Supporting Information

Incorporation of different end-groups in conjugated polymers using functional nickel initiators

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Supporting Information S1
General S2
Synthesis of tetrakistriphenylphosphinenickel(0) S3
Synthesis of 4-bromo-3-methylbenzylalcohol (2a) S3
1-bromo-4-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]methyl]-2-methylbenzene (2c) S3
Synthesis of 1-bromo-2-methyl-4-[2-(trimethylsilyl)ethynyl]benzene (2d) S4
Synthesis of bromo(phenyl)bis(triphenylphosphine)nickel(II) (3a) S4
Analysis of decomposition of 3a S5
Synthesis of bromo(*o*-tolyl)bis(triphenylphosphine)nickel(II) (3b) S5
Synthesis of bromo(2-(4-((tert-butyldimethylsilyloxy)methyl)-2-methylphenyl))bis(triphenylphosphine)nickel(II) (3c) S5
Synthesis of bromo(2-methyl-4-((trimethylsilyl)ethynyl)phenyl)bis(triphenylphosphine)nickel(II) (3d) S6
Synthesis of 2-bromo-3-hexyl-5-iodothiophene (4) S6
Synthesis of the polymers S6
Synthesis of P1 ..... S6
Synthesis of P2 ..... S7
Synthesis of P3 ..... S7
Synthesis of P4 ..... S7
Synthesis of P5 ..... S7
Synthesis of P6 ..... S7
Synthesis of P7 ..... S7
Synthesis of P8 ..... S8
Synthesis of P9 ..... S8

NMR spectra of initiators and monomers S9
^{1}H-NMR of 2a S9
^{1}H-NMR of 2c S9
^{13}C-NMR of 2c S10
^{1}H-NMR of 2d S10
^{13}C-NMR of 2d S11
^{1}H-NMR of decomposition of 3a S11
^{1}H-NMR of 3b S12
^{31}P-NMR of 3b S13
^{1}H-NMR of 3c S13
^{31}P-NMR of 3c S14
^{1}H-NMR of 3d S14
^{31}P-NMR of 3d S15
^{1}H-NMR of 4 ..... S15
NMR spectra of polymers S16
^{1}H-NMR of P1 ..... S16
1H-NMR of P2 ..... S16
^{1}H-NMR of P3 ..... S17
^{1}H-NMR of P4 ..... S17
^{1}H-NMR of P5 ..... S18
^{1}H-NMR of P6 ..... S18
^{1}H-NMR of P7 ..... S19
^{1}H-NMR of P8 ..... S19
1H-NMR of P9 ..... S20
MALDI-ToF spectra of polymers S21
MALDI-ToF of P1 ..... S21
MALDI-ToF of P2 ..... S22
MALDI-ToF of P3 ..... S23
MALDI-ToF of P4 ..... S24
MALDI-ToF of P5 ..... S25
MALDI-ToF of P6 ..... S26
MALDI-ToF comparison of P1, P5 and P6 ..... S27
MALDI-ToF of P7 ..... S27
MALDI-ToF of P8 ..... S28
MALDI-ToF of P9 ..... S29

General

All reagents were purchased from Sigma-Aldrich, Acros Organics, Merck, Fluka and Alfa Aesar. ^{1}H nuclear magnetic resonance (NMR) measurements were carried out with Bruker Avance 300 MHz, Bruker Avance 400 MHz and Bruker Avance II 600 MHz. Reagent grade solvents were dried and purified by distillation. *i*PrMgCl and *i*PrMgCl.LiCl were titrated before use with salicylaldehyde phenylhydrazone[1] in order to determine their exact concentration. 2-bromo-3-hexylthiophene[2], 5-bromo-2-bromomagnesio-3-(*S*)-3,7-dimethyloctylthiothiophene[3], 5-bromo-2-bromomagnesio-3-(*S*)-3,7-dimethyloctyloxythiophene[4] and 1-bromo-5-iodo-2,4-dioctyloxybenzene[5] were prepared according to literature procedures. MALDI mass spectra were recorded using

our Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analysis were performed in the reflectron mode at a resolution of about 10 000. The matrix, trans-2-[3-(4-*t*-Butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was prepared as 20 mg/mL solution in chloroform. The matrix solution (1 µL) was applied to a stainless steel target and air dried. Polymer samples were dissolved in chloroform to obtain 1mg/mL solutions. 1µL aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and then air dried.

Synthesis of tetrakistriphenylphosphinenickel(0)

$NiCl_2.6H_2O$ (9.51 g, 40.0 mmol) and PPh_3 (48.3 g, 184 mmol) were dissolved in ethanol (250 mL) and allowed to react for 30 minutes under reflux. The resulting dark green solution was allowed to cool to room temperature, after which zinc powder (3.92 g, 60.0 mmol) was added under a flow of argon. The mixture was then heated to reflux for two hours, during which a dark red precipitate was formed. After cooling to room temperature, the product was filtered and washed successively with ethanol (2x100 mL) and finally with diethylether (100 mL). The product was then dissolved in THF (500 mL) and precipitated in ice-cooled ethanol (1 L). Filtration under argon atmosphere yielded a dark purple, extremely air sensitive powder which was stored under N_2 atmosphere.
Yield: 23.2 g (53%)

Synthesis of 4-bromo-3-methylbenzylalcohol (2a)

A solution of methyl 4-bromo-3-methylbenzoate (4.58 g, 20.0 mmol) in dry THF (100 mL) was cannulated to an ice-cooled suspension of $LiAlH_4$ (0.759 g, 20.0 mmol) in dry THF (20 mL). The reaction was maintained at 0 ºC for 30 minutes and was then allowed to warm to room temperature. After completion of the reaction (TLC-monitoring, SiO_2, EtOAc/hexane (50/50)), water was carefully added and after addition of NH_4Cl, the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, and after filtration, the solvent was removed using rotary evaporation. This afforded white crystals, which were used without further purification.
Yield: 3.12 g (78%)
^{1}H-NMR: (300 MHz, CD_2Cl_2): 7.49 (1H, d, 7.8 Hz), 7.31 (1H, s), 7.11 (1H, d, 7.8 Hz), 4.57 (2H, d), 4.27 (1H, t), 2.36 (3H, s)
mp: 32.5-34.7 °C (lit: 31-32°C)[6]

1-bromo-2-methyl-4-[[[(t-butyl)dimethylsilyl]oxy]methyl]benzene (2c)

4-bromo-3-methylbenzylalcohol (1.01 g, 5.00 mmol) and imidazole (0.904 g, 6.00 mmol) were dissolved in dry DMF (50 mL), after which a solution of *tert*-butyldimethylsilyl

chloride in dry DMF (50 mL) was added. After completion of the reaction (TLC-monitoring, SiO_2, EtOAc/hexane (50/50)), water was added and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, and after filtration, the solvent was removed using rotary evaporation. The product was isolated as a white solid and used without further purification.
Yield: 1.38 g (87%)
mp: 130-143 °C
^{1}H-NMR: (300 MHz, CD_2Cl_2): 7.51 (1H, d, 7.8 Hz), 7.29 (1H, s), 7.11 (1H, d, 7.8 Hz), 4.71 (2H, s), 2.37 (3H, s), 0.93 (9H, s), 0.11 (6H, s)
^{13}C-NMR (75 MHz, CD_2Cl_2): 141.58, 138.26, 132.71, 129.27, 125.86, 123.61, 65.00, 26.50, 23.51, 19.03, -4.73
MS: 315 (M^+), 299 (M^+ -CH_3), 259 (M^+ -$C(CH_3)_3$), 183 (M^+ -TBDMS -CH_3)

Synthesis of 1-bromo-2-methyl-4-[2-(trimethylsilyl)ethynyl]benzene (2d)

$Pd(PPh_3)Cl_2$ (0.227 g, 0.36 mmol), CuI (22.9 mg, 0.120 mmol) and 2-bromo-5-iodotoluene (3.56 g, 12.0 mmol) were weighed in a flask and flushed with argon. Then, a solution of trimethylsilylacetylene (1.28 g, 13.0 mmol) in THF (45 mL) and Et_3N (45 mL) was cannulated into the flask. After completion of the reaction (TLC-monitoring, SiO_2, petroleum ether), water was added and the aqueous layer was extracted with petroleum ether. The combined organic layers were dried using $MgSO_4$, and after filtration, the solvents were removed using rotary evaporation. After having passed through a short column (SiO_2, petroleum ether), the product was isolated as a pale-yellow oil.
Yield: 3.11 g (97%)
^{1}H-NMR: (300 MHz, CD_2Cl_2): 7.46 (1H, d, 8.7 Hz), 7.33 (1H, s), 7.12 (1H, d, 8.7 Hz), 2.35 (3H, s), 0.23 (9H, s)
^{13}C-NMR: (75 MHz, CD_2Cl_2): 138.75, 134.48, 132.81, 131.04, 125.83, 122.85, 104.44, 95.55, 74.56, 23.02, 0.07
MS: 267 (M^+), 253 (M^+ -CH_3)

Synthesis of bromo(phenyl)bis(triphenylphosphine)nickel(II) (3a)

A solution of 2-bromobenzene (0.149 g, 0.950 mmol) in toluene (3.5 mL) was purged with argon and cannulated into a flask containing $Ni(PPh_3)_4$ (0.222 g, 0.200 mmol). The resulting mixture was stirred for 15 minutes and allowed to stand overnight, after which the crude product was dissolved in the smallest possible amount of toluene and immediately precipitated in *n*-hexane. After washing with *n*-hexane (100 mL), methanol (25 mL) and finally *i*PrOH (50 mL), the product was dried under vacuum to afford a yellow, air-stable powder.
Yield: 0.136 g (92%)

Analysis of decomposition of 3a

3a (0.129 g, 0.174 mmol) was dissolved under stirring in toluene (25 mL), during which the solution gradually lost its yellow color and a white; flocky precipitate formed. This reaction was allowed to proceed overnight, after which the toluene solution was filtered and concentrated in vacuo. The resulting product was purified using column chromatography (SiO_2, *n*-hexane/CH_2Cl_2 (8:2)) and found to consist of mainly biphenyl and PPh_3. A standard gravimetrical test for Ni^{2+}, using 40% NH_3 and dimethylglyoxime 1% in ethanol proved that the residue which was insoluble in toluene contained Ni^{2+}.

Synthesis of bromo-(o-tolyl)bis(triphenylphosphine)nickel(II) (3b)

A solution of 2-bromotoluene (0.513 g, 3.00 mmol) in toluene (25 mL) was purged with argon and cannulated into a flask containing $Ni(PPh_3)_4$ (2.21 g, 2.00 mmol). The reaction was allowed to proceed overnight, after which toluene (100 mL) was added and the resulting solution was filtered. The filtrate was then concentrated through rotary evaporation and the crude product was precipitated in *n*-hexane. After washing with pentane (100 mL), methanol (25 mL) and finally *i*PrOH (50 mL), the product was dried under vacuum to afford a yellow, air-stable powder.
Yield: 1.37 g (91%)
^{1}H-NMR: (300 Mhz, CD_2Cl_2): 7.50 (12H, m), 7.34 (6H, t), 7.24 (12H, t), 7.15 (1H, d, 7.4 Hz), 6.27 (2H, m), 5.90 (1H, d, 7.4 Hz), 2.06 (3H, s)
^{31}P-NMR: (162 MHz, CD_2Cl_2): 22.5 ppm vs H_3PO_4
mp: decomposes at 174°C

Synthesis of bromo-[2-methyl-2-[(tert-butyldimethylsilyloxy)-methyl]phenyl]bis(triphenylphosphine)nickel(II) (3c)

The synthesis is analogous to that of **3b**, using $Ni(PPh_3)_4$ (2.21 g, 2.00 mmol) and **2c** (0.631 g, 2.00 mmol).
Yield: 0.719 g (40%)
^{1}H-NMR: (300 MHz, CD_2Cl_2): 7.49 (12H, m), 7.32 (6H, m), 7.24 (8H, t), 7.06 (1H, d, 8.1 Hz), 6.26 (1H, d, 8.1 Hz), 5.90 (1H, s), 4.28 (2H, s), 2.02 (2H, s), 0.89 (9H, s), 0.04 (6H, s)
^{31}P-NMR: (162 MHz, CD_2Cl_2): 22.4 ppm vs H_3PO_4
mp: decomposes at 135°C

Synthesis of bromo-[2-methyl-4-[(trimethylsilyl)ethynyl]phenyl]bis(triphenylphosphine)nickel(II) (3d)

The synthesis is analogous to that of **3b**, using $Ni(PPh_3)_4$ (2.21 g, 2.00 mmol) and **2d** (0.802 g, 3.00 mmol).
Yield: 0.425 g (25%)
^{1}H-NMR: (300 MHz, CD_2Cl_2): 7.51 (12H, m), 7.38 (6H, t), 7.27 (12H, t), 7.08 (1H, dd, 21.0 Hz, 7.8 Hz), 6.32 (1H, m), 5.99 (1H, s), 2.06 (3H, s), 0.16 (9H, s)
^{31}P-NMR: (162 MHz, CD_2Cl_2): 22.3 ppm vs H_3PO_4
mp: decomposes at 183°C

Synthesis of 2-bromo-3-hexyl-5-iodothiophene (4)

2-bromo-3-hexylthiophene (30.9 g, 125 mmol) was dissolved in a mixture of $CHCl_3$ (120 mL) and acetic acid (60 mL) and shielded from light. Then, *N*-iodosuccinimide (38.3 g, 170 mmol) was added and the reaction was allowed to proceed overnight. The solution was then concentrated in vacuo, neutralized with $NaHCO_3$ and extracted with *n*-hexane. Next, the combined fractions were dried over $MgSO_4$ and the solvent was removed in vacuo. Finally, the product was then passed over a short column (SiO_2, petroleum ether) and distilled under vacuum (2 Torr, 135°C) to yield a yellow fluid.
Yield: 36.3 g (78%)
^{1}H-NMR: (300 MHz, $CDCl_3$): 6.96 (1H, s), 2.52 (2H, t), 1.54 (2H, m), 1.29 (6H, m), 0.89 (3H, t)
Lit: (105°C, 0.004 Torr)[7]

Synthesis of the polymers

Synthesis of P1

To a solution of 2-bromo-3-hexyl-5-iodothiophene (0.373 g, 1.00 mmol) in dry THF (15 mL) a solution of *i*PrMgCl in THF (0.530 mL, 1.05 mmol) was added and the mixture was allowed to react for 1h at room temperature. This solution was then cannulated to a solution containing **3b** (0.07 mmol) in dry THF (5 mL) The polymerization was then allowed to proceed for 2 hours, after which it was quenched with 1M HCl in THF. The polymer was precipitated in methanol (200 mL) and filtrated. After Soxhlet extractions using subsequently acetone and chloroform, the latter fraction, being the high-molecular weight fraction, was concentrated in vacuo and precipitated in methanol. Finally, filtration and drying under vacuum yielded a dark purple solid.
Yield: 84.7 mg (51%)

Synthesis of P2

A solution of **3b** (0.0226 g, 0.03 mmol) in dry THF (3 mL) was added via syringe to a solution of 5-bromo-2-bromomagnesio-3-(*S*)-3,7-dimethyloctyloxythiophene (0.254 g, 0.60 mmol) in dry THF (3 mL). The reaction was allowed to proceed at 0C for 3h after which it was quenched with HCl in MeOH. Finally, the polymer was precipitated in methanol, yielding a blue solid.
Yield: 96.6 mg (68%)

Synthesis of P3

The synthesis is analogous to that of **P2**, but using 5-bromo-2-bromomagnesio-3-(*S*)-3,7-dimethyloctylthiothiophene (0.263 g, 0.60 mmol). The polymer was isolated as a red solid.
Yield: 68.1 mg (45%)

