

Ni^{II} and Cu^{II} complexes of a salen ligand bearing ferrocenes in its secondary coordination sphere
sphere

Supporting Information

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Mass spectrometry

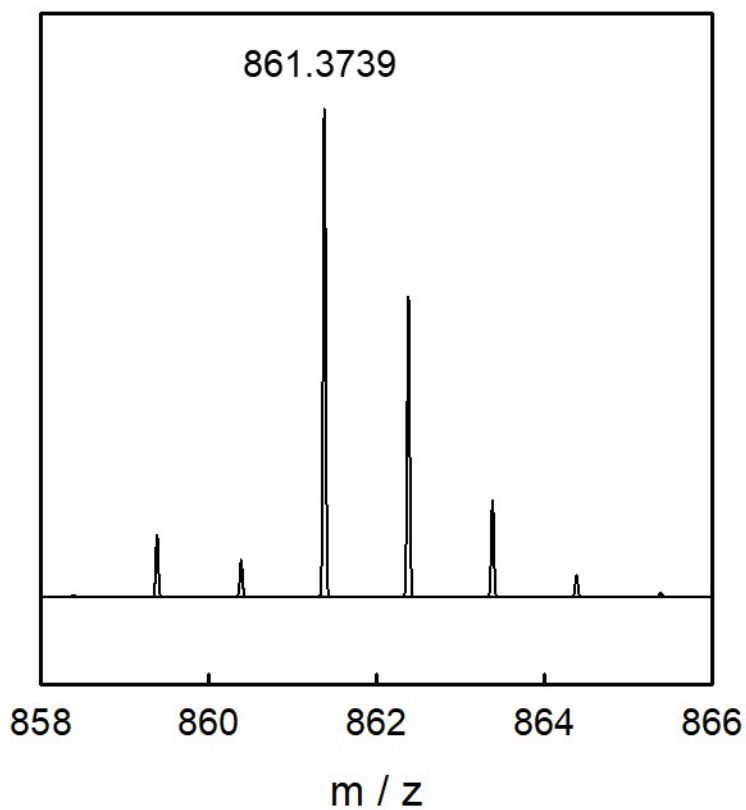
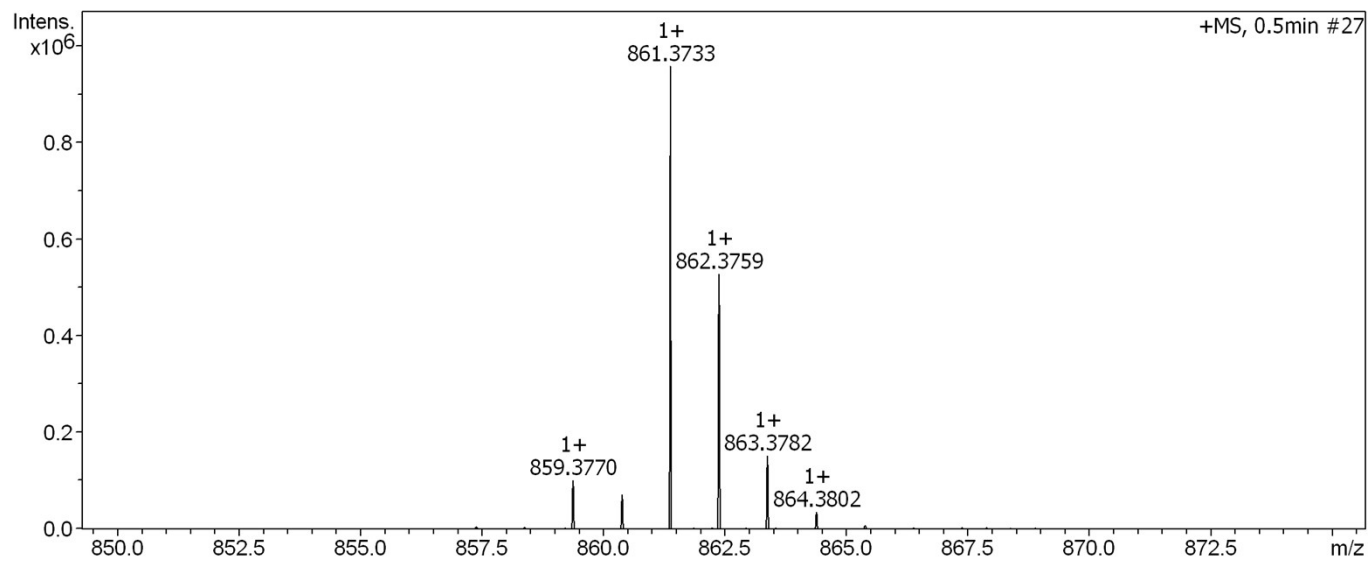


Figure S1. Experimental (top) and simulated (bottom) mass spectrum of $\text{H}_2(\text{Sal})^{\text{Fc}}$.

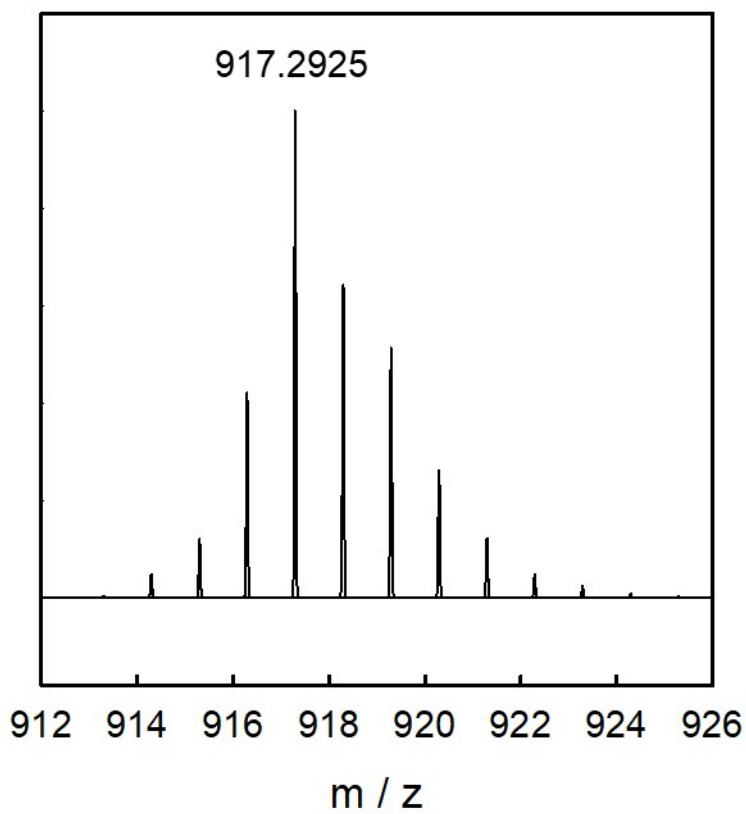
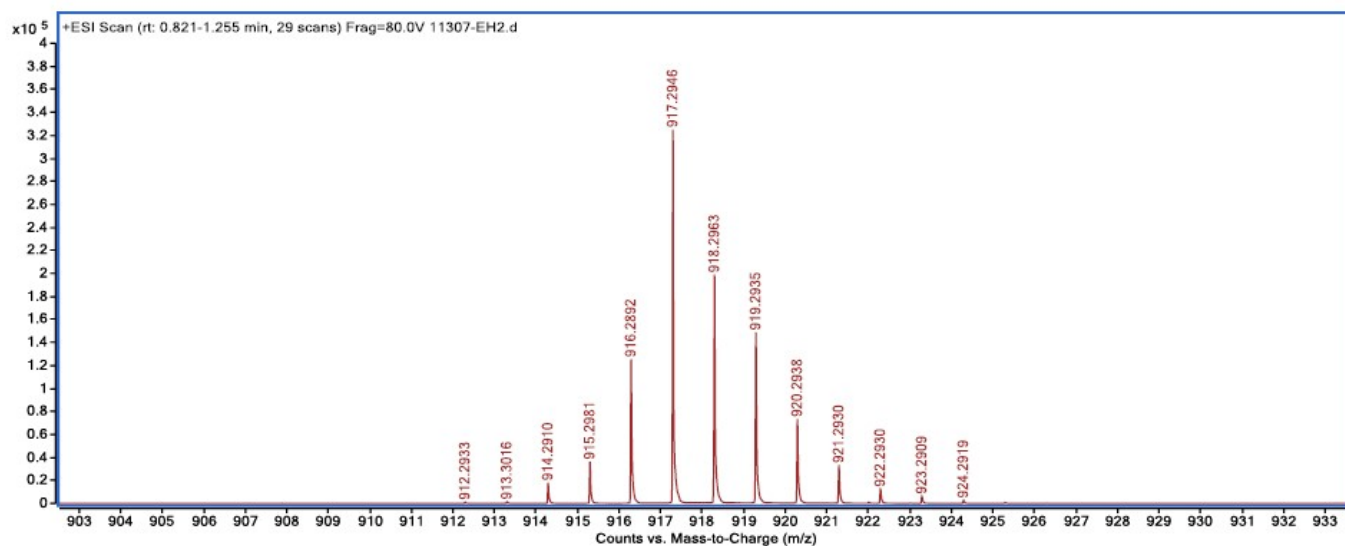


Figure S2. Experimental (top) and simulated (bottom) mass spectrum of Ni(Sal)^{Fc}.

