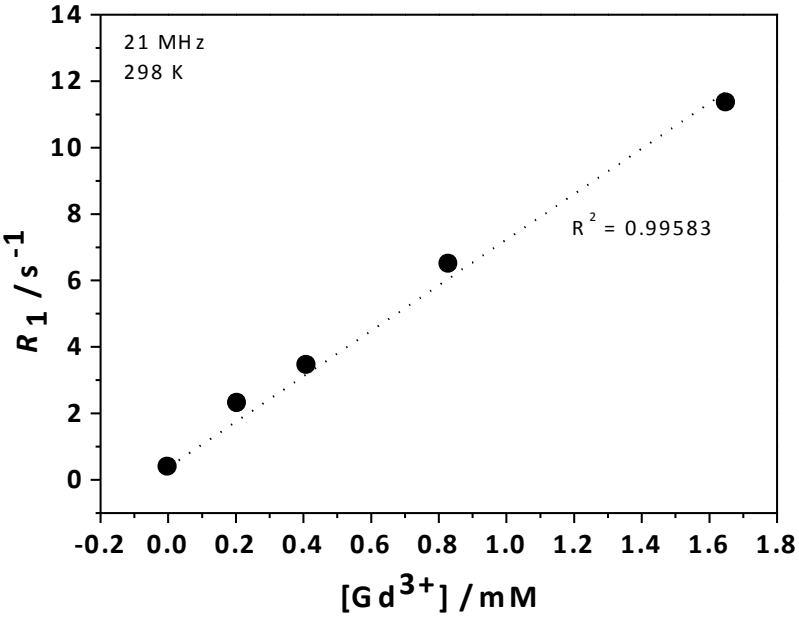

Figure S1. R_1 value of Gd-**7** at different concentrations

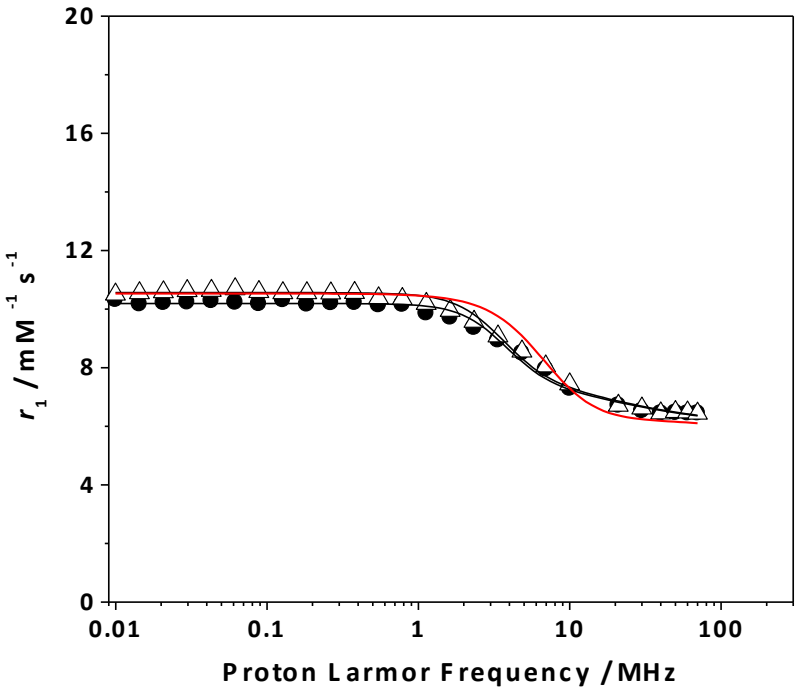

Figure S2. ^{1}H NMRD profiles of Gd-**5** (solid circles) and Gd-**7** (open triangles). The red line represent the best fitting results of the experimental data points by using q = 2 (Table S1).

Table S1: Best-fit parameters obtained from the analysis of the $1/T_1$ ^{1}H NMRD profiles collected at 298 K and ^{17}O NMR data using $q = 2$

Parameter	Gd-**7**
$^{298}\tau_M$ / ns	40 ± 8
$\Delta H_M^{\#}$ / kJ mol^{-1}	42.3 ± 1.2
$A/\hbar$ / 10^6 rad s^{-1}	–3.1 ± 0.1
$^{298}\tau_R$ / ps	68 ± 2.0
$^{298}\tau_V$ / ps	19.4 ± 2.1
Δ^2 / 10^{19} s^{-2}	5.9 ± 0.8