Synthesis of P4

To a solution of 1-bromo-4-iodo-2,5-dioctyloxybenzene in dry THF (3 mL) *i*PrMgCl.LiCl (0.488 mL, 0.60 mmol) in THF was added via syringe. The reaction was allowed to proceed for 2h at room temperature after which the solution was transferred through cannula to a solution of **3b** (22.6 mg, 0.0300 mmol) and dppe (12.0 mg, 0.0300 mmol) in dry THF (3 mL). After 3h at room temperature the polymer was precipitated in methanol, filtrated and dried in vacuo to yield a yellow solid.
Yield: 49.0 mg (25%)

Synthesis of P5

The synthesis is analogous to that of **P1**, but with addition of dppp (29.0 mg, 0.0700 mmol) to the solution of **3b** prior to monomer addition.
Yield: 74.8 mg (45%)

Synthesis of P6

The synthesis is analogous to that of **P1**, but with addition of dppp (58 mg, 0.140 mmol) to the solution of **3b** prior to monomer addition.
Yield: 106 mg (64%)

Synthesis of P7

The synthesis is analogous to that of **P6**, using **3c** (62.9 mg, 0.0700 mmol) instead of **3b.**
Yield: 40.9 mg (25%)

Synthesis of P8

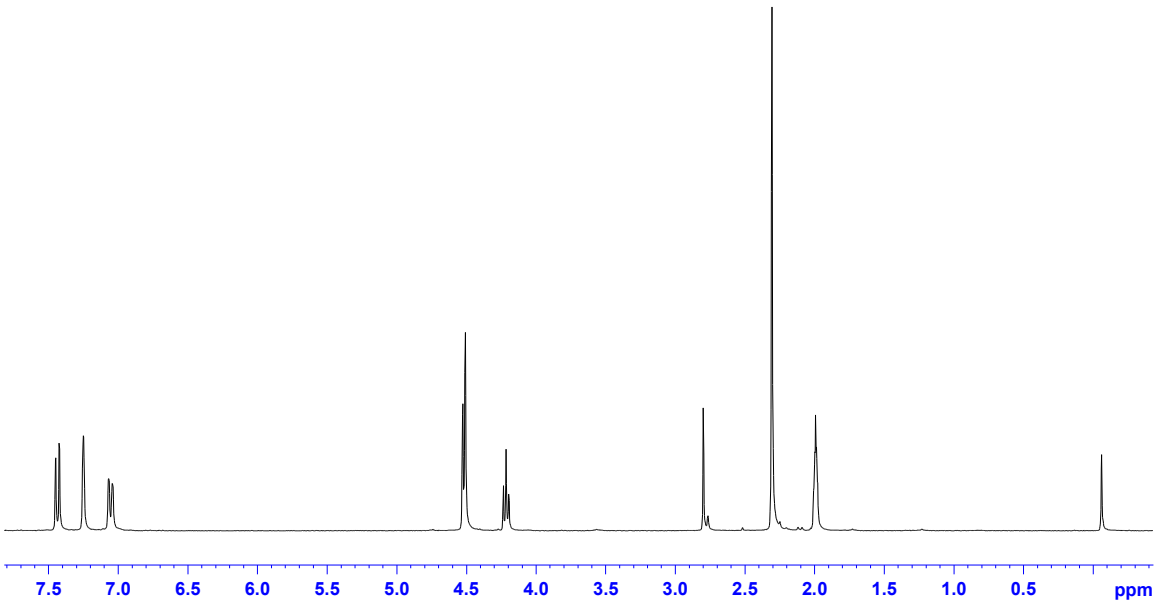
The synthesis is analogous to that of **P6**, using **3d** (59.5 mg, 0.0700 mmol) instead of **3b.**
Yield: 45.7 mg (28%)

Synthesis of P9

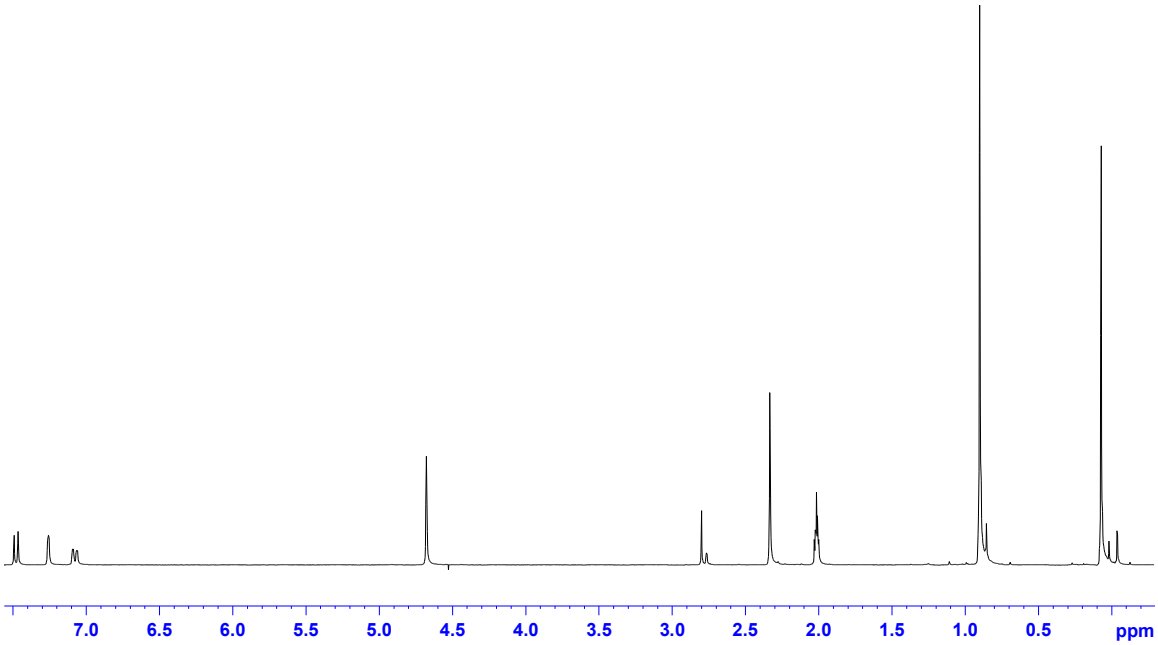
To a solution of 2-bromo-3-hexyl-5-iodothiophene (0.755 g, 2.00 mmol) in dry THF (25 mL) a solution of *i*PrMgCl in THF (1.10 mL, 2.10 mmol) was added and the mixture was allowed to react for 1h at room temperature. This solution was then cannulated to a solution containing **3b** (0.07 mmol) in dry THF (5 mL) and the polymerization was allowed to proceed for 30 min, after which one part of the mixture was quenched with HCl, while the other part was quenched with 4-chloromagnesio-anisol (1 mL, 1.00 mmol) in THF. The latter fraction was allowed to react for 30 min, after which the polymer was precipitated in methanol. After Soxhlet extractions using subsequently acetone and chloroform, the latter fraction, being the high-molecular weight fraction, was concentrated in vacuo and precipitated in methanol. Finally, filtration and drying under vacuum yielded a dark purple solid.
Yield: 27.5 mg (17%)

