Supramolecular motifs for the self-assembly of monosubstituted pillar[5]arenes with an amide fragment: from nanoparticles to supramolecular polymers

Nazarova A. A.[a], *Padnya P. L.*[a]., *Gilyazeva A. I..*[a], *Khannanov A. A.*[a], *Evtugyn V. G..*[a], *Kutyreva M. P.*[a], *Klochkov V. V.*[b], *Stoikov I. I.*[a,b]

[a]A.M.Butlerov Chemical Institute, Kazan Federal University, 420008 Kremlevskaya, 18, Kazan, Russian Federation. Fax:+7 843 275 2253; Tel: +7 843 233 7462; E-mail: Ivan.Stoikov@mail.ru

[b]Institute of Physics, Federal University, 420008 Kremlevskaya, 18, Kazan, Russian Federation. Tel: +7 843 233 7012; E-mail: Vladimir.Klochkov@kpfu.ru

*Corresponding author. Tel.: +7-843-2337462; fax: +7-843-2752253; e-mail: Ivan.Stoikov@mail.ru

Electronic Supplementary Information (71 pages)

Fig. S1. ^{1}H NMR spectrum of decamethoxypillar[5]arene (1), $CDCl_3$, 298 K, 400 MHz.

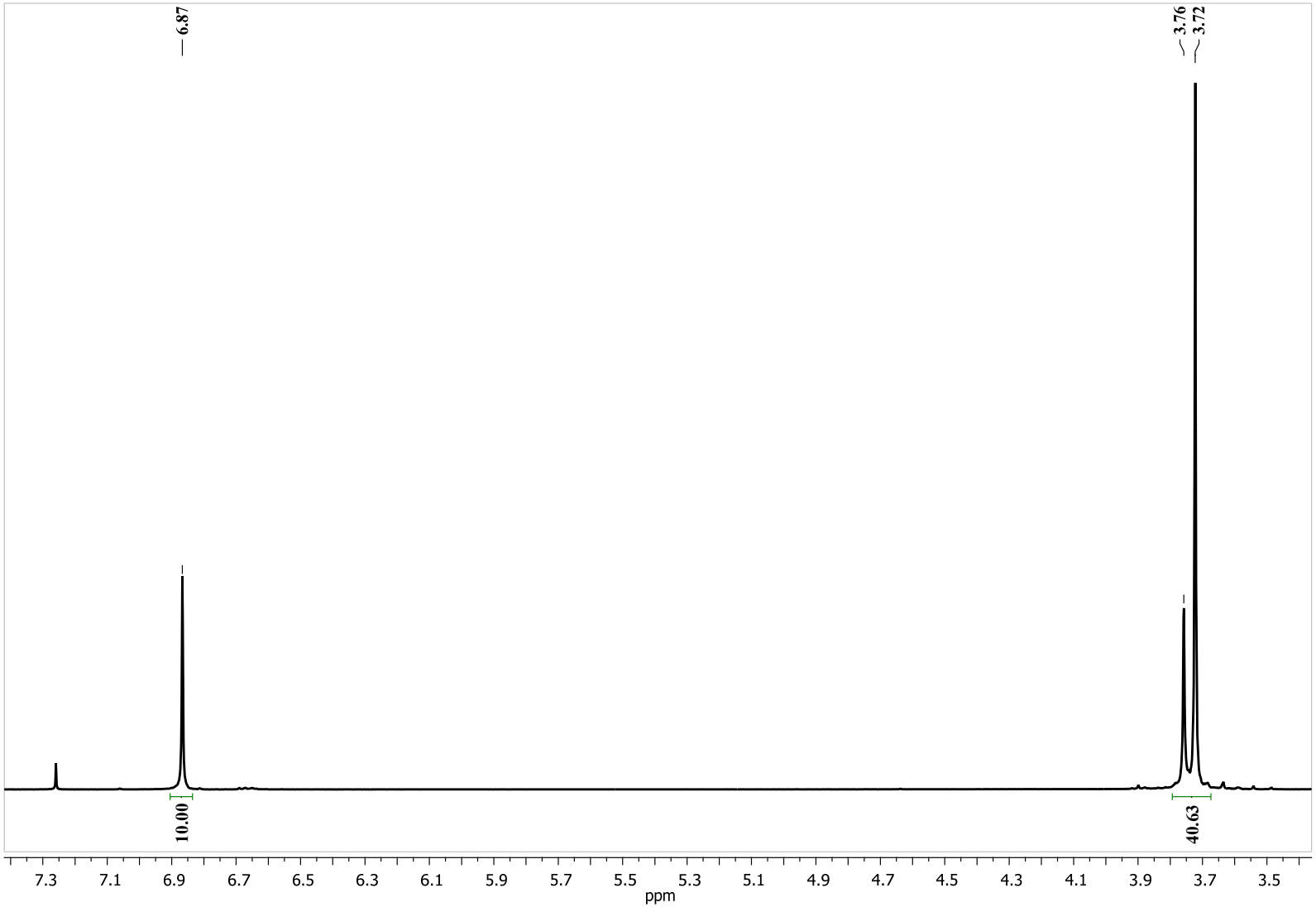

Fig. S2. ^{1}H NMR spectrum of 4-hydroxy-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (2), $CDCl_3$, 298 K, 400 MHz.

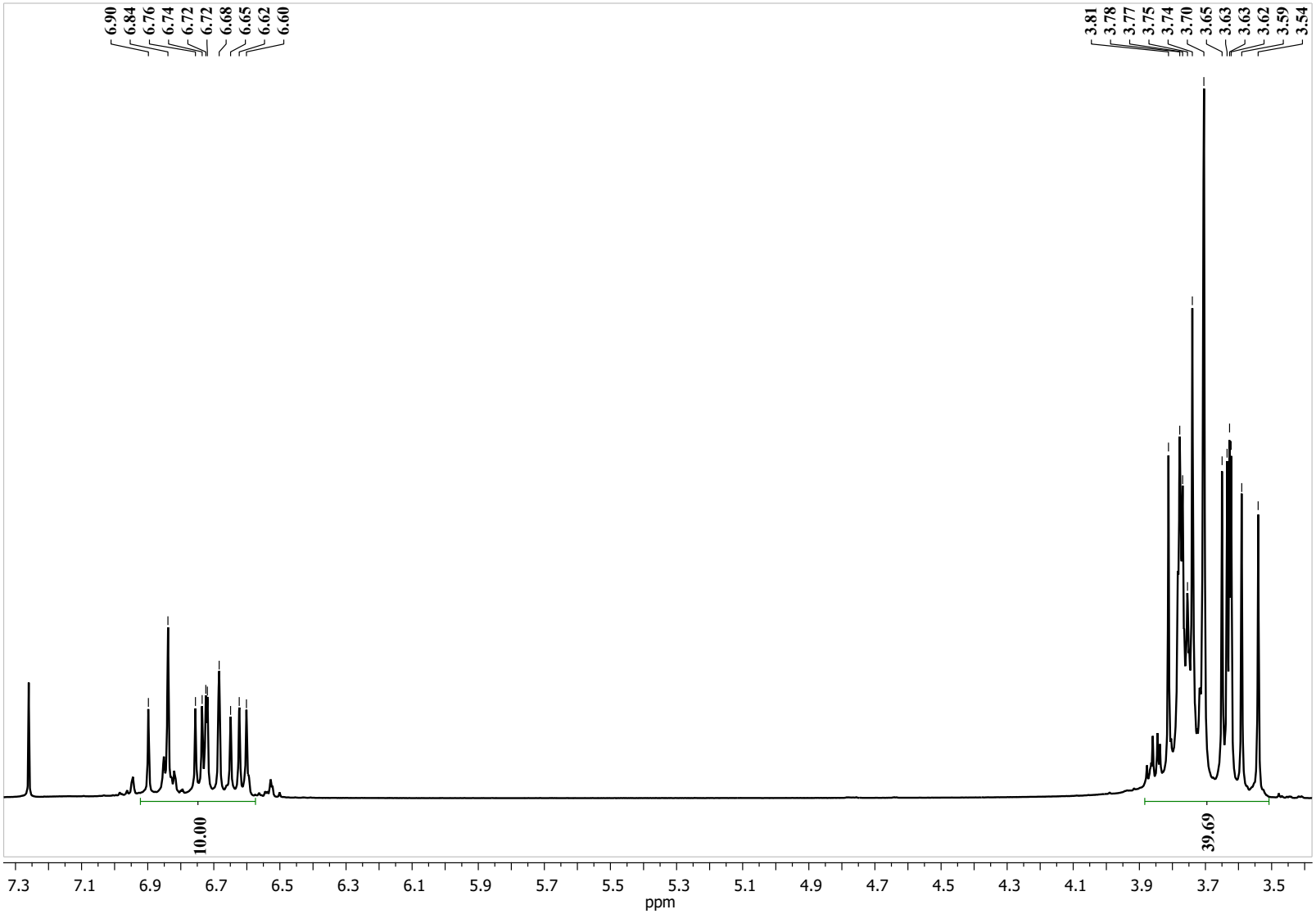

Fig. S3. ^{1}H NMR spectrum of 4-(ethoxycarbonylmethoxy)-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (3), $CDCl_3$, 298 K, 400 MHz.

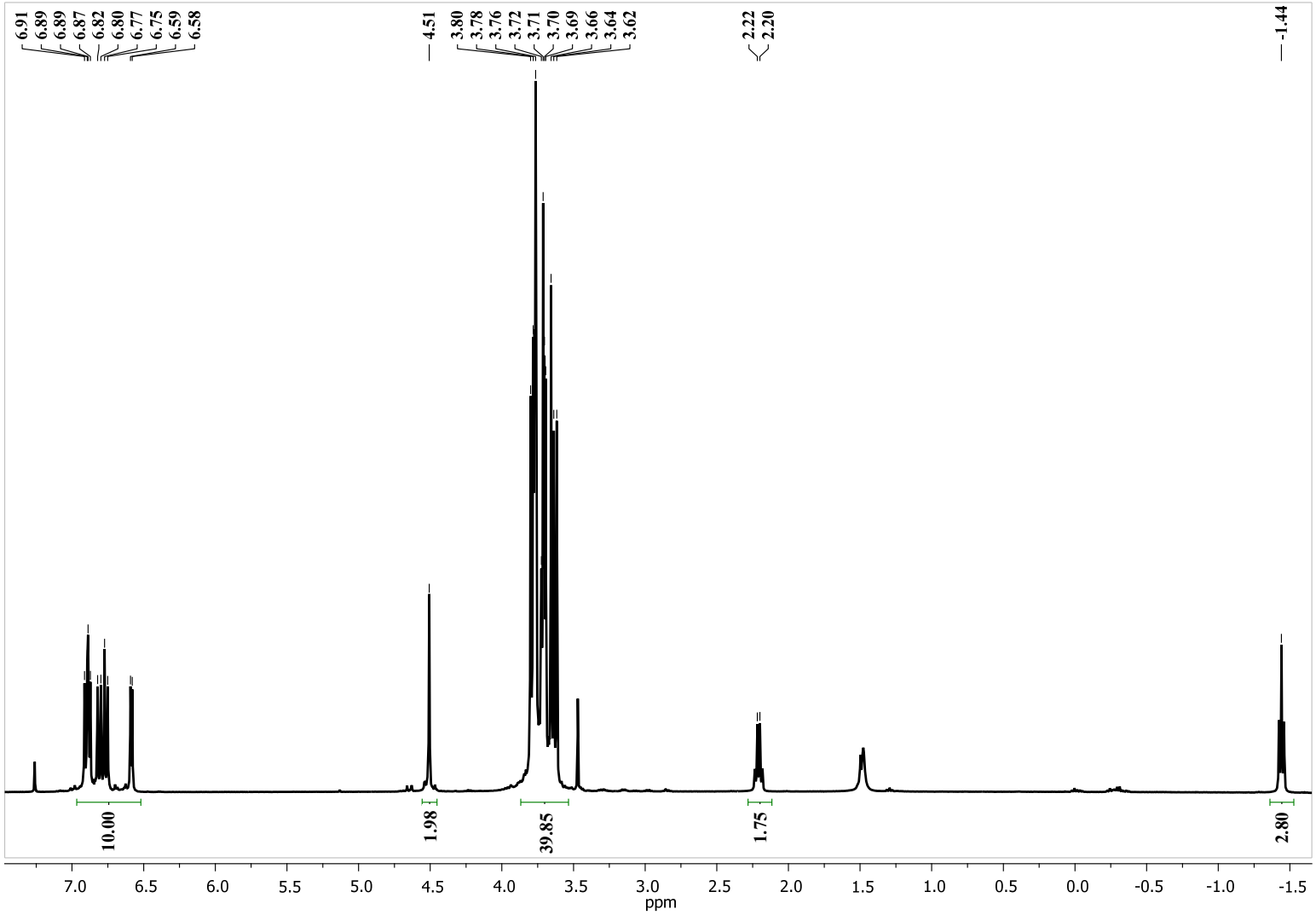

Fig. S4. ^{1}H NMR spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), $CDCl_3$, 298 K, 400 MHz.

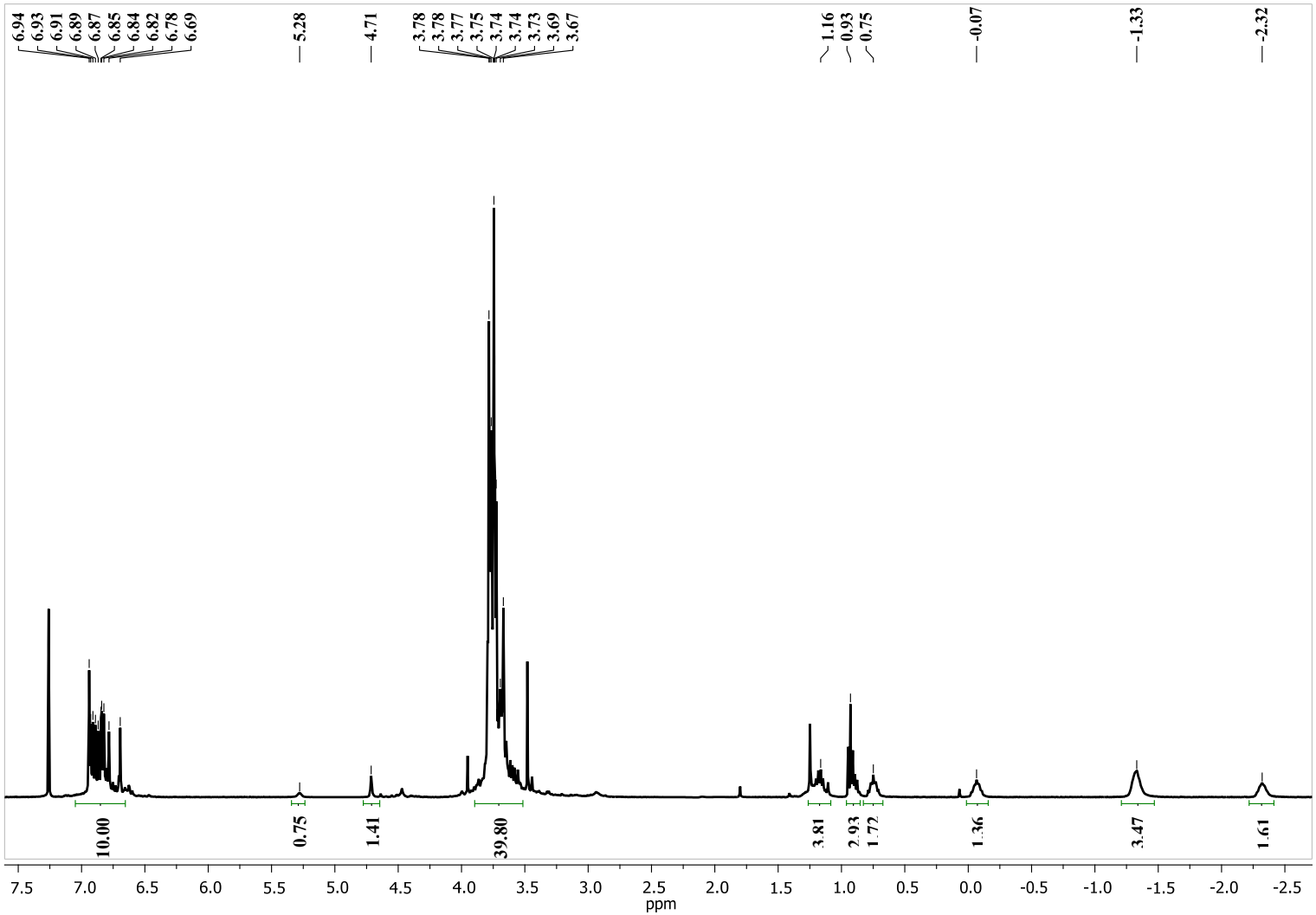

Fig. S5. ^{1}H NMR spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), DMSO-d_6, 298 K, 400 MHz.

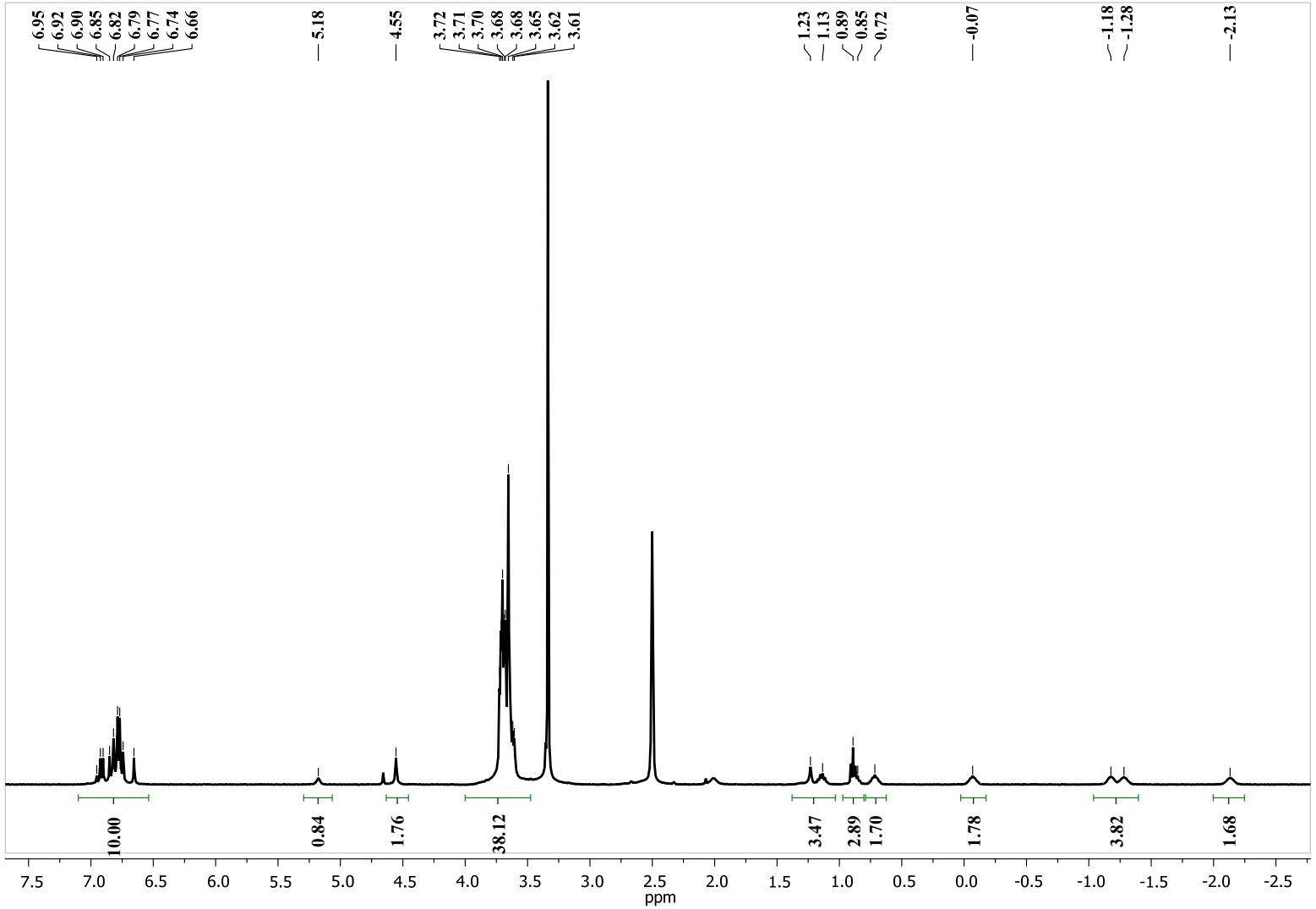

Fig. S6. ^{1}H NMR spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), $CDCl_3$, 298 K, 400 MHz.

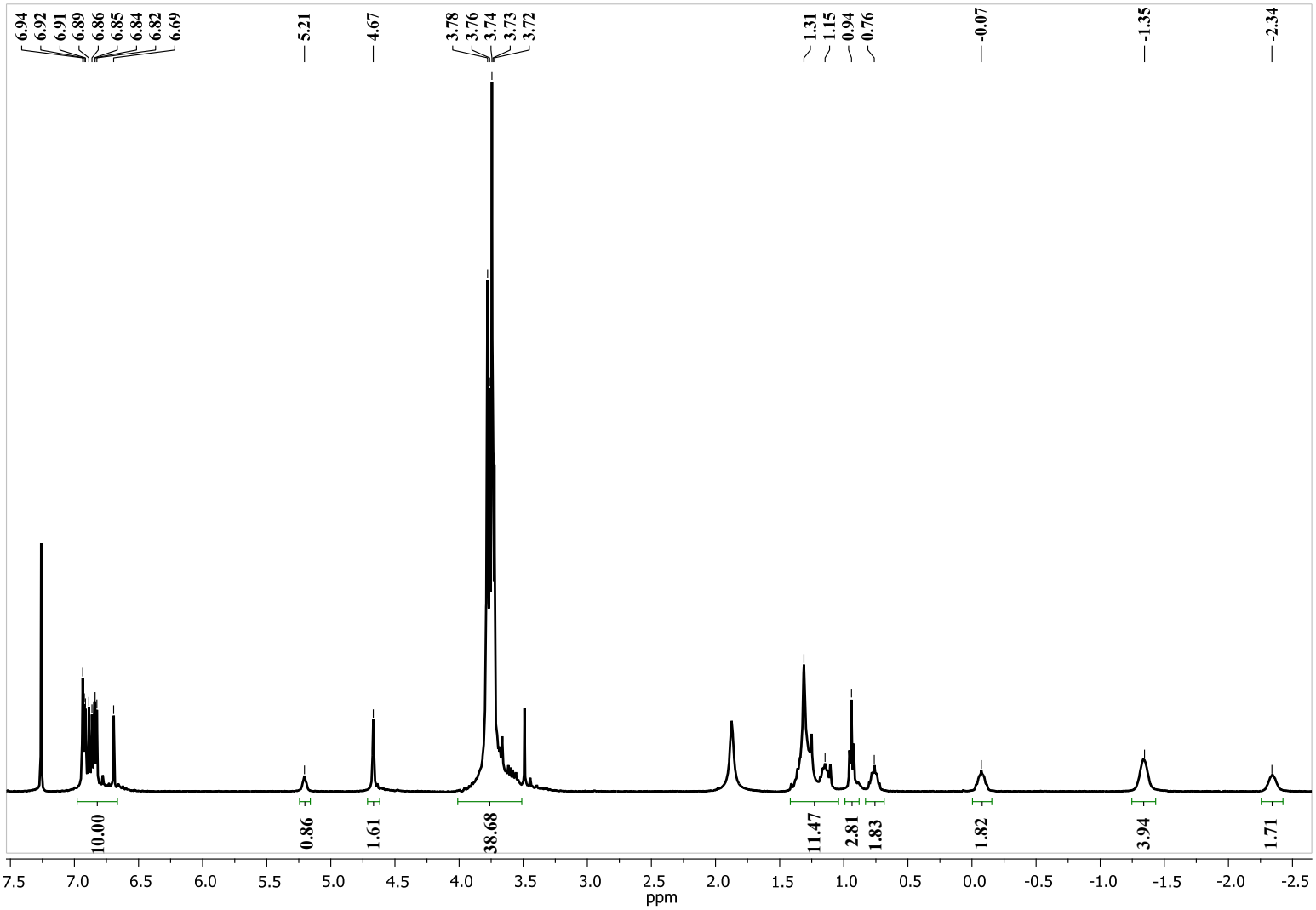

Fig. S7. ^{1}H NMR spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), DMSO-d_6, 298 K, 400 MHz.

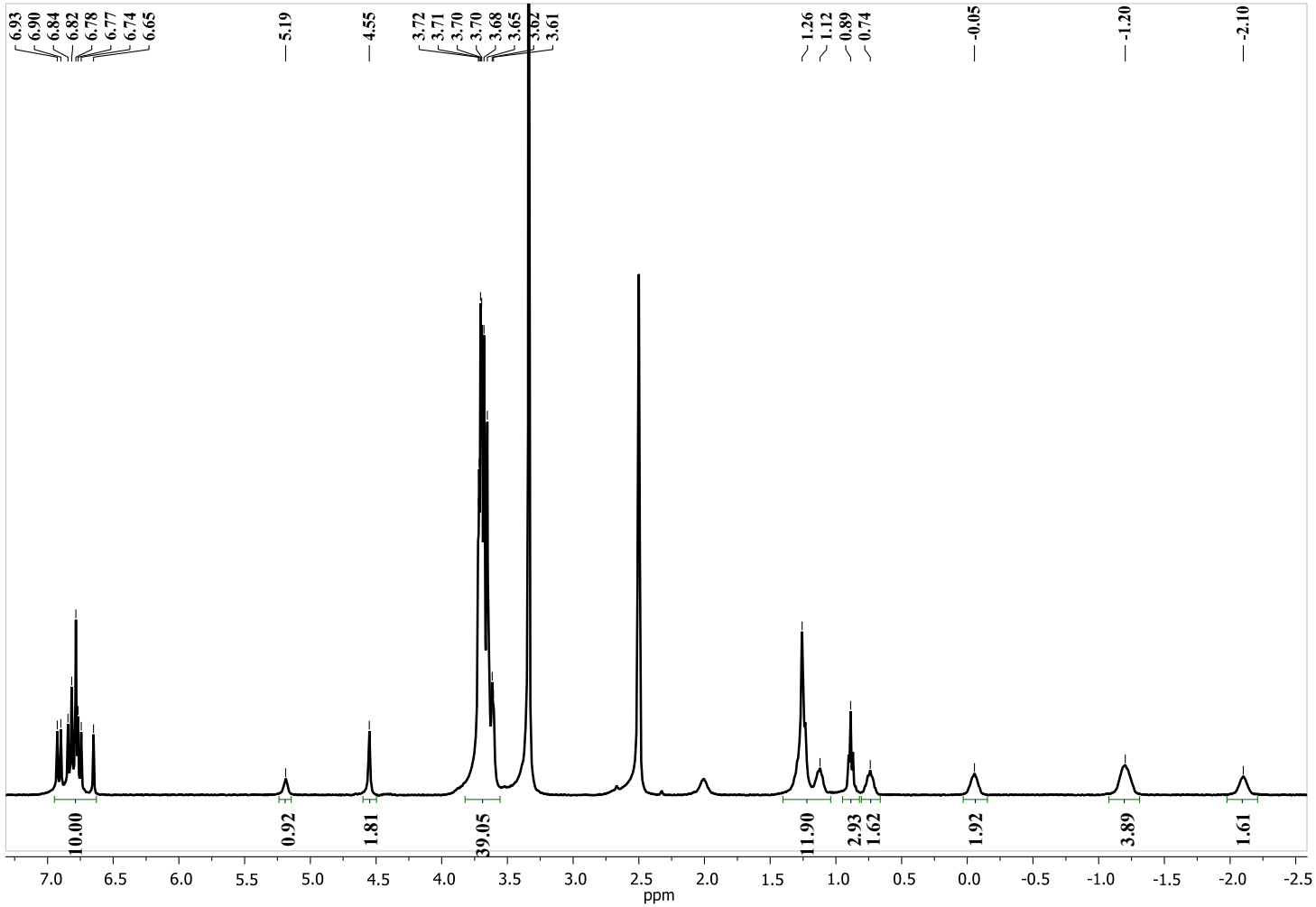

Fig. S8. ^{1}H NMR spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), $CDCl_3$, 298 K, 400 MHz.

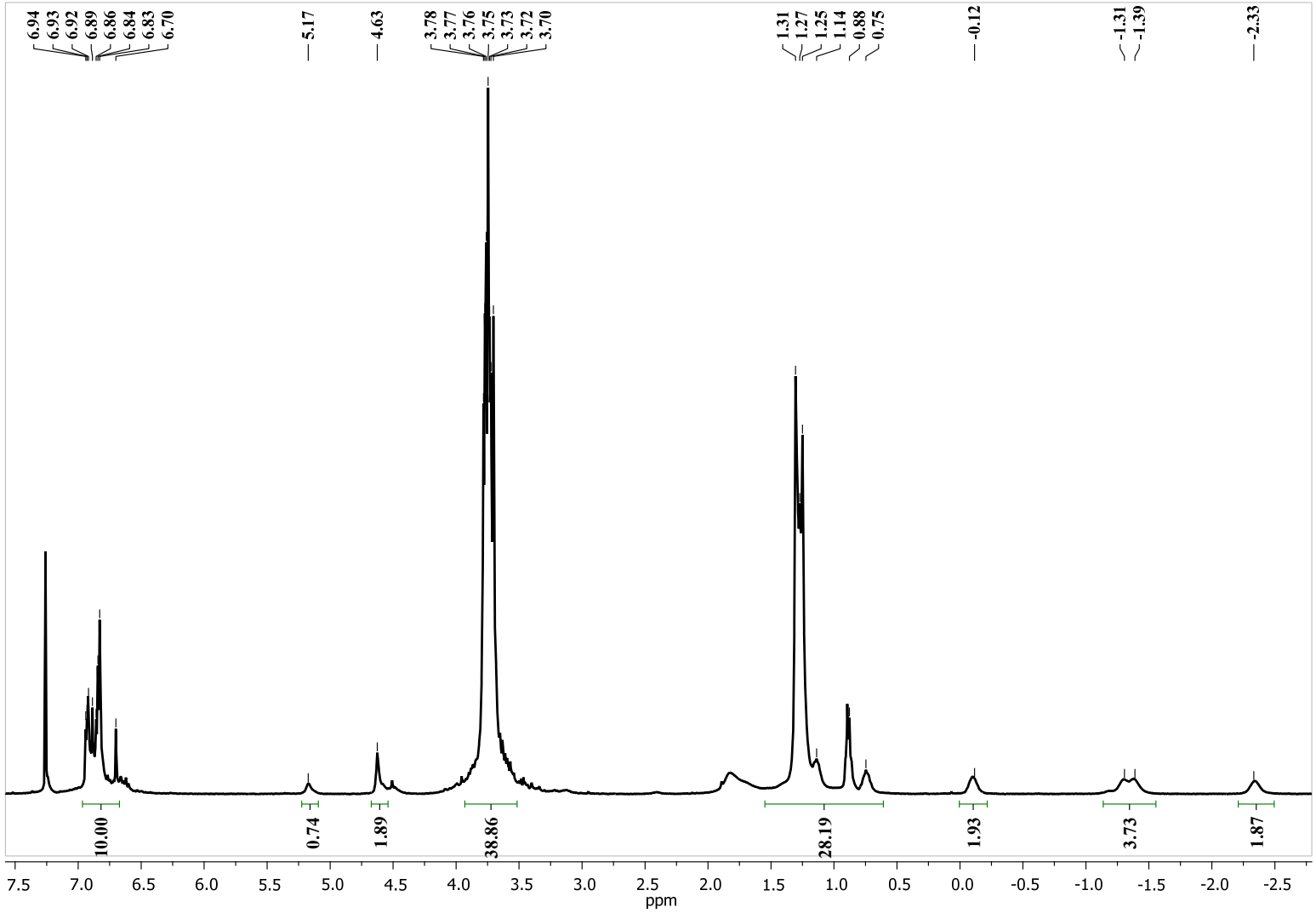

Fig. S9. ^{1}H NMR spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), DMSO-d_6, 298 K, 400 MHz.

