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Significant impact of lanthanide contraction on the structure of the phenanthroline complexes

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1. Experimental part

1.1 Materials

Ar-saturated solvents, purified and dried using standard techniques were used [S1]. Lanthanides nitrates $La(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}6H_2O$ and $Lu(NO_3)_3{\cdot}xH_2O$ were purchased from Sigma and used without further purification. Water content x in lutetium nitrate was determined as x = 3. Deuterated solvents for NMR spectra were purchased from commercial sources and used without further purification.

1.2 Methods

NMR spectra were recorded using standard 5 mm sample tubes on Agilent 400-MR spectrometer with operating frequencies of 400.1 MHz (^{1}H) and 100.6 MHz (^{13}C).

IR spectra were recorded on FTIR spectrometer Nicolet iS5 (Thermo Scientific) using an internal reflectance attachment with diamond optical element – attenuated total reflection (ATR) with 45° angle of incidence. Resolution 4 cm^{-1}, the number of scans is 32.

HRMS ESI - mass spectra were recorded on the MicroTof Bruker Daltonics and Orbitrap Elite instruments.

Single crystals of complexes **1-4** were obtained upon slow isothermal (25ºC) recrystallization of corresponding substances from CD_3CN.

X-ray diffraction data for complexes **1** and **4** were collected at 120 K with a Bruker APEXII DUO CCD diffractometer; those for **2** and **3** at 100 K with a Bruker D8 QUEST PHOTON-III CCD diffractometer, both using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Using Olex2 [S2], the structures were solved with the ShelXT [S3] structure solution program using Intrinsic Phasing and refined with the XL [S4] refinement package using Least-Squares minimization against F^2 in anisotropic approximation for non-hydrogen atoms. Positions of hydrogen atoms were calculated, and they were refined in isotropic approximation within the riding model. Crystal data and structure refinement parameters for **1-4** are given in Table S1. CCDC 2072995 (for **1**), 2073000

(for **2**), 2073001 (for **3**) and 2072996 (for **4**) contain the supplementary crystallographic data for this paper.

1.3 Synthesis and analytical data

***N,N,N',N'*-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L)** was synthesized as described [S5]. Yield 81% (1.99 g), white powder, m.p. 91-93°C, R_f 0.36 (acetone:hexane 1:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 8.2 Hz, 2H), 7.81 (s, 2H), 3.75 – 3.44 (m, 8H), 1.86 – 1.59 (m, 8H), 1.53 – 1.33 (m, 4H), 1.10 – 0.92 (m, 10H), 0.64 (t, J = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 154.7, 144.4, 136.9, 128.9, 127.2, 123.3, 49.2, 46.6, 31.4, 29.9, 20.5, 20.0, 14.1, 13.7; IR (cm^{-1}) 3054, 2959, 2929, 2897, 2871, 2856 (C-H stretching vibrations), 1634, 1621 (C=O), 1583, 1546, 1504, 1470, 1455 (C=C, C=N); HRMS (ESI-TOF) (*m*/*z*) $[M+H]^+$ calculated for $C_{30}H_{43}N_4O_2$ 491.3381, found 491.3377.

*General method for synthesis of complexes **1-4***

A solution of lanthanide nitrate (0.1 mmol) in dry acetonitrile (1 ml) was added dropwise to a solution of **L** (0.1 mmol) in $CHCl_3$ (1 ml). The mixture was then concentrated *in vacuo* (~20 Torr) to 1/5 of the initial volume and treated with diethyl ether (2 ml). The resulting precipitate of the complex was filtered, washed with a fresh portion of ether, dried in air, then at 80°C at ~2 Torr.

***N,N,N',N'*-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide lanthanum trinitrate 1.** Yield 46.4 mg (75%). Light yellow powder, T_{decomp}. 233-234 °C. IR (cm^{-1}) 1599(CO), 1480, 1293 (ONO_2). Anal. Calc. for $C_{30}H_{42}LaN_7O_{11}$: C, 44.18; H, 5.19; N, 12.02. Found: C, 45.35; H, 5.38; N, 11.95%.

***N,N,N',N'*-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide neodymium trinitrate 2.** Yield 45.1 mg (72%). Light pink powder, T_{decomp}. 254-255 °C. IR (cm^{-1}) 1604 (CO), 1486, 1287 (ONO_2). Anal. Calc. for $C_{30}H_{42}NdN_7O_{11}$: C, 43.89; H, 5.16; N, 11.94. Found: C, 44.06; H, 5.30; N, 11.95%.

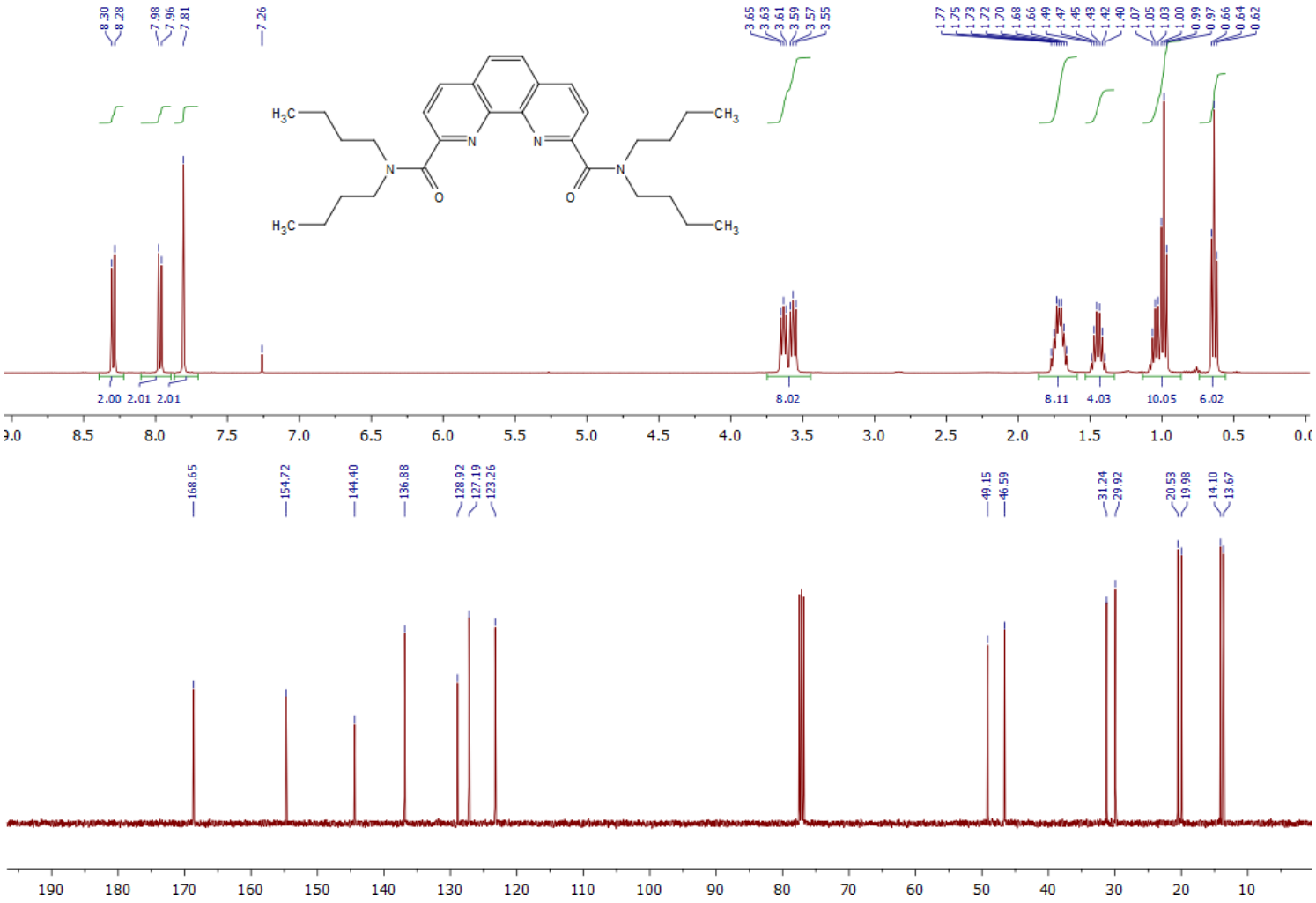
***N,N,N',N'*-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide europium trinitrate 3**. Yield 86 mg (91%). Light yellow powder. T_{decomp}. 232-233 °C. IR (cm^{-1}) 1601 (CO), 1479, 1300 (ONO_2). Anal. Calc. for $C_{30}H_{42}EuN_7O_{11}$: C, 43.48; H, 5.11; N, 11.83. Found: C, 43.52; H, 5.19; N, 11.98%.