NMR spectra of initiators and monomers

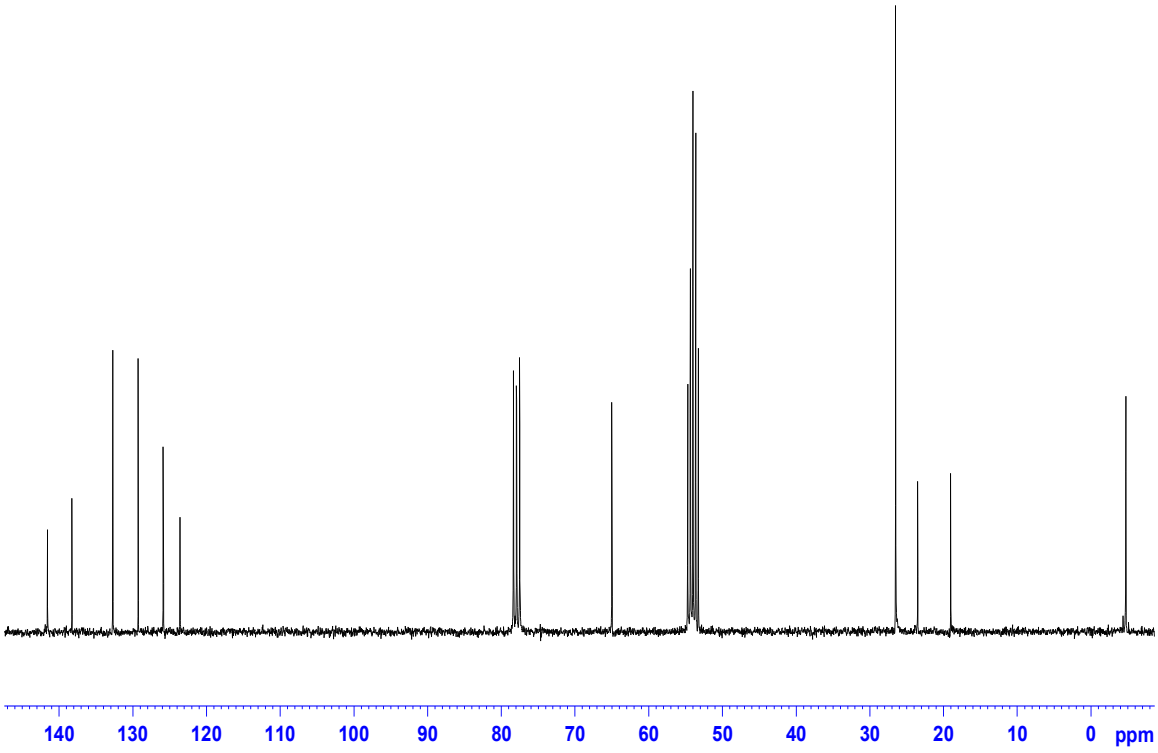
^{1}H-NMR of 2a



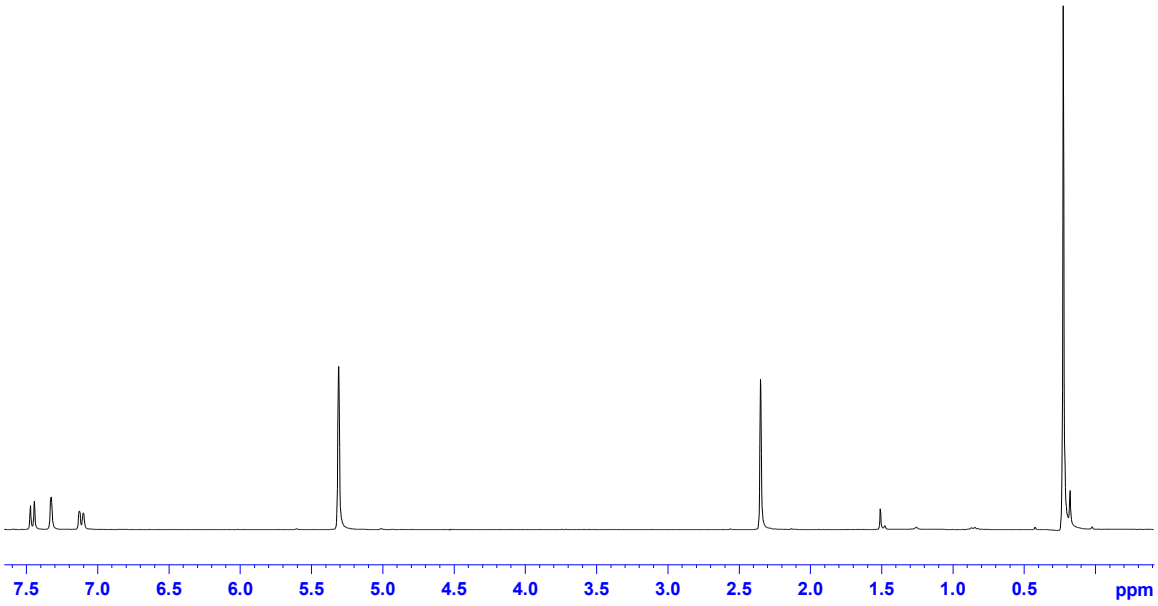
^{1}H-NMR of 2c



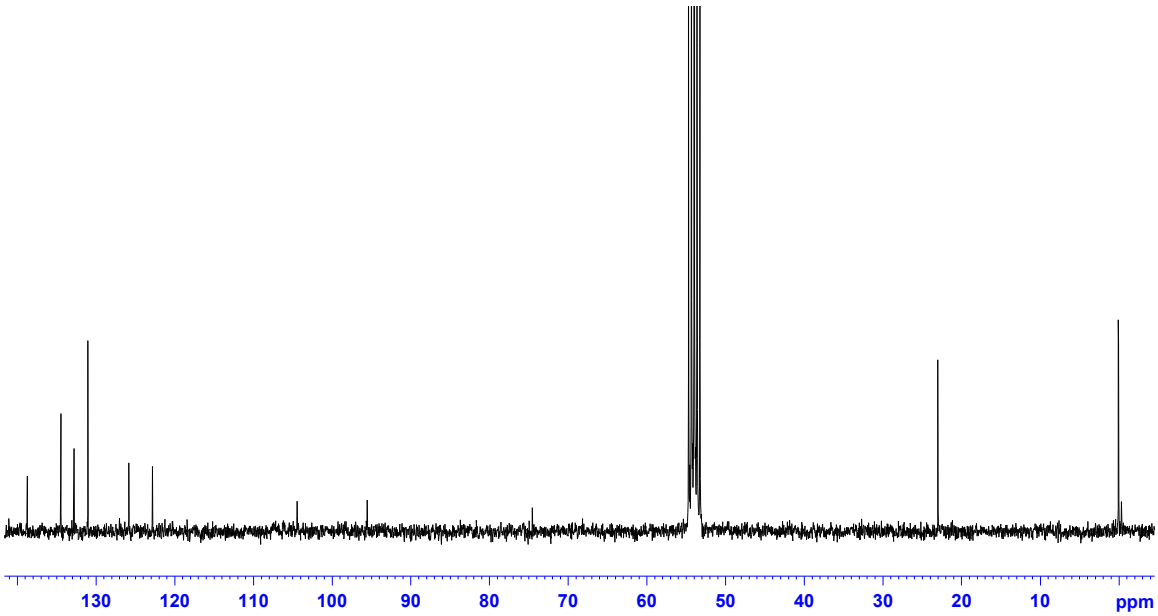
^{13}C-NMR of 2c



^{1}H-NMR of 2d

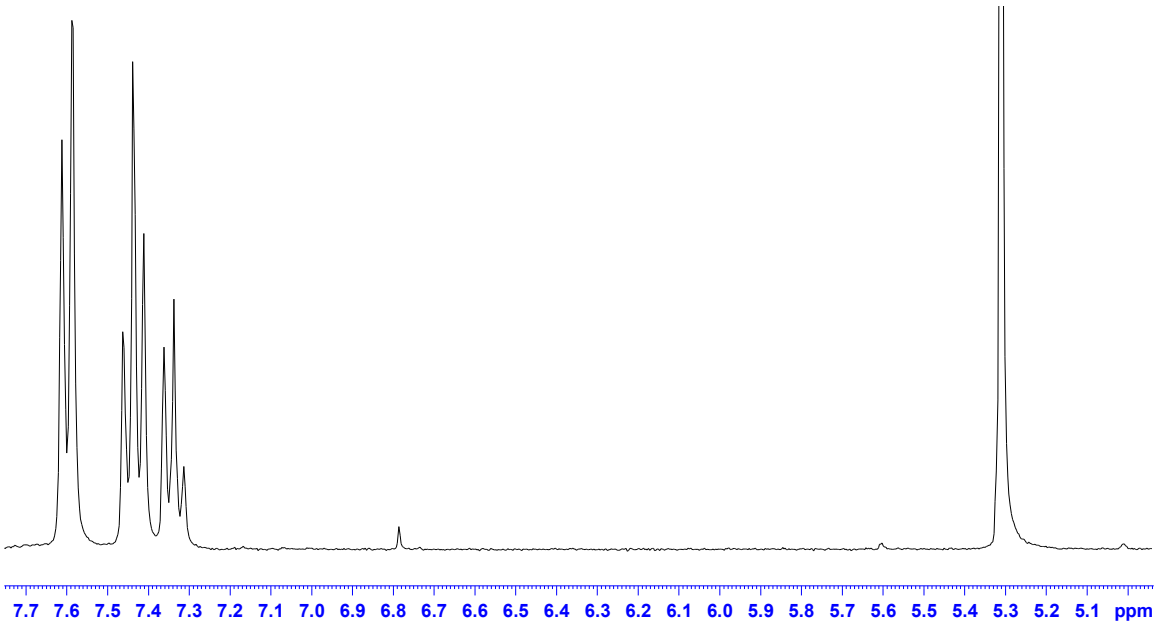


^{13}C-NMR of 2d

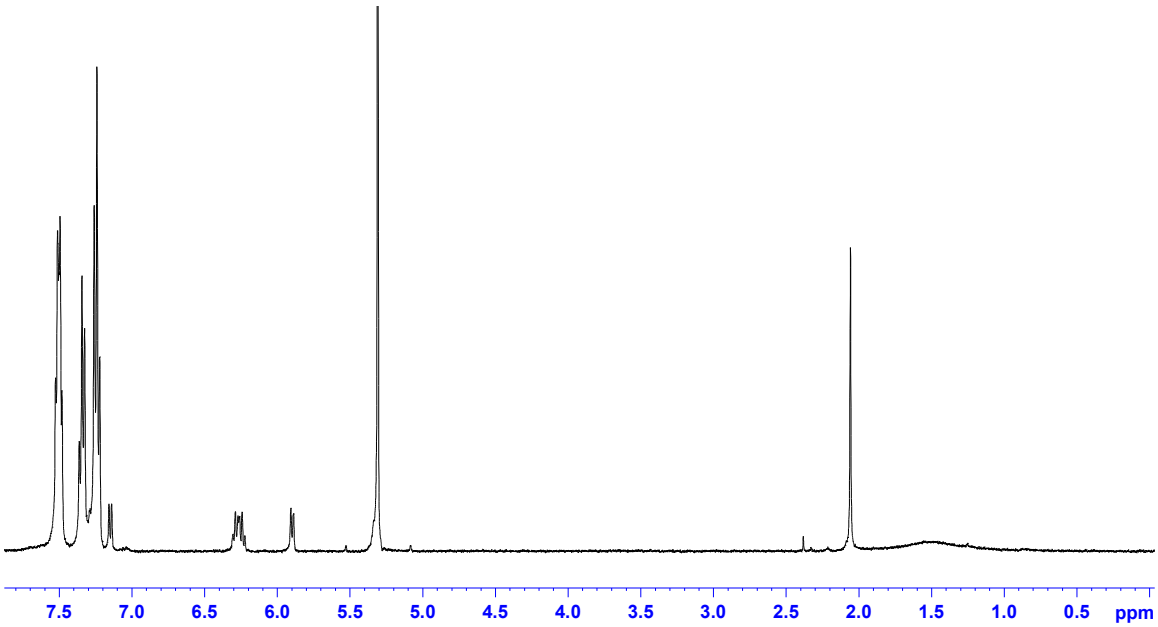


^{1}H-NMR of decomposition of 3a

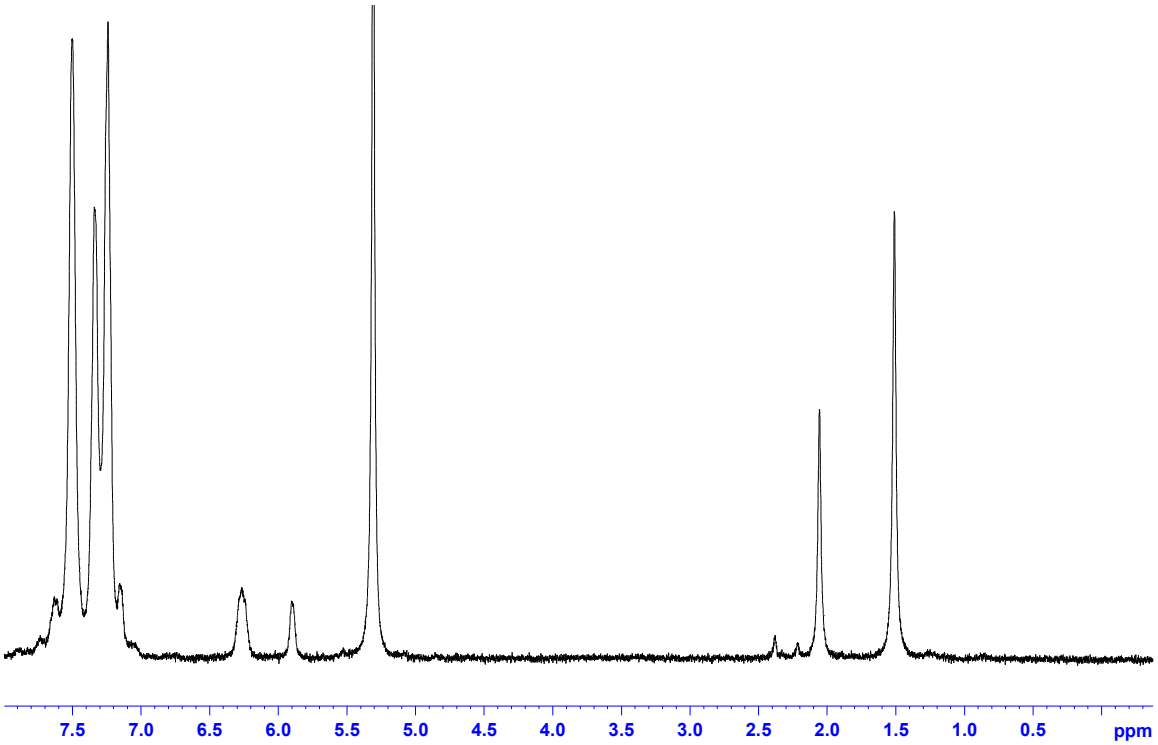
Biphenyl:



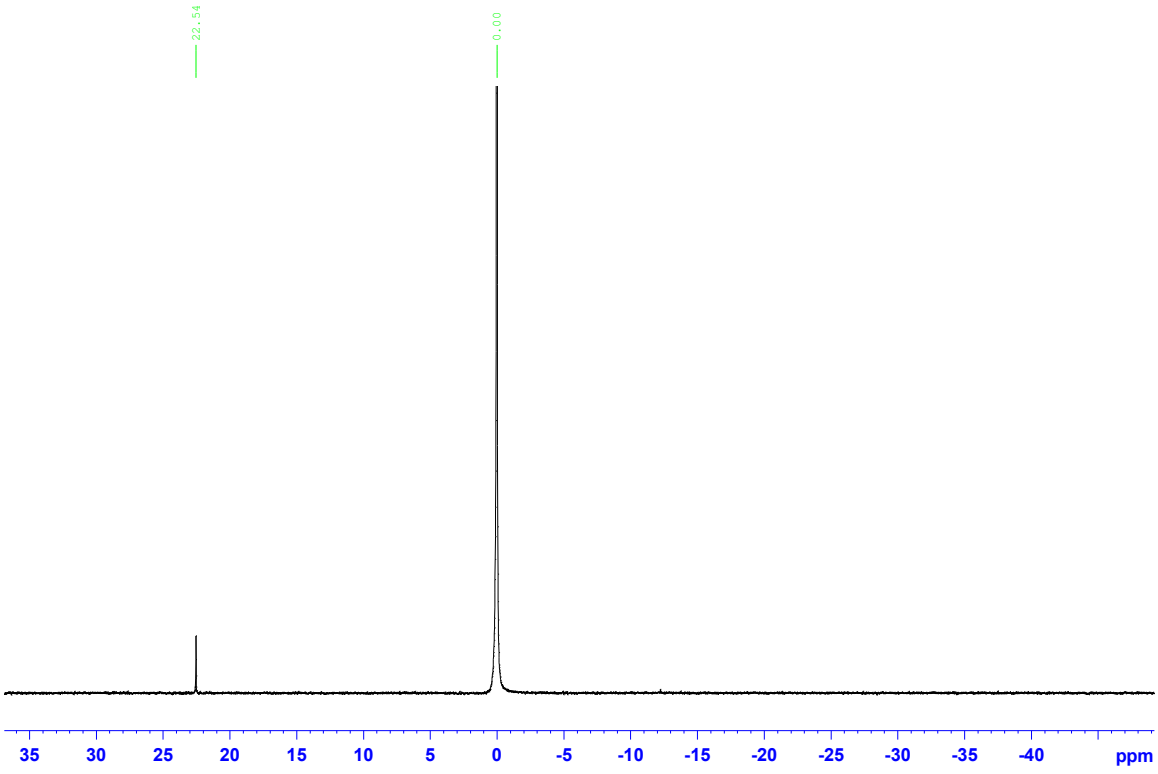
^{1}H-NMR of 3b



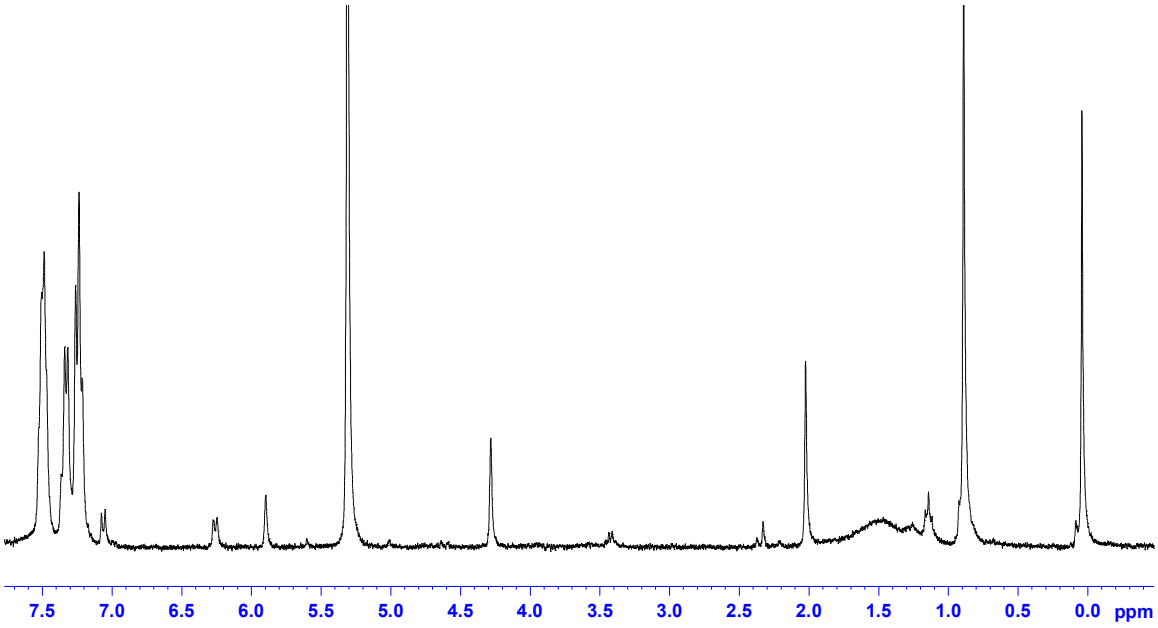
After 1 hour:



