

SUPPORTING INFORMATION

Origin of Enantioselectivity in Palladium-Catalyzed Asymmetric Allylic Alkylation Reactions Using Chiral N,N-Ligands with Different Rigidity and Flexibility

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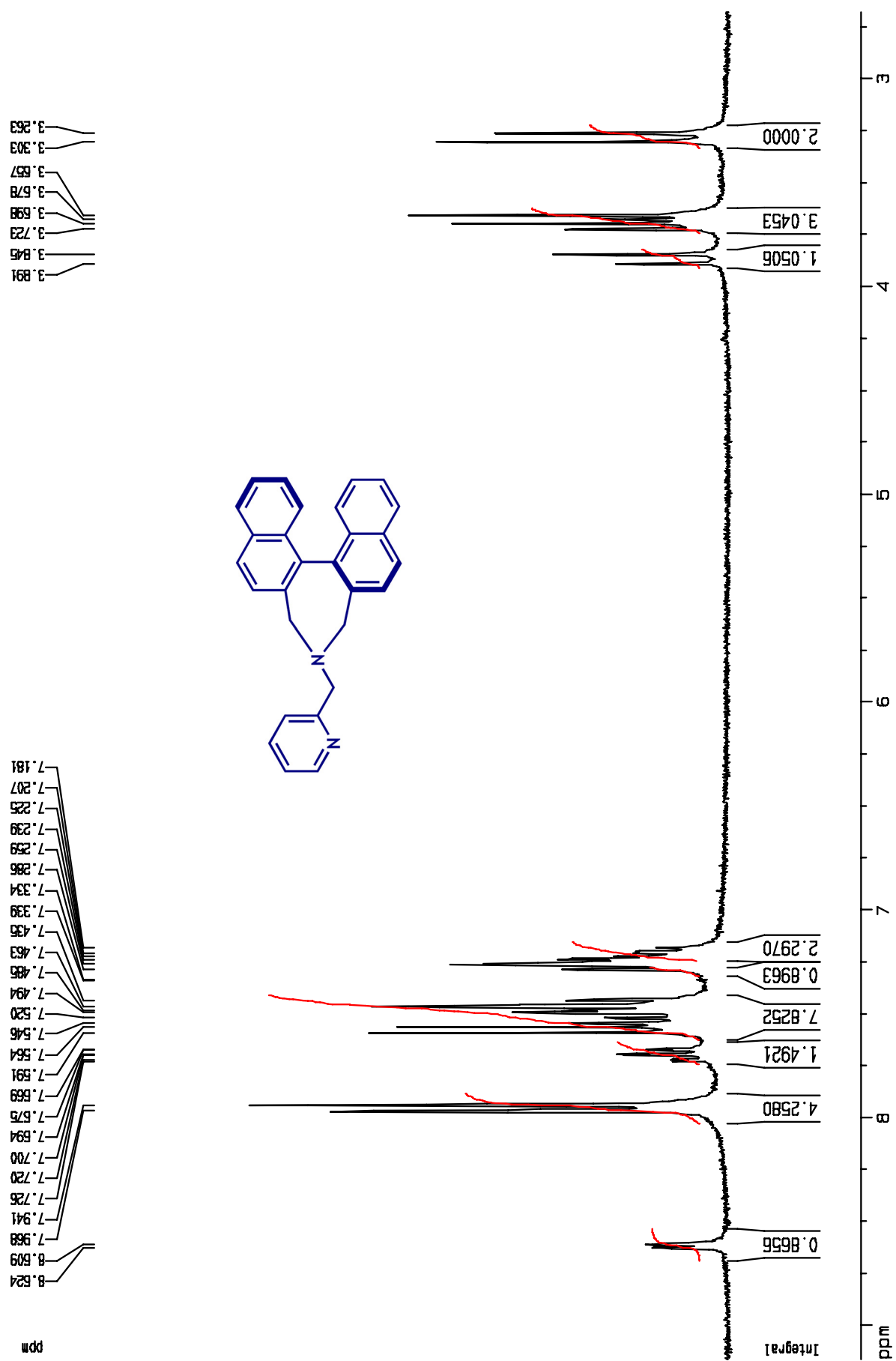
Table 1 DFT data	S2
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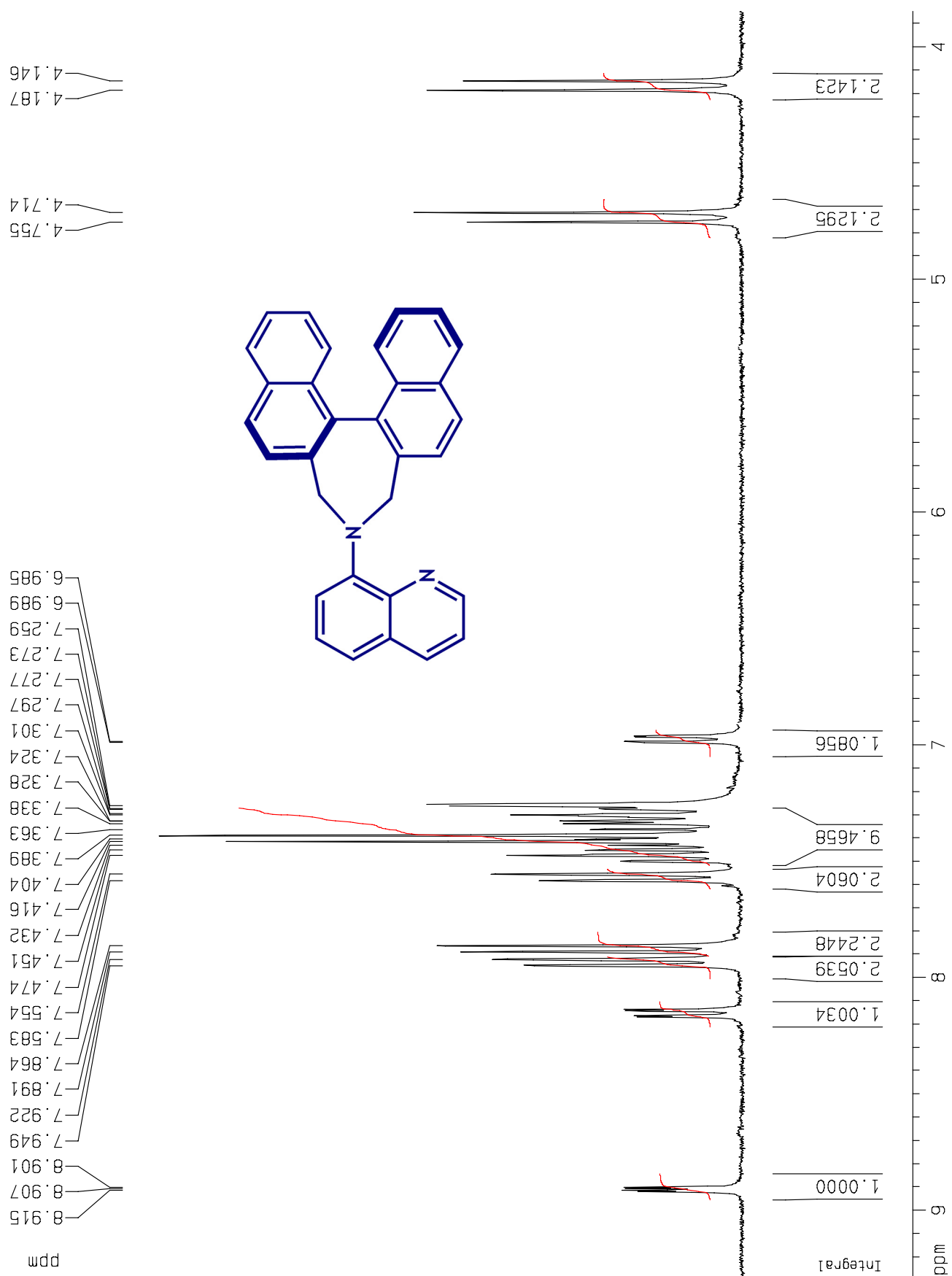
Table 1. Computed (DFT)distances (Å), angles (°) absolute (hartree) and relative energies (kcal and kj mol⁻¹) of 9 - 11 complexes

