Supporting Information

for

Synthesis and Characterization of 1-Hydroxy-4,5-benzotropylium Derivatives

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I. Crystallographic Informations.

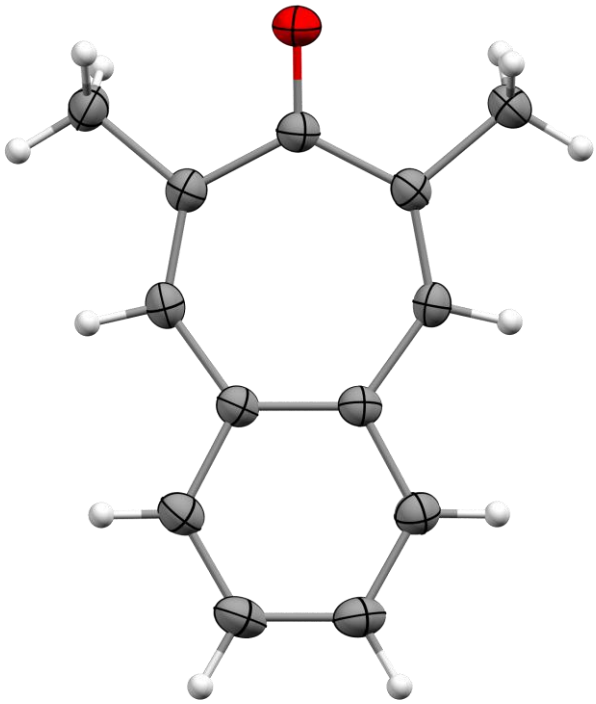


Figure S1. ORTEP drawing of **3b** with thermal ellipsoids set at the 50% probability level.[a]

[a]Crystal data for **3b**, orthorhombic, space group *P b c a* (no. 61), a = 13.2716(4) Å, b = 7.2879(2) Å, c =19.6548(7) Å, $\alpha = \beta = \gamma = 90$ °, V = 1901.05(11) Å^3, T = 123 K, Z = 8, $R1$ ($wR2$) = 0.0410 (0.1111) for 129 parameters and 1916 unique reflections. GOF = 1.073. CCDC 2047994.

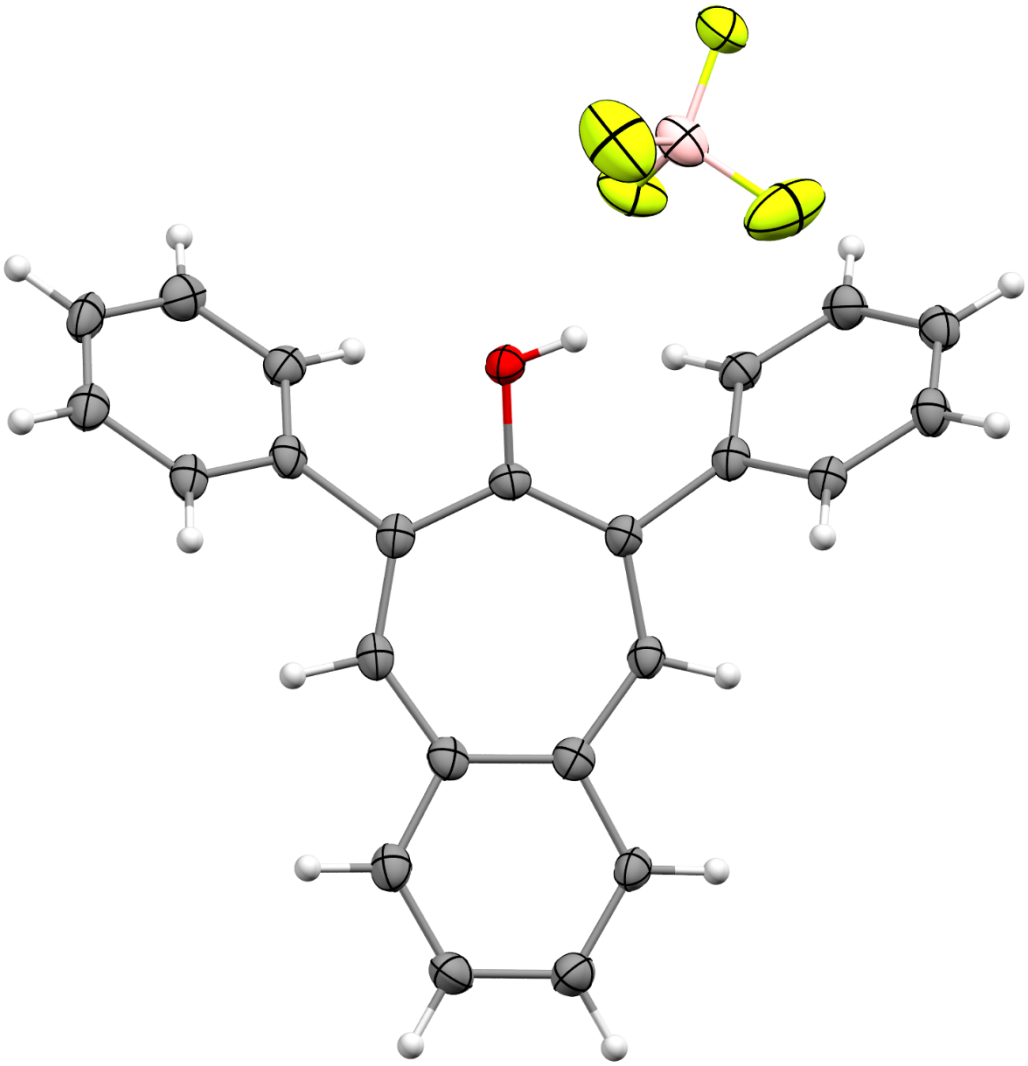


Figure S2. ORTEP drawing of **4a** with thermal ellipsoids set at the 30% probability level.[a]

[a]Crystal data for **4a**, orthorhombic, space group $P\,n\,a\,2_1$ (no. 33), a = 20.3702(7) Å, b = 7.5418(2) Å, c = 27.0101(9) Å, $\alpha = \beta = \gamma = 90$ °, V = 4149.5(2) Å^3, T = 123 K, Z = 4, $R1$ ($wR2$) = 0.0860 (0.2176) for 591 parameters and 7169 unique reflections. GOF = 1.039. CCDC 2047995.

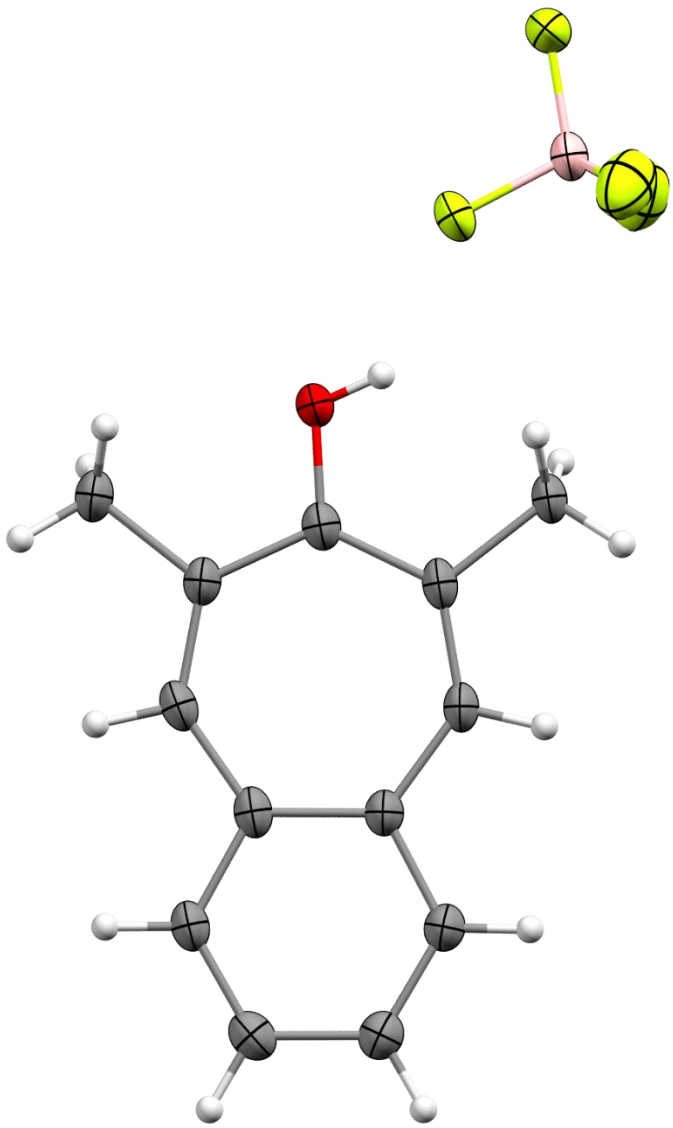


Figure S3. ORTEP drawing of **4b** with thermal ellipsoids set at the 50% probability level.[a]

[a]Crystal data for **4b**, orthorhombic, space group $P\,m\,n\,2_1$ (no. 31), a = 6.6500(3) Å, b = 8.6055(3) Å, c = 10.4614(4) Å, $\alpha = \beta = \gamma = 90$ °, V = 598.67(4) Å^3, T = 123 K, Z = 4, $R1$ ($wR2$) = 0.0408 (0.1086) for 115 parameters and 1022 unique reflections. GOF = 1.053. CCDC 2047997.

