

Electronic Supplementary information for New Journal of Chemistry

Supporting information

An efficient route for design of luminescent composite materials based on polyethylene containing europium dibenzoylmethanate

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Synthesis

S1 Synthesis of RI

In a glove box, a solution of (1,2-Ph₂-4-(4-MeOC₆H₄)C₅H₂)₂NdCl₂K(thf)₃¹ (0.279 g, 0,250 mmol) in toluene (25.7 ml) and a Bu₂Mg solution in heptane (1M, 10 ml, 10 mmol) were transferred into a 100 mL glass reactor equipped with a stirring bar, stainless steel and Teflon stopcocks. The reactor was degassed, placed into a thermostat and connected to an ethylene reservoir with a pressure sensor. Ethylene oligomerization was carried out at 38°C and at ethylene pressure of 0.2 MPa, which was kept constant during oligomerization. Ca. 8.985 g of ethylene was consumed, which was measured from the observed pressure drop in the reservoir until Mg(PE)₂ started to precipitate. The reactor was then disconnected from the ethylene source, degassed, filled with argon. A solution of I₂ (6.350 g, 25.0 mmol) in THF (35 ml) was added dropwise via cannula to the stirred cold (0-5°C) reaction mixture. The mixture was stirred for 1 h, and then consequentially washed with saturated NaHSO₃ water solution, water, 1M HCl, water. Organic layer and precipitate was extracted with CH₂Cl₂, washed with water till pH=7,

dried over Na₂SO₄. The organic layer was concentrated to 100 ml under reduced pressure and 150 ml of methanol was added to it. The resulting mixture was cooled to -20°C. The formed PE-I precipitate was filtered off, washed with cold methanol, and dried under vacuum. The yield was 11.134 g.

According to ¹H NMR spectral data, the 1-iodoalkane/alkane ratio was 81% : 19%; the presence of alkene was not detected; the averaged formula for 1-iodoalkane was C₂₈H₅₇-I. A MALDI-TOF mass-spectrum of a preliminary derivatized product with Ph₃P displayed the presence ions Ph₃P⁺(CH₂-CH₂)_nH with n=8-22 (the highest peaks for n=11-13)². Recalculated data for PE-I: M_n=499, M_w=508, PDI=1.018

S2 Reaction of 1 with RI

Na[Eu(DBM)₄] 2C₂H₅OH (1.564 g 1.34 mmol), RI 0.970 g (approx. 1.5 mmol), dry THF (50 ml) were placed in a 100 mL Schlenk flask. The reaction mixture was stirred under reflux for 50h under argon. The resulting solution obtained was separated from the insoluble precipitate. The solvent was evaporated under vacuum. The residue was extracted twice with hexane (2 x 50 mL), washed with CH₂Cl₂ (2 x 20 mL) and then again with hexane (20 mL), and dried under dynamic vacuum. These procedures left 0.389 g of yellowish powder, contained unidentified Europium compounds (21.39% Eu according to complexometric titration), which were impossible to isolate as individual compounds. NMR spectrum (Fig. S2).

The hexane extract was evaporated under vacuum, yielding 1.307 g of solid, which appeared to be a mixture of compounds, that cannot be separated. The mixture contained RI and unidentified organic compounds, according to the NMR spectrum (Fig. S3).

X-ray crystallography.

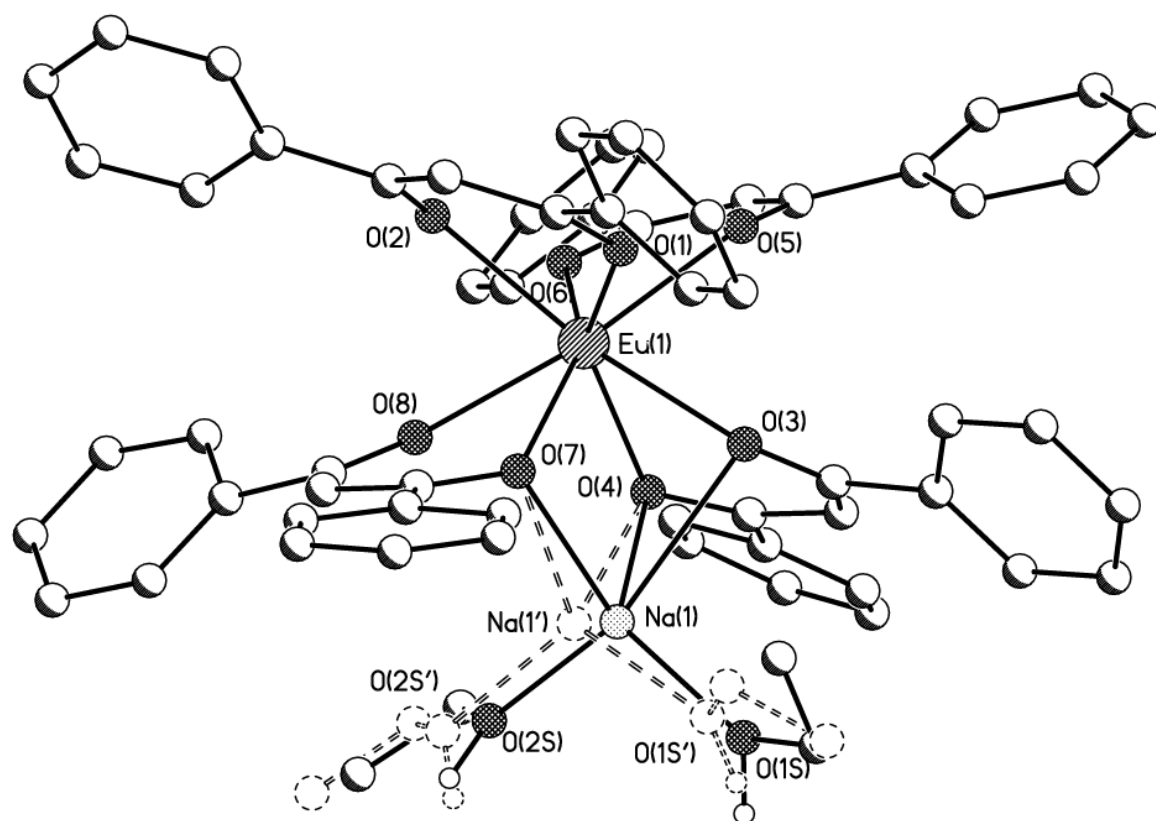


Fig. S1. The general view of **1** illustrating the disorder of $\text{Na}(\text{HOC}_2\text{H}_5)_2$ fragment.