***N,N,N',N'*-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide lutetium trinitrate 4**. Yield 44.8 mg (47%). Light yellow powder, T_{decomp}. 249-250 °C. IR (cm^{-1}) 1609 (CO), 1470, 1294 (ONO_2). Anal. Calc. for $C_{30}H_{42}LuN_7O_{11}$: C, 42.31; H, 4.97; N, 11.51. Found: C, 42.51; H, 5.08; N, 11.46%.

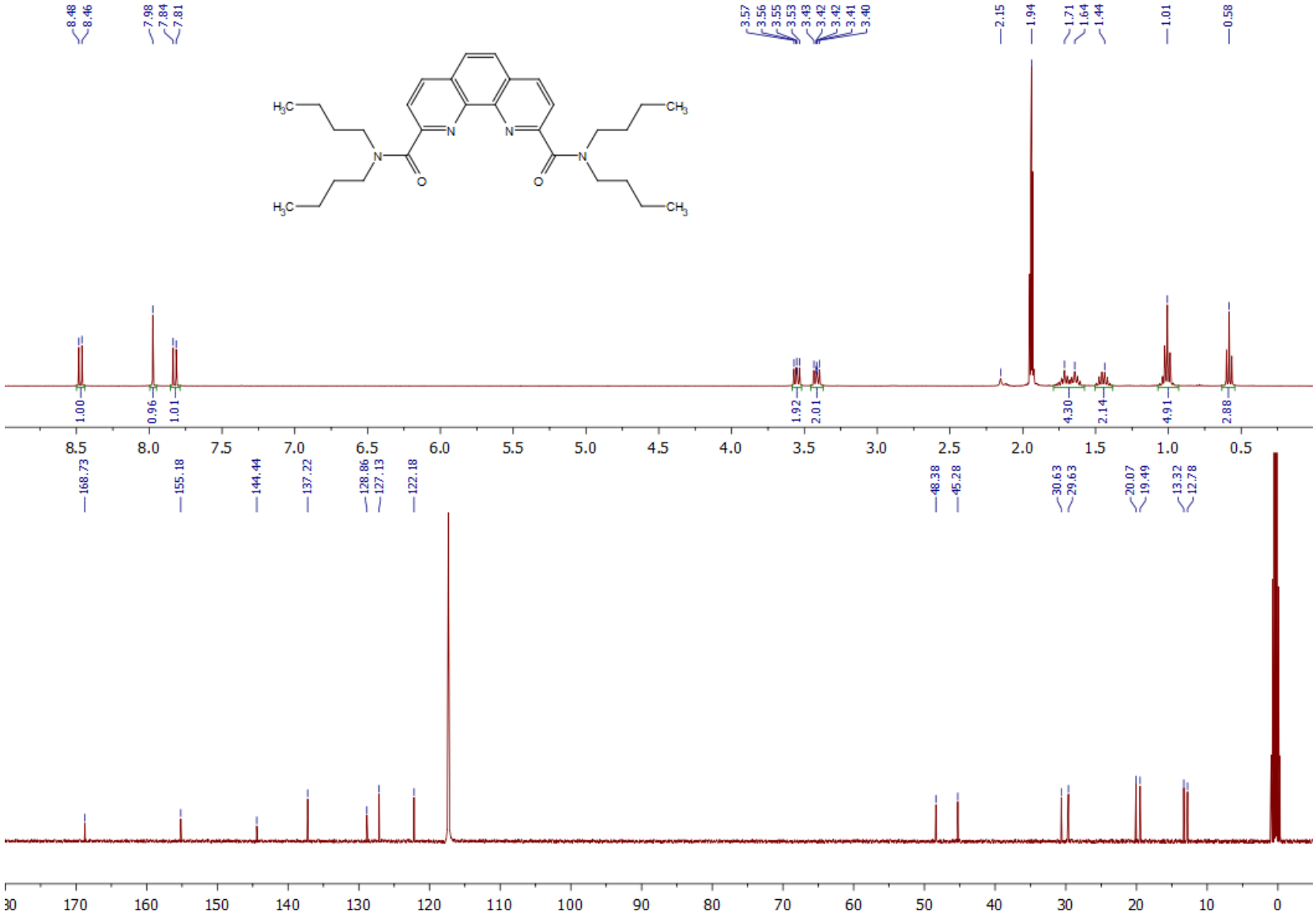
2. NMR, IR and HRMS spectra of synthesized compounds

N,*N*,*N*',*N*'-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (L)

