Supporting Information

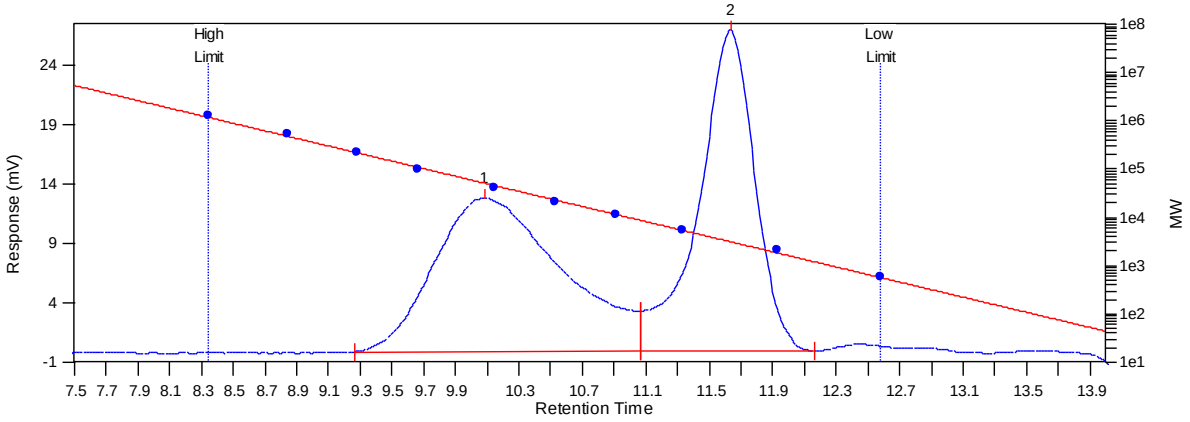
for

Regiodivergent Cobalt-Catalyzed Diels-Alder Reactions for the Synthesis of Bifunctional Building Blocks and their Suzuki-Cross-Coupling Polymerizations

Julian R. Kuttner, and Gerhard Hilt*

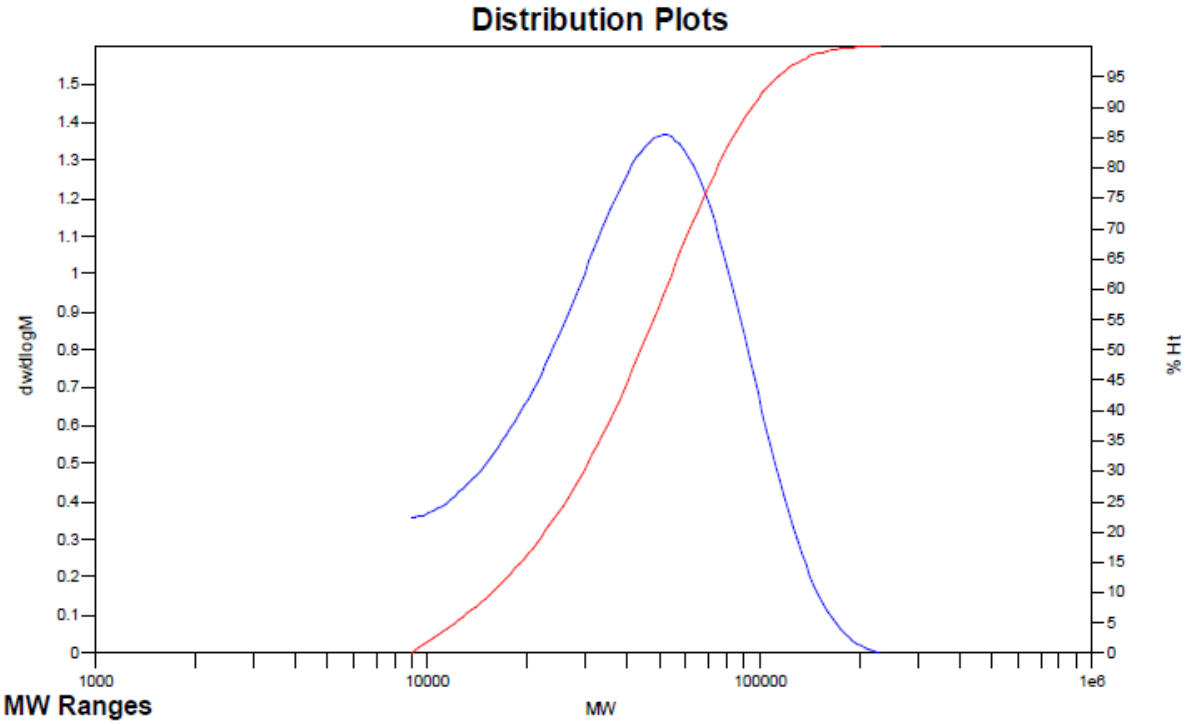
1. Chromatograms and relative molecular weight distributions

1.1. Poly-3a



MW Averages

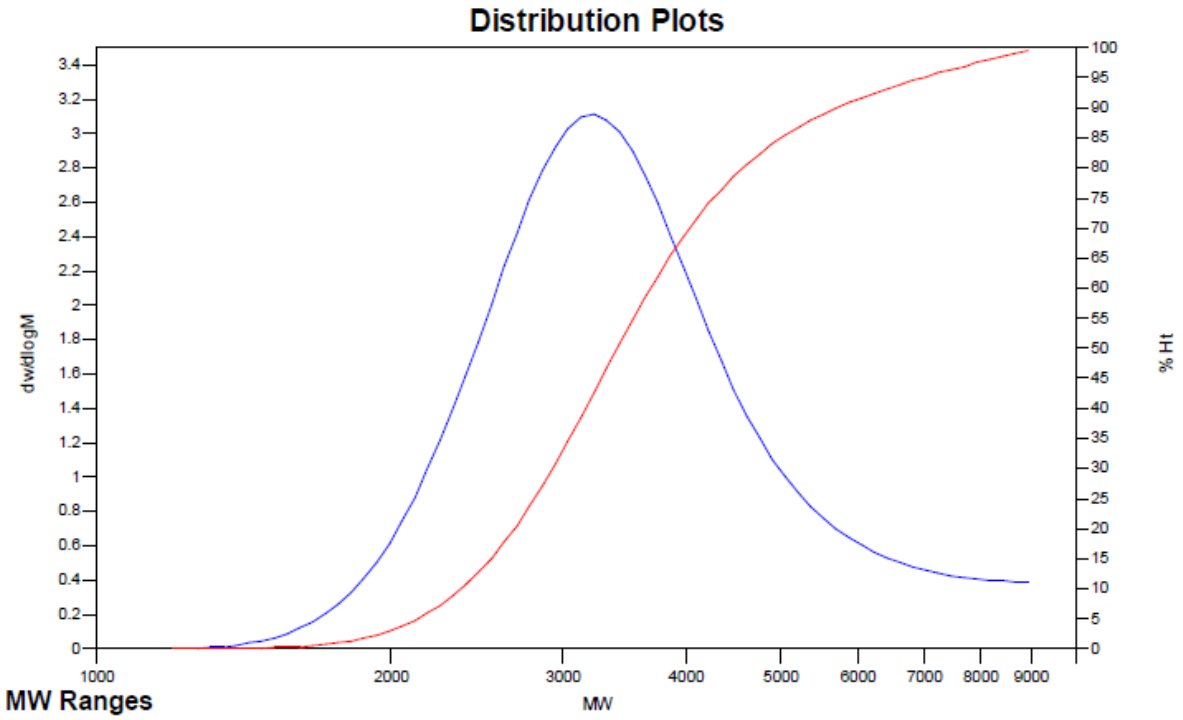
Mp: 51066	Mn: 32305	Mv: 47097	Mw: 49902
Mz: 69936	Mz+1: 89168	PD: 1.5447	



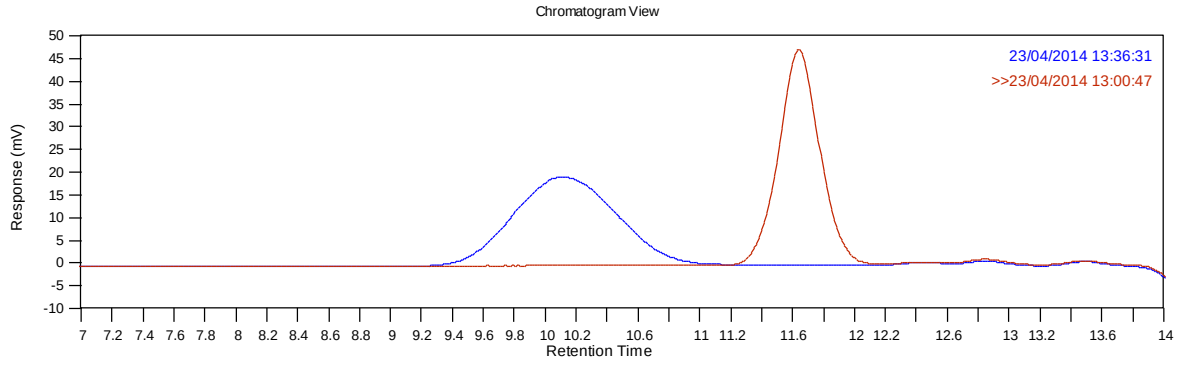
MW Ranges

MW Averages

Mp: 3219	Mn: 3292	Mv: 3632	Mw: 3703
Mz: 4244	Mz+1: 4915	PD: 1.1248	



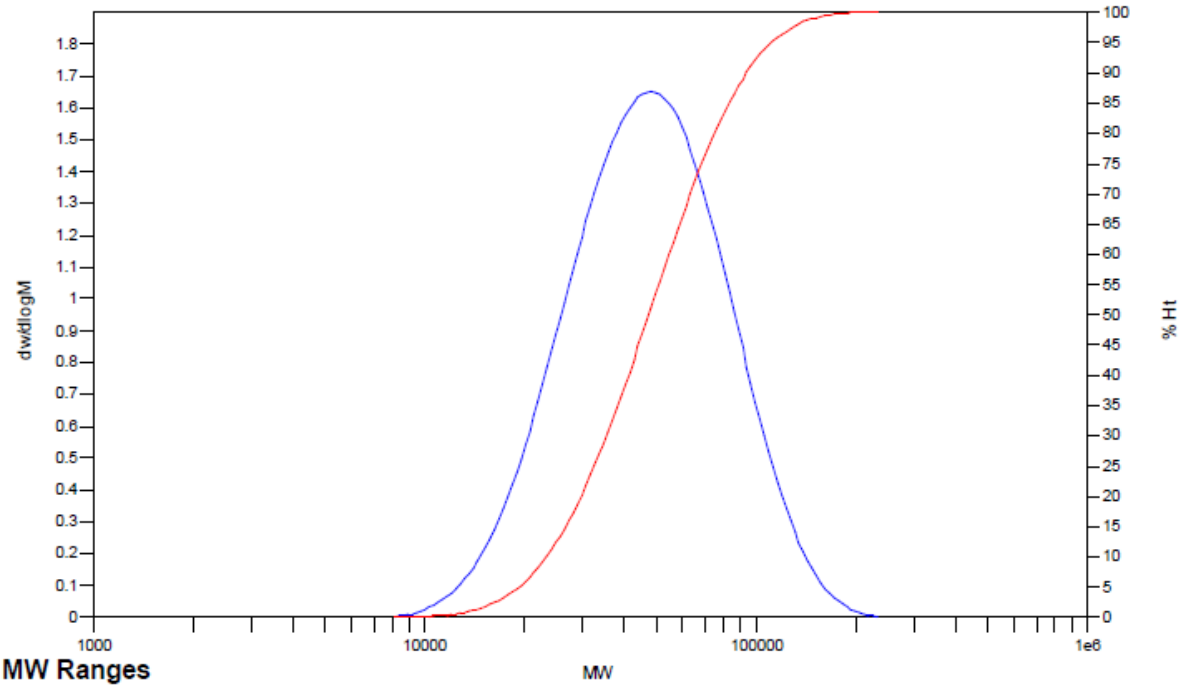
After chromatographic separation



MW Averages

Mp: 48217	Mn: 40112	Mv: 51011	Mw: 53131
Mz: 68751	Mz+1: 85720	PD: 1.3246	

Distribution Plots

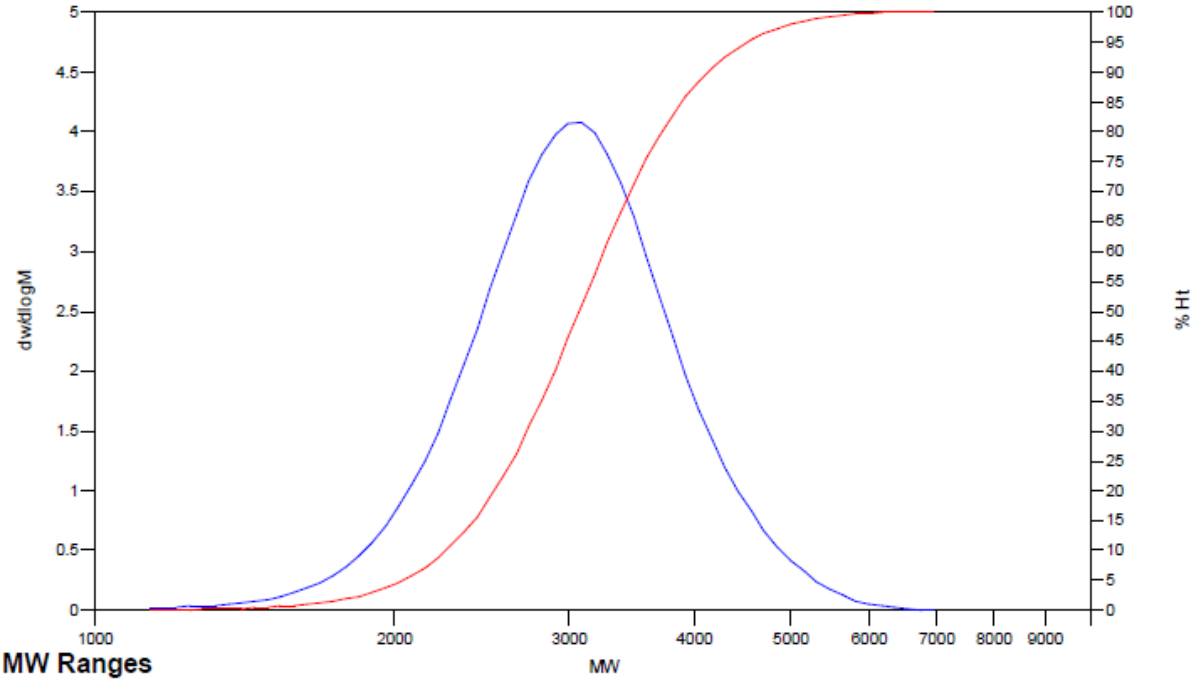


MW Ranges

MW Averages

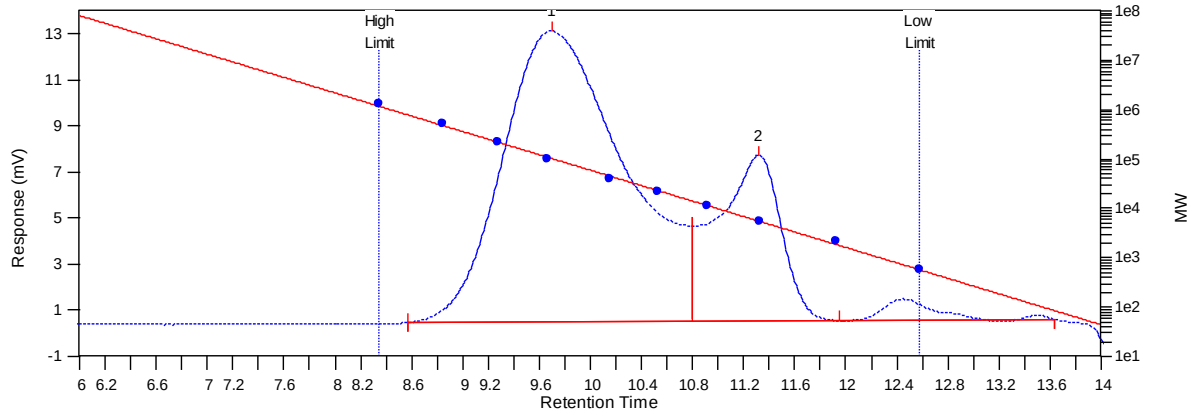
Mp: 3080	Mn: 2916	Mv: 3066	Mw: 3092
Mz: 3271	Mz+1: 3456	PD: 1.0604	

