Electronic Supplementary Information

Peculiarities of crystal structures and photophysical properties of Ga^{III}/Ln^{III} metallacrowns with a non-planar [12-MC-4] Core

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Table S1. Crystallographic details for **Tb-1** and **Yb-1**.

	Tb-1	**Yb-1**
mol formula	$C_{72}H_{58}N_{13}O_{21}Ga_4Tb$	$C_{73}H_{65.25}N_{13}O_{25.12}Ga_4Yb$
fw (g/mol)	1879.11	1978.55
cryst syst/ space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
T (K)	85(2)	85(2)
wavelength (Å)	1.54184	1.54184
a (Å)	16.19696(19)	14.3025(7)
b (Å)	16.7609(2)	16.1811(6)
c (Å)	17.6368(2)	19.1090(8)
α (deg)	95. 7057(11)	66.971(4)
β (deg)	105.3324(11)	81.148(4)
γ (deg)	110.4118(12)	78.481(4)
V (Å^3)	4229.24(10)	3973.9(3)
Z	2	2
density, ρ (g/cm^3)	1.476	1.654
abs coeff, μ (mm^{-1})	6.082	4.341
F(000)	1876	1978
θ range for data collection (deg)	2.658 to 73.989	3.003 to 69.921
limiting indices	$-19 \le h \le 20$ $-20 \le k \le 20$ $-21 \le l \le 21$	-17<=h<=17 -19<=k<=19 -22<=l<=23
reflns collected/ unique	133406 / 16660	59569 / 14459
completeness to θ (%)	98.7	98.0
no. of data/ restraints/ params	16660 / 337 / 1057	14459 / 328 / 1228
goodness of fit on F^2	1.044	1.110
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0456 wR_2 = 0.1332	R_1 = 0.0745 wR_2 = 0.2145
R indices (all data)	R_1 = 0.0462 wR_2 = 0.1341	R_1 = 0.0816 wR_2 = 0.2347
largest diff peak and hole (e$^-$ Å^{-3})	0.784 and -1.666	1.271 and -2.711

Table S2. Unit cell parameters of single crystals of **Ln-1** compounds.

Tb-1 a = 16.19696(19), b = 16.7609(2), c = 17.6368(2) α = 95.7057(11), β = 105.3324(11), γ = 110.4118(12) V = 4229.24(10)	**Yb-1** a = 14.3025(3), b = 16.1811(6), c = 19.1090(8) α = 66.971(4), β = 81.148(4), γ = 78.481(4) V = 3973.9(3)
Ho-1 a = 16.062, b = 16.745, c = 17.782 α = 95.78, β = 105.91, γ = 110.18 V = 4279.33	**Er-1** a = 14.347, b = 16.251, c = 19.185 α = 66.67, β = 81.29 , γ = 78.47 V = 4011.60
Gd-1 a = 16.060, b = 16.713, c = 17.813 α = 95.92, β = 106.05, γ = 110.01, V = 4275.73	**Tm-1** a = 14.360, b = 16.251, c = 19.180 α = 66.74, β = 81.25, γ = 78.45 V = 4015.66
Dy-1 a = 16.098, b = 16.780, c = 17.825 α = 95.82, β = 106.08, γ = 110.46 V = 4300.98	

Table S3. SHAPE analysis of nine-coordinate geometry in compound **Tb-1**.

EP (D_{9h})	OPY (C_{8v})	HBPY (D_{7h})	JTC (C_{3v})	JCCU (C_{4v})	CCU (C_{4v})	JCSAPR (C_{4v})	CSAPR (C_{4v})	JTCTPR (D_{3h})	**TCTPR (D_{3h})**	JTDIC (C_{3v})	HH (C_{2v})	MFF (C_s)
34.68	22.406	14.759	13.176	8.255	6.632	3.421	2.473	3.585	**2.115**	9.731	9.722	2.724

Abbreviations: EP – Enneagon, OPY – Octagonal pyramid, HBPY – Heptagonal bipyramid, JTC – Triangular cupola, JCCU – Capped cube (elongated square pyramid J8), CCU – Capped Cube, JCSAPR Capped square antiprism (Gyroelongated square pyramid J10), CSAPR – Capped square antiprism, JTCTPR – Tricapped trigonal prism (J51), TCTPR – Tricapped trigonal prism, JTDIC – Tridiminished icosahedron (J63), HH – Hula-hoop, MFF – Muffin

Table S4. SHAPE analysis of eight-coordinate geometry in compound **Yb-1**.