NMR spectra

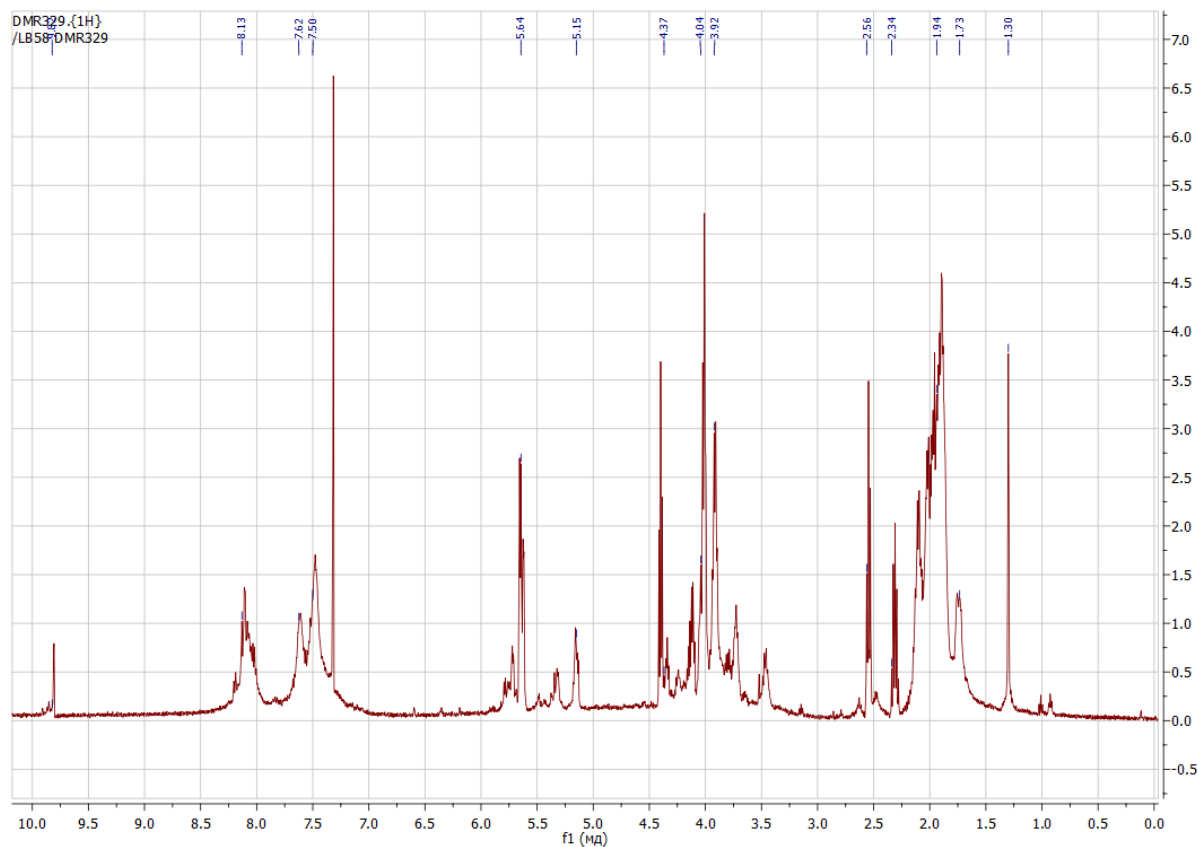


Figure S2 NMR spectrum of residue (S1) after extraction with hexane (CDCl_3)

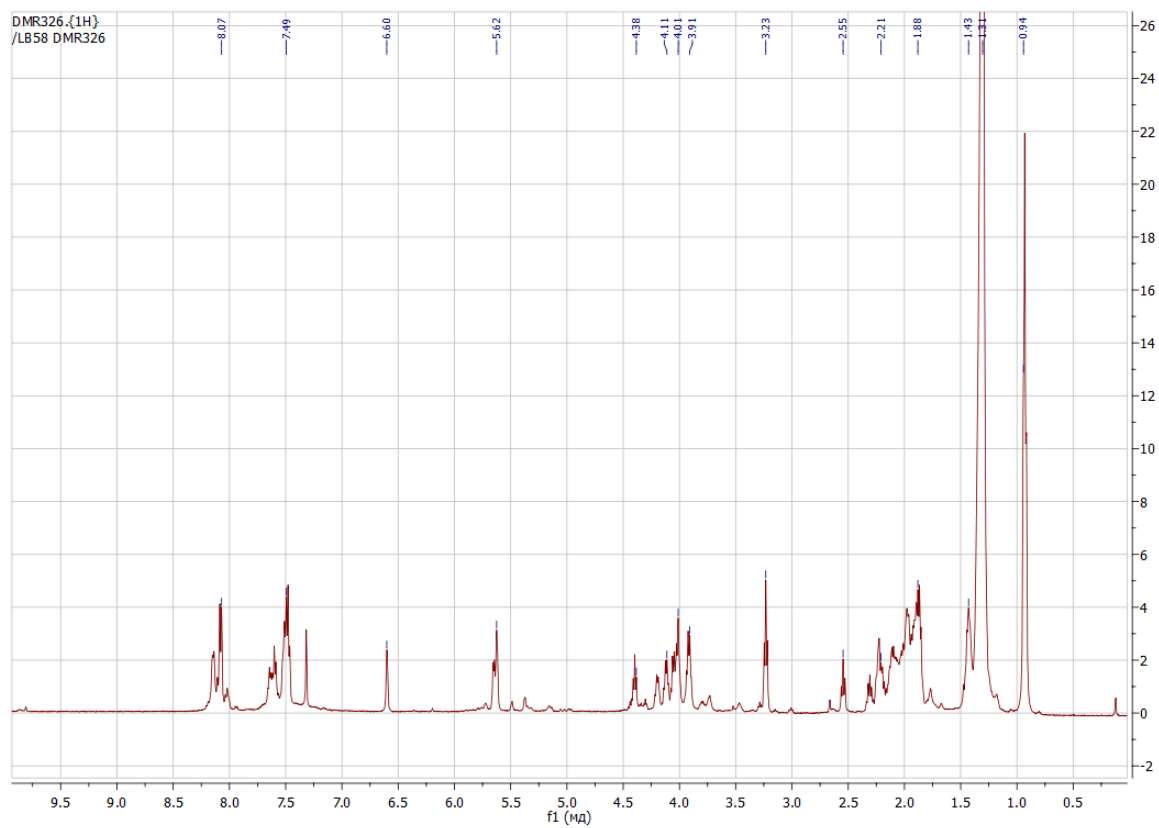


Figure S 3 NMR spectrum of residue (S1) from hexane extract (CDCl_3)