Distribution Plots



MW Ranges

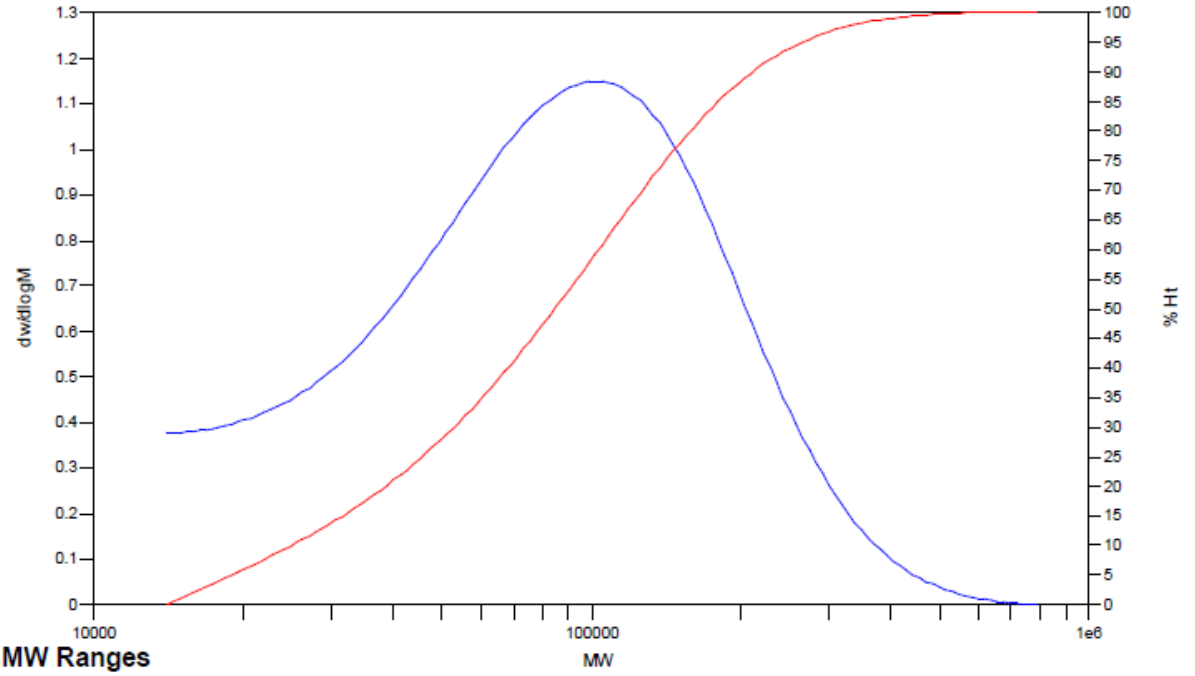
1.2. **Poly-4a**



MW Averages

Mp: 101910	Mn: 56857	Mv: 95916	Mw: 104034
Mz: 167280	Mz+1: 237171	PD: 1.8297	

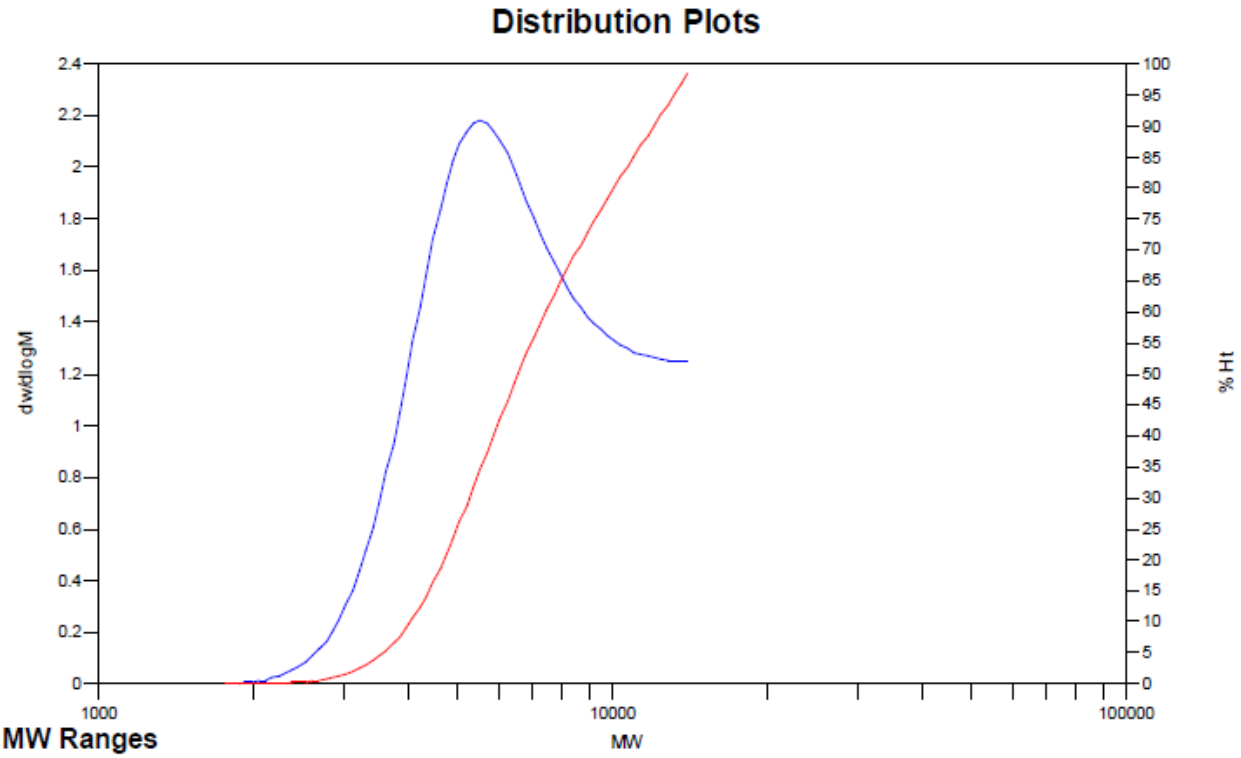
Distribution Plots



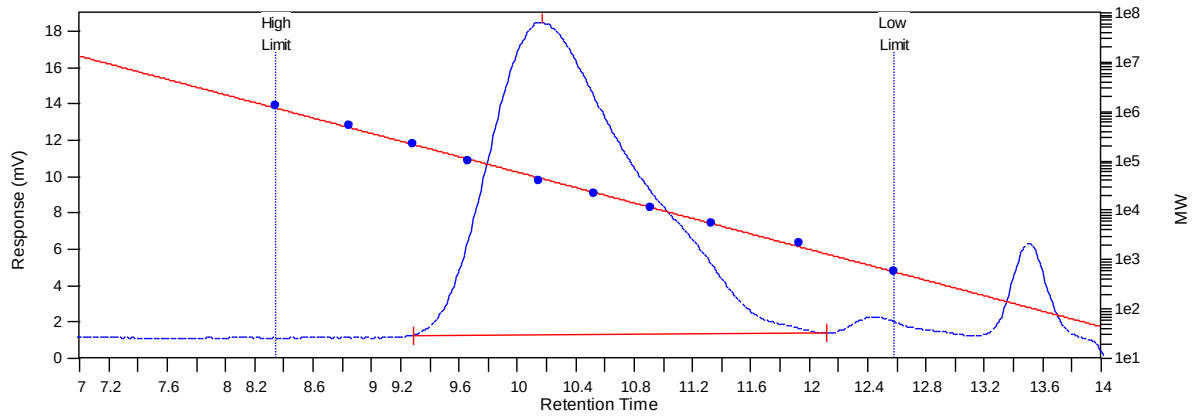
MW Ranges

MW Averages

Mp: 5529	Mn: 6132	Mv: 7027	Mw: 7196
Mz: 8372	Mz+1: 9497	PD: 1.1735	

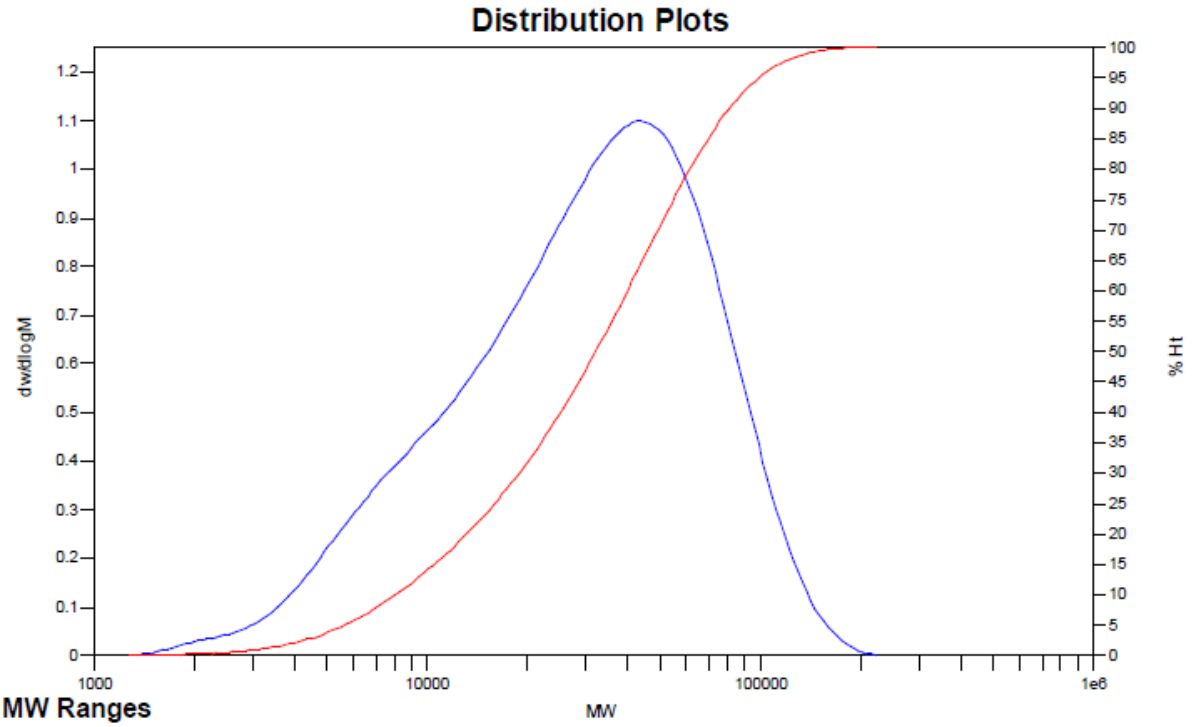


1.3. **Poly-3b**

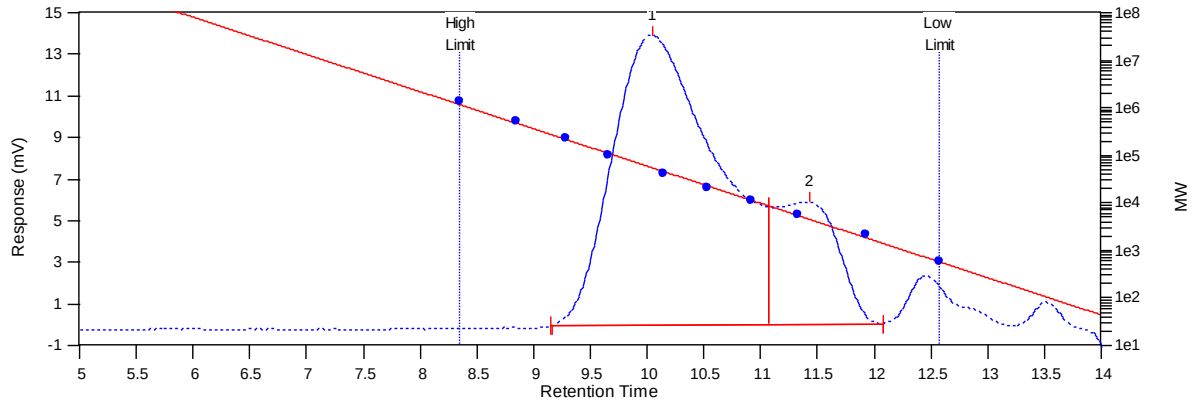


MW Averages

Mp: 43944	Mn: 18174	Mv: 35565	Mw: 38778
Mz: 61670	Mz+1: 82062	PD: 2.1337	



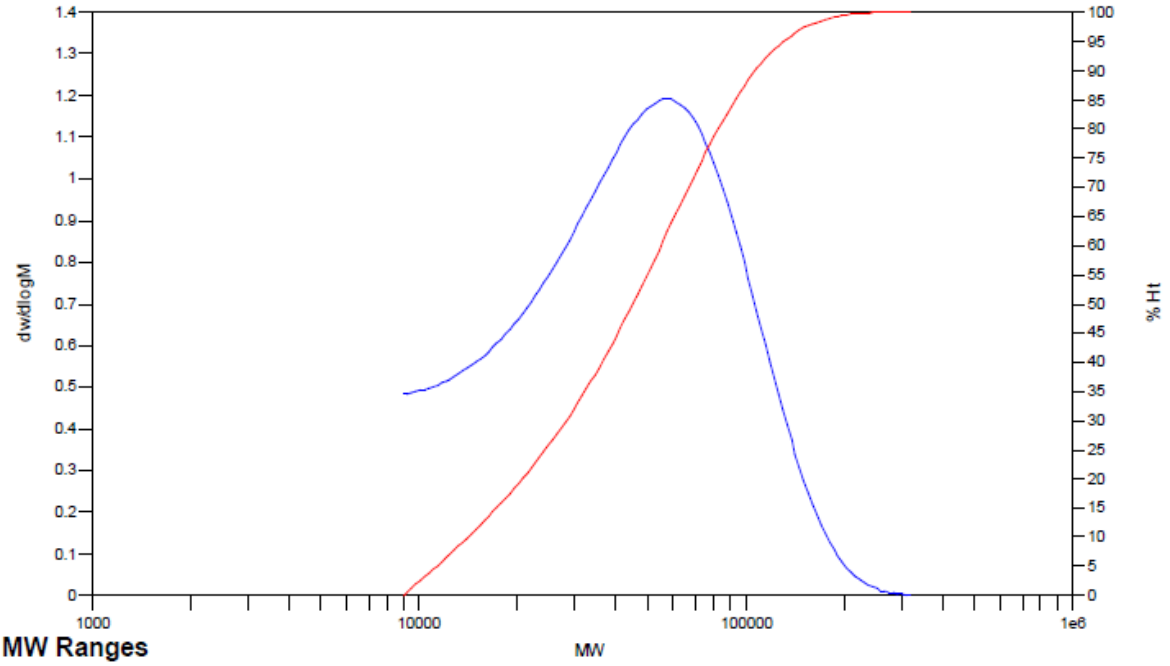
1.4. **Poly-4b**



MW Averages

Mp: 57587	Mn: 31424	Mv: 49814	Mw: 53509
Mz: 80652	Mz+1: 107021	PD: 1.7028	

Distribution Plots

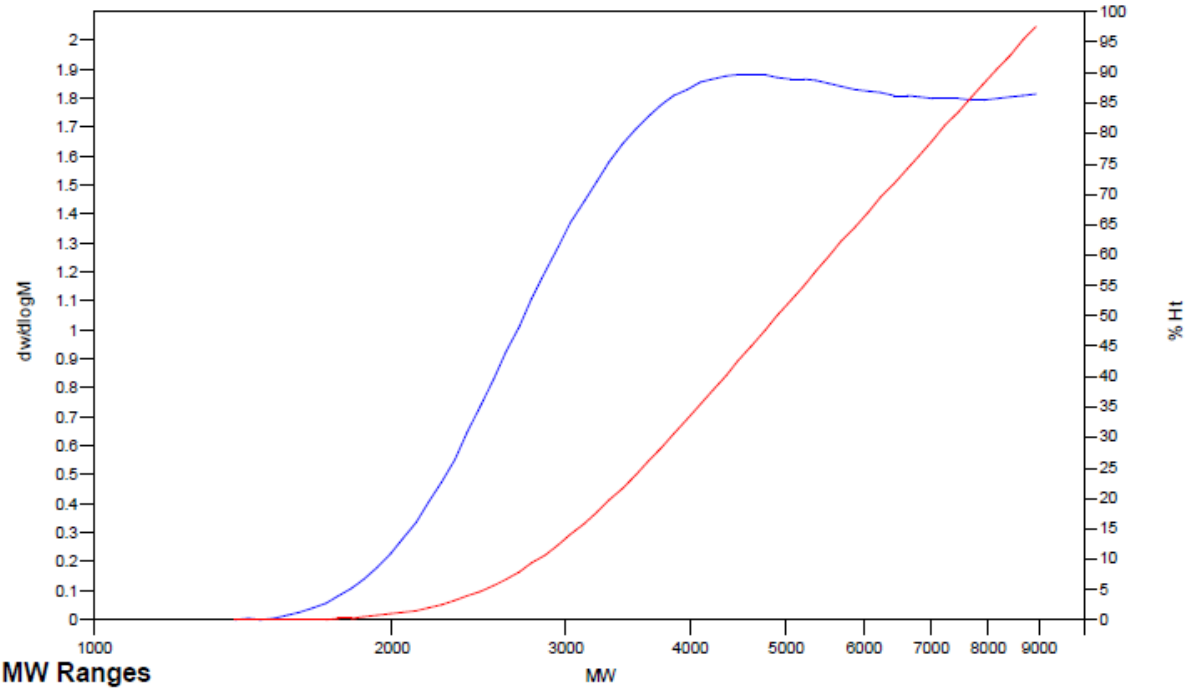


MW Ranges

MW Averages

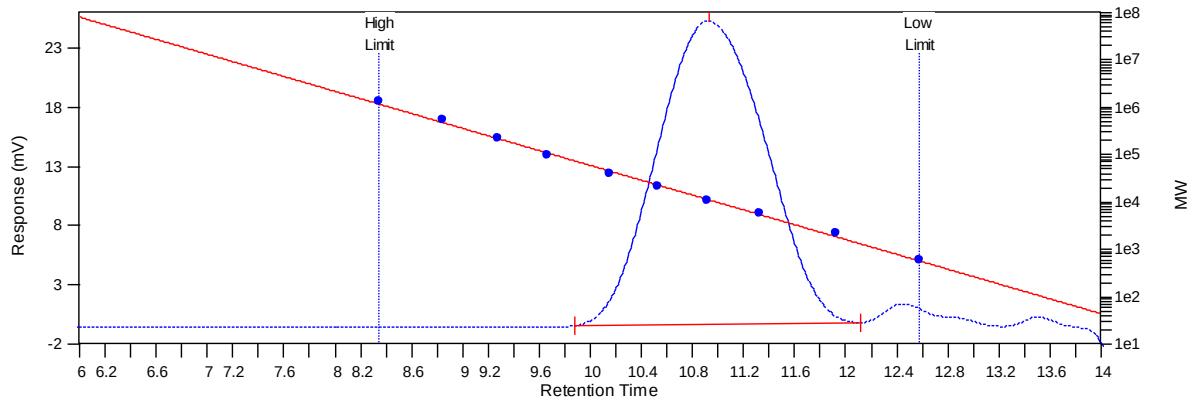
Mp: 4480	Mn: 4390	Mv: 5001	Mw: 5109
Mz: 5818	Mz+1: 6434	PD: 1.1638	

Distribution Plots



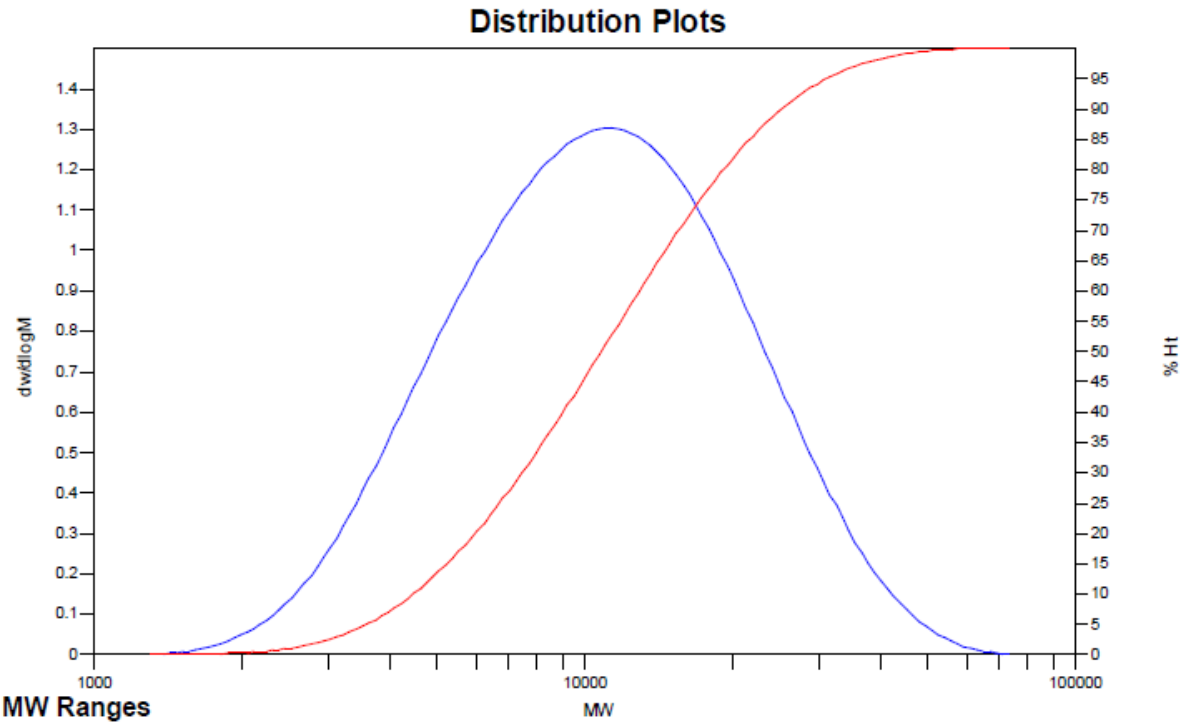
MW Ranges

1.5. **Poly-3c**



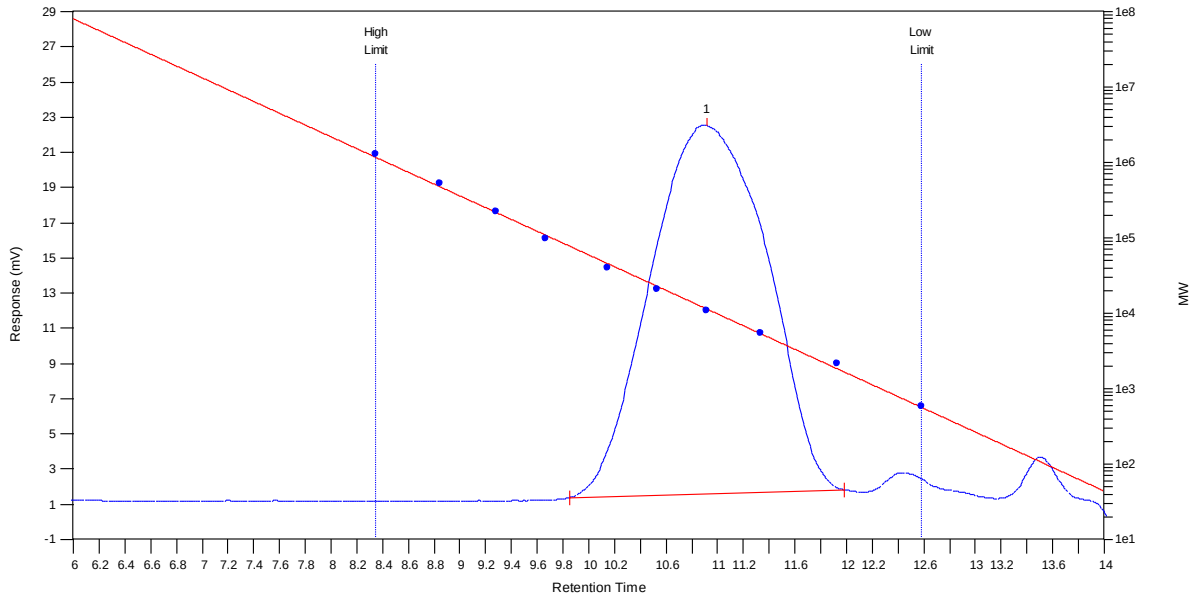
MW Averages

Mp: 11370	Mn: 8515	Mv: 12230	Mw: 13001
Mz: 18948	Mz+1: 25468	PD: 1.5268	



MW Ranges

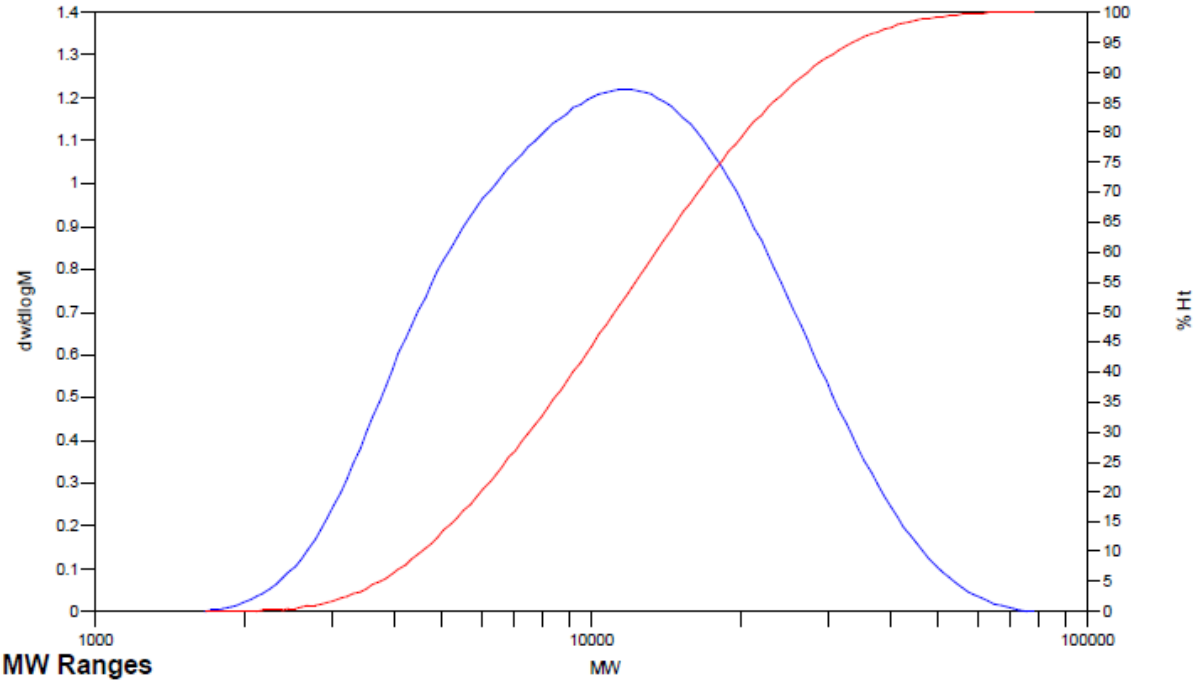
1.6. **Poly-4c**



MW Averages

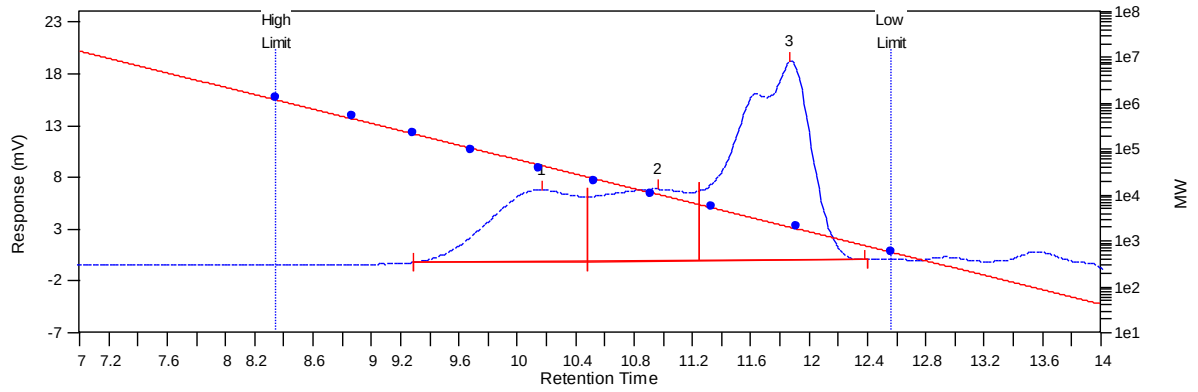
Mp: 11370	Mn: 8801	Mv: 12840	Mw: 13709
Mz: 20492	Mz+1: 27860	PD: 1.5577	

Distribution Plots



MW Ranges

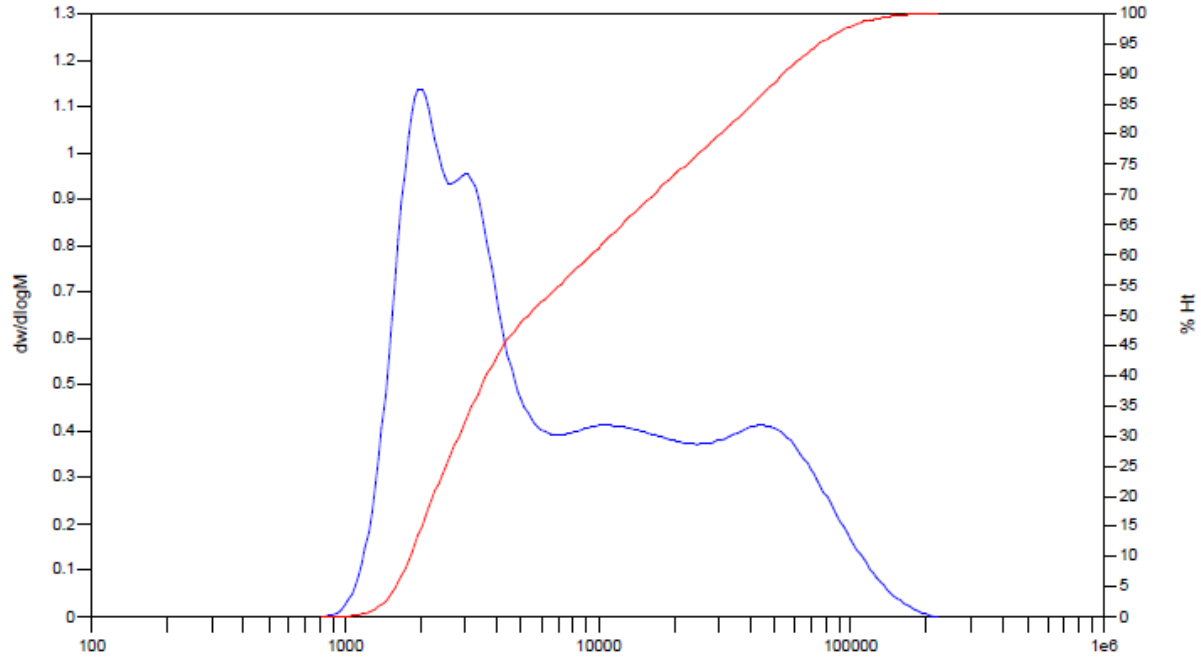
1.7. **Poly-3d**



MW Averages

Mp: 2017	Mn: 4097	Mv: 13984	Mw: 17802
Mz: 55478	Mz+1: 84543	PD: 4.3451	

Distribution Plots

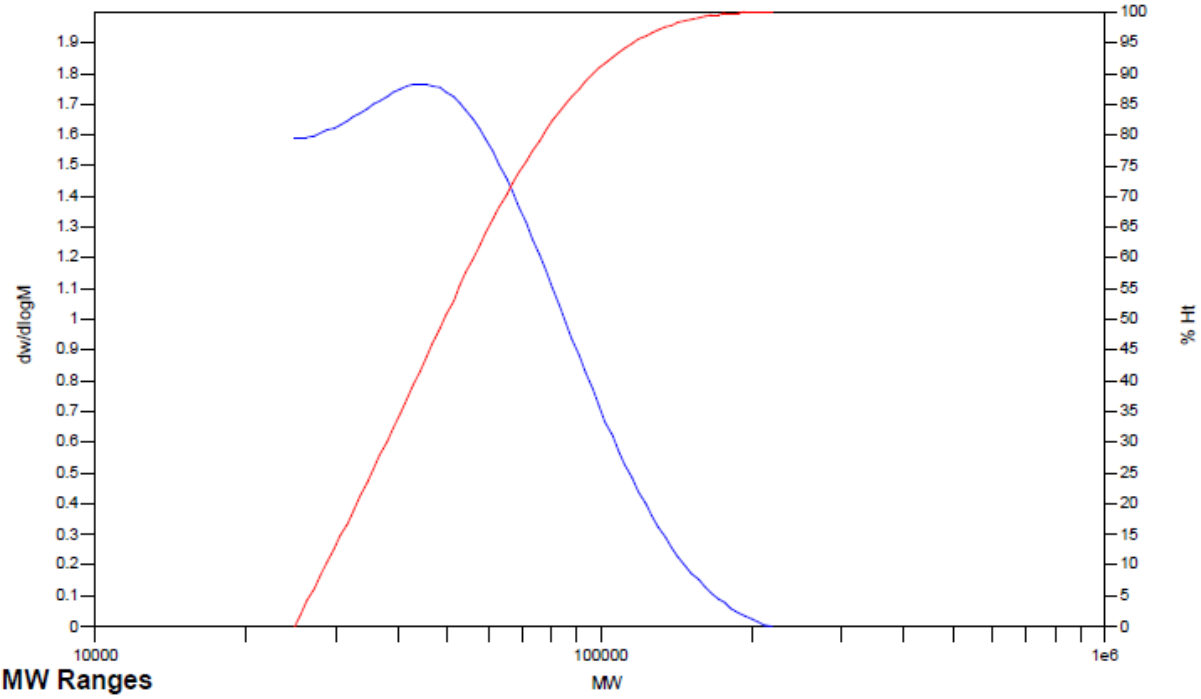


MW Ranges

MW Averages

Mp: 44037	Mn: 45887	Mv: 54509	Mw: 56389
Mz: 70995	Mz+1: 88389	PD: 1.2289	

Distribution Plots

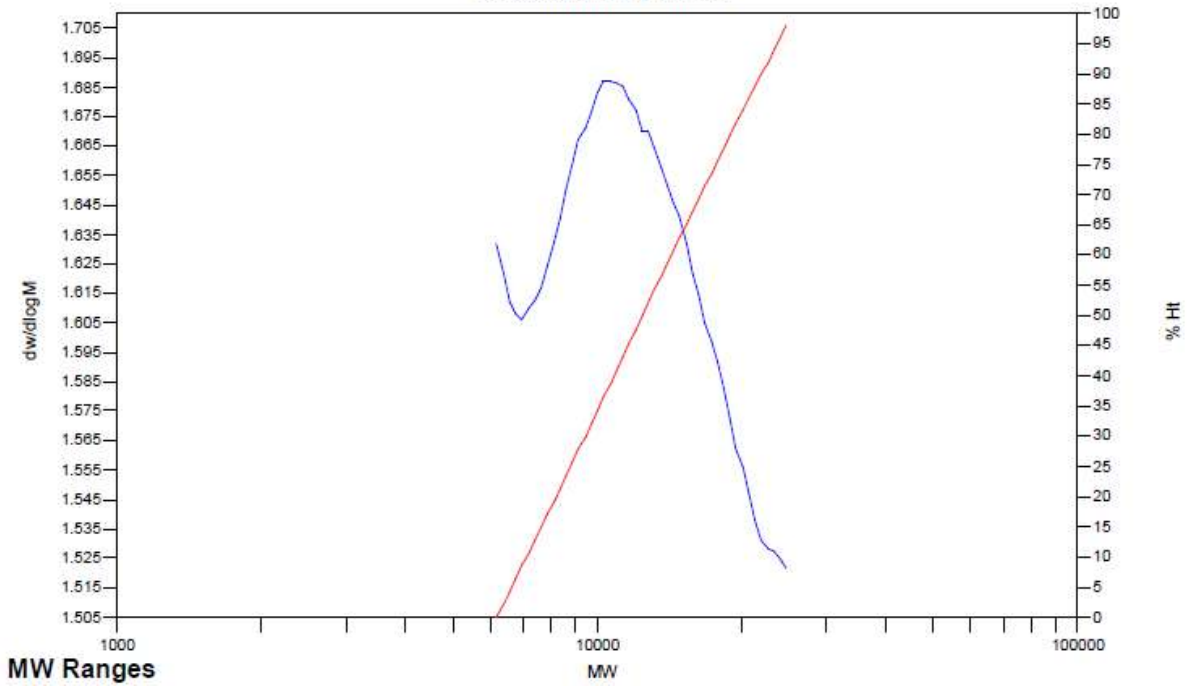


MW Ranges

MW Averages

Mp: 10638	Mn: 11326	Mv: 13002	Mw: 13318
Mz: 15465	Mz+1: 17403	PD: 1.1759	

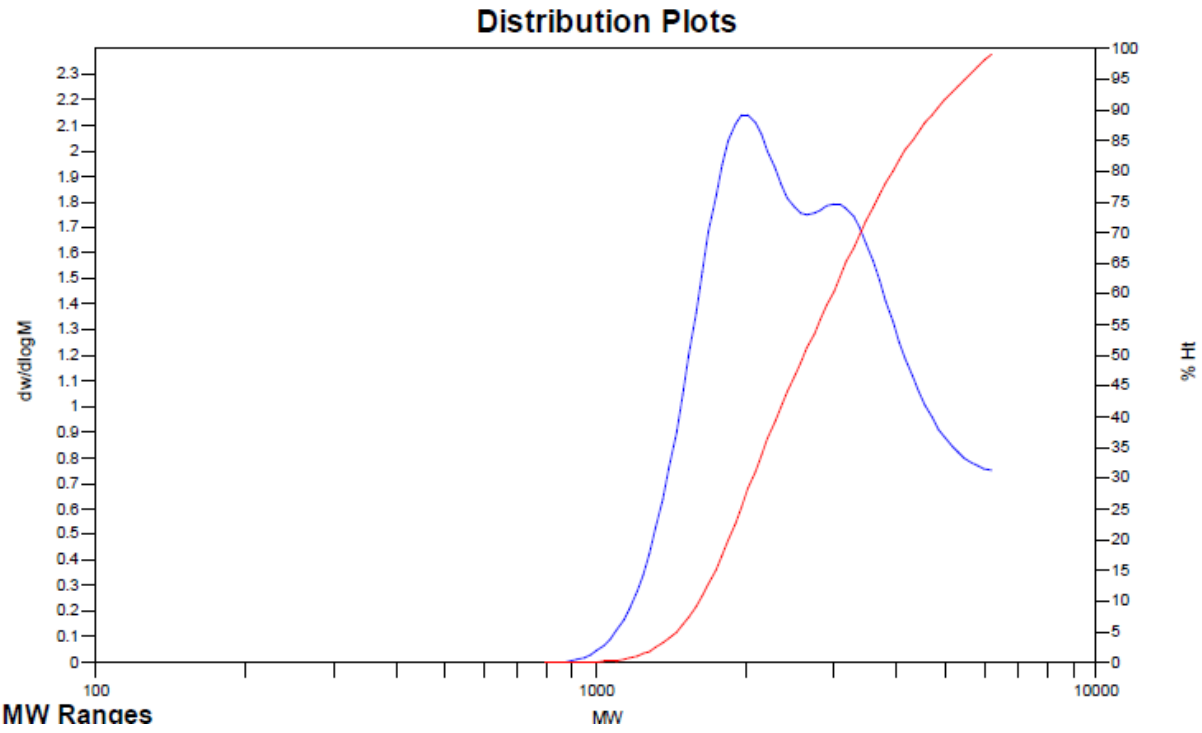
Distribution Plots



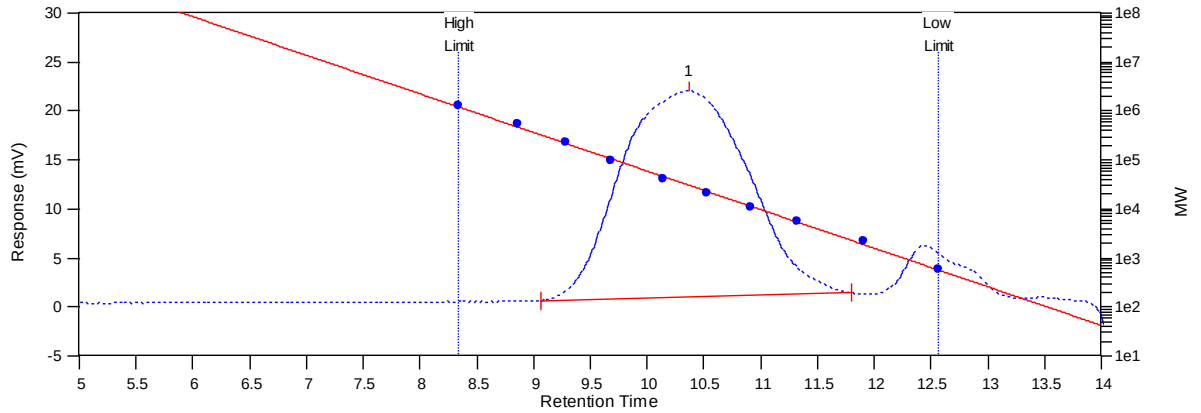
MW Ranges

MW Averages

Mp: 2017	Mn: 2437	Mv: 2799	Mw: 2871
Mz: 3379	Mz+1: 3893	PD: 1.1781	

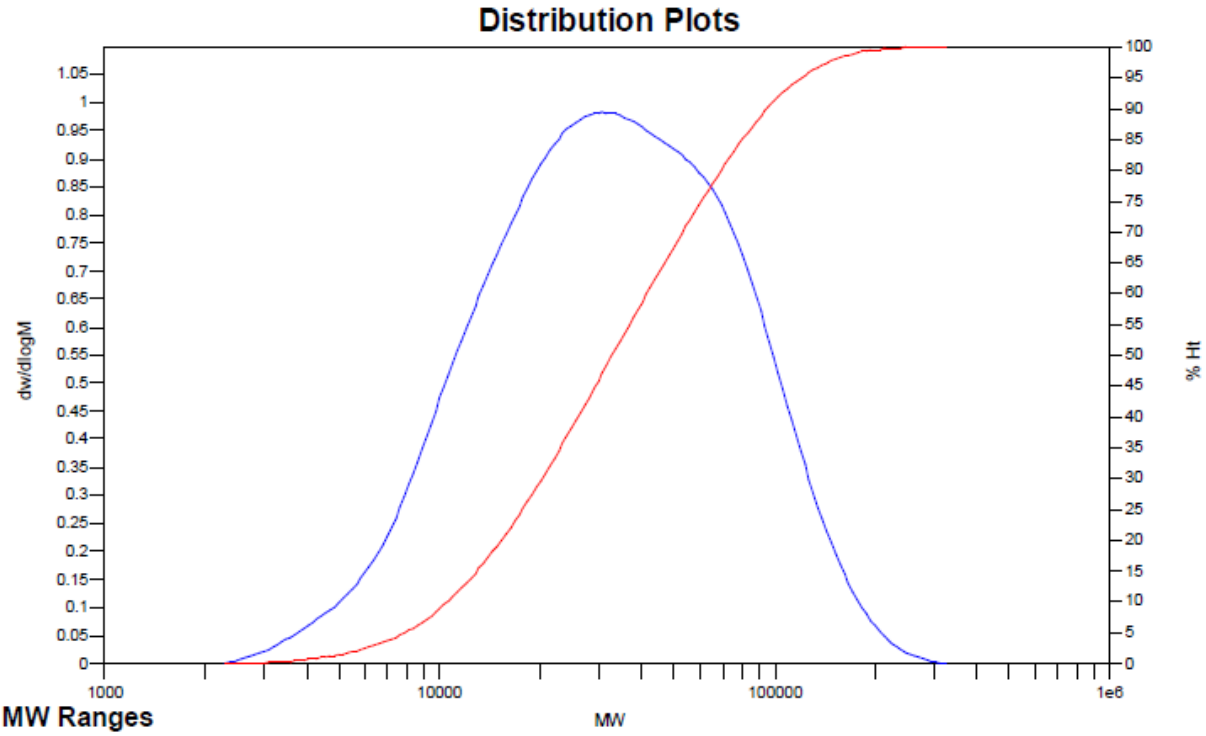


After chromatographic separation:

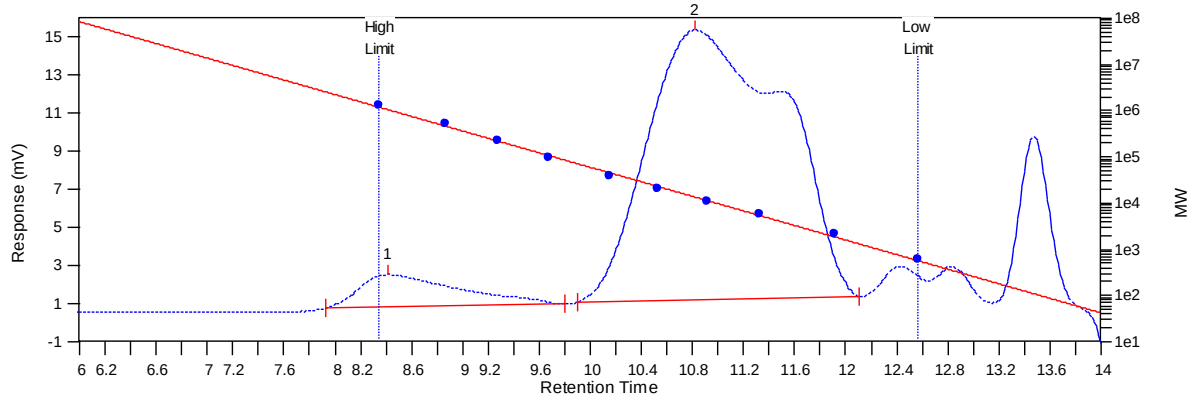


MW Averages

Mp: 30641	Mn: 22176	Mv: 40144	Mw: 44052
Mz: 75130	Mz+1: 107366	PD: 1.9865	



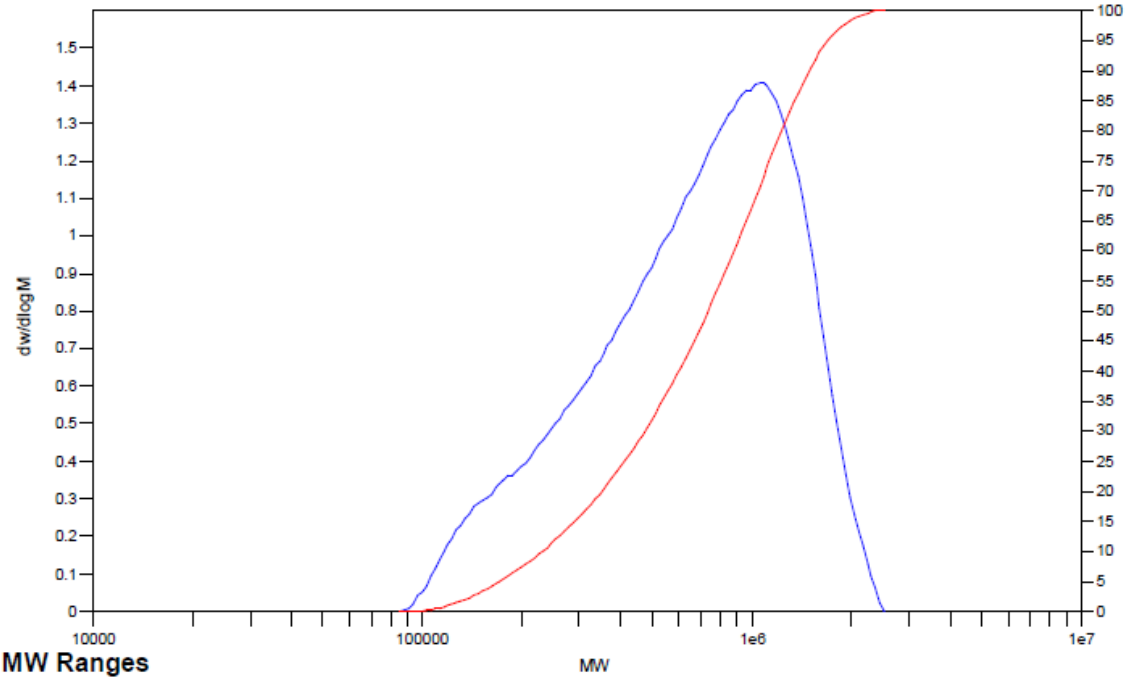
1.8. **Poly-4d**



MW Averages

Mp: 1052266	Mn: 493357	Mv: 753485	Mw: 797308
Mz: 1080619	Mz+1: 1296017	PD: 1.6161	

Distribution Plots

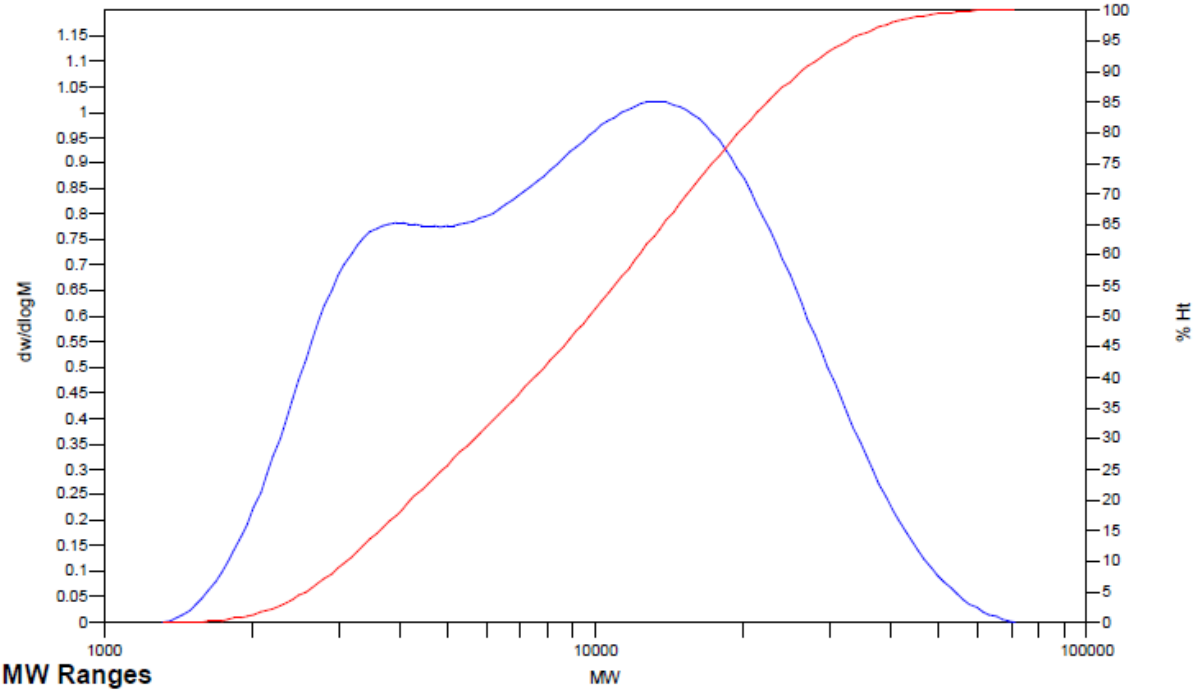


MW Ranges

MW Averages

Mp: 13548	Mn: 6760	Mv: 11382	Mw: 12394
Mz: 20121	Mz+1: 27513	PD: 1.8334	

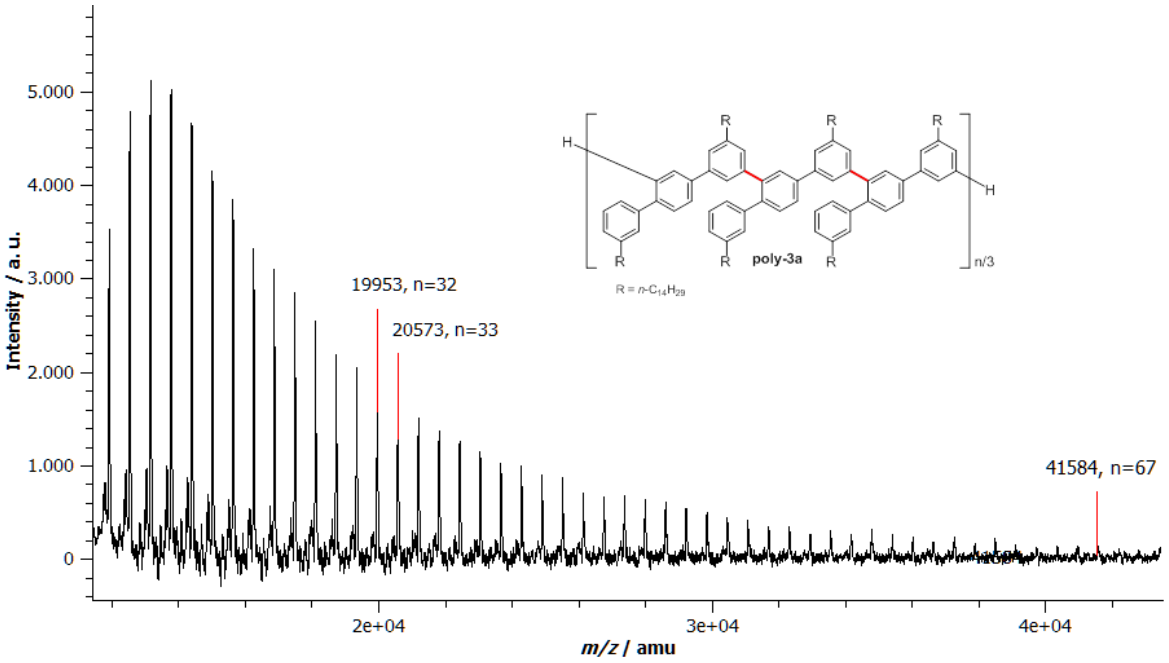
Distribution Plots

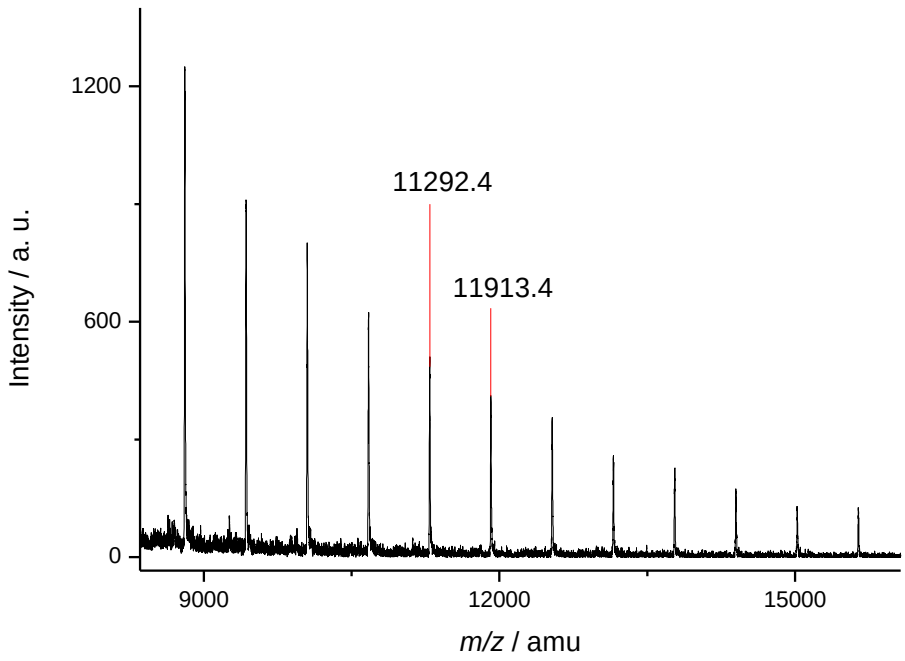


MW Ranges

2. MALDI-TOF mass spectra

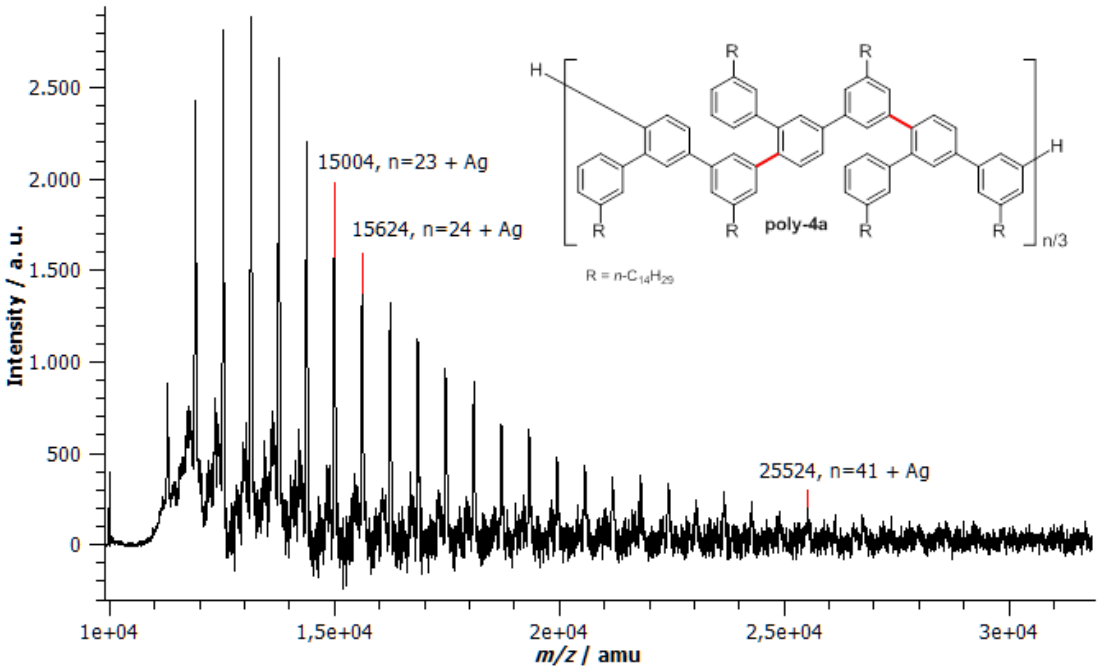
2.1. Poly-3a



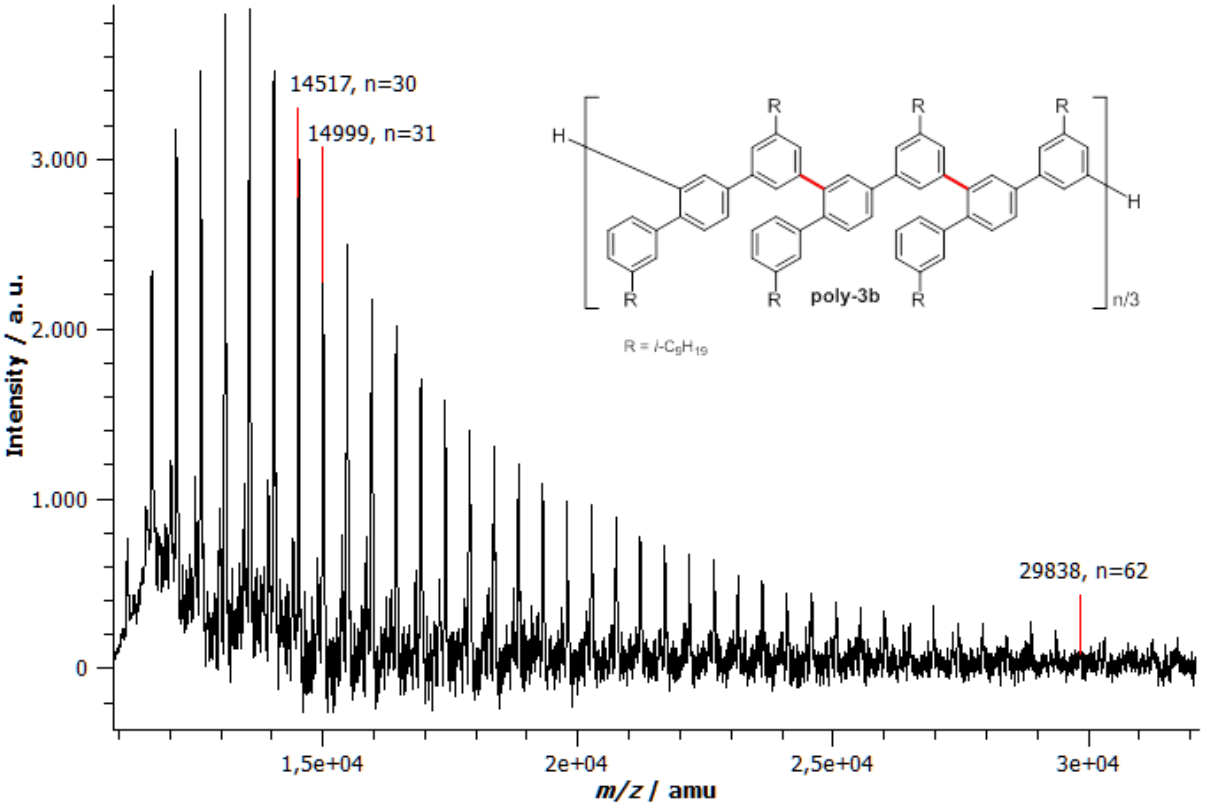


Detail from MALDI-TOF mass spectrum of **poly-3a** recorded with a method selective for lower molecular weights and higher resolution: Only peaks for proton end groups are present in the spectrum; calculated Molecular Weight (n=18+Ag) = 11288.5 g/mol.