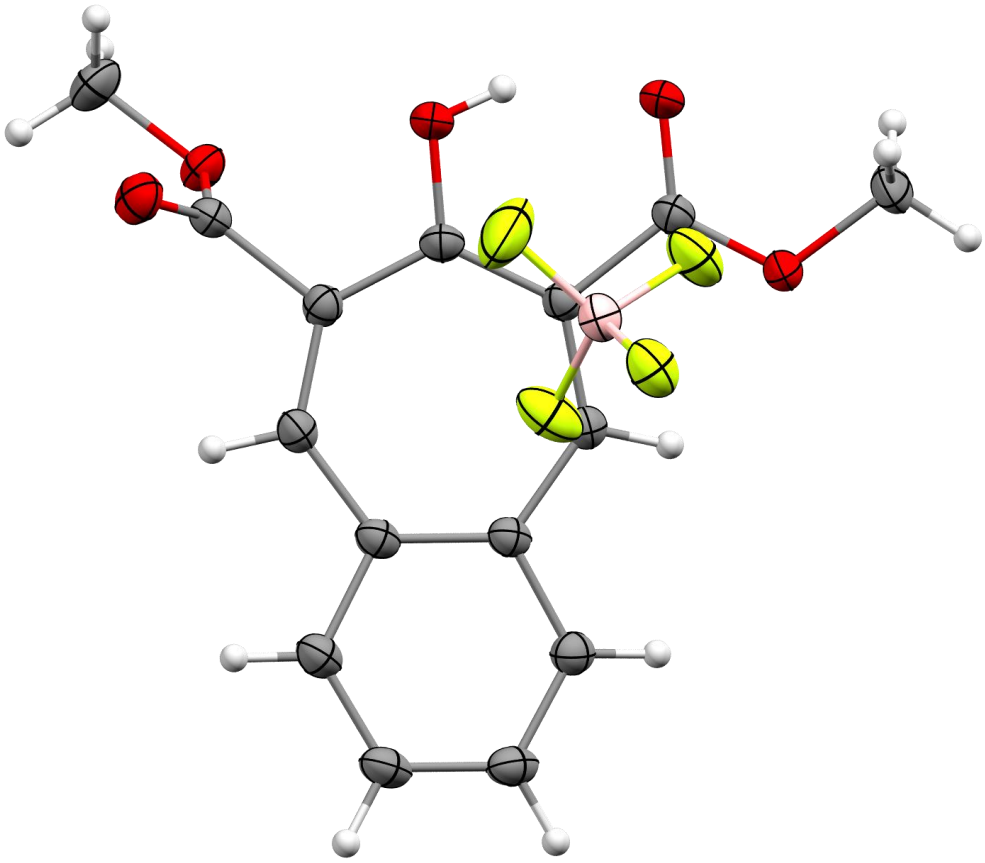


Figure S4. ORTEP drawing of **4c** with thermal ellipsoids set at the 50% probability level.[a]

[a]Crystal data for **4c**, monoclinic, space group $P\,2_1/c$ (no. 14), a = 8.3646(2) Å, b = 14.4140(3) Å, c = 12.6829(3) Å, α = 90 °, β = 91.602(2) °, γ = 90 °, V = 1528.55(6) Å^3, T = 123 K, Z = 4, $R1$ ($wR2$) = 0.0385 (0.1019) for 229 parameters and 3151 unique reflections. GOF = 1.074. CCDC 2047998.

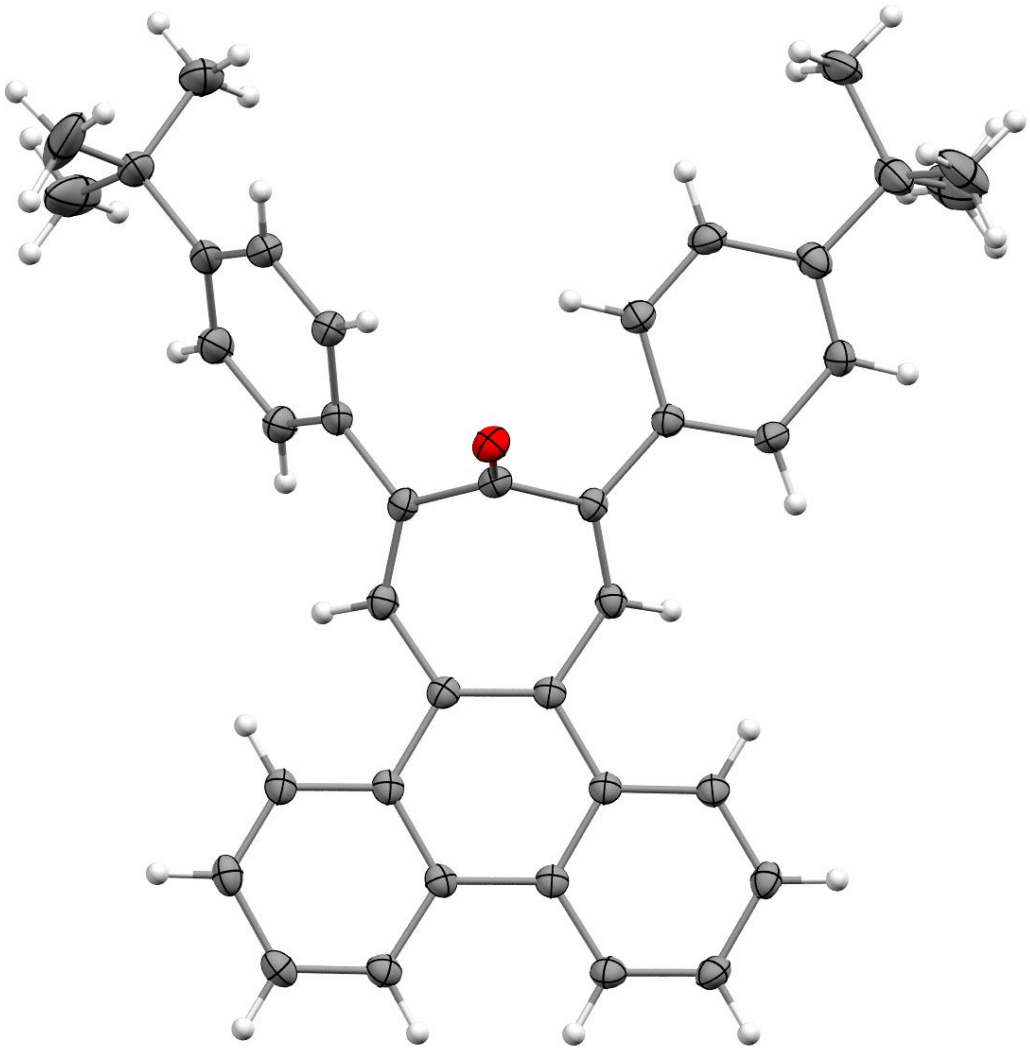


Figure S5. ORTEP drawing of **3i** with thermal ellipsoids set at the 50% probability level.[a]

[a]Crystal data for **3i**, orthorhombic, space group *P b c a* (no. 61), a = 11.6373(3) Å, b = 12.2407(3) Å, c = 41.5758(9) Å, $\alpha = \beta = \gamma = 90$ °, V = 5922.4(2) Å^3, T = 123 K, Z = 8, $R1$ ($wR2$) = 0.0636 (0.1763) for 434 parameters and 5337 unique reflections. GOF = 1.032. CCDC 2100026.

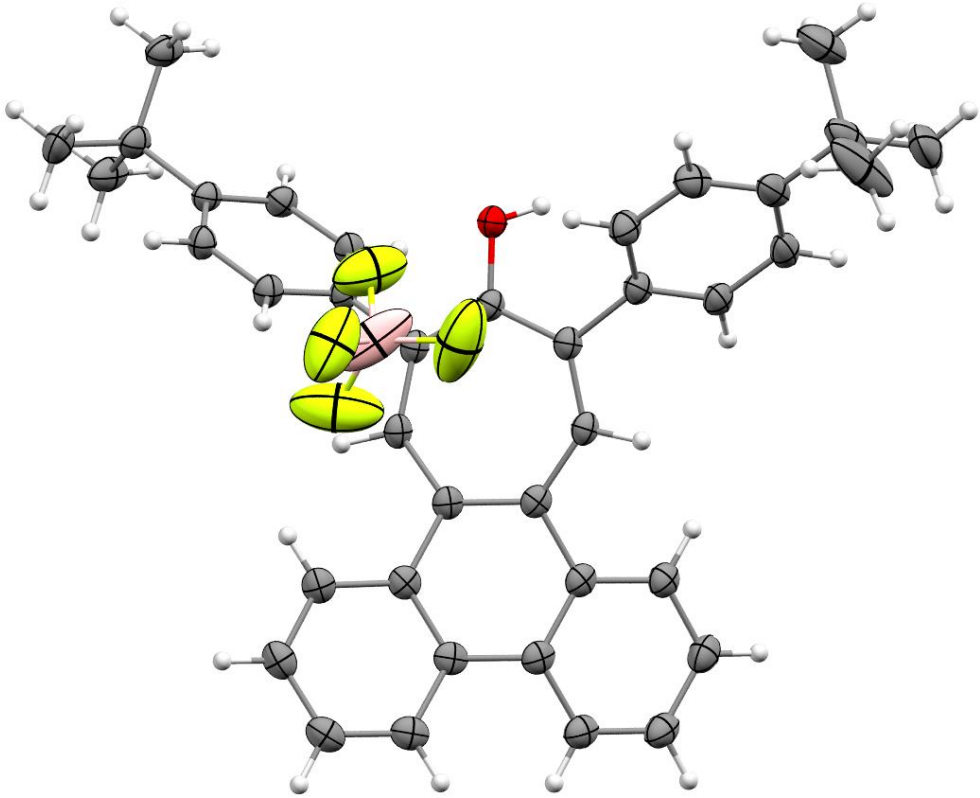


Figure S6. ORTEP drawing of **4i** with thermal ellipsoids set at the 30% probability level.[a]

[a]Crystal data for **4i**, monoclinic, space group *C* 2/*c* (no. 15), a = 20.7234(3) Å, b = 20.8474(3) Å, c = 16.3267(2) Å, $\alpha = \gamma = 90$ °, β = 93.6728(12) °, V = 7039.16(18) Å^3, T = 123 K, Z = 8, $R1$ ($wR2$) = 0.0693 (0.2055) for 391 parameters and 6958 unique reflections. GOF = 1.051. CCDC 2100259.