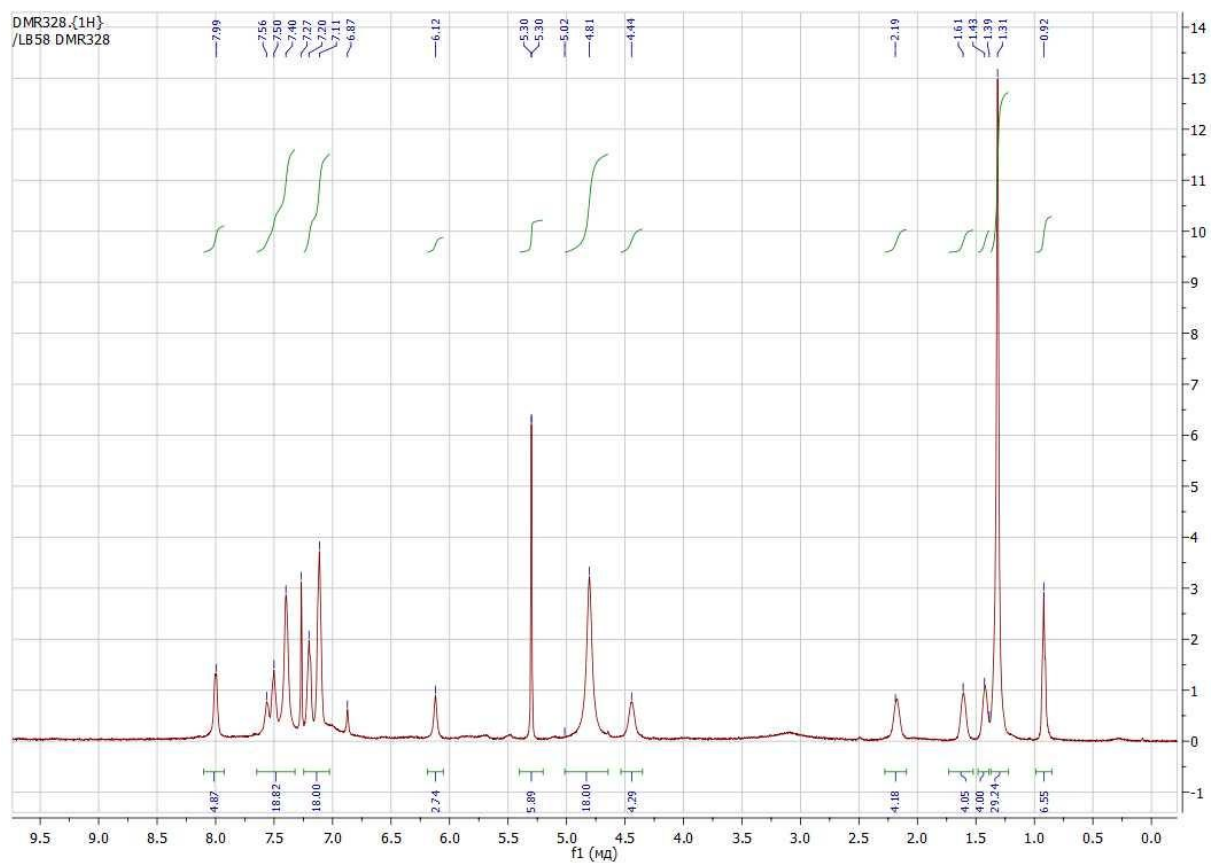


Figure S4 ^1H -NMR -spectrum of **2** (CDCl_3)

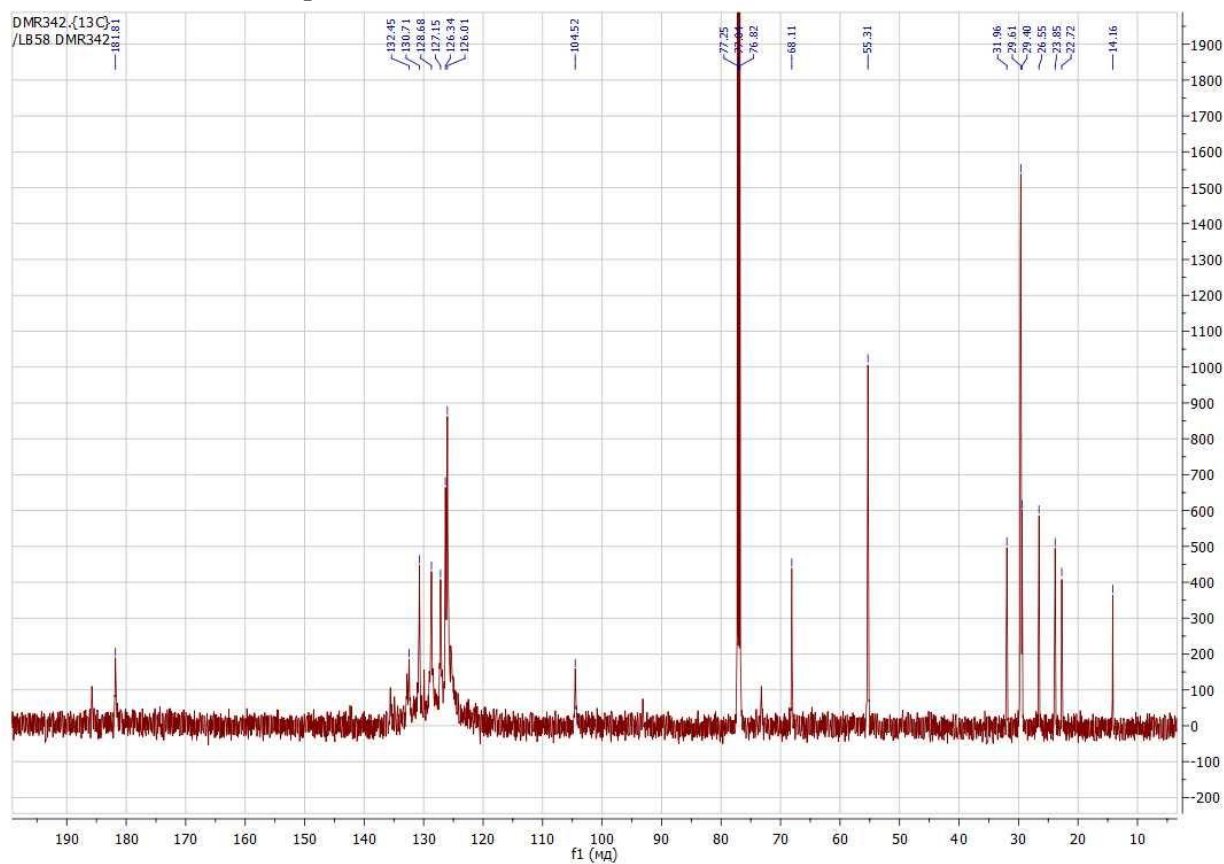


Figure S5 ^{13}C -NMR -spectrum of **2** (CDCl_3)