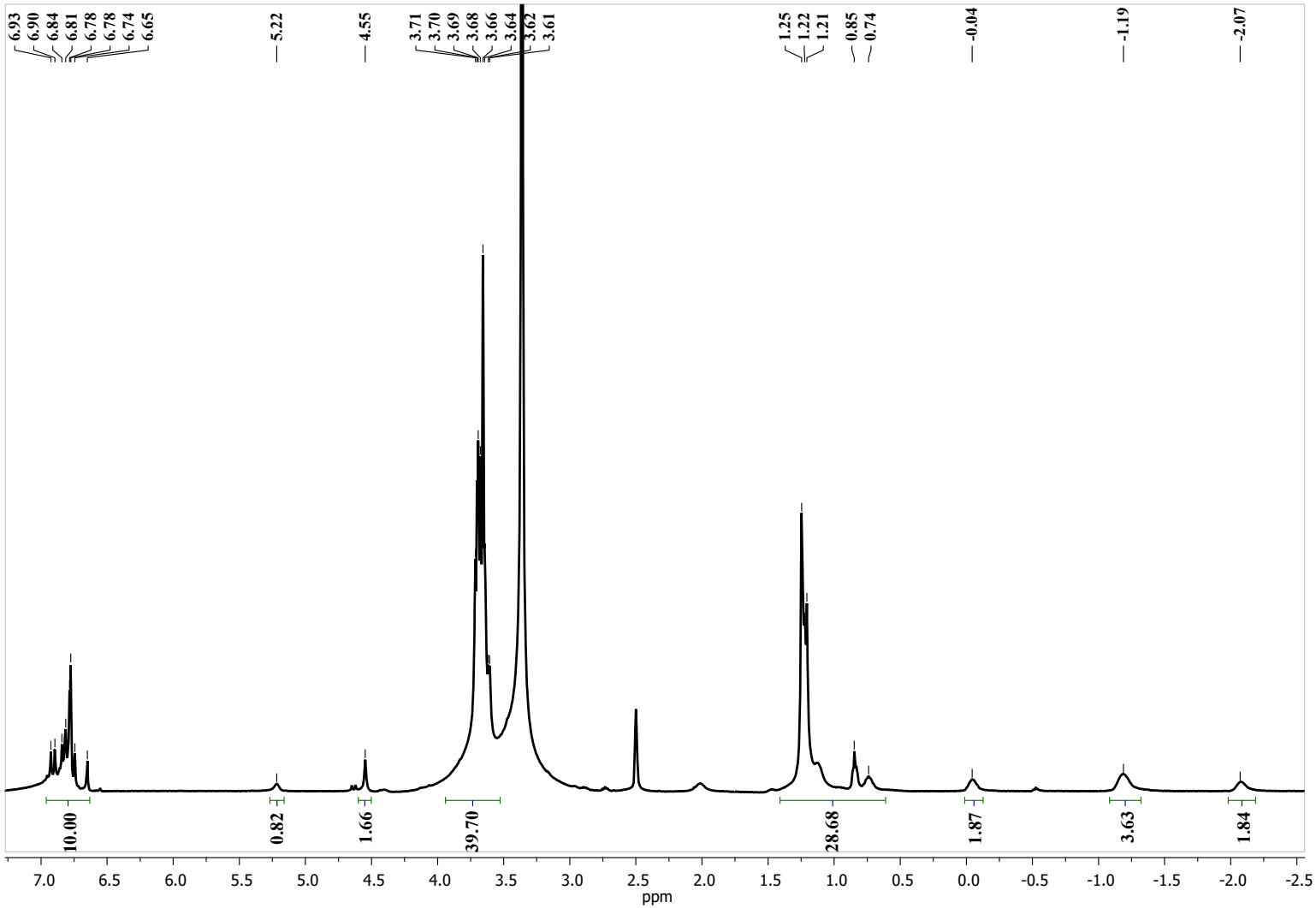

Fig. S10. ^{13}C NMR spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), $CDCl_3$, 298 K, 100 MHz.

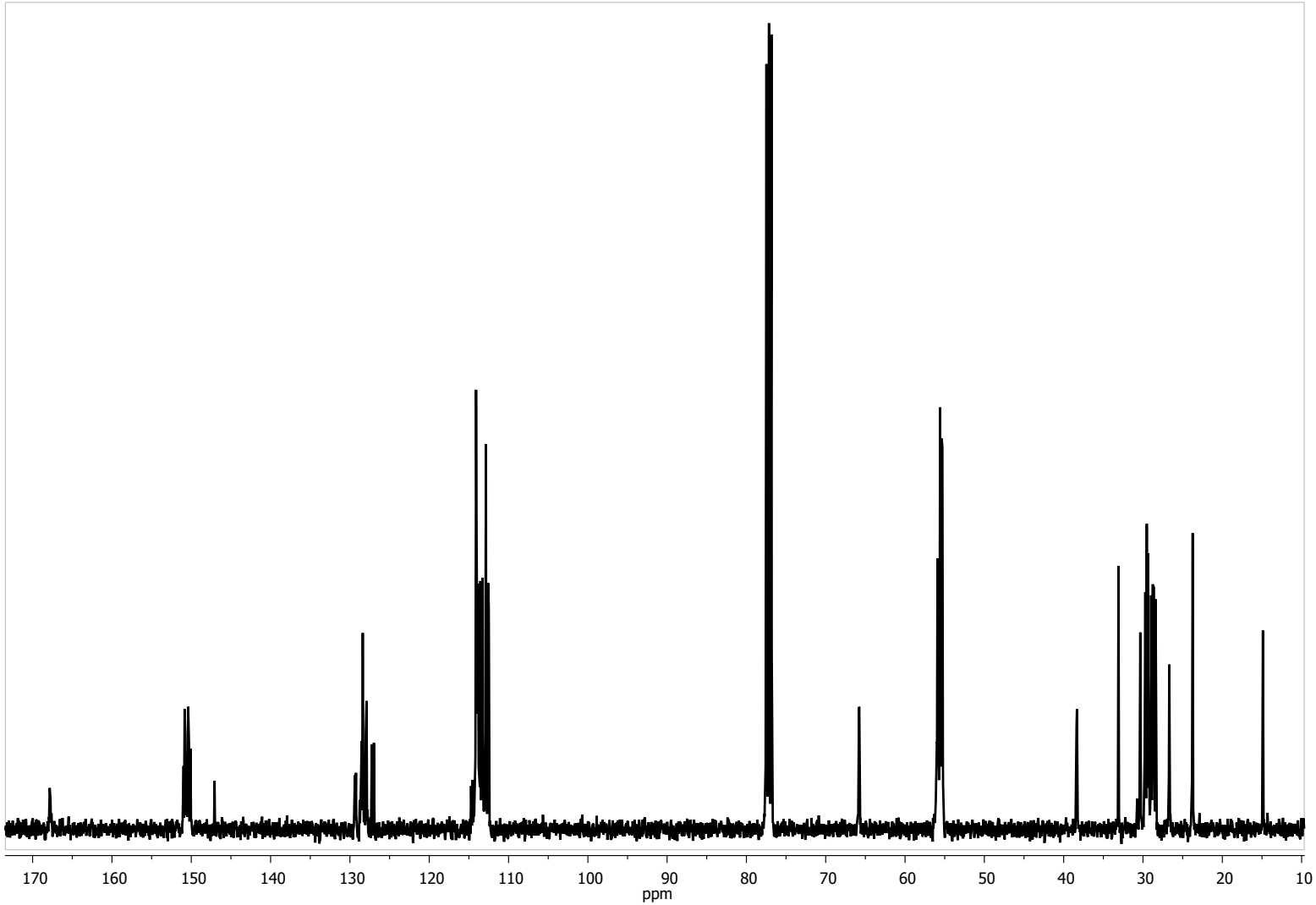

Fig. S11. ^{13}C NMR spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), $CDCl_3$, 298 K, 100 MHz.

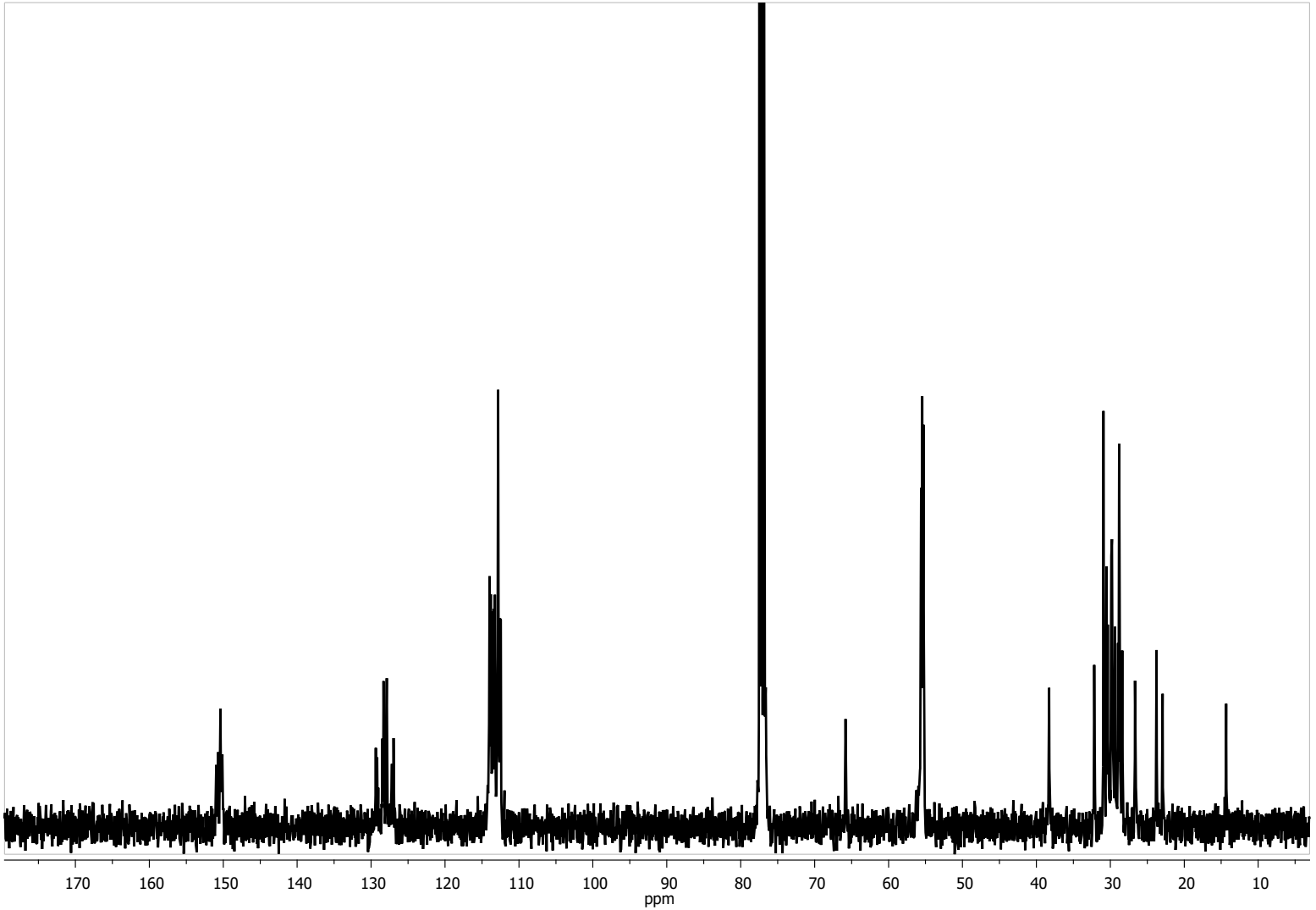

Fig. S12. ^{13}C NMR spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), $CDCl_3$, 298 K, 100 MHz.

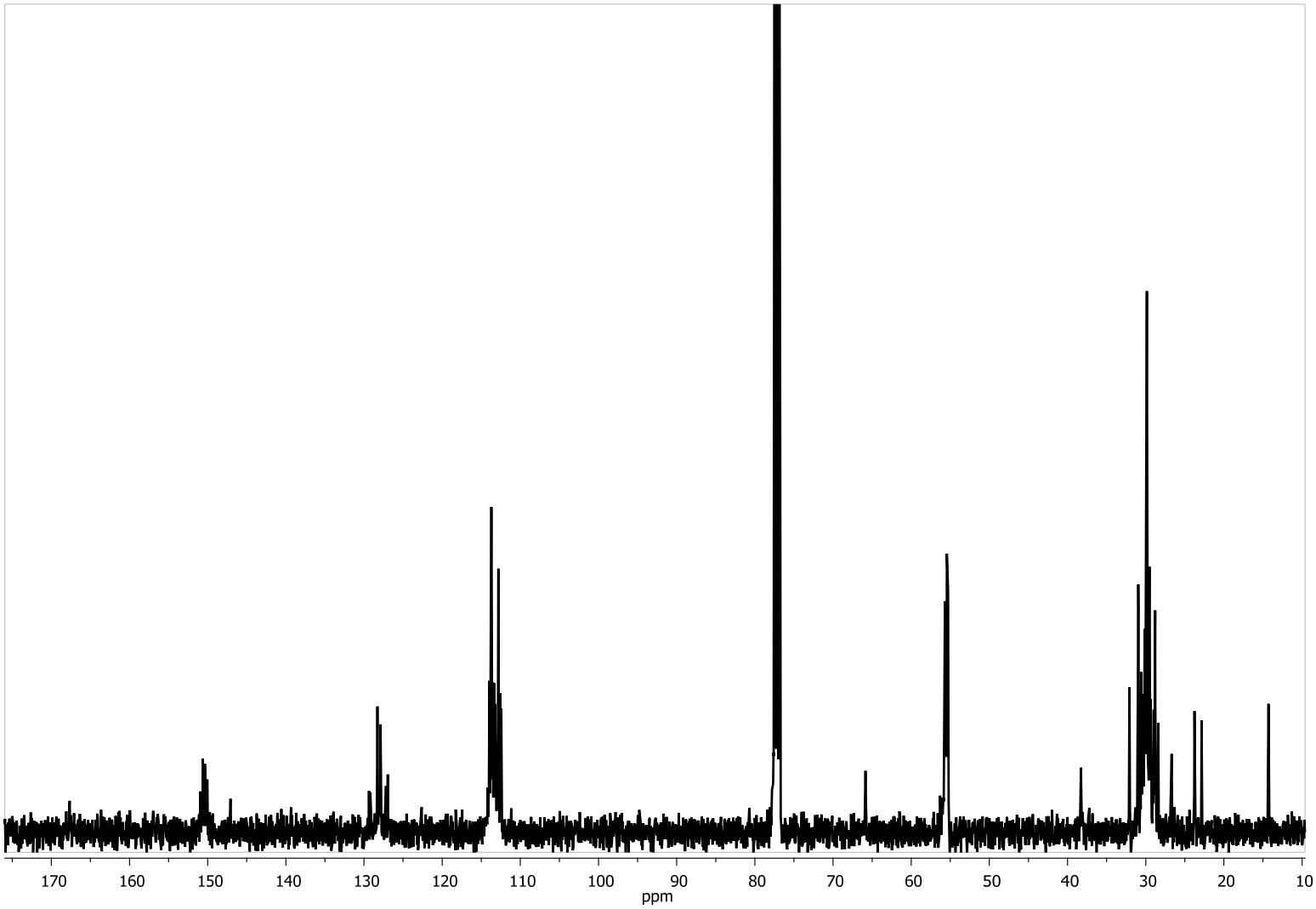

Fig. S13. Mass spectrum (MALDI-TOF) of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4).

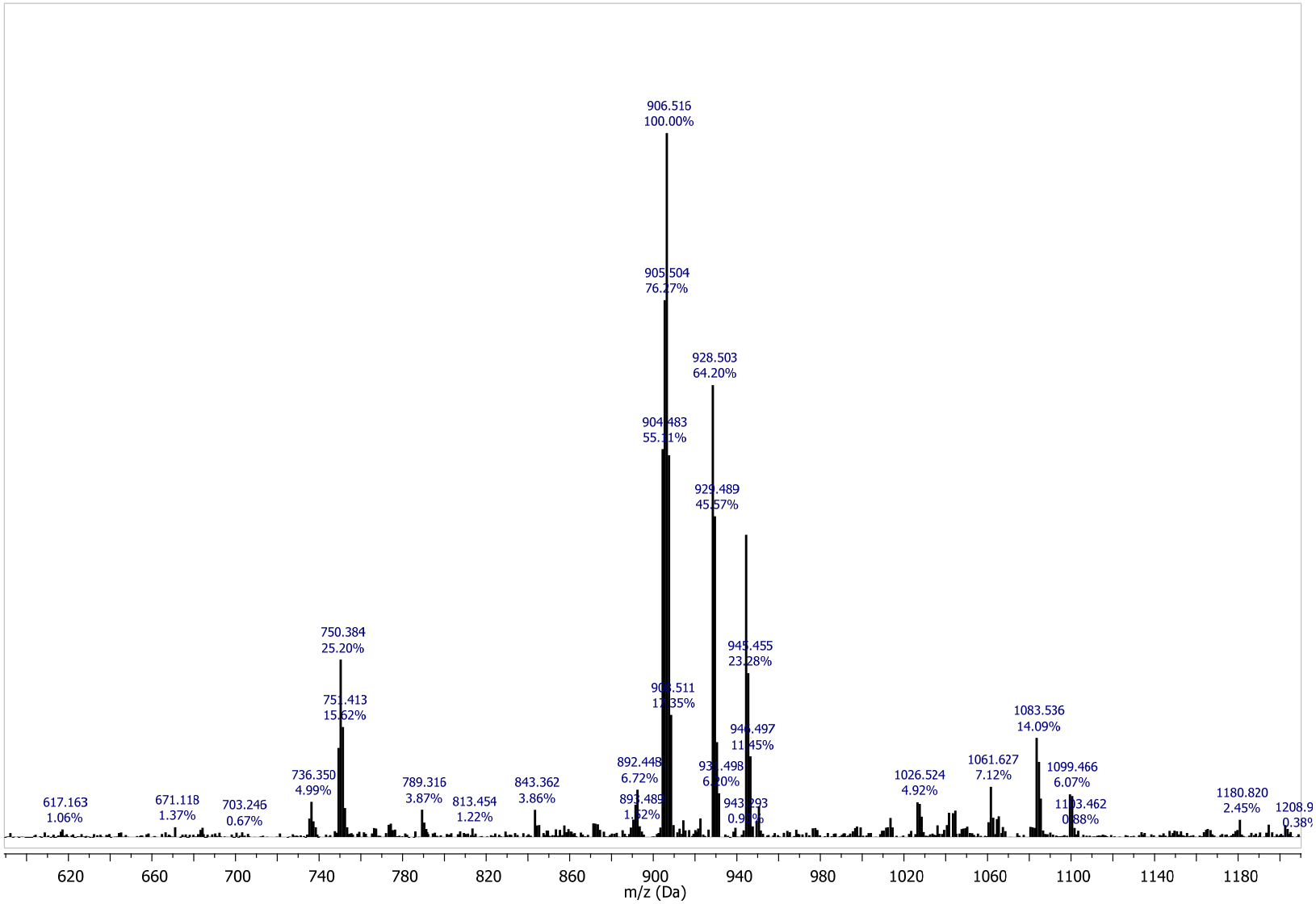

Fig. S14. Mass spectrum (MALDI-TOF) of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5).

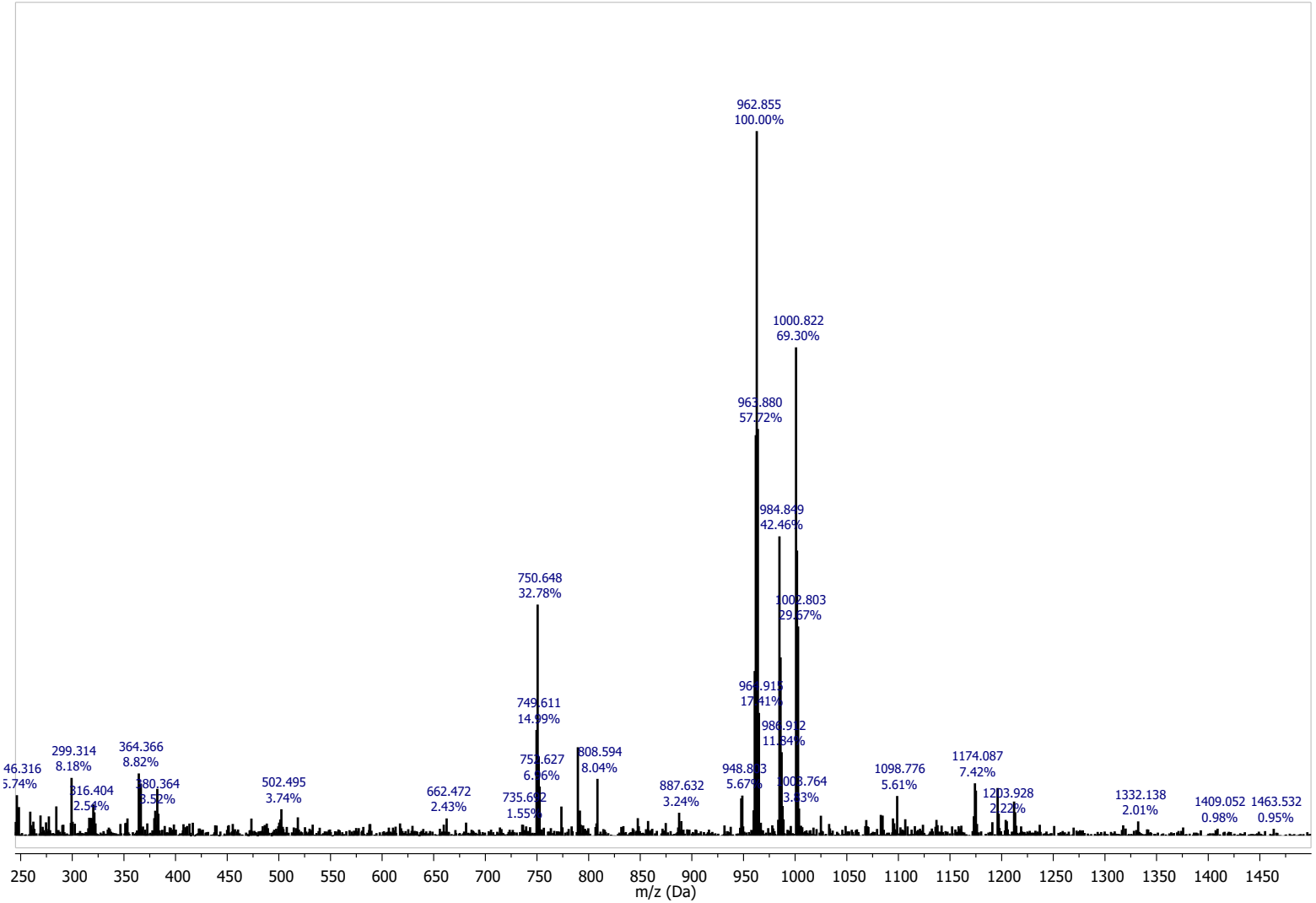

Fig. S15. Mass spectrum (MALDI-TOF) of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6).

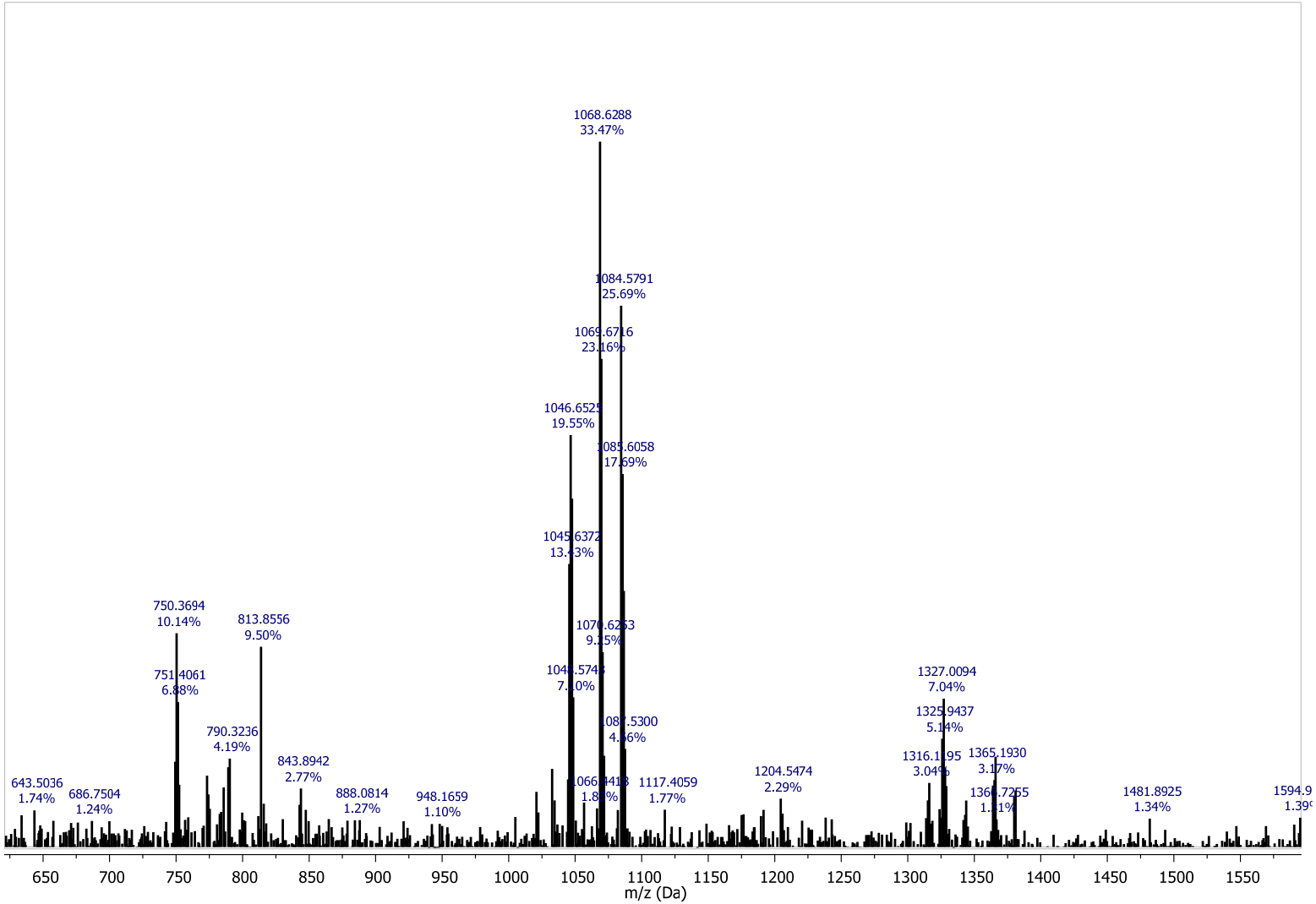

Fig. S16-S18. IR spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), 4-[(N-aminodoctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6).

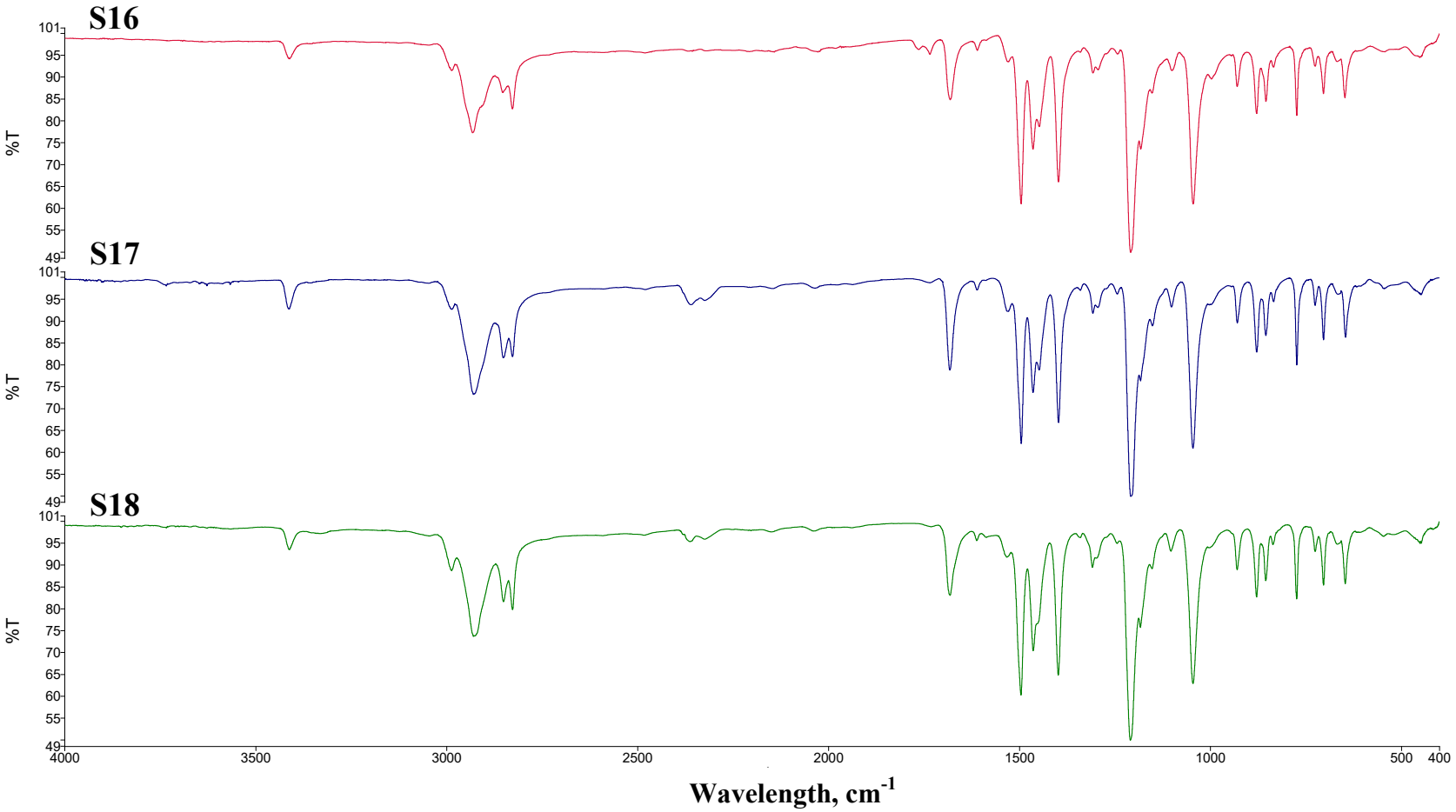

Fig. S19. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), $CDCl_3$, 293 K, 400 MHz.

