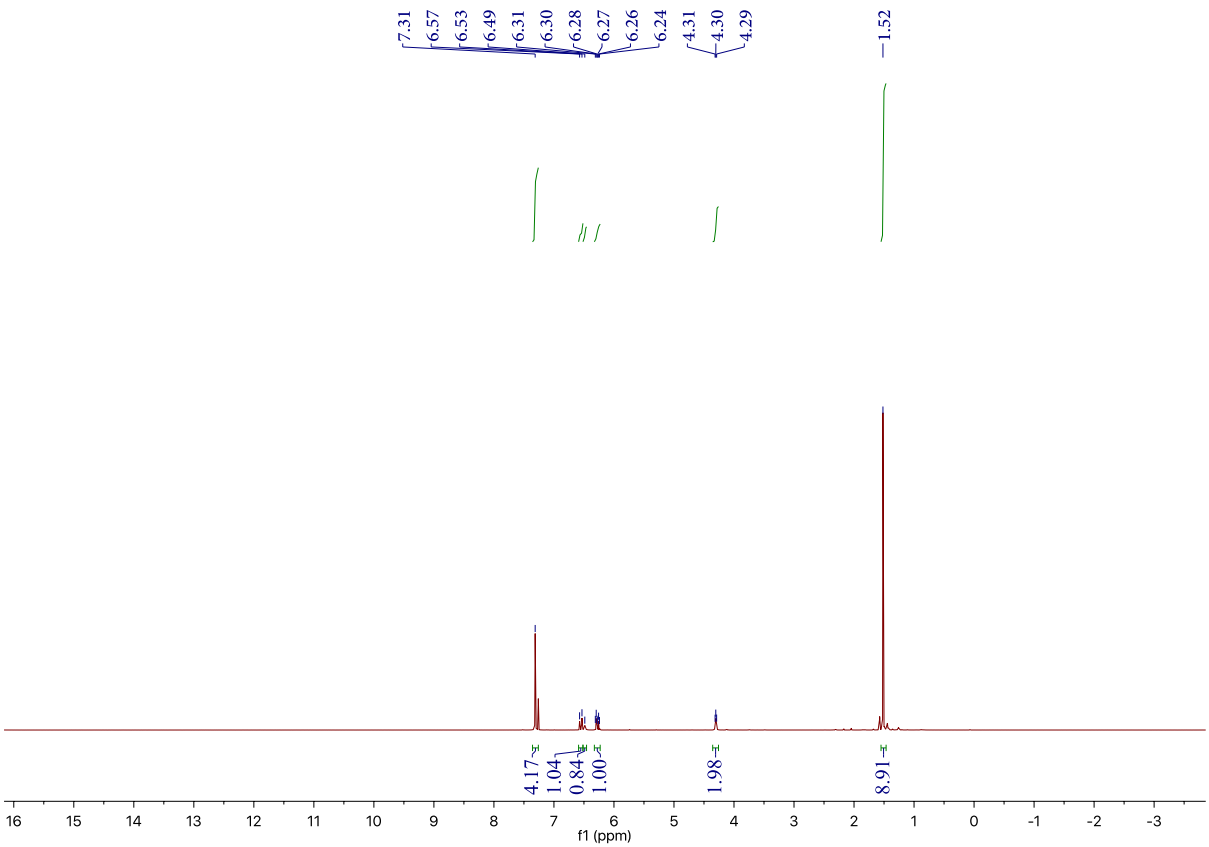


Figure S5 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA 3**

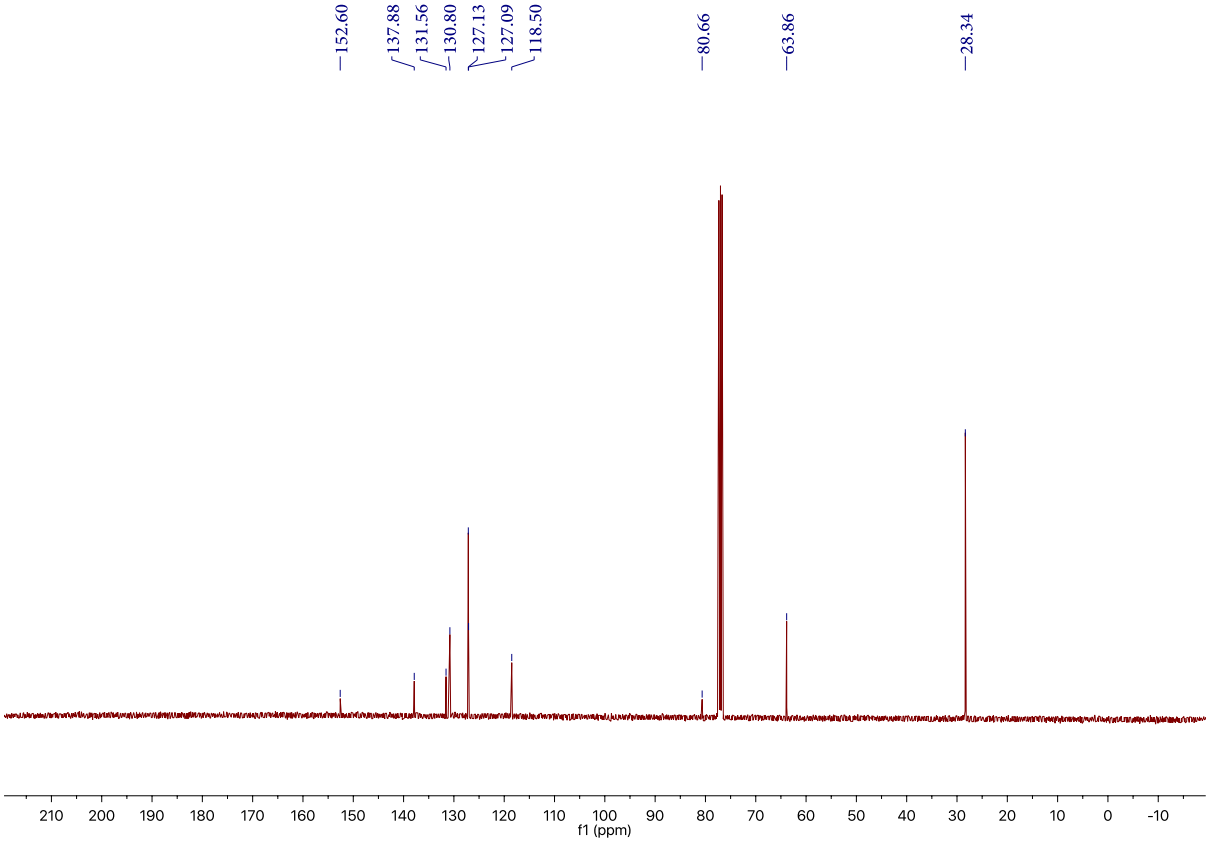


Figure S6 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA 3**

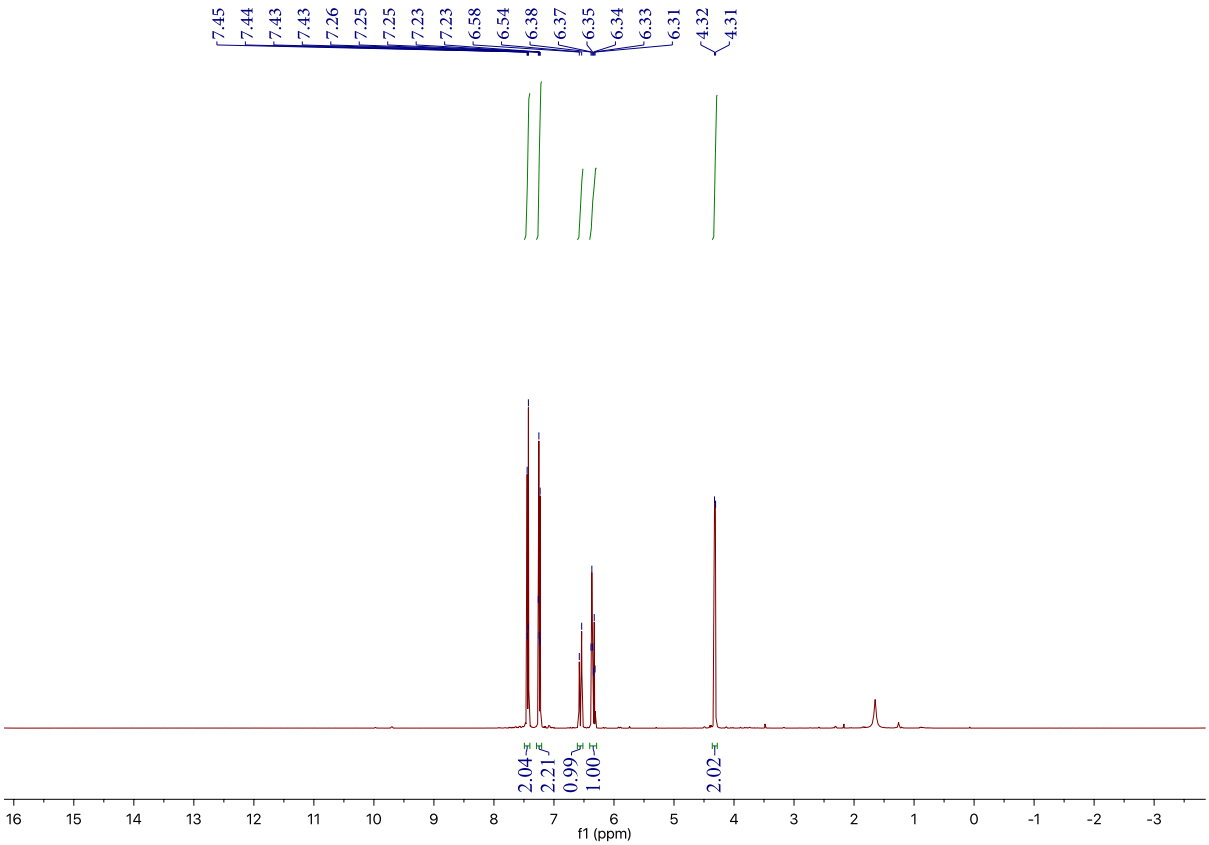


Figure S7 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA 4**

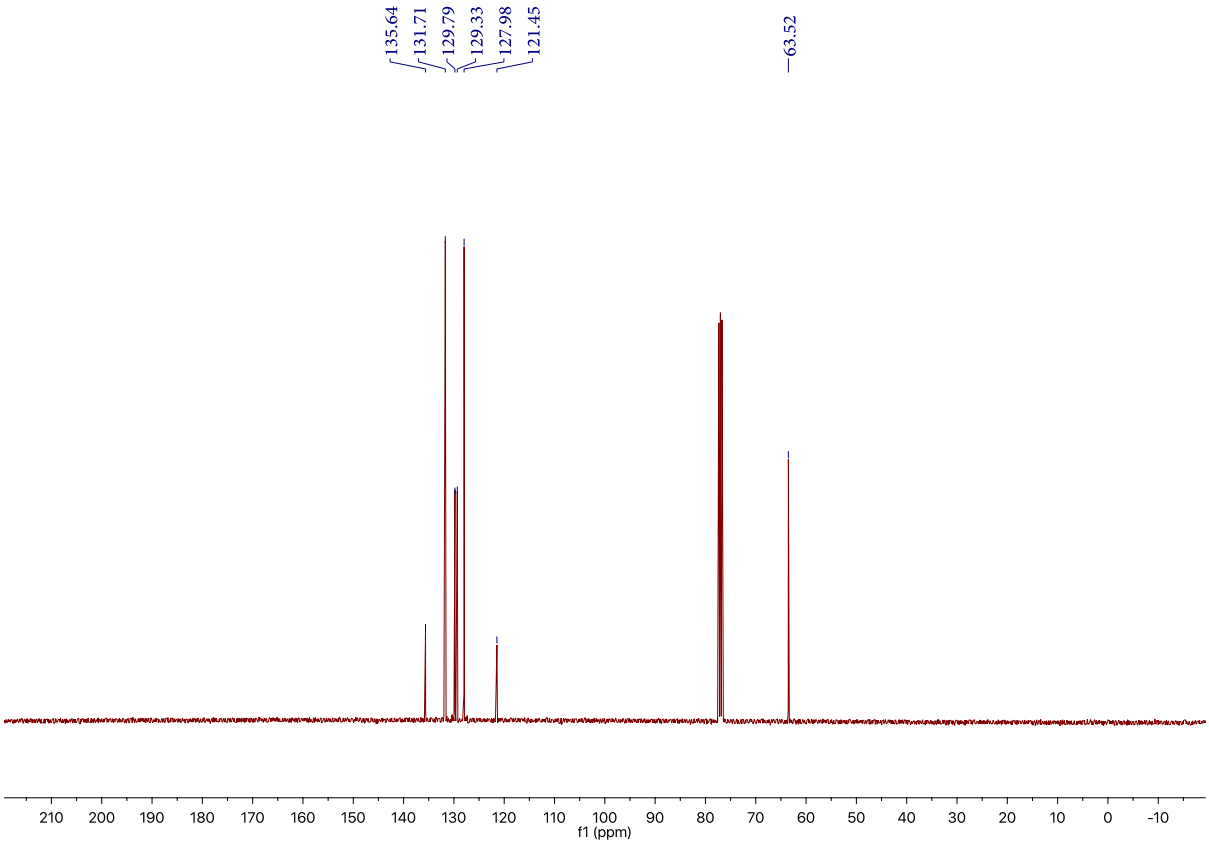


Figure S8 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA 4**

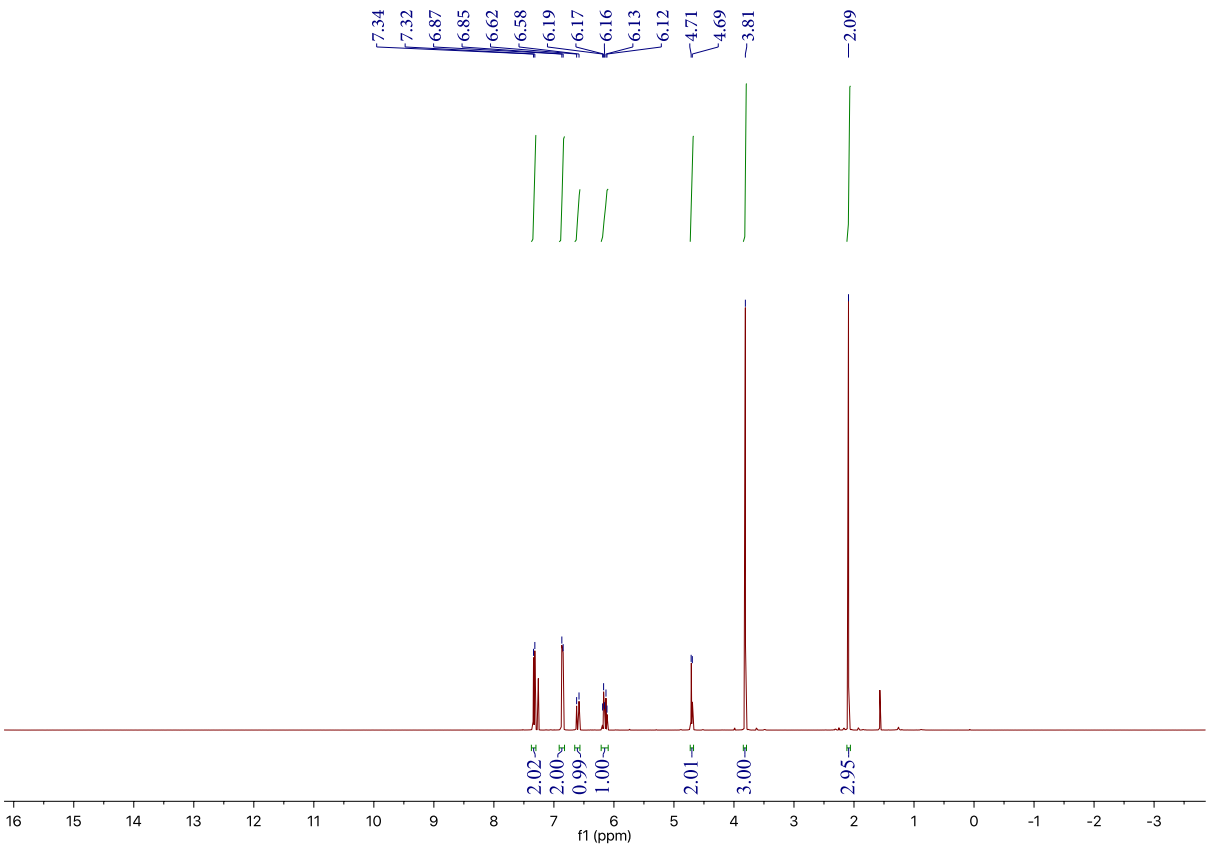


Figure S9[1]H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA 5**

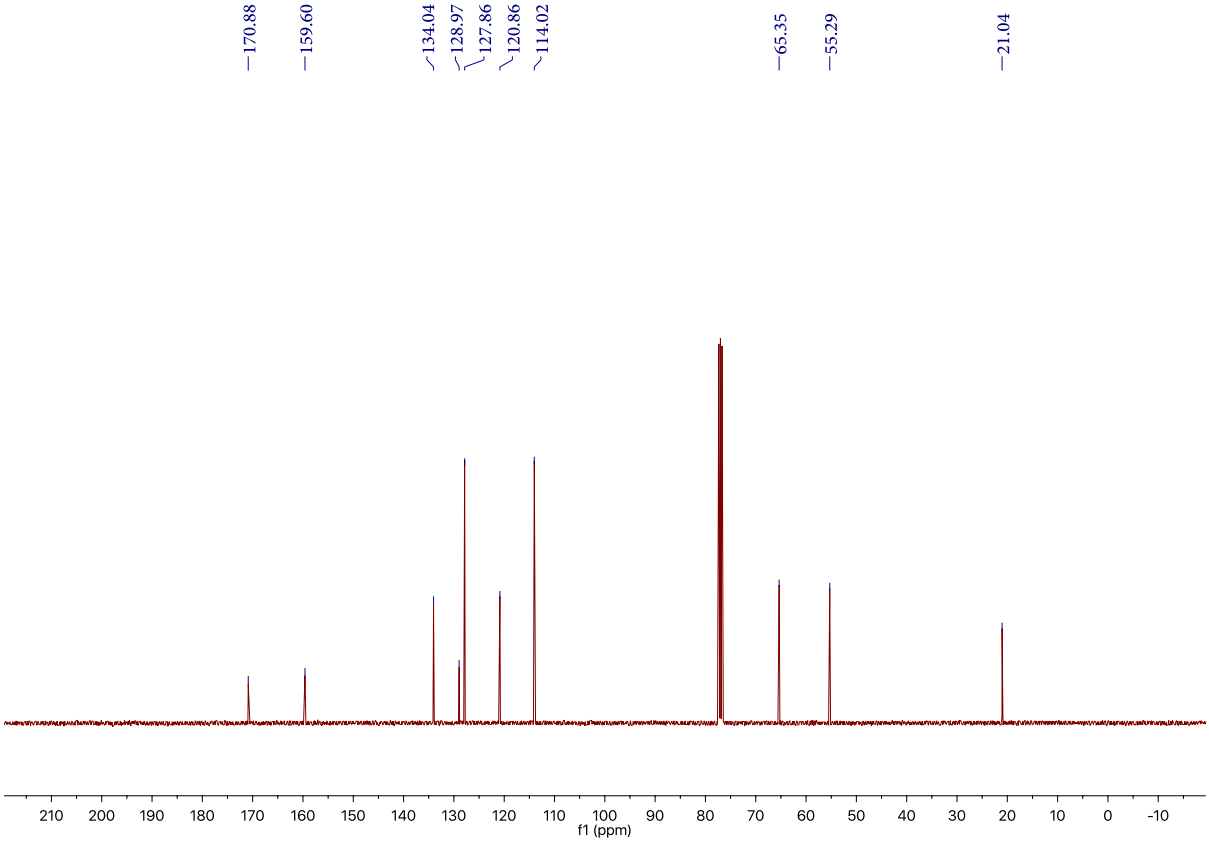


Figure S10 [13]C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA 5**

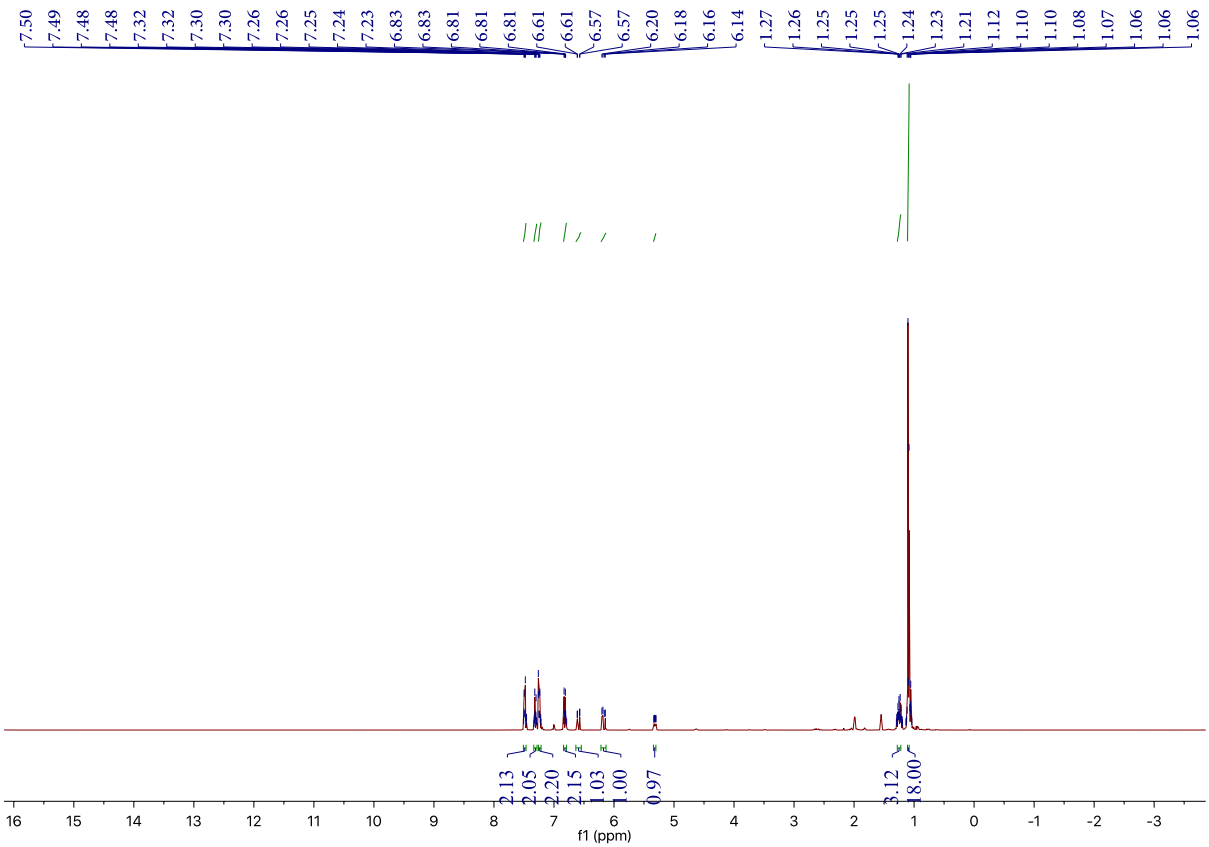


Figure S11 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **CTA 6**

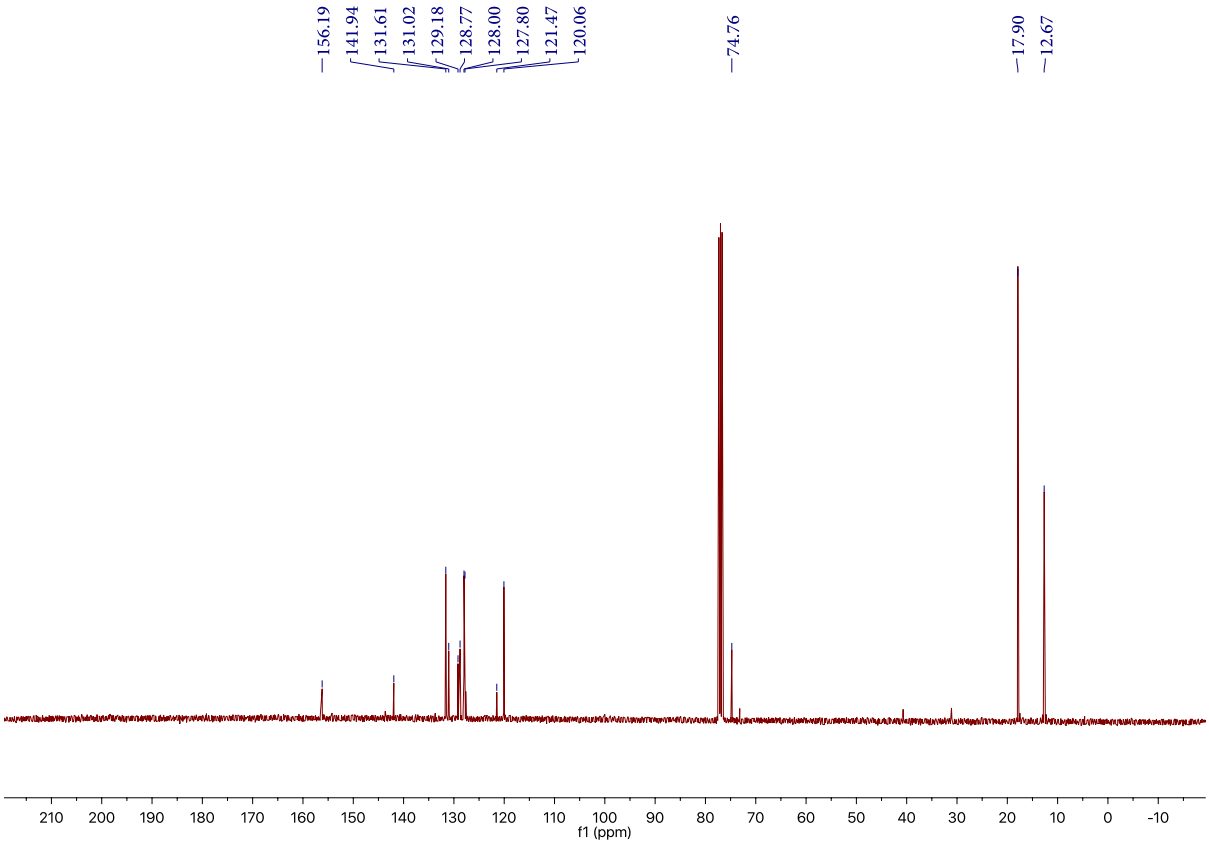


Figure S12 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **CTA 6**

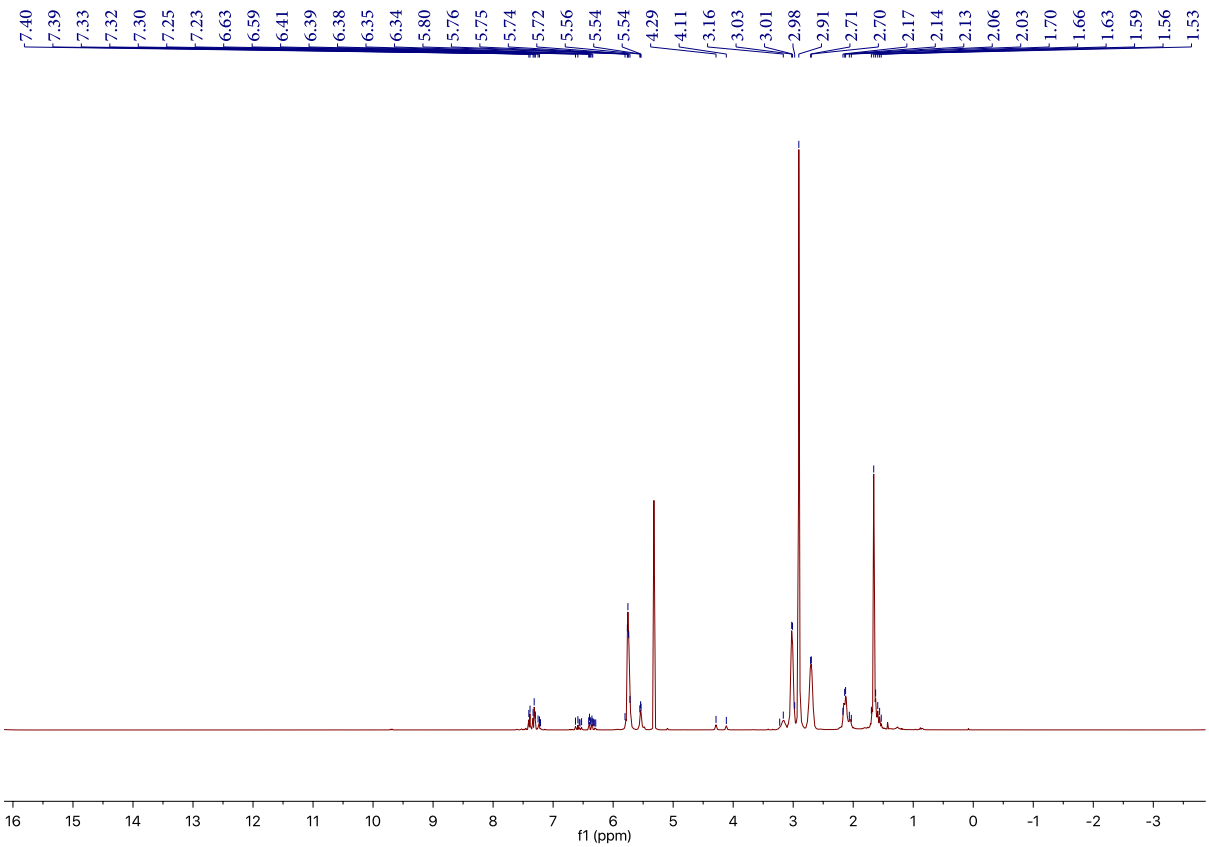


Figure S13 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 1**

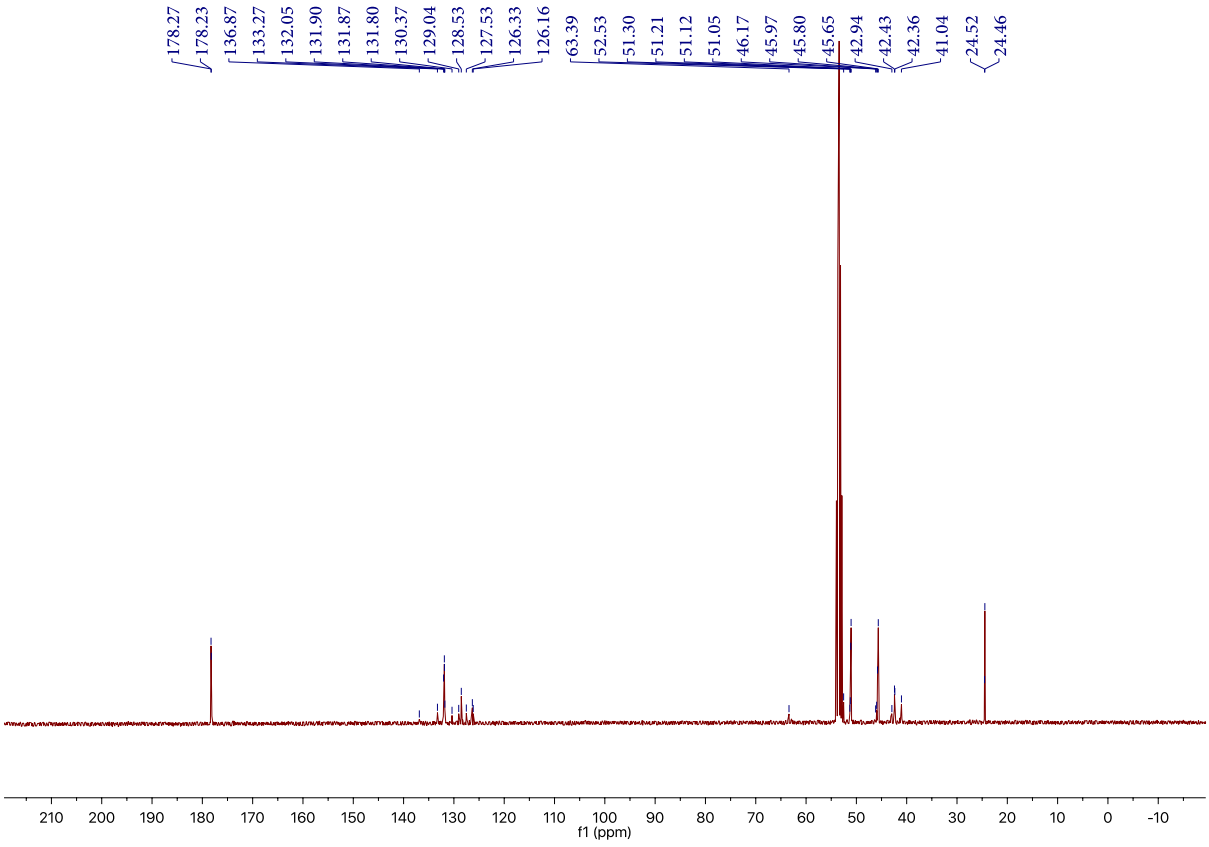


Figure S14 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 1**

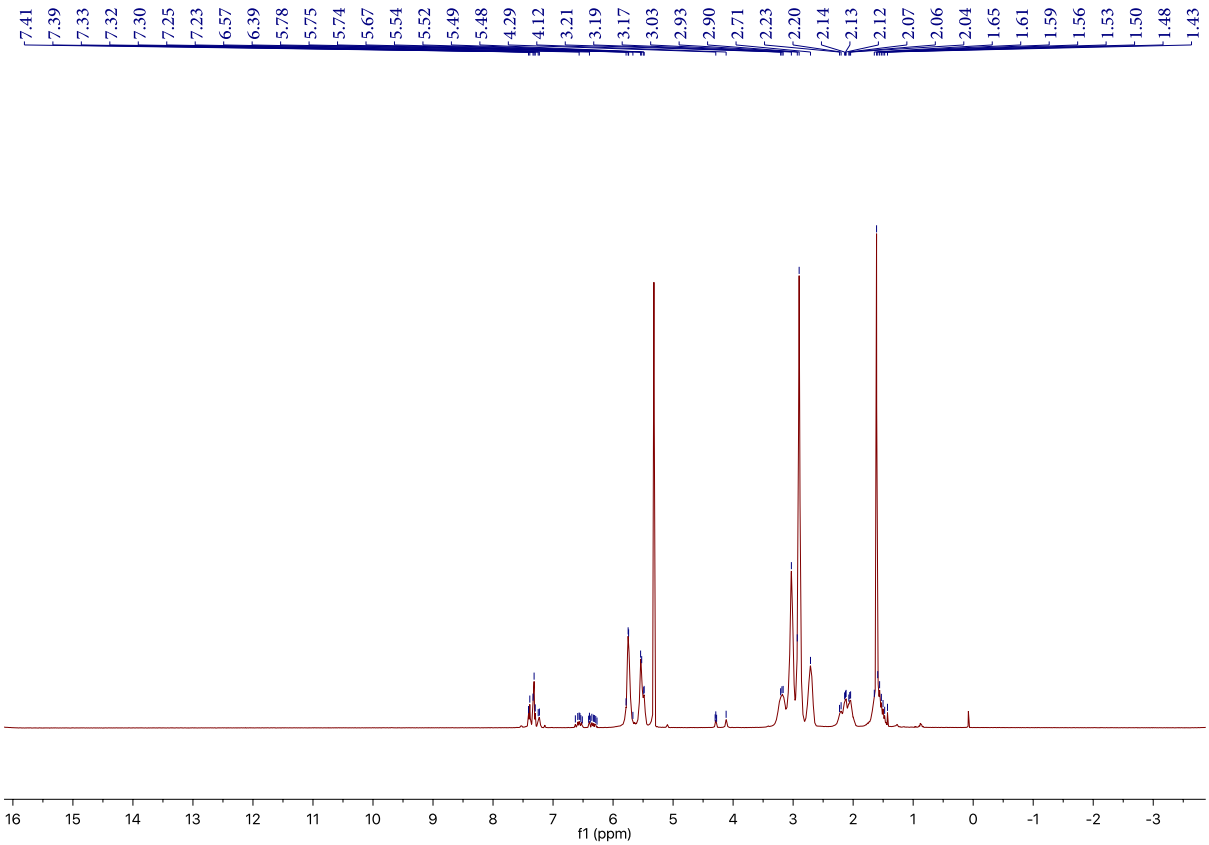


Figure S15 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 2**

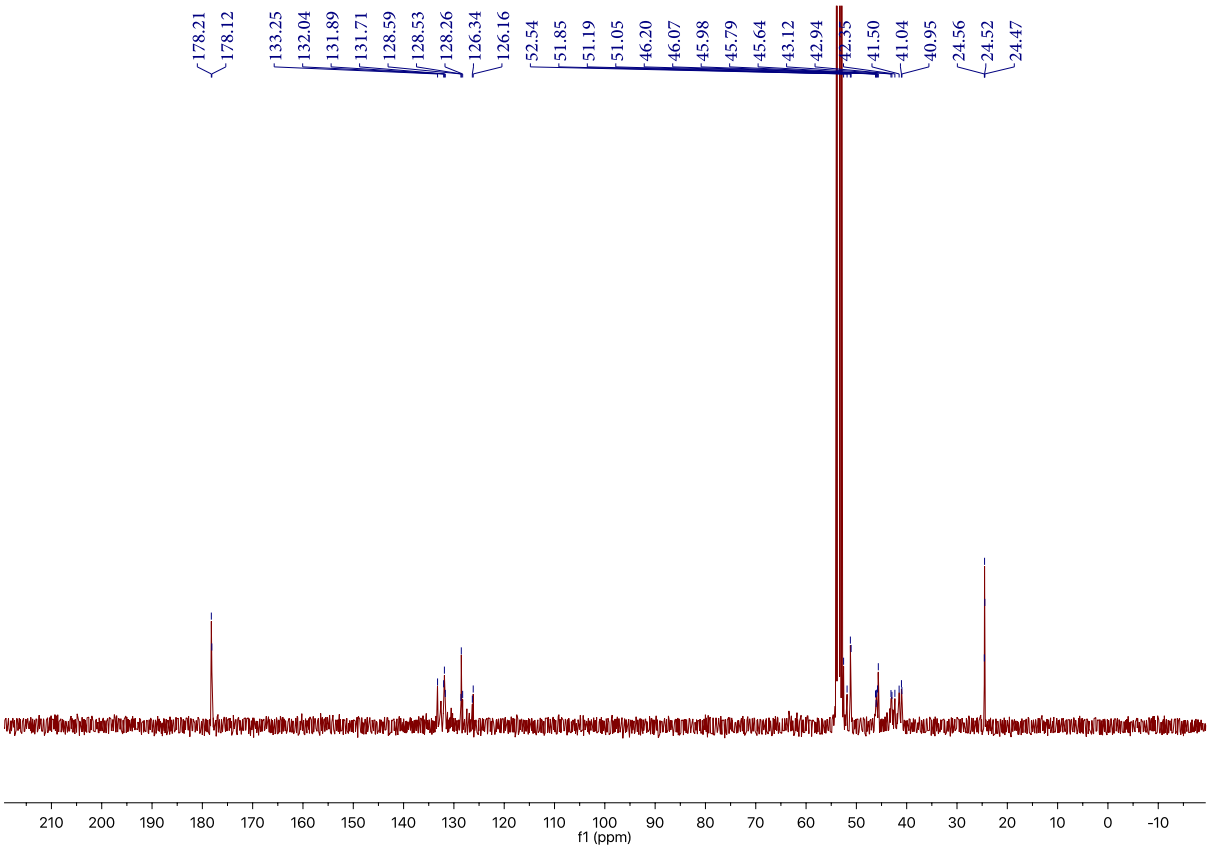


Figure S16 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 2**

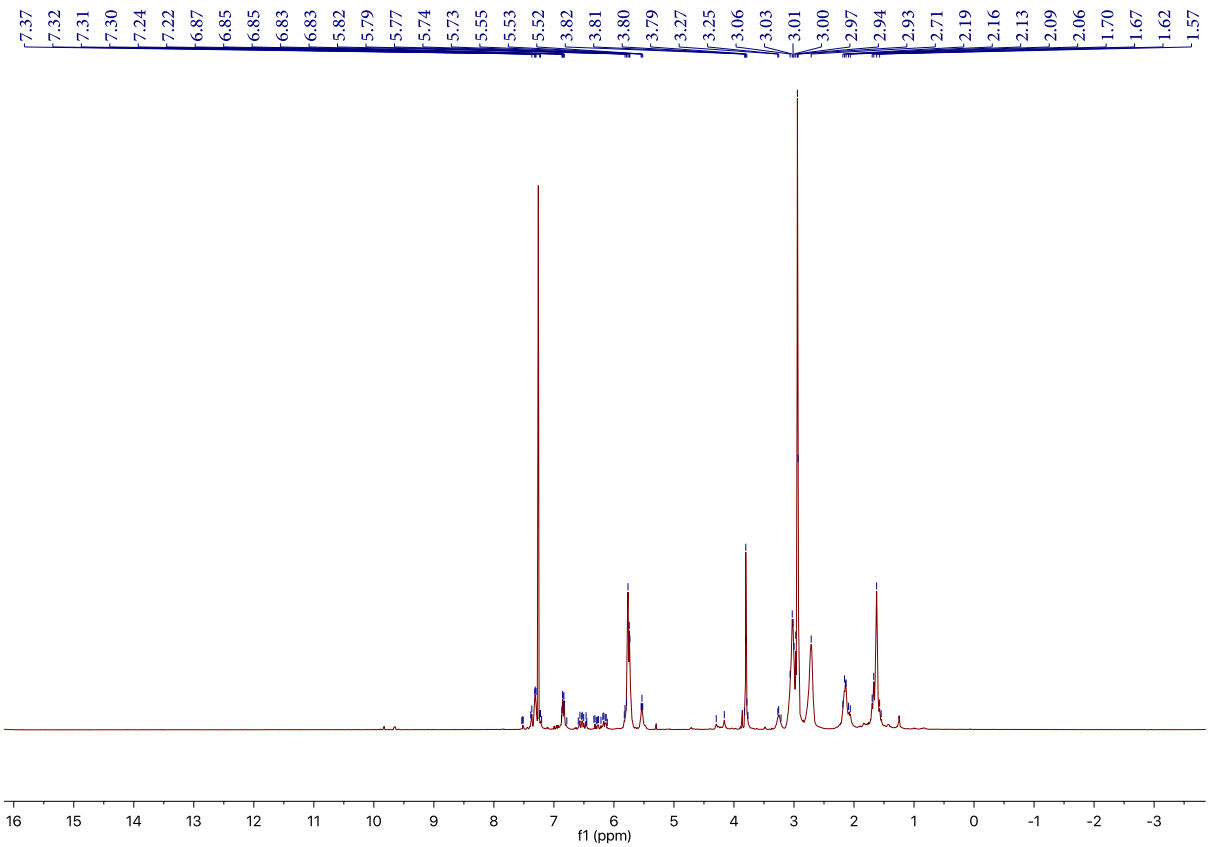


Figure S17 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 3**

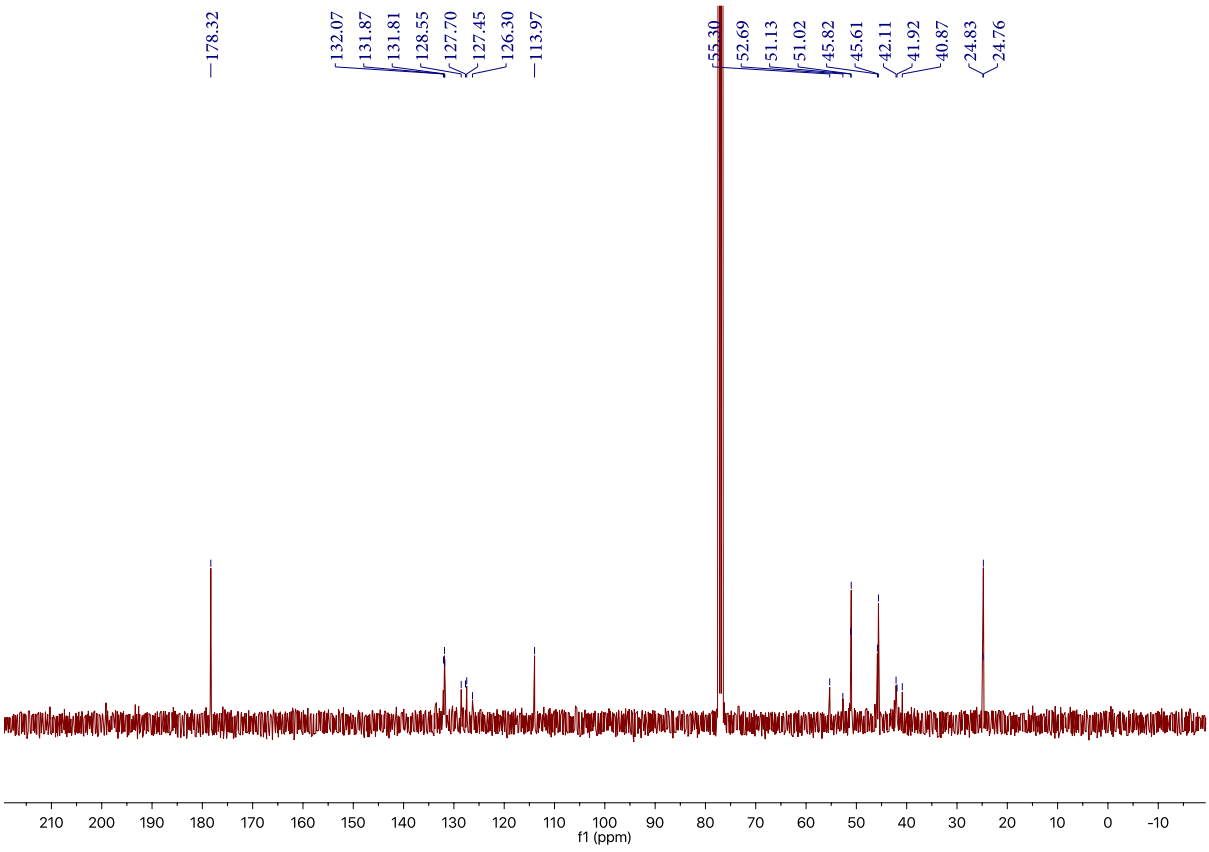