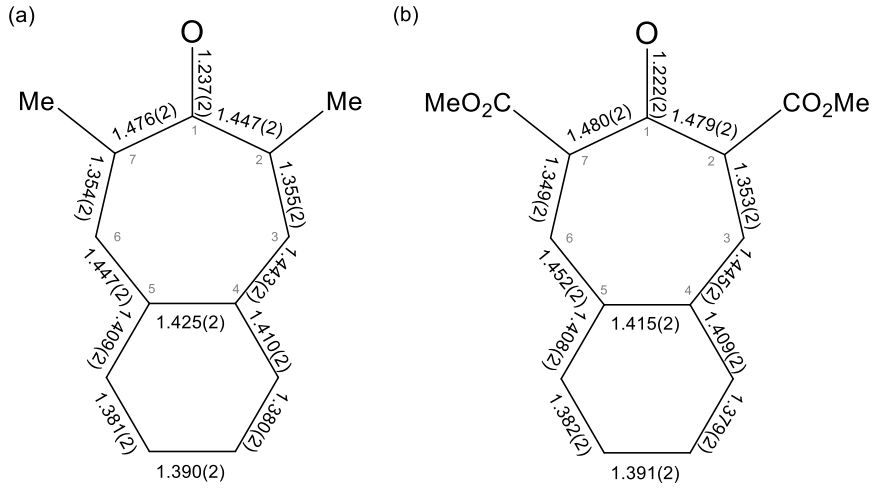


Figure S7. Selected bond lengths (Å) of (a) **3b** and (b) **3c** (CCDC 2036613).

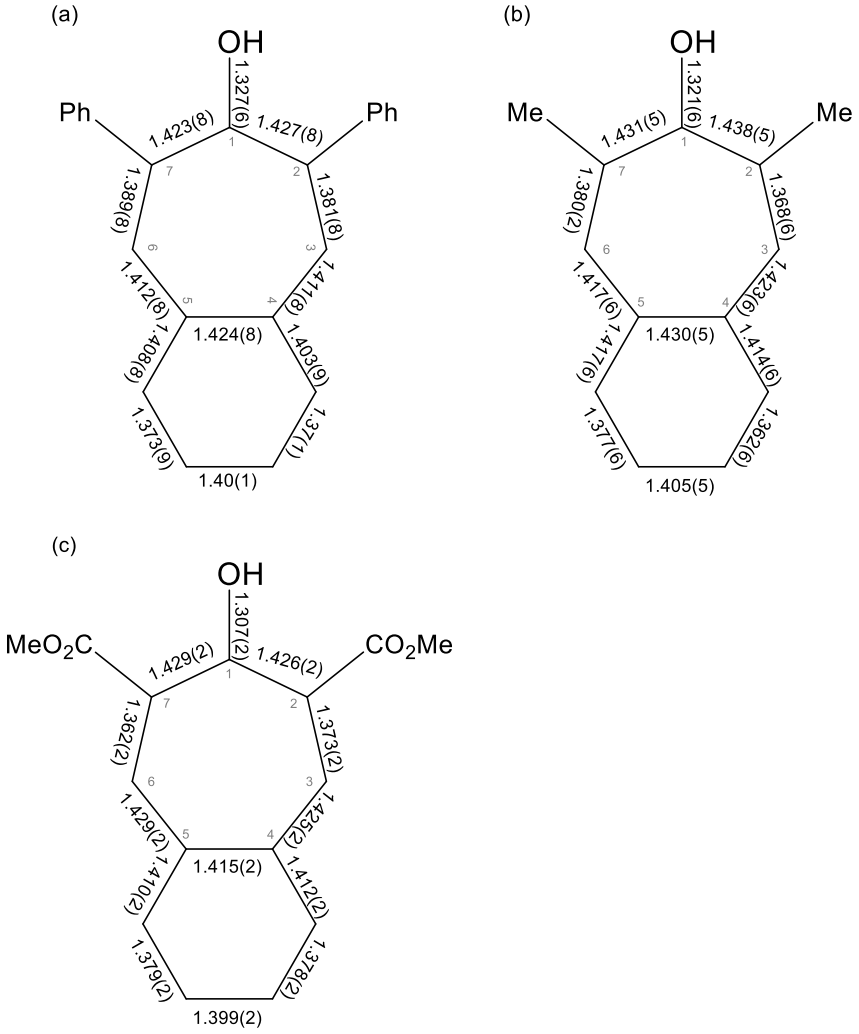


Figure S8. Selected bond lengths (Å) of (a) **4a** (b) **4b**, and (c) **3c**

Table S1. Selected Bond Length/Å of 4,5-Arene Fused Tropone Scaffold of **3a**–**3c**, **3i** and **4a**–**4c**, **4i** and HOMA Values.[a]

	bond length / Å				HOMA	
	O–C1	C1–C2/C7–C1	C2–C3/C6–C7	C3–C4/C5–C6	ring **A**	ring **B**
3a	1.217	1.486/1.477	1.350/1.354	1.448/1.447	–0.019	0.943
4a	1.327(6)	1.427(8)/1.423(8)	1.381(8)/1.389(8)	1.411(8)/1.412(8)	0.809	0.888
3b	1.237(2)	1.447(2)/1.476(2)	1.355(2)/1.354(2)	1.443(2)/1.447(2)	0.071	0.896
4b	1.321(6)	1.438(5)/1.431(5)	1.368(6)/1.380(2)	1.423(6)/1.417(6)	0.681	0.812
3c	1.222(2)	1.479(2)/1.480(2)	1.353(2)/1.349(2)	1.445(2)/1.452(2)	–0.015	0.927
4c	1.307(2)	1.426(2)/1.429(2)	1.373(2)/1.362(2)	1.425(2)/1.429(2)	0.678	0.869
3i	1.220(2)	1.487(3)/1.483(3)	1.352(3)/1.350(3)	1.461(3)/1.458(3)	–0.293	0.127
4i	1.329(2)	1.425(3)/1.412(3)	1.385(3)/1.378(3)	1.415(3)/1.412(3)	0.863	0.075

[a]Structural parameters for **3a** (CCDC 1145437) and **3c** (CCDC 2036613) were abstracted from the Cambridge Structural Data Base.

II. NMR-Titration Measurements.

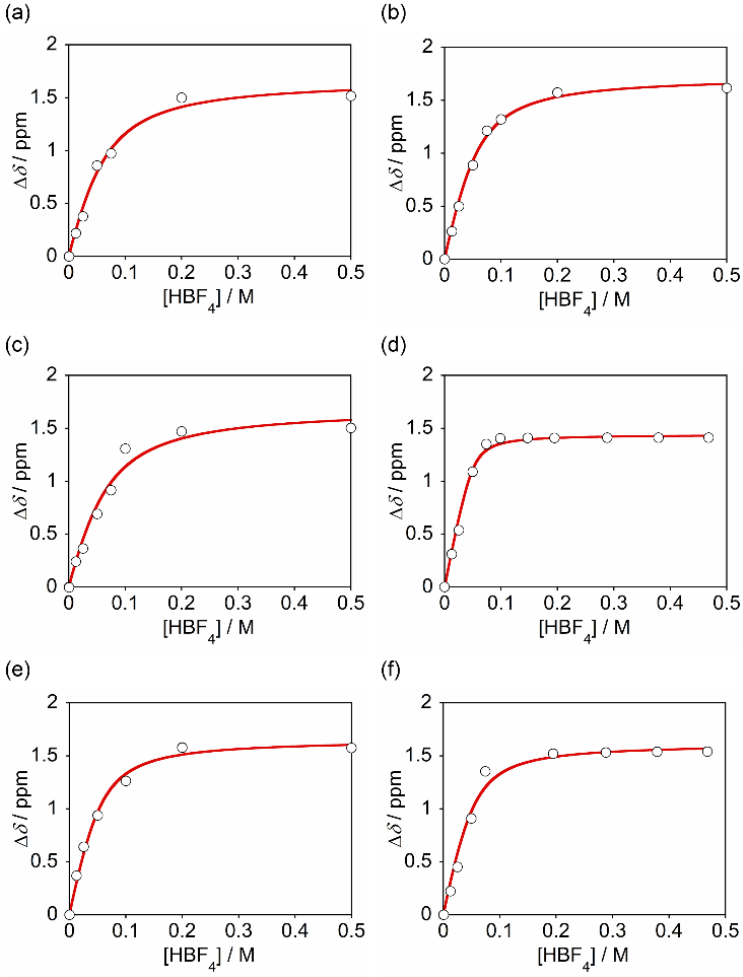


Figure S9. Changes in the ^{1}H chemical shifts of β-protons for $\Delta\delta$ for (a) **3d**, (b) **3e**, (c) **3f**, (d) **3g**, (e) **3h**, and (f) **3i** as a function of HBF_4 concentration along with curve fitting by the non-linear least squares (red line).

Table S2. K_b and $\Delta\delta_{sat}$ for **3d**–**3i** determined by non-linear least squares and the pK_a values for the corresponding conjugated acids.

	3d	**3e**	**3f**	**3g**	**3h**	**3i**
K_b	34.8 ± 8.34	50.4 ± 7.05	30.8 ± 9.59	299 ± 89.9	68.2 ± 18.4	78.1 ± 25.3
$\Delta\delta_{sat}$ / ppm	1.67 ± 0.08	1.72 ± 0.04	1.69 ± 0.12	1.44 ± 0.02	1.66 ± 0.06	1.62 ± 0.06
pK_a[a]	1.54	1.70	1.48	2.48	1.83	1.89

[a]For the corresponding conjugated acids.

