Electronic Supporting Information

Low coordinate potassium alkoxide - an efficient trap for arenes: the role of η^n non-covalent bonding in substrate activation for C-H bond metalation

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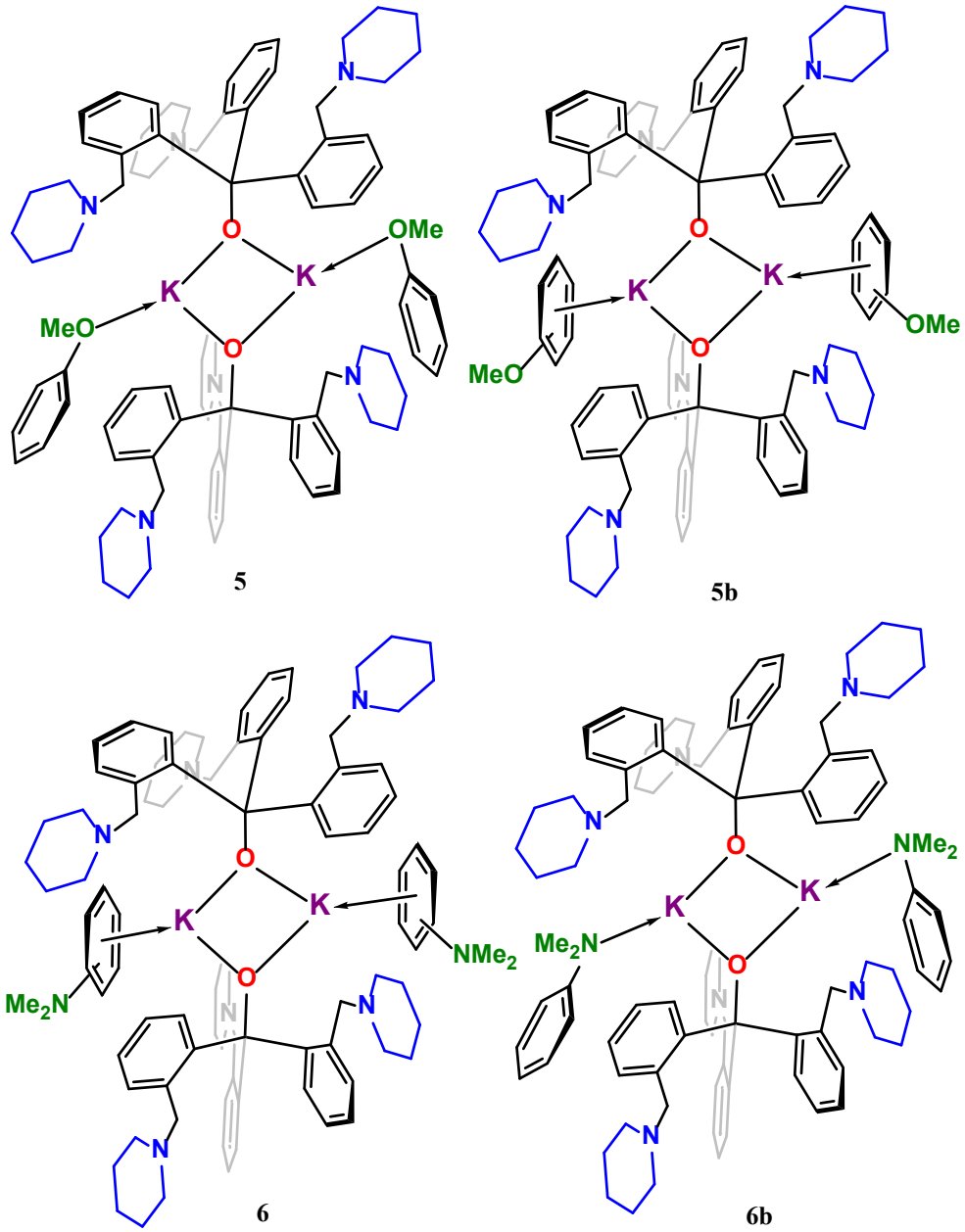
Table S1. Crystal data and structure refinement parameters for **1**, **2**, **3** and **4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{82}H_{116}K_2N_6O_4$	$C_{98}H_{120}K_2N_6O_2$	$C_{102}H_{127}K_2N_6O_2$	$C_{94}H_{112}K_2N_6O_2$
Formula weight	1328.00	1492.19	1547.29	1436.09
T, K	100	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	P-1
Z	2	2	2	1
a, Å	14.6214(5)	16.6965(19)	16.1563(3)	12.1208(5)
b, Å	12.9345(4)	14.0000(17)	14.0953(3)	13.8895(5)
c, Å	22.6282(7)	18.5478(17)	19.3873(3)	13.9198(5)
α, °	90	90	90	118.070(2)
β, °	102.170(2)	103.263(6)	105.0040(10)	103.177(2)
γ, °	90	90	90	94.963(2)
V, Å^3	4183.3(2)	4219.9(8)	4264.51(14)	1961.45(13)
D_{calc} (g cm^{-1})	1.054	1.174	1.205	1.216
Linear absorption, μ (cm^{-1})	1.61	1.65	1.66	1.75
F(000)	1440	1608	1670	772
$2\theta_{max}$, °	54	54	56	56
Reflections measured	34480	79604	52157	47238
Independent reflections	8997	9214	10311	9418
Observed reflections [$I > 2\sigma(I)$]	5918	3579	7408	7175
Parameters	434	483	507	469
R1	0.0717	0.1177	0.0465	0.0450
wR2	0.1727	0.2899	0.1126	0.1090
GOF	1.031	1.016	1.019	1.017
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	0.678/-0.467	0.519/-0.585	0.409/-0.339	0.460/-0.267

Table S2. Crystal data and structure refinement parameters for **5**, **6**, **7** and **8**.

	5	**6**	**7**	**8**
Empirical formula	$C_{88}H_{112}K_2N_6O_4$	$C_{90}H_{118}K_2N_8O_2$	$C_{80}H_{102}K_2N_6O_2$	$C_{78}H_{100}K_2N_6O_2S$
Formula weight	1396.03	1422.12	1257.87	1263.89
T, K	100	100	100	100
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	$Pca2_1$	P-1	P-1	P-1
Z	4	1	1	1
a, Å	21.9048(12)	12.1575(2)	9.4334(2)	9.5095(17)
b, Å	14.7155(9)	13.7797(3)	13.5138(3)	13.644(2)
c, Å	26.2038(15)	13.9883(3)	16.9113(4)	16.946(3)
α, °	90	117.7860(10)	113.3940(10)	113.687(4)
β, °	90	103.1450(10)	92.4760(10)	92.326(4)
γ, °	90	95.3970(10)	105.2320(10)	105.616(4)
V, $Å^3$	8446.5(8)	1963.69(7)	1882.46(7)	1911.3(6)
D_{calc} (g cm^{-1})	1.098	1.203	1.110	1.098
Linear absorption, μ (cm^{-1})	1.62	1.75	1.74	1.97
F(000)	3008	768	678	680
$2\theta_{max}$, °	54	54	56	50
Reflections measured	149530	22435	22735	17505
Independent reflections	18427	8557	9074	6724
Observed reflections [$I > 2\sigma(I)$]	8654	7152	6848	3177
Parameters	895	481	425	429
R1	0.0870	0.0422	0.0721	0.0788
wR2	0.2749	0.1085	0.1994	0.2451
GOF	1.003	1.020	1.023	0.897
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e $Å^{-3}$)	0.668/-0.523	0.303/-0.251	1.773/-1.703	0.681/-0.527



Scheme S1. The calculated isomers of complexes **5** and **6**.

Table S3 The distanced (d, Å) and energy values (E_{cont}, kcal/mol) for K…X (X = O, C, N) interactions

Molecule	Level of theory	X-Ray geometry[a]		r^2-SCAN-3c		r^2-SCAN-3c CPCM(Hexane)	
	BCP	d	E_{cont}	d	E_{cont}	d	E_{cont}
1 L= Et_2O	K99…O103	2.723	4.3	2.686	4.8	2.684	4.8
	K1…O5	2.723	4.1	2.796	3.4	2.797	3.4
2 L= C_6H_6	K1…C93	3.331	1.1	3.374	1.0	3.376	1.0
	K103…C195	3.331	1.1	3.375	1.0	3.375	1.0
3 L = Toluene	K106…C193	3.338	1.1	3.344	1.1	3.345	1.1
	K1…C88	3.337	1.1	3.344	1.1	3.345	1.1
4 L = Naphthalene	K1…C95	3.114	1.6	3.309	1.1	3.306	1.1
	K109…C203	3.114	1.6	3.304	1.1	3.303	1.1
5 L = PhOMe	K1…O6	2.740	4.1	2.780	3.6	2.784	3.6
	K2…O8	2.691	4.7	2.781	3.6	2.785	3.6
5b L = PhOMe	K105…C173			3.285	1.2	3.283	1.2
	K1…C68			3.284	1.2	3.284	1.2
6 L = $PhNMe_2$	K1…C68	3.080	1.9	3.284	1.2	3.280	1.2
	K109…C177	3.080	1.9	3.284	1.2	3.282	1.2
6b L = $PhNMe_2$	K1…N8			3.194	1.7	3.204	1.7
	K109…N116			3.202	1.7	3.204	1.7
8a L =Thiophene	K11…C88			3.351	1.2	3.378	1.1
	K11…C87			3.355	–	3.377	1.1
	K11…S13			3.489	1.1	3.495	1.1
	K10…C2			3.369	1.1	3.359	1.1
	K10…C1			3.353	1.2	3.356	1.1
	K10…S5			3.459	1.2	3.478	1.1
10b	K1…N94			2.939	2.8	2.934	2.9
	K91…N4			2.869	3.5	2.864	3.5
11b	K1…N67			2.877	3.4	2.869	3.5
	K64…N4			2.824	3.9	2.822	4.0

[a]The X-ray geometry parameters were used for QTAIM analysis at the r^2-SCAN-3c/Def2-TZVP level.

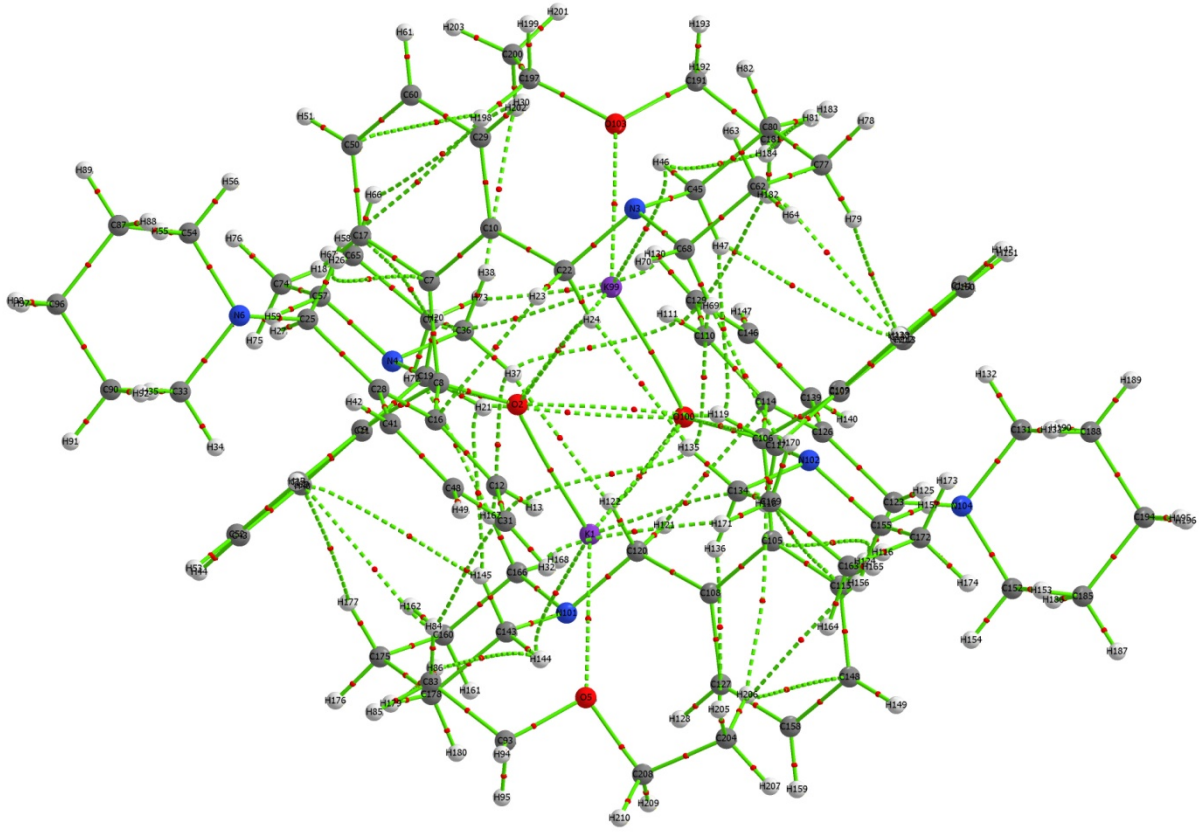


Figure S1. QTAIM molecular graph for **1** (L= Et_2O) with X-ray geometry.

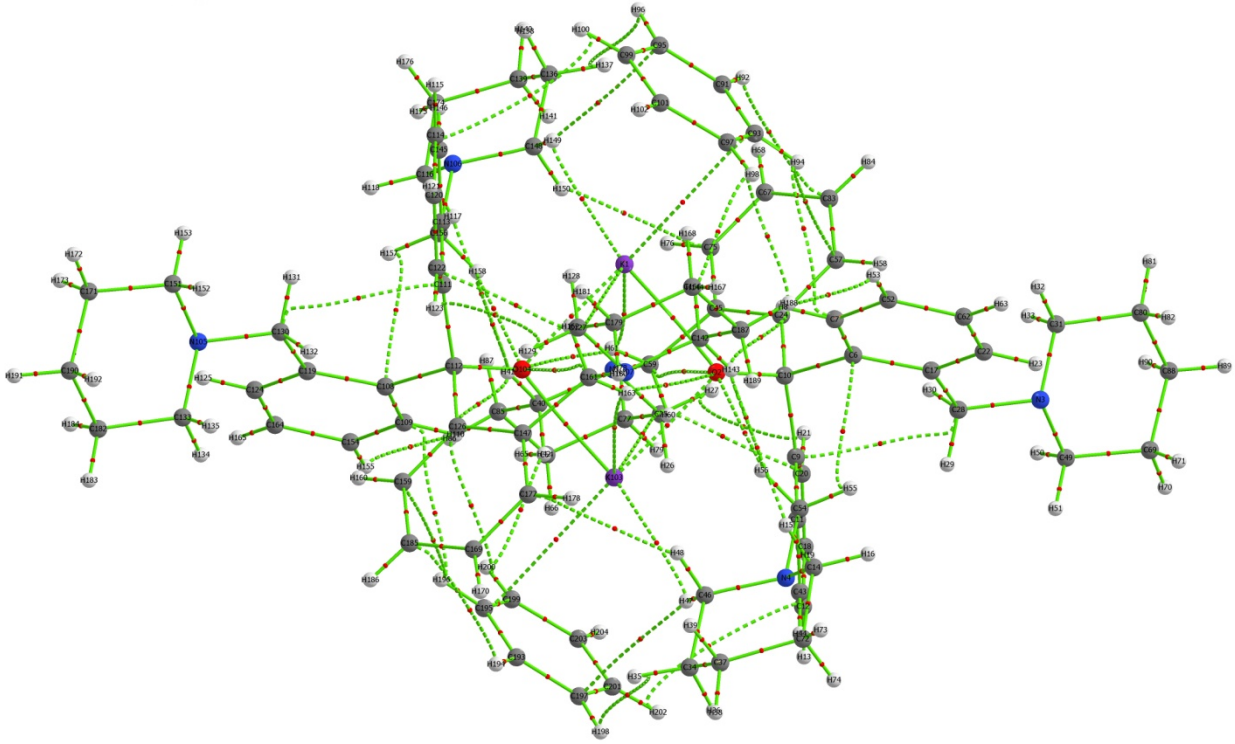


Figure S2. QTAIM molecular graph for **2** (L= C_6H_6) with X-ray geometry.

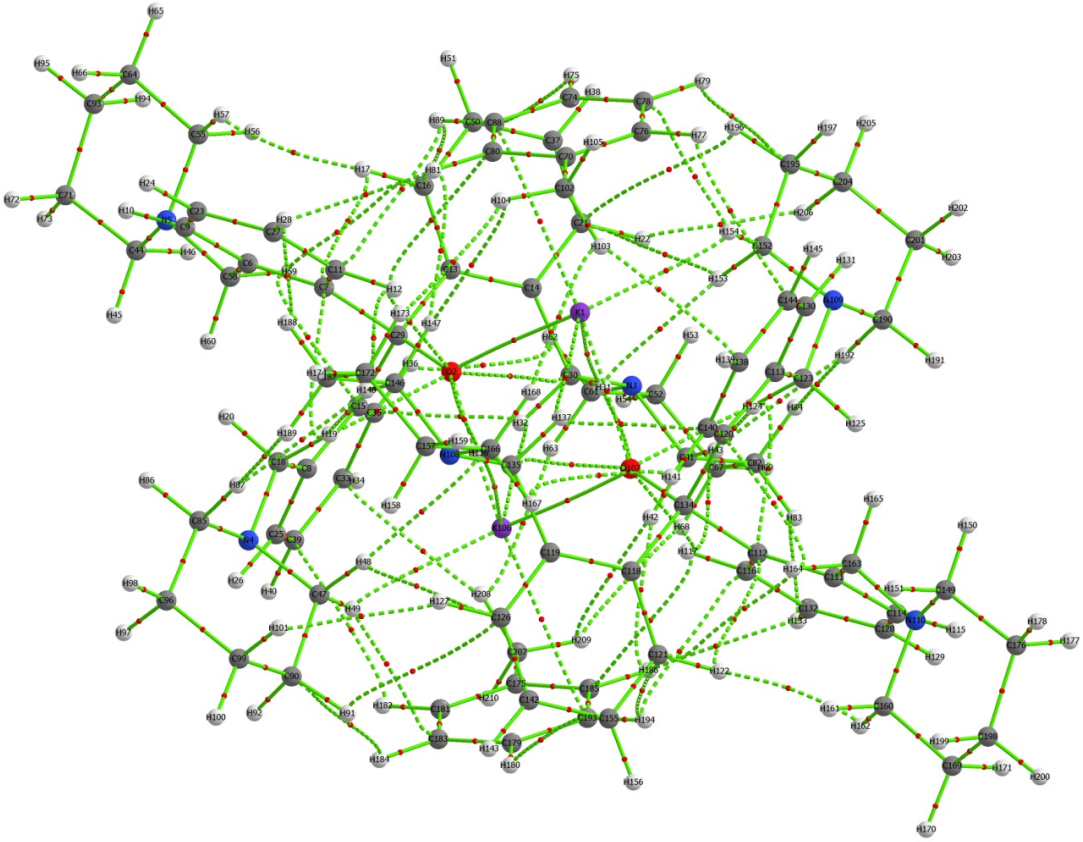


Figure S3. QTAIM molecular graph for **3** (L = Toluene) with X-ray geometry.

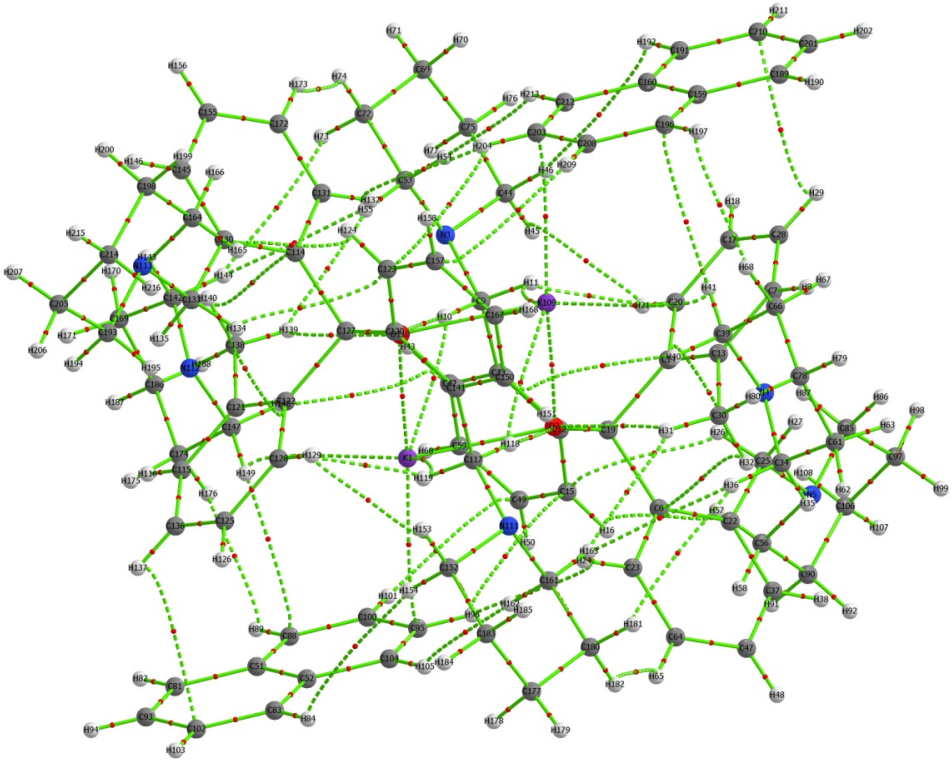


Figure S4. QTAIM molecular graph for **4** (L = Naphthalene) with X-ray geometry.

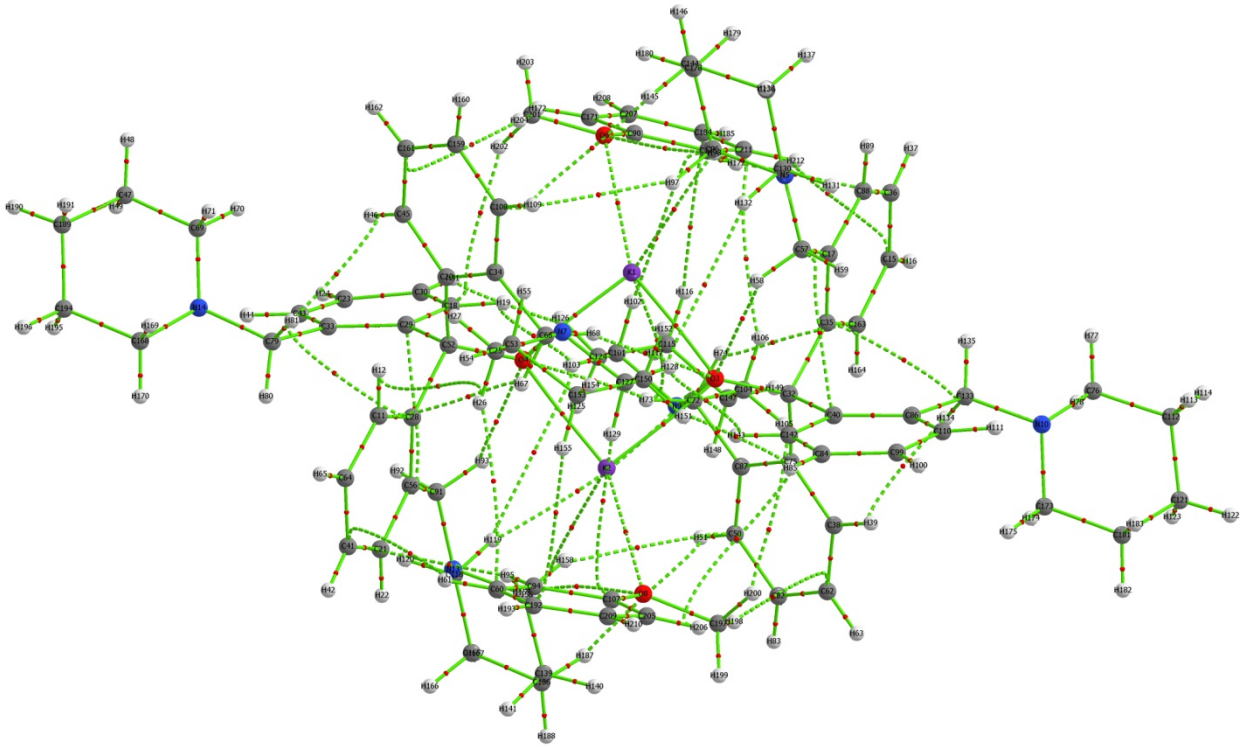


Figure S5. QTAIM molecular graph for **5** (L = PhOMe) with X-ray geometry.

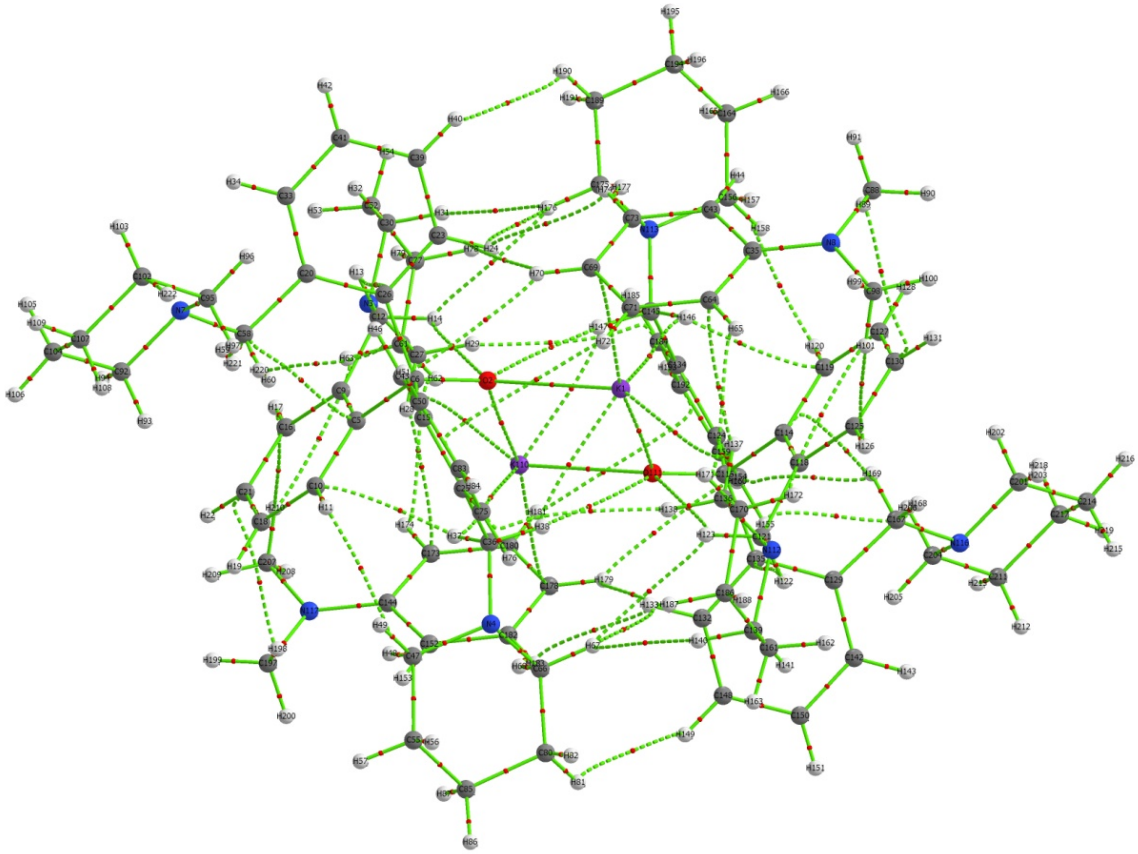


Figure S6. QTAIM molecular graph for **6** (L = $PhNMe_2$) with X-ray geometry.

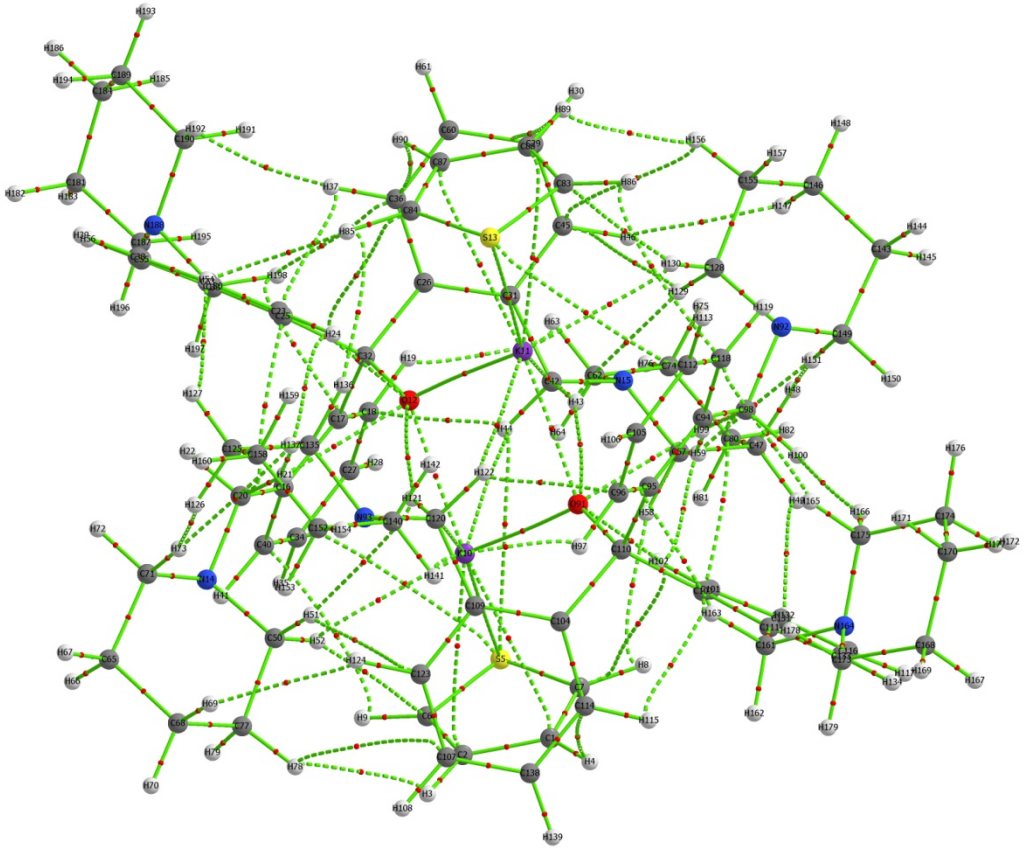


Figure S7. QTAIM molecular graph for **8a** (L = thiophene) optimized at the r^2-SCAN-3c/Def2-TZVP/CPCM(hexane) level.

