Electronic Supplementary Material (ESI) for Dalton Transactions

Systematic study of the formation of the lanthanoid cubane cluster motif mediated by steric modification of diketonate ligands

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Supplementary information

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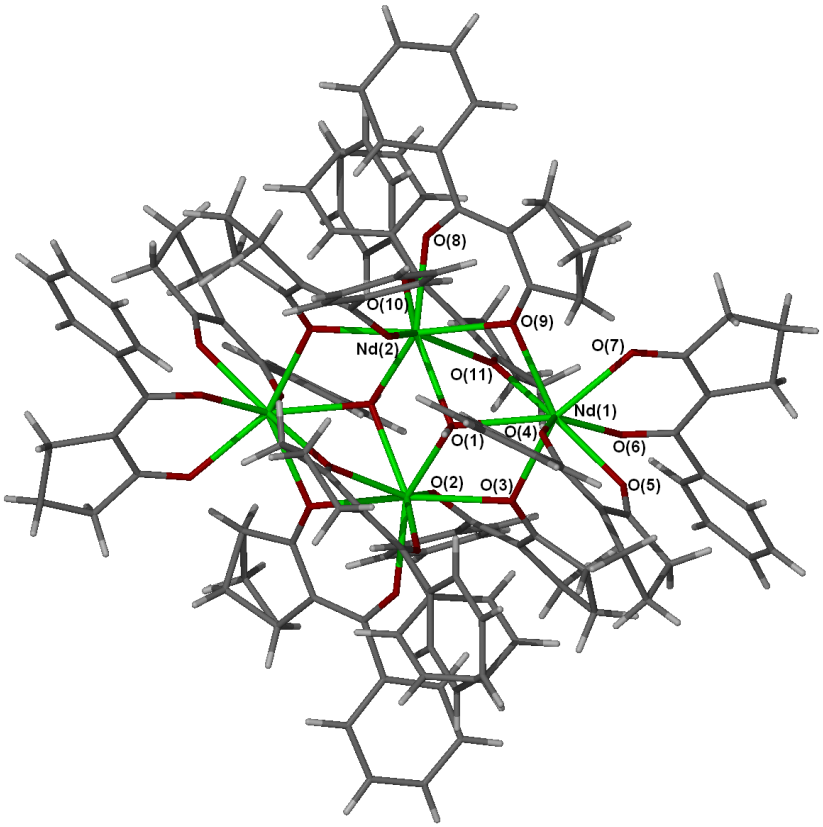
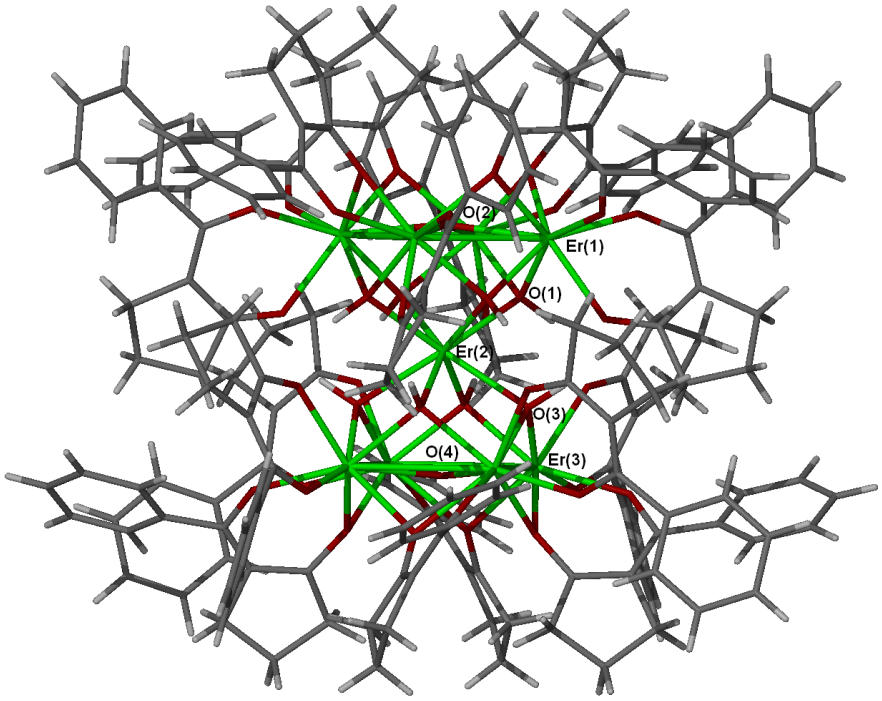
Molecular structure of cluster 1.



