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New enantiopure binaphthyl-cinchona thiosquaramides: synthesis and application for enantioselective organocatalysis

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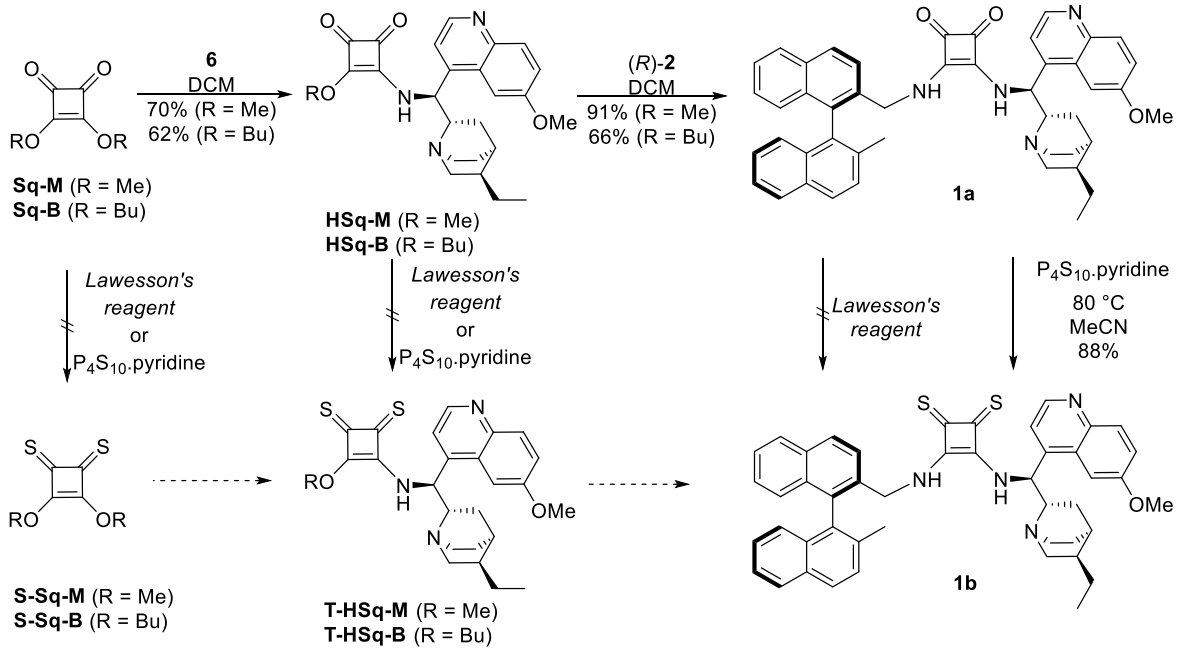
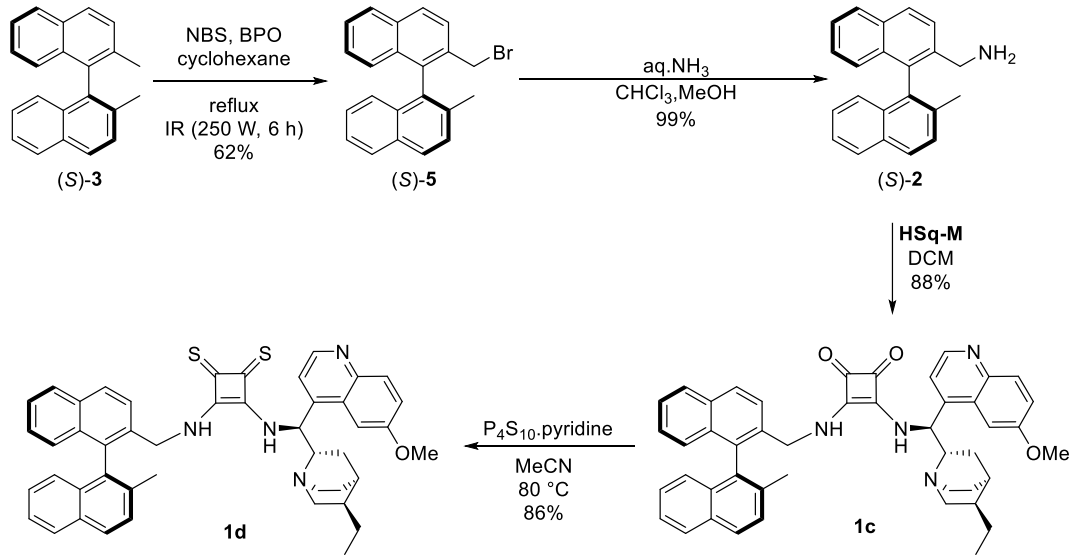
Electronic Supplementary Materials

1, Reaction pathways to squaramide (**1a**, **1c**) and thiosquaramide (**1b**, **1d**) catalysts in detail

The synthesis of binaphthyl-cinchona thiosquaramide **1b** was attempted in many ways (see Scheme 4. and Scheme S1), but it was successful only by thionation of its dioxo form **1a** using P_4S_{10}·pyridine complex. The thionation of squaric acid esters (**Sq-M** or **Sq-B**) or of cinchona half-squaramides (**HSq-M** or **HSq-B**) was unsuccessful using thionating agents such as *Lawesson*'s reagent or P_4S_{10}·pyridine complex. In these reactions the corresponding products were not isolated, although the starting materials were run out.



Scheme S1. Original reaction path to **1b** thiosquaramide



Scheme S2. Reaction path to **1c** and **1d** catalysts

2, FT-IR spectra

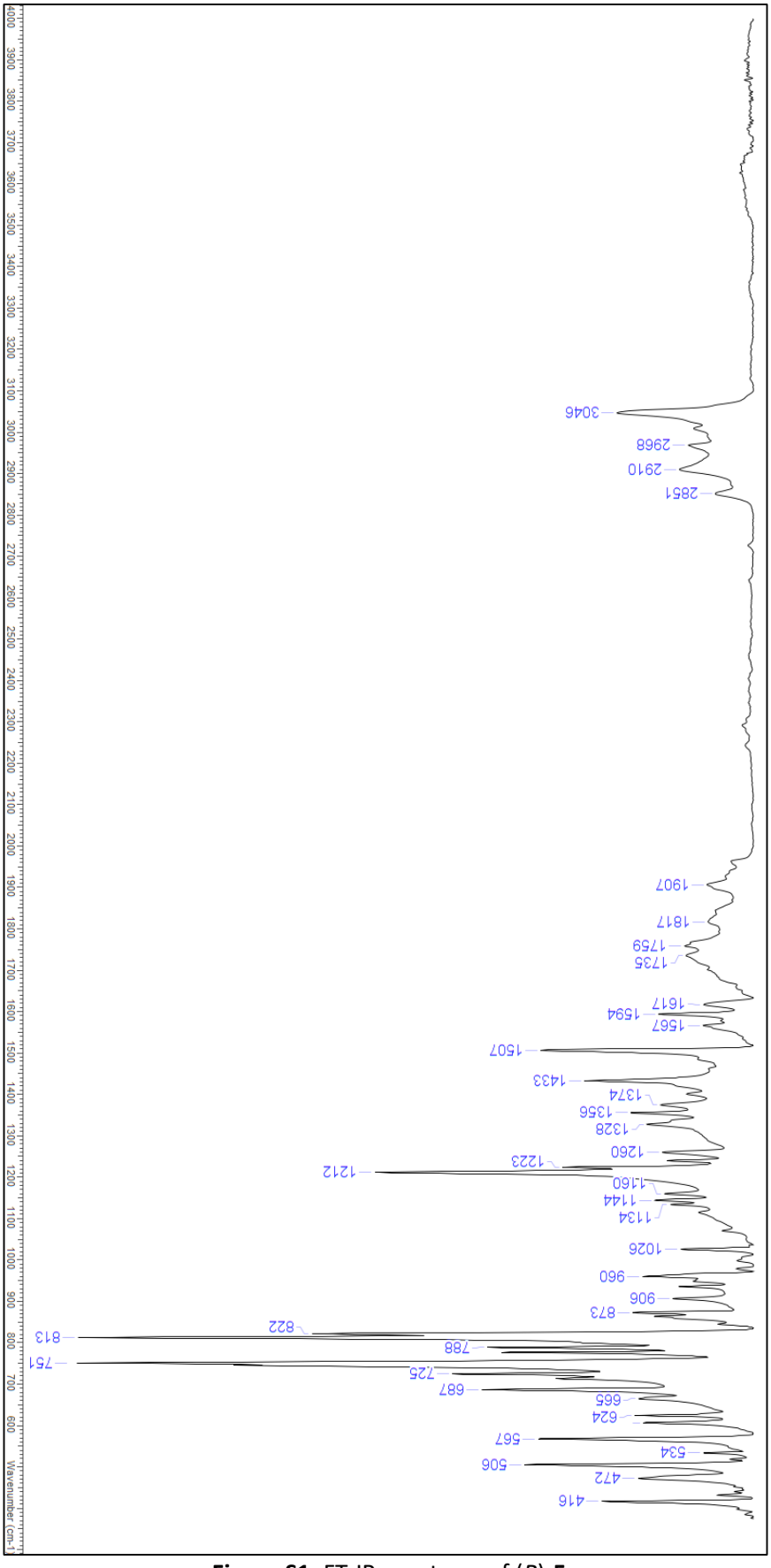


Figure S1. FT-IR spectrum of (*R*)-**5**

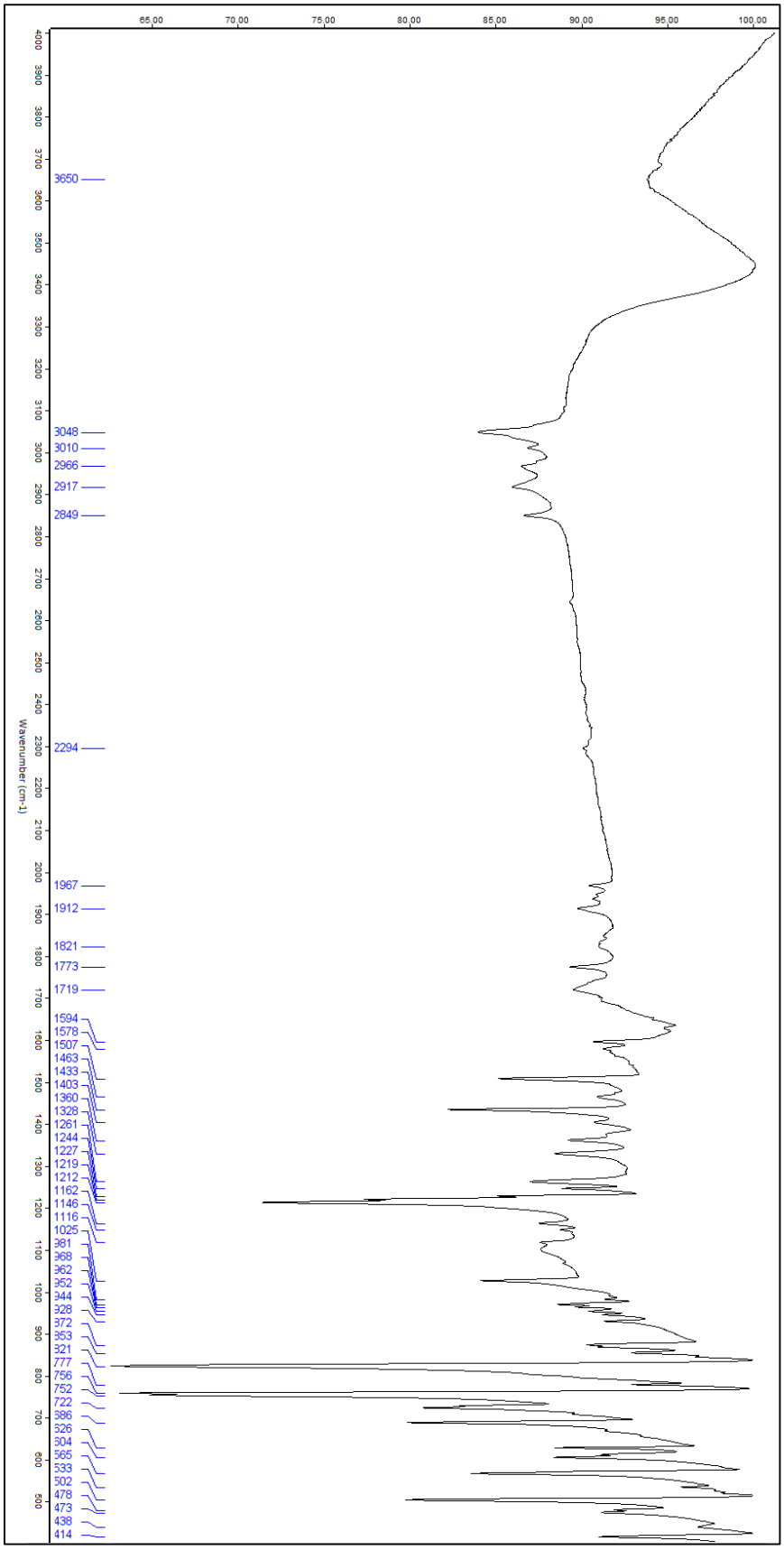


Figure S2. FT-IR spectrum of (*R*)-**5b**

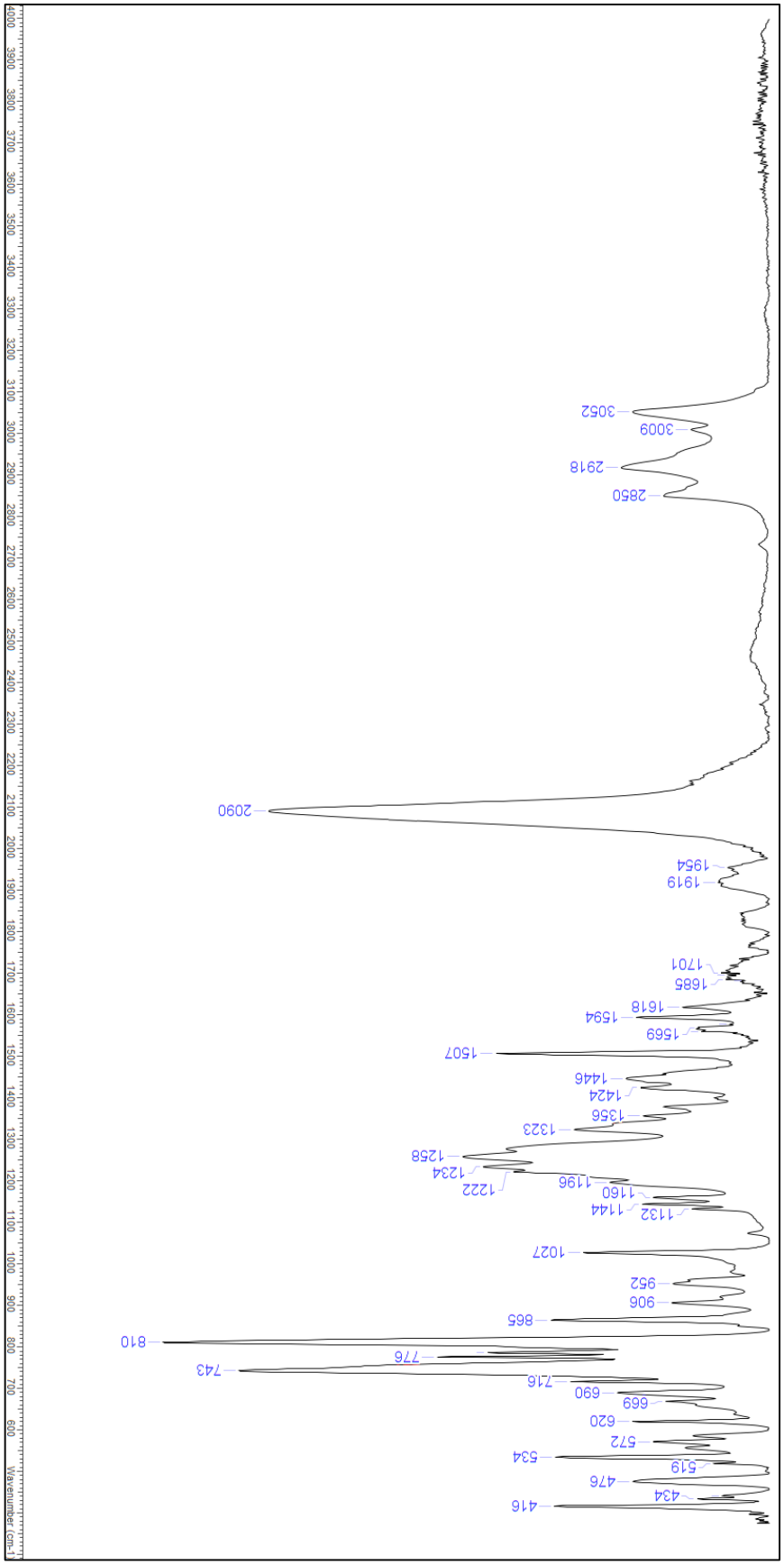


Figure S3. FT-IR spectrum of (*R*)-**16**

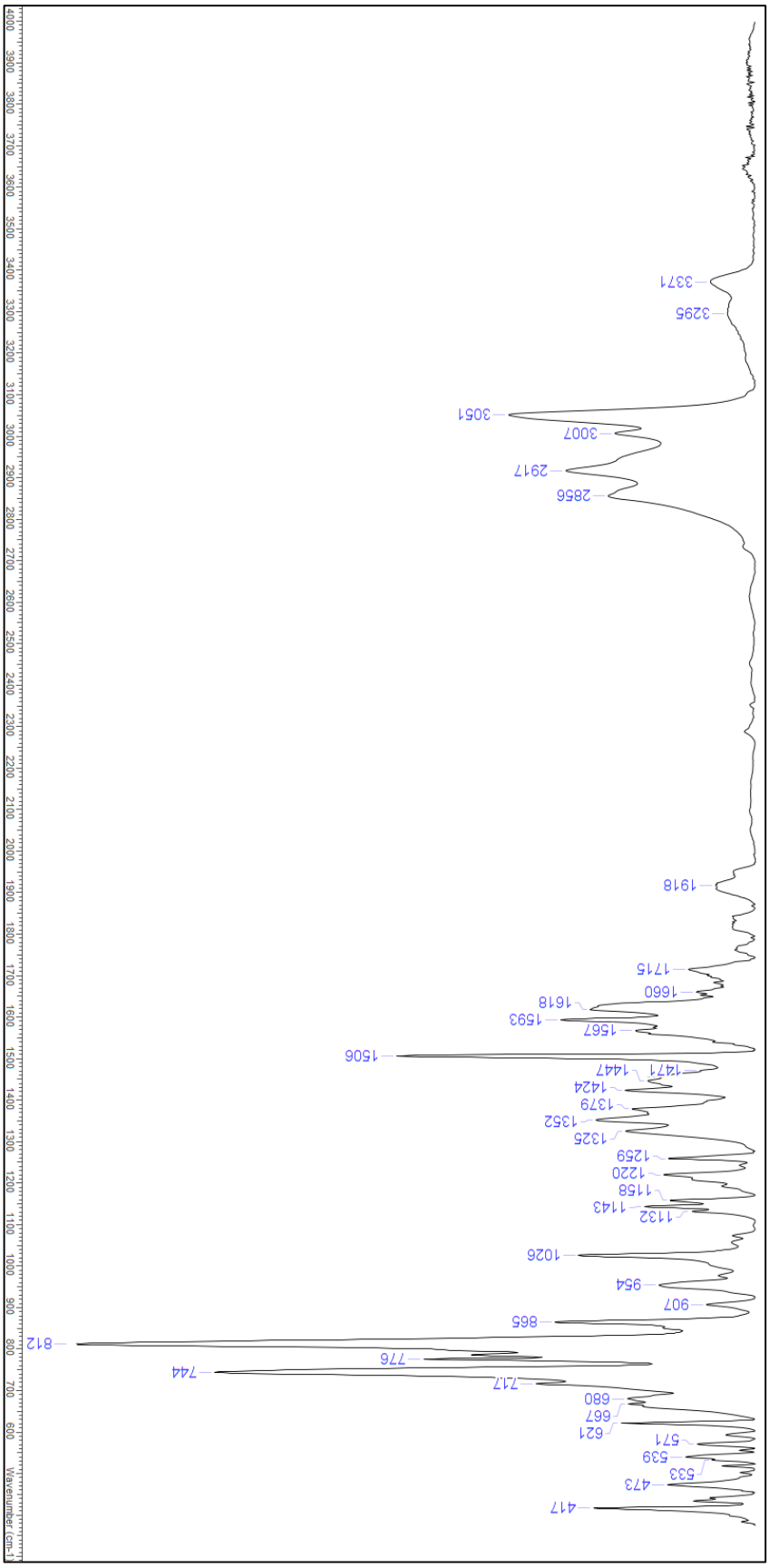


Figure S4. FT-IR spectrum of (*R*)-**2**

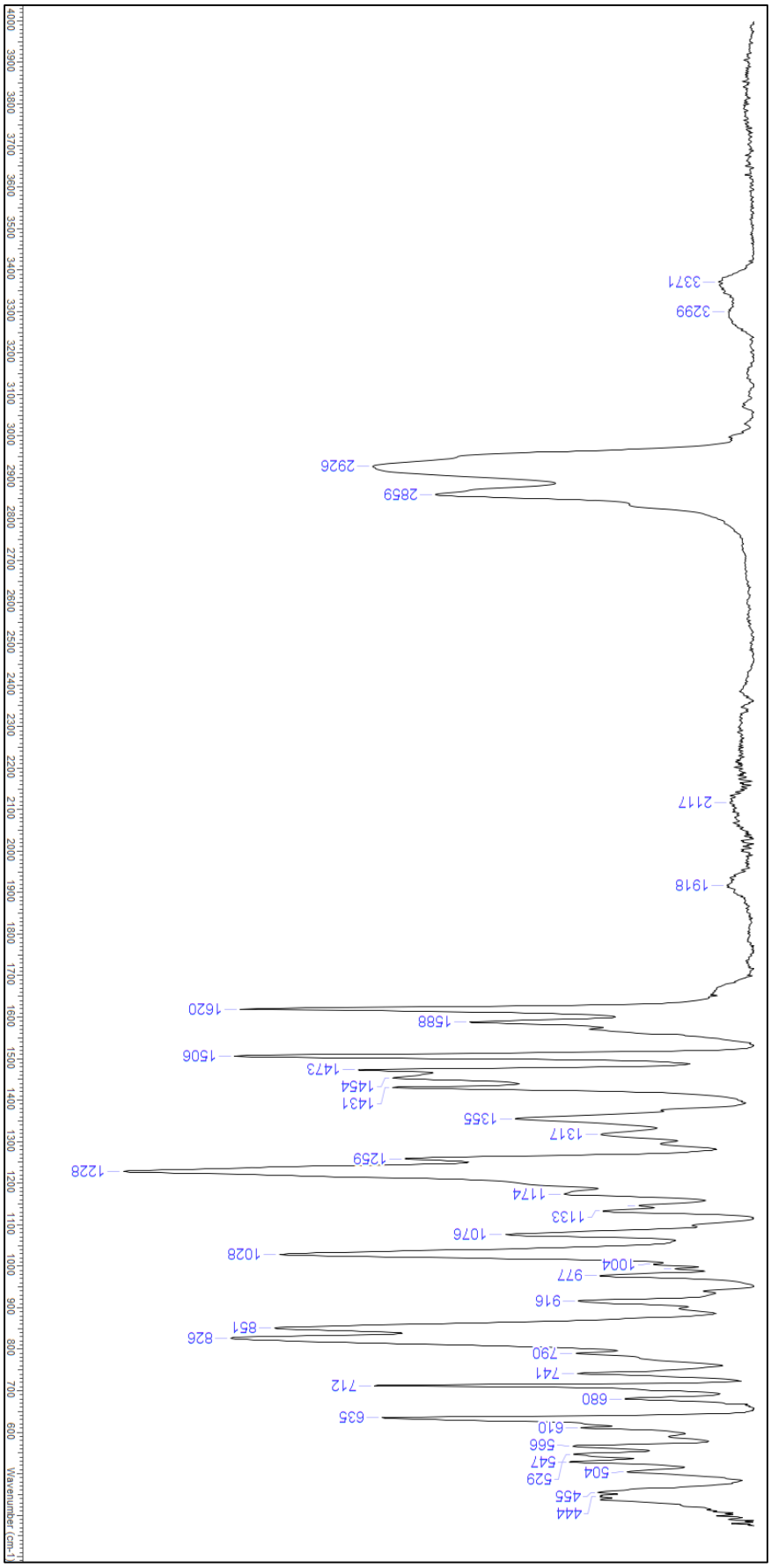


Figure S5. FT-IR spectrum of **6**

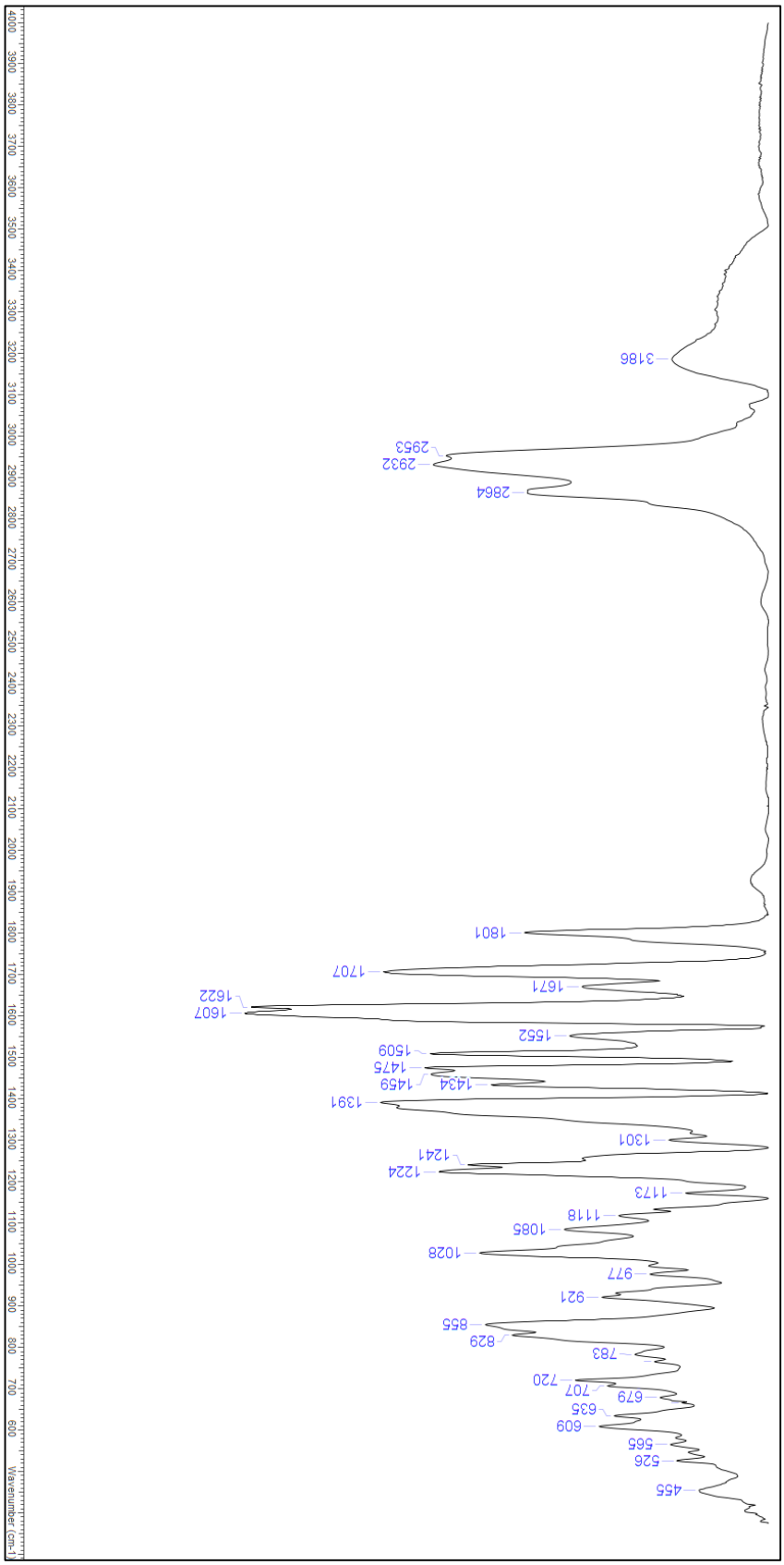


Figure S6. FT-IR spectrum of **HSq-M**

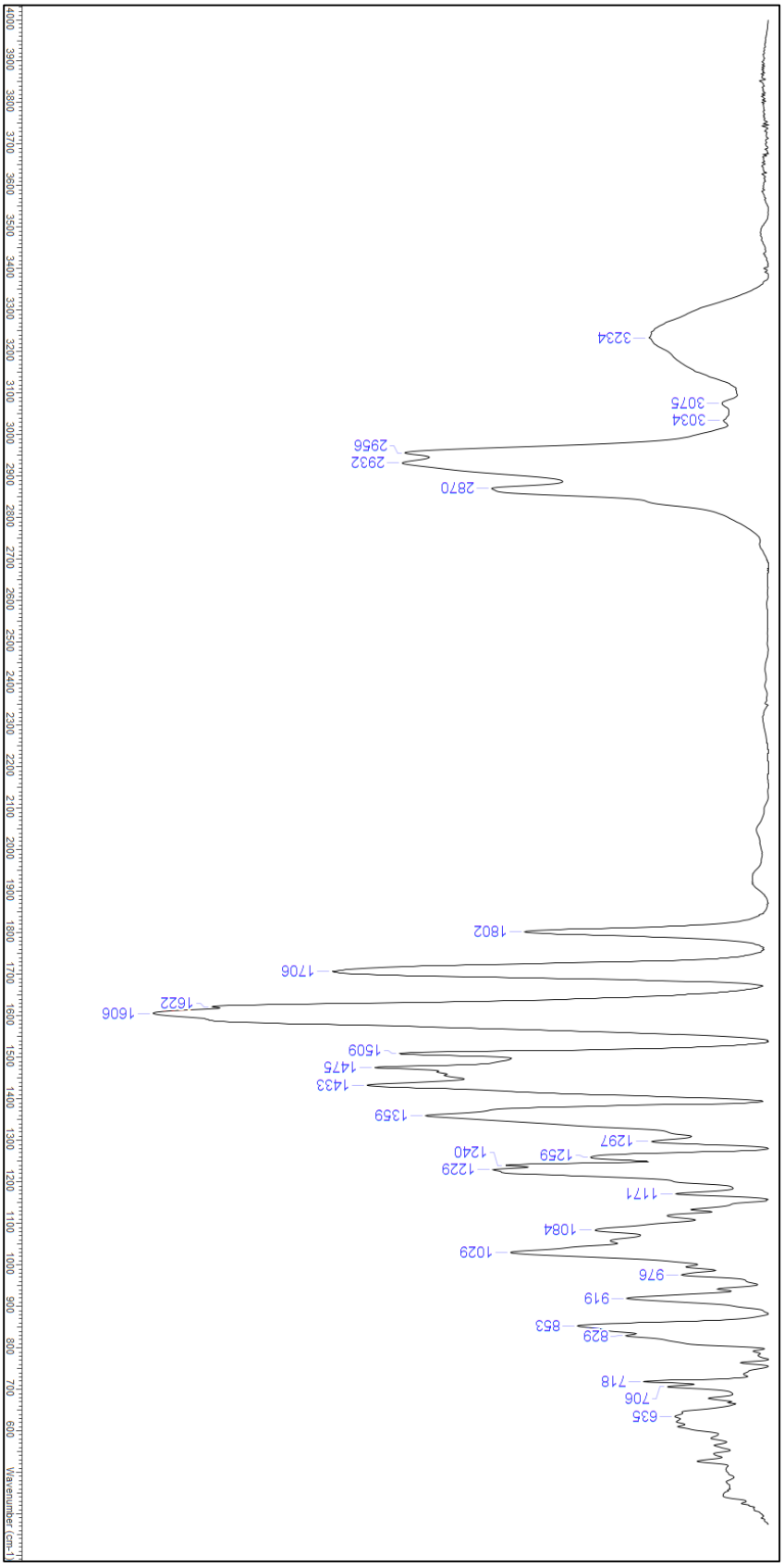


Figure S7. FT-IR spectrum of **HSq-B**

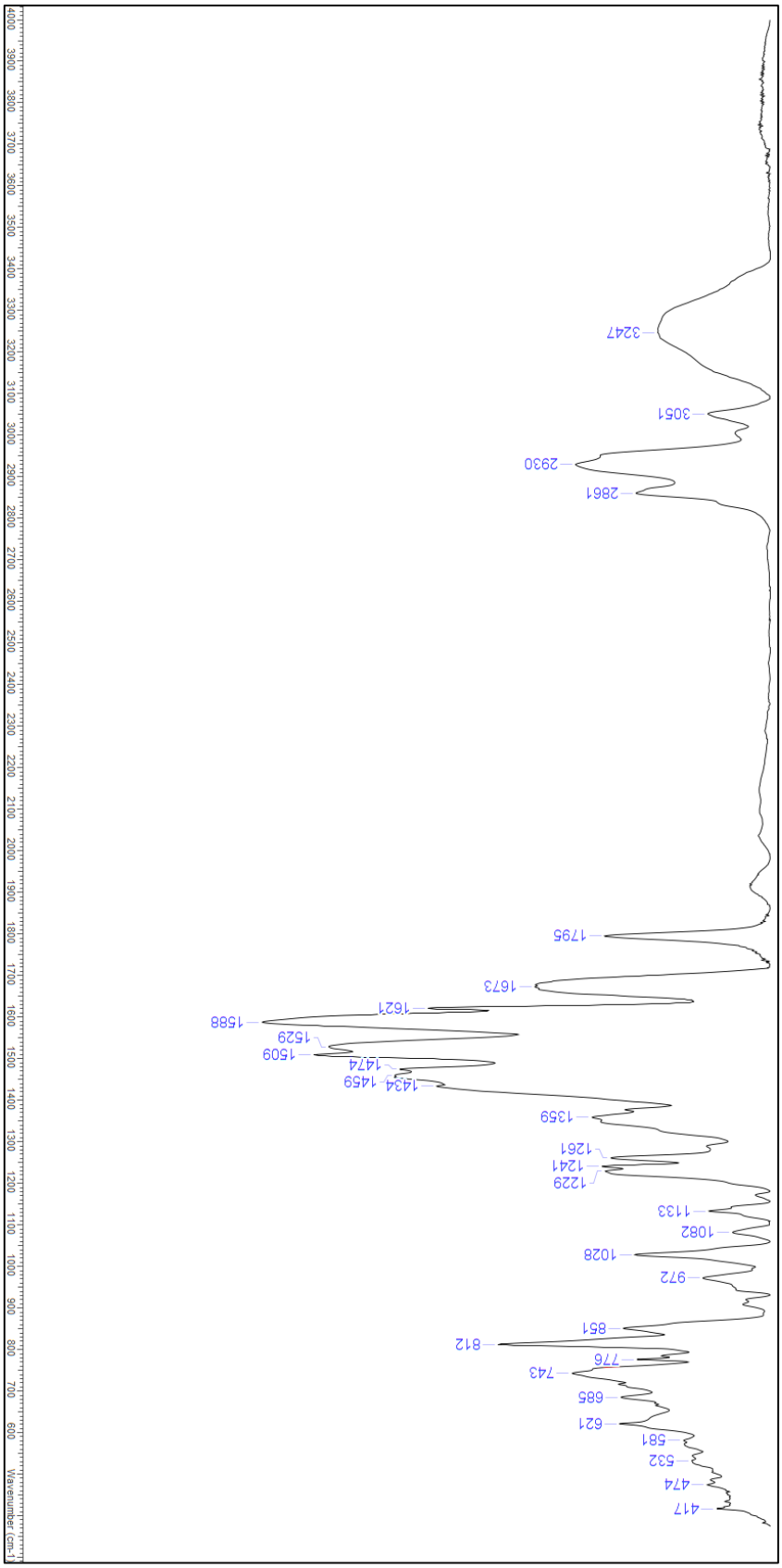


Figure S8. FT-IR spectrum of **1a**

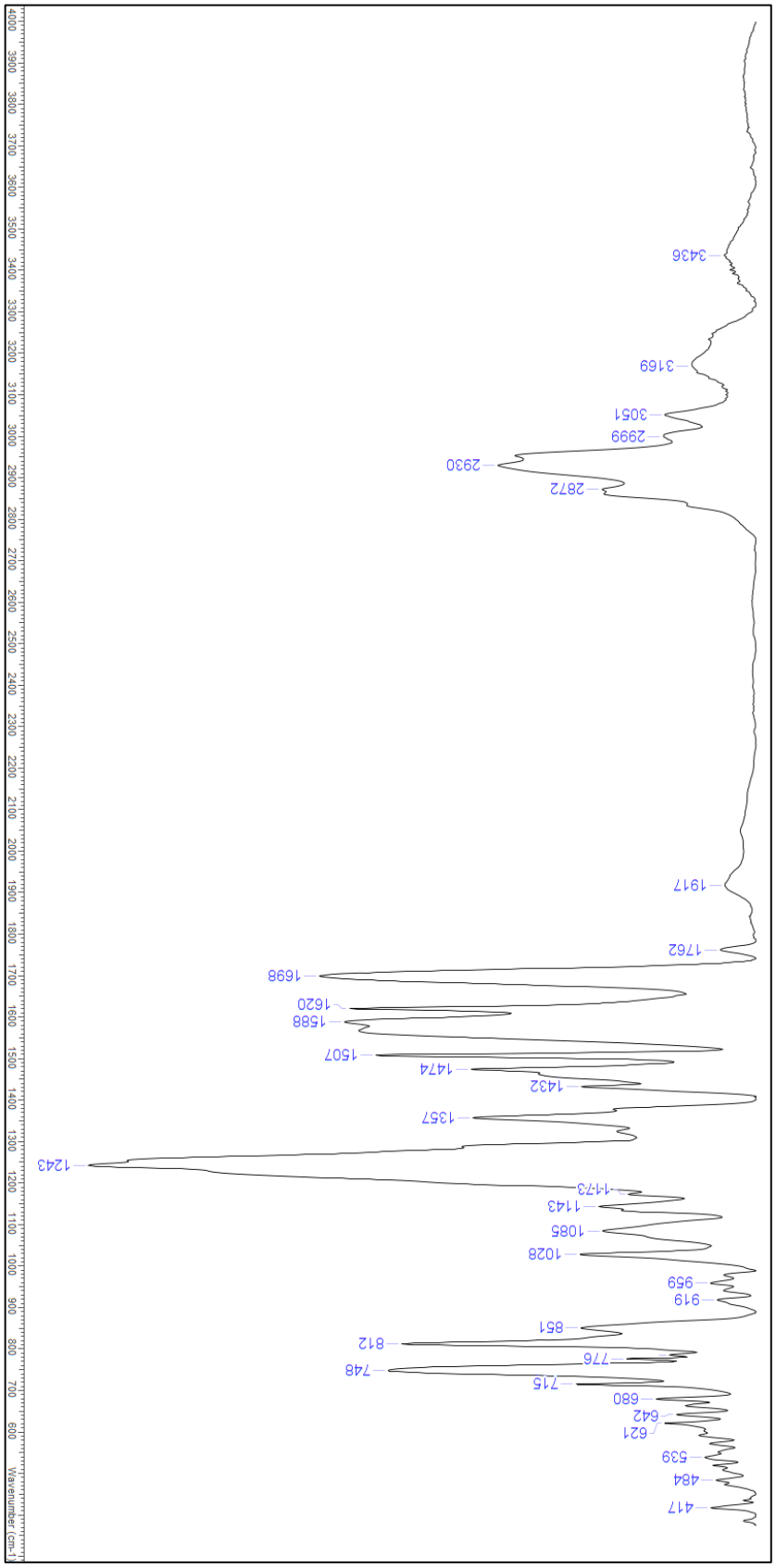


Figure S9. FT-IR spectrum of **1b**

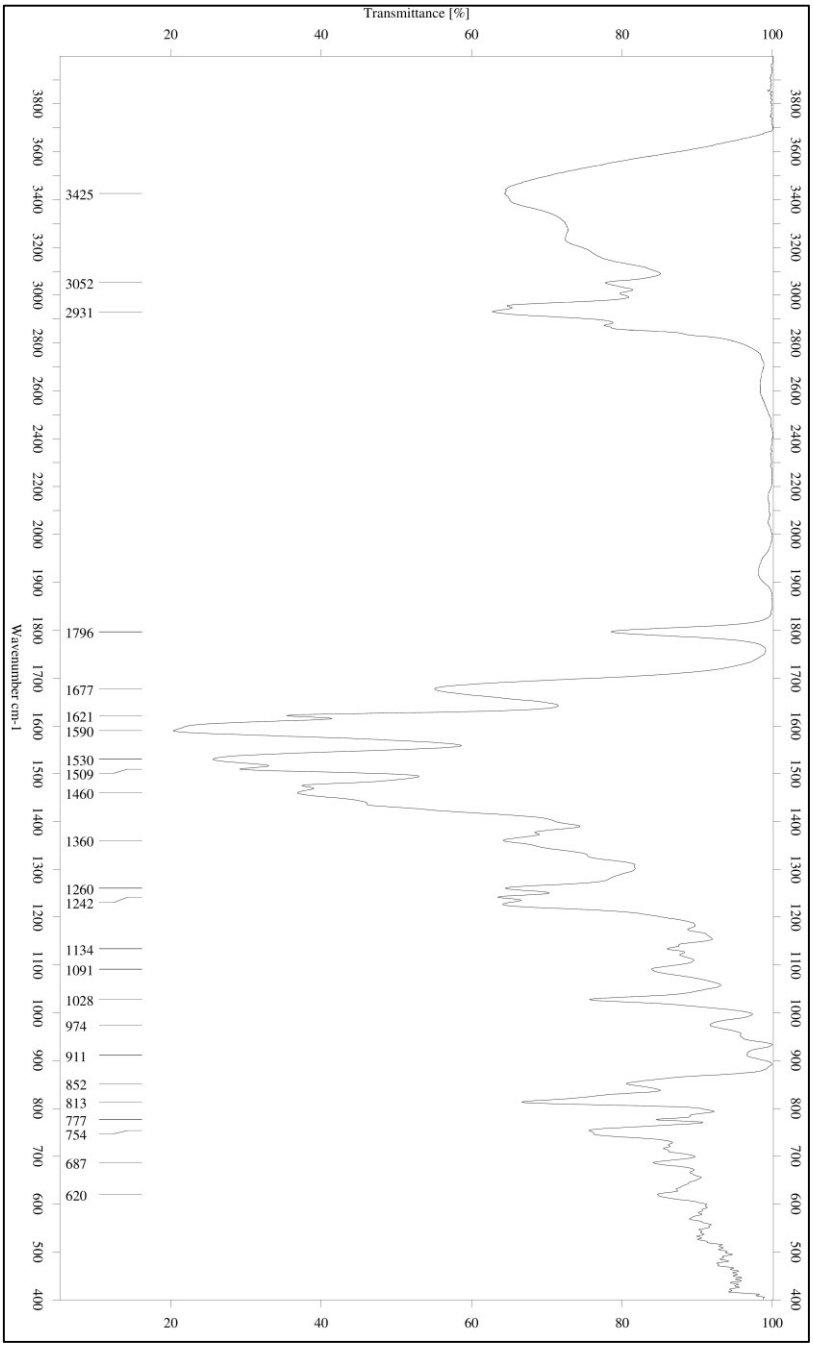


Figure S10. FT-IR spectrum of **1c**

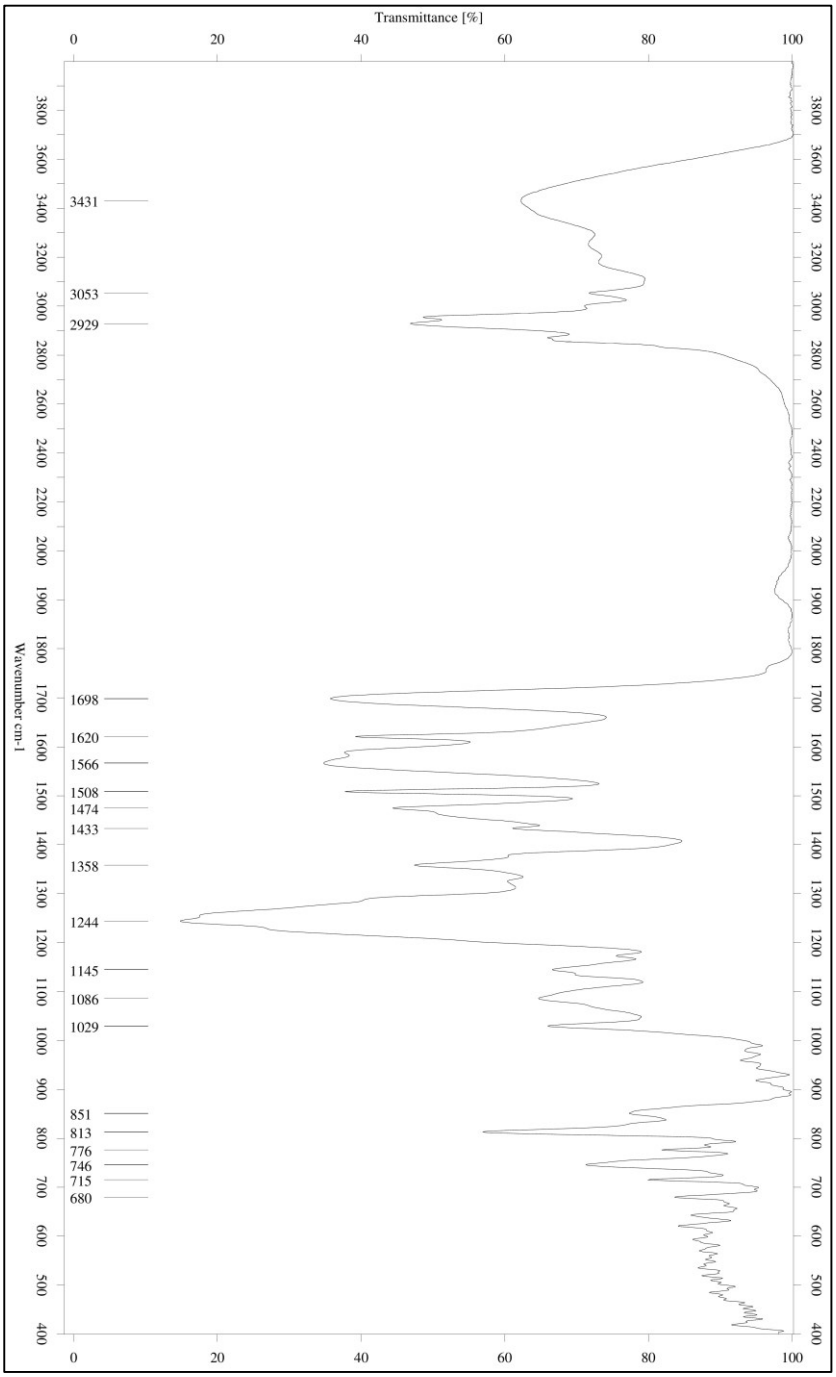


Figure S11. FT-IR spectrum of **1d**

3, NMR spectra

NMR spectra of (*R*)-**5**

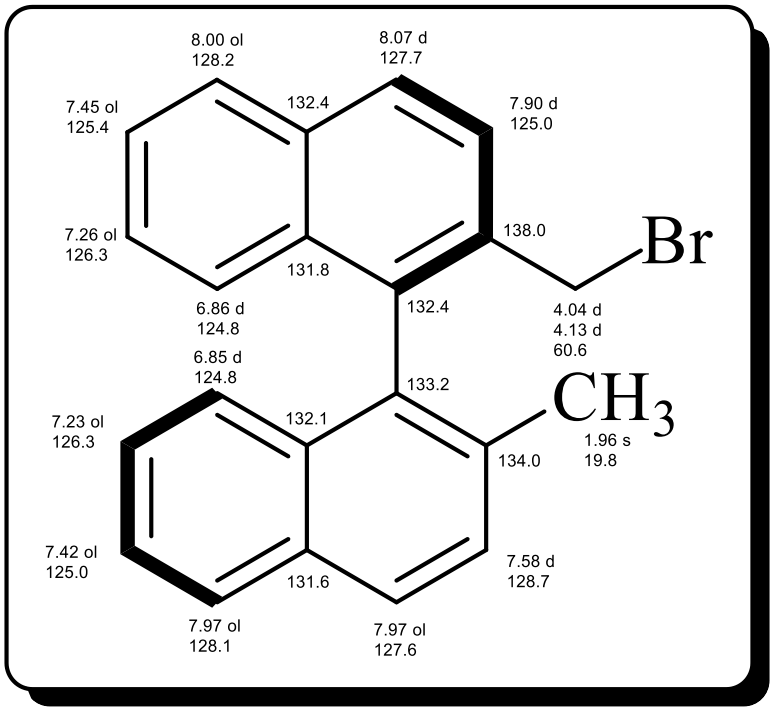


Figure S12. Molecule structure, ^{1}H and ^{13}C assignment of (*R*)-**5**

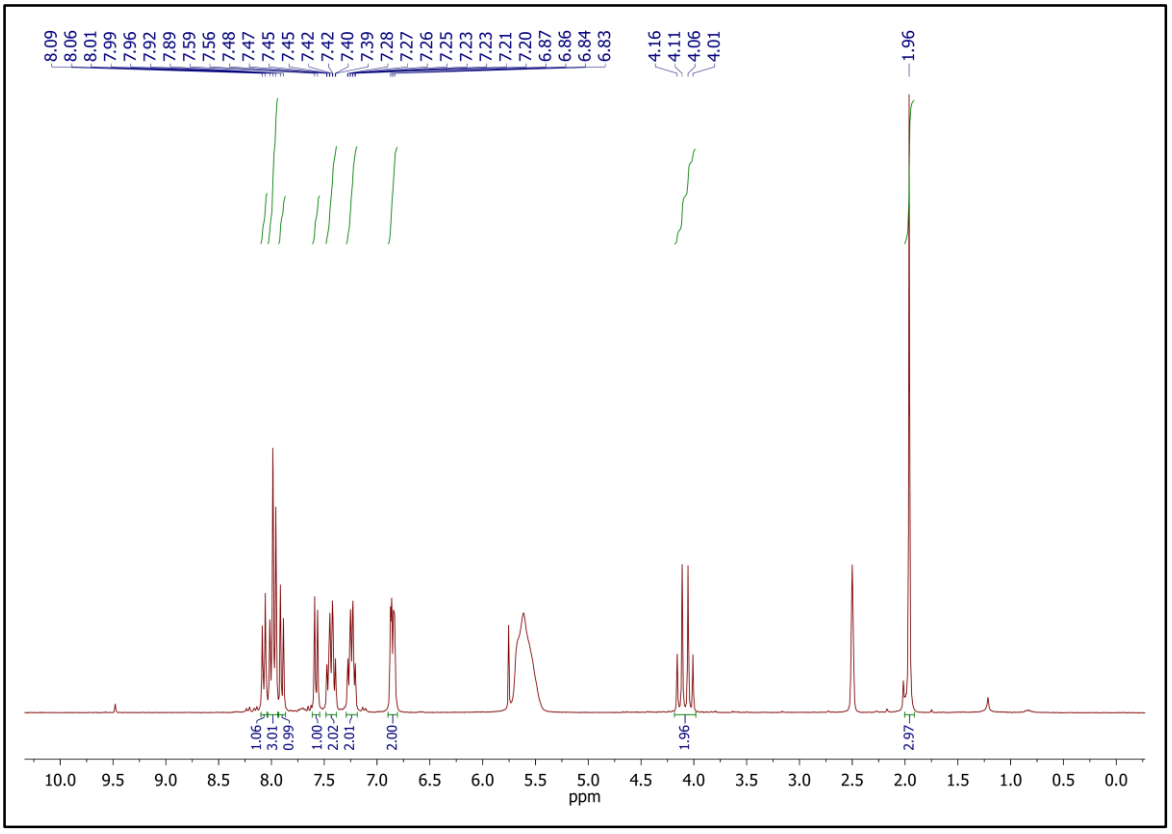


Figure S13. ^{1}H NMR spectrum of (*R*)-**5** (300 MHz, DMSO, 25 °C)