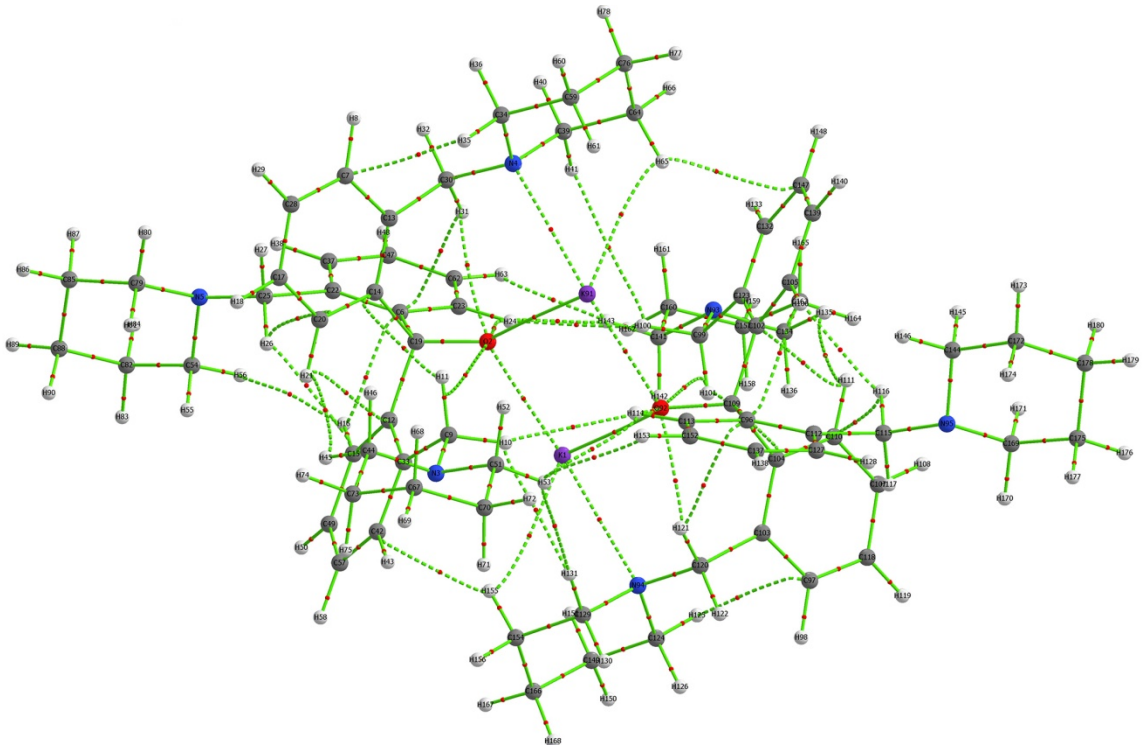


Figure S8. QTAIM molecular graph for **10b** optimized at the r^2-SCAN-3c/Def2-TZVP/CPCM(hexane) level.

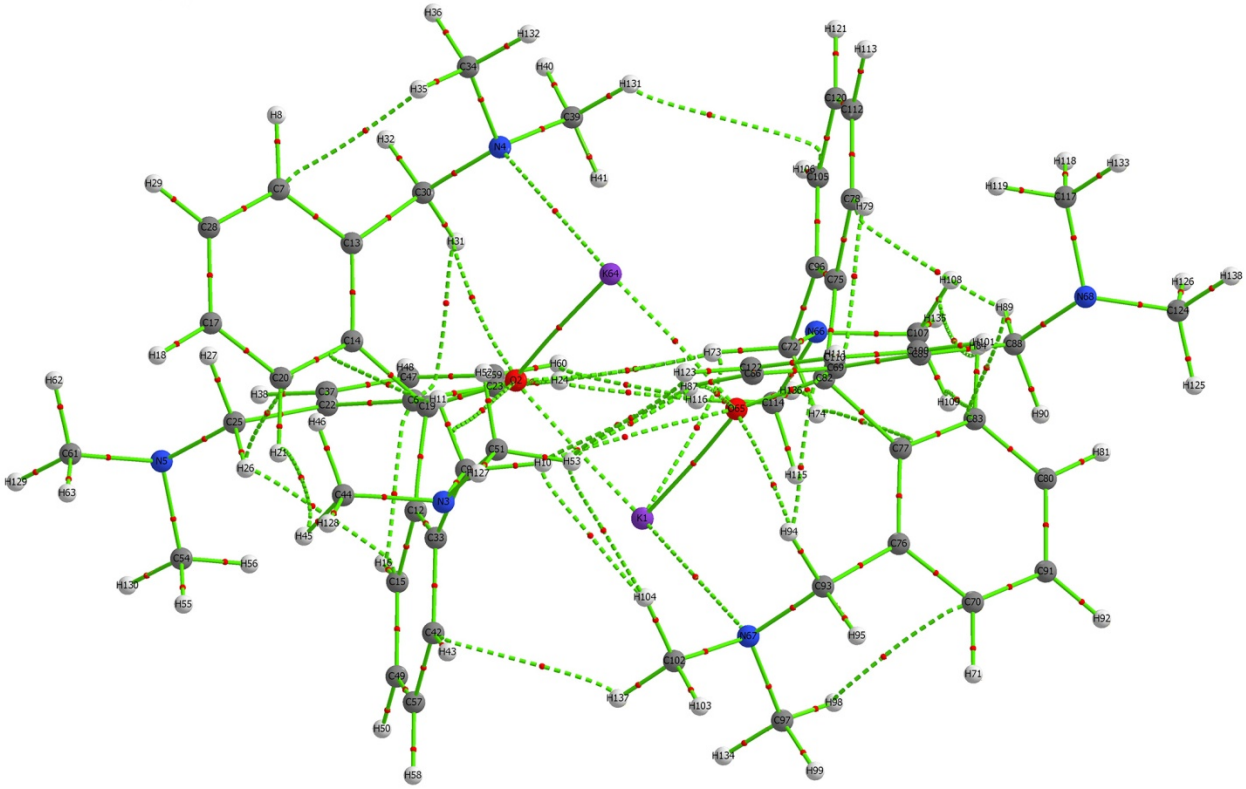


Figure S9. QTAIM molecular graph for **11b** optimized at the r^2-SCAN-3c/Def2-TZVP/CPCM(hexane) level.

Table S4. QTAIM data for K…X interaction in **1**-**6** for the X-Ray geometry calculated at the r^2-SCAN-3c/Def2-TZVP level

BCP #	Distance, Å	ρ(**r**), a.u.	Δρ(**r**),a.u.	K(**r**), a.u.	V(**r**),a.u.	E_{cont}, kcal/mol
1 (L= Et_2O)						
K99 - O103	2.723	0.01670	0.08436	-0.00367	-0.01376	**4.3**
K1 - O5	2.723	0.01590	0.08246	-0.00377	-0.01308	**4.1**
K99 - O100	2.578	0.02760	0.14168	-0.00381	-0.02779	8.7
O2 - K99	2.578	0.02466	0.12004	-0.00345	-0.02310	7.2
K1 - O100	2.501	0.02466	0.11992	-0.00345	-0.02308	7.2
K1 - O2	2.501	0.02762	0.14167	-0.00381	-0.02780	8.7
K1 - H118	2.800	0.00646	0.02940	-0.00164	-0.00407	1.3
K1 - H144	2.868	0.00569	0.02538	-0.00148	-0.00338	1.1
K99 -H46-	2.868	0.00568	0.02537	-0.00149	-0.00337	1.1
2 (L= C_6H_6)						
K1 - C93	3.331	0.00658	0.02528	-0.00140	-0.00352	**1.1**
K103 - C195	3.331	0.00658	0.02528	-0.00140	-0.00352	**1.1**
K1 - O104	2.596	0.02350	0.11428	-0.00350	-0.02157	6.8
K103 - O104	2.526	0.02694	0.13400	-0.00357	-0.02635	8.3
O2 - K103	2.596	0.02350	0.11428	-0.00350	-0.02157	6.8
K1 - O2	2.526	0.02694	0.13400	-0.00357	-0.02635	8.3
K1 - H149	2.777	0.00662	0.02895	-0.00161	-0.00402	1.3
K1 - H162	2.765	0.00666	0.02981	-0.00165	-0.00416	1.3
K1 - H61	2.734	0.00596	0.02761	-0.00158	-0.00374	1.2
K103 - H163	2.734	0.00596	0.02761	-0.00158	-0.00374	1.2
H47 - K103	2.777	0.00662	0.02895	-0.00161	-0.00402	1.3
5 (L = PhOMe)						
K1 - O6	2.740	0.01632	0.08154	-0.00358	-0.01322	**4.1**
K2 - O8	2.691	0.01775	0.09067	-0.00383	-0.01501	**4.7**
K2 - O4	2.519	0.02729	0.13683	-0.00360	-0.02700	8.5
K1 - O3	2.510	0.02787	0.13985	-0.00359	-0.02778	8.7
K1 - O4	2.499	0.02887	0.14362	-0.00345	-0.02901	9.1
K2 - O3	2.514	0.02792	0.13875	-0.00349	-0.02770	8.7
K1 - H73	2.798	0.00645	0.03037	-0.00170	-0.00420	1.3
K1 - H98	2.919	0.00759	0.03445	-0.00189	-0.00483	1.5
K2 - H158	2.794	0.00727	0.03303	-0.00185	-0.00457	1.4
6 (L = $PhNMe_2$)						
K1 - C69	3.080	0.01011	0.03777	-0.00169	-0.00606	**1.9**
K110 - C178	3.080	0.01012	0.03780	-0.00169	-0.00608	**1.9**
K1 - O2	2.538	0.02614	0.13000	-0.00361	-0.02528	7.9
K110 - O111	2.538	0.02611	0.13003	-0.00362	-0.02527	7.9
O2 - K110	2.577	0.02457	0.11972	-0.00349	-0.02296	7.2
K1 - O111	2.577	0.02456	0.11979	-0.00349	-0.02296	7.2
K1 - H137	3.018	0.00426	0.01881	-0.00116	-0.00239	0.8
K1 - H146	2.874	0.00541	0.02395	-0.00137	-0.00326	1.0
K1 - H38	2.761	0.00562	0.02618	-0.00152	-0.00351	1.1

K110 - H147	2.761	0.00562	0.02614	-0.00152	-0.00350	1.1
H28 - K110	3.018	0.00426	0.01882	-0.00116	-0.00240	0.8
H37 - K110	2.874	0.00544	0.02396	-0.00136	-0.00327	1.0
4 (L = Naphthalene)						
K1 - C95	3.114	0.00890	0.03297	-0.00157	-0.00511	**1.6**
K109 - C203	3.114	0.00890	0.03297	-0.00157	-0.00511	**1.6**
K109 - O110	2.574	0.02687	0.13408	-0.00360	-0.02632	8.3
K1 - O2	2.525	0.02687	0.13408	-0.00360	-0.02632	8.3
O2 - K109	2.574	0.02488	0.12070	-0.00345	-0.02328	7.3
K1 - O110	2.574	0.02488	0.12070	-0.00345	-0.02328	7.3
K109 - H41	3.017	0.00416	0.01808	-0.00110	-0.00231	0.7
K109 - H118	2.692	0.00645	0.02999	-0.00171	-0.00407	1.3
K109 - H11	2.867	0.00542	0.02394	-0.00137	-0.00325	1.0
K1 - H10	2.692	0.00645	0.02999	-0.00171	-0.00407	1.3
K1 - H119	2.867	0.00542	0.02394	-0.00137	-0.00325	1.0
K1 - H149	3.017	0.00416	0.01808	-0.00110	-0.00231	0.7
3 (L = Toluene)						
K106 - C193	3.338	0.00609	0.02478	-0.00141	-0.00338	**1.1**
O2 - K106	2.611	0.02215	0.10924	-0.00368	-0.01995	6.3
K106 - O107	2.512	0.02567	0.12942	-0.00383	-0.02470	7.8
K1 - O2	2.512	0.02567	0.12943	-0.00383	-0.02471	7.8
K1 - O107	2.611	0.02215	0.10924	-0.00368	-0.01995	6.3
K1 - C88	3.337	0.00609	0.02478	-0.00141	-0.00338	**1.1**
K106 - H49	2.764	0.00738	0.03160	-0.00172	-0.00447	1.4
K106 - H136	2.801	0.00588	0.02606	-0.00147	-0.00357	1.1
K106 -H32	2.779	0.00637	0.02773	-0.00155	-0.00384	1.2
K1 - H137	2.779	0.00637	0.02773	-0.00155	-0.00384	1.2
K1 - H154	2.764	0.00737	0.03158	-0.00172	-0.00446	1.4
K1 - H31	2.801	0.00588	0.02606	-0.00147	-0.00357	1.1

Table S5. QTAIM data for K…X interaction in **1**-**6**, **8a**,**9b** and **10b** optimized at the r^2-SCAN-3c/Def2-TZVP level

BCP	Distance, Å	ρ(**r**), a.u.	Δρ(**r**),a.u.	H(**r**), a.u.	V(**r**),a.u.	E_{cont}, kcal/mol
1 (L= Et_2O)						
K99 - O103	2.686	0.01785	0.09216	0.00392	-0.01520	4.8
K1 - O5	2.796	0.01399	0.07031	0.00344	-0.01069	3.4
K99 - O100	2.508	0.02749	0.14051	0.00387	-0.02738	8.6
O2 - K99	2.568	0.02472	0.12275	0.00369	-0.02331	7.3
K1 - O100	2.508	0.02349	0.11658	0.00371	-0.02174	6.8
K1 - O2	2.532	0.02573	0.13227	0.00396	-0.02514	7.9
K1 - H86	2.968	0.00452	0.01940	0.00118	-0.00249	0.8
K99-H46	2.773	0.00754	0.03402	0.00189	-0.00473	1.5
2 (L= C_6H_6)						
K1 - C93	3.374	0.00585	0.02429	0.00141	-0.00326	**1.0**
K103 - C195	3.375	0.00584	0.02424	0.0014	-0.00325	**1.0**
K1 - O104	2.628	0.02166	0.10619	0.00364	-0.01927	6.0
K103 - O104	2.524	0.02558	0.12945	0.00386	-0.02464	7.7
O2 - K103	2.628	0.02165	0.10617	0.00364	-0.01927	6.0
K1 - O2	2.542	0.02555	0.12929	0.00386	-0.02460	7.7
5 (L = PhOMe)						
K1 - O6	2.780	0.01472	0.07430	0.00352	-0.01153	3.6
K2 - O8	2.781	0.014674	0.074056	0.00351	-0.01149	3.6
K2 - O4	2.566	0.024955	0.123343	0.00365	-0.02355	7.4
K1 - O3	2.567	0.02494	0.12323	0.00364	-0.02352	7.4
K1 - O4	2.512	0.02674	0.13860	0.00402	-0.02661	8.3
K2 - O3	2.508	0.02697	0.13994	0.00403	-0.02693	8.4
5b (L = PhOMe)						
K1 - O107	2.609	0.02254	0.11092	0.00366	-0.02040	6.4
K1 - O2	2.539	0.02576	0.13044	0.00387	-0.02488	7.8
O2 - K106	2.609	0.02253	0.11081	0.00366	-0.02039	6.4
K106 - O107	2.539	0.02574	0.13022	0.00386	-0.02484	7.8
K106 - C174	3.285	0.00681	0.02665	0.00146	-0.00374	**1.2**
K1 - C69	3.284	0.00678	0.02656	0.00146	-0.00373	**1.2**
6 (L = $PhNMe_2$)						
K1 - O110	2.615	0.02218	0.10934	0.00368	-0.01998	6.3
K1 - O2	2.550	0.02521	0.12698	0.00383	-0.02408	7.6
O2 - K109	2.615	0.02218	0.10936	0.00368	-0.01999	6.3
K109 - O110	2.549	0.02524	0.12715	0.00383	-0.02412	7.6
K109 - C177	3.284	0.00689	0.02717	0.00148	-0.00384	**1.2**
K1 - C68	3.284	0.00689	0.02716	0.00148	-0.00384	**1.2**
6b (L = $PhNMe_2$)						
K1 - O110	2.558	0.023811	0.111391	0.00312	-0.02161	6.8
O2 - K109	2.557	0.023848	0.11163	0.00313	-0.02166	6.8
K1 - O2	2.565	0.024953	0.112433	0.00271	-0.0227	7.1
K1 - N8	3.194	0.008137	0.03157	0.00131	-0.00528	**1.7**
K109 - O110	2.567	0.024945	0.112397	0.00271	-0.02269	7.1
K109 - N116	3.202	0.008123	0.031515	0.00131	-0.00527	**1.7**
4 (L = Naphthalene)						
K1 - O2	2.533	0.02593	0.13174	0.00389	-0.02516	7.9
K109 - O110	2.531	0.02612	0.13255	0.00387	-0.02539	8.0
O2 - K109	2.609	0.02259	0.11086	0.00365	-0.02042	6.4

K1 - O110	2.531	0.02254	0.11072	0.00365	-0.02037	6.4
K1 - C95	3.309	0.00634	0.02485	0.00139	-0.00342	**1.1**
K109 - C203	3.304	0.00634	0.02461	0.00138	-0.00340	**1.1**
3 (L = Toluene)						
K1 - O107	2.615	0.02215	0.10924	0.00368	-0.01995	6.3
K1 - O2	2.542	0.02567	0.12943	0.00383	-0.02471	7.8
O2 - K106	2.615	0.02215	0.10924	0.00368	-0.01995	6.3
K106 - O107	2.542	0.02567	0.12942	0.00383	-0.02470	7.8
K106 - C193	3.344	0.00609	0.02478	0.00141	-0.00338	**1.1**
K1 - C88	3.344	0.00609	0.02478	0.00141	-0.00338	**1.1**
8a (L = Thiophene)						
K11 - C88	3.351	0.00626	0.02665	0.00149	-0.00368	**1.2**
K11 - O12	2.528	0.02659	0.13408	0.00381	-0.02591	8.1
K11 - O91	2.592	0.02321	0.11531	0.00373	-0.02136	6.7
K11 - S13	3.489	0.00593	0.02651	0.00157	-0.00348	**1.1**
C2 - K10	3.369	0.00609	0.02621	0.00147	-0.00361	**1.1**
C1 - K10	3.353	0.00623	0.02681	0.00151	-0.00368	**1.2**
S5 - K10	3.459	0.00631	0.02797	0.00164	-0.00371	**1.2**
K10 - O12	2.586	0.02352	0.11695	0.00374	-0.02176	6.8
K10 - O91	2.525	0.02678	0.13502	0.0038	-0.02616	8.2
K10 - H121	2.779	0.00560	0.02498	0.00143	-0.00339	1.1
K10 - H44	2.814	0.00599	0.02603	0.00146	-0.00359	1.1
K10 - H52	2.738	0.00735	0.03164	0.00171	-0.00448	1.4
K11 - H122	2.782	0.00643	0.02821	0.00158	-0.00390	1.2
K11 - H130	2.735	0.00724	0.03087	0.00167	-0.00438	1.4
K11 - H43	2.755	0.00589	0.02634	0.0015	-0.00358	1.1
10b						
K1 - O92	2.478	0.02746	0.14924	0.00454	-0.02824	8.9
K1 - O2	2.651	0.02122	0.10189	0.00348	-0.01852	5.8
K1 - N94	2.939	0.01355	0.05475	0.00234	-0.00902	**2.8**
K1 - H155	2.931	0.00450	0.01873	0.00112	-0.00245	0.8
K91 - O92	2.640	0.02204	0.10526	0.00343	-0.01947	6.1
K91 - O2	2.478	0.02765	0.14948	0.00448	-0.02840	8.9
K91 - N4	2.869	0.01577	0.06428	0.00248	-0.01112	**3.5**
K91 - H65	2.904	0.00481	0.02012	0.00119	-0.00266	0.8
11b						
K1 - O65	2.494	0.02670	0.14353	-0.00444	-0.02701	8.5
K1 - O2	2.669	0.02044	0.09784	-0.00346	-0.01754	5.5
K1 - N67	2.877	0.01530	0.06310	-0.00251	-0.01076	**3.4**
K1 - H73	2.841	0.00560	0.02532	-0.00145	-0.00344	1.1
O2 - K64	2.486	0.02721	0.14637	-0.00445	-0.02770	8.7
K64 - O65	2.625	0.02265	0.10880	-0.00346	-0.02027	6.4
N4 - K64	2.824	0.01711	0.07103	-0.00260	-0.01257	**3.9**

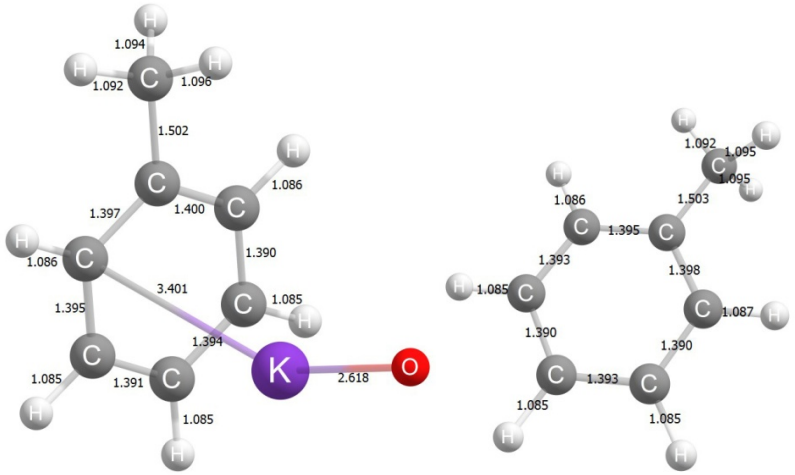
Table S6. QTAIM data for K…X interaction in **1**-**6**, **8a**,**9b** and **10b** optimized at the r^2-SCAN-3c/Def2-TZVP level with CPCM(Hexane).

BCP #	Distance, Å	ρ(**r**), a.u.	Δρ(**r**),a.u.	H(**r**), a.u.	V(**r**),a.u.	E_{cont}, kcal/mol
1 (L= Et_2O)						
K1 - O2	2.538	0.02534	0.13031	0.00397	-0.02463	7.7
K1 - O5	2.797	0.01402	0.07032	0.00344	-0.01070	3.4
K99 - O100	2.513	0.02718	0.13900	0.00389	-0.02698	8.5
O2 - K99	2.573	0.02441	0.12115	0.00369	-0.02291	7.2
K99 - O103	2.684	0.01797	0.09260	0.00392	-0.01531	4.8
K1 - O5	2.593	0.01402	0.07032	0.00344	-0.01070	3.4
2 (L= C_6H_6)						
K103 - O104	2.546	0.02532	0.12812	0.00386	-0.02430	7.6
K1 - O104	2.546	0.02153	0.10557	0.00364	-0.01912	6.0
O2 - K103	2.630	0.02152	0.10554	0.00364	-0.01911	6.0
K1 - O2	2.630	0.02530	0.12805	0.00386	-0.02428	7.6
K1 - C93	3.376	0.00585	0.02425	0.00141	-0.00325	**1.0**
K103 - C195	3.375	0.00585	0.02422	0.0014	-0.00325	**1.0**
5 (L = PhOMe)						
K1 - O3	2.570	0.02477	0.12235	0.00364	-0.02330	7.3
K2 - O3	2.512	0.02669	0.13849	0.00403	-0.02656	8.3
K1 - O4	2.516	0.02657	0.13778	0.00403	-0.02639	8.3
K2 - O4	2.569	0.02478	0.12244	0.00365	-0.02332	7.3
K1 - O6	2.784	0.01459	0.07354	0.0035	-0.01139	3.6
K2 - O8	2.785	0.01456	0.07338	0.0035	-0.01135	3.6
5b (L = PhOMe)						
K1 - O106	2.616	0.02230	0.10969	0.00366	-0.02011	6.3
K1 - O2	2.541	0.02555	0.12936	0.00387	-0.02460	7.7
K1 - C68	3.284	0.00676	0.02645	0.00145	-0.00371	**1.2**
K105 - O106	2.542	0.02555	0.12934	0.00387	-0.02460	7.7
O2 - K105	2.614	0.02231	0.10969	0.00366	-0.02011	6.3
K105 - C173	3.283	0.00677	0.02646	0.00145	-0.00371	**1.2**
6 (L = $PhNMe_2$)						
K1 - O110	2.619	0.02218	0.09849	0.00256	-0.01950	6.1
K1 - O2	2.552	0.02512	0.11756	0.00313	-0.02312	7.3
O2 - K109	2.619	0.02219	0.09851	0.00256	-0.01950	6.1
K1 - C68	3.280	0.00718	0.02647	0.00139	-0.00383	**1.2**
K109 - O110	2.552	0.02512	0.11757	0.00313	-0.02313	7.3
K109 - C177	3.282	0.00718	0.02648	0.00139	-0.00383	**1.2**
6b (L = $PhNMe_2$)						
O2 - K109	2.561	0.02385	0.11163	0.00313	-0.02166	6.8
K1 - O2	2.561	0.02495	0.11243	0.00271	-0.02270	7.1
K1 - O110	2.563	0.02381	0.11139	0.00312	-0.02161	6.8
K1 - N8	3.204	0.00814	0.03157	0.00131	-0.00528	**1.7**
K109 - O110	2.561	0.02495	0.11240	0.00271	-0.02269	7.1
K109 - N116	3.204	0.00812	0.03152	0.00131	-0.00527	**1.7**
4 (L = Naphthalene)						
O2 - K109	2.612	0.022418	0.110079	0.00365	-0.02022	6.3

K1 - O110	2.612	0.022397	0.11002	0.00365	-0.0202	6.3
K1 - O2	2.537	0.025752	0.130753	0.00389	-0.02492	7.8
K109 - O110	2.535	0.025897	0.131399	0.00388	-0.02509	7.9
K1 - C95	3.306	0.00634	0.024715	0.00138	-0.00341	**1.1**
K109 - C203	3.303	0.006352	0.024608	0.00138	-0.0034	**1.1**
3 (L = Toluene)						
K106 - C193	3.344	0.00608	0.02476	0.00141	-0.00337	**1.1**
K106 - O107	2.544	0.02551	0.12861	0.00383	-0.02449	7.7
K1 - O107	2.618	0.02201	0.10854	0.00368	-0.01978	6.2
K1 - O2	2.544	0.02551	0.12861	0.00383	-0.02449	7.7
K1 - C88	3.345	0.00608	0.02474	0.00141	-0.00337	**1.1**
O2 - K106	2.618	0.02201	0.10853	0.00368	-0.01978	6.2
8a (L = Thiophene)						
K11 - O12	2.533	0.02619	0.13224	0.00383	-0.02541	8.0
K11 - O91	2.599	0.02285	0.11332	0.00372	-0.02089	6.6
K10 - O91	2.530	0.02644	0.13337	0.00381	-0.02572	8.1
K11 - C87	3.377	0.00587	0.02532	0.00145	-0.00343	1.1
K11 - C88	3.378	0.00595	0.02534	0.00144	-0.00346	1.1
K11 - S13	3.495	0.00585	0.02594	0.00155	-0.00339	1.1
C2 - K10	3.359	0.00618	0.02640	0.00148	-0.00363	1.1
S5 - K10	3.478	0.00606	0.02698	0.0016	-0.00355	1.1
C1 - K10	3.356	0.00612	0.02647	0.0015	-0.00362	1.1
K10 - H121	2.785	0.00553	0.02458	0.00141	-0.00333	1.0
K10 - H44	2.810	0.00602	0.02611	0.00146	-0.00360	1.1
K10 - H52	2.748	0.00725	0.03128	0.0017	-0.00441	1.4
K11 - H122	2.782	0.00643	0.02819	0.00158	-0.00390	1.2
K11 - H130	2.748	0.00715	0.03063	0.00167	-0.00432	1.4
K11 - H43	2.755	0.00587	0.02613	0.00149	-0.00356	1.1
10b						
K1 - O92	2.481	0.02726	0.14811	0.00453	-0.02796	8.8
K1 - O2	2.657	0.02096	0.10059	0.00347	-0.01820	5.7
K1 - N94	2.934	0.01371	0.05544	0.00235	-0.00917	**2.9**
K1 - H155	2.926	0.00456	0.01895	0.00113	-0.00249	0.8
K91 - H65	2.903	0.00483	0.02019	0.00119	-0.00267	0.8
K91 - N4	2.864	0.01593	0.06491	0.00248	-0.01127	**3.5**
K91 - O92	2.643	0.02186	0.10441	0.00343	-0.01925	6.0
O2 - K91	2.482	0.02739	0.14797	0.00448	-0.02804	8.8
11b						
K1 - H73	2.839	0.02545	0.00146	-0.00345	0.02545	1.1
K1 - N67	2.869	0.06428	0.00252	-0.01102	0.06428	**3.5**
K1 - O2	2.671	0.09732	0.00346	-0.01741	0.09732	5.5
K1 - O65	2.498	0.14211	0.00443	-0.02667	0.14211	8.4
K64 - O65	2.631	0.10732	0.00347	-0.01990	0.10732	6.2
K64 -O2	2.492	0.14420	0.00443	-0.02718	0.14420	8.5
K64 - N4	2.822	0.07135	0.00259	-0.01265	0.07135	**4.0**

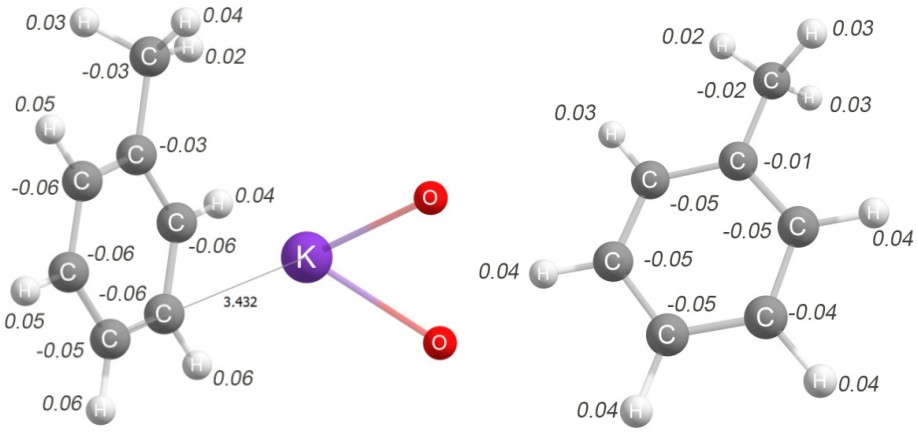
Table S7. The E_{tot} (a.u.) values estimated

	r^2-SCAN-3c/Def2-TZVP	r^2-SCAN-3c/Def2-TZVP, CPCM(Hexane)
Et_2O	-233.602979	-233.602979
C_6H_6	-232.190761	-232.192680
PhOMe	-346.693772	-346.696665
$PhNMe_2$	-366.124311	-366.124311
Naphthalene	-385.805166	-385.807856
Toluene	-271.496010	-271.498006
Thiophene	-552.962441	-552.962441
1 (L= Et_2O)	-5023.050493	-5023.062204
2 (L= C_6H_6)	-5020.227090	-5020.239101
5 (L = PhOMe)	-5249.256454	-5249.268938
5b (L = PhOMe) Ar-isomer	-5249.247853	-5249.261870
6 (L = $PhNMe_2$)	-5288.096879	-5288.110561
6b (L = $PhNMe_2$) N-isomer	-5288.091559	-5288.104558
4 (L = Naphthalene)	-5327.458020	-5327.471941
3 (L = Toluene)	-5098.842076	-5098.853946
8a (L = Thiophene)	-5661.763892	-5661.776554
10a Free $(KOAr)_2$	-4555.802971	-4555.813719
10b Free $(KOAr)_2$ N-isomer	-4555.808895	-4555.818926
11a	-3855.499884	-3855.510588
11b	-3855.514289	-3855.524304



a ***b***

Figure S10. The comparison of the bond length of toluene in symmetrical independent moiety of the complex **3** (***a***) and free molecule (***b***) optimized at the r^2-SCAN-3c/Def2-TZVP/CPCM(hexane) level.



a ***b***

Figure S11. QTAIM charges of toluene in the complex **3** (***a***) and free molecule (***b***) calculated at the r^2-SCAN-3c/Def2-TZVP/CPCM(hexane) level.