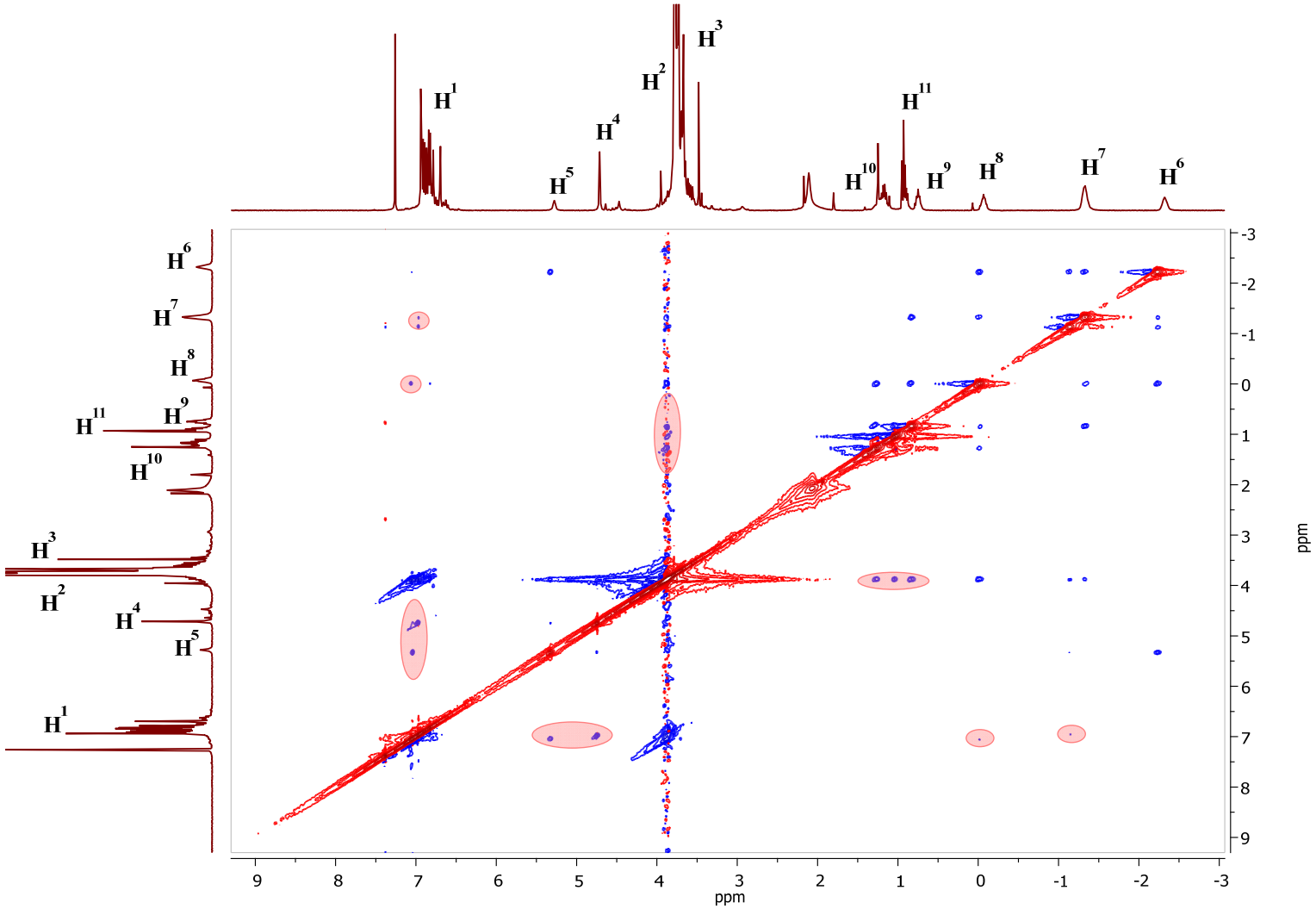

Fig. S20. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), DMSO-d_6, 293 K, 400 MHz.

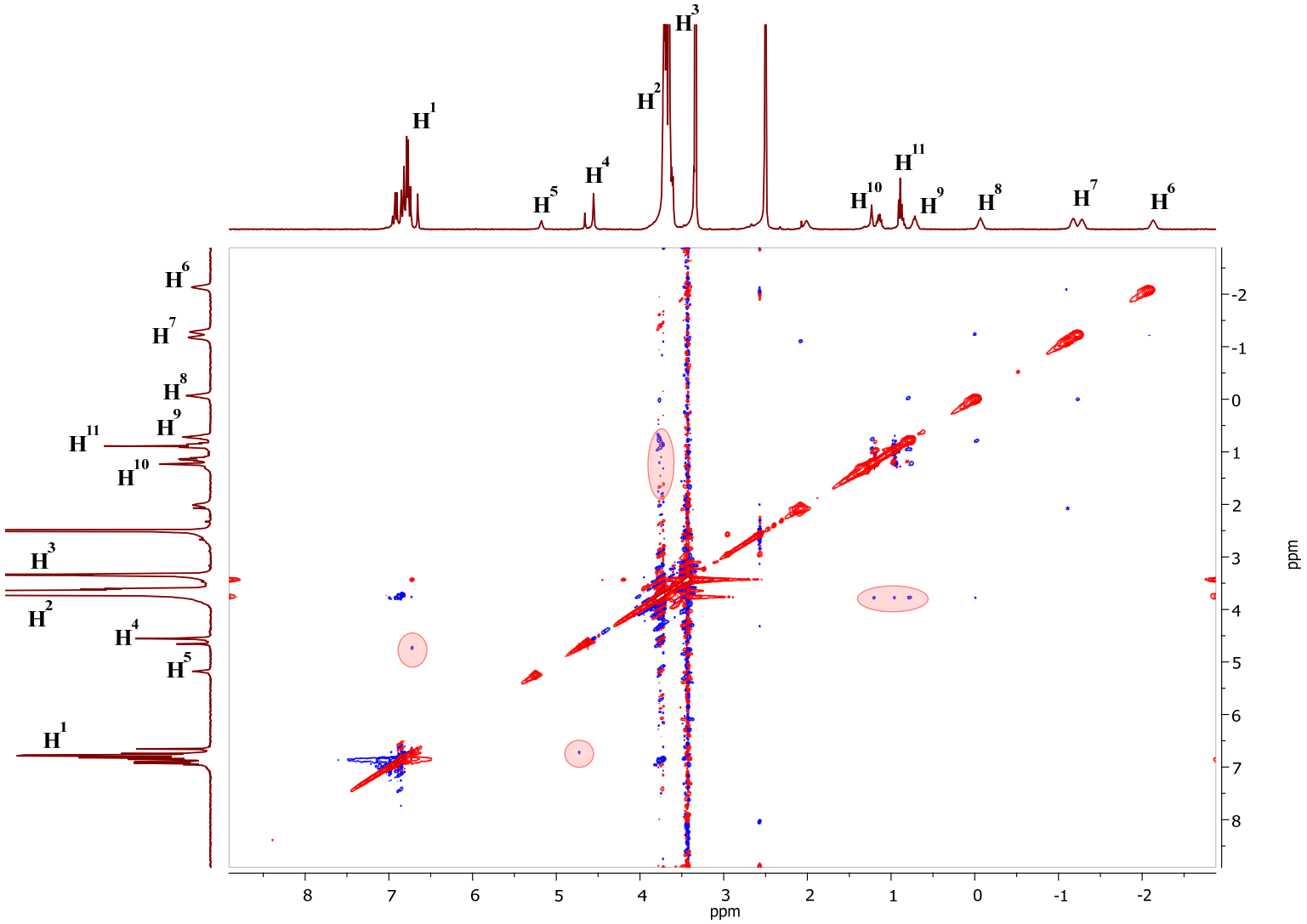

Fig. S21. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), $CDCl_3$, 293 K, 400 MHz.

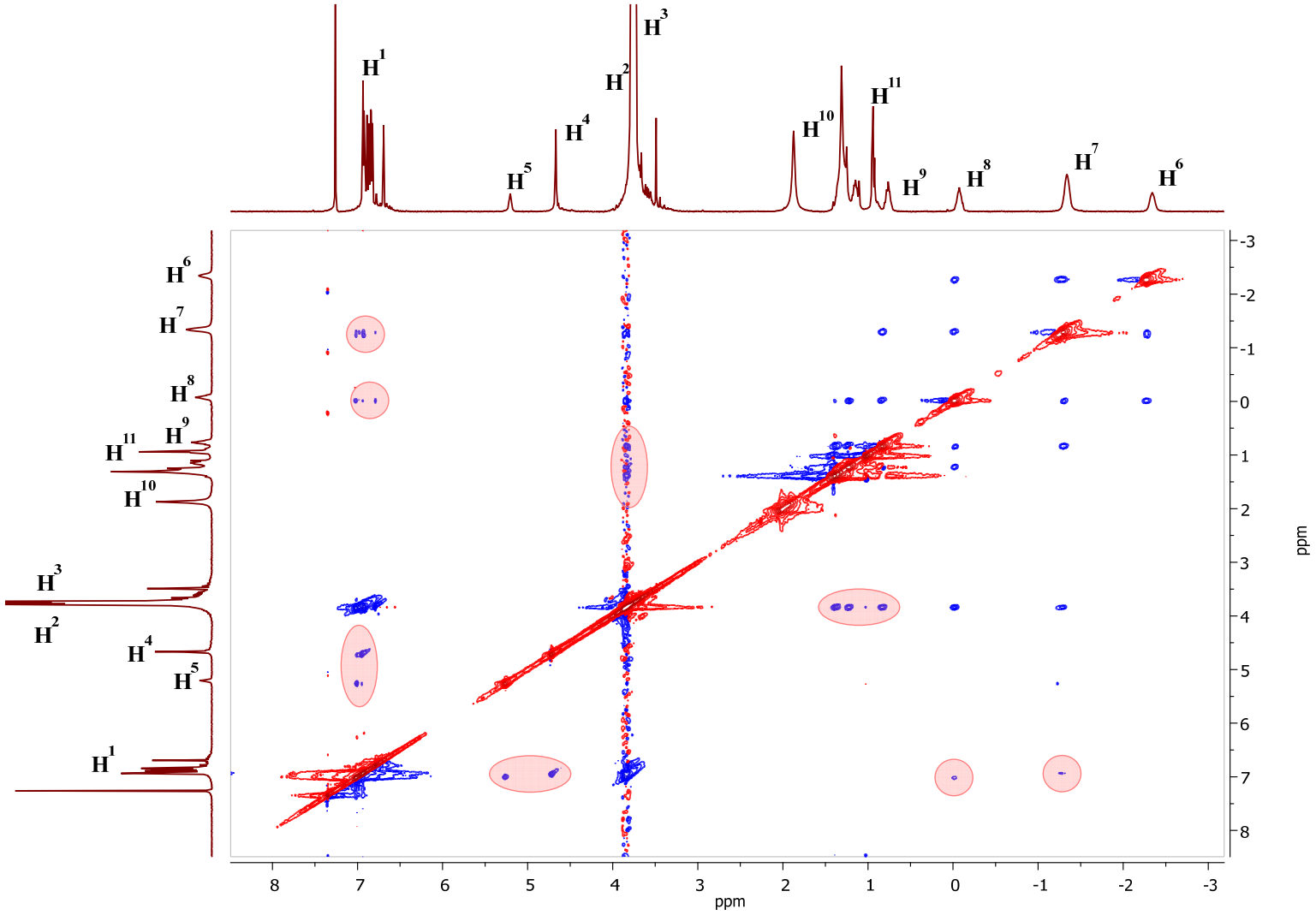

Fig. S22. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), DMSO-d_6, 293 K, 400 MHz.

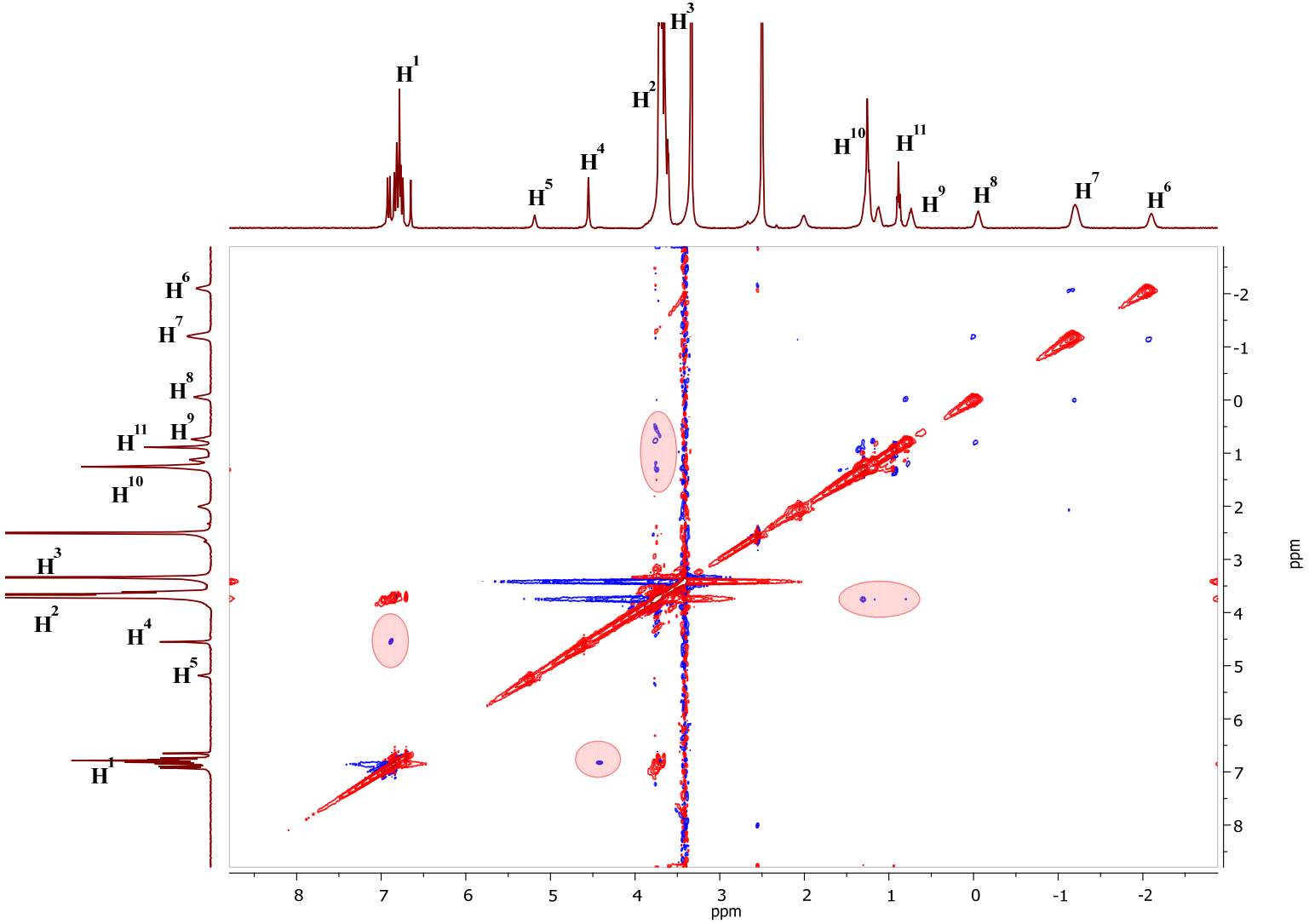

Fig. S23. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), $CDCl_3$, 293 K, 400 MHz.

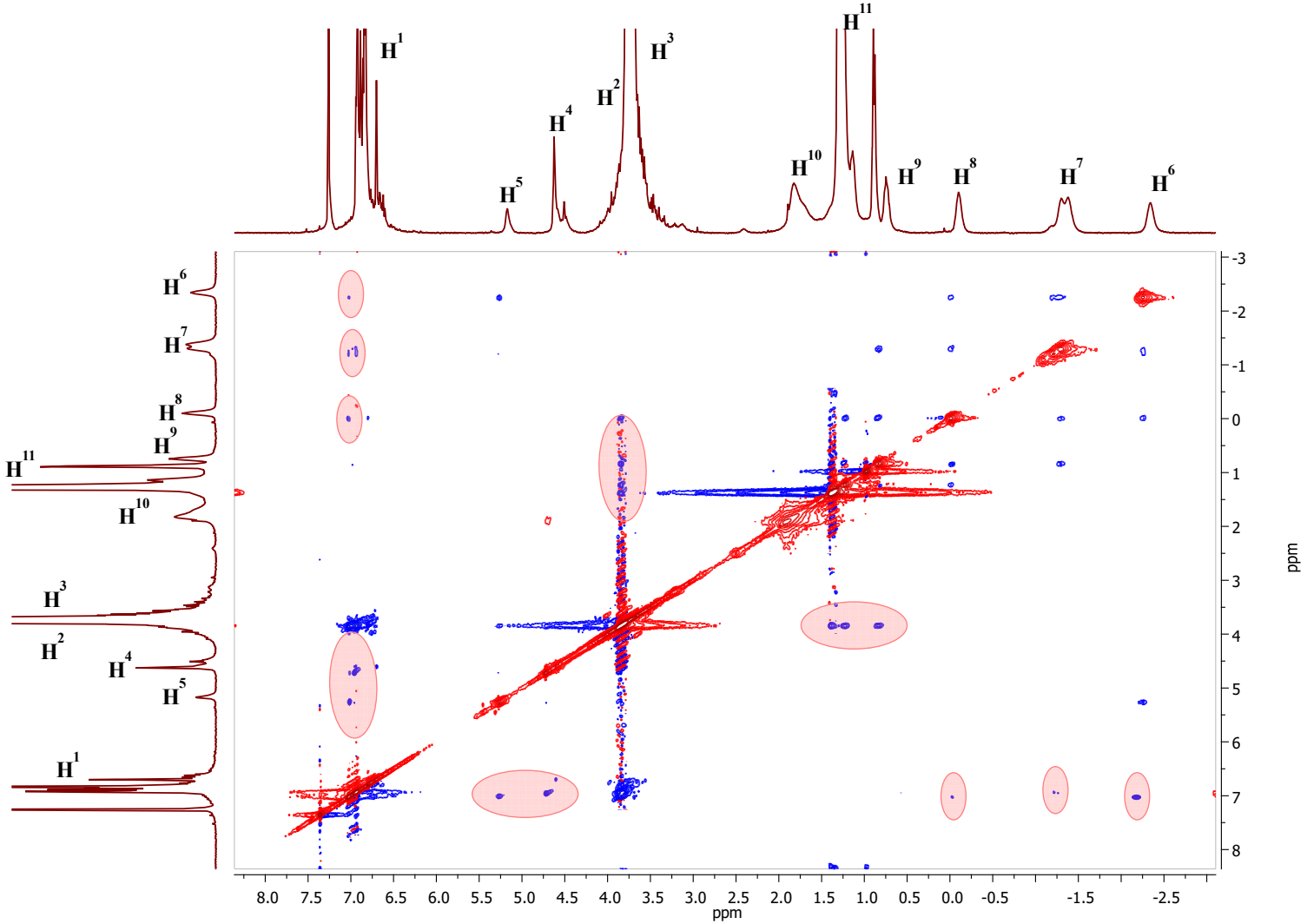

Fig. S24. 2D NMR NOESY ^{1}H-^{1}H spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), DMSO-d_6, 293 K, 400 MHz.

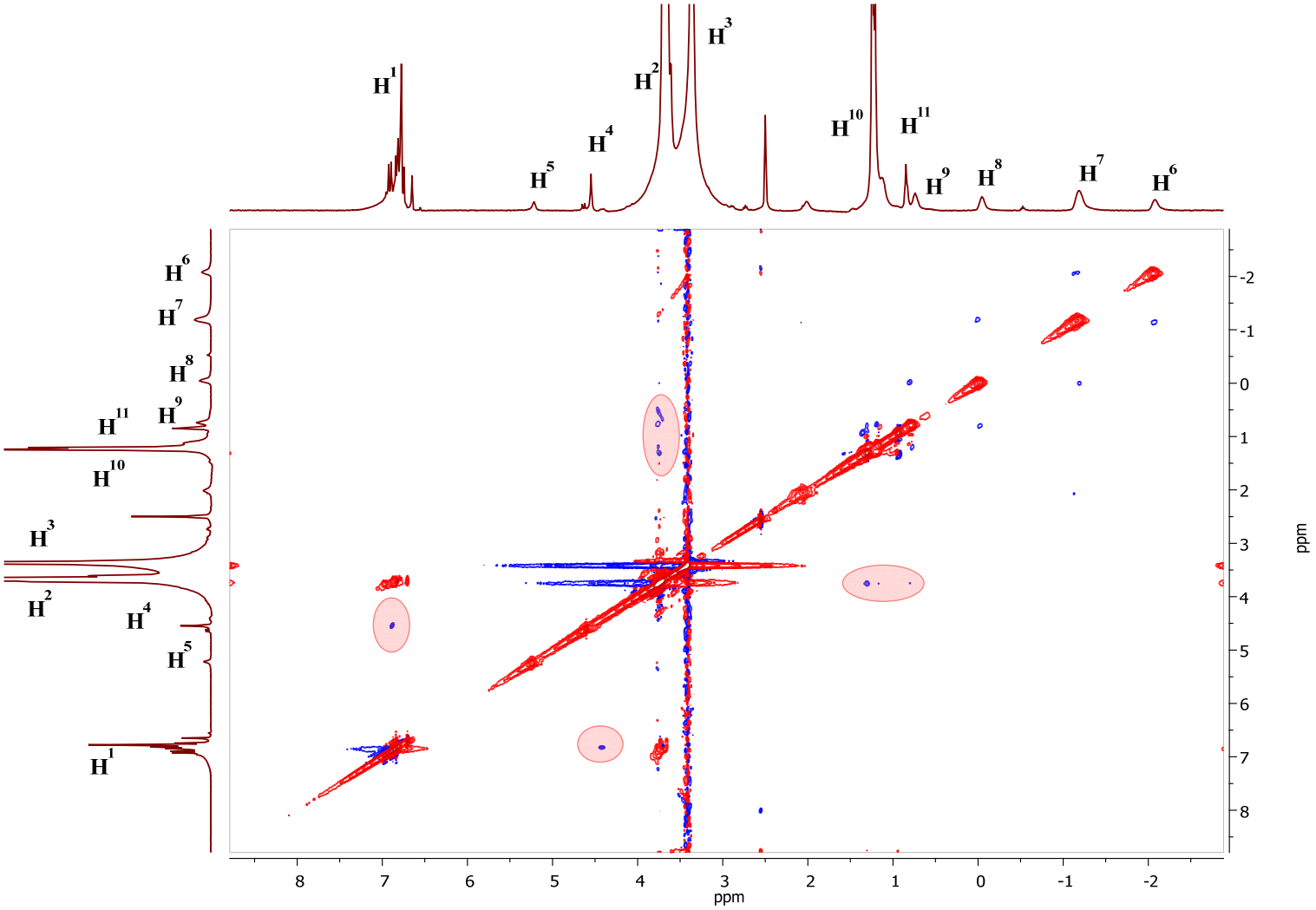

Fig. S25. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), 1×10^{-2} M, $CDCl_3$, 293 K, 400 MHz.

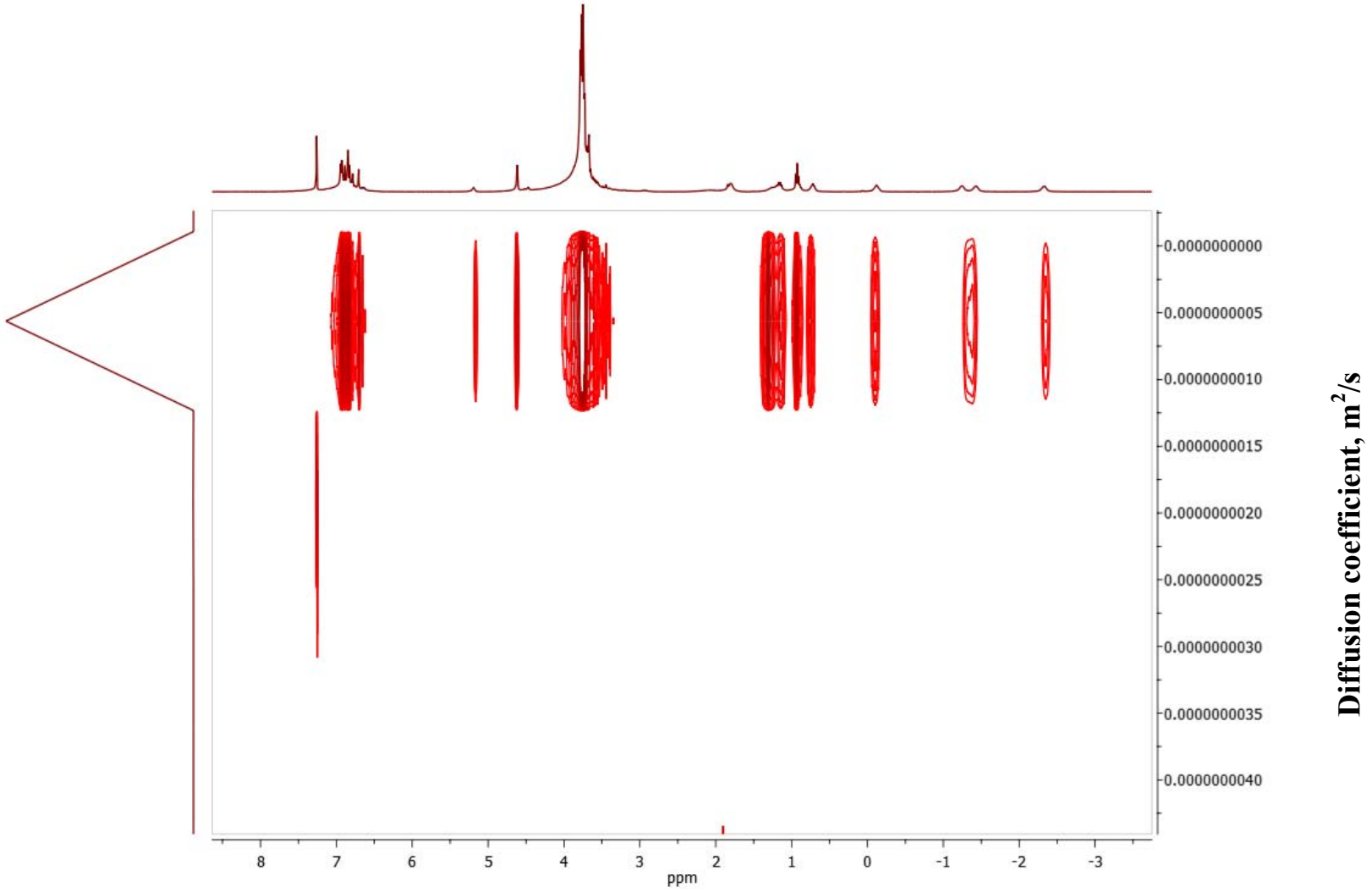

Fig. S26. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), 5×10^{-3} M, $CDCl_3$, 293 K, 400 MHz.

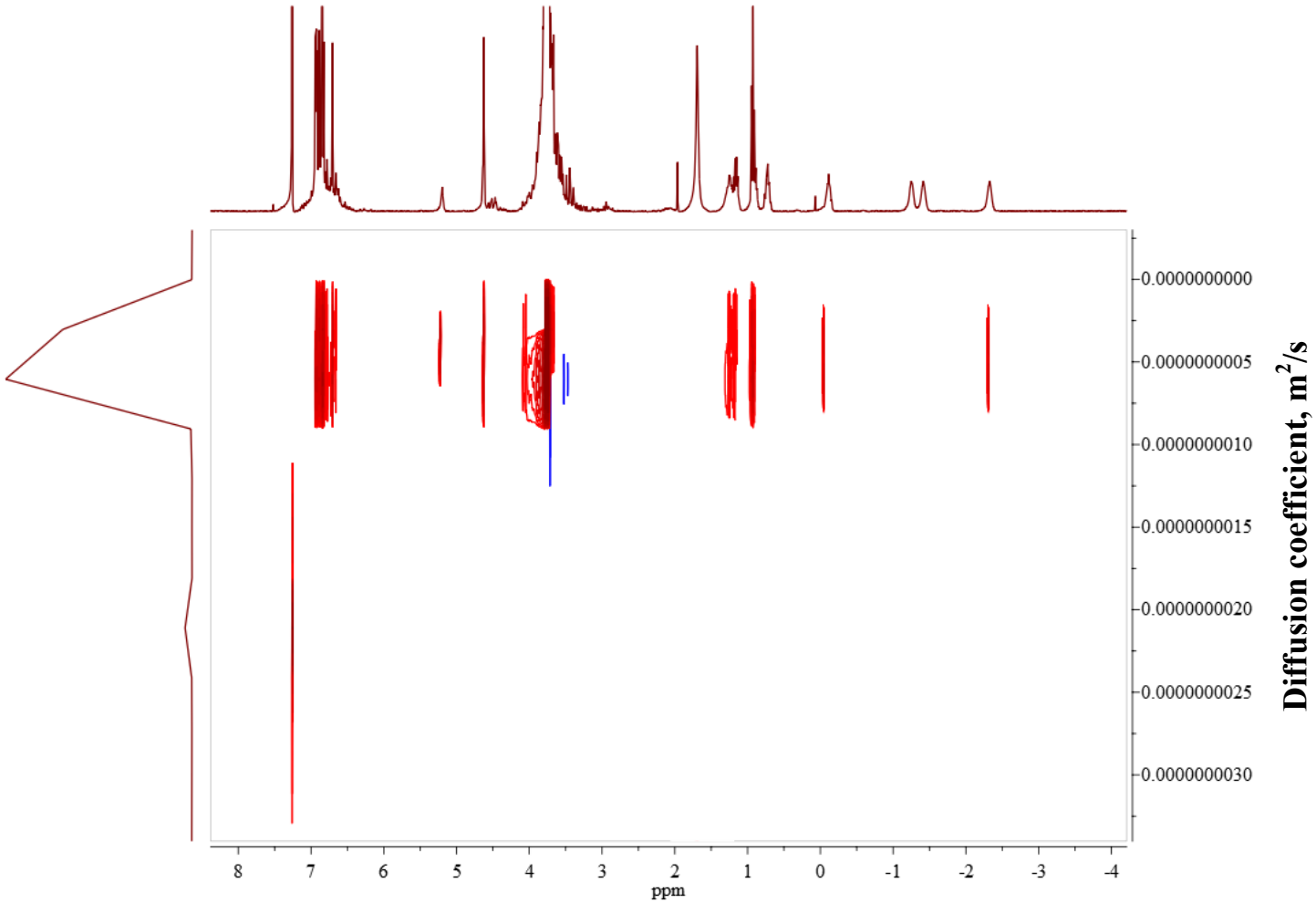

Fig. S27. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), 1×10^{-3} M, $CDCl_3$, 293 K, 400 MHz.