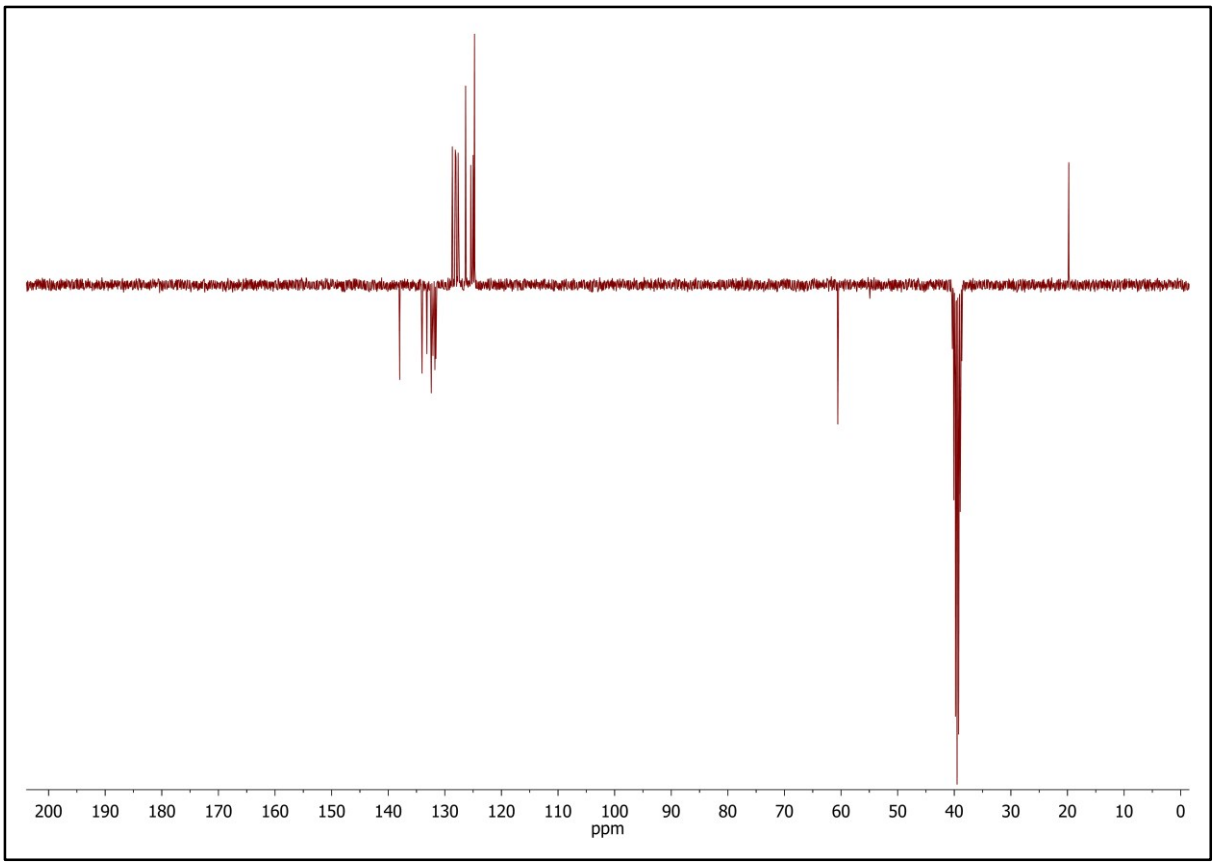


Figure S14. ^{13}C DEPT NMR spectrum of (*R*)-**5** (75 MHz, DMSO, 25 °C)

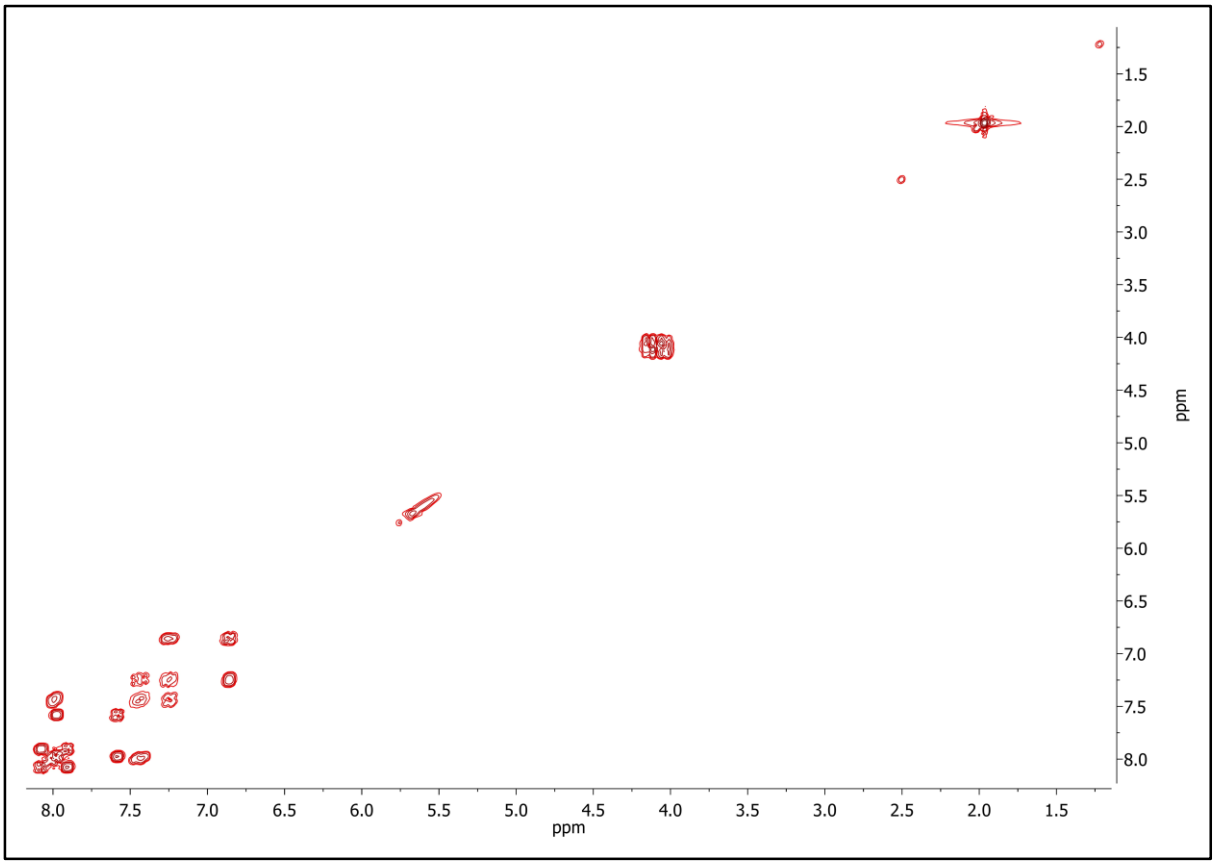


Figure S15. COSY NMR spectrum of (*R*)-**5** (DMSO, 25 °C)

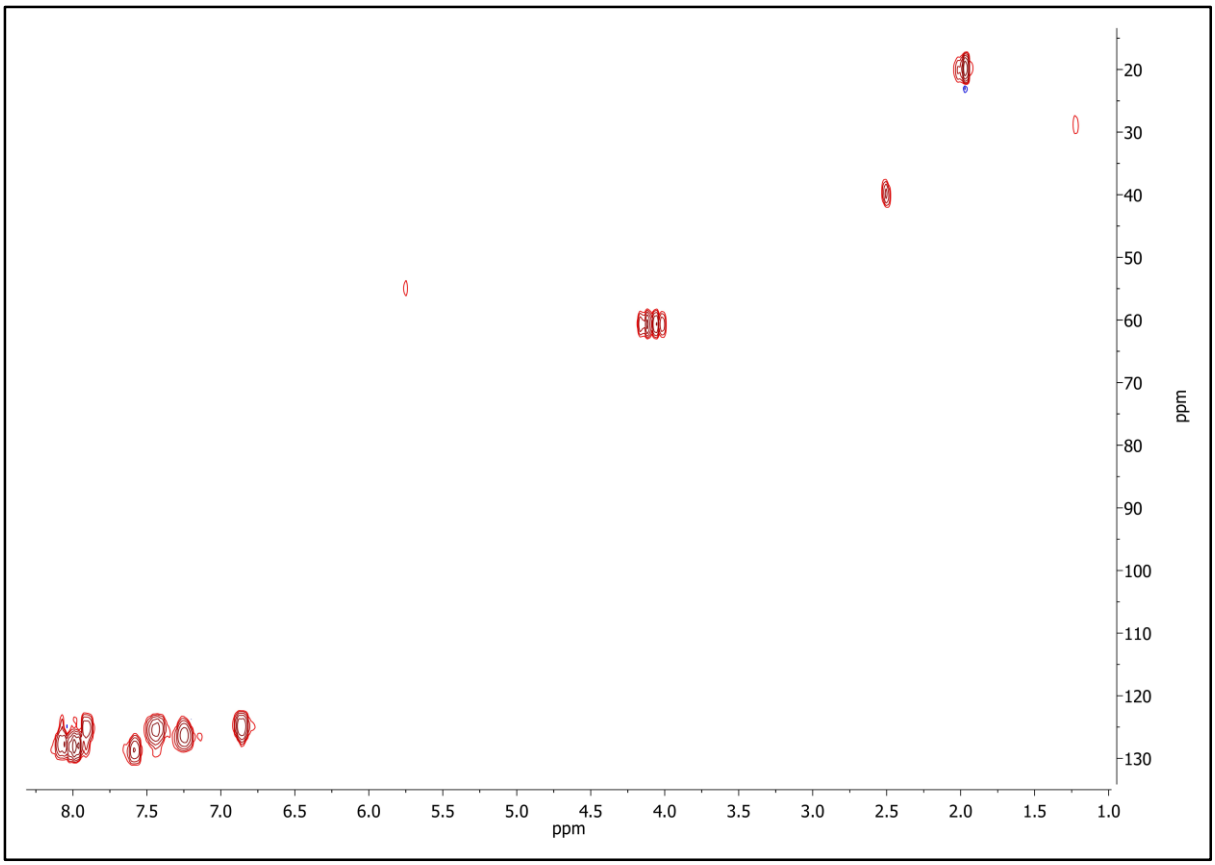


Figure S16. HSQC NMR spectrum of (*R*)-**5** (DMSO, 25 °C)

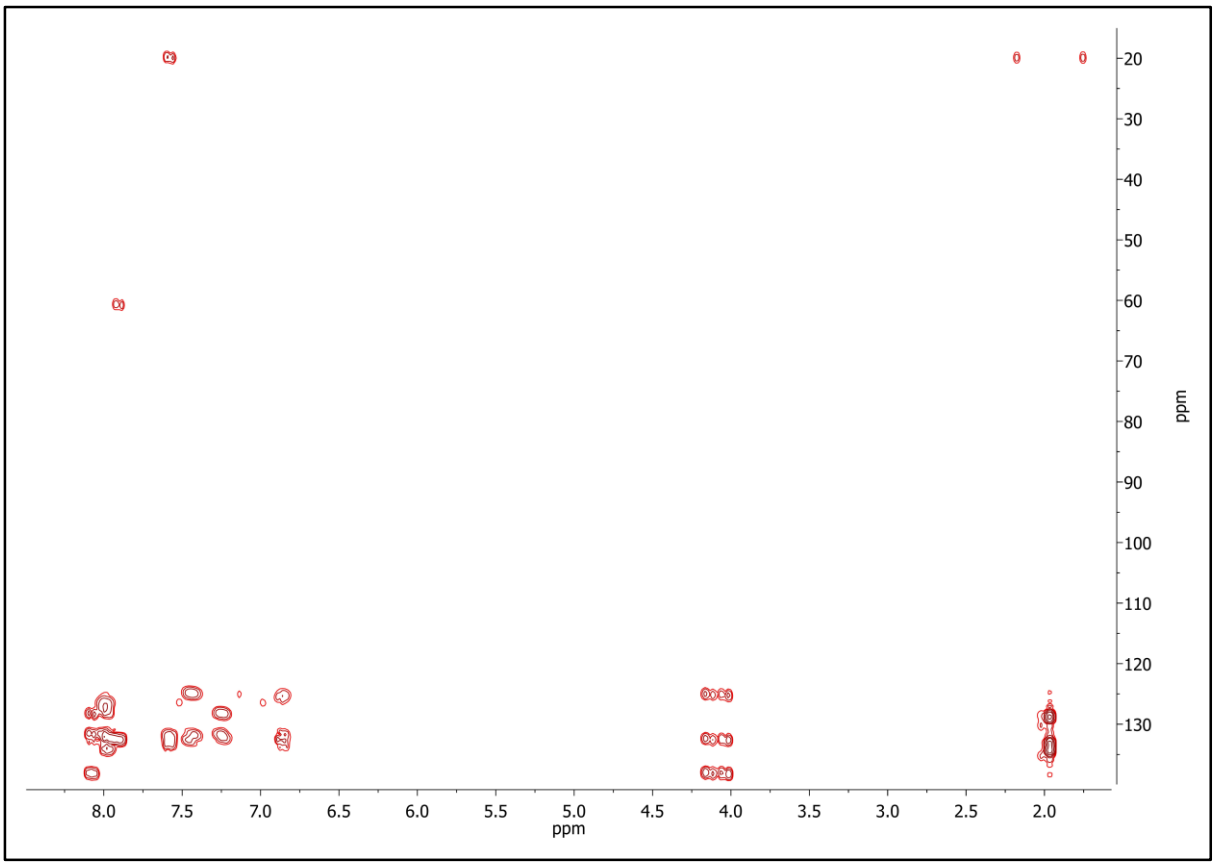


Figure S17. HMBC NMR spectrum of (*R*)-**5** (DMSO, 25 °C)

NMR spectra of (*R*)-**5**

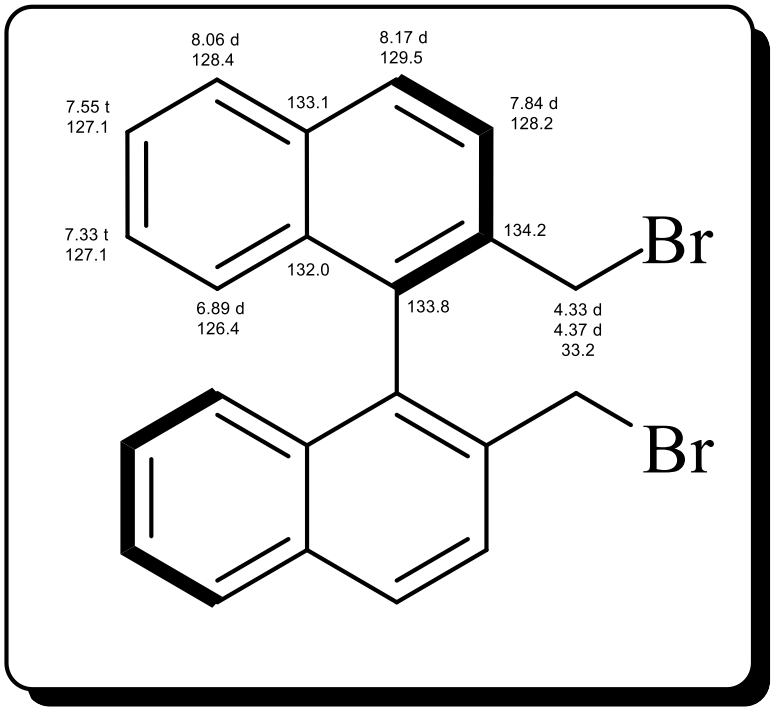


Figure S18. Molecule structure, ^{1}H and ^{13}C assignment of (*R*)-**5b**

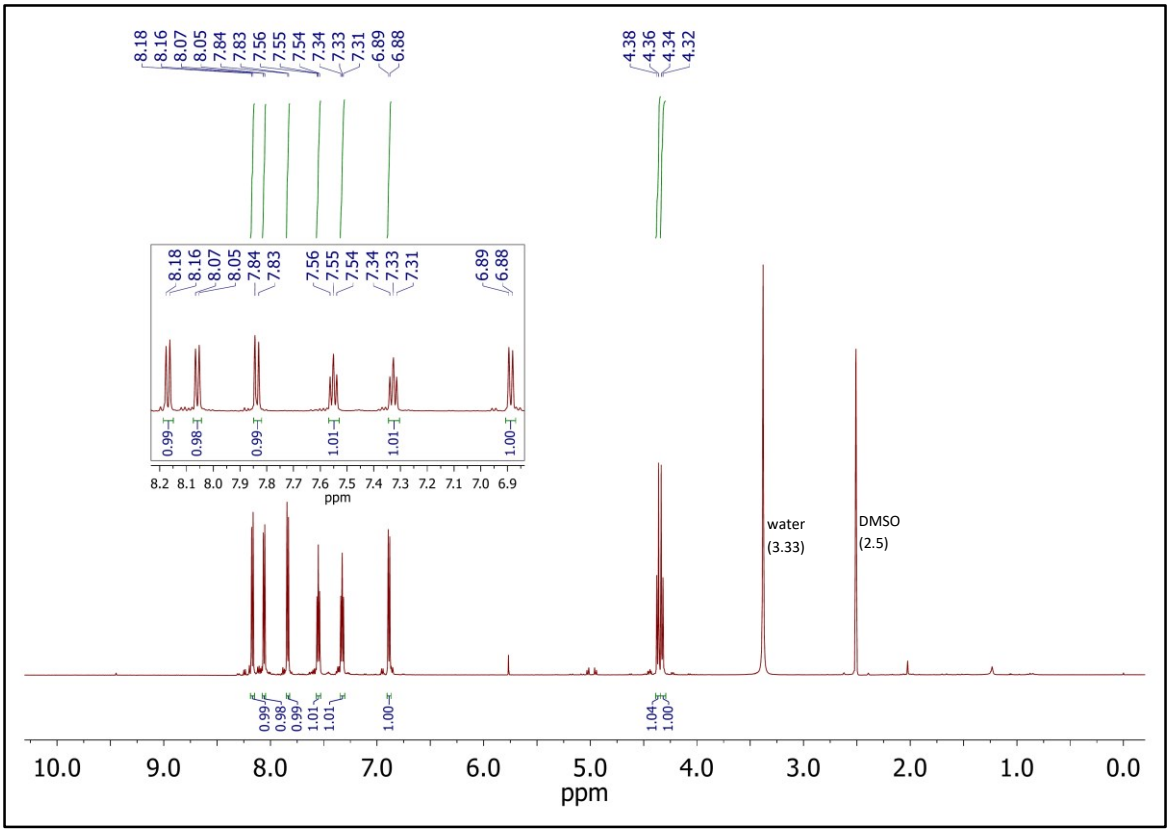


Figure S19. ^{1}H NMR spectrum of (*R*)-**5b** (600 MHz, DMSO, 25 °C)

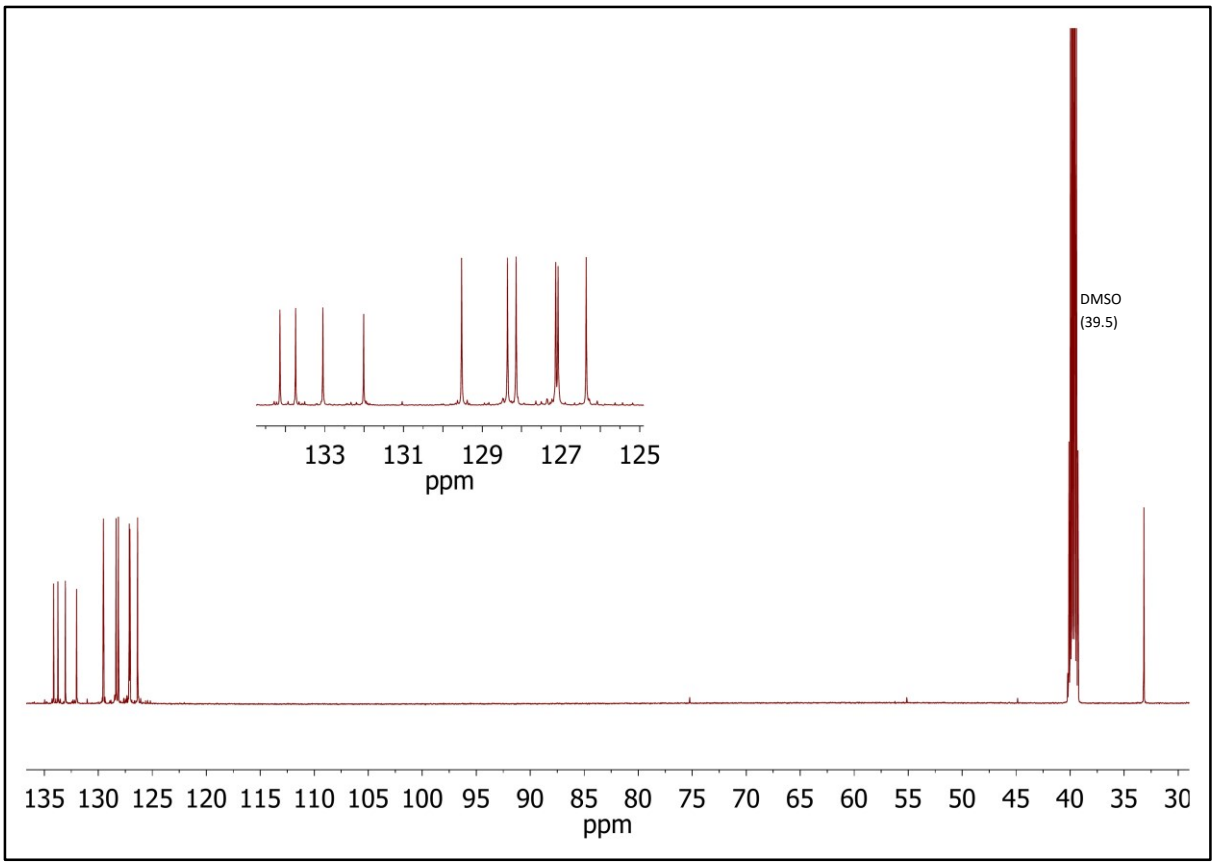


Figure S20. ^{13}C NMR spectrum of (*R*)-**5b** (150 MHz, DMSO, 25 °C)

NMR spectra of (*R*)-**16**

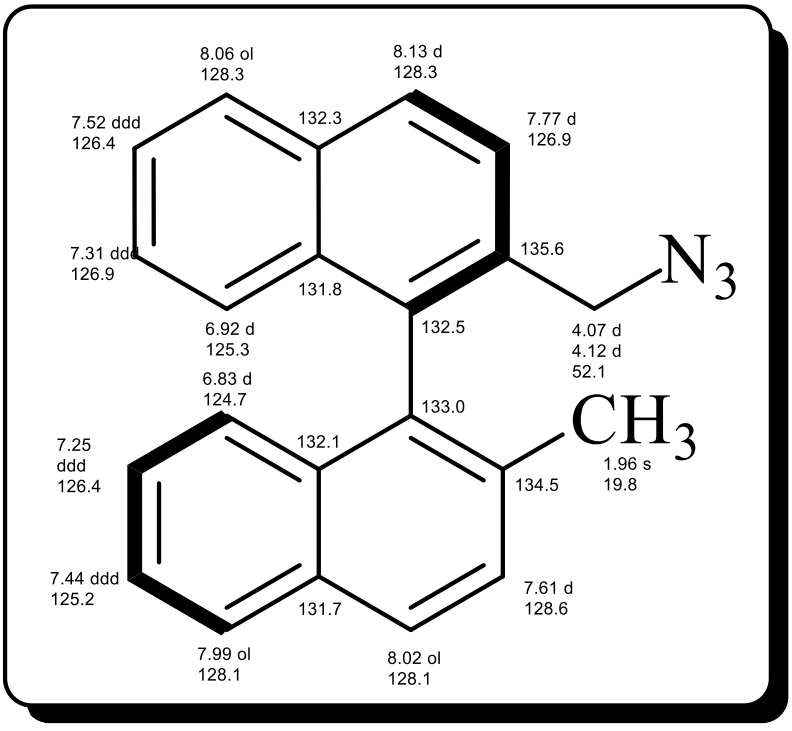


Figure S21. Molecule structure, ^{1}H and ^{13}C assignment of (*R*)-**16**

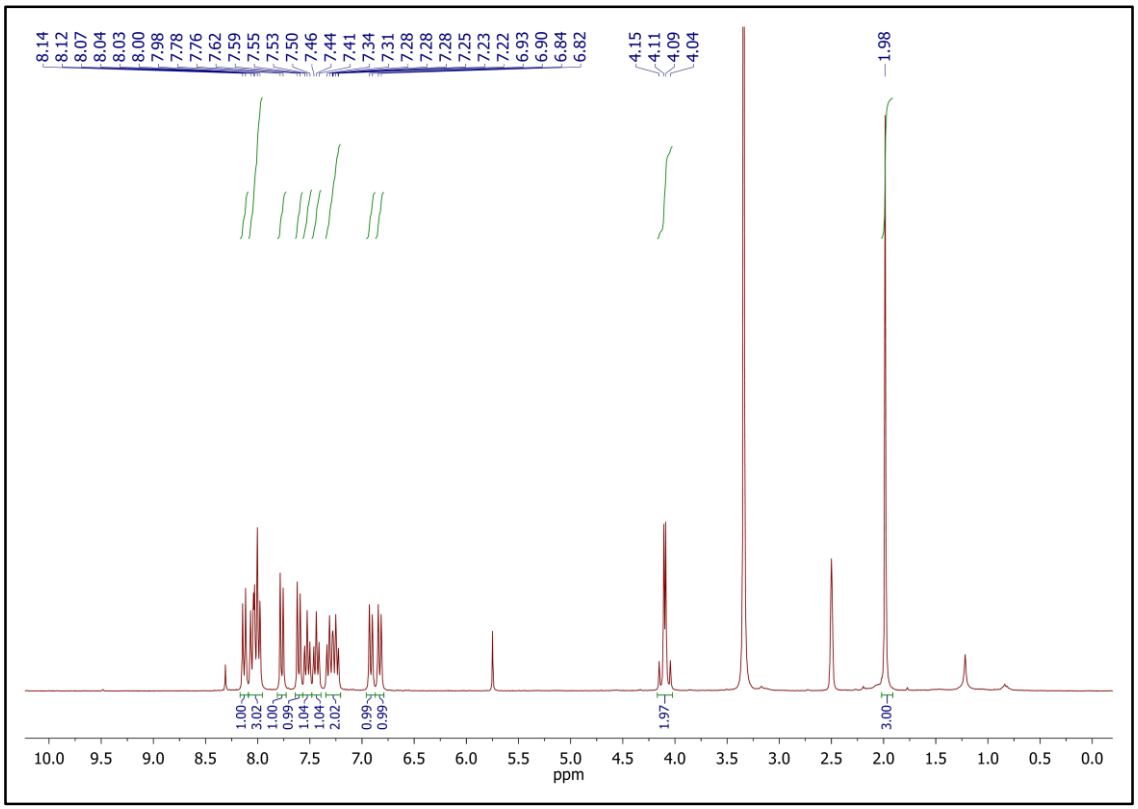


Figure S22. ^{1}H NMR spectrum of (*R*)-**16** (300 MHz, DMSO, 25 °C)

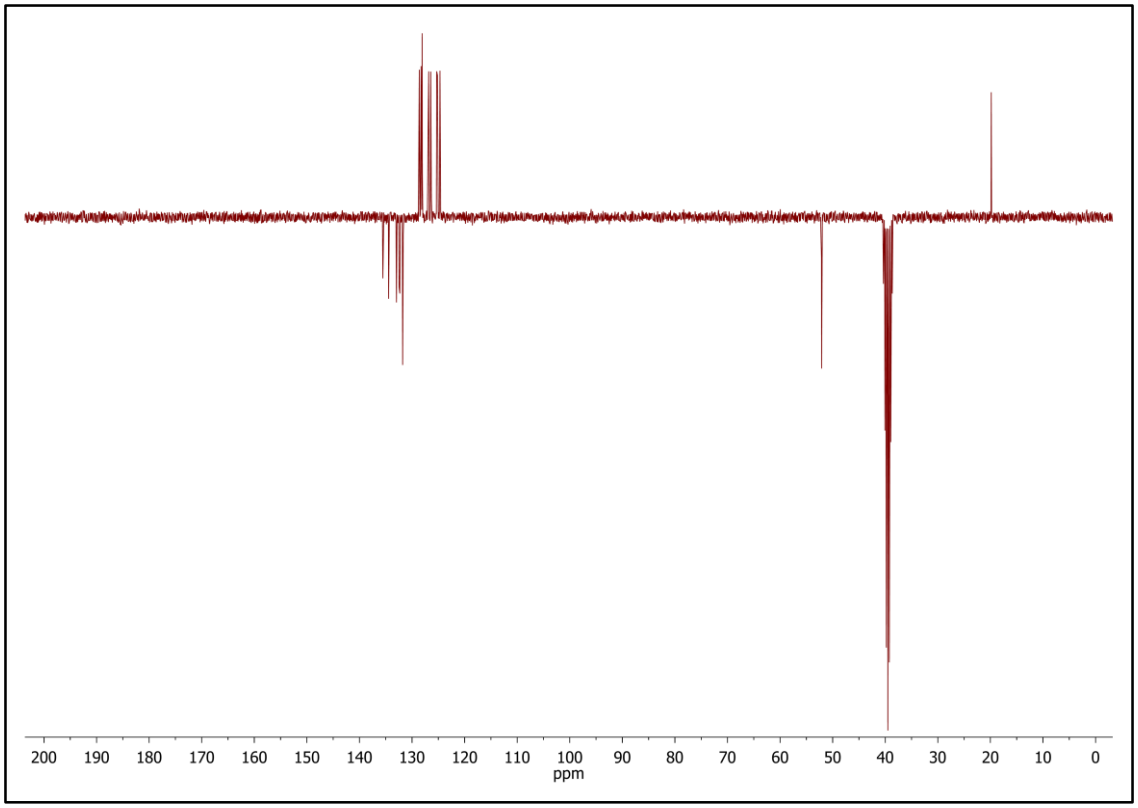


Figure S23. ^{13}C NMR spectrum of (*R*)-**16** (75 MHz, DMSO, 25 °C)

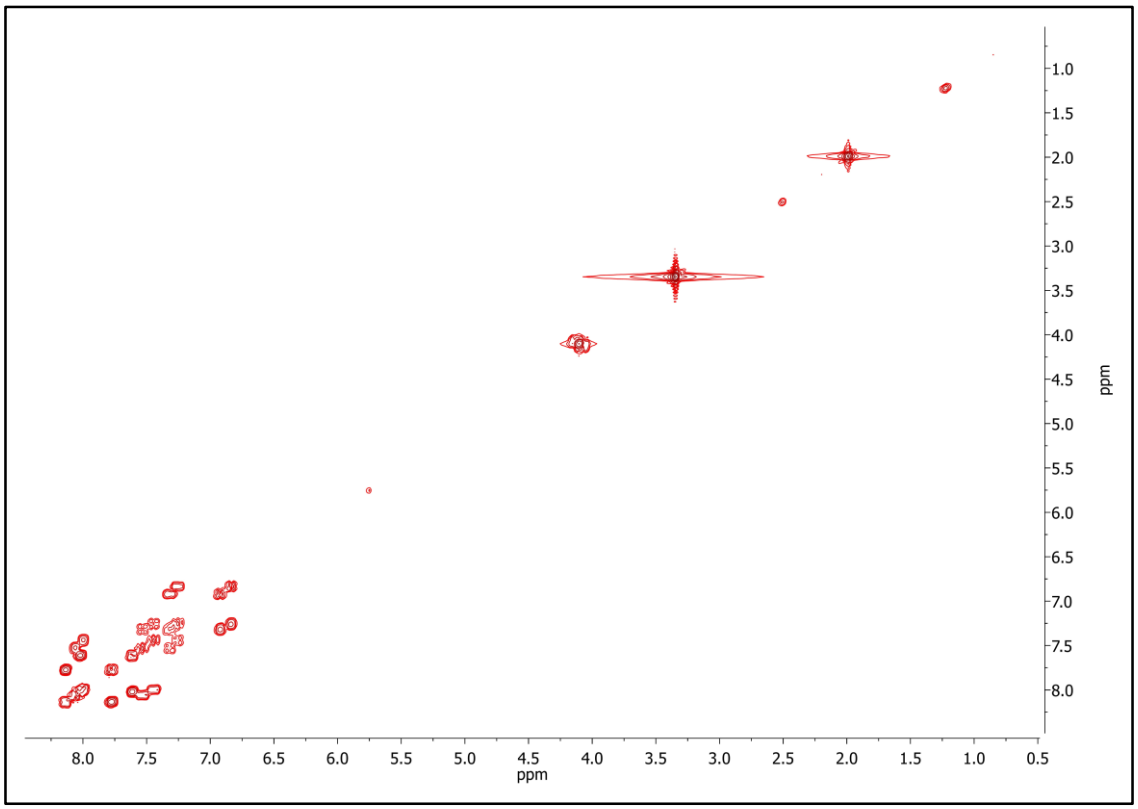


Figure S24. COSY NMR spectrum of (*R*)-**16** (DMSO, 25 °C)

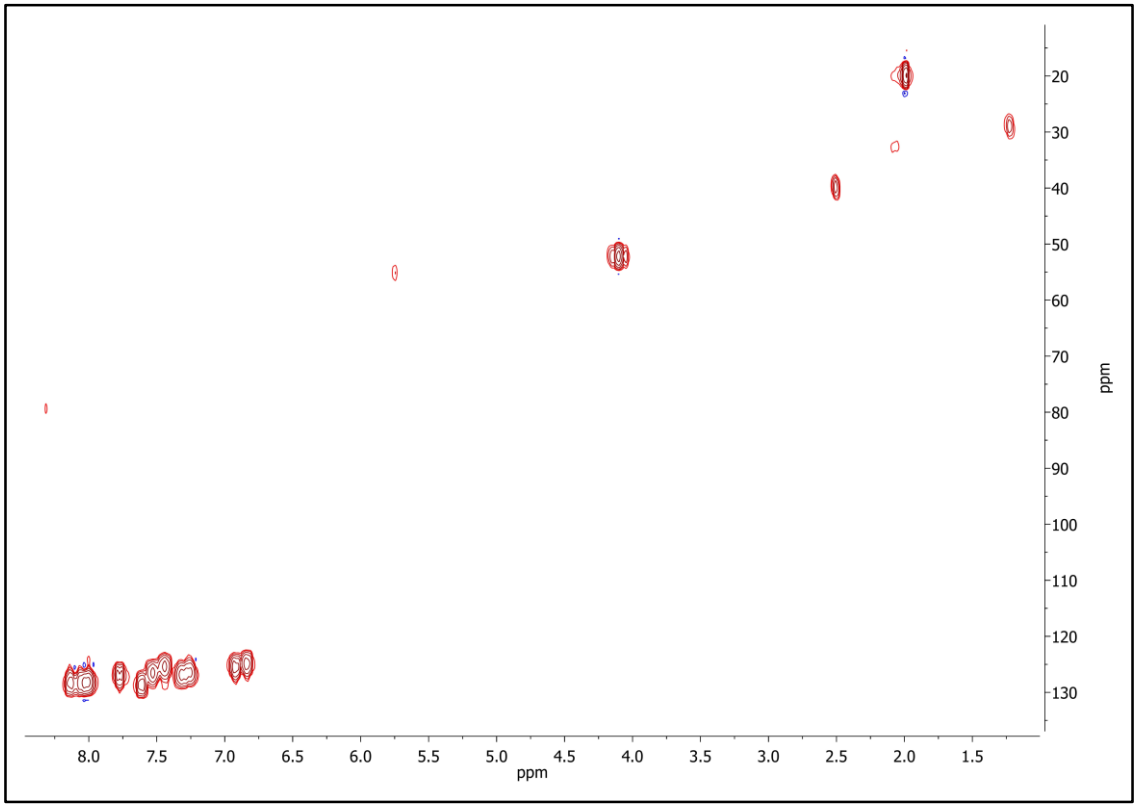


Figure S25. HSQC NMR spectrum of (*R*)-**16** (DMSO, 25 °C)

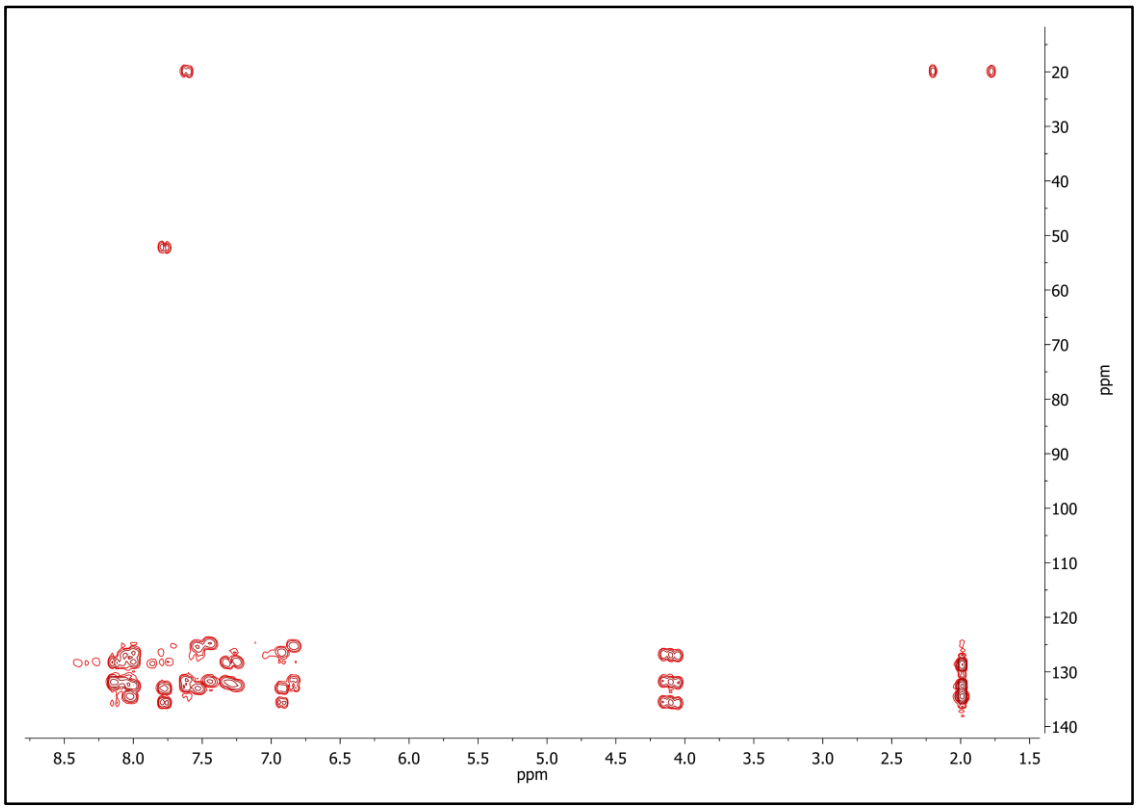


Figure S26. HMBC NMR spectrum of (*R*)-**16** (DMSO, 25 °C)

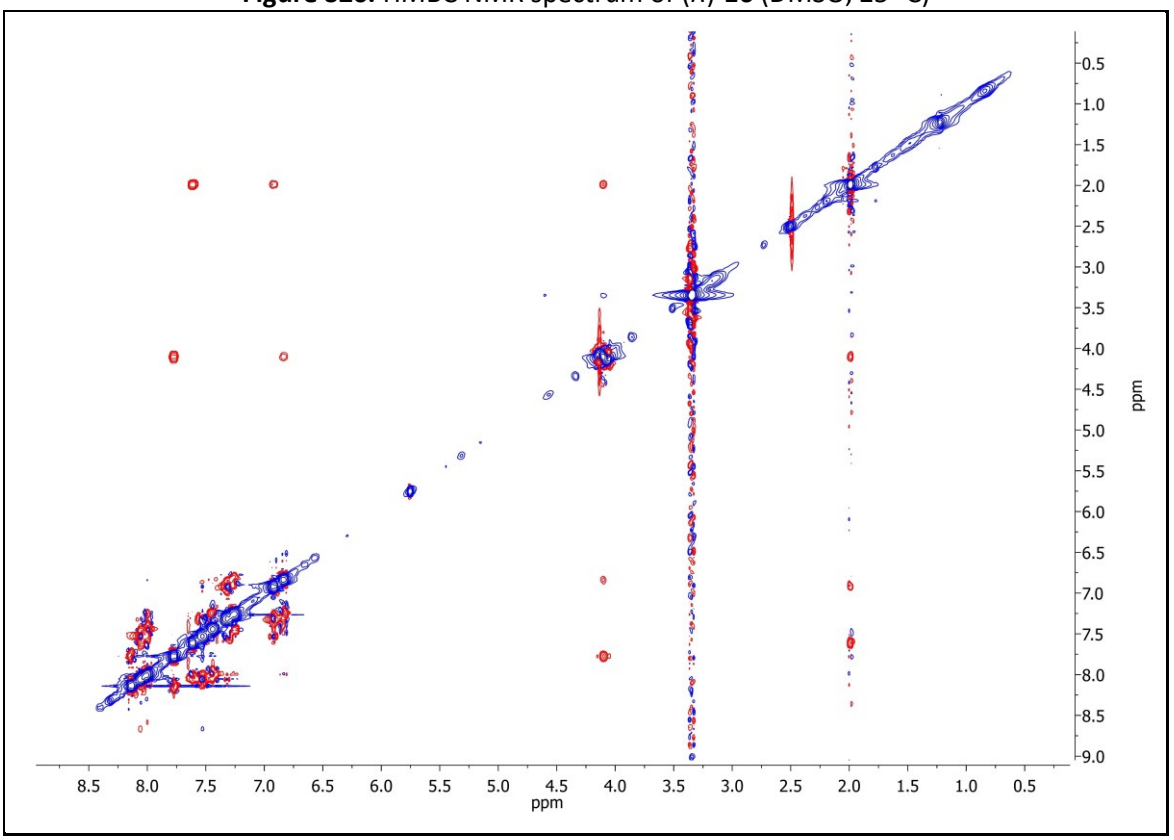


Figure S27. NOESY NMR spectrum of (*R*)-**16** (DMSO, 25 °C)

NMR spectra of (*R*)-**2**

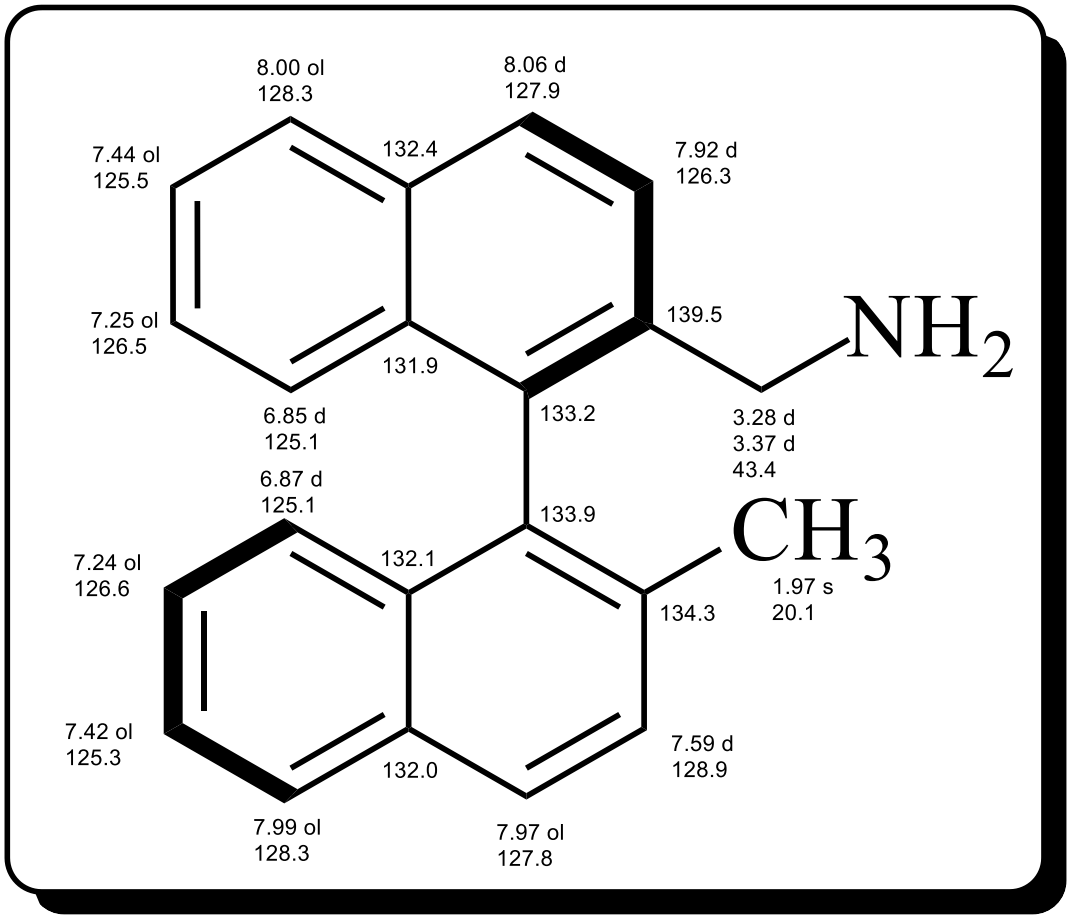


Figure S28. Molecule structure, ^{1}H and ^{13}C assignment of (*R*)-**2**

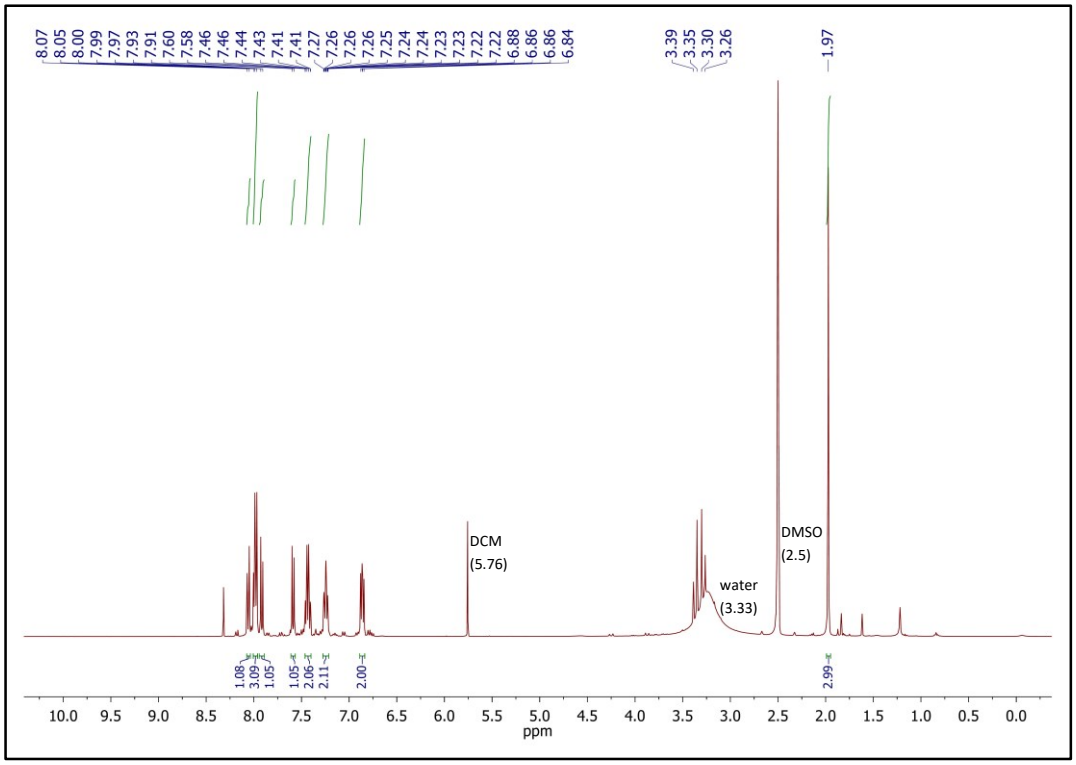


Figure S29. ^{1}H NMR spectrum of (*R*)-**2** (600 MHz, DMSO, 25 °C)

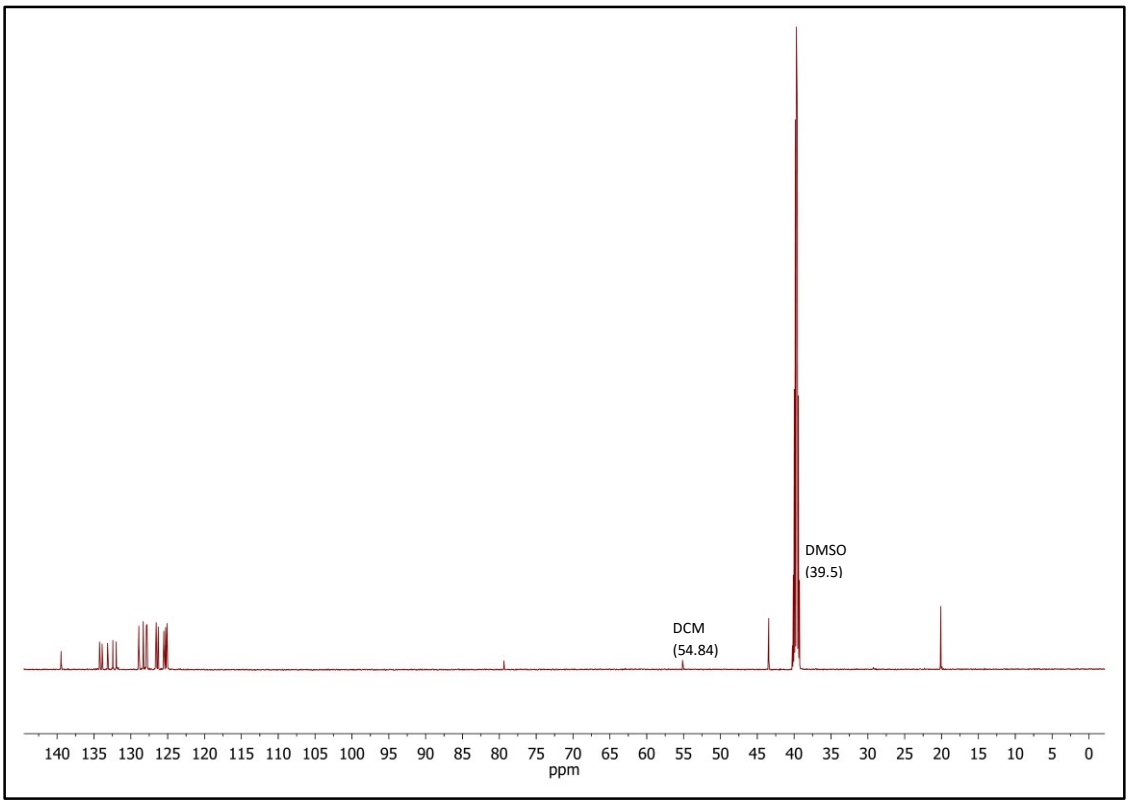


Figure S30. ^{13}C NMR spectrum of (*R*)-**2** (150 MHz, DMSO, 25 °C)