To elucidate possible activation of the toluene ring coordinated in the complex **3**, bond length distribution (Fig. S11) and QTAIM charges (Fig. S12) are compared for toluene moiety as a part of the complex **3** and free toluene at the r^2-SCAN-3c/Def2-TZVP/CPCM(hexane) level of theory. During complex formation, only small elongation (0.002 Å) of aromatic C-C bond is observed. As can be seen from molecular graph of **3** (Fig. S4), the H atoms are not involved in any interaction with K or O atoms. Furthermore, changes to the QTAIM charges are within error limits (±0.01 ē), as illustrated in Fig. S12. Therefore, the results of the DFT analysis demonstrated that there was no evidence of pre-activation of toluene moiety in the complex **3**.

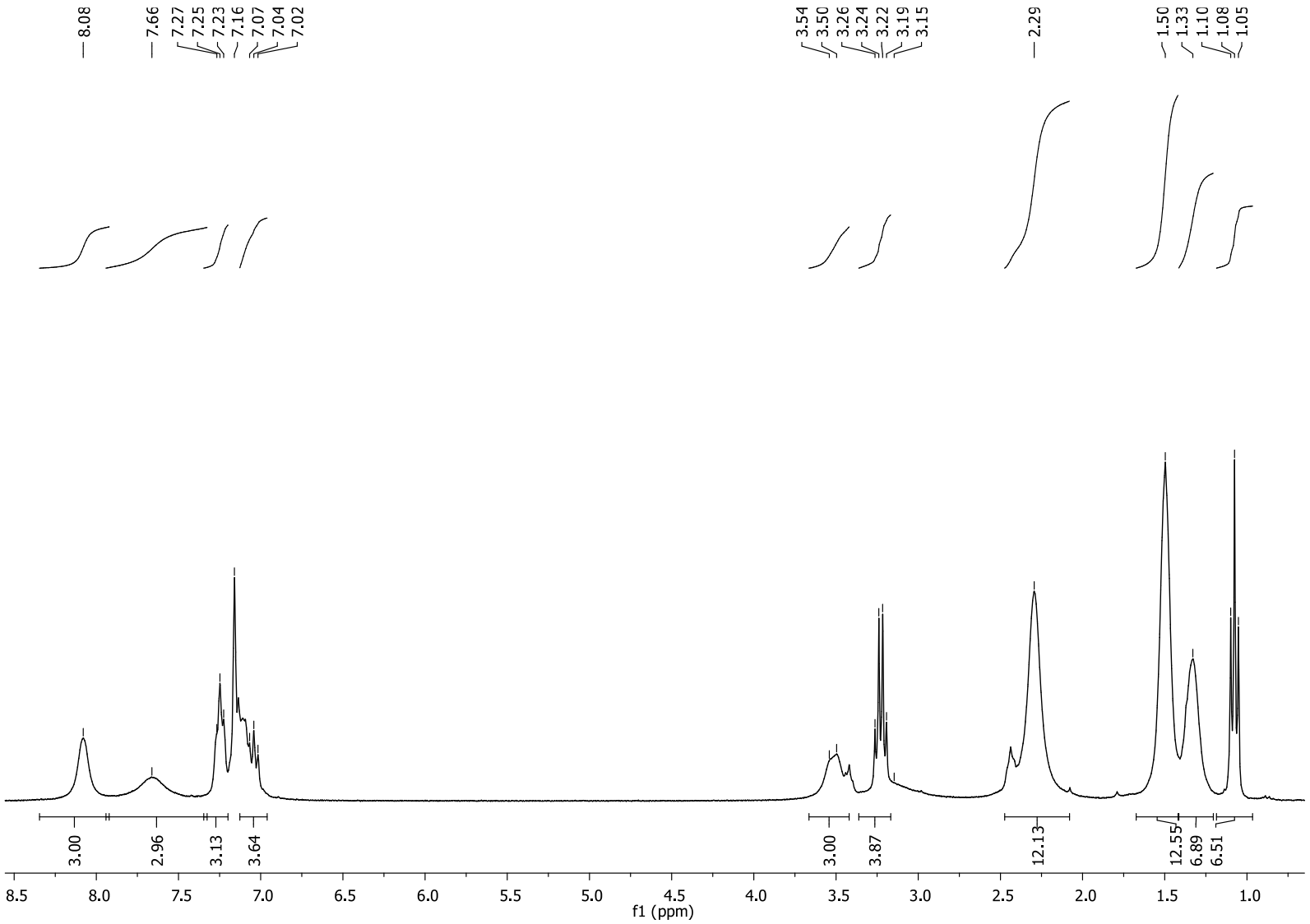


Figure S12. ^{1}H NMR spectrum of **1** (400 MHz, C_6D_6, 293 K).

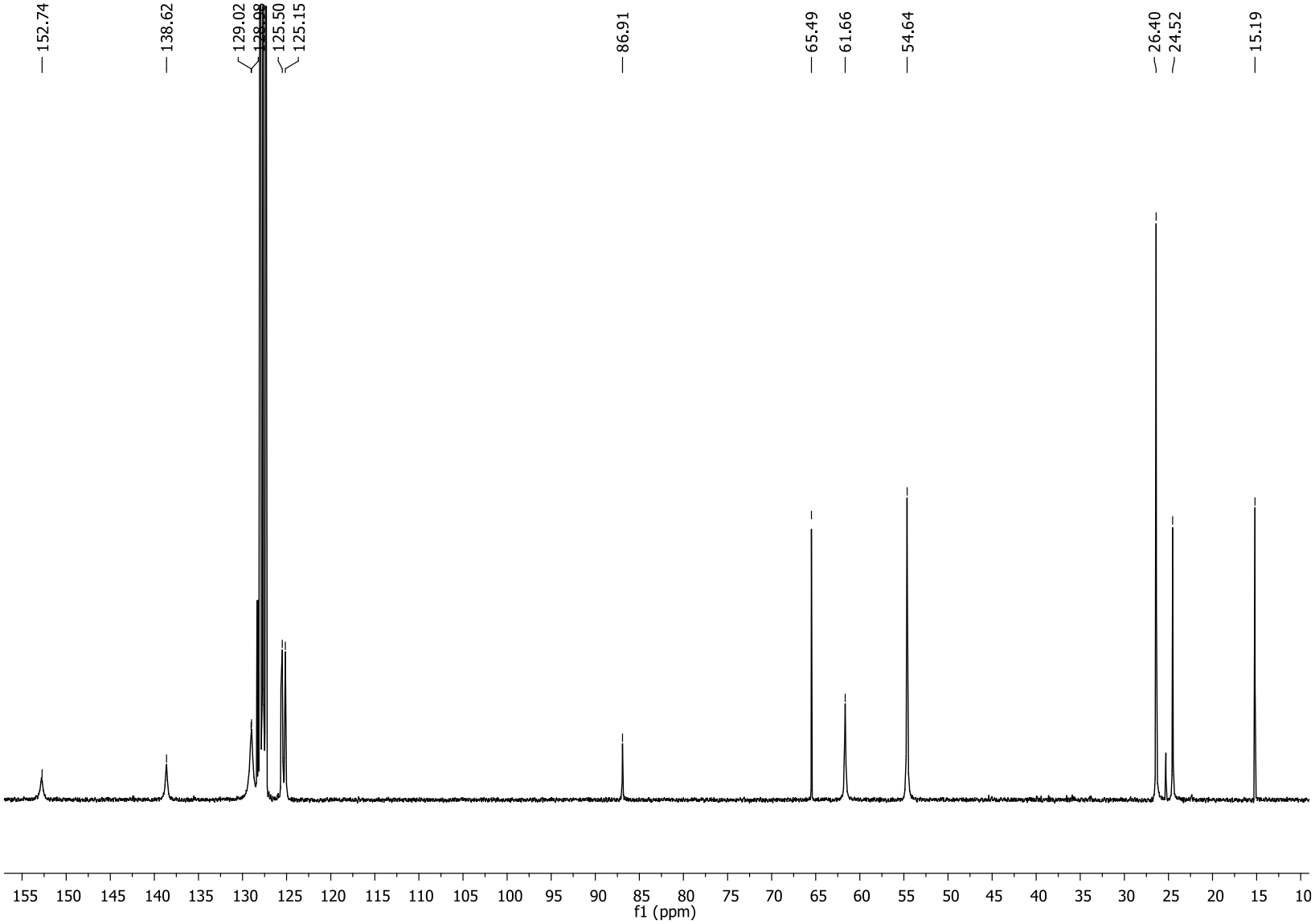


Figure S13. ^{13}C {^{1}H} NMR spectrum of **1** (100 MHz, C_6D_6, 293 K).

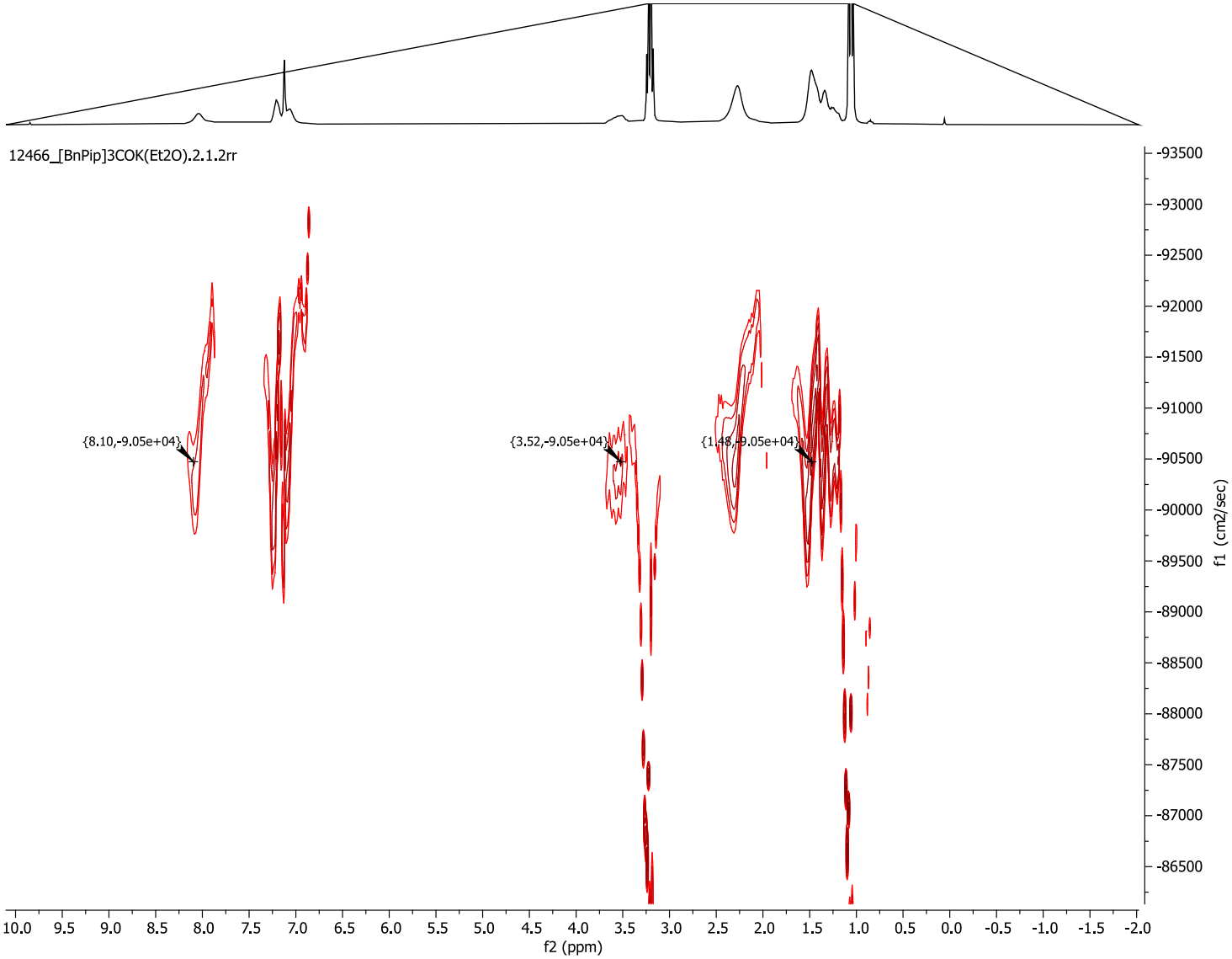


Figure S14. ^{1}H DOSY NMR spectrum of **1** (300 MHz, C_6D_6, 293 K).

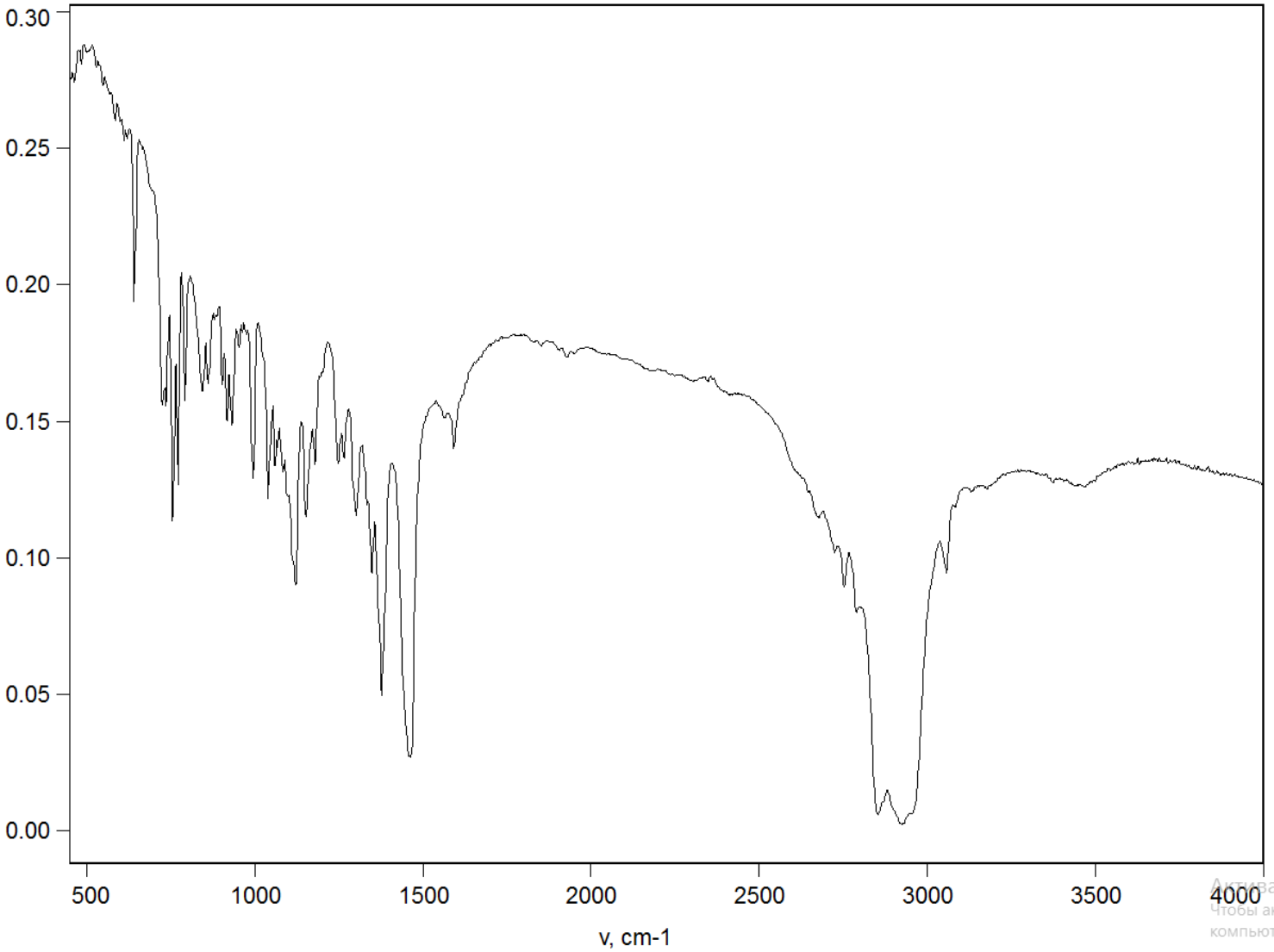


Figure S15. IR (KBr, Nujol) spectrum of complex **1**.

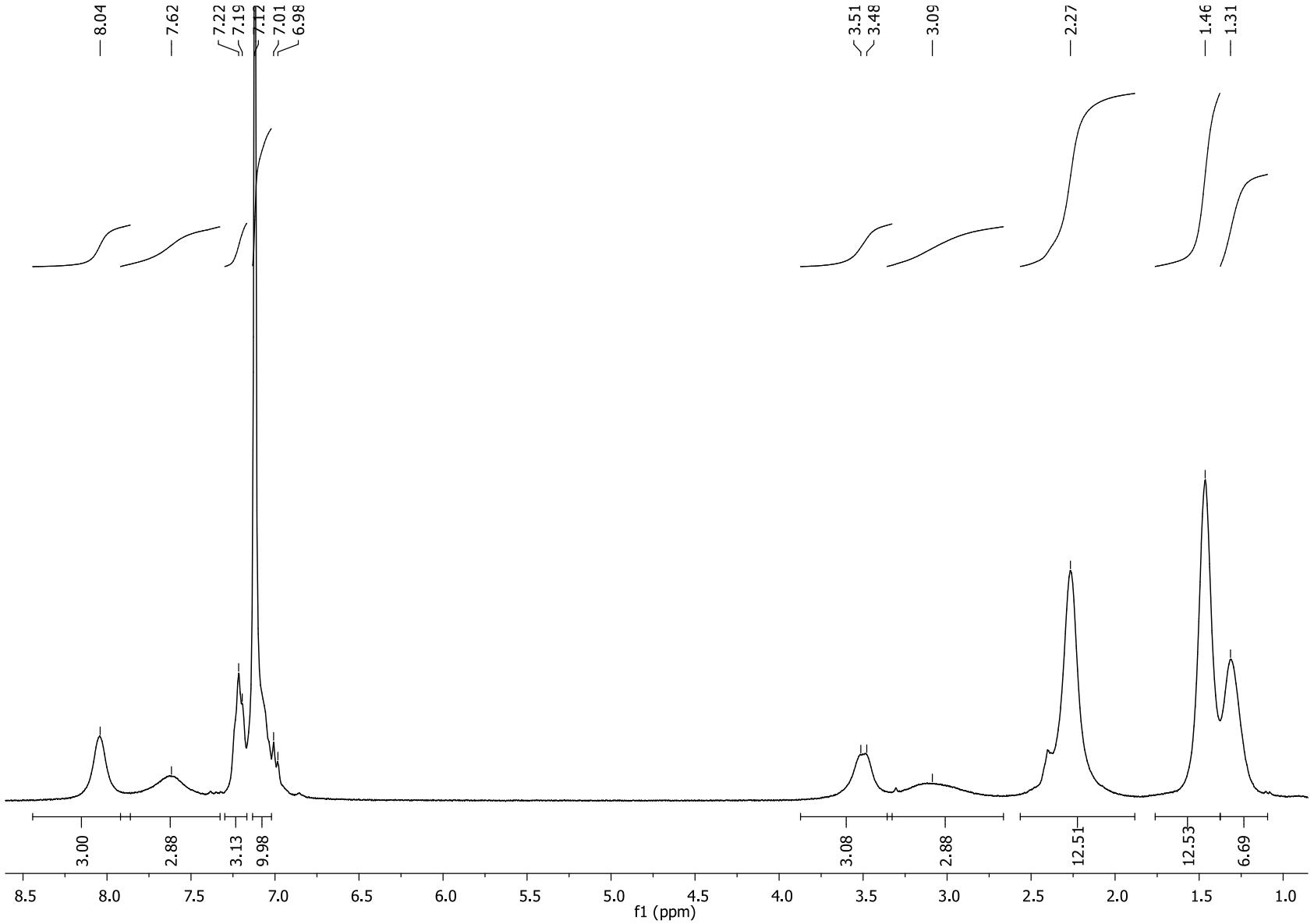


Figure S16. ^{1}H NMR spectrum of **2** (300 MHz, C_6D_6, 293 K).

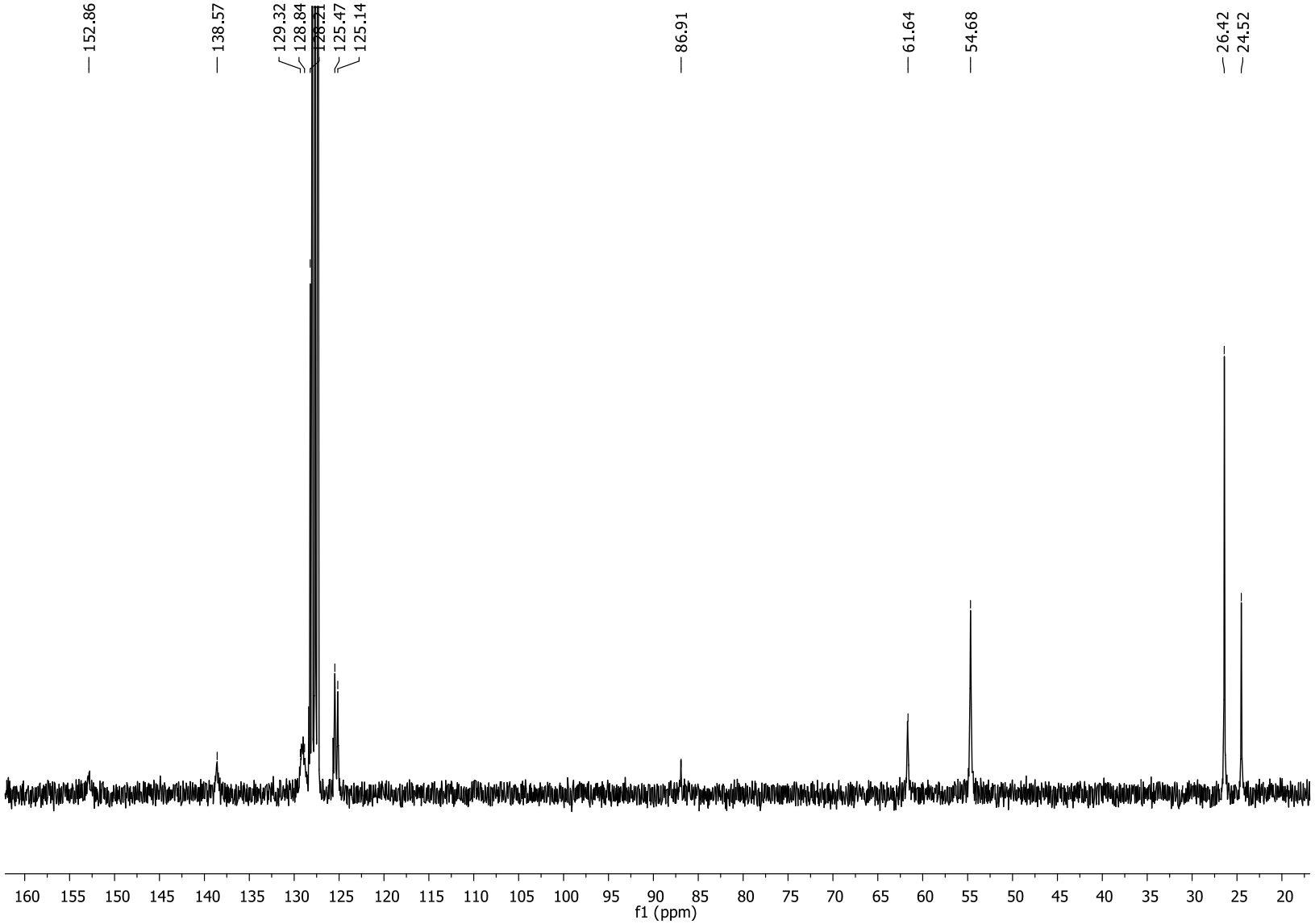


Figure S17. ^{13}C {^{1}H} NMR spectrum of **2** (75 MHz, C_6D_6, 293 K).