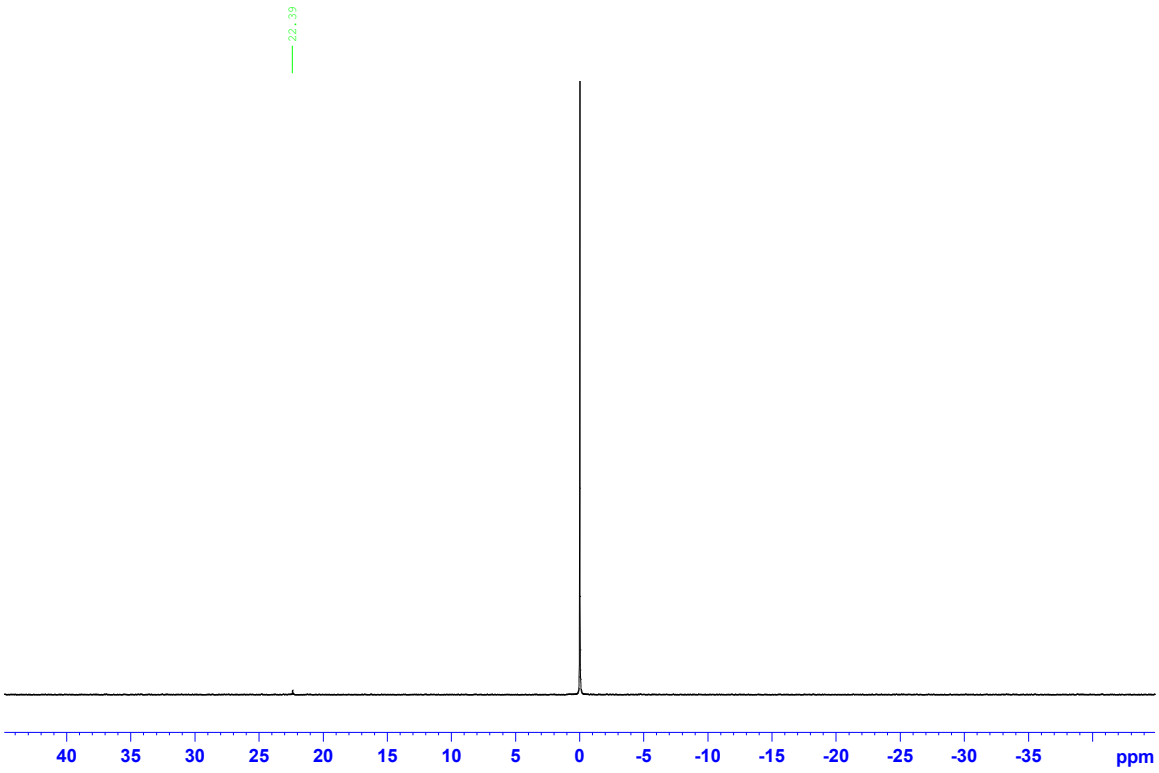
^{31}P-NMR of 3b



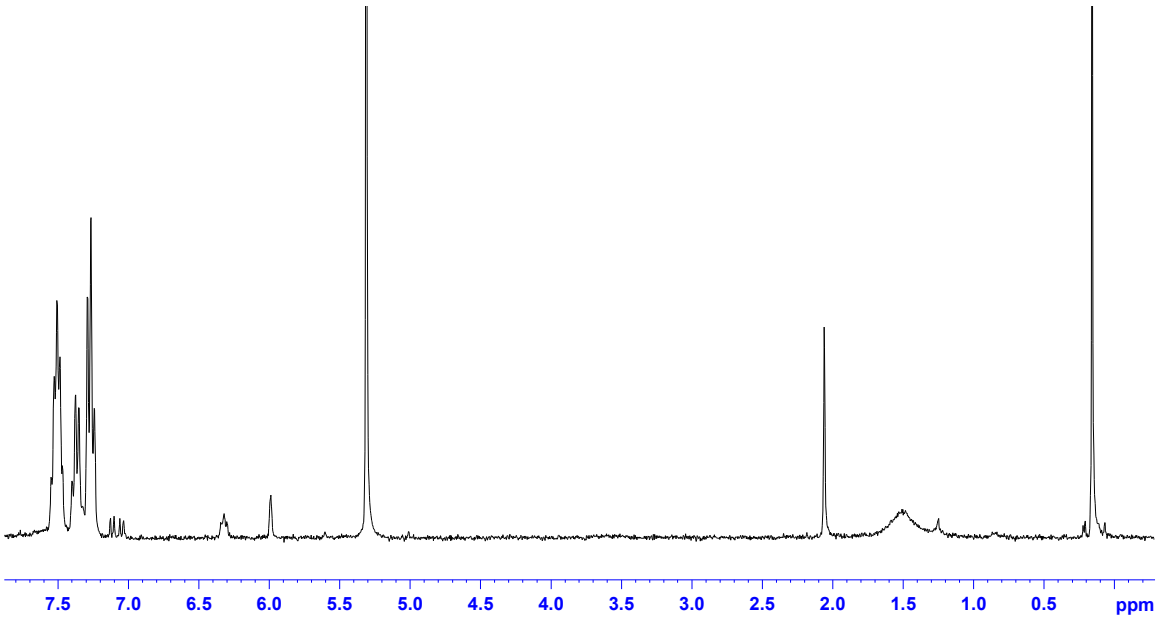
^{1}H-NMR of 3c



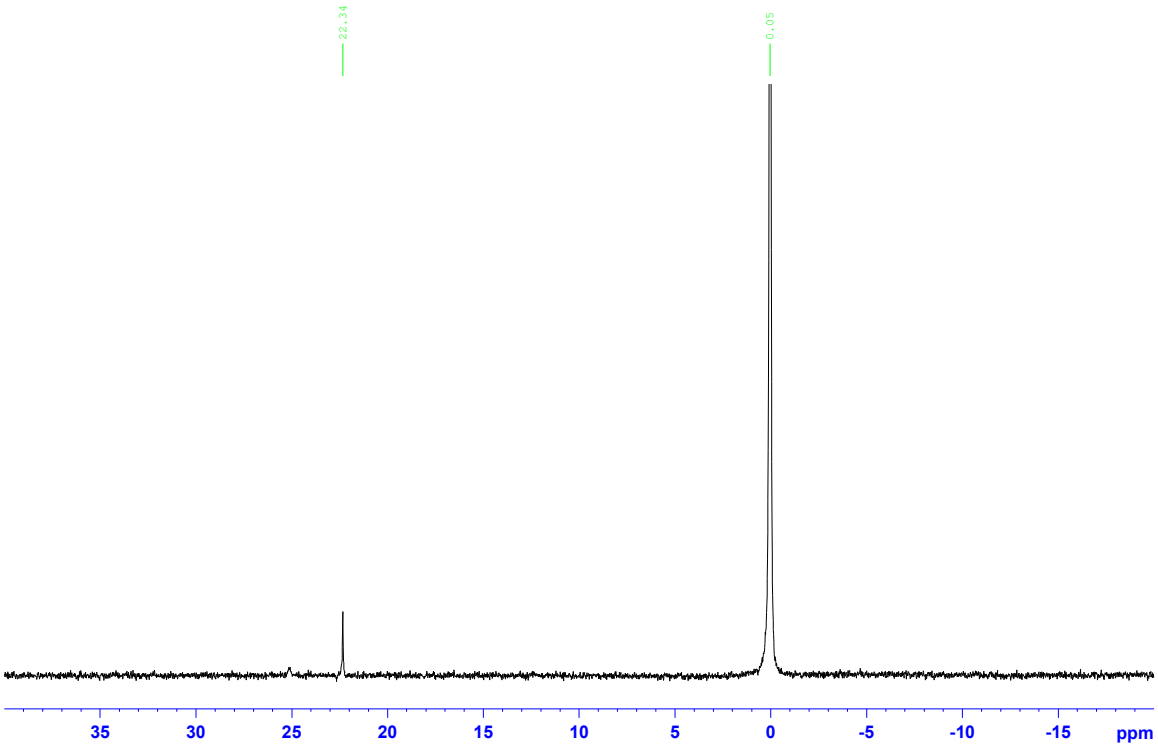
^{31}P-NMR of 3c



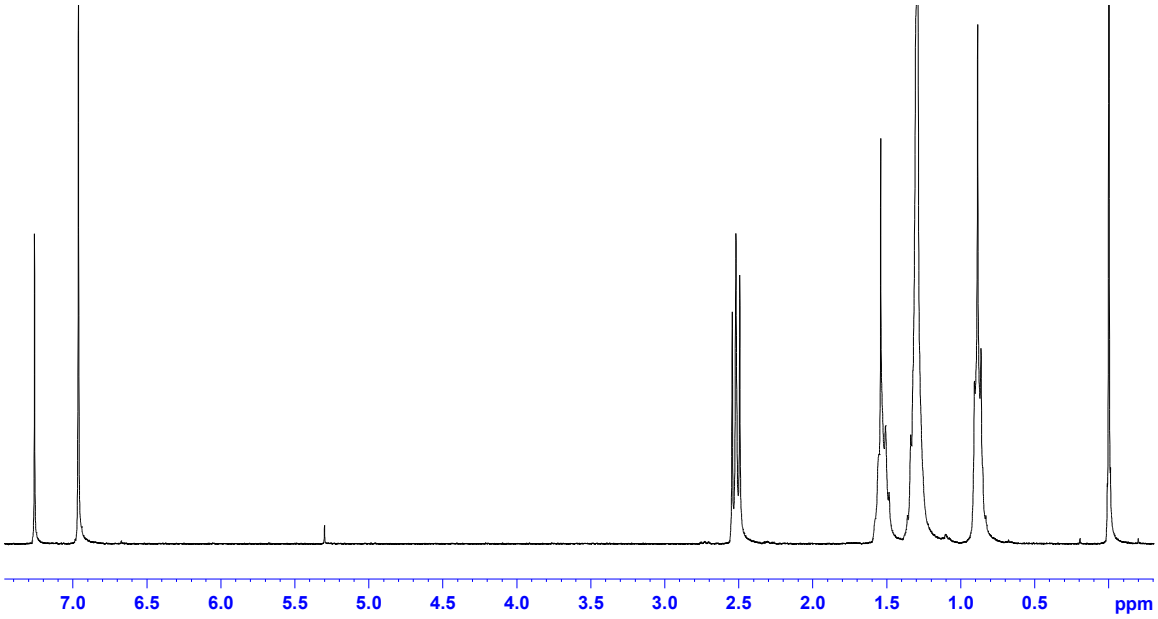
^{1}H-NMR of 3d



^{31}P-NMR of 3d

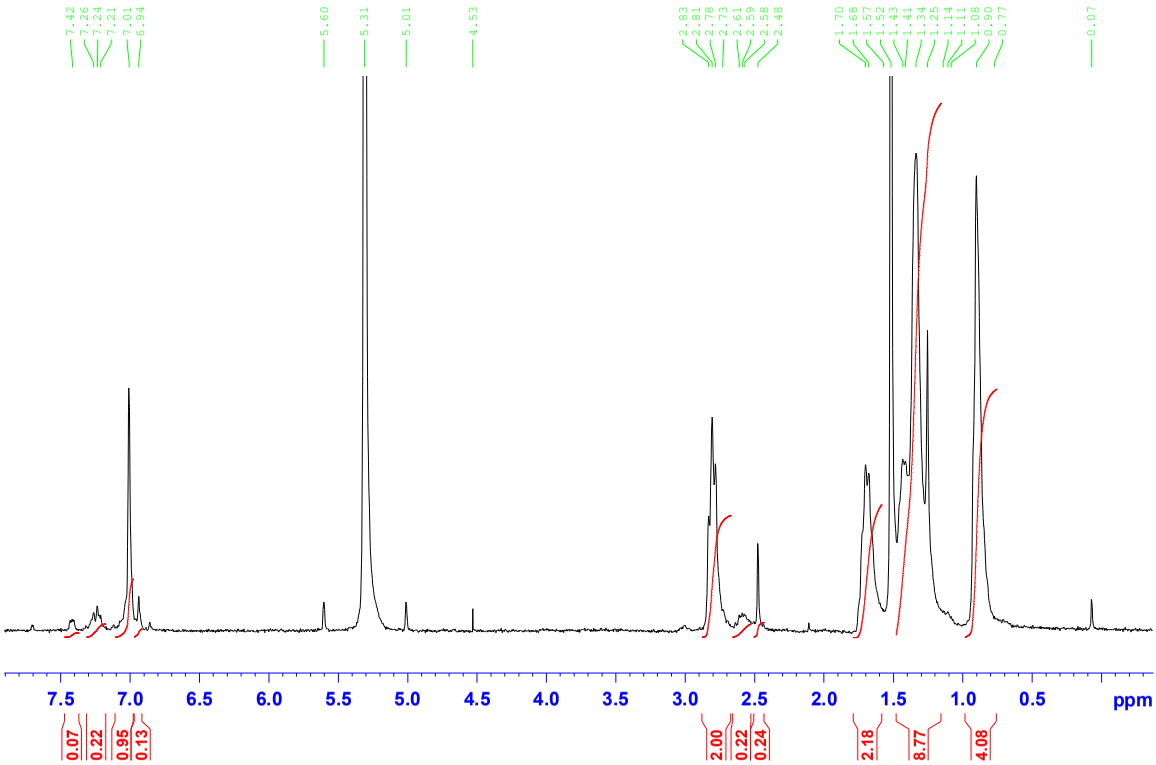


^{1}H-NMR of 4

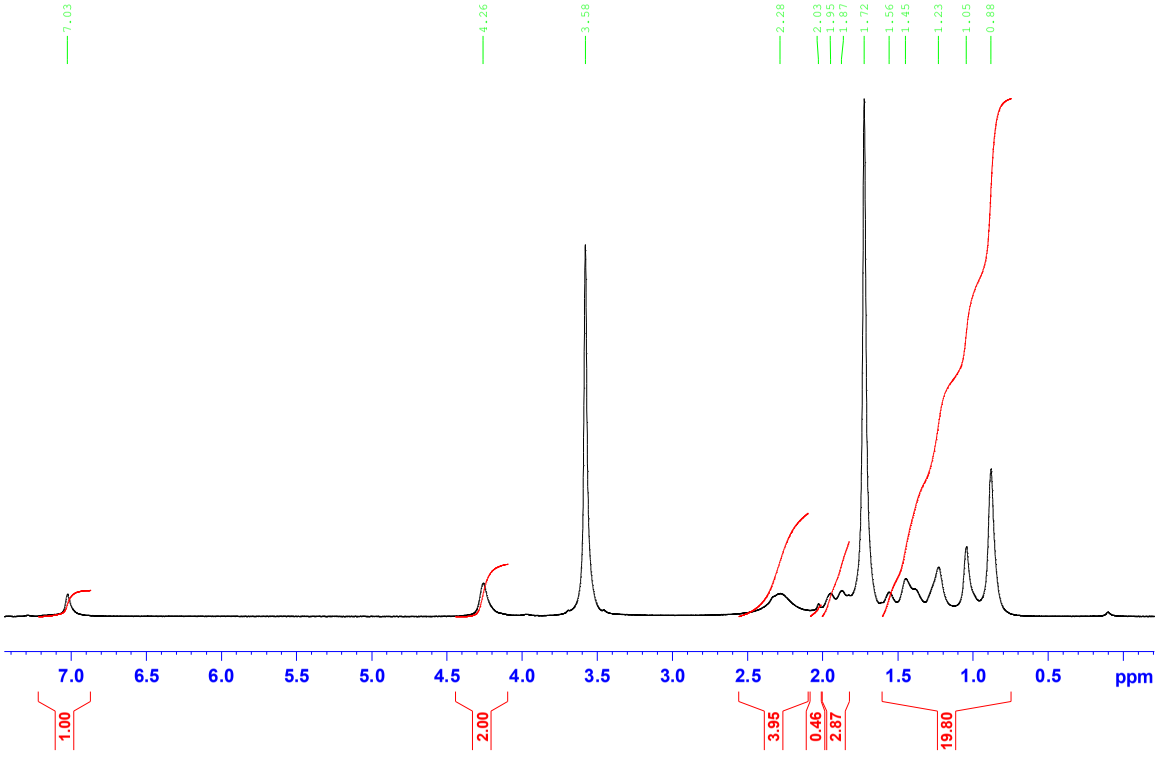


NMR spectra of polymers

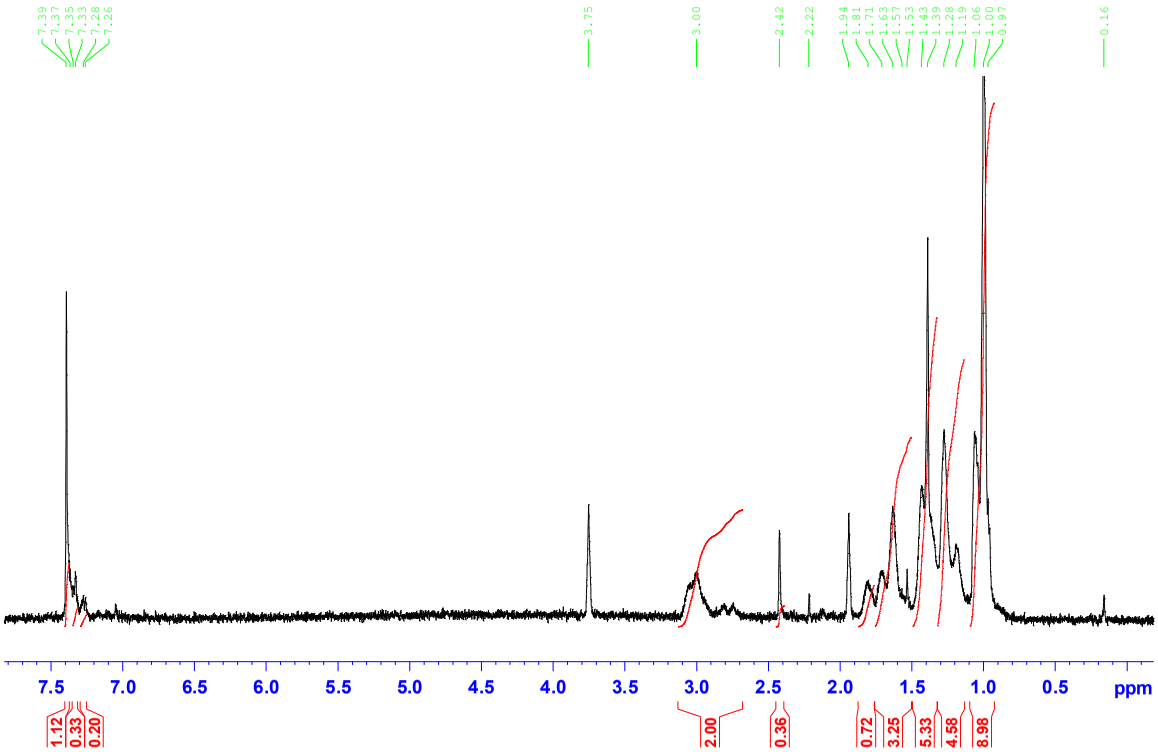
^{1}H-NMR of P1



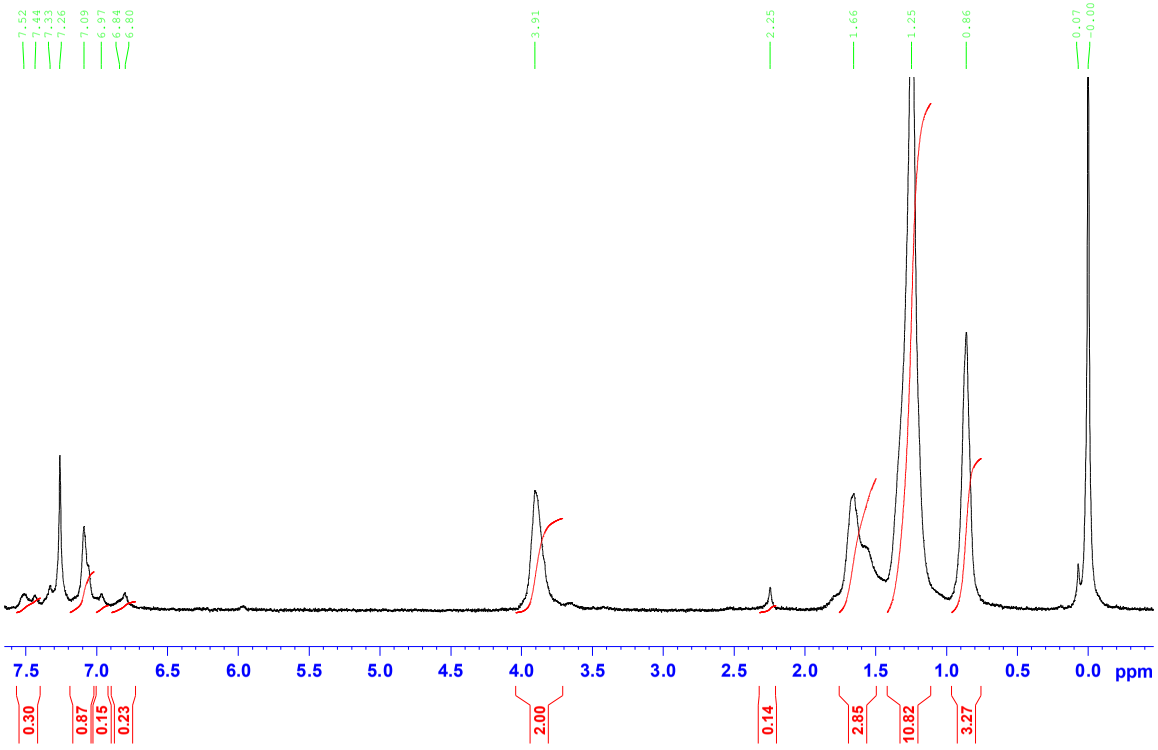
