First 4,7-oxygenated 1,10-phenanthroline-2,9-diamides: synthesis, tautomerism and complexation with REE nitrates

Nane A. Avagyan,[a] Pavel S. Lemport,[a] Vitaly A. Roznyatovsky,[a] Alexei D. Averin,[a] Alexei A. Yakushev,[a] Konstantin A. Lyssenko,[a] Pavel D. Perfilyev,[a] Ksenia L. Isakovskaya,[b] Svetlana A. Aksenova,[b,c] Yulia V. Nelyubina,[b] Mikhail F. Vokuev,[a] Igor A. Rodin,[a] Igor P. Gloriozov,[a] Yuri A. Ustynyuk,[a] Valentine G. Nenajdenko[a*]

[a] Department of Chemistry, Lomonosov Moscow State University, Leninskie gory 1 bld. 3, Moscow, Russia; nenajdenko@gmail.com (V.N.)

[b] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119334, Moscow, Russia

[c] Moscow Institute of Physics and Technology, National Research University, Institutskiy per. 9, Dolgoprudny, 141700 Moscow Region, Russia

***** Correspondence to: nenajdenko@gmail.com (V.N.)

Supplementary Materials

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1. NMR and IR spectra of synthesized compounds

N^2,N^2,N^9,N^9-tetrabutyl-7-chloro-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (4a)

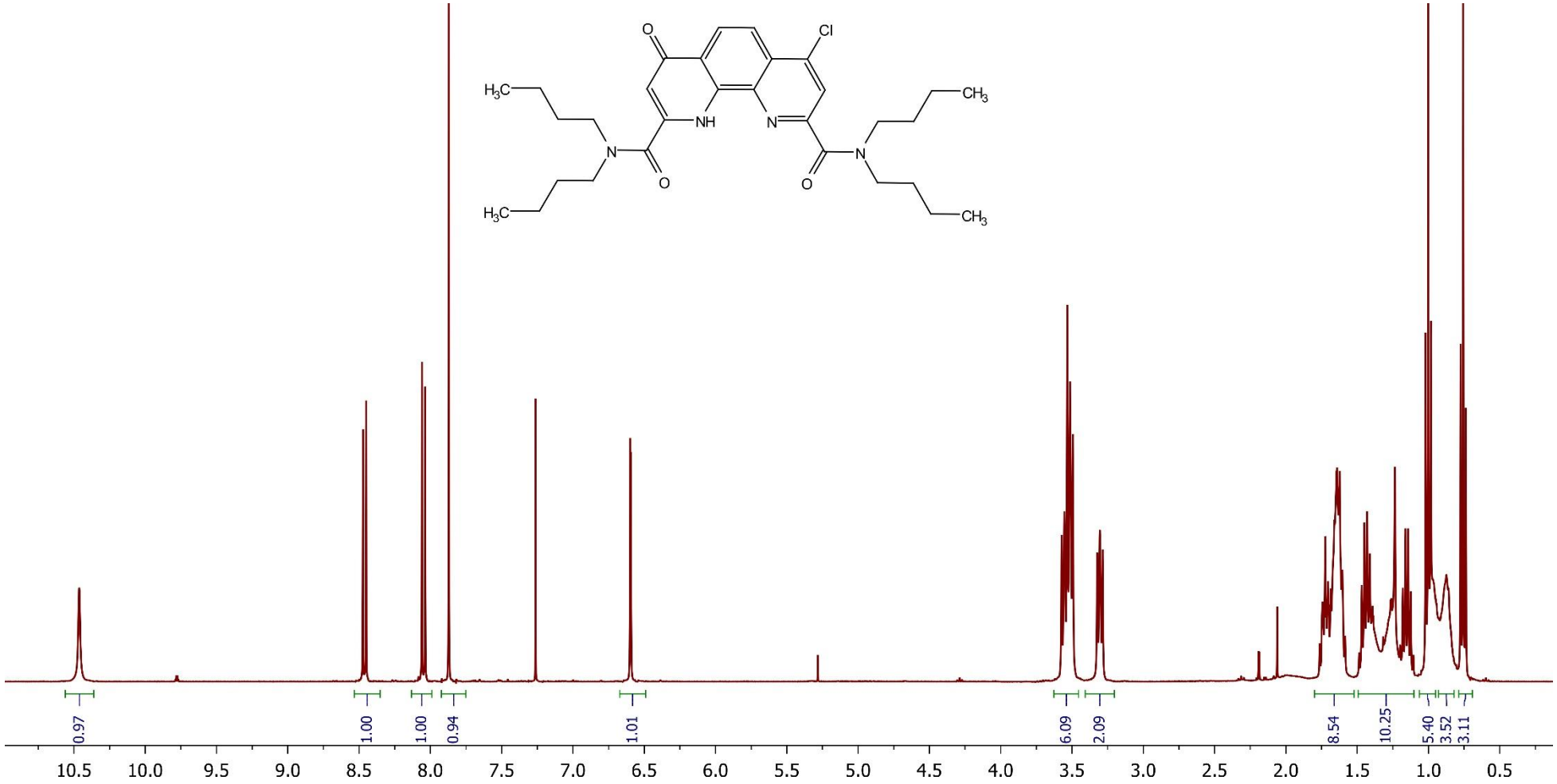

Figure S1. ^{1}H NMR spectrum in $CDCl_3$ at 25ºC

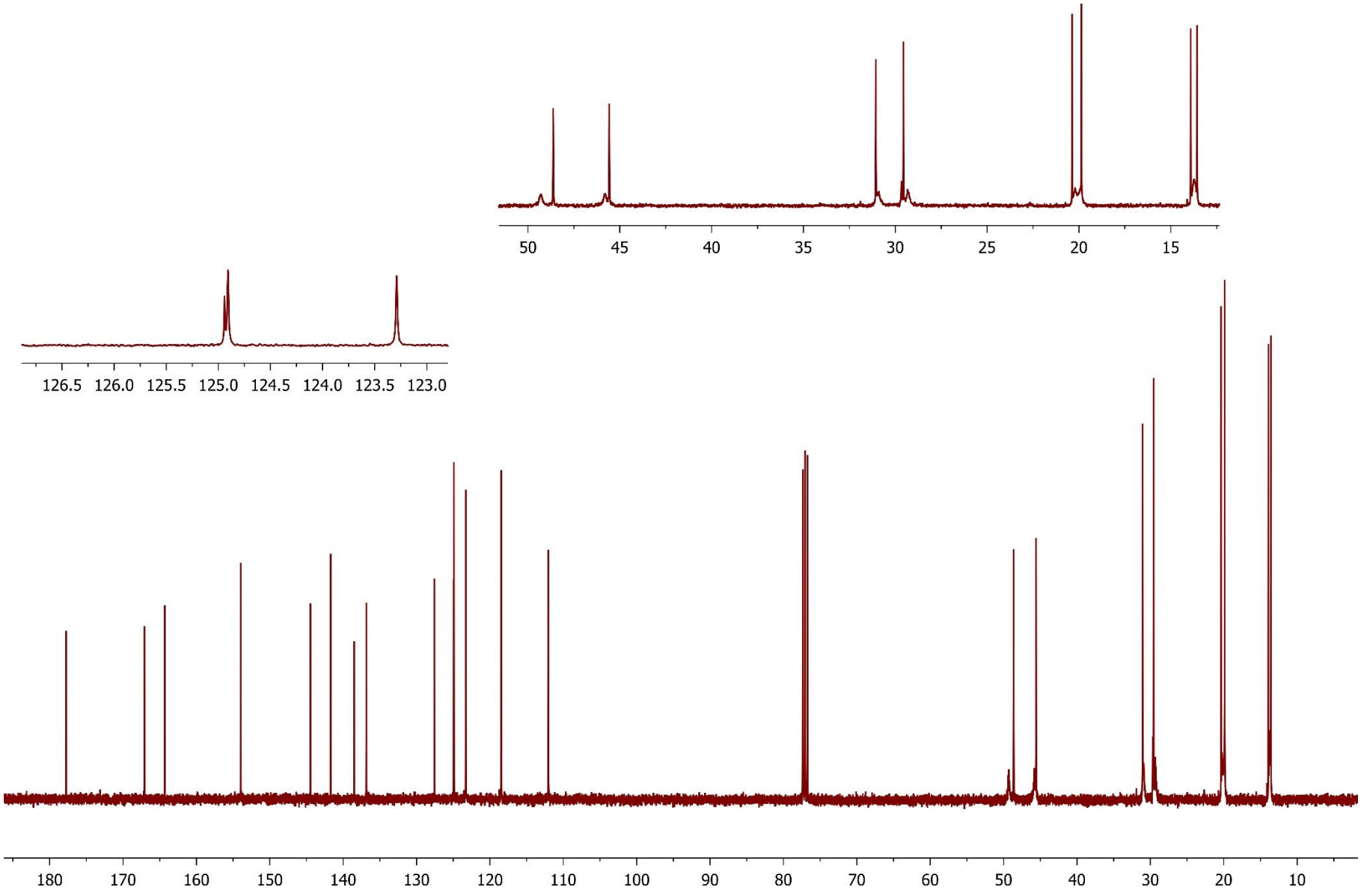

Figure S2. ^{13}C NMR spectrum in $CDCl_3$ at 25ºC

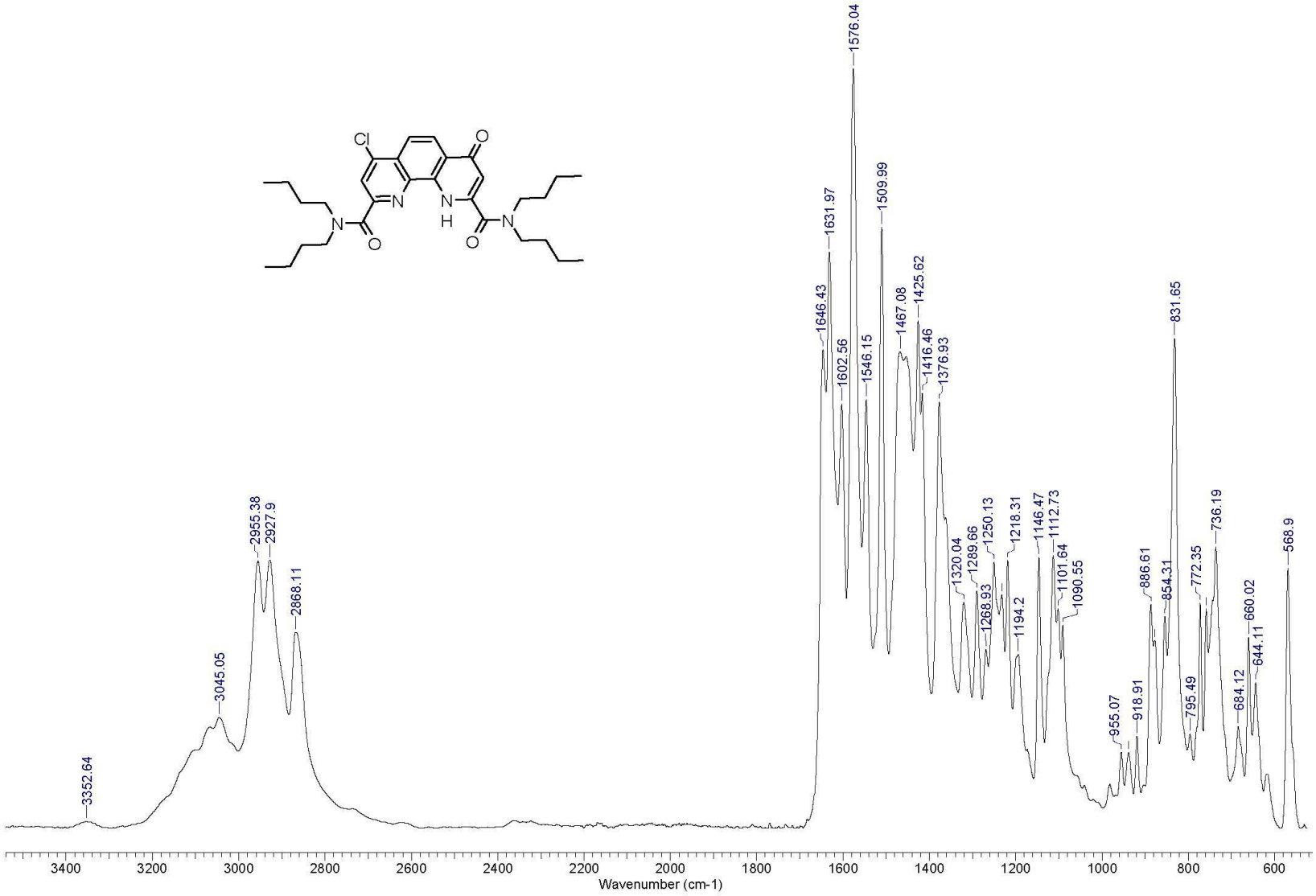

Figure S3. Solid-state IR spectrum at 25ºC

N^2,N^9-bis(4-butylphenyl)-7-chloro-N^2,N^9-diethyl-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (4d)

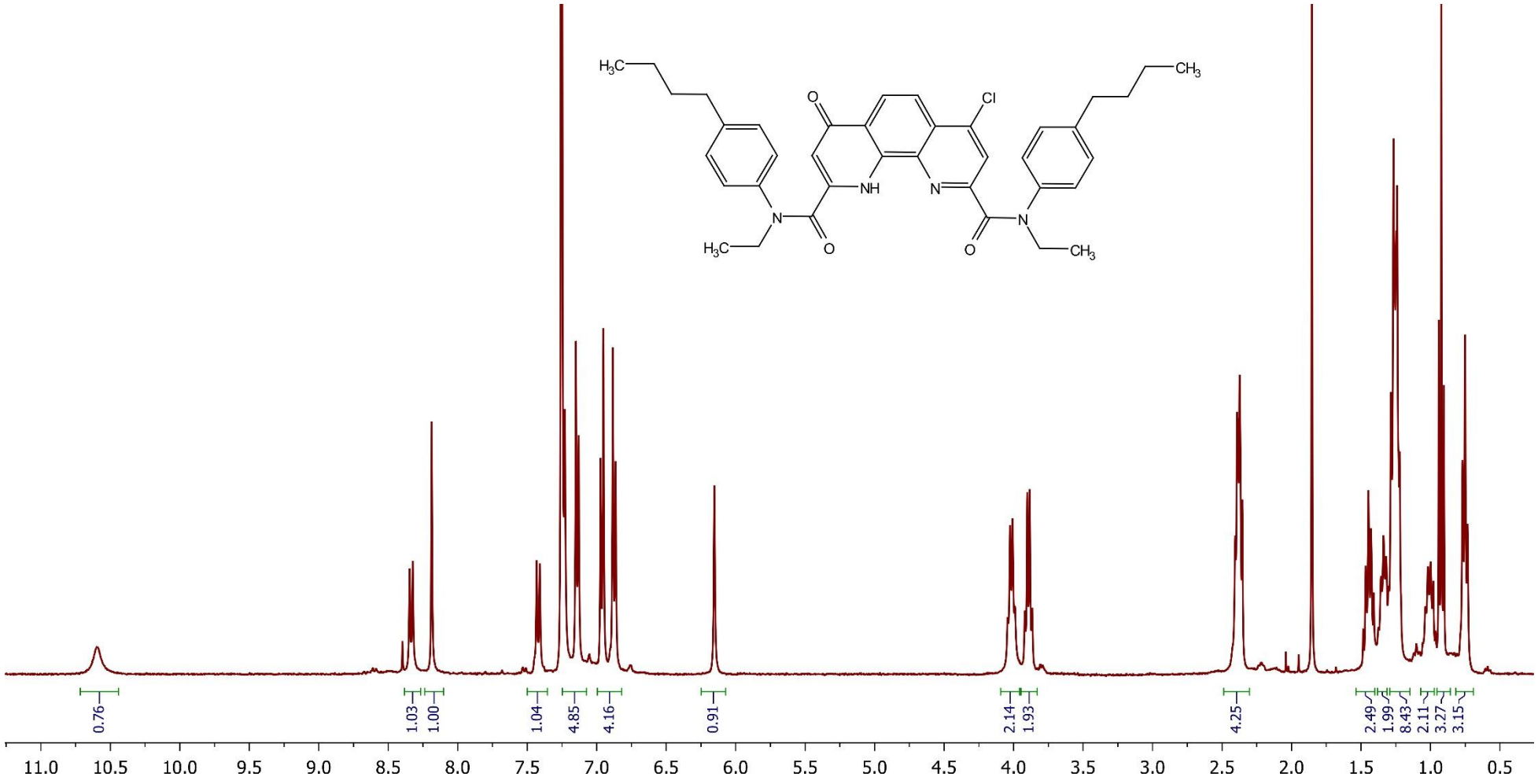

Figure S4. ^{1}H NMR spectrum in C_6D_6 at 25ºC

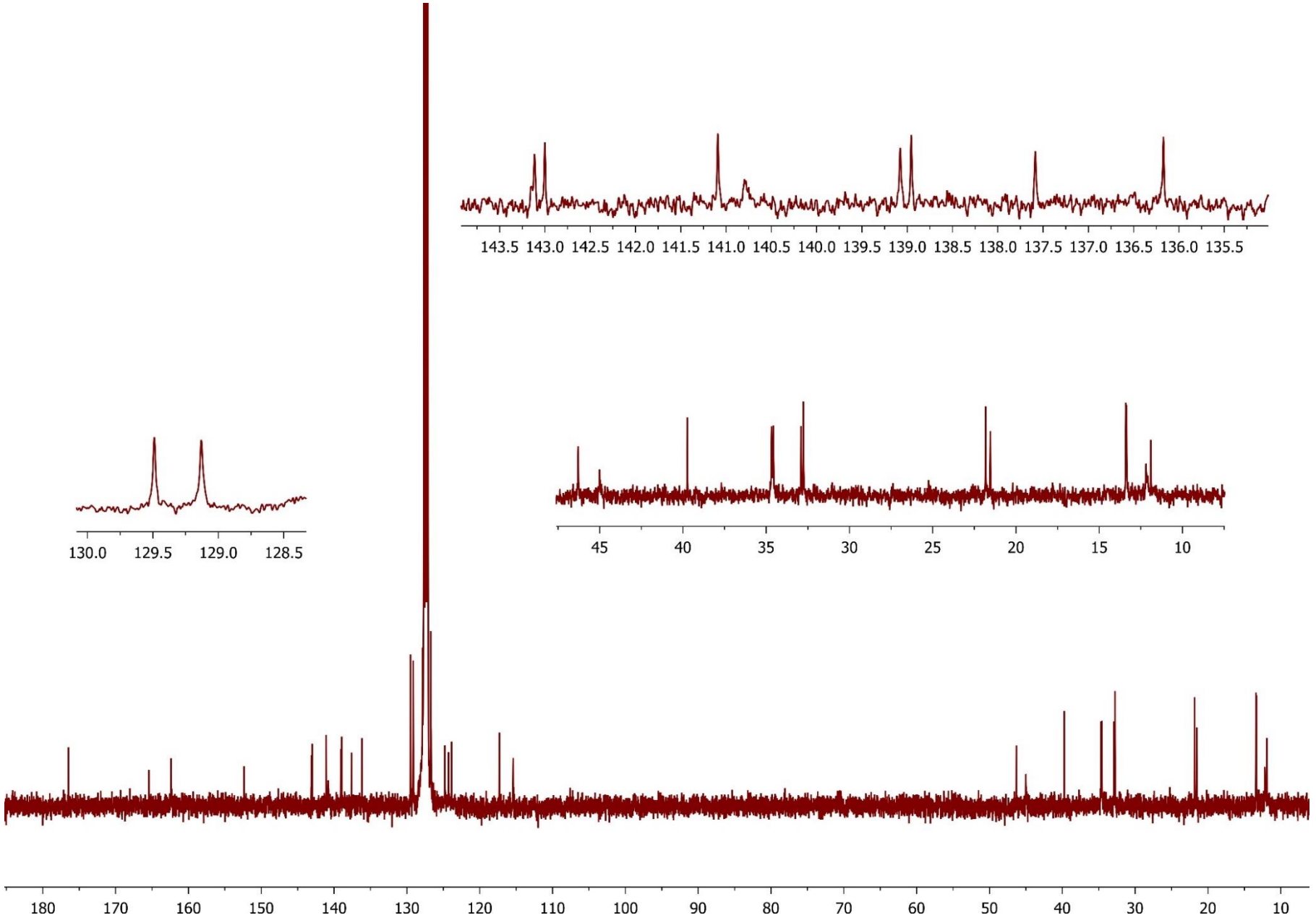

Figure S5. ^{13}C NMR spectrum in C_6D_6 at 25ºC

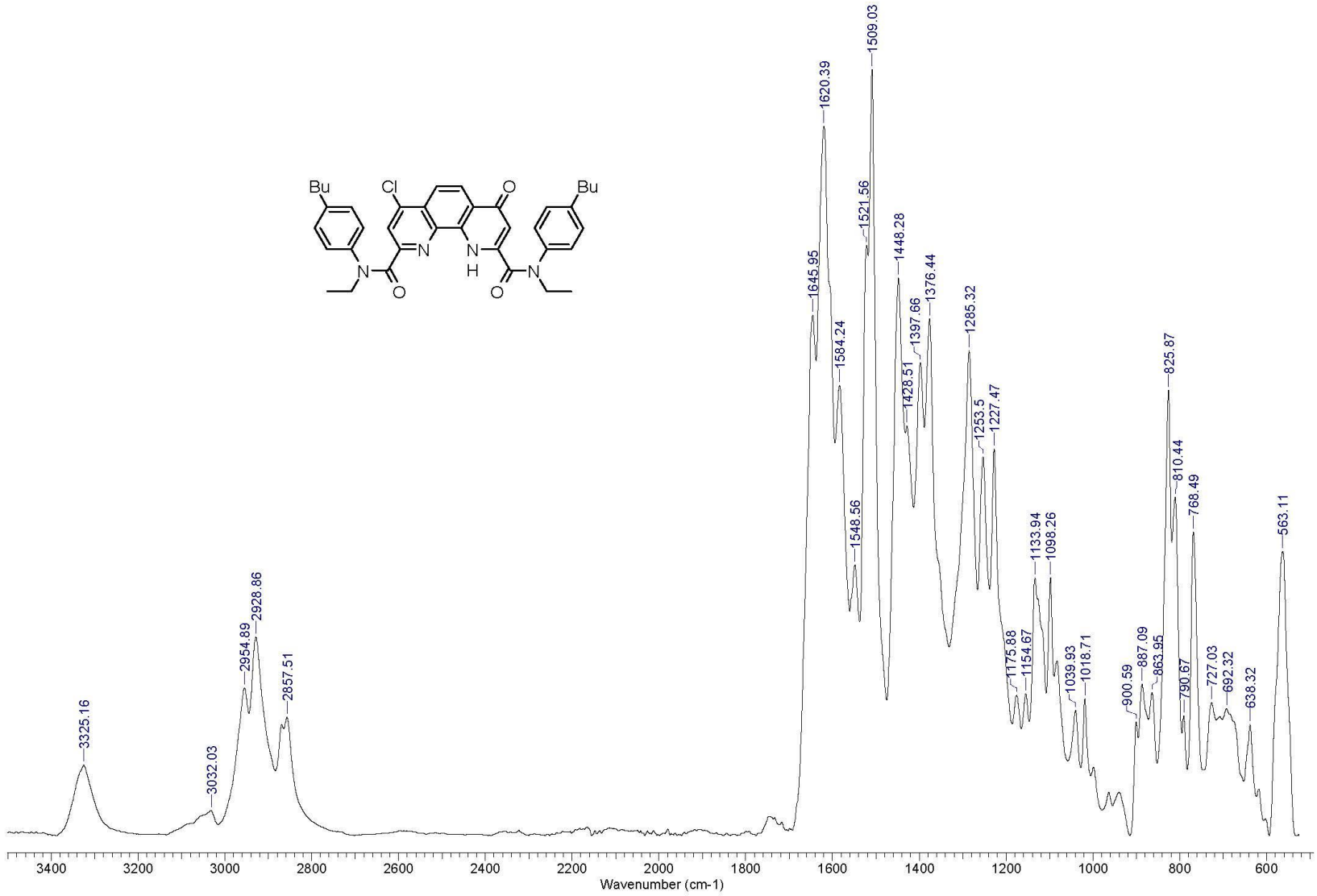

Figure S6. Solid-state IR spectrum at 25ºC

N^2,N^2,N^9,N^9-tetrabutyl-7-hydroxy-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (5a)

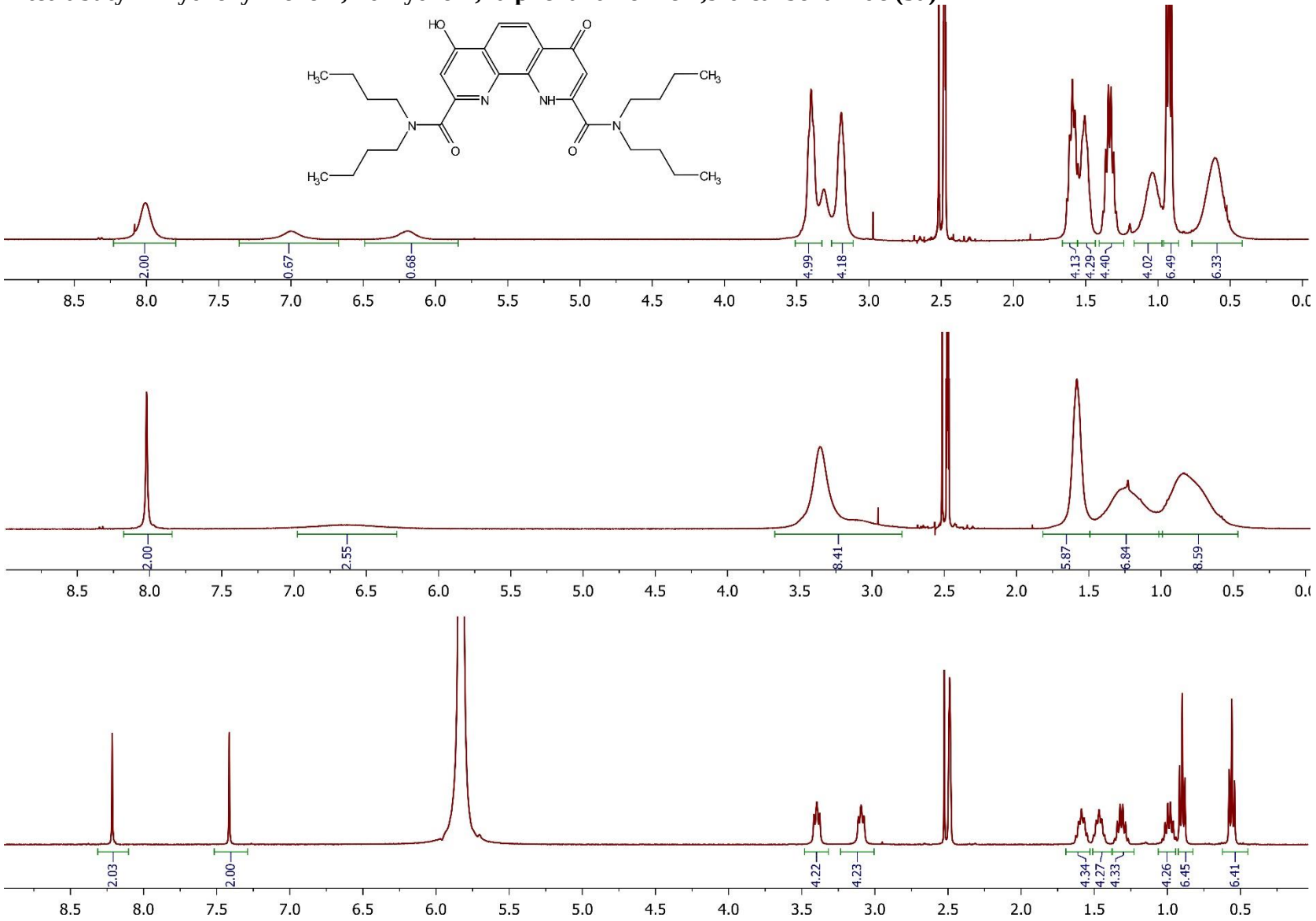

Figure S7. ^{1}H NMR spectra in DMSO-d_6 at (upper) 25ºC, (middle) 60ºC and (bottom) after adding H^+