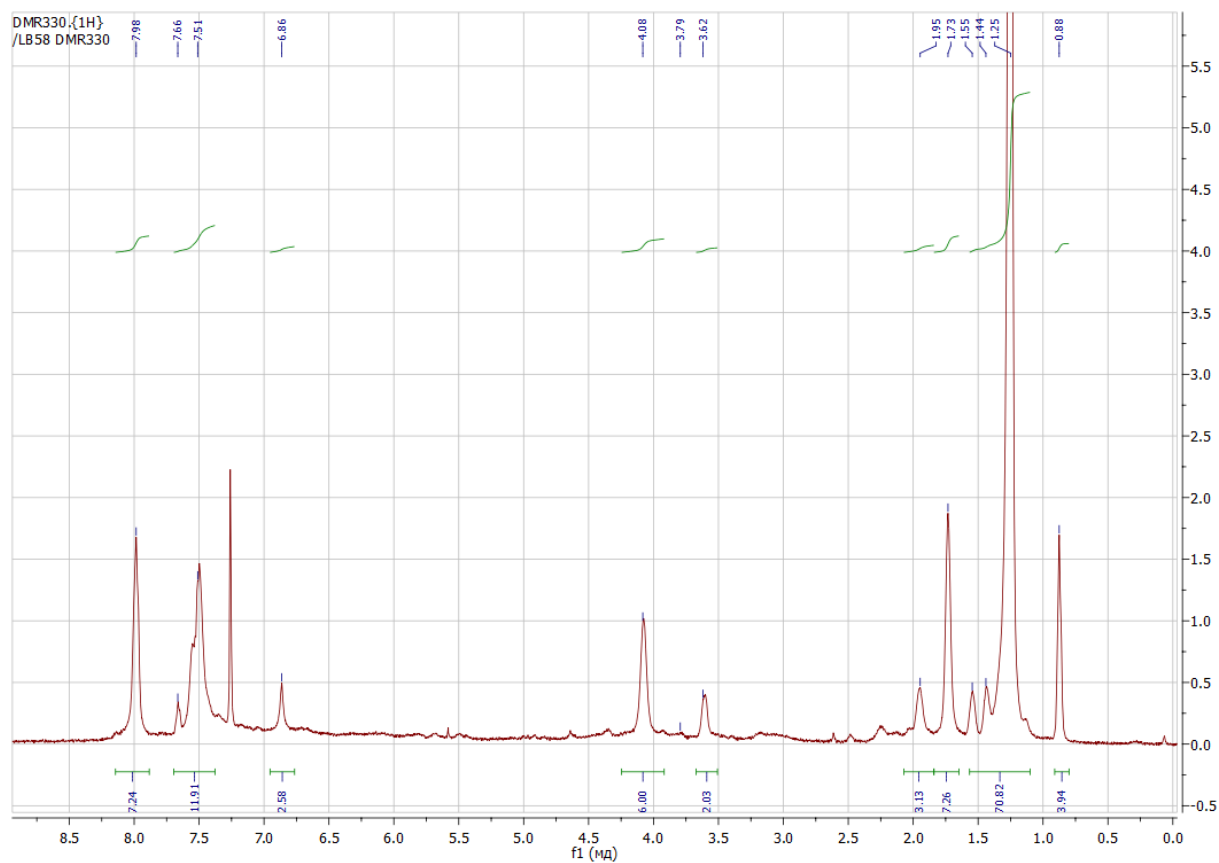


Figure S6 ^1H -NMR -spectrum of **3** (CDCl_3)

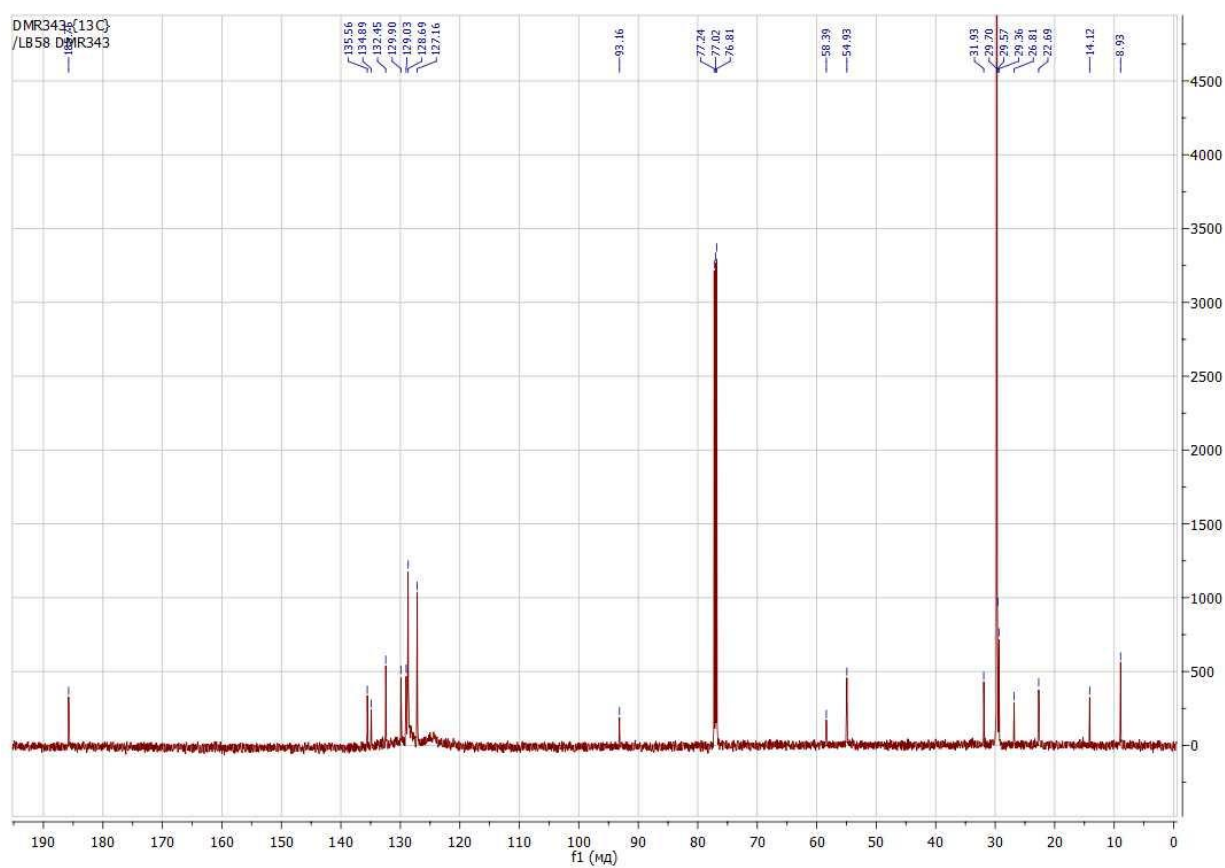


Figure S7 ^{13}C -NMR -spectrum of **3** (CDCl_3)