Complex	Conf	Pd-C1	Pd-C2	Pd-C3	Pd-N1	Pd-N2	N1-C4	N1-C5	N1-C6	N1-Pd-N2	N1-Pd-C1	N2-Pd-C3	C1-Pd-C3
9	ENSS	2.2476	2.2041	2.2203	2.2245	2.1358	1.5221	1.5299	1.5072	79.21	108.08	105.60	66.69
9	EXSS	2.2717	2.2038	2.2035	2.2265	2.1382	1.5206	1.5302	1.5081	78.58	108.06	105.40	66.44
9	EXAS	2.2412	2.1825	2.2390	2.2157	2.1320	1.5221	1.5301	1.5085	79.33	106.51	105.24	68.65
9	ENAS	2.2523	2.1802	2.2184	2.2218	2.1485	1.5232	1.5313	1.5044	79.30	107.26	106.17	67.61
9	EXSA	2.2787	2.1851	2.1914	2.2291	2.1359	1.5202	1.5293	1.5092	78.32	108.47	104.97	67.43
9	EXAA	2.2355	2.1563	2.2244	2.2131	2.1250	1.5250	1.5308	1.5089	79.49	104.86	105.33	70.21
10SS	ENSS	2.2710	2.2026	2.2283	2.2569	2.1300	1.5525	1.5318	1.5033	79.97	110.12	103.59	66.19
10SS	EXSS	2.2986	2.2142	2.2068	2.2625	2.1287	1.5524	1.5325	1.5035	79.67	109.88	103.40	66.00
10SS	EXAS	2.2314	2.1781	2.2662	2.2413	2.1222	1.5441	1.5303	1.5039	80.36	106.68	104.44	67.86
10SS	ENSA	2.2733	2.1766	2.2888	2.2827	2.1419	1.5534	1.5417	1.5026	79.54	110.89	103.22	66.24
10SS	EXAA	2.2532	2.1584	2.2251	2.2457	2.1168	1.5447	1.5308	1.5049	80.15	107.06	102.77	69.75
11SS	ENSS	2.2904	2.2073	2.2230	2.2548	2.1083	1.5712	1.5599	1.4776	80.64	108.78	104.50	65.95
11SS	EXSS	2.2917	2.2156	2.2131	2.2593	2.1061	1.5708	1.5626	1.4776	80.63	108.30	104.19	65.98
11SS	EXAS	2.2511	2.1798	2.2600	2.2501	2.0998	1.5827	1.5490	1.4766	80.85	106.40	104.65	67.75
11SS	ENSA	2.2999	2.1850	2.1914	2.2502	2.1099	1.5773	1.5563	1.4762	80.74	109.34	103.35	67.13
11SS	EXAA	2.2873	2.1609	2.2096	2.2470	2.0988	1.5809	1.5525	1.4761	80.94	106.70	103.01	69.39
Complex	Conf	E(au) B3LYP/SDD		E(kcal)	E(kJ)								
9	ENSS	-1589.46464		0	0								
9	EXSS	-1589.46252		1.33	5.56								
9	EXAS	-1589.45646		5.13	21.46								
9	ENSA	-1589.45440		6.43	26.90								
9	EXSA	-1589.45313		7.22	30.22								
9	EXAA	-1589.44127		14.66	61.34								
10SS	ENSS	-1284.65125		0	0								
10SS	EXSS	-1284.65005		0.75	3.15								

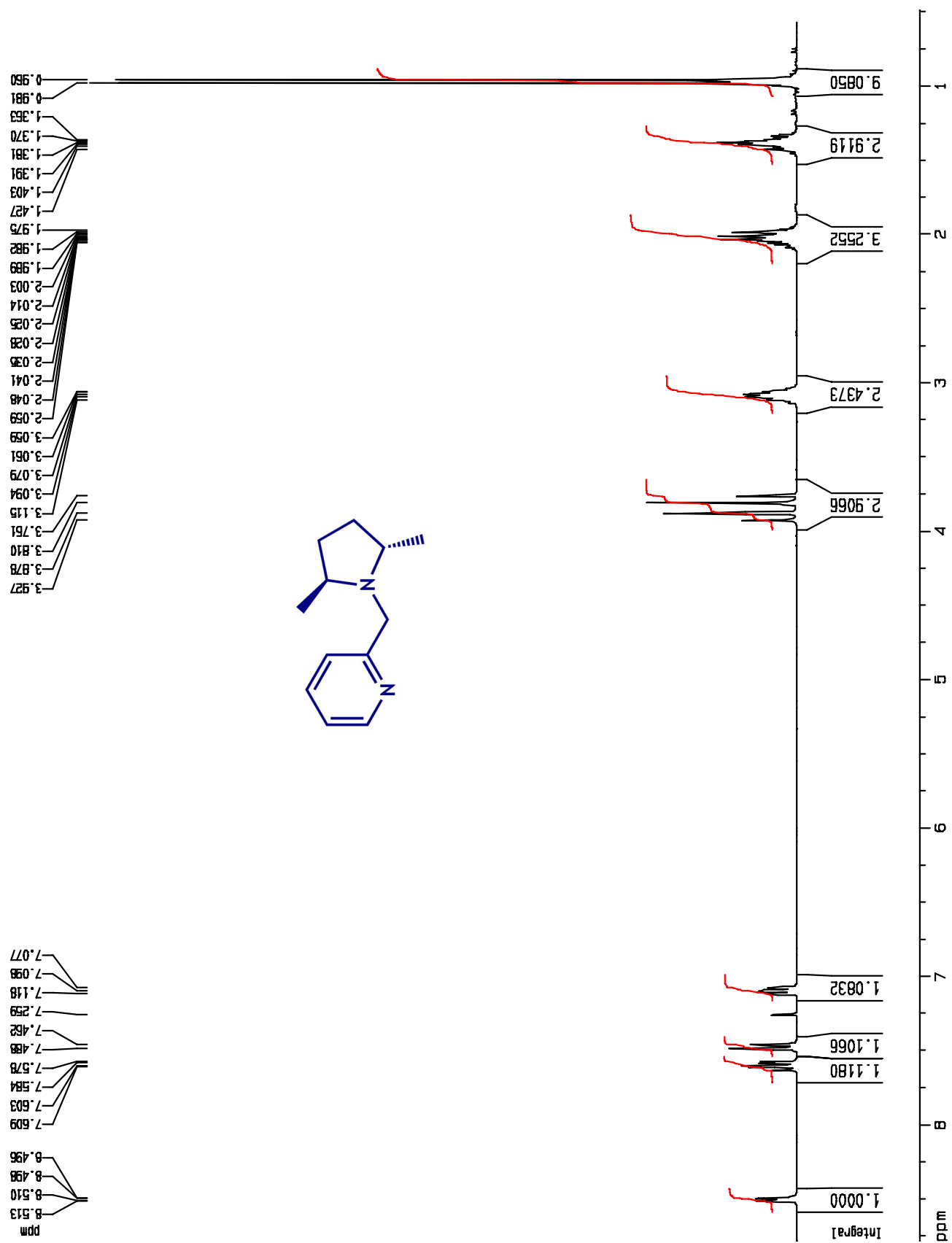
Complex	Conf	E(au) B3LYP/SDD	E(kcal)	E(kJ)
10SS	EXAS	-1284.64517	3.82	15.96
10SS	ENSA	-1284.63210	12.02	50.28
10SS	EXAA	-1284.63001	13.33	55.77
11SS	ENSS	-1398.95982	0	0
11SS	EXSS	-1398.95909	0.46	1.91
11SS	EXAS	-1398.95257	4.55	19.03
11SS	ENSA	-1398.95072	5.15	21.53
11SS	EXAA	-1398.93579	15.08	63.09