^{1}H-NMR of P2



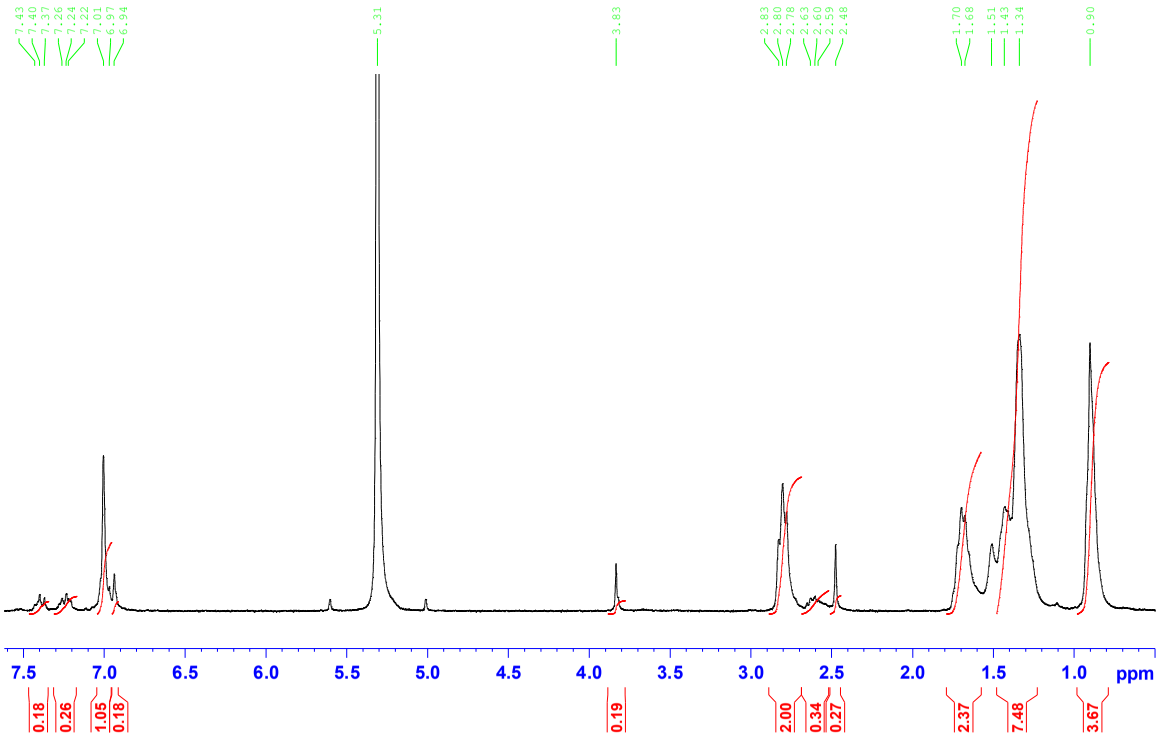
^{1}H-NMR of P3



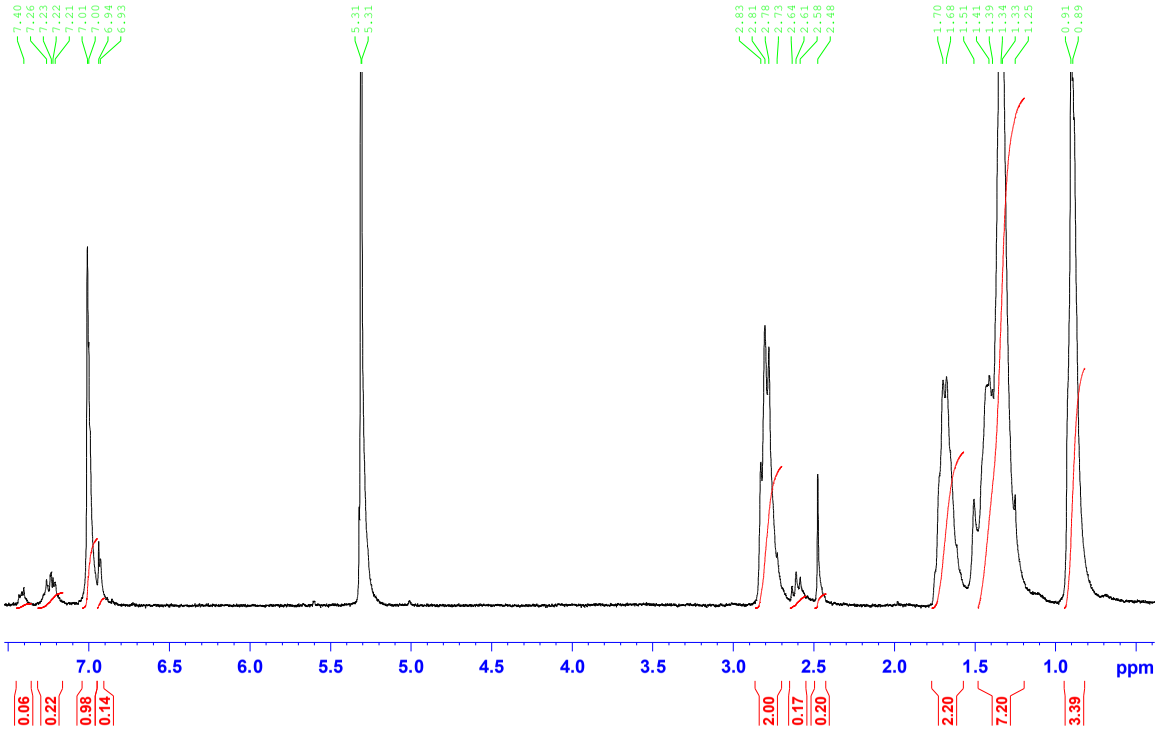
^{1}H-NMR of P4



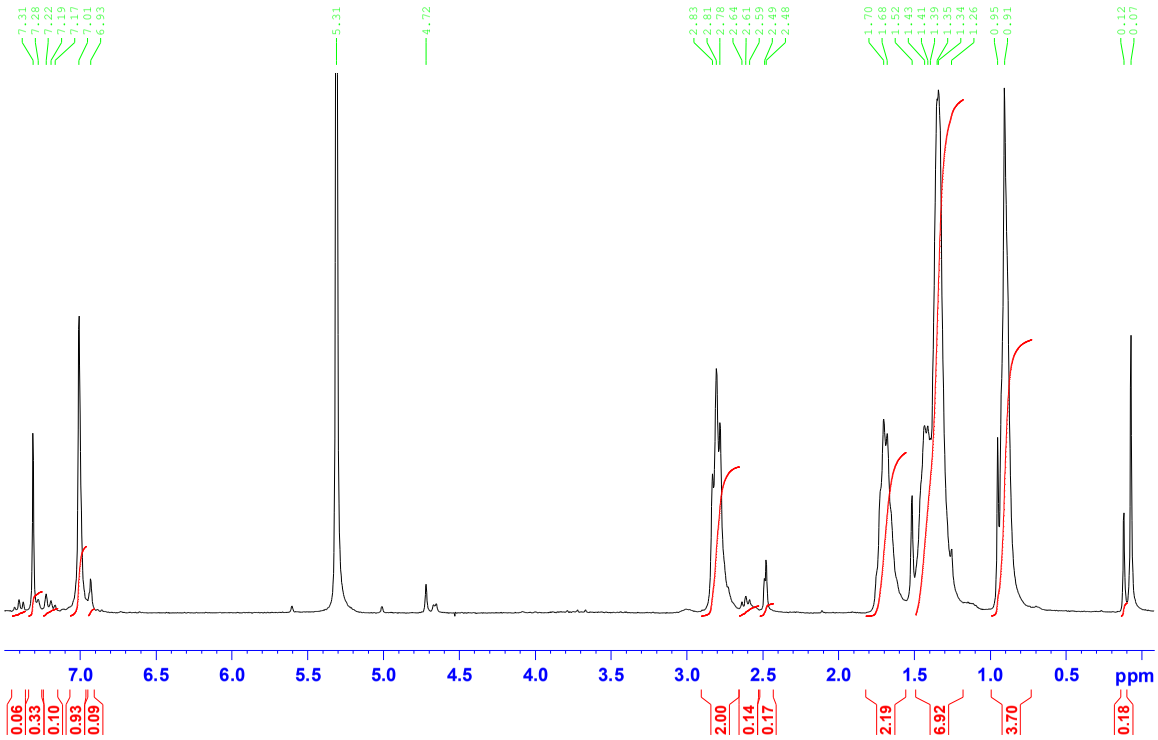
^{1}H-NMR of P5



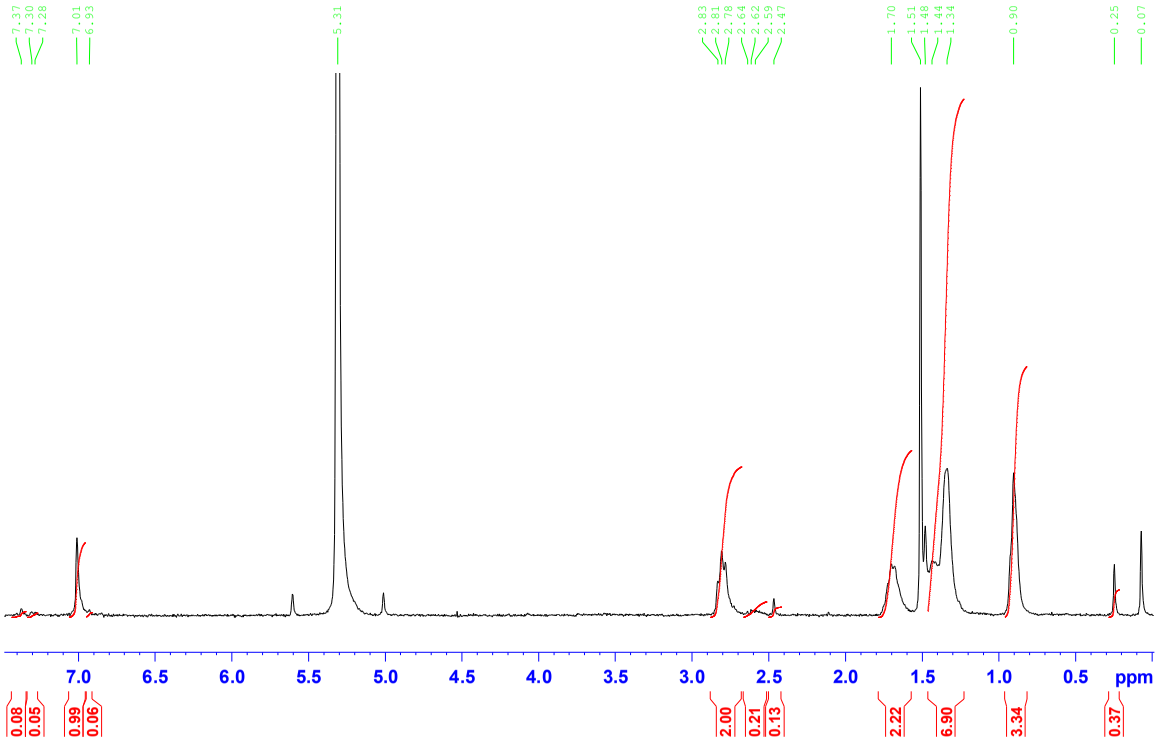
^{1}H-NMR of P6



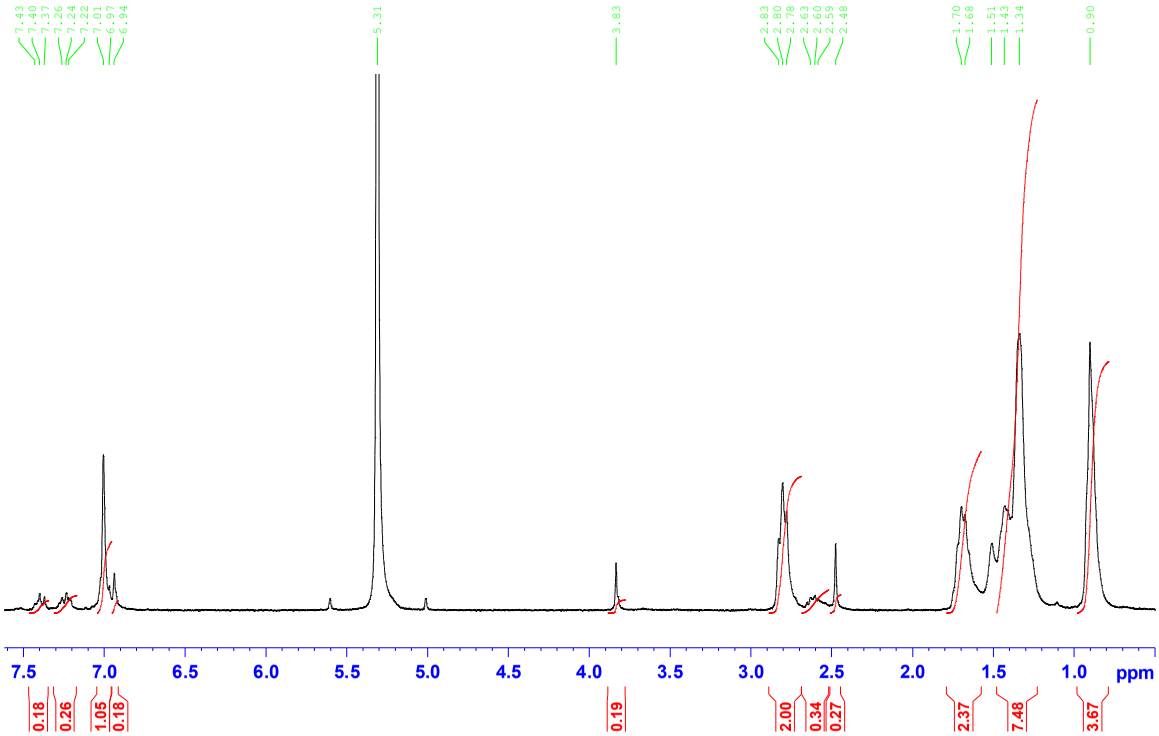
^{1}H-NMR of P7



^{1}H-NMR of P8



1H-NMR of P9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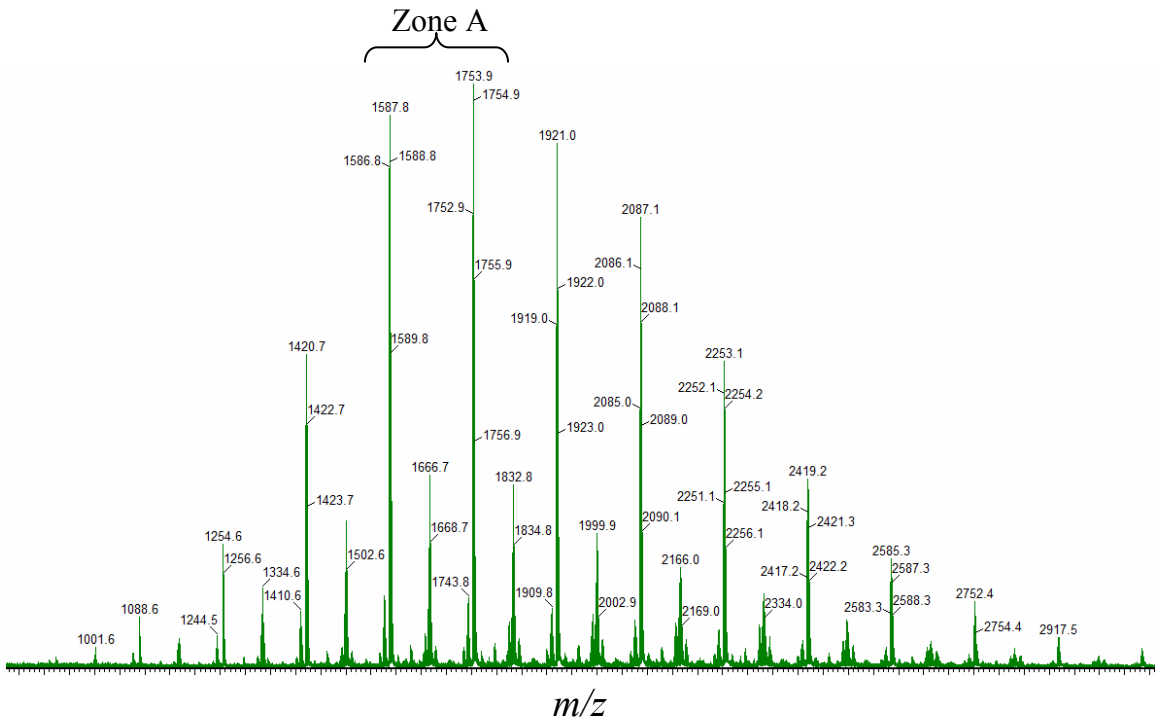
7.40
7.37
7.26
