

Electronic Supplementary Information

Investigations into the Effects of Linker Length Elongation on the Behaviour of Calcium-responsive MRI Probes

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Supplementary Figures

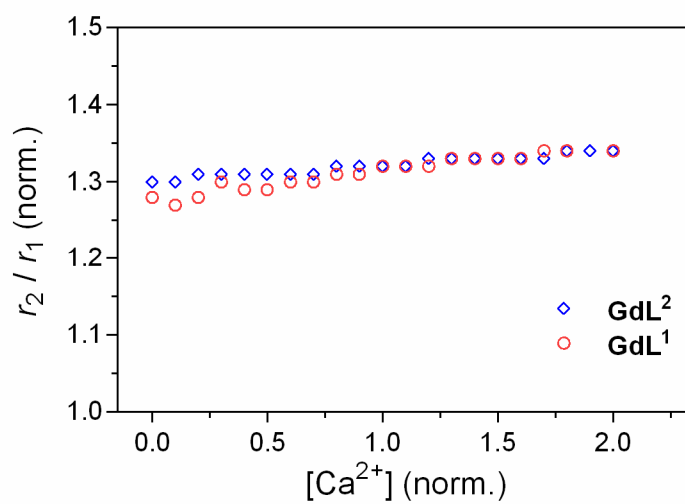


Figure S1. Relaxometric titration curves (300 MHz, 25 °C) showing the r_2/r_1 ratio change of **GdL¹** and **GdL²** upon addition of Ca^{2+} .

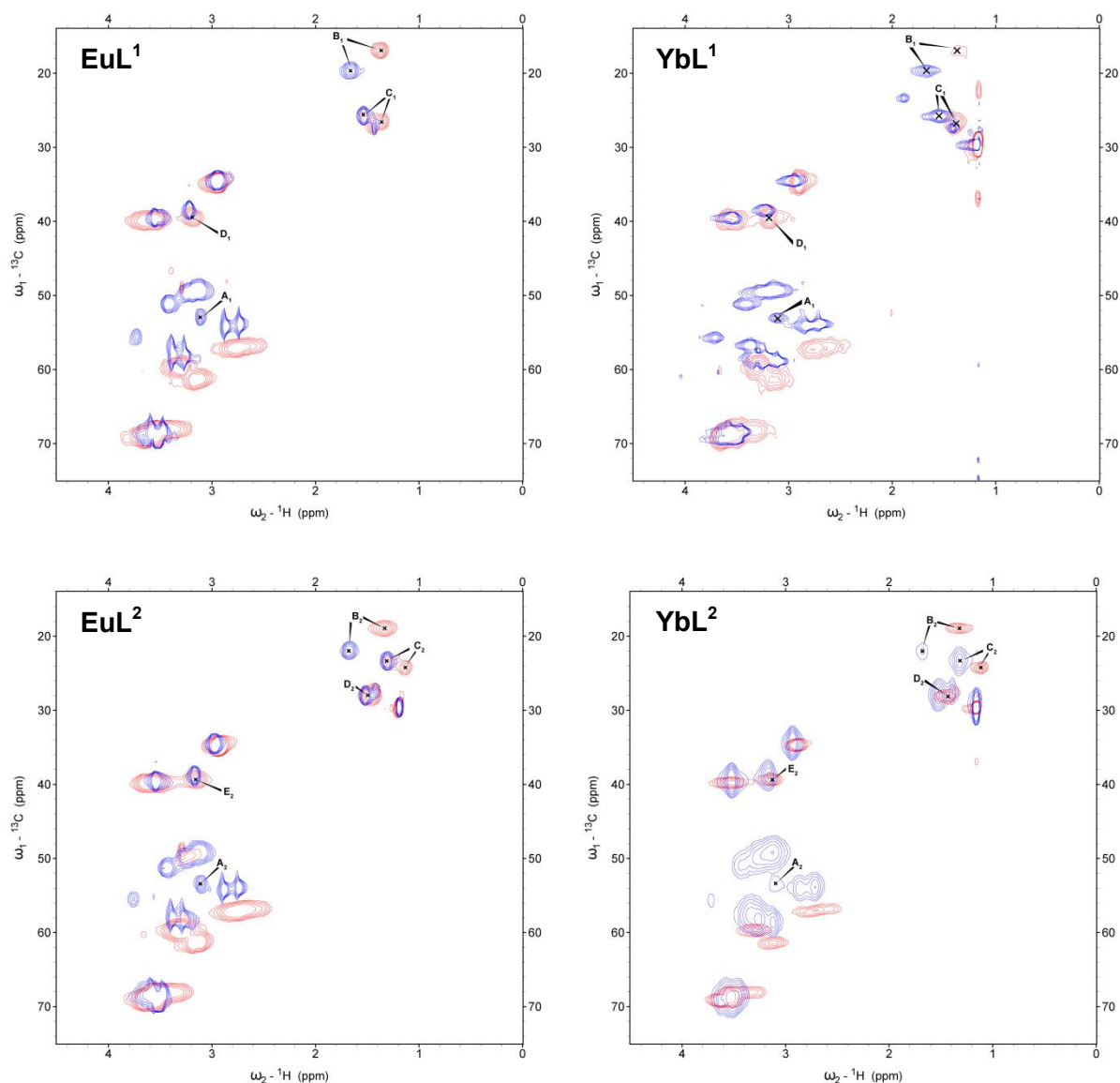


Figure S2. HSQC spectra of Eu^{3+} (left) and Yb^{3+} (right) complexes of L^1 (top) and L^2 (bottom) with the signals of interest assigned pre-(blue) and post- Ca^{2+} (red) addition. Chemical structures of studied complexes with the methylene units of interest labelled are presented in Figures 2-3.

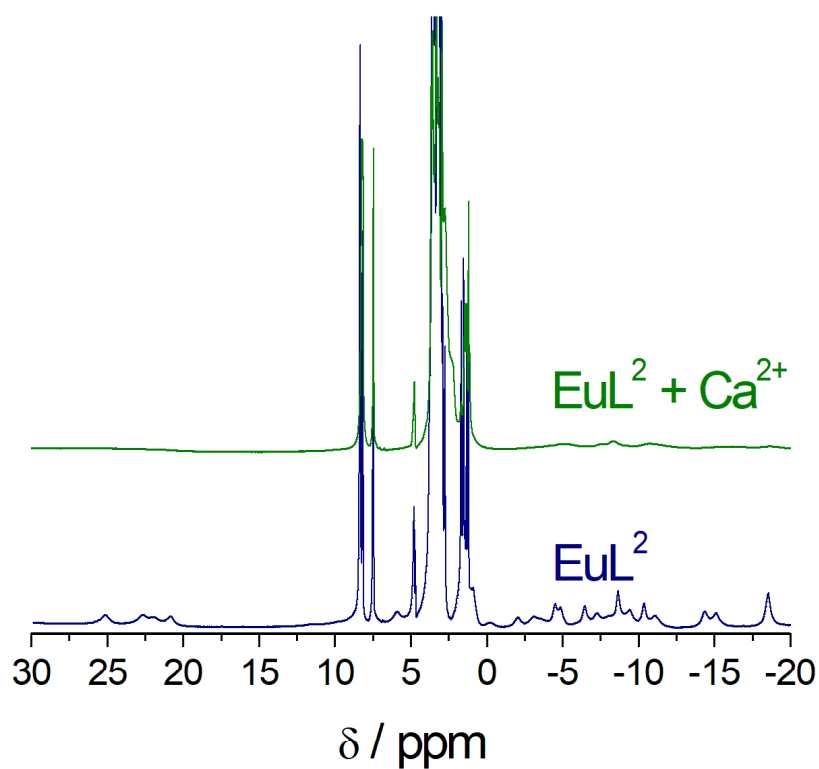
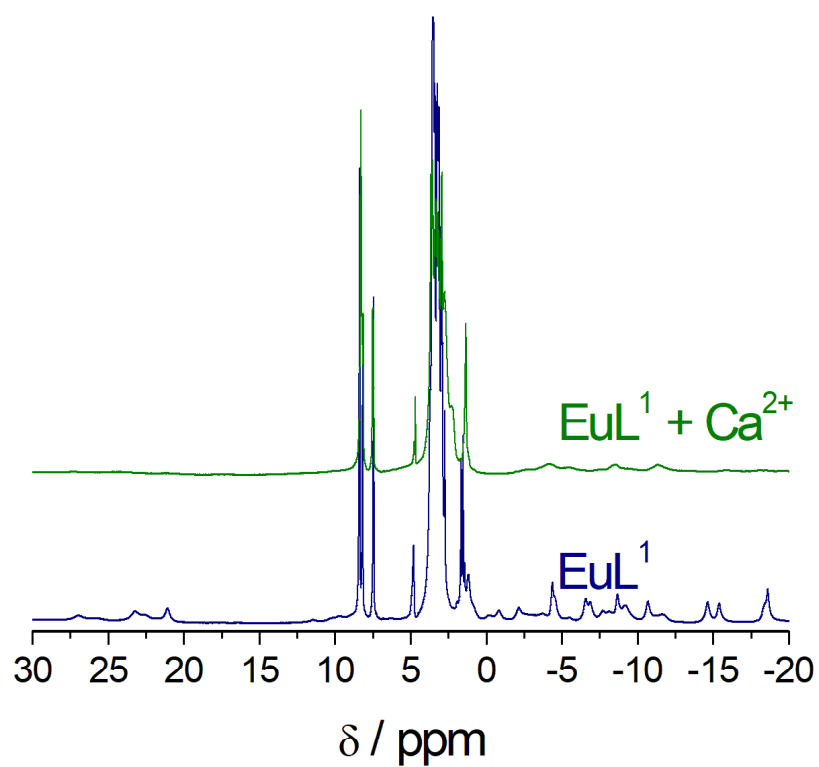


Figure S3. ¹H NMR spectra of **EuL¹** (top) and **EuL²** (bottom) in absence and presence of 2 equiv. Ca²⁺ (800 MHz, 25 °C, pD 7).

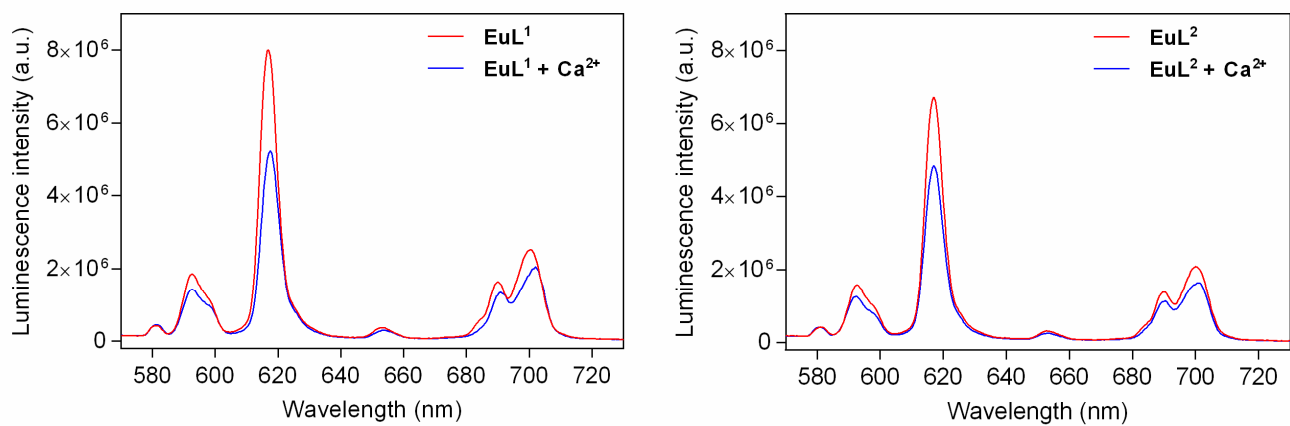


Figure S4. Luminescence emission spectra of **EuL¹** (left) and **EuL²** (right) in absence and presence of 2 equiv. Ca²⁺ (H₂O, 25 °C, pH 7).