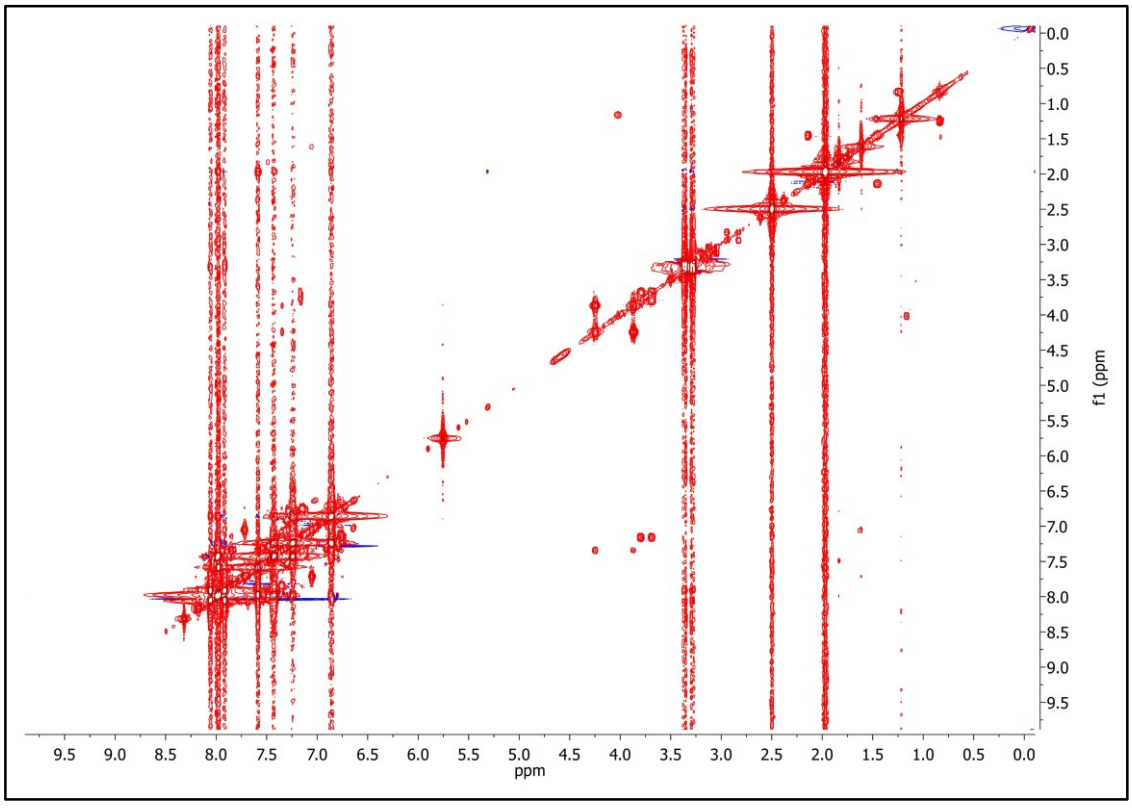


Figure S31. COSY NMR spectrum of (*R*)-**2** (DMSO, 25 °C)

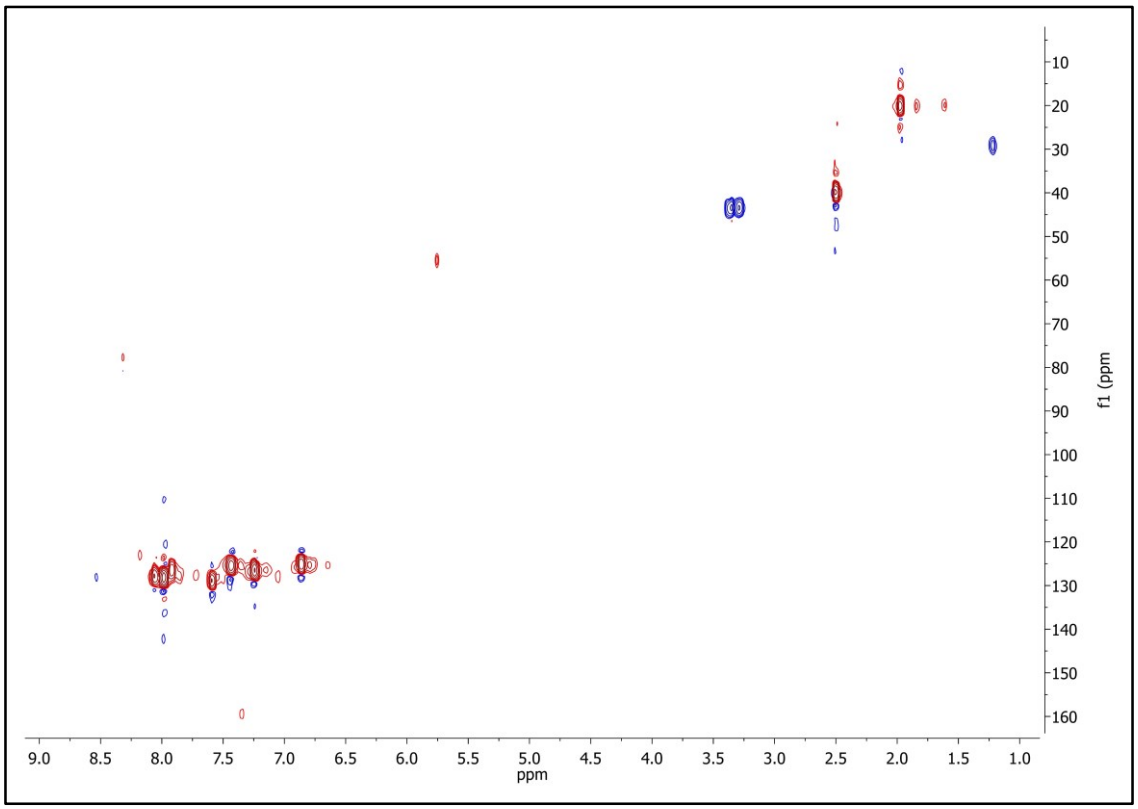


Figure S32. HSQC NMR spectrum of (*R*)-**2** (DMSO, 25 °C)

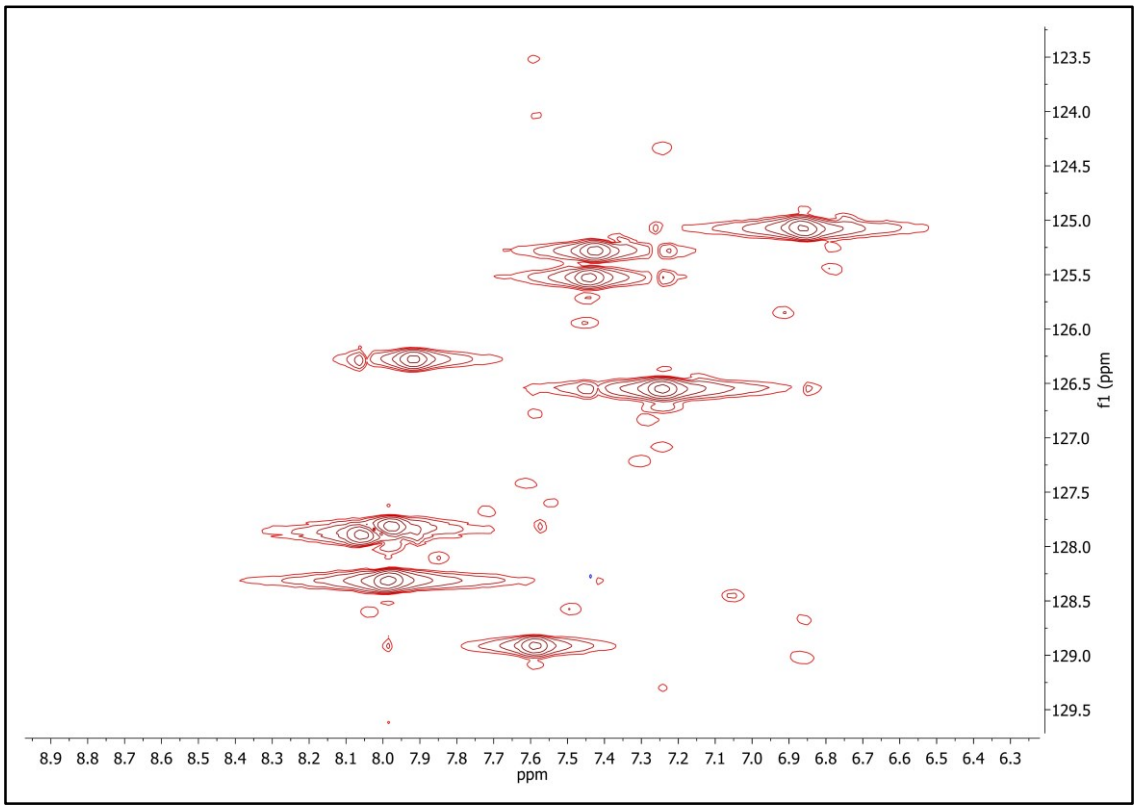


Figure S33. Selective HSQC NMR spectrum of (*R*)-**2** (DMSO, 25 °C)

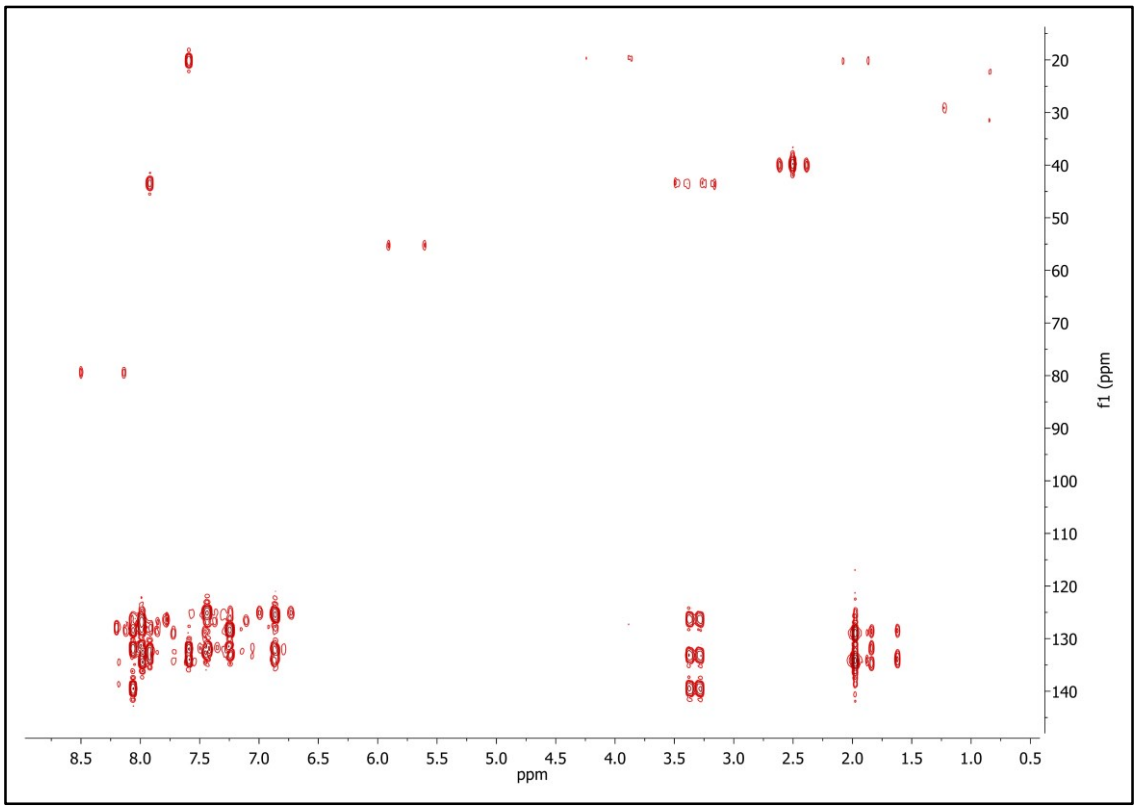


Figure S34. HMBC NMR spectrum of (*R*)-**2** (DMSO, 25 °C)

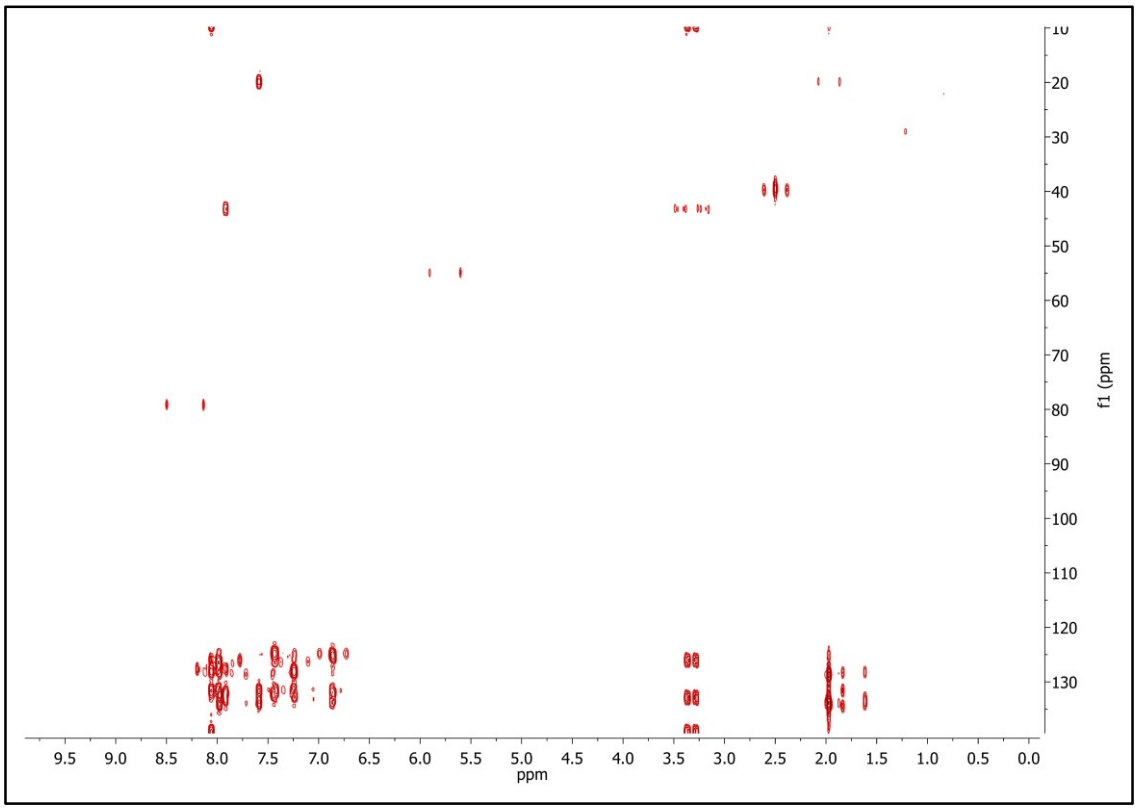


Figure S35a. Selective HMBC NMR spectrum of (*R*)-**2** (DMSO, 25 °C)

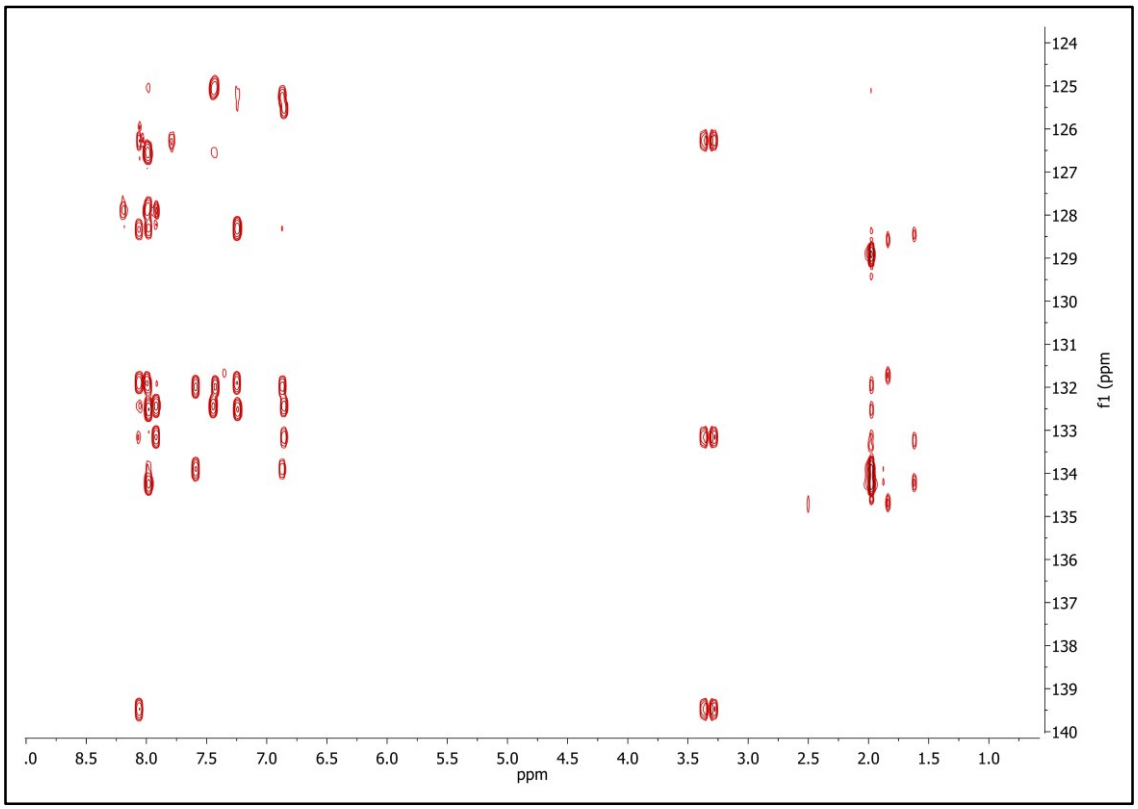


Figure S35b. Selective HMBC NMR spectrum of (*R*)-**2** (DMSO, 25 °C)

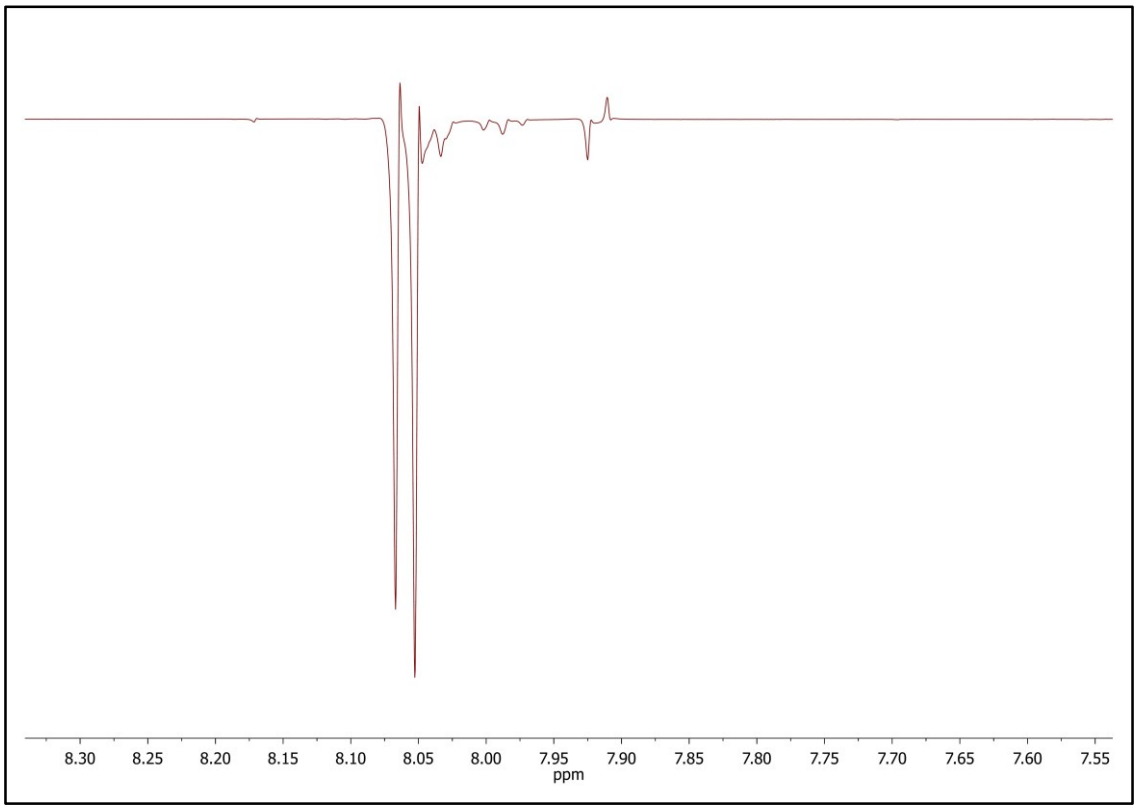


Figure S36. Selective gradient NOESY NMR spectrum of (*R*)-**2** (DMSO, 25 °C)

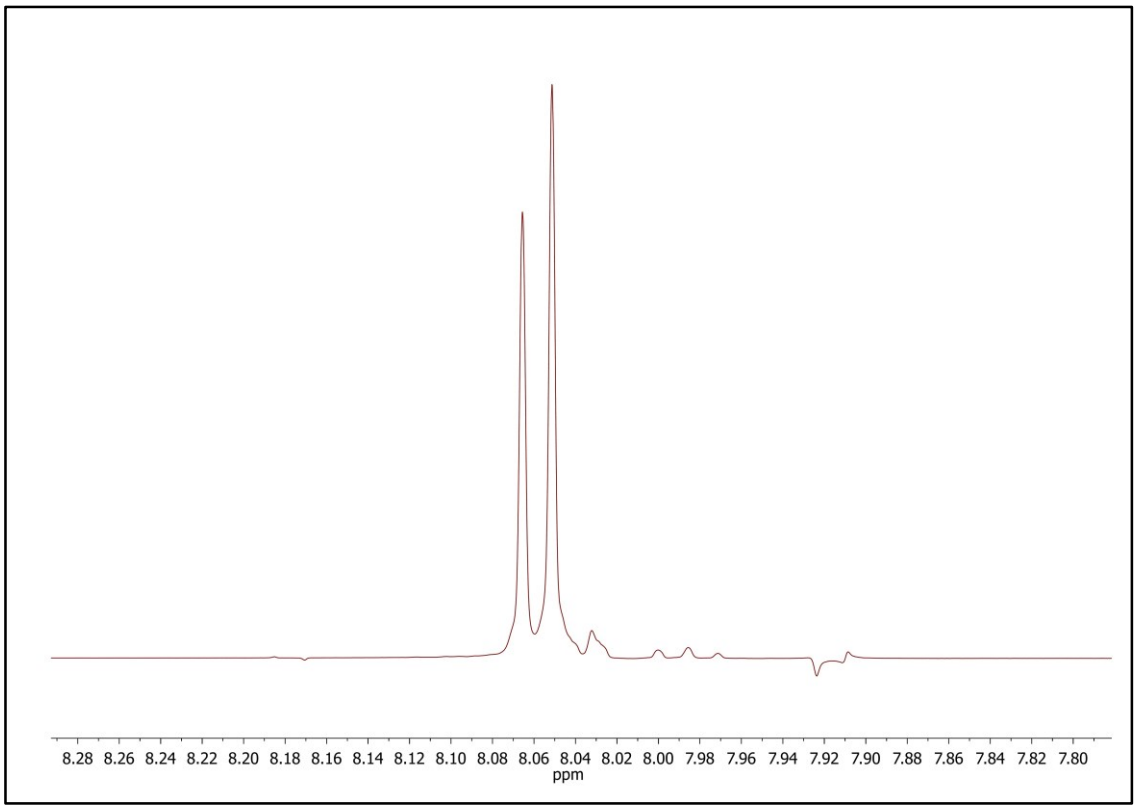


Figure S37. Selective gradient ROESY NMR spectrum of (*R*)-**2** (DMSO, 25 °C)

NMR spectra of **6**

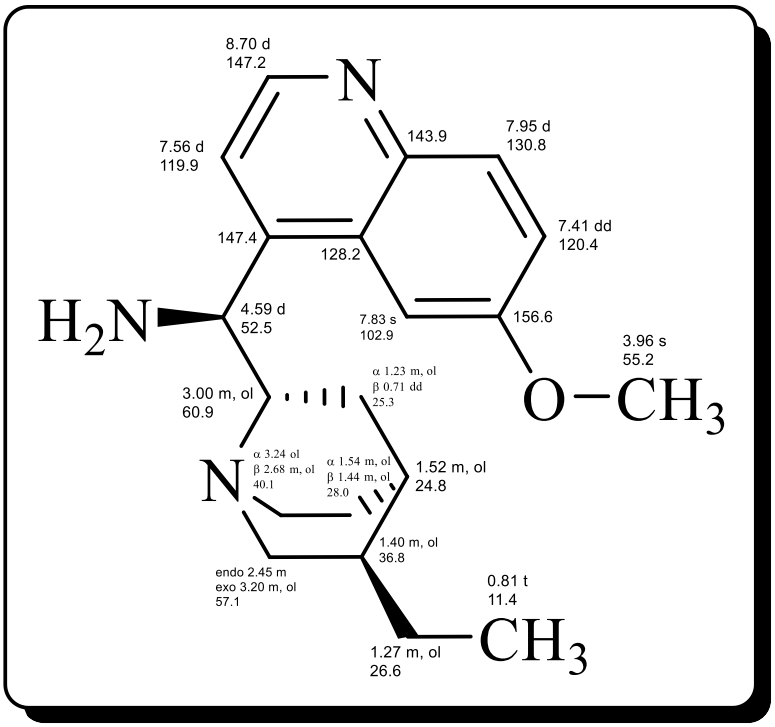


Figure S38. Molecule structure, ^{1}H and ^{13}C assignment of **6**

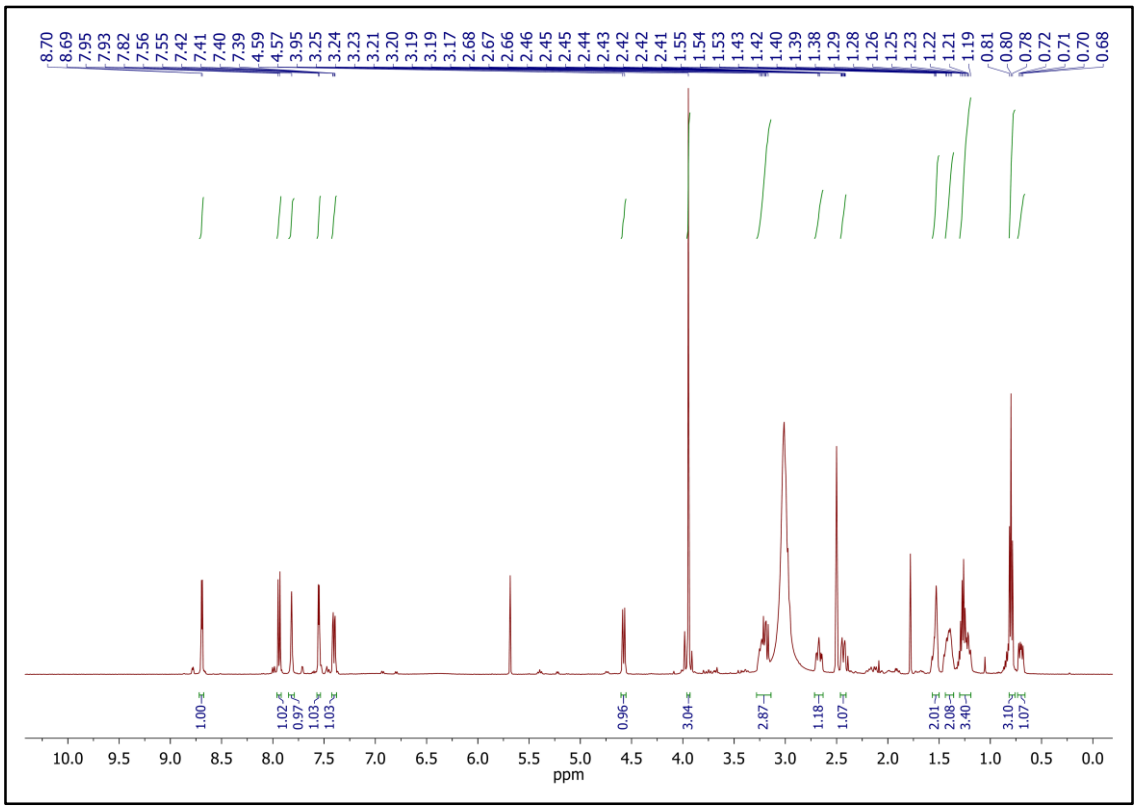


Figure S39. ^{1}H NMR spectrum of **6** (500 MHz, DMSO, 80 °C)

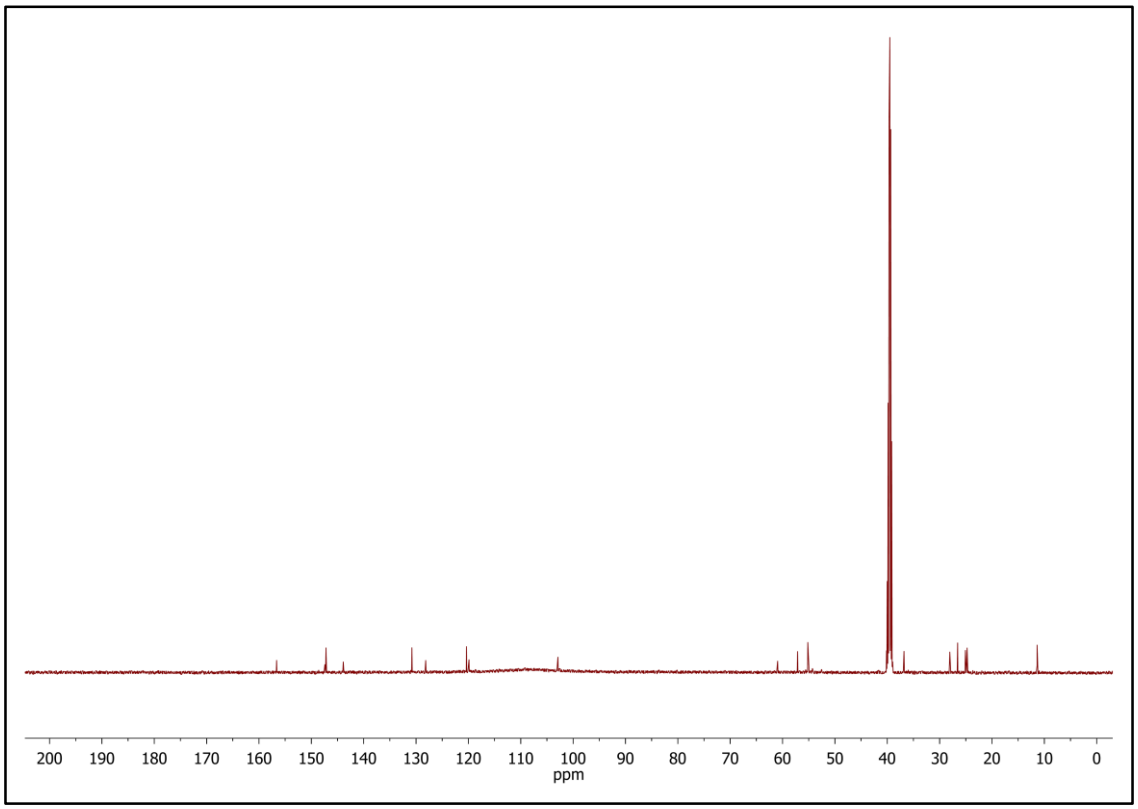


Figure S40. ^{13}C NMR spectrum of **6** (125 MHz, DMSO, 80 °C)

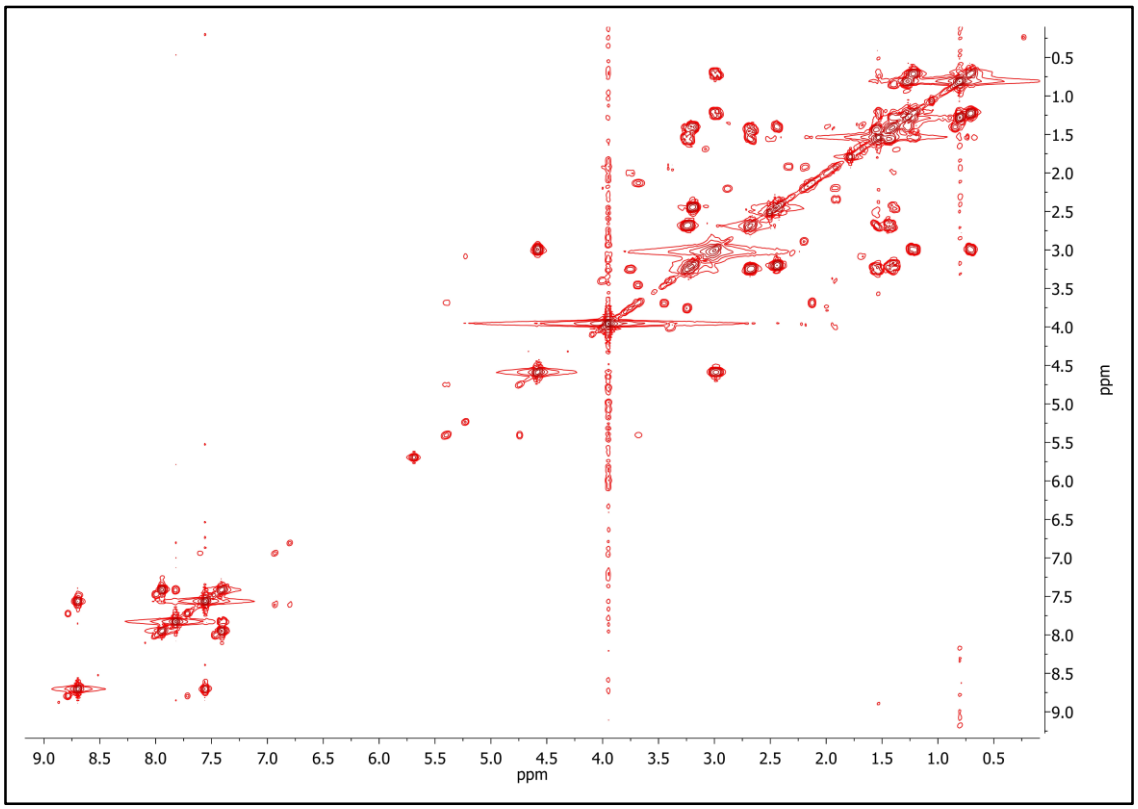


Figure S41. COSY spectrum of **6** (DMSO, 80 °C)

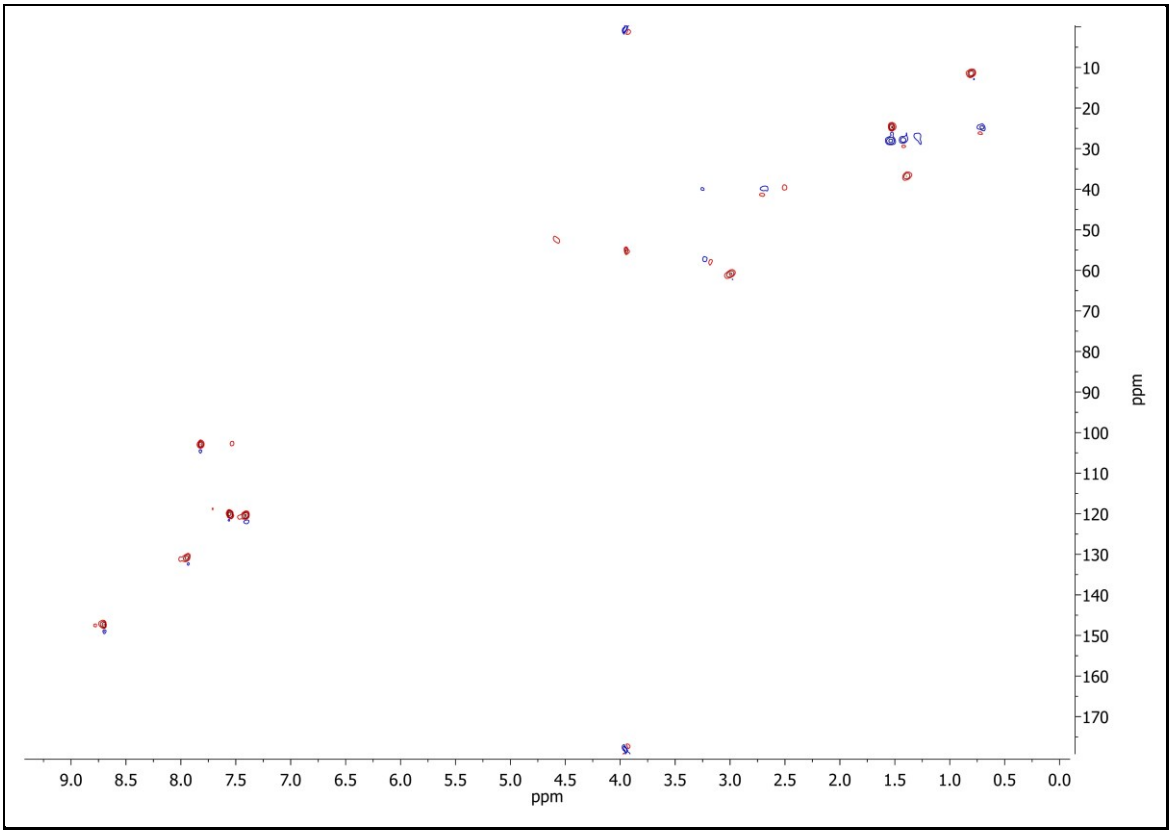


Figure S42. HSQC spectrum of **6** (DMSO, 80 °C)

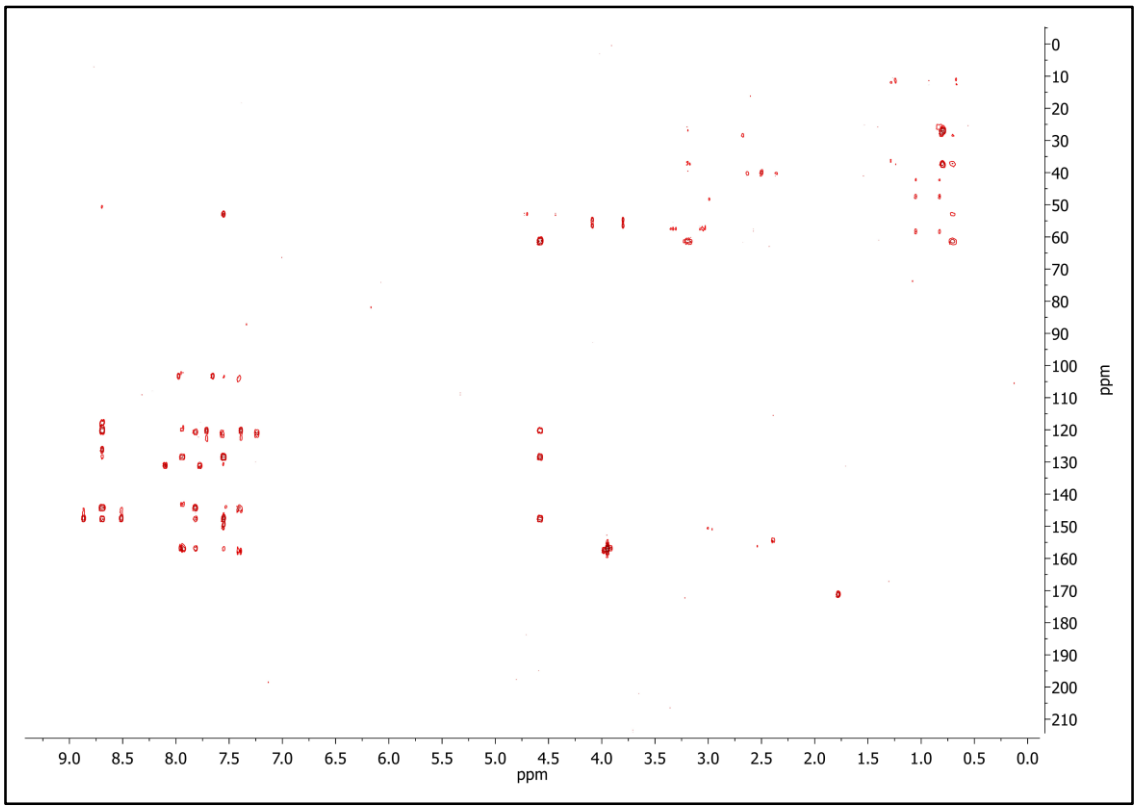


Figure S43. HMBC spectrum of **6** (DMSO, 80 °C)

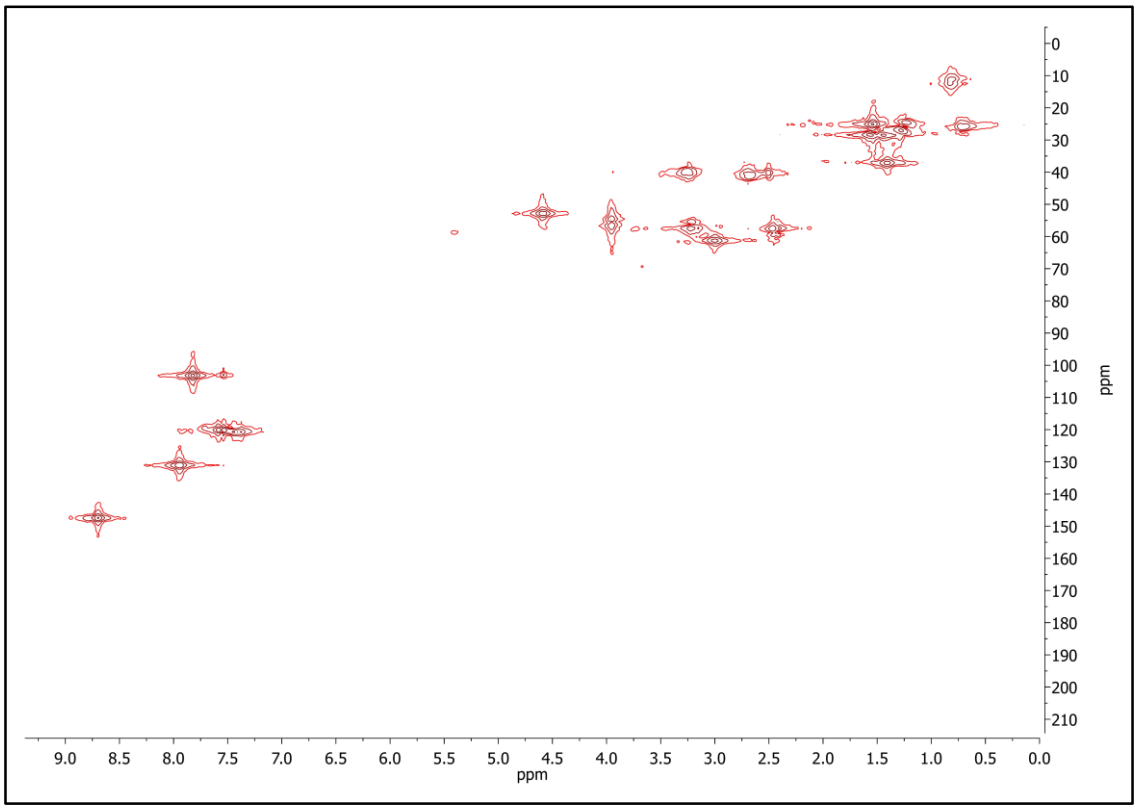


Figure S44. HMQC spectrum of **6** (DMSO, 80 °C)

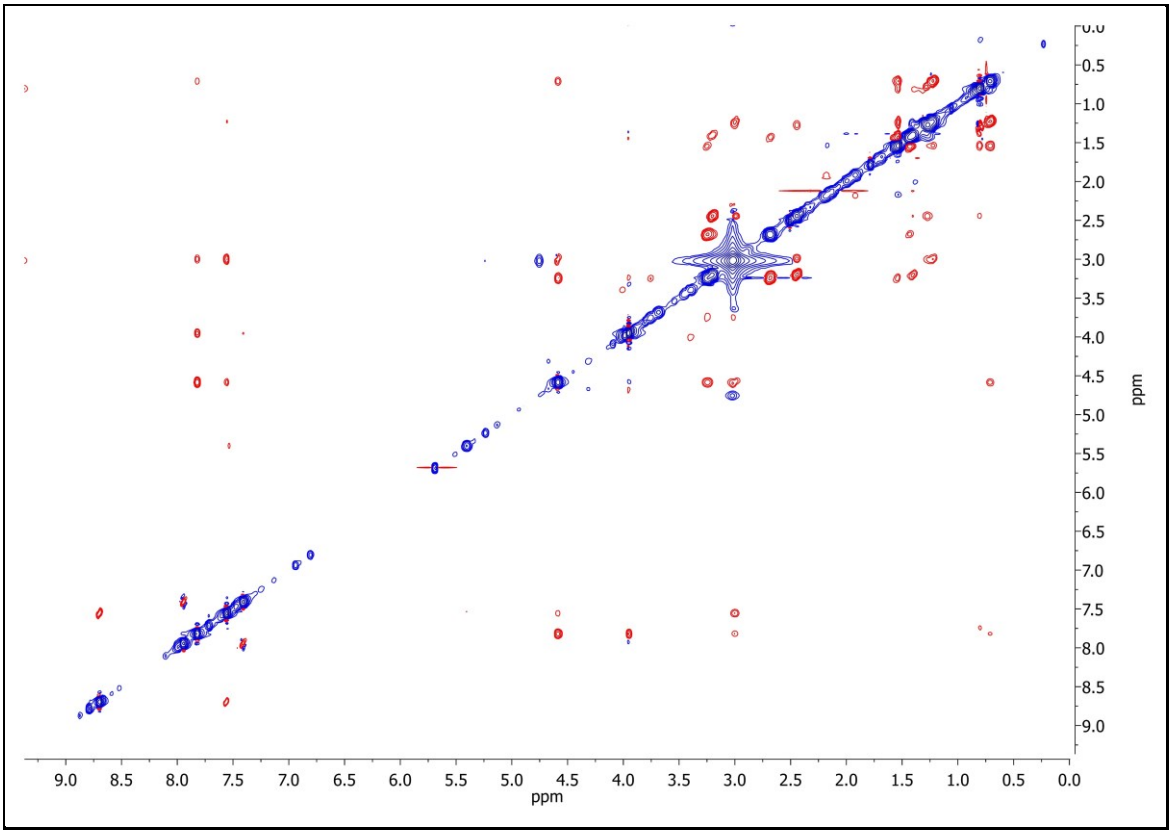


Figure S45. NOESY spectrum of **6** (DMSO, 80 °C)

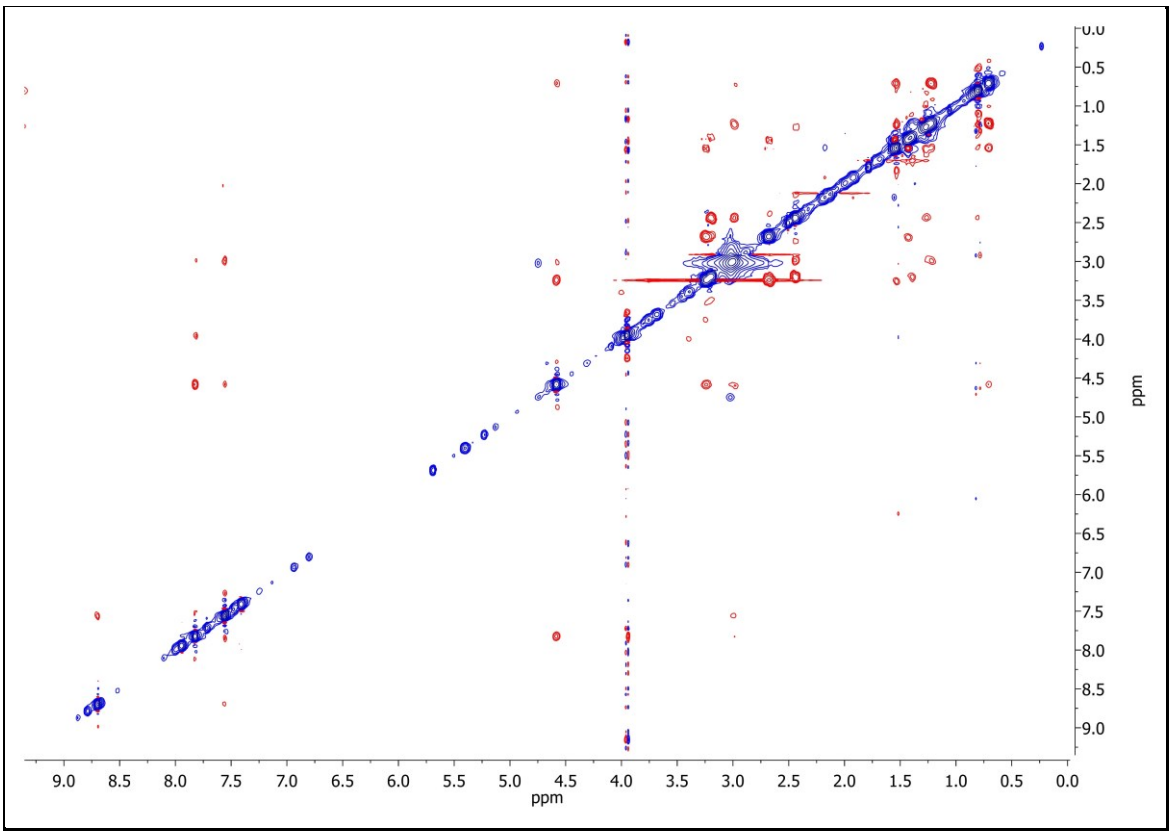


Figure S46. NOESY spectrum of **6** (DMSO, 80 °C)

NMR spectra of **HSq-M**

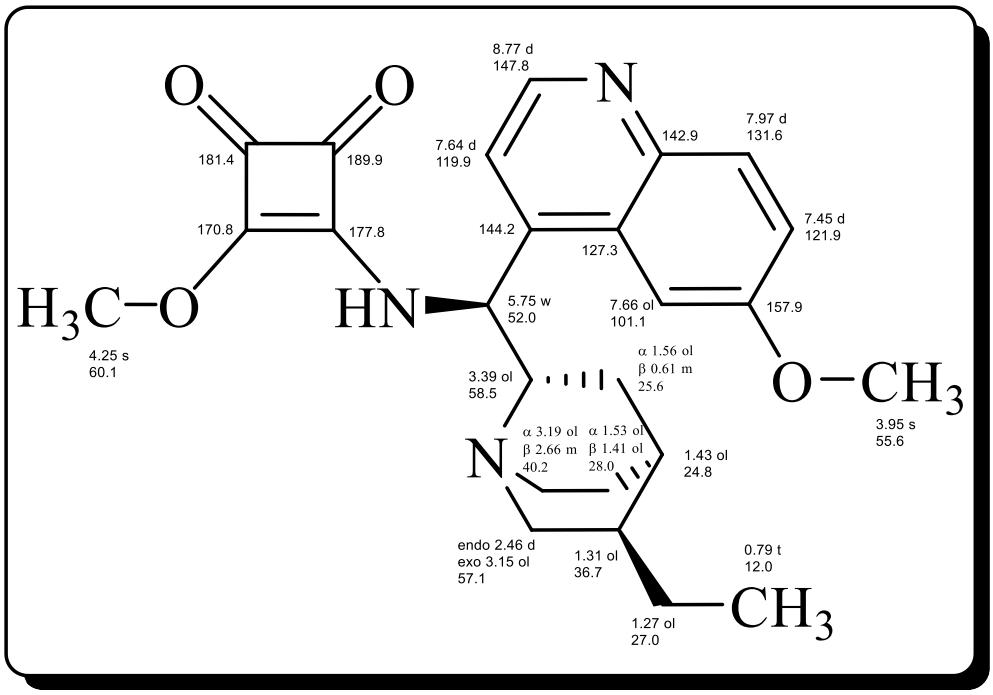


Figure S47. Molecule structure, ^{1}H and ^{13}C assignment of **HSq-M**

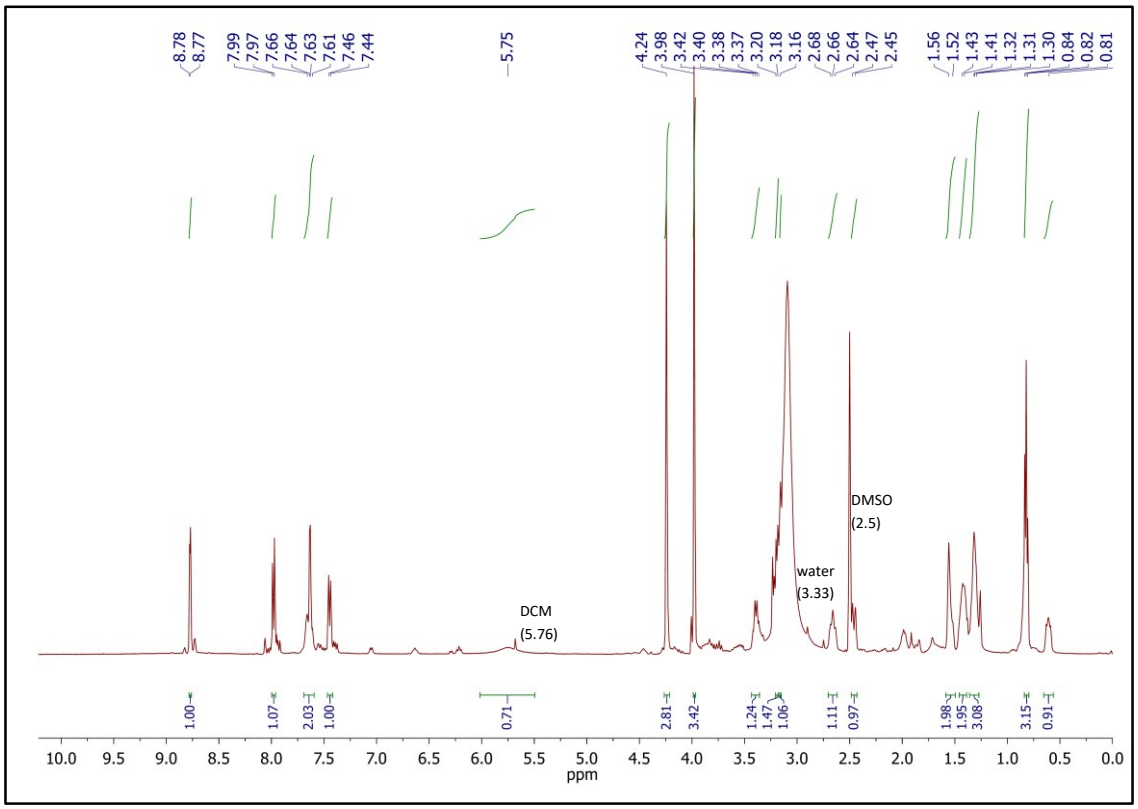


Figure S48. ^{1}H NMR spectrum of **HSq-M** (500 MHz, DMSO, 80 °C)

