

## Electronic Supplementary Information

# Homoselenacalix[4]arenes: synthetic exploration and metallo-supramolecular chemistry

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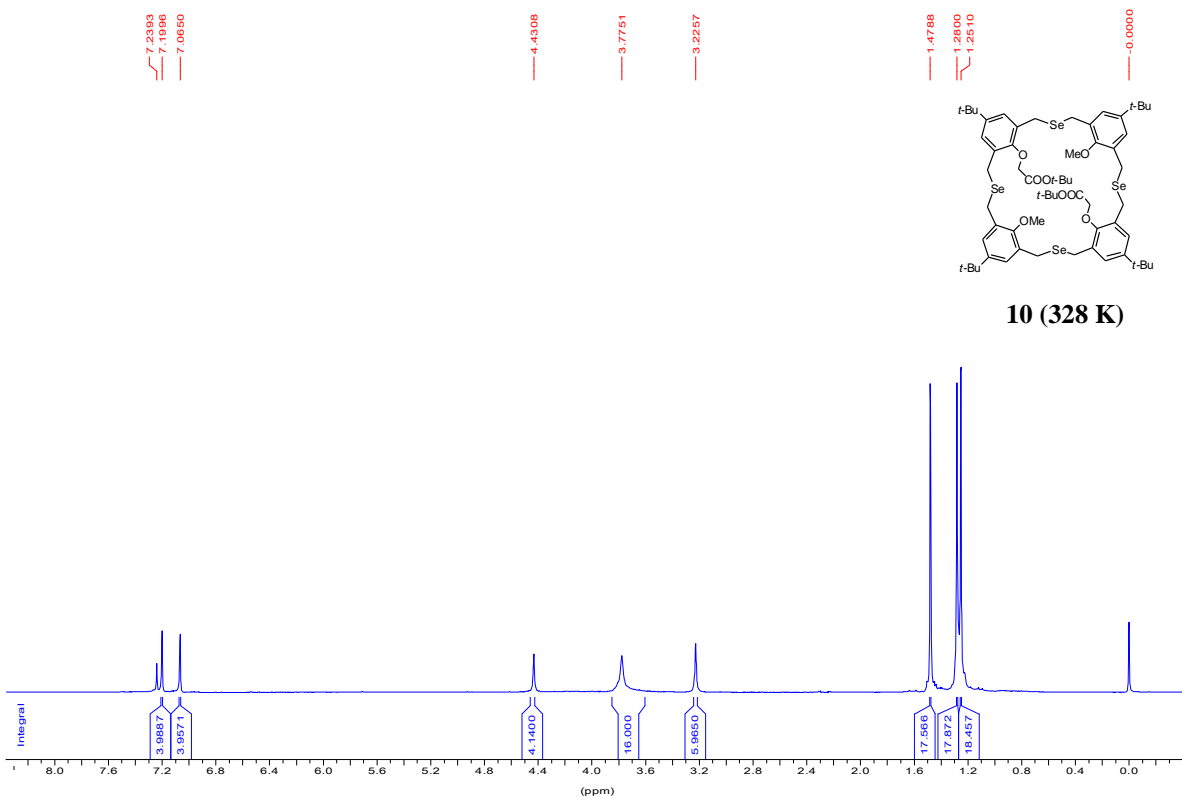
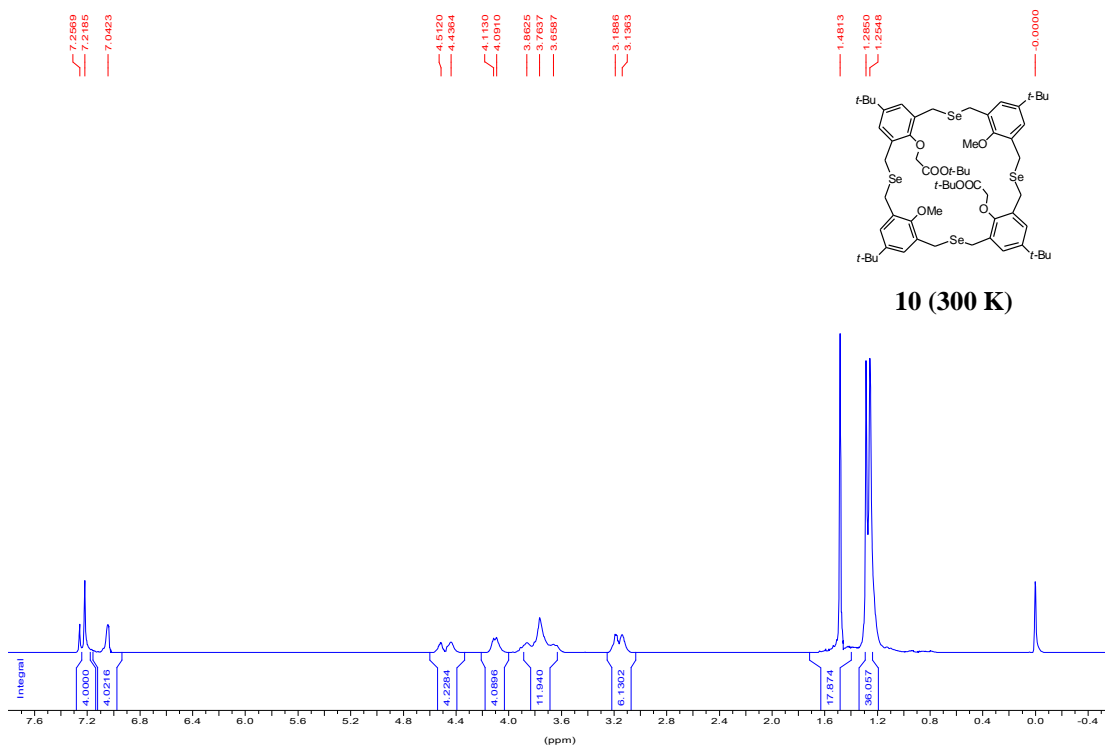
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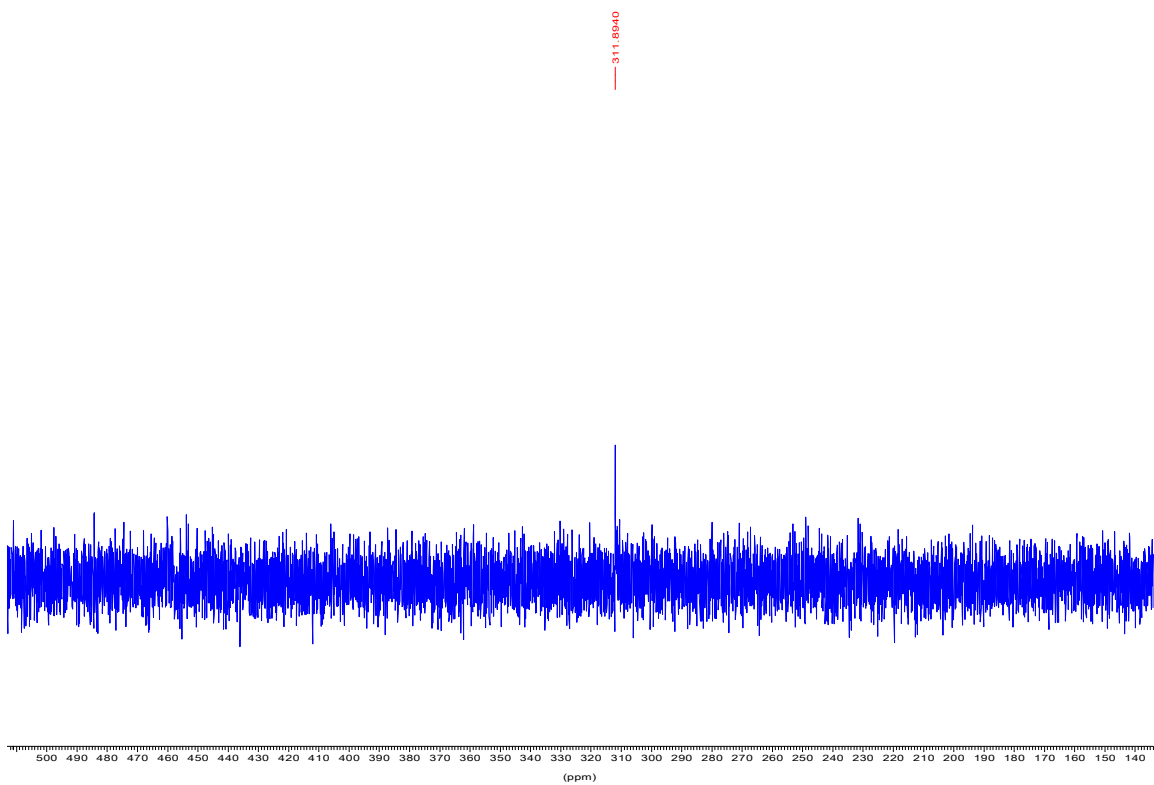
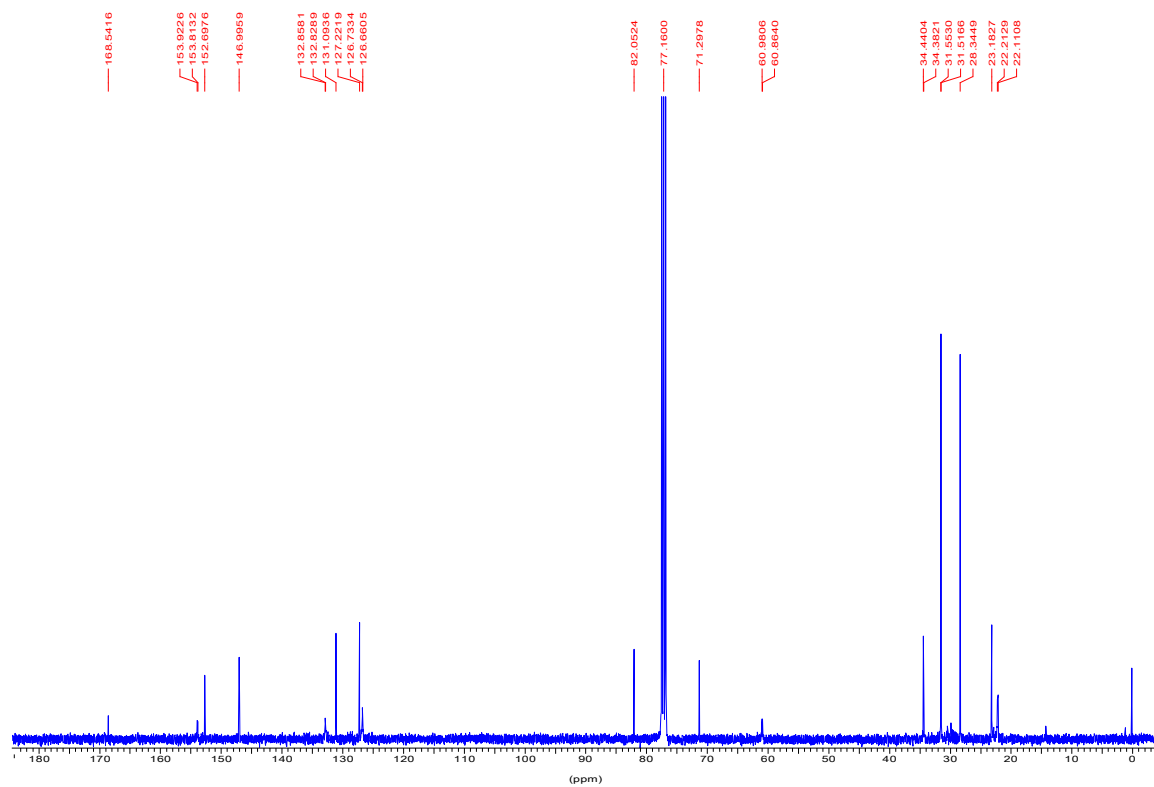