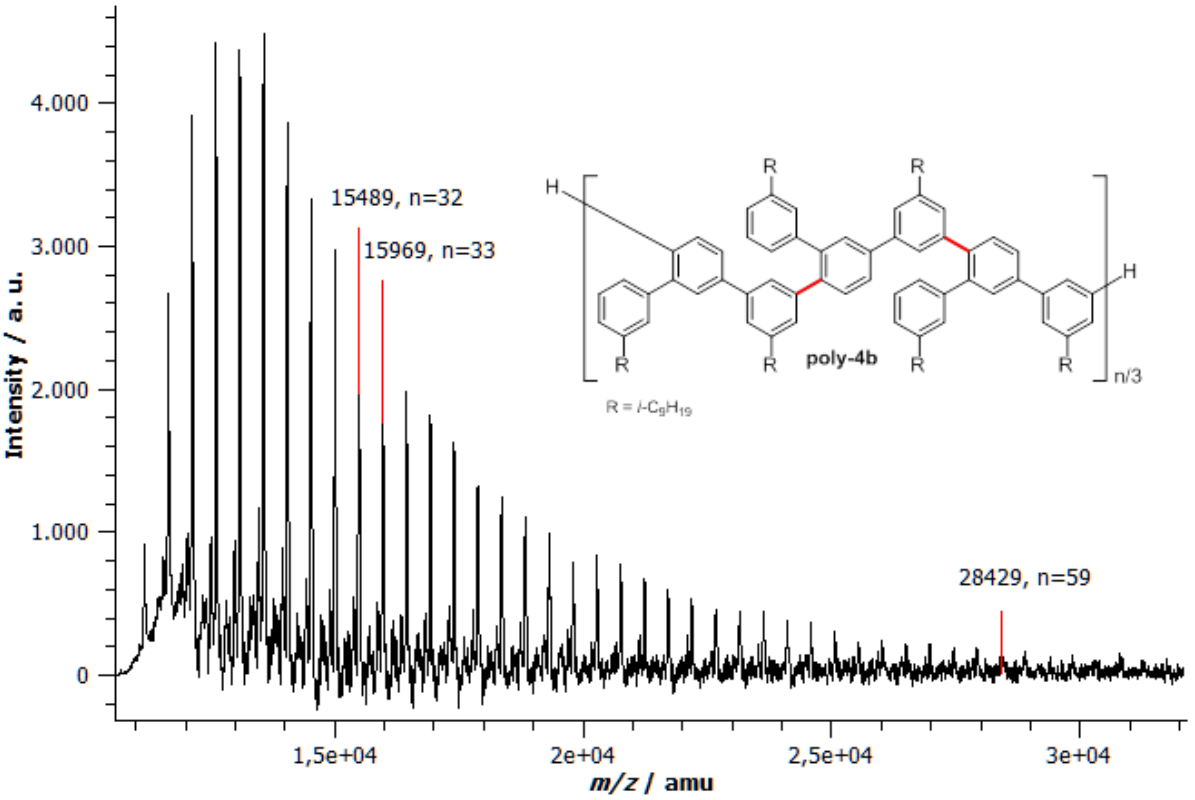
2.2. **Poly-4a**



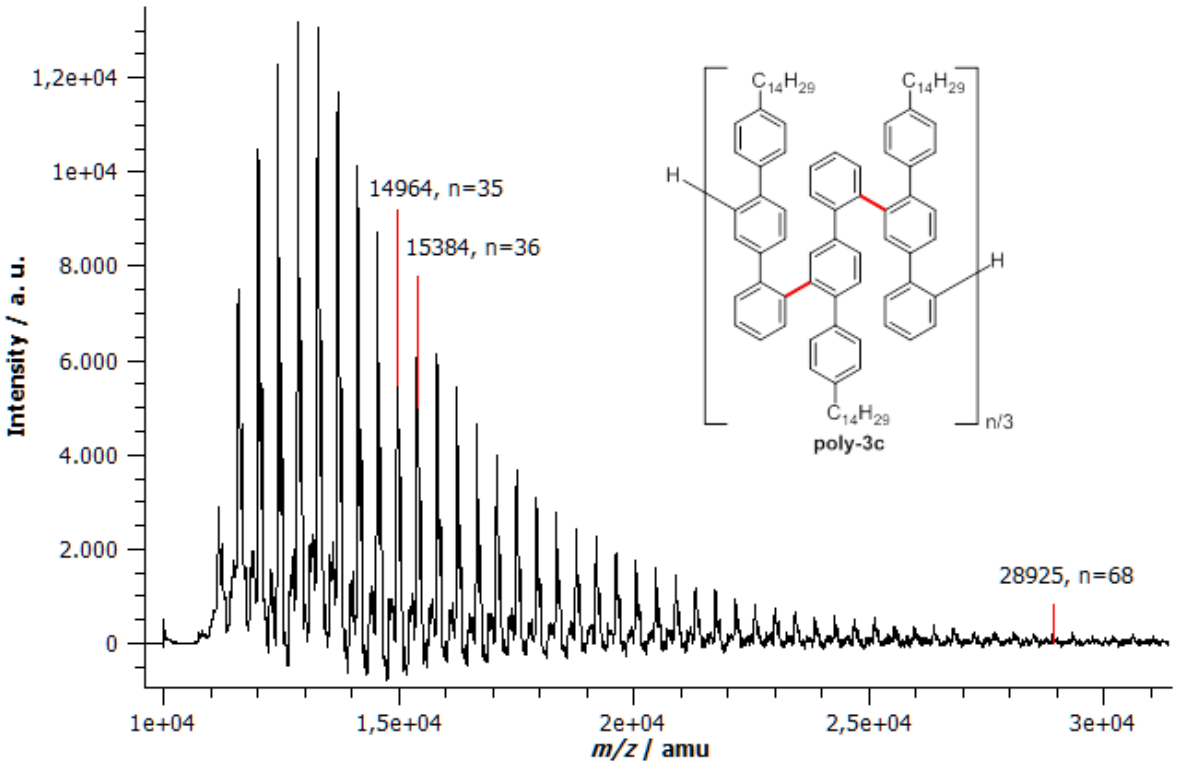
2.3. **Poly-3b**



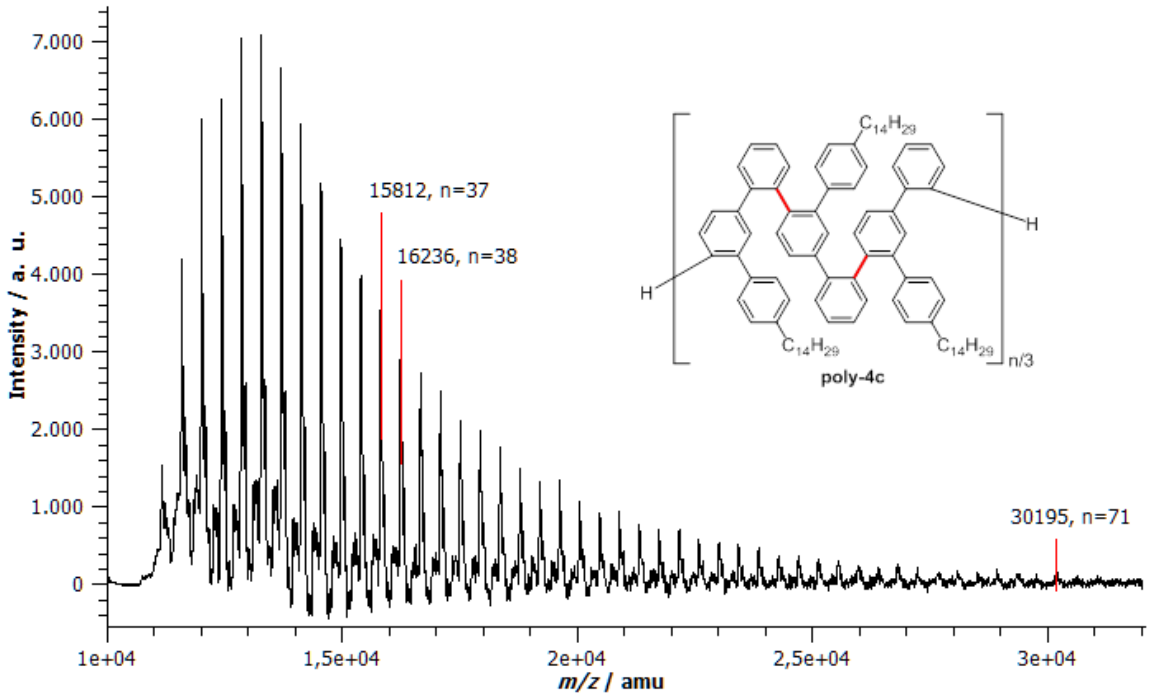
2.4. **Poly-4b**



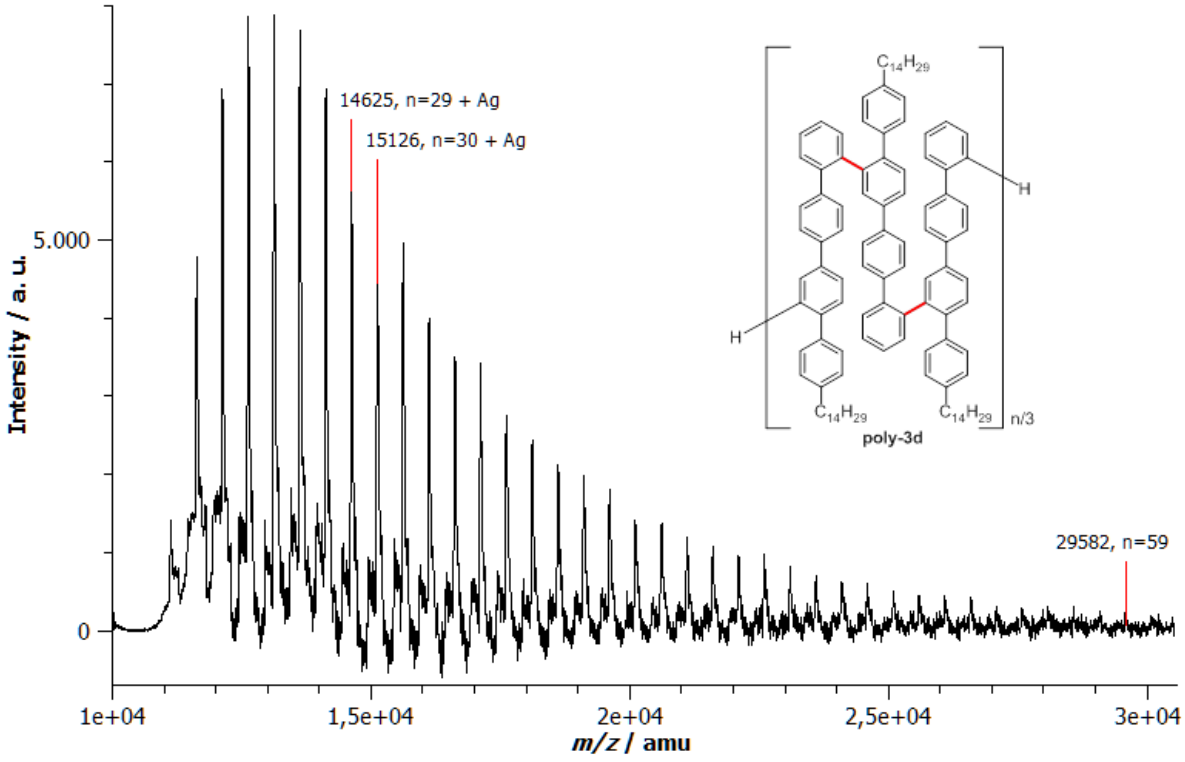
2.5. **Poly-3c**



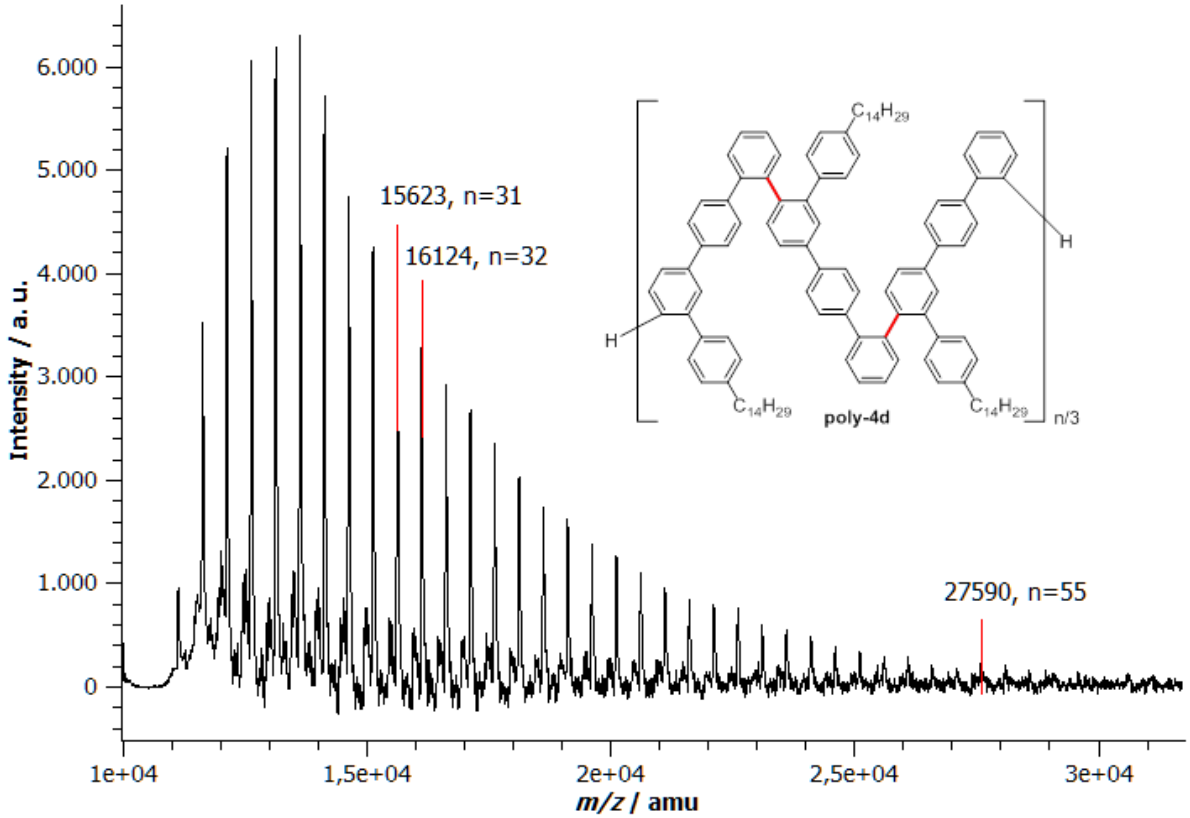
2.6. **Poly-4c**



2.7. **Poly-3d**



2.8. **Poly-4d**

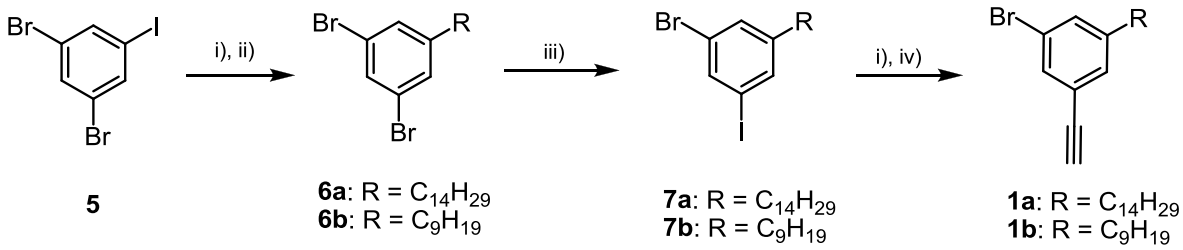


3. Synthesis of bis(tri-*tert*-butylphosphine)palladium(0)

In a dry Schlenk tube $Pd(dba)_2$ (575 mg, 1.0 mmol) was suspended in DMF (10 mL). To the suspension a solution of tri-*tert*-butylphosphine (484 mg, 2.4 mmol) in 5 mL of DMF was added via syringe and the mixture was stirred for 15 h at room temperature. The precipitate was collected by filtration over a ceramic frit, rinsed with DMF until the washing was colourless and dissolved in diethyl ether. The grey turbid solution was taken up in a syringe and filtered over Celite to remove black insoluble material resulting in a colourless to slightly yellowish solution. The solvent was evaporated under reduced pressure to afford bis(tri-*tert*-butylphosphine)palladium(0) (395 mg, 0.77 mmol, 77%) as colourless crystalline solid. The ^{31}P NMR spectrum (101 MHz, THF, δ = 85.5 ppm) matched with the literature.[1]

(1) Proutiere, F.; Aufiero M.; Schoenebeck, F. *J. Am. Chem. Soc.* **2012**, *134*, 606−612.

4. Synthesis of alkynes 1a, 1b, 1d and 2a-c



5 **6a**: R = $C_{14}H_{29}$ **6b**: R = C_9H_{19} **7a**: R = $C_{14}H_{29}$ **7b**: R = C_9H_{19} **1a**: R = $C_{14}H_{29}$ **1b**: R = C_9H_{19}

i) $Pd(PPh_3)_2Cl_2$ or $Pd(OAc)_2$, PPh_3, CuI, alkyne, amine, THF; ii) H_2, PtO_2, MeOH, toluene; iii) -78 °C, *n*BuLi, I_2, Et_2O, THF; iv) K_2CO_3, MeOH, CH_2Cl_2

4.1. 1,3-Dibromo-5-tetradecylbenzene **6a**

$Pd(PPh_3)_2Cl_2$ (100 mg, 2 mol%), CuI (53 mg, 3 mol%), and 1,3-dibromo-5-iodobenzene (3.16 g, 8.7 mmol) were dissolved in triethylamine (30 mL) and THF (10 mL). Tetradec-1-yne (1.70 g, 8.7 mmol) was added and the mixture was stirred for 16 h at room temperature. The mixture was filtered and the solvent evaporated. The residue was taken up in pentane (100 mL), washed with 1 M HCl, and the phases were separated. The aqueous phase was washed twice with pentane (50 mL) and the combined organic phases were dried over $MgSO_4$ and filtered over silica gel (pentane). Evaporation of the solvent gave 1,3-dibromo-5-(tetradec-1-ynyl)benzene (3.72 g, 8.7 mmol, 100%) as light yellow oil which was taken up in MeOH and toluene (100 mL, 9:1). $PtO_2 \cdot H_2O$ (50 mg, 2 mol%) was added and the mixture was stirred under an atmosphere of hydrogen for 2 d. The solvent was evaporated and the residue was filtered over silica gel (pentane). The filtrate was concentrated yielding 1,3-dibromo-5-tetradecylbenzene (**6a**) (3.69 g, 8.5 mmol, 98%) as colourless solid.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.47 (t, J = 1.7 Hz, 1H, H_{Ar}), 7.25 (d, J = 1.7 Hz, 2H, H_{Ar}), 2.60-2.47 (m, 2H, CH_2), 1.65-1.51 (m, 2H, CH_2), 1.36-1.20 (m, 22H, CH_2), 0.88 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 146.9, 131.3, 130.3, 122.7, 35.4, 31.9, 31.0, 29.68, 29.65 (3C), 29.62, 29.5, 29.37, 29.36, 29.1, 22.7, 14.1; IR (film, CH_2Cl_2): ν = 2922,

2852, 1584, 1553, 1460, 1424, 1369, 1205, 1103, 991, 884, 849, 740, 679; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{20}H_{32}Br^{81}Br$, 432.0850; found, 432.0859.

4.2. 1,3-Dibromo-5-(3-ethylheptyl)benzene **6b**

According to the above procedure $Pd(PPh_3)_2Cl_2$ (45 mg, 1 mol%), CuI (24 mg, 2 mol%), 1,3-dibromo-5-iodobenzene (2.10 g, 5.8 mmol), and 3-ethylhept-1-yne (720 mg,5.8 mmol) were reacted in NEt_3 (20 mL) and THF (15 mL). 1,3-Dibromo-5-(3-ethylhept-ynyl)benzene (2.07 g, 5.8 mmol, 100%) was obtained as yellow oil which was dissolved in MeOH and toluene (50 mL, 4:1) in an autoclave vessel. $PtO_2 \cdot H_2O$ (33 mg, 2 mol%) was added, the autoclave was filled with hydrogen (8 bars), and the mixture was stirred at room temperature for 2 d. The solvent was evaporated and the residue was filtered over silica gel (pentane). The filtrate was concentrated yielding **6b** (1.98 g, 5.5 mmol, 95%) as a colourless oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.47 (t, *J* = 1.7 Hz, 1H, H_{Ar}), 7.26 (d, *J* = 1.6 Hz, 2H, H_{Ar}), 2.63-2.41 (m, 2H, CH_2), 1.63-1.45 (m, 2H, CH_2), 1.42-1.19 (m, 9H, CH/CH_2), 0.99-0.77 (m, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 147.3, 131.2, 130.2, 122.7, 38.6, 34.8, 32.7, 32.6, 28.8, 25.7, 23.1, 14.1, 10.8; IR (film, CH_2Cl_2): *v* = 2957, 2923, 2860, 1583, 1552, 1458, 1422, 1377, 1289, 1206, 1102, 1021, 990, 889, 848, 739, 678; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{15}H_{22}Br^{81}Br$, 362.0068; found, 362.0068.

4.3. 1-Bromo-3-iodo-5-tetradecylbenzene **7a**

A solvent mixture of 190 mL Et_2O/THF (1:1 v/v) was cooled to -78 °C and a solution of 1,3-dibromo-5-tetradecylbenzene (**6a**) (2.82 g, 6.5 mmol) in 10 mL Et_2O/THF (1:1 v/v) was added dropwise with stirring. To the suspension an *n*-butyl lithium solution (3.0 mL,

7.5 mmol, 2.5 M in hexanes) was added dropwise and the mixture was stirred for 1 h at -78 °C after which a solution of iodine (2.16 g, 8.5 mmol) in THF (5 mL) was added quickly in one portion. The mixture was allowed to warm to room temperature and a saturated aqueous solution of NH_4Cl (100 mL) was added. The phases were separated and the aqueous phase was extracted twice with pentane (50 mL). The combined organic phases were washed twice with a 10% solution of NaS_2O_3 in water (50 mL) and once with brine (50 mL), dried with $MgSO_4$ and filtered. The filtrate was concentrated and the oily residue was chromatographically purified on silica gel (pentane) to obtain 1-bromo-3-iodo-5-tetradecylbenzene (**7a**) (3.01 g, 6.3 mmol, 96%) as light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.66 (t, *J* = 1.6 Hz, 1H, H_{Ar}), 7.45 (t, *J* = 1.5 Hz, 1H, H_{Ar}), 7.28 (t, *J* = 1.5 Hz, 1H, H_{Ar}), 2.57-2.45 (m, 2H, CH_2), 1.64-1.49 (m, 2H, CH_2), 1.38-1.18 (m, 22H, CH_2), 0.93-0.84 (m, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 147.0, 136.8, 136.2, 130.9, 122.7, 94.3, 35.2, 31.9, 31.0, 29.7 (5C), 29.5, 29.4 (2C), 29.1, 22.7, 14.1; IR (neat): *ν* = 2913, 2846, 1577, 1544, 1462, 1416, 1374, 1201, 1100, 880, 847, 722, 683, 607; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{20}H_{32}BrI$, 478.0732; found, 478.0725.

4.4. 1-Bromo-3-iodo-5-(3-ethylheptyl)benzene **7b**

According to the above procedure 1,3-dibromo-5-(3-ethylheptyl)benzene (**6b**) (5.46 g, 15.1 mmol) was reacted with *n*-butyl lithium (7.0 mL, 17.5 mmol, 2.5 M in hexanes) and iodine (4.95 g, 19.5 mmol) in THF (130 mL) and Et_2O (220 mL). 1-Bromo-3-iodo-5-(3-ethylheptyl)benzene (**7b**) (6.04 g,14.8 mmol, 98%) was obtained as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.68 (t, *J* = 1.5, 1.5 Hz, 1H, H_{Ar}), 7.48 (s, 1H, H_{Ar}), 7.31 (s, 1H, H_{Ar}), 2.55-2.46 (m, 2H, CH_2), 1.59-1.48 (m, 2H, CH_2), 1.41-1.20 (m, 9H, CH/CH_2), 0.99-0.83 (m, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 147.5, 136.8, 136.1, 130.9, 122.7, 94.3,

38.6, 34.8, 32.6, 32.6, 28.9, 25.7, 23.1, 14.1, 10.8; IR (neat): ν = 2953, 2922, 2859, 2158, 1578, 1545, 1458, 1287, 1204, 1100, 994, 886, 848, 759, 722, 679; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{15}H_{22}BrI$, 407.9950; found, 407.9947.

4.5. 1-Brom-3-ethynyl-5-tetradecylbenzol **1a**

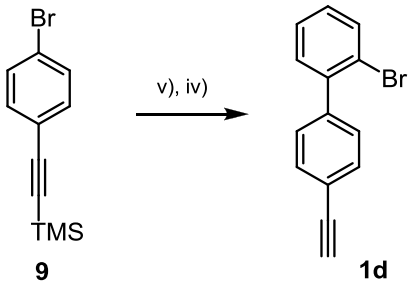
Following the procedure for **6a** 1-bromo-3-iodo-5-tetradecylbenzene (**7a**) (3.01 g, 6.3 mmol) was reacted with trimethylsilylacetylene (638 mg, 6.5 mmol), $Pd(OAc)_2$ (14 mg, 1 mol%), triphenylphosphine (33 mg, 2 mol%), and CuI (24 mg, 2 mol%) in HN^iPr_2 (20 mL) and THF (20 mL). The product obtained was taken up in $MeOH/CH_2Cl_2$ (150 mL, 2:1 v/v), K_2CO_3 (1.93 g, 14.0 mmol) was added, and the mixture was stirred for 16 h at room temperature. The solvent was evaporated and the residue was taken up in pentane (100 mL) and 1 M HCl (50 mL). The phases were separated and the aqueous phase was extracted twice with pentane (50 mL). The combined organic phases were dried over $MgSO_4$ and filtered over silica gel. Concentration of the filtrate gave 1-bromo-3-ethynyl-5-tetradecylbenzene (**1a**) (2.21 g, 5.9 mmol, 93%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.45 (t, J = 1.5 Hz, 1H, H_{Ar}), 7.31 (t, J = 1.6 Hz, 1H, H_{Ar}), 7.23 (s, 1H, H_{Ar}), 3.08 (s, 1H, $C_{sp}H$), 2.61-2.48 (m, 2H, CH_2), 1.65-1.49 (m, 2H, CH_2), 1.37-1.18 (m, 22H, CH_2), 0.88 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 145.2, 132.1, 132.1, 130.8, 123.7, 121.9, 82.4, 77.9, 35.4, 31.9, 31.0, 29.68, 29.65 (3C), 29.63, 29.5, 29.39, 29.35, 29.1, 22.7, 14.1; IR (neat): ν = 3305, 2921, 2852, 1593, 1560, 1461, 1373, 1237, 895, 864, 808, 722, 685, 649, 614, 544; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{22}H_{33}Br$, 376.1766; found, 376.1771.

4.6. 1-Bromo-3-ethynyl-5-(3-ethylheptyl)benzene **1b**

Following the procedure for **6a** 1-bromo-3-iodo-5-(3-ethylheptyl)benzene (**7b**) (6.03 g, 13.6 mmol) was reacted with trimethylsilylacetylene (1.38 g, 14.0 mmol), $Pd(OAc)_2$ (34 mg, 1 mol%), triphenylphosphine (80 mg, 2 mol%), and CuI (60 mg, 2 mol%) in HN^iPr_2 (20 mL) and THF (40 mL). The product obtained was taken up in $MeOH/CH_2Cl_2$ (300 mL, 2:1 v/v), K_2CO_3 (4.15 g, 30.0 mmol) was added, the mixture was stirred for 16 h at room temperature. Work up according to the above procedure gave 1-bromo-3-ethynyl-5-(3-ethylheptyl)benzene (**1b**) (3.97 g, 12.9 mmol, 95%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.45 (t, J = 1.6 Hz, 1H, H_{Ar}), 7.32 (t, J = 1.7 Hz, 1H, H_{Ar}), 7.24 (s, 1H, H_{Ar}), 3.08 (s, 1H, $C_{sp}H$), 2.59-2.44 (m, 2H, CH_2), 1.59-1.45 (m, 2H, CH_2), 1.40-1.19 (m, 9H, CH/CH_2), 0.97-0.80 (m, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 145.6, 132.1, 132.0, 130.8, 123.7, 121.9, 82.3, 78.0, 38.5, 34.8, 32.7, 32.6, 28.8, 25.7, 23.1, 14.1, 10.7; IR (neat): ν = 3302, 2957, 2924, 2860, 1593, 1560, 1459, 1378, 1295, 1239, 1112, 994, 932, 896, 863, 810, 728, 685, 649, 614, 545; HRMS (EI, 70 eV) m/z: calcd for $C_{17}H_{23}Br$, 306.0983; found, 306.0988.

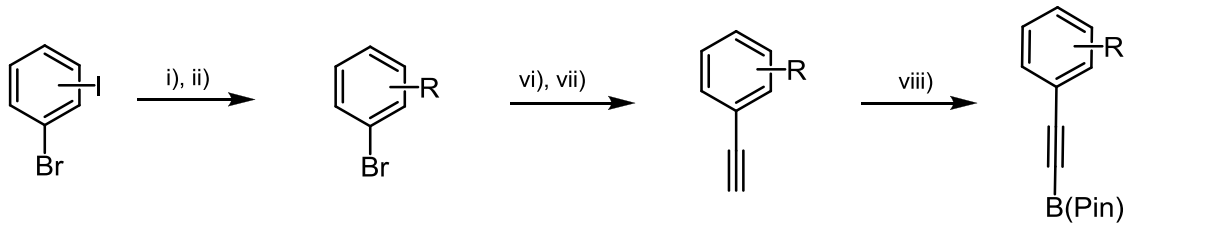


v) *n*-butyl lithium, $ZnBr_2$, 2-bromoiodobenzene, $Pd(PPh_3)_4$, Et_2O, THF; iv) K_2CO_3, MeOH, CH_2Cl_2

4.7. 2-Bromo-4‘-ethynylbiphenyl **1d**

((4-Bromophenyl)ethinyl)trimethylsilane (**9**) (1.99 g, 7.9 mmol) was dissolved in Et_2O (60 mL) and the solution was cooled to -78 °C. *n*-Butyl lithium (5.0 mL, 12.5 mmol, 2.5 M in hexanes) was added dropwise and the mixture was stirred for 1.5 h after which it was warmed to -40 °C. Zinc bromide (3.15 g, 14.0 mmmol) was added and the mixture was slowly warmed to 0 °C. At this temperature it was diluted by addition of THF (20 mL) and 2-bromoiodobenzene (3.93 g, 13.9 mmol) and $Pd(PPh_3)_4$ (252 mg, 2.8 mol%) were added. The mixture was allowed to warm to room temperature and stirred for 20 h. The reaction was stopped by addition of a saturated aqueous NH_4Cl solution (50 mL), the phases were separated, and the aqueous phase was extracted twice with Et_2O (50 mL each). The combined organic phases were washed with water and brine (80 mL each), dried over $MgSO_4$, and filtered. After evaporation of the solvent the oily residue was chromatographed on silica gel (pentane) yielding ((2‘-bromobiphenyl-4-yl-)ethynyl)trimethylsilane (1.48 g, 4.5 mmol). The product was desilylated as described for **1a** applying K_2CO_3 (1.50 g, 10.9 mmol) in $MeOH/CH_2Cl_2$ (120 mL, 2:1 v/v). 2-Bromo-4‘-ethynylbiphenyl (**1d**) (1.15 g, 4.5 mmol, 57%) was obtained as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.68 (dd, J = 8.0, 1.1 Hz, 1H, H_{Ar}), 7.56 (d, J = 8.3 Hz, 2H, H_{Ar}), 7.41-7.28 (m, 4H, H_{Ar}), 7.22 (ddd, J = 7.9, 7.2, 2.0 Hz, 1H, H_{Ar}), 3.13 (s, 1H, $C_{sp}H$); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 141.8, 141.5, 133.2, 131.8, 131.1, 129.4, 129.0, 127.4, 122.4, 121.4, 83.4, 77.7; IR (neat): ν = 3288, 3055, 2106, 1917, 1561, 1505, 1463, 1429, 1396, 1245, 1111, 1065, 1024, 1001, 947, 866, 835, 755, 709, 648, 616, 560, 507, 475, 446; HRMS (EI, 70 eV) m/z: calcd for $C_{14}H_9Br$, 255.9888; found, 255.9886.



10a: R = 3-$C_{14}H_{29}$
10b: R = 3-C_9H_{19}
10c: R = 4-$C_{14}H_{29}$

11a: R = 3-$C_{14}H_{29}$
11b: R = 3-C_9H_{19}
11c: R = 4-$C_{14}H_{29}$

2a: R = 3-$C_{14}H_{29}$
2b: R = 3-C_9H_{19}
2c: R = 4-$C_{14}H_{29}$

i) $Pd(PPh_3)_2Cl_2$ or $Pd(OAc)_2$, PPh_3, CuI, alkyne, amine, THF; ii) H_2, PtO_2, MeOH, toluene; vi) $Pd(OAc)_2$, PPh_3, 2-methylbut-3-yn-2-ol, K_3PO_4, toluene, DMSO; vii) KOH, toluene; viii) *n*-butyl lithium, *i*-PrOB(Pin), BF3 · OEt_2 or HCl, Et_2O

4.8. 1-Bromo-3-tetradecylbenzene **10a**

Following the procedure for **6a** 3-bromoiodobenzene (4.24 g, 15.0 mmol) was reacted with tetradec-1-yne (2.92 g, 15.0 mmol), $Pd(OAc)_2$ (34 mg, 1 mol%), triphenylphosphine (79 mg, 2 mol%), and CuI (29 mg, 1 mol%) in HN*i*-Pr_2 (25 mL) and THF (50 mL). The product obtained was dissolved in MeOH and toluene (50 mL, 4:1) in an autoclave vessel. $PtO_2 \cdot H_2O$ (58 mg, 1 mol%) was added, and the mixture was stirred under an atmosphere of hydrogen (8 bars). Work up as described for **6a** gave 1-bromo-3-tetradecylbenzene (**10a**) (5.06 g, 14.3 mmol, 95%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.36-7.28 (m, 2H, H_{Ar}), 7.17-7.07 (m, 2H, H_{Ar}), 2.62-2.53 (m, 2H, CH_2), 1.65-1.53 (m, 2H, CH_2), 1.39-1.18 (m, 22H, CH_2), 0.89 (t, *J* = 6.7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 145.3, 131.4, 129.8, 128.7, 127.0, 122.3, 35.6, 31.9, 31.2, 29.7 (5C), 29.6, 29.4, 29.4, 29.2, 22.7, 14.1; IR (neat): *v* = 2921, 2852, 1594, 1567, 1464, 1373, 1299, 1202, 1072, 997, 880, 846, 774, 720, 690, 669, 434; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{20}H_{33}Br$, 352.1766; found, 352.1774.

4.9. 1-Bromo-3-(3-ethylheptyl)benzene **10b**

Following the procedure for **6a** 3-bromoiodobenzene (3.82 g, 13.5 mmol) was reacted with 3-ethylhept-1-yne (1.67 g, 13.5 mmol), $Pd(OAc)_2$ (20 mg, 1 mol%), triphenylphosphine (60 mg, 2 mol%), and CuI (40 mg, 2 mol%) in HN*i*-Pr_2 (25 mL) and THF (50 mL). The product obtained was dissolved in MeOH and toluene (40 mL, 3:1) in an autoclave vessel. $PtO_2 \cdot H_2O$ (80 mg, 2 mol%) was added, and the mixture was stirred under an atmosphere of hydrogen (8 bars). Work up as described for **6a** gave 1-bromo-3-(3-ethylheptyl)benzene (**10b**) (3.49 g, 12.3 mmol, 91%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.34 (s, 1H, H_{Ar}), 7.31 (dt, *J* = 7.1, 1.9 Hz, 1H, H_{Ar}), 7.18-7.08 (m, 2H, H_{Ar}), 2.61-2.50 (m, 2H, CH_2), 1.62-1.48 (m, 2H, CH_2), 1.42-1.21 (m, 9H, CH/CH_2), 0.96-0.83 (m, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 145.7, 131.4, 129.8, 128.6, 127.0, 122.3, 38.6, 35.0, 32.9, 32.7, 28.9, 25.7, 23.1, 14.1, 10.8; IR (neat): *ν* = 2957, 2923, 2860, 1594, 1567, 1464, 1426, 1378, 1204, 1071, 997, 879, 853, 775, 690, 670, 434; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{15}H_{23}Br$, 282.0983; found, 282.0967.