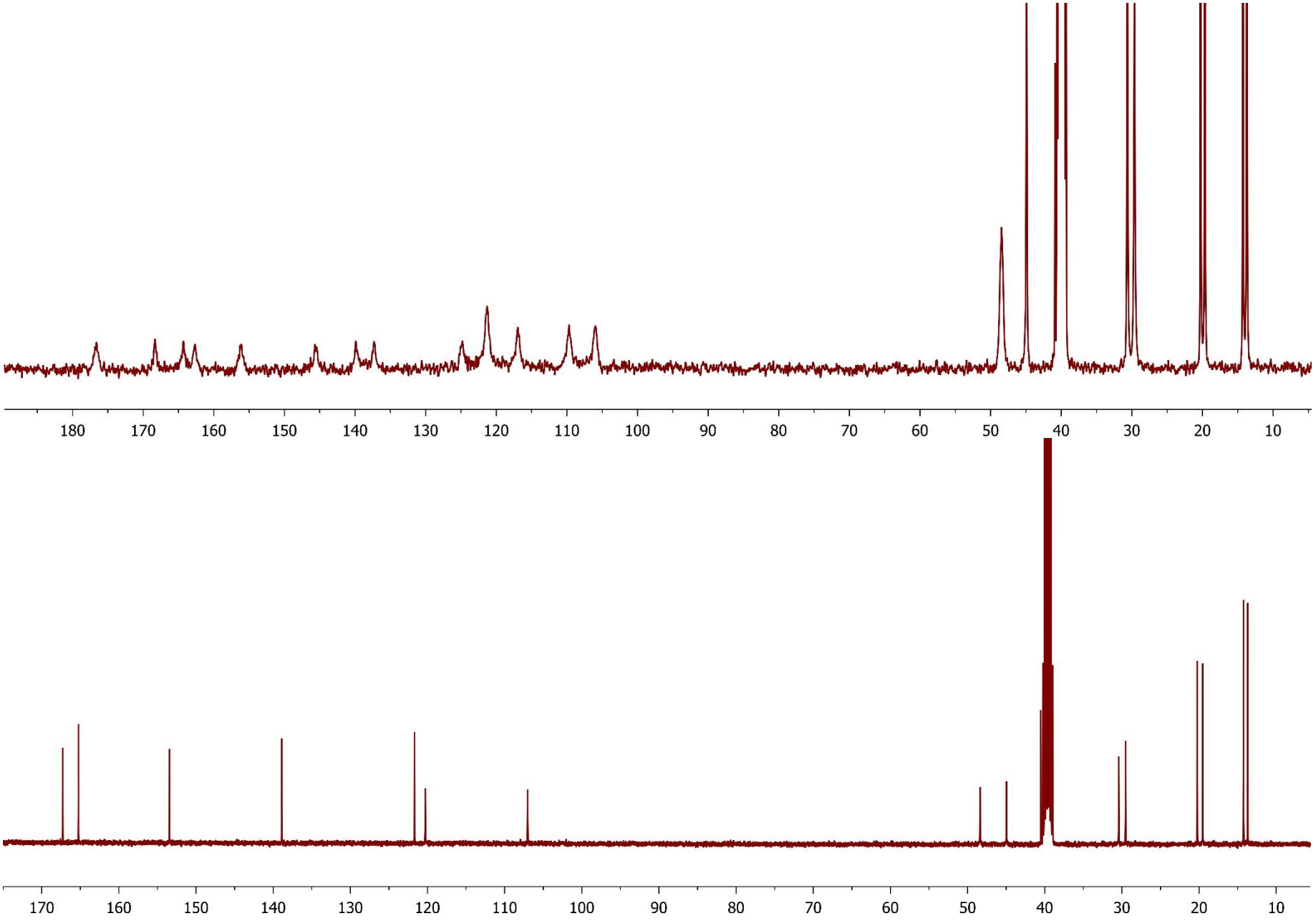

Figure S8. ^{13}C NMR spectra in in DMSO-d_6 at (upper) 25ºC and (bottom) after adding H^+