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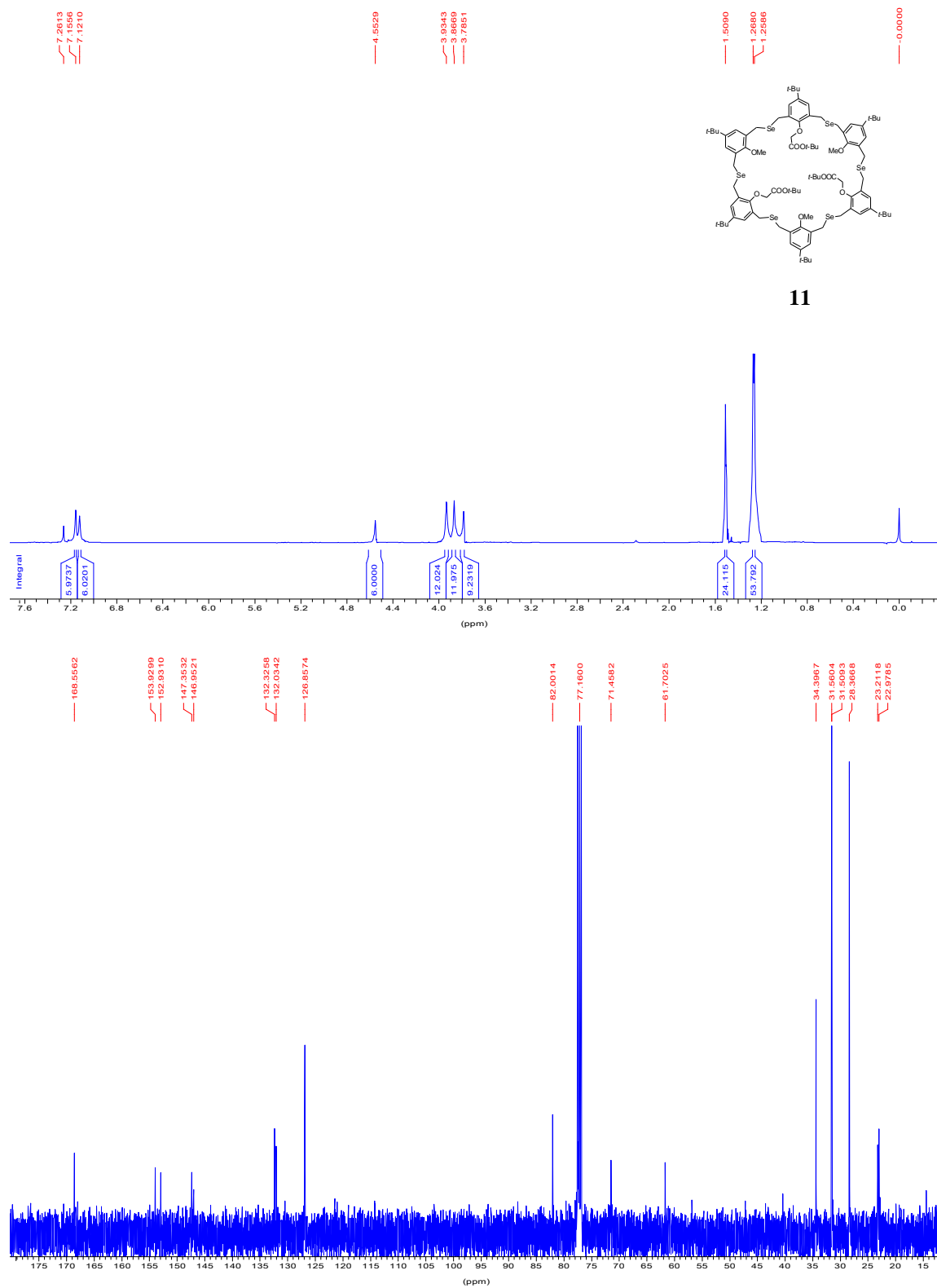
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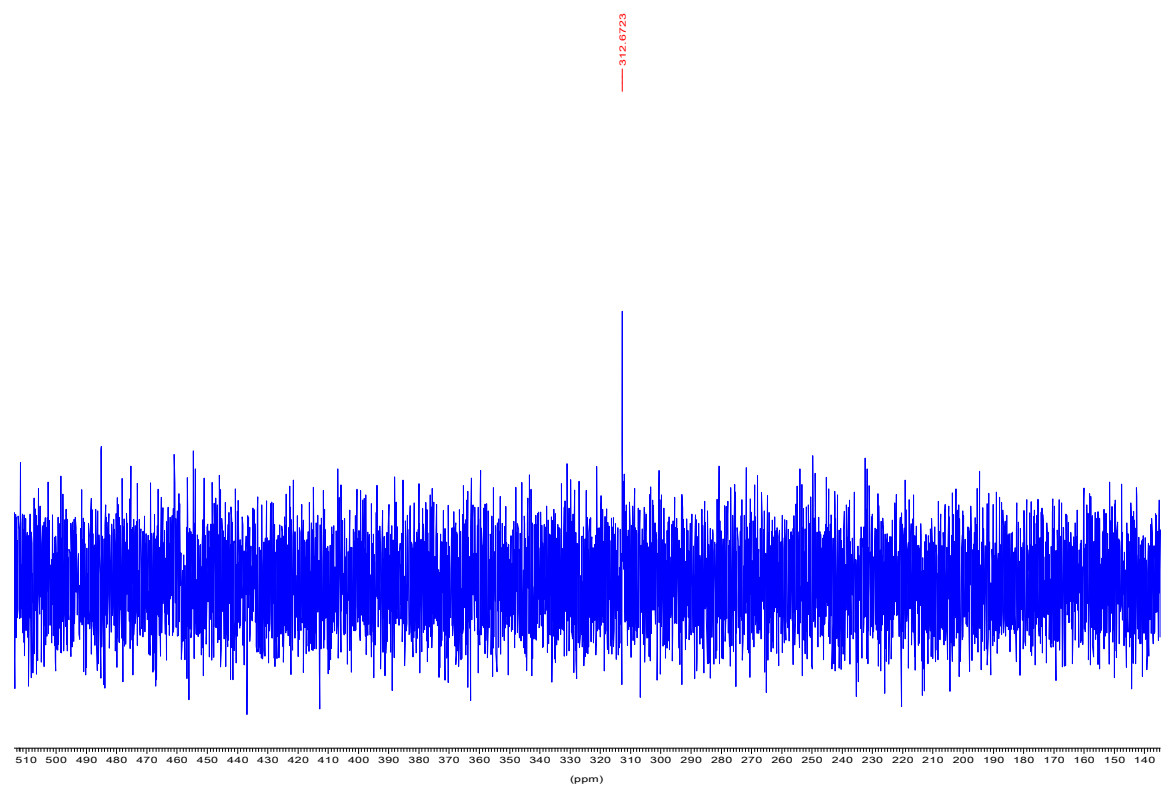
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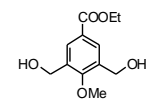
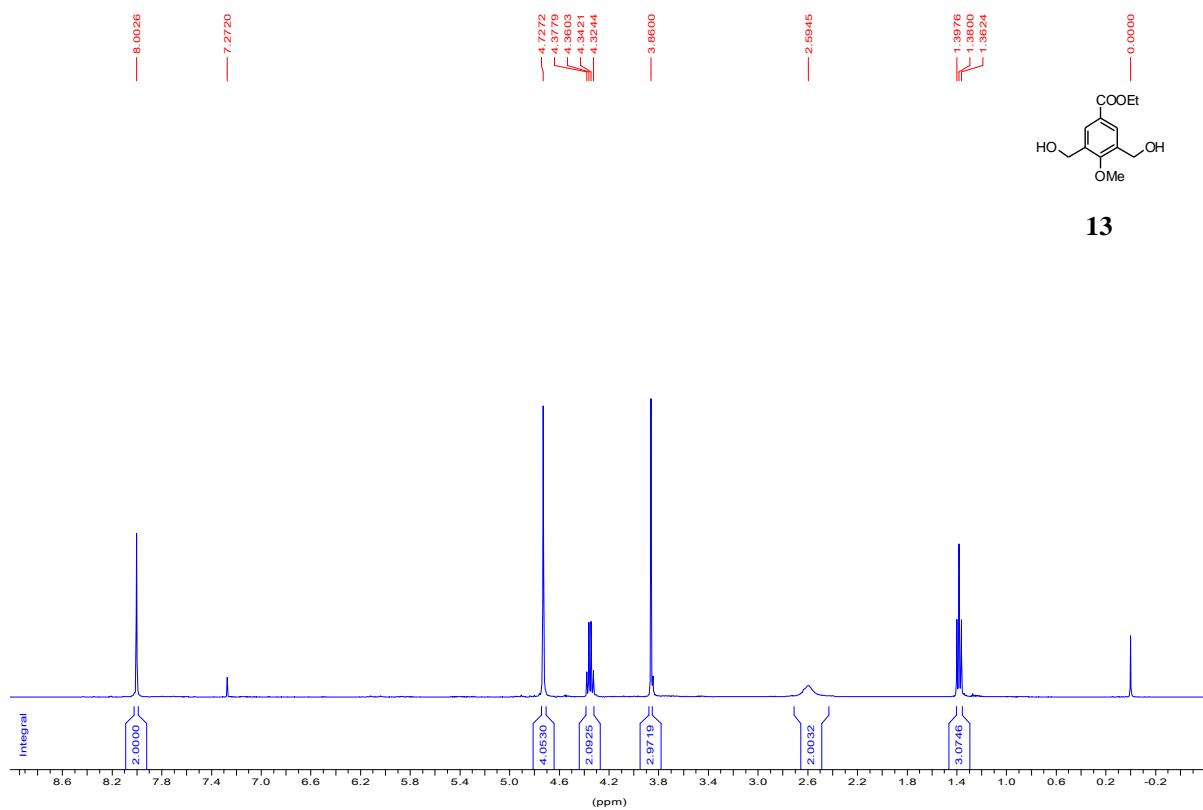
# 1. $^1\text{H}$ , $^{13}\text{C}$ and $^{77}\text{Se}$ NMR spectra for the novel precursors and homoselenacalix[*n*]arenes