4.10. 1-Bromo-4-tetradecylbenzene **10c**

Following the procedure for **6a** 4-bromoiodobenzene (1.13 g, 4.0 mmol) was reacted with tetradec-1-yne (778 mg, 4.0 mmol), $Pd(OAc)_2$ (9 mg, 1 mol%), triphenylphosphine (21 mg, 2 mol%), and CuI (20 mg, 3 mol%) in HN*i*-Pr_2 (15 mL) and THF (30 mL). The product obtained was dissolved in MeOH (22 mL) and toluene (3 mL) in an autoclave vessel. $PtO_2 \cdot H_2O$ (14 mg, 1.5 mol%) was added, and the mixture was stirred under an atmosphere of hydrogen (8 bars). Work up as described for **6a** gave 1-bromo-4-tetradecylbenzene (**10c**) (1.36 g, 3.9 mmol, 98%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.45-7.38 (d, *J* = 8.4 Hz, 2H, H_{Ar}), 7.07 (d, *J* = 8.4 Hz, 2H, H_{Ar}), 2.64-2.50 (m, 2H, CH_2), 1.66-1.55 (m, 2H, CH_2), 1.40-1.20 (m, 22H, CH_2), 0.91 (t, *J* = 6.7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 141.8, 131.2, 130.2, 119.2, 35.3, 31.9, 31.3, 29.7 (5C), 29.6, 29.5, 29.4, 29.2, 22.7, 14.1; IR (neat): *v* = 2956, 2916, 2847, 1486, 1460, 1403, 1376, 1193, 1117, 1069, 1005, 885, 808, 759, 724, 699, 633, 515, 493, 459, 434; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{20}H_{33}Br$, 352.1766; found, 352.1752.

4.11. 1-Ethynyl-3-tetradecylbenzene **11a**

In a Schlenk tube $Pd(OAc)_2$ (79 mg, 5 mol%), triphenylphosphine (370 mg, 20 mol%) and K_3PO_4 (1.80 g, 8.5 mmol) were suspended in DMSO (14 mL). 1-Bromo-3-tetradecylbenzene (**10a**) (2.50 g, 7.1 mmol), toluene (2 mL) and 2-methylbut-3-yn-2-ol (883 mg, 10.5 mmol) were added and the mixture was stirred for 6 h at 80 °C. The mixture was cooled to room temperature and taken up in pentane/Et_2O (150 mL, 5:1 v/v) and 1 M HCl (70 mL). The phases were separated and the aqueous phase was extracted twice with pentane (50 mL). The combined organic phases were dried over $MgSO_4$ and filtered. After evaporation of the solvent the orange oily residue was purified by column chromatography on silica gel (pentane:diethyl ether = 5:1) yielding 2-methyl-4-(3-tetradecylphenyl)but-3-yn-2-ol (2.15 g, 6.0 mmol, 85%) as yellow oil. The product was dissolved in toluene (10 mL) and powdered KOH (1.20 g, 21.4 mmol) was added. The mixture was stirred at 100 °C for 5 h and cooled to room temperature. It was taken up in pentane (150 mL) and 1 M HCl (70 mL), the mixture was cautiously shaken, the phases were separated and the aqueous phase was extracted thrice with pentane (50 mL). The combined organic phases were washed with brine (70 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated and the oily residue was filtered over silica gel (pentane). Concentration of the filtrate gave 1-ethynyl-3-tetradecylbenzene (**11a**) (1.63 g, 5.4 mmol, 90%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.36-7.29 (m, 2H, H_{Ar}), 7.26-7.20 (m, 1H, H_{Ar}), 7.16 (dt, *J* = 7.6, 1.5 Hz, 1H, H_{Ar}), 3.05 (s, 1H, $C_{sp}H$), 2.63-2.54 (m, 2H, CH_2), 1.66-1.54 (m, 2H, CH_2), 1.38-1.19 (m, 22H, CH_2), 0.89 (t, *J* = 6.7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 143.1, 132.1, 129.4, 129.1, 128.2, 121.9, 84.0, 76.6, 35.7, 31.9, 31.3, 29.7 (5C), 29.6, 29.5, 29.4, 29.2, 22.7, 14.1; IR (neat): *v* = 3309, 2922, 2852, 2109, 1598, 1462, 1373, 1251, 1207, 1087, 895, 846, 790, 721, 694, 644, 606, 528, 462; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{22}H_{34}$, 298.2661; found, 298.2665.

4.12. 1-Ethynyl-3-(3-ethylheptyl)benzene **11b**

Following the procedure for **11a** 1-bromo-3-(3-ethylheptyl)benzene (**10c**) (3.47 g, 12.3 mmol) was reacted with 2-methylbut-3-in-2-ol (1.55 g, 18.4 mmol), $Pd(OAc)_2$ (54 mg, 2 mol%), triphenylphosphine (257 mg, 8 mol%), and K_3PO_4 (3.90 g, 18.4 mmol) in DMSO (25 mL) and toluene (5 mL). 2-Methyl-4-(3-(3-ethylheptyl)phenyl)but-3-yn-2-ol (2.67 g, 9.3 mmol, 76%) was obtained as yellow oil. The product was deprotected applying powdered KOH (1.57 g, 28.0 mmol) in toluene (30 mL) at 100 °C. Work up as described for **11a** gave 1-ethynyl-3-(3-ethylheptyl)benzene (**11c**) (1.94 g, 8.5 mmol, 91%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.36-7.29 (m, 2H, H_{Ar}), 7.27-7.14 (m, 2H, H_{Ar}), 3.06 (s, 1H, $C_{sp}H$), 2.62-2.51 (m, 2H, CH_2), 1.62-1.49 (m, 2H, CH_2), 1.41-1.20 (m, 9H, CH/CH_2), 0.96-0.83 (m, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 143.5, 132.0, 129.4, 129.0, 128.2, 121.9, 84.0, 76.6, 38.6, 35.0, 32.9, 32.7, 28.9, 25.7, 23.1, 14.1, 10.8; IR (neat): *v* = 3306, 2957, 2924, 2860, 2108, 1599, 1459, 1377, 1210, 1085, 890, 791, 727, 692, 644, 606, 528, 460; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{17}H_{24}$, 228.1878; found, 228.1884.

4.13. 1-Ethynyl-4-tetradecylbenzene **11c**

Following the procedure for **11a** 1-bromo-4-tetradecylbenzene (**10c**) (3.88 g, 11.0 mmol) was reacted with 2-methylbut-3-in-2-ol (1.38 g, 16.4 mmol), $Pd(OAc)_2$ (74 mg, 3 mol%), triphenylphosphine (346 mg, 12 mol%), and K_3PO_4 (3.48 g, 16.4 mmol) in DMSO (30 mL) and toluene (10 mL). 2-Methyl-4-(4-tetradecylphenyl)but-3-yn-2-ol (2.97 g, 8.3 mmol, 76%) was obtained as yellow solid. A part of the product (1.37 g, 3.8 mmol) was deprotected applying powdered KOH (672 mg, 12.0 mmol) in toluene (20 mL). Work up as described for **11a** gave 1-ethynyl-4-tetradecylbenzene (**11c**) (930 mg, 3.1 mmol, 82%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.41 (d, J = 8.2 Hz, 2H, H_{Ar}), 7.13 (d, J = 8.3 Hz, 2H, H_{Ar}), 3.03 (s, 1H, $C_{sp}H$), 2.67-2.53 (m, 2H, CH_2), 1.58 (m, 2H, CH_2), 1.40-1.15 (m, 22H, CH_2), 0.88 (t, J = 6.7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 144.0, 132.0, 128.4, 119.2, 83.9, 76.4, 35.9, 31.9, 31.2, 29.68, 29.66 (4C), 29.6, 29.5, 29.4, 29.2, 22.7, 14.1; IR (neat): ν = 3310, 2921, 2852, 2108, 1608, 1505, 1461, 1373, 1210, 1116, 1020, 821, 722, 644, 605, 554, 519, 407; HRMS (EI, 70 eV) m/z: calcd for $C_{22}H_{34}$, 298.2661; found, 298.2655.

4.14. 4,4,5,5-Tetramethyl-2-((3-tetradecylphenyl)ethynyl)-1,3,2-dioxaborolane **2a**

1-Ethynyl-3-tetradecylbenzene (**11a**) (1.94 g, 6.5 mmol) were dissolved in THF/Et_2O (100 mL, 1:1 v/v) and the solution was cooled to -78 °C. *n*-Butyl lithium (2.8 mL, 7.0 mmol, 2.5 M in hexanes) was added and the mixture was stirred for 30 min. 2-Isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.1 mL, 10 mmol) was added and the mixture was vigorously stirred at -78 °C for 2 h becoming a jelly consistence. HCl (2.0 mL, 8.0 mmol, 4 M in Et_2O) was added at -78 °C upon which the mixture became less viscous. It was allowed to warm to room temperature and all salts were precipitated from the mixture by addition of an equal volume of pentane. It was filtered over Celite and the solvent evaporated, giving 2.65 g

of a mixture **2a**:**11a** = 5:1 (NMR-analysis) as yellow oil, which was used in the cycloaddition step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.39-7.30 (m, 2H, H_{Ar}), 7.24-7.14 (m, 2H, H_{Ar}), 2.62-2.49 (m, 2H, CH_2), 1.65-1.49 (m, 2H, CH_2), 1.32 (s, 12H, CH_3), 1.30-1.22 (m, 22H, CH_2), 0.88 (t, *J* = 6.7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 143.0, 132.6, 129.8, 129.7, 128.1, 121.6, 84.4, 35.6, 31.9, 31.1, 29.7 (5C), 29.54, 29.46, 29.4, 29.2, 24.7, 22.7, 14.1 (the sp-carbon bound to the benzene ring is not resolved); ^{11}B NMR (128 MHz, $CDCl_3$, δ): 24.0; IR (neat): *ν* = 2915, 2850, 2197, 1471, 1343, 1135, 970, 840, 799, 654; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{28}H_{45}BO_2$, 424.3513; found, 424.3506.

4.15. 2-((3-(3-Ethylheptyl)phenyl)ethynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2b**

Following the above procedure 1-ethynyl-3-(3-ethylheptyl)benzene (**11c**) (912 mg, 4.0 mmol) was reacted with *n*-butyl lithium (2.0 mL, 5.0 mol, 2.5 M in hexanes), 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.1 mL, 5.0 mmol), and BF_3 etherate (710 mg, 5.0 mmol) in Et_2O (70 mL). Filtration and concentration gave almost pure **2b** (1.62 g) containing about 5% of the alkyne **11b** (NMR-analysis) as yellow oil, which was used in the cycloaddition step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37 (s, 1H, H_{Ar}), 7.34 (dt, *J* = 7.3, 1.4 Hz, 1H, H_{Ar}), 7.21 (t, *J* = 7.5 Hz, 1H, H_{Ar}), 7.34 (dt, *J* = 7.7, 1.5 Hz, 1H, H_{Ar}), 2.58-2.49 (m, 2H, CH_2), 1.58-1.46 (m, 2H, CH_2), 1.32 (s, 12H, CH_3), 1.30-1.23 (m, 9H, CH/CH_2), 0.94-0.82 (m, 6H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 143.4, 132.6, 129.75, 129.67, 128.2, 121.6, 102.2, 84.4, 38.5, 34.9, 32.8, 32.7, 28.8, 25.7, 24.7, 23.1, 14.1, 10.7; ^{11}B NMR (128 MHz, $CDCl_3$, δ): 22.3; IR (neat): *ν* = 2961, 2926, 2862, 2195, 1476, 1452, 1380, 1345, 1270, 1231, 1139, 970, 849, 792, 689, 661; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{23}H_{35}BO_2$, 354.2730; found, 354.2719.

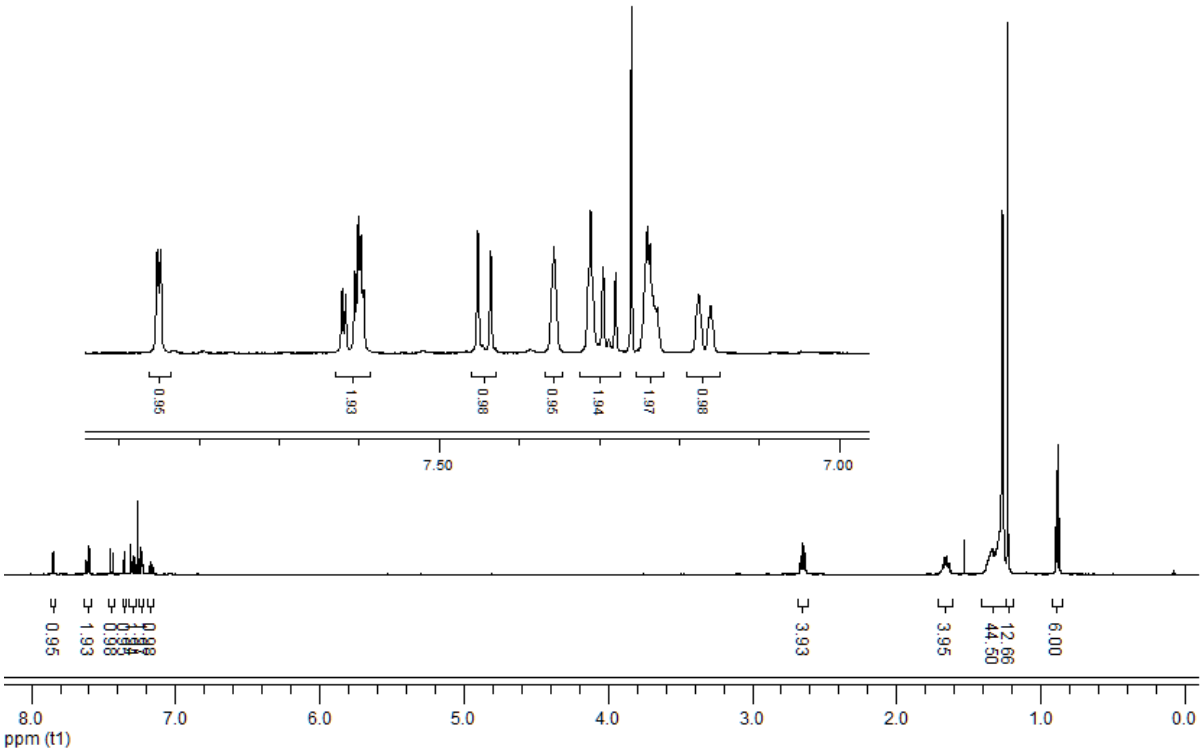
4.16. 4,4,5,5-Tetramethyl-2-((4-tetradecylphenyl)ethynyl)-1,3,2-dioxaborolane **2c**

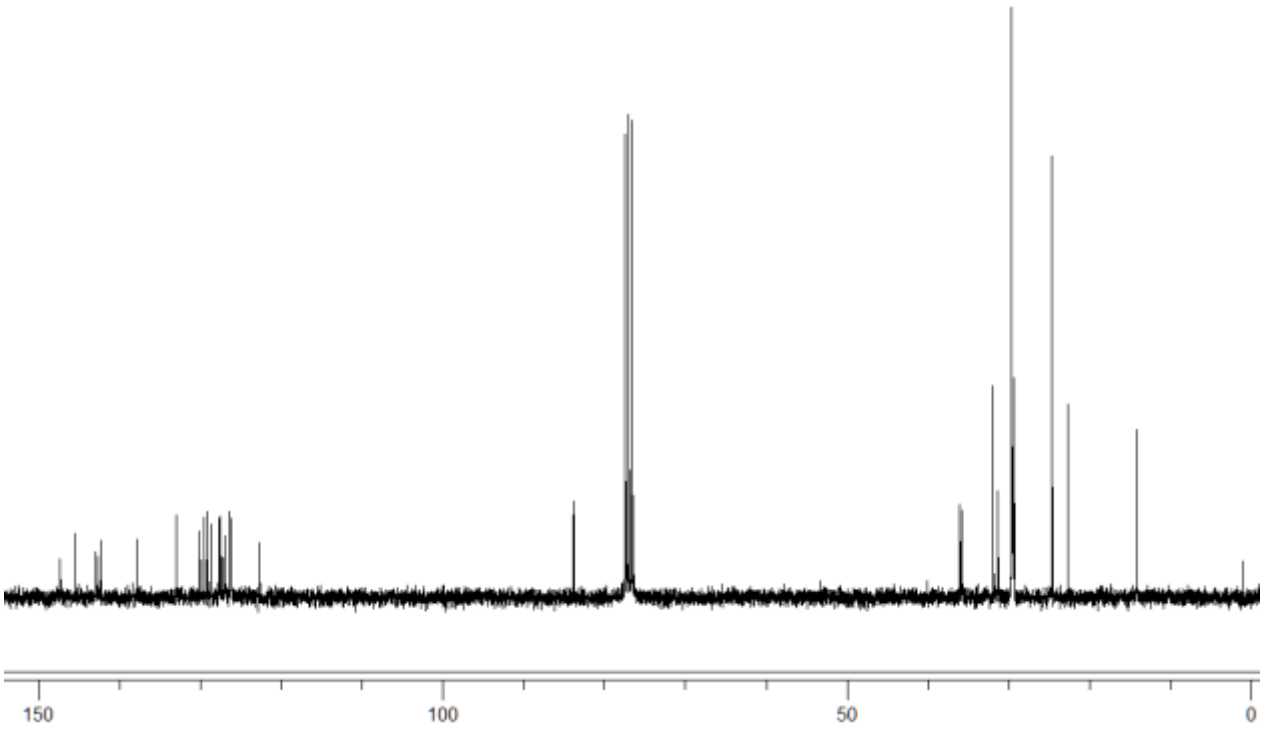
Following the above procedure 1-ethynyl-4-tetradecylbenzene (**11c**) (3.04 g, 10.2 mmol) was reacted with *n*-butyl lithium (4.8 mL, 12.0 mol, 2.5 M in hexanes), 2-isopropyloxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.5 mL, 12.0 mmol), and BF_3 etherate (1.6 mL, 12.0 mmol) in Et_2O (130 mL). Filtration and concentration gave 4.77 g of a mixture **2c**:**11c** = 5:1 (NMR-analysis) as a yellow solid, which was used in the cycloaddition step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.43 (d, J = 8.2 Hz, 2H, H_{Ar}), 7.11 (d, J = 8.2 Hz, 2H, H_{Ar}), 2.61-2.56 (m, 2H, CH_2), 1.63-1.54 (m, 2H, CH_2), 1.32 (s, 12H, CH_3), 1.30-1.22 (m, 22H, CH_2), 0.88 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 144.7, 132.5, 128.3, 119.0, 102.2, 84.3, 35.9, 31.9, 31.1, 29.65, 29.63, 29.62 (2C), 29.60, 29.5, 29.4, 29.3, 29.2, 24.7, 22.6, 14.1; ^{11}B NMR (128 MHz, $CDCl_3$, δ): 24.2; IR (neat): ν = 3215, 2915, 2849, 2191, 1501, 1465, 1383, 1347, 1318, 1271, 1200, 1134, 965, 841, 812, 719,680, 656, 569, 544; HRMS (EI, 70 eV) *m*/*z*: calcd for $C_{28}H_{45}BO_2$, 424.3513; found, 424.3496.

