Supplementary information for

First 24-membered macrocyclic 1,10-phenanthroline-2,9-diamides – an efficient switch from acidic to alkaline extraction of *f*-elements

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1. Spectra drawings
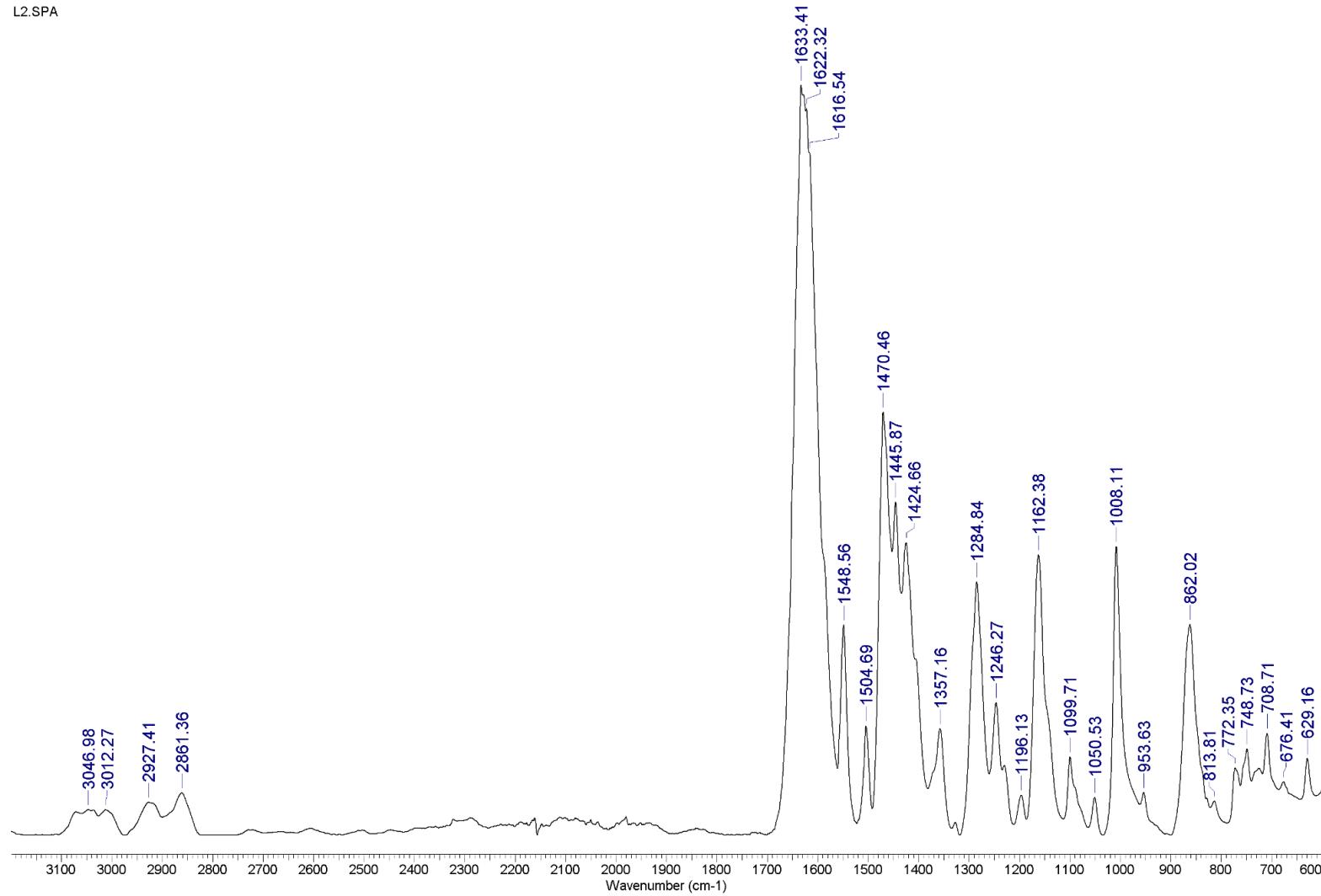
Figure S1. Solid-state IR spectrum of macrocycle **L2** at 25°C
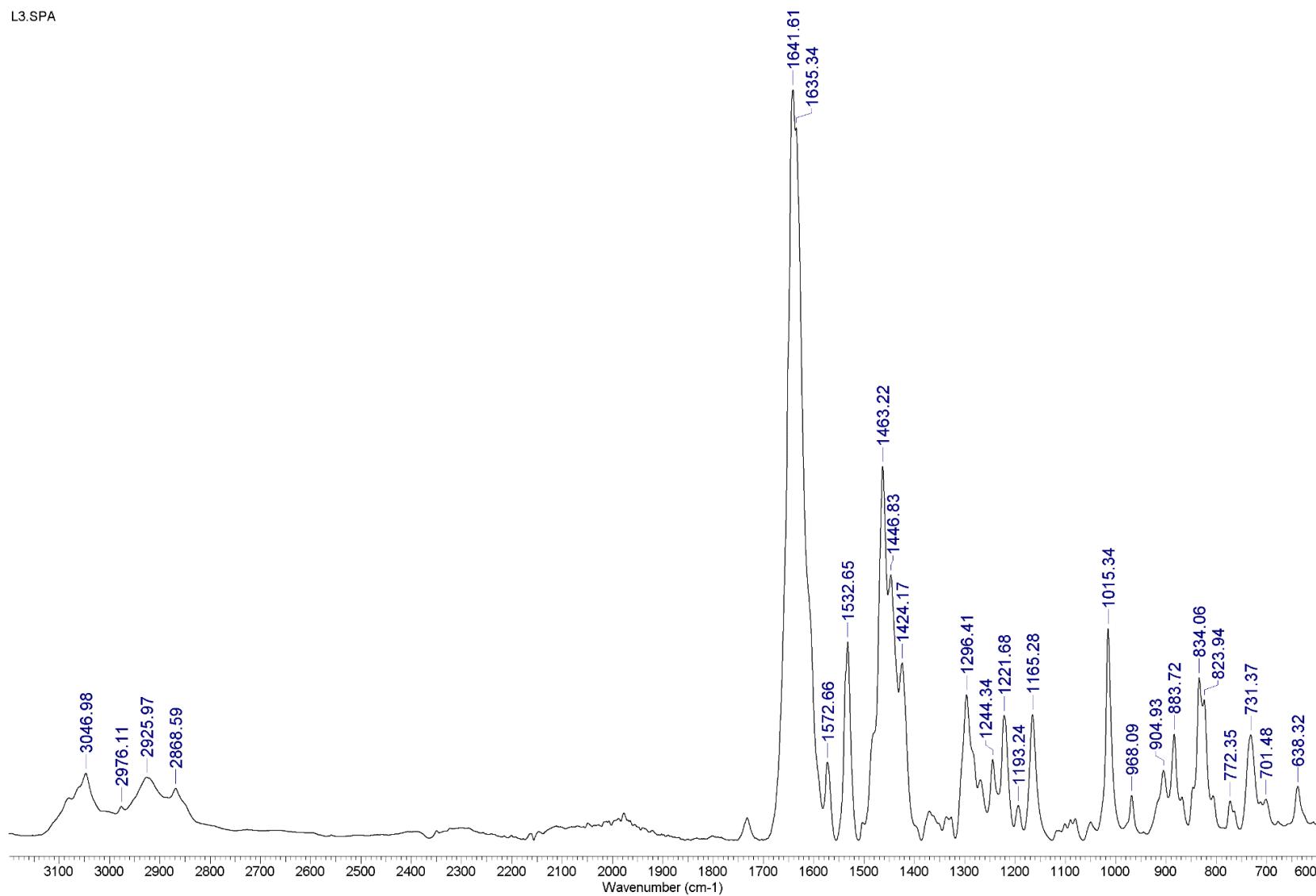
Figure S2. Solid-state IR spectrum of **L3** at 25°C
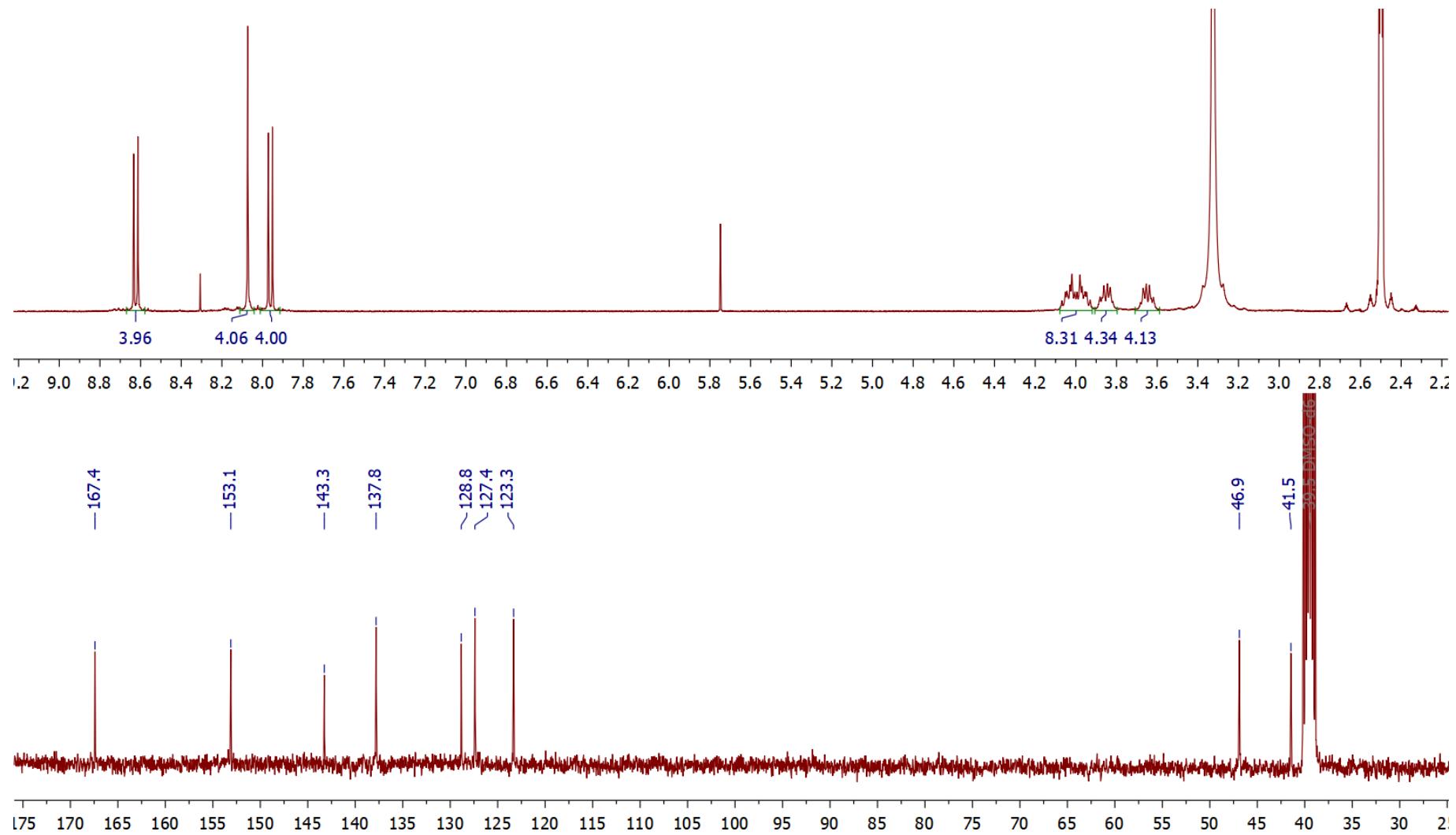
Figure S3. ^{1}H and ^{13}C NMR spectra of **L2** (DMSO-d_6, 25°C).
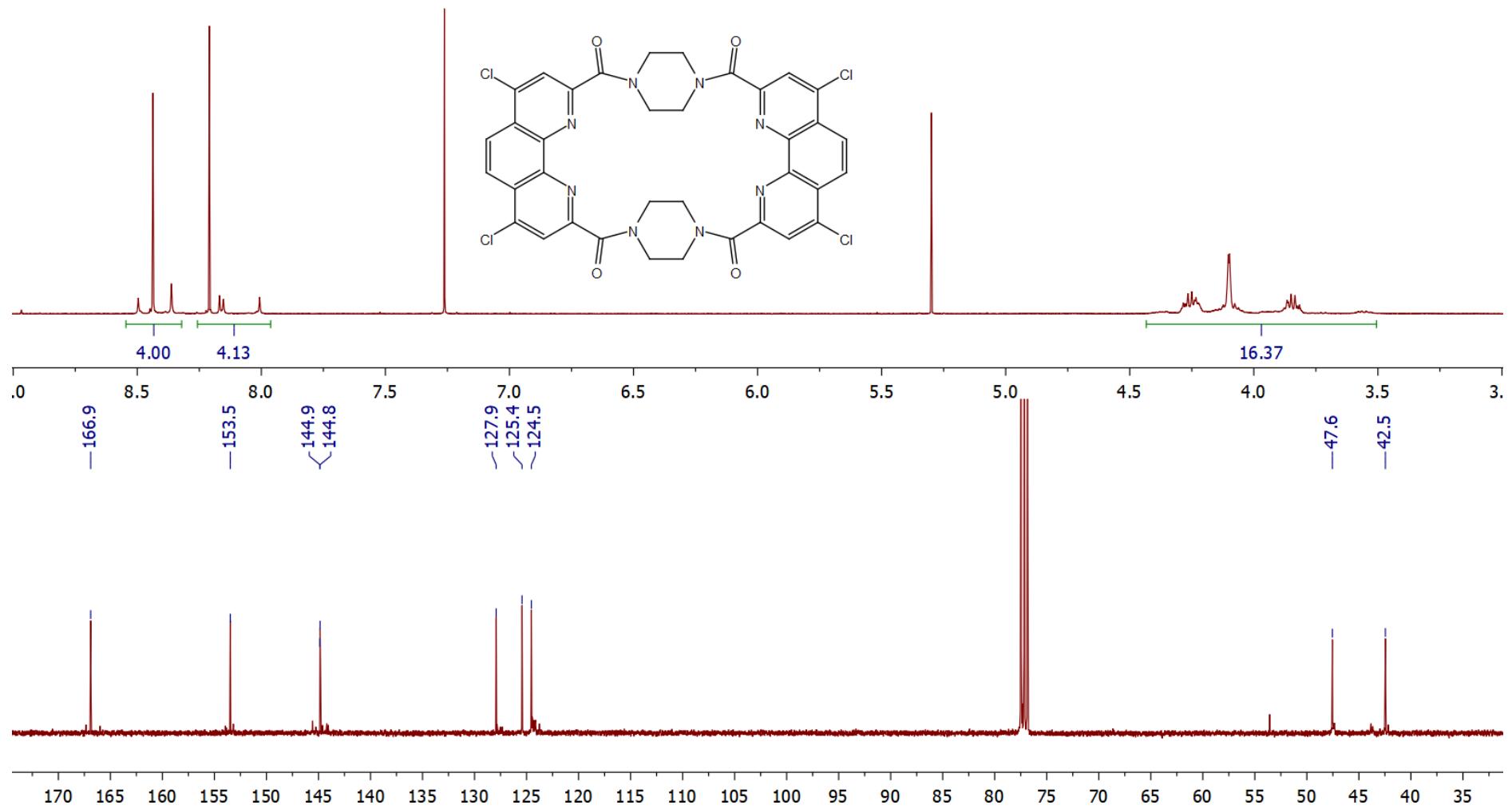
Figure S4. ^{1}H and ^{13}C NMR spectra (CDCl$_3$, 25°C)
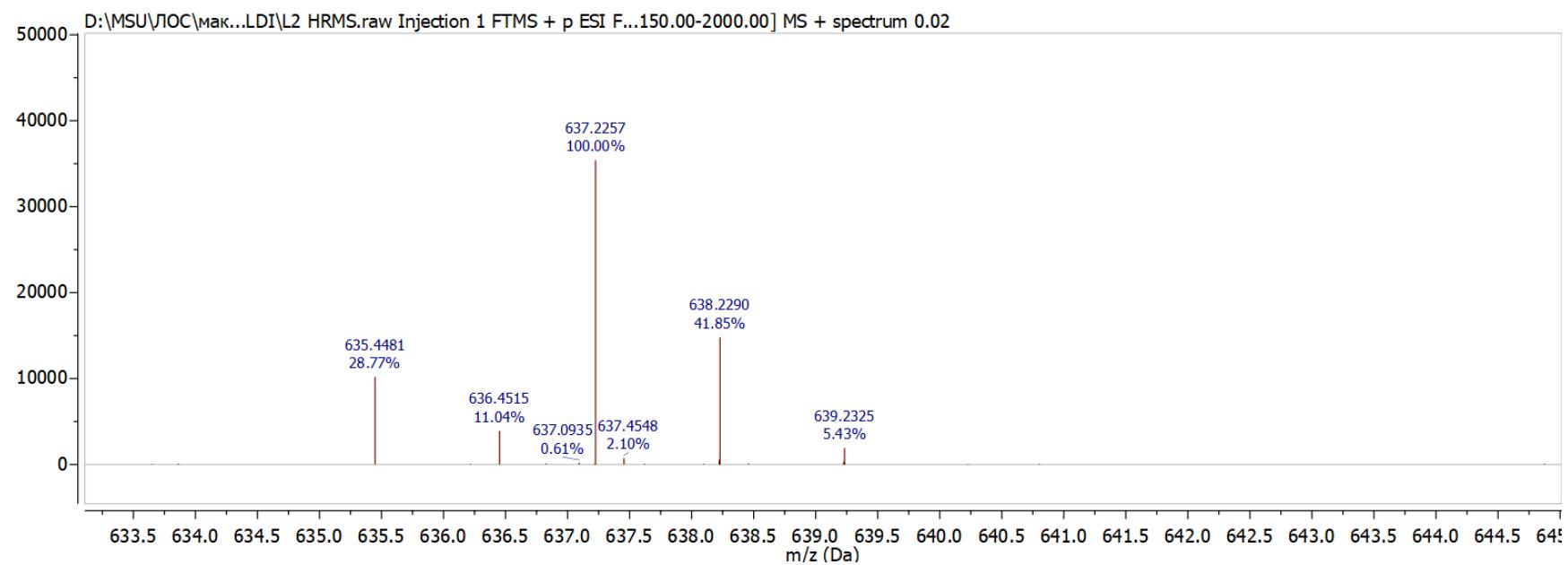
Figure S5. Fragmental view of HRMS ESI spectrum of **L2**

