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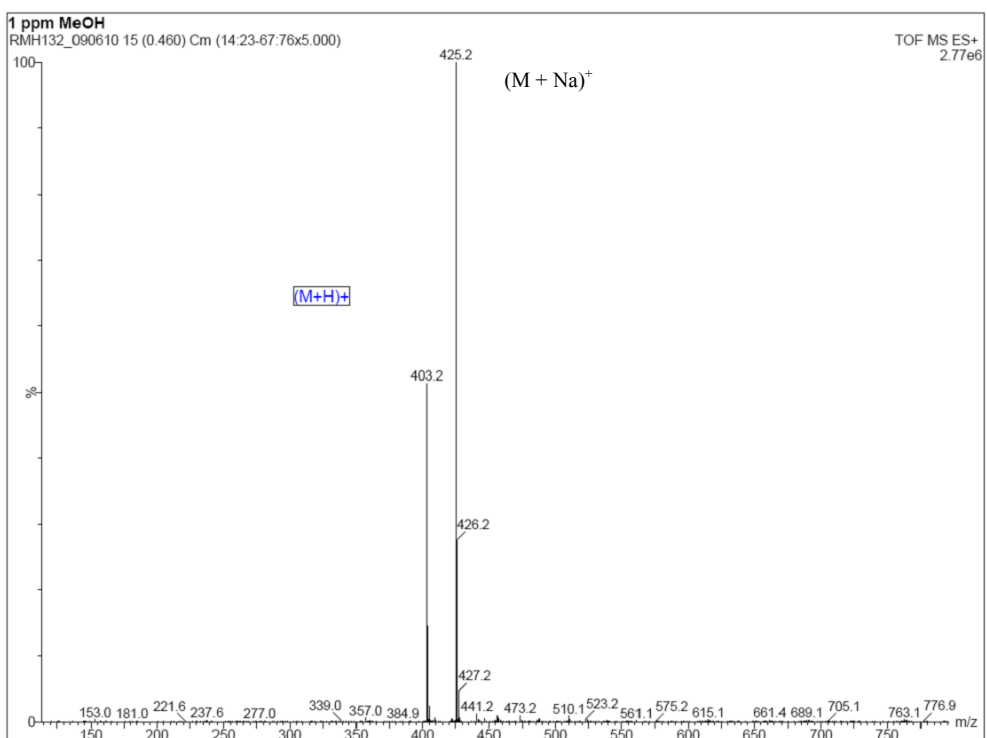
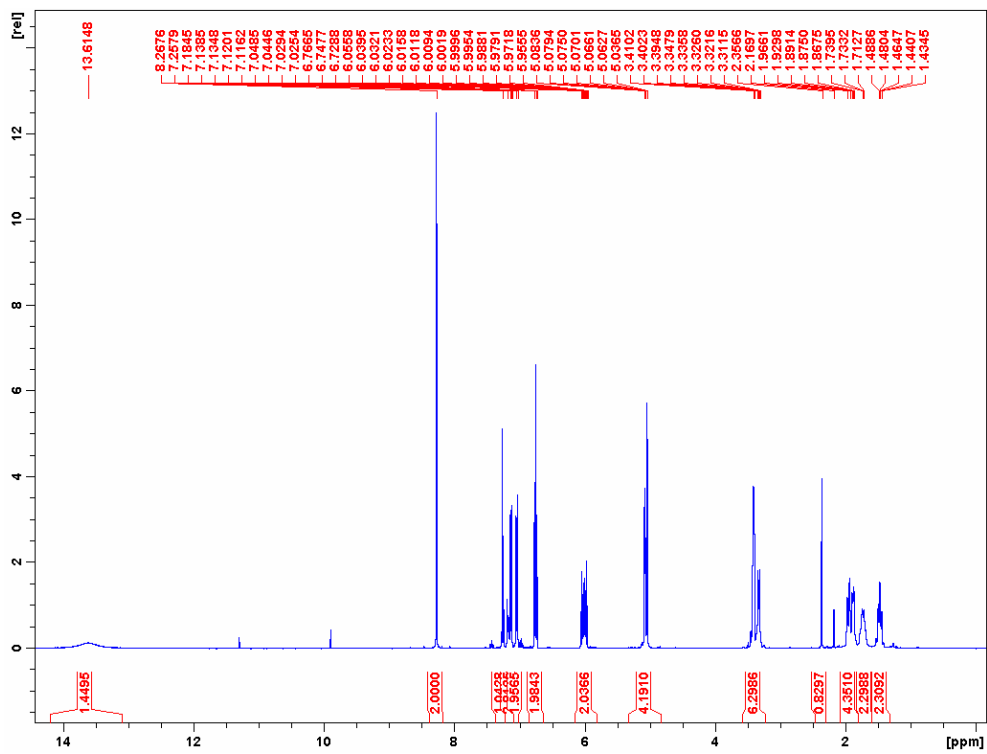
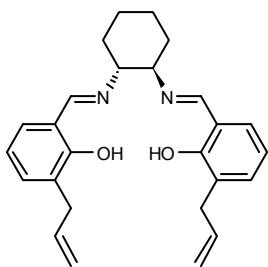
**Olefin metathesis as a tool for multinuclear Co(III)salen catalyst  
construction: Access to cooperative catalysts**

*Robert M. Haak, Marta Martínez Belmonte, Eduardo C. Escudero-Adán, Jordi Benet-  
Buchholz and Arjan W. Kleij\**

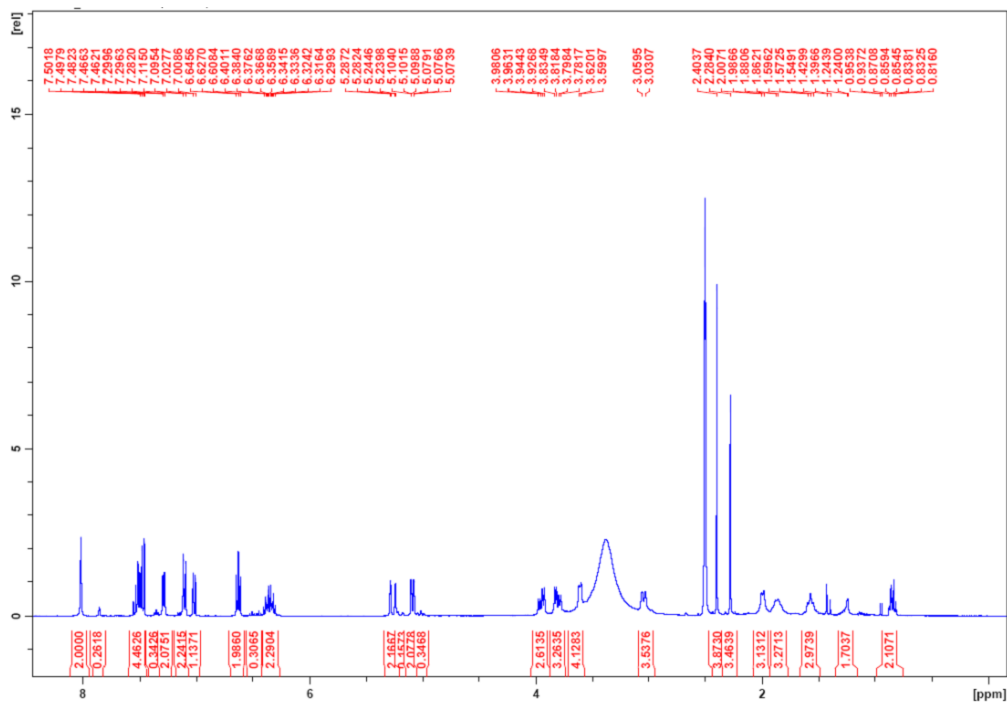
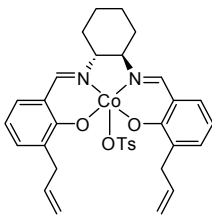
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3a