7.24
7.22
7.01
6.97
6.94
5.31
3.83
2.83
2.80
2.78
2.63
2.60
2.59
2.48
1.70
1.68
1.51
1.43
1.34
0.90
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.18
0.26
1.05
0.18
0.19
2.00
0.34
0.27
2.37
7.48
3.67

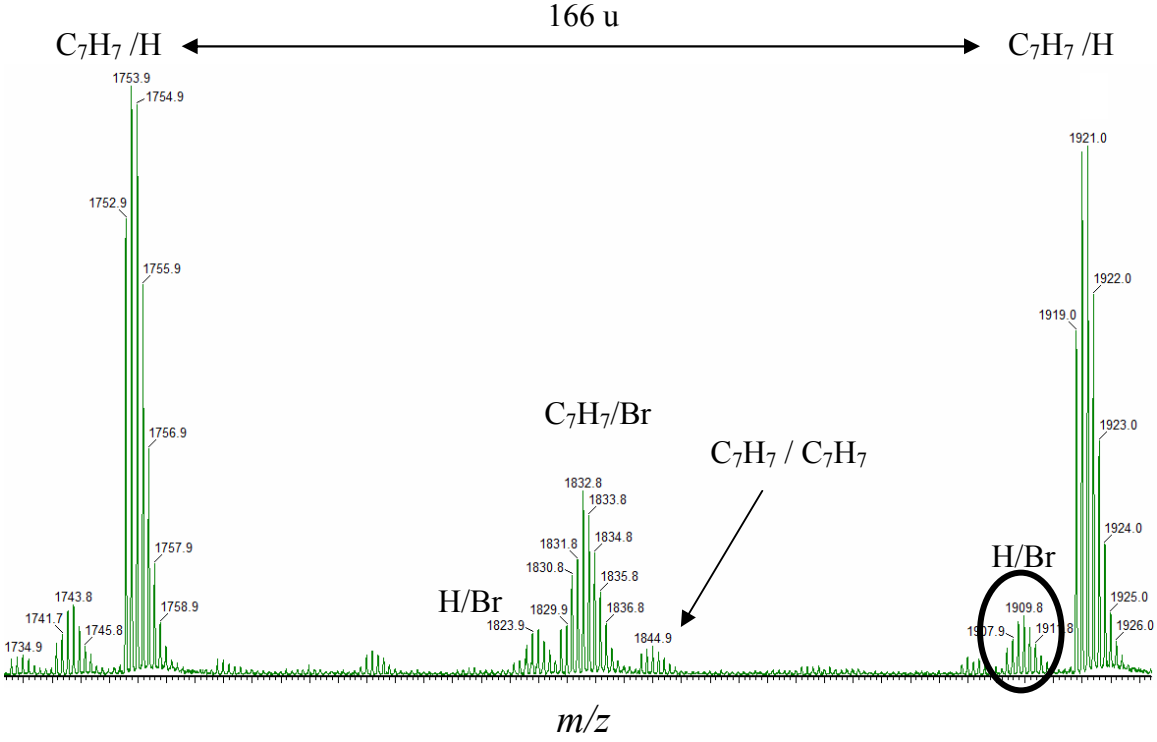
MALDI-ToF spectra of polymers

MALDI-ToF of P1

P1

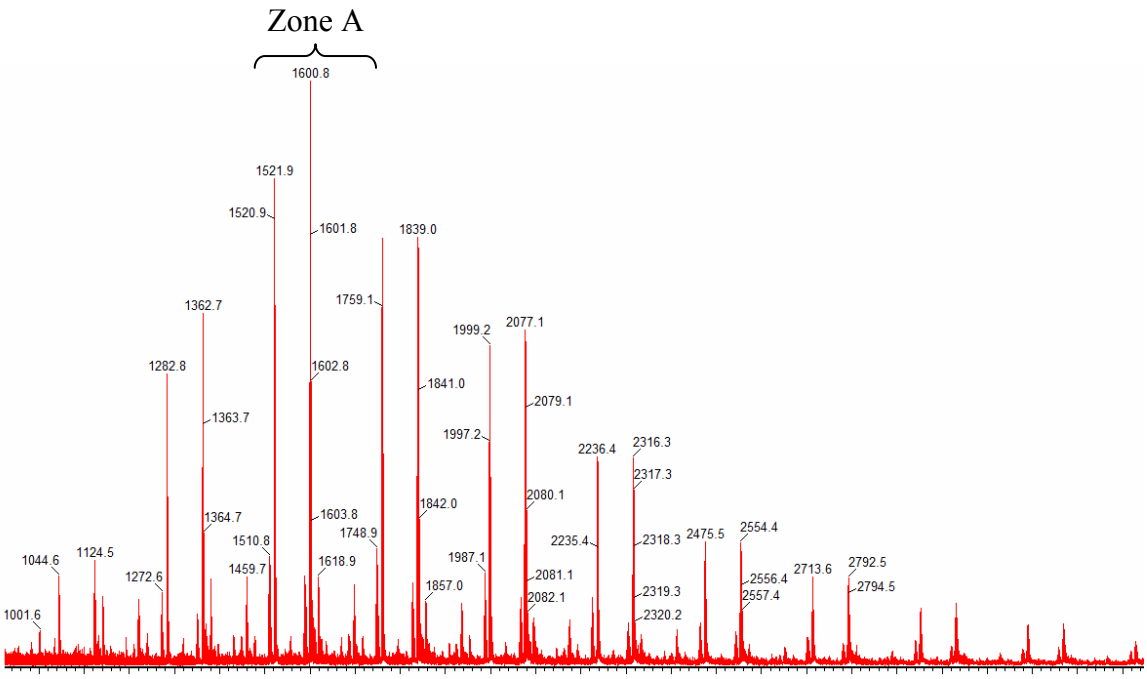


Zone A :

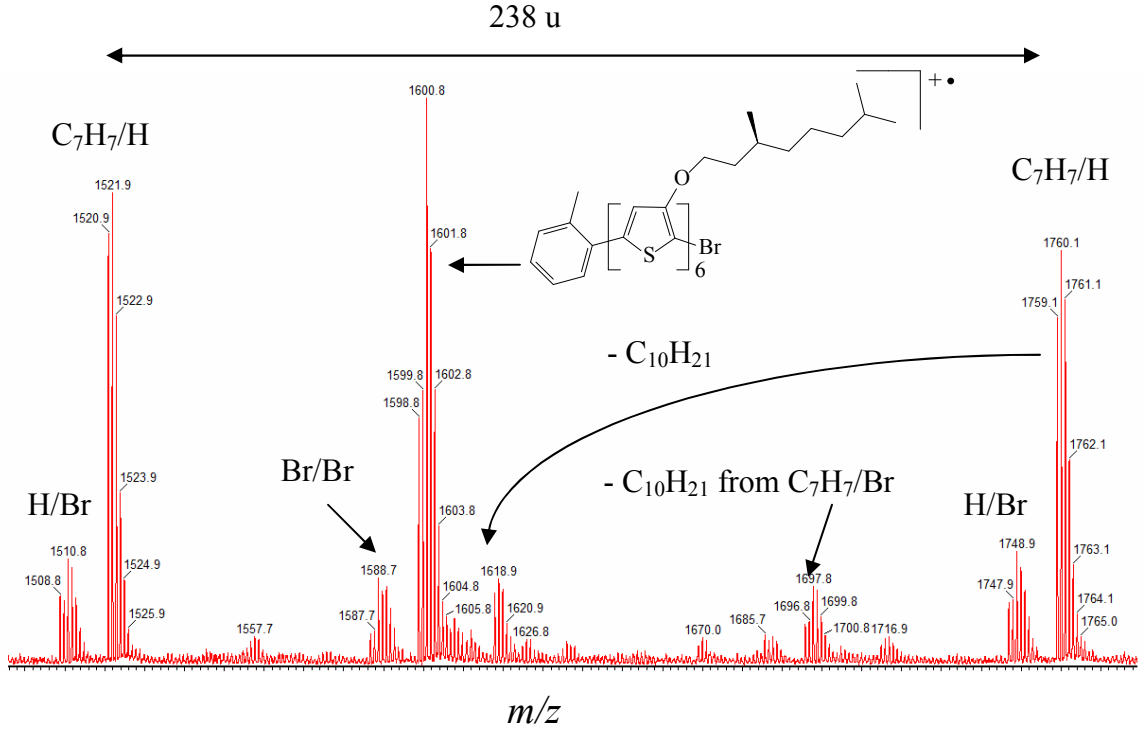


MALDI-ToF of P2

P2

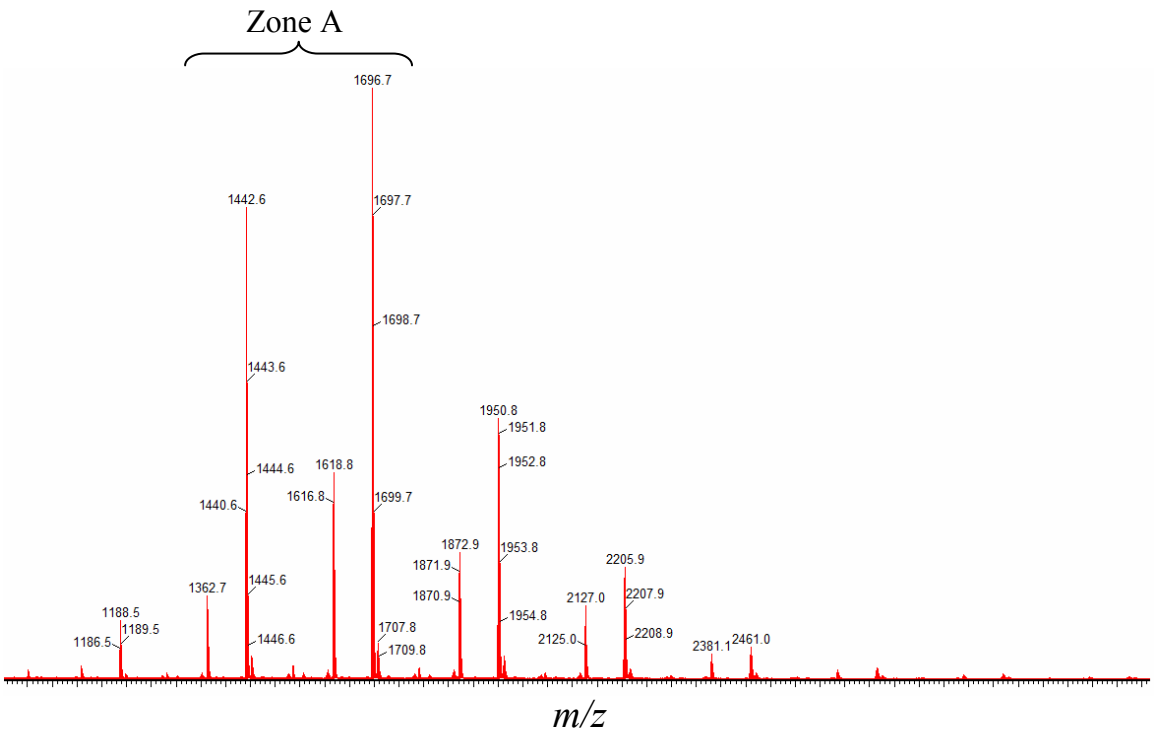


Zone A :