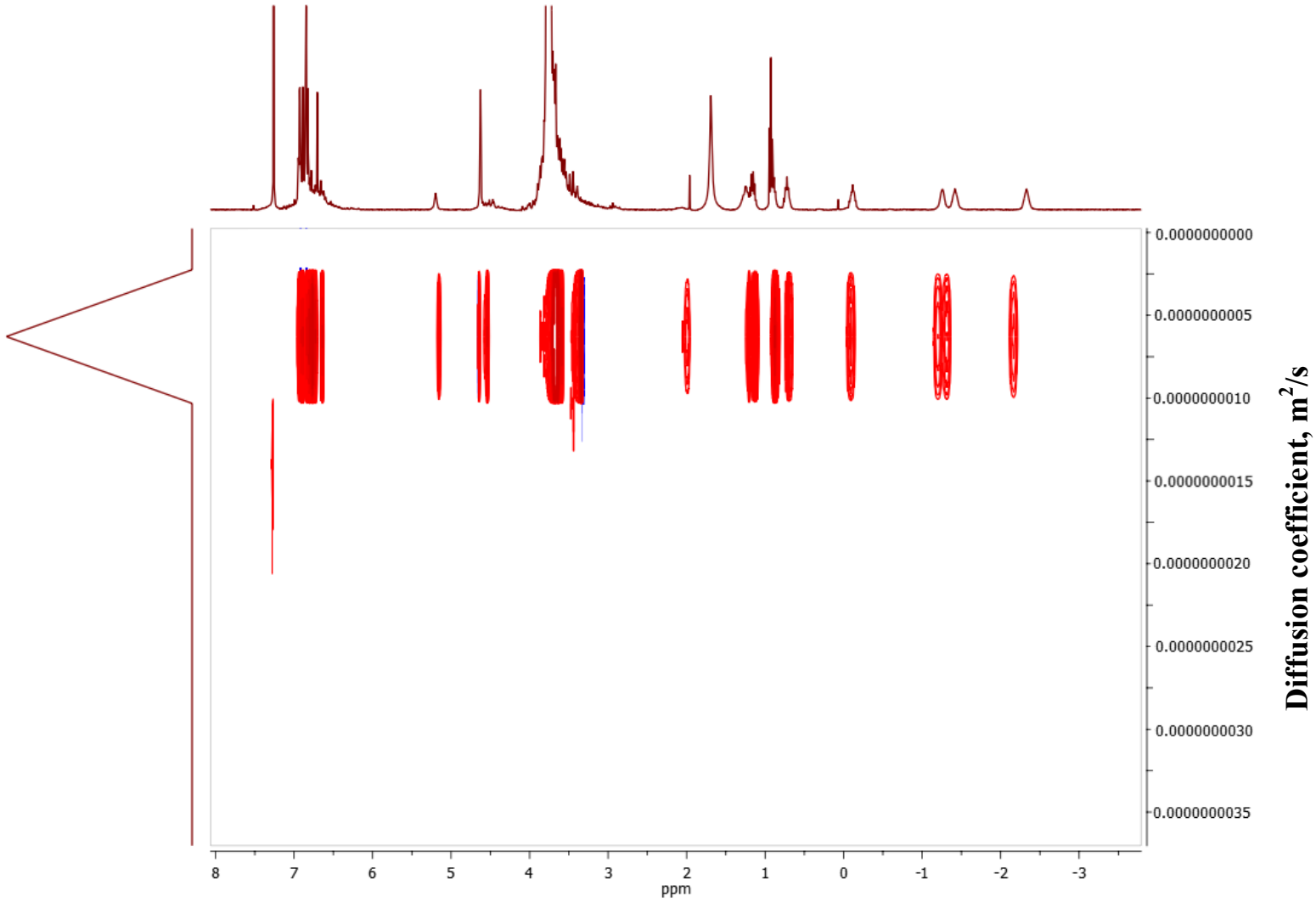

Fig. S28. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), 1×10^{-2} M, DMSO-d_6, 293 K, 400 MHz.

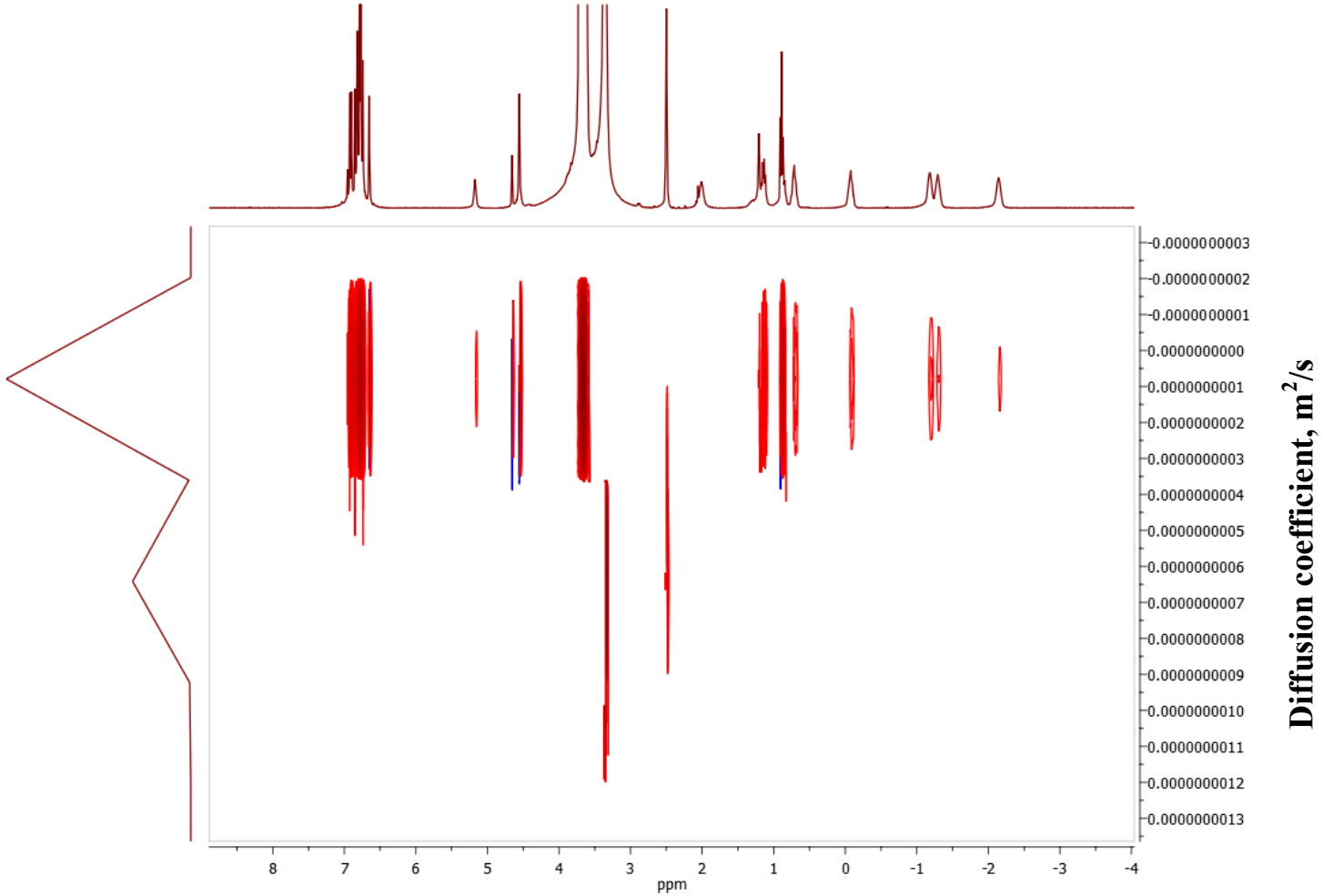

Fig. S29. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), 5×10^{-3} M, DMSO-d_6, 293 K, 400 MHz.

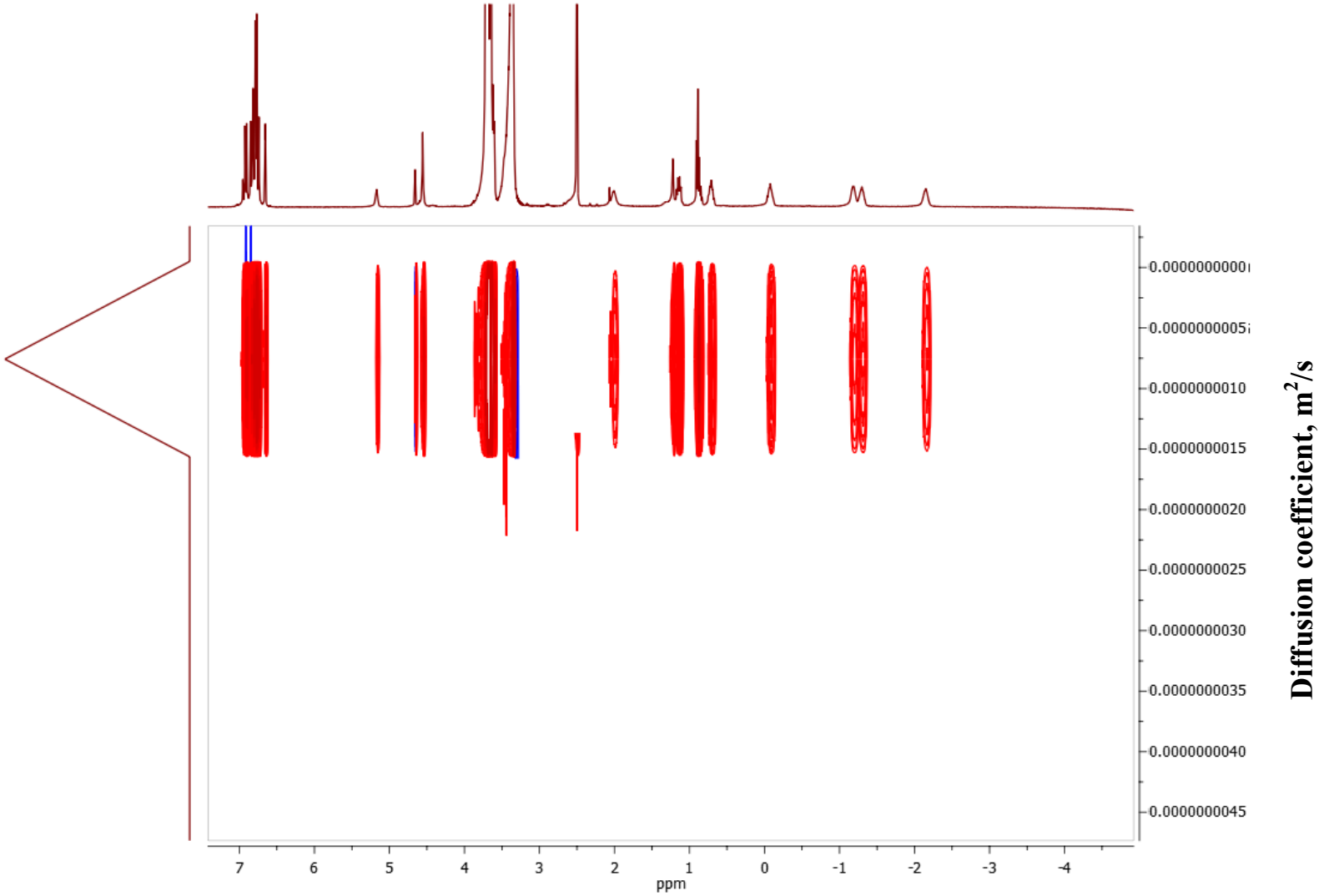

Fig. S30. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (4), 1×10^{-3} M, DMSO-d_6, 293 K, 400 MHz.

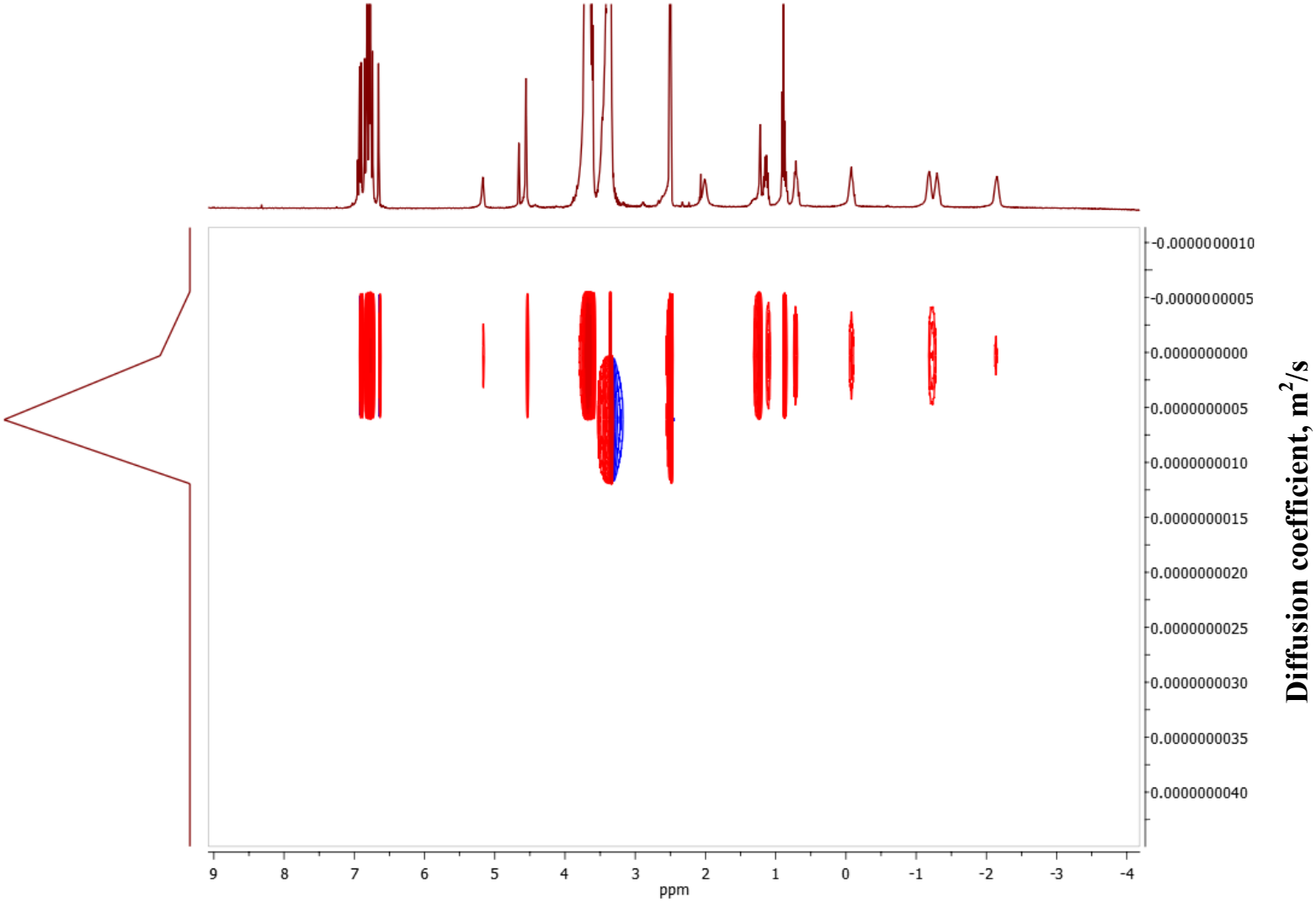

Fig. S31. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), 1×10^{-2} M, $CDCl_3$, 293 K, 400 MHz.

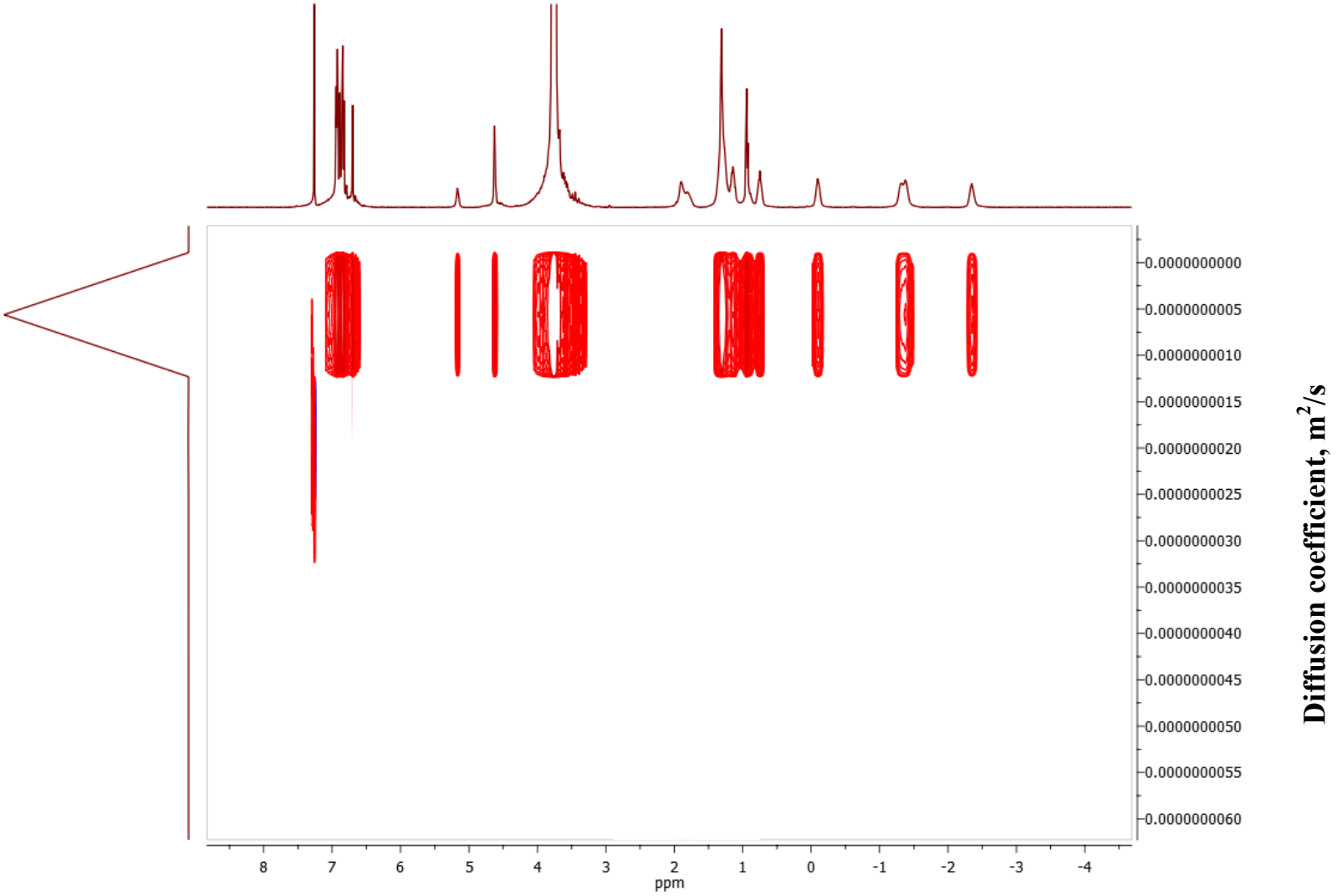

Fig. S32. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), 5×10^{-3} M, $CDCl_3$, 293 K, 400 MHz.

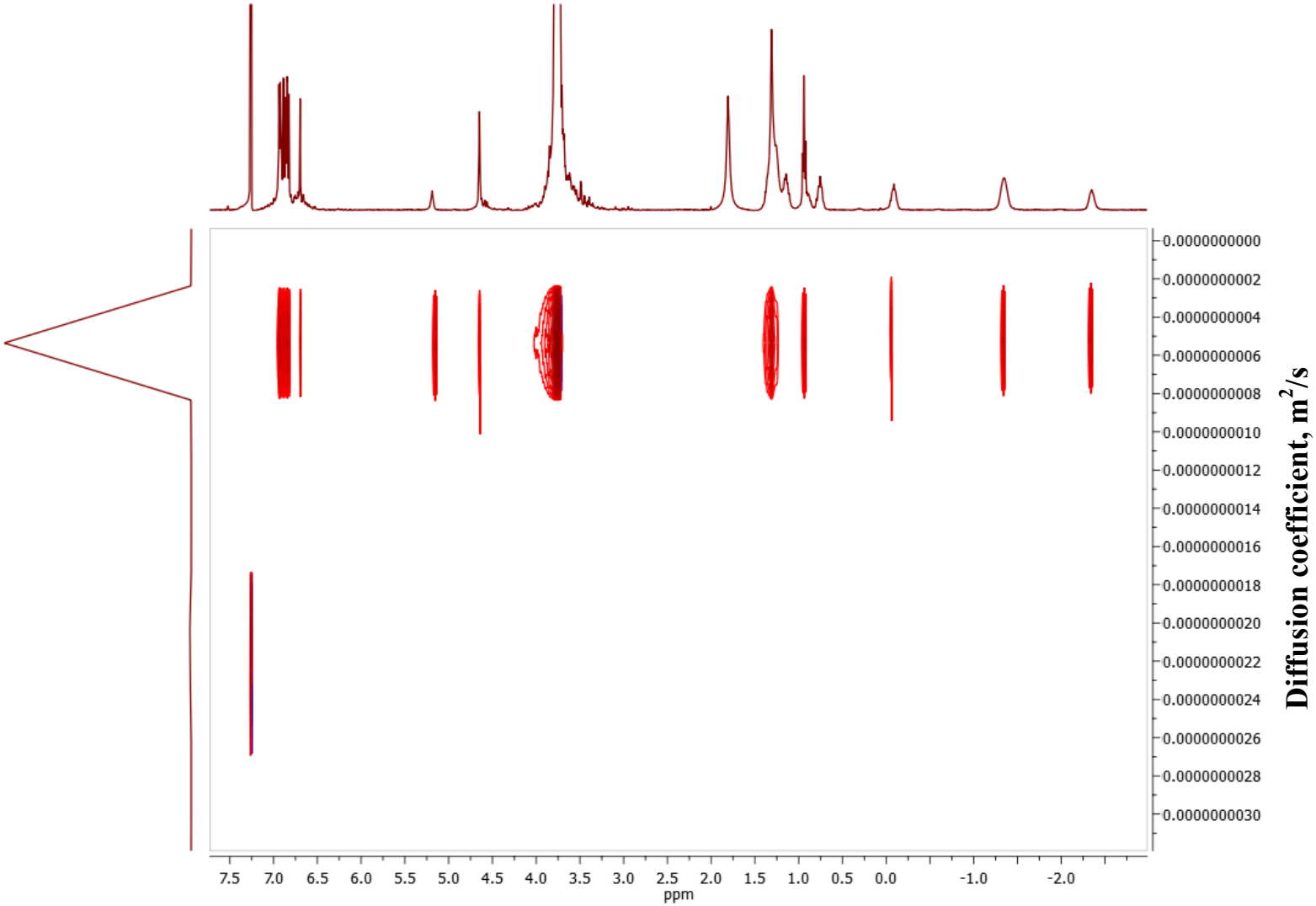

Fig. S33. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), 1×10^{-3} M, $CDCl_3$, 293 K, 400 MHz.

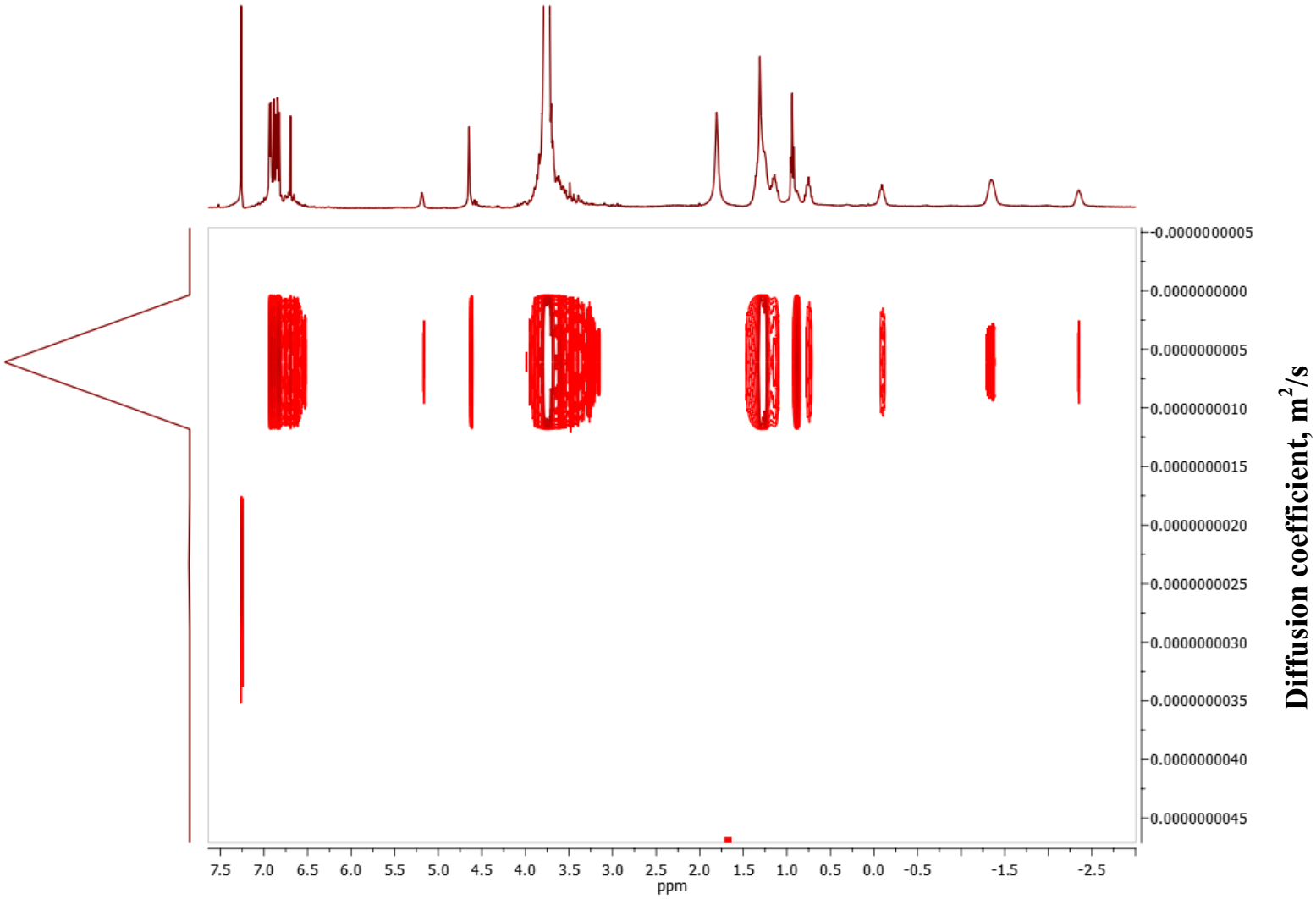

Fig. S34. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), 1×10^{-2} M, DMSO-d_6, 293 K, 400 MHz.

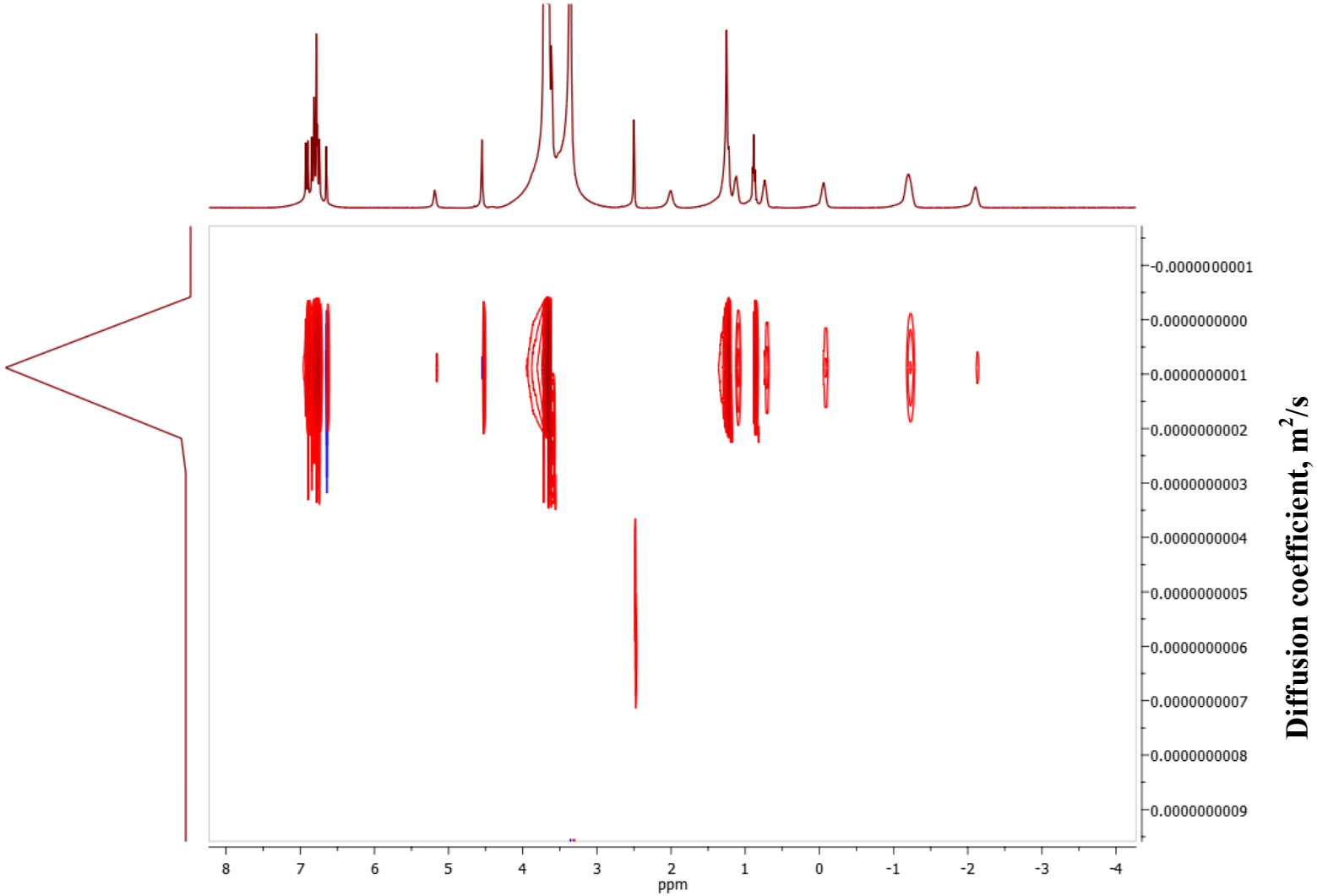

Fig. S35. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), 5×10^{-3} M, DMSO-d_6, 293 K, 400 MHz.