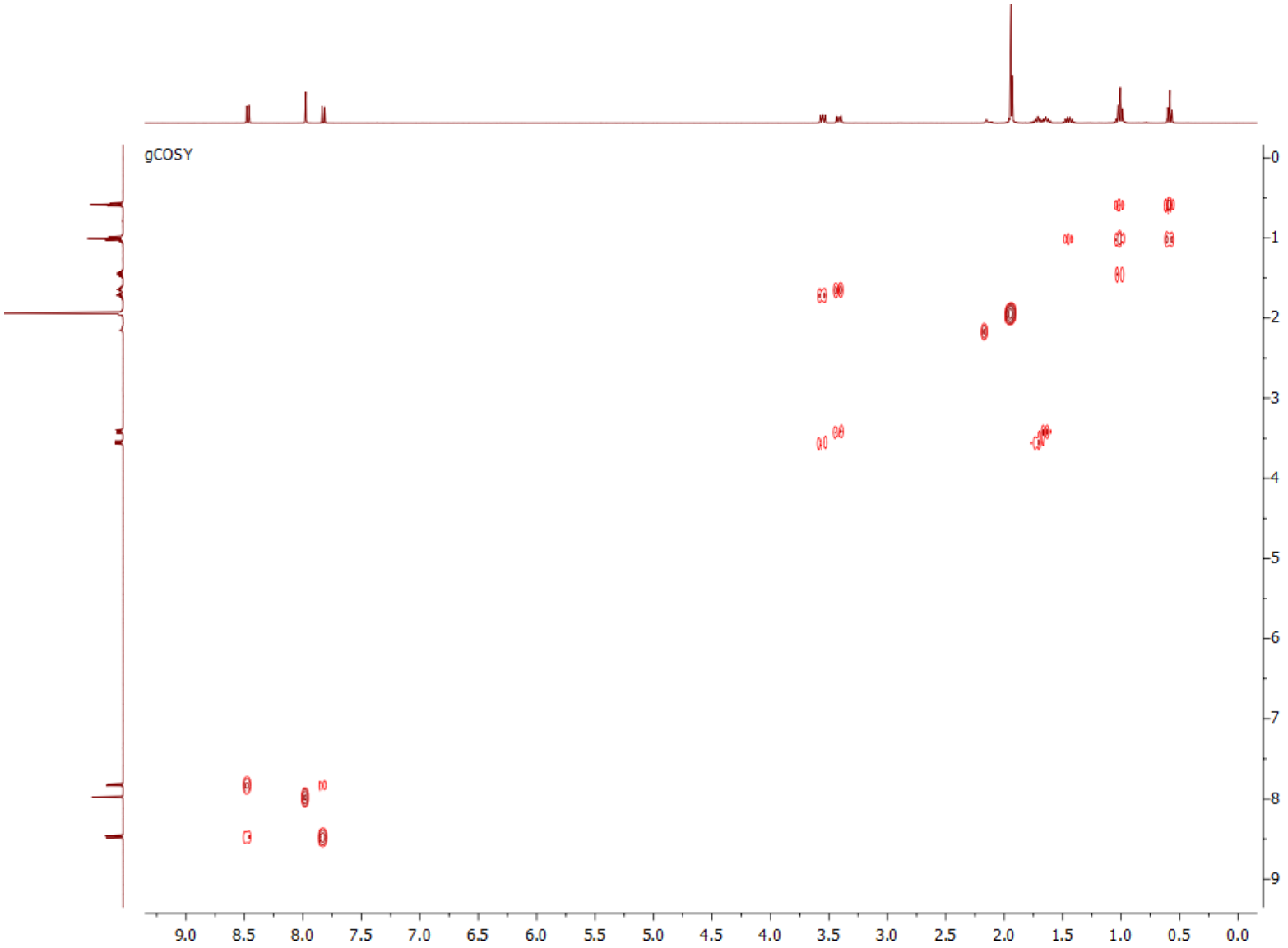
^{1}H NMR (above) and ^{13}C NMR (below) spectra in $CDCl_3$ at 25ºC



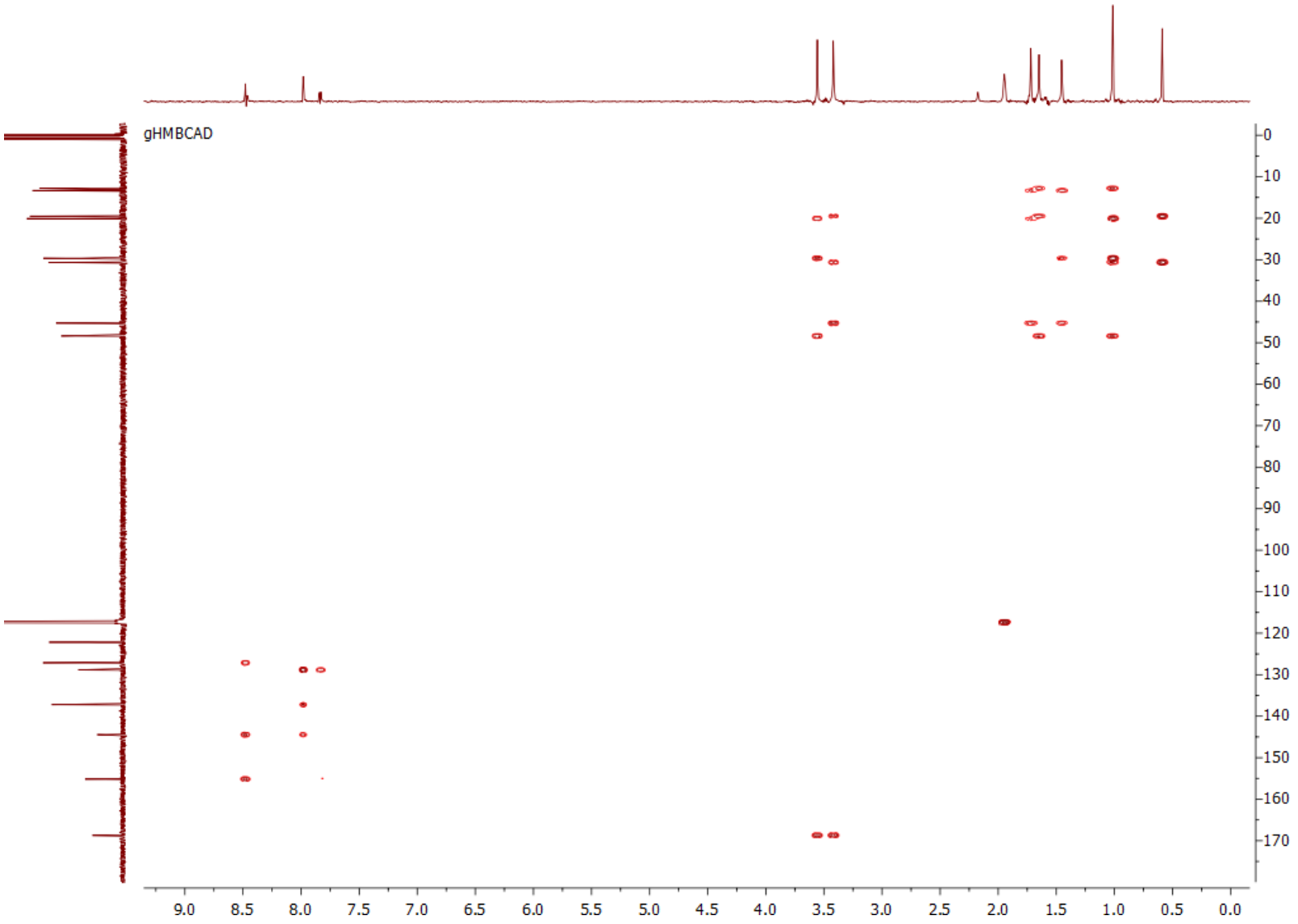
^{1}H NMR (above) and ^{13}C NMR (below) spectra in CD_3CN at 25ºC



