SUPPORTING INFORMATION

4′-Methoxyphenacyl-Assisted Synthesis of *β*-Kdo Glycosides

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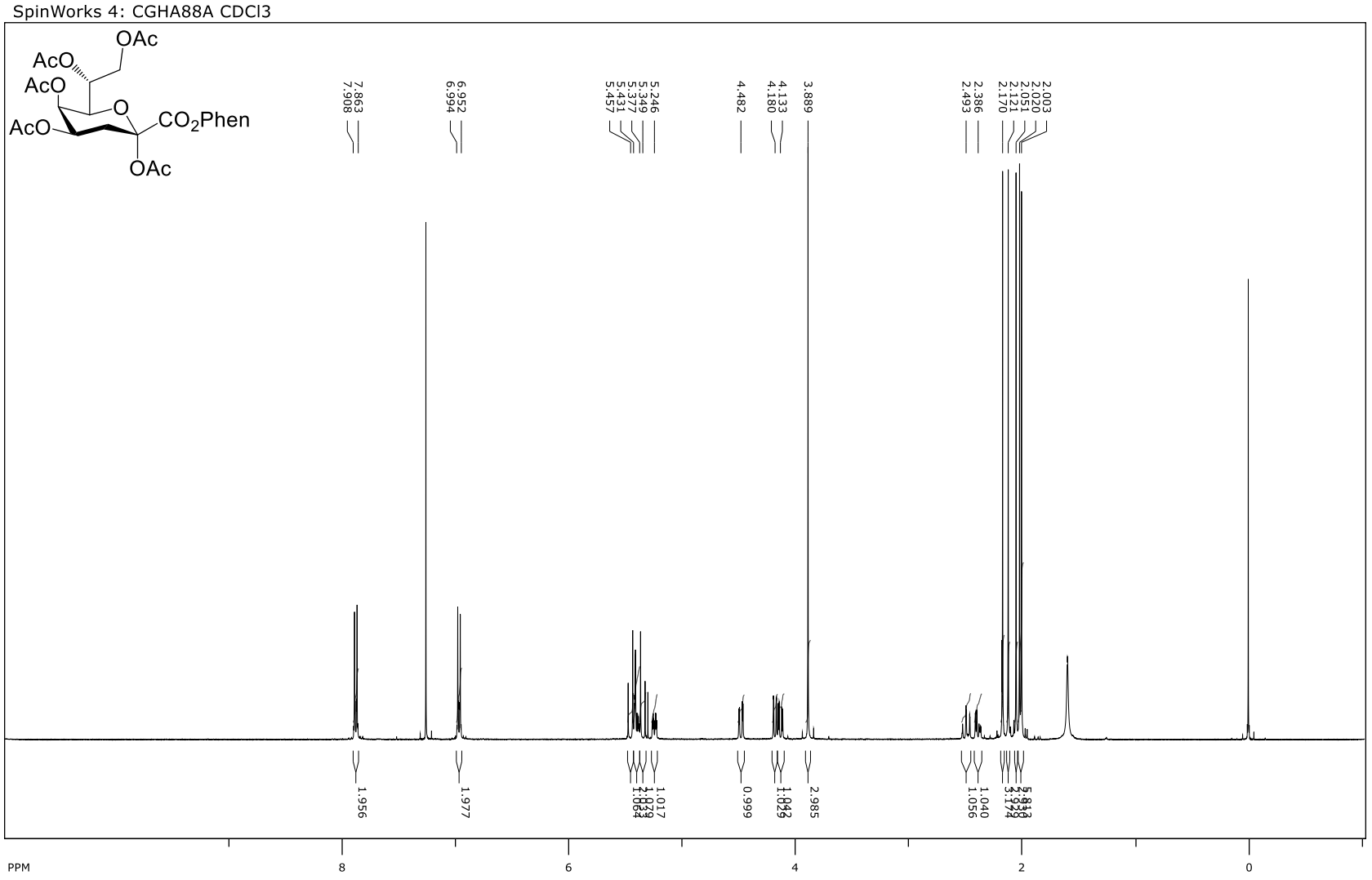
^{1}H NMR spectra (400 MHz, $CDCl_3$) of 4′-methoxyphenacyl (2,4,5,7,8-penta-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranosyl)onate.



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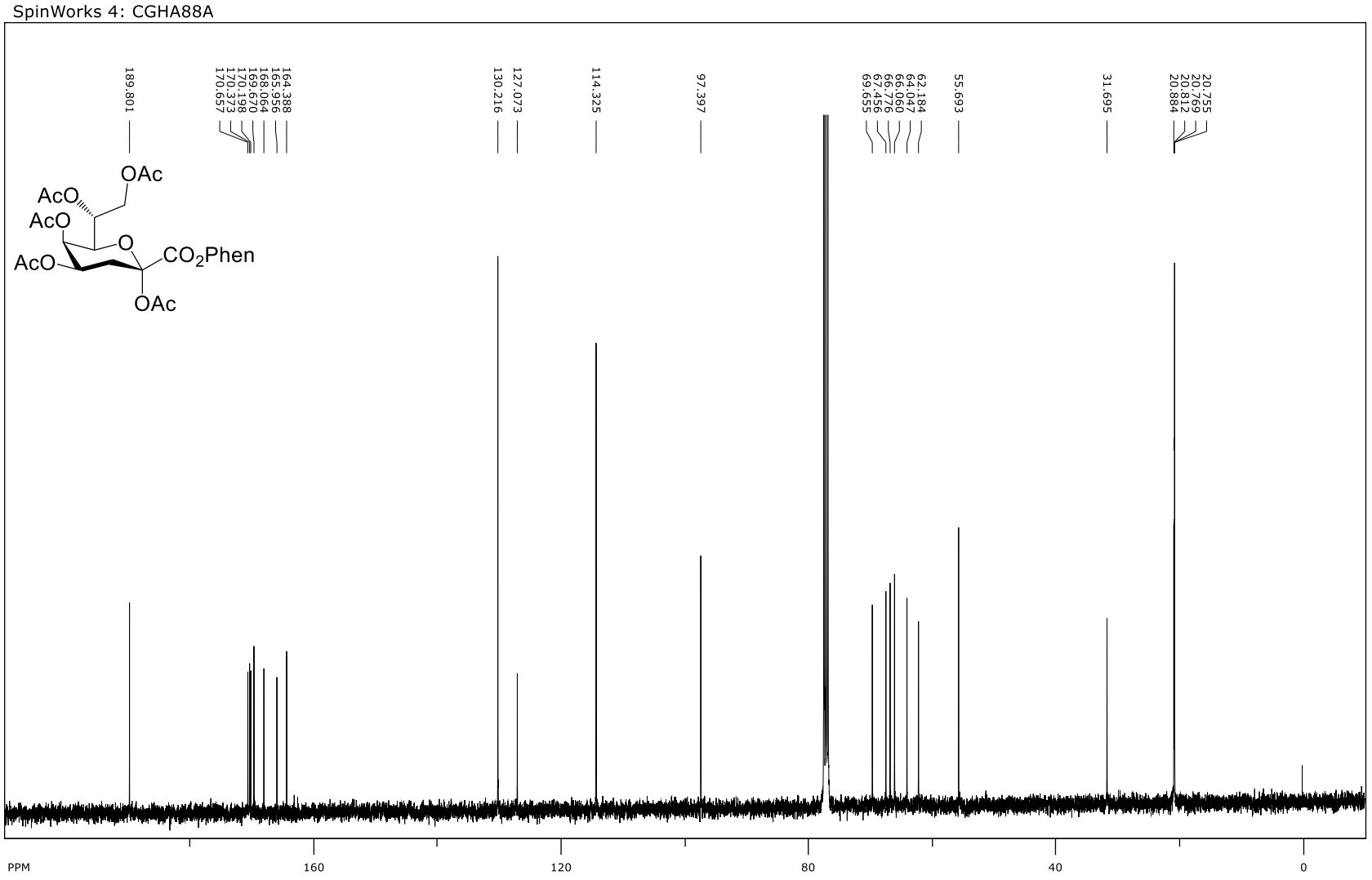

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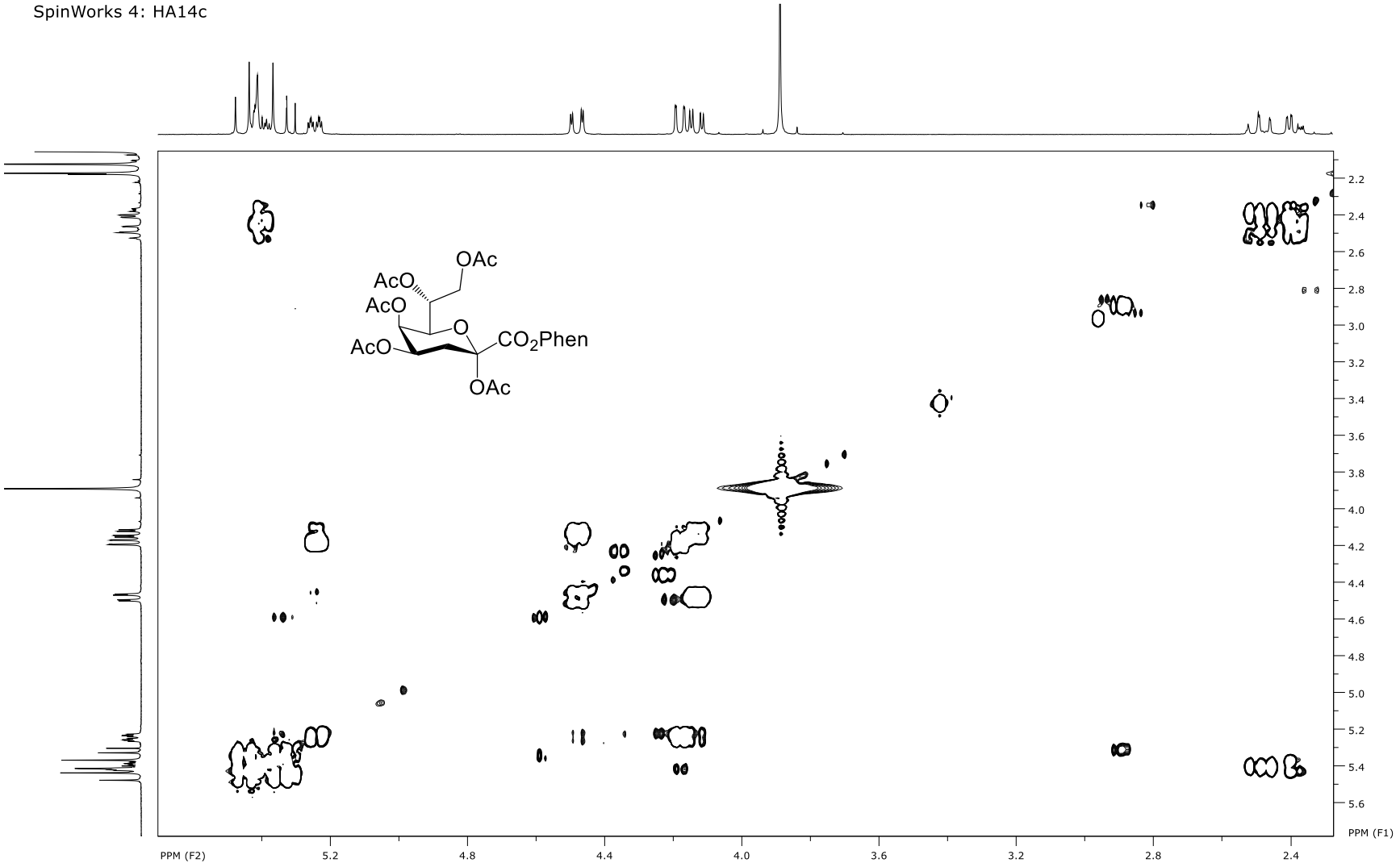

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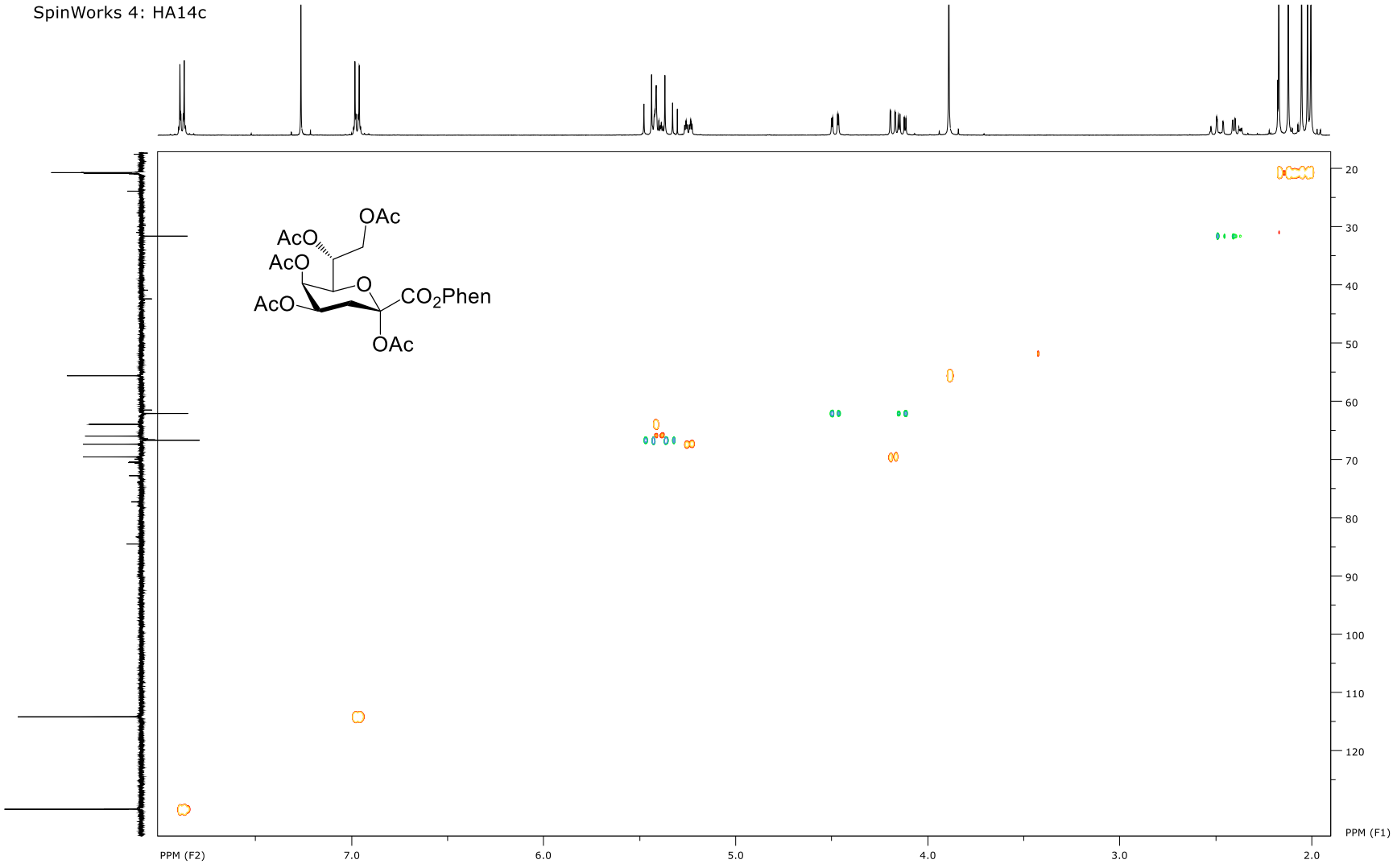
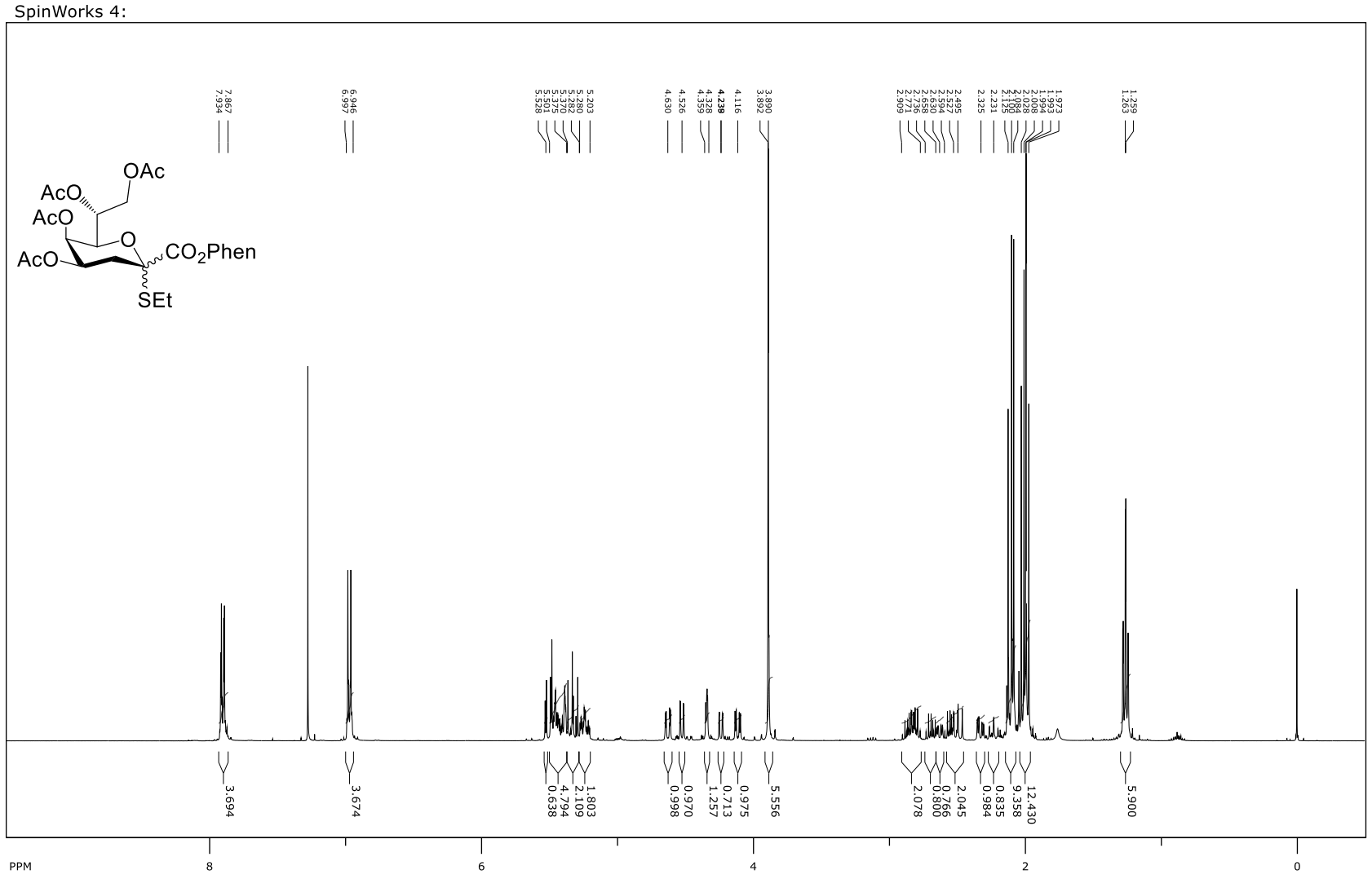
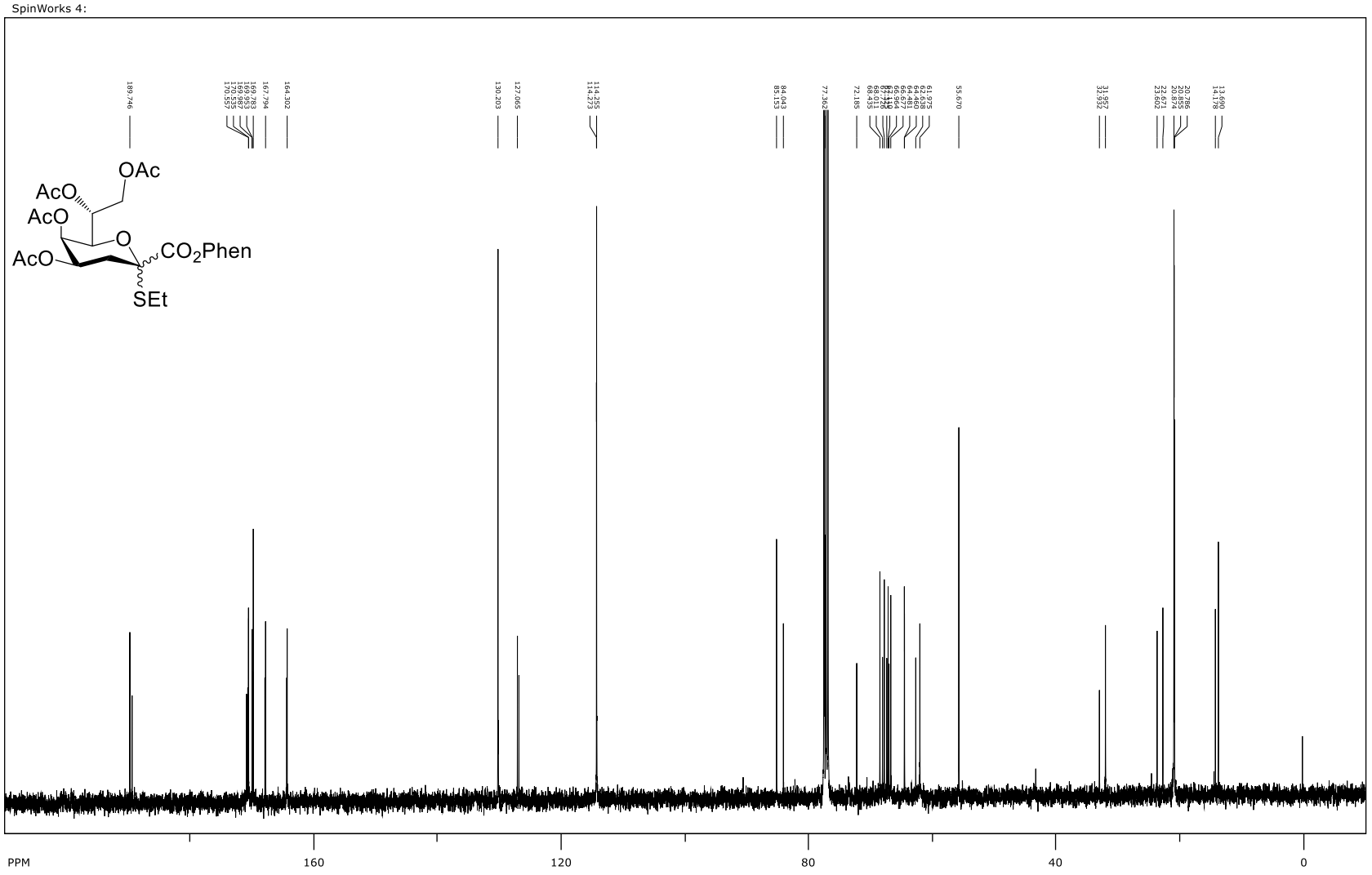


^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **2** (ratio α/β ~ 1:1).



^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **2** (ratio α/β ~ 1:1).



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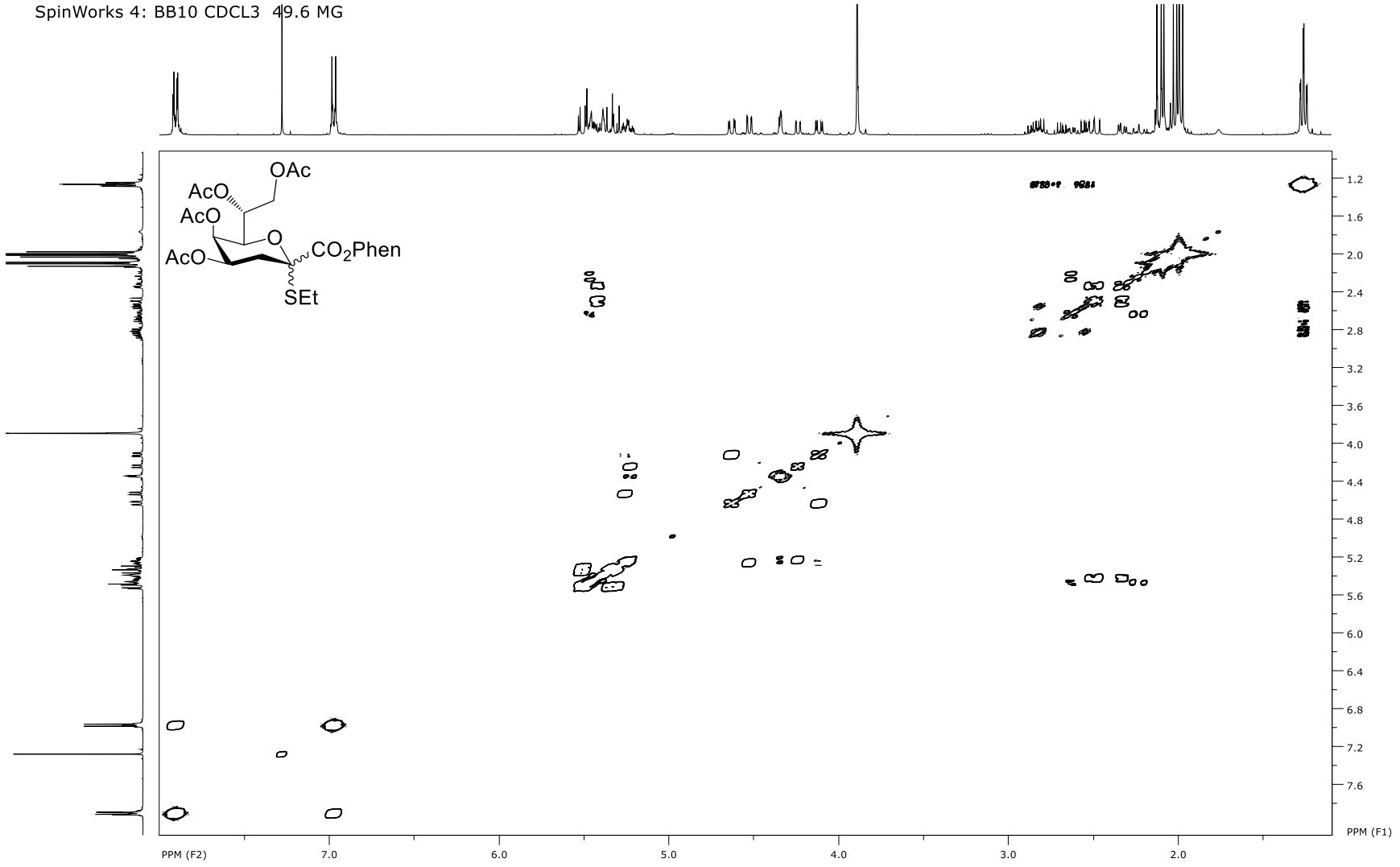

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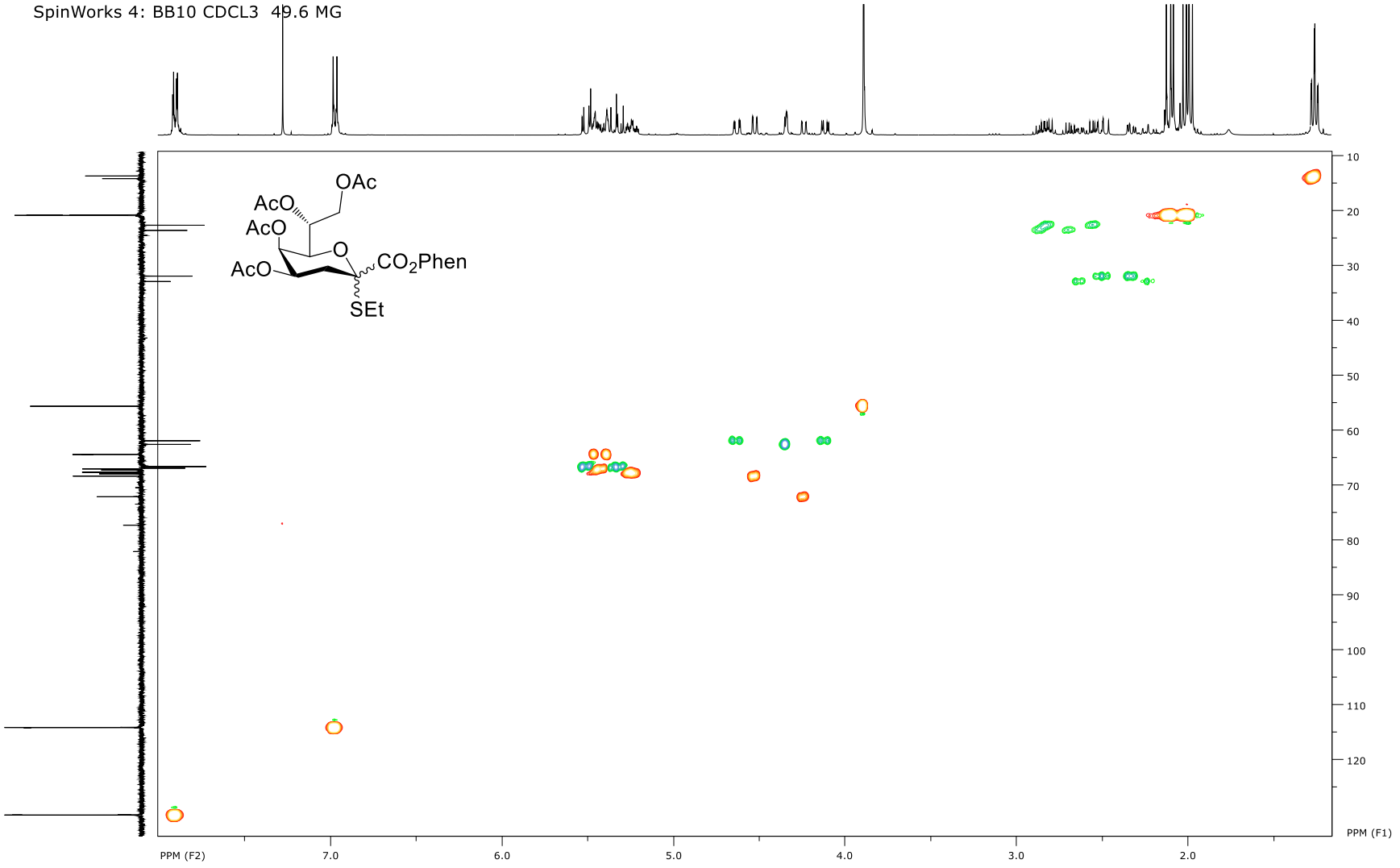
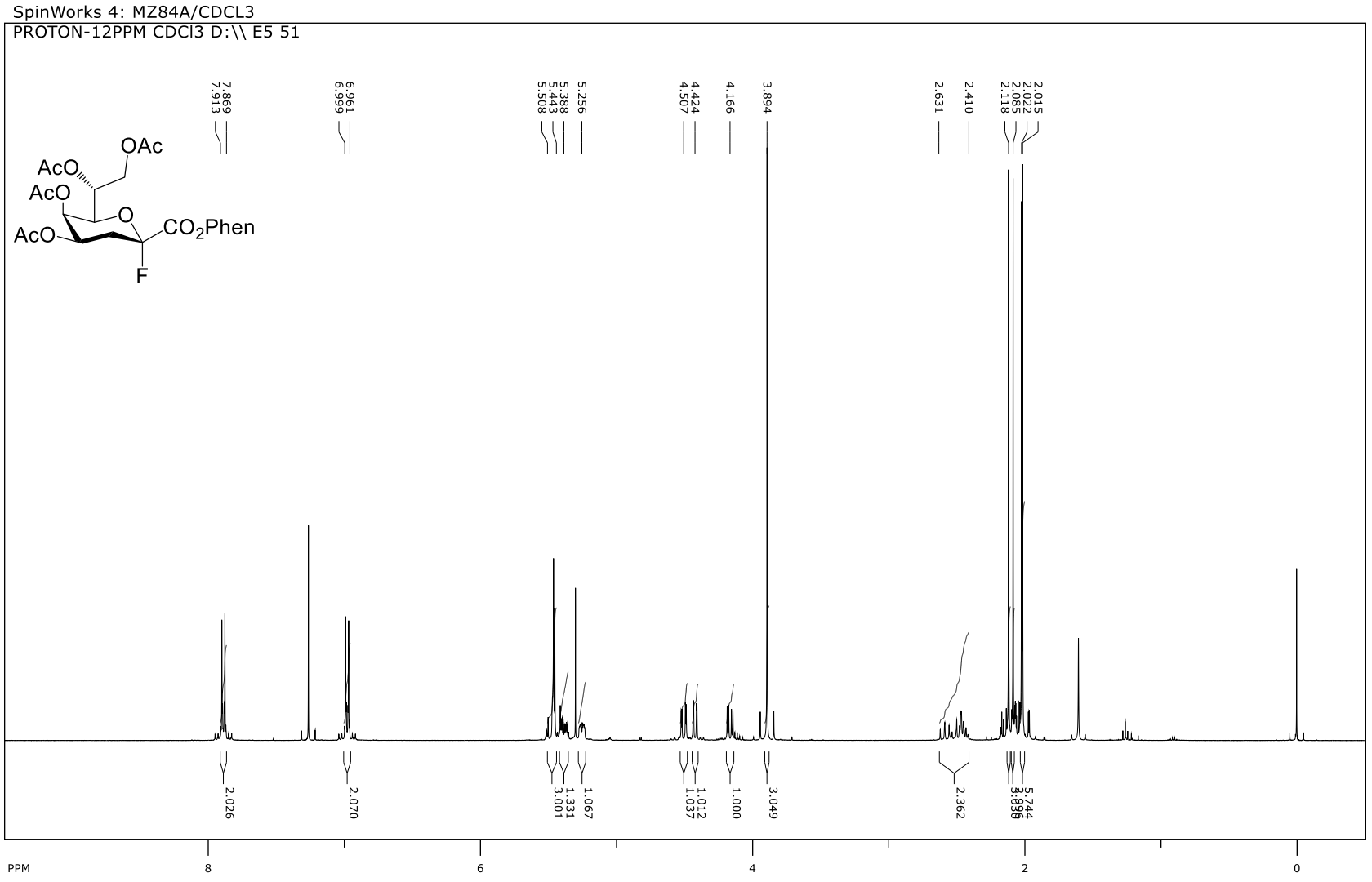
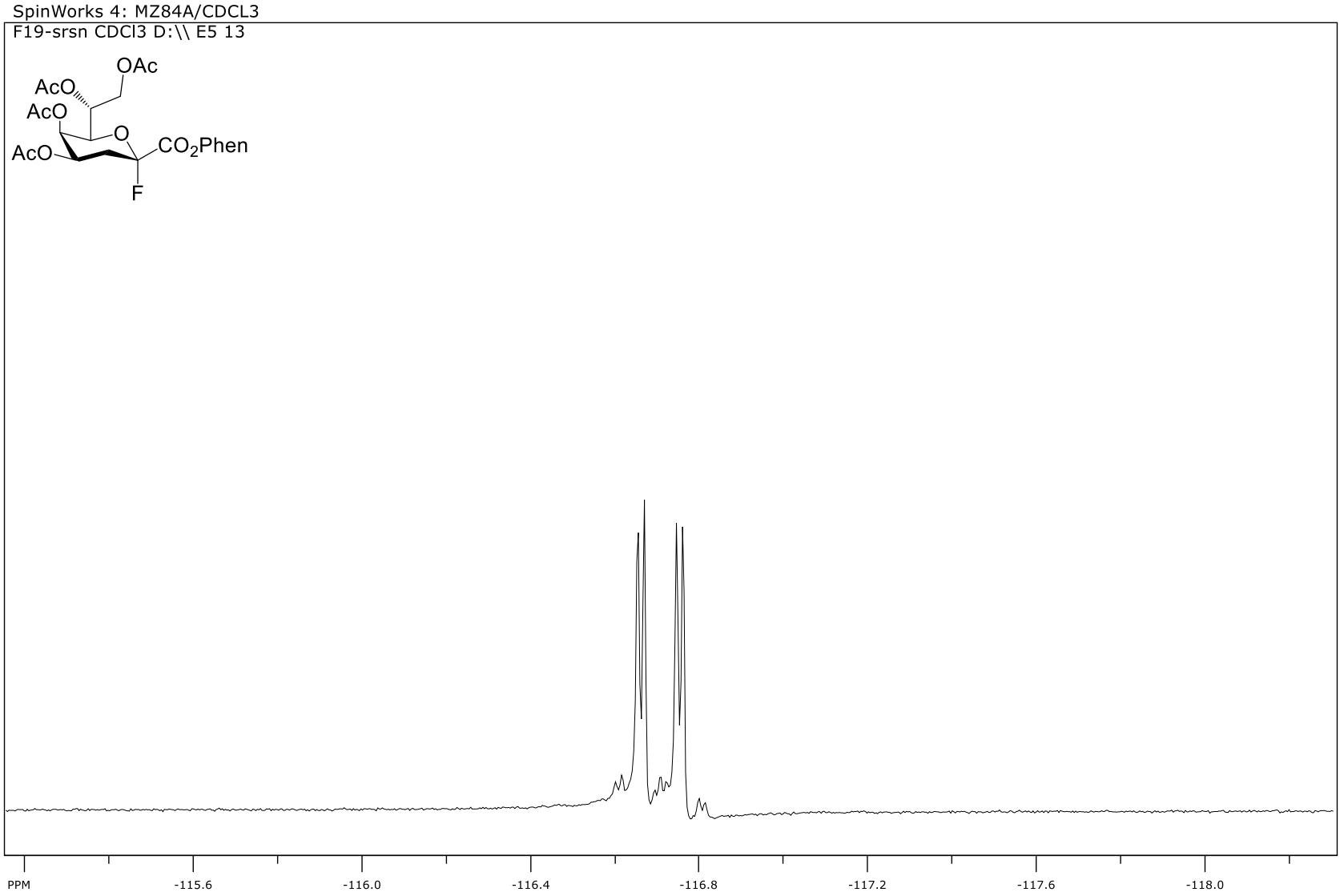


^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **4**.



^{19}F NMR spectra (376 MHz, $CDCl_3$) of compound **4**.



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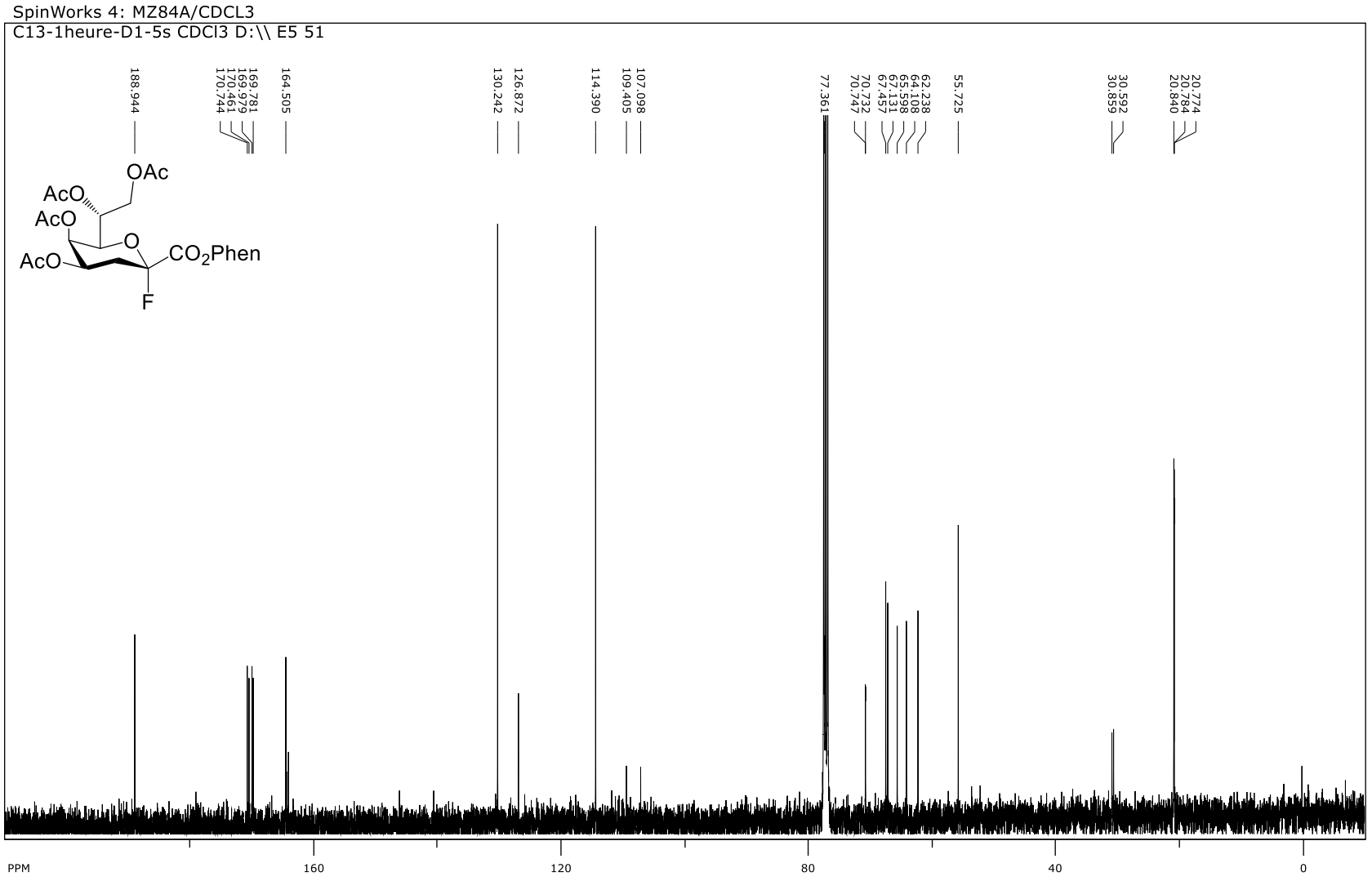

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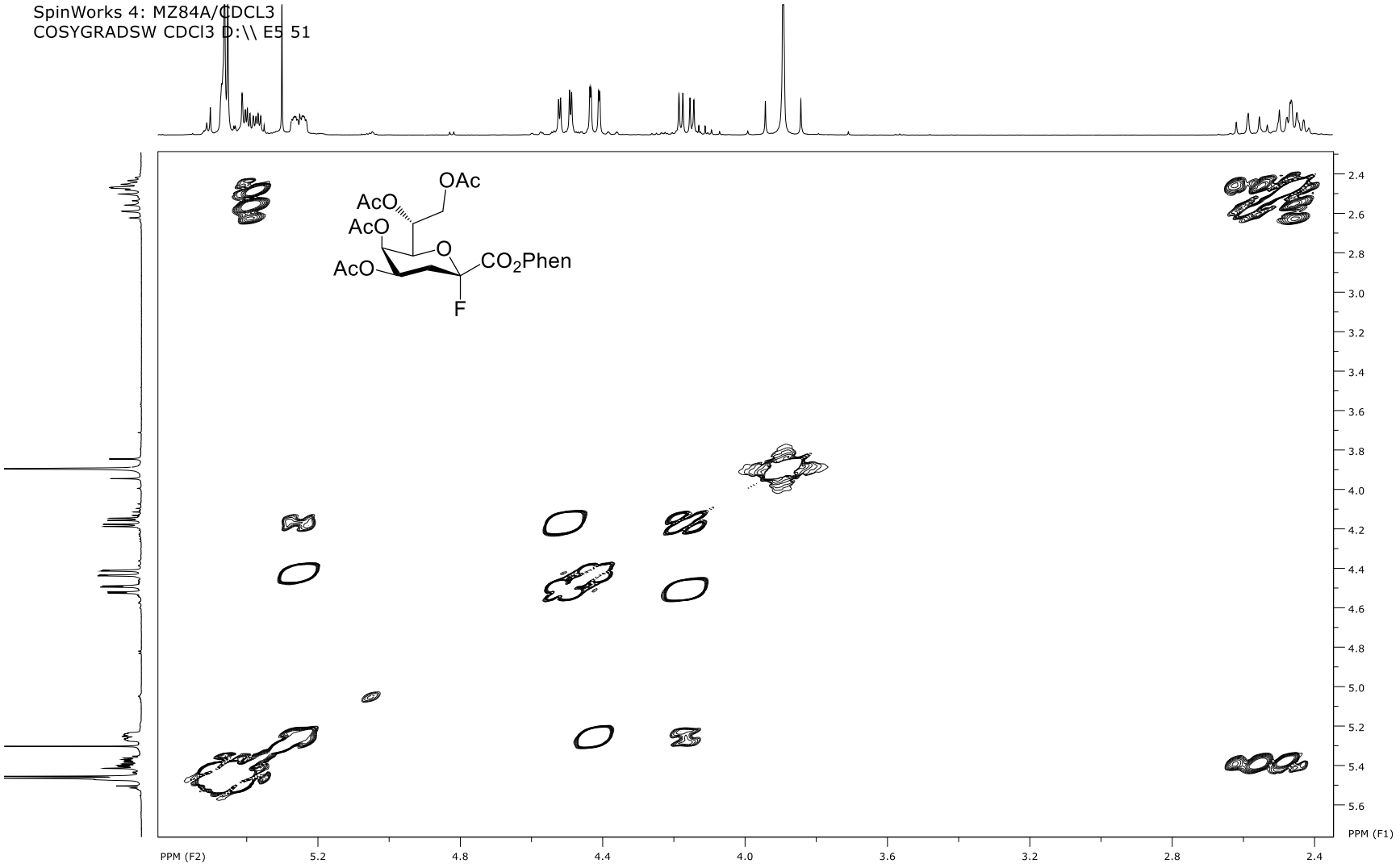

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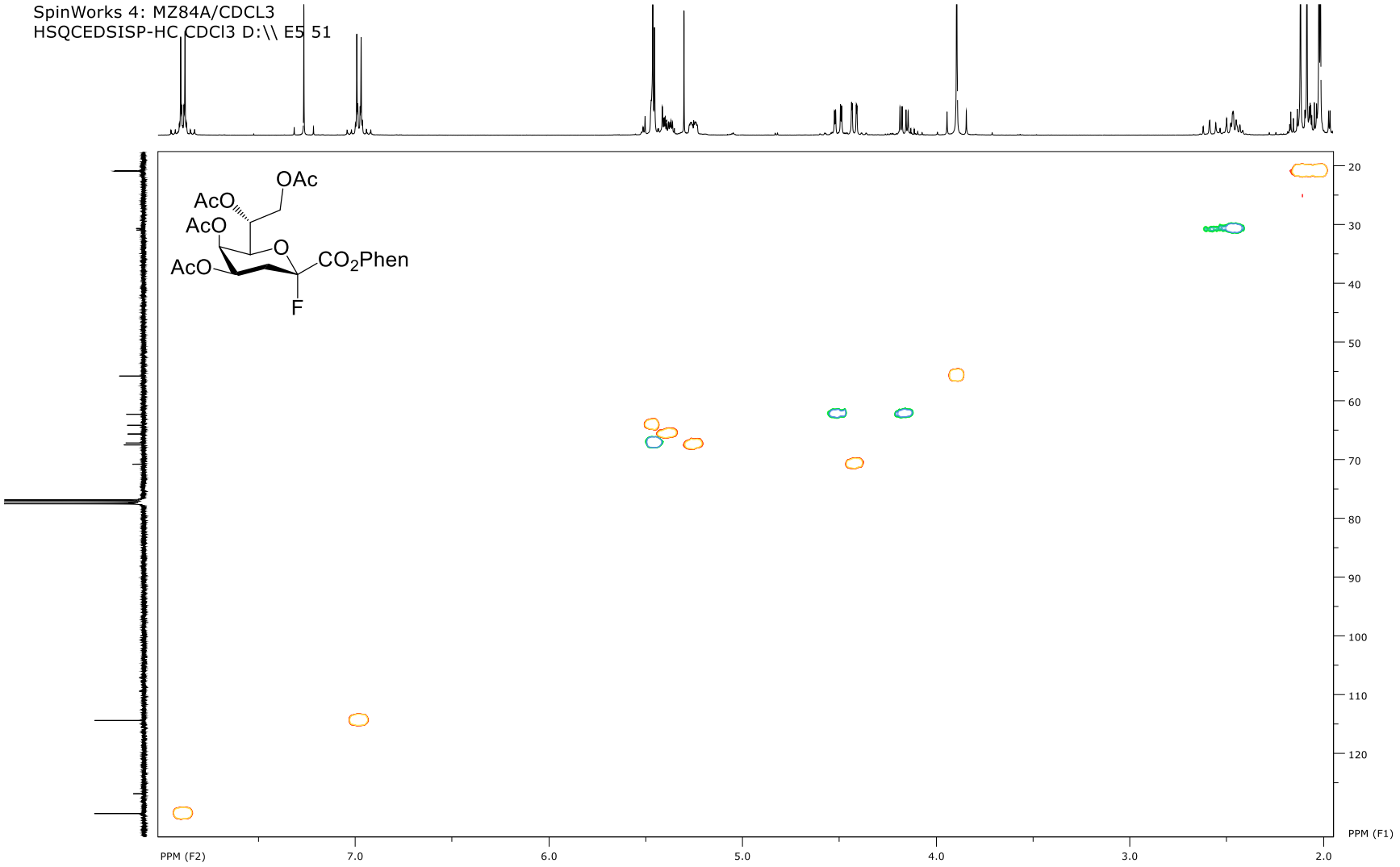
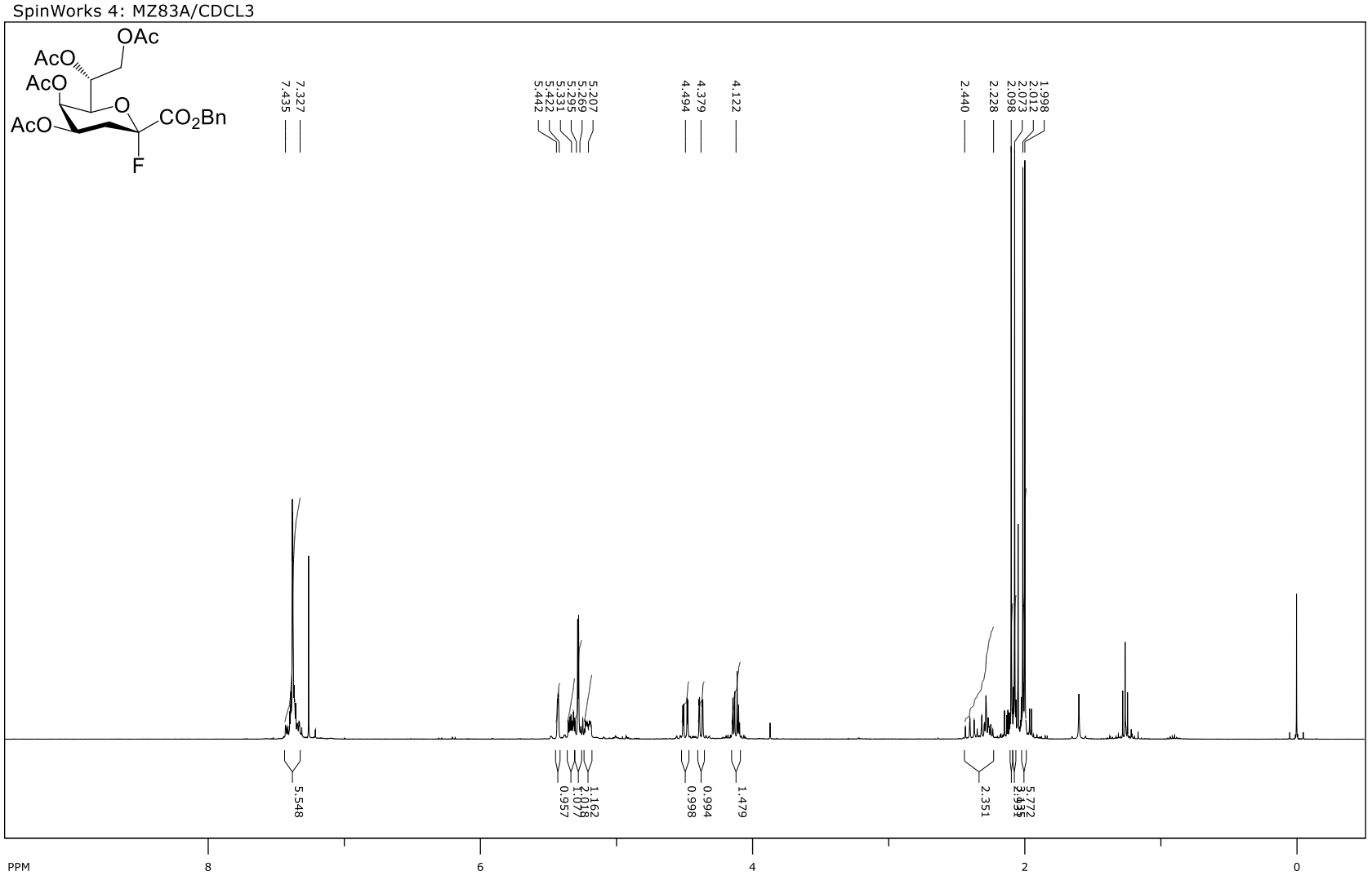


^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **5**.