$[Nd_4(\mu_3\text{-}OH)_2(\mathbf{pmc})_{10}]$ (**1**)

Empirical formula	$C_{120}H_{112}Nd_4O_{22}$
Formula weight	2483.06
Temperature	100(2) K
Wavelength	0.773747861 Å (synchrotron)
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	a = 12.378(3) Å α = 66.73(3) deg. b = 15.353(3) Å β = 69.06(3) deg. c = 15.713(3) Å γ = 74.93(3) deg.
Volume	2537.3(9) Å^3
F(000)	1248
Crystal size	0.03 x 0.03 x 0.02 mm
Theta range for data collection	1.84 to 25.00 deg.
Limiting indices	-13<=h<=13, -16<=k<=16, -17<=l<=17
Reflections collected / unique	25247 / 6477 [R(int) = 0.0344]
Completeness to theta = 25.00	93.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6477 / 2 / 659
Goodness-of-fit on F^2	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1073
R indices (all data)	R1 = 0.0500, wR2 = 0.1143

Molecular structure of cluster 2.



$[HNEt_3][Er_9(\mu_4\text{-}O)_2(\mu_3\text{-}OH)_8(\mathbf{pmc})_{16}]$ (**2**)

Empirical formula	$C_{192}H_{184}Er_9O_{42}$
Formula weight	4668.73
Temperature	173(2) K
Wavelength	0.773747861 Å (synchrotron)
Crystal system, space group	Tetragonal, *I*4
Unit cell dimensions	a = 21.708(3) Å α = 90 deg. b = 21.708(3) Å β = 90 deg. c = 25.682(5) Å γ = 90 deg.
Volume	12103(3) Å^3
F(000)	4568
Crystal size	0.09 x 0.08 x 0.06 mm
Theta range for data collection	1.23 to 24.99 deg.
Limiting indices	-19<=h<=25, -18<=k<=25, -23<=l<=30
Reflections collected / unique	22589 / 10010 [R(int) = 0.1029]
Completeness to theta = 25.00	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10010 / 66 / 434
Goodness-of-fit on F^2	0.996
Final R indices [I>2sigma(I)]	R1 = 0.0660, wR2 = 0.1572
R indices (all data)	R1 = 0.1035, wR2 = 0.1712

Table S1: Selected bond lengths (Å) and angles (°) for **3**.

Bond Lengths, Å			
Er(1)-O(1)	2.365(7)	Er(2)-O(2)	2.361(7)
Er(1)-O(4)	2.366(8)	Er(2)-O(3)	2.426(10)
Er(3)-O(1)	2.337(8)	Er(4)-O(2)	2.345(8)
Er(3)-O(4)	2.307(8)	Er(4)-O(3)	2.310(9)
Er(1)-O(2)	2.357(7)	Er(2)-O(2)	2.361(7)
Er(3)-O(3)	2.365(8)	Er(4)-O(4)	2.406(8)
Bond Angles, °			
O(1)-Er(1)-O(4)	74.0(3)	O(2)-Er(2)-O(3)	74.0(3)
O(4)-Er(3)-O(1)	75.7(3)	O(3)-Er(4)-O(2)	76.5(3)
O(2)-Er(1)-O(1)	69.1(2)	O(1)-Er(2)-O(2)	69.7(2)
O(2)-Er(1)-O(4)	68.7(3)	O(1)-Er(2)-O(3)	68.9(3)
O(1)-Er(3)-O(3)	69.8(3)	O(3)-Er(4)-O(4)	70.2(3)
O(4)-Er(3)-O(3)	71.0(3)	O(2)-Er(4)-O(4)	68.2(3)

Table S2: Selected bond lengths (Å) and angles (°) for **7**.

