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Xanthanoltrimer A-C：Three Xanthanolide Sesquiterpene Trimers from the Fruits of *Xanthium italicum* Moretti by HPLC-MS-SPE-NMR

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Supporting Information

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List of Contents

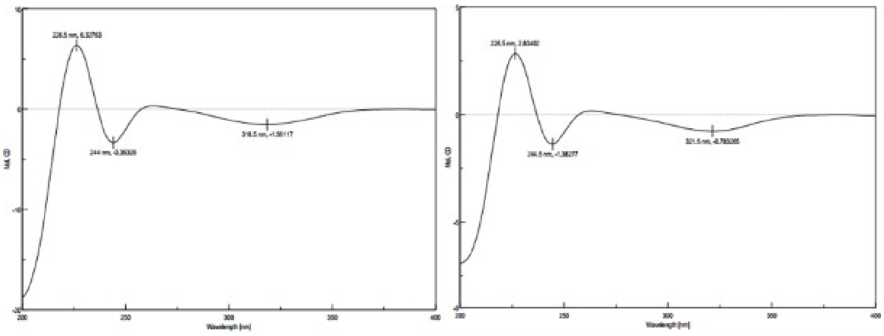

Figure S1. Experimental ECD spectra of Xanthanoltrimer B (**2**) and Xanthanoltrimer A (**1**)

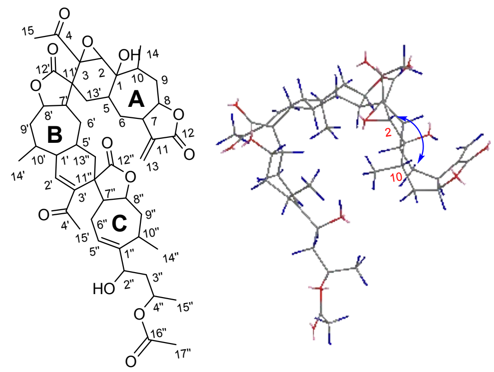

Figure S2. Selected NOESY correlations of compound Xanthanoltrimer C (**3**)

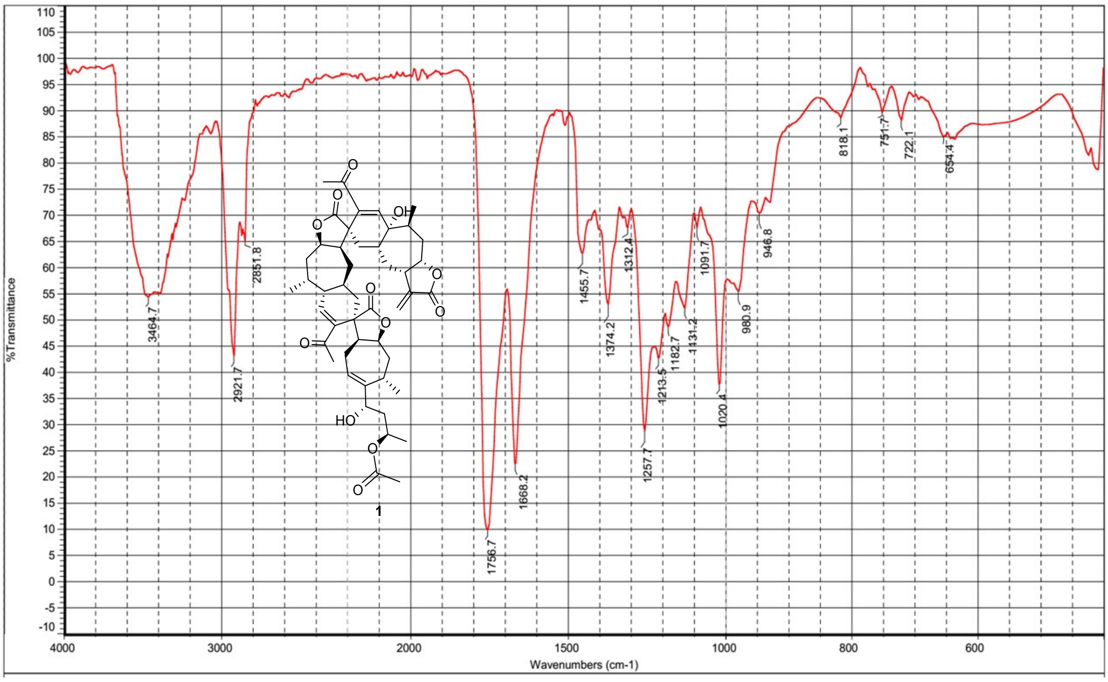

Figure S4. IR spectrum of Xanthanoltrimer A (**1**)

MS Formula Results: + Scan (7.640 min) Sub (2017112401.d)

m/z	Ion	Formula	Abundance
839.397	(M+Na)+	C47 H60 Na O12	567225.2

Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
✓	C47 H60 O12	C47 H60 Na O12	99.89		816.4078	816.4085	839.3977	0.83	0.83	99.98	99.69	99.95	18
	C48 H56 N4 O8	C48 H56 N4 Na O8	99.67		816.4078	816.4098	839.399	2.45	2.45	99.79	99.23	99.96	23
	C42 H60 N2 O14	C42 H60 N2 Na O14	99.54		816.4078	816.4045	839.3937	-4.11	4.11	99.42	99.39	99.97	14
	C51 H60 O7 S	C51 H60 Na O7 S	99.34		816.4078	816.406	839.3952	-2.25	2.25	99.83	97.98	99.99	22
	C39 H64 N2 O14 S	C39 H64 N2 Na O14 S	99.29		816.4078	816.4078	839.397	0	0	100	97.55	99.96	9
	C52 H56 N4 O3 S	C52 H56 N4 Na O3 S	99.25		816.4078	816.4073	839.3965	-0.63	0.63	99.99	97.4	99.99	27
	C44 H64 O12 S	C44 H64 Na O12 S	99.23		816.4078	816.4118	839.4011	4.94	4.94	99.16	98.71	99.98	13
	C45 H60 N4 O8 S	C45 H60 N4 Na O8 S	99.03		816.4078	816.4132	839.4024	6.56	6.56	98.53	99.09	99.98	18
	C46 H60 N2 O9 S	C46 H60 N2 Na O9 S	98.85		816.4078	816.402	839.3912	-7.19	7.19	98.23	98.93	99.98	18
	C54 H56 O7	C54 H56 Na O7	98.65		816.4078	816.4026	839.3918	-6.36	6.36	98.62	97.63	99.94	27
	C35 H64 N2 O19	C35 H64 N2 Na O19	98.6		816.4078	816.4103	839.3995	3.09	3.09	99.67	95.67	99.98	5
	C55 H52 N4 O3	C55 H52 N4 Na O3	98.58		816.4078	816.4039	839.3932	-4.75	4.75	99.23	96.37	99.95	32
	C40 H64 O17	C40 H64 Na O17	98.52		816.4078	816.4144	839.4036	8.03	8.03	97.8	98.51	99.97	9
	C48 H64 O7 S2	C48 H64 Na O7 S2	98.48		816.4078	816.4093	839.3986	1.86	1.86	99.88	94.96	99.9	17
	C53 H56 N2 O6	C53 H56 N2 Na O6	98.46		816.4078	816.4138	839.4031	7.39	7.39	98.14	97.75	99.95	27
	C43 H64 N2 O9 S2	C43 H64 N2 Na O9 S2	98.41		816.4078	816.4053	839.3945	-3.08	3.08	99.67	95.11	99.86	13
	C49 H60 N4 O3 S2	C49 H60 N4 Na O3 S2	98.38		816.4078	816.4107	839.3999	3.48	3.48	99.58	95.1	99.9	22
	C57 H56 N2 O S	C57 H56 N2 Na O S	98.3		816.4078	816.4113	839.4006	4.31	4.31	99.36	95.1	100	31
	C41 H60 N4 O13	C41 H60 N4 Na O13	98.28		816.4078	816.4157	839.4049	9.64	9.64	96.85	99.26	99.97	14
	C60 H52 N2 O	C60 H52 N2 Na O	98.19		816.4078	816.408	839.3972	0.19	0.19	100	93.71	99.94	36
	C34 H64 N4 O16 S	C34 H64 N4 Na O16 S	98.06		816.4078	816.4038	839.393	-4.95	4.95	99.16	94.68	99.93	5
	C37 H60 N4 O16	C37 H60 N4 Na O16	97.99		816.4078	816.4004	839.3897	-9.05	9.05	97.21	97.63	99.98	10
	C49 H56 N2 O9	C49 H56 N2 Na O9	97.71		816.4078	816.3986	839.3878	-11.3	11.3	95.69	99.19	99.96	23
	C55 H60 O2 S2	C55 H60 Na O2 S2	97.52		816.4078	816.4035	839.3927	-5.33	5.33	99.03	93	99.95	26
	C36 H68 N2 O14 S2	C36 H68 N2 Na O14 S2	97.38		816.4078	816.4112	839.4004	4.11	4.11	99.42	91.99	99.79	4
	C50 H60 N2 O6 S	C50 H60 N2 Na O6 S	97.37		816.4078	816.4172	839.4064	11.5	11.5	95.54	98.22	99.99	22
	C30 H64 N4 O21	C30 H64 N4 Na O21	97.27		816.4078	816.4063	839.3955	-1.86	1.86	99.88	90.66	99.99	1
	C41 H60 N4 O11 S	C41 H60 N4 Na O11 S	97.25		816.4078	816.3979	839.3872	-12.14	12.14	95.05	98.66	99.96	14
	C38 H64 N4 O11 S2	C38 H64 N4 Na O11 S2	97.17		816.4079	816.4013	839.3905	-8.03	8.03	97.8	93.92	99.8	9
	C58 H56 O2 S	C58 H56 Na O2 S	97.07		816.4078	816.4001	839.3893	-9.44	9.44	96.97	94.79	100	31
	C33 H68 O20 S	C33 H68 Na O20 S	97		816.4078	816.4025	839.3917	-6.55	6.55	98.53	92.01	99.93	0
	C36 H64 O20	C36 H64 Na O20	96.99		816.4078	816.3991	839.3883	-10.66	10.66	96.16	95.88	99.97	5
	C41 H68 O12 S2	C41 H68 Na O12 S2	96.96		816.4078	816.4152	839.4044	9.06	9.06	97.21	94.12	99.85	8
	C54 H60 N2 O S2	C54 H60 N2 Na O S2	96.95		816.4078	816.4147	839.4039	8.42	8.42	97.58	93.41	99.94	26
	C42 H64 N4 O8 S2	C42 H64 N4 Na O8 S2	96.8		816.4078	816.4166	839.4058	10.67	10.67	96.15	95.35	99.84	13
	C32 H68 N2 O19 S	C32 H68 N2 Na O19 S	96.79		816.4078	816.4137	839.4029	7.19	7.19	98.23	91.78	99.92	0

page 1

Figure S5. (+)-HRESIMS data of Xanthanoltrimer A (**1**)

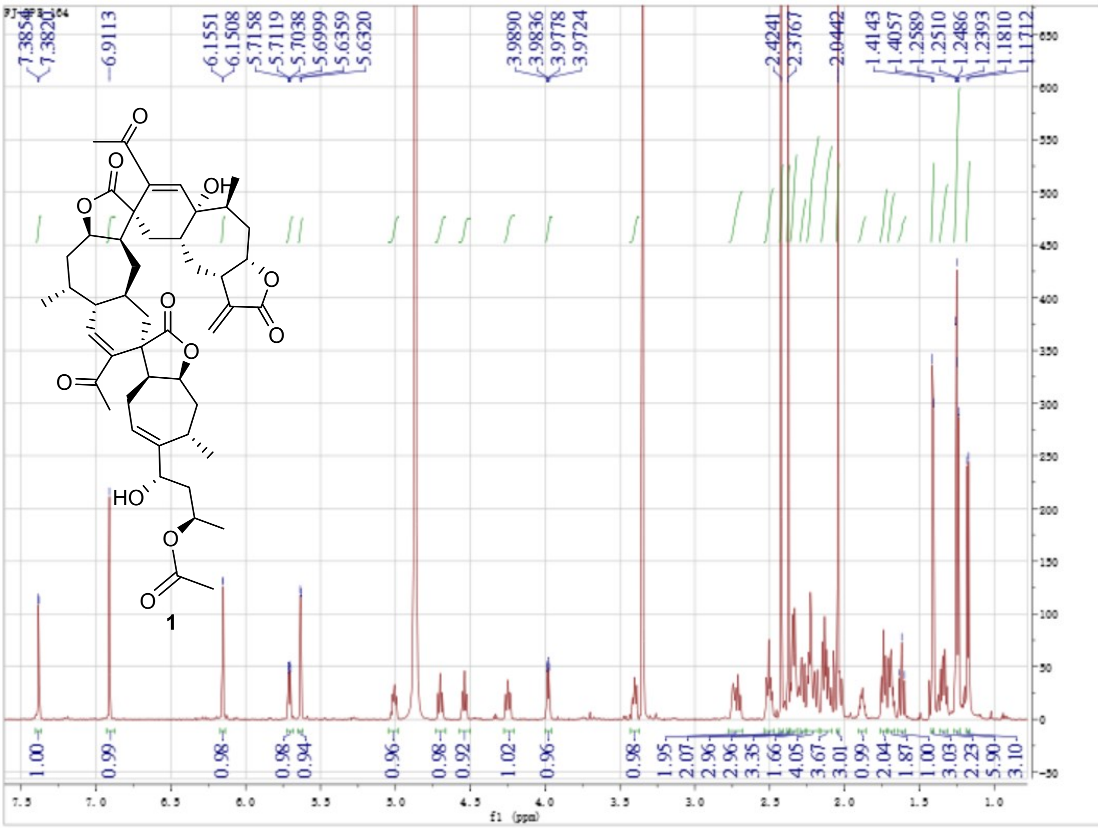

Figure S6. ^{1}H NMR spectrum of Xanthanoltrimer A (**1**) (800 MHz, in CD_3OD)

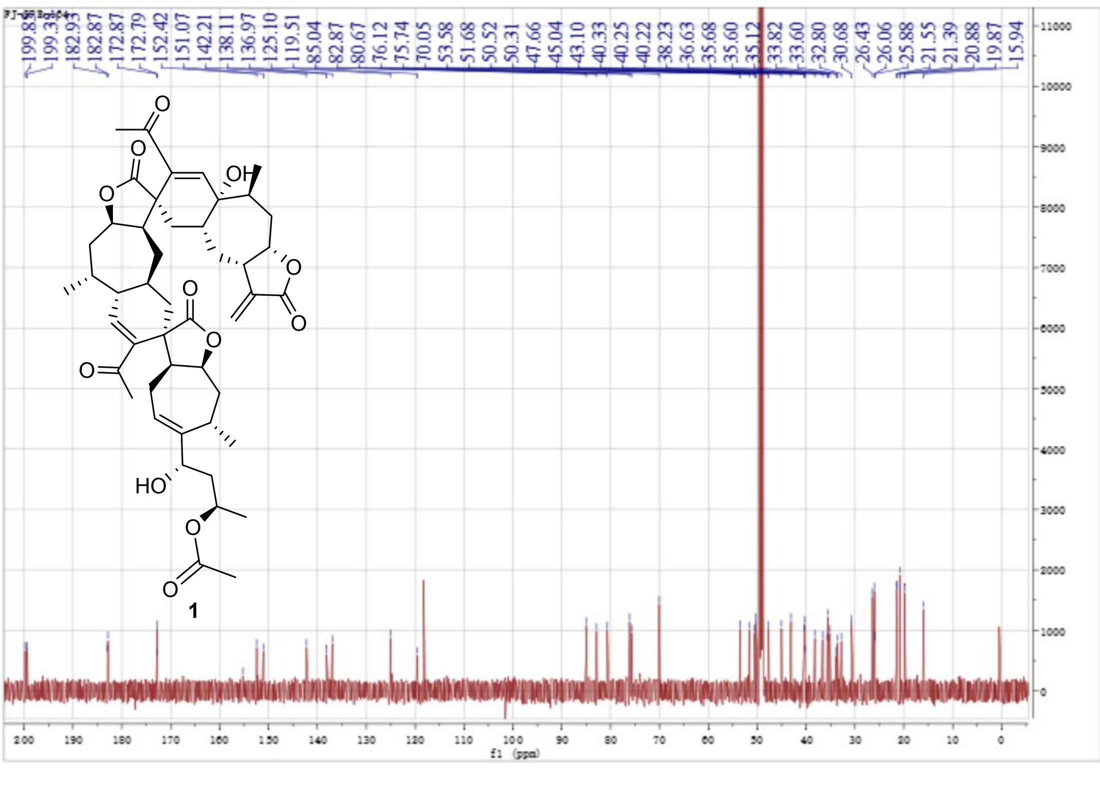

Figure S7. ^{13}C NMR spectrum of Xanthanoltrimer A (**1**) (200 MHz, in CD_3OD)

Figure S8. DEPT spectrum of Xanthanoltrimer A (**1**) (150 MHz, in CD_3OD)

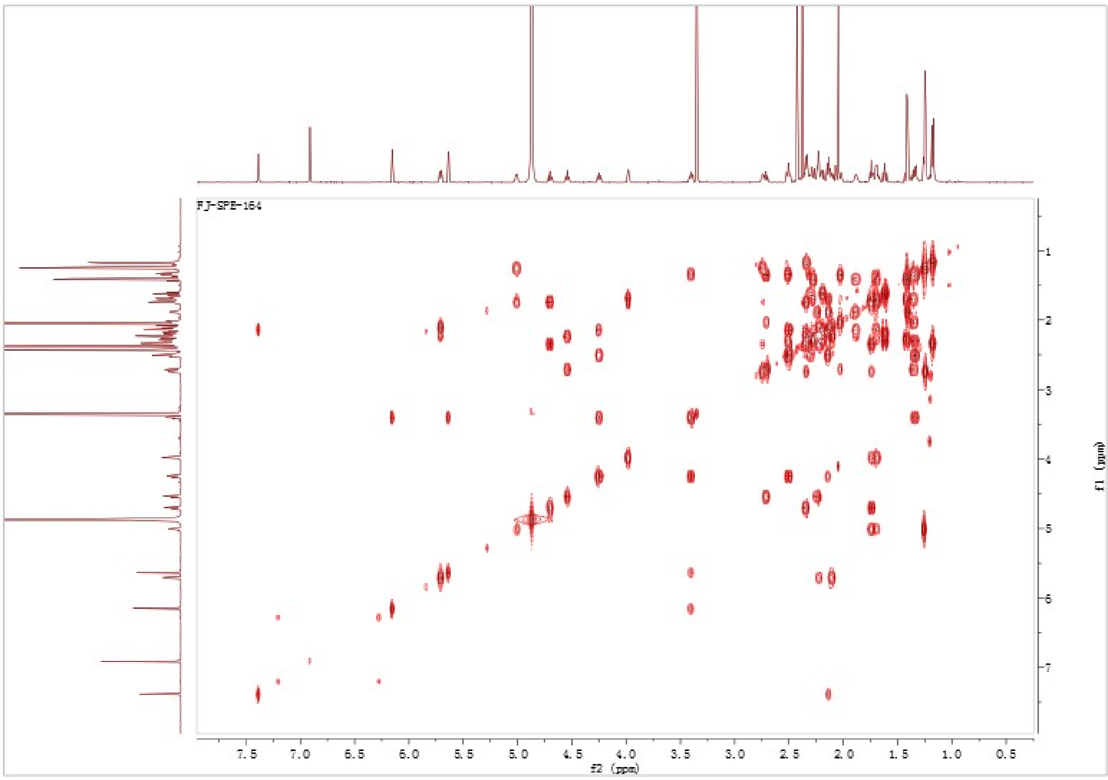

Figure S9. ^1H-^1H COSY spectrum of Xanthanoltrimer A (**1**)