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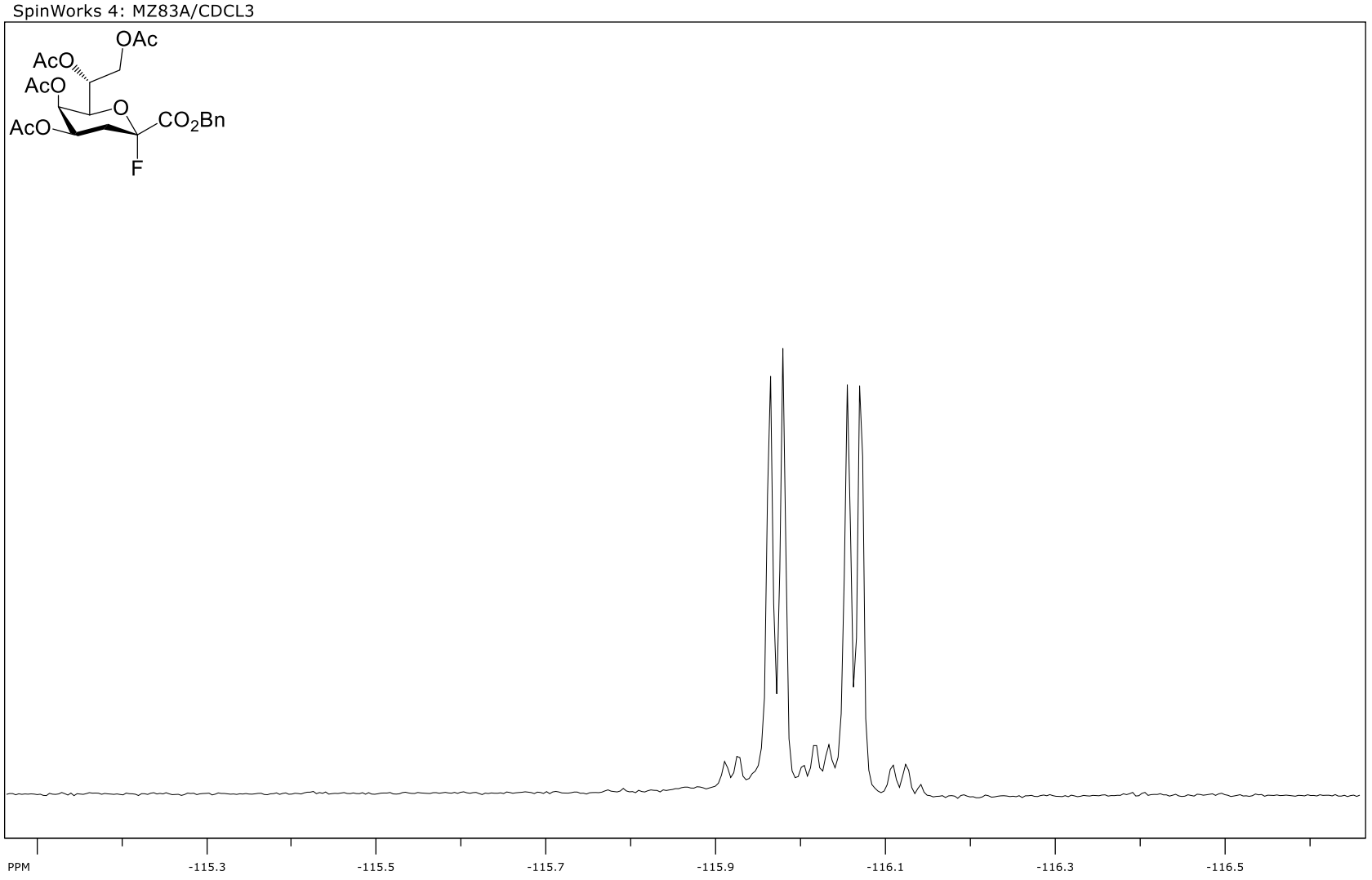
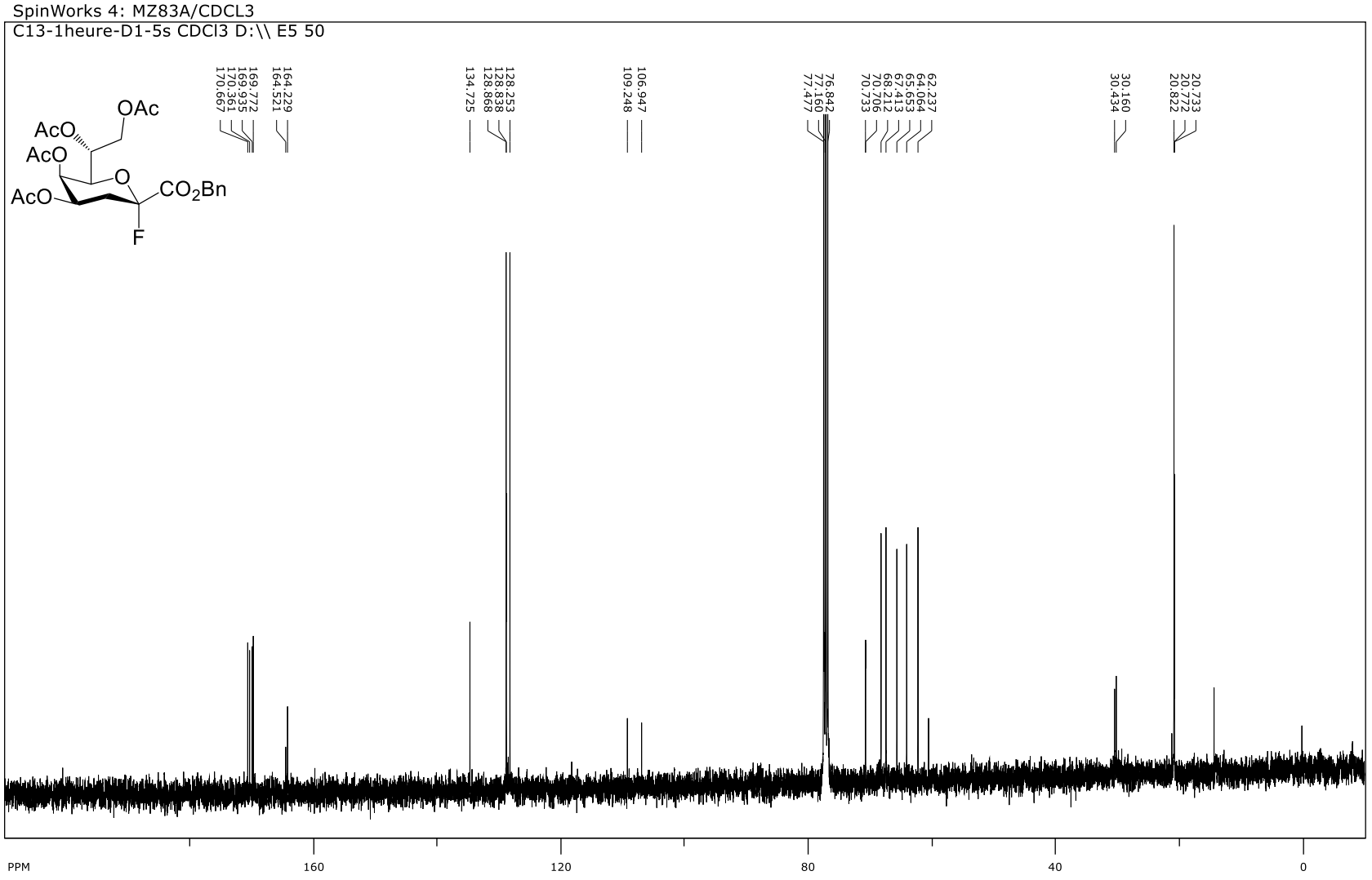


^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **5**.



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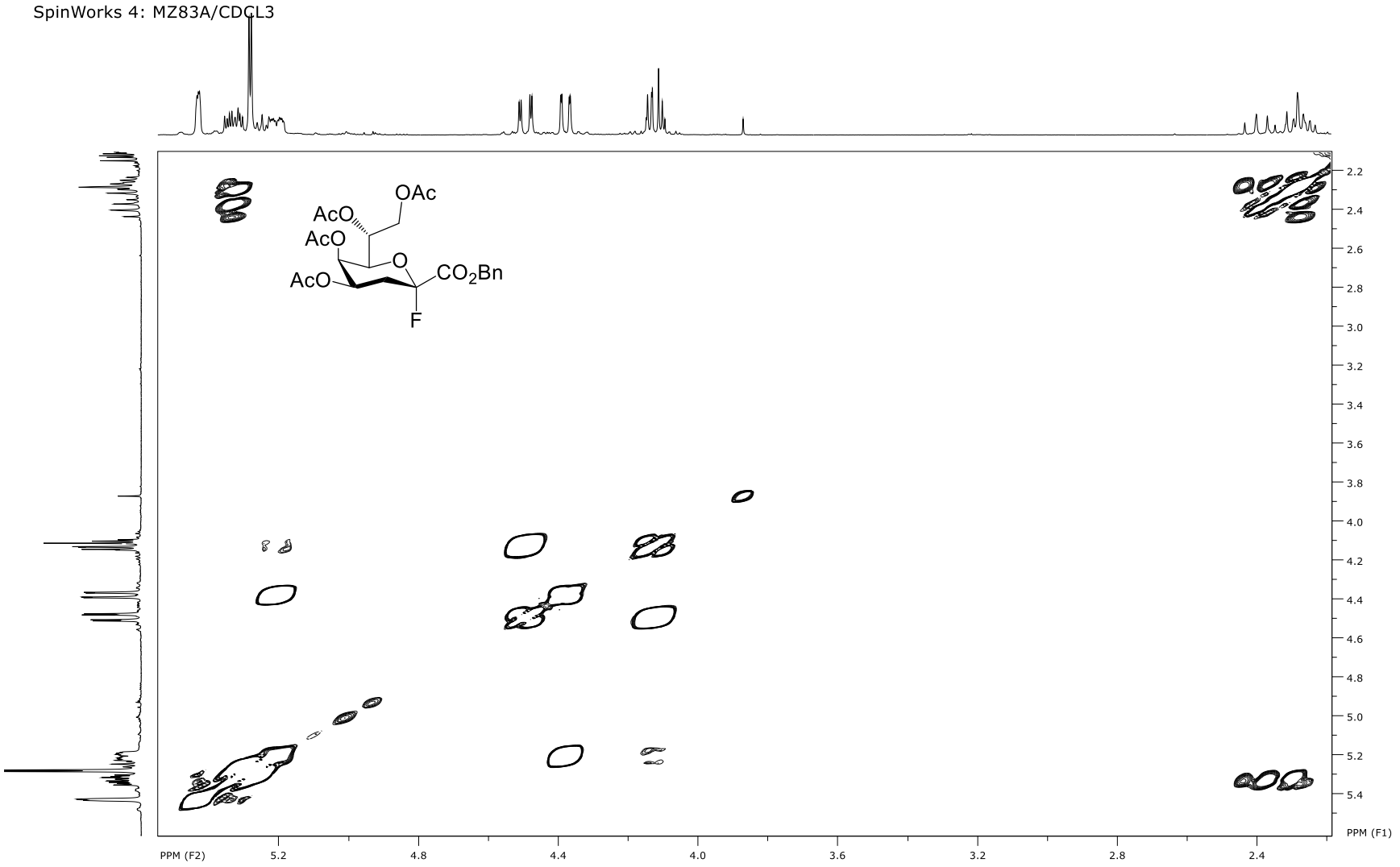

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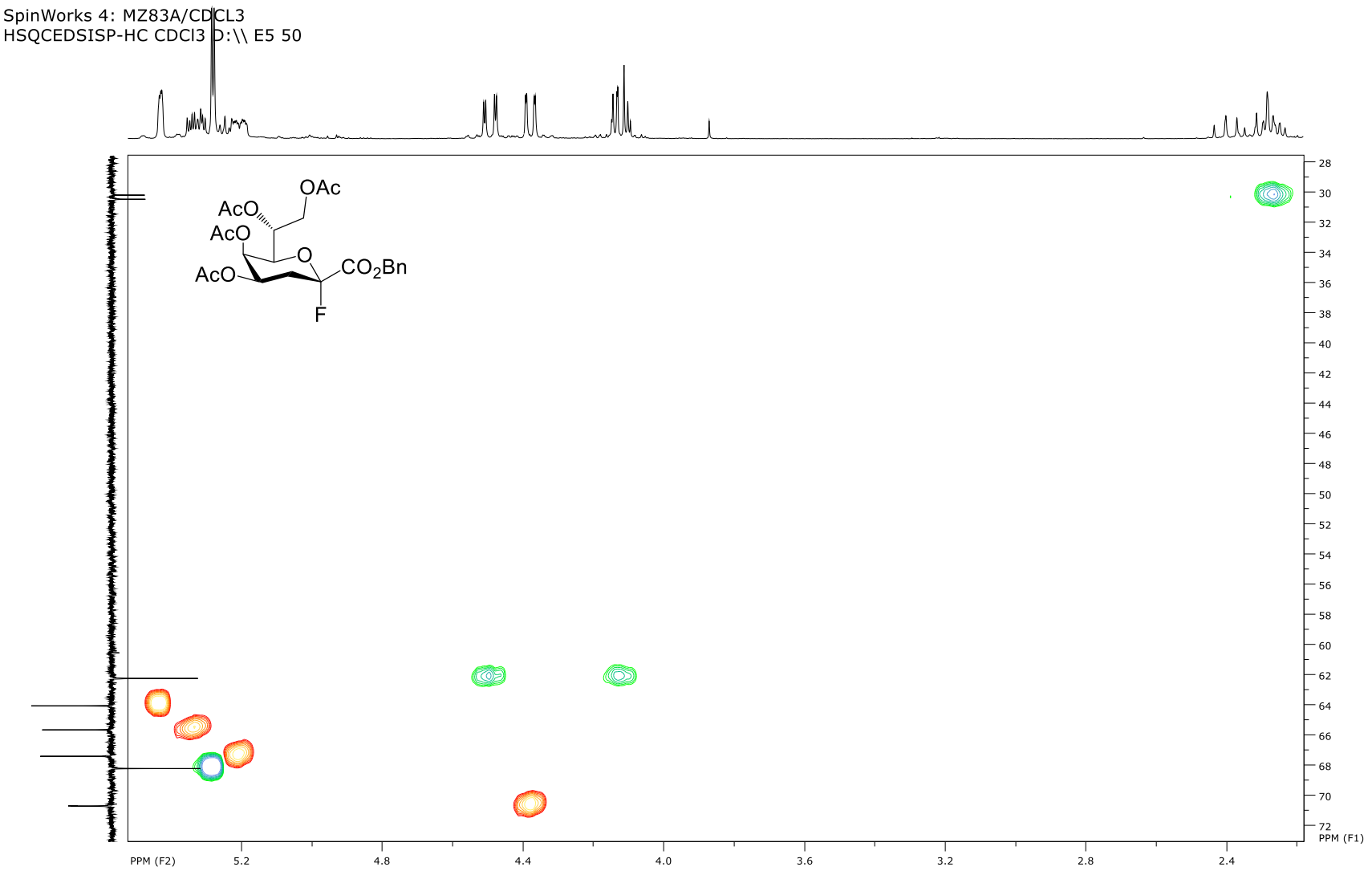
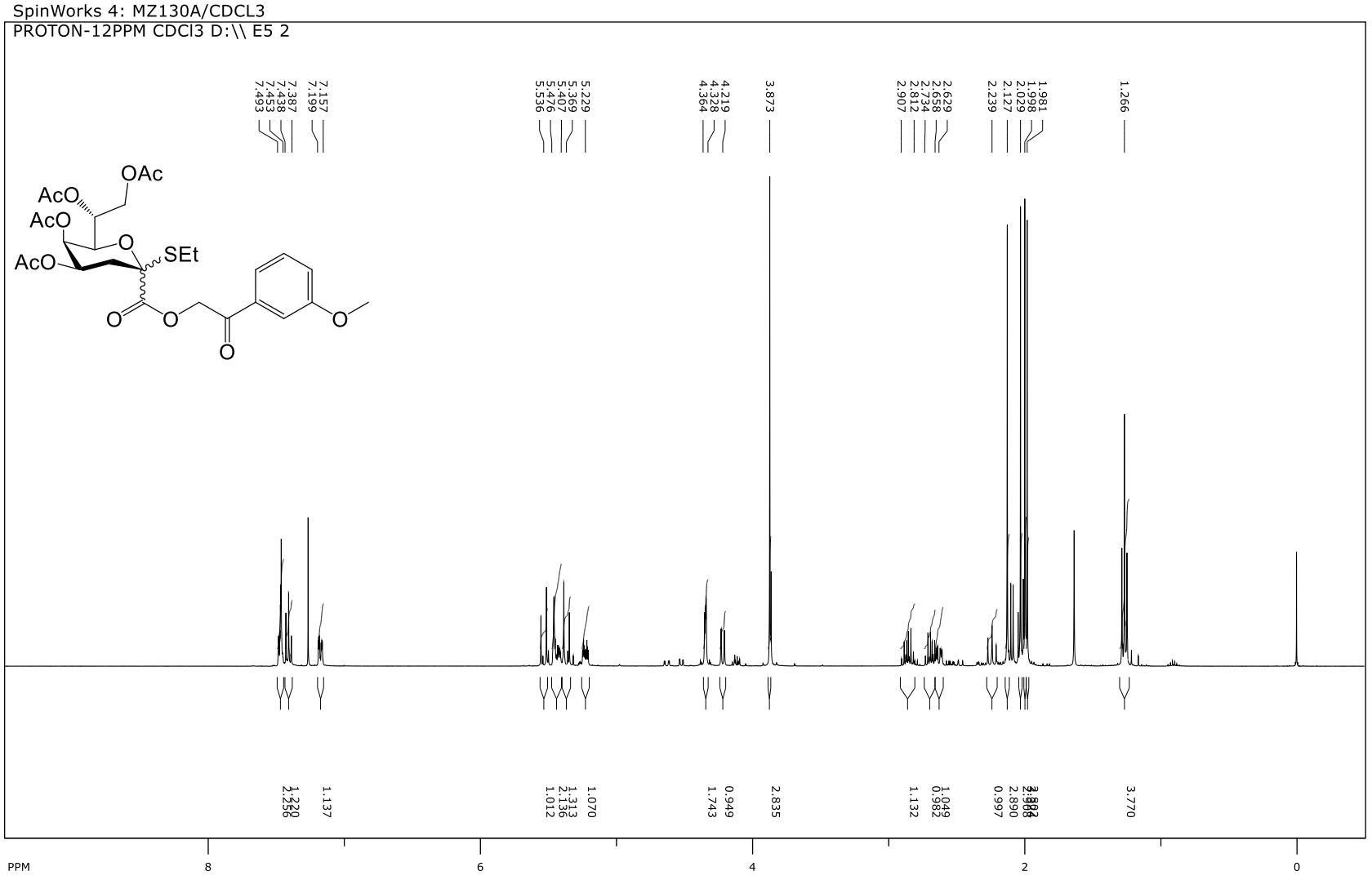
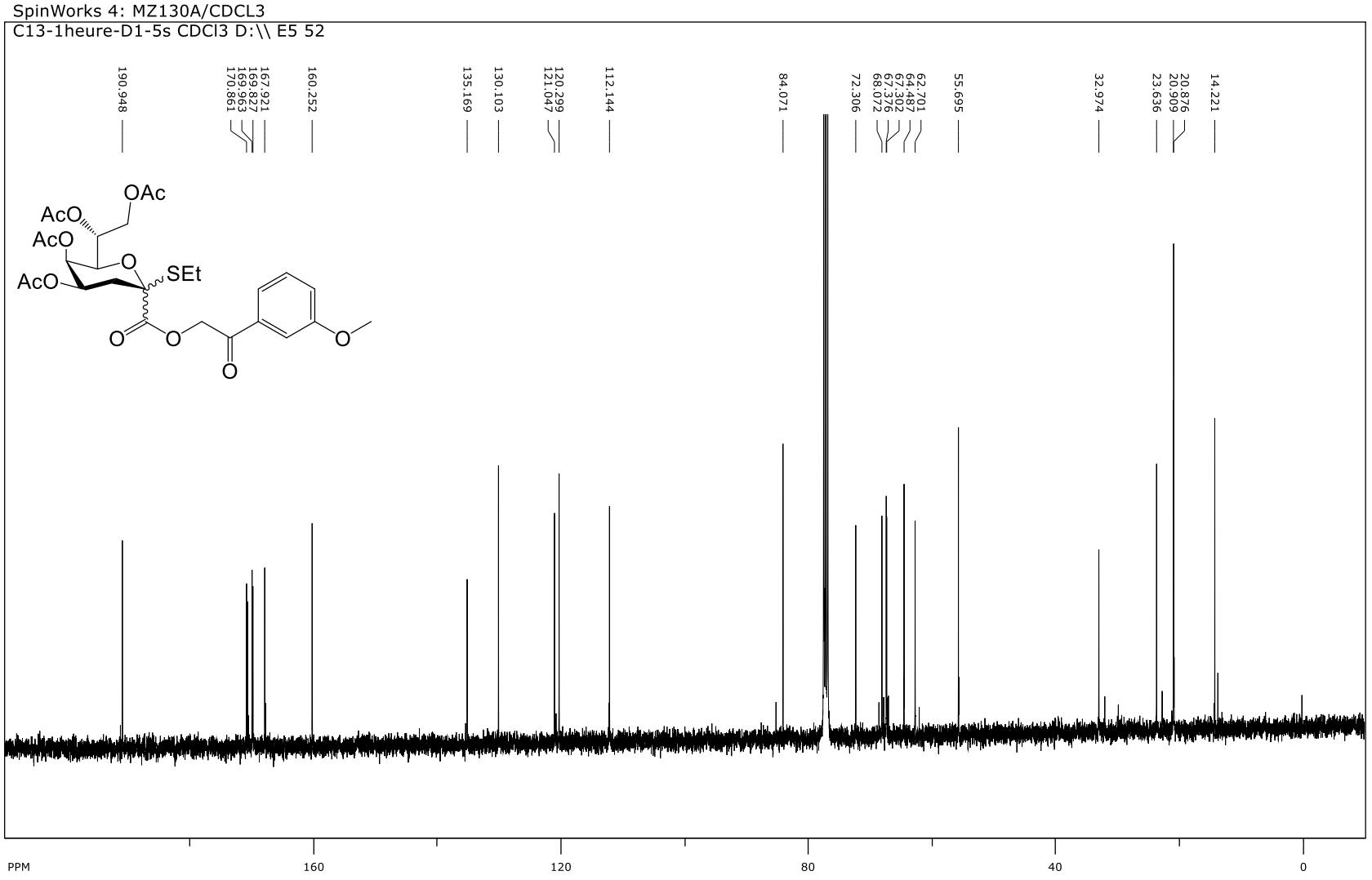


^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **6**.



^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **6**.



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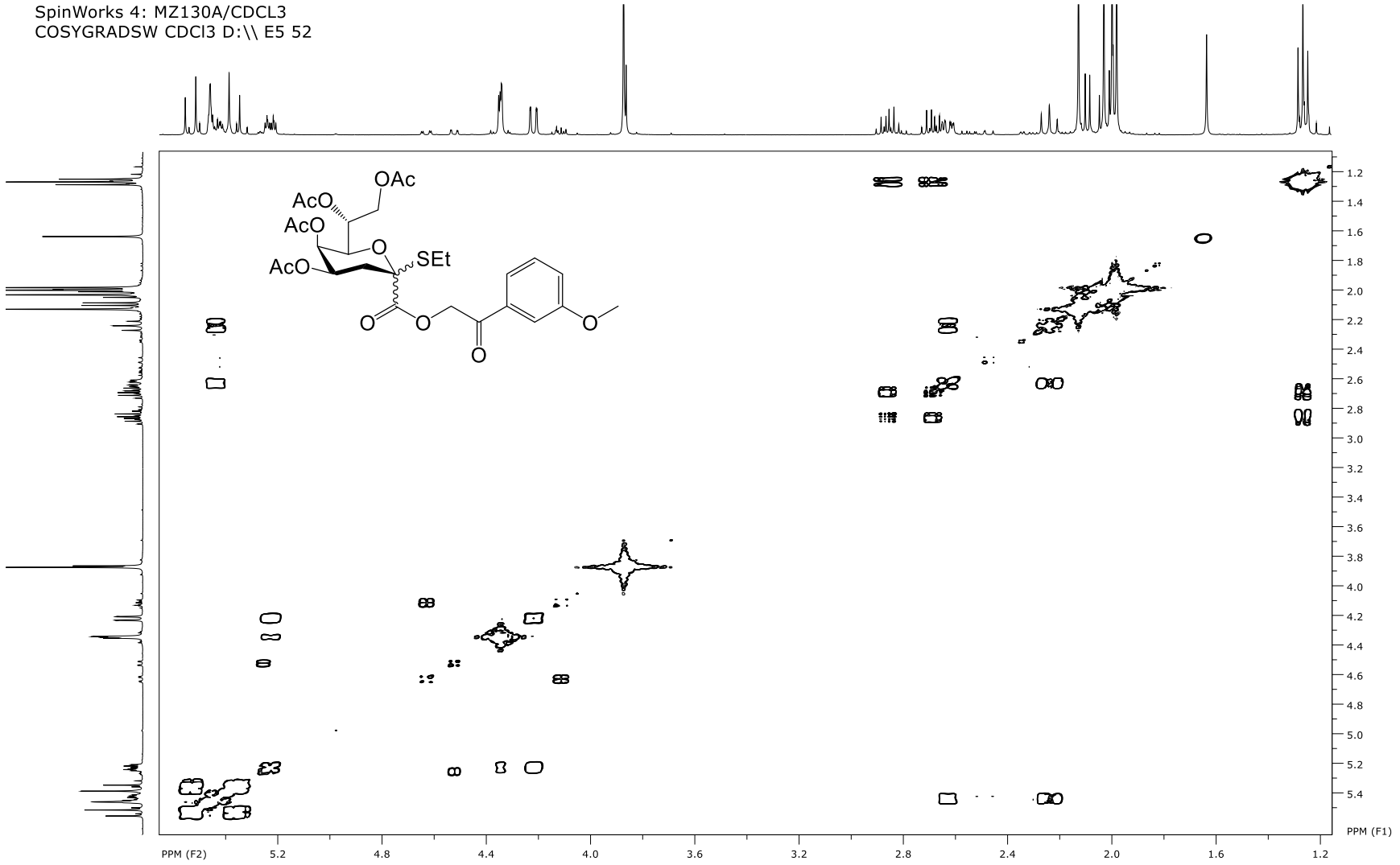

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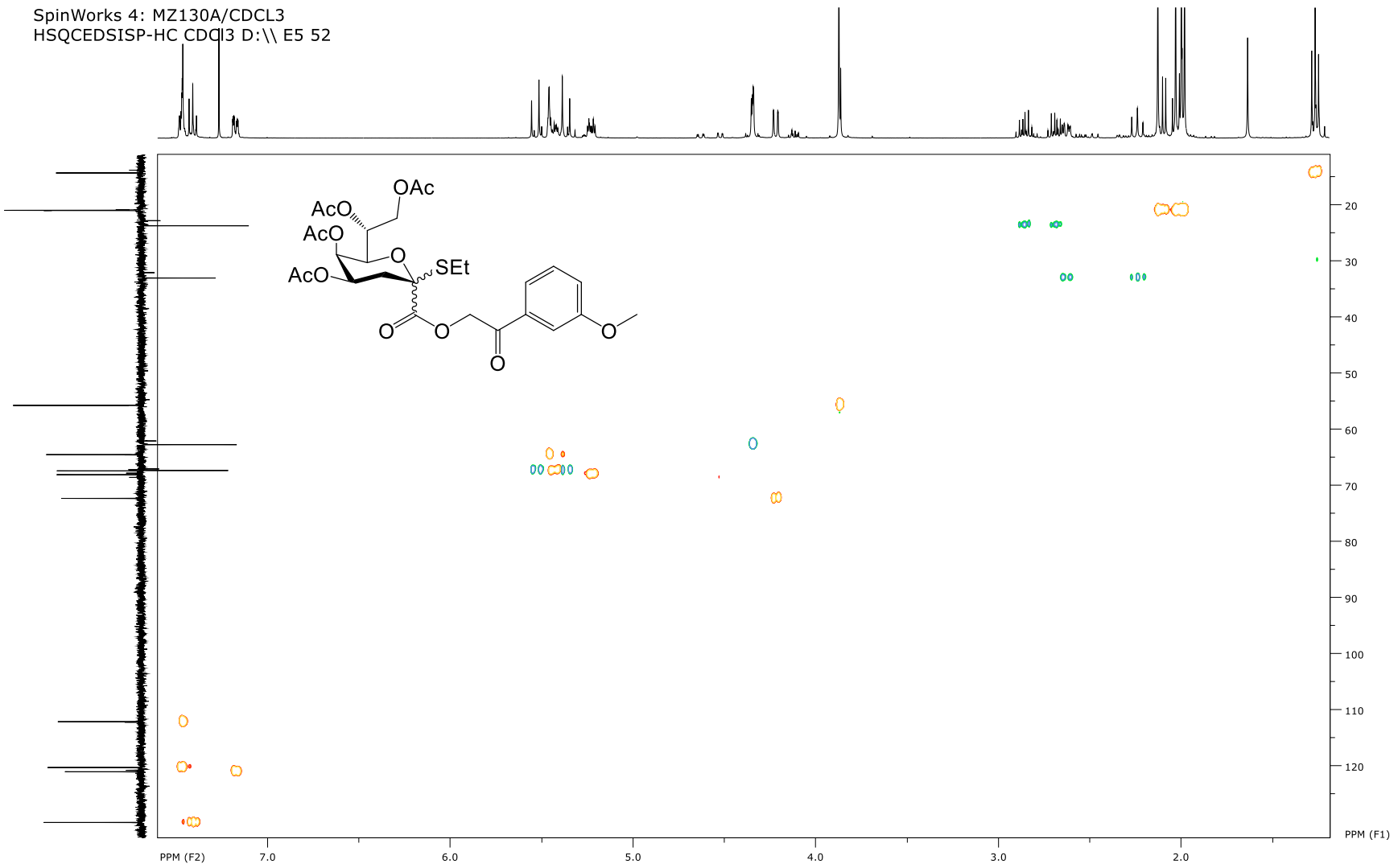
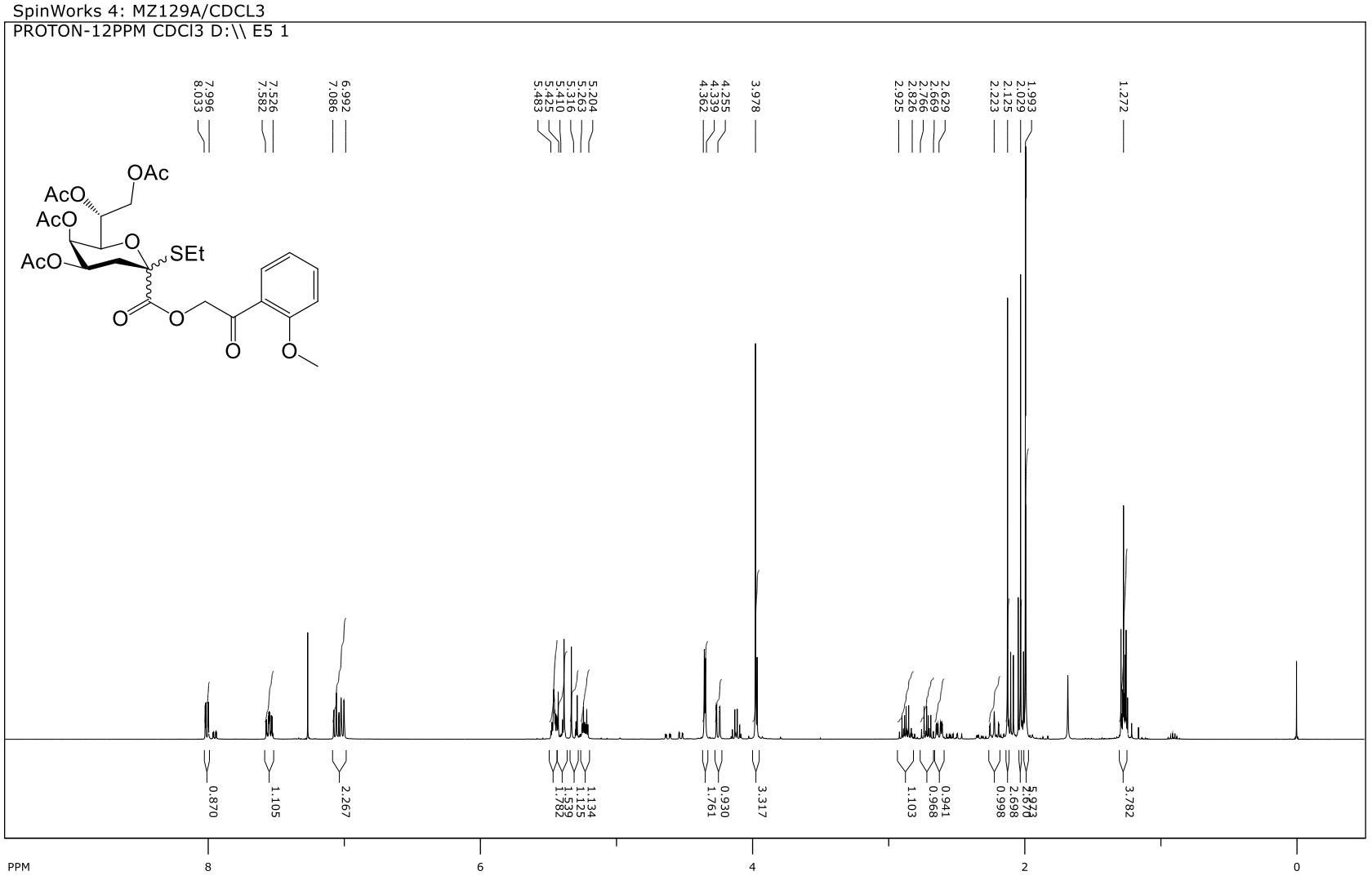


^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **7**.



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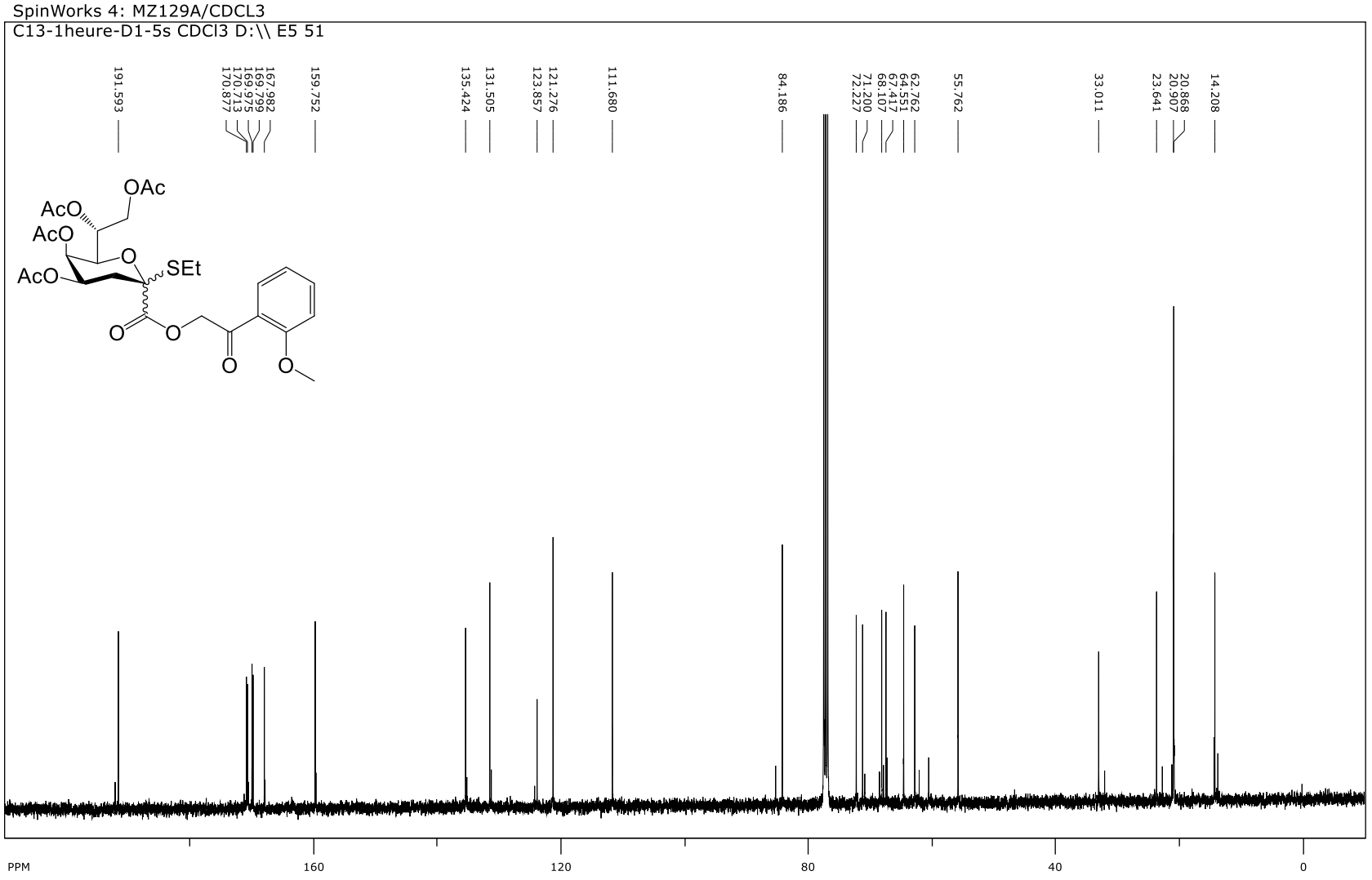

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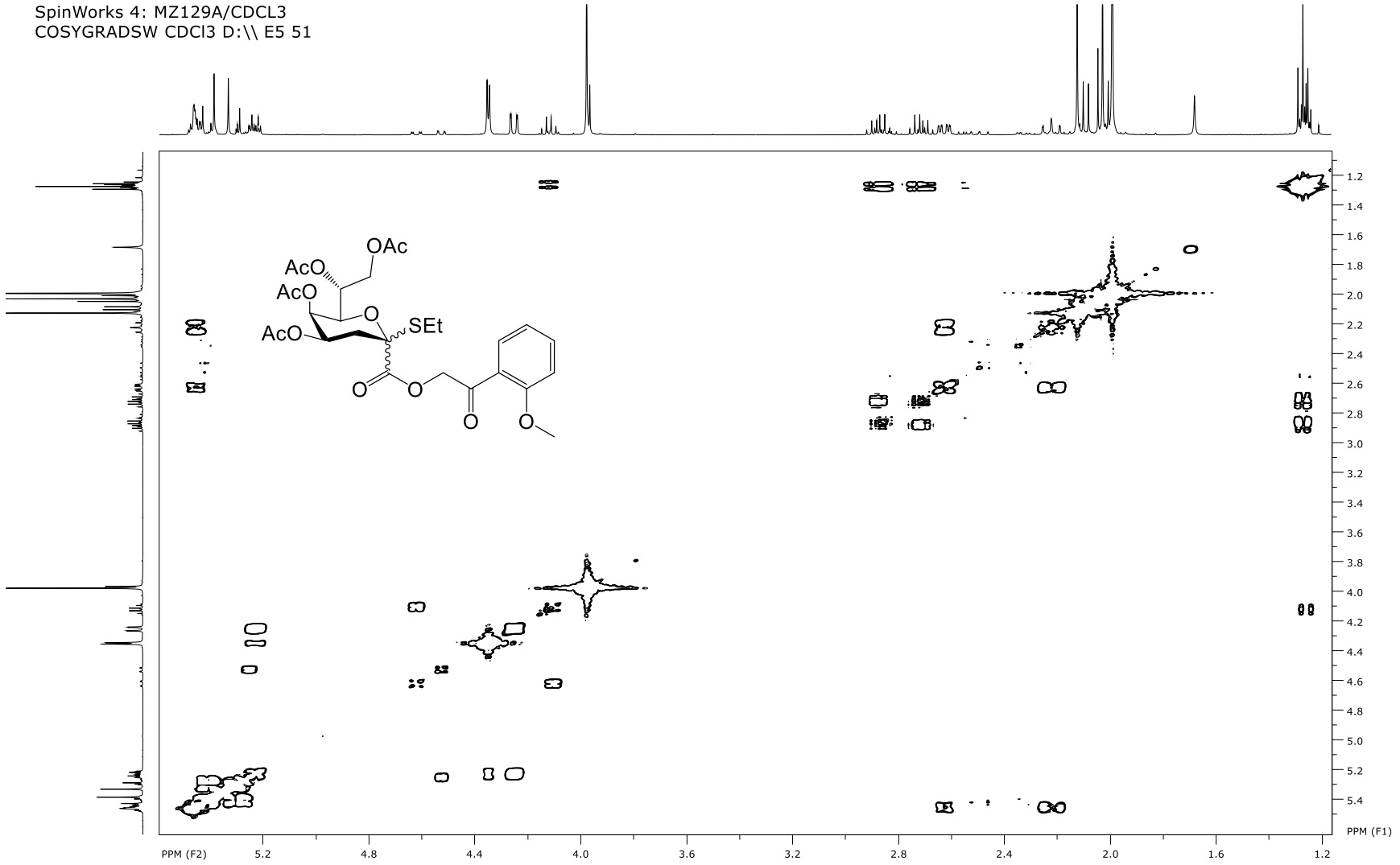

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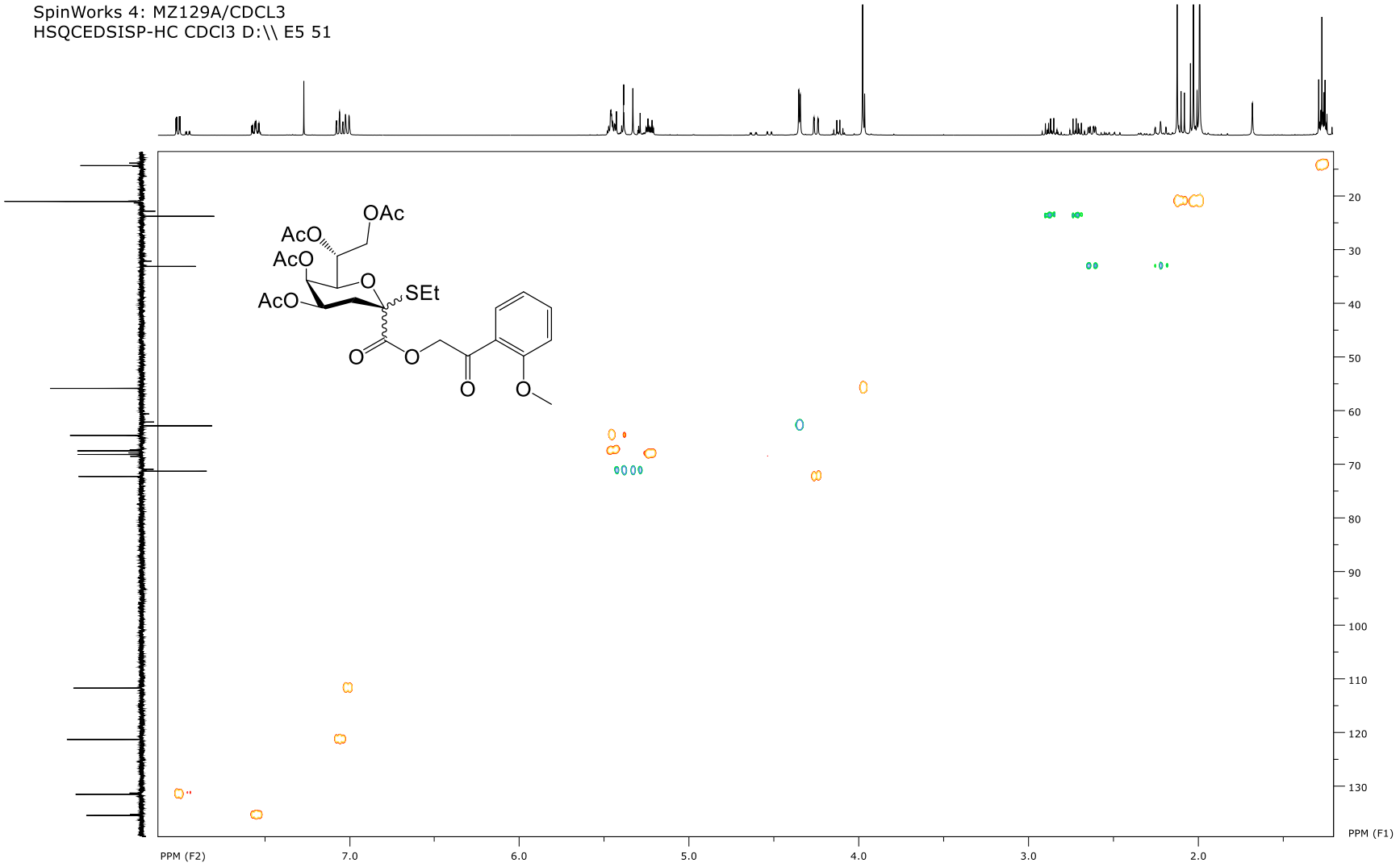

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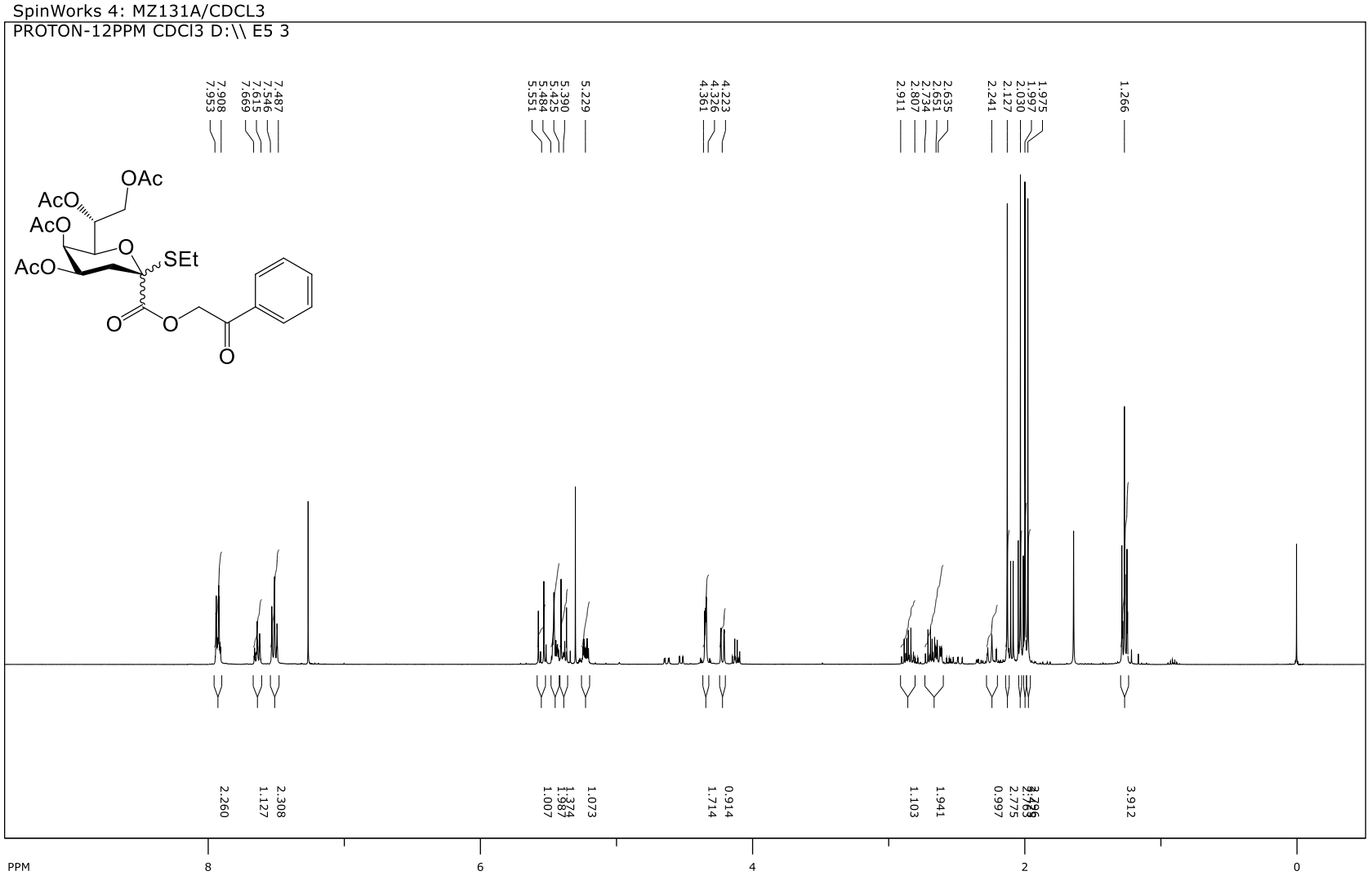