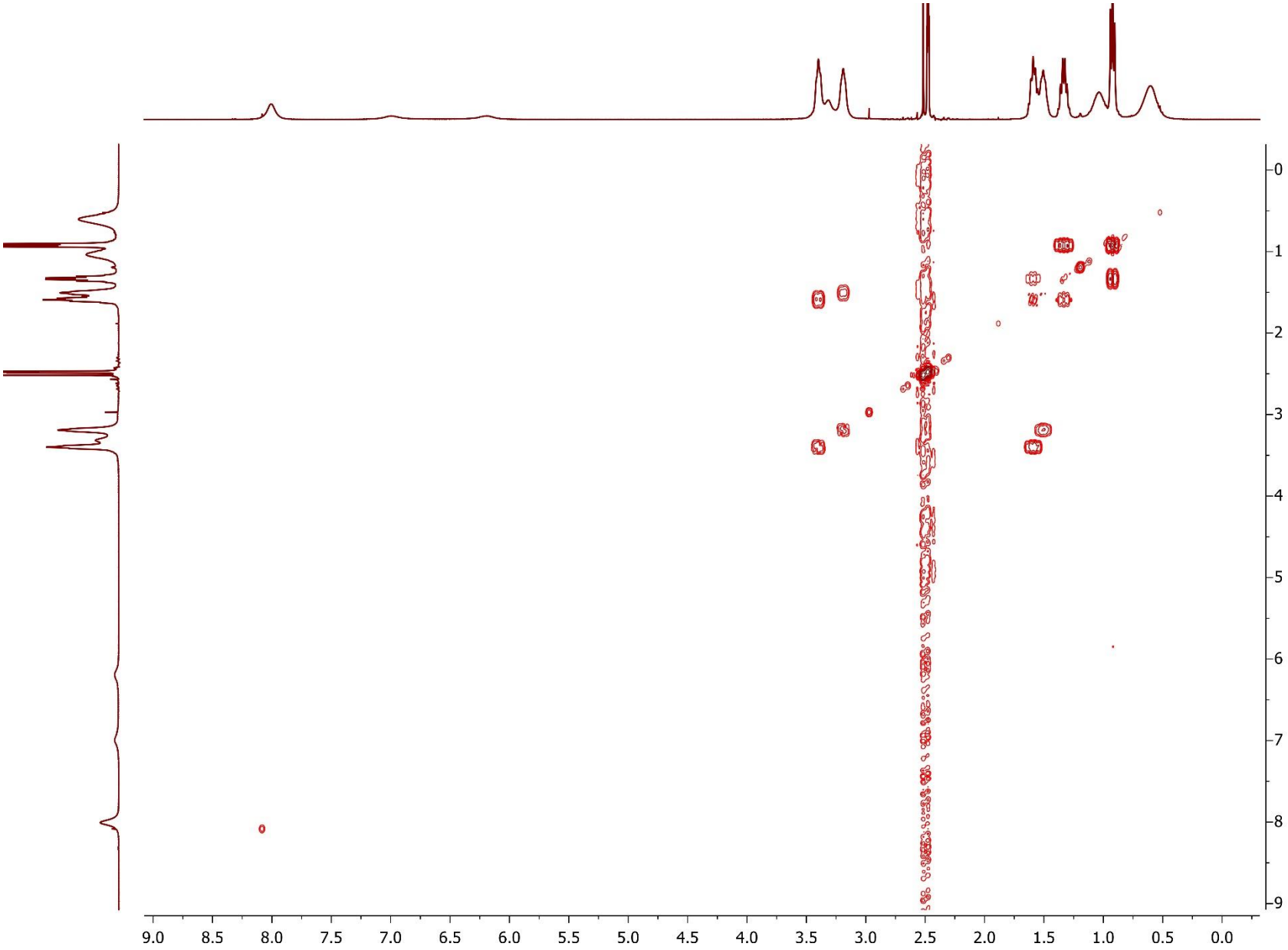

Figure S9. $^{1}H/^{1}H$ COSY NMR spectrum in DMSO-d_6 at 25ºC

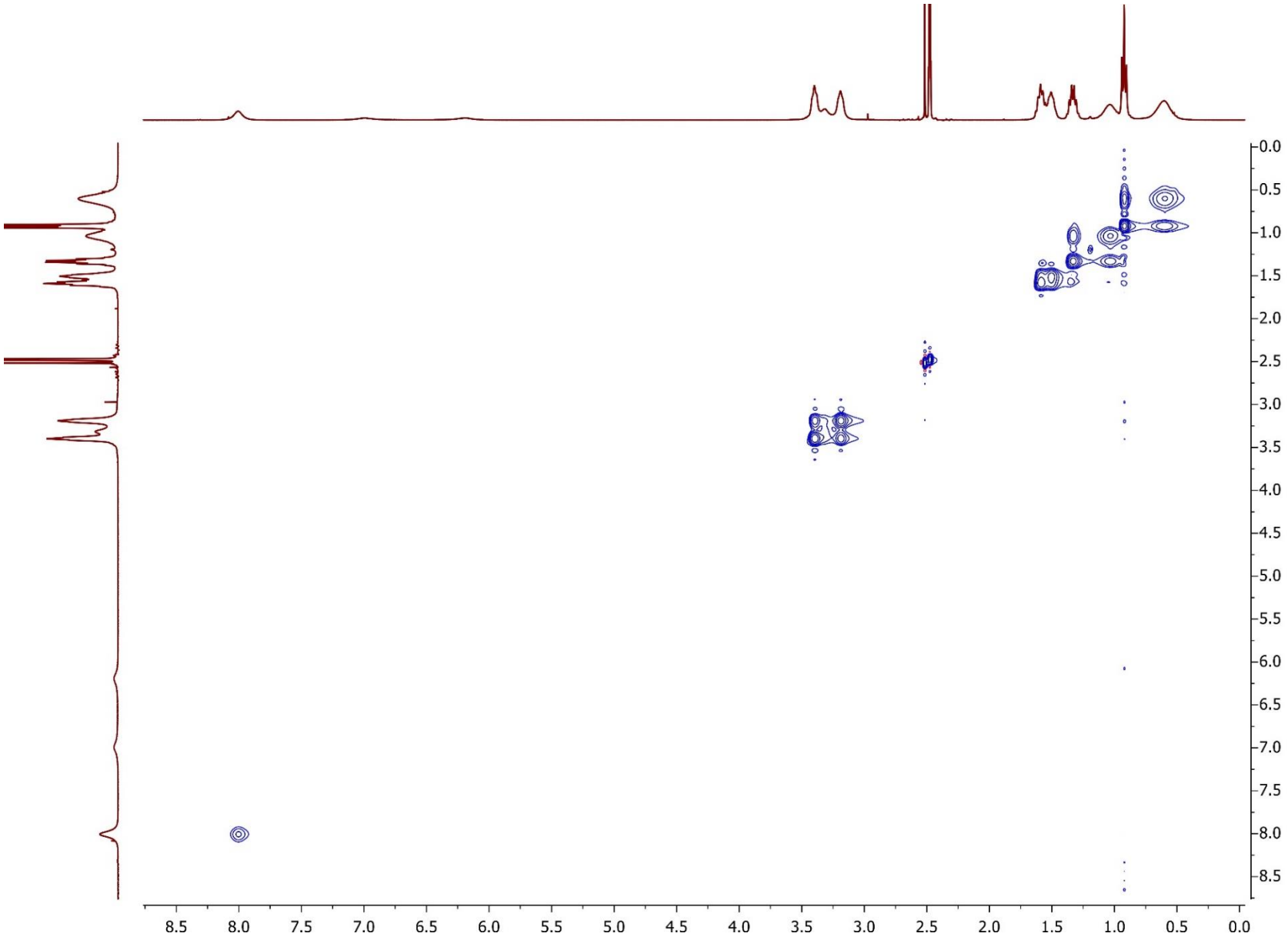

Figure S10. $^{1}H/^{1}H$ NOESY NMR spectrum in DMSO-d_6 at 25ºC

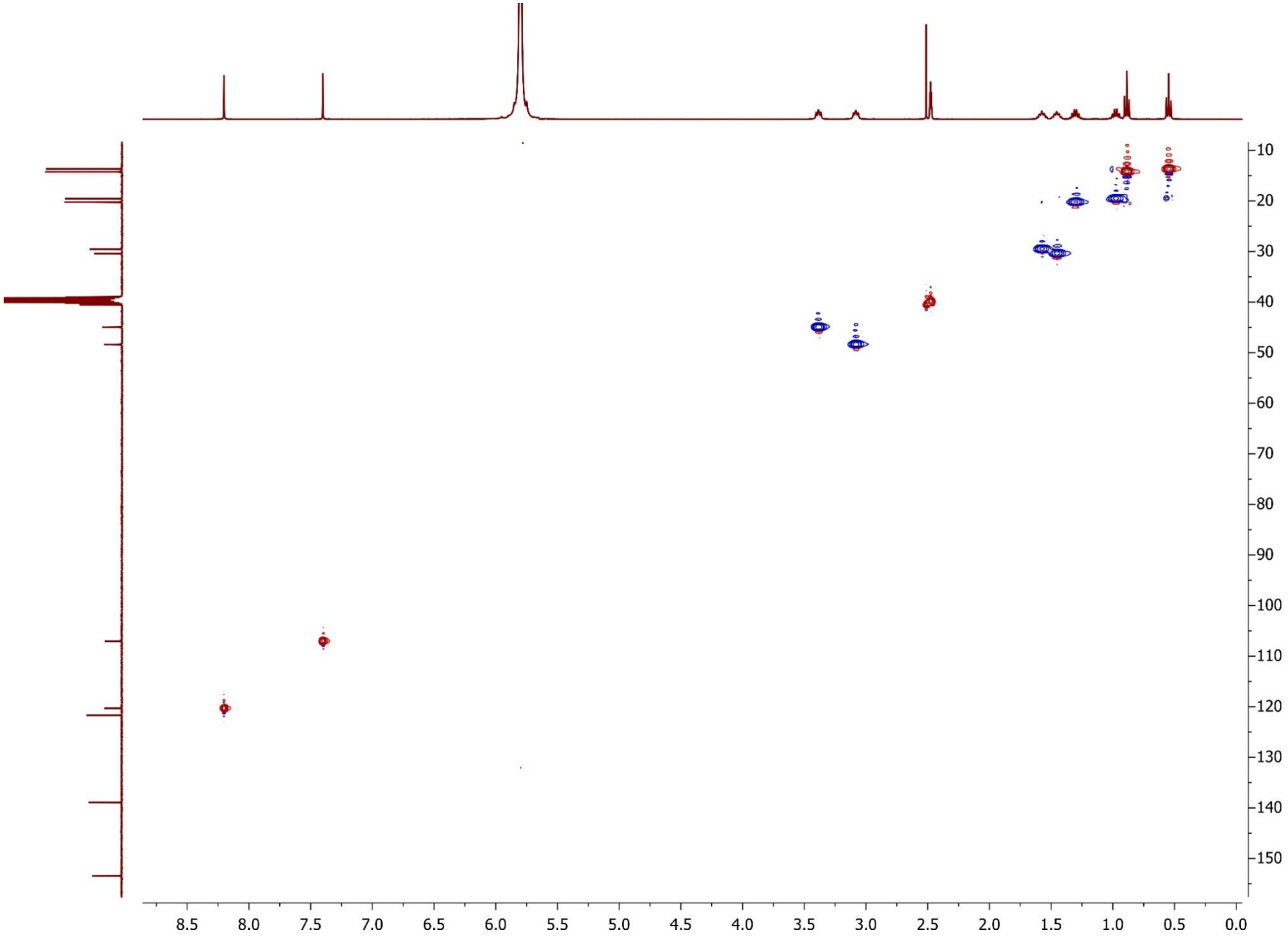

Figure S11. $^{1}H/^{13}C$ HSQC NMR spectrum in DMSO-d_6 after adding H^+

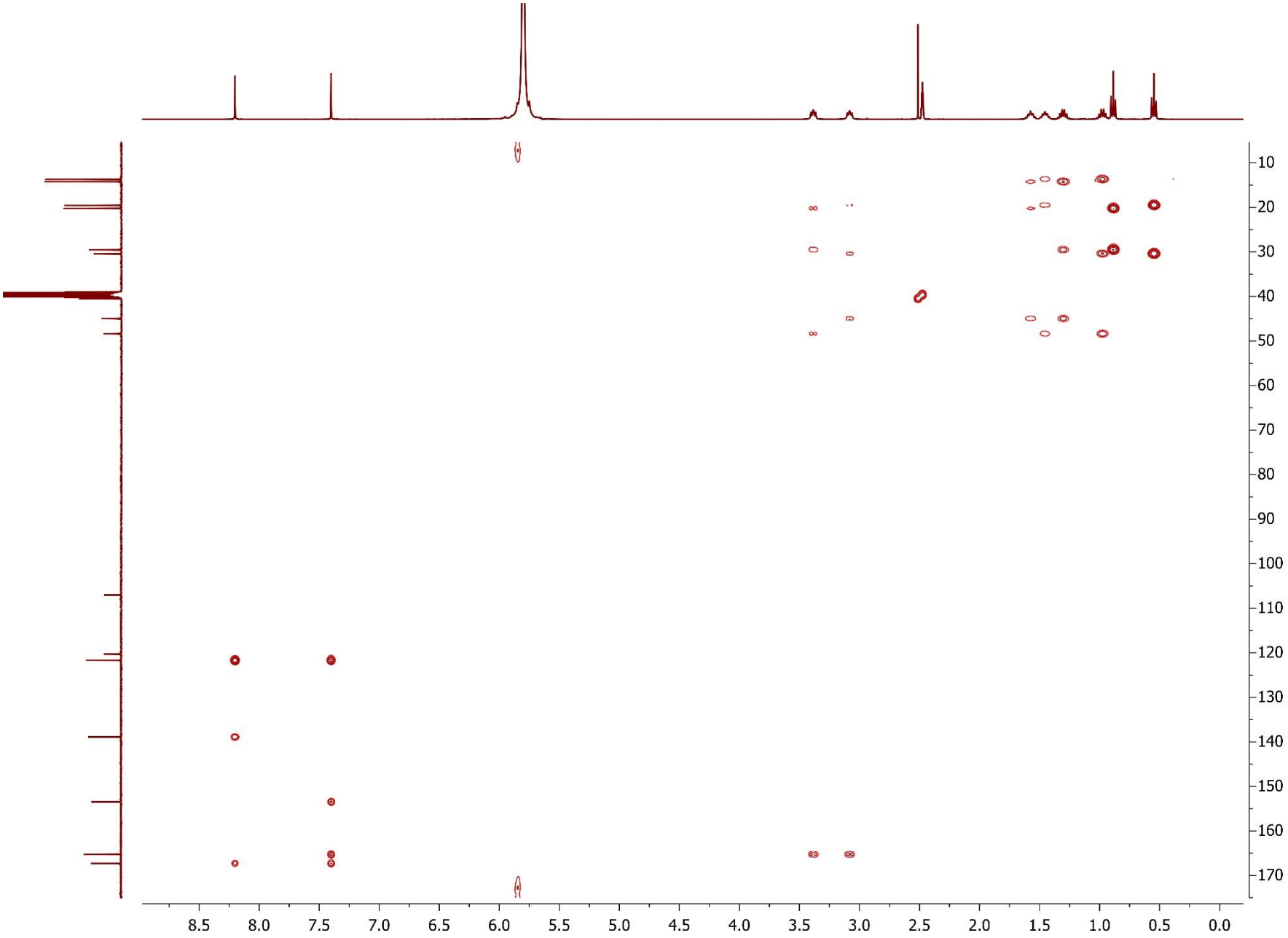

Figure S12. $^{1}H/^{13}C$ HMBC NMR spectrum in DMSO-d_6 after adding H^+

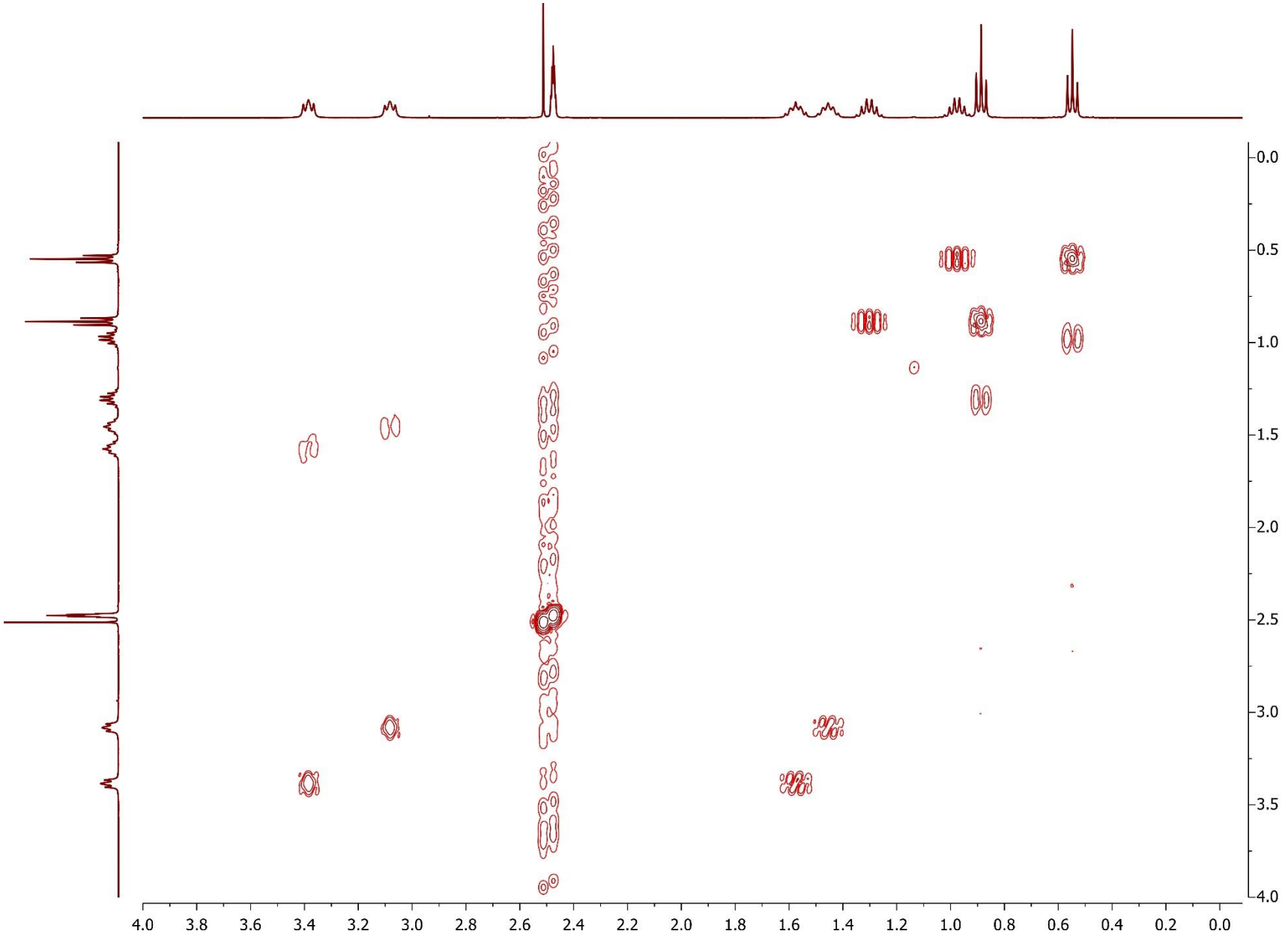

Figure S13. $^{1}H/^{1}H$ COSY NMR spectrum in DMSO-d_6 after adding H^+

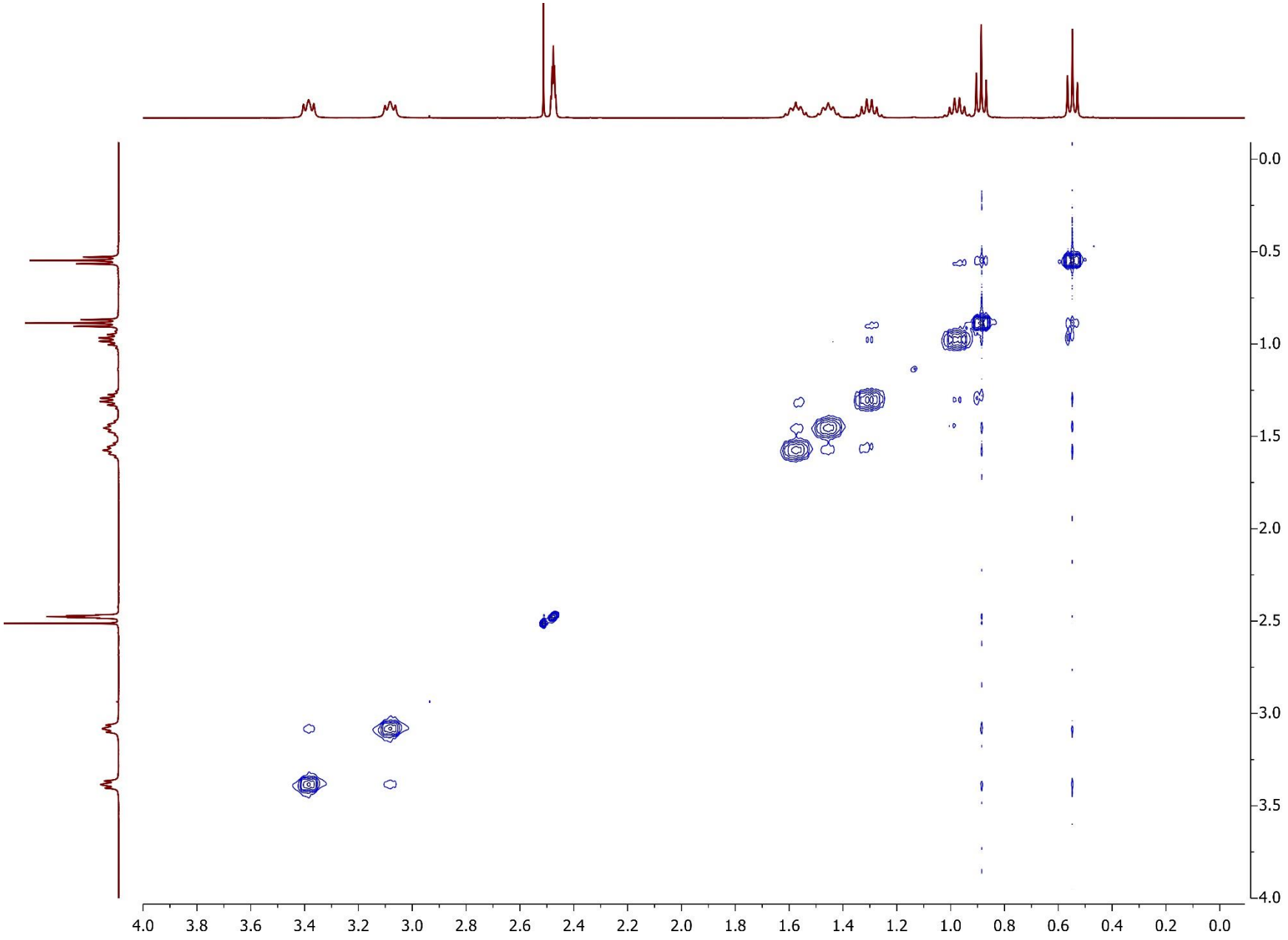

Figure S14. $^{1}H/^{1}H$ NOESY NMR spectrum in DMSO-d_6 after adding H^+

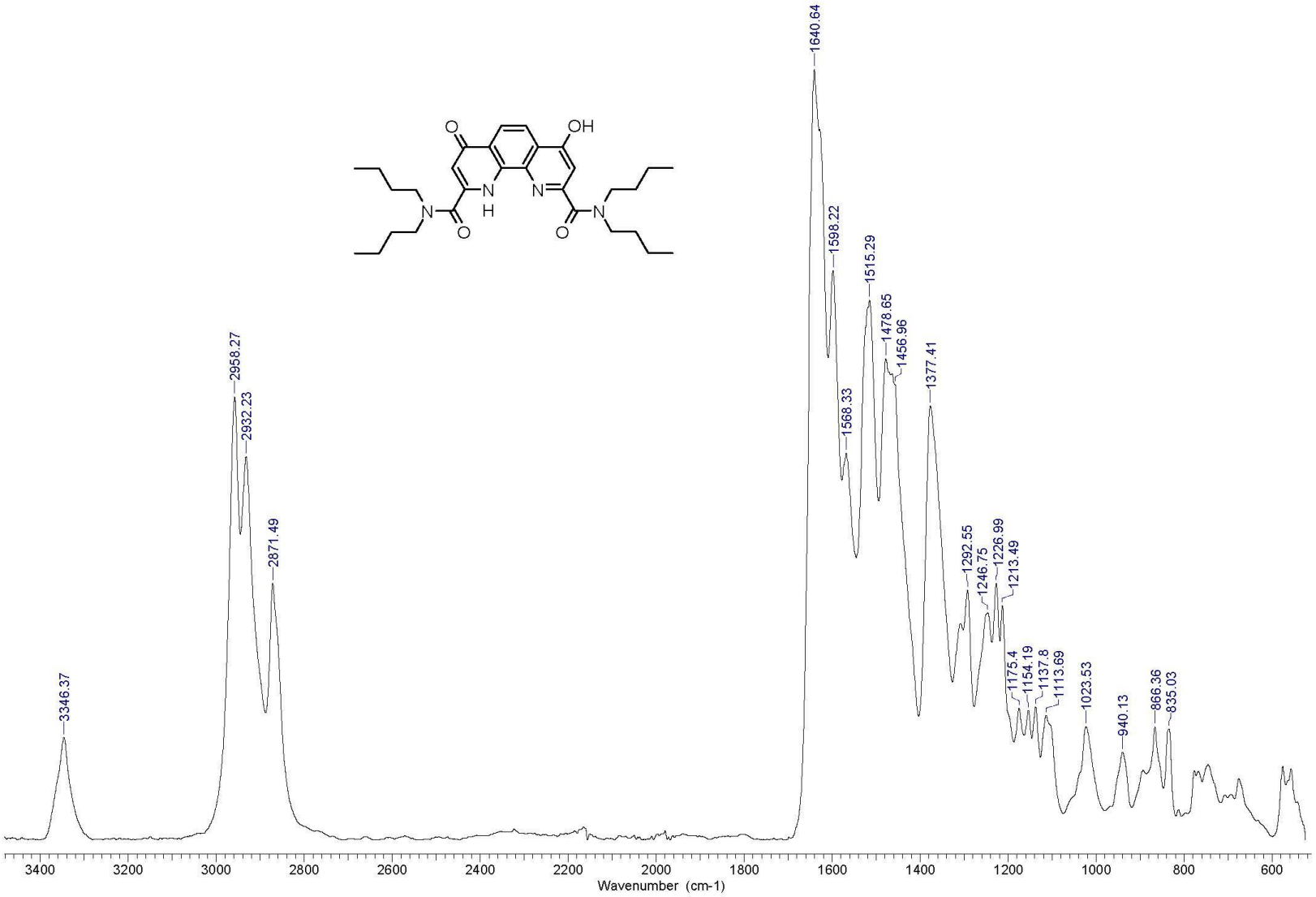

Figure S15. Solid-state IR spectrum at 25ºC

N^2,N^9-diethyl-7-hydroxy-4-oxo-N^2,N^9-di-p-tolyl-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (5c)

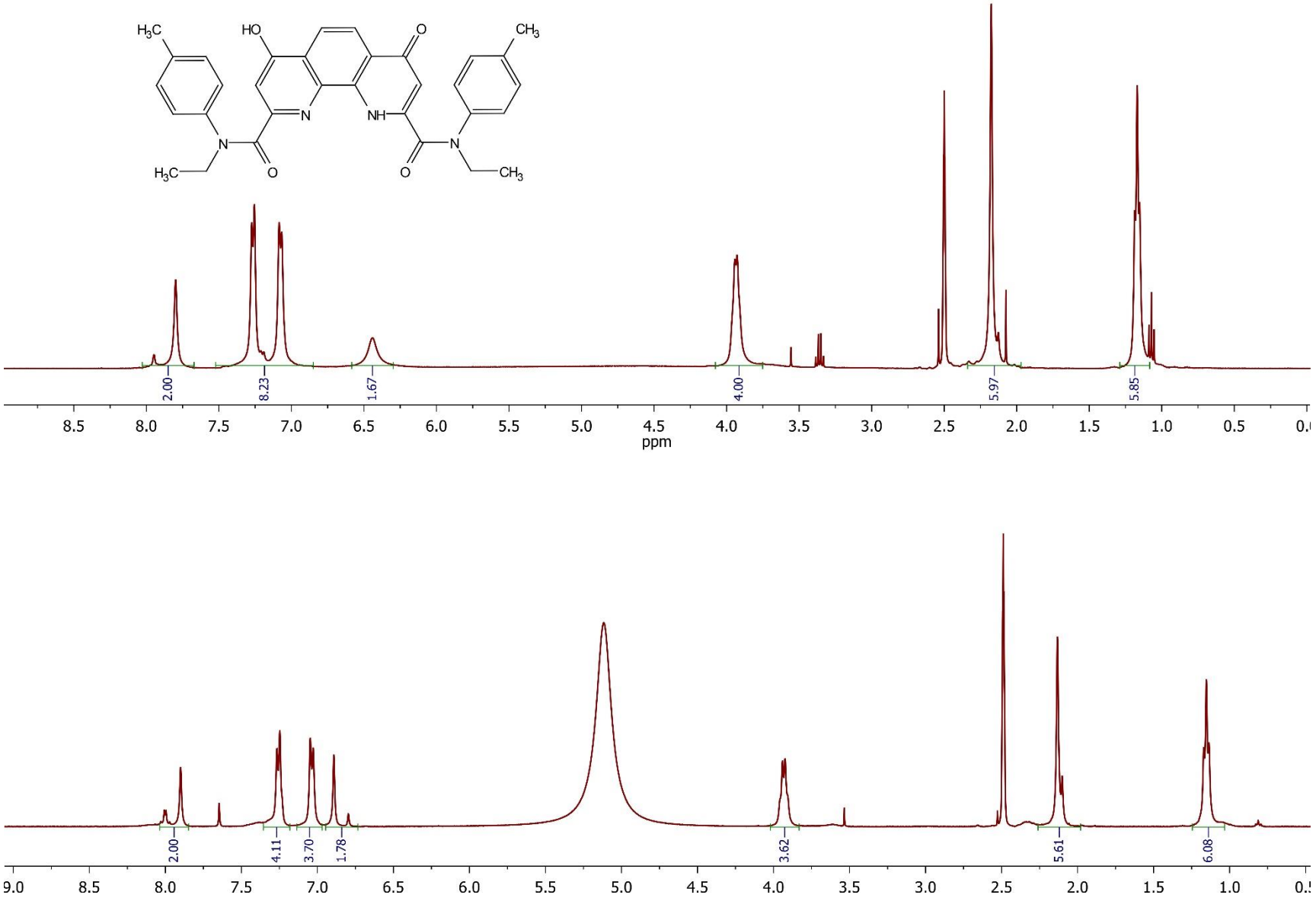

Figure S16. ^{1}H NMR spectra in DMSO-d_6 at (upper) 25ºC and (bottom) after adding H^+

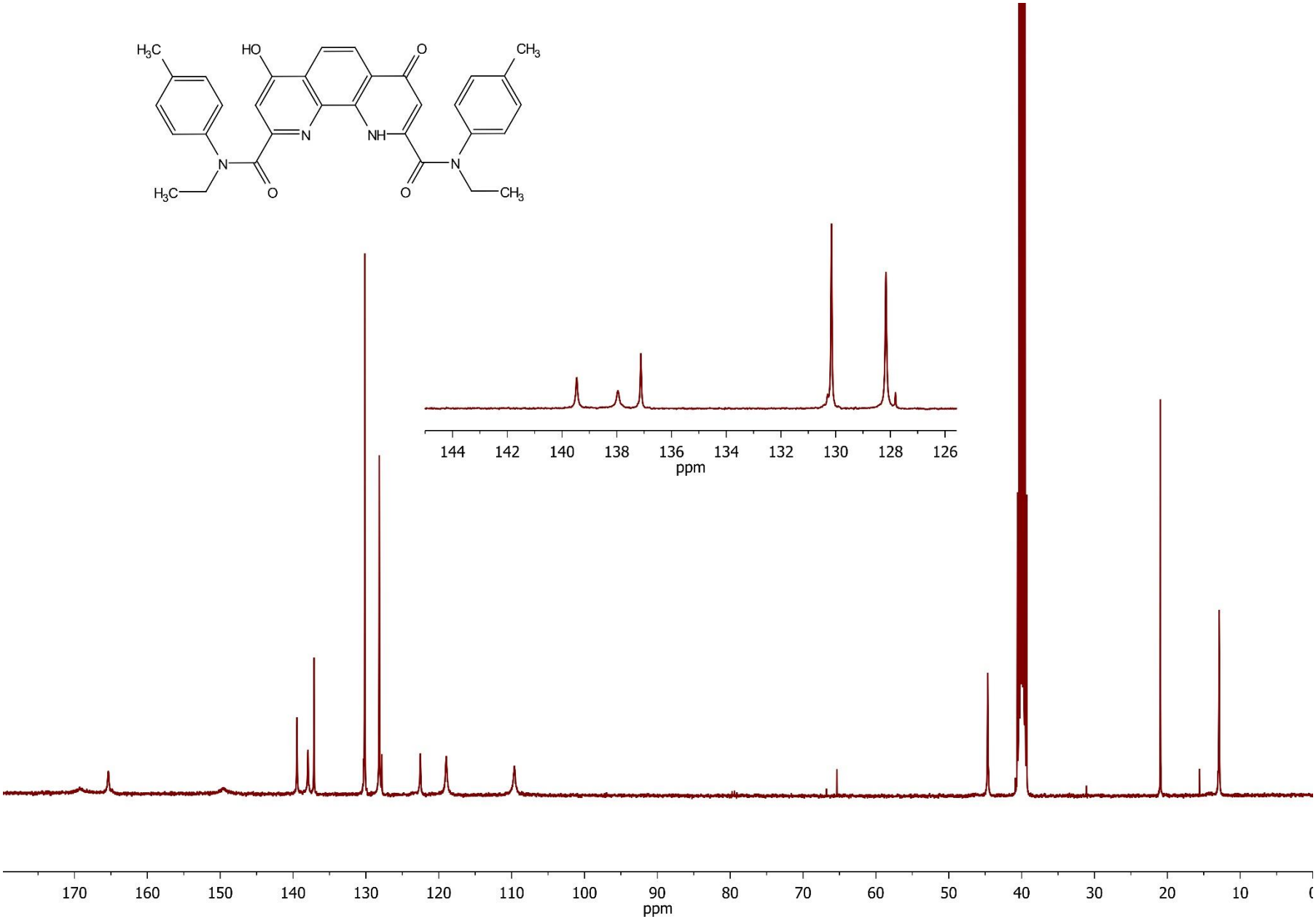

Figure S17. ^{13}C NMR spectra in DMSO-d_6

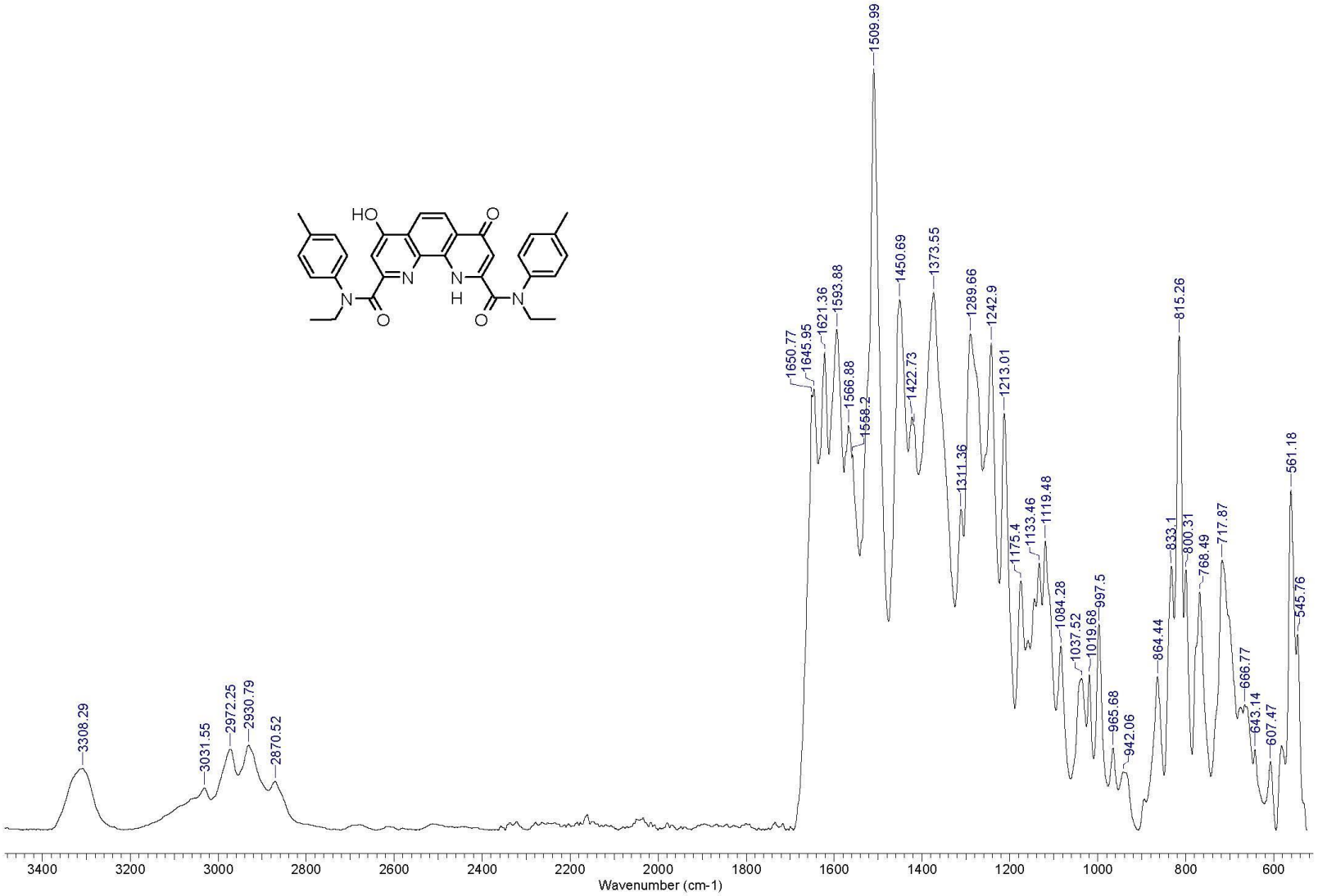

Figure S18. Solid-state IR spectrum at 25ºC

N^2,N^9-bis(4-butylphenyl)-N^2,N^9-diethyl-7-hydroxy-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (5d)

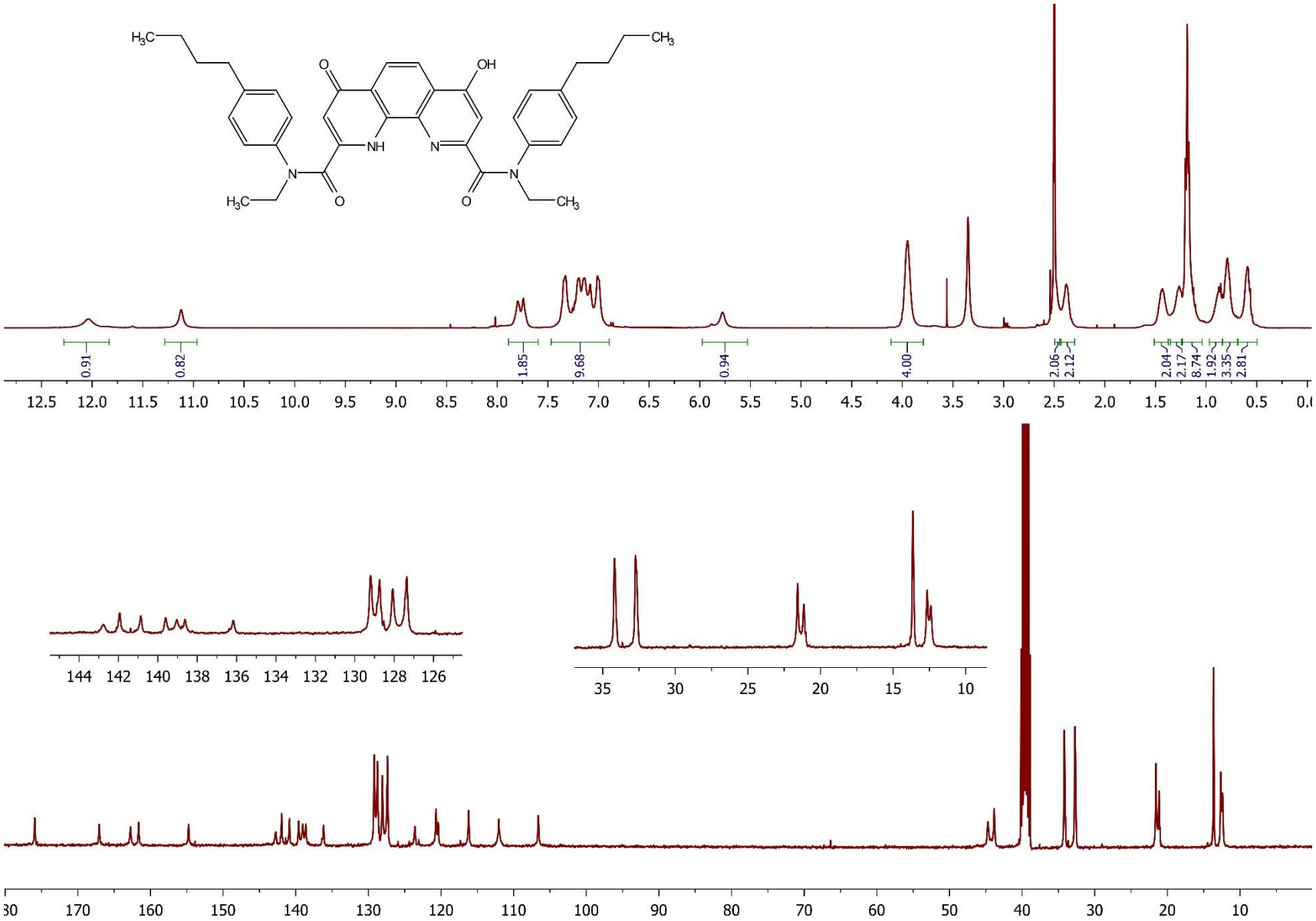

Figure S19. ^{1}H (upper) and ^{13}C (bottom) NMR spectra in DMSO-d_6 at 25°C

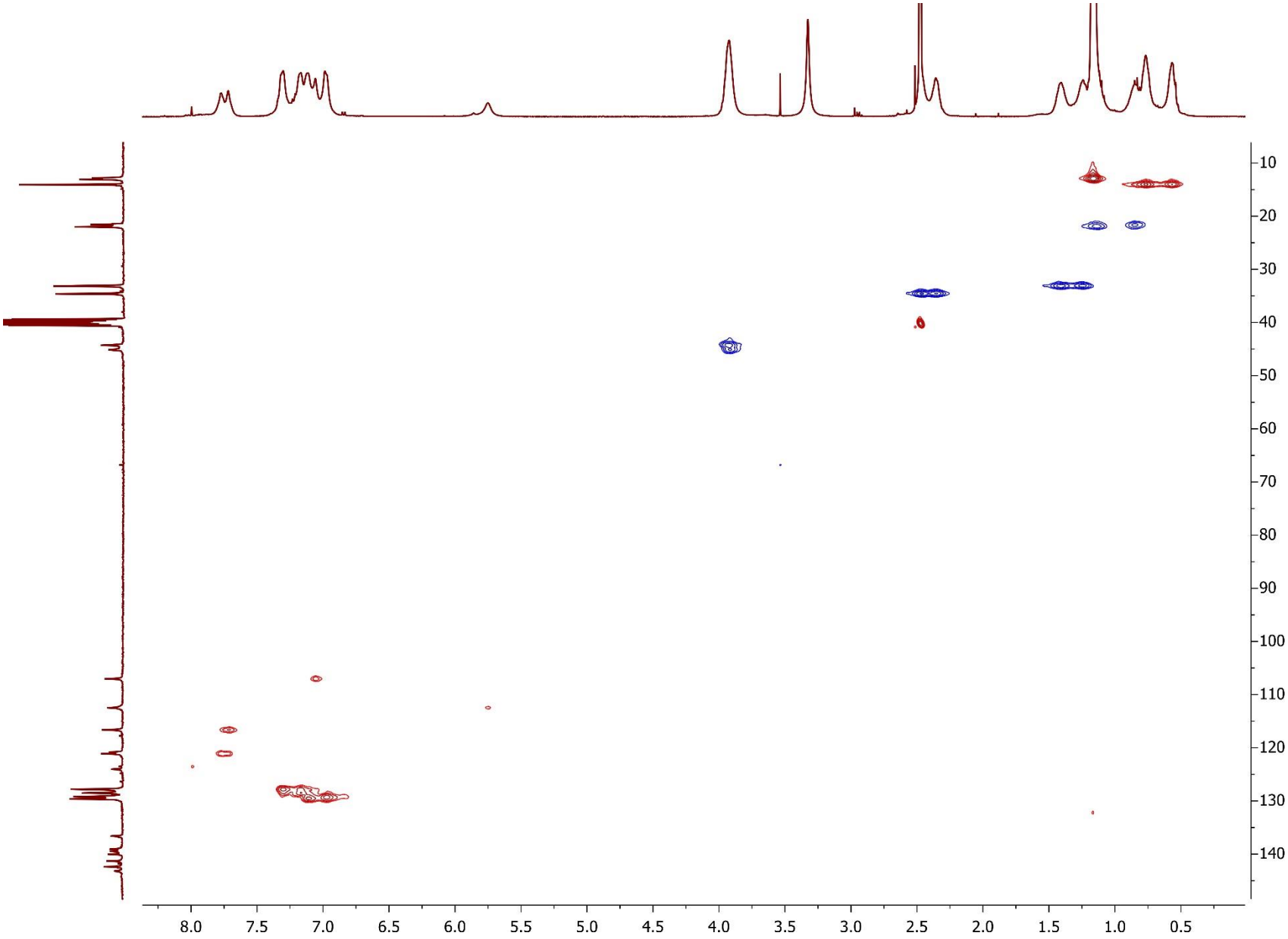

Figure S20. $^{1}H/^{13}C$ HSQC NMR spectrum in DMSO-d_6 at 25°C

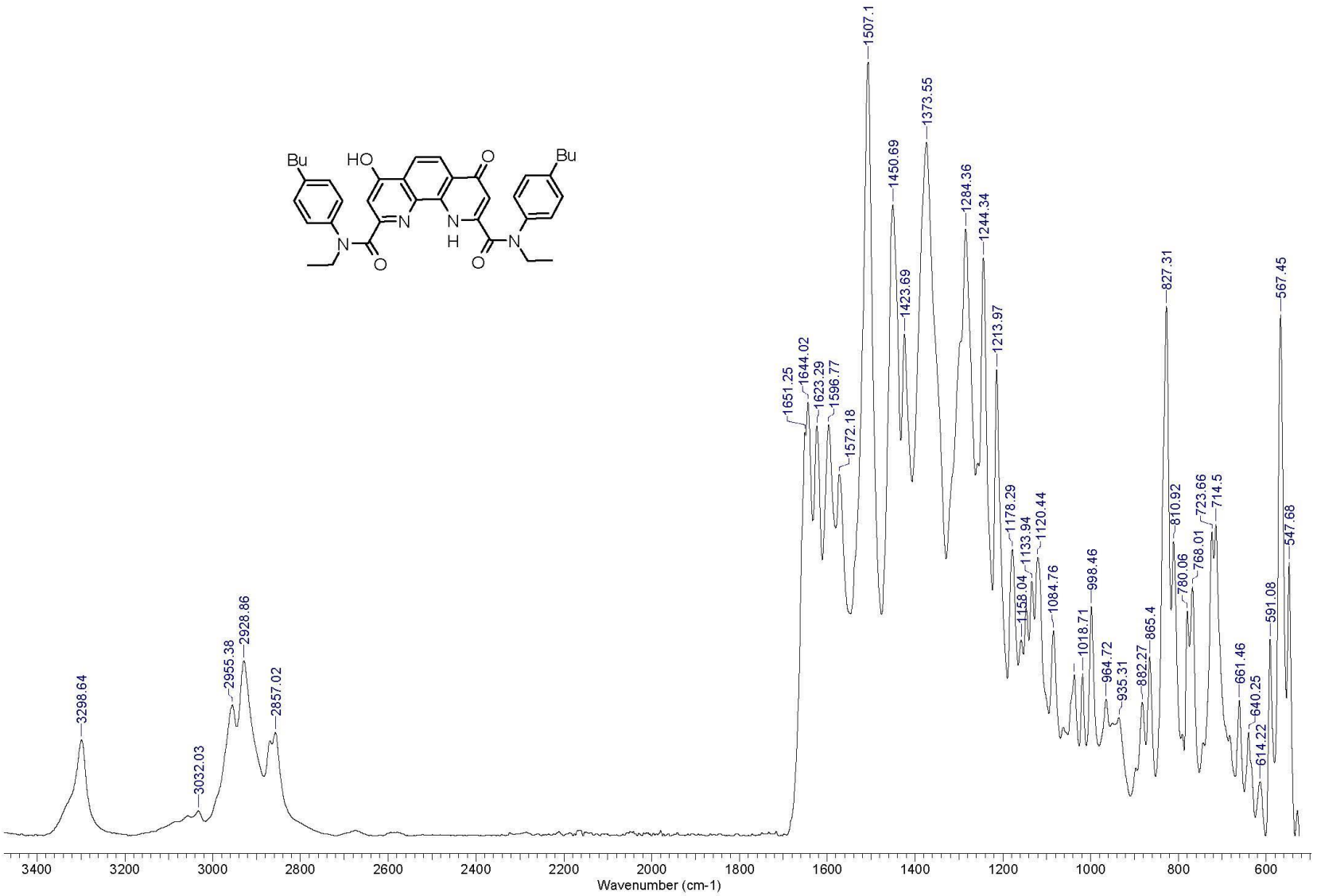

Figure S21. Solid-state IR spectrum at 25ºC

N^2,N^2,N^9,N^9-tetrabutyl-4,7-dihydroxy-1,10-phenanthroline-2,9-dicarboxamide lanthanum trinitrate 5a•$La(NO_3)_3$