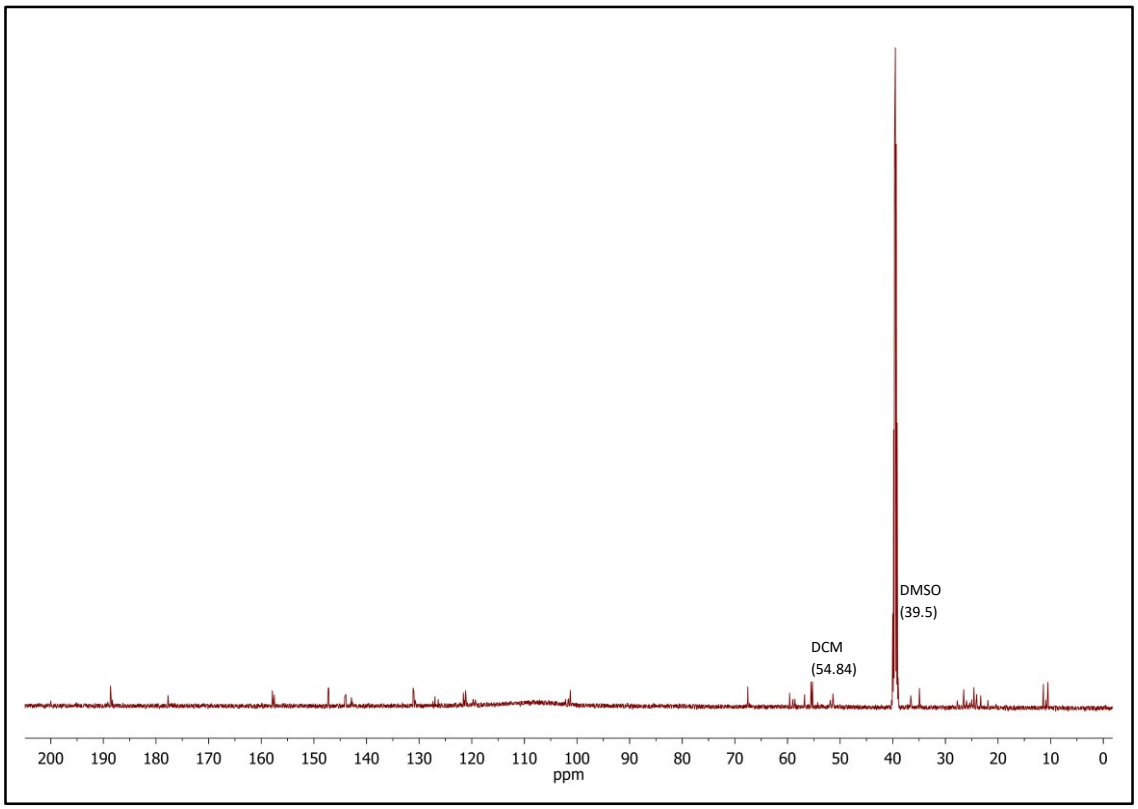


Figure S49. ^{13}C NMR spectrum of **HSq-M** (125 MHz, DMSO, 80 °C)

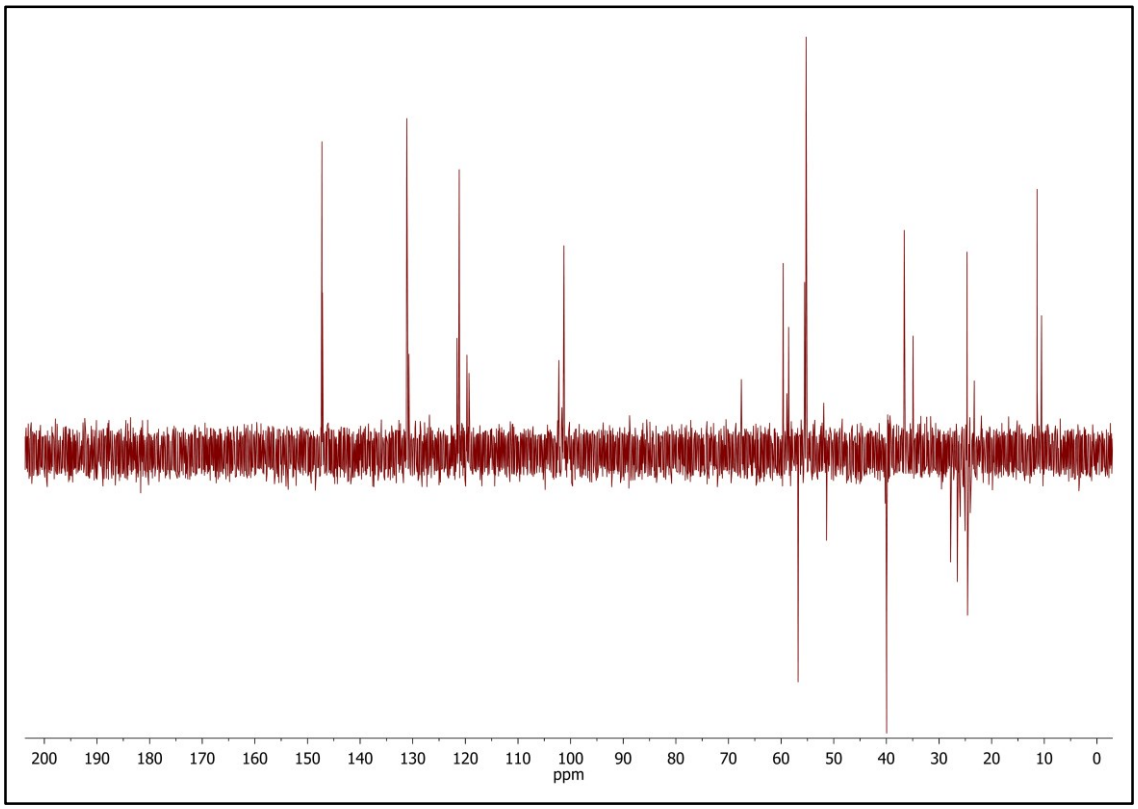


Figure S50. ^{13}C NMR DEPT spectrum of **HSq-M** (125 MHz, DMSO, 80 °C)

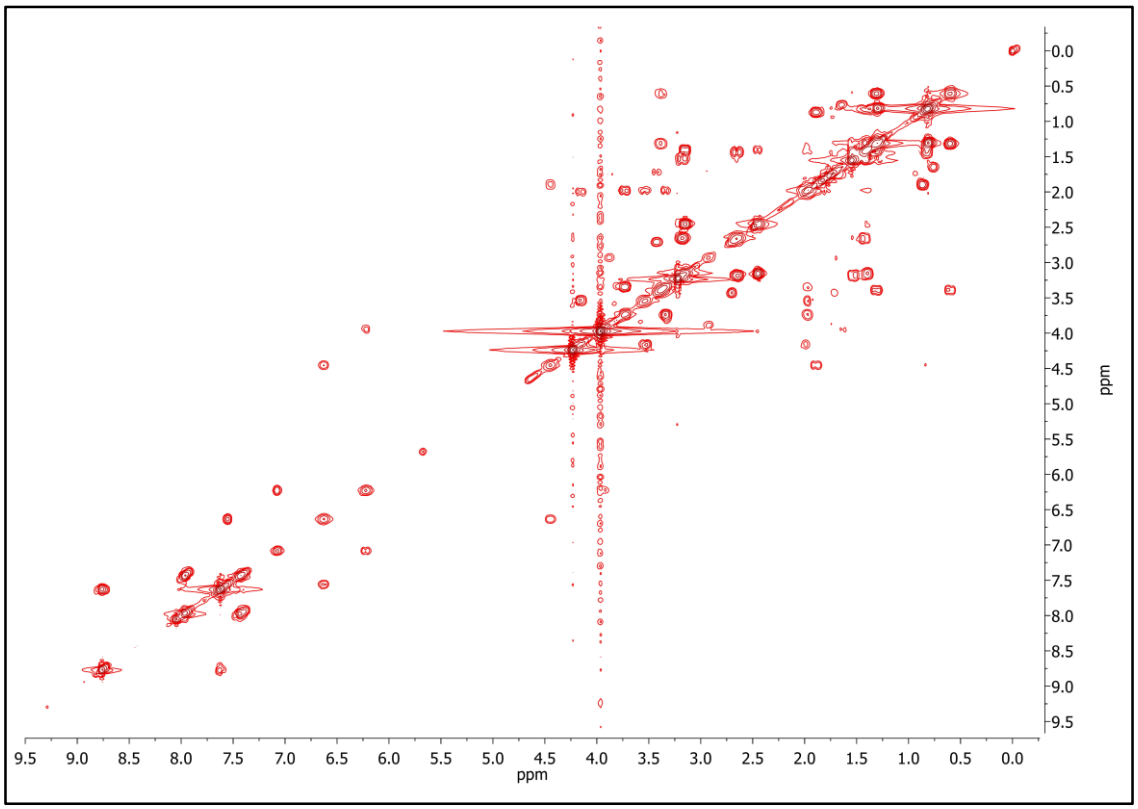


Figure S51. COSY spectrum of **HSq-M** (DMSO, 80 °C)

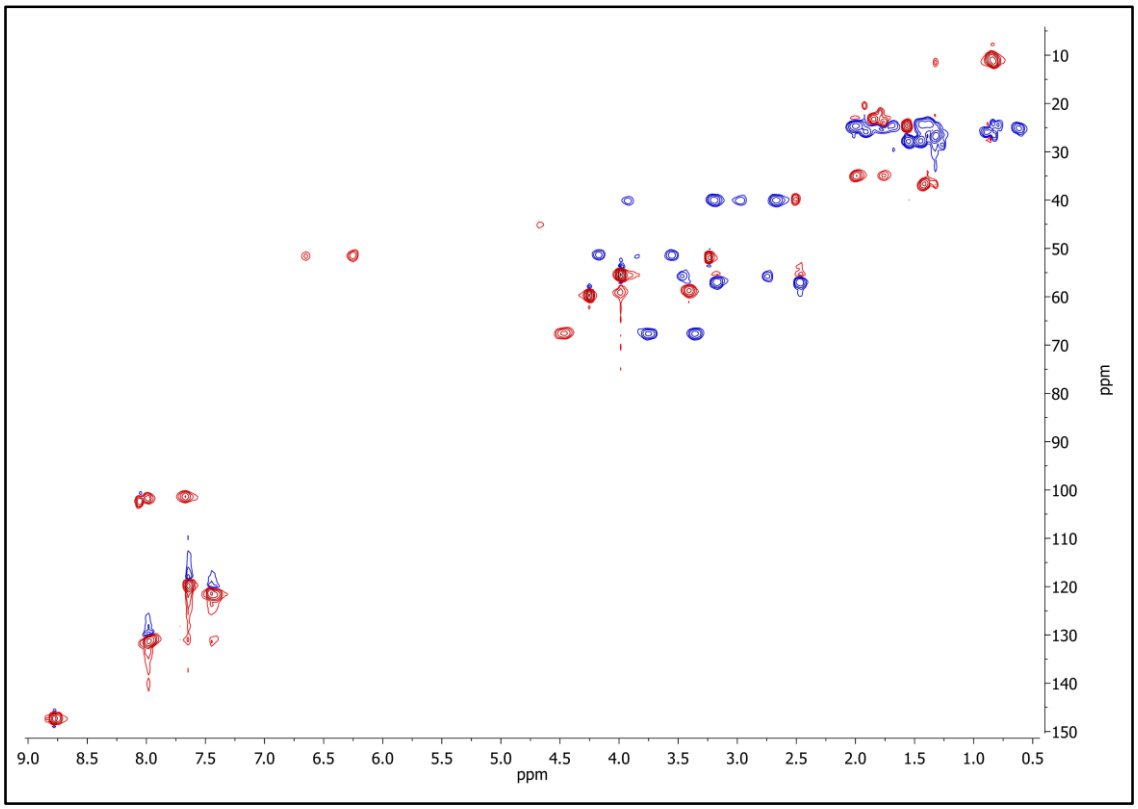


Figure S52. HSQC spectrum of **HSq-M** (DMSO, 80 °C)

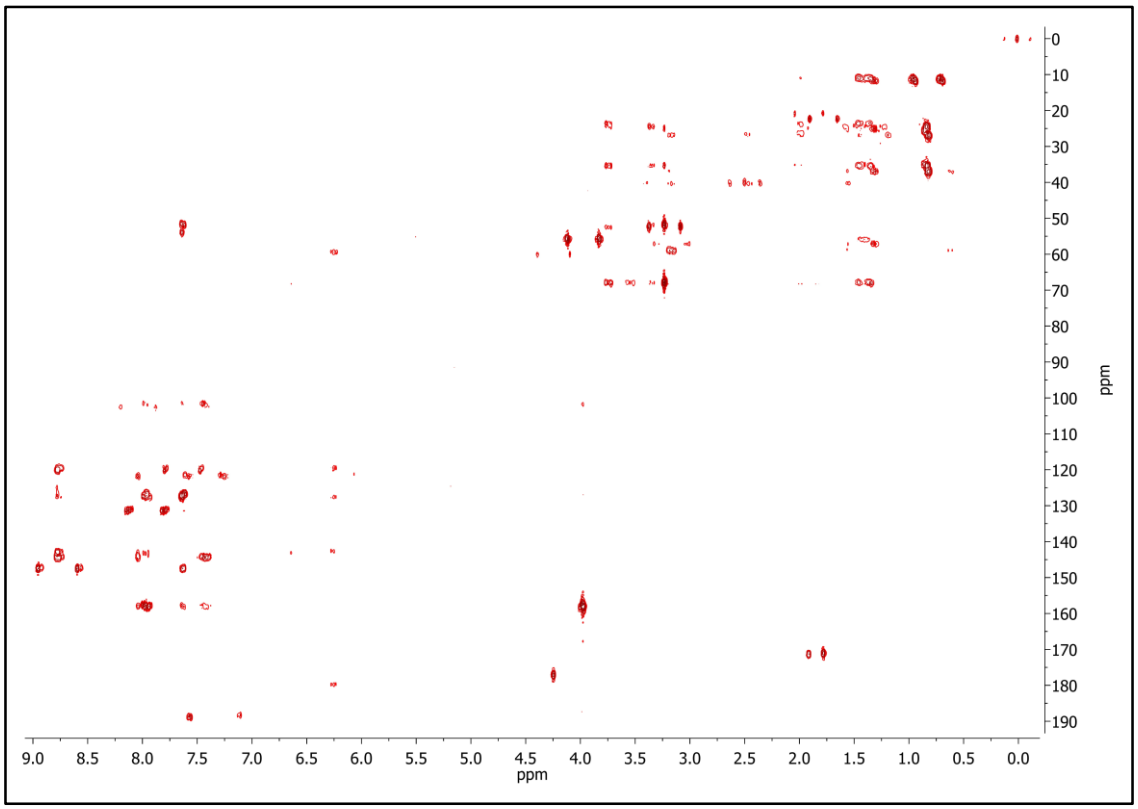


Figure S53. HMBC spectrum of **HSq-M** (DMSO, 80 °C)

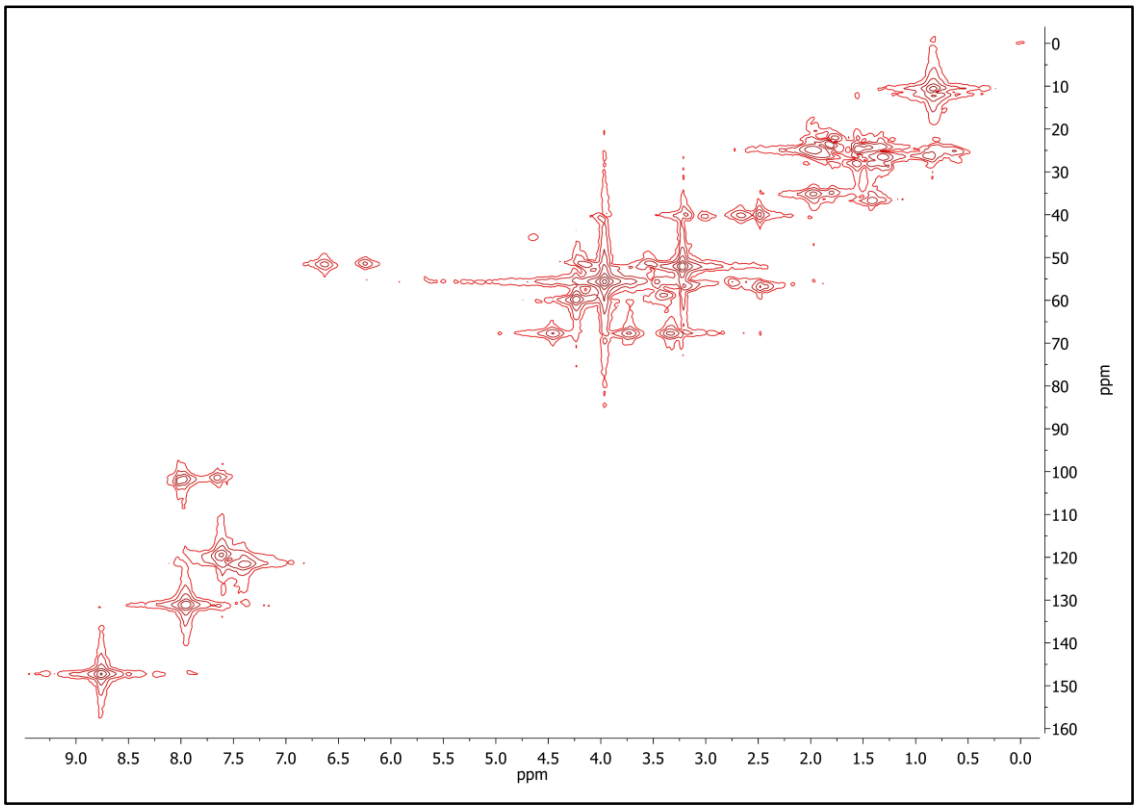


Figure S54. HMQC spectrum of **HSq-M** (DMSO, 80 °C)

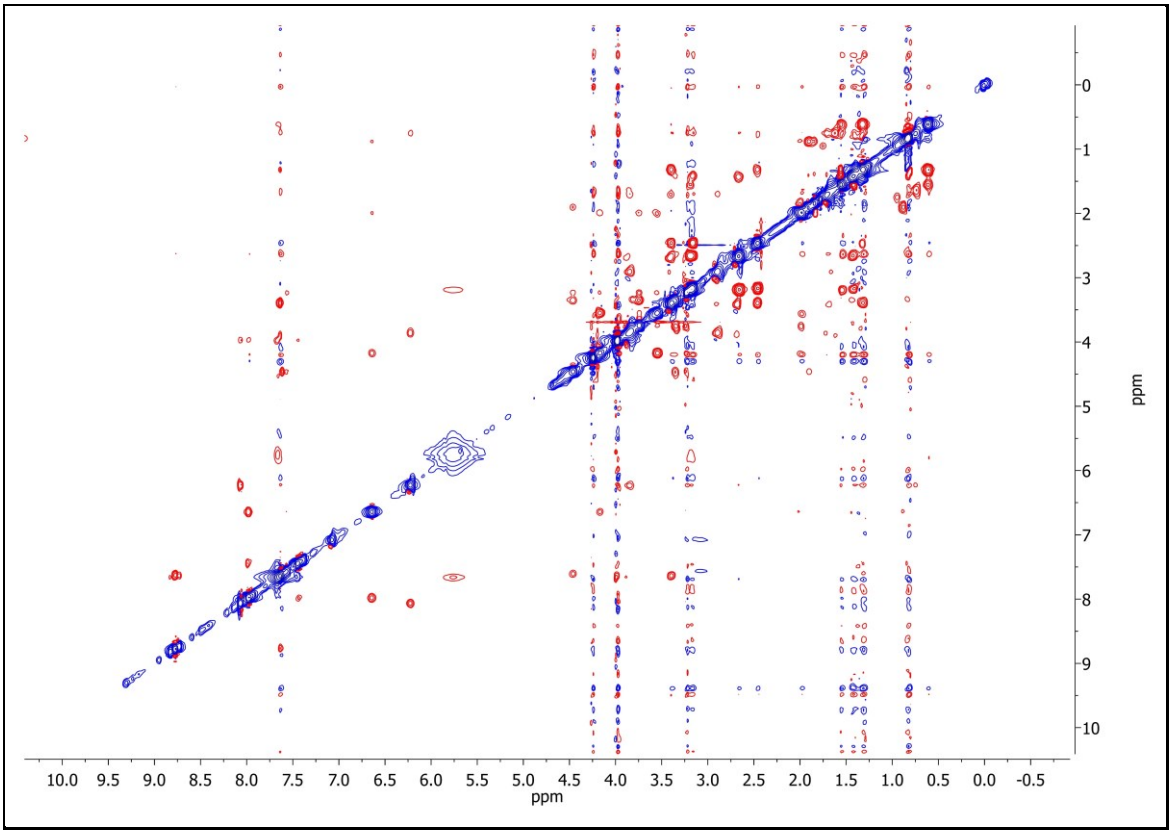


Figure S55. NOESY spectrum of **HSq-M** (DMSO, 80 °C)

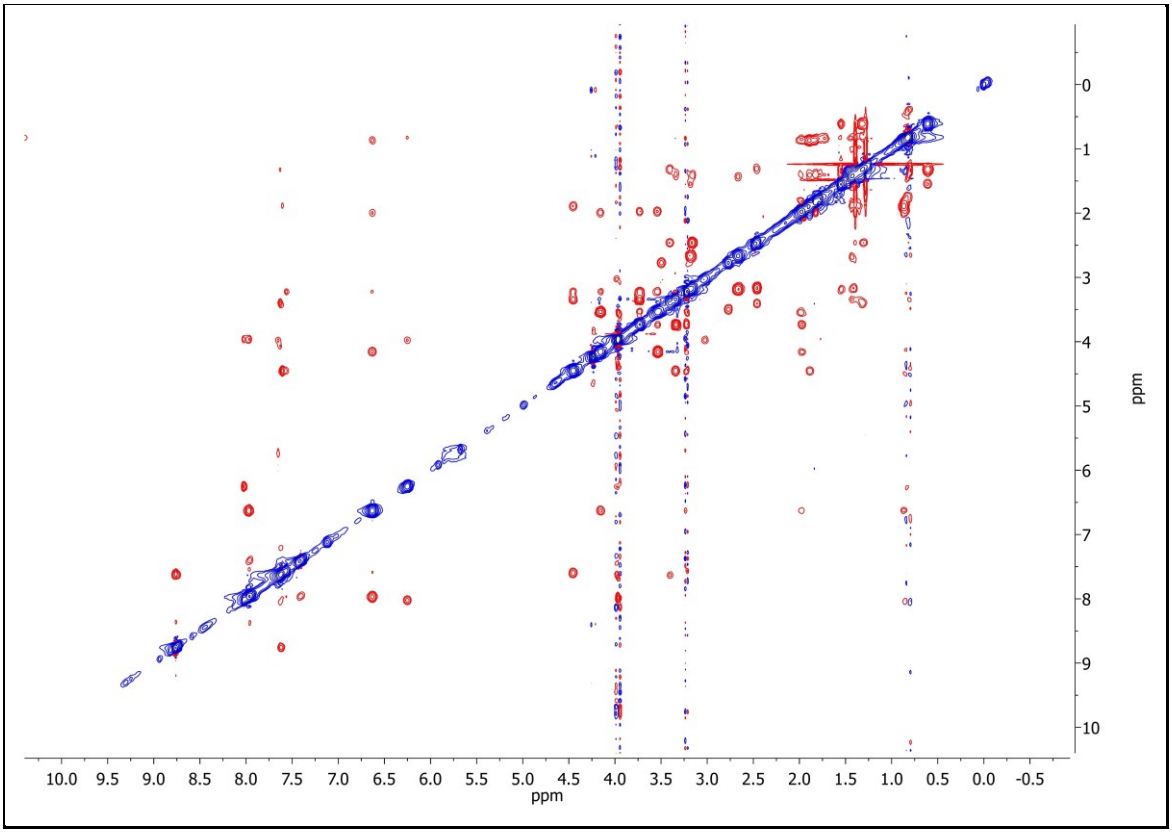


Figure S56. ROESY spectrum of **HSq-M** (DMSO, 80 °C)

NMR spectra of **HSq-B**

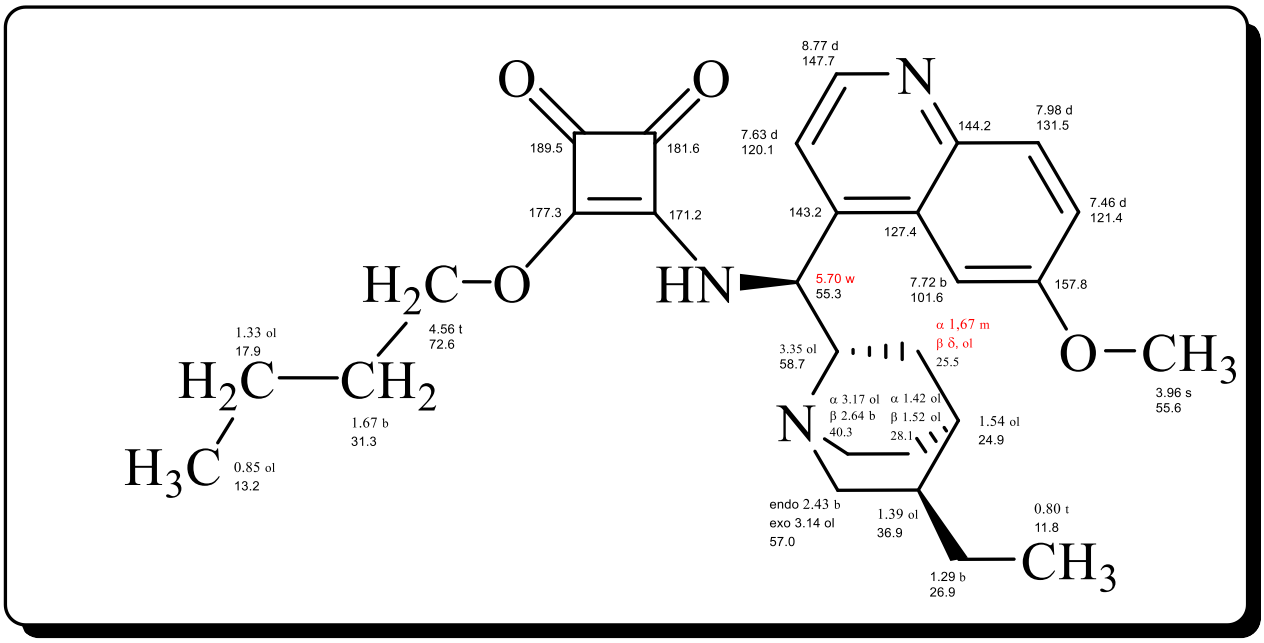


Figure S57. Molecule structure, ^{1}H and ^{13}C assignment of **HSq-B**

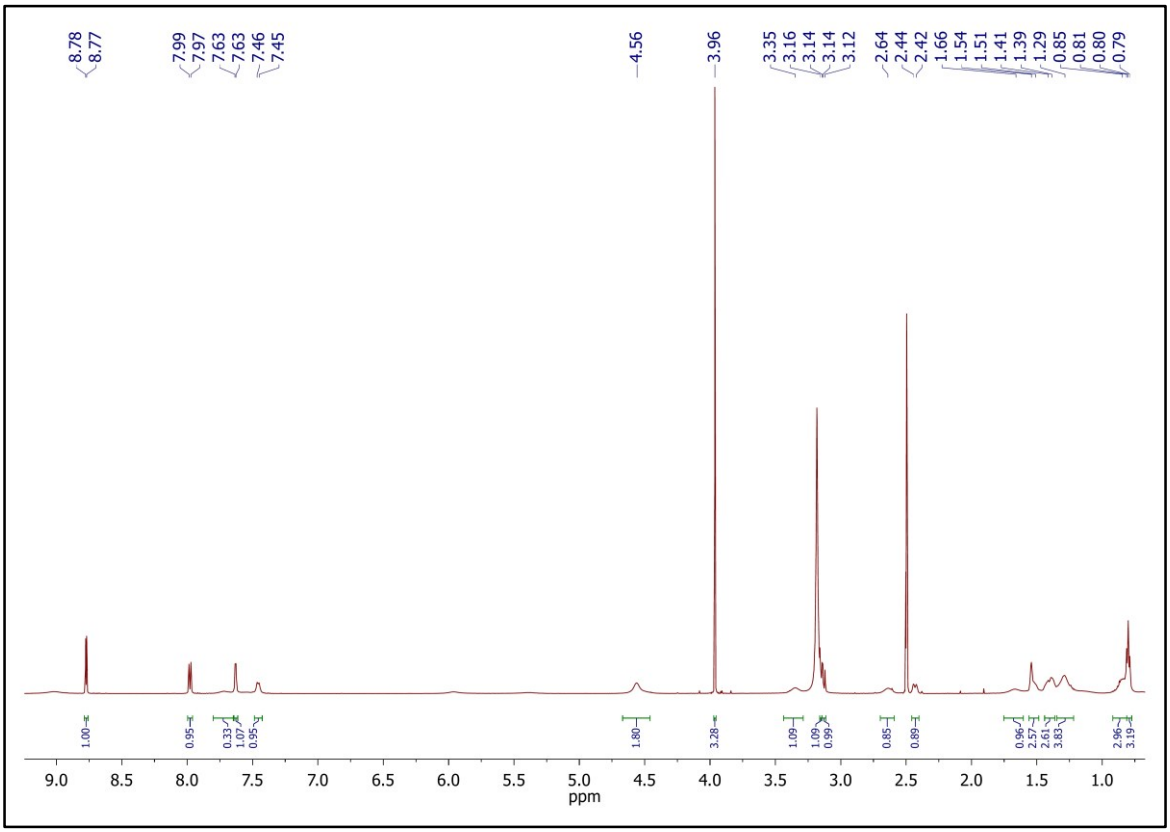


Figure S58. ^{1}H NMR spectrum of **HSq-B** (600 MHz, DMSO, 60 °C)

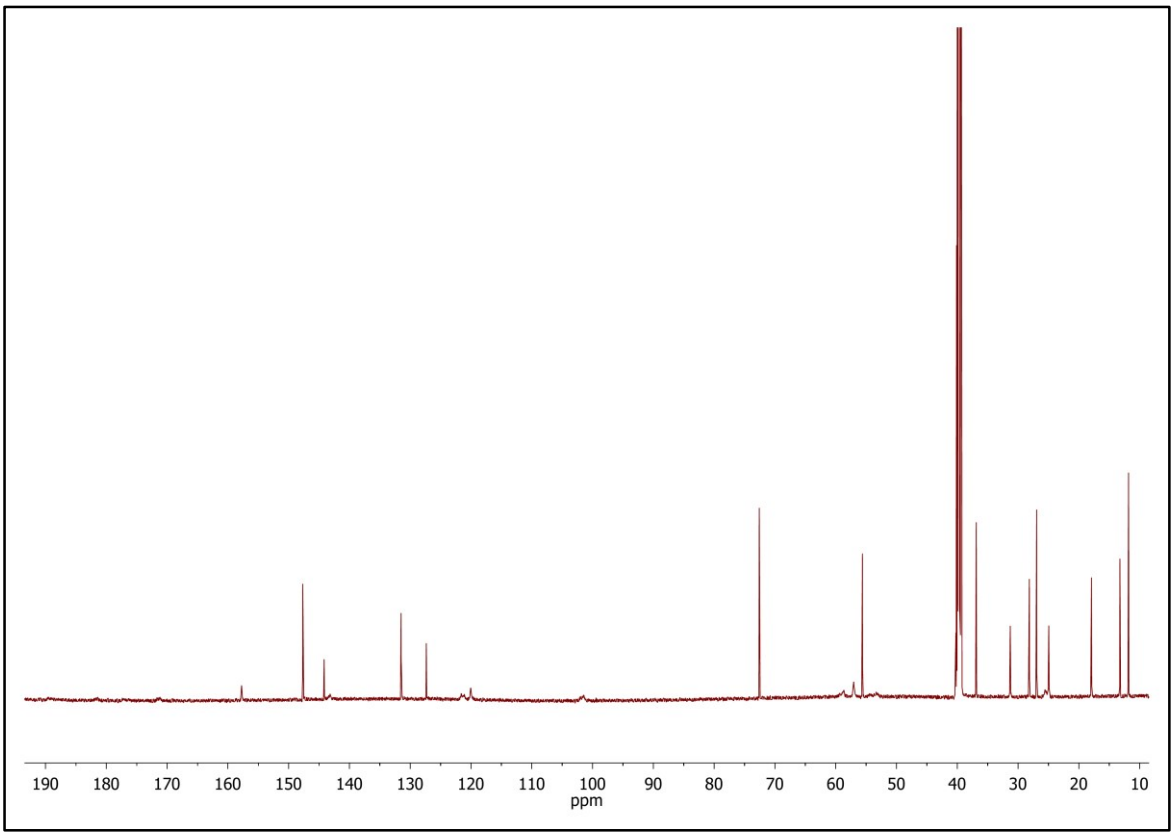


Figure S59. ^{13}C NMR spectrum of **HSq-B** (150 MHz, DMSO, 60 °C)

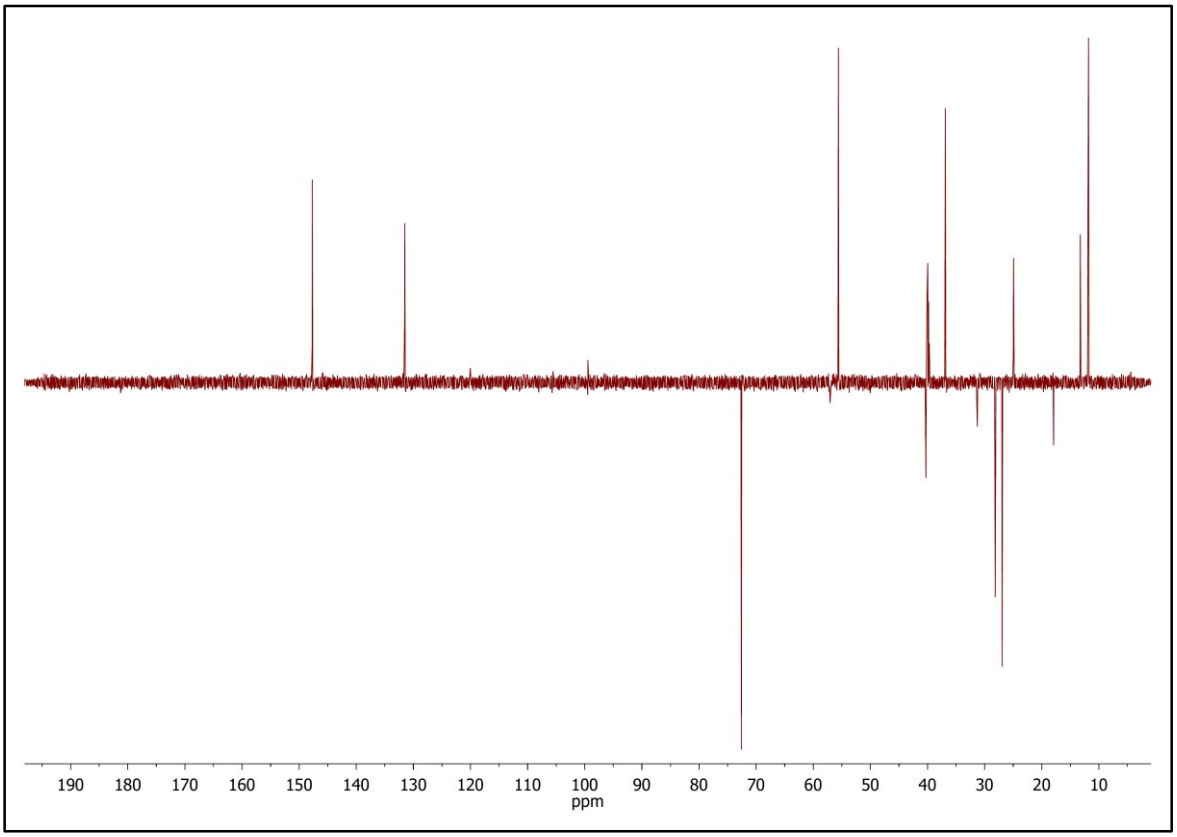


Figure S60. DEPT ^{13}C NMR spectrum of **HSq-B** (DMSO, 60 °C)

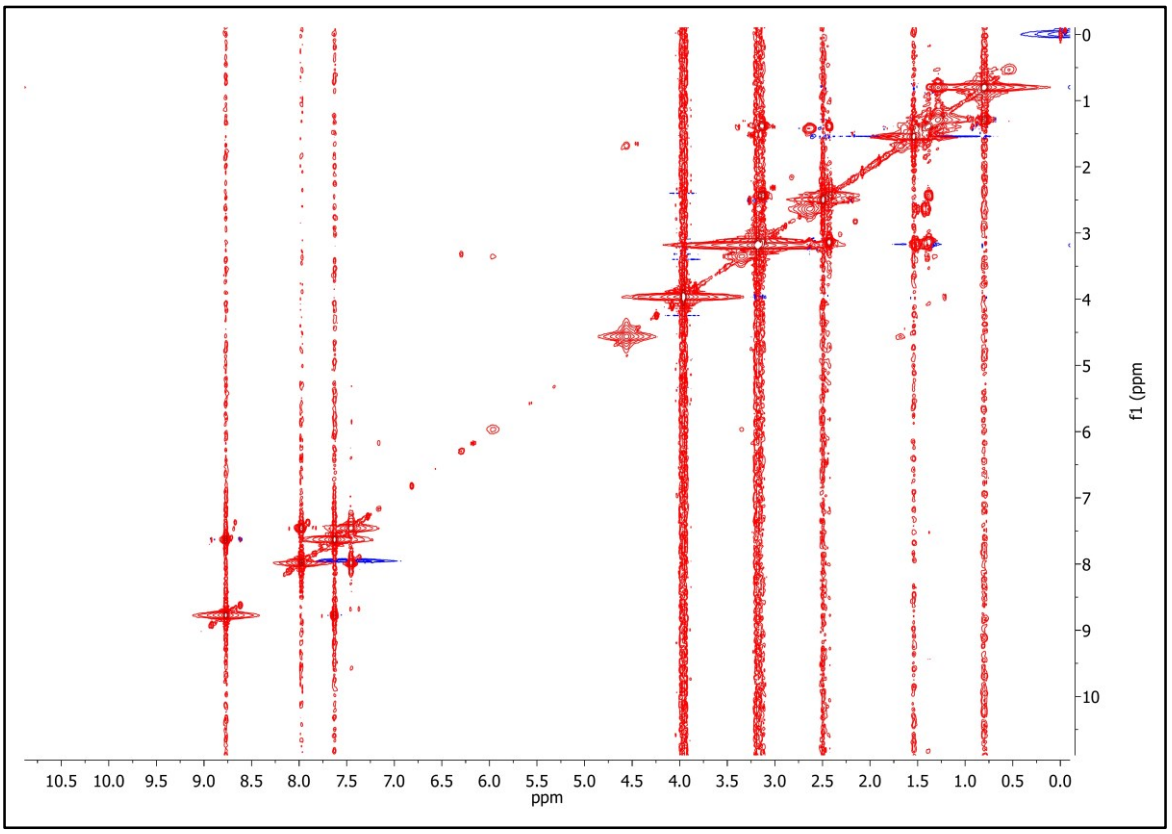


Figure S61. COSY spectrum of **HSq-B** (DMSO, 60 °C)

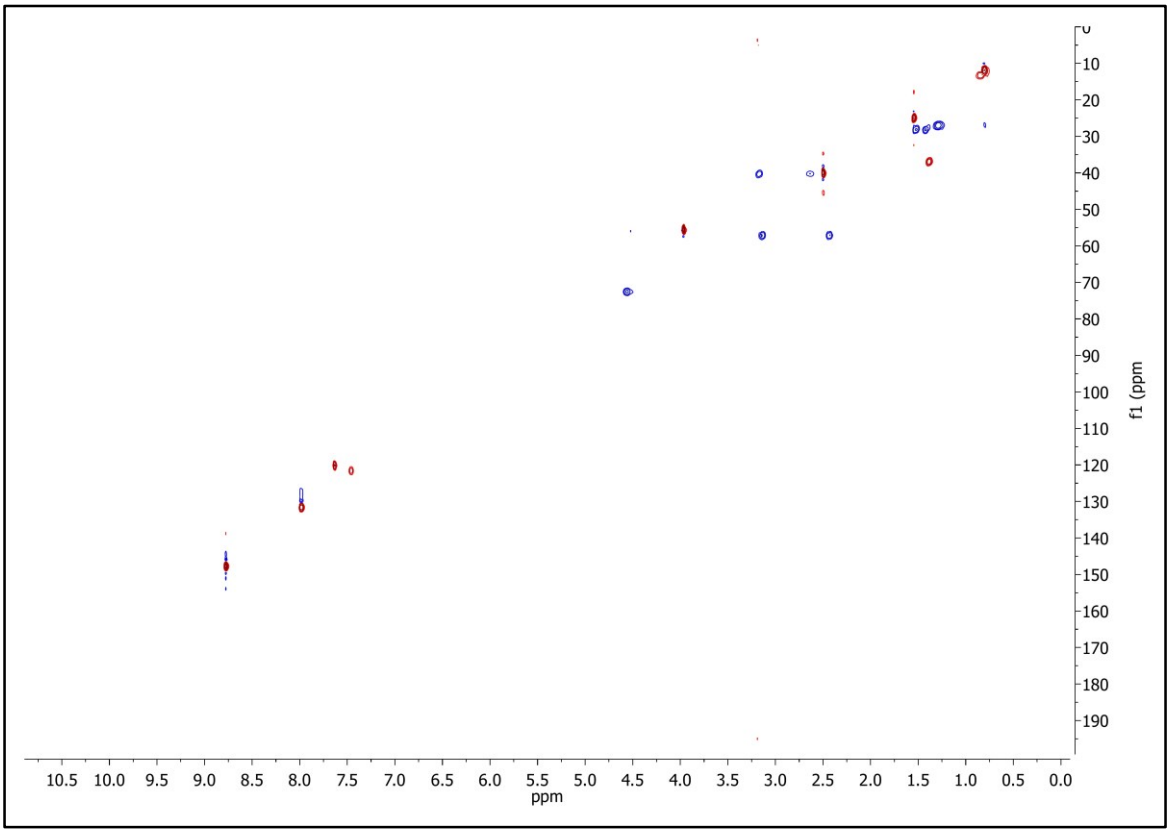


Figure S62a. HSQC spectrum of **HSq-B** (DMSO, 60 °C)

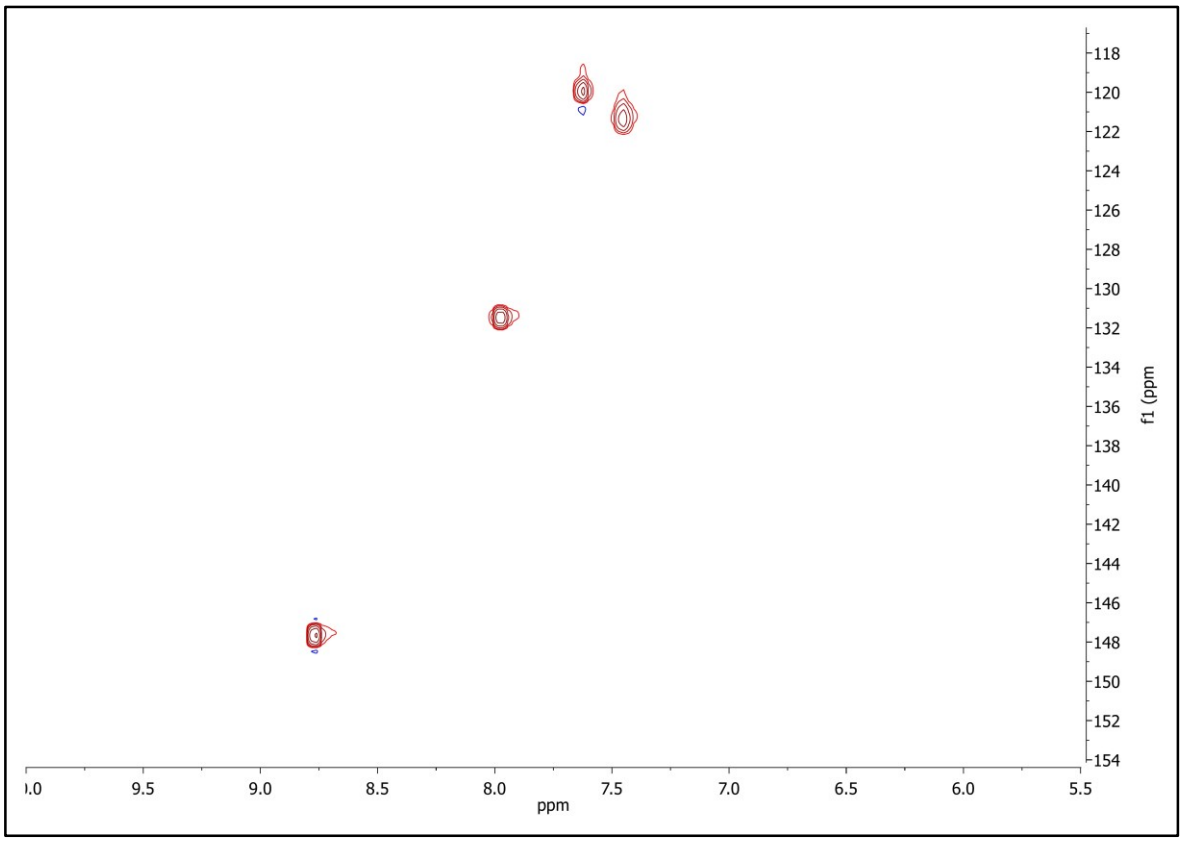


Figure S62b. HSQC spectrum of **HSq-B** (DMSO, 60 °C)

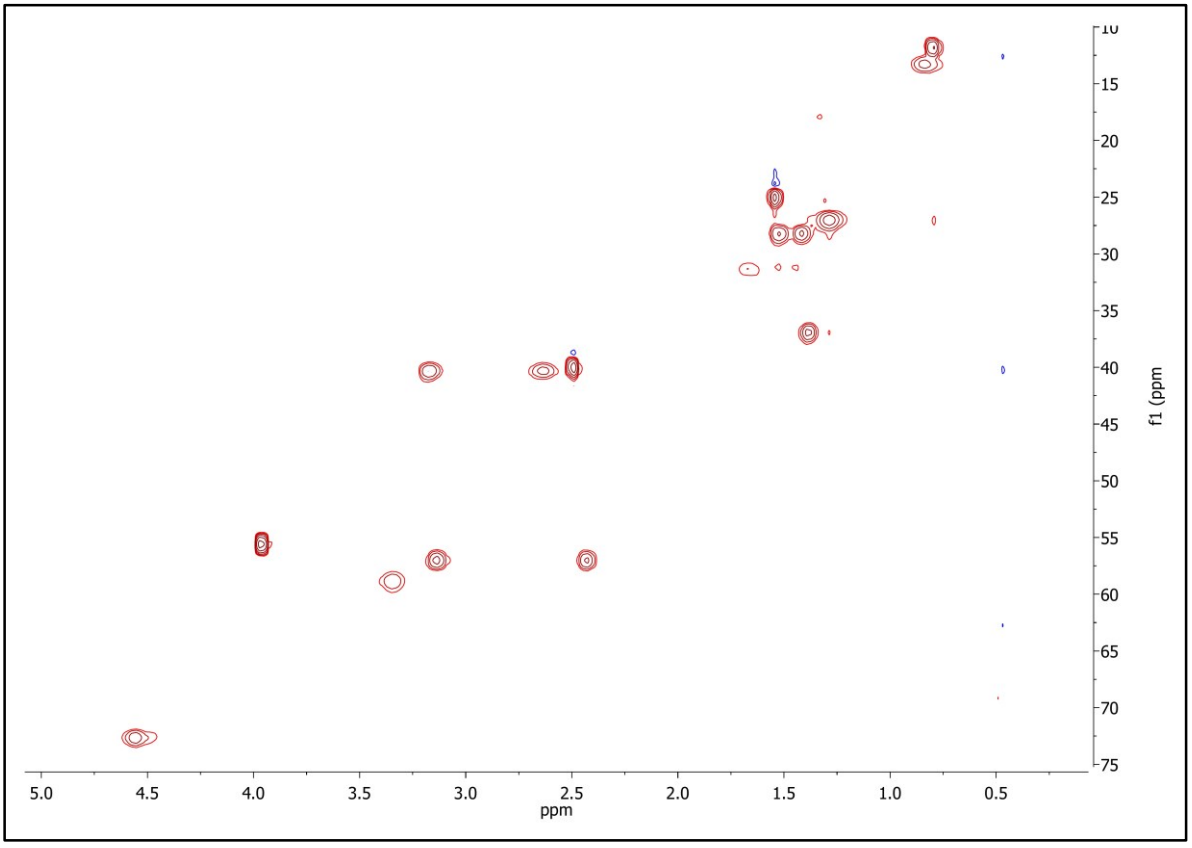


Figure S62c. HSQC spectrum of **HSq-B** (DMSO, 60 °C)

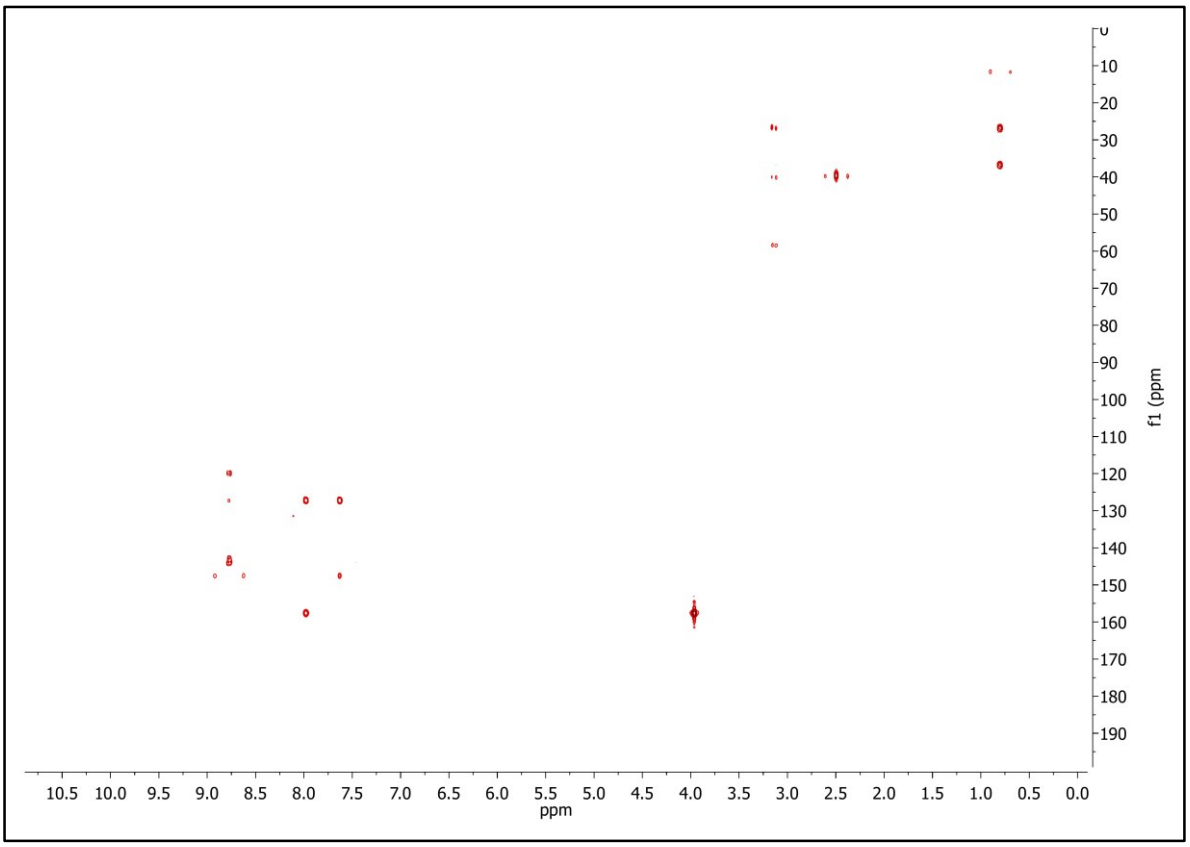


Figure S63a. HMBC spectrum of **HSq-B** (DMSO, 60 °C)