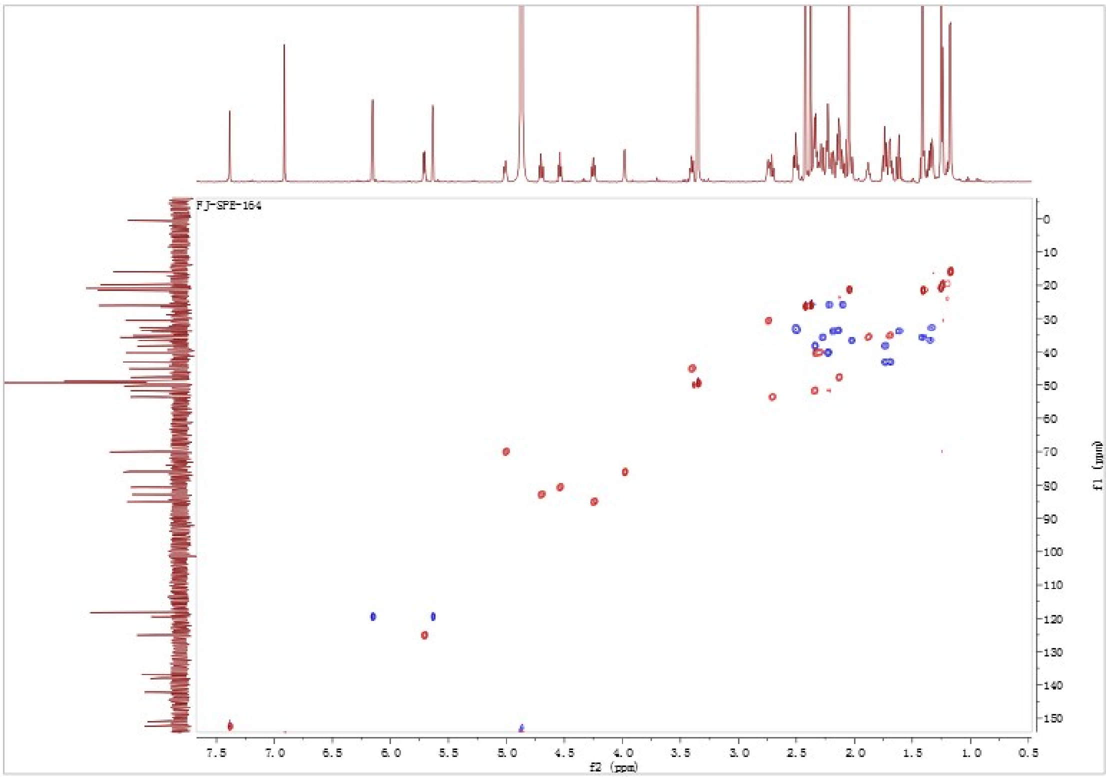

Figure S10. HSQC spectrum of Xanthanoltrimer A (**1**)

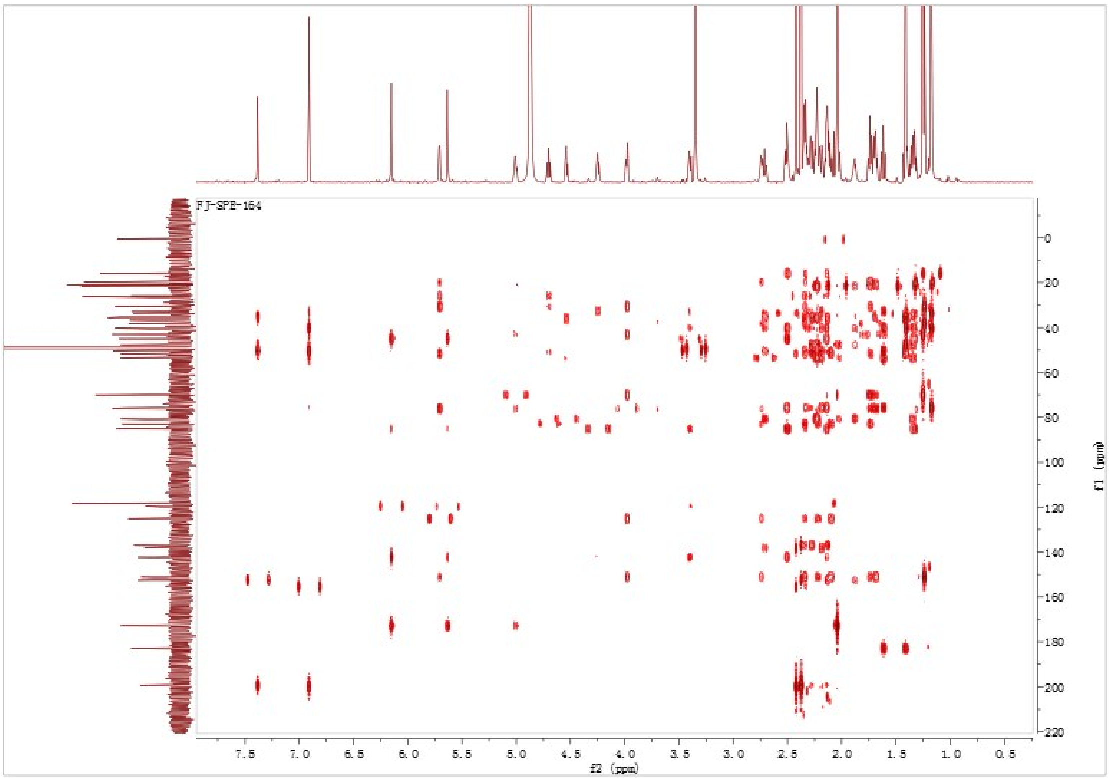

Figure S11. HMBC spectrum of Xanthanoltrimer A (**1**)

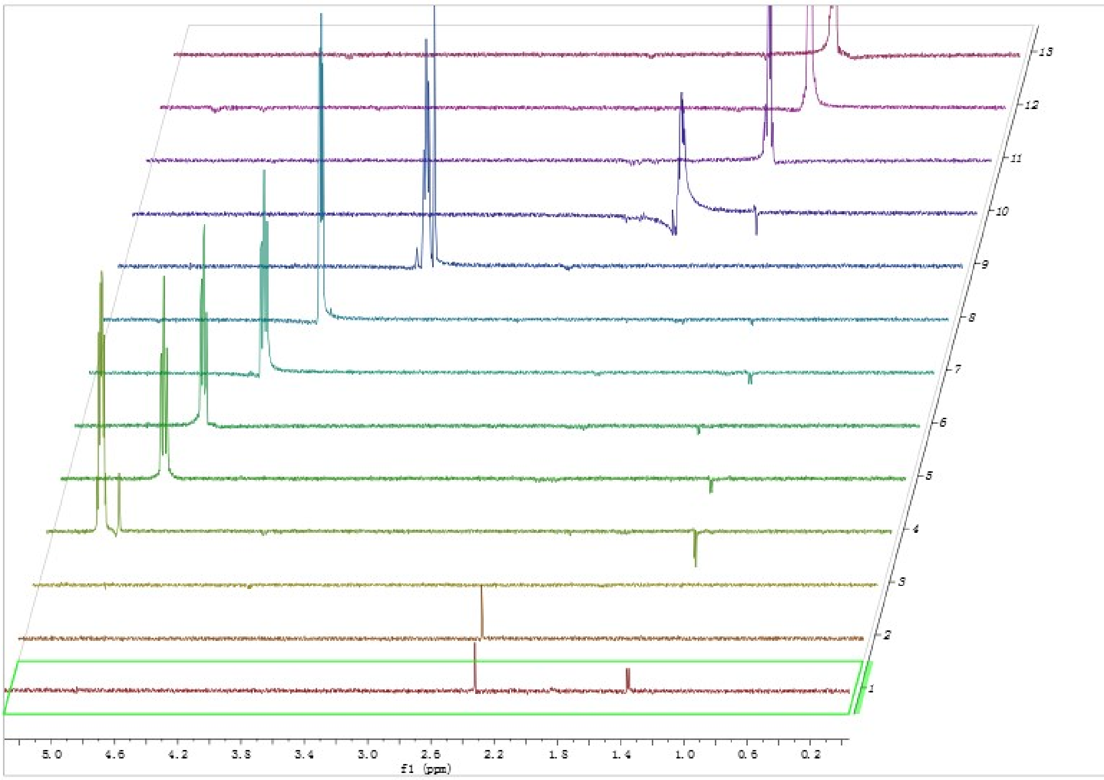

Figure S12. NOE spectrum of Xanthanoltrimer A (**1**) (600 MHz, in CD_3OD)

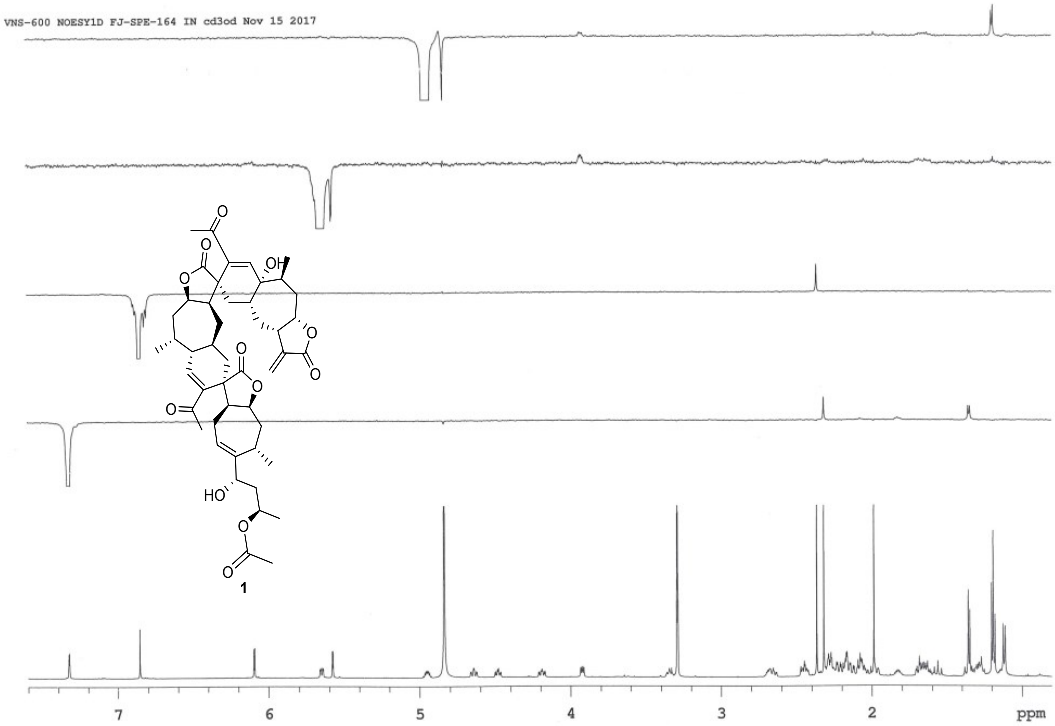

Figure S13. NOE spectrum of Xanthanoltrimer A (**1**) (600 MHz, in CD_3OD)

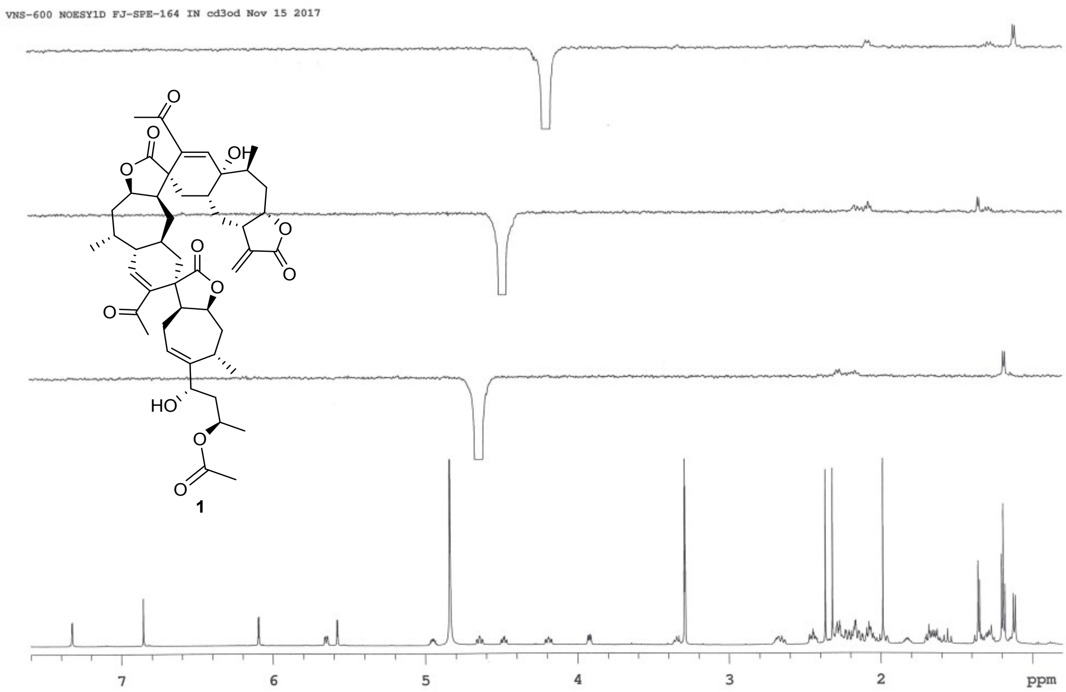

Figure S14. NOE spectrum of Xanthanoltrimer A (**1**) (600 MHz, in CD_3OD)

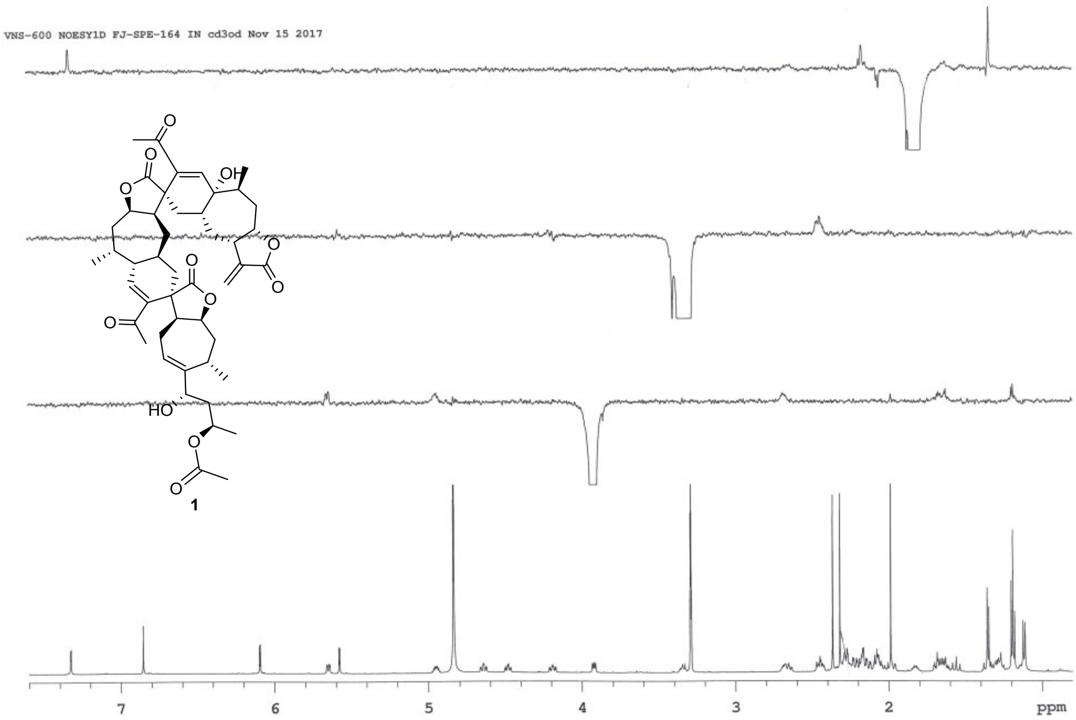

Figure S15. NOE spectrum of Xanthanoltrimer A (**1**) (600 MHz, in CD_3OD)

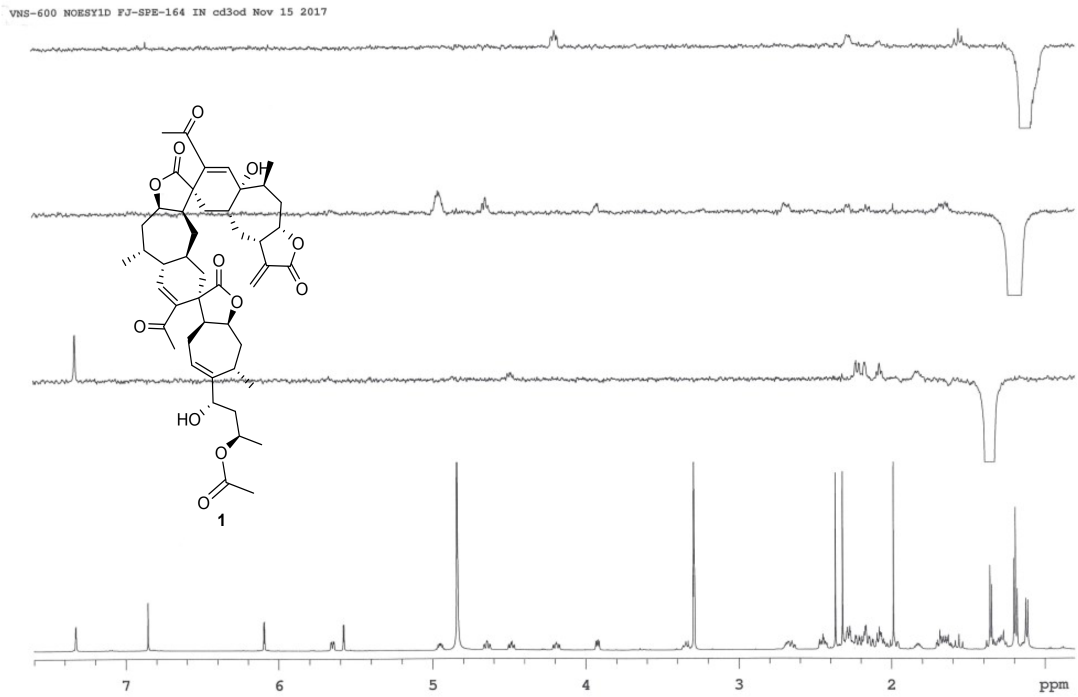

Figure S16. NOE spectrum of Xanthanoltrimer A (**1**) (600 MHz, in CD_3OD)

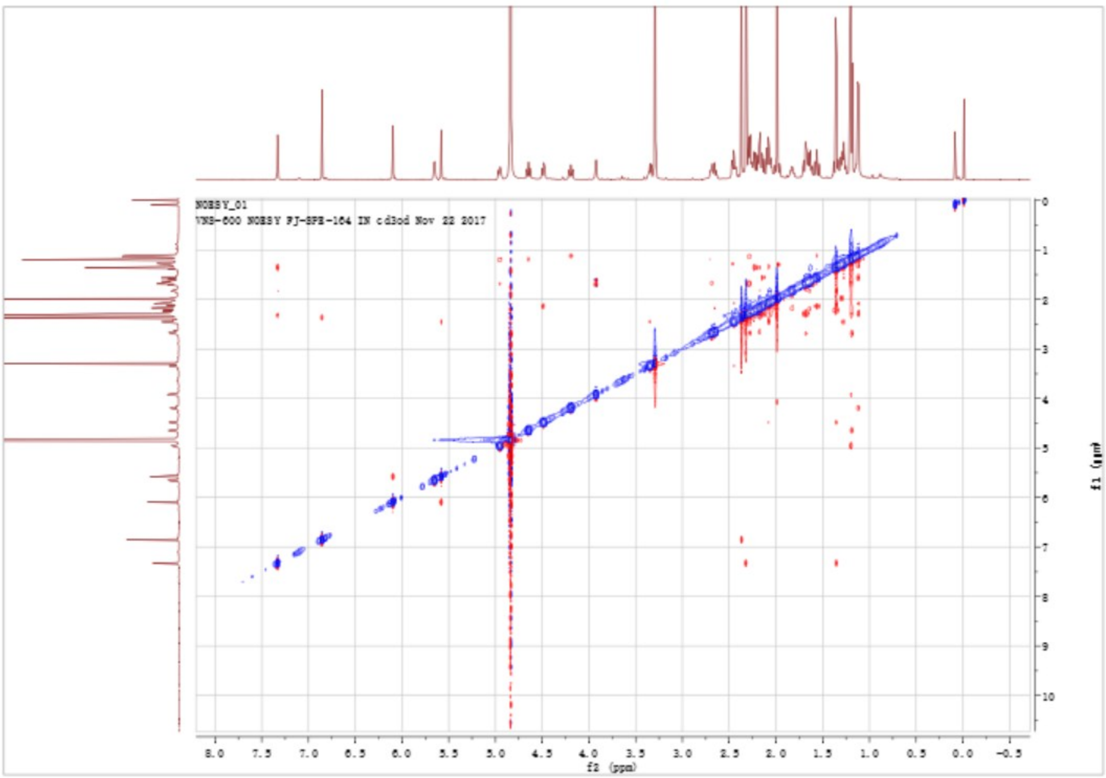

Figure S17. NOESY spectrum of Xanthanoltrimer A (**1**) (600 MHz, in CD_3OD)

