Design, Synthesis, and Evaluation of 1,4,7,10-Tetraazacyclododecane-1,4,7-triacetic Acid-Derived, Redox-Sensitive Contrast Agents for Magnetic Resonance Imaging

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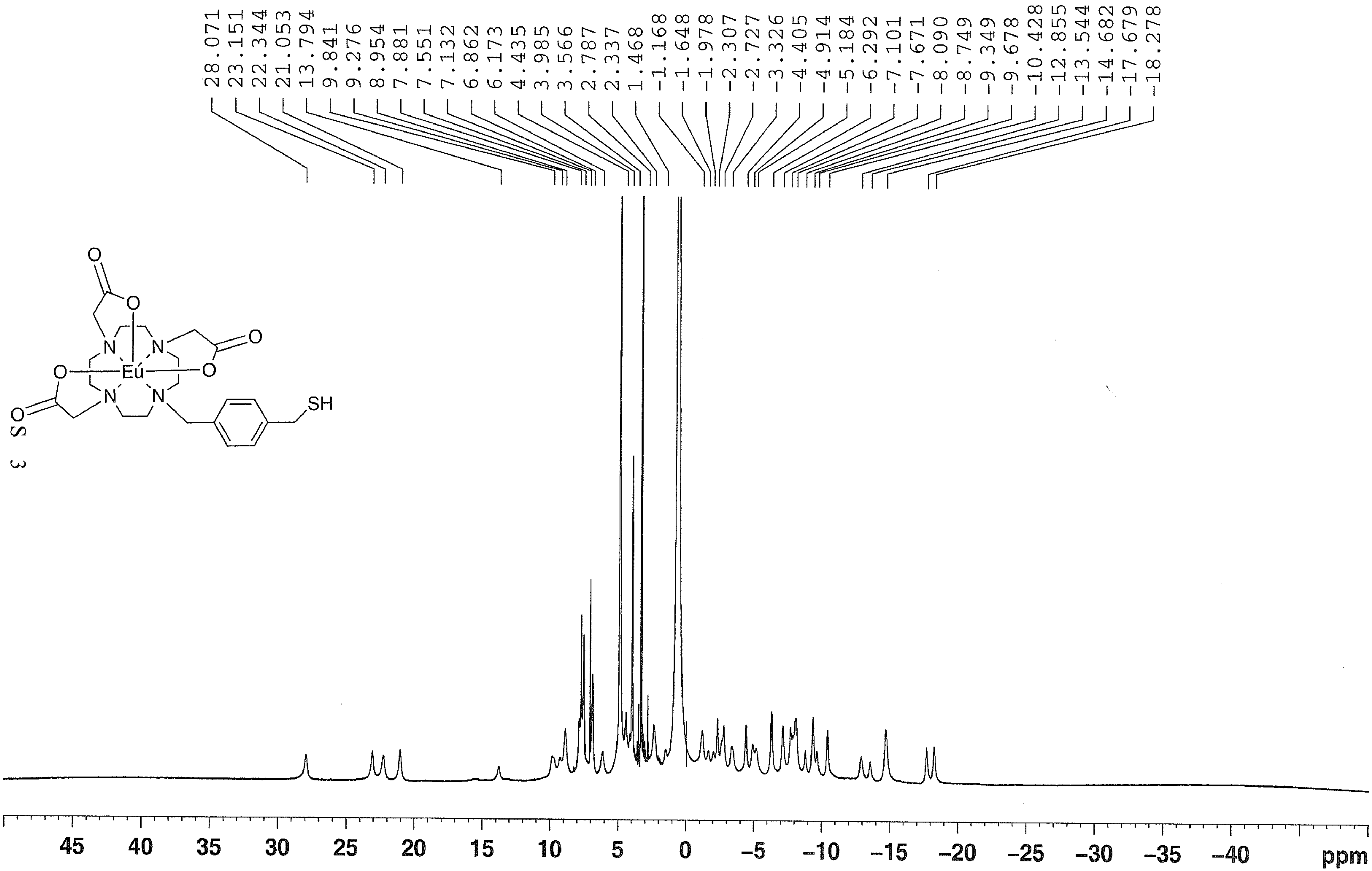
Supporting Information

General Experimental

Reactions were conducted in flame-dried glassware under a positive pressure of argon, except as otherwise noted. Hydroscopic solvents were transferred via an oven-dried syringe or cannula. All the reagents and solvents were commercially available and were used as received. Solutions were concentrated in vacuo using a rotary evaporator. Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel 60 F-254 glass plates. TLC visualization required using UV light and/or staining. An anisaldehyde stain (100 mL anisaldehyde, 50 mL glacial AcOH, 100 mL conc H_2SO_4, 1 L 95% EtOH) and a PMA stain (5 g phosphomolybdic acid, 100 mL 95% EtOH) were the most commonly used TLC stains. Flash and gravity chromatography were performed using silica gel 60 (230-400 mesh). Melting points are uncorrected. Nuclear Magnetic Resonance (NMR) experiments were performed on 500 MHz or 600 MHz spectrometers. NMR spectra were referenced to TMS in $CDCl_3$ (0.00 ppm), $CDCl_3$ (7.24 ppm, 77.0 ppm), or TFA-*d* (11.5 ppm, 164.4 ppm). Mass spectrometry was conducted using ESI.

The purity of the lanthanide complexes tested was established as ≥95% by reversed phase thin-layer chromatographic analysis. The purity of isolated synthetic intermediates was established as ≥95% by elemental analysis and/or normal phase thin-layer chromatographic analysis.



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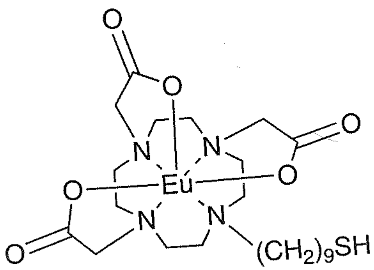

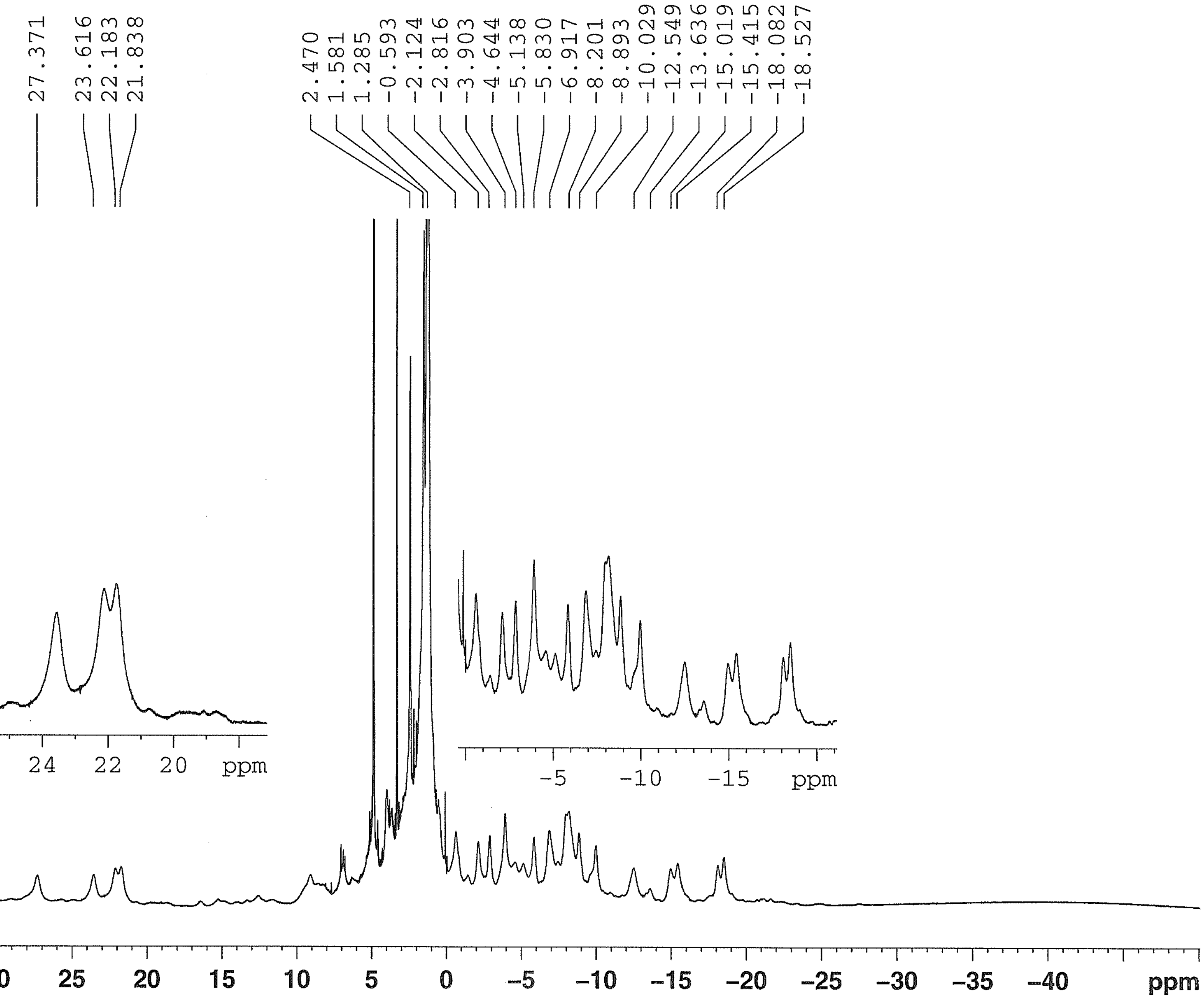

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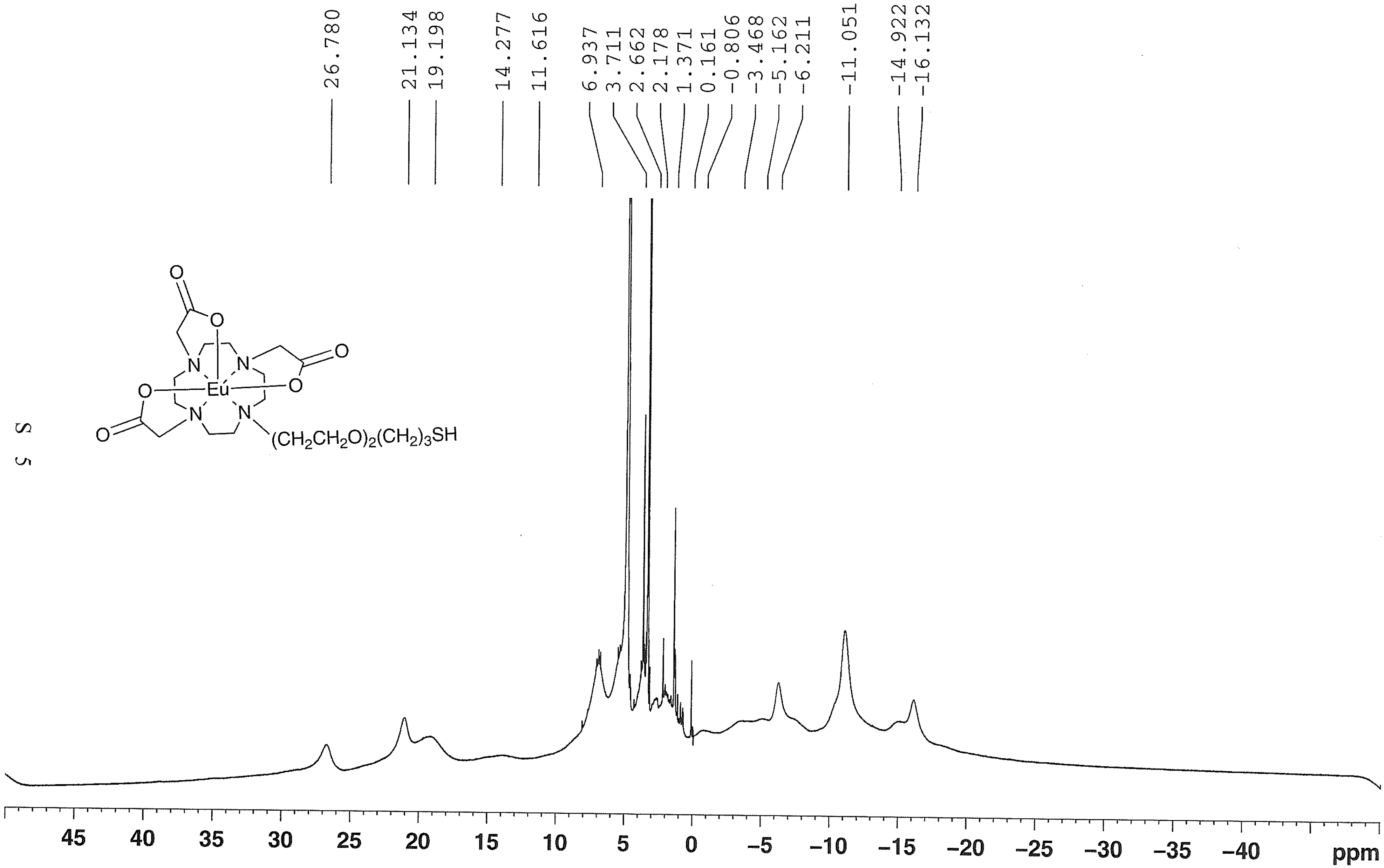

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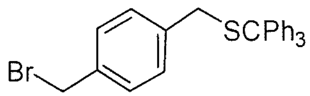

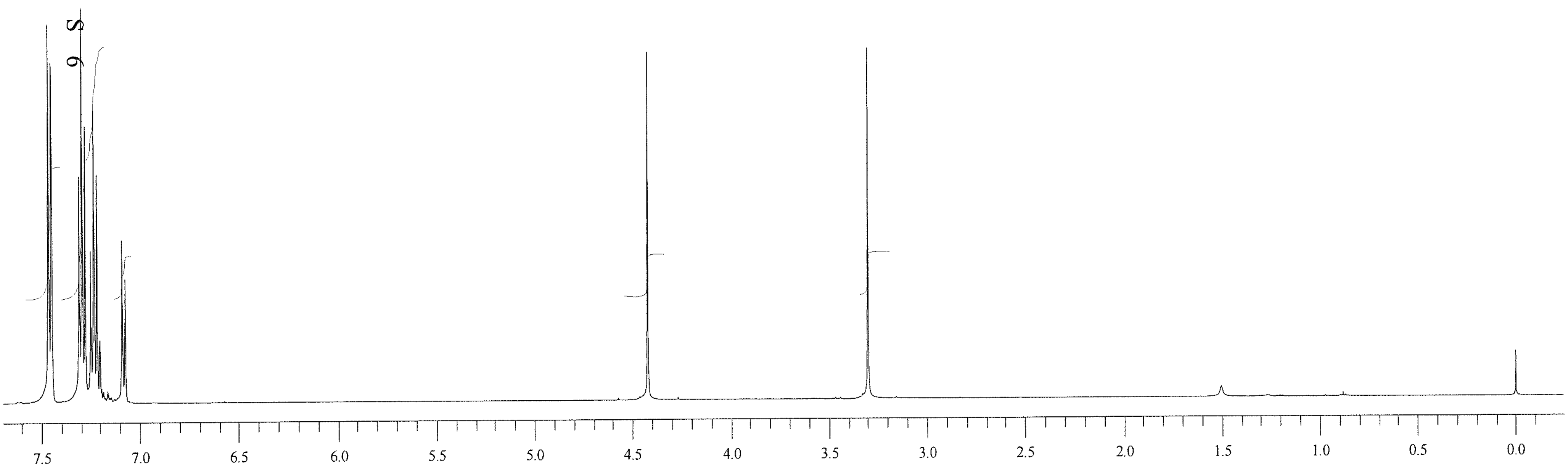

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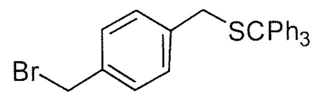