Bond Lengths, Å			
Er(1)-O(1)	2.305(4)	Er(1)-O(6)	2.236(3)
Er(1)-O(1)^{a}	2.330(3)	Er(1)-O(7)	2.306(4)
Er(1)-O(1)^{b}	2.375(5)	Er(1)-Er(1)^{a}	3.6413(3)
Er(1)-O(2)	2.269(4)	Er(1)-Er(1)^{b}	3.8197(5)
Er(1)-O(3)	2.255(4)	Er(1)-Er(1)^{c}	3.6413(3)
Bond Angles, °			
O(1)^{a}-Er(1)-O(1)	74.67(13)	O(1)^{a}-Er(1)-O(1)^{b}	73.35(13)
O(1)^{b}-Er(1)-O(1)	69.86(11)		

Symmetry Transformations: a = -x+1,-y+1,z; b = -y+1,x,-z+2; c = y,-x+1,-z+2.

Table S3: Selected bond lengths (Å) and angles (°) for **8**.

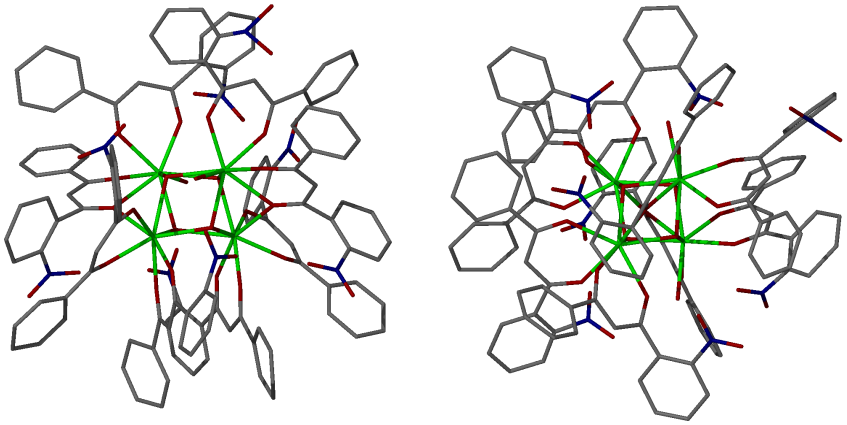
Bond Lengths, Å			
Er(1)-O(1)	2.369(12)	Er(3)-O(1)	2.311(11)
Er(1)-O(2)	2.319(10)	Er(3)-O(3)	2.313(13)
Er(1)-O(3)	2.330(10)	Er(3)-O(4)	2.346(11)
Er(2)-O(1)	2.333(11)	Er(4)-O(2)	2.353(9)
Er(2)-O(2)	2.302(11)	Er(4)-O(3)	2.341(11)
Er(2)-O(4)	2.337(10)	Er(4)-O(4)	2.362(11)
Bond Angles, °			
O(2)-Er(1)-O(3)	68.5(3)	O(2)-Er(1)-O(1)	75.0(4)
O(3)-Er(1)-O(1)	72.4(4)	O(1)-Er(3)-O(4)	68.1(4)
O(2)-Er(2)-O(1)	76.1(4)	O(3)-Er(3)-O(4)	77.1(4)
O(2)-Er(2)-O(4)	76.2(4)	O(3)-Er(4)-O(2)	67.7(3)
O(1)-Er(2)-O(4)	67.9(4)	O(3)-Er(4)-O(4)	76.2(4)
O(1)-Er(3)-O(3)	73.8(4)	O(2)-Er(4)-O(4)	74.7(4)

Table S4: Selected bond lengths (Å) and angles (°) for **9**.