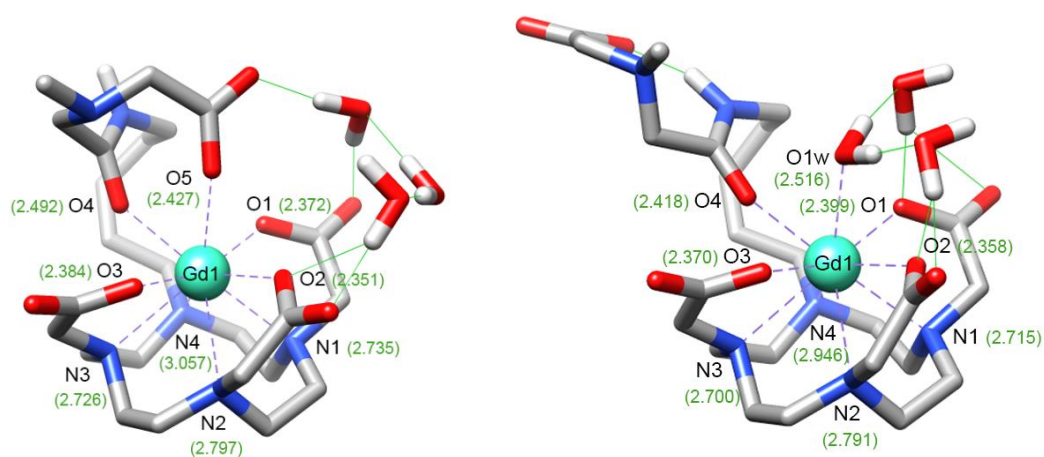


Figure S5. Optimized structures of the GdL^{2+} system obtained with DFT calculations showing the coordination of the carboxylate group of the side chain (left) or the coordination of a water molecule (right). The numbers represent the calculated bond distances (\AA) between the metal center and the ligand donor atoms.

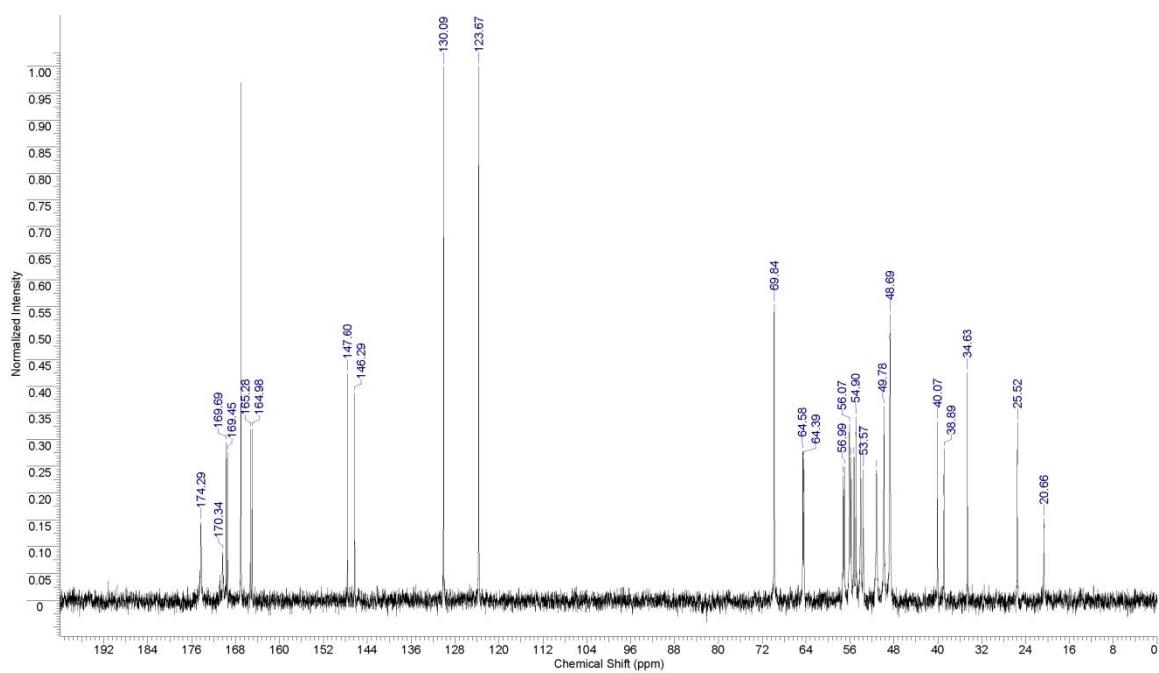
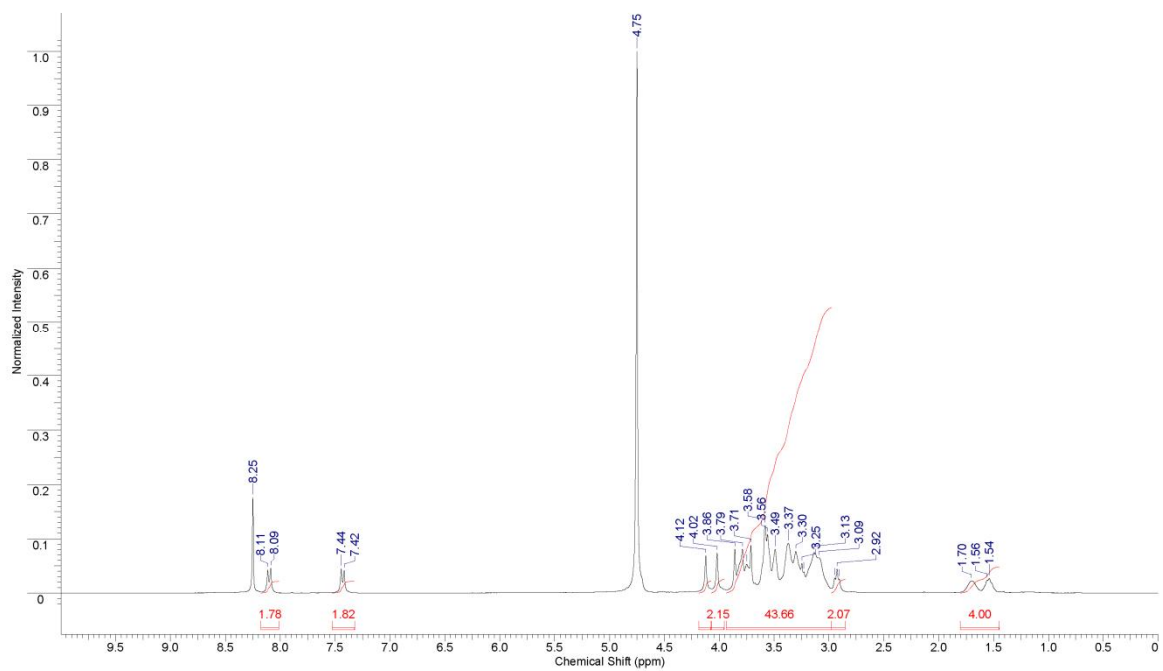


Figure S6. ¹H NMR (top) and ¹³C NMR (bottom) spectra of **L**¹ (300 MHz, 25 °C, D₂O).

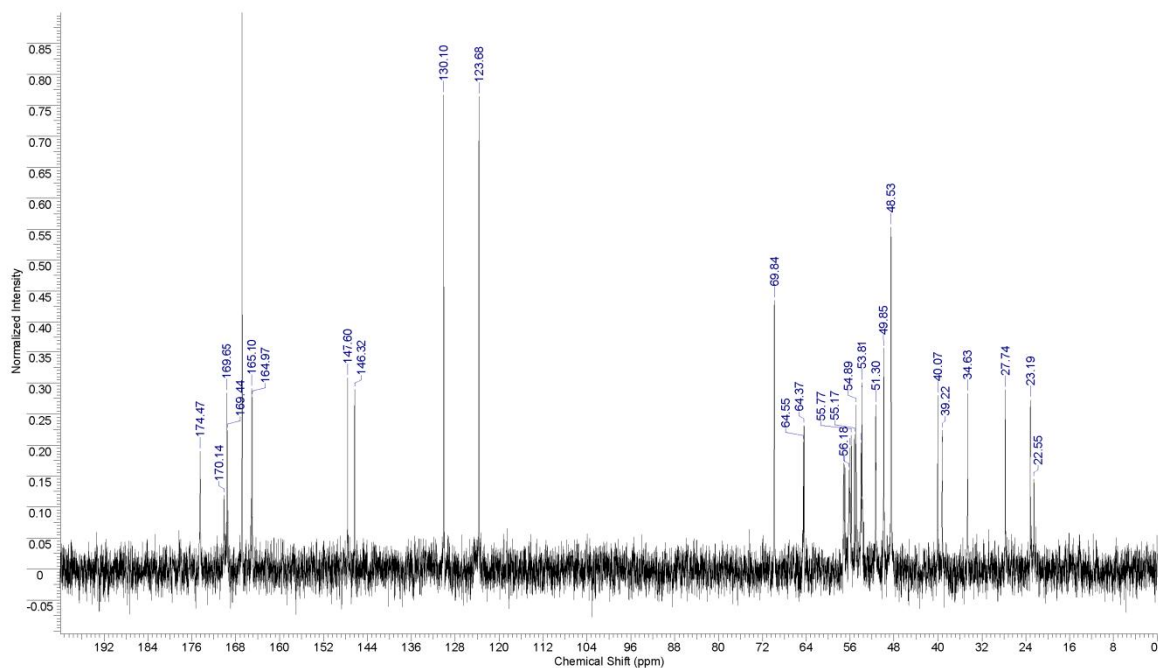
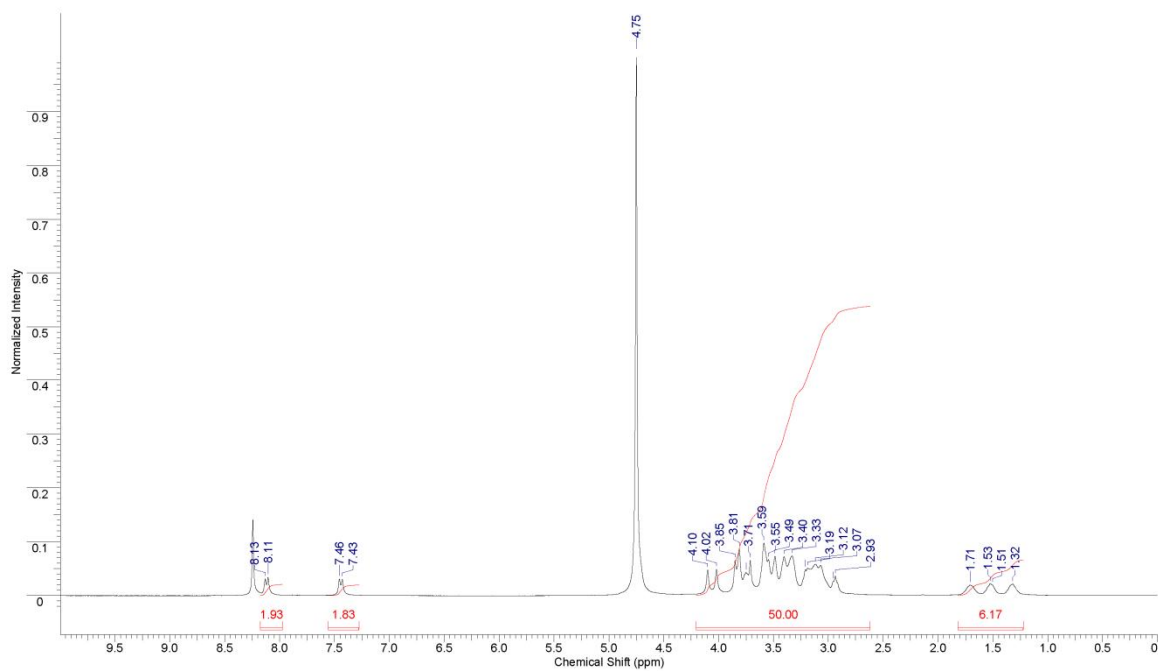


Figure S7. ¹H NMR (top) and ¹³C NMR (bottom) spectra of L² (300 MHz, 25 °C, D₂O).