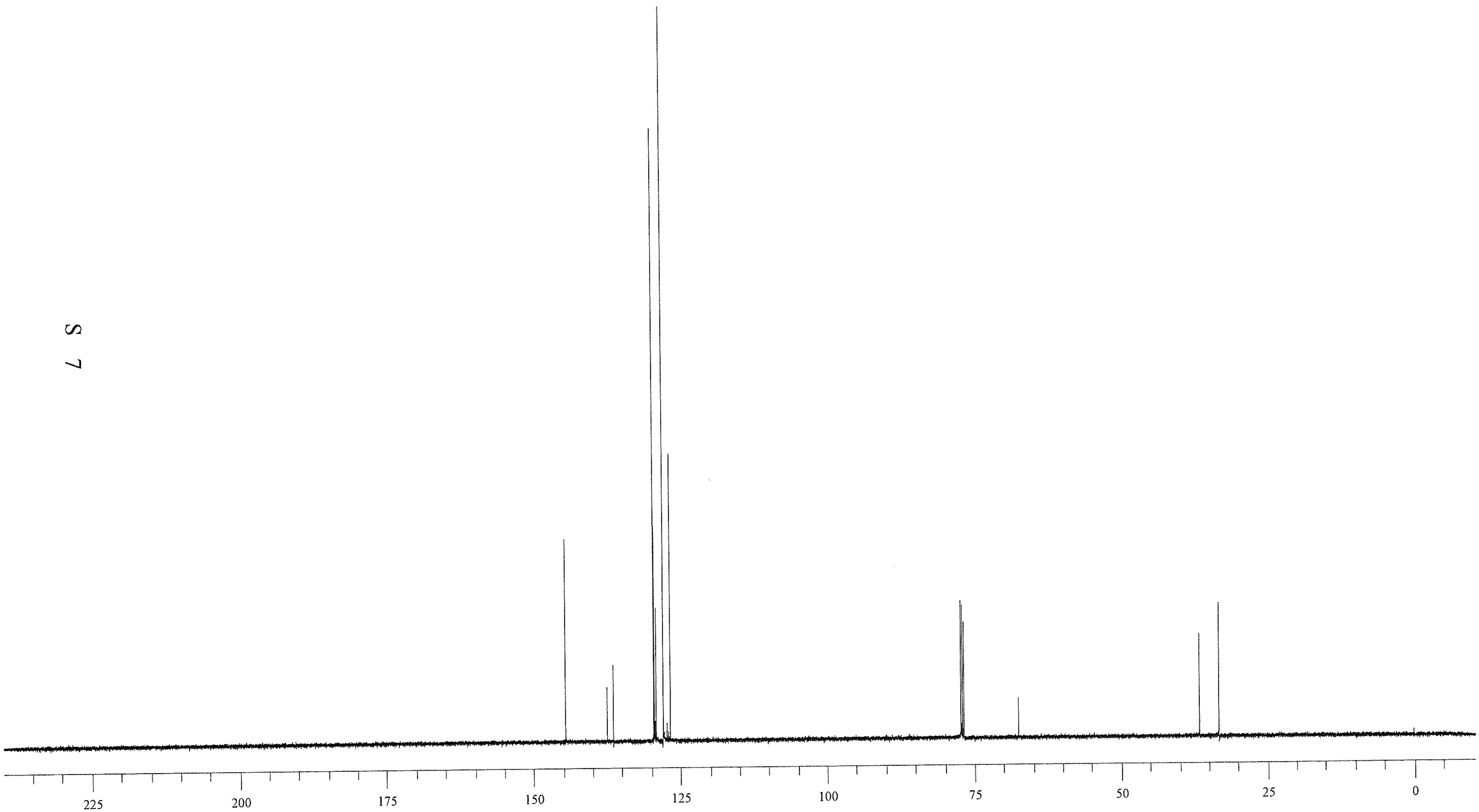

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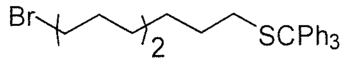

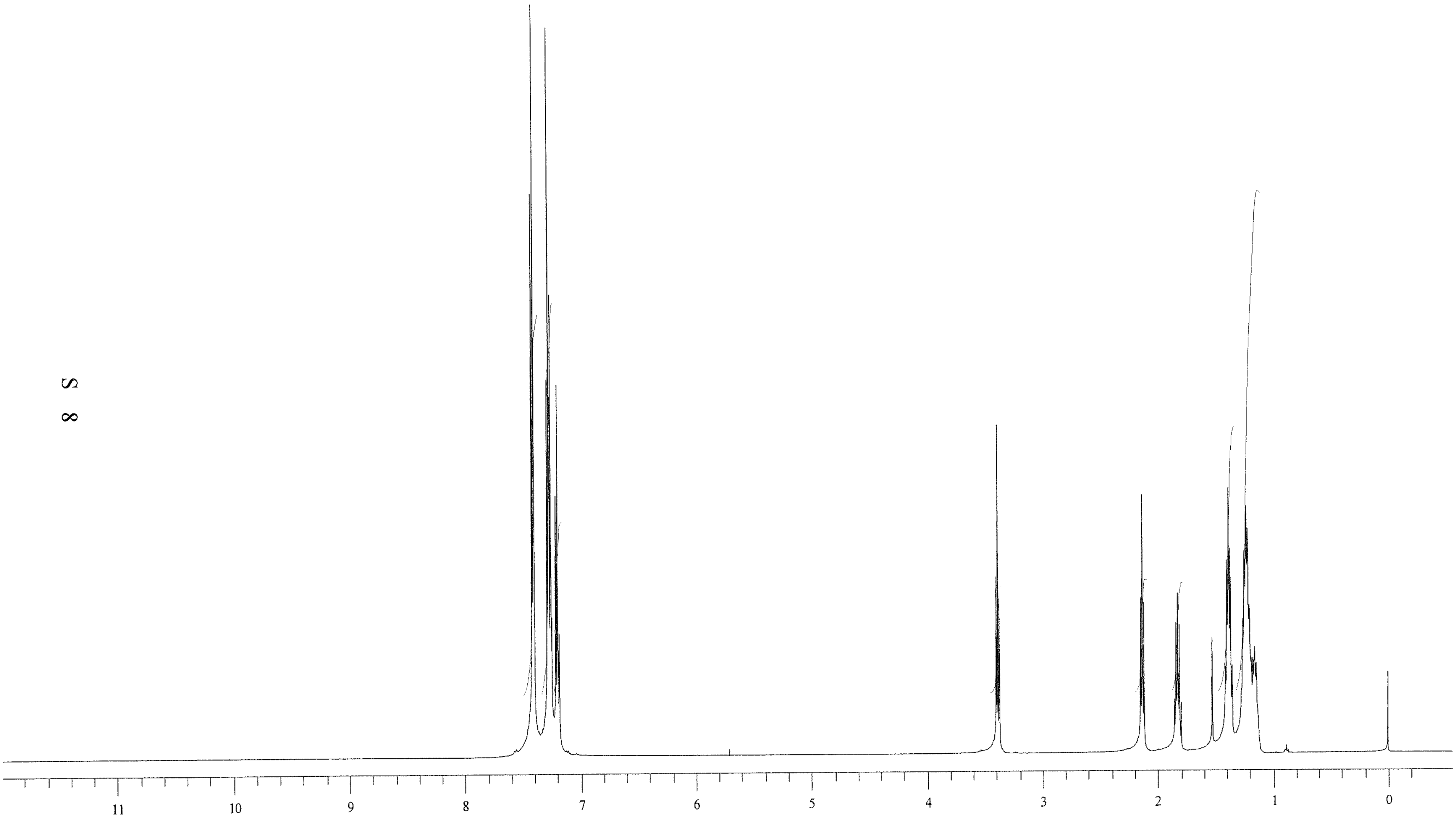

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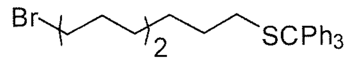

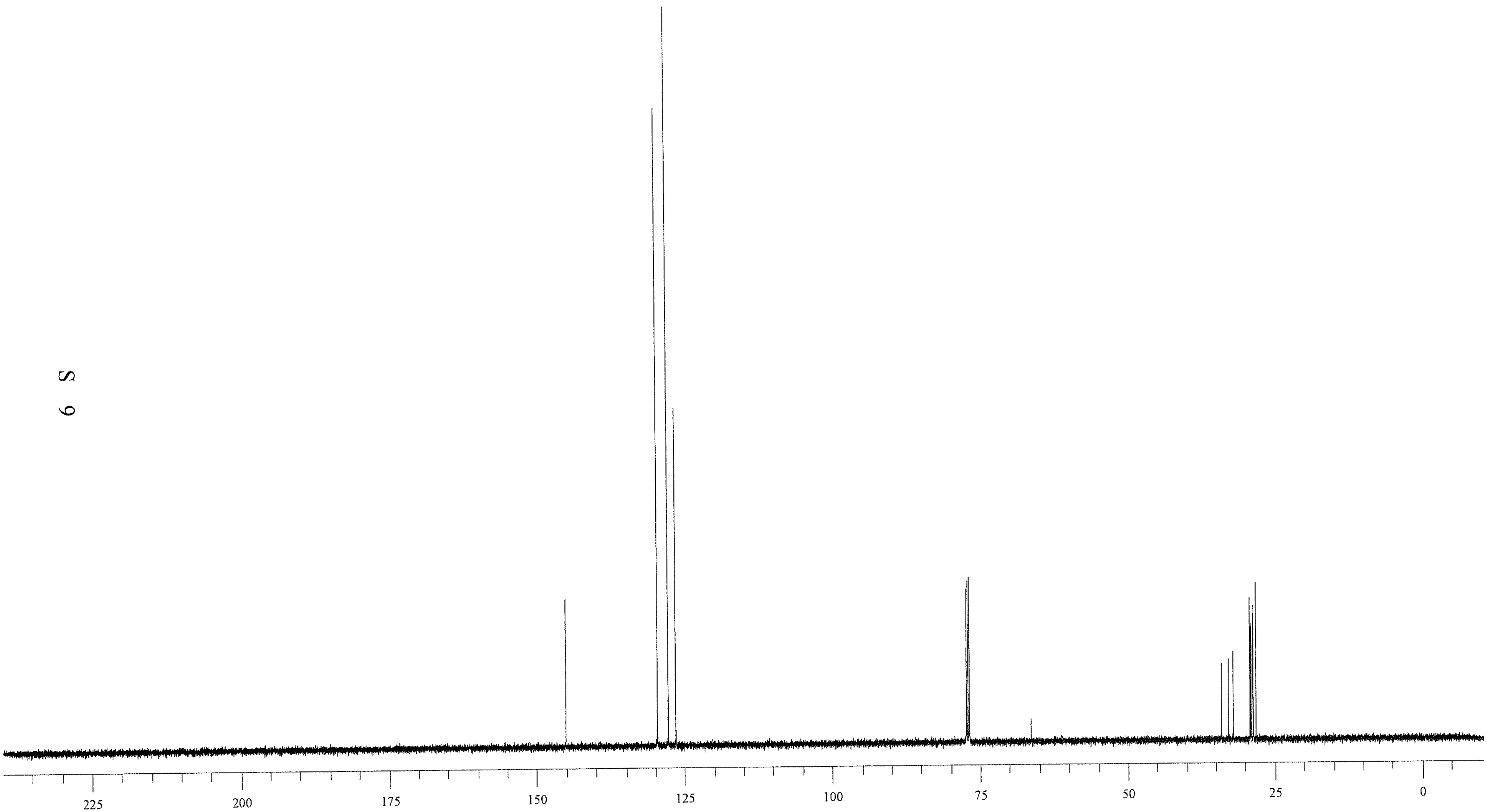

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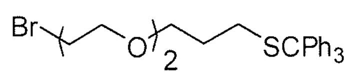

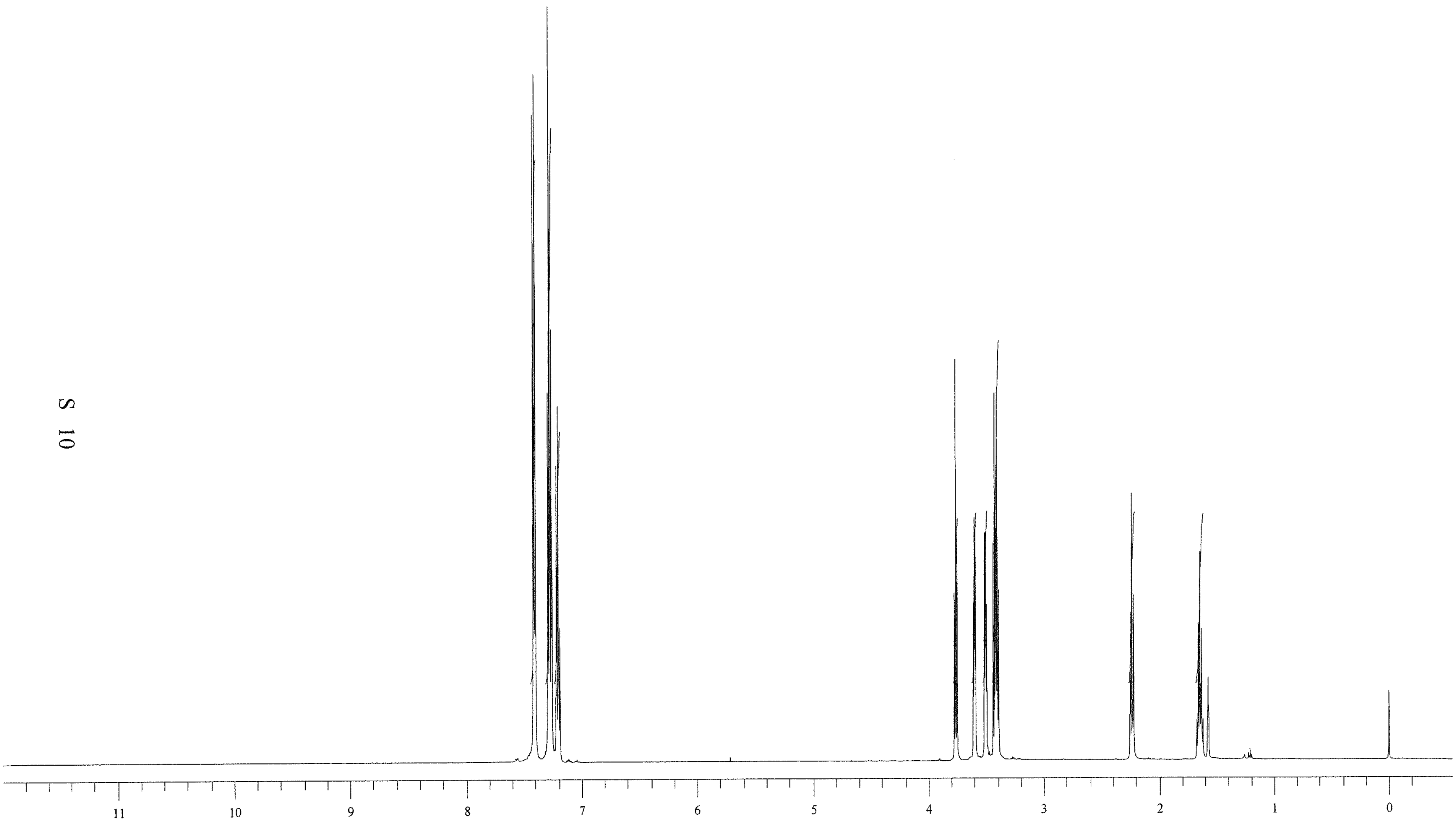

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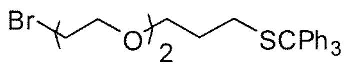