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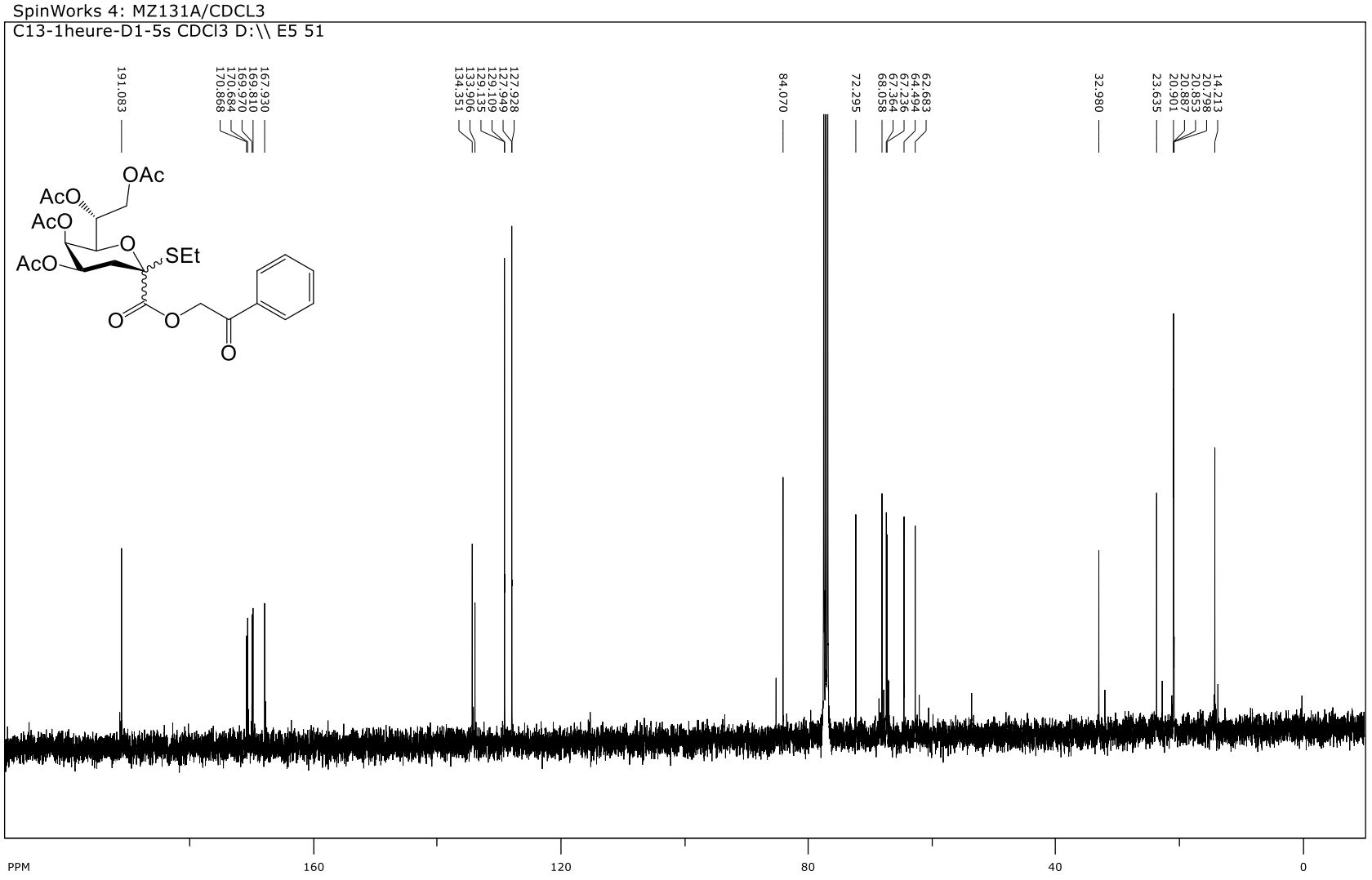

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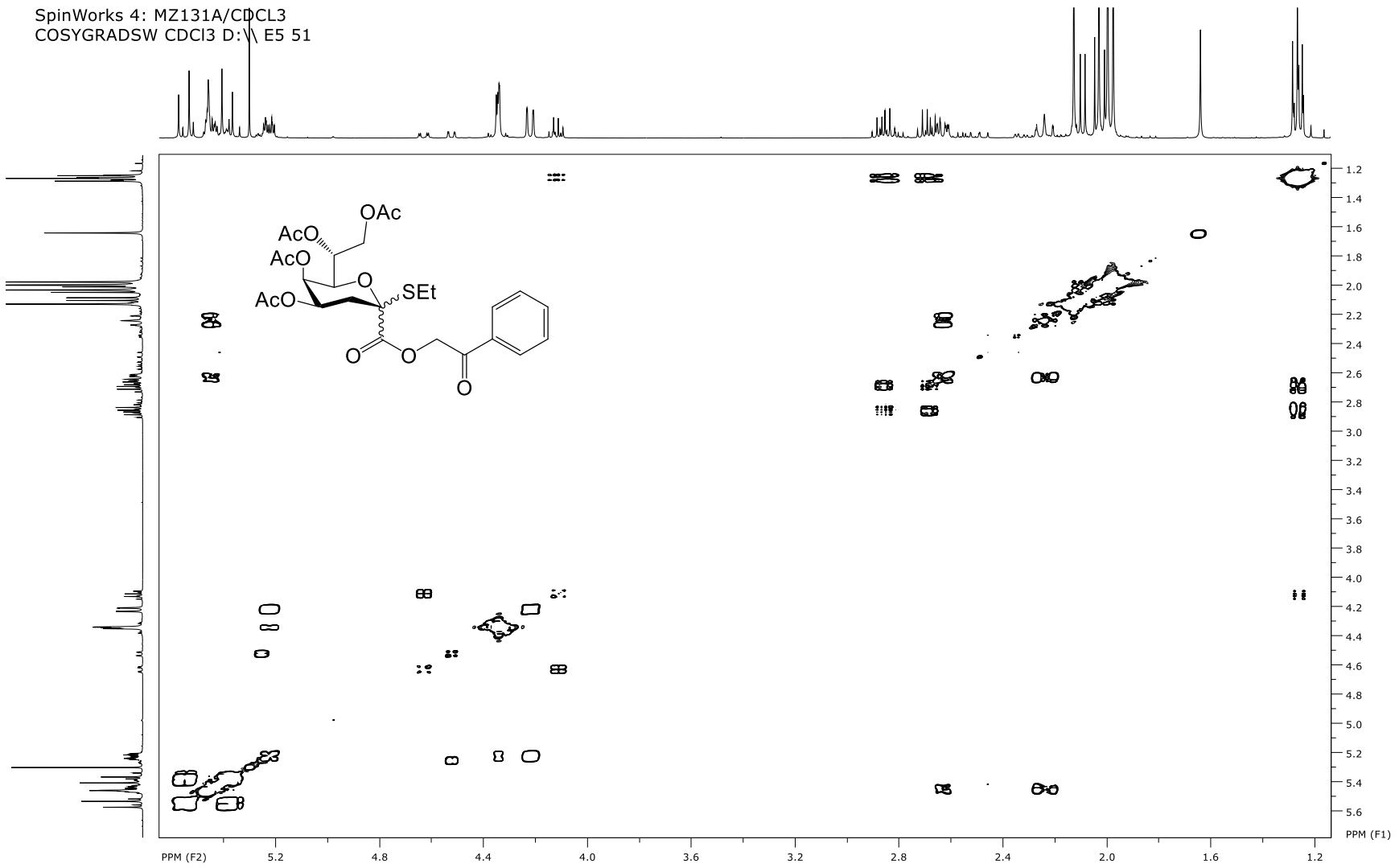
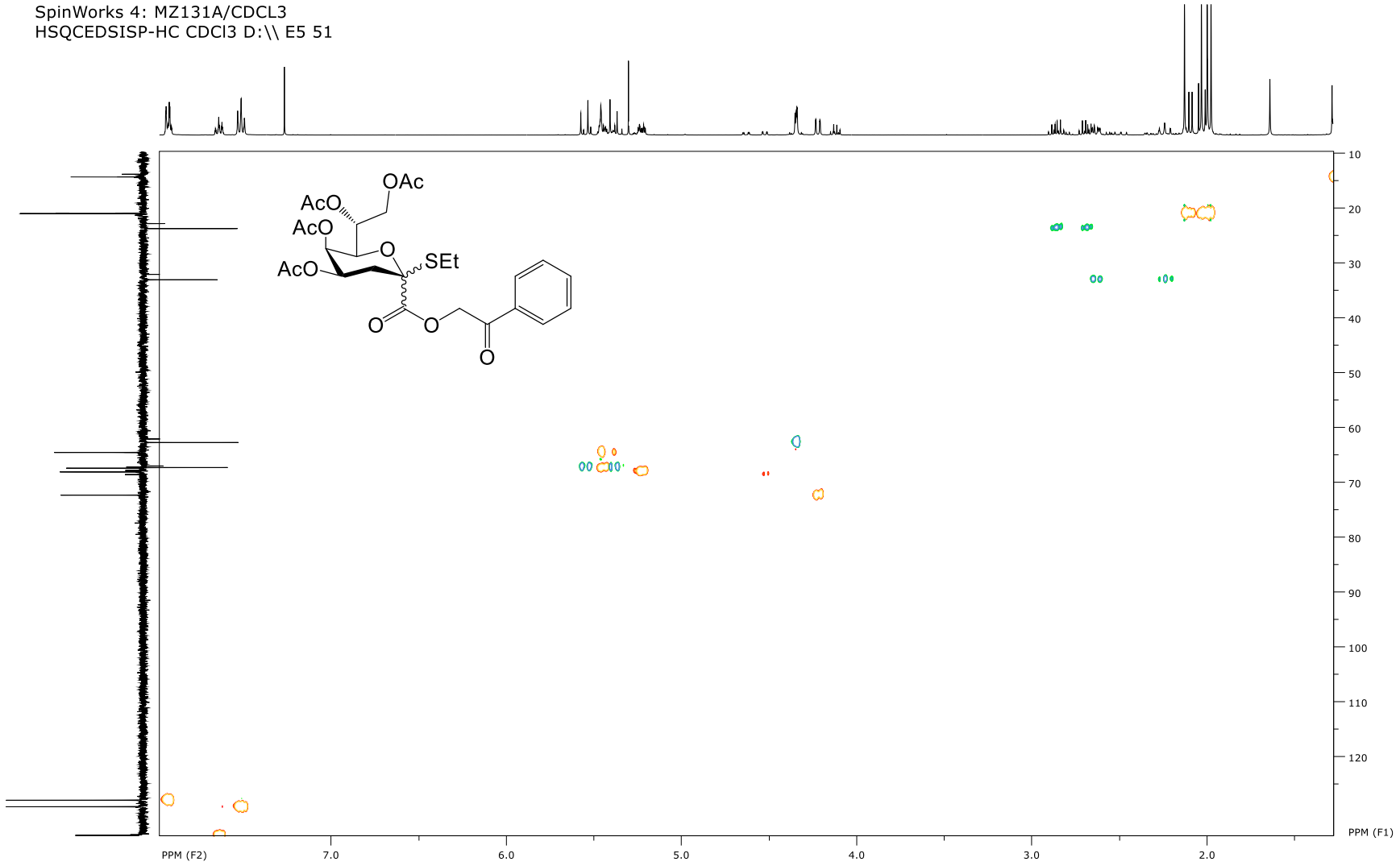
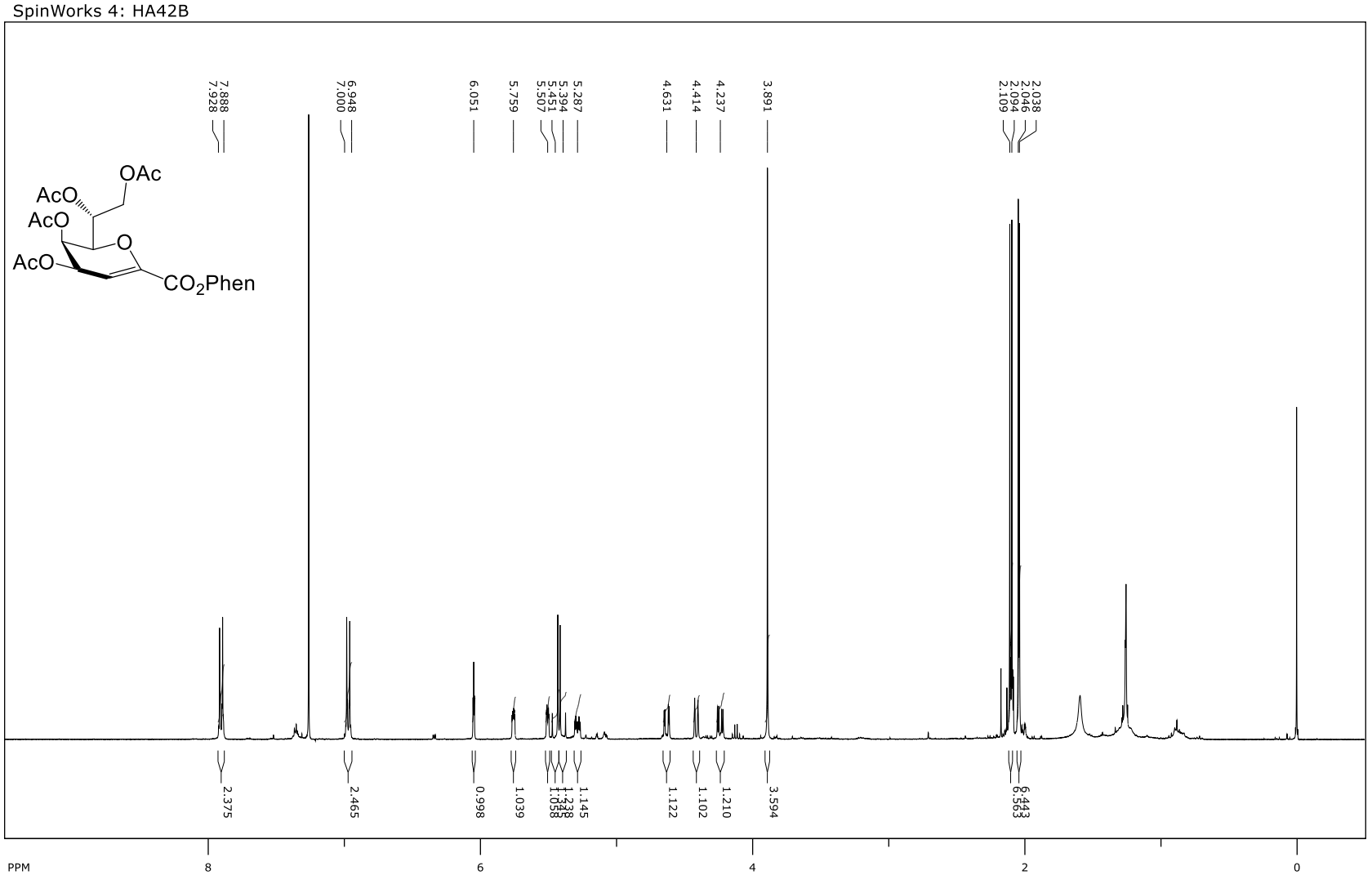


2D HSQC spectra (400 MHz, $CDCl_3$) of compound **8**.



^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **16**.



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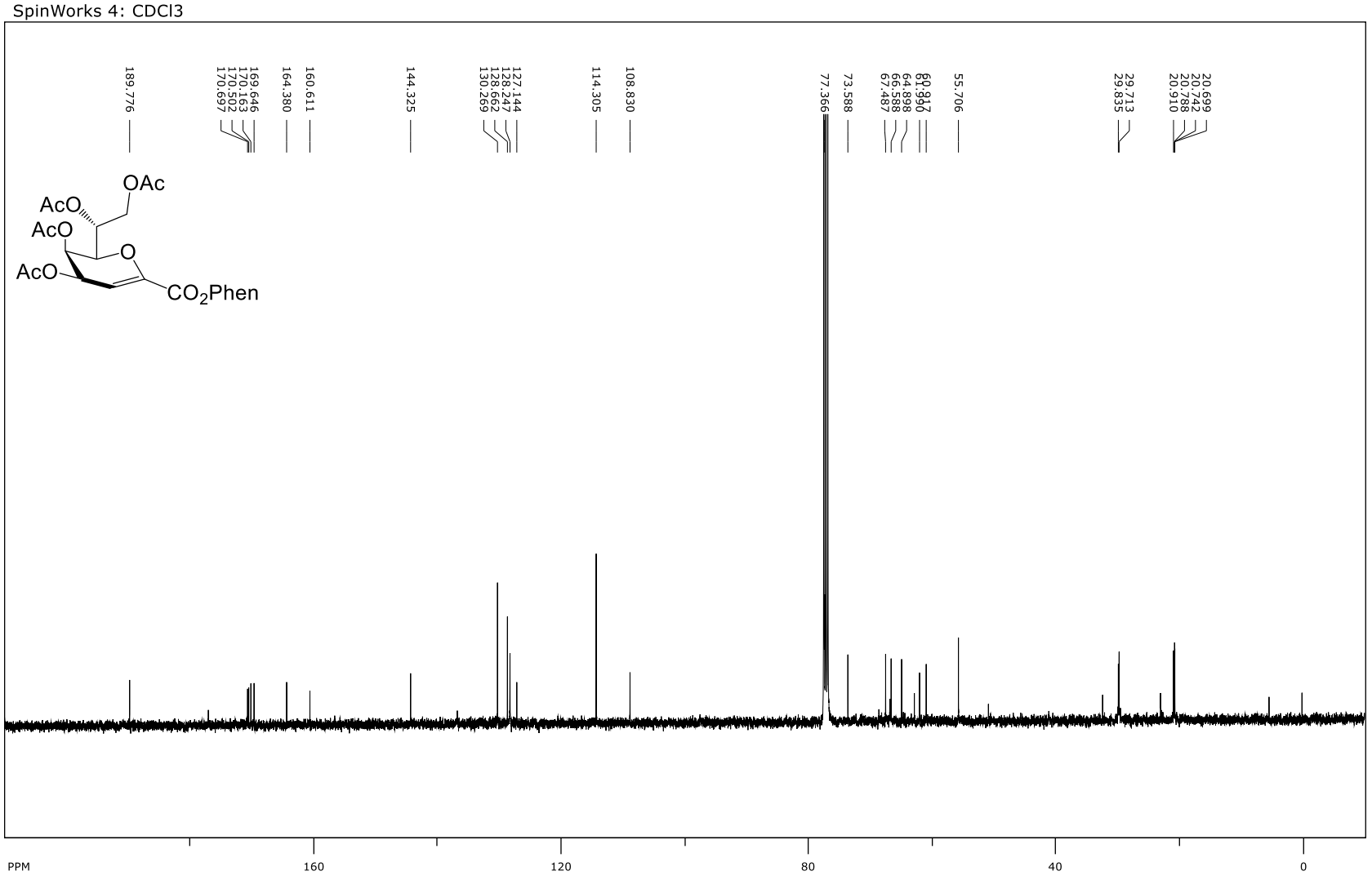

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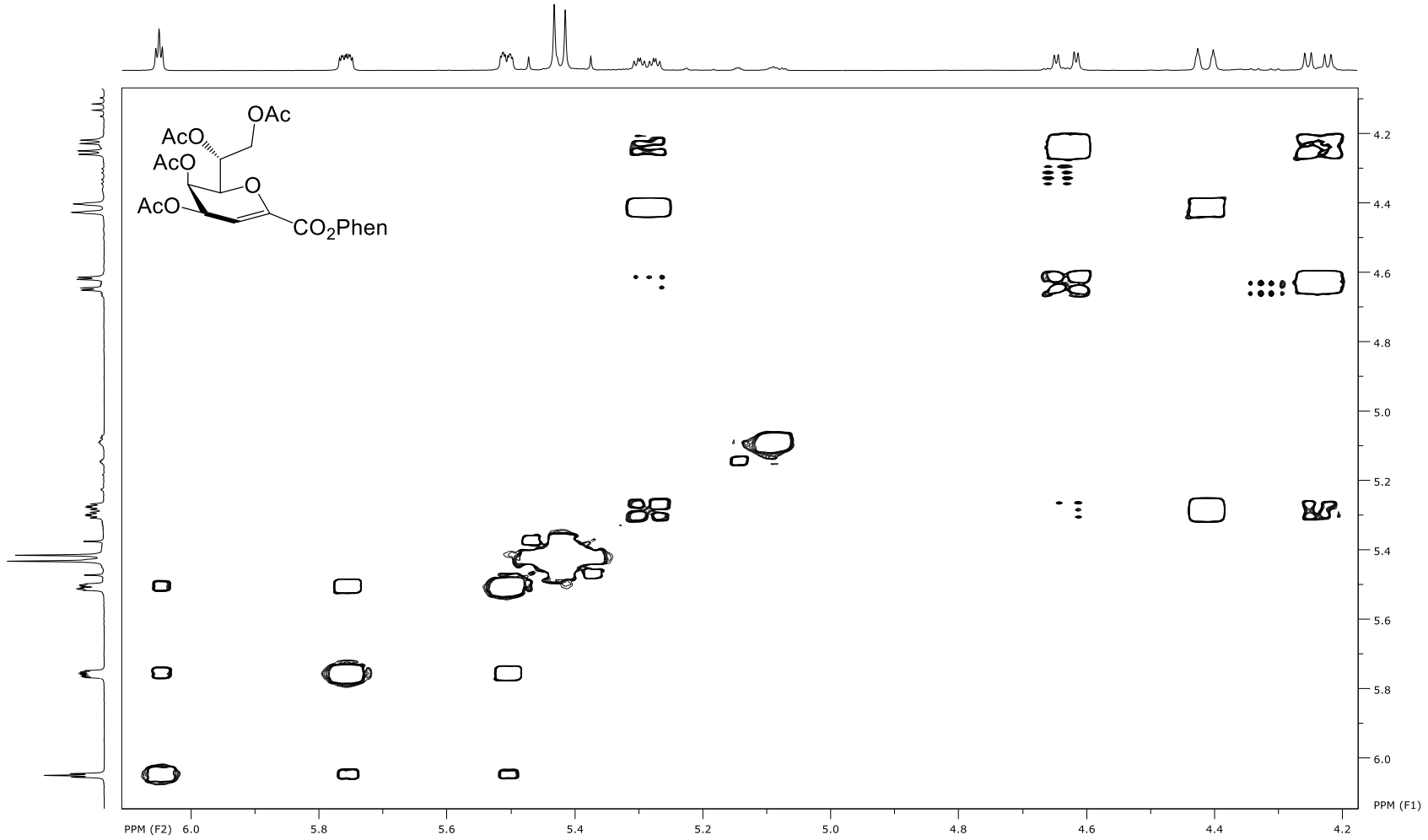

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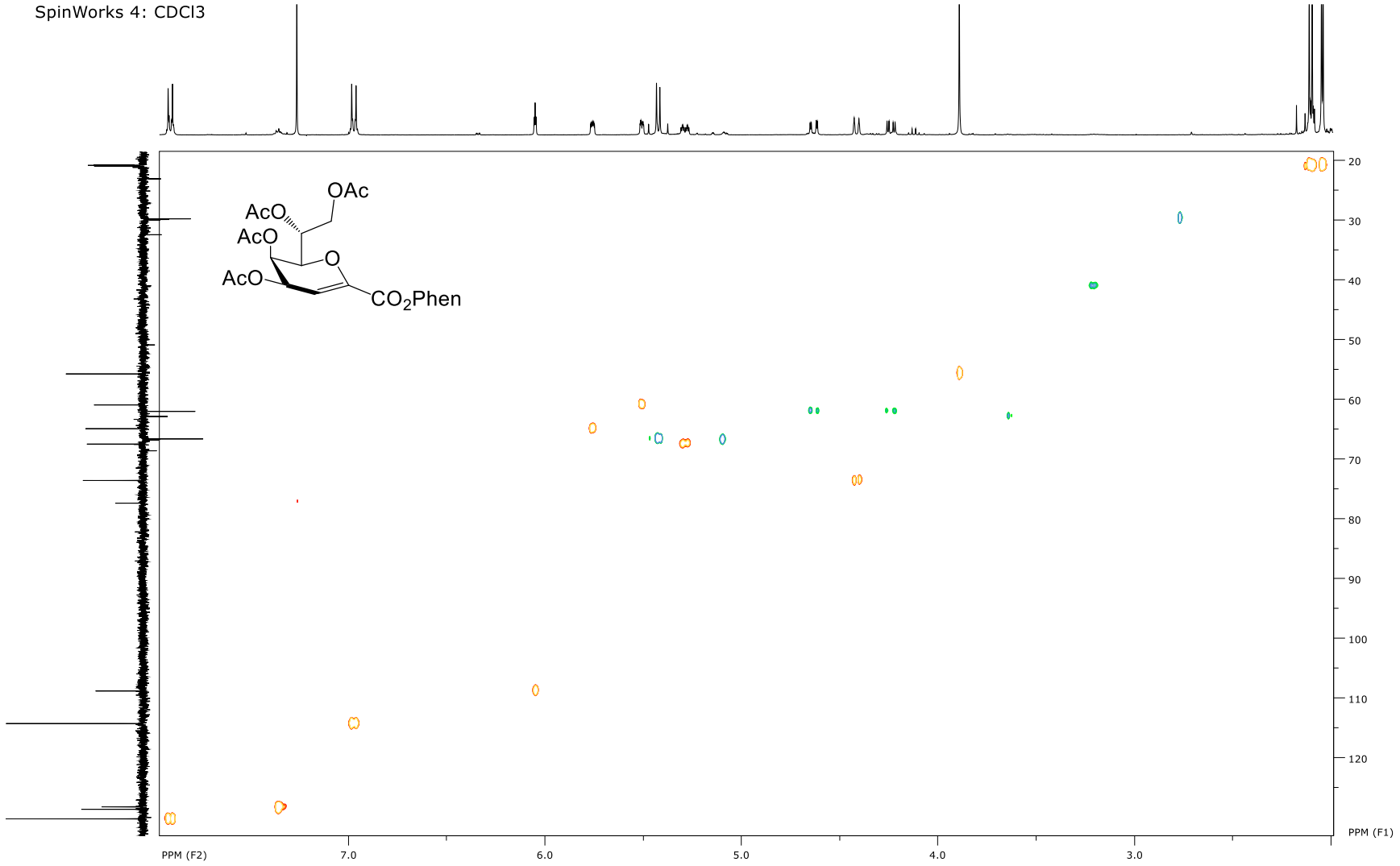
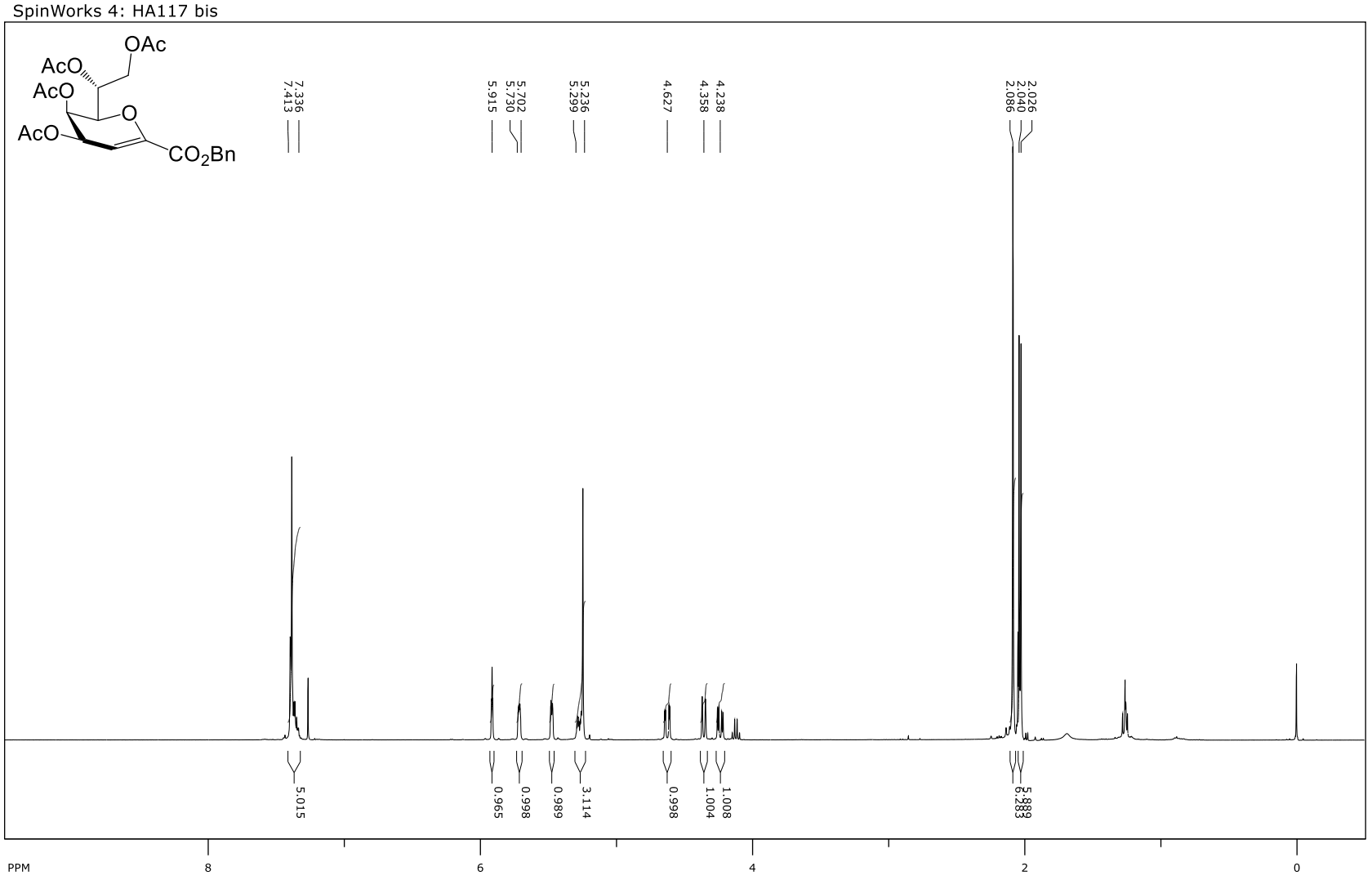
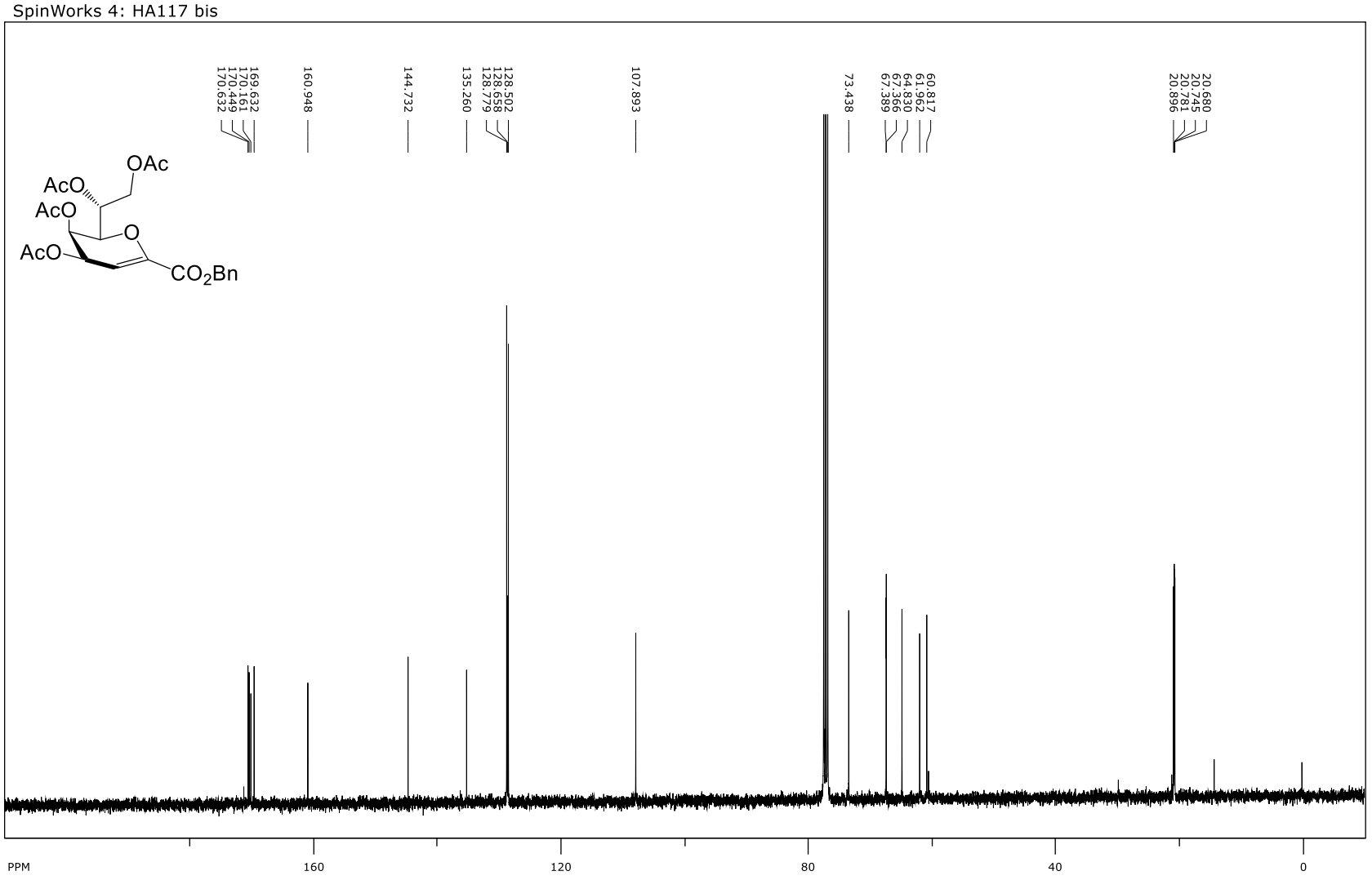


^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **18**.



^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **18**.



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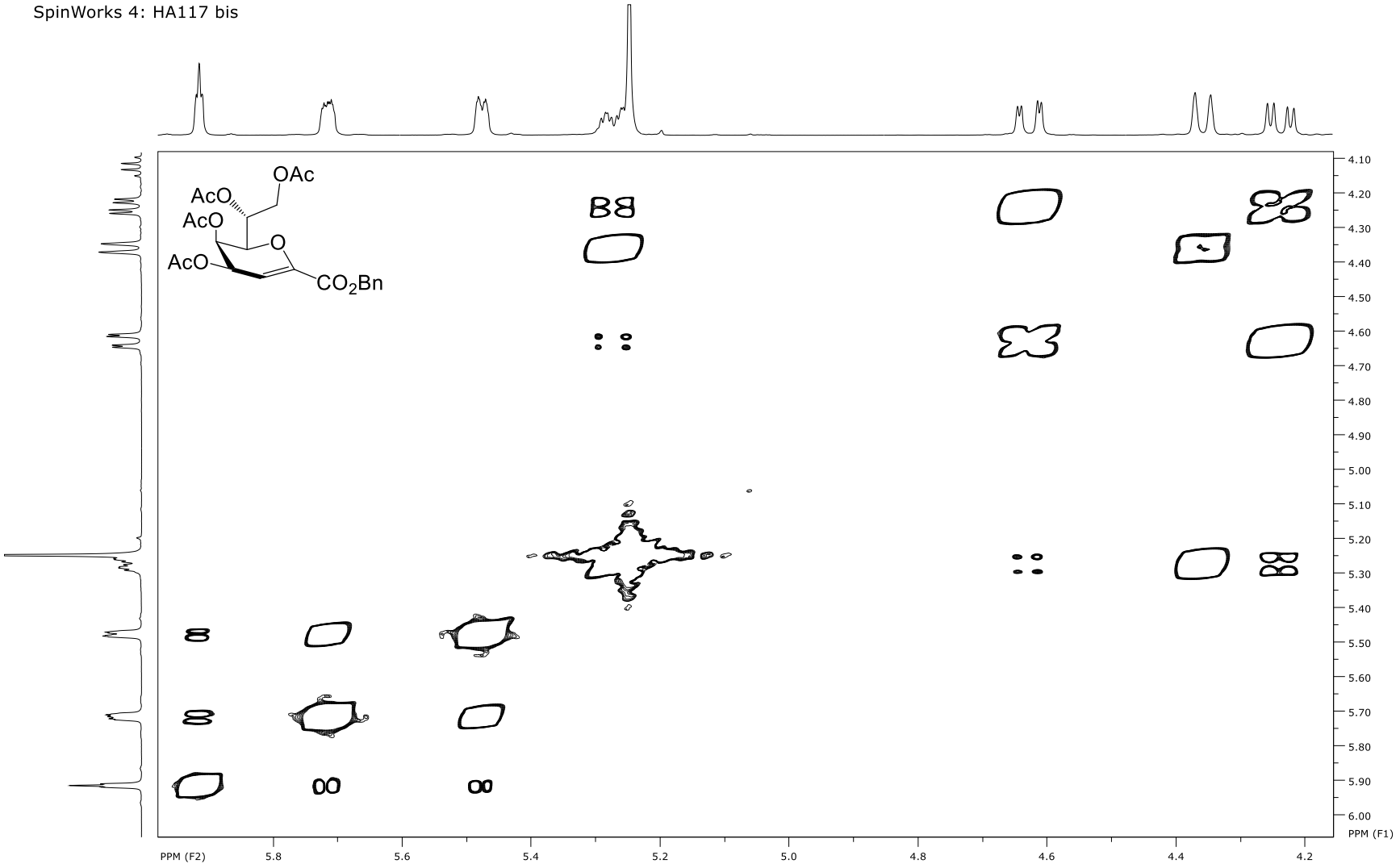
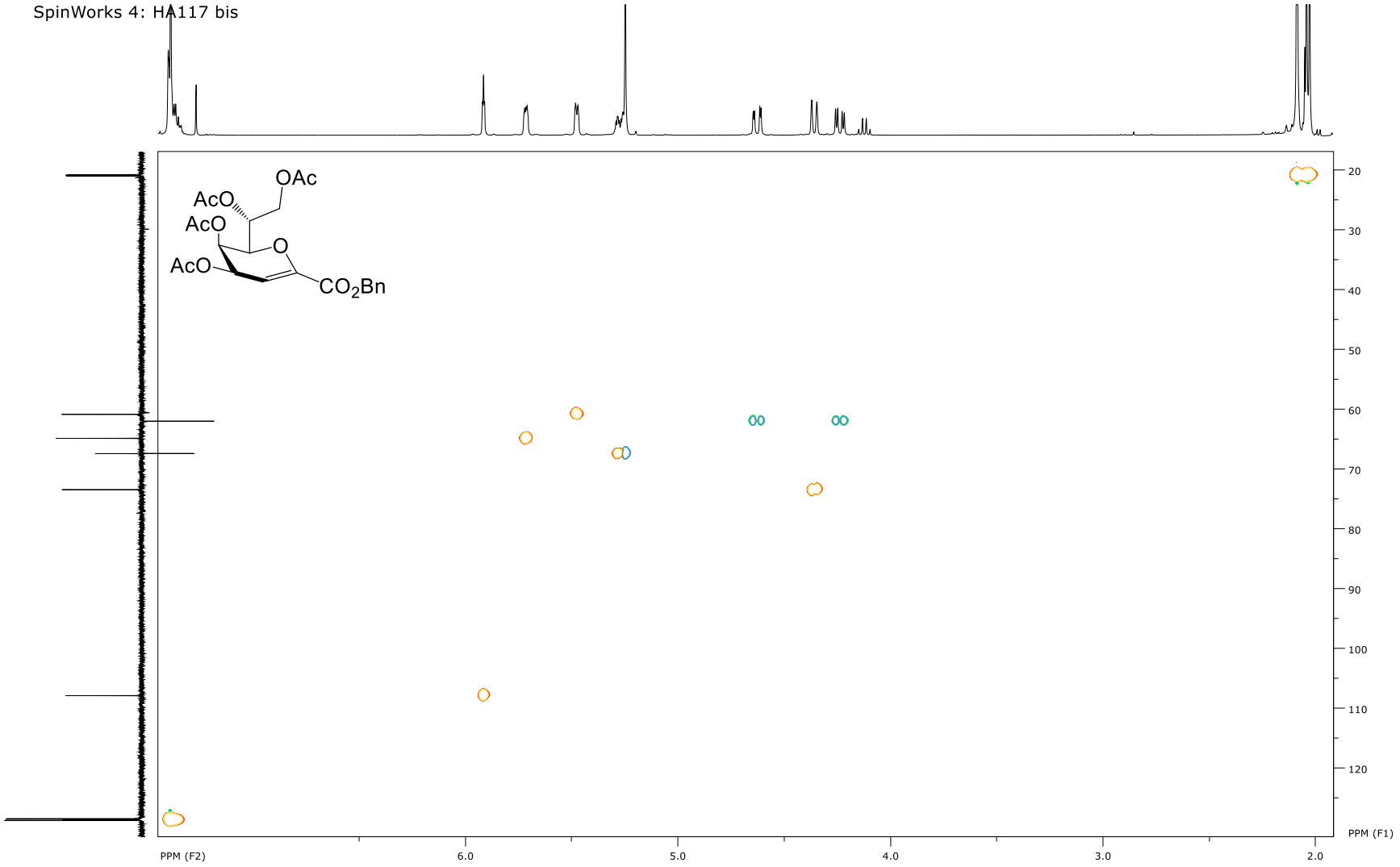
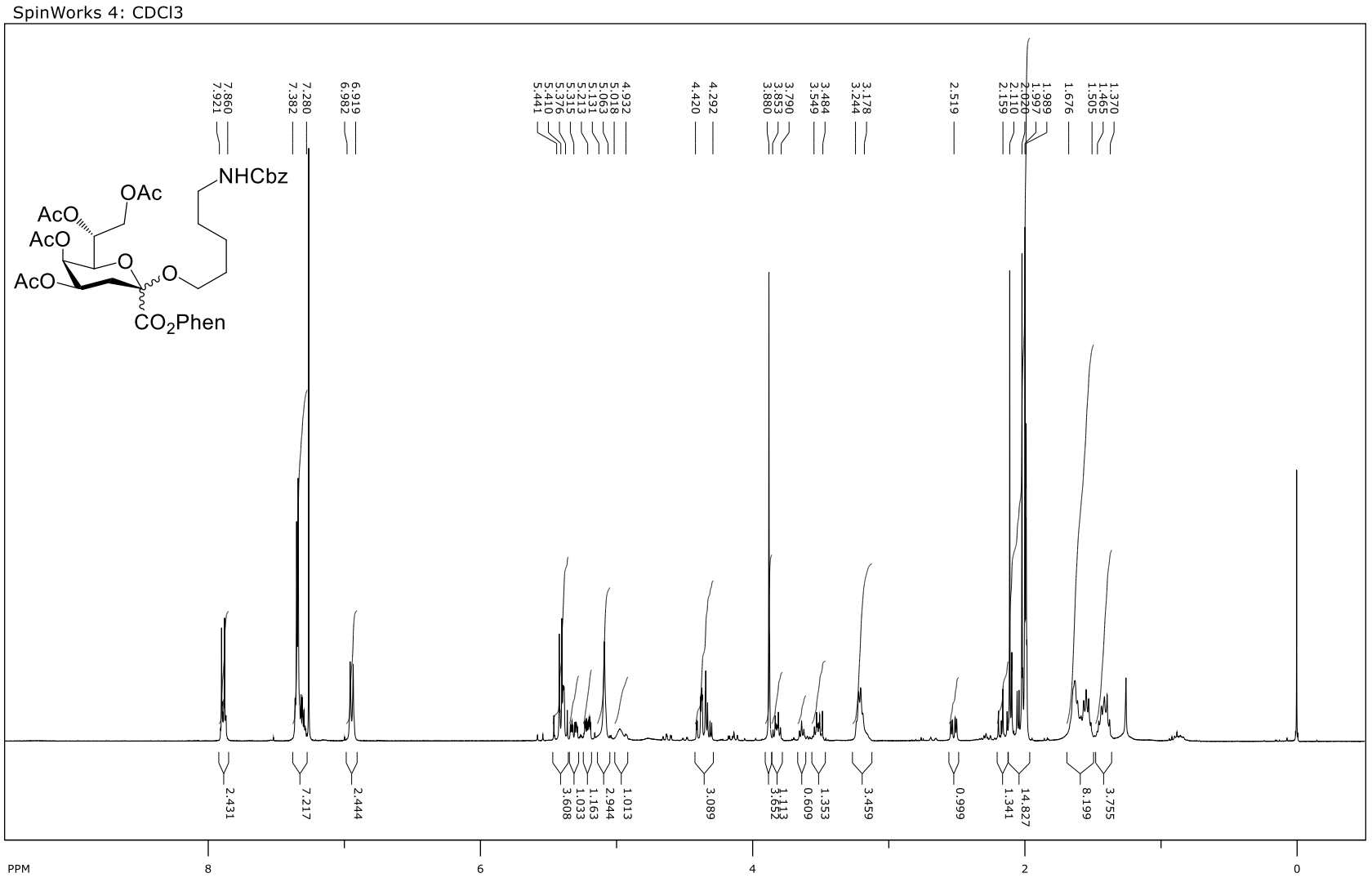


2D HSQC spectra (400 MHz, $CDCl_3$) of compound **18**.



^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **15** (β majo).



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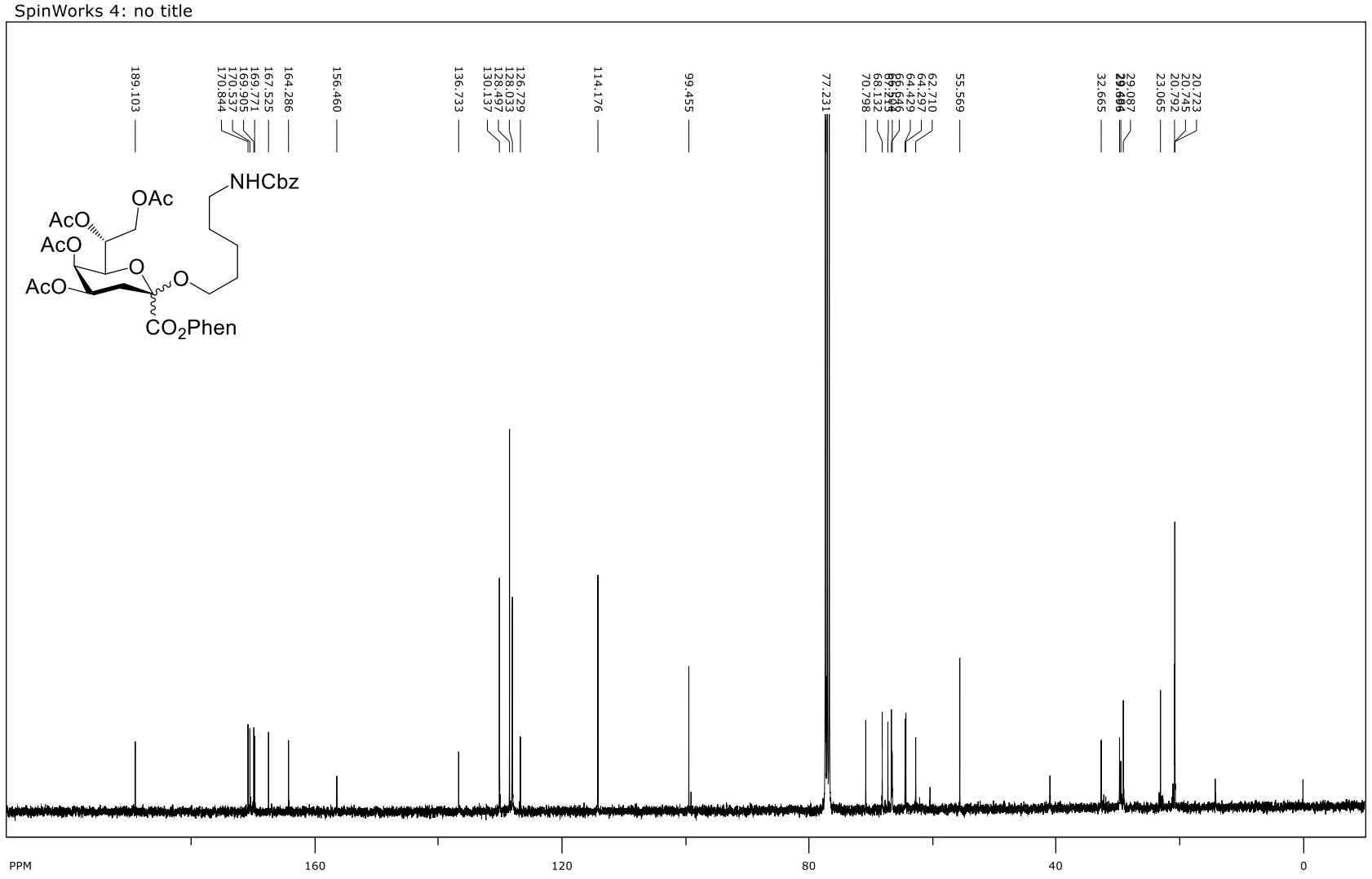
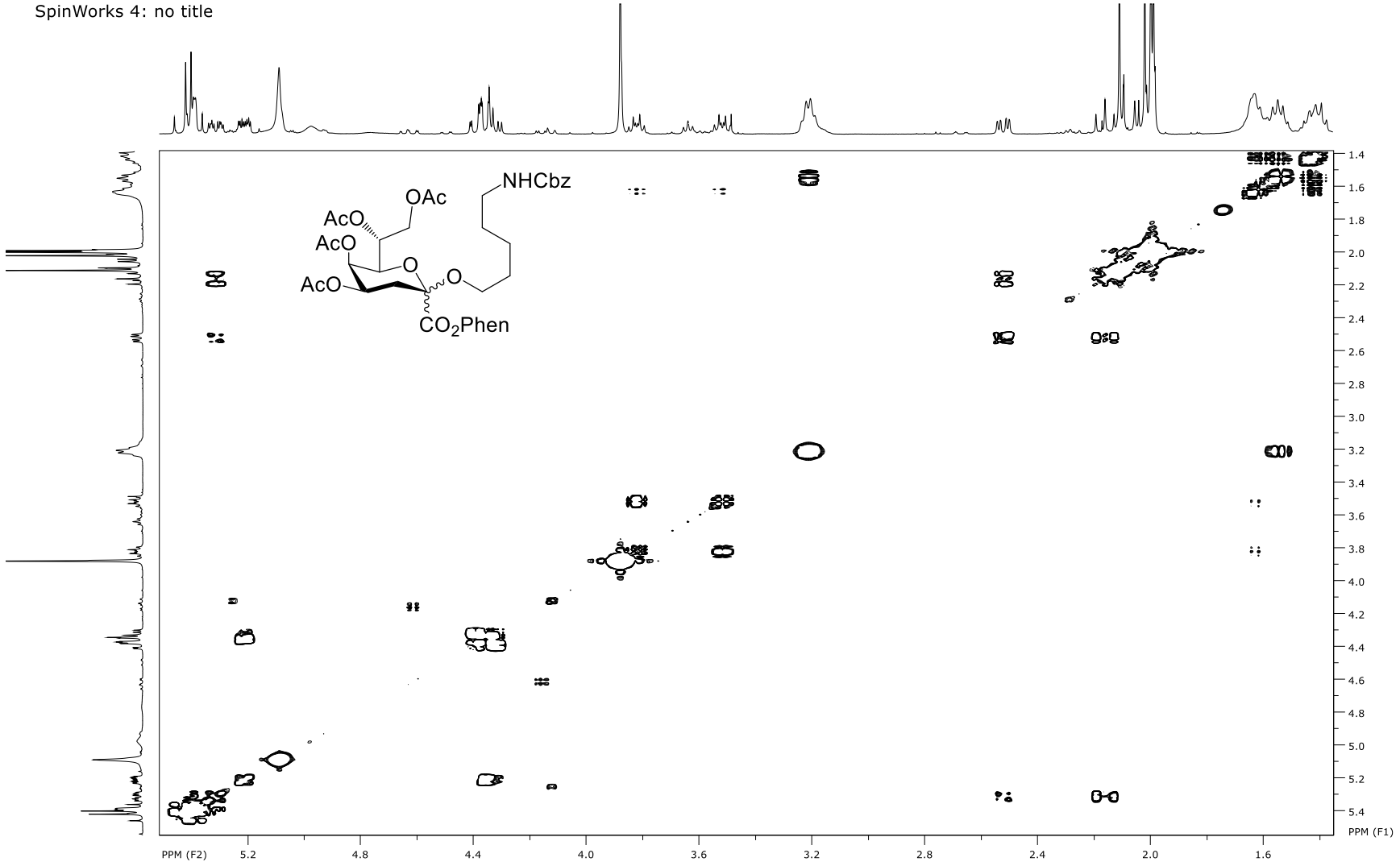
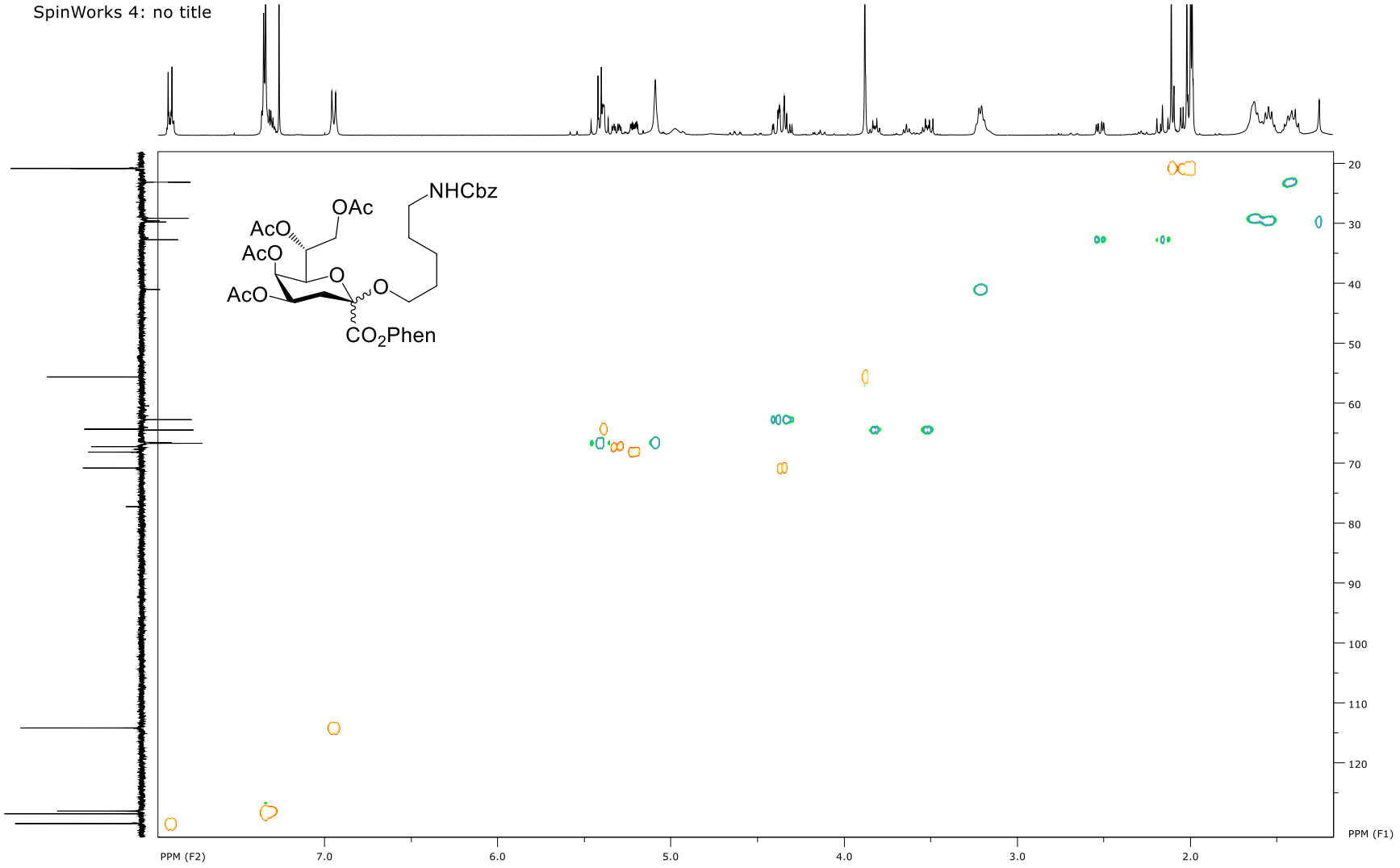


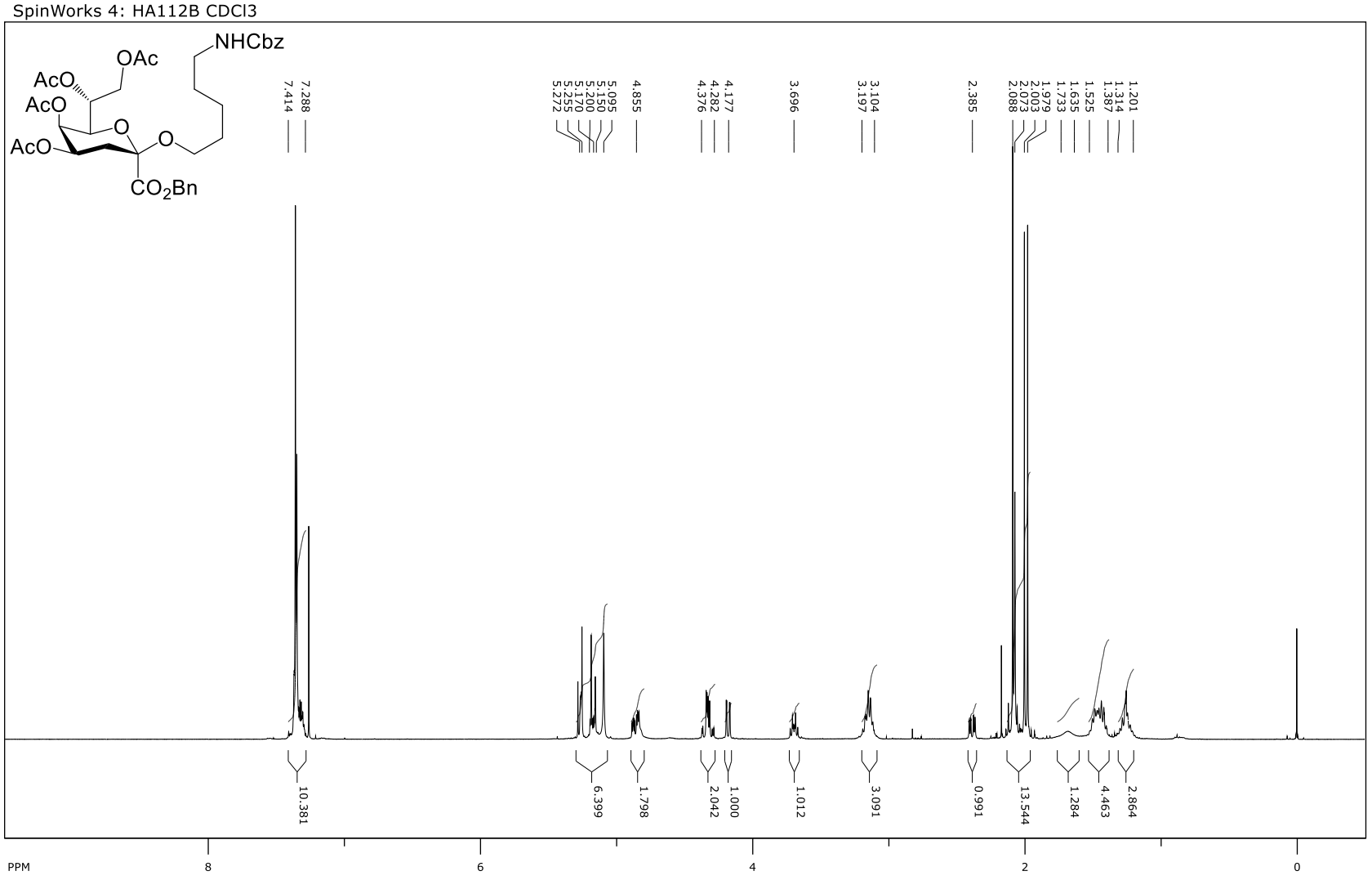
2D COSY spectra (400 MHz, $CDCl_3$) of compound **15** (β majo).