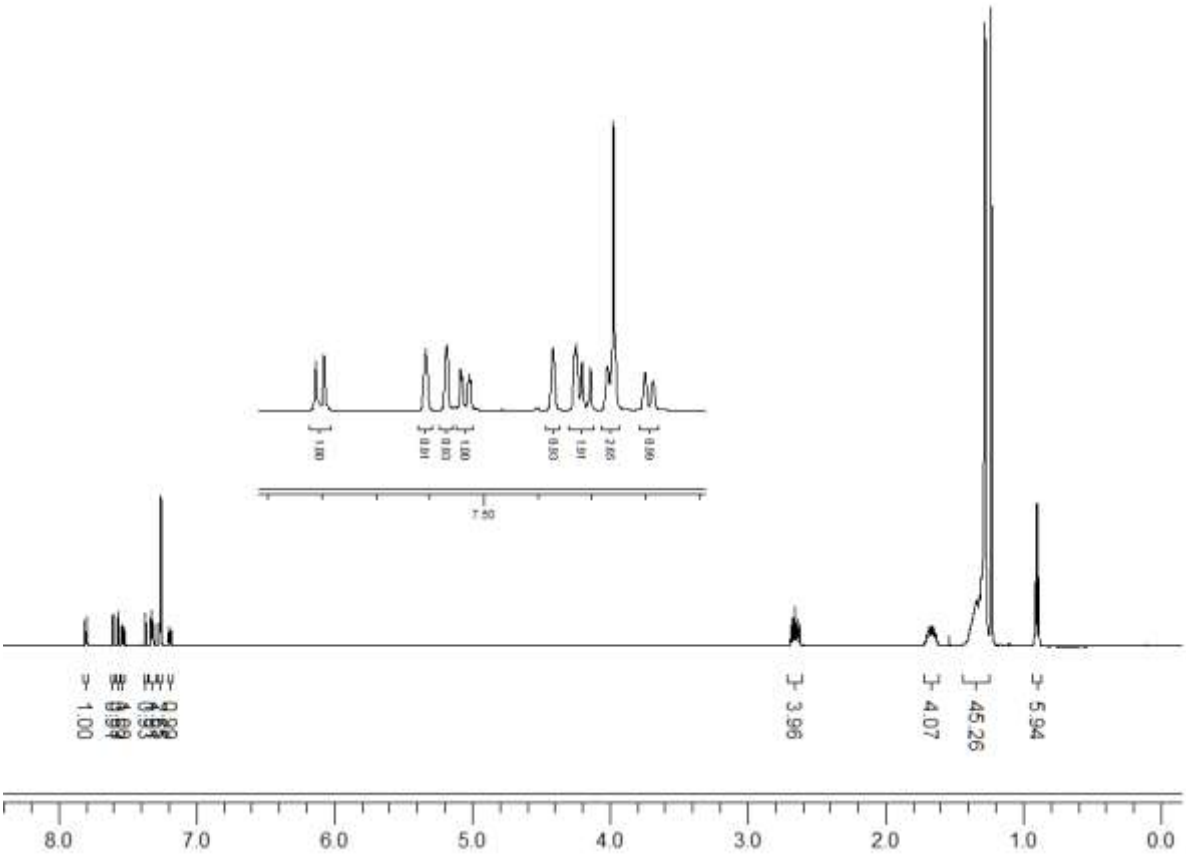
4. NMR-spectra of monomers and polymers

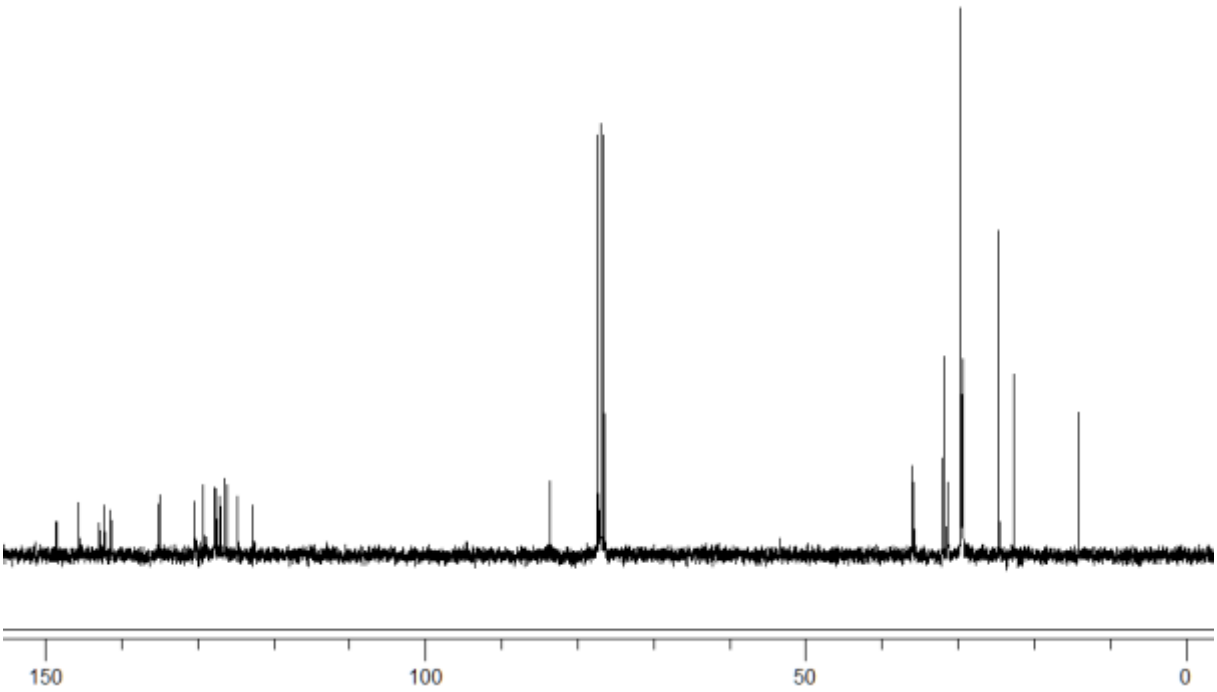
4.1. Monomer **3a**



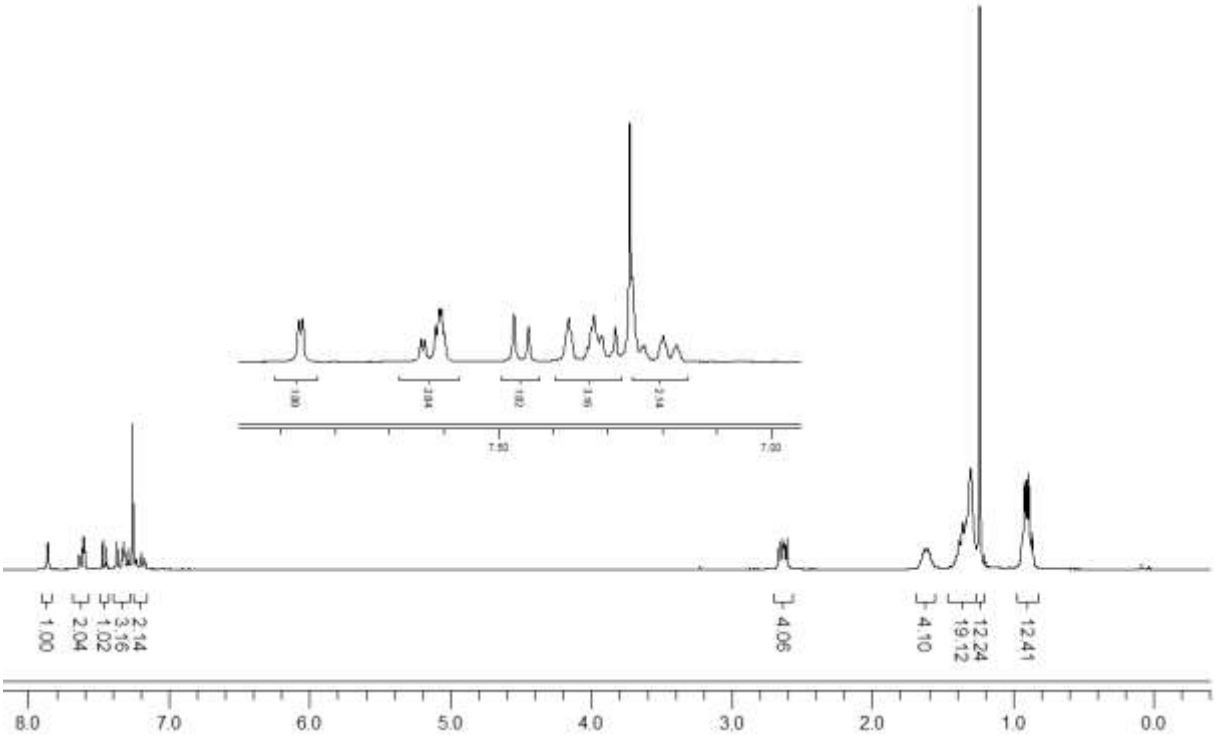


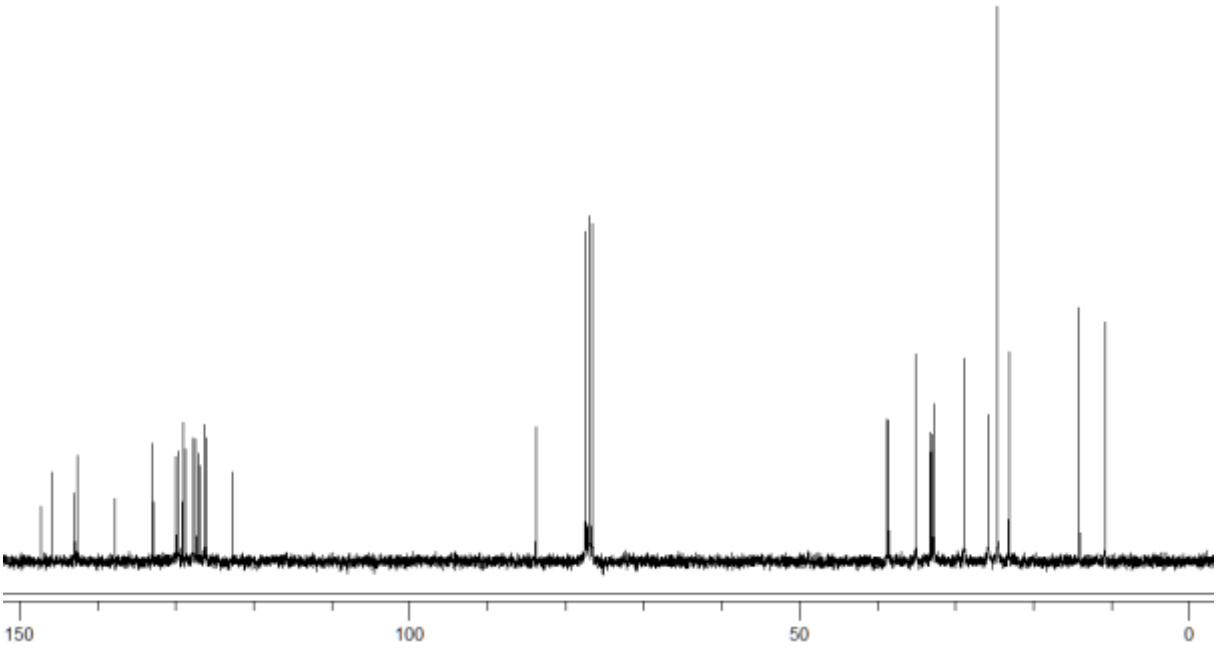
4.2. Monomer **4a**



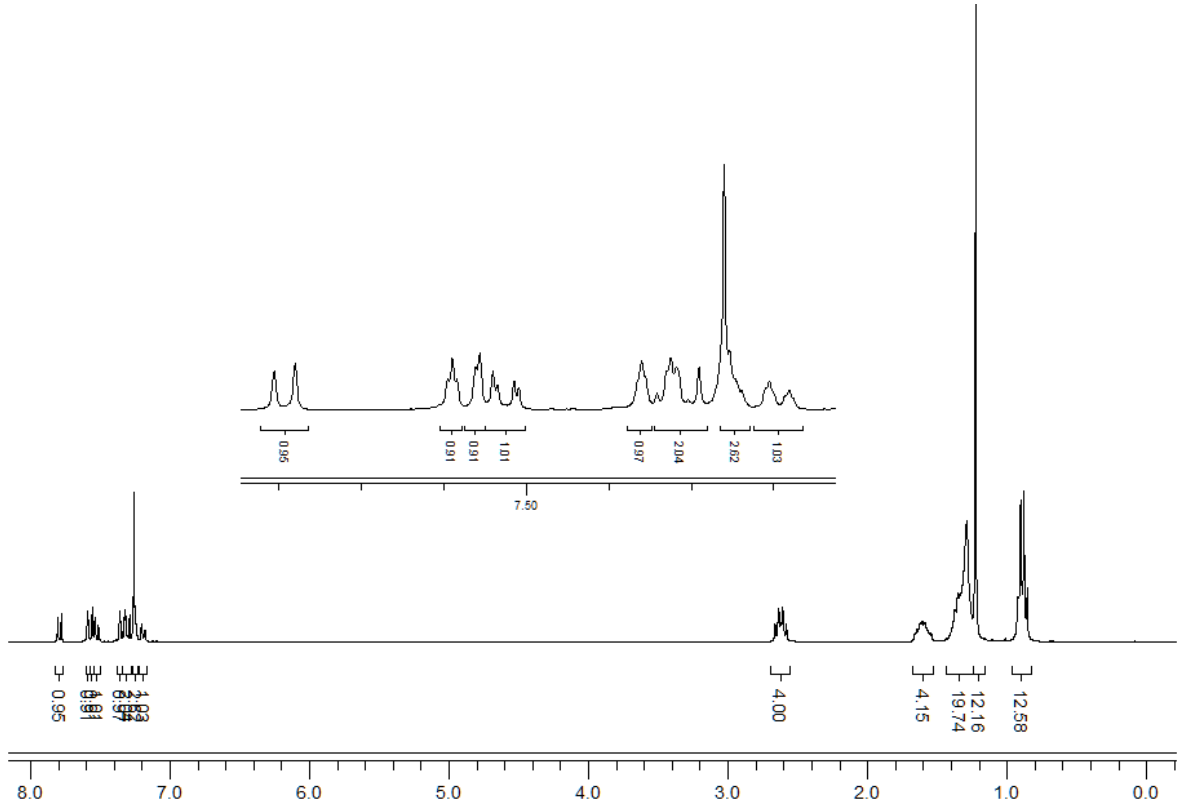


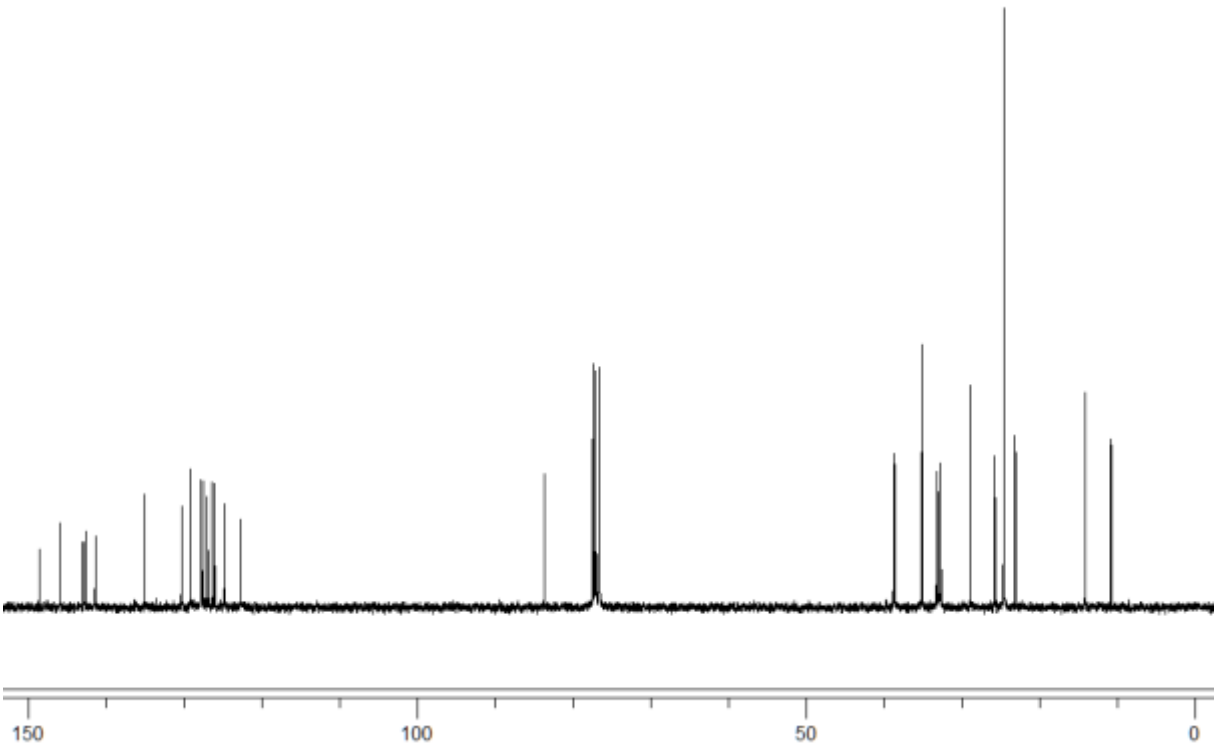
4.3. Monomer **3b**



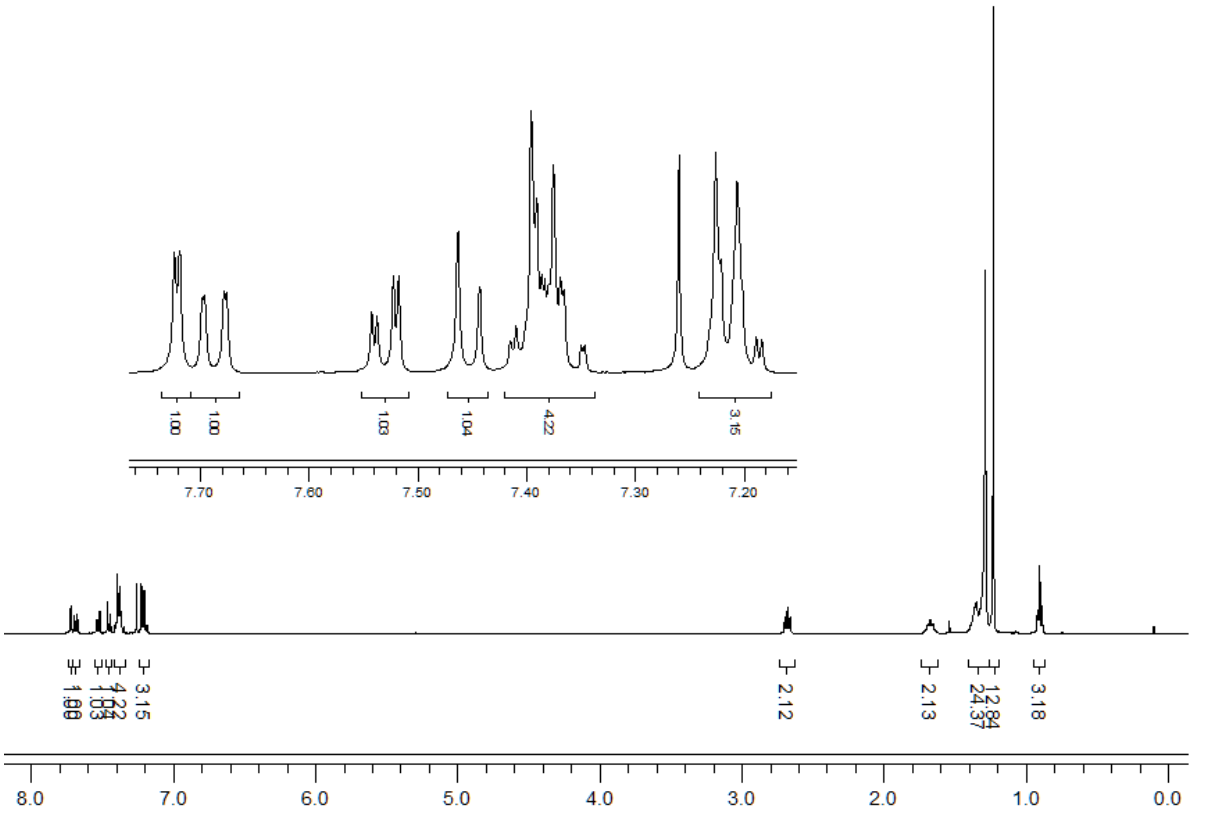


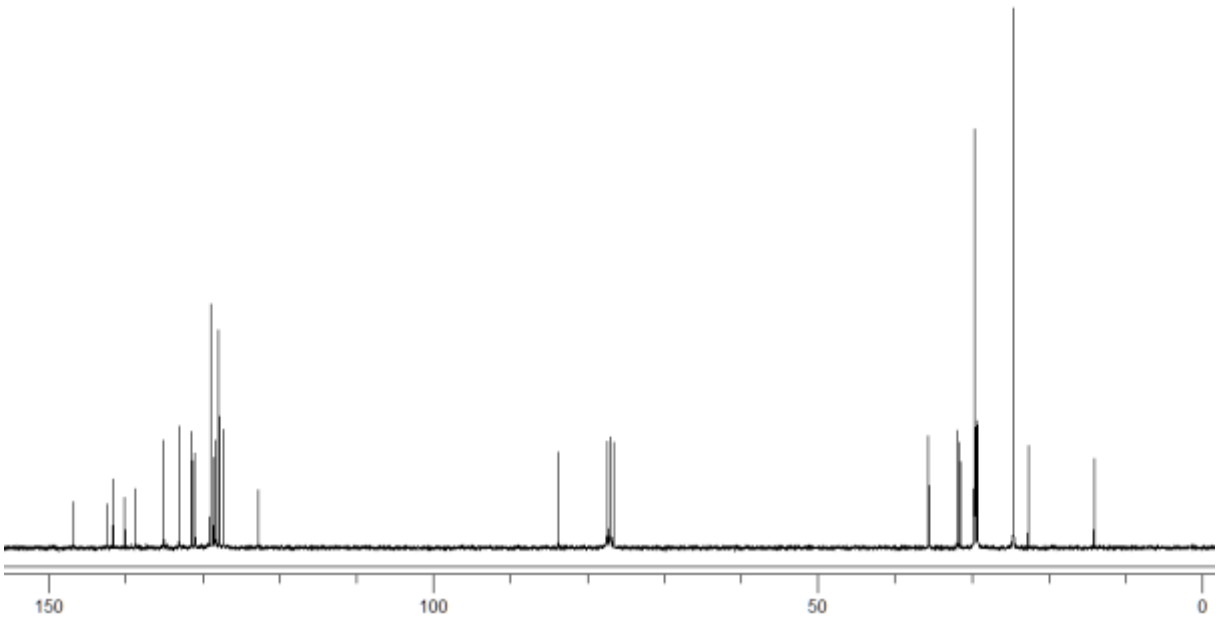
4.4. Monomer **4b**



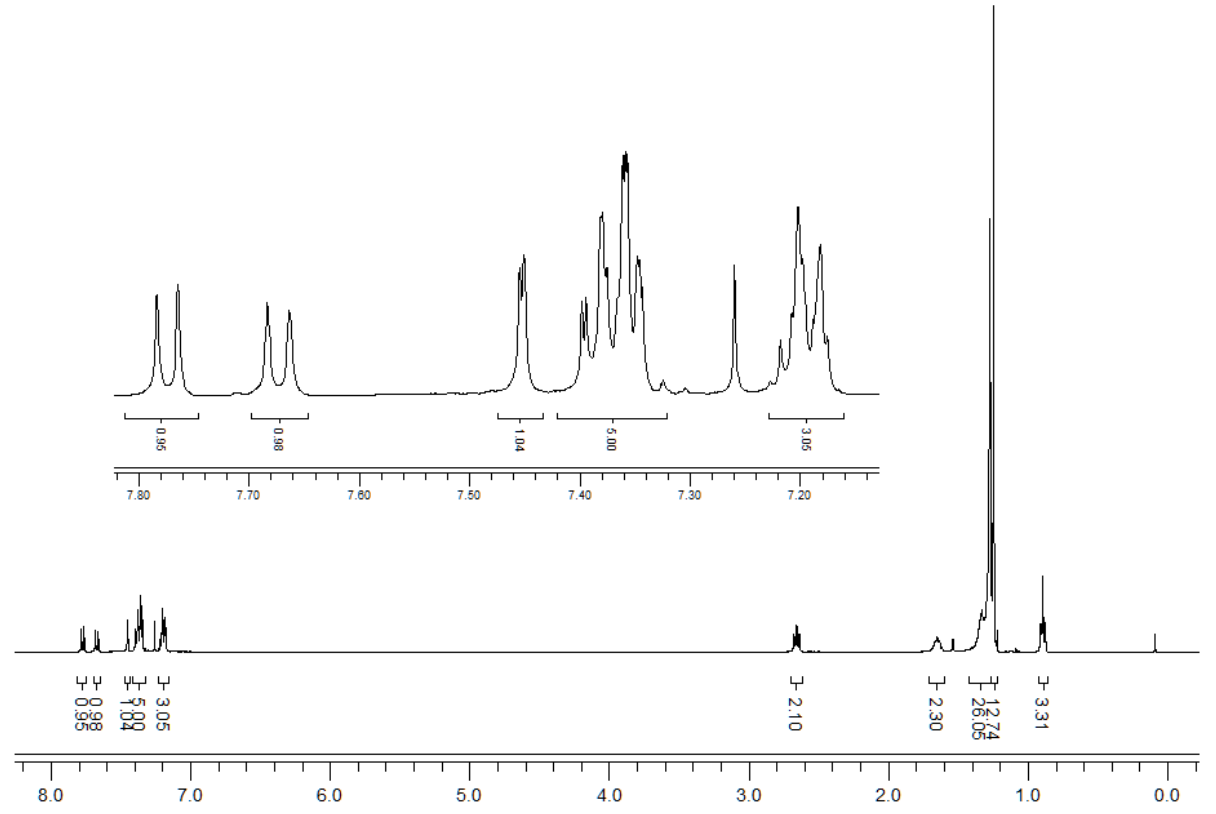


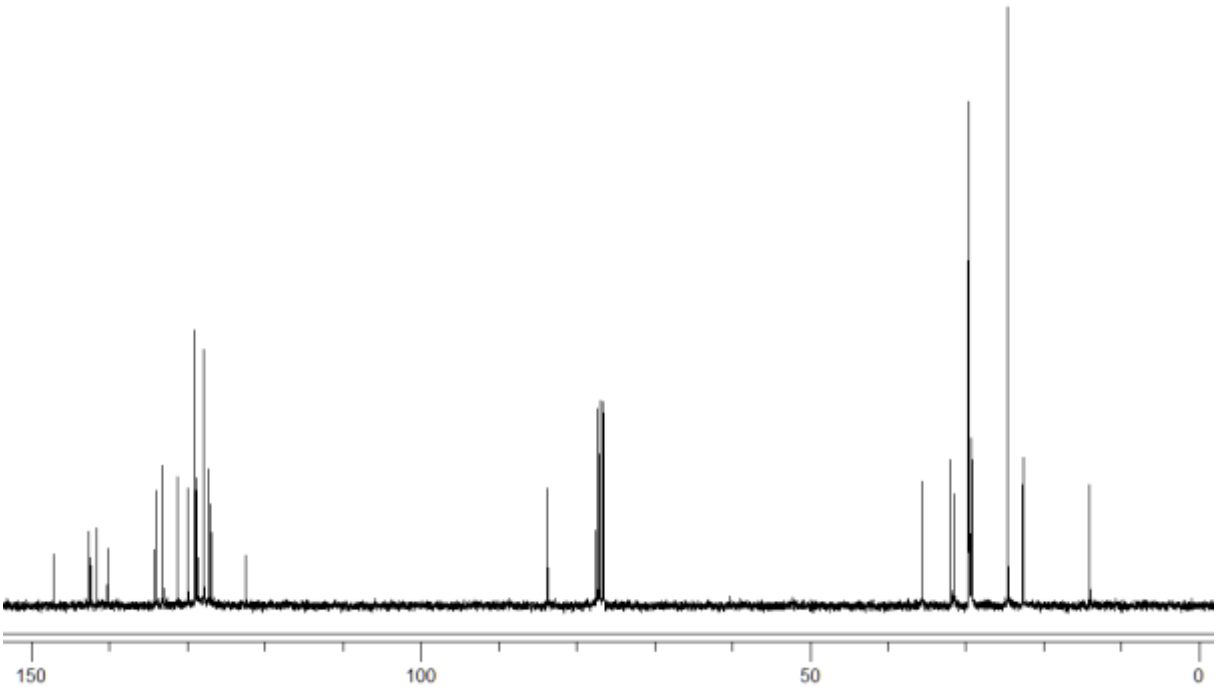
4.5. Monomer **3c**



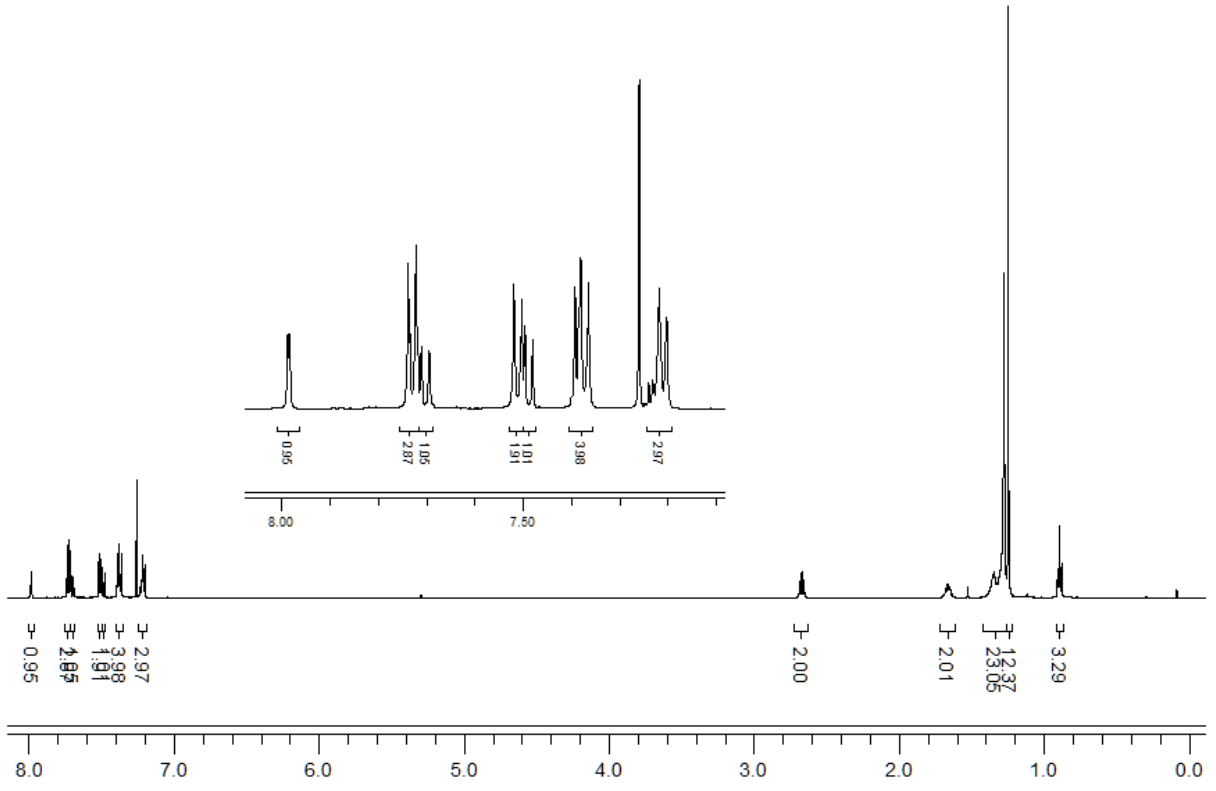


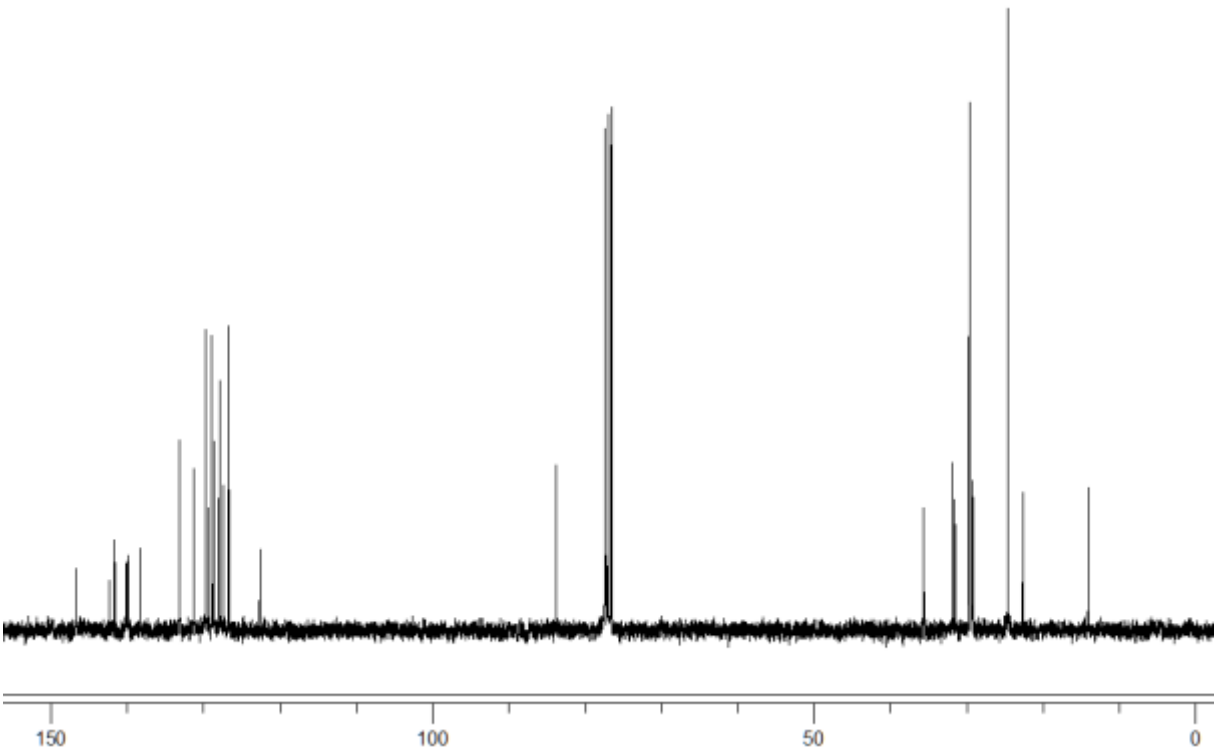
4.6. Monomer **4c**



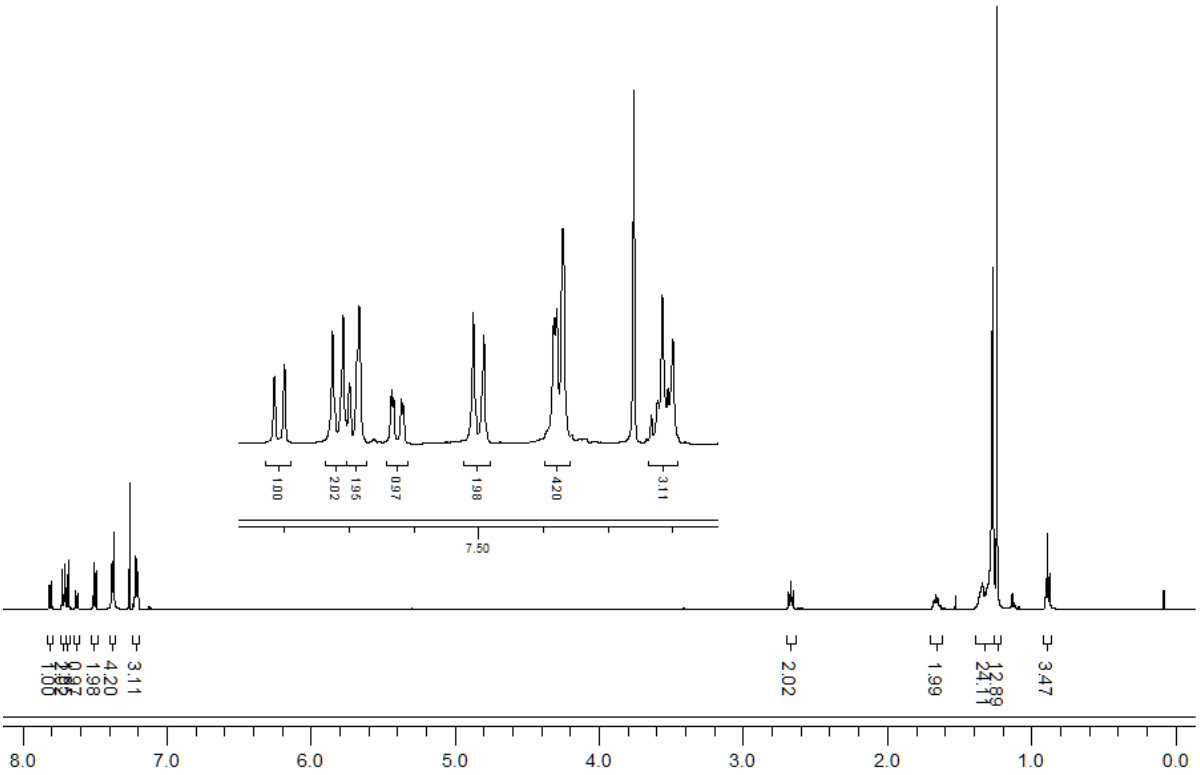


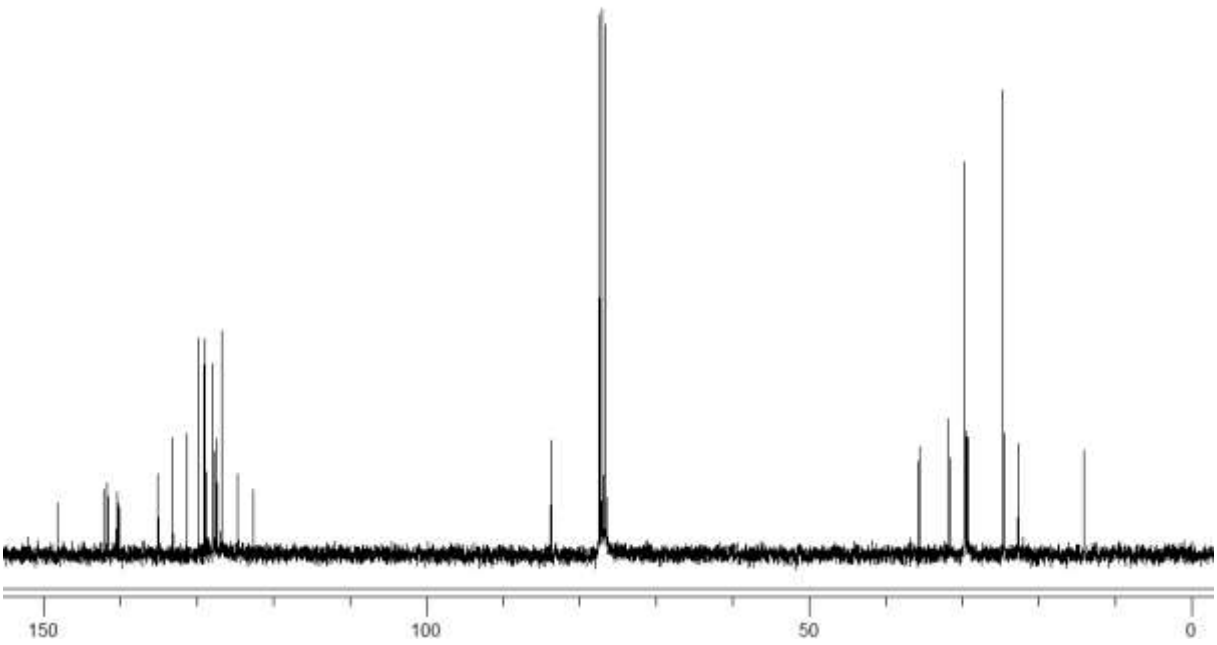
4.7. Monomer **3d**



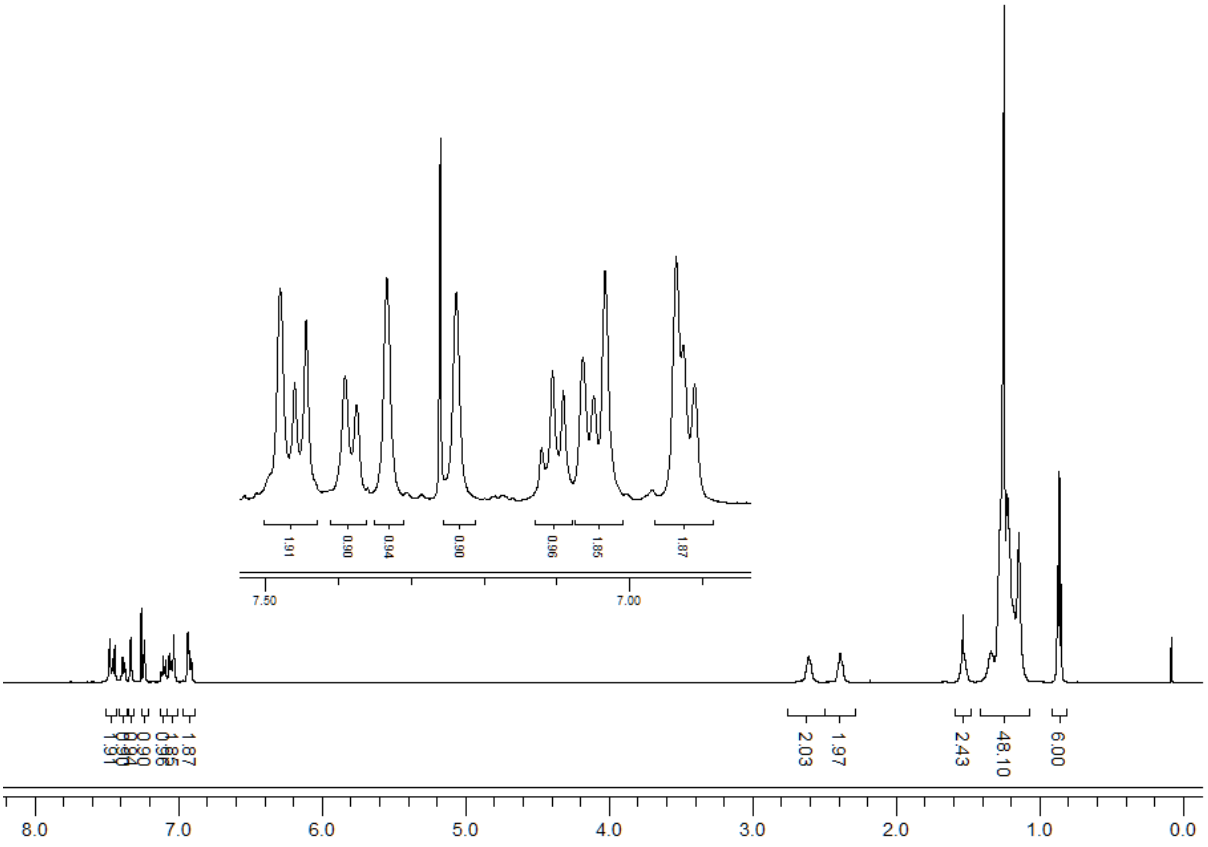


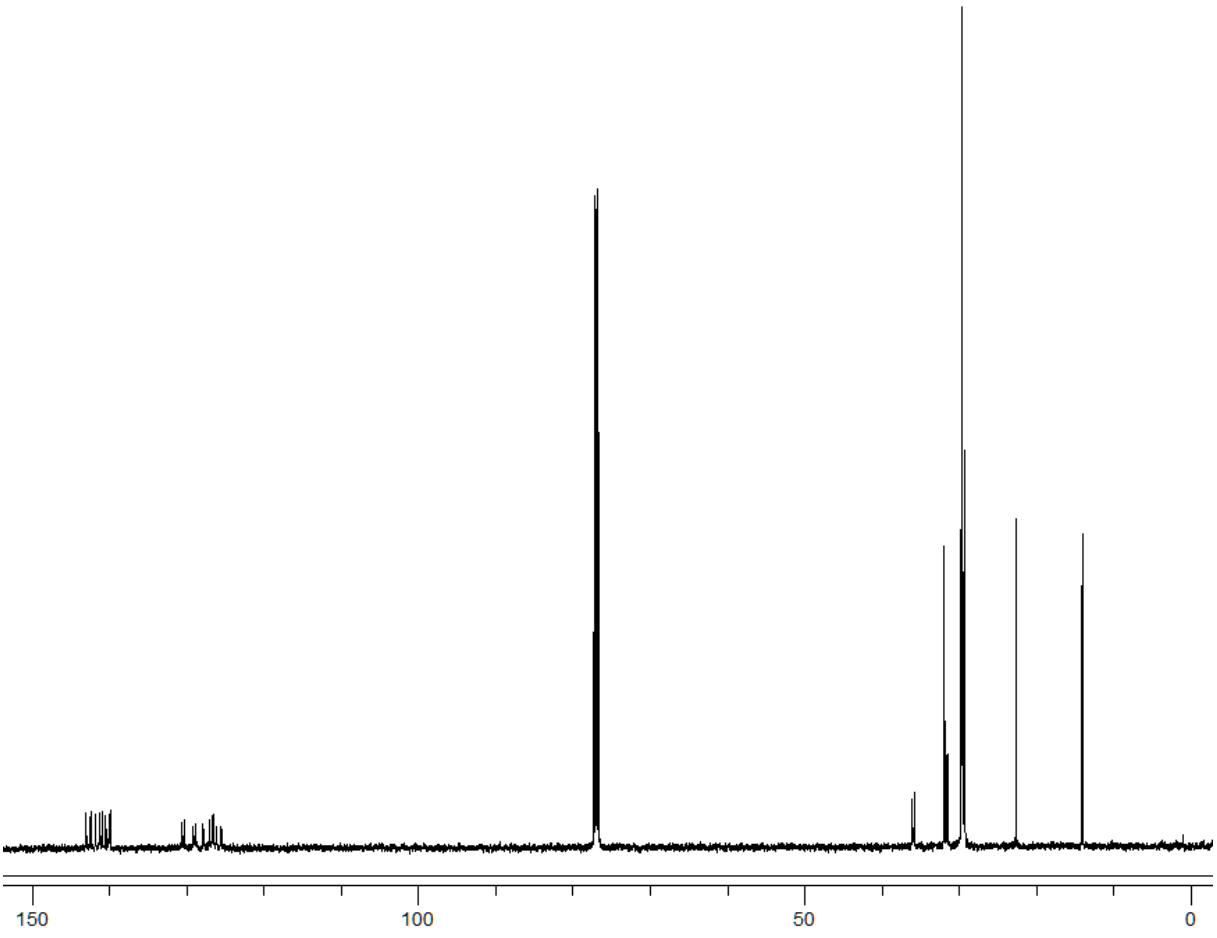
4.8. Monomer **4d**



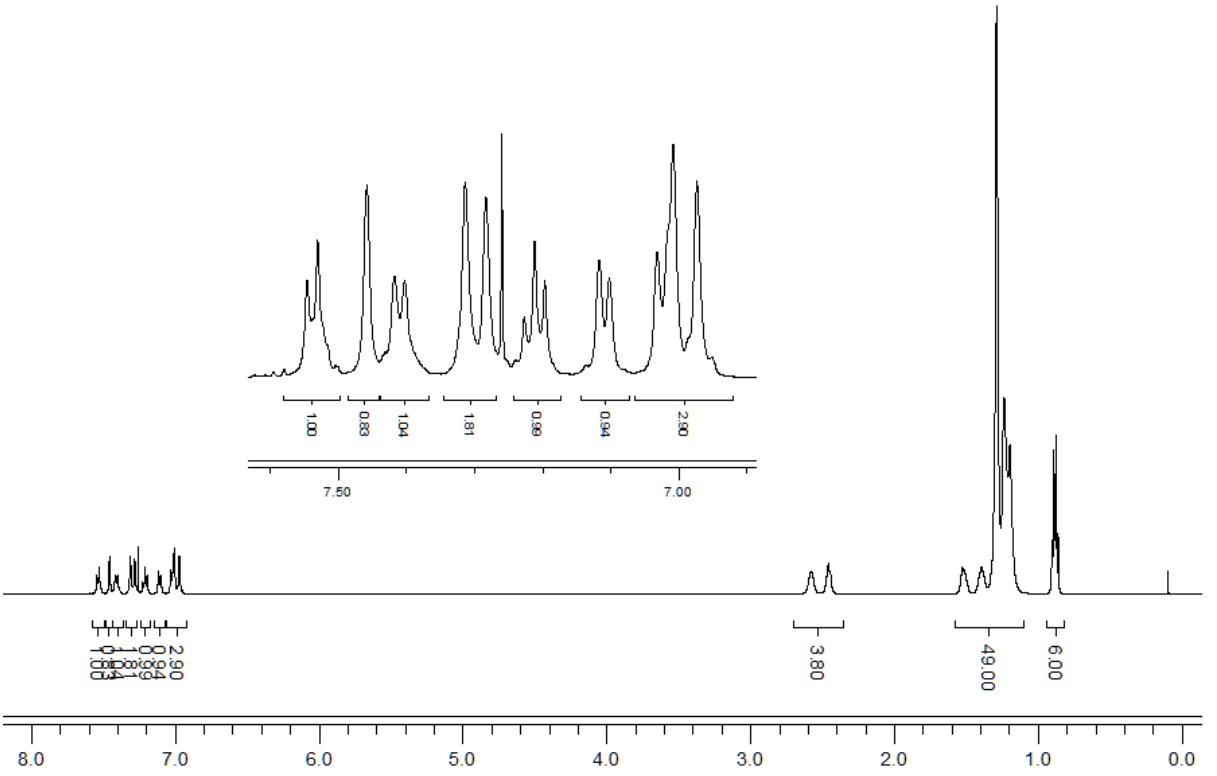


4.9. **poly-3a** (high molecular weight fraction $M_n = 4.0 \cdot 10^4$ Da)





4.10. **poly-4a**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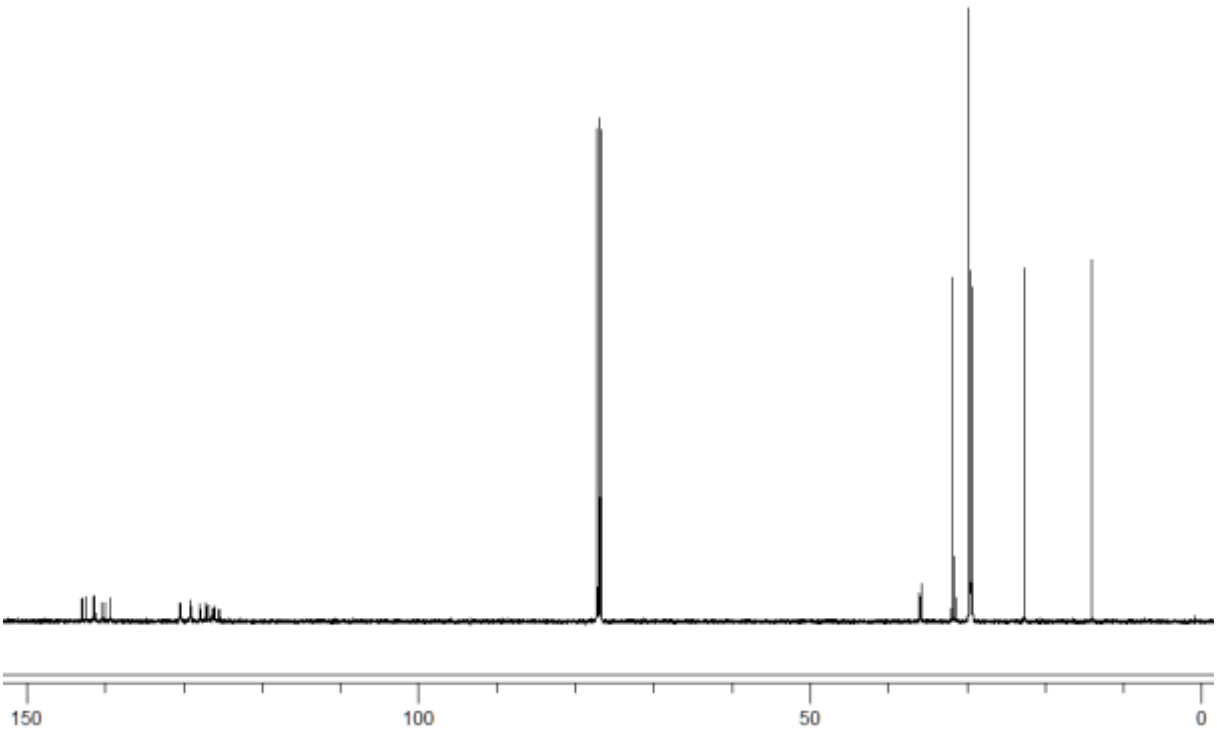
1.81
0.99
0.94
2.00
7.50
7.00
1.00
0.84
1.81
0.99
