Supporting Information for:

Access to multinuclear salen complexes using olefin metathesis

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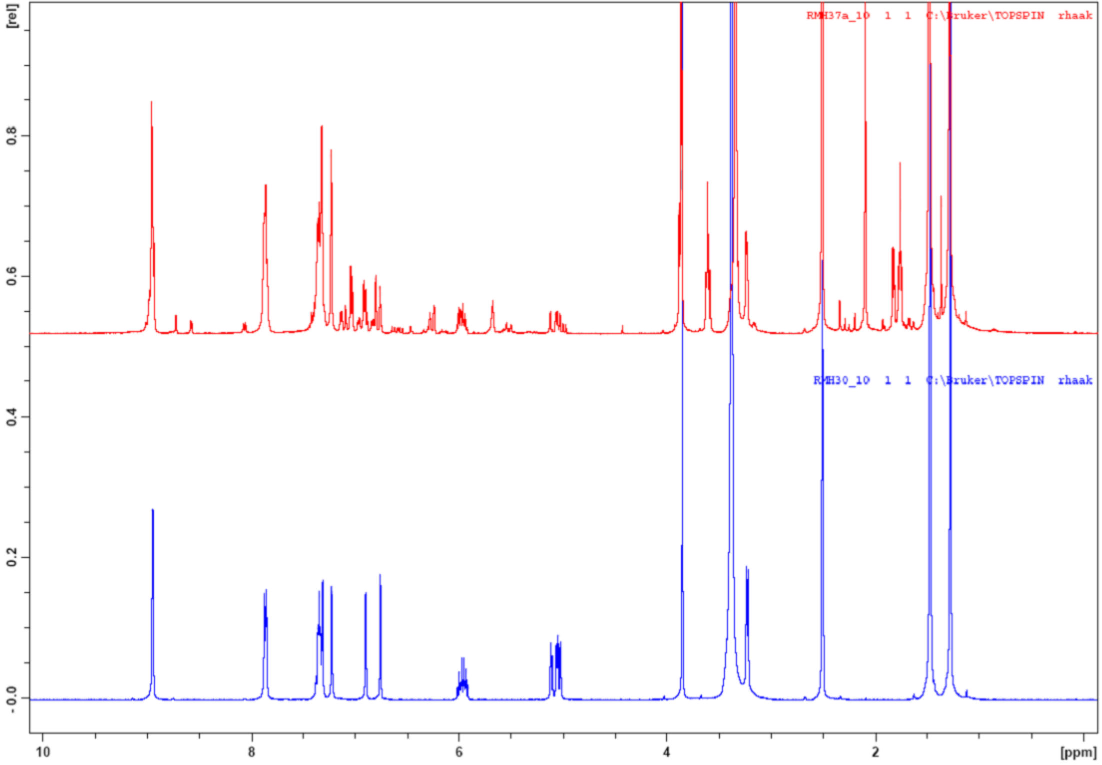
Contents:

Table 1, entry 1

Scale: 0.1 mmol, cat. **C** (5 mol%), THF, 100 mM, 72 h, 61% conv.

^{1}H NMR of starting material **4** (below) and product di-**4** (above):



MS (MALDI+) of the product mixture:

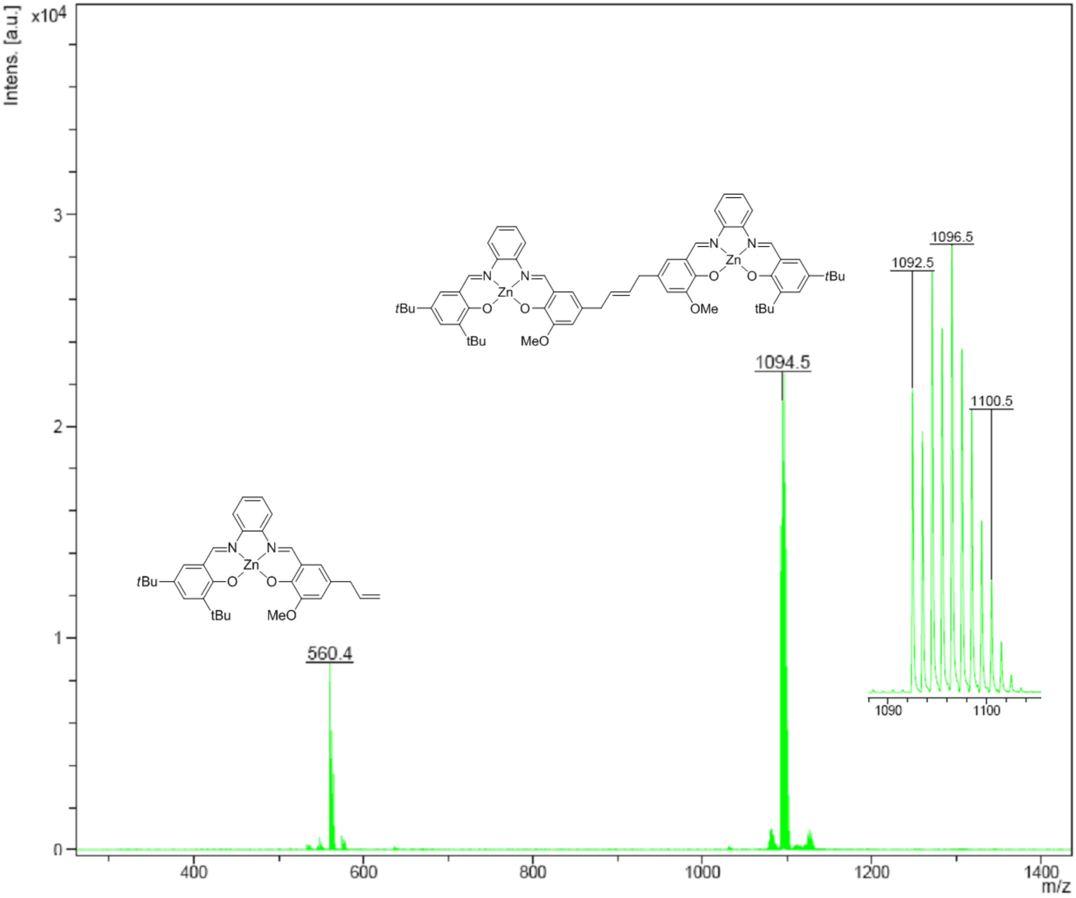
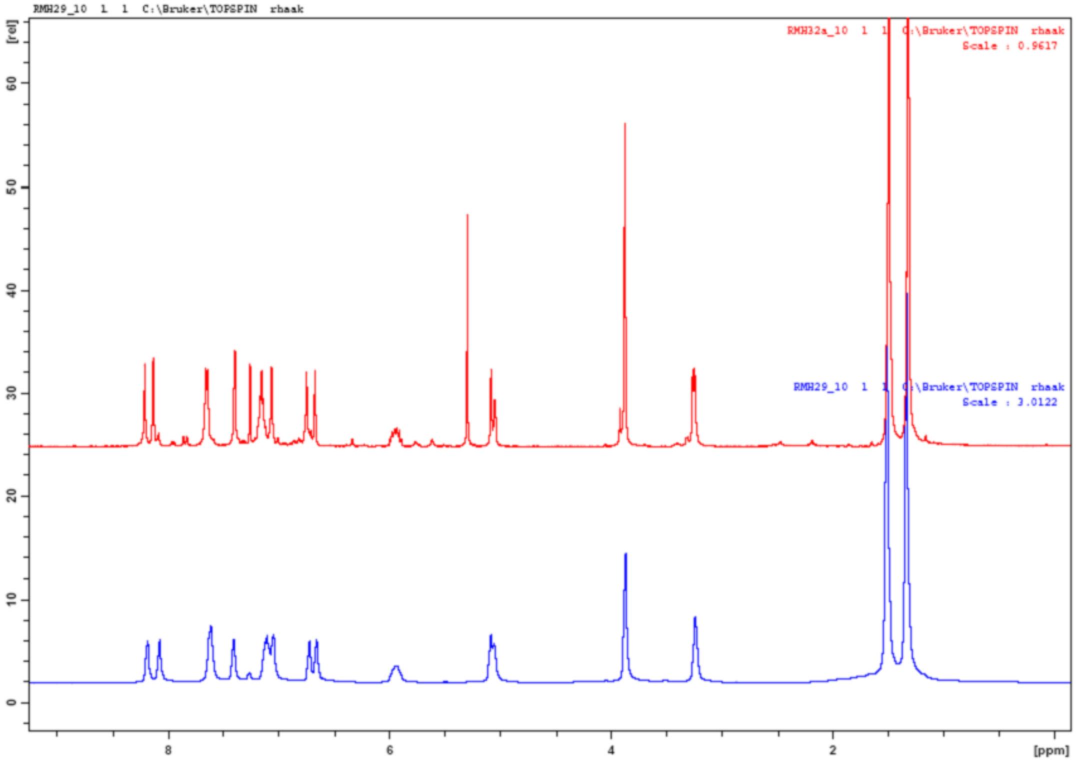


Table 1, entry 2

Scale: 0.1 mmol, cat. **C** (5 mol%), DCM, 100 mM, 24 h, 29% conv.

^{1}H NMR of starting material **5** (below) and product di-**5** (above):



MS (MALDI+) of the product mixture containing **5** and di-**5**.

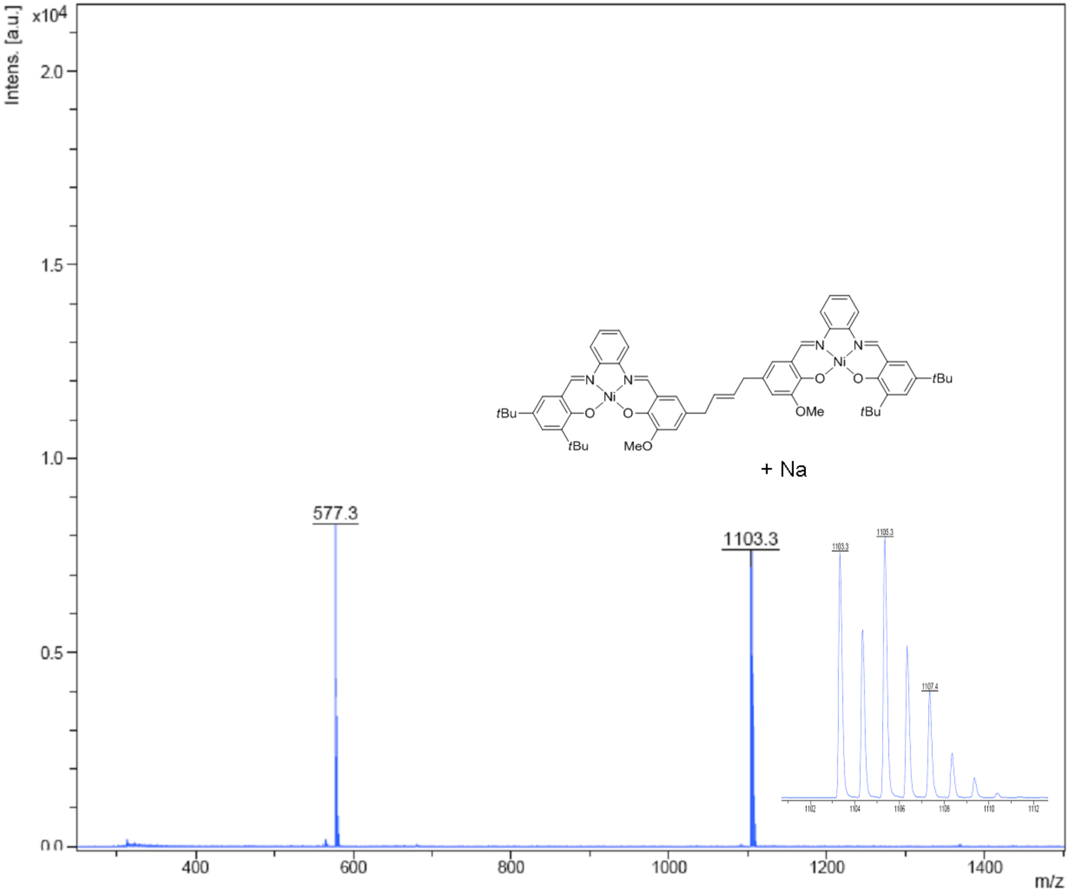
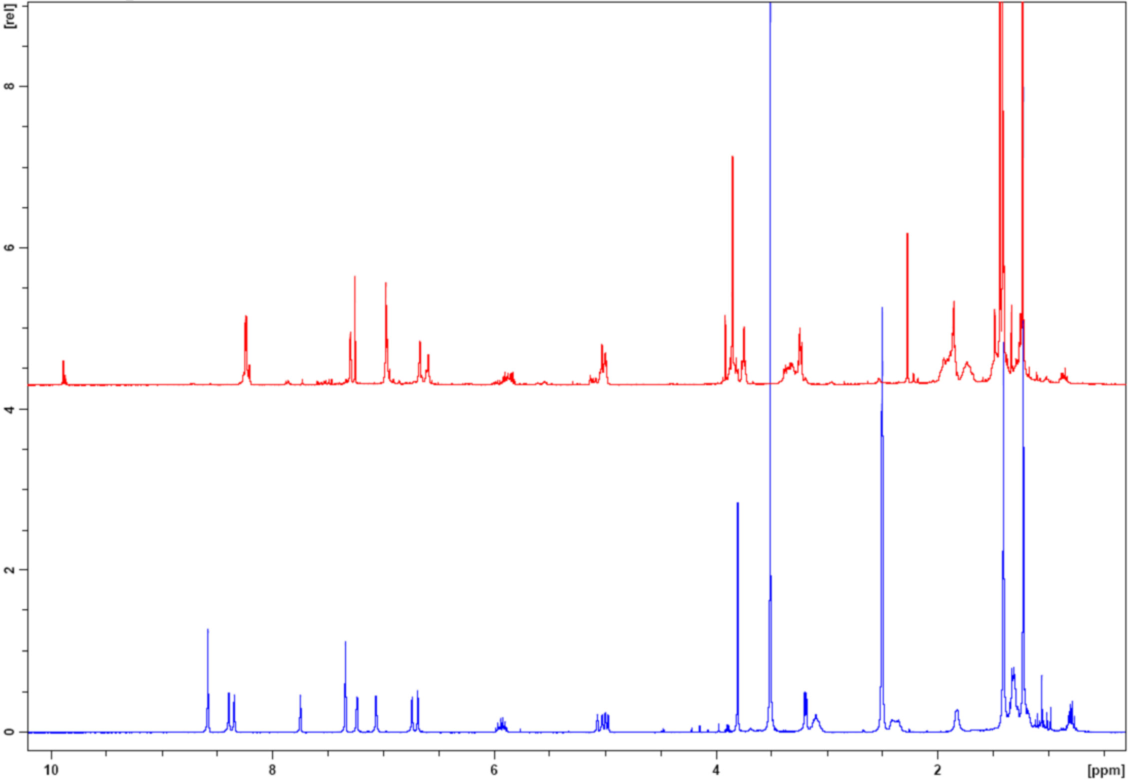


Table 1, entry 3
Scale: 0.1 mmol, cat. **C** (7 mol%), THF, 50 mM, 48 h, 10% conv.
^{1}H NMR of starting material (*R*,*R*)-**9** (below) and product (above):

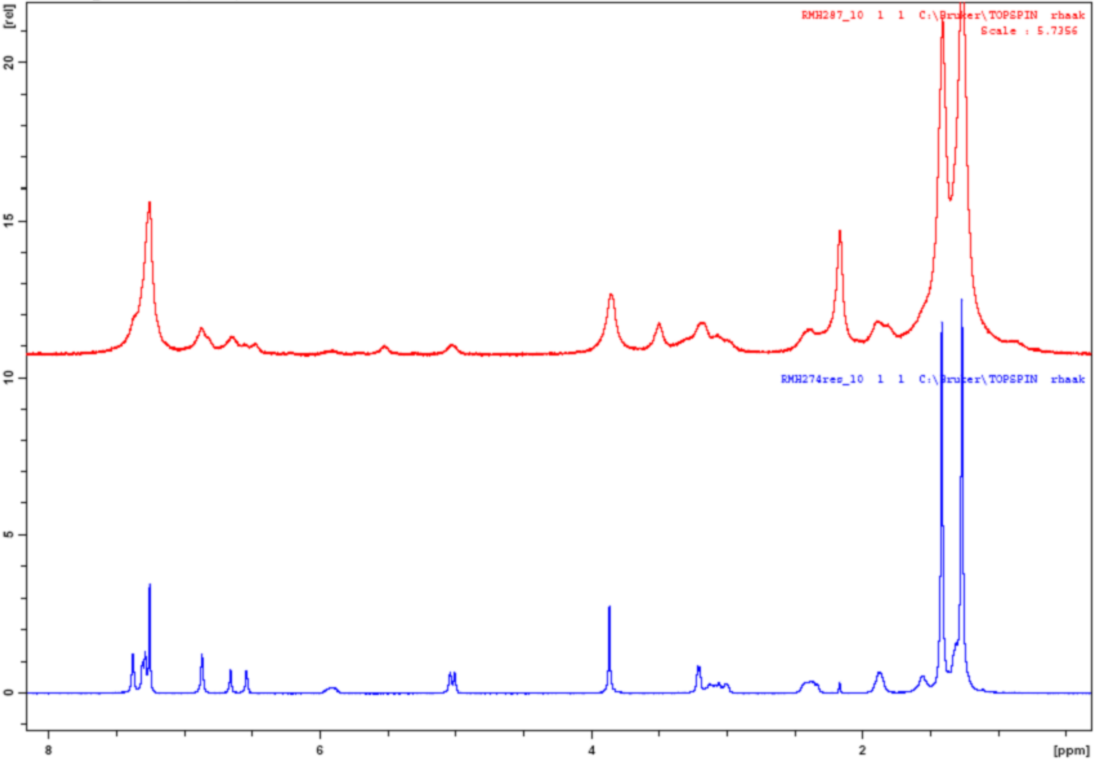


In this case, the reaction was performed without isolating the product, hence no mass spectrometric analysis was obtained.

Table 1, entry 4

Scale: 0.1 mmol, cat. **C** (14 mol%), DCM, 100 mM, 24 h, 59% conv.

^{1}H NMR of starting material (*R*,*R*)-**10** (below) and product di-(*R*,*R*)-**10** (above):



MS (MALDI+) of the product mixture:

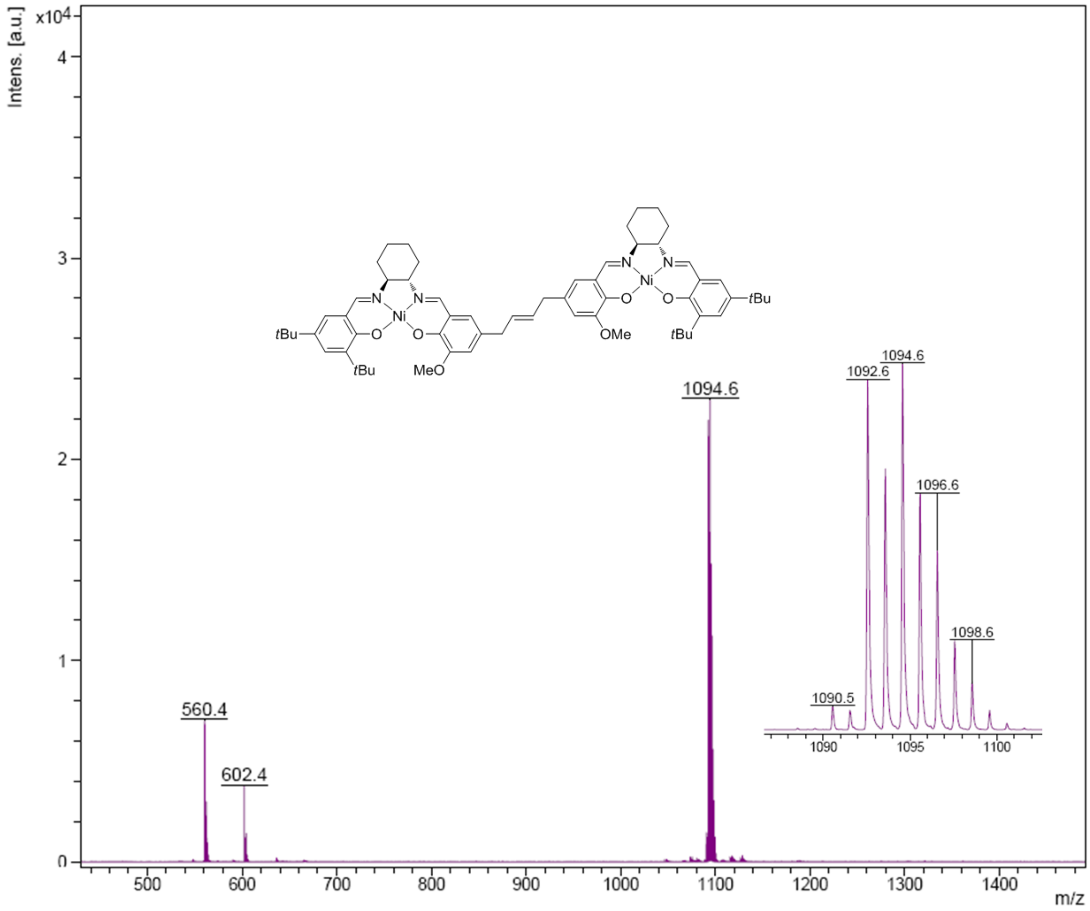
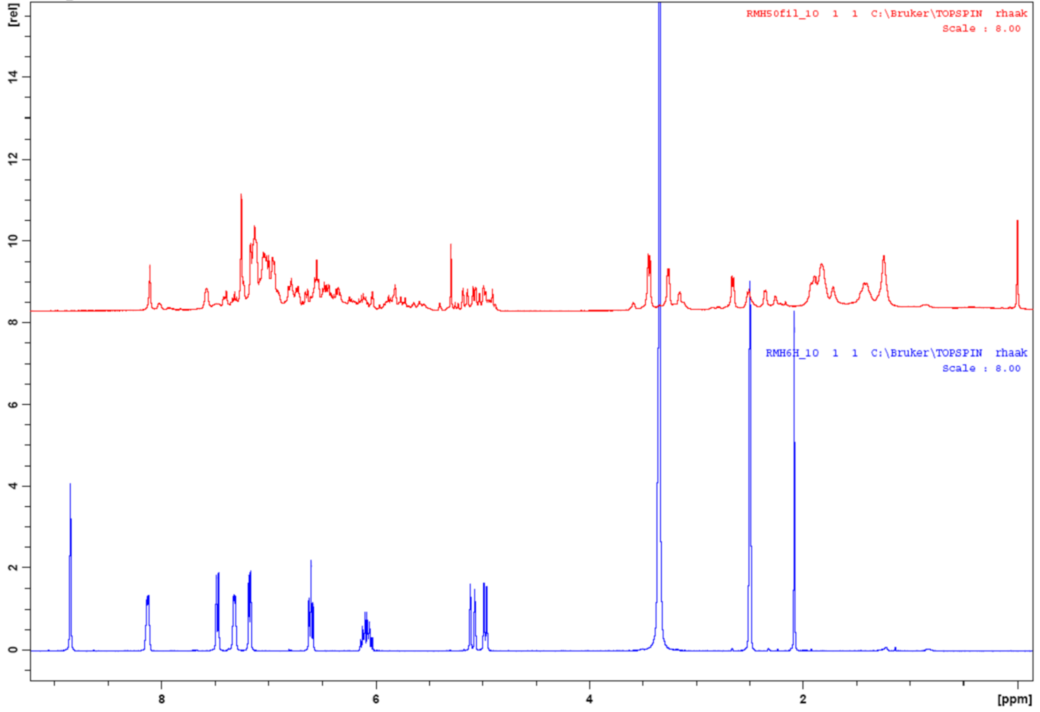


Table 2, entry 1

Scale 0.5 mmol, cat. **A** (14 mol%), DCM, 167 mM, 48 h, >95% conv.