TGA and DSC data for compounds 2 and 3

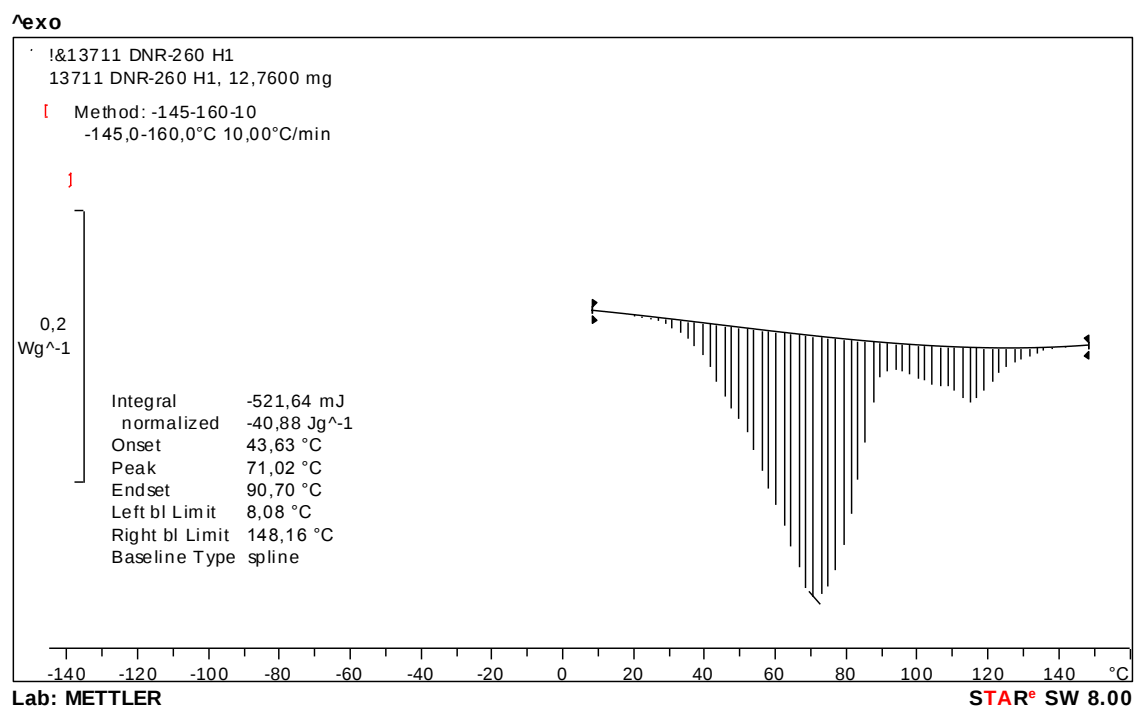
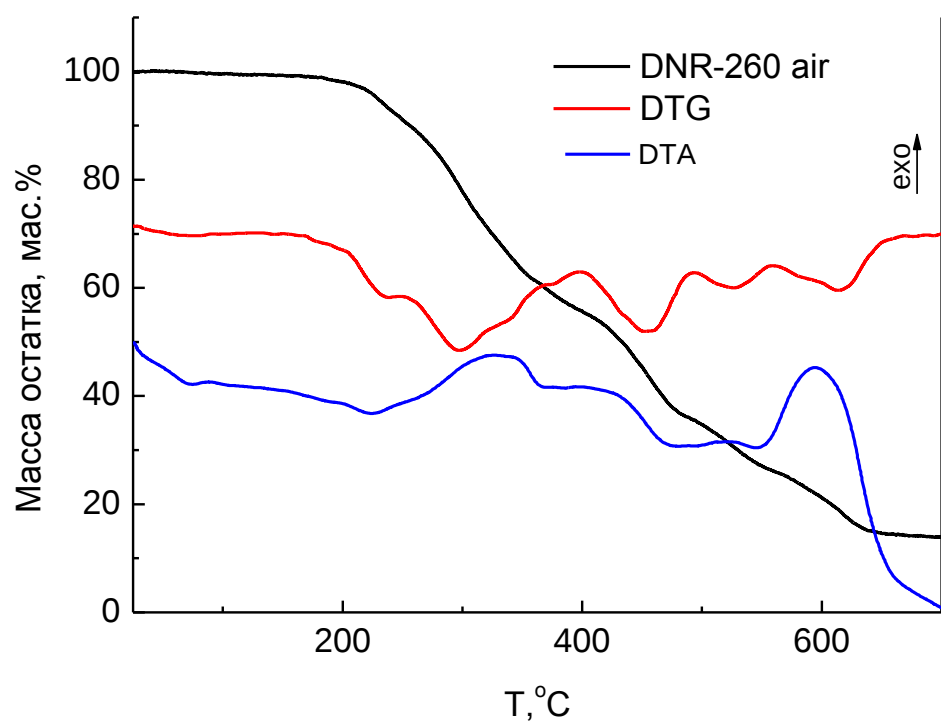