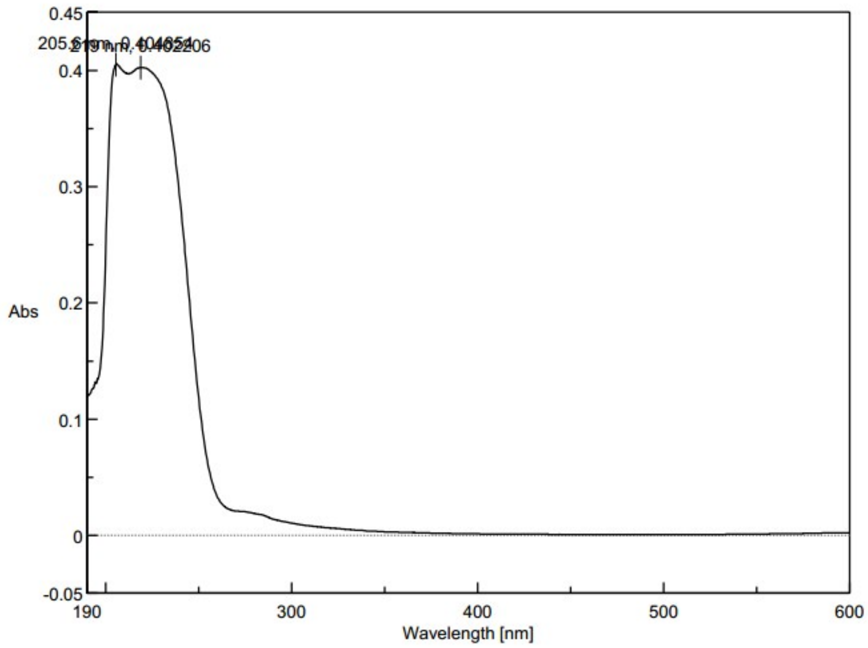

Figure S18. Experimental UV spectrum of Xanthanoltrimer A (**1**) in MeOH

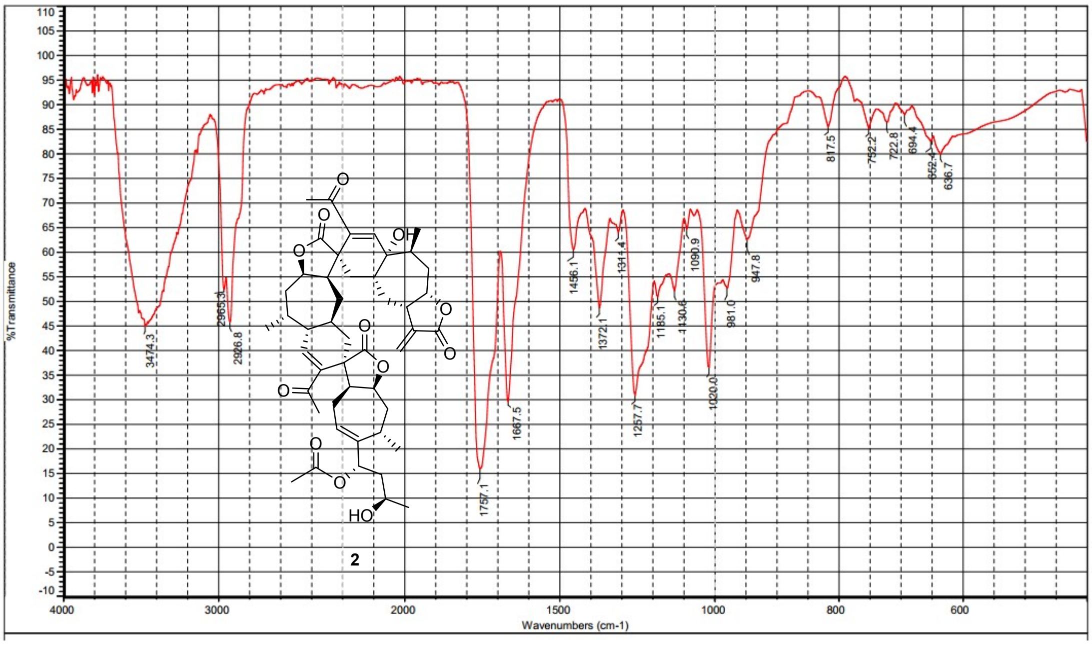

Figure S19. IR spectrum of Xanthanoltrimer B (**2**)

MS Formula Results: - Scan (7.551 min) Sub (2017111602.d)

m/z	Ion	Formula	Abundance
861.4036	(M+COOH)-	C48 H61 O14	30473.8

Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
✓	C47 H60 O12	C48 H61 O14	99.43		816.4051	816.4085	861.4067	4.14	4.14	99.44	99.23	99.66	18
	C51 H60 O7 S	C52 H61 O9 S	99.64		816.4051	816.406	861.4042	1.05	1.05	99.96	99.02	99.74	22
	C46 H60 N2 O9 S	C47 H61 N2 O11 S	99.63		816.4051	816.402	861.4002	-3.9	3.9	99.5	99.74	99.76	18
	C42 H60 N2 O14	C43 H61 N2 O16	99.55		816.4051	816.4045	861.4027	-0.81	0.81	99.98	98.71	99.69	14
	C52 H56 N4 O3 S	C53 H57 N4 O5 S	99.38		816.4051	816.4073	861.4055	2.66	2.66	99.77	98.41	99.77	27
	C39 H64 N2 O14 S	C40 H65 N2 O16 S	99.29		816.4051	816.4078	861.406	3.29	3.29	99.65	98.33	99.75	9
	C43 H64 N2 O9 S2	C44 H65 N2 O11 S2	99.14		816.4052	816.4053	861.4035	0.21	0.21	100	97.25	99.69	13
	C54 H56 O7	C55 H57 O9	99.1		816.4051	816.4026	861.4008	-3.06	3.06	99.69	97.64	99.65	27
	C48 H56 N4 O8	C49 H57 N4 O10	99.05		816.4051	816.4098	861.408	5.75	5.75	98.92	98.7	99.71	23
	C55 H52 N4 O3	C56 H53 N4 O5	98.87		816.4051	816.4039	861.4021	-1.44	1.44	99.93	96.41	99.69	32
	C48 H64 O7 S2	C49 H65 O9 S2	98.71		816.4051	816.4093	861.4075	5.15	5.15	99.13	97.19	99.71	17
	C34 H64 N4 O16 S	C35 H65 N4 O18 S	98.62		816.4052	816.4038	861.402	-1.66	1.66	99.91	95.54	99.75	5
	C55 H60 O2 S2	C56 H61 O4 S2	98.56		816.4051	816.4035	861.4017	-2.03	2.03	99.86	95.4	99.73	26
	C37 H60 N4 O16	C38 H61 N4 O18	98.5		816.4051	816.4004	861.3986	-5.75	5.75	98.92	96.77	99.73	10
	C38 H64 N4 O11 S2	C39 H65 N4 O13 S2	98.45		816.4052	816.4013	861.3995	-4.74	4.74	99.27	96.06	99.67	9
	C60 H52 N2 O	C61 H53 N2 O3	98.09		816.4051	816.408	861.4062	3.5	3.5	99.6	94.27	99.66	36
	C33 H68 O20 S	C34 H69 O22 S	97.82		816.4051	816.4025	861.4007	-3.26	3.26	99.65	93.2	99.71	0
	C30 H64 N4 O21	C31 H65 N4 O23	97.13		816.4051	816.4063	861.4045	1.44	1.44	99.93	90.27	99.75	1
	C31 H68 N4 O16 S2	C32 H69 N4 O18 S2	97.12		816.4052	816.4072	861.4054	2.44	2.44	99.8	90.56	99.62	0

Figure S20. (+)-HRESIMS data of Xanthanoltrimer B (**2**)

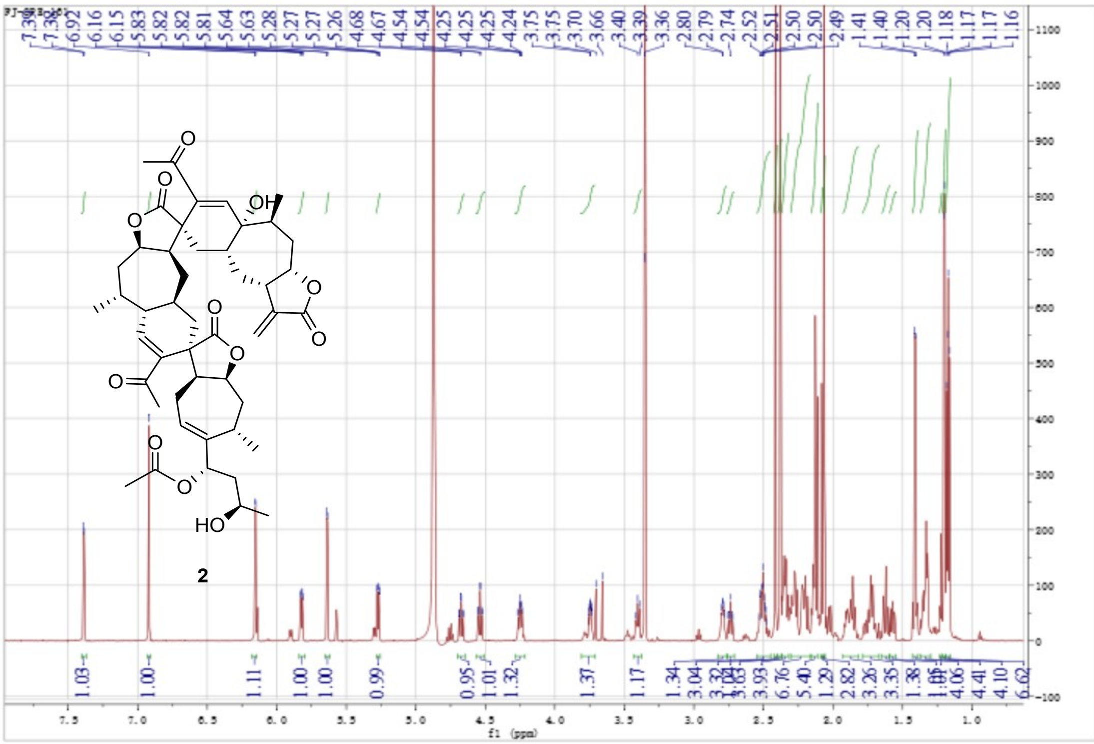

Figure S21. ^{1}H-NMR spectrum of Xanthanoltrimer B (**2**) (800 MHz, in CD_3OD)

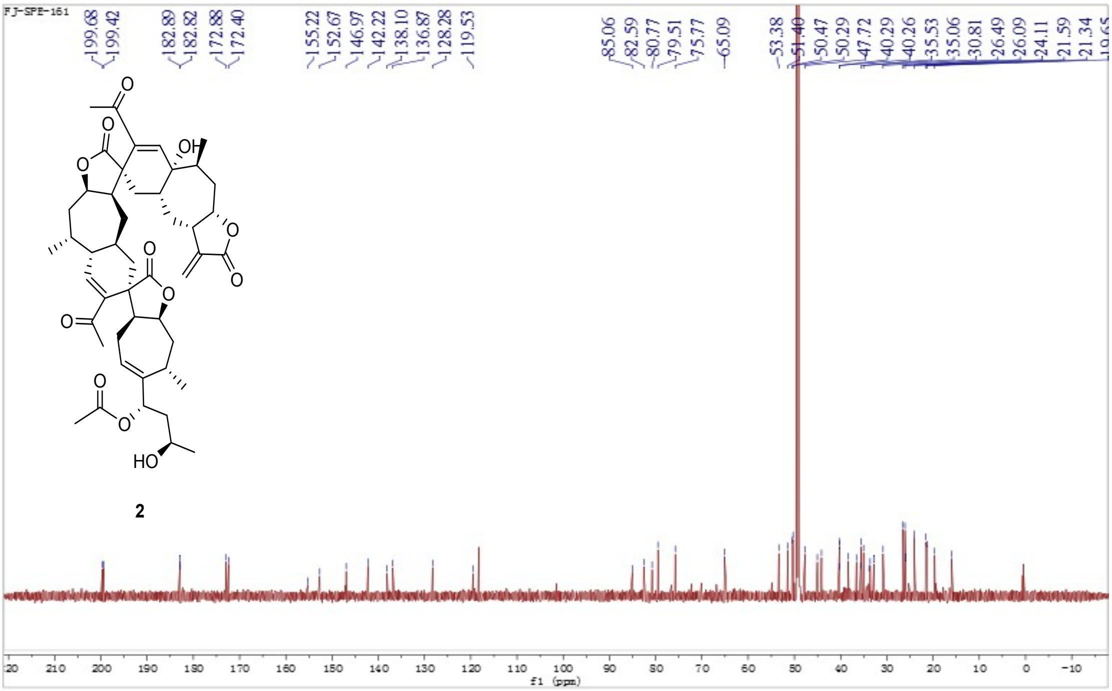

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Figure S22. ^{13}C-NMR spectrum of Xanthanoltrimer B (**2**) (200 MHz, in CD_3OD)

Figure S23. DEPT spectrum of Xanthanoltrimer B (**2**) (150 MHz, in CD_3OD)

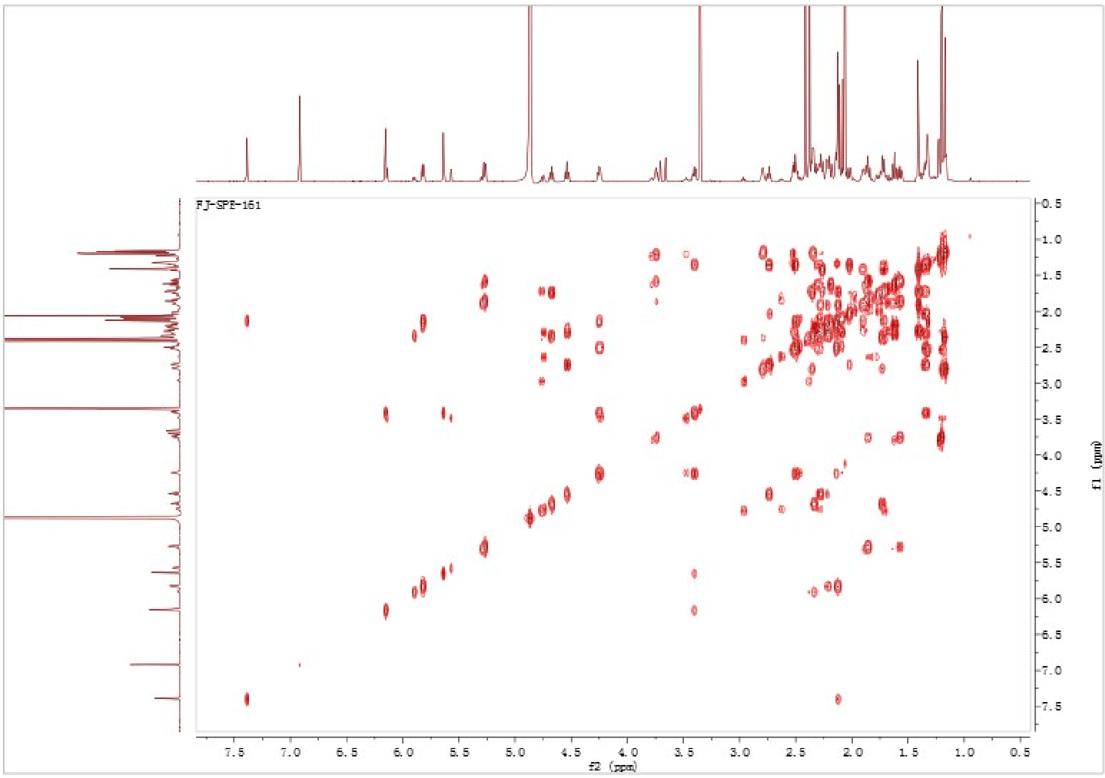


Figure S24. ^{1}H-^{1}H COSY spectrum of Xanthanoltrimer B (**2**) (800 MHz, in CD_3OD)

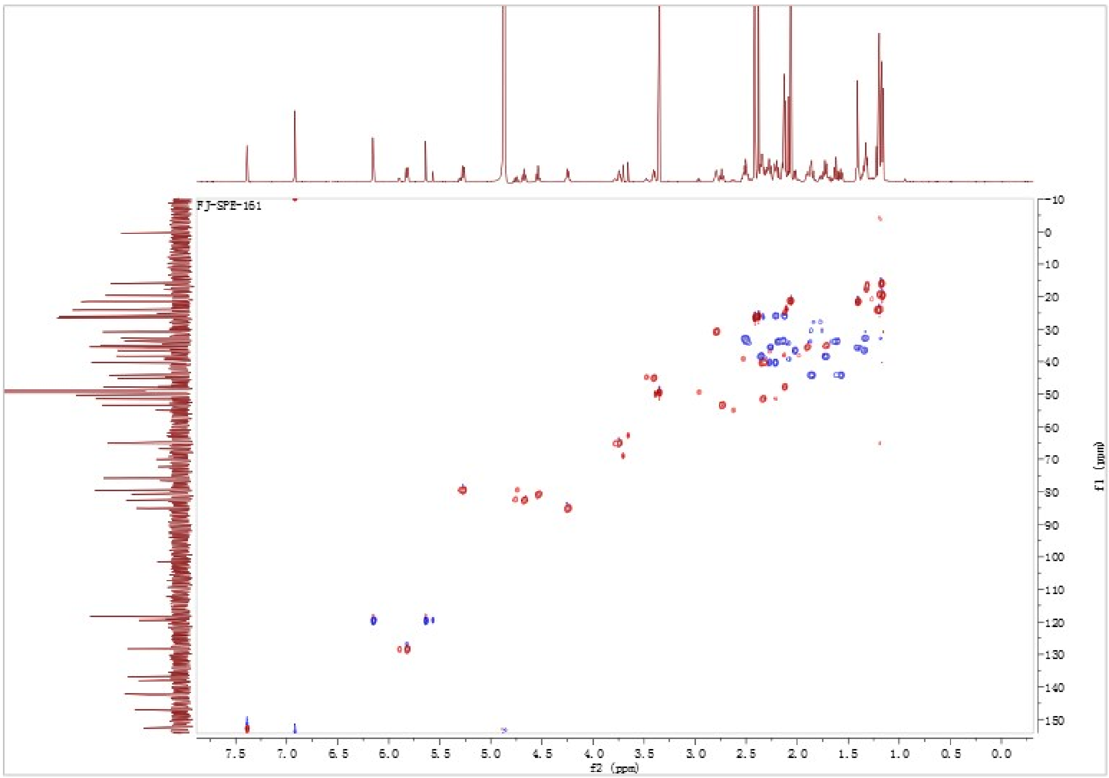


Figure S25. HSQC spectrum of Xanthanoltrimer B (**2**)