Display Report

Analysis Info　　　　　　　　　　　　　　　　　　Acquisition Date　30.09.2020 18:55:47

Analysis Name	D:\Data\Kolotyrkina\2020\Muzalevsky\0930038.d	
Method	tune_50-1600.m	
Sample Name	/MUSE PVS-076	Operator　BDAL@DE
Comment	C36H24Cl4N8O4 mH 773.0747 calibrant added, CH3CN	Instrument / Ser#　micrOTOF　10248

Acquisition Parameter

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

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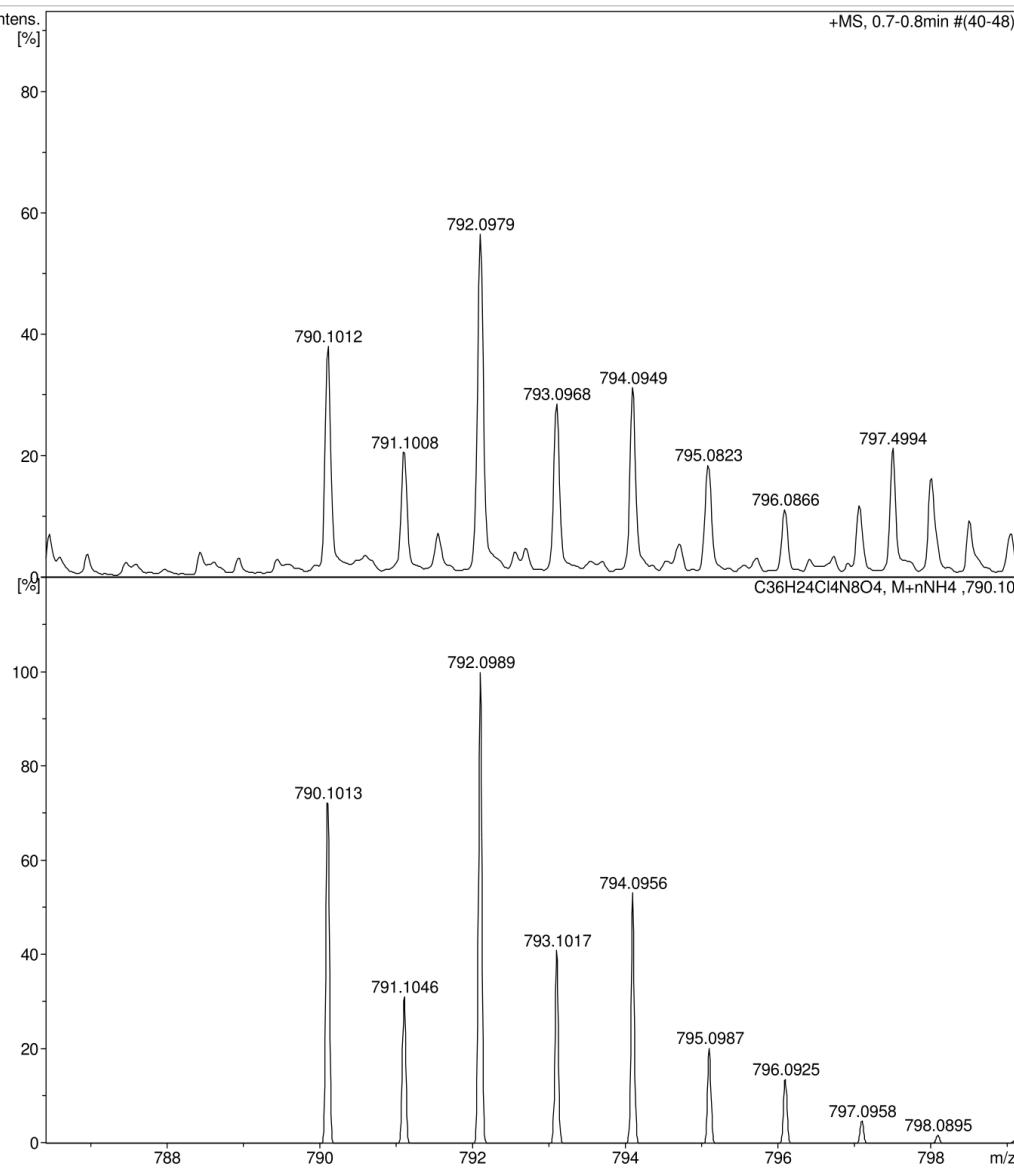
Figure S6. Fragmental view of HRMS ESI spectrum of **L3**

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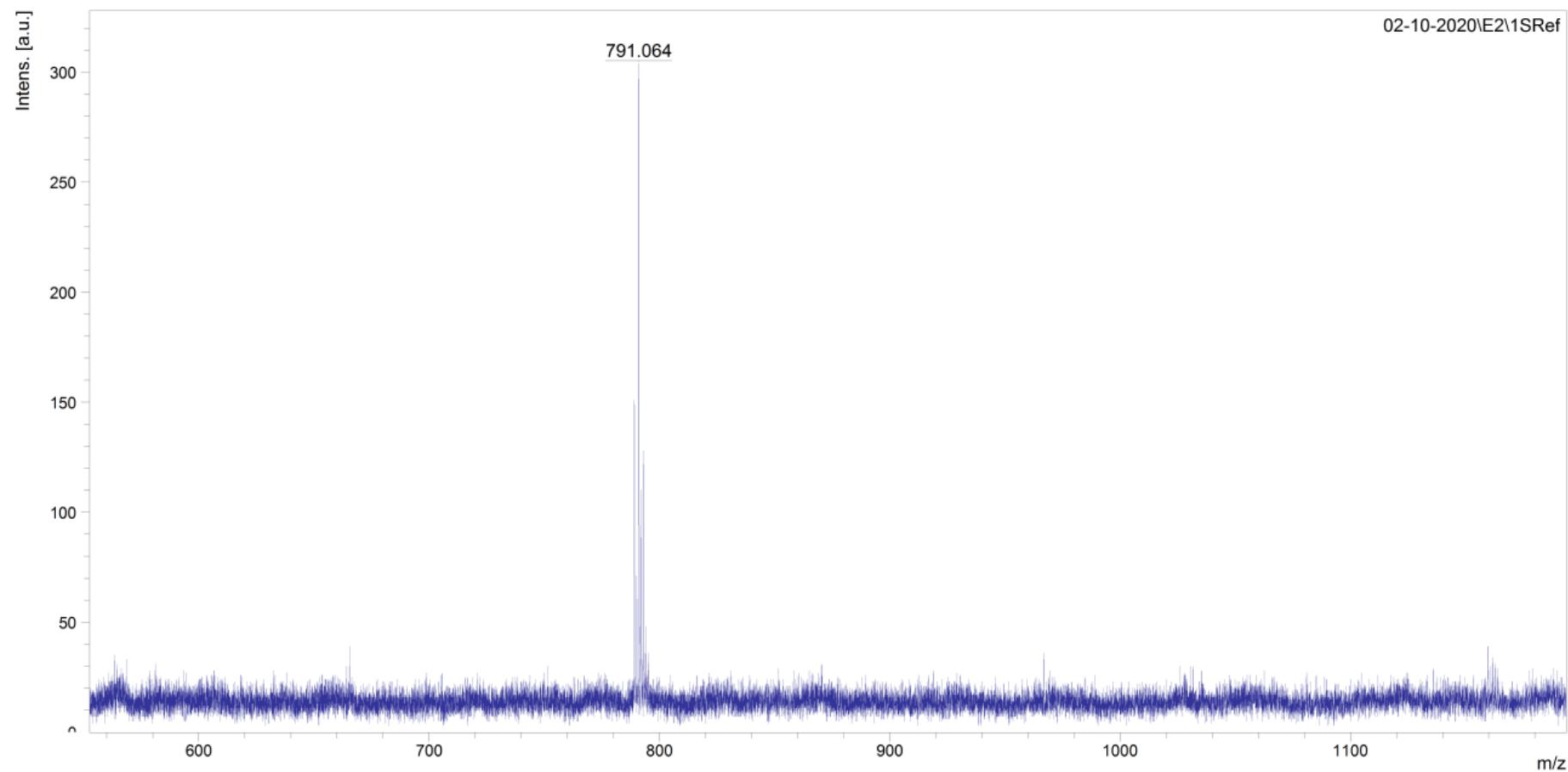
Figure S7. MALDI spectrum of macrocycle **L3**.

2. X-ray analysis data

Table S1. Crystal data and structure refinement details for **L2**·2.75DMF, **L3**·2CHCl₃ and **L3**·3DMF.