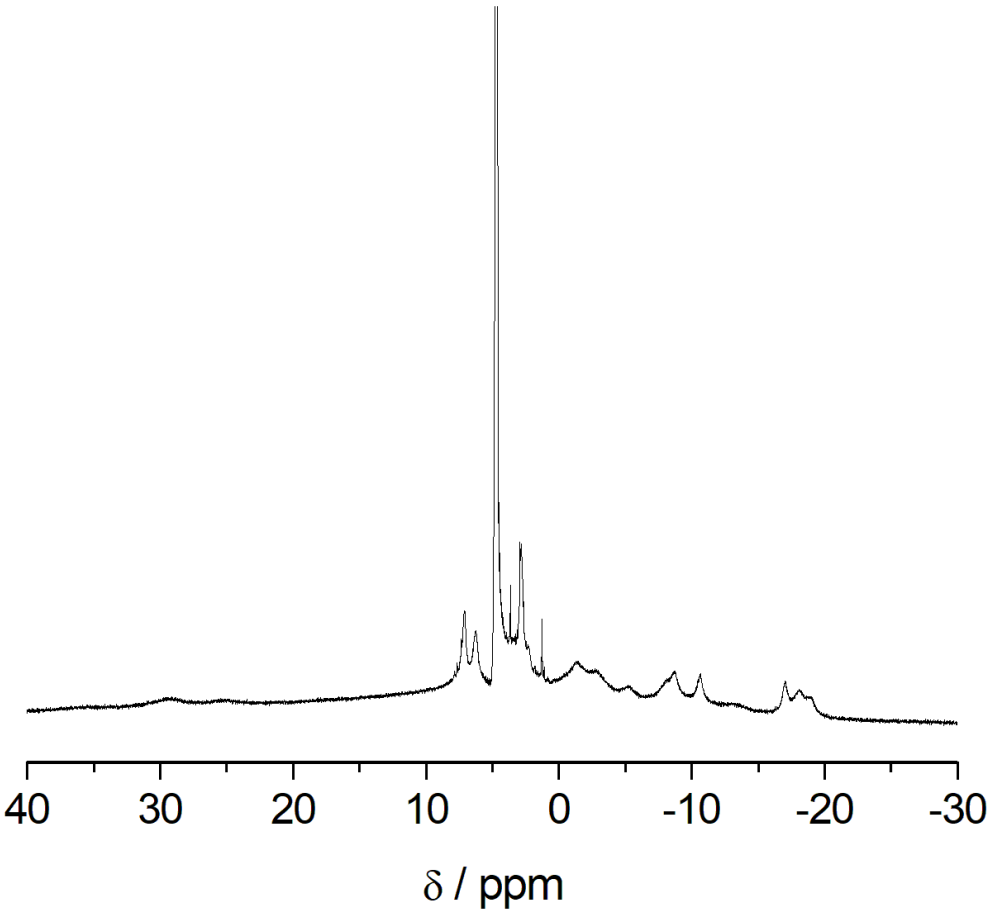

Figure S3. ^{1}H NMR spectrum of Eu-**7**.

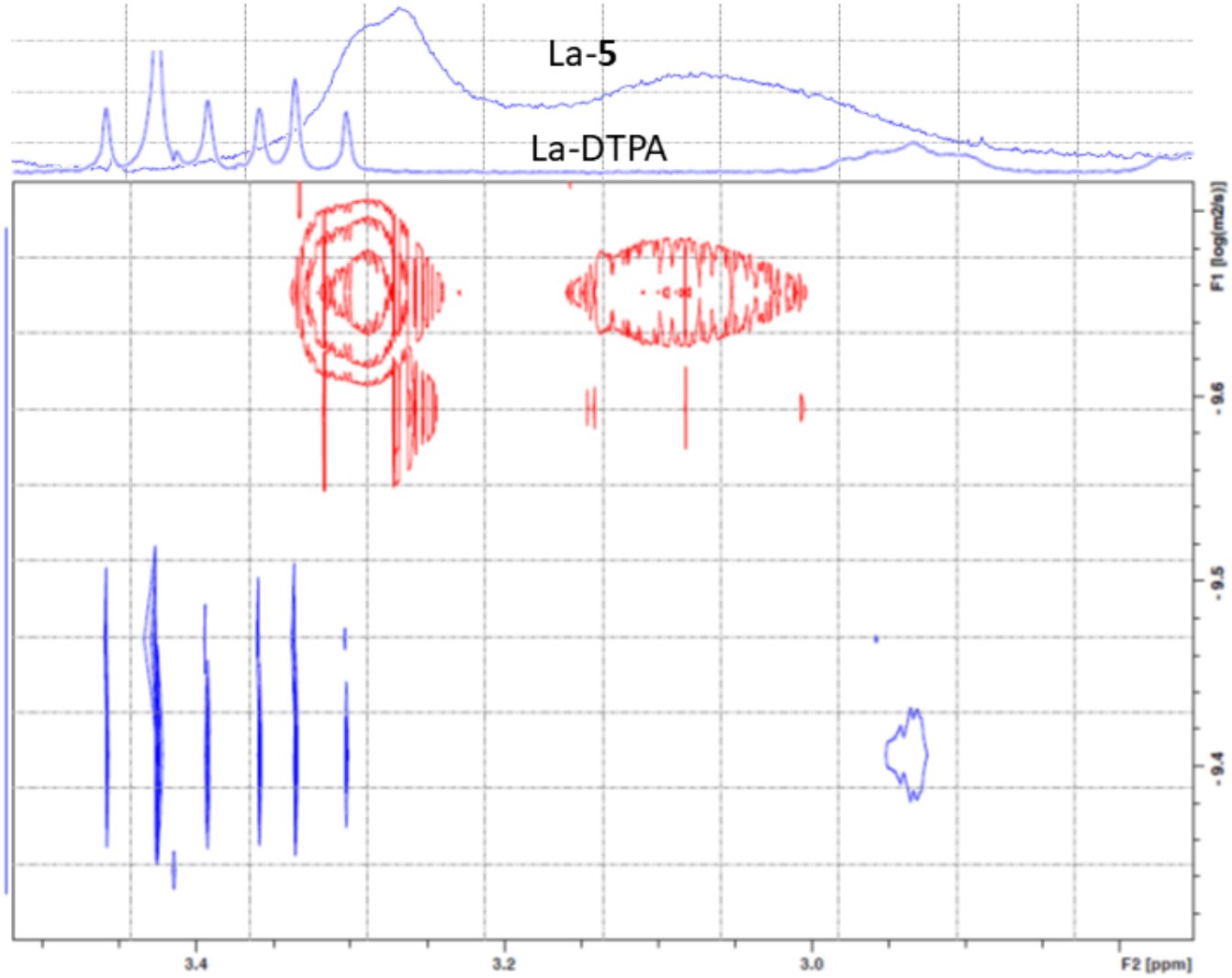

Figure S4. ^{1}H NMR DOSY spectra of La-**5** compared to LaDTPA.