SS = carbon ligand configuration ; EN=endo; EX=exo, AA=anti-anti, SS=syn-syn, AS=anti-syn, SA=syn-anti

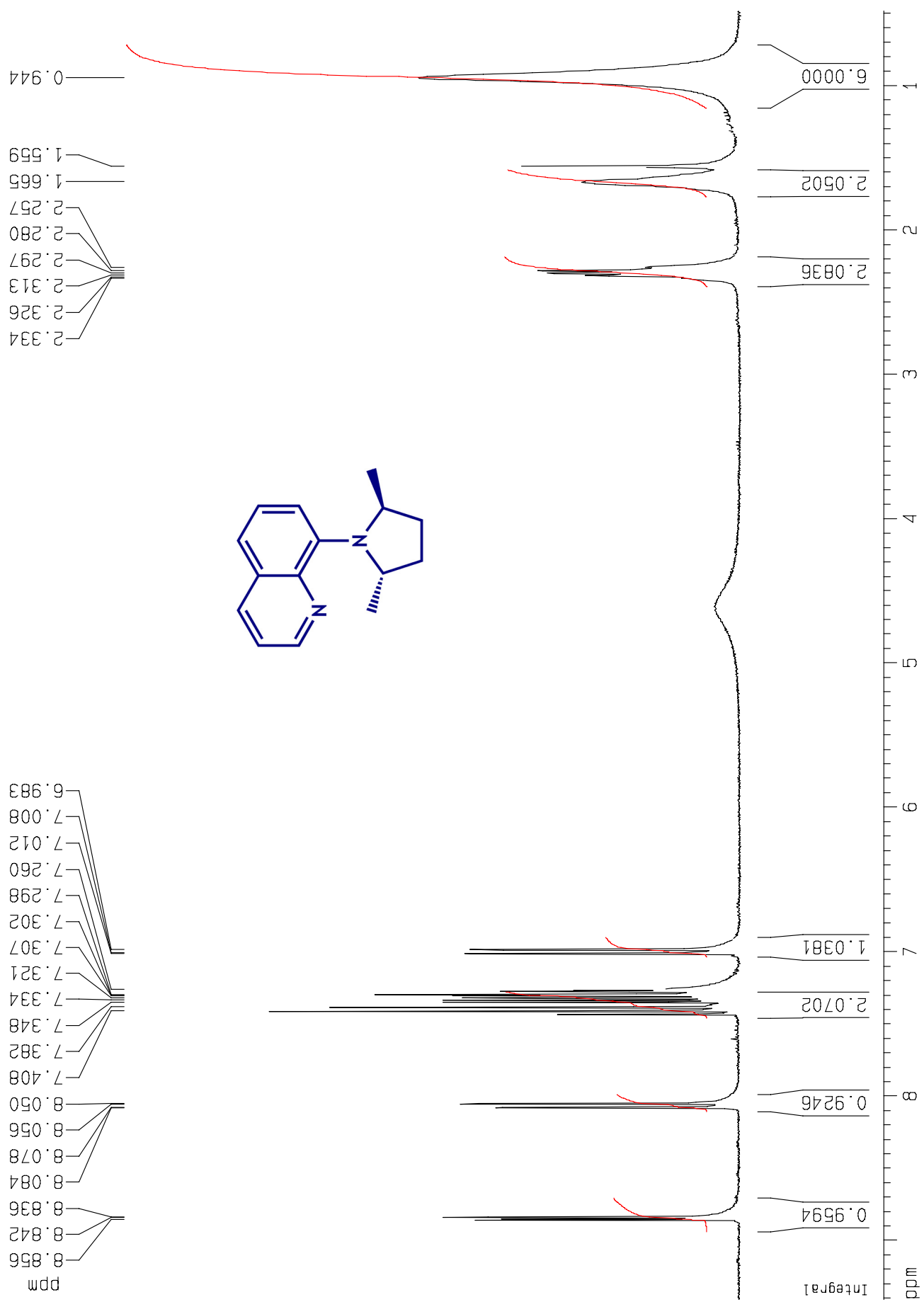


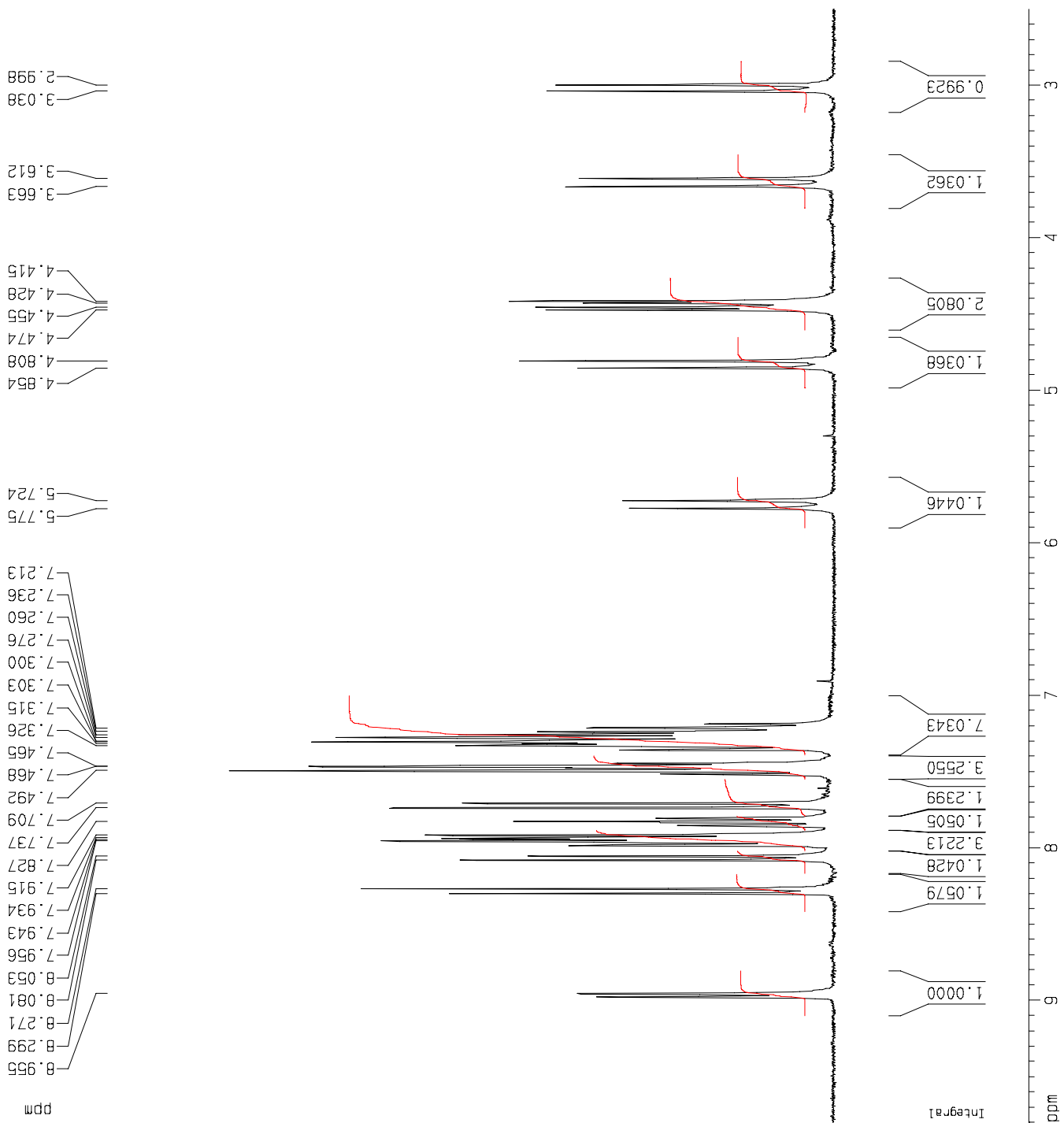