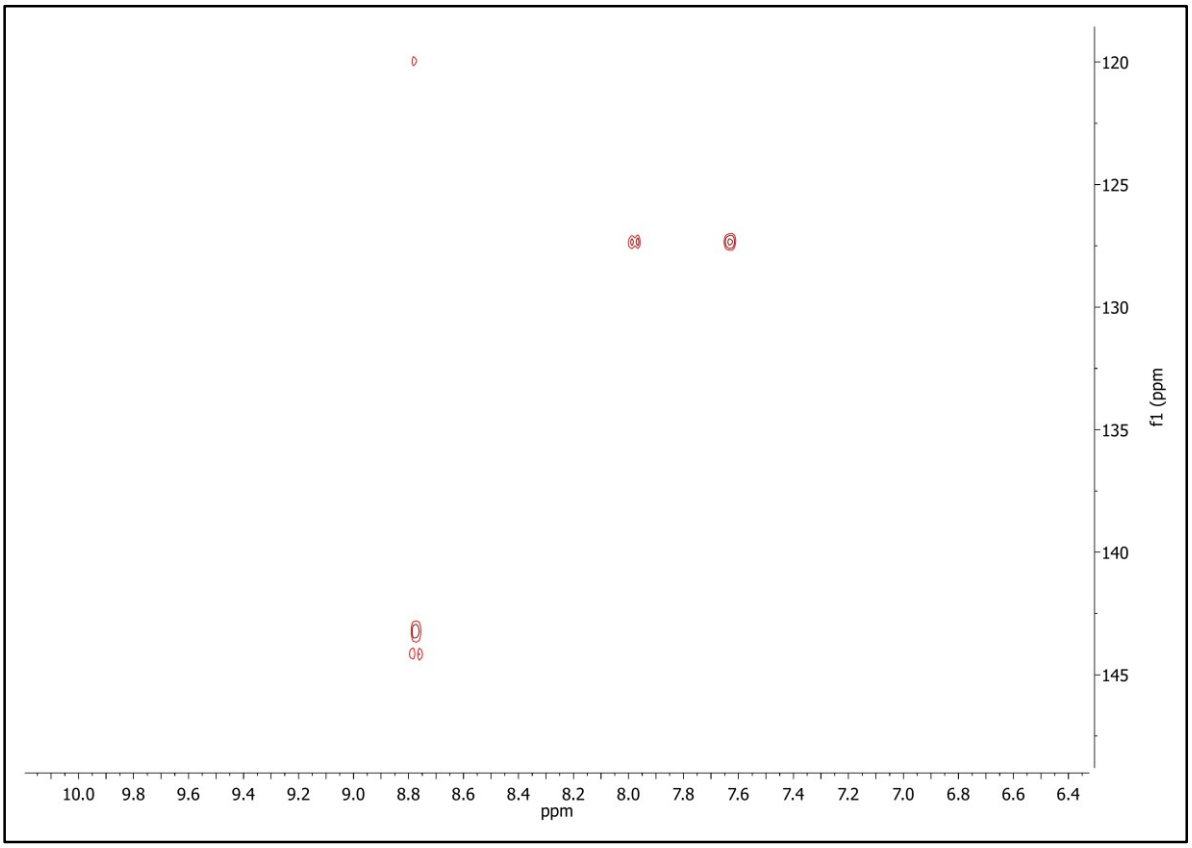


Figure S63b. HMBC spectrum of **HSq-B** (DMSO, 60 °C)

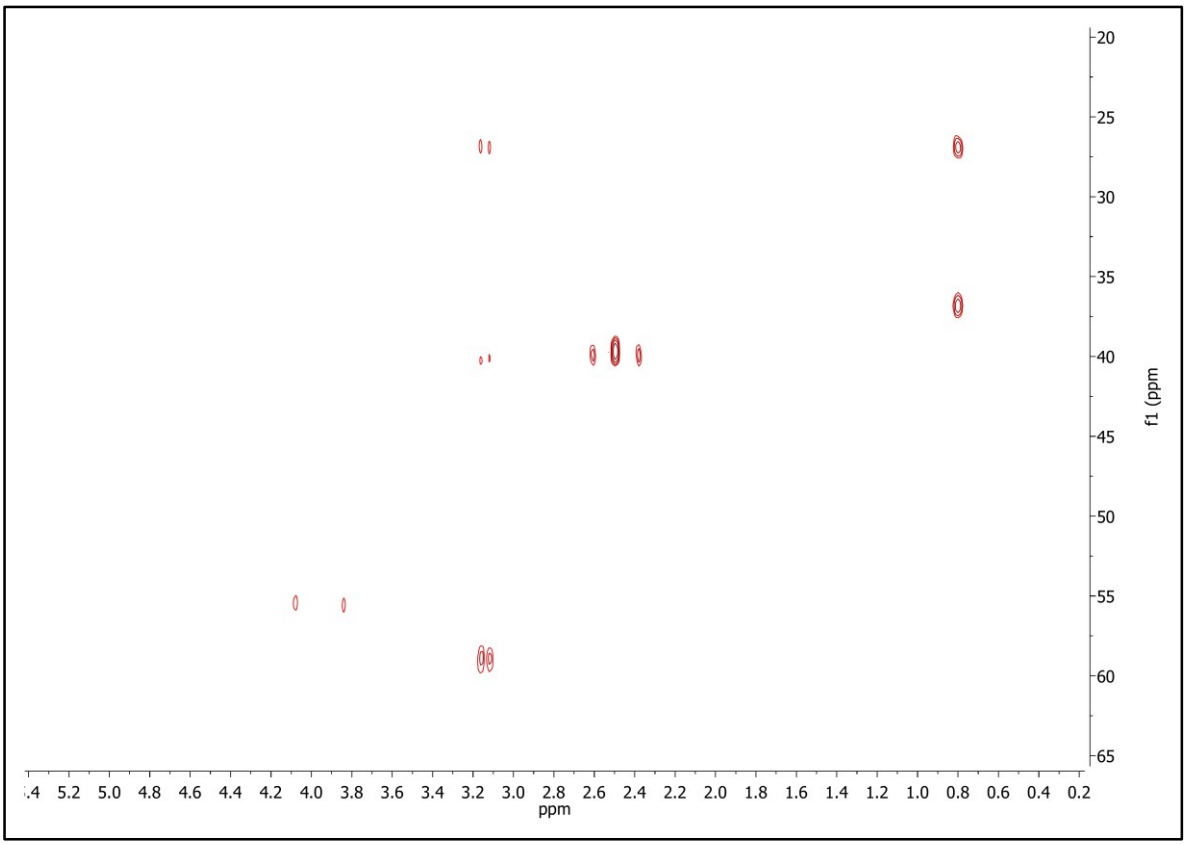


Figure S63c. HMBC spectrum of **HSq-B** (DMSO, 60 °C)

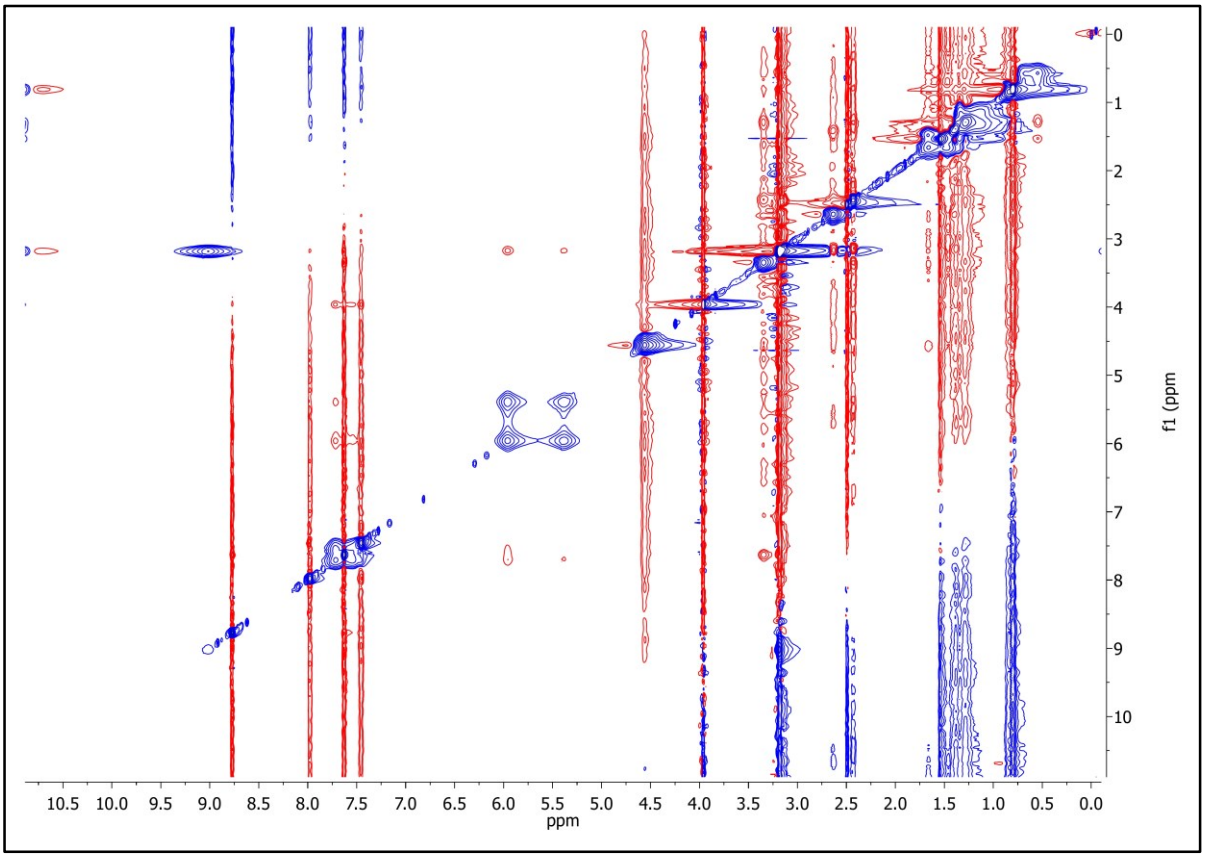


Figure S64. NOESY NMR spectrum of **HSq-B** (DMSO, 60 °C)

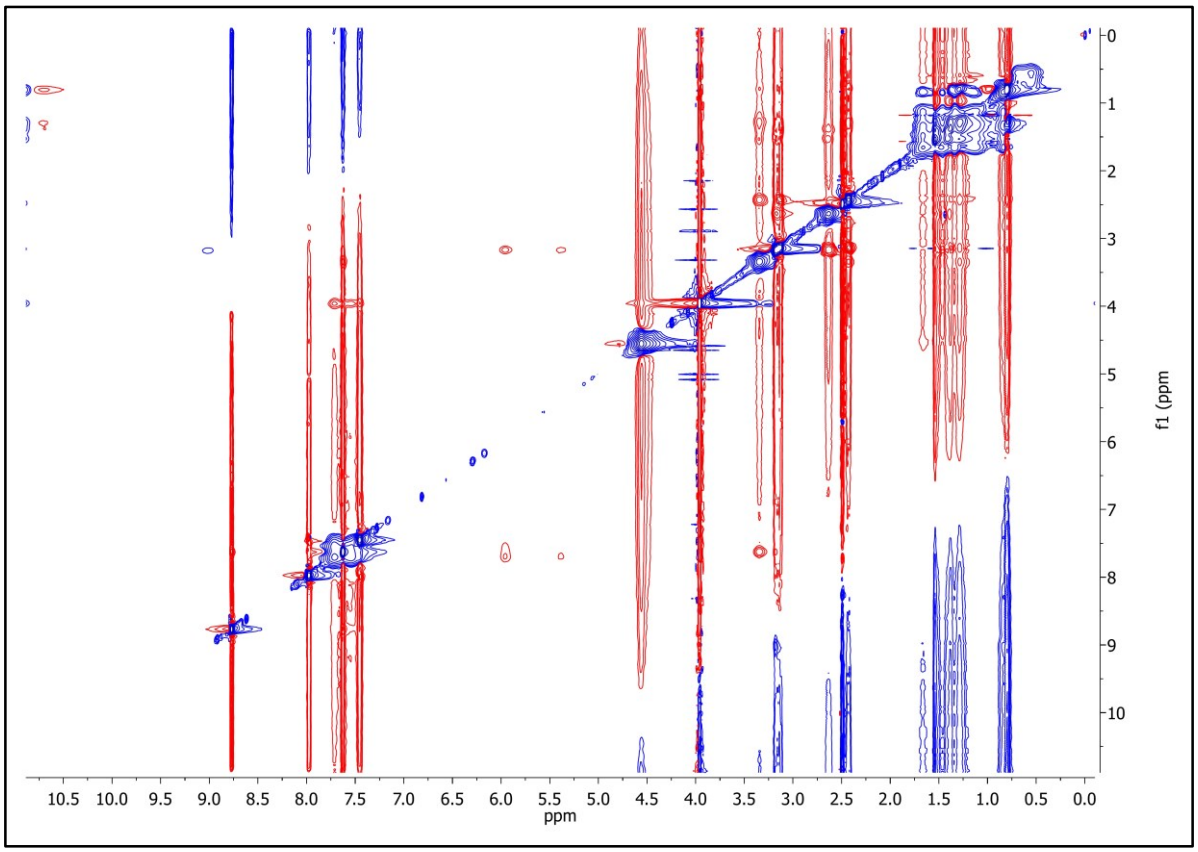


Figure S65. ROESY NMR spectrum of **HSq-B** (DMSO, 60 °C)

NMR spectra of **1a**

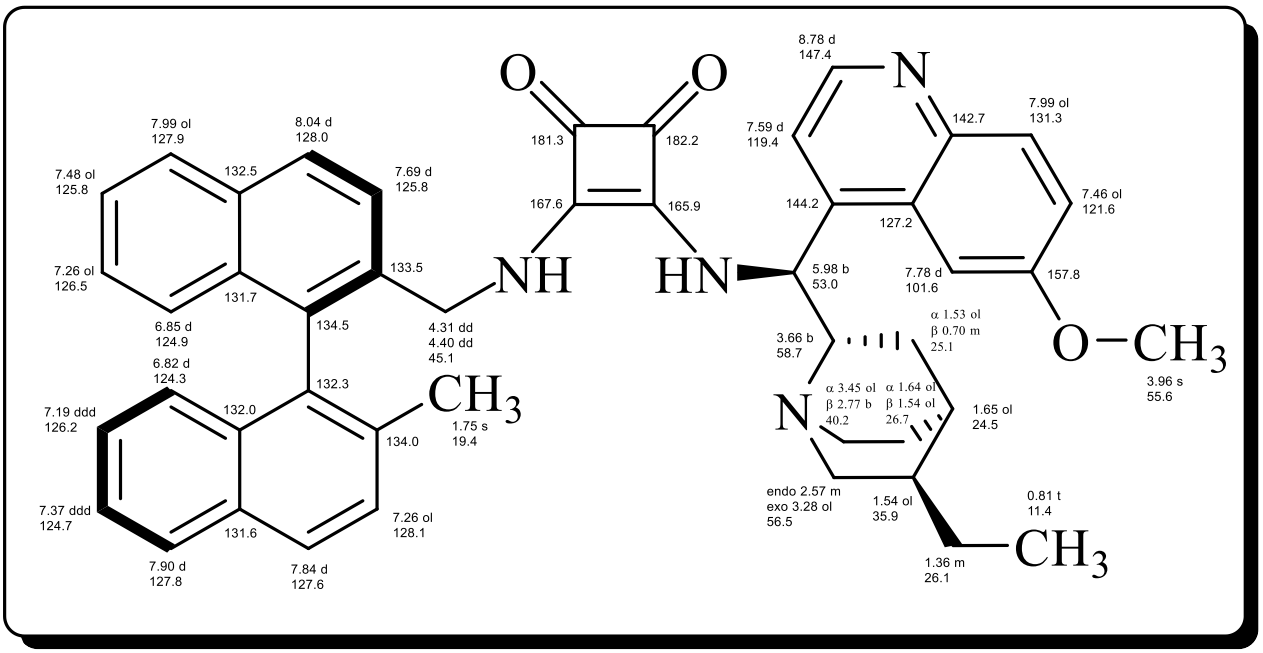


Figure S66. Molecule structure, ^{1}H and ^{13}C assignment of **1a**

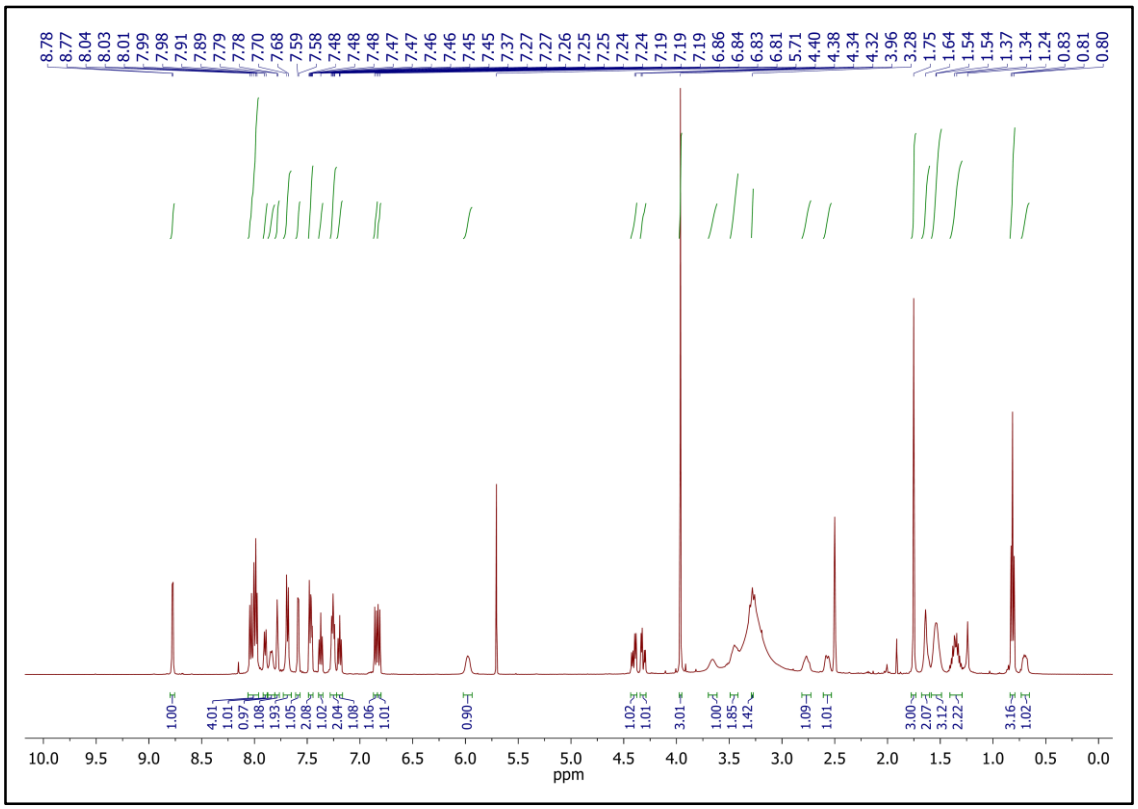


Figure S67a. ^{1}H NMR spectrum of **1a** (500 MHz, DMSO, 60 °C)

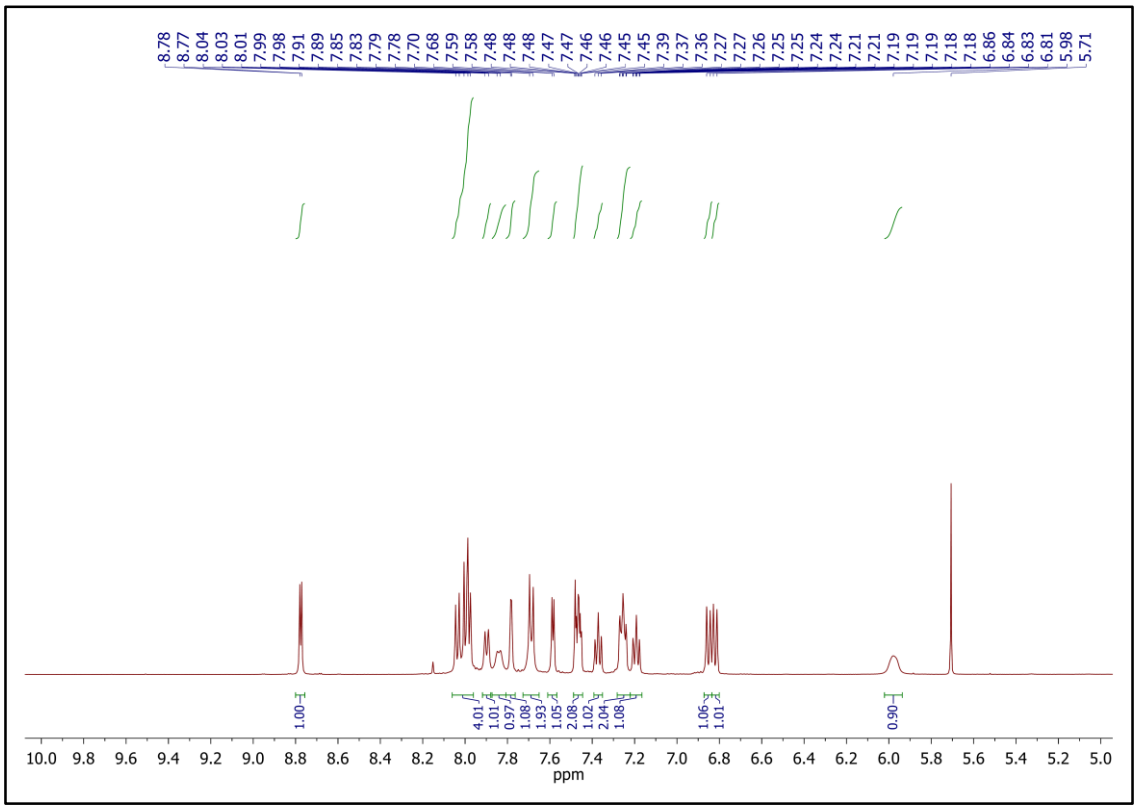


Figure S67b. ^{1}H NMR spectrum of **1a** (500 MHz, DMSO, 60 °C)

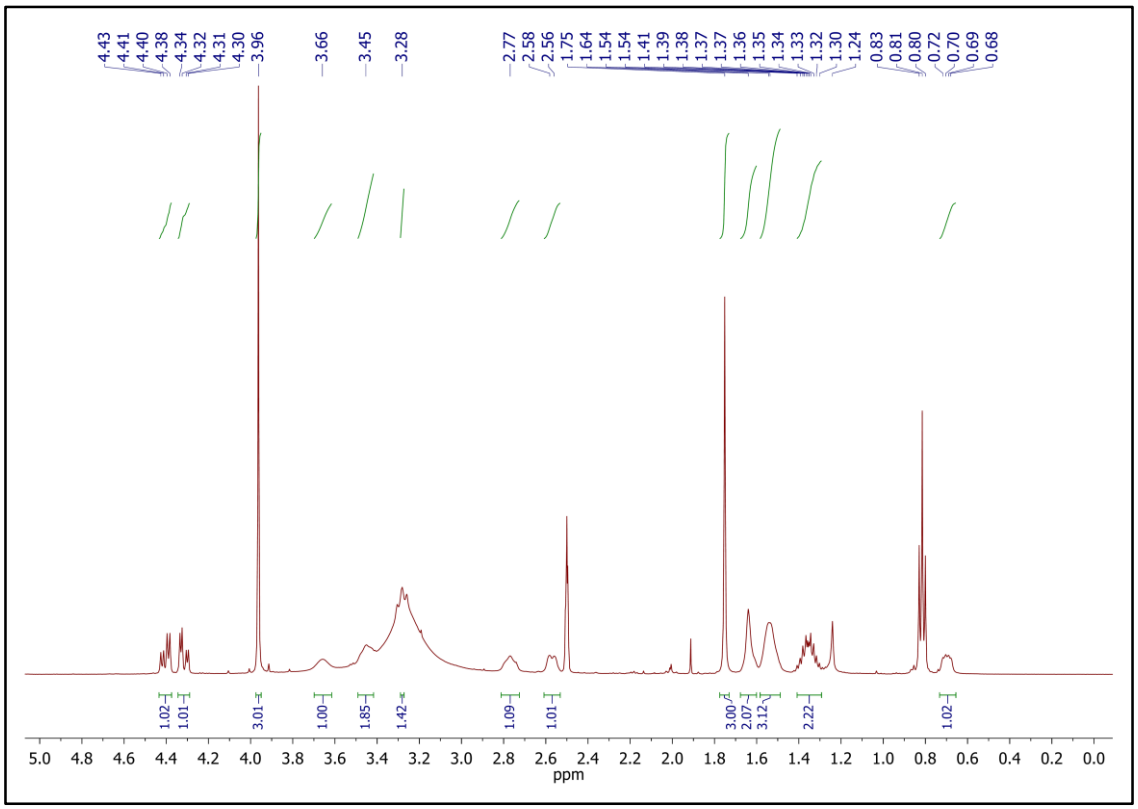


Figure S67c. ^{1}H NMR spectrum of **1a** (500 MHz, DMSO, 60 °C)

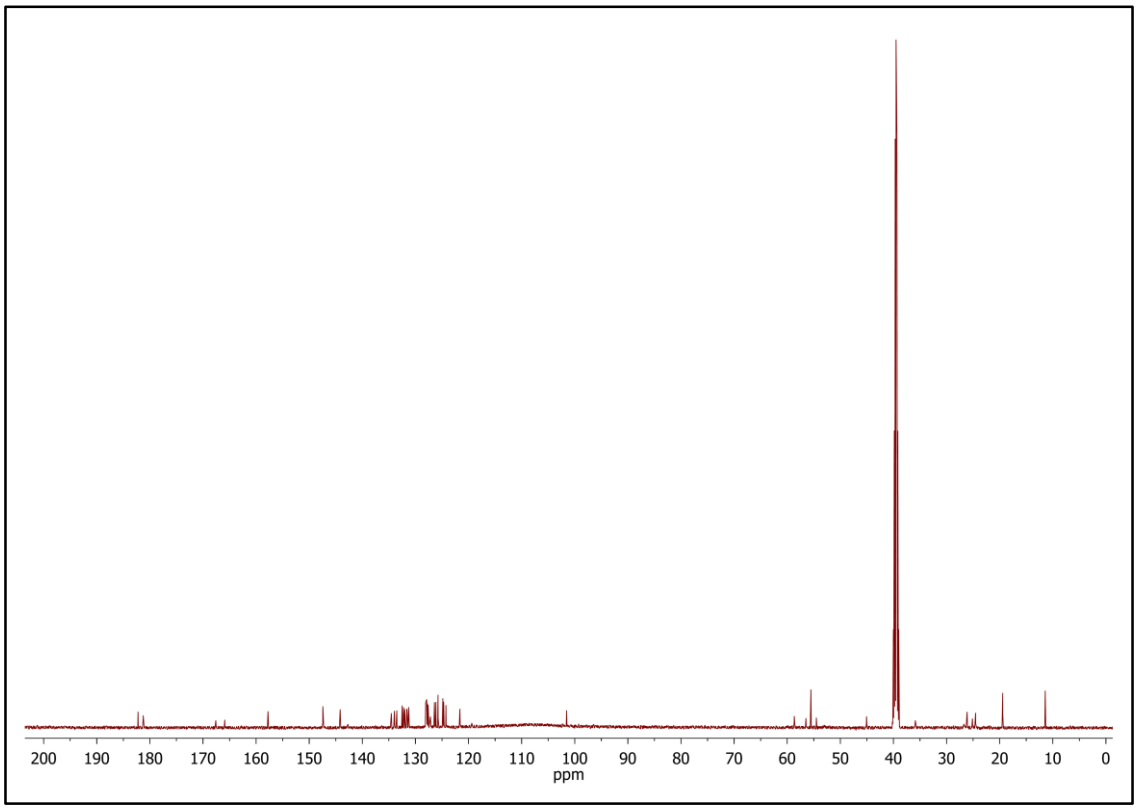


Figure S68. ^{13}C NMR spectrum of **1a** (125 MHz, DMSO, 60 °C)

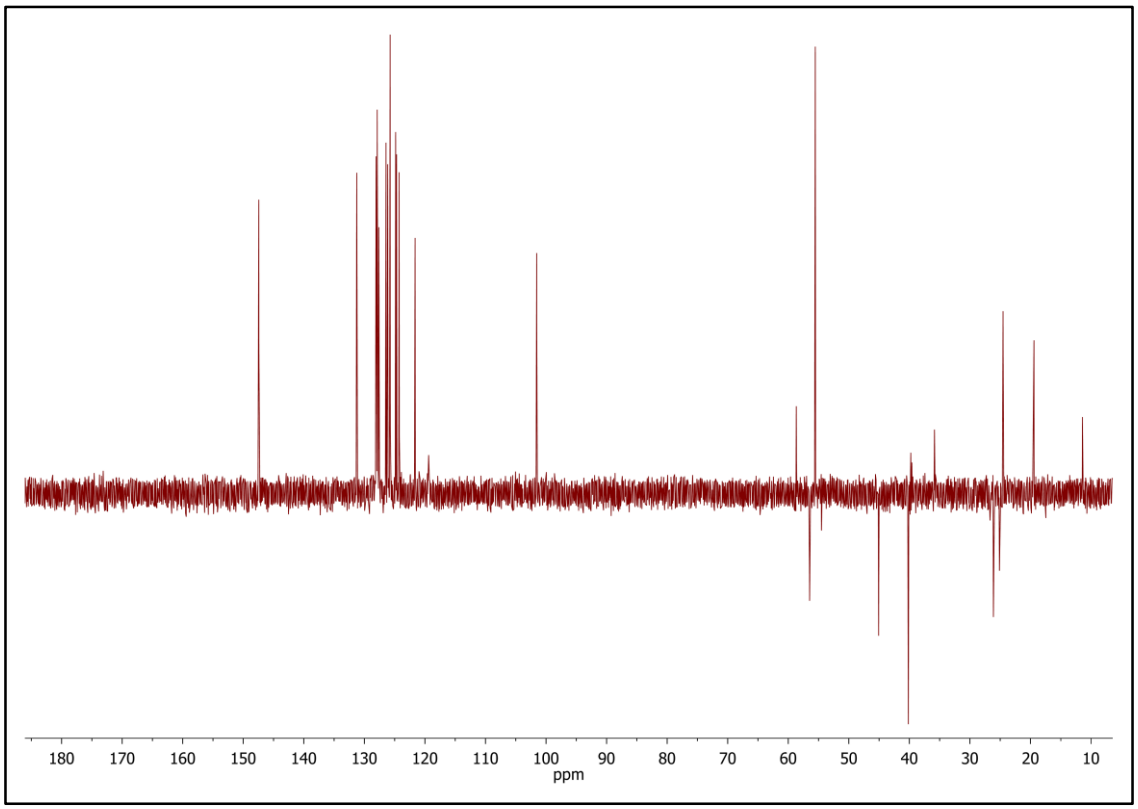


Figure S69. ^{13}C DEPT NMR spectrum of **1a** (125 MHz, DMSO, 60 °C)

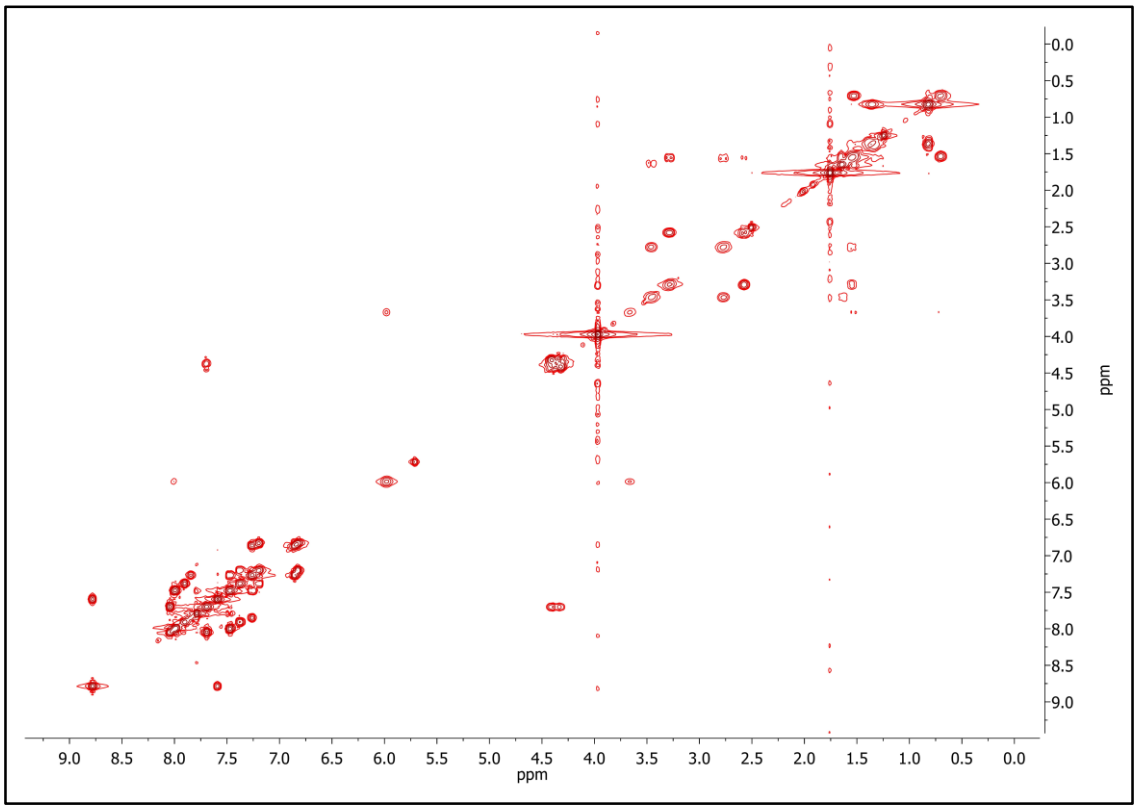


Figure S70. COSY NMR spectrum of **1a** (DMSO, 60 °C)

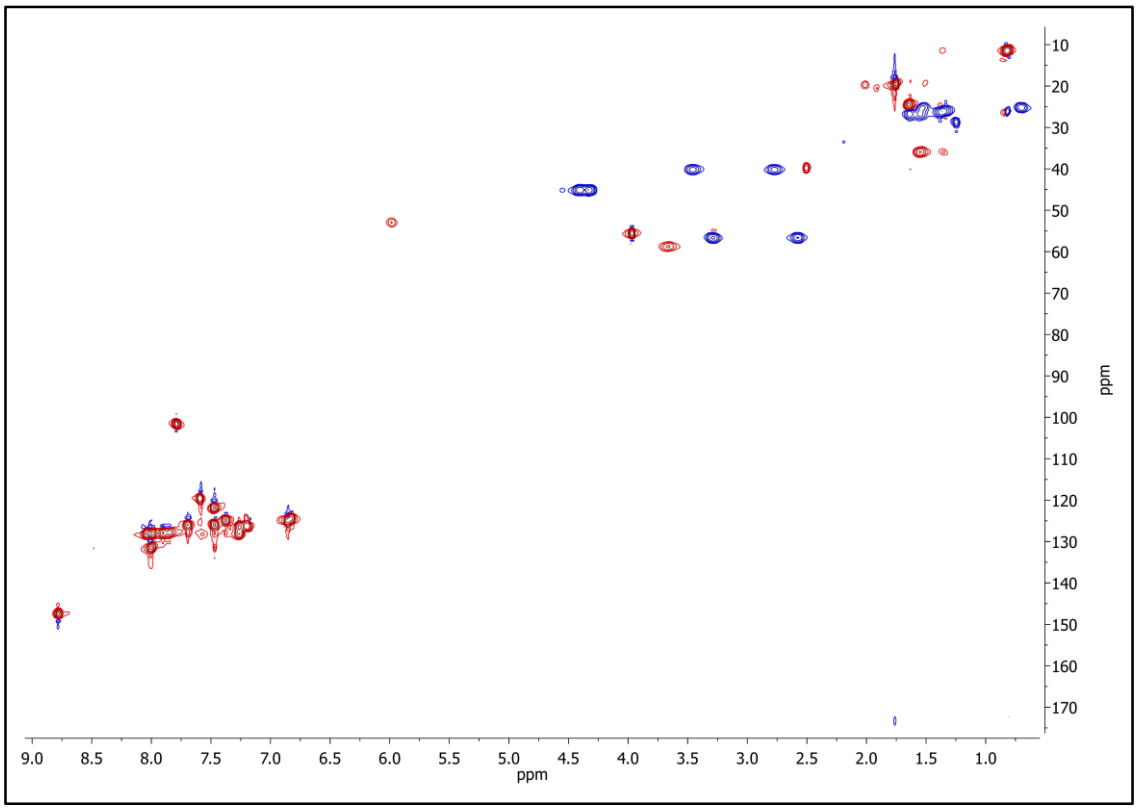


Figure S71. HSQC NMR spectrum of **1a** (DMSO, 60 °C)

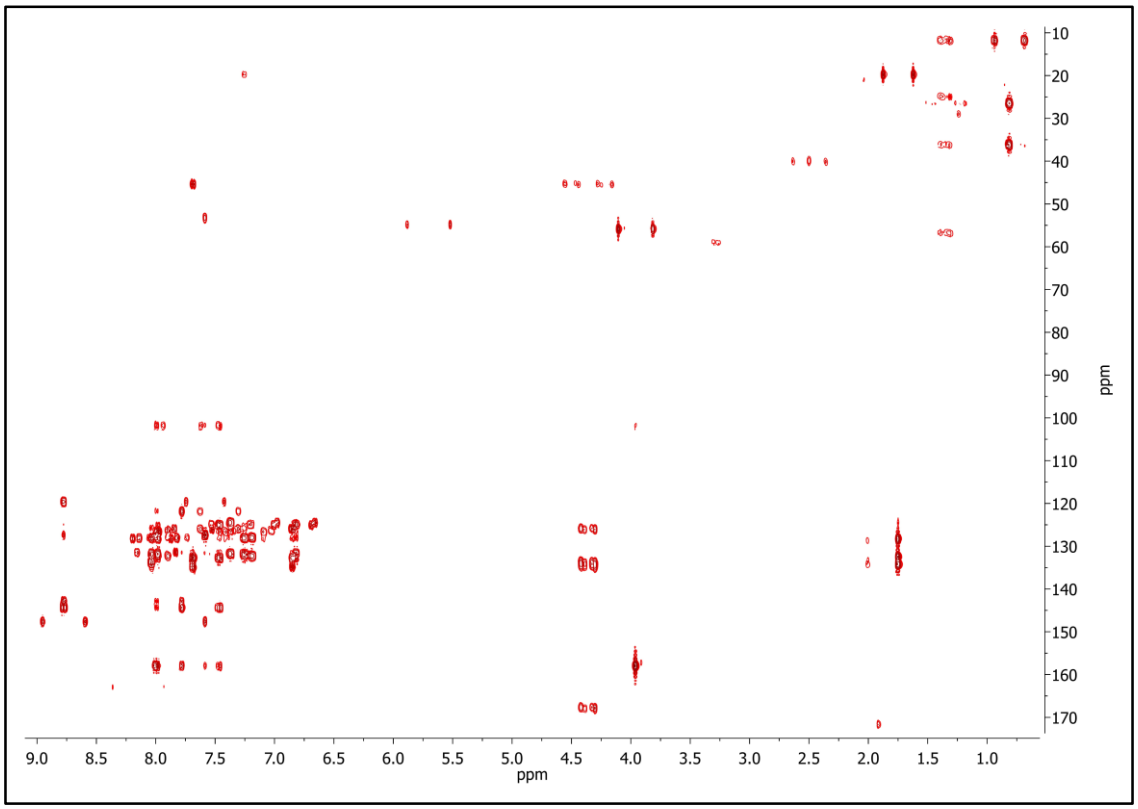


Figure S72. HMBC NMR spectrum of **1a** (DMSO, 60 °C)

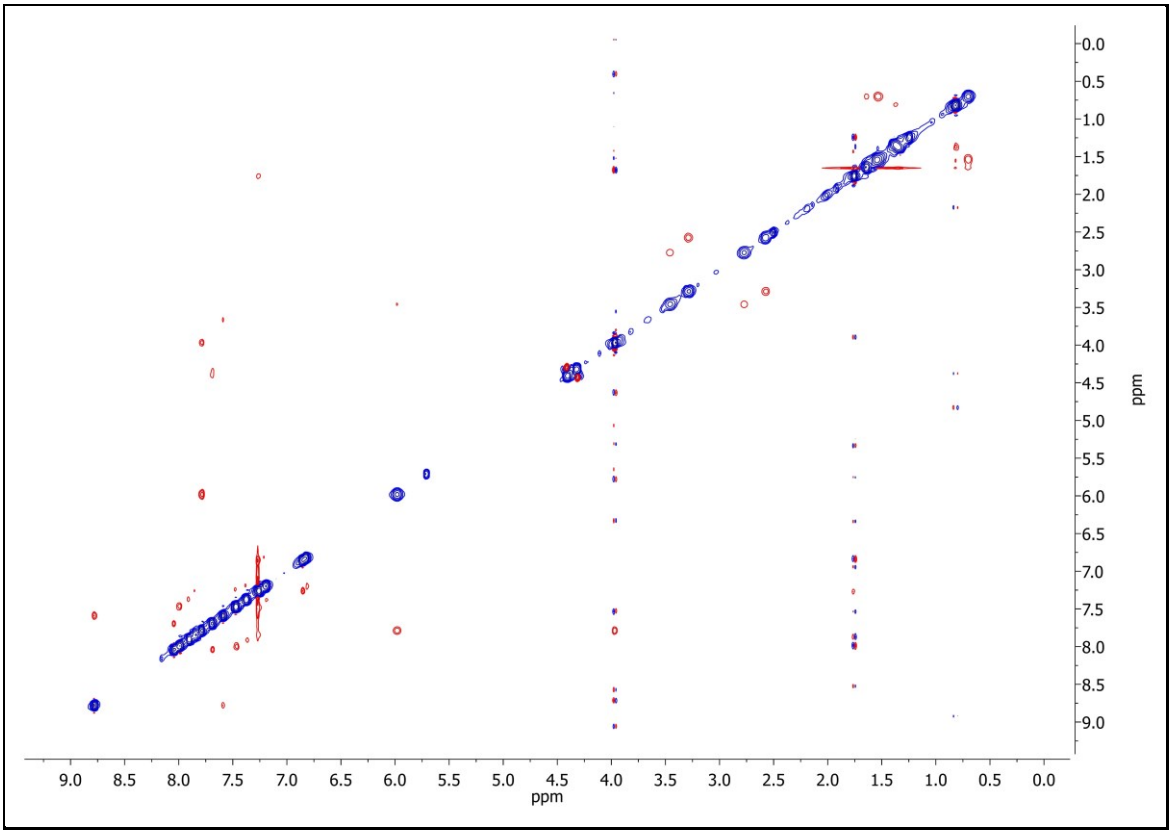


Figure S73. ROESY NMR spectrum of **1a** (DMSO, 60 °C)

NMR spectra of **1b**

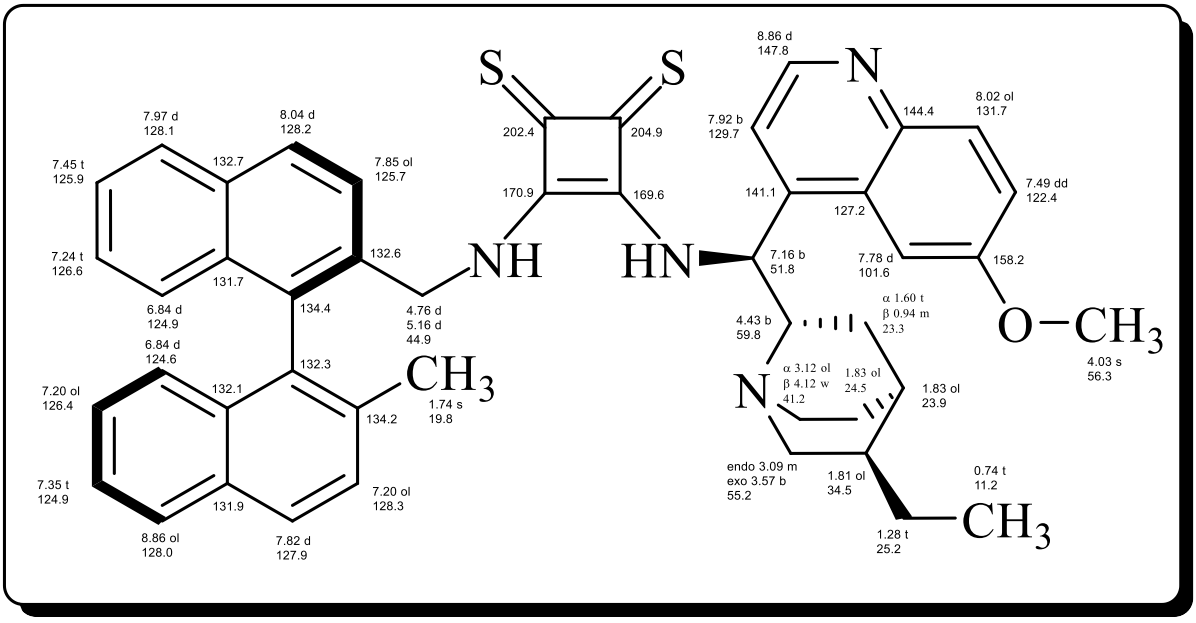


Figure S74. Molecule structure, ^{1}H and ^{13}C assignment of **1b**

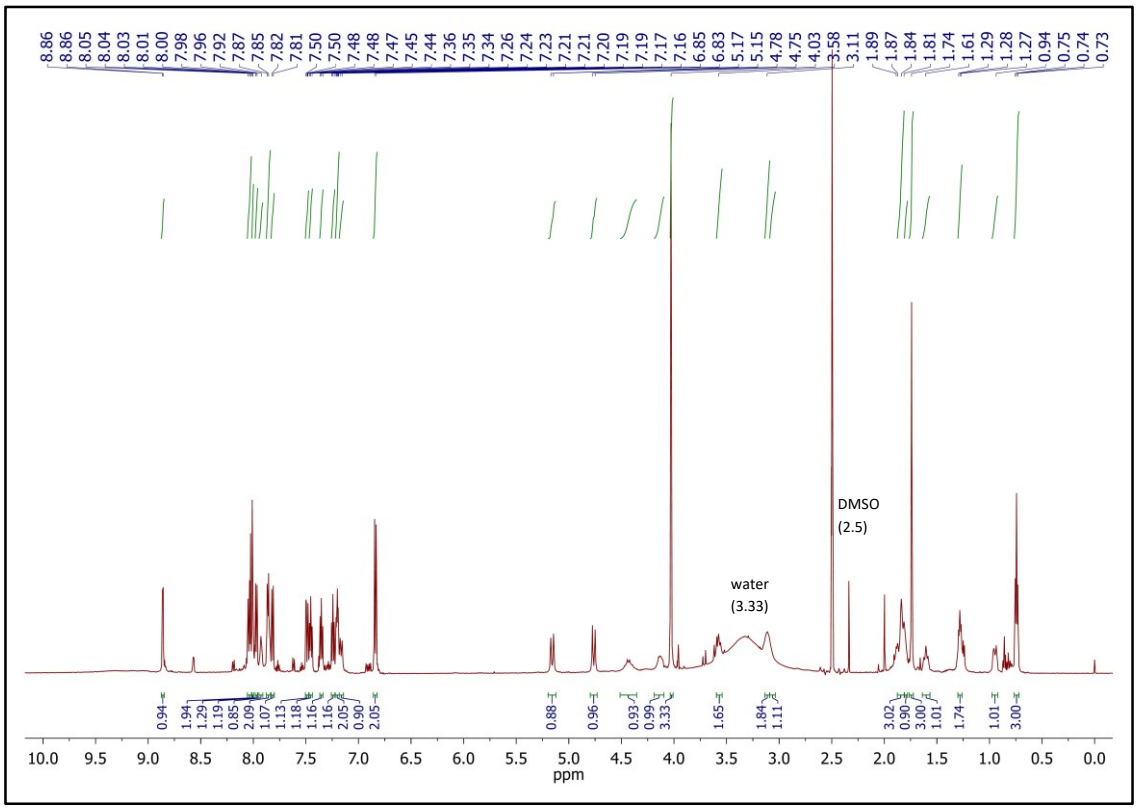


Figure S75a. ^{1}H NMR spectrum of **1b** (600 MHz, DMSO, 60 °C)

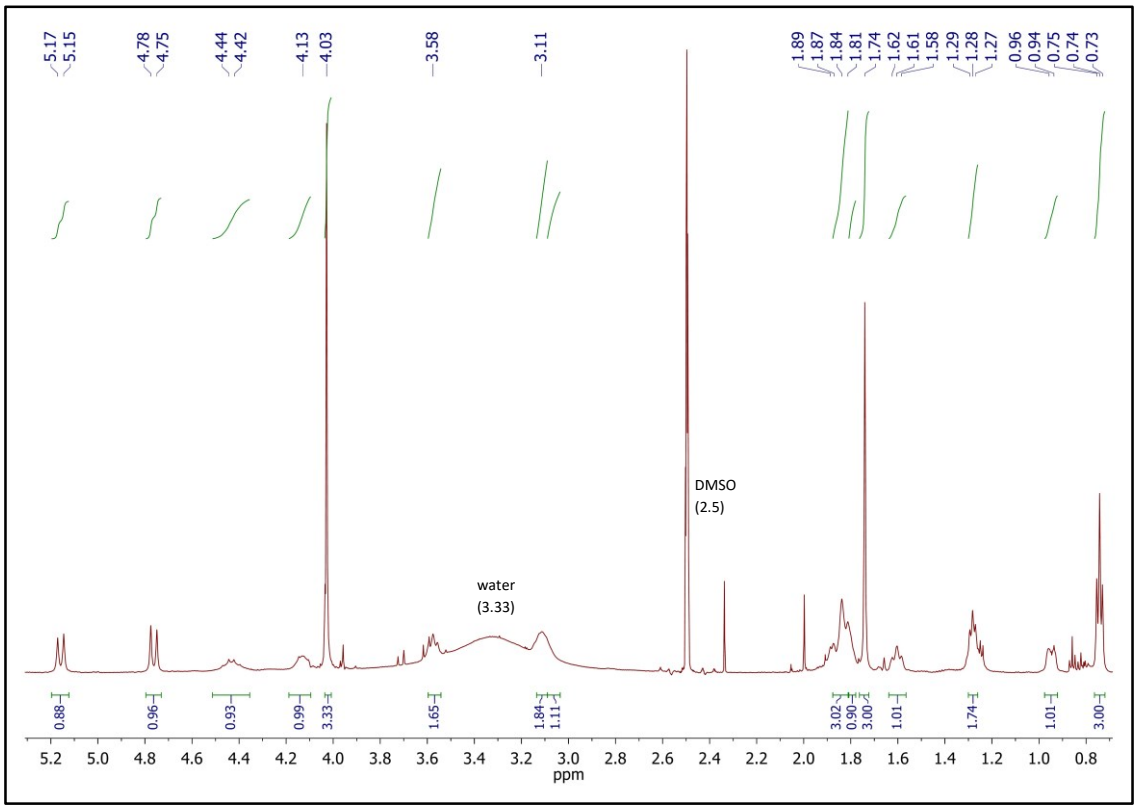


Figure S75b. ^{1}H NMR spectrum of **1b** (600 MHz, DMSO, 60 °C)