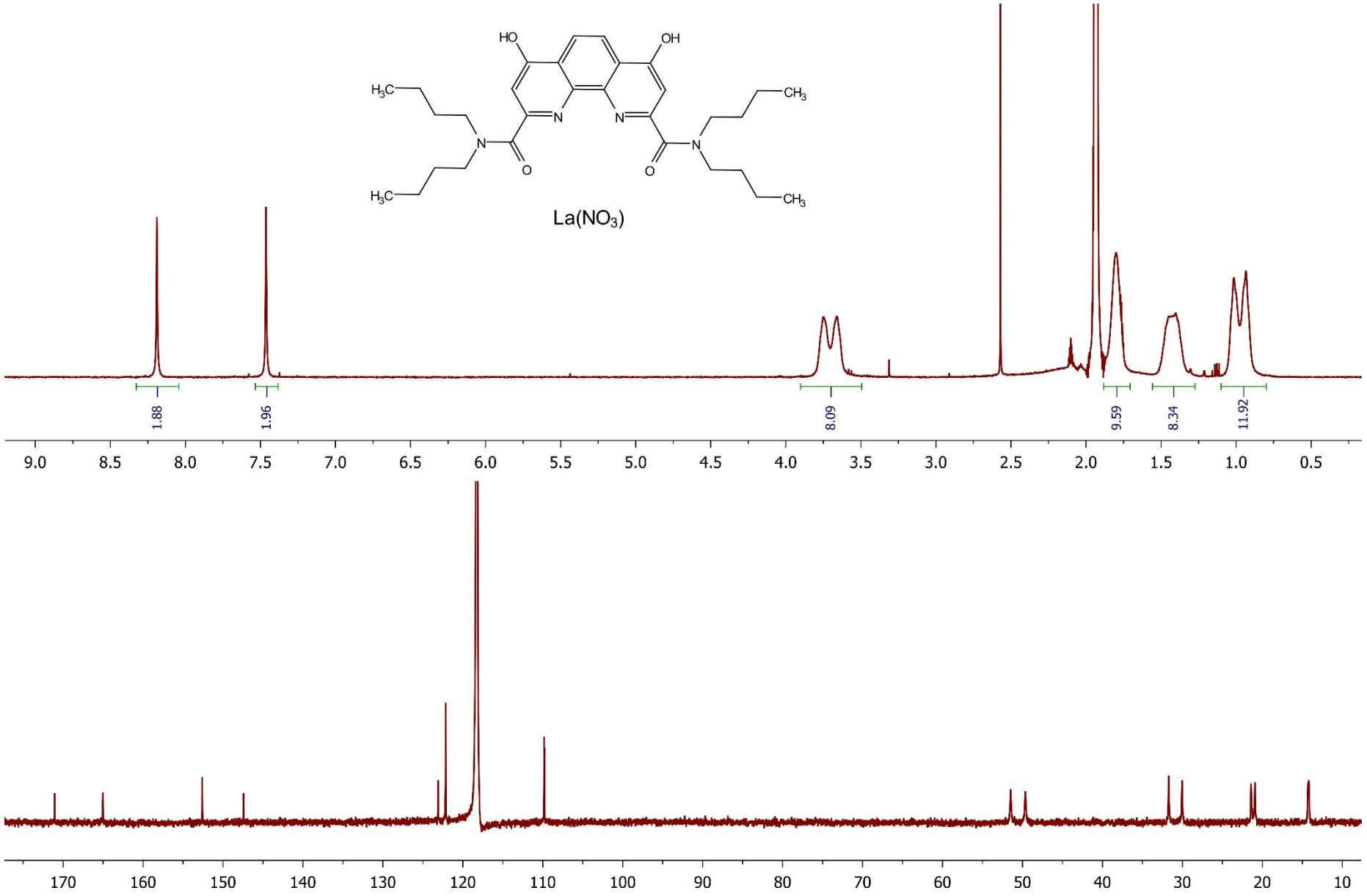

Figure S22. (Upper) ^{1}H and (bottom) ^{13}C NMR spectra in CD_3CN at 60ºC

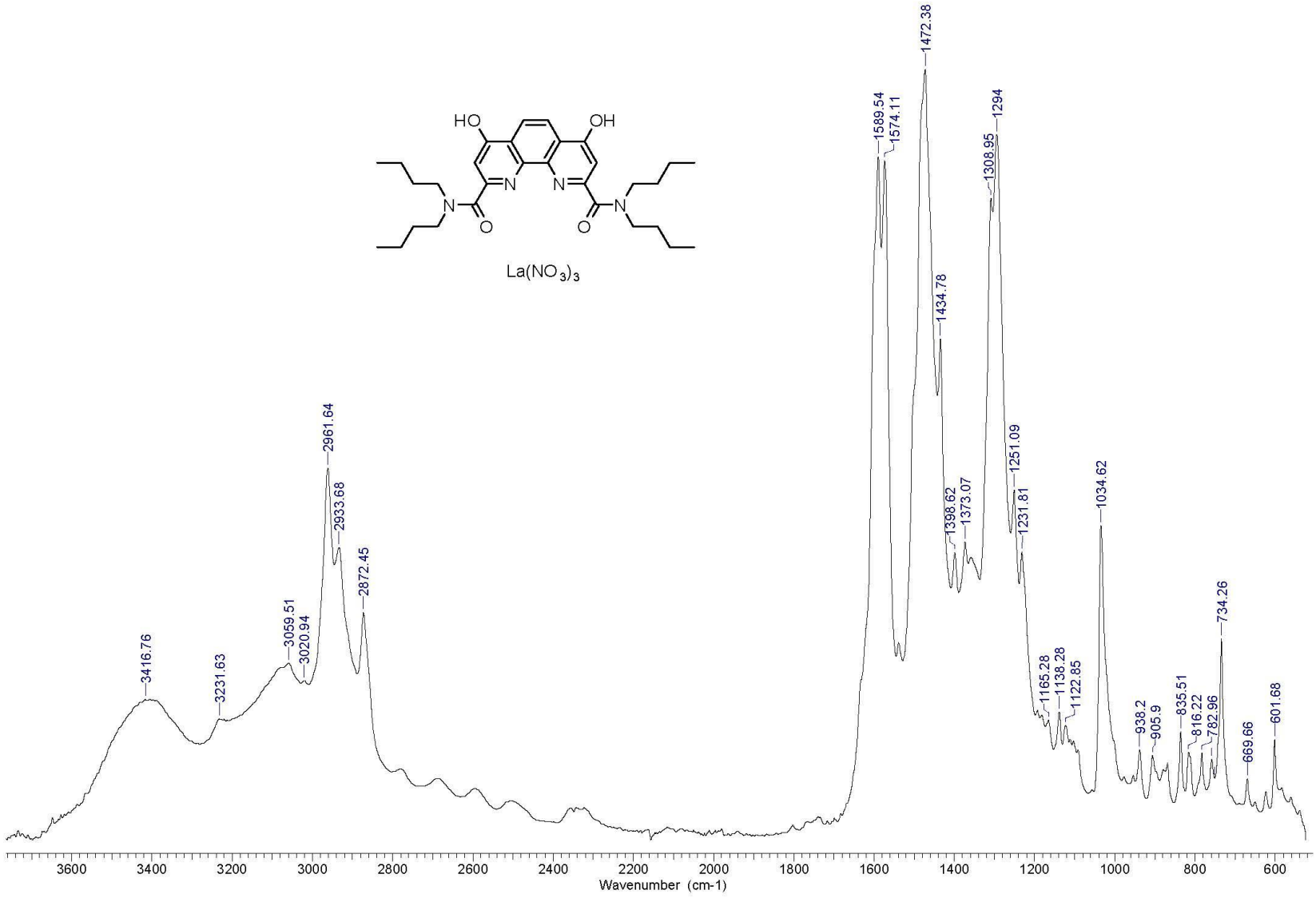

Figure S23. Solid-state IR spectrum at 25ºC

N^2,N^2,N^9,N^9-tetrabutyl-4,7-dihydroxy-1,10-phenanthroline-2,9-dicarboxamide neodymium trinitrate 5a•$Nd(NO_3)_3$

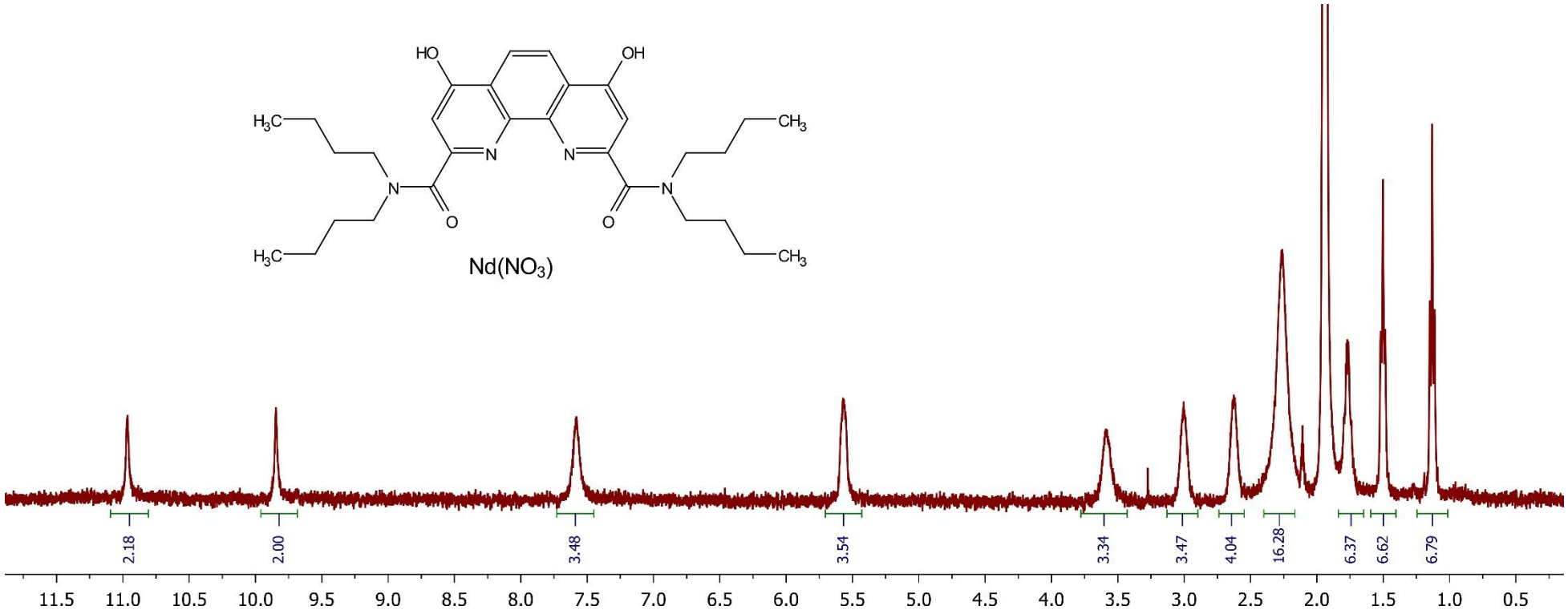

Figure S24. ^{1}H and ^{13}C NMR spectrum in CD_3CN at 25ºC

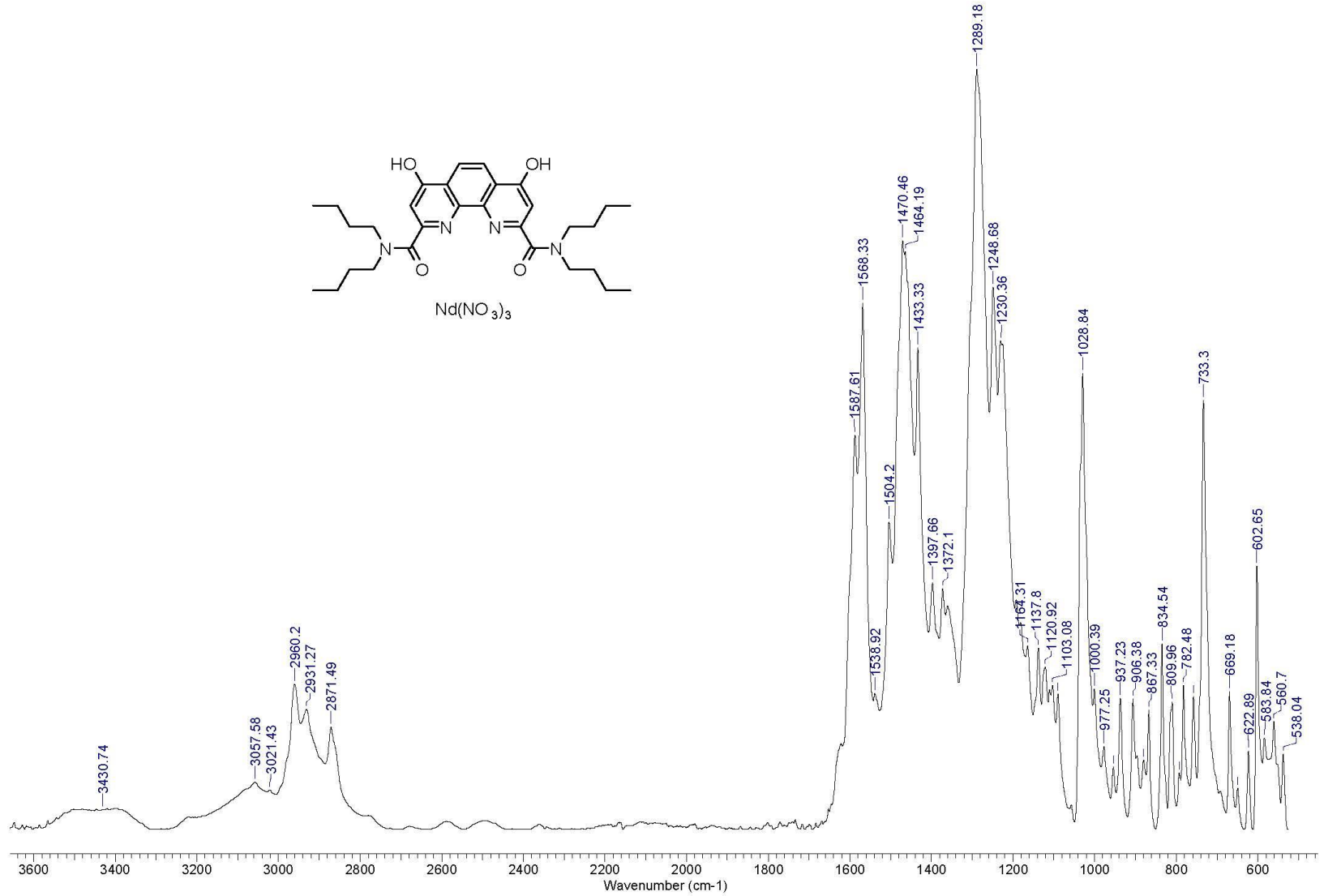

Figure S25. Solid-state IR spectrum at 25ºC

N^2,N^2,N^9,N^9-tetrabutyl-4,7-dihydroxy-1,10-phenanthroline-2,9-dicarboxamide europium trinitrate 5a•$Eu(NO_3)_3$

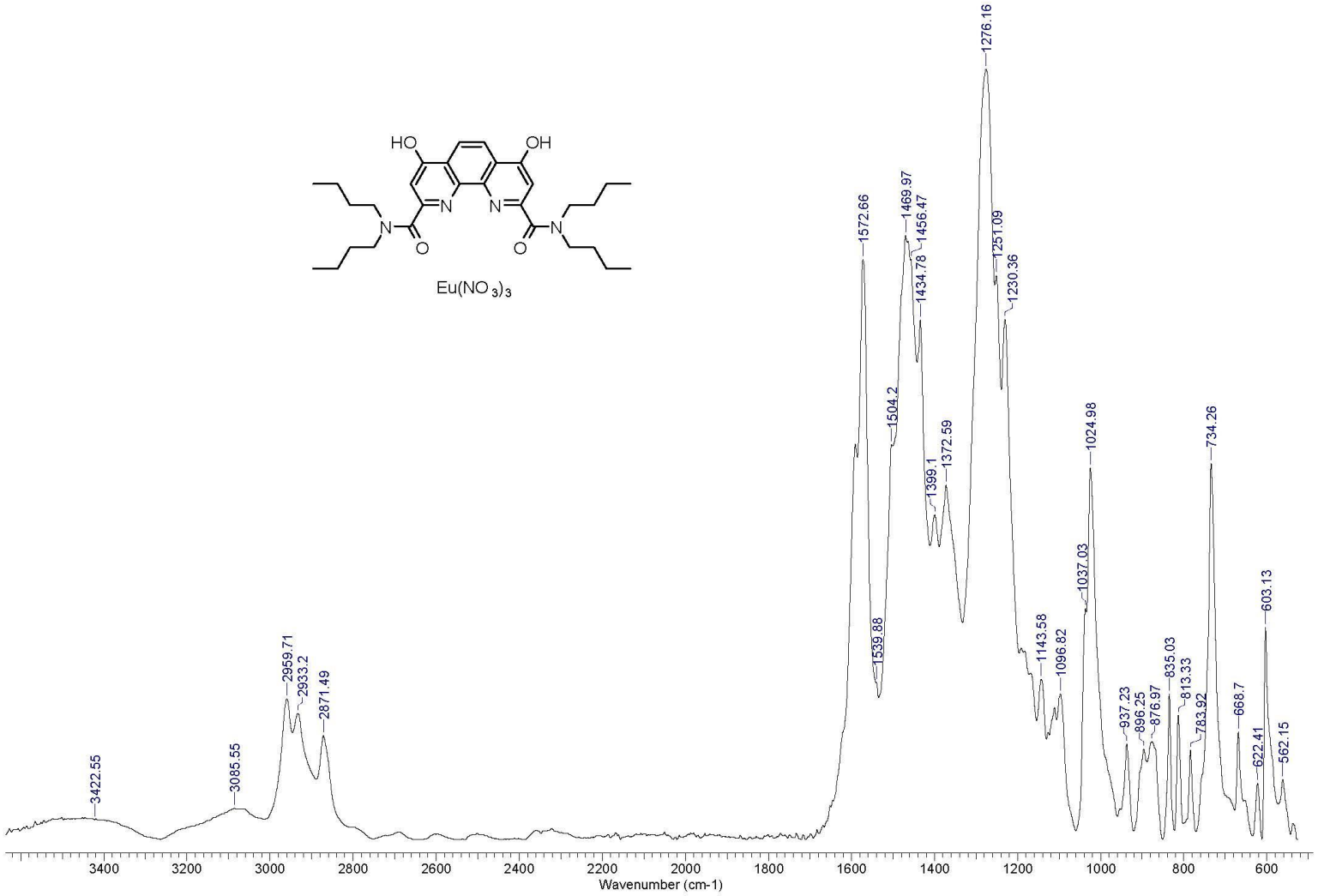

Figure S26. Solid-state IR spectrum at 25ºC

N^2,N^2,N^9,N^9-tetrabutyl-4,7-dihydroxy-1,10-phenanthroline-2,9-dicarboxamide lutetium trinitrate 5a•$Lu(NO_3)_3$

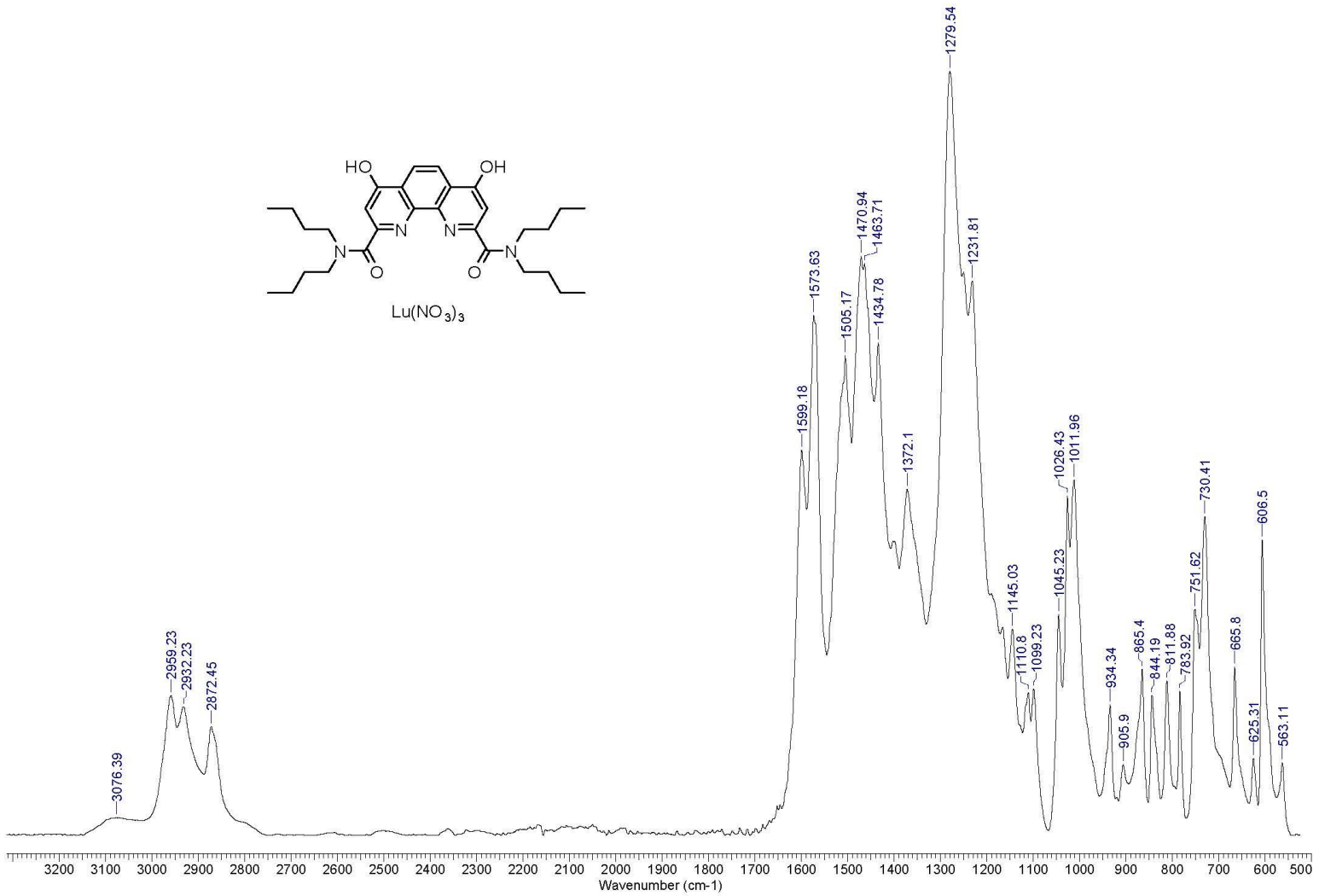

Figure S27. Solid-state IR spectrum at 25ºC

N^2,N^9-diethyl-4,7-dihydroxy-N^2,N^9-di-p-tolyl-1,10-phenanthroline-2,9-dicarboxamide lanthanum trinitrate 5c•$La(NO_3)_3$

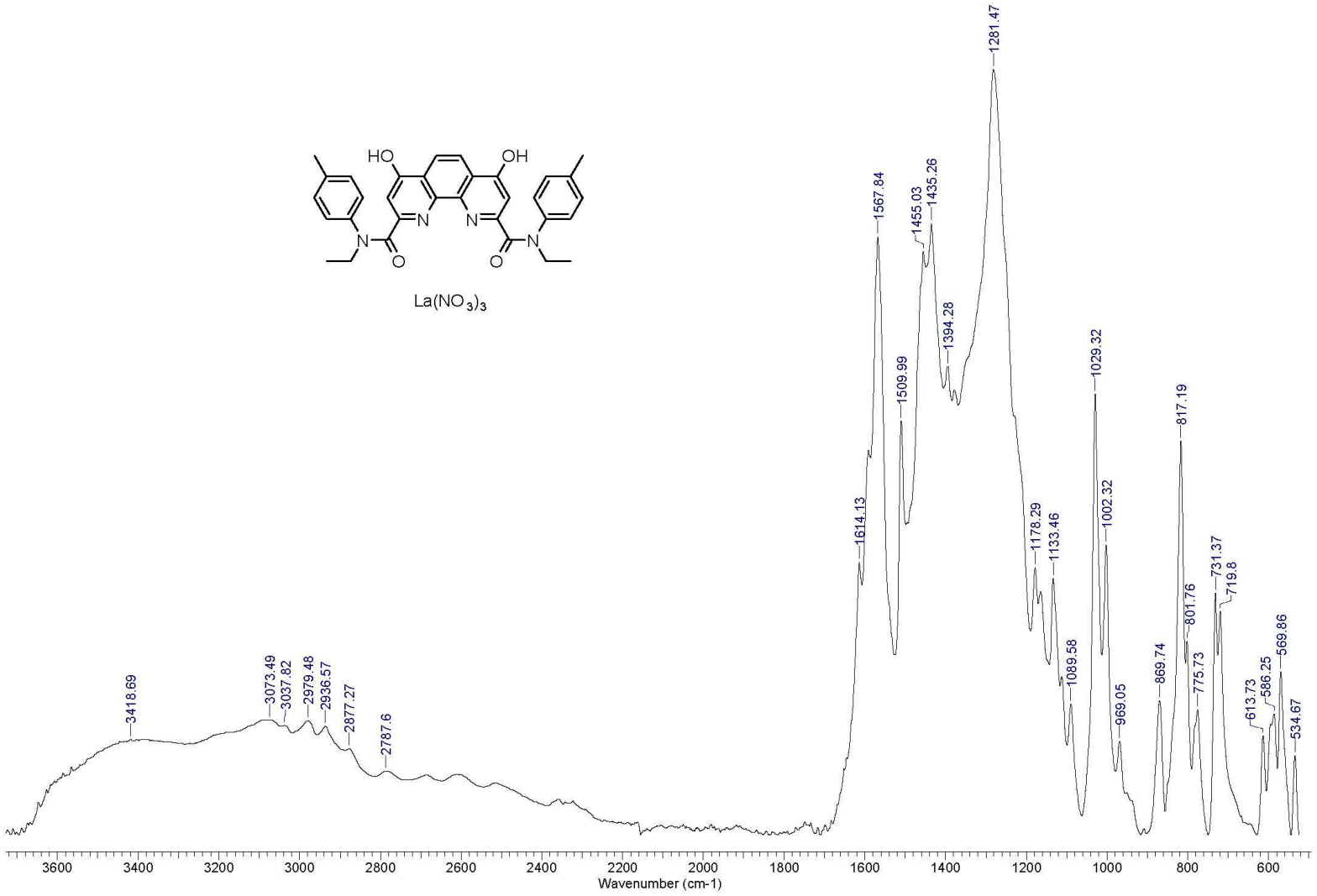

Figure S28. Solid-state IR spectrum at 25ºC

N^2,N^9-diethyl-4,7-dihydroxy-N^2,N^9-di-p-tolyl-1,10-phenanthroline-2,9-dicarboxamide neodymium trinitrate 5c•$Nd(NO_3)_3$