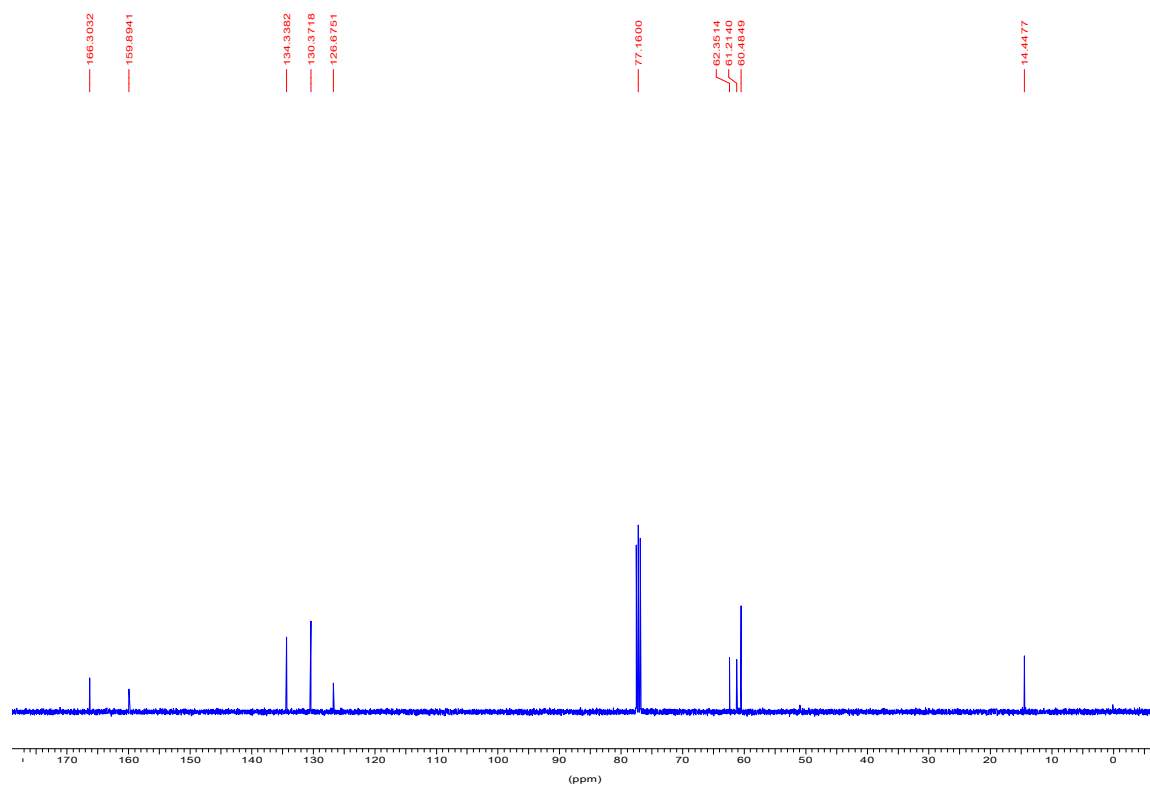


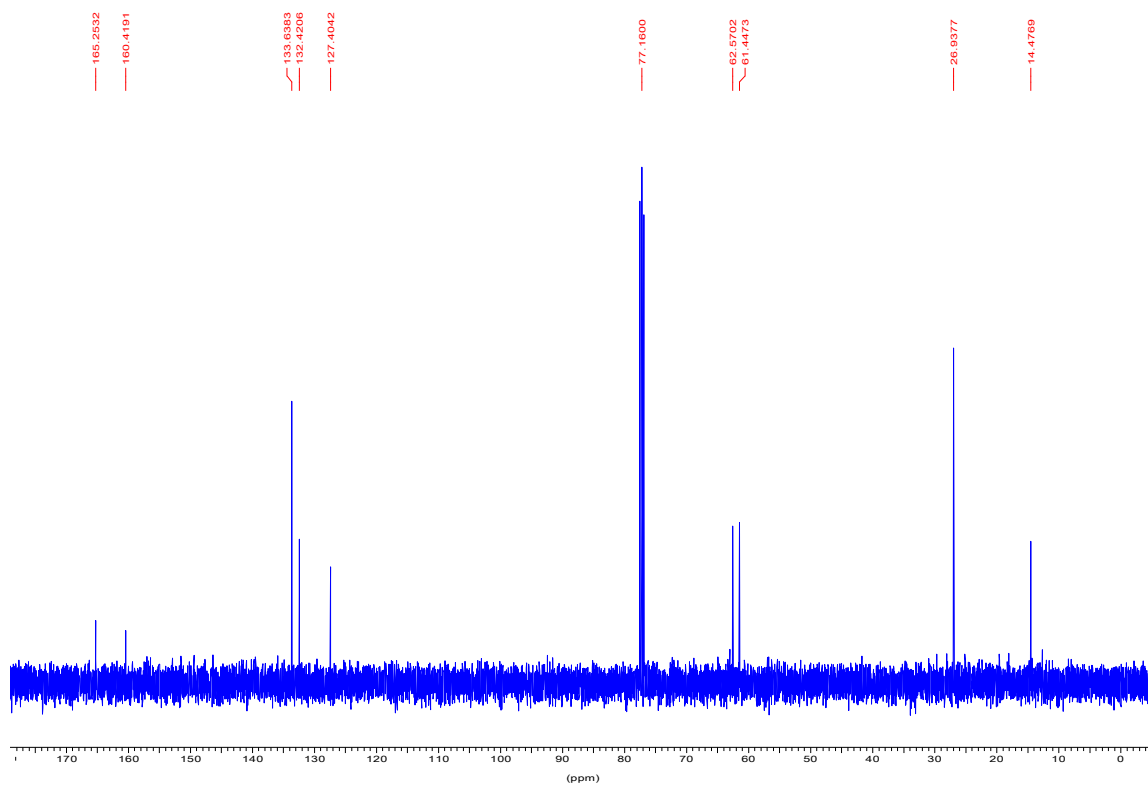
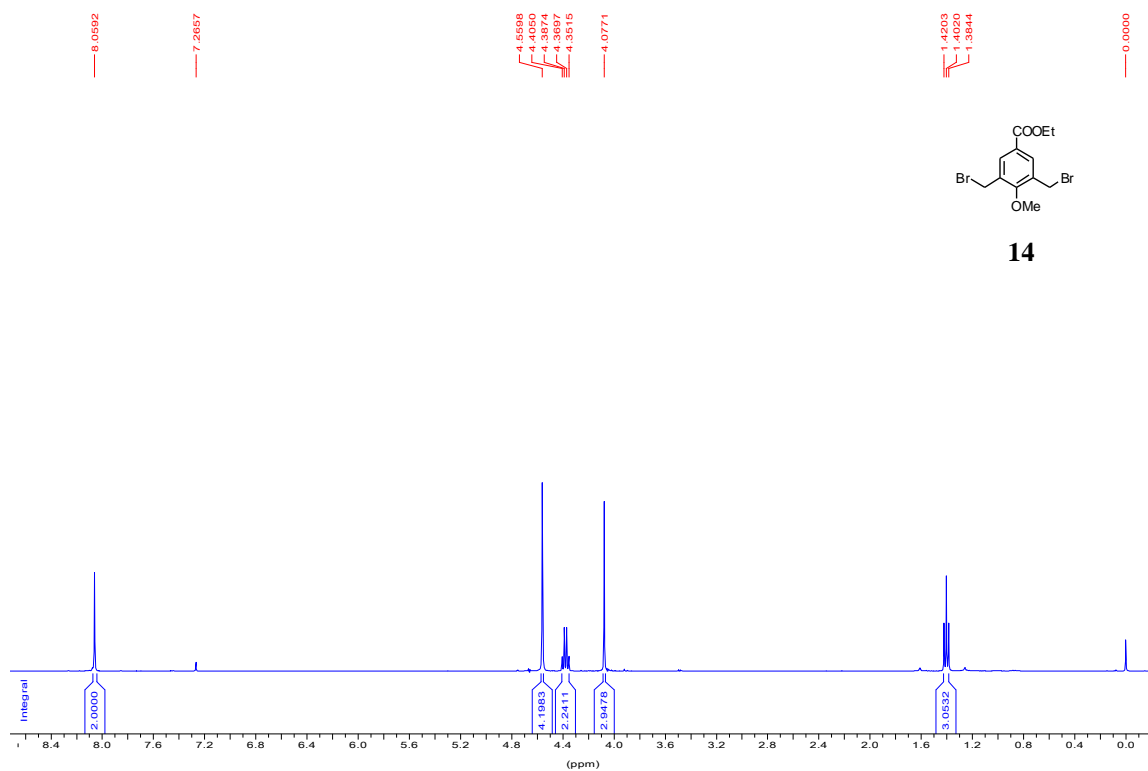