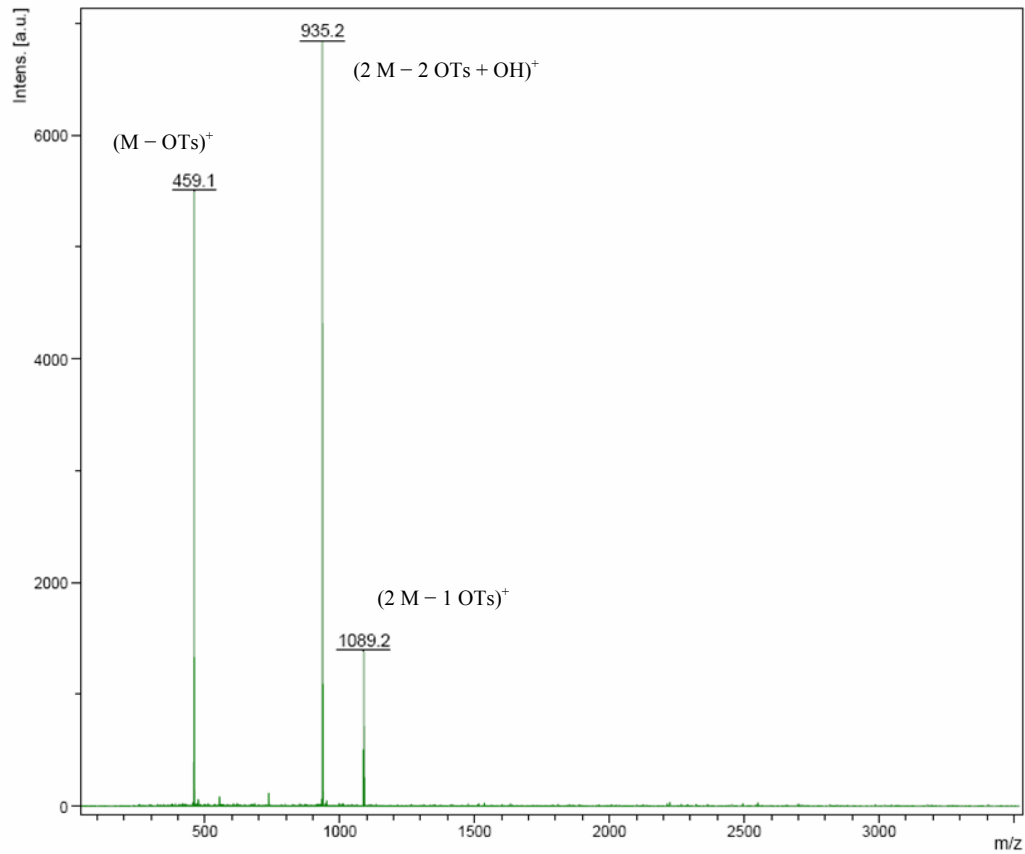


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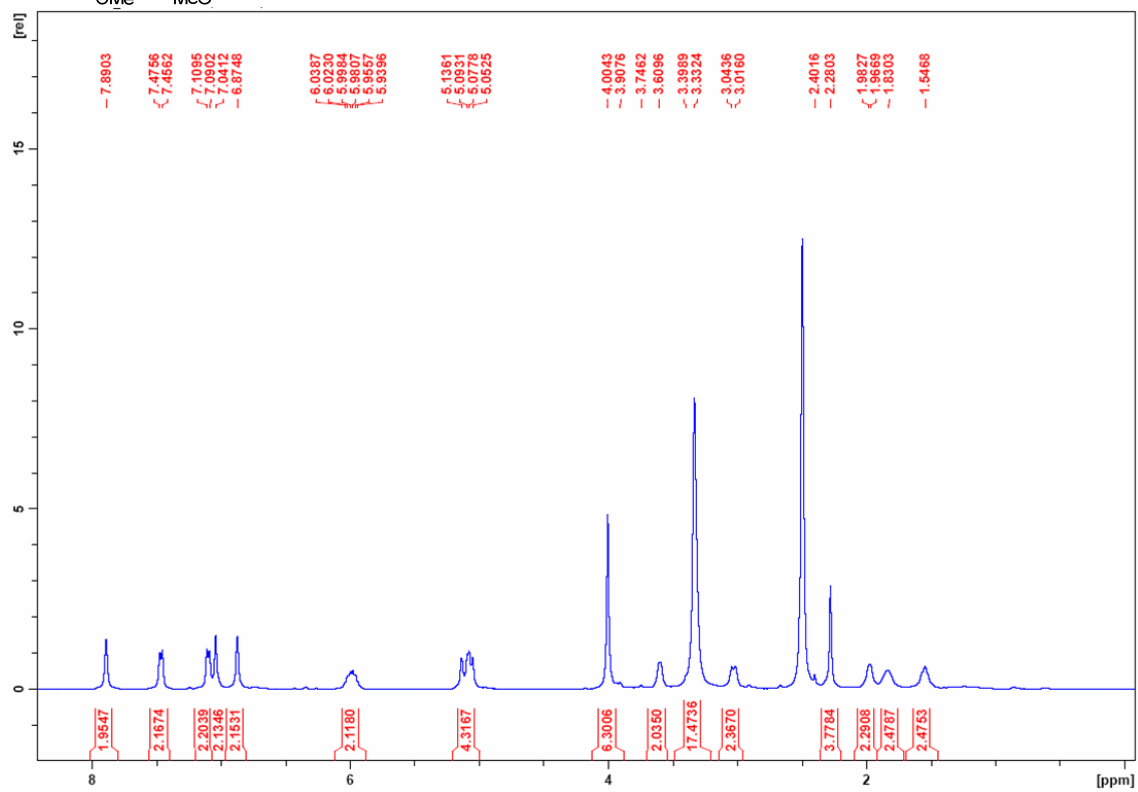
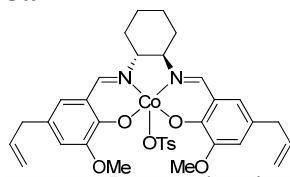


Comment 1  
 Comment 2

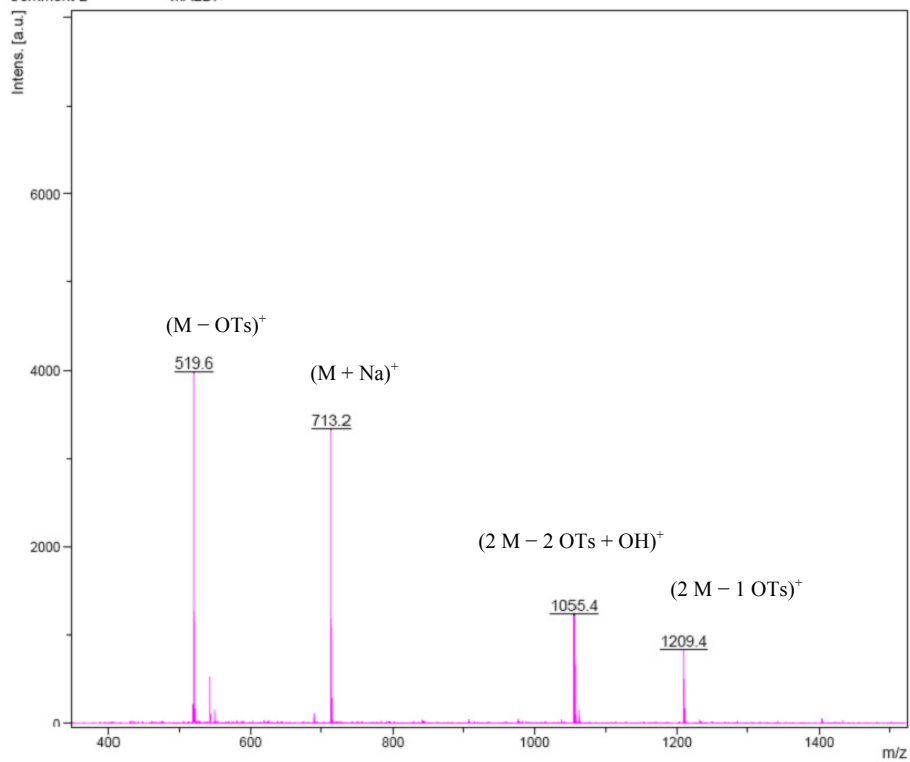
dctb/CH2Cl2  
 MALDI+



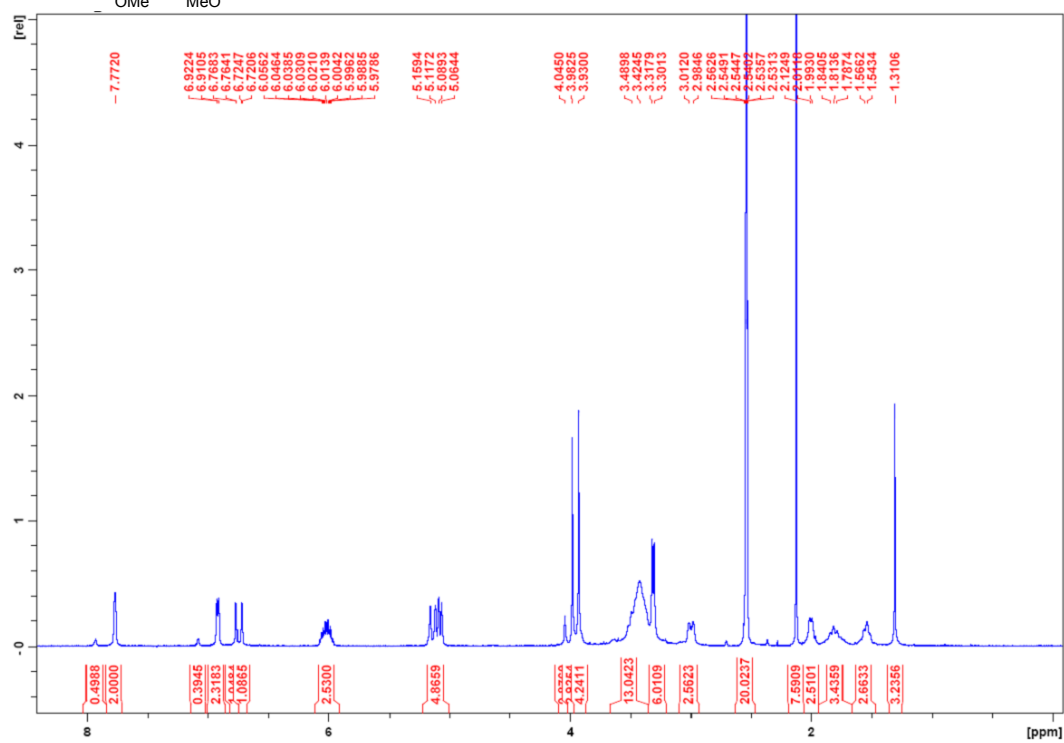
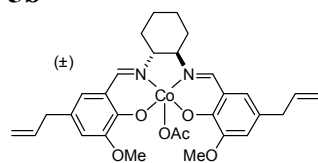
### 5a