¹H NMR (300 MHz, CDCl₃) Spectrum of (S_a)-2

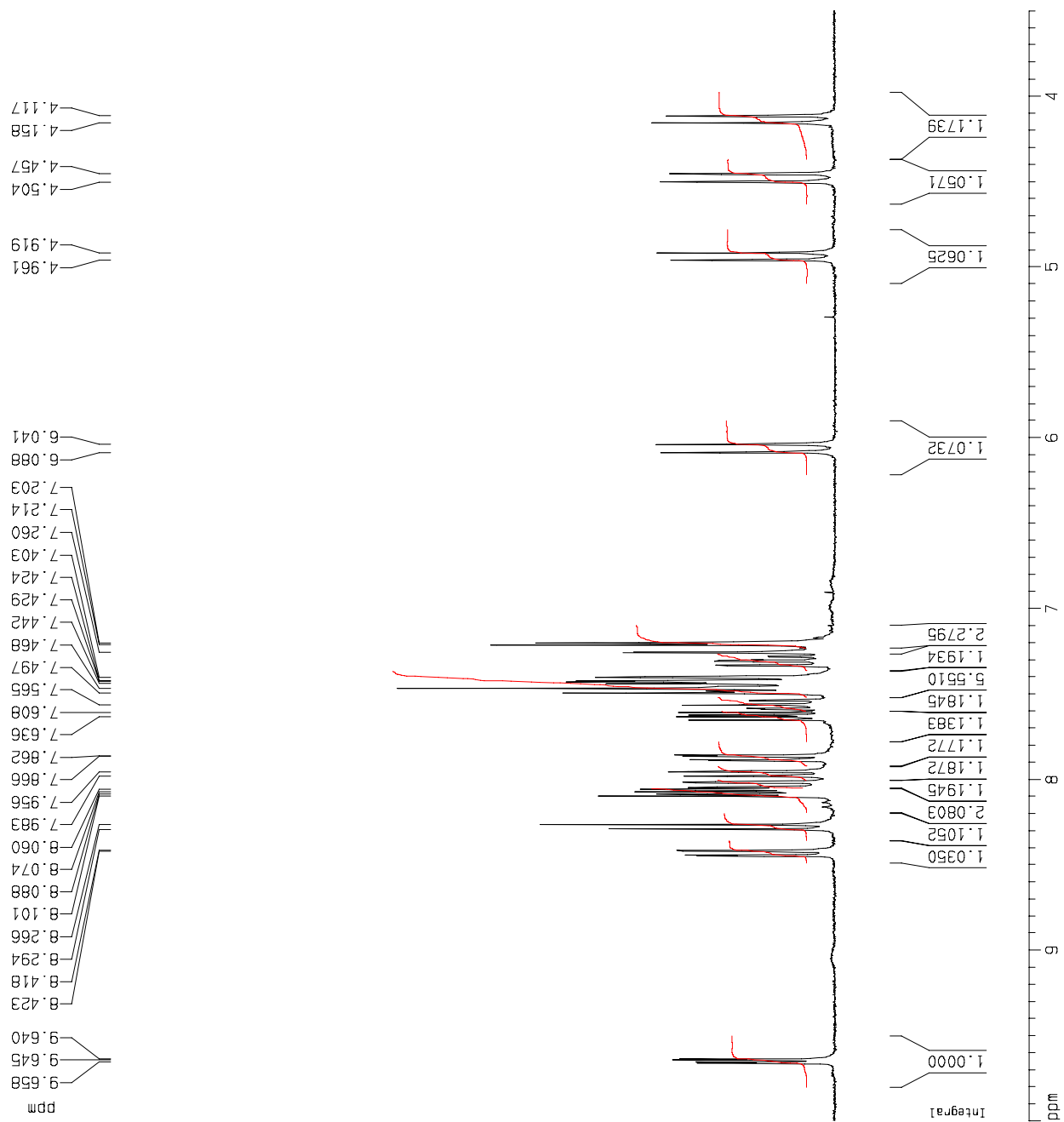


^1H NMR (300 MHz, CDCl_3) Spectrum of (S,S)-3

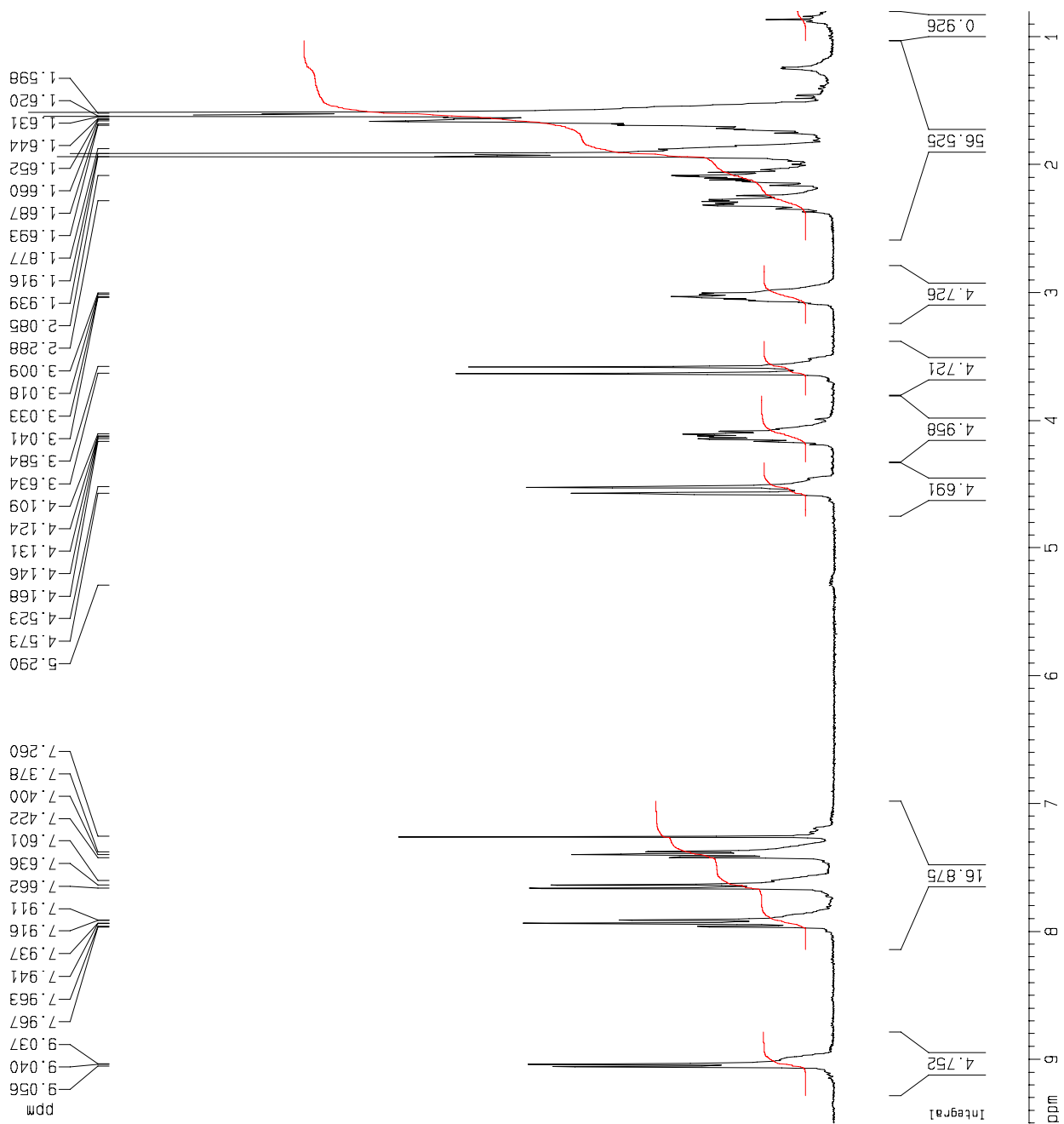
^1H NMR (300 MHz, CDCl_3) Spectrum of (S,S)-4