Figure S18 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 3**

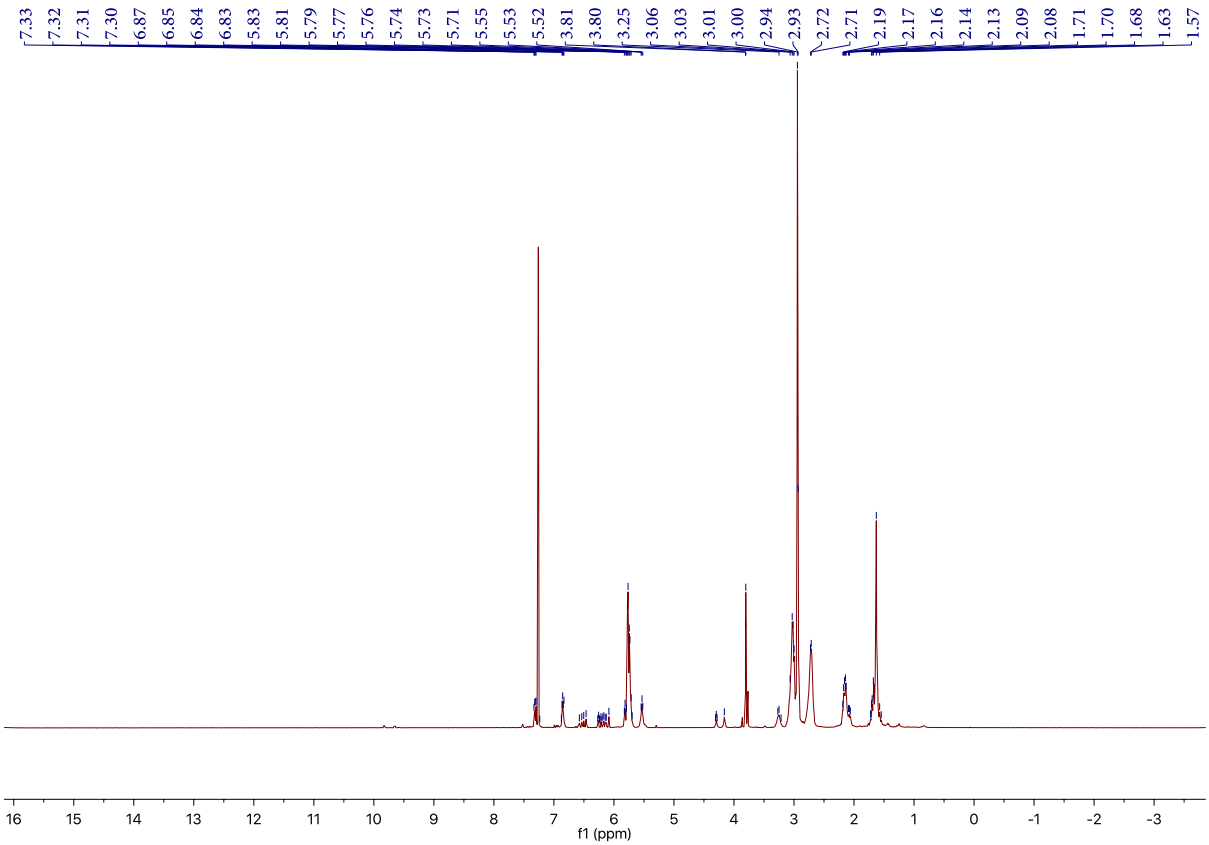


Figure S19 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 4A**

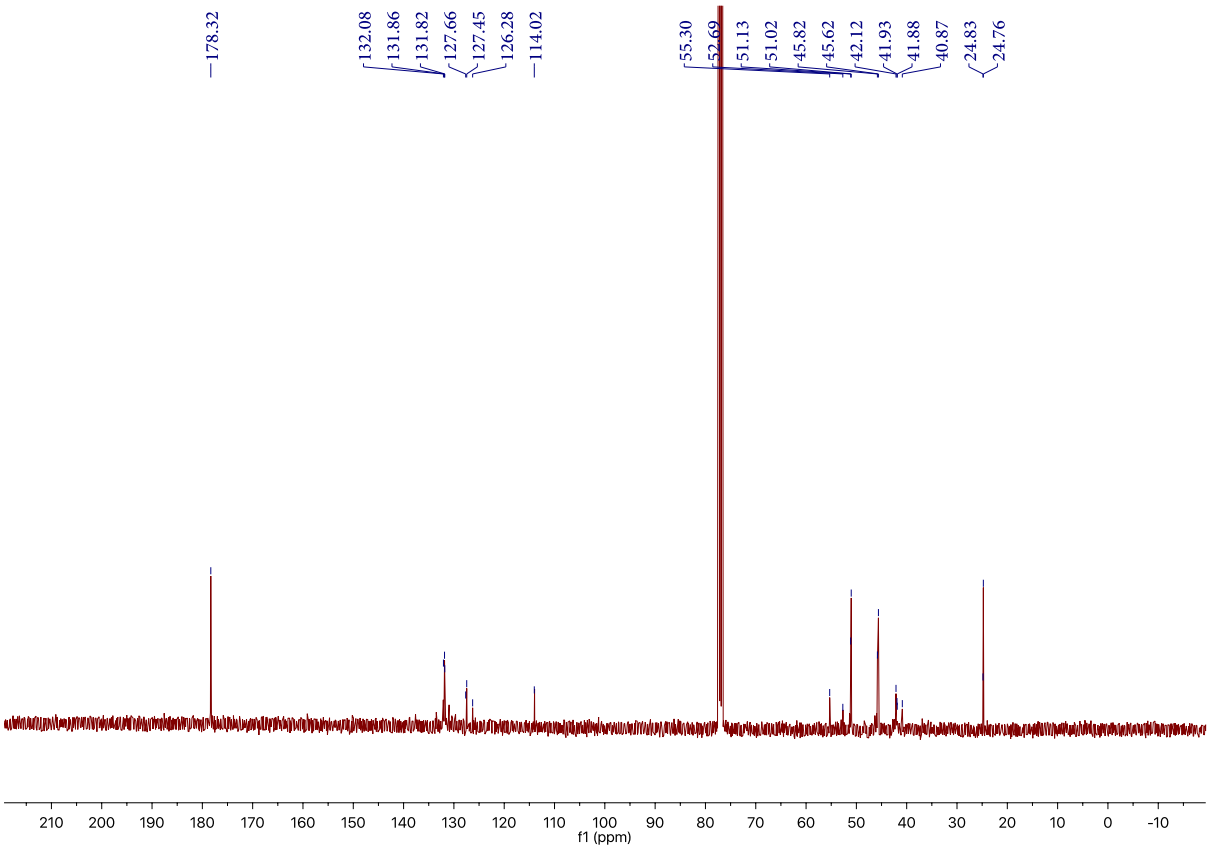


Figure S20 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 4A**

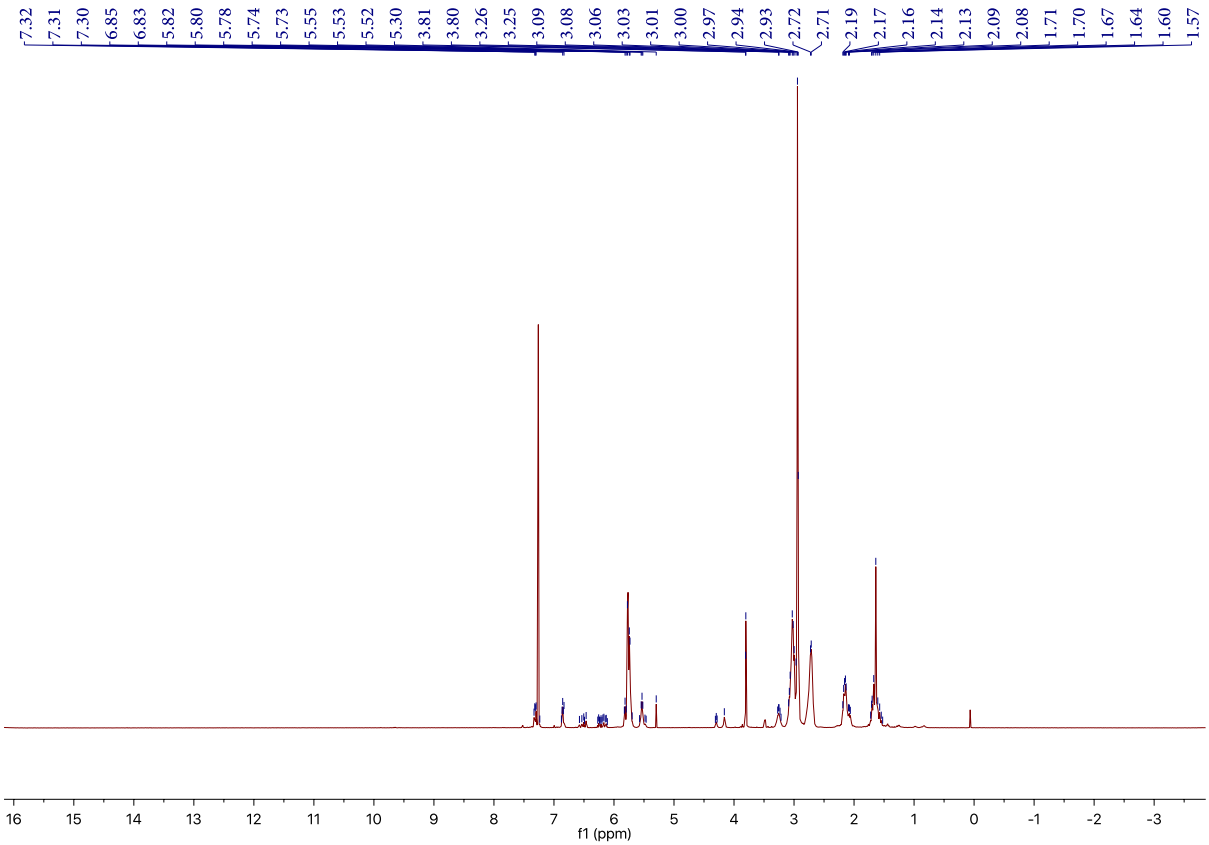


Figure S21 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 4B**

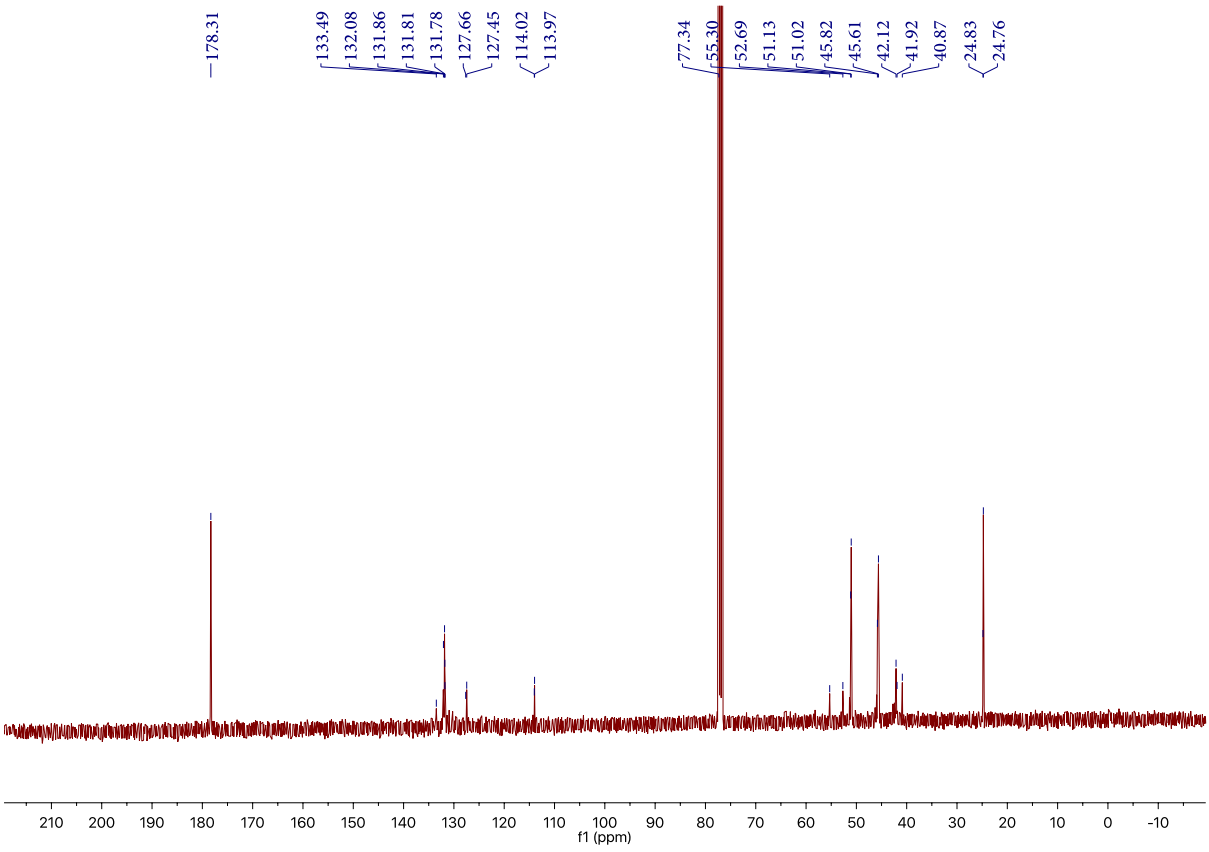


Figure S22 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 4B**

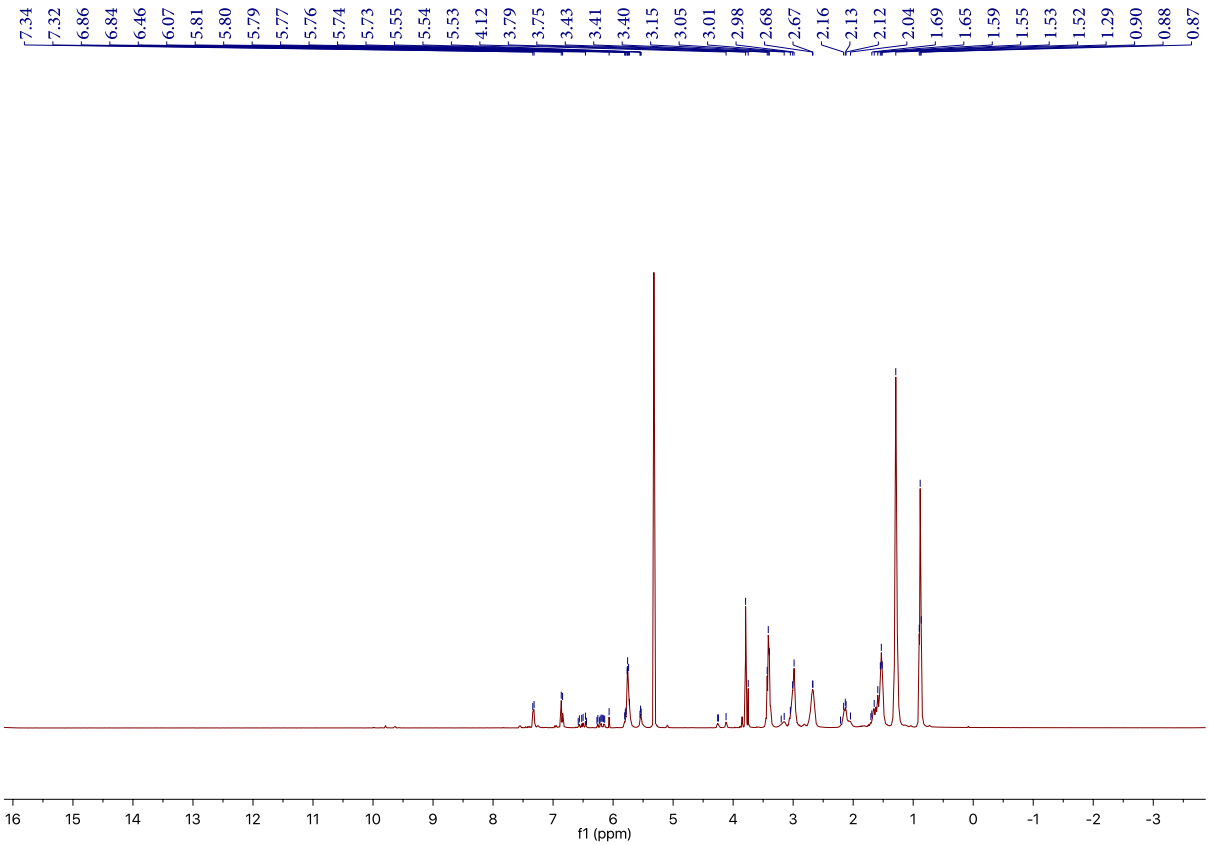


Figure S23 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 5**

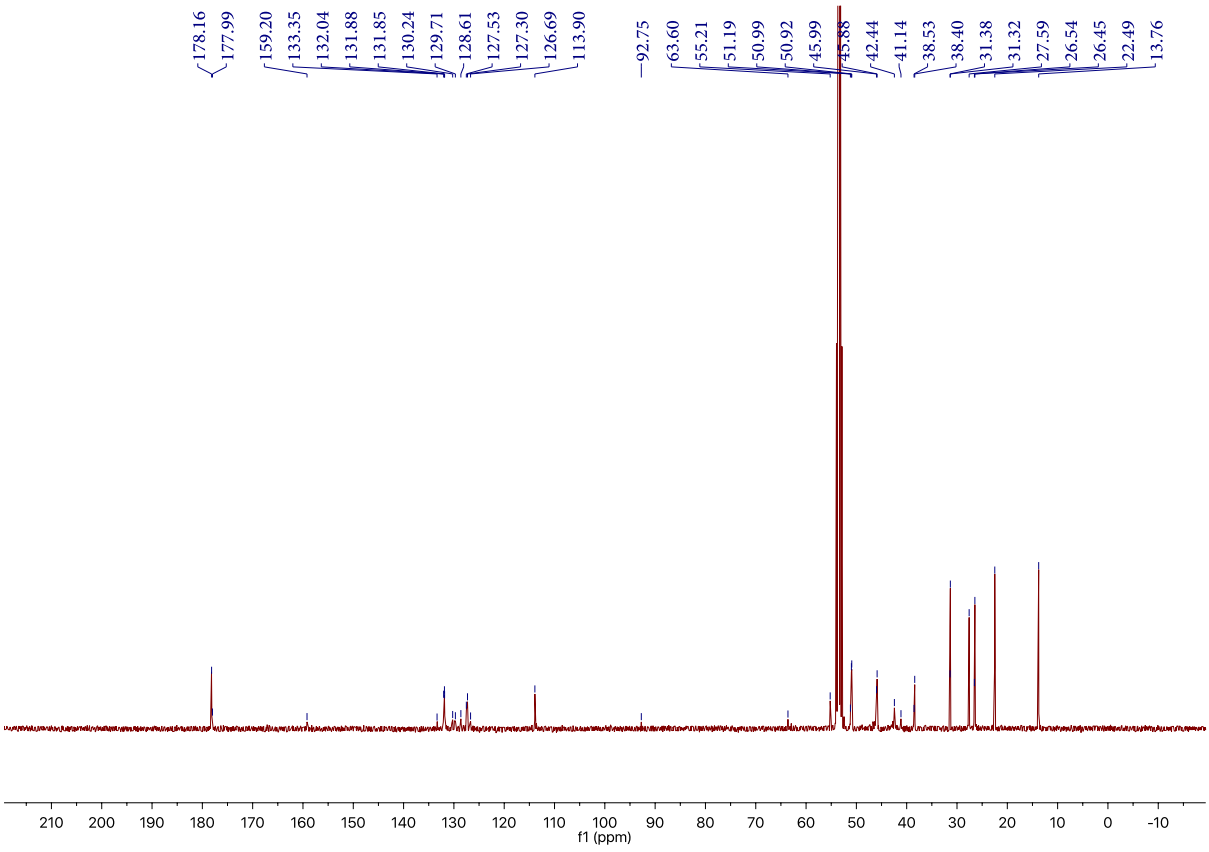


Figure S24 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 5**

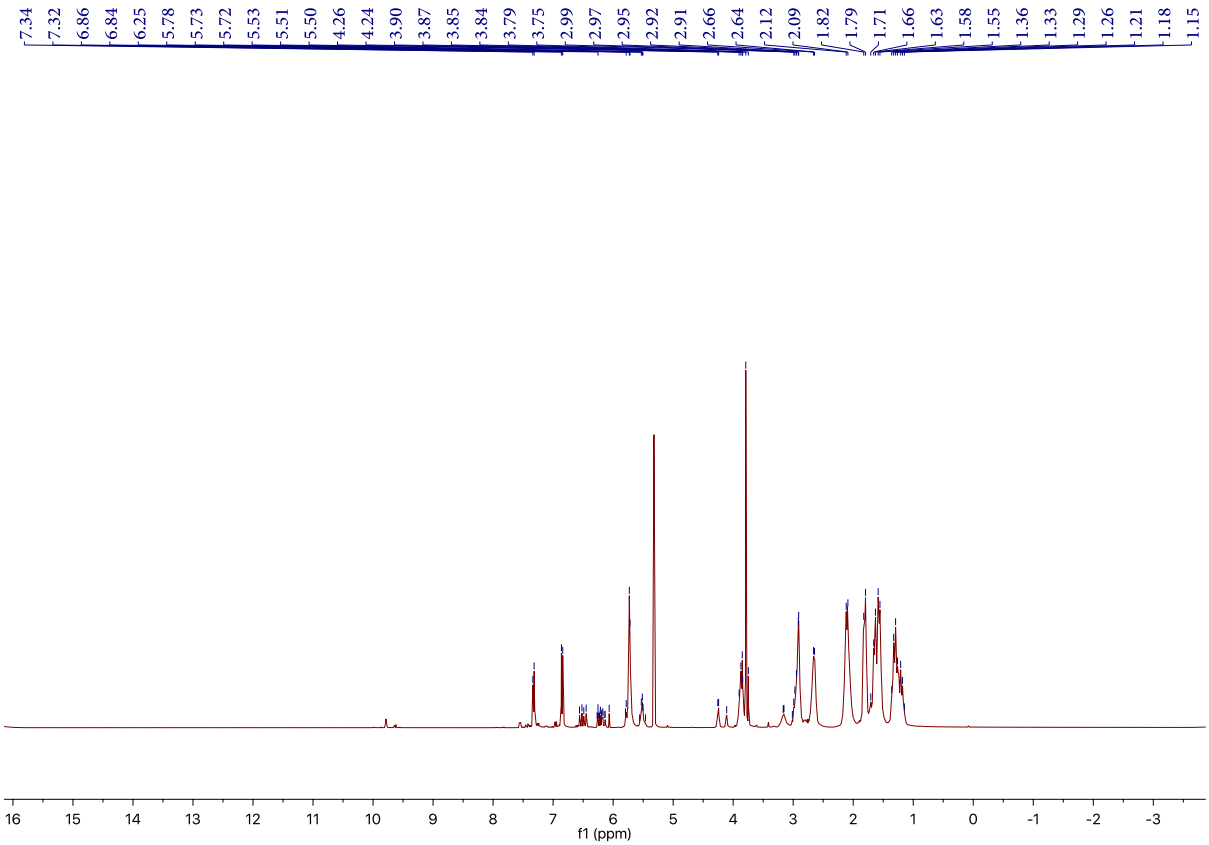


Figure S25 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 6**

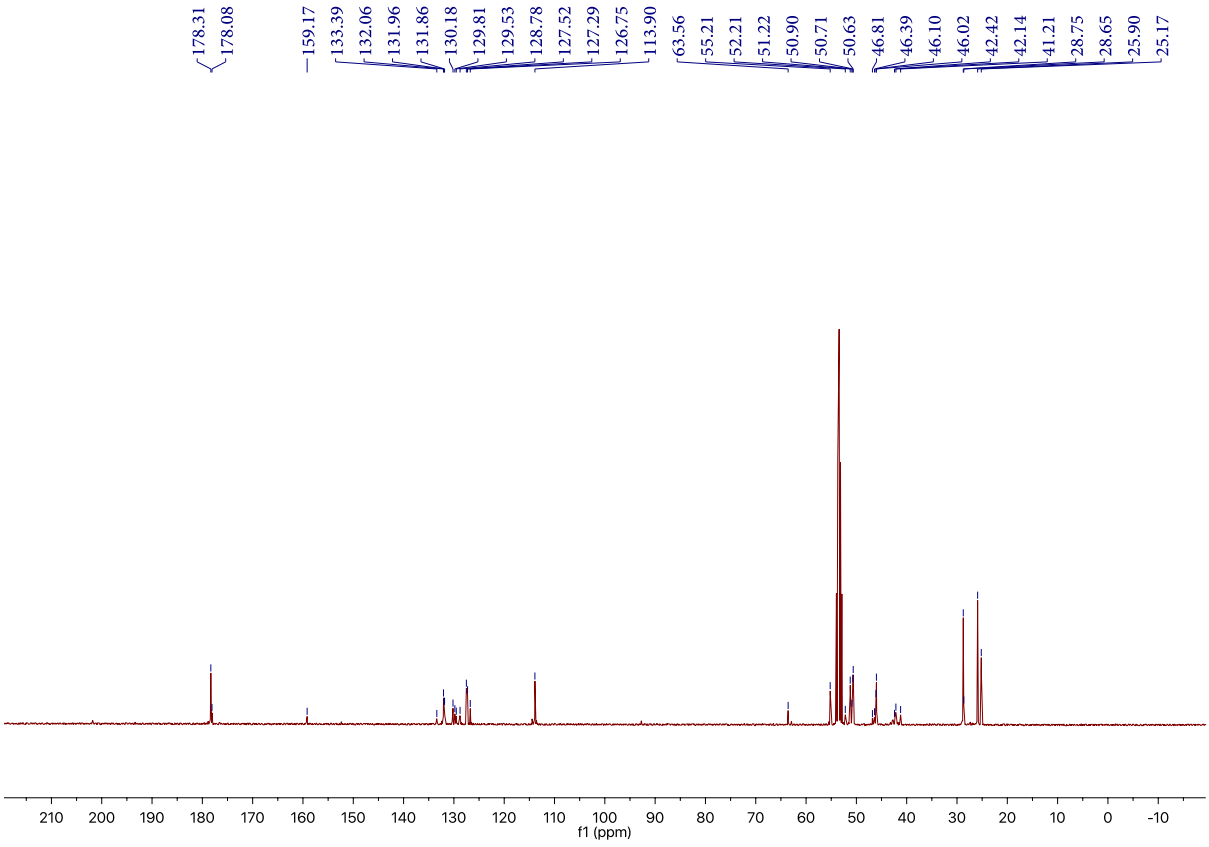


Figure S26 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 6**

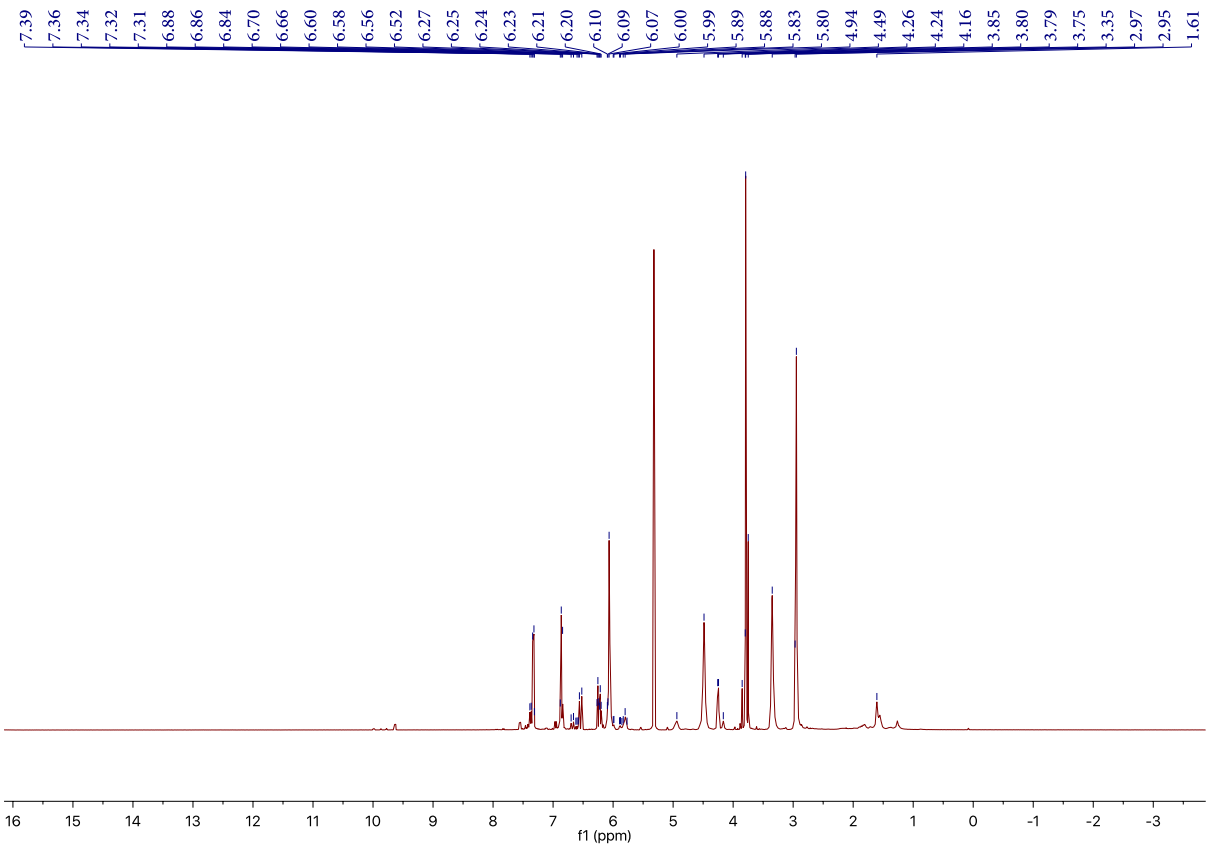


Figure S27 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 7**

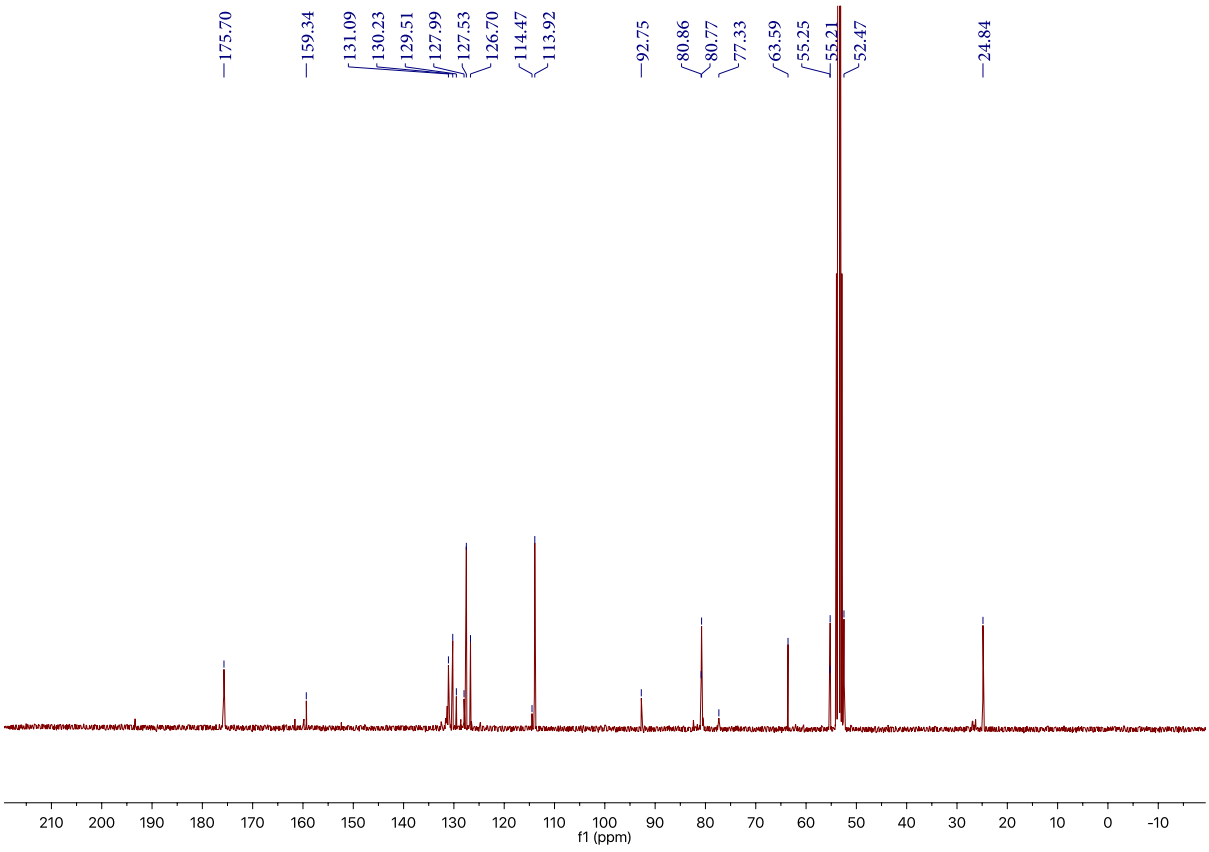


Figure S28 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 7**

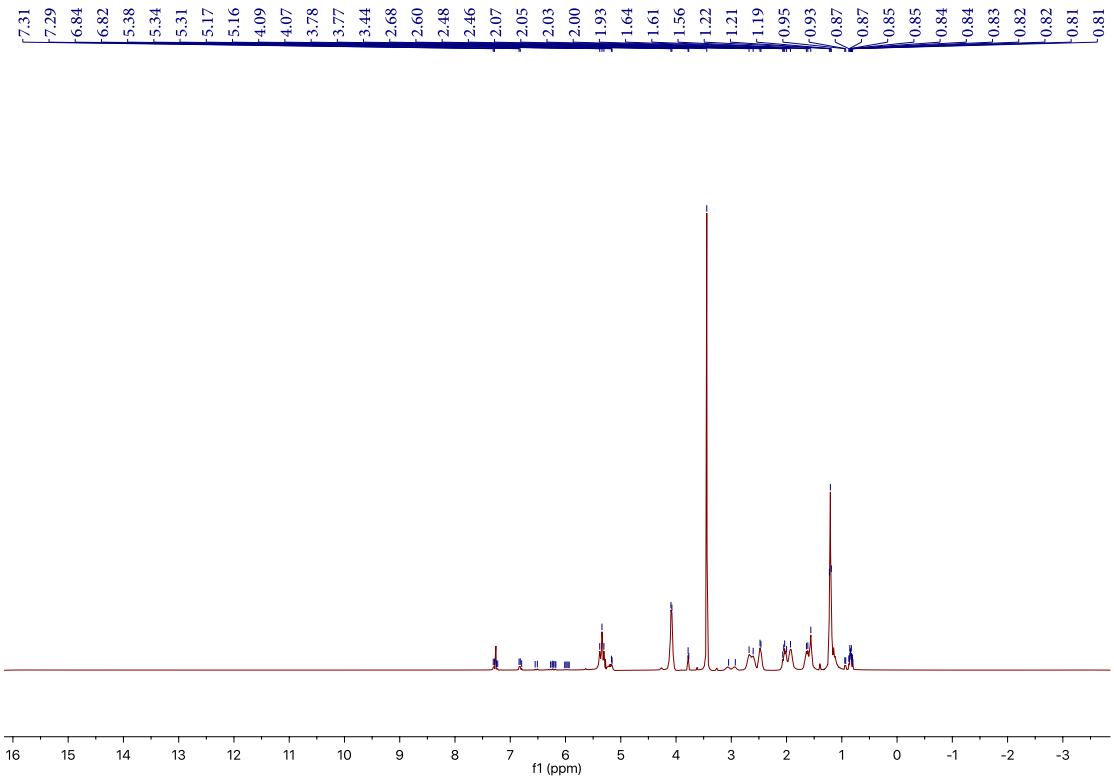


Figure S29 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 8**

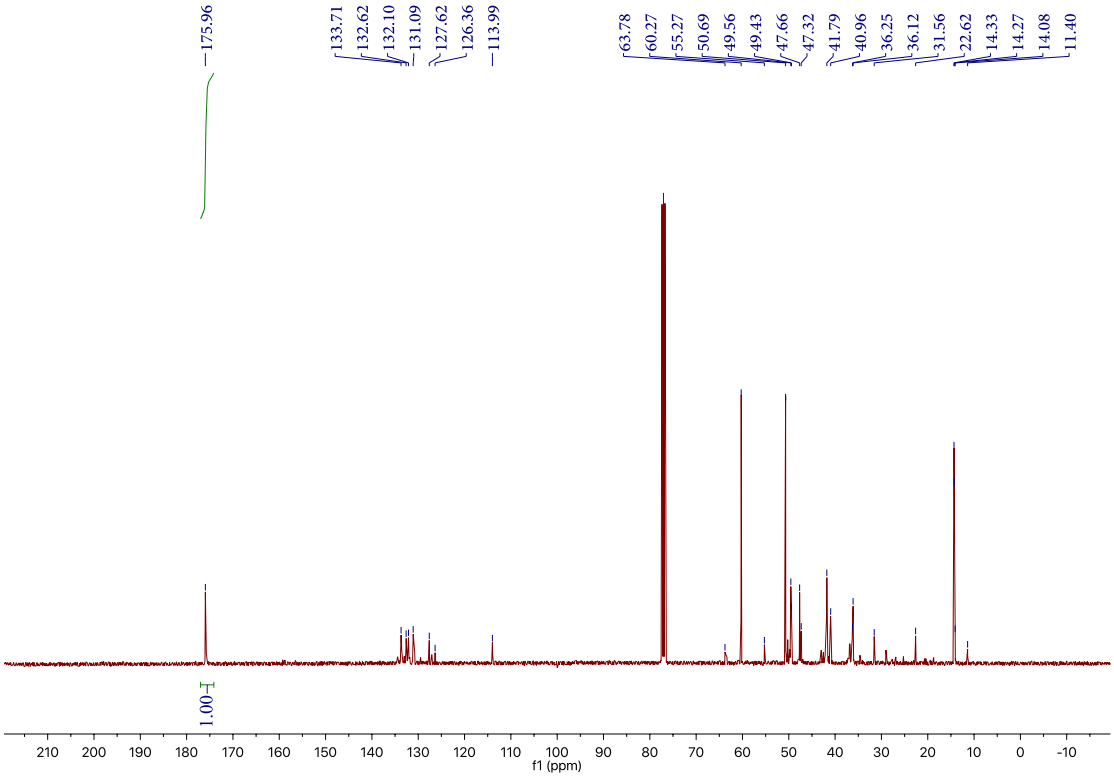


Figure S30 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 8**

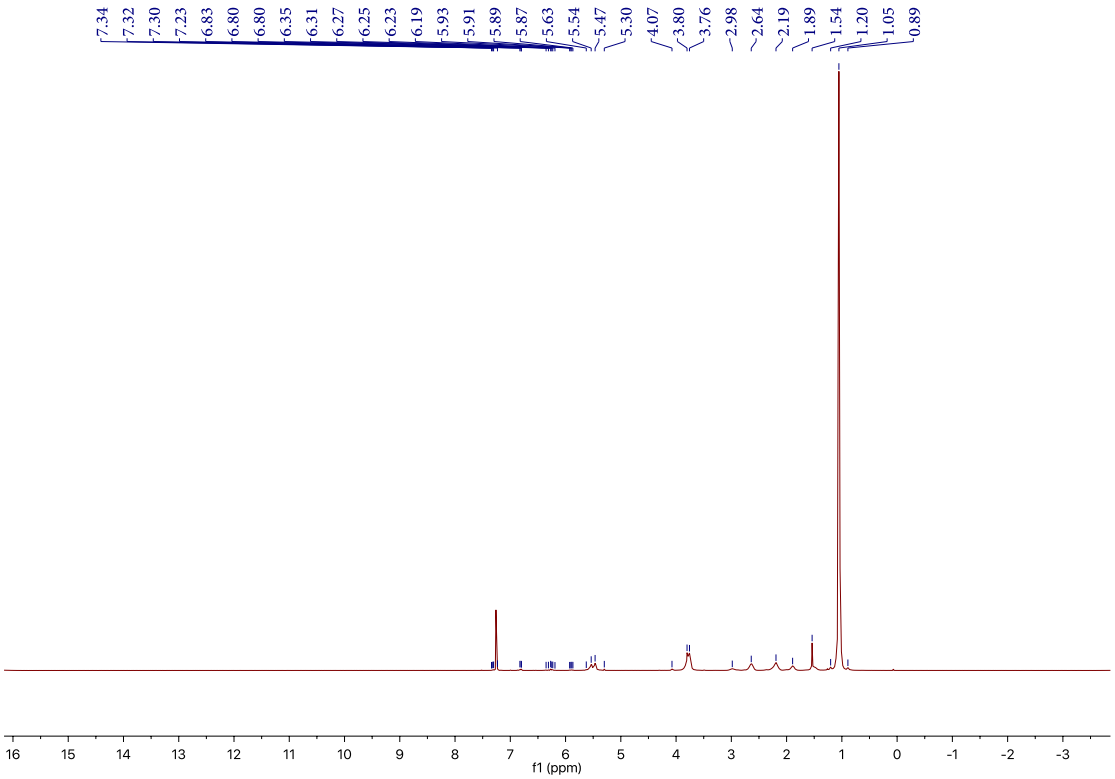


Figure S31 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 9**