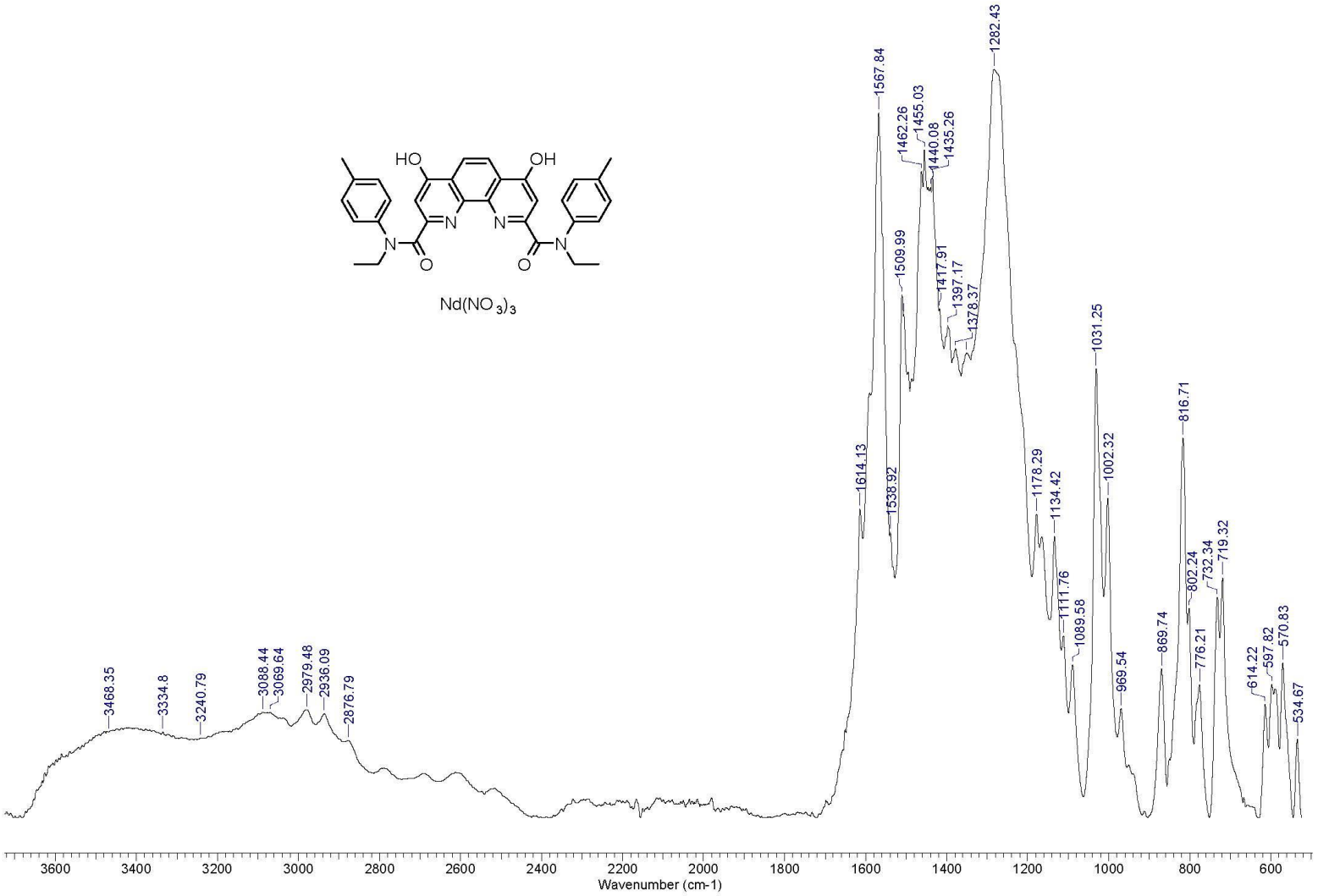

Figure S29. Solid-state IR spectrum at 25ºC

N^2,N^9-diethyl-4,7-dihydroxy-N^2,N^9-di-p-tolyl-1,10-phenanthroline-2,9-dicarboxamide europium trinitrate 5c•$Eu(NO_3)_3$

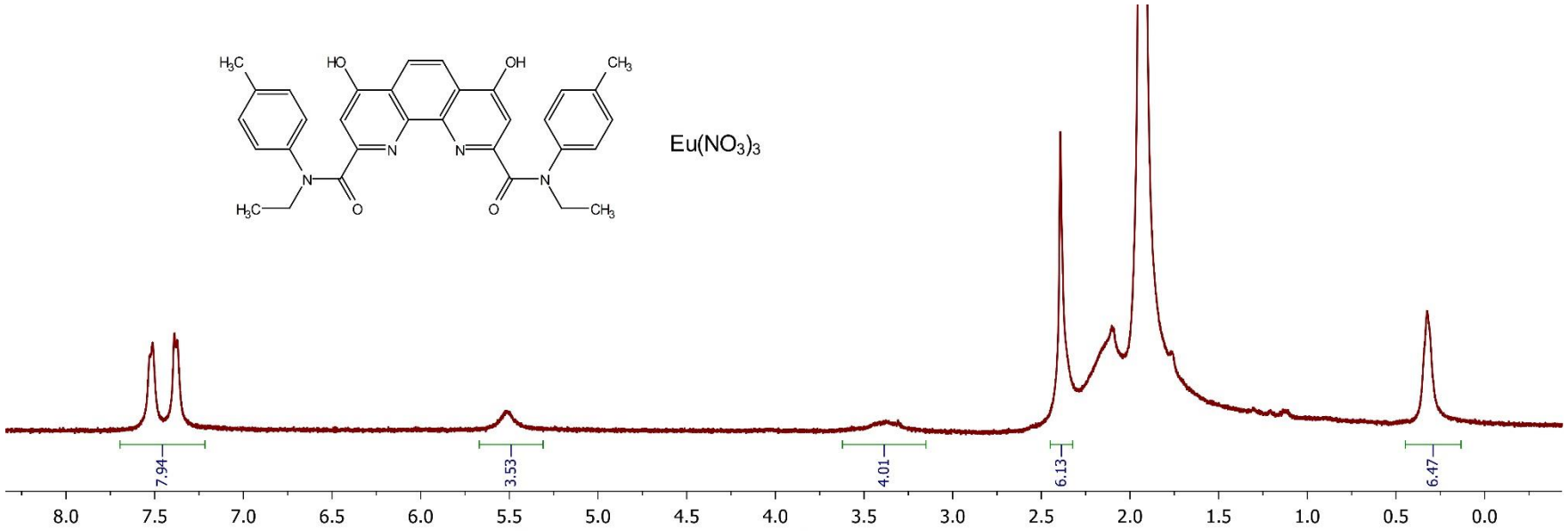

Figure S30. ^{1}H NMR spectrum in CD_3CN at 60ºC

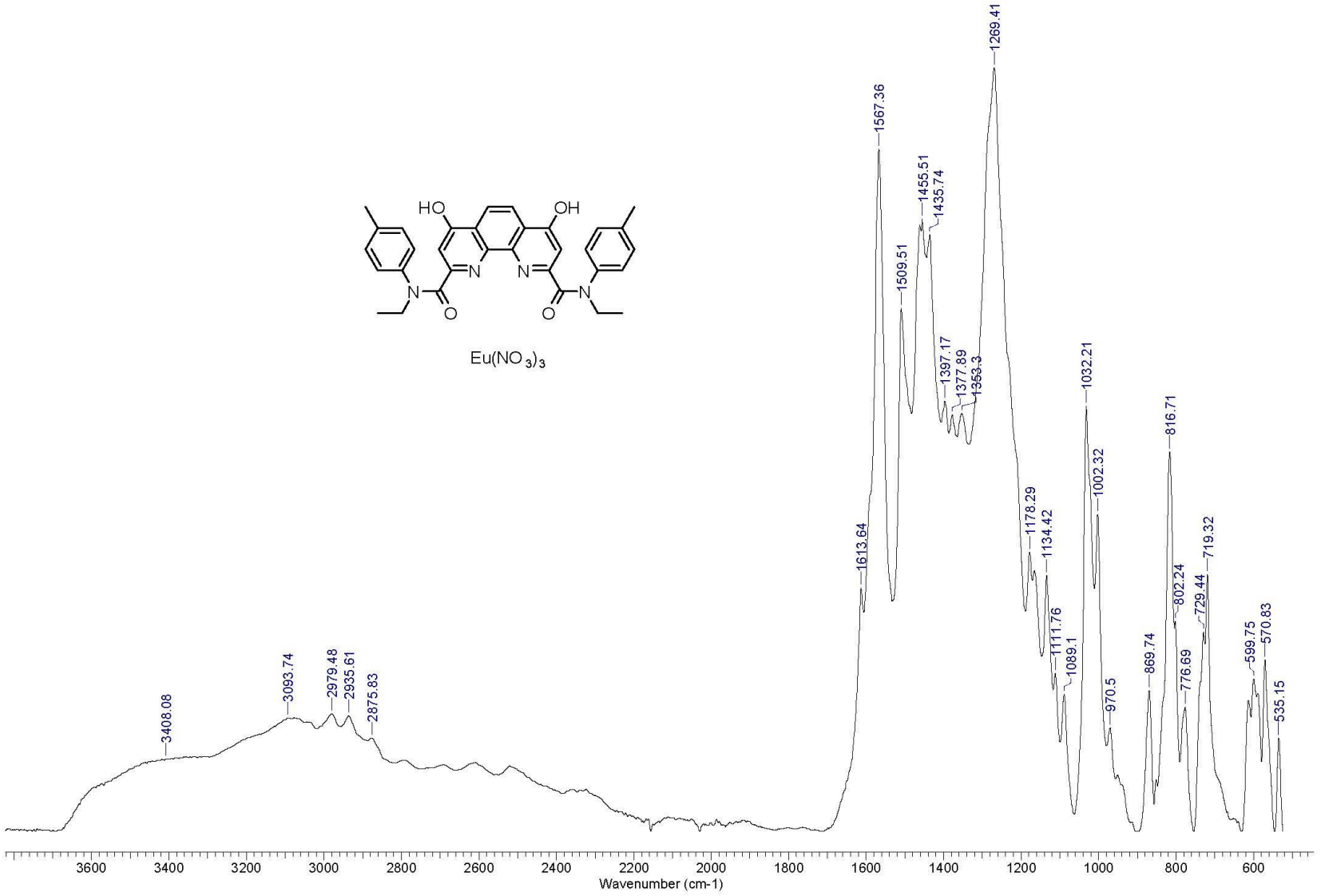

Figure S31. Solid-state IR spectrum at 25ºC

N^2,N^9-diethyl-4,7-dihydroxy-N^2,N^9-di-p-tolyl-1,10-phenanthroline-2,9-dicarboxamide lutetium trinitrate 5c•$Lu(NO_3)_3$

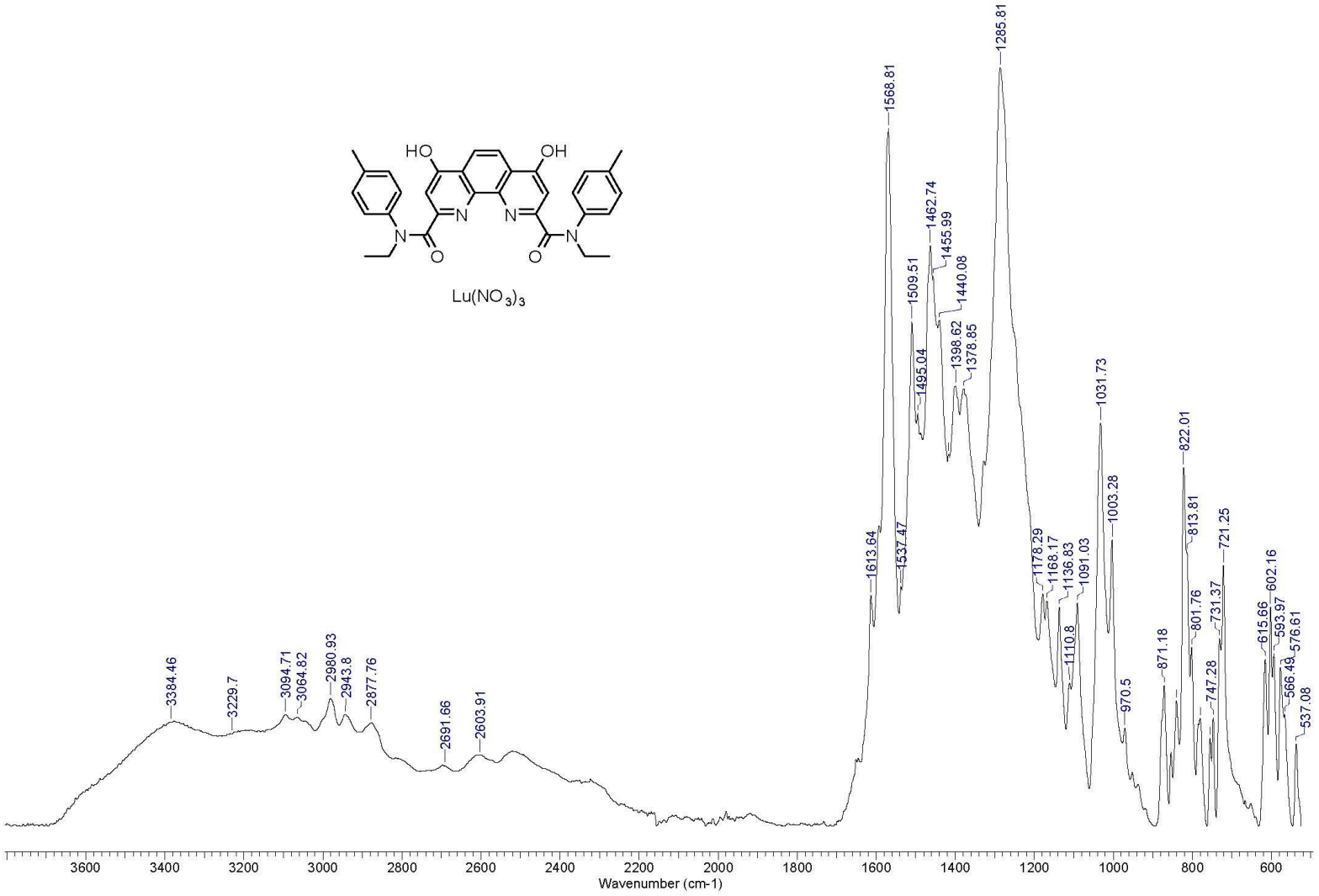

Figure S32. Solid-state IR spectrum at 25ºC

2. NMR spectra of hydrolysis experiments

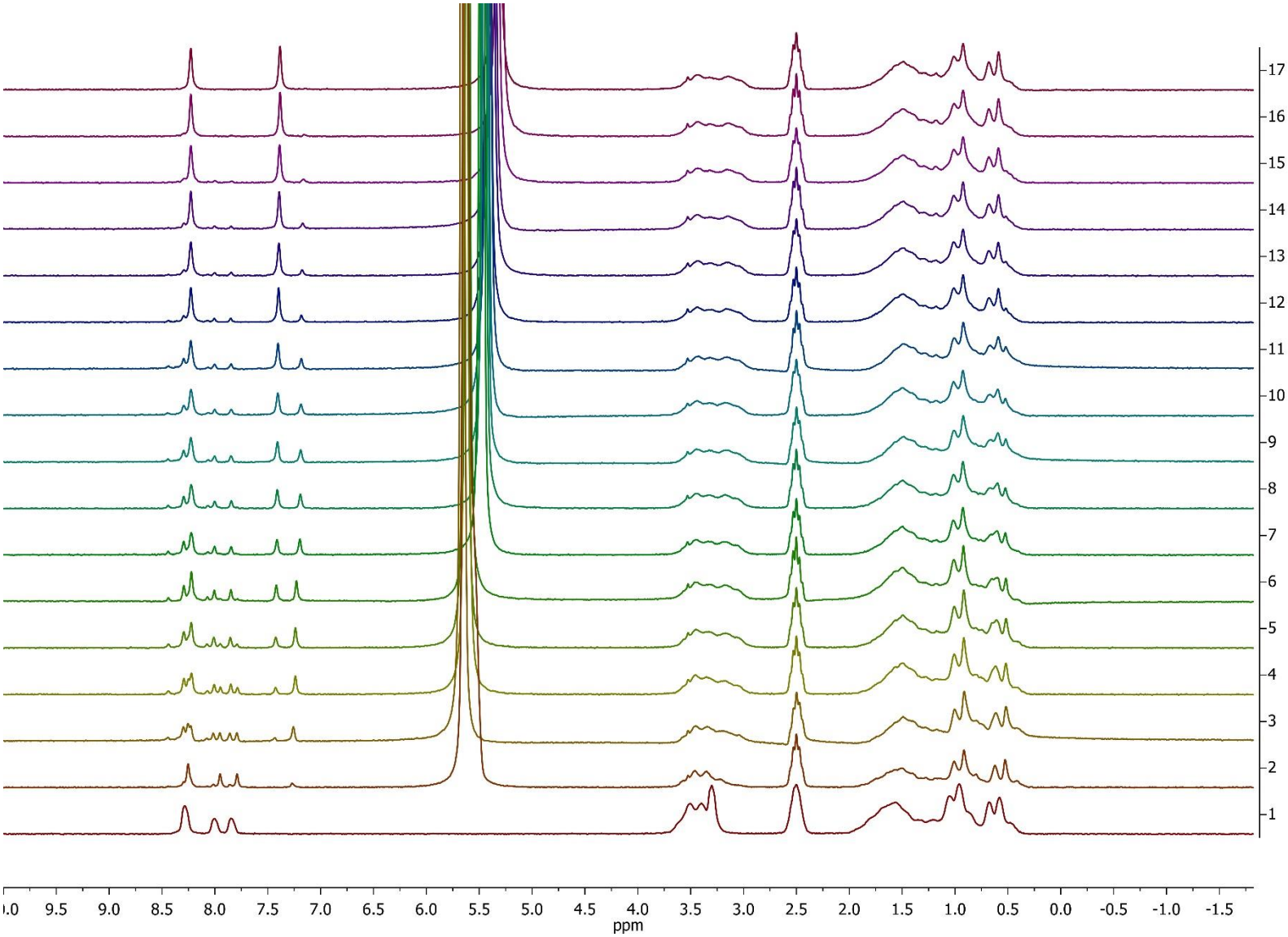

Figure S33. Hydrolysis of **1a** (1) after 0.3h (2), 1.5h (3), 2h (4), 2.5h (5), 3h (6), 3.5h (7), 4h (8), 4.5h(9), 5h (10), 5.5h (11), 8.3h (12), 9.2h (13), 10.2h (14), 12.2h (15), 16.2h (16), 20h (17)

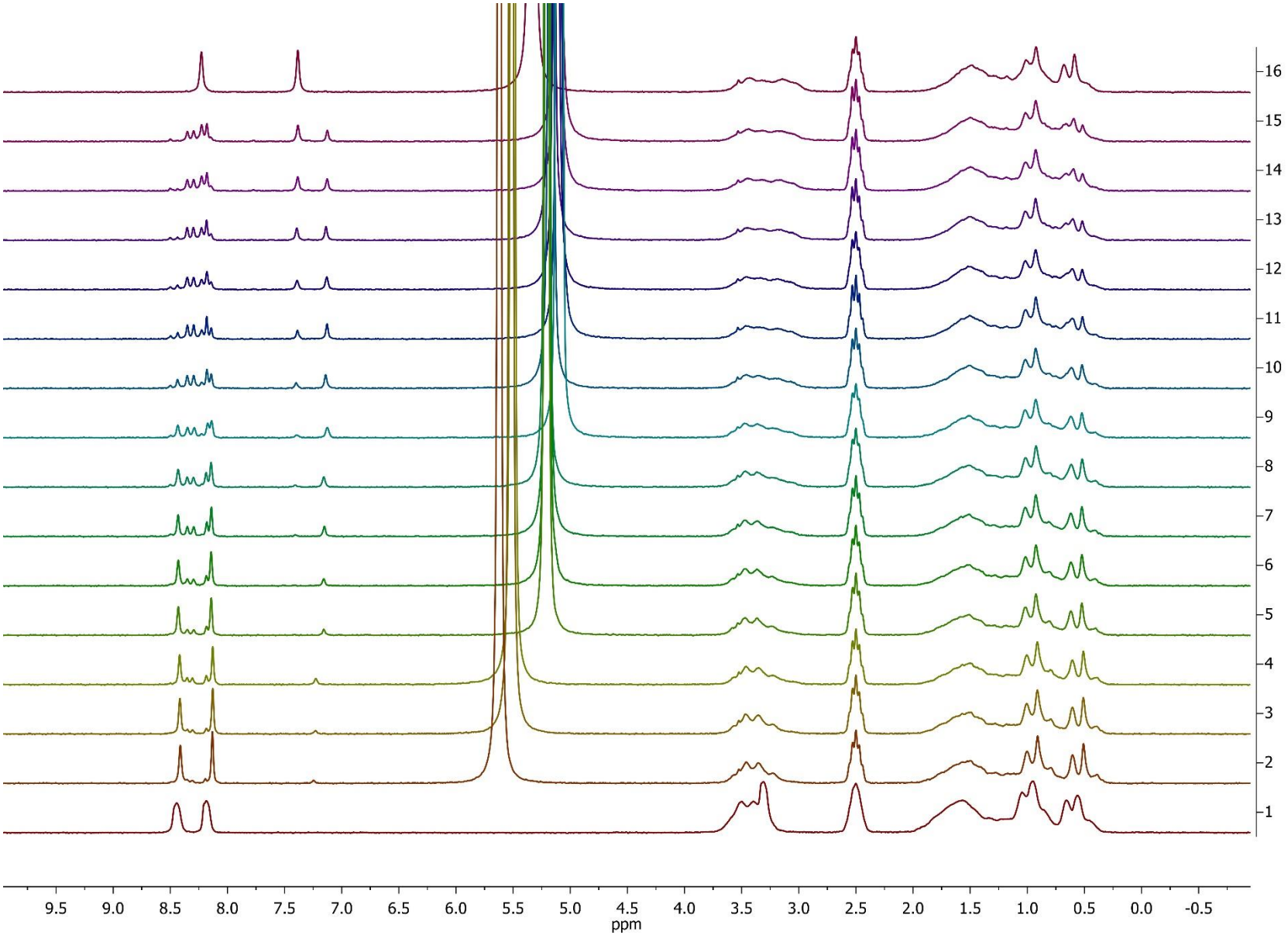

Figure S34. Hydrolysis of **3a** (1) after 1.5h (2), 2h (3), 3h (4), 4h (5), 5h (6), 6.5h (7), 7.5h (8), 9.5h(9), 13.5h (10), 16.5h (11), 19.5h (12), 22.5h (13), 26.5h (14), 30.5h (15), 72h (16)

3. NMR titration

N^2,N^2,N^9,N^9-tetrabutyl-4,7-difluoro-1,10-phenanthroline-2,9-dicarboxamide (1a) with **neodymium trinitrate**

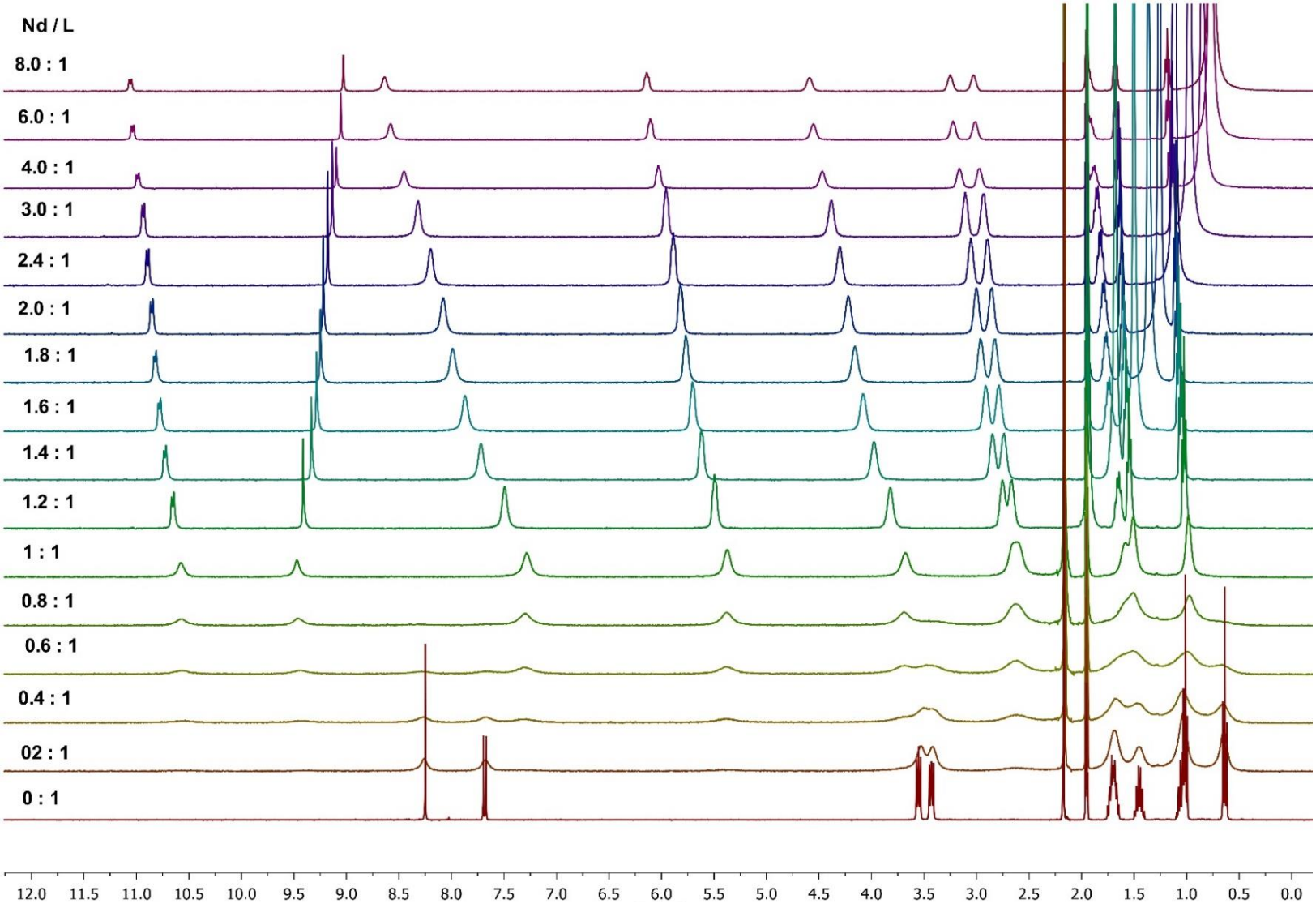

Figure S35. NMR titration of **1a** with $Nd(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^2,N^9,N^9-tetrabutyl-4,7-difluoro-1,10-phenanthroline-2,9-dicarboxamide (1a) with **lutetium trinitrate**