^{1}H NMR of starting material **15** (below) and product (above):



MS (MALDI+) of the product mixture:

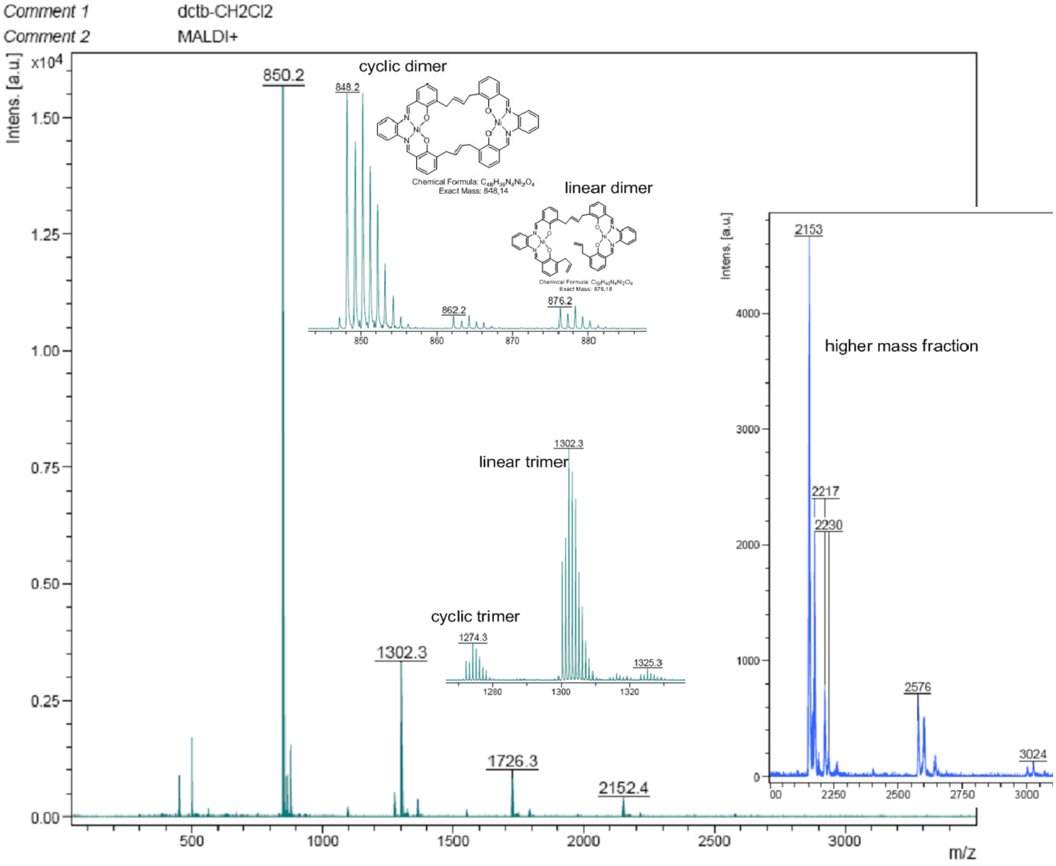
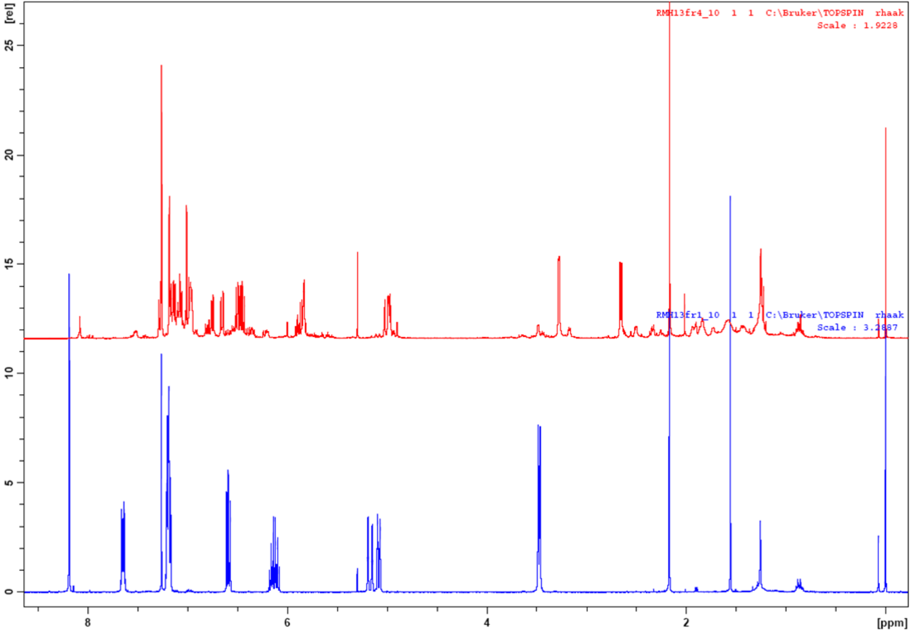


Table 2, entry 2

Scale 0.1 mmol, cat. **B** (5 mol%), DCM, 5 mM, 72 h, >95% conv.

^{1}H NMR of starting material **15** (below) and product (above):



MS of crude product di-**15**:

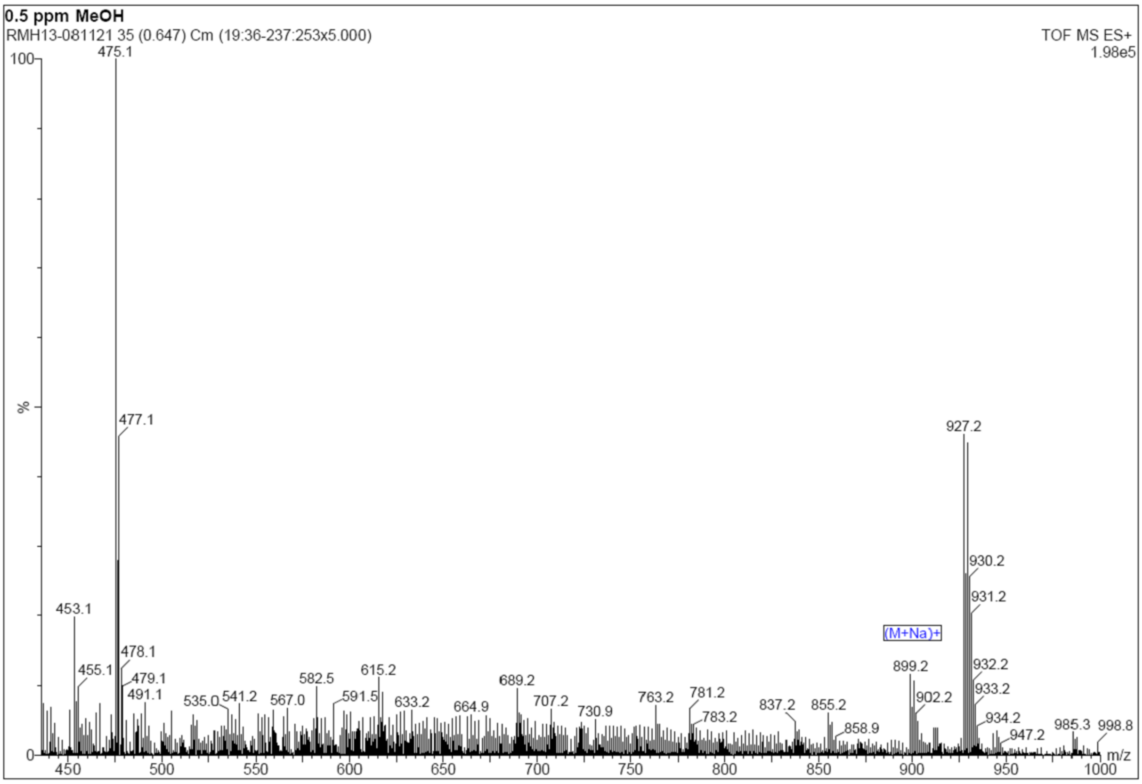
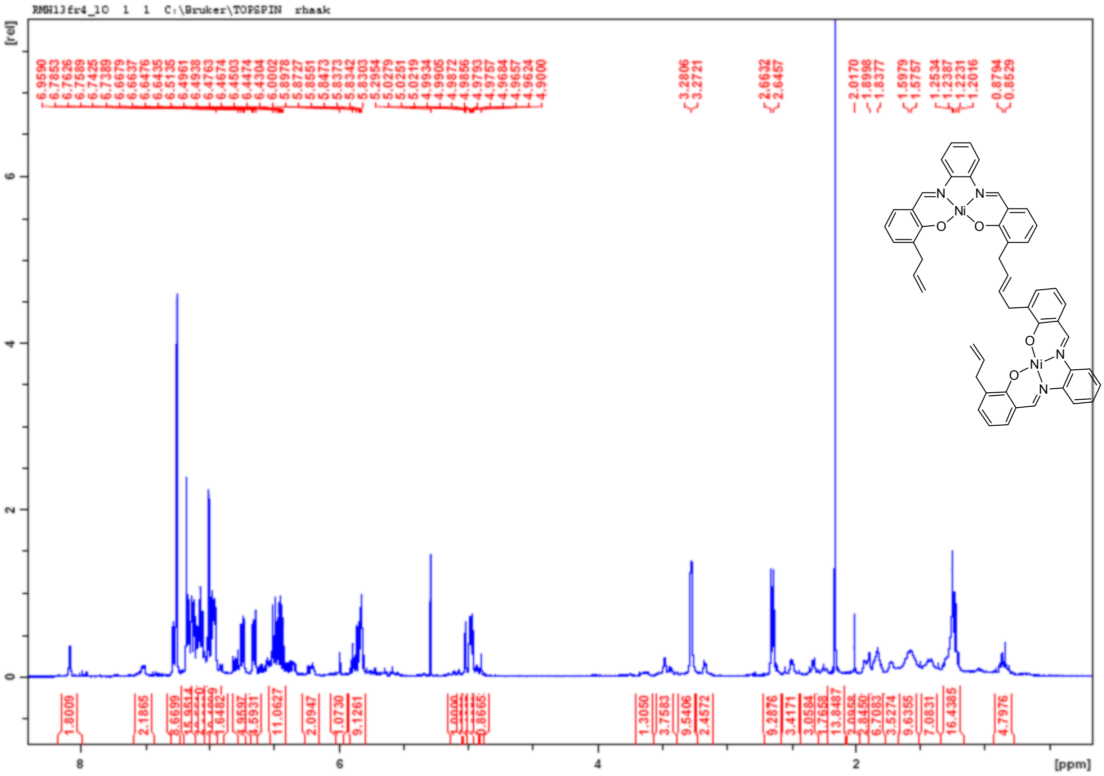


Table 2, entry 2 (contd.)

^{1}H NMR and MS (ES+) of di-**15** isolated after column chromatography (33% yield):



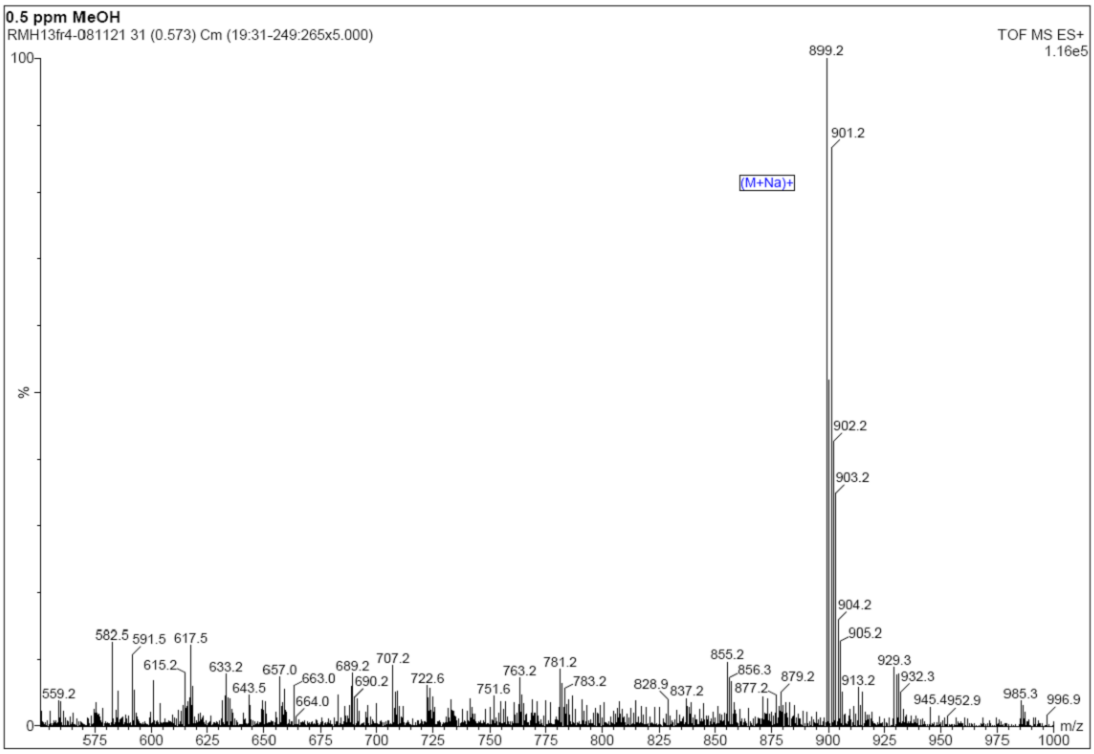
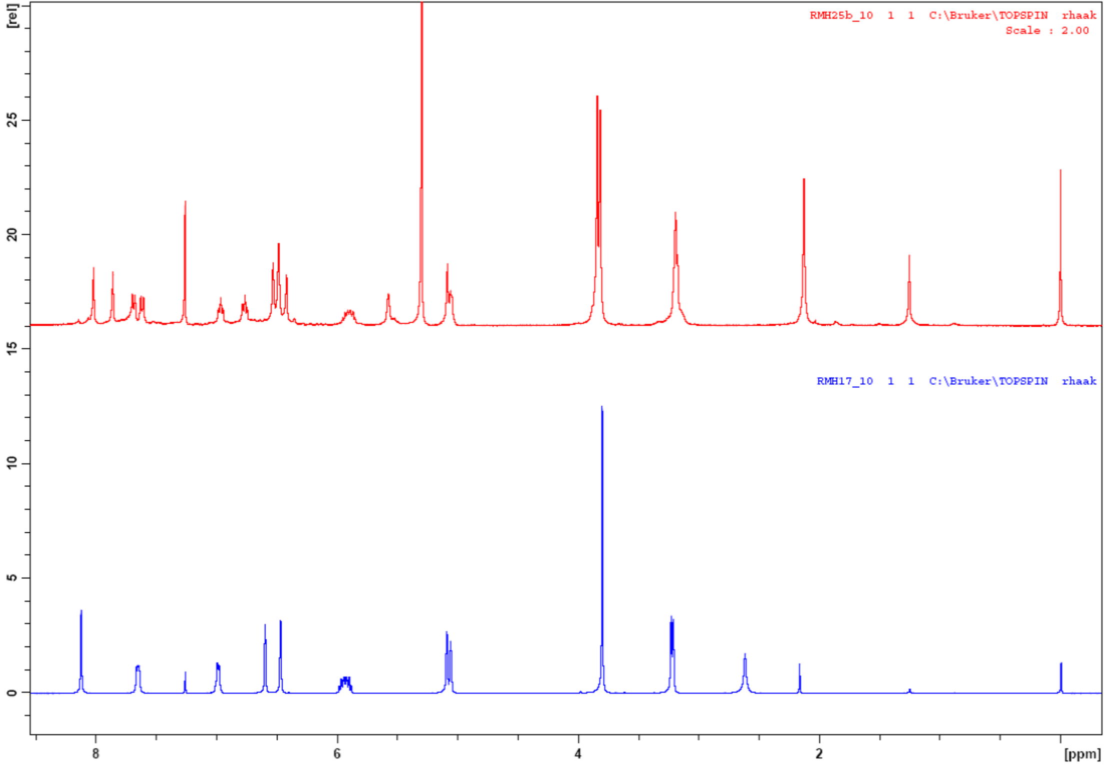


Table 2, entry 3

Scale 0.1 mmol, cat. **B** (5 mol%), DCM, 100 mM, 72 h, 50% conv.

^{1}H NMR of **17** (below) and product di-**17** (above):



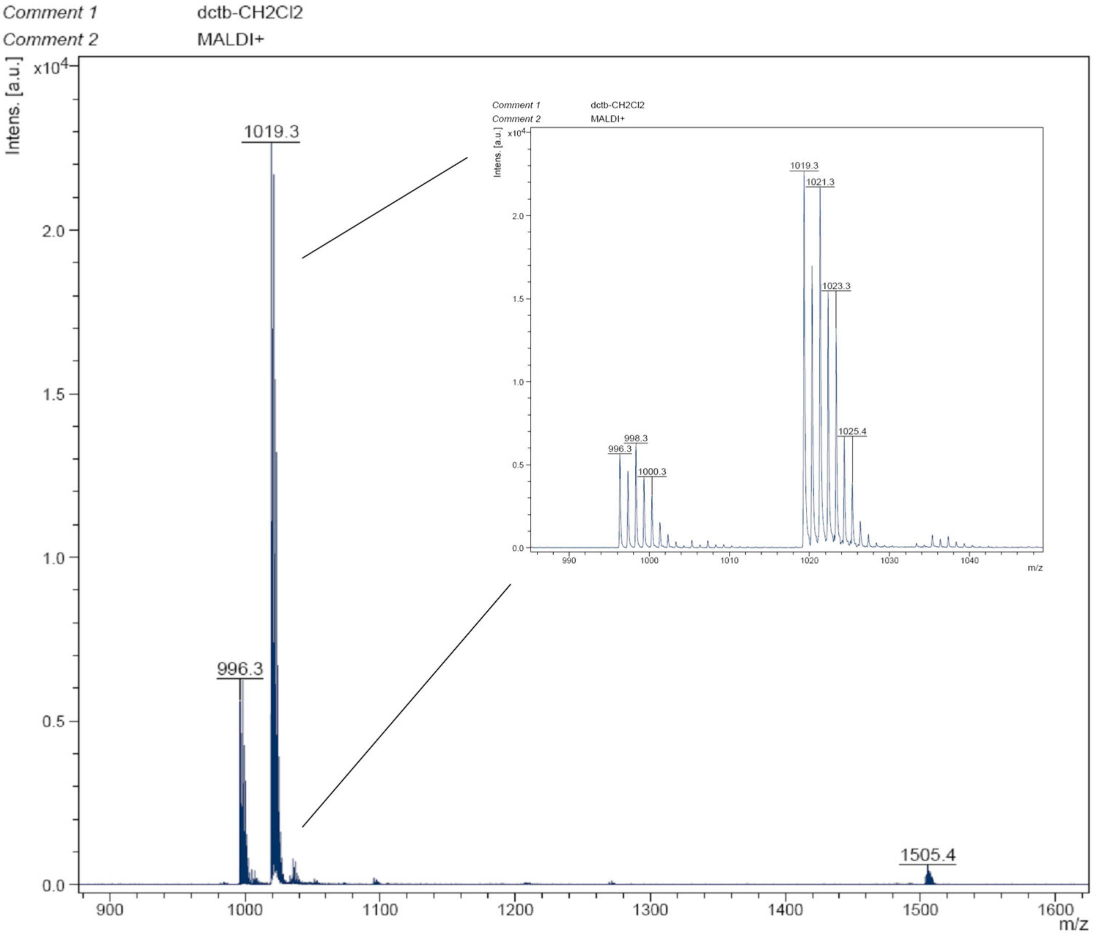
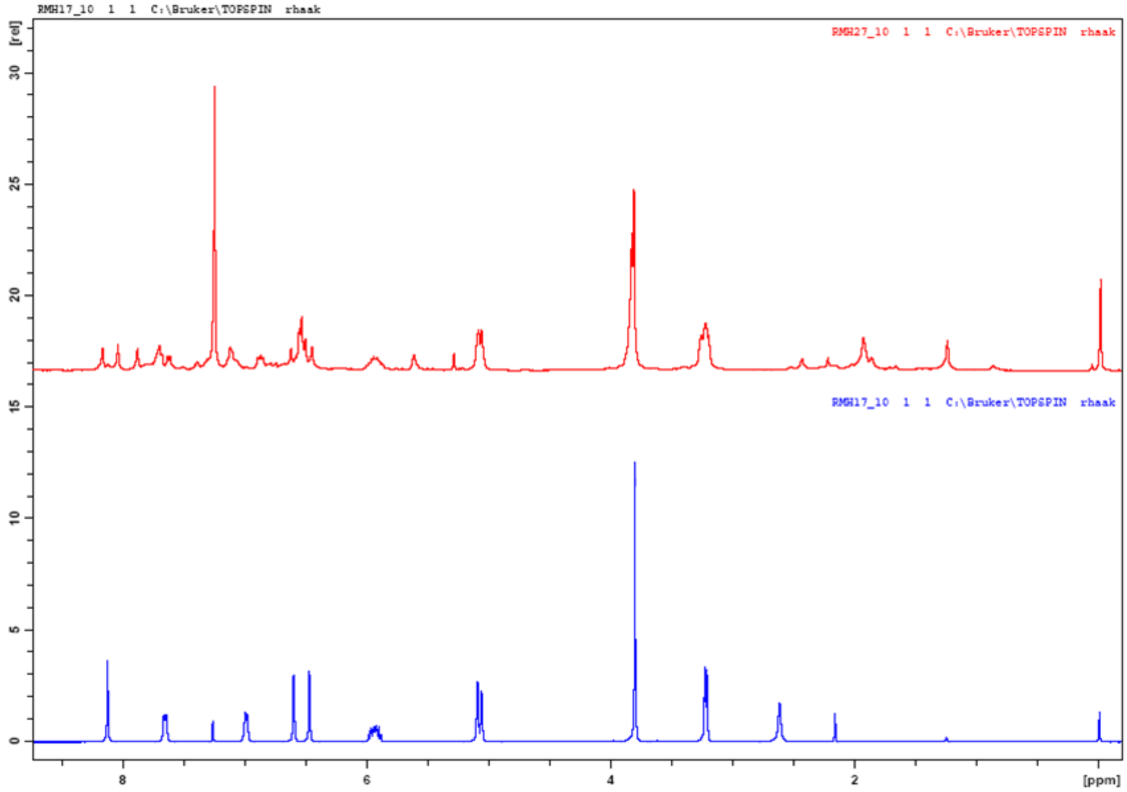


Table 2, entry 4

Scale 0.1 mmol, cat. **C** (5 mol%), DCM, 100 mM, 24 h, 57% conv.