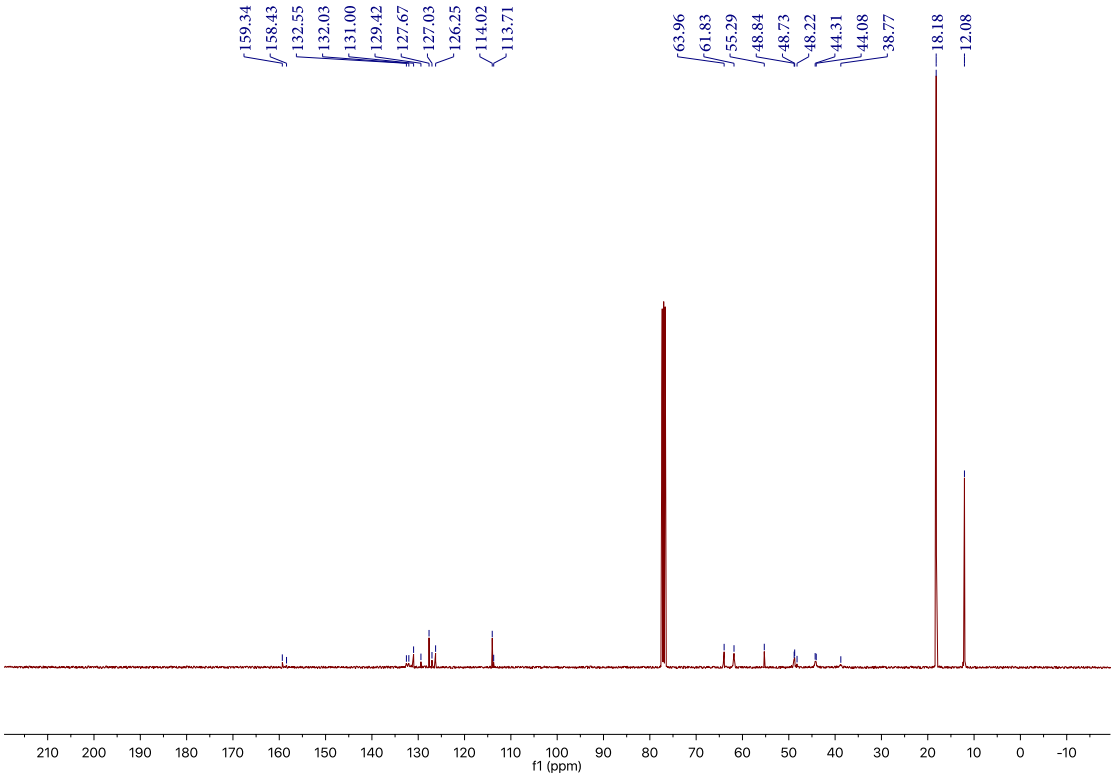


Figure S32 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 9**

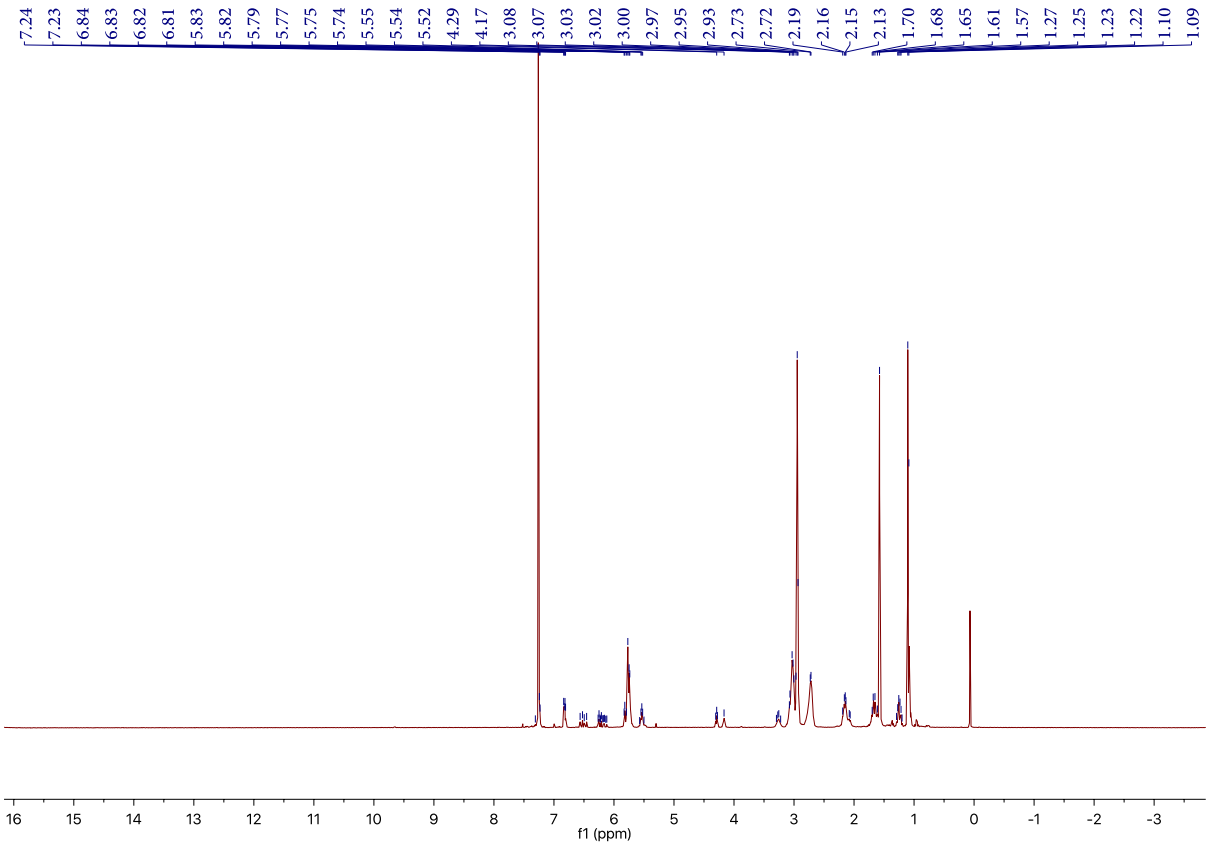


Figure S33 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 10**

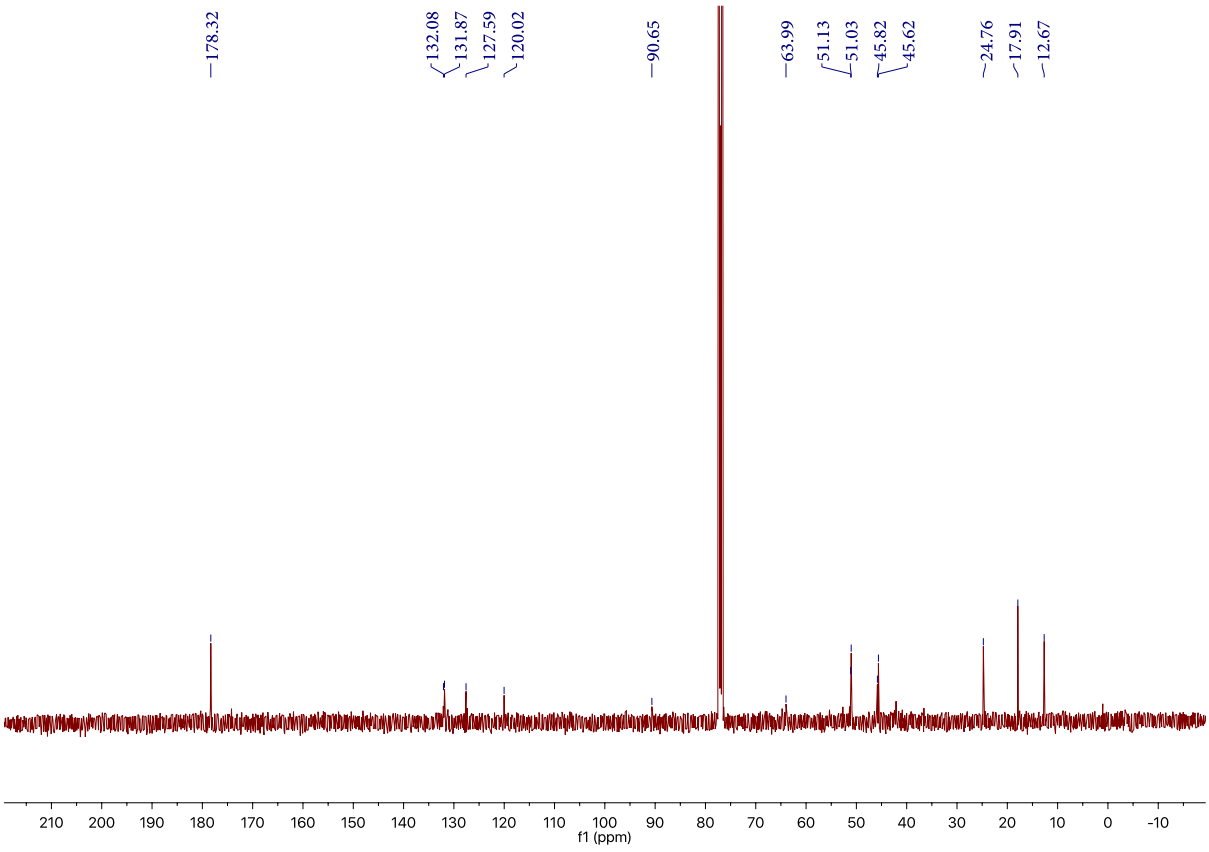


Figure S34 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 10**

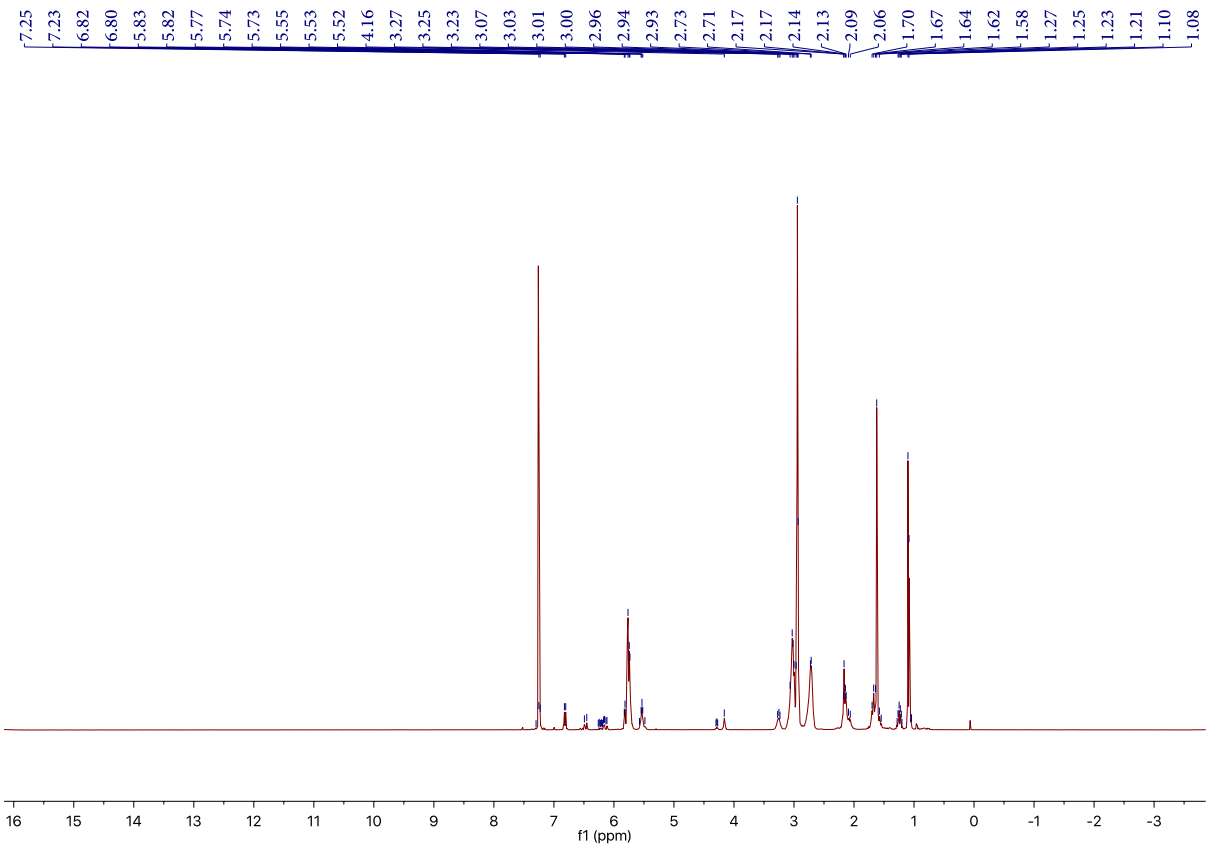


Figure S35 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 11**

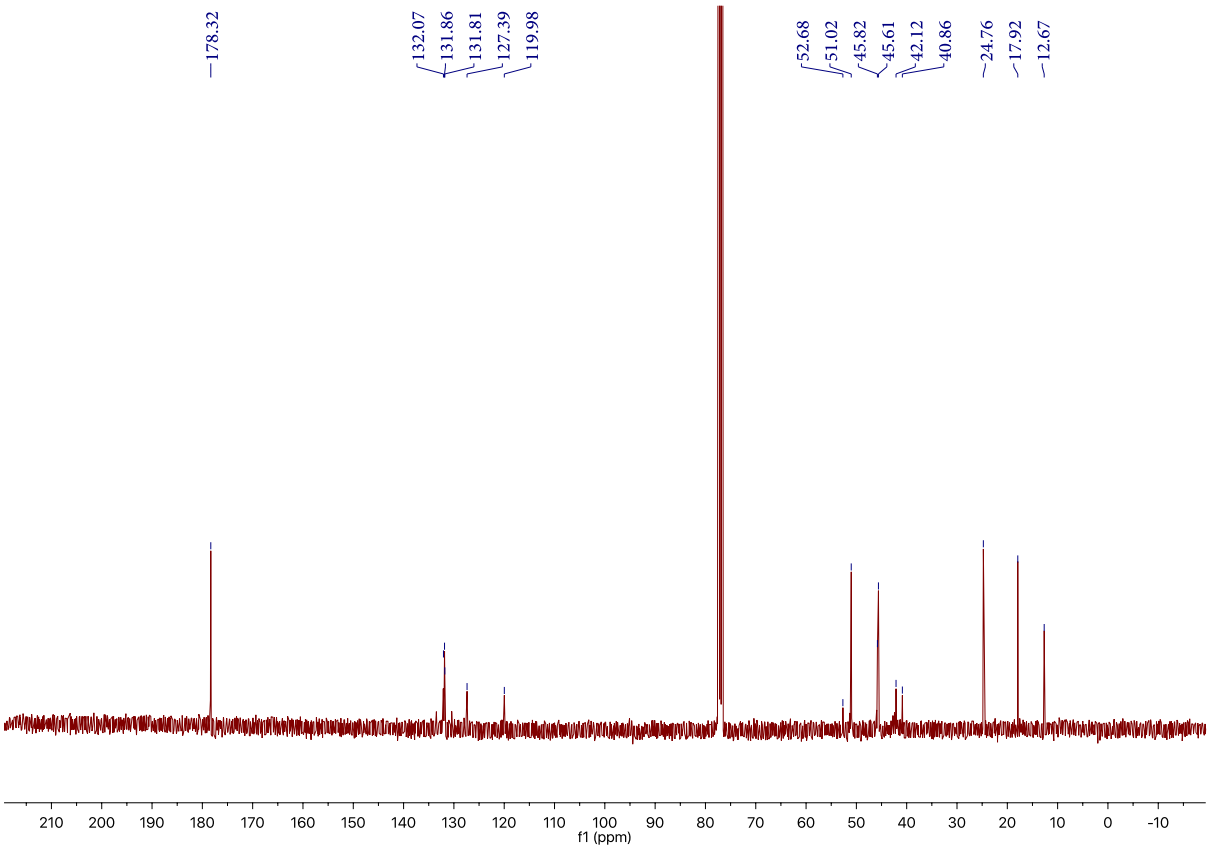


Figure S36 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 11**

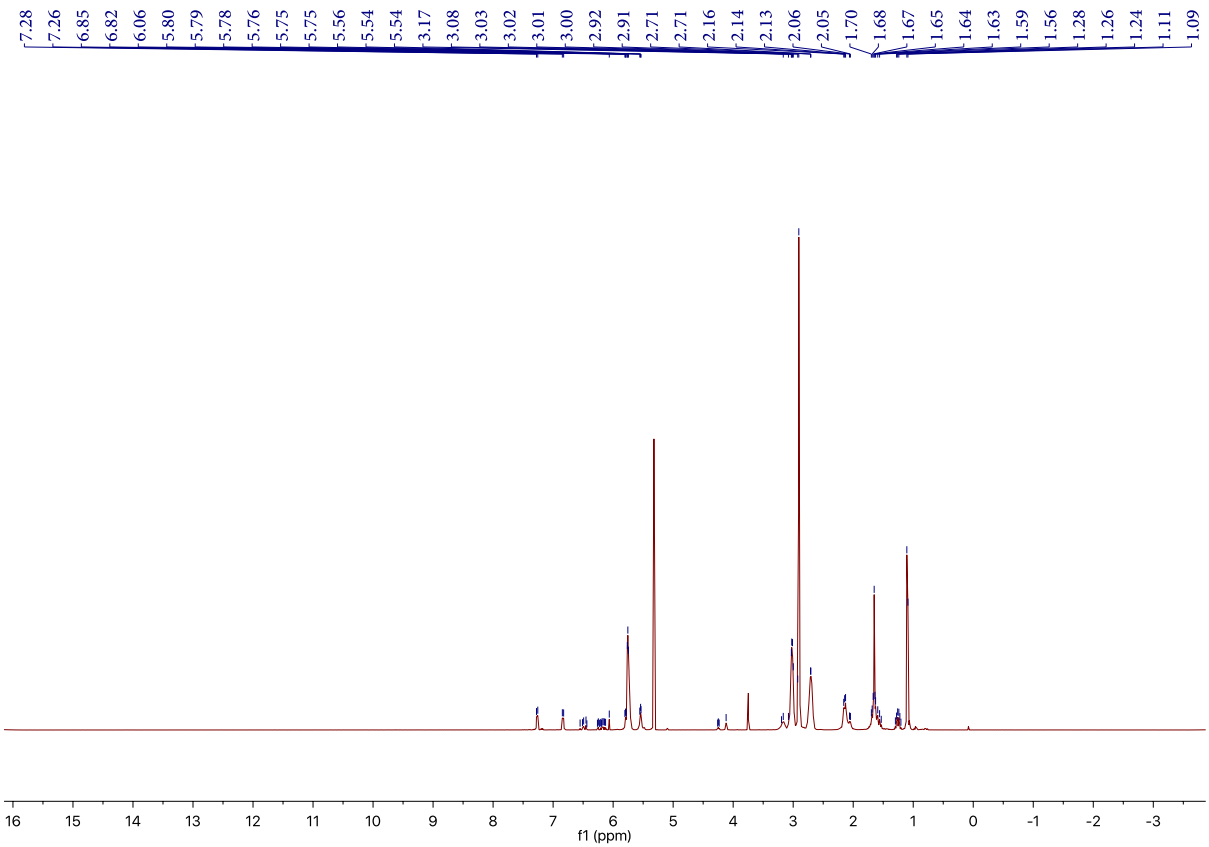


Figure S37 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 12**

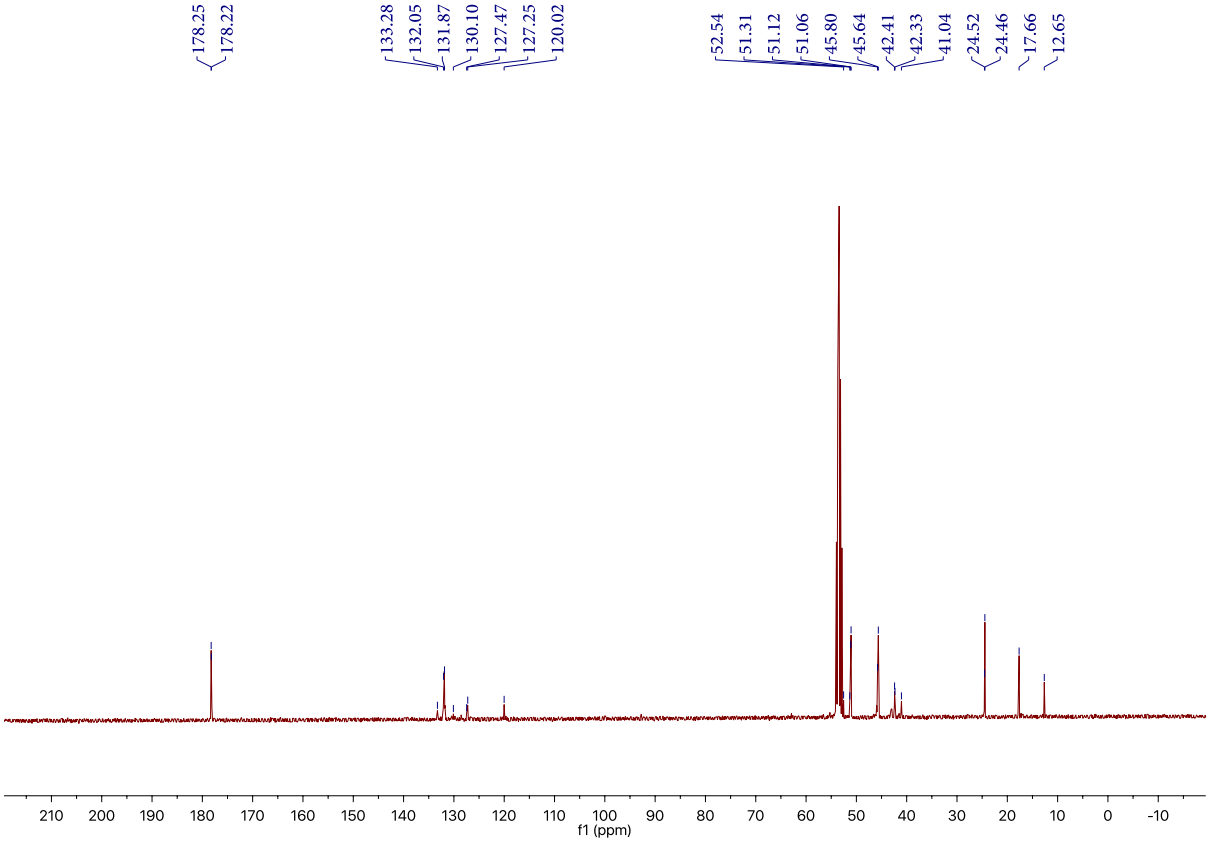


Figure S38 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 12**

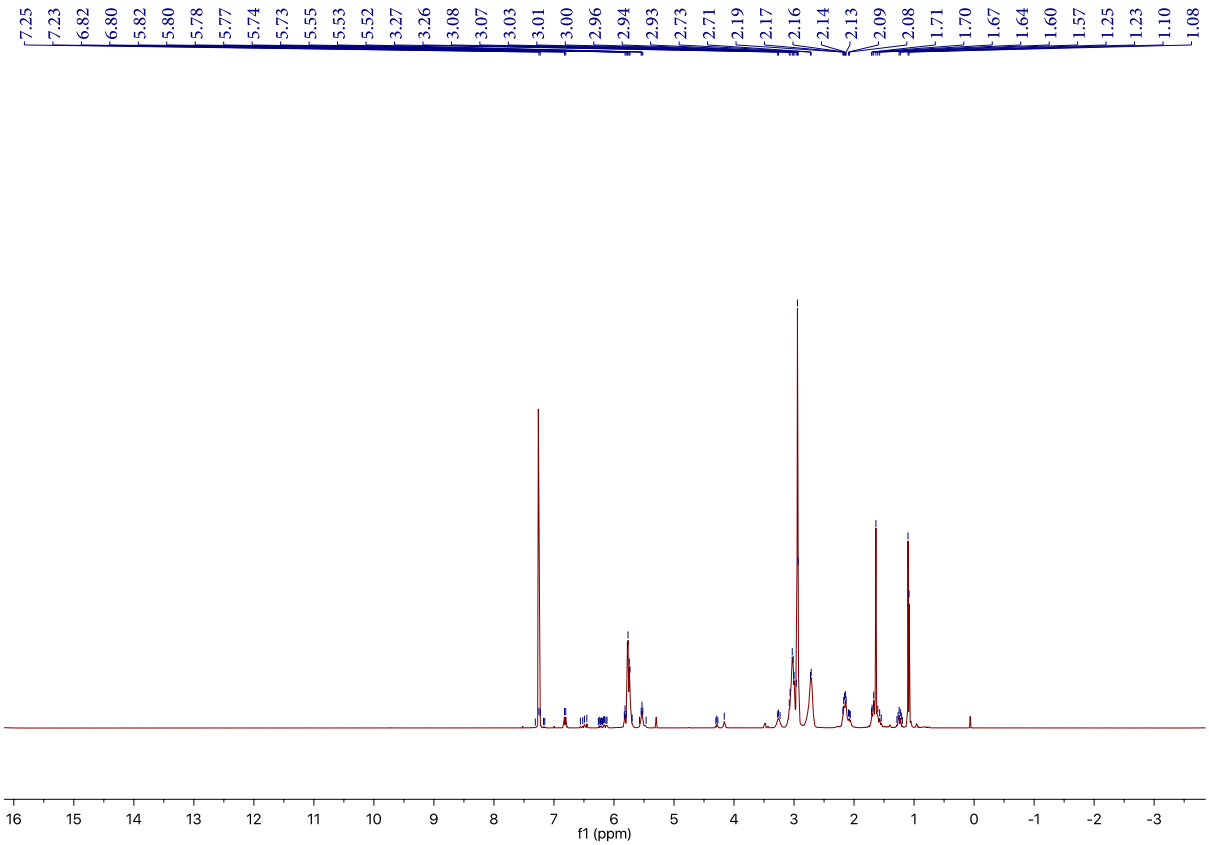


Figure S39 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 13**

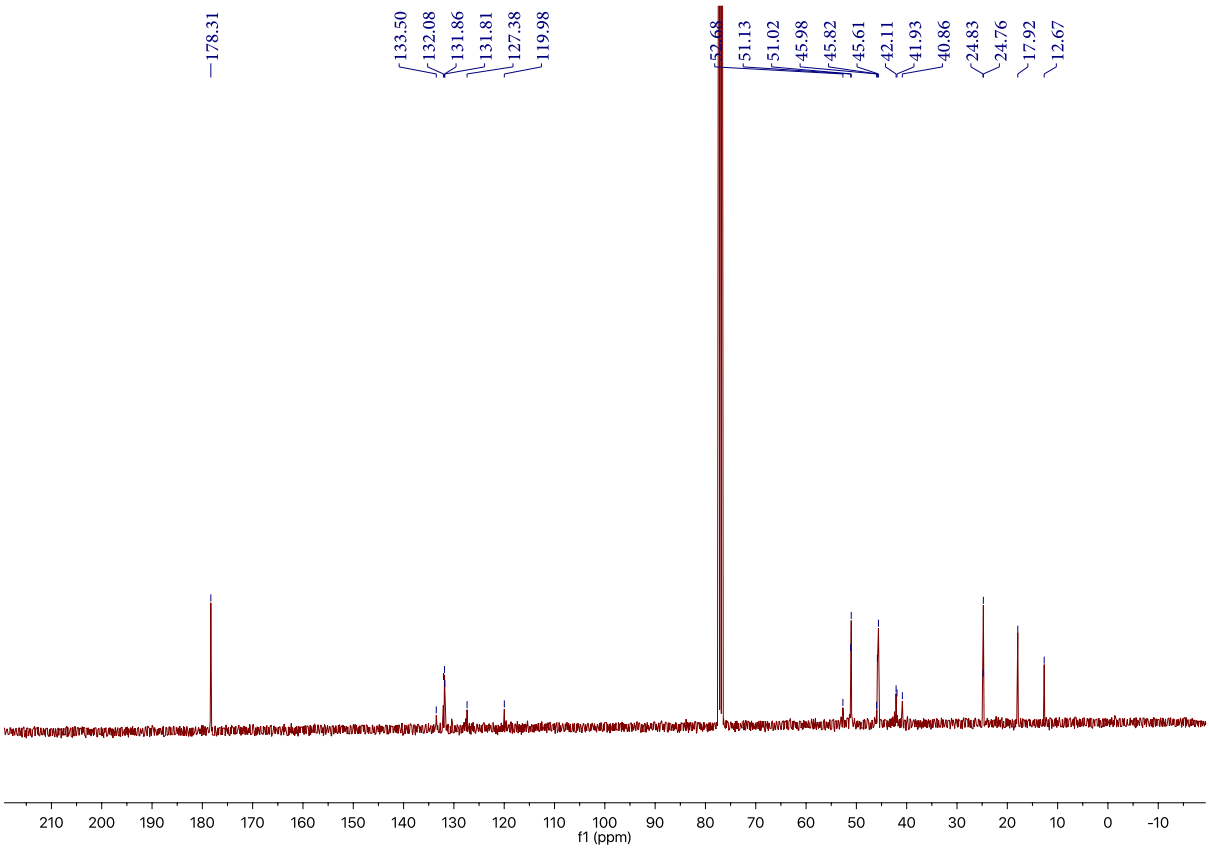


Figure S40 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 13**

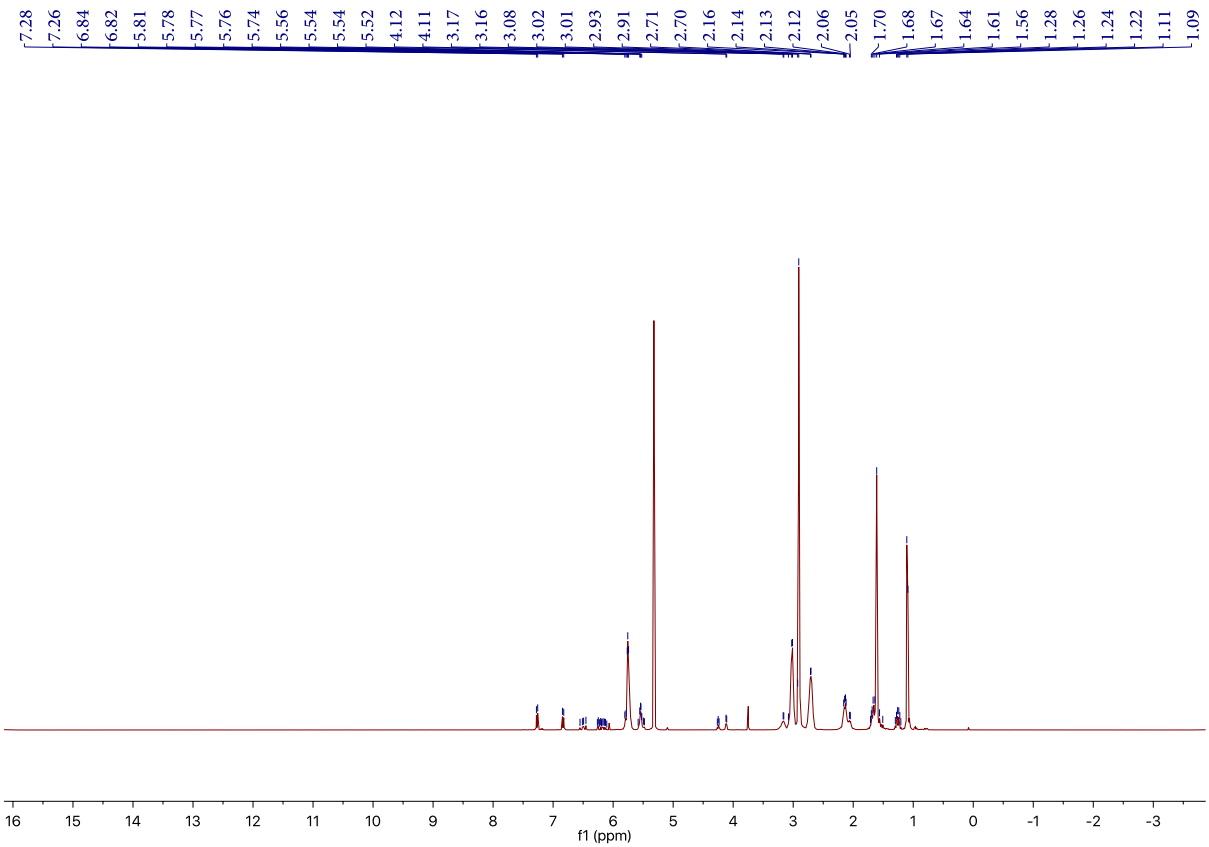


Figure S41 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 14**

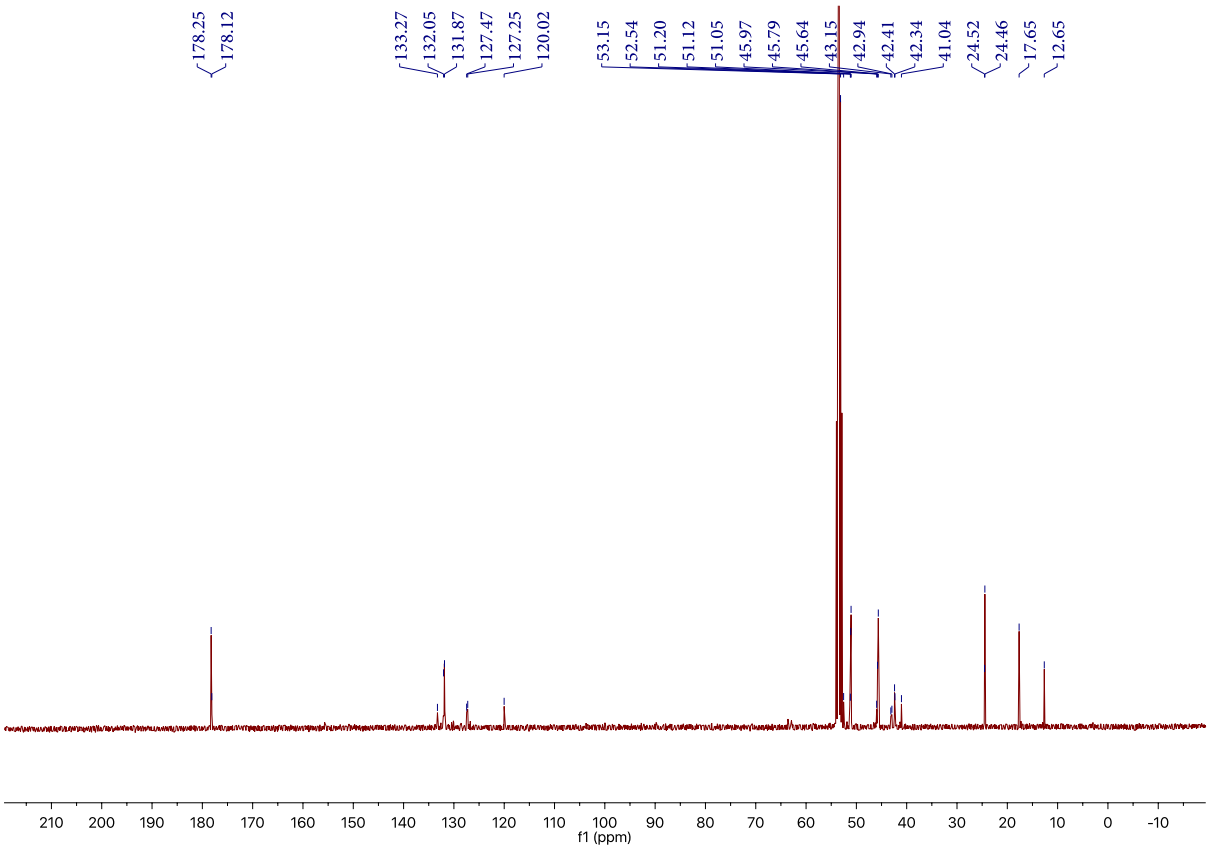


Figure S42 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 14**

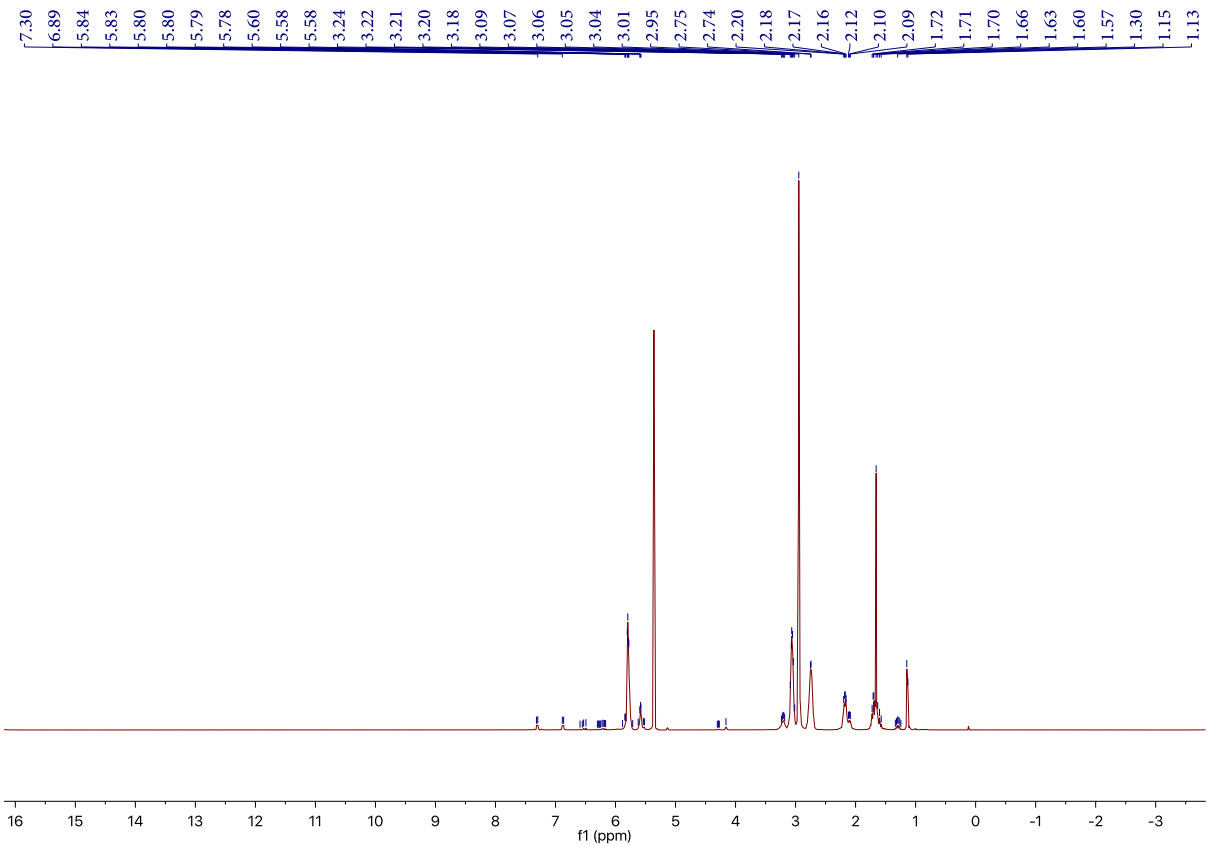


Figure S43 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 15**

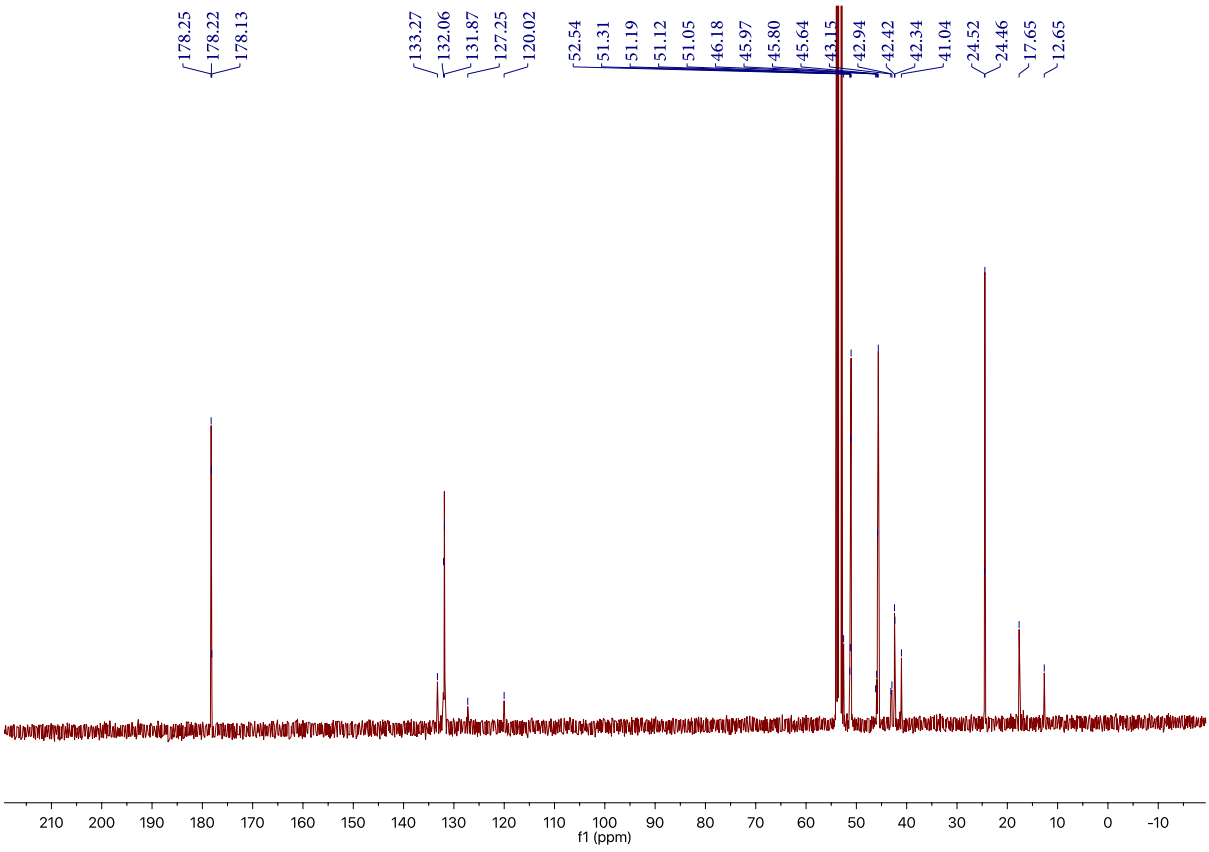


Figure S44 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 15**

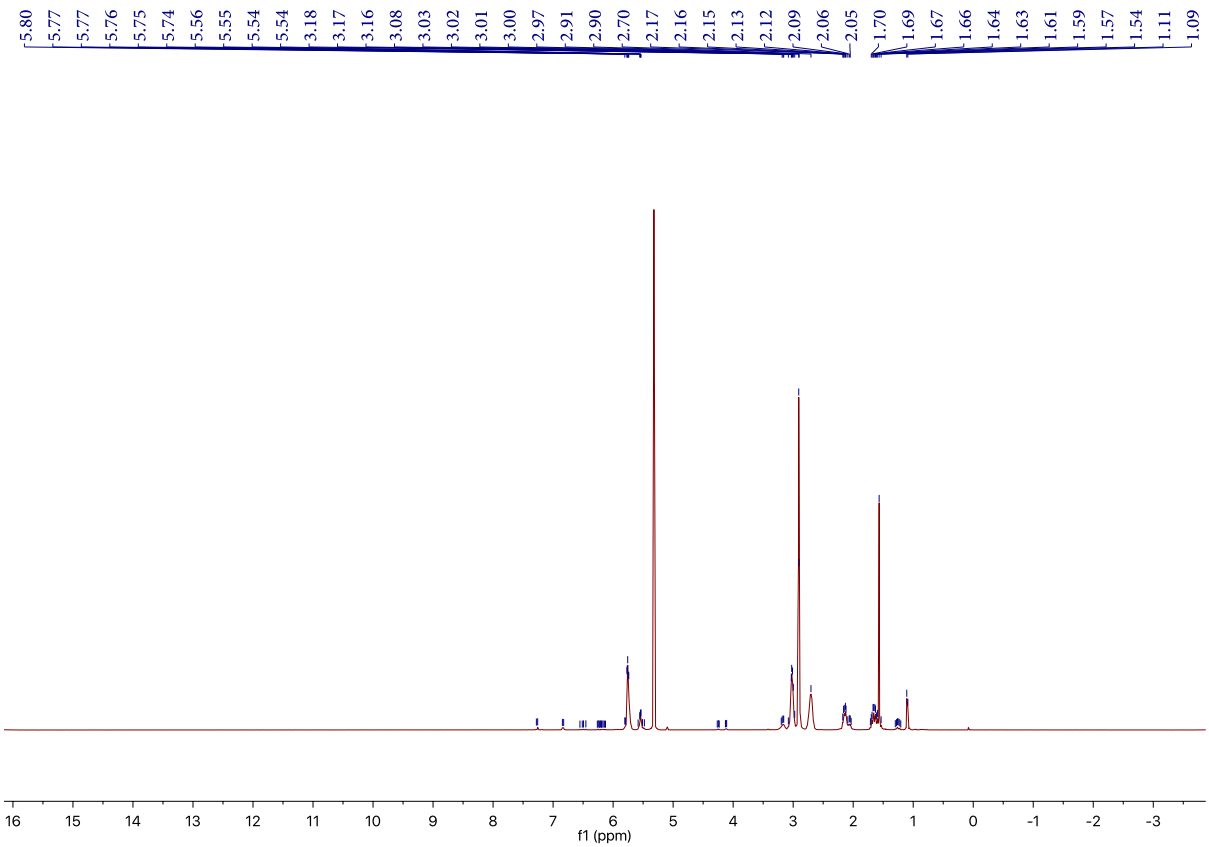


Figure S45 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 16**