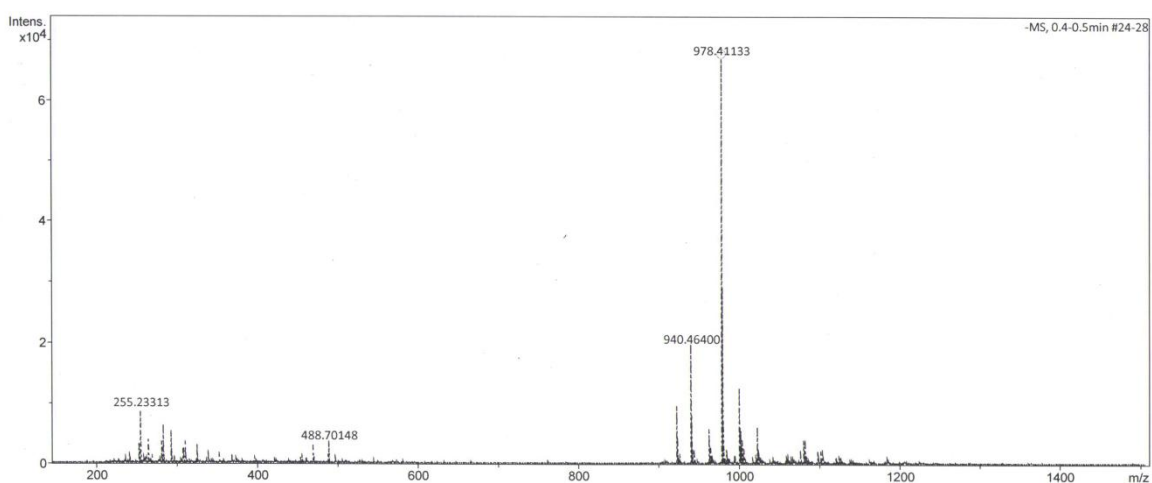
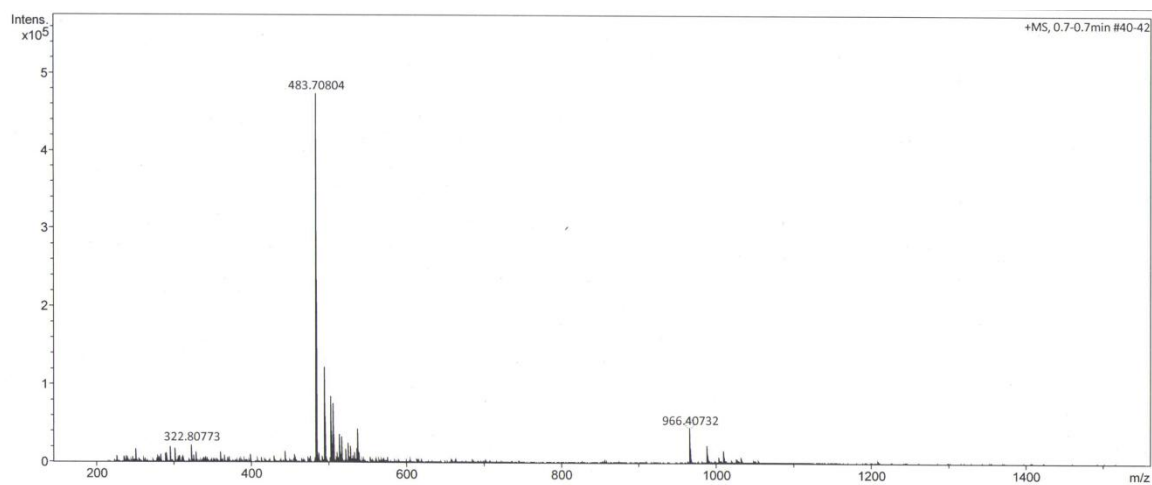


Figure S8. HRMS spectra of L^1 (top) and L^2 (bottom).

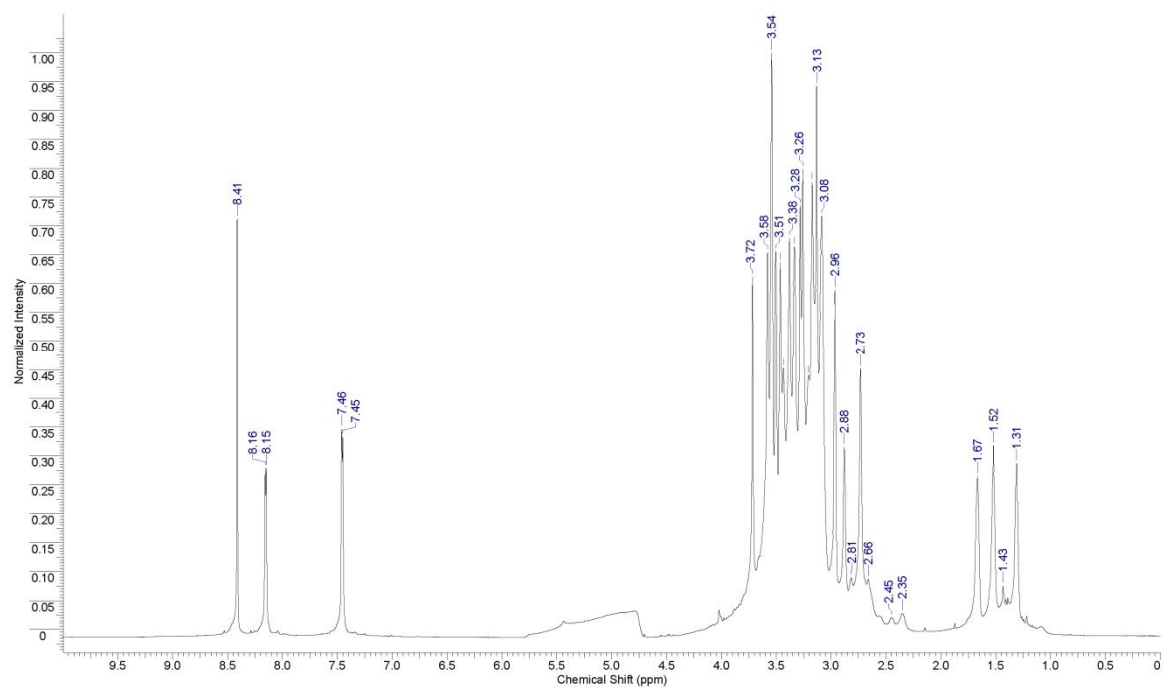
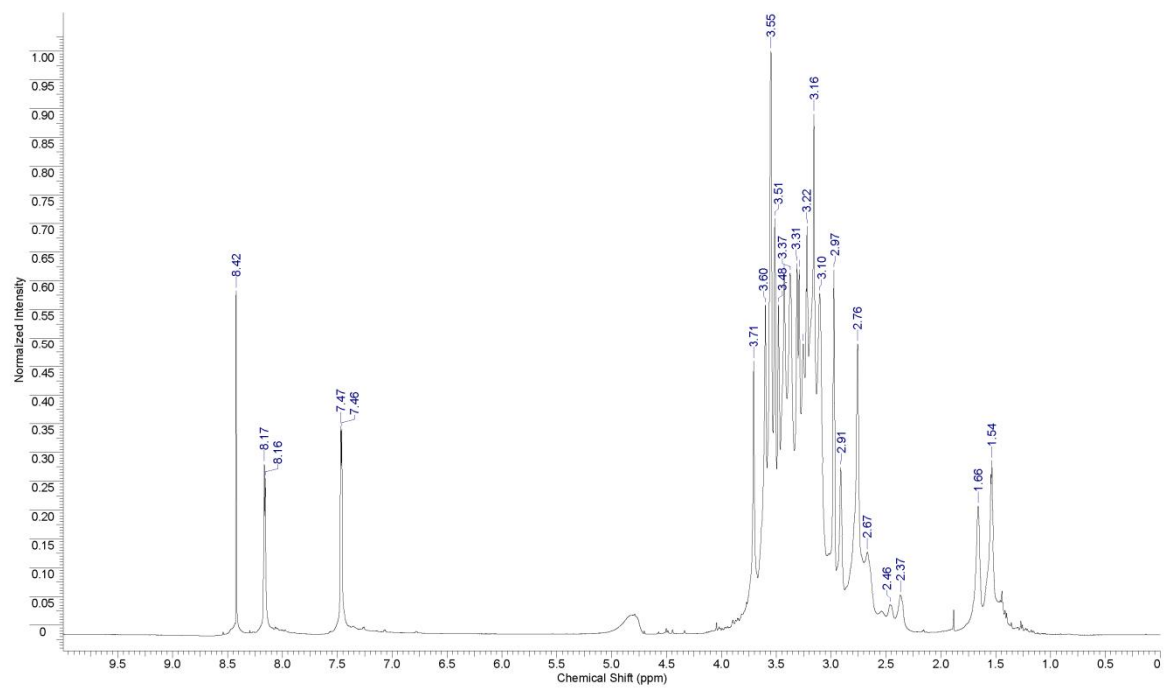


Figure S9. ¹H NMR spectra of YL¹ (top) and YL² (bottom) (300 MHz, 25 °C, D₂O).

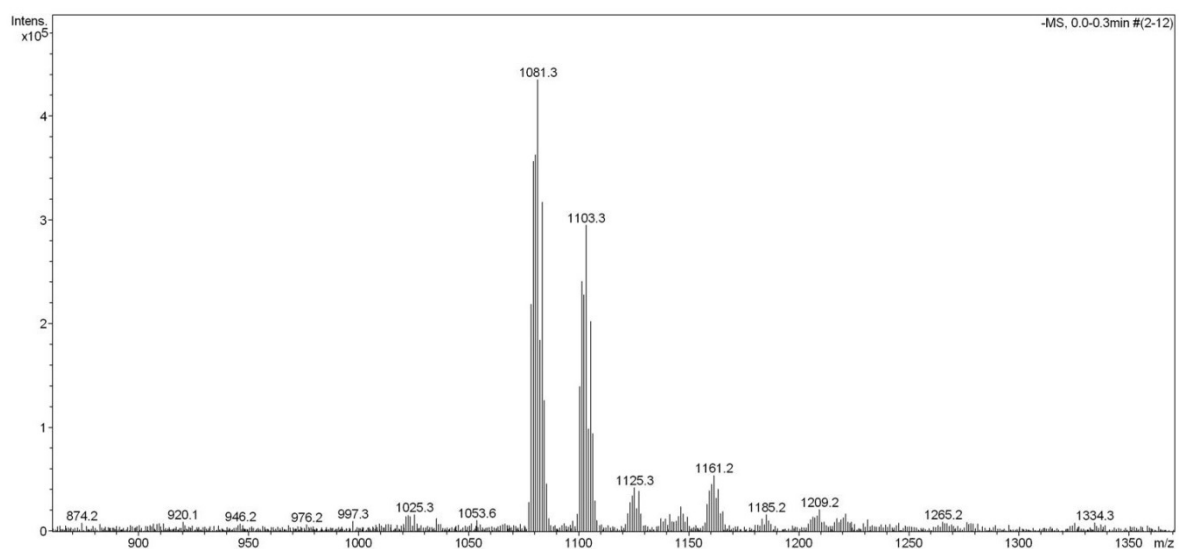


Figure S10. ESI-LRMS spectra of GdL¹.

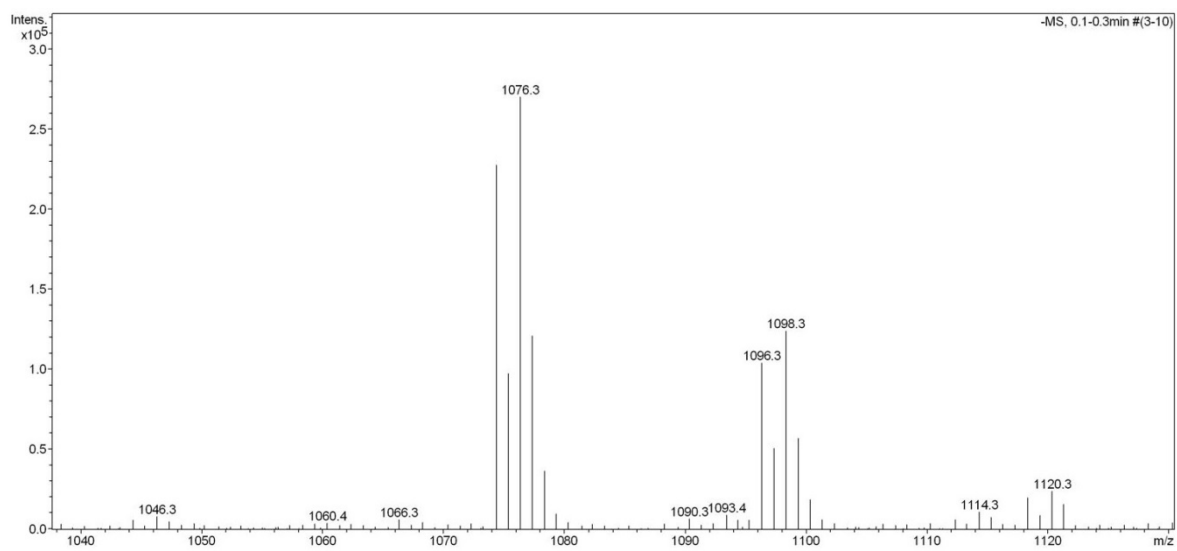


Figure S11. ESI-LRMS spectra of EuL¹.