^{1}H NMR of **17** (below) and product di-**17** (above):



MS (MALDI+) of di-**17**:

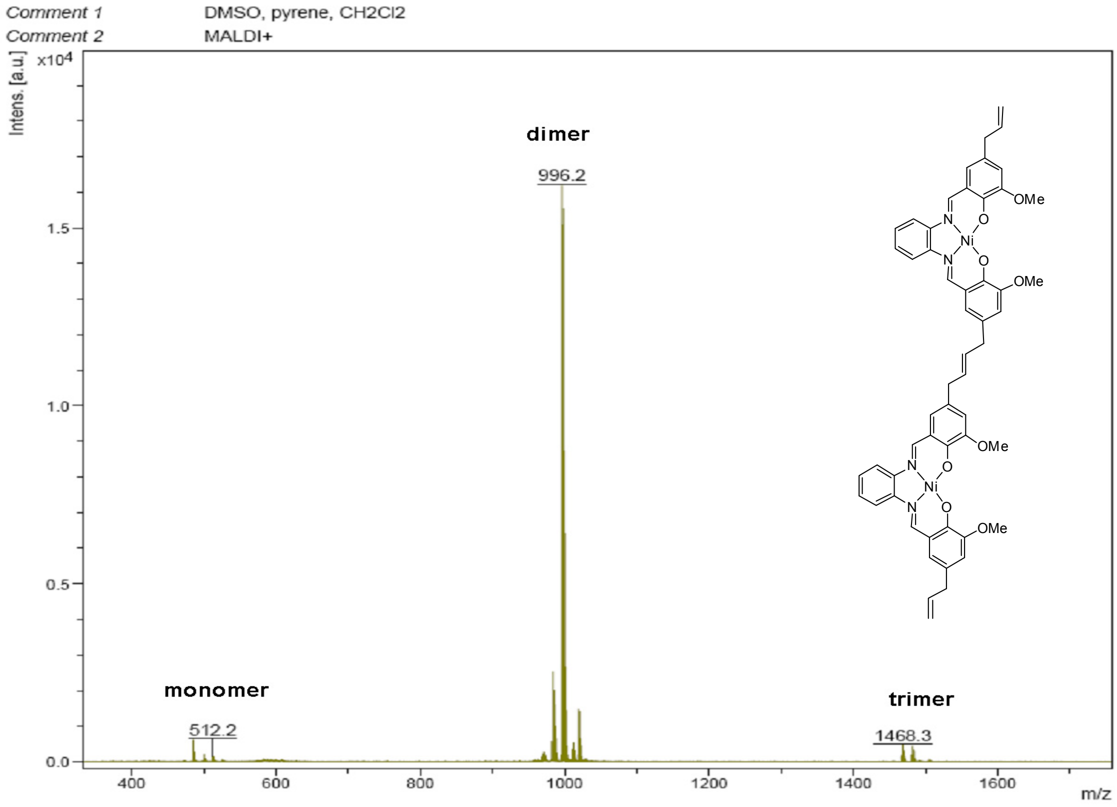
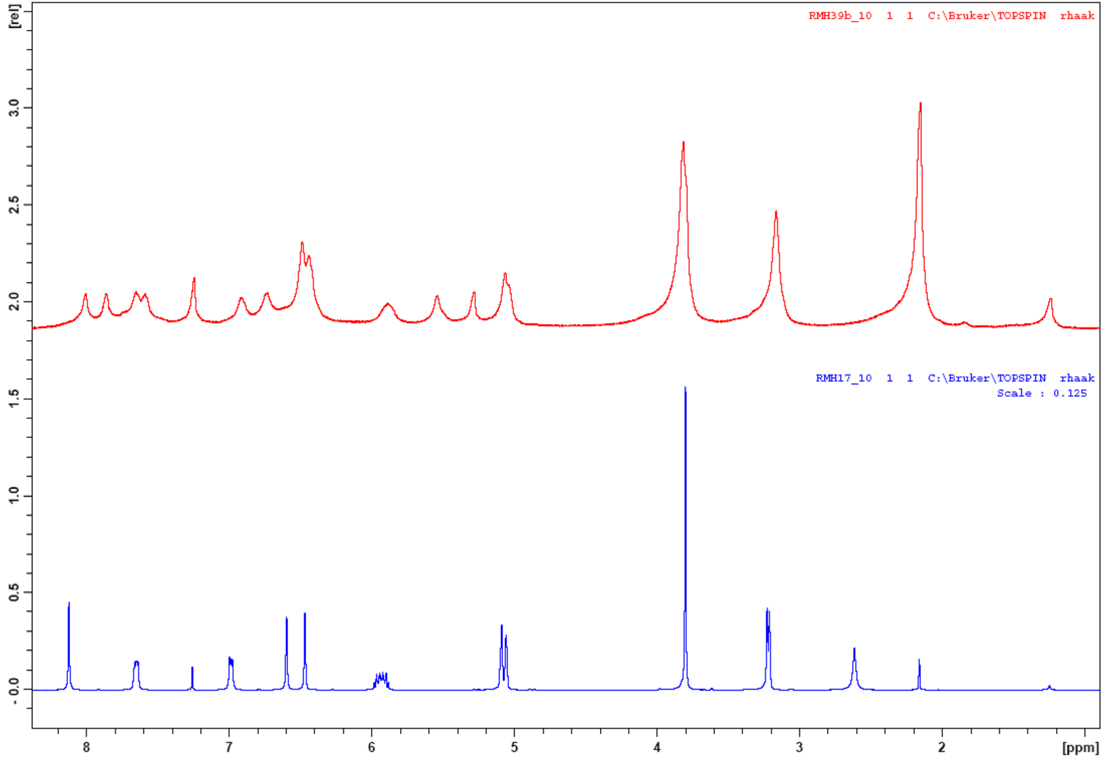


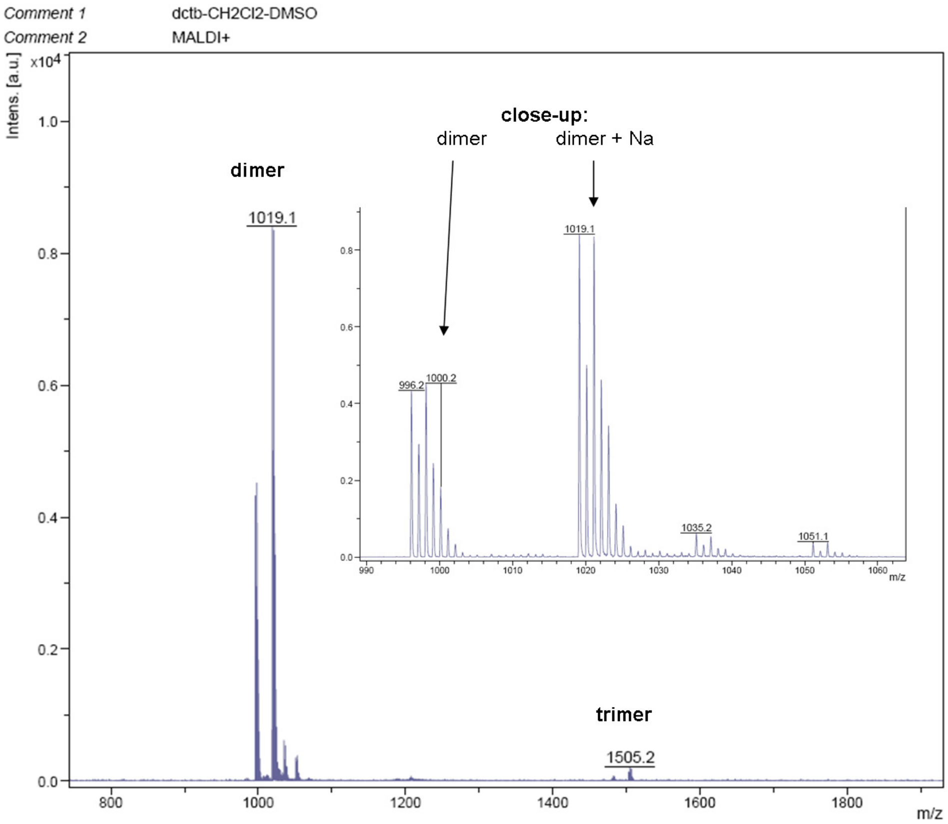
Table 2, entry 5

Scale 0.1 mmol, cat. **C** (5 mol%), THF, 62 mM, 24 h, 93% conv.

^{1}H NMR of **17** (below) and product di-**17** (above):



MS (MALDI+) of di-**17**:

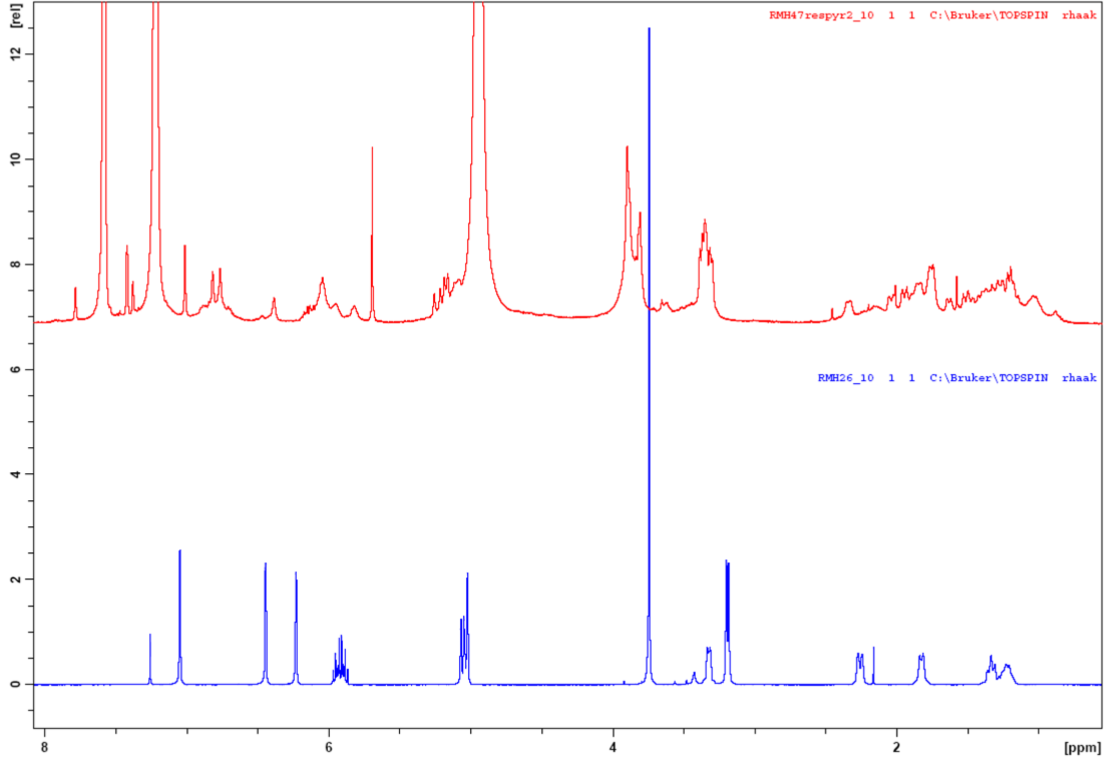


N.B. When using THF as solvent, the product mixture partly consisted of completely insoluble material not amenable to detailed analysis. The MALDI shown above is that of the soluble part of the product mixture.

Table 2, entry 6

Scale 0.5 mmol, cat. **A** (21 mol%), DCM, 100 mM, 48 h, >95% conv.

^{1}H NMR of starting material (±)-**19** (below) and product oligo-(±)-**19** (above):



MS (MALDI+) of oligo-(±)-**19** (bottom):

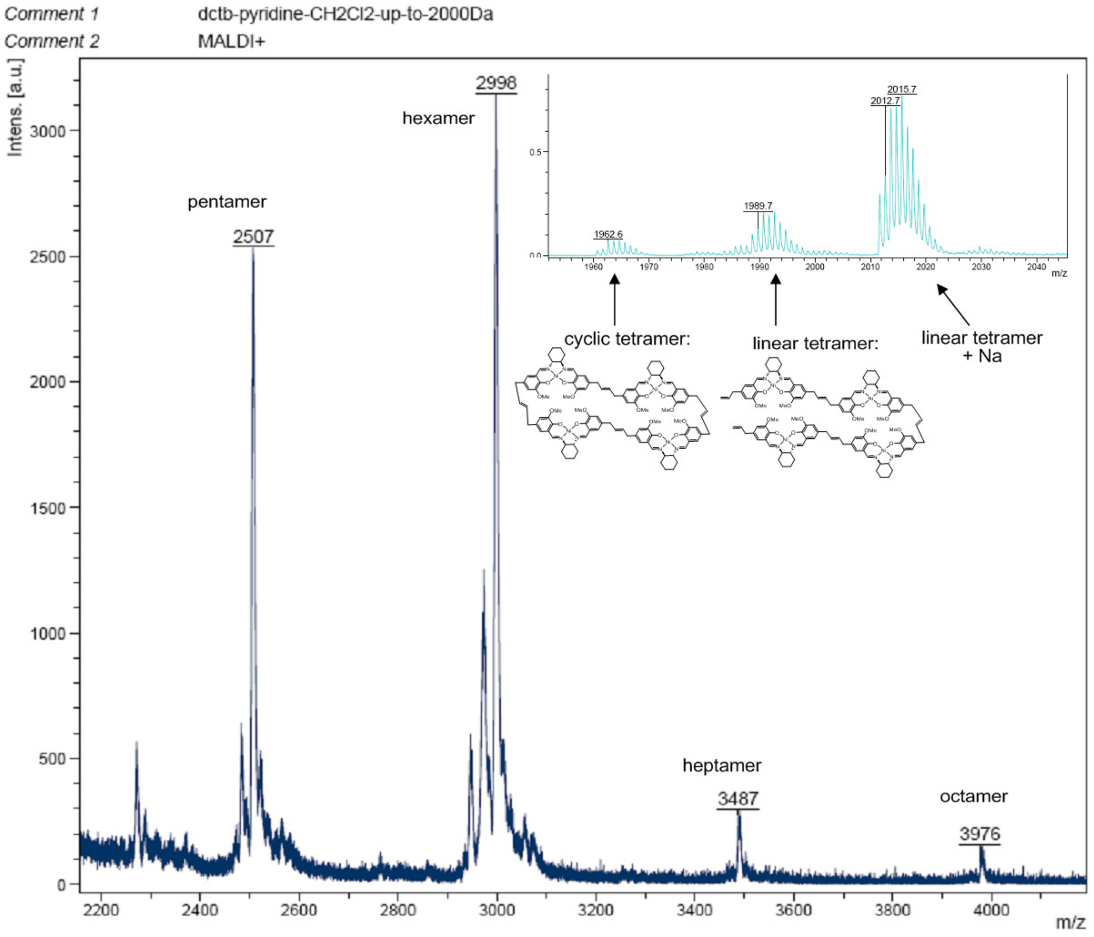


Table 2, entry 6 (contd.)

Attempted separation of the oligomers in oligo-(±)-19

In order to access individual compounds from the mixtures of oligomers, it was attempted to separate oligo-(±)-**19** using GPS. However, no separation was obtained. Chromatography was hampered by the low solubility of oligo-(±)-**19**. Using reversed phase HPLC, some separation could be achieved (see chromatogram below). However, none of the fractions corresponded to any of the the expected products; furthermore, some of the fractions did not contain nickel as judged from their mass spectra. Possibly, demetallation of the nickel complexes with consecutive product decomposition takes place during chromatography.

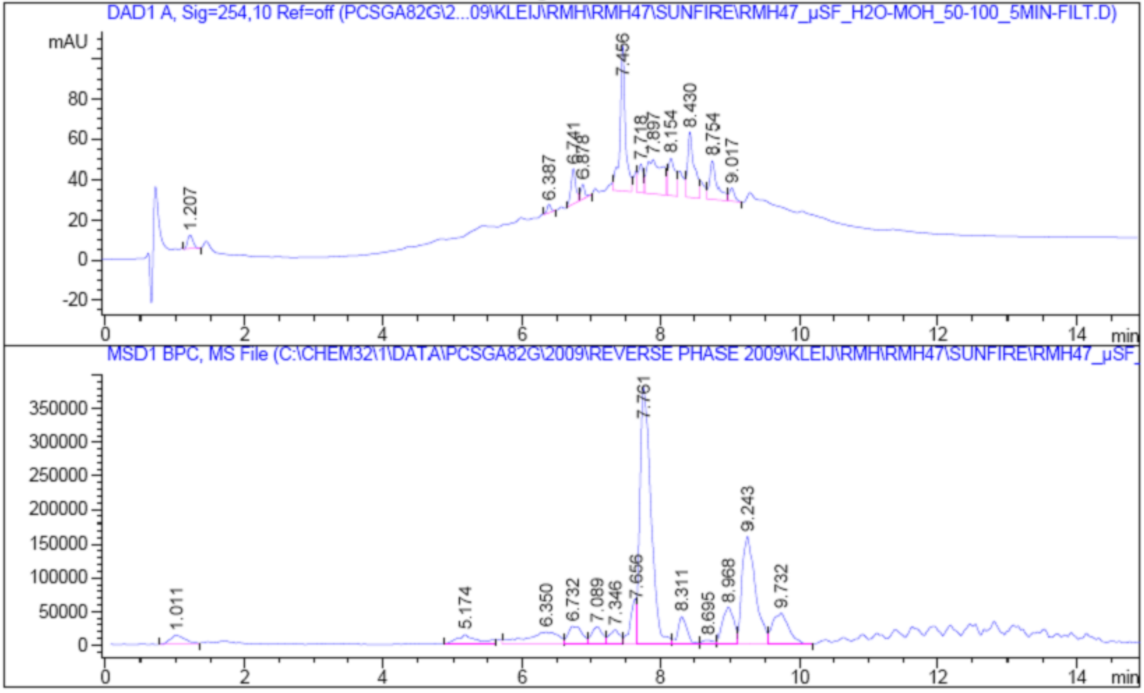
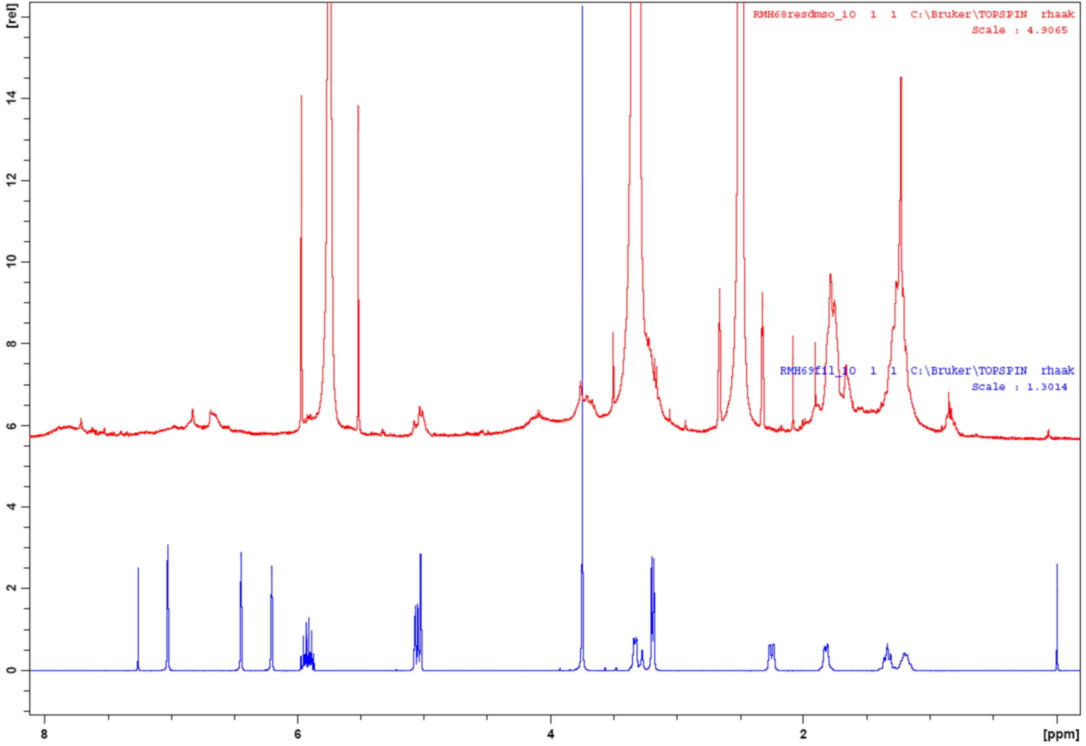


Table 2, entry 7

Scale 0.5 mmol, cat. **A** (14 mol%), DCM, 5 mM, 96 h, >95% conv.