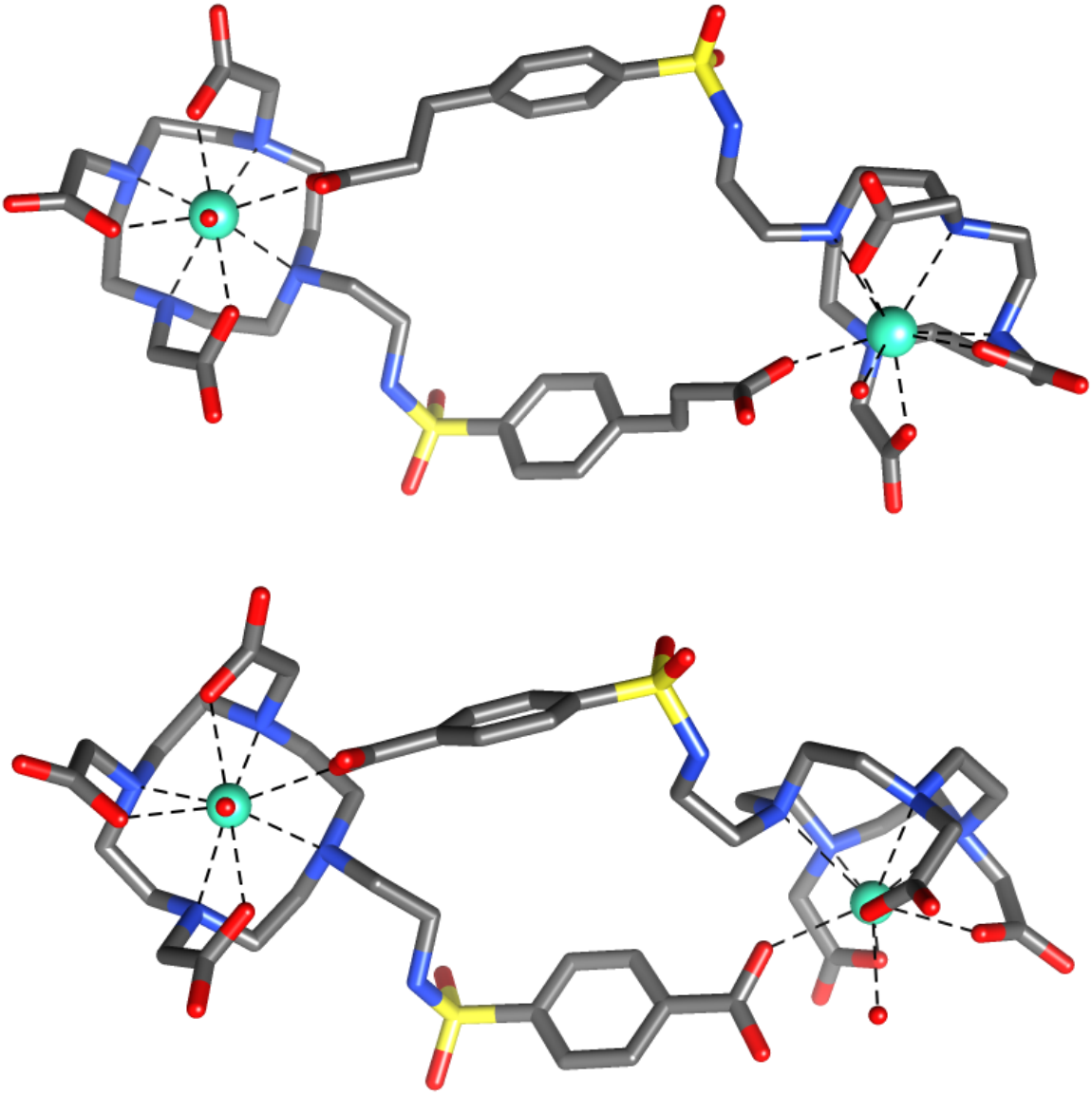

Figure S5. Geometries of the SAP conformers of $[Gd_2(\mathbf{5})_2(H_2O)_2]$ and $[Gd_2(\mathbf{7})_2(H_2O)_2]$ (bottom), obtained from DFT calculations at the TPSSh/LCRECP/6-31G(d) level.

Table S2. Optimized Cartesian coordinates (Å) obtained for the SAP isomer of [Gd(DO3A-SA-$(CH_2)_2$-COO)$(H_2O)]_2$ (TPSSh/LCRECP/6-31G(d) level, aqueous solution, 0 imaginary frequencies).

N	-8.73085600	2.03819900	-0.06312700
C	-10.15895400	1.87847800	0.32080000
C	-10.37262400	0.72781500	1.29975600
N	-9.91245800	-0.58543700	0.78092000
C	-9.69786300	-1.51778500	1.91904200
C	-8.36045100	-1.26951700	2.61084500
N	-7.19415800	-1.44818800	1.70835500
C	-5.97533300	-0.84916800	2.31943000
C	-5.97033300	0.67961200	2.30338400
N	-5.95757200	1.24916900	0.93127300
C	-6.49099600	2.63637200	0.92890100
C	-8.00740100	2.69648600	1.05128200
C	-8.63298400	2.85339400	-1.29849600
C	-7.33793800	2.64151800	-2.10243100
O	-6.82576500	1.45076900	-2.03723200
O	-6.91006300	3.57474800	-2.79520900
C	-10.90911000	-1.14016000	-0.16402100
C	-10.81473400	-0.52944400	-1.57270600
O	-11.83028800	-0.51975800	-2.28540600
O	-9.64082600	-0.11348500	-1.91954100
C	-6.97169100	-2.89371900	1.45415700
C	-7.83267700	-3.48641500	0.32222800
O	-8.04644000	-4.70857600	0.33696800
O	-8.22060200	-2.65943600	-0.59314300
C	-4.59391800	1.22045900	0.33868500
C	-3.49706800	2.10082000	0.96935500
H	-9.44597200	2.53764900	-1.96041800
H	-8.76377700	3.92327600	-1.08324700
H	-11.93318400	-1.03332200	0.22147600
H	-10.69354300	-2.20658500	-0.28028000
H	-7.11139600	-3.48342700	2.37095300
H	-5.93571000	-3.01441300	1.12818800
H	-4.25004300	0.18710100	0.38193800
H	-4.70707700	1.46720400	-0.72207500
H	-10.73330800	1.70590200	-0.58988800
H	-10.54338800	2.80371700	0.77891300
H	-11.44272500	0.67869300	1.55686000
H	-9.83976000	0.92864800	2.23236200
H	-10.50405500	-1.42182100	2.66286500
H	-9.73976800	-2.53855600	1.53428200
H	-8.27396800	-1.94587400	3.47626800
H	-8.33569000	-0.25054200	3.00495400
H	-5.85379000	-1.19189400	3.35913300
H	-5.12430600	-1.21727300	1.74269800
H	-6.84806400	1.06948900	2.82401200
H	-5.10271500	1.02232400	2.88604300
H	-6.16684600	3.11363300	0.00248800
H	-6.05671800	3.22505200	1.74940000
H	-8.32077800	2.22044500	1.98367600
H	-8.30763800	3.75496800	1.12152100
H	-2.52615100	1.68285000	0.66764100
H	-3.54086600	2.08586500	2.06097900
N	-3.61599800	3.51377100	0.55361300
H	-3.55394500	3.64435900	-0.45795700