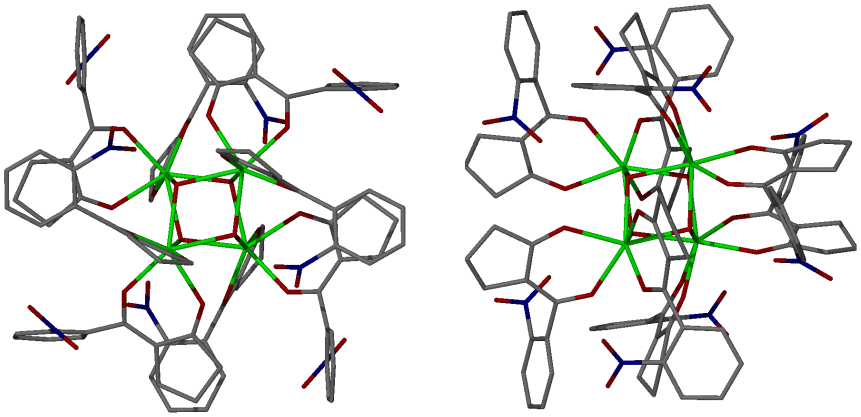
Bond Lengths, Å			
Er(1)-O(1)	2.350(10)	Er(2)-O(2)	2.315(8)
Er(1)-O(4)	2.313(10)	Er(2)-O(3)	2.305(11)
Er(3)-O(4)	2.298(10)	Er(4)-O(1)	2.418(10)
Er(1)-O(2)	2.379(9)	Er(4)-O(3)	2.353(10)
Er(3)-O(3)	2.335(10)	Er(4)-O(4)	2.374(9)
Bond Angles, °			
O(4)-Er(1)-O(1)	78.1(3)	O(2)-Er(2)-O(3)	74.8(3)
O(4)-Er(3)-O(2)	67.9(3)	O(3)-Er(4)-O(1)	67.6(4)
O(1)-Er(1)-O(2)	68.2(3)	O(1)-Er(2)-O(2)	69.6(3)
O(4)-Er(1)-O(2)	67.2(3)	O(1)-Er(2)-O(3)	69.8(3)
O(2)-Er(3)-O(3)	73.7(3)	O(3)-Er(4)-O(4)	68.5(3)
O(4)-Er(3)-O(3)	70.1(3)	O(1)-Er(4)-O(4)	75.6(3)

Figure S3: Examples of 'capping' and 'peripheral' faces for clusters **3**,**7** and **8**.

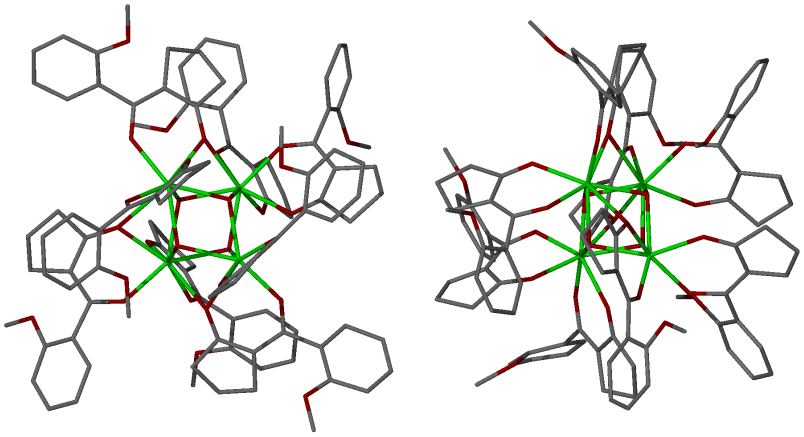
Erbium cluster **3**:



Erbium cluster **7**



Erbium cluster **8**



In each instance the capping face is on the left and a peripheral face on the right. The capping face either possesses or resembles a fourfold rotation axis (C_4) while the peripheral faces posses or resembles a twofold rotation axis (C_2) (seen as horizontal here).

Figure S4: Mass spectra of intermediate species for motif **3**.