Figure S8 TGA (top) and DSC (bottom) for **3**

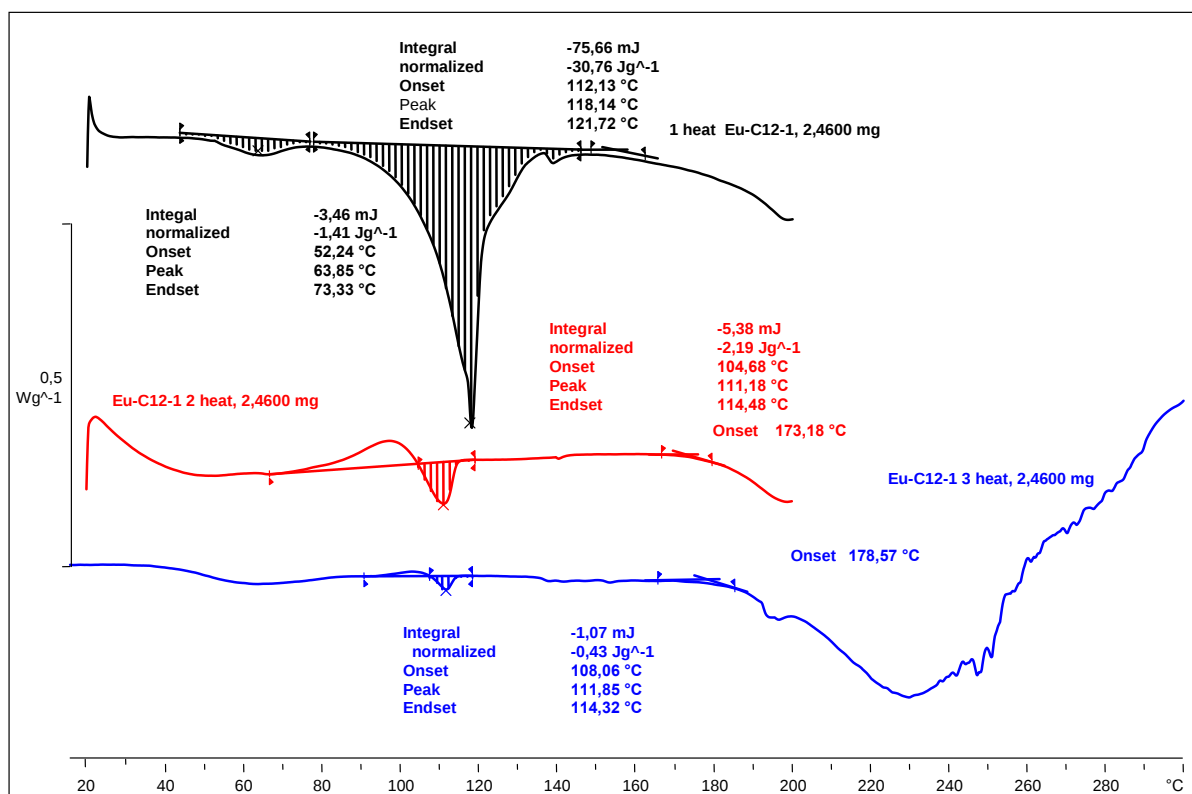
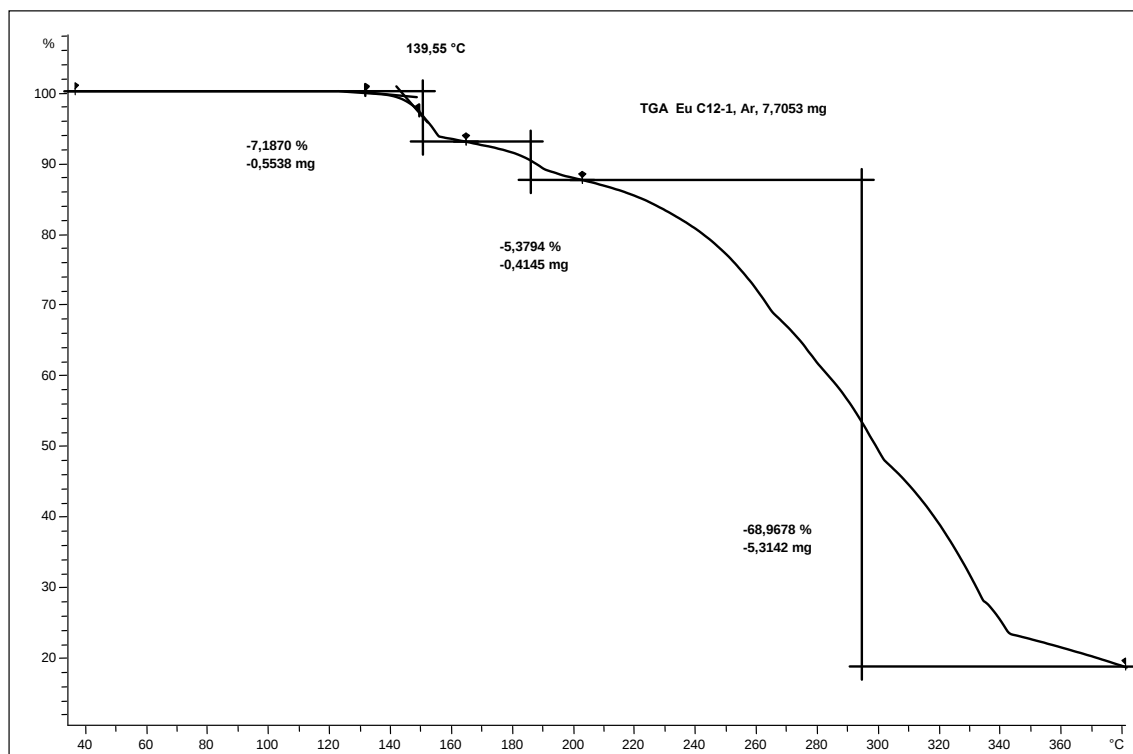
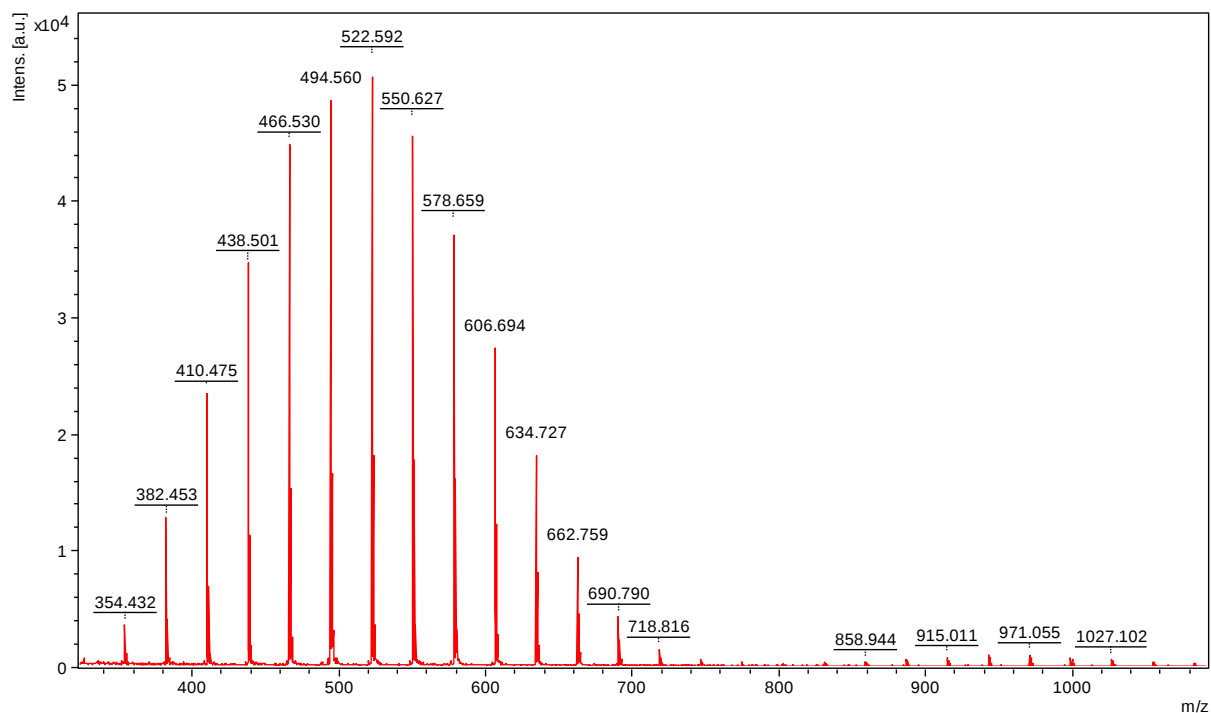


Figure S 9 TGA (top) and DSC (bottom) for 2 .