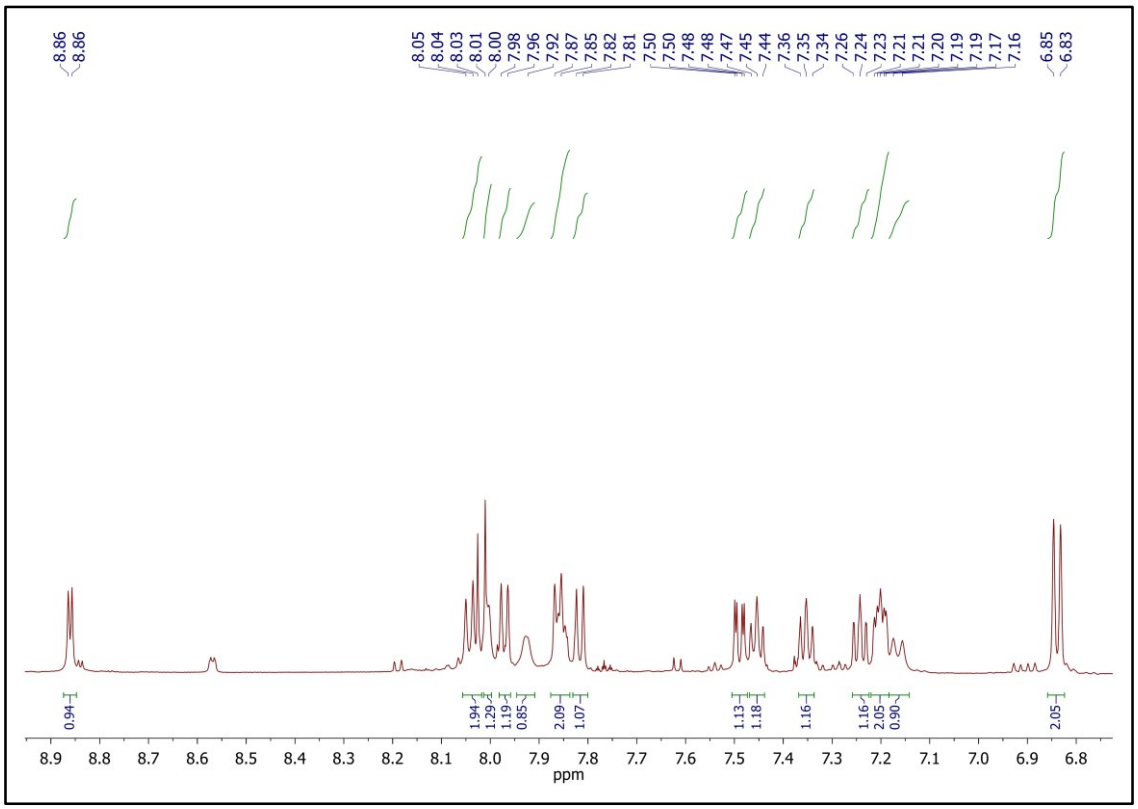


Figure S75c. ^{1}H NMR spectrum of **1b** (600 MHz, DMSO, 60 °C)

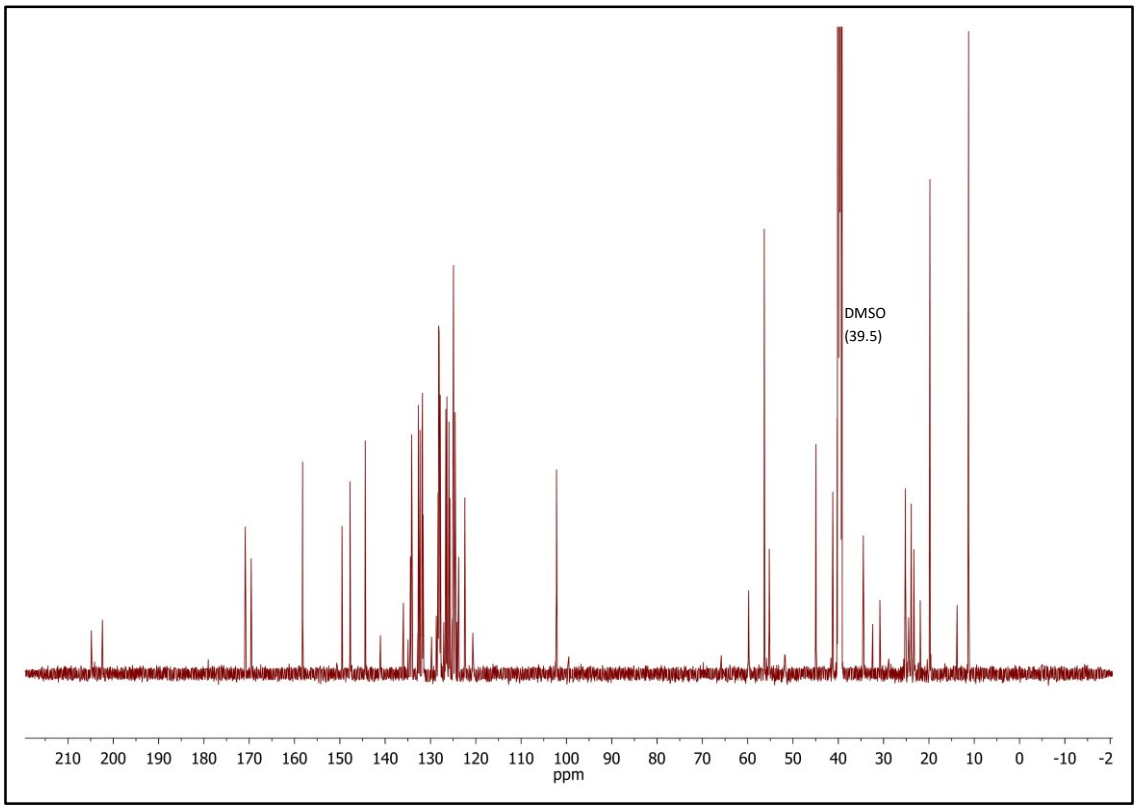


Figure S76. ^{1}H NMR spectrum of **1b** (150 MHz, DMSO, 60 °C)

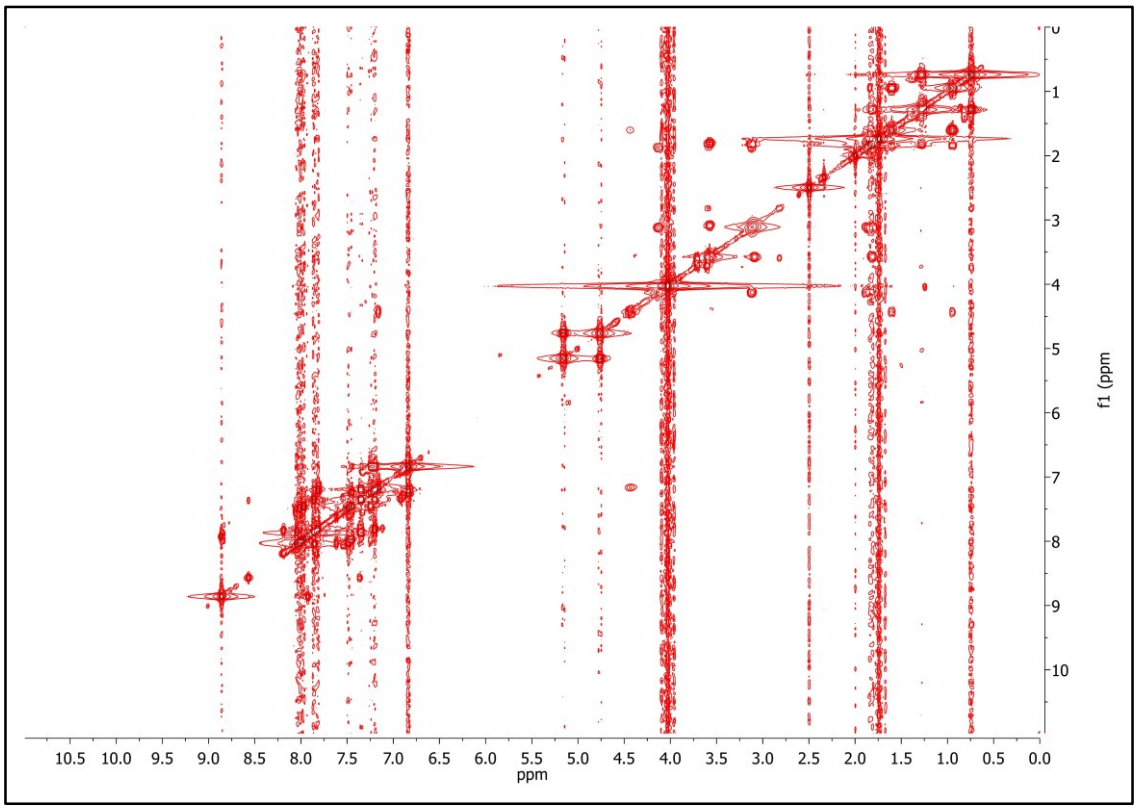


Figure S77. COSY spectrum of **1b** (DMSO, 60 °C)

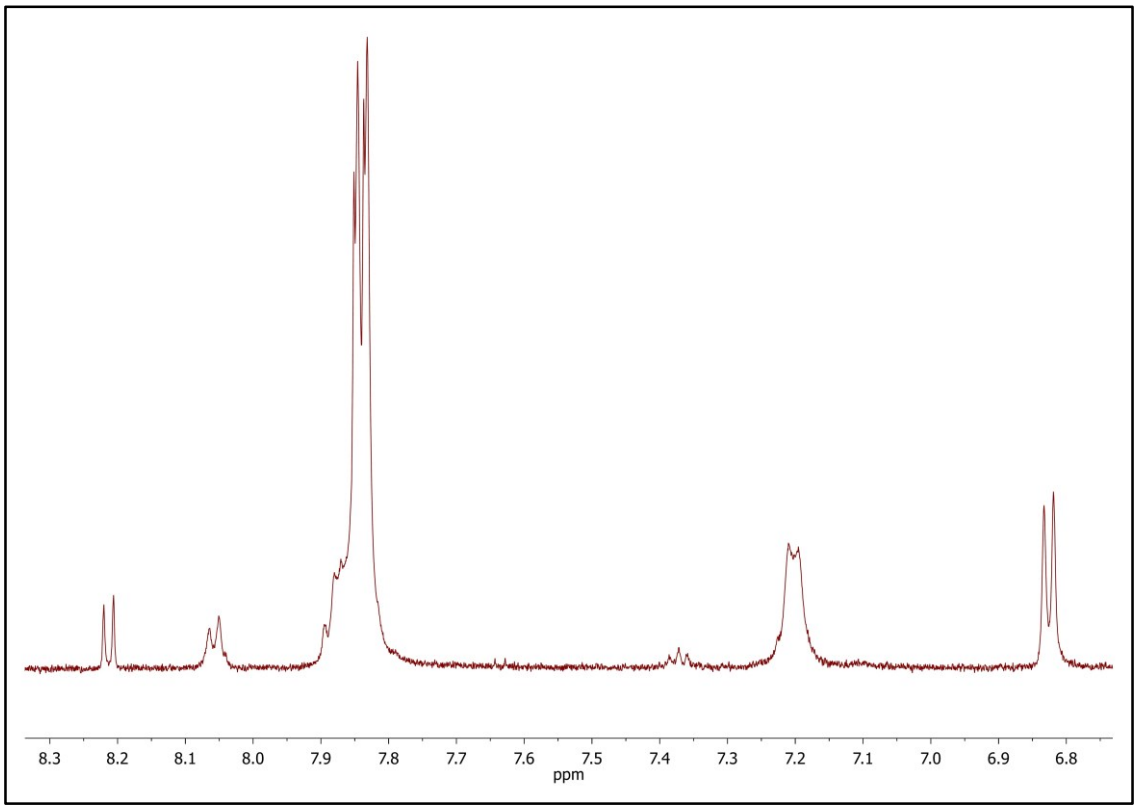


Figure S78a. Selective gradient TOCSY spectrum of **1b** (DMSO, 60 °C)

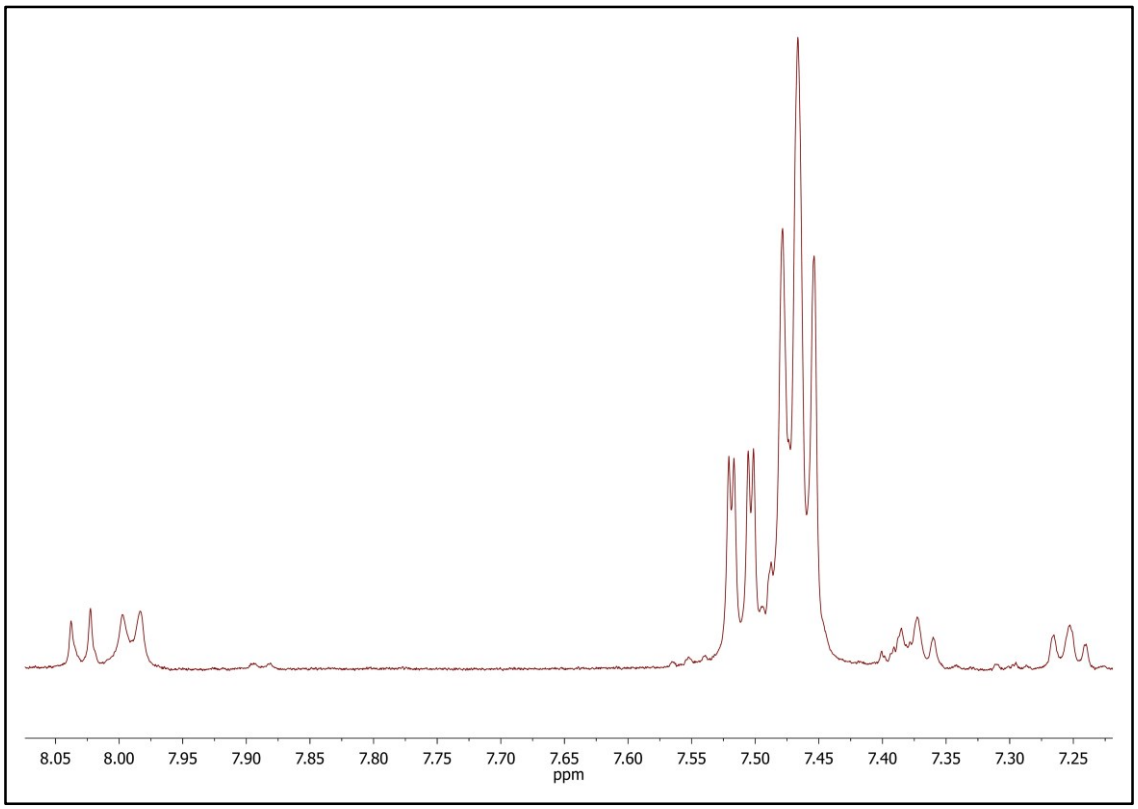


Figure S78b. Selective gradient TOCSY spectrum of **1b** (DMSO, 60 °C)

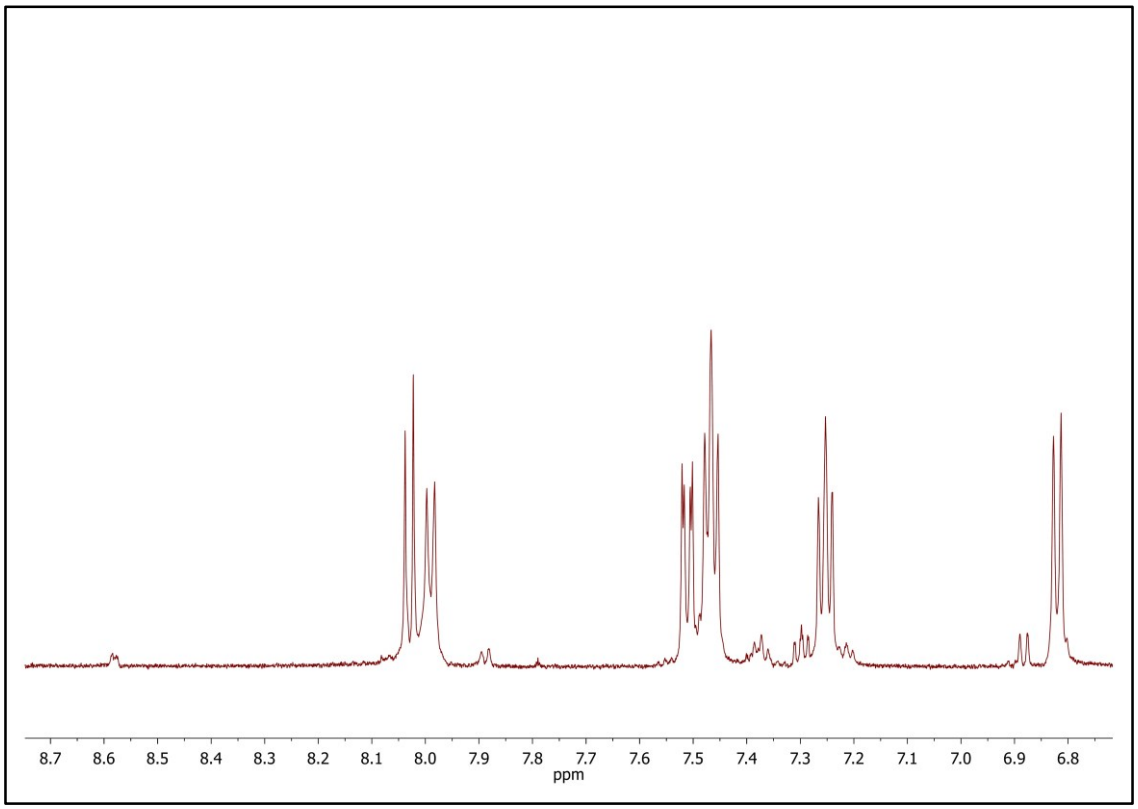


Figure S78c. Selective gradient TOCSY spectrum of **1b** (DMSO, 60 °C)

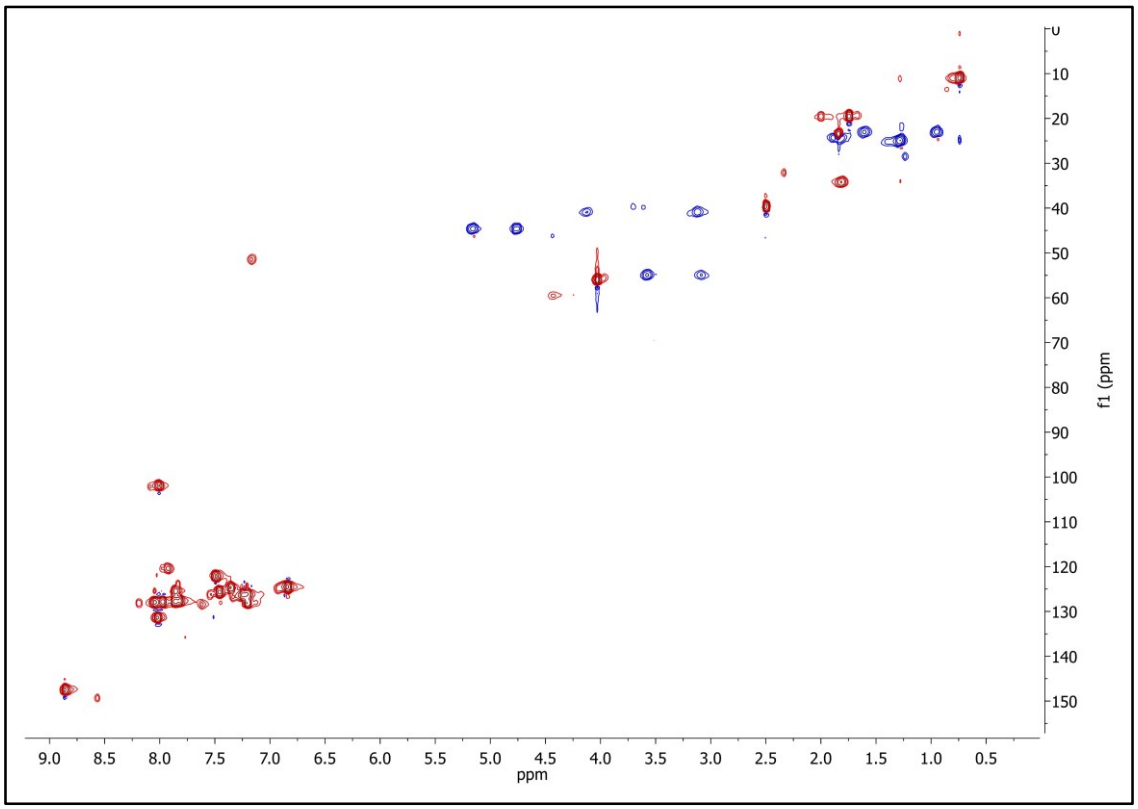


Figure S79a. Selective gradient HSQC spectrum of **1b** (DMSO, 60 °C)

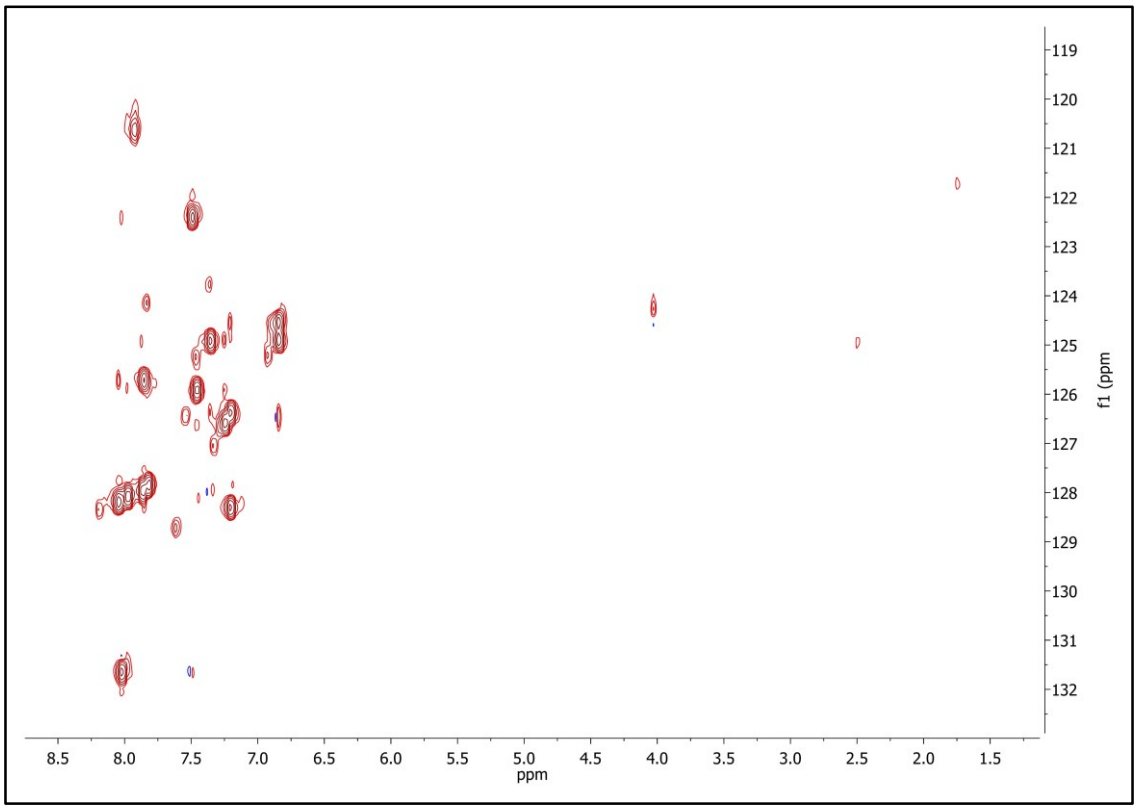


Figure S79b. Selective gradient HSQC spectrum of **1b** (DMSO, 60 °C)

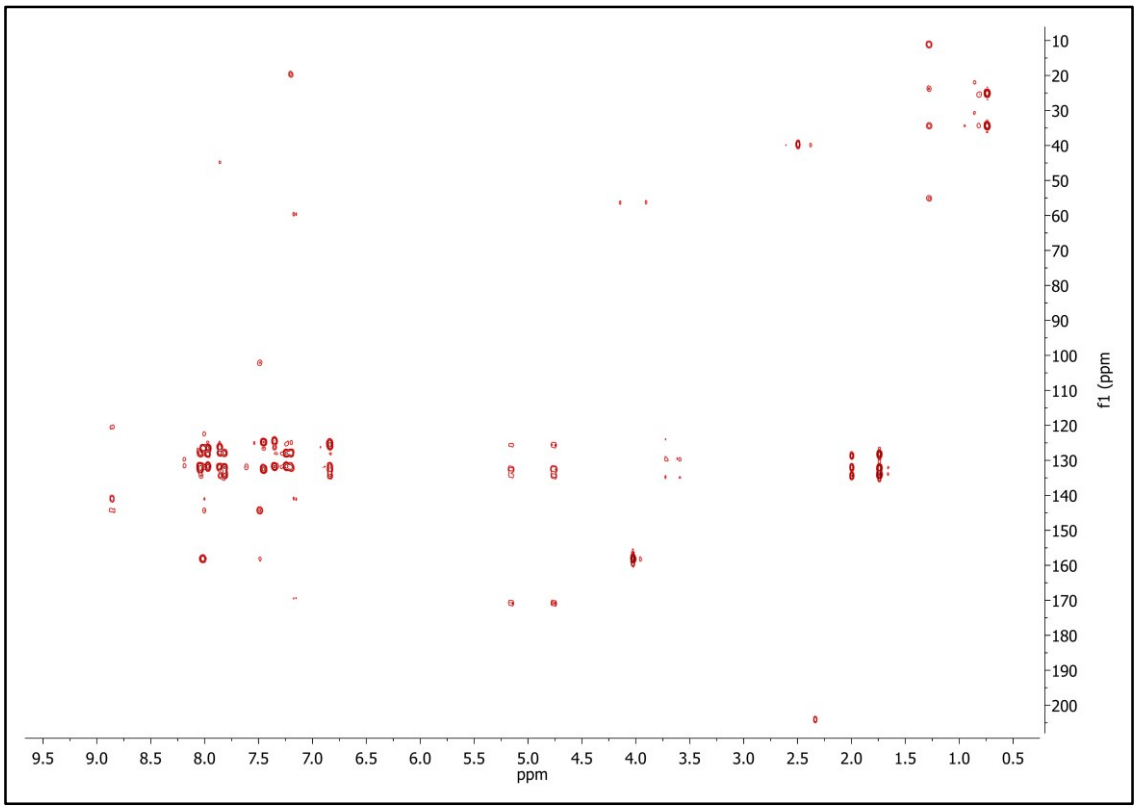


Figure S80a. Selective gradient HMBC spectrum of **1b** (DMSO, 60 °C)

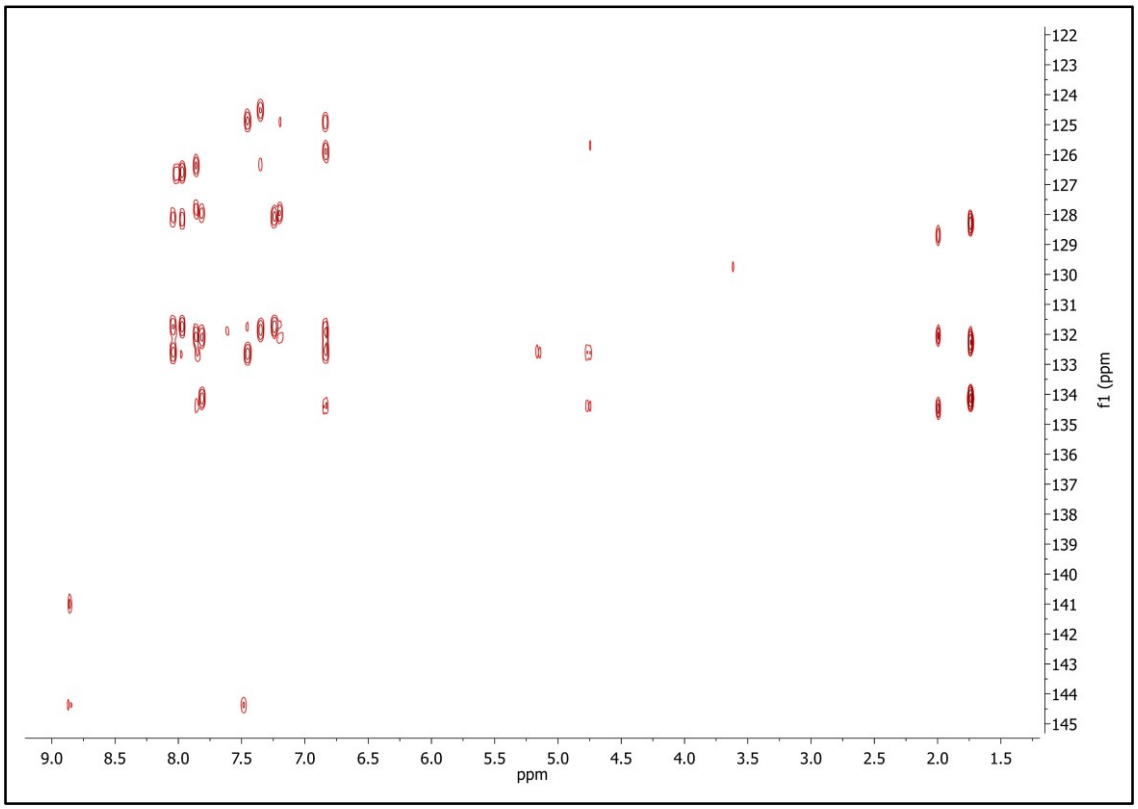


Figure S80b. Selective gradient HMBC spectrum of **1b** (DMSO, 60 °C)

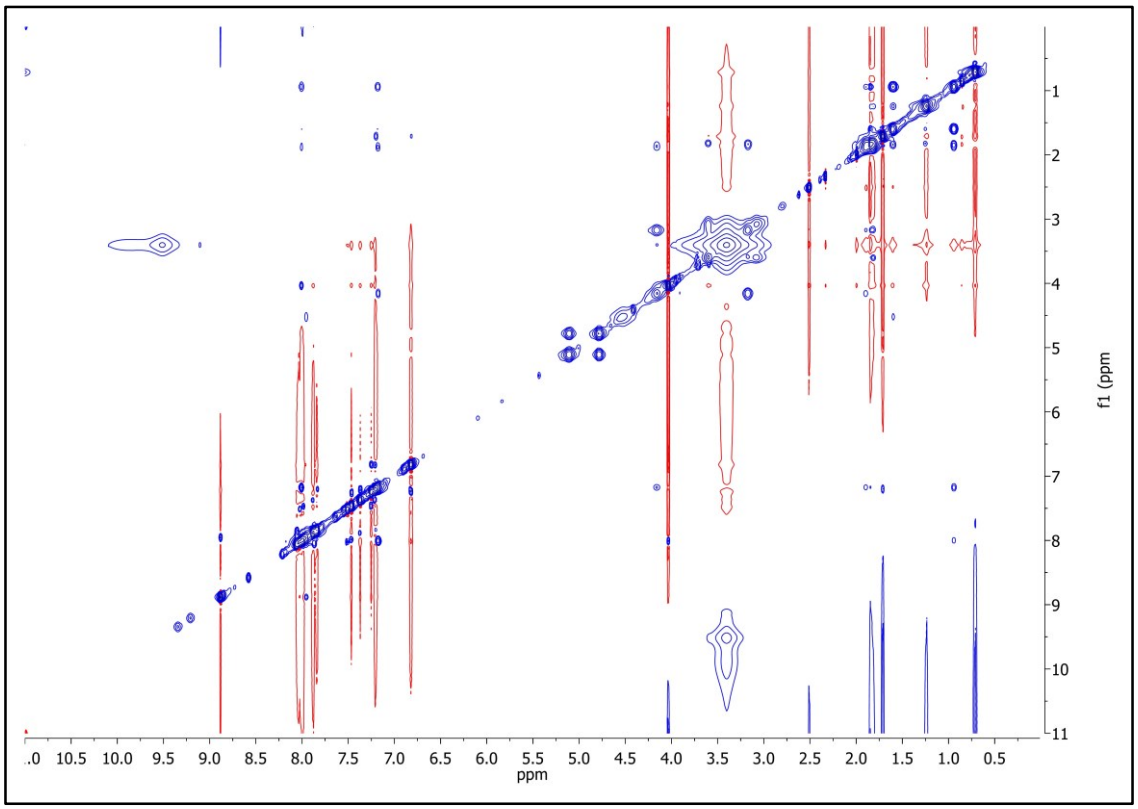


Figure S81. NOESY spectrum of **1b** (DMSO, 60 °C)

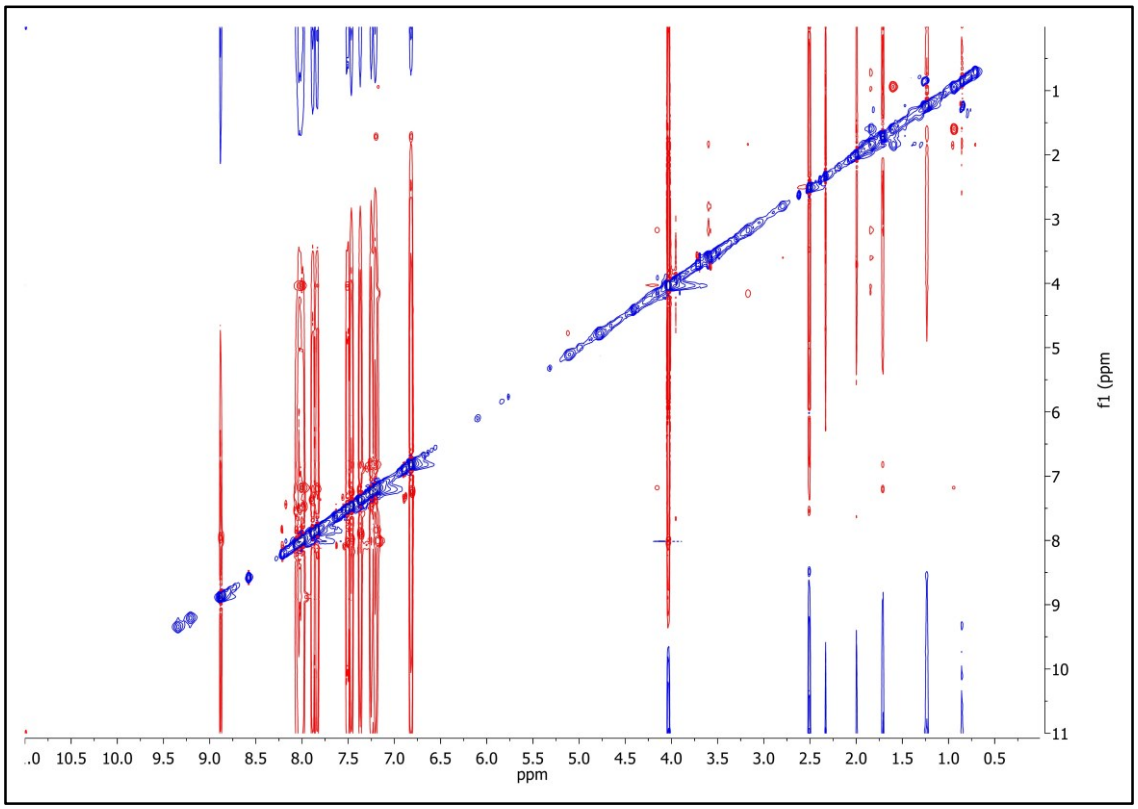


Figure S82. NOESY spectrum of **1b** (DMSO, 60 °C)

NMR spectra of **1c**

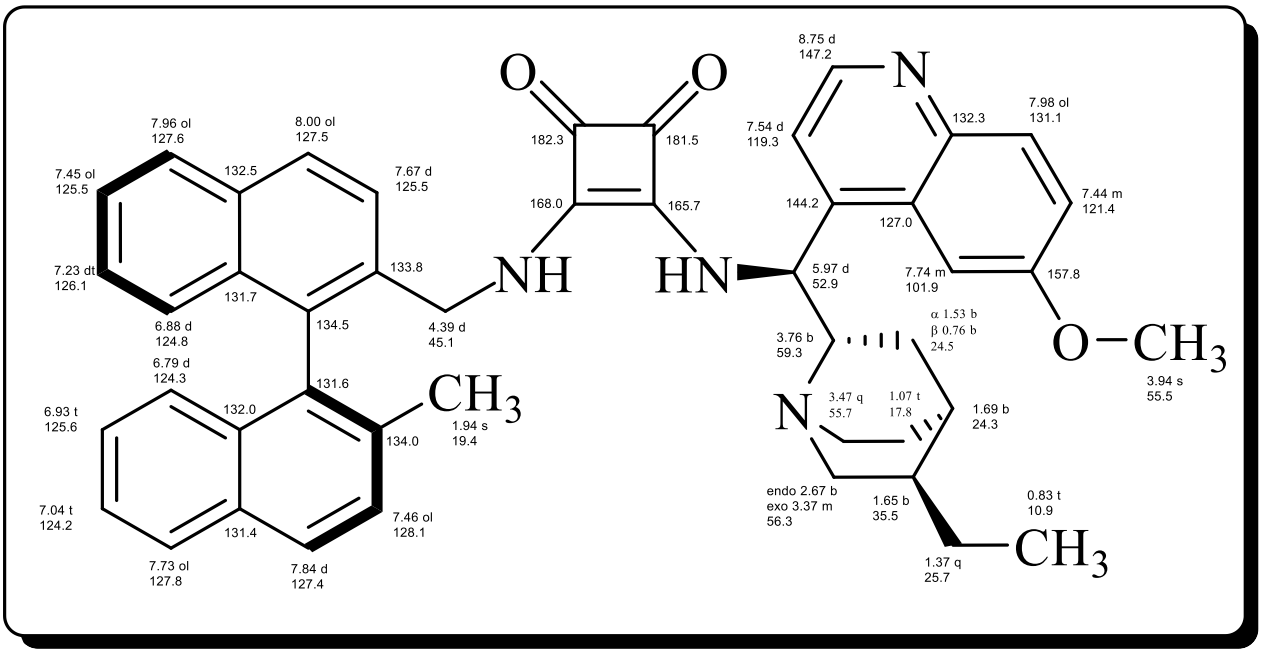


Figure S83. Molecule structure, ^{1}H and ^{13}C assignment of **1c**

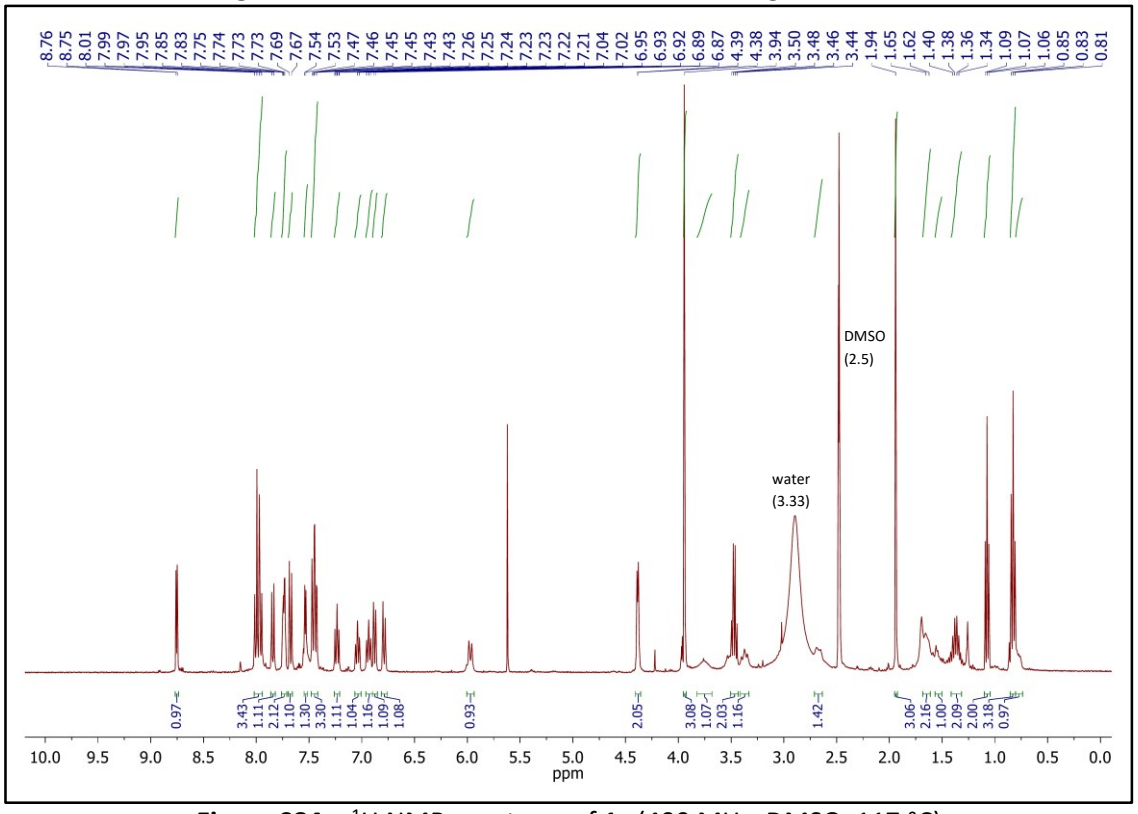


Figure S84a. ^{1}H NMR spectrum of **1c** (400 MHz, DMSO, 117 °C)

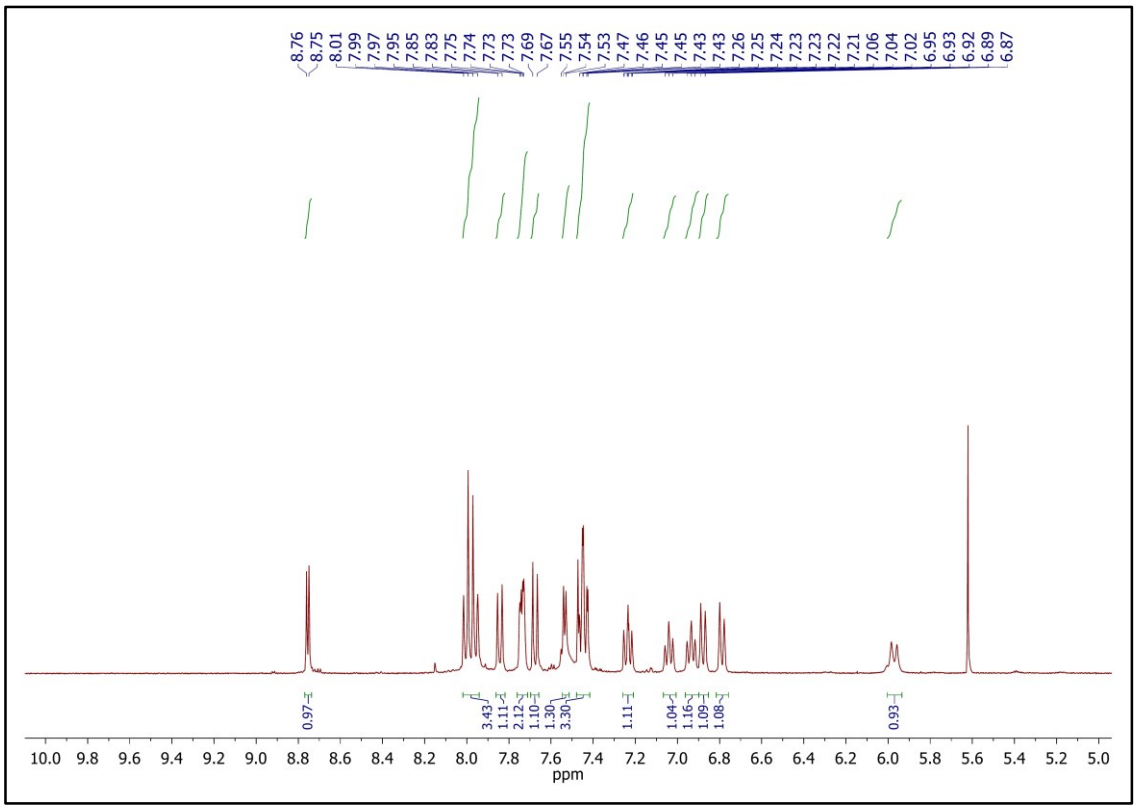


Figure S84b. ^{1}H NMR spectrum of **1c** (400 MHz, DMSO, 117 °C)

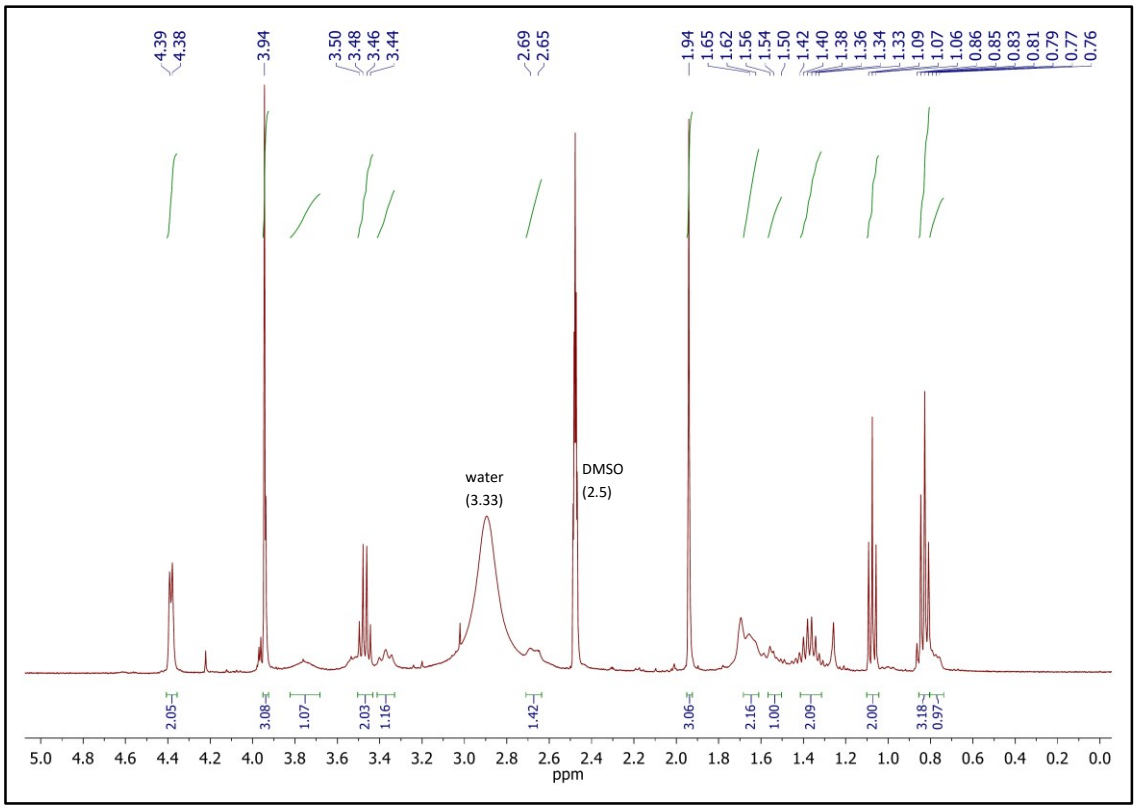


Figure S84c. ^{1}H NMR spectrum of **1c** (400 MHz, DMSO, 117 °C)

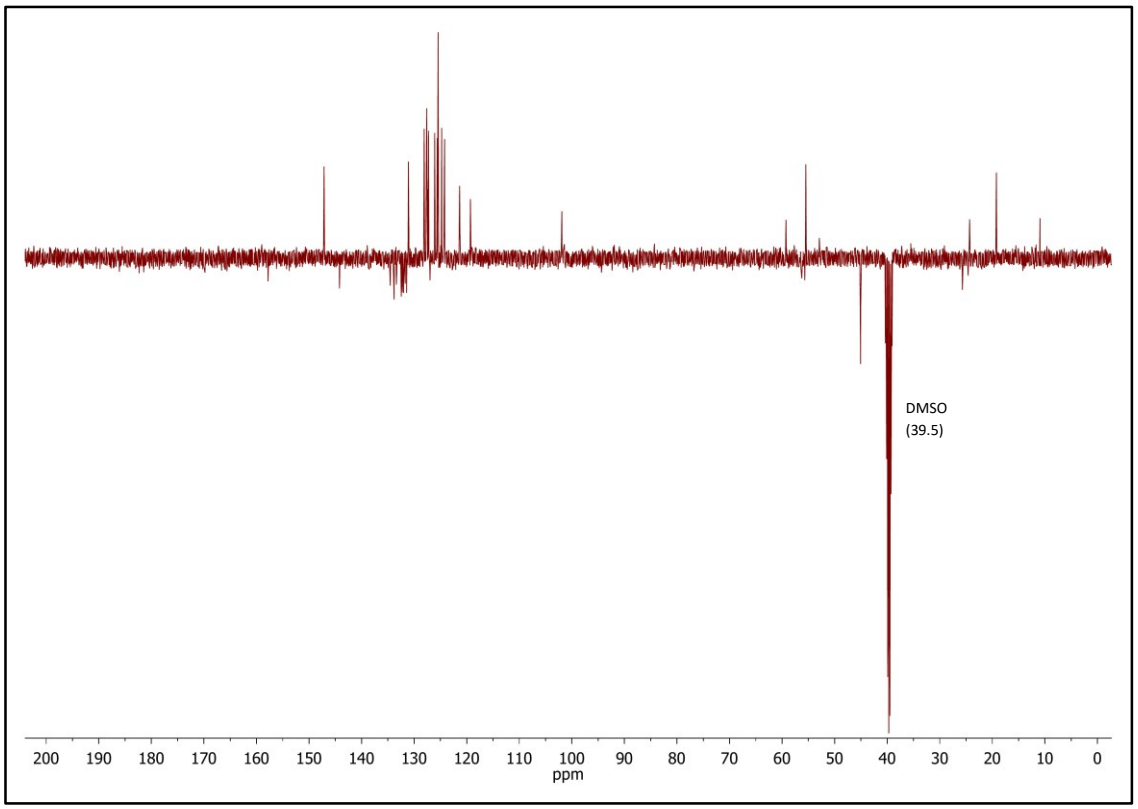


Figure S85. ^{13}C DEPT NMR spectrum of **1c** (100 MHz, DMSO, 117 °C)

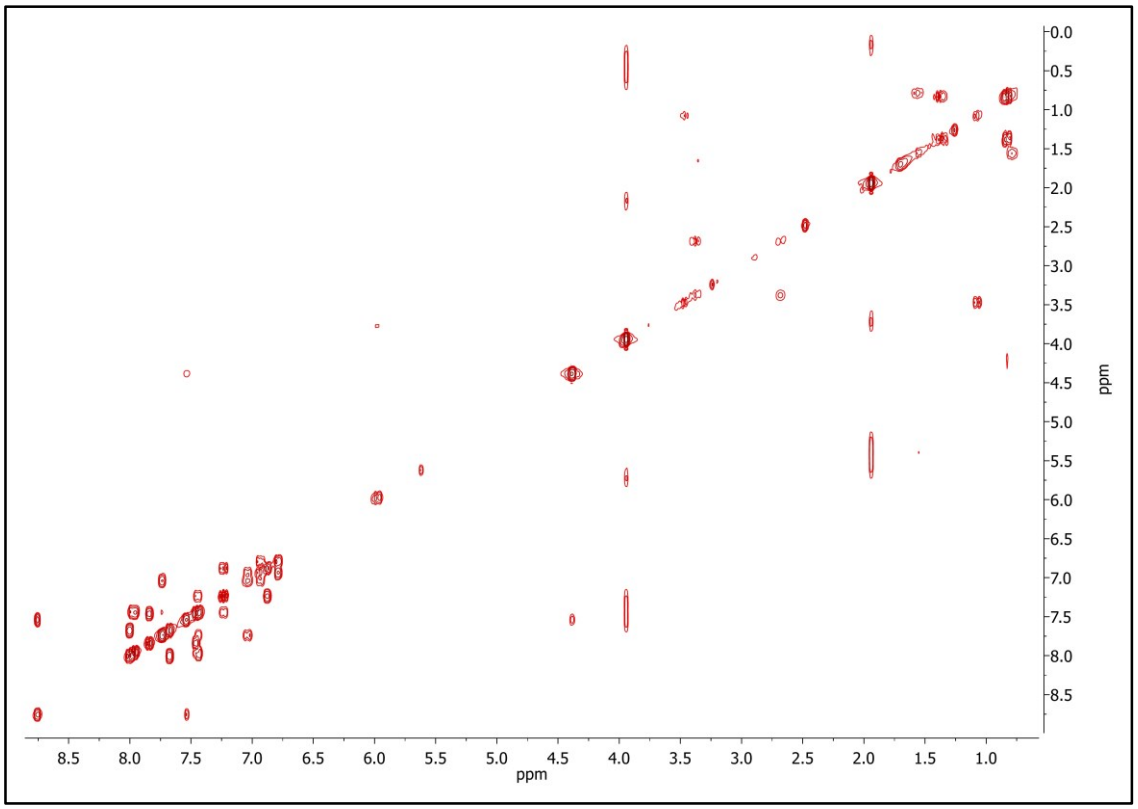


Figure S86. COSY NMR spectrum of **1c** (DMSO, 117 °C)