|	**L2·2.75DMF**	**L3·2CHCl₃**	**L3·3DMF**
a, Å	10.9660(11)	13.3836(3)	21.7930(10)
b, Å	14.2860(14)	14.7558(4)	13.8810(10)
c, Å	15.1070(15)	22.1736(5)	15.4230(10)
α, °	69.625(10)	90.0	90.0
β, °	79.528(11)	105.844(3)	90.0
γ, °	69.554(10)	90.0	90.0
V, Å³	2074.0(4)	4212.61(19)	4665.6(5)
Z	2	4	4
Sp. gr.	P-1	P2₁/c	Pbcn
λ, Å	0.75270	1.54186	0.71073
T, K	100	295	295
Θ_{max}, °	30.981	67.686	25.995
$N_{measured}$	30844	32127	58030
$N_{averaged}$/N(I>2σ)	10892 / 7534	7363 / 3592	4580 / 2064
R_{int}	0.0479	0.0813	0.1352
R (I>2σ)	0.0580	0.0476	0.0866
wR² (all)	0.1634	0.1262	0.1581
GoF	1.052	0.830	1.002
Δ_{ϱ}, e Å⁻³	0.596/-0.594	0.445/-0.248	0.238/-0.201
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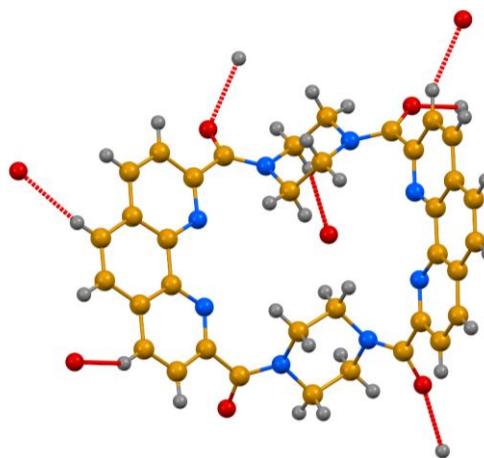
Figure S8. The C-H...O hydrogen bonds formed by **L2** molecule in **L2**·2.75DMF
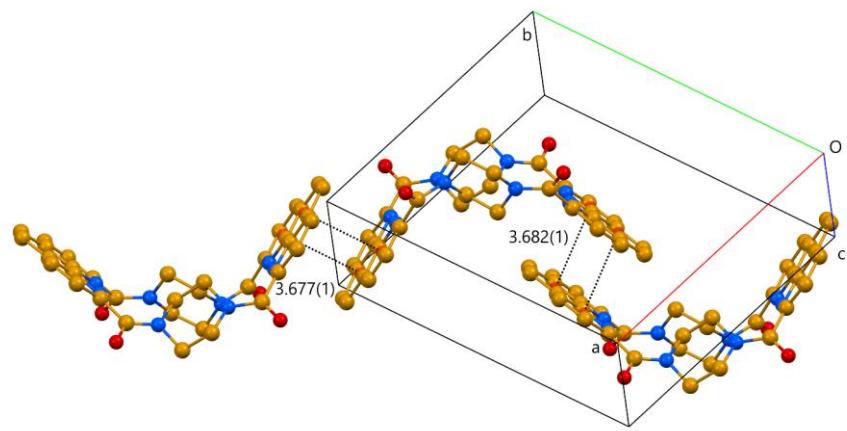
Figure S9. Stacking interactions in **L2**·2.75DMF.
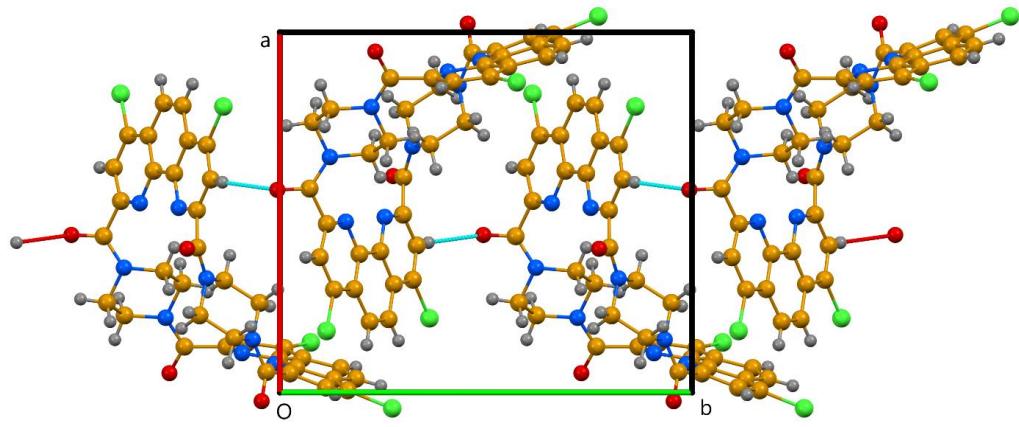
**Figure S10**. Chains of hydrogen-bonded **L3** molecules in **L3**·2CHCl$_3$.
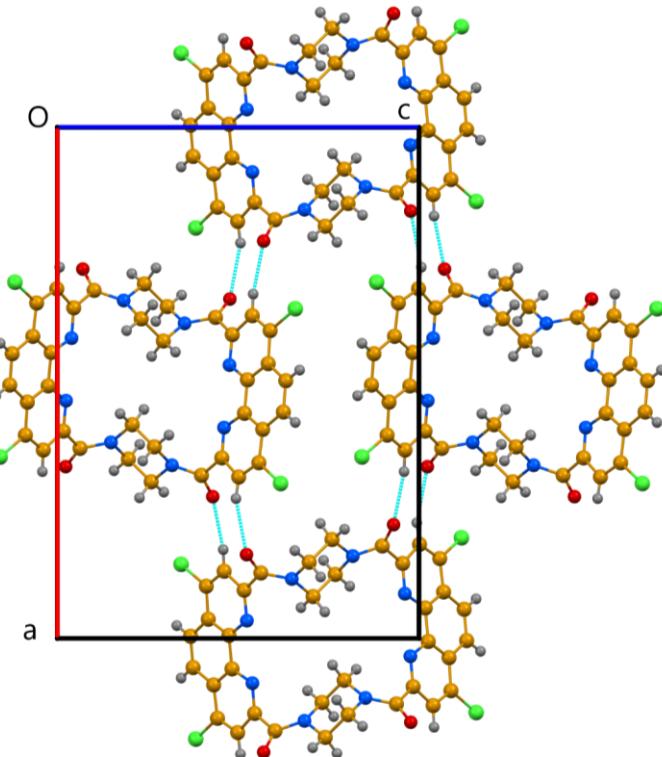
**Figure S11**. Layers of hydrogen-bonded **L3** molecules in **L3**·3DMF.
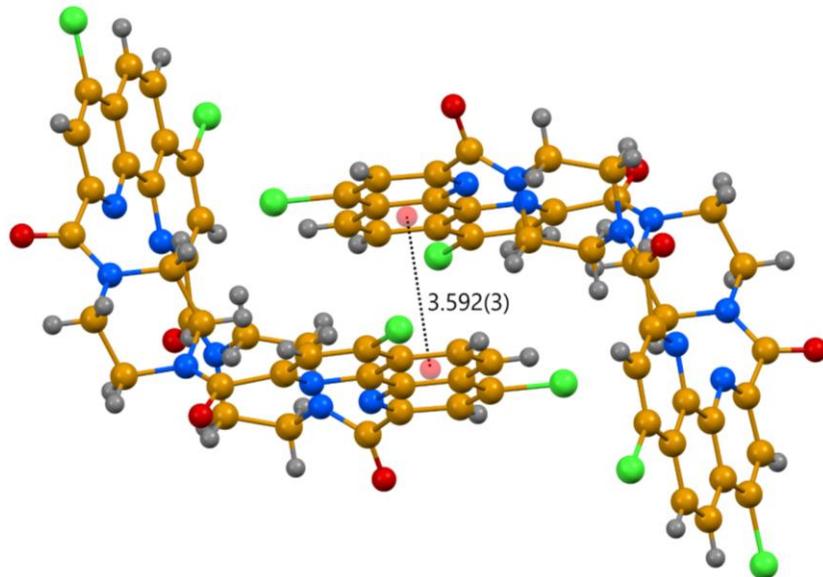
Figure S12. Stacking dimers in **L3**·3DMF.

Table S2. Non-classic C-H...O hydrogen bonds in the structures **L2**·2.75DMF, **L3**·2CHCl₃ and **L3**·3DMF.

C-H⋯O contact, symmetry operation	C-H, Å	H⋯O, Å	C⋯O, Å	∠ C-H⋯O, °
L2·2.75DMF				
C15-H15B⋯O1A(1-x,2-y,1-z)	0.99	2.24	3.180(2)	159
C8A-H8A⋯O1(1-x,2-y,1-z)	0.95	2.41	3.281(2)	153
C7-H7⋯O2A(x,-1+y,z)	0.95	2.41	3.267(3)	150
L3·2CHCl₃				
C3-H3..O2(1-x,1/2+y,3/2-z)	0.93	2.34	3.172(5)	149
L3·3DMF				
C3-H3..O2(-1/2+x,1/2-y,1-z)	0.93	2.29	3.204(6)	167
C8-H8..O1(1/2+x,1/2-y,1-z)	0.93	2.42	3.310(6)	162