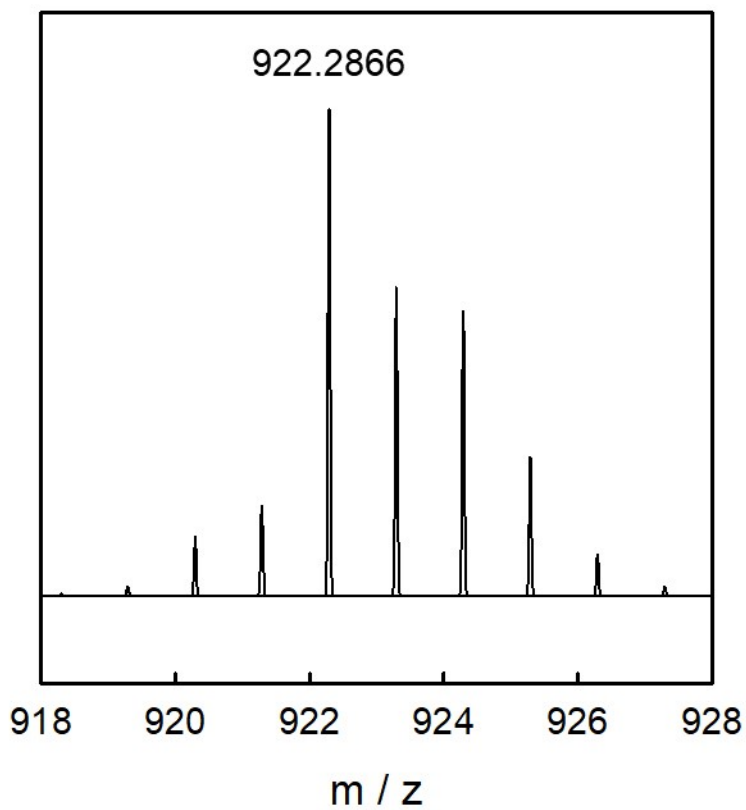
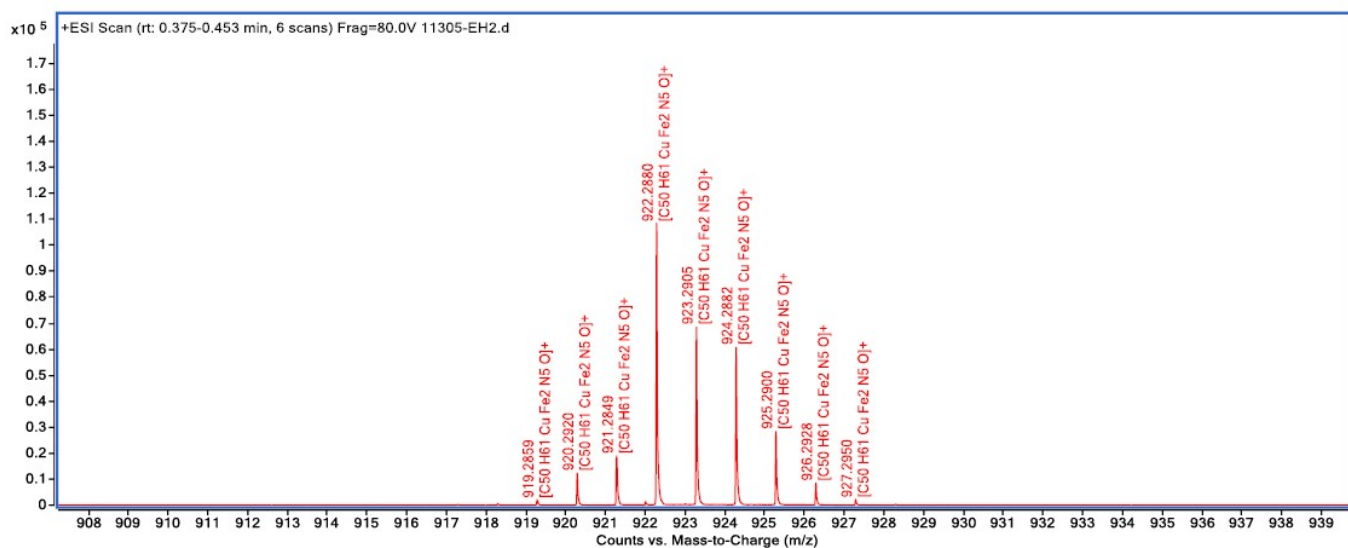


Figure S3. Experimental (top) and simulated (bottom) mass spectrum of **Cu(Sal)^{Fc}**.

NMR spectroscopy:

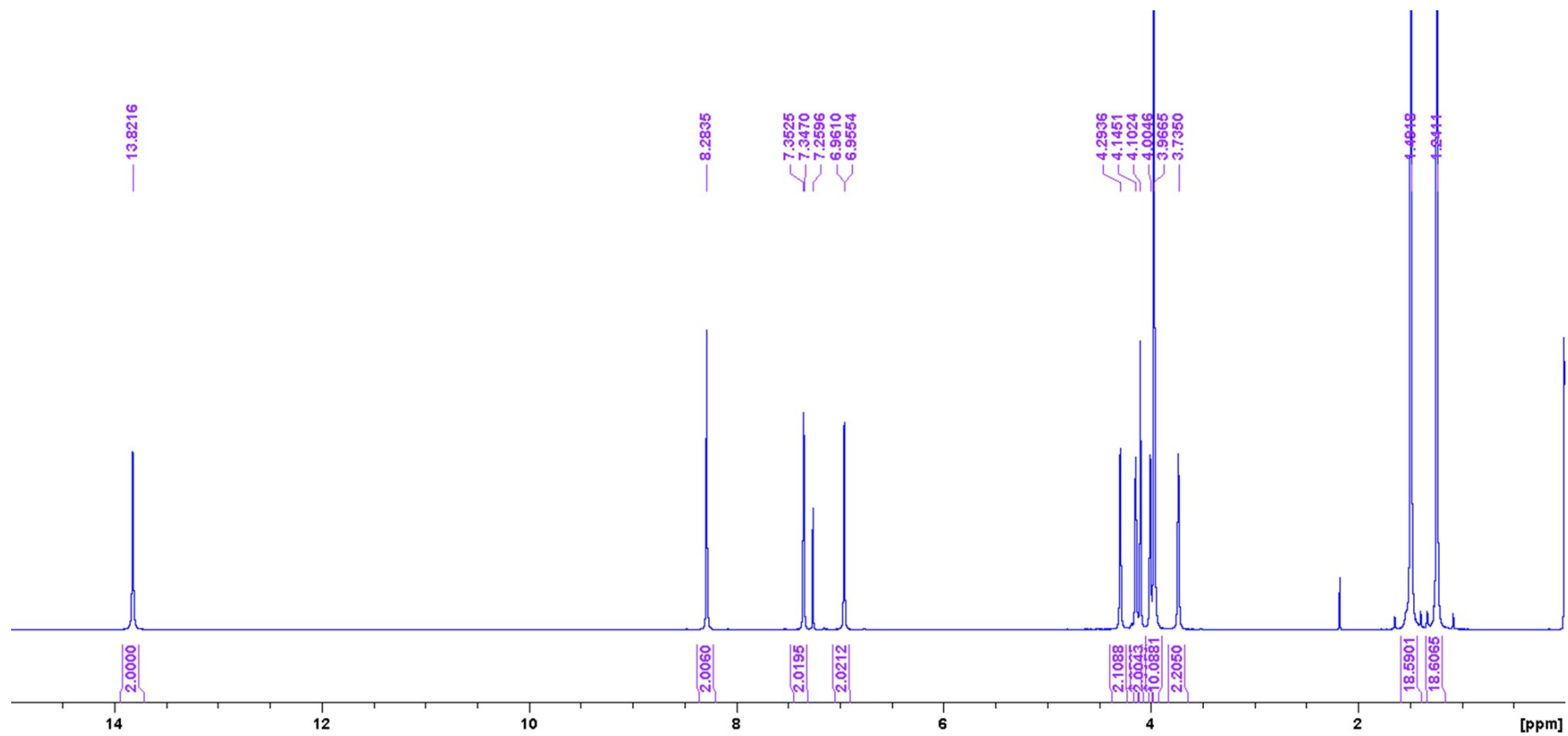


Figure S4. ^1H NMR spectrum of $\text{H}_2(\text{Sal})^{\text{Fc}}$ recorded in CDCl_3 at 298 K.

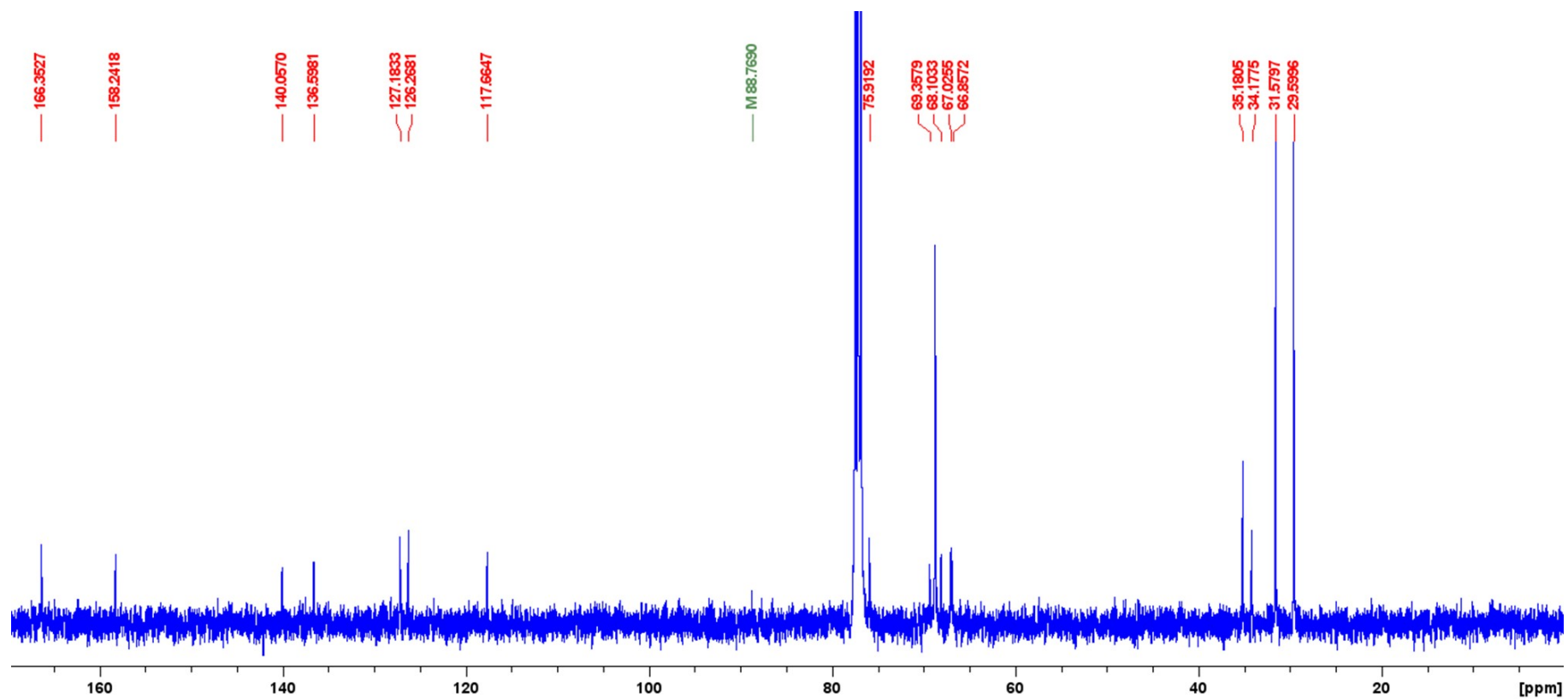


Figure S5. ^{13}C NMR spectrum of $\text{H}_2(\text{Sal})^{\text{Fc}}$ recorded in CDCl_3 at 298 K.