^{1}H NMR of starting material (±)-**19** (below) and product oligo-(±)-**19** (above):



MS (MALDI+) of the product mixture containing dimers and tetramers:

Comment 1 dctb-pyridine-CH2Cl2-(450-5000Da)

Comment 2 MALDI+

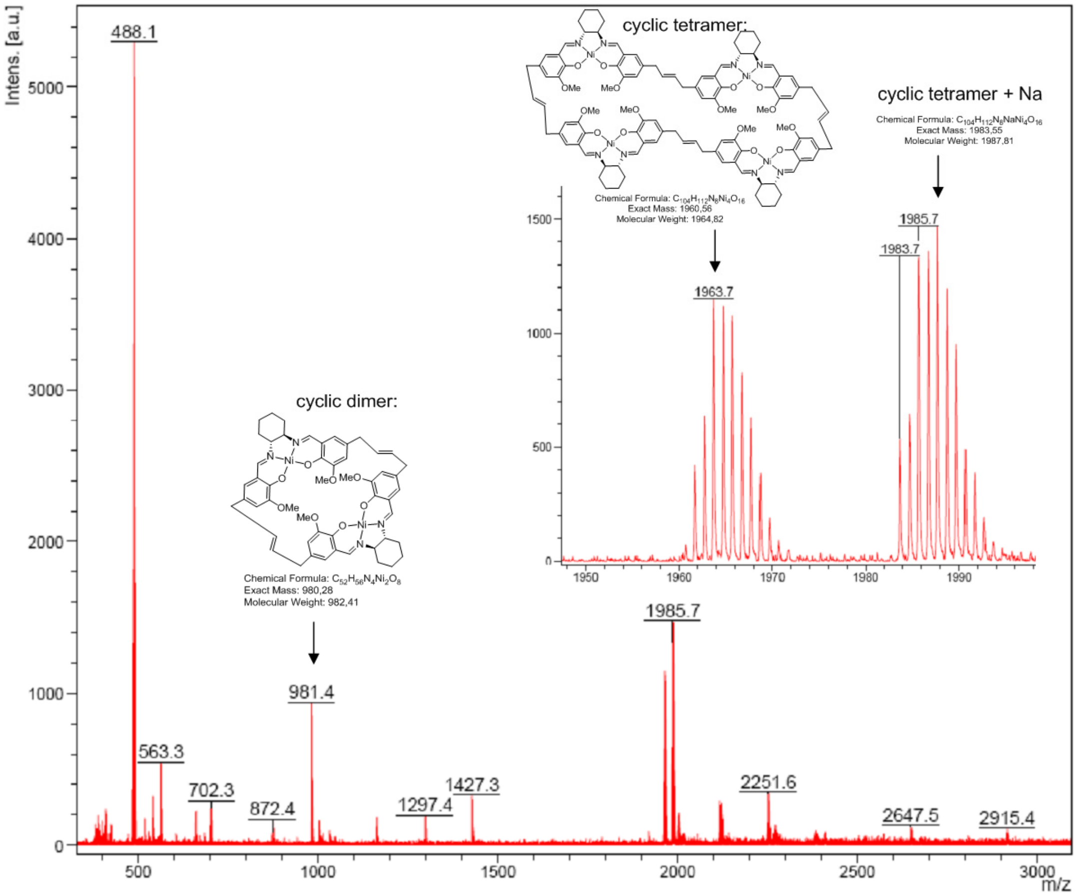
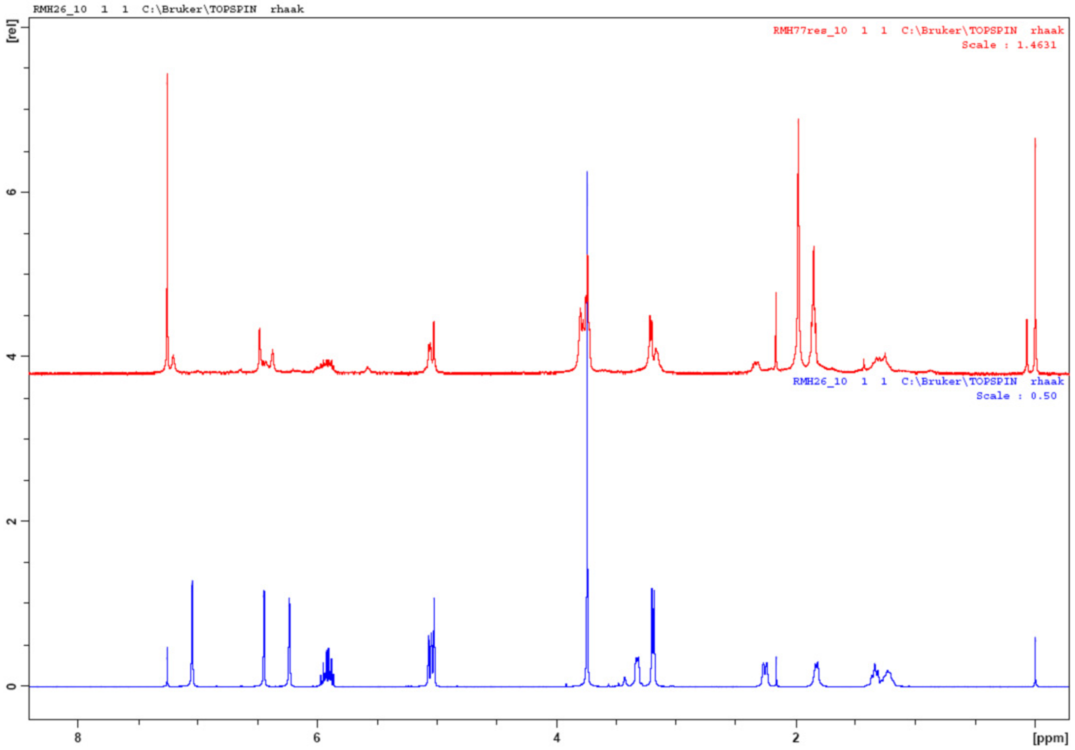


Table 2, entry 8

Scale 0.5 mmol, cat. **B** (3 mol%), DCM / THF 1:4, 20 mM, 3 h, >95% conv.

^{1}H NMR of starting material (±)-**19** (below) and product (above):



MS (MALDI+) of the product mixture:

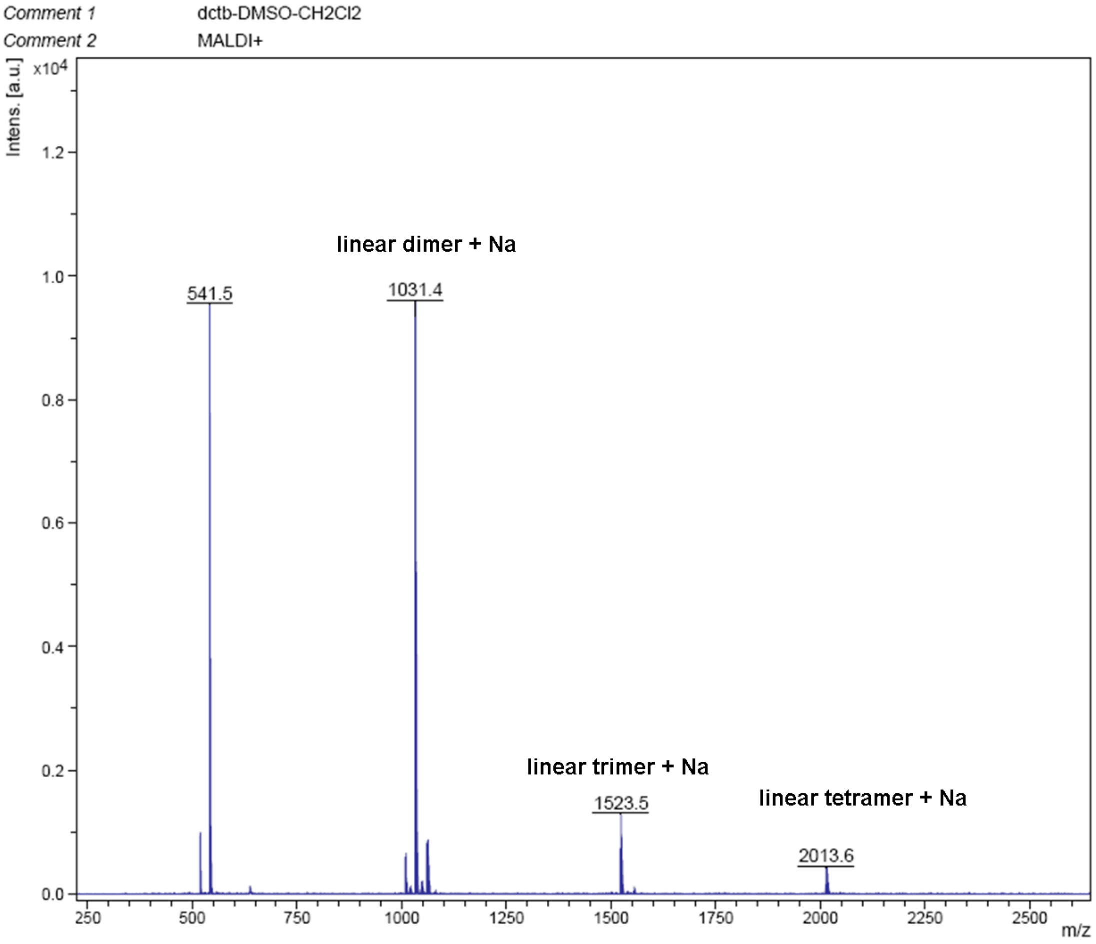
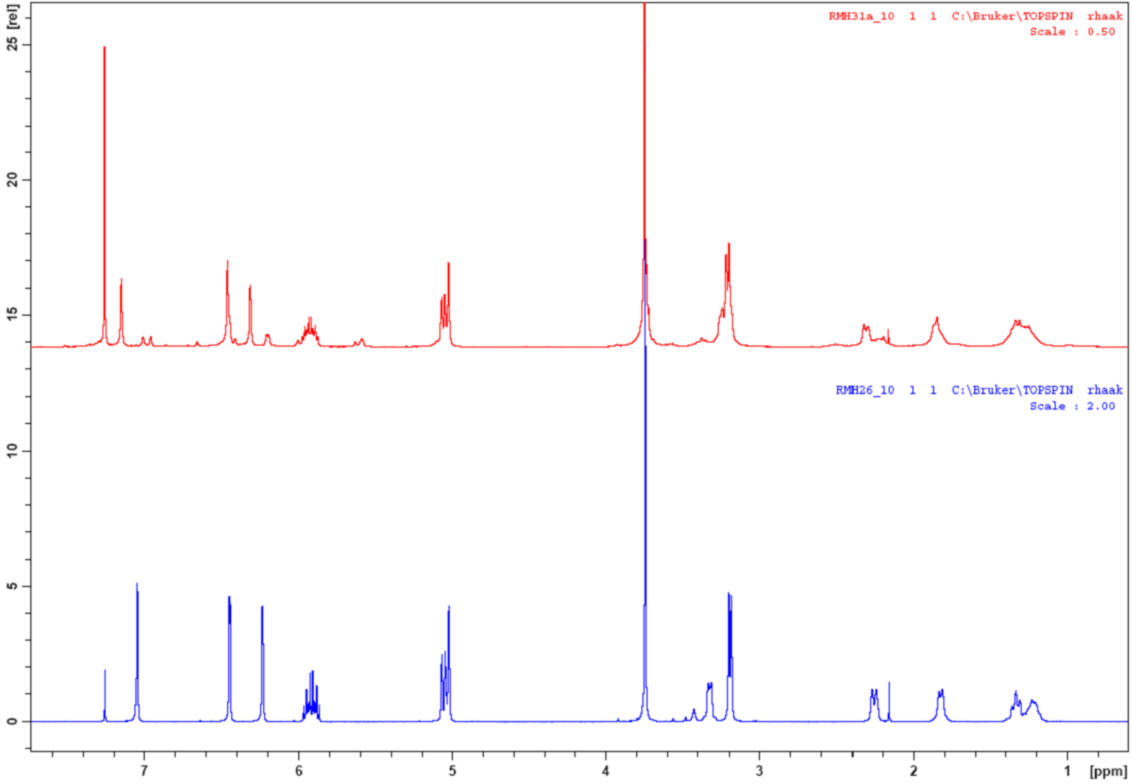


Table 2, entry 9

Scale 0.1 mmol, cat. **C** (5 mol%), DCM, 100 mM, 96 h, 21% conv.

^{1}H NMR of (±)-**19** (below) and product oligo-(±)-**19** (above):



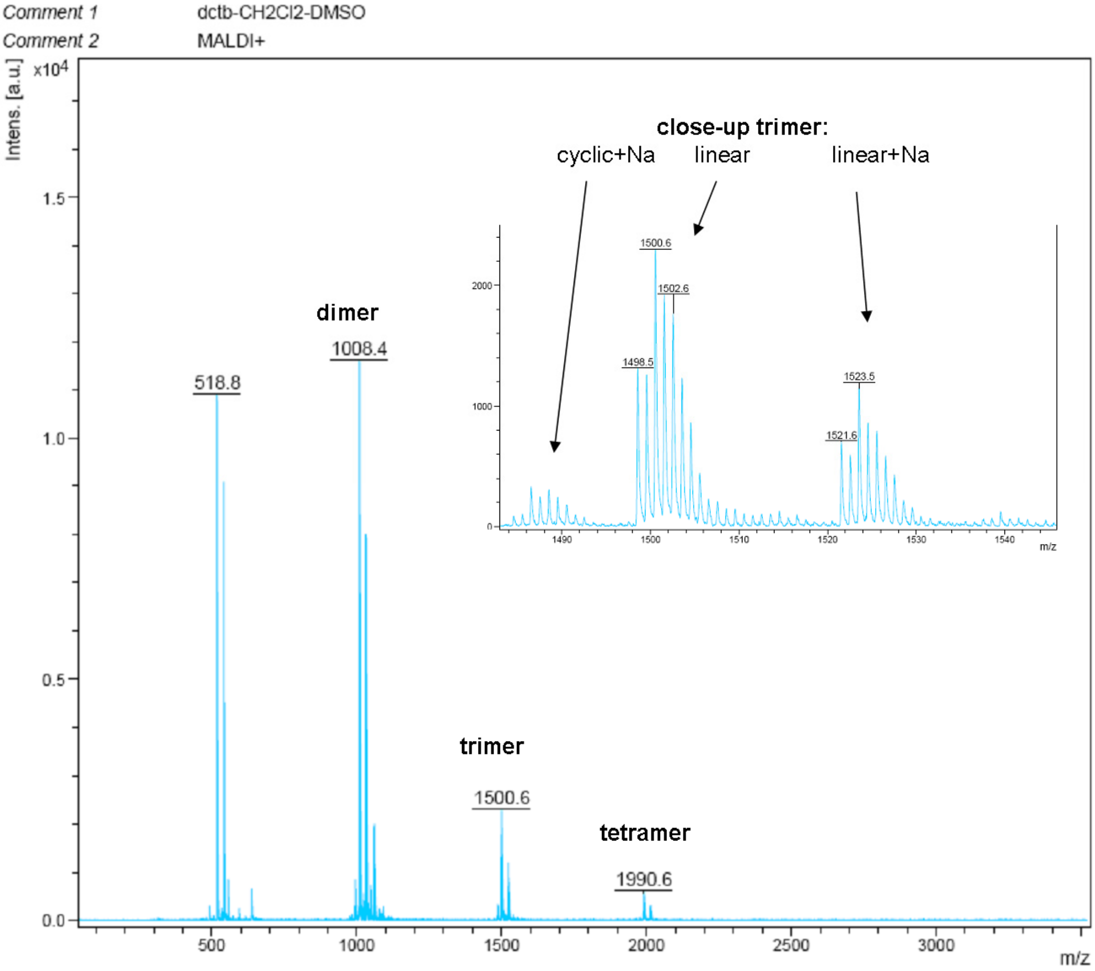
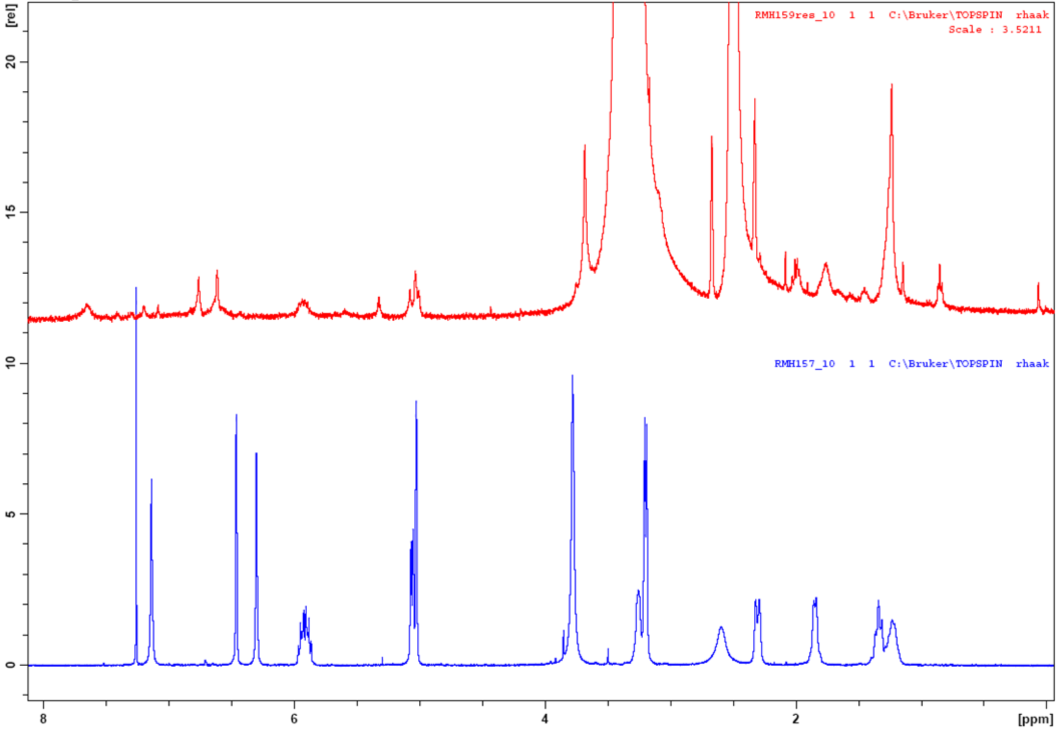


Table 2, entry 10

Scale: 0.05 mmol, cat. **B** (5 mol%), DCM, 25 mM, 24 h, >95% conv.