3. DLS cumulative fits

Figure captions indicate conditions: solvent, ultrasonic treatment, presence of pentafluorobenzoic acid, recrystallisation from ethanol
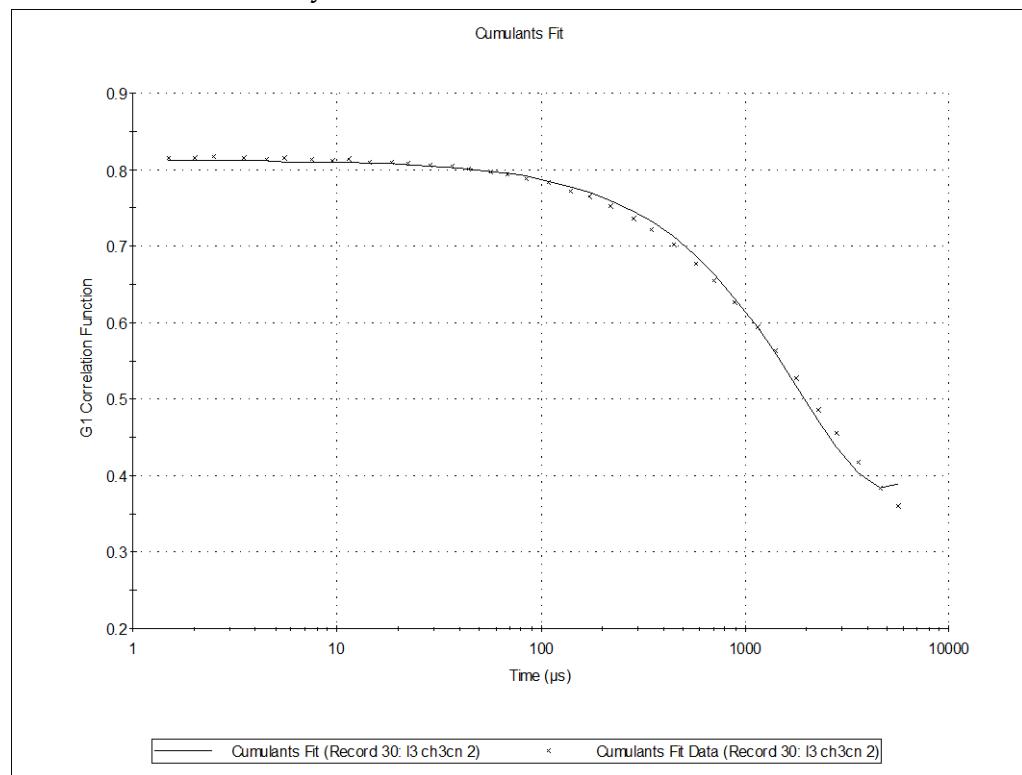
Figure S13. Acetonitrile
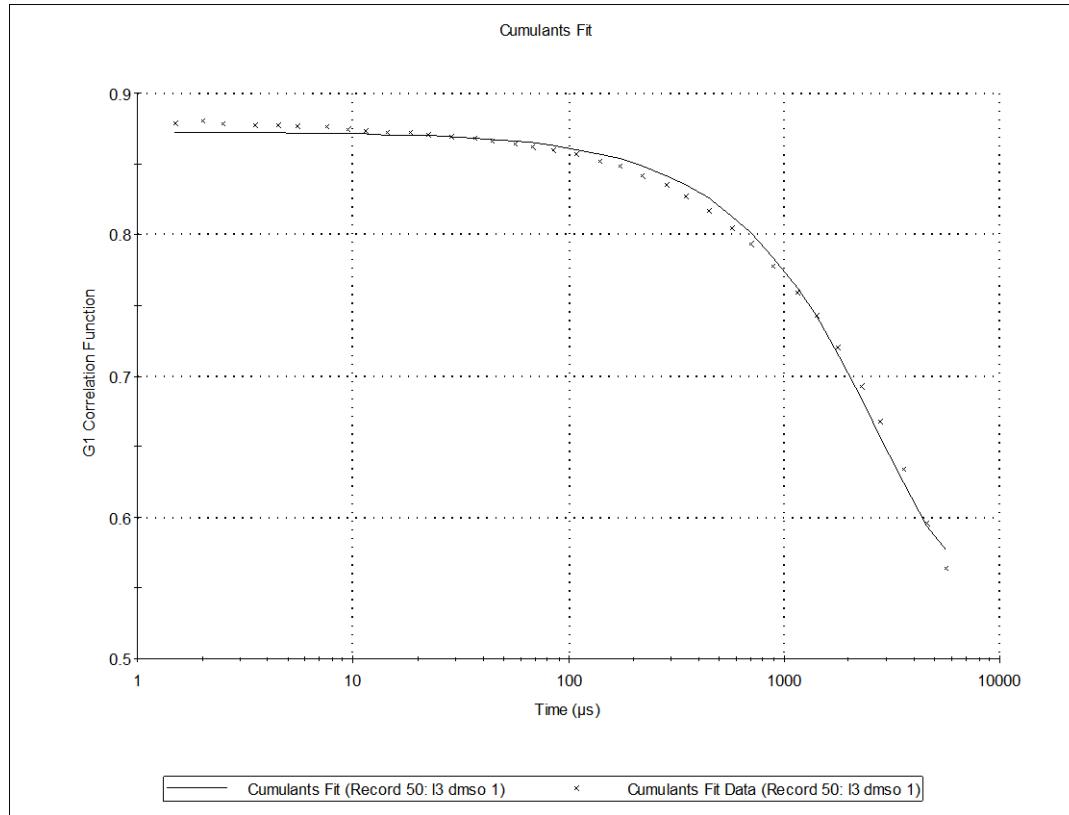
Figure S14. Chloroform
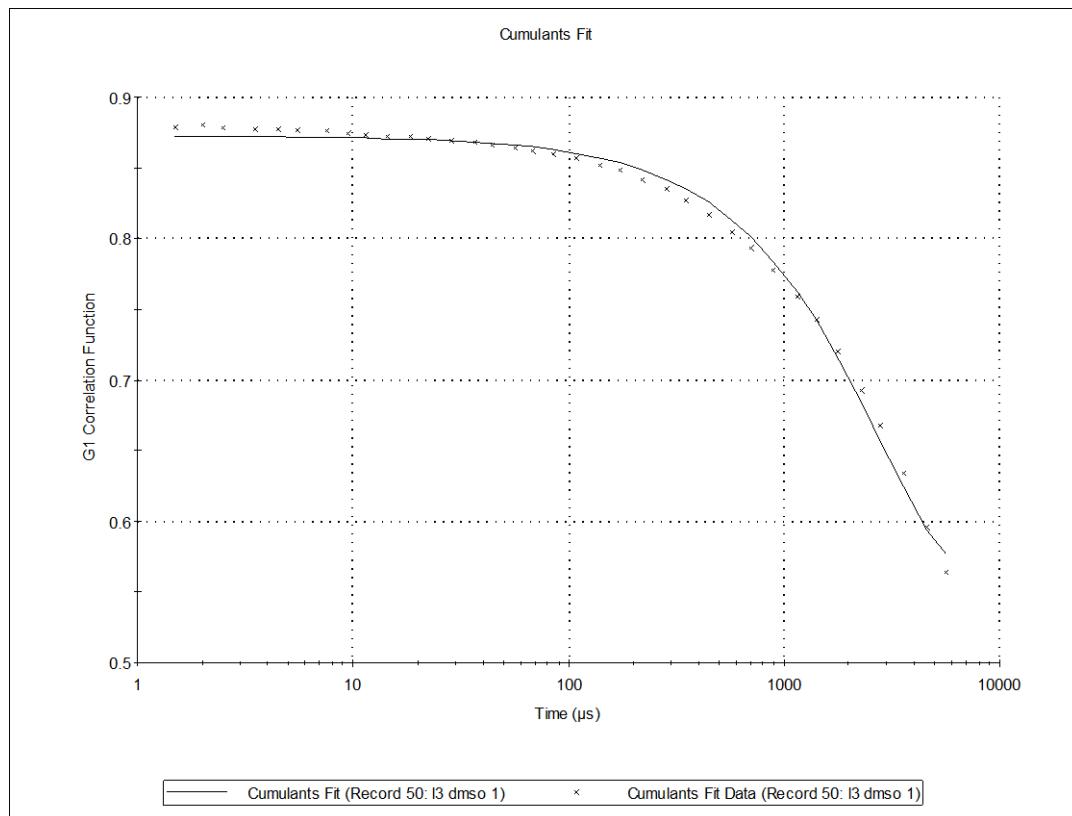
Figure S15. DMSO
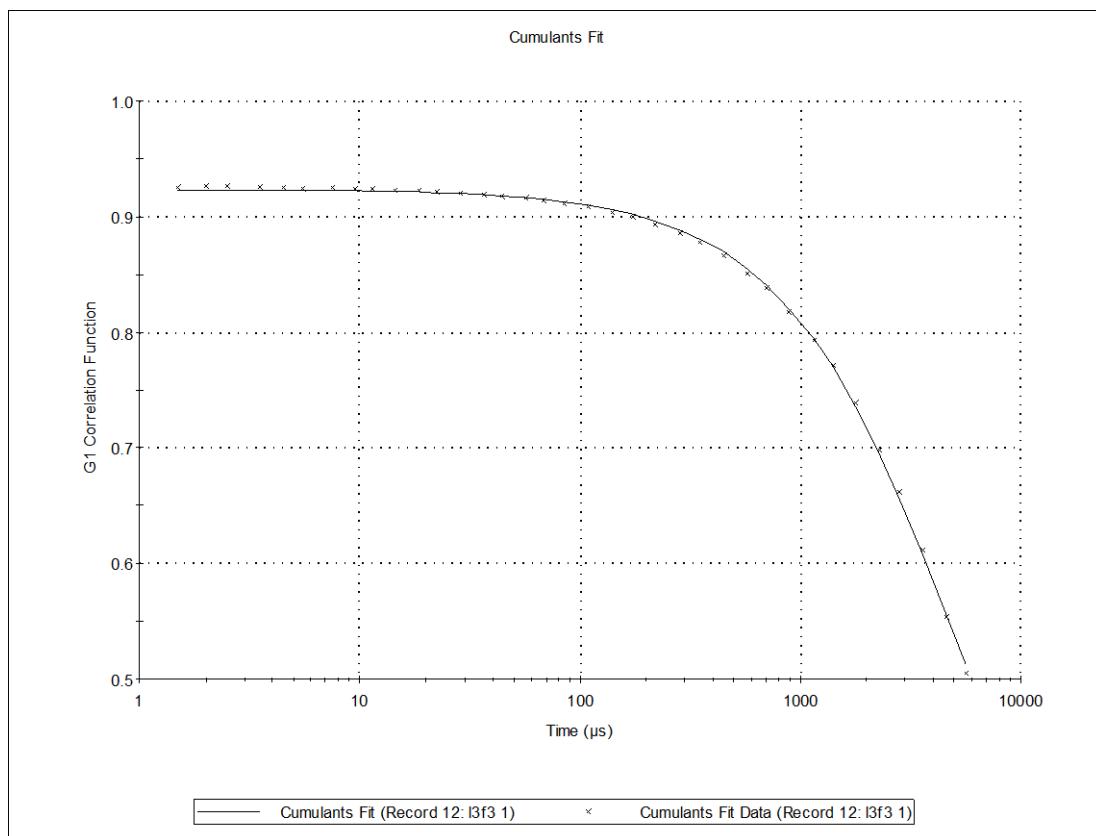
Figure S16. F-3
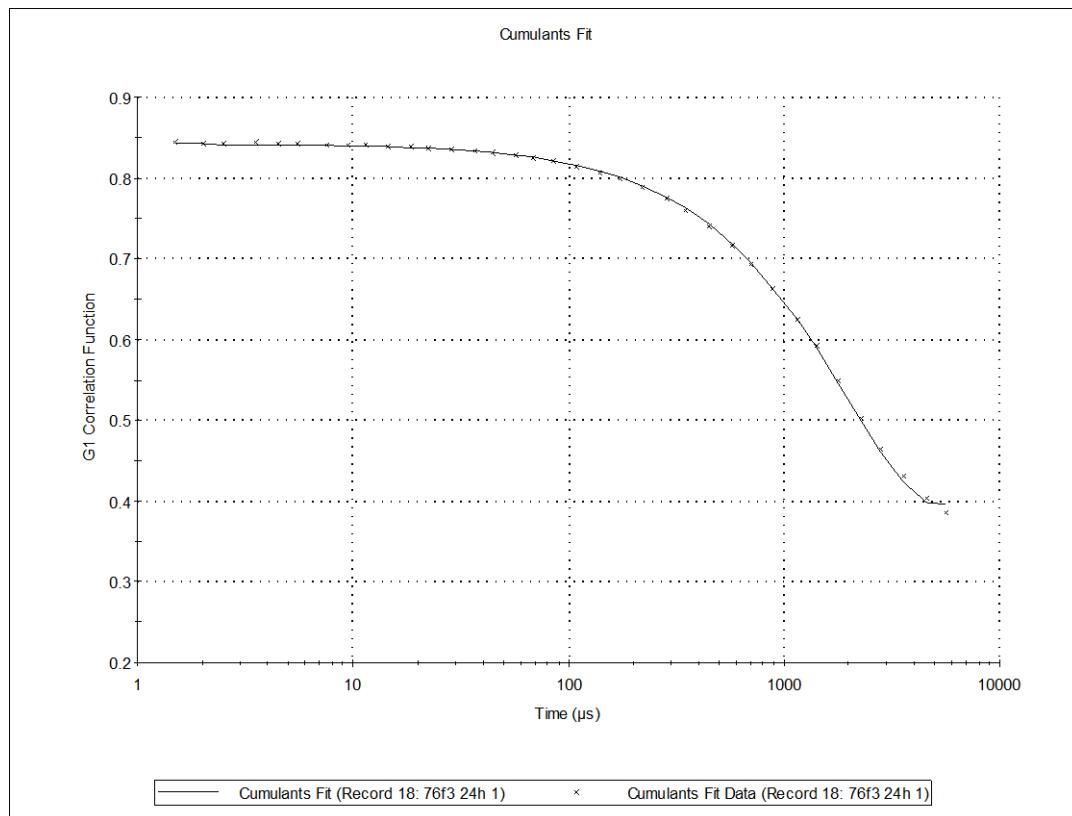