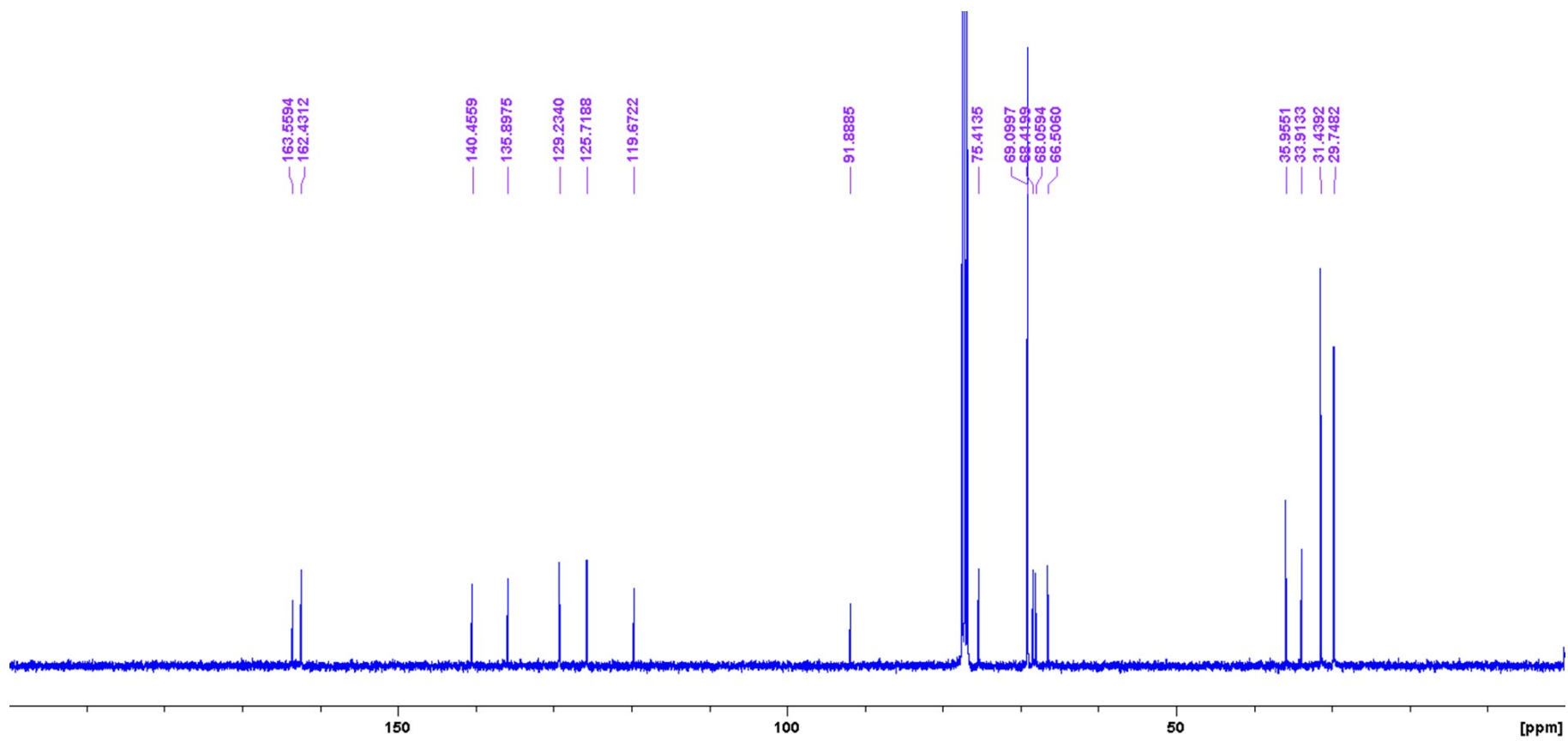


Figure S6. ^{13}C NMR spectrum of $\text{Ni}(\text{Sal})^{\text{Fc}}$ recorded in CDCl_3 at 298 K.

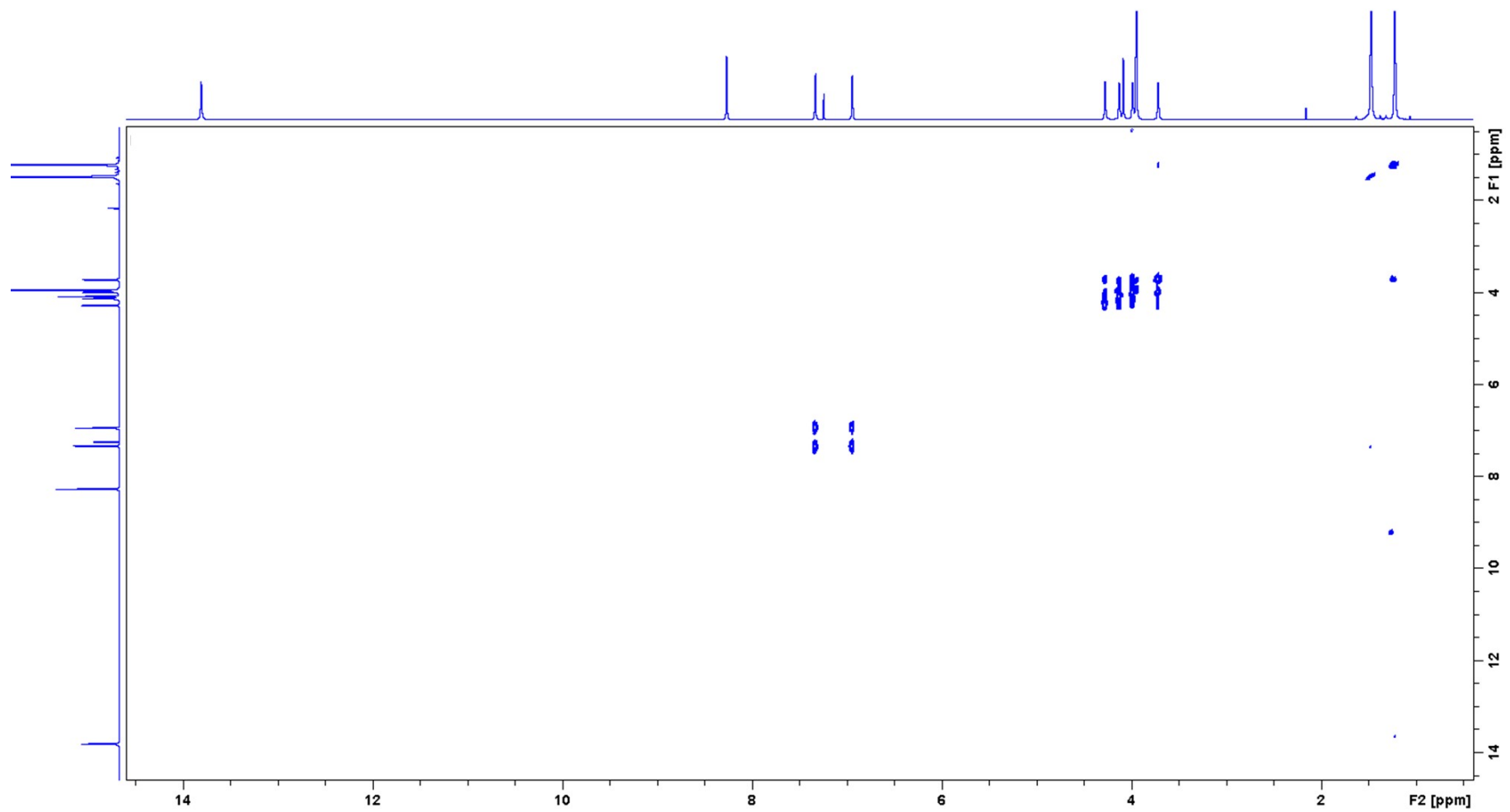


Figure S7. Full ¹H-¹H COSY spectrum of **H₂(Sal)^{Fc}** recorded in CDCl₃ at 298 K.