III. Electronic Absorption and Emission Spectra.

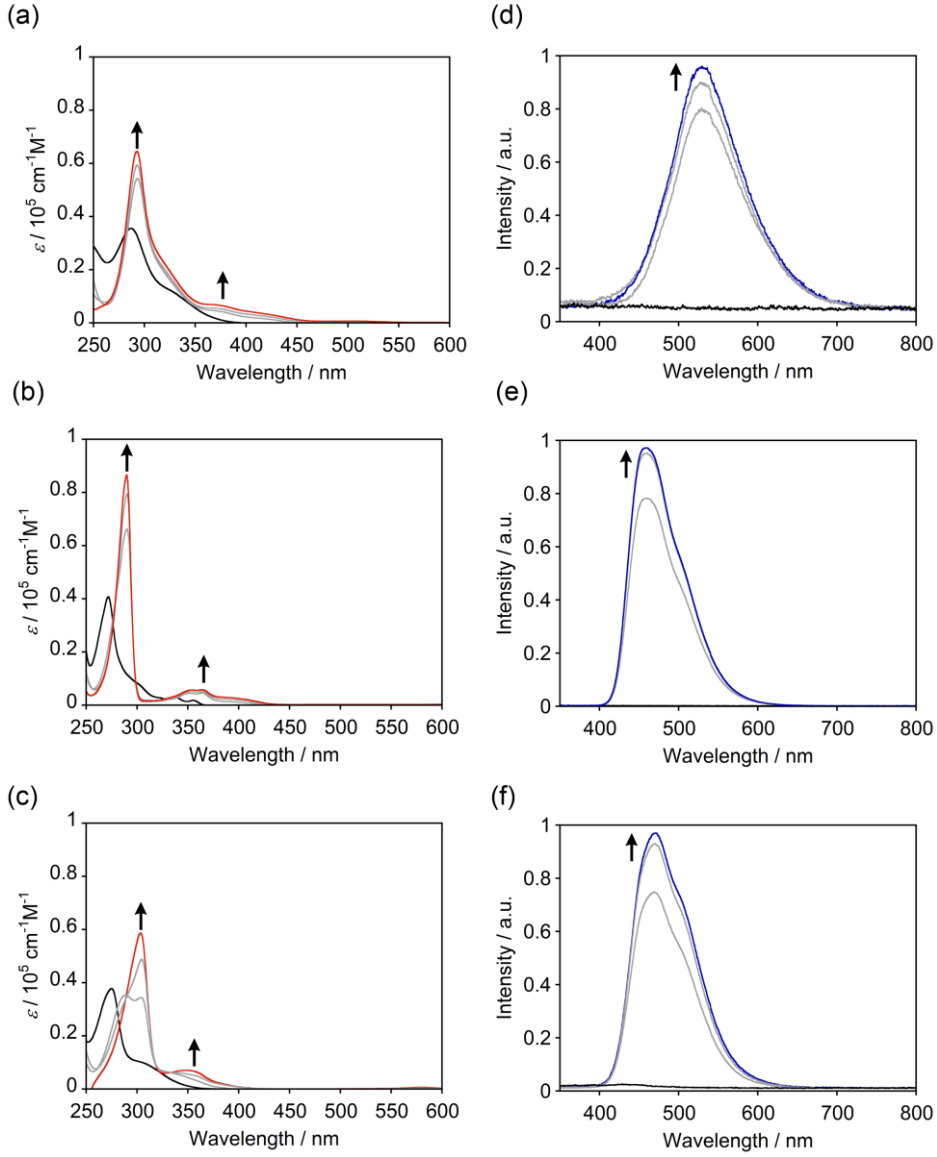
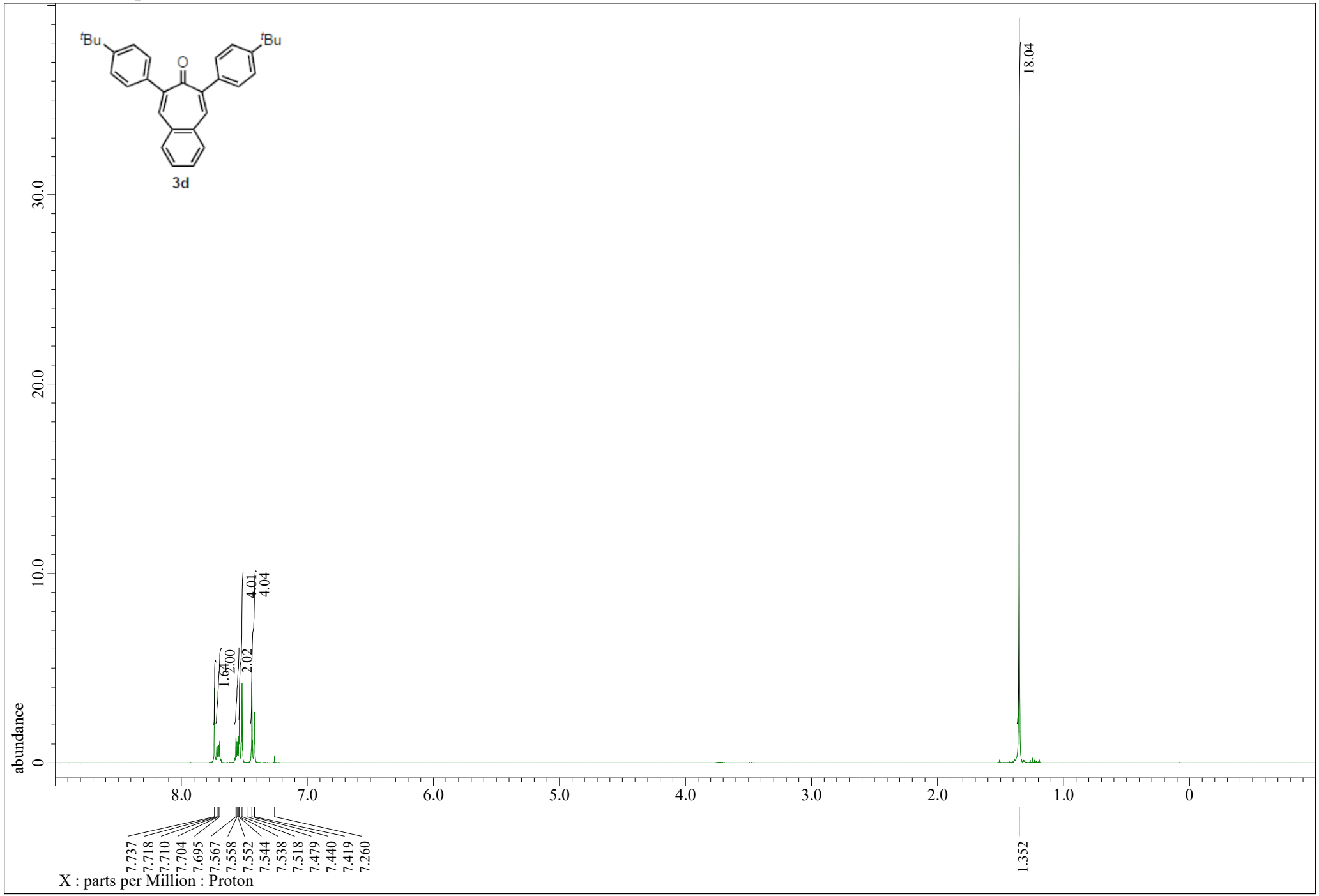


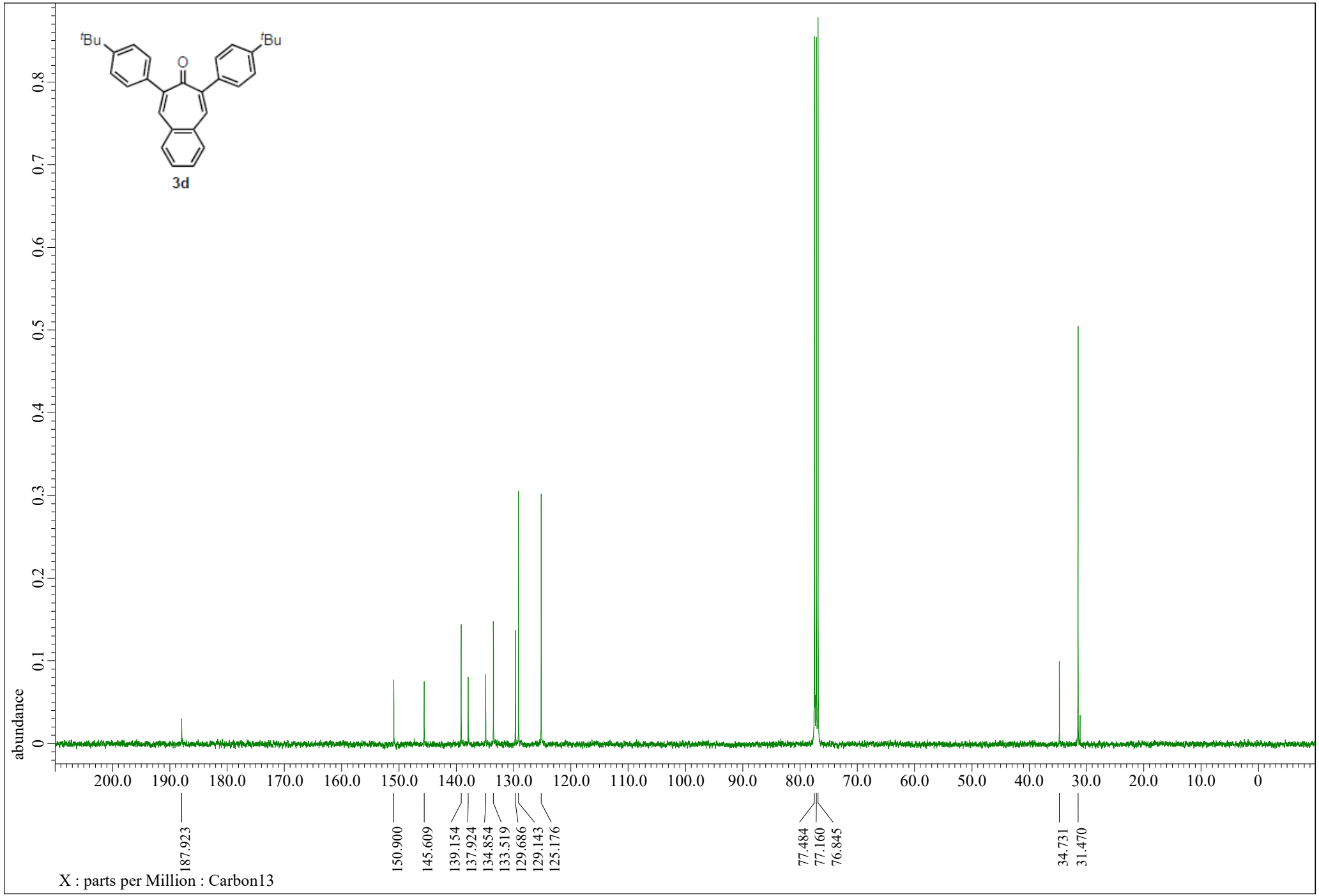
Figure S10. Electronic absorption spectra of (a) **3a**; (b) **3b**; (c) **3c** and emission spectra of (d) **3a** (λ_{ex} = 290 nm); (e) **3b** (λ_{ex} = 280 nm); (f) **3c** (λ_{ex} = 305 nm) (2.0×10^{-5} M in 0 [black]–20 [red/blue]% TFA/CH_2Cl_2 (*v*/*v*), rt).