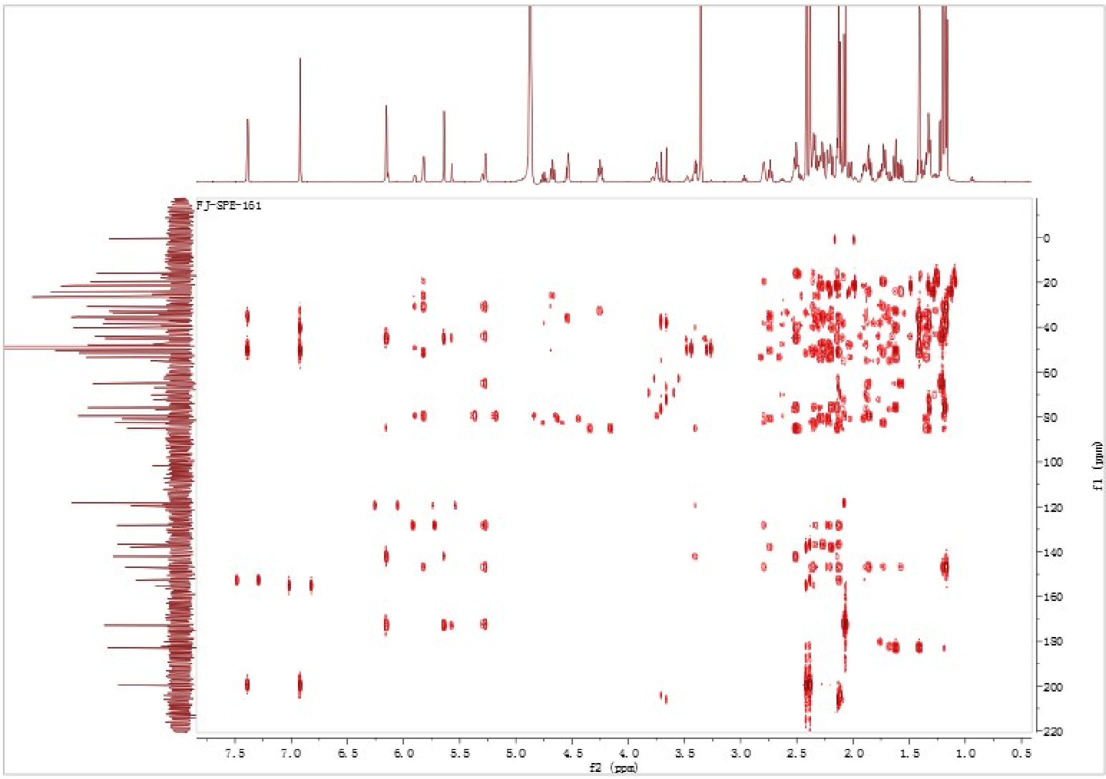


Figure S26. HMBC spectrum of Xanthanoltrimer B (**2**)

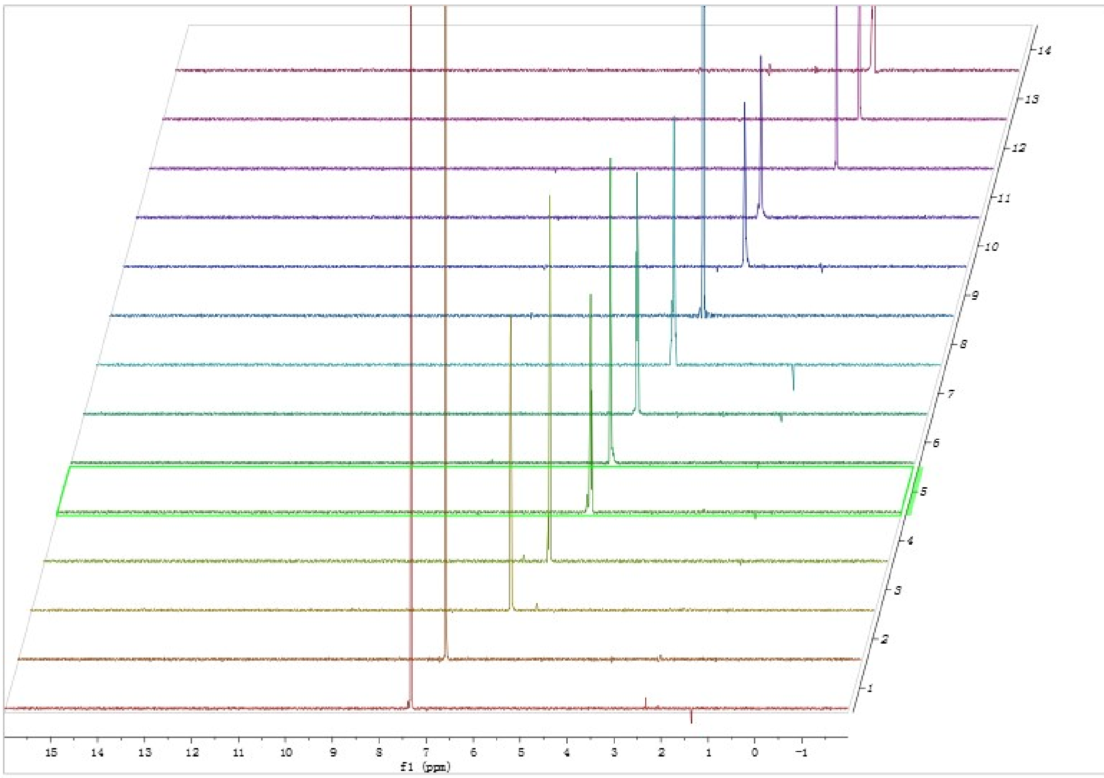


Figure S27. NOE spectrum of Xanthanoltrimer B (**2**) (600 MHz, in CD_3OD)

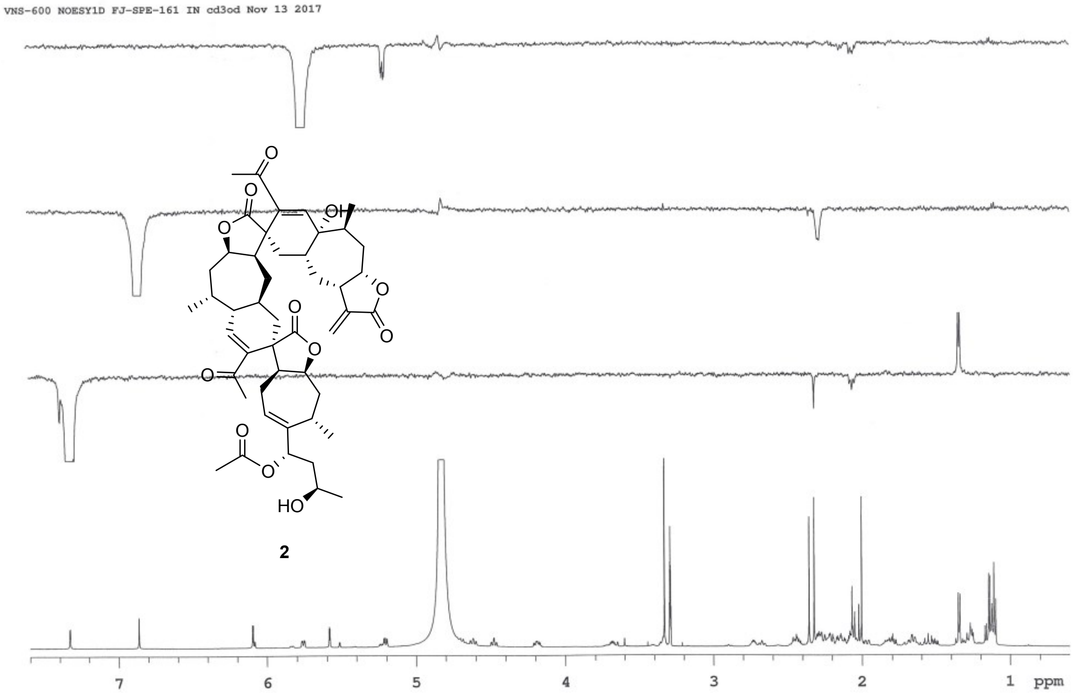


Figure S28. NOE spectrum of Xanthanoltrimer B (**2**) (600 MHz, in CD_3OD)

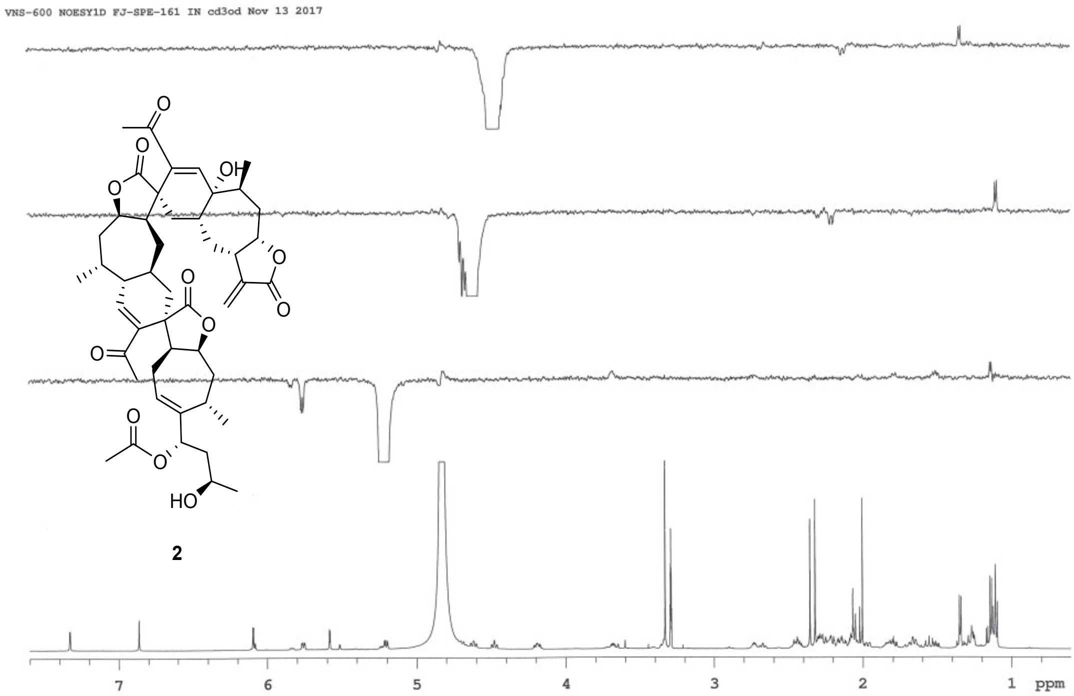


Figure S29. NOE spectrum of Xanthanoltrimer B (**2**) (600 MHz, in CD_3OD)

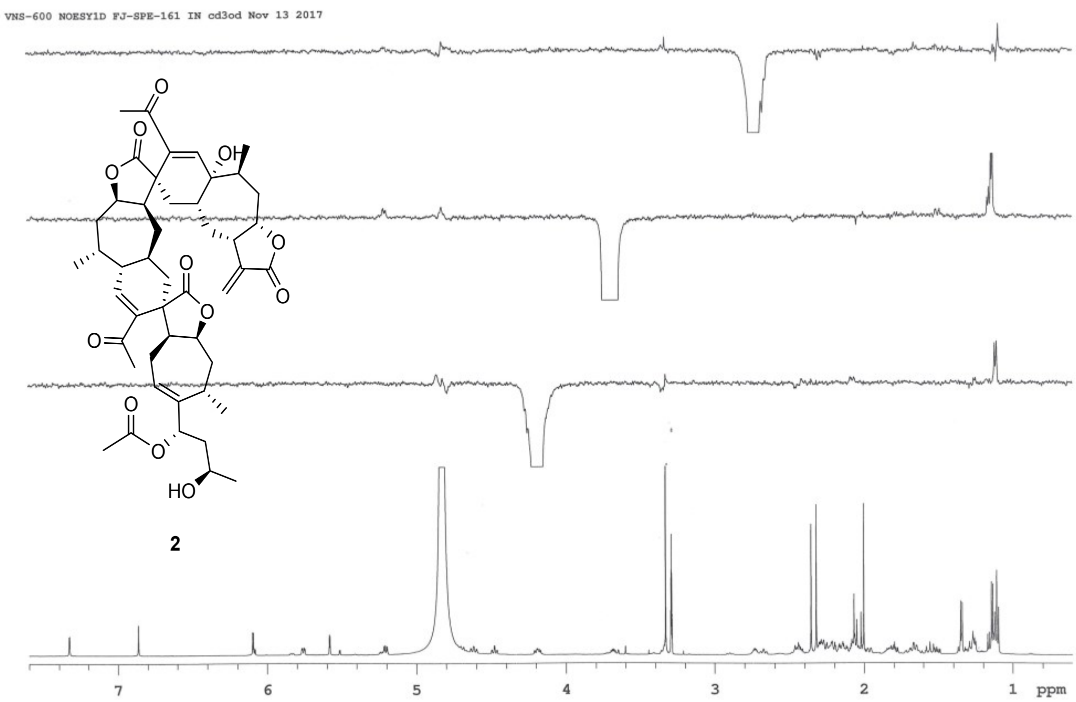


Figure S30. NOE spectrum of Xanthanoltrimer B (**2**) (600 MHz, in CD_3OD)

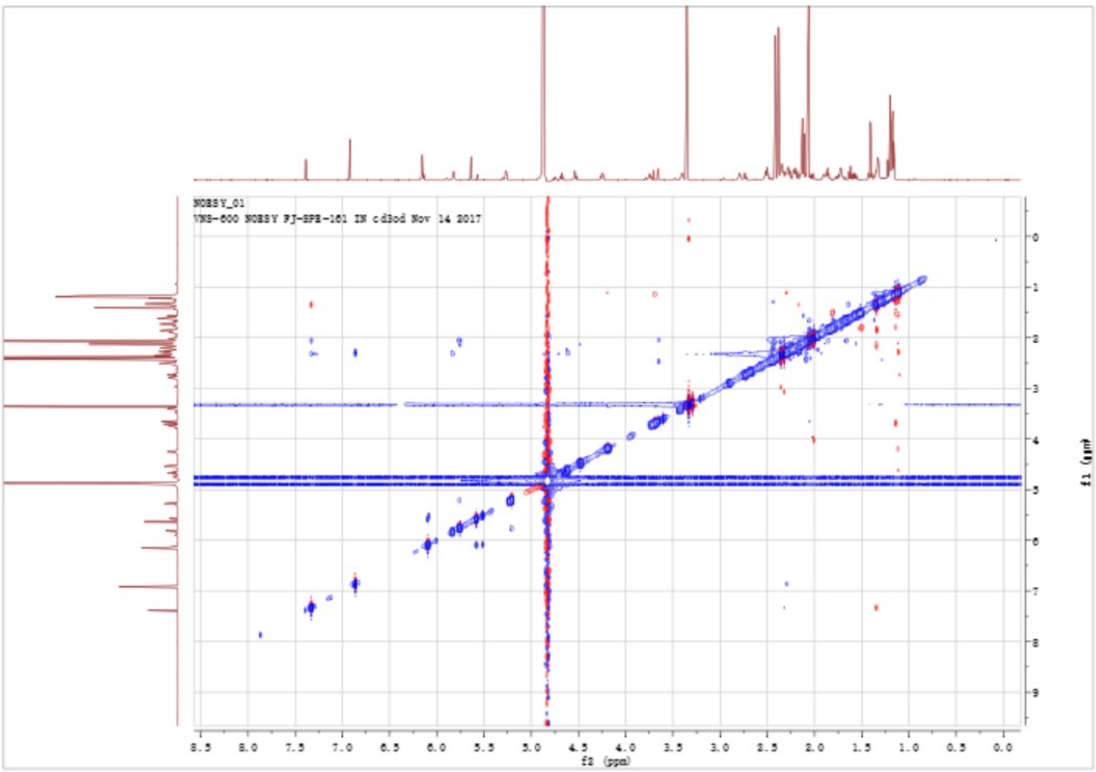


Figure S31. NOESY spectrum of Xanthanoltrimer B (**2**) (600 MHz, in CD_3OD)

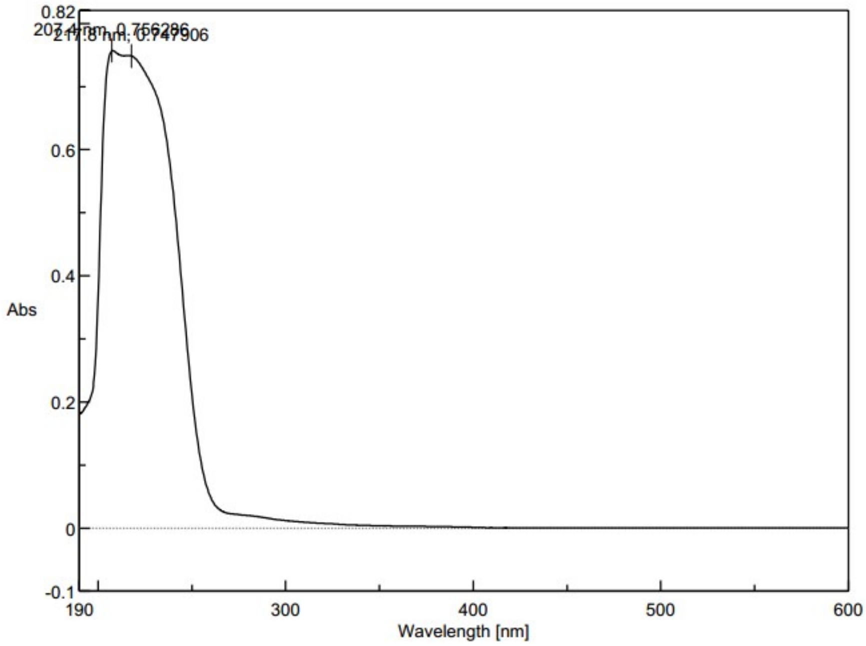


Figure S32. Experimental UV spectrum of Xanthanoltrimer B (**2**) in MeOH

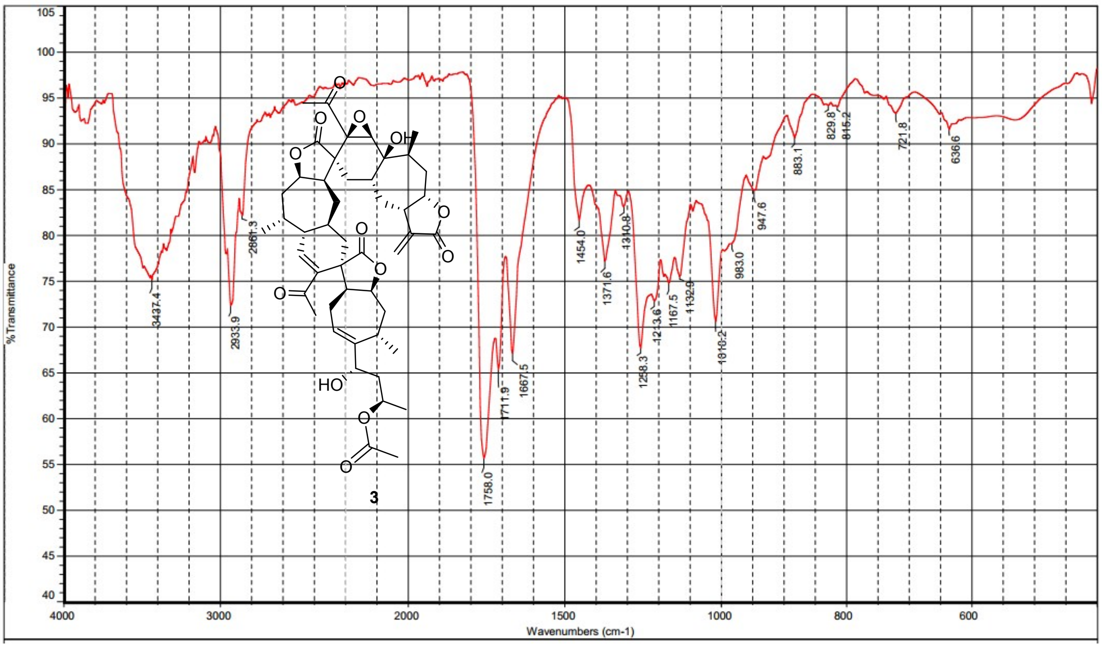


Figure S33. IR spectrum of Xanthanoltrimer C (**3**)