OP (D_{8h})	HPY (C_{7v})	HBPY (D_{6h})	CU (O_h)	SAPR (D_{4d})	**TDD (D_{2d})**	JGBF (D_{2d})	JETBPY (D_{3h})	JBTP (C_{2v})	BTPR (C_{2v})	JSD (D_{2d})	TT (T_d)	ETBPY (D_{3h})
24.016	19.543	13.913	12.322	6.328	**4.698**	13.750	24.693	5.557	5.425	6.705	12.409	21.022

Abbreviations: OP – Octagon, HPY – Heptagonal pyramid, HBPY – Hexagonal bipyramid, CU – cube, SAPR – Square antiprism, TDD – Triangular dodecahedron, JGBF – Johnson - Gyrobifastigium (J26), JETBPY – Johnson elongated triangular bipyramid (J14), JBTP – Biaugmented trigonal prism (J50), BTPR – Biaugmented trigonal prism, JSD – Snub diphenoid (J84), TT – Triakis tetrahedron, ETBPY – Elongated trigonal bipyramid

Table S5. Relative integral intensities of $^5D_4 \rightarrow {}^7F_J$ (J = 6–0) transitions in the emission spectra of **Tb-1** MC in the solid state.

State/Solvent	$\int_{4-6}$	$\int_{4-5}$	$\int_{4-4}$	$\int_{4-3}$	$\int_{4-2,1,0}$
Solid	0.34	1.00	0.23	0.14	0.05

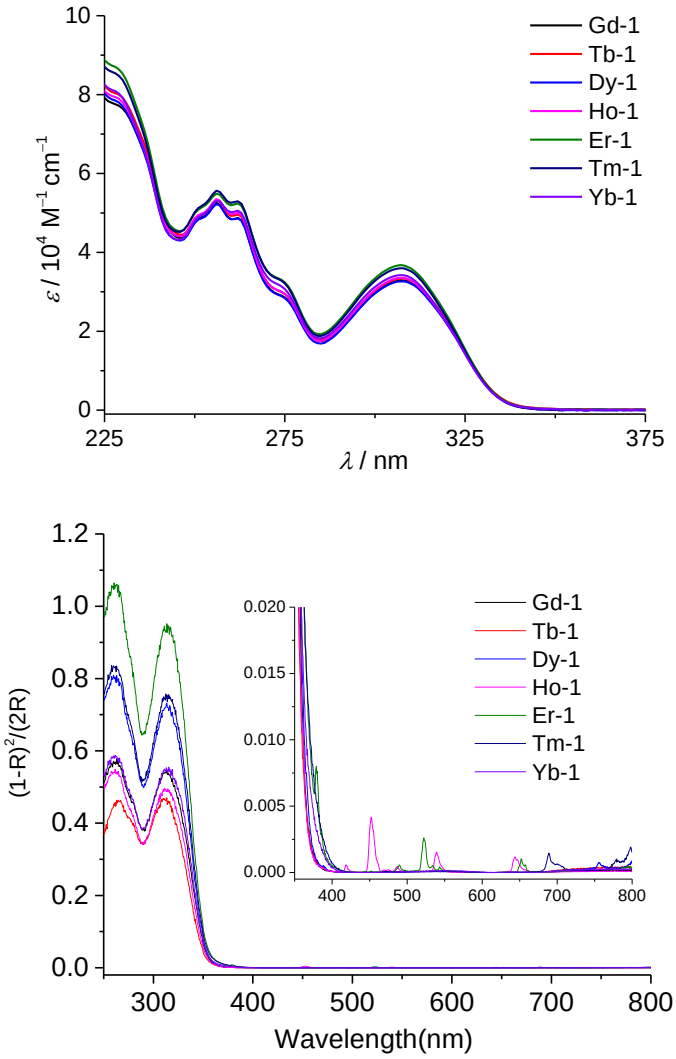


Figure S1. (Top) UV-Vis absorption spectra in methanol (0.5 mM), and (bottom) diffuse reflectance spectra presented as Kubelka-Munk function *vs*. wavelength of the **Ln-1** MCs at room temperature.

