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Supporting Information

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From {Bi₂₂O₂₆} to Chiral Ligand-Protected {Bi₃₈O₄₅}-Based Bismuth Oxido Clusters

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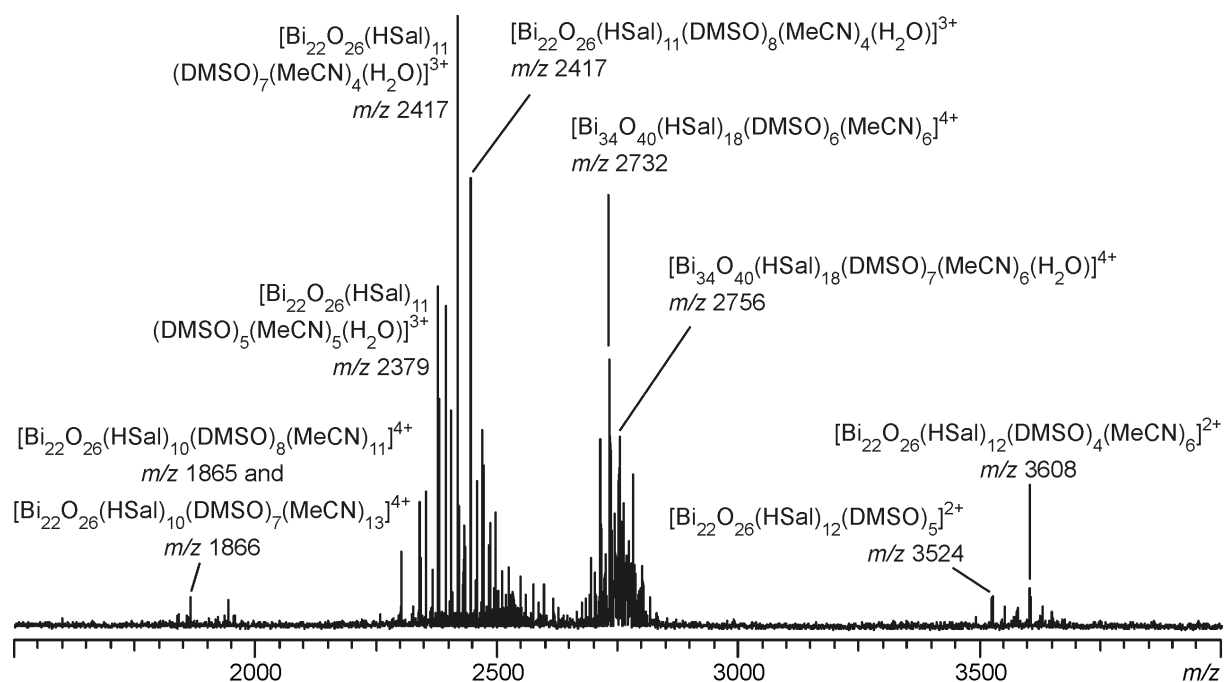


Figure S1. ESI mass spectrum of $[\text{Bi}_{22}\text{O}_{24}(\text{HSal})_{14}]$ (2) containing a new bismuth oxide species $[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{22}]$. In order to give an overview of the species observed, some of the major peaks in the spectrum are assigned to their fragments.