MS Formula Results: + Scan (7.751 min) Sub (2017112402.d)

m/z	Ion	Formula	Abundance
855.3937	(M+Na)+	C47 H60 Na O13	139559

Best	Formula (M)	Ion Formula	Score	Cross Sco	Mass	Calc Mass	Calc m/z	Diff (ppm)	Abs Diff (ppm)	Mass Match	Abund Match	Spacing Match	DBE
✓	C47 H60 O13	C47 H60 Na O13	99.91		832.4044	832.4034	855.3926	-1.21	1.21	99.95	99.79	99.97	18
	C48 H56 N4 O9	C48 H56 N4 Na O9	99.91		832.4044	832.4047	855.394	0.37	0.37	100	99.7	99.98	23
	C52 H56 N4 O4 S	C52 H56 N4 Na O4 S	99.51		832.4044	832.4022	855.3914	-2.65	2.65	99.76	98.72	99.97	27
	C45 H60 N4 O9 S	C45 H60 N4 Na O9 S	99.46		832.4044	832.4081	855.3973	4.4	4.4	99.33	99.26	99.95	18
	C44 H64 O13 S	C44 H64 Na O13 S	99.43		832.4044	832.4068	855.396	2.82	2.82	99.73	98.52	99.95	13
	C51 H60 O8 S	C51 H60 Na O8 S	99.4		832.4044	832.4009	855.3901	-4.24	4.24	99.38	98.96	99.97	22
	C53 H56 N2 O7	C53 H56 N2 Na O7	99.27		832.4044	832.4088	855.398	5.22	5.22	99.06	99.02	99.97	27
	C57 H56 N2 O2 S	C57 H56 N2 Na O2 S	99.08		832.4044	832.4062	855.3955	2.19	2.19	99.83	97.07	99.98	31
	C42 H60 N2 O15	C42 H60 N2 Na O15	99		832.4044	832.3994	855.3886	-6.06	6.06	98.74	98.63	99.98	14
	C39 H64 N2 O15 S	C39 H64 N2 Na O15 S	98.94		832.4044	832.4027	855.392	-2.03	2.03	99.86	96.59	99.92	9
	C49 H60 N4 O4 S2	C49 H60 N4 Na O4 S2	98.85		832.4045	832.4056	855.3948	1.38	1.38	99.93	96.19	99.85	22
	C60 H52 N2 O2	C60 H52 N2 Na O2	98.82		832.4044	832.4029	855.3921	-1.84	1.84	99.88	96.08	99.96	36
	C48 H64 O8 S2	C48 H64 Na O8 S2	98.75		832.4044	832.4043	855.3935	-0.2	0.2	100	95.74	99.85	17
	C55 H52 N4 O4	C55 H52 N4 Na O4	98.71		832.4044	832.3989	855.3881	-6.68	6.68	98.47	98.06	99.97	32
	C40 H64 O18	C40 H64 Na O18	98.66		832.4044	832.4093	855.3985	5.85	5.85	98.82	97.28	99.98	9
	C41 H60 N4 O14	C41 H60 N4 Na O14	98.64		832.4044	832.4106	855.3998	7.42	7.42	98.11	98.4	99.99	14
	C54 H56 O8	C54 H56 Na O8	98.59		832.4044	832.3975	855.3867	-8.26	8.26	97.67	98.99	99.96	27
	C46 H60 N2 O10 S	C46 H60 N2 Na O10 S	98.42		832.4044	832.3969	855.3861	-9.08	9.08	97.19	99.18	99.95	18
	C50 H60 N2 O7 S	C50 H60 N2 Na O7 S	98.36		832.4044	832.4121	855.4013	9.25	9.25	97.09	99.14	99.97	22
	C43 H64 N2 O10 S2	C43 H64 N2 Na O10 S2	98.17		832.4044	832.4002	855.3895	-5.06	5.06	99.12	95.22	99.8	13
	C35 H64 N2 O20	C35 H64 N2 Na O20	98.12		832.4044	832.4052	855.3945	1	1	99.97	93.49	99.99	5
	C54 H60 N2 O2 S2	C54 H60 N2 Na O2 S2	97.94		832.4044	832.4096	855.3988	6.23	6.23	98.67	95.1	99.89	26
	C58 H56 O5	C58 H56 Na O5	97.62		832.4044	832.4128	855.402	10.06	10.06	96.56	97.46	99.96	31
	C55 H60 O3 S2	C55 H60 Na O3 S2	97.62		832.4044	832.3984	855.3876	-7.26	7.26	98.2	94.74	99.9	26
	C46 H60 N2 O12	C46 H60 N2 Na O12	97.49		832.4044	832.4146	855.4038	12.27	12.27	94.93	99.69	99.98	18
	C42 H64 N4 O9 S2	C42 H64 N4 Na O9 S2	97.48		832.4045	832.4115	855.4007	8.42	8.42	97.58	95.39	99.79	13
	C41 H68 O13 S2	C41 H68 Na O13 S2	97.43		832.4044	832.4101	855.3994	6.85	6.85	98.39	93.85	99.79	8
	C36 H68 N2 O15 S2	C36 H68 N2 Na O15 S2	97.31		832.4045	832.4061	855.3953	1.99	1.99	99.86	91.04	99.73	4
	C34 H64 N4 O17 S	C34 H64 N4 Na O17 S	97.19		832.4045	832.3987	855.3879	-6.89	6.89	98.37	92.97	99.88	5
	C49 H56 N2 O10	C49 H56 N2 Na O10	97.18		832.4044	832.3935	855.3827	-13.11	13.11	94.23	99.76	99.97	23
	C58 H56 O3 S	C58 H56 Na O3 S	97.03		832.4044	832.395	855.3842	-11.29	11.29	95.69	96.81	99.98	31
	C37 H60 N4 O17	C37 H60 N4 Na O17	96.91		832.4044	832.3953	855.3846	-10.91	10.91	95.97	95.89	99.99	10
	C38 H64 N4 O14 S	C38 H64 N4 Na O14 S	96.87		832.4044	832.414	855.4032	11.44	11.44	95.57	96.49	99.91	9
	C37 H68 O18 S	C37 H68 Na O18 S	96.81		832.4044	832.4126	855.4019	9.87	9.87	96.69	94.42	99.91	4
	C59 H52 N4 O	C59 H52 N4 Na O	96.72		832.4044	832.4141	855.4033	11.65	11.65	95.42	96.19	99.97	36
	C32 H68 N2 O20 S	C32 H68 N2 Na O20 S	96.61		832.4044	832.4086	855.3978	5.02	5.02	99.13	89.7	99.87	0

page 1

Figure S34. (+)-HRESIMS data of Xanthanoltrimer C (**3**)

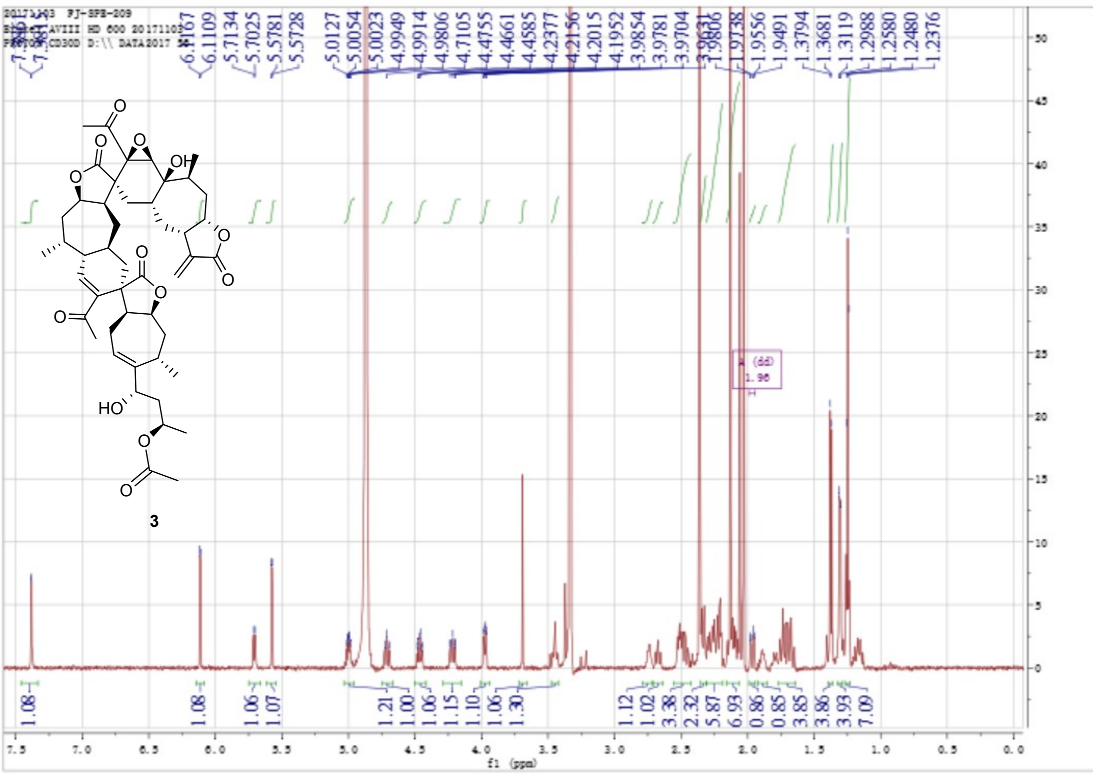


Figure S35. ^{1}H-NMR spectrum of Xanthanoltrimer C (**3**) (600 MHz, in CD_3OD)

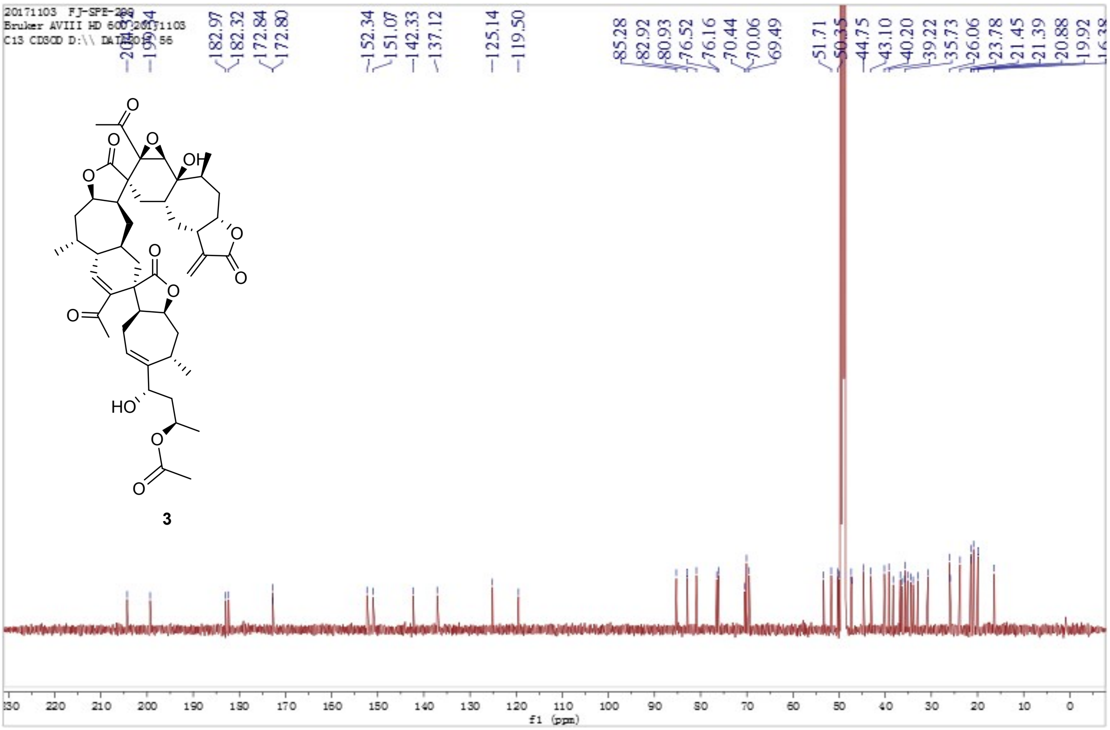


Figure S36. [13]C-NMR spectrum of Xanthanoltrimer C (**3**) (150 MHz, in CD_3OD)

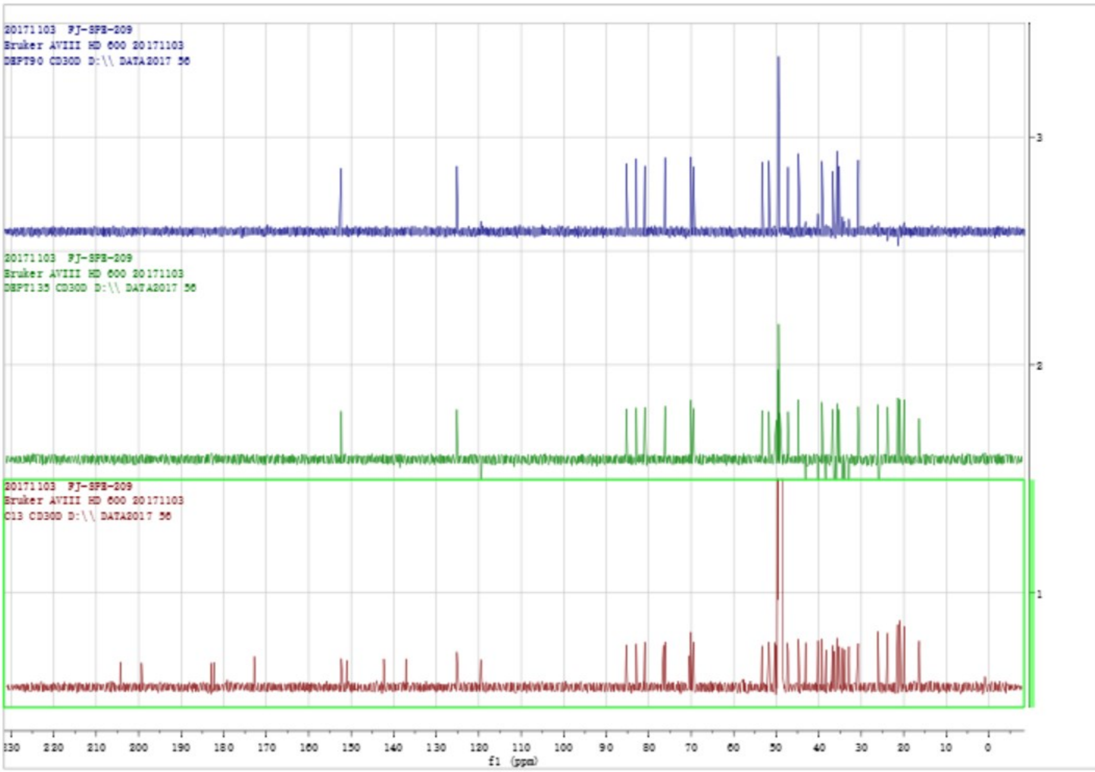


Figure S37. DEPT spectrum of Xanthanoltrimer C (**3**) (150 MHz, in CD_3OD)

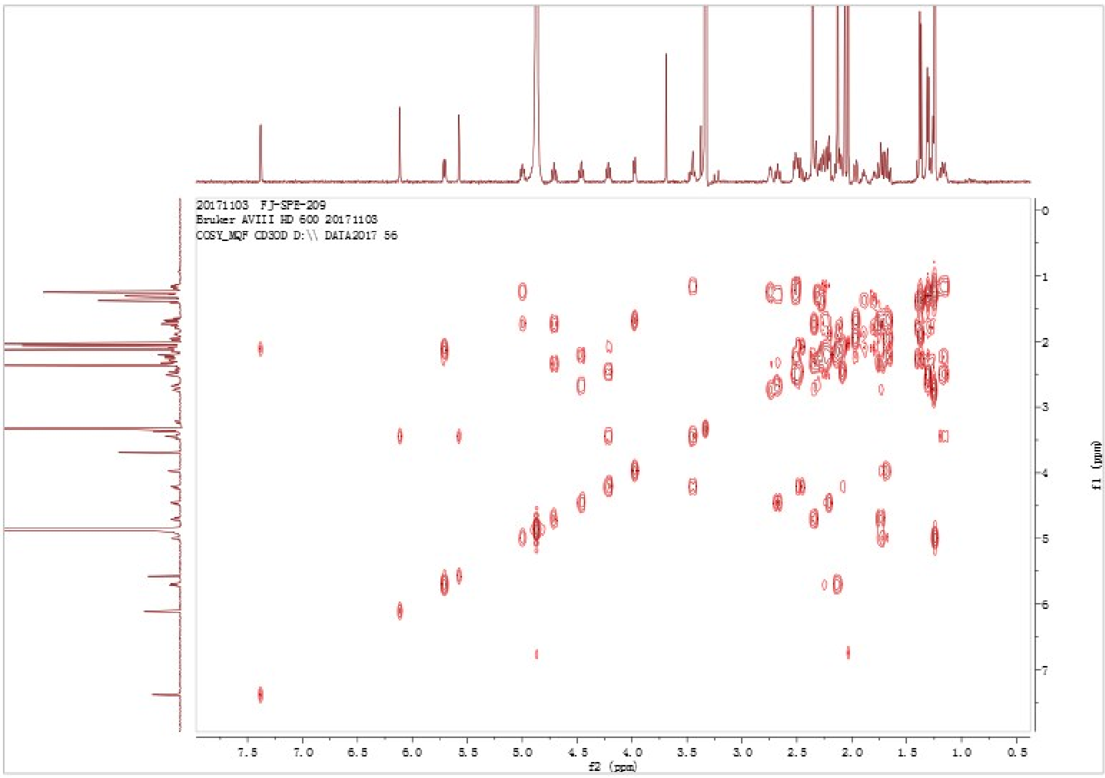


Figure S38. ^{1}H-^{1}H COSY spectrum of Xanthanoltrimer C (**3**) (600 MHz, in CD_3OD)

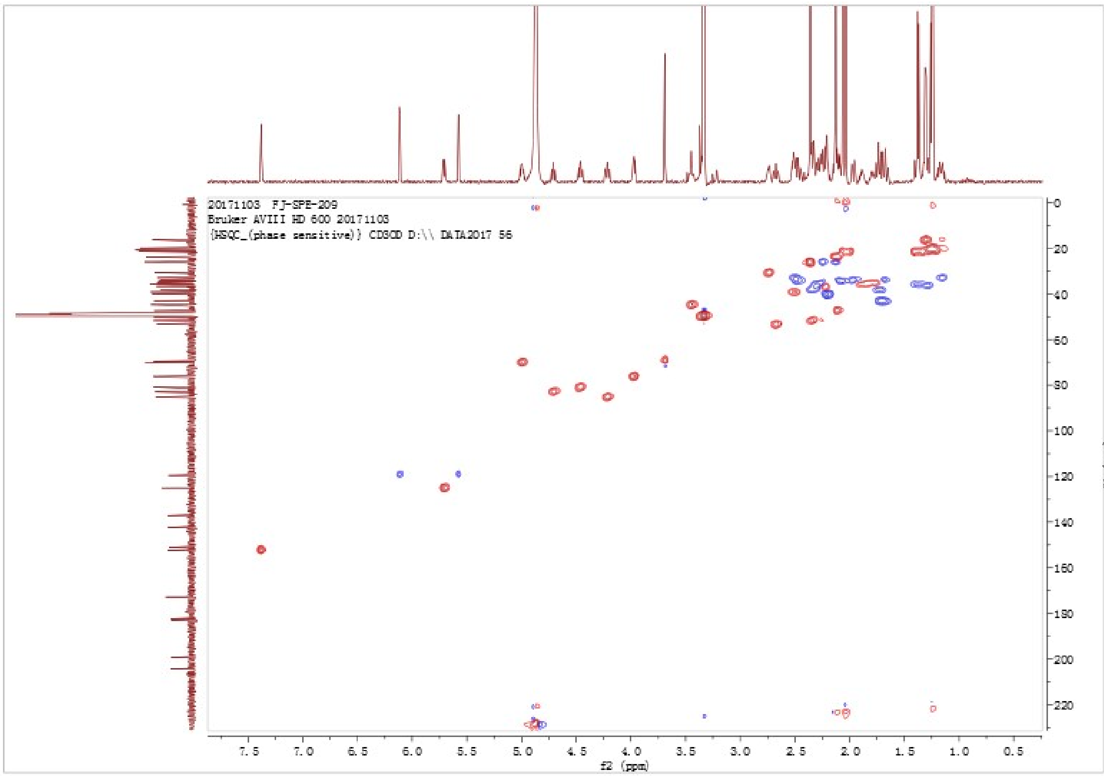


Figure S39. HSQC spectrum of Xanthanoltrimer C (**3**)