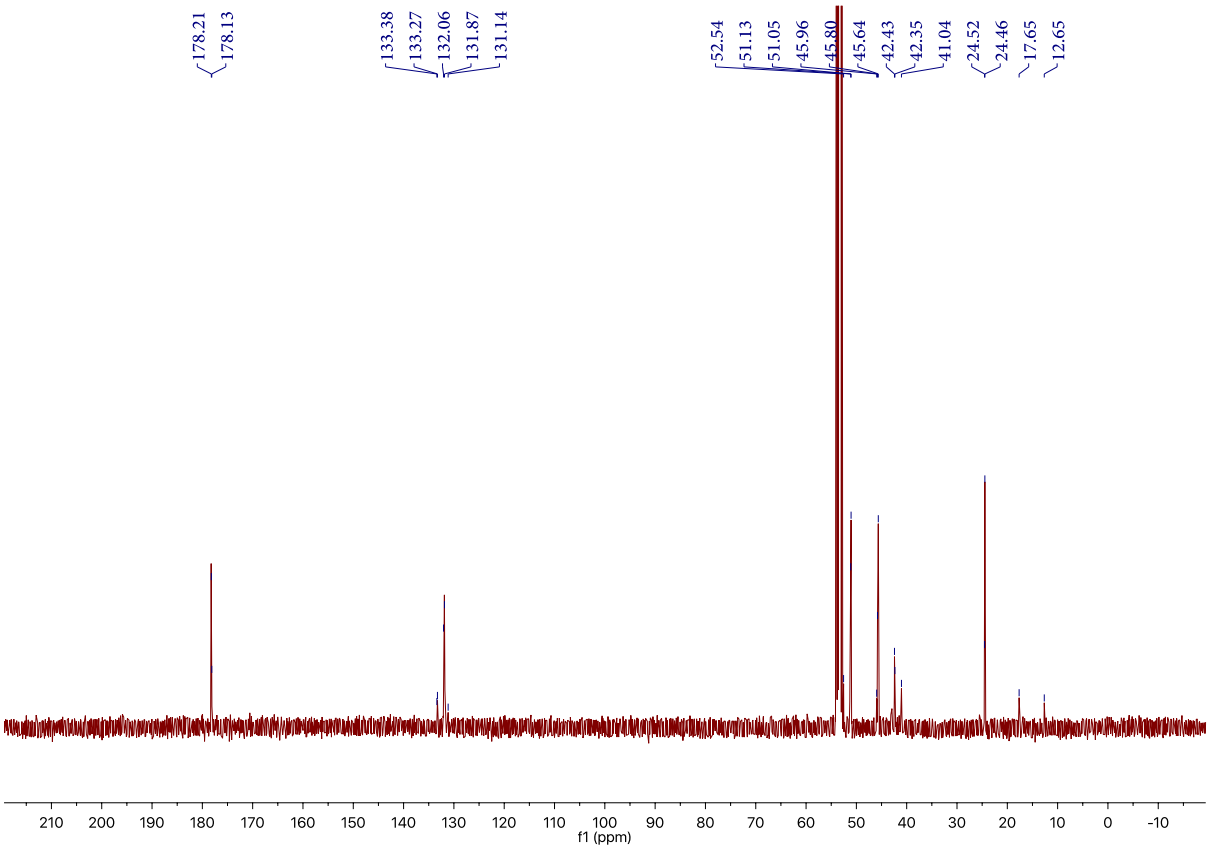


Figure S46 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 16**

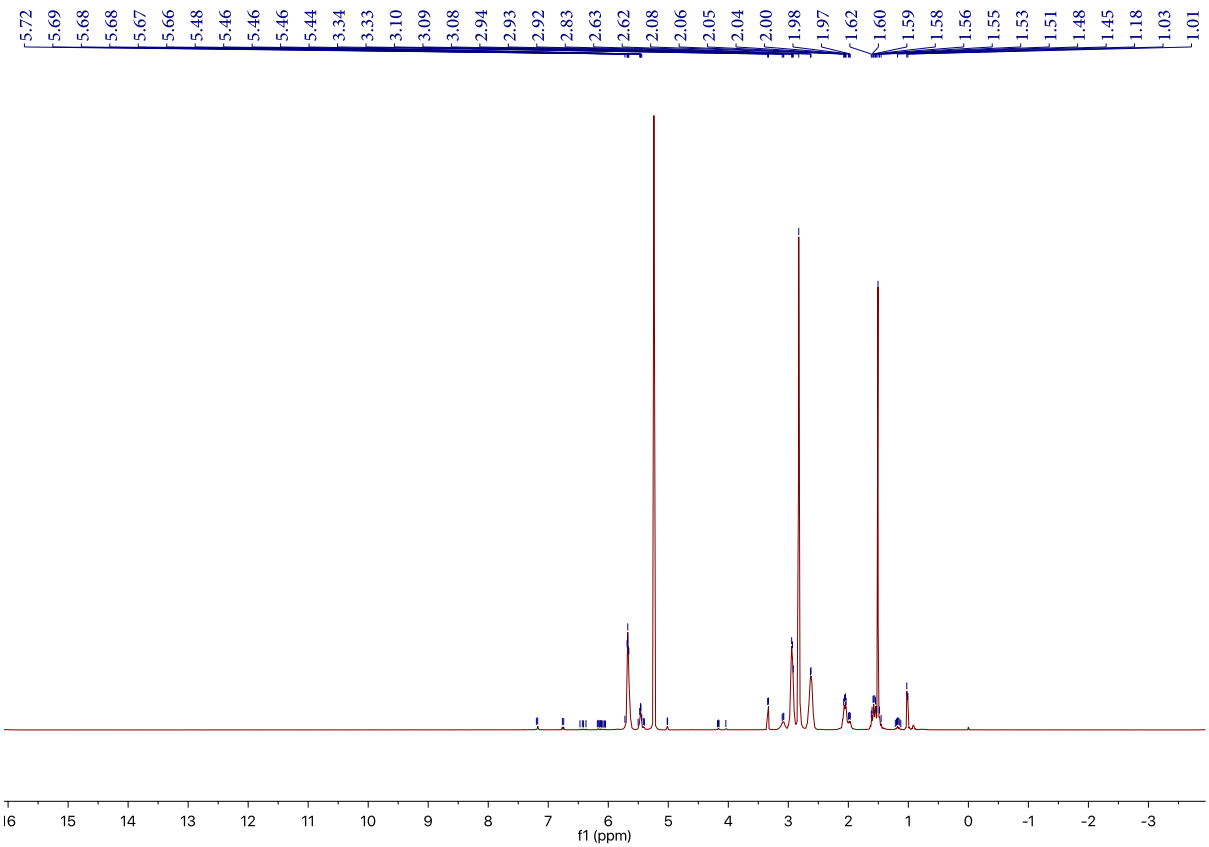


Figure S47 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 17**

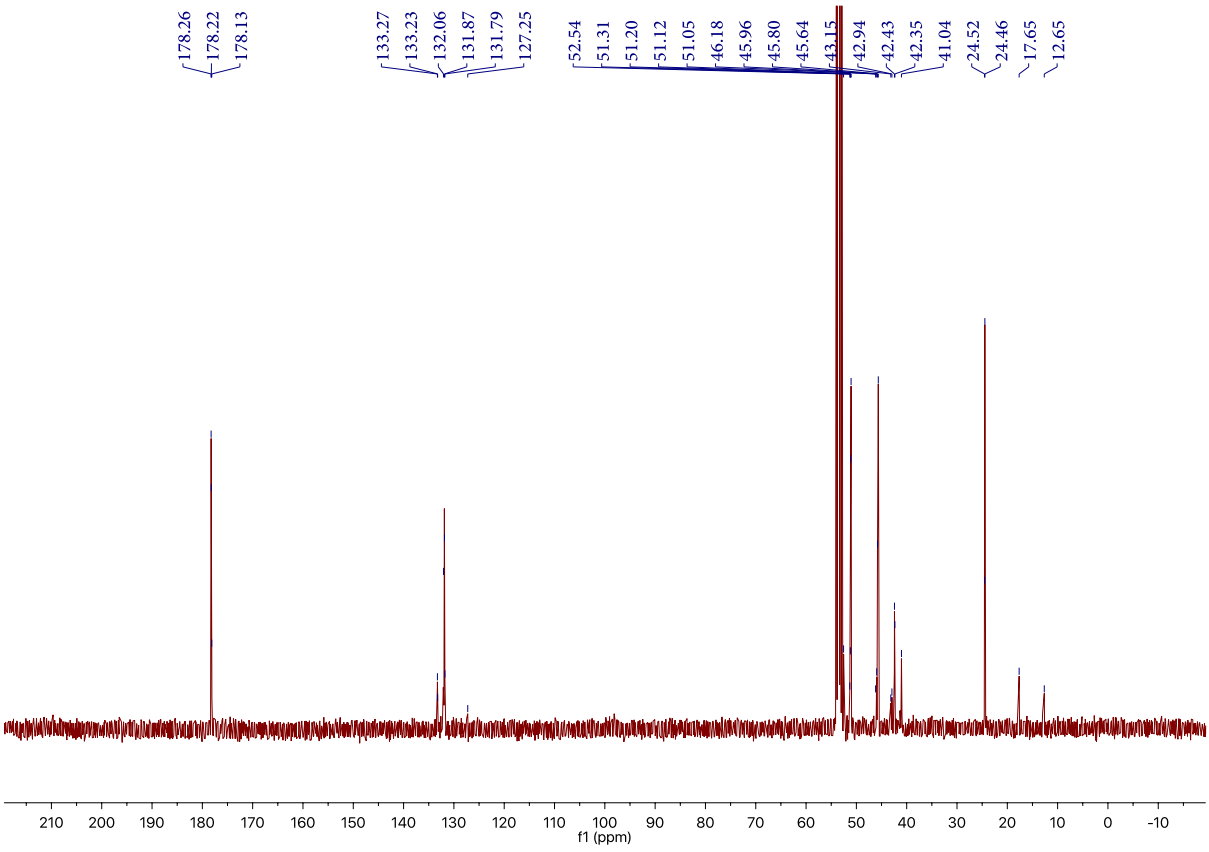


Figure S48 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 17**

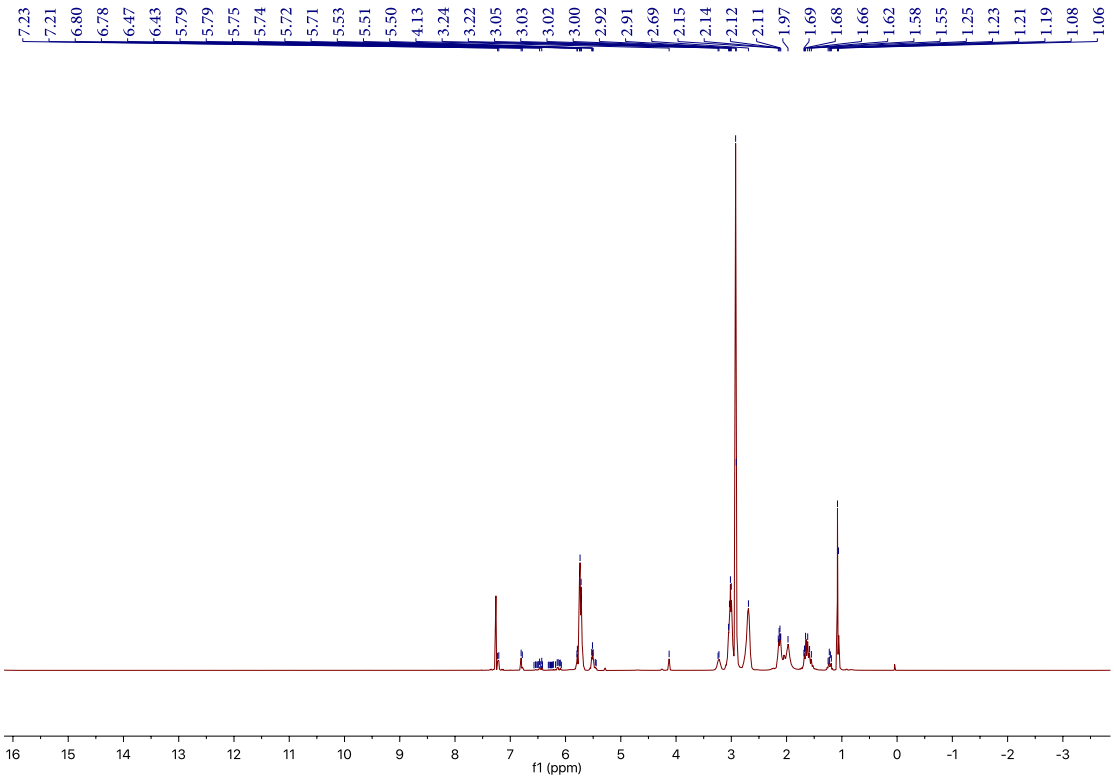


Figure S49 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 18**

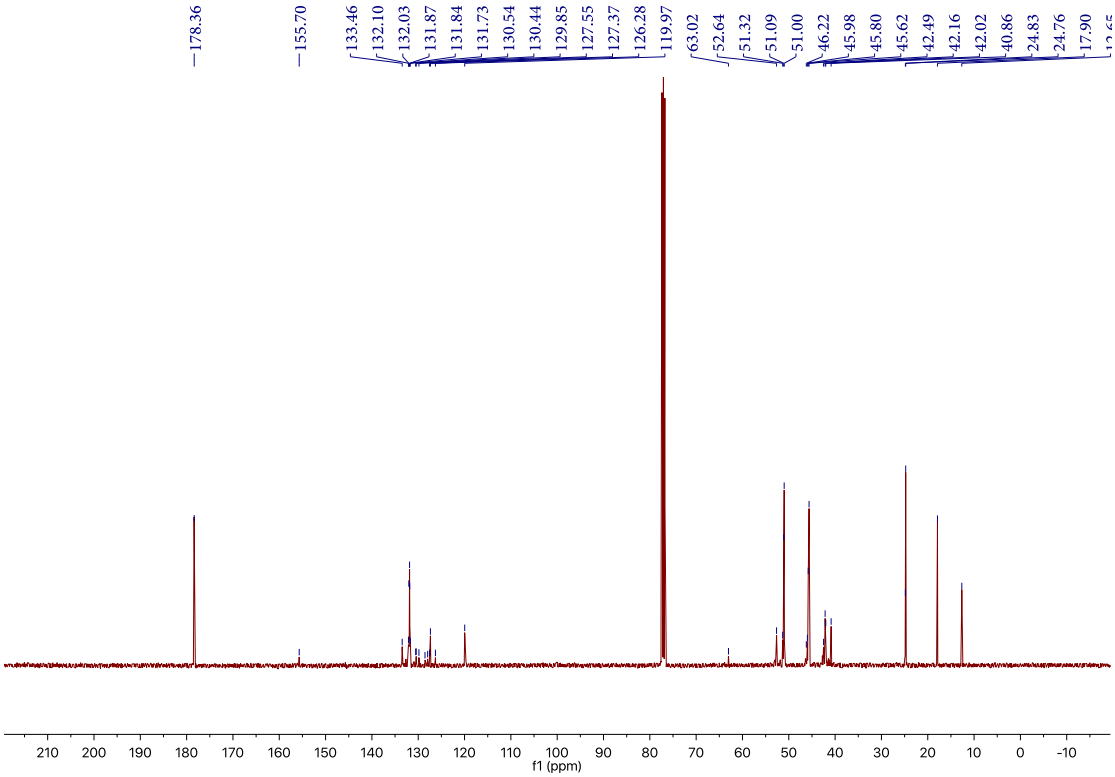


Figure S50 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 18**

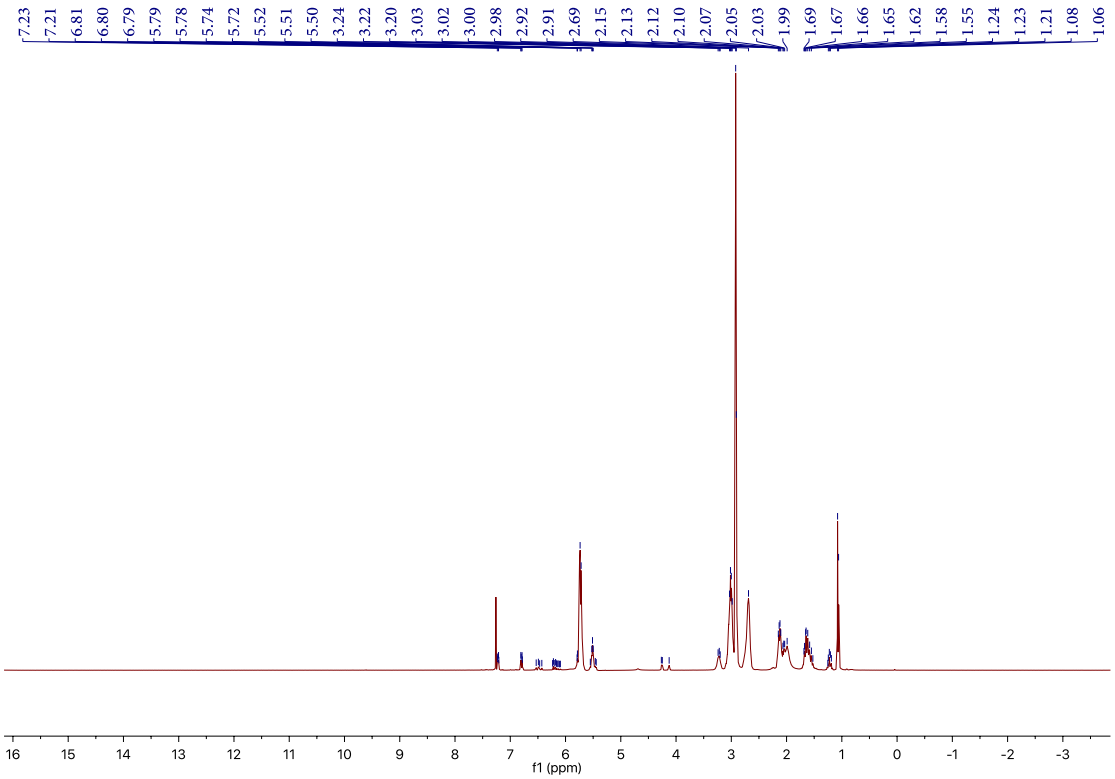


Figure S51 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 19**

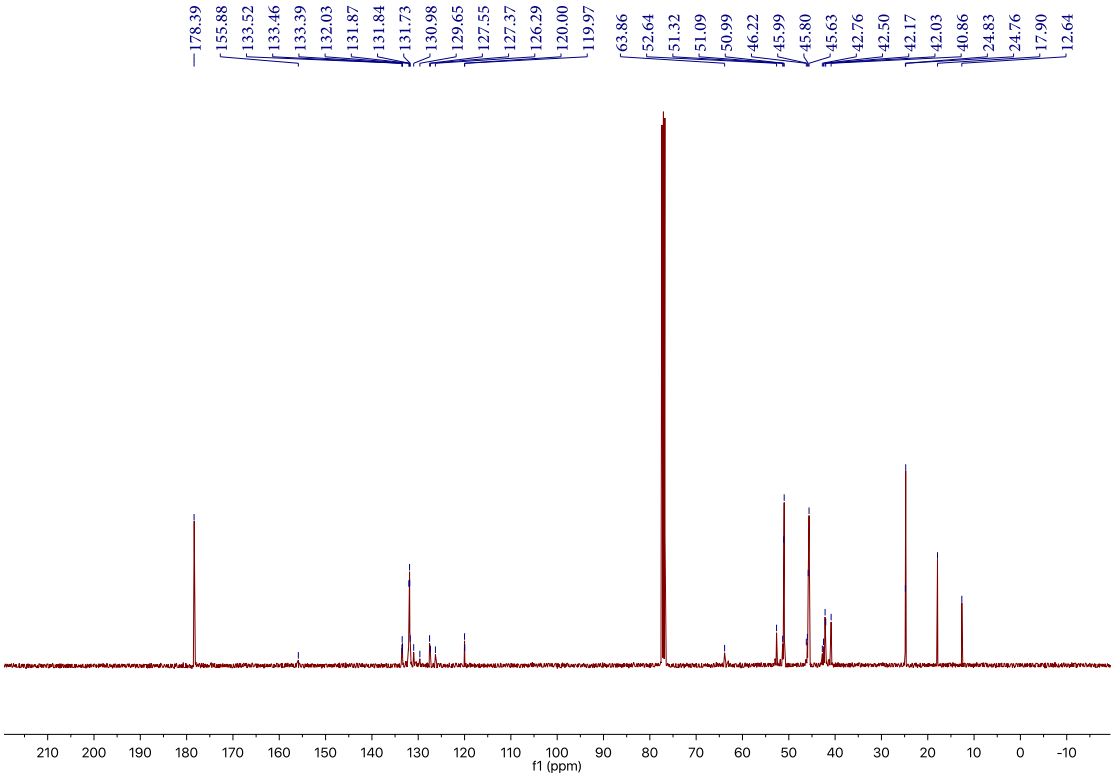


Figure S52 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 19**

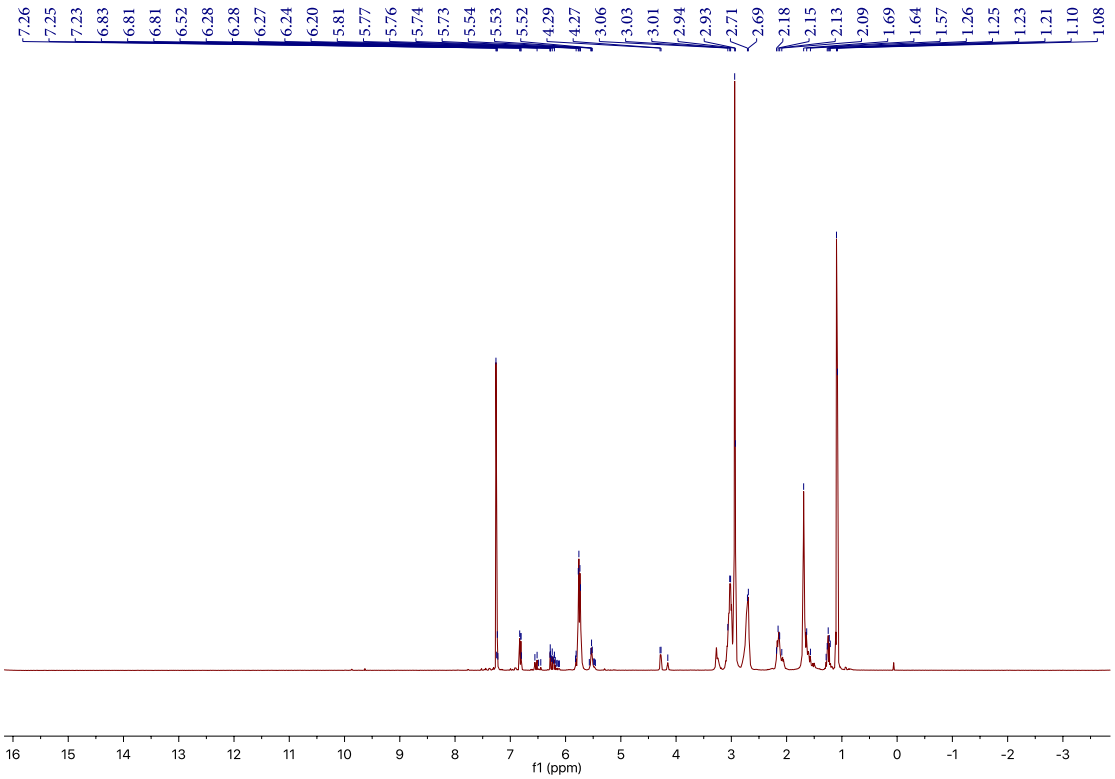


Figure S53 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 20**

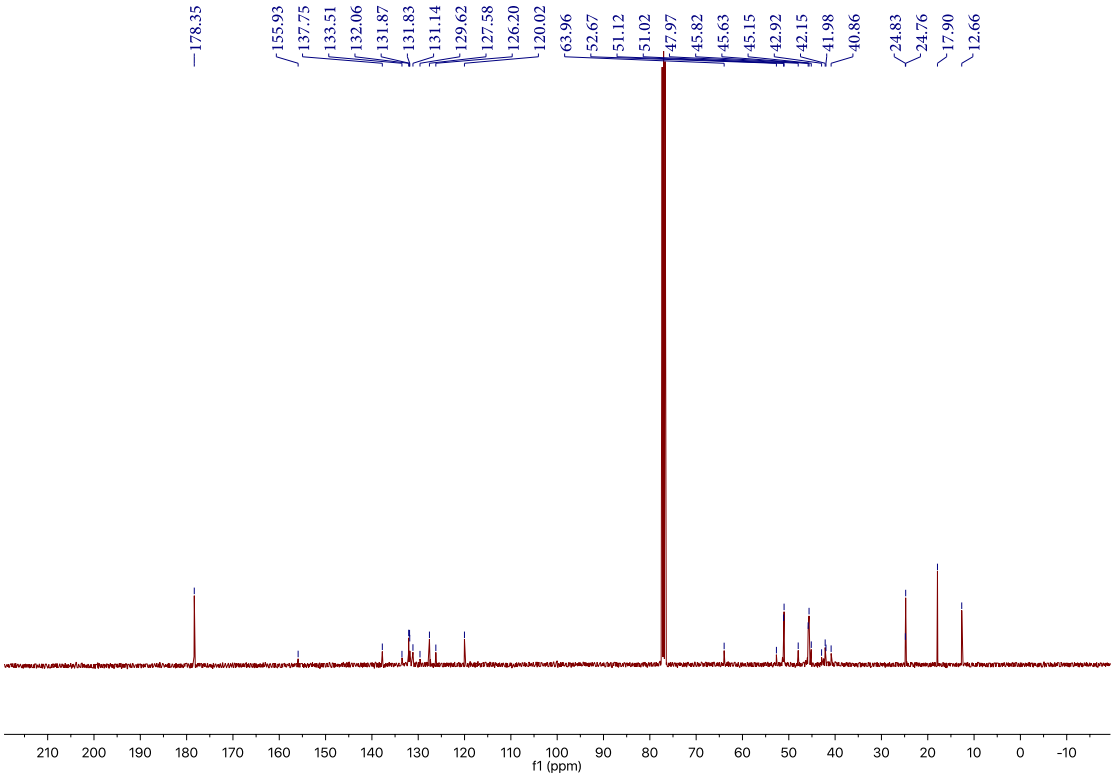


Figure S54 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 20**

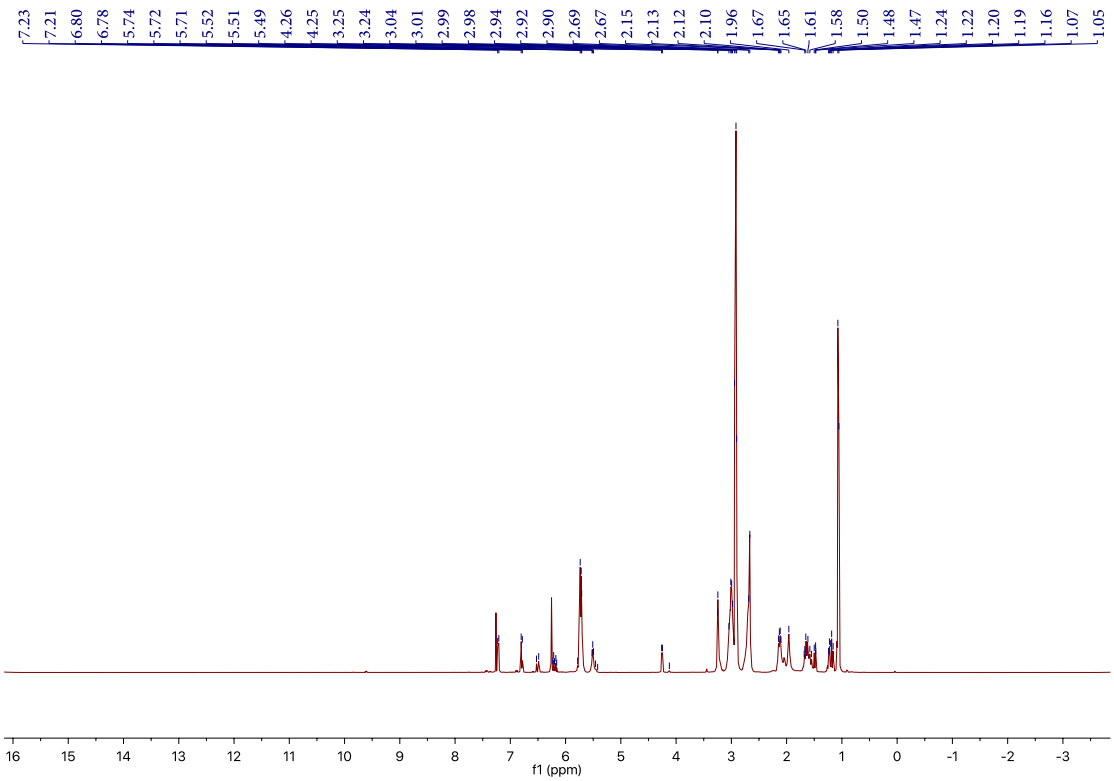


Figure S55 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 21**

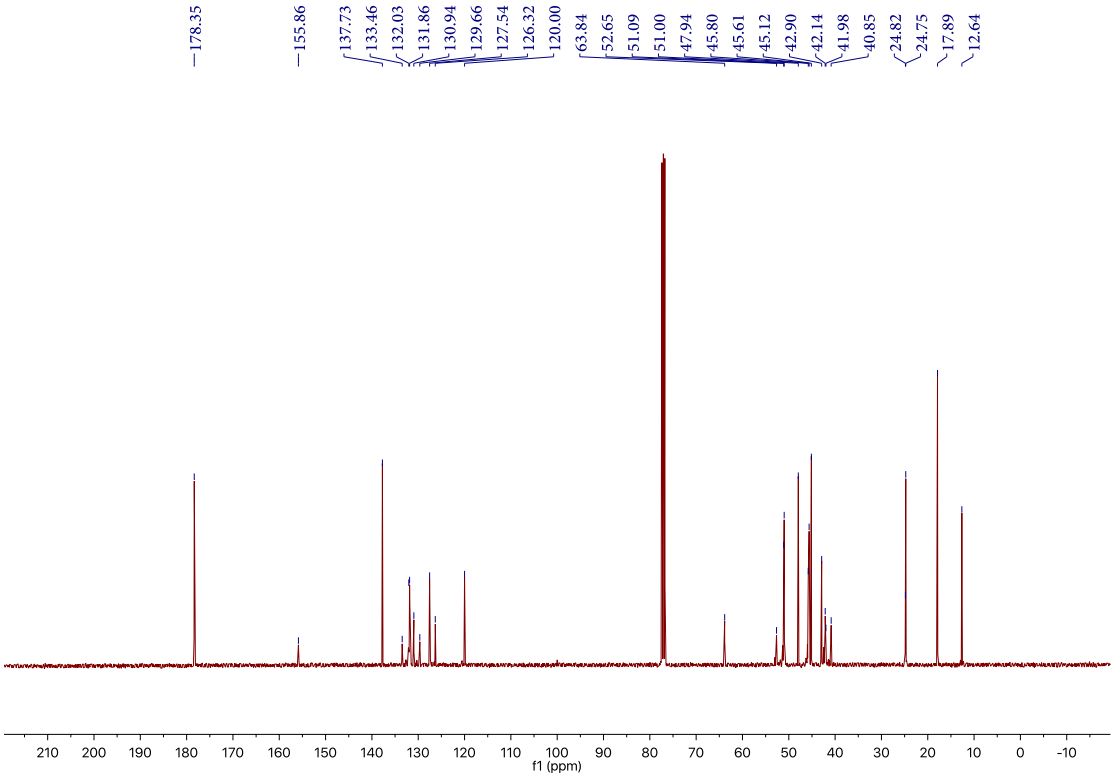


Figure S56 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 21**

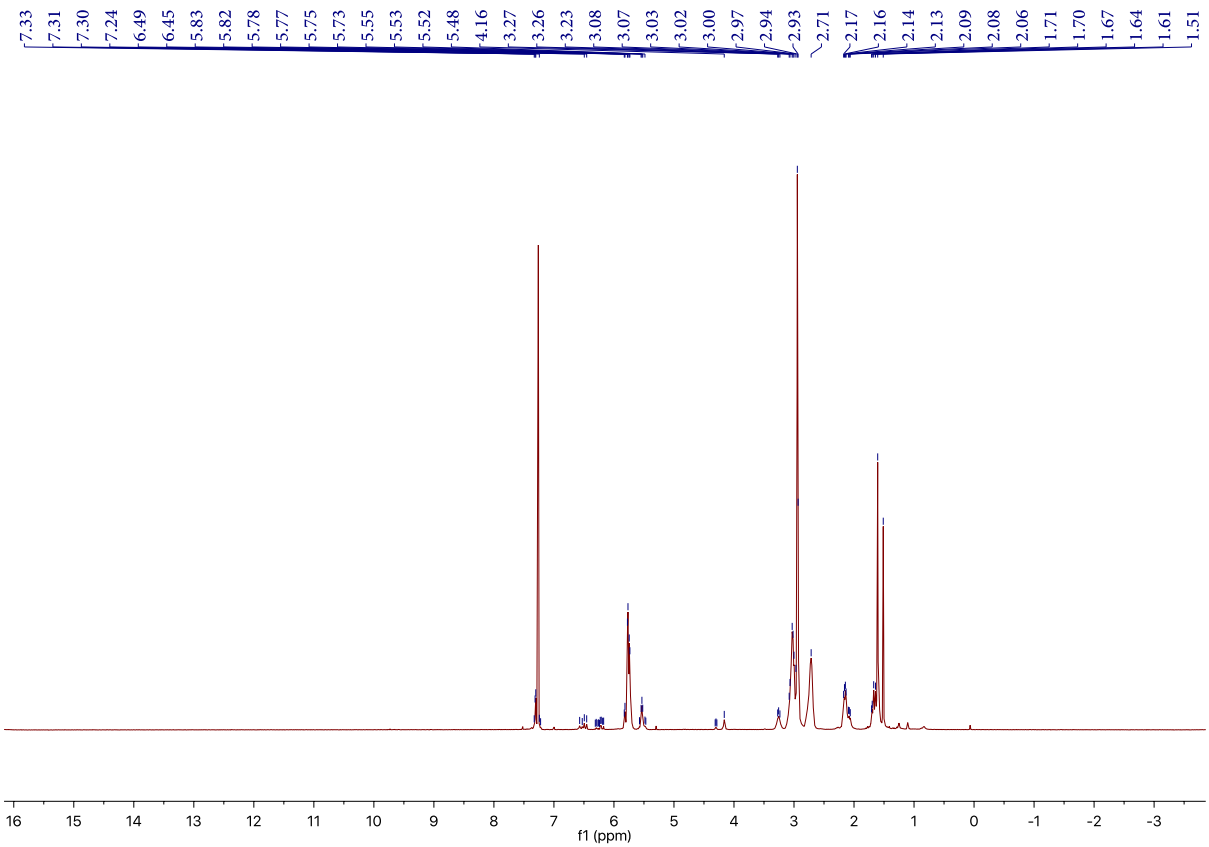


Figure S57 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 22**

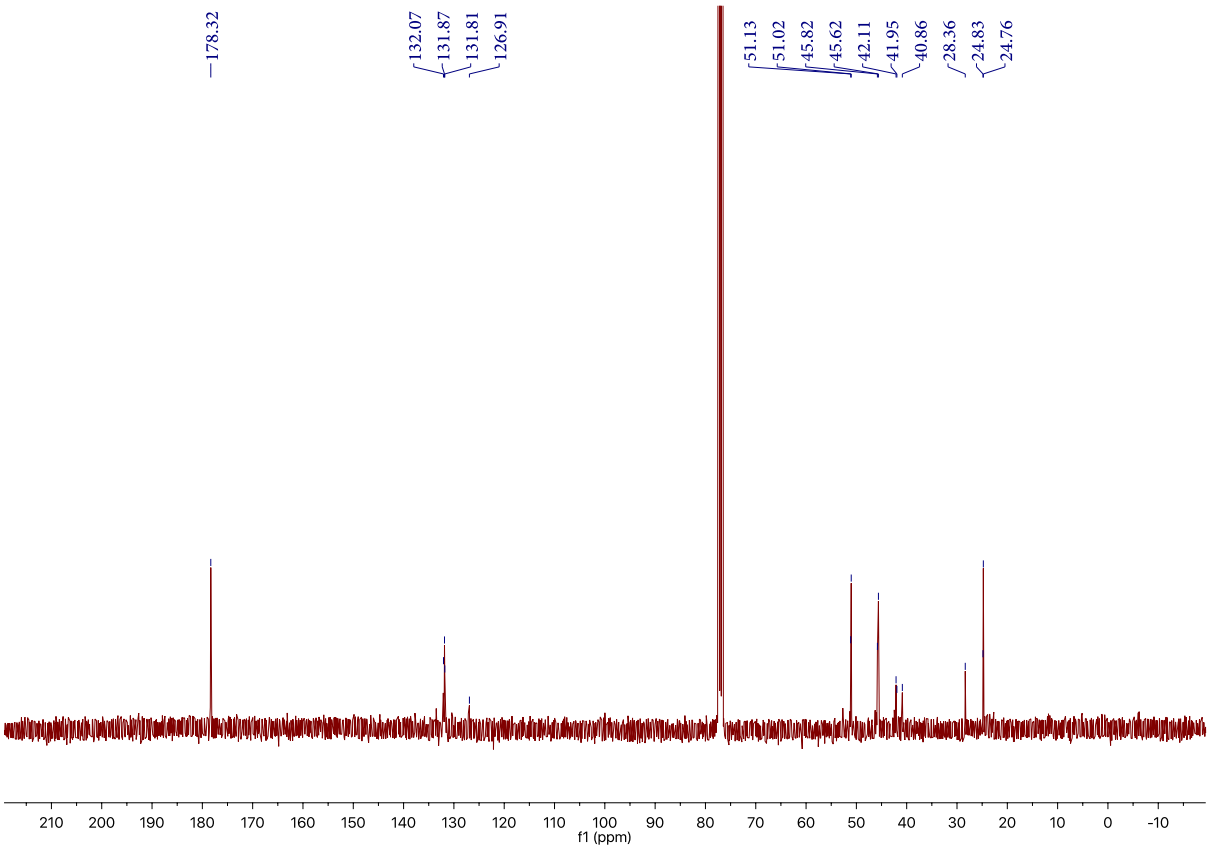


Figure S58 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 22**

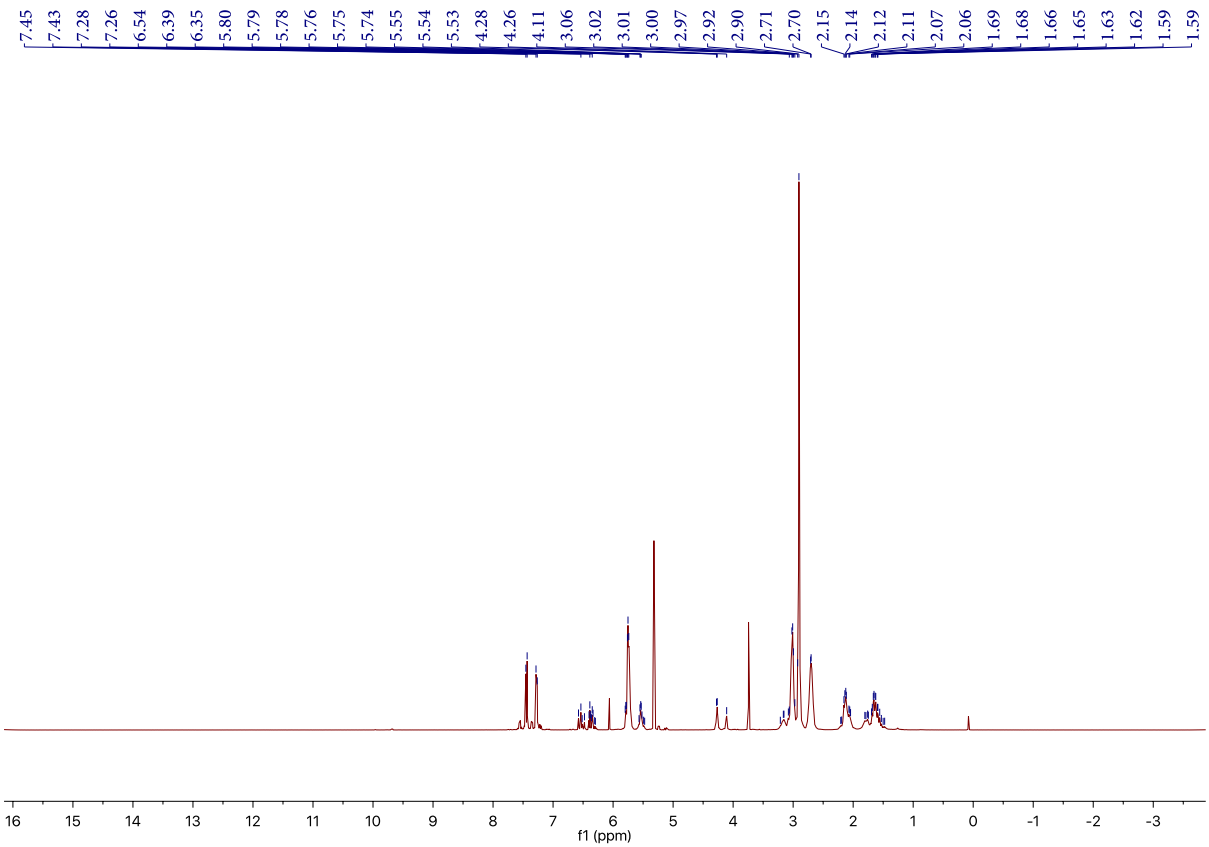