2.90
3.80
49.00
6.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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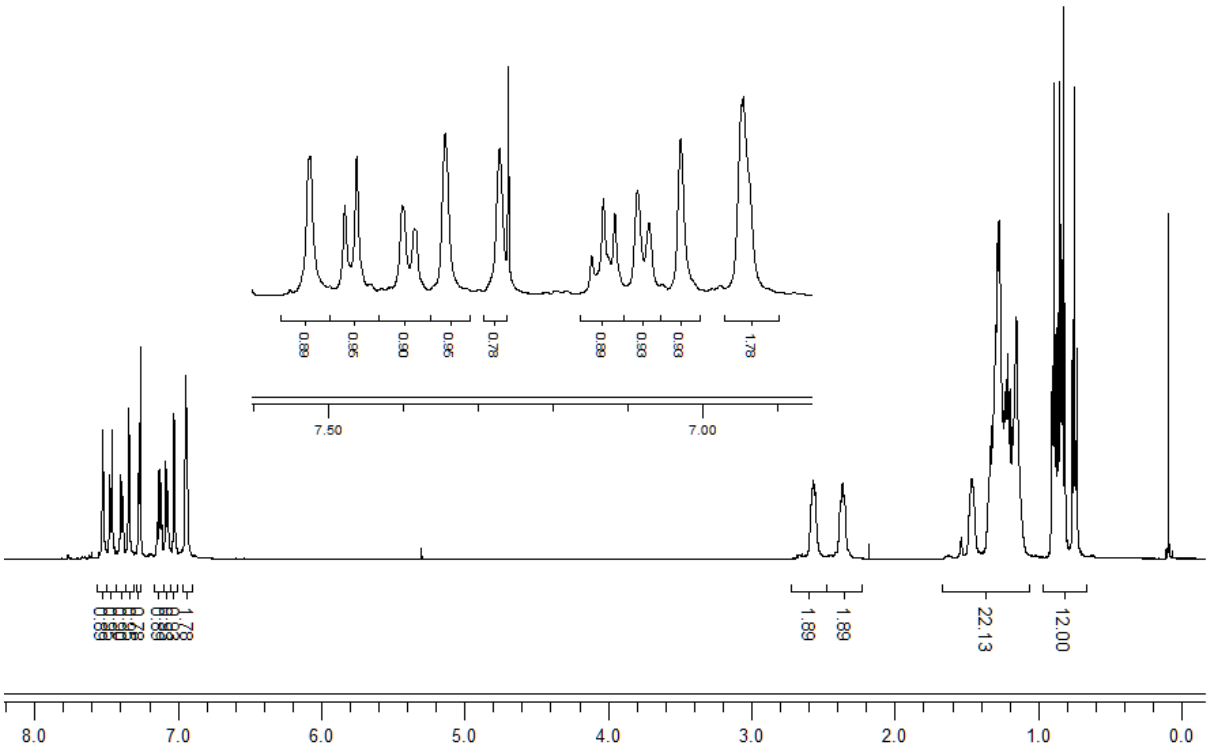
100
50
0

4.11. **poly-3b**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0.78
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0.93
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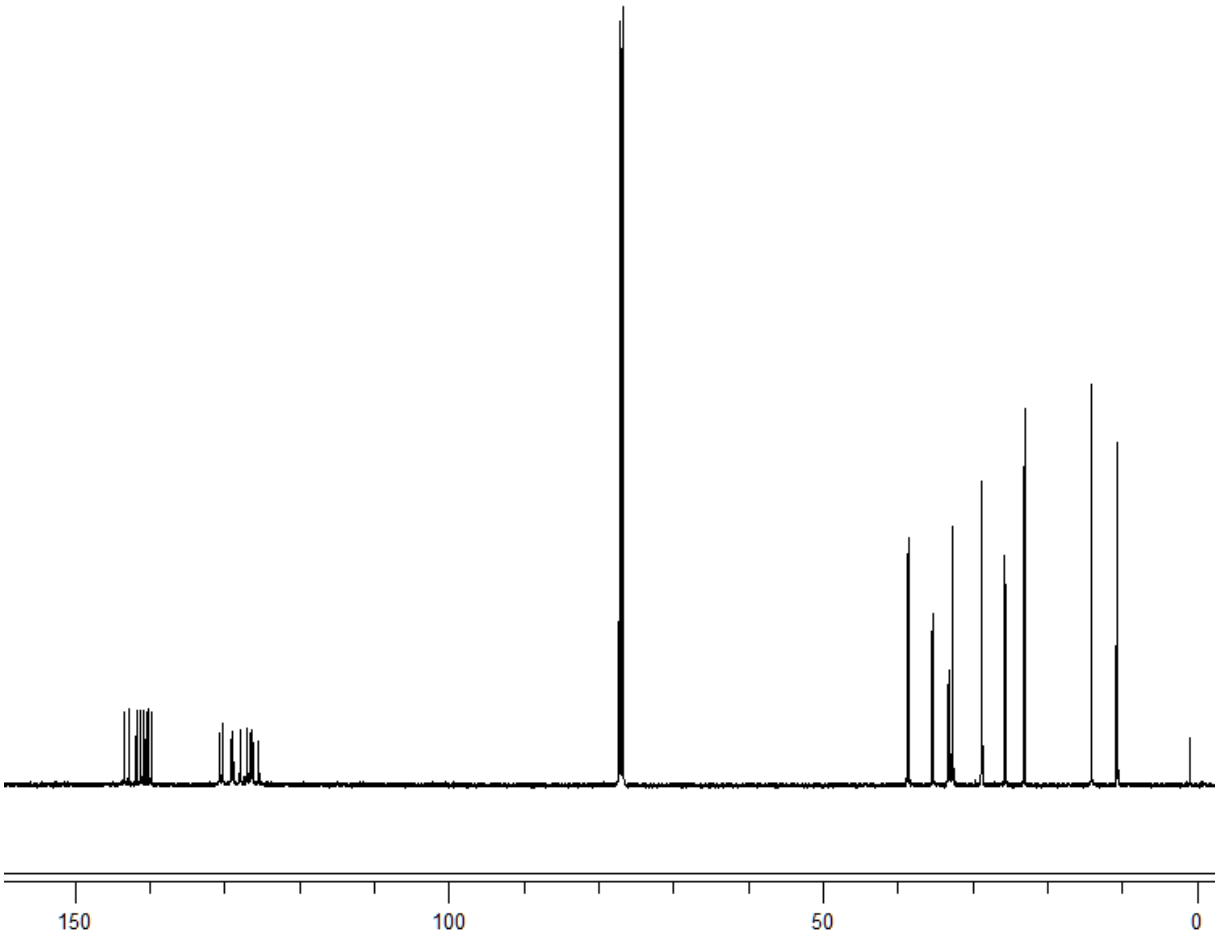
7.00
1.89
1.89
22.13
12.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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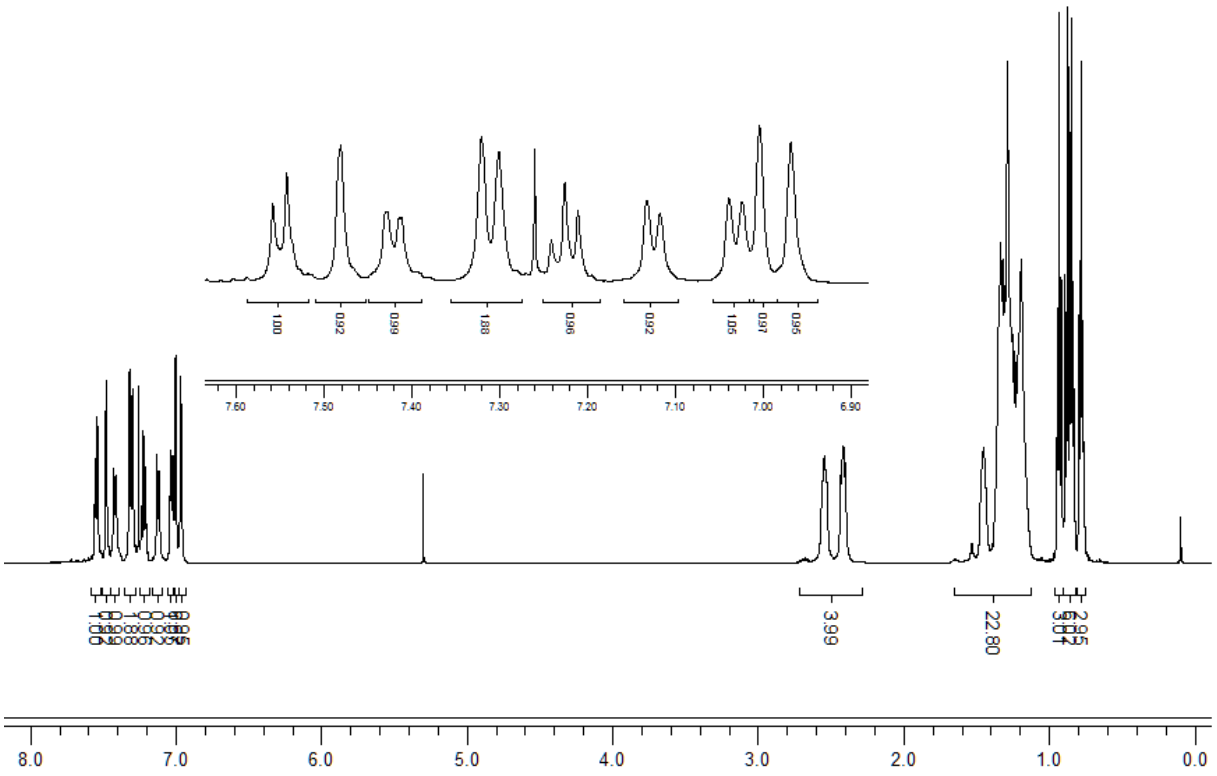
4.12 **poly-4b**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1.05
0.97
0.95
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
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22.80
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7.0
6.0
5.0
4.0
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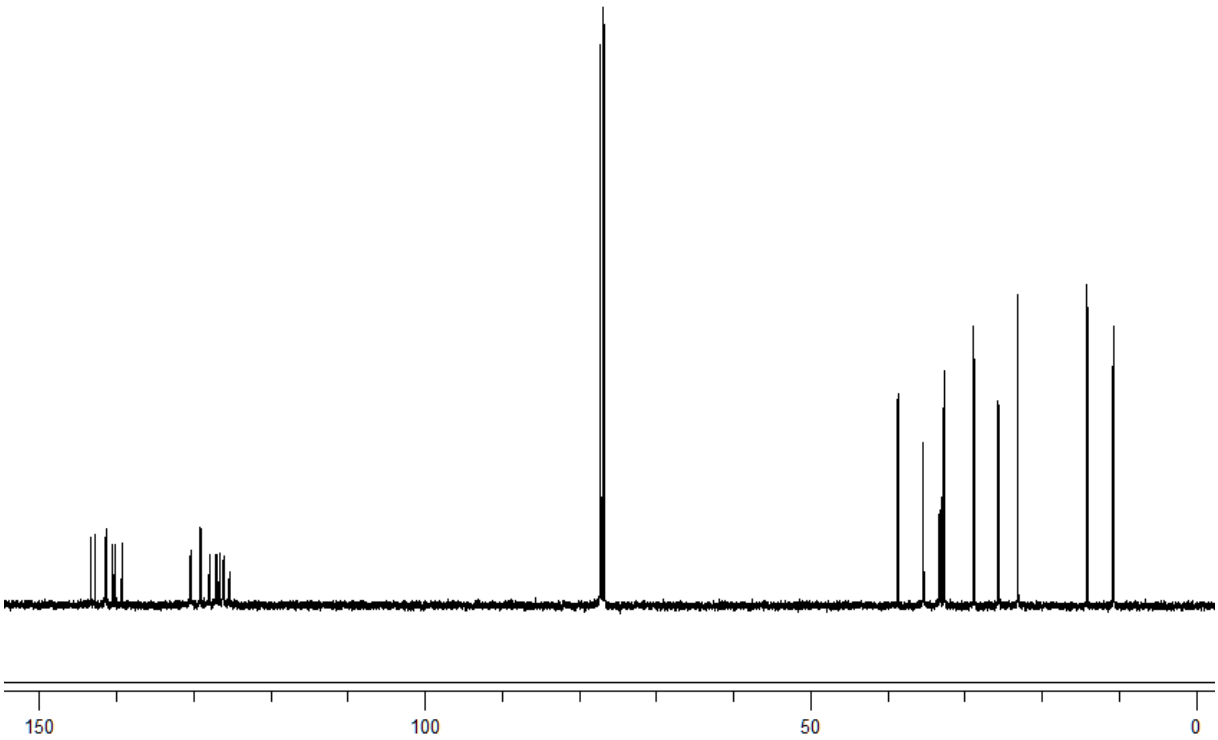
2.0
1.0
0.0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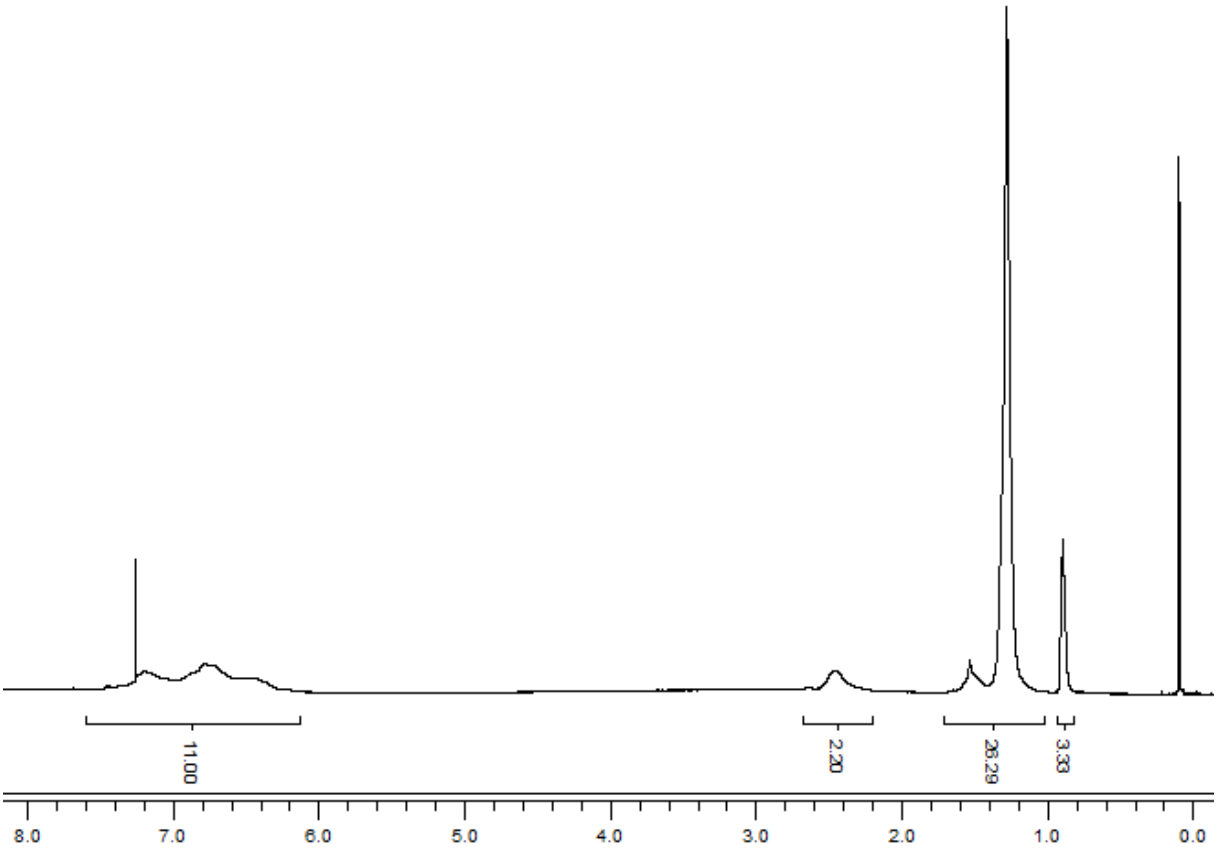
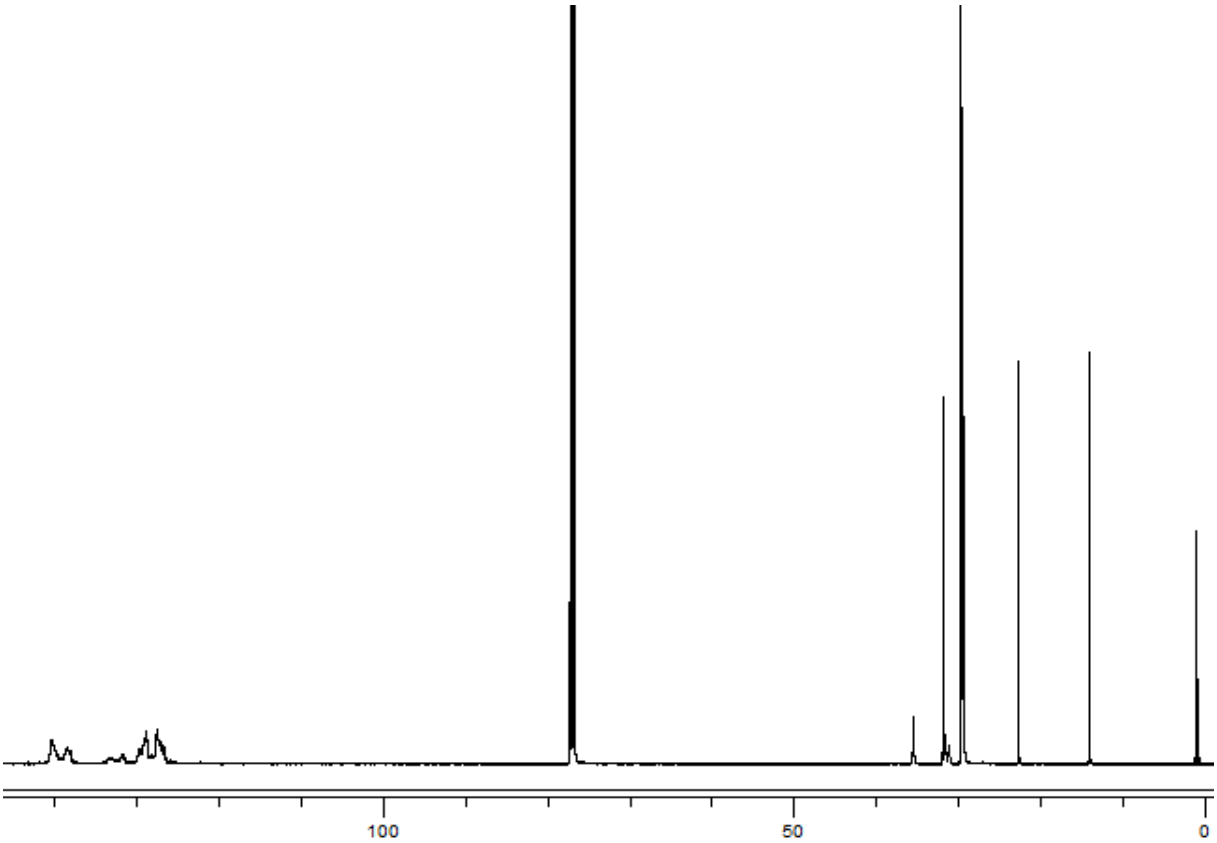
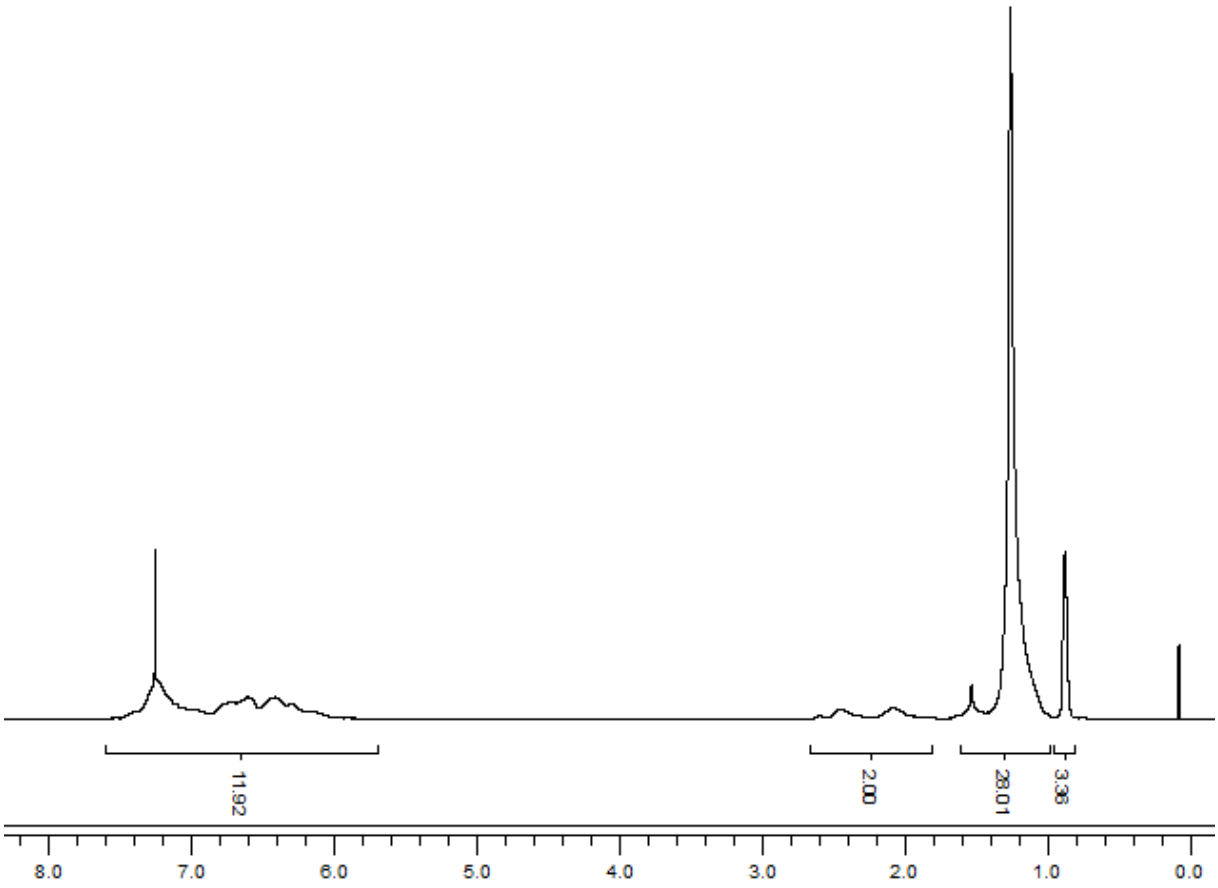
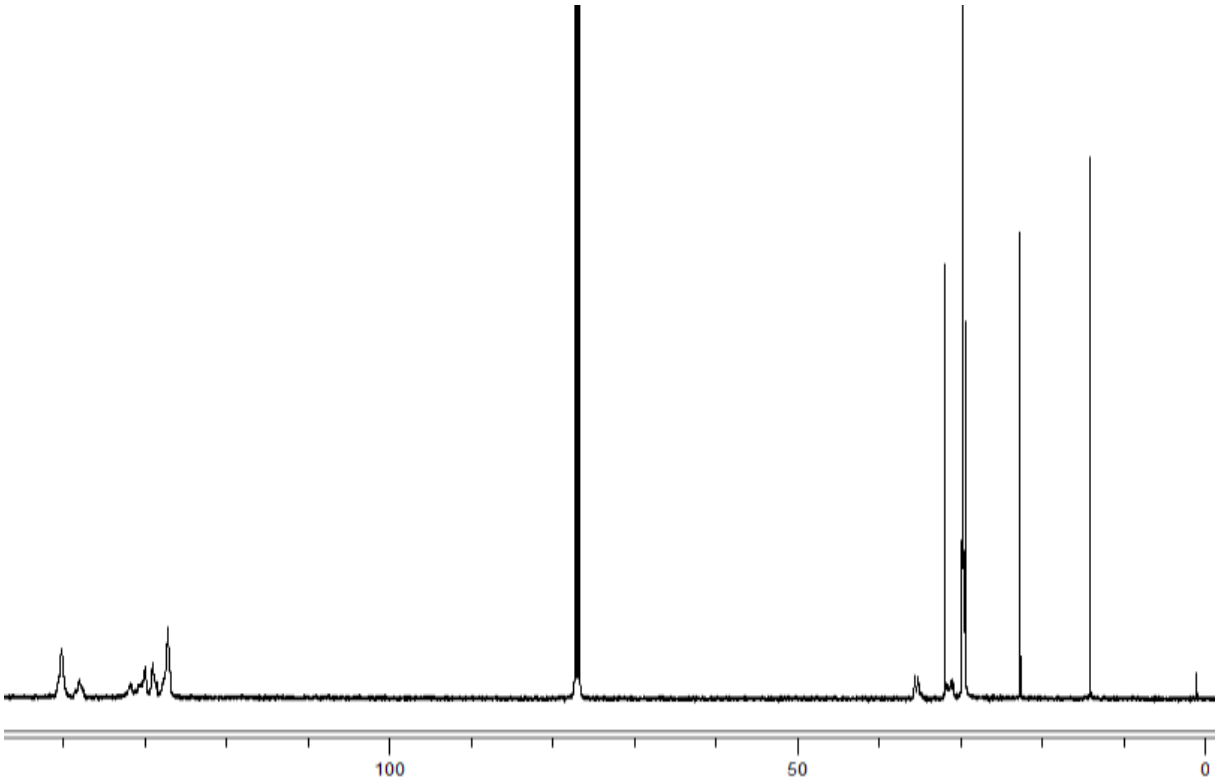
4.13. **poly-3c**