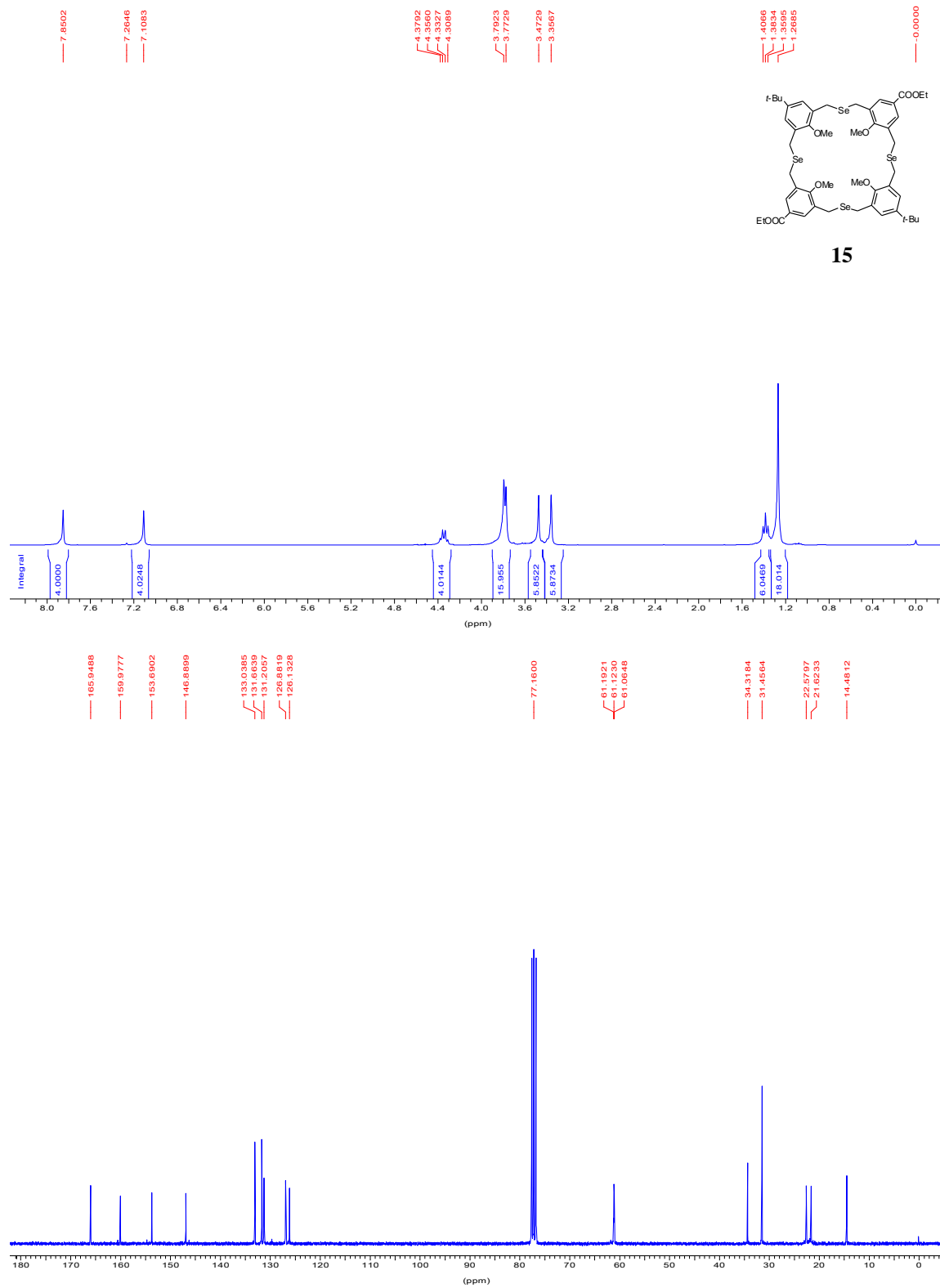




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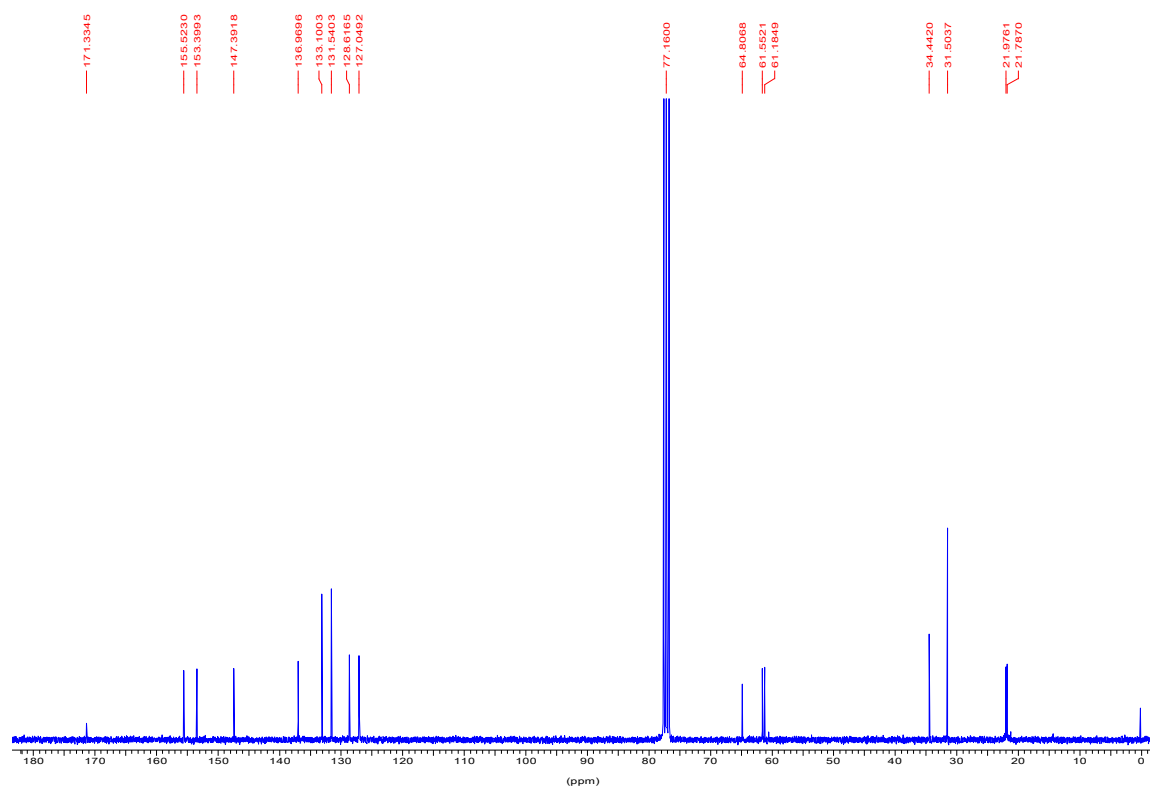