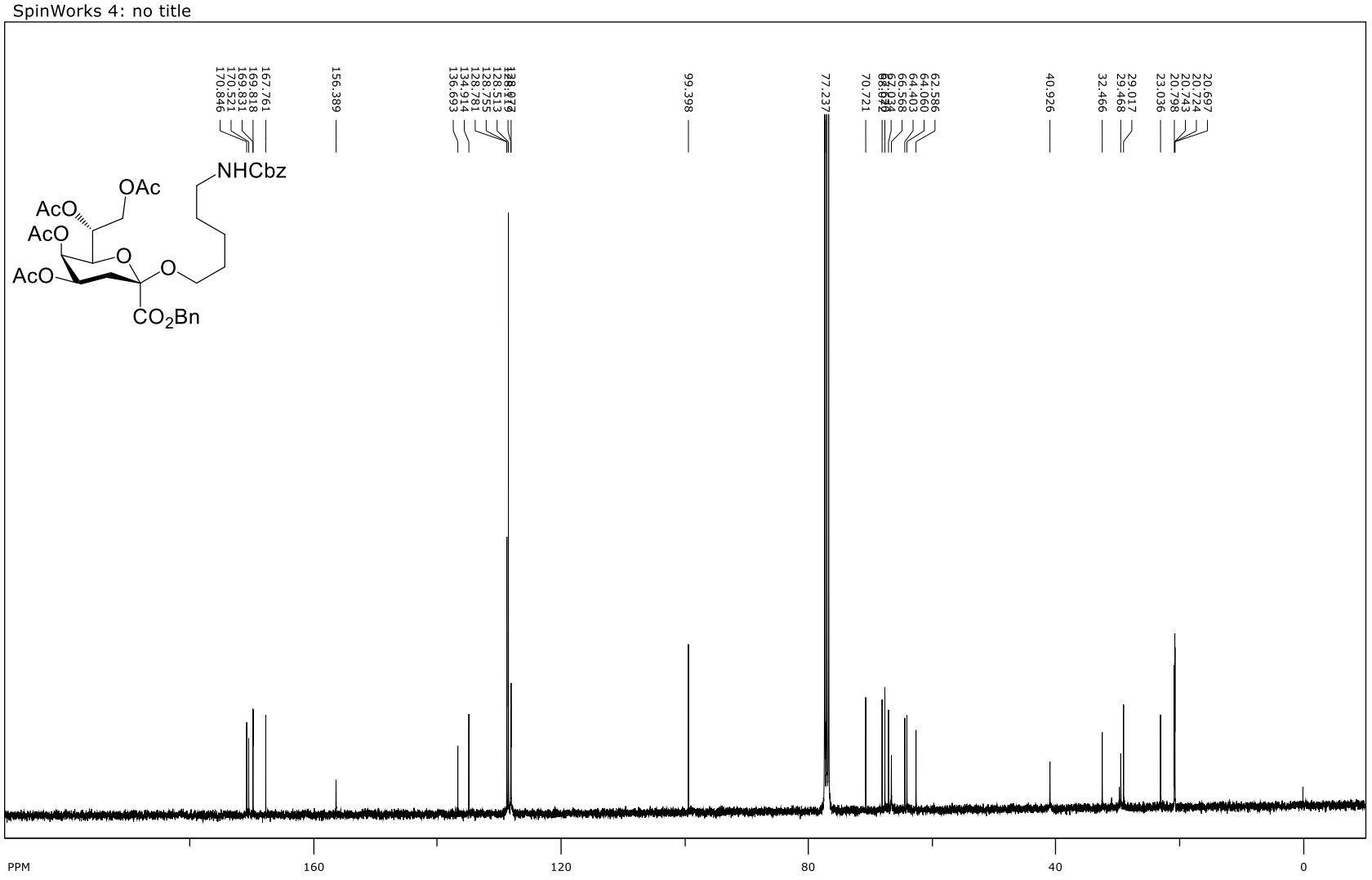
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **15** (β majo).



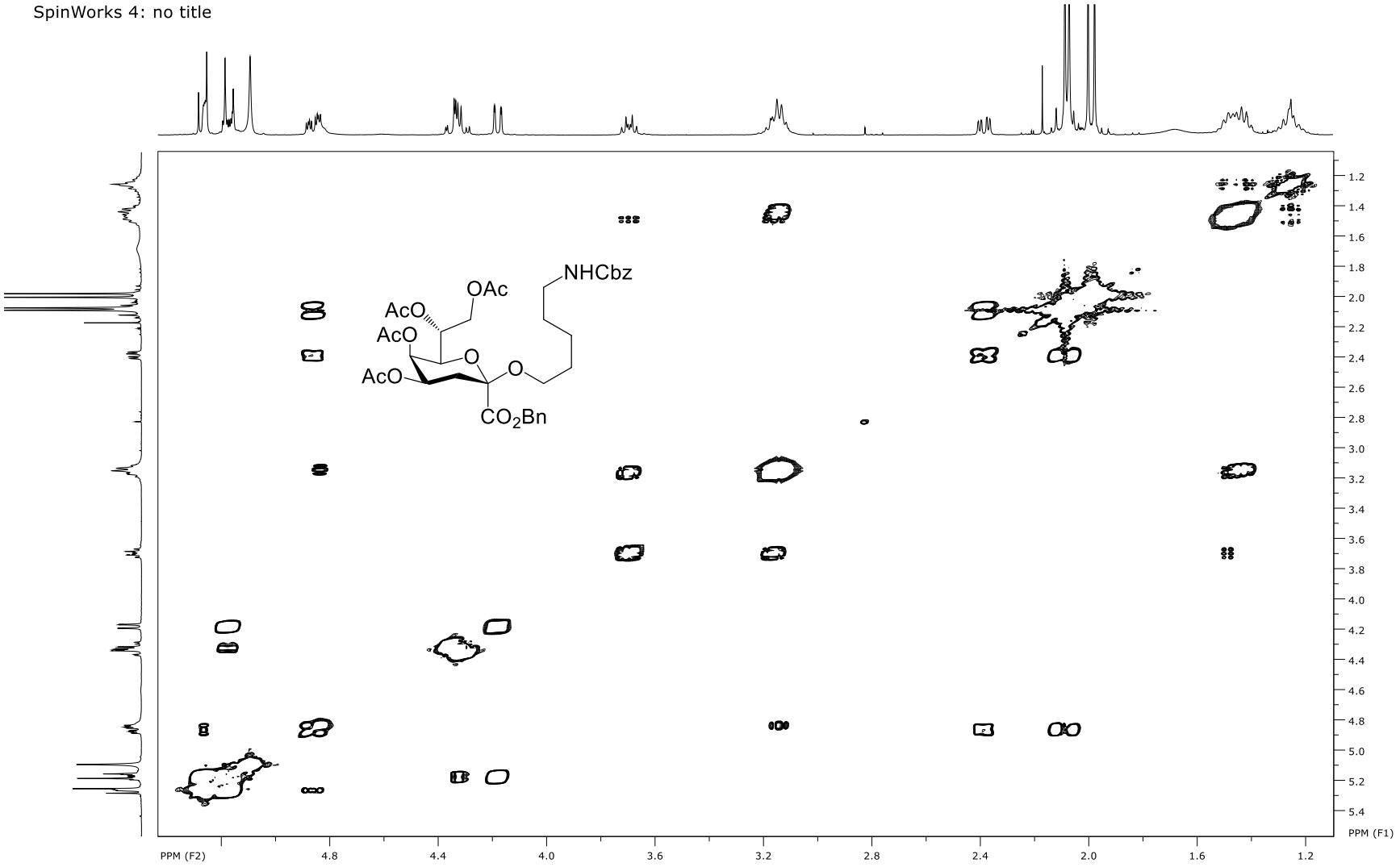
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **17*β***.



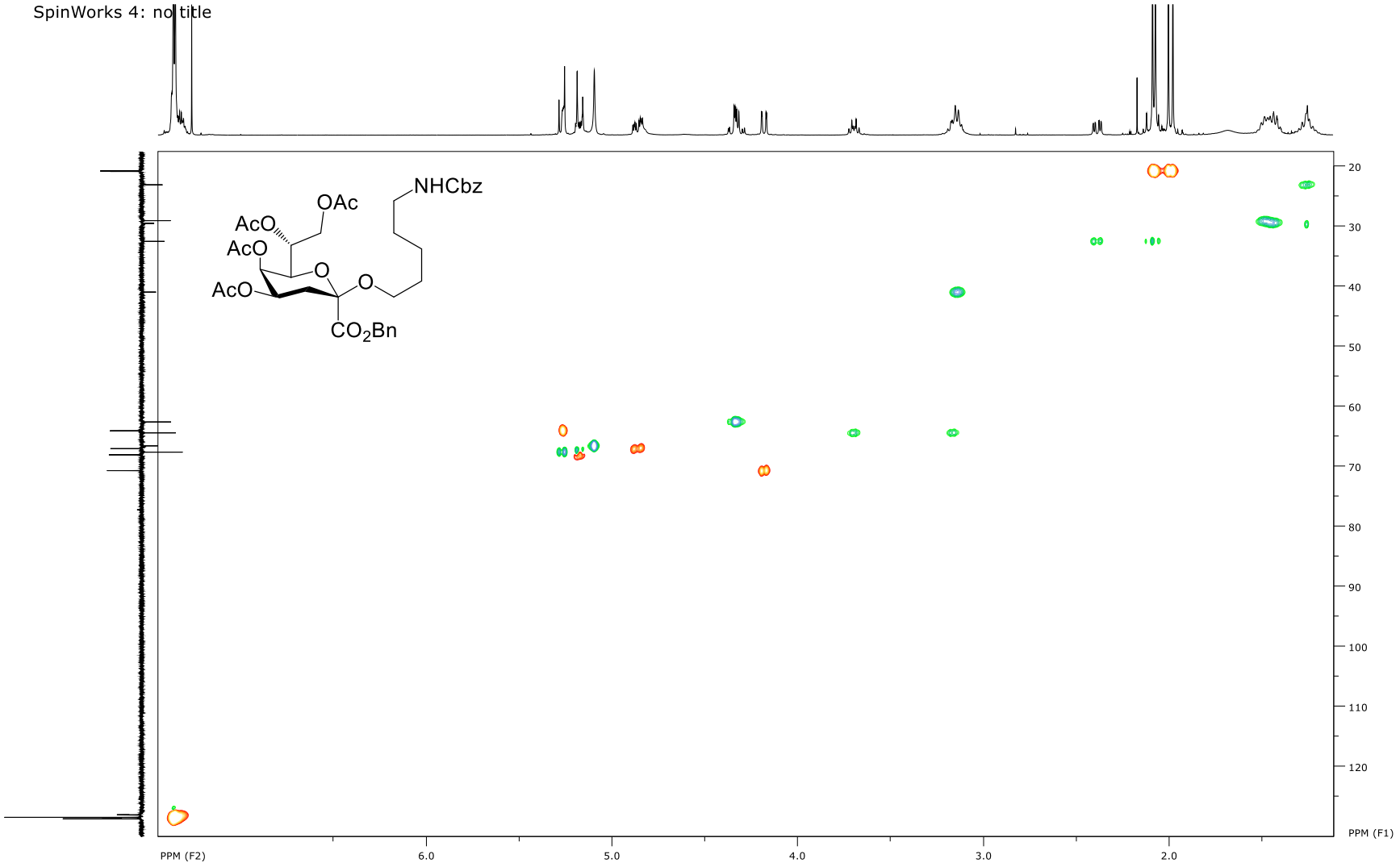
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **17*β***.



2D COSY spectra (400 MHz, $CDCl_3$) of compound **17*β***.



2D HSQC spectra (400 MHz, $CDCl_3$) of compound **17*β***.



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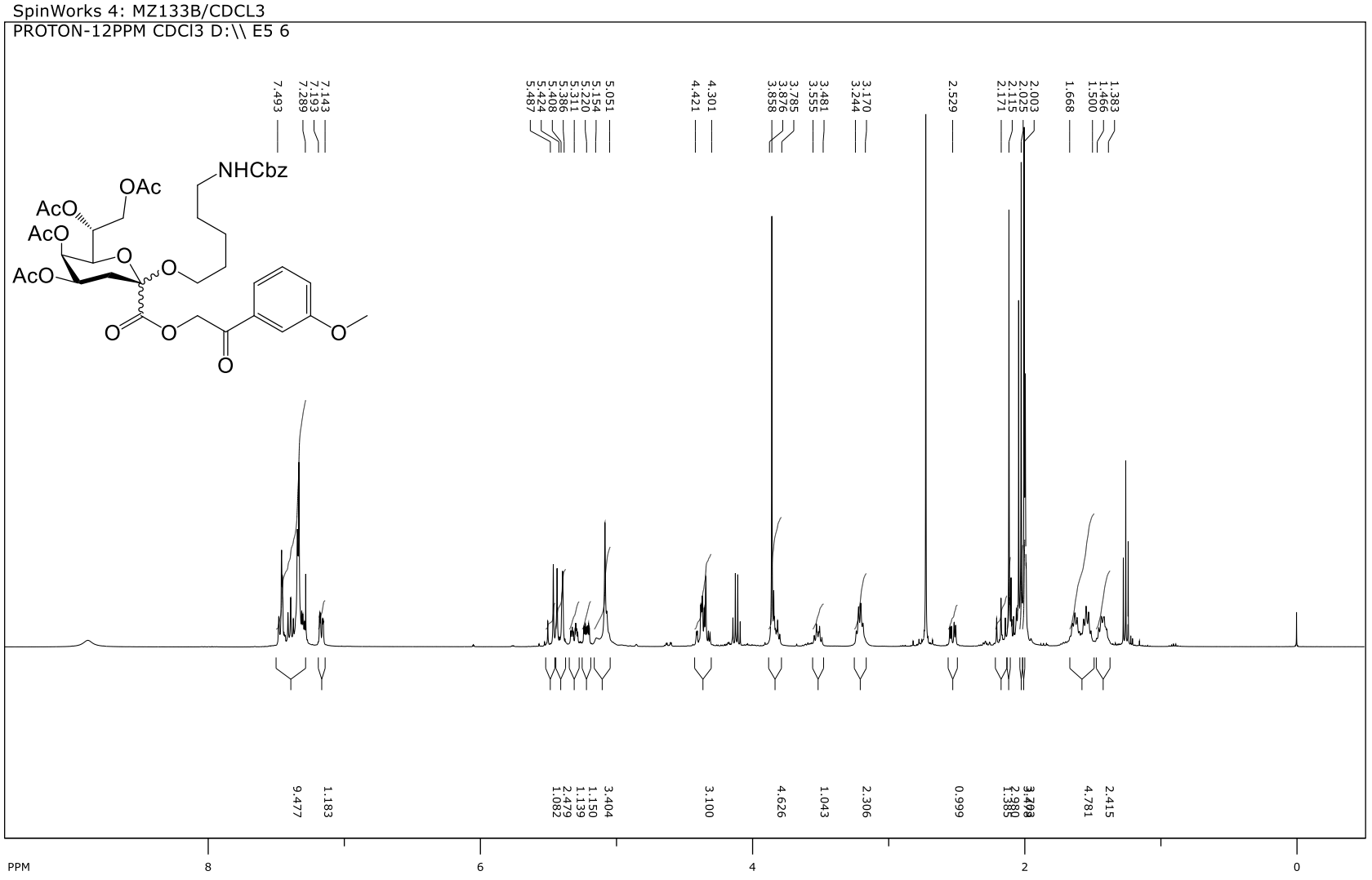
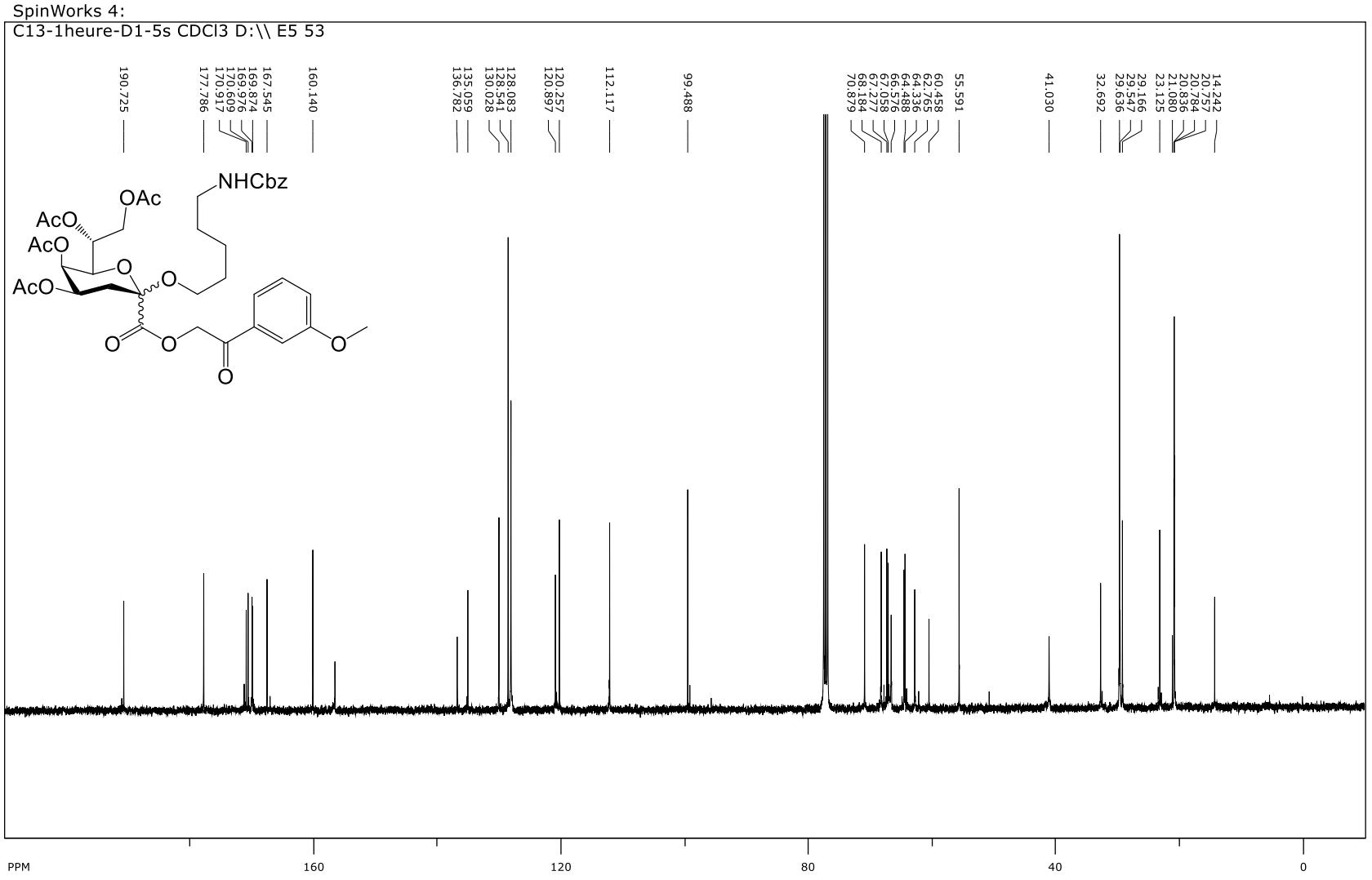


^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **19**.



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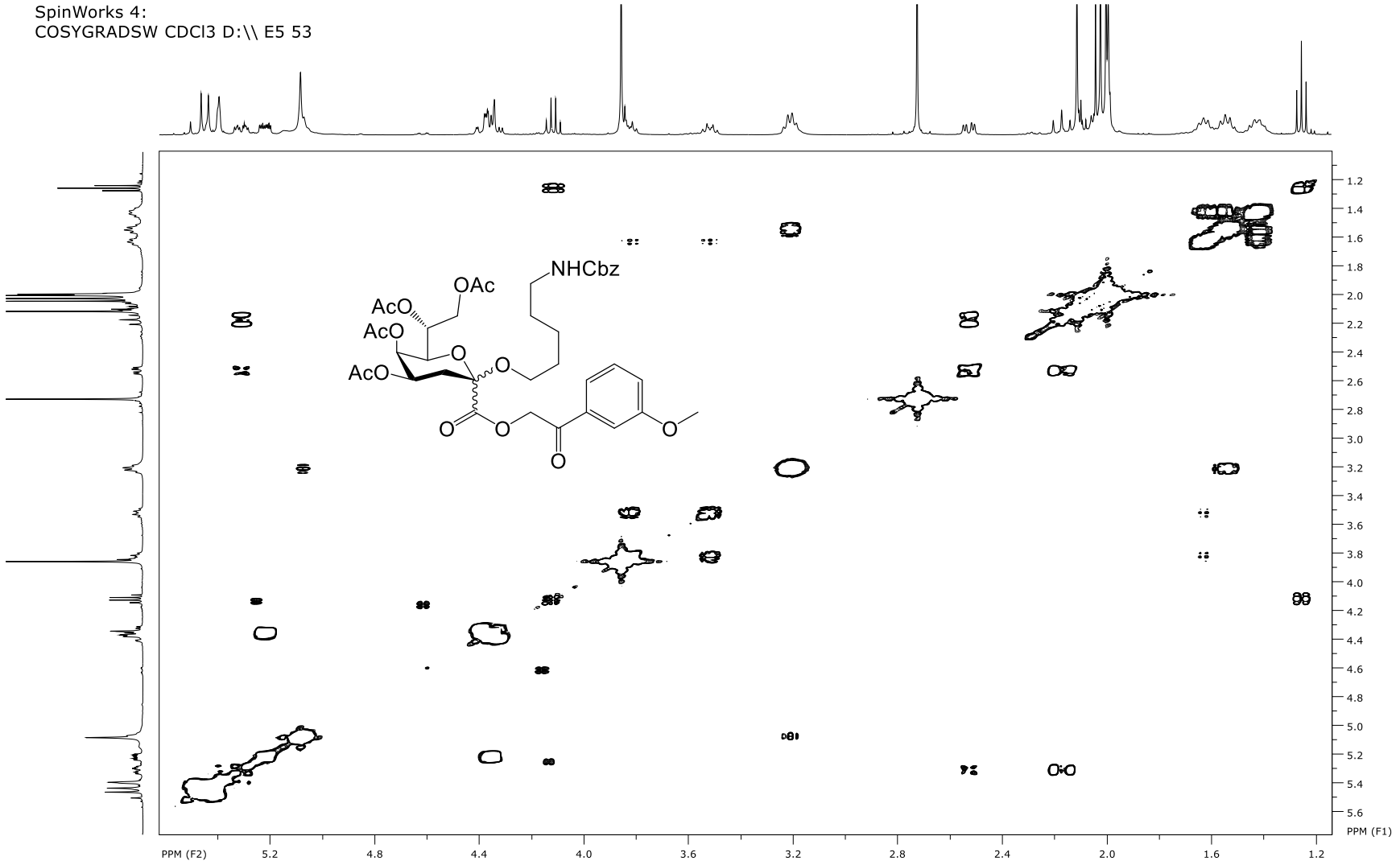
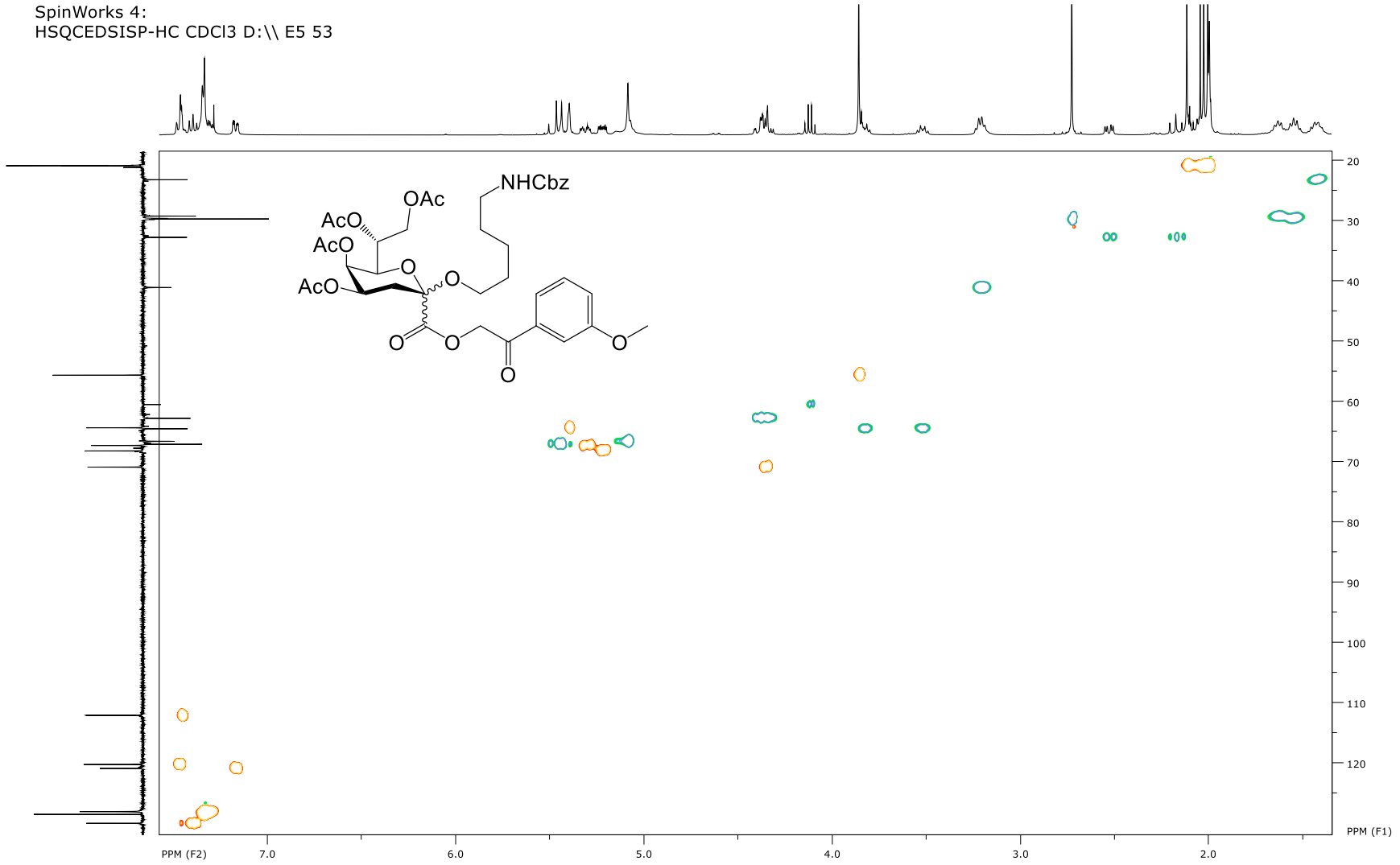
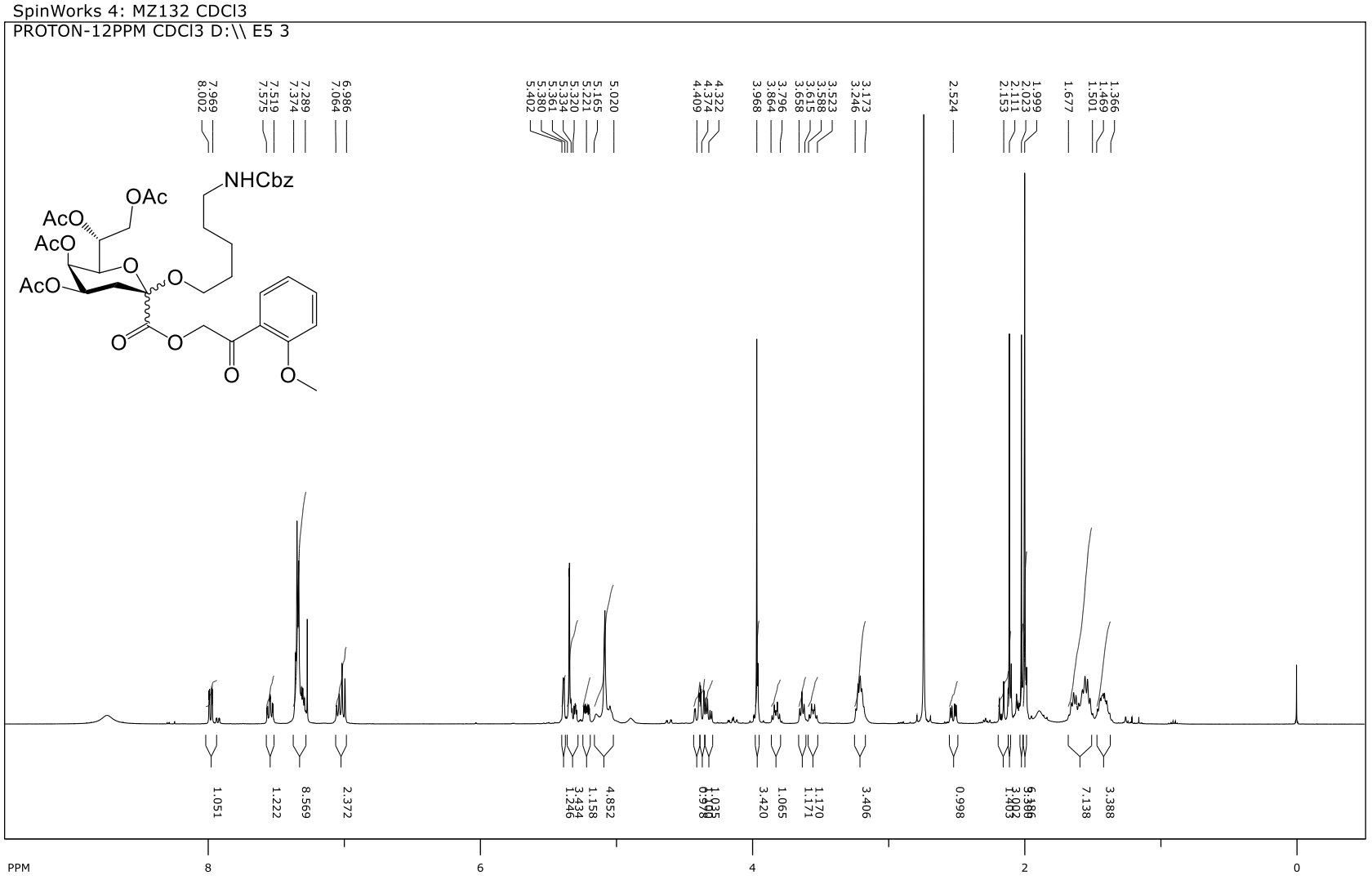


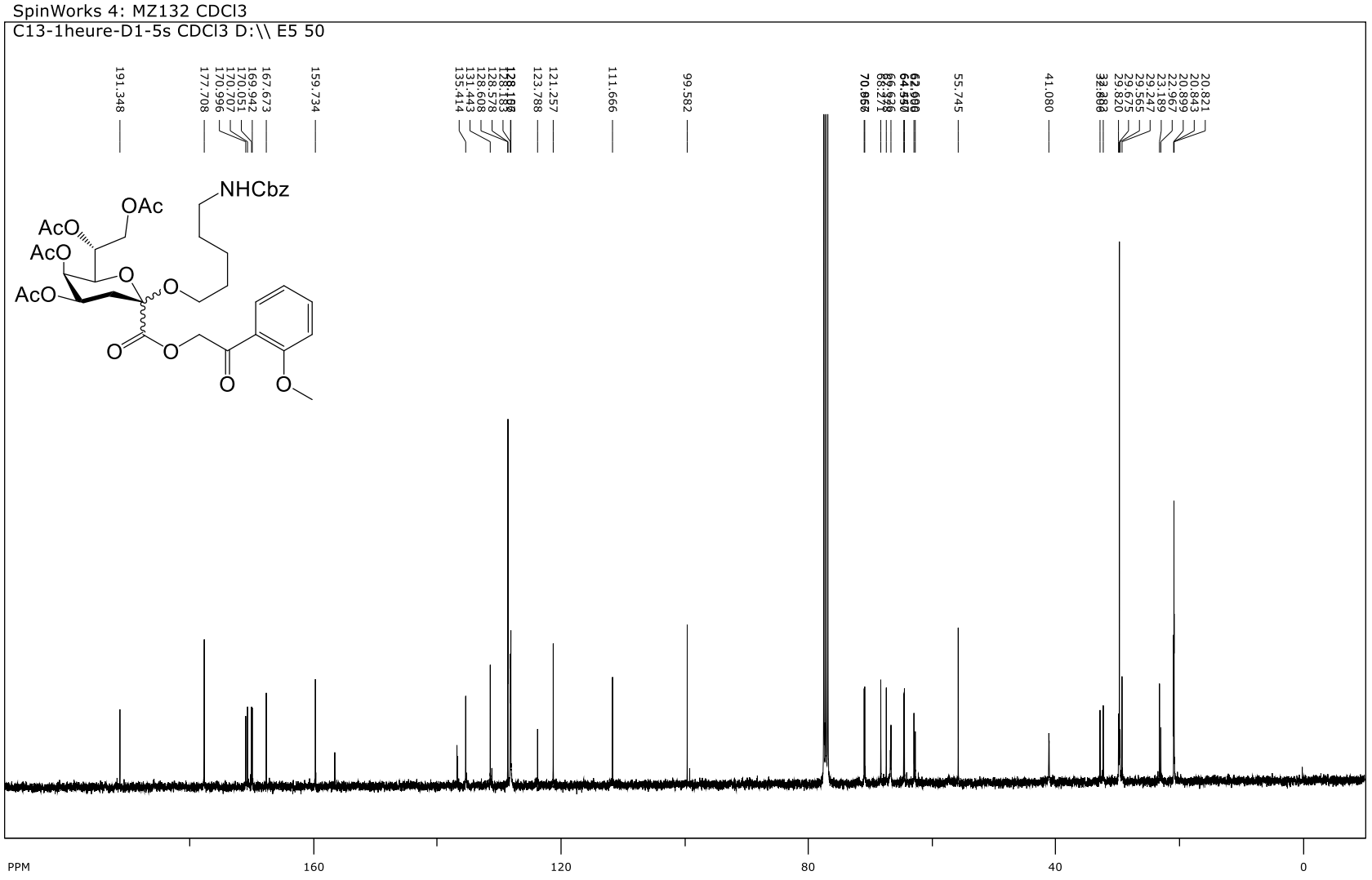
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **19**.



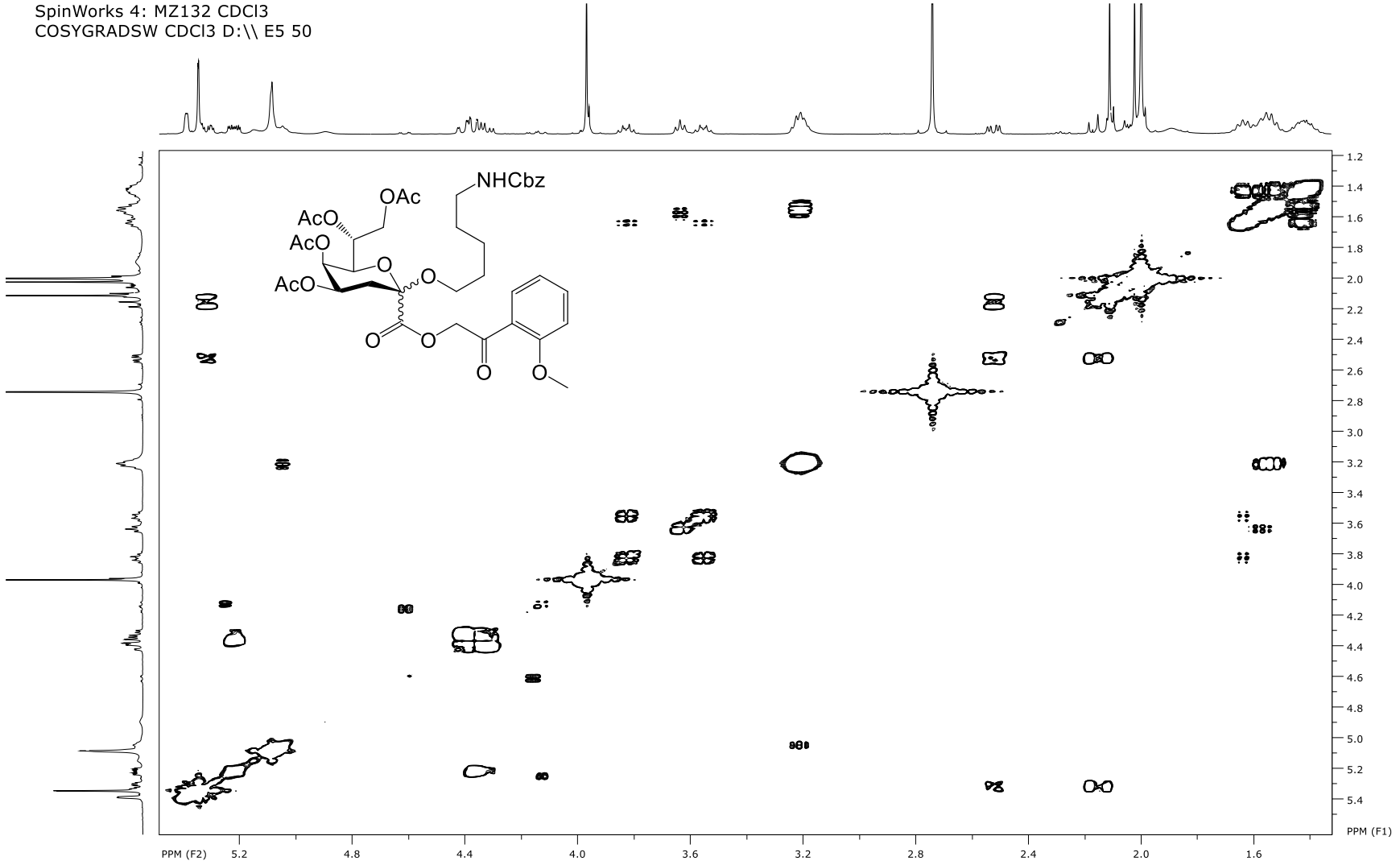
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **20**.



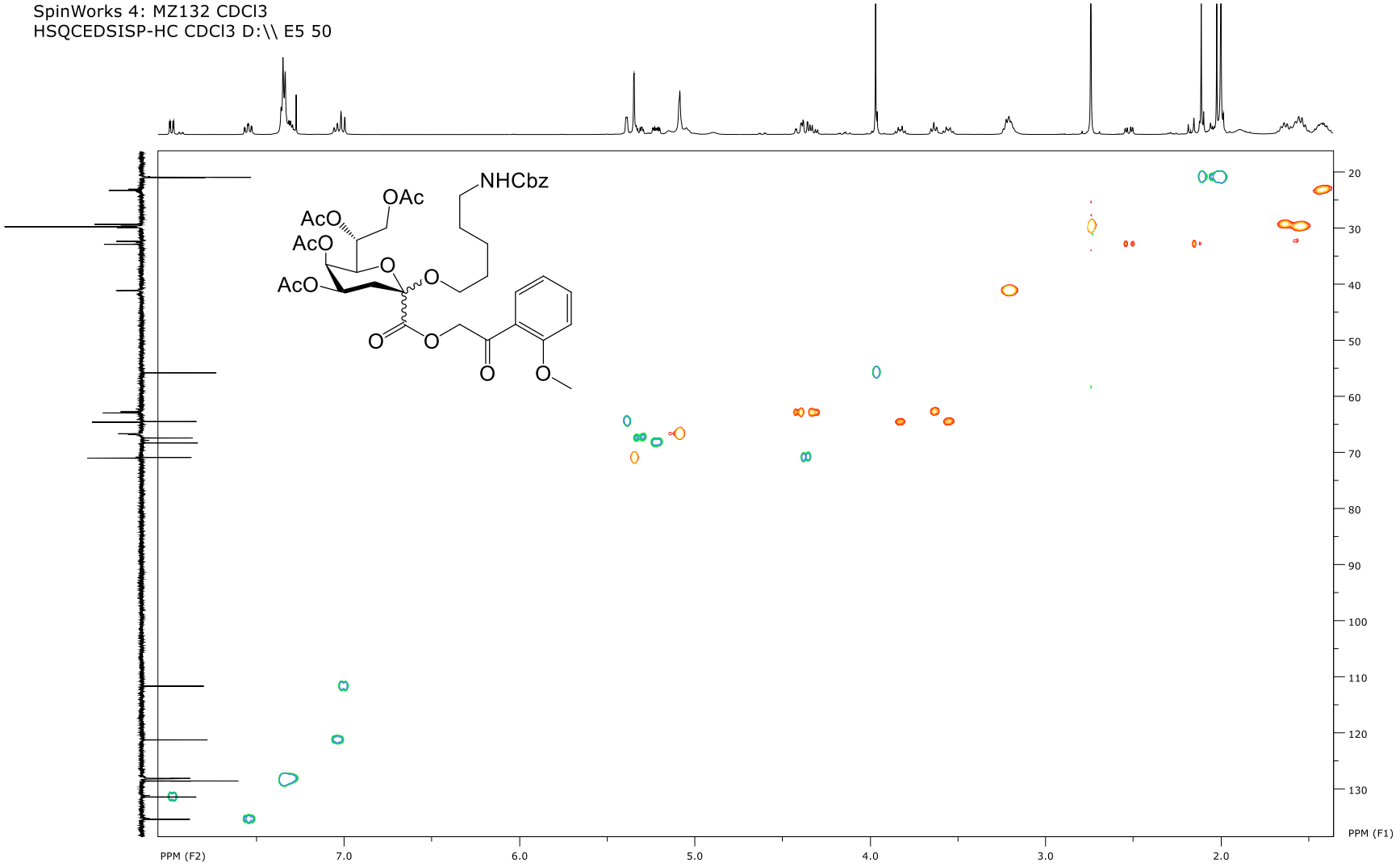
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **20**.



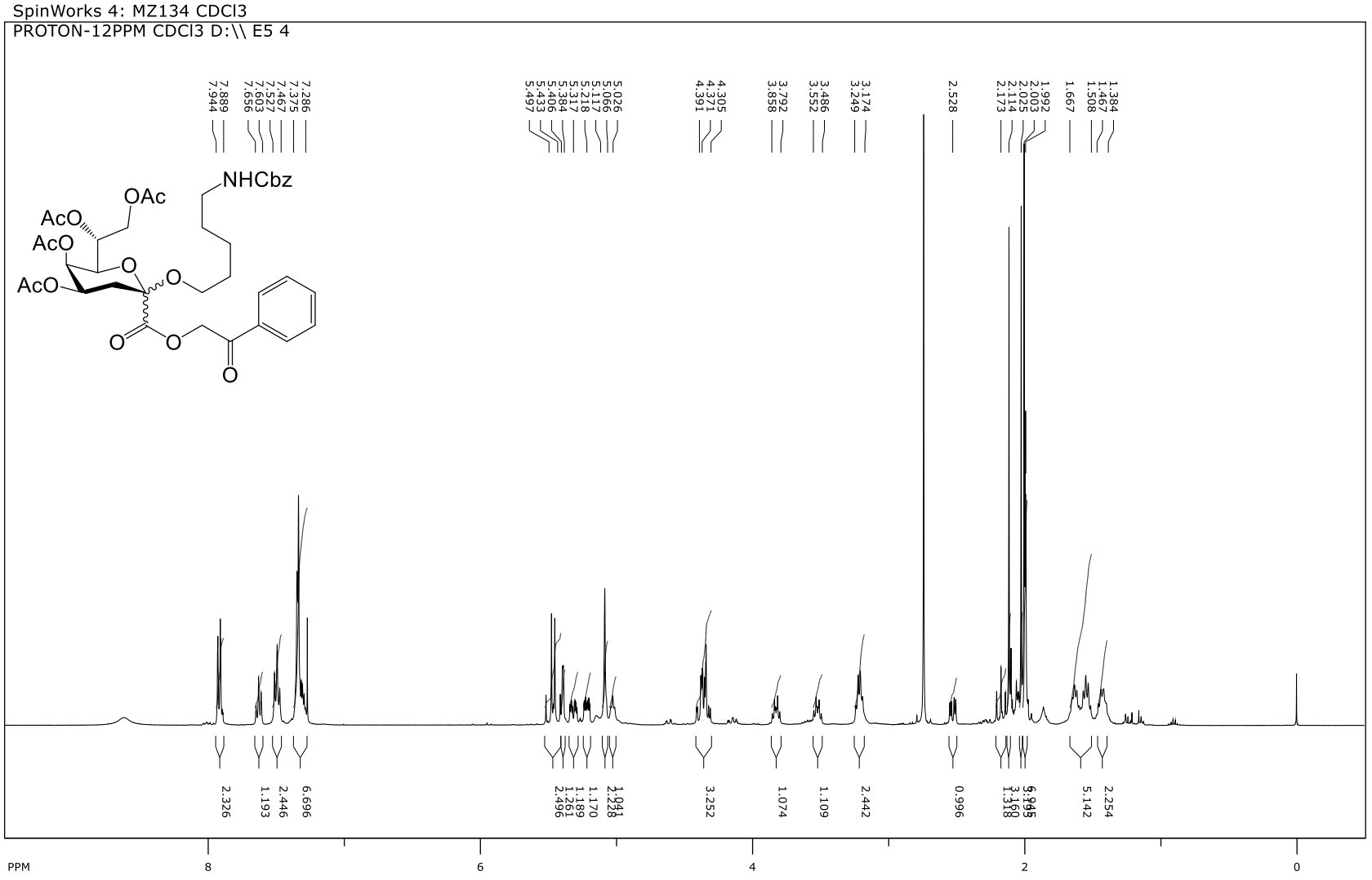
2D COSY spectra (400 MHz, $CDCl_3$) of compound **20**.