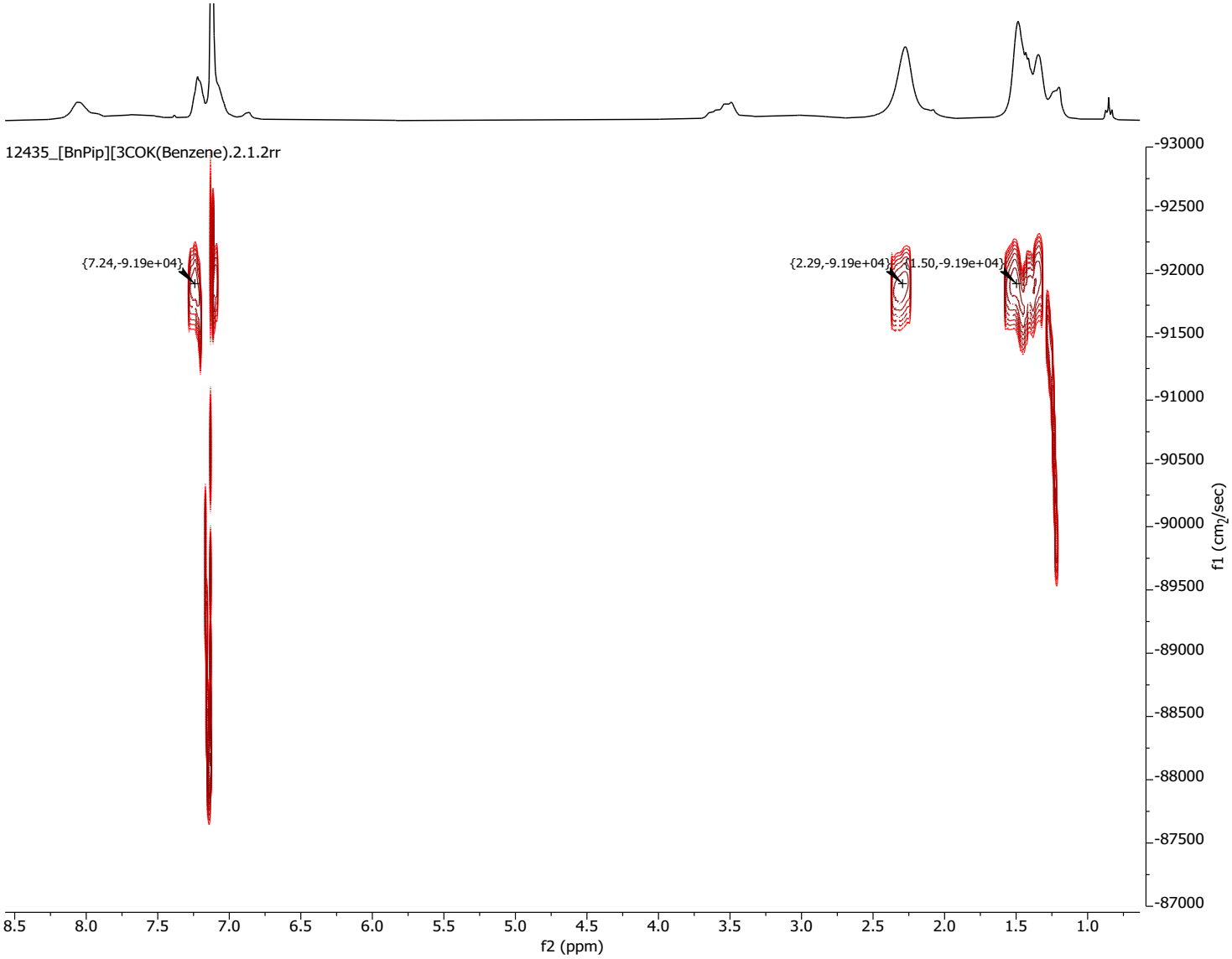


Figure S18. ^{1}H DOSY NMR spectrum of **2** (400 MHz, C_6D_6, 293 K).

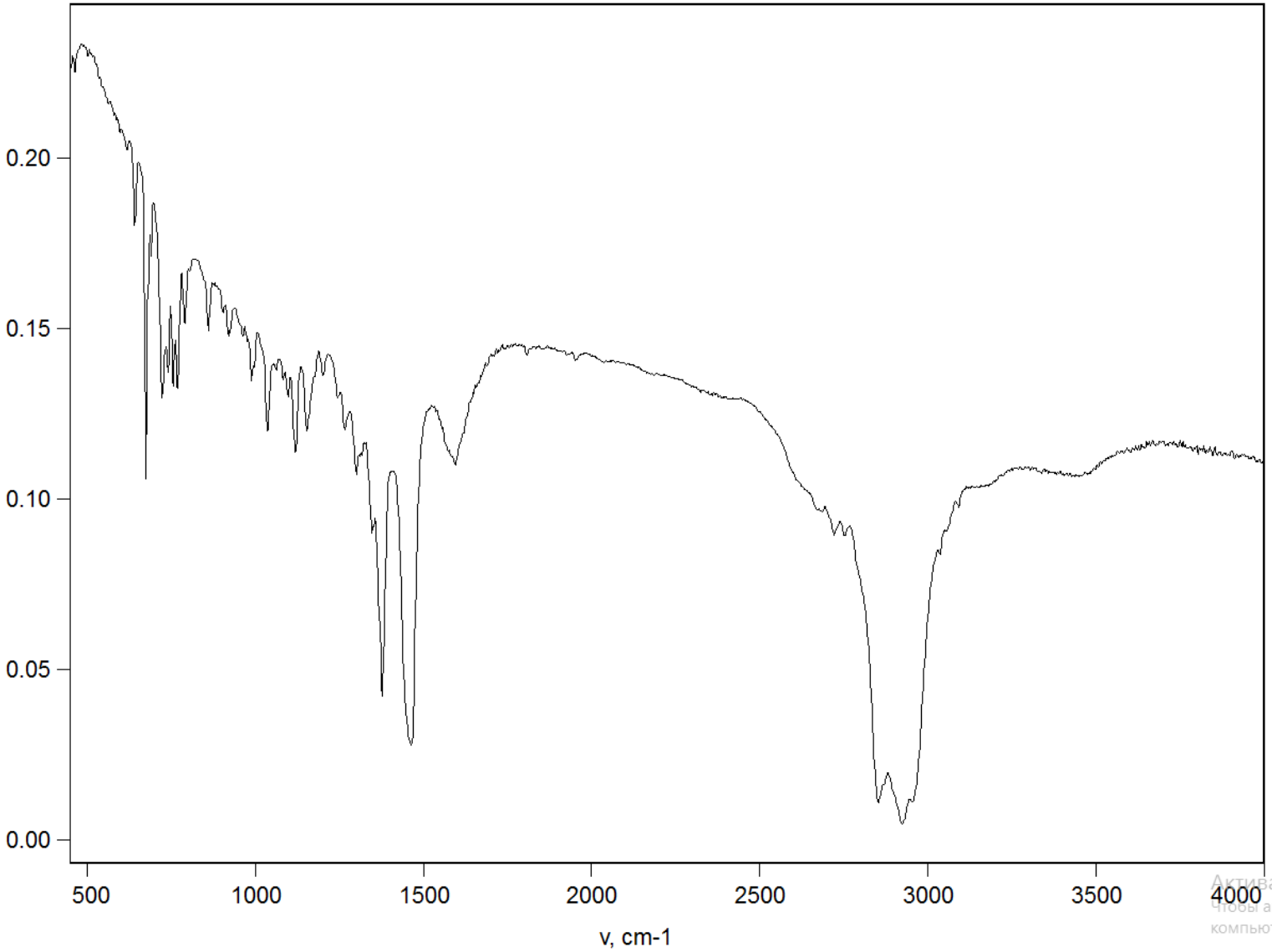


Figure S19. IR (KBr, Nujol) spectrum of complex **2**.

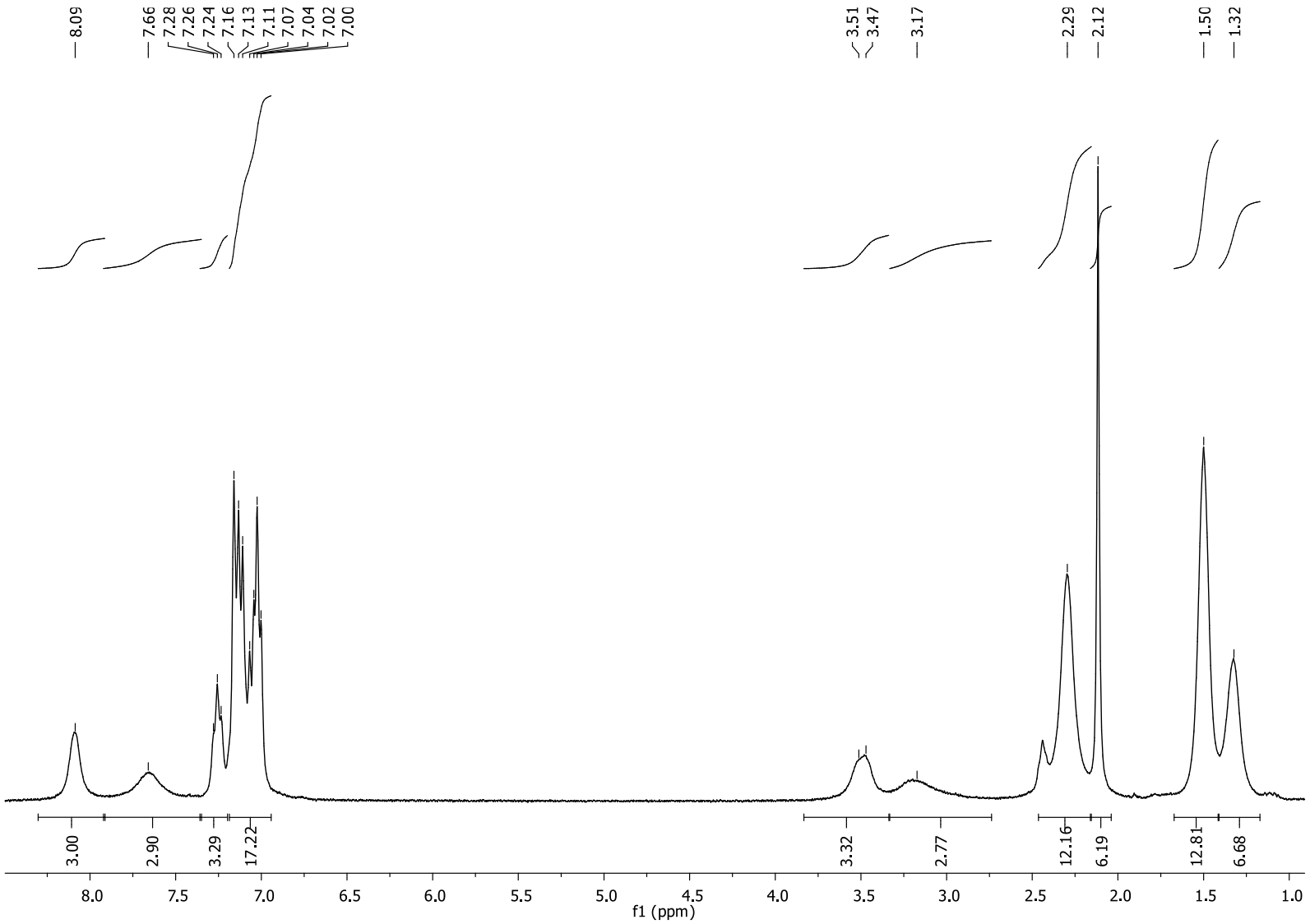


Figure S20. ^{1}H NMR spectrum of **3** (400 MHz, C_6D_6, 293 K).

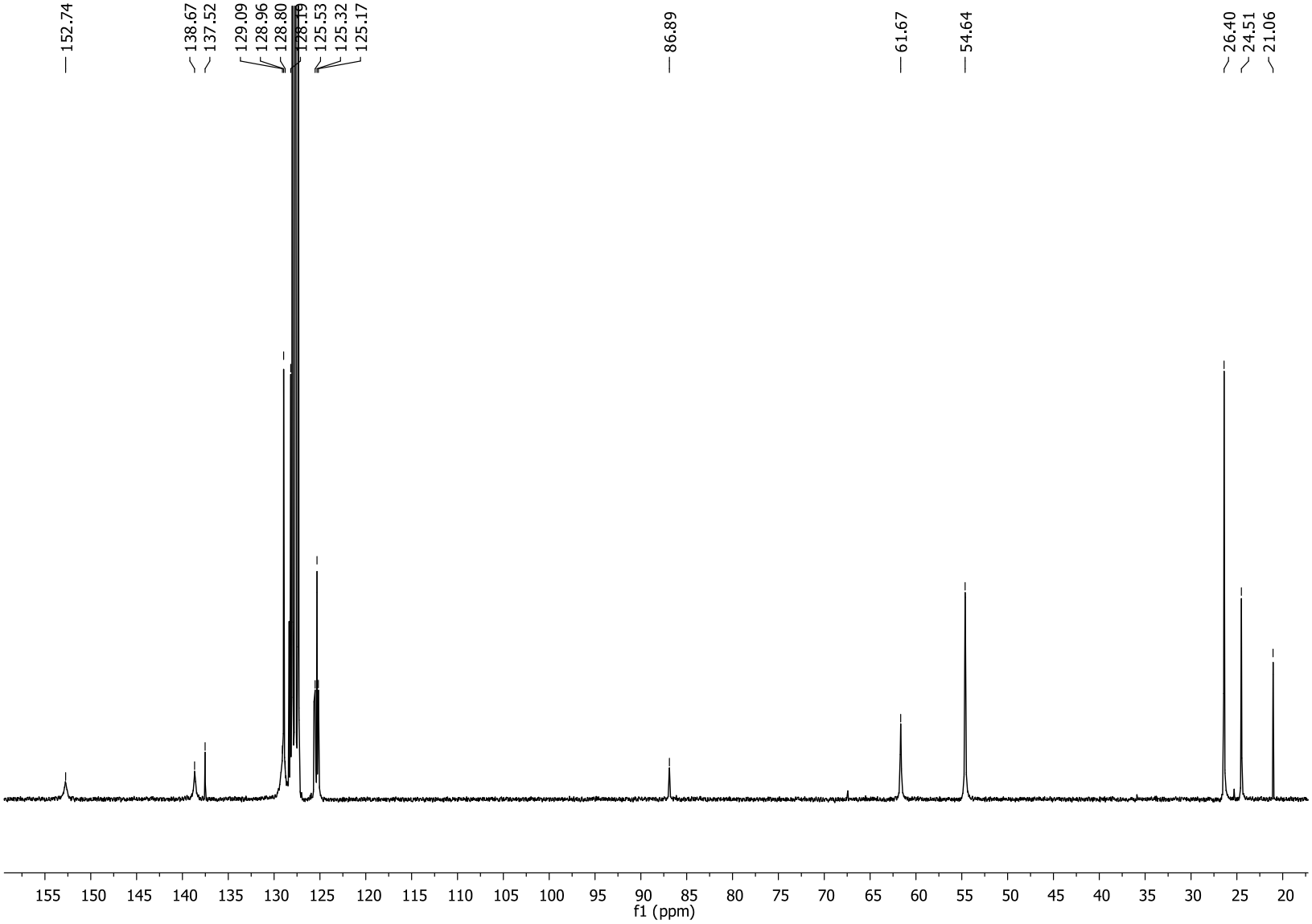


Figure S21. ^{13}C {^{1}H} NMR spectrum of **3** (100 MHz, C_6D_6, 293 K).

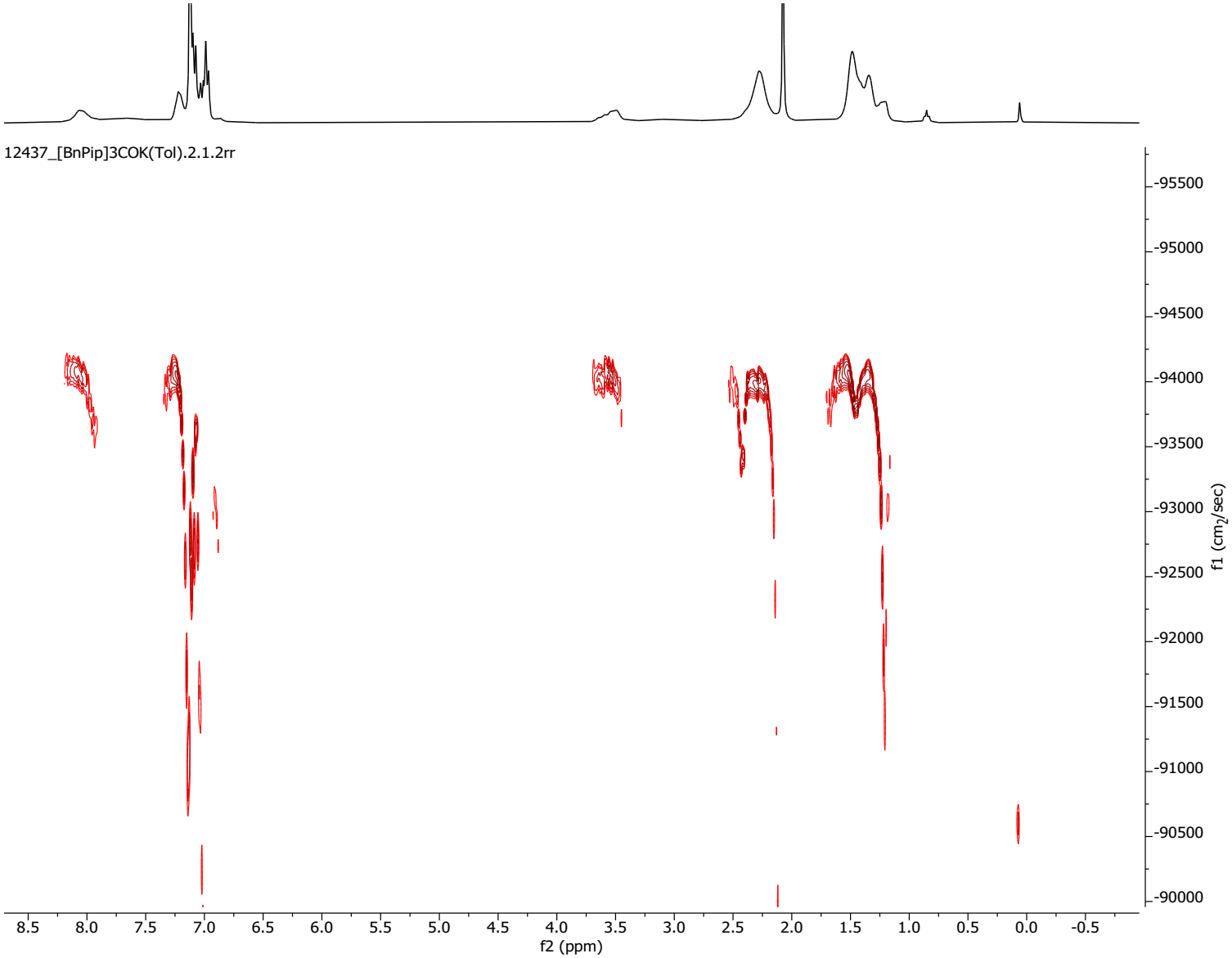


Figure S22. ^{1}H DOSY NMR spectrum of **3** (300 MHz, C_6D_6, 293 K).

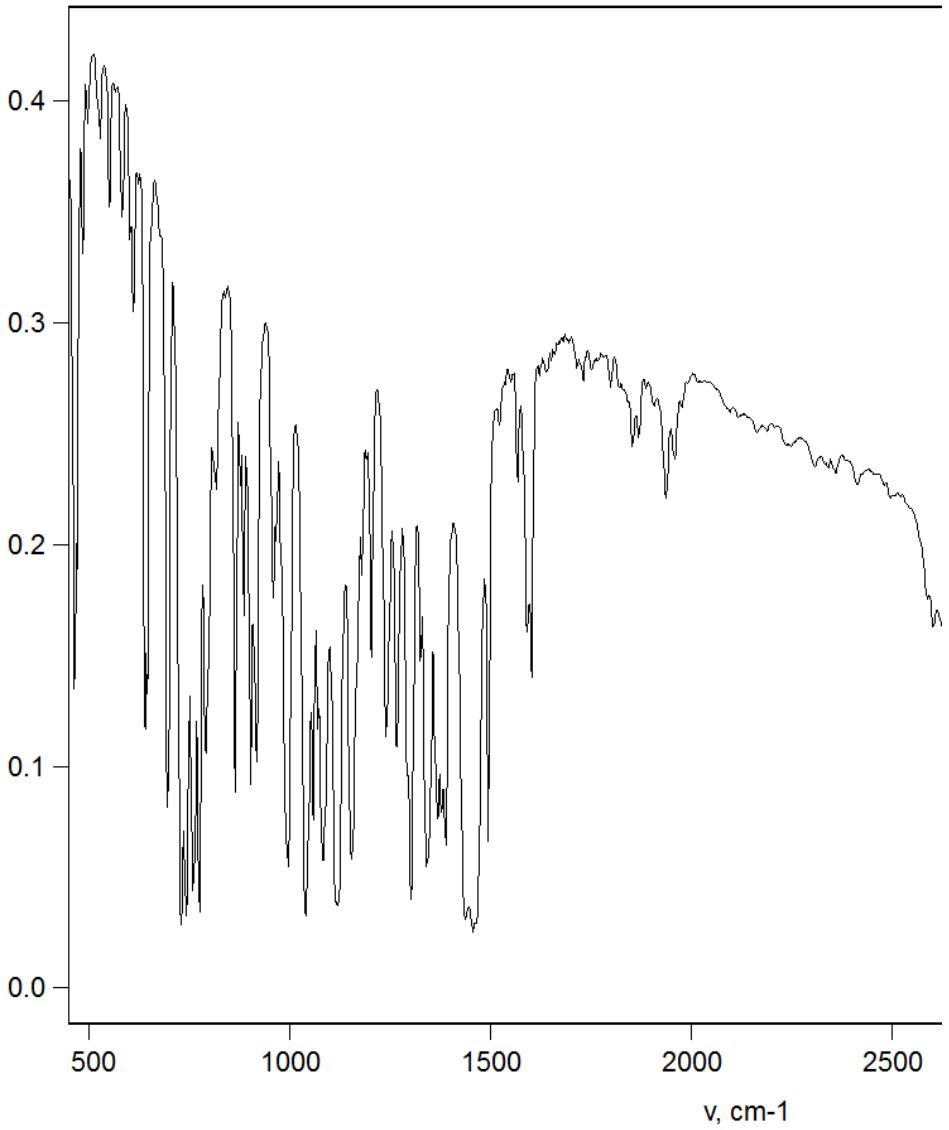


Figure S23. IR (KBr, Nujol) spectrum of complex **3**.

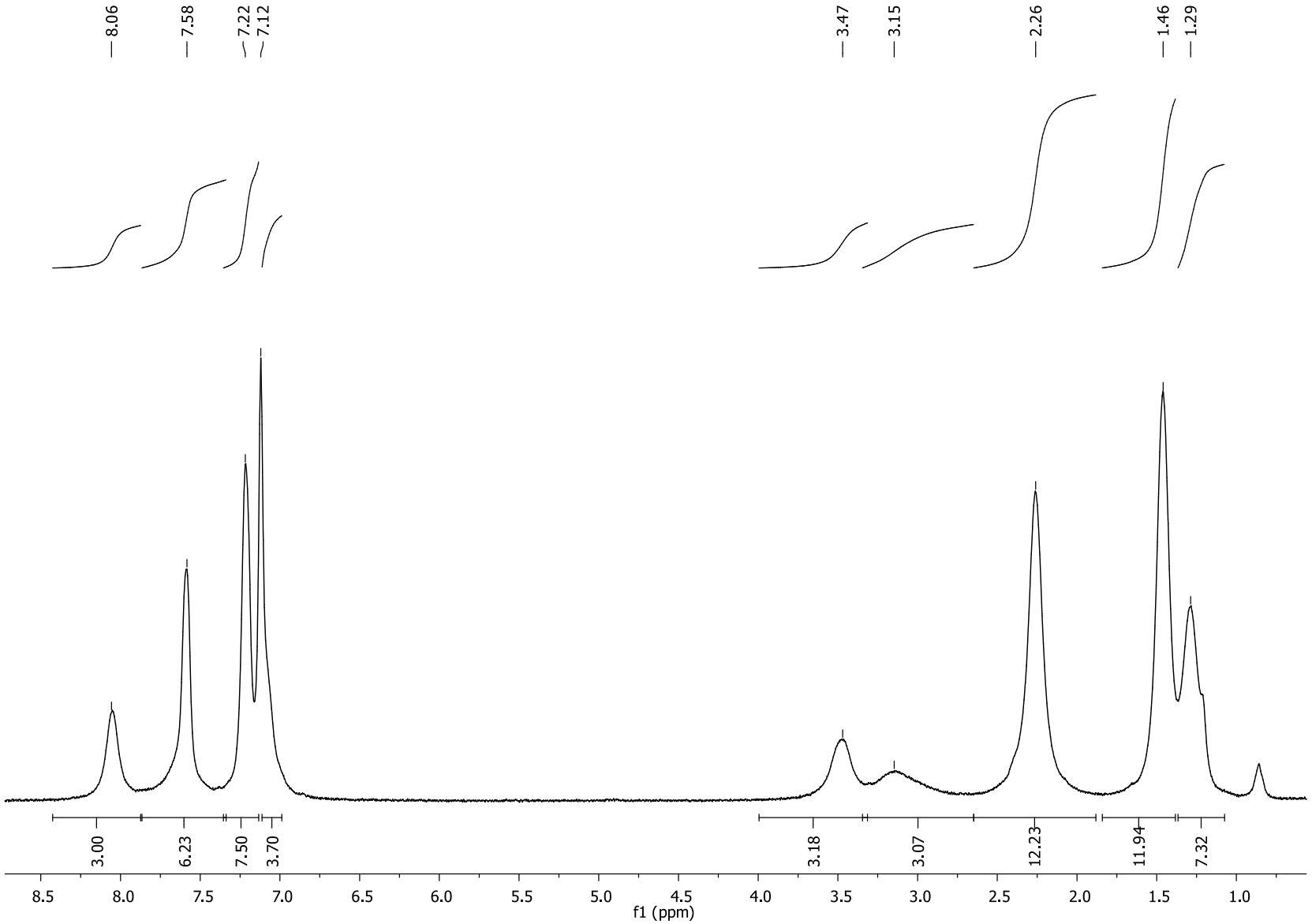


Figure S24. ^{1}H NMR spectrum of **4** (300 MHz, C_6D_6, 293 K).

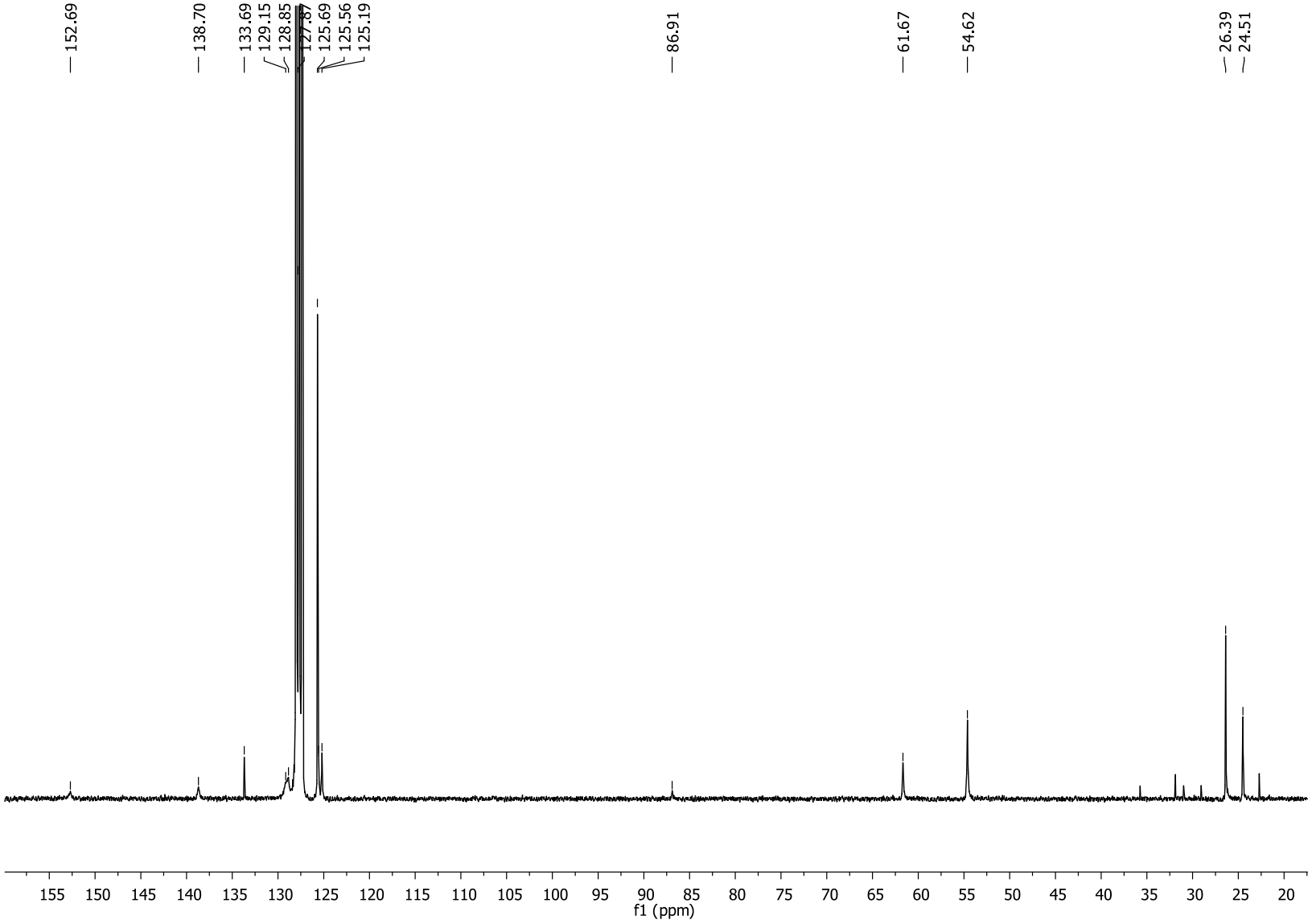


Figure S25. ^{13}C {^{1}H} NMR spectrum of **4** (75 MHz, C_6D_6, 293 K).