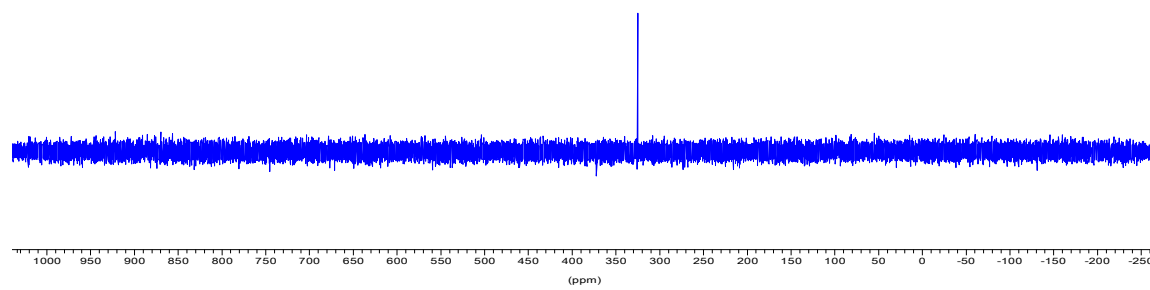


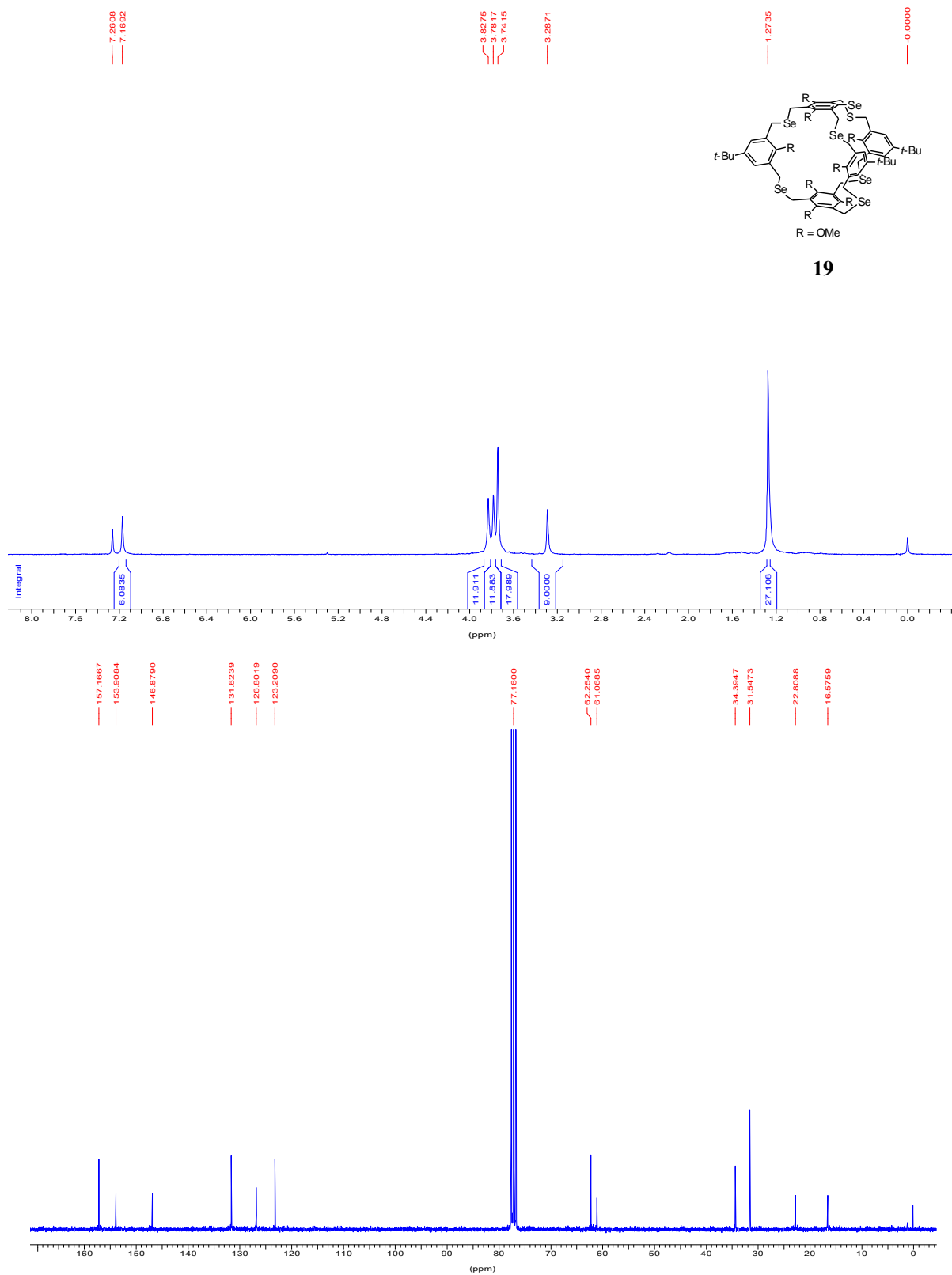


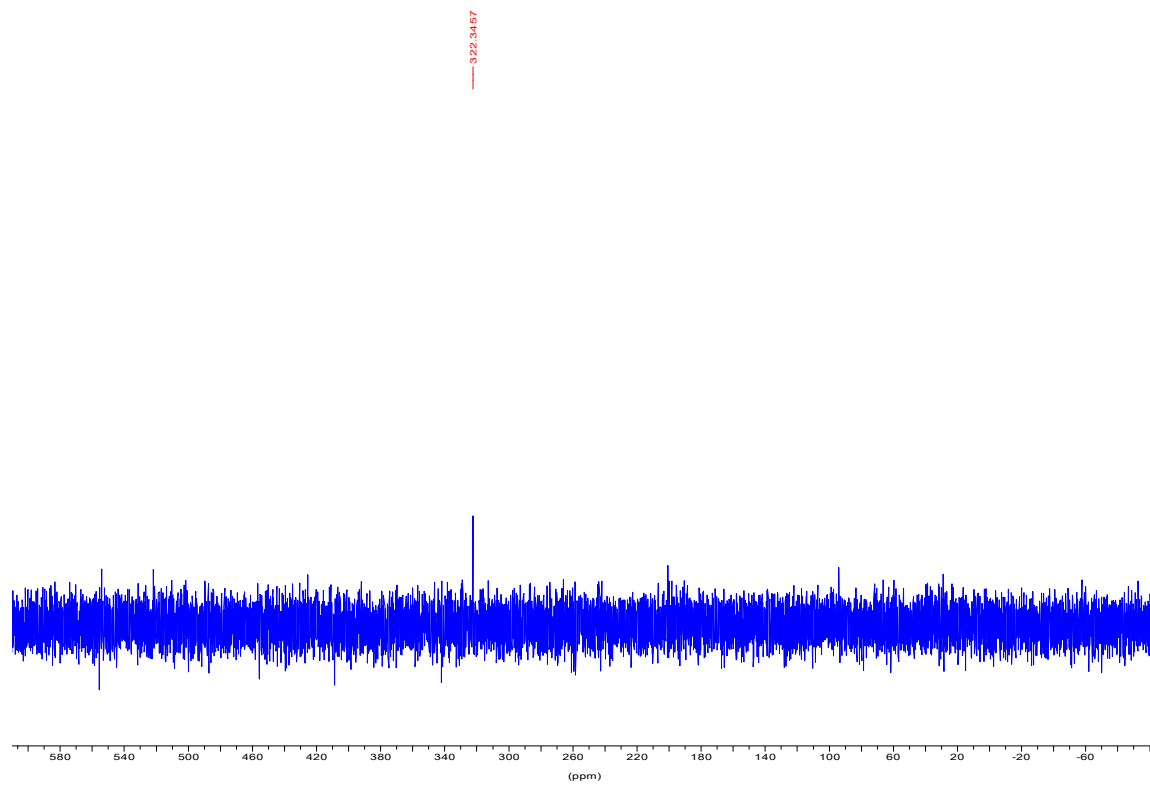




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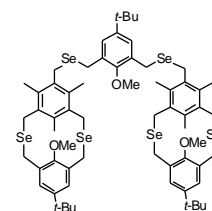
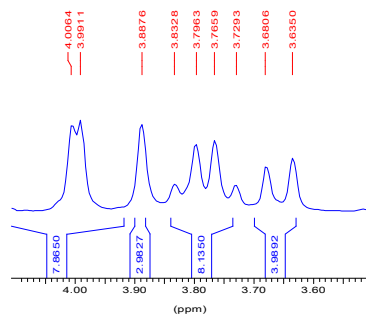
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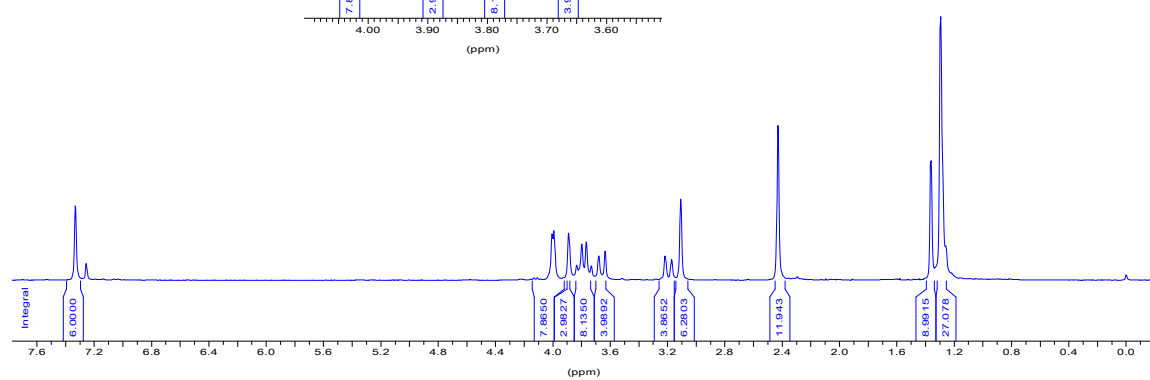