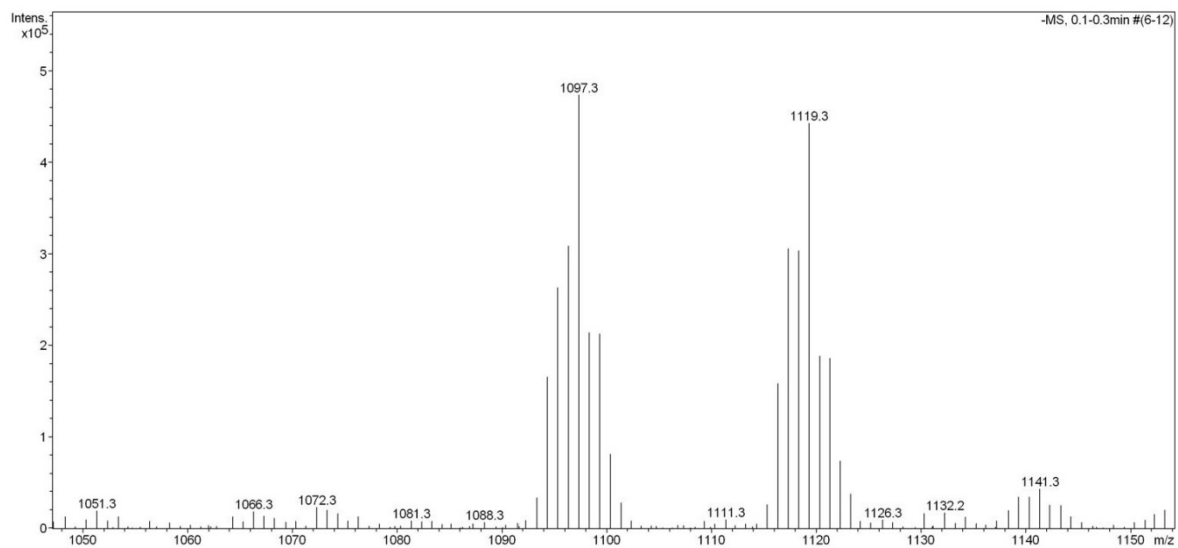


Figure S12. ESI-LRMS spectra of YbL¹.

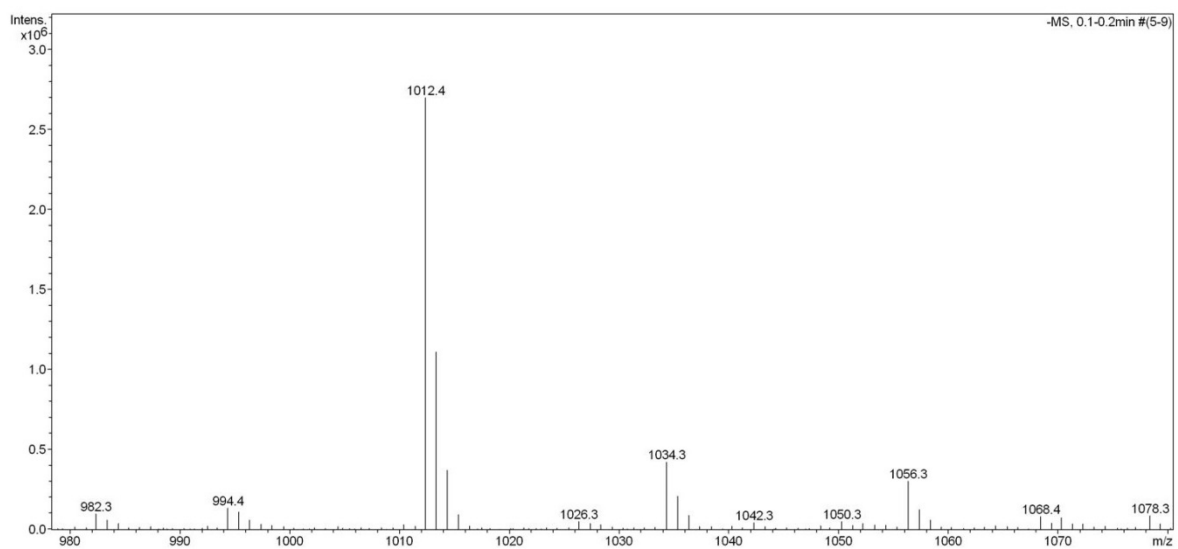


Figure S13. ESI-LRMS spectra of YL¹.

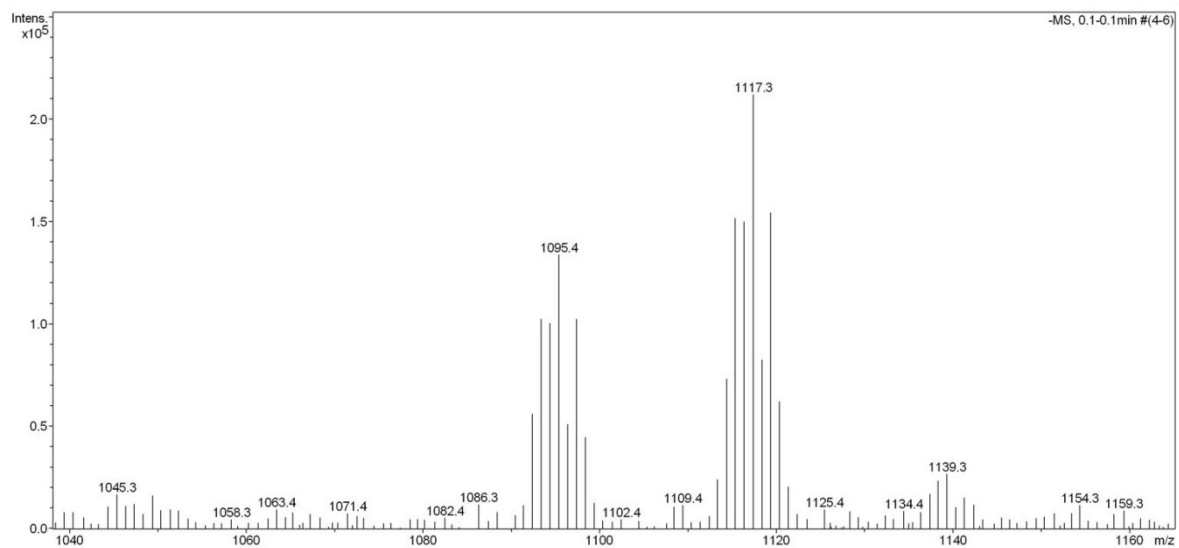


Figure S14. ESI-LRMS spectra of GdL².

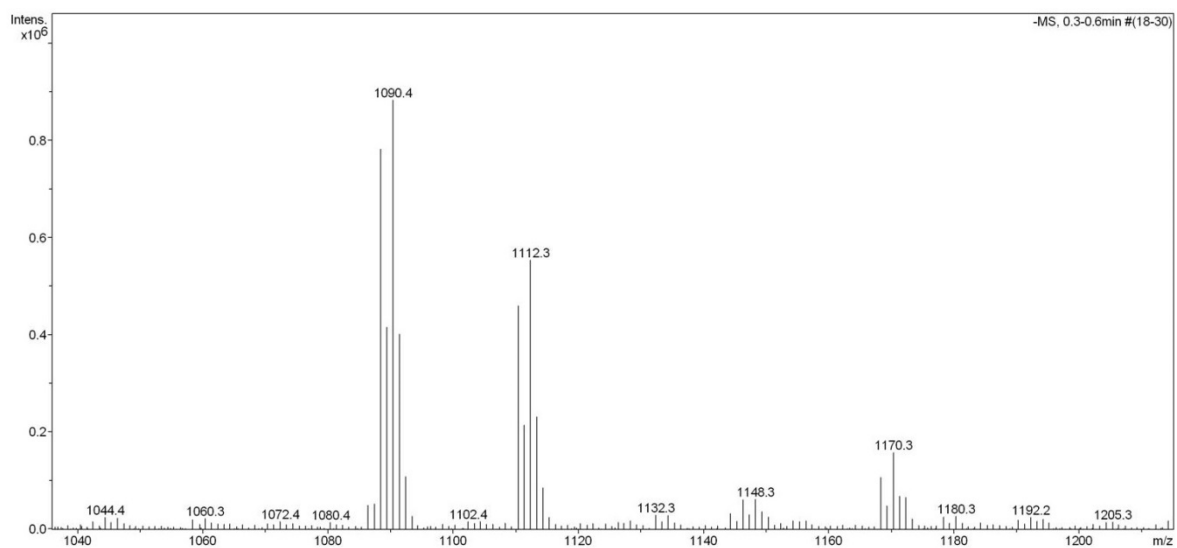


Figure S15. ESI-LRMS spectra of EuL².

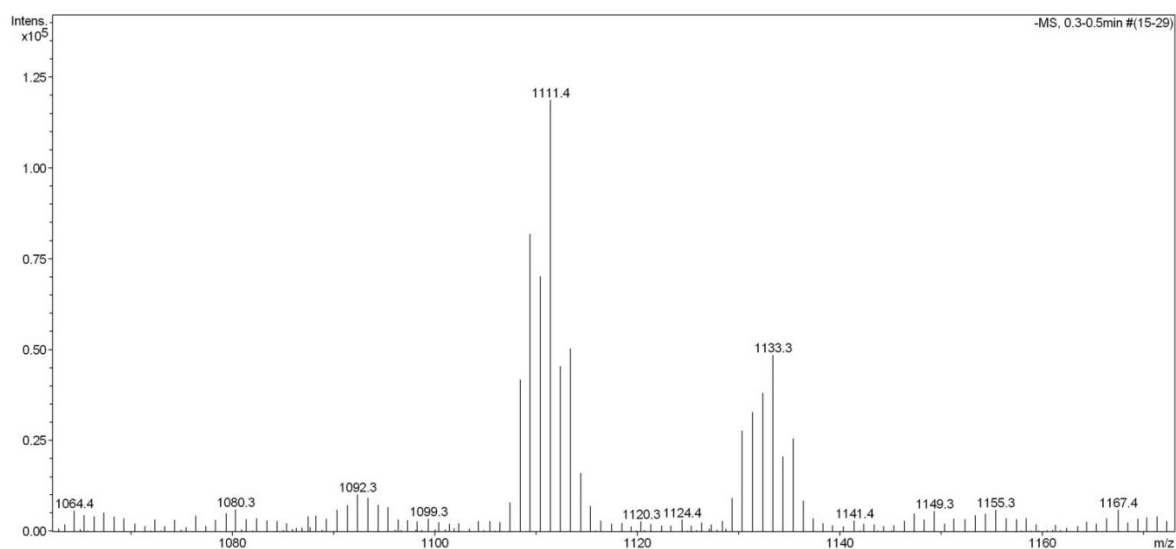


Figure S16. ESI-LRMS spectra of YbL².