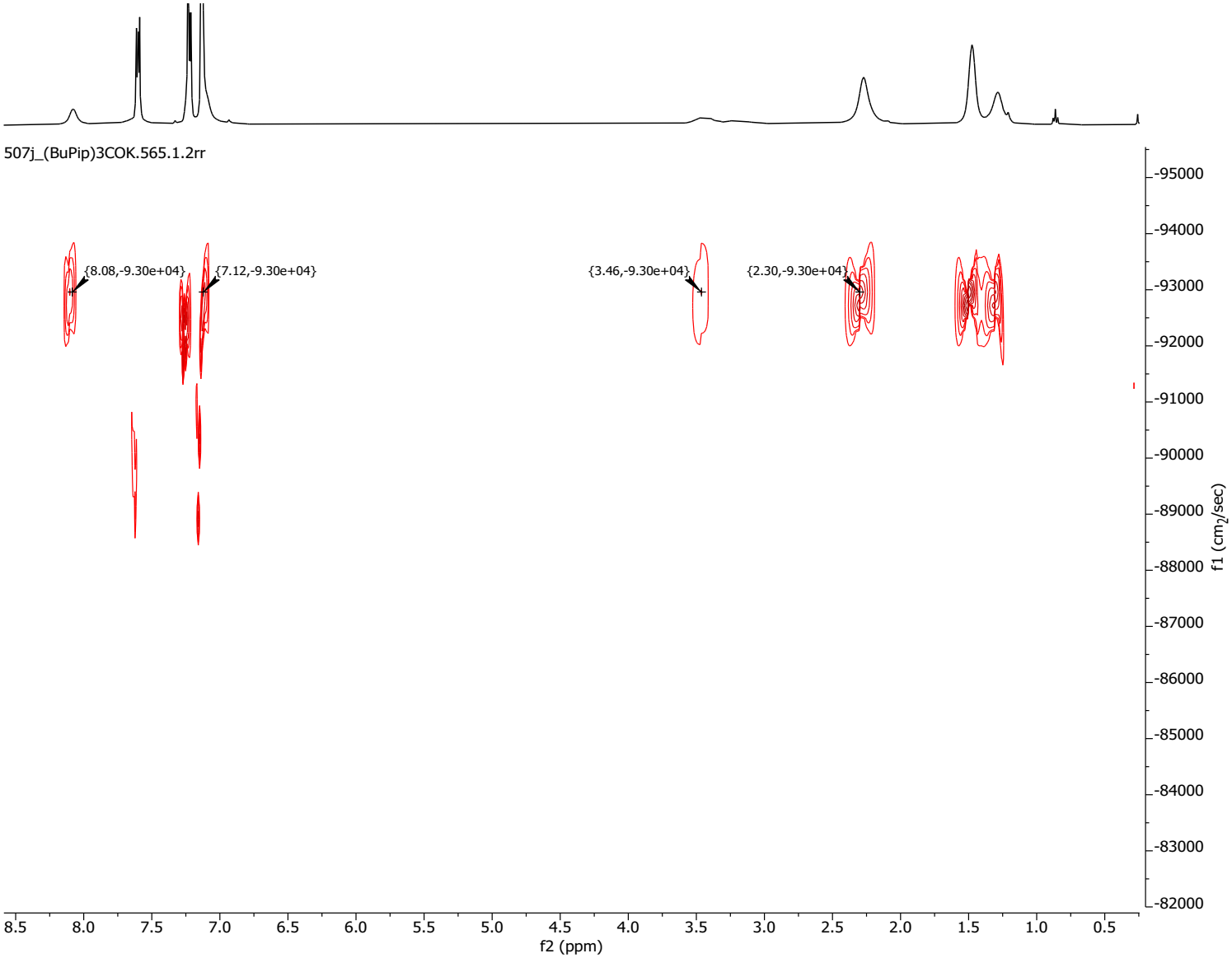


Figure S26. ^{1}H DOSY NMR spectrum of **4** (300 MHz, C_6D_6, 293 K).

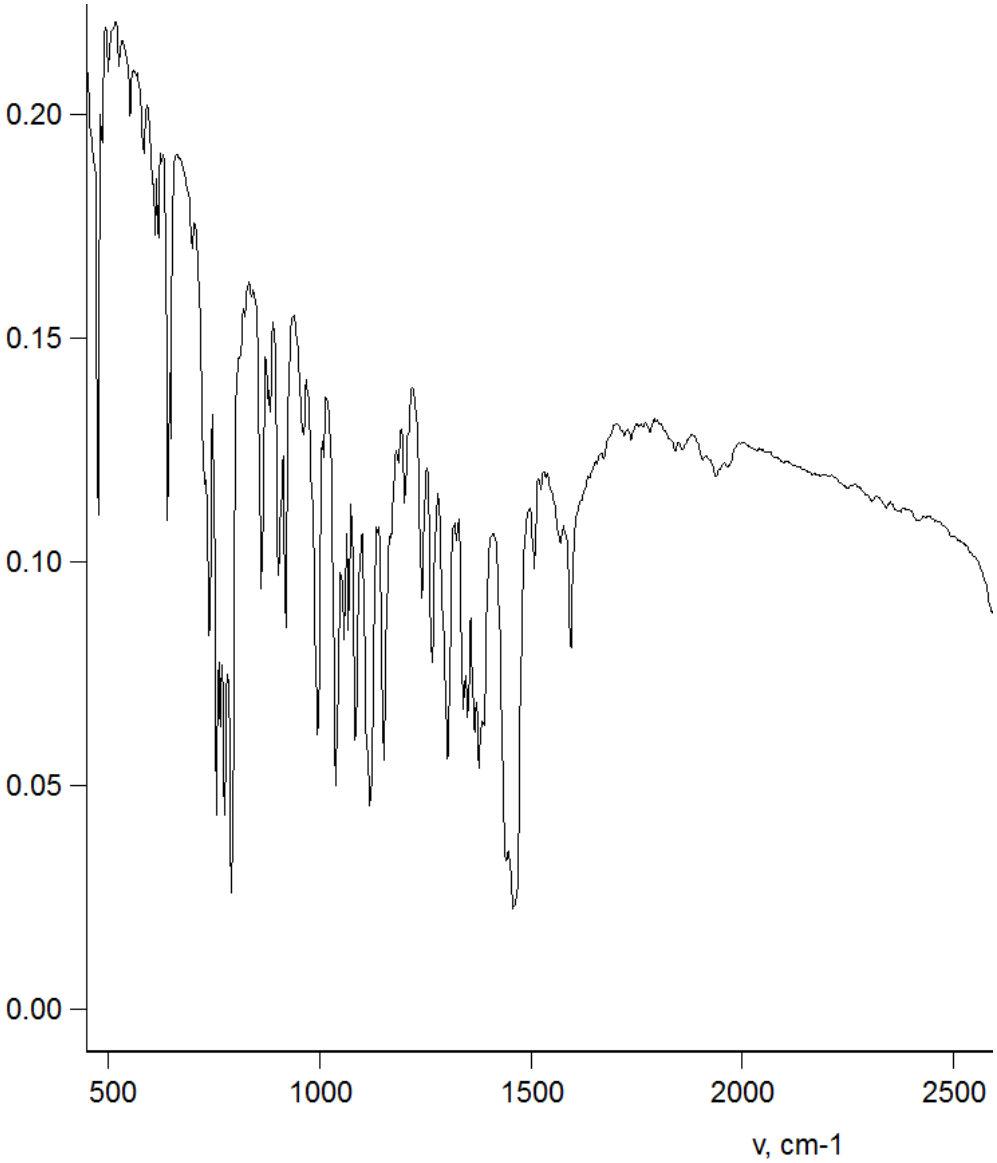


Figure S27. IR (KBr, Nujol) spectrum of complex **4**.

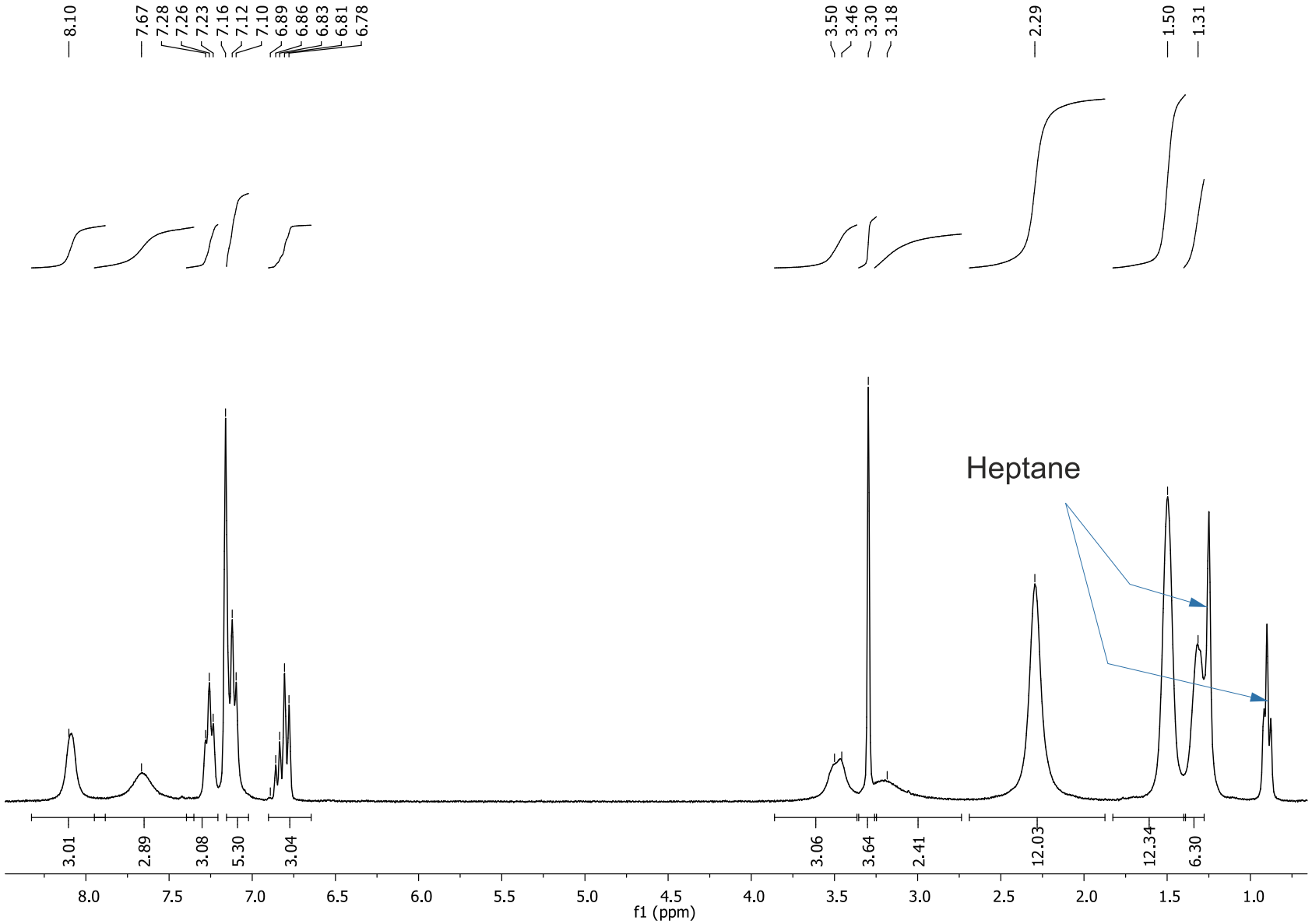


Figure S28. ^{1}H NMR spectrum of **5** (300 MHz, C_6D_6, 293 K).

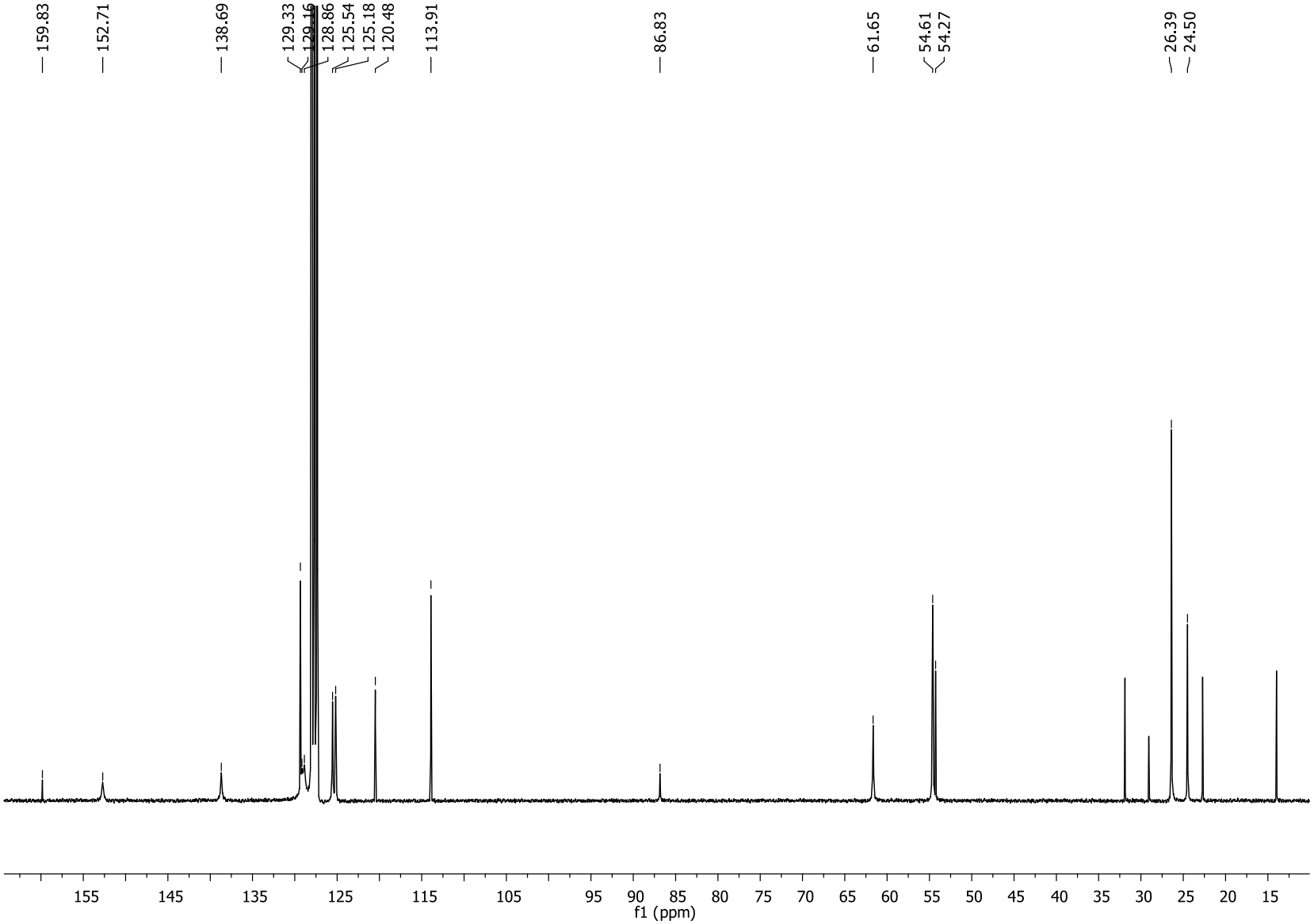


Figure S29. ^{13}C {^{1}H} NMR spectrum of **5** (75 MHz, C_6D_6, 293 K).

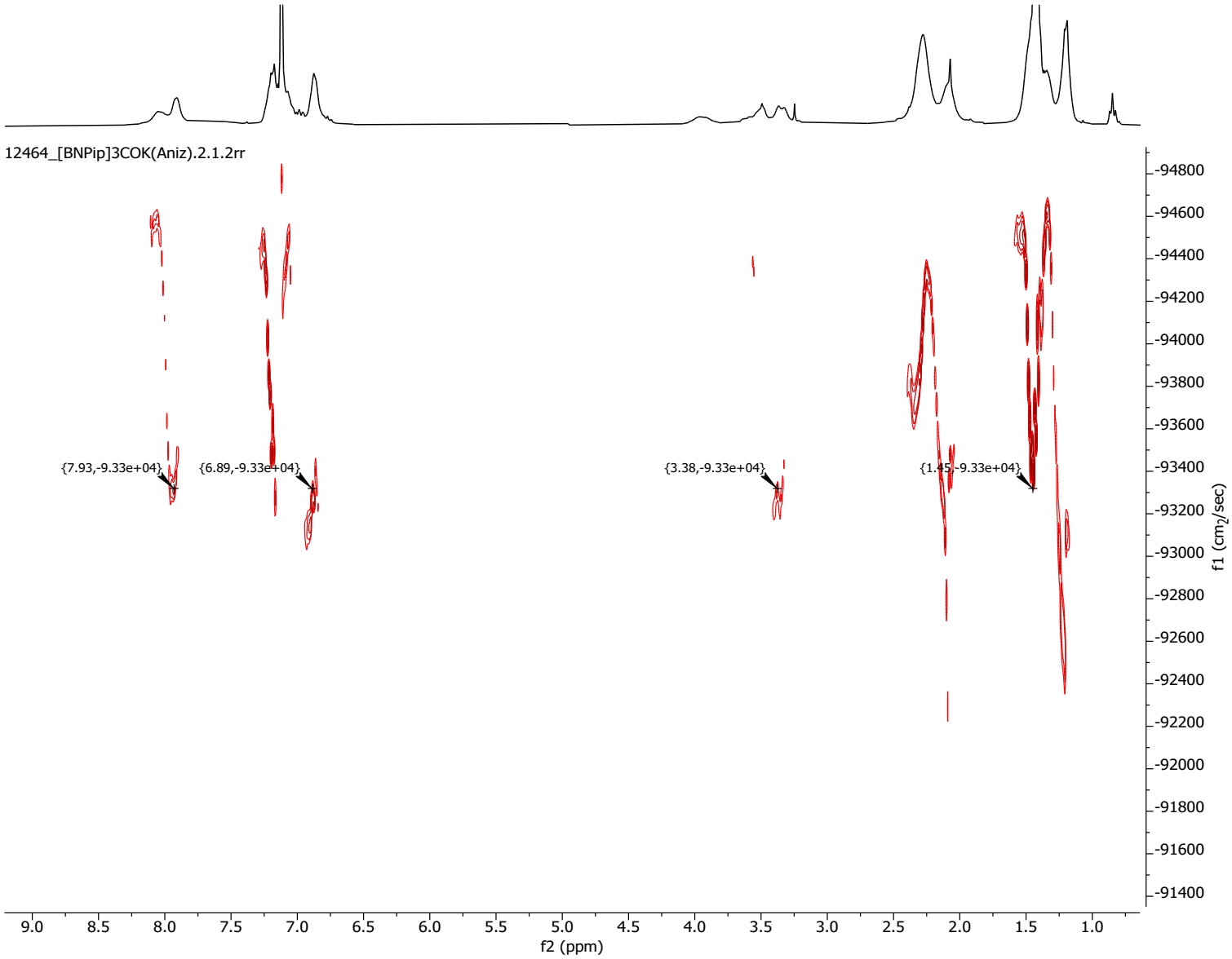


Figure S30. ^{1}H DOSY NMR spectrum of **5** (300 MHz, C_6D_6, 293 K).

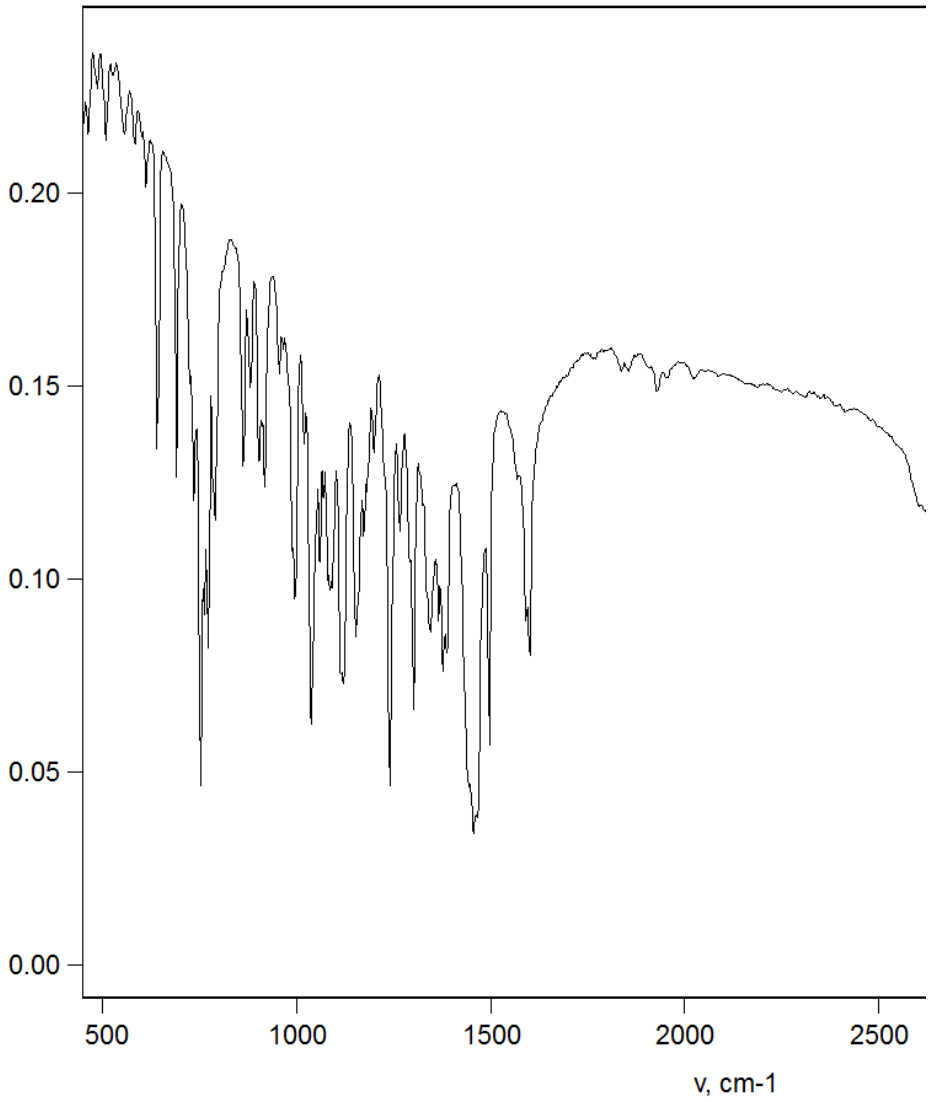


Figure S31. IR (KBr, Nujol) spectrum of complex **5**.

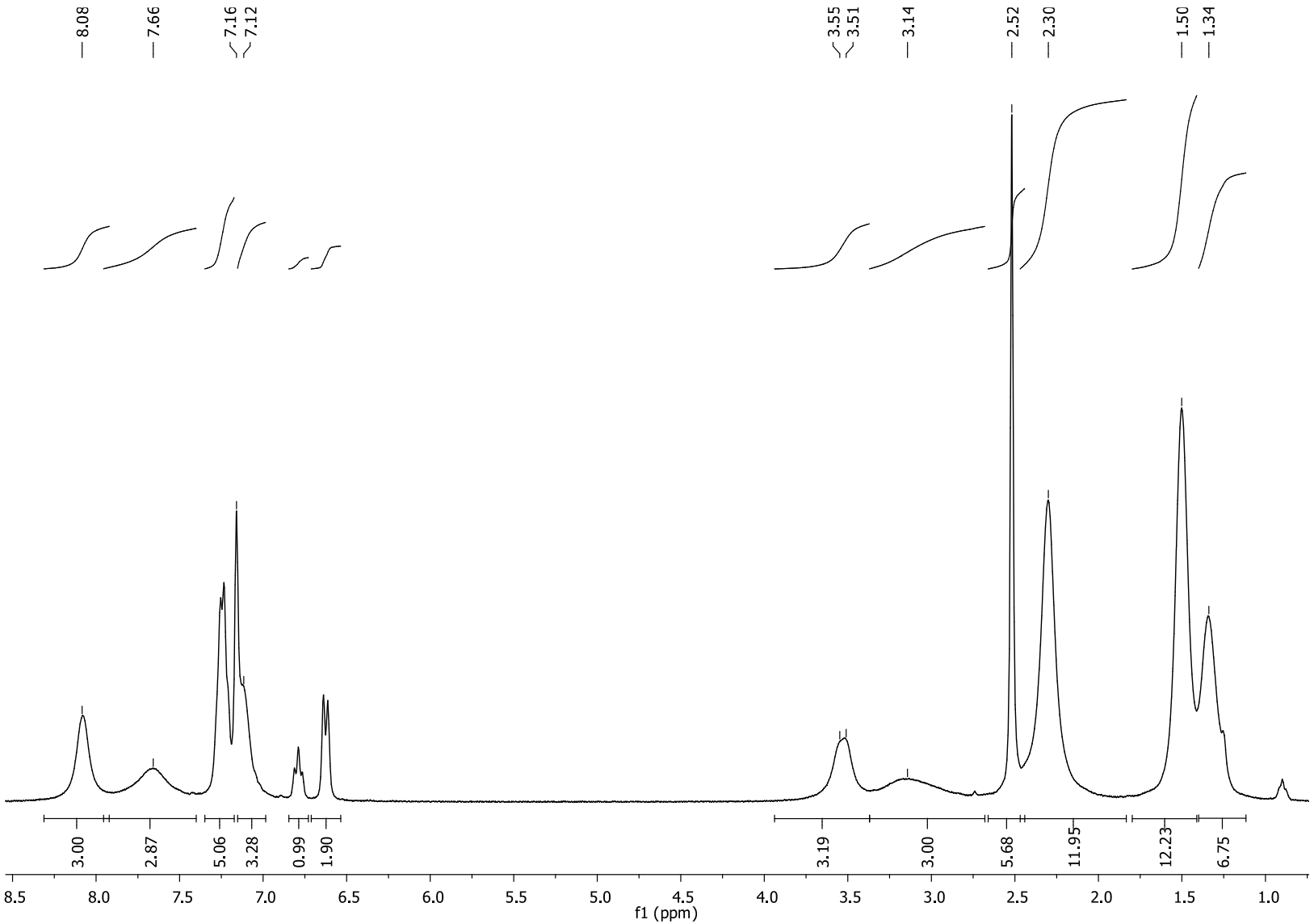


Figure S32. ^{1}H NMR spectrum of **6** (300 MHz, C_6D_6, 293 K).

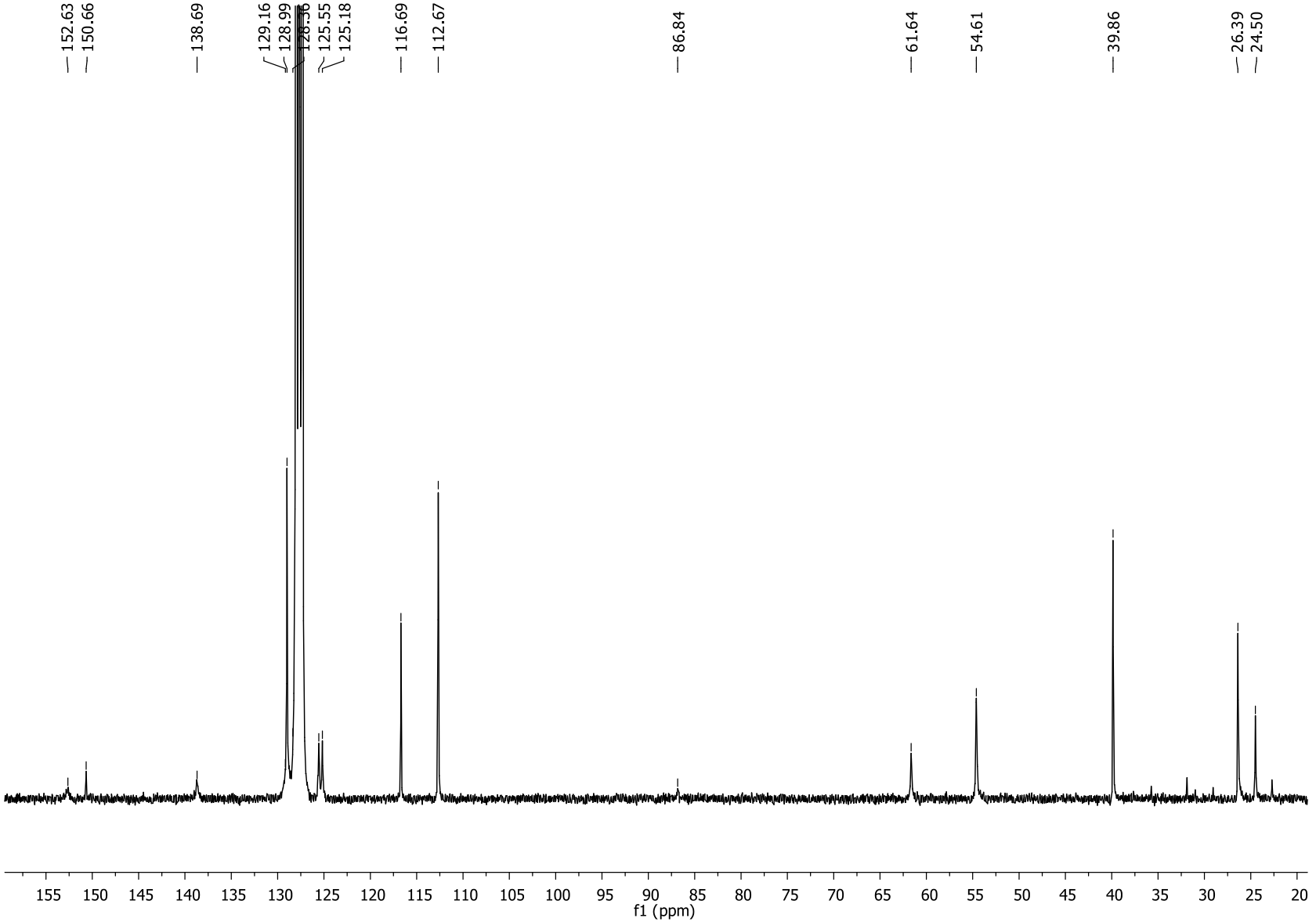


Figure S33. ^{13}C {^{1}H} NMR spectrum of **6** (75 MHz, C_6D_6, 293 K).