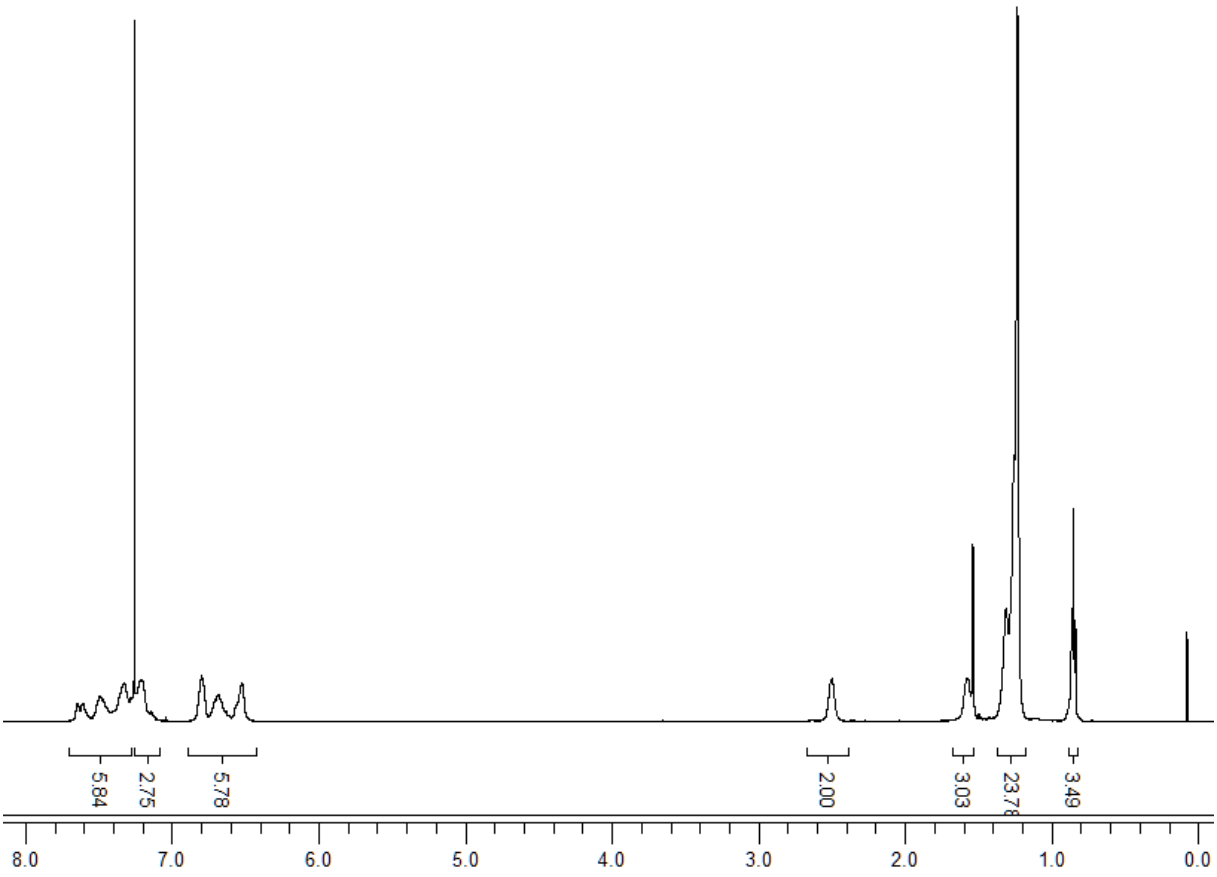


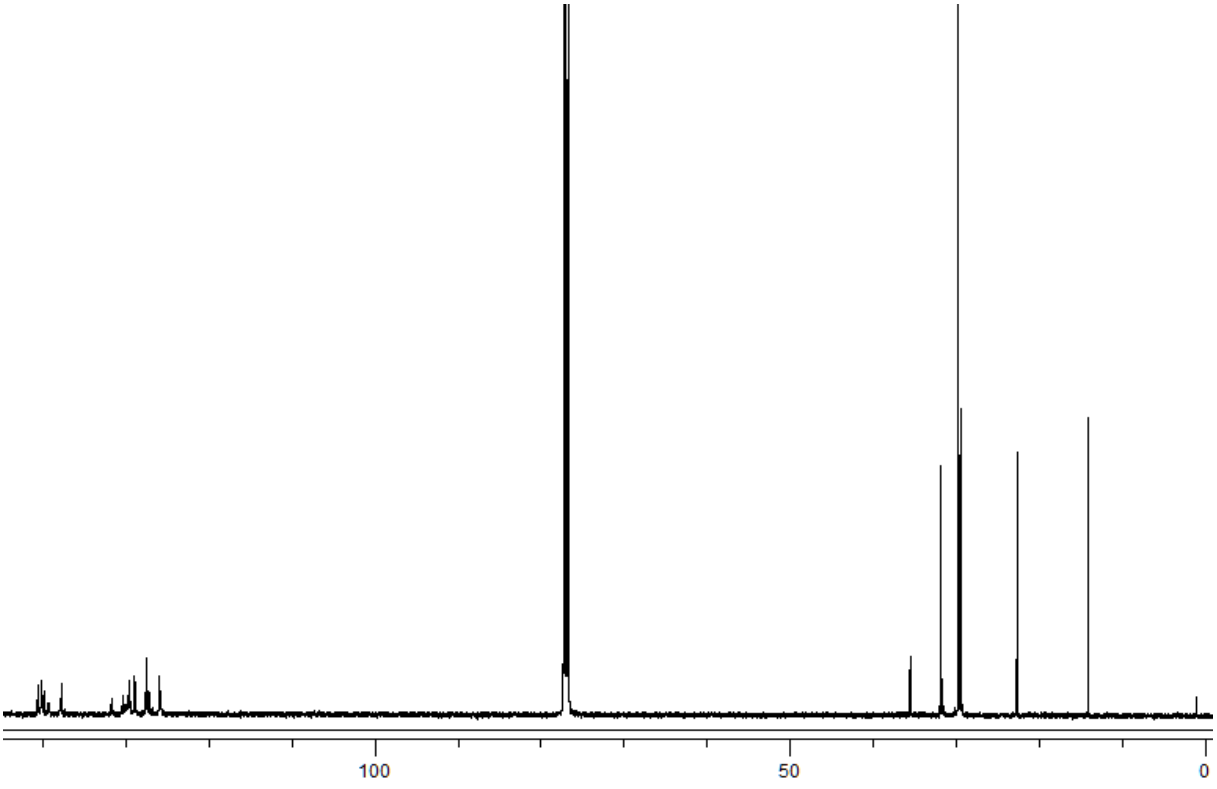
4.14. **poly-4c**



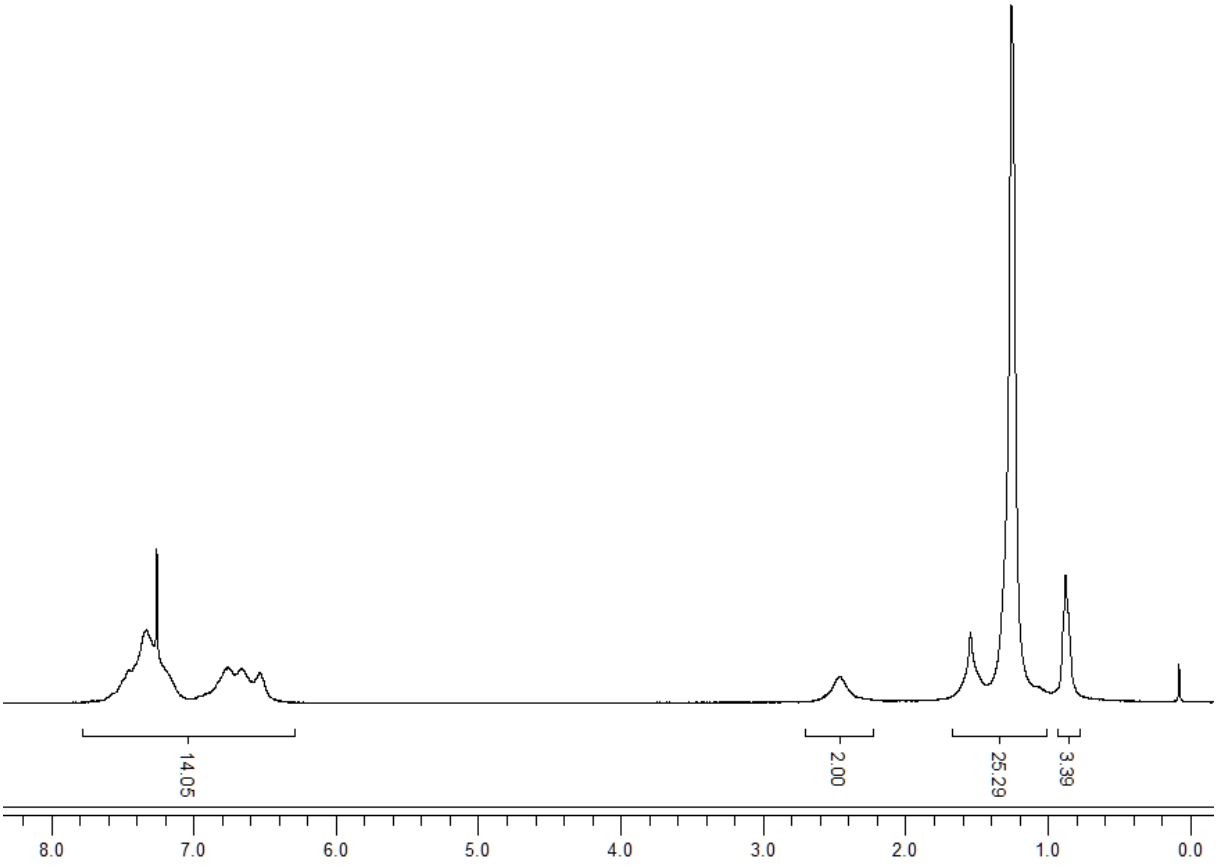


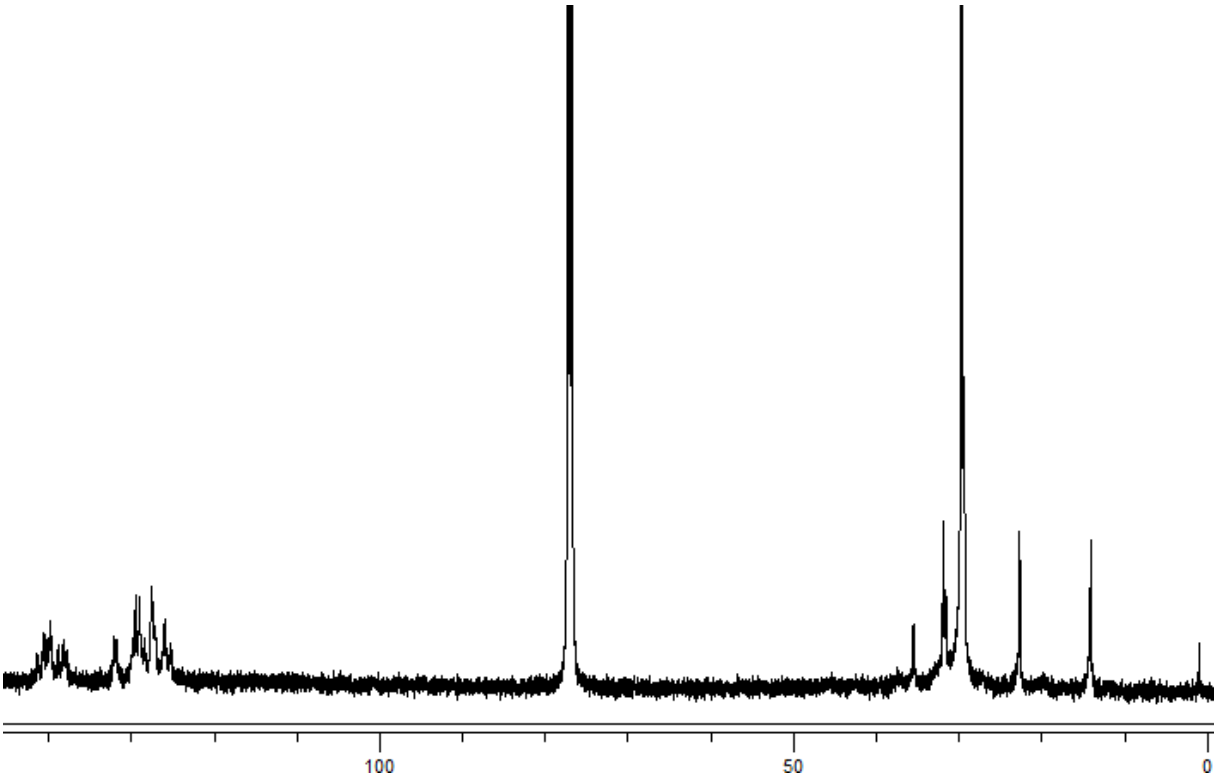
4.15. **poly-3d** (high molecular weight fraction $M_n = 2.2 \cdot 10^4$ Da)



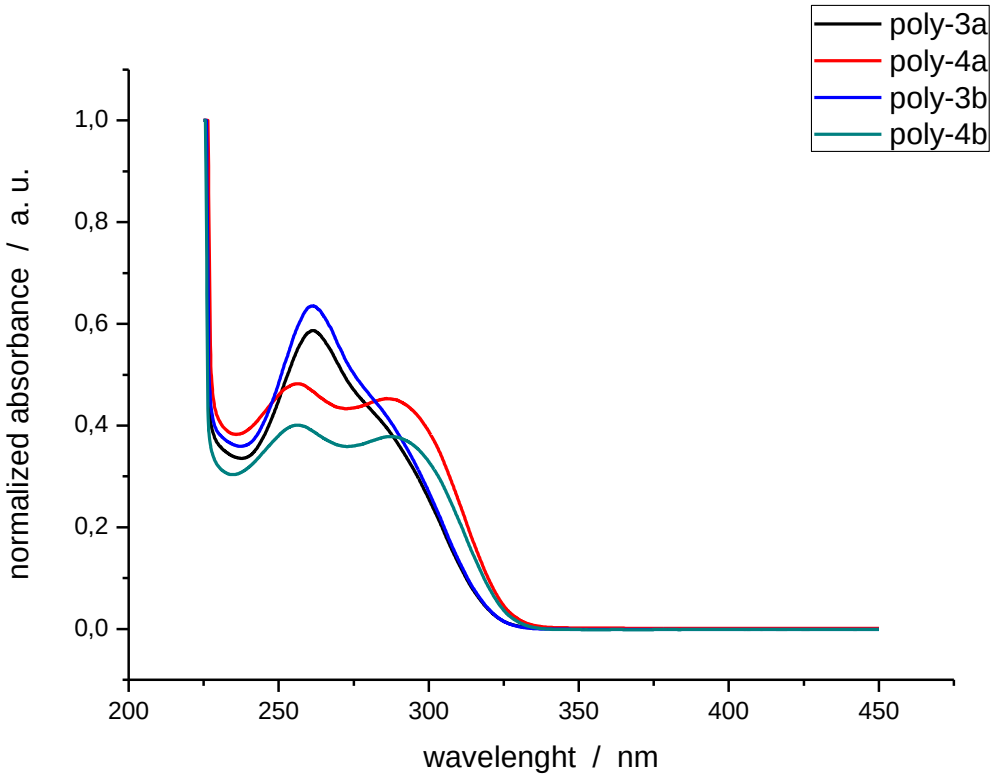


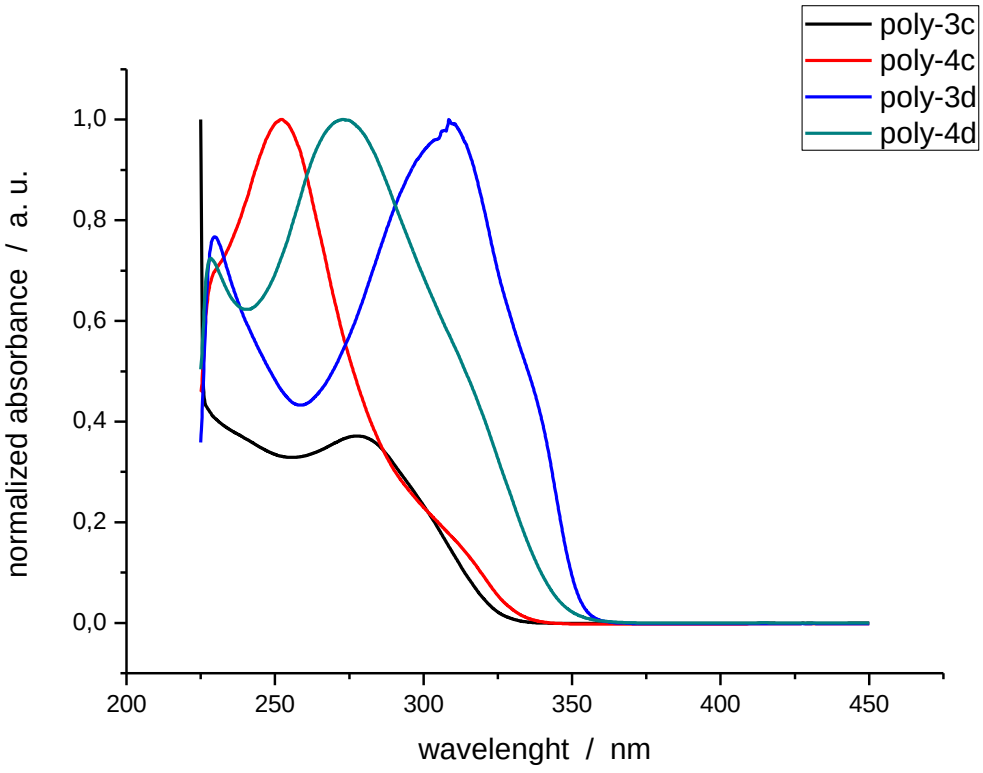
4.16. **poly-4d**





5. Absorption spectra of the polymers





6. Emission spectra of the polymers