O	-7.21622700	-0.99969500	-3.08802000
H	-6.28569100	-1.41298000	-3.07746200
H	-7.06950700	-0.06362500	-3.33951700
S	-2.65160300	4.64799500	1.33055800
O	-2.98714400	5.93808500	0.70689500
O	-2.85568100	4.42817100	2.77206500
C	-0.94252100	4.28578200	0.95697100
C	-0.34165200	4.89638000	-0.15069000
C	-0.23787400	3.37181600	1.74901800
C	0.98002000	4.58188400	-0.46222200
H	-0.89713800	5.61578900	-0.74308300
C	1.08288600	3.06525800	1.41612800
H	-0.70697200	2.92676400	2.62031900
C	1.70905500	3.65964500	0.30880000
H	1.45503200	5.06360500	-1.31301700
H	1.63651800	2.36099400	2.03172800
C	3.12636000	3.29349500	-0.07232700
Gd	-7.63477900	-0.36266700	-0.69595900
N	8.73066400	-2.03863500	-0.06307100
C	10.15885000	-1.87892700	0.32054900
C	10.37274200	-0.72817400	1.29936000
N	9.91265900	0.58510600	0.78053100
C	9.69828700	1.51748700	1.91865700
C	8.36095800	1.26933300	2.61064200
N	7.19458100	1.44811100	1.70825600
C	5.97571700	0.84931800	2.31950600
C	5.97053600	-0.67947600	2.30362600
N	5.95772000	-1.24921900	0.93157800
C	6.49094600	-2.63648700	0.92941100
C	8.00734500	-2.69671300	1.05155700
C	8.63246900	-2.85394300	-1.29833700
C	7.33703300	-2.64220700	-2.10165500
O	6.82553500	-1.45109300	-2.03723000
O	6.90845000	-3.57567700	-2.79367500
C	10.90923500	1.13972900	-0.16453300
C	10.81448900	0.52937900	-1.57336000
O	11.82971600	0.52084300	-2.28655500
O	9.64076100	0.11263000	-1.91977400
C	6.97231100	2.89366800	1.45394700
C	7.83311600	3.48615500	0.32176400
O	8.04718700	4.70827000	0.33648600
O	8.22067900	2.65911600	-0.59369200
C	4.59407100	-1.22039400	0.33894700
C	3.49712200	-2.10059100	0.96965300
H	9.44516300	-2.53808900	-1.96057200
H	8.76344900	-3.92379100	-1.08303400
H	11.93336400	1.03254400	0.22072400
H	10.69401300	2.20624900	-0.28053800
H	7.11230400	3.48343700	2.37066100
H	5.93627300	3.01451600	1.12820700
H	4.25031400	-0.18698500	0.38207700
H	4.70722500	-1.46727100	-0.72177900
H	10.73299300	-1.70645600	-0.59028600
H	10.54332400	-2.80414800	0.77866500
H	11.44287700	-0.67915600	1.55632900
H	9.83998200	-0.92889200	2.23205500
H	10.50458700	1.42147600	2.66236400
H	9.74019900	2.53825500	1.53388700

H	8.27466600	1.94574400	3.47603600
H	8.33612800	0.25037000	3.00479400
H	5.85430600	1.19214200	3.35919000
H	5.12469100	1.21747700	1.74280700
H	6.84823300	-1.06936900	2.82432600
H	5.10287100	-1.02202300	2.88629300
H	6.16660400	-3.11390200	0.00314500
H	6.05669900	-3.22493800	1.75008700
H	8.32091700	-2.22057700	1.98383600
H	8.30745700	-3.75523000	1.12187700
H	2.52623600	-1.68255900	0.66793600
H	3.54092700	-2.08564100	2.06127600
N	3.61603200	-3.51356300	0.55392500
H	3.55435500	-3.64407500	-0.45767600
O	7.21547800	0.99910400	-3.08783400
H	6.28546700	1.41376700	-3.07690400
H	7.06760800	0.06320600	-3.33926700
S	2.65135300	-4.64778300	1.33050500
O	2.98698800	-5.93782300	0.70678600
O	2.85509200	-4.42809500	2.77207800
C	0.94238800	-4.28546100	0.95655500
C	0.34182600	-4.89568800	-0.15147200
C	0.23753600	-3.37178000	1.74874800
C	-0.97976100	-4.58109200	-0.46325600
H	0.89746200	-5.61490100	-0.74396100
C	-1.08315200	-3.06513000	1.41560900
H	0.70642200	-2.92702400	2.62031200
C	-1.70900000	-3.65913300	0.30788300
H	-1.45456900	-5.06254400	-1.31432000
H	-1.63699500	-2.36112900	2.03132200
C	-3.12622300	-3.29287200	-0.07341400
Gd	7.63475900	0.36228800	-0.69600500
H	3.65247000	4.18581200	-0.43278200
H	3.66357600	2.92505600	0.80684300
H	-3.65228800	-4.18499000	-0.43442700
H	-3.66365900	-2.92487900	0.80580300
C	3.15241400	2.21097800	-1.17518200
H	2.67024300	1.30208800	-0.79196200
H	2.58149300	2.55002200	-2.04418500
C	-3.15196900	-2.20975700	-1.17567300
H	-2.58063200	-2.54814200	-2.04465200
H	-2.66999400	-1.30103200	-0.79175400
C	4.56641800	1.85040800	-1.64055000
O	4.82094700	1.99103400	-2.86902600
O	5.39055300	1.42051100	-0.75848000
C	-4.56584400	-1.84904300	-1.64137400
O	-5.39061000	-1.42074900	-0.75910100
O	-4.81963800	-1.98793200	-2.87018500

E(RTPSSh) =-5021.56476 Hartree

Zero-point correction =	1.293035
Thermal correction to Energy =	1.379007
Thermal correction to Enthalpy =	1.379951
Thermal correction to Gibbs Free Energy =	1.165884
Sum of electronic and zero-point Energies =	-5020.271725
Sum of electronic and thermal Energies =	-5020.185753
Sum of electronic and thermal Enthalpies =	-5020.184809
Sum of electronic and thermal Free Energies =	-5020.398876

Table S3. Optimized Cartesian coordinates obtained for the TSAP isomer of [Gd(DO3A-SA-$(CH_2)_2$-COO)$(H_2O)]_2$ (TPSSh/LCRECP/6-31G(d) level, aqueous solution, 0 imaginary frequencies).