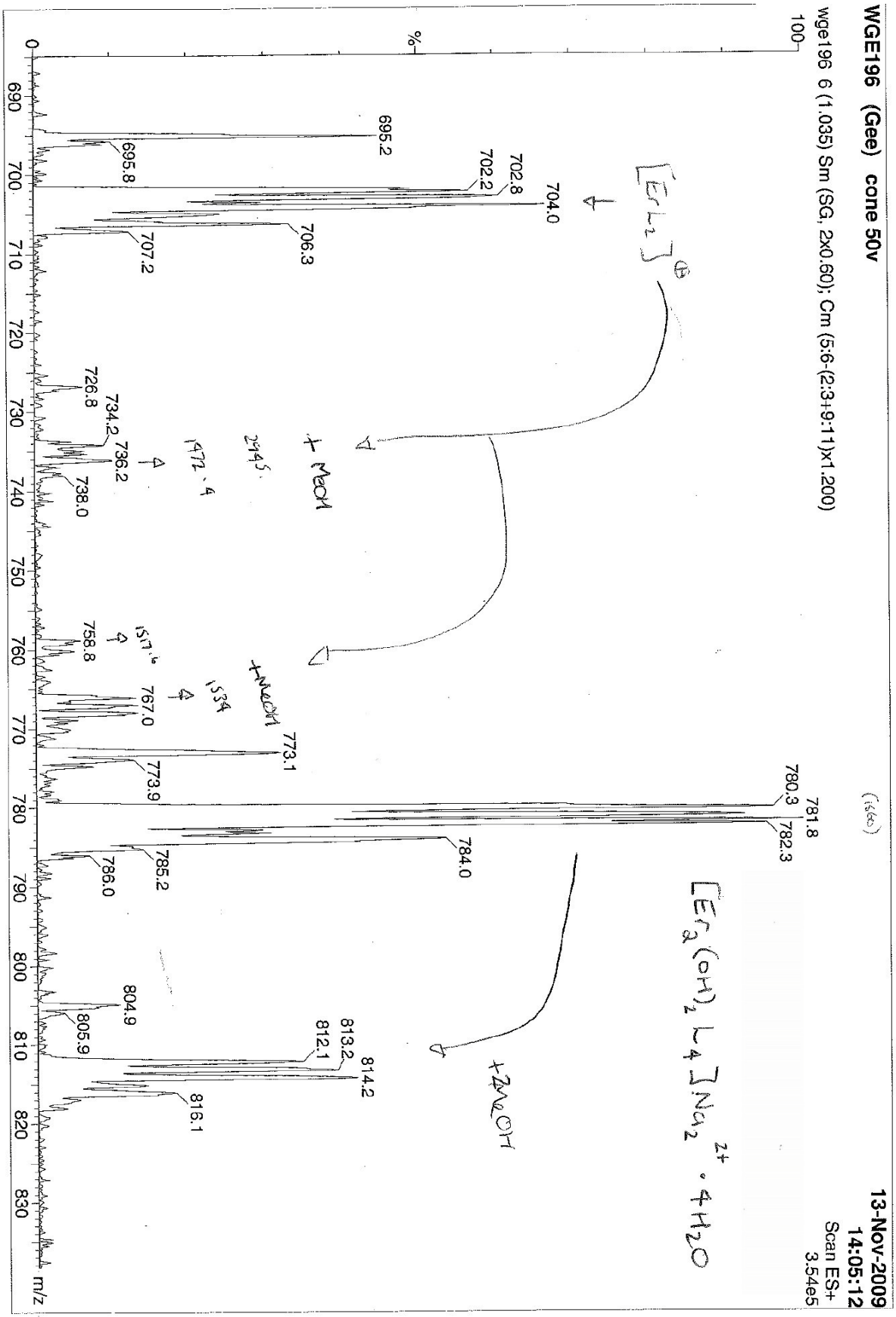


Figure S5: Mass spectra of intermediate species for motif **8**.