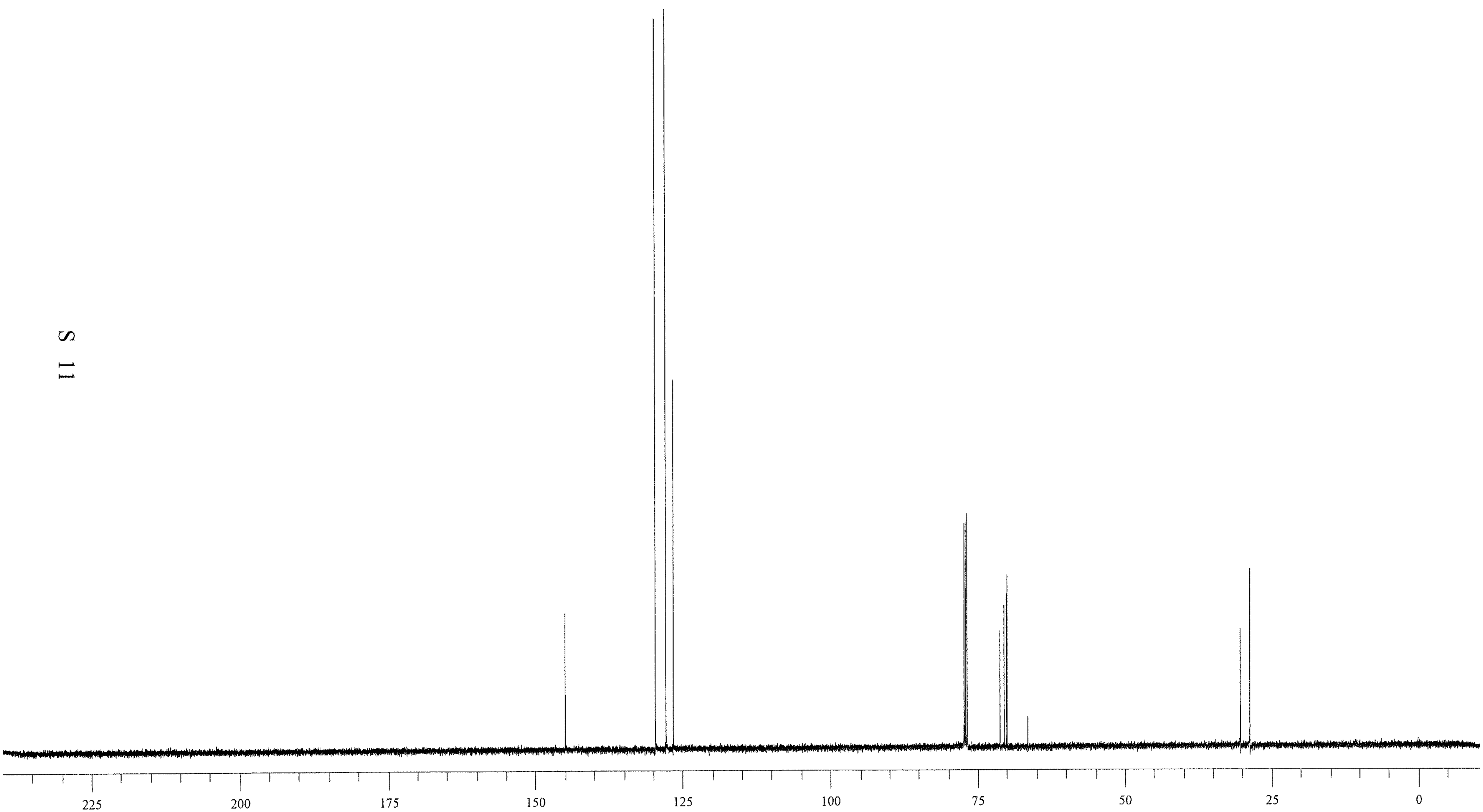

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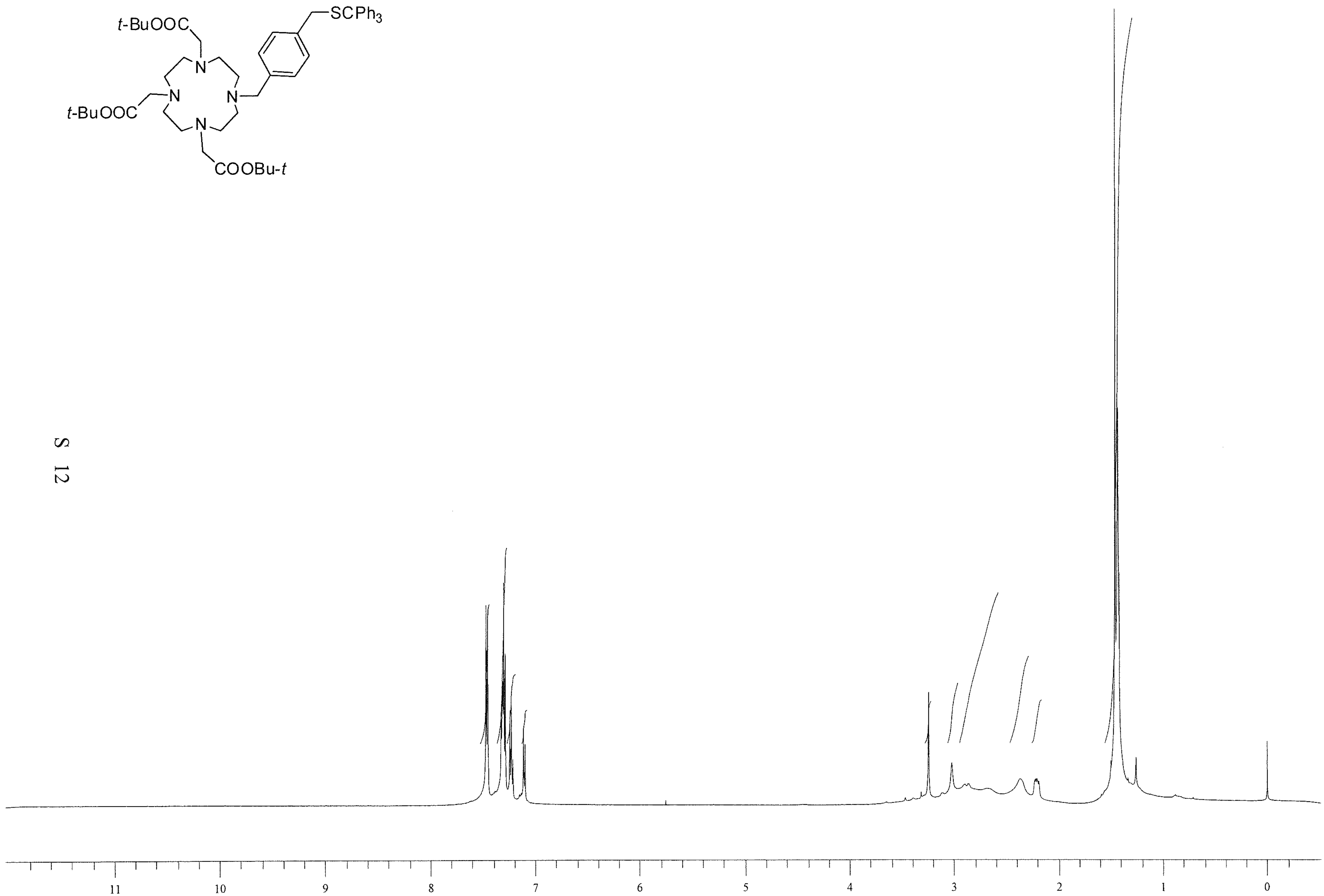

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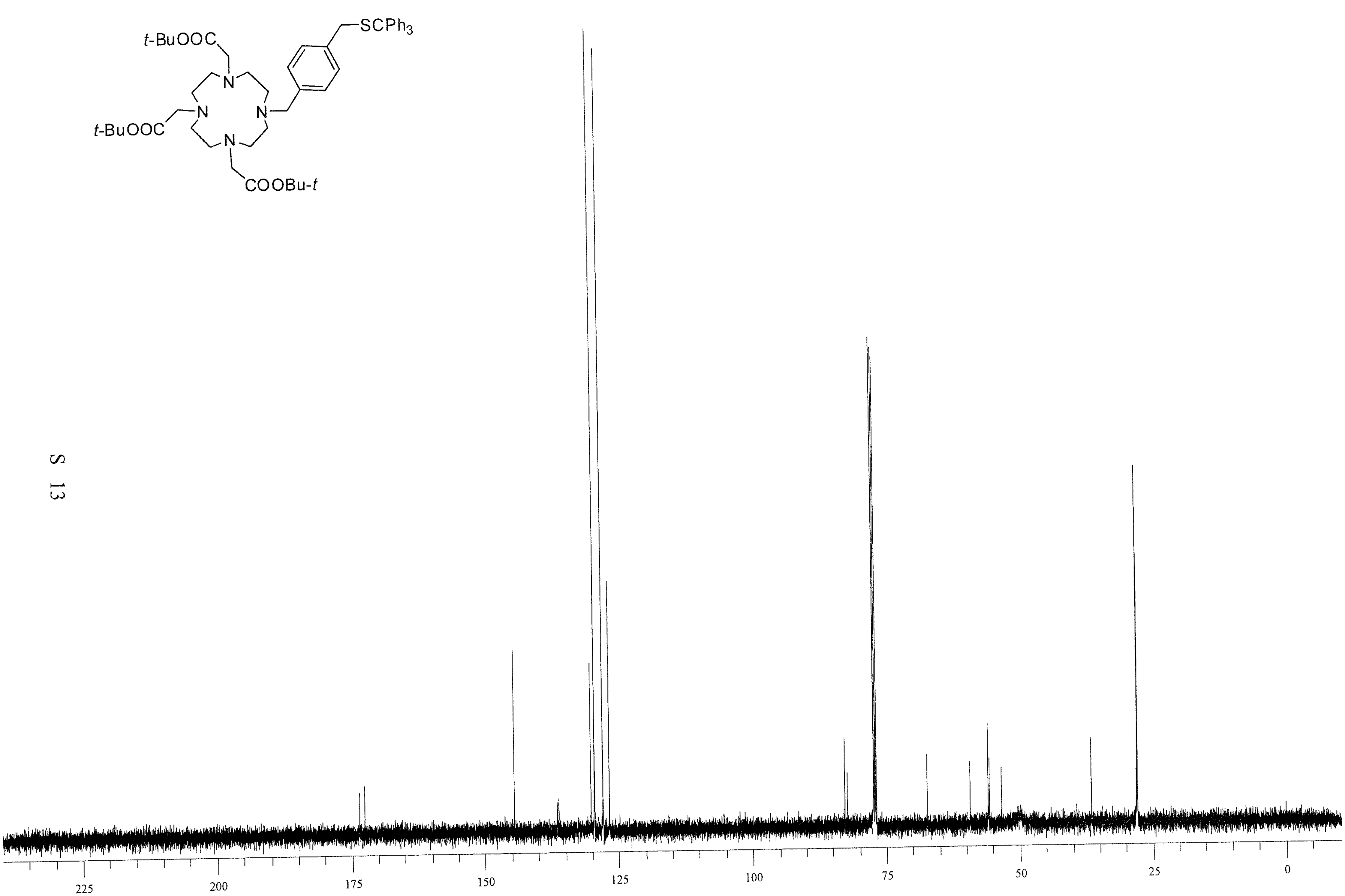

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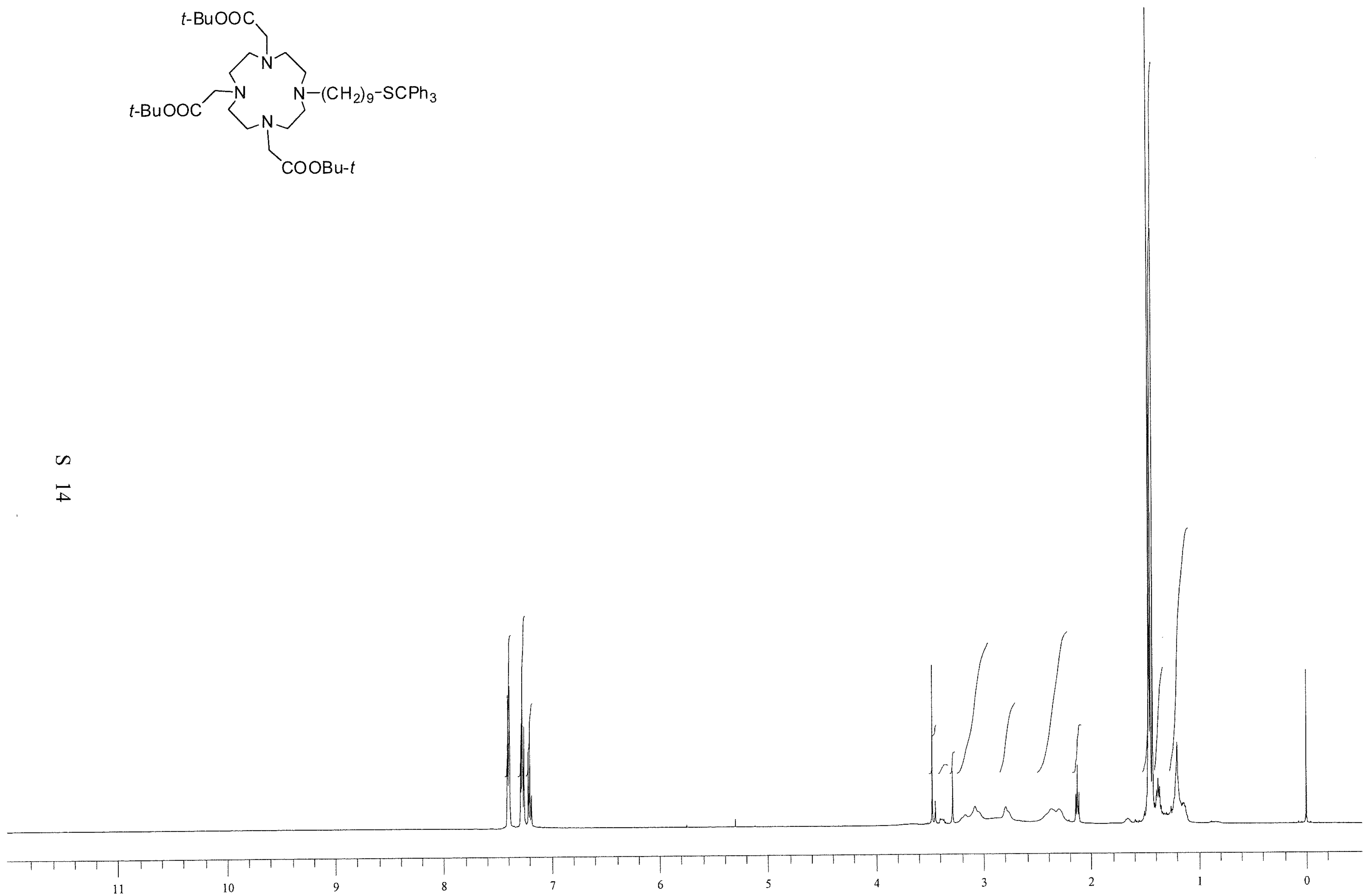

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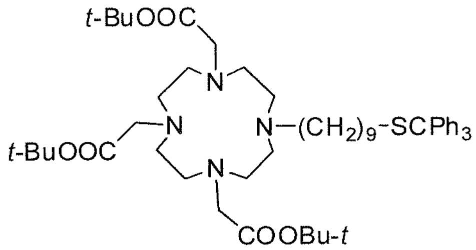