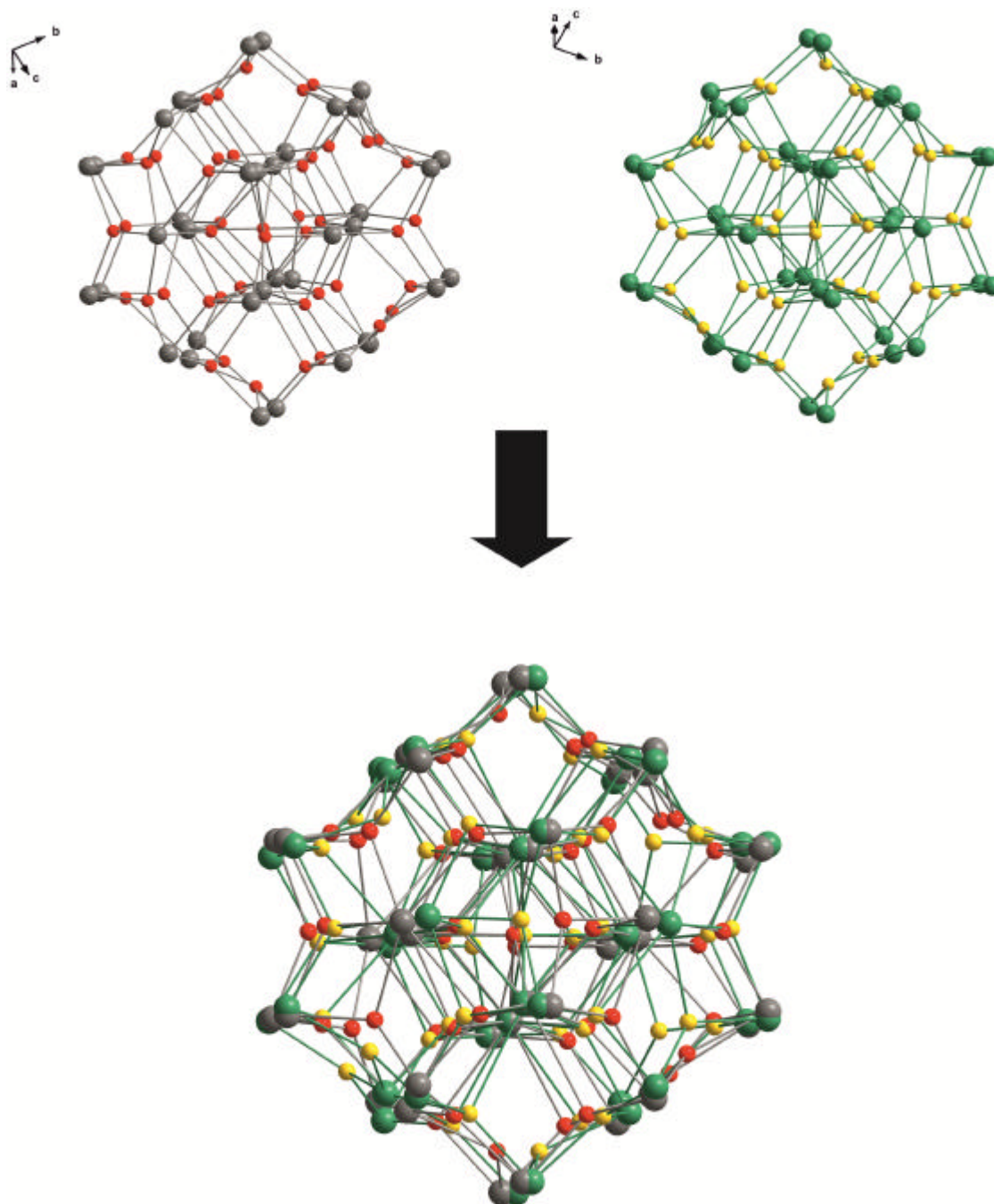


Figure S2. Overlay of the inner core structure of $[\text{Bi}_{38}\text{O}_{45}(\text{HSal})_{22}(\text{OH})_2(\text{DMSO})_{16.5}] \cdot \text{DMSO} \cdot \text{H}_2\text{O}$ ($3 \cdot \text{DMSO} \cdot \text{H}_2\text{O}$) (left, Bi: gray, O: red) and its non-superimposable mirror image (right, Bi: green, O: yellow).