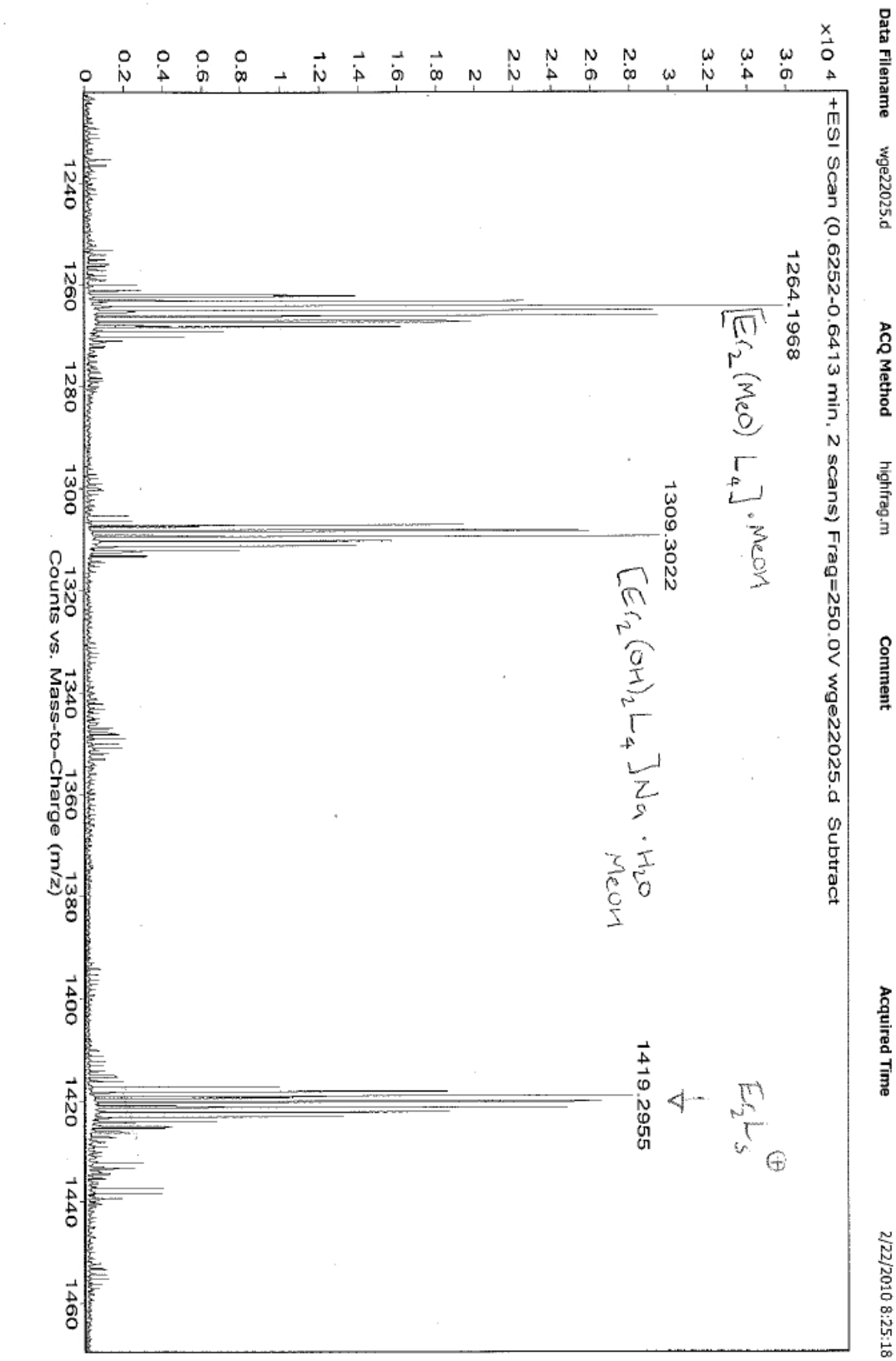


Figure S5: Mass spectra of intermediate species for motif **9**.