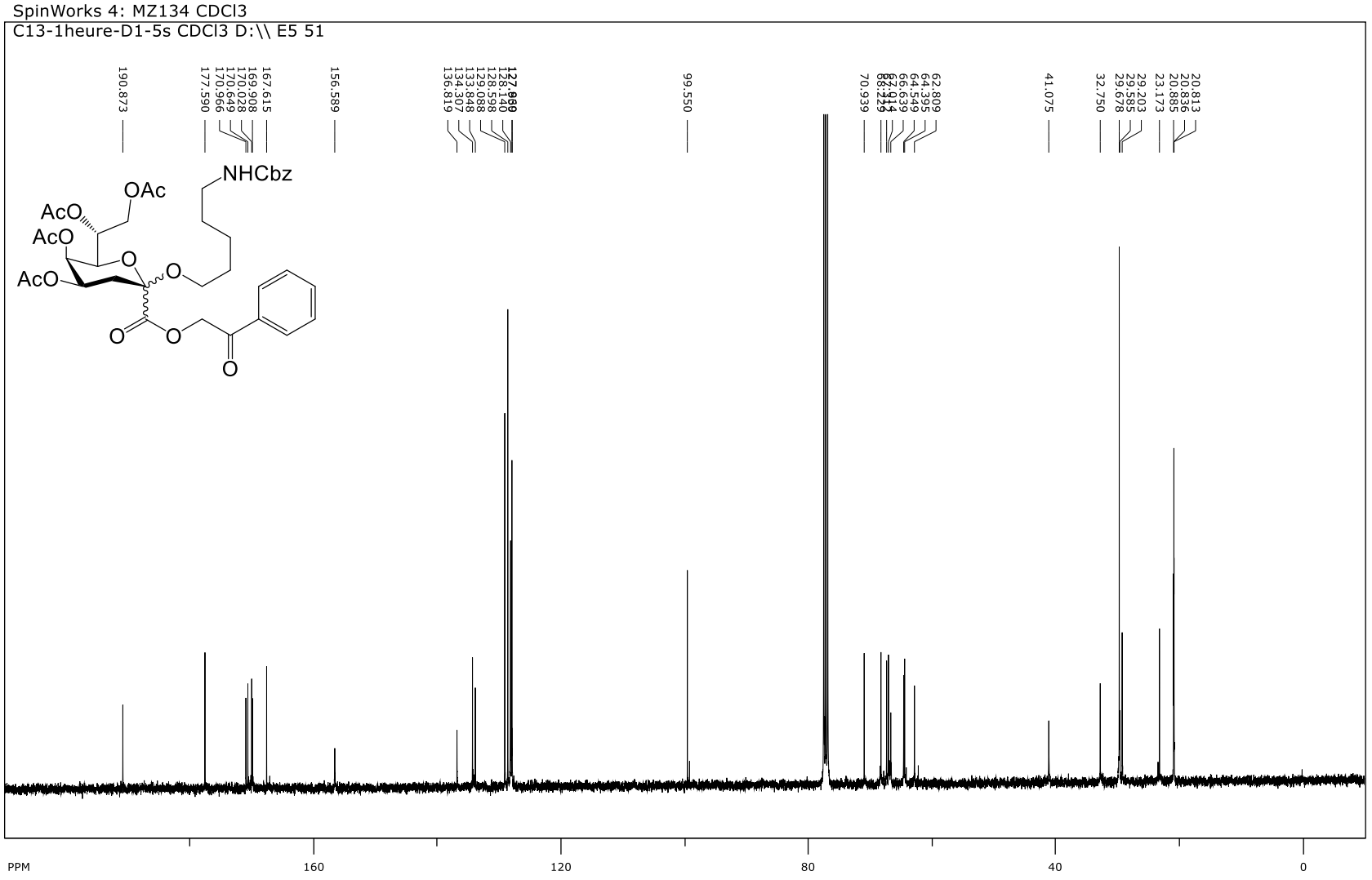
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **20**.



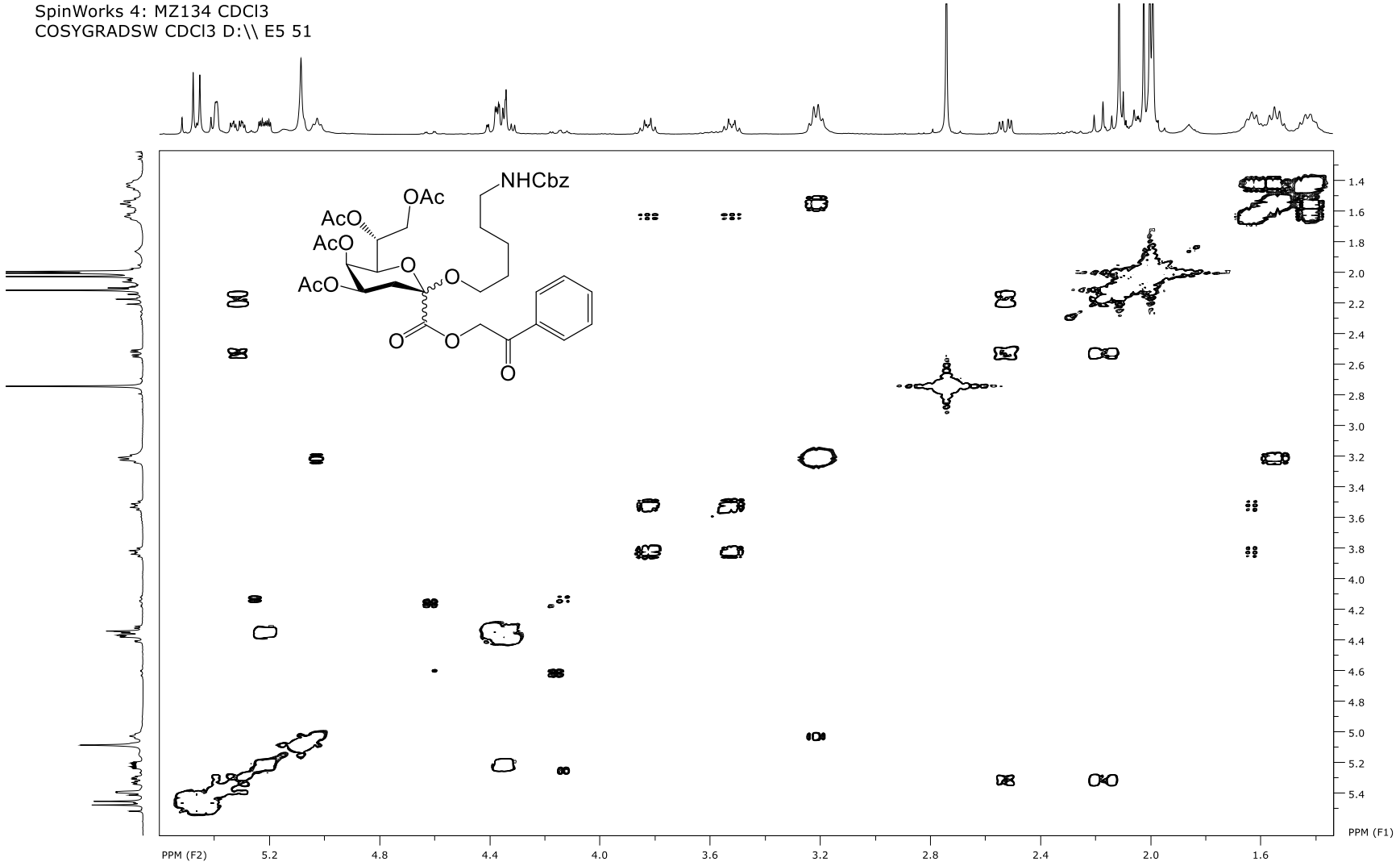
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **21**.



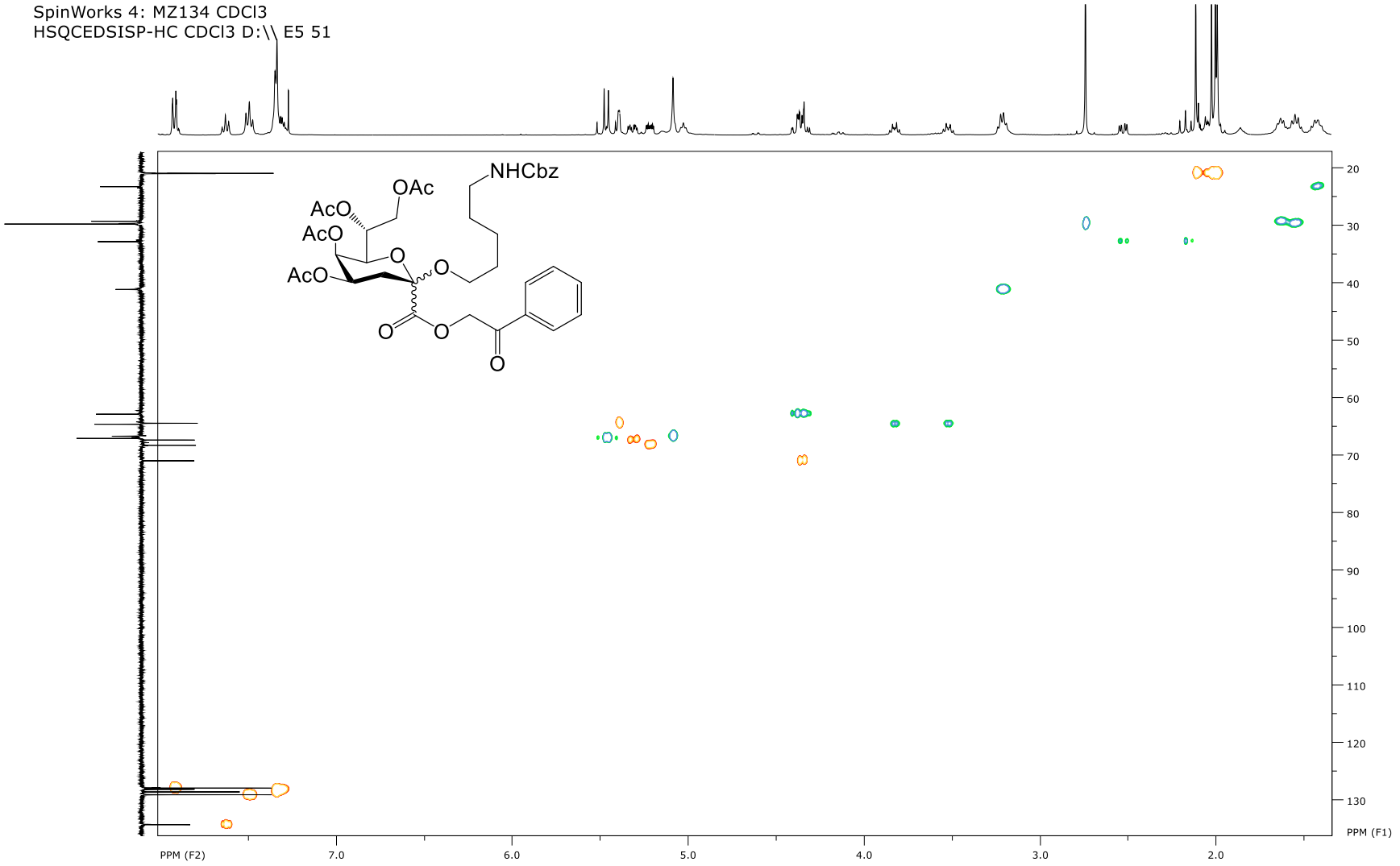
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **21**.



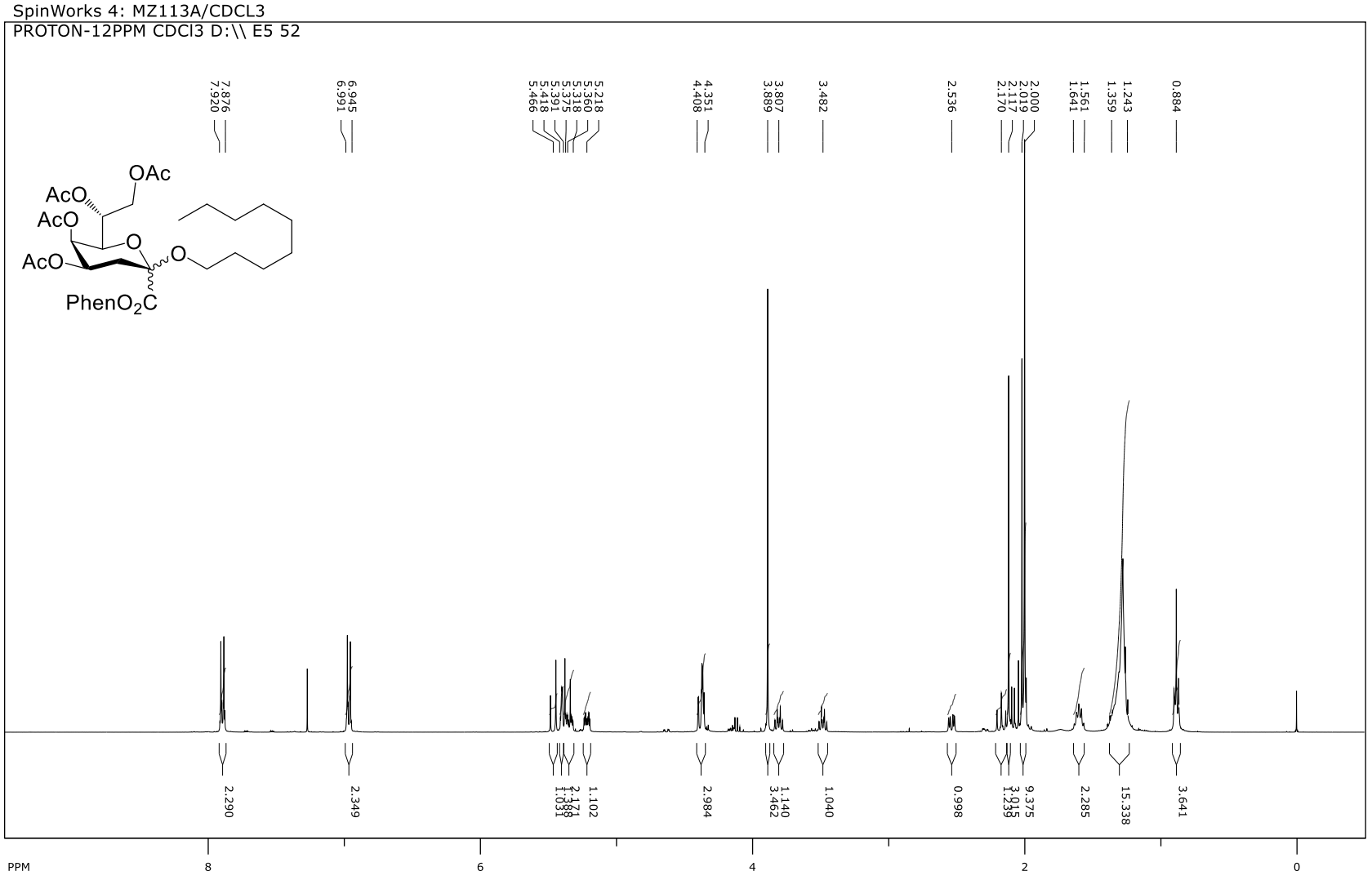
2D COSY spectra (400 MHz, $CDCl_3$) of compound **21**.



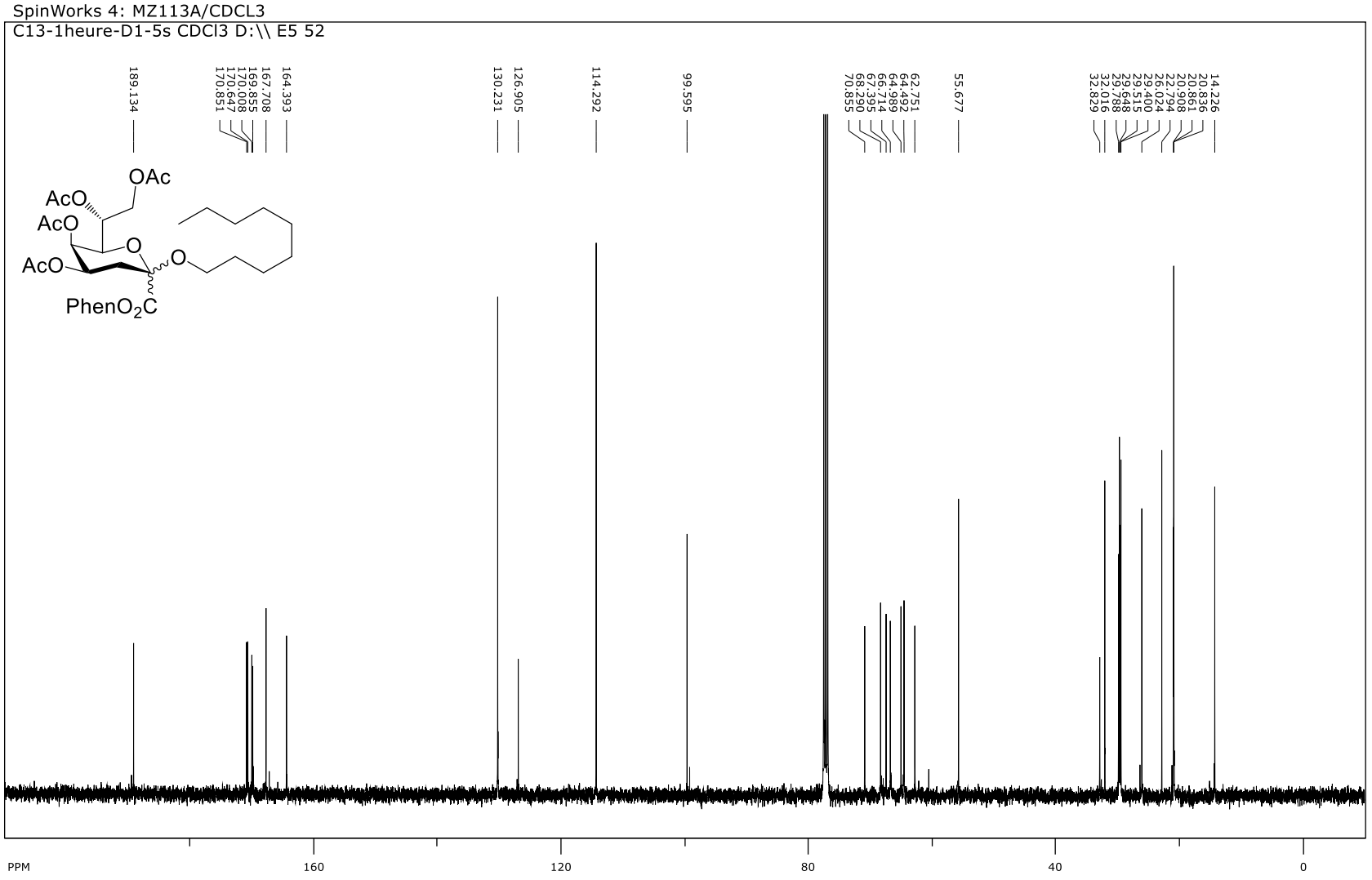
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **21**.



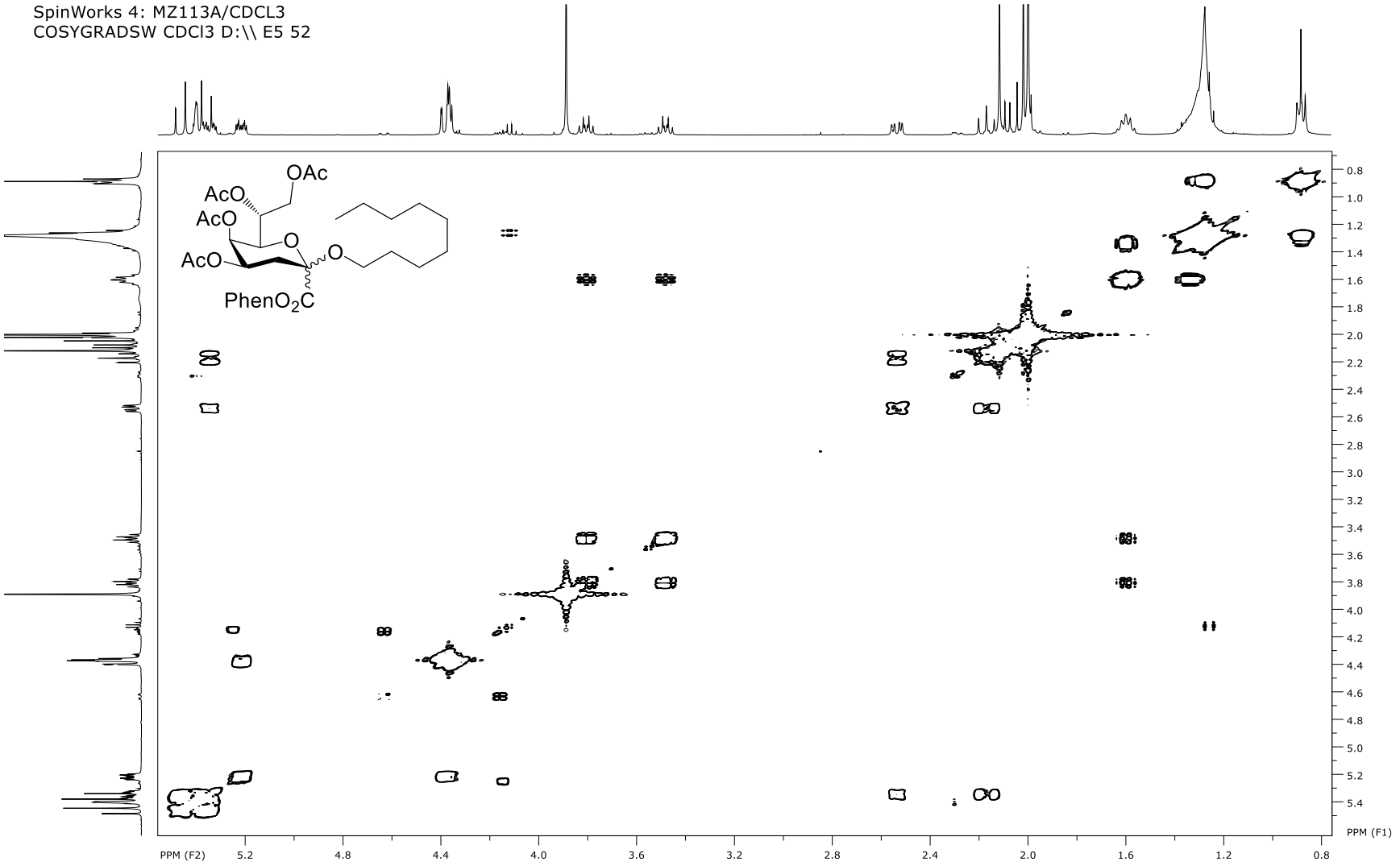
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **22**.



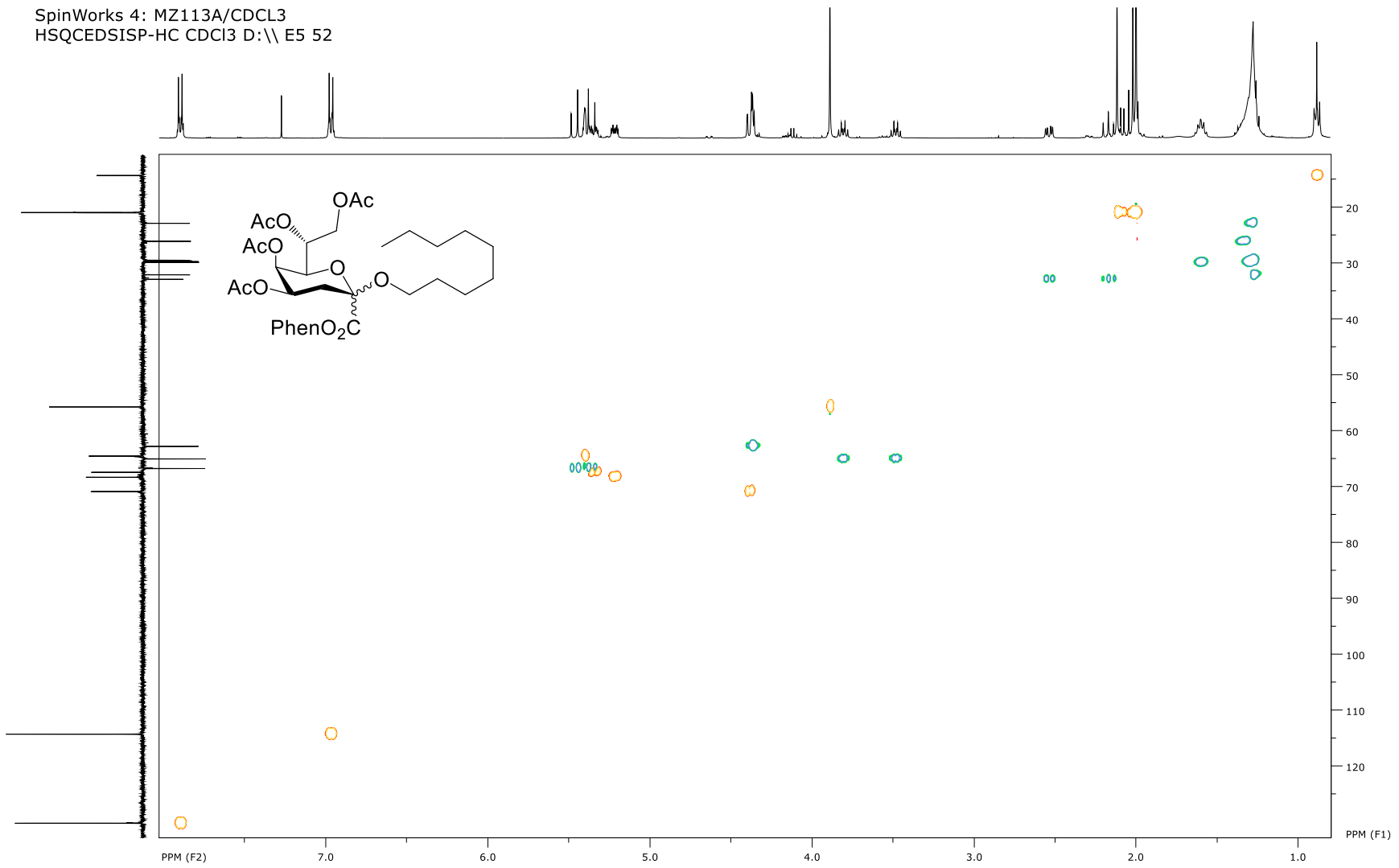
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **22**.



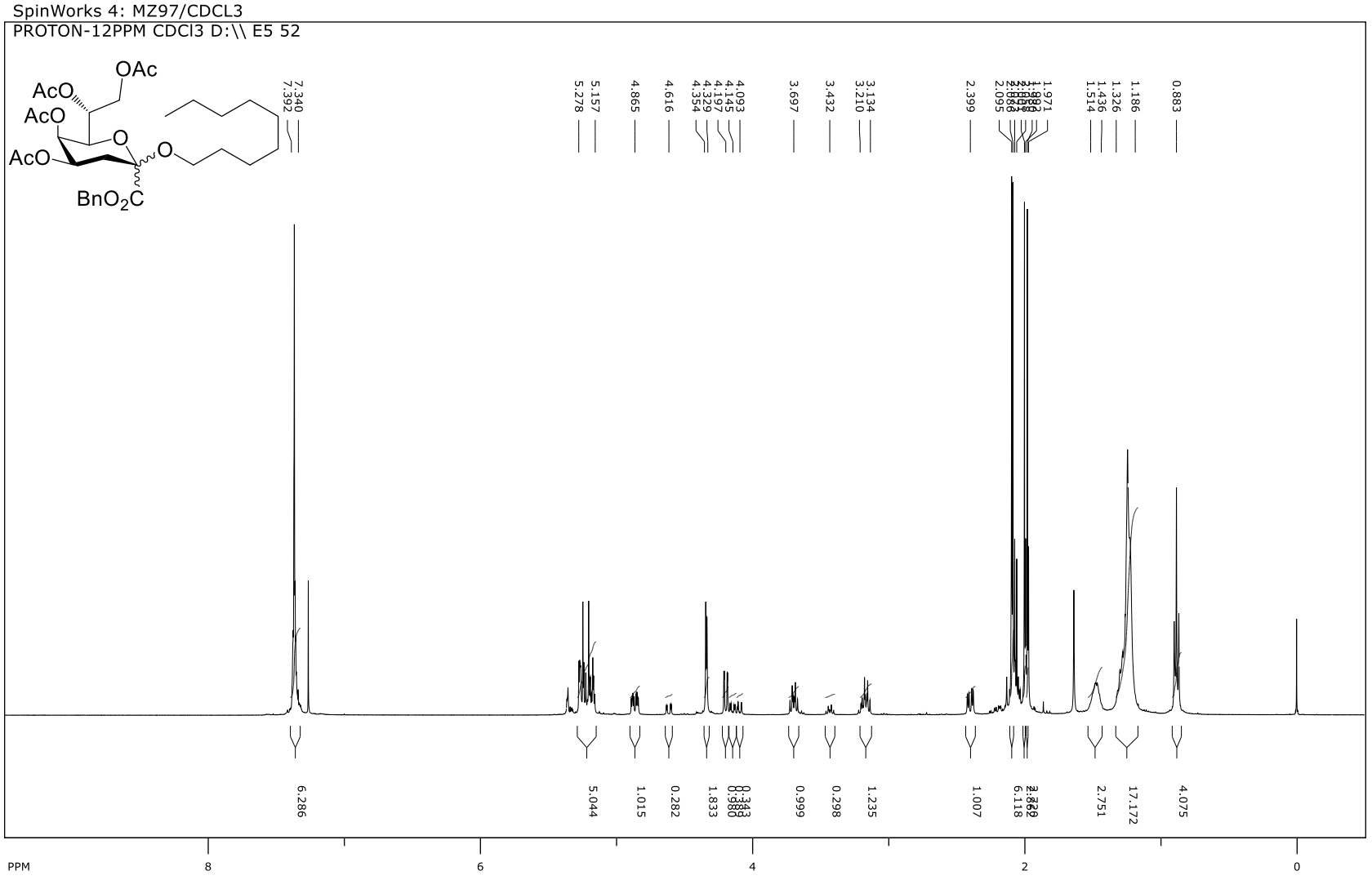
2D COSY spectra (400 MHz, $CDCl_3$) of compound **22**.



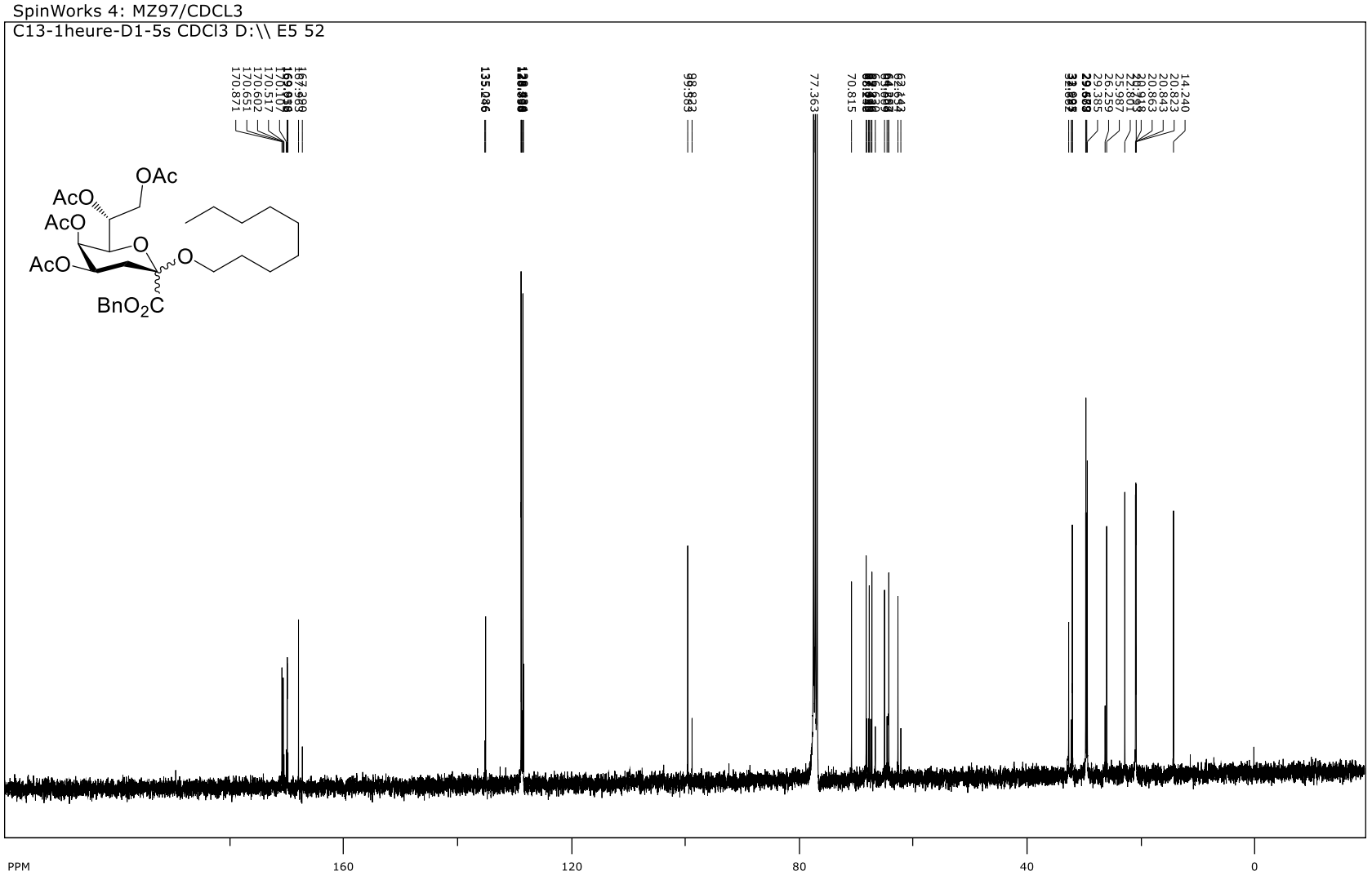
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **22**.



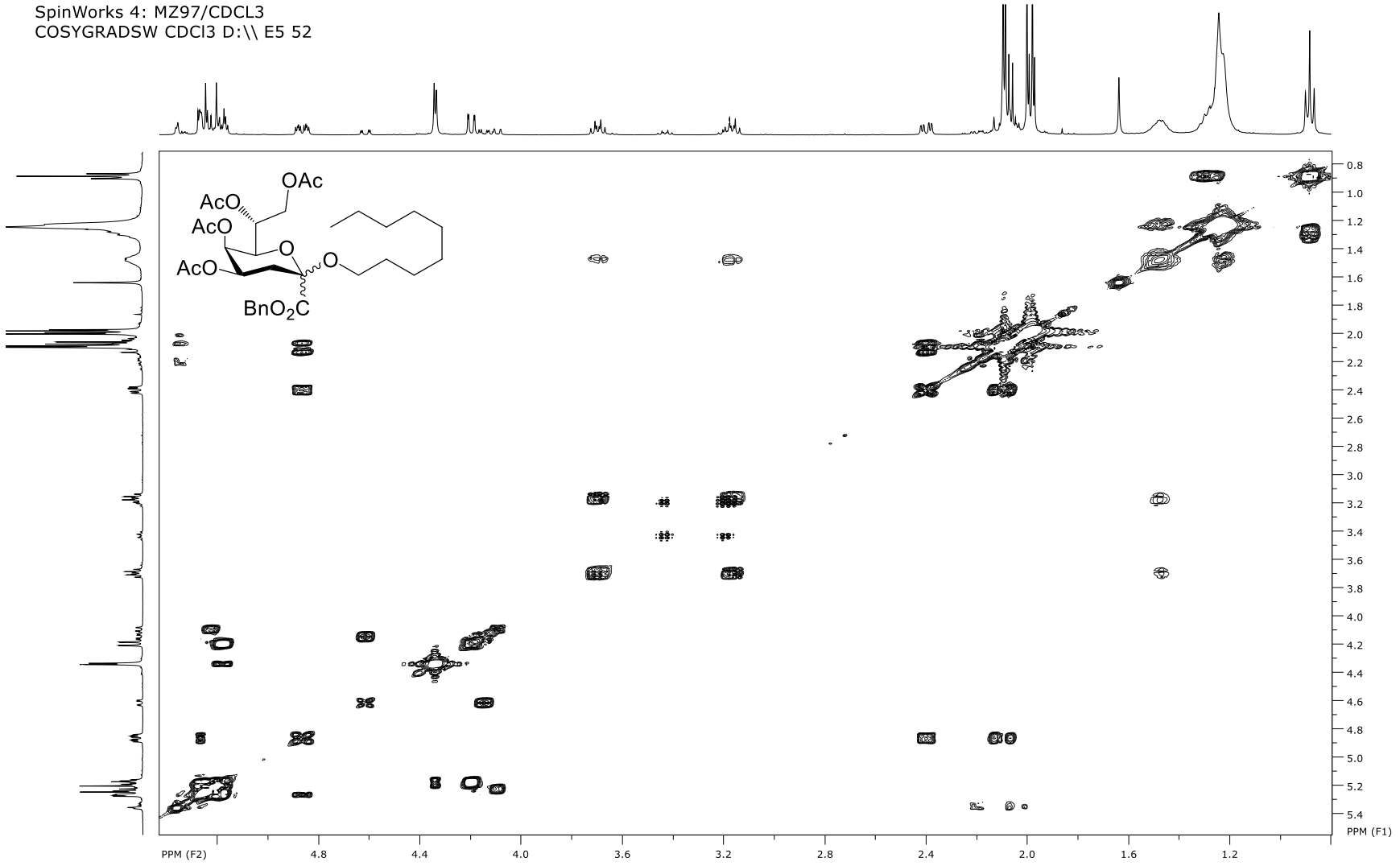
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **23**.



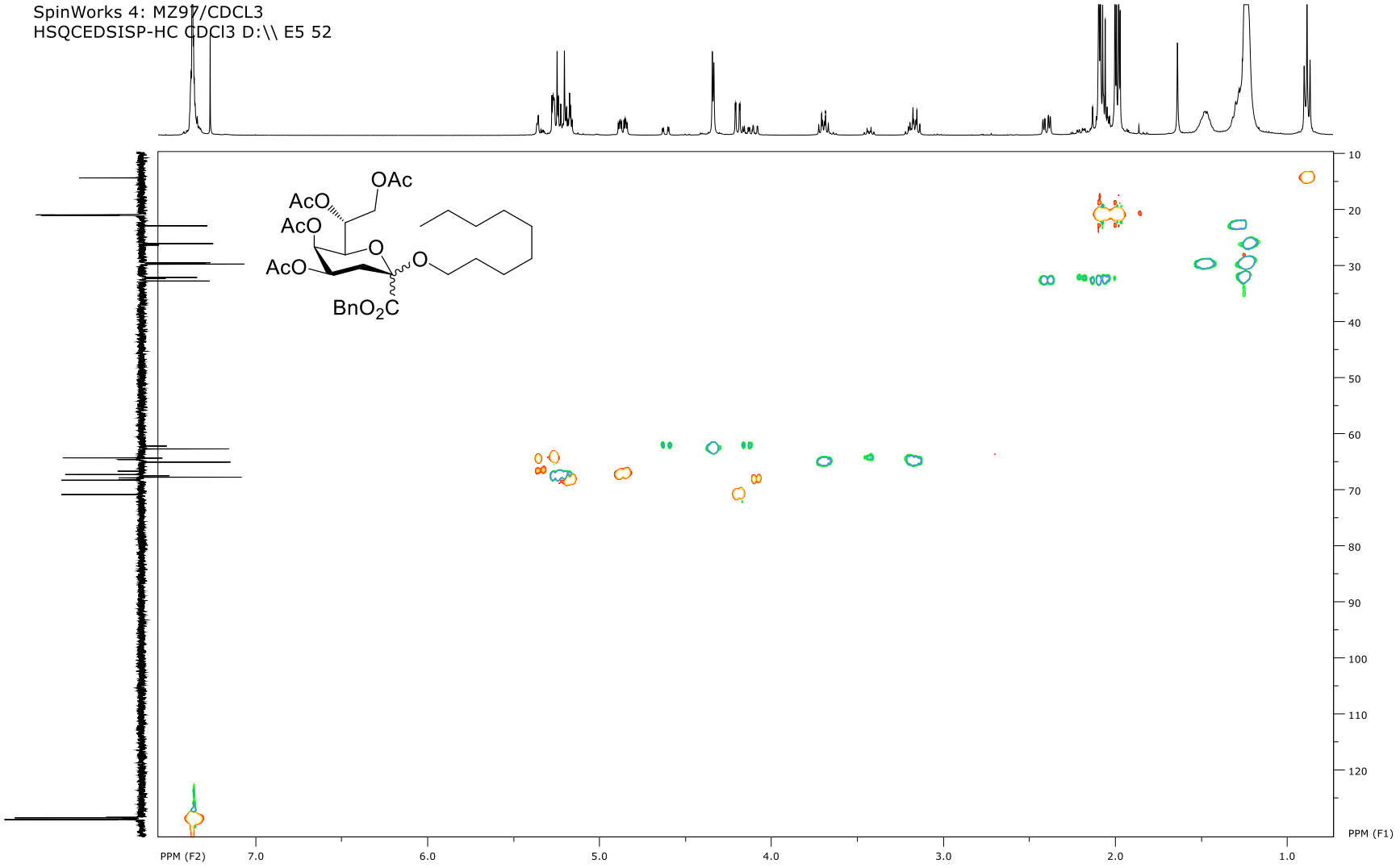
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **23**.



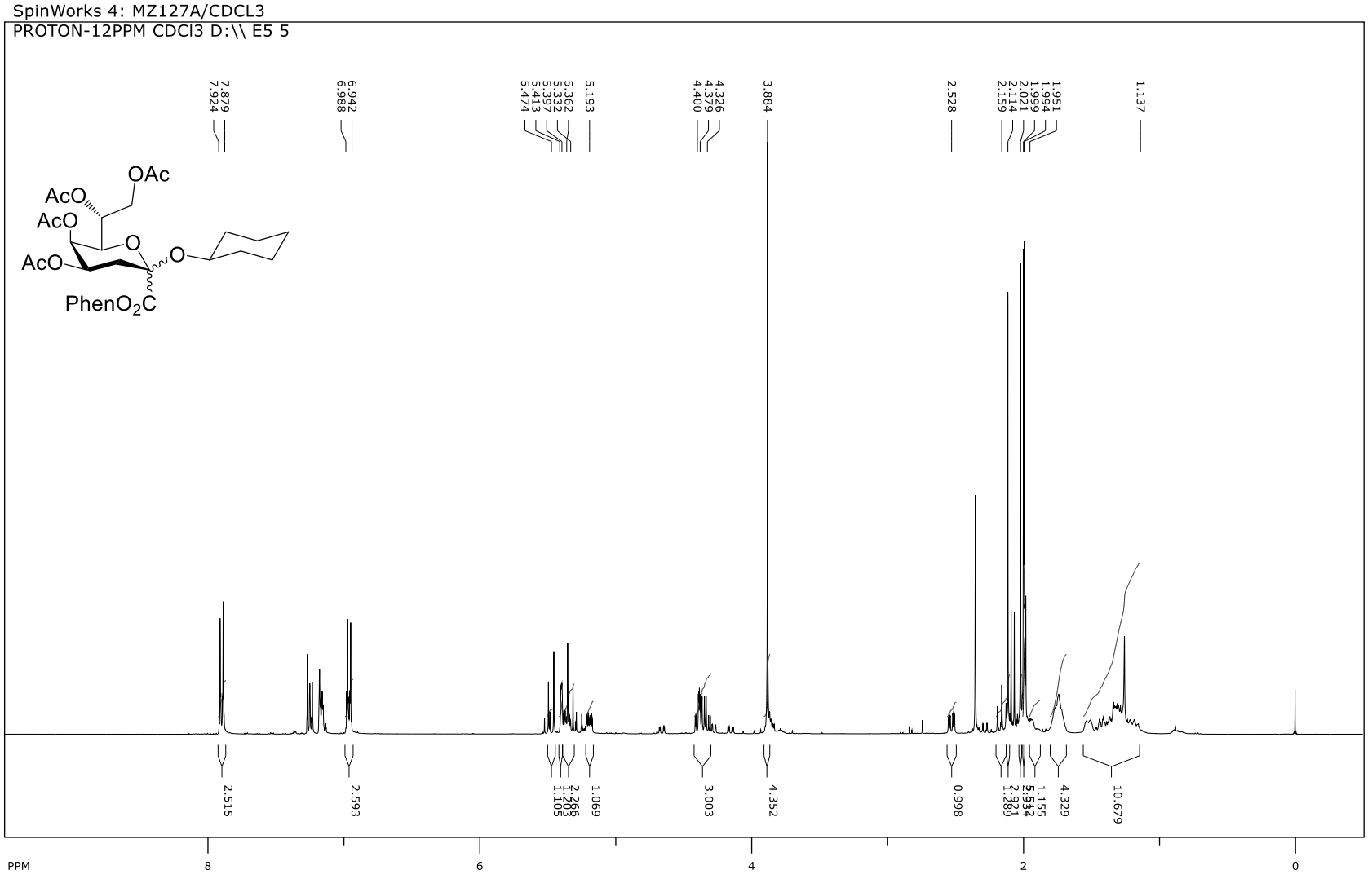
2D COSY spectra (400 MHz, $CDCl_3$) of compound **23**.



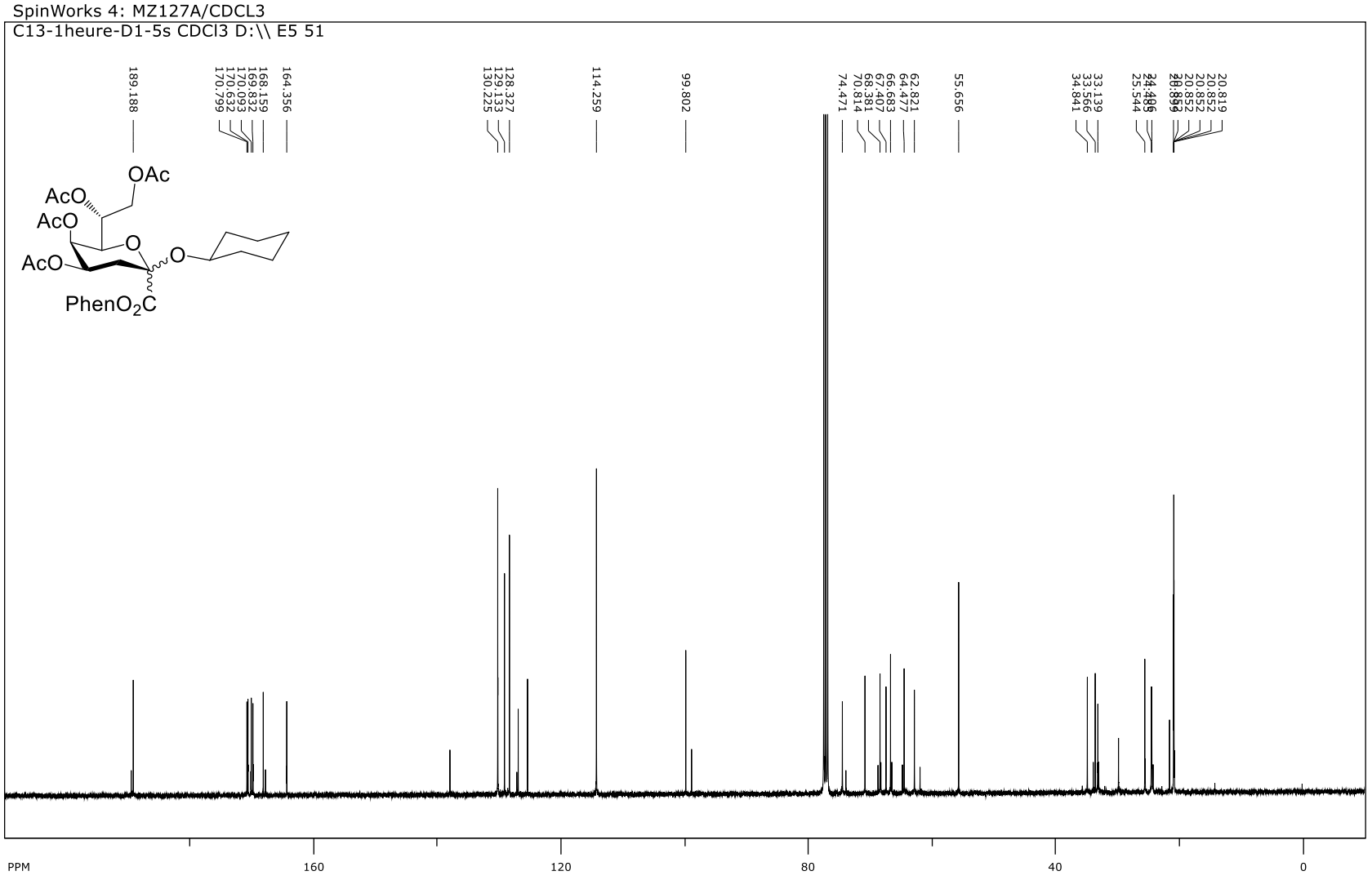
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **23**.