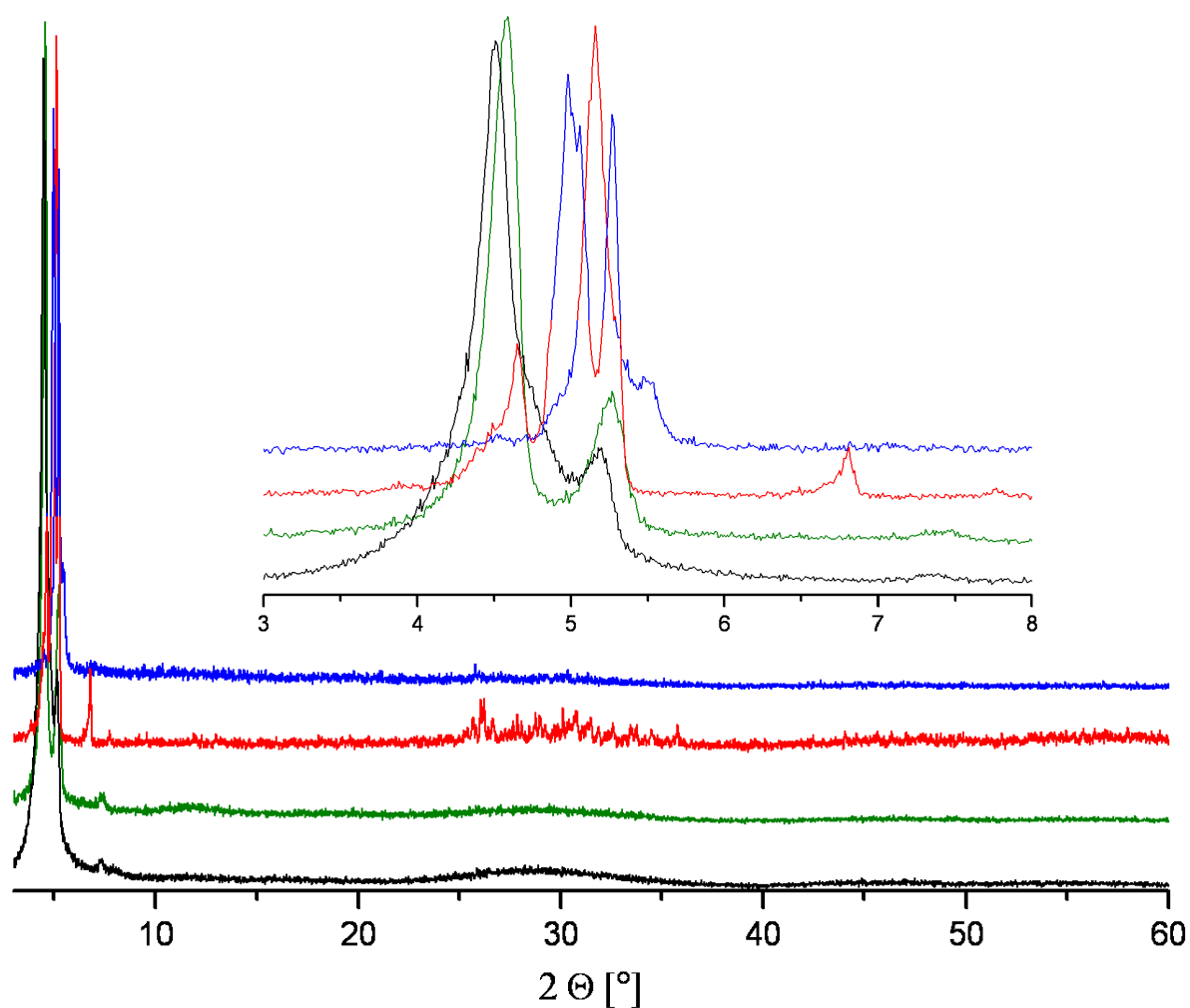


Figure S3. X-ray powder diffraction pattern of $[\text{Bi}_{22}\text{O}_{24}(\text{HSal})_{14}]$ (**2**, red), $[\text{Bi}_{38}\text{O}_{45}(\text{HSal})_{22}(\text{OH})_2(\text{DMSO})_{16.5}] \cdot \text{DMSO} \cdot \text{H}_2\text{O}$ (**3**·DMSO·H₂O, blue), $[\text{Bi}_{38}\text{O}_{45}(\text{BOC-ValO})_{22}(\text{OH})_2]$ (**4**, green) and $[\text{Bi}_{38}\text{O}_{45}(\text{BOC-PheO})_{22}(\text{OH})_2]$ (**5**, black).

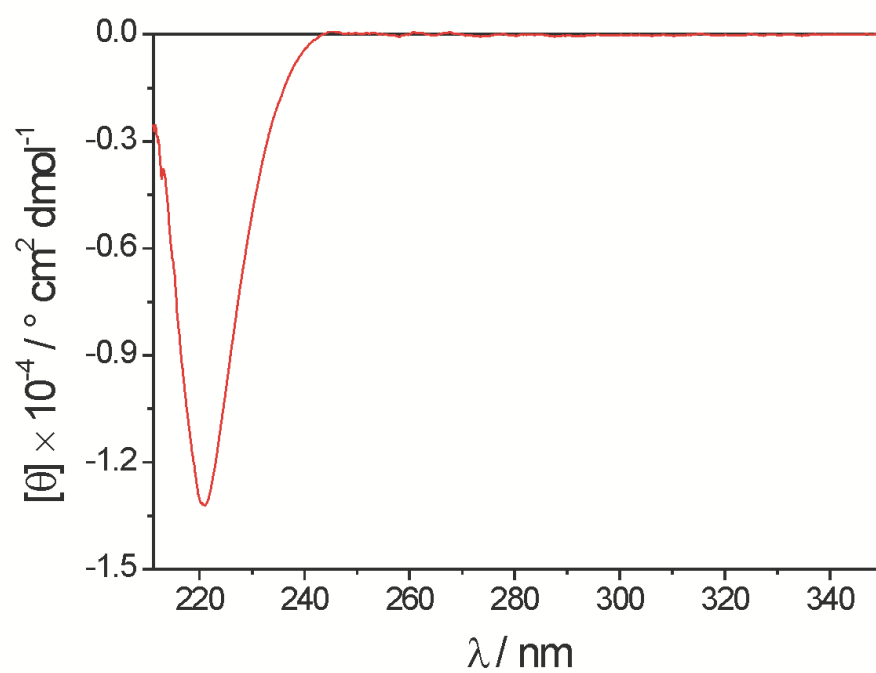


Figure S4. CD Spectrum of BOC-D-PheOH.