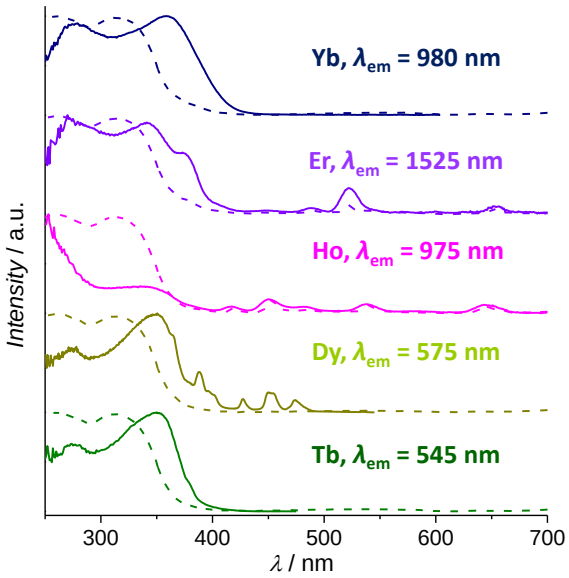


Figure S2. Corrected and normalized excitation (solid lines) under monitoring of the main transitions of the corresponding Ln^{3+} ions and superimposed reflectance (dashed) spectra of the **Ln-1** (Ln^{III} = Tb, Dy, Ho, Er, Yb) MCs in the solid state at room temperature.

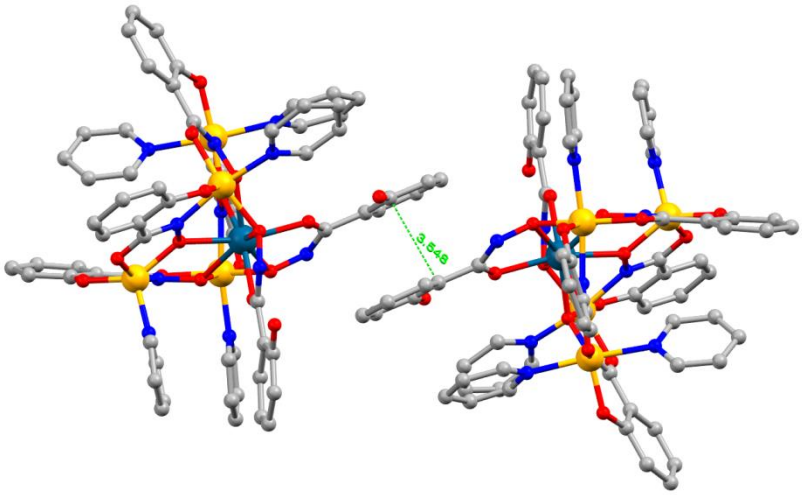
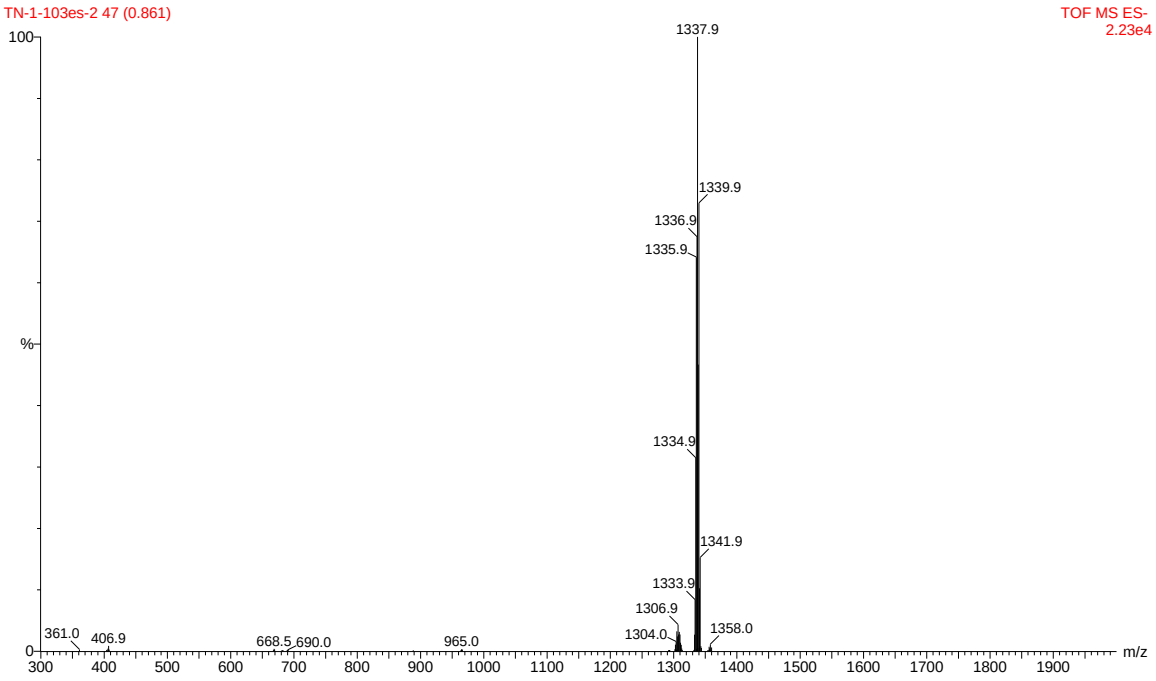