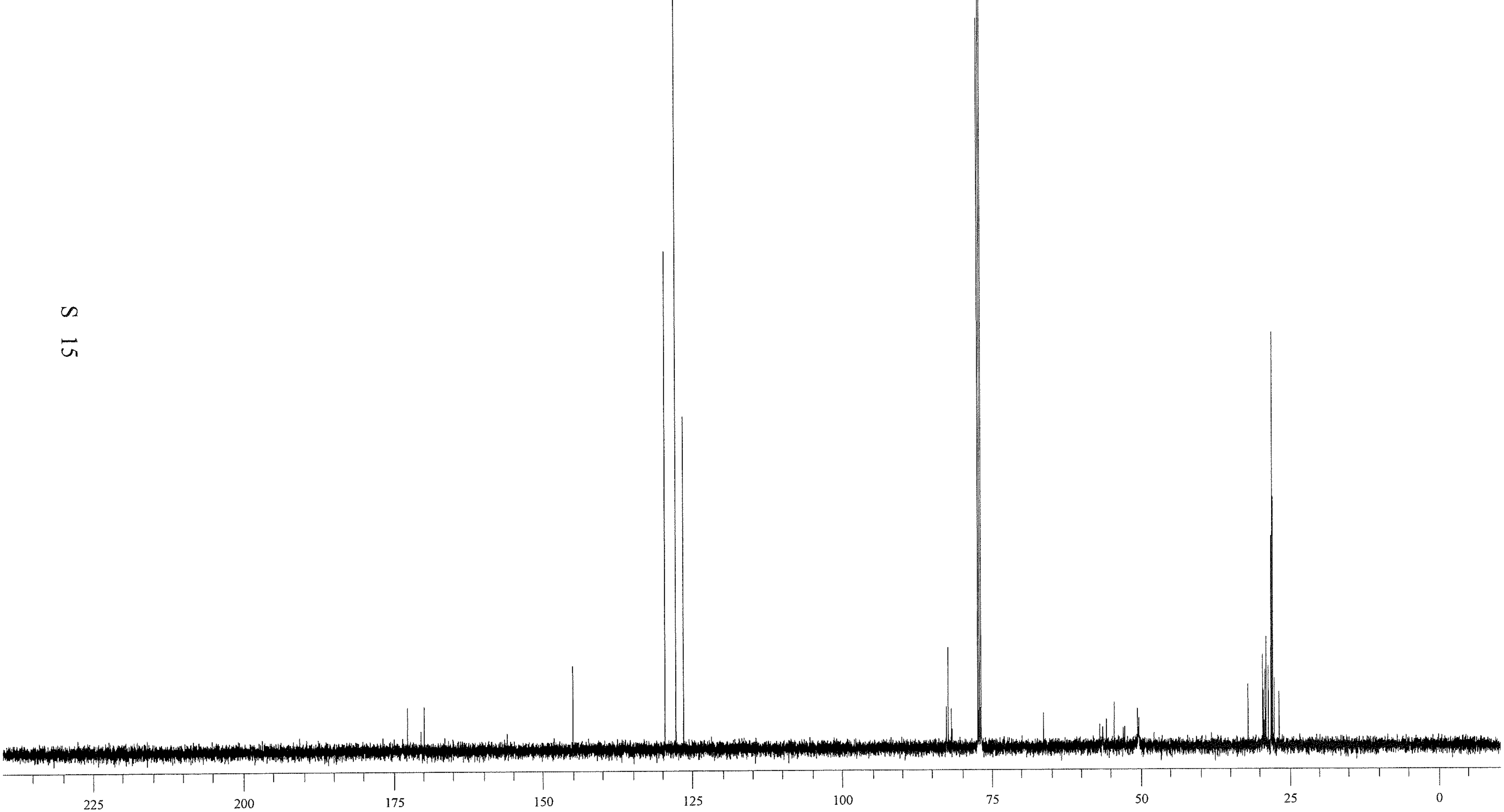

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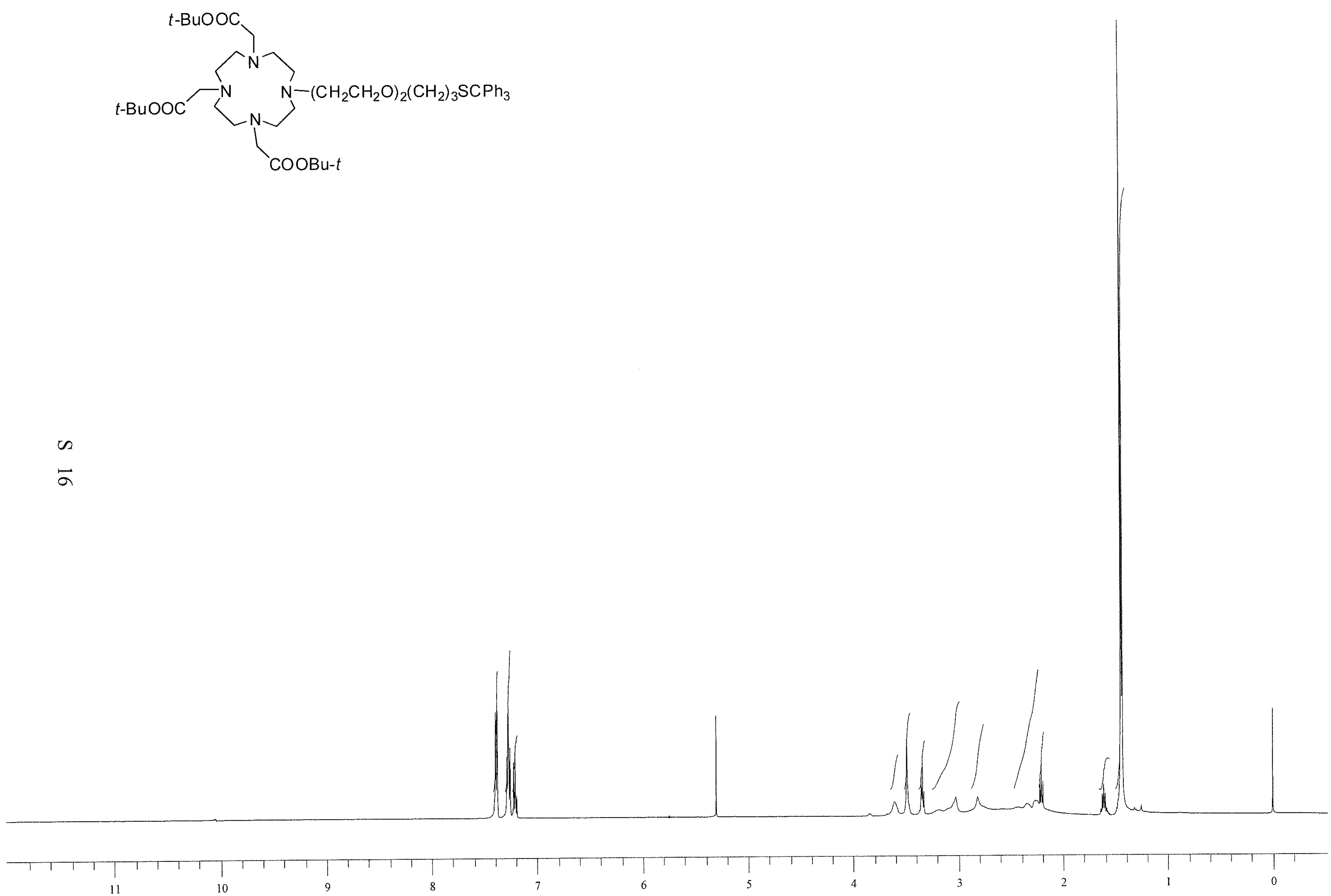

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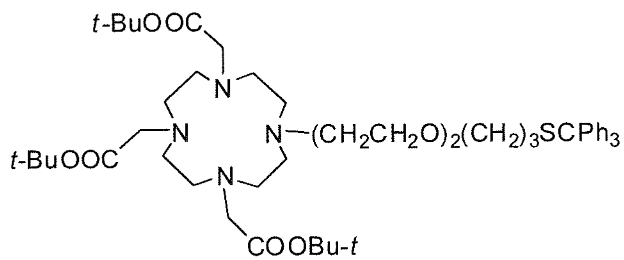

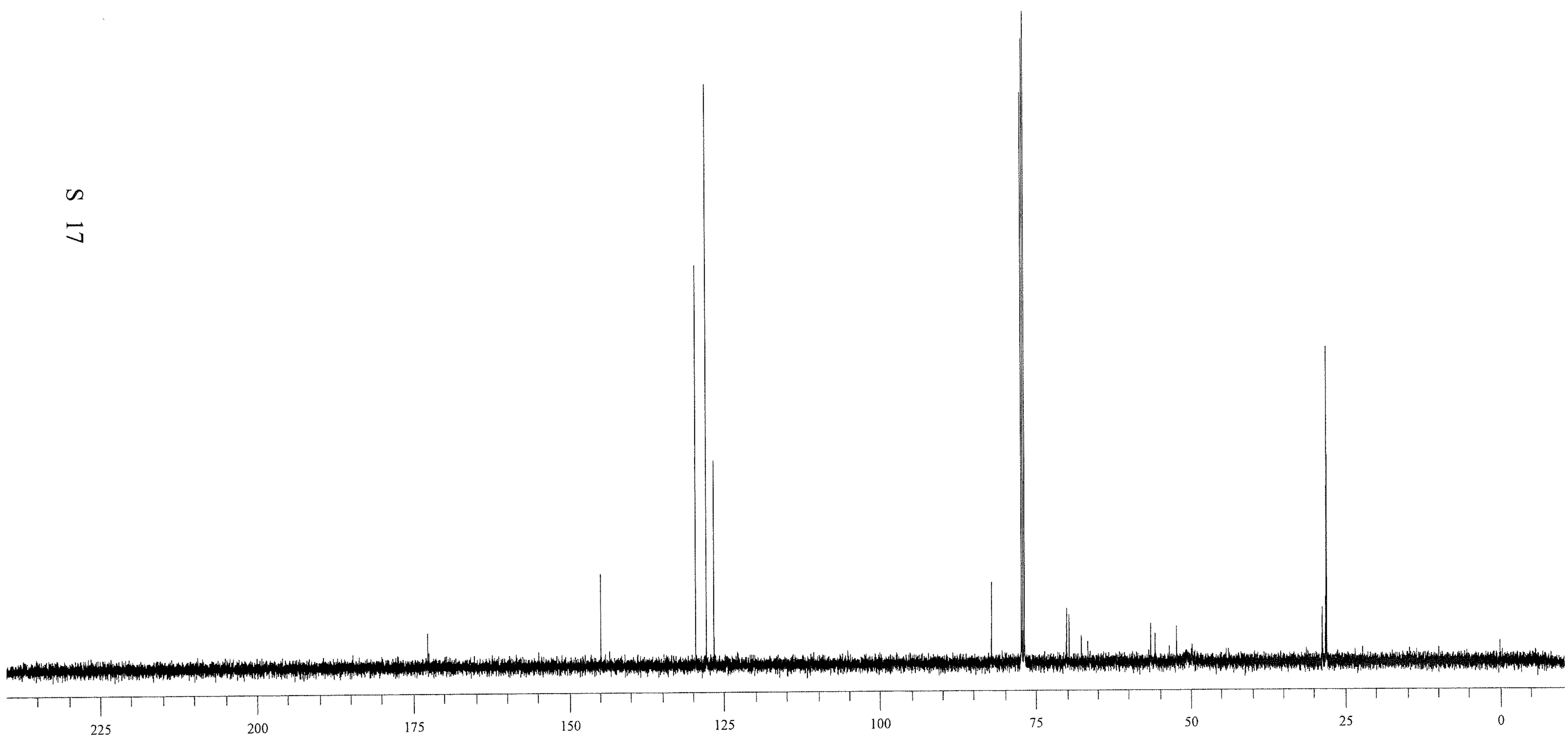

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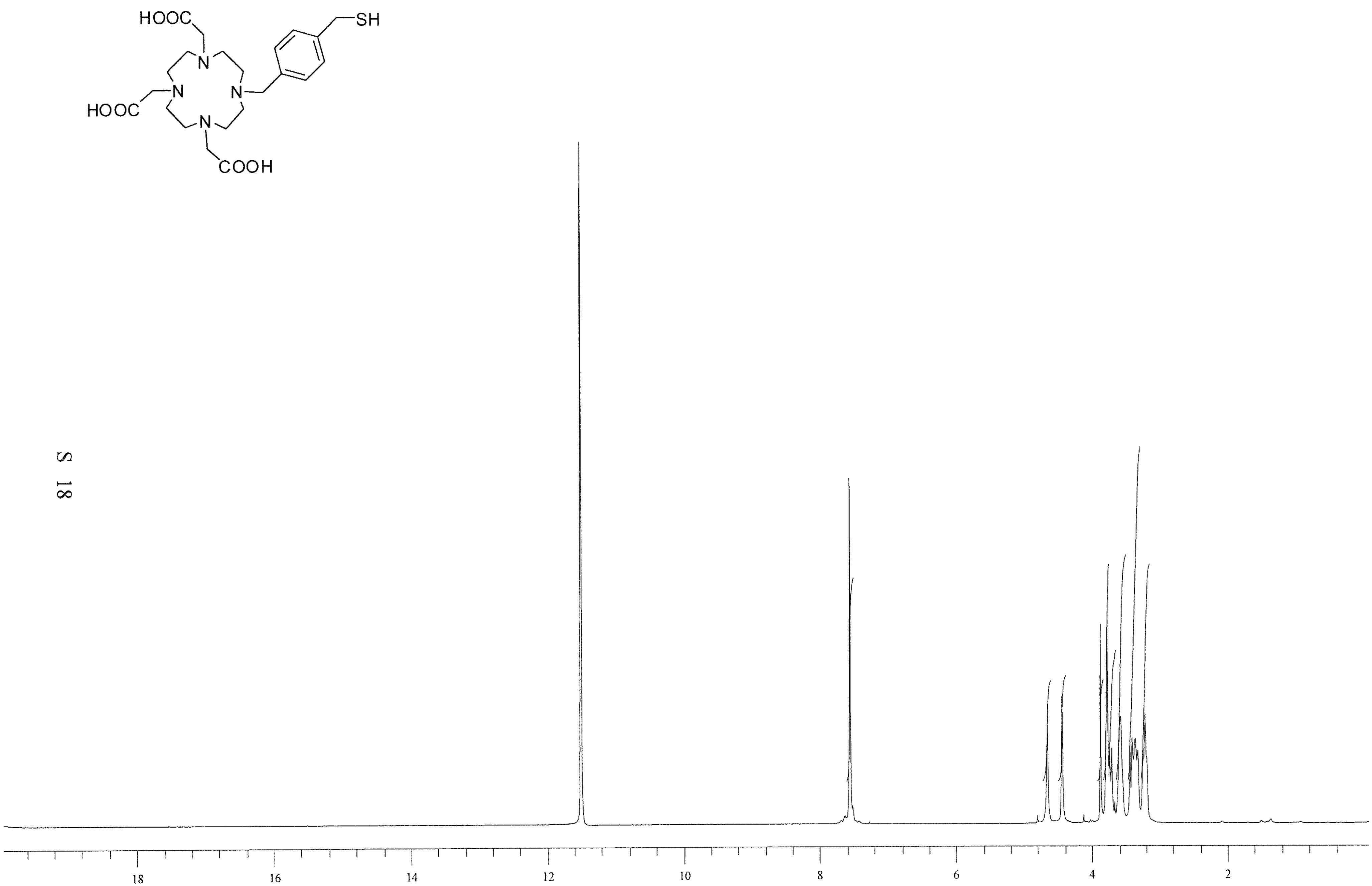

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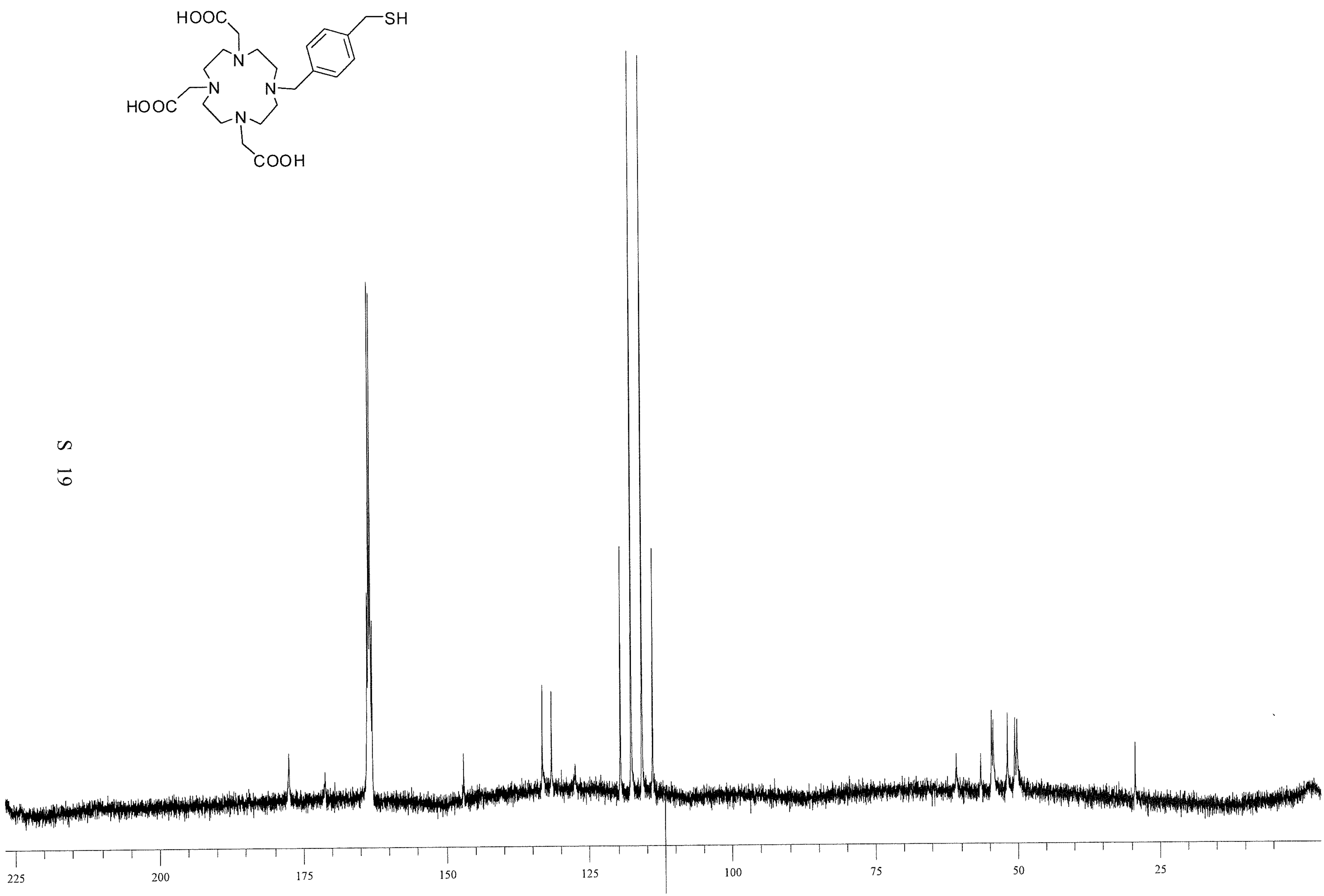