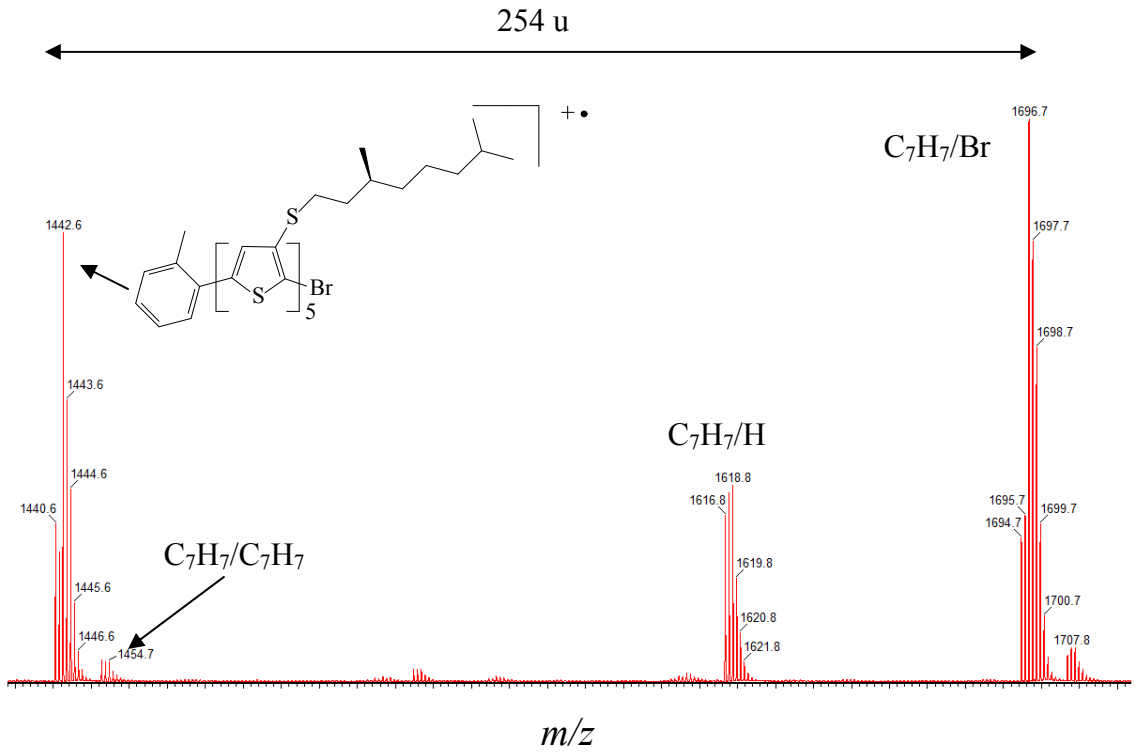


MALDI-ToF of P3

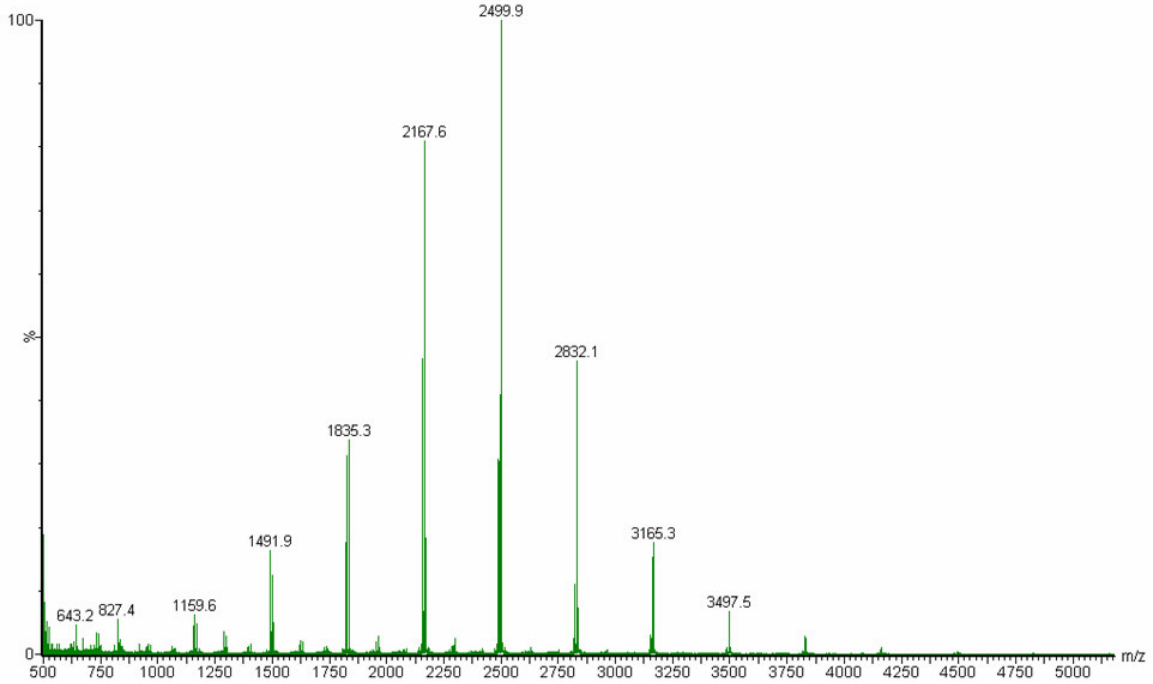
P3

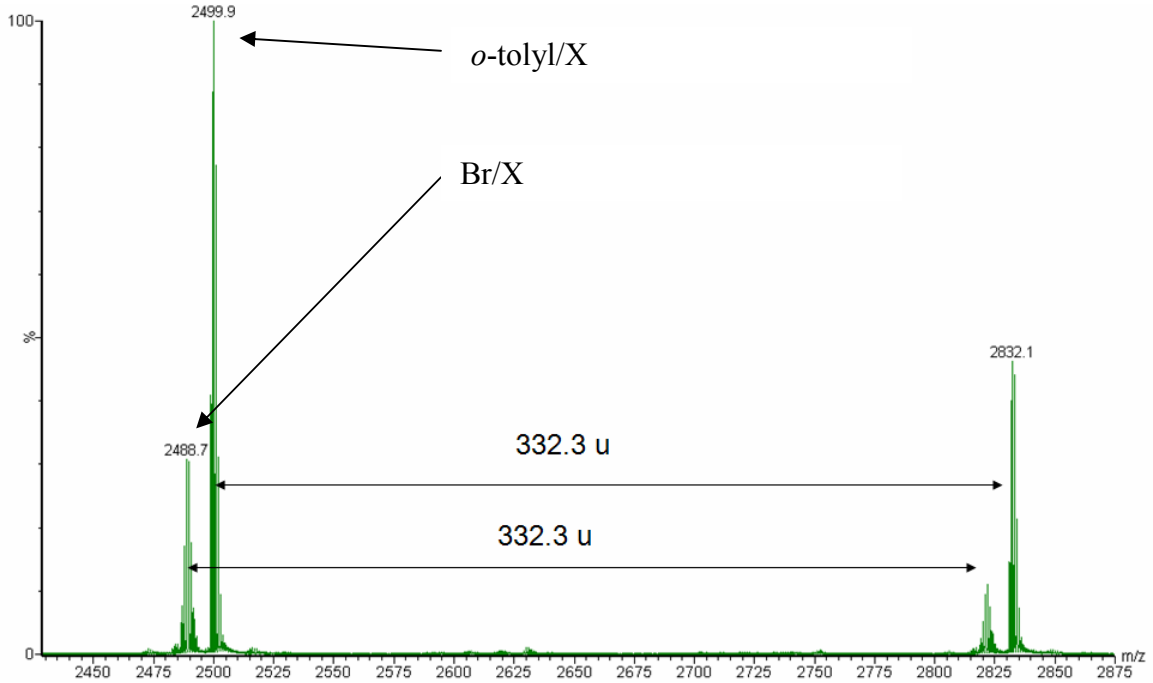


Zone A :