^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **3d**

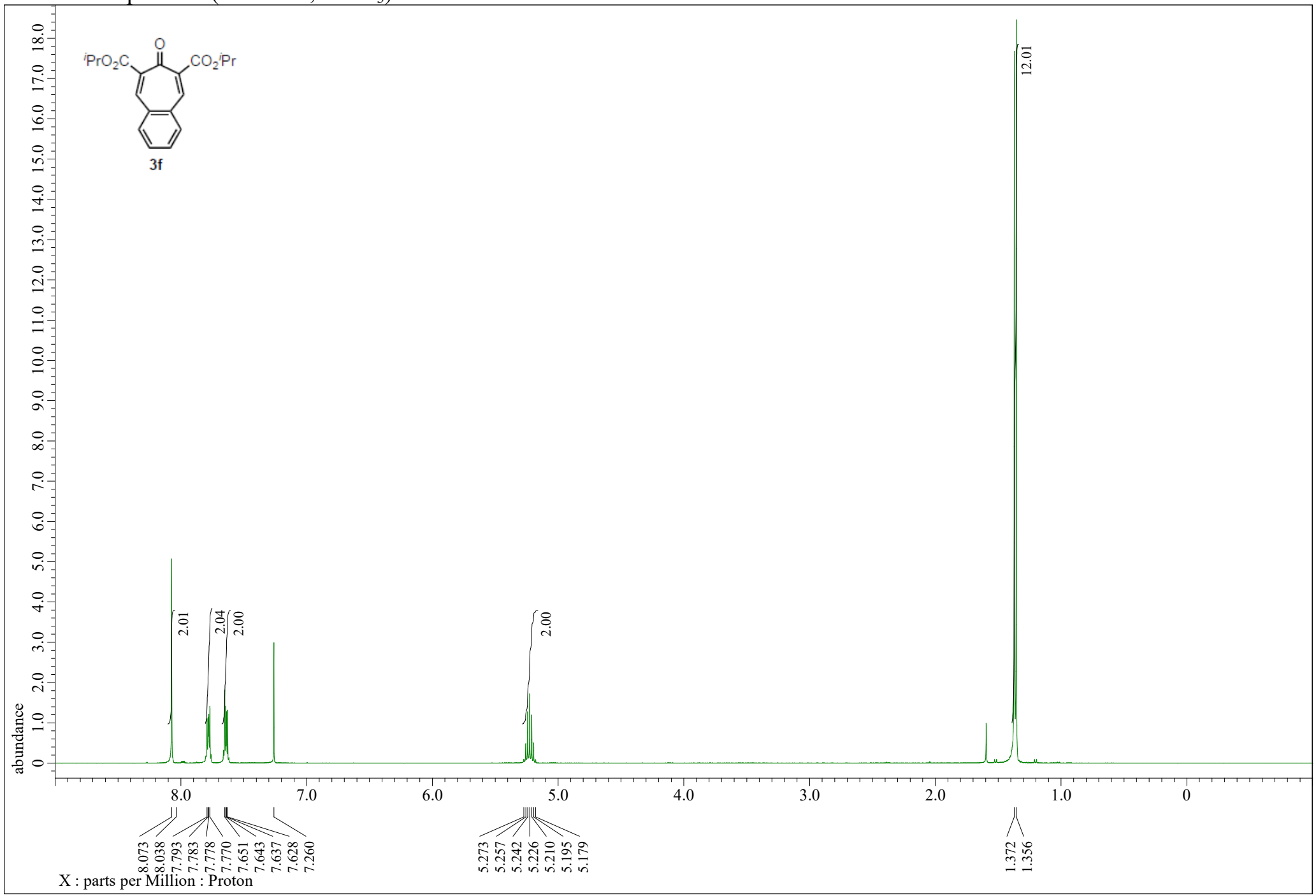


II. Copies of ^{1}H and ^{13}C NMR Spectra

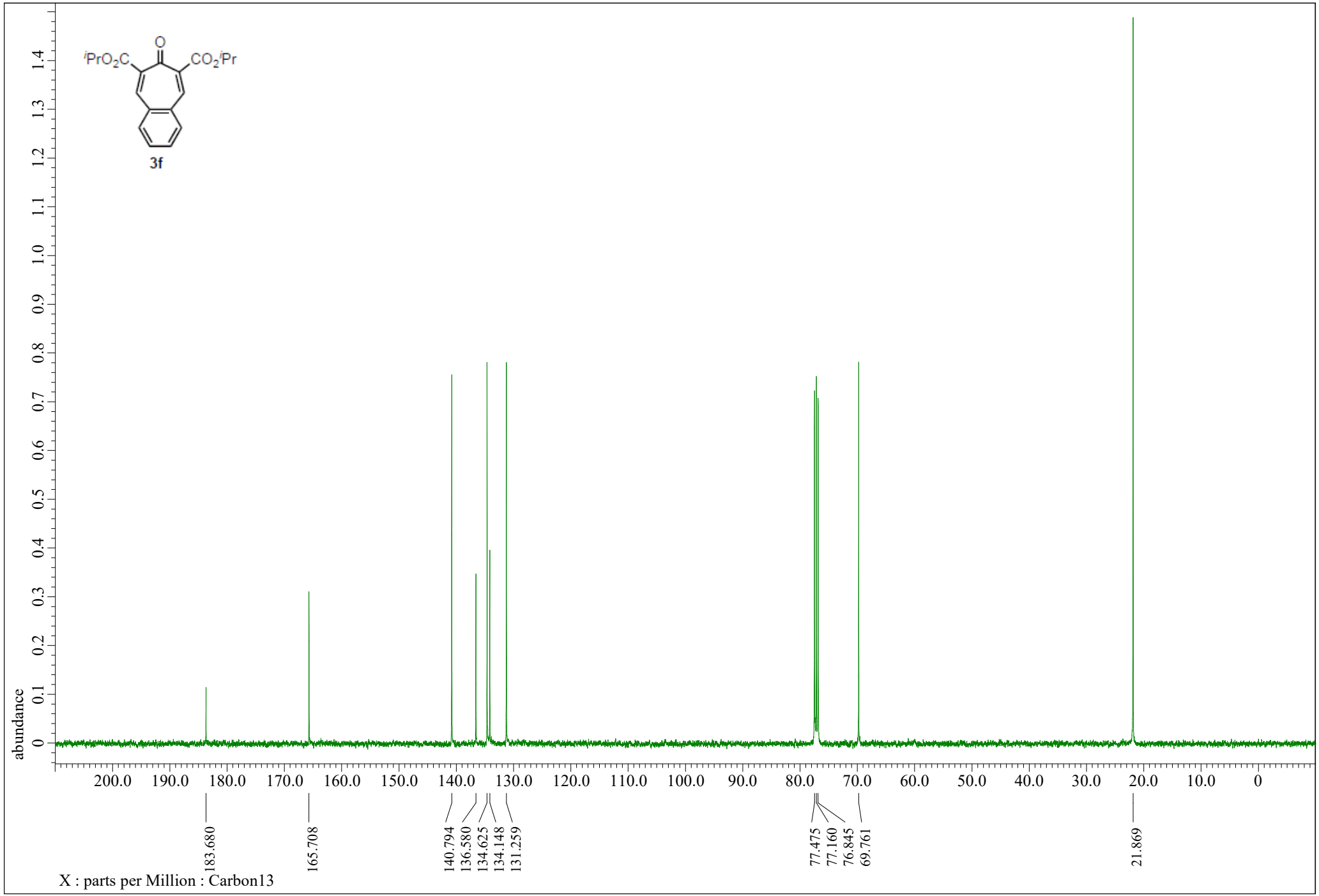
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, $CDCl_3$) of **3d**