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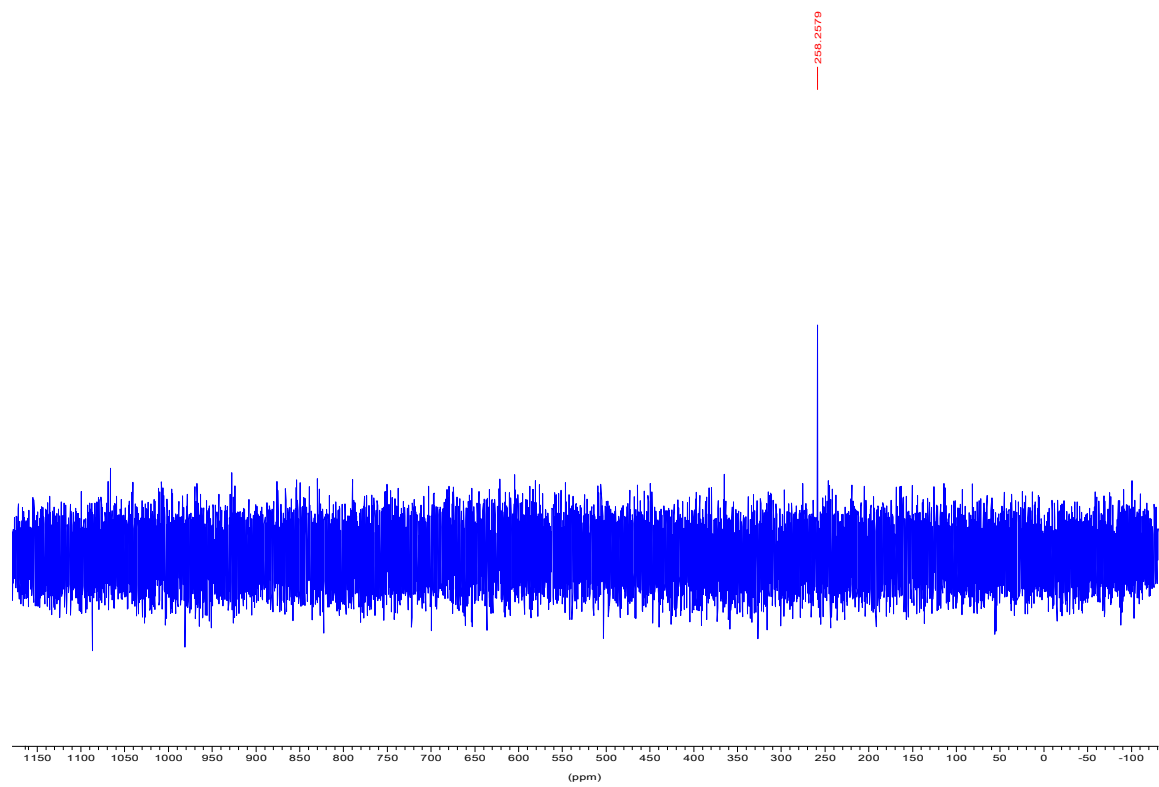
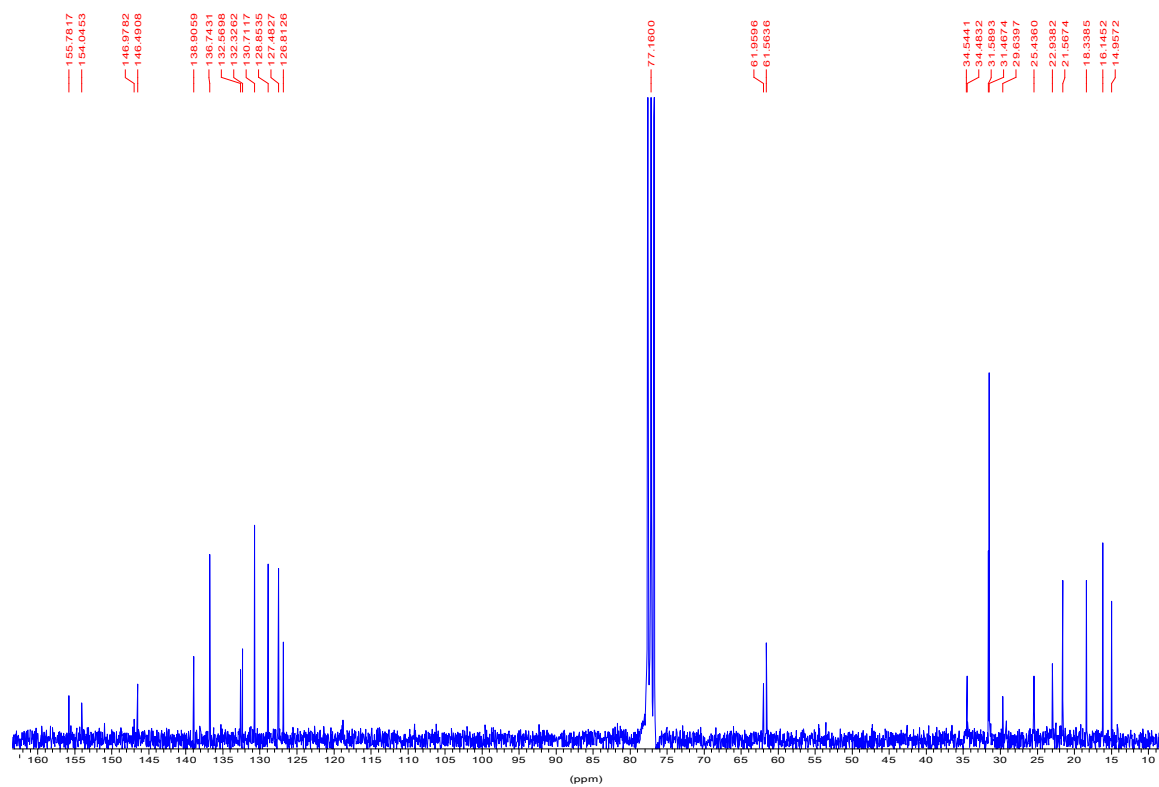
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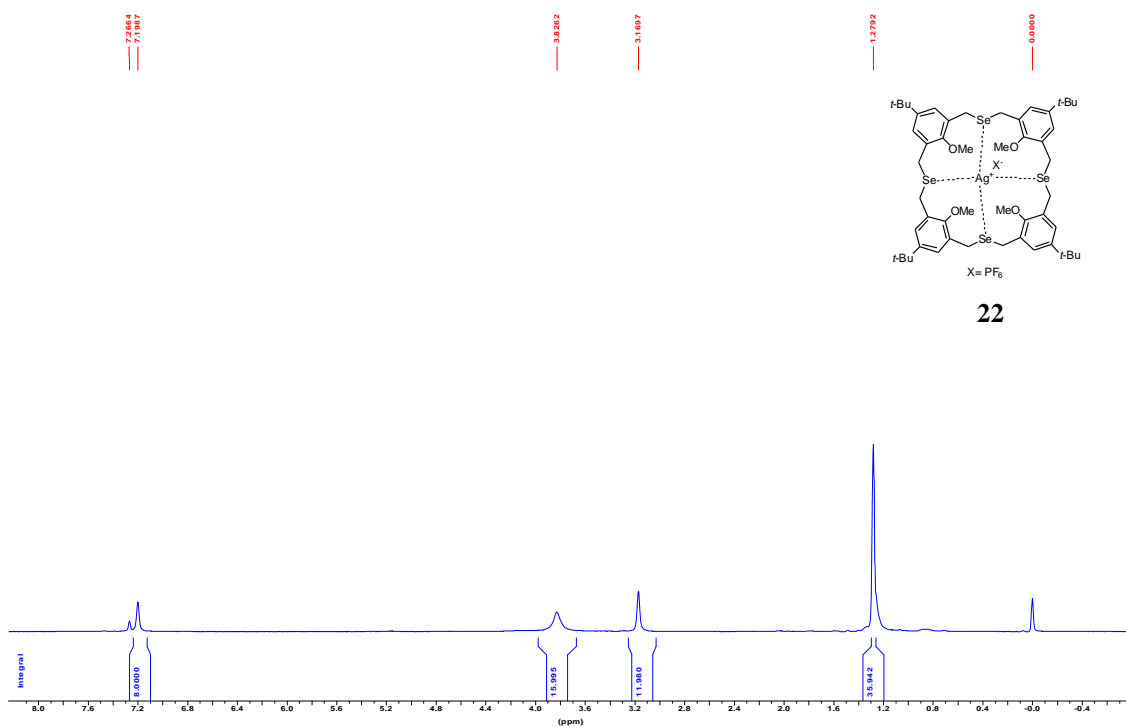
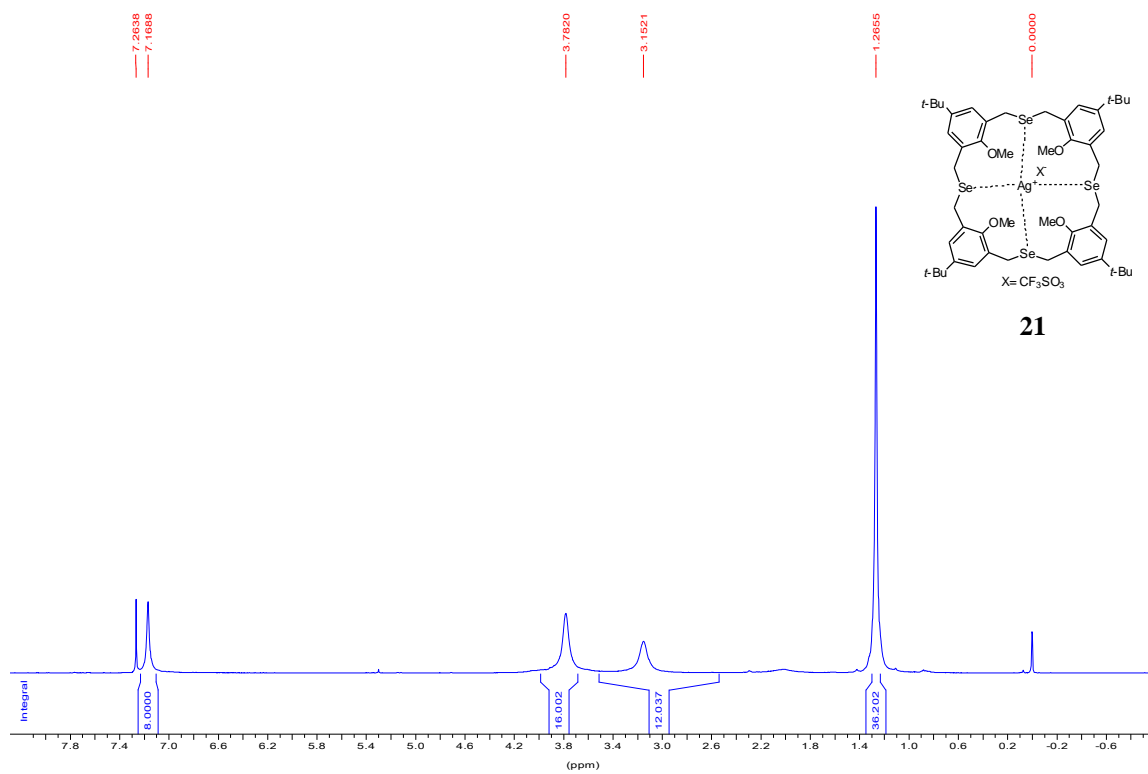
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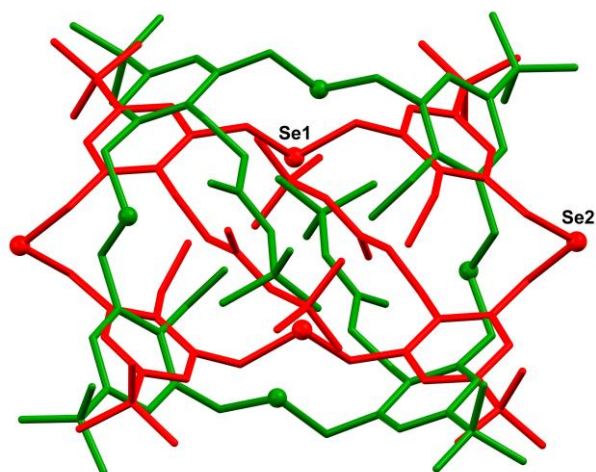