Comment 1 dctb-CH2Cl2  
Comment 2 MALDI+

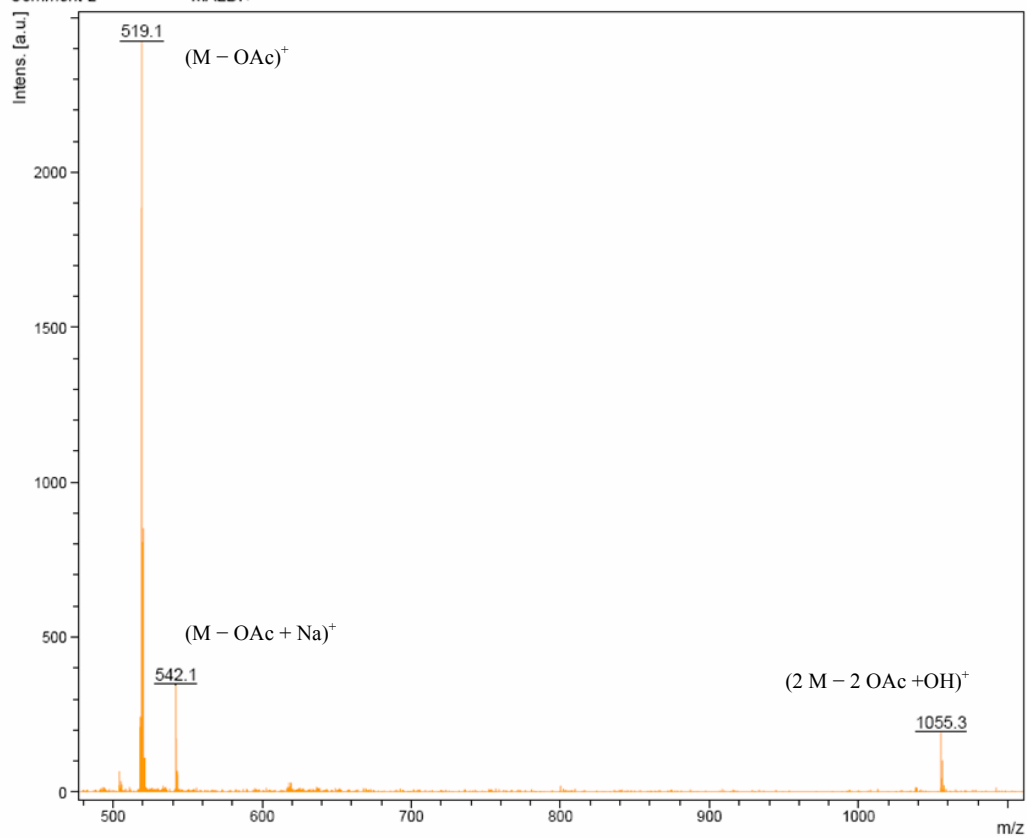


5b

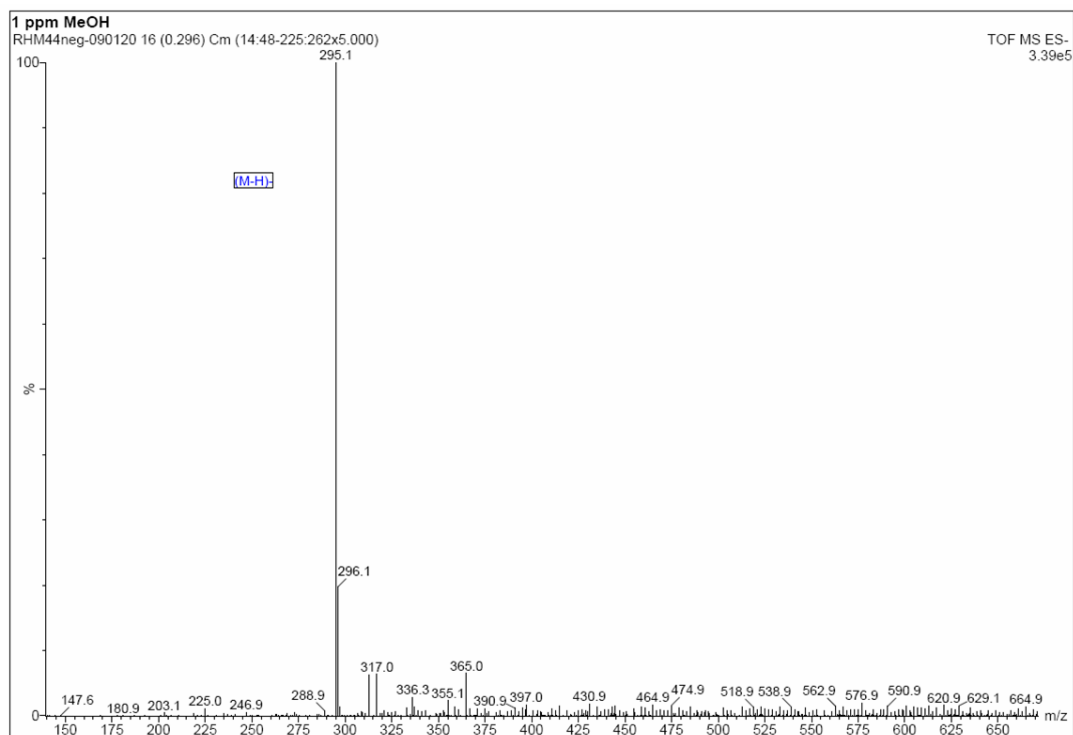
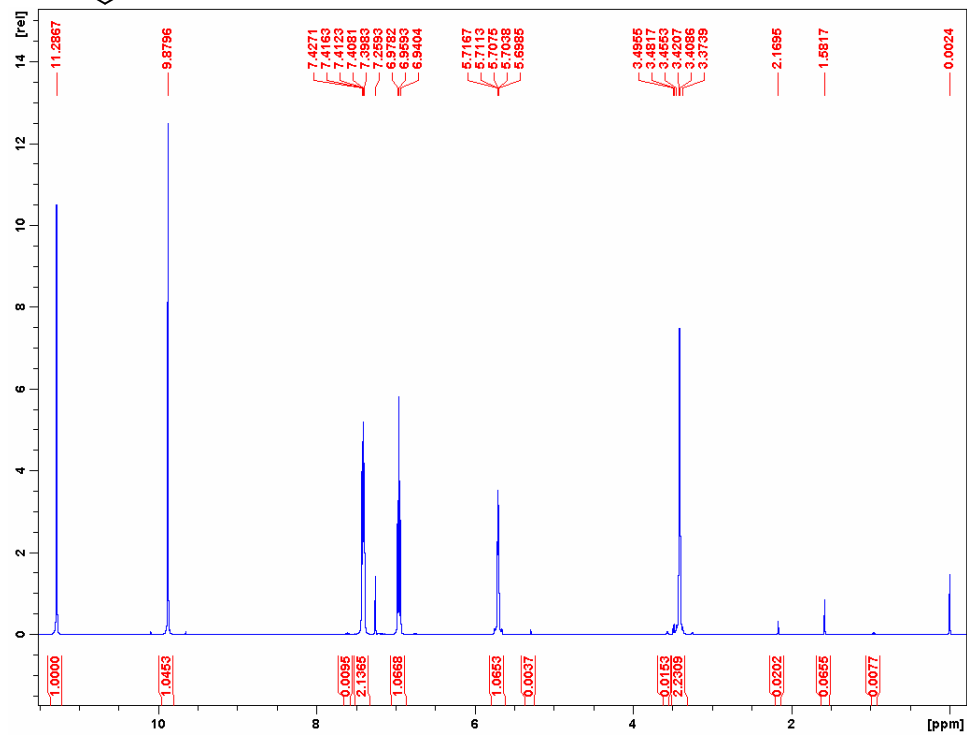
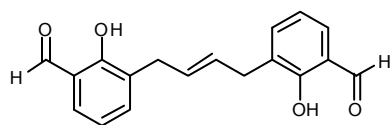