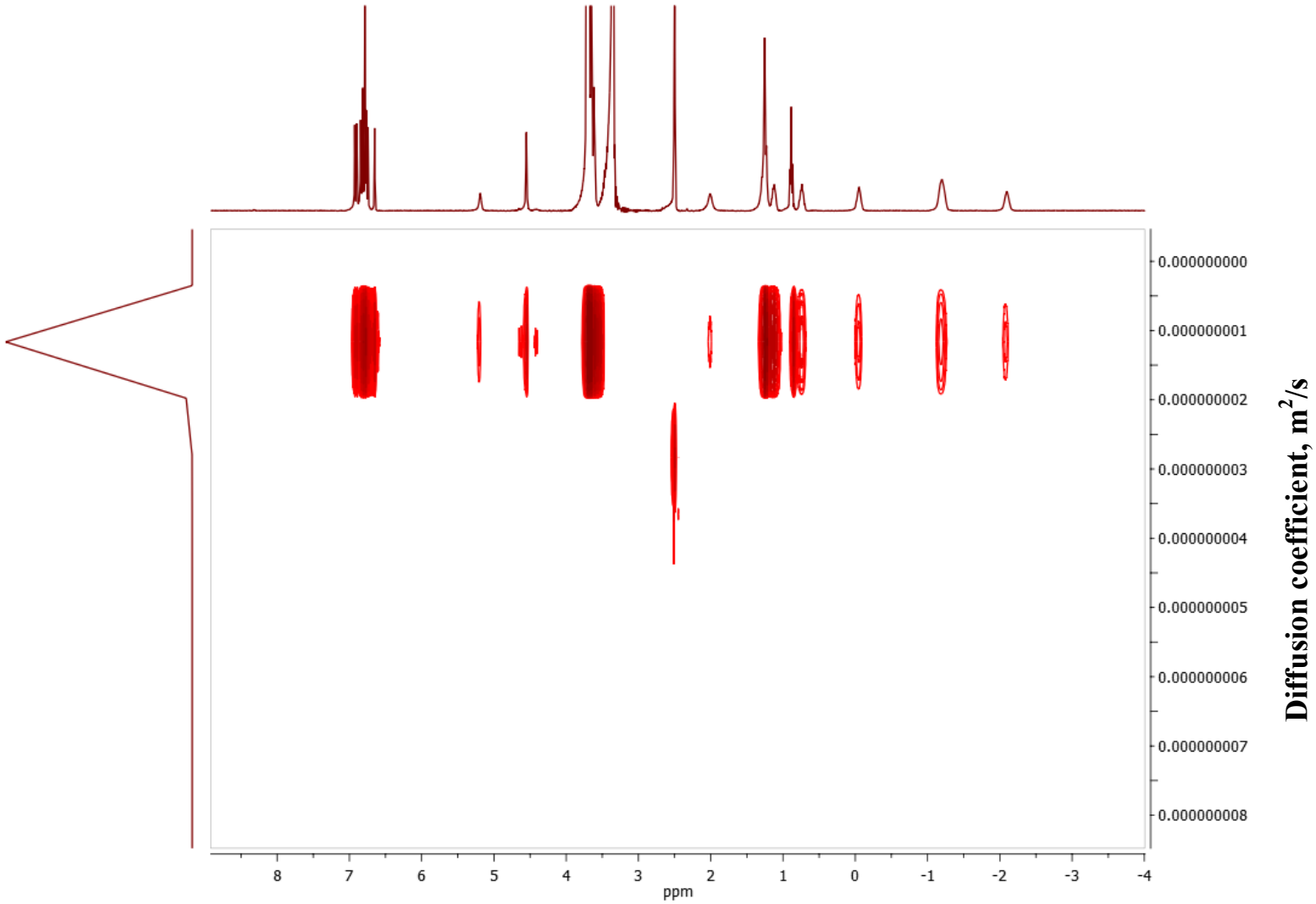

Fig. S36. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminododecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (5), 1×10^{-3} M, DMSO-d_6, 293 K, 400 MHz.

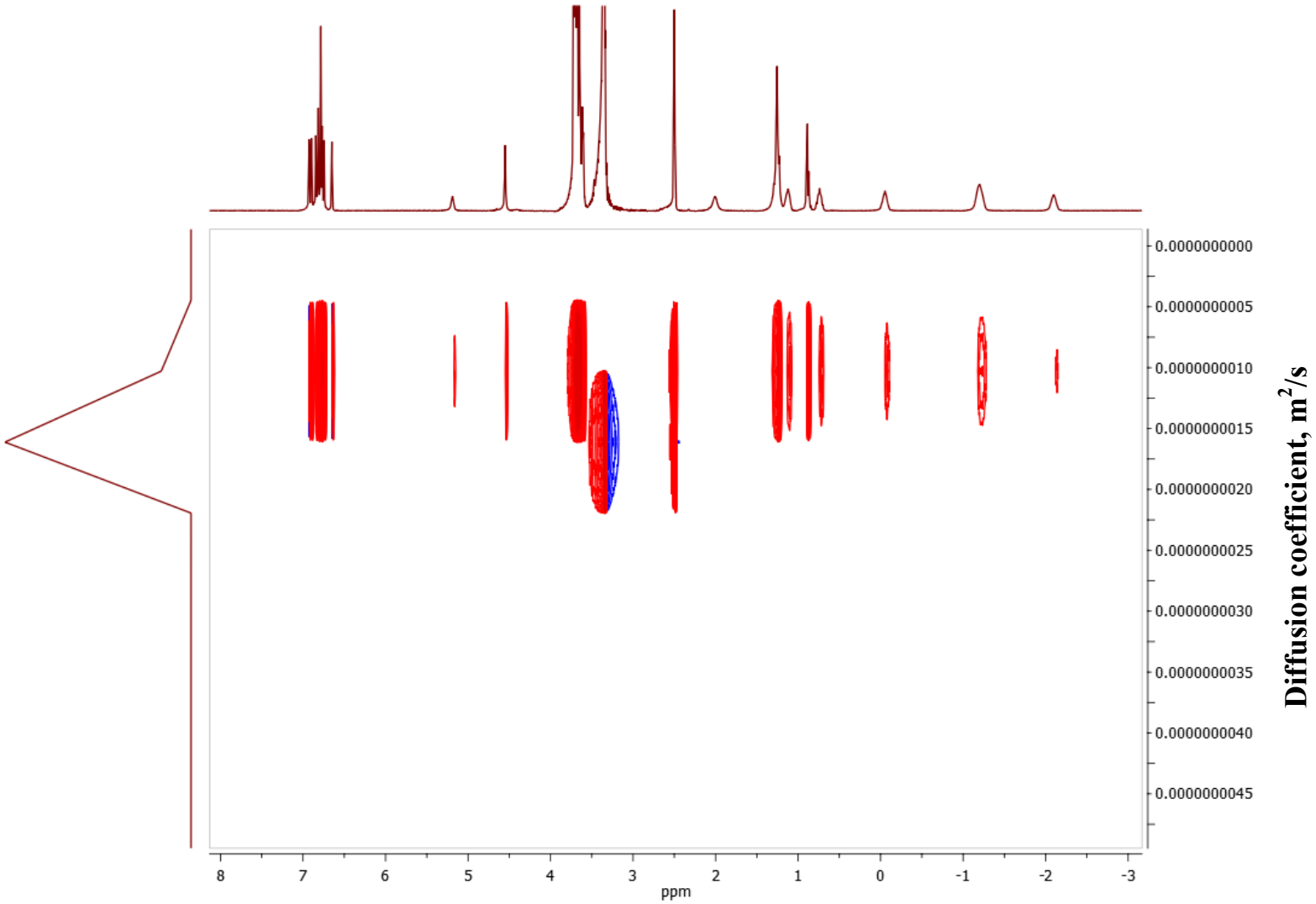

Fig. S37. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), 1×10^{-2} M, $CDCl_3$, 293 K, 400 MHz.

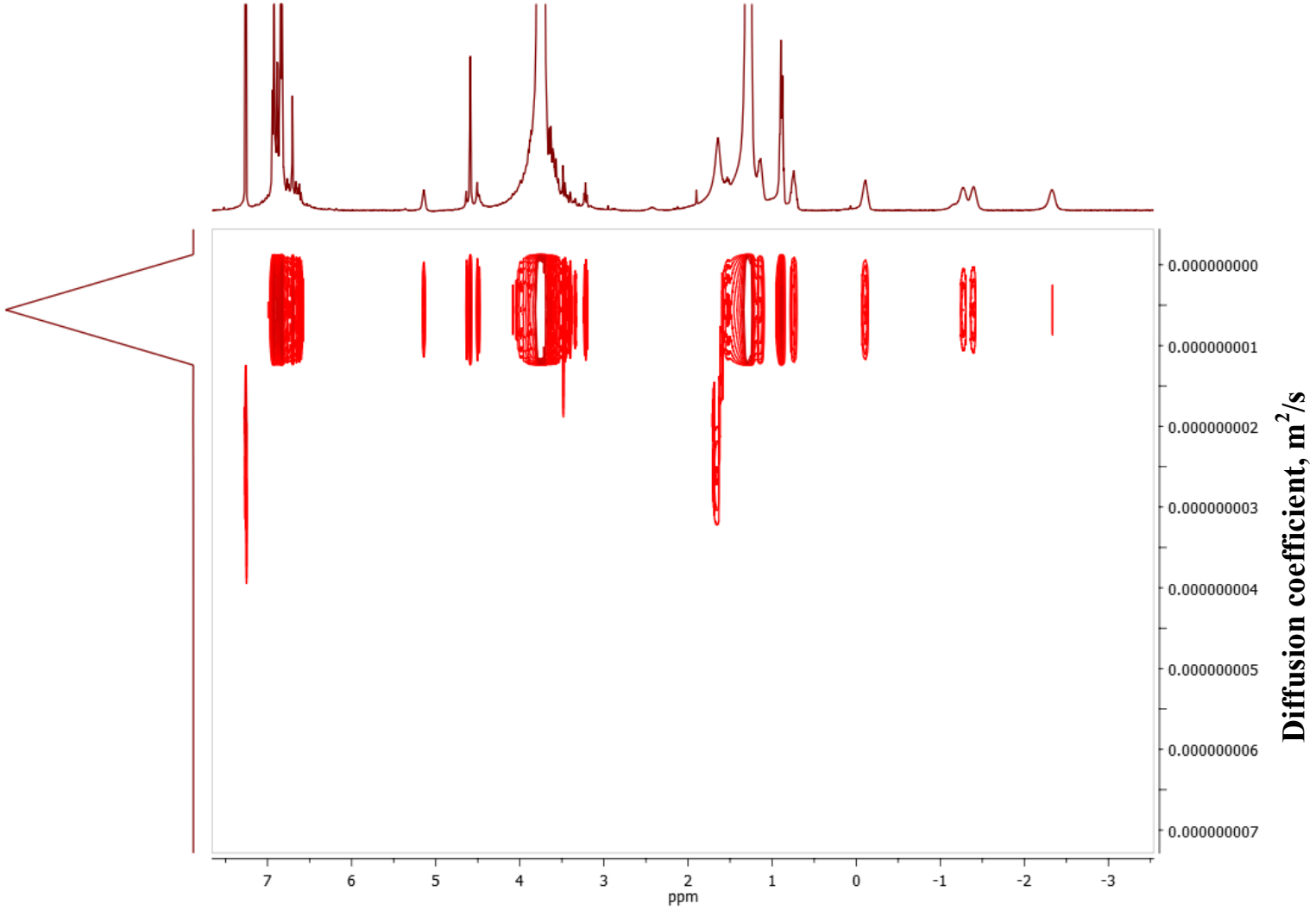

Fig. S38. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), 5×10^{-3} M, $CDCl_3$, 293 K, 400 MHz.

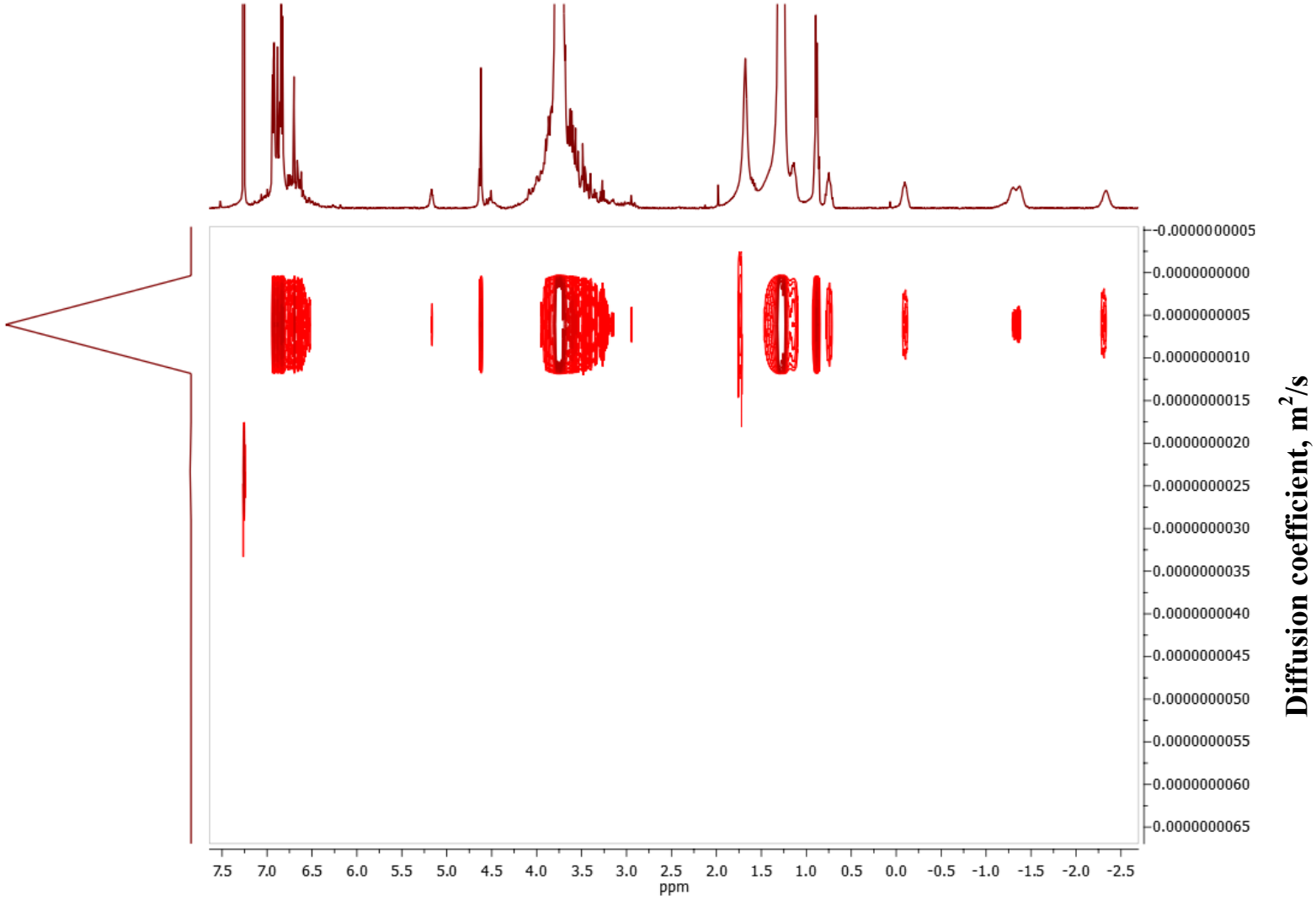

Fig. S39. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), 1×10^{-3} M, $CDCl_3$, 293 K, 400 MHz.

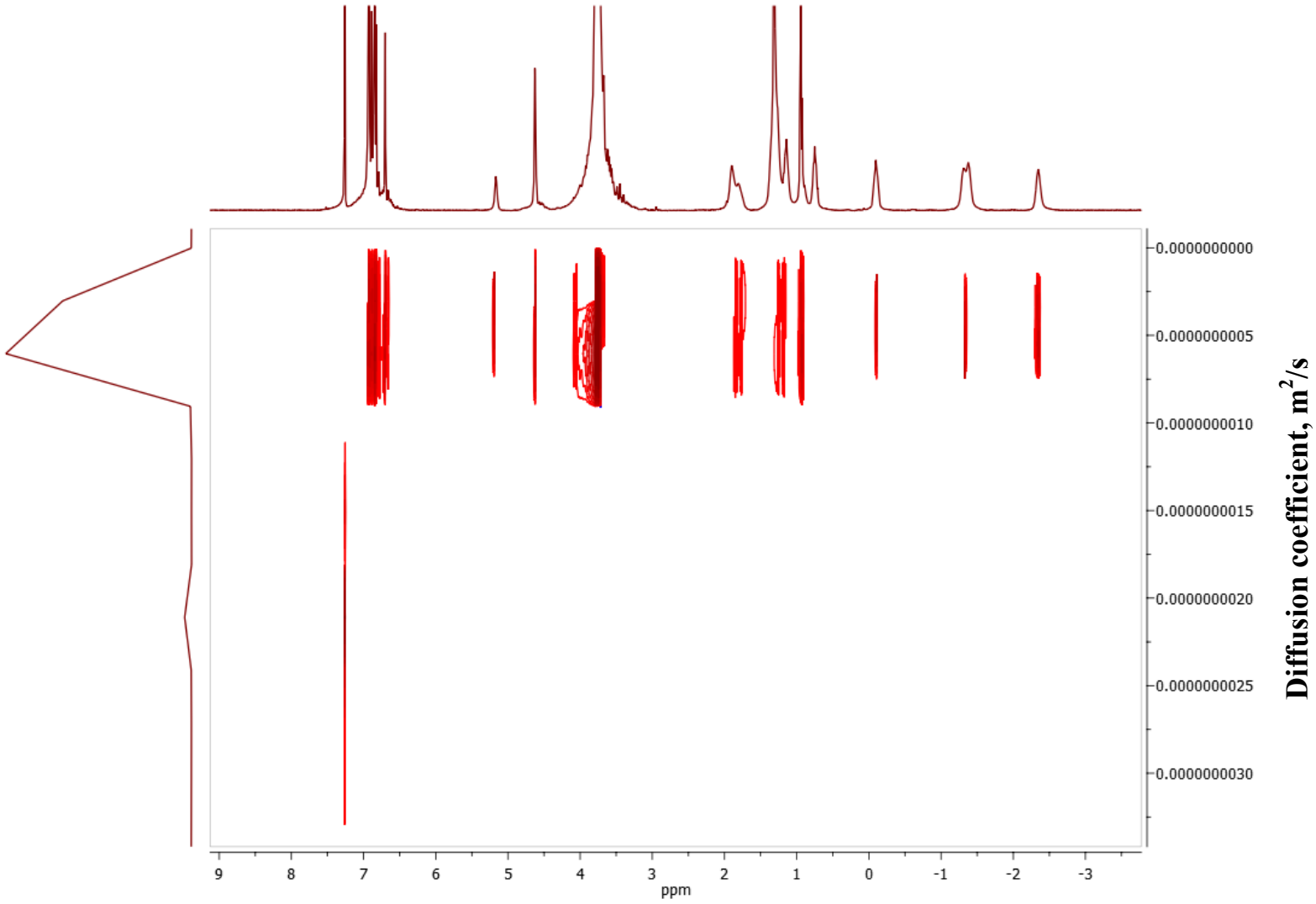

Fig. S40. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), 1×10^{-2} M, DMSO-d_6, 293 K, 400 MHz.

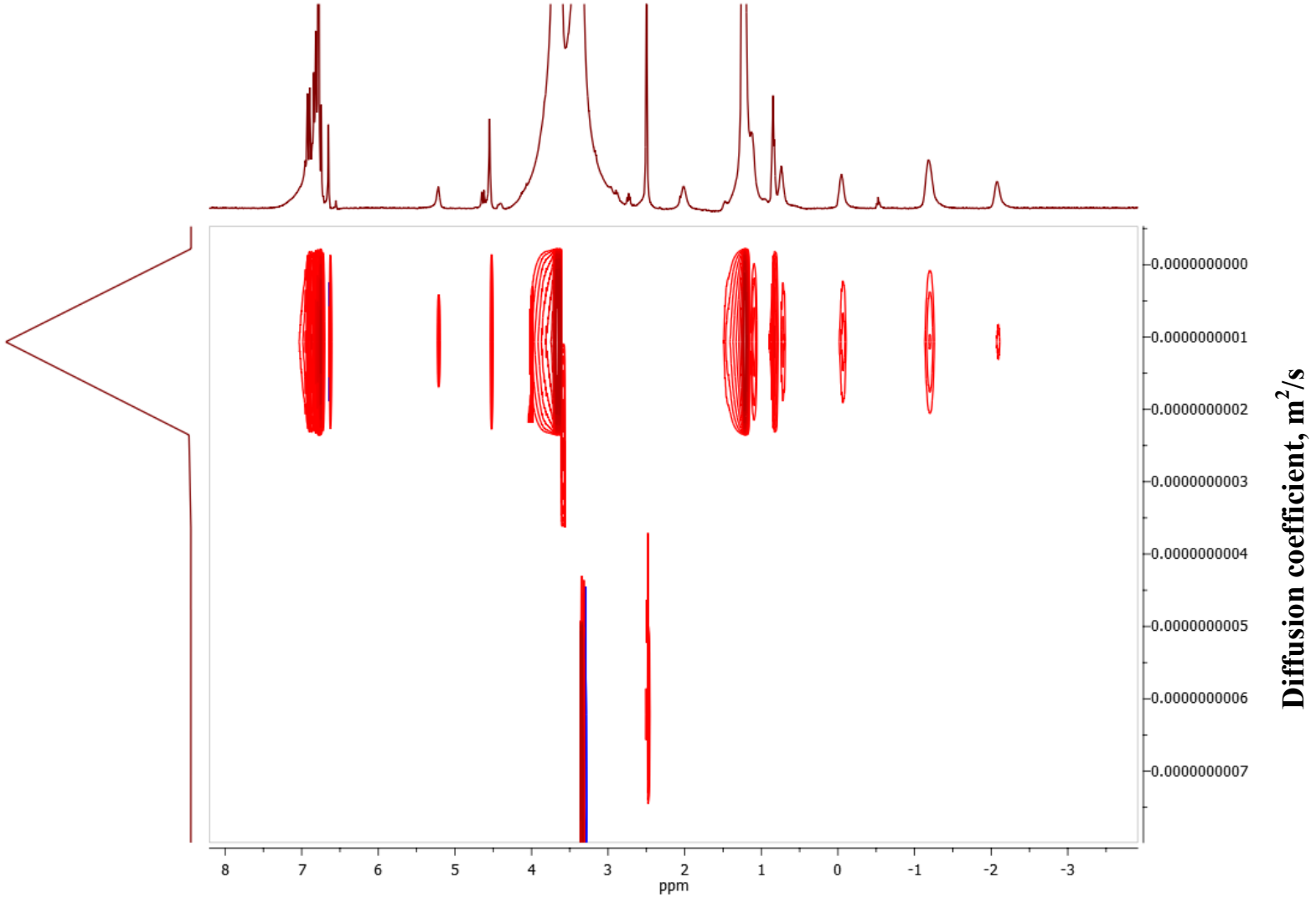

Fig. S41. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), 5×10^{-3} M, DMSO-d_6, 293 K, 400 MHz.

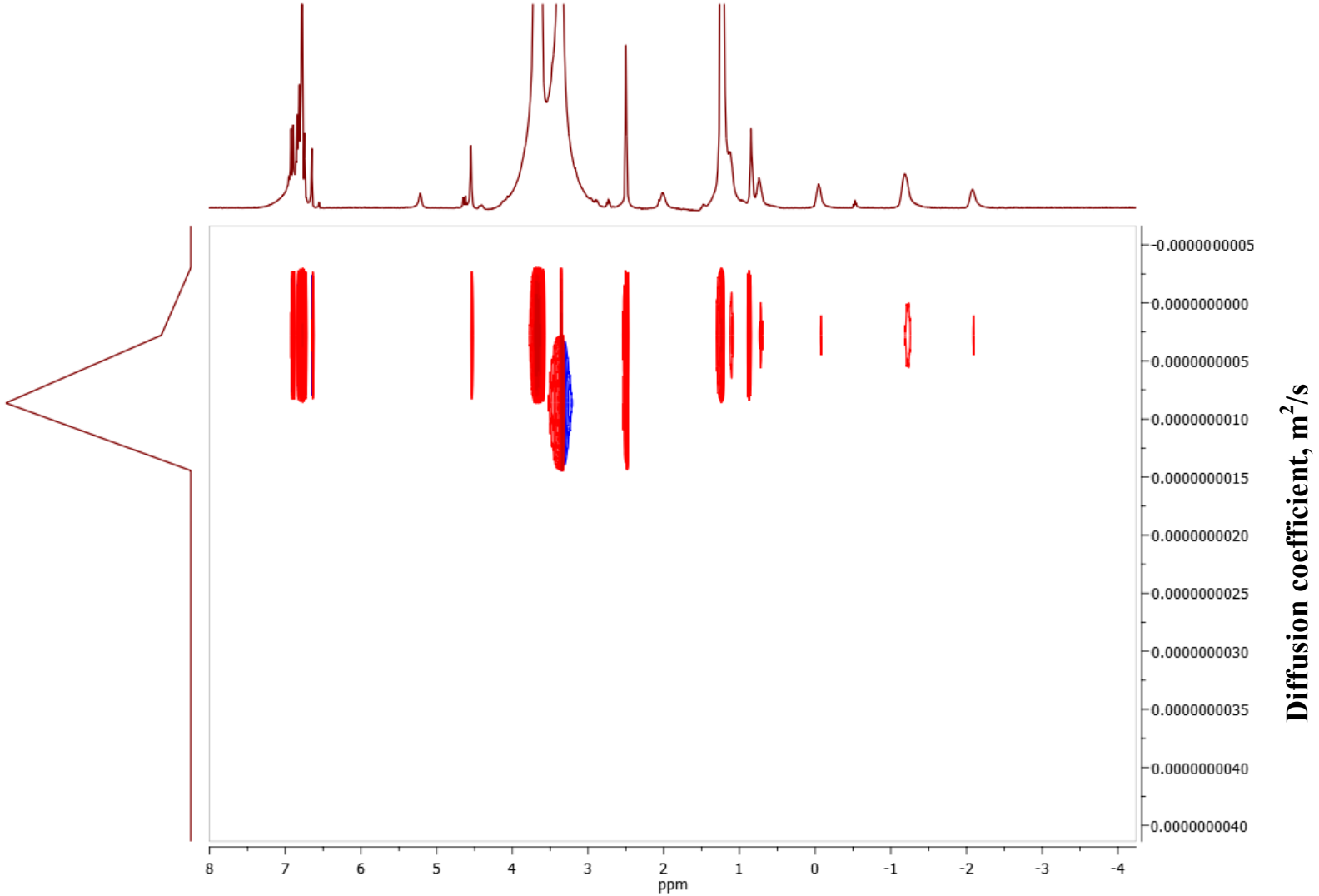

Fig. S42. ^{1}H NMR (DOSY) spectrum of 4-[(N-aminooctadecyl)-carbamoylmethoxy]-8,14,18,23,26,28,31,32,35-nonamethoxypillar[5]arene (6), 1×10^{-3} M, DMSO-d_6, 293 K, 400 MHz.

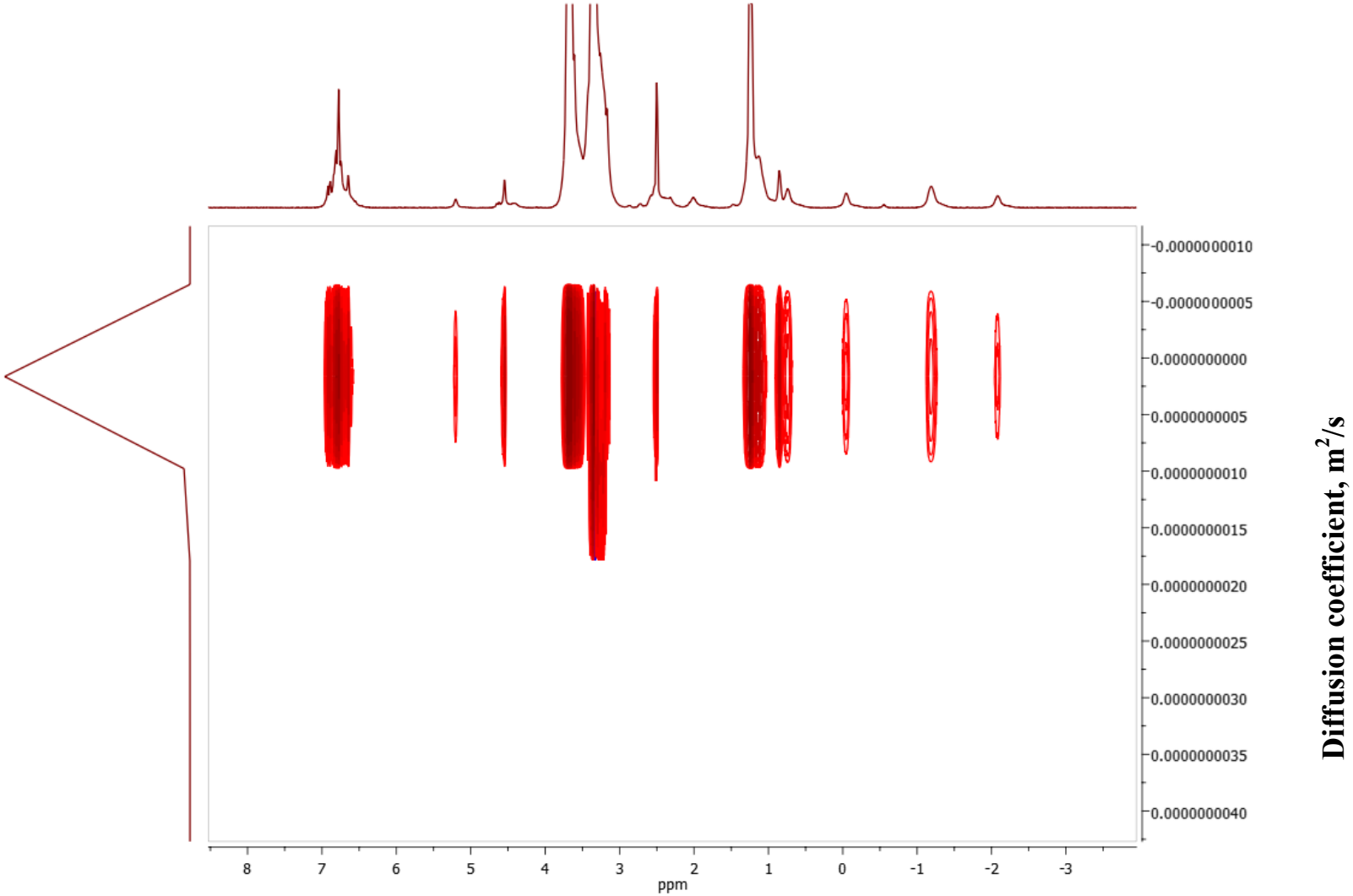

Table S1. The size distribution by number and polydispersity index of pillar[5]arenes 4-6 (1×10^{-5} - 1×10^{-3} M) in $CHCl_3$ and DMSO.