^{1}H NMR of starting material (*R*,*R*)-**19** (below) and product oligo-(*R*,*R*)-**19** (above):



MS (MALDI+) of the product mixture containing dimer, trimer, and tetramers:

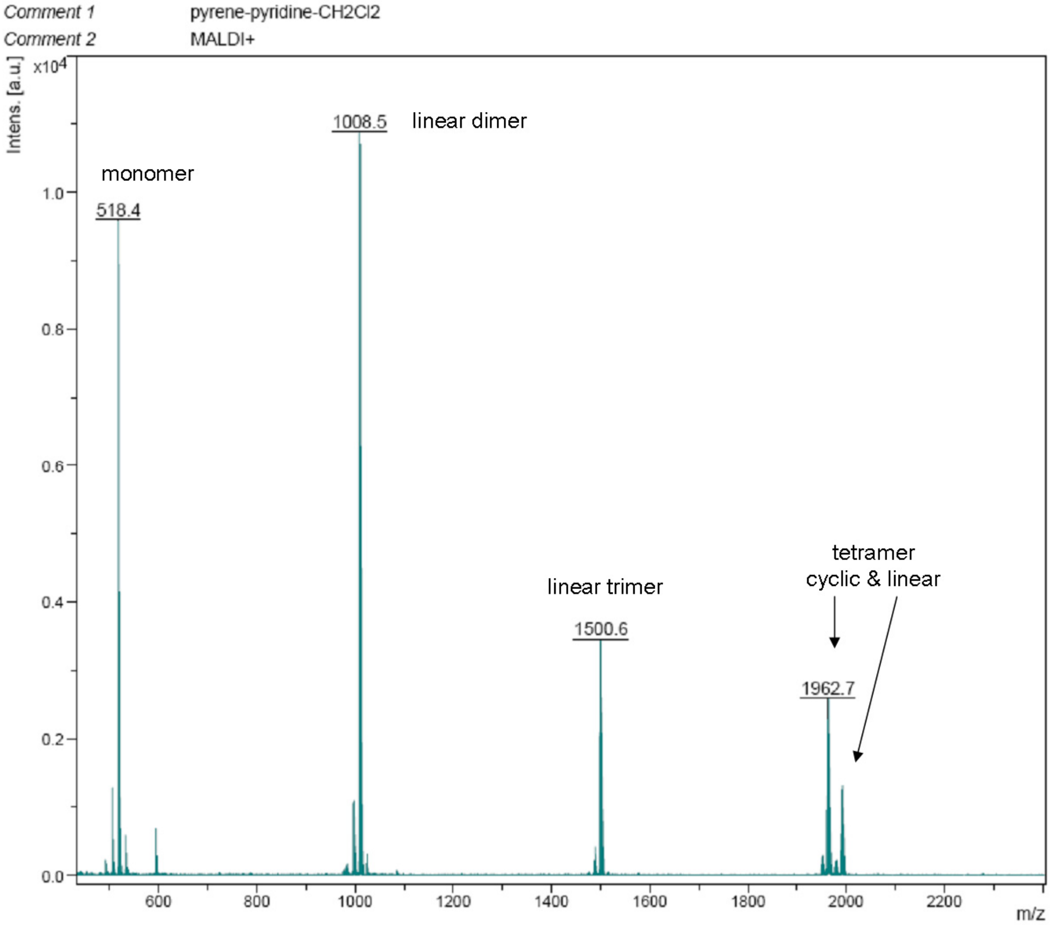
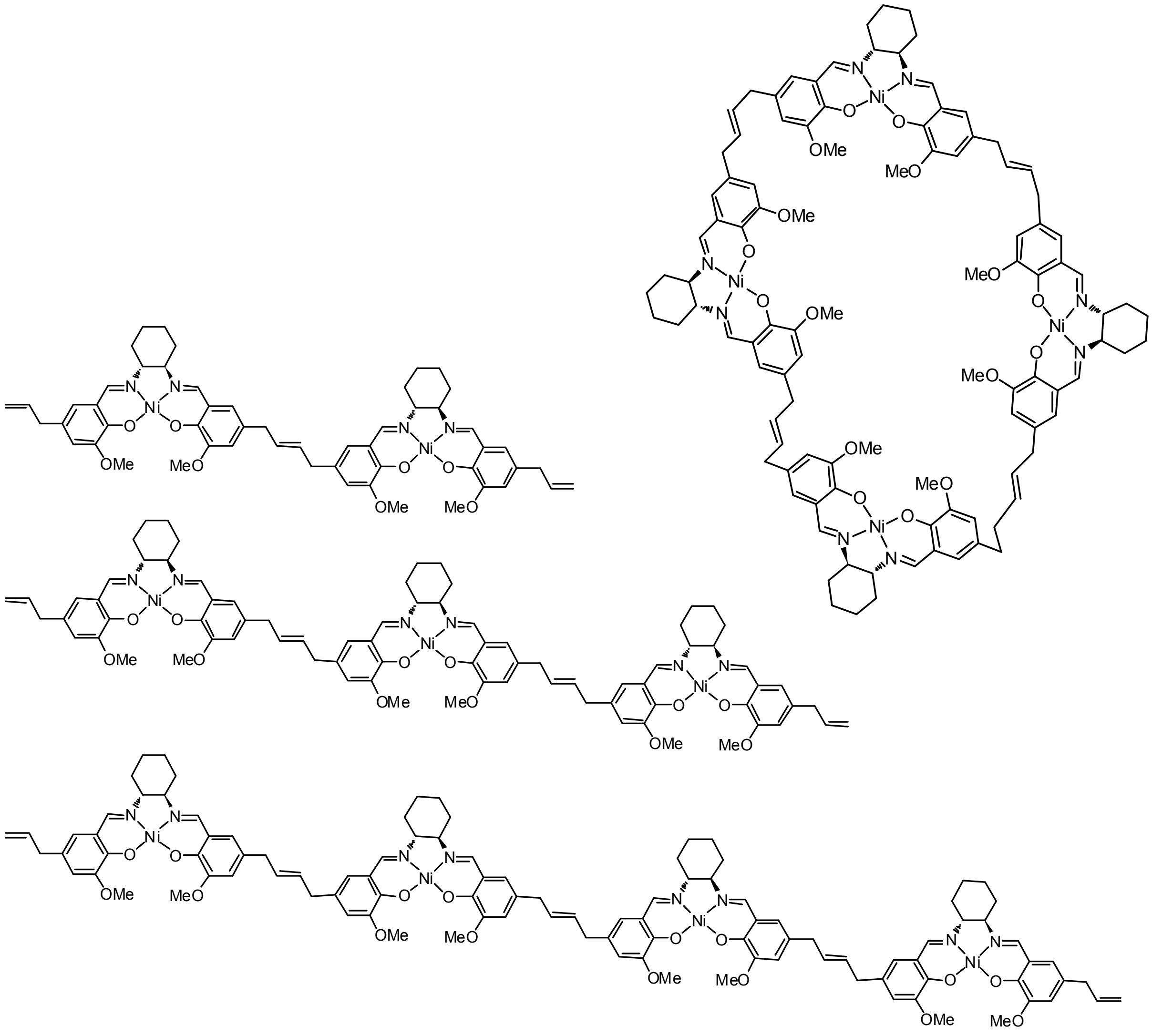


Table 2, entry 10 (contd.)



CD spectra of (*R*,*R*)-**19** (pink) and oligo-(*R*,*R*)-**19** (blue) in DCM ($1.0 \cdot 10^{-4}$ M):

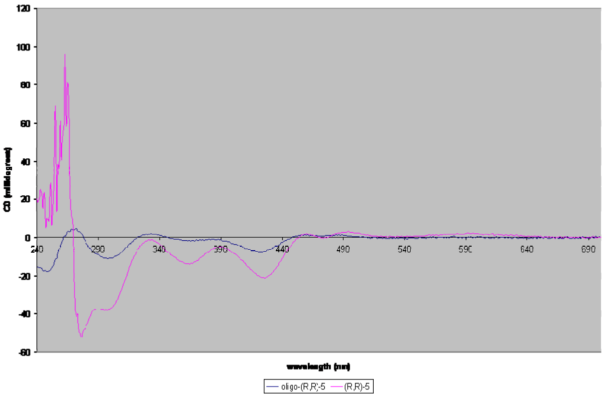
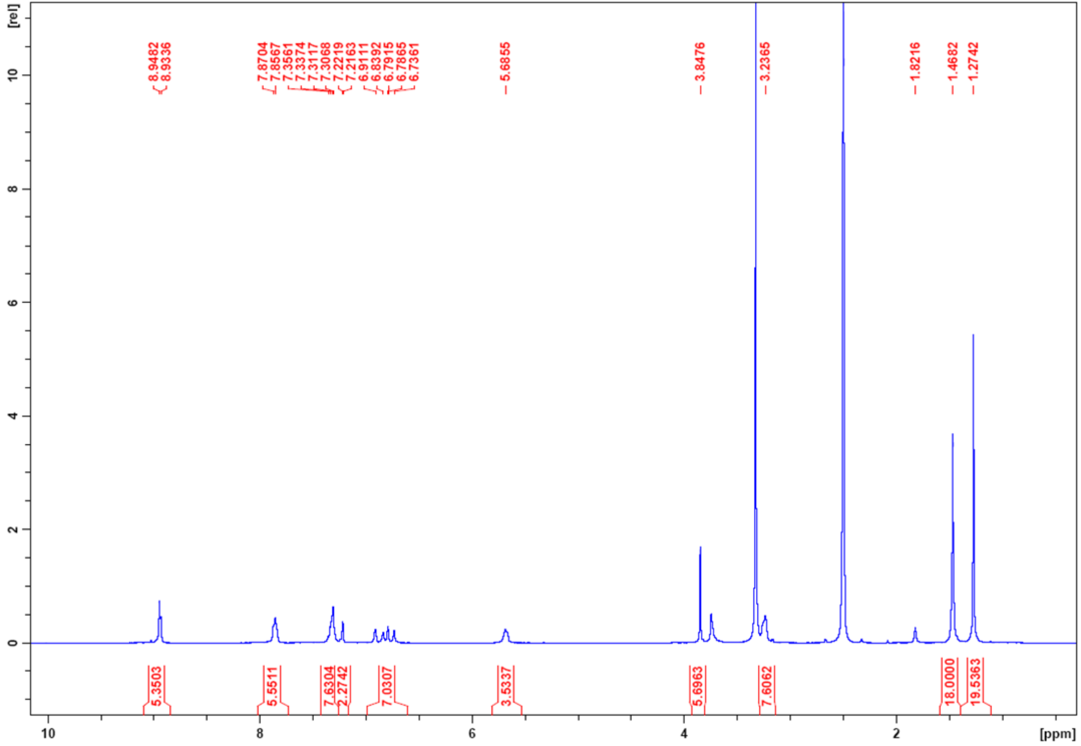


Table 3

^{1}H NMR and MS of starting material di-**4**.



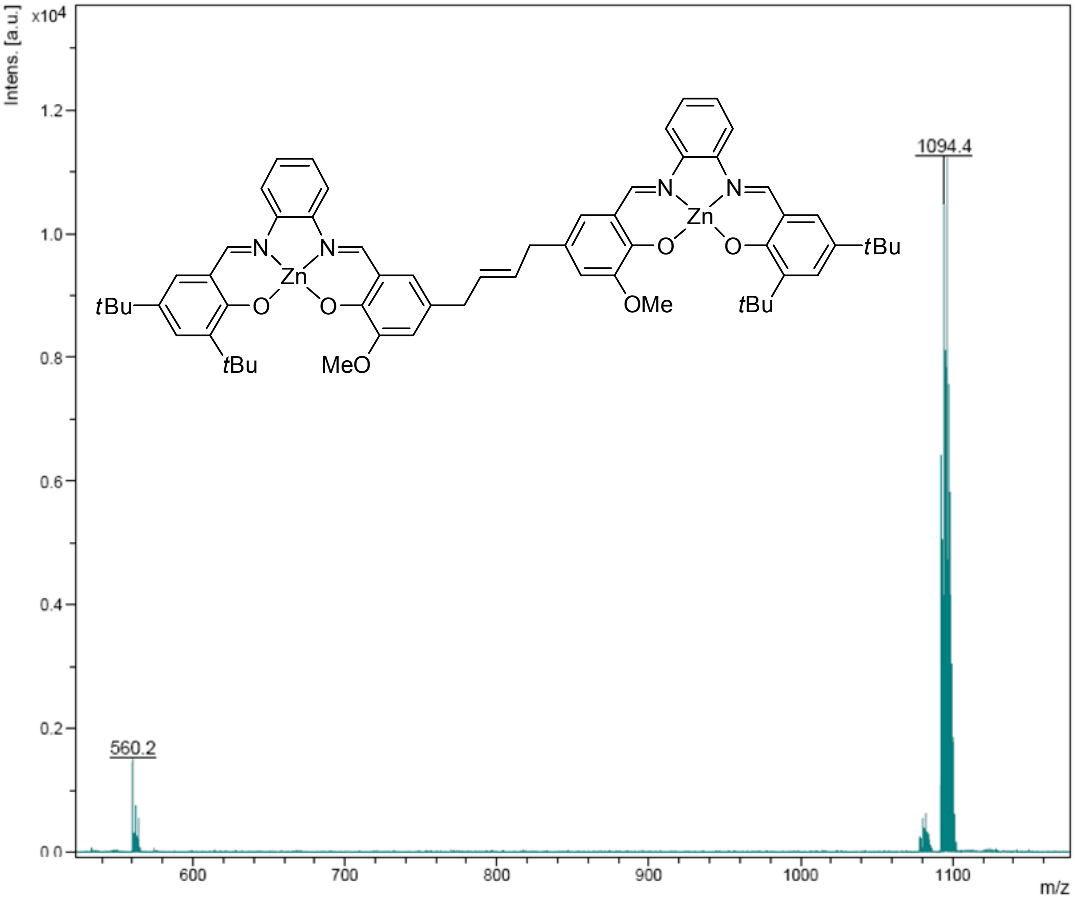
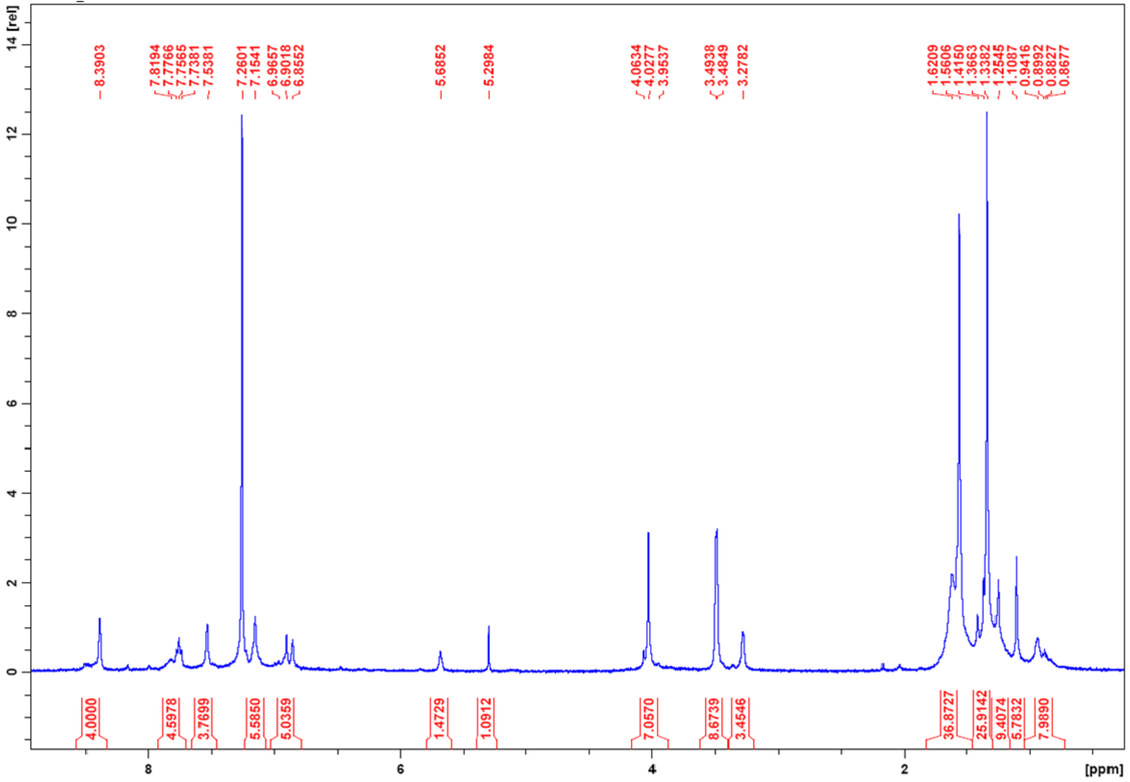


Table 3, entry 1



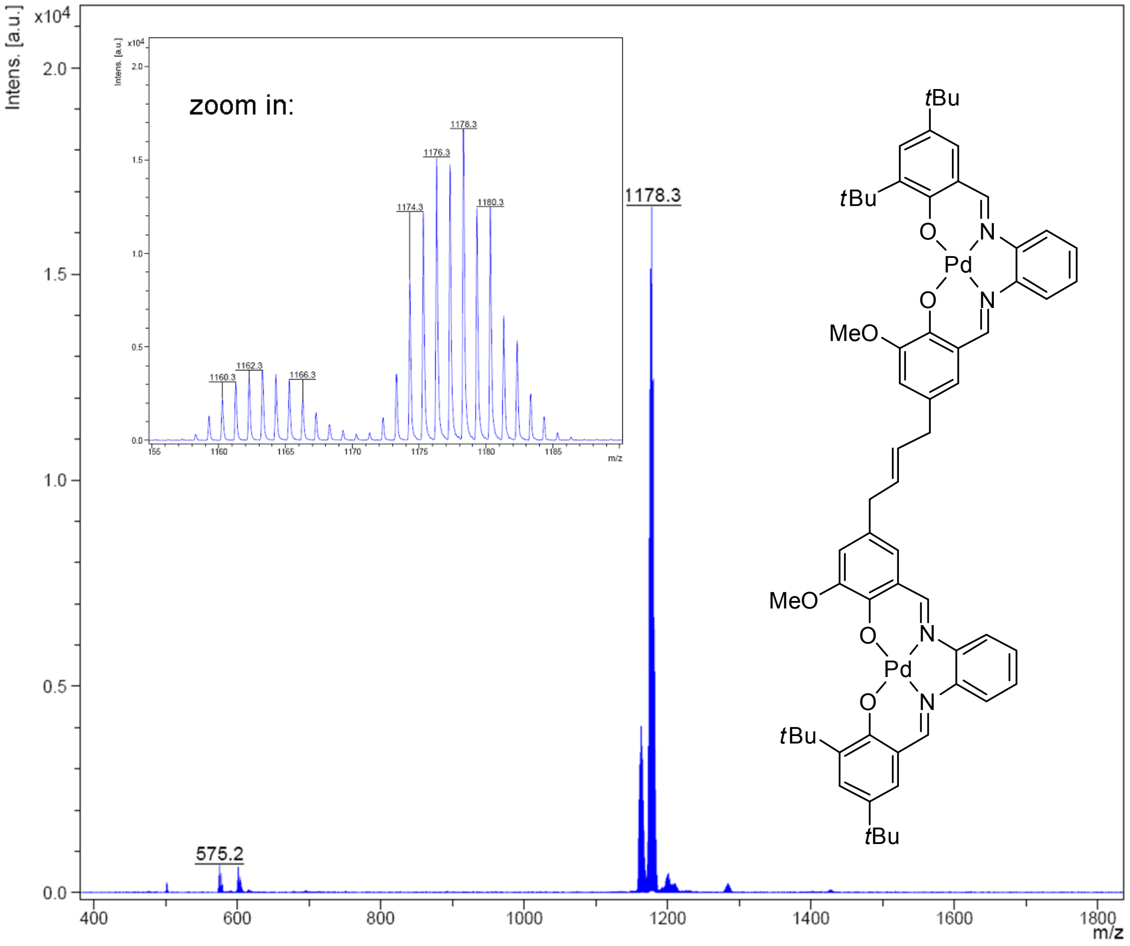
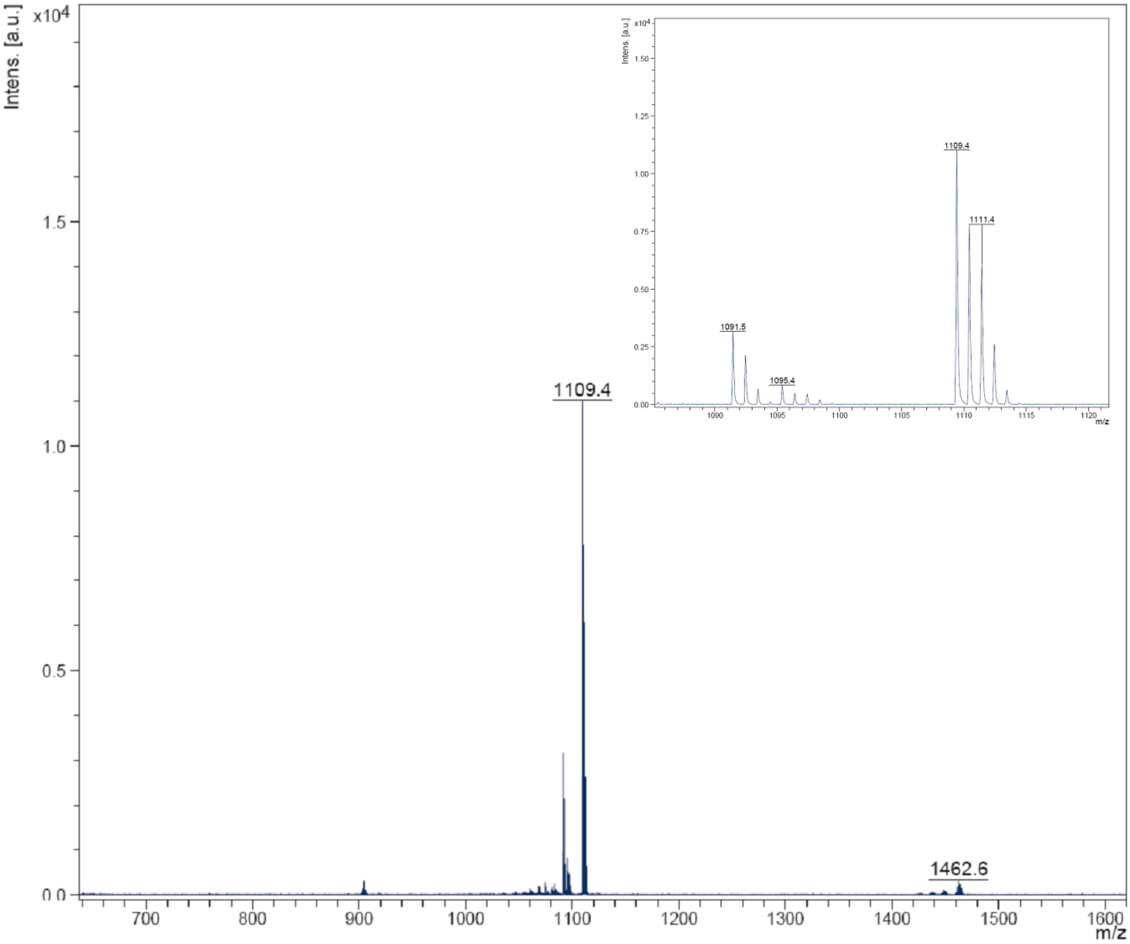