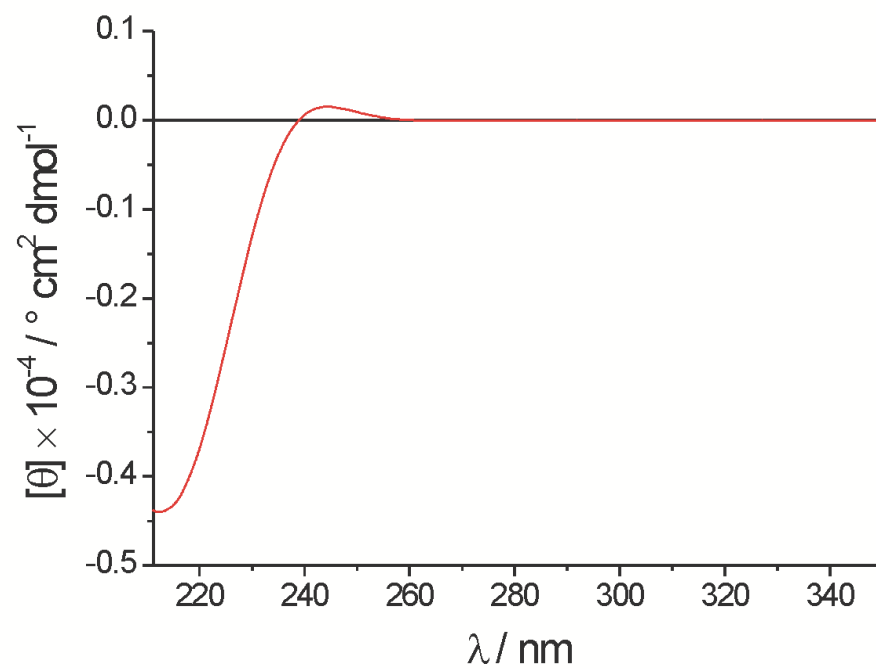


Figure S5. CD spectrum of BOC-D-ValOH.

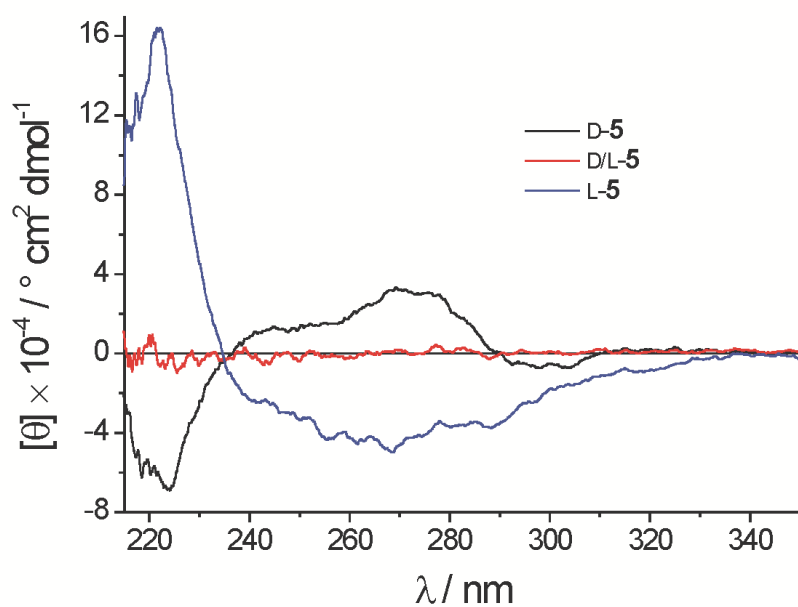


Figure S6. CD spectra of **5** based on BOC-D-PheOH (D-**5**), BOC-L-PheOH (L-**5**) and BOC-D/L-PheOH (D/L-**5**).

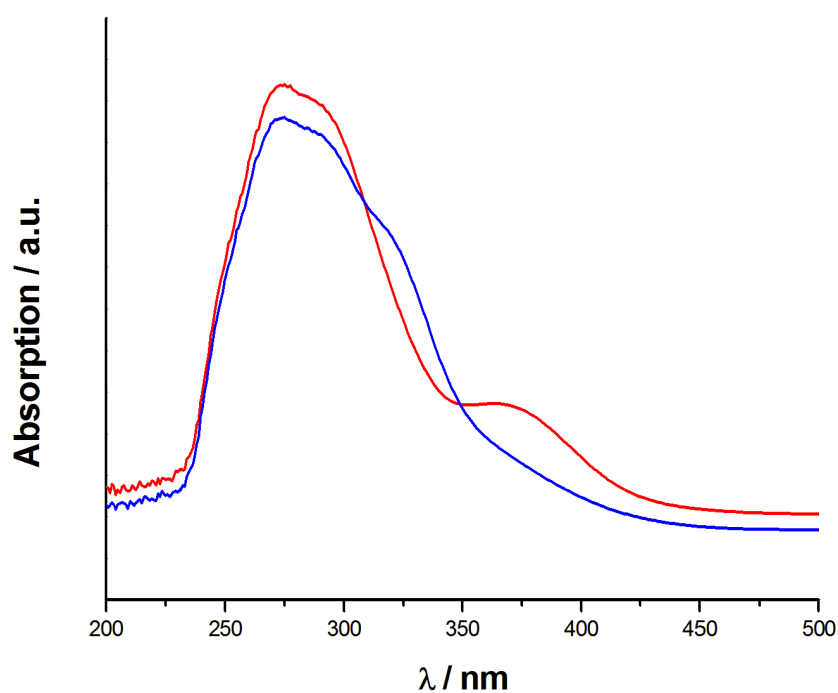


Figure S7. UV vis reflectance spectra of solid $[\text{Bi}_{38}\text{O}_{45}(\text{BOC-D/L-ValO})_{22}(\text{OH})_2]$ (**4**, red) and $[\text{Bi}_{38}\text{O}_{45}(\text{BOC-D/L-PheO})_{22}(\text{OH})_2]$ (**5**, blue).