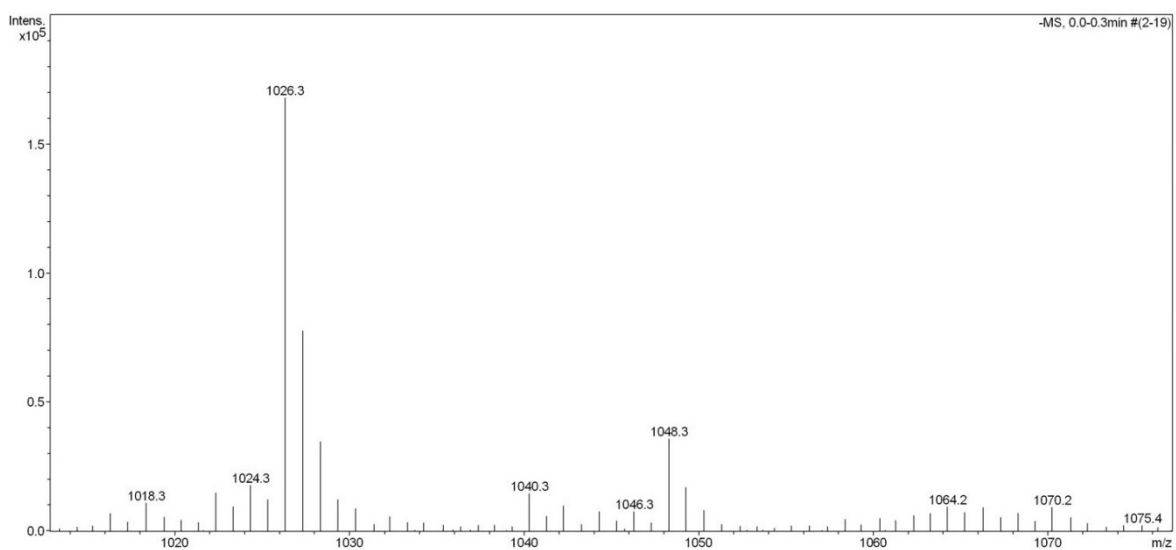


Figure S17. ESI-LRMS spectra of YL².

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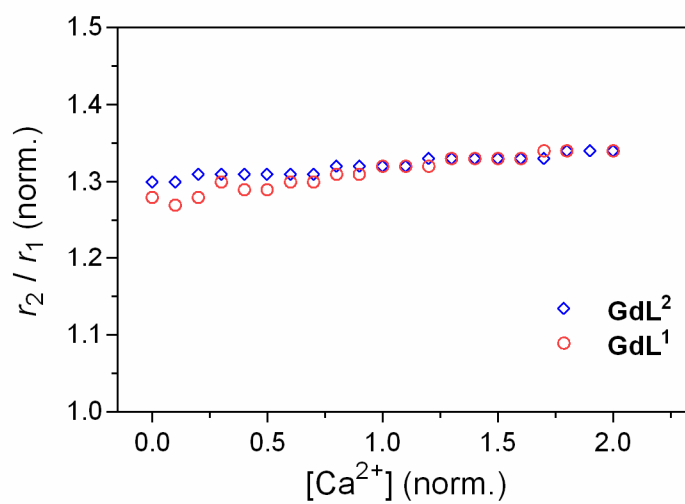


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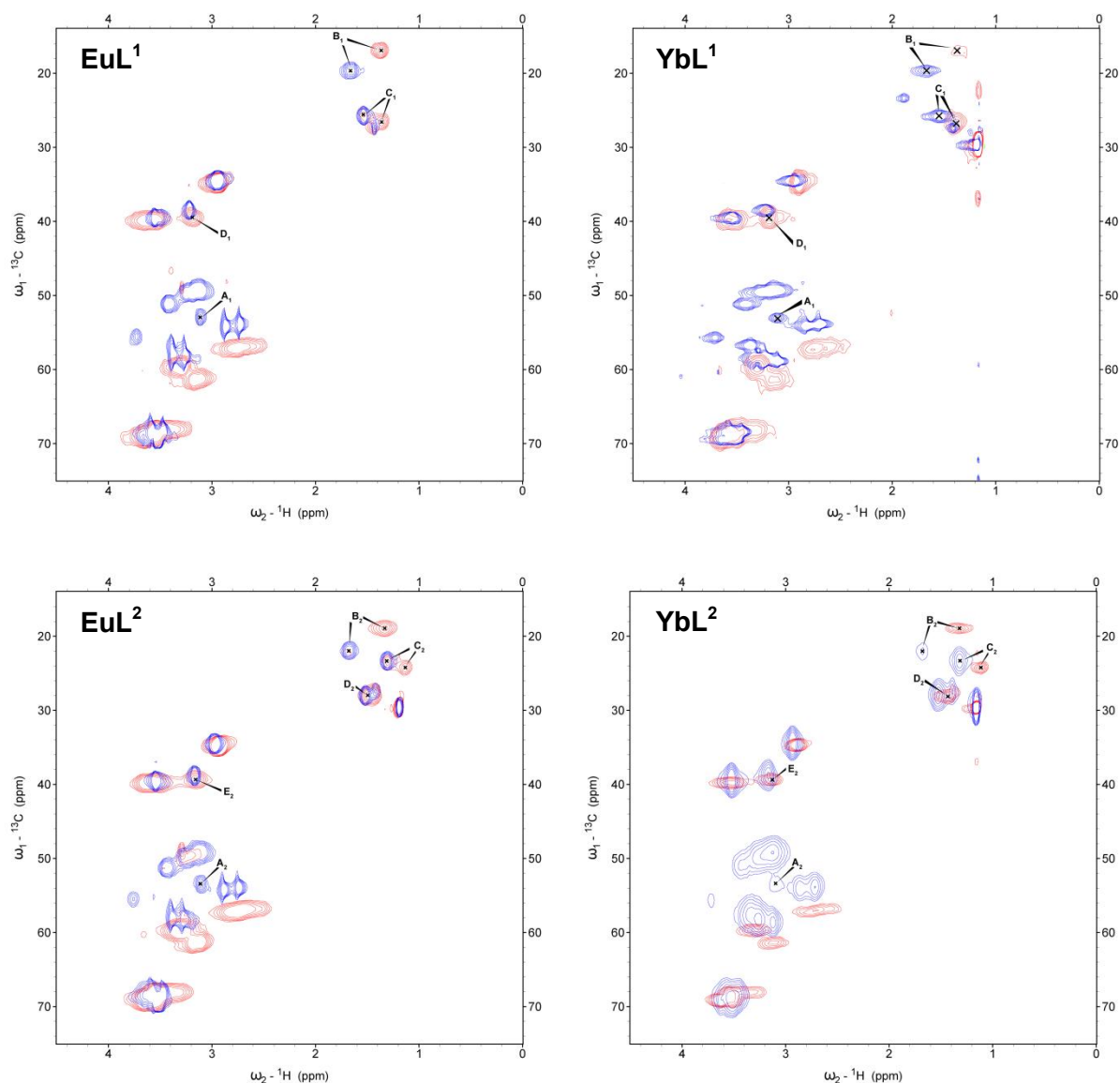


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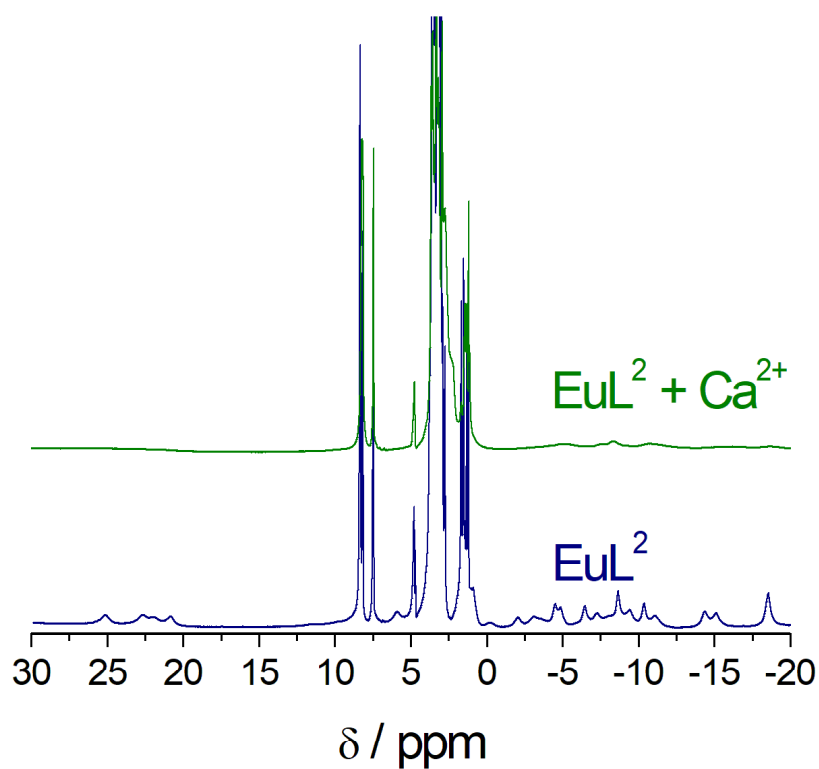
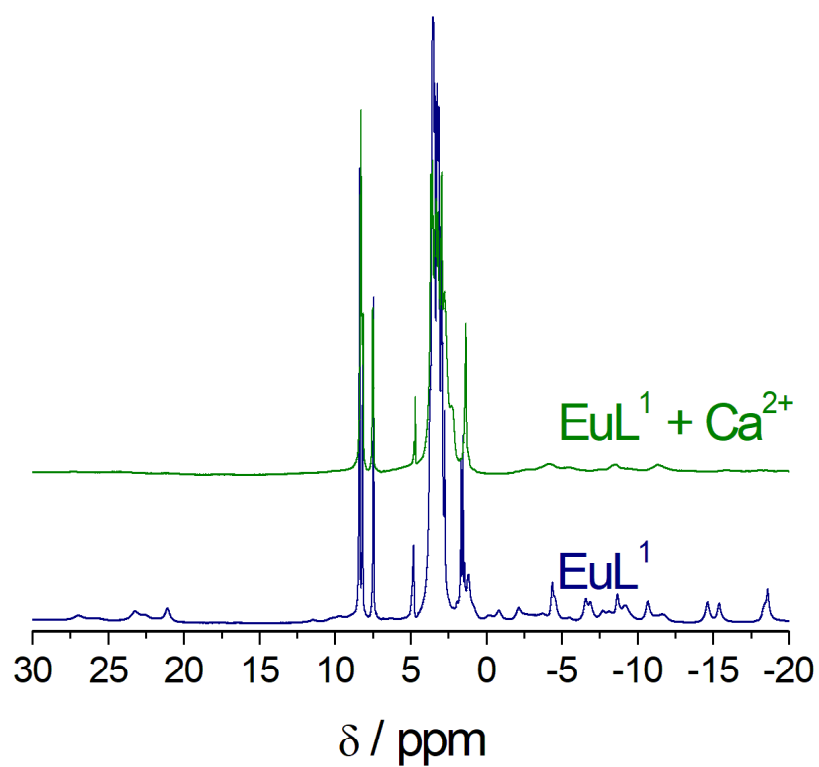


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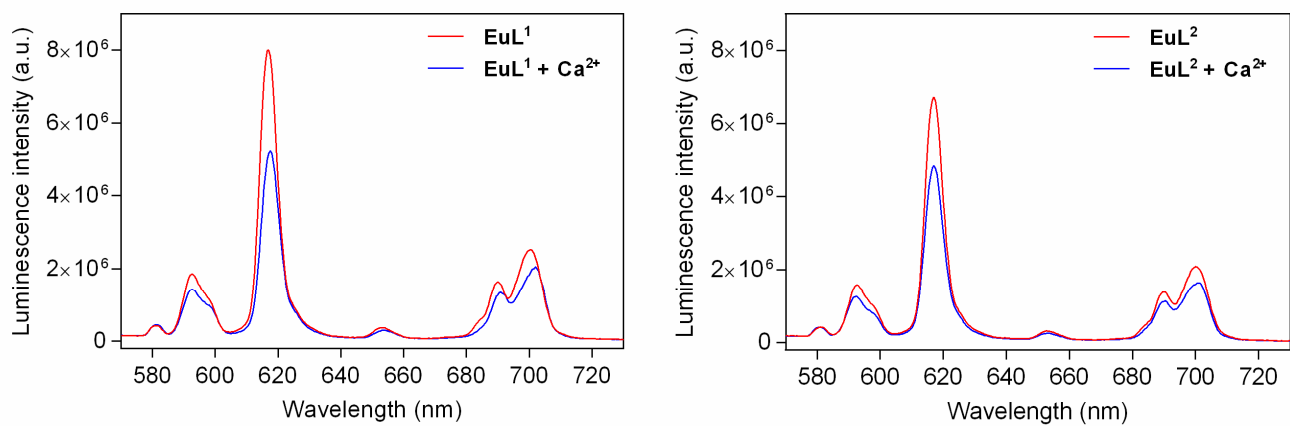