Figure S59 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 23**

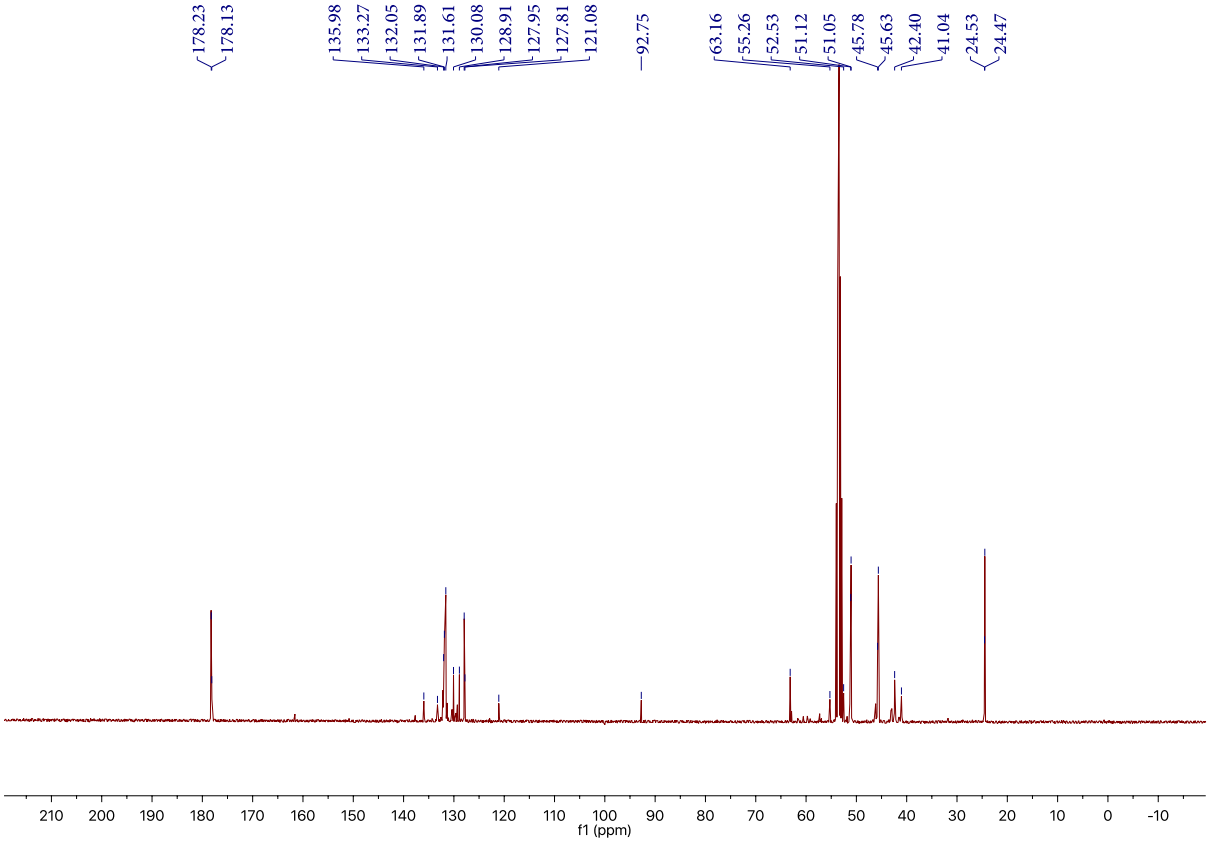


Figure S60 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 23**

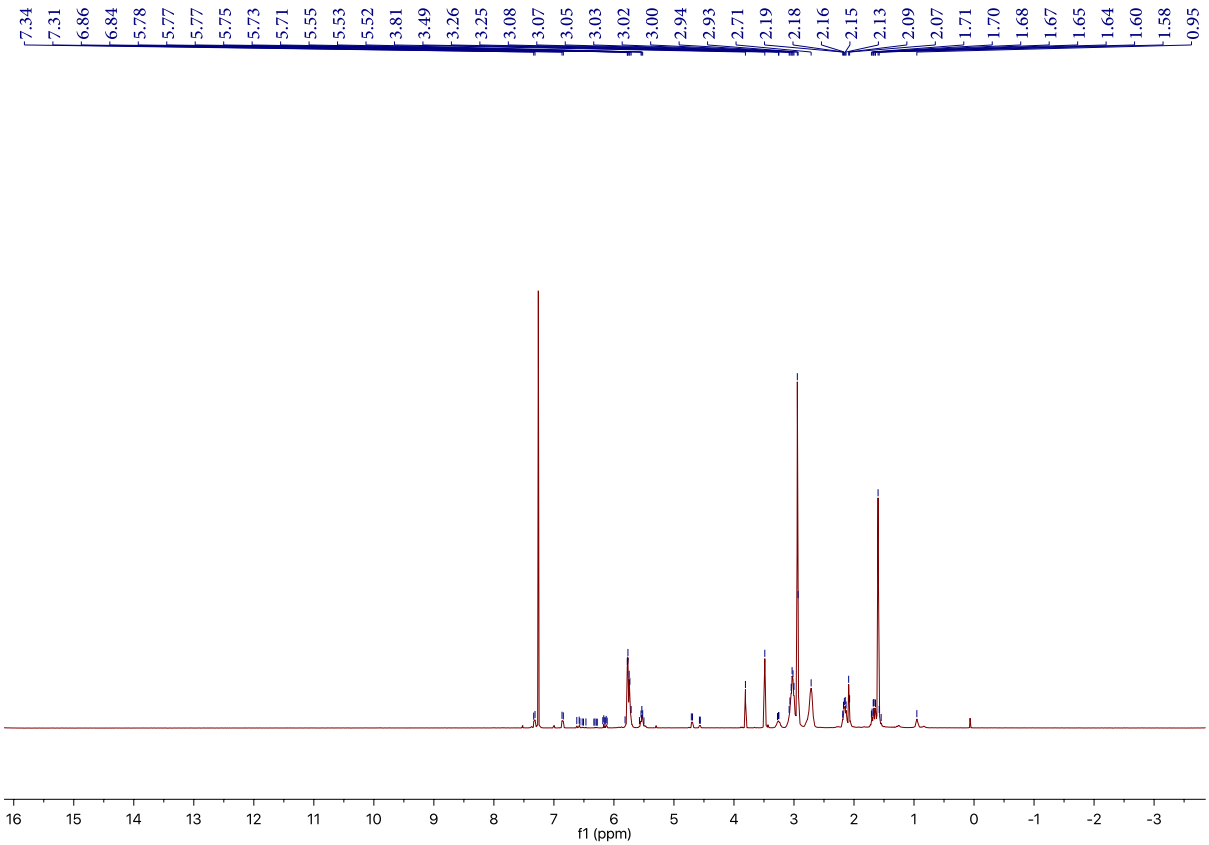


Figure S61 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 24**

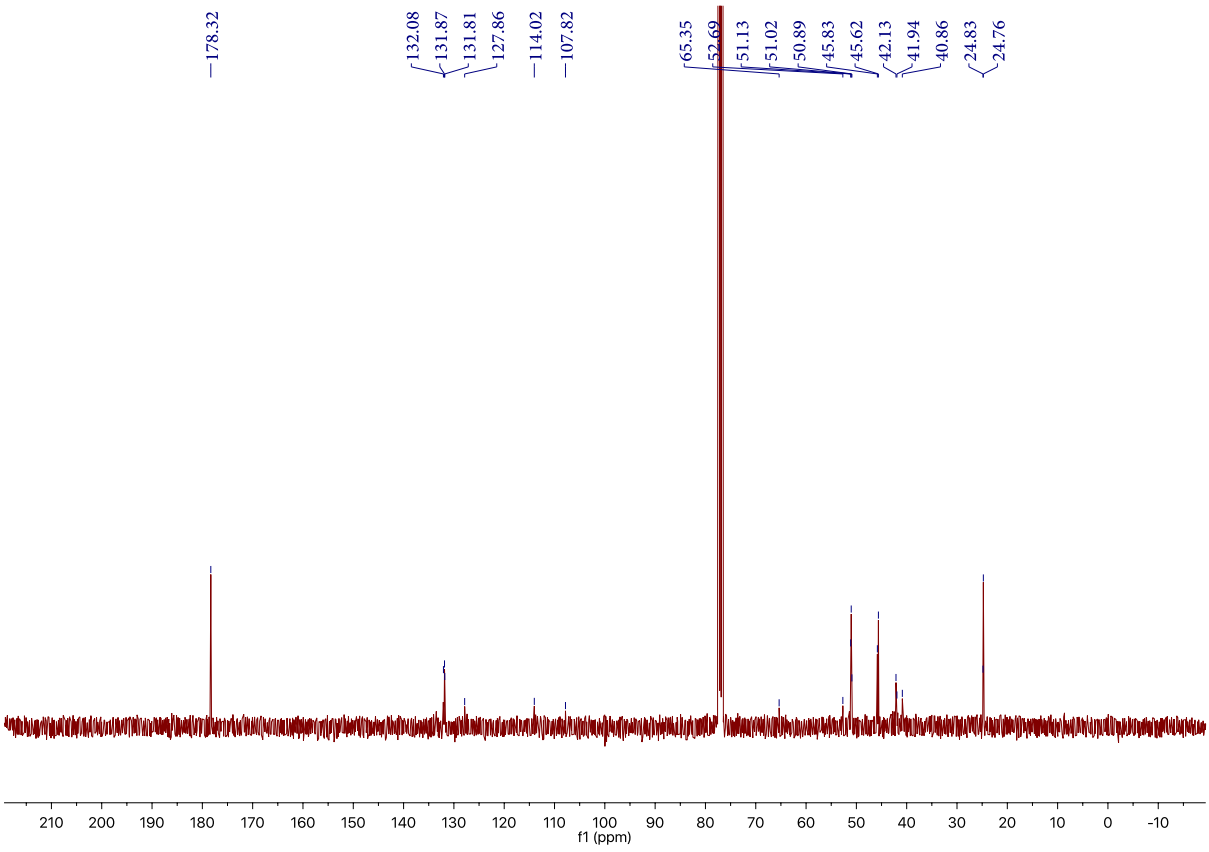


Figure S62 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 24**

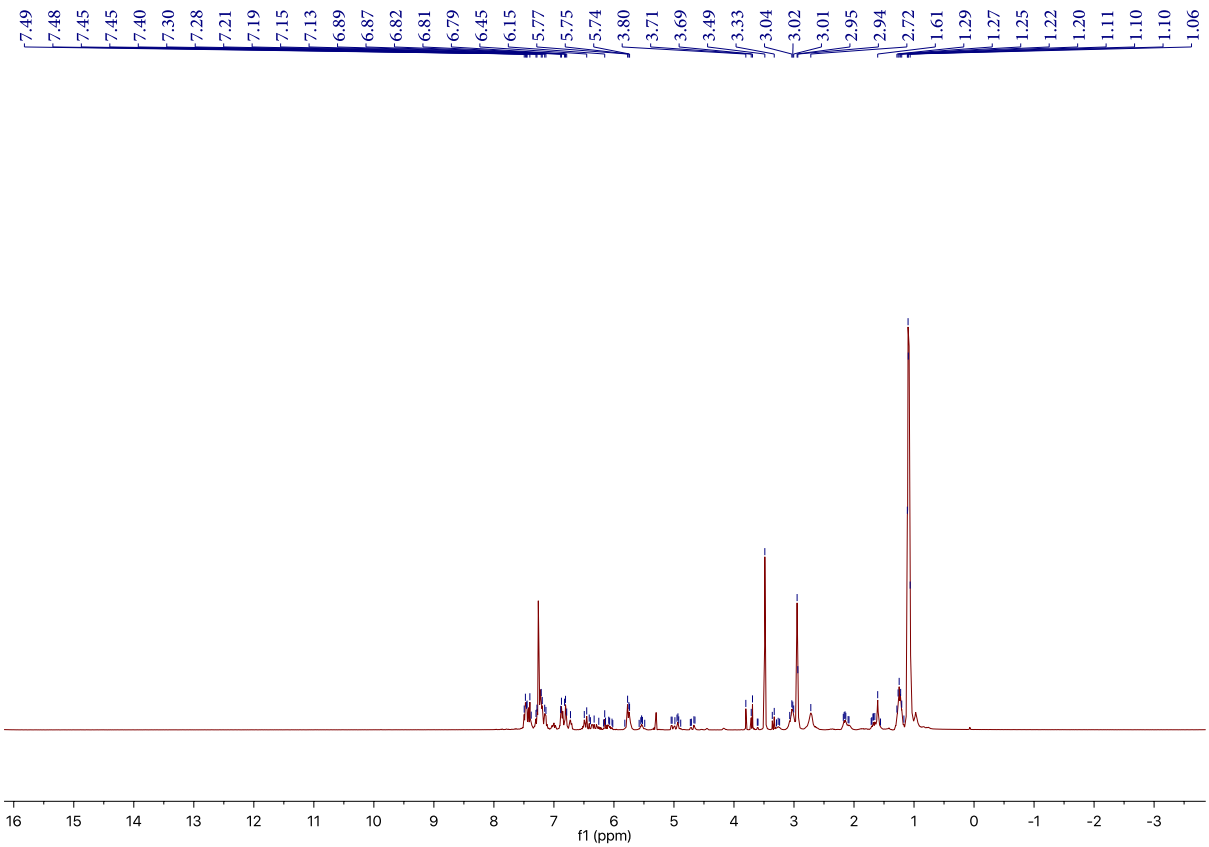


Figure S63 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 25**

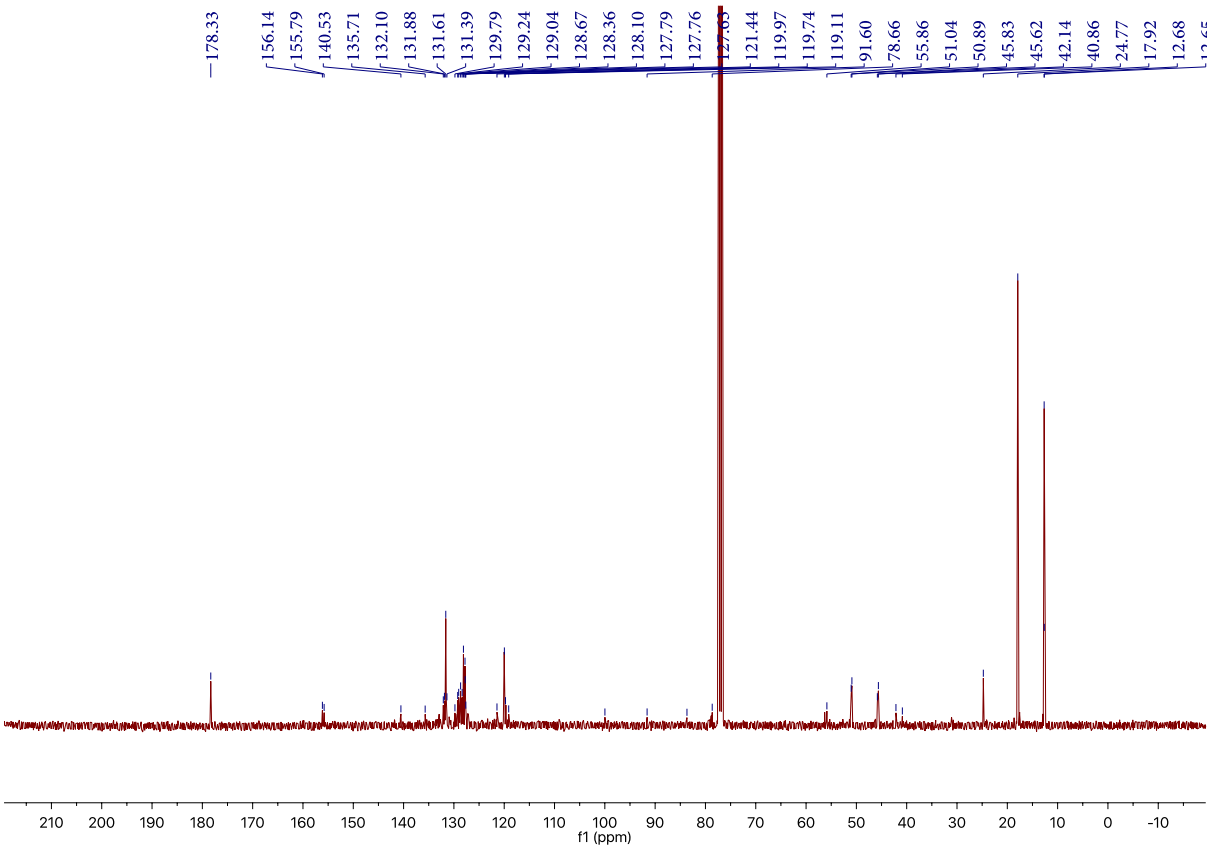


Figure S64 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 25**

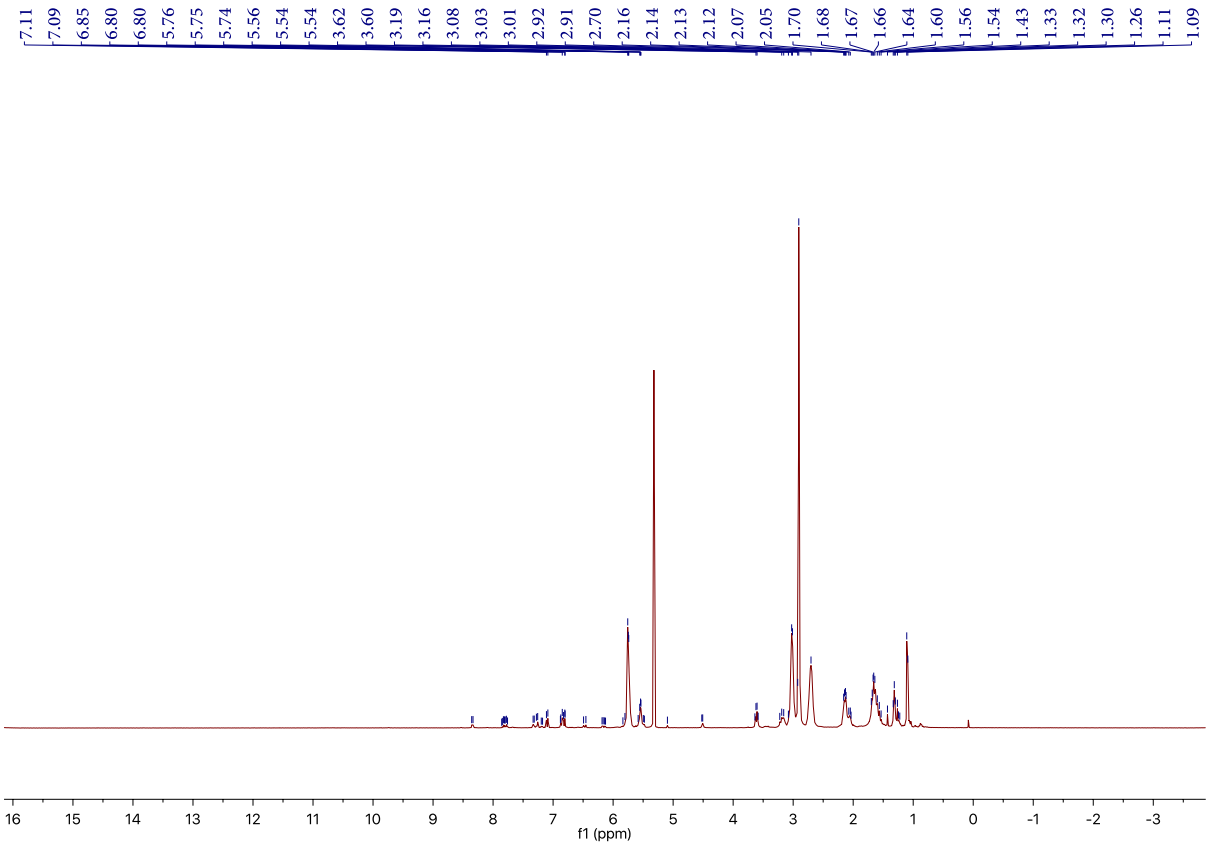


Figure S65 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 26**

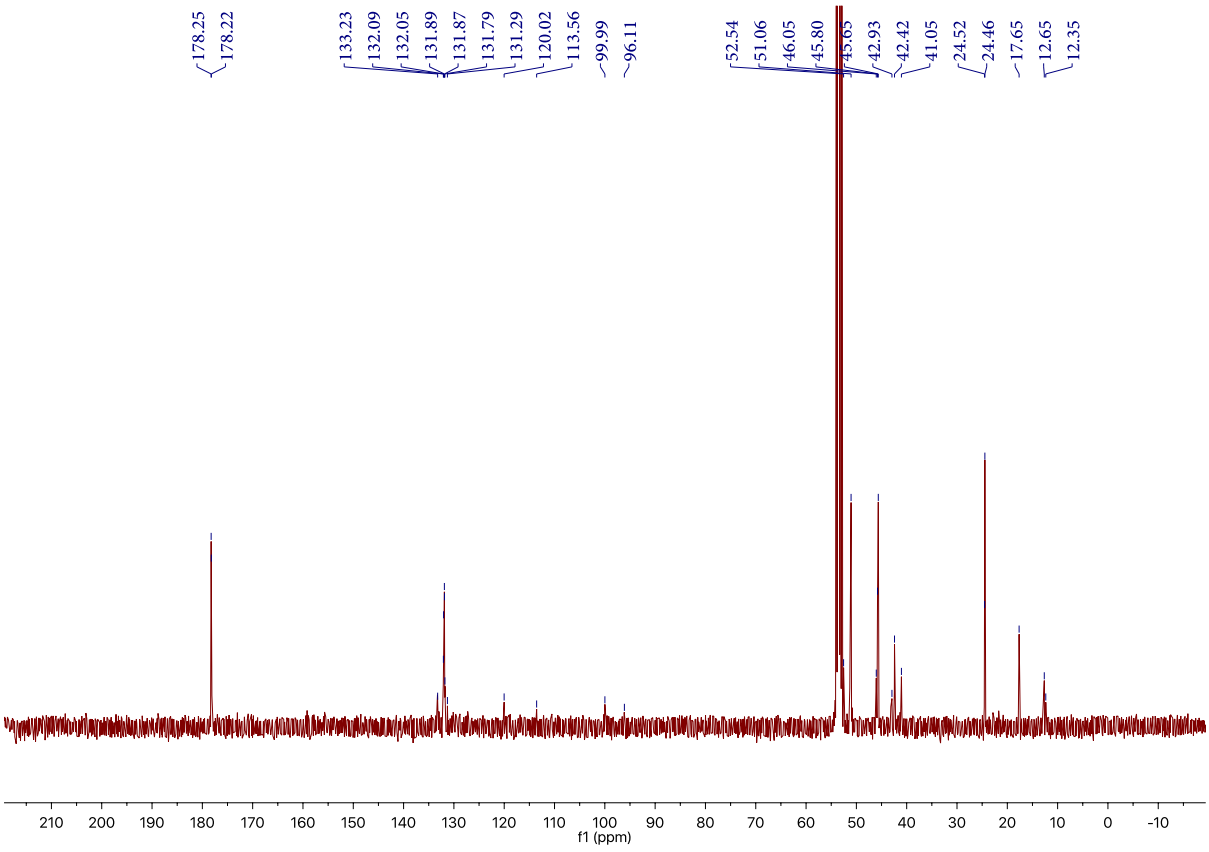


Figure S66 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 26**

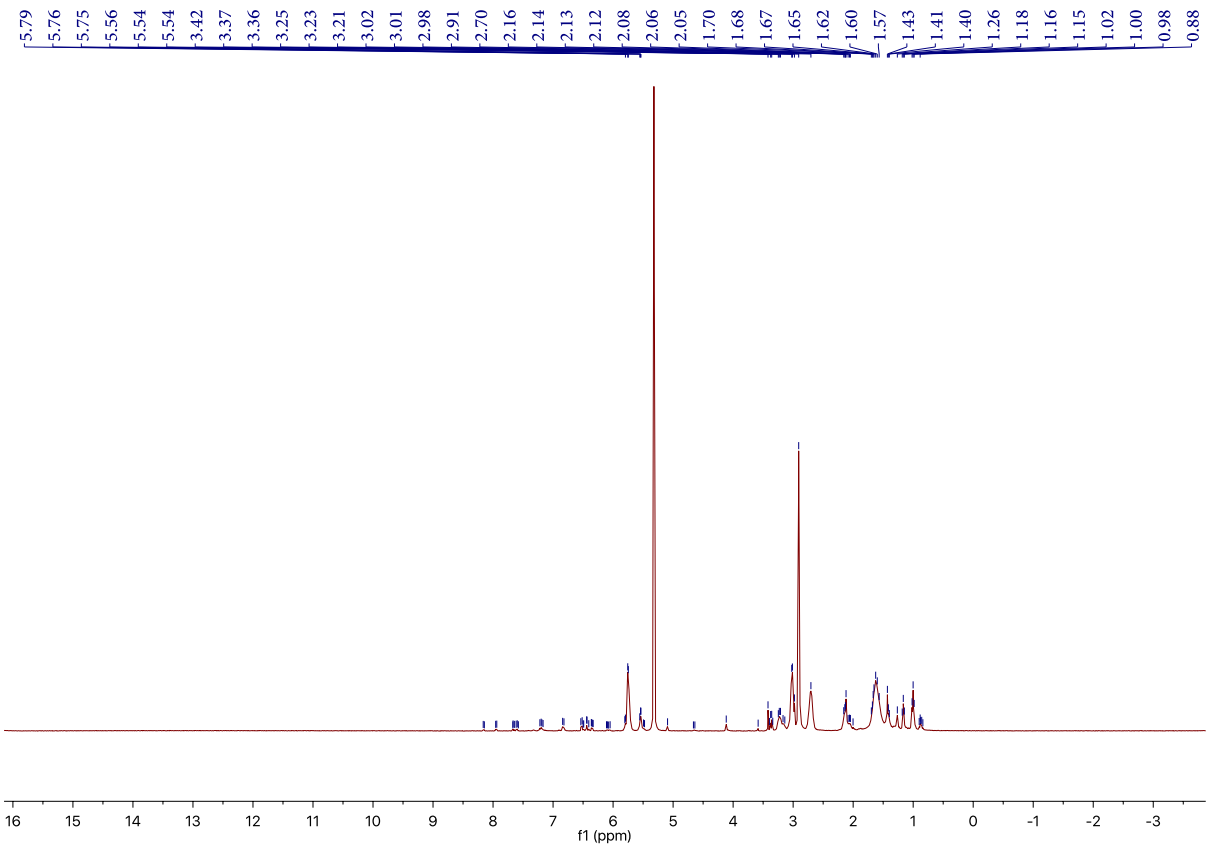


Figure S67 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 27**

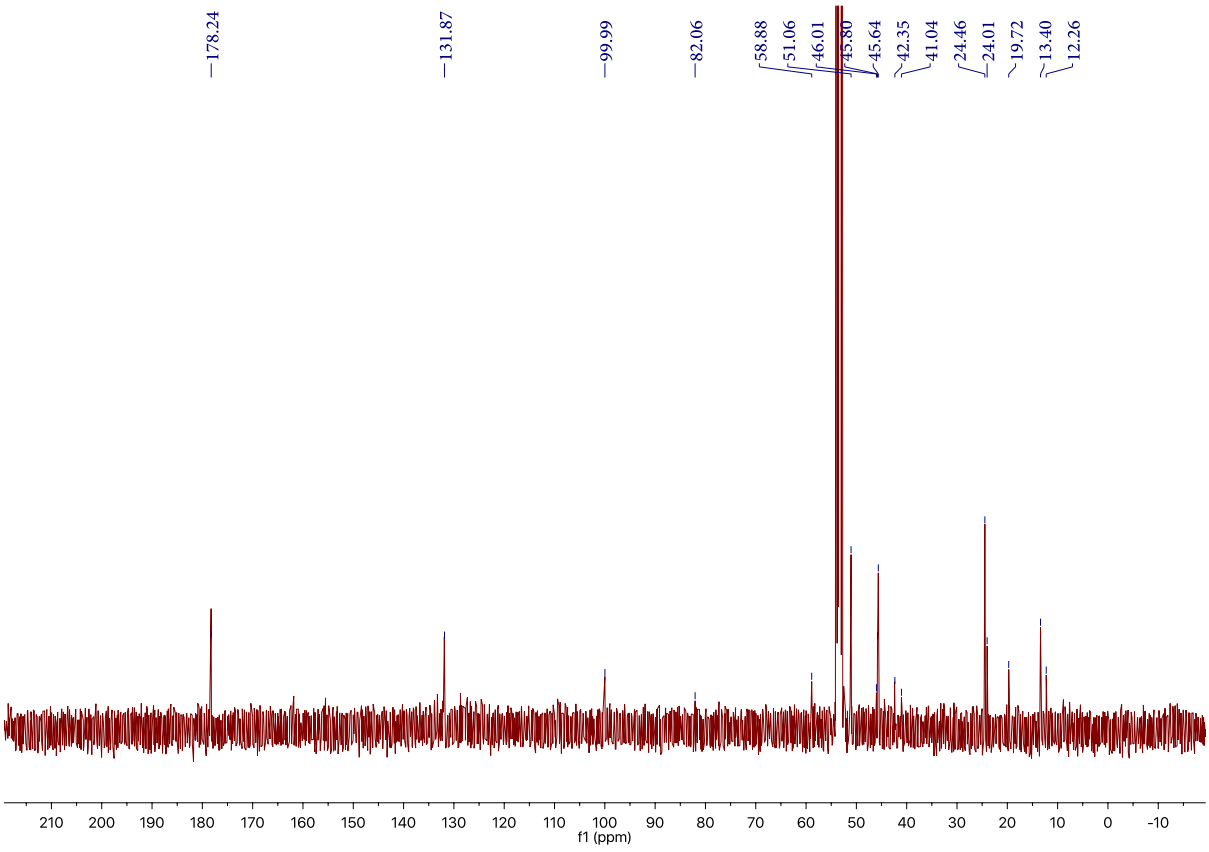


Figure S68 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 27**

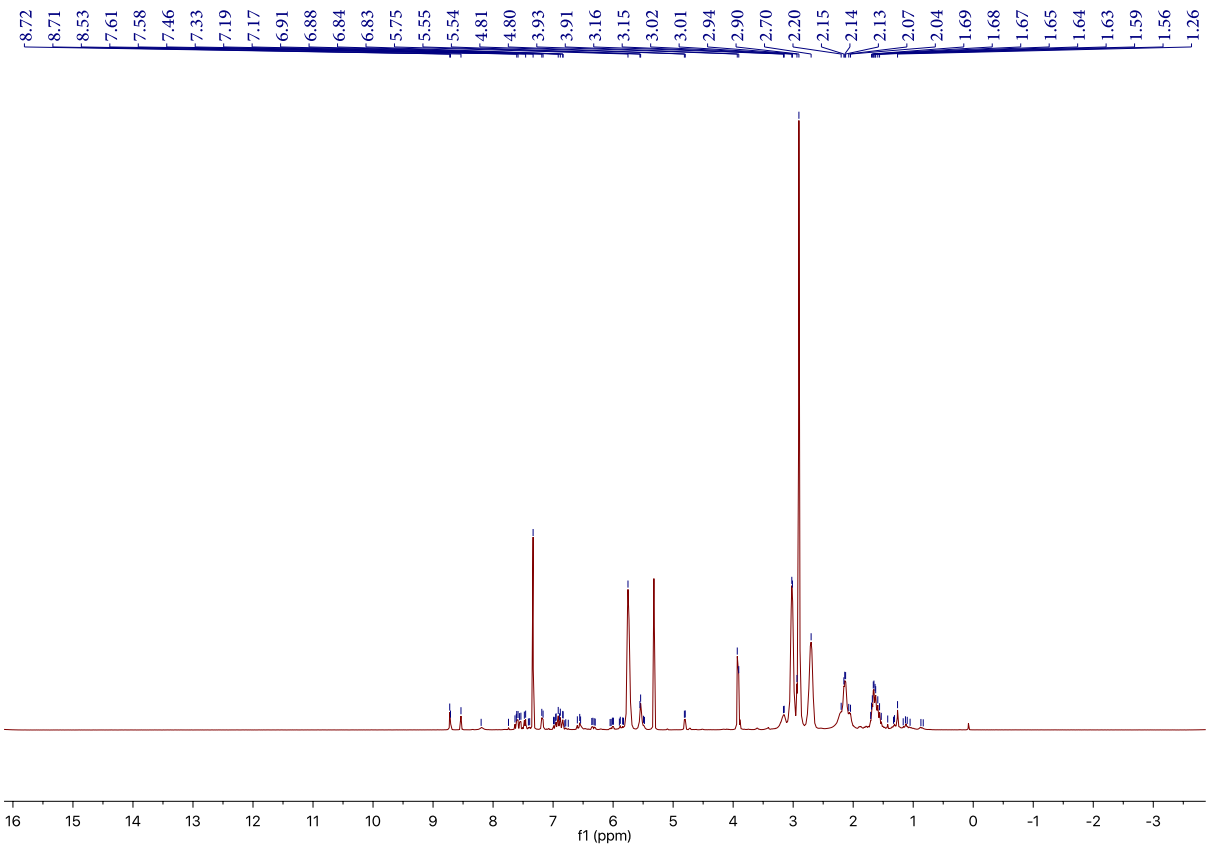


Figure S69 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of **Polymer 28**

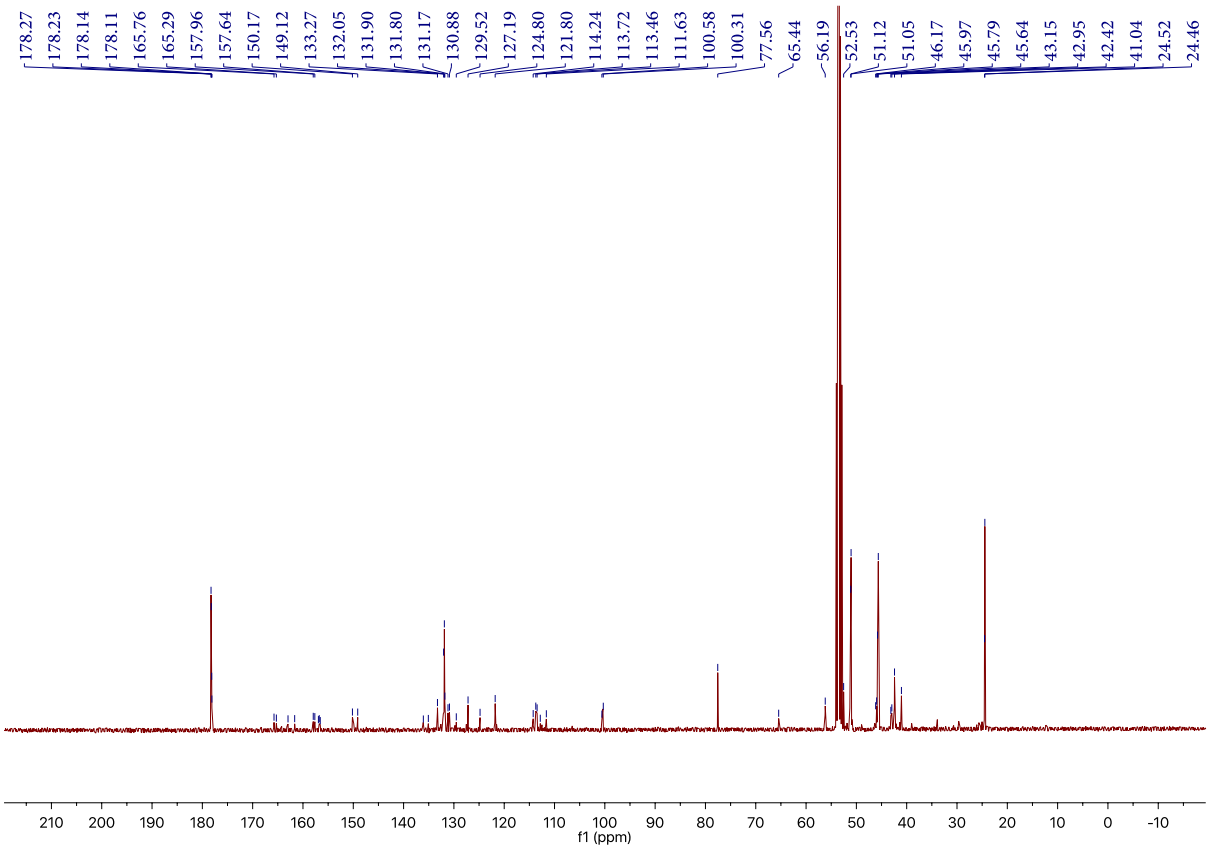


Figure S70 ^{13}C-NMR spectrum (101 MHz, CD_2Cl_2) of **Polymer 28**

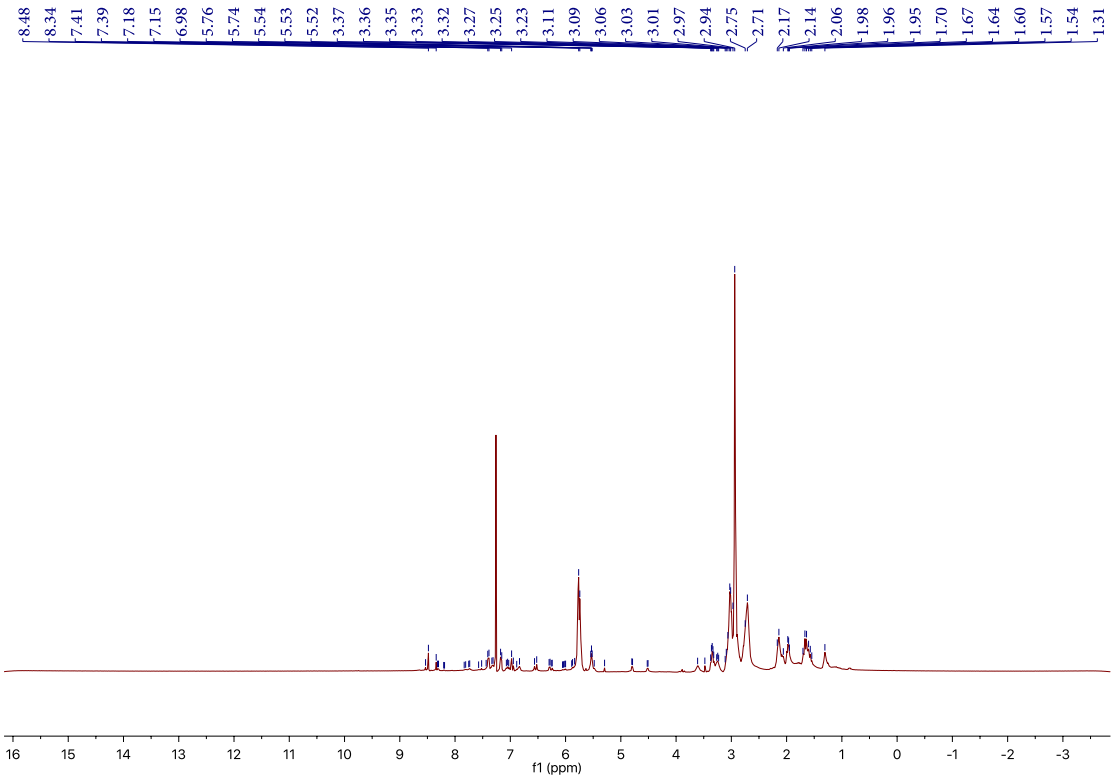


Figure S71 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **Polymer 29**

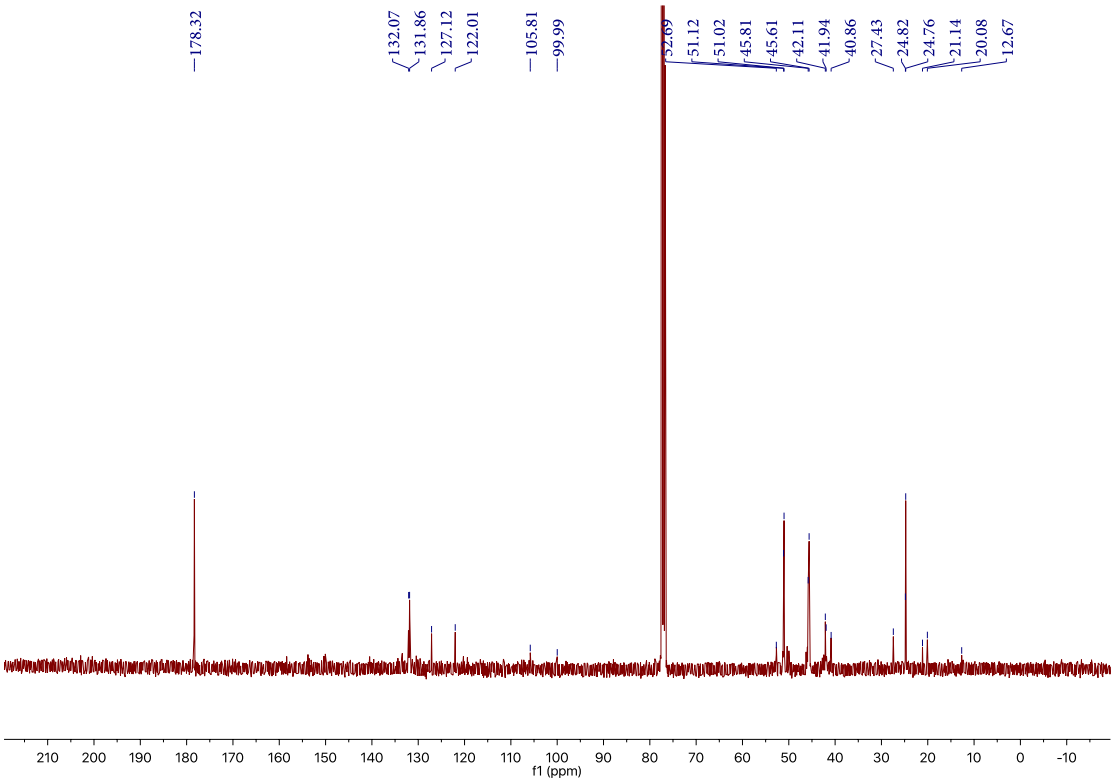
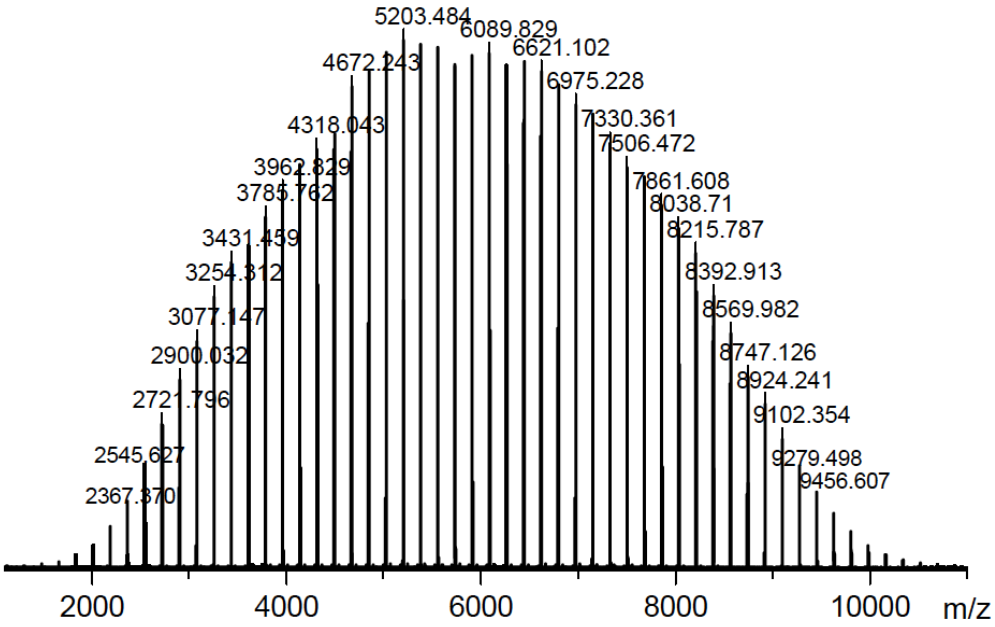