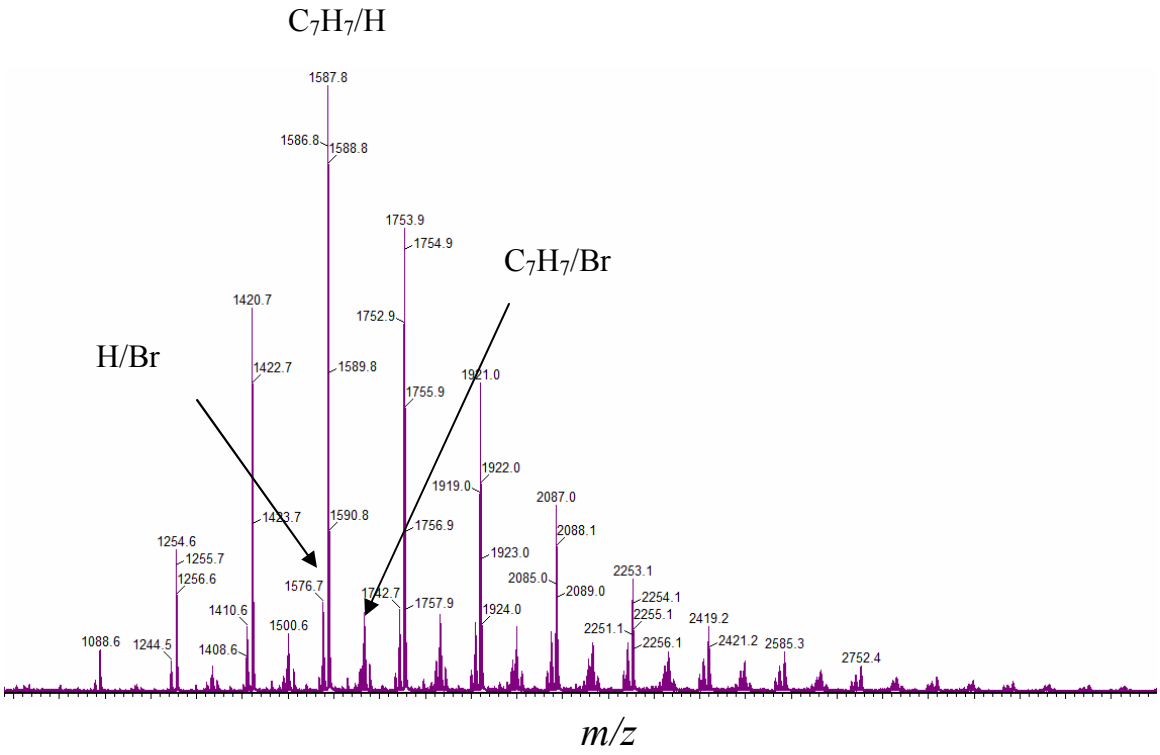
MALDI-ToF of P4





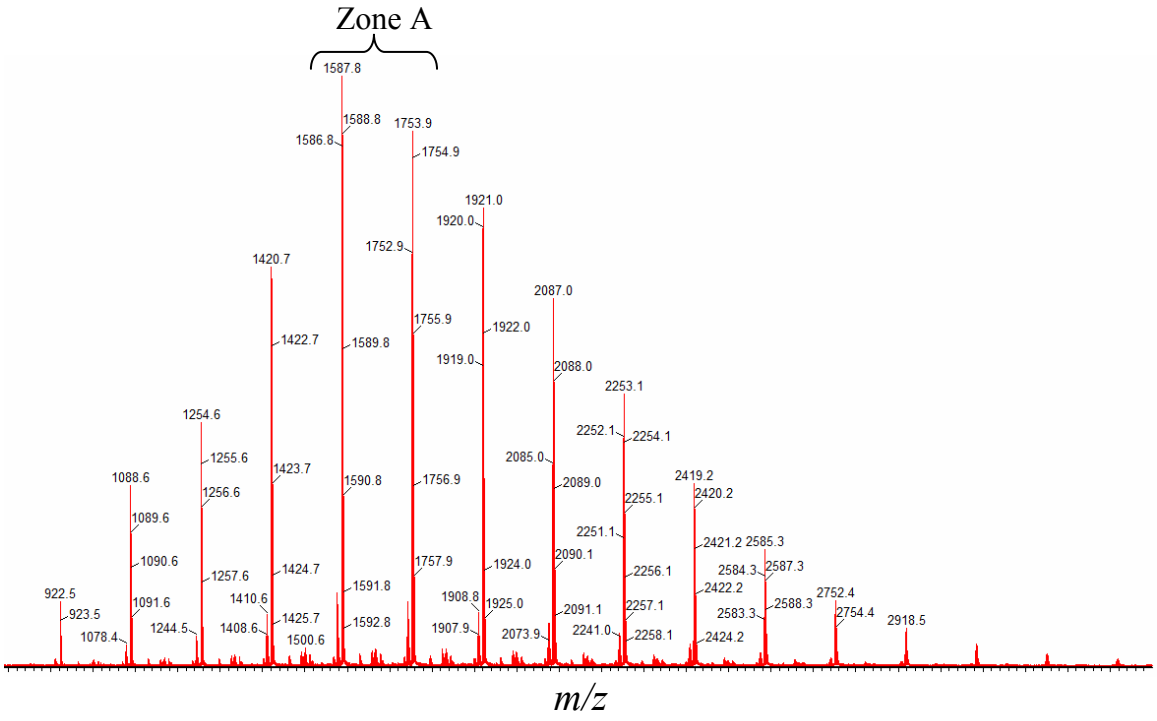
MALDI-ToF of P5

P5

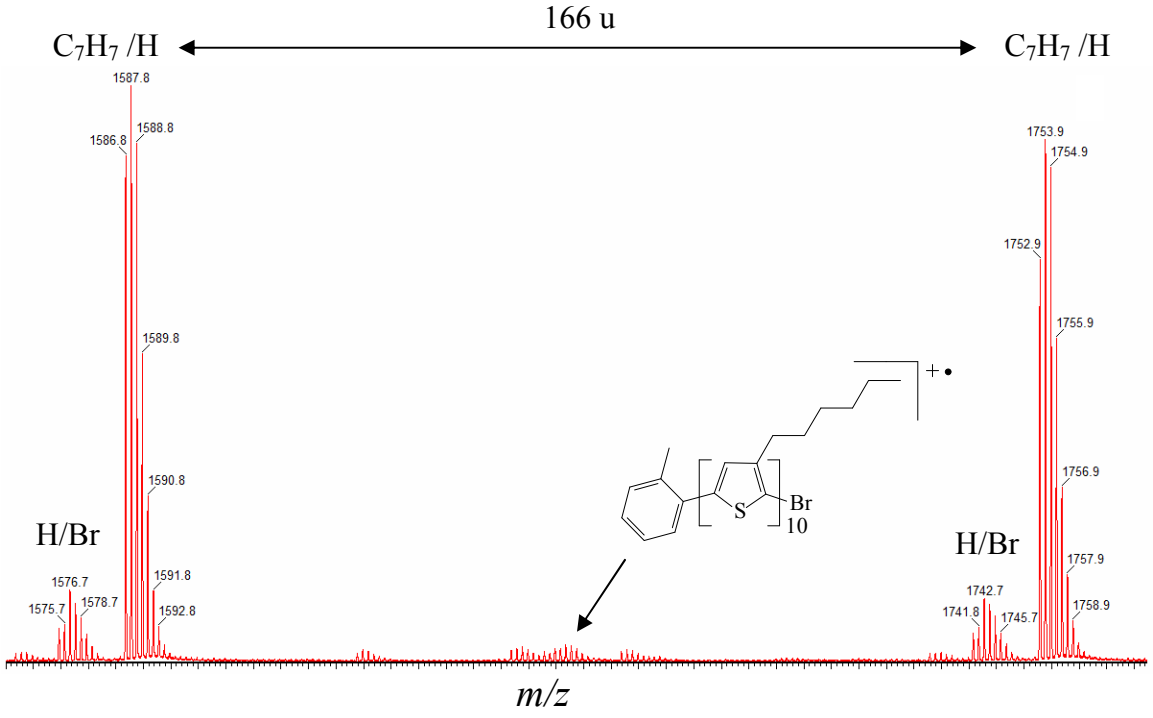


MALDI-ToF of P6

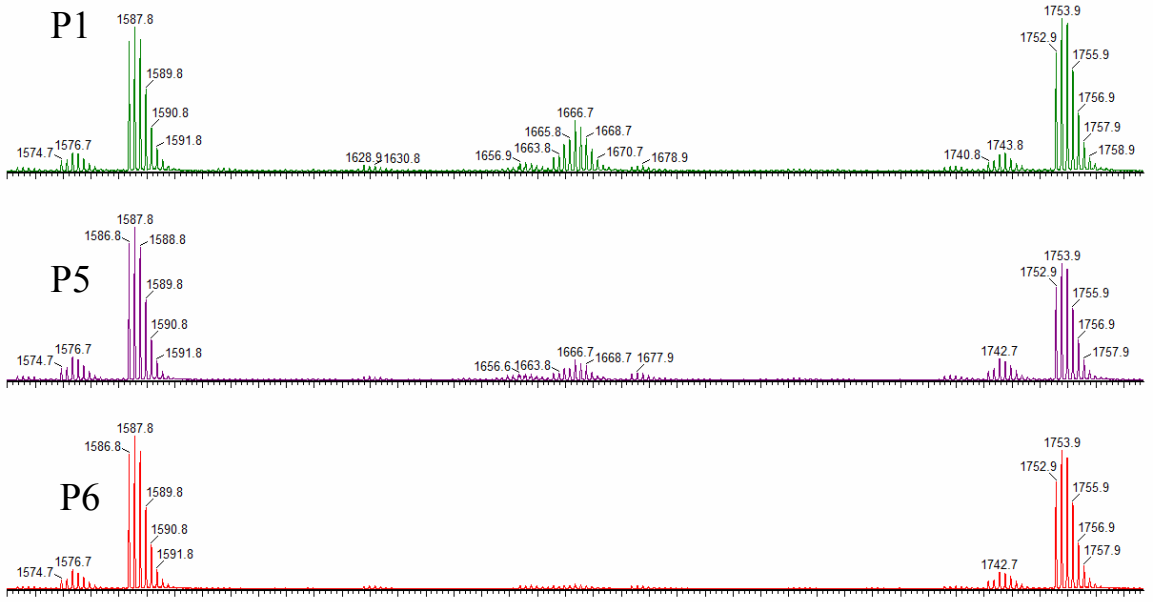
P6



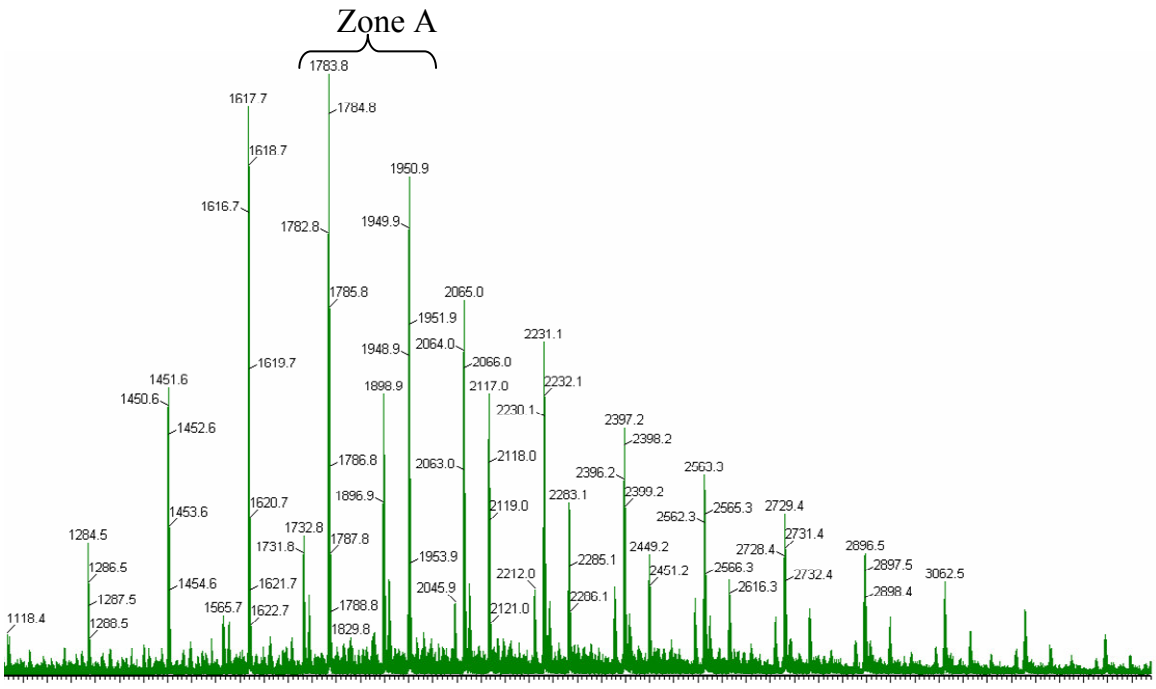
Zone A :



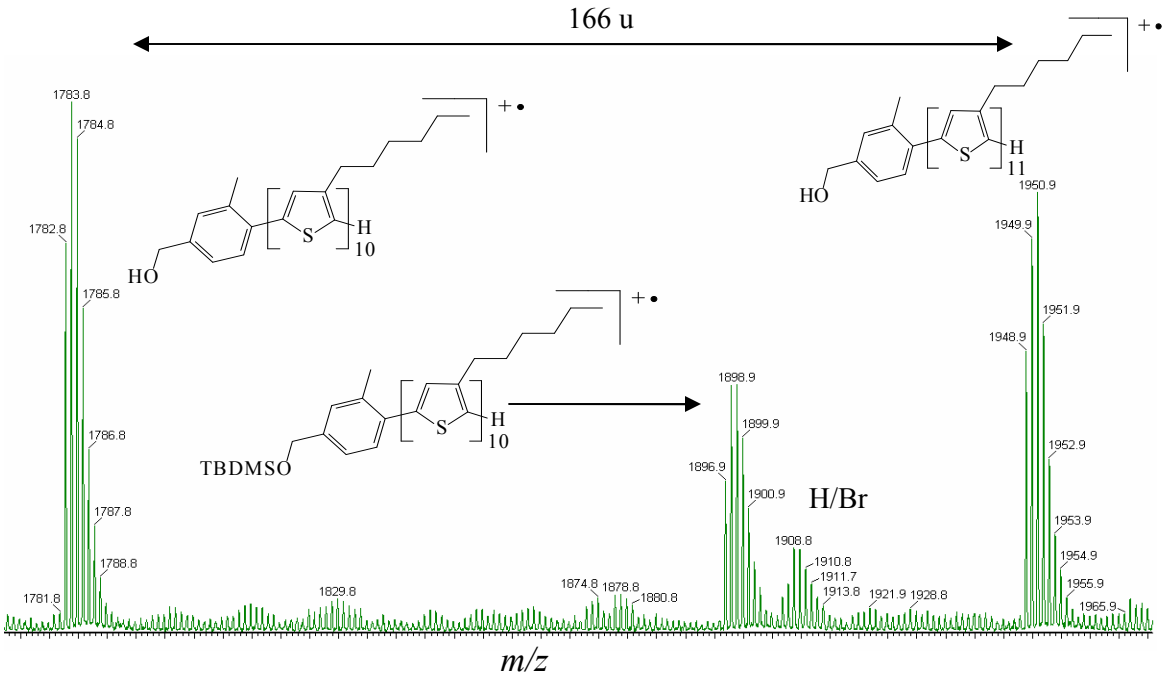
MALDI-ToF comparison of P1, P5 and P6



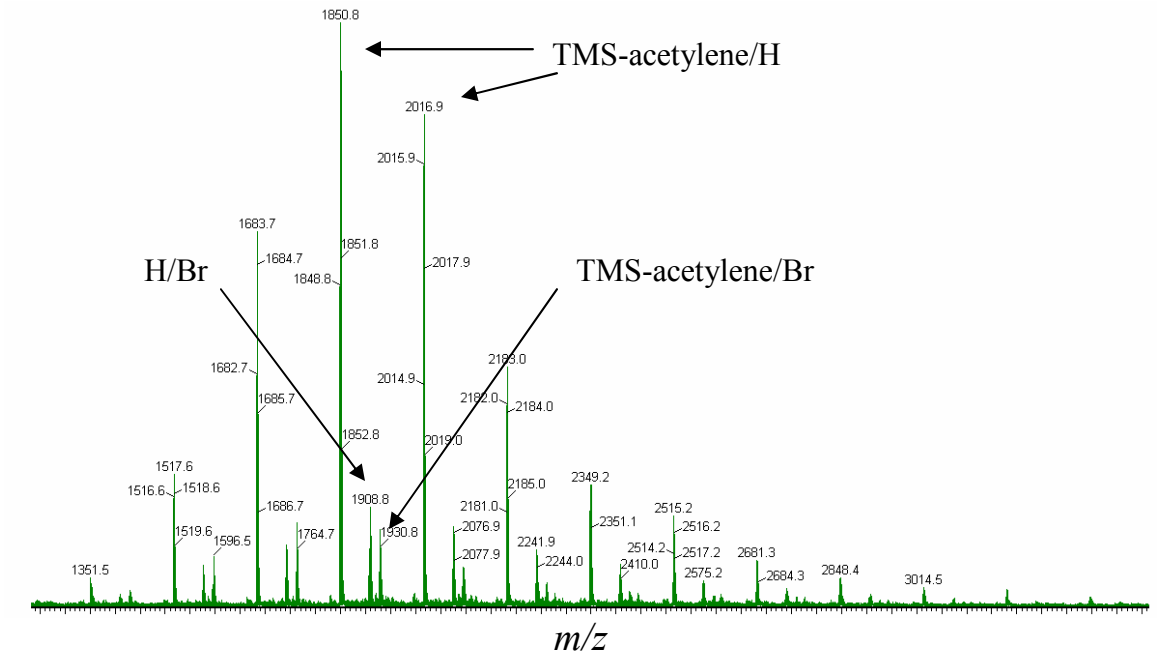
MALDI-ToF of P7



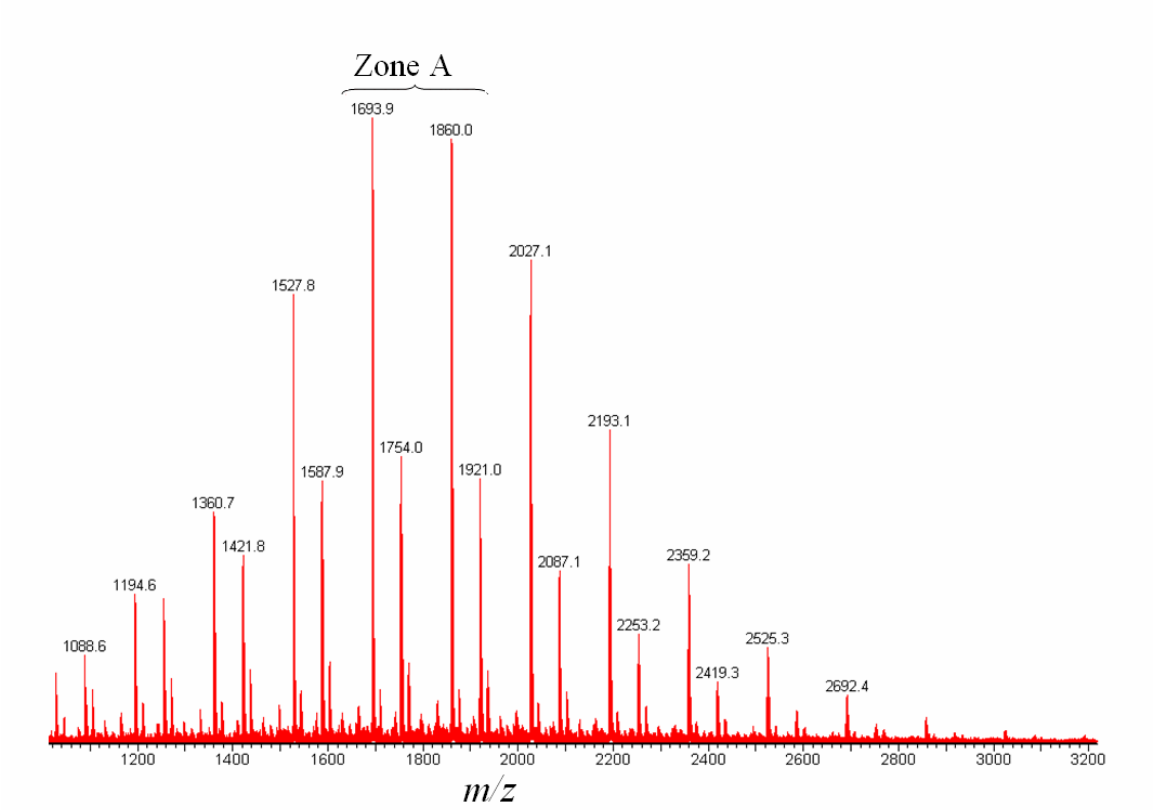
Zone A :



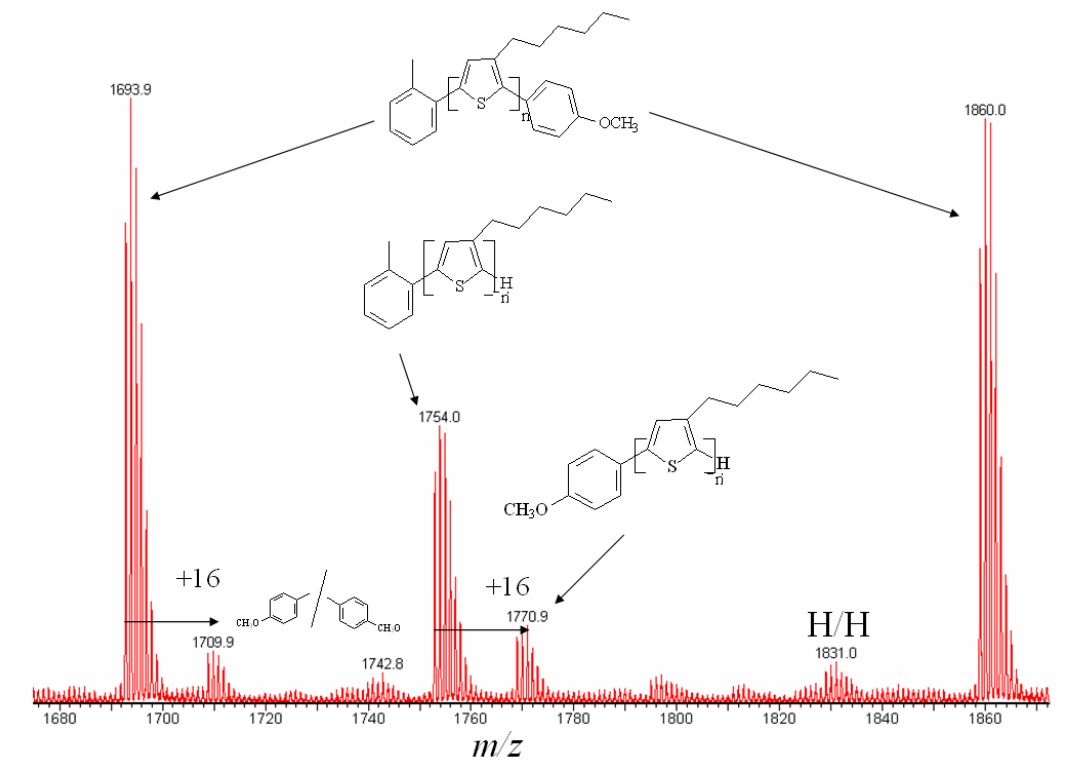
MALDI-ToF of P8



MALDI-ToF of P9



Zone A :



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