C	-8.64105700	2.79743800	-1.38121400
C	-7.69556100	2.35601800	-2.51207200
O	-6.98654500	1.29318900	-2.26772400
O	-7.69612400	2.99613000	-3.57066800
C	-10.77943400	-0.94051200	0.37549800
C	-10.79716200	-0.79723500	-1.15850900
O	-11.76584800	-1.25008400	-1.78552300
O	-9.75760100	-0.21988100	-1.67240600
C	-6.78645800	-2.72143700	1.59727300
C	-7.51625500	-3.41019800	0.42701500
O	-7.34245200	-4.62793400	0.27113300
O	-8.23983000	-2.64045500	-0.32292900
C	-4.52649700	1.24495900	-0.07323700
C	-3.34170500	2.05715100	0.48553100
H	-9.62901800	2.38905300	-1.61610800
H	-8.72017800	3.89468000	-1.37218300
H	-11.79221100	-0.78844400	0.77788000
H	-10.47072300	-1.96456300	0.60194200
H	-6.84100500	-3.35530600	2.49499100
H	-5.73799300	-2.63167500	1.30883800
H	-4.16251000	0.26777500	-0.38967100
H	-4.92478800	1.73408300	-0.96704400
H	-2.42097200	1.72721200	-0.01242800
H	-3.21815800	1.89223200	1.55902600
N	-3.55018200	3.50979800	0.29004700
H	-3.50618400	3.79260200	-0.69070400
O	-7.43485500	-1.22054100	-2.98375100
H	-6.55765700	-1.72919300	-3.00498400
H	-7.21994300	-0.31719500	-3.30469200
S	-2.63633600	4.56644400	1.22411900
O	-2.98455100	5.91284500	0.74269500
O	-2.88191800	4.17490600	2.62241900
C	-0.90814300	4.27500900	0.87722300
C	-0.27650100	4.99780500	-0.14233500
C	-0.21812600	3.29833800	1.60444500
C	1.06109600	4.73116200	-0.43211700
H	-0.82008400	5.76458000	-0.68444200
C	1.11798700	3.04142000	1.29389900
H	-0.71092600	2.76498400	2.41061700
C	1.77533400	3.74681400	0.27335900
H	1.55868400	5.29942400	-1.21378000
H	1.65920200	2.28727300	1.85945700
Gd	-7.62782200	-0.35699900	-0.62181000
C	8.64099500	-2.79752800	-1.38102900
C	7.69531800	-2.35638800	-2.51184400
O	6.98657800	-1.29330600	-2.26770600
O	7.69552600	-2.99684100	-3.57022500
C	10.77948100	0.94050600	0.37540500
C	10.79719600	0.79713200	-1.15859100
O	11.76588400	1.24995300	-1.78562400
O	9.75765800	0.21971100	-1.67244900
C	6.78651100	2.72161000	1.59708000
C	7.51631300	3.41025500	0.42674800
O	7.34267600	4.62800900	0.27084500

O	8.23973100	2.64039000	-0.32321800
C	4.52634900	-1.24464800	-0.07322000
C	3.34158600	-2.05687000	0.48555600
H	9.62887600	-2.38901100	-1.61605000
H	8.72025500	-3.89475800	-1.37186500
H	11.79225200	0.78842200	0.77778600
H	10.47081000	1.96458400	0.60178200
H	6.84110100	3.35555700	2.49474200
H	5.73803400	2.63186800	1.30868200
H	4.16233100	-0.26743900	-0.38954400
H	4.92459400	-1.73370000	-0.96709100
H	2.42086900	-1.72703500	-0.01251300
H	3.21793700	-1.89180500	1.55901900
N	3.55015100	-3.50951700	0.29027900
H	3.50627000	-3.79244900	-0.69043900
O	7.43490600	1.22023700	-2.98395600
H	6.55762700	1.72871800	-3.00526400
H	7.22015500	0.31675200	-3.30465100
S	2.63638900	-4.56611500	1.22444100
O	2.98482400	-5.91255600	0.74329900
O	2.88176700	-4.17430400	2.62270000
C	0.90819400	-4.27498100	0.87729100
C	0.27676800	-4.99795800	-0.14225900
C	0.21796000	-3.29832300	1.60433900
C	-1.06083200	-4.73152200	-0.43222700
H	0.82053500	-5.76470600	-0.68422500
C	-1.11814500	-3.04161200	1.29361200
H	0.71057500	-2.76480800	2.41051600
C	-1.77528300	-3.74720300	0.27305900
H	-1.55825400	-5.29991700	-1.21389800
H	-1.65951300	-2.28746500	1.85902200
Gd	7.62789500	0.35692300	-0.62184300
N	7.31979300	1.36693600	1.86332500
N	9.80863600	-0.00001200	0.97414100
N	8.21806500	-2.27296600	-0.06558600
N	5.66446300	-0.96866900	0.84872800
C	10.36169900	-1.37291600	0.84176400
H	10.85341200	-1.43575000	-0.13134400
H	11.13270900	-1.55160200	1.60776600
C	7.00497000	-3.00765100	0.38104100
H	7.28328700	-3.98941800	0.79436200
H	6.38008300	-3.19583000	-0.49474900
C	8.63115000	1.52585900	2.54920300
H	8.47823000	1.73473000	3.61922400
H	9.11773100	2.40455100	2.11985800
C	5.22925600	-0.03986800	1.92536000
H	4.64804400	0.74740400	1.43902500
H	4.57147400	-0.54494000	2.65039900
C	9.53899600	0.31275500	2.39528600
H	9.07116100	-0.56486700	2.85127000
H	10.47670100	0.49323400	2.94483100
C	9.29166900	-2.44936600	0.94259000
H	9.76258700	-3.43947700	0.83859700
H	8.83055200	-2.42706000	1.93348400
C	6.21998200	-2.21970500	1.42012000
H	6.87953400	-1.94755100	2.24711700
H	5.42671400	-2.85118000	1.84051800
C	6.38678900	0.58095800	2.70975400