Table 3, entry 2



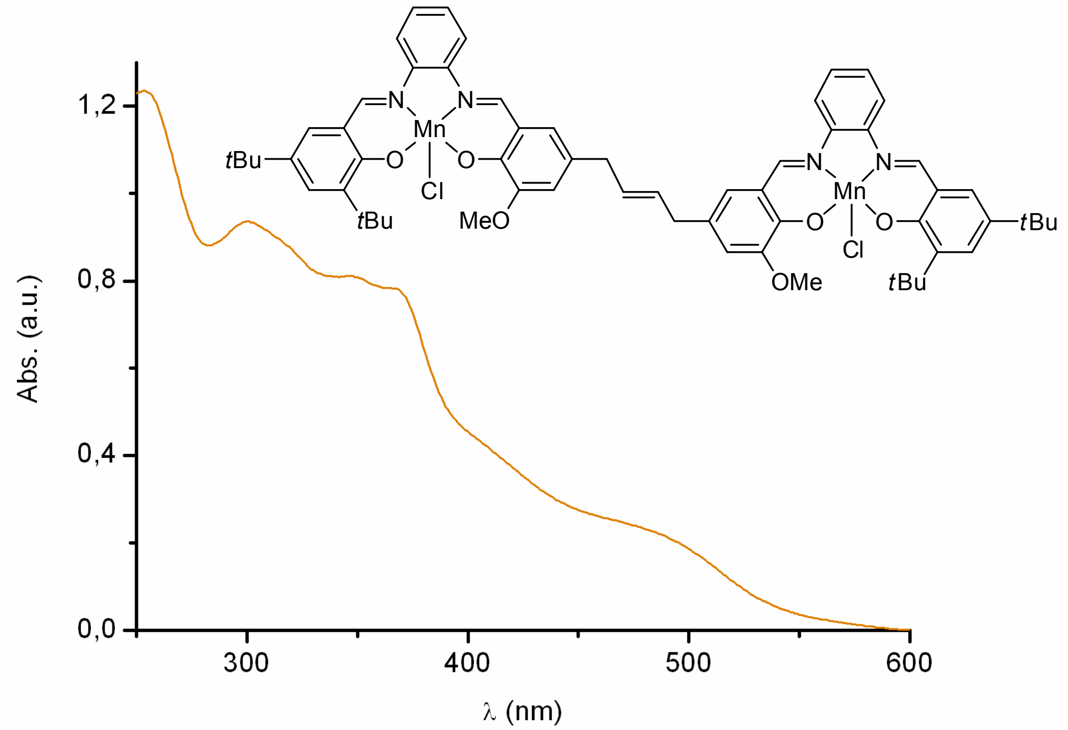
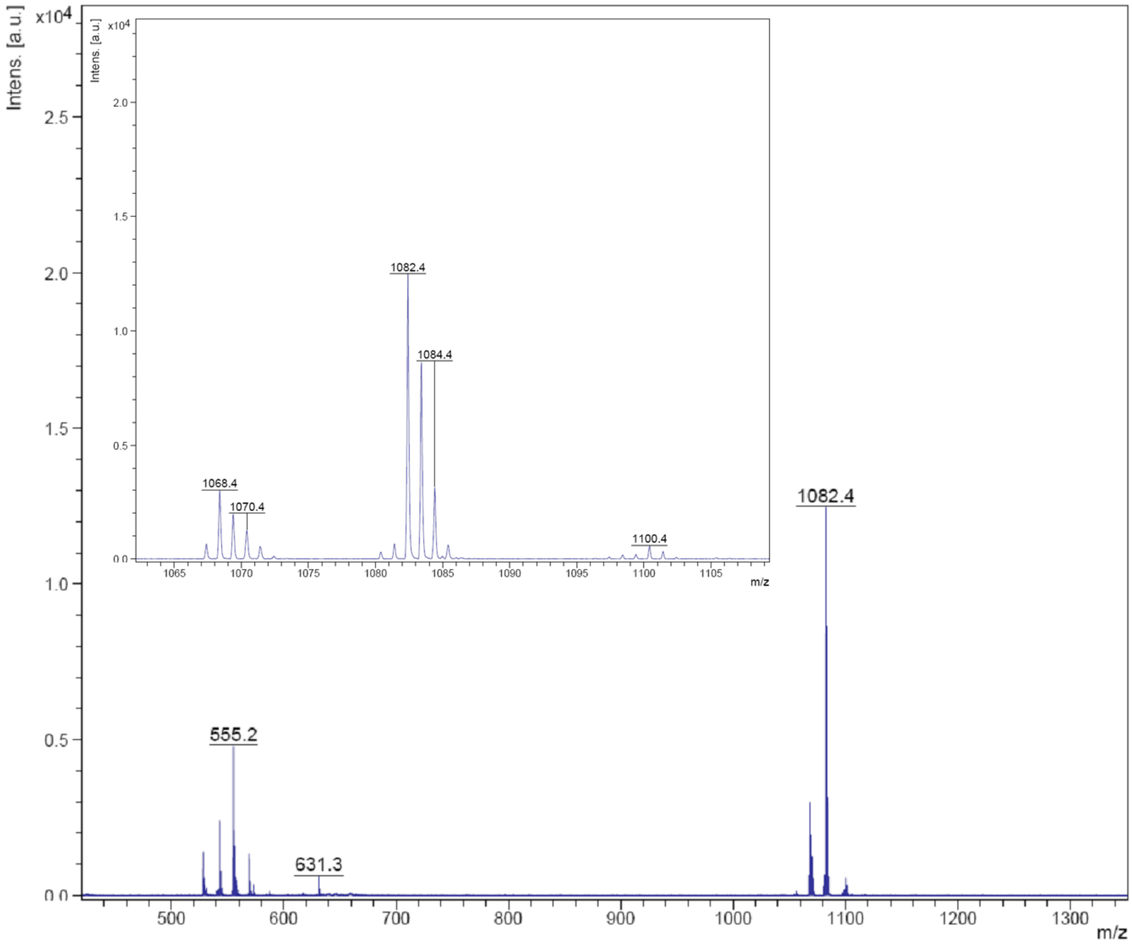


Table 3, entry 3



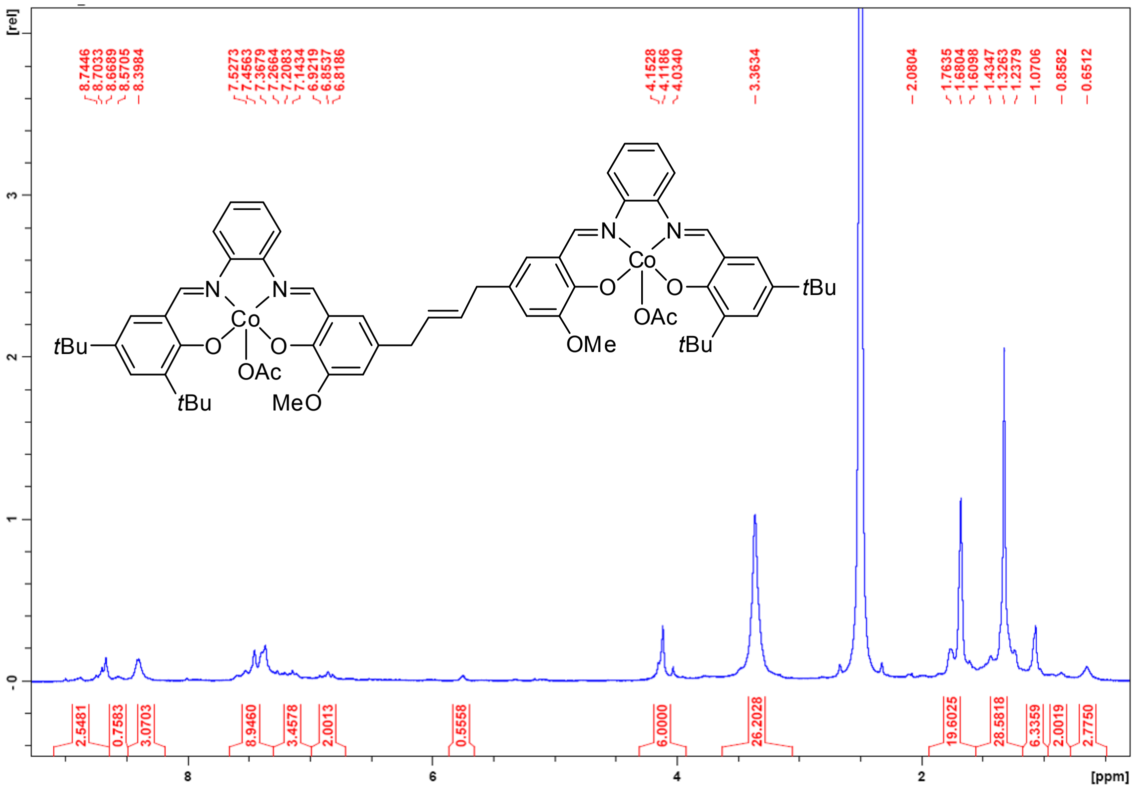
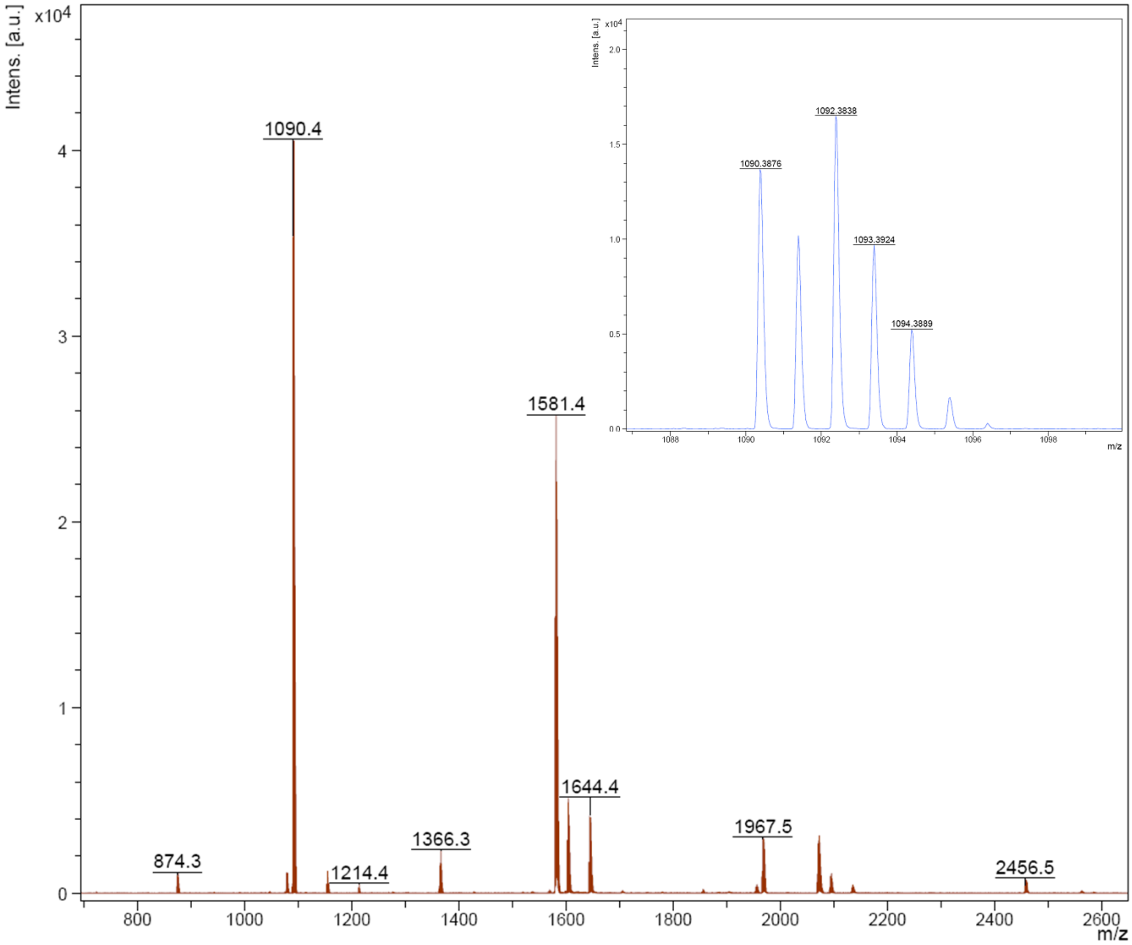


Table 3, entry 4



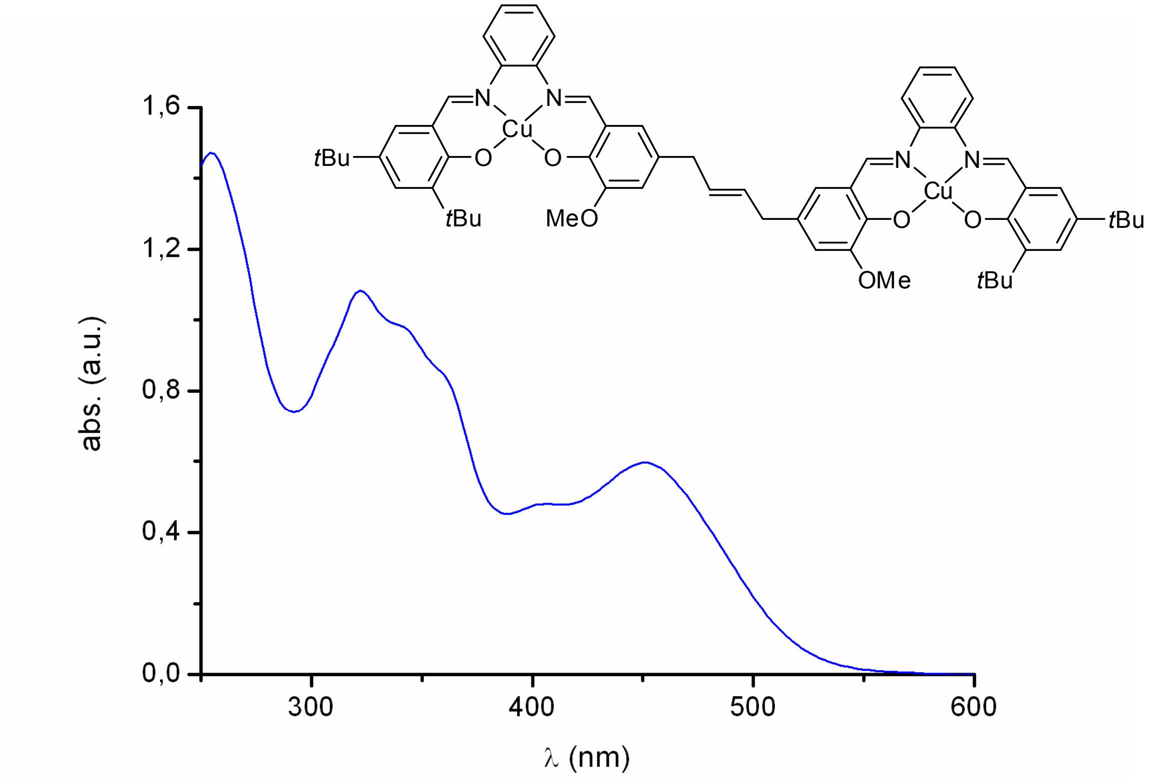
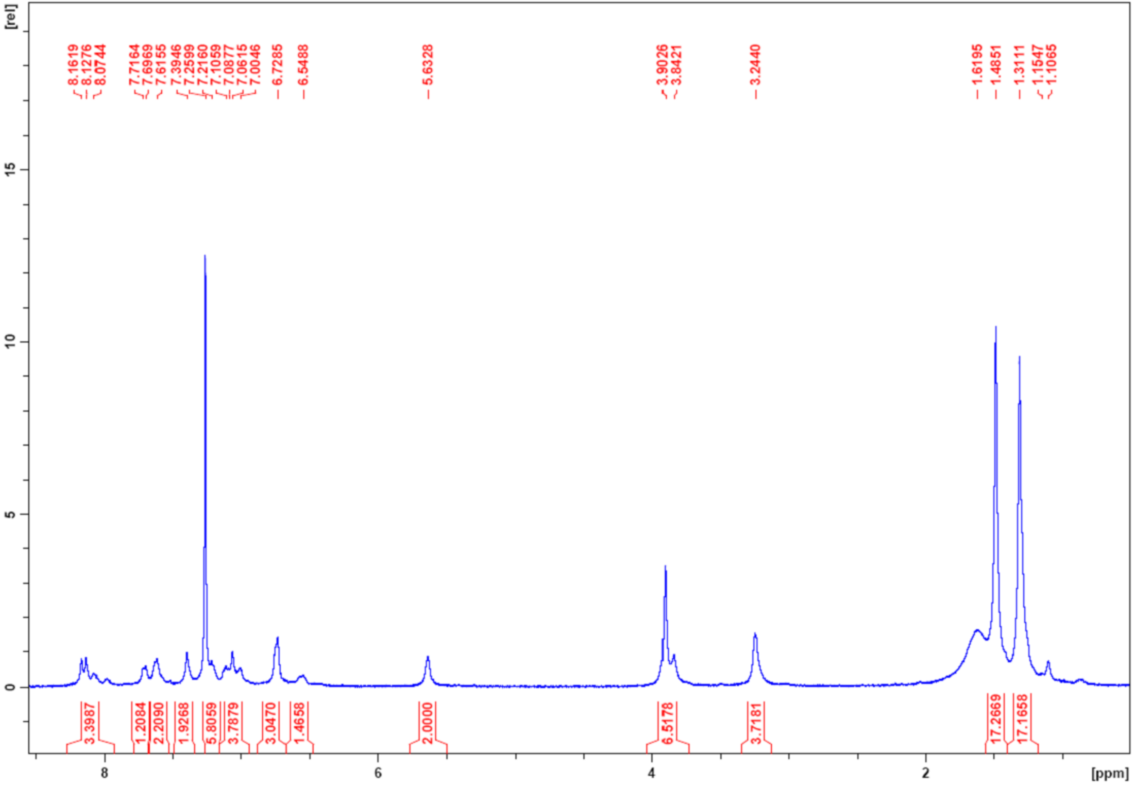
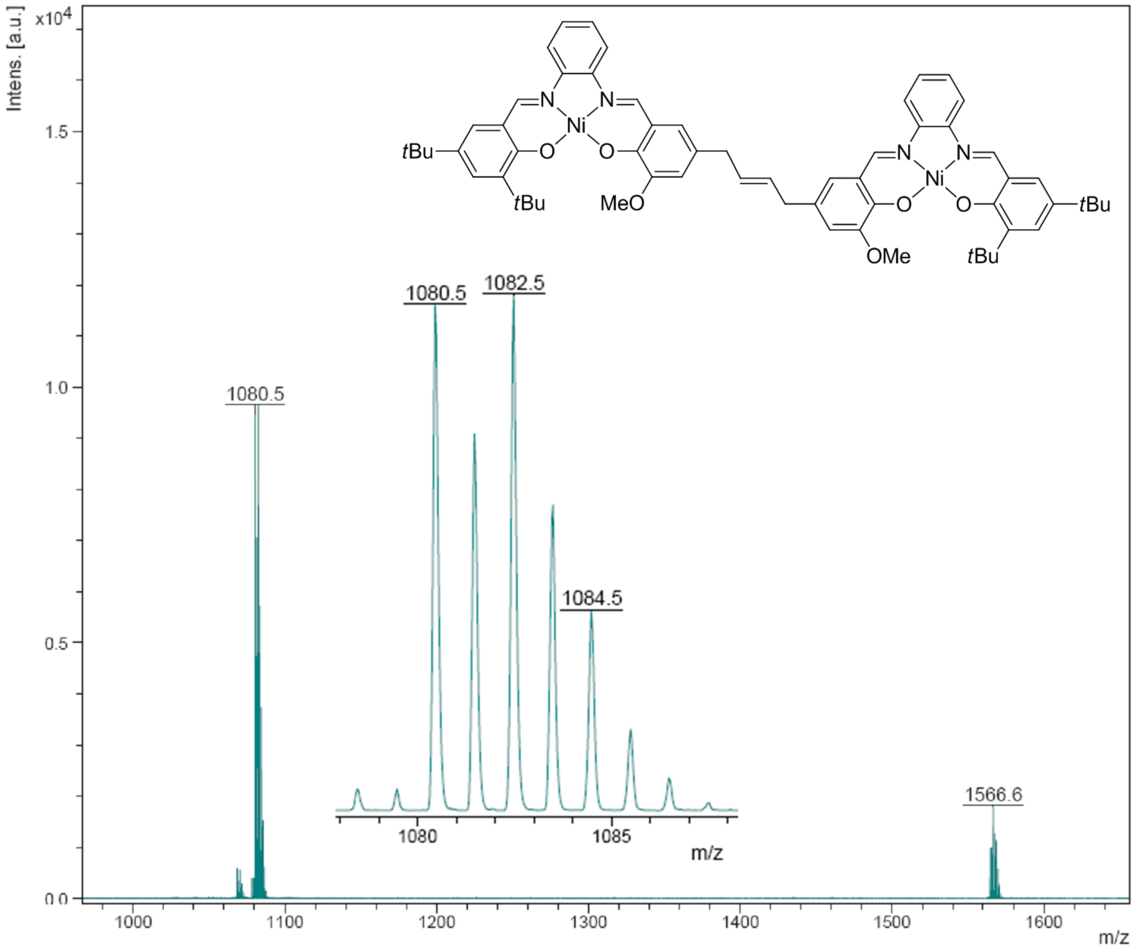
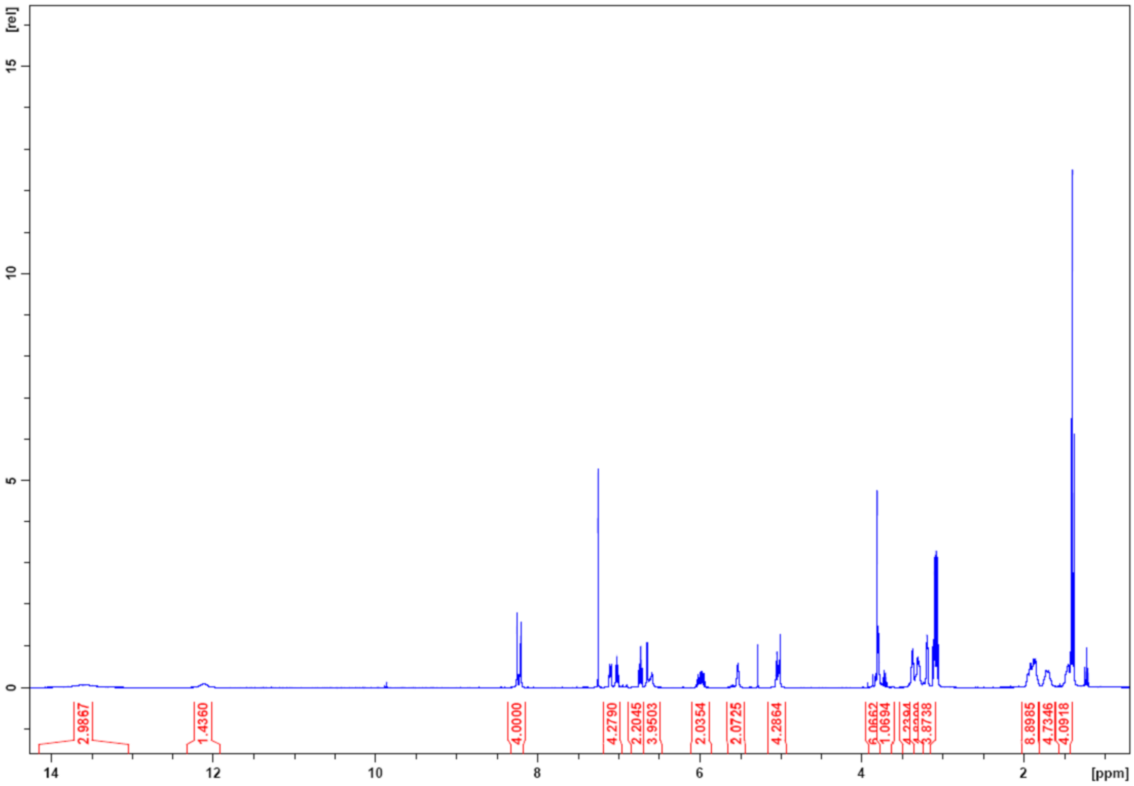