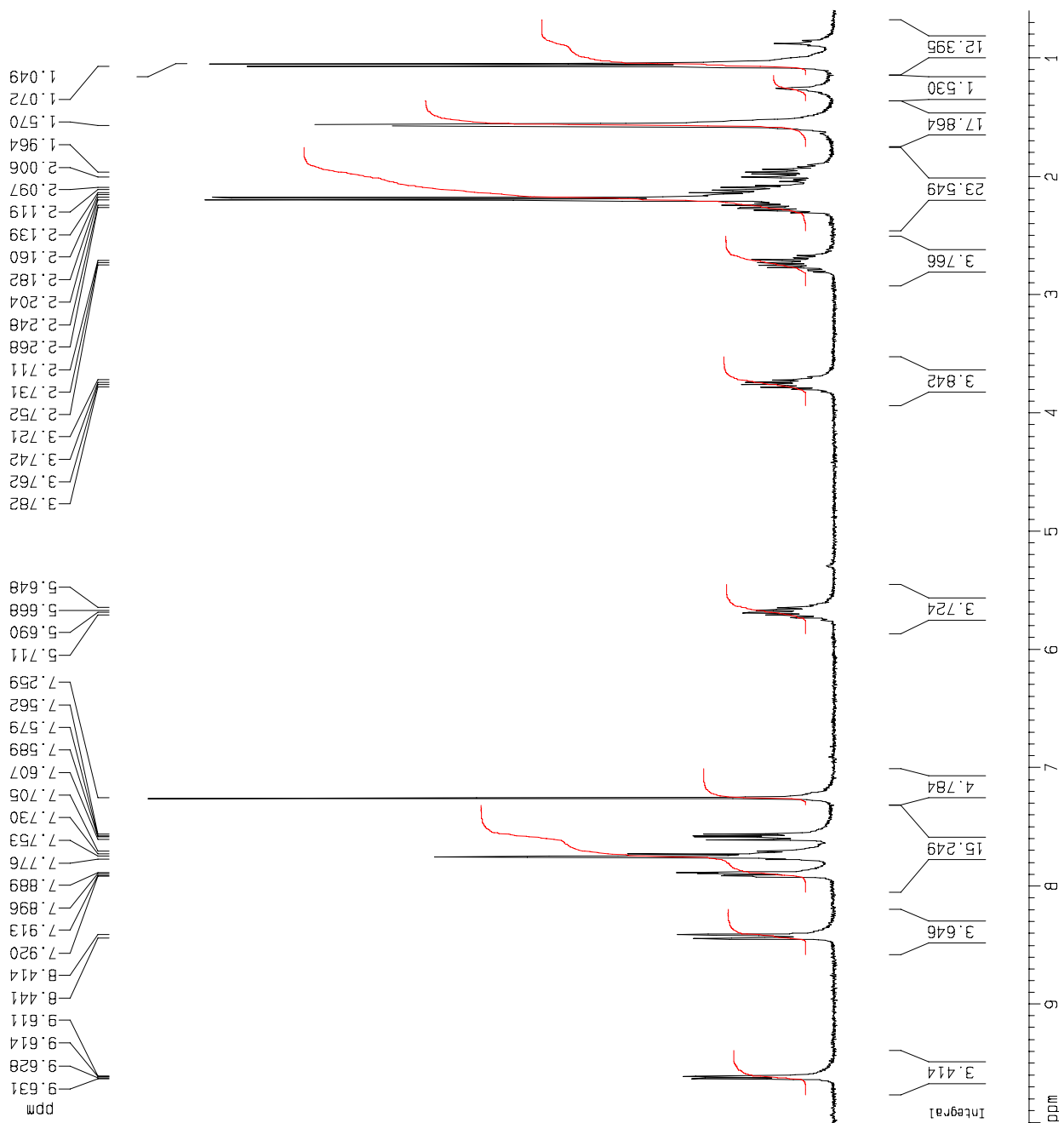
^1H NMR (300 MHz, CDCl_3) Spectrum of $[\text{Pd}(\text{S}_a\text{-1})\text{Cl}_2]$ (**5**).