Figure S72 ^{13}C-NMR spectrum (101 MHz, $CDCl_3$) of **Polymer 29**

MALDI-ToF Mass Spectrometric Data of Polymers



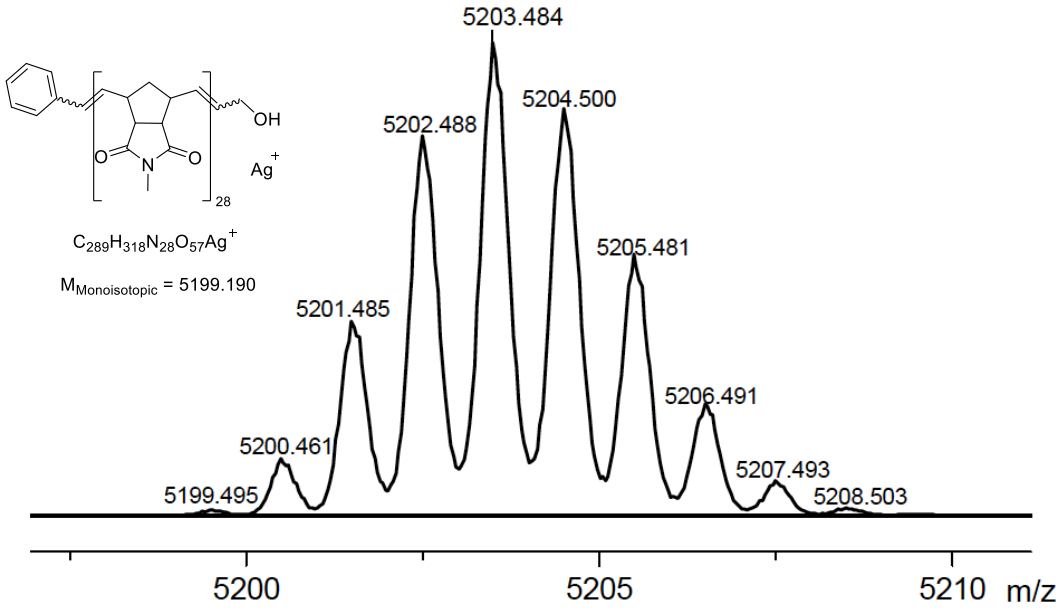


Figure S73 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 1**

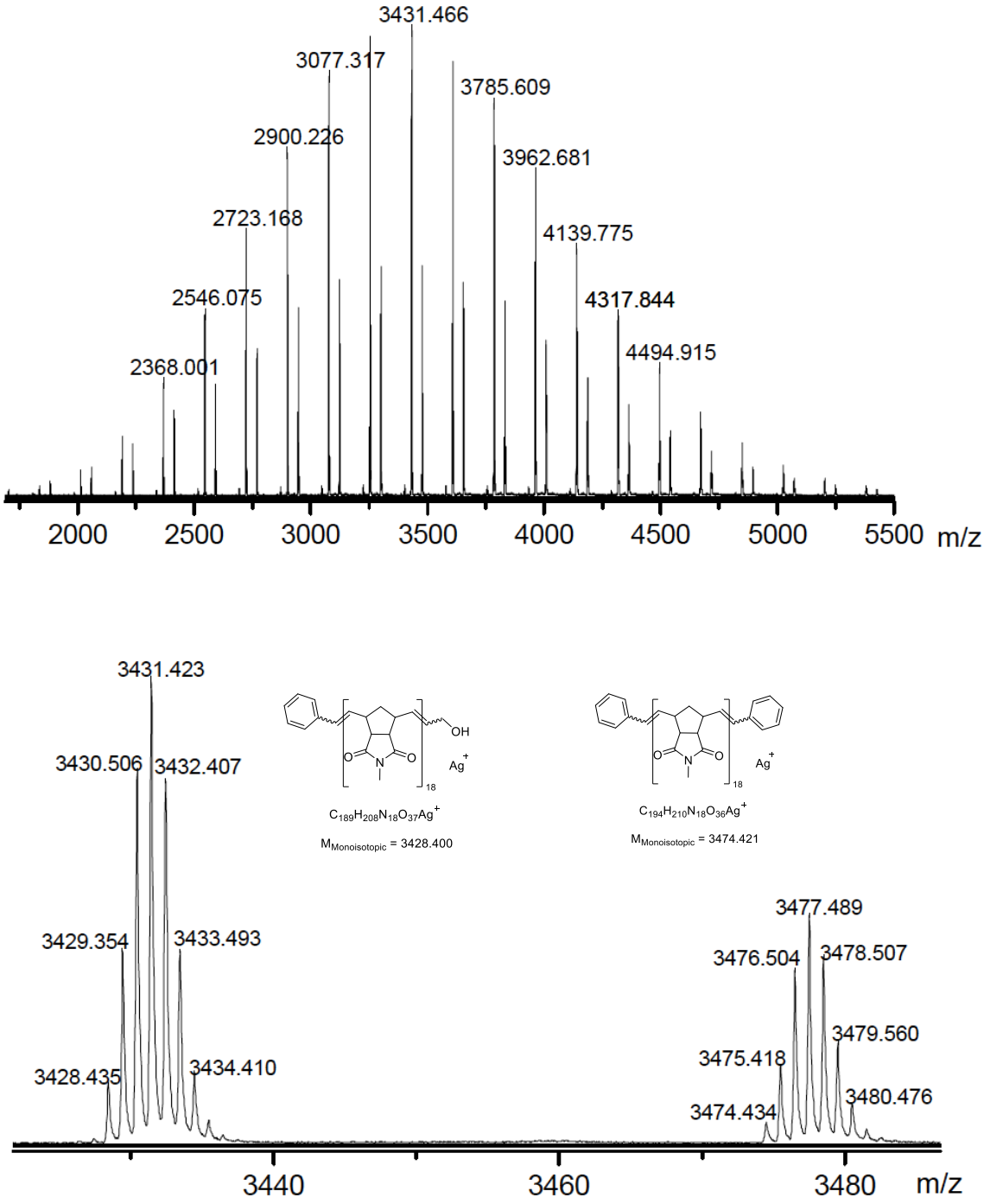


Figure S74 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 2**

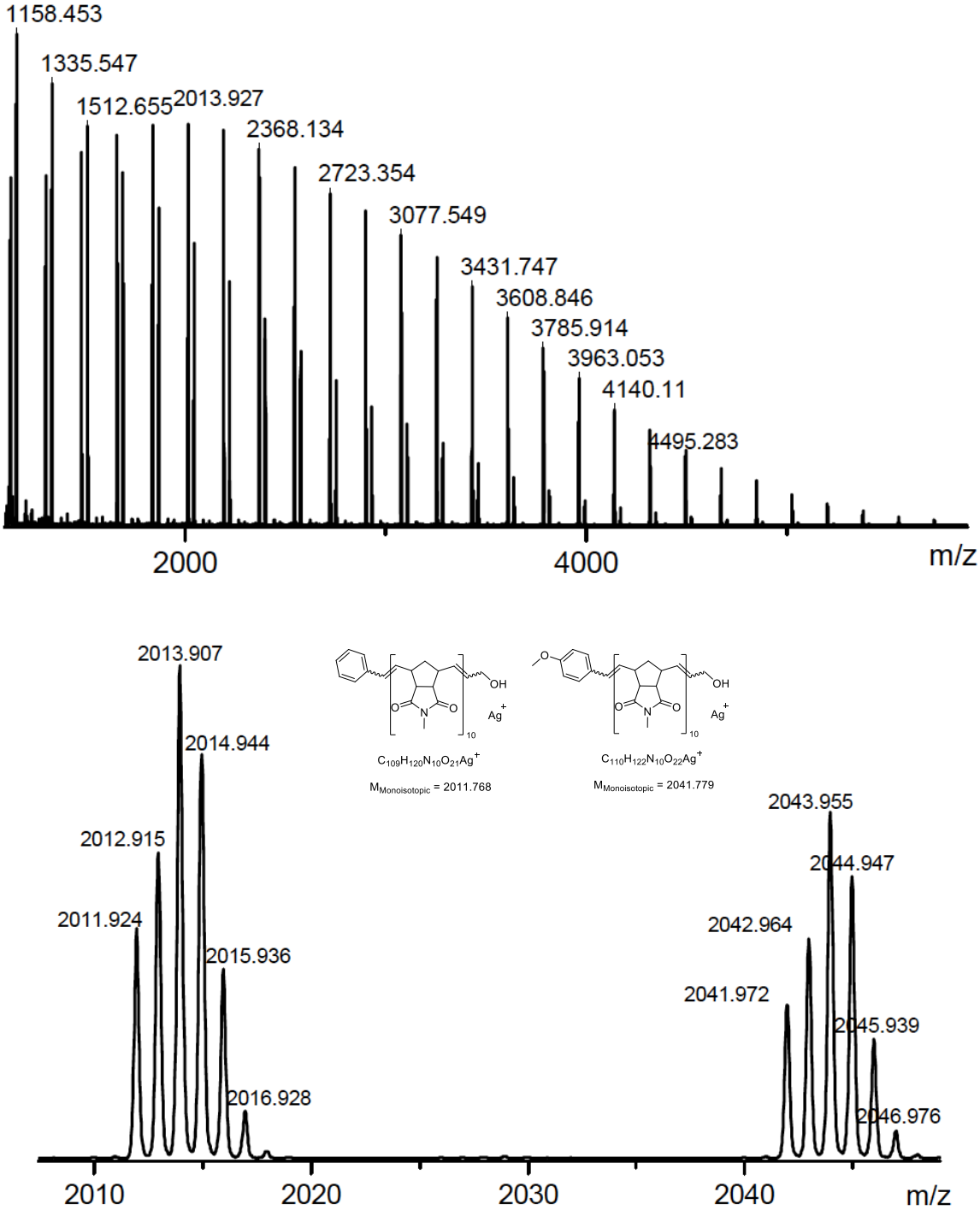


Figure S75 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 3**

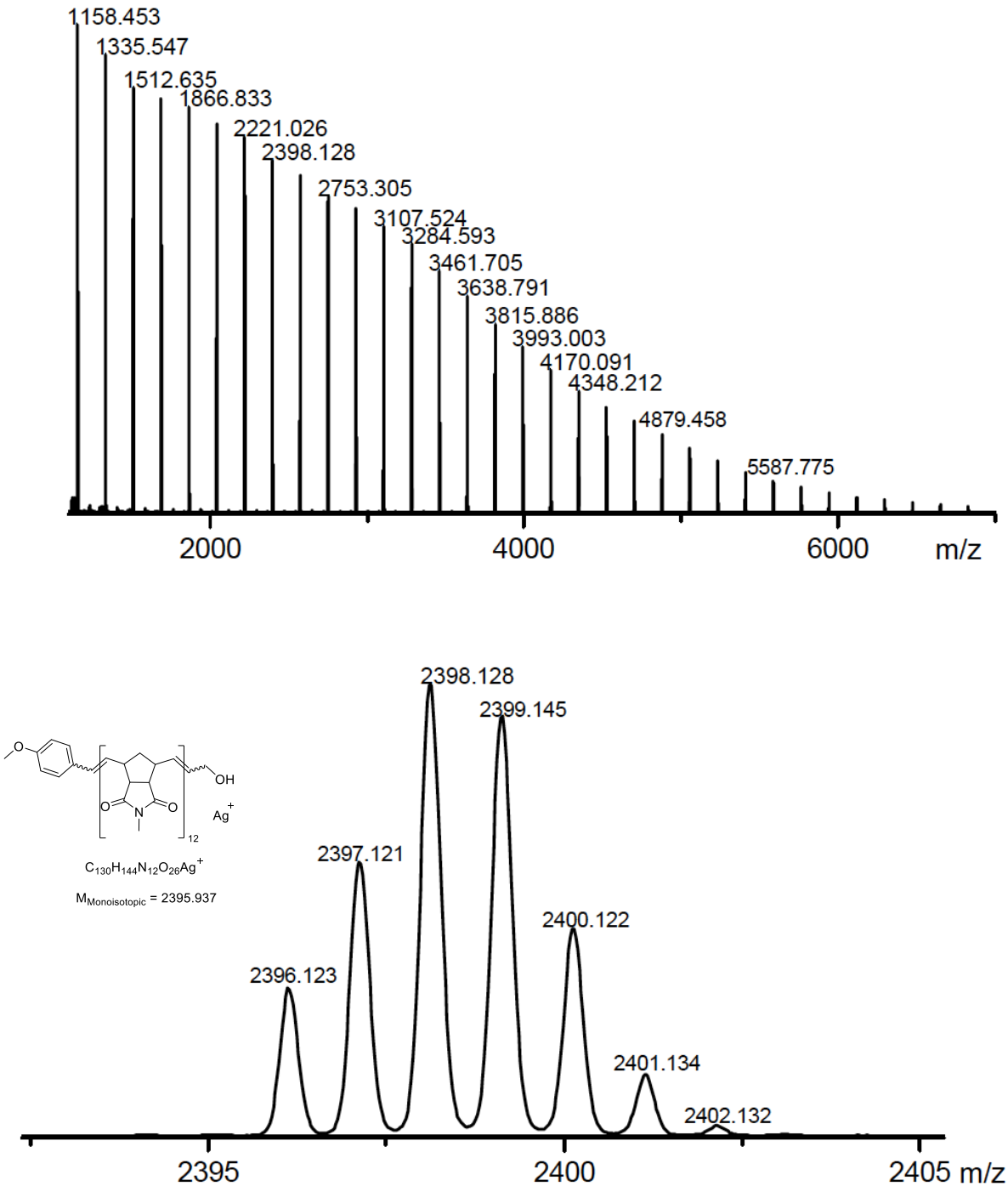


Figure S76 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 4A**

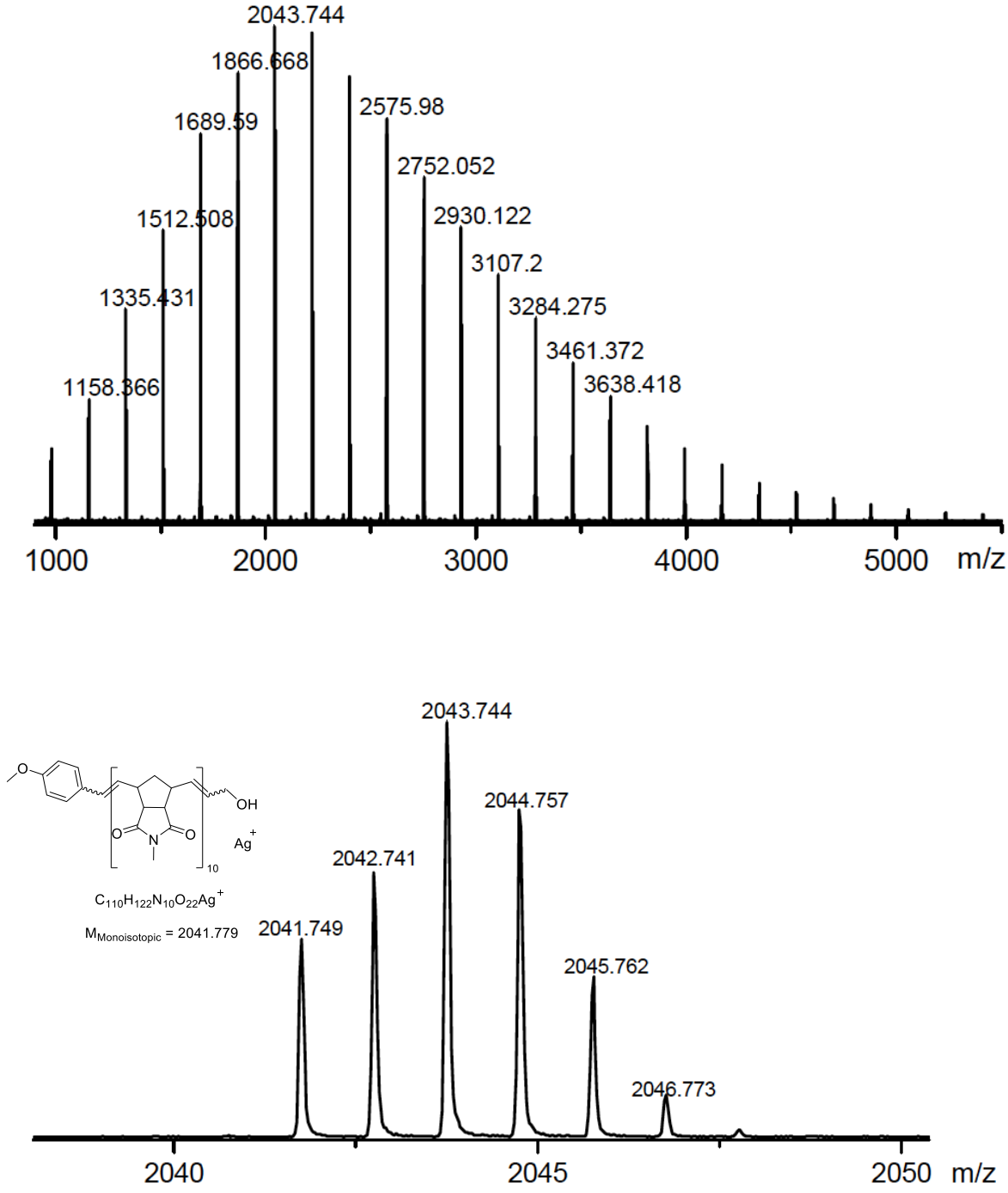


Figure S77 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 4B**

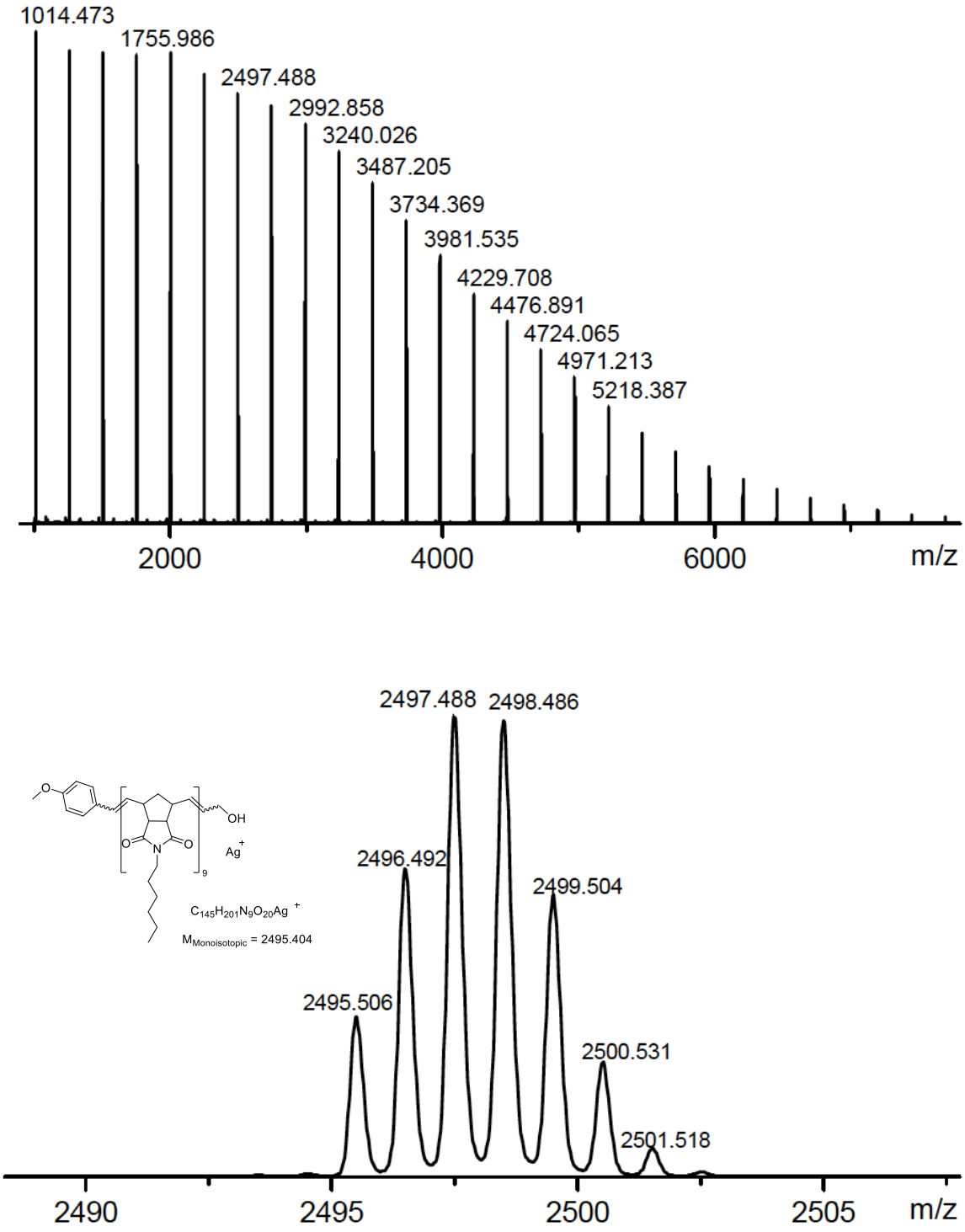


Figure S78 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 5**

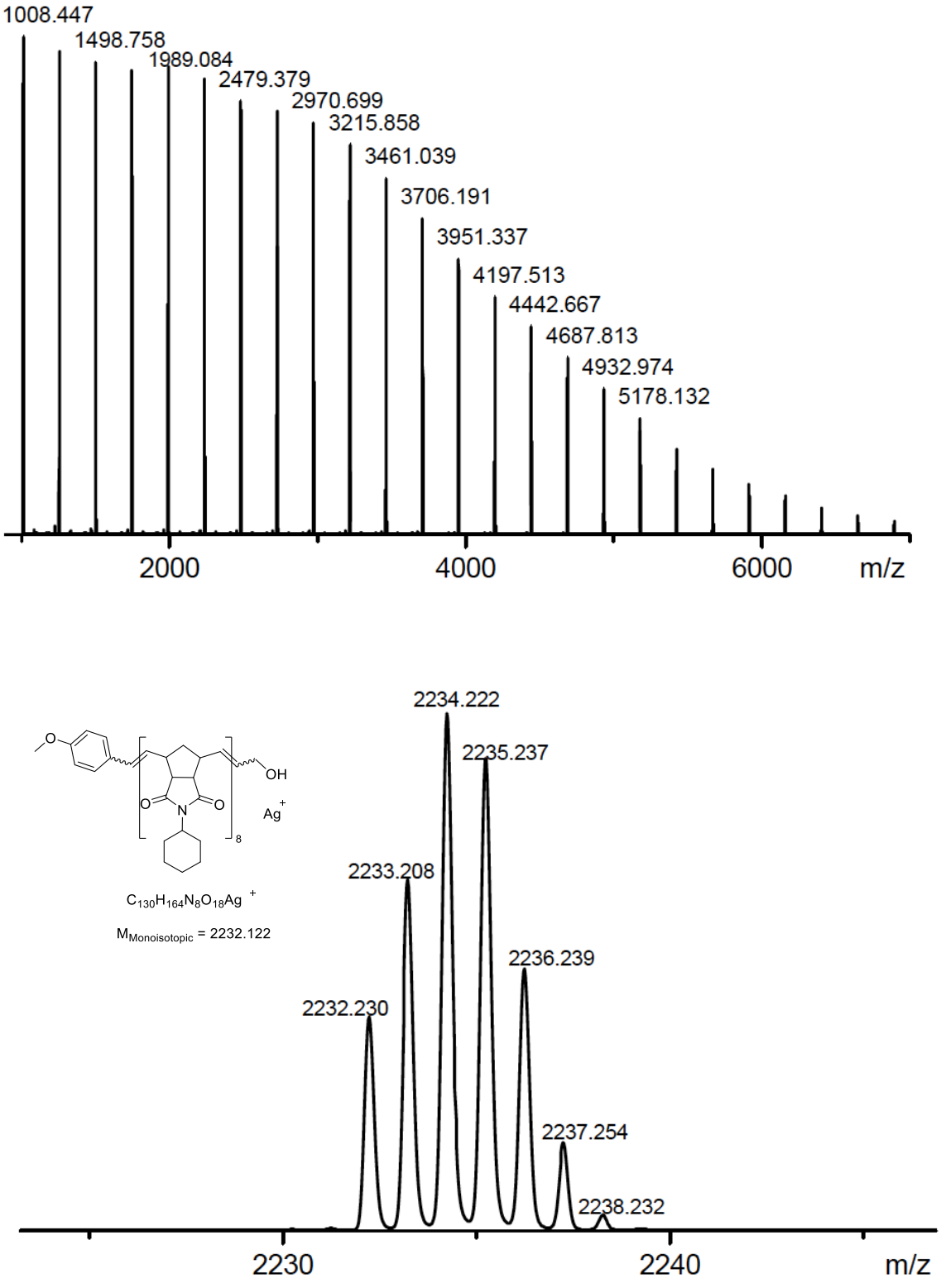


Figure S79 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 6**

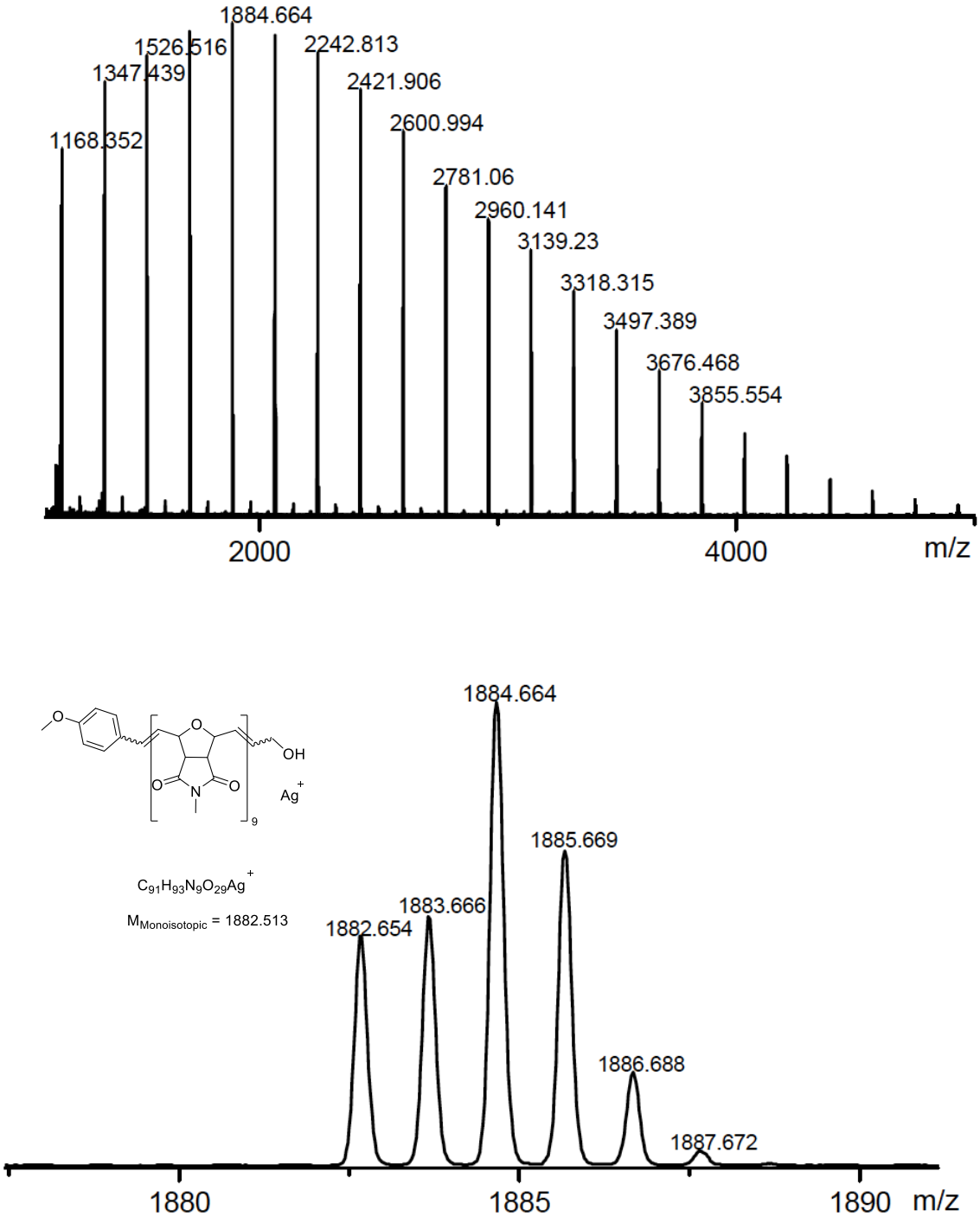


Figure S80 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 7**

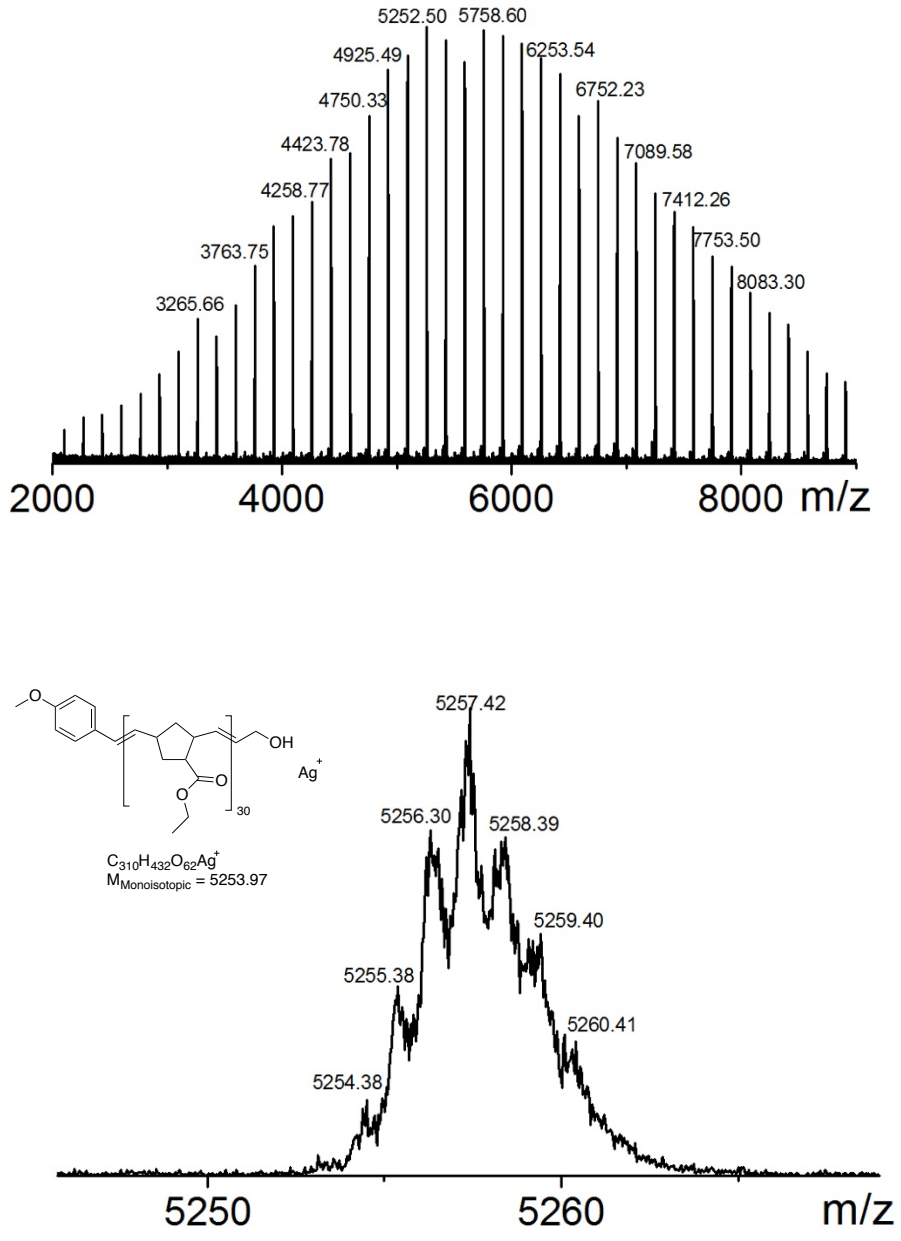


Figure S81 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 8**

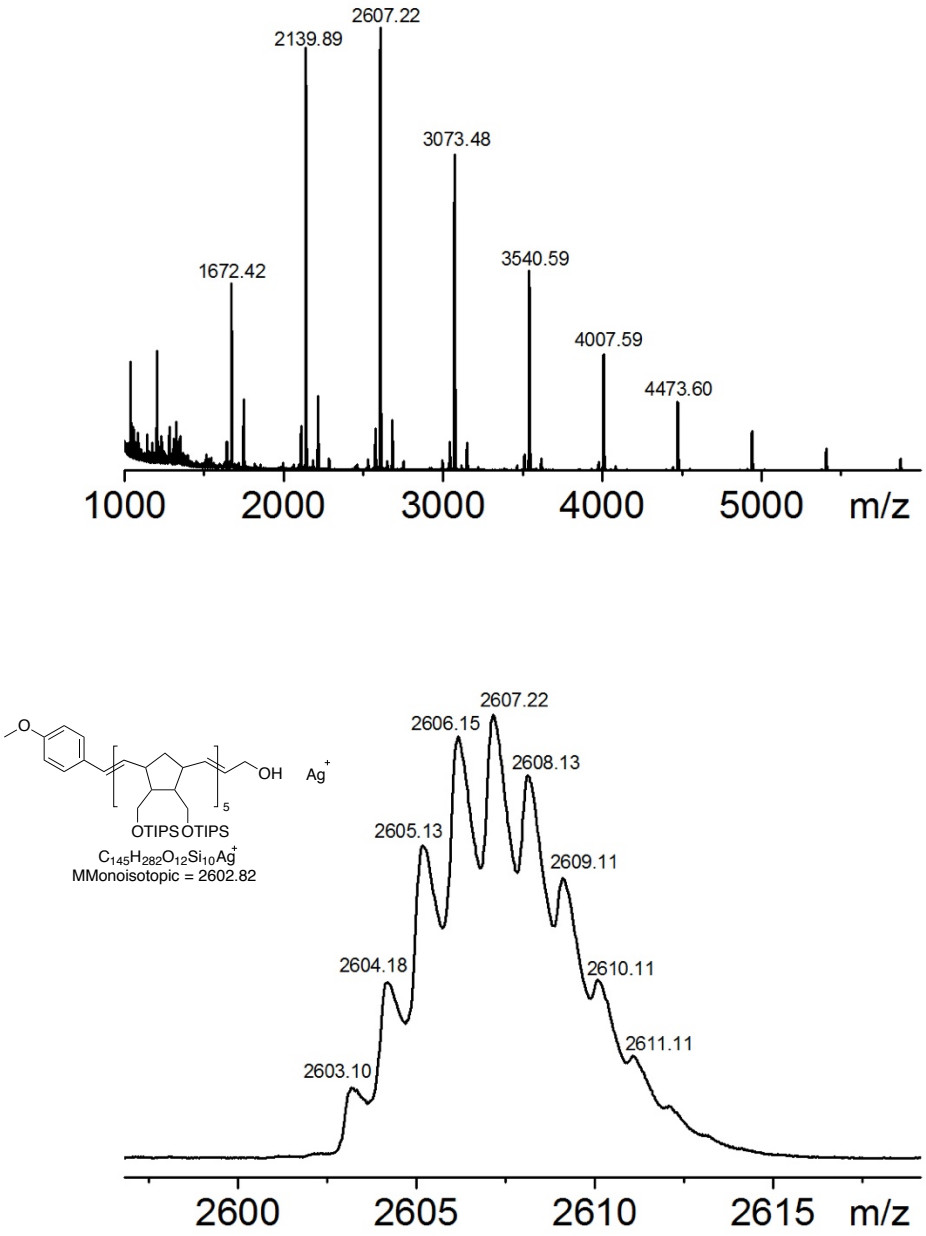


Figure S82 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 9**

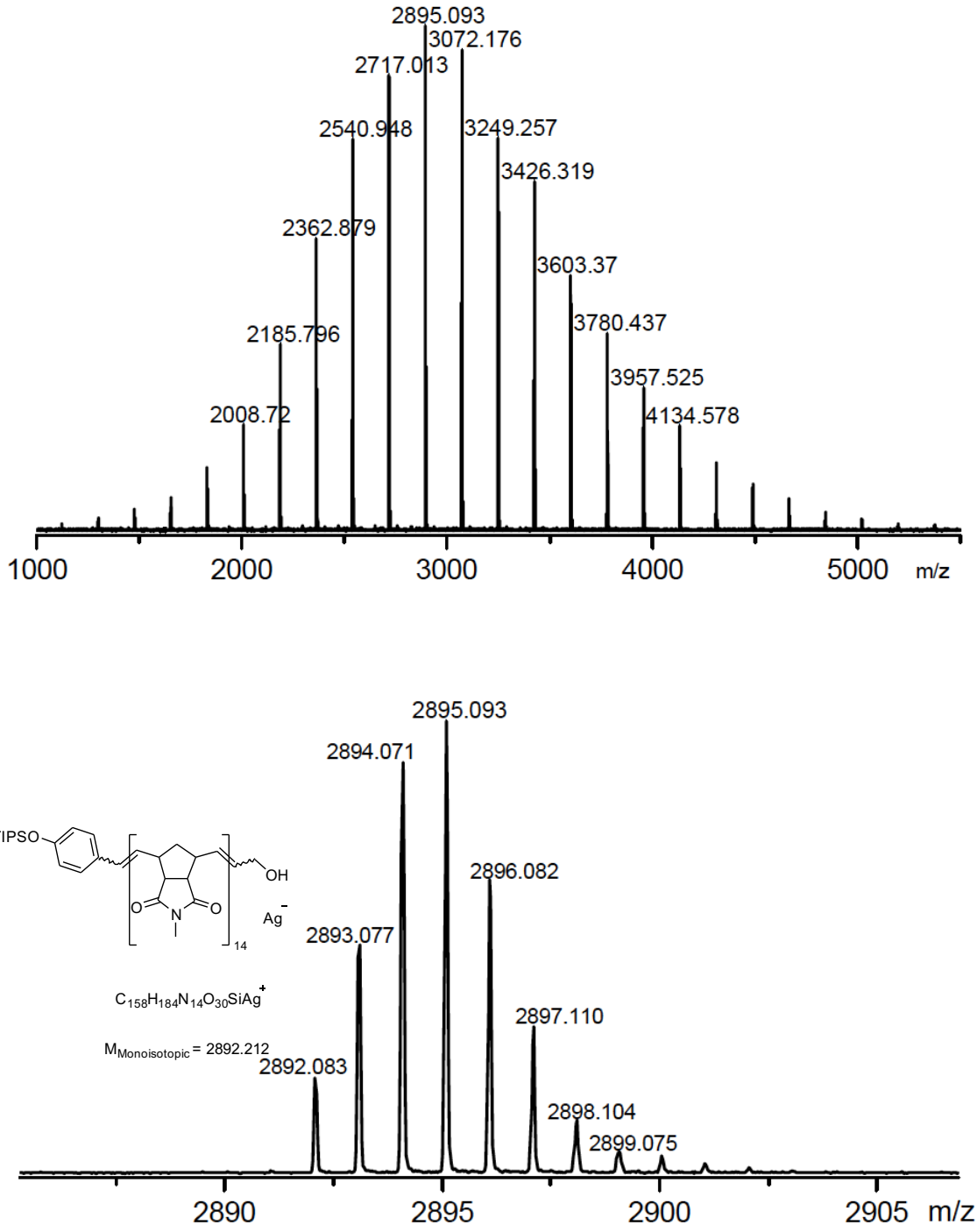


Figure S83 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 10**

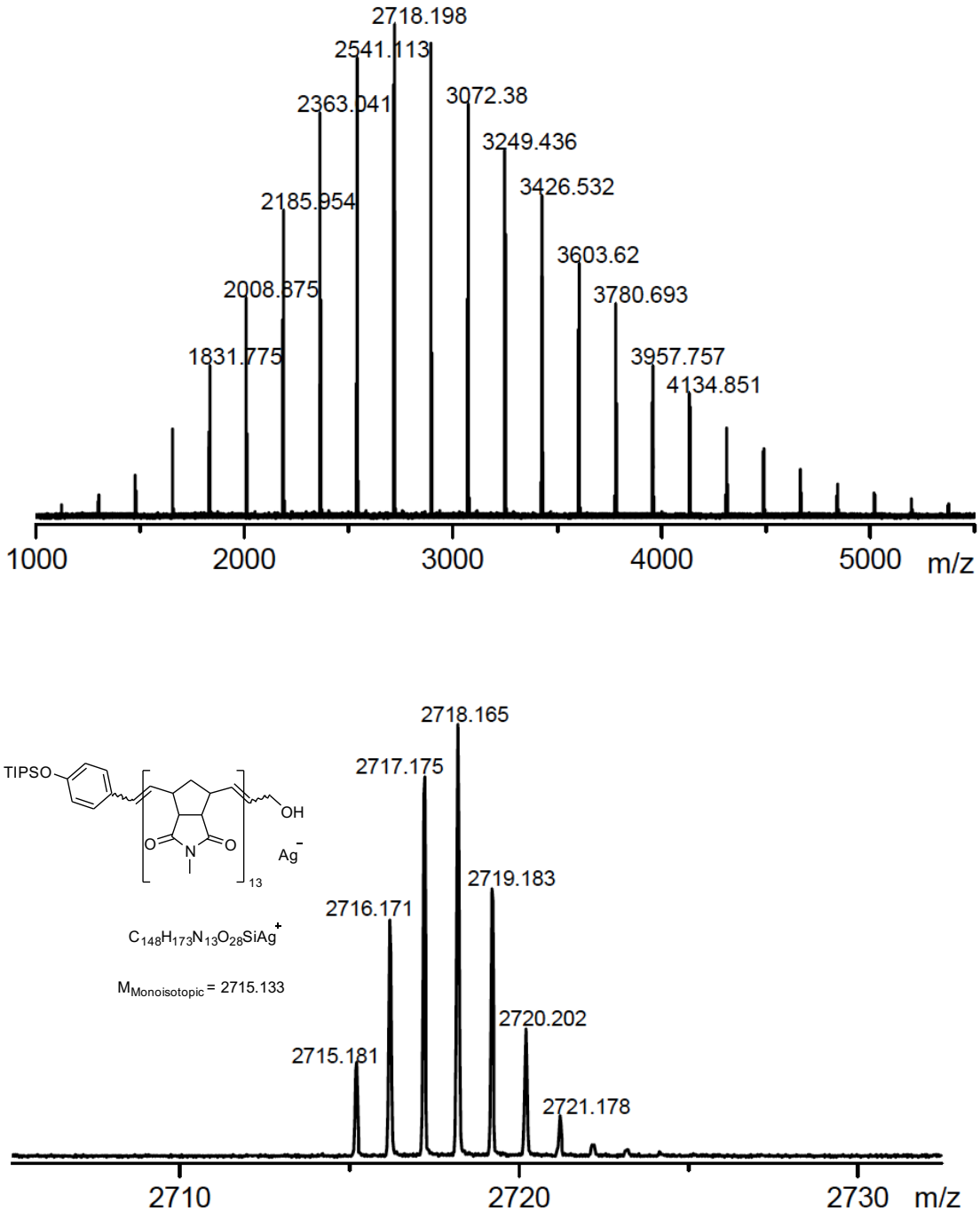


Figure S84 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 11**

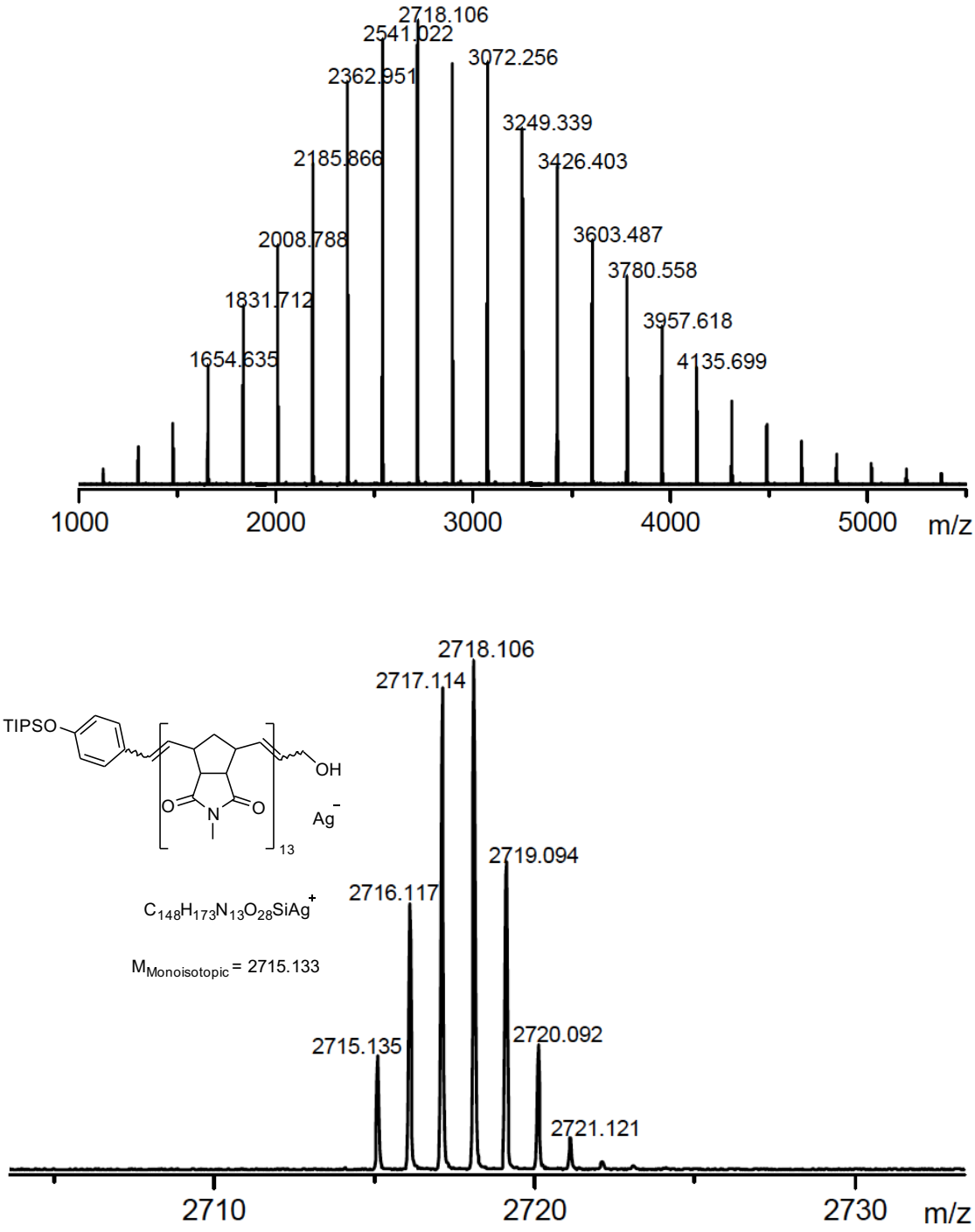
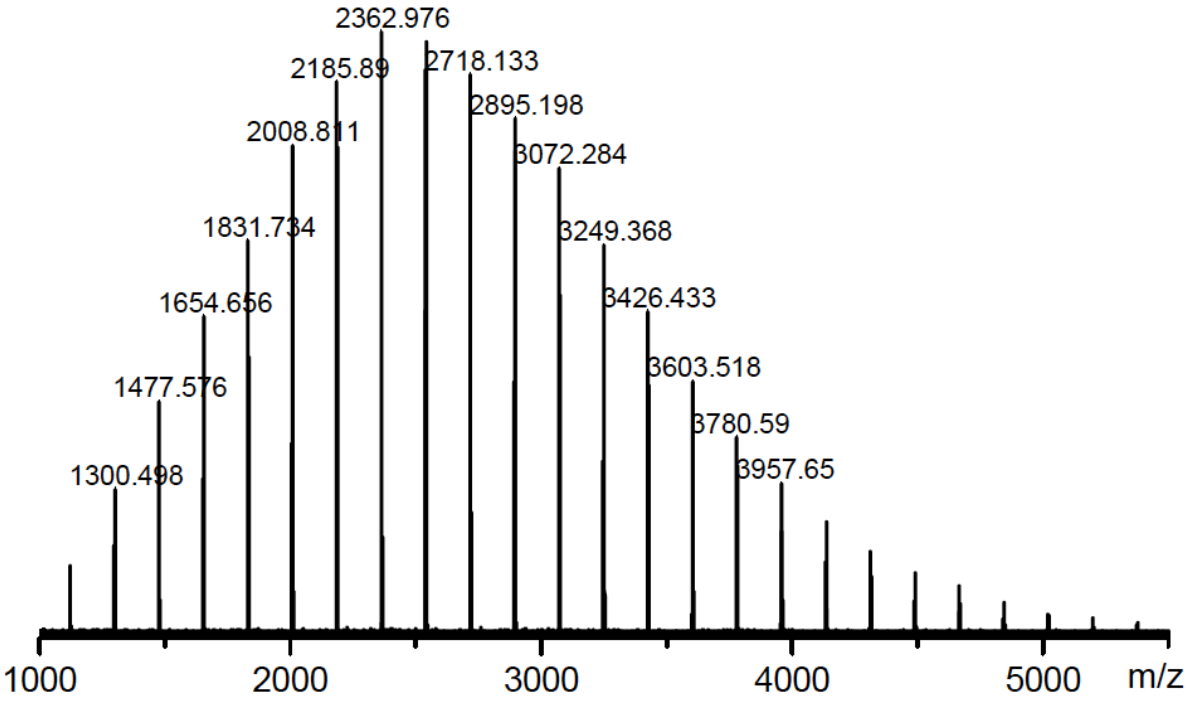


Figure S85 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 12**



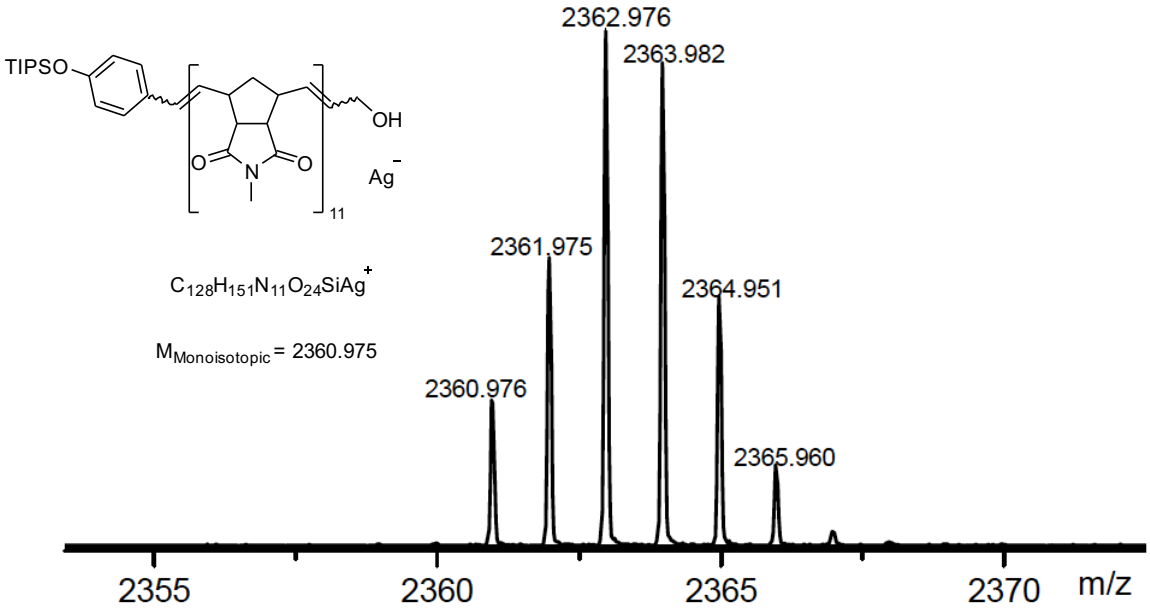


Figure S86 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 13**

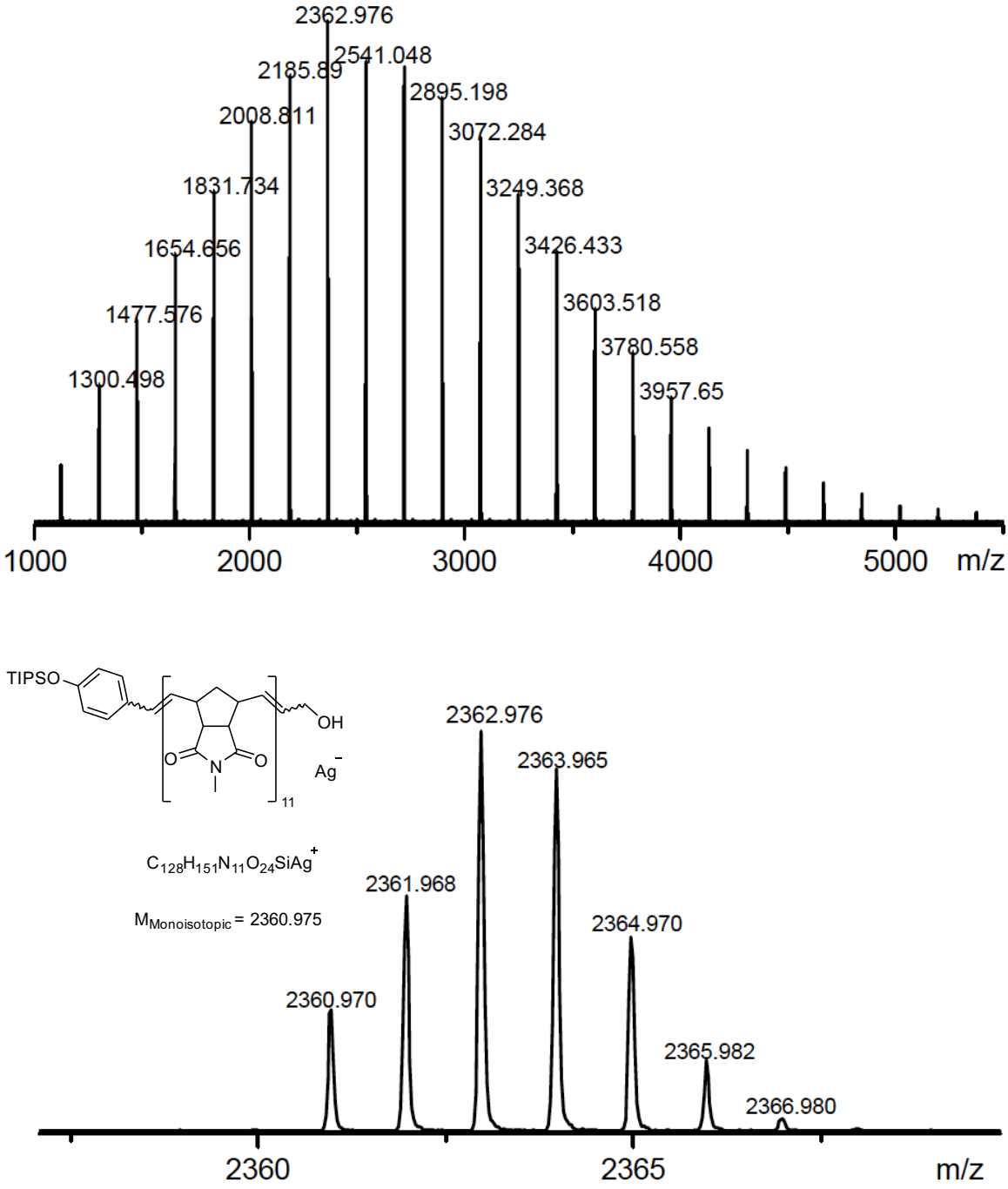
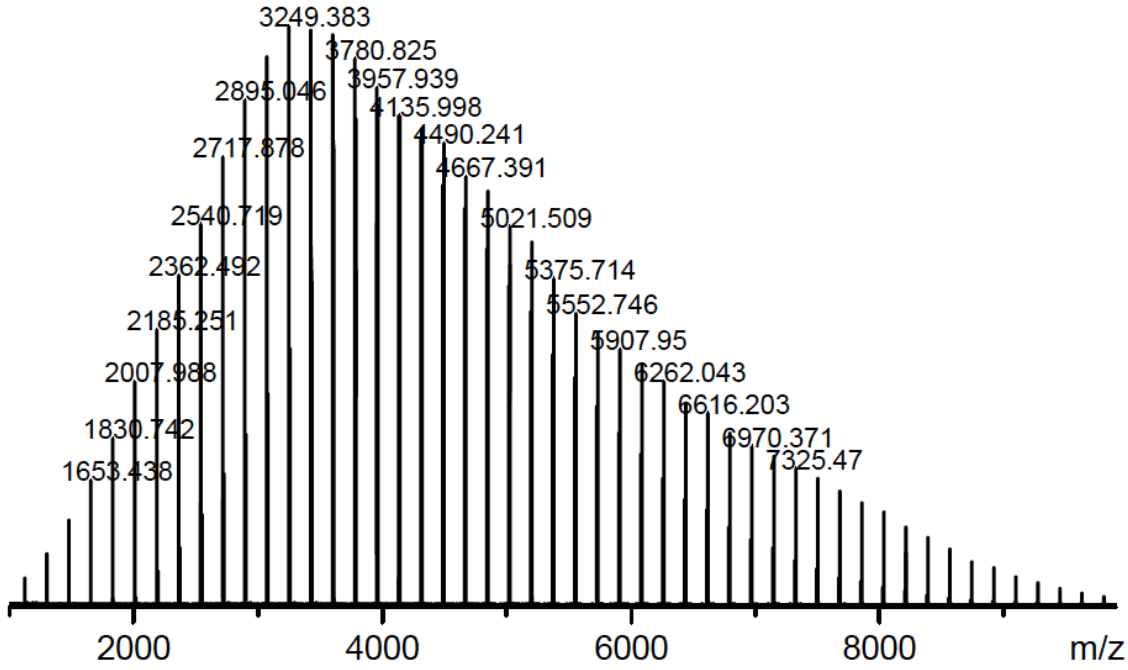