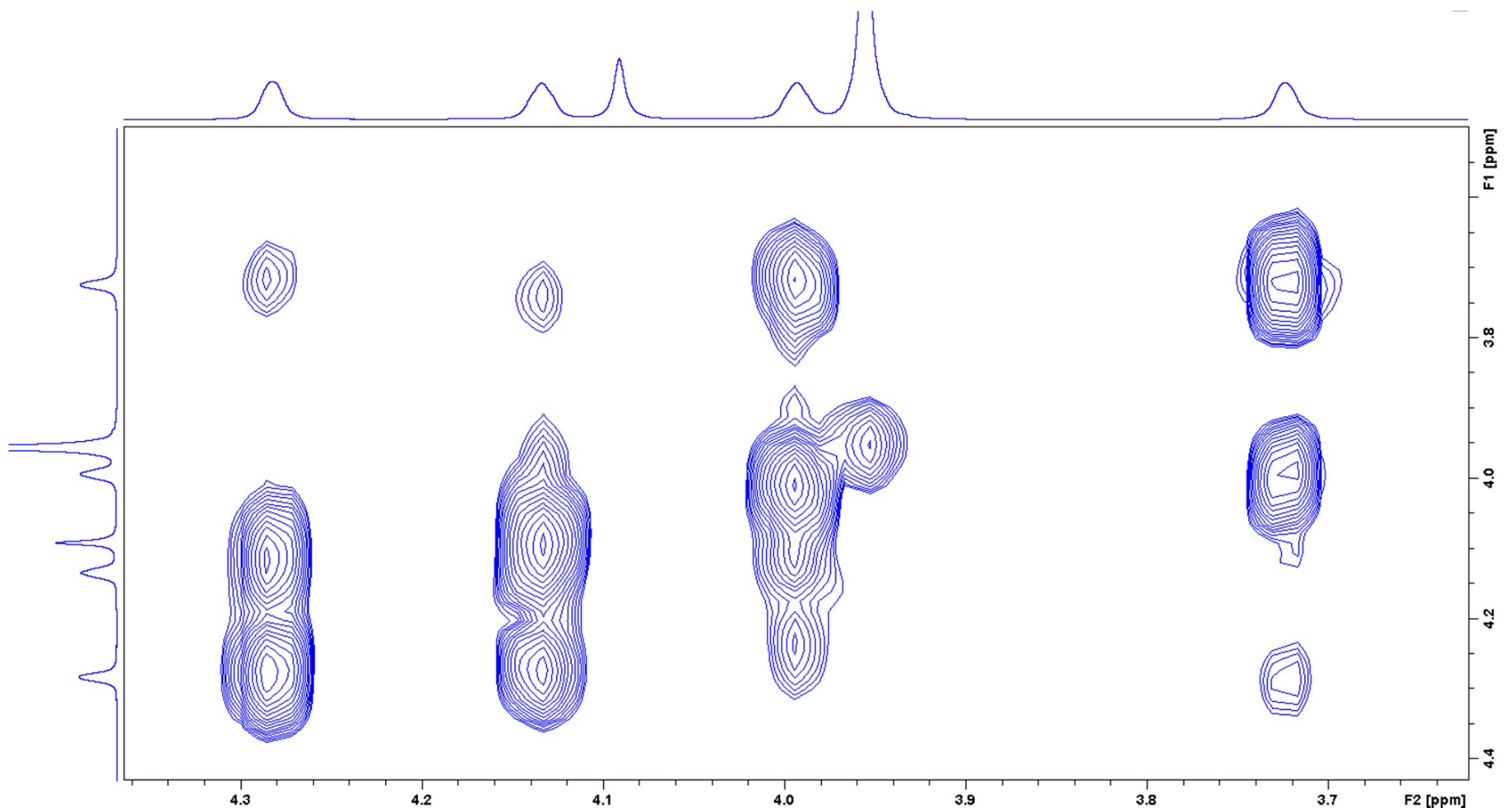


Figure S8. Magnified ¹H-¹H COSY spectrum of **H₂(Sal)^{Fc}** recorded in CDCl₃ at 298 K.

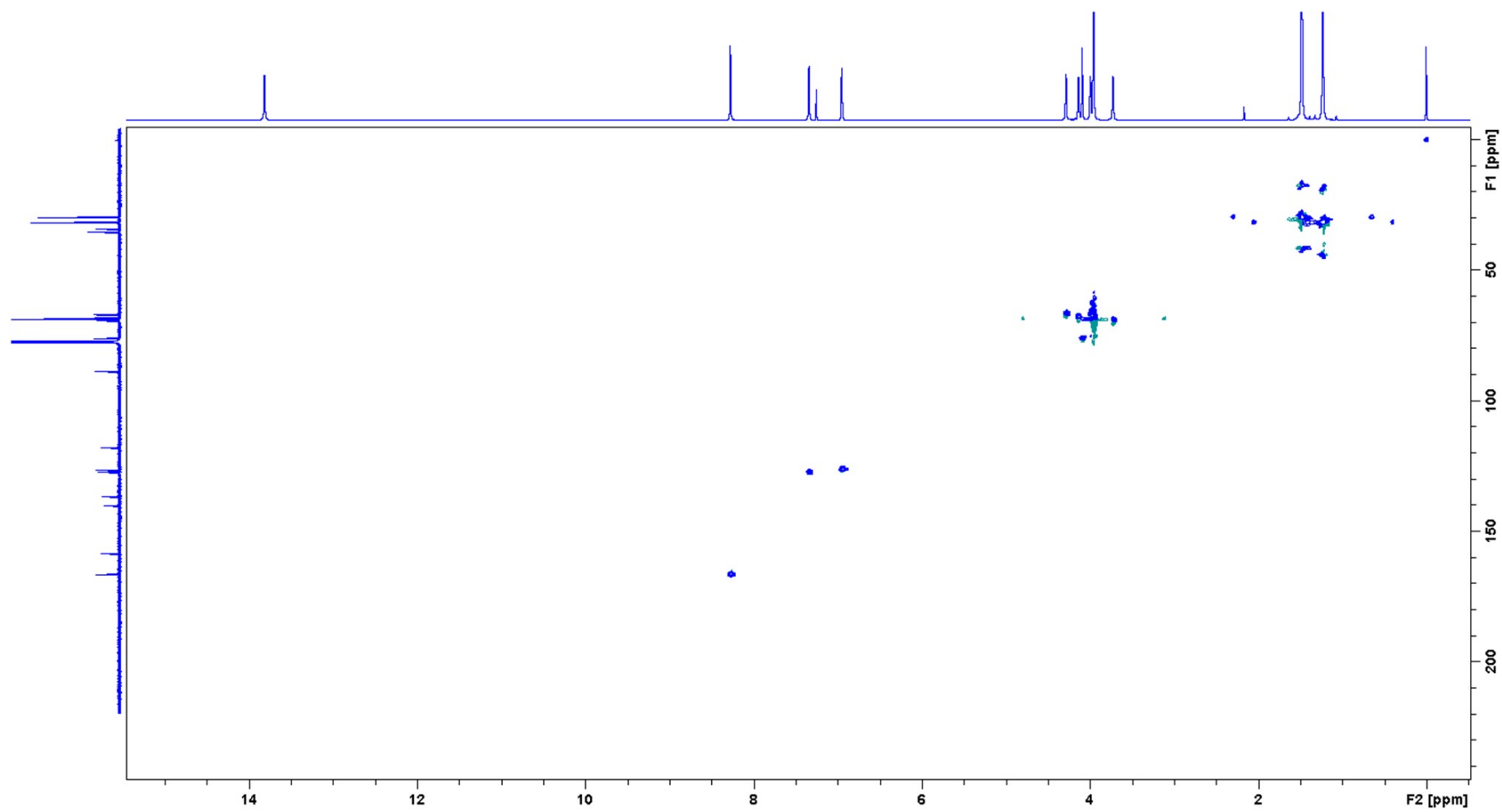


Figure S9. Full ^1H - ^{13}C HSQC spectrum of $\text{H}_2(\text{Sal})^{\text{Fc}}$ recorded in CDCl_3 at 298 K.

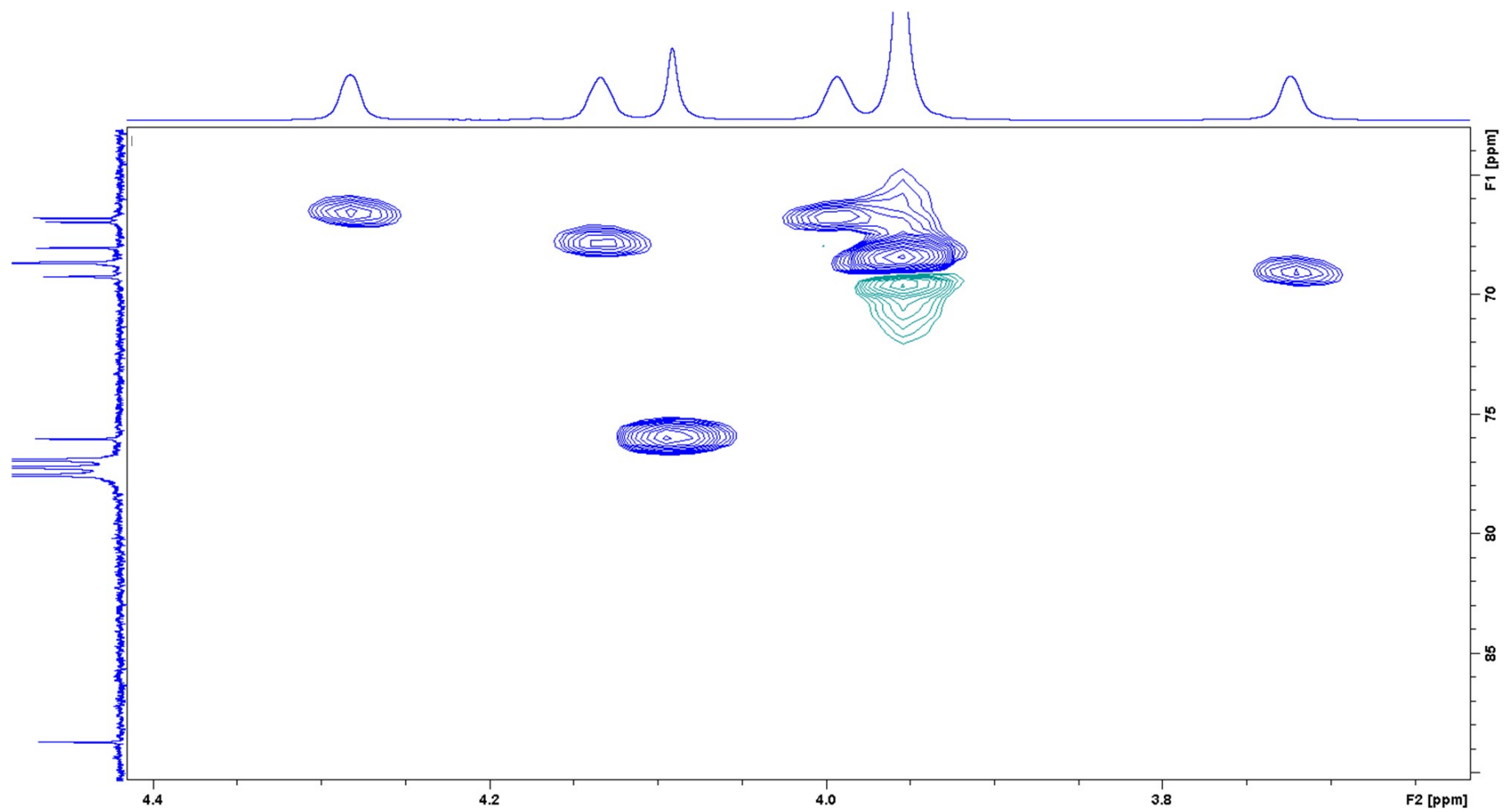


Figure S10. Magnified ^1H - ^{13}C HSQC spectrum of $\text{H}_2(\text{Sal})^{\text{Fc}}$ recorded in CDCl_3 at 298 K.