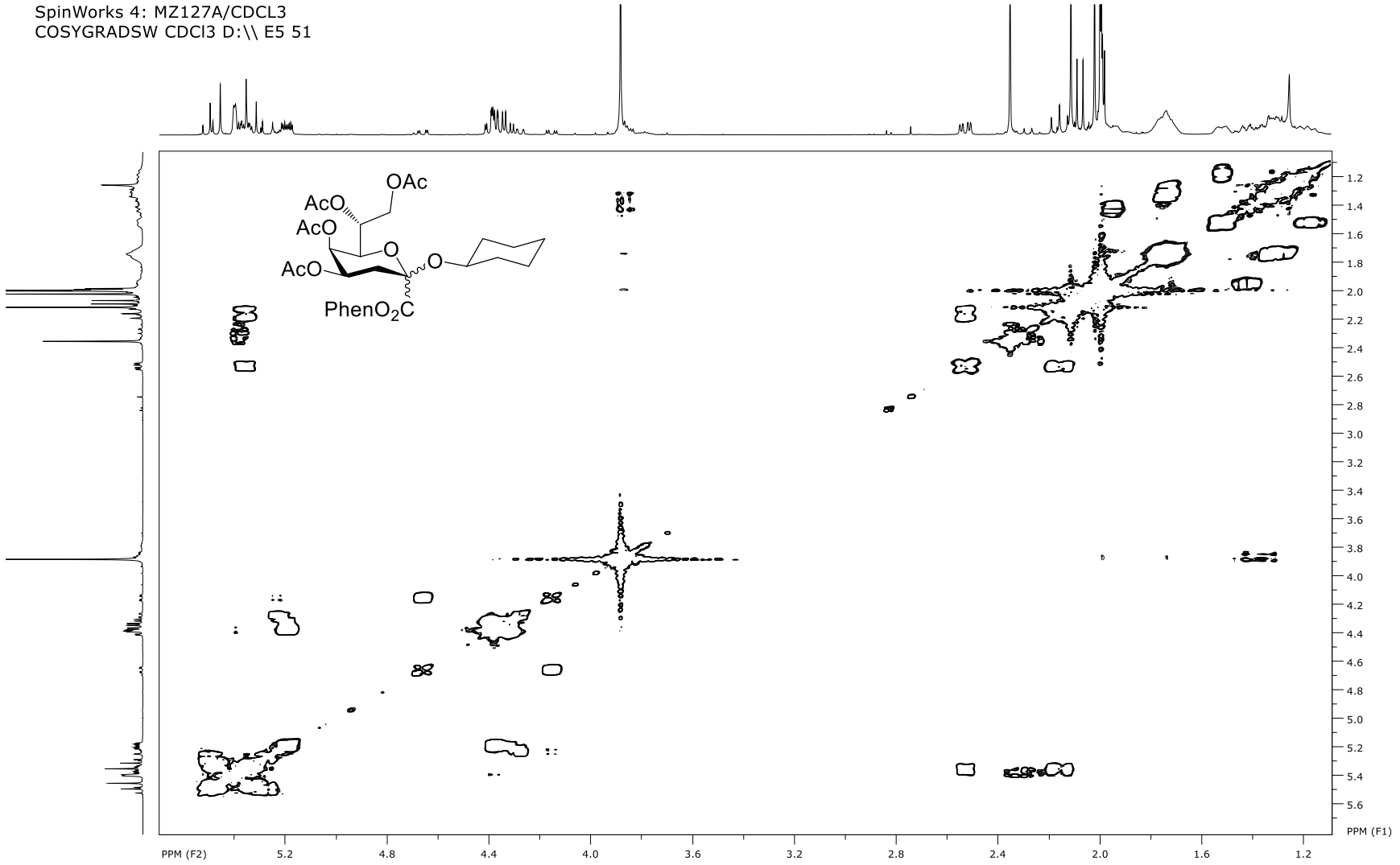
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **24**.



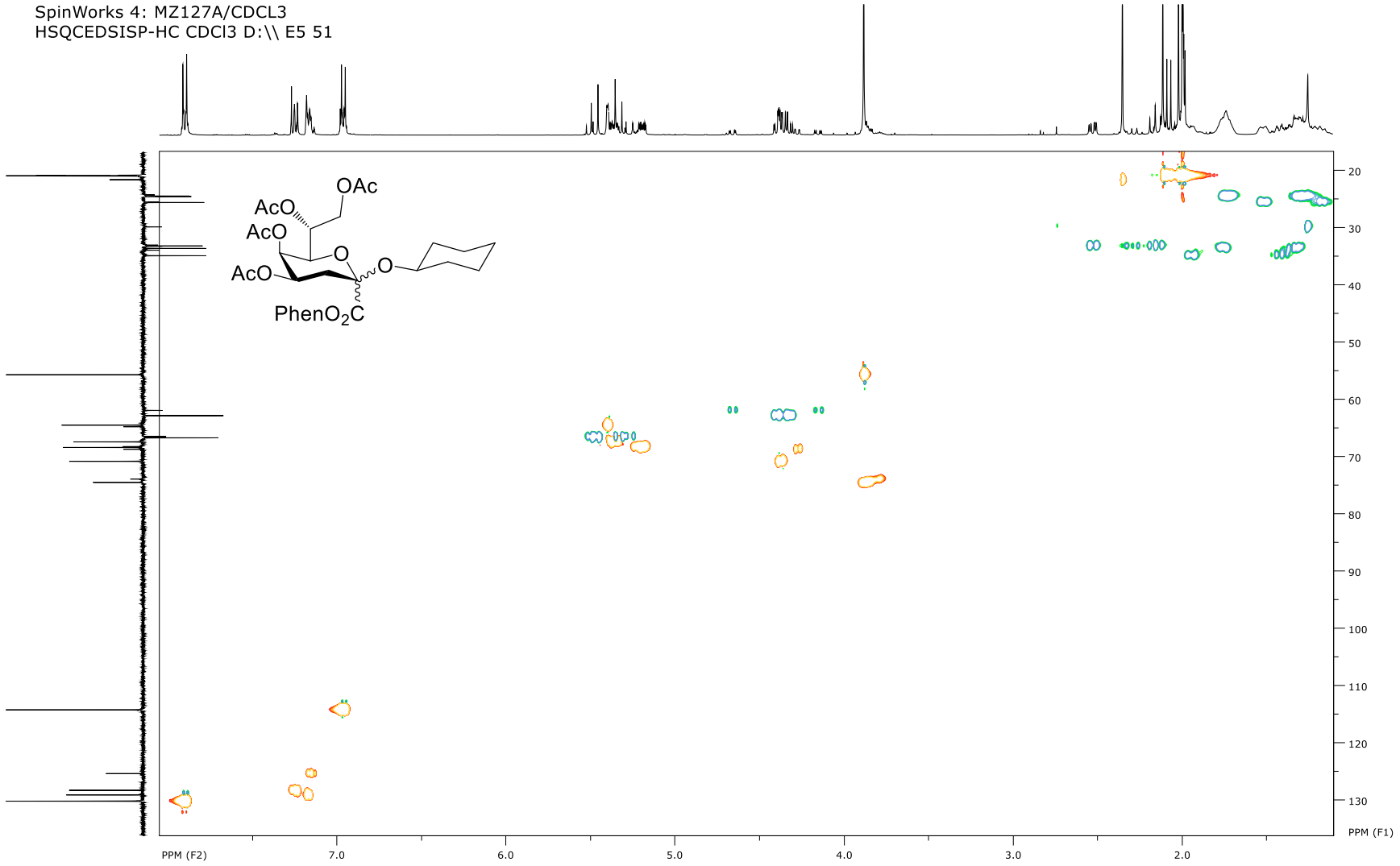
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **24**.



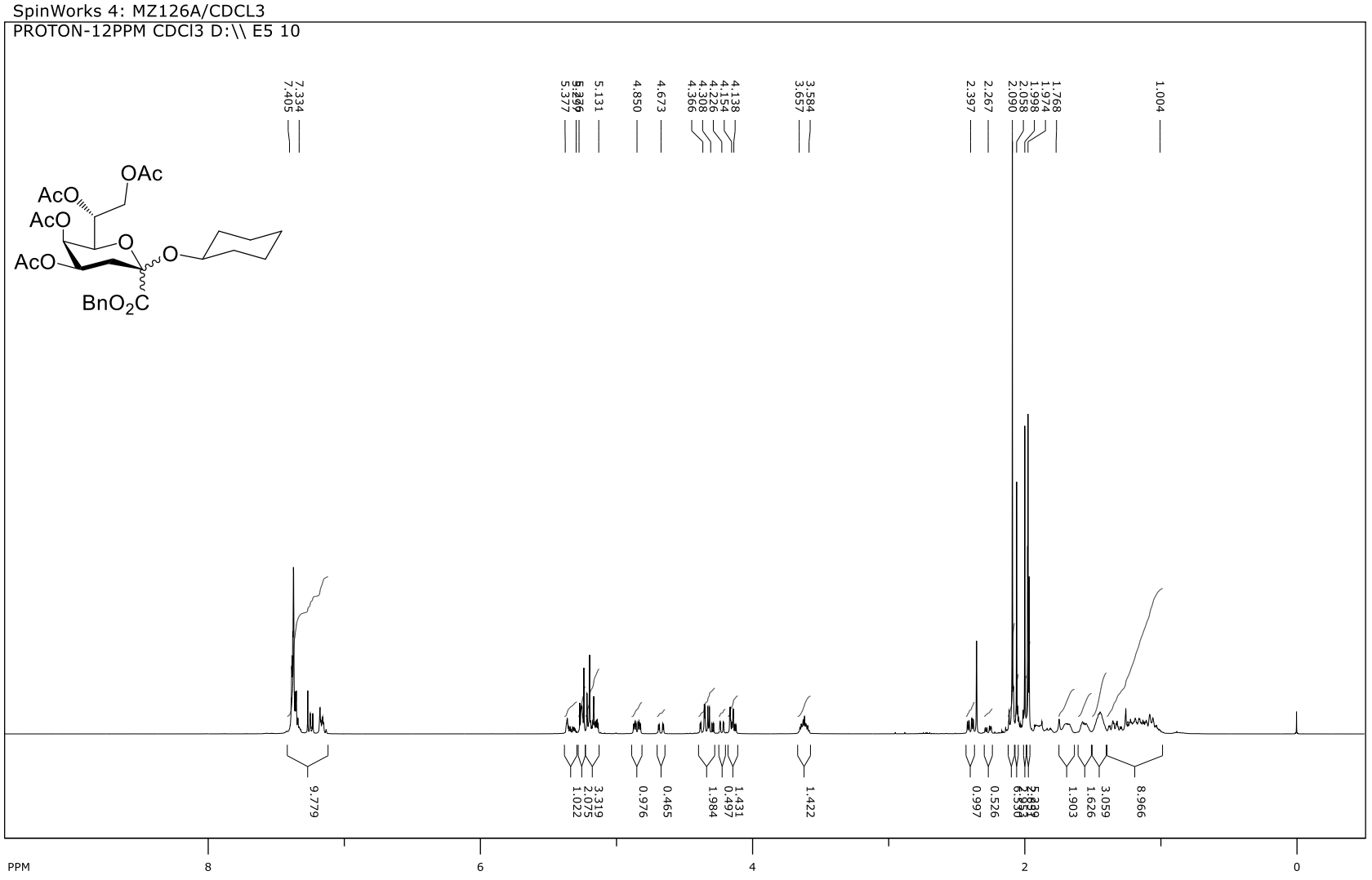
2D COSY spectra (400 MHz, $CDCl_3$) of compound **24**.



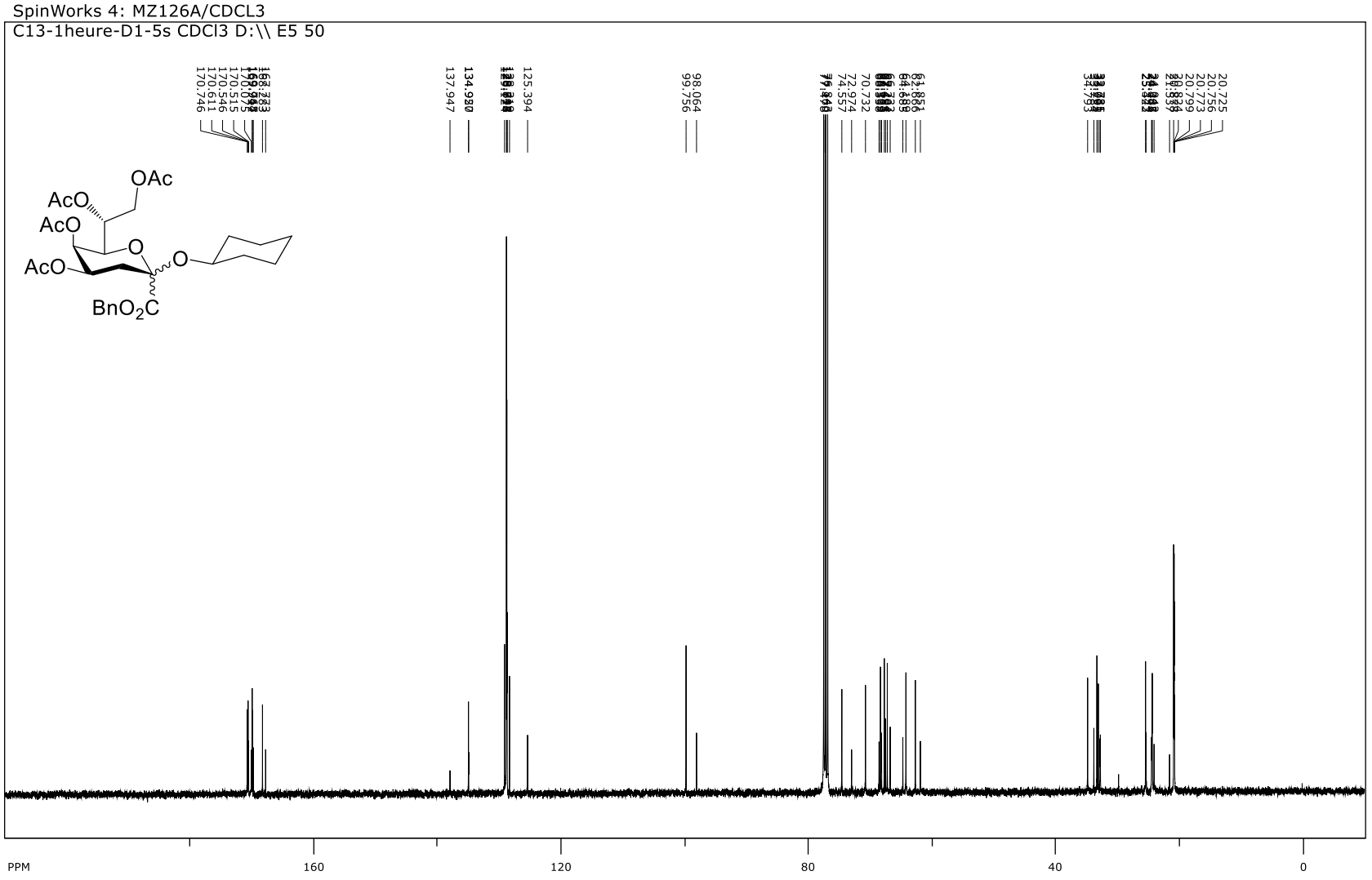
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **24**.



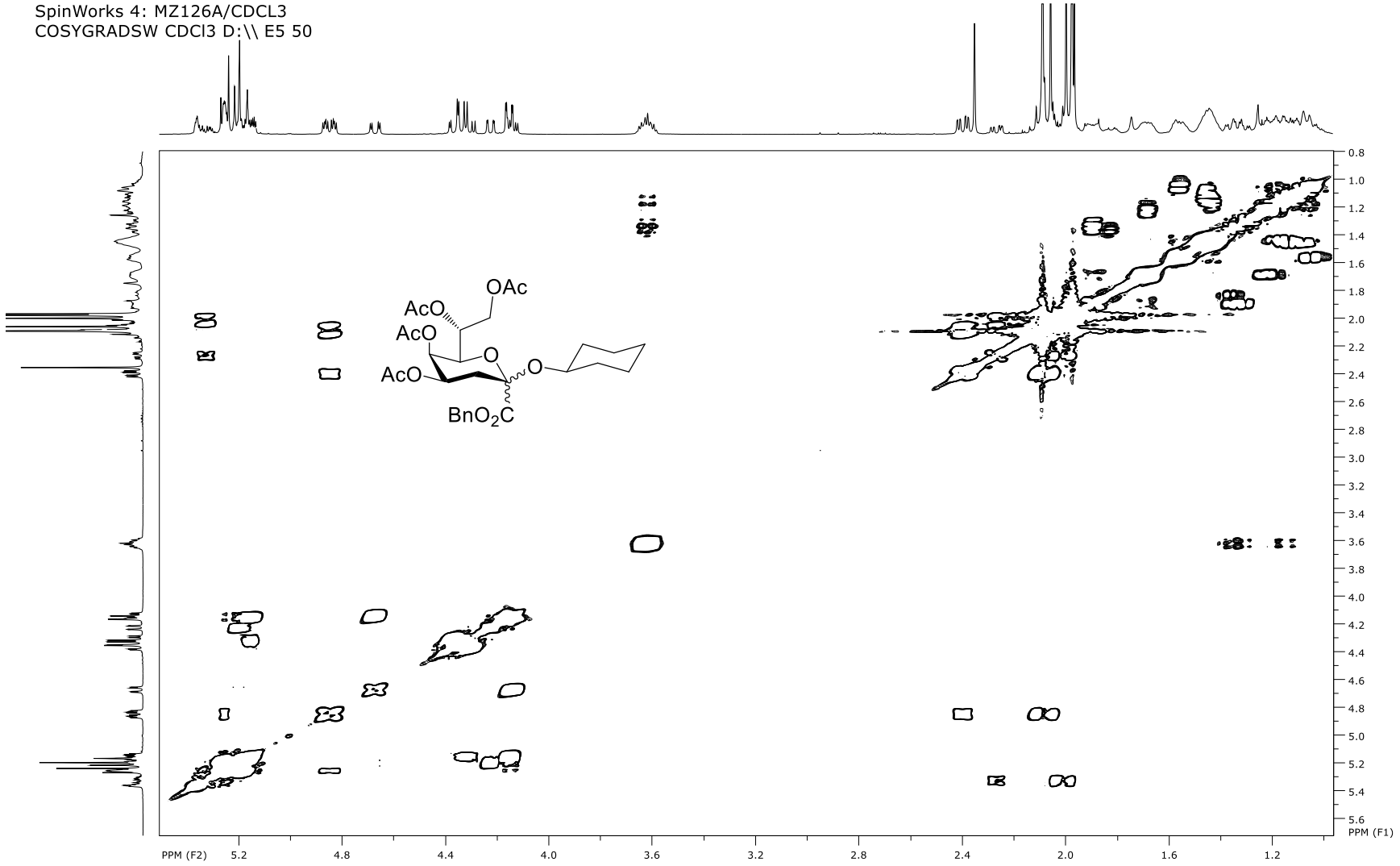
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **25**.



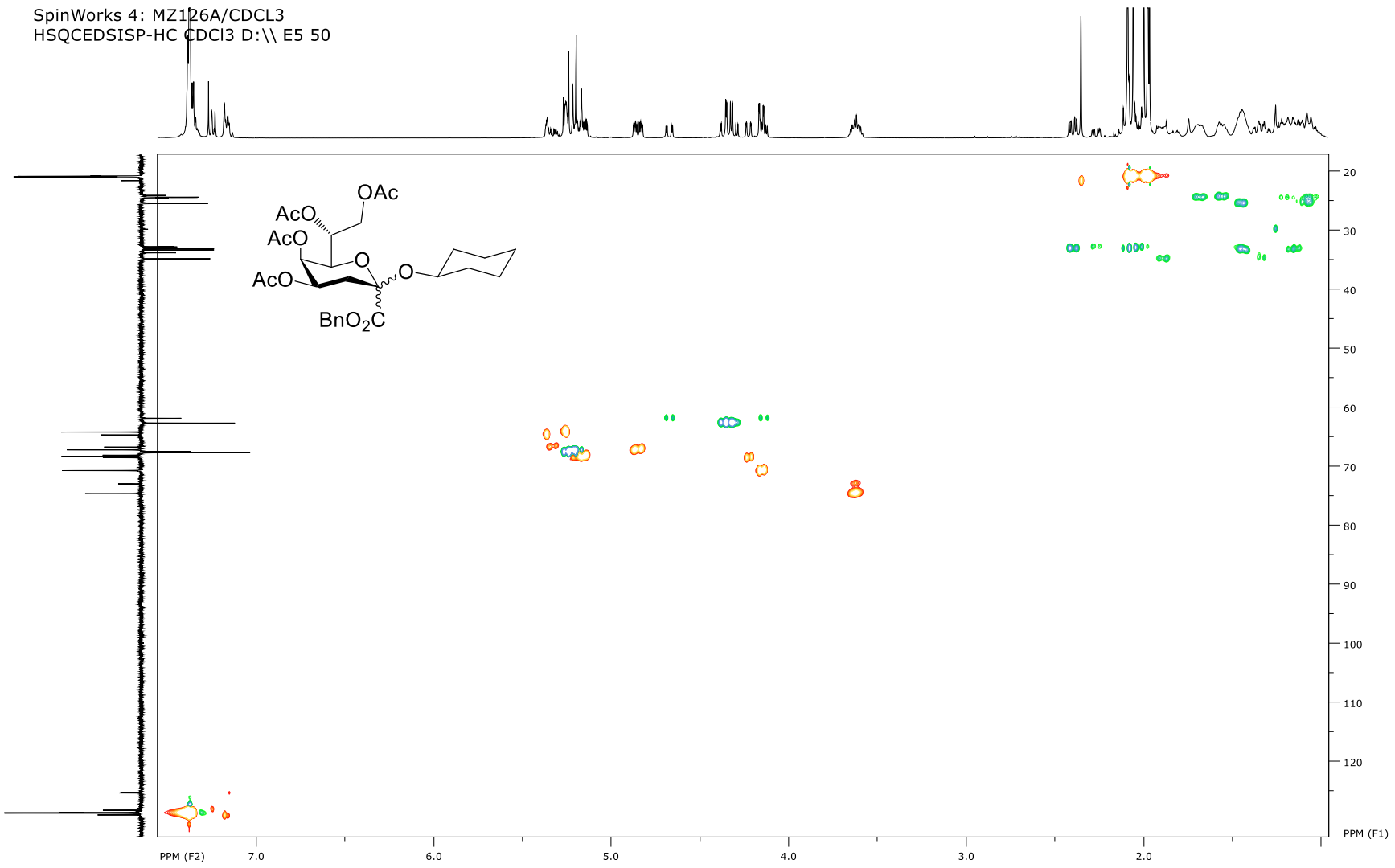
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **25**.



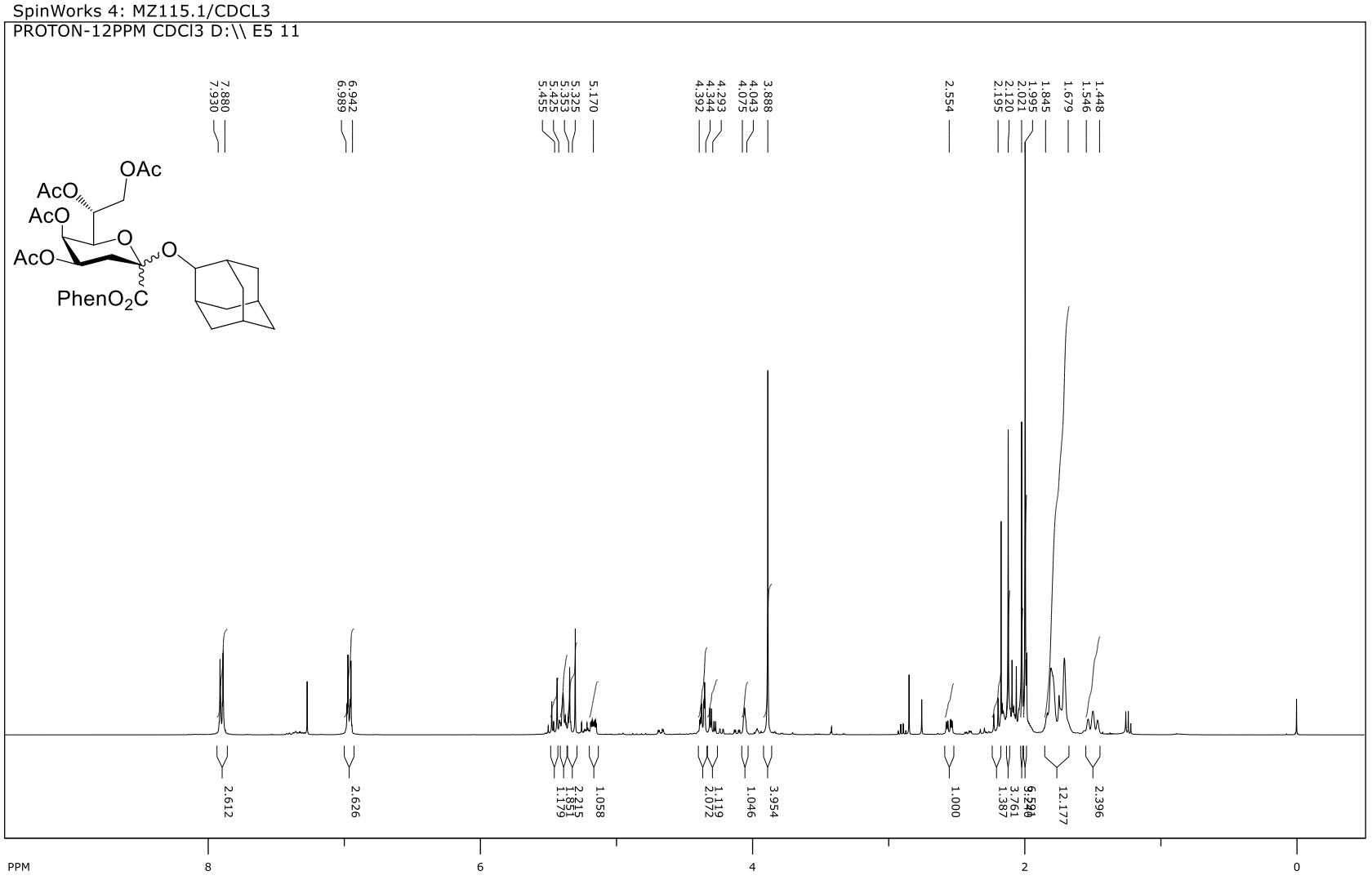
2D COSY spectra (400 MHz, $CDCl_3$) of compound **25**.



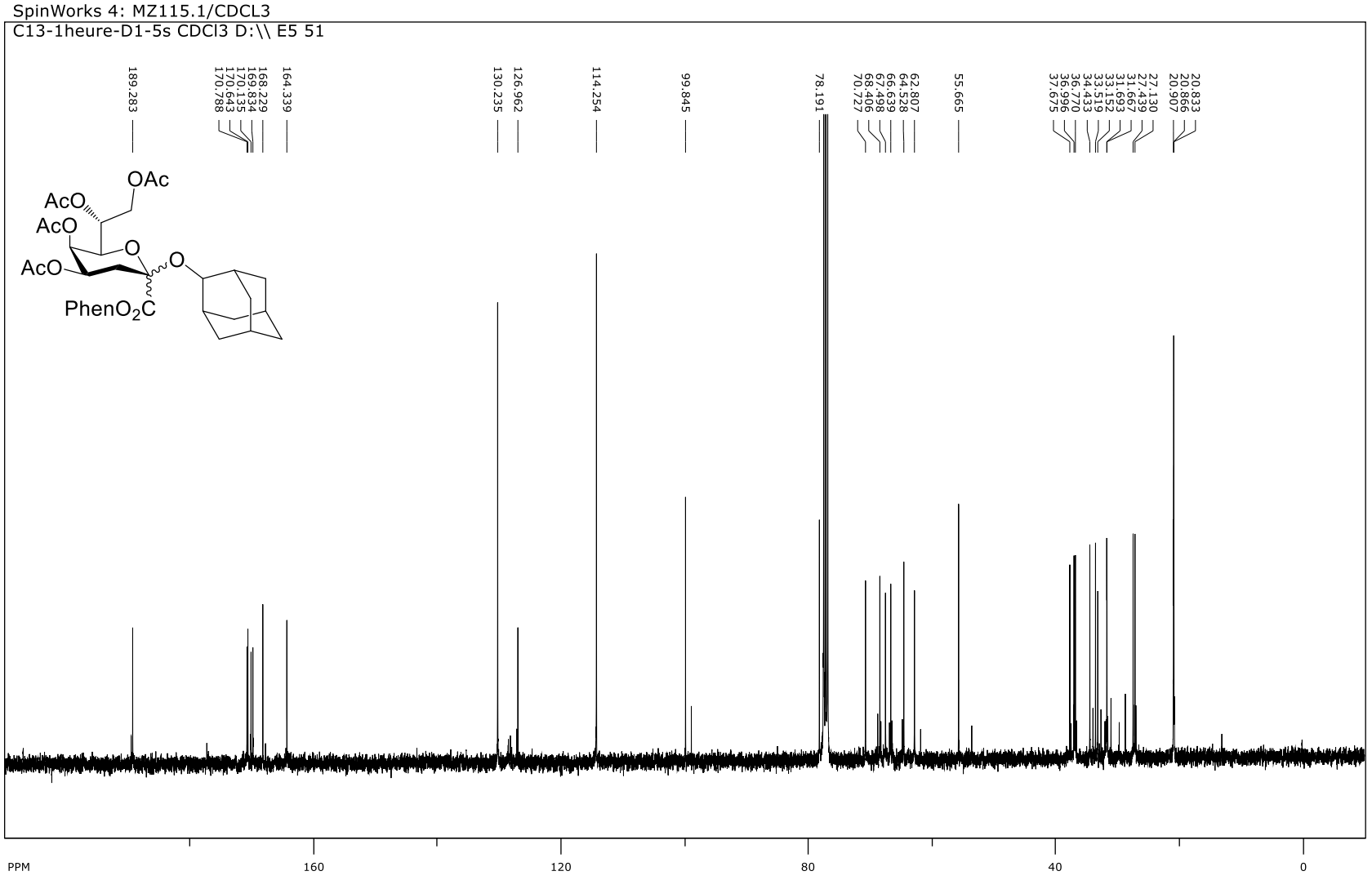
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **25**.



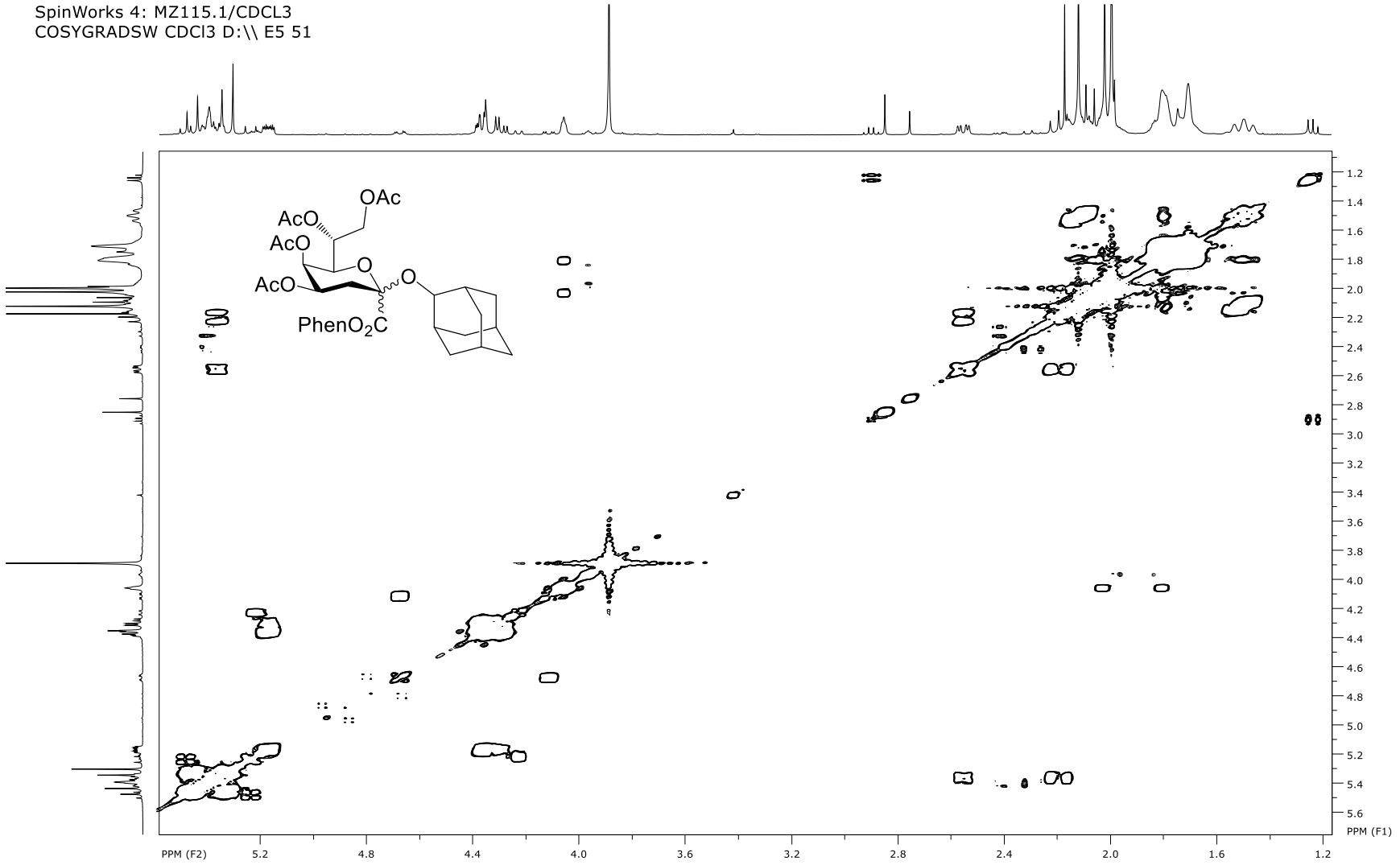
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **26**.



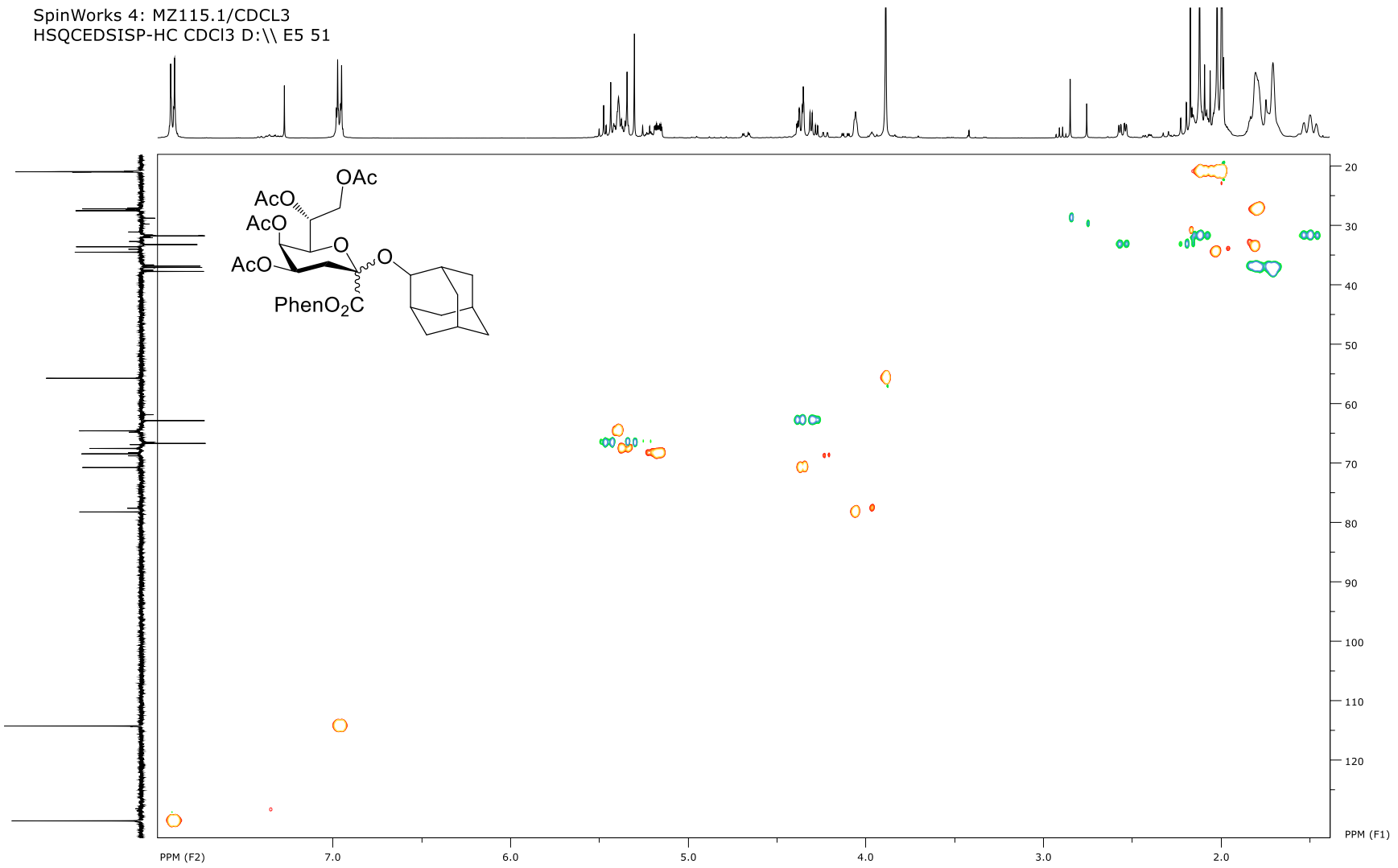
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **26**.



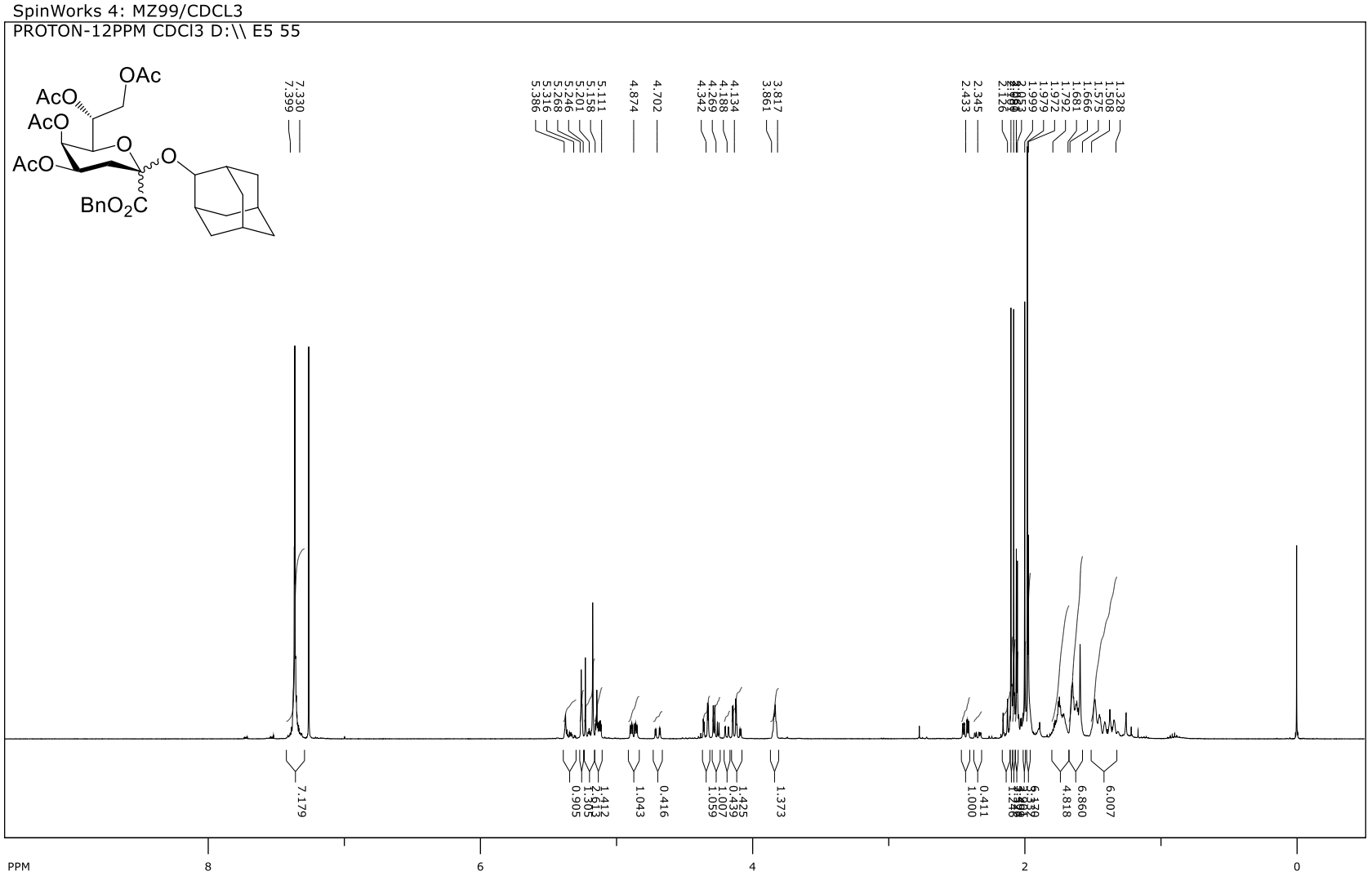
2D COSY spectra (400 MHz, $CDCl_3$) of compound **26**.



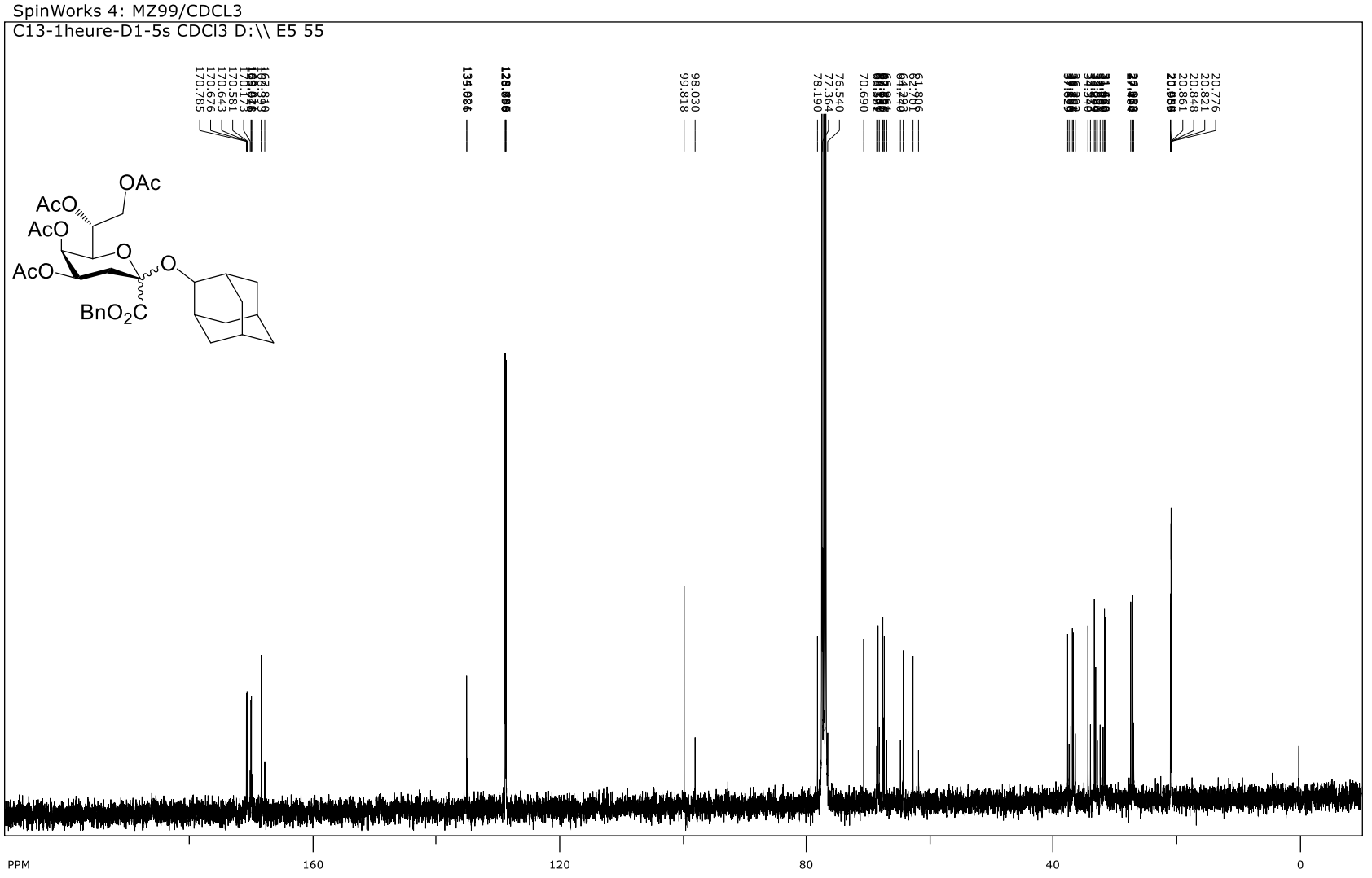
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **26**.



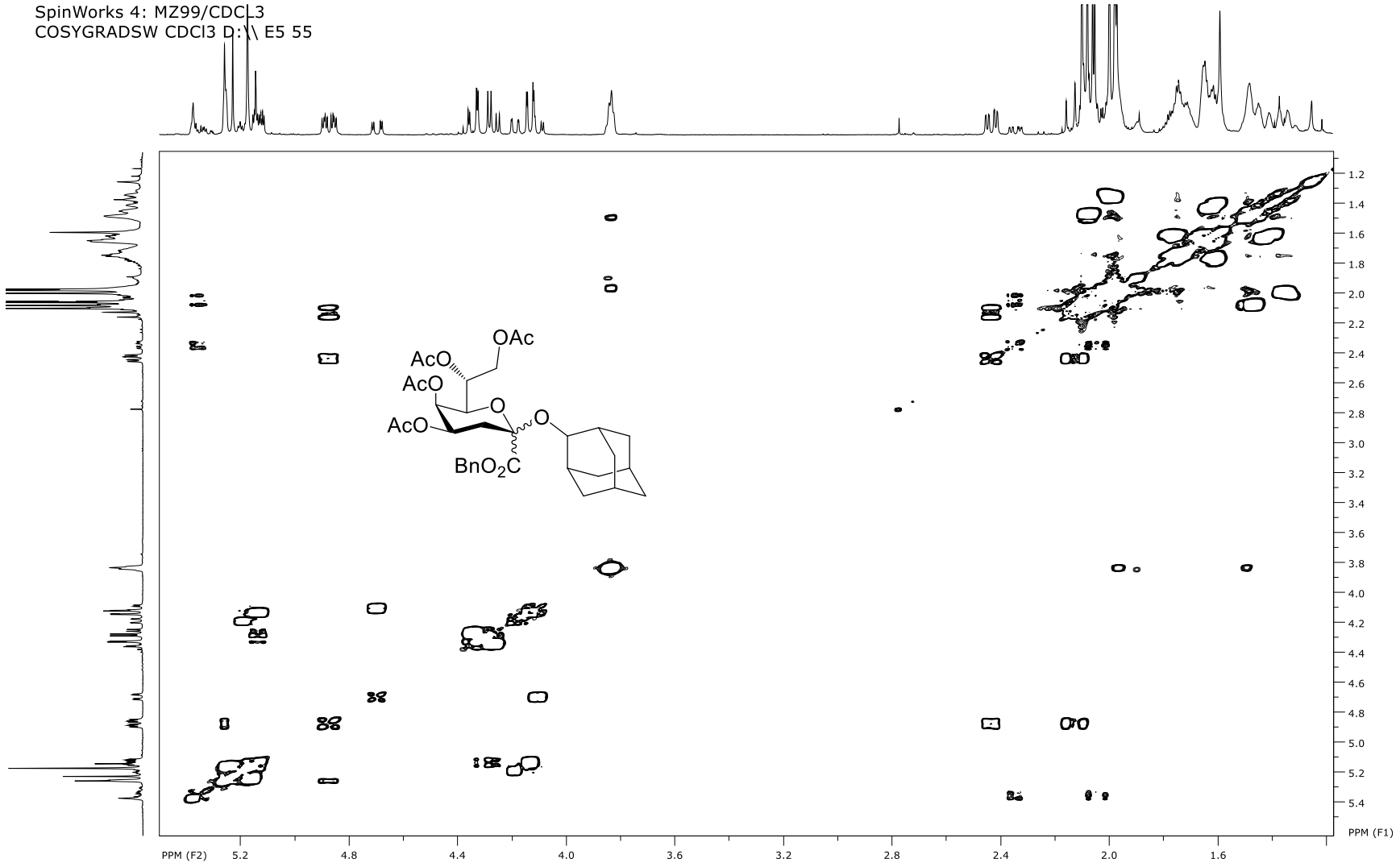
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **27**.



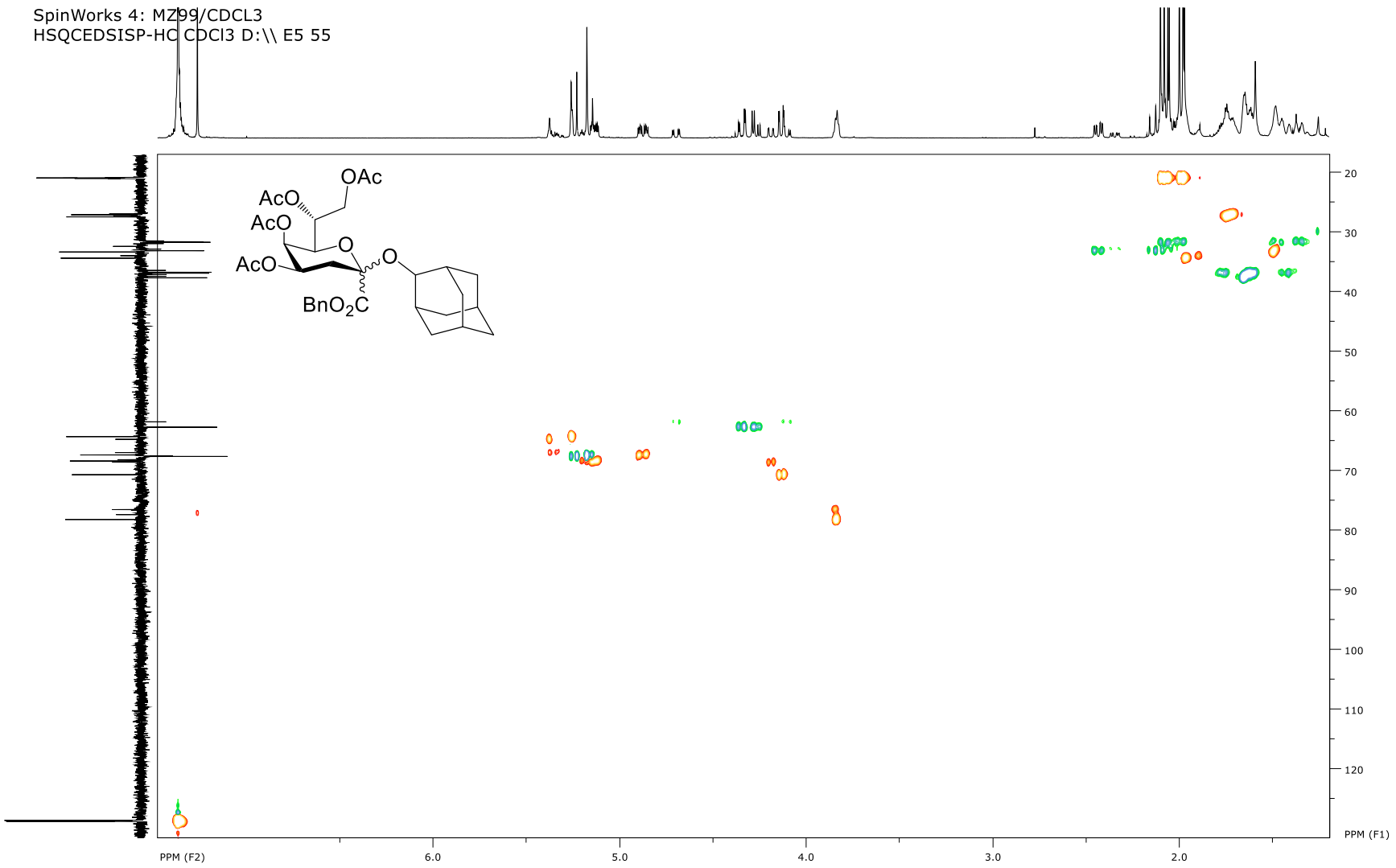
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **27**.