MS -spectra



M_n	M_w	PD
526	536	1.019

Figure S10 MALDI-TOF mass-spectrum of $[(RNEt_3)]^+I^-$

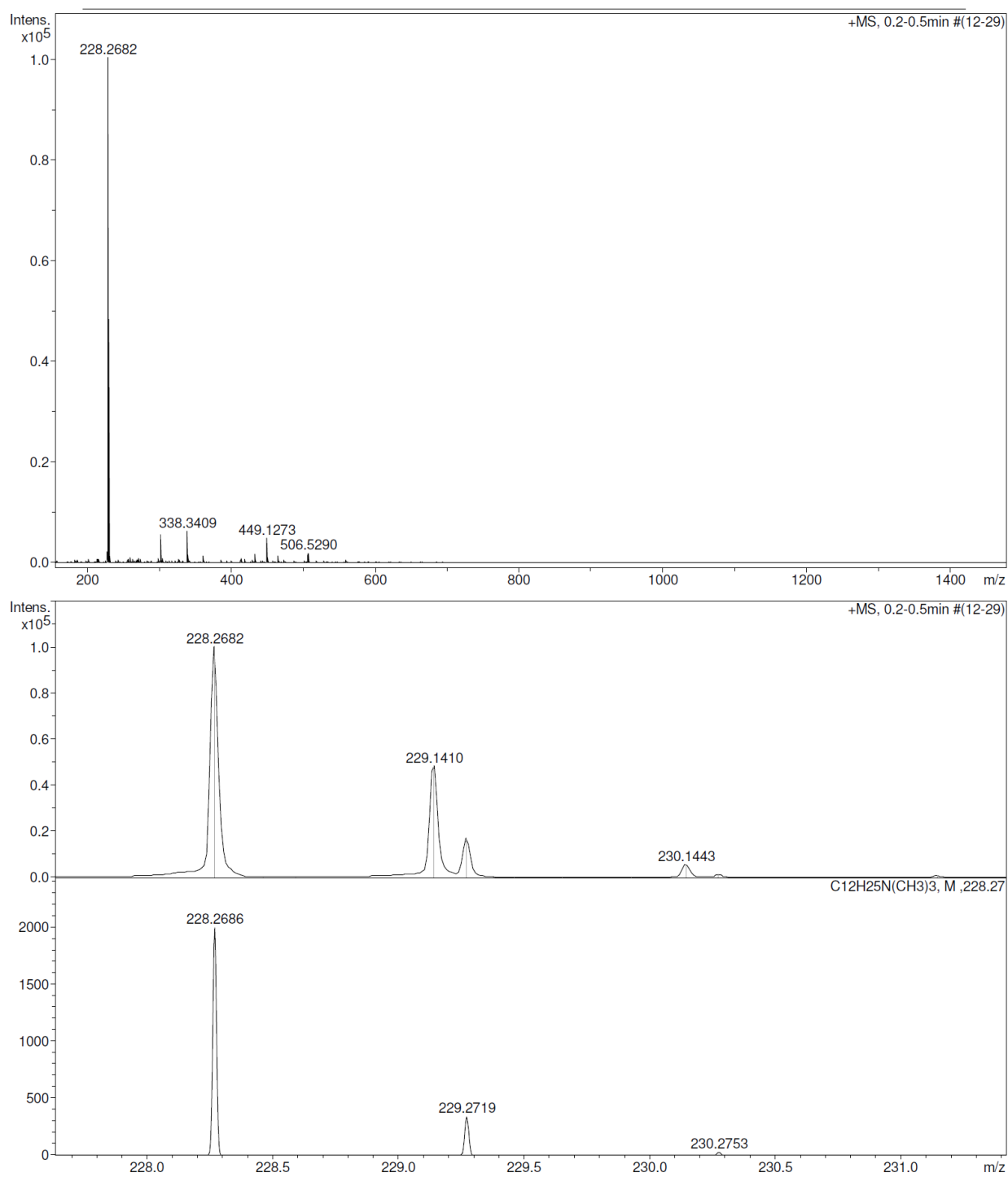


Figure S11 ESI MS spectrum of 2 (positive mode)