Figure S17. F-3, recrystallisation from ethanol
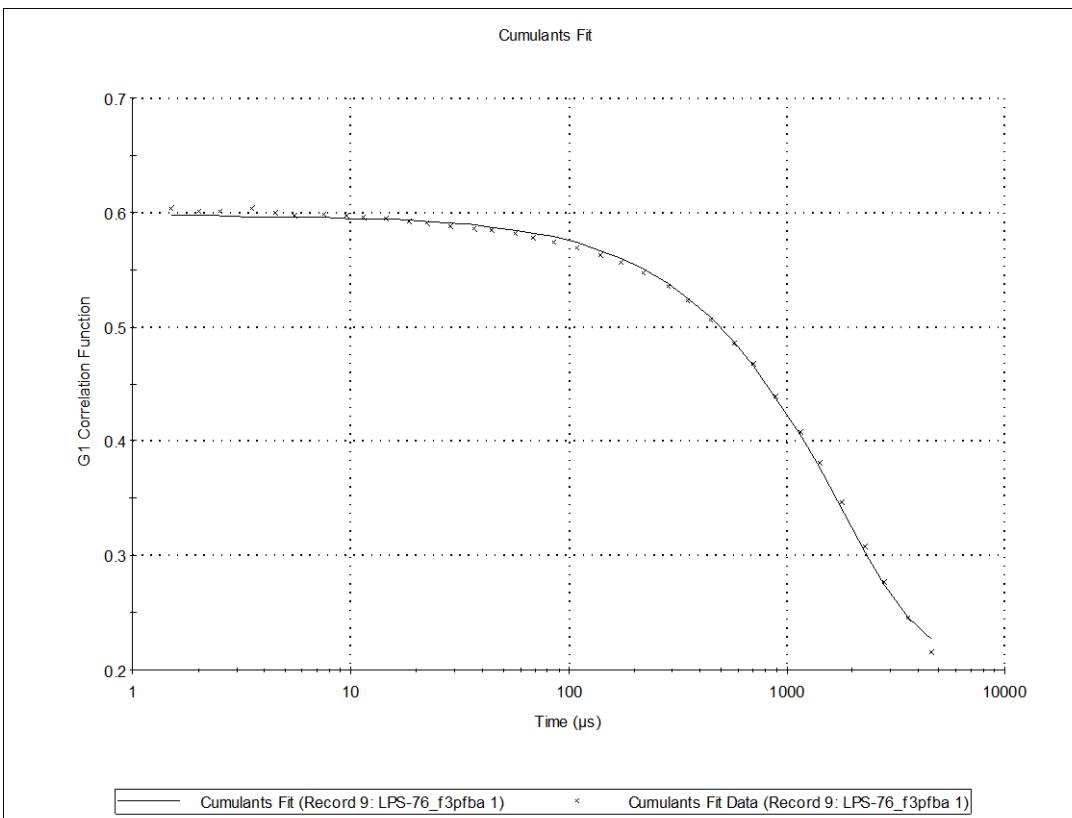
Figure S18. F-3, pentafluorobenzoic acid
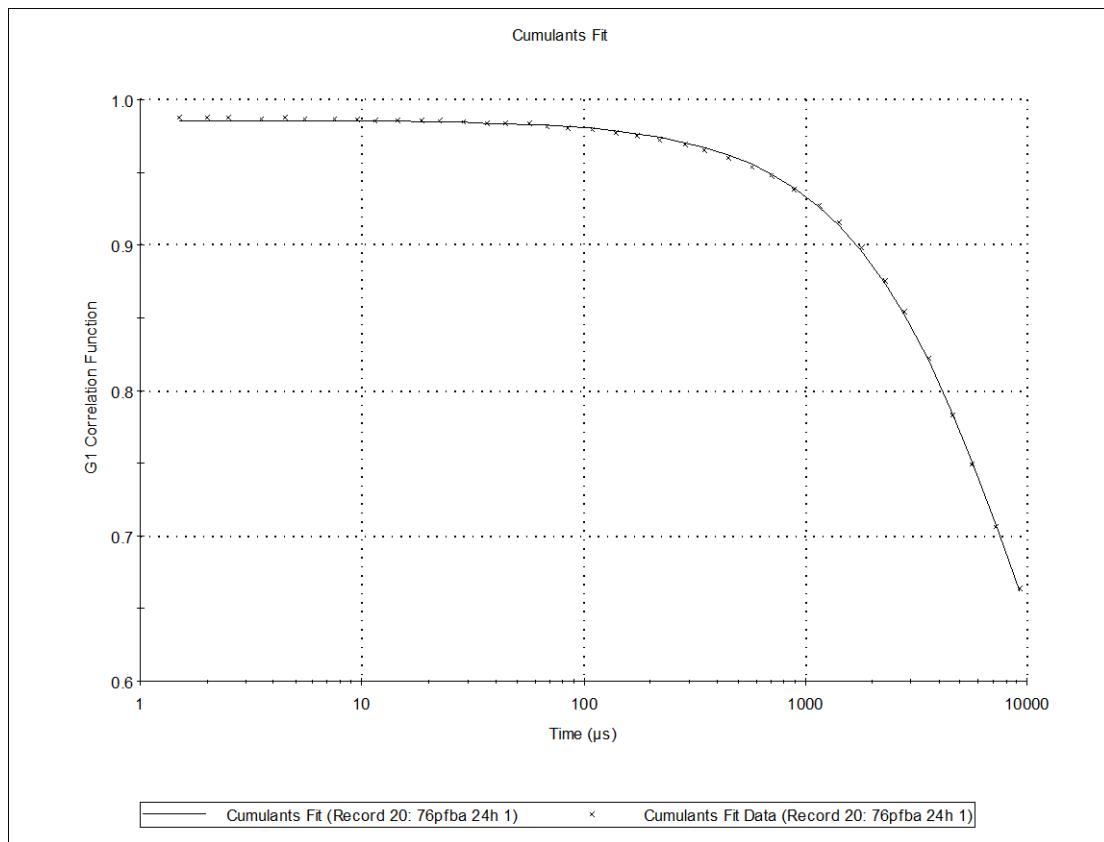
Figure S19. F-3, pentafluorobenzoic acid, recrystallisation from ethanol
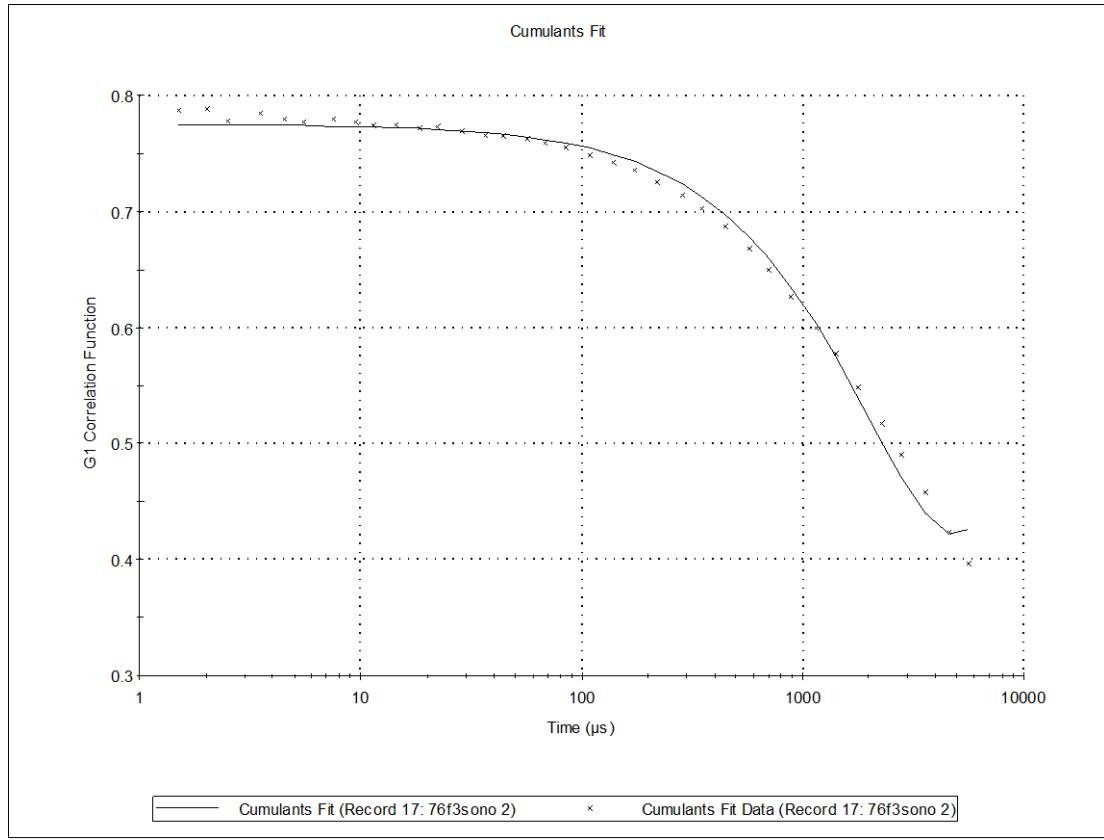
Figure S20. F-3, ultrasonic
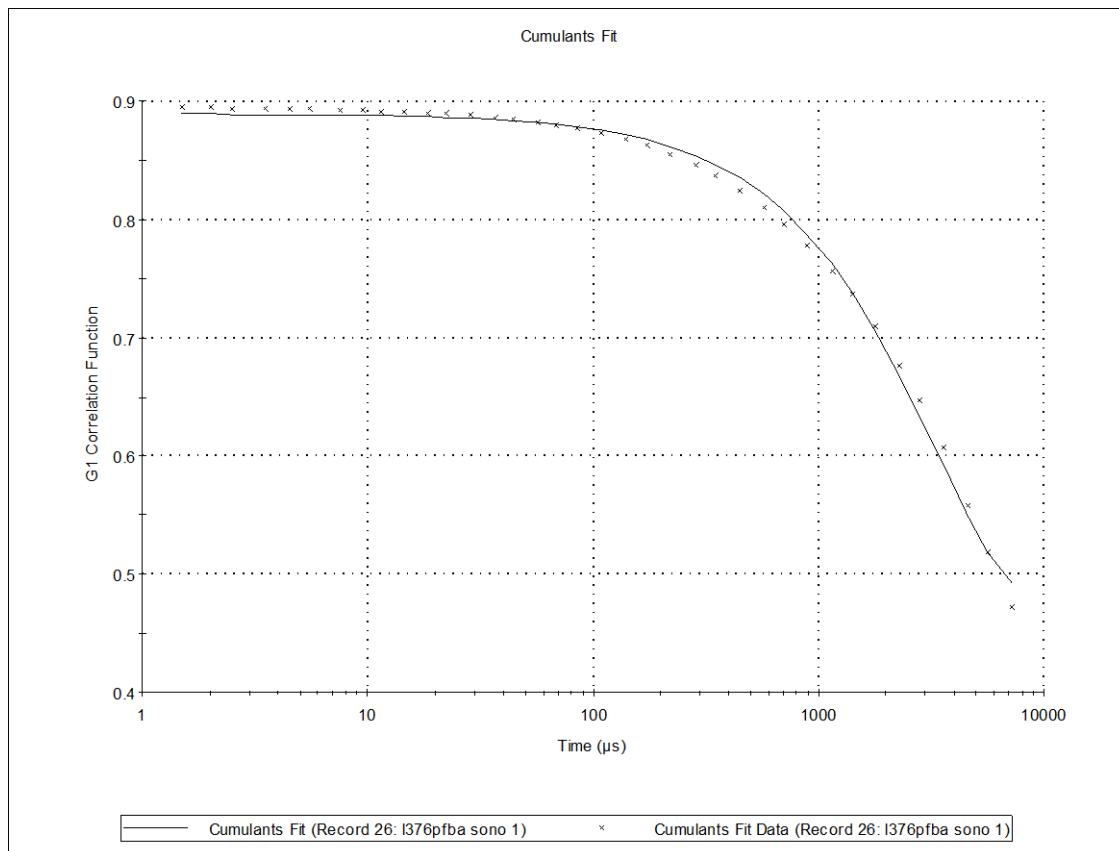
Figure S21. F-3, pentafluorobenzoic acid, ultrasonic