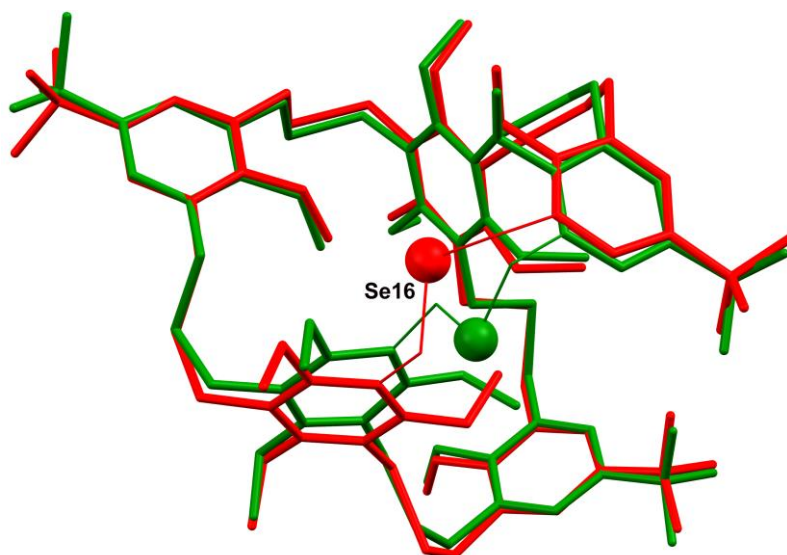


## 2. X-ray crystallographic general experimental data and additional figures for the structures of homoselenacalix[*n*]arenes 4·THF, **10**, **19**, **20**, **21** and **22**

Single crystal X-ray diffraction data for compounds **10**, **19**, **20** and **21** were collected on a SMART 6000 diffractometer with CCD detector using CuK $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ , crossed Goebel mirrors) and phi and omega scans.<sup>1</sup> Cell refinement and data reduction were performed using the program SAINT.<sup>2</sup> Measurements for 4·THF and **22** were performed on a Kuma KM4CCD  $\kappa$ -axis diffractometer with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data collection and data reduction were carried out with the Oxford Diffraction programs.<sup>3</sup> The structures were solved by direct methods and refined by full-matrix least squares on  $|F^2|$  using the SHELXS-97 program.<sup>4</sup> All data collections were carried out at 100(2) K to minimize solvent loss, possible structural disorder and thermal motion effects. All non-hydrogen atoms were anisotropically refined and the hydrogen atoms were placed on calculated positions with temperature factors fixed at 1.2 times  $U_{eq}$  of the parent atoms and 1.5 times  $U_{eq}$  for methyl groups. The program Mercury was used to prepare molecular graphics images.<sup>5</sup> Some of the *tert*-butyl groups were disordered over two orientations, namely C26 in **10**, C70 in **19** and C34 in **21** as well as the counter ions in **21** and **22** ( $\text{PF}_6^-$  located on a special position).

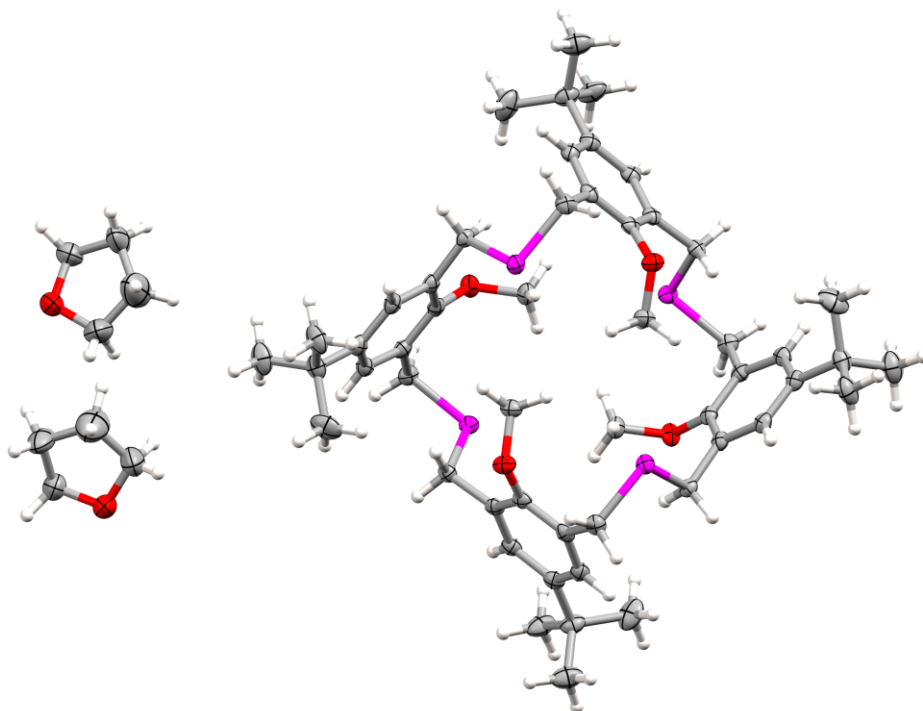


**Fig. S1** Overlay of the structure of homoselenacalix[4]arene **10** (shown in red) with the previously reported analogous homothiocalix[4]arene<sup>6</sup> (shown in green); Se/S atoms are represented by balls.

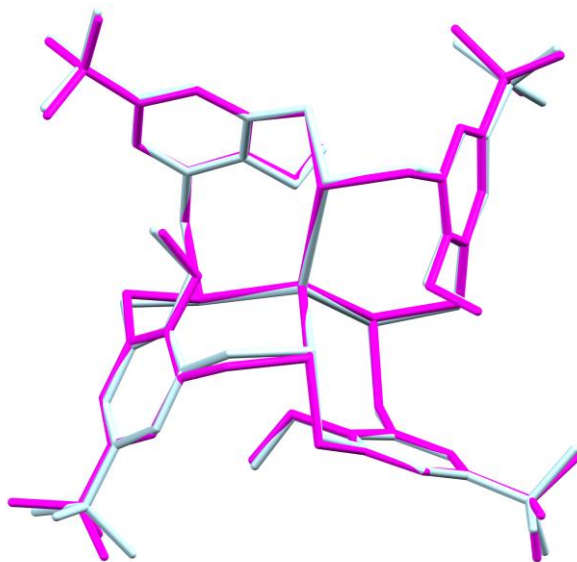


**Fig. S2** Overlay of bicyclohomoselenacalix[4]arene **19** (shown in red) with the earlier reported analogous bicyclohomothiocalix[4]arene<sup>6</sup> (shown in green), showing a different geometry around one of the heteroatom bridges.

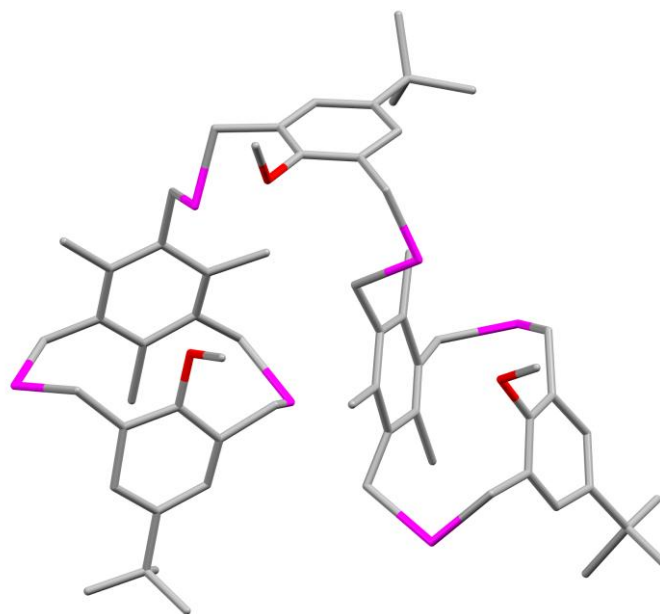




**Fig. S3** Molecular structure of the THF solvate of homoselenacalix[4]arene **4** (thermal ellipsoids are drawn at 50% probability).