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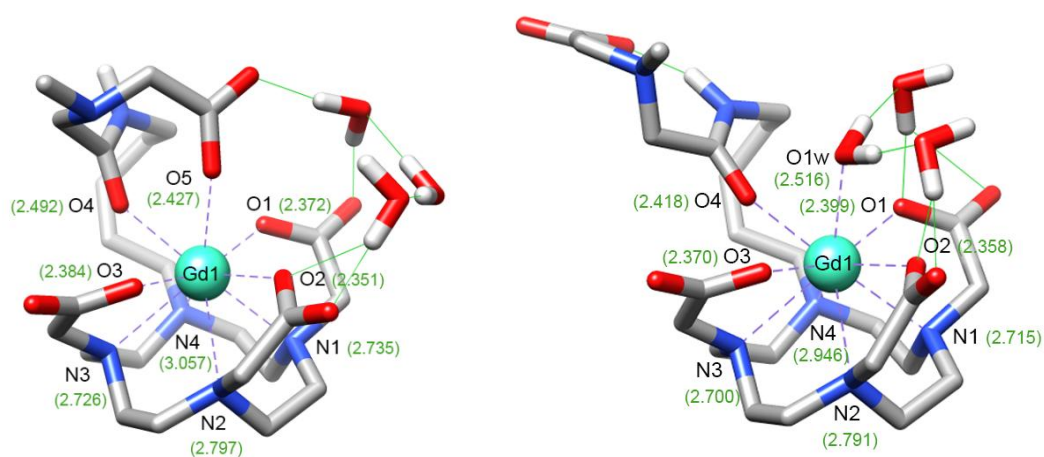


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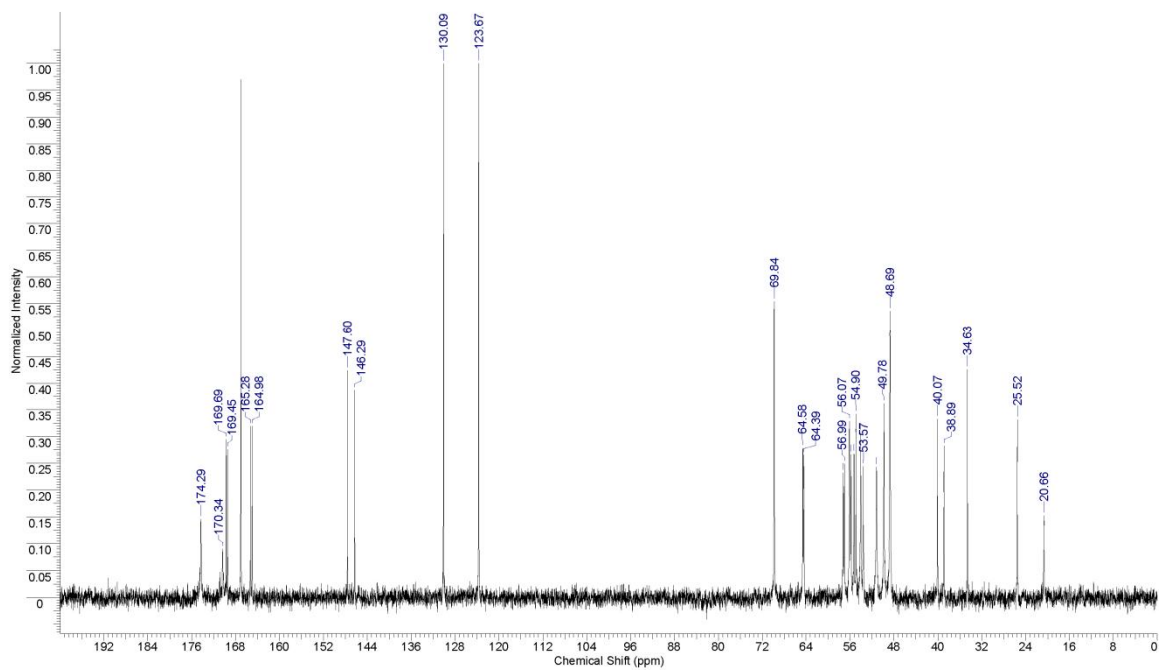
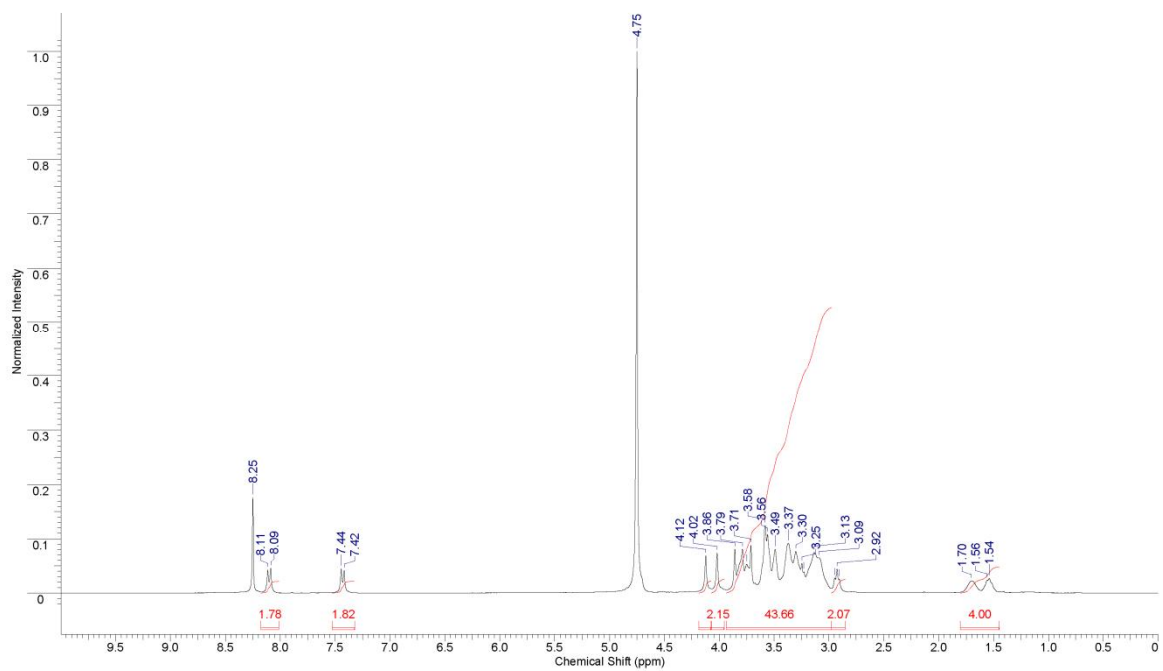


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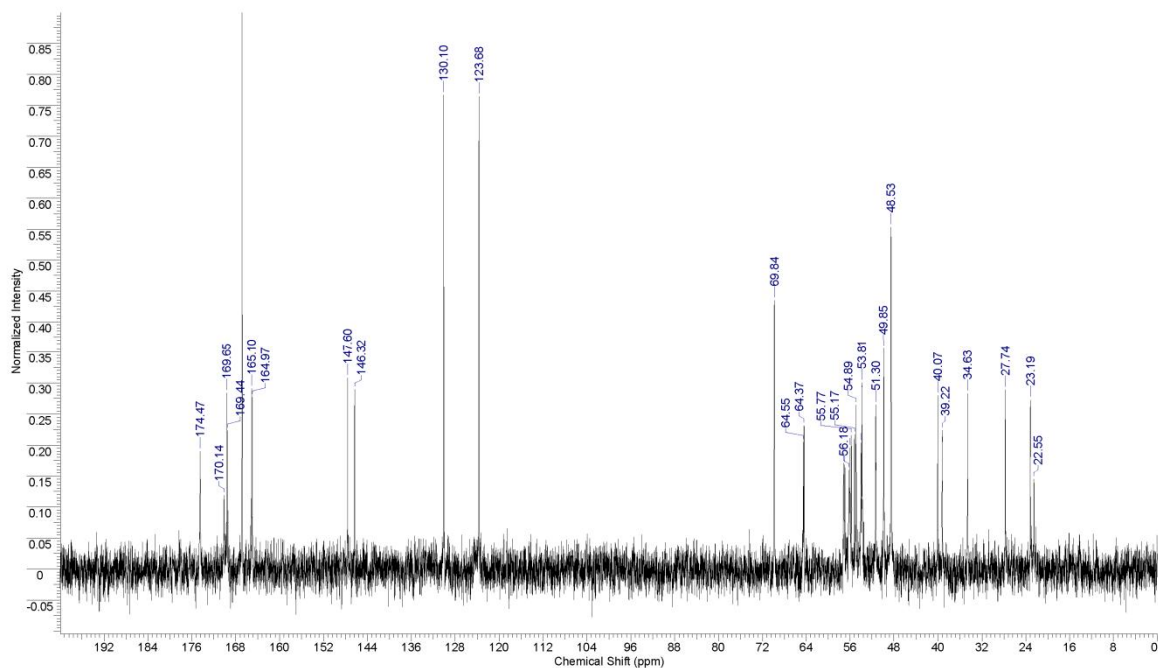
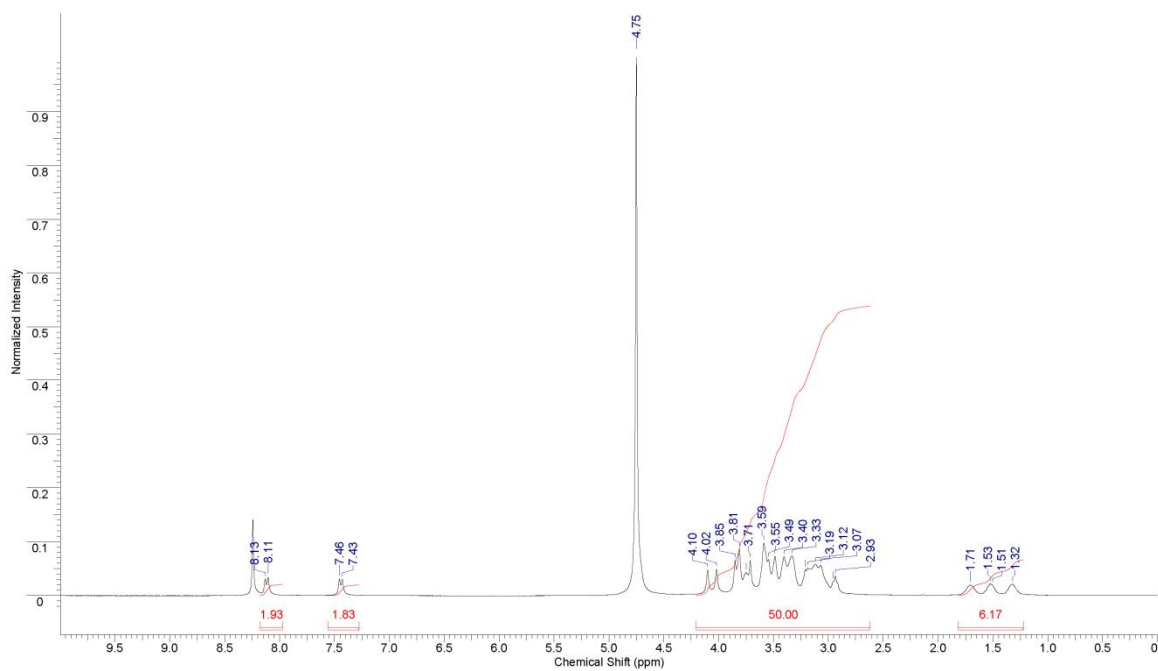