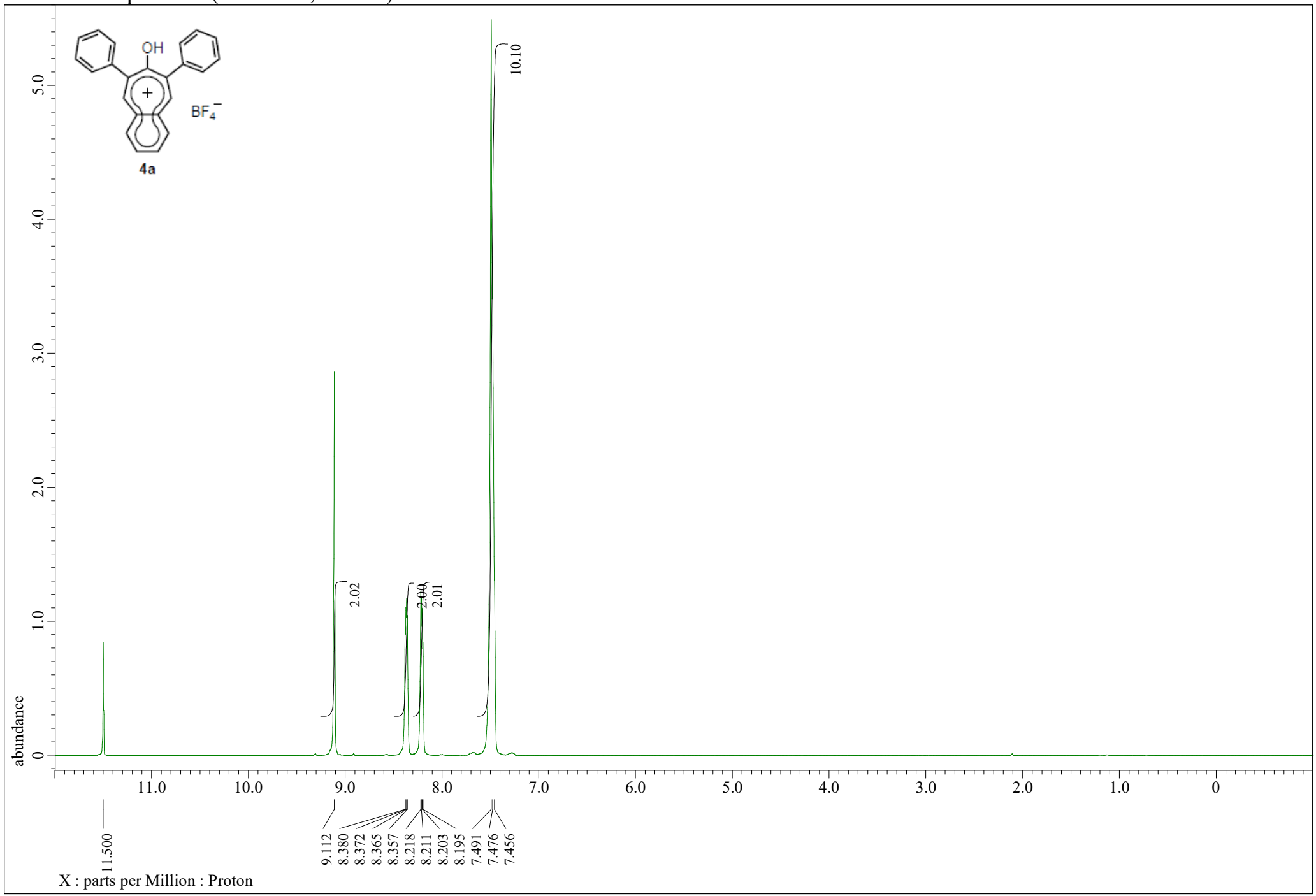
^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **3f**



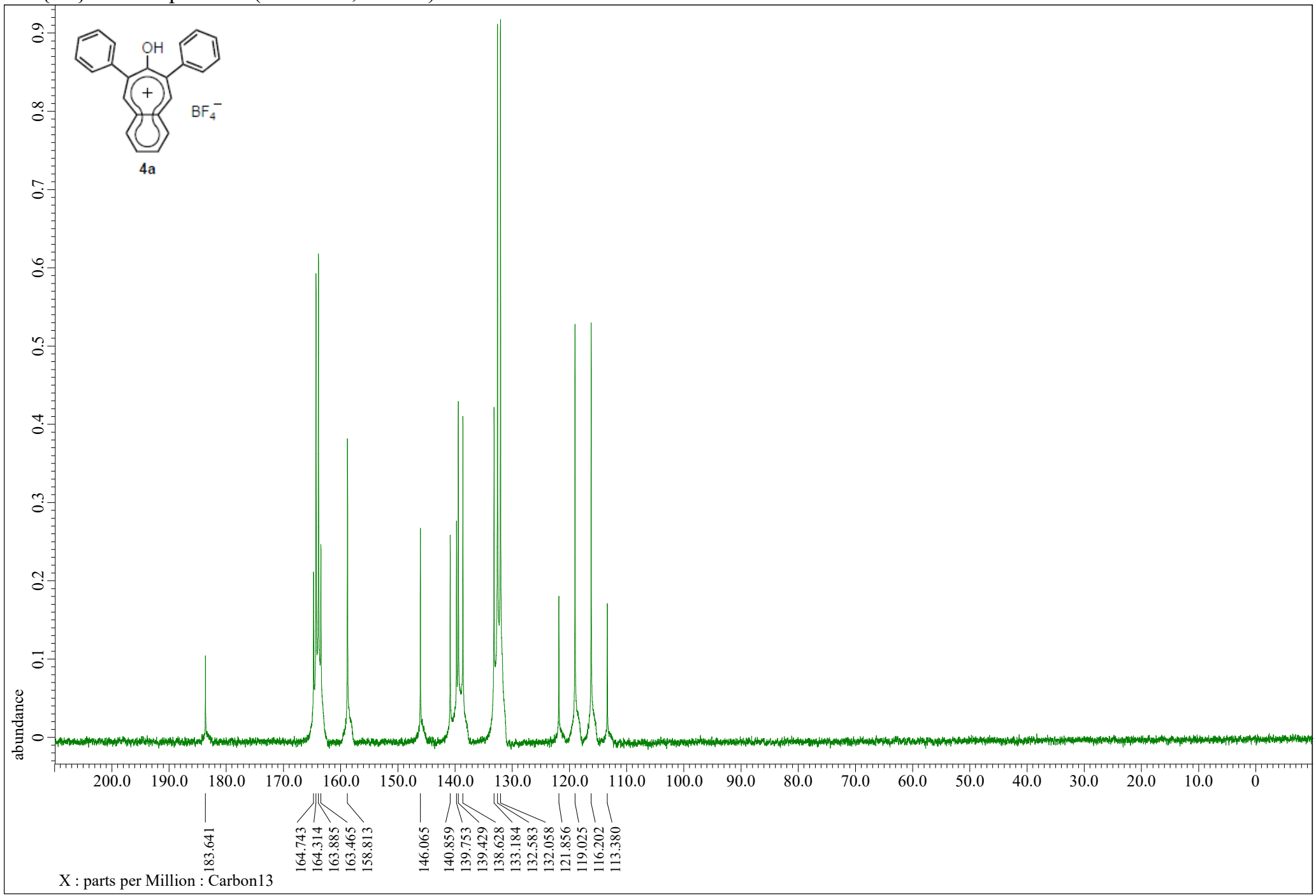
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, $CDCl_3$) of **3f**



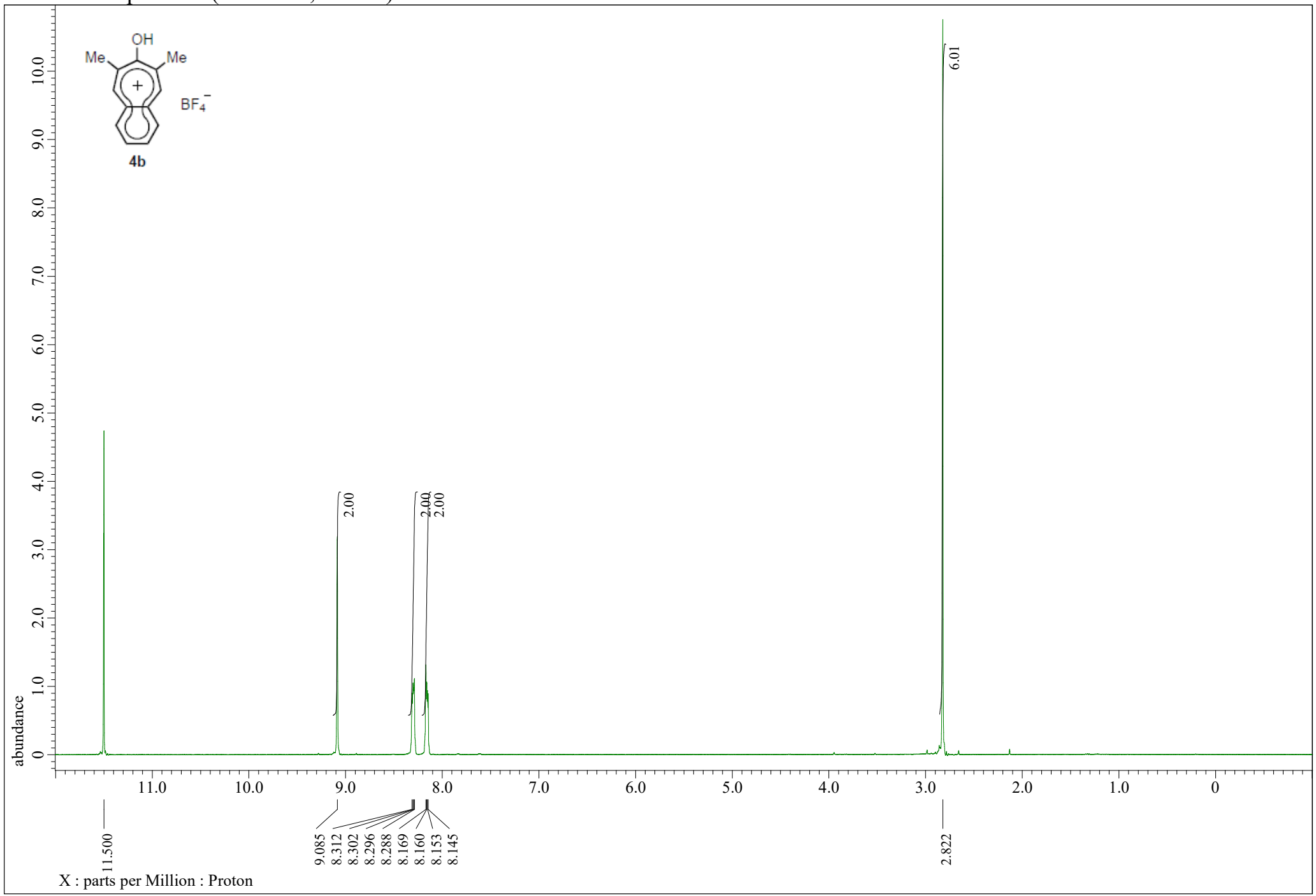
^{1}H-NMR spectrum (400 MHz, TFA-*d*) of **4a**