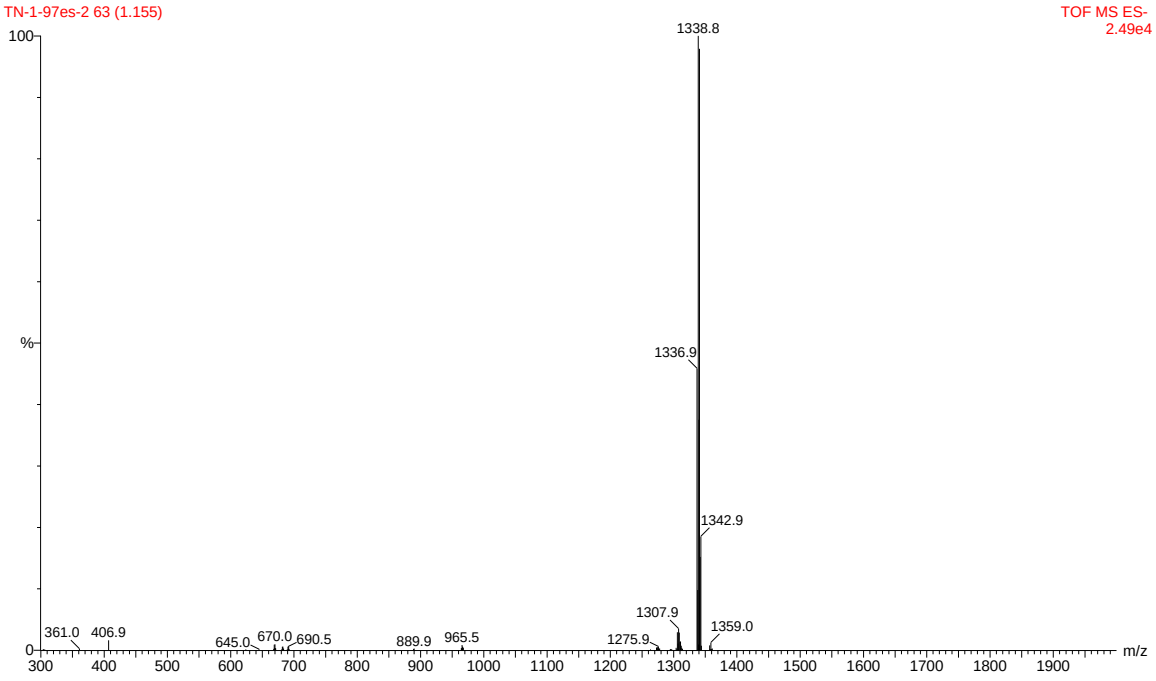
Figure S3. π-π stacking between Ga_4Yb molecules.

Mass-spectra of **Ln-1** complexes.