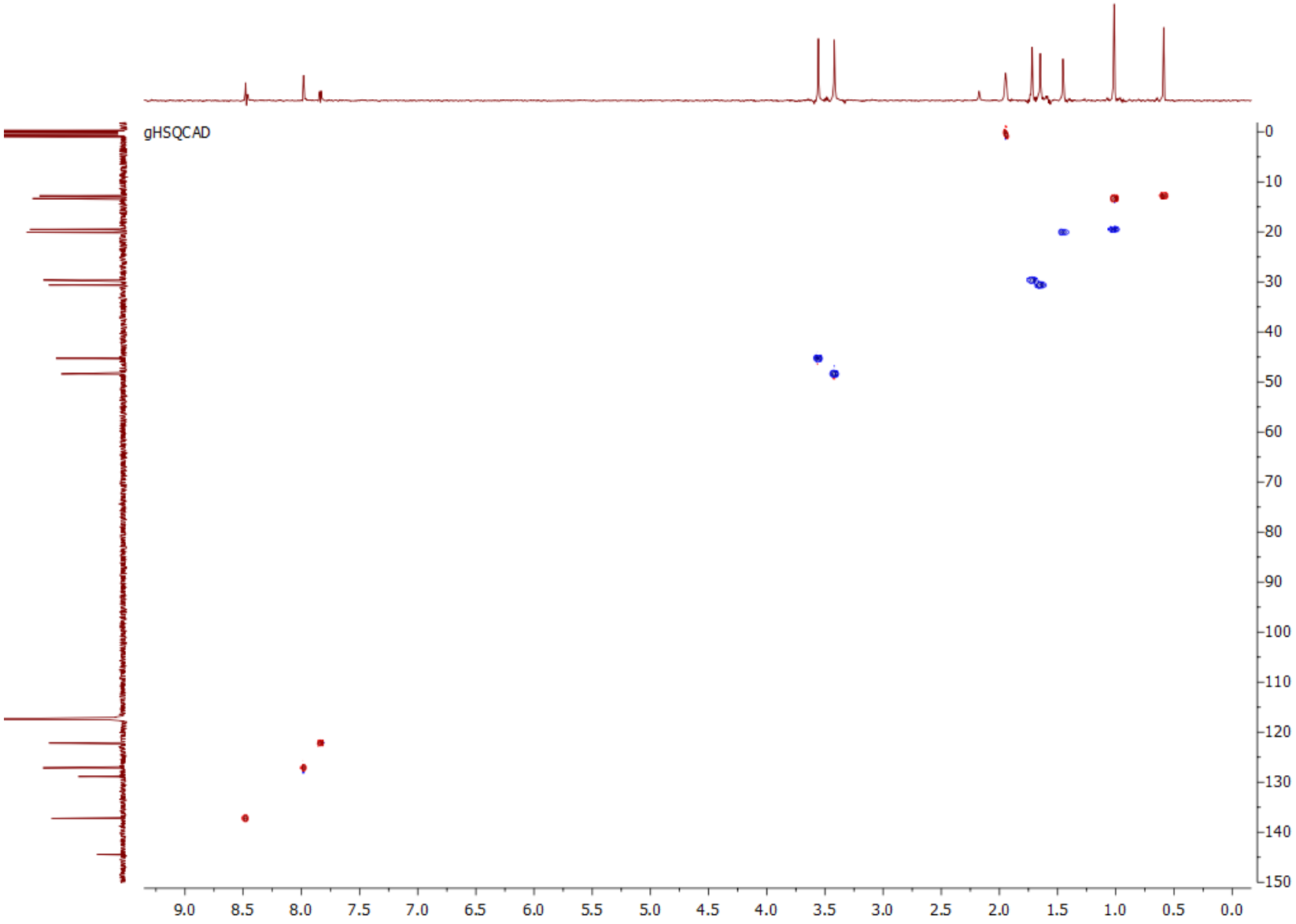
gCOSY spectra



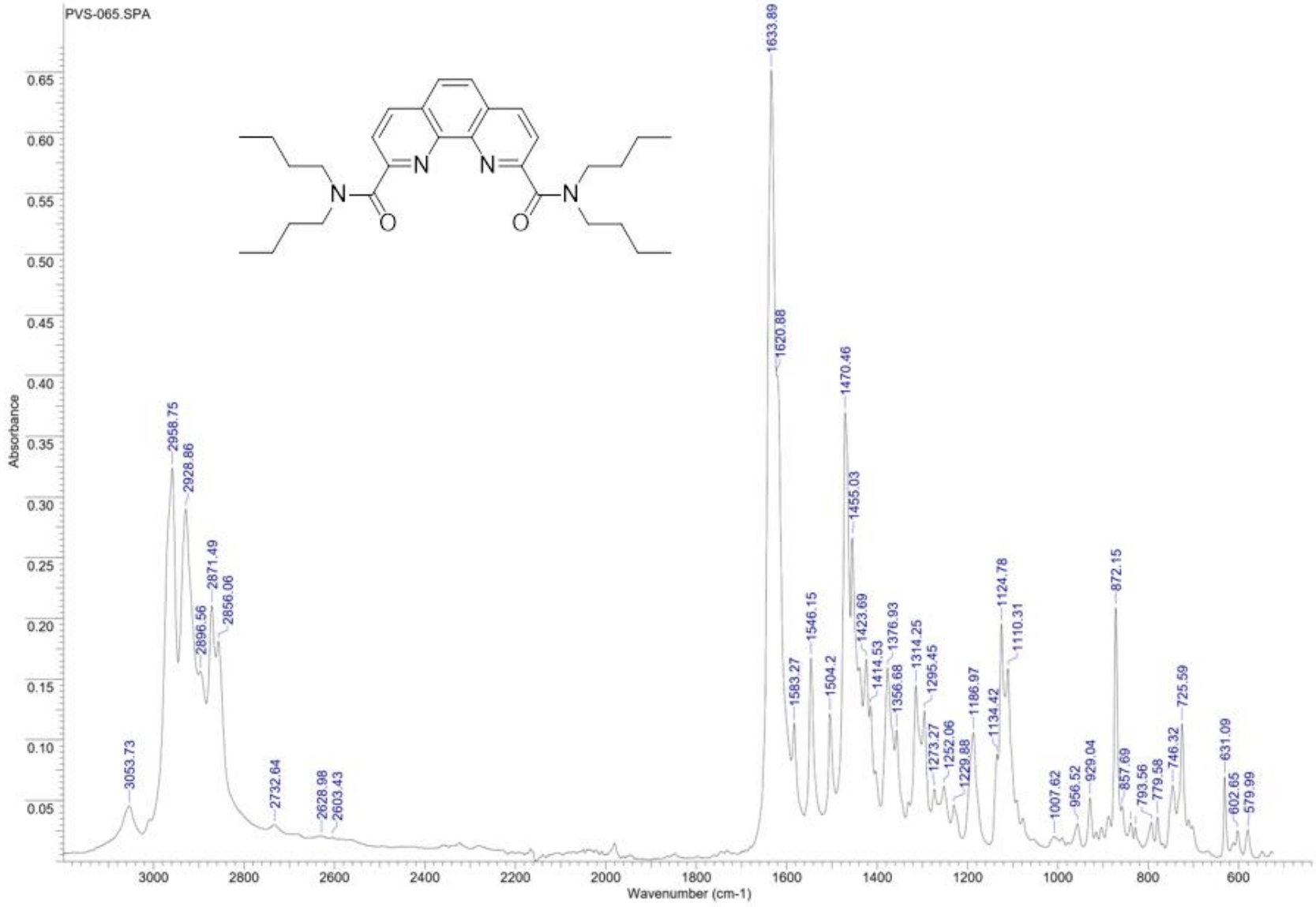
gHMBCAD spectra



gHSQCAD spectra



IR spectra at 25ºC



HRMS spectra

Display Report

Analysis Info

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Comment	C30H42N4O2 mH 491.3380 calibrant added CH3CN		