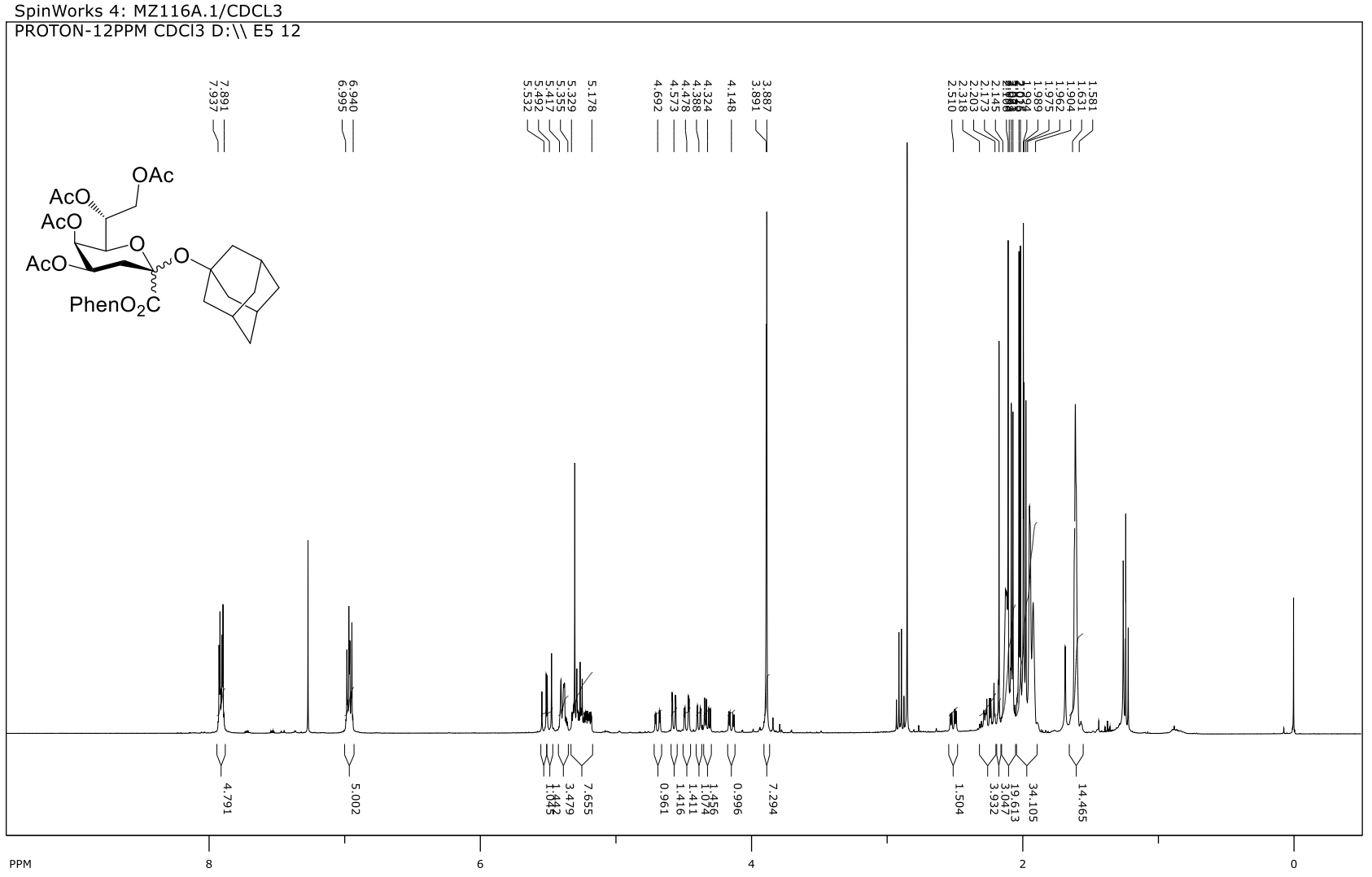
2D COSY spectra (400 MHz, $CDCl_3$) of compound **27**.



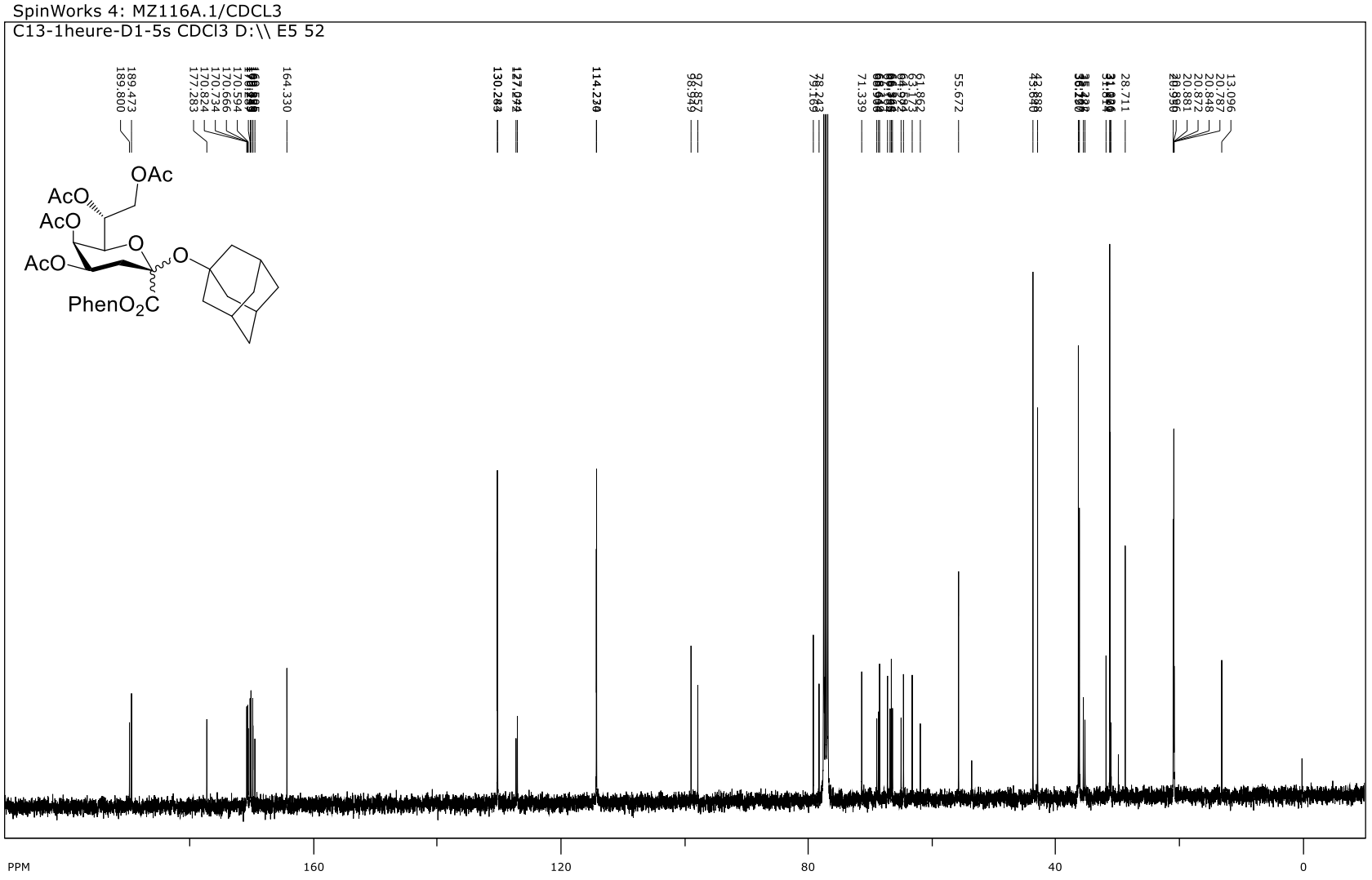
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **27**.



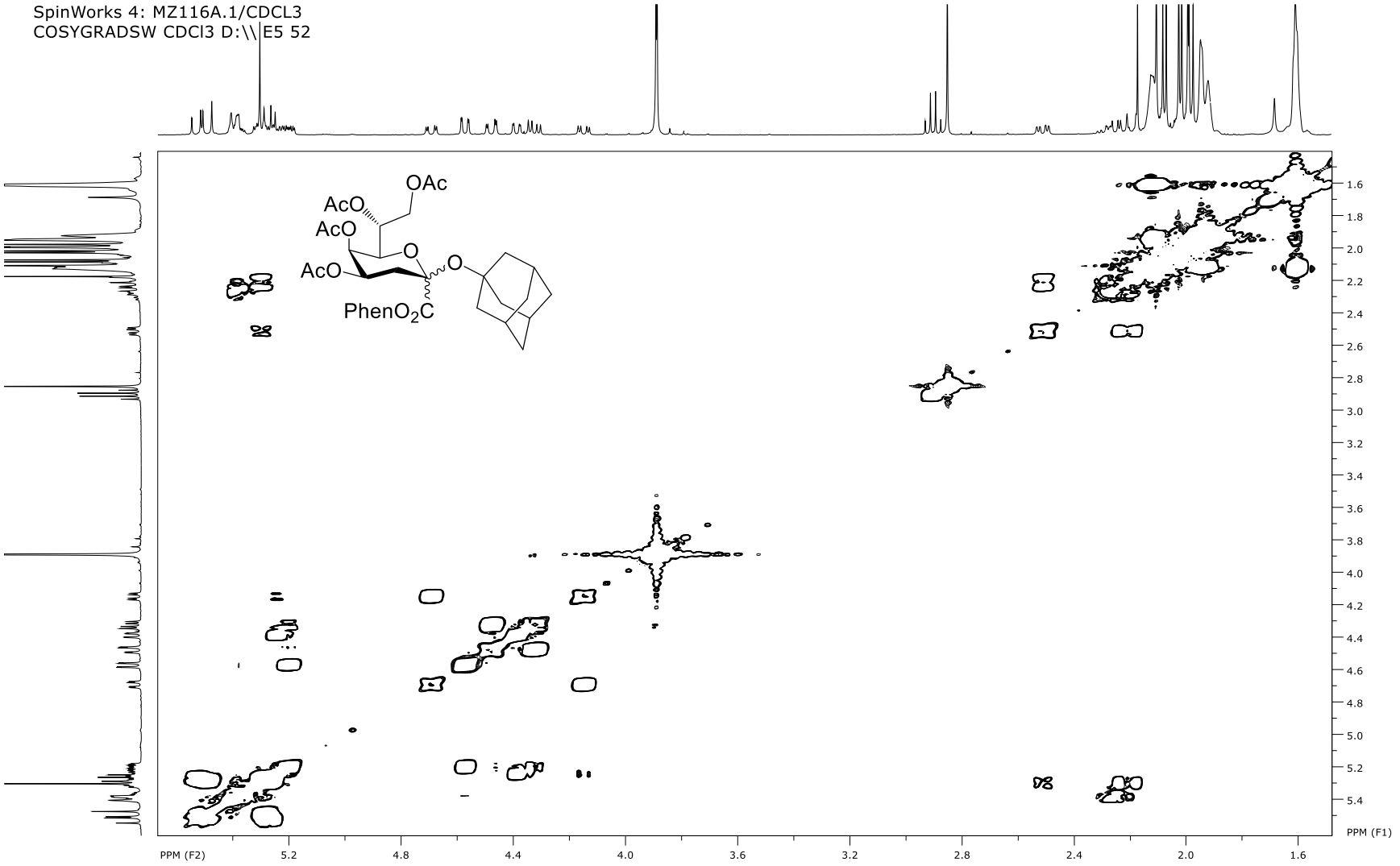
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **28**.



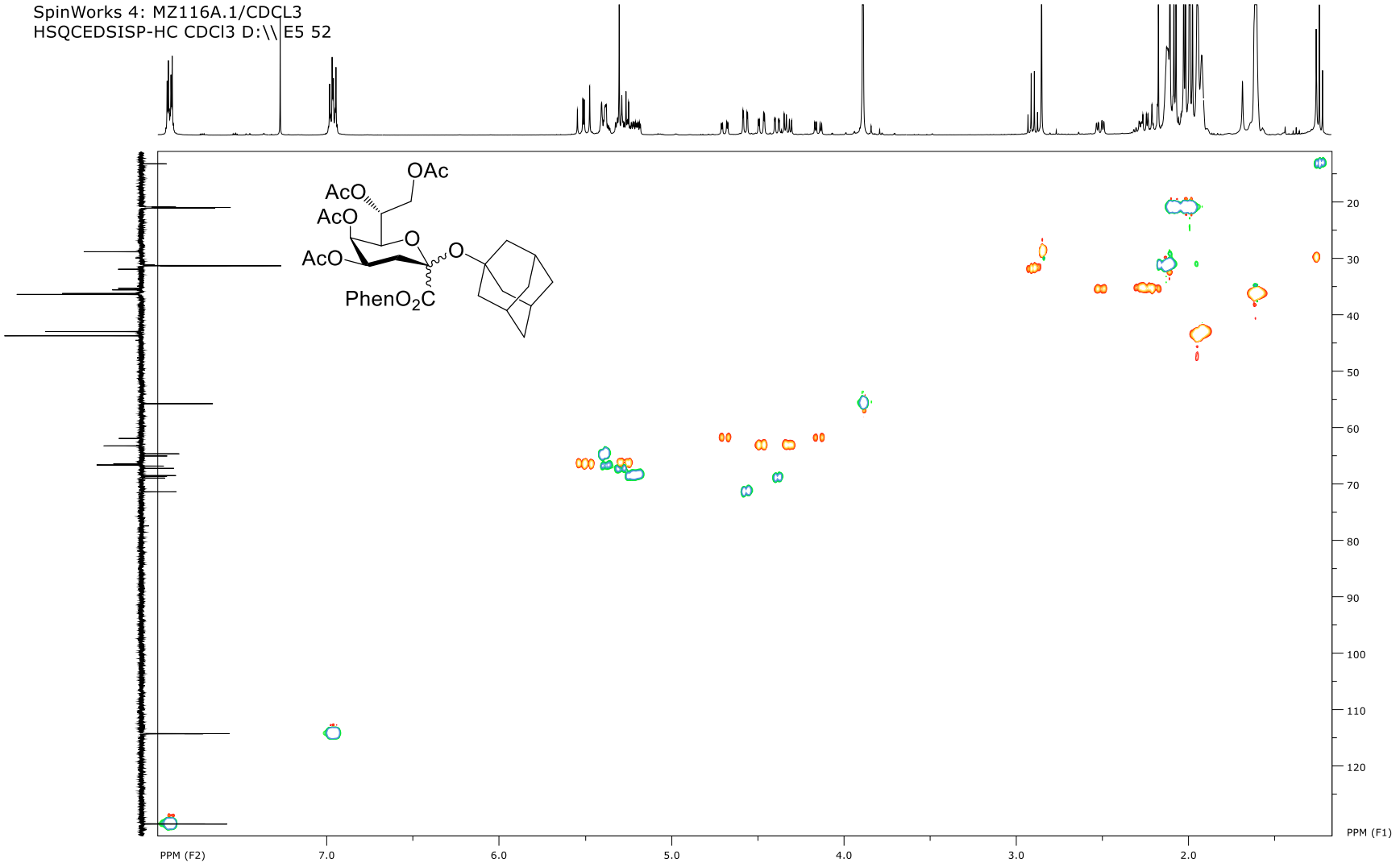
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **28**.



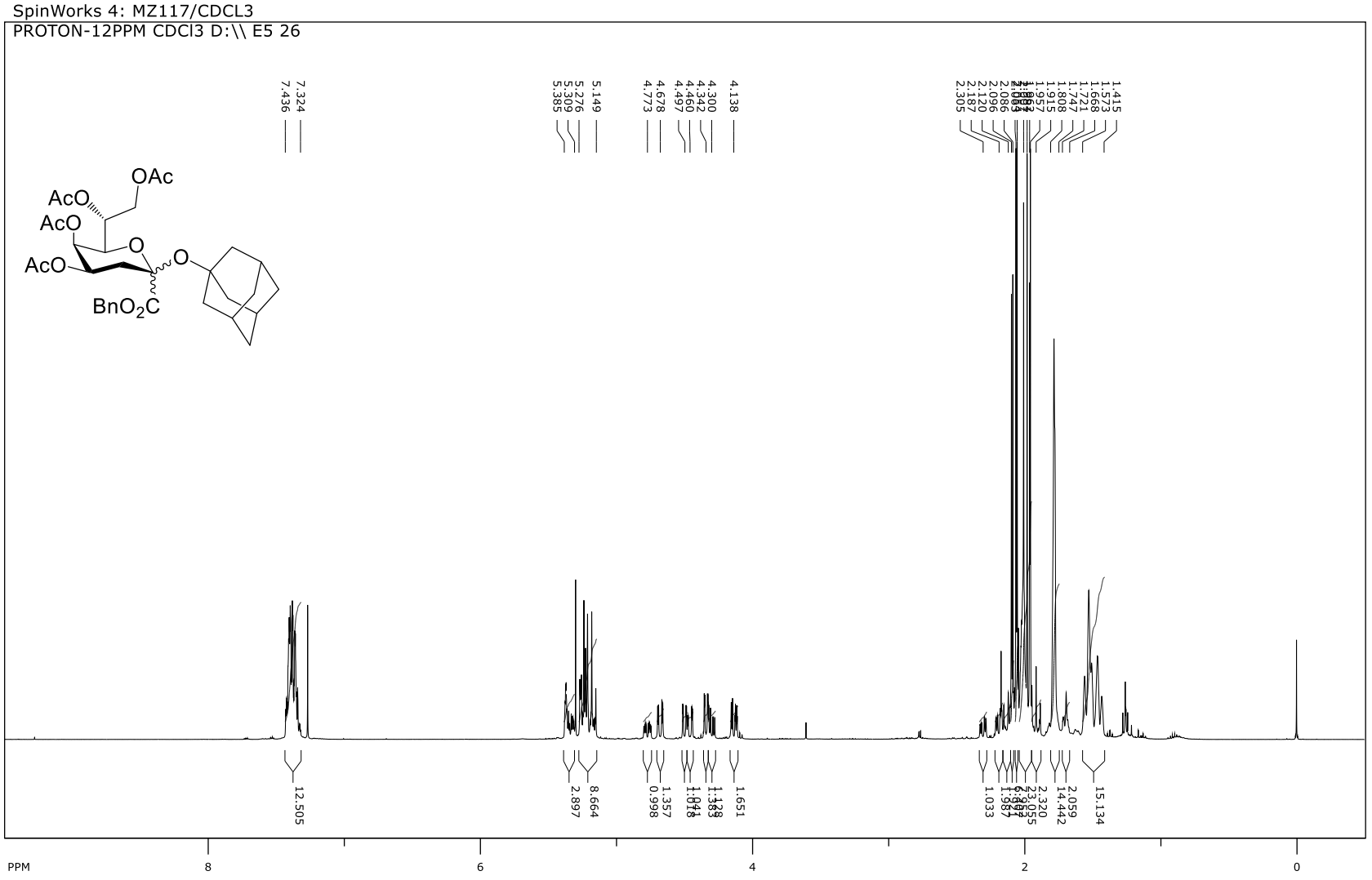
2D COSY spectra (400 MHz, $CDCl_3$) of compound **28**.



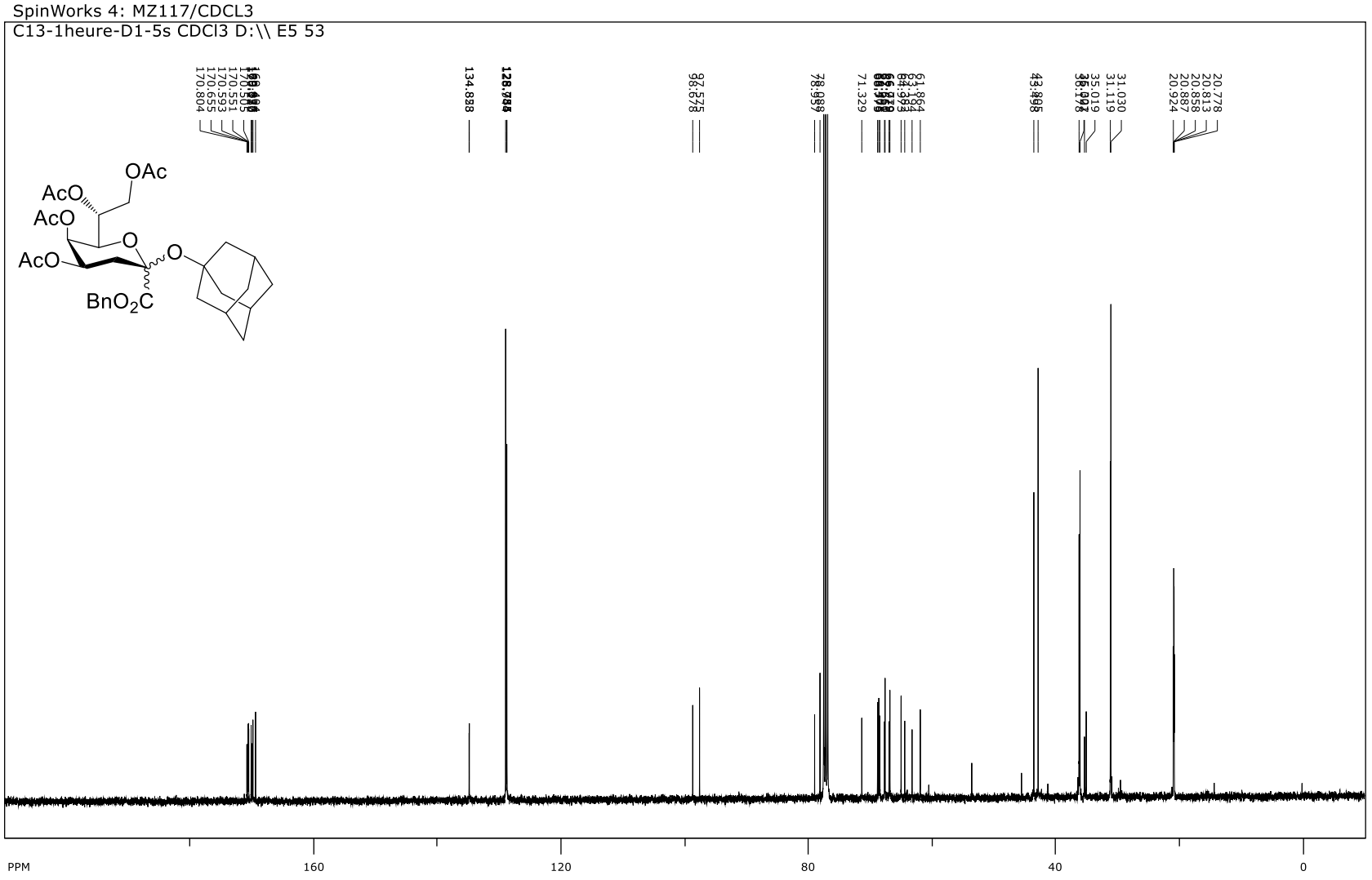
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **28**.



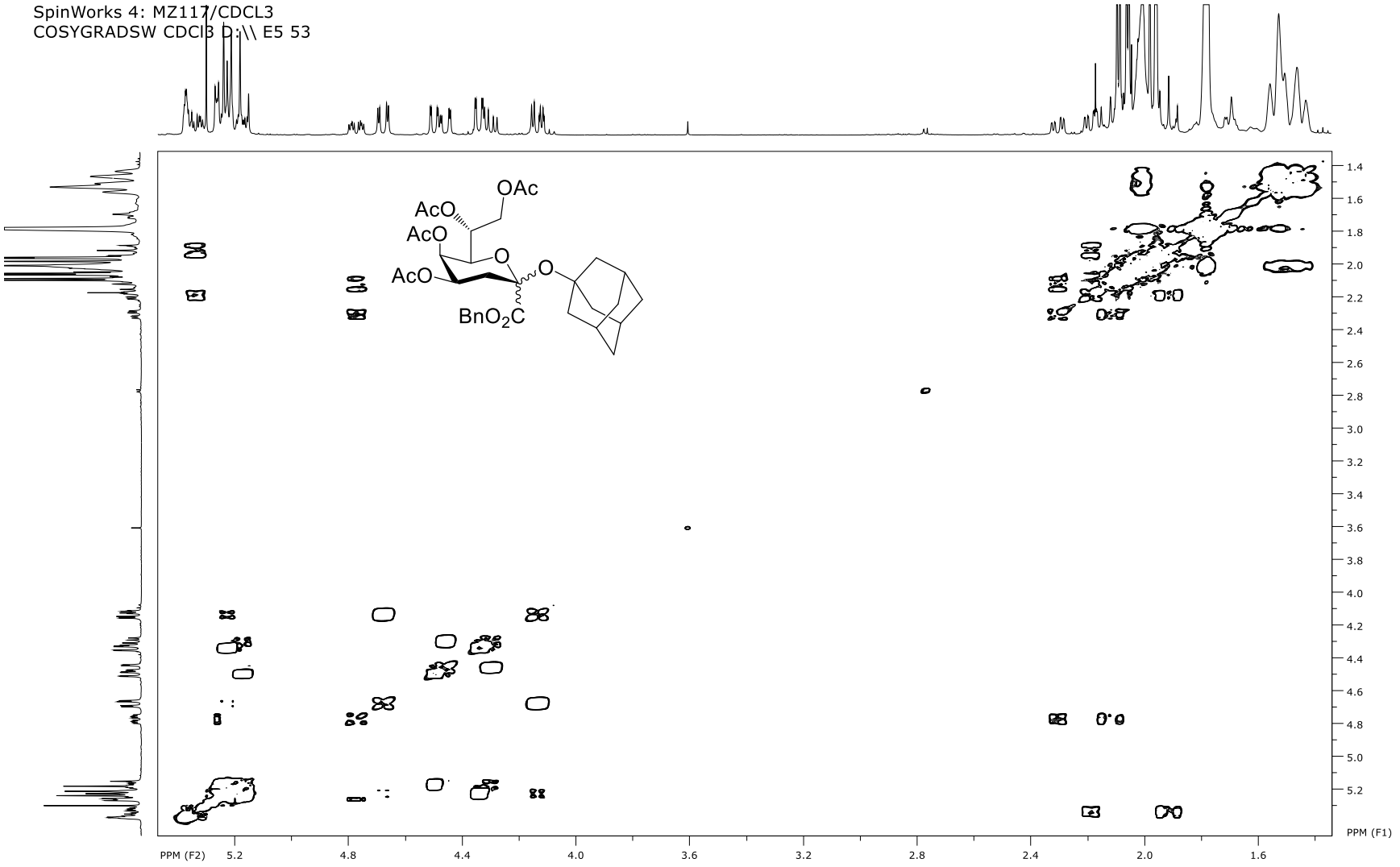
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **29**.



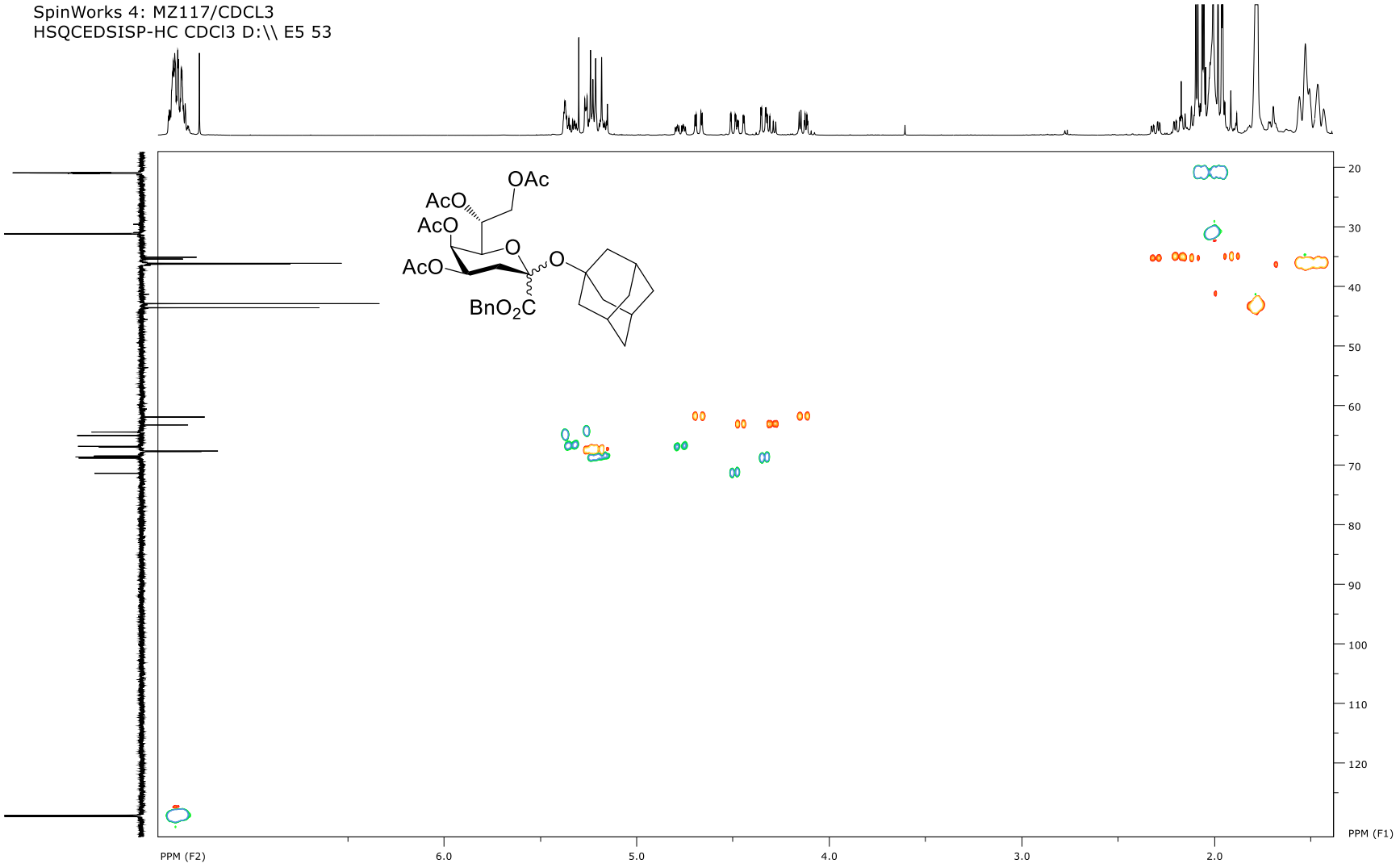
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **29**.



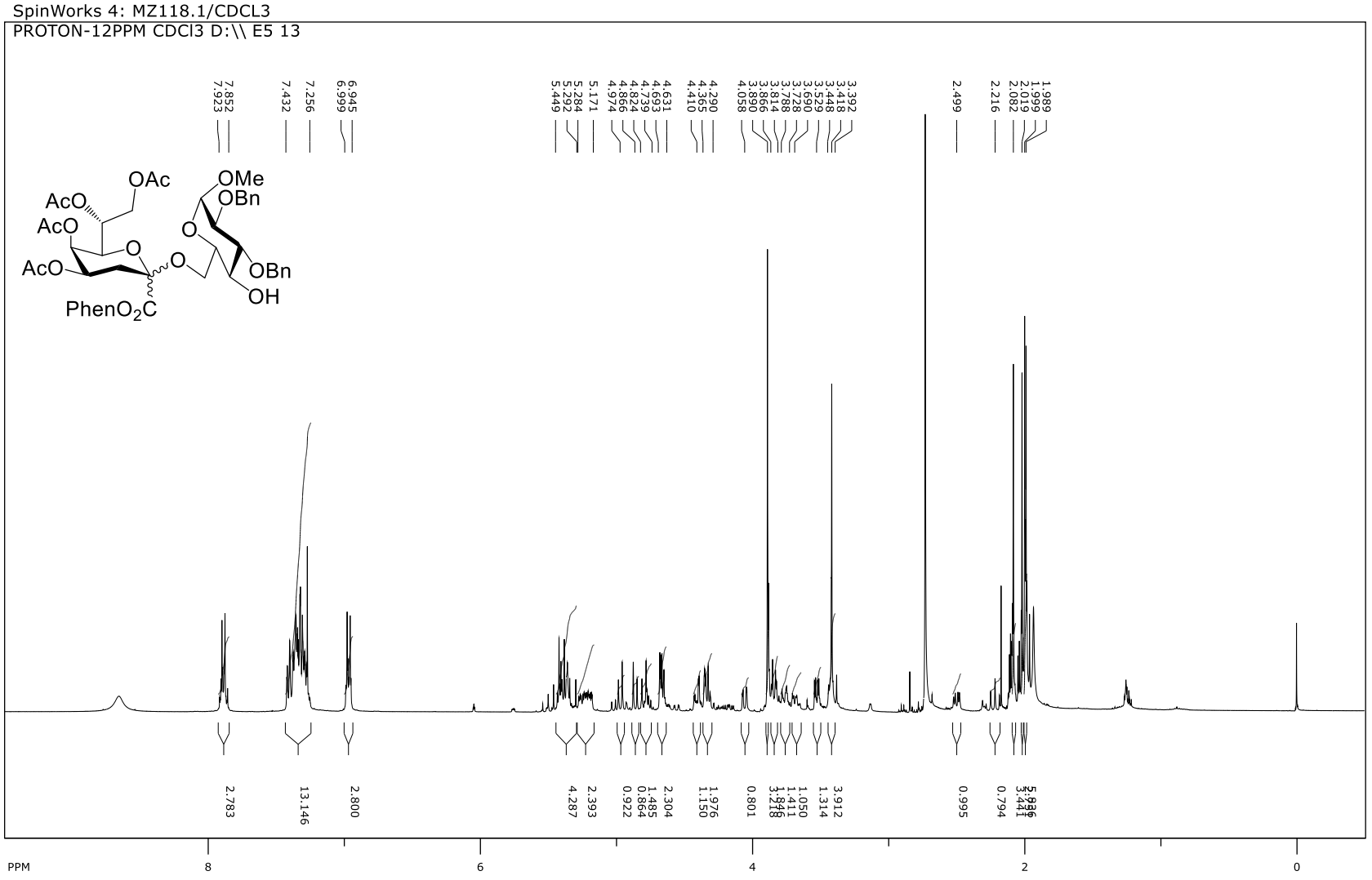
2D COSY spectra (400 MHz, $CDCl_3$) of compound **29**.



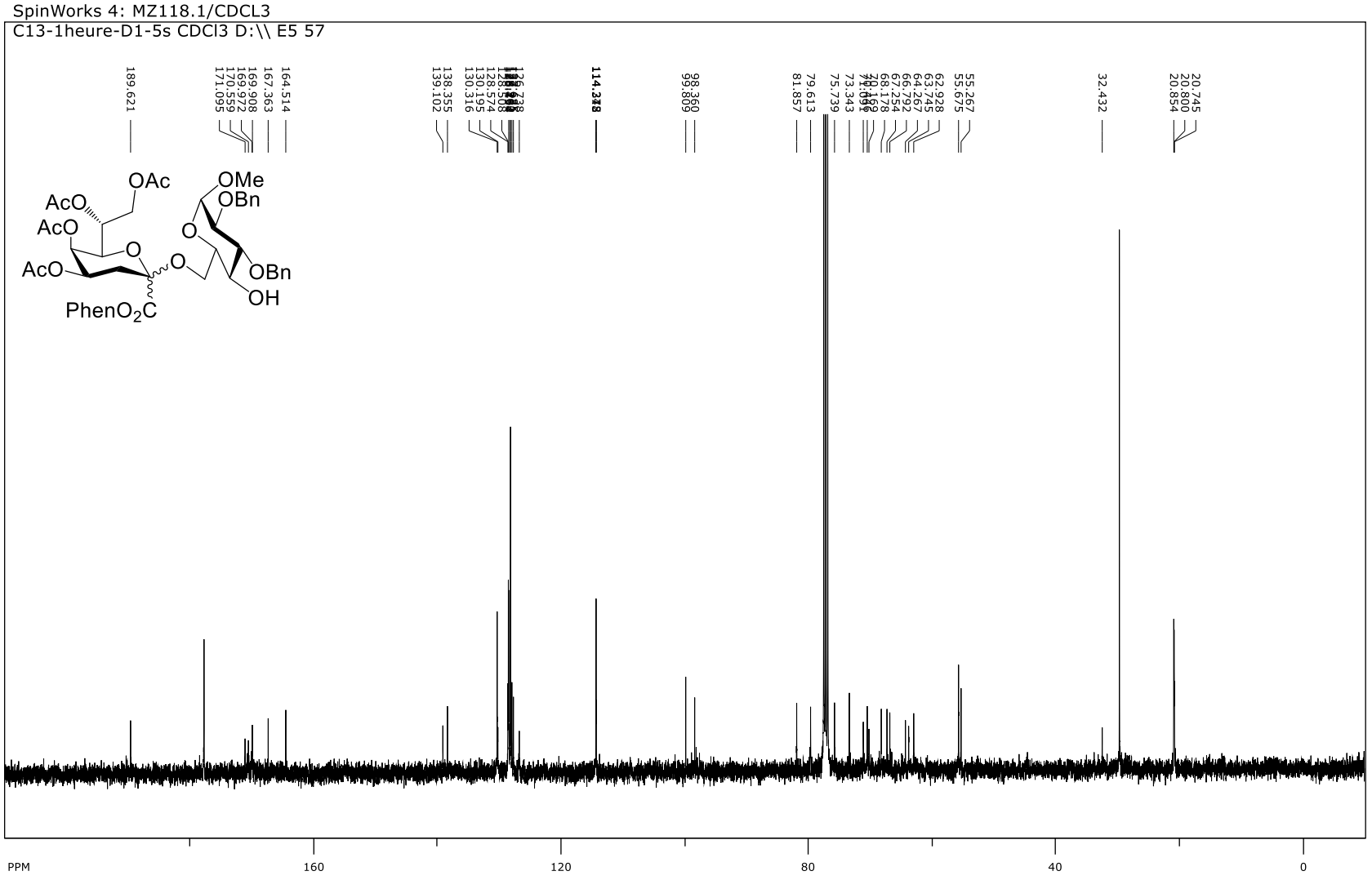
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **29**.



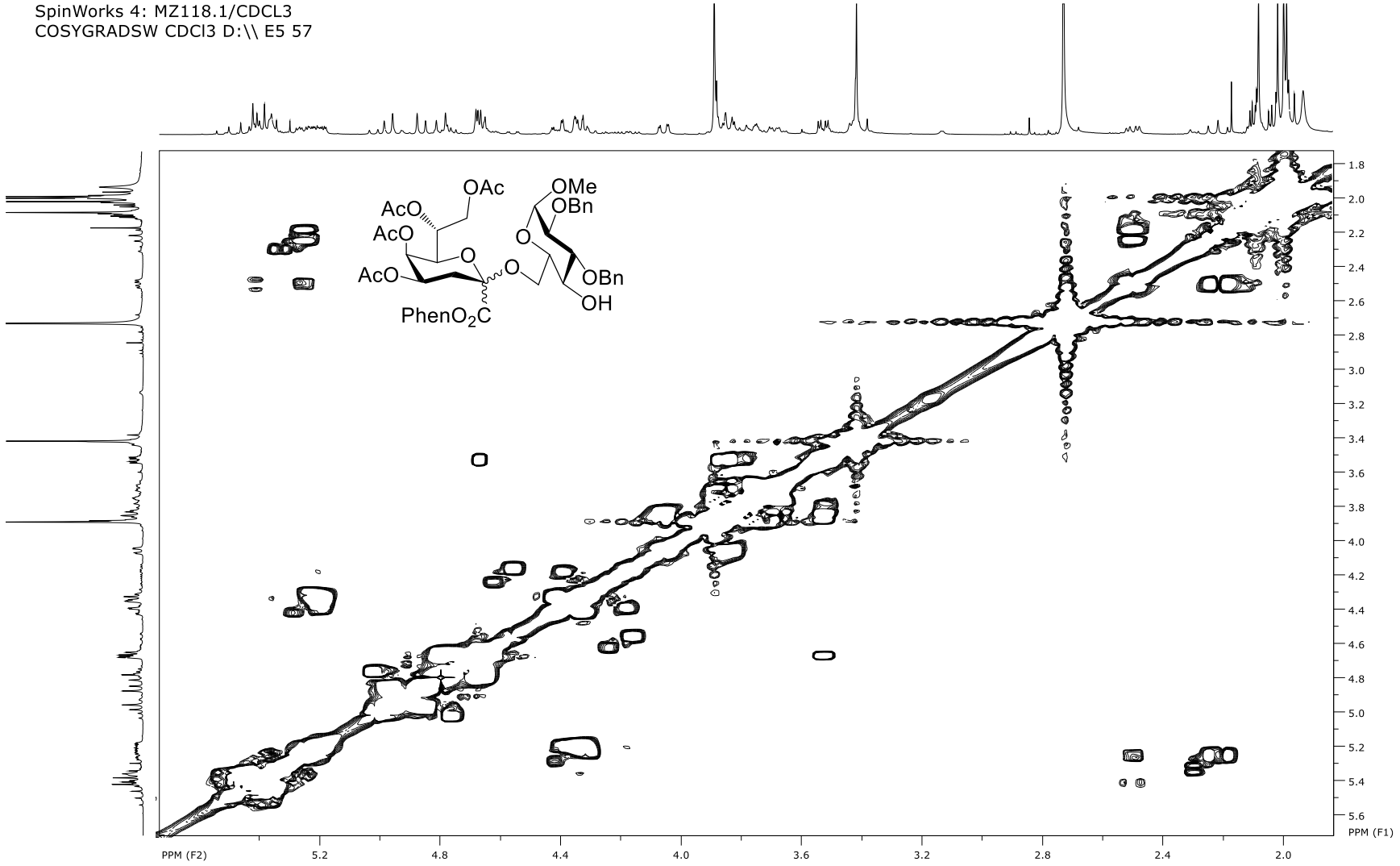
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **30**.



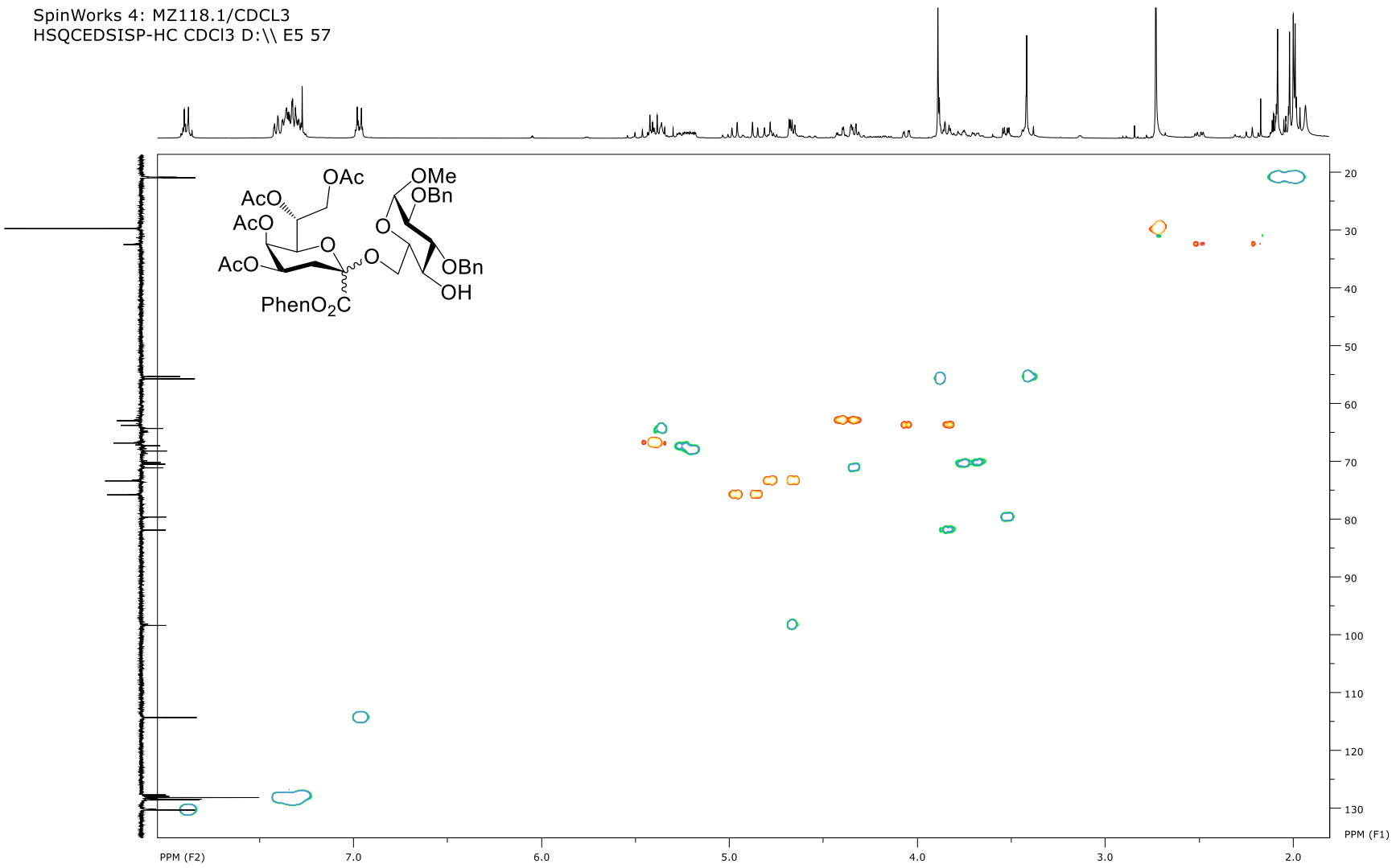
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **30**.



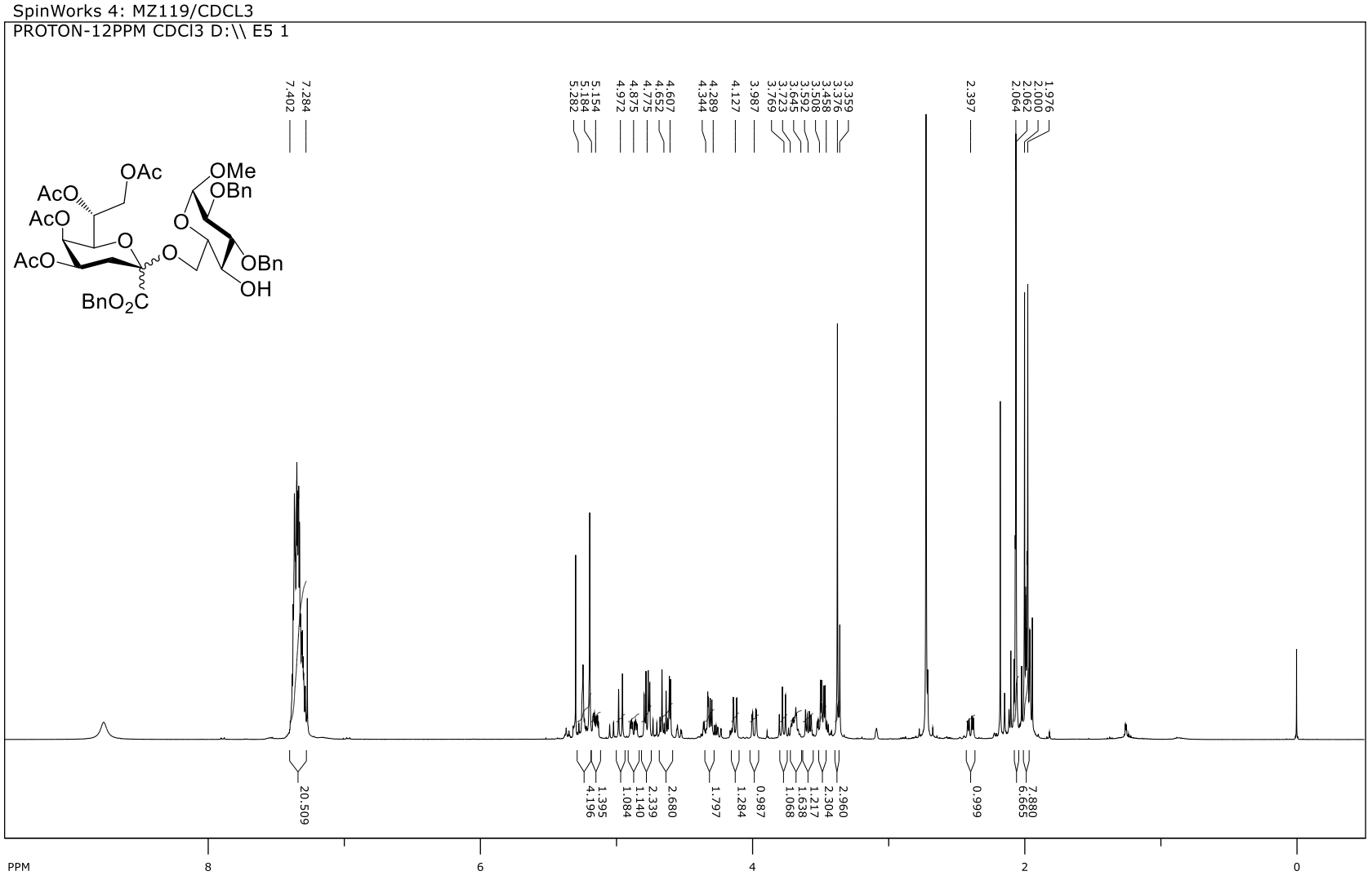
2D COSY spectra (400 MHz, $CDCl_3$) of compound **30**.



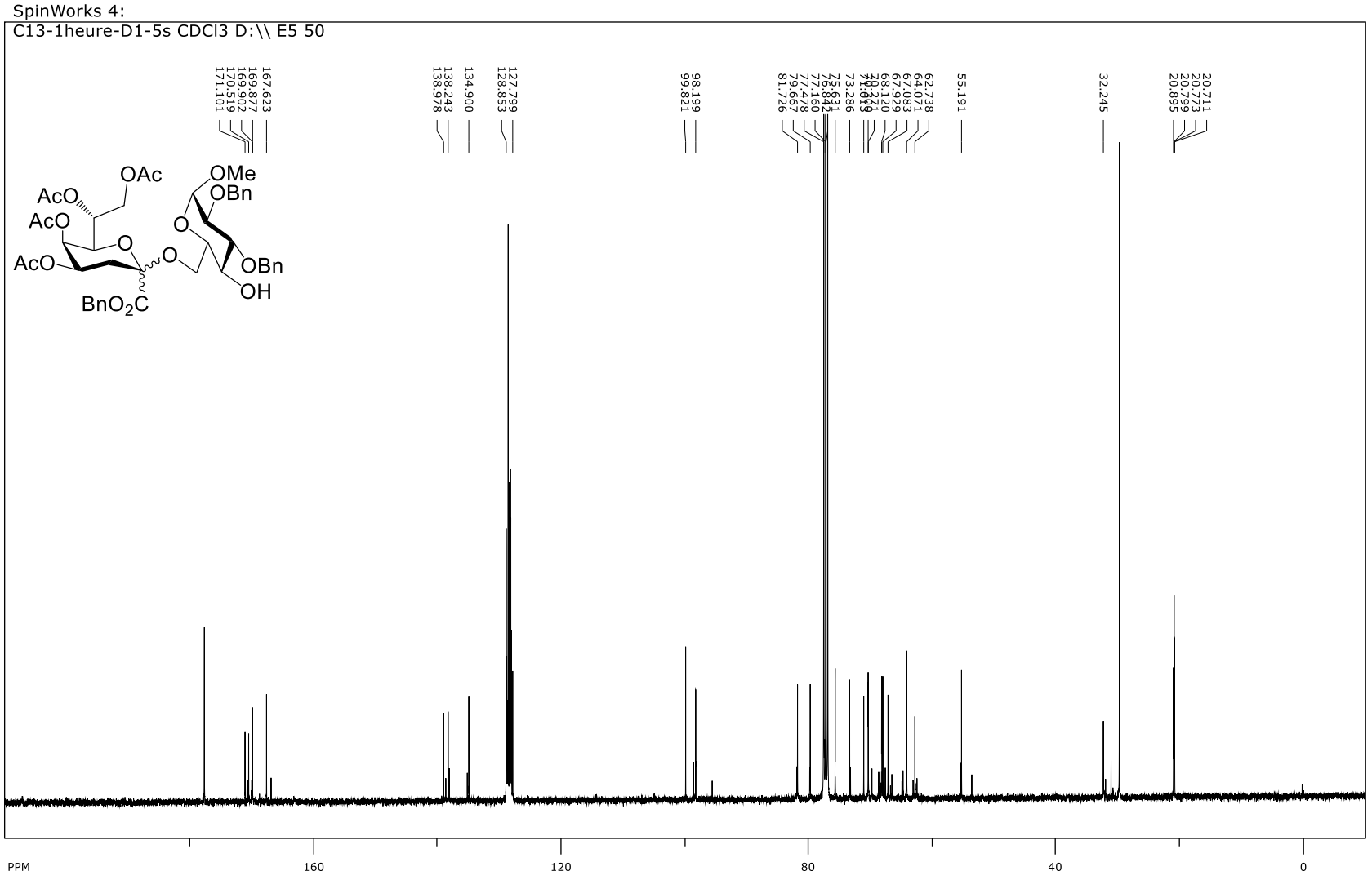
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **30**.