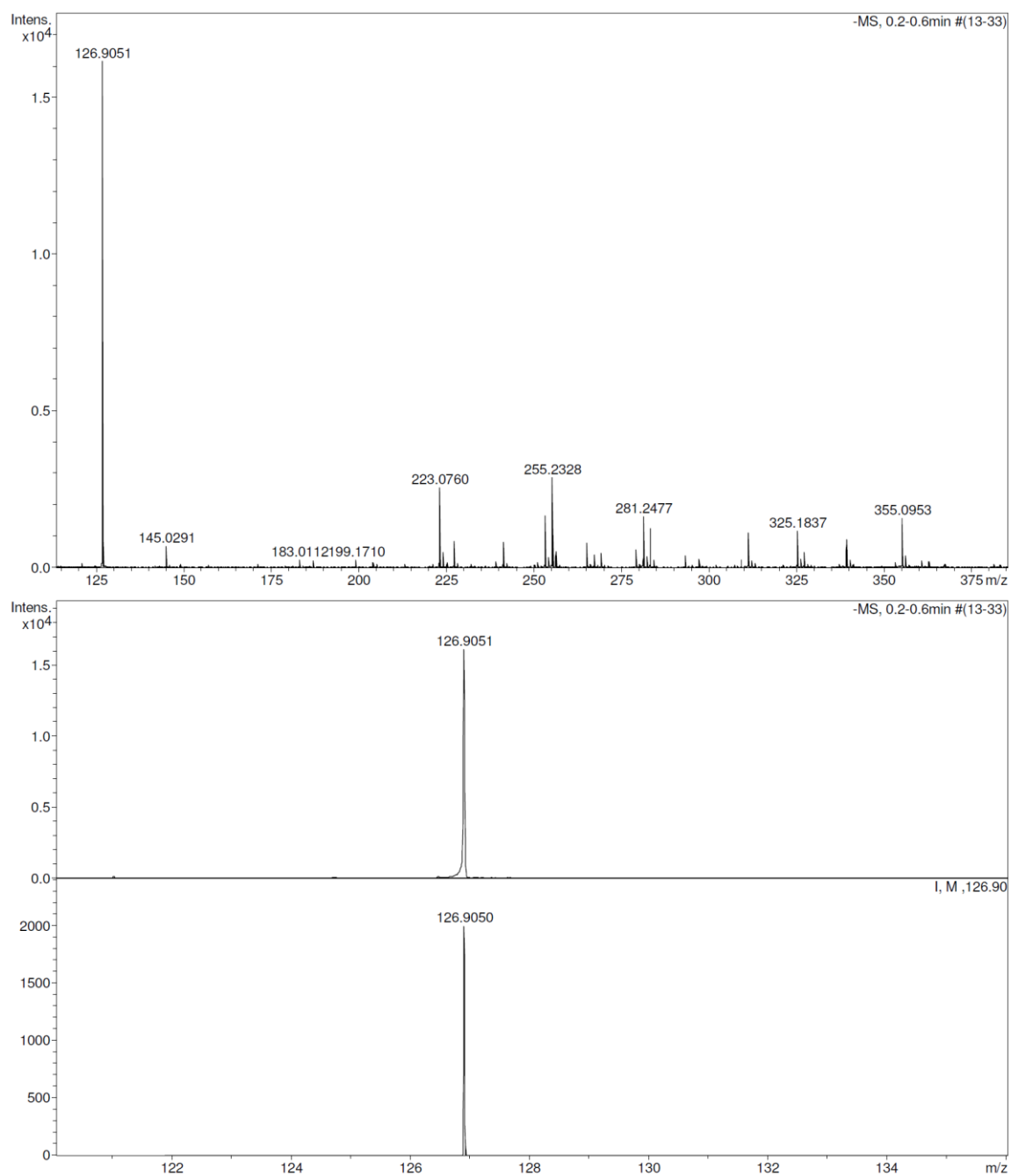


Figure S12 ESI MS -spectrum of 2 in the negative ion mode

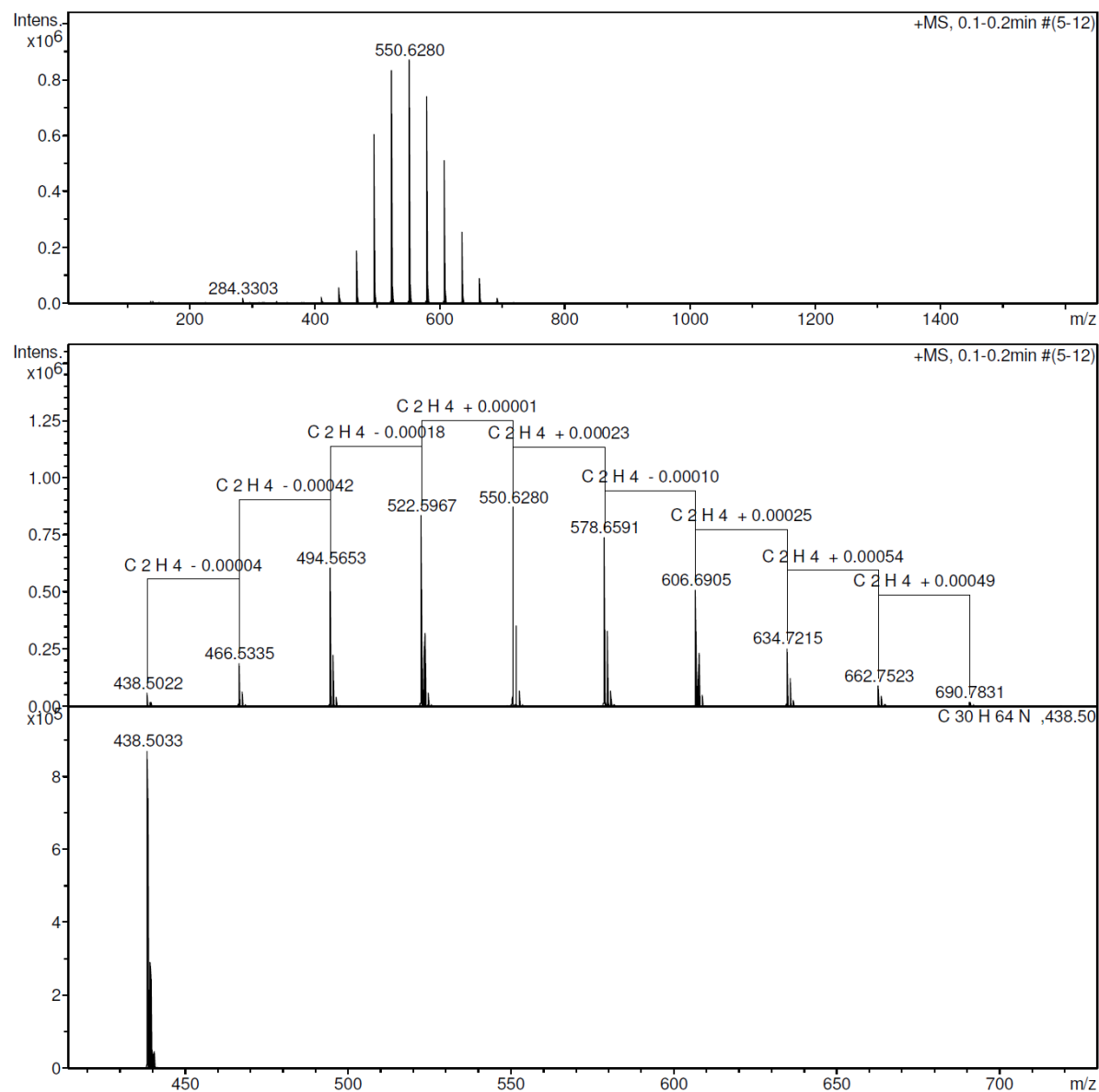


Figure S13 ESI MS -spectrum of **3**

Literature

1. M.E. Minyaev, A.A. Vinogradov, D.M. Roitershtein, R.S. Borisov, I.V. Ananyev, A.V. Churakov, I.E. Nifant'ev *J.Organomet.Chem.*, 2016, **818**, 28.
2. V.G. Zaikin, R.S. Borisov, N.Y. Polovkov, D.I. Zhilyaev, A.A. Vinogradov, A.V. Ivanyuk, *Eur. J. Mass Spectrom.* 2013, **19**, 163.