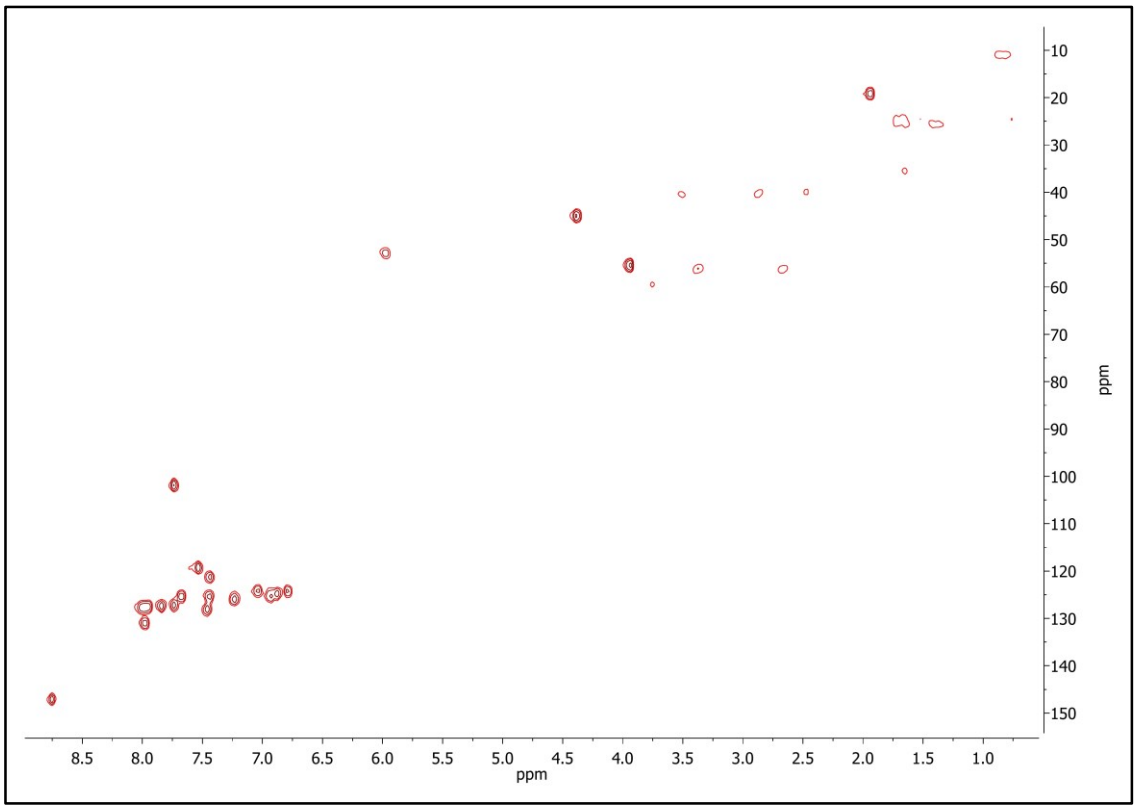


Figure S87. HSQC NMR spectrum of **1c** (DMSO, 117 °C)

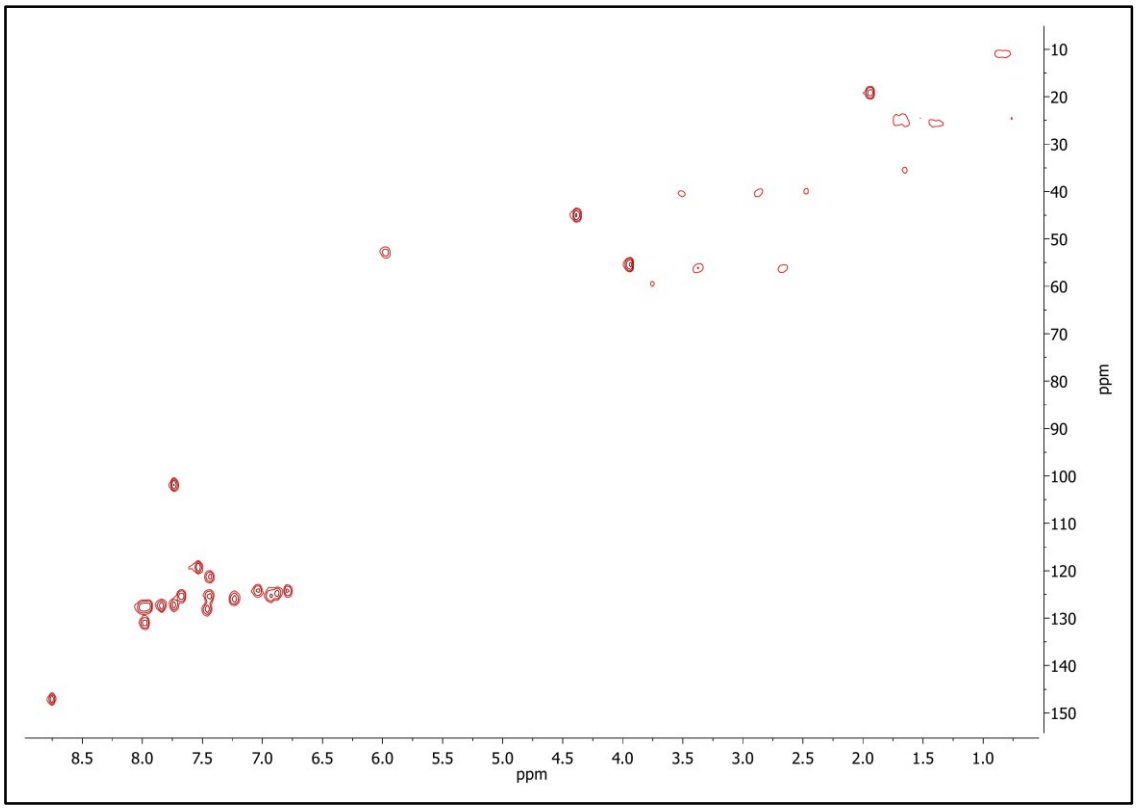


Figure S88. HMBC NMR spectrum of **1c** (DMSO, 117 °C)

NMR spectra of **1d**

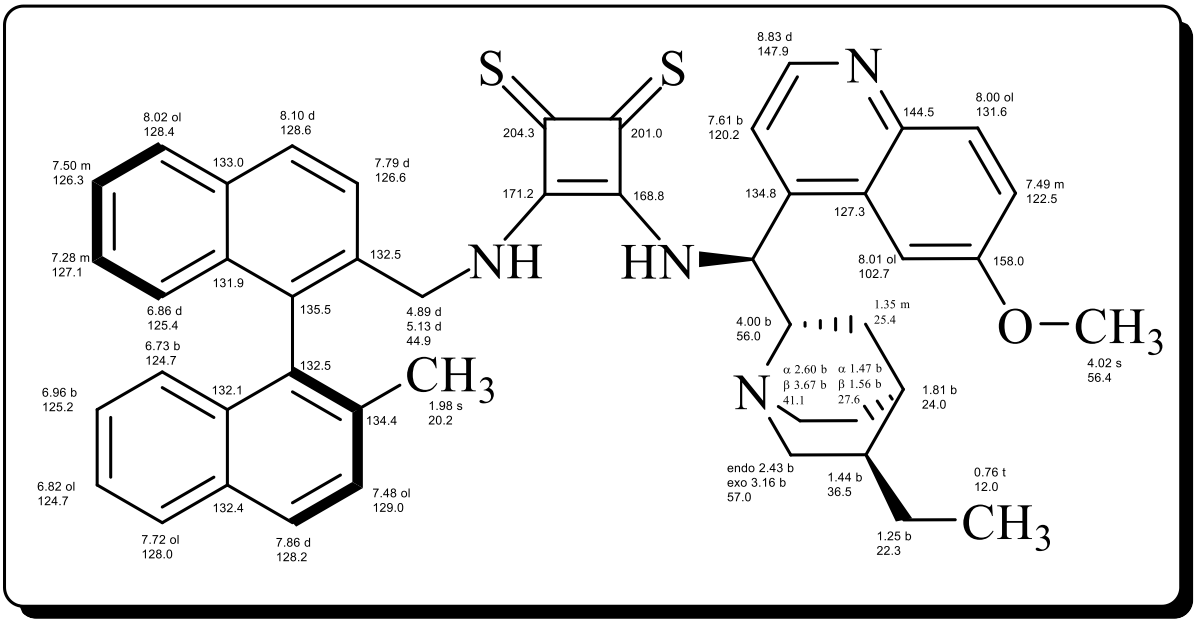


Figure S89. Molecule structure, ^{1}H and ^{13}C assignment of **1d**

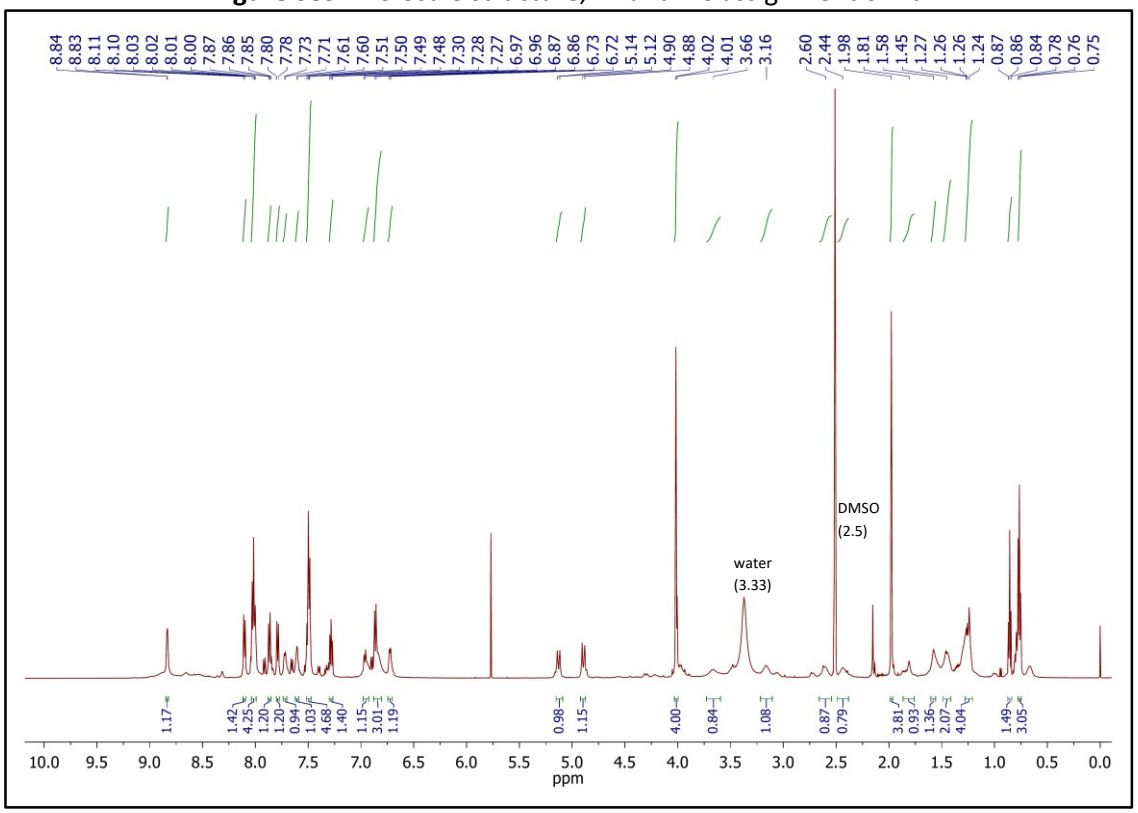


Figure S90a. ^{1}H NMR spectrum of **1d** (600 MHz, DMSO, 22 °C)

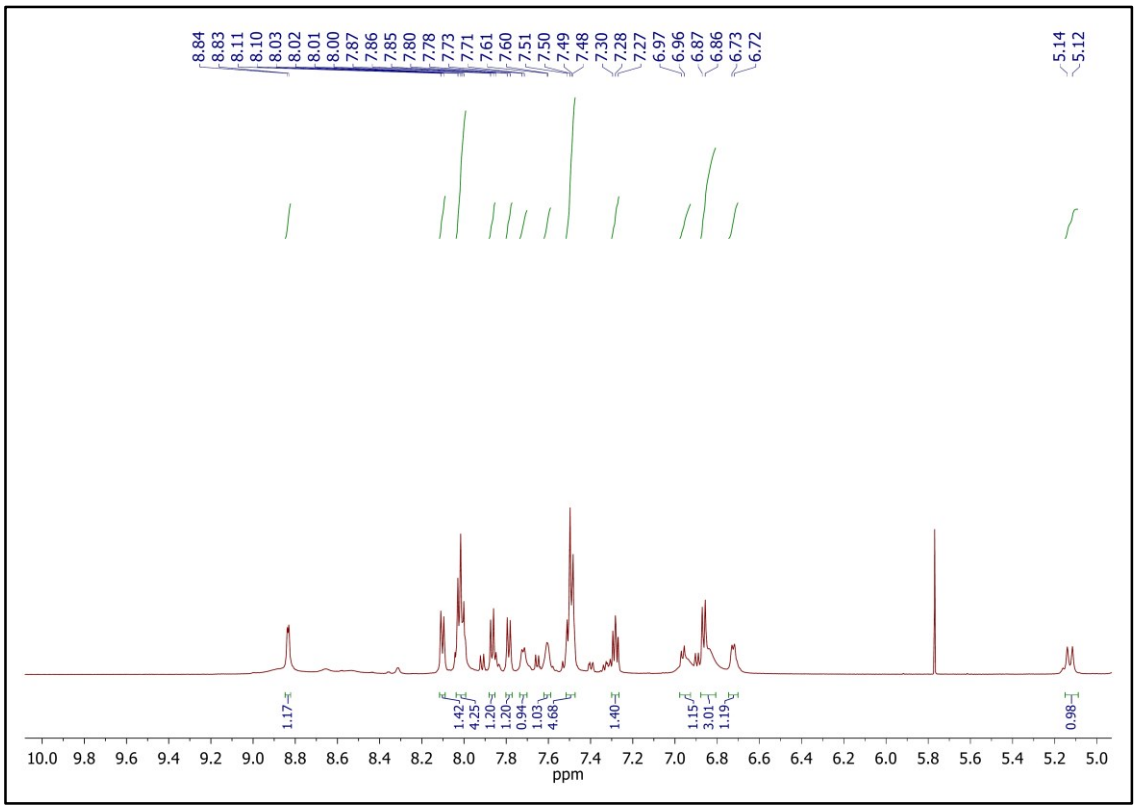


Figure S90b. ^{1}H NMR spectrum of **1d** (600 MHz, DMSO, 22 °C)

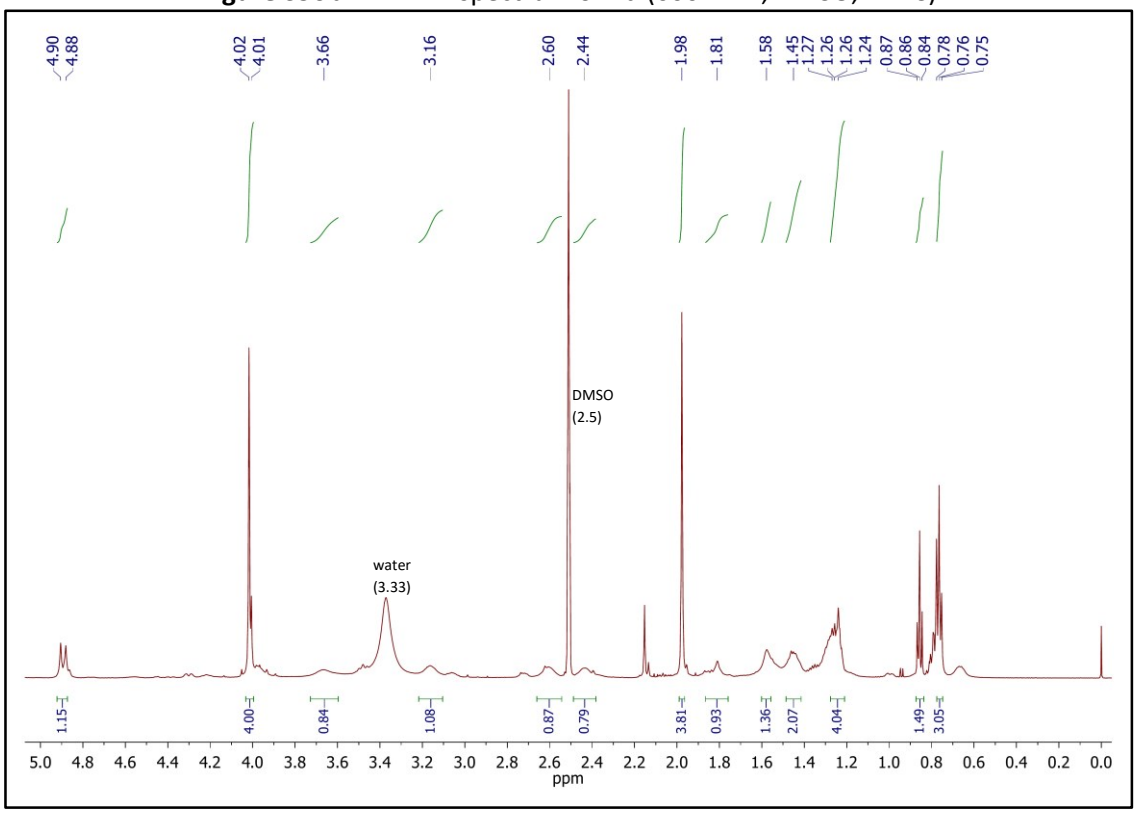


Figure S90c. ^{1}H NMR spectrum of **1d** (600 MHz, DMSO, 22 °C)

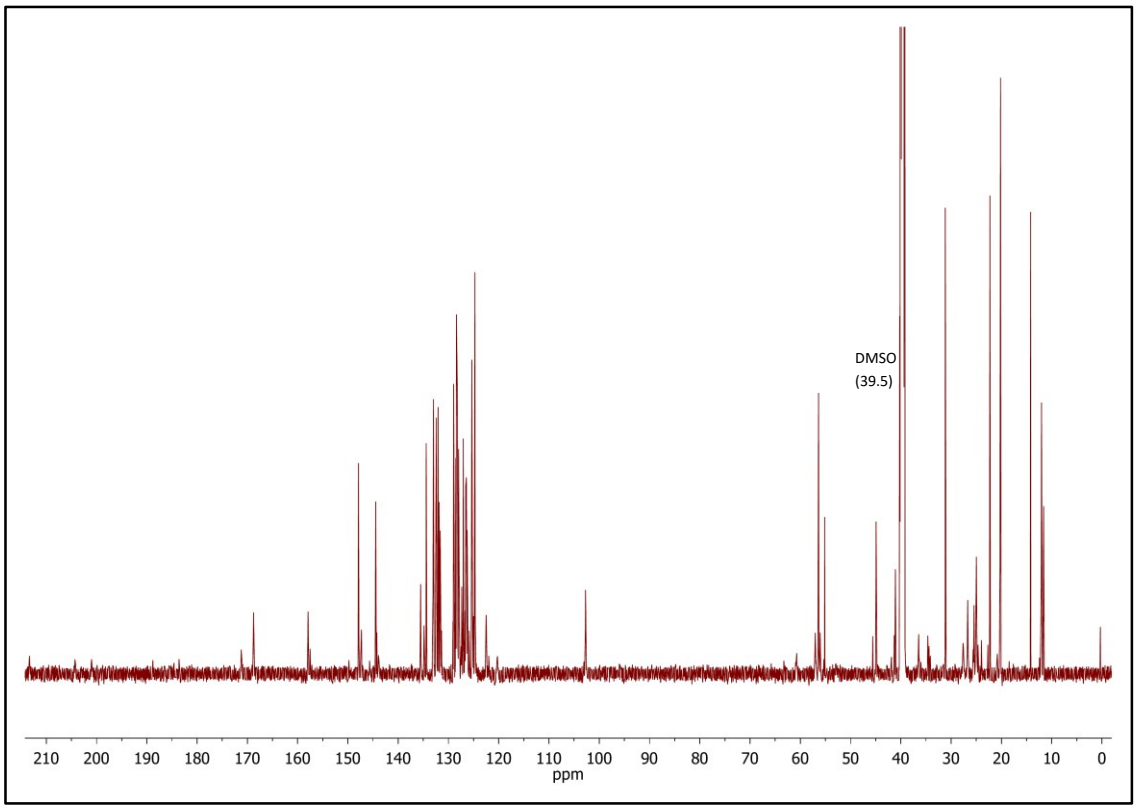


Figure S91. ^{1}H NMR spectrum of **1d** (150 MHz, DMSO, 22 °C)

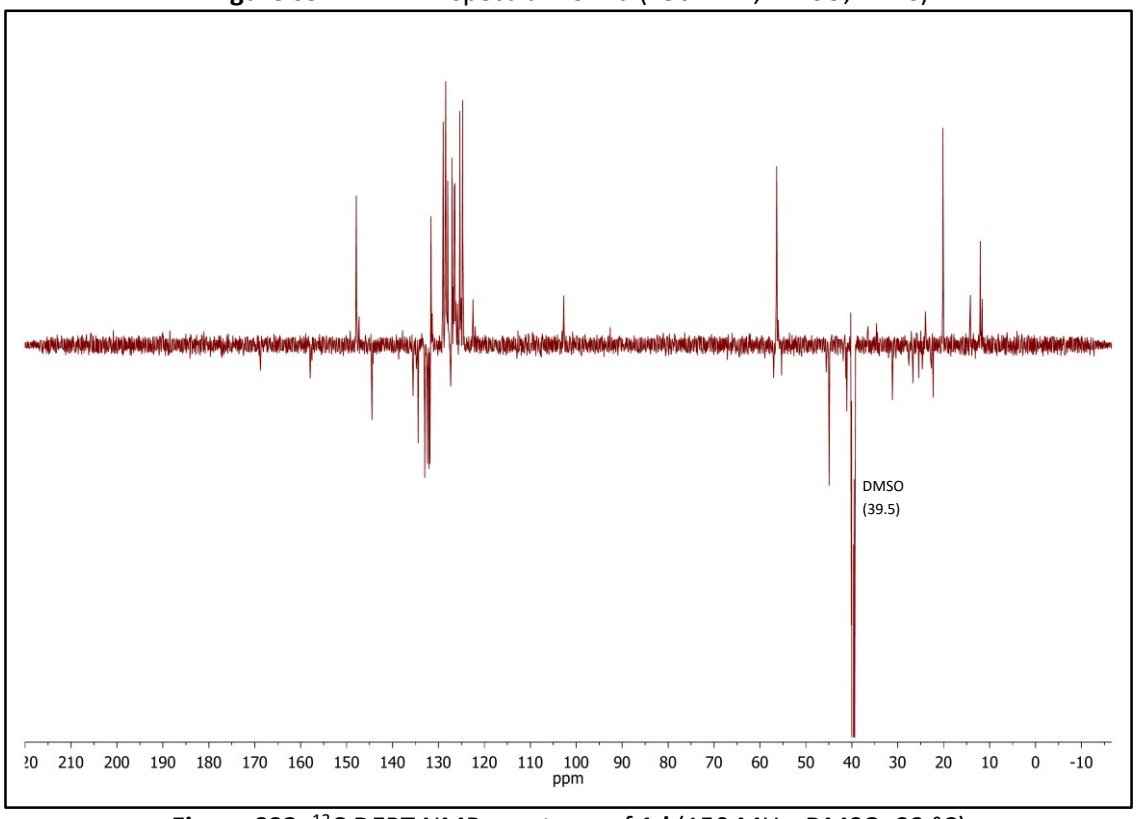


Figure S92. ^{13}C DEPT NMR spectrum of **1d** (150 MHz, DMSO, 22 °C)

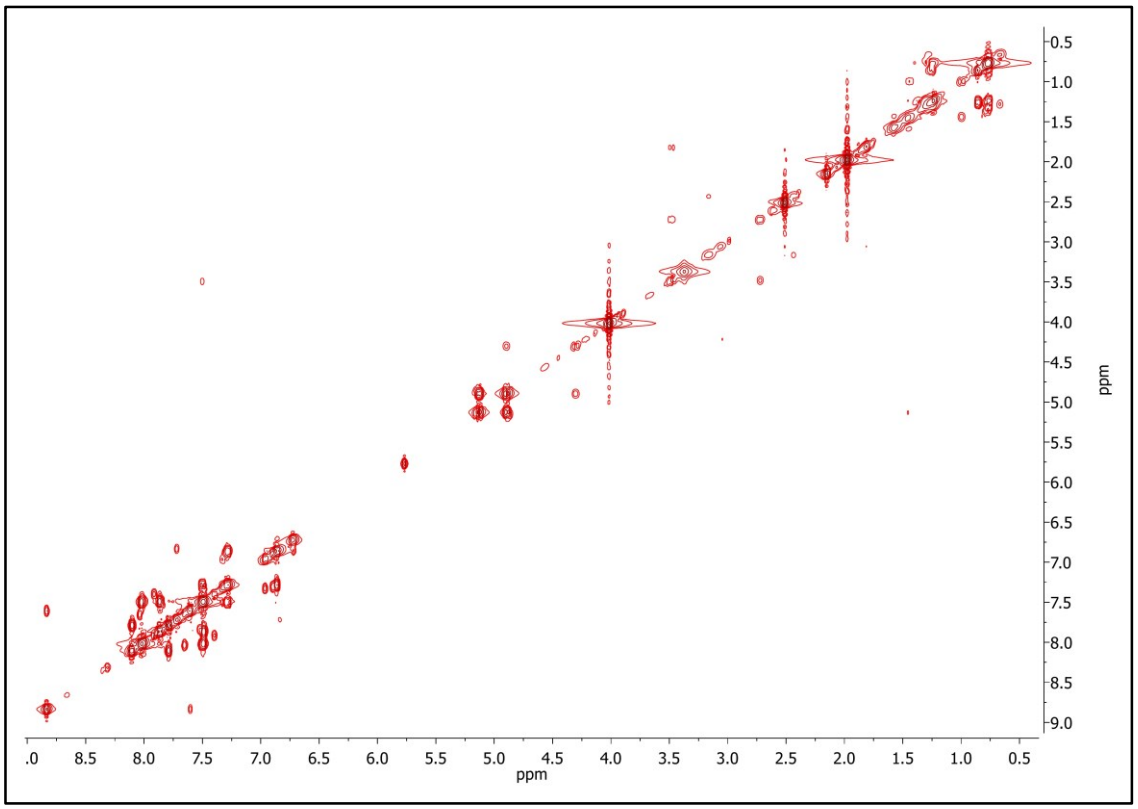


Figure S93. COSY spectrum of **1d** (DMSO, 22 °C)

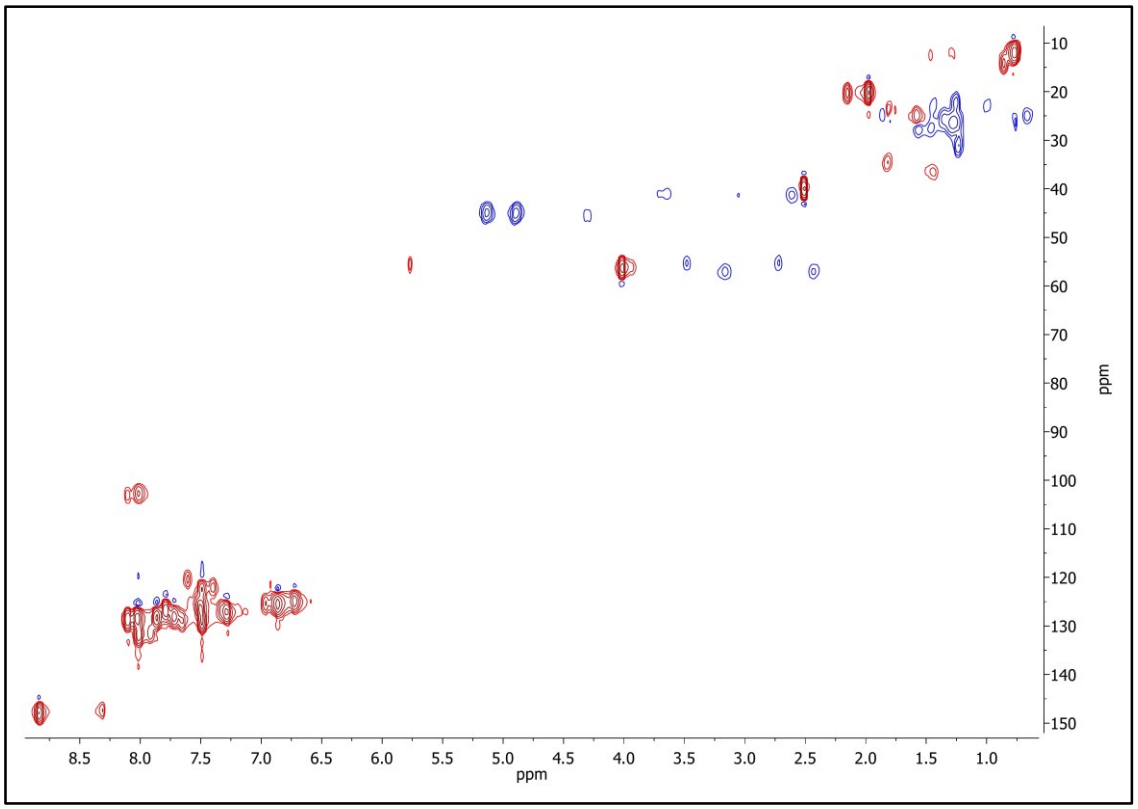


Figure S94. HSQC spectrum of **1d** (DMSO, 22 °C)

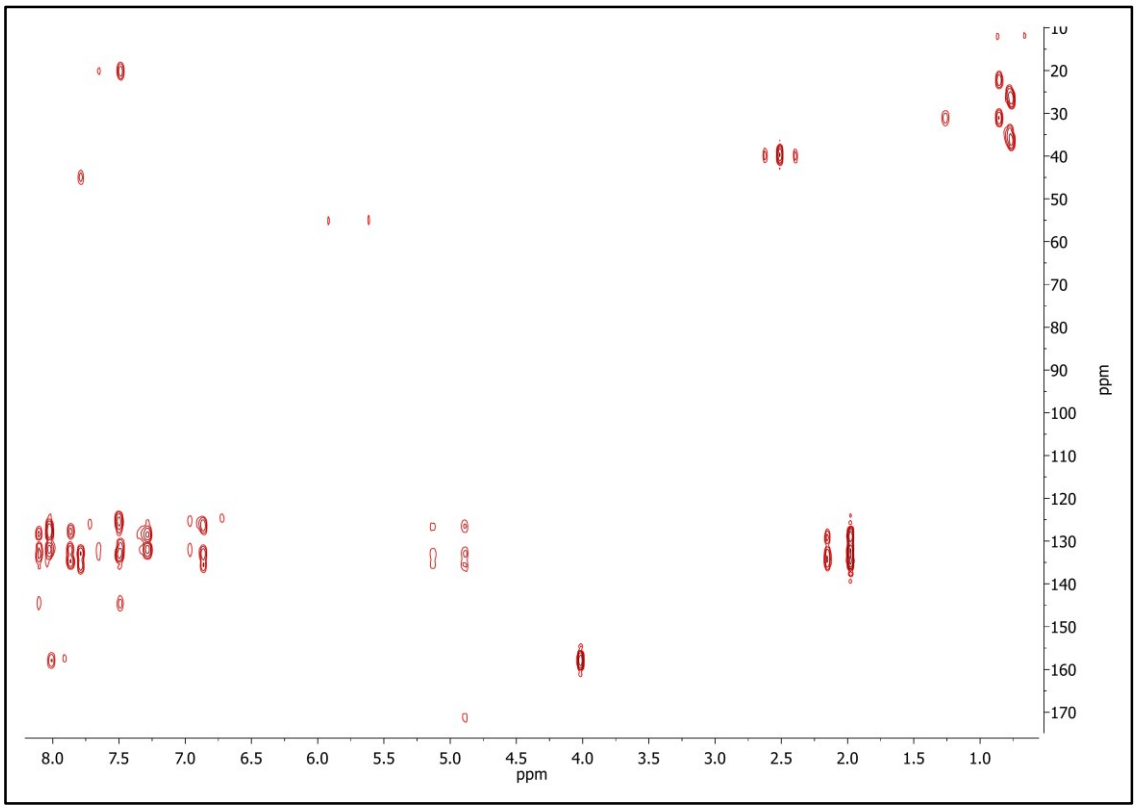


Figure S95. HMBC spectrum of **1d** (DMSO, 22 °C)

4, MS spectra

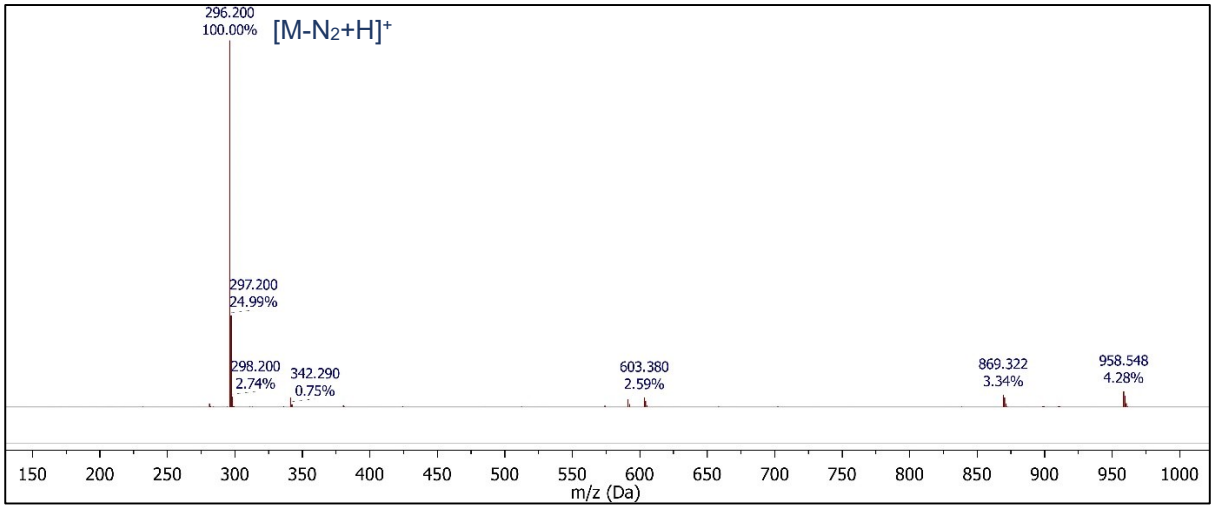


Figure S96. MS spectrum of (*R*)-**16**

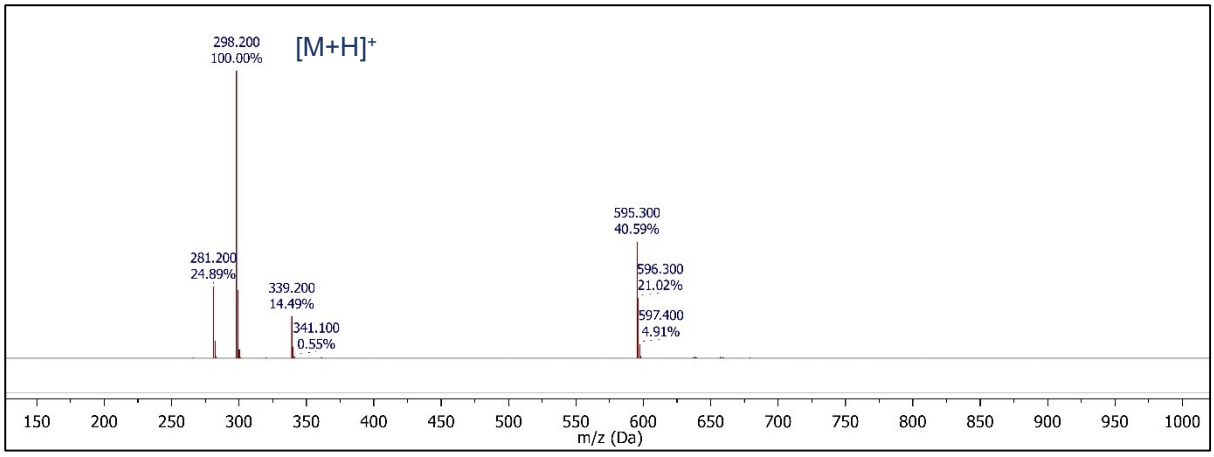


Figure S97. MS spectrum of (*R*)-**2**

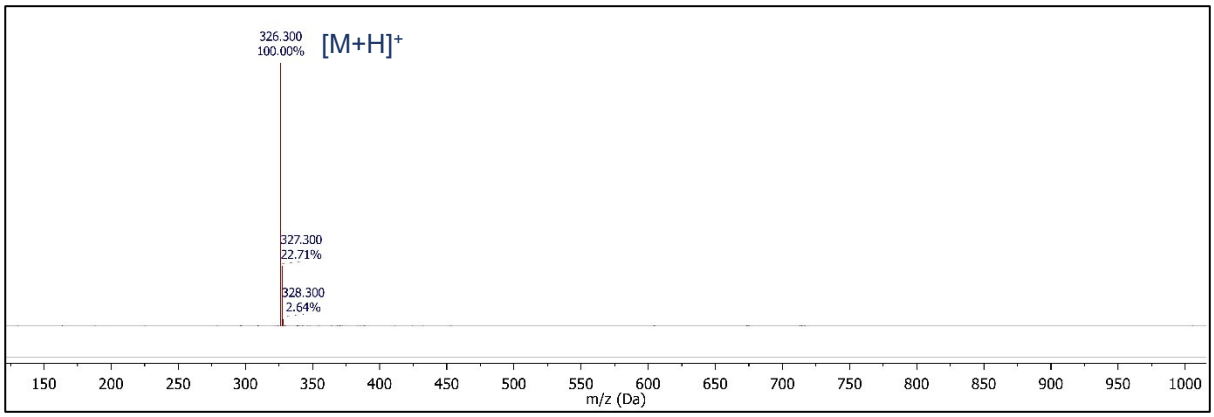


Figure S98. MS spectrum of **6**

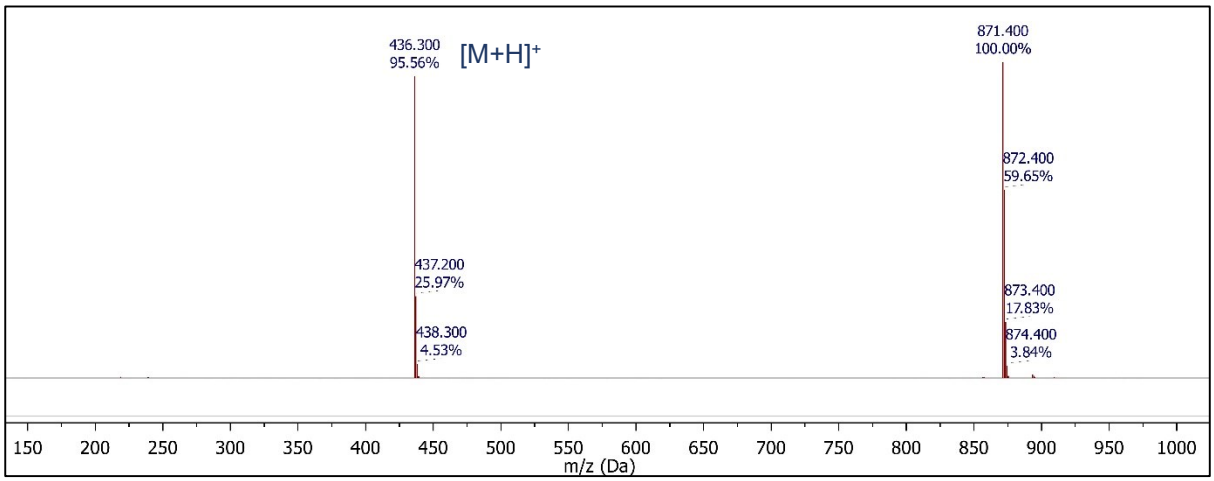


Figure S99. MS spectrum of **HSq-M**

[2M+H]+

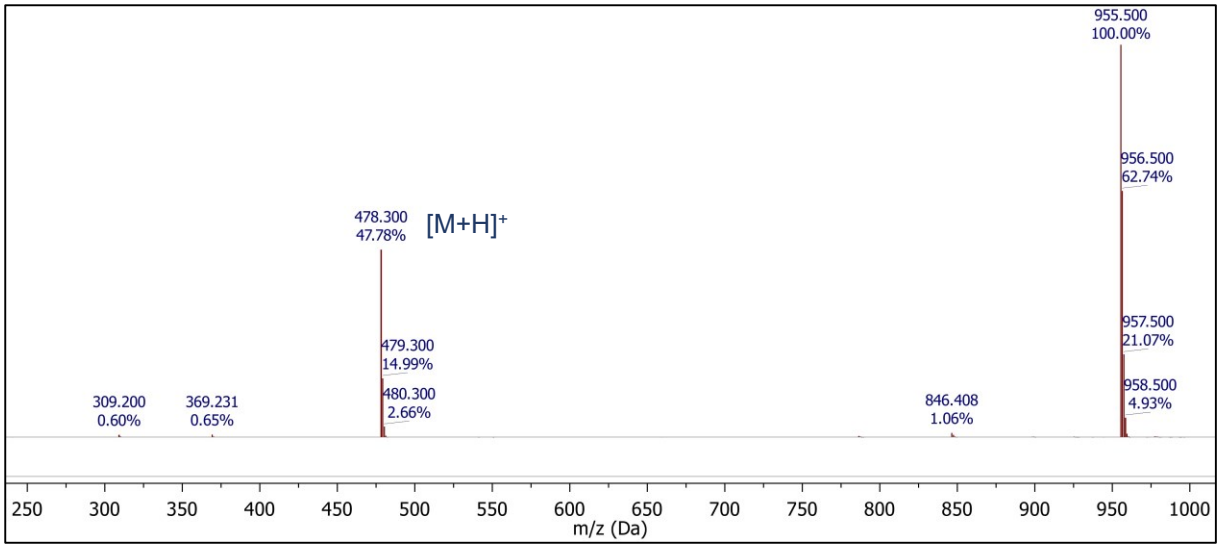


Figure S100. MS spectrum of **HSq-B**

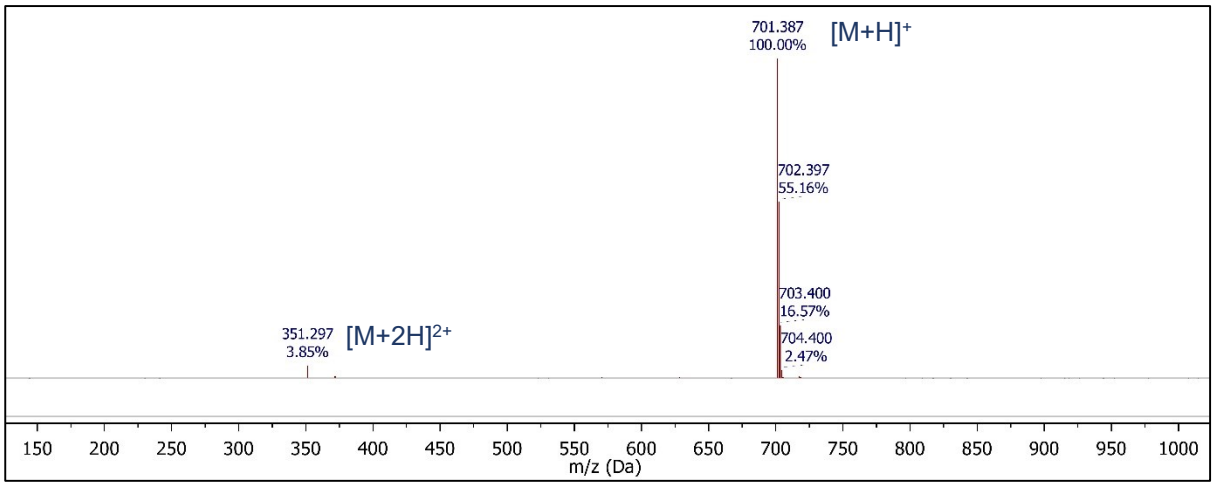


Figure S101. MS spectrum of **1a**

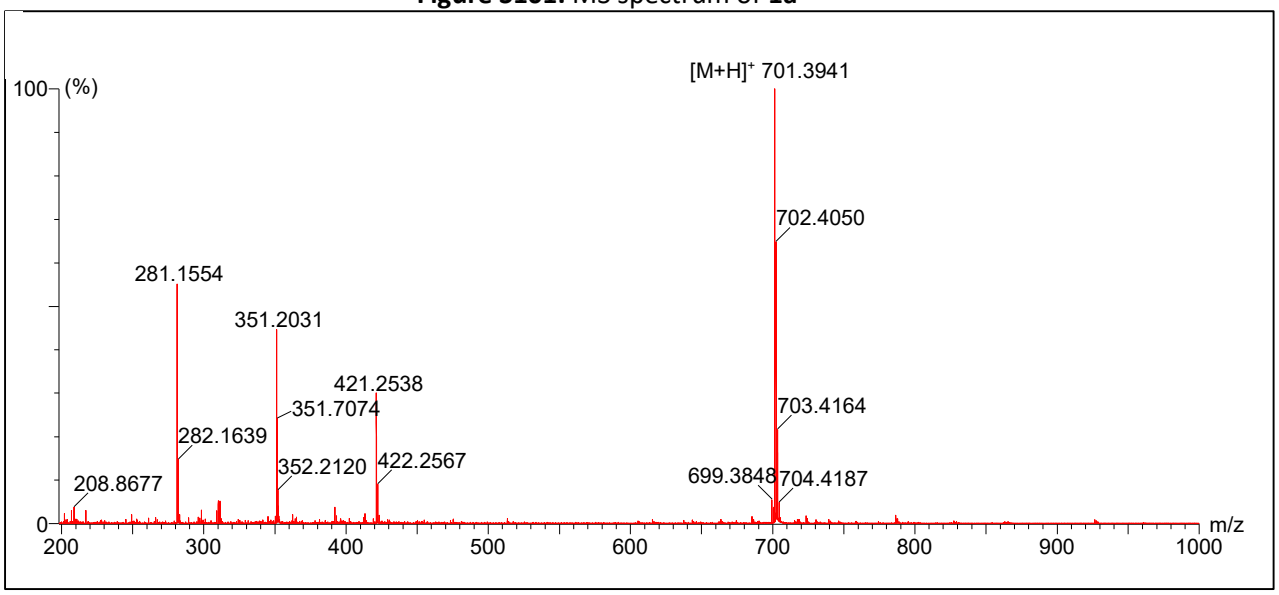


Figure S102. HRMS spectrum of **1a**

[M+H]+

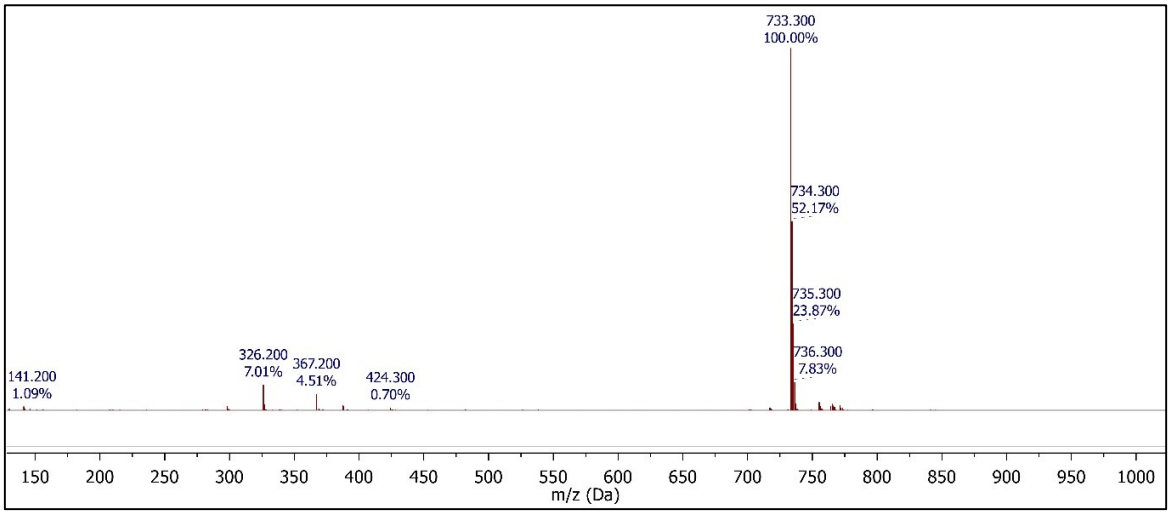


Figure S103. MS spectrum of **1b**

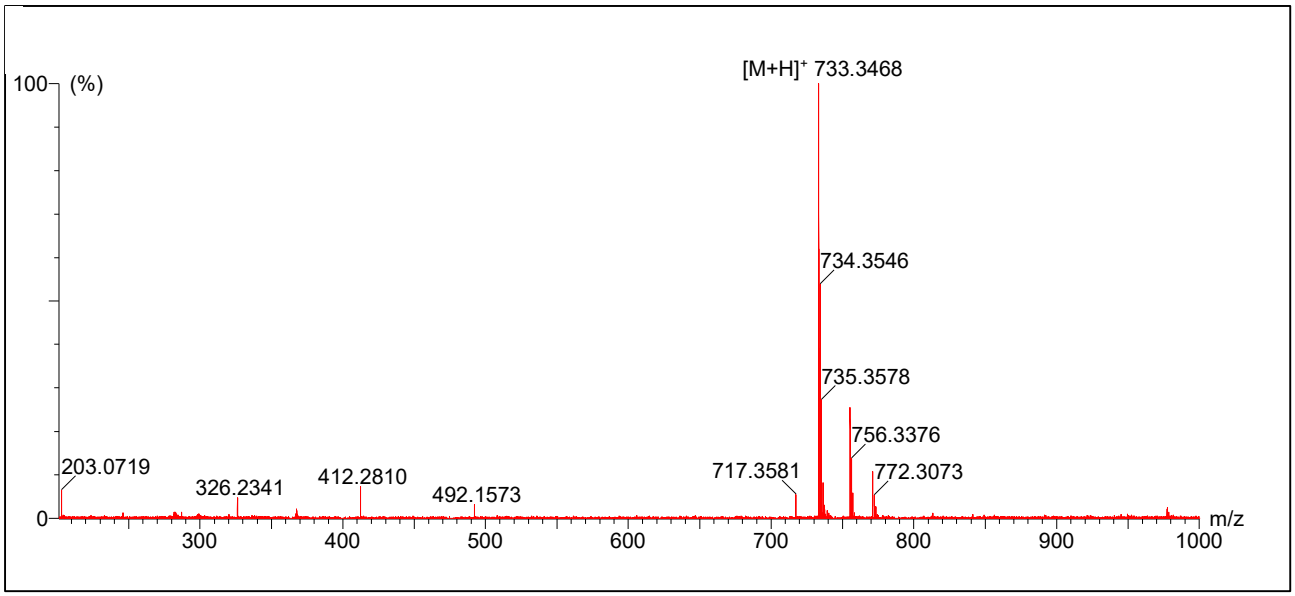


Figure S104. HRMS spectrum of **1b**

5, Thermoanalytical measurements

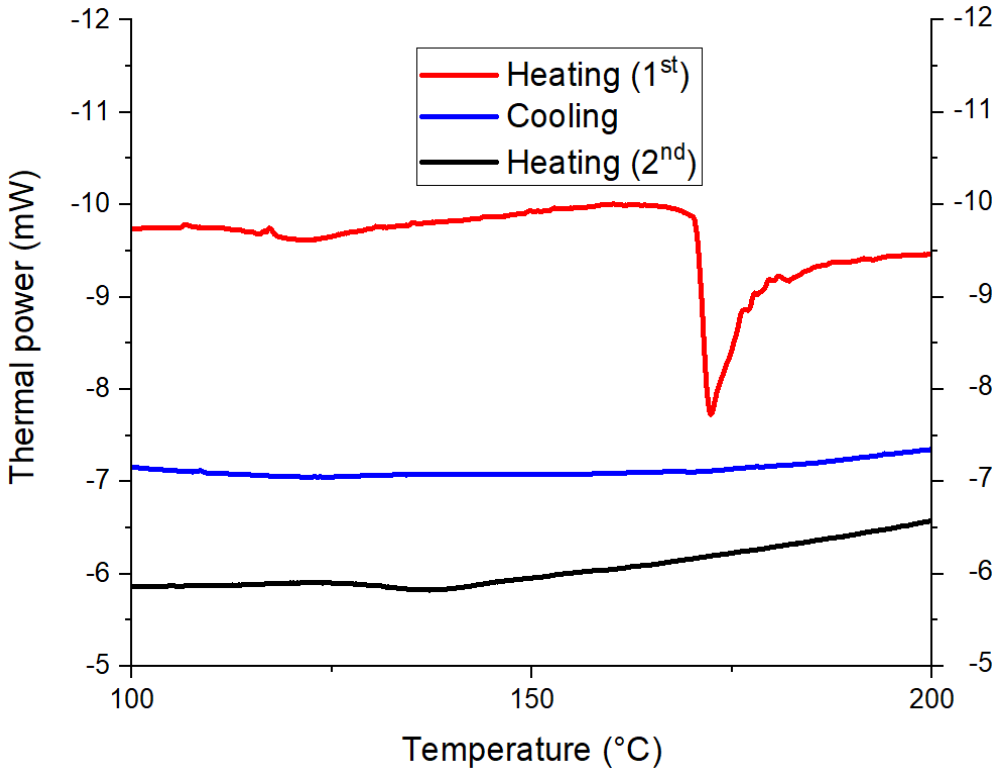


Figure S105. DSC result of **1a** (sample weight: 3.530 mg, method: hold at 30 °C, then heat to 200 °C by 10 °C/min, hold at 200 °C for 10 min, then cool to 30 °C by 10 °C/min, hold at 30 °C for 10 min, then heat to 200 °C by 10 °C/min)