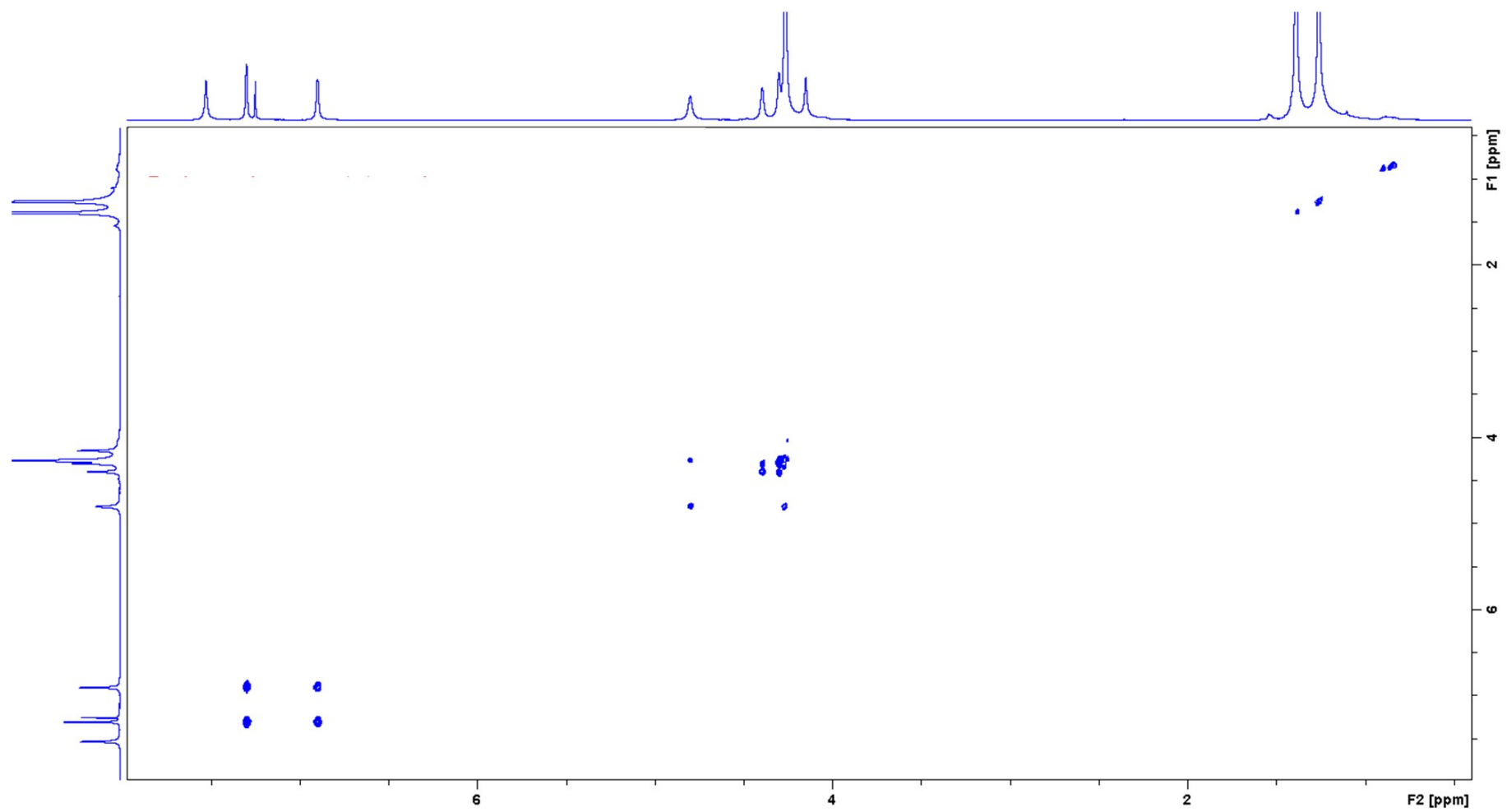


Figure S11. Full ^1H - ^1H COSY spectrum of $\text{Ni}(\text{Sal})^{\text{Fc}}$ recorded in CDCl_3 at 298 K.

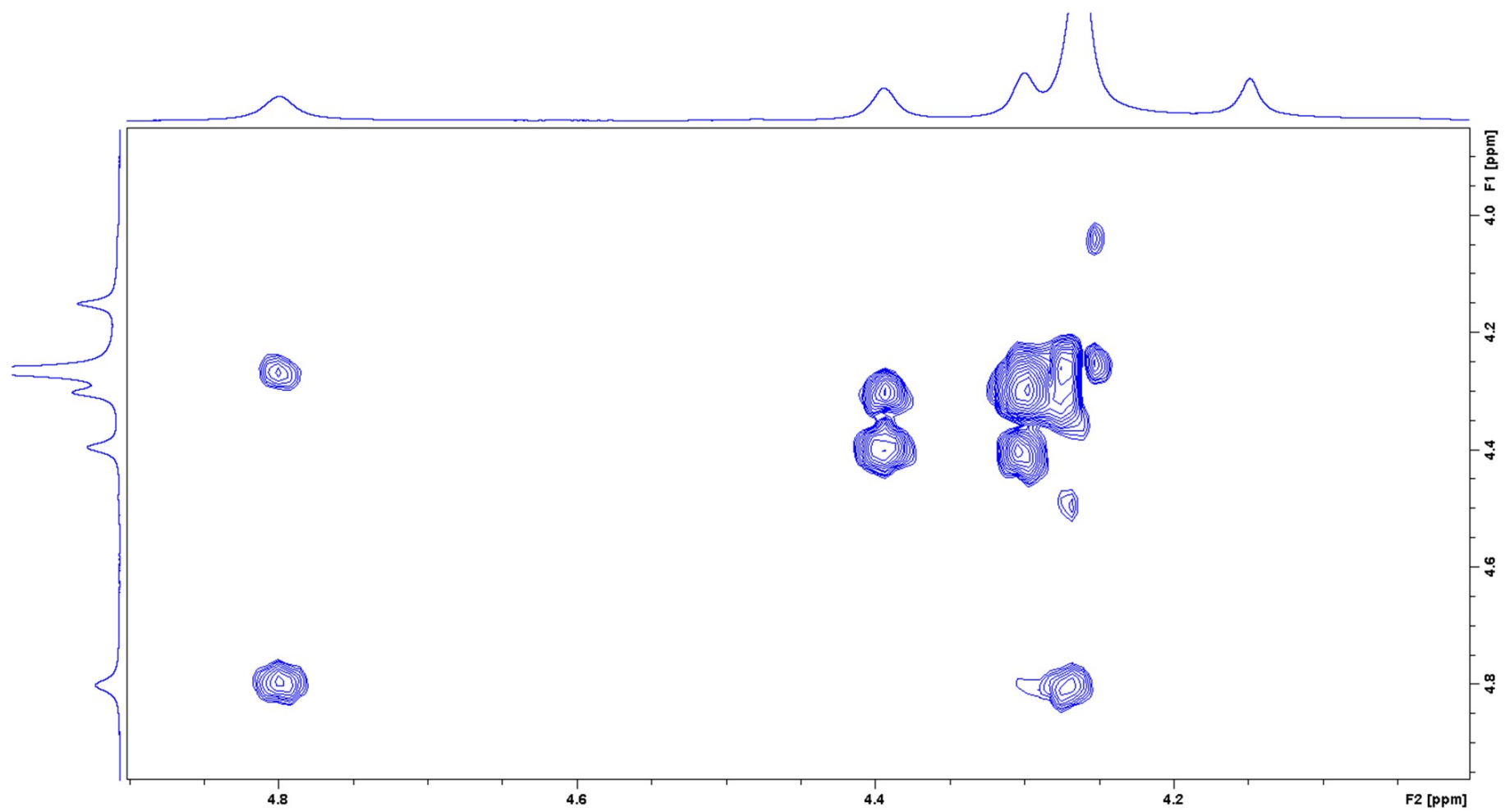


Figure S12. Magnified ^1H - ^1H COSY spectrum of $\text{Ni}(\text{Sal})^{\text{Fc}}$ recorded in CDCl_3 at 298 K.