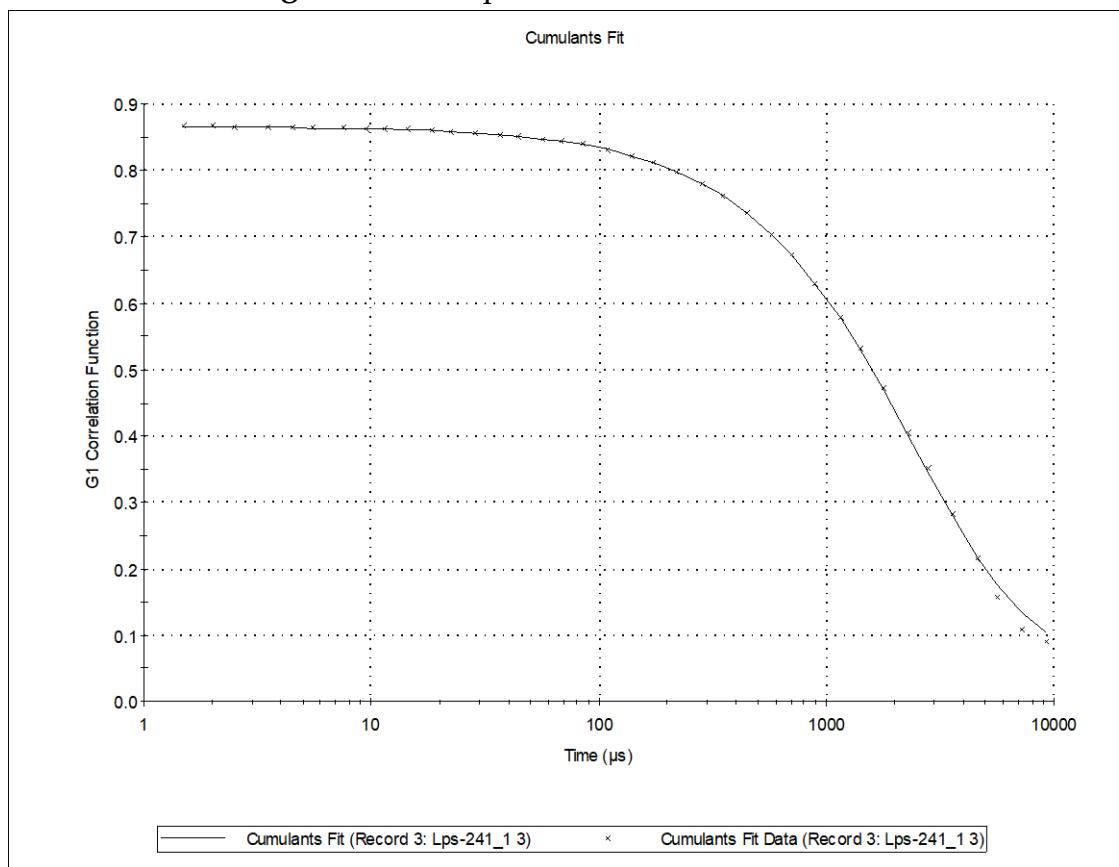
Figure S22. F-3, recrystallization from ethanol
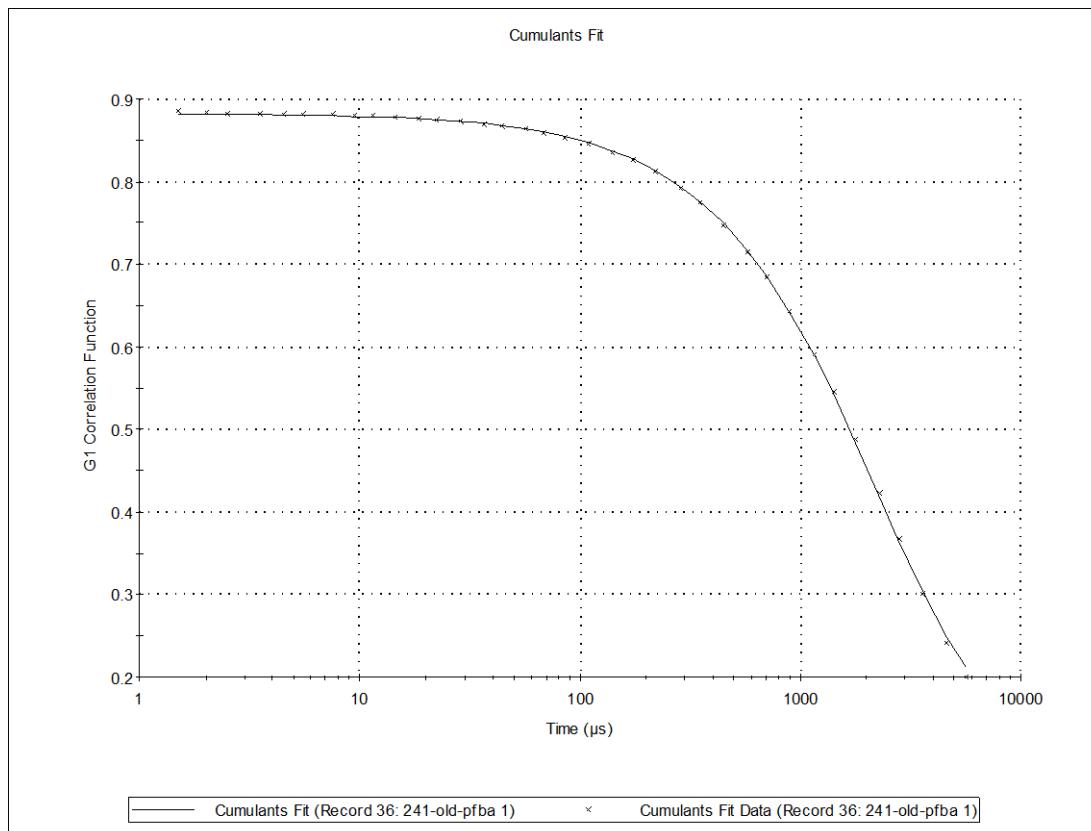
Figure S23. F-3, recrystallization from ethanol, ultrasonic
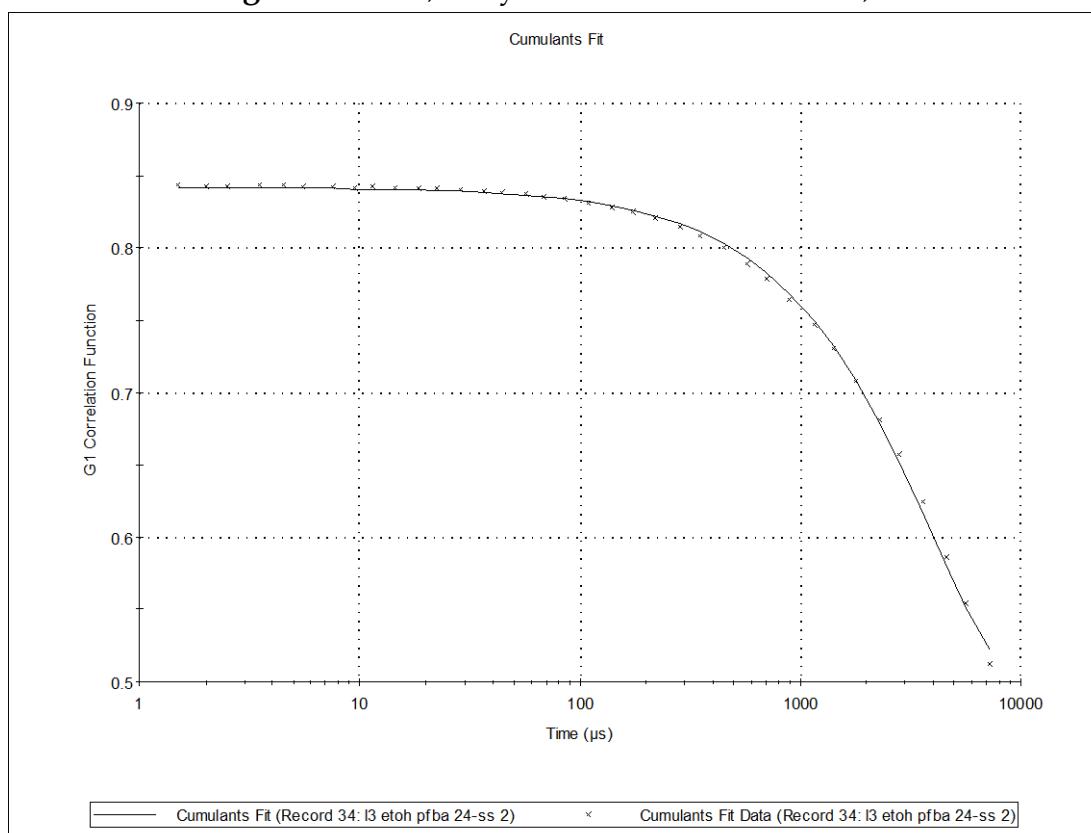
Figure S24. F-3, pentafluorobenzoic acid, recrystallization from ethanol
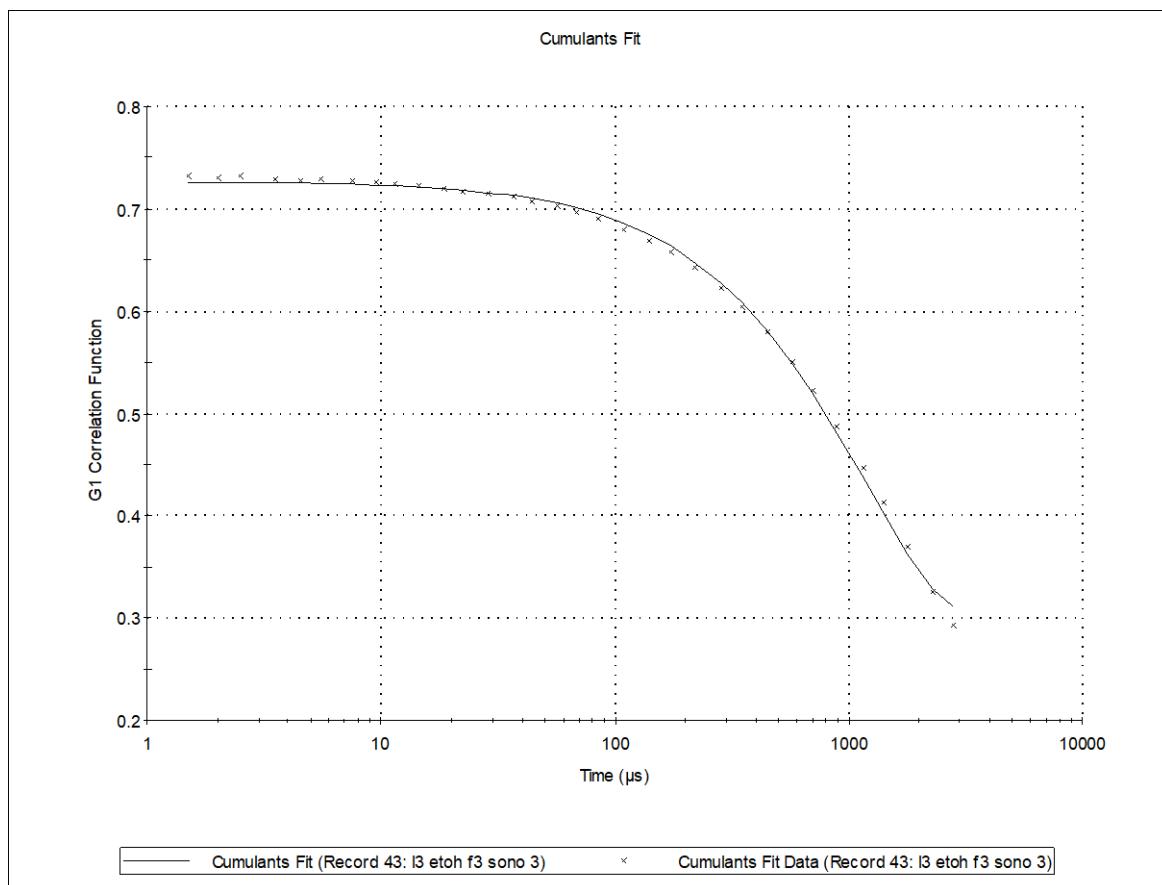
Figure S25. F-3, pentafluorobenzoic acid, recrystallization from ethanol, ultrasonic