Table S1. First part of the ESI-MS data of [Bi₂₂O₂₄(HSal)₁₄] (2).

m/z	classification	m/z	classification
1826	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₆ (MeCN) ₁₁] ⁴⁺	2521	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₁ (MeCN) ₄ (H ₂ O)] ³⁺
1836	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₆ (MeCN) ₁₂] ⁴⁺	2527	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₂ (MeCN) ₃] ³⁺
1845	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₇ (MeCN) ₁₁] ⁴⁺	2533	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₂ (MeCN) ₃ (H ₂ O)] ³⁺
1847	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₆ (MeCN) ₁₃] ⁴⁺	2541	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₂ (MeCN) ₄] ³⁺
1856	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₇ (MeCN) ₁₂] ⁴⁺	2547	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₂ (MeCN) ₄ (H ₂ O)] ³⁺
1857	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₆ (MeCN) ₁₄] ⁴⁺	2554	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₂ (MeCN) ₅] ³⁺
1865	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₈ (MeCN) ₁₁] ⁴⁺	2561	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₂ (MeCN) ₅ (H ₂ O)] ³⁺
1866	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₇ (MeCN) ₁₃] ⁴⁺	2567	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₃ (MeCN) ₄] ³⁺
1875	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₈ (MeCN) ₁₂] ⁴⁺	2673	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₃ (MeCN) ₄ (H ₂ O)] ³⁺
1876	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₇ (MeCN) ₁₄] ⁴⁺	2681	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₃ (MeCN) ₅] ³⁺
1885	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₉ (MeCN) ₁₁] ⁴⁺	2687	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₃ (MeCN) ₅ (H ₂ O)] ³⁺
1886	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₈ (MeCN) ₁₃] ⁴⁺	2594	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₃ (MeCN) ₆] ³⁺
1895	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₉ (MeCN) ₁₂] ⁴⁺	2600	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₃ (MeCN) ₆ (H ₂ O)] ³⁺
1896	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₈ (MeCN) ₁₄] ⁴⁺	2607	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₄ (MeCN) ₅] ³⁺
1905	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₉ (MeCN) ₁₃] ⁴⁺	2613	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₄ (MeCN) ₅ (H ₂ O)] ³⁺
1906	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₈ (MeCN) ₁₅] ⁴⁺	2619	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₅ (MeCN) ₄] ³⁺
1915	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₁₀ (MeCN) ₁₂] ⁴⁺	2633	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₅ (MeCN) ₅] ³⁺
1916	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₉ (MeCN) ₁₄] ⁴⁺		
1919	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₁₀ (MeCN) ₁₂ (H ₂ O)] ⁴⁺	2693	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₄ (MeCN) ₆] ⁴⁺
1920	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₉ (MeCN) ₁₄ (H ₂ O)] ⁴⁺	2712	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₅ (MeCN) ₆] ⁴⁺
1925	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₁₁ (MeCN) ₁₁] ⁴⁺	2732	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₆ (MeCN) ₆] ⁴⁺
1926	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₁₀ (MeCN) ₁₃] ⁴⁺	2736	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₆ (MeCN) ₆ (H ₂ O)] ⁴⁺
1934	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₁₁ (MeCN) ₁₂] ⁴⁺	2741	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₇ (MeCN) ₅] ⁴⁺
1935	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₁₀ (MeCN) ₁₃] ⁴⁺	2746	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₇ (MeCN) ₅ (H ₂ O)] ⁴⁺
1954	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₁₂ (MeCN) ₁₂] ⁴⁺	2752	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₇ (MeCN) ₆] ⁴⁺
1955	[Bi ₂₂ O ₂₆ (HSal) ₁₀ (DMSO) ₁₁ (MeCN) ₁₃] ⁴⁺	2756	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₇ (MeCN) ₆ (H ₂ O)] ⁴⁺
		2761	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₇ (MeCN) ₇] ⁴⁺
2299	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₃ (MeCN) ₃ (H ₂ O)] ³⁺	2766	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₇ (MeCN) ₇ (H ₂ O)] ⁴⁺
2339	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₄ (MeCN) ₄ (H ₂ O)] ³⁺	2770	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₉ (MeCN) ₄] ⁴⁺
2351	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₅ (MeCN) ₃ (H ₂ O)] ³⁺	2771	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₈ (MeCN) ₆] ⁴⁺
2364	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₅ (MeCN) ₄ (H ₂ O)] ³⁺	2775	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₉ (MeCN) ₄ (H ₂ O)] ⁴⁺
2379	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₅ (MeCN) ₅ (H ₂ O)] ³⁺	2776	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₈ (MeCN) ₆ (H ₂ O)] ⁴⁺
2391	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₅ (MeCN) ₆ (H ₂ O)] ³⁺	2780	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₉ (MeCN) ₅] ⁴⁺
2404	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₆ (MeCN) ₅ (H ₂ O)] ³⁺	2785	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₉ (MeCN) ₅ (H ₂ O)] ⁴⁺
2417	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₇ (MeCN) ₄ (H ₂ O)] ³⁺	2790	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₁₀ (MeCN) ₄] ⁴⁺
2429	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₈ (MeCN) ₃ (H ₂ O)] ³⁺	2791	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₉ (MeCN) ₆] ⁴⁺
2443	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₈ (MeCN) ₄ (H ₂ O)] ³⁺	2795	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₉ (MeCN) ₆ (H ₂ O)] ⁴⁺
2456	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₈ (MeCN) ₅ (H ₂ O)] ³⁺	2800	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₁₀ (MeCN) ₅] ⁴⁺
2469	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₉ (MeCN) ₄ (H ₂ O)] ³⁺	2803	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₁₁ (MeCN) ₃ (H ₂ O)] ⁴⁺
2484	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₉ (MeCN) ₅ (H ₂ O)] ³⁺	2805	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₁₀ (MeCN) ₅ (H ₂ O)] ⁴⁺
2495	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₀ (MeCN) ₄ (H ₂ O)] ³⁺	2809	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₁₁ (MeCN) ₄] ⁴⁺
2502	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₀ (MeCN) ₅] ³⁺	2810	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₁₀ (MeCN) ₆] ⁴⁺
2509	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₀ (MeCN) ₅ (H ₂ O)] ³⁺	2815	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₁₀ (MeCN) ₆ (H ₂ O)] ⁴⁺
2515	[Bi ₂₂ O ₂₆ (HSal) ₁₁ (DMSO) ₁₁ (MeCN) ₄] ³⁺	2819	[Bi ₃₄ O ₄₀ (HSal) ₁₈ (DMSO) ₁₁ (MeCN) ₅] ⁴⁺