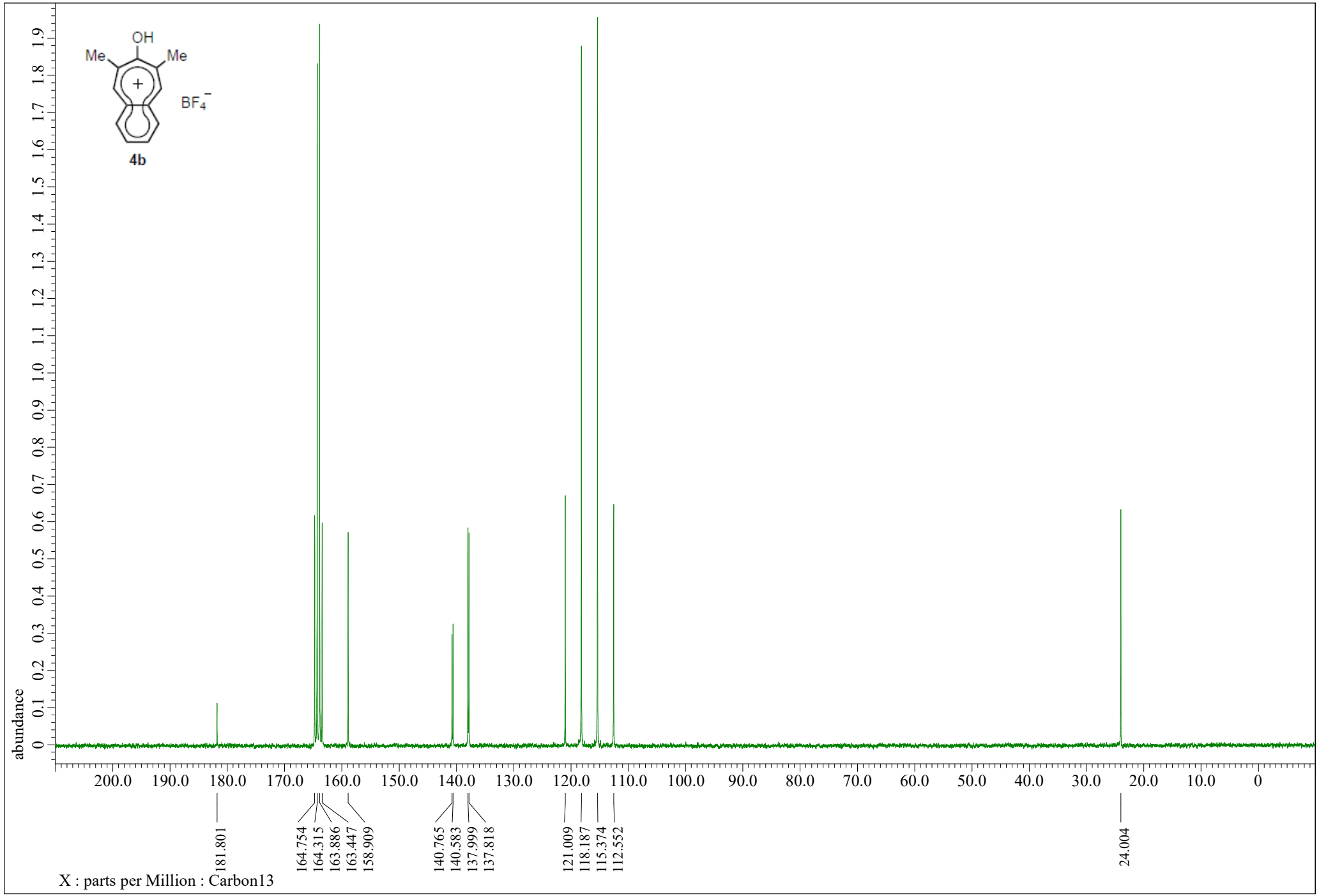
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, TFA-*d*) of **4a**



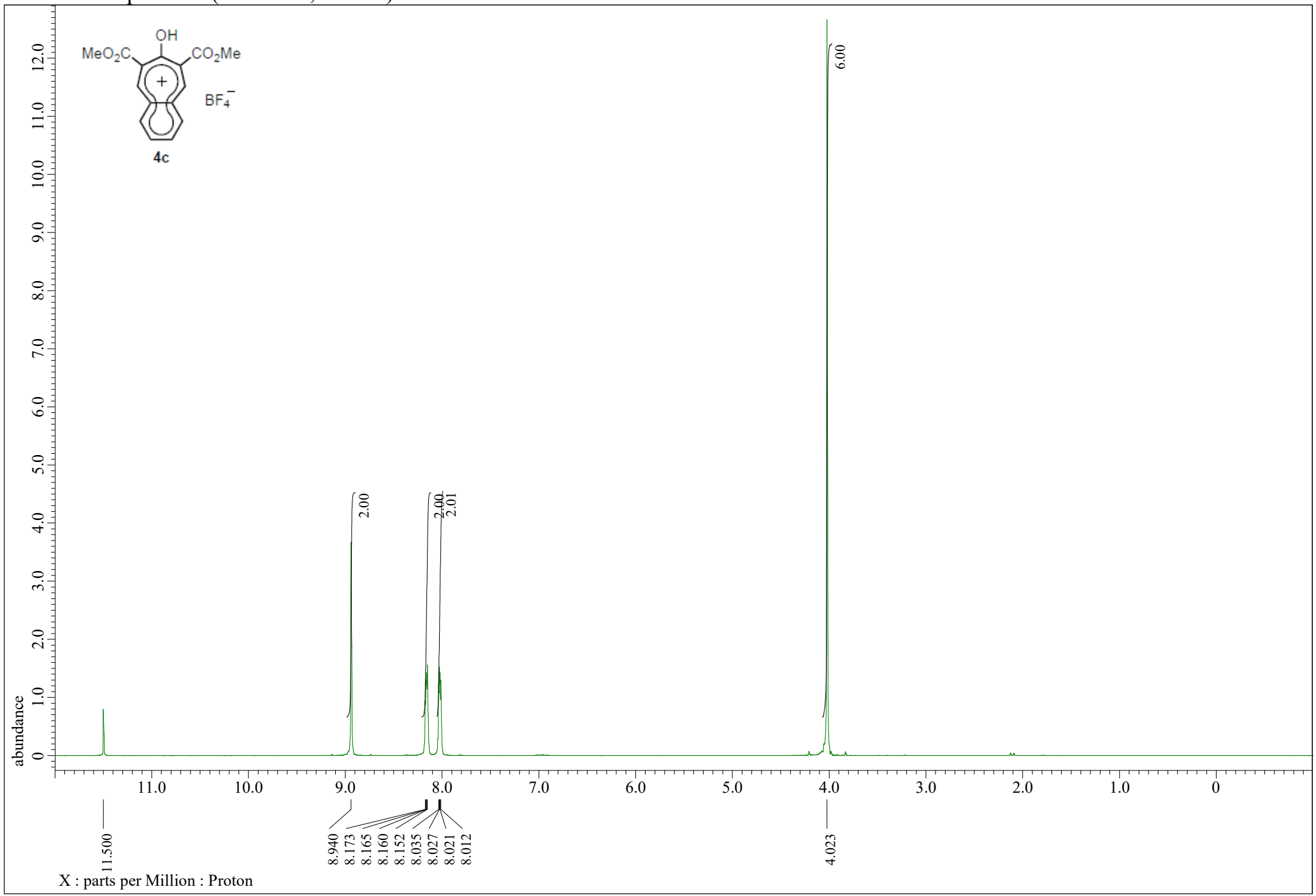
^{1}H-NMR spectrum (400 MHz, TFA-*d*) of **4b**