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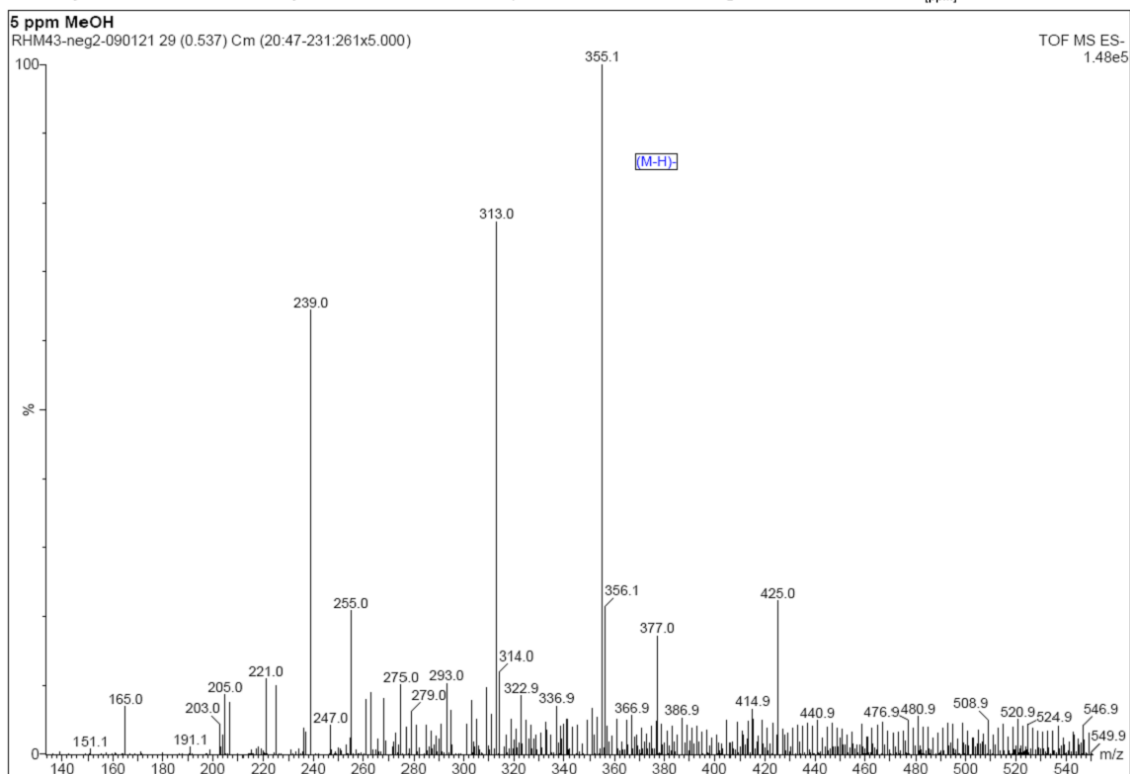
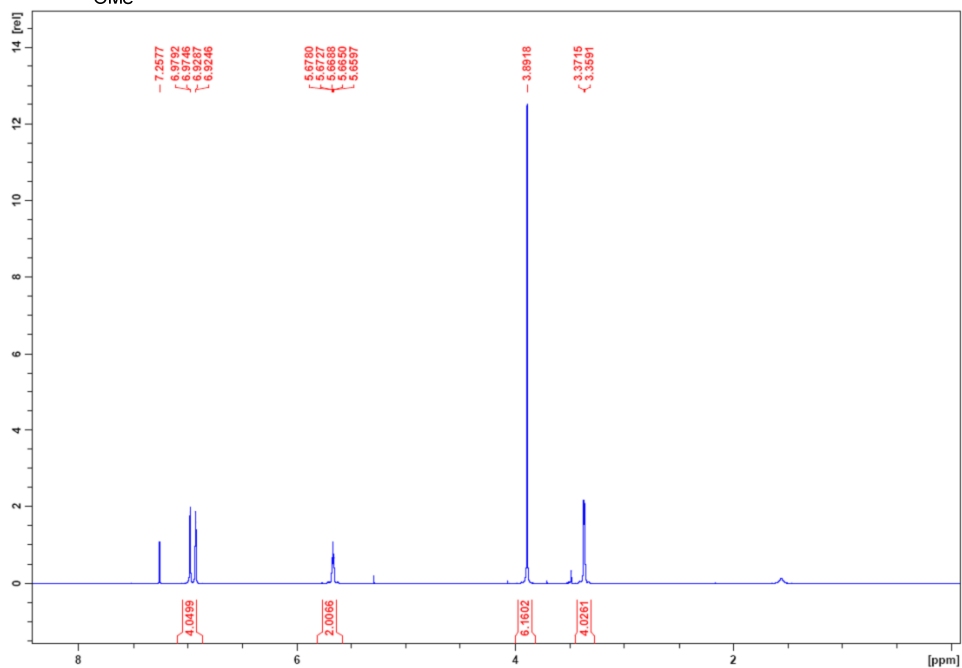
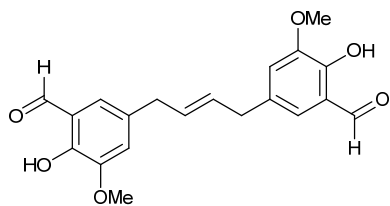
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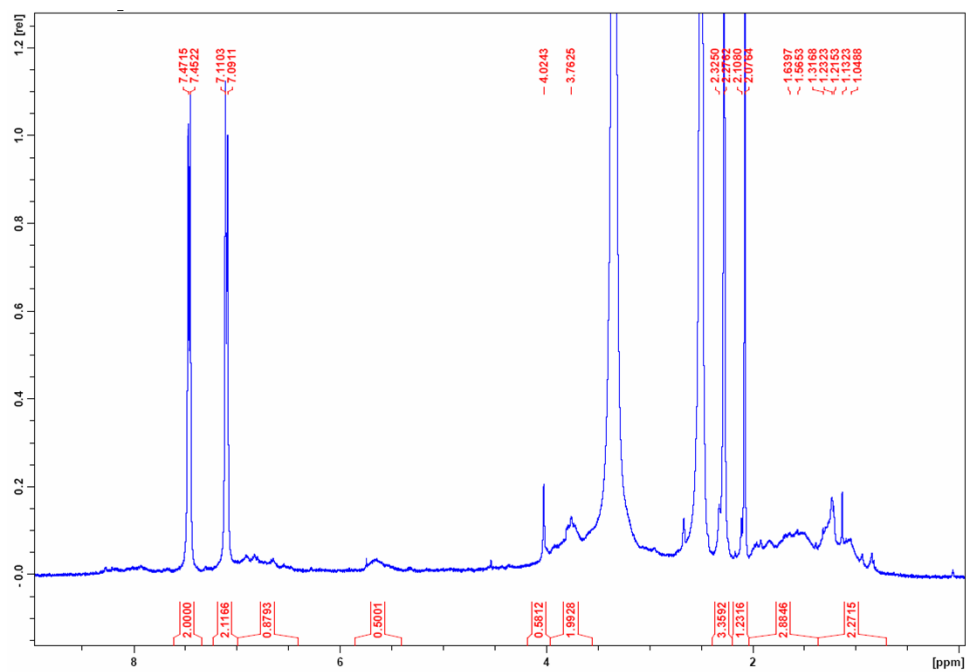
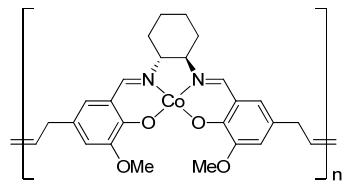
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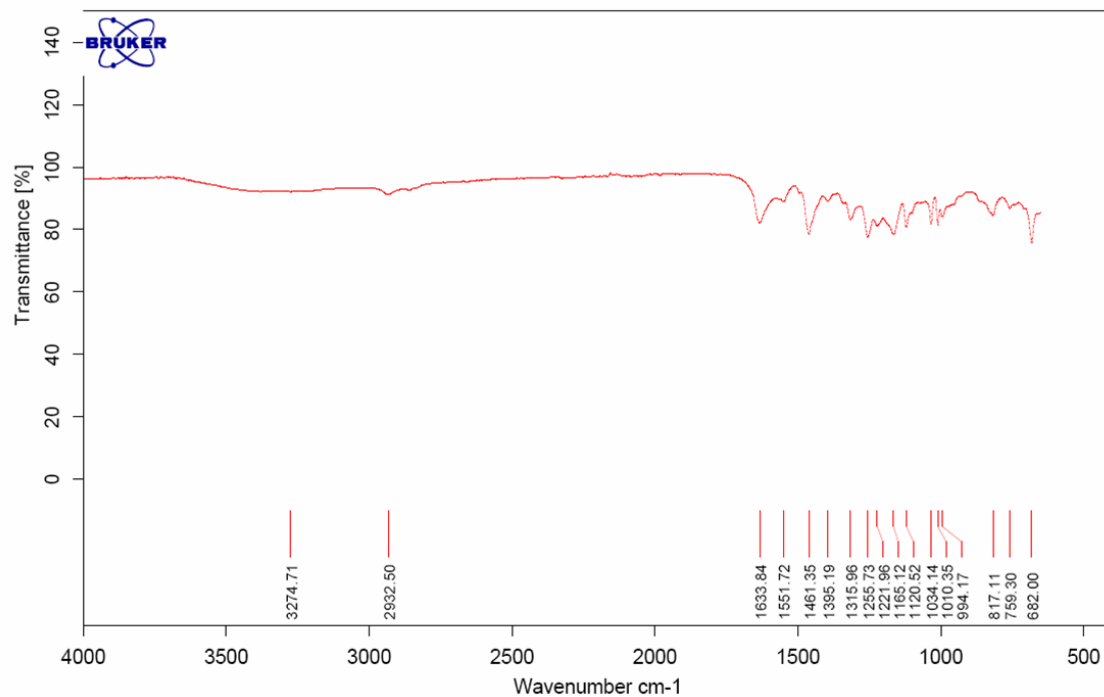
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9