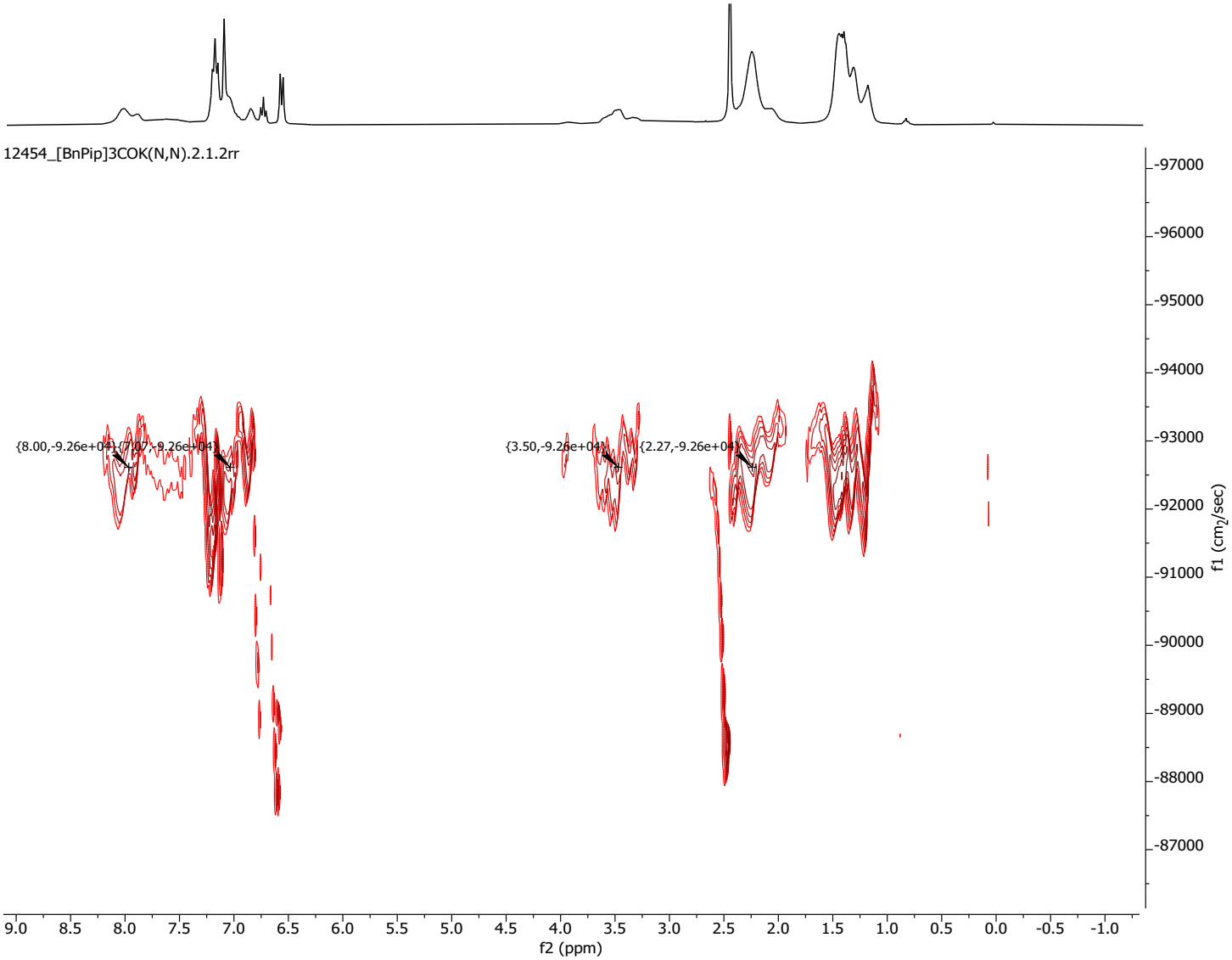


Figure S34. ^{1}H DOSY NMR spectrum of **6** (300 MHz, C_6D_6, 293 K).

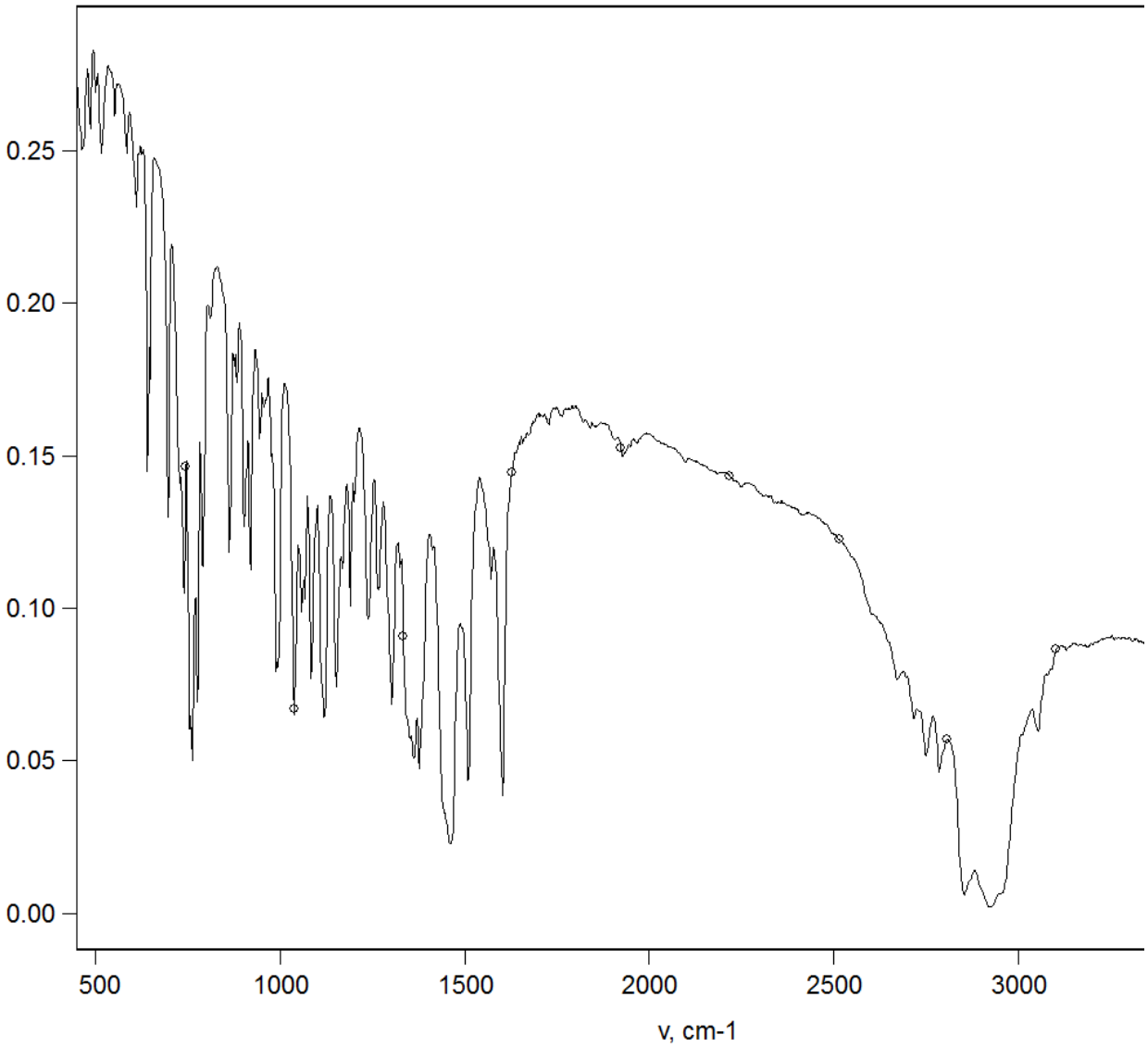


Figure S35. IR (KBr, Nujol) spectrum of complex **6**.

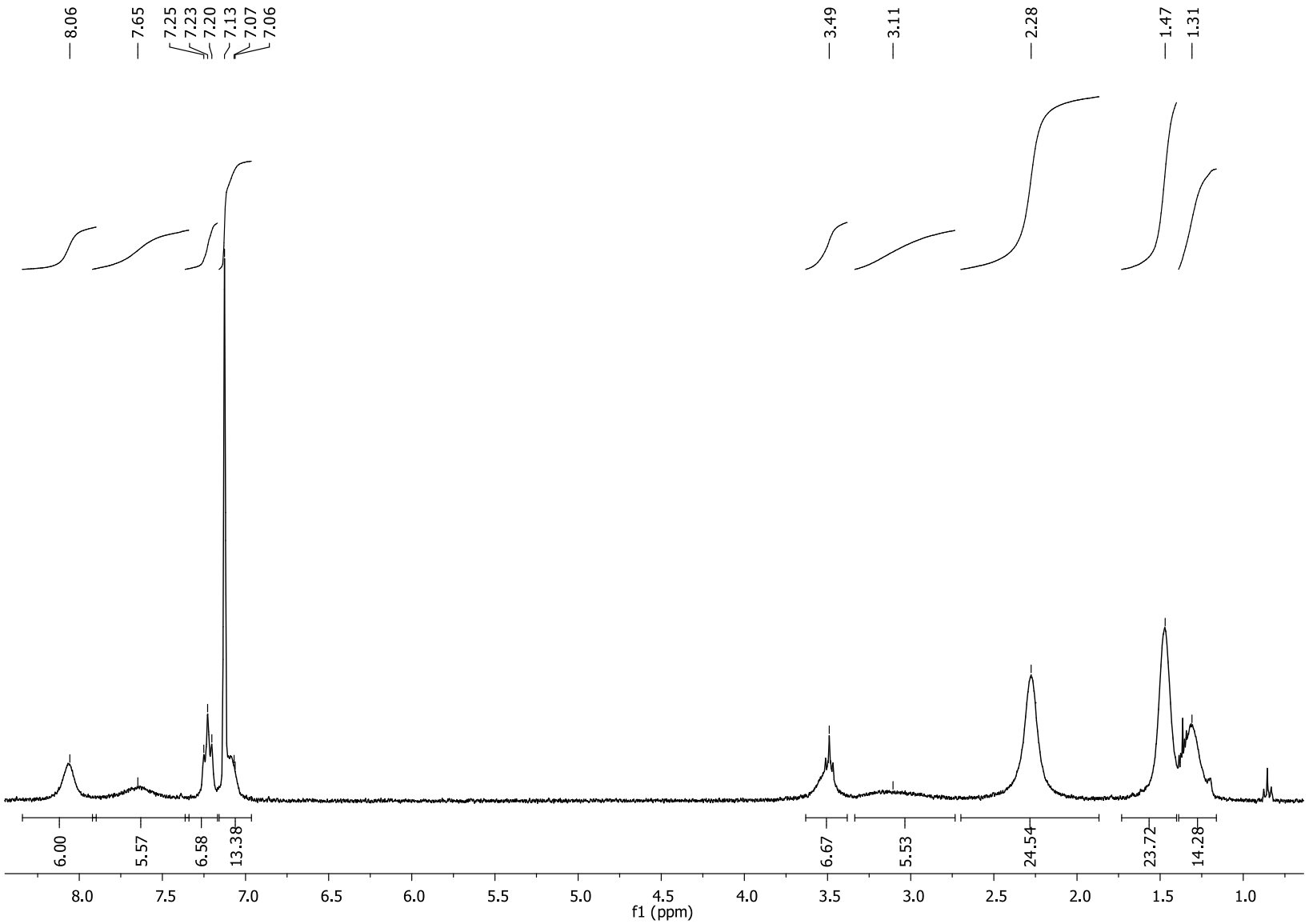


Figure S36. ^{1}H NMR spectrum of **7** (300 MHz, C_6D_6, 293 K).

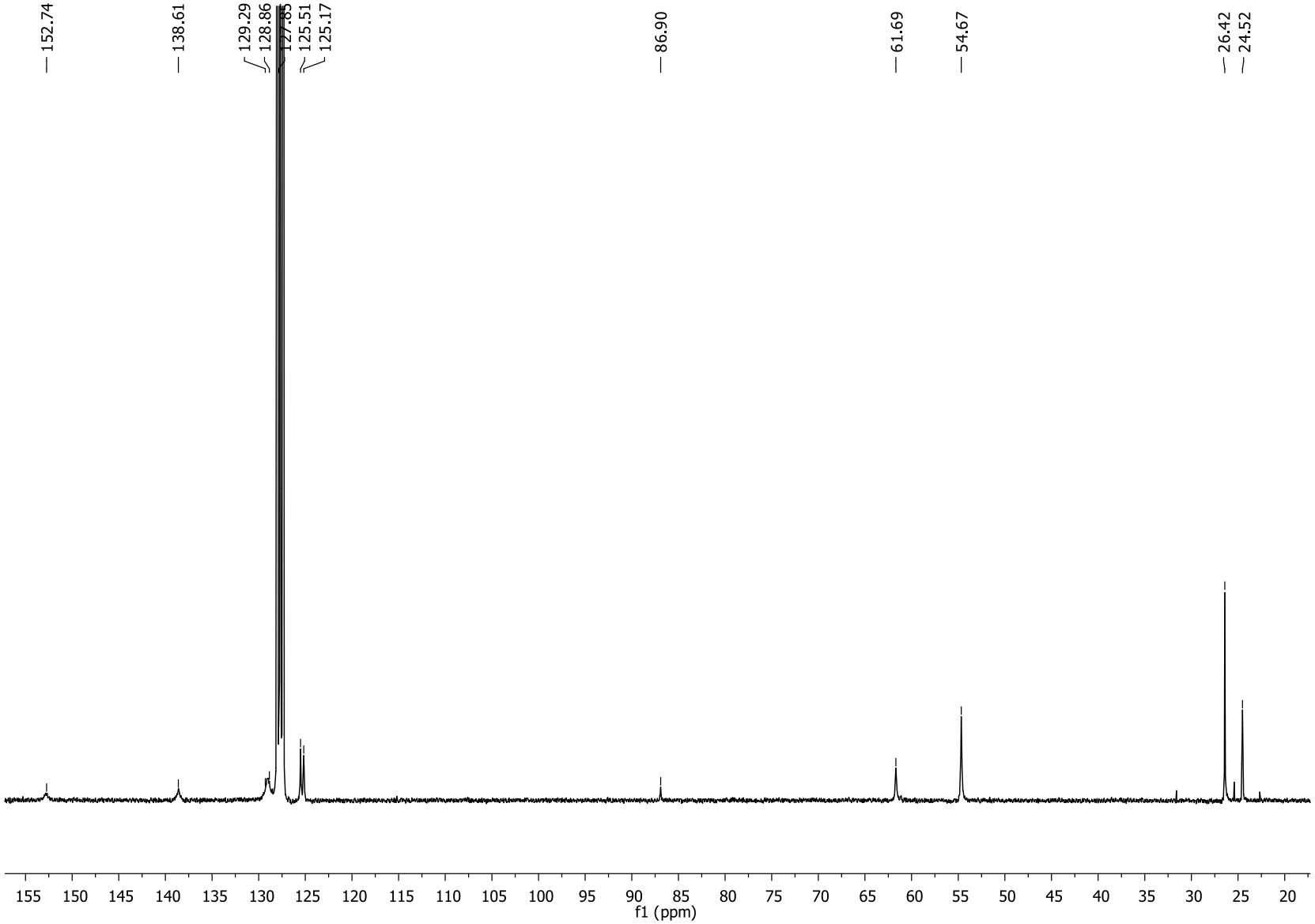


Figure S37. ^{13}C {^{1}H} NMR spectrum of **7** (75 MHz, C_6D_6, 293 K).

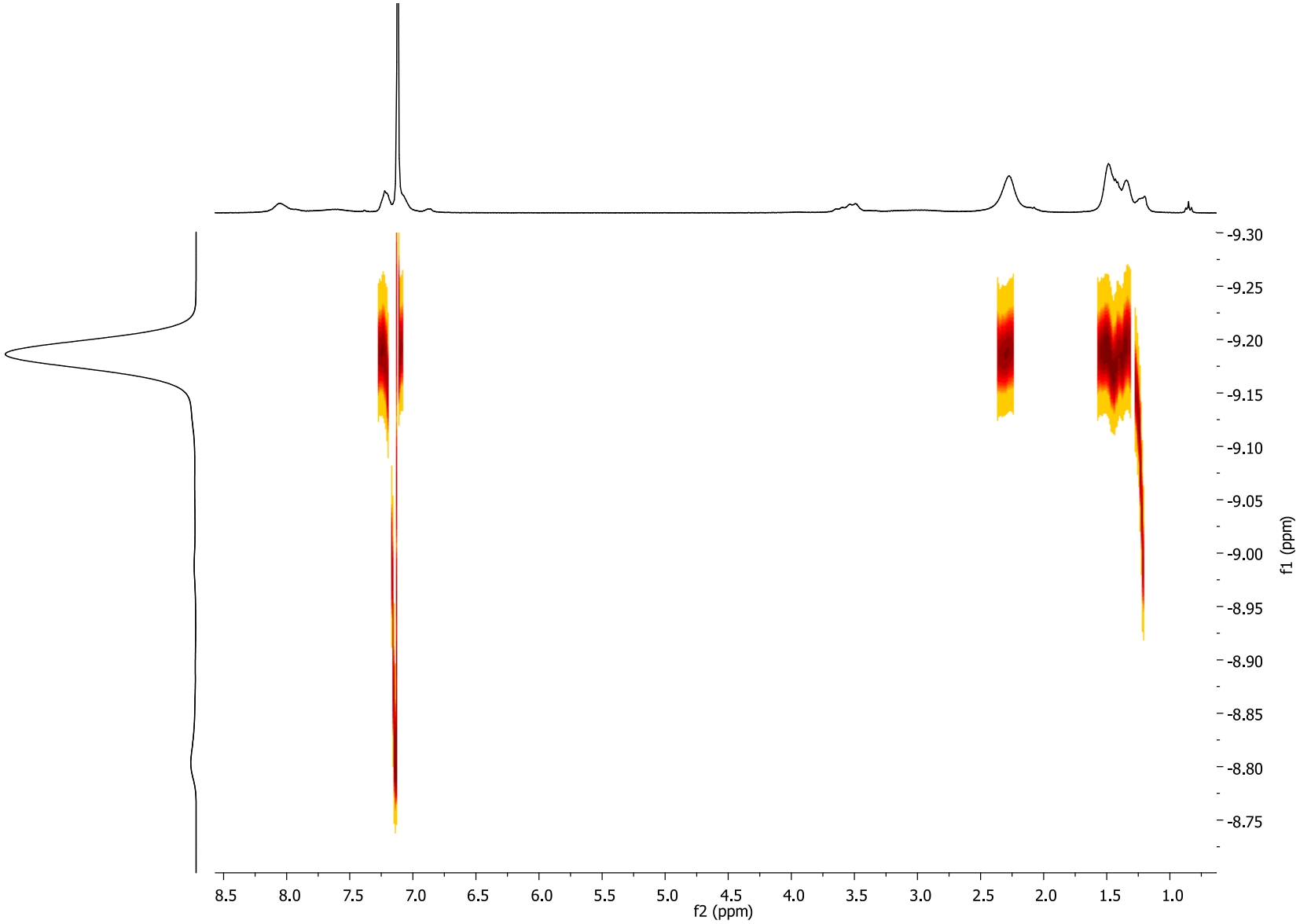


Figure S38. ^{1}H DOSY NMR spectrum of **7** (300 MHz, C_6D_6, 293 K).

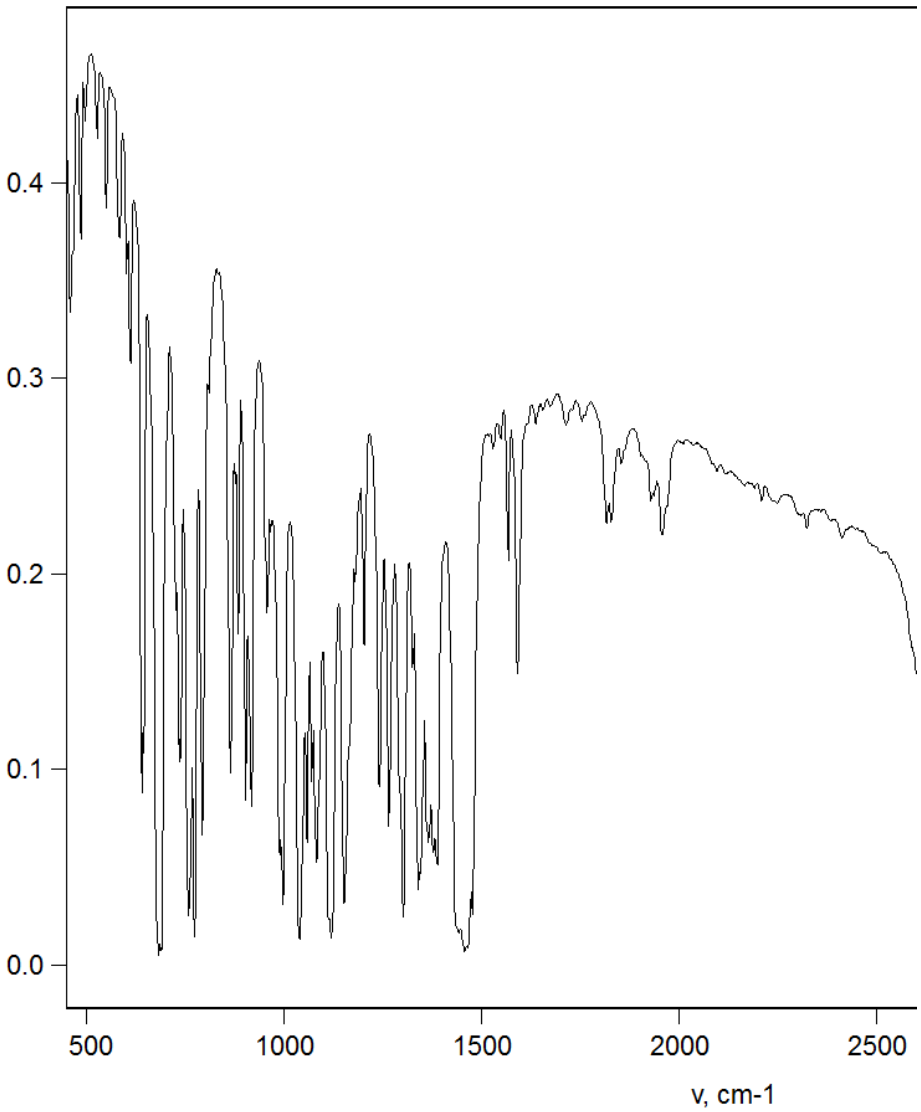


Figure S39. IR (KBr, Nujol) spectrum of complex **7**.

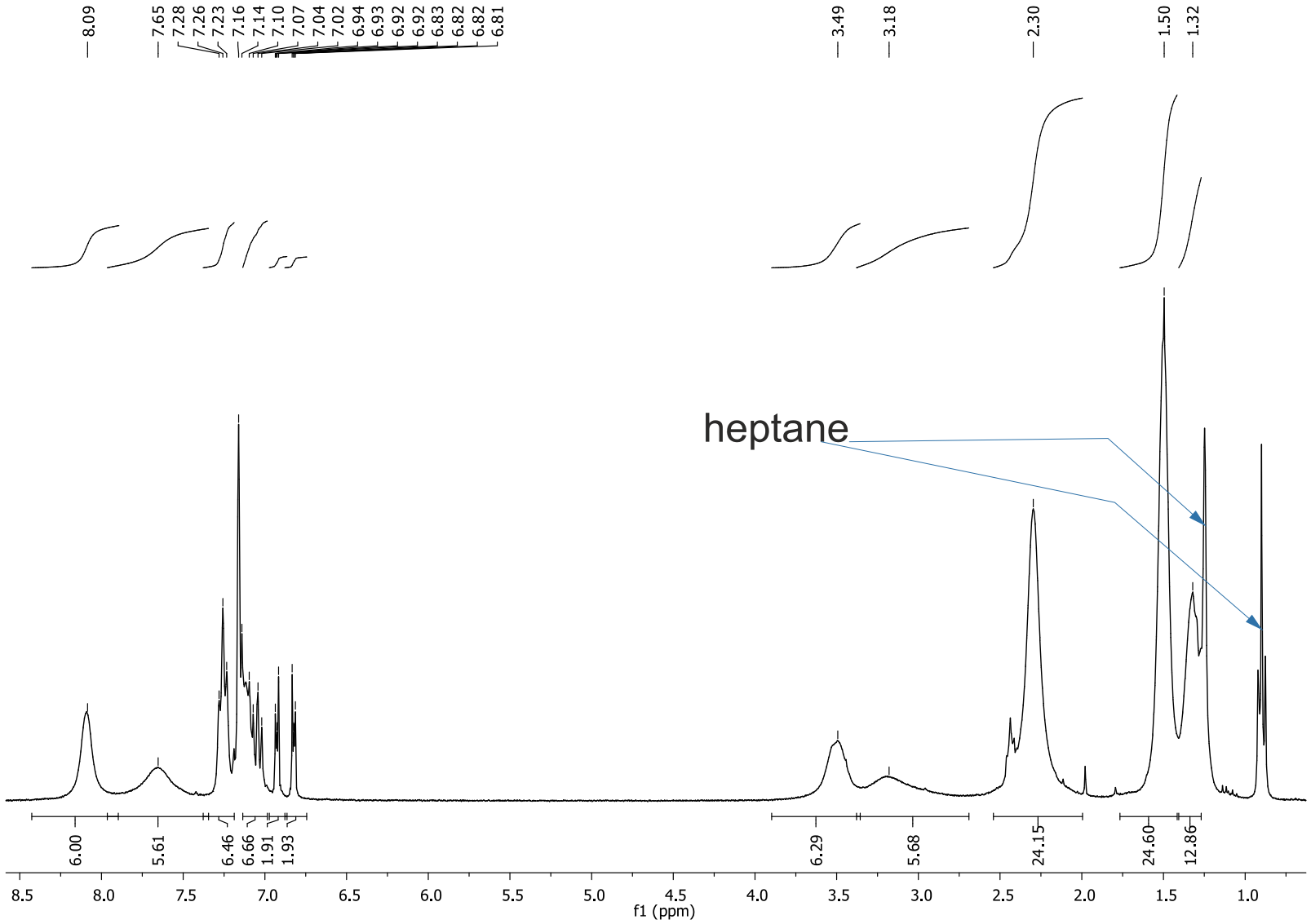


Figure S40. ^{1}H NMR spectrum of **8** (300 MHz, C_6D_6, 293 K).

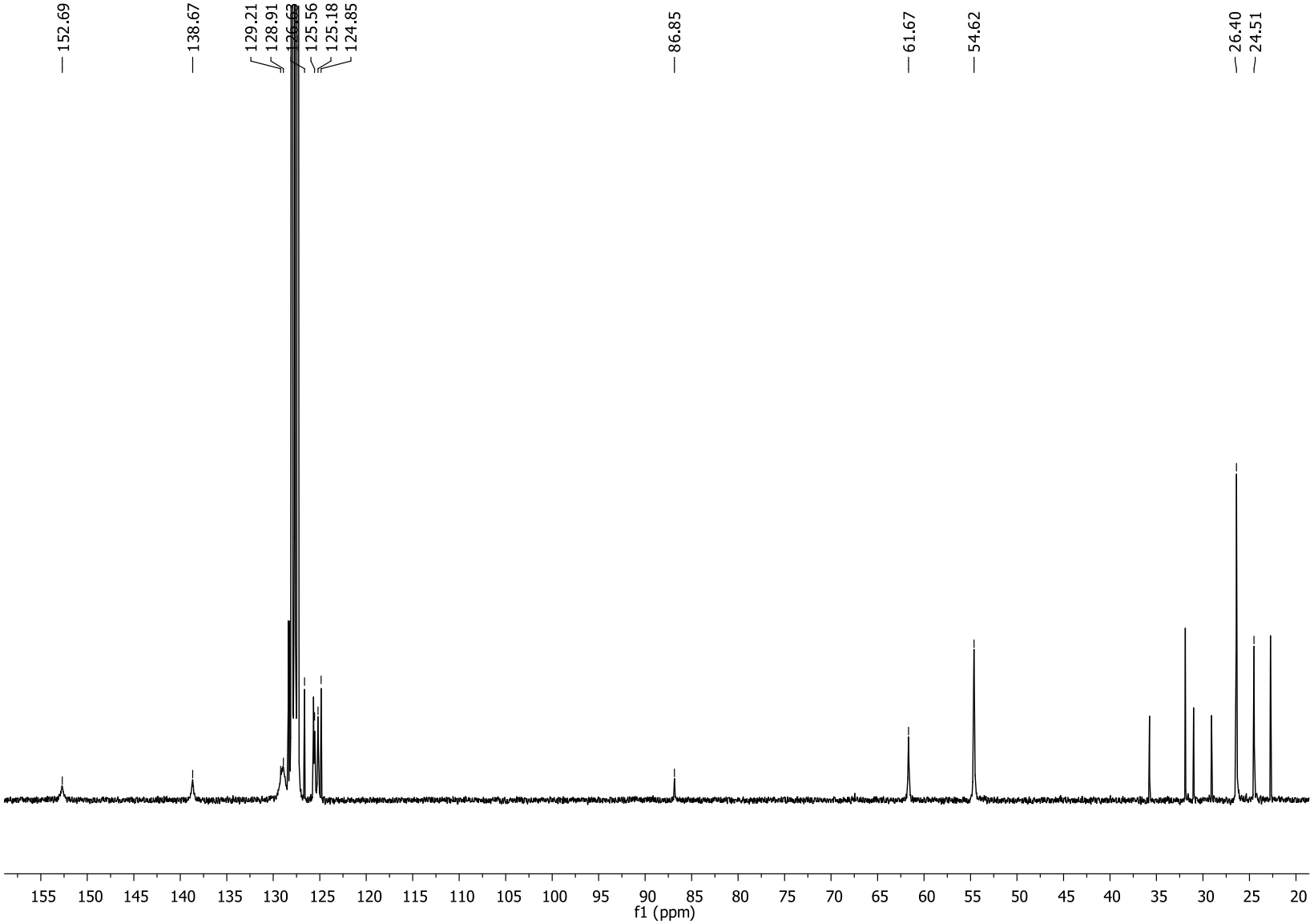


Figure S41. ^{13}C {^{1}H} NMR spectrum of **8** (75 MHz, C_6D_6, 293 K).