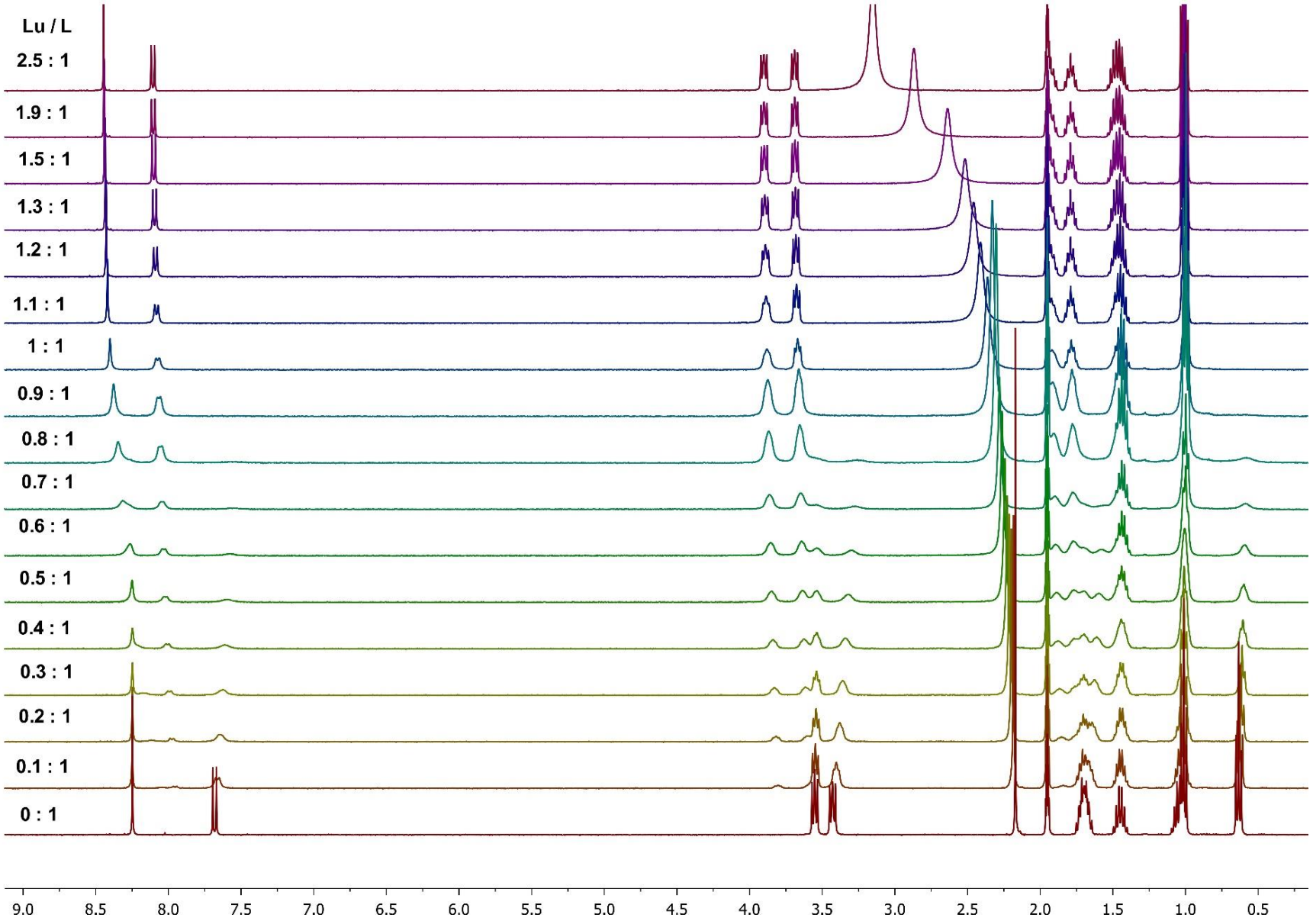

Figure S36. NMR titration of **1a** with $Lu(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^2,N^9,N^9-tetrabutyl-7-fluoro-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (2a) with **neodymium trinitrate**

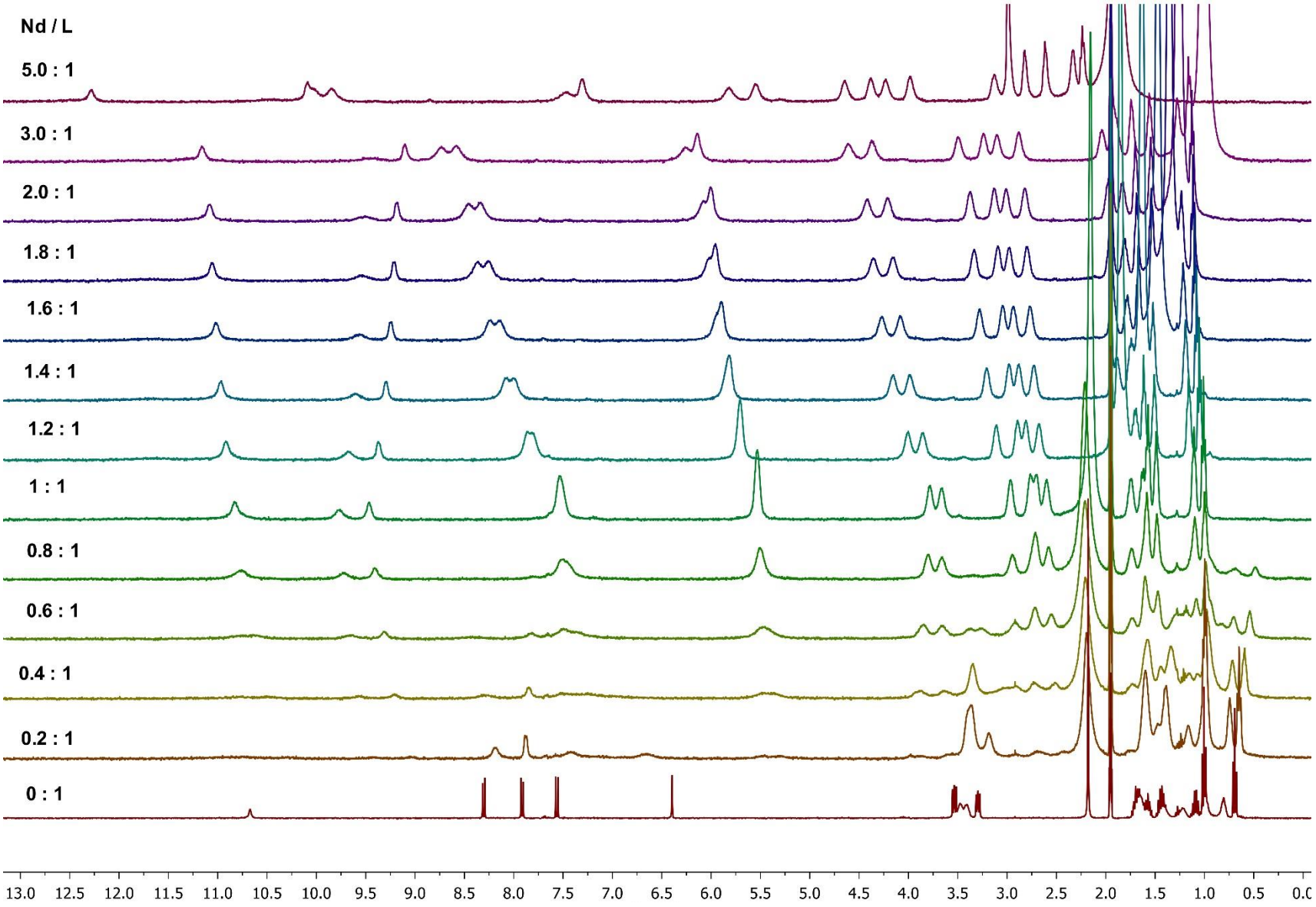

Figure S37. NMR titration of **2a** with $Nd(NO_3)_3.6H_2O$ in CD_3CN

N^2,N^2,N^9,N^9-tetrabutyl-7-fluoro-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (2a) with **lutetium trinitrate**

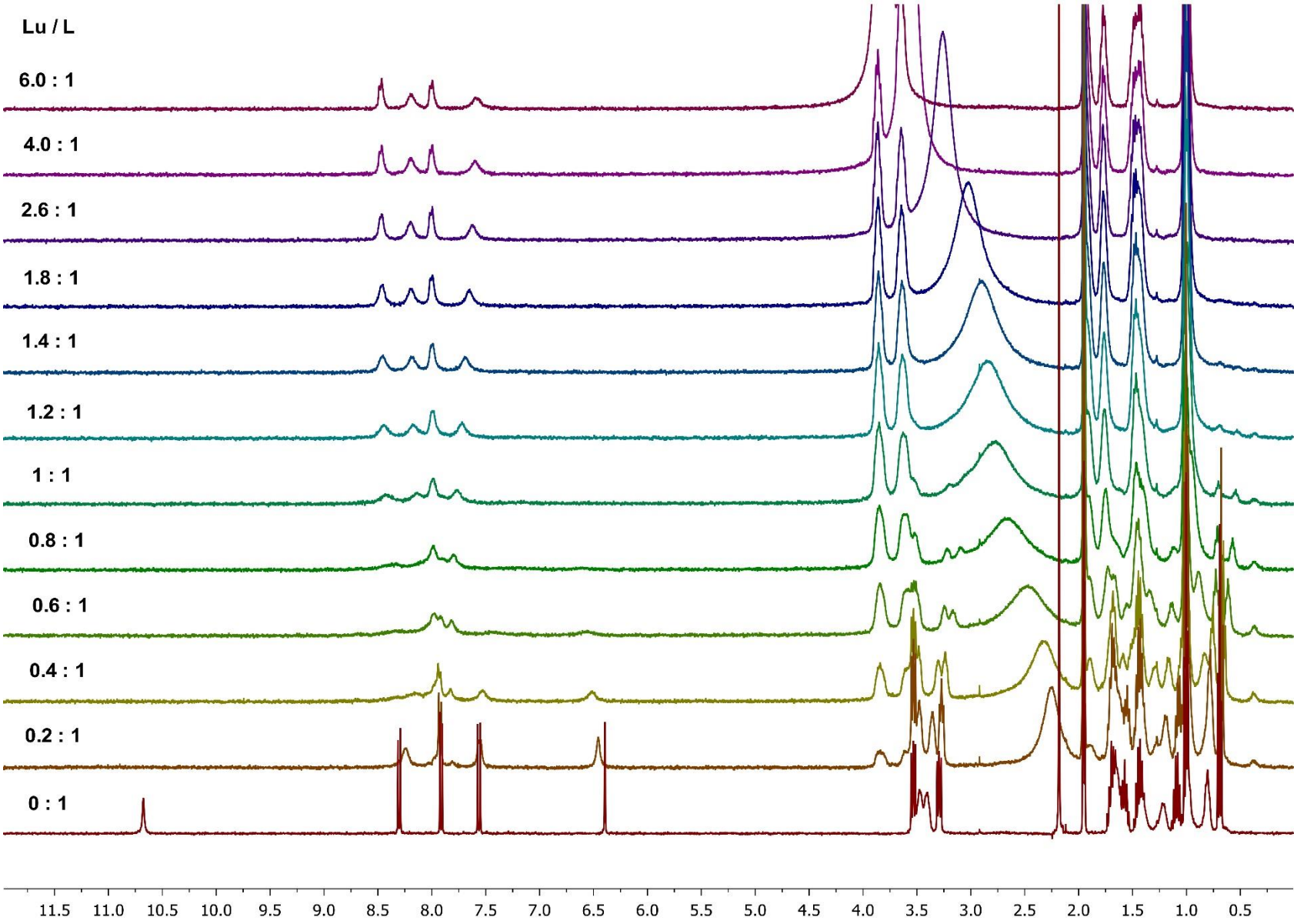

Figure S38. NMR titration of **2a** with $Lu(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^9-bis(p-tolyl)-4,7-difluoro-N^2,N^9-diethyl-1,10-phenanthroline-2,9-dicarboxamide (1c) with **lanthanum trinitrate**

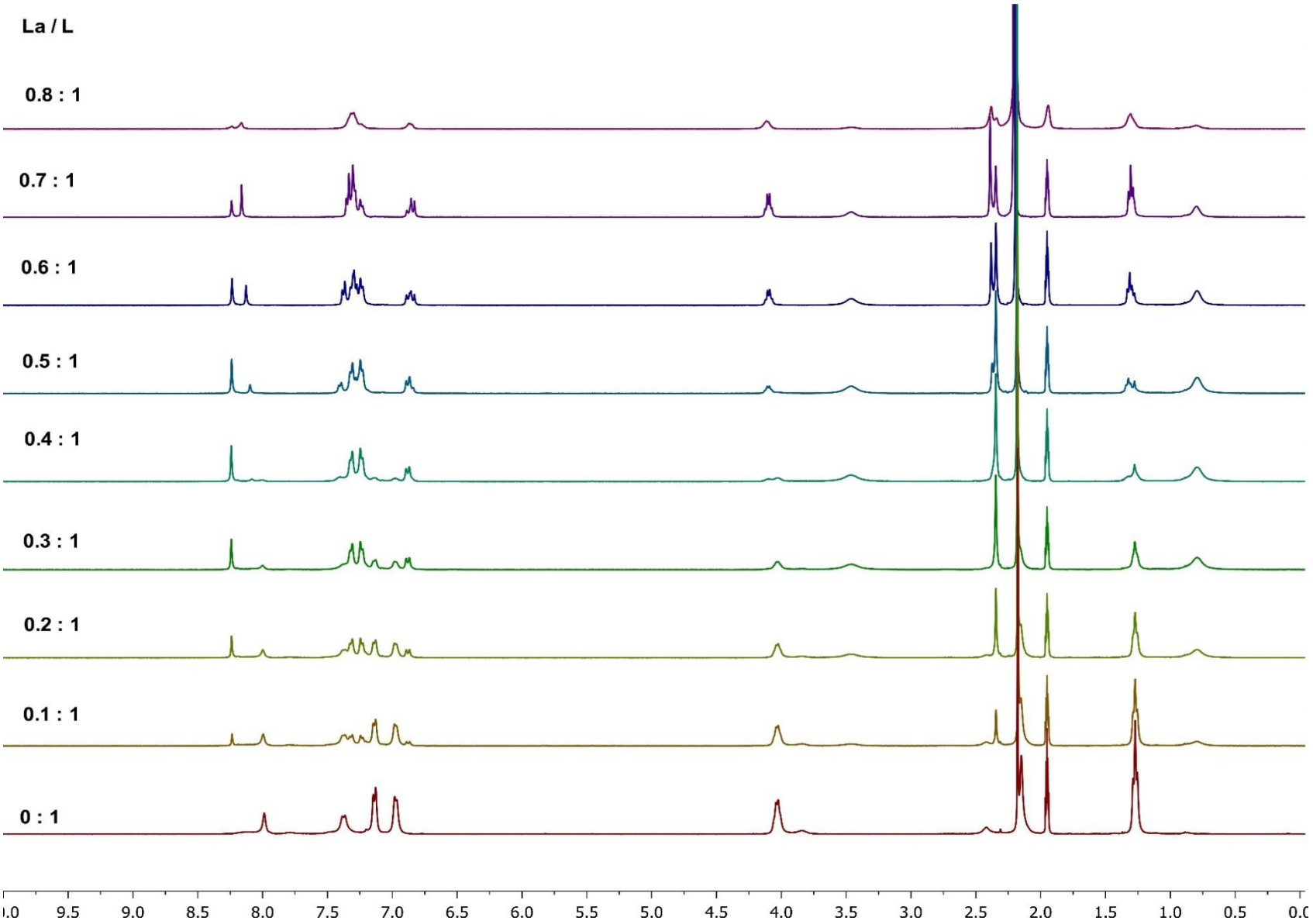

Figure S39. NMR titration of **1c** with $La(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^9-bis(p-tolyl)-4,7-difluoro-N^2,N^9-diethyl-1,10-phenanthroline-2,9-dicarboxamide (1c) with **neodymium trinitrate**

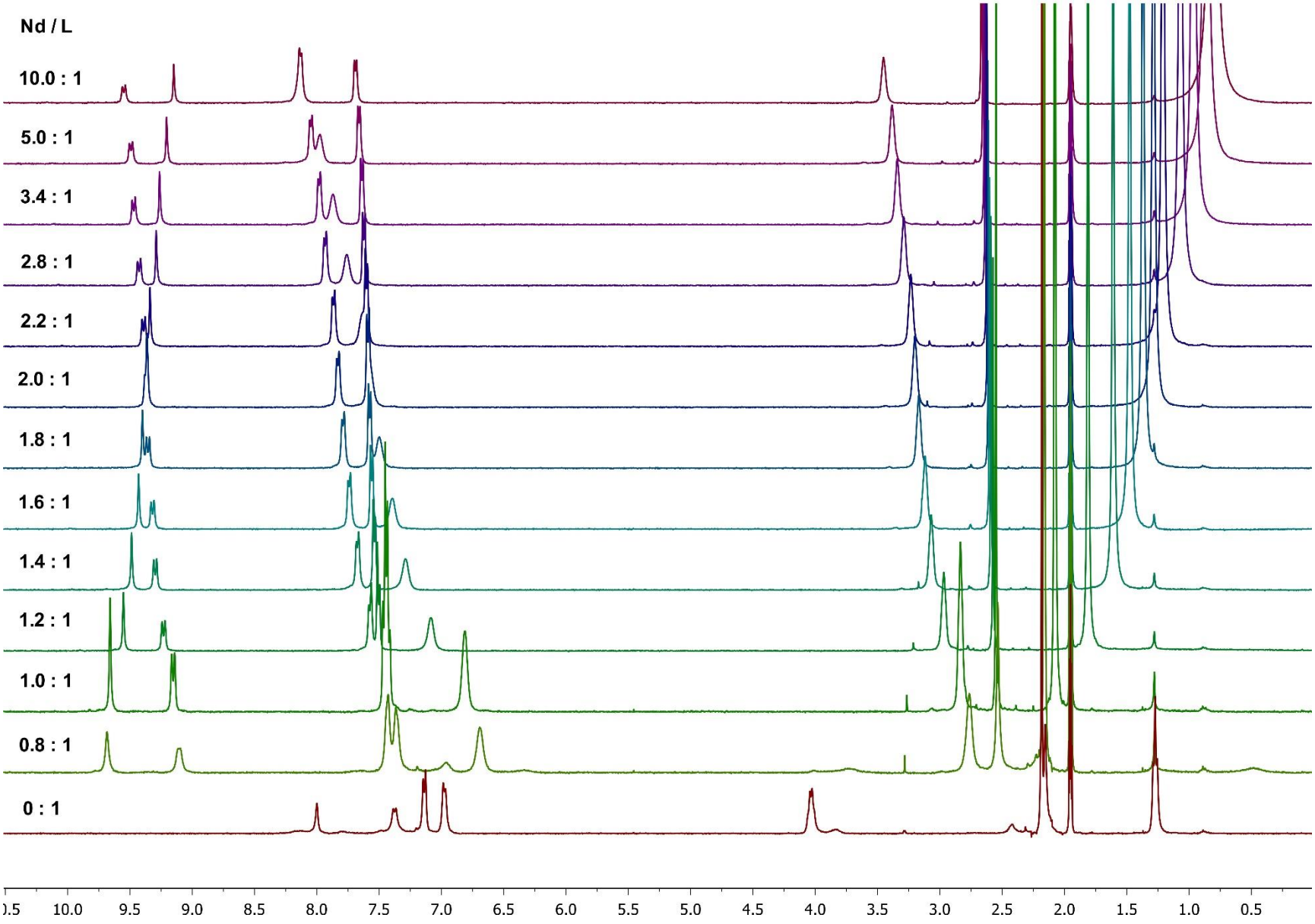

Figure S40. NMR titration of **1c** with $Nd(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^9-bis(p-tolyl)-4,7-difluoro-N^2,N^9-diethyl-1,10-phenanthroline-2,9-dicarboxamide (1c) with **europium trinitrate**

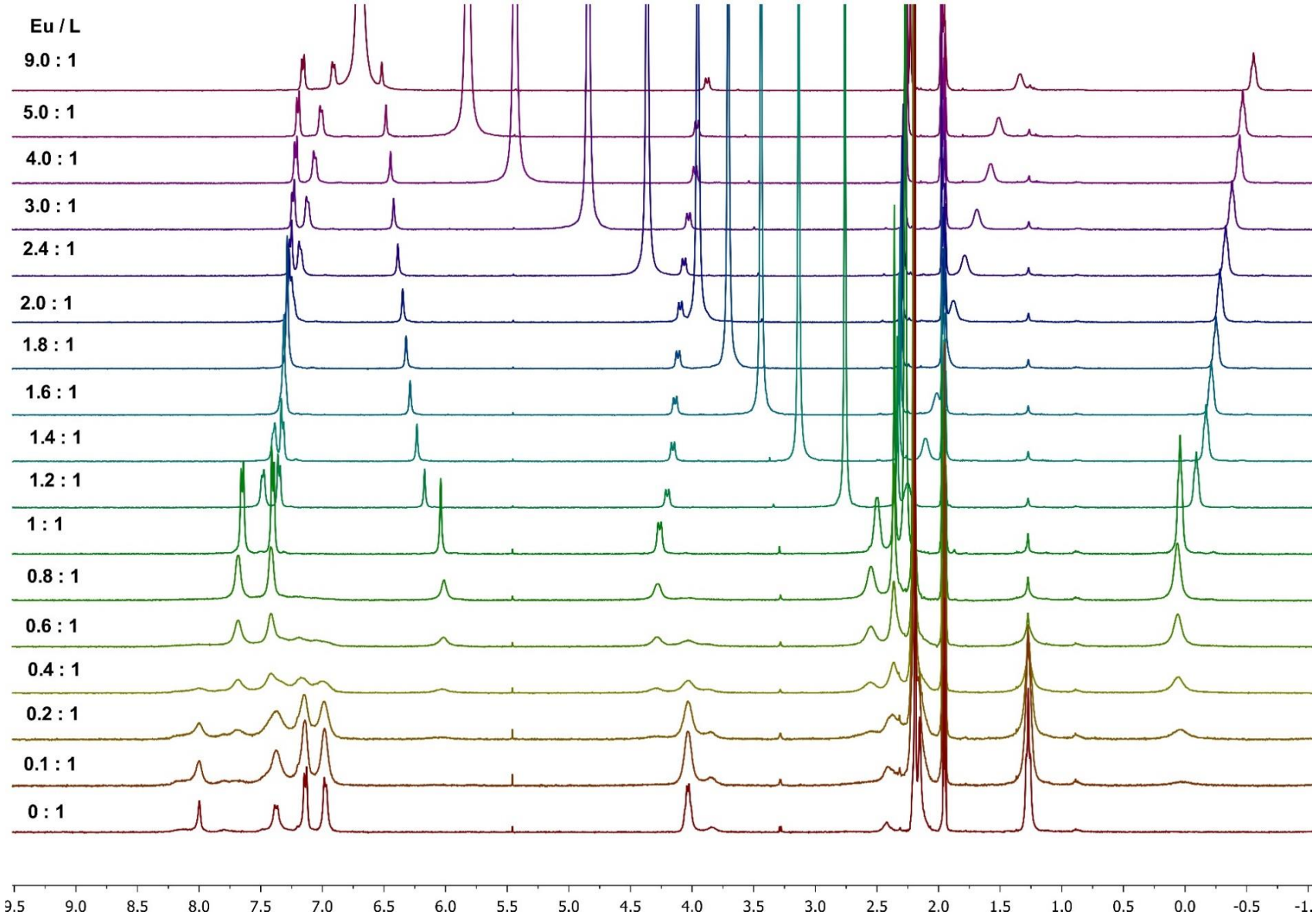

Figure S41. NMR titration of **1c** with $Eu(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^9-bis(p-tolyl)-4,7-difluoro-N^2,N^9-diethyl-1,10-phenanthroline-2,9-dicarboxamide (1c) with **lutetium trinitrate**

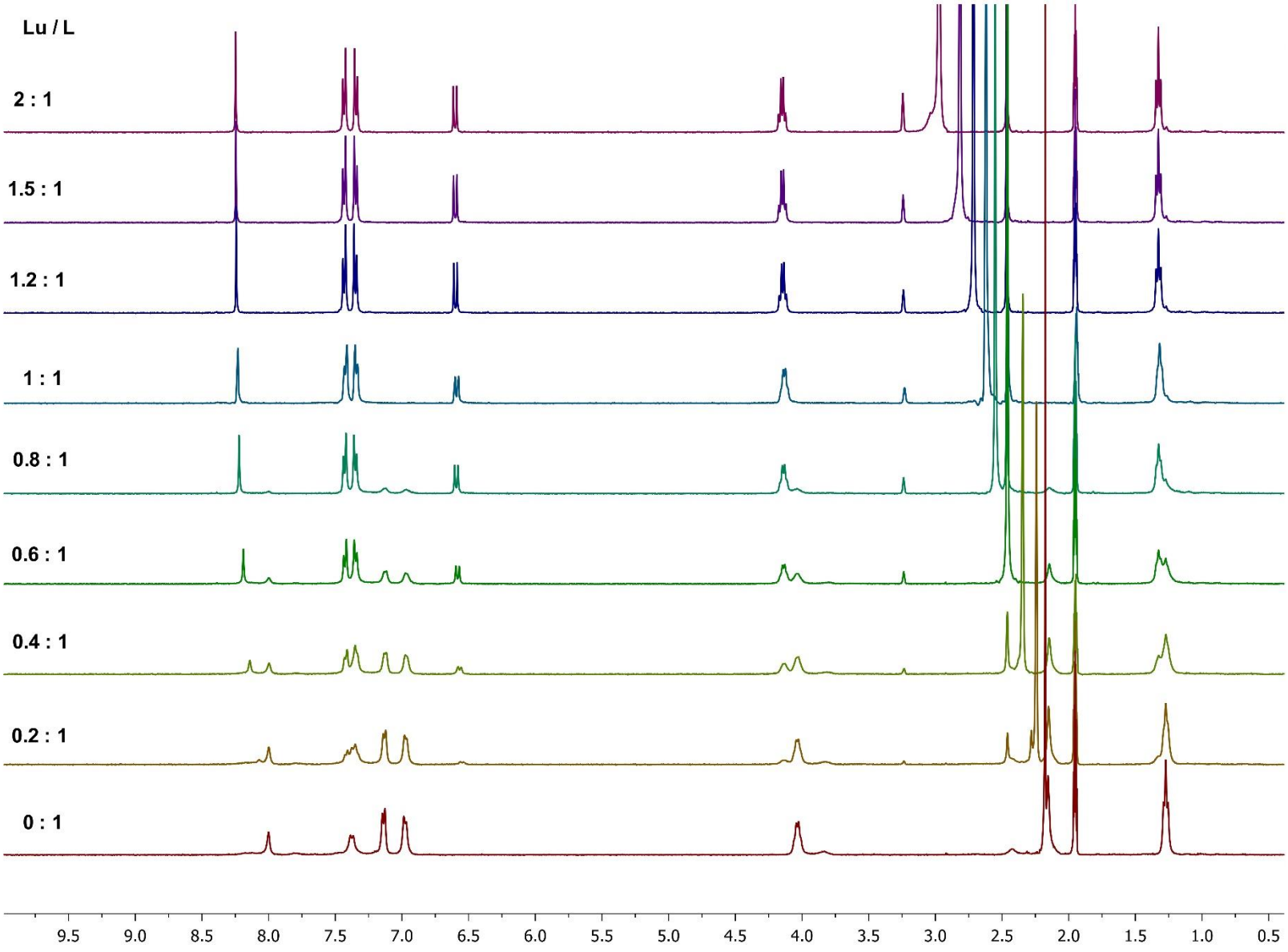

Figure S42. NMR titration of **1c** with $Lu(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^9-bis(p-tolyl)-N^2,N^9-diethyl-7-fluoro-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (2c) with **lanthanum trinitrate**