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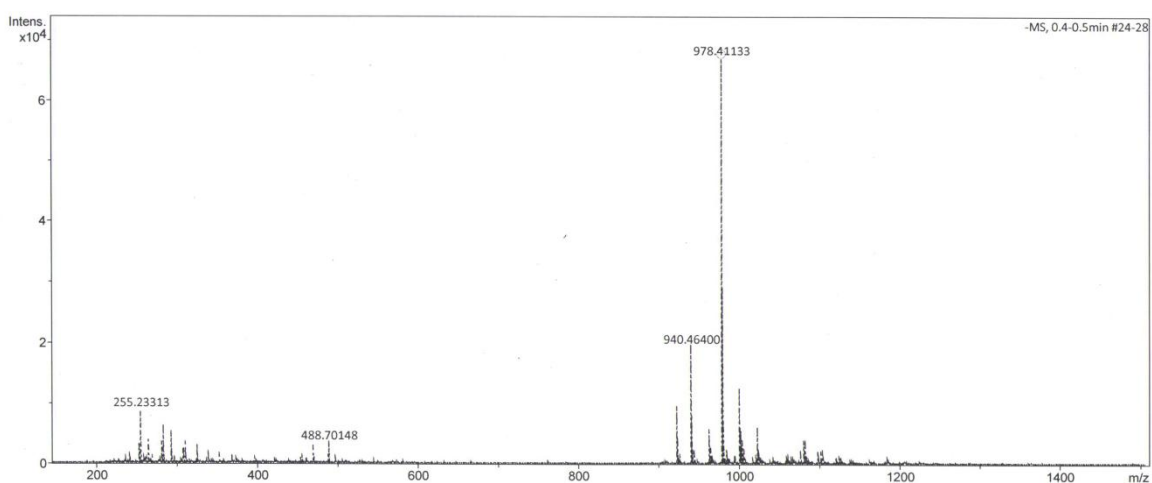
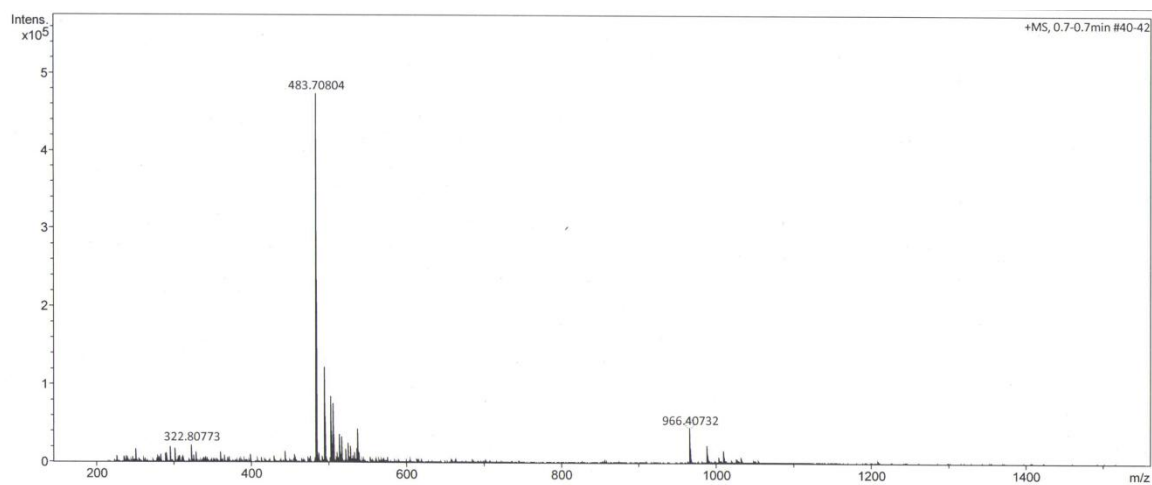


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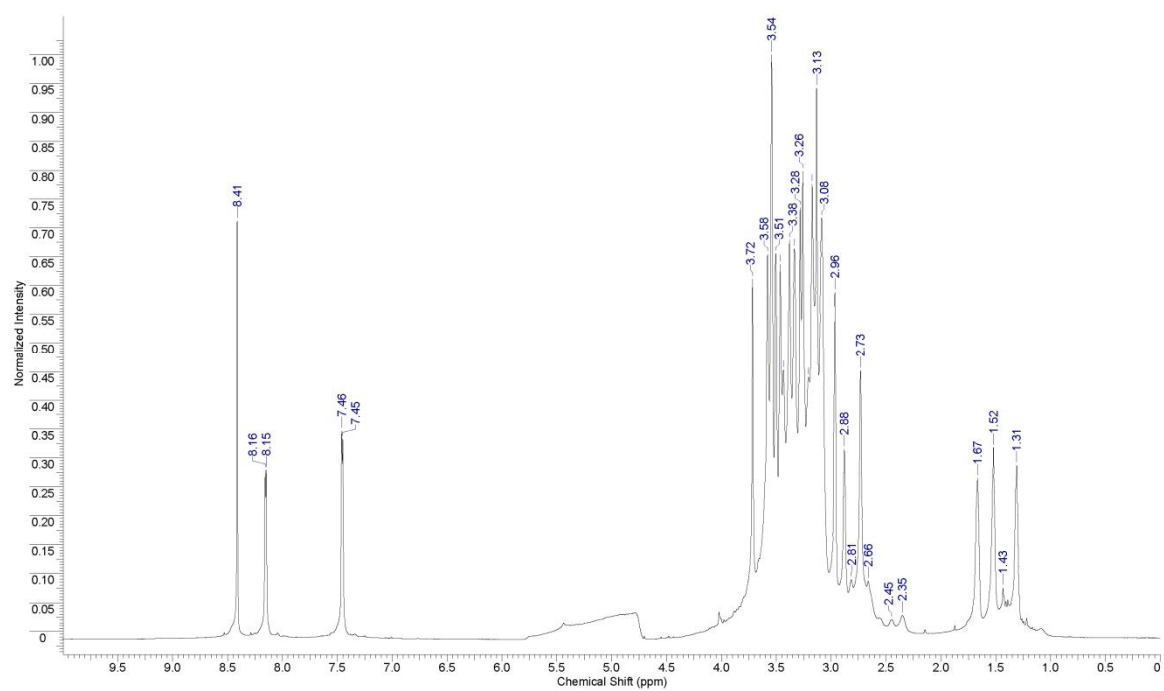
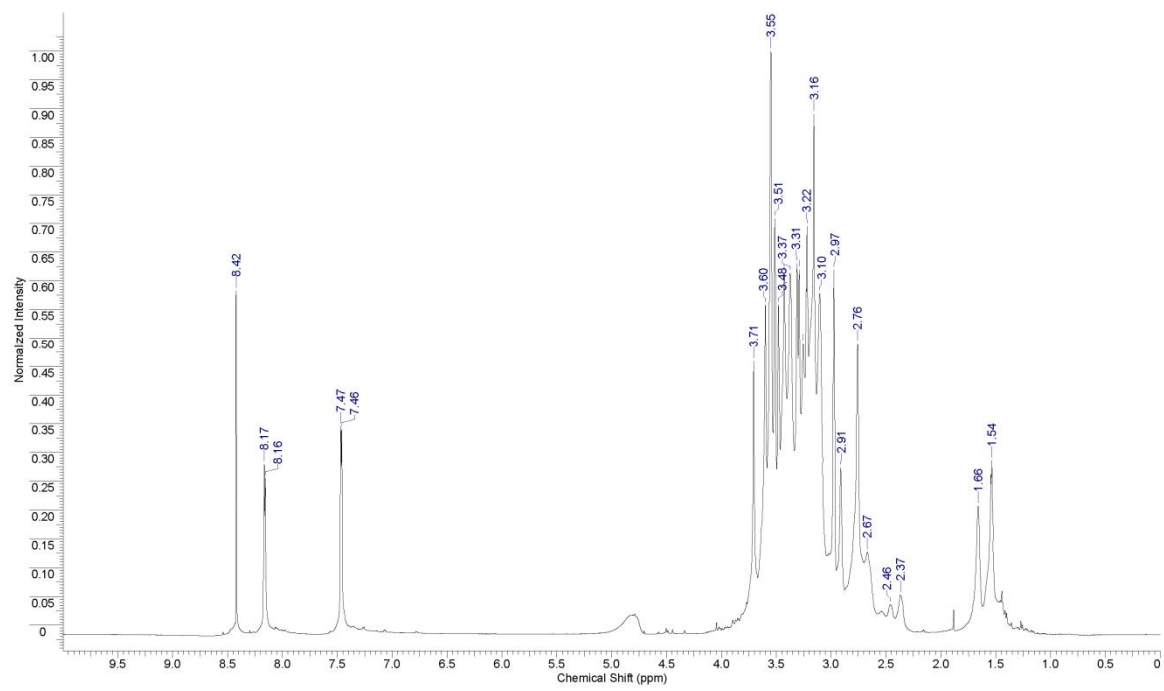


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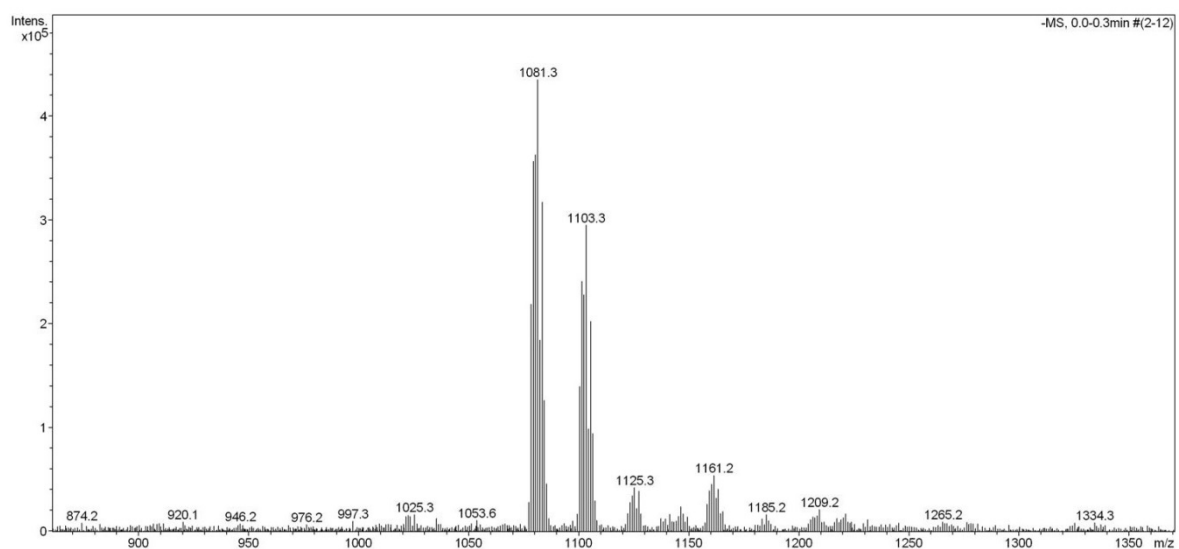


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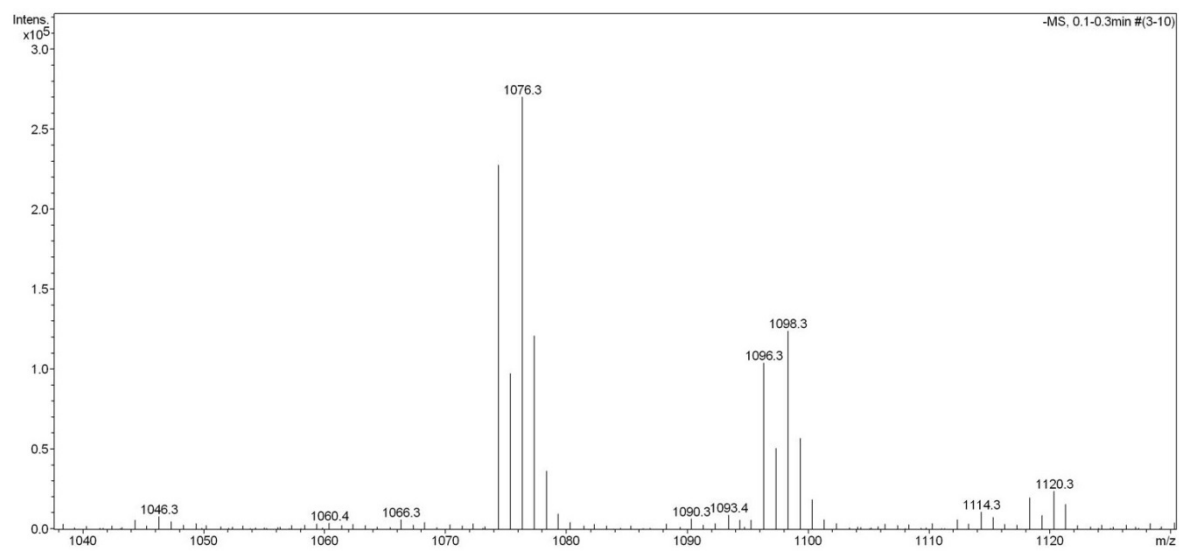