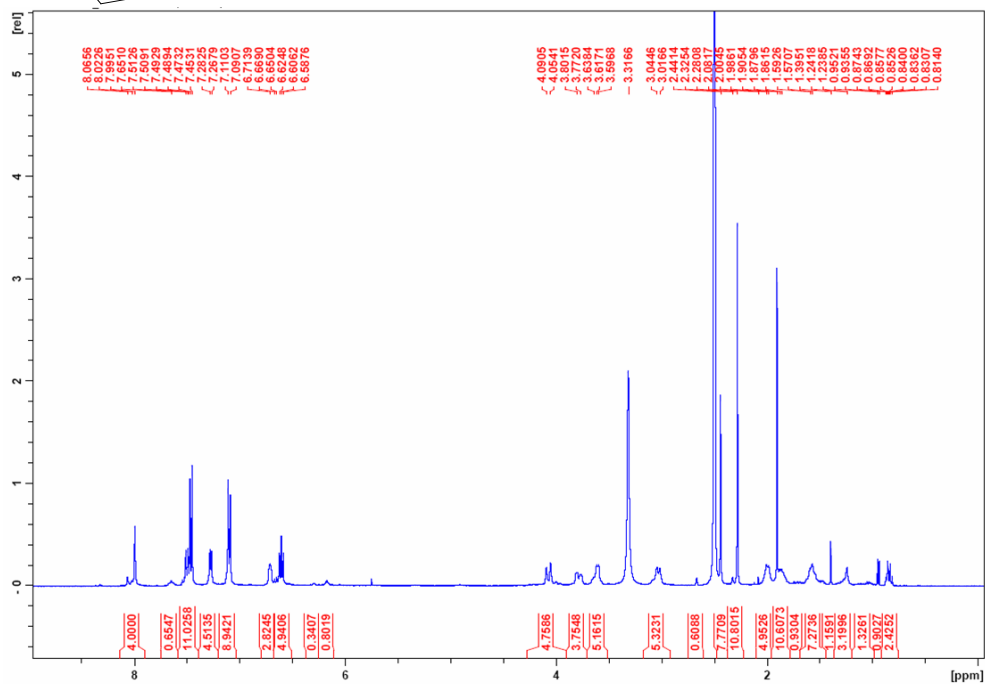
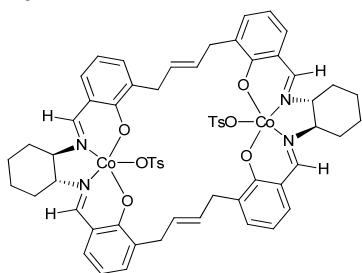


Please note that due to poor solubility features, no mass spectrum of 9 could be obtained; an IR spectrum is given instead.