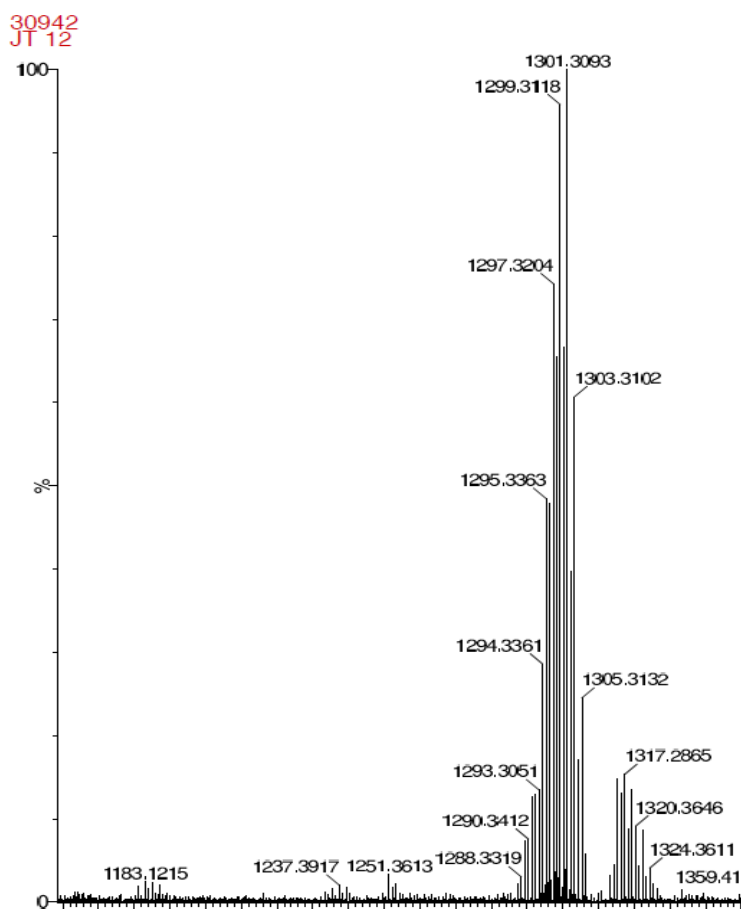


**Fig. S4** Overlay of Ag(I) complexes **21** (purple) and **22** (blue-grey), presenting approximately the same conformation of the calixarene units adopted after complexation.

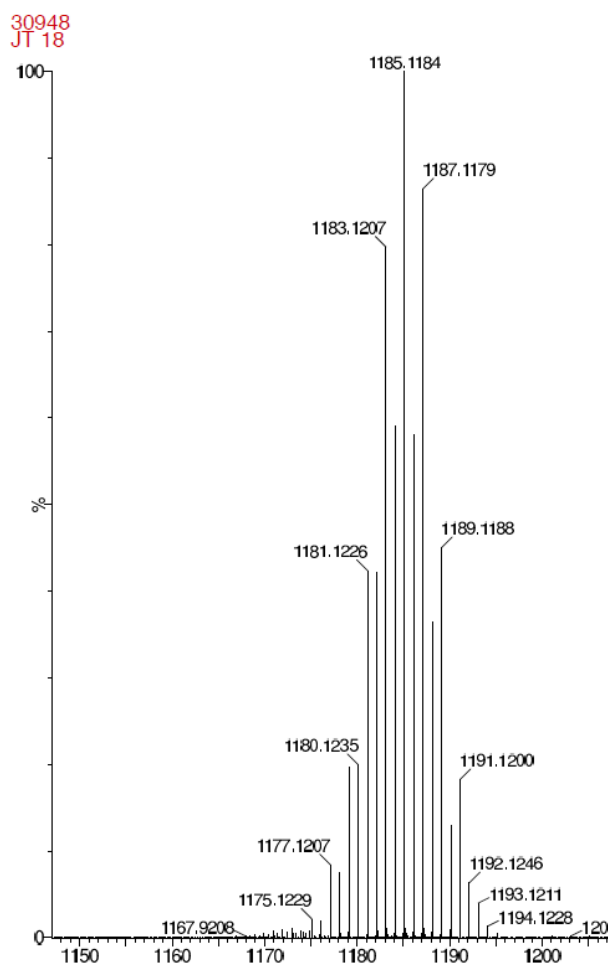


**Fig. S5** Capped-sticks representation of the (non-refined) structure of bis(selenacyclophane) 20.

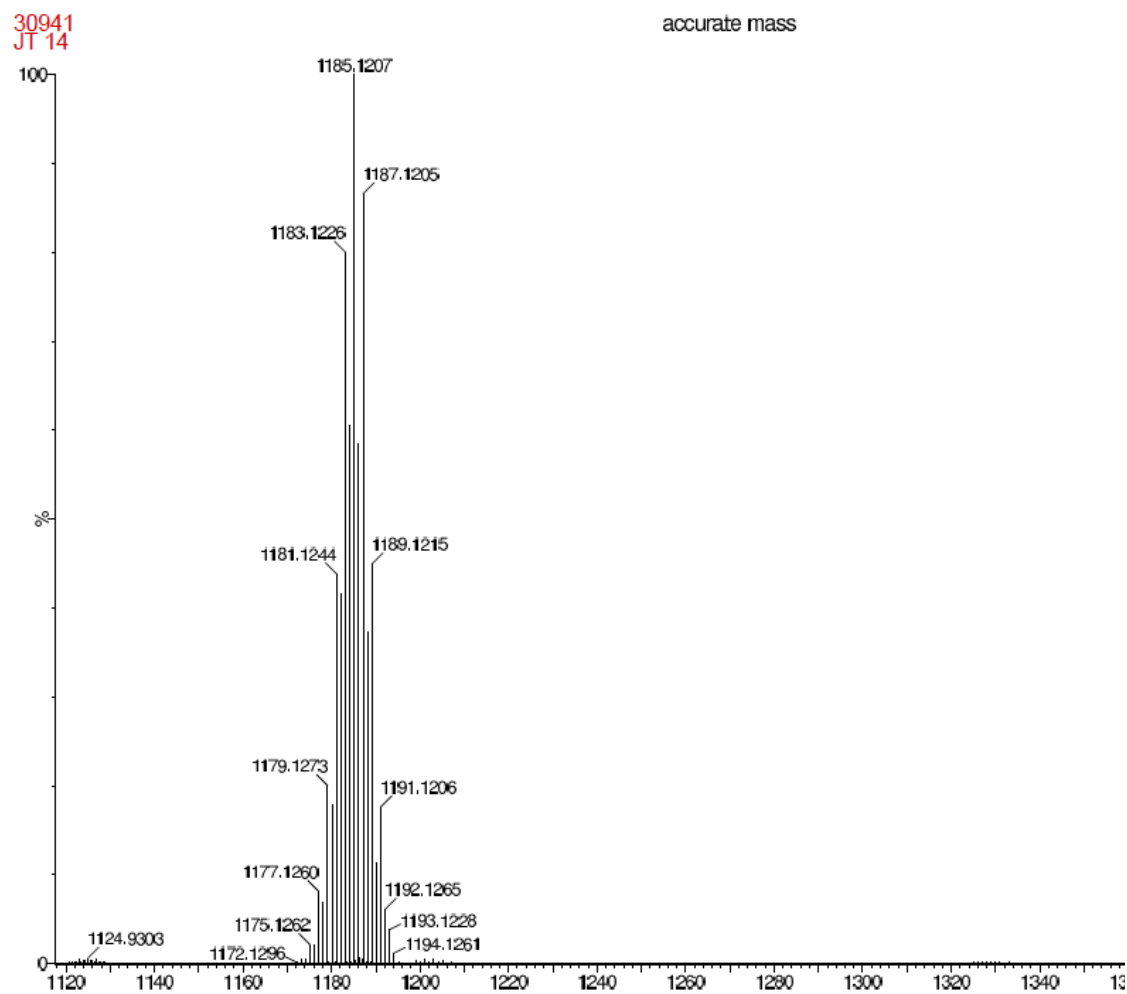
### 3. FTMS (ESI<sup>+</sup>) isotopic patterns for homoselenacalix[4]arene **10** and metal complexes **21** and **22**



**Fig. S6** Observed high resolution FTMS (ESI<sup>+</sup>) isotopic pattern for homoselenacalix[4]arene **10** ([M+Na]<sup>+</sup>).



**Fig. S7** Observed high resolution FTMS (ESI<sup>+</sup>) isotopic pattern for complex **21** ([M-CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>).



**Fig. S8** Observed high resolution FTMS ( $\text{ESI}^+$ ) isotopic pattern for complex **22** ( $[\text{M-PF}_6]^+$ ).

#### 4. References

- 1 SMART, Version 5.625, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
- 2 SAINT, Version 5/6.0, Bruker AXS Inc., Madison, Wisconsin, USA, 1997.
- 3 CrysAlis CCD and CrysAlis RED, Version 1.171.33.52, Oxford Diffraction Ltd, Abingdon, Oxfordshire, England, 2009.
- 4 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
- 5 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466.
- 6 J. Thomas, K. Van Hecke, K. Robeyns, W. Van Rossom, M. P. Sonawane, L. Van Meervelt, M. Smet, W. Maes and W. Dehaen, *Chem. Eur. J.*, 2011, **17**, 10339.