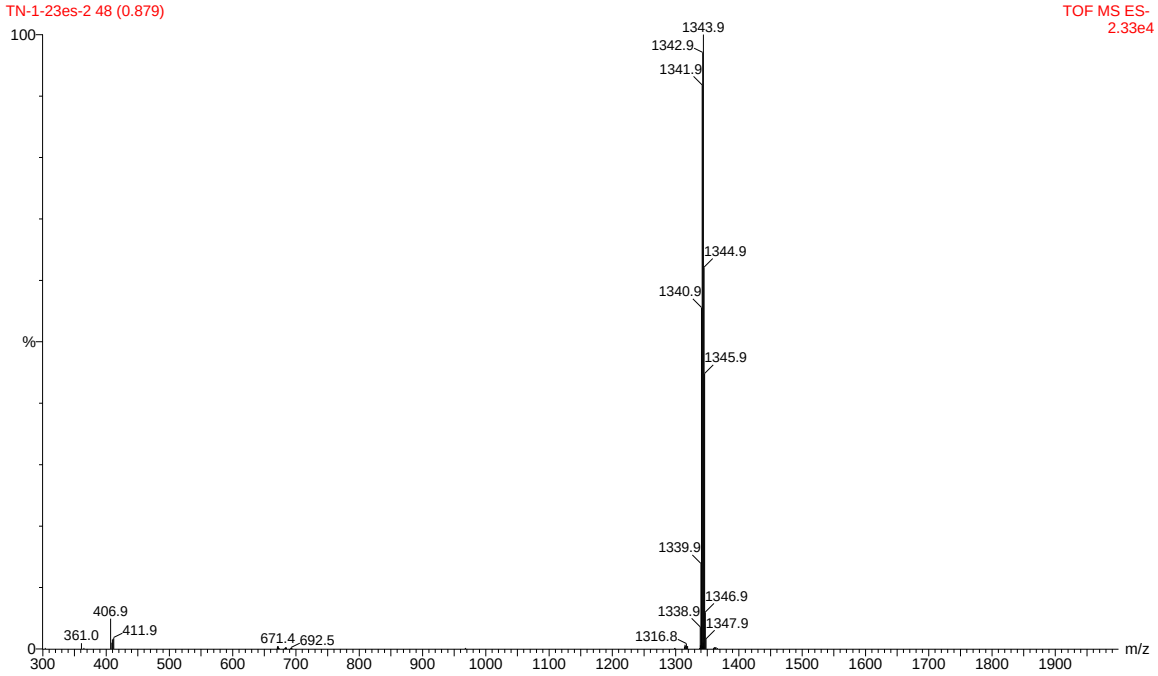
Gd-1



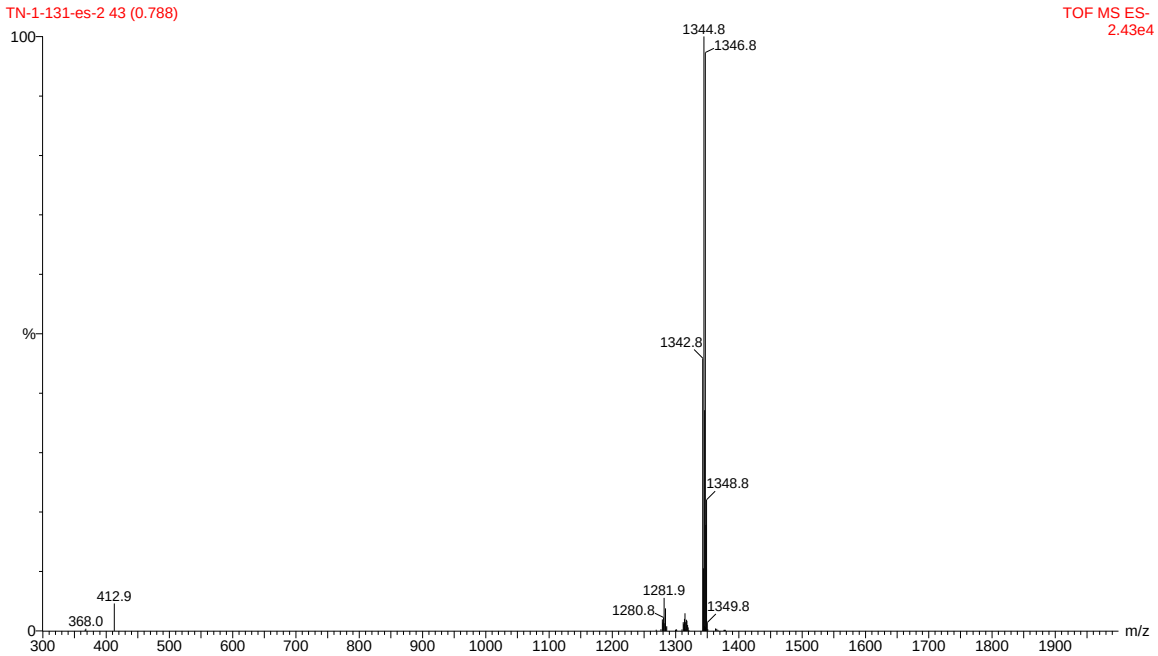
Tb-1



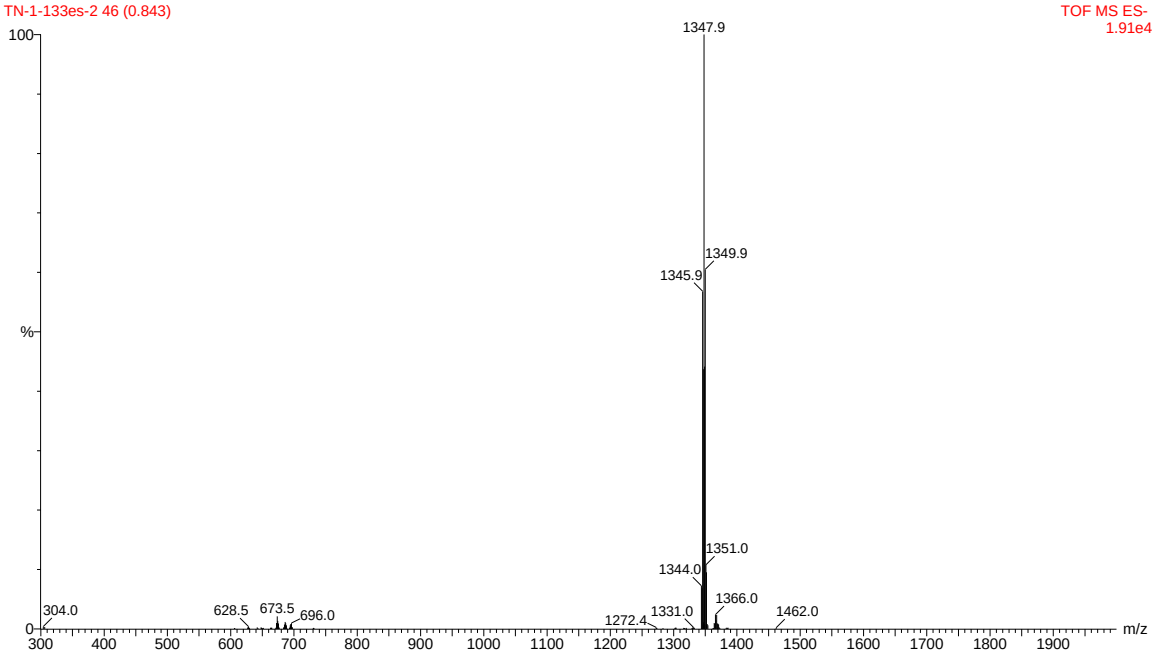
Dy-1


TN-1-23es-2 48 (0.879)
TOF MS ES-
2.33e4
100
%
0
1343.9
1342.9
1341.9
1344.9
1340.9
1345.9
1339.9
1346.9
1338.9
1347.9
406.9
361.0
411.9
671.4
692.5
1316.8
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
m/z

Ho-1


TN-1-131-es-2 43 (0.788)
TOF MS ES-
2.43e4
100
%
0
1344.8
1346.8
1342.8
1348.8
1281.9
1280.8
1349.8
412.9
368.0
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
m/z