Concentration of pillar[5]arene	The particle size (d), nm / PDI					
	4		**5**		**6**	
	DMSO	$CHCl_3$	DMSO	$CHCl_3$	DMSO	$CHCl_3$
1×10^{-3}	714±61(0.71)	523±103 (0.82)	943±33 (1)	1729±76 (1)	785±55 (0.57)	2970±308 (0.98)
1×10^{-4}	813±38 (0.70)	477±46 (0.41)	855±22 (0.37)	1159±306 (0.54)	796±21 (0.52)	1591 (0.71)
1×10^{-5}	841±38 (0.62)	100±3 (0.28)	851±50 (0.35)	365±20 (0.22)	885±50 (0.49)	472±66 (0.26)

Table S2. Size of particles based on self-associates obtained with macrocycles 4-6 by using NTA method in $CHCl_3$.

Compound	Concentration	Bin Center (nm)	Concentration (10^6 particles/ml)	Mean Mode Average D_h (nm)	Total Concentration Average concentration (10^6 particles/ml)
4	1×10^{-5}	51	0.013	121±18	35±3
		66	0.016		
		87	0.021		
		104	0.083		
		144	0.197		
		185	0.200		
		236	0.199		
		288	0.099		
		353	0.041		
	1×10^{-4}	33	0.031	150±27	59±7
		42	0.062		
		63	0.053		
		93	0.205		
		120	0.298		
		142	0.325		
		177	0.235		
		254	0.155		
		347	0.062		
	1×10^{-3}	38	0.015	168±13	68 ± 2
		52	0.047		
		63	0.75		
		112	0.124		
		141	0.265		

		181	0.269		
		224	0.268		
		280	0.166		
		343	0.081		
		405	0.035		
5	1×10^{-5}	26	0.10	103±7	38±1
		56	0.15		
		66	0.17		
		90	0.25		
		104	0.21		
		130	0.22		
		205	0.12		
		286	0.06		
	1×10^{-4}	25	0.13	130±5	42±1
		41	0.12		
		55	0.14		
		71	0.15		
		131	0.35		
		190	0.12		
		244	0.07		
		333	0.02		
	1×10^{-3}	50	0.04	157±8	68±5
		76	0.15		
		94	0.14		
		117	0.20		
		147	0.40		
		170	0.37		
		277	0.19		
		378	0.05		
		577	0.01		
6	1×10^{-5}	52	0.02	123±8	40±4
		71	0.08		
		86	0.16		

		110	0.34		
		127	0.37		
		182	0.15		
		243	0.05		
		317	0.05		
	1×10^{-4}	33	0.07	136±5	51±2
		52	0.08		
		71	0.14		
		92	0.17		
		132	0.33		
		156	0.29		
		228	0.132		
		296	0.09		
	1×10^{-3}	30	0.05	138±4	118±5
		48	0.11		
		60	0.18		
		80	0.33		
		114	0.62		
		141	0.76		
		181	0.52		
		268	0.23		
		334	0.08		

Table S3. Size of particles based on self-associates obtained with macrocycles 4-6 by using NTA method in DMSO.

Compound	Concentration	Bin Center (nm)	Concentration (10^6 particles/ml)	Mean Mode Average D_h (nm)	Total Concentration Average concentration (10^6 particles/ml)
4	1×10^{-5}	50	0.06	92±5	21±1
		77	0.15		
		101	0.19		
		123	0.15		
		160	0.10		
		210	0.04		
	1×10^{-4}	44	0.48	100±3	138±2
		73	1.21		
		90	1.37		
		111	1.16		
		151	0.54		
		193	0.18		
	1×10^{-3}	57	1.31	110±5	555±18
		105	4.49		
		126	4.27		
		189	1.86		
5	1×10^{-5}	69	0.87	82±8	89±9
		82	0.86		
		128	0.58		
		181	0.24		
		281	0.03		
	1×10^{-4}	52	0.51	110±5	111±5
		81	0.59		

		110	0.74		
		134	0.62		
		160	0.48		
		253	0.11		
		323	0.05		
6	1×10^{-5}	52	0.38	82±6	71±5
		70	0.47		
		82	0.49		
		105	0.52		
		138	0.39		
		180	0.24		
		260	0.05		
	1×10^{-4}	34	0.20	93±3	122±8
		46	0.30		
		98	1.17		
		118	0.87		
		167	0.40		
		252	0.13		
		349	0.064		

Fig. S43. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 4 (0.01 M) + 1% MeOH; b) 4 (0.01 M).

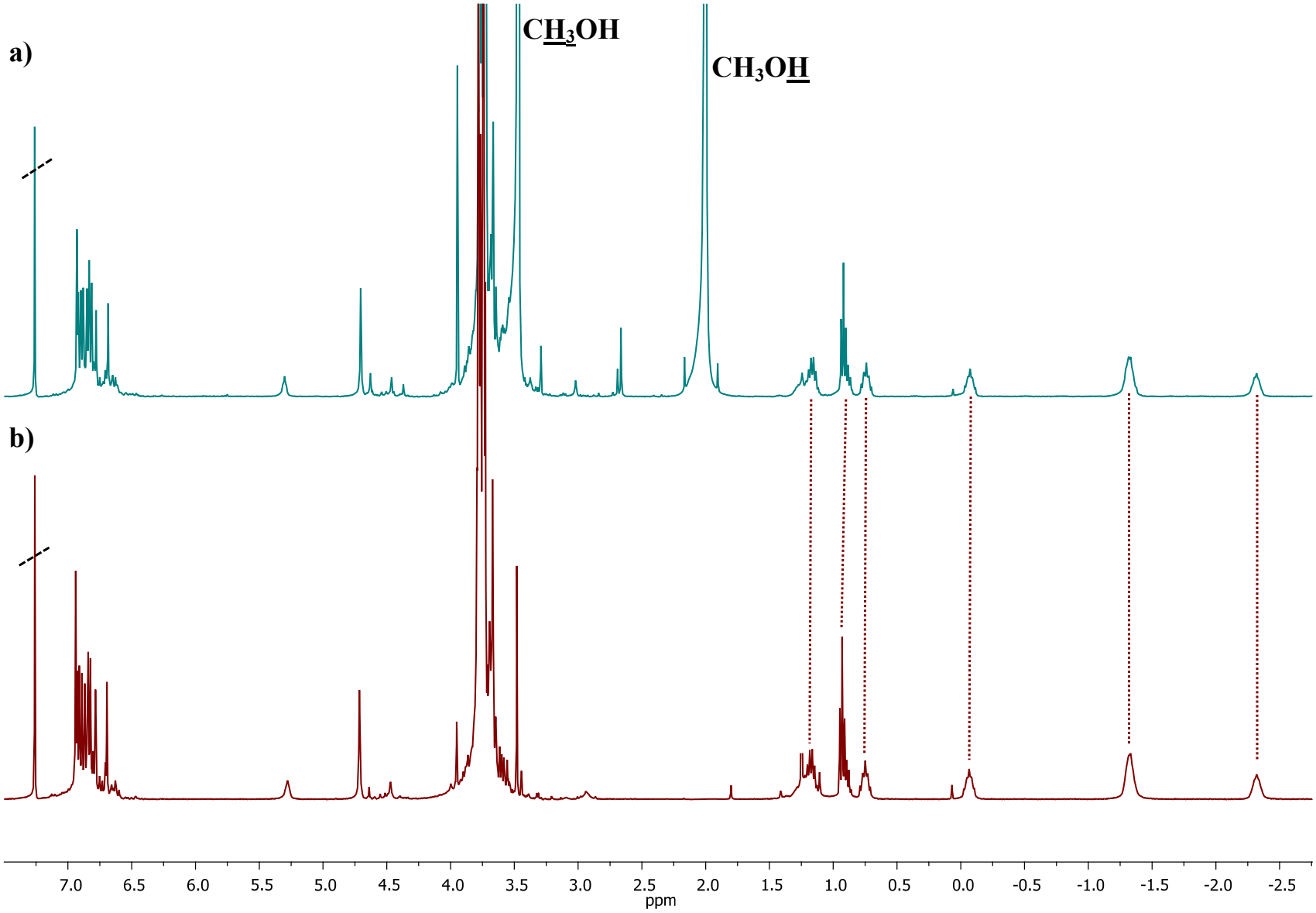

Fig. S44. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 4 (0.01 M) + 1% MeOH; b) 4 (0.01 M).

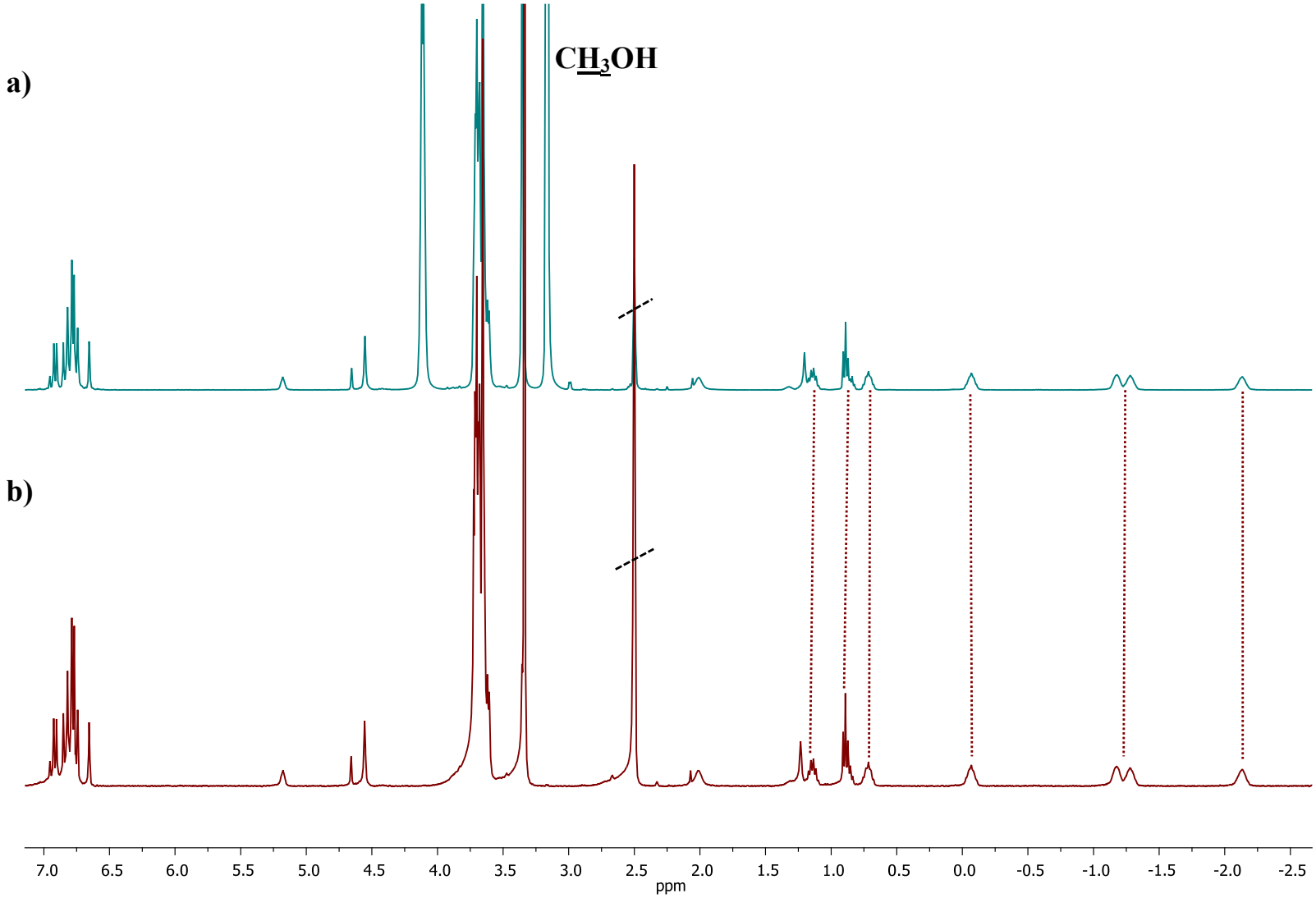

Fig. S45. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 5 (0.01 M) + 1% MeOH; b) 5 (0.01 M).

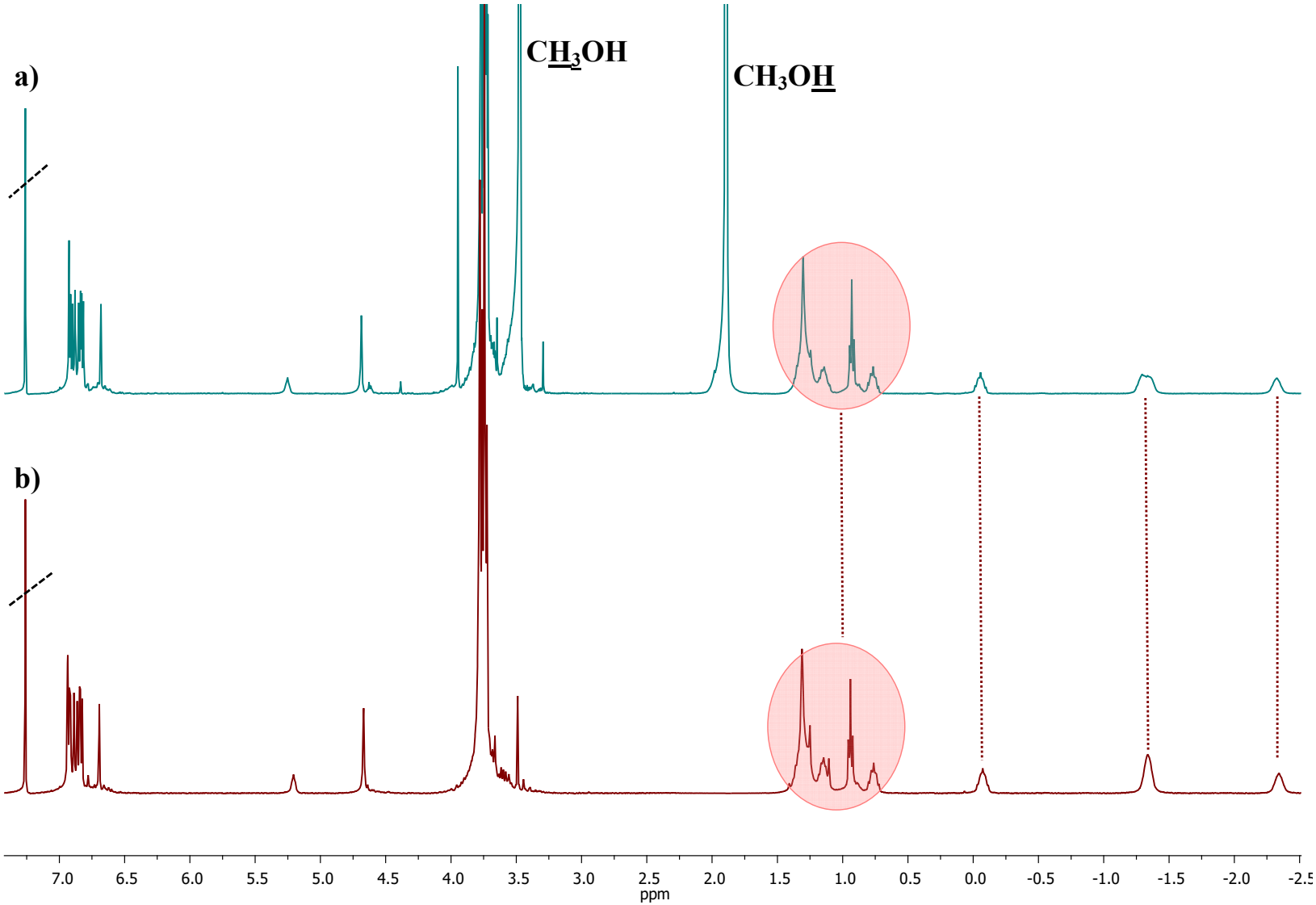

Fig. S46. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 5 (0.01 M) + 1% MeOH; b) 5 (0.01 M).

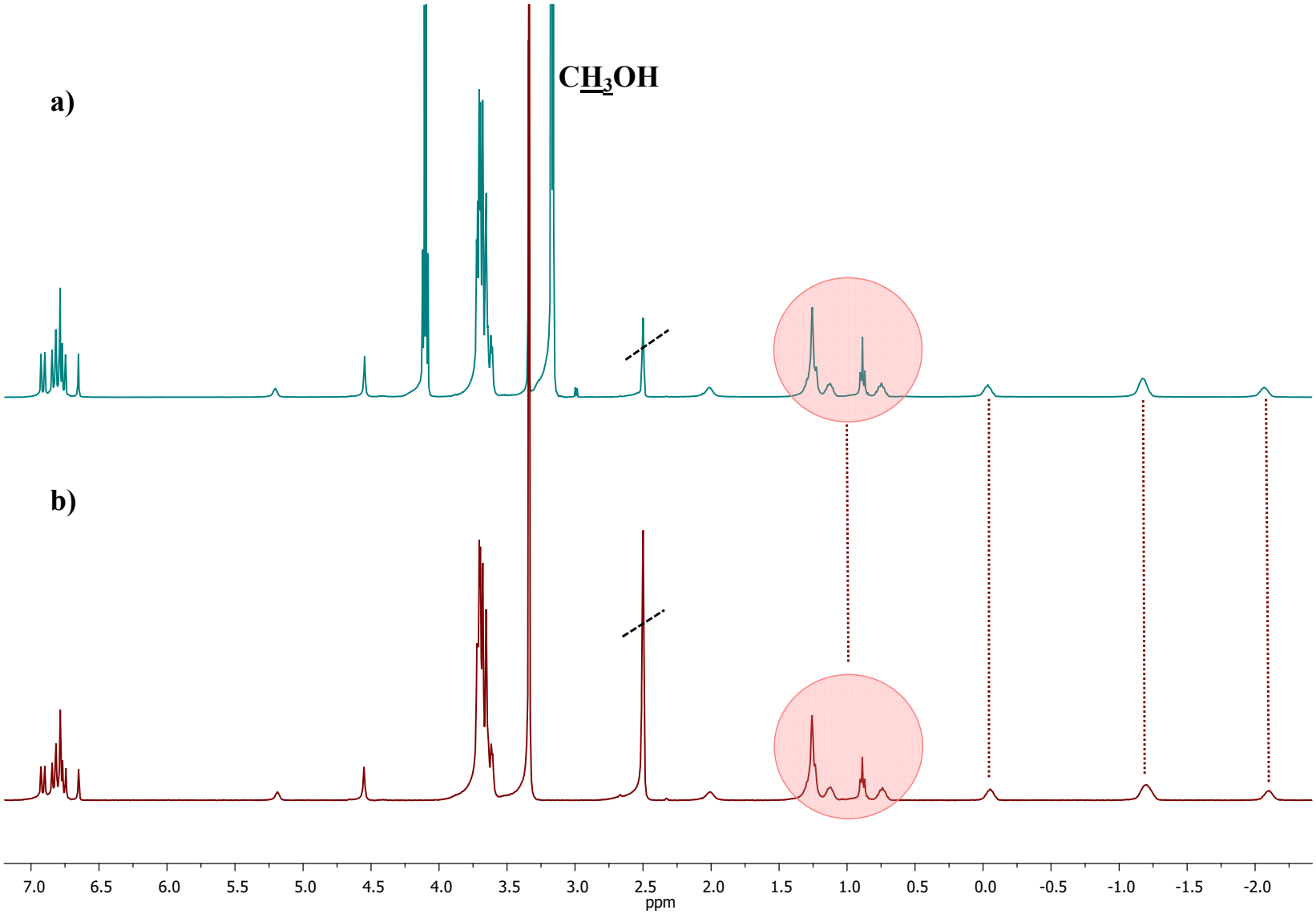

Fig. S47. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 6 (0.01 M) + 1% MeOH; b) 6 (0.01 M).

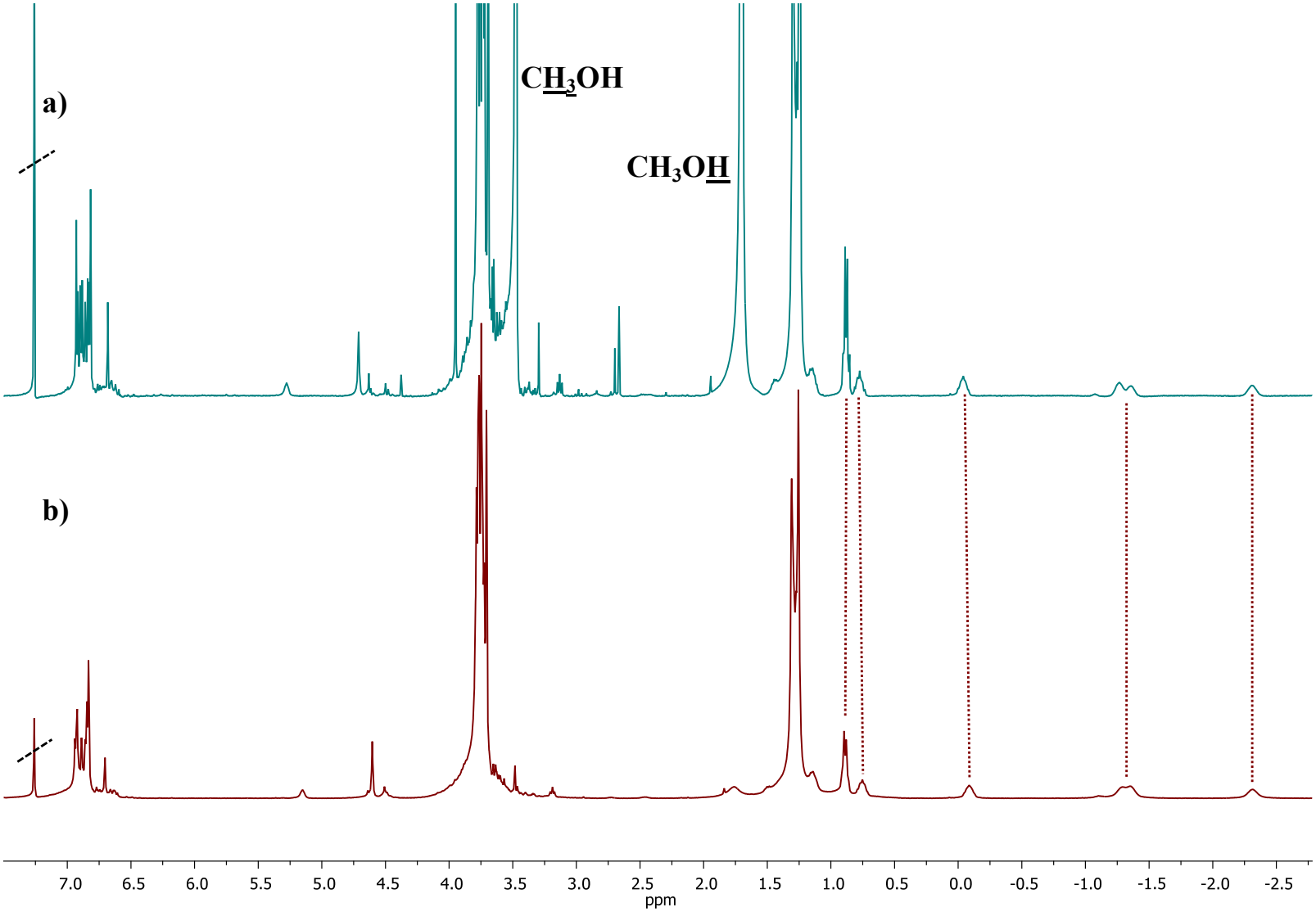

Fig. S48. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 6 (0.01 M) + 1% MeOH; b) 6 (0.01 M).

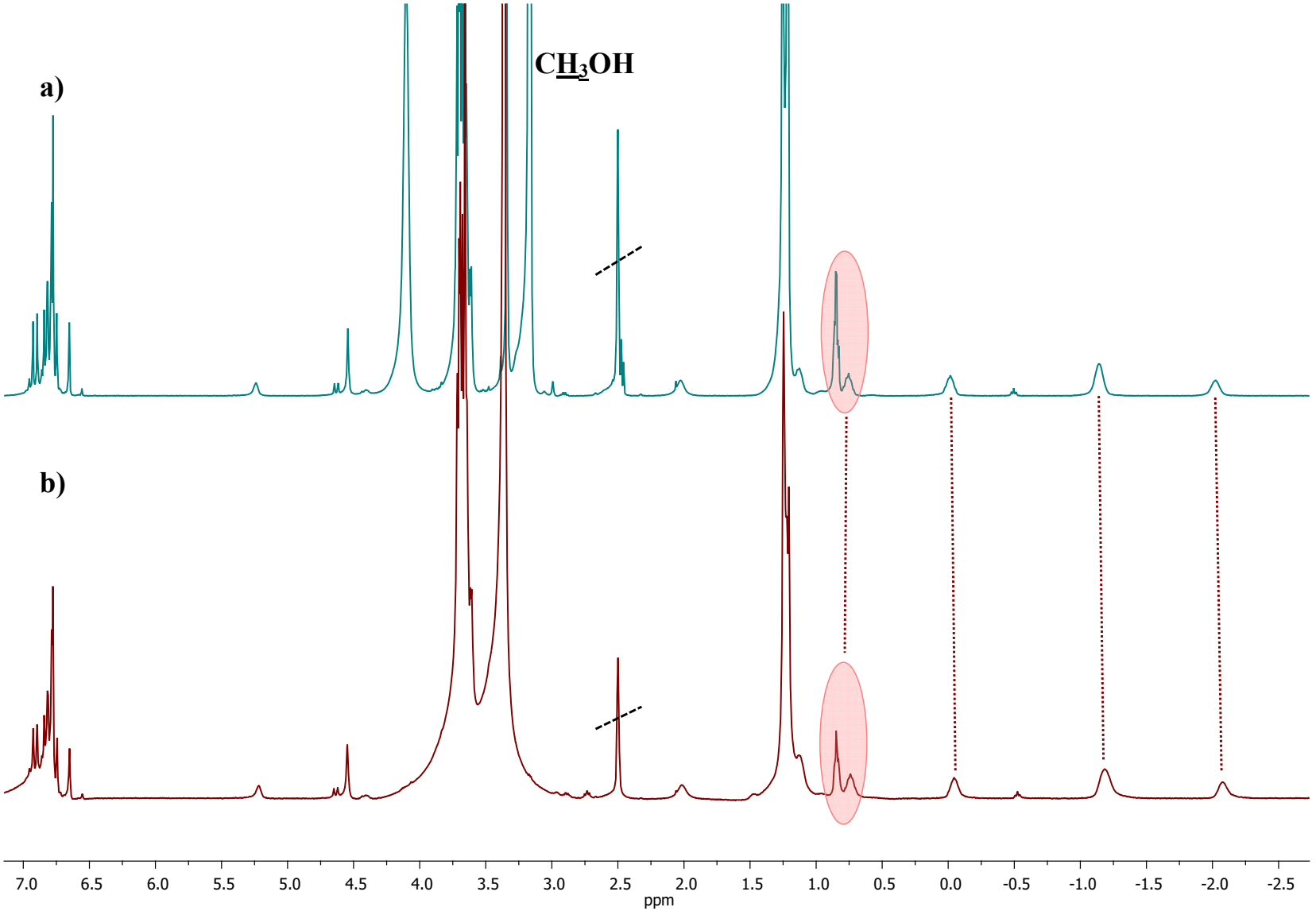

Fig. S49. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 4 (0.01 M) + 1% CH_3CN; b) 4 (0.01 M).

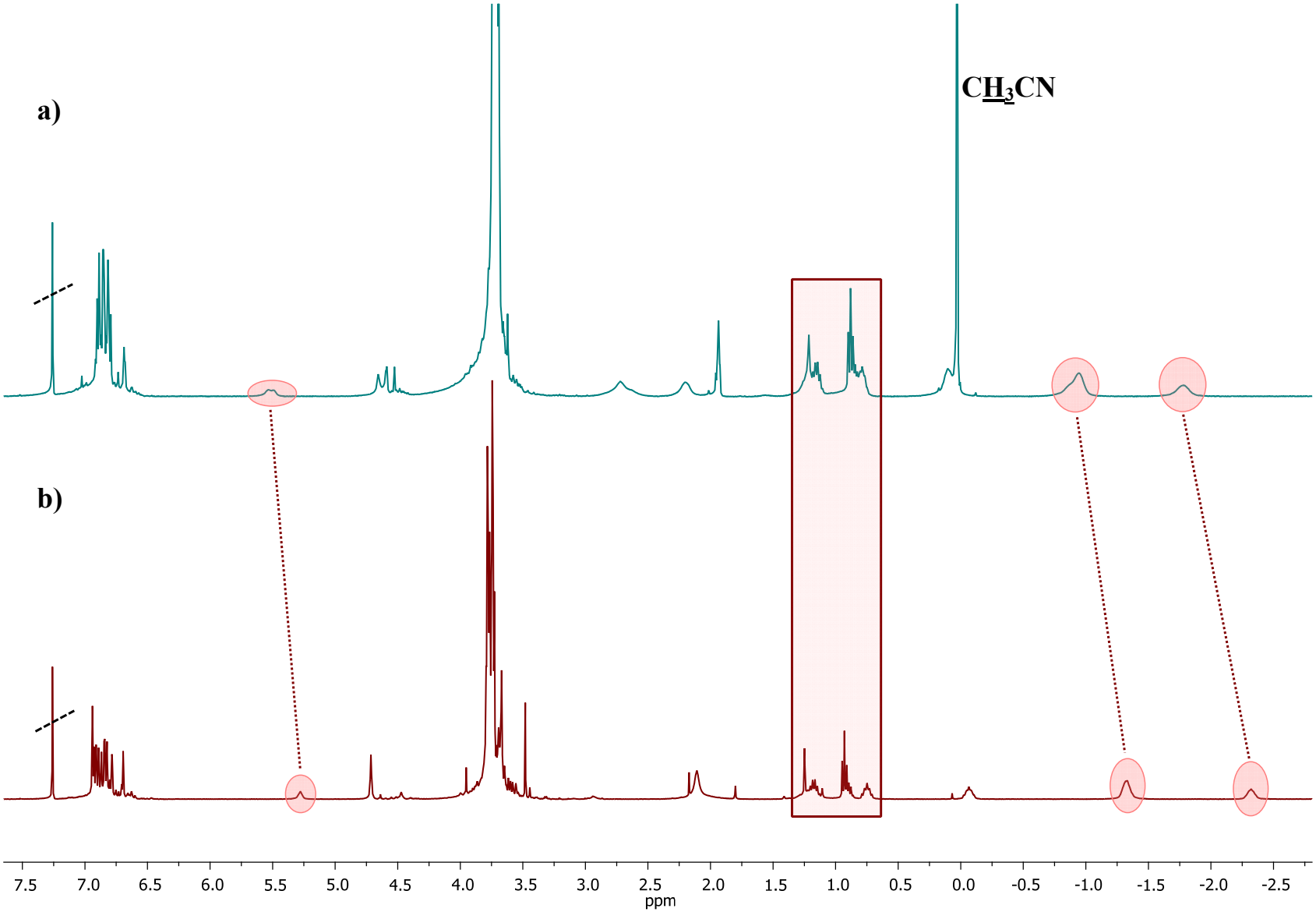

Fig. S50. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 4 (0.01 M) + 1% CH_3CN; b) 4 (0.01 M).