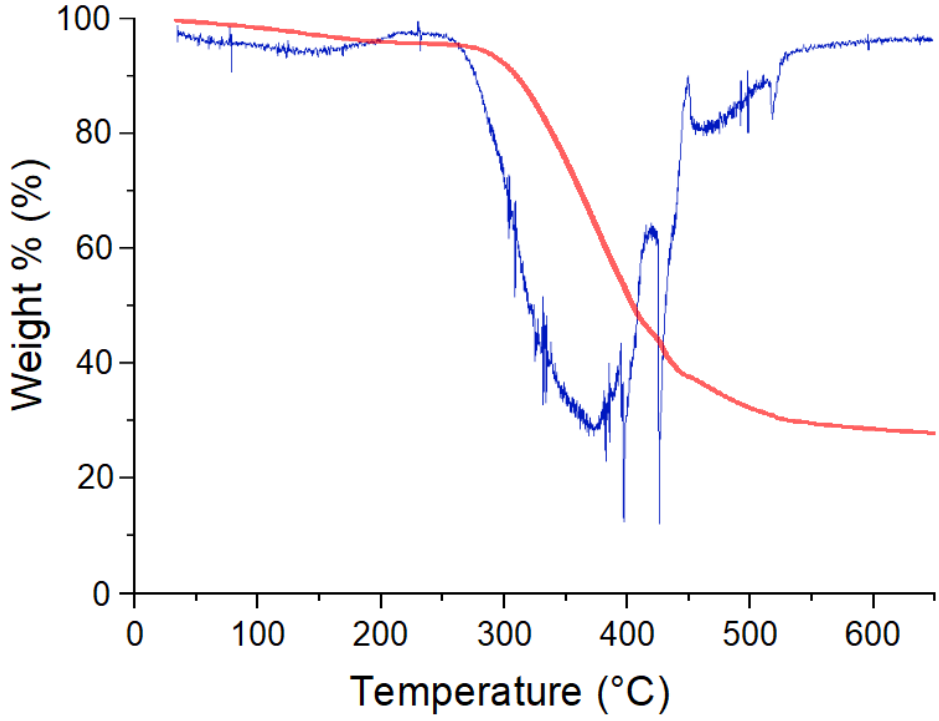


Figure S106. TGA result of **1a** (sample weight: 10.372 mg; method: hold for 1. min at 30 °C, then heat to 700 °C by 10 °C/min, and hold at 700 °C for 10 min, N_2 purge)

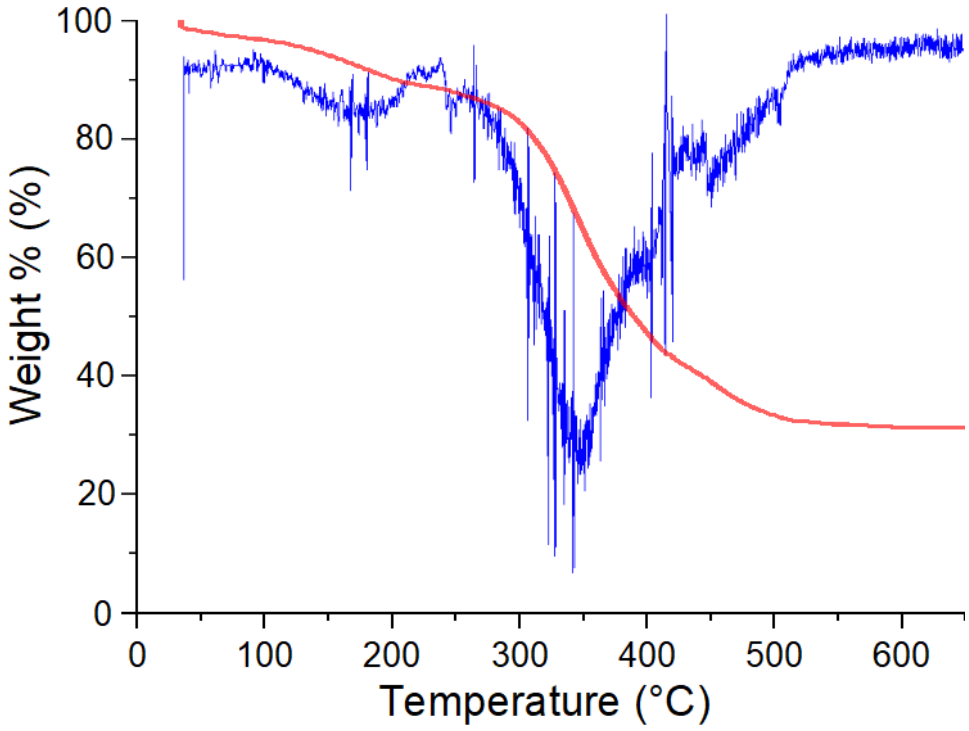


Figure S107. DSC result of **1b** (sample weight: 3.480 mg, method: hold at 30 °C, then heat to 200 °C by 10 °C/min, hold at 200 °C for 10 min, then cool to 30 °C by 10 °C/min, hold at 30 °C for 10 min, then heat to 200 °C by 10 °C/min)

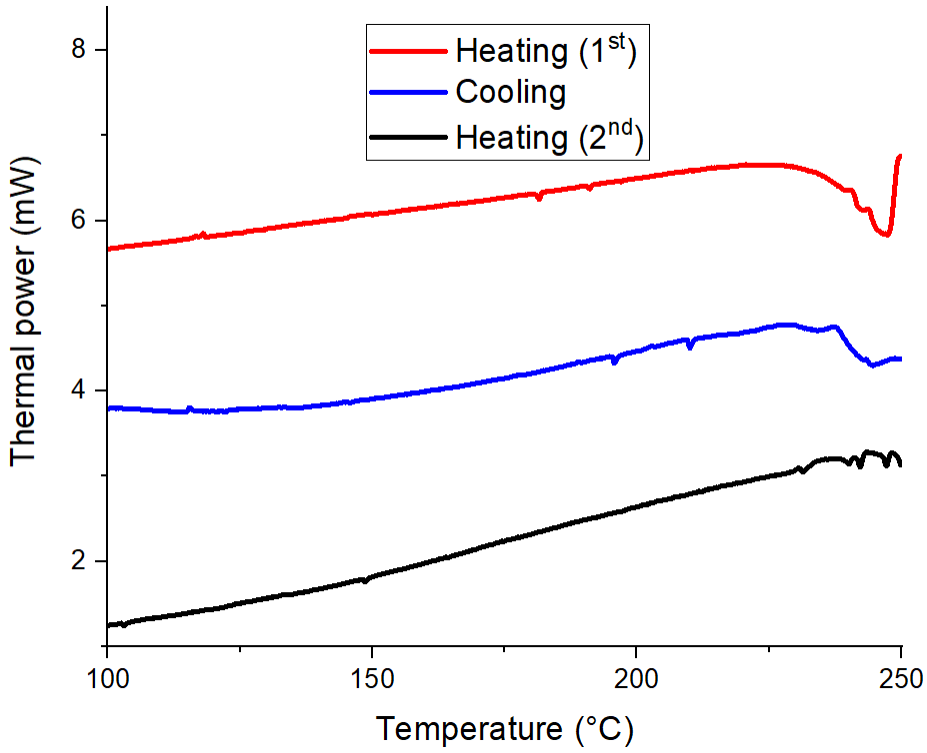
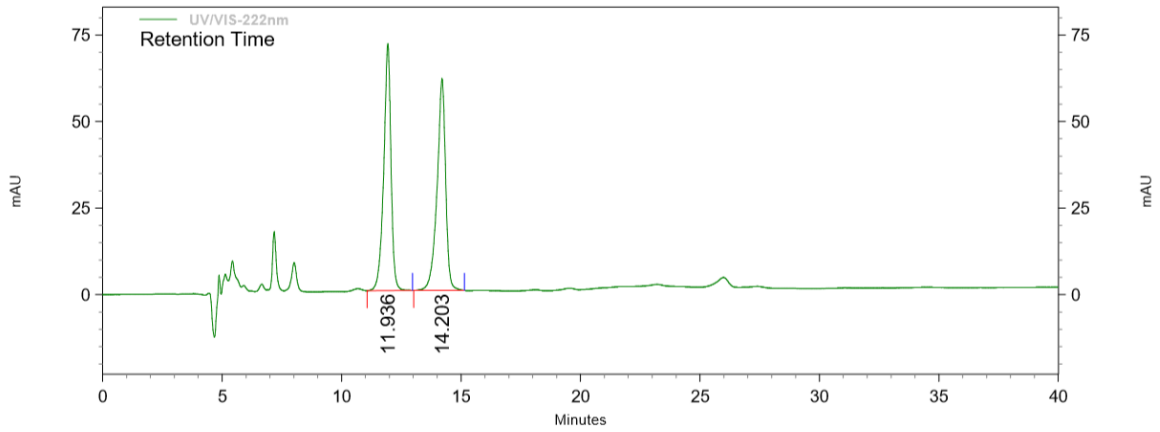


Figure S108. TGA result of **1b** (sample weight: 8.254 mg; method: hold for 1. min at 30 °C, then heat to 700 °C by 10 °C/min, and hold at 700 °C for 10 min, N_2 purge)

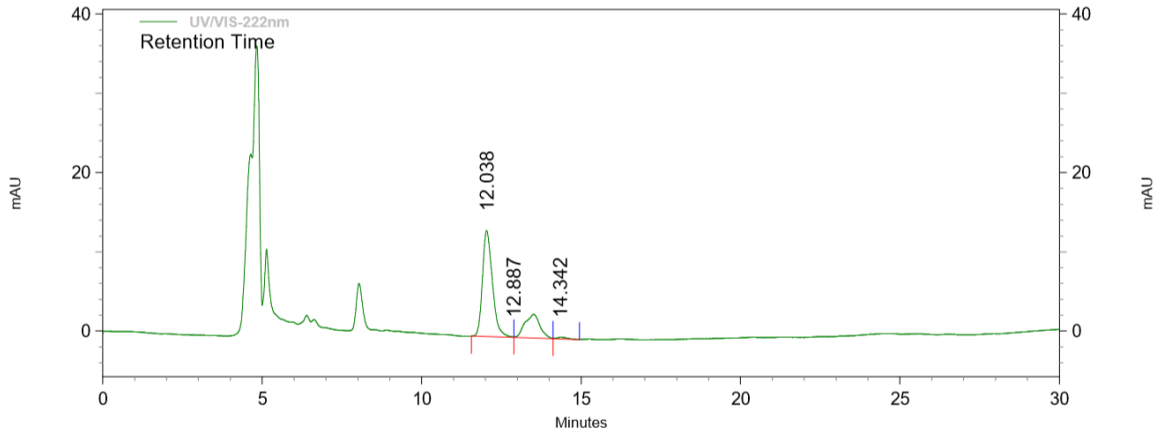
6, Chiral HPLC profiles of **9** *Michael*-, and **12** conjugate adducts

HPLC: Phenomonex Lux Cellulose-3 column (3 µm, 250 × 4.6 mm), eluent CH_3CN/20 mM NH_4OAc in H_2O = 40/60, isocratic mode; 0.6 mL·min^{-1}; UV detector 222 nm, 5 µL or 10 µL injection, 20 °C. Retention time for (*S*)-**9**: 11.94 min, for (*R*)-**9**: 14.20 min.



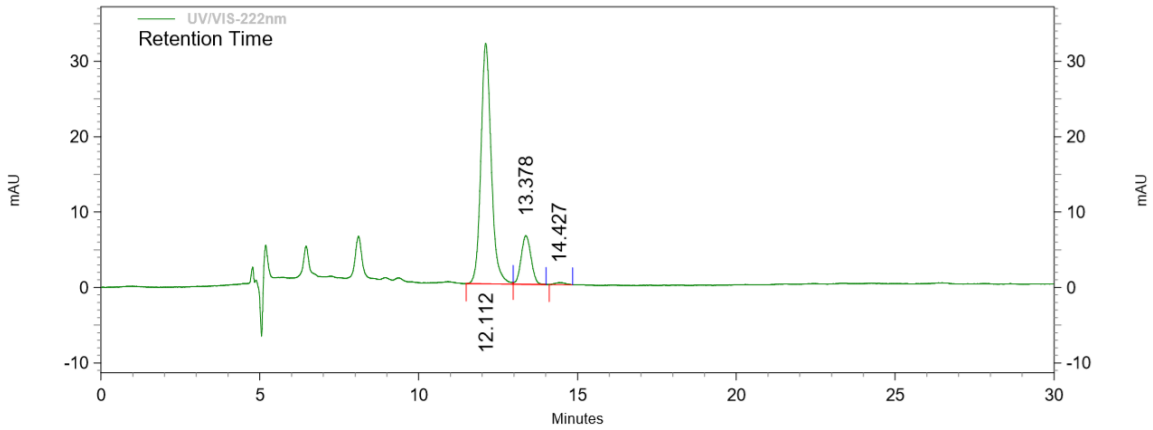
Name	Retention Time	Area	Area Percent	Integration Codes
	11.936	1512904	49.812	MM
	14.203	1524328	50.188	MM
Totals		3037232	100.000	

Figure S109. HPLC chromatogram of racemic **9**



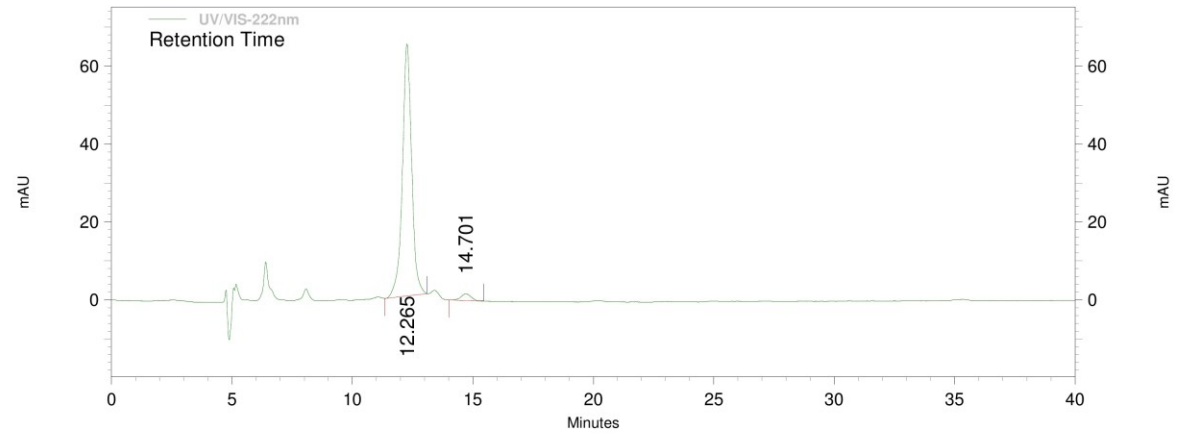
Name	Retention Time	Area	Area Percent	Integration Codes
	12.038	387502	98.774	Mx
	12.887	0	0.000	MM
	14.342	4810	1.226	xM
Totals		392312	100.000	

Figure S110. HPLC chromatogram of enantiomeric enriched **9** (Table 2, Entry 1)



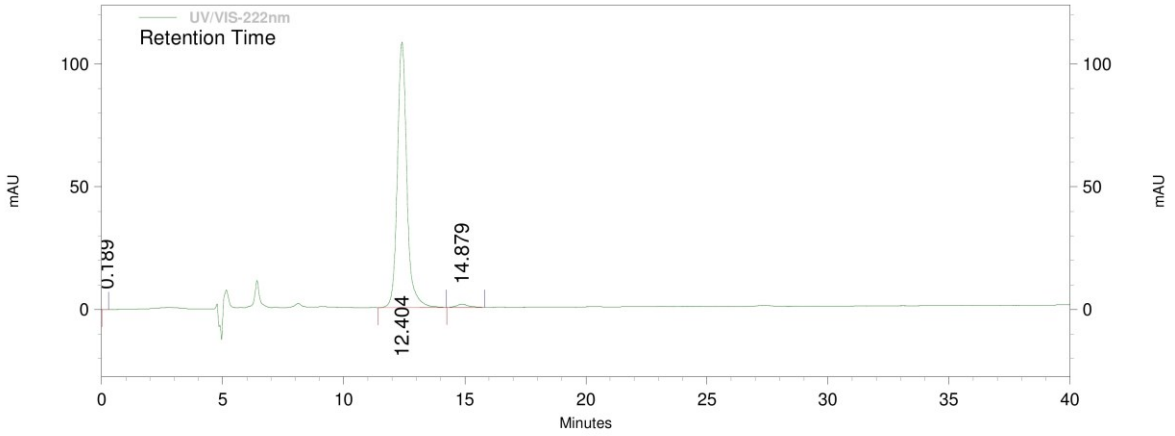
Name	Retention Time	Area	Area Percent	Integration Codes
	12.112	721572	83.277	Mx
	13.378	138926	16.033	xM
	14.427	5976	0.690	MM
Totals		866474	100.000	

Figure S111. HPLC chromatogram of enantiomeric enriched **9** (Table 2, Entry 6)



Name	Retention Time	Area	Area Percent	Integration Codes
	12.265	1732924	97.215	MM
	14.701	49648	2.785	MM
Totals		1782572	100.000	

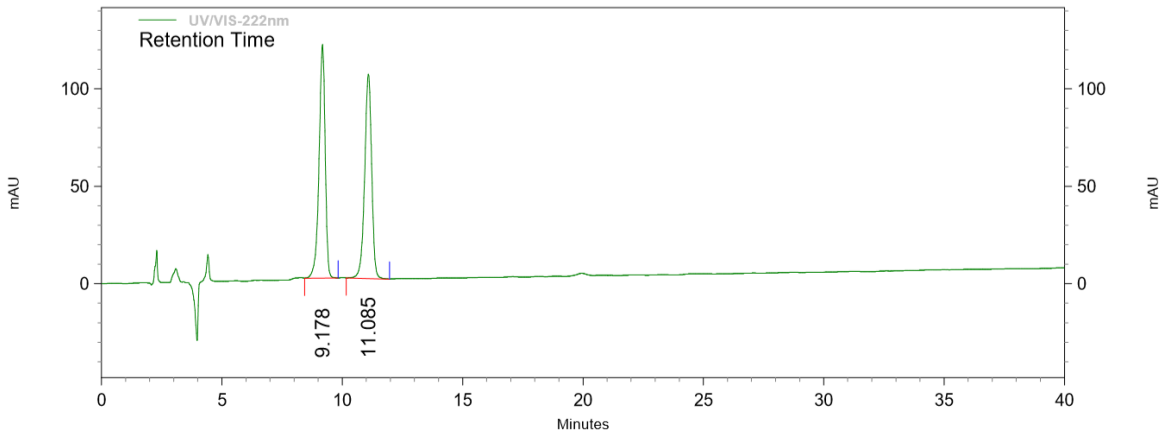
Figure S112. HPLC chromatogram of enantiomeric enriched **9** (Table 5, Entry 2)



Name	Retention Time	Area	Area Percent	Integration Codes
	0.189	202	0.007	BI
	12.404	2935973	98.678	MM
	14.879	39117	1.315	MM
Totals		2975292	100.000	

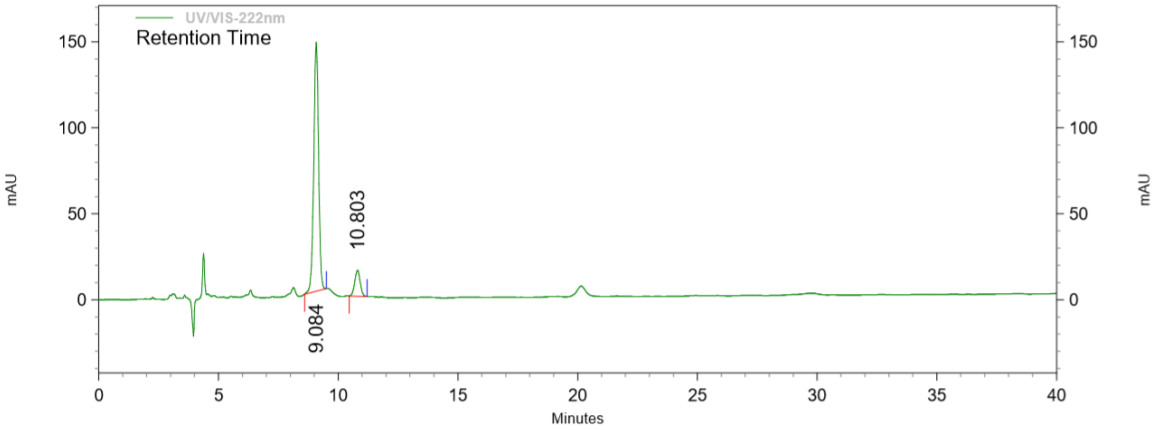
Figure S113. HPLC chromatogram of enantiomeric enriched **9** (Table 5, Entry 7)

HPLC: Phenomonex Lux Cellulose-1 column (3 µm, 250 × 4.6 mm); eluent CH_3CN/0.1% AcOH in H_2O and = 40:60, isocratic mode; 0.8 mL·min^{-1}; UV detector 222 nm ; 5 µL or 10 µL injection, 25 °C. Retention time for (*R*)-**12** 9.18 min, for(*S*)-**12** 11.09 min.



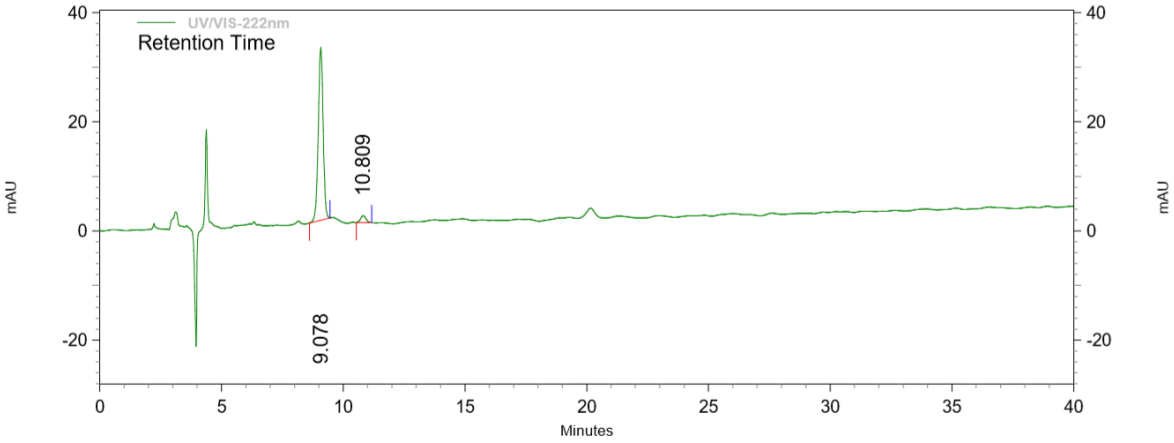
Name	Retention Time	Area	Area Percent	Integration Codes
	9.178	2123017	50.019	MM
	11.085	2121371	49.981	MM
Totals		4244388	100.000	

Figure S114. HPLC chromatogram of racemic **12**



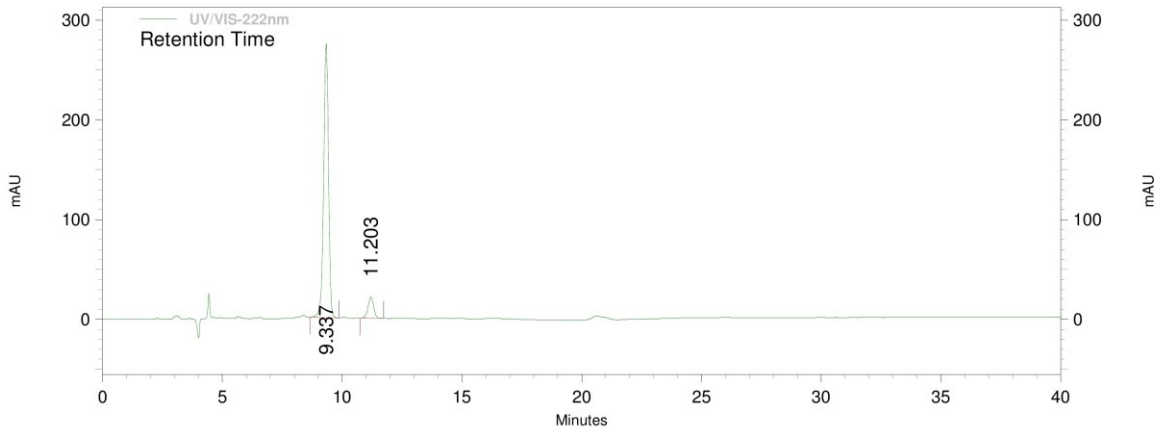
Name	Retention Time	Area	Area Percent	Integration Codes
	9.084	2015418	89.386	MM
	10.803	239329	10.614	MM
Totals		2254747	100.000	

Figure S115. HPLC chromatogram of enantiomeric enriched **12** (Table 3, Entry 1)



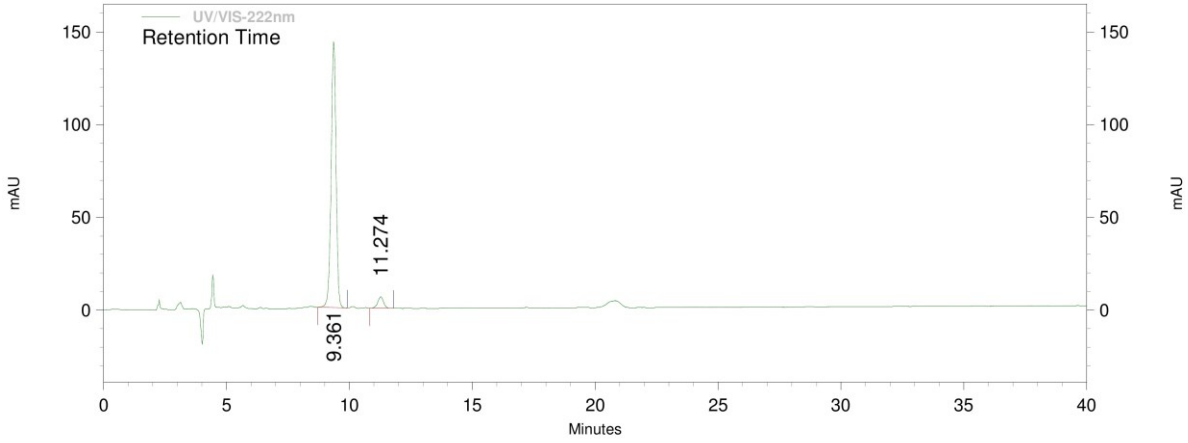
Name	Retention Time	Area	Area Percent	Integration Codes
	9.078	437759	95.792	MM
	10.809	19230	4.208	MM
Totals		456989	100.000	

Figure S116. HPLC chromatogram of enantiomeric enriched **12** (Table 3, Entry 4)



Name	Retention Time	Area	Area Percent	Integration Codes
	9.337	3834244	91.656	MM
	11.203	349058	8.344	MM
Totals		4183302	100.000	

Figure S117. HPLC chromatogram of enantiomeric enriched **12** (Table 6, Entry 1)



Name	Retention Time	Area	Area Percent	Integration Codes
	9.361	1994813	95.281	MM
	11.274	98806	4.719	MM
Totals		2093619	100.000	

Figure S118. HPLC chromatogram of enantiomeric enriched **12** (Table 6, Entry 4)

7, Theoretical calculations

XYZ coordinates and total energies

1. XYZ coordinates (in Å) and total energy (in atomic units) of binaphthalene-cinchona squaramide (**1a**) optimized in gas phase

E = -2223.39342911886

C	-2.8446185526	4.7009310605	0.2983075300
C	-2.9962357149	5.1471153419	-0.9871062854
C	-2.8594398767	3.3123199628	0.5930556936
C	-3.0274821021	2.3713436934	-0.4617419302
C	-3.1900767033	4.2181578493	-2.0358714025
C	-3.2116311348	2.8719562020	-1.7804657653
C	-2.7073688932	2.8385334466	1.9188278695
C	-2.6972862498	1.4947680601	2.1711285986
C	-2.8184144523	0.5405870183	1.1286646590
C	-2.9876217754	0.9651945357	-0.1796050283
C	-3.1659767435	-0.0219123919	-1.2923915087
C	-4.4044565295	-0.7470535738	-1.3643965822
C	-2.1874094044	-0.2363257797	-2.2469398451
C	-2.3935491685	-1.2184257272	-3.2530495994
C	-4.5838206305	-1.7275673404	-2.3770745701
C	-3.5422582744	-1.9503092676	-3.3119731783
C	-5.4764623289	-0.5173105032	-0.4600368436
C	-6.6422099290	-1.2356834227	-0.5452507916
C	-6.8058550132	-2.2241702349	-1.5400491547
C	-5.7964078275	-2.4586930724	-2.4365663409
C	-2.6404698750	-0.9169402636	1.5141561051
C	-0.8871986793	0.5253057740	-2.3057090549
C	-1.3253440101	-2.8725670462	-0.5360302506
C	0.0551881357	-2.9325631772	-1.2109769147
C	0.5542652601	-2.1240367599	-0.0885638840
C	3.5530875396	-2.1372886359	1.9025806927
C	3.6085679004	-2.7954161365	3.1062692454
C	4.7924245248	-3.4450130632	3.5231575878
C	4.7376870061	-2.1423161119	1.0921874662
C	5.8718172212	-2.8400078323	1.6083930284
C	7.0622493505	-2.8806176801	0.8442586530
C	7.1553889202	-2.2697876381	-0.3782817975
C	6.0341755998	-1.5759090002	-0.8934623240
C	4.8606512863	-1.5191384235	-0.1726569951
N	5.8901019337	-3.4775667283	2.8126503198
O	6.0282150140	-0.9333956571	-2.0860116290
C	7.1891690437	-0.9829849076	-2.8869820395
N	1.8242101340	-1.6938906628	0.1714730040
C	-0.7094902255	-1.9433702480	0.4568135917

N	-1.2199717328	-1.2762710482	1.5031626716
C	2.2496580064	-1.4308385734	1.5520105244
C	2.2908876688	0.0556413472	1.9947310547
C	3.2858781519	1.0071477518	1.2970246313
C	2.6985575848	2.4320480219	1.3555381778
C	1.5400689704	2.4726853845	0.3405227226
N	0.9461657196	0.6696163992	2.0020274370
C	0.6358367784	1.2600380392	0.6847788866
C	0.7416596821	3.7802910139	0.2909080316
C	1.5806613959	5.0135068005	-0.0331292414
C	0.9568636626	1.7480648980	3.0050140008
C	2.1572070624	2.7016781437	2.7689396564
H	-2.7059094839	5.4045468869	1.1152904252
H	-2.9773832528	6.2108452310	-1.2040543052
H	-3.3271712693	4.5767090689	-3.0515723516
H	-3.3665330654	2.1671890891	-2.5902570136
H	-2.5998247445	3.5559790289	2.7286127280
H	-2.5745561779	1.1368932911	3.1909627204
H	-3.1684554235	-1.5983265810	0.8459245371
H	-3.0324630990	-1.0749444716	2.5245883726
H	-0.5766487482	-0.6034499909	1.9399756142
H	2.4971939233	-2.1907240234	-0.3989068304
H	1.4866898021	-1.8756648911	2.2014019611
H	2.7357135211	-2.8283555636	3.7525059338
H	4.8132623562	-3.9605481242	4.4815319259
H	4.0446830961	-0.9630385499	-0.6147931886
H	8.0831646764	-2.3223133385	-0.9359352937
H	7.9033985709	-3.4187809515	1.2680008858
H	8.0448021539	-0.5106349647	-2.3880340306
H	7.4479054977	-2.0138285706	-3.1588911945
H	6.9493927442	-0.4238180121	-3.7917521916
H	2.5789113120	-0.0169580600	3.0512594347
H	4.2686695675	0.9487829313	1.7758957926
H	3.4222668722	0.7351374181	0.2465915891
H	3.4711742581	3.1617803229	1.0950469774
H	1.9719106903	2.3166997615	-0.6581114471
H	-0.0447188159	3.6663923038	-0.4670842300
H	0.2075250838	3.9336951400	1.2379027703
H	0.9450355968	5.8968772393	-0.1511298228
H	2.1386190603	4.8746046547	-0.9666125672
H	2.3068709134	5.2289262463	0.7588164248
H	-0.4154976981	1.5564603107	0.7003311151
H	0.7434885098	0.4739736946	-0.0600549171
H	0.9922225514	1.2977983903	4.0027579854
H	0.0032062788	2.2776680855	2.9182604928
H	1.8511642413	3.7471075315	2.8783408317
H	2.9496289844	2.5256010116	3.5060302841

H	-0.7785993493	1.0053198525	-3.2851412205
H	-0.8184087449	1.3035154910	-1.5469882647
H	-0.0351991047	-0.1543445555	-2.1859711007
H	-1.5957504704	-1.3989762945	-3.9684951837
H	-3.6702977299	-2.7155506395	-4.0723874835
H	-5.9088313280	-3.2141834828	-3.2098111960
H	-7.7299069170	-2.7918980537	-1.5927649026
H	-7.4476863744	-1.0402876919	0.1566747346
H	-5.3705255014	0.2439355441	0.3056131710
O	-2.4139939429	-3.3775528991	-0.6607758757
O	0.5634271103	-3.3969325596	-2.2065046248

2. XYZ coordinates (in Å) and total energy (in atomic units) of binaphthalene-cinchona squaramide (**1a**)optimized in acetyl acetone

E = -2223.43717985901

C	-3.0602976883	4.6409607100	0.4893974922
C	-3.3498701482	5.1408968032	-0.7519581092
C	-2.9898723706	3.2408961819	0.7122619448
C	-3.2158839799	2.3446830636	-0.3708050219
C	-3.5953377573	4.2559107130	-1.8262893291
C	-3.5342064873	2.8992213470	-1.6411721832
C	-2.6951387321	2.7130905824	1.9936705539
C	-2.6036457889	1.3619885966	2.1765709964
C	-2.7831541552	0.4539817490	1.1013951787
C	-3.0944441765	0.9300529073	-0.1608889226
C	-3.3316124339	-0.0116863711	-1.3025575765
C	-4.5663799189	-0.7450222687	-1.3412908317
C	-2.4047060706	-0.1704038023	-2.3164921739
C	-2.6684264491	-1.0900196552	-3.3670433552
C	-4.8046972338	-1.6620521723	-2.4012678834
C	-3.8198424765	-1.8182683506	-3.4088273468
C	-5.5782453184	-0.5872560653	-0.3560478213
C	-6.7443971425	-1.3075845730	-0.4136316834
C	-6.9685173913	-2.2275497968	-1.4605684422
C	-6.0173956729	-2.3952847877	-2.4327613266
C	-2.5089672633	-1.0096563101	1.3896854826
C	-1.1089525539	0.5943362486	-2.3856297266
C	-1.1347254840	-2.8714283534	-0.7468248868
C	0.2450102765	-2.9226523877	-1.3920321204
C	0.7245006101	-2.1062504957	-0.2735253402
C	3.5646635799	-2.1369521720	1.8980598146
C	3.4861275183	-2.8060433061	3.0948339736
C	4.5965915874	-3.5123067560	3.6038453139
C	4.8159950690	-2.1843346955	1.1960051892
C	5.8679753664	-2.9422560899	1.7936118683

C	7.1143649996	-3.0294244679	1.1309553526
C	7.3381082299	-2.4042972741	-0.0671104447
C	6.3011103522	-1.6450286291	-0.6613056551
C	5.0750197791	-1.5428110720	-0.0379409761
N	5.7505517094	-3.5949465858	2.9871495083
O	6.4320510744	-0.9841867139	-1.8366320871
C	7.6741325481	-1.0575404012	-2.5181290602
N	1.9649652645	-1.6685526842	0.0466743599
C	-0.5589167208	-1.9417517231	0.2548213090
N	-1.0745307670	-1.2783395104	1.2915584353
C	2.3190141902	-1.3827001090	1.4441728002
C	2.3652828599	0.1103261501	1.8566115006
C	3.3486309491	1.0550701796	1.1387006285
C	2.7669539250	2.4824105175	1.2161795170
C	1.6001647047	2.5364105328	0.2108137432
N	1.0147977064	0.7194181998	1.8599501895
C	0.6969762962	1.3200343988	0.5497625958
C	0.8062877354	3.8483986768	0.1845522282
C	1.6454572202	5.0807361580	-0.1393027811
C	1.0290279689	1.7930567722	2.8696305753
C	2.2348362892	2.7397417733	2.6359465548
H	-2.8766775811	5.3110088101	1.3249222955
H	-3.3968886939	6.2130382399	-0.9141269279
H	-3.8361060933	4.6546233057	-2.8067543253
H	-3.7272742769	2.2310245350	-2.4734204836
H	-2.5431000034	3.3964102594	2.8248006411
H	-2.3699250845	0.9635627802	3.1606560460
H	-3.0279331947	-1.6779519599	0.7020885295
H	-2.8426921668	-1.2513727654	2.4038881569
H	-0.4441468563	-0.5959783817	1.7421521623
H	2.6906098929	-2.0814974668	-0.5256150525
H	1.5040785763	-1.7912173012	2.0493841395
H	2.5625457186	-2.8066690280	3.6656913852
H	4.5125306786	-4.0350501454	4.5541066264
H	4.3269229700	-0.9316585689	-0.5254470286
H	8.3062195515	-2.4956862949	-0.5447265092
H	7.8927950867	-3.6128338404	1.6113380367
H	8.4874394877	-0.6294062426	-1.9213950379
H	7.9196048930	-2.0877173984	-2.7999595107
H	7.5497356107	-0.4639676806	-3.4240356193
H	2.6569674110	0.0583366283	2.9124943033
H	4.3426359746	0.9920616156	1.5921534342
H	3.4555224477	0.7842078324	0.0828301862
H	3.5392686832	3.2130648972	0.9562305220
H	2.0212252740	2.3915300114	-0.7944879370
H	0.0089187142	3.7467096252	-0.5638657495
H	0.2874457966	3.9975430494	1.1407251953

H	1.0145369901	5.9699591441	-0.2397913945
H	2.1908322329	4.9528552039	-1.0821776954
H	2.3839645716	5.2895696127	0.6430713147
H	-0.3562065789	1.6173682236	0.5766371779
H	0.7939981309	0.5423587526	-0.2087723054
H	1.0623517129	1.3383710625	3.8645571983
H	0.0786411444	2.3287510472	2.7876666766
H	1.9382628012	3.7862442658	2.7602521244
H	3.0299454916	2.5515510831	3.3667370431
H	-1.0529528930	1.1684811814	-3.3175987920
H	-0.9915923743	1.2946776548	-1.5600397928
H	-0.2536829179	-0.0918577491	-2.3809217929
H	-1.9173814267	-1.2186752390	-4.1422473181
H	-3.9952622324	-2.5276465512	-4.2126893713
H	-6.1775250744	-3.0982806052	-3.2457642512
H	-7.8922807463	-2.7964607757	-1.4940440417
H	-7.5024919222	-1.1670082274	0.3506975576
H	-5.4253180610	0.1200349515	0.4519022653
O	-2.2146451084	-3.4061003325	-0.8968764231
O	0.7622036720	-3.4164558074	-2.3784613253

3. XYZ coordinates (in Å) and total energy (in atomic units) of binaphthalene-cinchona thiosquaramide (**1b**) optimized in gas phase

E = -2869.33005160762

C	-2.6739769775	4.8317447635	-0.2778597016
C	-2.8014022996	5.0862058293	-1.6170774298
C	-2.7265480126	3.5027029232	0.2178045208
C	-2.9117054700	2.4211628563	-0.6889800935
C	-3.0081055808	4.0176988018	-2.5204140913
C	-3.0693362962	2.7248625686	-2.0696963884
C	-2.5941780382	3.2270896860	1.6004728639
C	-2.6113221730	1.9354193075	2.0479719265
C	-2.7506495493	0.8427344336	1.1550770834
C	-2.9130966063	1.0716267784	-0.2018872256
C	-3.1409999618	-0.0602091624	-1.1568990827
C	-4.4240783303	-0.7068611765	-1.1389401411
C	-2.1756885292	-0.4712868235	-2.0591398919
C	-2.4458140315	-1.5636286159	-2.9256403186
C	-4.6687886892	-1.7983938836	-2.0165559307
C	-3.6440272502	-2.2126911544	-2.9041466406
C	-5.4771915478	-0.2936690506	-0.2783544402
C	-6.6863489301	-0.9415779377	-0.2765663521
C	-6.9158667554	-2.0384527876	-1.1353886730
C	-5.9263538210	-2.4518057778	-1.9880681482
C	-2.6040738938	-0.5456031264	1.7469693604

C	-0.8266928349	0.1856637898	-2.2048729689
C	-1.1602682102	-2.9034487731	0.1509557882
C	0.1953670274	-2.9937474082	-0.4670082113
C	0.6625488418	-2.0522134786	0.5114335581
C	3.6970511017	-1.6341816279	2.4764576006
C	3.8293254549	-1.9503655845	3.8089278282
C	5.0487351555	-2.4455458576	4.3112836807
C	4.8352582949	-1.8282883497	1.6317923432
C	6.0070242313	-2.3625328480	2.2429155368
C	7.1559706873	-2.6132787627	1.4406587019
C	7.1529403480	-2.3647243130	0.1013640817
C	5.9902284449	-1.8297081368	-0.5136481938
C	4.8712472924	-1.5499013225	0.2344330227
N	6.1064606330	-2.6555278159	3.5657563253
O	6.0882710661	-1.6295570946	-1.8446648668
C	4.9261993027	-1.2196248325	-2.5393352810
N	1.9225548899	-1.6321927428	0.7455555738
C	-0.6464093392	-1.7896725916	0.9616673575
N	-1.1831757945	-0.9070530760	1.7955488825
C	2.3527455692	-1.0712970448	2.0295699259
C	2.3535862346	0.4733158855	2.1528800930
C	3.3648418058	1.2755729296	1.3064417507
C	2.7682496578	2.6770382051	1.0650410867
C	1.6409121563	2.5021891582	0.0300200179
N	1.0043099596	1.0570692018	1.9998145177
C	0.7273447311	1.3790565406	0.5849356654
C	0.8417128527	3.7661291808	-0.3073482781
C	1.6856102693	4.9190753360	-0.8430286458
C	0.9819158400	2.3140143334	2.7705105721
C	2.1849790109	3.2129364888	2.3830539642
H	-2.5250968462	5.6445887974	0.4284037012
H	-2.7540334032	6.1055094570	-1.9880470613
H	-3.1248732801	4.2254117477	-3.5796833810
H	-3.2352271780	1.9122644052	-2.7686577431
H	-2.4780123544	4.0535035469	2.2972266666
H	-2.5007301810	1.7294466833	3.1102482025
H	-3.1327807113	-1.3096771757	1.1762037555
H	-3.0002664754	-0.5578381680	2.7673610751
H	-0.5299108496	-0.1853324277	2.1347779822
H	2.5901779663	-2.2280107545	0.2671992772
H	1.6180423435	-1.4017075192	2.7738157441
H	2.9886636378	-1.8300322821	4.4868838892
H	5.1388565448	-2.6868442393	5.3685617967
H	4.0185050493	-1.0978954927	-0.2487555056
H	8.0178354719	-2.5665626478	-0.5213122116
H	8.0284467591	-3.0200319664	1.9404754438
H	4.1015573128	-1.9283940806	-2.3904222439

H	4.6076727074	-0.2164204172	-2.2266114975
H	5.2012529371	-1.1957060372	-3.5937234013
H	2.6122905732	0.6225916033	3.2086331858
H	4.3318533807	1.3241834053	1.8170920617
H	3.5380978457	0.7990075566	0.3368012407
H	3.5429467841	3.3505554847	0.6864226169
H	2.1030748261	2.1502536126	-0.9032661003
H	0.0825174122	3.4961872570	-1.0533603339
H	0.2737225516	4.0992482196	0.5710393322
H	1.0483070779	5.7506753789	-1.1600733790
H	2.2800309889	4.6035913074	-1.7087103549
H	2.3791528749	5.3018459972	-0.0858819302
H	-0.3230902743	1.6718658426	0.5205688803
H	0.8459452909	0.4645802554	0.0069335119
H	0.9898265894	2.0695916387	3.8380284089
H	0.0300981436	2.8072877464	2.5540346132
H	1.8705393159	4.2560541173	2.2762287270
H	2.9568799590	3.1930713946	3.1610793809
H	-0.6508874374	0.4488518600	-3.2538800672
H	-0.7367219031	1.0969790991	-1.6151028919
H	-0.0265552382	-0.5055518473	-1.9130764746
H	-1.6594215388	-1.8950918664	-3.5981190803
H	-3.8231196982	-3.0613867994	-3.5579558030
H	-6.0882404573	-3.2929600403	-2.6569161157
H	-7.8745901571	-2.5477015422	-1.1191532807
H	-7.4755918491	-0.6060823717	0.3898128707
H	-5.3220271140	0.5520666620	0.3830399396
S	-2.5451499556	-3.7571389059	0.0857975065
S	0.9383953356	-3.7588015382	-1.7139527685

4. XYZ coordinates (in Å) and total energy (in atomic units) of binaphthalene-cinchona thiosquaramide (**1b**) optimized in acetyl acetone

E = -2869.38400140379

C	-2.8532260812	4.7358565010	-0.0822554987
C	-3.1732766802	5.0615436253	-1.3733200008
C	-2.8188666882	3.3808587548	0.3387554756
C	-3.1220350723	2.3487160135	-0.5937969092
C	-3.4855642613	4.0412383484	-2.3002688592
C	-3.4666499569	2.7240238111	-1.9211904101
C	-2.4811297340	3.0302468212	1.6694704695
C	-2.3999894431	1.7163476964	2.0366408659
C	-2.6589515203	0.6741708983	1.1100238930
C	-3.0465702763	0.9761046723	-0.1828269967
C	-3.4496224375	-0.0980874614	-1.1465969837
C	-4.7806808104	-0.6281482093	-1.0423355300

C	-2.6019857741	-0.5468689475	-2.1400103641
C	-3.0545340723	-1.5448119537	-3.0448351144
C	-5.2120324195	-1.6237509048	-1.9612456440
C	-4.3113572205	-2.0673541588	-2.9635029218
C	-5.7019197929	-0.1855761222	-0.0552724744
C	-6.9678836098	-0.7085634807	0.0197727560
C	-7.3874959145	-1.7033679607	-0.8894320687
C	-6.5254848238	-2.1471048605	-1.8583379784
C	-2.3941164031	-0.7437129022	1.5715011471
C	-1.2100212230	-0.0080143570	-2.3315293588
C	-0.8483728634	-3.0566983456	-0.0965865168
C	0.5017684018	-3.1359975549	-0.6808802919
C	0.9379597694	-2.1419709070	0.2592969536
C	3.6733064018	-1.6754057381	2.5136642161
C	3.5442132366	-2.0782114527	3.8226710043
C	4.6301775405	-2.6577276996	4.5055661902
C	4.9455331516	-1.8631812678	1.8866783404
C	5.9687752363	-2.4783100532	2.6626597511
C	7.2424874601	-2.7039607202	2.0719381276
C	7.4986139903	-2.3454639529	0.7824390251
C	6.4855676097	-1.7249550651	0.0055273544
C	5.2447068157	-1.4869718827	0.5479535253
N	5.8063332952	-2.8663922379	3.9577583622
O	6.8484168479	-1.4020885923	-1.2563022958
C	5.8660191620	-0.8065317626	-2.0899128646
N	2.1446359399	-1.6717299429	0.5615579738
C	-0.4024010314	-1.9058572665	0.6875782356
N	-0.9550557472	-1.0038233717	1.4678831310
C	2.4470970655	-1.0470039530	1.8578588736
C	2.4759985597	0.4984461665	1.8991708040
C	3.4711456979	1.2679814889	1.0110589774
C	2.8884482494	2.6790476462	0.7798371547
C	1.7520078544	2.5148691547	-0.2475945630
N	1.1209656555	1.0745012714	1.7256307861
C	0.8415790730	1.3886182868	0.3092518917
C	0.9555221889	3.7856314852	-0.5696548080
C	1.8049349108	4.9440615056	-1.0837399384
C	1.1012617586	2.3370613361	2.4884732954
C	2.3164535320	3.2189298545	2.1013461878
H	-2.6155137378	5.5124876535	0.6395725963
H	-3.1908080937	6.0999899746	-1.6883806350
H	-3.7442727044	4.3035228738	-3.3213089655
H	-3.7092086333	1.9498975366	-2.6410750405
H	-2.2792984645	3.8193072640	2.3887574516
H	-2.1192963658	1.4545150129	3.0535844425
H	-2.9266515749	-1.4863075160	0.9778336134
H	-2.6939034041	-0.8657901399	2.6164533366

H	-0.3212845802	-0.2546031205	1.8079664147
H	2.9009016424	-2.1317298646	0.0658898219
H	1.6092467490	-1.3078958848	2.5101519687
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H	8.4674371178	-2.5185028025	0.3265902256
H	8.0006912109	-3.1742304374	2.6890044681
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H	5.5409109836	0.1619780759	-1.6918257158
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H	2.7387756405	0.6960741212	2.9448968849
H	4.4599604022	1.2997098562	1.4781061877
H	3.5849882358	0.7829992896	0.0350306193
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H	2.2036381913	2.1694107495	-1.1882860791
H	0.2005090733	3.5297725445	-1.3245972733
H	0.3843735702	4.1107087082	0.3101055138
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H	-2.3686205312	-1.9002840447	-3.8092259630
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H	-6.8367929795	-2.9112509622	-2.5655137654
H	-8.3902777673	-2.1129927644	-0.8202482338
H	-7.6540142819	-0.3527775479	0.7820635481
H	-5.3976137929	0.5818264962	0.6479561628
S	-2.2162448042	-3.9763080874	-0.1836365311
S	1.2636356858	-4.0003527330	-1.8746862553