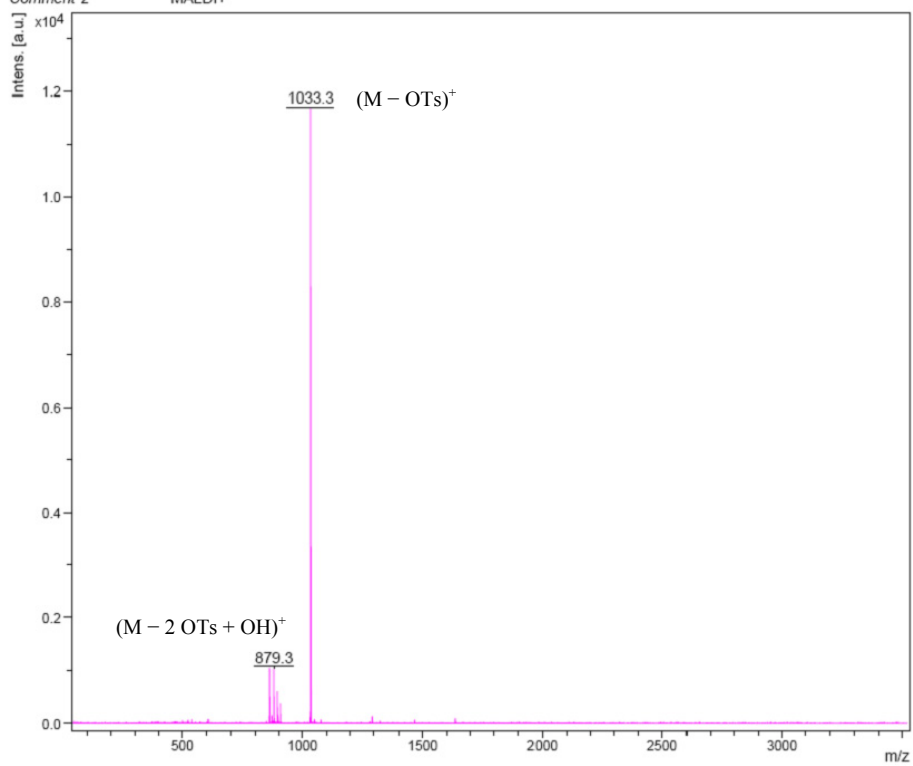




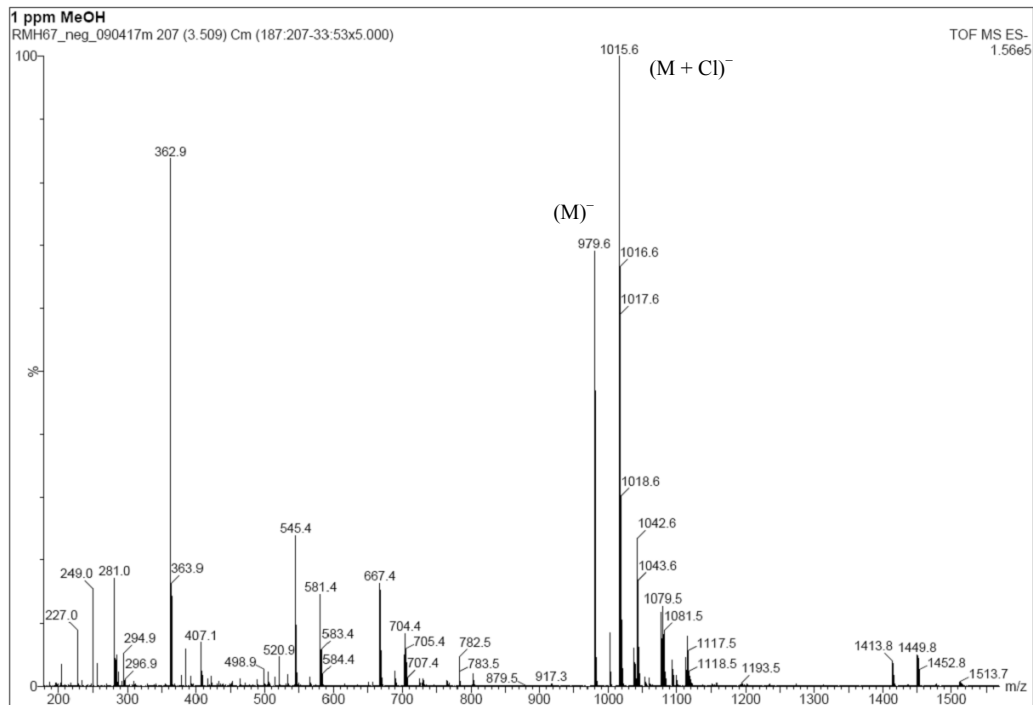
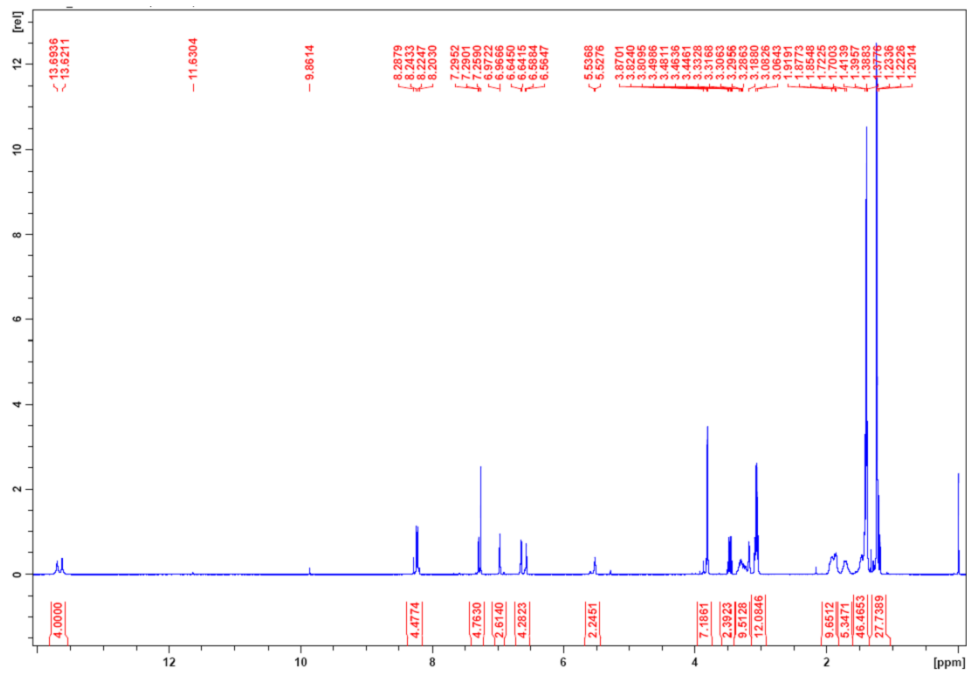
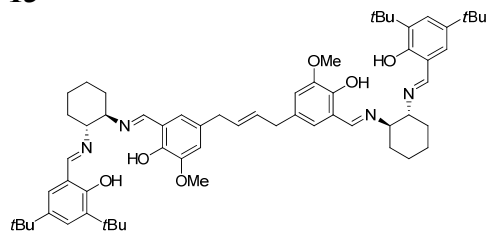
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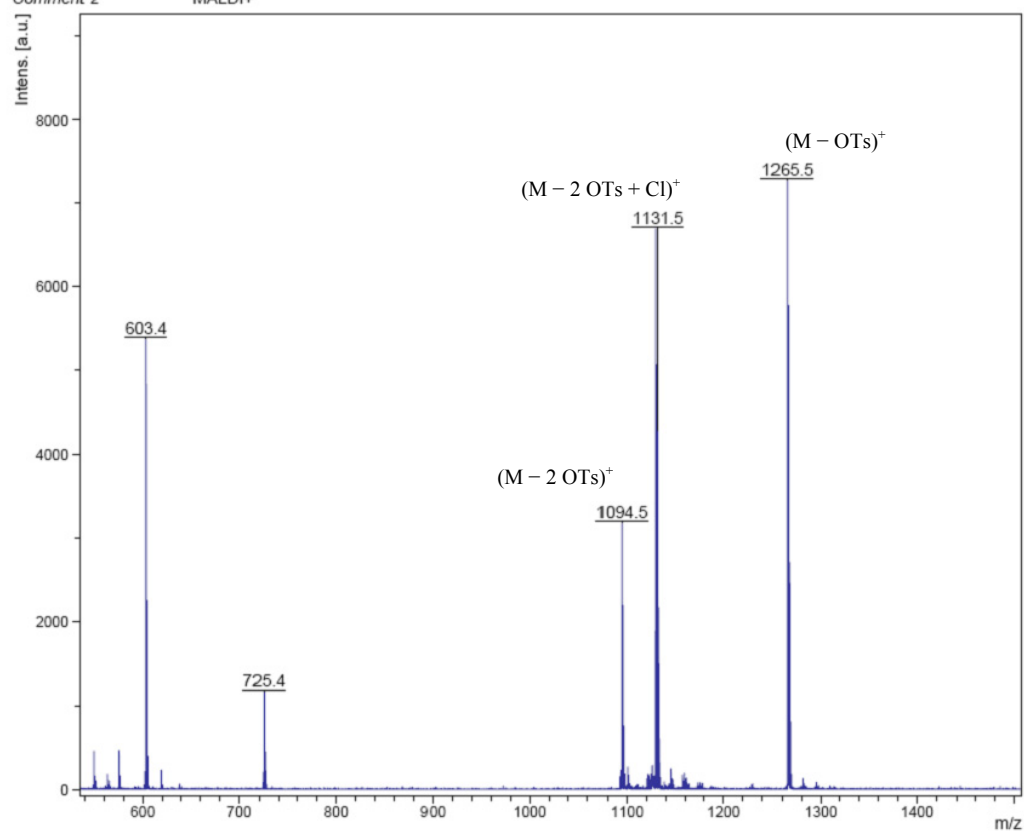
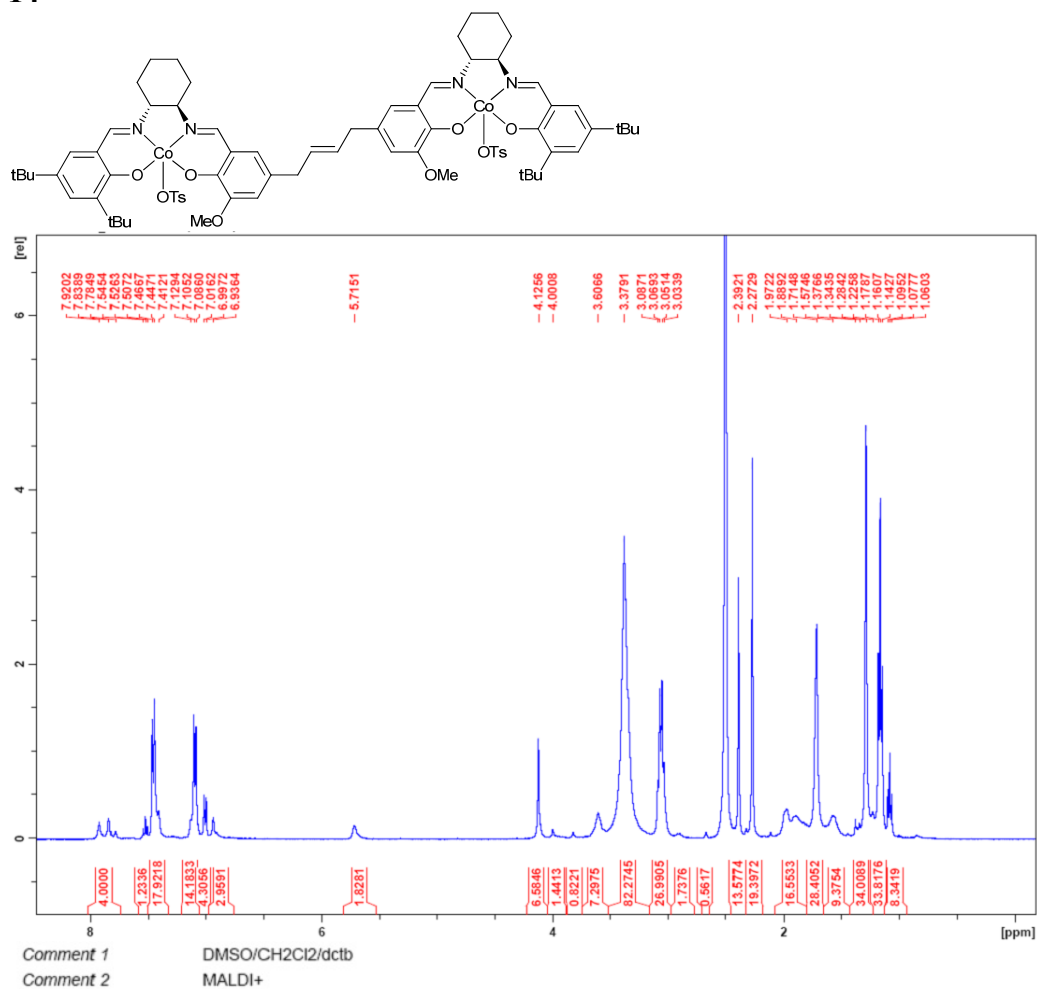
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Comment 2 MALDI+