Table S2. Second part of the ESI-MS data of $[\text{Bi}_{22}\text{O}_{24}(\text{HSal})_{14}]$ (2).

m/z	classification	m/z	classification
2824	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{11}(\text{MeCN})_5(\text{H}_2\text{O})]^{4+}$	3588	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_4(\text{MeCN})_5]^{2+}$
2830	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{11}(\text{MeCN})_6]^{4+}$	3597	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_4(\text{MeCN})_5(\text{H}_2\text{O})]^{2+}$
2834	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{11}(\text{MeCN})_6(\text{H}_2\text{O})]^{4+}$	3602	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_7]^{2+}$
2843	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{12}(\text{MeCN})_5(\text{H}_2\text{O})]^{4+}$	3608	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_4(\text{MeCN})_6]^{2+}$
2844	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{11}(\text{MeCN})_7(\text{H}_2\text{O})]^{4+}$	3615	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_5(\text{MeCN})_4(\text{H}_2\text{O})]^{2+}$
2849	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{12}(\text{MeCN})_6]^{4+}$	3617	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_4(\text{MeCN})_6(\text{H}_2\text{O})]^{2+}$
2854	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{12}(\text{MeCN})_6(\text{H}_2\text{O})]^{4+}$	3623	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_7(\text{MeCN})]^{2+}$
2864	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{12}(\text{MeCN})_7(\text{H}_2\text{O})]^{4+}$	3628	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_5(\text{MeCN})_5]^{2+}$
2868	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{13}(\text{MeCN})_6]^{4+}$	3636	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_5(\text{MeCN})_5(\text{H}_2\text{O})]^{2+}$
2883	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{13}(\text{MeCN})_7(\text{H}_2\text{O})]^{4+}$	3642	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_8]^{2+}$
2903	$[\text{Bi}_{34}\text{O}_{40}(\text{HSal})_{18}(\text{DMSO})_{14}(\text{MeCN})_7(\text{H}_2\text{O})]^{4+}$	3648	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_5(\text{MeCN})_6]^{2+}$
3490	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_2(\text{MeCN})_4]^{2+}$	3662	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_8(\text{MeCN})]^{2+}$
3524	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_5]^{2+}$	3668	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_5(\text{MeCN})_7]^{2+}$
3550	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_3(\text{MeCN})_5]^{2+}$	3675	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_6(\text{MeCN})_5(\text{H}_2\text{O})]^{2+}$
3554	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_5(\text{MeCN})(\text{H}_2\text{O})]^{2+}$	3695	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_6(\text{MeCN})_6(\text{H}_2\text{O})]^{2+}$
3563	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_6]^{2+}$	3707	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_6(\text{MeCN})_7]^{2+}$
3568	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_4(\text{MeCN})_4]^{2+}$	3716	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_6(\text{MeCN})_7(\text{H}_2\text{O})]^{2+}$
3570	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_3(\text{MeCN})_6]^{2+}$	3722	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_9(\text{MeCN})_2]^{2+}$
3576	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_4(\text{MeCN})_4(\text{H}_2\text{O})]^{2+}$	3740	$[\text{Bi}_{22}\text{O}_{26}(\text{HSal})_{12}(\text{DMSO})_{10}(\text{MeCN})]^{2+}$