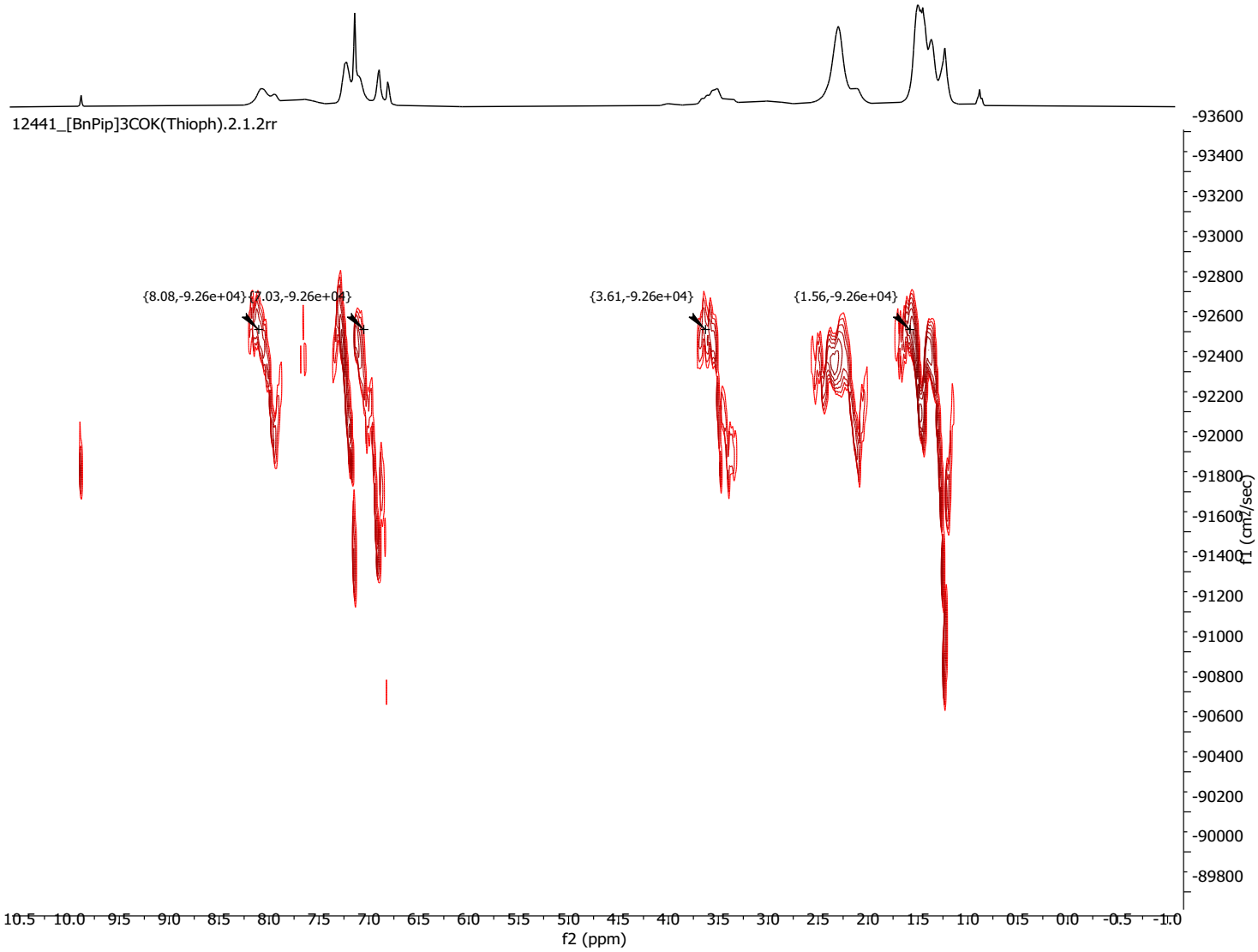


Figure S42. ^{1}H DOSY NMR spectrum of **8** (300 MHz, C_6D_6, 293 K).

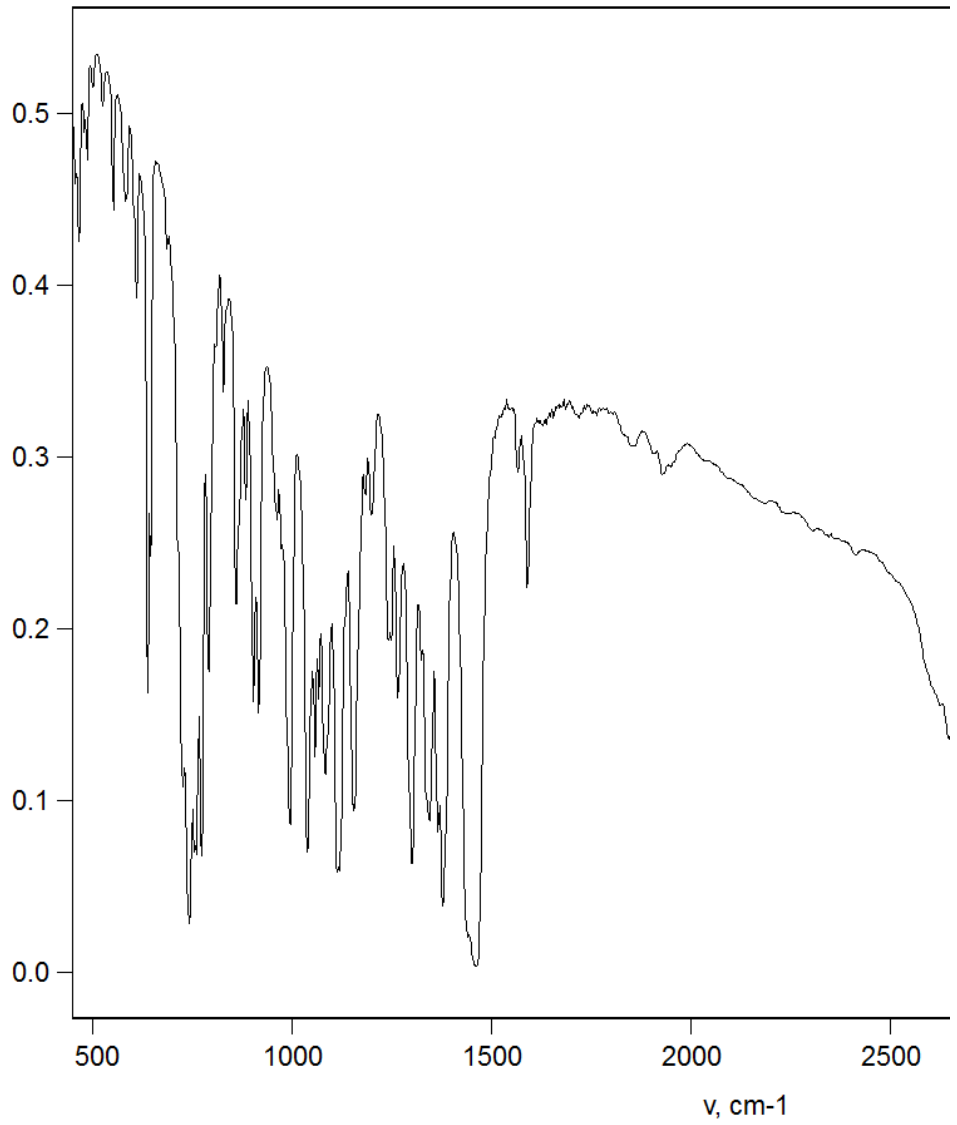


Figure S43. IR (KBr, Nujol) spectrum of complex **8**.

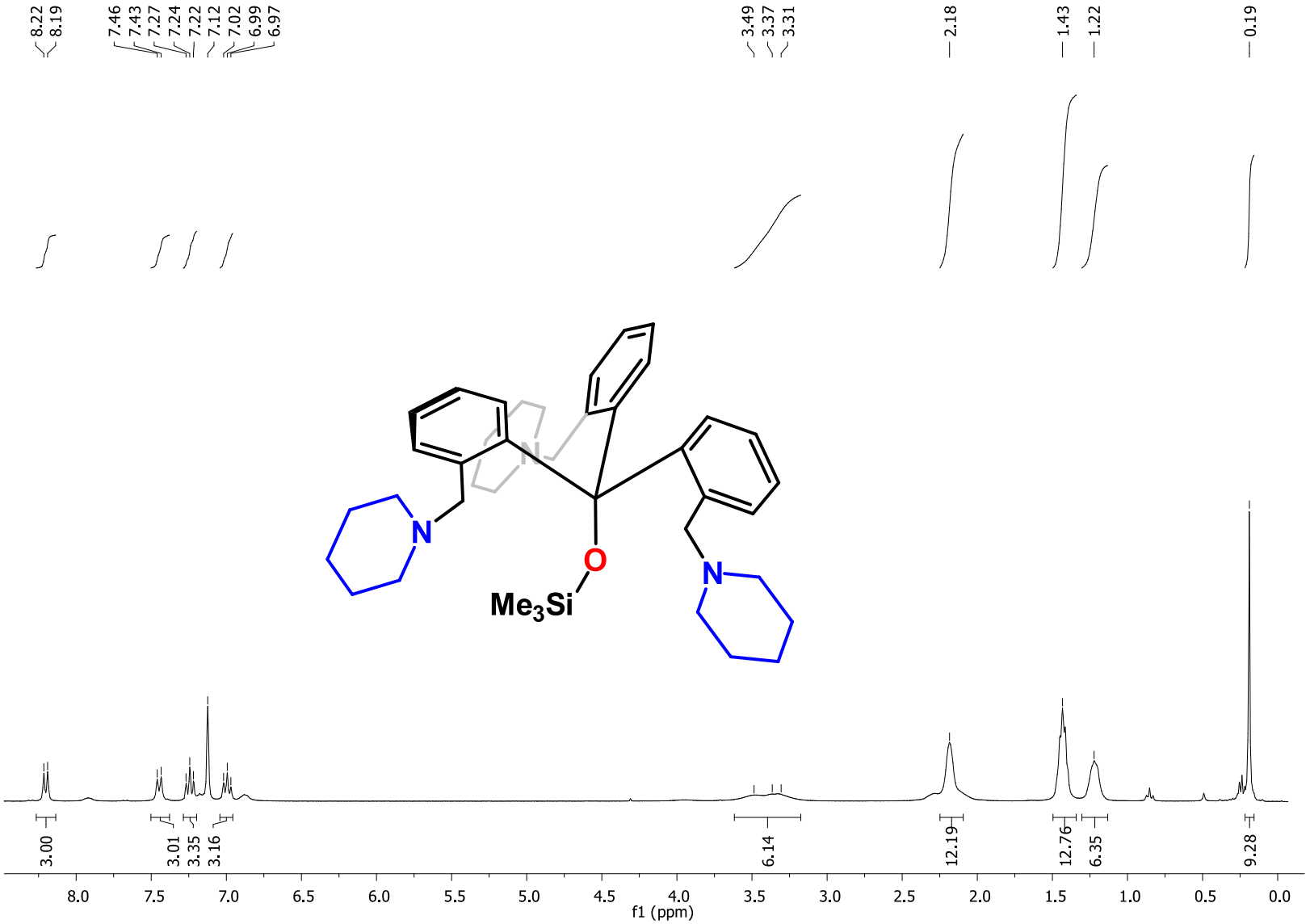


Figure S44. ^{1}H NMR spectrum of **[(C$_5$H$_{10}$N)CH$_2$C$_6$H$_4$-*o*]$_3$COSiMe$_3$** (300 MHz, C$_6$D$_6$, 293 K).

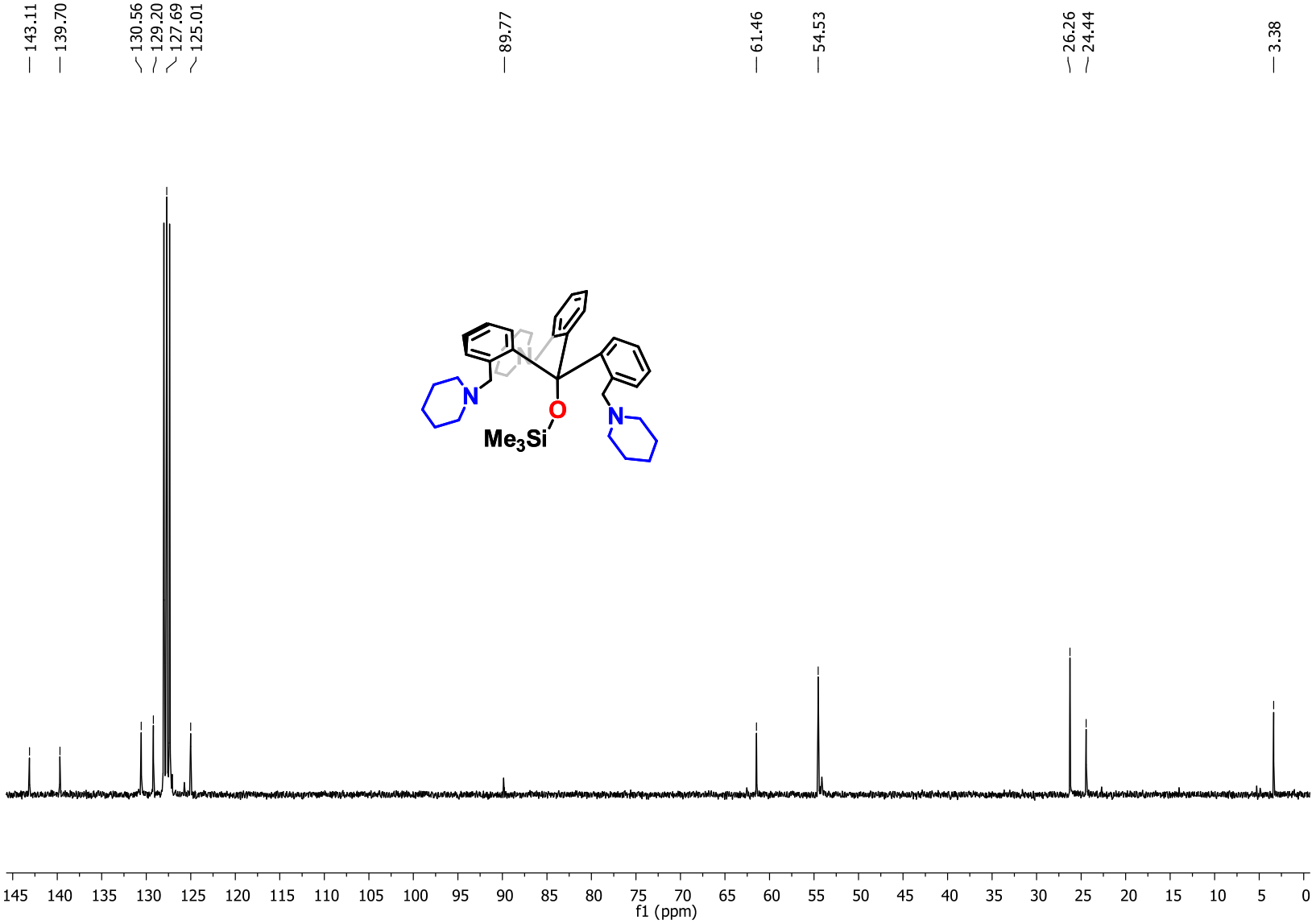


Figure S45. ^{13}C {^{1}H} NMR spectrum of **[($C_5H_{10}N$)$CH_2C_6H_4$-*o*]$_3$COSiMe_3** (75 MHz, C_6D_6, 293 K).

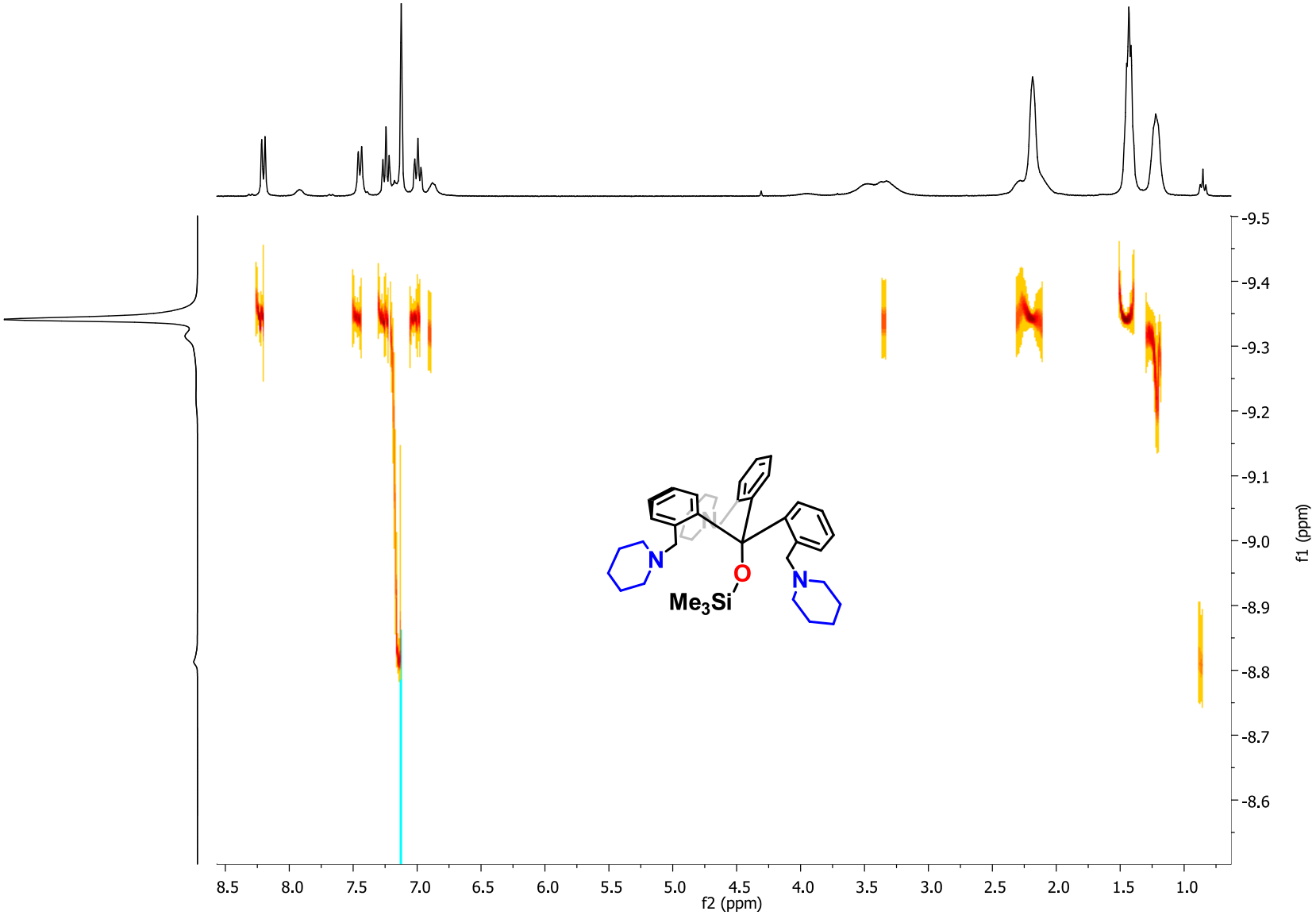


Figure S46. ^{1}H DOSY NMR spectrum of **[(C$_5$H$_{10}$N)CH$_2$C$_6$H$_4$-*o*]$_3$COSiMe$_3$** (300 MHz, C$_6$D$_6$, 293 K).

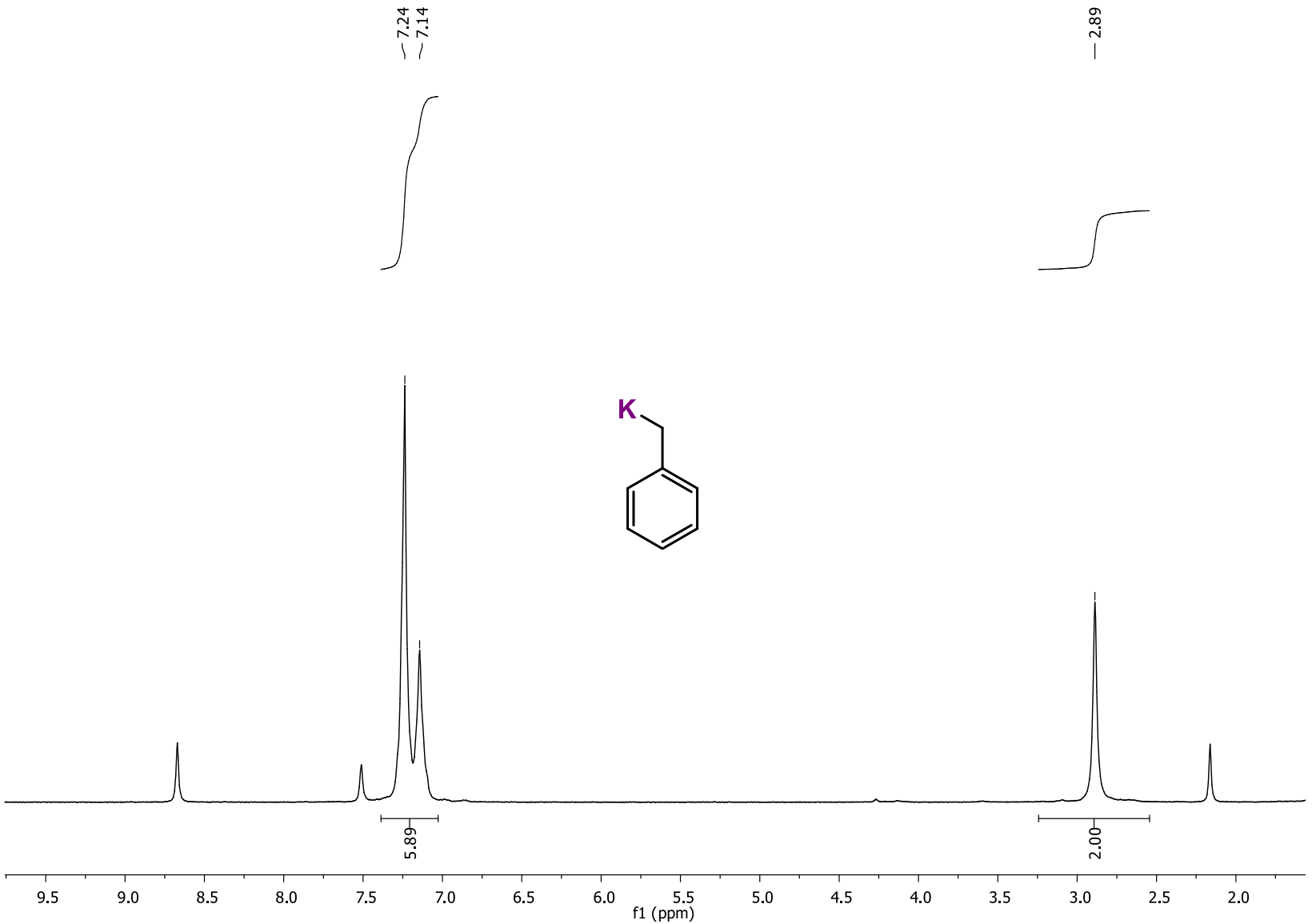


Figure S47. ^{1}H NMR spectrum of **BnK** (300 MHz, C_5D_5N, 298 K).

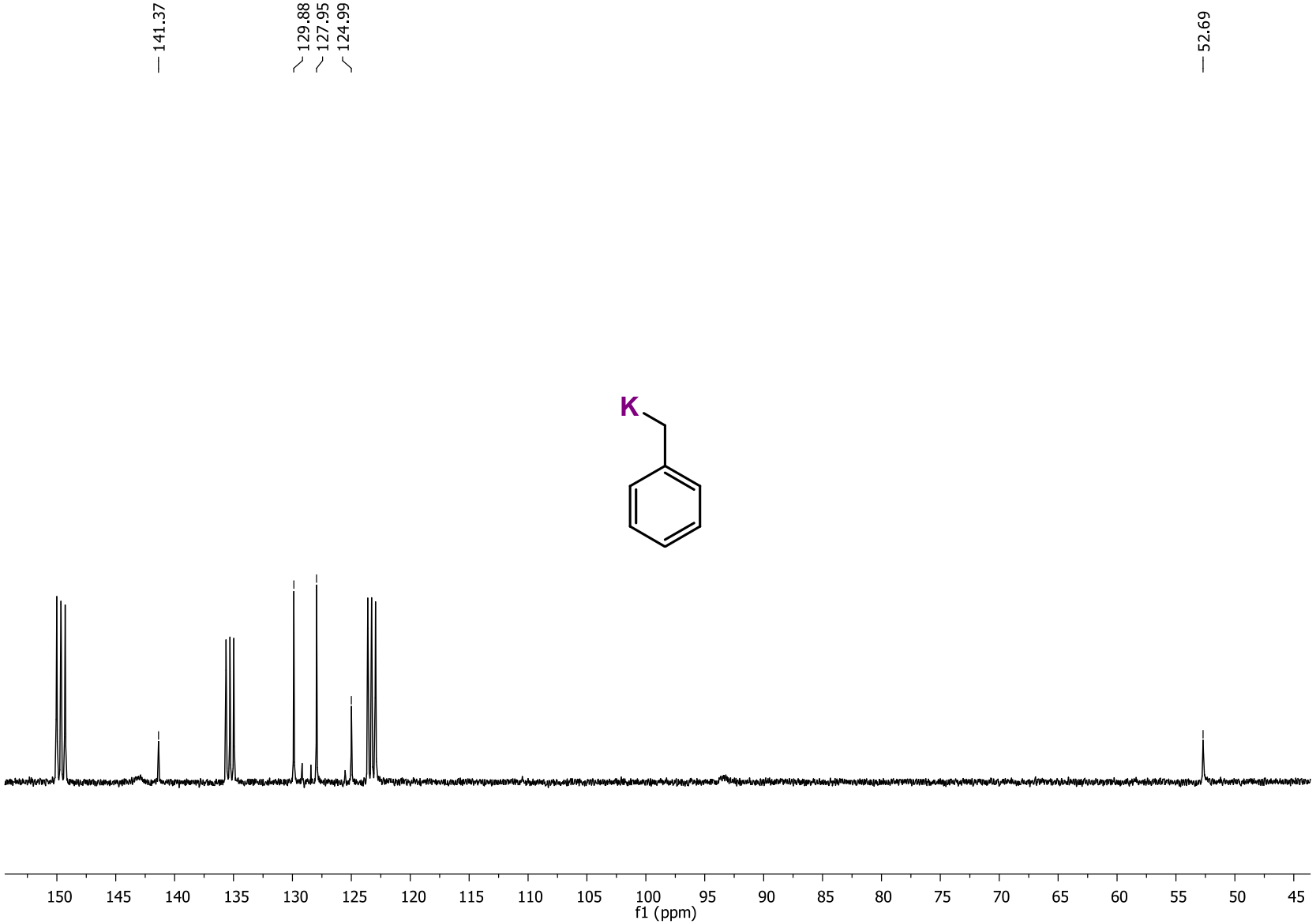


Figure S48. ^{13}C {^{1}H} NMR spectrum of **BnK** (75 MHz, C_5D_5N, 298 K).