Acquisition Parameter

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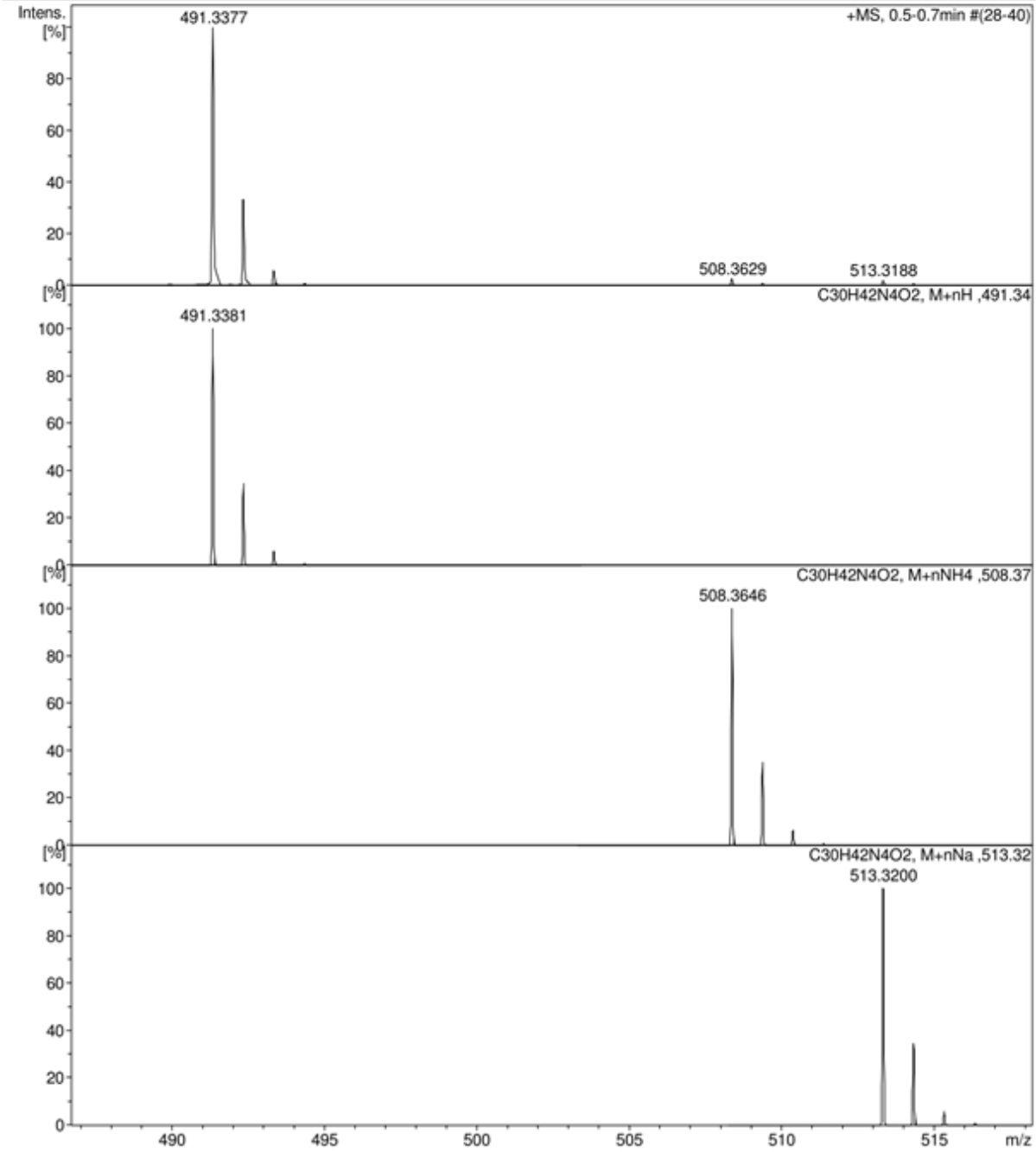
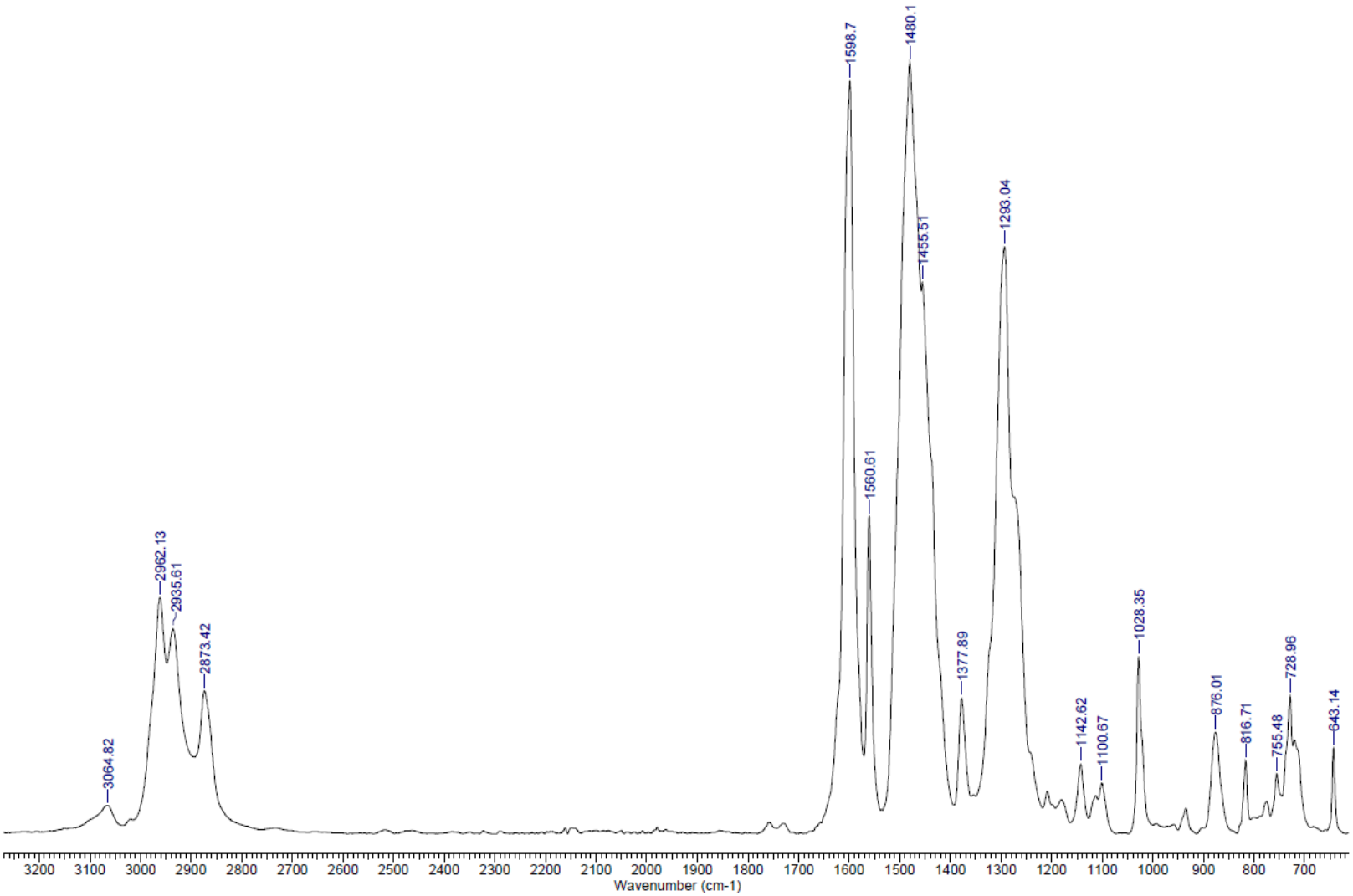
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Bruker Compass DataAnalysis 4.0 printed: 16.09.2020 18:56:41 Page 1 of 1