Figure S87 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 14**



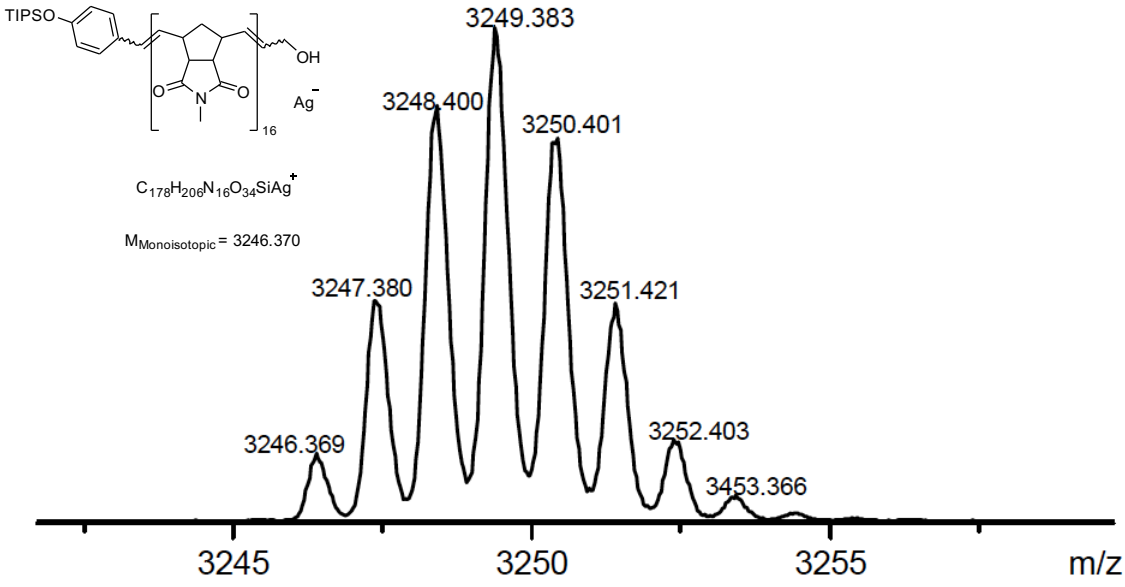


Figure S88 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 15**

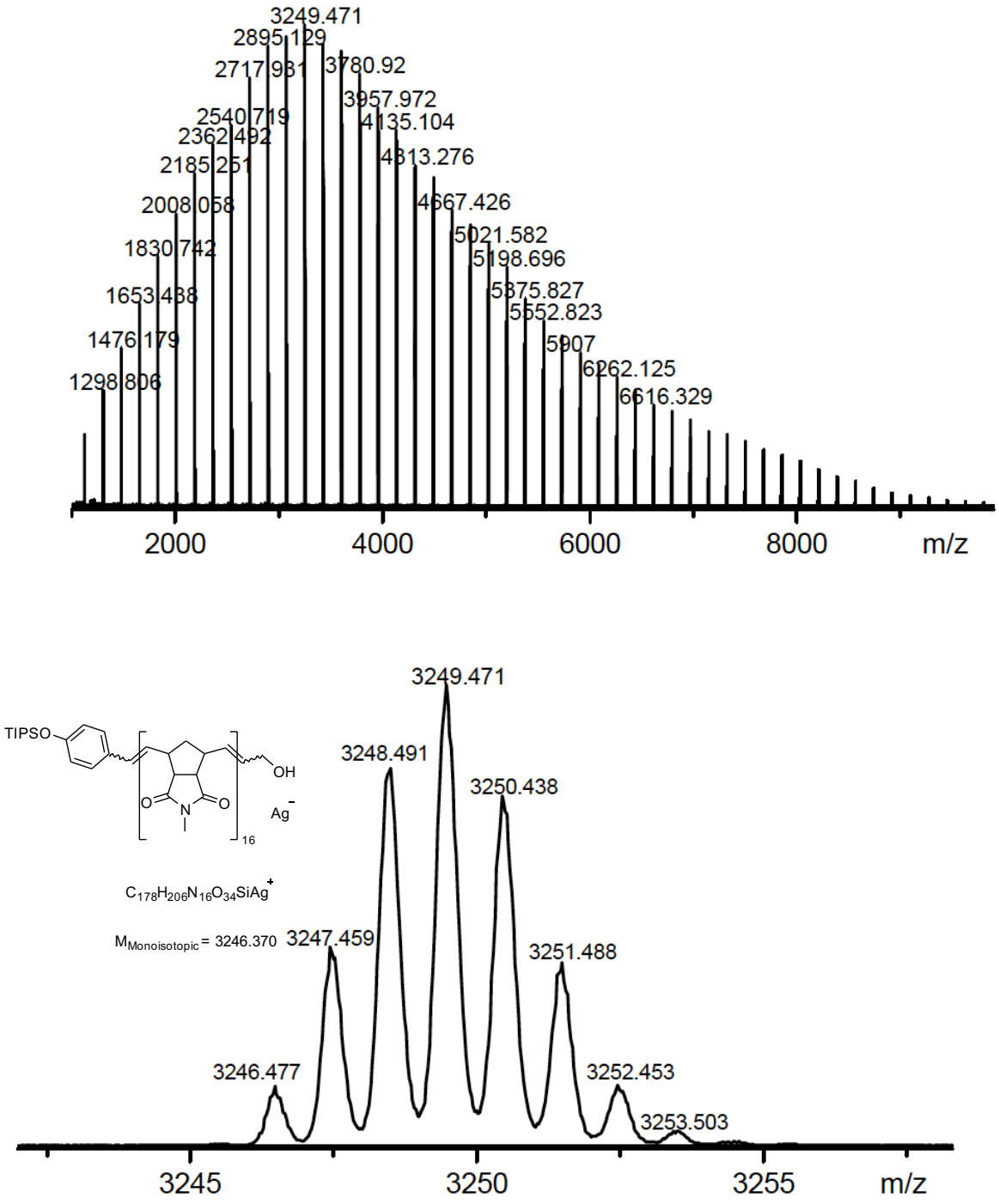


Figure S89 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 16**

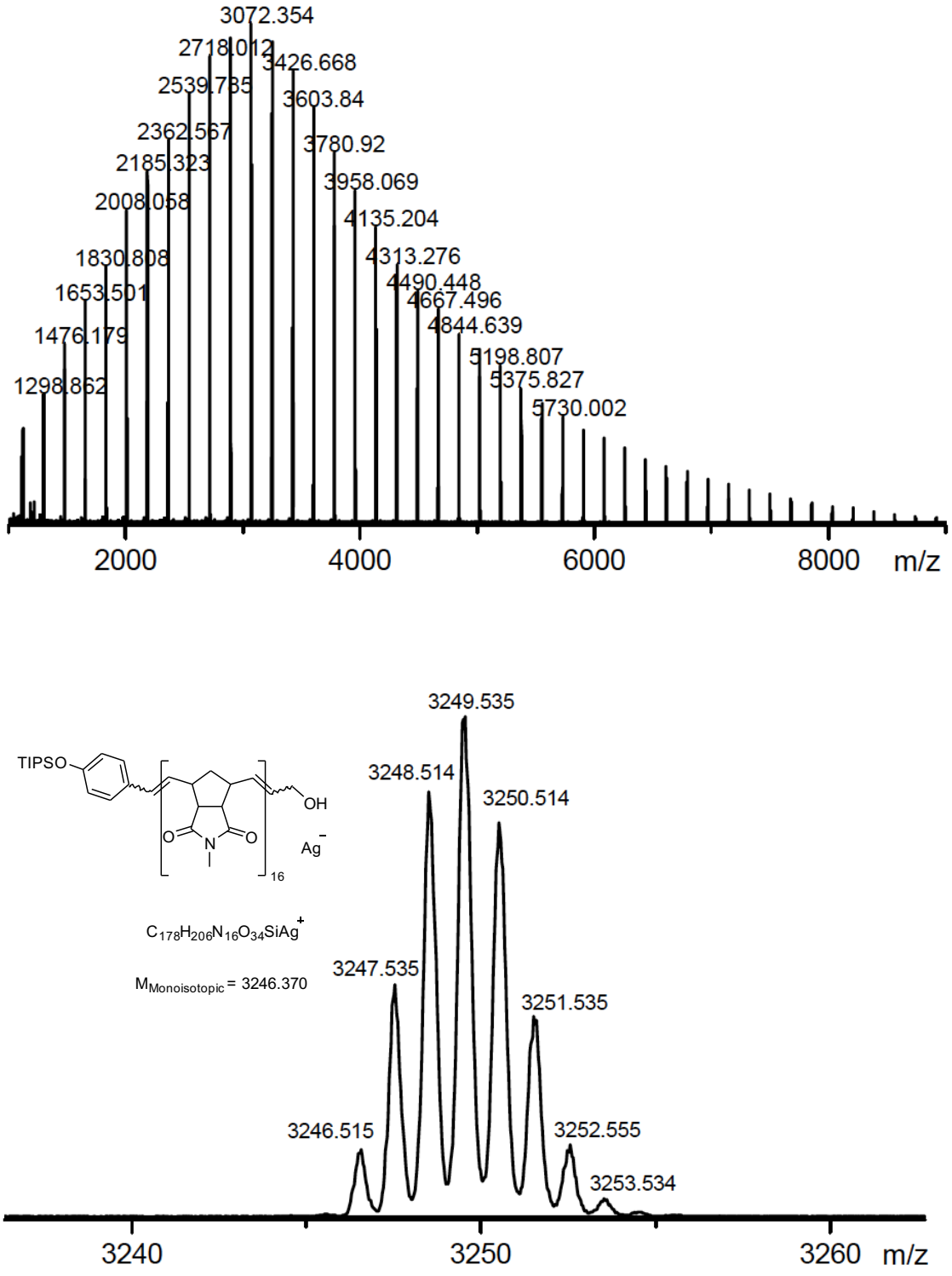


Figure S90 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 17**

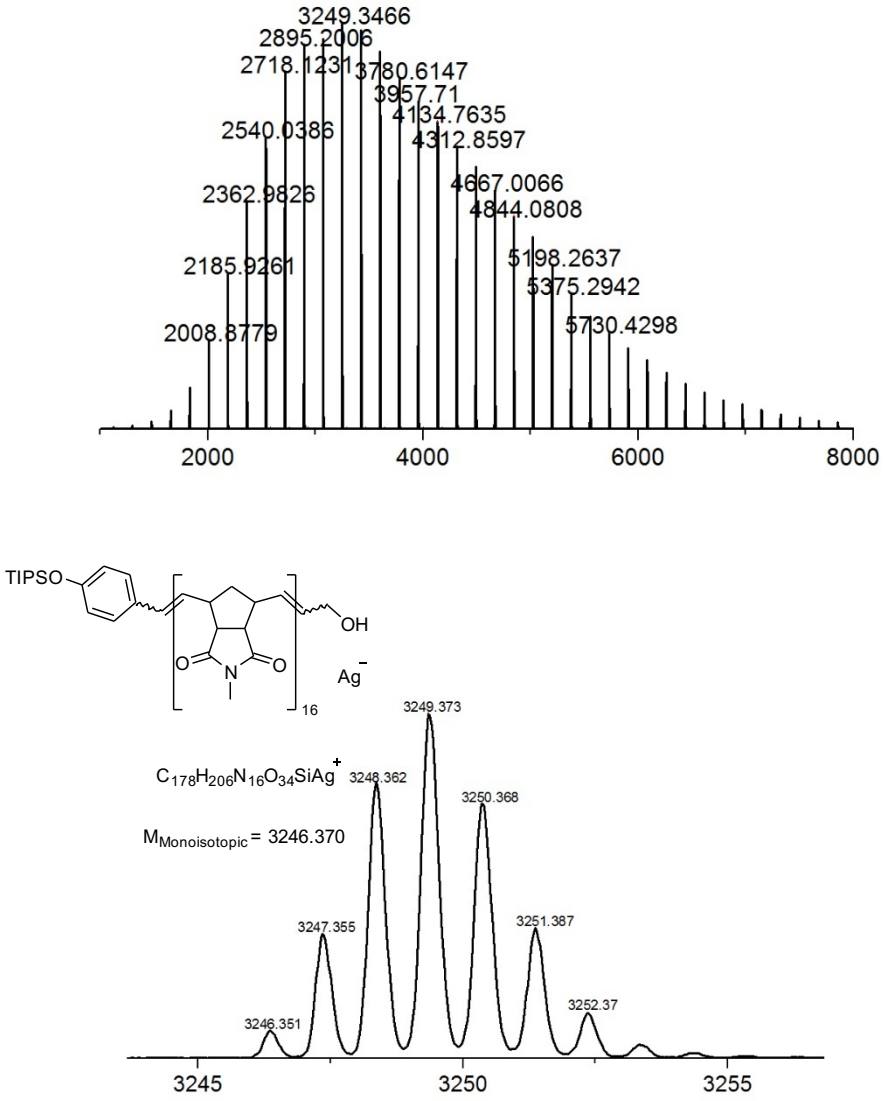


Figure S91 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 18**

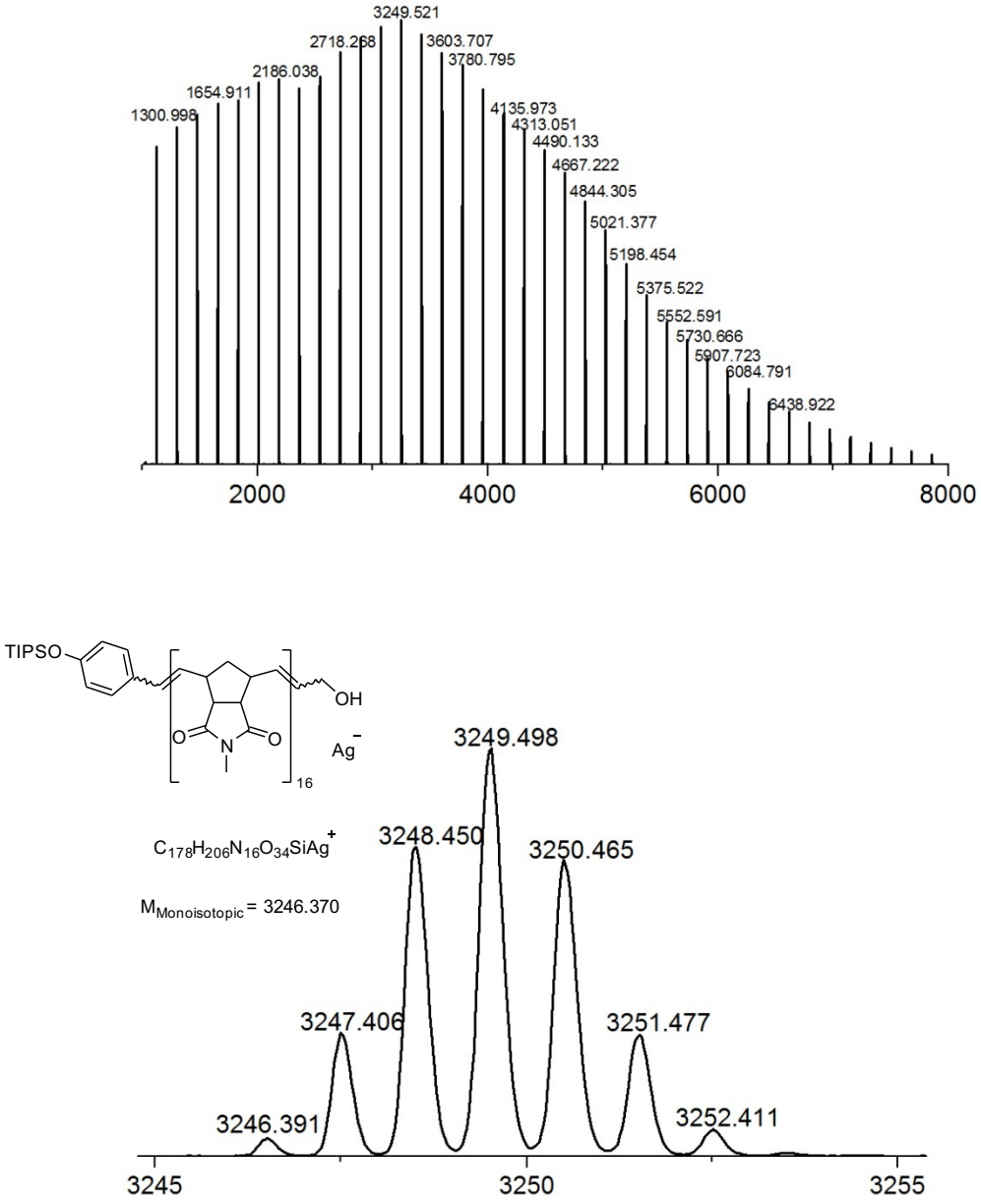


Figure S92 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 19**

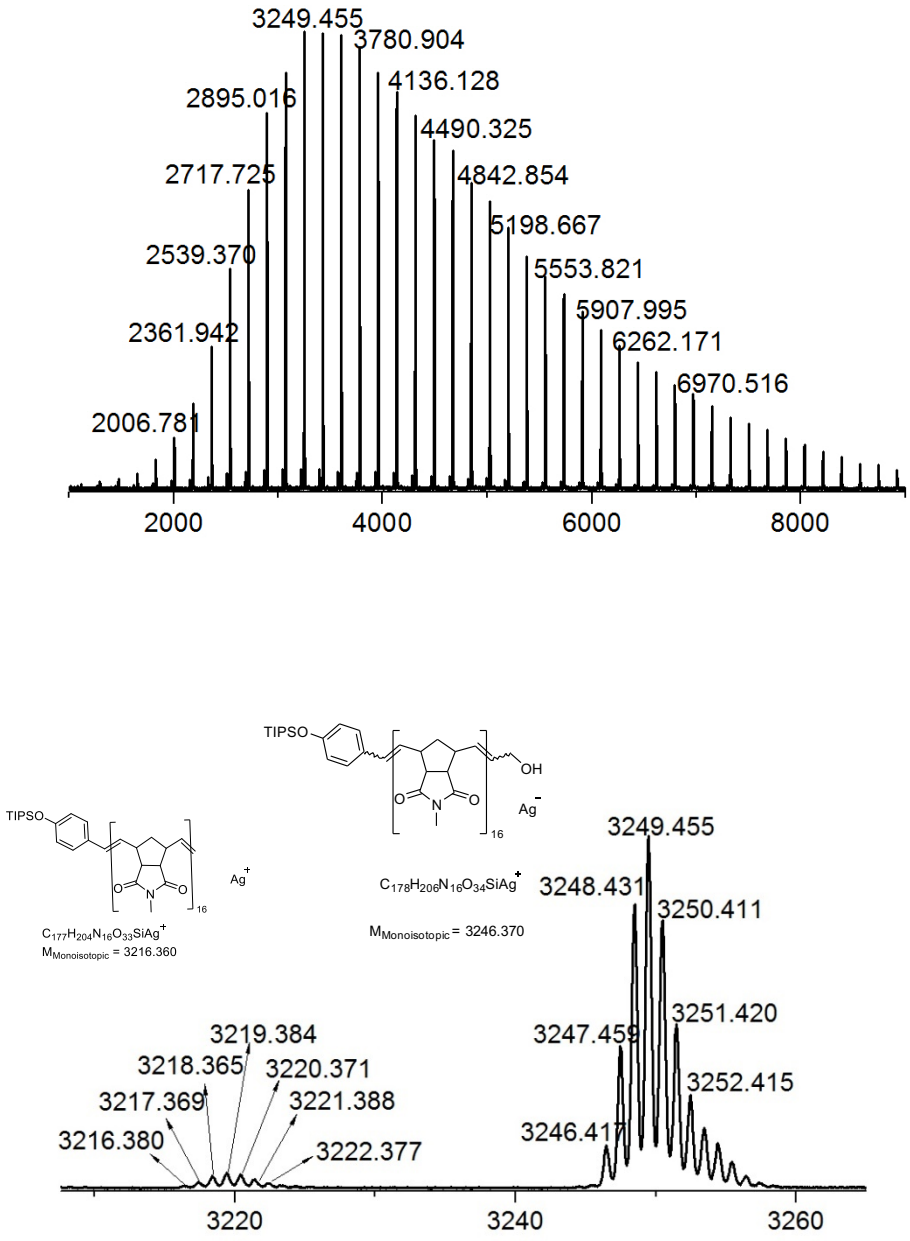


Figure S93 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 20**

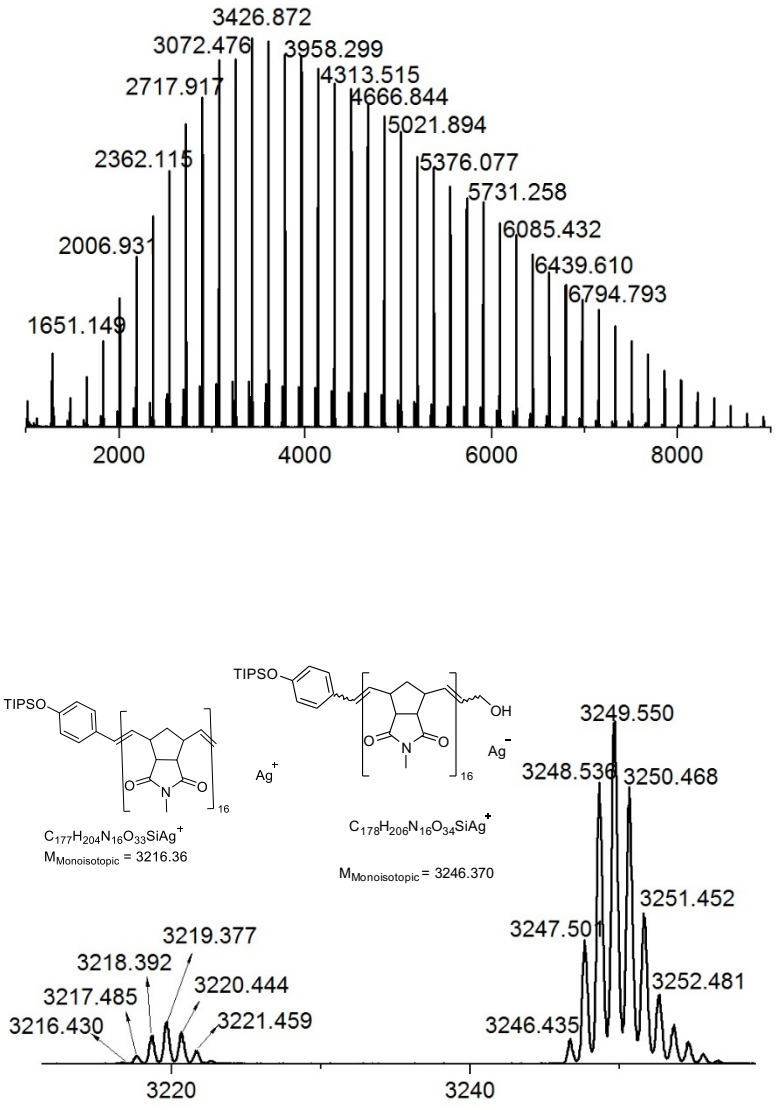


Figure S94 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 21**

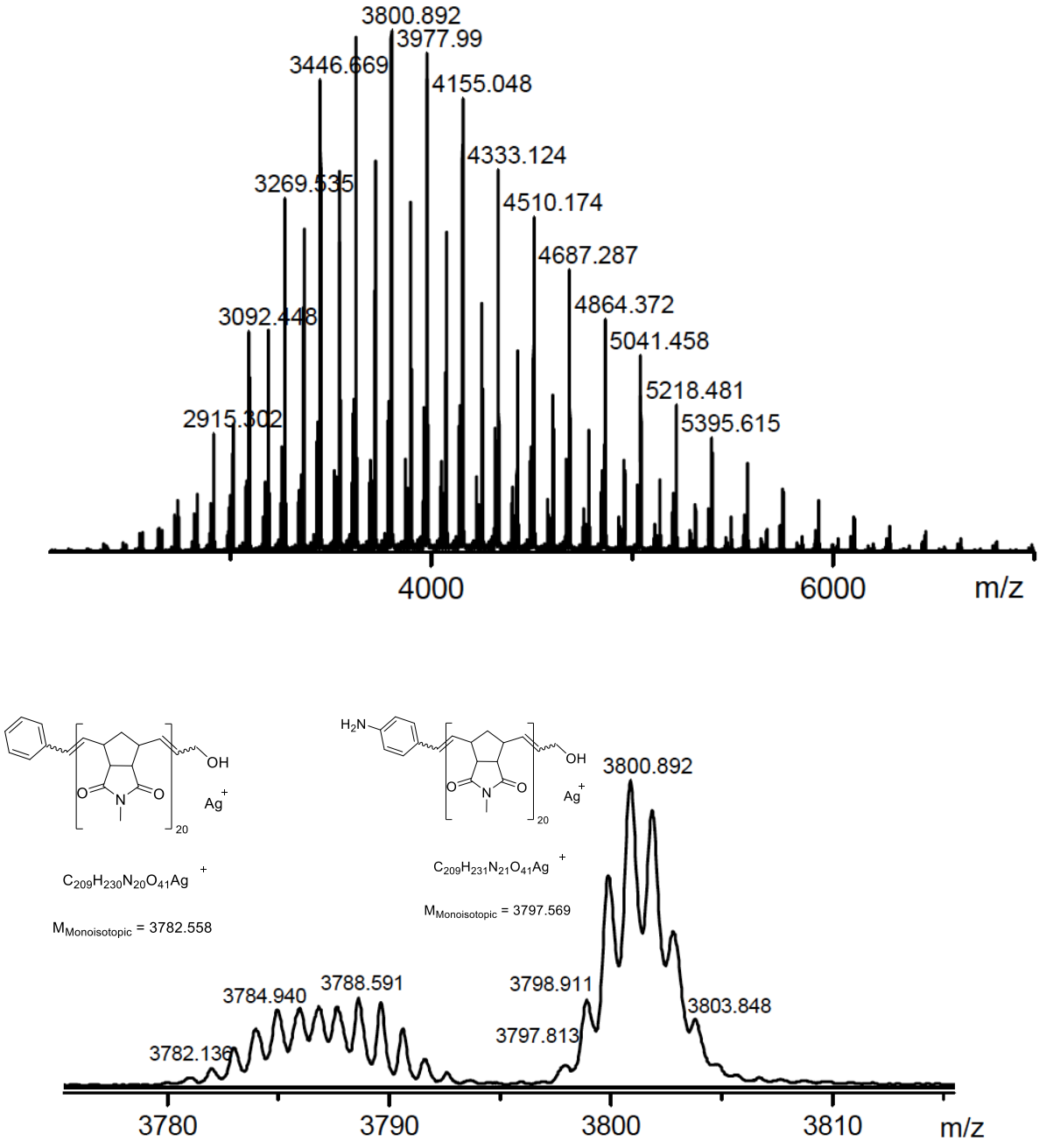


Figure S95 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 22**

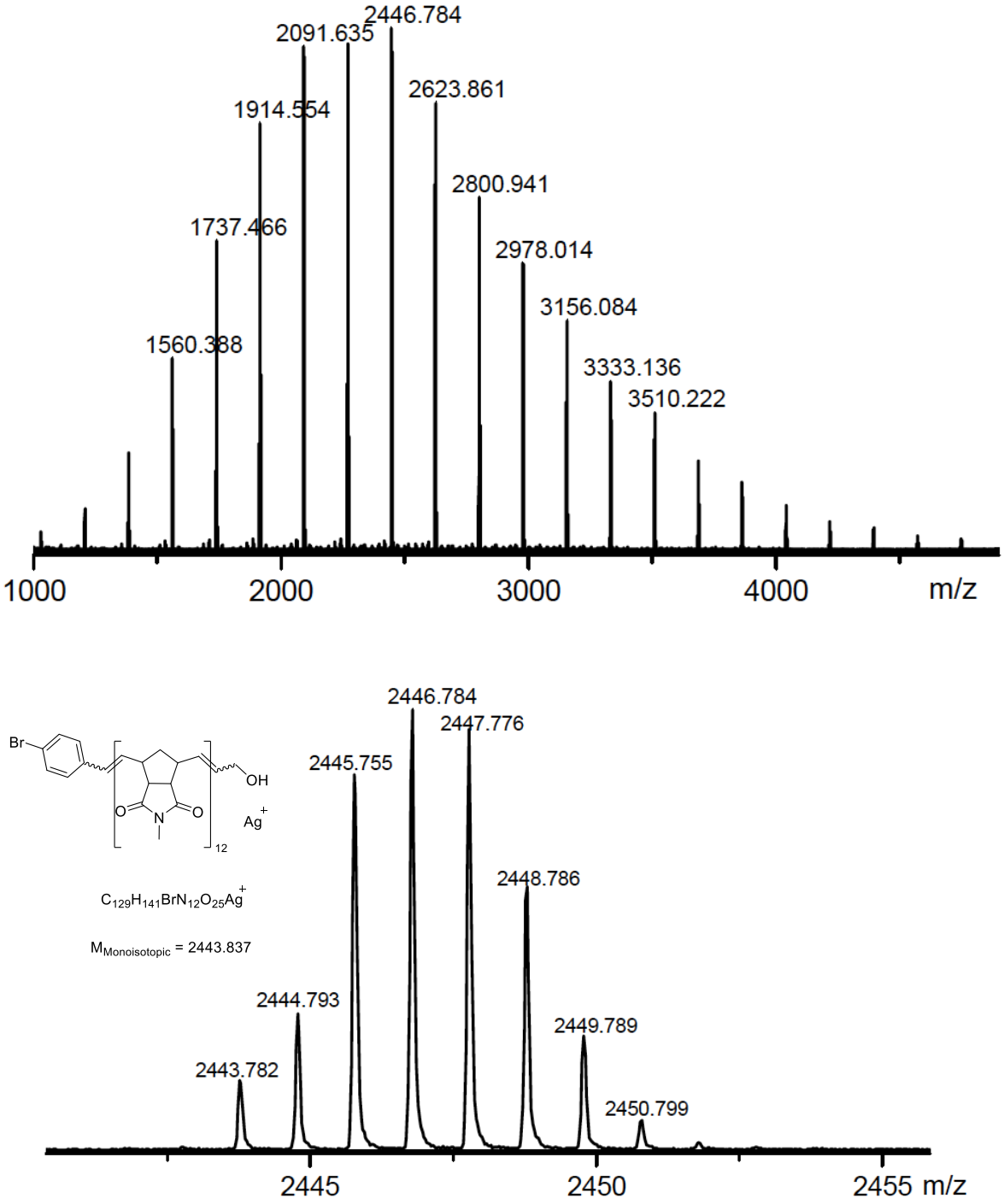


Figure S96 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 23**

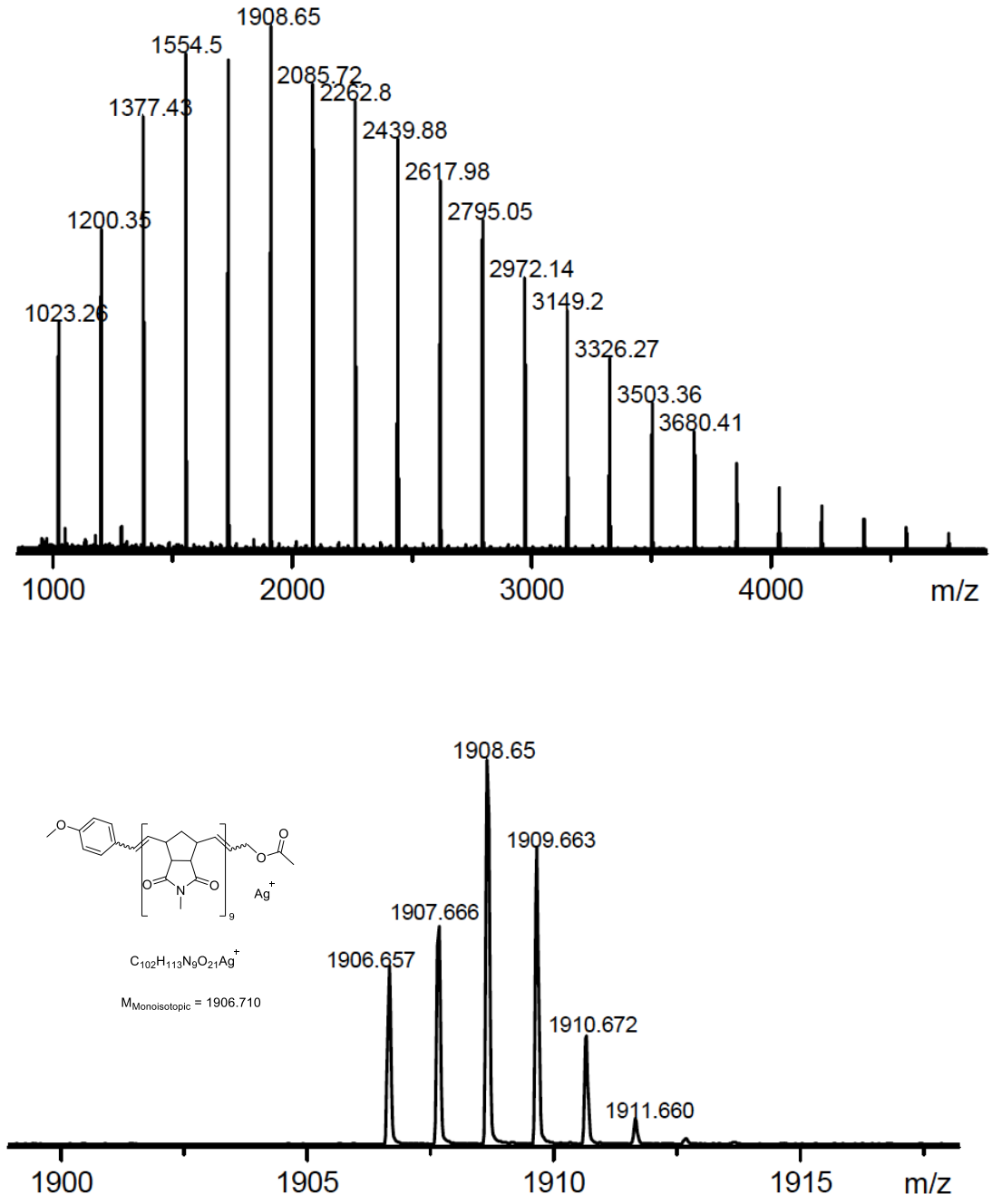
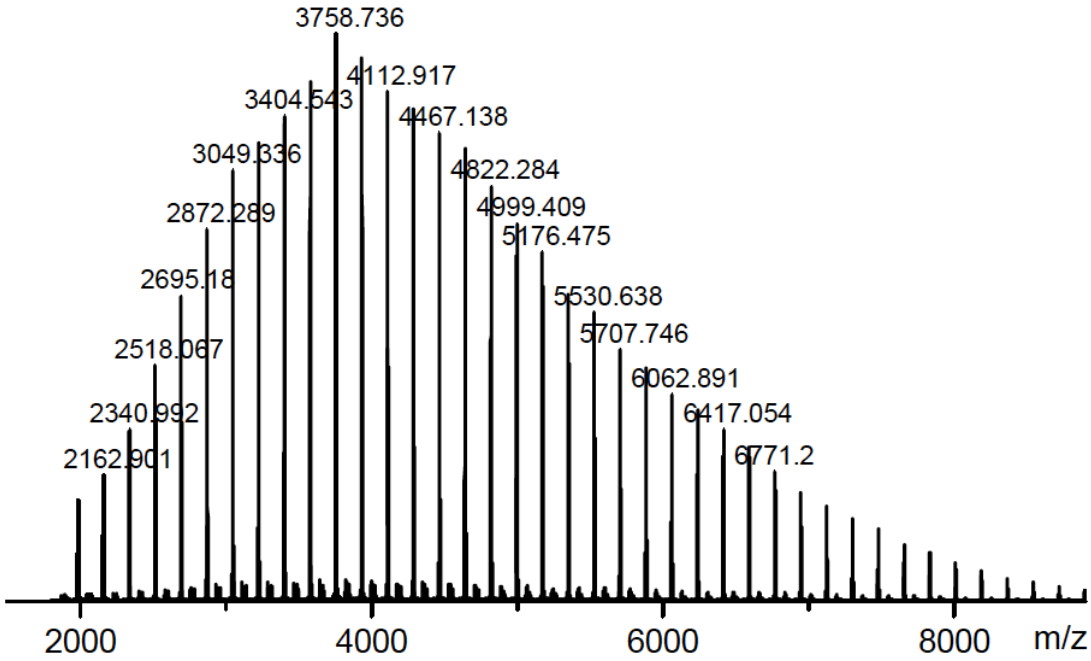


Figure S97 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 24**



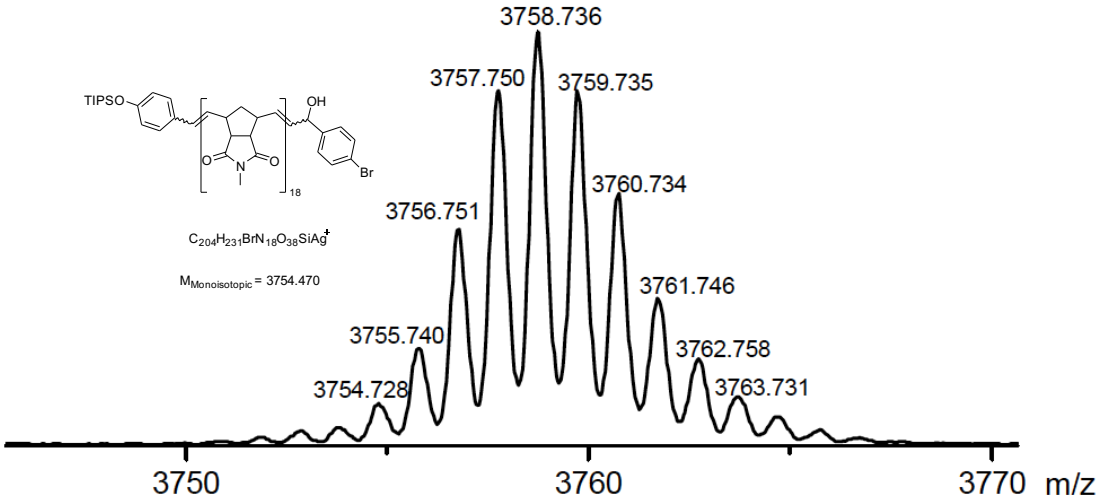


Figure S98 MALDI-ToF Mass Spectrum (DCTB, AgTFA) of **Polymer 25**

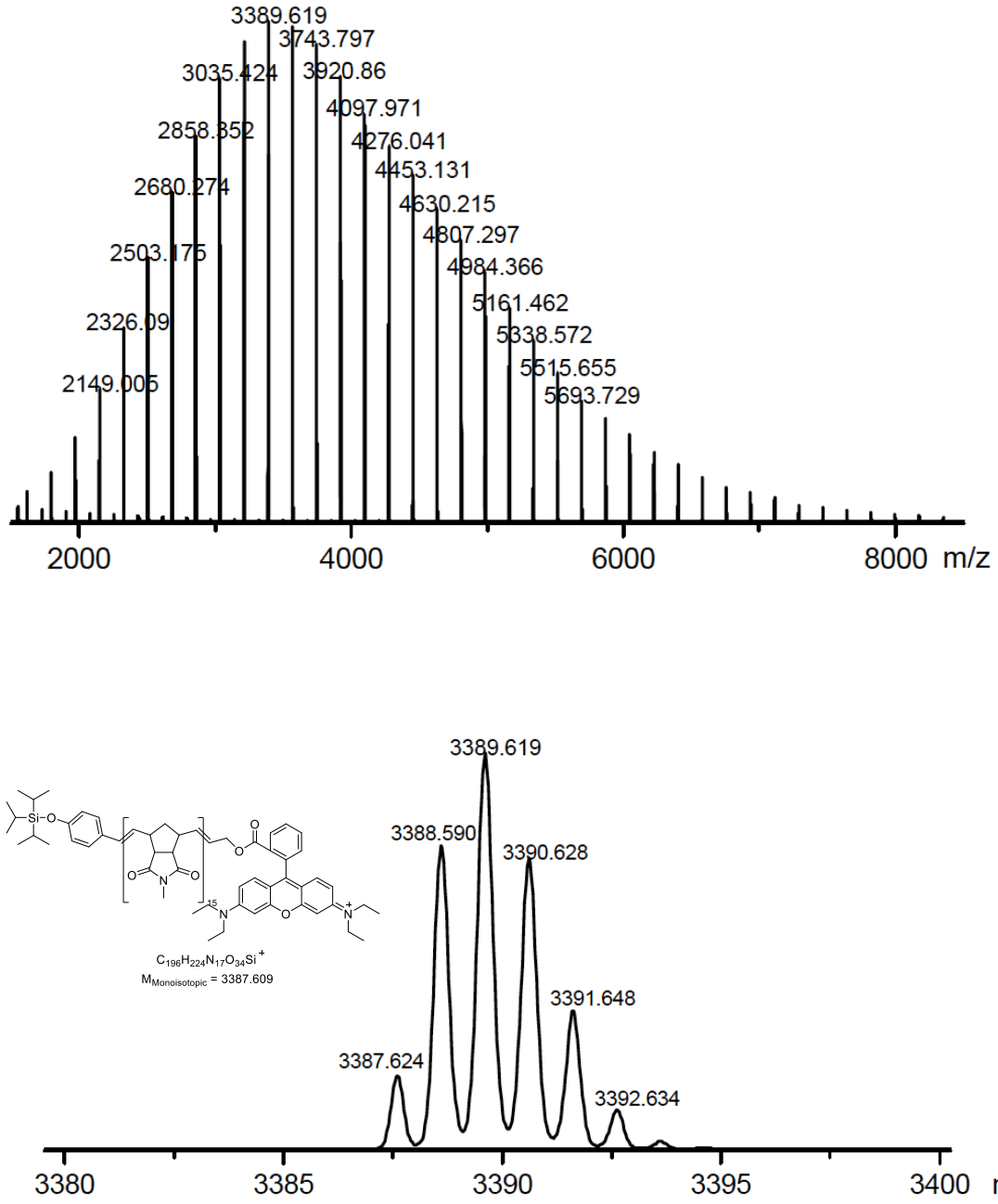


Figure S99 MALDI-ToF Mass Spectrum (DCTB) of **Polymer 26**

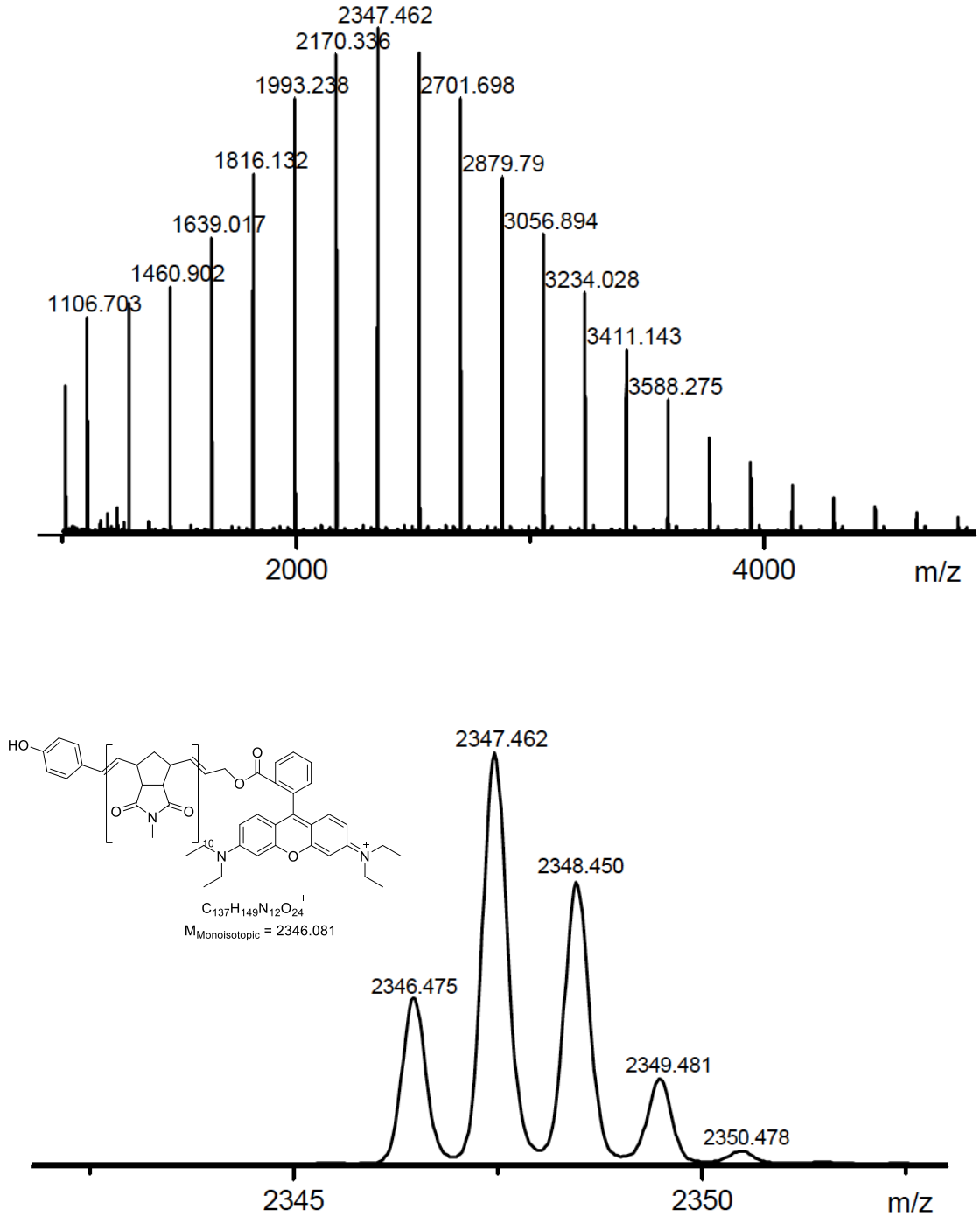


Figure S100 MALDI-ToF Mass Spectrum (DCTB) of **Polymer 27**

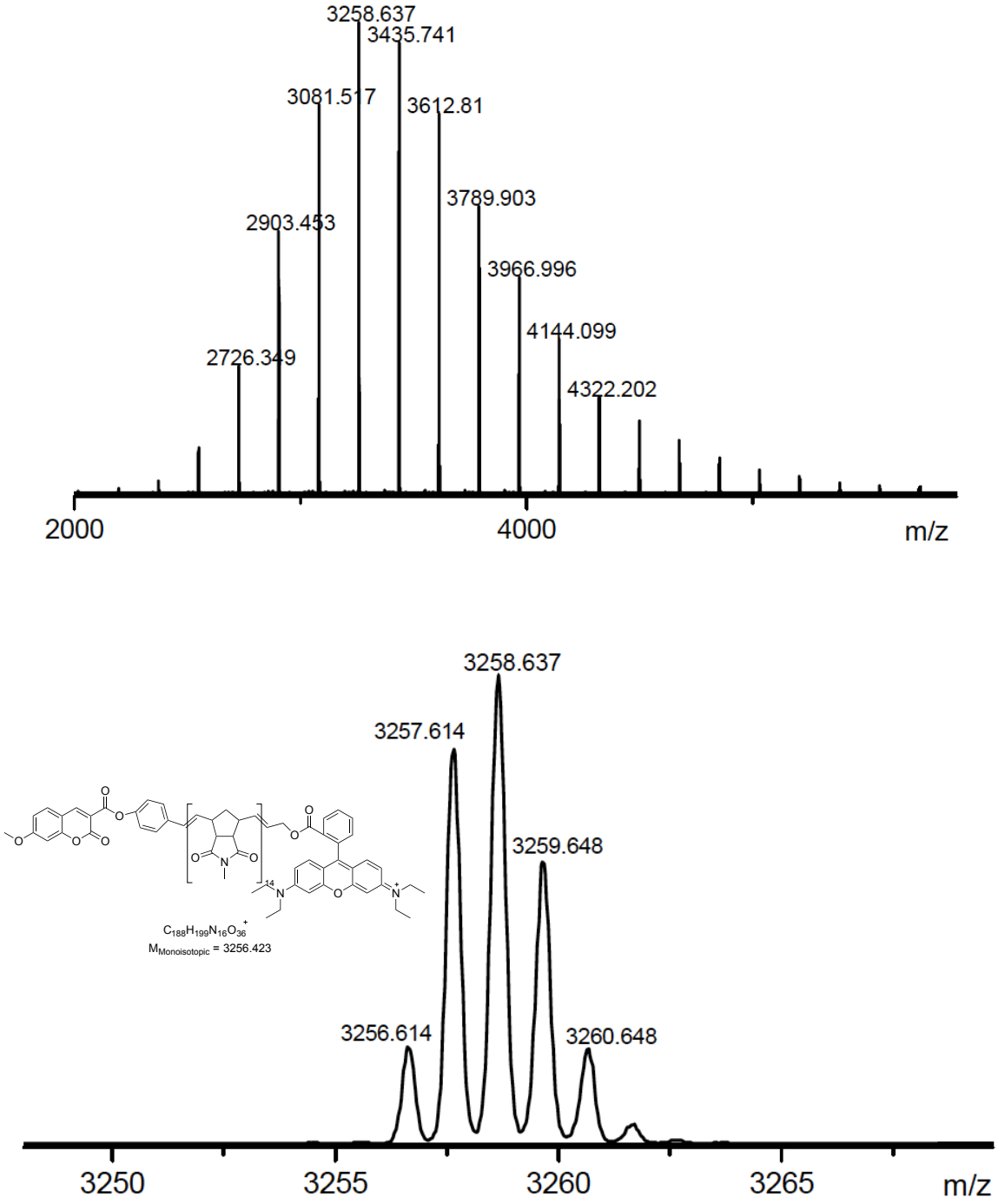


Figure S101 MALDI-ToF Mass Spectrum (DCTB) of **Polymer 28**

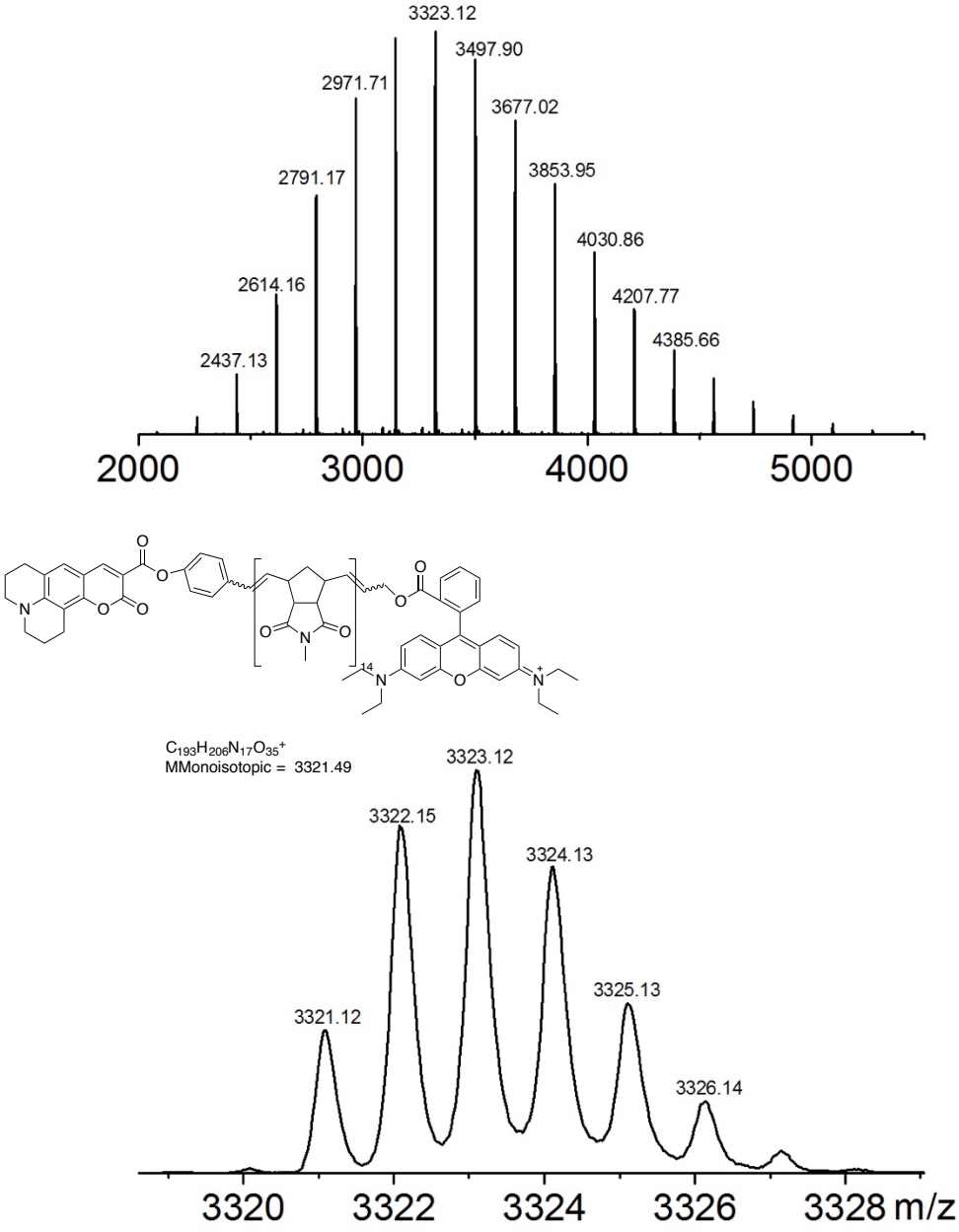


Figure S102 MALDI-ToF Mass Spectrum (DCTB) of **Polymer 29**

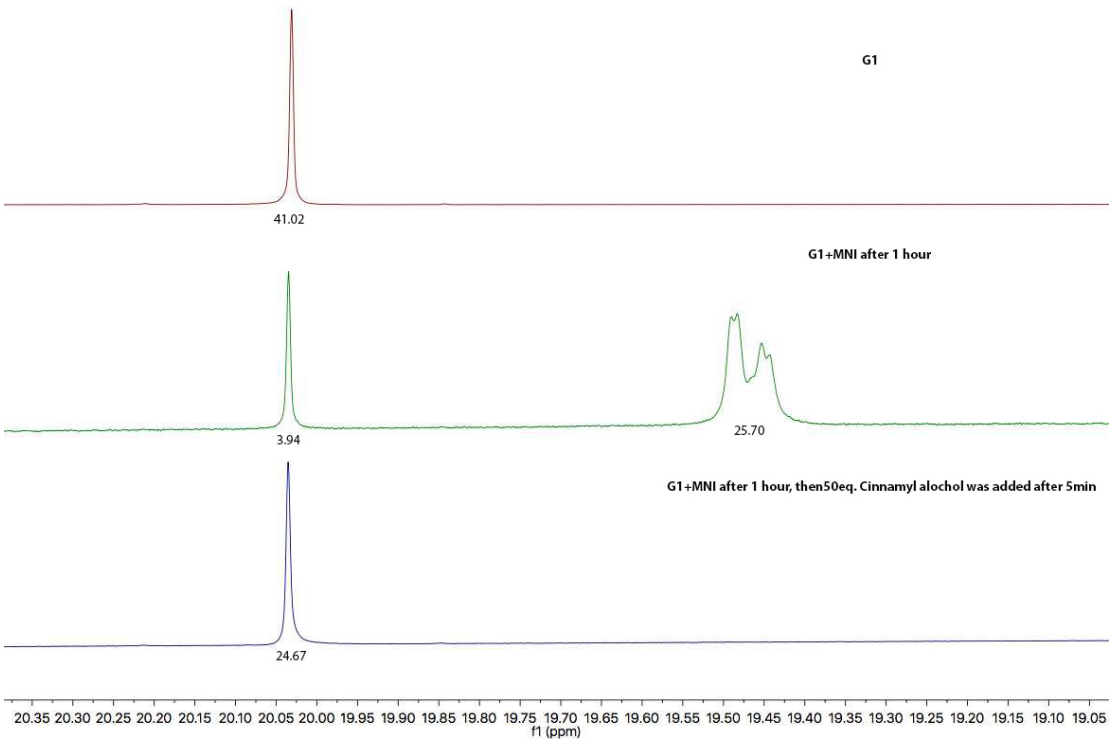


Figure S103 ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of following the reaction of **Polymer 1** (integrated with respect to residual protic solvent as internal standard)

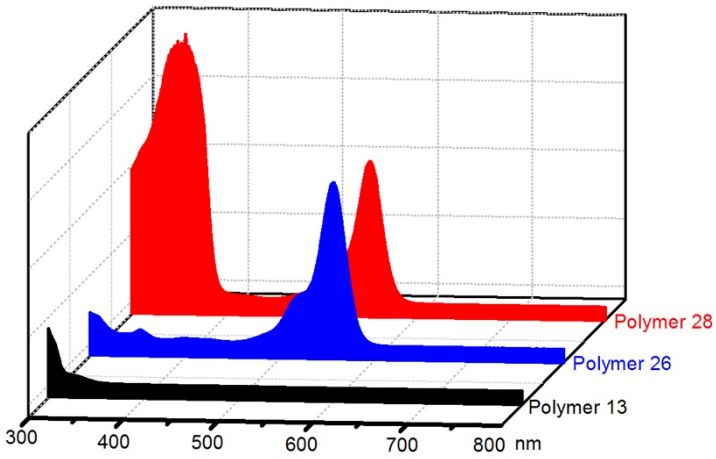


Figure S104 Labelling experiment. UV absorption spectra of **Polymer 13** (black), **Polymer 26** (blue), **Polymer 28** (red).

Photographs of polymers

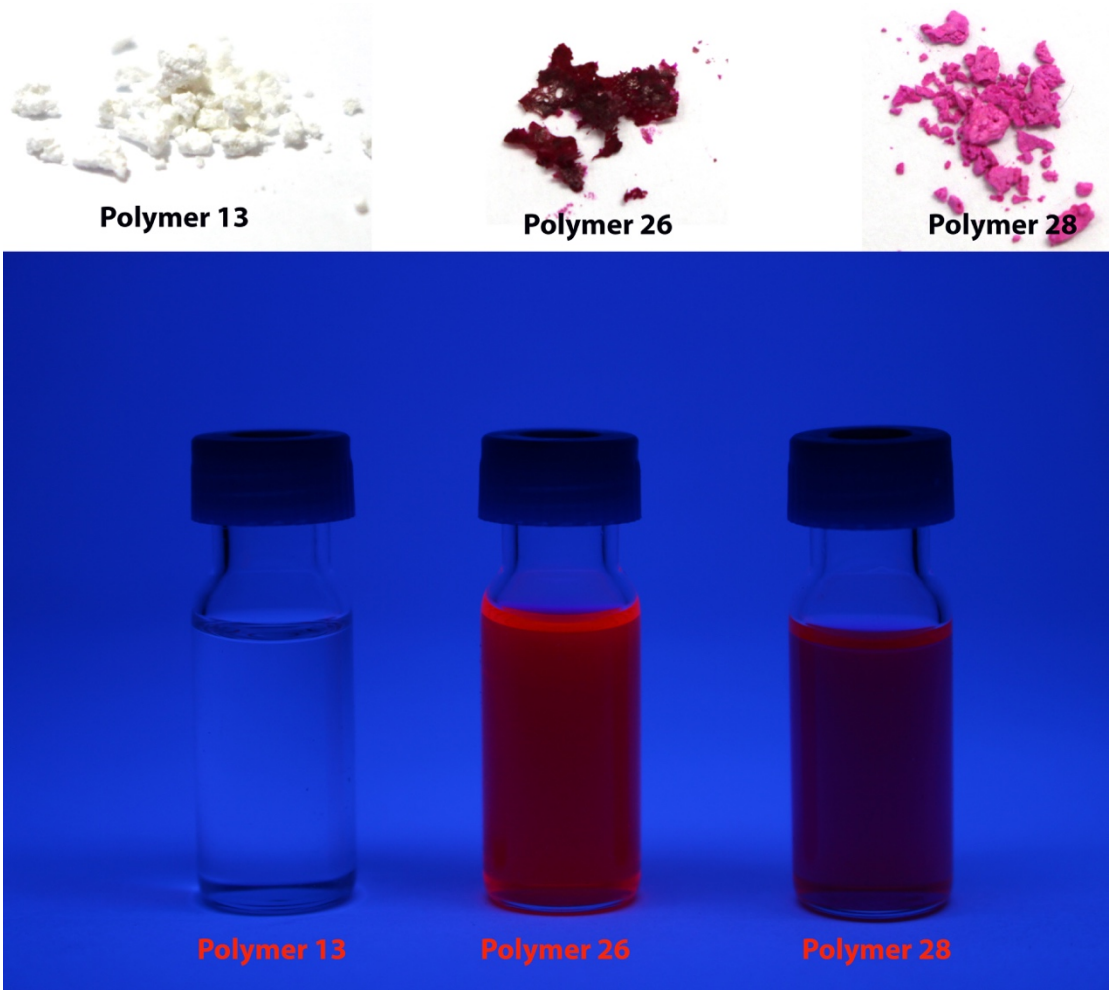


Figure S105 *Top*: Photographs of solid polymer powders. *Bottom*: Solution of Polymers in DCM under UV light 366nm)

FRET experiment