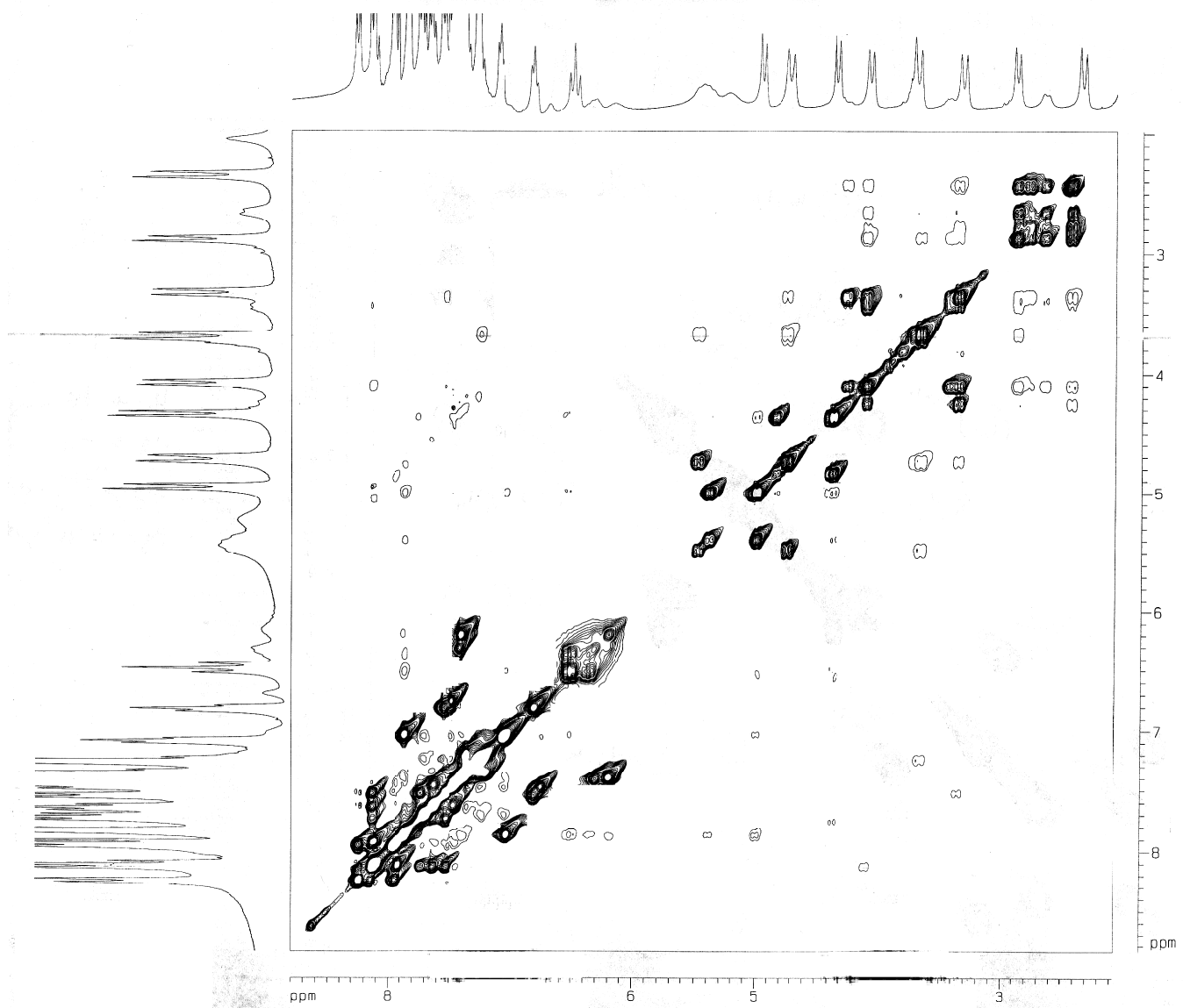
^1H NMR (300 MHz, CDCl_3) Spectrum of $[\text{Pd}(\text{S}_a\text{-2})\text{Cl}_2]$ (6)



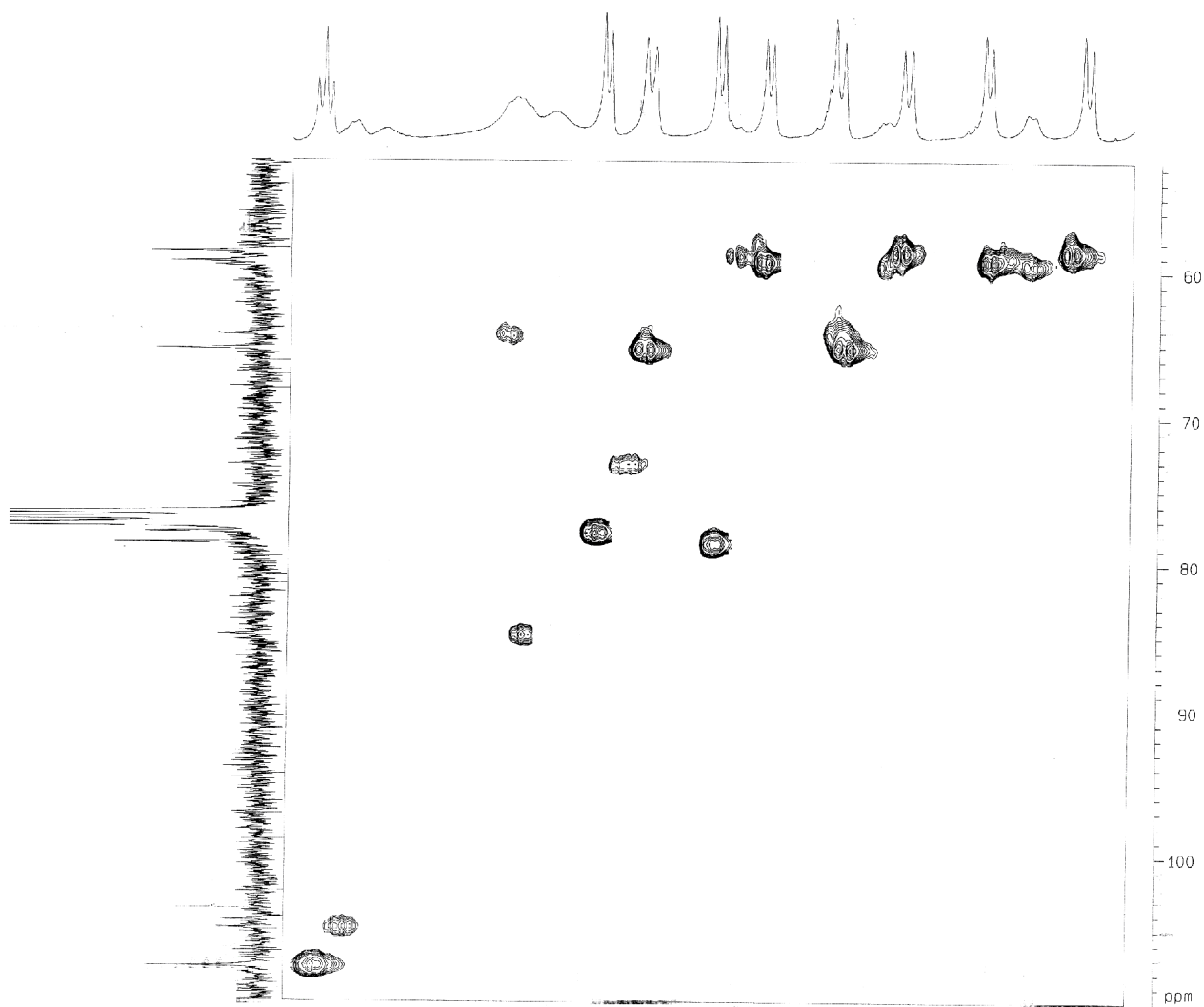
^1H NMR (300 MHz, CDCl_3) Spectrum of $[\text{Pd}(\text{S,S-3})\text{Cl}_2]$ (7)