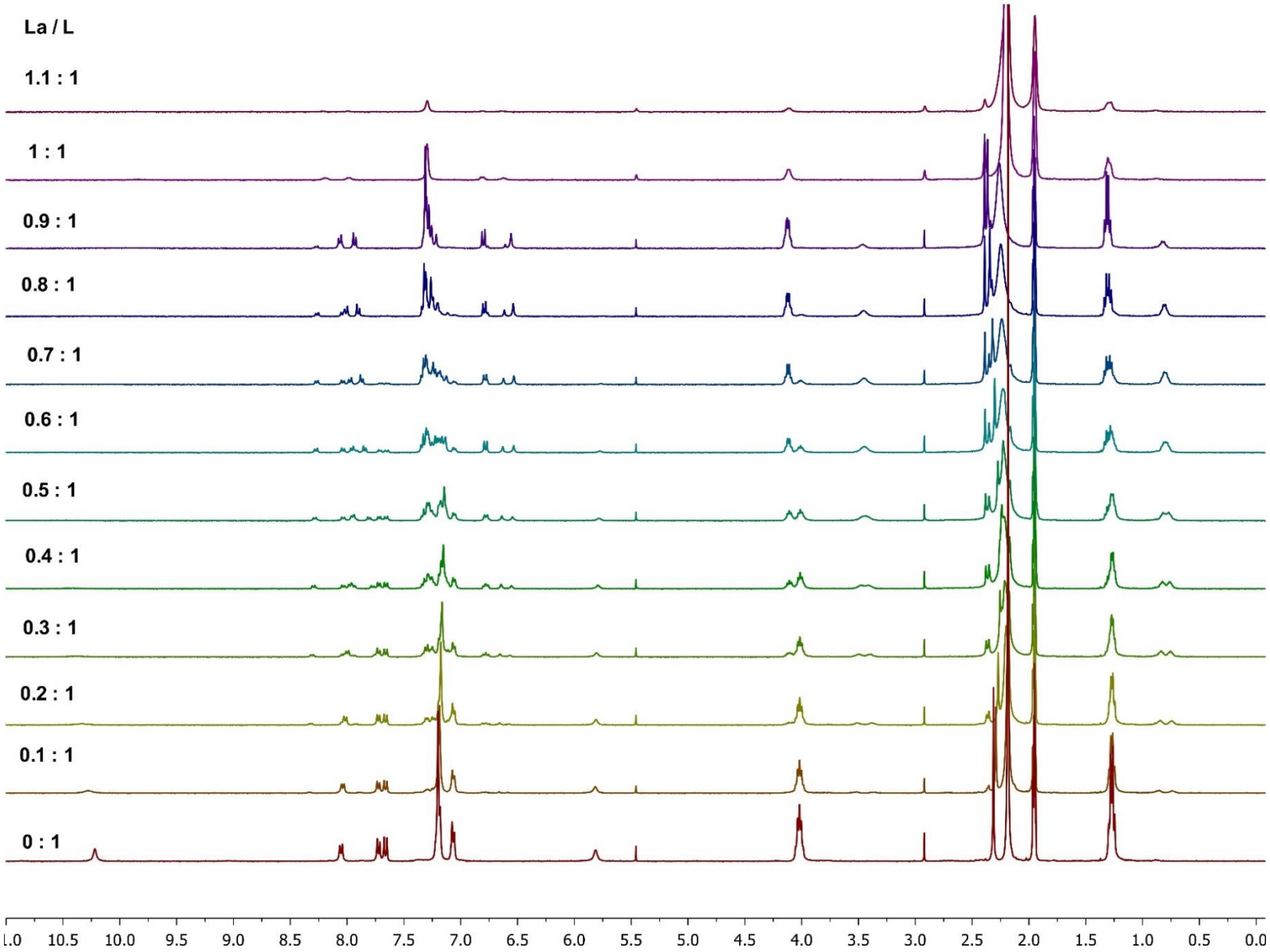

Figure S43. NMR titration of **2c** with $La(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^9-bis(p-tolyl)-N^2,N^9-diethyl-7-fluoro-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (2c) with **neodymium trinitrate**

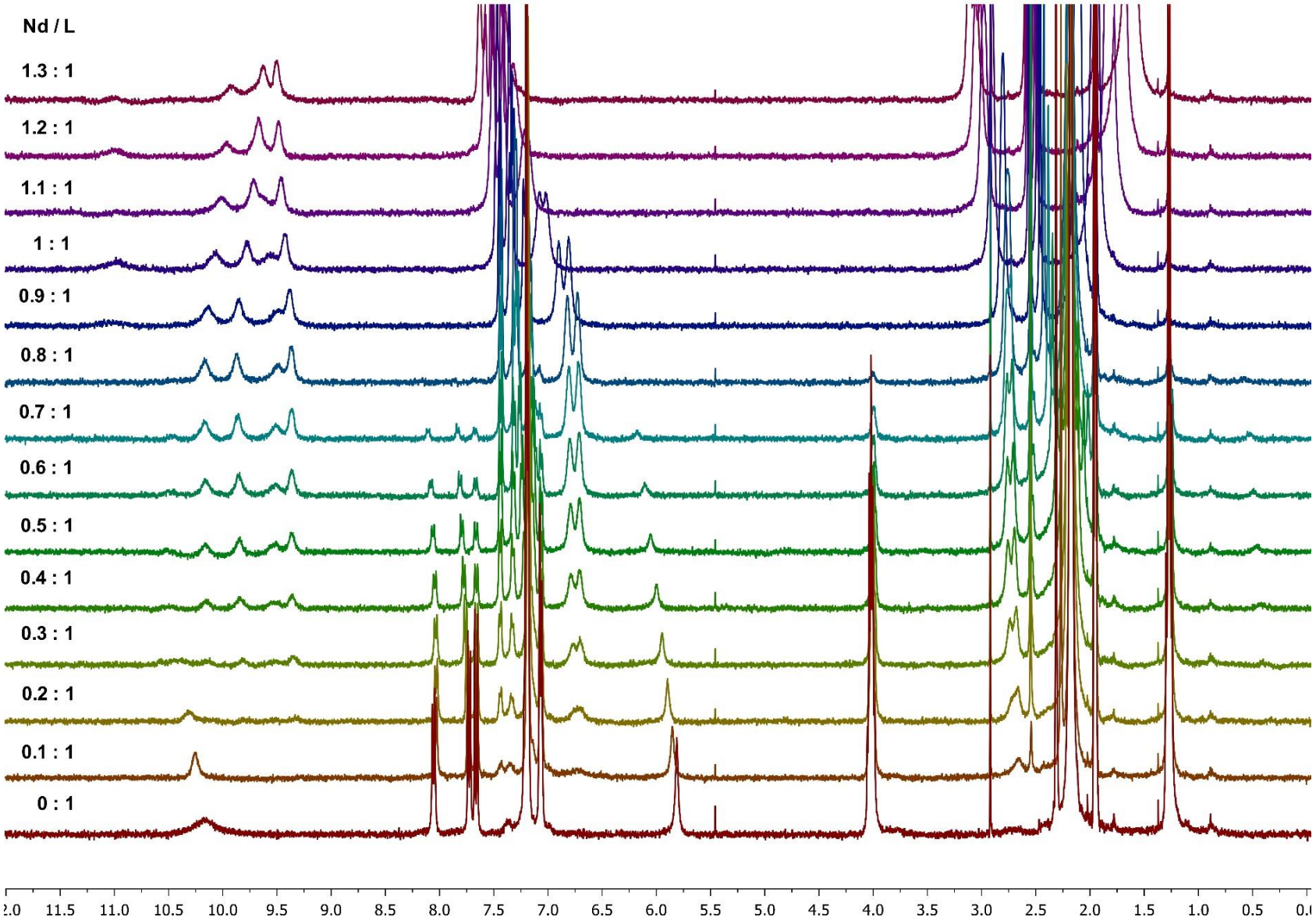

Figure S44. NMR titration of **2c** with $Nd(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^9-bis(p-tolyl)-N^2,N^9-diethyl-7-fluoro-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (2c) with **europium trinitrate**

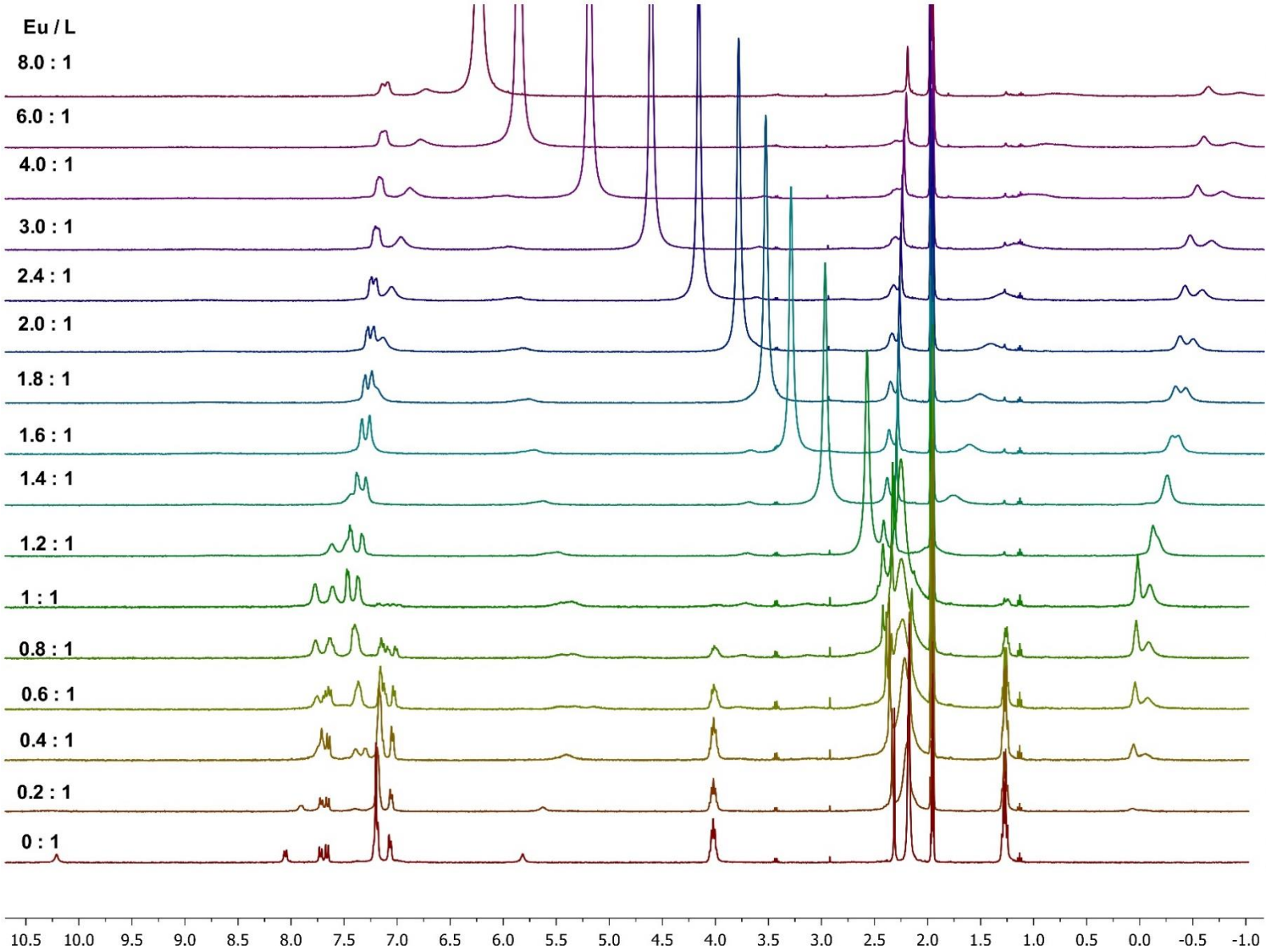

Figure S45. NMR titration of **2c** with $Eu(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^9-bis(p-tolyl)-N^2,N^9-diethyl-7-fluoro-4-oxo-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (2c) with **lutetium trinitrate**

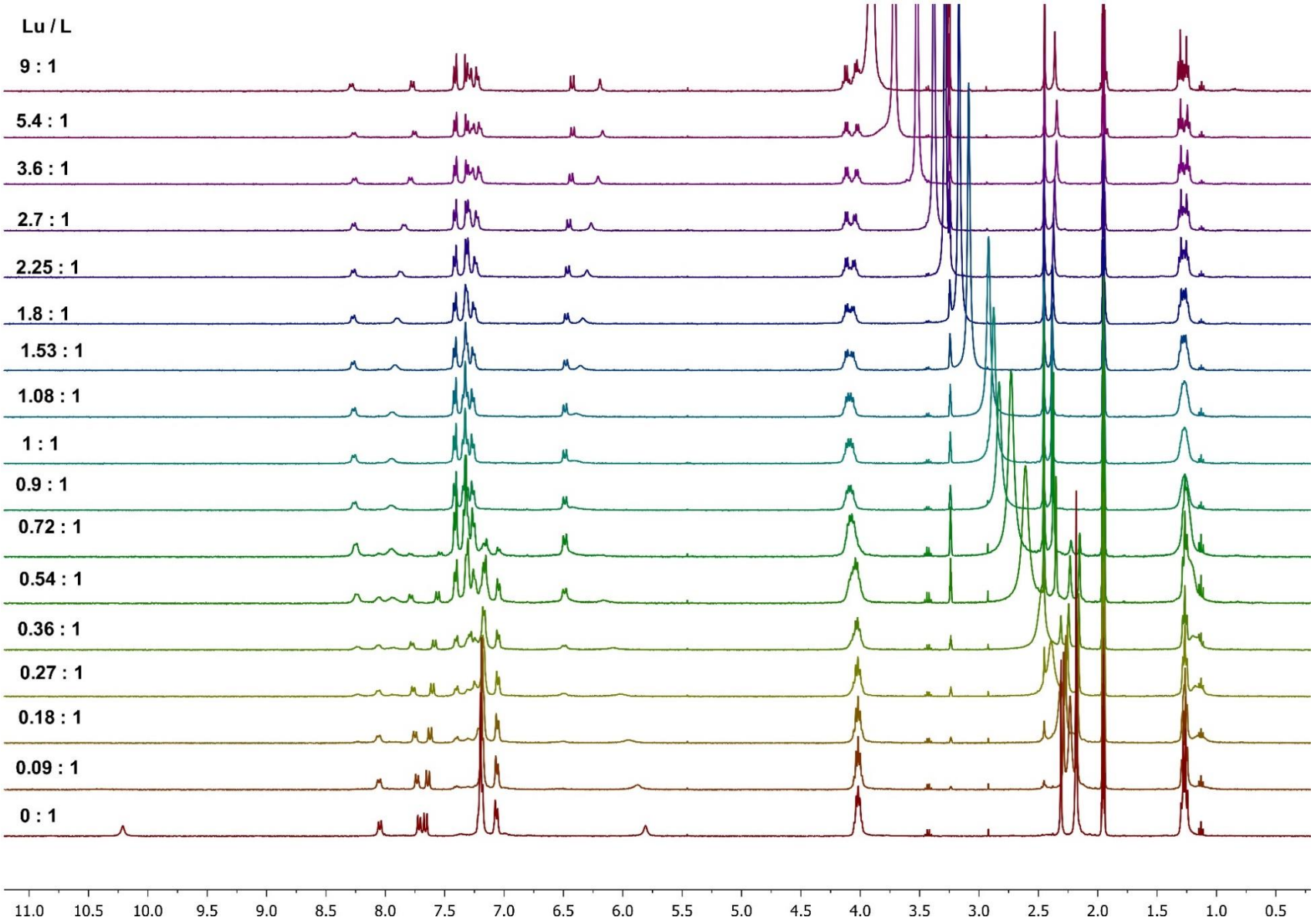

Figure S46. NMR titration of **2c** with $Lu(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^2,N^9,N^9-tetrabutyl-4,7-dihydroxy-1,10-phenanthroline-2,9-dicarboxamide (5a) with **neodymium trinitrate**

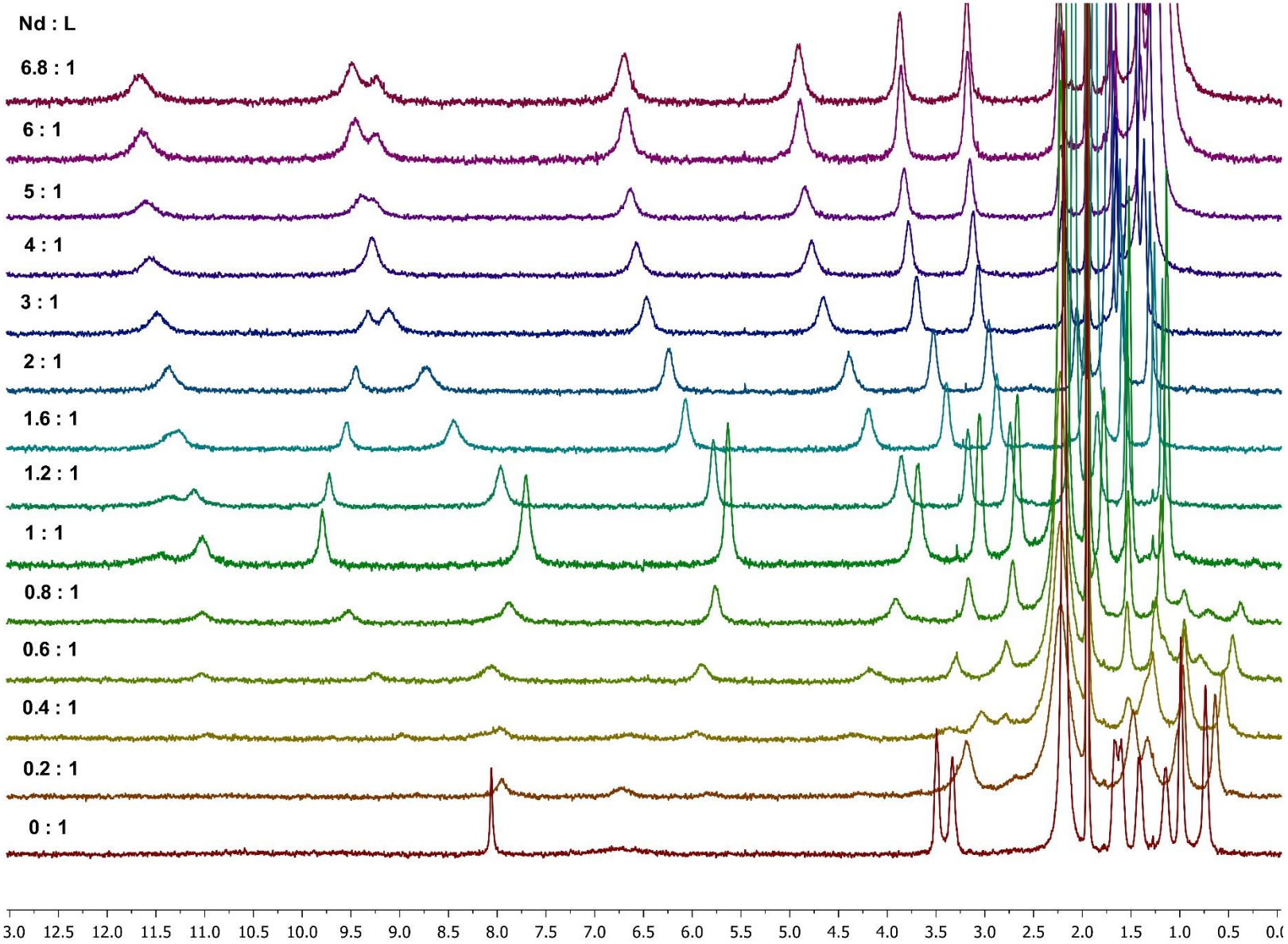

Figure S47. NMR titration of **5a** with $Nd(NO_3)_3.6H_2O$ in CD_3CN

N^2,N^2,N^9,N^9-tetrabutyl-4,7-dihydroxy-1,10-phenanthroline-2,9-dicarboxamide (5a) with **europium trinitrate**

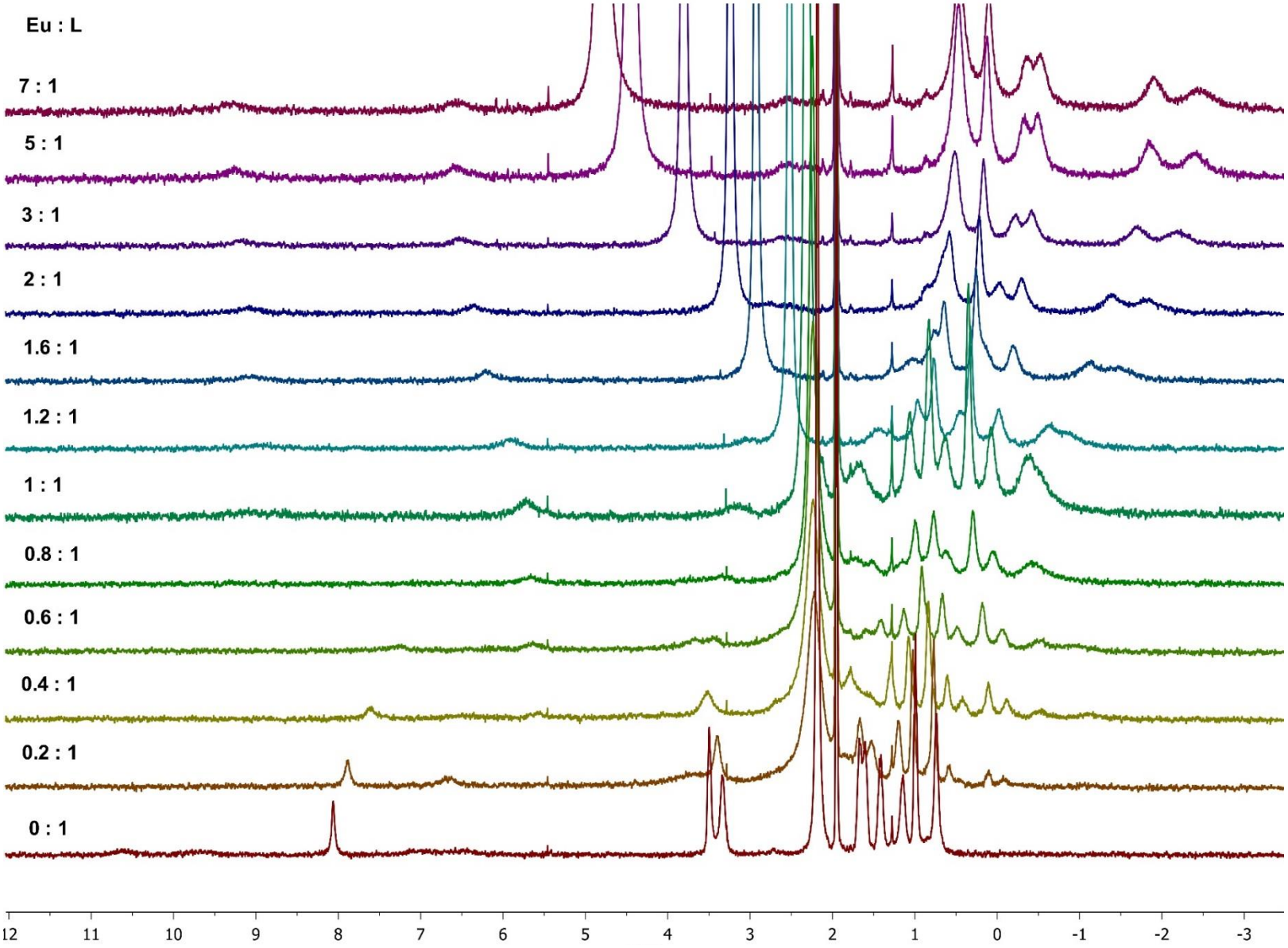

Figure S48. NMR titration of **5a** with $Eu(NO_3)_3{\cdot}6H_2O$ in CD_3CN

N^2,N^2,N^9,N^9-tetrabutyl-4,7-dihydroxy-1,10-phenanthroline-2,9-dicarboxamide (5a) with **lutetium trinitrate**