H	5.96410600	1.21465500	3.50482400
H	6.96589300	-0.19773000	3.21282400
N	-9.80862600	0.00009000	0.97415700
N	-8.21813900	2.27301300	-0.06570400
N	-5.66457400	0.96889300	0.84874400
N	-7.31976900	-1.36675100	1.86342900
C	-8.63112500	-1.52565400	2.54934000
H	-9.11767500	-2.40439700	2.12006700
H	-8.47816700	-1.73441800	3.61937300
C	-9.53898200	-0.31258200	2.39533200
H	-9.07117700	0.56507600	2.85127100
H	-10.47669700	-0.49304900	2.94486600
C	-7.00509500	3.00778100	0.38090900
H	-6.38018400	3.19598800	-0.49485800
H	-7.28348200	3.98954100	0.79420200
C	-6.22013900	2.21993600	1.42007900
H	-6.87972000	1.94783400	2.24707000
H	-5.42688600	2.85144200	1.84045200
C	-5.22928400	0.04013800	1.92538500
H	-4.64803100	-0.74709900	1.43904200
H	-4.57152500	0.54525000	2.65041600
C	-6.38678000	-0.58070900	2.70981000
H	-5.96410100	-1.21435100	3.50492400
H	-6.96589500	0.19801400	3.21281400
C	-10.36174800	1.37296400	0.84168900
H	-10.85344600	1.43570100	-0.13143200
H	-11.13278700	1.55166400	1.60765800
C	-9.29176100	2.44945800	0.94244100
H	-9.76269700	3.43955800	0.83839600
H	-8.83065300	2.42723700	1.93334300
C	3.21180700	3.43004400	-0.07944200
H	3.75970600	4.35675400	-0.28843700
H	3.69614200	2.94607900	0.77361200
C	-3.21174900	-3.43061000	-0.07993500
H	-3.75932800	-4.35733200	-0.28966500
H	-3.69644400	-2.94728400	0.77327400
C	-3.30245700	-2.49809800	-1.30915900
H	-2.75547400	-1.57181800	-1.08984100
H	-2.82639100	-2.97139400	-2.17254900
C	3.30258500	2.49830300	-1.30919000
H	2.75527200	1.57202700	-1.09062400
H	2.82685800	2.97221900	-2.17243400
C	4.73999000	2.12988500	-1.69145900
O	5.13171500	2.44406800	-2.84746700
O	5.44097400	1.50545100	-0.81585200
C	-4.73993900	-2.12996500	-1.69138800
O	-5.44091800	-1.50548500	-0.81580800
O	-5.13187200	-2.44472000	-2.84715300

E(RTPSSh) = -5021.5652485 Hartree
Zero-point correction = 1.292363
Thermal correction to Energy = 1.378258
Thermal correction to Enthalpy = 1.379202
Thermal correction to Gibbs Free Energy = 1.165956
Sum of electronic and zero-point Energies = -5020.272886
Sum of electronic and thermal Energies = -5020.186991
Sum of electronic and thermal Enthalpies = -5020.186046
Sum of electronic and thermal Free Energies = -5020.399293

Table S4. Optimized Cartesian coordinates obtained for the SAP isomer of $[Gd(DO3A\text{-}SA\text{-}COO)(H_2O)]_2$ (TPSSh/LCRECP/6-31G(d) level, aqueous solution, 0 imaginary frequencies).

N	7.77469000	-2.20329500	-0.02525300
C	9.13320800	-2.22344800	0.58005600
C	9.24747800	-1.29041700	1.78227300
N	8.94310300	0.12899700	1.46593900
C	8.62575500	0.85795900	2.72089200
C	7.19625300	0.59272500	3.18161800
N	6.17325300	1.00603800	2.18618800
C	4.86622600	0.37986700	2.52373300
C	4.80256200	-1.10939900	2.18993400
N	4.94493600	-1.39043000	0.73856200
C	5.38528900	-2.79329700	0.51694700
C	6.86151600	-3.01320500	0.81842500
C	7.82749900	-2.75414200	-1.40170500
C	6.67429100	-2.30165900	-2.31477900
O	6.19584500	-1.11893300	-2.07178800
O	6.32466500	-3.04415100	-3.24178700
C	10.09597600	0.75900100	0.78081800
C	10.16878900	0.42381000	-0.71822400
O	11.27269100	0.45828900	-1.28280800
O	9.03372500	0.17786700	-1.28703400
C	6.04467200	2.48575100	2.17849500
C	7.08595700	3.21161200	1.30365700
O	7.35071900	4.39209900	1.57683900
O	7.56382900	2.53747700	0.30843500
C	3.67839800	-1.13136200	0.00017600
C	2.45900300	-2.02479700	0.30380900
H	8.74103400	-2.37399600	-1.87024300
H	7.88015300	-3.85196600	-1.39130400
H	11.04608200	0.49834300	1.26861000
H	9.96295400	1.84337600	0.84293800
H	6.07342000	2.89171700	3.19915700
H	5.07237600	2.73103900	1.74223000
H	3.39292400	-0.09856200	0.19930800
H	3.92196800	-1.18647800	-1.06573400
H	9.84815100	-1.93180100	-0.18984500
H	9.39930400	-3.24280800	0.90162300
H	10.26449800	-1.37435200	2.19734700
H	8.56389600	-1.61519200	2.57073600
H	9.31693900	0.57053400	3.52836100
H	8.77211200	1.92439100	2.53952800
H	7.02373400	1.11483900	4.13612100
H	7.06705200	-0.47397900	3.38008400
H	4.63424400	0.51382100	3.59178400
H	4.10363600	0.91052200	1.95229900
H	5.59405400	-1.64813400	2.71523700
H	3.85632900	-1.50753000	2.58436000
H	5.16896400	-3.04674500	-0.52200300
H	4.80097000	-3.48978000	1.13528800
H	7.06589200	-2.77367100	1.86502500
H	7.08518800	-4.08517600	0.69270200
H	1.55541600	-1.46221500	0.03138500
H	2.38872800	-2.27238100	1.36564900
N	2.52593600	-3.30380700	-0.43401600
H	2.55518100	-3.18533800	-1.44853200