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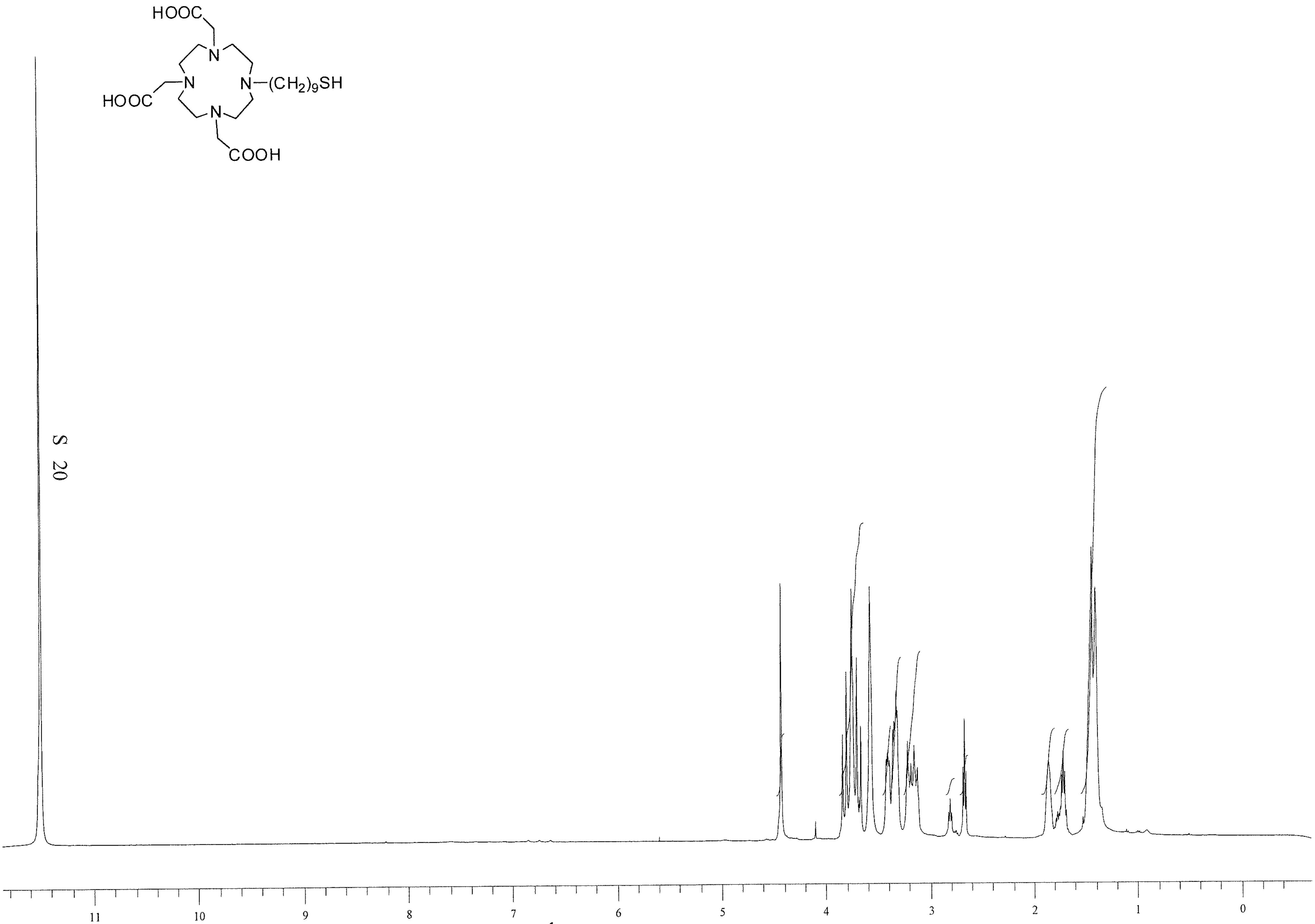

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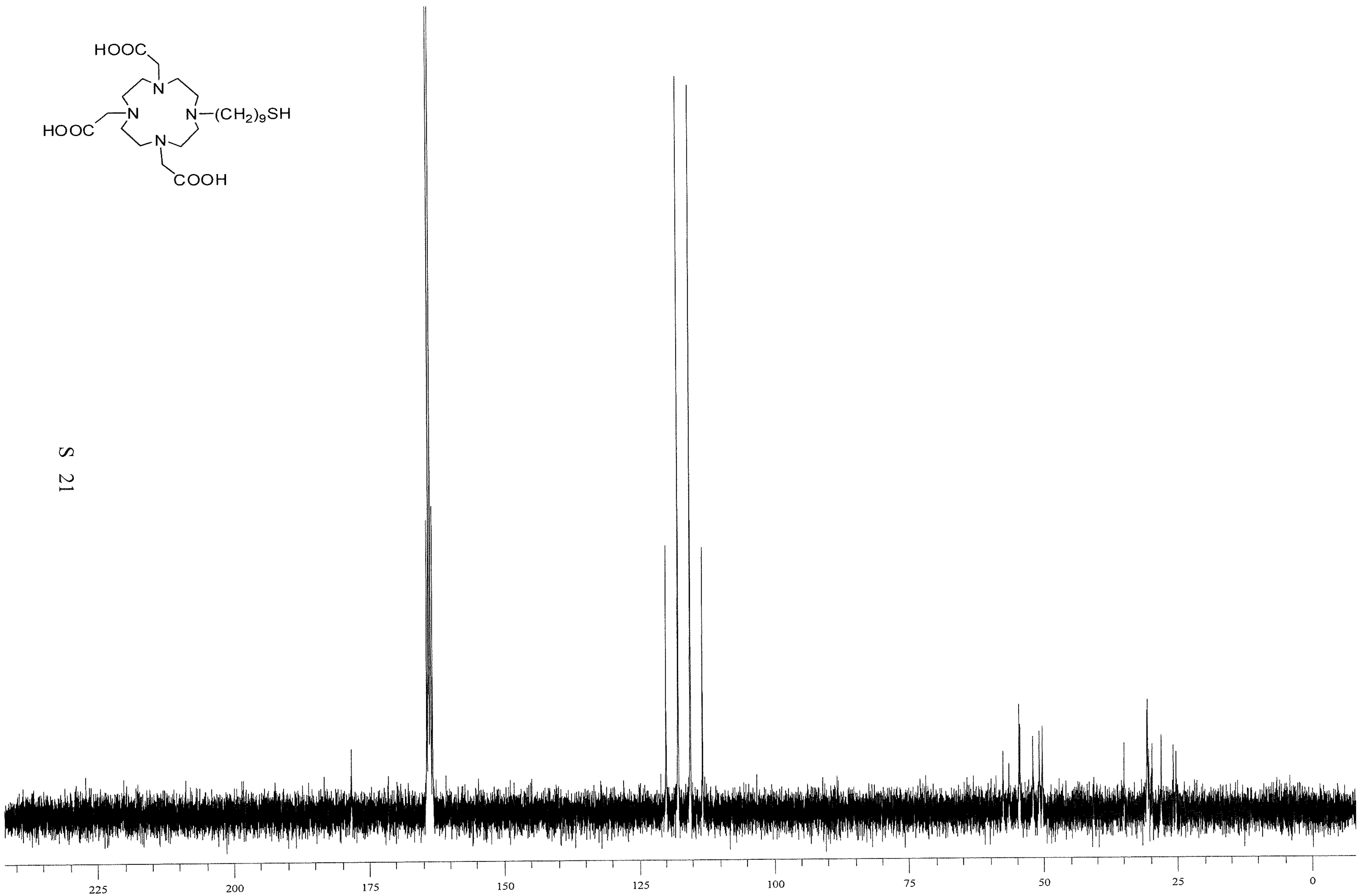

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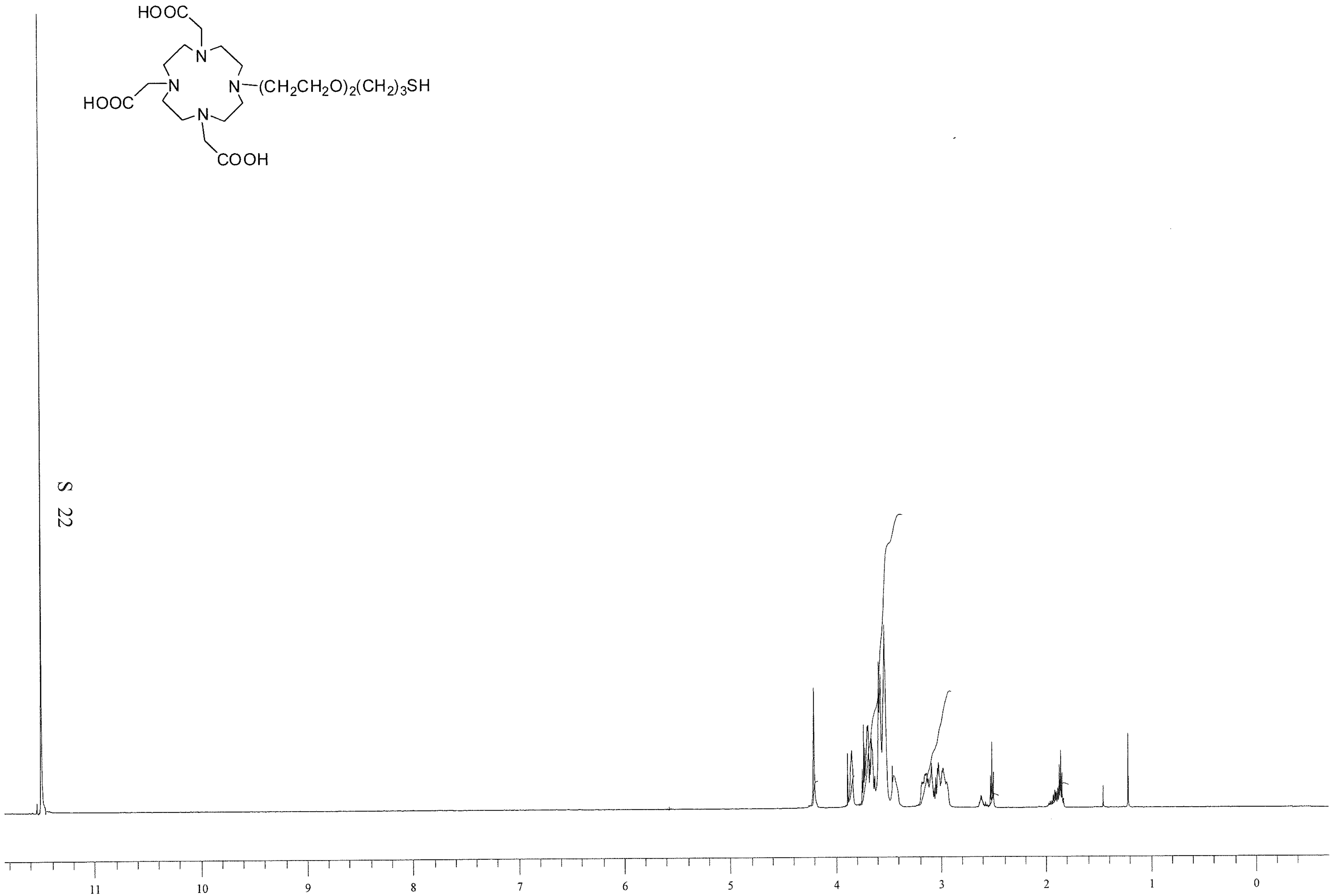

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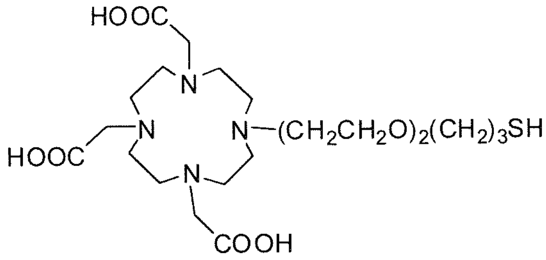