Förster resonance energy transfer (FRET) was investigated in polymer **29**, bearing Coumarin 343 and Rhodamine B fluorophores, which are expected to act as donor and acceptor, respectively. To investigate the sensitized emission of the acceptor, polymer **29** was compared to polymer **26**, bearing only one unit of Rhodamine B. Two optically diluted solutions of **29** and **26** in $CHCl_3$ were prepared and their concentrations adjusted in order to show the same absorption in the Rhodamine region (500-600 nm, Figure

S106).

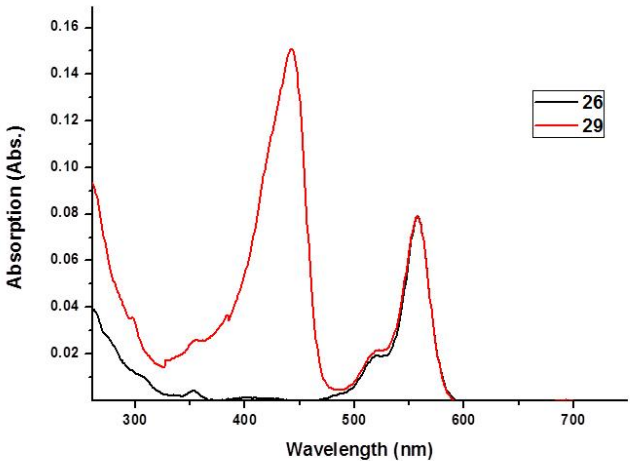


Figure S106. Absorption spectra of solutions of polymers **26** (black) and **29** (red) in $CHCl_3$ used in FRET experiment.

The solutions were irradiated at 417.75 nm, where **29** shows an absorbance of 0.1 (to avoid inner filter effect) and the emission spectra of the two compounds were compared (Figure S107). As expected, whilst **26** shows only Rhodamine emission (λ_{max} = 575 nm), **29** shows a dual emission with a prominent peak centred at 468 nm (belonging to the Coumarin) and a peak at 575 nm (belonging to the Rhodamine). Remarkably, the intensity of the Rhodamine peak in **29** is almost 8-fold higher than the Rhodamine peak in **26**, suggesting the presence of a FRET.

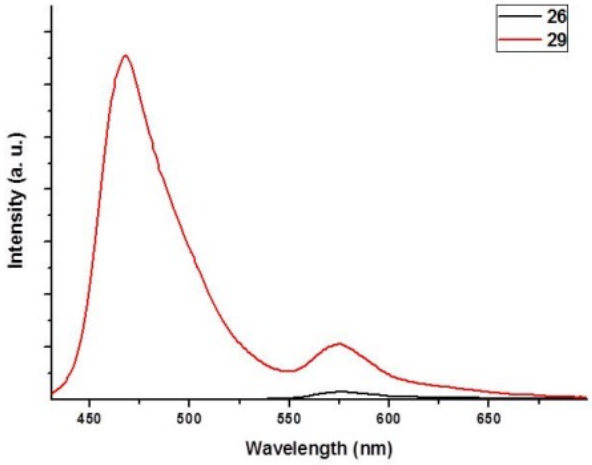


Figure S107. Emission spectra of **26** (black) and **29** (red) in $CHCl_3$ (λ_{exc} = 417.75 nm). FRET efficiency was evaluated according to equation (1)

$$E = \left(1 + \frac{\varphi_{Rhod}}{\varphi_{Coum}} \frac{I_{DA}}{I_{AD} - I_A}\right)^{-1} \quad (1)$$

Where φ_{Rhod} and φ_{Coum} are respectively the quantum yields of Rhodamine B and Coumarin 343, I_{DA} and I_{AD} are the emission intensities Coumarin and Rhodamine in **29** and I_A is the emission intensity of Rhodamine in **26**.[3] The calculated FRET efficiency of 12% is in good agreement with the expected value (13%) for this FRET pair at a distance of 68 Å, which is the size of a polymer of 14 units estimated according to semiempirical (PM6) models.

References

(1) Bai, Y.; Xing, H.; Lu, Y.; et. al. *ACS Nano* **2015**, *9*, 10227;
(2) Hillmyer, M. A.; Grubbs, R. H.; et. al. *Macromolecules* **1992**, *25*, 3345.
(3) Medintz, I. and Hildebrandt, N. (eds) (**2013**), in FRET - Förster Resonance Energy Transfer: From Theory to Applications, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. Chapter 5.