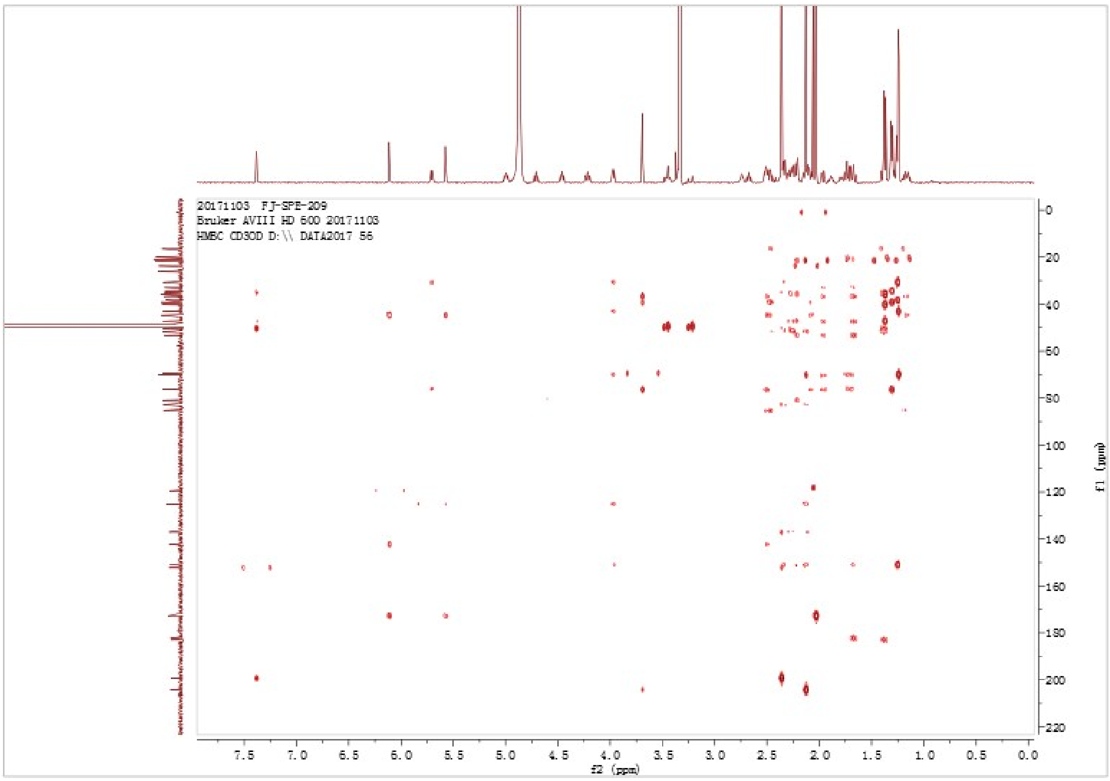


Figure S40. HMBC spectrum of Xanthanoltrimer C (**3**)

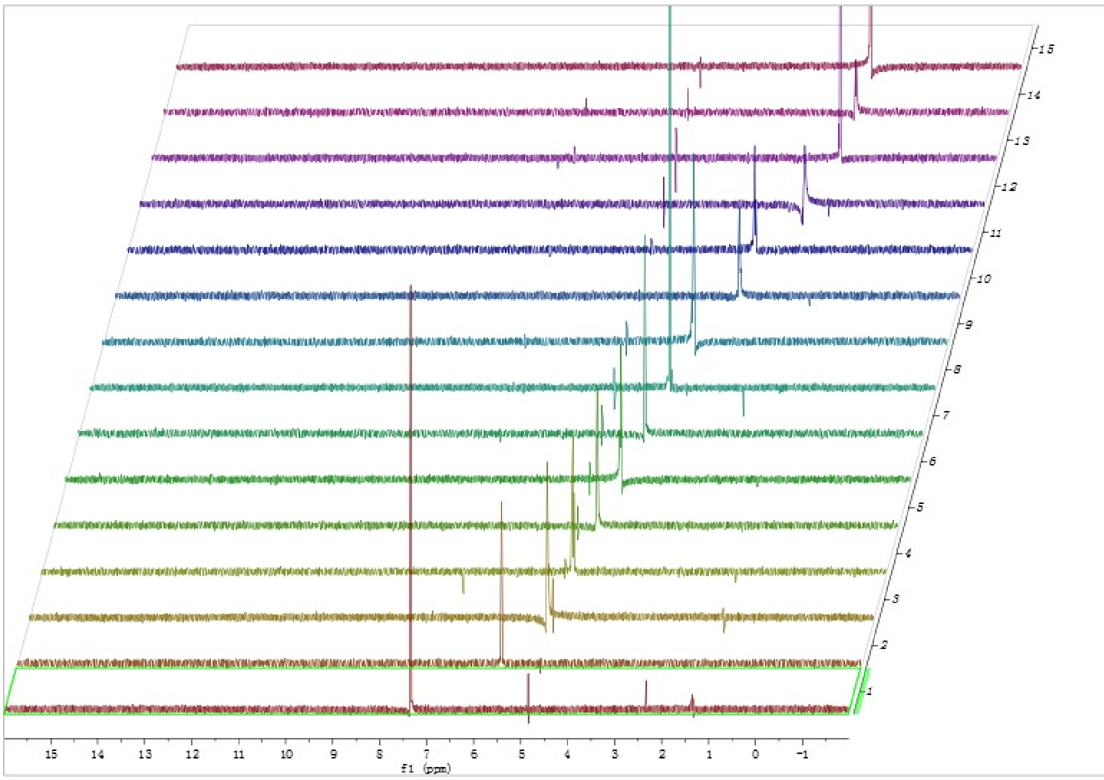


Figure S41. NOE spectrum of Xanthanoltrimer C (**3**) (600 MHz, in CD_3OD)

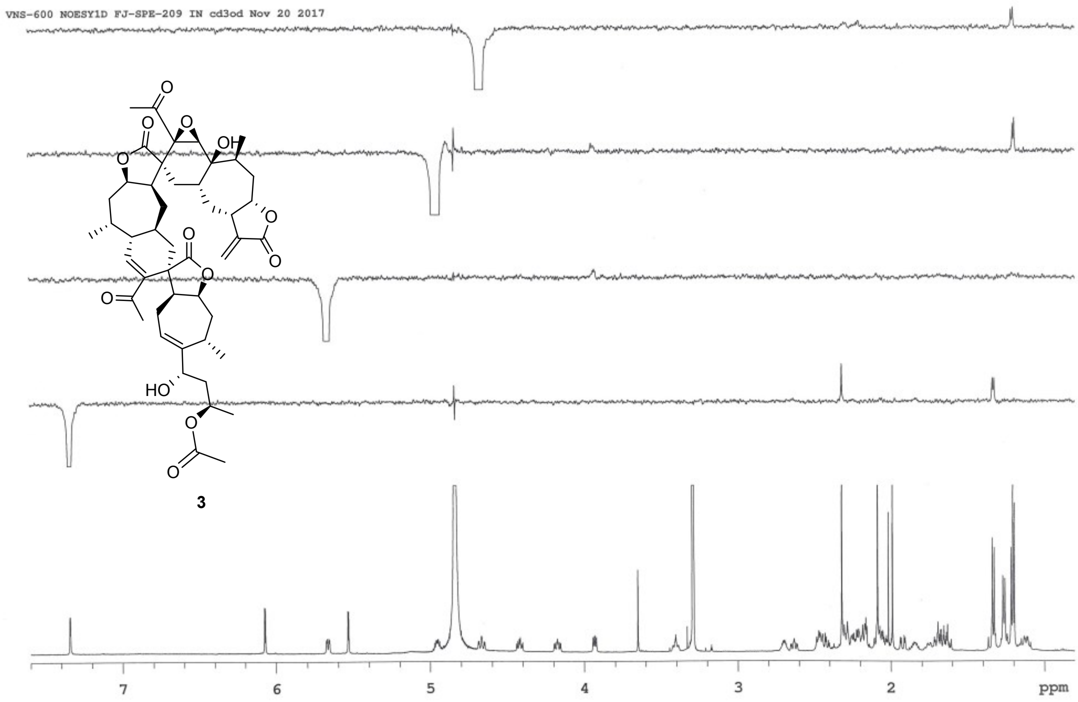


Figure S42. NOE spectrum of Xanthanoltrimer C (**3**) (600 MHz, in CD_3OD)

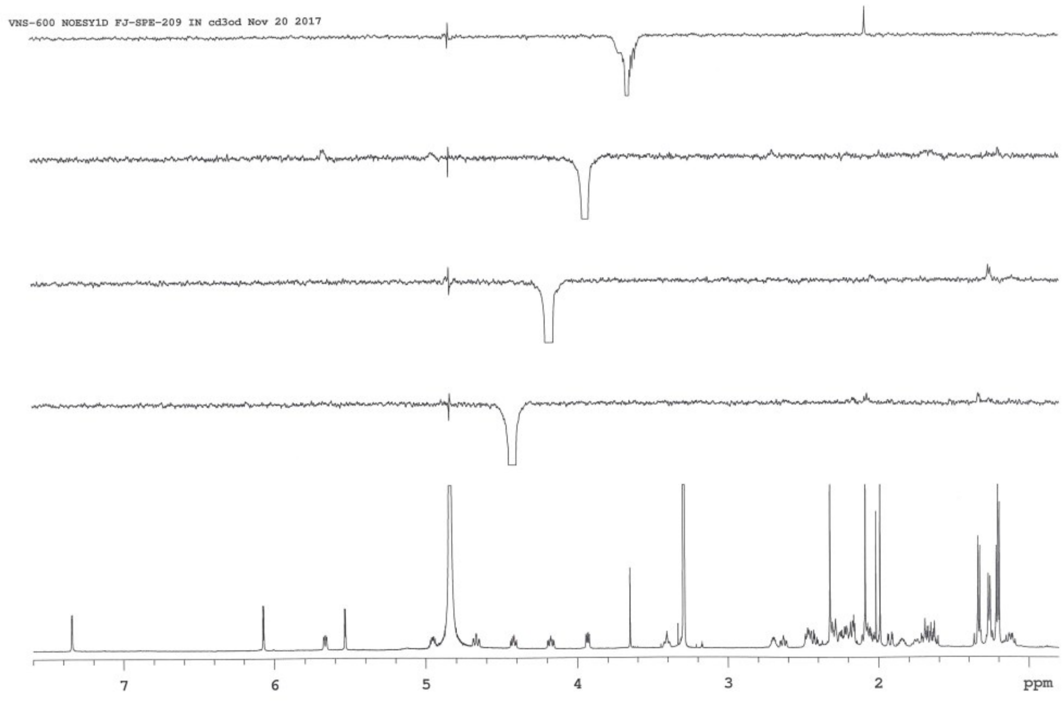


Figure S43. NOE spectrum of Xanthanoltrimer C (**3**) (600 MHz, in CD_3OD)

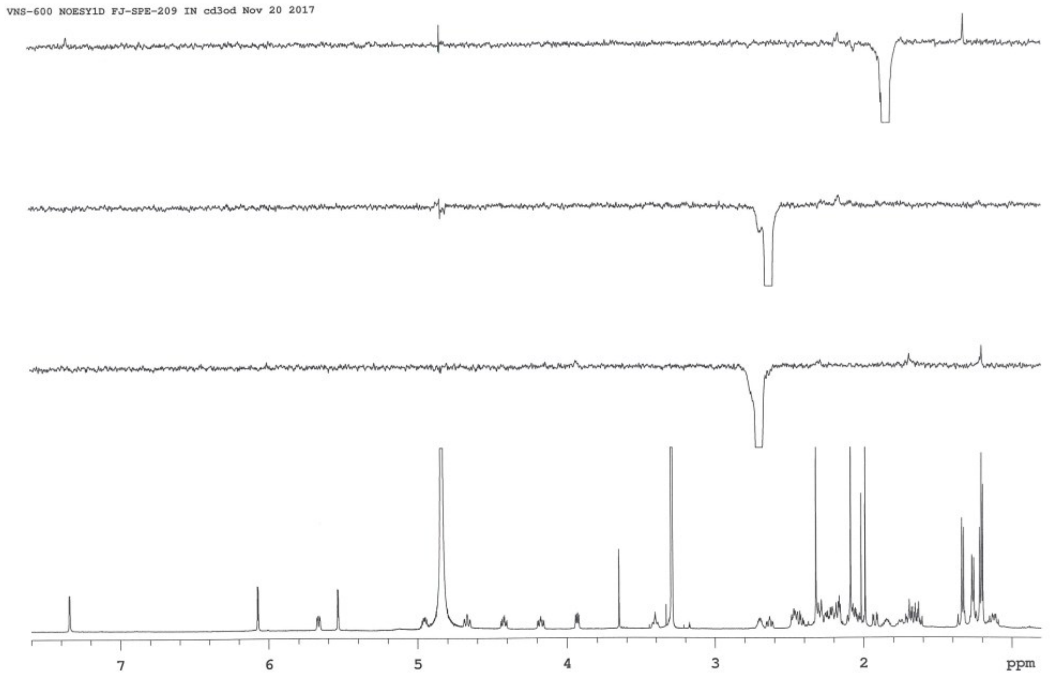


Figure S44. NOE spectrum of Xanthanoltrimer C (**3**) (600 MHz, in CD_3OD)

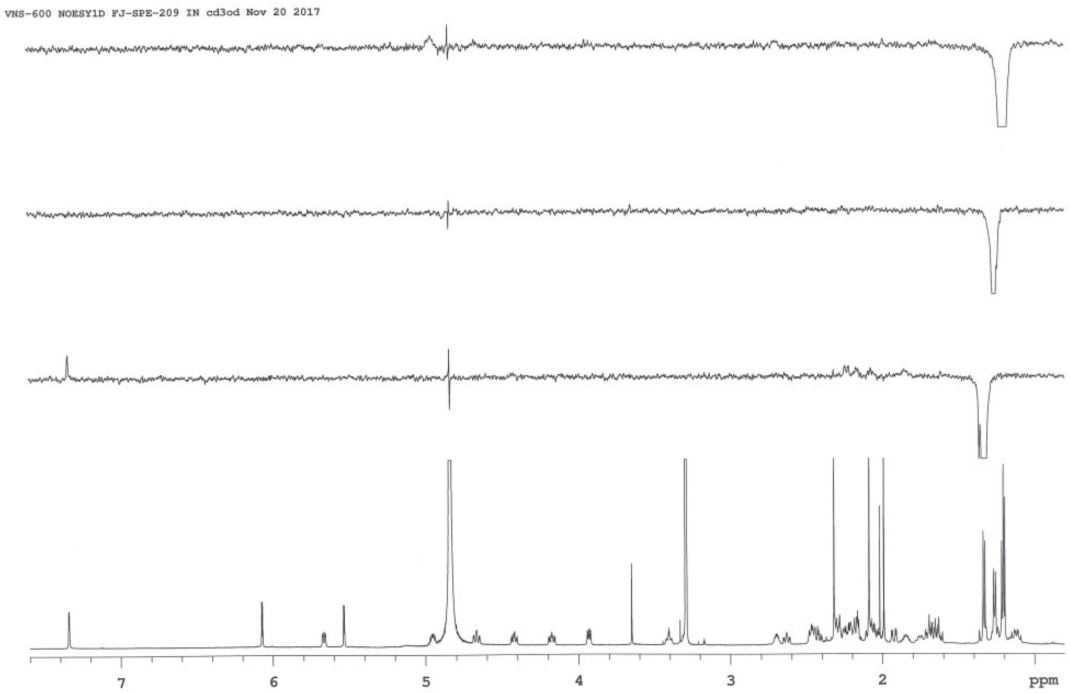


Figure S45. NOE spectrum of Xanthanoltrimer C (**3**) (600 MHz, in CD_3OD)

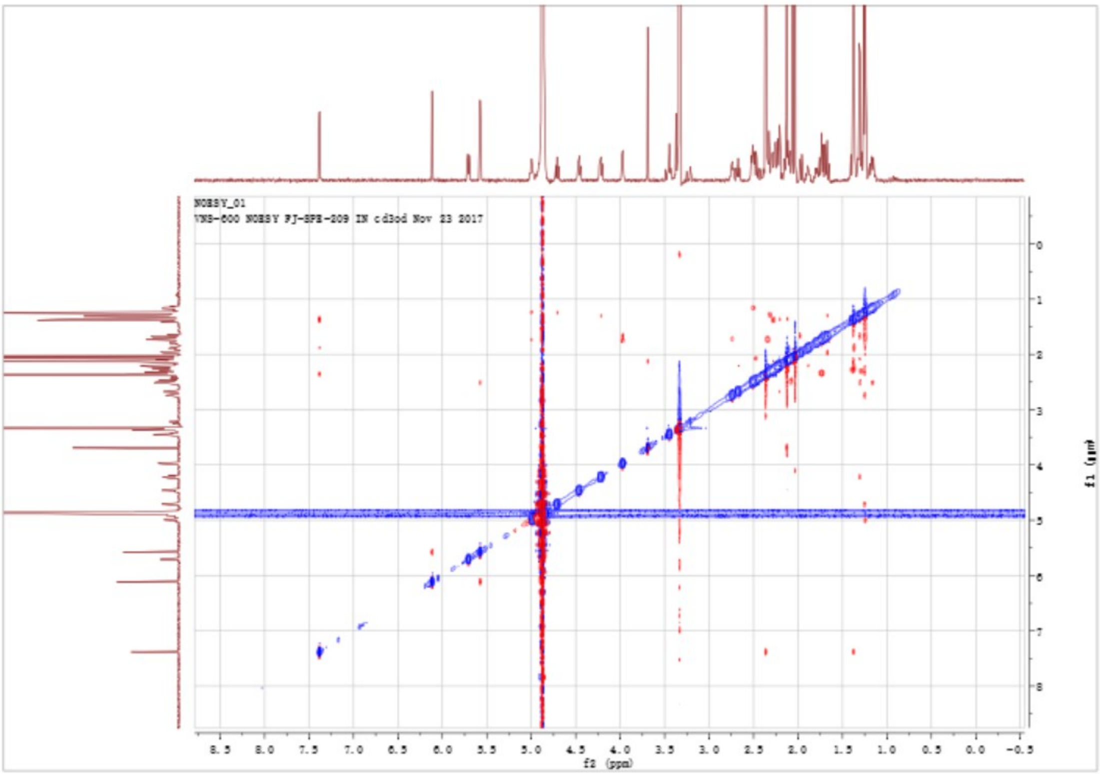


Figure S46. NOESY spectrum of Xanthanoltrimer C (**3**) (600 MHz, in CD_3OD)

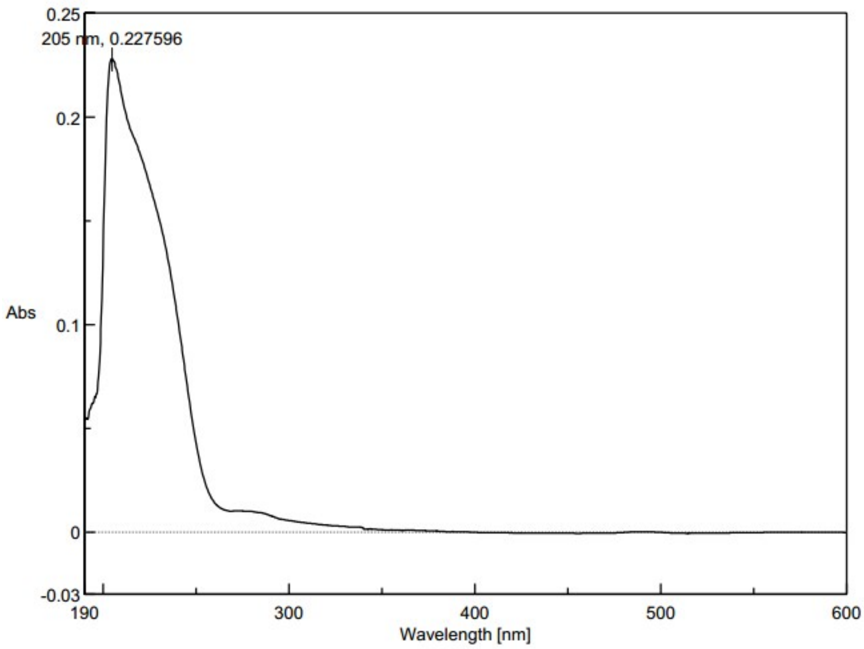
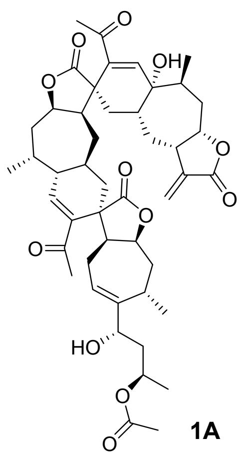


Figure S47. Experimental UV spectrum of Xanthanoltrimer C (**3**) in MeOH

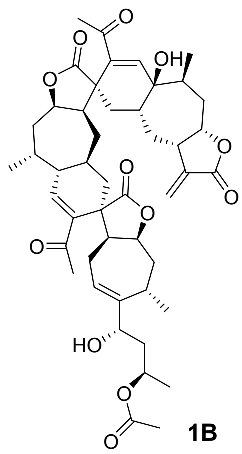
NMR chemical shifts and ECD calculation of Xanthanoltrimer A (1).