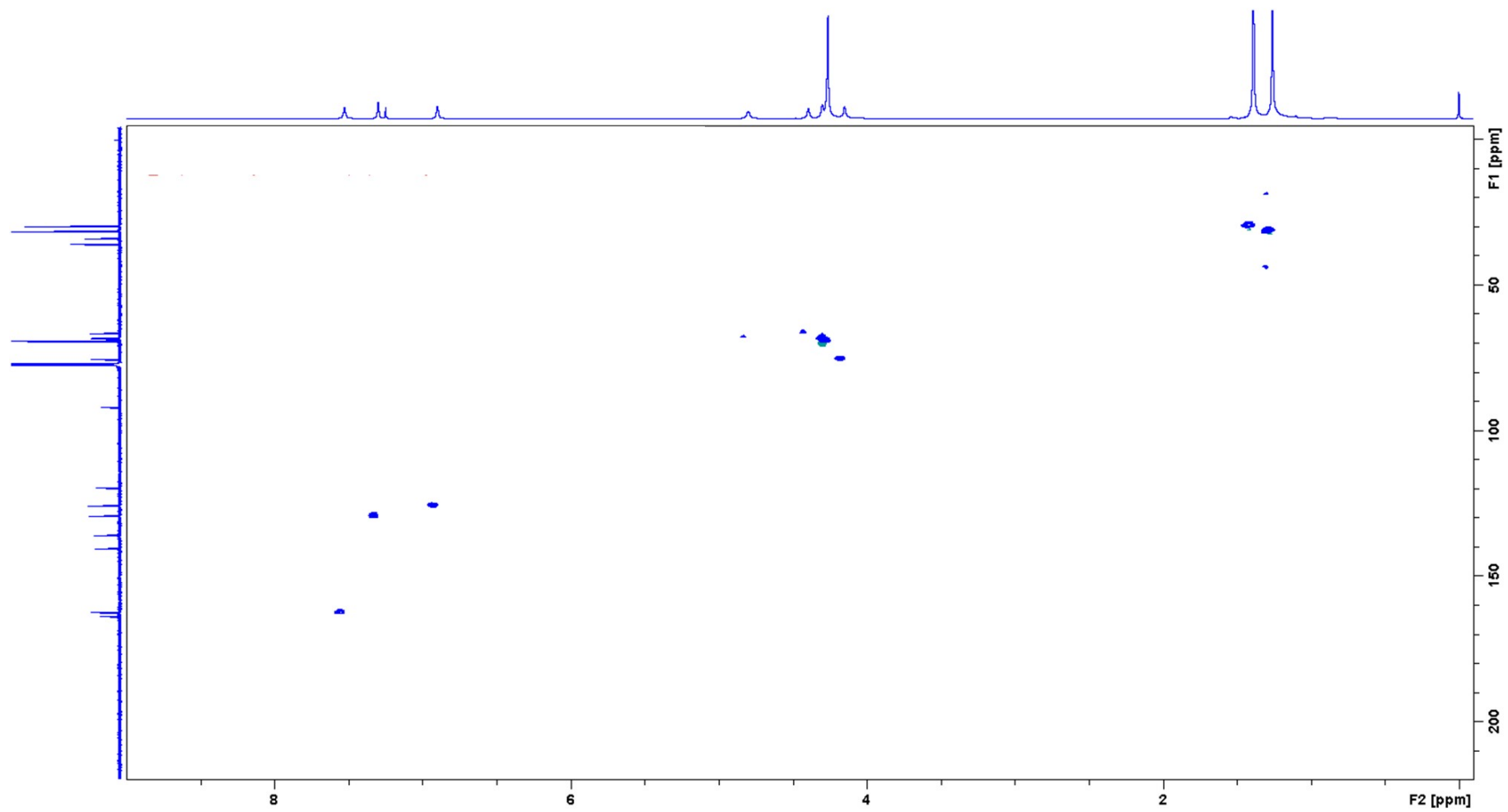


Figure S13. Full ^1H - ^{13}C HSQC spectrum of $\text{Ni}(\text{Sal})^{\text{Fe}}$ recorded in CDCl_3 at 298 K.

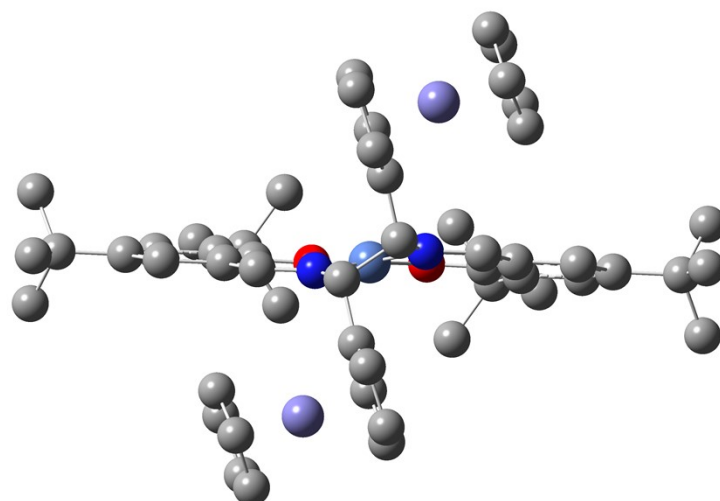


Figure S14. DFT optimized structure of $\text{Ni}(\text{Sal})^{\text{Fc}}$. H-atoms have been omitted for clarity.

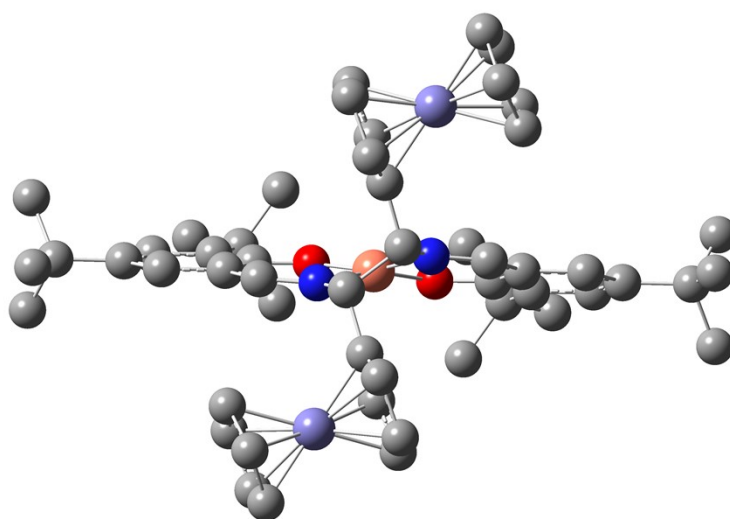


Figure S15. DFT optimized structure of $\text{Cu}(\text{Sal})^{\text{Fc}}$. H-atoms have been omitted for clarity.

Table S1. Select DFT computed bond distances (Å). See experimental section for computational details.

Bond	$\text{Ni}(\text{Sal})^{\text{Fc}}$	$\text{Ni}(\text{Sal})^{\text{Ph}}$	$\text{Cu}(\text{Sal})^{\text{Fc}}$	$\text{Cu}(\text{Sal})^{\text{Ph}}$
M-N1	1.842	1.843	1.928	1.931
M-N2	1.842	1.843	1.928	1.930
M-O1	1.856	1.857	1.904	1.904
M-O2	1.856	1.857	1.904	1.905
C1-O1	1.309	1.309	1.306	1.305
C7-O2	1.308	1.309	1.306	1.305

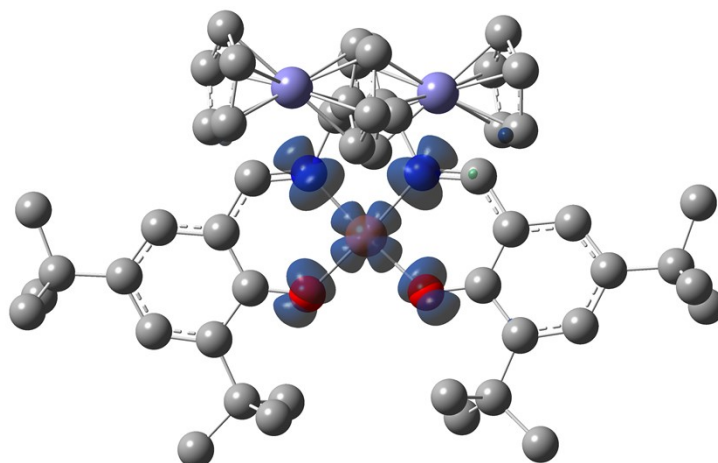


Figure S16. Spin density plot of $\text{Cu}(\text{Sal})^{\text{Fc}}$ (Isovalue: 0.0021).

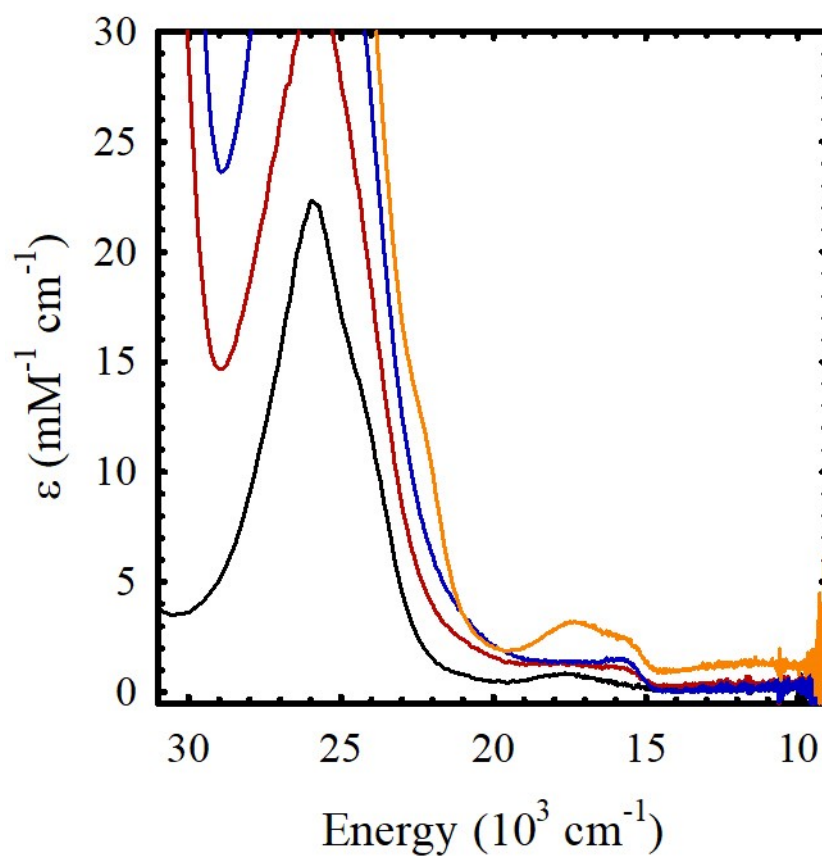


Figure S17. Sequential chemical oxidation of $\text{Ni}(\text{Sal})^{\text{Fc}}$ (black) to its one-electron oxidized (red), two-electron oxidized (blue), and three-electron oxidized (orange) species. Inset: Near-IR region. Conditions: 0.4 mM $\text{Ni}(\text{Sal})^{\text{Fc}}$ in CH_2Cl_2 , 195 K.