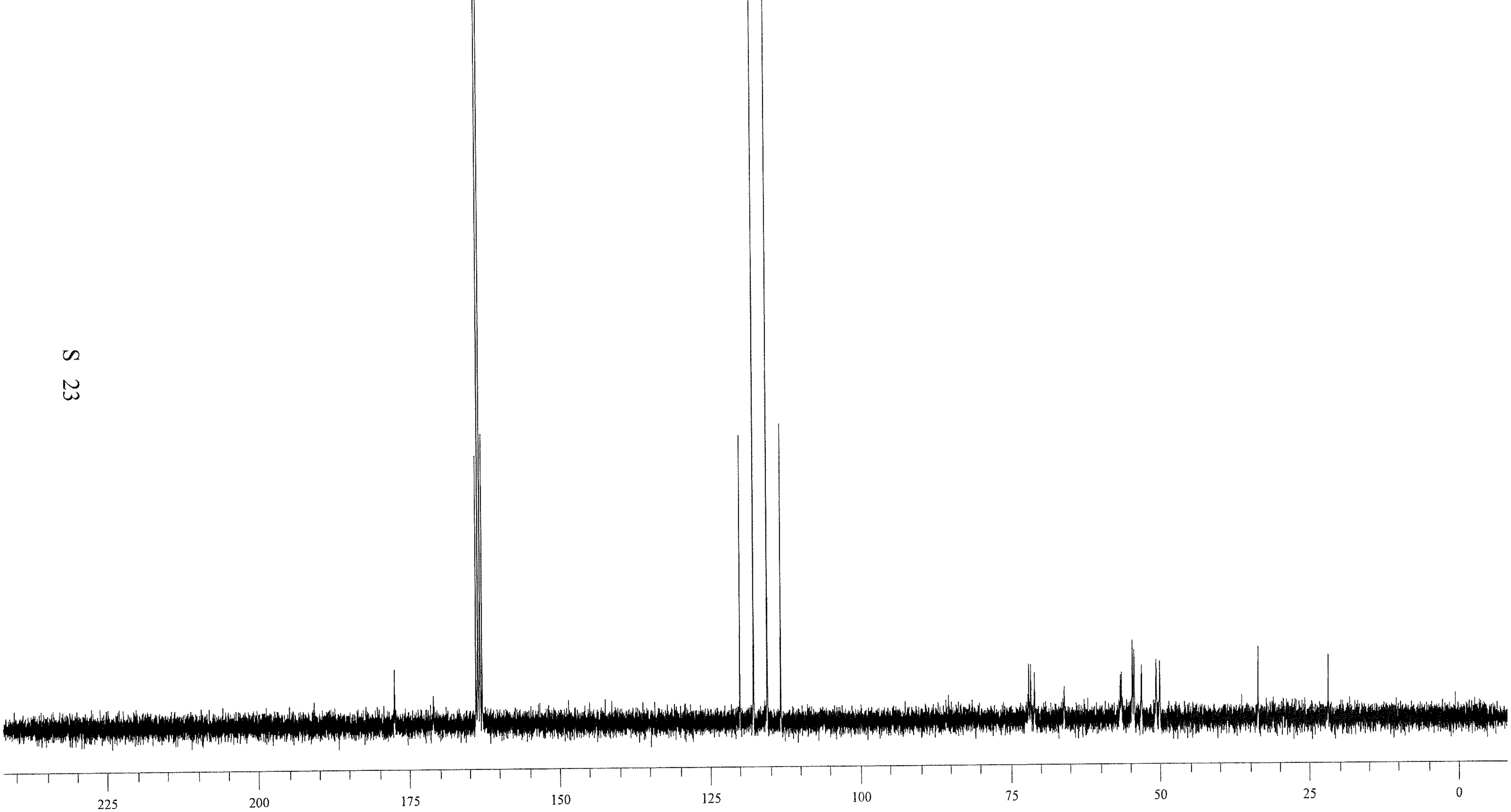

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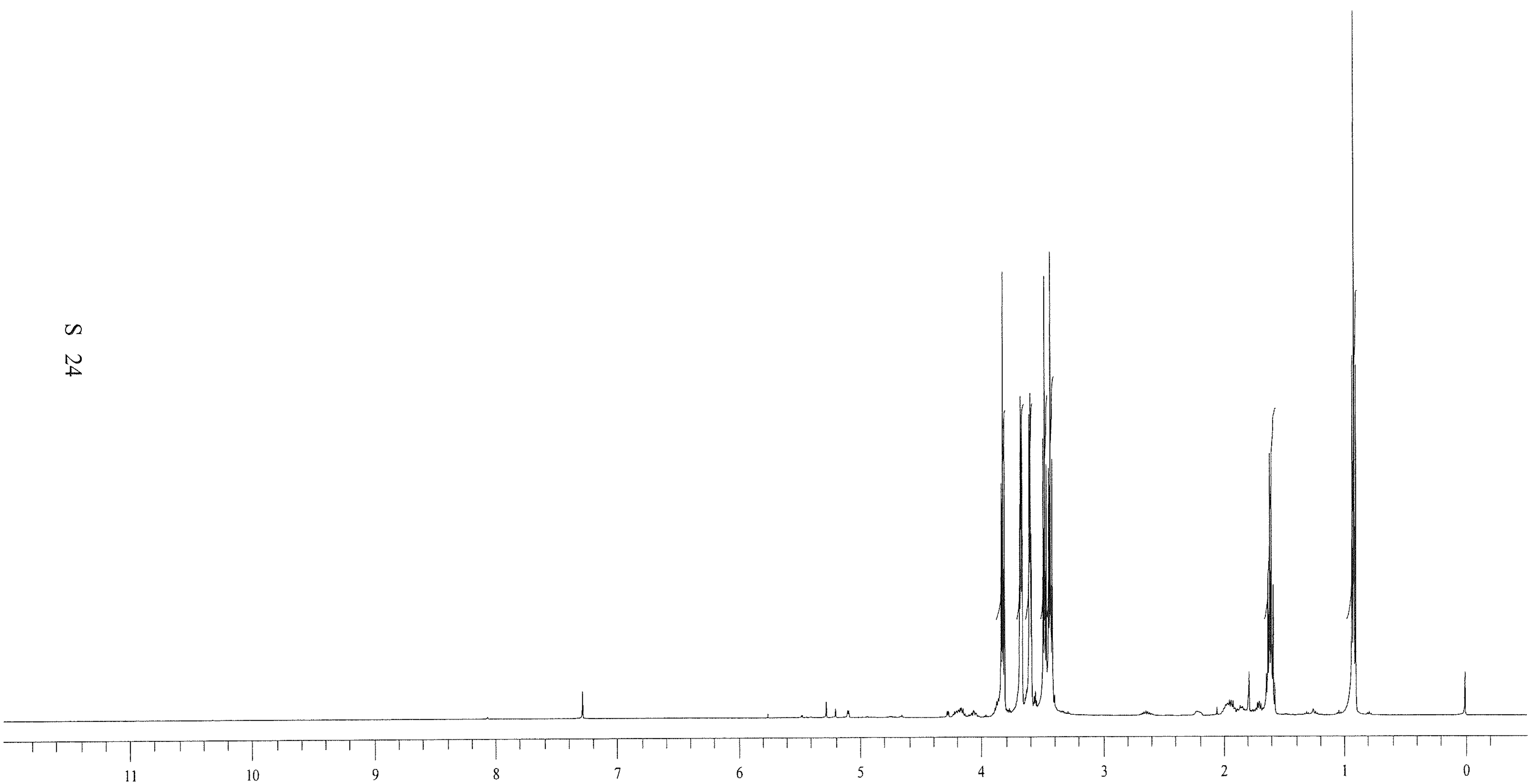

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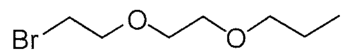

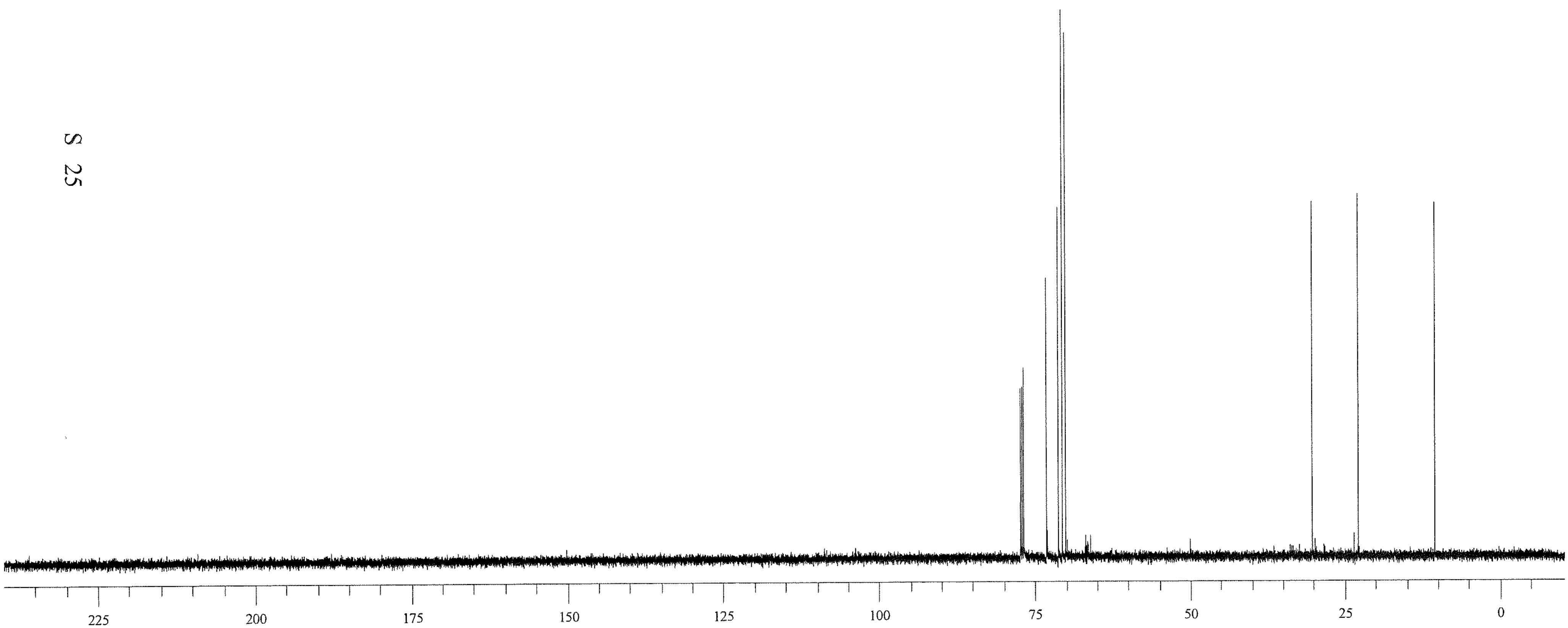

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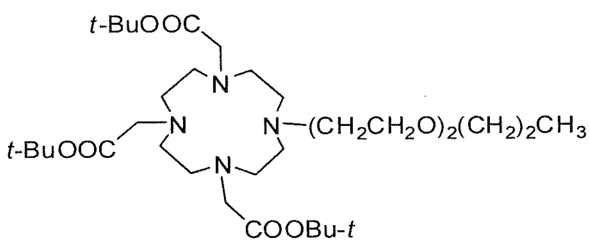

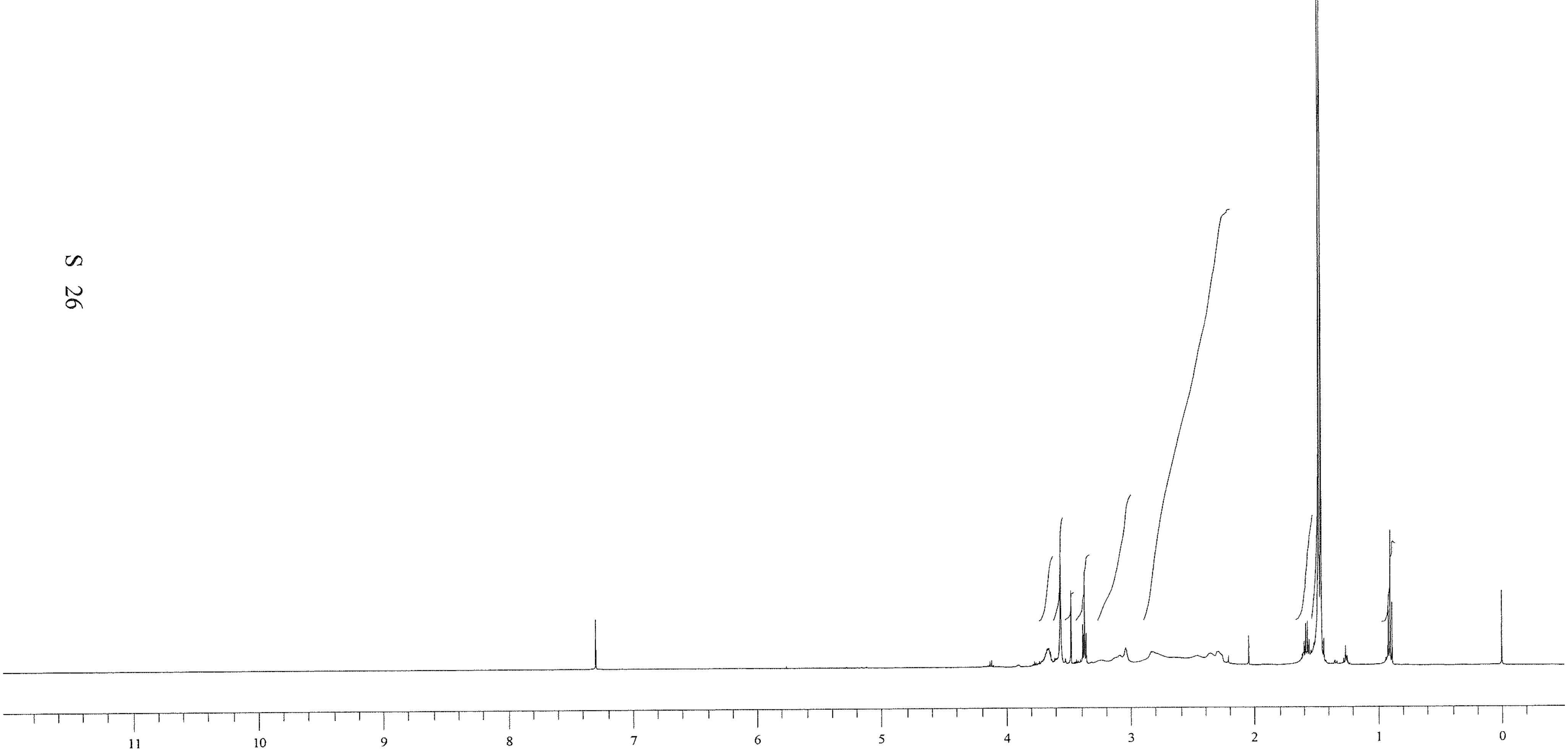

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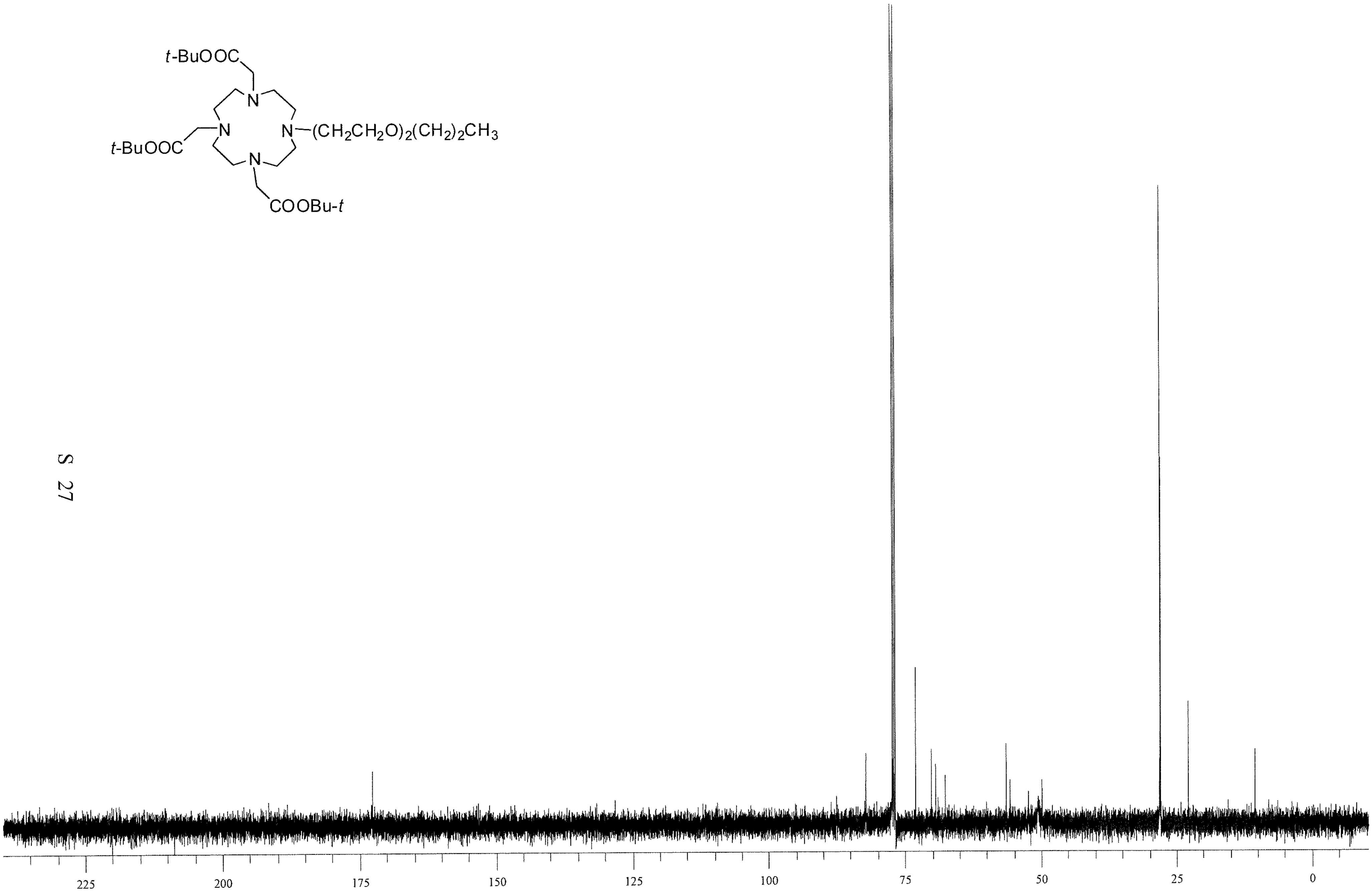

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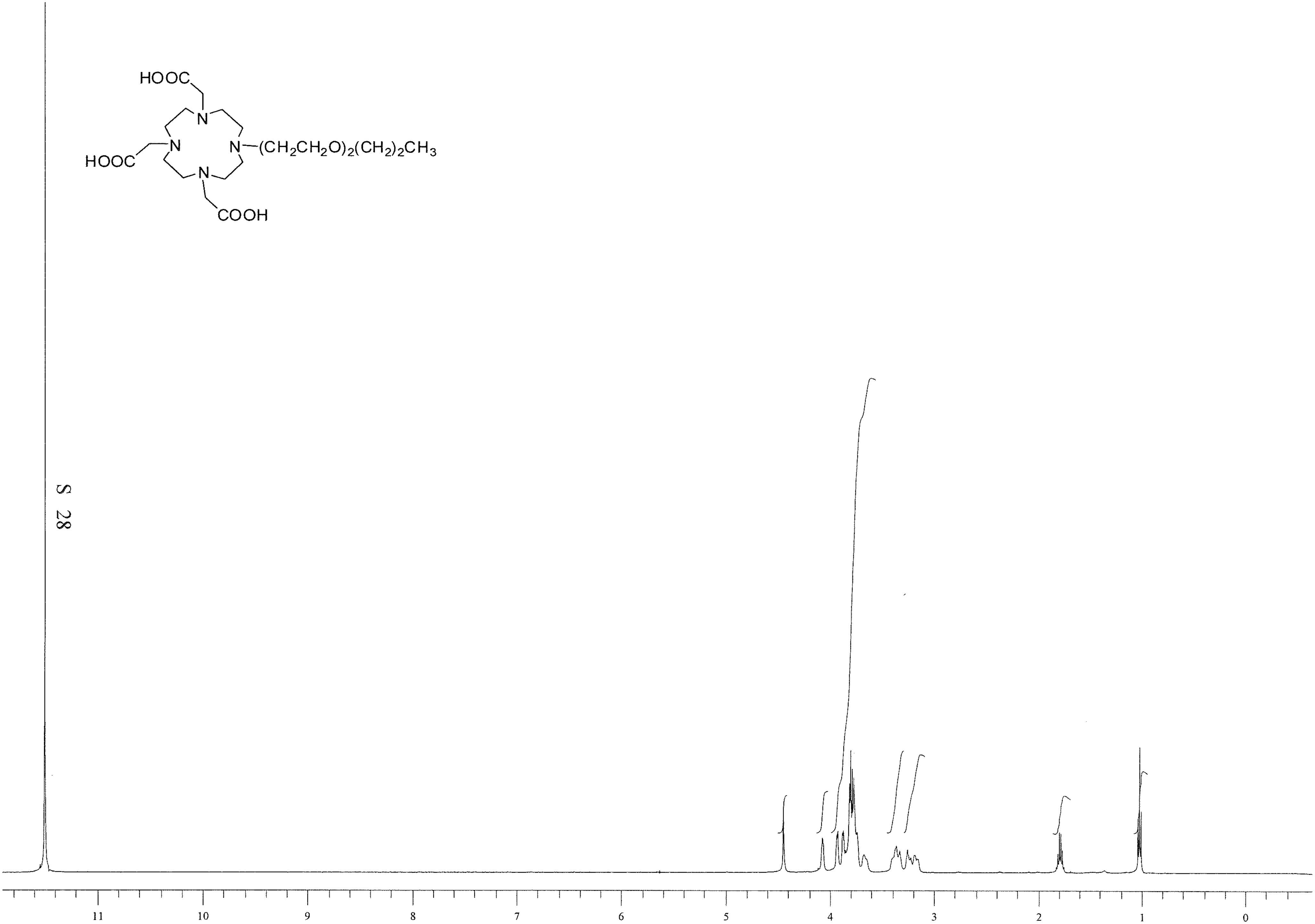