Conformational analysis of the **1A** and **1B** (Fig. S48) were carried out via Monte Carlo searching with the MMFF94s molecular mechanics force field using the spartan 14 software. 3 of **1A** and 2 of **1B** geometries having relative energies within 5 kcal/mol were optimized using DFT at the B3LYP/6-31+G (d, p) level in vacuum with the Gaussian 09 program, respectively. NMR chemical shifts calculation for those B3LYP/6-31+G (d, p)-optimized conformers with their Boltzmann distribution (≧1%, Table S2, S4) were carried out at PCM/mPW1PW91/6-311+G (d, p) level in methanol with GIAO method. After Boltzmann weighing of the calculated chemical shift of each isomers, the DP4+ parameters were calculated using the excel file (Table. S5), which was provided by Ariel M. Sarotti.

In addition, those stable conformers with their Boltzmann distribution (≧1%) also were carried out at the TDDFT CAM-B3LYP/6-311+G(2d,p) level in the methanol for ECD computation. Boltzmann statistics were performed for ECD simulations with a standard deviation of σ 0.3 eV. The final ECD spectra of **1A** and **1B** were obtained according to the Boltzmann distribution theory and their relative Gibbs free energy (ΔG), respectively.



1A



1B

Figure S48. The Structures of **1A** and **1B**

Table S1. Free energies (Δ*G*), and Boltzmann distribution abundances of conformers of **1A**.

Conf.	B3LYP/6-31+G(d, p) Gibbs free energy (298.15 K)		
	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
1A-C1	-2729.074051	1.2410	0.109
1A-C2	-2729.076028	0.0000	0.884
1A-C3	-2729.071505	2.8380	0.007

Table S2. Experimental ^{13}C-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of **1A**

No.	Exptl.	1A-C1	1A-C2	1A-C3	Averaged[a]	Unscaled shifts (δ_U)[b]	Scaled shifts (δ_S)[c]
4	199.8	-24.2677	-22.773	-22.8147	-22.9362	211	200.4
4'	199.4	-19.8732	-19.88	-19.6676	-19.8778	207.9	197.5
12'	182.9	-2.1674	-1.7316	-1.9395	-1.7806	189.8	180.2
12"	182.9	-1.8479	-1.829	-1.9019	-1.8316	189.9	180.3
16"	172.8	7.2434	3.7175	5.3591	4.1133	183.9	174.5
12	172.9	8.8939	9.2225	8.1473	9.179	178.9	169.8
2'	152.4	20.2918	20.575	21.1474	20.5481	167.5	158.9
2	155.3	25.9869	24.6578	24.1562	24.7992	163.2	154.8
1"	151.1	27.5825	32.1139	26.1563	31.5783	156.5	148.4
11	142.2	38.4248	38.7495	37.8163	38.7076	149.3	141.5
3	138.1	41.2892	41.6497	41.0494	41.6062	146.4	138.7
3'	137	42.1104	41.1067	42.9115	41.2287	146.8	139.1
5"	125.1	47.0173	46.6989	52.6286	46.7751	141.3	133.9
13	119.5	56.7783	54.1096	58.5223	54.4314	133.6	126.5
8'	80.7	104.5752	105.8987	105.1879	105.7495	82.3	77.5
8	85	105.4358	105.7089	105.6745	105.6789	82.4	77.6
8"	82.9	107.7236	106.5067	107.6005	106.6470	81.4	76.6
1	75.7	110.1608	110.8988	110.2205	110.8136	77.2	72.6
2"	76.1	113.3342	108.4663	111.9112	109.0210	79	74.3
4"	70	115.4472	113.0899	106.8831	113.3034	74.7	70.2
7"	51.7	129.9109	129.8832	130.7033	129.8920	56.4	52.8
11"	50.3	130.8012	131.784	131.5733	131.6754	58.2	54.5
7	45	131.3955	130.2133	130.5957	130.3448	57.7	54
1'	47.7	132.2261	132.0372	130.8537	132.0495	56	52.4
7'	53.6	134.1143	131.9252	132.7065	132.1693	55.9	52.3
3"	43.1	141.0022	143.8861	142.0056	143.5586	44.5	41.4
7	45	141.341	140.2309	141.6118	140.3616	47.7	44.4
10	40.3	142.5357	143.8457	144.6051	143.7082	45	41.9
13'	33.8	142.854	143.079	143.3633	143.0565	44.3	41.2
13"	35.7	143.3568	143.0022	143.4267	143.0438	45	41.9
10"	30.7	144.8651	149.8488	145.1026	149.2724	38.8	35.9

10'	35.6	148.3974	147.76	148.0268	147.8313	40.2	37.3
9'	40.2	149.3384	150.8572	149.3516	150.6811	37.4	34.6
6'	36.6	150.1421	151.3641	150.955	151.2280	36.8	34
5	40.2	151.5593	151.6731	152.0533	151.6634	38.6	35.8
9"	38.2	151.6116	149.1854	151.2756	149.4645	36.4	33.6
5'	35.1	153.1788	154.6064	152.8255	154.4383	37.9	35.1
9	33.6	153.2698	149.6976	151.3235	150.0984	33.6	31
6	32.8	154.954	150.1934	153.3478	150.7344	37.3	34.5
15	26.4	158.3344	158.8158	158.6012	158.7618	29.3	26.9
6"	25.9	158.5352	160.2168	159.3212	160.0272	28	25.6
15'	26.1	158.8347	158.7384	158.9428	158.7503	29.3	26.9
17"	21.4	164.0893	164.0688	164.3076	164.0727	24	21.8
15"	20.9	166.8515	166.0492	167.6106	166.1476	21.9	19.8
14"	19.9	168.1743	166.4981	167.7568	166.6896	21.4	19.3
14	15.9	171.6931	172.0643	172.1729	172.0246	16	14.2
14'	21.5	172.6394	173.3598	173.2471	173.2805	14.8	13

[a]Averaged according to the Boltzmann-calculated contribution at B3LYP/6-31+G(d,p) level. [b]δ_U = Calculated Shielding Value (TMS) – Calculated Shielding value (Averaged). $\delta_S = (\delta_U - 1.1724)/1.0469$

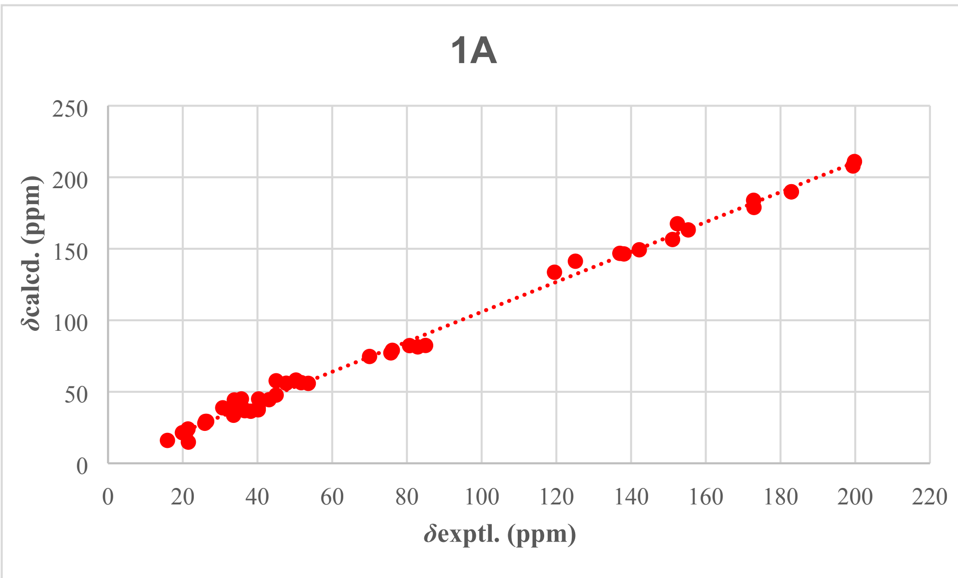


Figure S49. Correlation plots of experimental ^{13}C-NMR chemical shifts versus corresponding calculated ^{13}C-NMR chemical shifts for **1A.**

Table S3. Experimental ^{1}H-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of 1A

No.	Exptl.	1A-C1	1A-C2	1AC3	Averaged[a]
2	6.91	24.305	24.4577	24.4542	24.44103
5	2.33	29.8498	29.9036	29.9367	29.89797
6a	2.5	29.5004	29.4104	29.4049	29.42017
6b	1.33	30.2577	30.6646	30.3358	30.61795

7	3.4	27.9387	28.5437	28.0845	28.47454
8	4.25	26.8685	26.8991	26.7558	26.89476
9a	2.5	29.2172	29.0354	29.1778	29.05621
9b	2.13	29.9984	29.6432	30.0049	29.68445
10	2.33	29.4389	29.4406	29.579	29.44138
13a	6.15	25.2582	25.0086	25.2481	25.03748
13b	5.63	25.9652	25.6107	25.8648	25.65112
14	1.18	30.83897	30.96503	30.8491	30.95048
15	2.42	29.2891	29.39903	29.37873	29.38691
1'	2.13	29.3344	29.2479	29.3801	29.25825
2'	7.38	24.1027	24.2941	24.3824	24.27386
5'	1.69	30.4588	30.4381	30.4581	30.4405
6'a	2.03	29.8416	29.6717	29.7802	29.69098
6'b	1.35	30.958	30.9617	31.0787	30.96212
7'	2.71	29.0029	29.1931	29.2627	29.17286
8'	4.54	26.5914	26.6771	26.7188	26.66805
9'a	2.22	28.9943	29.3427	29.3111	29.3045
9'b	2.22	29.5234	29.3326	29.3649	29.35362
10'	1.88	29.2807	29.1601	29.2529	29.1739
13'a	2.19	30.0172	30.1185	30.0962	30.1073
13'b	1.62	30.0958	30.1412	30.3043	30.13739
14'	1.41	30.9022	30.95183	30.95337	30.94643
15'	2.38	29.3842	29.4759	29.42033	29.46552
2''	3.98	27.8946	28.3093	27.6726	28.25964
3''a	1.73	29.8553	30.0055	30.5773	29.99313
3''b	1.69	30.0648	30.4013	29.0408	30.3551
4''	5.01	27.121	26.8155	27.3277	26.85238
5''	5.7	25.3011	25.7065	25.4109	25.66024
6''a	2.22	28.7024	29.0619	29.228	29.02388
6''b	2.1	30.2811	30.4374	30.3562	30.41979
7''	2.34	29.248	29.2891	29.3067	29.28474
8''	4.7	26.8799	26.8801	26.9088	26.88028
9''a	2.34	28.9143	29.0499	29.1508	29.03583
9''b	1.73	29.4808	29.6461	29.5874	29.62767
10''	2.74	29.1613	29.2073	29.0227	29.20099
13''a	2.27	30.112	30.1172	30.0659	30.11627
13''b	1.42	30.4243	30.4585	30.4784	30.45491
14''	1.24	30.74543	30.6216	30.9147	30.63715
15''	1.25	30.84587	30.5342	30.48803	30.56785
17''	2.04	29.78927	29.65277	29.84767	29.66901

Table S4. Free energies (ΔG), and Boltzmann distribution abundances of conformers of **1B**.

Conf.	B3LYP/6-31+G(d, p) Gibbs free energy (298.15 K)		
	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
1B-C1	-2729.066919	0.0000	0.781
1B-C2	-2729.065721	0.7520	0.219

Table S5. Experimental ^{13}C-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of **1B**

No.	Exptl.	1B-C1	1B-C2	Averaged[a]	Unscaled shifts (δ_U)[b]	Scaled shifts (δ_S)[c]
4	199.8	-24.8753	-24.6777	-24.8320	212.9	202.1
4'	199.4	-20.2708	-20.0028	-20.2121	208.3	197.7
12'	182.9	-1.5909	-1.6106	-1.5952	189.6	179.8
12"	182.9	-2.2873	-2.5158	-2.3373	190.4	180.6
16"	172.8	6.674	6.171	6.5638	181.5	172.1
12	172.9	9.2066	9.2054	9.2063	178.8	169.5
2'	152.4	20.503	20.4711	20.4960	167.6	158.8
2	155.3	23.705	23.5886	23.6795	164.4	155.7
1"	151.1	26.9961	31.1864	27.9138	160.1	151.6
11	142.2	37.5159	37.8527	37.5897	150.5	142.4
3	138.1	40.6094	40.7337	40.6367	147.4	139.5
3'	137	42.1643	41.9158	42.1099	145.9	138
5"	125.1	46.4679	49.1159	47.0478	141	133.4
13	119.5	54.5141	54.6721	54.5487	133.5	126.2
8'	80.7	105.5879	105.2782	105.5201	82.5	77.4
8	85	107.1732	106.762	107.0831	81	76
8"	82.9	107.9584	107.907	107.9471	80.1	75.1
1	75.7	107.6414	107.4685	107.6035	80.4	75.4
2"	76.1	113.1089	113.4848	113.1912	74.9	70.2
4"	70	115.4572	114.8813	115.3311	72.7	68.1
7"	51.7	129.9327	129.8751	129.9201	56	52.1
11"	50.3	132.049	132.2494	132.0929	58.1	54.1
7	45	131.6246	131.3151	131.5569	56.5	52.6
1'	47.7	132.1092	132.0732	132.1013	55.9	52
7'	53.6	133.4664	132.9841	133.3608	54.7	50.9
3"	43.1	141.1913	140.4954	141.0389	47	43.5
7	45	144.2361	144.4108	144.2744	43.8	40.4
10	40.3	141.4942	141.8267	141.5670	40	36.8
13'	33.8	142.8835	142.3149	142.7590	46.5	43
13"	35.7	147.9469	148.274	148.0185	45.3	41.9
10"	30.7	145.4311	145.6631	145.4819	42.6	39.3
10'	35.6	148.2532	148.3585	148.2763	39.8	36.6

9'	40.2	149.8029	149.1306	149.6557	38.4	35.3
6'	36.6	148.9969	149.4287	149.0915	39	35.9
5	40.2	150.4739	150.8581	150.5580	45.2	41.8
9"	38.2	142.8203	142.8835	142.8341	37.5	34.4
5'	35.1	149.7776	149.714	149.7637	34.2	31.3
9	33.6	154.0048	153.4025	153.8729	38.3	35.2
6	32.8	150.507	150.3134	150.4646	37.6	34.5
15	26.4	158.3848	158.4189	158.3923	29.7	27
6"	25.9	158.7659	158.7152	158.7548	29.3	26.6
15'	26.1	158.5936	158.7546	158.6289	29.4	26.7
17"	21.4	164.1396	164.2383	164.1612	23.9	21.4
15"	20.9	166.9745	166.7797	166.9318	21.1	18.7
14"	19.9	167.5435	168.0417	167.6526	20.4	18.1
14	15.9	169.3172	169.1502	169.2806	18.8	16.5
14'	21.5	172.9887	172.9559	172.9815	15.1	13

[a]Averaged according to the Boltzmann-calculated contribution at B3LYP/6-31+G(d,p) level. [b]δ_U = Calculated Shielding Value (TMS) – Calculated Shielding value (Averaged). $\delta_S = (\delta_U - 1.4871)/1.0462$

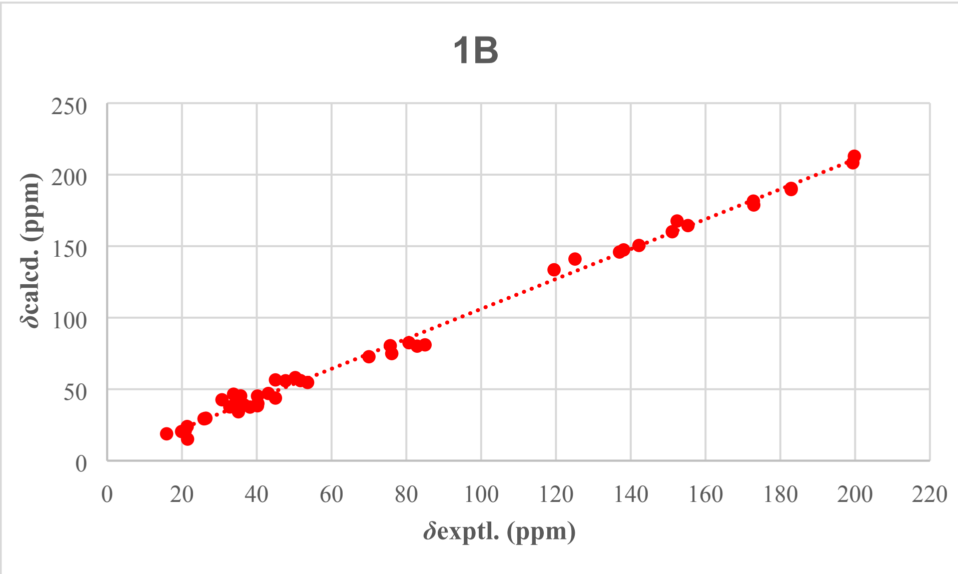


Figure S50. Correlation plots of experimental ^{13}C-NMR chemical shifts versus corresponding calculated ^{13}C-NMR chemical shifts for **1B.**

Table S6. Experimental ^{1}H-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of 1B

No.	Exptl.	1B-C1	1B-C2	Averaged[a]
2	6.91	24.4611	24.4481	24.45825
5	2.33	29.9034	29.8498	29.89166
6a	2.5	30.1538	30.0925	30.14038
6b	1.33	29.5725	29.6096	29.58062
7	3.4	28.2441	28.2708	28.24995

8	4.25	25.9539	25.9308	25.94884
9a	2.5	30.0441	30.0176	30.03830
9b	2.13	29.1995	29.203	29.20027
10	2.33	29.7231	29.6974	29.71747
13a	6.15	25.2441	25.2016	25.23479
13b	5.63	25.7662	25.6727	25.74572
14	1.18	30.53143	30.5054	30.52573
15	2.42	29.29777	29.3161	29.30178
1'	2.13	29.4868	29.4361	29.47570
2'	7.38	24.1731	24.1494	24.16791
5'	1.69	30.4986	30.4488	30.48769
6'a	2.03	30.3097	30.0383	30.25026
6'b	1.35	30.8287	30.8206	30.82693
7'	2.71	29.2818	29.2062	29.26524
8'	4.54	26.7607	26.719	26.75157
9'a	2.22	29.0647	29.1633	29.08629
9'b	2.22	29.696	29.603	29.67563
10'	1.88	29.2871	29.3348	29.29755
13'a	2.19	30.0562	30.0339	30.05132
13'b	1.62	30.1276	30.1132	30.12445
14'	1.41	30.95757	30.9455	30.95492
15'	2.38	29.46273	29.44383	29.45859
2''	3.98	27.9628	27.8615	27.94062
3''a	1.73	29.8095	30.1317	29.88006
3''b	1.69	30.0689	29.7034	29.98886
4''	5.01	27.103	27.1869	27.12137
5''	5.7	25.4568	25.7227	25.51503
6''a	2.22	28.795	28.8402	28.80490
6''b	2.1	30.3232	30.3473	30.32848
7''	2.34	29.3955	29.3156	29.37800
8''	4.7	26.8254	26.7057	26.79919
9''a	2.34	29.5938	29.5789	29.59054
9''b	1.73	29.0655	29.133	29.08028
10''	2.74	29.2667	29.2053	29.25325
13''a	2.27	30.2558	30.1652	30.23596
13''b	1.42	30.4322	30.3519	30.41461
14''	1.24	30.756	30.70833	30.74556
15''	1.25	30.61137	30.61537	30.61224
17''	2.04	29.80897	29.74703	29.79540

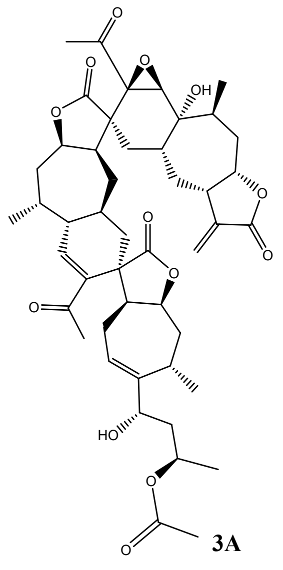
Table S7. Experimental chemical shifts, the calculated shielding tensors for **1A** (isomer 1) and **1B** (isomer 2), and the DP4+ probability of **1A** and **1B**