Table 3, entry 5

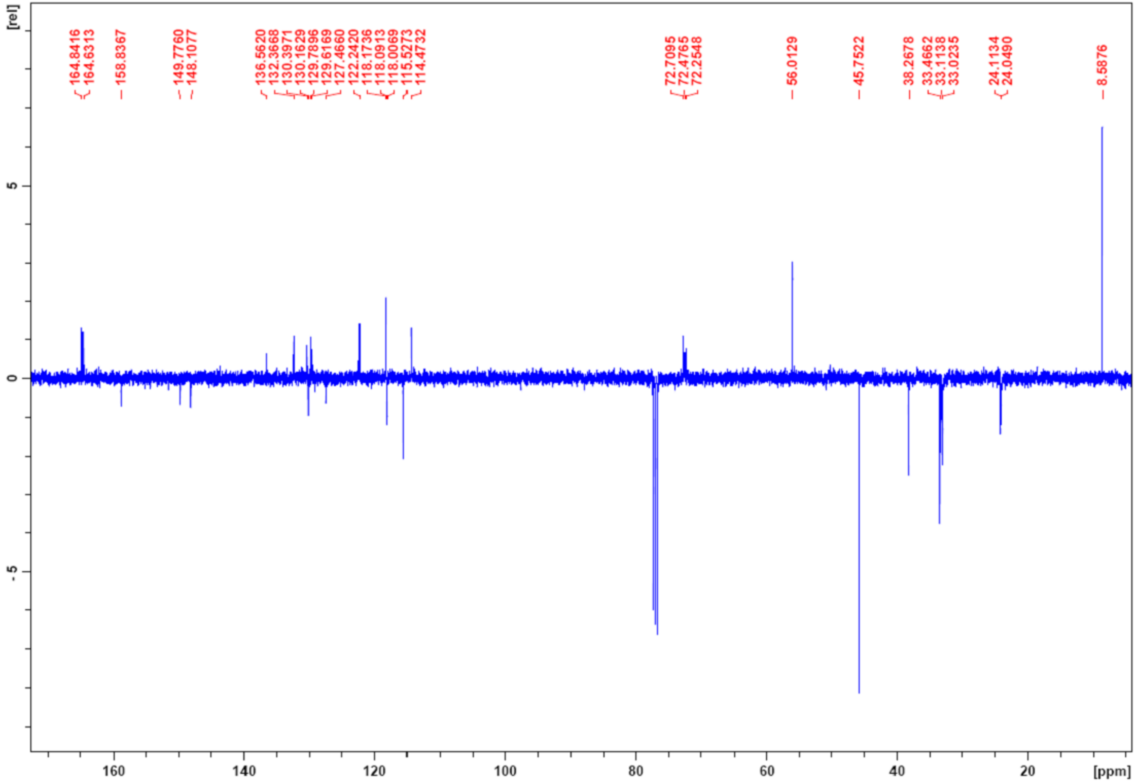




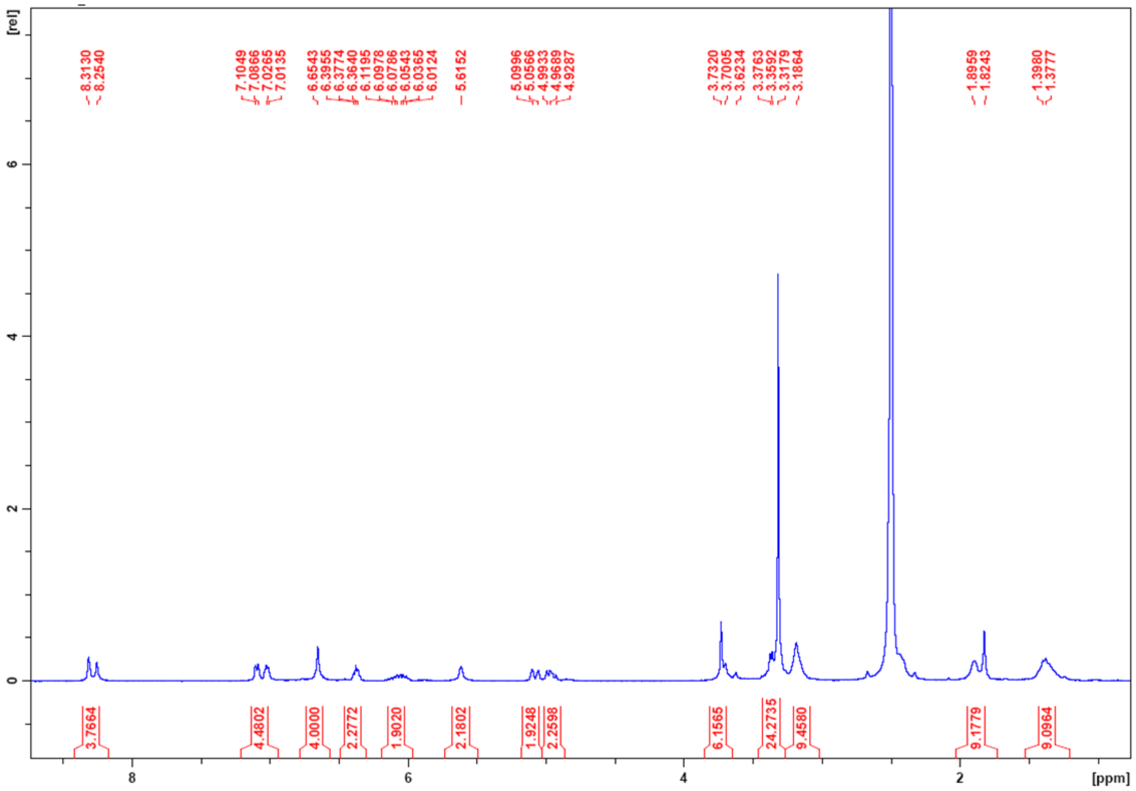
^{1}H NMR of **29**:



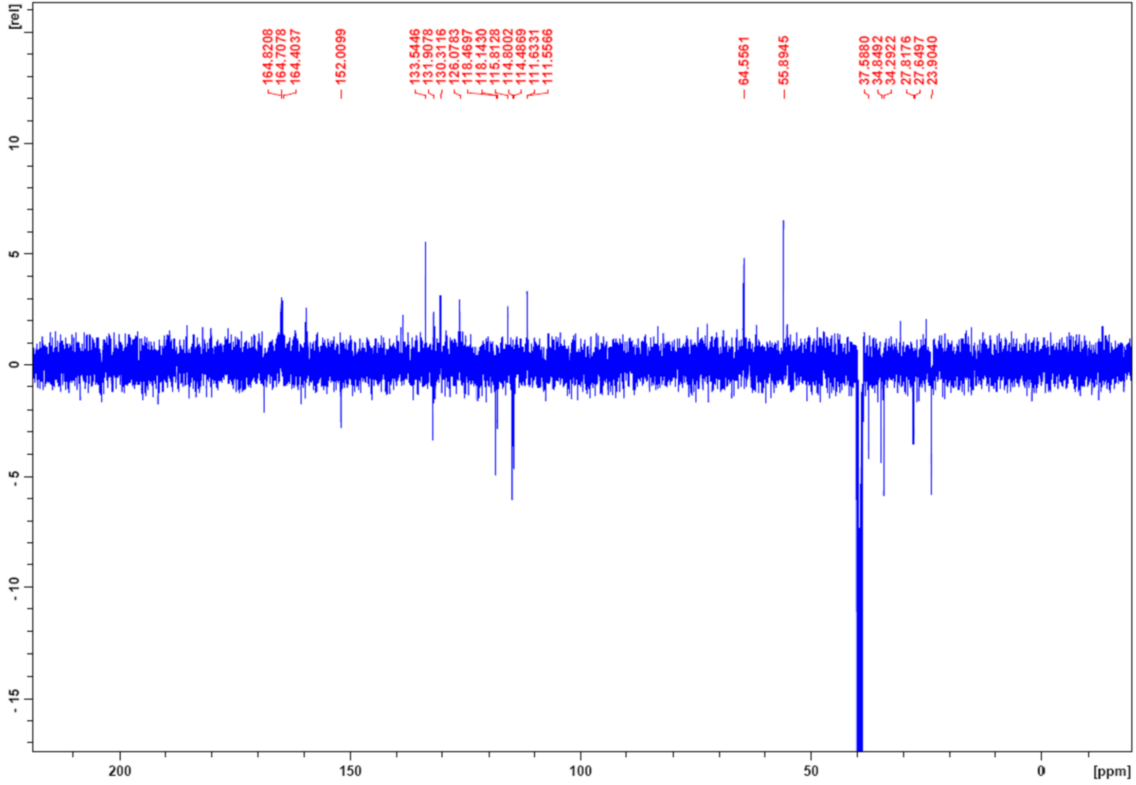
^{13}C NMR (DEPTQ) of **29**:



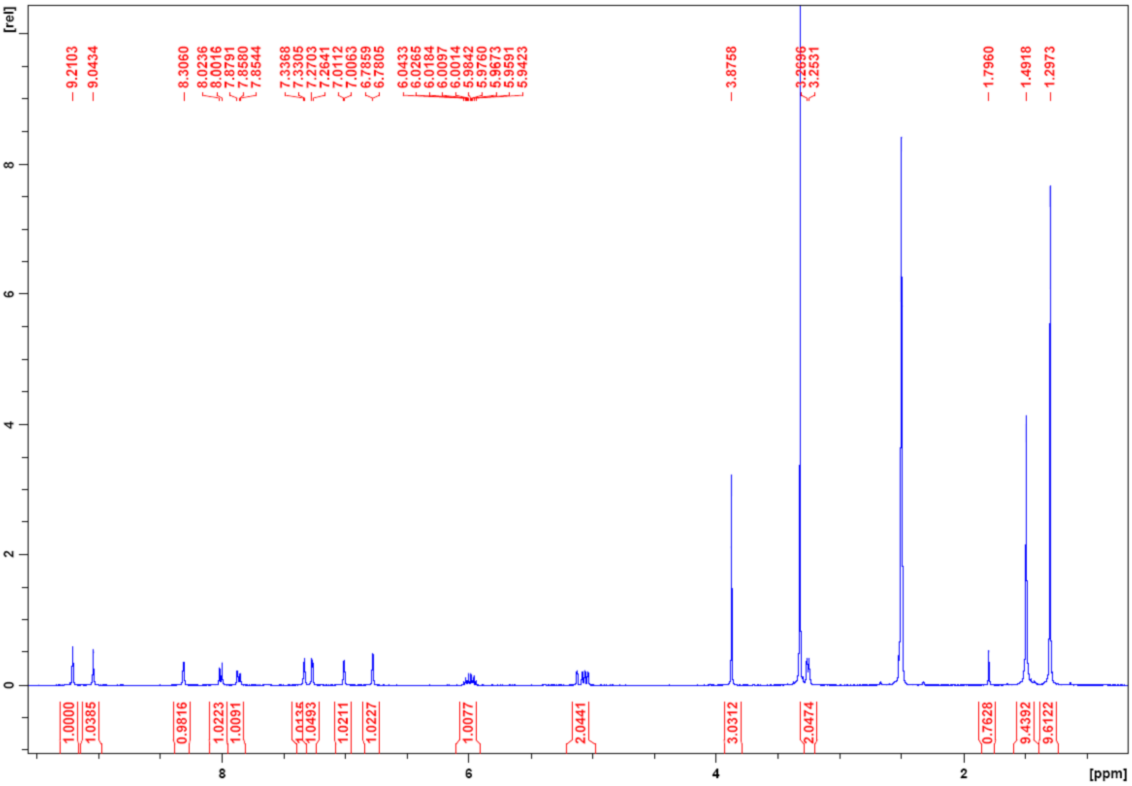
^{1}H NMR of **30**:



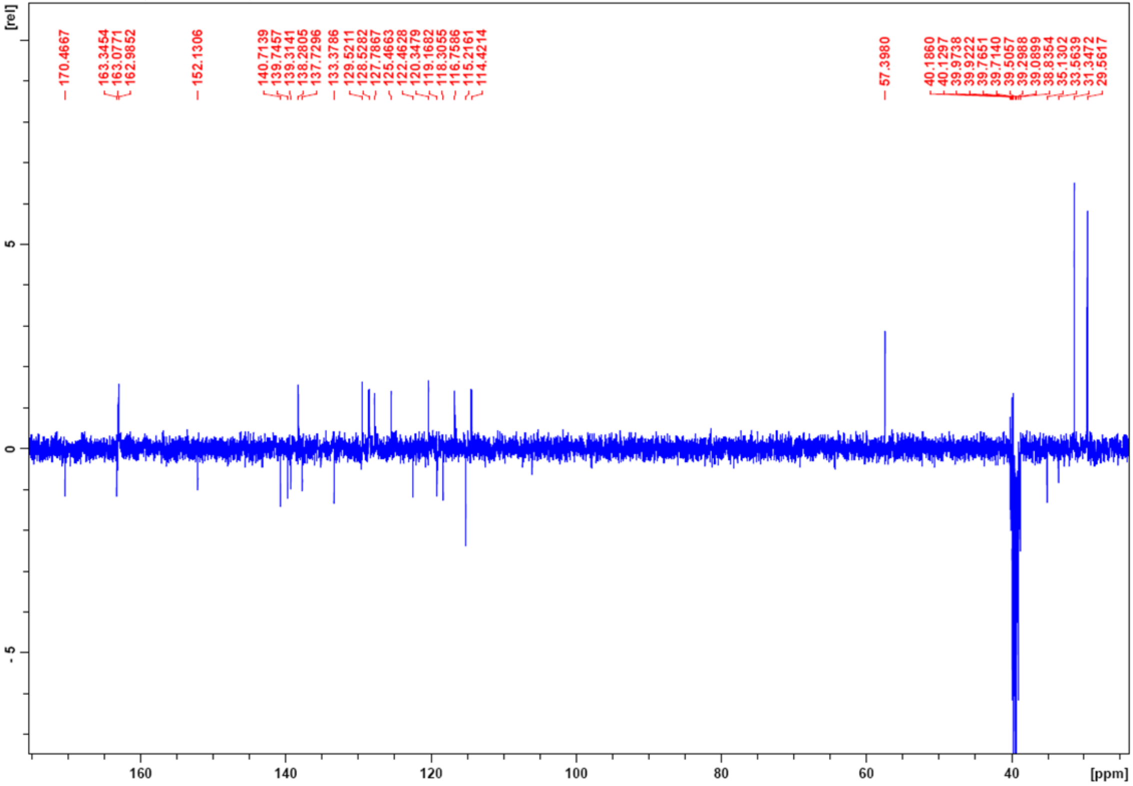
^{13}C NMR (DEPTQ) of **30**:



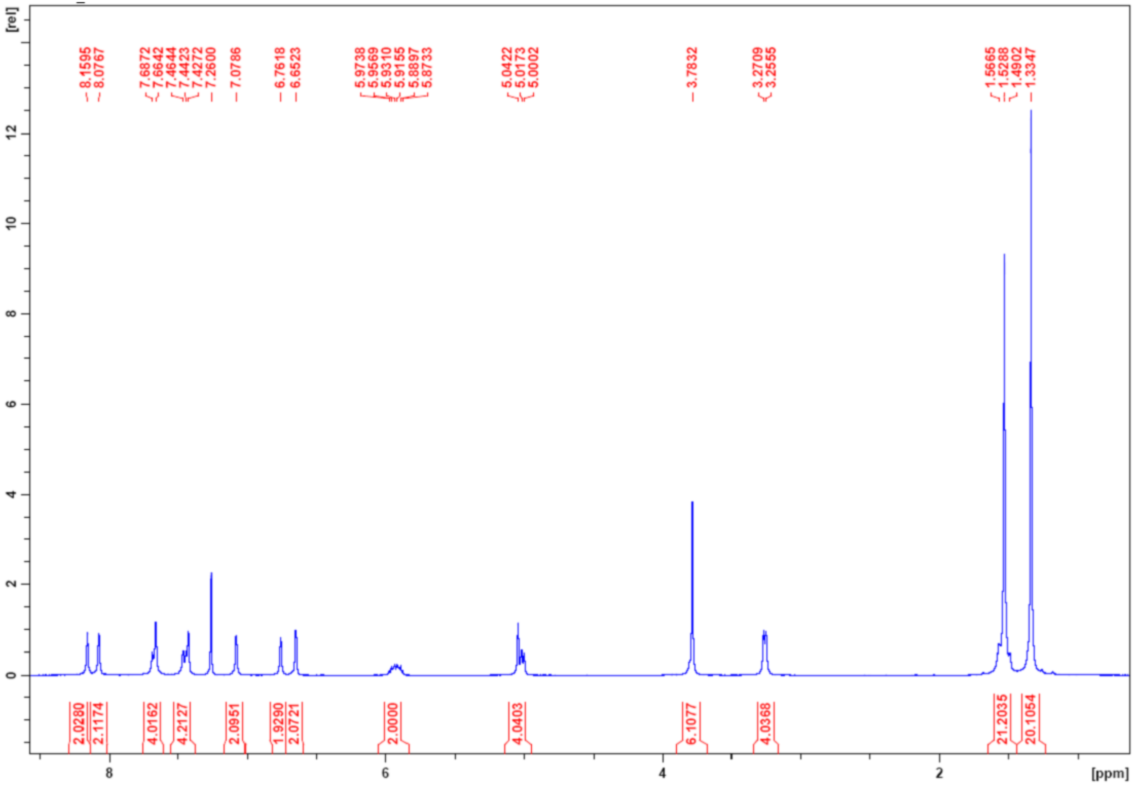
^{1}H NMR of **33**:



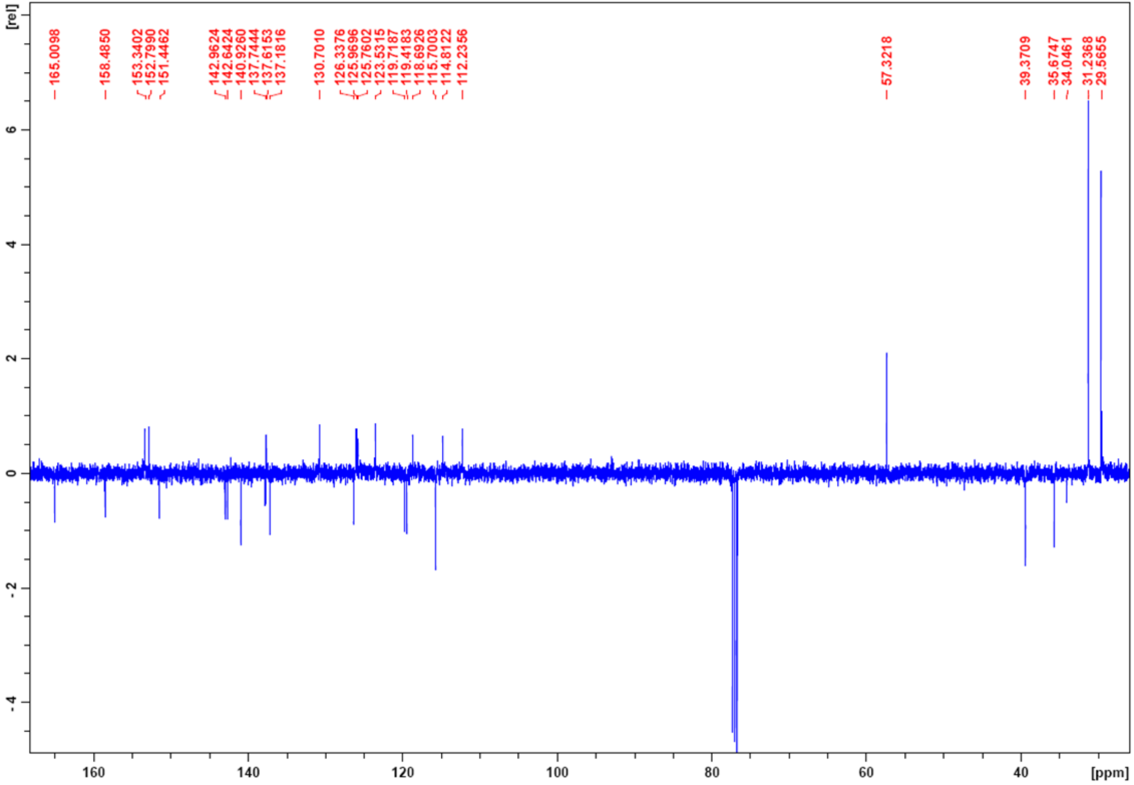
^{13}C NMR (DEPTQ) of **33**:



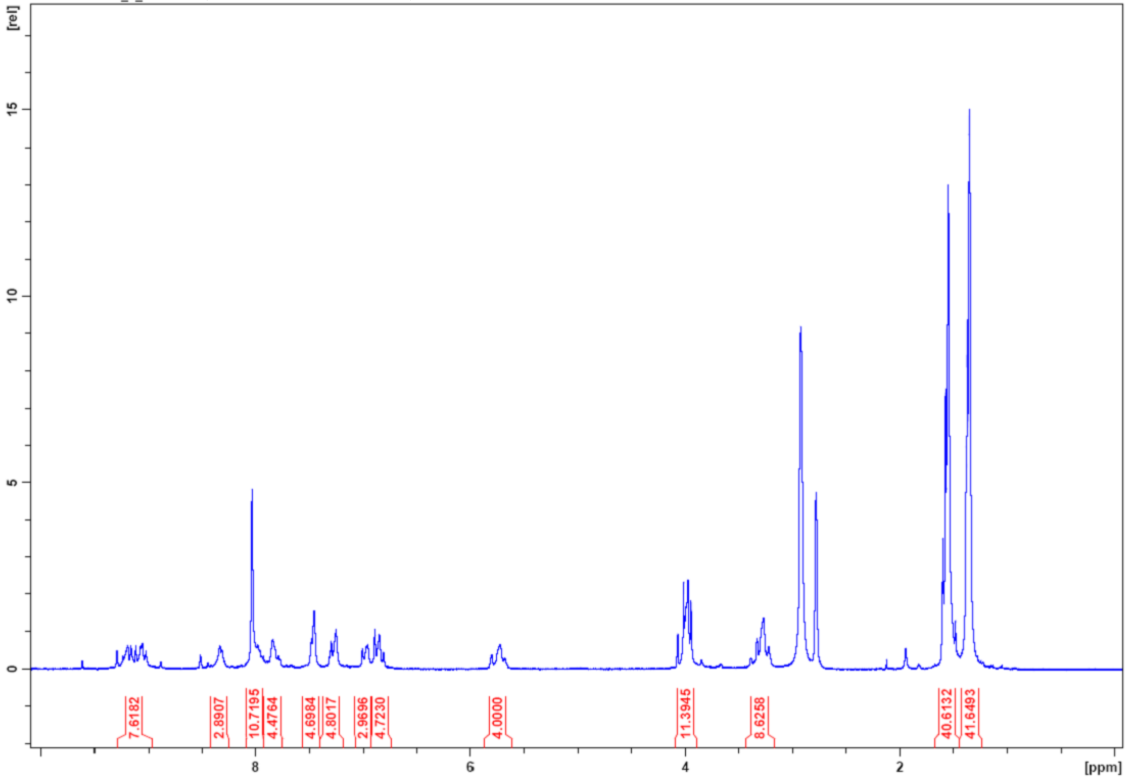
^{1}H NMR of **34**:



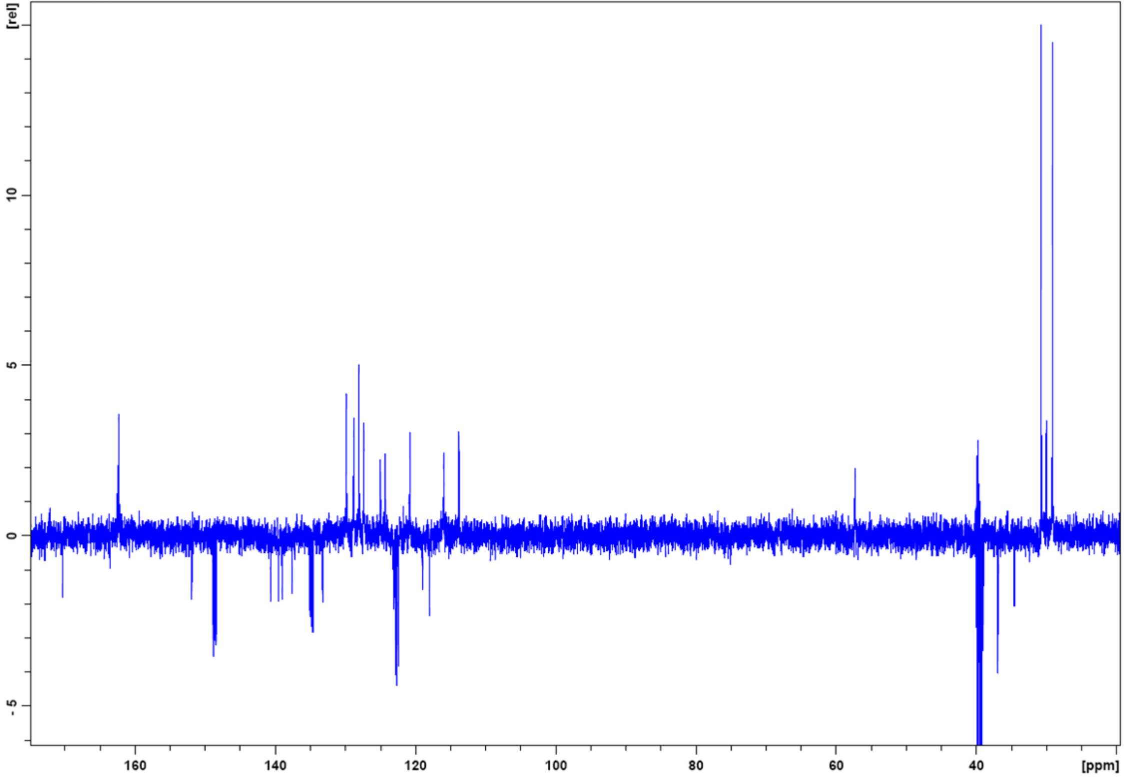
^{13}C NMR (DEPTQ) of **34**:



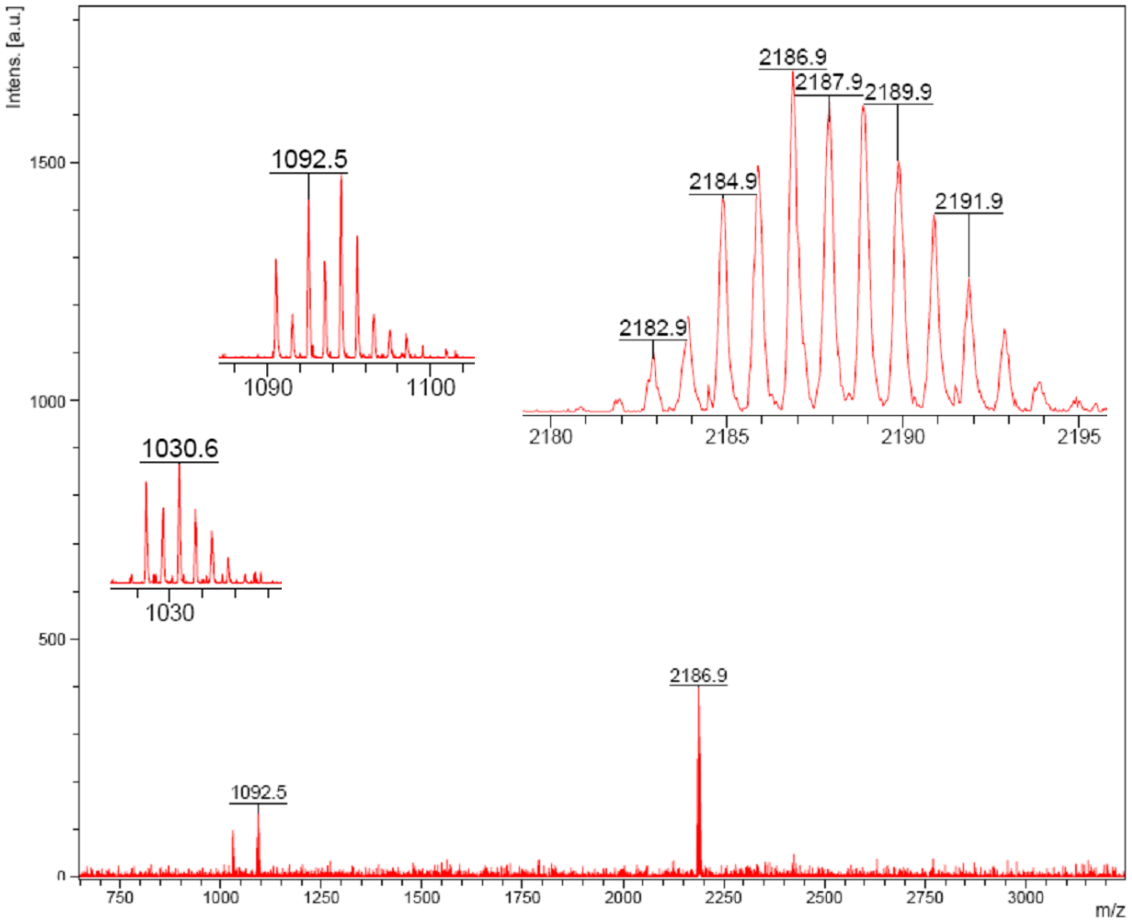
^{1}H NMR of **35** (DMF-d_7, 378 K):



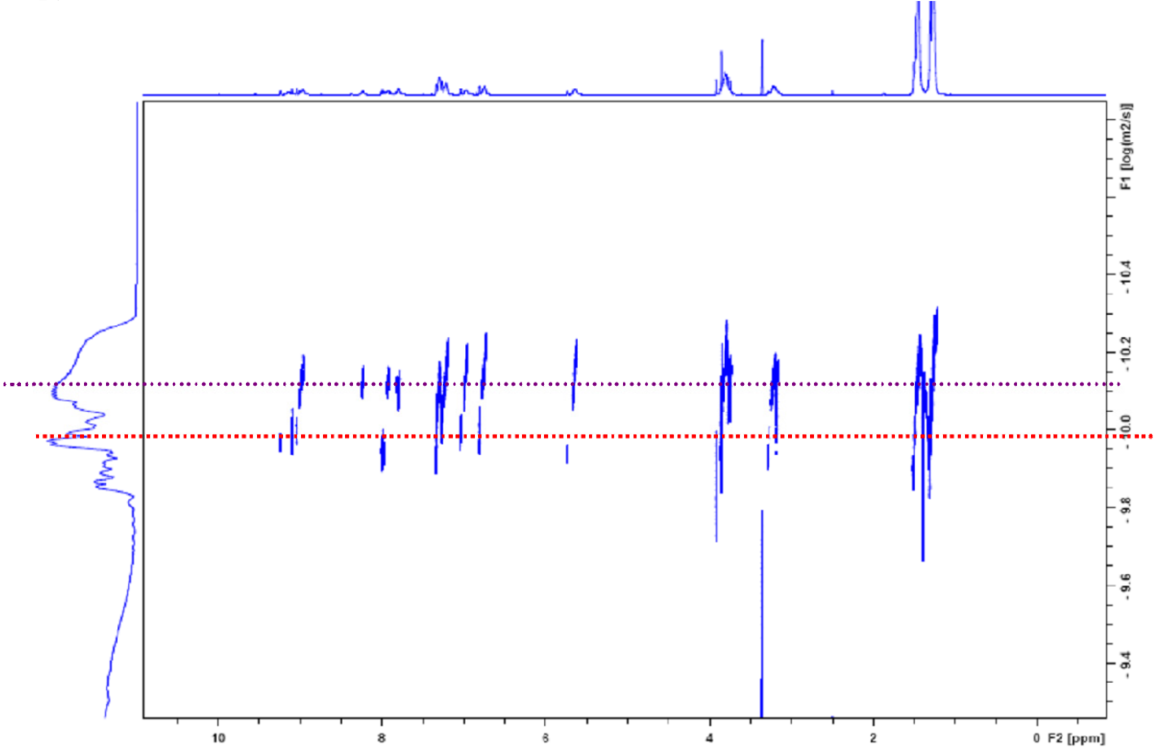
^{13}C NMR of **35** (DMSO-d_6 / pyridine-d_5 9:1, 378 K):



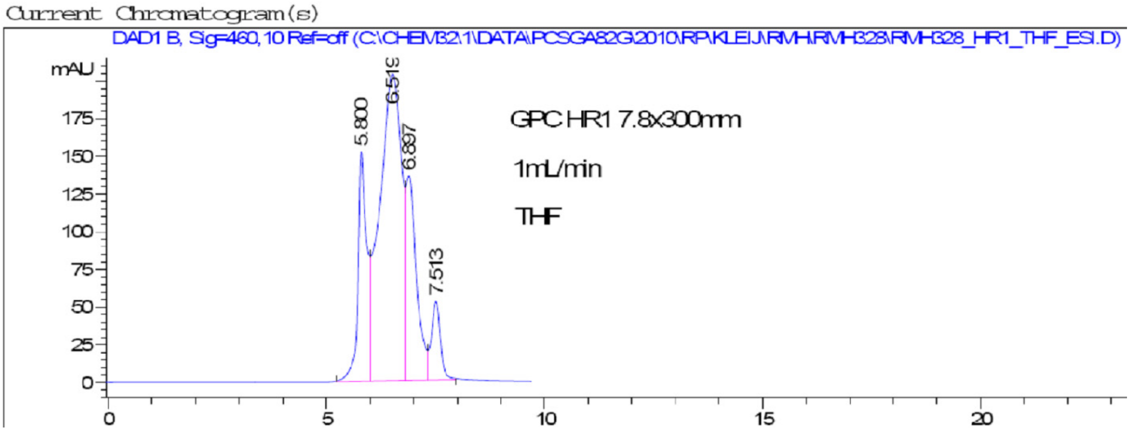
MS (MALDI) **35**:

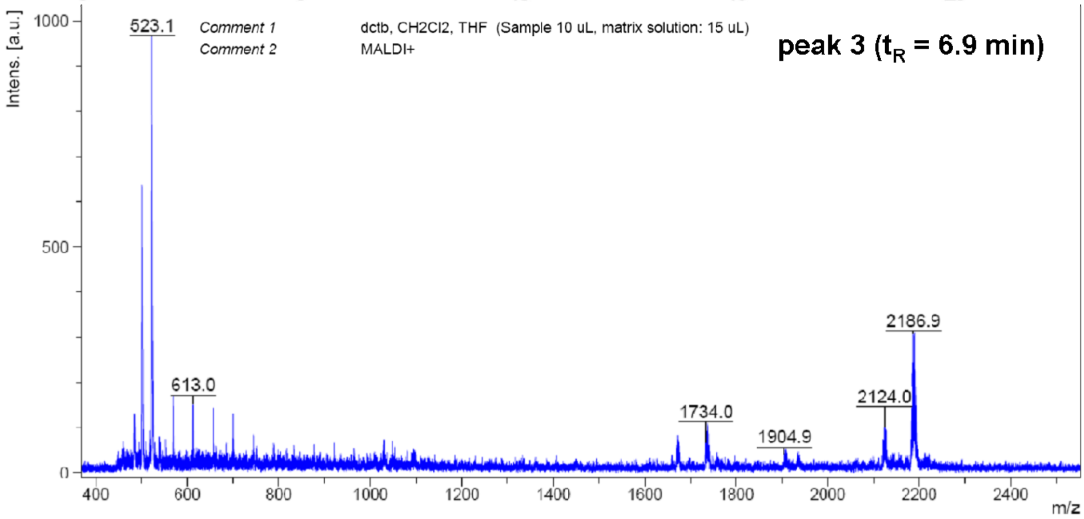


Copy of DOSY **35**:

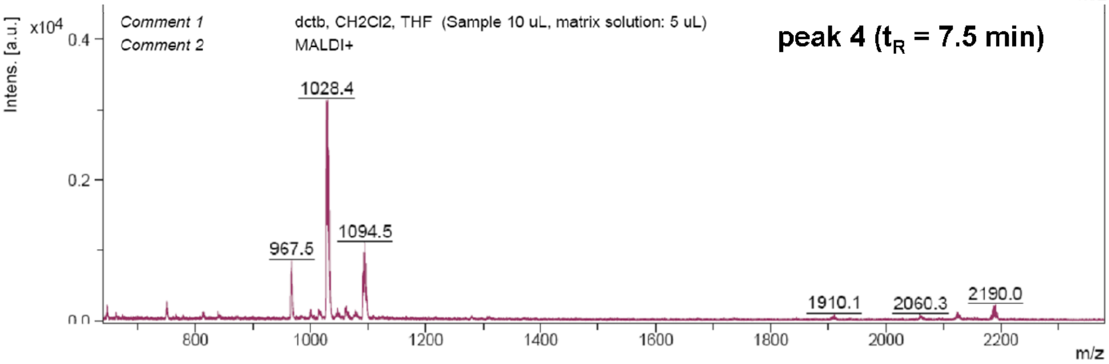


GPC of **35**:





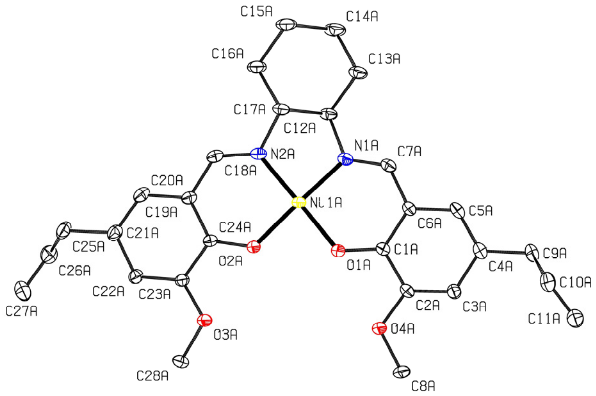
peak 3 (t_R = 6.9 min)



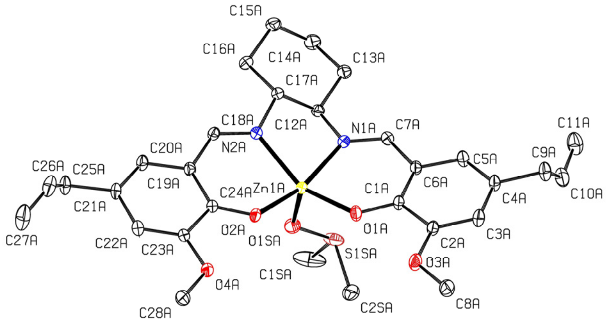
peak 4 (t_R = 7.5 min)

Transmetallation of 35: Zn-compound **35** (15.0 mg, 6.83·10^{-3} mmol) was dissolved in $CHCl_3$ (2 mL), after which a solution of $Ni(OAc)_2{\cdot}4H_2O$ (9.1 mg, 38.1·10^{-3} mmol) in MeOH (2 mL) was added. An immediate color change was observed, after which the mixture was allowed to stir at rt for 1 h. The mixture was then filtered and the residue was washed with water and dried. Characterization of the resulting material was found to be impossible due to its insolubility in a wide range of NMR solvents.

Additional comments for the X-ray diffraction studies carried out for complexes **19** and **20**.



Complex 19: Compound **19** crystallizes in a triclinic crystal which can be solved and refined in the chiral space group $P1$ and in centrosymmetric space group *P*-1. Since the compound analyzed is chiral the space group $P1$ was selected. It the asymmetric unit two independent molecules can be observed which are related by pseudo centro symmetry. The Flack parameter refined to 0.016(6). Alternatively the structure can be solved and refined in the centrosymmetric space group P-1 with only one independent molecule and the chiral rest disordered in two orientations.



Complex 20: Compound **20** crystallizes in a monoclinic space which can be solved and refined in the chiral space group $P2_1$ and in the centrosymmetric space group $P2_1/c$. Since the compound analyzed is chiral the space group $P2_1$ was selected. It the asymmetric unit two independent molecules can be observed which are related by pseudo centro symmetry. The Flack parameter refined to 0.000(5). Alternatively the structure can be solved and refined in the centro-symmetric space group $P2_1/c$ with only one independent molecule and the chiral rest disordered in two orientations.