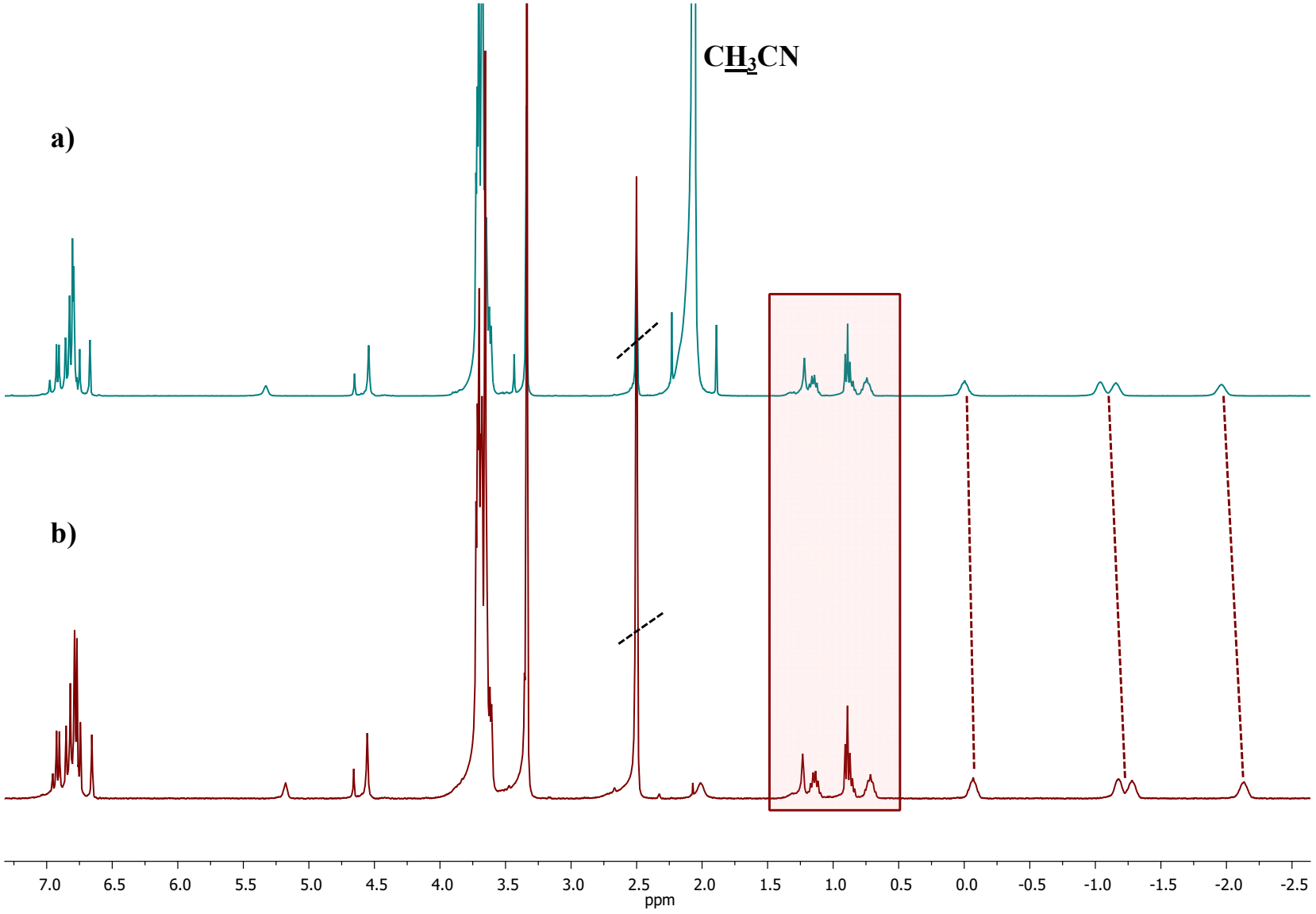

Fig. S51. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 5 (0.01 M) + 1% CH_3CN; b) 5 (0.01 M).

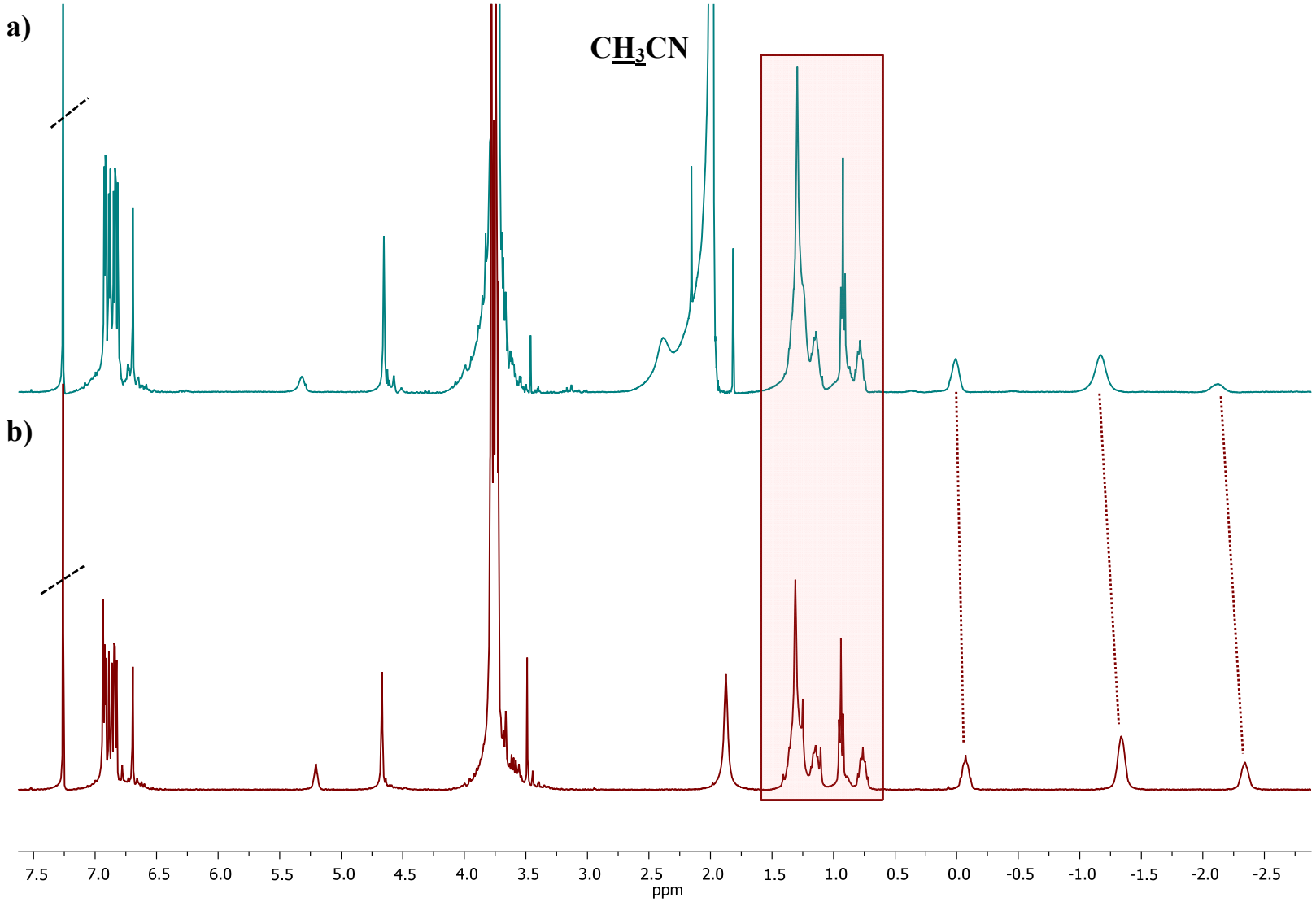

Fig. S52. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 5 (0.01 M) + 1% CH_3CN; b) 5 (0.01 M).

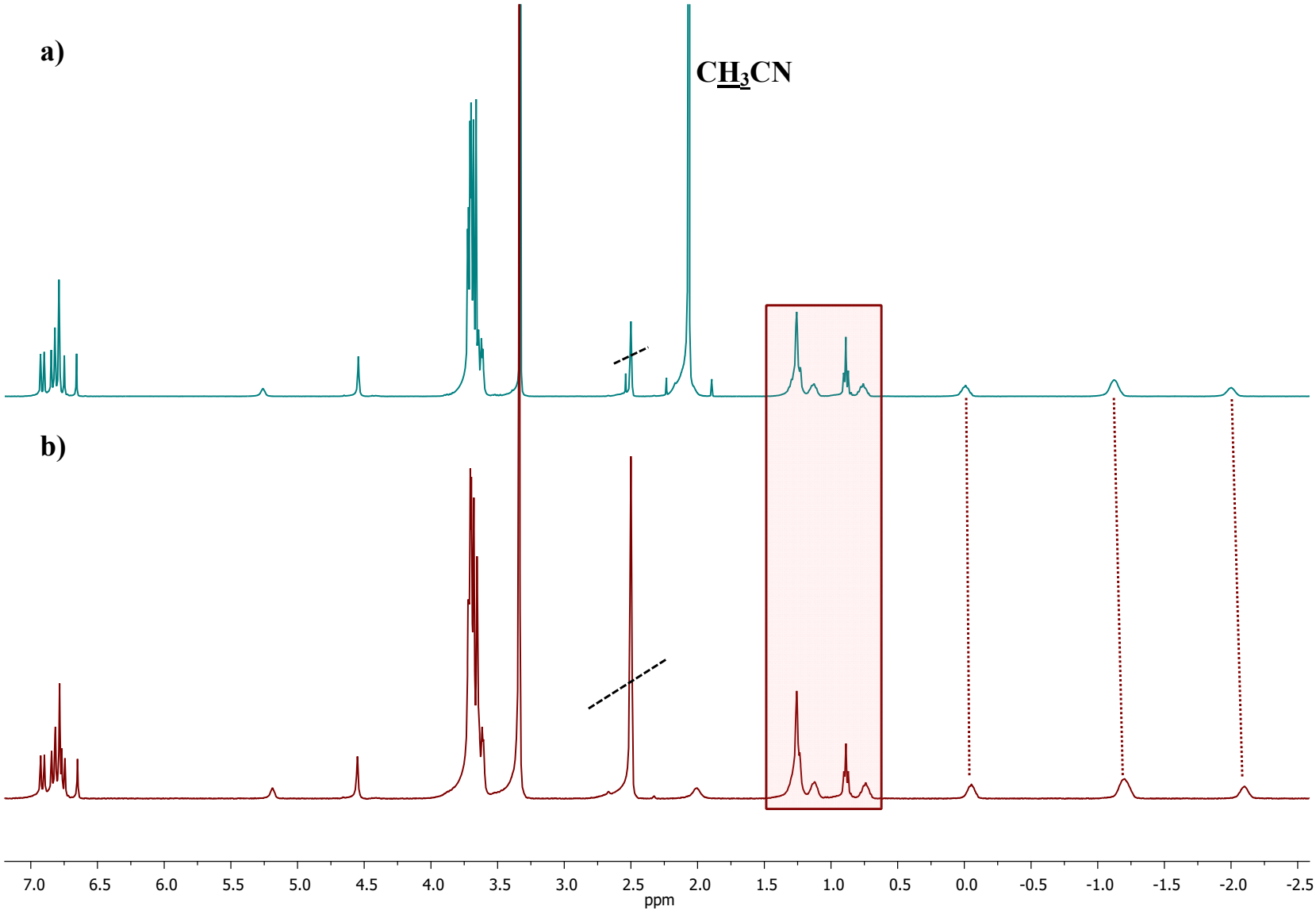

Fig. S53. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 6 (0.01 M) + 1% CH_3CN; b) 6 (0.01 M).

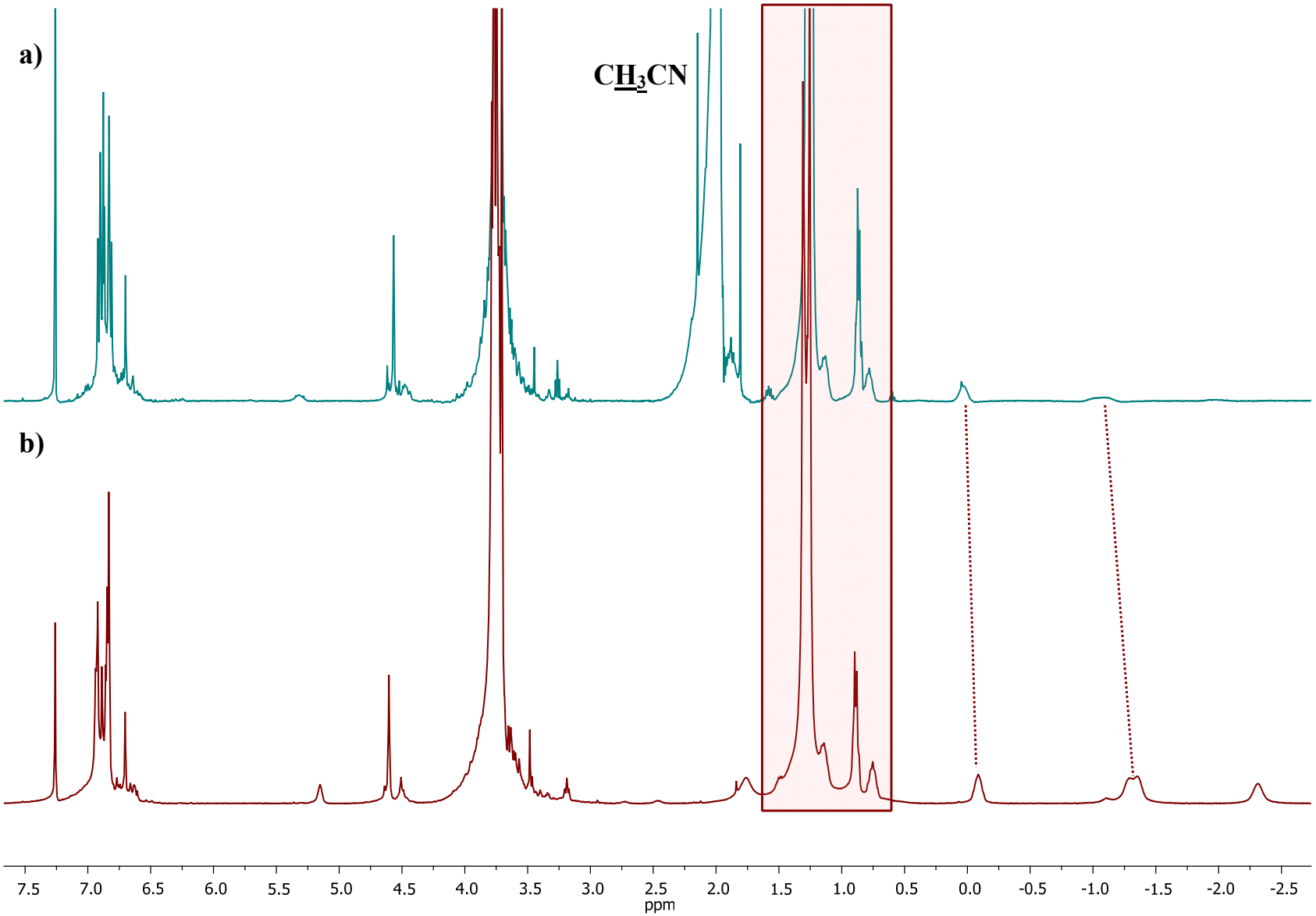

Fig. S54. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 6 (0.01 M) + 1% CH_3CN; b) 6 (0.01 M).

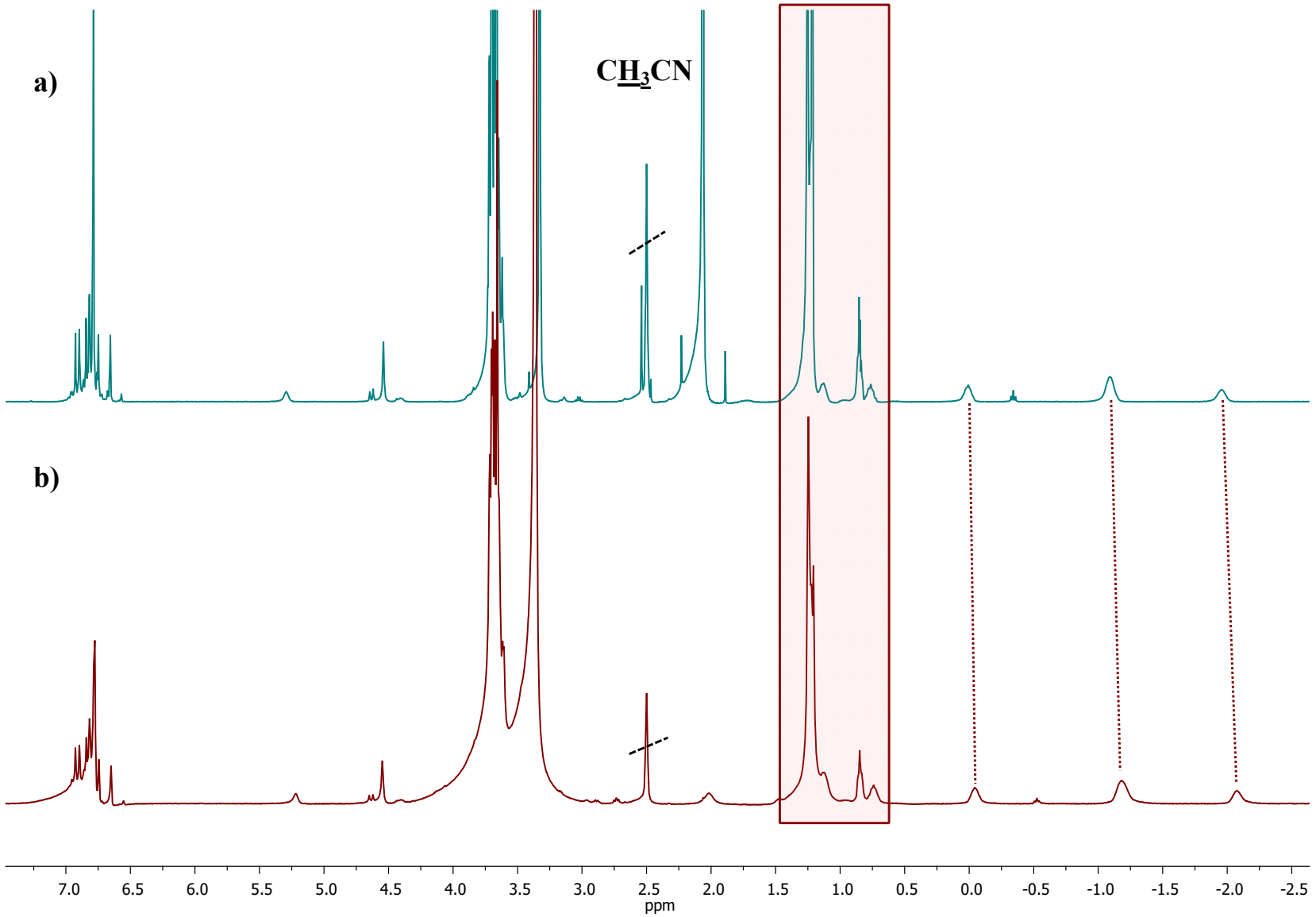

Fig. S55. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 4 (0.01 M) + 1% H_2O; b) 4 (0.01 M).

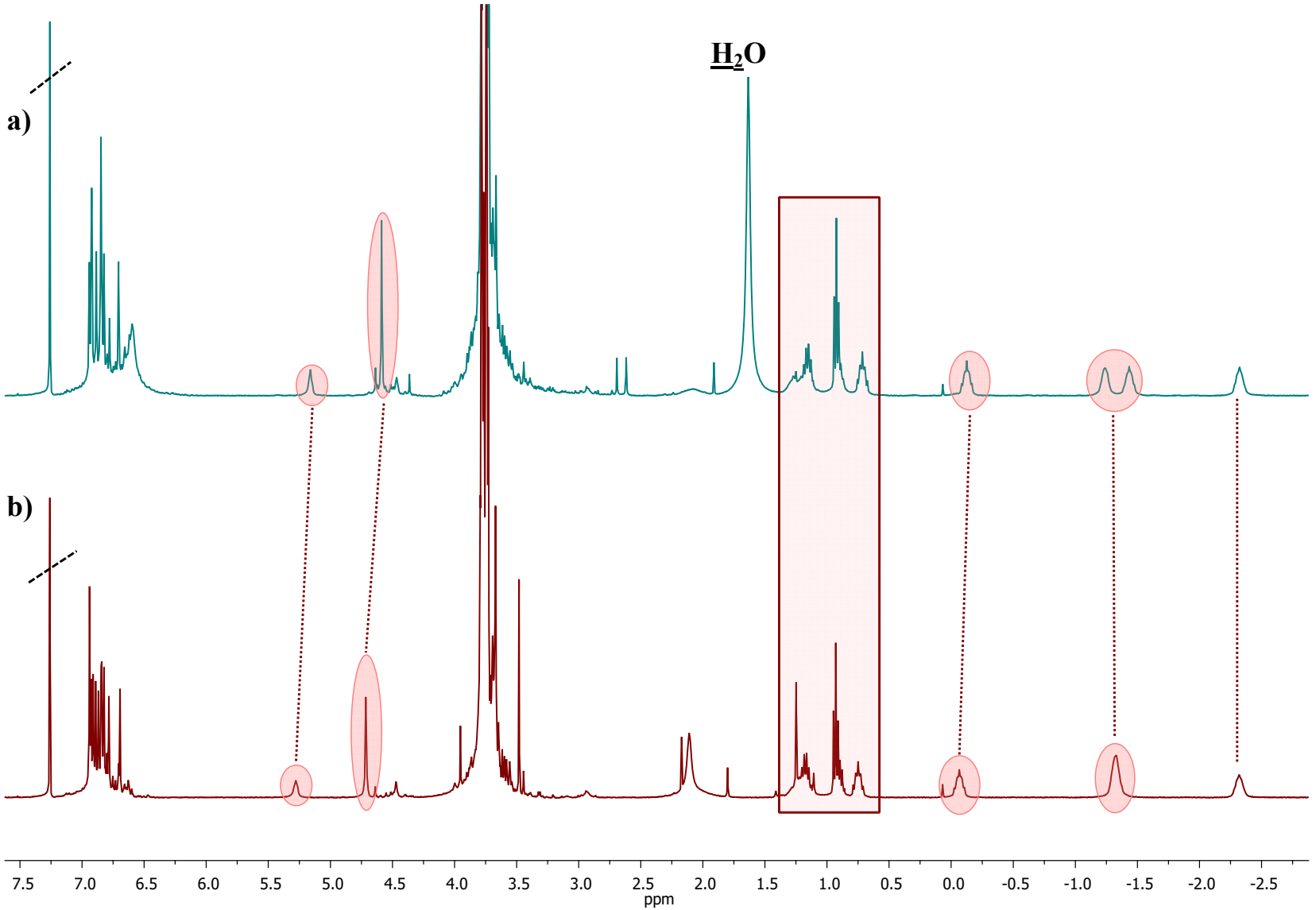

Fig. S56. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 4 (0.01 M) + 1% H_2O; b) 4 (0.01 M).

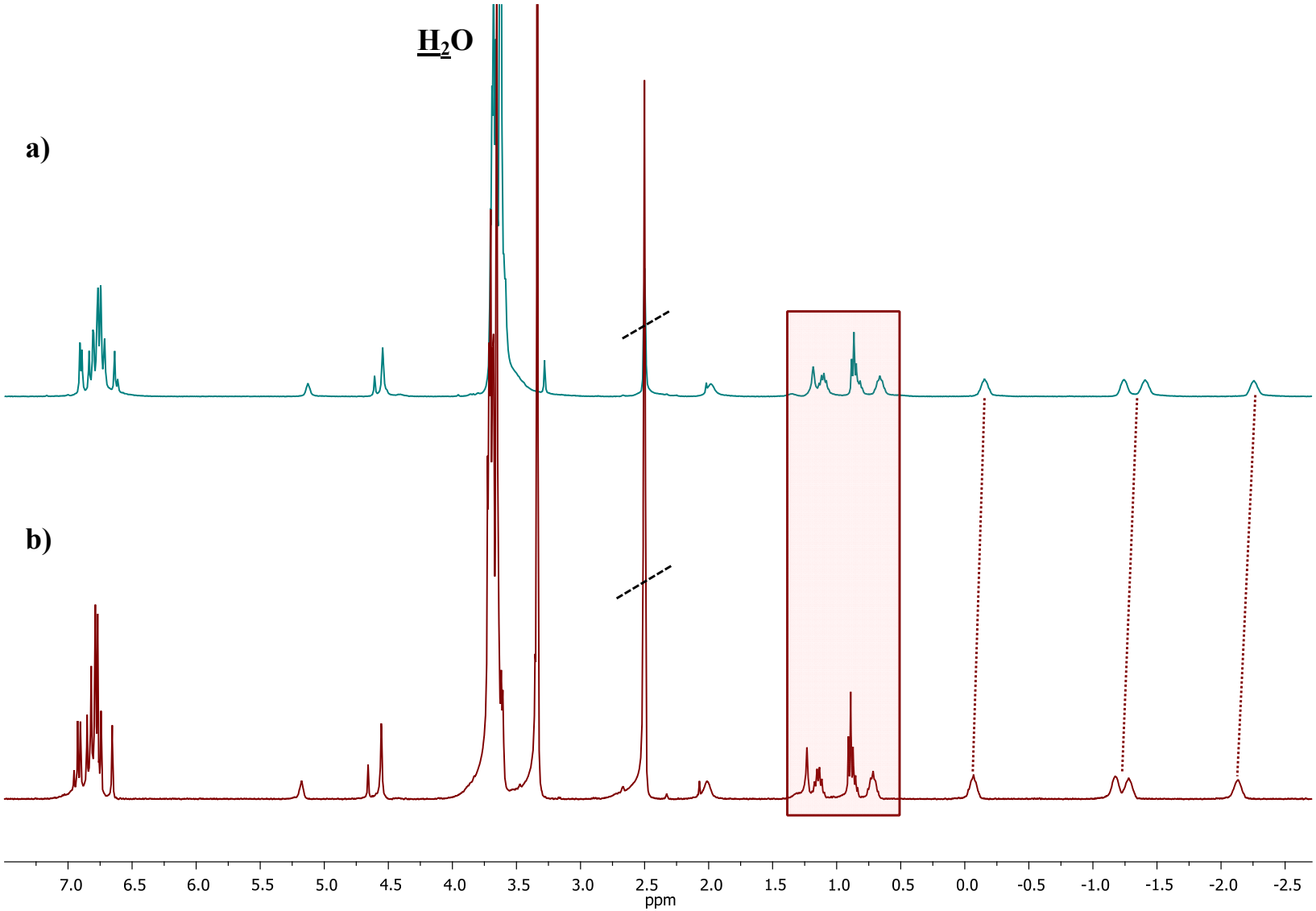

Fig. S57. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 5 (0.01 M) + 1% H_2O; b) 5 (0.01 M).

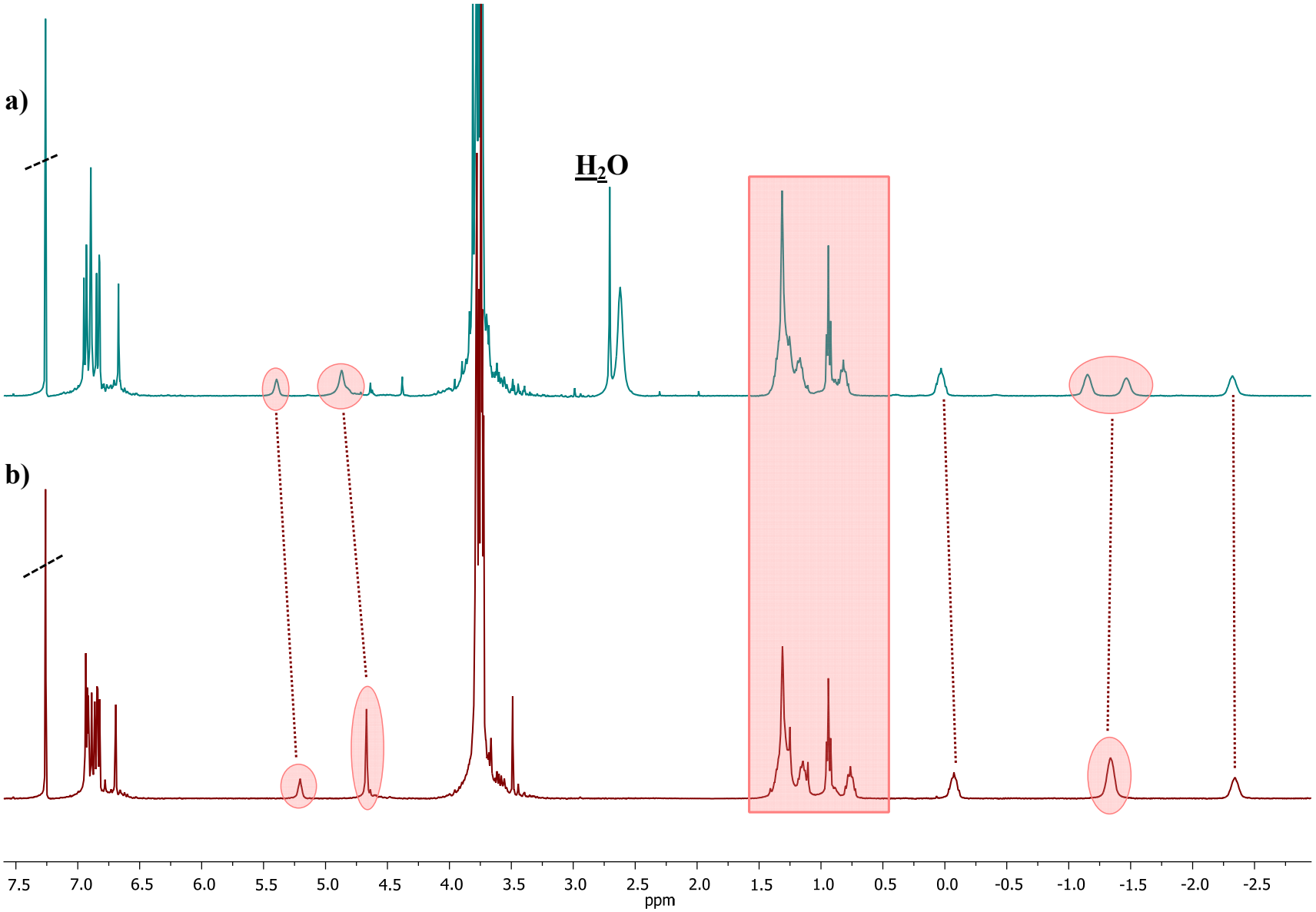

Fig. S58. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 5 (0.01 M) + 1% H_2O; b) 5 (0.01 M).