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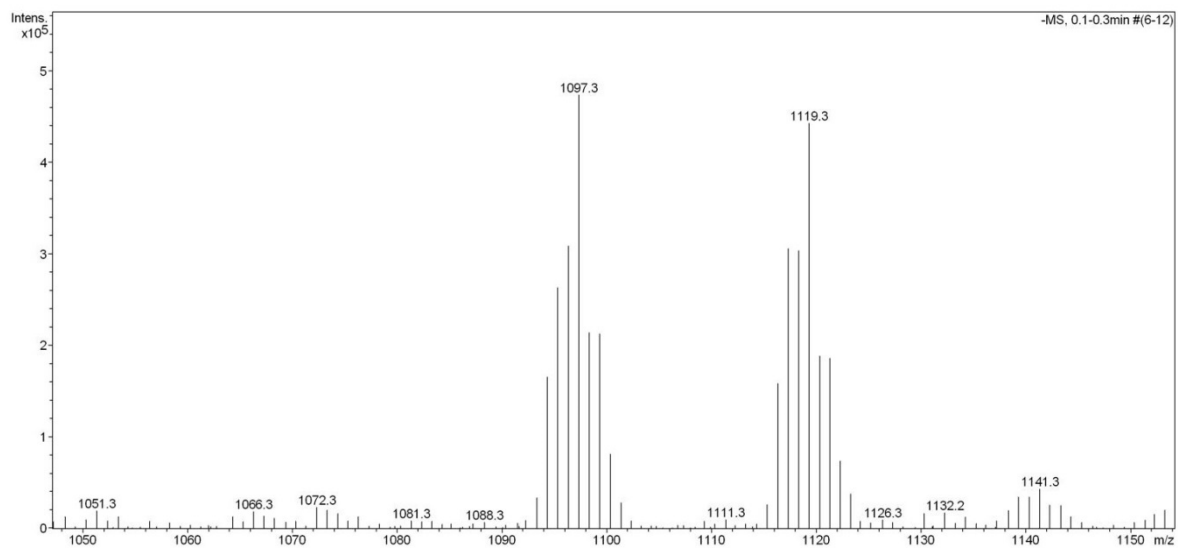


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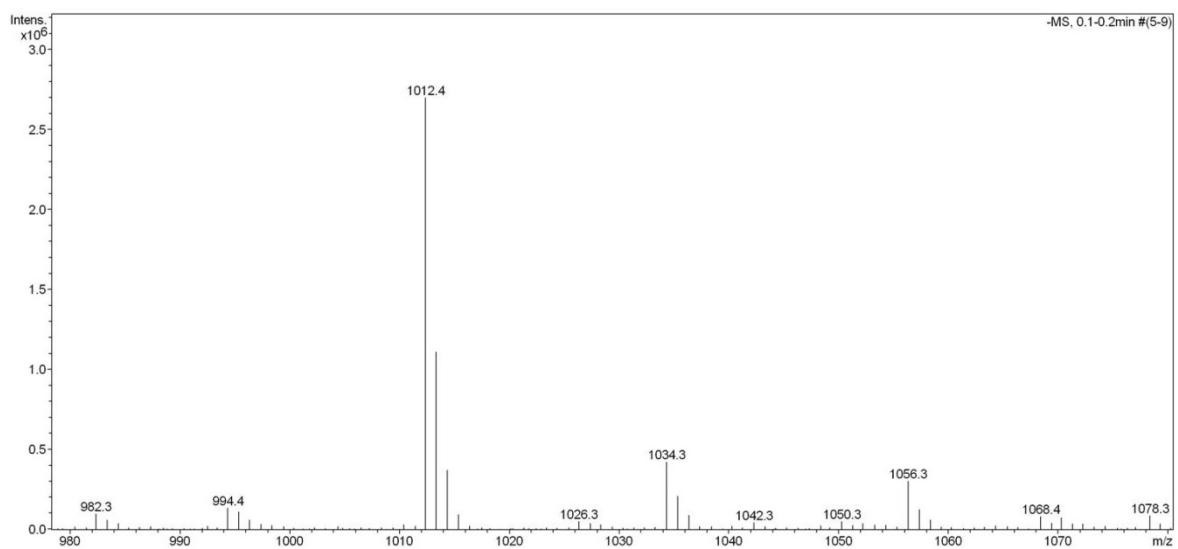


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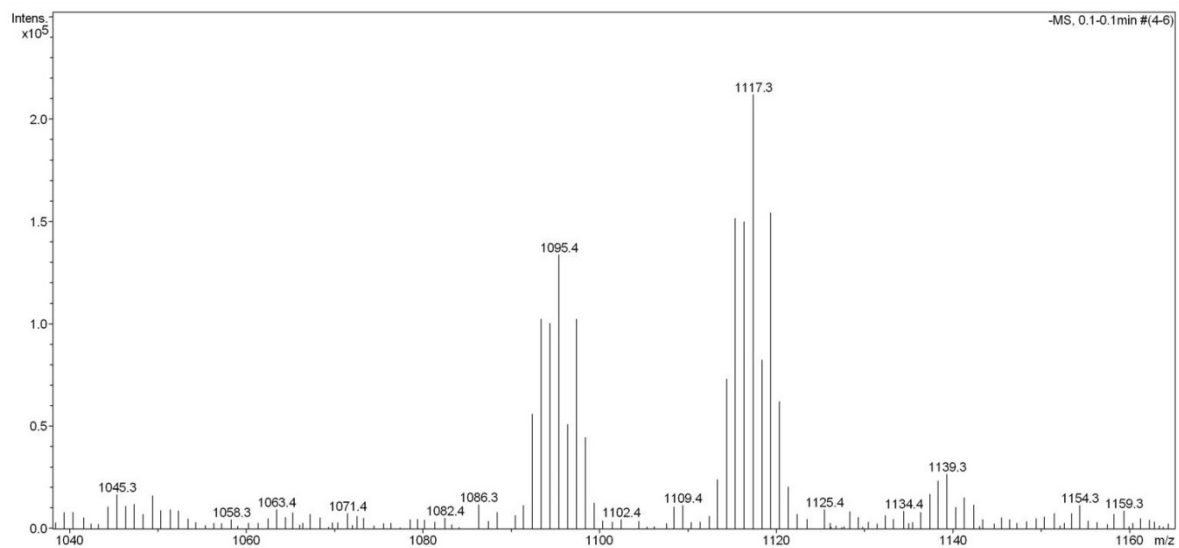


Figure S14. ESI-LRMS spectra of GdL².

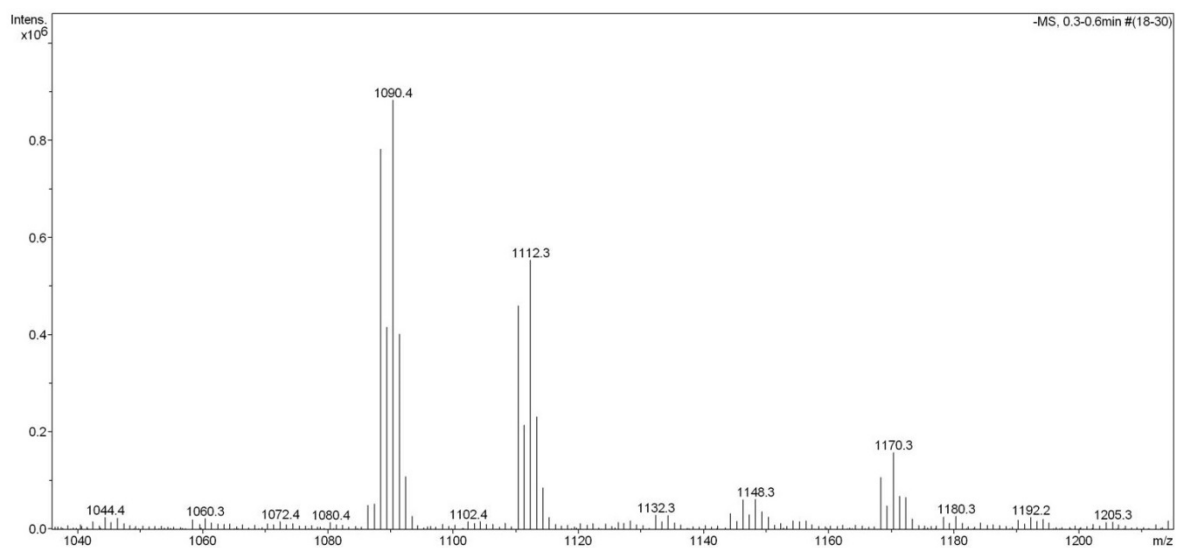


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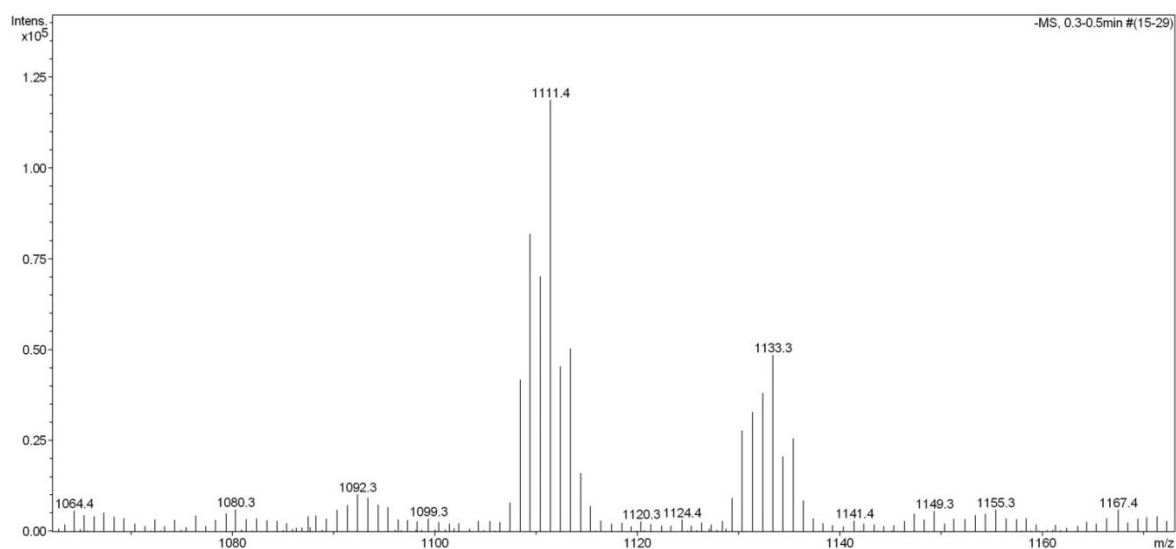


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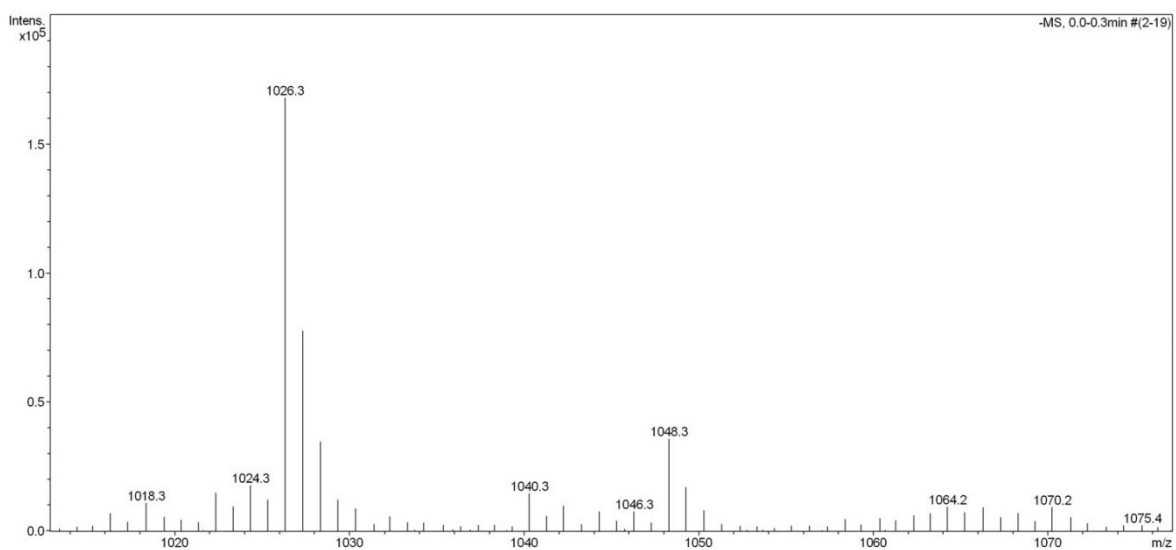


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