4. Luminescence titration data
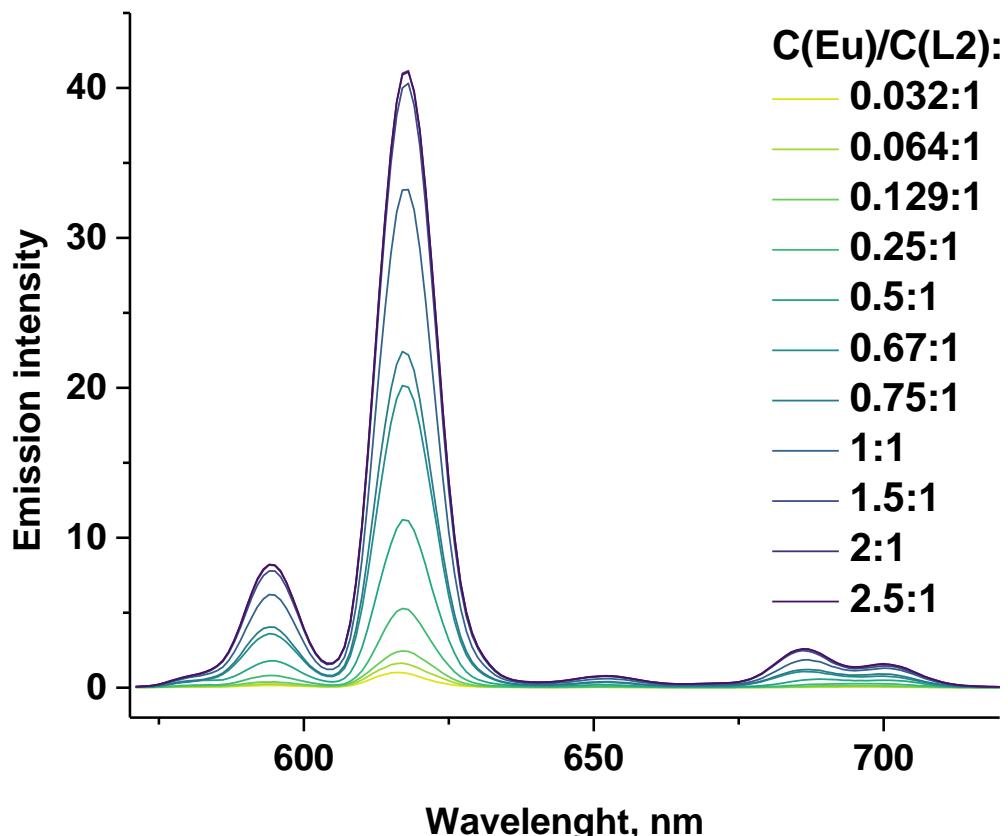
Figure S26. General view of the fluorescence spectra of europium complexes when excited at 300 nm.