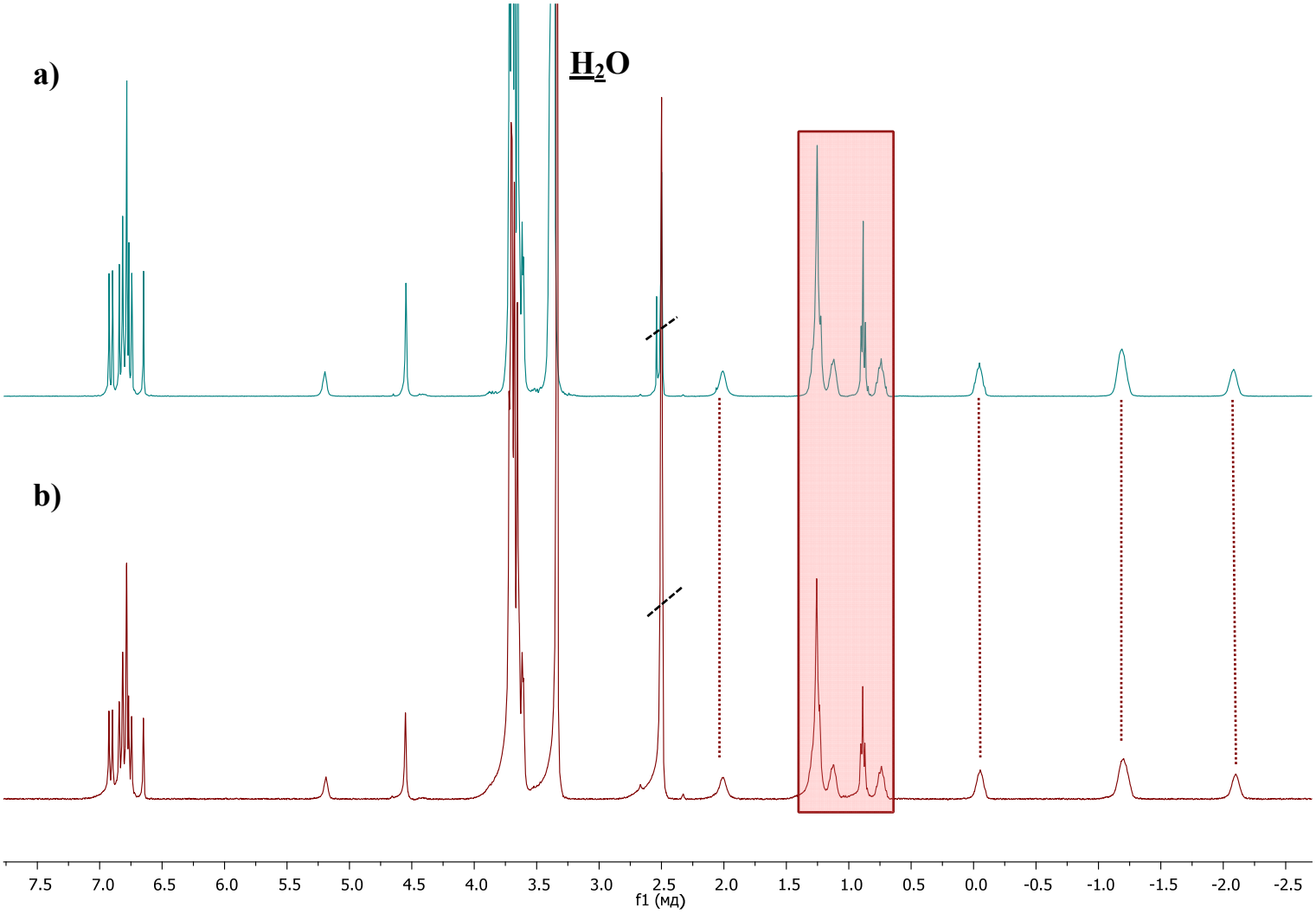

Fig. S59. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) 6 (0.01 M) + 1% H_2O; b) 6 (0.01 M).

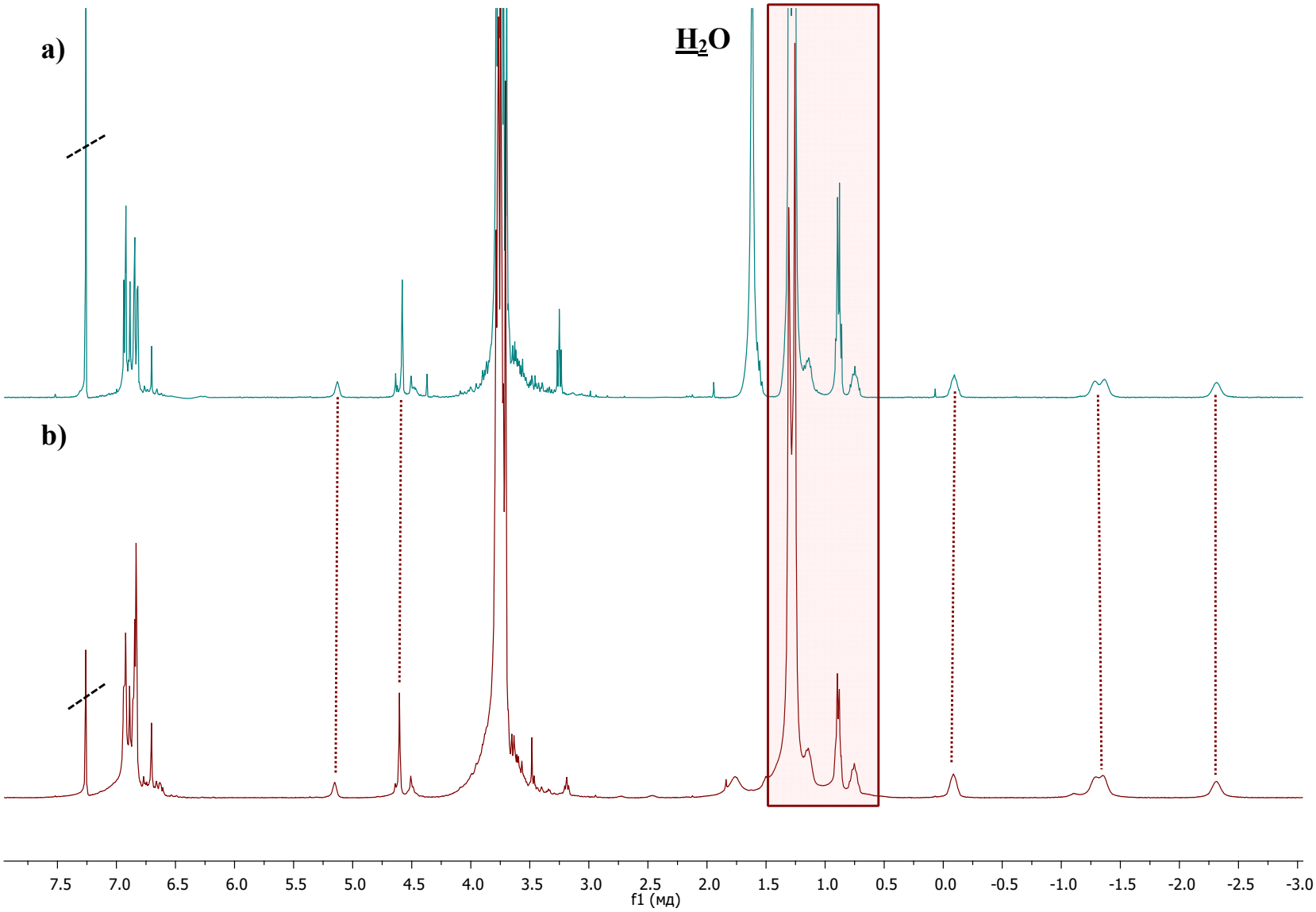

Fig. S60. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) 6 (0.01 M) + 1% H_2O; b) 6 (0.01 M).

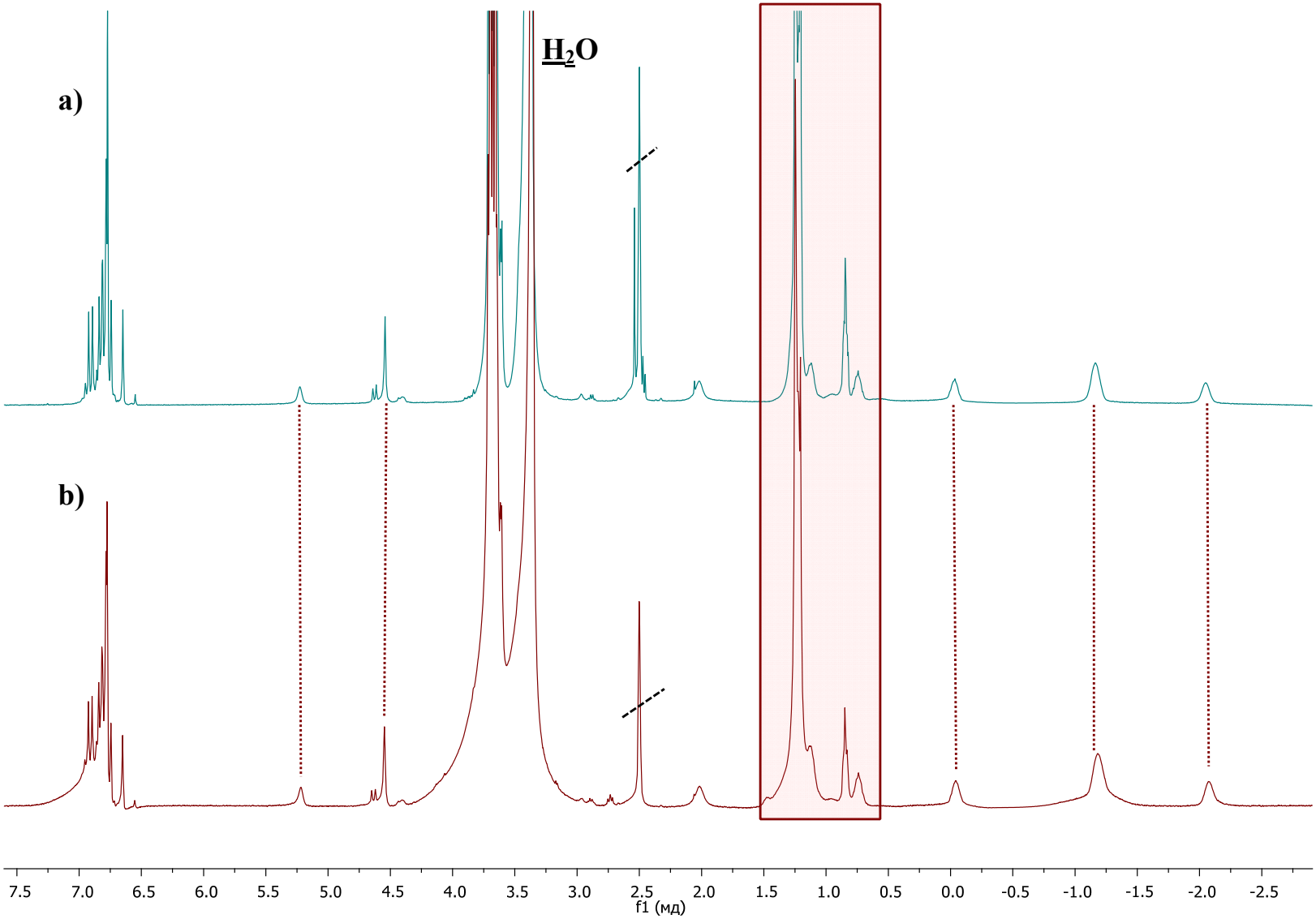

Fig. S61. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) BMIIm (0.01 M); b) 4 (0.01 M) + BMIIm (0.01 M); c) 4 (0.01 M).

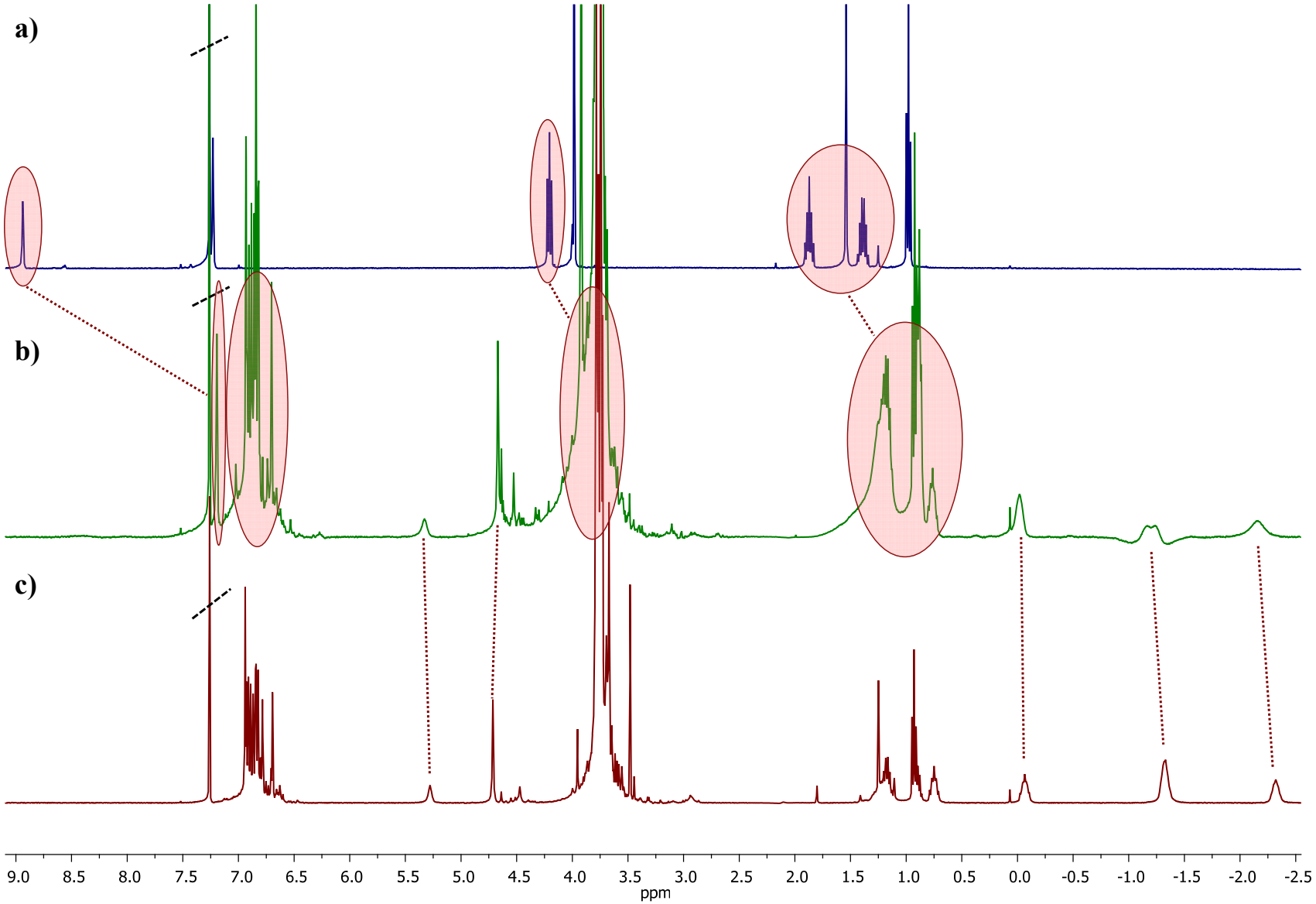

Fig. S62. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) BMIIm (0.01 M); b) 4 (0.01 M) + BMIIm (0.01 M); c) 4 (0.01 M).

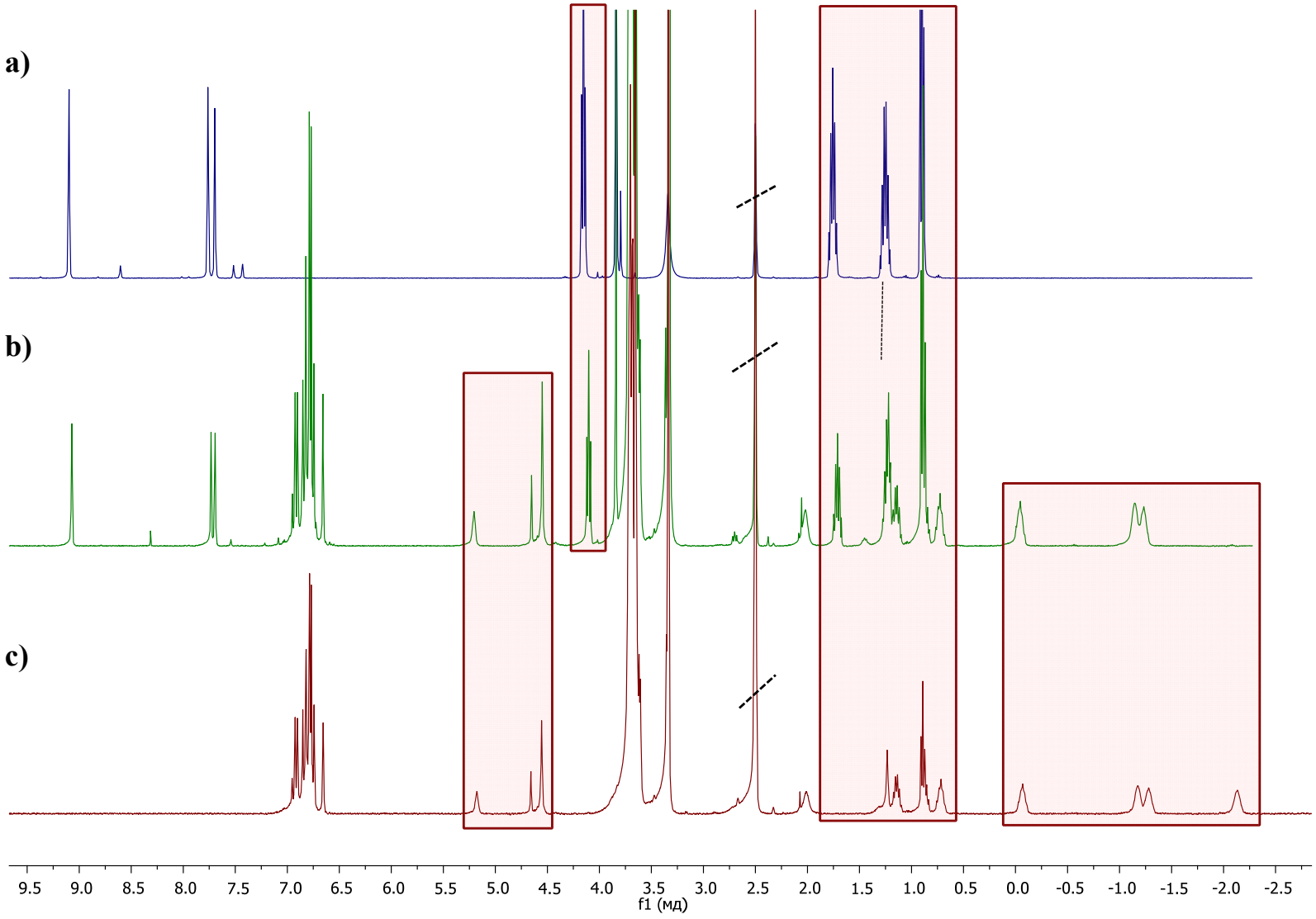

Fig. S63. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) BMIIm (0.01 M); b) 5 (0.01 M) + BMIIm (0.01 M); c) 5 (0.01 M).

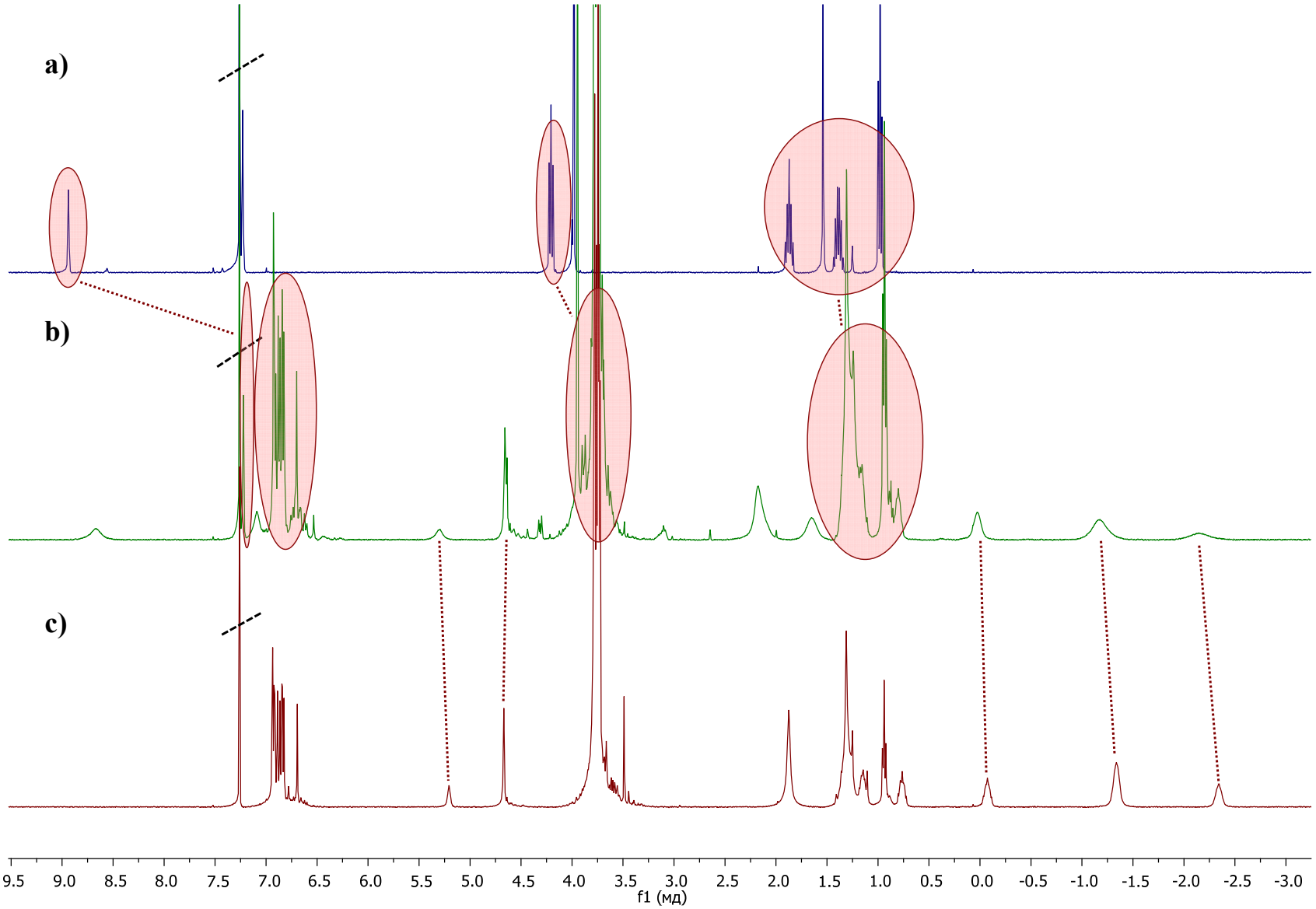

Fig. S64. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) BMIIm (0.01 M); b) 5 (0.01 M) + BMIIm (0.01 M); c) 5 (0.01 M).

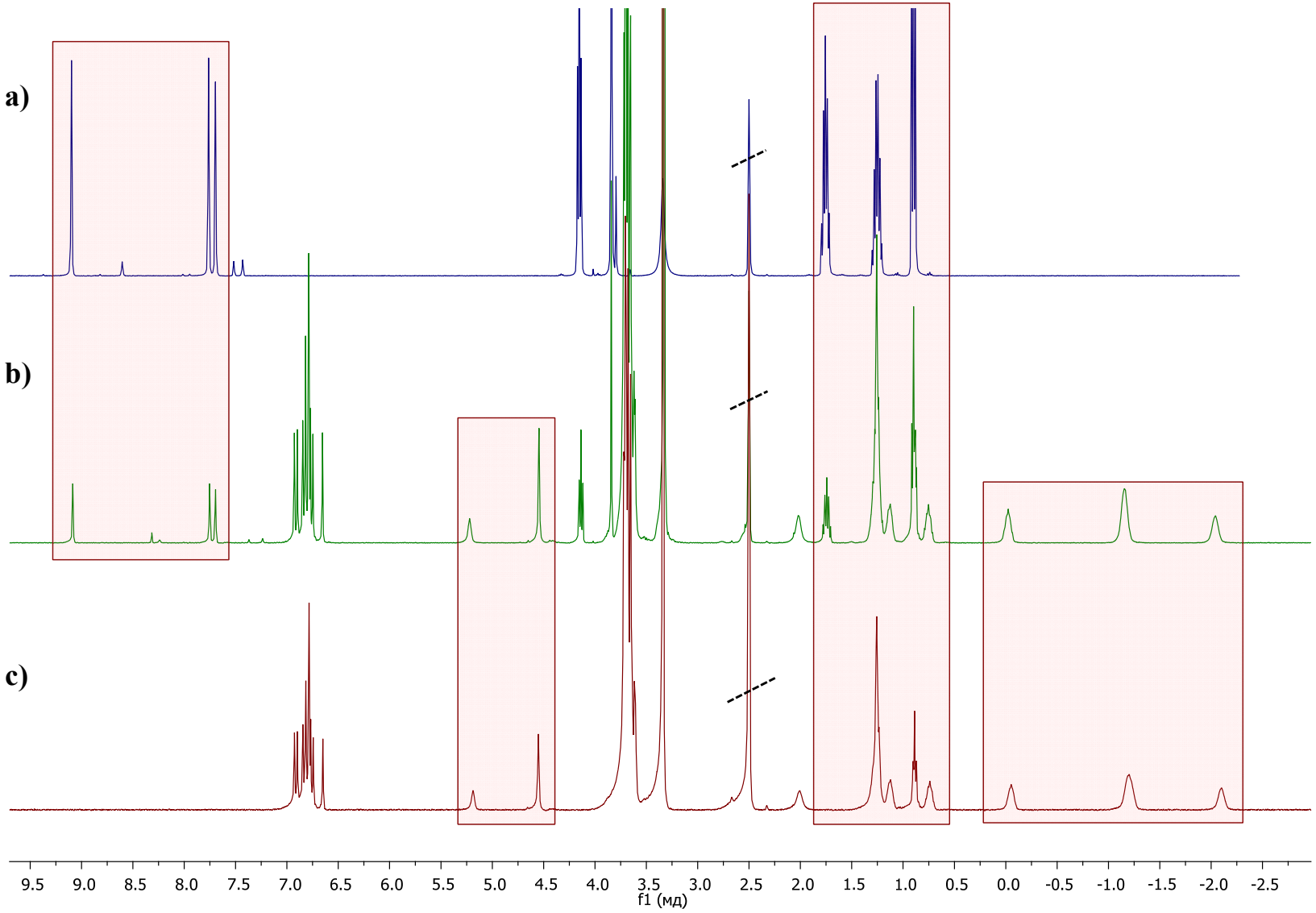

Fig. S65. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K): a) BMIIm (0.01 M) ; b) 6 (0.01 M) + BMIIm (0.01 M); c) 6 (0.01 M).

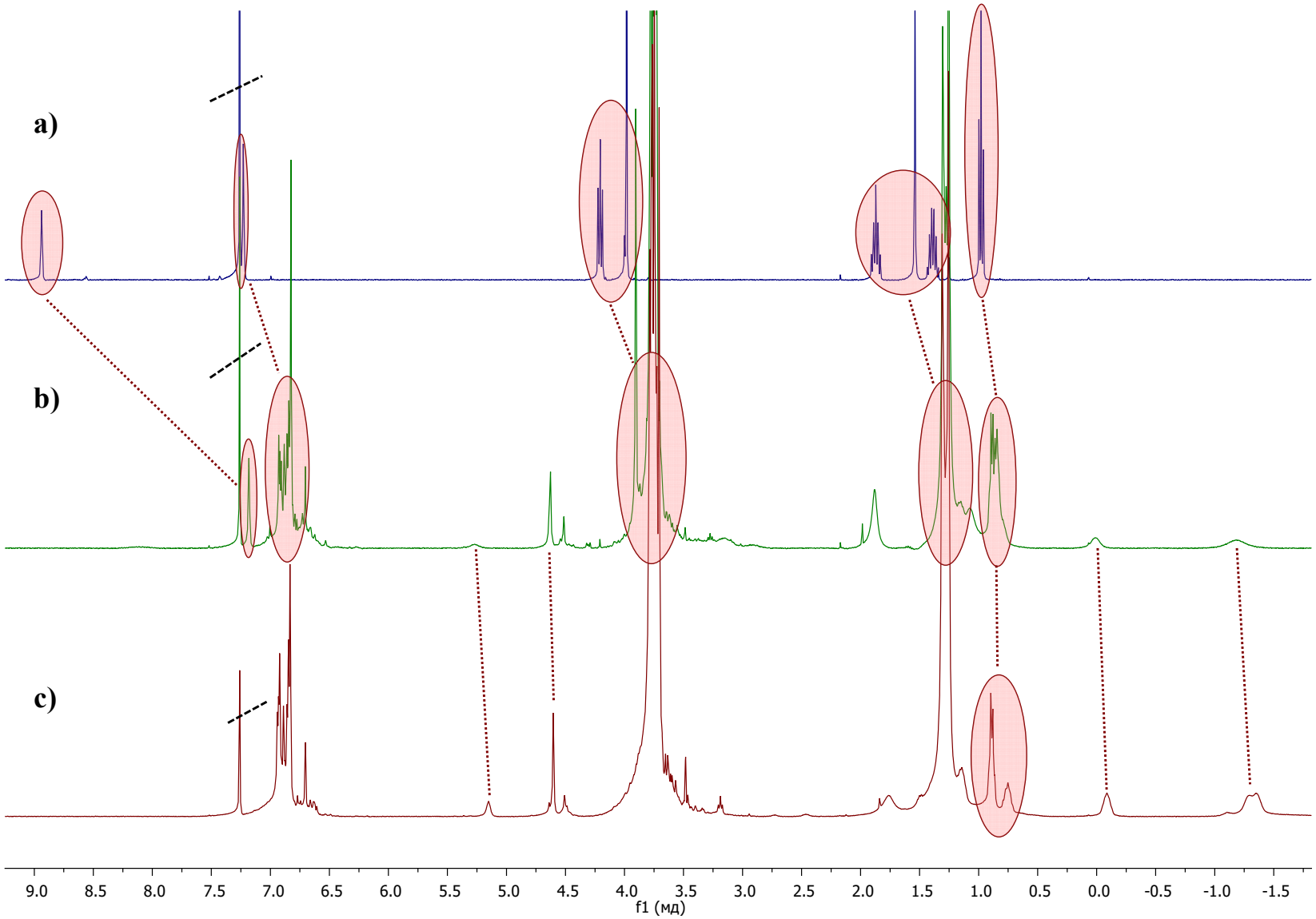

Fig. S66. ^{1}H NMR spectra (DMSO-d_6, 400 MHz, 298 K): a) BMIIm (0.01 M); b) 6 (0.01 M) + BMIIm (0.01 M); c) 6 (0.01 M).