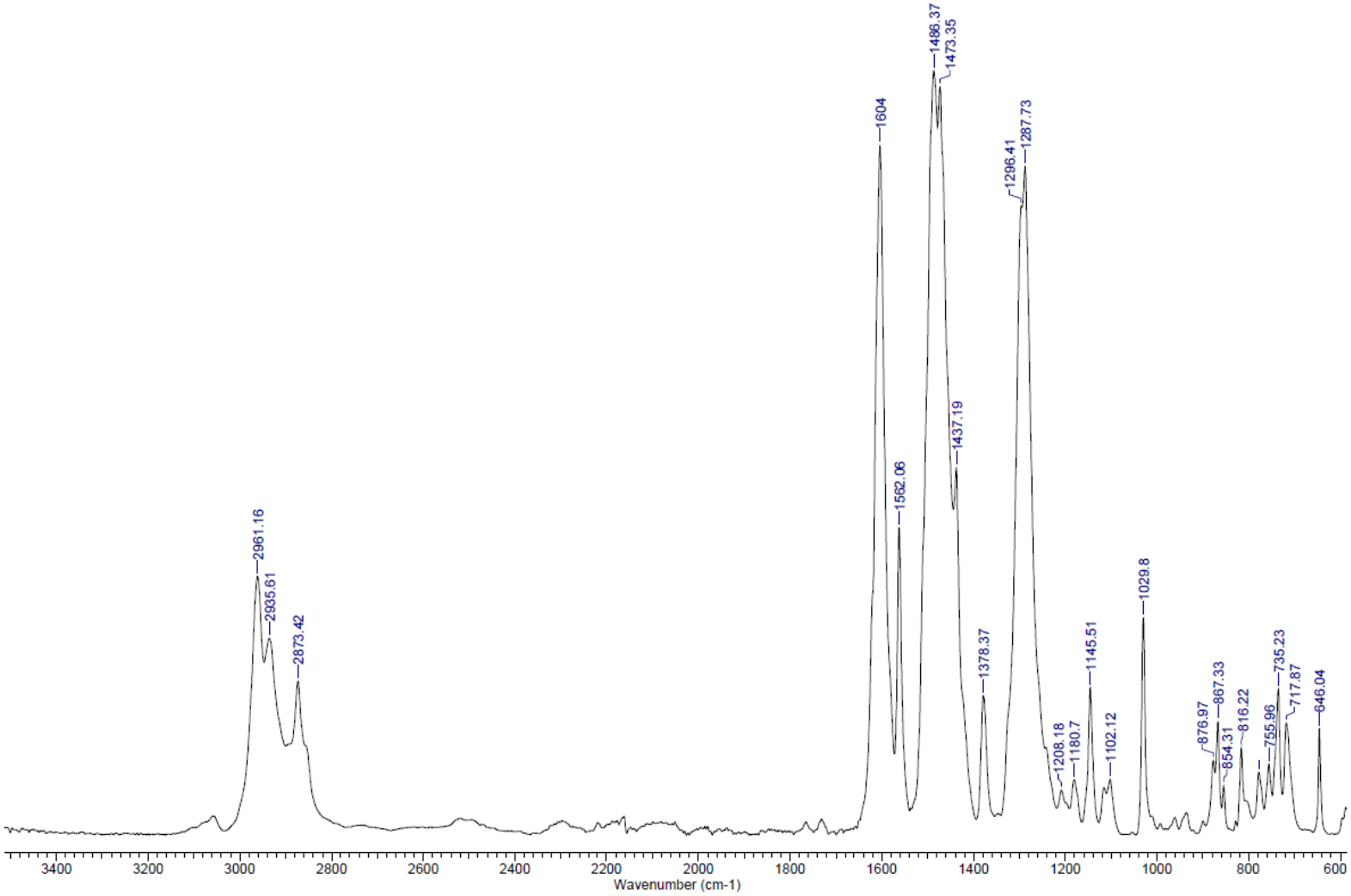
***N*,*N*,*N*',*N*'-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide lanthanum trinitrate (1)**