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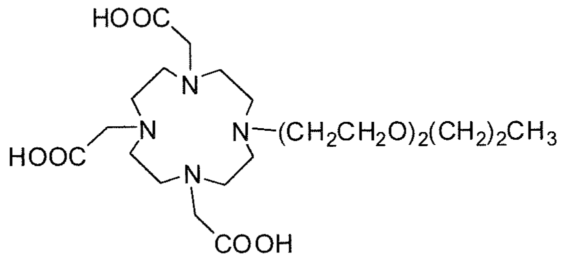

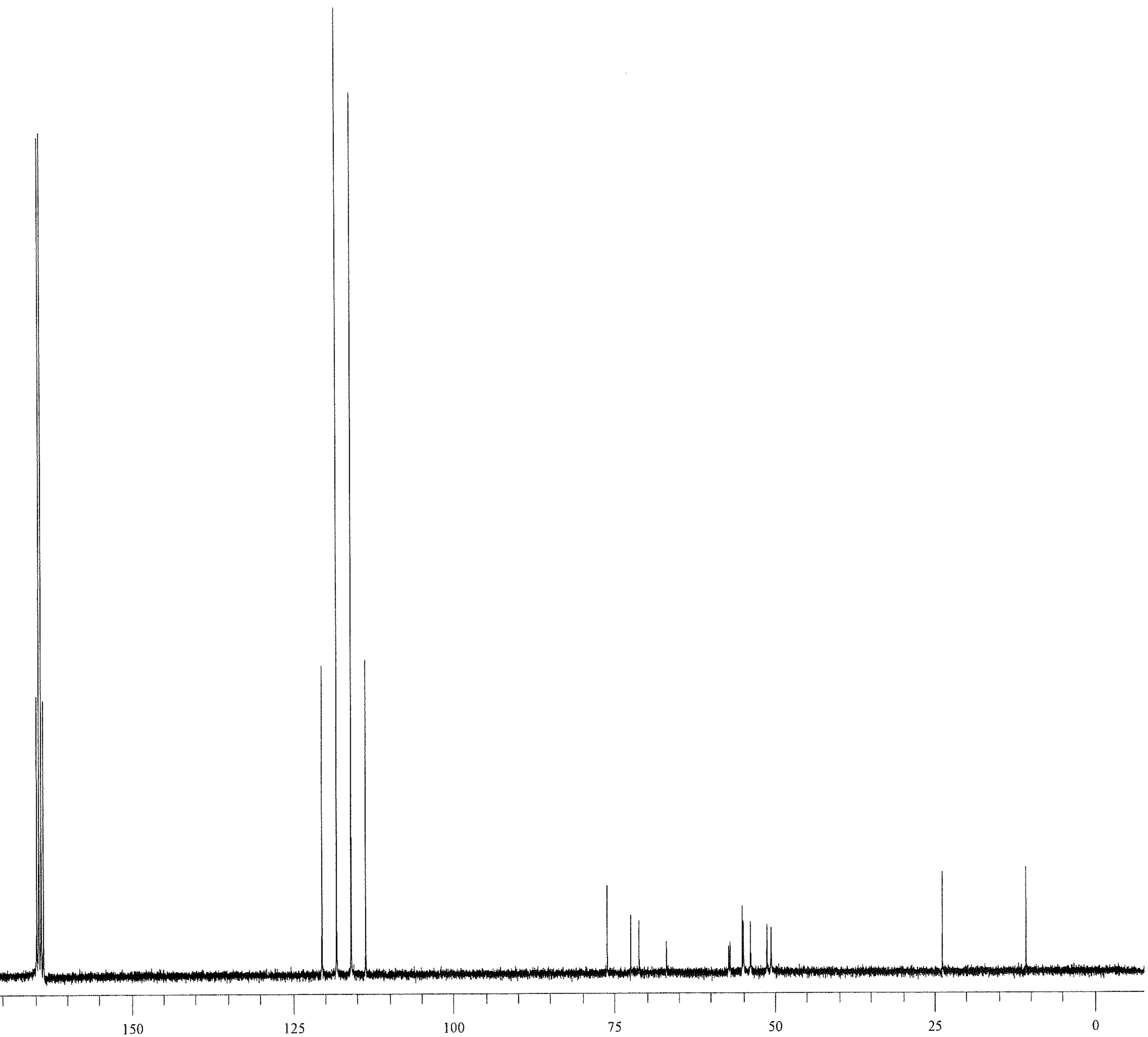

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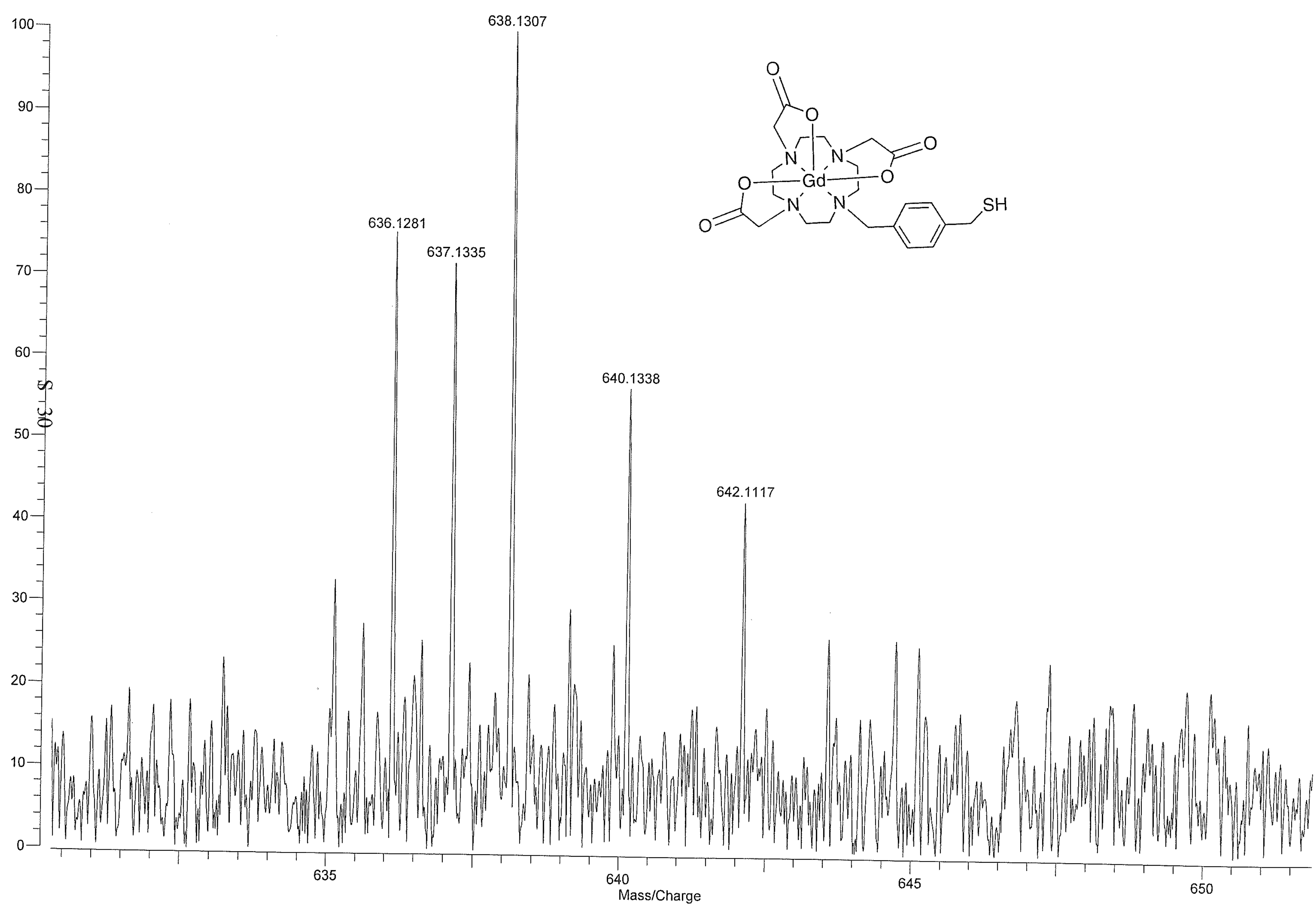

MS of Compound **3a**

Generic Display Report

Analysis Info

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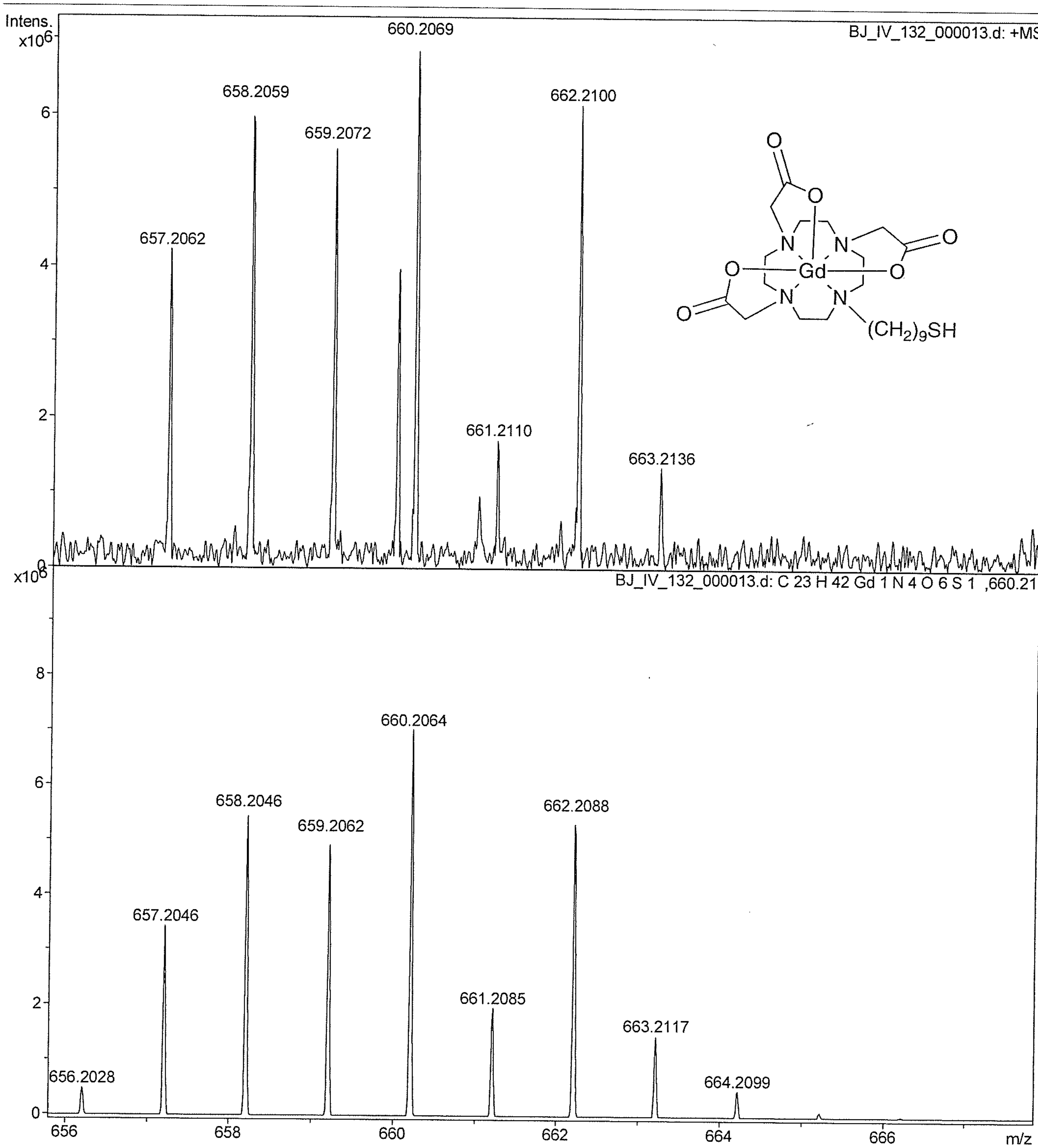

MS of Compound **4a**

Generic Display Report

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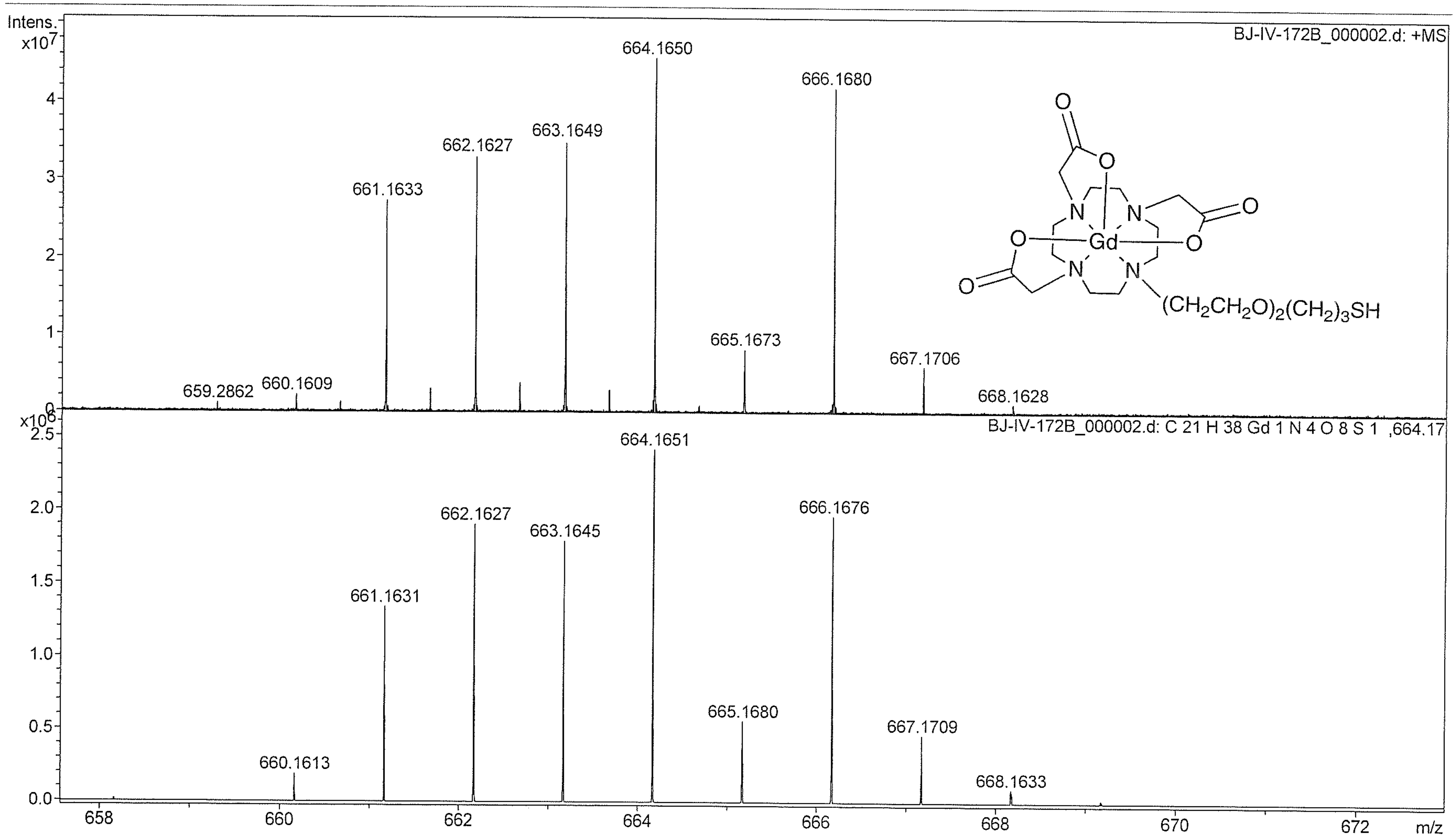