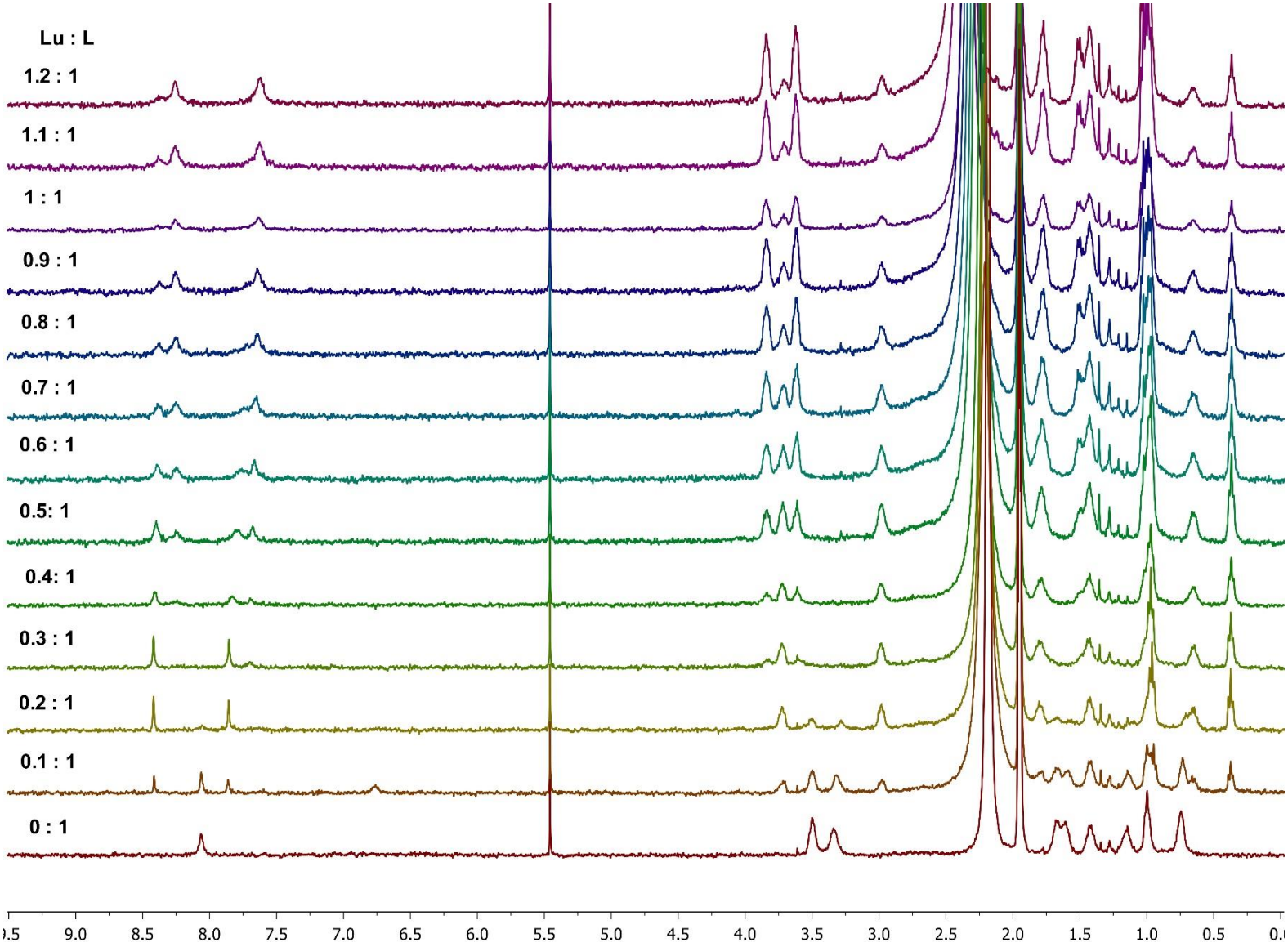

Figure S49. NMR titration of **5a** with $Lu(NO_3)_3.6H_2O$ in CD_3CN

N^2,N^9-diethyl-7-hydroxy-4-oxo-N^2,N^9-di-p-tolyl-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (5c) with **neodymium trinitrate**

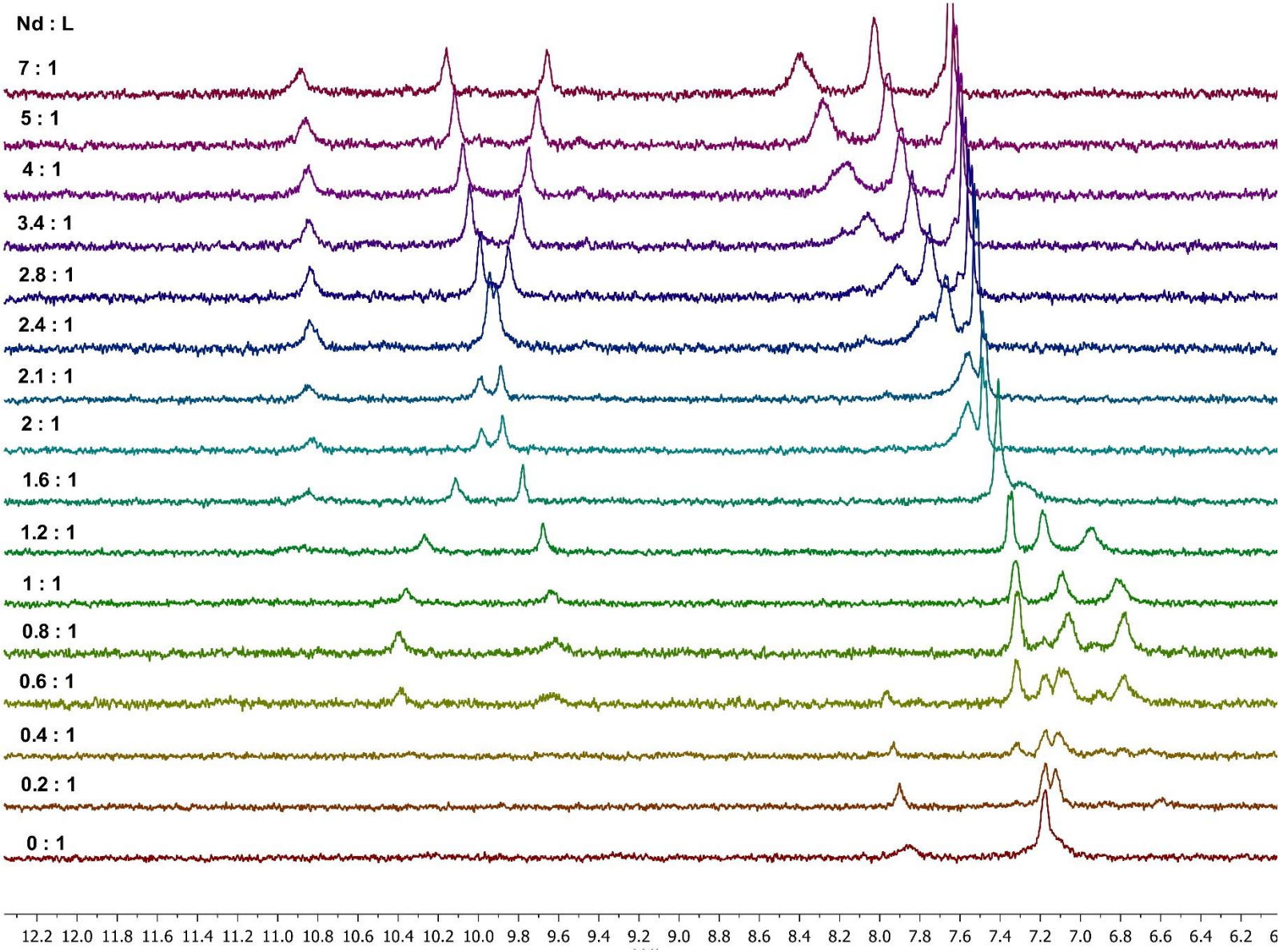

Figure S50. Fragmental view of NMR titration of **5c** with $Nd(NO_3)_3.6H_2O$ in CD_3CN

N^2,N^9-diethyl-7-hydroxy-4-oxo-N^2,N^9-di-p-tolyl-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (5c) with **europium trinitrate**

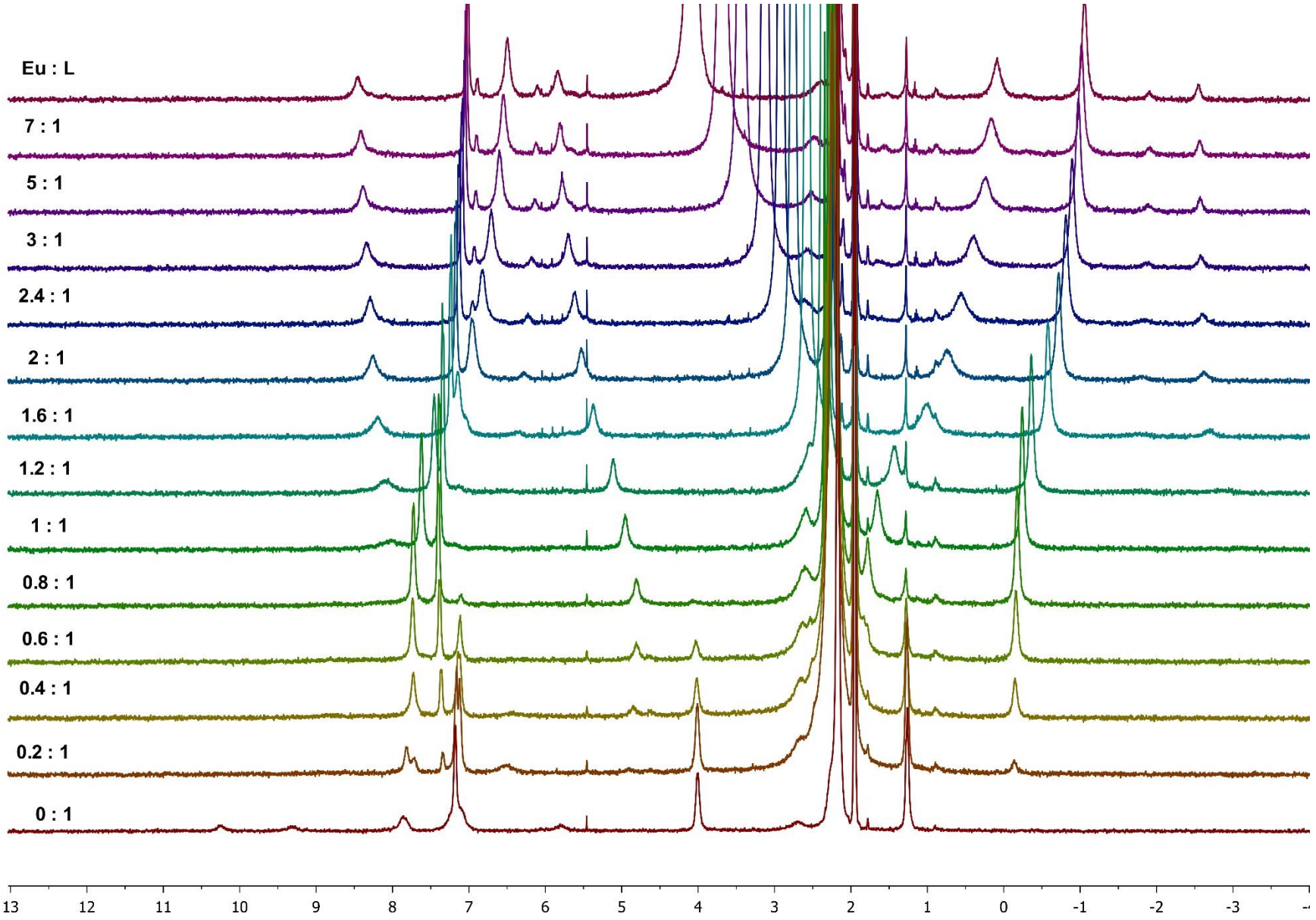

Figure S51. NMR titration of **5c** with $Eu(NO_3)_3.6H_2O$ in CD_3CN

N^2,N^9-diethyl-7-hydroxy-4-oxo-N^2,N^9-di-p-tolyl-1,4-dihydro-1,10-phenanthroline-2,9-dicarboxamide (5c) with **lutetium trinitrate**

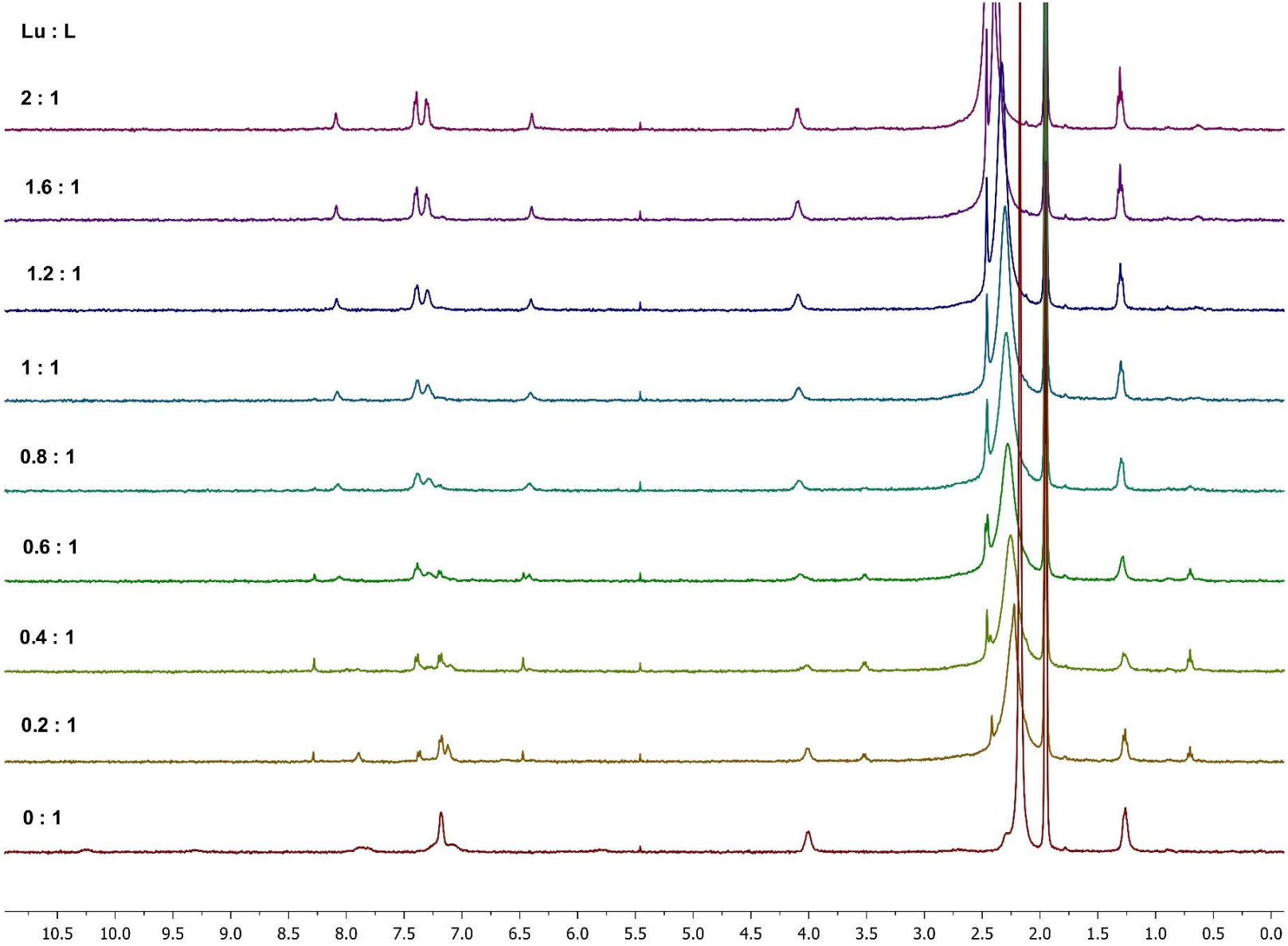

Figure S52. NMR titration of **5c** with $Lu(NO_3)_3{\cdot}6H_2O$ in CD_3CN

4. UV-vis titration

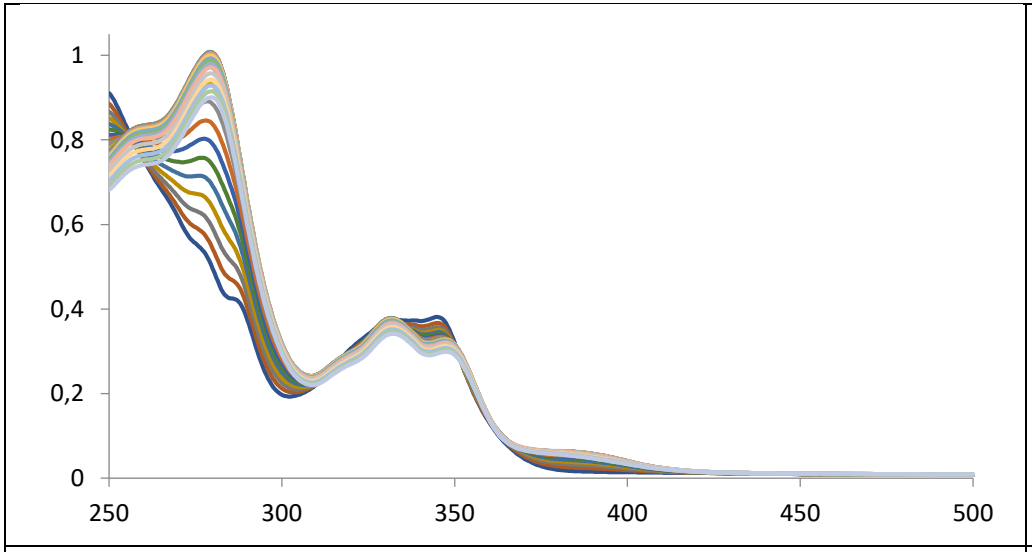

Figure S53. Spectrophotometric titration of **5a** with $La(NO_3)_3$ in CH_3CN solution

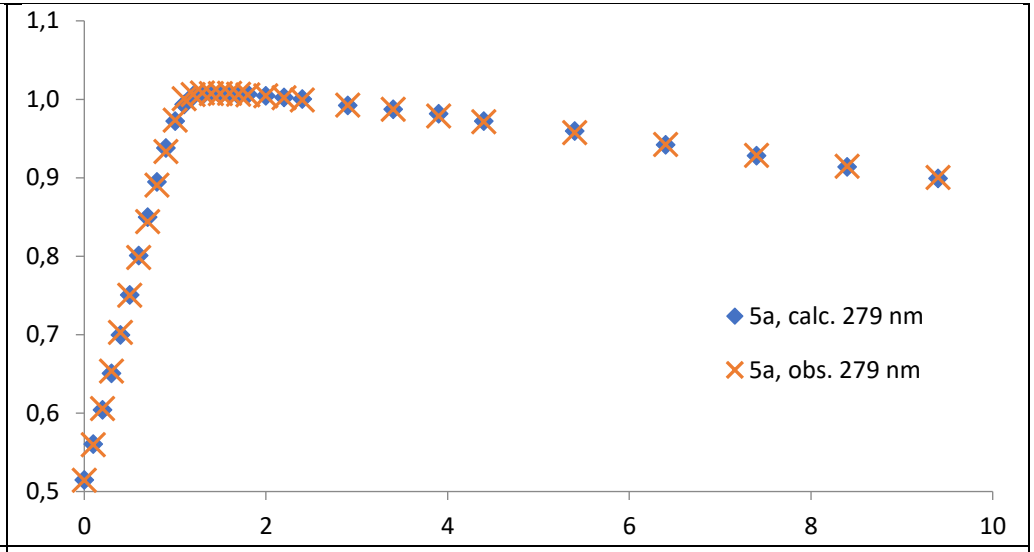

Figure S54. Titration curves of **5a** with La (III) at 279 nm, calculated *vs* observed

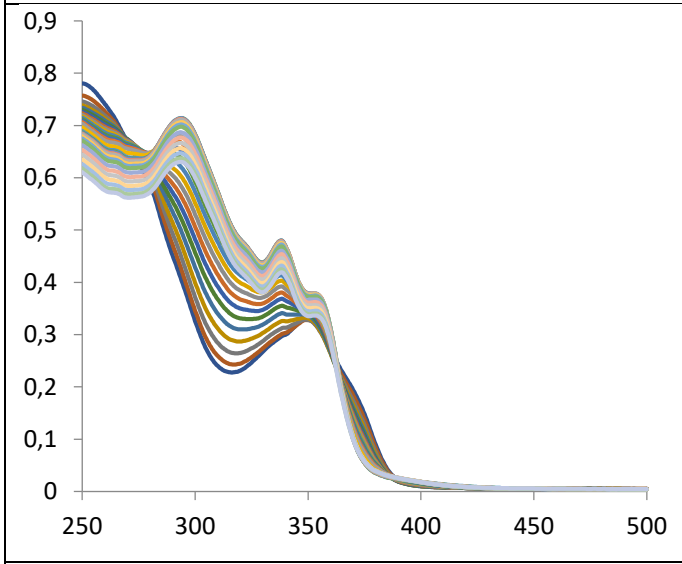

Figure S55. Spectrophotometric titration of **5c** with $La(NO_3)_3$ in CH_3CN solution

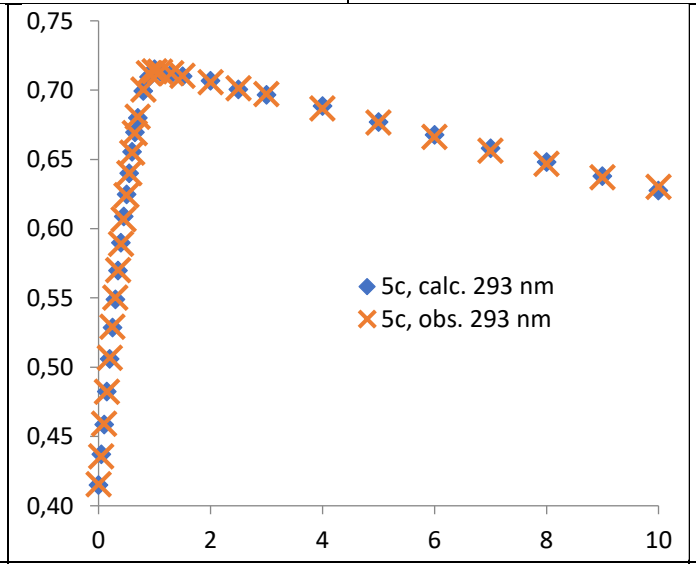

Figure S56. Titration curves of **5c** with La (III) at 293 nm, calculated *vs* observed

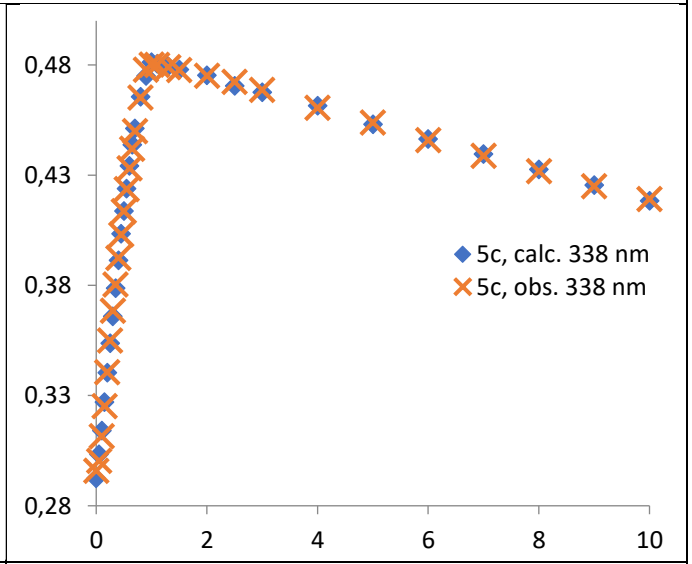

Figure S57. Titration curves of **5c** with La (III) at 338 nm, calculated *vs* observed

5. Theoretical computations

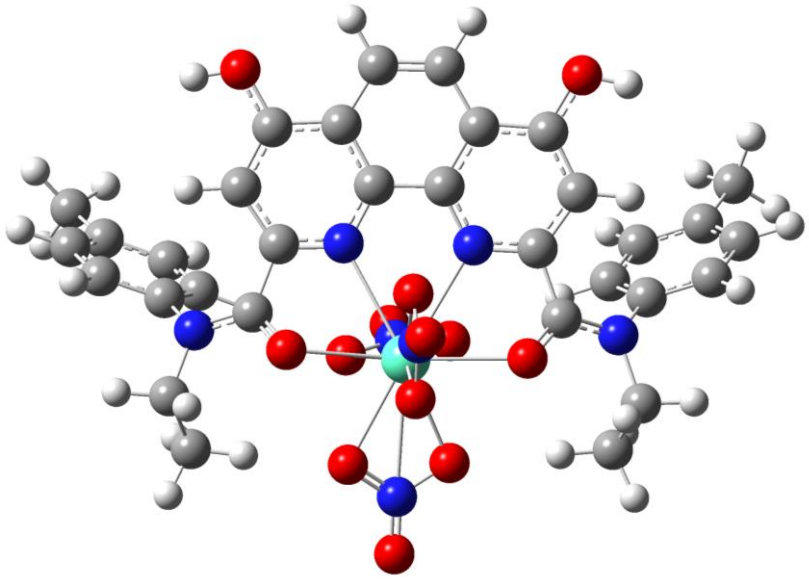

Figure S58. DFT optimized geometry of **5c•Eu(NO$_3$)$_3$**

Cartesian Coordinates

Eu	1.272052	2.073416	5.146673
O	3.529477	2.003227	4.047808
O	-1.188142	1.776782	5.595258
O	2.471614	-0.258486	8.297168
O	0.526920	1.638627	2.849710
O	0.907337	-0.084570	4.113131
N	5.454310	3.207699	4.154906
O	0.957777	0.940539	7.257781
N	2.060017	4.120033	3.531412
N	-2.907579	2.852090	6.619393
O	0.669357	3.907362	6.819370
N	2.128260	0.403694	7.339155
N	-0.507321	3.946161	4.236746
O	0.170867	-0.377002	2.069463
N	0.519430	0.358192	2.971858
O	2.069754	5.420024	7.560881
O	2.892535	0.627374	6.335876
N	1.847082	4.387557	6.947366
O	2.783868	3.719291	6.378643
C	-3.473902	4.112307	7.017833

C	4.140003	3.071028	3.864000
C	7.873506	6.035940	3.904033
H	8.780889	6.280768	3.357144
C	-0.192670	4.851857	3.291513
C	3.348850	4.191161	3.222878
C	-4.864765	4.278456	7.032649
H	-5.508396	3.458774	6.724833
C	1.199779	4.956806	2.920849
C	7.242493	4.816118	3.667636
H	7.649375	4.118683	2.940069
C	6.179603	2.010085	4.658582
H	7.210851	2.102318	4.304599
H	5.724127	1.1419370	4.180727
C	-1.766972	3.851582	4.635563
C	0.600872	6.734925	1.323822
H	0.920606	7.448857	0.572553
C	2.975001	5.956769	1.634056
C	-0.718244	6.628118	1.666755
H	-1.464609	7.254583	1.191968
C	-2.805282	4.614031	4.069055
H	-3.827441	4.495651	4.411823
C	6.074680	4.487964	4.366342
C	3.857313	5.099933	2.278291
H	4.918508	5.125928	2.054503
C	-3.085396	1.697068	7.539160
H	-2.894127	0.795392	6.955176
H	-4.137928	1.701244	7.837966
C	-1.142488	5.688646	2.660998
C	7.358931	6.950613	4.835677
C	1.588510	5.904188	1.944874
C	-5.413845	5.496446	7.426190
H	-6.495088	5.616847	7.430272
C	-1.943413	2.761716	5.672119
C	6.188766	6.602886	5.523338
H	5.773057	7.290786	6.255719

C	5.550429	5.380671	5.308785
H	4.661014	5.111903	5.874026
C	-3.209078	6.380138	7.802874
H	-2.555000	7.192271	8.109603
C	-2.641974	5.161990	7.421703
H	-1.563086	5.023424	7.434512
C	-2.494064	5.528457	3.072558
C	-4.596148	6.571419	7.812074
C	8.068604	8.254403	5.114543
H	7.375602	9.016100	5.483720
H	8.558689	8.645818	4.217399
C	-2.167720	1.751518	8.760883
H	-1.118866	1.661800	8.468587
H	-2.4082810	0.915634	9.426670
H	-2.309440	2.681546	9.321076
C	-5.205401	7.889610	8.229303
H	-5.862098	7.766860	9.098557
H	-5.814875	8.320121	7.425403
C	6.132875	1.870458	6.179870
H	6.542827	2.756695	6.674120
H	6.736951	1.007031	6.478003
H	5.110184	1.703094	6.523433
H	8.846151	8.122682	5.877726
H	-4.435473	8.619807	8.492191
O	3.361470	6.854769	0.700206
H	4.318930	6.806086	0.571439
O	-3.418829	6.302932	2.460672
H	-4.295250	6.118980	2.826027