IR



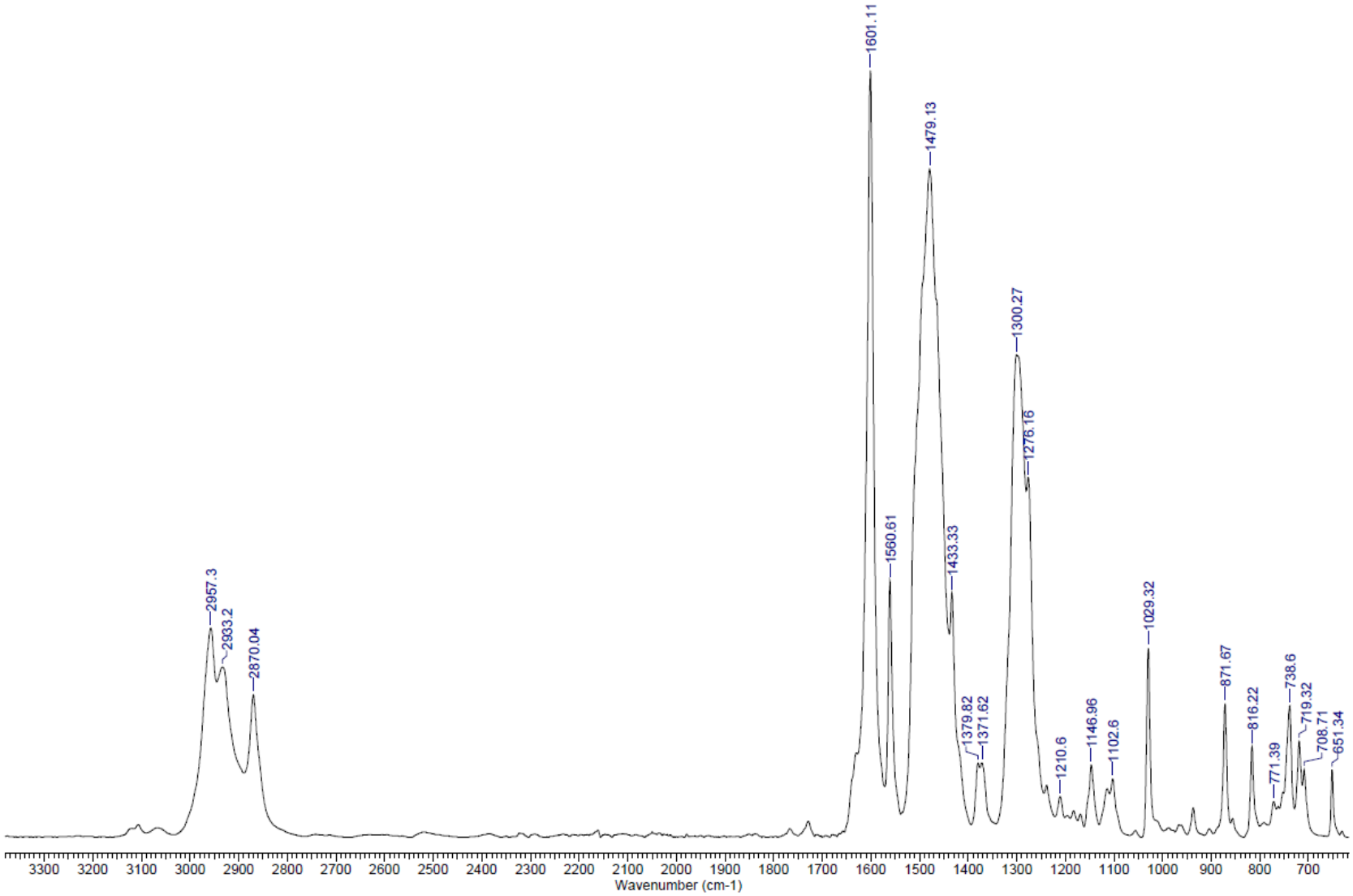
***N*,*N*,*N*',*N*'-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide neodymium trinitrate (2)**

IR



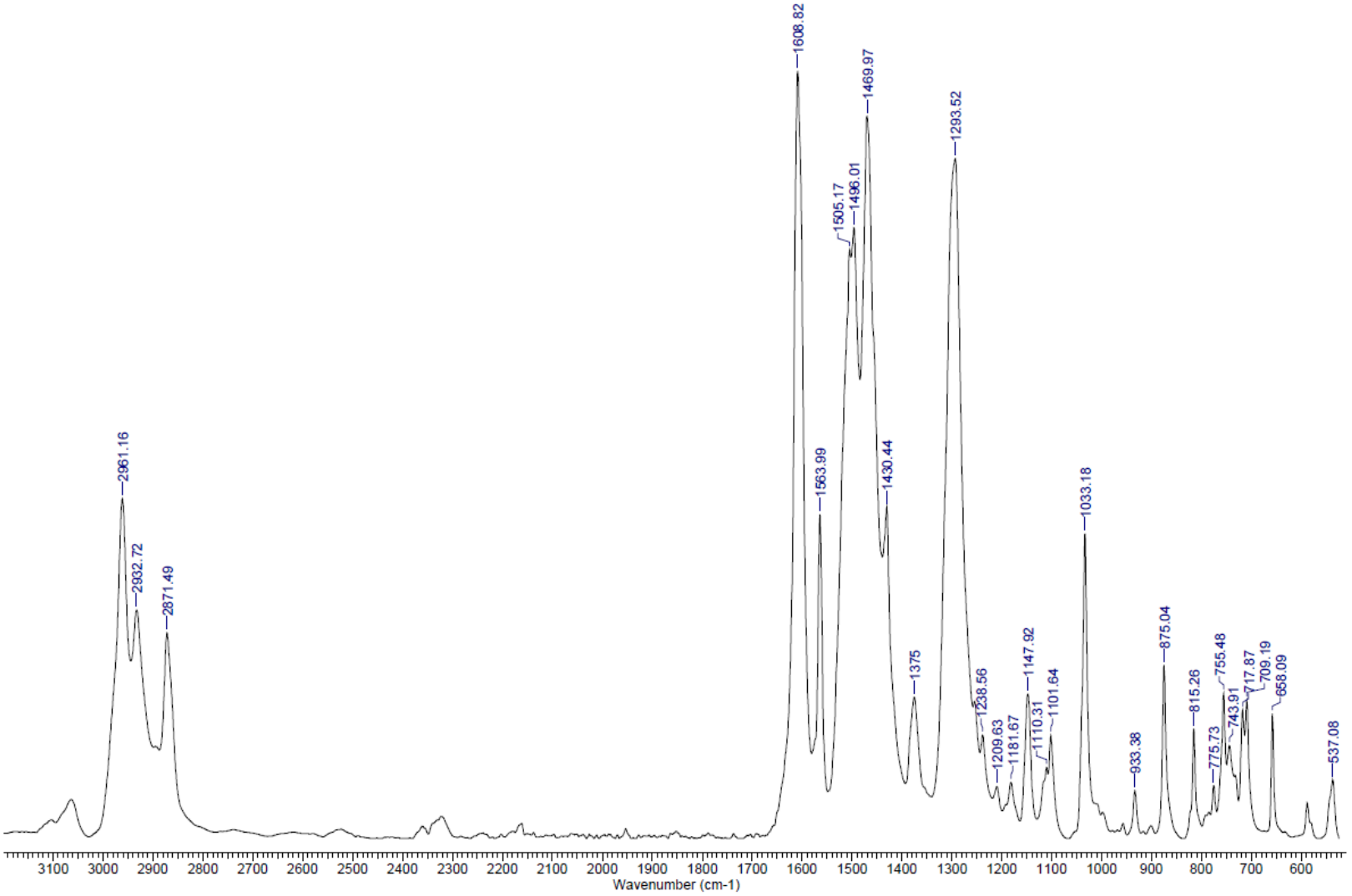
***N*,*N*,*N'*,*N'*-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide europium trinitrate (3)**