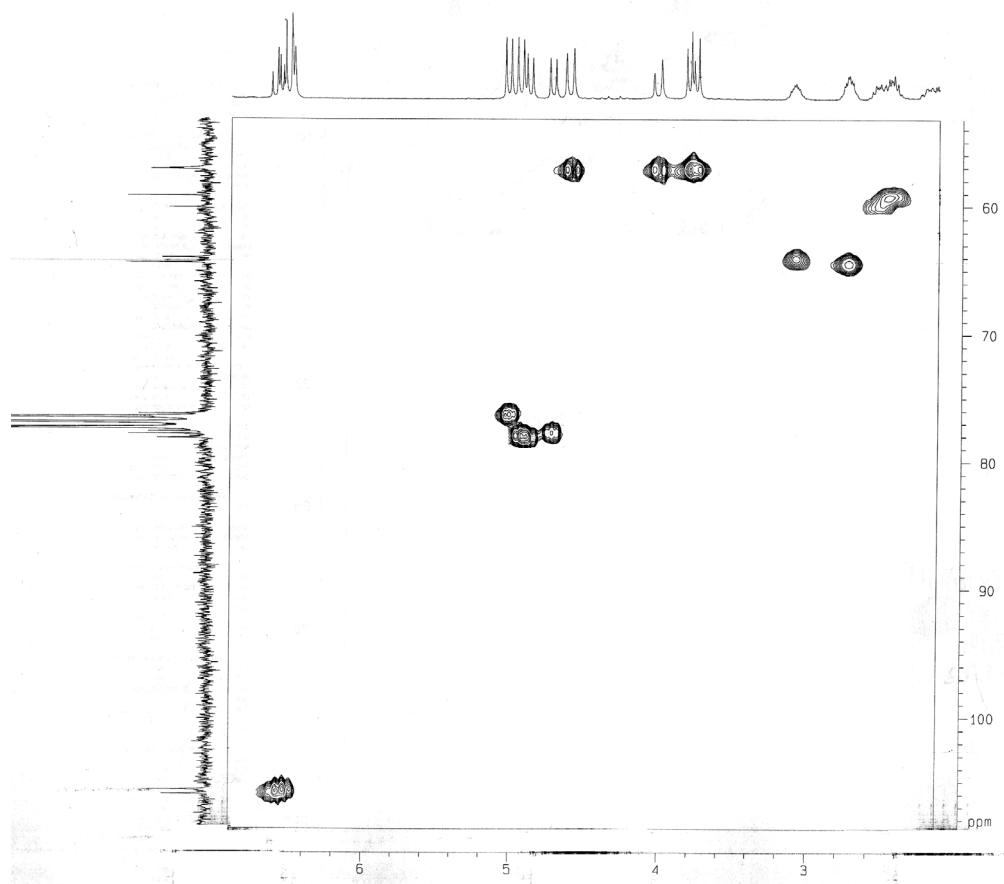
^1H NMR (300 MHz, CDCl_3) Spectrum of $[\text{Pd}(\text{S,S-4})\text{Cl}_2]$ (**8**)



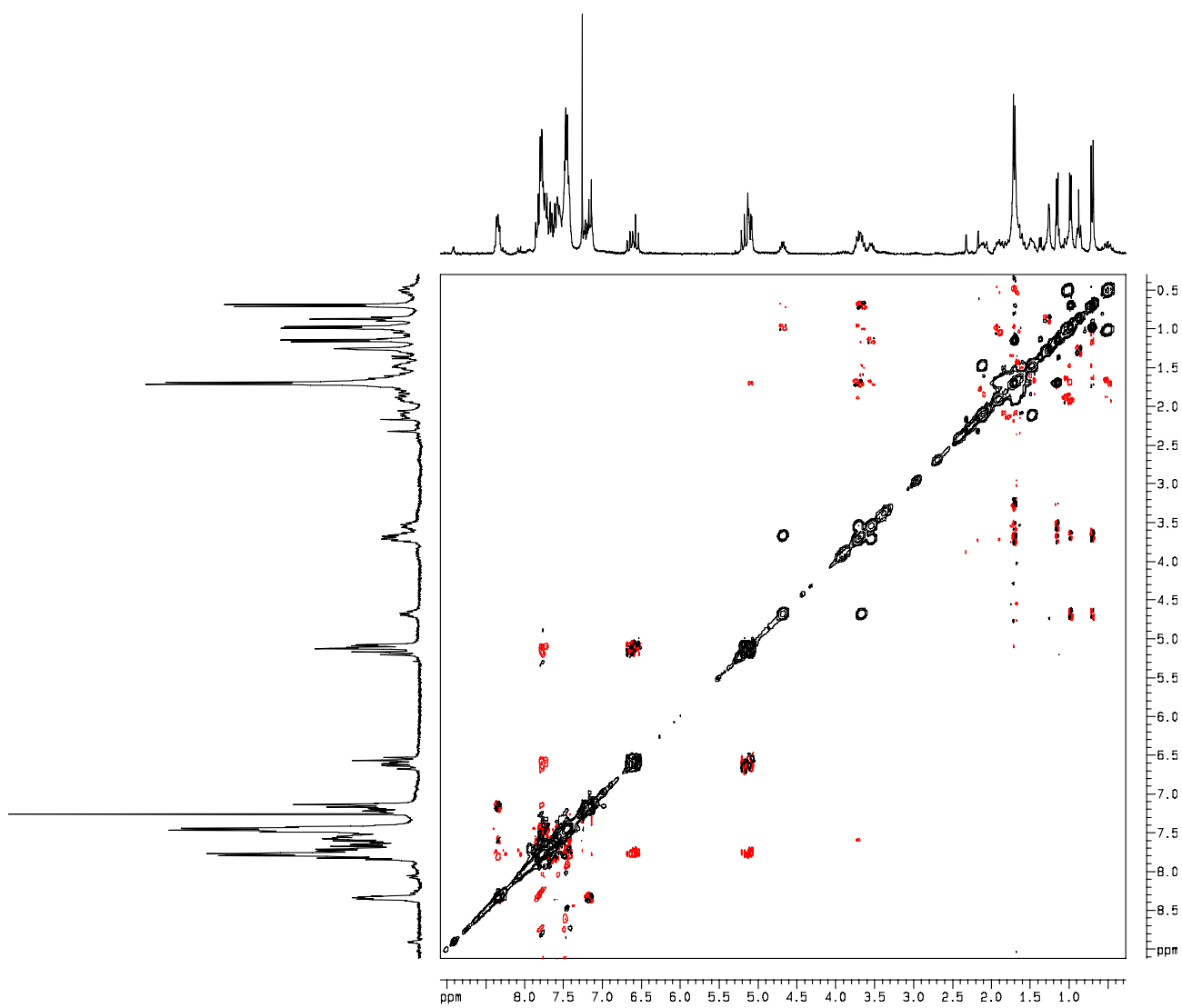
NOESY NMR (300 MHz, CDCl_3) Spectrum of $[\text{Pd}(\eta^3\text{-PhCHCHCHPh})(\text{Sa-1})]\text{CF}_3\text{SO}_3$ (**9**).