O	6.85637700	1.42628800	-2.58267200
H	5.97203300	1.92023800	-2.62390800
H	6.68230800	0.56112500	-3.01080600
S	1.42633000	-4.50498300	-0.03288600
O	1.70825100	-5.61933300	-0.95087800
O	1.52787000	-4.67766200	1.42505600
C	-0.21948000	-3.89748700	-0.39301300
C	-0.75114700	-4.08055000	-1.67606200
C	-0.93352500	-3.21994900	0.60121800
C	-2.01721700	-3.57329800	-1.95890800
H	-0.18734600	-4.62165200	-2.42872300
C	-2.19808200	-2.71272400	0.29679600
H	-0.51440800	-3.10890600	1.59556000
C	-2.74898200	-2.88019200	-0.98061700
H	-2.45889000	-3.70779500	-2.94001300
H	-2.76398300	-2.19181500	1.05988200
C	-4.11692200	-2.33651000	-1.34146500
O	-4.55107300	-2.63642100	-2.48848500
O	-4.72495100	-1.61669500	-0.47699800
Gd	6.89477700	0.35106200	-0.31227100
N	-7.77468300	2.20325500	-0.02512500
C	-9.13319800	2.22333100	0.58018200
C	-9.24746300	1.29020400	1.78232700
N	-8.94310100	-0.12919600	1.46592200
C	-8.62572500	-0.85816800	2.72085900
C	-7.19623200	-0.59287400	3.18156800
N	-6.17323900	-1.00610800	2.18610000
C	-4.86621800	-0.37990500	2.52363800
C	-4.80259500	1.10939000	2.18995900
N	-4.94488200	1.39054300	0.73859600
C	-5.38531200	2.79340200	0.51710000
C	-6.86155600	3.01318300	0.81858900
C	-7.82757400	2.75417200	-1.40154600
C	-6.67445300	2.30169100	-2.31472700
O	-6.19614500	1.11886900	-2.07191200
O	-6.32454700	3.04439000	-3.24146100
C	-10.09600100	-0.75919600	0.78083900
C	-10.16887300	-0.42403900	-0.71821400
O	-11.27277900	-0.45861900	-1.28277900
O	-9.03384100	-0.17797200	-1.28703300
C	-6.04458200	-2.48581400	2.17837800
C	-7.08584700	-3.21172400	1.30355500
O	-7.35061900	-4.39219400	1.57679300
O	-7.56378900	-2.53760900	0.30834800
C	-3.67828300	1.13158000	0.00026000
C	-2.45893600	2.02507800	0.30388400
H	-8.74114100	2.37403200	-1.87002500
H	-7.88022400	3.85199600	-1.39109400
H	-11.04609100	-0.49853900	1.26866400
H	-9.96297700	-1.84357000	0.84296700
H	-6.07328200	-2.89180000	3.19903400
H	-5.07228500	-2.73104100	1.74208100
H	-3.39273100	0.09881100	0.19944200
H	-3.92180400	1.18663000	-1.06566400
H	-9.84813800	1.93174900	-0.18974500
H	-9.39930100	3.24266100	0.90183800
H	-10.26447900	1.37411800	2.19741500
H	-8.56387600	1.61492800	2.57080700

H	-9.31691100	-0.57078100	3.52833900
H	-8.77204600	-1.92460200	2.53947900
H	-7.02366600	-1.11499800	4.13605600
H	-7.06707800	0.47383400	3.38005200
H	-4.63422100	-0.51392400	3.59167700
H	-4.10362600	-0.91050800	1.95215600
H	-5.59413200	1.64805500	2.71527000
H	-3.85639500	1.50752000	2.58446200
H	-5.16898200	3.04697600	-0.52181600
H	-4.80103900	3.48985600	1.13551700
H	-7.06591600	2.77358400	1.86517800
H	-7.08529700	4.08514800	0.69293100
H	-1.55533500	1.46248200	0.03153800
H	-2.38870100	2.27275000	1.36570800
N	-2.52582100	3.30401600	-0.43407100
H	-2.55500100	3.18544700	-1.44857800
O	-6.85636600	-1.42651000	-2.58257300
H	-5.97212000	-1.92063400	-2.62376400
H	-6.68215400	-0.56142000	-3.01080700
S	-1.42624500	4.50523700	-0.03301100
O	-1.70814200	5.61950100	-0.95111500
O	-1.52783000	4.67805100	1.42491100
C	0.21956800	3.89769700	-0.39305000
C	0.75127900	4.08072200	-1.67608300
C	0.93355800	3.22014600	0.60121400
C	2.01734300	3.57342500	-1.95888300
H	0.18751700	4.62183300	-2.42876600
C	2.19811000	2.71288200	0.29684000
H	0.51441400	3.10913300	1.59554800
C	2.74906000	2.88032300	-0.98055900
H	2.45905300	3.70791100	-2.93997300
H	2.76397500	2.19197200	1.05994800
C	4.11703800	2.33669900	-1.34133900
O	4.72502300	1.61680400	-0.47689700
O	4.55101300	2.63626200	-2.48851200
Gd	-6.89488300	-0.35113700	-0.31232100

E(RTPSSh) = -4864.3023017 Hartree
Zero-point correction = 1.178375
Thermal correction to Energy = 1.258969
Thermal correction to Enthalpy = 1.259913
Thermal correction to Gibbs Free Energy = 1.059552
Sum of electronic and zero-point Energies = -4863.123926
Sum of electronic and thermal Energies = -4863.043333
Sum of electronic and thermal Enthalpies = -4863.042388
Sum of electronic and thermal Free Energies = -4863.242750

Table S5. Optimized Cartesian coordinates obtained for the TSAP isomer of [Gd(DO3A-SA-COO)(H_2O)]$_2$ (TPSSh/LCRECP/6-31G(d) level, aqueous solution, 0 imaginary frequencies).

C	7.80819300	-2.59081800	-1.60400200
C	7.04155800	-1.82550400	-2.69533500
O	6.35163300	-0.80259300	-2.28167800
O	7.15442800	-2.19264800	-3.87102600
C	9.88679100	0.43120100	1.23381500
C	10.09816500	0.64514300	-0.27683600
O	11.16907600	1.13265300	-0.66539500
O	9.09704500	0.30614700	-1.02633400
C	5.83950200	2.19681000	2.38800100
C	6.76342400	3.08448900	1.52910900
O	6.69857800	4.31224100	1.68217900
O	7.52546700	2.45977400	0.68663000
C	3.62035200	-1.05133000	-0.43175000
C	2.33206400	-1.87199000	-0.22039300
H	8.83572300	-2.21365800	-1.61463200
H	7.83637100	-3.66185700	-1.85351900
H	10.82625300	0.10139600	1.70154300
H	9.61152400	1.39746900	1.66468500
H	5.79432200	2.58975700	3.41431000
H	4.83985500	2.26256700	1.95417100
H	3.35235200	0.00094700	-0.53062700
H	4.09884500	-1.34163400	-1.37162600
H	1.49302100	-1.34796100	-0.69453900
H	2.10162000	-1.97587700	0.84317700
N	2.47074700	-3.23830400	-0.77413800
H	2.47233000	-3.26248300	-1.79515800
O	7.04505200	1.74638900	-2.32639400
H	6.21034700	2.31532300	-2.35294300
H	6.83182800	0.95125400	-2.86405300
S	1.46511200	-4.44183800	-0.17910600
O	1.73999000	-5.62537700	-1.00858200
O	1.68173600	-4.46761700	1.27689800
C	-0.23330700	-3.94458100	-0.45380400
C	-0.84302400	-4.22249300	-1.68392400
C	-0.91173700	-3.25493500	0.55658000
C	-2.15199400	-3.79549700	-1.89763900
H	-0.30574800	-4.77274800	-2.44936500
C	-2.21668300	-2.82189700	0.31826000
H	-0.43168300	-3.07555600	1.51246800
C	-2.84570000	-3.08157700	-0.90637800
H	-2.65434000	-4.00702400	-2.83509800
H	-2.75415800	-2.29068300	1.09447300
C	-4.25667000	-2.61069600	-1.19520000
O	-4.81342300	-3.10234400	-2.21406500
O	-4.76906500	-1.74300900	-0.40483000
Gd	6.86624200	0.36534100	-0.22111300
C	-7.80933000	2.59097900	-1.60319900
C	-7.04415400	1.82495200	-2.69502100
O	-6.35137800	0.80390000	-2.28150400
O	-7.16059800	2.19009600	-3.87099000
C	-9.88644500	-0.43160100	1.23429900
C	-10.09792300	-0.64523300	-0.27638200
O	-11.16885800	-1.13257700	-0.66501700
O	-9.09675000	-0.30621400	-1.02584600