Table S3. ESI-MS data of $[\text{Bi}_{38}\text{O}_{45}(\text{HSal})_{22}(\text{OH})_2(\text{DMSO})_{16.5}] \cdot \text{DMSO}$ (3·DMSO).

m/z	classification
3544	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO}) - 2 \text{H}_2\text{O} - 5 \text{H}_2\text{Sal}]^{3+}$
3550	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO}) - \text{H}_2\text{O} - 5 \text{H}_2\text{Sal}]^{3+}$
3570	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_2 - 2 \text{H}_2\text{O} - 5 \text{H}_2\text{Sal}]^{3+}$
3576	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_2 - \text{H}_2\text{O} - 5 \text{H}_2\text{Sal}]^{3+}$
3596	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_3 - 2 \text{H}_2\text{O} - 5 \text{H}_2\text{Sal}]^{3+}$
3602	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_3 - \text{H}_2\text{O} - 5 \text{H}_2\text{Sal}]^{3+}$
3616	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_2 - 2 \text{H}_2\text{O} - 4 \text{H}_2\text{Sal}]^{3+}$
3622	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_2 - \text{H}_2\text{O} - 4 \text{H}_2\text{Sal}]^{3+}$
3628	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_2 - 4 \text{H}_2\text{Sal}]^{3+}$
3642	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_3 - 2 \text{H}_2\text{O} - 4 \text{H}_2\text{Sal}]^{3+}$
3648	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_3 - \text{H}_2\text{O} - 4 \text{H}_2\text{Sal}]^{3+}$
3668	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_2 - \text{H}_2\text{O} - 3 \text{H}_2\text{Sal}]^{3+}$
3688	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_3 - 2 \text{H}_2\text{O} - 3 \text{H}_2\text{Sal}]^{3+}$
3694	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_3 - \text{H}_2\text{O} - 3 \text{H}_2\text{Sal}]^{3+}$
3714	$[\text{Bi}_{38}\text{O}_{46}(\text{HSal})_{19}(\text{DMSO})_2 - \text{H}_2\text{O} - 2 \text{H}_2\text{Sal}]^{3+}$

Table S4. ESI-MS data of $[\text{Bi}_{38}\text{O}_{45}(\text{BOC-ValO})_{22}(\text{OH})_2]$ (**4**).

m/z	classification
3082	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})_3(\text{BOC-ValO})_{15}(\text{EtOH})]^{4+}$
3089	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})_3(\text{BOC-ValO})_{15}(\text{EtOH})_2 - \text{H}_2\text{O}]^{4+}$
3097	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})_2(\text{BOC-ValO})_{16}]^{4+}$
3099	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})_3(\text{BOC-ValO})_{15}(\text{EtOH})_2(\text{H}_2\text{O})]^{4+}$
3108	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})_2(\text{BOC-ValO})_{16}(\text{EtOH})]^{4+}$
3115	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})_2(\text{BOC-ValO})_{16}(\text{EtOH})_2 - \text{H}_2\text{O}]^{4+}$
3122	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})(\text{BOC-ValO})_{17}]^{4+}$
3136	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})_2(\text{BOC-ValO})_{16}(\text{EtOH})_3(\text{H}_2\text{O})]^{4+}$
3143	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})(\text{BOC-ValO})_{17} - \text{H}_2\text{O}]^{4+}$
3158	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-ValO})_{18}(\text{EtOH})]^{4+}$
3161	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})(\text{BOC-ValO})_{17}(\text{EtOH})_3(\text{H}_2\text{O})]^{4+}$
3165	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-ValO})_{18}(\text{EtOH})_2 - \text{H}_2\text{O}]^{4+}$
3172	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{ValO})(\text{BOC-ValO})_{18}]^{4+}$
3193	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-ValO})_{18}(\text{EtOH})_4]^{4+}$
3197	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-ValO})_{19}]^{4+}$
3204	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-ValO})_{18}(\text{EtOH})_5]^{4+}$
3222	$[\text{Bi}_{38}\text{O}_{45}(\text{ValO})(\text{BOC-ValO})_{19}]^{4+}$
3247	$[\text{Bi}_{38}\text{O}_{45}(\text{BOC-ValO})_{20}]^{4+}$
4183	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{ValO})_3(\text{BOC-ValO})_{16}(\text{EtOH})]^{3+}$
4206	$[\text{Bi}_{38}\text{O}_{45}(\text{ValO})_6(\text{BOC-ValO})_{15}(\text{EtOH})_3(\text{H}_2\text{O})]^{3+}$
4265	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{ValO})_3(\text{BOC-ValO})_{17}(\text{EtOH})_2]^{3+}$
4293	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-ValO})_{19}(\text{EtOH})_2 - \text{H}_2\text{O}]^{3+}$
4329	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-ValO})_{19}(\text{EtOH})_4]^{3+}$
4401	$[\text{Bi}_{38}\text{O}_{45}(\text{BOC-ValO})_{21}]^{3+}$
4488	$[\text{Bi}_{38}\text{O}_{45}(\text{BOC-ValO})_{21}(\text{EtOH})_6 - \text{H}_2\text{O}]^{3+}$