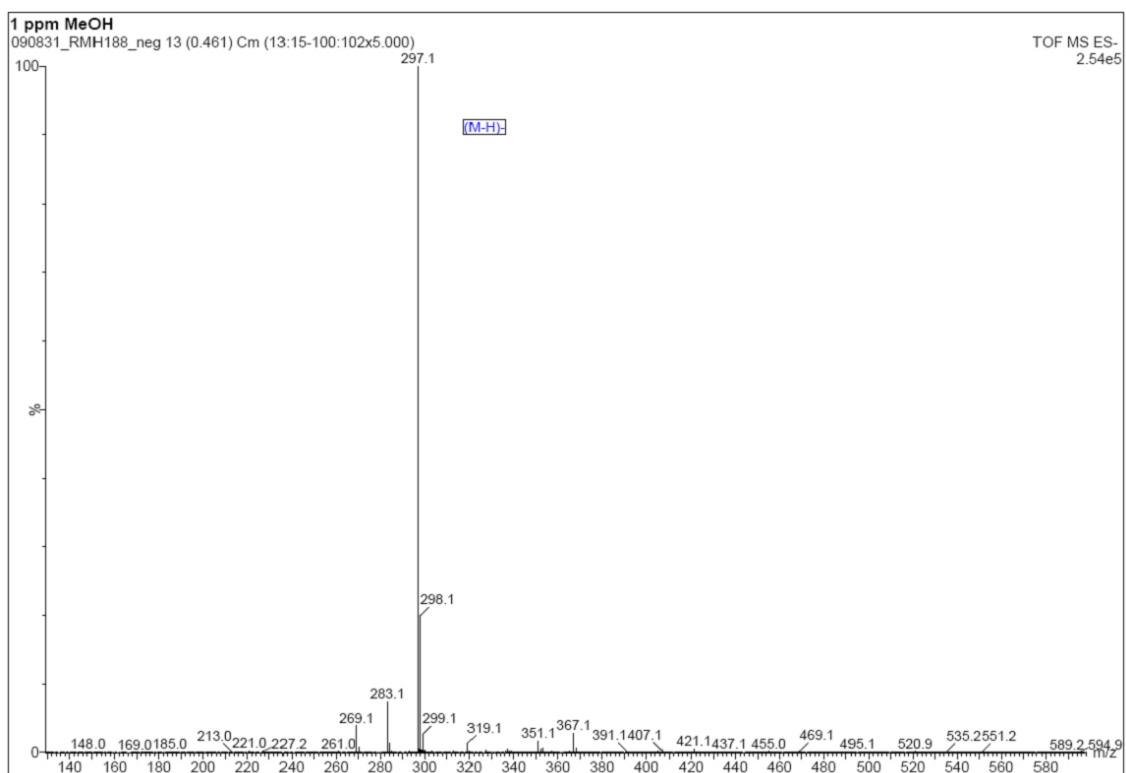
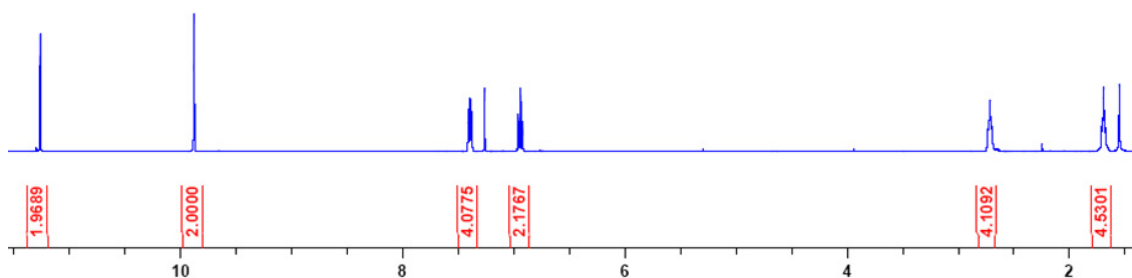
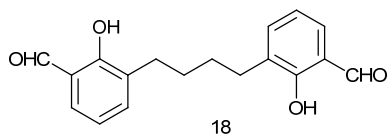
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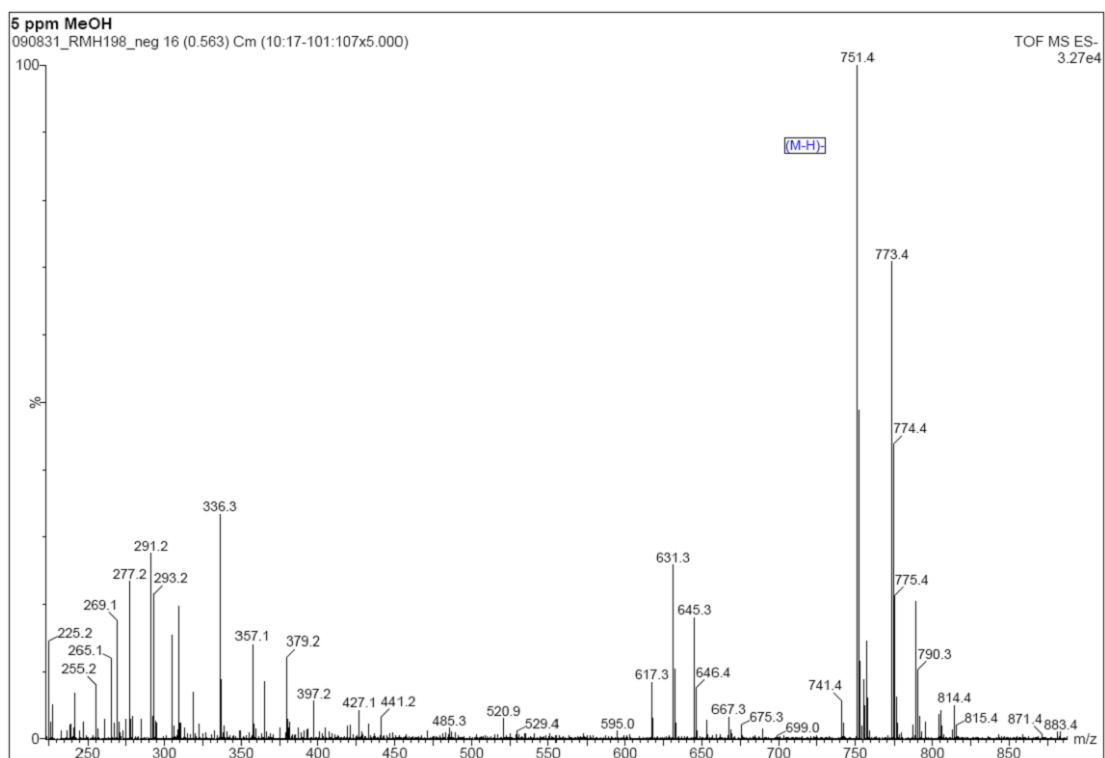
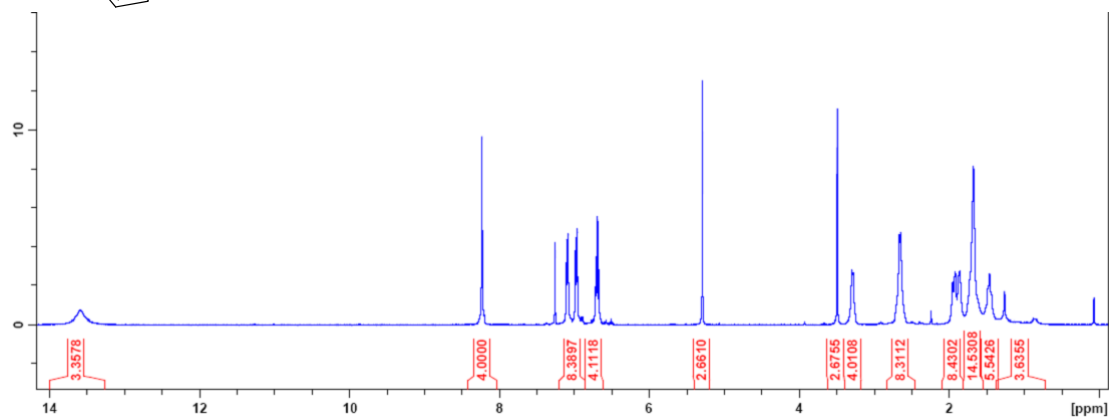
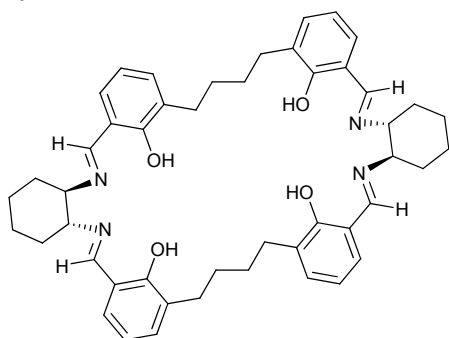
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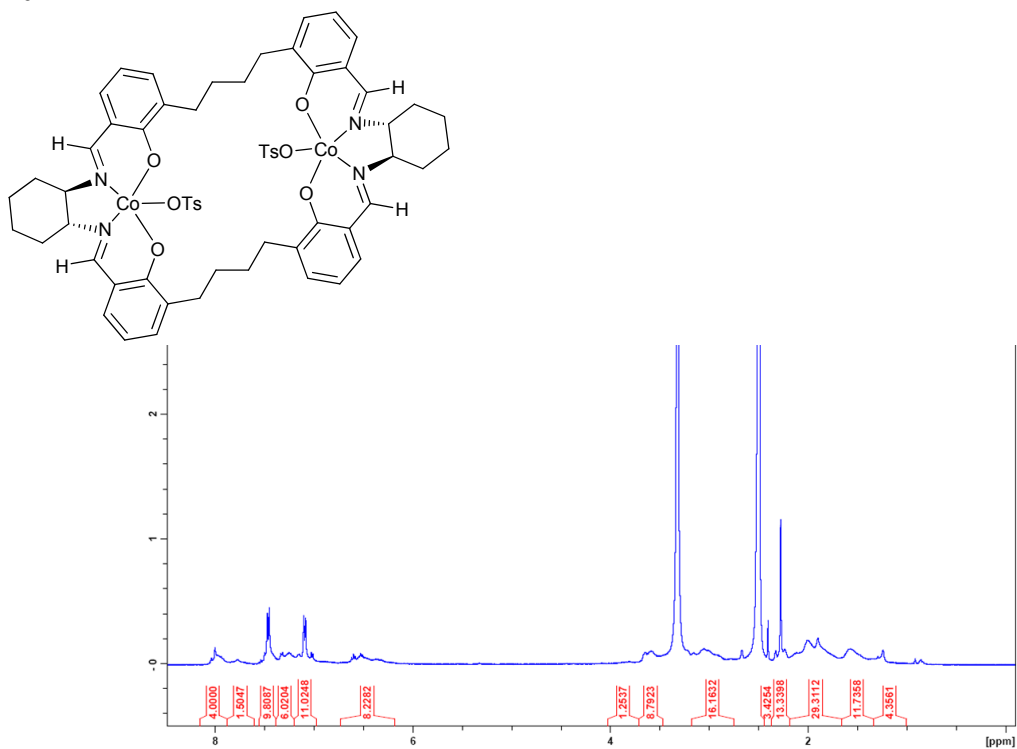
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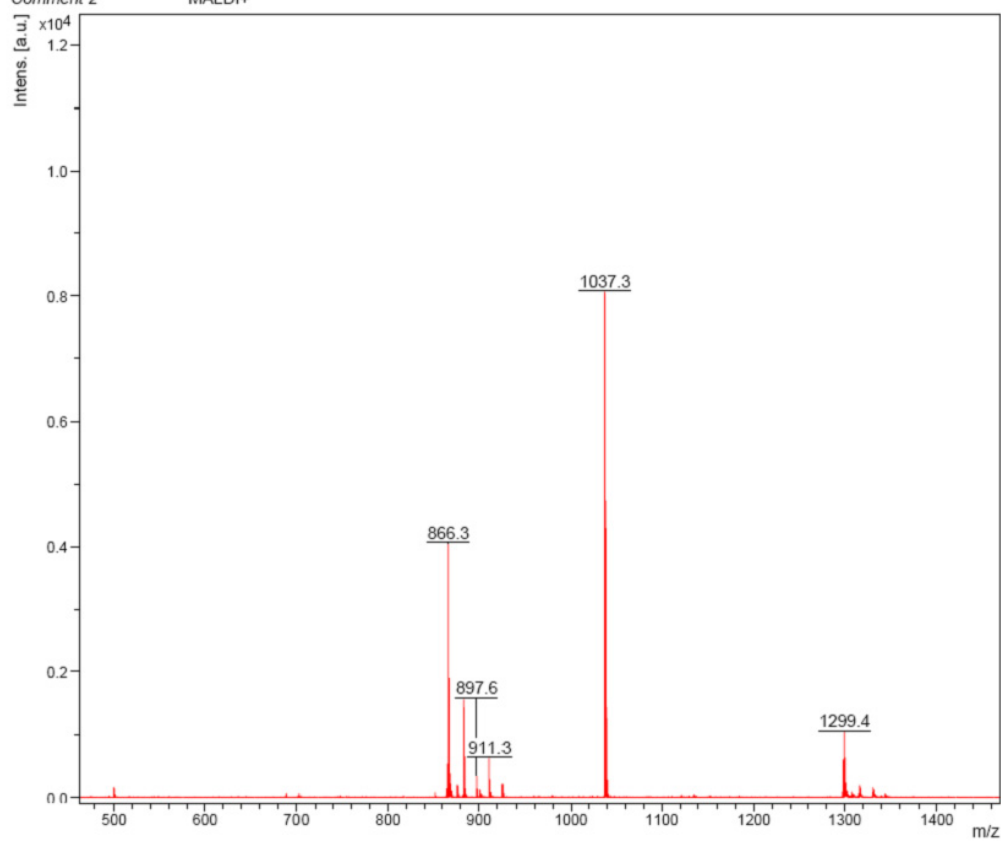