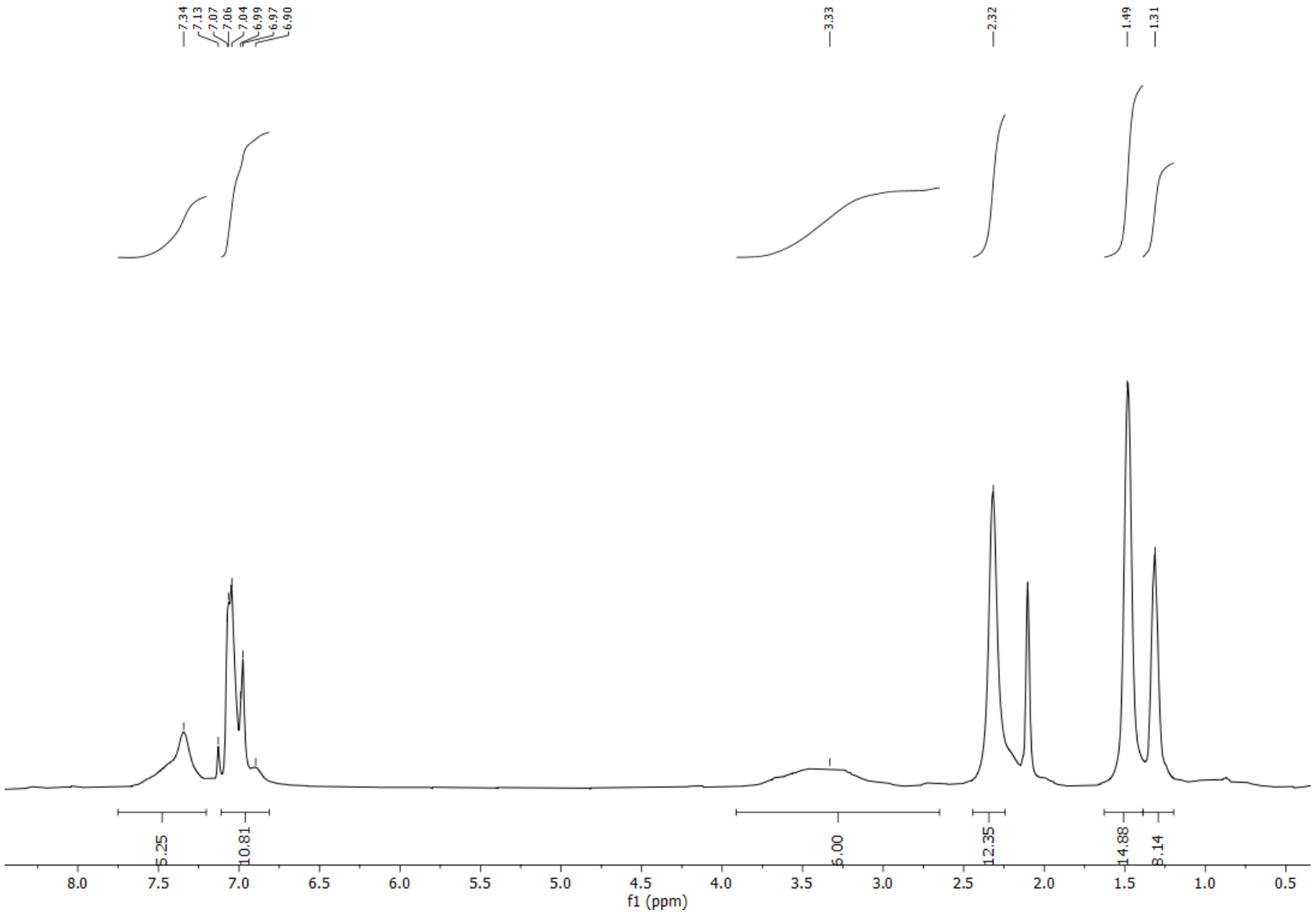


Figure S49. ^{1}H NMR spectrum of **9** (400 MHz, C_7D_8, 373 K).

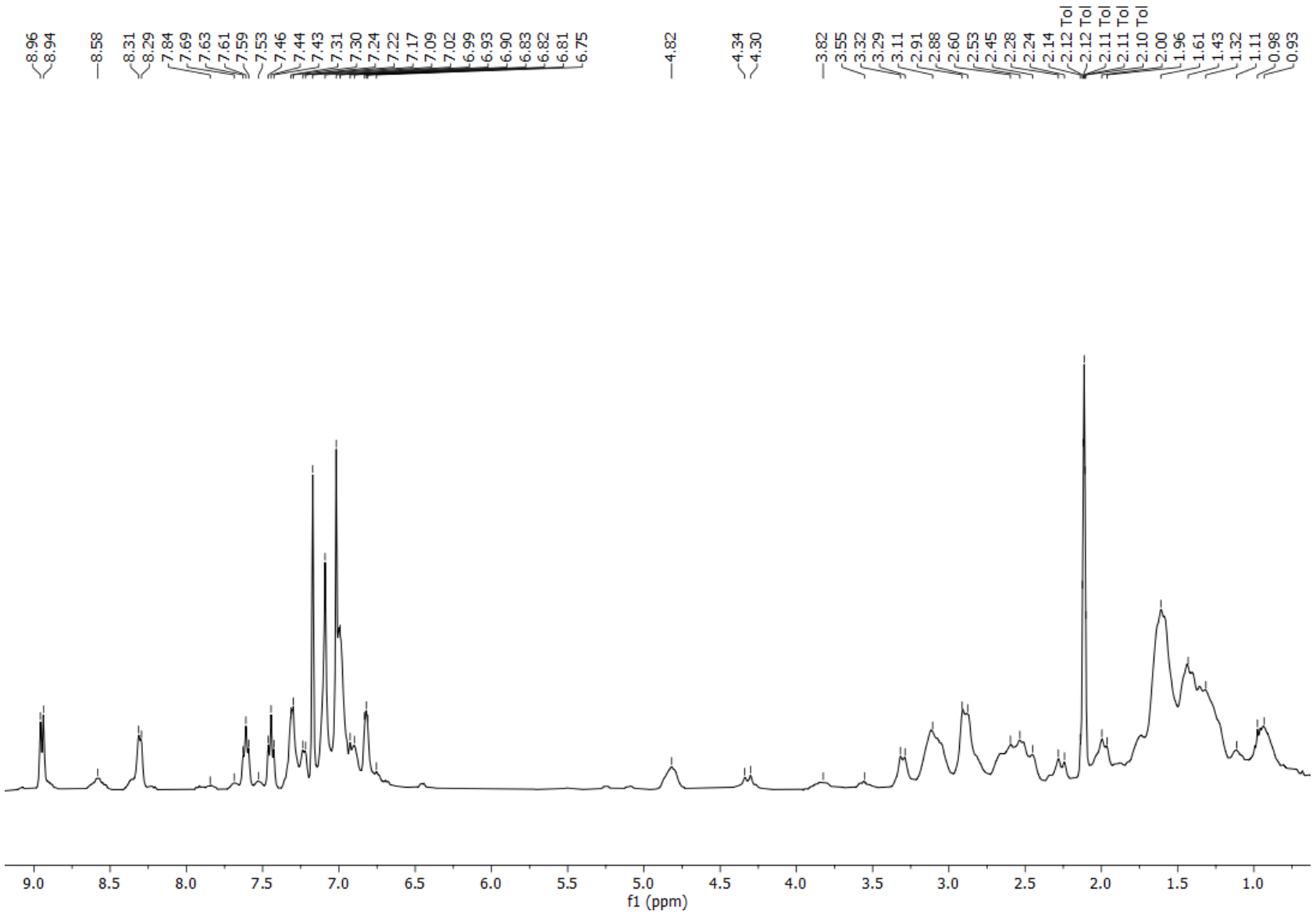


Figure S50. ^{1}H NMR spectrum of **9** (400 MHz, C_7D_8, 213 K).

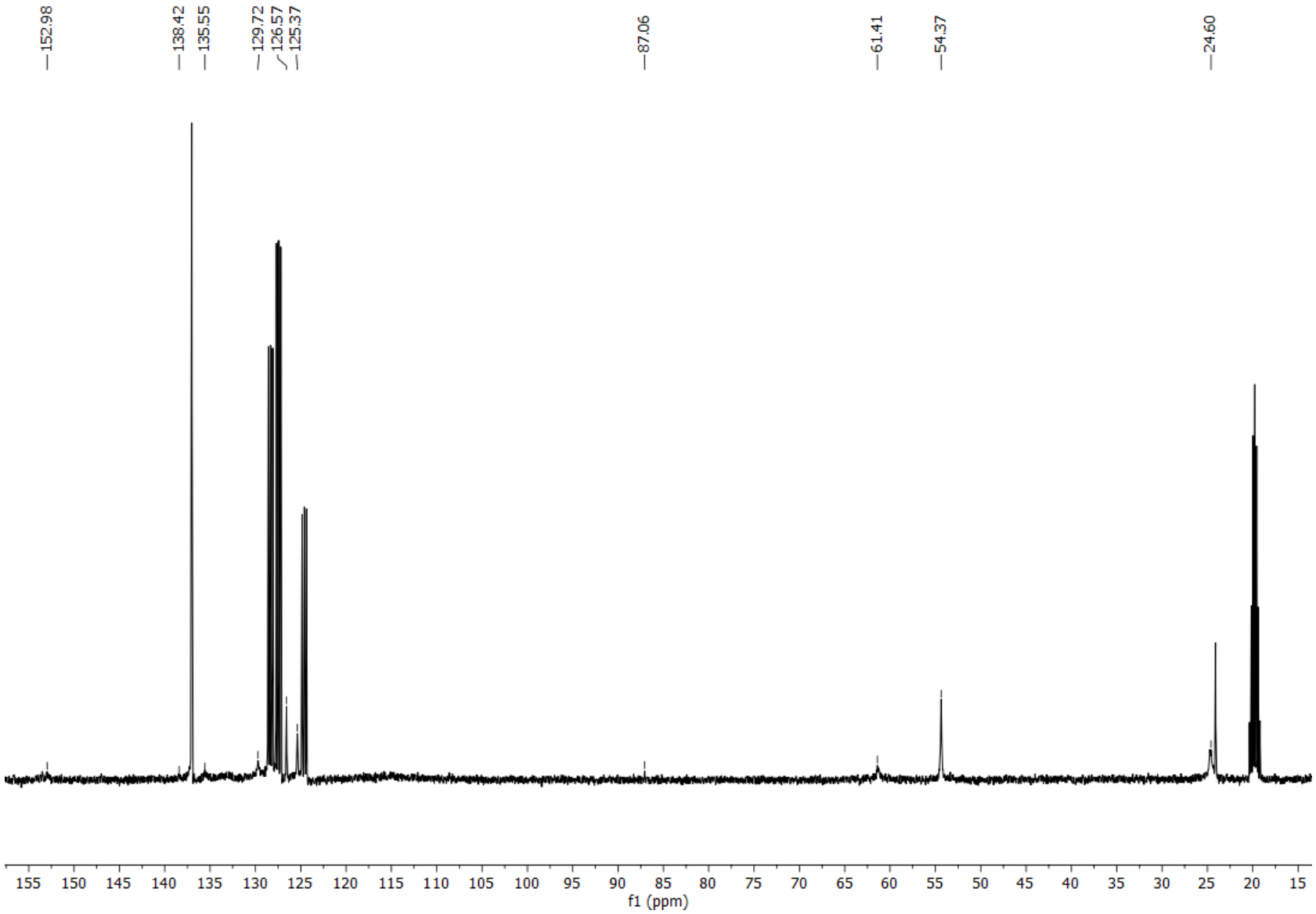


Figure S51. $^{13}C\ \{^{1}H\}$ NMR spectrum of **9** (100 MHz, C_7D_8, 373 K).

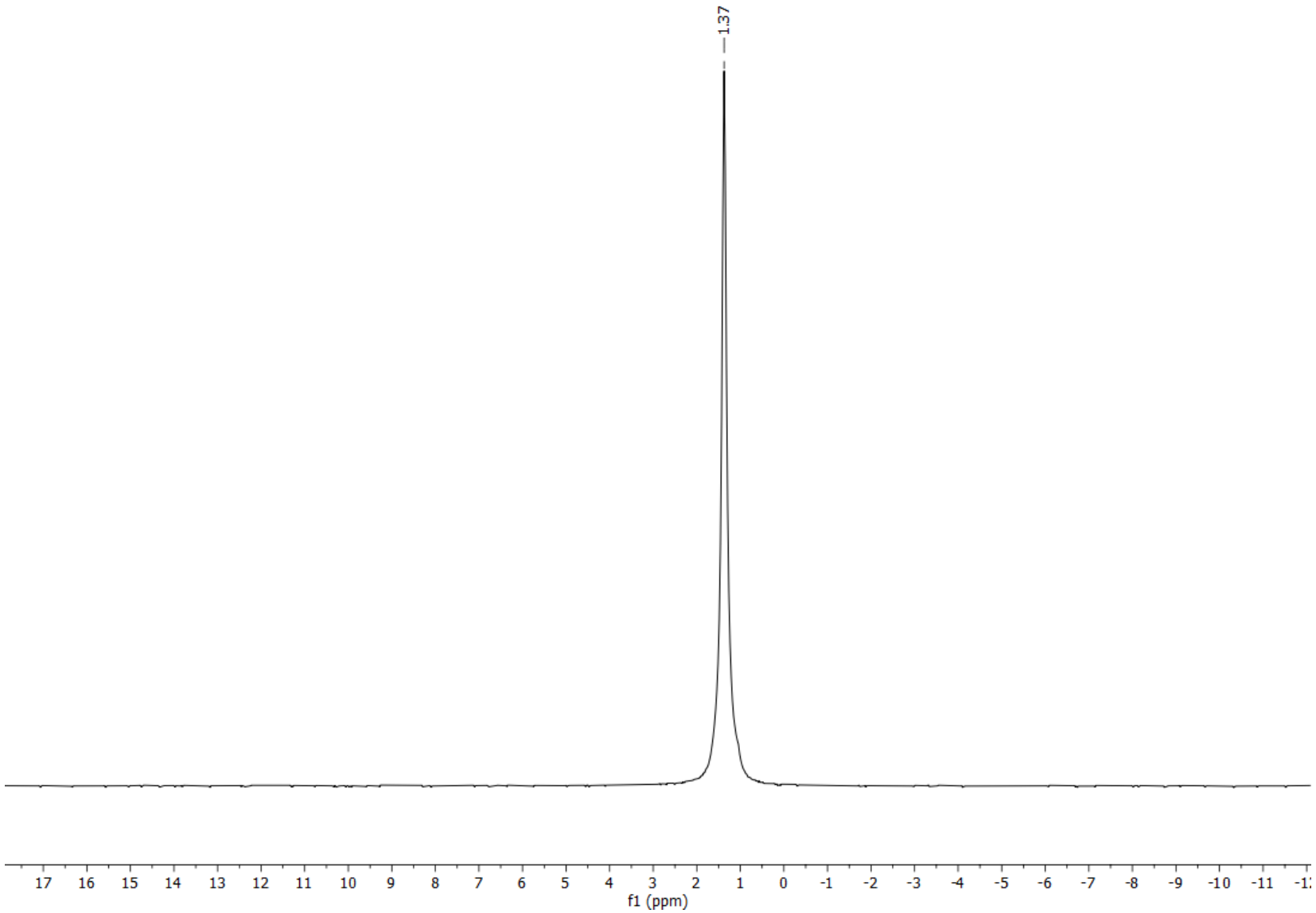


Figure S52. ^{7}Li NMR spectrum of **9** (155 MHz, C_7D_8, 293 K).

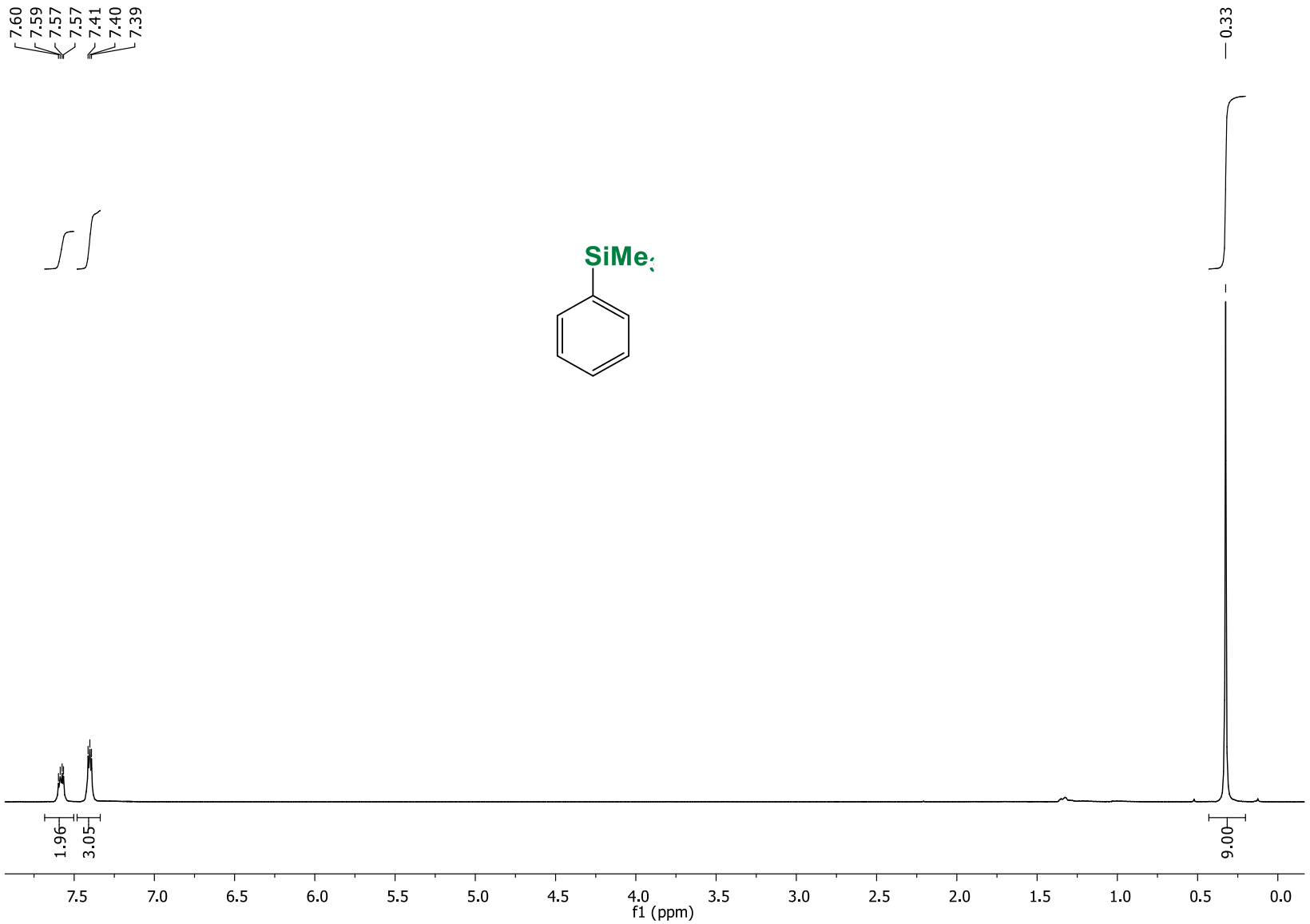


Figure S53. ^{1}H NMR spectrum of **$C_6H_5SiMe_3$** (300 MHz, $CDCl_3$, 298 K).

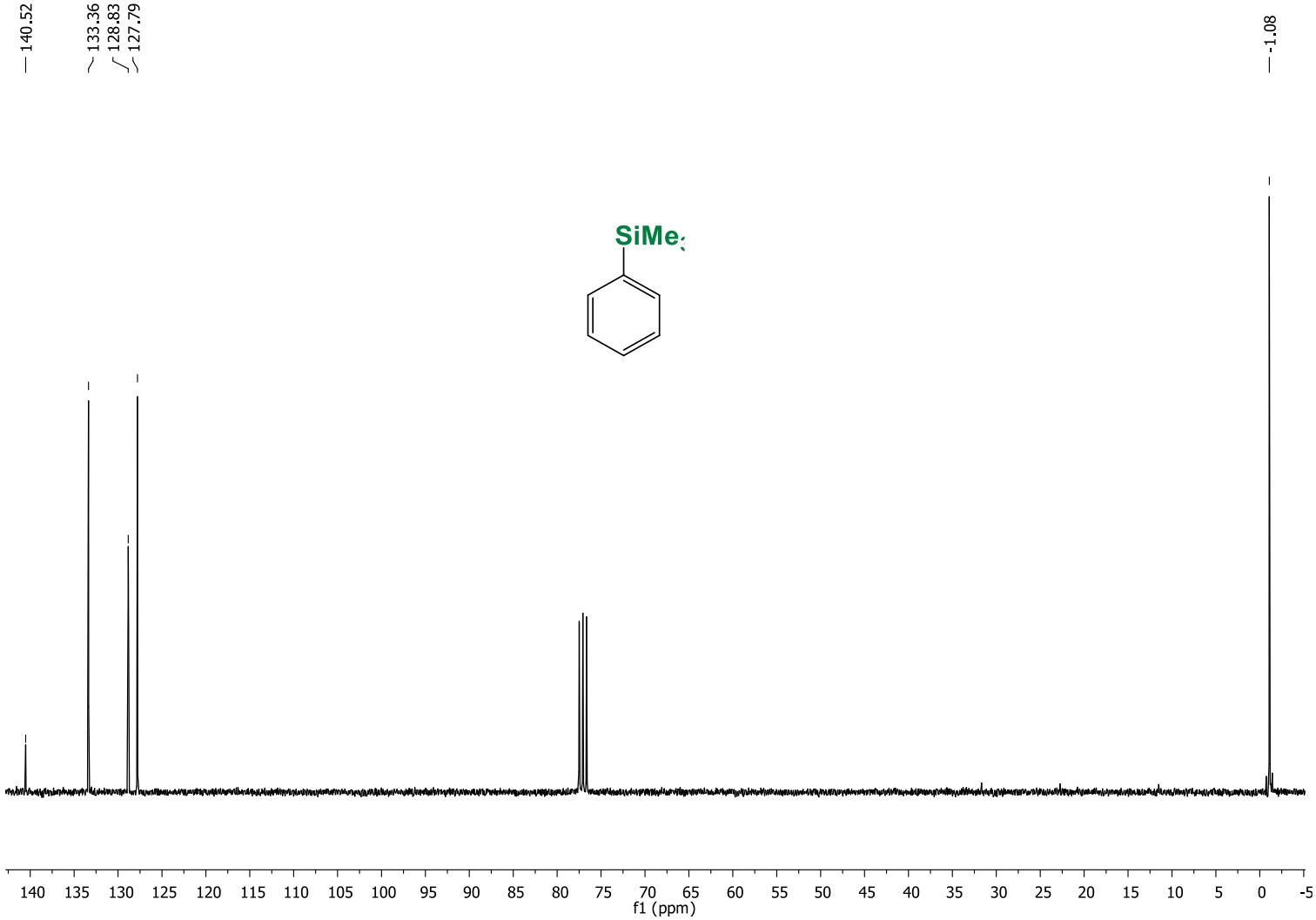


Figure S54. ^{13}C {^{1}H} NMR spectrum of **$C_6H_5SiMe_3$** (75 MHz, $CDCl_3$, 298 K).

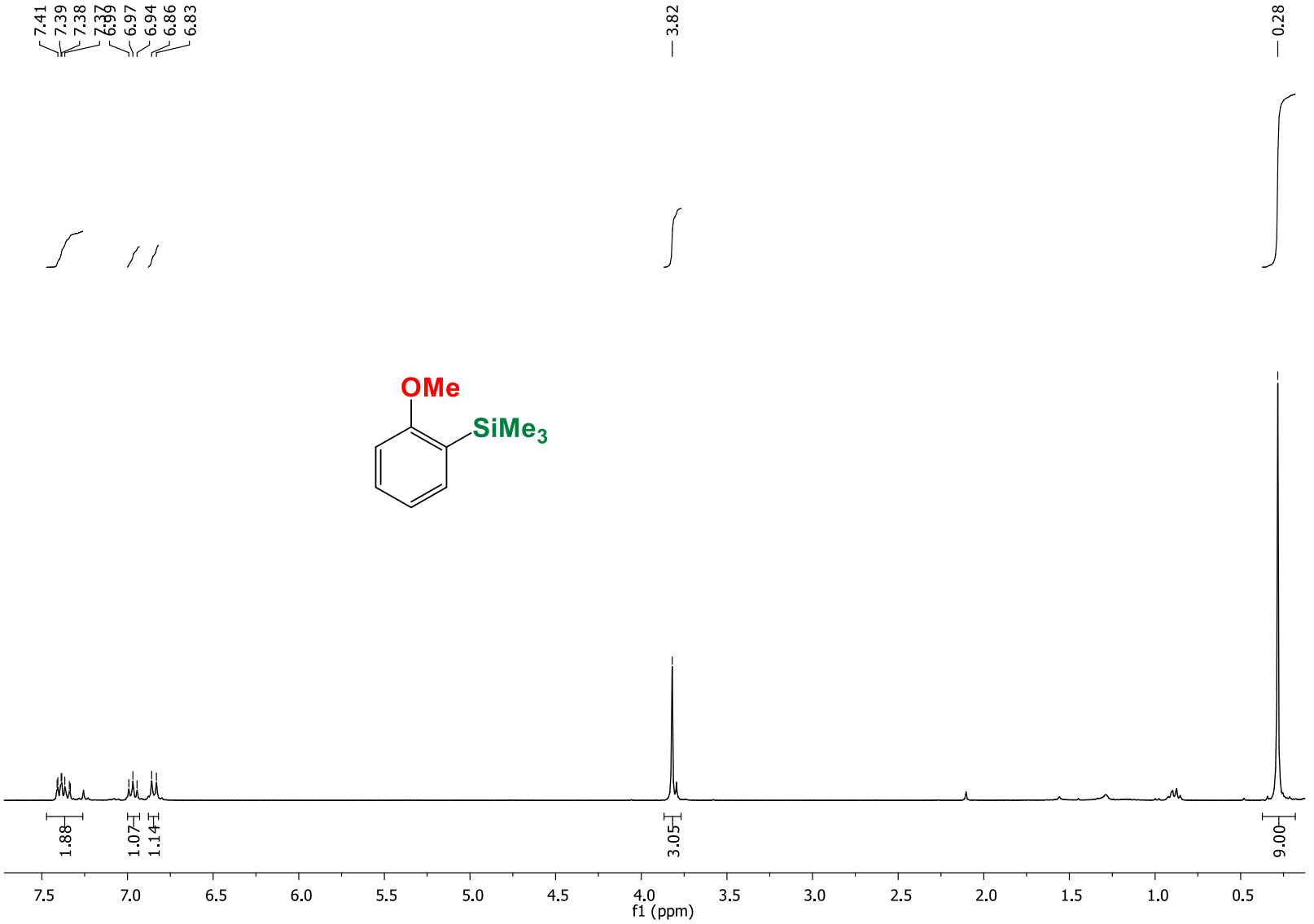


Figure S55. ^{1}H NMR spectrum of ***o*-MeOC$_6$H$_5$SiMe$_3$** (300 MHz, $CDCl_3$, 298 K).

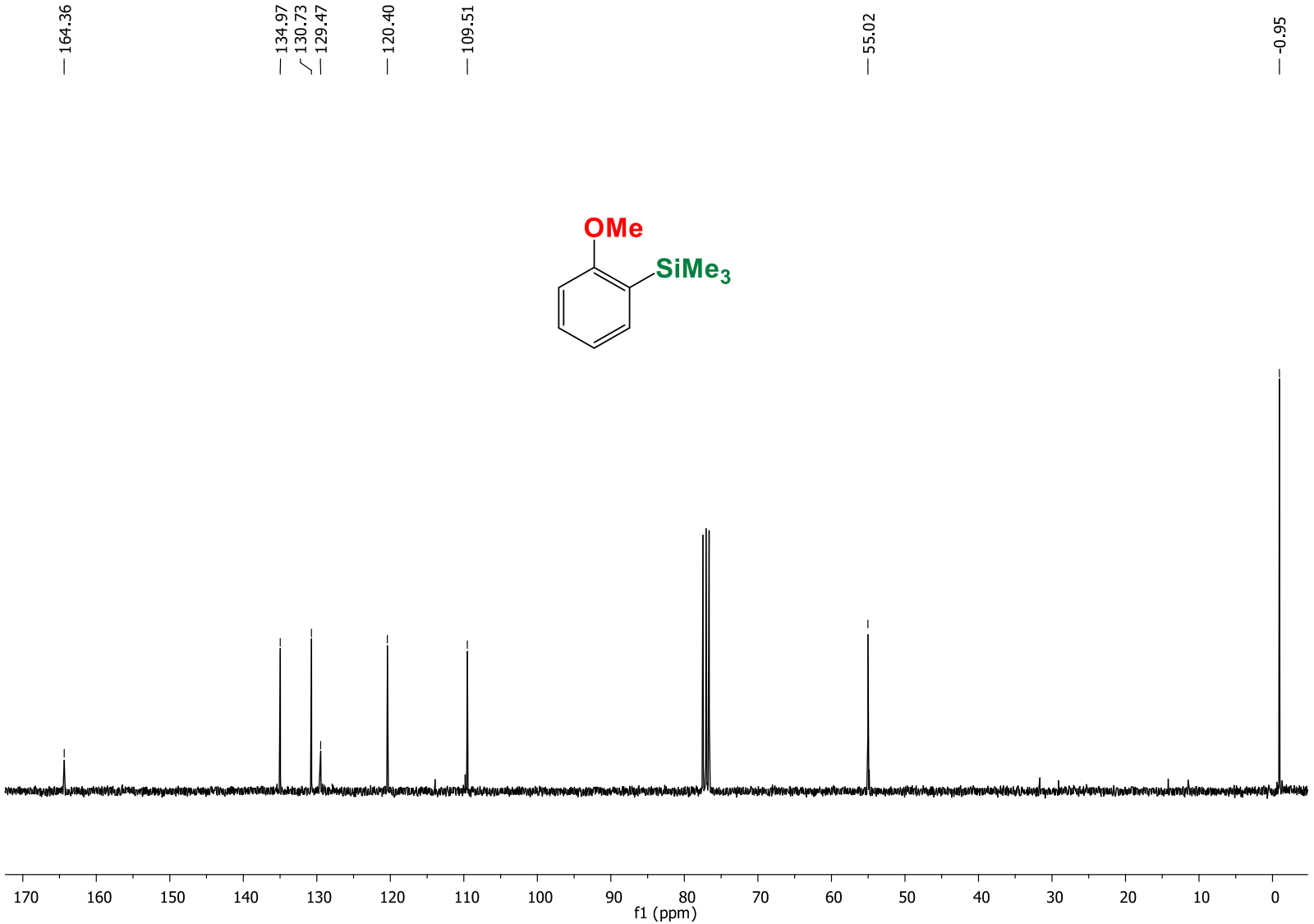


Figure S56. ^{13}C {^{1}H} NMR spectrum of ***o*-MeOC$_6$H$_5$SiMe$_3$** (75 MHz, $CDCl_3$, 298 K).