Functional		Solvent?		Basis Set		Type of Data	
mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
		DP4+	100.00%	0.00%	-	-	-
Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
C	x	199.8	-22.9	-24.8			
C	x	199.4	-19.9	-20.2			
C	x	182.9	-1.8	-1.6			
C	x	182.9	-1.8	-2.3			
C	x	172.8	4.1	6.6			
C	x	172.9	9.2	9.2			
C	x	152.4	20.5	20.5			
C	x	155.3	24.8	23.7			
C	x	151.1	31.6	27.9			
C	x	142.2	38.7	37.6			
C	x	138.1	41.6	40.6			
C	x	137	41.23	42.11			
C	x	125.1	46.78	47.05			
C	x	119.5	54.43	54.55			
C		80.7	105.75	105.52			
C		85	105.68	107.08			
C		82.9	106.65	107.95			
C		75.7	110.81	107.60			
C		76.1	109.02	113.19			
C		70	113.30	115.33			
C		51.7	131.68	132.09			
C		50.3	129.89	129.92			
C		45	130.34	131.56			
C		47.7	132.05	132.10			
C		53.6	132.17	133.36			
C		43.1	143.5585914	141.0388979			
C		45	140.3615672	144.2743593			
C		40.3	143.0438229	148.0185349			
C		33.8	143.7082258	141.5670175			
C		35.7	143.0564651	142.7589766			
C		30.7	149.2723533	145.481908			
C		35.6	147.8313442	148.2762607			
C		40.2	150.6811116	149.6556663			
C		36.6	151.2280383	149.0914642			
C		40.2	149.4644872	142.8341408			
C		38.2	151.6633572	150.5580398			
C		35.1	150.0983511	153.8728963			
C		33.6	154.4383253	149.7636716			
C		32.8	150.7343862	150.4646016			
C		26.4	158.7618252	158.3922679			
C		25.9	160.0272364	158.7547967			
C		26.1	158.7503275	158.628859			
C		21.4	164.0727061	164.1612153			
C		20.9	166.1475805	166.9318388			
C		19.9	166.6896167	167.6526058			
C		15.9	172.0245994	169.280627			
C		21.5	173.2804875	172.9815168			
H	x	6.91	24.4410312	24.458253			
H		2.33	29.8979675	29.8916616			
H		2.5	29.4201715	30.1403753			
H		1.33	30.6179463	29.5806249			
H		3.4	28.4745406	28.2499473			
H		4.25	26.8947615	25.9488411			
H		2.5	29.056213	30.0382965			
H		2.13	29.6844487	29.2002665			
H		2.33	29.4413835	29.7174717			
H	x	6.15	25.0374829	25.2347925			
H	x	5.63	25.6511192	25.7457235			
H		1.18	30.95048053	30.52573203			
H		2.42	29.3869085	29.30178167			
H		2.13	29.2582539	29.4756967			
H	x	7.38	24.2738555	24.1679097			
H		1.69	30.4404963	30.4876938			
H		2.03	29.6909786	30.2502634			
H		1.35	30.9621157	30.8269261			
H		2.71	29.1728554	29.2652436			
H		4.54	26.6680506	26.7515677			
H		2.22	29.3045032	29.0862934			
H		2.22	29.3536233	29.675633			
H		1.88	29.173895	29.2975463			
H		2.19	30.1073022	30.0513163			
H		1.62	30.1373931	30.1244464			
H		1.41	30.94643403	30.95492407			
H		2.38	29.46551573	29.45859423			
H		3.98	28.2596408	27.9406153			
H		1.73	29.9931308	29.8800618			
H		1.69	30.355098	29.9888555			
H		5.01	26.8523849	27.1213741			
H	x	5.7	25.6602422	25.5150321			
H		2.22	29.0238772	28.8048988			
H		2.1	30.4197949	30.3284779			
H		2.34	29.2847433	29.3780019			
H		4.7	26.8802791	26.7991857			
H		2.34	29.0358259	29.5905369			
H		1.73	29.6276714	29.0802825			
H		2.74	29.2009938	29.2532534			
H		2.27	30.1162741	30.2359586			
H		1.42	30.4549115	30.4146143			
H		1.24	30.63714953	30.745561			
H		1.25	30.5678485	30.61224267			
H		2.04	29.66900947	29.79540327			

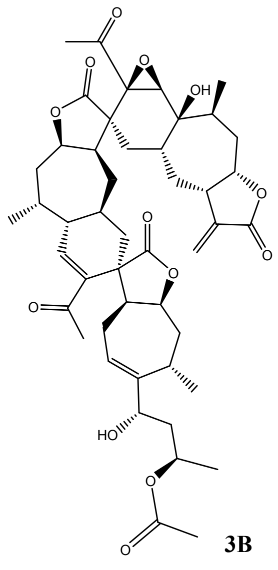
NMR chemical shifts and ECD calculation of Xanthanoltrimer C (3).

Conformational analysis of the **3A** and **3B** (Fig. S52) were carried out via Monte Carlo searching with the MMFF94s molecular mechanics force field using the spartan 14 software. 4 of **3A** and 3 of **3B** geometries having relative energies within 5 kcal/mol were optimized using DFT at the B3LYP/6-31+G (d, p) level in vacuum with the Gaussian 09 program, respectively. NMR chemical shifts calculation for those B3LYP/6-31+G (d, p)-optimized conformers with their Boltzmann distribution (≧1%, Table S7, S9) were carried out at PCM/mPW1PW91/6-311+G (d, p) level in methanol with GIAO method. After Boltzmann weighing of the calculated chemical shift of each isomers, the DP4+ parameters were calculated using the excel file (Table S10), which was provided by Ariel M. Sarotti.

In addition, those stable conformers with their Boltzmann distribution (≧1%) also were carried out at the TDDFT CAM-B3LYP/6-311+G (2d,p) level in the methanol for ECD computation. Boltzmann statistics were performed for ECD simulations with a standard deviation of σ 0.3 eV. The final ECD spectra of **3A** and **3B** were obtained according to the Boltzmann distribution theory and their relative Gibbs free energy (ΔG), respectively.



3A



3B

Figure S51. The Structures of **3A** and **3B**

Table S8. Free energies (ΔG), and Boltzmann distribution abundances of conformers of **3A**.

Conf.	B3LYP/6-31+G(d, p) Gibbs free energy (298.15 K)		
	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
3A-C1	-2804.262217	0.0000	0.897
3A-C2	-2804.260176	1.2810	0.103

Table S9. Experimental ^{13}C-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of **3A**

No.	**Exptl.**	**3A-C1**	**3A-C2**	**Averaged**[a]	**Unscaled shifts (δ_U)**[b]	**Scaled shifts (δ_S)**[c]
4	204.2	-29.6037	-28.5664	-29.4969	217.5	207.0
4'	199.3	-19.7955	-20.7359	-19.8924	207.9	197.8
12"	182.3	-1.8659	-2.2823	-1.9088	190	180.8
12'	183	-0.8444	-0.8146	-0.8413	188.9	179.7
16"	172.8	6.0155	6.35	6.05	182	173.1
12	172.8	9.6429	7.8256	9.4557	178.6	169.9
2'	152.3	20.7299	19.7725	20.6313	167.4	159.2
1"	151.1	30.8206	30.314	30.7684	157.3	149.6
11	142.3	38.3448	36.7051	38.1759	149.9	142.5
3'	137.1	41.8775	41.4416	41.8326	146.2	139.0
5"	125.1	50.204	55.2829	50.7271	137.3	130.5
13	119.5	53.0657	55.3092	53.2968	134.7	128.0
8'	80.9	104.7651	105.4789	104.8386	83.2	78.9
8	85.3	104.8426	104.9205	104.8506	83.2	78.9
8"	82.9	107.7099	106.71	107.6069	80.4	76.2
1	76.5	109.9418	108.5113	109.7945	78.3	74.2
2"	76.2	113.8062	113.9305	113.819	74.2	70.3
4"	70.1	114.2146	113.7985	114.1717	73.9	70.0
2	69.5	118.1292	121.8472	118.5122	69.5	65.8
3	70.4	120.4723	120.9966	120.5263	67.5	63.9
11"	50.3	131.0446	130.5895	130.9977	57	53.9
7'	53.4	131.2497	130.9898	131.2229	56.8	53.7
1'	47.2	131.304	130.9622	131.2688	56.8	53.7
7"	51.7	131.9726	131.8217	131.9571	56.1	53.0
11'	50	133.4041	132.9509	133.3574	54.7	51.7
7	44.7	139.6141	138.4495	139.4941	48.6	45.8
10	39.2	141.2416	148.0515	141.943	46.1	43.5
3"	43.1	143.4354	145.5185	143.65	44.4	41.8
13'	36	143.8926	144.9385	144.0003	44	41.5
13"	35.8	144.1194	142.8479	143.9884	44.1	41.6
10"	30.7	144.968	148.2151	145.3025	42.7	40.2

9'	40.2	147.9103	148.3761	147.9583	40.1	37.7
10'	35.7	148.4287	148.3531	148.4209	39.6	37.3
6	32.9	150.8172	151.3464	150.8717	37.2	35.0
5	39.2	150.8371	151.6122	150.9169	37.1	34.9
9"	38.3	151.3871	150.5154	151.2973	36.7	34.5
5'	35.2	151.5417	151.0637	151.4925	36.6	34.4
6'	36.4	152.6446	152.3071	152.6098	35.4	33.2
9	34.4	154.5713	151.9658	154.3029	33.7	31.6
6"	25.9	158.4871	159.8707	158.6296	29.4	27.5
15'	26.1	158.8534	158.7144	158.8391	29.2	27.3
15	23.8	160.6654	159.782	160.5744	27.5	25.7
17"	21.4	163.9453	164.0901	163.9602	24.1	22.5
15"	20.9	166.9581	167.3877	167.0023	21	19.5
14"	19.9	167.4372	167.8088	167.4755	20.6	19.1
14	16.4	172.5881	171.4576	172.4717	15.6	14.4
14'	21.5	172.8748	172.8051	172.8676	15.2	14.0

[a]Averaged according to the Boltzmann-calculated contribution at B3LYP/6-31+G(d,p) level. [b]δ_U = Calculated Shielding Value (TMS) – Calculated Shielding value (Averaged). $\delta_S = (\delta_U - 0.5514)/1.0481$

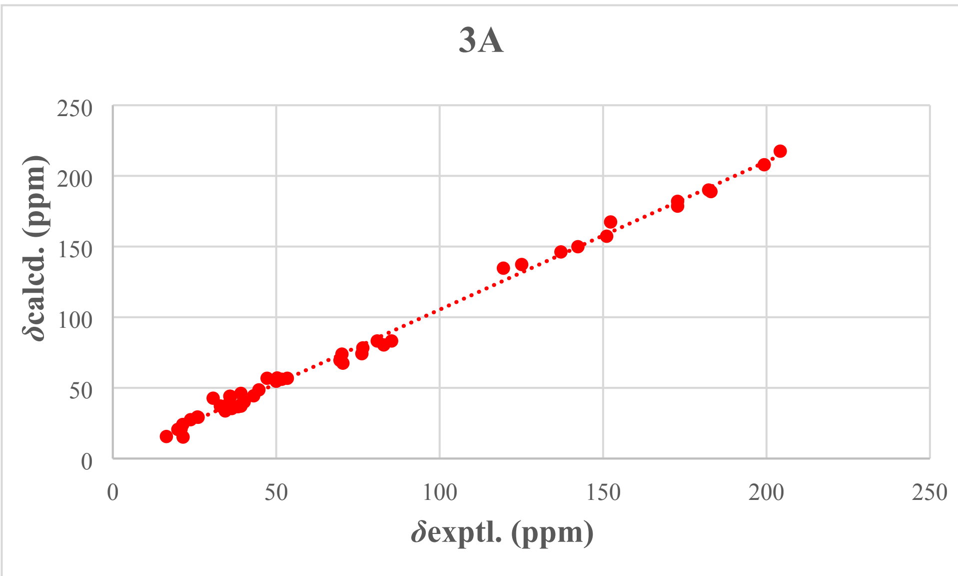


Figure S52. Correlation plots of experimental ^{13}C-NMR chemical shifts versus corresponding calculated ^{13}C-NMR chemical shifts for **3A.**

Table S10. Free energies (ΔG), and Boltzmann distribution abundances of conformers of **3B**.

Conf.	B3LYP/6-31+G(d, p) Gibbs free energy (298.15 K)		
	G (Hartree)	ΔG (Kcal/mol)	Boltzmann Distribution
3B-C1	-2804.260692	0.0000	0.902
3B-C2	-2804.258595	1.3160	0.098

Table S11. Experimental ^{13}C-NMR chemical shifts and GIAO isotropic magnetic shielding values calculated for PCM/mPW1PW91/6-311+G (d, p) geometries of **3B**

No.	Exptl.	3B-C1	3B-C2	Averaged^a	Unscaled shifts (δ_U)^b	Scaled shifts (δ_S)^c
4	204.2	-28.0474	-28.0752	-28.0501	216.1	205.8
4'	199.3	-20.6664	-20.4835	-20.6485	208.7	198.7
12"	182.3	-1.9648	-2.1188	-1.9799	190	180.9
12'	183	-1.1951	-1.2103	-1.1966	189.2	180.1
16"	172.8	6.042	5.9882	6.0367	182	173.3
12	172.8	8.903	8.9388	8.9065	179.1	170.5
2'	152.3	19.9845	20.1223	19.998	168	159.9
1"	151.1	30.4217	34.251	30.797	157.2	149.6
11	142.3	37.349	37.2971	37.3439	150.7	143.4
3'	137.1	42.5643	42.3315	42.5415	145.5	138.4
5"	125.1	53.8948	53.9583	53.901	132.8	126.3
13	119.5	55.4543	53.4395	55.2568	134.1	127.6
8'	80.9	105.8006	105.6093	105.7819	82.3	78.1
8	85.3	106.9248	106.9304	106.9253	80.2	76.1
8"	82.9	107.236	107.1674	107.2293	80.8	76.7
1	76.5	107.8086	107.7575	107.8036	81.1	77
2"	76.2	113.5137	114.2215	113.5831	74.5	70.7
4"	70.1	113.973	114.2179	113.997	74	70.2
2	69.5	114.4404	114.37	114.4335	70.4	66.8
3	70.4	117.6323	117.6178	117.6309	73.6	69.8
11"	50.3	130.0791	130.2168	130.0926	58	54.9
7'	53.4	130.5794	130.5776	130.5792	55.5	52.5
1'	47.2	132.0504	132.1229	132.0575	57.5	54.5
7"	51.7	132.5494	132.5377	132.5483	56	53
11'	50	133.479	133.5293	133.4839	54.6	51.7
7	44.7	142.3039	142.3827	142.3116	43.4	41
10	39.2	143.7862	143.6385	143.7717	37	34.9
3"	43.1	144.6768	144.6601	144.6752	43	40.6
13'	36	145.167	143.8253	145.0355	44.3	41.9
13"	35.8	146.5159	146.2114	146.4861	45.7	43.2
10"	30.7	147.1285	147.2662	147.142	41.6	39.3
9'	40.2	147.9166	147.9732	147.9221	38.8	36.6
10'	35.7	149.2838	149.1143	149.2672	40.1	37.8
6	32.9	150.2121	150.223	150.2132	37.8	35.7
5	39.2	150.9328	151.0972	150.9489	40.9	38.6
9"	38.3	151.0294	151.0325	151.0297	36	33.9
5'	35.2	151.123	151.1108	151.1218	37.1	35
6'	36.4	152.0613	151.8884	152.0444	35.8	33.7
9	34.4	152.2917	152.225	152.2852	36.9	34.8
6"	25.9	158.4673	158.4997	158.4705	28.1	26.4

15'	26.1	159.9501	160.2244	159.977	29.6	27.8
15	23.8	160.31	160.3853	160.3174	27.7	26
17"	21.4	164.0776	164.0701	164.0769	24	22.5
15"	20.9	167.6969	167.455	167.6732	20.4	19
14"	19.9	168.4364	168.3289	168.4259	19.6	18.3
14	16.4	170.2777	170.3516	170.2849	17.8	16.6
14'	21.5	173.3459	173.2753	173.339	14.7	13.6

[a]Averaged according to the Boltzmann-calculated contribution at B3LYP/6-31+G(d,p) level. [b]δ_U = Calculated Shielding Value (TMS) – Calculated Shielding value (Averaged). $\delta_S = (\delta_U - 0.4378)/1.0479$

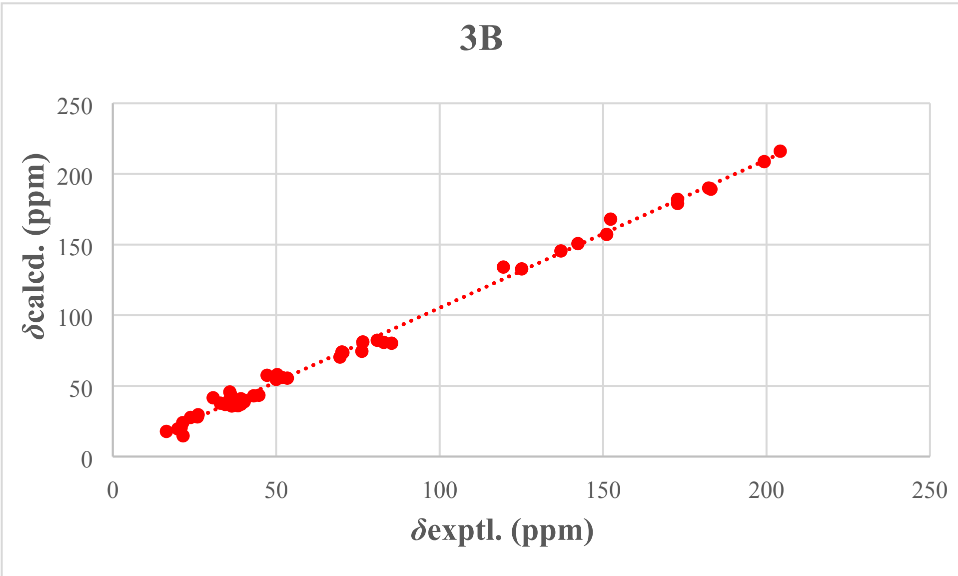


Figure S53. Correlation plots of experimental ^{13}C-NMR chemical shifts versus corresponding calculated ^{13}C-NMR chemical shifts for **3B.**

Table S12. Experimental chemical shifts, the calculated shielding tensors for **3A** (isomer 1) and **3B** (isomer 2), and the DP4+ probability of **3A** and **3B**

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311+G(d,p)		Shielding Tensors	
3								
12			DP4+	0.01%	99.99%	-	-	-
14	Nuclei	sp2?	Experimental	Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5
15	C	x	204.2	-29.5	-28.1			
16	C	x	199.3	-19.9	-20.6			
17	C	x	182.3	-1.9	-2.0			
18	C	x	183	-0.8	-1.2			
19	C	x	172.8	6.0	6.0			
20	C	x	172.8	9.5	8.9			
21	C	x	152.3	20.6	20.0			
22	C	x	151.1	30.8	30.8			
23	C	x	142.3	38.2	37.3			
24	C	x	137.1	41.8	42.5			
25	C	x	125.1	50.7	55.3			
26	C	x	119.5	53.30	53.90			
27	C		80.9	104.84	105.78			
28	C		85.3	104.85	107.80			
29	C		82.9	107.61	107.23			
30	C		76.5	109.79	106.93			
31	C		76.2	113.82	113.58			
32	C		70.1	114.17	114.00			
33	C		69.5	118.51	117.63			
34	C		70.4	120.53	114.43			
35	C		50.3	131.00	130.09			
36	C		53.4	131.22	132.55			
37	C		47.2	131.27	130.58			
38	C		51.7	131.96	132.06			
39	C		50	133.36	133.48			
40	C		44.7	139.4941462	144.6751634			
41	C		39.2	141.9430197	151.0297038			
42	C		43.1	143.6499593	145.0355134			
43	C		36	144.0003277	143.7717254			
44	C		35.8	143.9884355	142.3116224			
45	C		30.7	145.3024513	146.486059			
46	C		40.2	147.9582774	149.267189			
47	C		35.7	148.4209132	147.9221468			
48	C		32.9	150.8717076	150.2131682			
49	C		39.2	150.9169353	147.1419946			
50	C		38.3	151.2973149	152.0443558			
51	C		35.2	151.492466	150.9489112			
52	C		36.4	152.6098375	152.2851634			
53	C		34.4	154.3029335	151.1218044			
54	C		25.9	158.6296108	159.9769814			
55	C		26.1	158.839083	158.4704752			
56	C		23.8	160.5744098	160.3173794			
57	C		21.4	163.9602144	164.076865			
58	C		20.9	167.0023488	167.6731938			
59	C		19.9	167.4754748	168.425865			
60	C		16.4	172.4716585	170.2849422			
61	C		21.5	172.8676209	173.3389812			