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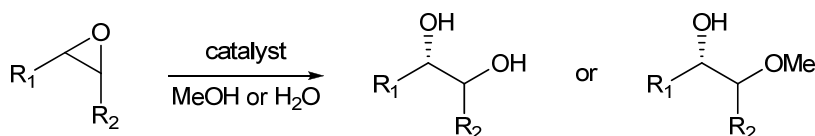


Comment 1  
Comment 2

CH<sub>2</sub>Cl<sub>2</sub>, dcb  
MALDI+



### Overview of analytical separation methods:



R<sub>1</sub>, R<sub>2</sub> = *n*-C<sub>4</sub>H<sub>9</sub>, H (1,2-epoxyhexane, **15a**)

- GC: HP-5 column (60.0 m × 320 μm × 0.25 μm), 50 °C to 140 °C at 10 °C min<sup>-1</sup>, t<sub>R</sub> = 2.23 min (epoxide), 3.95 min (β-methoxyalcohol).
- chiral GC: HP CHIRAL (30 m × 0.25 mm × 0.25 μm), 40 °C for 35 min, then 90 °C for 40 min, t<sub>R</sub> = 26.3 min (epoxide, major enantiomer), 27.0 min (epoxide, minor enantiomer), 47.0 min (β-methoxyalcohol, major enantiomer), 47.7 min (β-methoxyalcohol, minor enantiomer). For the diol, no chiral separation was obtained.

R<sub>1</sub>, R<sub>2</sub> = PhCH<sub>2</sub>OCH<sub>2</sub>, H (benzyl glycidyl ether, **15b**)

- GC: HP-5 column (60.0 m × 320 μm × 0.25 μm), 140 °C to 175 °C at 5 °C min<sup>-1</sup>, t<sub>R</sub> = 2.56 (epoxide), 3.73 (β-methoxyalcohol), 4.22 (diol).
- chiral HPLC: Chiralcel OD, 25 °C, heptane/IPA 92:8, 1.0 mL/min, t<sub>R</sub> = 5.9 min (epoxide, minor enantiomer), 6.2 min (epoxide, major enantiomer), 15.9 min (diol, minor enantiomer), 17.4 min (diol, major enantiomer).
- chiral HPLC, Chiralcel OD, 25 °C, heptane/IPA 98:2, 1.0 mL/min, t<sub>R</sub> = 20.0 min (β-methoxyalcohol, minor enantiomer), 21.4 min (β-methoxyalcohol, major enantiomer).

R<sub>1</sub>, R<sub>2</sub> = Ph, H (styrene oxide, **15c**)

- GC: HP-5 column (60.0 m × 320 μm × 0.25 μm), 50 °C to 140 °C at 10 °C min<sup>-1</sup>, t<sub>R</sub> = 5.10 min (epoxide), 7.06 min (β-methoxyalcohol), 8.43 min (diol).
- chiral GC: Chiraldex G-TA 30 m × 0.25 mm × 0.12 μm, 100 °C isothermic, t<sub>R</sub> = 9.1 min (epoxide, major enantiomer), 11.5 min (epoxide, minor enantiomer), 24.2 min (β-methoxyalcohol, minor enantiomer), 28.7 min (β-methoxyalcohol, major enantiomer).

R<sub>1</sub>, R<sub>2</sub> = ClCH<sub>2</sub>, H (epichlorohydrin, **15d**)

- GC: HP-5 column (60.0 m × 320 μm × 0.25 μm), 50 °C to 140 °C at 10 °C min<sup>-1</sup>, t<sub>R</sub> = 1.75 min (epoxide), 2.84 min (β-methoxyalcohol).
- chiral GC, Chiraldex G-TA 30 m × 0.25 mm × 0.12 μm, 50 °C to 150 °C at 15 °C min<sup>-1</sup>, t<sub>R</sub> = 3.8 min (epoxide, major enantiomer), 4.0 min (epoxide, minor enantiomer), 5.6 (β-methoxyalcohol, minor enantiomer), 5.8 (β-methoxyalcohol, major enantiomer).

R<sub>1</sub>, R<sub>2</sub> = -(CH<sub>2</sub>)<sub>4</sub>- (cyclohexene oxide, **15e**)

- GC: HP-5 column (60.0 m × 320 μm × 0.25 μm), 50 °C to 140 °C at 10 °C min<sup>-1</sup>, t<sub>R</sub> = 2.71 min (epoxide), 4.62 (β-methoxyalcohol).
- chiral GC, Chiraldex G-TA 30 m × 0.25 mm × 0.12 μm, 70°C isothermic, t<sub>R</sub> = 38.3 min (β-methoxyalcohol, major enantiomer), 36.3 (β-methoxyalcohol, minor enantiomer).

Crystallographic comments/details:

**Single Crystal X-ray Diffraction Data:**

X-ray structure determinations: Crystals of **5c** were obtained by slow evaporation of solution in acetone. Crystals of **6** and **7** were obtained from CH<sub>2</sub>Cl<sub>2</sub>/MeOH at 4°C. Although the measured crystals are stable under atmosphere conditions, they were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

*Data Collection:* Measurements were made on a Bruker-Nonius diffractometer equipped with an APPEX 2 4K CCD area detector, a FR591 rotating anode with MoK $\alpha$  radiation, Montel mirrors as monochromator and a Kryoflex low temperature device ( $T = -173$  °C). Full-sphere data collection was used with  $\omega$  and  $\varphi$  scans.

*Programs used:* Data collection Apex2 V2009.1-0 (Bruker-Nonius 2009), data reduction Saint+ V7.60A (Bruker-Nonius 2009) and absorption correction SADABS Version 2008/1.

*Structure Solution and Refinement.* SHELXTL Version 6.14 (Sheldrick, 2008) was used.



***Comments to the structures:***

**Co(III)salen complex 5c:** Complex **5c** crystallized in the centro-symmetric, triclinic space group  $P\bar{1}$  together with one acetone molecule in the unit cell. Additionally, one molecule of acetone and a water molecule are coordinated to the cobalt atom of the complex. The hydrogen atoms of the water molecule were located experimentally from the rest electron density and its positions were refined freely and with isotropical thermal displacement parameters. The cyclohexane rest (C11-C16) of the main complex is disordered in two inverted conformations in concordance with the typical pseudo-rotation observed in alkane rings. The disorder ratio is 89:11. The atoms of the smaller disordered fraction were refined with restrained anisotropical thermal displacement parameters in order to avoid correlation with the major fraction of the disordered cyclohexane ring.

**Bis-aldehyde 6:** For this sample, data from an excellently diffracting crystal were collected, but unfortunately a breakdown of the diffractometer did not allow getting a complete data set. Only an 83.7 % of the data were collected but it was considered sufficient for a definitive structure elucidation.