C	-5.83897700	-2.19702800	2.38776300
C	-6.76269600	-3.08461800	1.52854400
O	-6.69748300	-4.31240600	1.68110300
O	-7.52491800	-2.45977900	0.68630700
C	-3.62073600	1.05164200	-0.43223900
C	-2.33224900	1.87205400	-0.22111700
H	-8.83717100	2.21469000	-1.61325600
H	-7.83691700	3.66200100	-1.85290100
H	-10.82593400	-0.10206000	1.70217300
H	-9.61101500	-1.39792200	1.66495400
H	-5.79398500	-2.59013400	3.41402000
H	-4.83925500	-2.26268900	1.95411600
H	-3.35283100	-0.00064100	-0.53138700
H	-4.09944200	1.34216000	-1.37194100
H	-1.49344000	1.34788200	-0.69551300
H	-2.10150800	1.97579200	0.84240100
N	-2.47069500	3.23844300	-0.77473200
H	-2.47225700	3.26276800	-1.79574500
O	-7.04372600	-1.74483800	-2.32770300
H	-6.20908400	-2.31381500	-2.35402300
H	-6.82954200	-0.94884300	-2.86383200
S	-1.46499600	4.44181200	-0.17951500
O	-1.73968500	5.62543700	-1.00893500
O	-1.68176400	4.46750100	1.27647100
C	0.23344600	3.94448300	-0.45404500
C	0.84331600	4.22253000	-1.68405000
C	0.91177200	3.25477000	0.55636900
C	2.15234500	3.79561800	-1.89762800
H	0.30613100	4.77284400	-2.44951200
C	2.21675700	2.82179100	0.31818100
H	0.43160200	3.07532600	1.51218900
C	2.84593700	3.08162000	-0.90635100
H	2.65480600	4.00729600	-2.83499000
H	2.75416200	2.29053900	1.09441500
C	4.25694700	2.61081600	-1.19504700
O	4.76913100	1.74272300	-0.40498800
O	4.81394800	3.10290400	-2.21358200
Gd	-6.86600600	-0.36517500	-0.22097400
N	-6.27230600	-0.78117400	2.37304400
N	-8.79184900	0.53396900	1.47239000
N	-7.23649700	2.36160800	-0.26016500
N	-4.64807000	1.10906000	0.64648000
C	-9.28194900	1.88274200	1.08398600
H	-9.90021200	1.76244700	0.19187900
H	-9.92881200	2.29655100	1.87325700
C	-5.93696200	3.07699500	-0.16265400
H	-6.10409000	4.15029300	0.01750500
H	-5.42801400	2.98990200	-1.12527000
C	-7.49530500	-0.67859000	3.21880800
H	-7.21781000	-0.64924000	4.28351200
H	-8.07380700	-1.59226800	3.06474000
C	-4.13100600	0.44691100	1.87257400
H	-3.63916500	-0.47097000	1.54632900
H	-3.37406700	1.06762300	2.37743400
C	-8.35448100	0.53375200	2.88658500
H	-7.79000800	1.45335700	3.06494400
H	-9.22089200	0.55797800	3.56657200
C	-8.15142000	2.85931000	0.79468600

H	-8.57907400	3.83349500	0.51034900
H	-7.56350100	3.03092600	1.70010300
C	-5.05819800	2.50555700	0.94036100
H	-5.60773200	2.50370100	1.88462800
H	-4.18412700	3.15309300	1.08557200
C	-5.21329800	0.11570700	2.89939100
H	-4.72909300	-0.33581100	3.77911000
H	-5.69389000	1.03306300	3.24951100
N	8.79203500	-0.53424500	1.47176400
N	7.23581300	-2.36150000	-0.26075800
N	4.64793100	-1.10888800	0.64669300
N	6.27273400	0.78094600	2.37311400
C	7.49585500	0.67803200	3.21869100
H	8.07445400	1.59167700	3.06477900
H	7.21856000	0.64841900	4.28343100
C	8.35479900	-0.53435900	2.88598800
H	7.79008700	-1.45387000	3.06407600
H	9.22124600	-0.55904500	3.56591800
C	5.93634700	-3.07690700	-0.16285200
H	5.42705400	-2.98990100	-1.12530300
H	6.10350300	-4.15020600	0.01726700
C	5.05797900	-2.50540800	0.94043100
H	5.60785400	-2.50361600	1.88450800
H	4.18388000	-3.15285800	1.08592700
C	4.13110700	-0.44686400	1.87293600
H	3.63920500	0.47105000	1.54688400
H	3.37425200	-1.06762400	2.37788000
C	5.21361300	-0.11582700	2.89956200
H	4.72959200	0.33576800	3.77933700
H	5.69407800	-1.03327500	3.24961200
C	9.28182800	-1.88296800	1.08289400
H	9.89981600	-1.76255500	0.19061300
H	9.92886900	-2.29704400	1.87188600
C	8.15109500	-2.85938300	0.79373000
H	8.57859500	-3.83352800	0.50902800
H	7.56345500	-3.03119900	1.69929100

E(RTPSSh) = =-4864.3024836 Hartree
Zero-point correction = 1.178506
Thermal correction to Energy = 1.259006
Thermal correction to Enthalpy = 1.259950
Thermal correction to Gibbs Free Energy = 1.059749
Sum of electronic and zero-point Energies = -4863.123978
Sum of electronic and thermal Energies = -4863.043478
Sum of electronic and thermal Enthalpies = -4863.042533
Sum of electronic and thermal Free Energies = -4863.242735