5. Computation data

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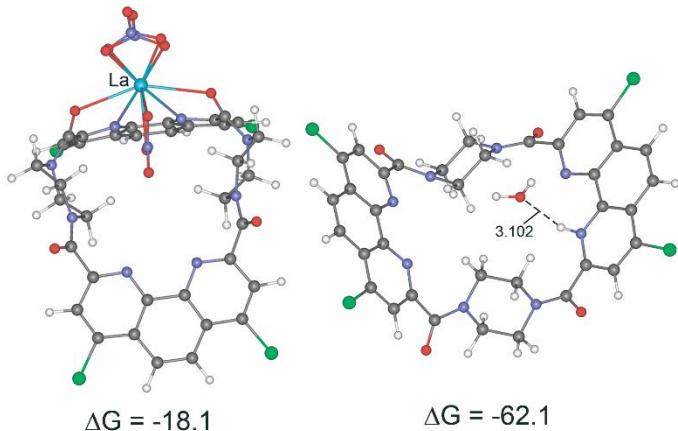
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6	-6.46977944	-1.84404465	-0.80330954
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6	-6.61965642	-1.22304863	0.40409028
1	-7.60433891	-0.88980166	0.73591077
6	-5.50688623	-1.02529789	1.27402787
6	-5.61916002	-0.46297342	2.57483467
6	-4.51246989	-0.37925698	3.39081835
1	-4.57492716	-0.02716165	4.42035782
6	-3.26749227	-0.79536084	2.87138966
6	-4.19707891	-1.42978360	0.86886693
6	-4.03501204	-2.08159904	-0.42868253
6	-2.11744622	-0.81324309	3.86842887
6	0.26344675	-0.81022188	4.38517900
1	1.03204233	-1.49358865	3.98373091
1	-0.16438156	-1.23064327	5.30614599
6	0.87306615	0.56072473	4.67643014
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1	1.78195641	0.47670367	5.28843477
6	0.18170356	1.32284181	2.42358856
1	0.57242758	1.73402334	1.48274048
1	-0.62301972	1.98330725	2.80086220
6	-0.40579746	-0.07438570	2.16004151
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1	0.36606363	-0.71037489	1.68677566
6	2.43637572	1.90368748	3.39047929
8	3.26553446	1.90417021	4.29696252
8	4.36844480	-1.62586705	-2.56425776
8	0.04252513	1.77045963	-1.06306493
1	-0.11837480	2.67656614	-1.38381269
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