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MS of Compound **5a**

Generic Display Report

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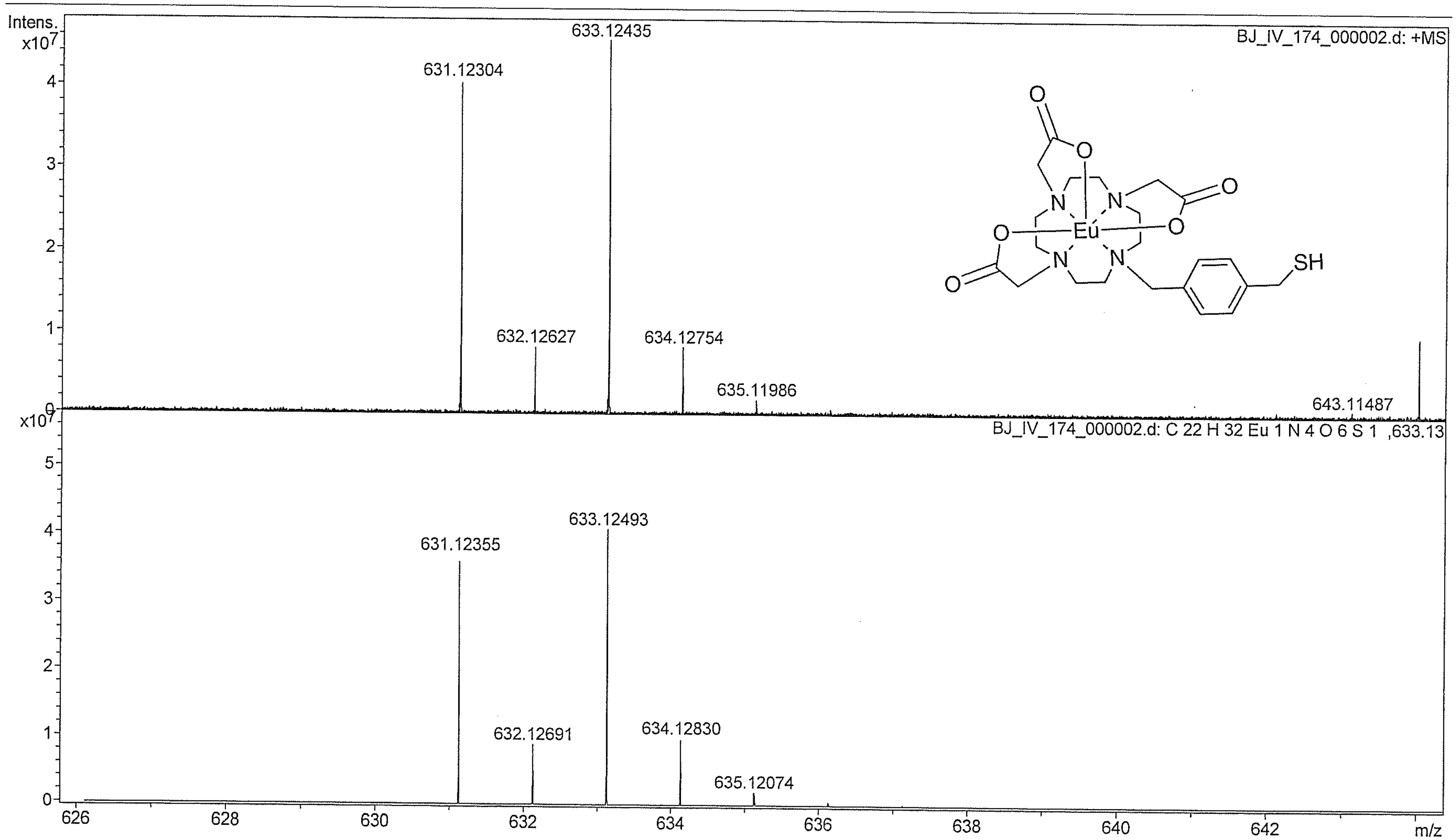

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MS of Compound **3b**

Generic Display Report

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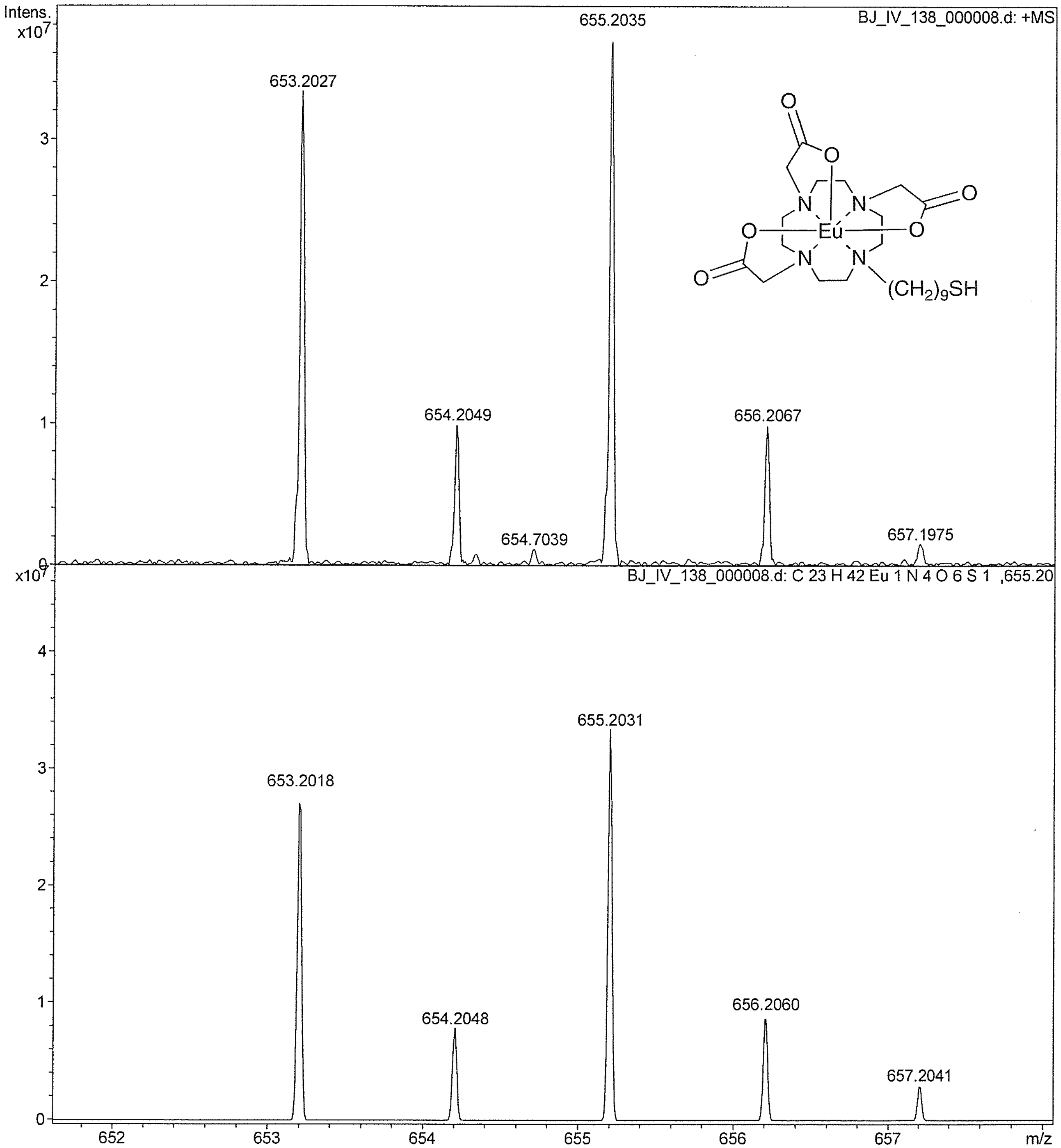

MS of Compound **4b**

Generic Display Report

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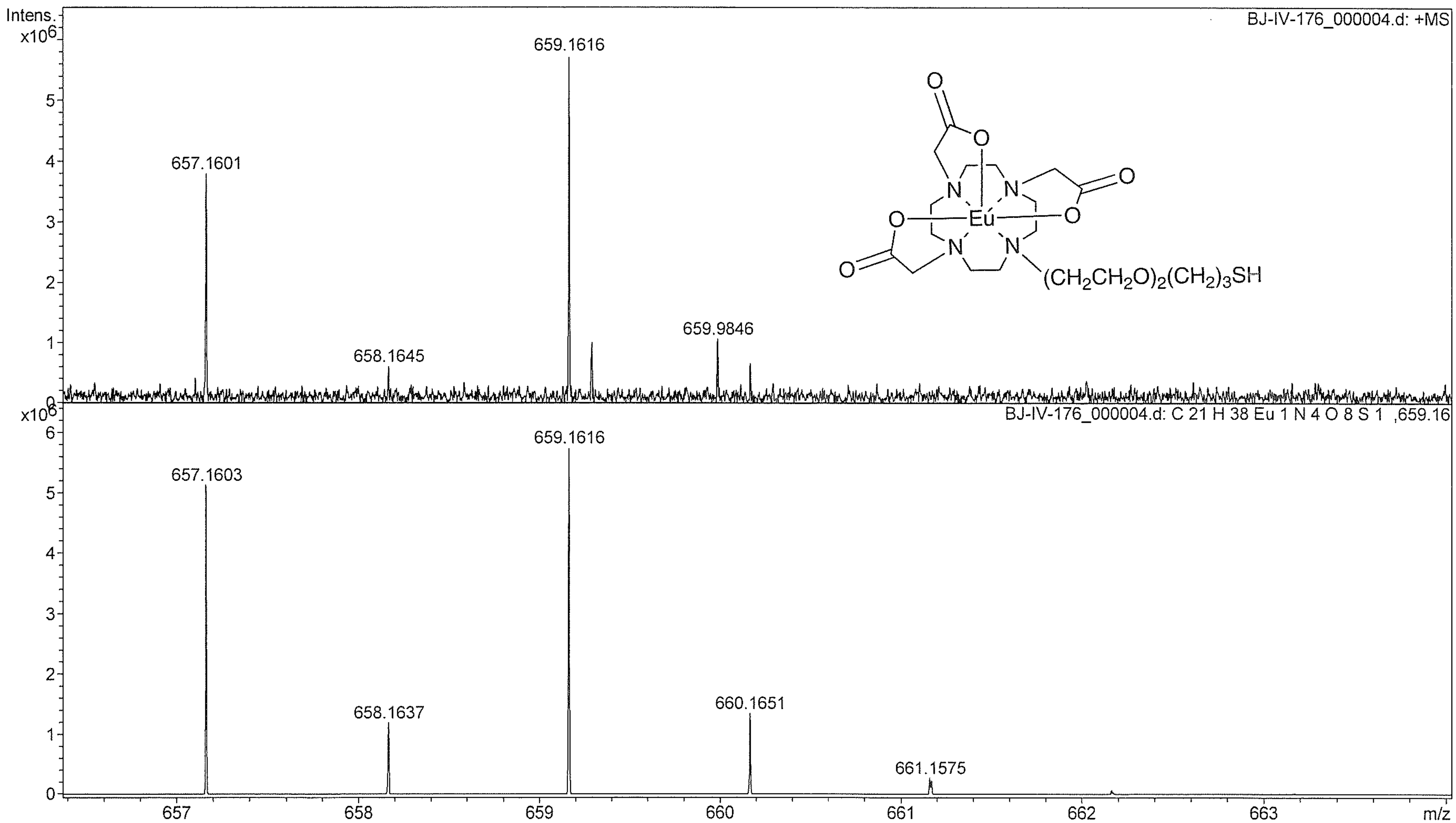

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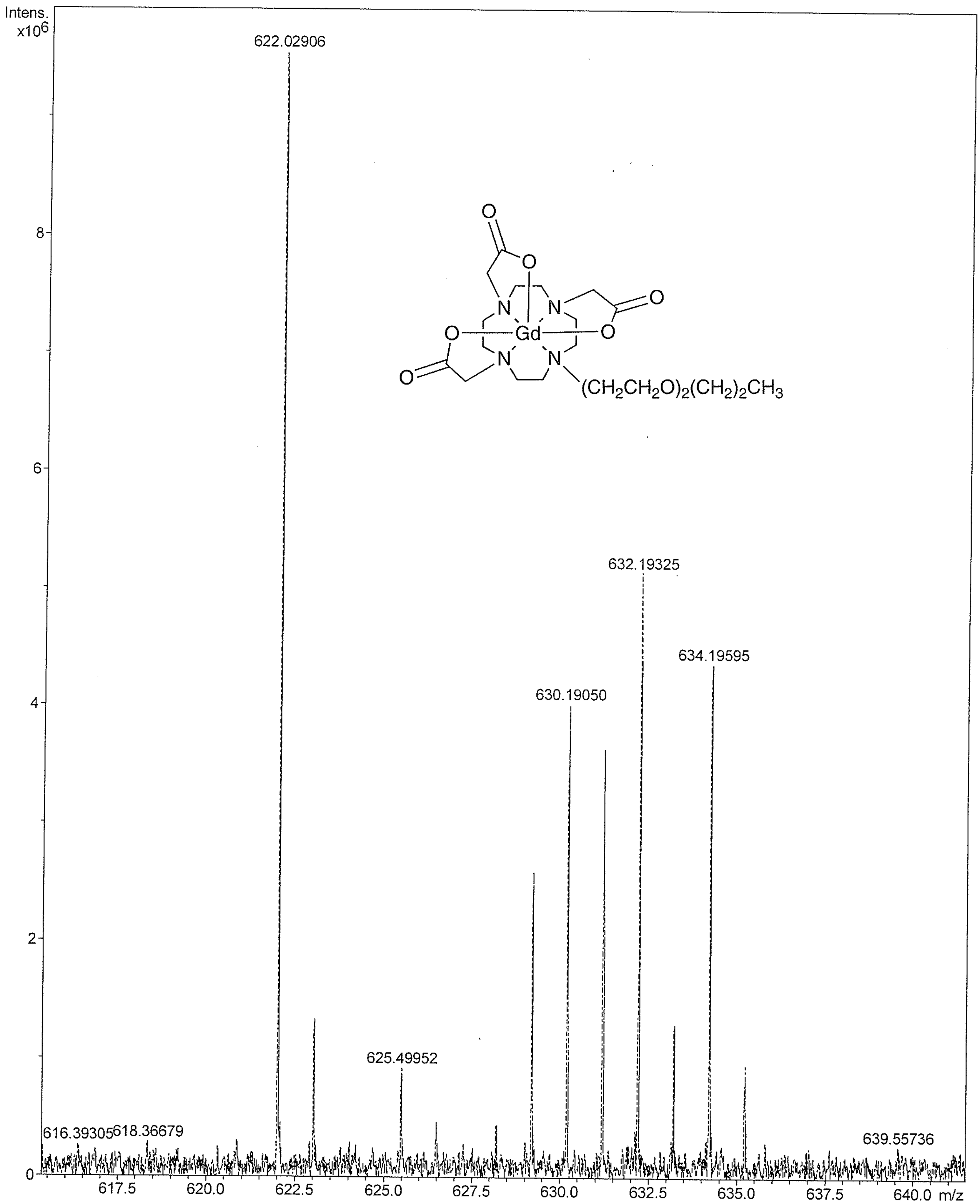
MS of Compound **5b**

Generic Display Report (all)



MS of Compound **24**