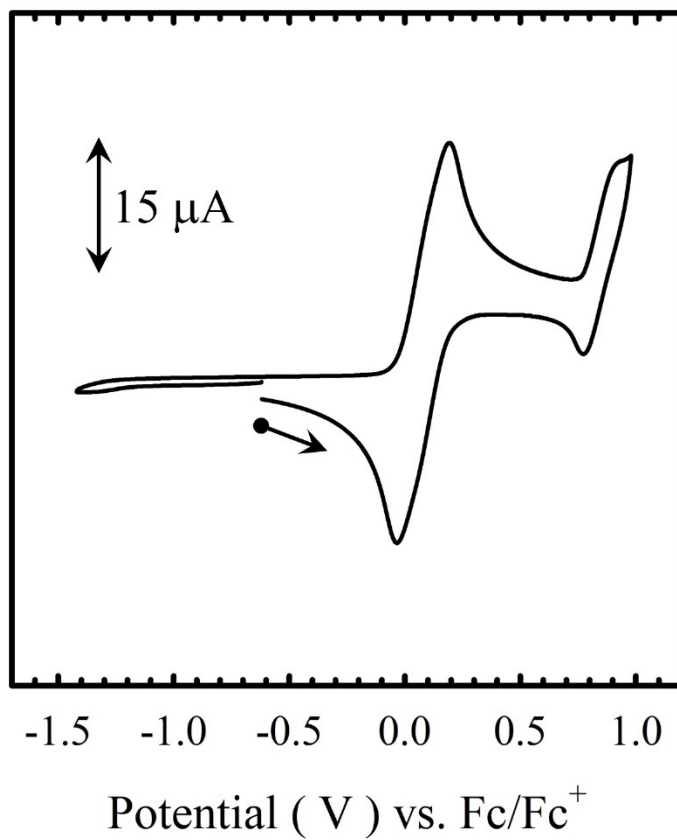


Figure S18. Cyclic voltammograms of *ca.* 1.5 mM solutions of $\text{H}_2(\text{Sal})^{\text{Fc}}$ in CH_2Cl_2 .

Optimized XYZ Coordinates of neutral **M(Sal)^{Fc}** using the B3LYP functional with PCM = CH₂Cl₂.

Ni(Sal)^{Fc}				Cu(Sal)^{Fc}			
C(Fragment=2)	2.51651608	1.75600244	-0.62649469	C(Fragment=2)	2.59272581	1.77875997	-0.66002377
N(Fragment=2)	1.25656068	-0.82417873	-0.05347441	N(Fragment=2)	1.29832869	-0.79975320	0.06975184
O(Fragment=2)	1.25743653	1.85686547	-0.28486515	O(Fragment=2)	1.31621970	1.93058939	-0.43167836
C(Fragment=2)	4.62044815	2.76200595	-1.30086995	C(Fragment=2)	4.75350599	2.71272598	-1.26188692
H(Fragment=2)	5.19141297	3.64730587	-1.55306723	H(Fragment=2)	5.35611457	3.57291161	-1.52790857
C(Fragment=2)	5.30680033	1.52017716	-1.34744980	C(Fragment=2)	5.41570977	1.45885622	-1.19510566
O(Fragment=2)	-1.25716050	1.85704836	0.28434853	O(Fragment=2)	-1.31601488	1.93104640	0.42966699
C(Fragment=2)	4.56425506	0.40256431	-1.03412342	C(Fragment=2)	4.63563171	0.37457235	-0.85553947
H(Fragment=2)	5.00924951	-0.58769045	-1.05098986	H(Fragment=2)	5.06634021	-0.61978920	-0.78559332
C(Fragment=2)	2.51343359	-0.71698385	-0.36656403	C(Fragment=2)	2.55222367	-0.70370220	-0.24676439
H(Fragment=2)	3.10650266	-1.63350082	-0.39043547	H(Fragment=2)	3.14816799	-1.62227944	-0.26720929
C(Fragment=2)	3.19381208	0.49585480	-0.68004603	C(Fragment=2)	3.24850940	0.50226187	-0.58254865
C(Fragment=2)	7.35409588	0.04439562	-1.72756265	C(Fragment=2)	7.45207881	-0.07071400	-1.37078158
H(Fragment=2)	6.83125822	-0.60112993	-2.44277196	H(Fragment=2)	6.95657576	-0.74916230	-2.07489385
H(Fragment=2)	7.28050722	-0.41454649	-0.73484094	H(Fragment=2)	7.31563014	-0.46845454	-0.35848821
H(Fragment=2)	8.41341083	0.05890885	-2.00789930	H(Fragment=2)	8.52519931	-0.09008875	-1.59214421
C(Fragment=2)	6.79413808	1.47926225	-1.73690306	C(Fragment=2)	6.92164736	1.36999463	-1.49557538
C(Fragment=2)	6.97620913	2.05738315	-3.16082293	C(Fragment=2)	7.19490994	1.85936838	-2.93804836
H(Fragment=2)	6.41763582	1.46699569	-3.89649105	H(Fragment=2)	6.66677194	1.23573376	-3.66877993
H(Fragment=2)	8.03529786	2.04339854	-3.44658476	H(Fragment=2)	8.26786449	1.81078584	-3.16150291
H(Fragment=2)	6.62789805	3.09366800	-3.22853053	H(Fragment=2)	6.87177267	2.89546825	-3.08606149
C(Fragment=2)	7.61822311	2.32373440	-0.73567319	C(Fragment=2)	7.70501739	2.25867038	-0.49988117
H(Fragment=2)	8.68063158	2.31143934	-1.00889814	H(Fragment=2)	8.78060793	2.21291697	-0.71088576
H(Fragment=2)	7.52408904	1.92564160	0.28138768	H(Fragment=2)	7.54623003	1.92321149	0.53165132
H(Fragment=2)	7.29225538	3.36932038	-0.71789748	H(Fragment=2)	7.39915490	3.30865480	-0.56160994
C(Fragment=2)	2.63962432	4.33293924	-0.97095097	C(Fragment=2)	2.78120769	4.32923055	-1.11721423
C(Fragment=2)	2.10363706	4.67495568	0.43927159	C(Fragment=2)	2.18889524	4.74348220	0.25193491
H(Fragment=2)	1.62645069	5.66317819	0.43226234	H(Fragment=2)	1.73519106	5.74014623	0.17974765
H(Fragment=2)	2.92555483	4.70503608	1.16558972	H(Fragment=2)	2.97626350	4.78826502	1.01468522
H(Fragment=2)	1.37211756	3.93931029	0.77334796	H(Fragment=2)	1.42527989	4.03840995	0.58264041
C(Fragment=2)	3.63723231	5.44306987	-1.36108604	C(Fragment=2)	3.81747420	5.40248764	-1.50982032
H(Fragment=2)	4.04190590	5.30310641	-2.37030044	H(Fragment=2)	4.26582252	5.20721273	-2.49108759
H(Fragment=2)	4.47711335	5.51141825	-0.65969982	H(Fragment=2)	4.62526329	5.48822219	-0.77353801
H(Fragment=2)	3.11880412	6.40859864	-1.34706489	H(Fragment=2)	3.31929622	6.37712524	-1.56484581
C(Fragment=2)	1.49004179	4.36578477	-2.00684841	C(Fragment=2)	1.67440414	4.34438031	-2.19993410
H(Fragment=2)	1.00443700	5.34970359	-2.00299387	H(Fragment=2)	1.22709690	5.34427132	-2.26651759
H(Fragment=2)	0.73743077	3.60788935	-1.78629955	H(Fragment=2)	0.88614259	3.62611970	-1.97023247
H(Fragment=2)	1.87898084	4.18718278	-3.01706845	H(Fragment=2)	2.09384234	4.09881959	-3.18355963
C(Fragment=2)	0.72052238	-2.15255598	0.28942984	C(Fragment=2)	0.69922285	-2.10646496	0.35703421
C(Fragment=2)	-0.72074410	-2.15245376	-0.28952829	C(Fragment=2)	-0.69968225	-2.10644153	-0.35708701
N(Fragment=2)	-1.25658760	-0.82401038	0.05344796	N(Fragment=2)	-1.29857215	-0.79957159	-0.07014676
C(Fragment=2)	3.28471291	2.93209284	-0.96380213	C(Fragment=2)	3.40373084	2.91992875	-1.01603492
C(Fragment=2)	-2.51341727	-0.71664227	0.36659527	C(Fragment=2)	-2.55231680	-0.70325637	0.24687771
H(Fragment=2)	-3.10659103	-1.63308473	0.39055322	H(Fragment=2)	-3.14835402	-1.62176062	0.26795342
C(Fragment=2)	-3.19361209	0.49630771	0.68007653	C(Fragment=2)	-3.24831116	0.50292587	0.58249211
C(Fragment=2)	-4.56401360	0.40320396	1.03435345	C(Fragment=2)	-4.63528942	0.37548978	0.85632021
H(Fragment=2)	-5.00912670	-0.58699691	1.05129640	H(Fragment=2)	-5.06614113	-0.61885412	0.78700722
C(Fragment=2)	-5.30638302	1.52093141	1.34768134	C(Fragment=2)	-5.41506735	1.45998828	1.19589395
C(Fragment=2)	-4.61989945	2.76268225	1.30083086	C(Fragment=2)	-4.75268841	2.71380784	1.26183682
H(Fragment=2)	-5.19072780	3.64807091	1.55302291	H(Fragment=2)	-5.35504621	3.57416759	1.52786477
C(Fragment=2)	-3.28421115	2.93258832	0.96348669	C(Fragment=2)	-3.40303055	2.92077103	1.01514236
C(Fragment=2)	-2.51618859	1.75636346	0.62625125	C(Fragment=2)	-2.59236058	1.77938871	0.65904907
C(Fragment=2)	-2.63897608	4.33337190	0.97030330	C(Fragment=2)	-2.78029104	4.33004147	1.11553496
C(Fragment=2)	-1.48927572	4.36626037	2.00606307	C(Fragment=2)	-1.67303327	4.34535234	2.19779848
H(Fragment=2)	-1.00348467	5.35008613	2.00192272	H(Fragment=2)	-1.22546632	5.34516531	2.26383934
H(Fragment=2)	-0.73682672	3.60817188	1.78561892	H(Fragment=2)	-0.88501993	3.62683948	1.96802347