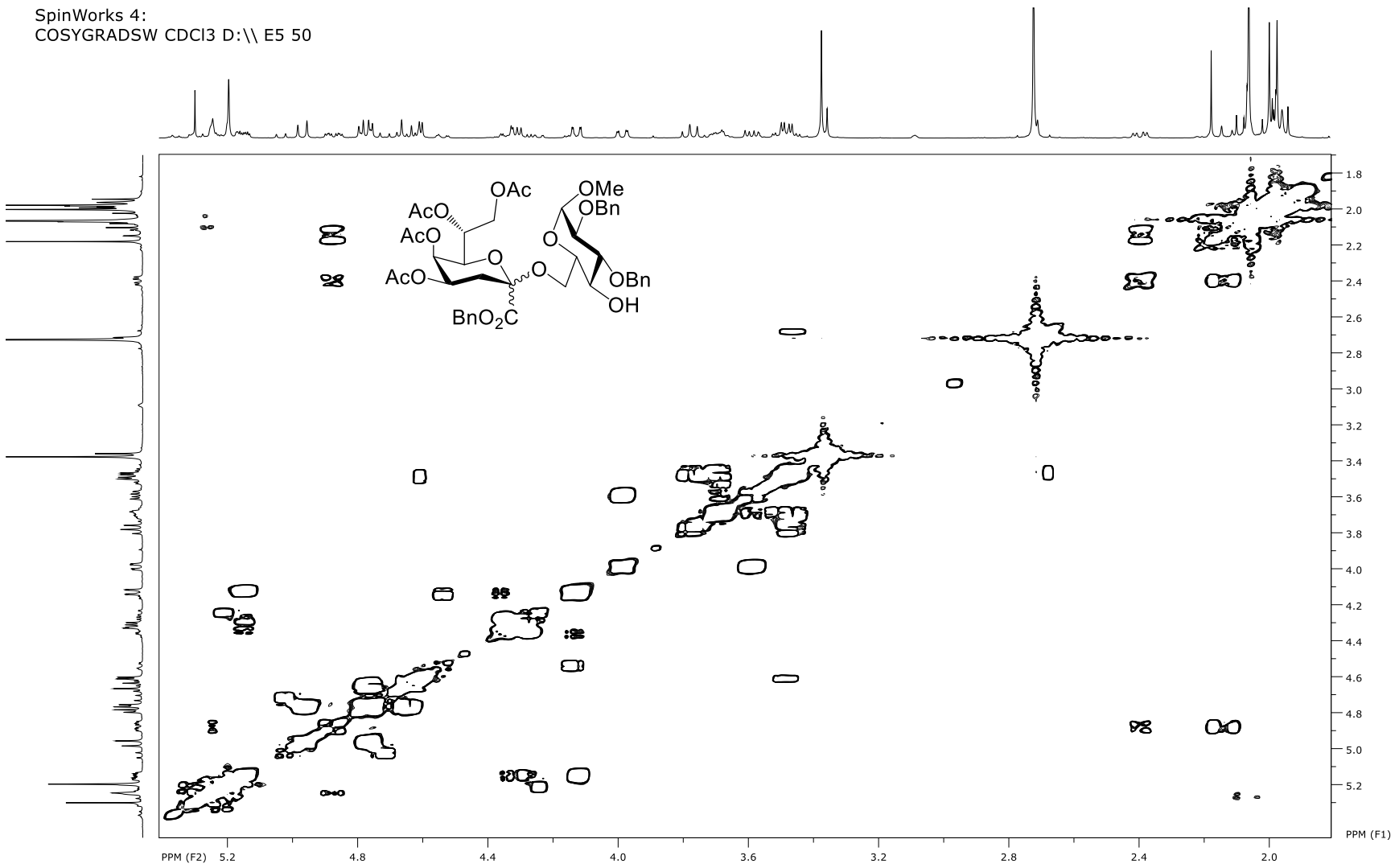
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **31**.



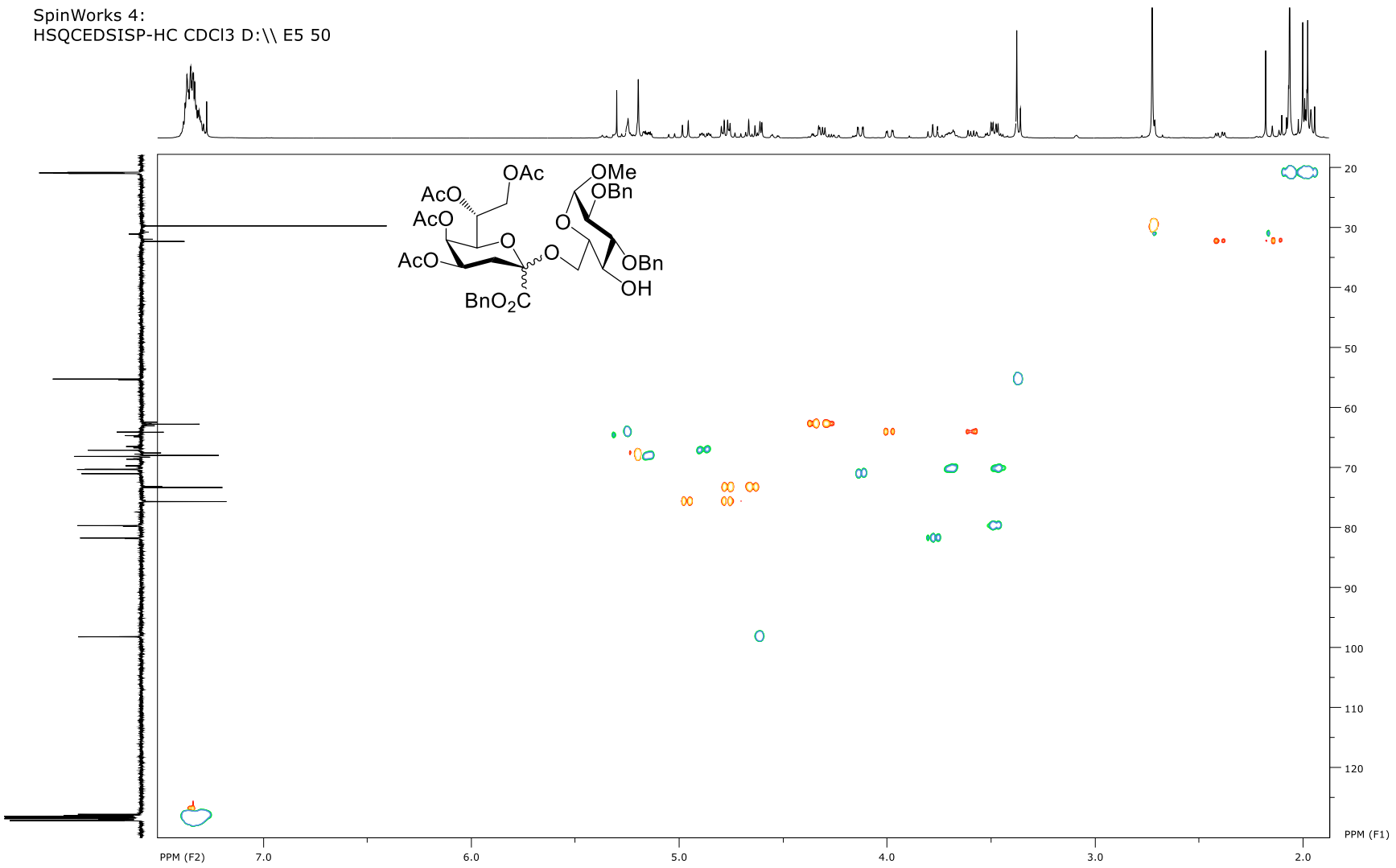
^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **31**.



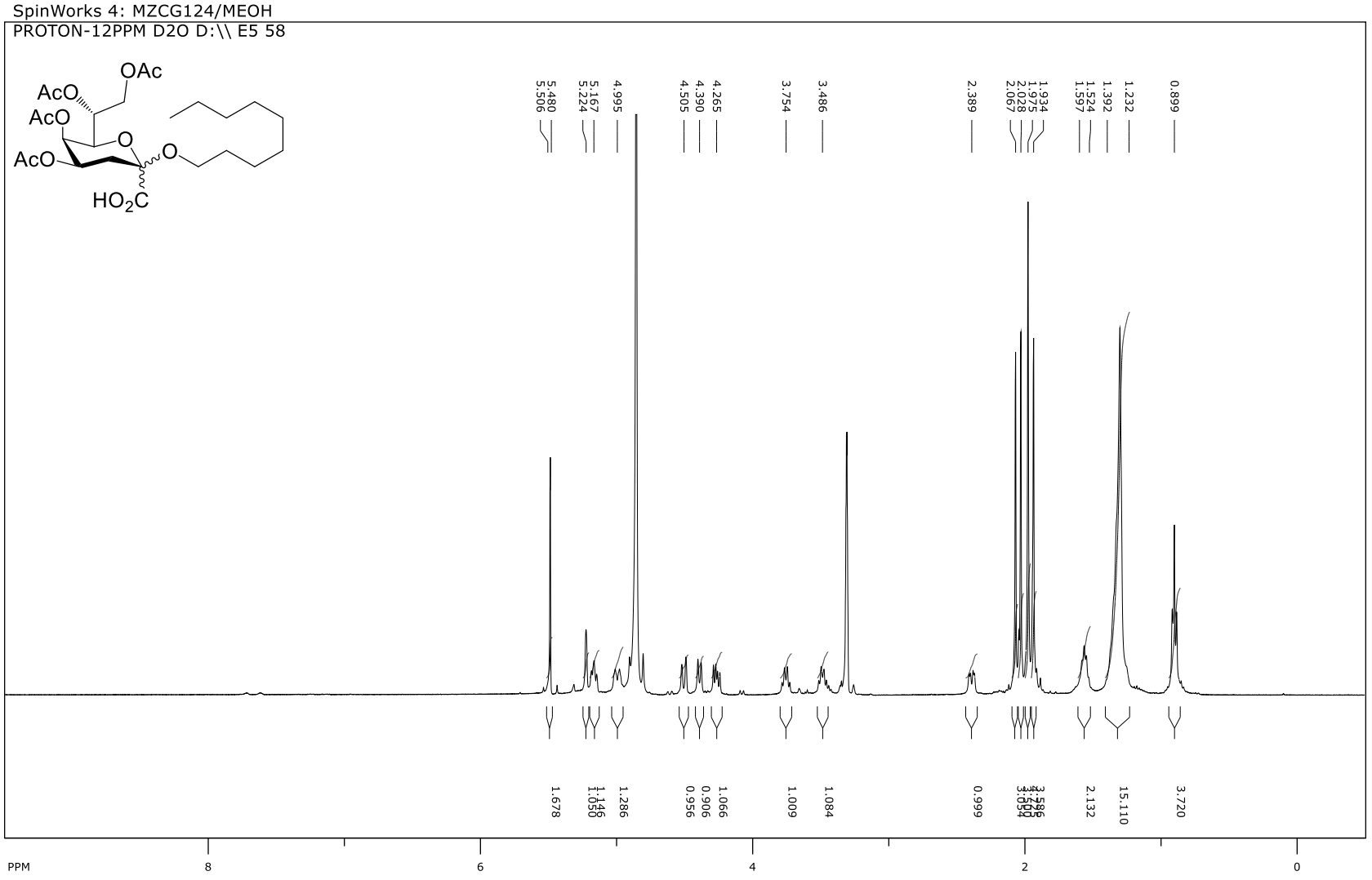
2D COSY spectra (400 MHz, $CDCl_3$) of compound **31**.



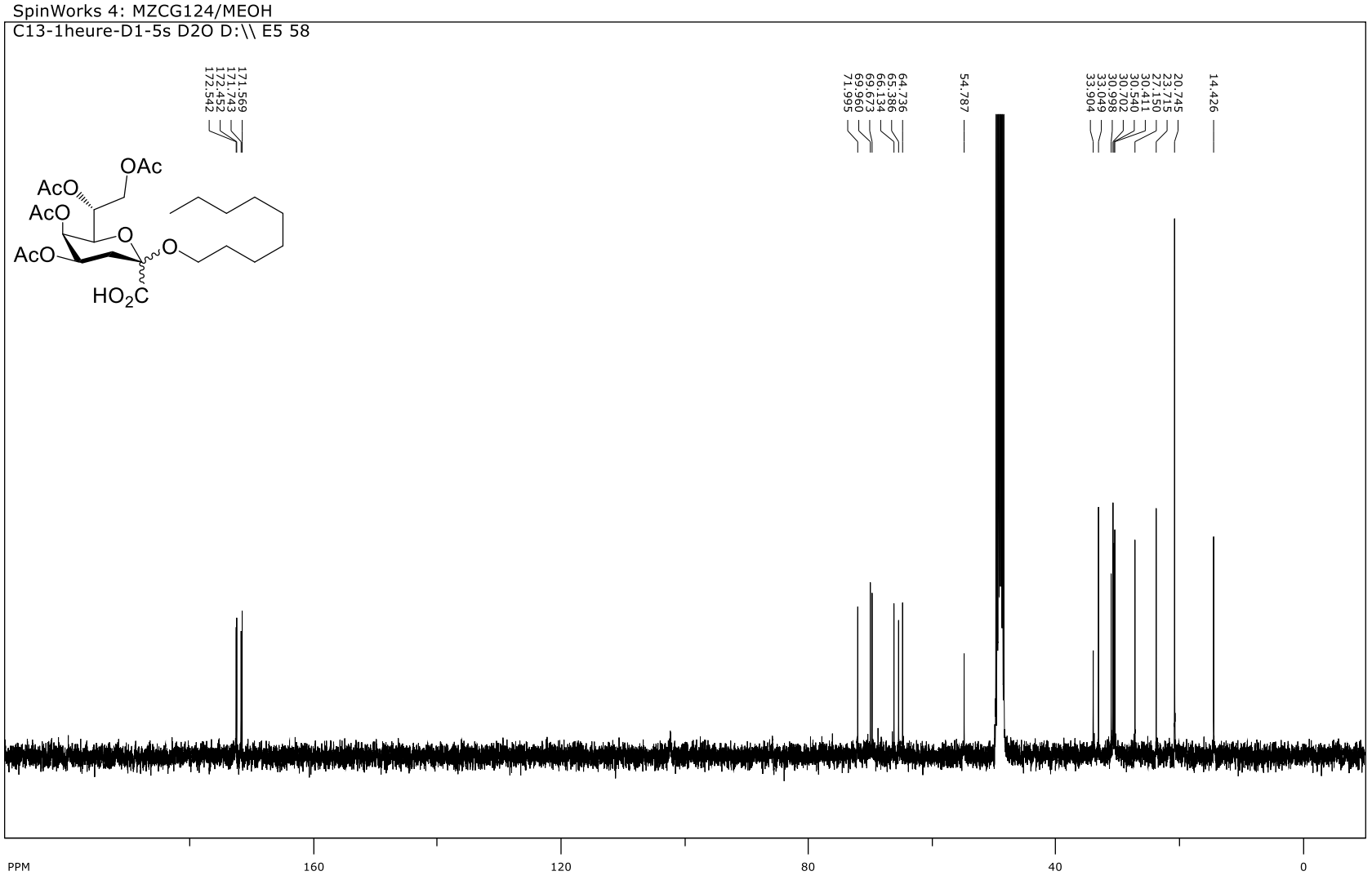
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **31**.



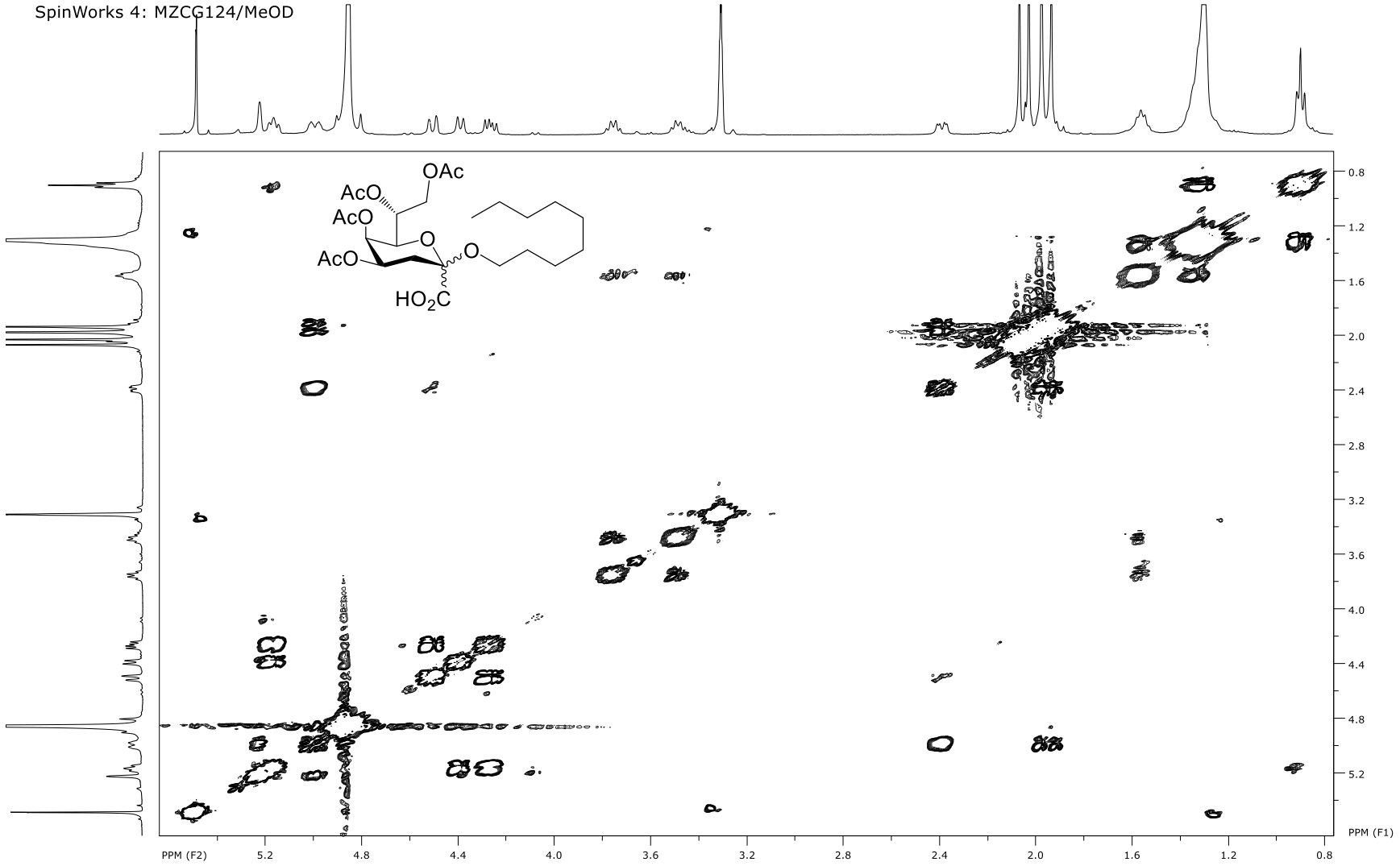
^{1}H NMR spectra (400 MHz, MeOD) of compound **32**.



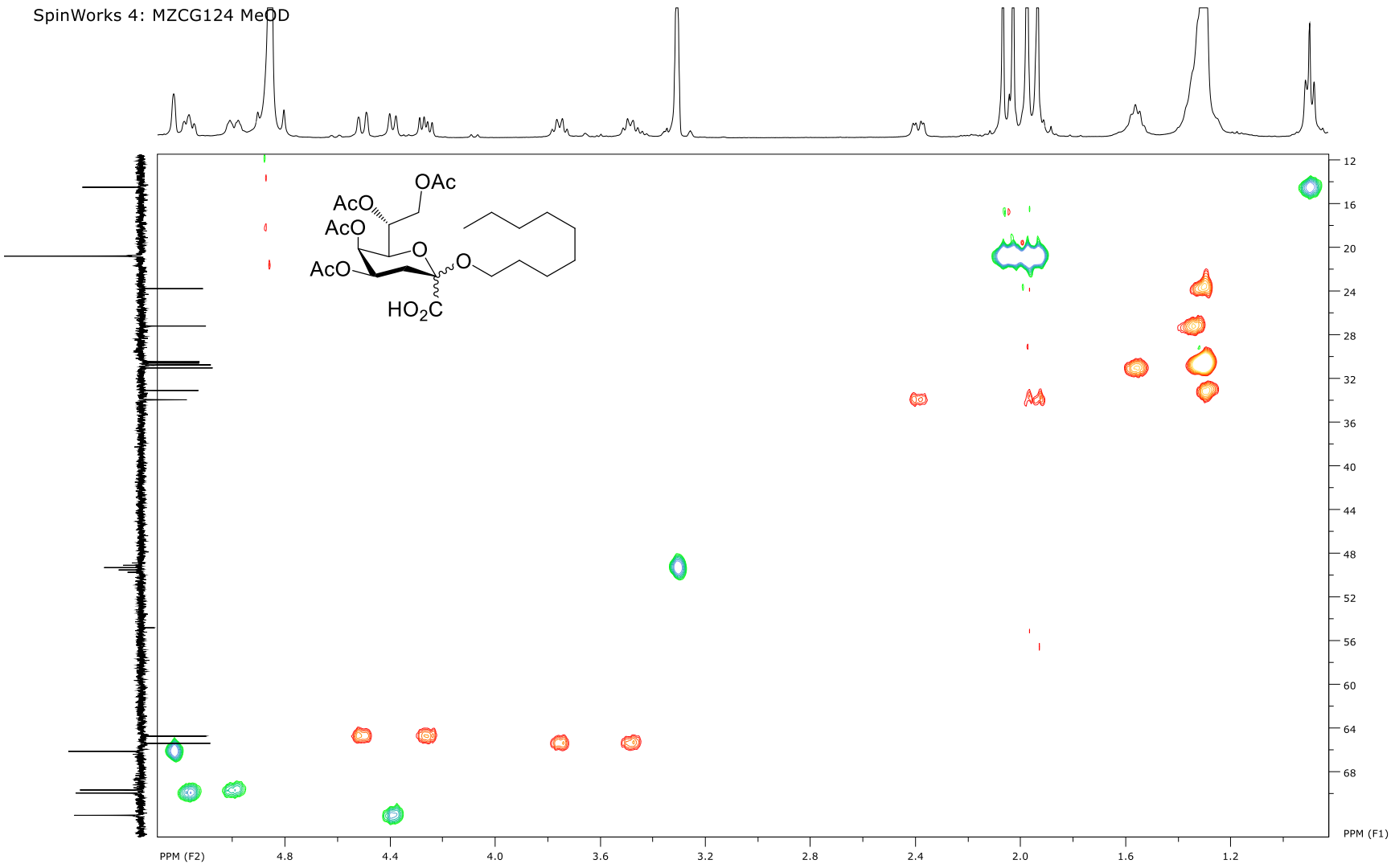
^{13}C NMR spectra (100 MHz, MeOD) of compound **32**.



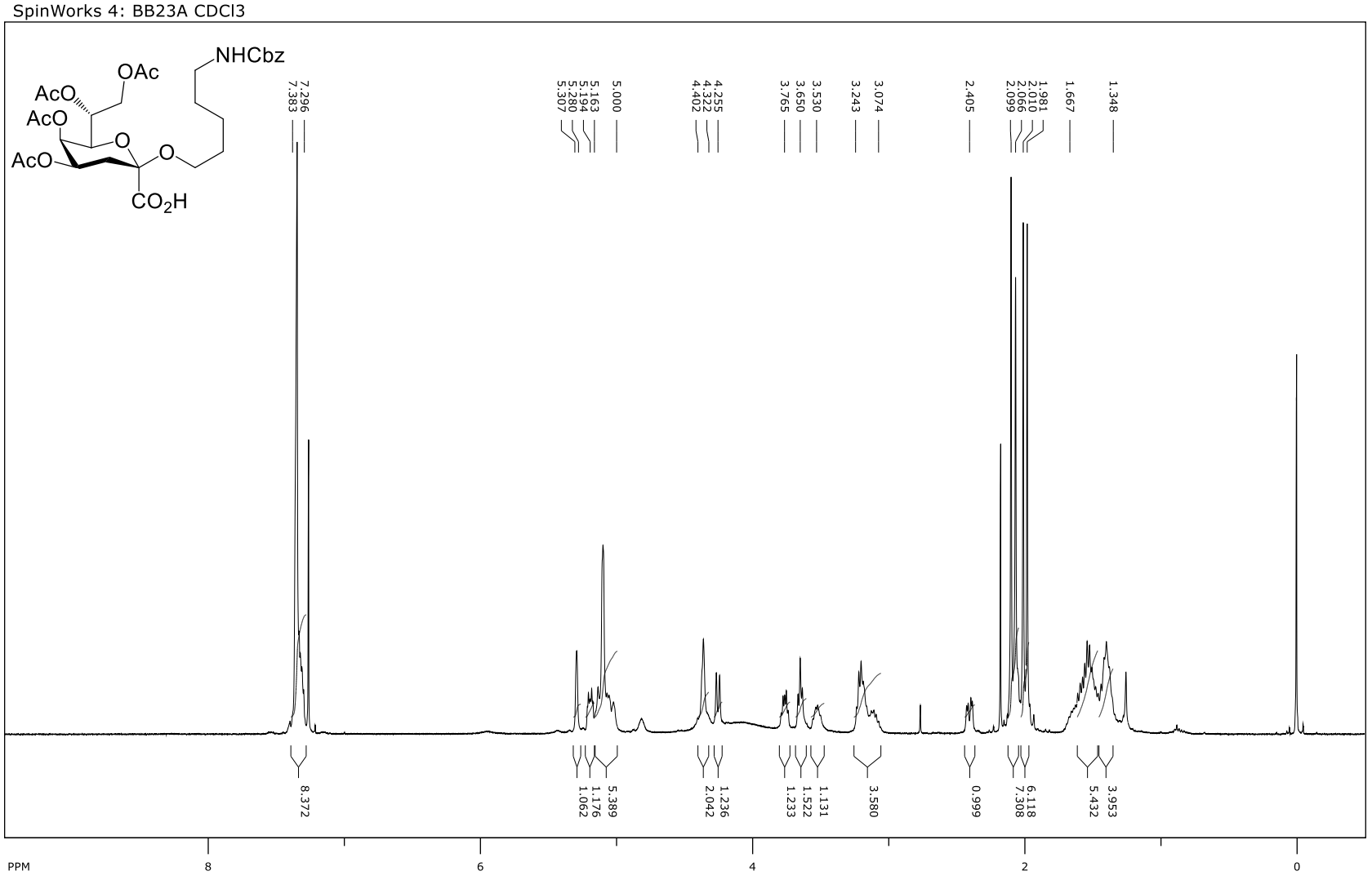
2D COSY spectra (400 MHz, $CDCl_3$) of compound **32**.



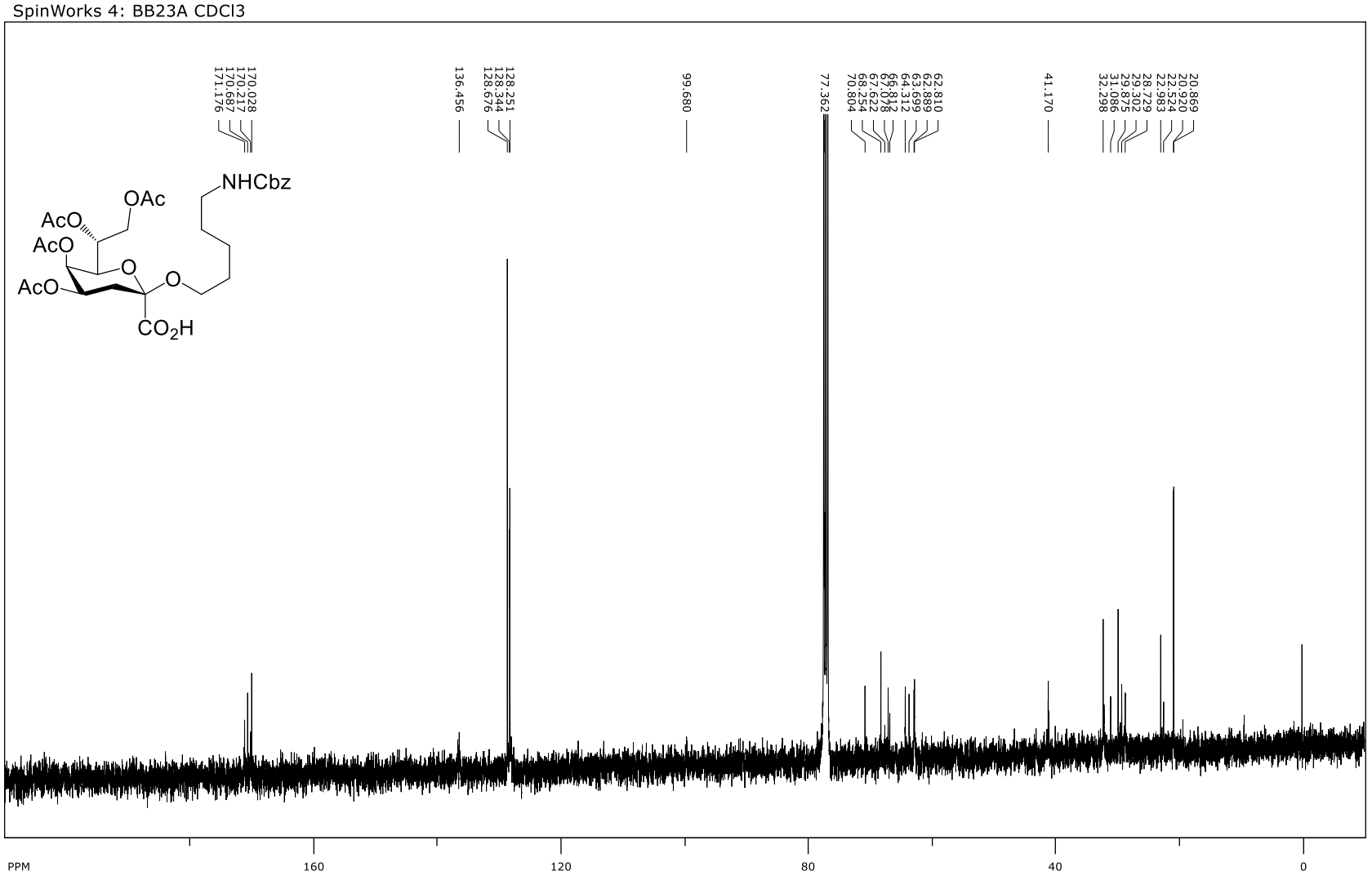
2D HSQC spectra (400 MHz, $CDCl_3$) of compound **32**.



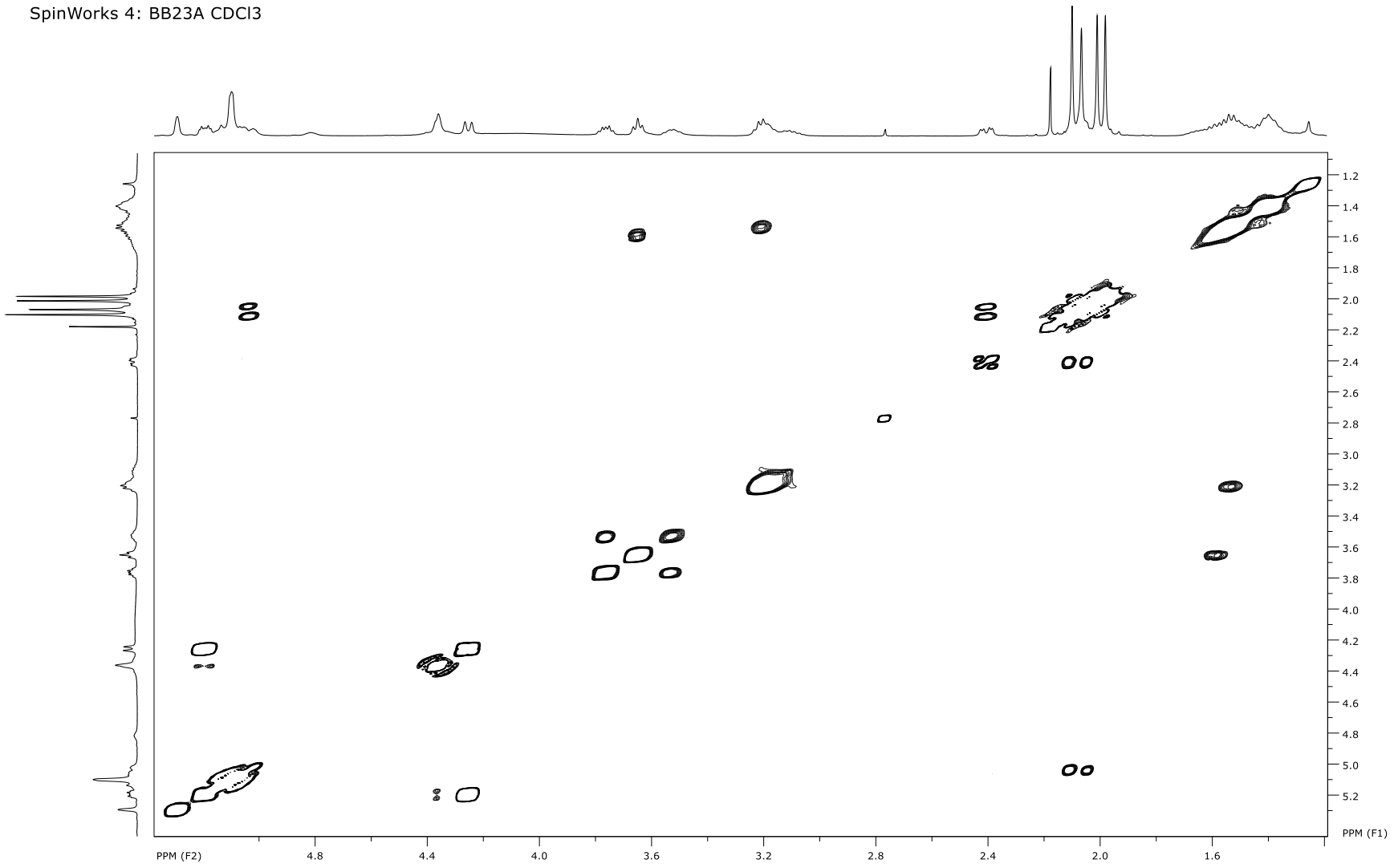
^{1}H NMR spectra (400 MHz, $CDCl_3$) of compound **33**.



^{13}C NMR spectra (100 MHz, $CDCl_3$) of compound **33**.



2D COSY spectra (400 MHz, $CDCl_3$) of compound **33**.



2D HSQC spectra (400 MHz, $CDCl_3$) of compound **33**.

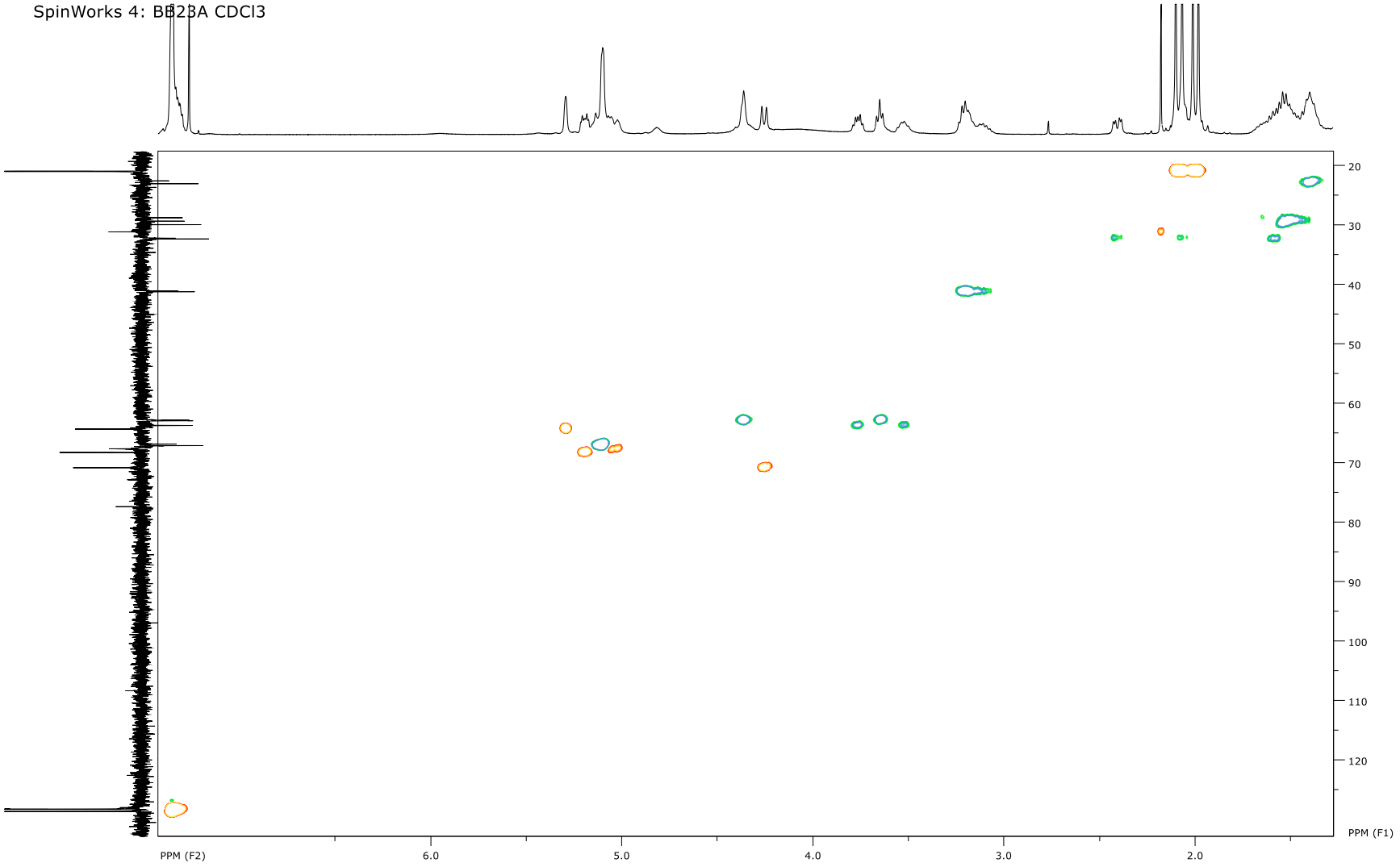


Figure S1. Structures and energies (in Hartree) of α-spiroPhen, β-spiroPhen, and oxocarbenium most stable conformers.

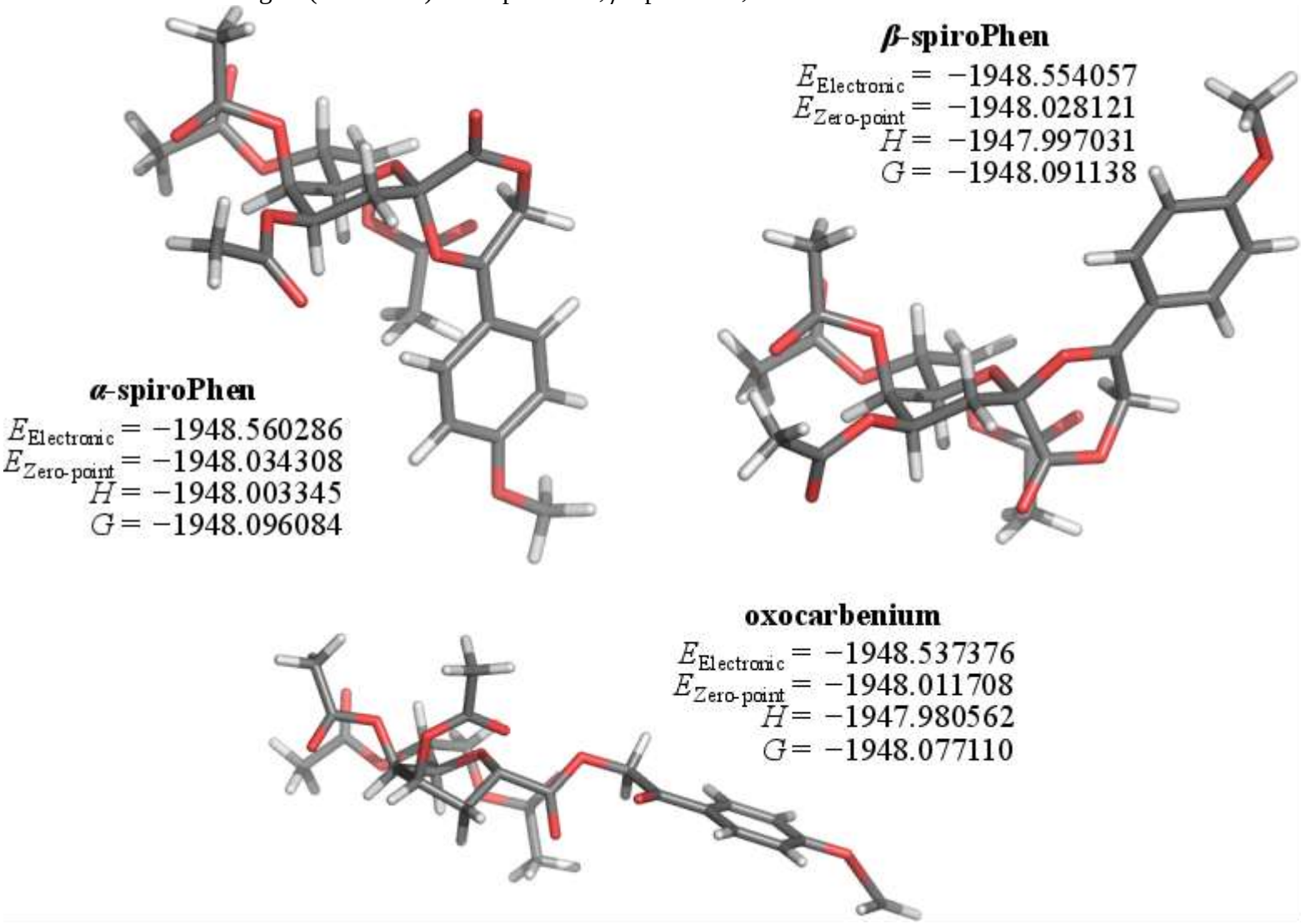


Table S1. Coordinated of *α*-spiroPhen, *β*-spiroPhen, and oxocarbenium most stable conformers.

Atom	*α*-spiroPhen			*β*-spiroPhen			oxocarbenium		
	X	Y	Z	X	Y	Z	X	Y	Z
C	−0.1658	−1.6473	2.9335	0.4232	0.8562	−2.4374	−0.7907	−0.4979	0.4361
O	1.0232	−1.2969	3.4407	1.4403	1.7270	−2.3977	−1.3949	−0.5927	−0.7346
O	−0.9900	−2.2102	3.5950	−0.4205	0.9163	−3.2889	−1.2117	0.0214	1.4381
C	−0.3780	−1.2932	1.4482	0.3987	−0.1887	−1.3001	0.6618	−0.9980	0.3751
C	−1.3963	−2.1880	0.7668	−0.3727	−1.4567	−1.6352	1.2441	−1.4422	1.7029
H	−0.9976	−3.1985	0.6903	−0.0939	−1.8076	−2.6282	1.1967	−0.6357	2.4329
H	−2.2858	−2.2062	1.3958	−0.0857	−2.2077	−0.8976	0.6774	−2.2838	2.0992
C	−1.7586	−1.6370	−0.6102	−1.8757	−1.2175	−1.5500	2.6798	−1.8207	1.3956
H	−0.9123	−1.7176	−1.2945	−2.2145	−0.5559	−2.3466	3.1876	−2.3190	2.2128
O	−2.8748	−2.3598	−1.1542	−2.5006	−2.5048	−1.6913	2.6668	−2.8676	0.3376
C	−2.6117	−3.5263	−1.7974	−3.8061	−2.5248	−2.0713	1.7052	−2.9792	−0.5001
O	−1.4939	−3.9728	−1.9142	−4.4204	−1.5256	−2.3631	0.6885	−2.1937	−0.5333
C	−3.8764	−4.1463	−2.3141	−4.3483	−3.9222	−2.0426	1.7800	−4.0581	−1.5034
H	−4.5397	−4.3712	−1.4758	−4.5102	−4.1990	−0.9972	2.2531	−3.6343	−2.3966
H	−3.6429	−5.0584	−2.8583	−3.6335	−4.6251	−2.4713	0.7771	−4.3883	−1.7690
H	−4.3947	−3.4396	−2.9651	−5.2950	−3.9611	−2.5771	2.3929	−4.8765	−1.1327
C	−2.1713	−0.1734	−0.5143	−2.2496	−0.5948	−0.2047	3.4966	−0.6012	0.8794
H	−2.3798	0.2271	−1.5046	−3.3123	−0.3626	−0.1850	4.0961	−0.2312	1.7119
O	−3.3386	−0.0562	0.3189	−1.9238	−1.5104	0.8589	4.3495	−0.9484	−0.2121
C	−4.5178	0.3069	−0.2571	−2.9294	−2.2354	1.4165	5.5106	−1.6024	0.0852
O	−4.6318	0.5568	−1.4333	−4.0773	−2.1684	1.0439	5.7723	−1.9636	1.2063
C	−5.6014	0.3892	0.7748	−2.4138	−3.0681	2.5503	6.3470	−1.7683	−1.1447
H	−5.5778	−0.4844	1.4271	−2.2108	−2.4000	3.3915	7.2680	−2.2904	−0.8972
H	−6.5686	0.4789	0.2855	−1.4807	−3.5601	2.2737	6.5651	−0.7819	−1.5608
H	−5.4205	1.2755	1.3888	−3.1641	−3.8004	2.8403	5.7860	−2.3286	−1.8959
C	−1.0362	0.6176	0.1259	−1.4443	0.6813	0.0109	2.5466	0.5065	0.4228
H	−0.1740	0.5780	−0.5446	−1.7566	1.4184	−0.7358	2.1988	1.0426	1.3078
O	−0.6619	0.0591	1.4160	−0.0228	0.4344	−0.1118	1.3994	−0.0266	−0.2768
C	−1.3968	2.0727	0.4291	−1.6188	1.2658	1.4153	3.1583	1.5254	−0.5358
H	−2.1772	2.0932	1.1906	−1.2562	0.5466	2.1497	3.5748	1.0259	−1.4094

Atom	*α*-spiroPhen			*β*-spiroPhen			oxocarbenium		
	X	Y	Z	X	Y	Z	X	Y	Z
O	−1.9000	2.6296	−0.8001	−3.0348	1.4712	1.5929	4.2180	2.1492	0.2167
C	−3.1013	3.2721	−0.7777	−3.6546	0.8764	2.6495	5.4522	2.2454	−0.3524
O	−3.7509	3.4231	0.2297	−3.0733	0.2013	3.4658	5.7008	1.8608	−1.4698
C	−3.4955	3.7057	−2.1568	−5.1277	1.1547	2.6208	6.4209	2.8722	0.6063
H	−2.6375	4.0973	−2.7031	−5.5773	0.8491	3.5628	6.0424	3.8421	0.9347
H	−4.2878	4.4487	−2.0953	−5.5730	0.5820	1.8028	7.3900	2.9883	0.1269
H	−3.8677	2.8246	−2.6868	−5.3140	2.2121	2.4294	6.5150	2.2372	1.4903
C	−0.2217	2.8946	0.9277	−0.8795	2.5737	1.6176	2.1430	2.5575	−1.0066
H	−0.5325	3.9290	1.0757	−1.1221	2.9891	2.5960	2.6624	3.3953	−1.4717
H	0.1460	2.4886	1.8683	0.1940	2.4080	1.5494	1.4601	2.1051	−1.7228
O	0.8270	2.8939	−0.0676	−1.3047	3.5256	0.6182	1.4020	3.0702	0.1220
C	2.0980	2.6402	0.3124	−0.3688	4.2150	−0.0691	0.0488	2.9805	0.1113
O	2.4152	2.3610	1.4490	0.8243	4.0709	0.0941	−0.5900	2.5569	−0.8252
C	3.0330	2.7200	−0.8590	−1.0091	5.1566	−1.0467	−0.5305	3.4272	1.4223
H	4.0531	2.5428	−0.5273	−1.6169	5.8857	−0.5063	0.0636	4.2229	1.8702
H	2.9542	3.7008	−1.3311	−1.6733	4.6003	−1.7112	−0.5266	2.5670	2.0979
H	2.7474	1.9720	−1.6023	−0.2414	5.6666	−1.6238	−1.5608	3.7464	1.2760
C	3.1183	−0.8774	0.3845	3.9251	−0.1271	−0.3541	−5.1557	−0.4268	−0.1885
C	4.3596	−0.3779	0.8708	4.0592	−1.4490	0.1673	−5.5410	0.7916	−0.7809
H	4.4849	−0.1264	1.9145	3.2097	−2.1178	0.1401	−4.8112	1.4450	−1.2424
C	5.4274	−0.1941	0.0289	5.2389	−1.8785	0.7150	−6.8660	1.1861	−0.7875
H	6.3571	0.1899	0.4217	5.3136	−2.8815	1.1086	−7.1687	2.1217	−1.2411
C	5.2954	−0.5119	−1.3430	6.3446	−0.9939	0.7662	−7.8482	0.3720	−0.1998
O	6.2574	−0.3644	−2.2370	7.5236	−1.3069	1.2738	−9.1132	0.8433	−0.2569
C	7.5467	0.1677	−1.8505	7.7666	−2.6264	1.8173	−10.1743	0.0685	0.3204
H	7.4347	1.1779	−1.4537	7.1033	−2.8148	2.6630	−10.2595	−0.9047	−0.1706
H	8.1292	0.1880	−2.7668	8.8002	−2.6077	2.1500	−11.0814	0.6440	0.1512
H	8.0216	−0.4868	−1.1180	7.6344	−3.3839	1.0434	−10.0200	−0.0670	1.3942
C	4.0697	−1.0214	−1.8449	6.2310	0.3226	0.2537	−7.4809	−0.8454	0.3953
H	4.0016	−1.2507	−2.9001	7.0967	0.9699	0.3014	−8.2193	−1.4883	0.8532
C	3.0088	−1.1982	−1.0054	5.0539	0.7469	−0.2943	−6.1479	−1.2287	0.3944

Atom	*α*-spiroPhen			*β*-spiroPhen			oxocarbenium		
	X	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
H	2.0710	−1.5716	−1.3929	5.0000	1.7511	−0.6907	−5.8586	−2.1667	0.8519
C	2.0043	−1.0069	1.2226	2.7007	0.2872	−0.8876	−3.7561	−0.8932	−0.1566
O	0.9091	−1.5238	0.7236	1.7551	−0.6166	−1.0214	−3.4137	−1.9415	0.3665
C	1.9495	−0.5362	2.6447	2.3691	1.6871	−1.2965	−2.7048	−0.0040	−0.8301
H	1.6741	0.5226	2.6485	1.9412	2.2243	−0.4434	−2.9008	0.0768	−1.8984
H	2.9078	−0.6469	3.1424	3.2437	2.2293	−1.6408	−2.6826	0.9956	−0.3938