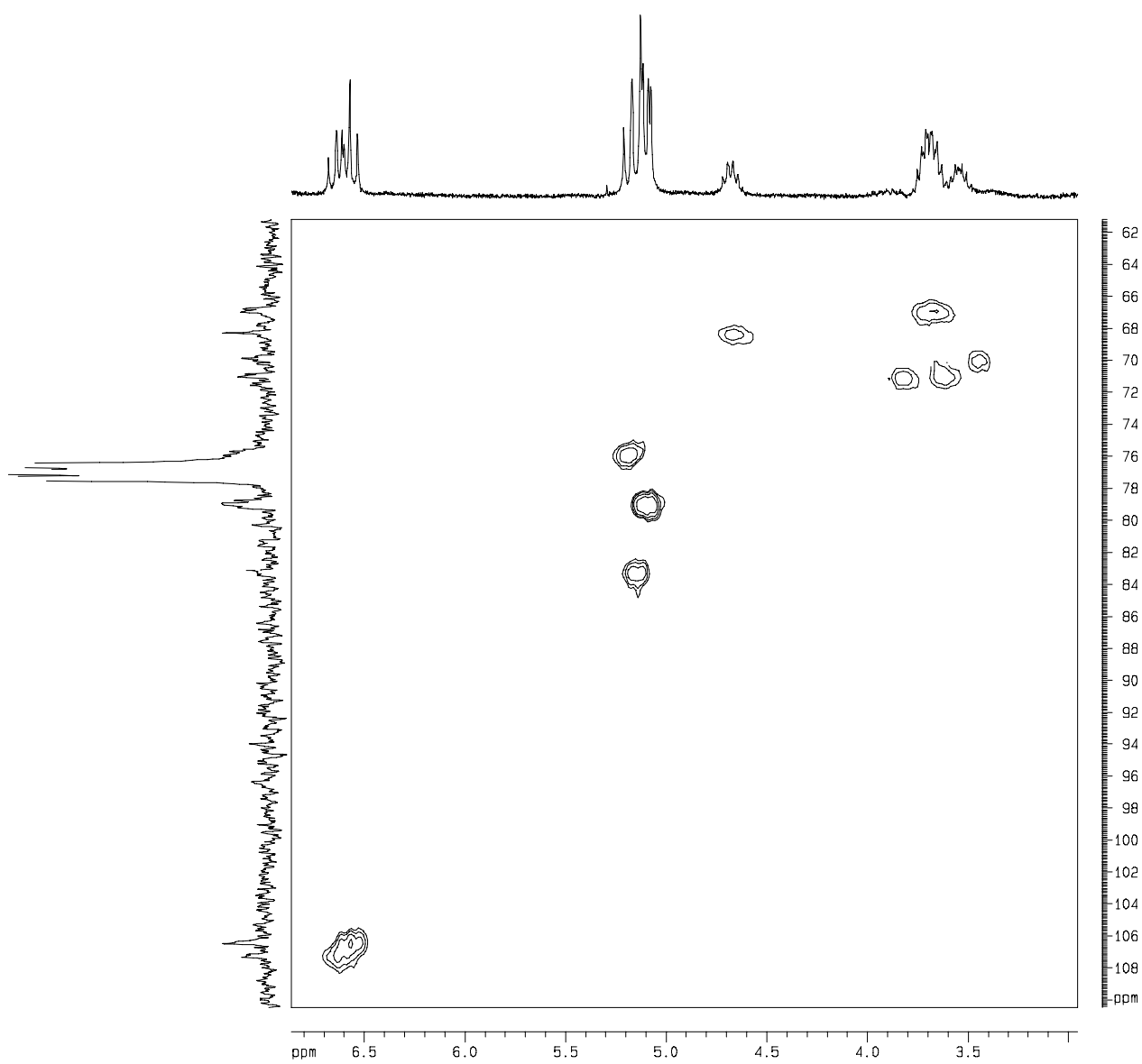
HMQC NMR (300 MHz, CDCl_3) Allylic Section Spectrum of $[\text{Pd}(\eta^3\text{-PhCHCHCHPh})(\text{S}_a\text{-1})]\text{CF}_3\text{SO}_3$ (**9**)



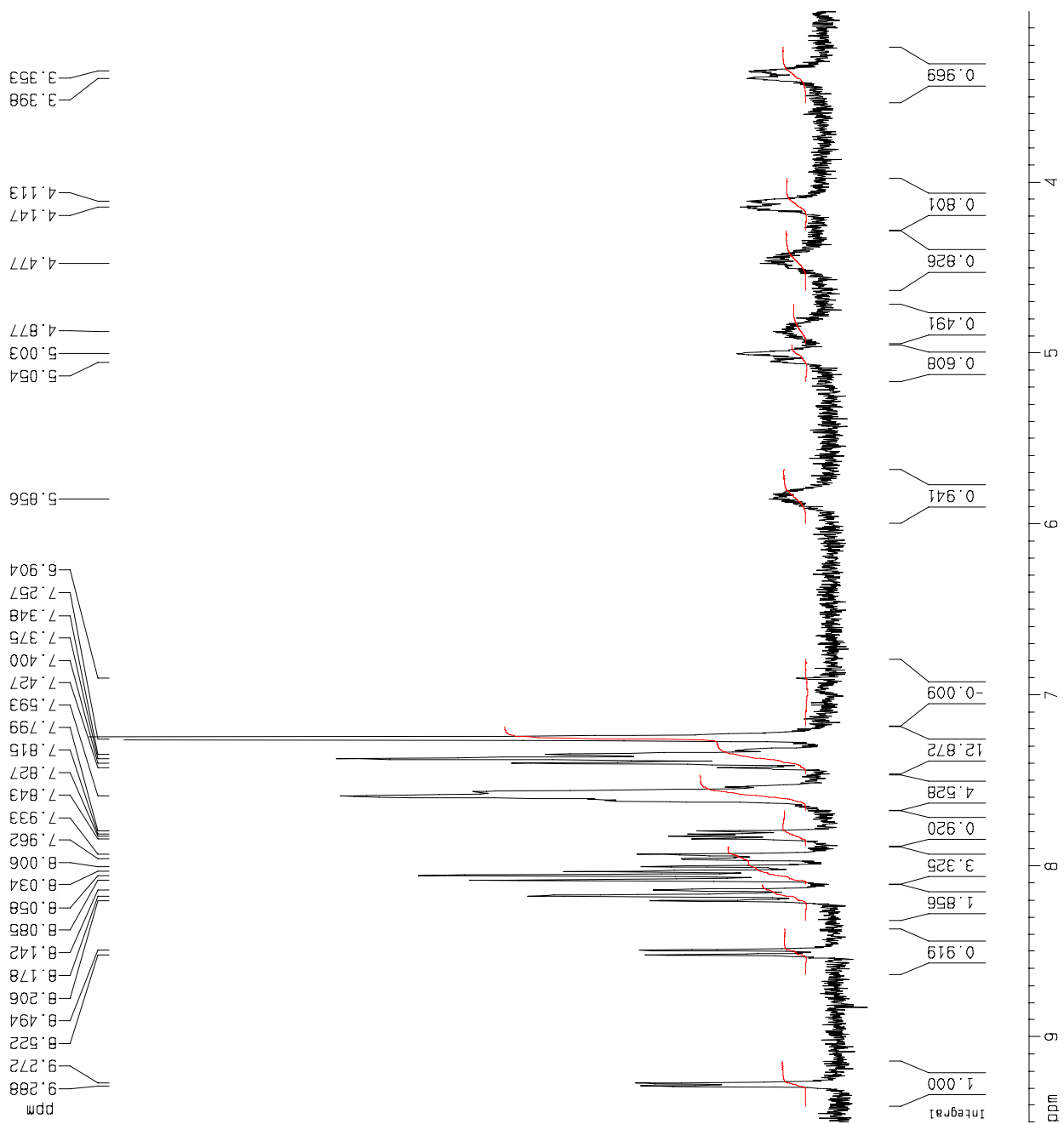
HMQC NMR (300 MHz, CDCl₃) Allylic Section Spectrum of [Pd(η³-PhCHCHCHPh)(S,S-3)]CF₃SO₃ (**10**)



NOESY NMR (300 MHz, CDCl_3) Spectrum of $[\text{Pd}(\eta^3\text{-PhCHCHCHPh})(\text{S,S-4})]\text{CF}_3\text{SO}_3$ (**11**).



HMQC NMR (300 MHz, CDCl_3) Allylic Section Spectrum of $[\text{Pd}(\eta^3\text{-PhCHCHCHPh})(\text{S,S-4})]\text{CF}_3\text{SO}_3$ (**11**)



^1H NMR (300 MHz, CDCl_3) Spectrum of $[\text{Pd}(\eta^3\text{-H}_2\text{CCHCH}_2)(\text{S}_a\text{-2})]\text{CF}_3\text{SO}_3$ (**12**).