H(Fragment=2)	-1.87813803	4.18796919	3.01636740	H(Fragment=2)	-2.09211225	4.10023372	3.18168491
C(Fragment=2)	-2.10311996	4.67508286	-0.44005056	C(Fragment=2)	-2.18846774	4.74378230	-0.25398728
H(Fragment=2)	-2.92512857	4.70512663	-1.16626665	H(Fragment=2)	-2.97613126	4.78841079	-1.01644235
H(Fragment=2)	-1.37171893	3.93930655	-0.77409694	H(Fragment=2)	-1.42508169	4.03847707	-0.58471206
H(Fragment=2)	-1.62583636	5.66325984	-0.43326622	H(Fragment=2)	-1.73463863	5.74042119	-0.18229737
C(Fragment=2)	-3.63641176	5.44368541	1.36034929	C(Fragment=2)	-3.81624765	5.40355034	1.50823324
H(Fragment=2)	-3.11788706	6.40915883	1.34604168	H(Fragment=2)	-3.31793302	6.37815259	1.56266362
H(Fragment=2)	-4.04094656	5.30398923	2.36965627	H(Fragment=2)	-4.26416744	5.20870386	2.48978152
H(Fragment=2)	-4.47639202	5.51196351	0.65907553	H(Fragment=2)	-4.62436522	5.48909141	0.77228819
C(Fragment=2)	-6.79365764	1.48022890	1.73738721	C(Fragment=2)	-6.92084825	1.37140005	1.49722858
C(Fragment=2)	-7.35376546	0.04541892	1.72831730	C(Fragment=2)	-7.45156800	-0.06924462	1.37292350
H(Fragment=2)	-8.41302506	0.06007007	2.00885595	H(Fragment=2)	-8.52456557	-0.08843053	1.59489760
H(Fragment=2)	-6.83085346	-0.60007892	2.44349721	H(Fragment=2)	-6.95576961	-0.74767887	2.07684142
H(Fragment=2)	-7.28041472	-0.41364277	0.73563308	H(Fragment=2)	-7.31575270	-0.46713484	0.36060382
C(Fragment=2)	-6.97542505	2.05854469	3.16126682	C(Fragment=2)	-7.19321287	1.86100686	2.93979484
H(Fragment=2)	-6.62698067	3.09479663	3.22878912	H(Fragment=2)	-6.86986906	2.89709043	3.08746787
H(Fragment=2)	-6.41680089	1.46818154	3.89691593	H(Fragment=2)	-6.66471805	1.23741289	3.67030226
H(Fragment=2)	-8.03446827	2.04471984	3.44720471	H(Fragment=2)	-8.26604253	1.81257778	3.16388304
C(Fragment=2)	-7.61782718	2.32466521	0.73619496	C(Fragment=2)	-7.70465522	2.26005967	0.50186831
H(Fragment=2)	-7.29176044	3.37021717	0.71824345	H(Fragment=2)	-7.39859889	3.31000716	0.56327244
H(Fragment=2)	-8.68019078	2.31250417	1.00959933	H(Fragment=2)	-8.78012945	2.21450195	0.71350744
H(Fragment=2)	-7.52390145	1.92644408	-0.28083491	H(Fragment=2)	-7.54652436	1.92443553	-0.52971138
Ni(Fragment=1)	0.00007917	0.52105666	-0.00008736	Cu(Fragment=1)	0.00001179	0.62427509	-0.00054356
C(Fragment=2)	-0.71488746	-2.41888758	-1.77785871	C(Fragment=2)	-0.54908904	-2.35382644	-1.84081989
C(Fragment=2)	-0.59807691	-3.72435041	-2.35968757	C(Fragment=2)	-0.32915761	-3.64258096	-2.42969619
C(Fragment=2)	-0.65874611	-1.46899022	-2.84710367	C(Fragment=2)	-0.45913644	-1.38491857	-2.89150953
C(Fragment=2)	-0.47112681	-3.57710605	-3.77340087	C(Fragment=2)	-0.10759811	-3.46640802	-3.82862761
H(Fragment=2)	-0.61576618	-4.66090650	-1.81576032	H(Fragment=2)	-0.34357869	-4.58820779	-1.90160700
C(Fragment=2)	-0.51278690	-2.18246977	-4.07407790	C(Fragment=2)	-0.19132207	-2.07079482	-4.11365188
H(Fragment=2)	-0.74427270	-0.39599231	-2.74288878	H(Fragment=2)	-0.60468006	-0.31850677	-2.78377348
H(Fragment=2)	-0.39102717	-4.38288896	-4.49181736	H(Fragment=2)	0.06158384	-4.25585563	-4.54970034
H(Fragment=2)	-0.47007044	-1.74108921	-5.06149780	H(Fragment=2)	-0.09745875	-1.61188680	-5.08944637
C(Fragment=2)	0.71452499	-2.41905459	1.77775598	C(Fragment=2)	0.54855738	-2.35350161	1.84081345
C(Fragment=2)	0.59785919	-3.72456324	2.35951744	C(Fragment=2)	0.32851080	-3.64211675	2.42994775
C(Fragment=2)	0.65795023	-1.46920891	2.84702853	C(Fragment=2)	0.45840402	-1.38435223	2.89125787
C(Fragment=2)	0.47060283	-3.57739910	3.77321419	C(Fragment=2)	0.10668711	-3.46562475	3.82879364
H(Fragment=2)	0.61588357	-4.66109654	1.81556127	H(Fragment=2)	0.34303661	-4.58786121	1.90207030
C(Fragment=2)	0.51192135	-2.18276243	4.07395222	C(Fragment=2)	0.19036305	-2.06994114	4.11351313
H(Fragment=2)	0.74329524	-0.39619043	2.74287014	H(Fragment=2)	0.60394564	-0.31796198	2.78329486
H(Fragment=2)	0.39048321	-4.38322188	4.49158390	H(Fragment=2)	-0.06262391	-4.25490555	4.55001890
H(Fragment=2)	0.46887720	-1.74142317	5.06137676	H(Fragment=2)	0.09632265	-1.61080613	5.08918393
Fe(Fragment=2)	-2.23548485	-2.75972247	-3.12332667	Fe(Fragment=2)	-1.94994651	-2.73954191	-3.29611529
Fe(Fragment=2)	2.23488813	-2.75960362	3.12349250	Fe(Fragment=2)	1.94914382	-2.73888807	3.29648595
C(Fragment=2)	3.70622334	-3.30568992	4.44925674	C(Fragment=2)	3.29676298	-3.32859185	4.73113774
C(Fragment=2)	3.81618145	-4.06711591	3.24665543	C(Fragment=2)	3.45637387	-4.11334576	3.54964779
C(Fragment=2)	3.83397235	-1.92455301	4.11096041	C(Fragment=2)	3.51030930	-1.96008721	4.38489277
H(Fragment=2)	3.53253469	-3.70464797	5.44047040	H(Fragment=2)	3.03580680	-3.70330168	5.71263441
C(Fragment=2)	4.01151376	-3.15619333	2.16463990	C(Fragment=2)	3.76811737	-3.22967970	2.47186594
H(Fragment=2)	3.74470970	-5.14425264	3.16618566	H(Fragment=2)	3.34179783	-5.18741918	3.47851289
C(Fragment=2)	4.02284281	-1.83093952	2.69935405	C(Fragment=2)	3.80196132	-1.89775380	2.98892004
H(Fragment=2)	3.77536409	-1.09229302	4.80054204	H(Fragment=2)	3.44107901	-1.11511120	5.05784487
H(Fragment=2)	4.12514883	-3.42738284	1.12281373	H(Fragment=2)	3.94014046	-3.52155112	1.44368012
H(Fragment=2)	4.14032412	-0.91535776	2.13466473	H(Fragment=2)	4.00007999	-0.99762459	2.42182434
C(Fragment=2)	-3.70688767	-3.30680016	-4.44860770	C(Fragment=2)	-3.29779510	-3.33030260	-4.73012615
C(Fragment=2)	-3.81664067	-4.06753397	-3.24554273	C(Fragment=2)	-3.45738624	-4.11402486	-3.54795550
C(Fragment=2)	-3.83475749	-1.92547201	-4.11111725	C(Fragment=2)	-3.51111211	-1.96147197	-4.38502790
H(Fragment=2)	-3.53327089	-3.70633374	-5.43960144	H(Fragment=2)	-3.03699788	-3.70588257	-5.71133231
C(Fragment=2)	-4.01199802	-3.15599802	-2.16405630	C(Fragment=2)	-3.76889051	-3.22939728	-2.47089052
H(Fragment=2)	-3.74504679	-5.14461476	-3.16445232	H(Fragment=2)	-3.34295864	-5.18805418	-3.47592065
C(Fragment=2)	-4.02352008	-1.83105497	-2.69954773	C(Fragment=2)	-3.80260065	-1.89790193	-2.98907422

H(Fragment=2)	-3.77633291	-1.09362184	-4.80120760	H(Fragment=2)	-3.44183603	-1.11708417	-5.05871311
H(Fragment=2)	-4.12554313	-3.42646007	-1.12203084	H(Fragment=2)	-3.94086743	-3.52037033	-1.44244426
H(Fragment=2)	-4.14108075	-0.91517531	-2.13535413	H(Fragment=2)	-4.00051506	-0.99726481	-2.42271155
H(Fragment=2)	-1.30613812	-2.93105754	0.21185319	H(Fragment=2)	-1.30496313	-2.90904570	0.08146075
H(Fragment=2)	1.30583254	-2.93122883	-0.21194428	H(Fragment=2)	1.30437743	-2.90926674	-0.08132443