Table S5. ESI-MS data of $[\text{Bi}_{38}\text{O}_{45}(\text{BOC-PheO})_{22}(\text{OH})_2]$ (**5**).

m/z	classification
3360	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{PheO})_4(\text{BOC-PheO})_{14}(\text{DMSO})_5]^{4+}$
3380	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{PheO})_4(\text{BOC-PheO})_{14}(\text{DMSO})_6]^{4+}$
3385	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{PheO})_3(\text{BOC-PheO})_{15}(\text{DMSO})_5]^{4+}$
3410	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{PheO})_2(\text{BOC-PheO})_{16}(\text{DMSO})_5]^{4+}$
3436	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{PheO})(\text{BOC-PheO})_{17}(\text{DMSO})_5]^{4+}$
3453	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})_2(\text{BOC-PheO})_{17}(\text{DMSO})_4]^{4+}$
3461	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-PheO})_{18}(\text{DMSO})_5]^{4+}$
3476	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-PheO})_{18}(\text{DMSO})_6 - \text{H}_2\text{O}]^{4+}$
3481	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-PheO})_{18}(\text{DMSO})_6]^{4+}$
3503	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{19}(\text{DMSO})_4]^{4+}$
3507	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{19}(\text{DMSO})_4(\text{H}_2\text{O})]^{4+}$
3525	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})_3(\text{BOC-PheO})_{16}(\text{DMSO})_9]^{4+}$
3531	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})_2(\text{BOC-PheO})_{17}(\text{DMSO})_8]^{4+}$
3550	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})_2(\text{BOC-PheO})_{17}(\text{DMSO})_9]^{4+}$
3554	$[\text{Bi}_{38}\text{O}_{45}(\text{PheO})_2(\text{BOC-PheO})_{18}(\text{DMSO})_6]^{4+}$
3573	$[\text{Bi}_{38}\text{O}_{45}(\text{PheO})_2(\text{BOC-PheO})_{18}(\text{DMSO})_7]^{4+}$
3578	$[\text{Bi}_{38}\text{O}_{45}(\text{PheO})(\text{BOC-PheO})_{19}(\text{DMSO})_6]^{4+}$
3596	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{19}(\text{DMSO})_9 - \text{H}_2\text{O}]^{4+}$
3604	$[\text{Bi}_{38}\text{O}_{45}(\text{BOC-PheO})_{20}(\text{DMSO})_6]^{4+}$
3620	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{19}(\text{DMSO})_{10}]^{4+}$
3626	$[\text{Bi}_{38}\text{O}_{45}(\text{BOC-PheO})_{20}(\text{DMSO})_7(\text{H}_2\text{O})]^{4+}$
3650	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})(\text{BOC-PheO})_{18}(\text{DMSO})_{13} - \text{H}_2\text{O}]^{4+}$
3668	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})_2(\text{BOC-PheO})_{17}(\text{DMSO})_{15}]^{4+}$
3673	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})(\text{BOC-PheO})_{18}(\text{DMSO})_{14}]^{4+}$
3674	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{19}(\text{DMSO})_{13} - \text{H}_2\text{O}]^{4+}$
4632	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})_6(\text{BOC-PheO})_{13}(\text{DMSO})_{10}]^{3+}$
4665	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})_5(\text{BOC-PheO})_{14}(\text{DMSO})_{10}]^{3+}$
4689	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{PheO})(\text{BOC-PheO})_{18}(\text{DMSO})_6 - \text{H}_2\text{O}]^{4+}$
4702	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{19}(\text{DMSO})_5]^{3+}$
4724	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{PheO})_2(\text{BOC-PheO})_{18}(\text{DMSO})_5 + \text{H}_2\text{O}]^{4+}$
4733	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{20}(\text{DMSO})_3]^{3+}$
4759	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{20}(\text{DMSO})_4]^{3+}$
4765	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})(\text{BOC-PheO})_{20}(\text{DMSO})_4 + \text{H}_2\text{O}]^{4+}$
4787	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{BOC-PheO})_{19}(\text{DMSO})_8 + \text{H}_2\text{O}]^{4+}$
4798	$[\text{Bi}_{38}\text{O}_{45}(\text{OH})_2(\text{PheO})(\text{BOC-PheO})_{18}(\text{DMSO})_{10}]^{4+}$