Er-1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TOF MS ES-
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100
%
0
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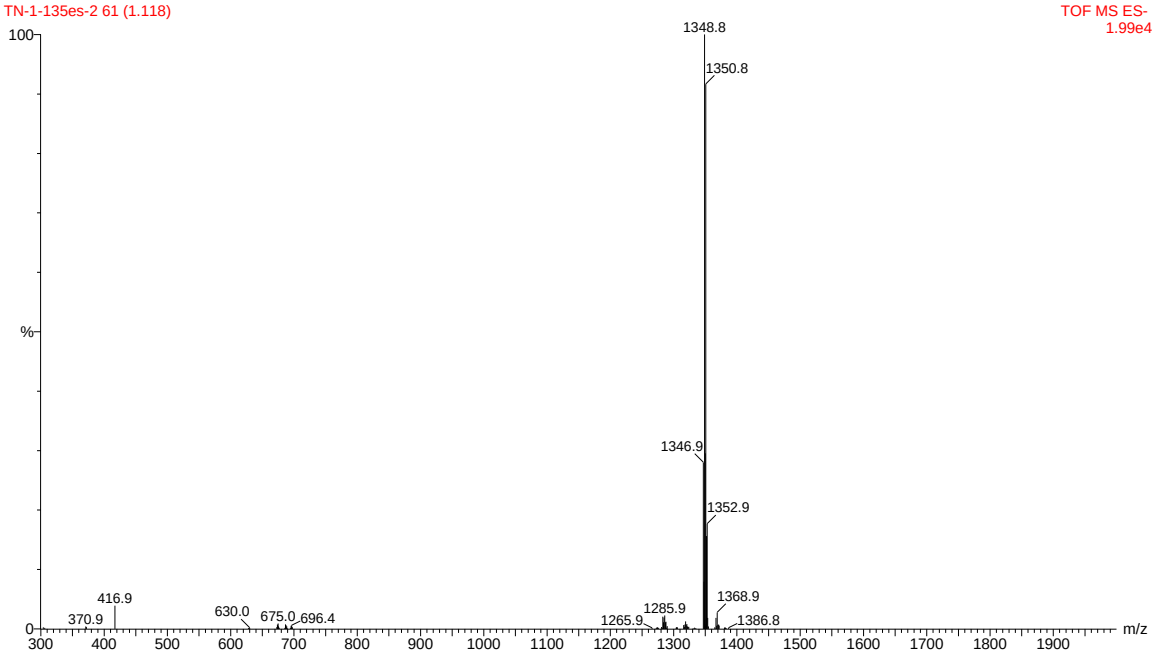
1349.9
1345.9
1351.0
1344.0
1366.0
304.0
628.5
673.5
696.0
1272.4
1331.0
1462.0
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
m/z

Tm-1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TOF MS ES-
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100
%
0
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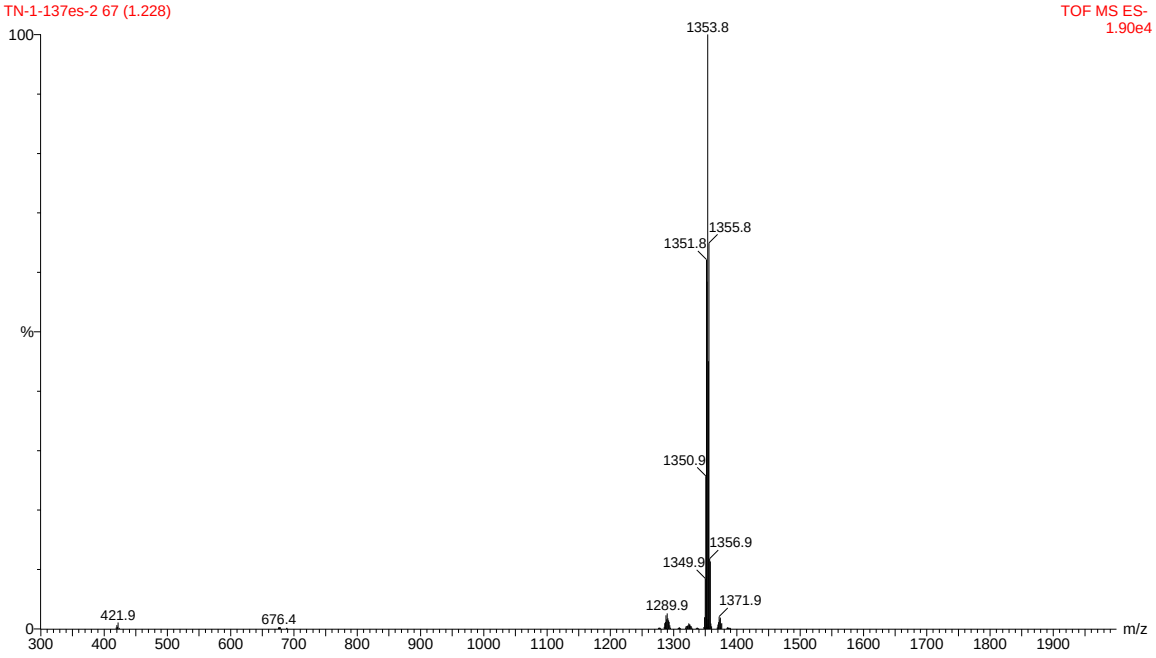
1350.8
1346.9
1352.9
416.9
370.9
630.0
675.0
696.4
1265.9
1285.9
1368.9
1386.8
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
m/z

Yb-1


TN-1-137es-2 67 (1.228)
TOF MS ES-
1.90e4
100
%
0
1353.8
1355.8
1351.8
1350.9
1356.9
1349.9
1371.9
1289.9
421.9
676.4
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
m/z