IR



***N*,*N*,*N*',*N*'-Tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide lutetium trinitrate (4)**

IR



3. X-ray diffraction data

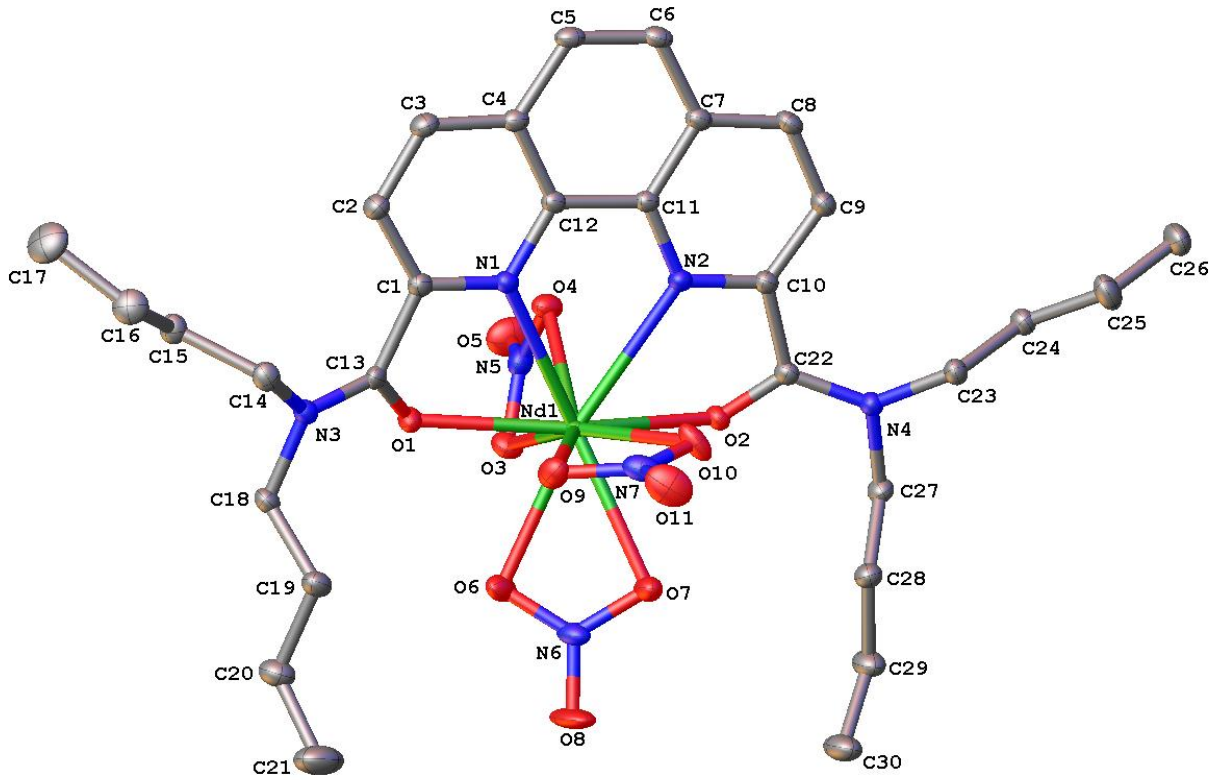


Figure S1 General view of **2**; solvent acetonitrile molecules and the minor component of the disordered nitrate anions are not shown.

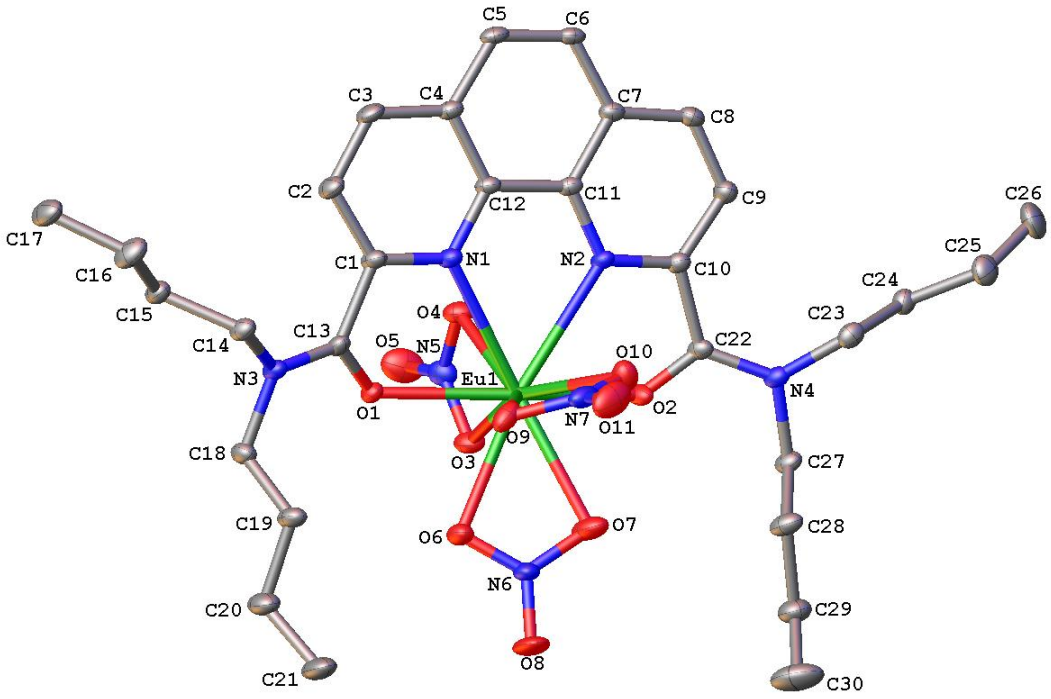


Figure S2 General view of the **3**; solvent acetonitrile molecules and the minor component of the disordered nitrate anions are not shown.

Table S1 Crystal data and structure refinement parameters for complexes **1-4**.

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{34}H_{48}LaN_9O_{11}$	$C_{34}H_{48}N_9NdO_{11}$	$C_{34}H_{48}N_9O_{11}Eu$	$C_{30}H_{42}LuN_7O_{11}$
Formula weight	897.72	903.05	910.77	851.67
T, K	120	100	100	120
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	$P2_1/n$
Z	2	2	2	4
a, Å	12.8066(15)	12.7265(2)	12.7052(2)	12.5387(9)
b, Å	13.1723(15)	13.0852(3)	13.0357(2)	13.2104(9)
c, Å	14.0055(16)	13.9425(3)	13.9381(2)	20.5389(14)
α/°	74.188(2)	74.1023(7)	74.0920(10)	90
β/°	67.870(3)	68.3360(6)	68.5940(10)	94.300(2)
γ/°	66.735(2)	66.7703(6)	66.6940(10)	90
V, Å^3	1989.3(4)	1960.38(7)	1951.00(6)	3392.5(4)
D_{calc} (g cm^{-1})	1.499	1.530	1.550	1.667
Linear absorption, μ (cm^{-1})	11.42	13.93	16.77	29.79
F(000)	920	926	932	1720
$2\theta_{max}$, °	62	56	56	56
Reflections measured	67046	47825	41028	38724
Independent reflections	12112	9429	9406	8199
Observed reflections [$I > 2\sigma(I)$]	9758	9010	8852	5767
Parameters	502	516	516	446
R1	0.0498	0.0178	0.0206	0.0377
wR2	0.0940	0.0444	0.0474	0.0742
GOF	1.065	1.038	1.037	1.002
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	0.925/-1.393	0.700/-0.493	0.769/-0.752	0.984/-1.237

References

[S1] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weincheim, 1988.

[S2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

[S3] G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3.

[S4] G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

[S5] M. Alyapyshev, J. Ashina, D. Dar'in, E. Kenf, D. Kirsanov, L. Tkachenko, A. Legin, G. Starova and V. Babain, *RSC Adv.*, 2016, **6**, 68642.