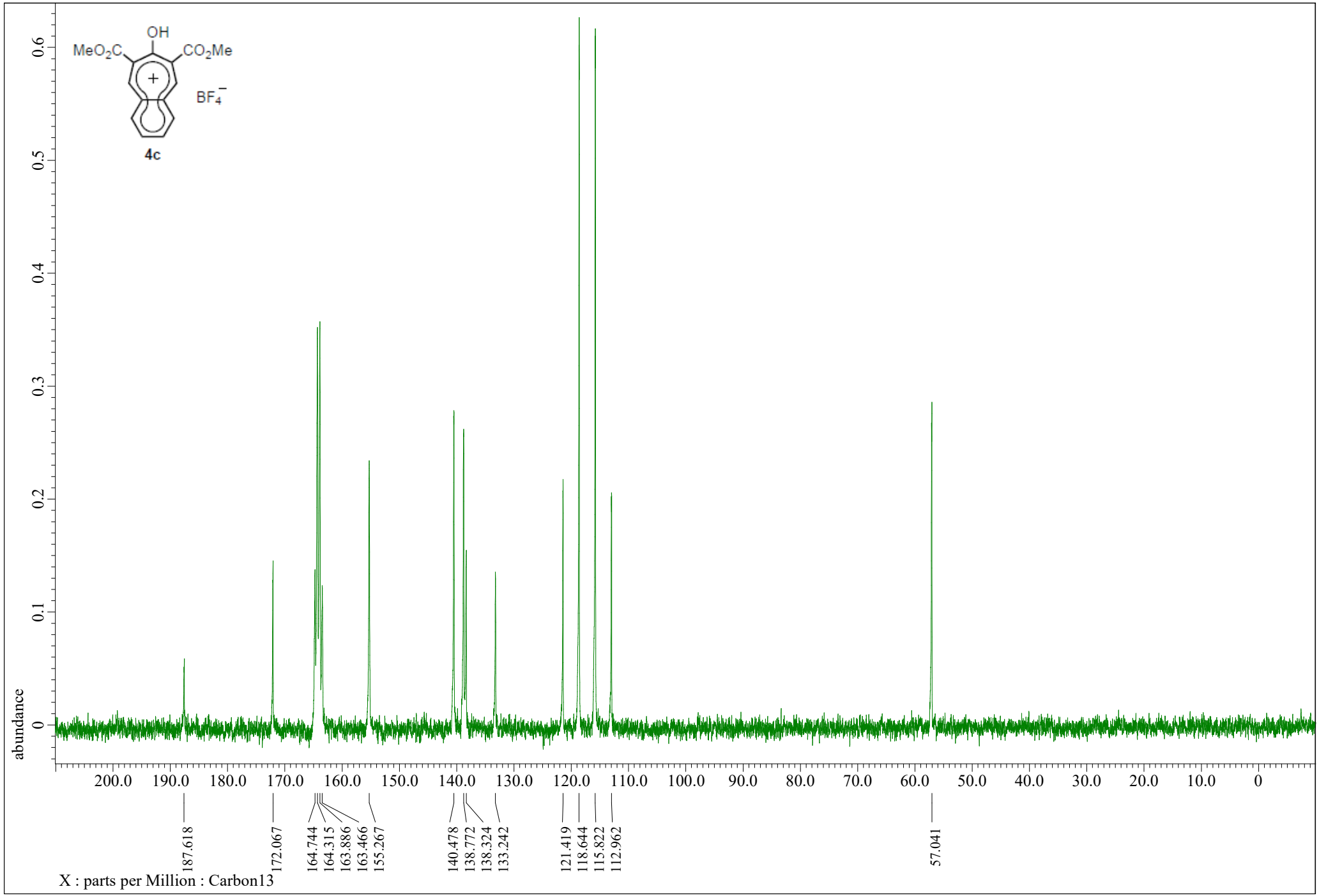
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, TFA-*d*) of **4b**



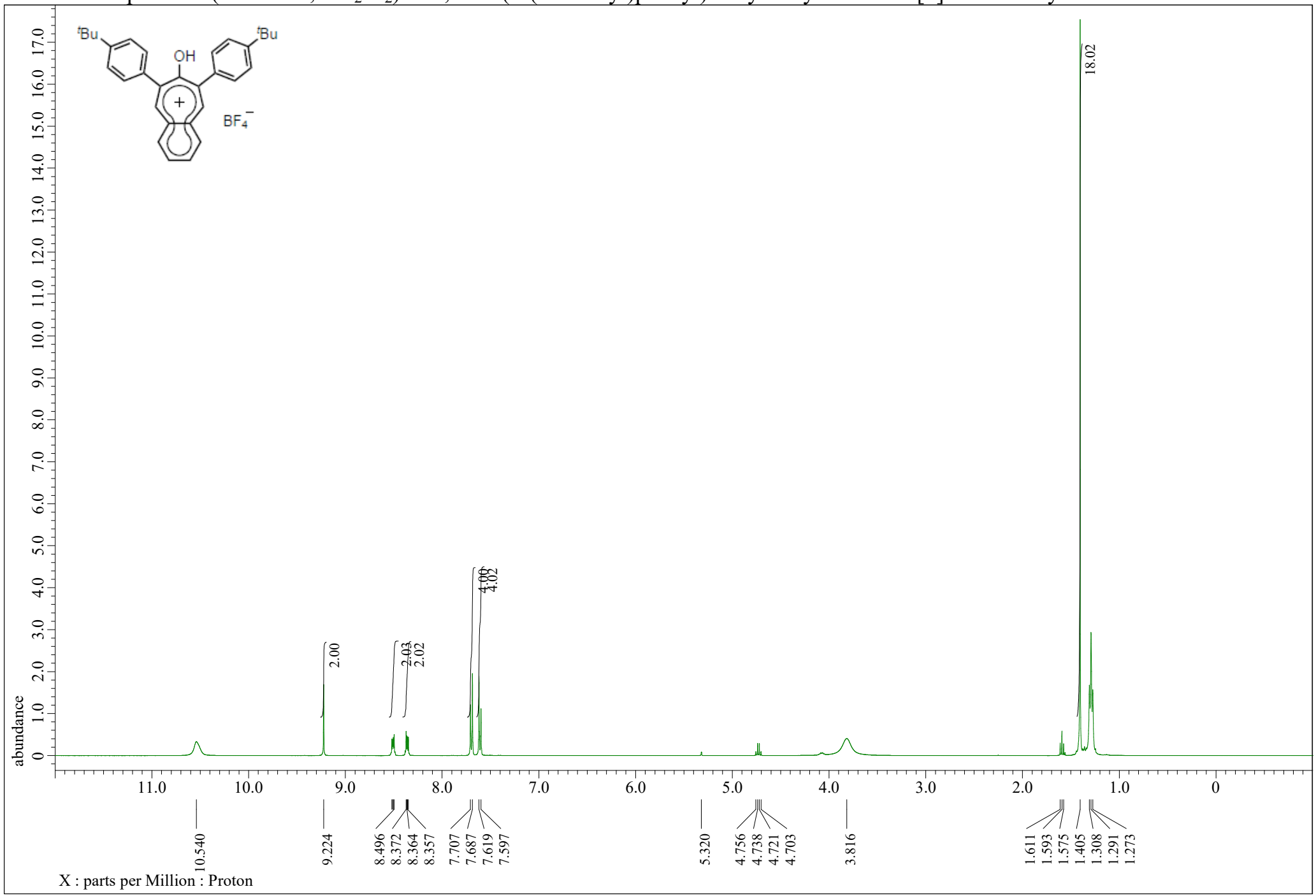
^{1}H-NMR spectrum (400 MHz, TFA-*d*) of **4c**



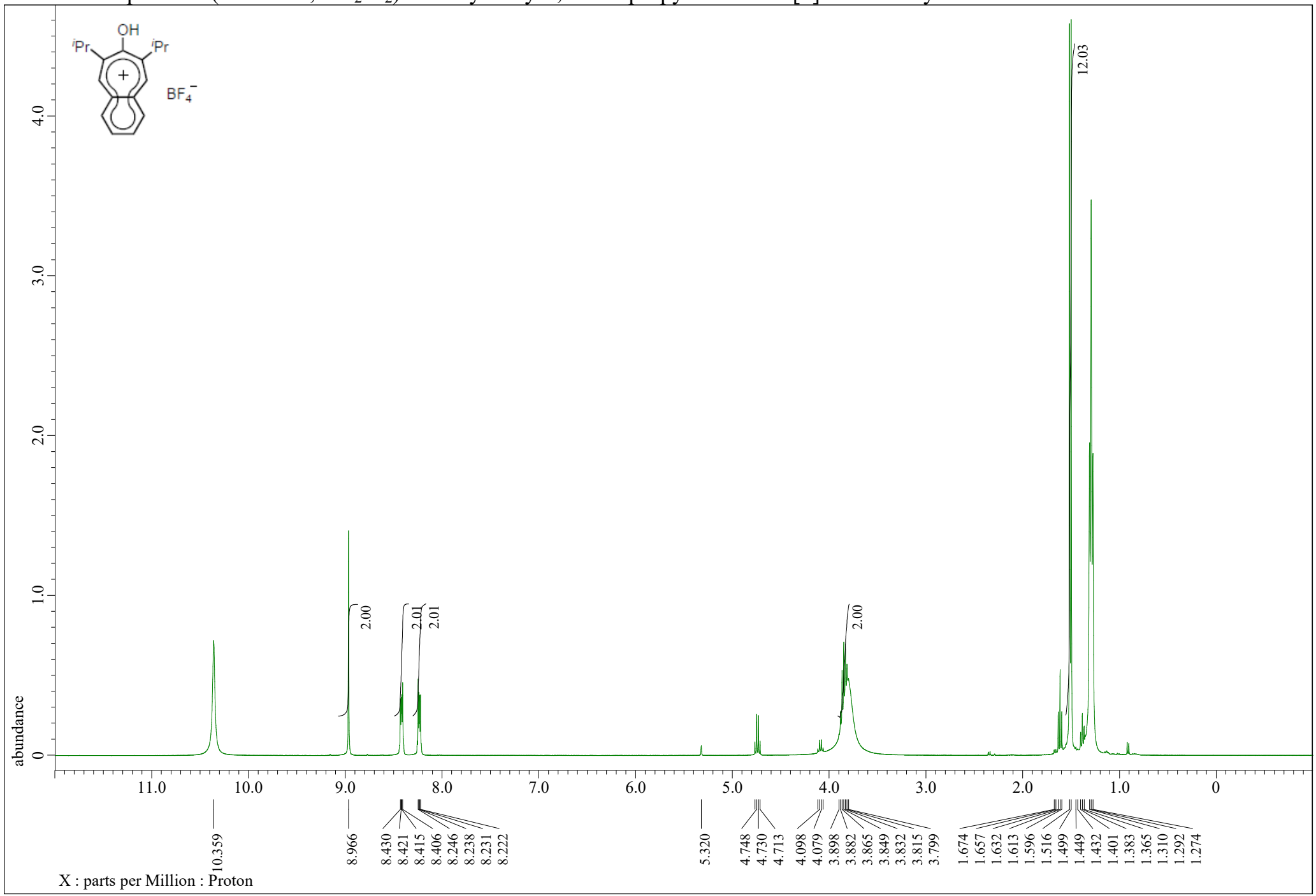
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, TFA-*d*) of **4c**



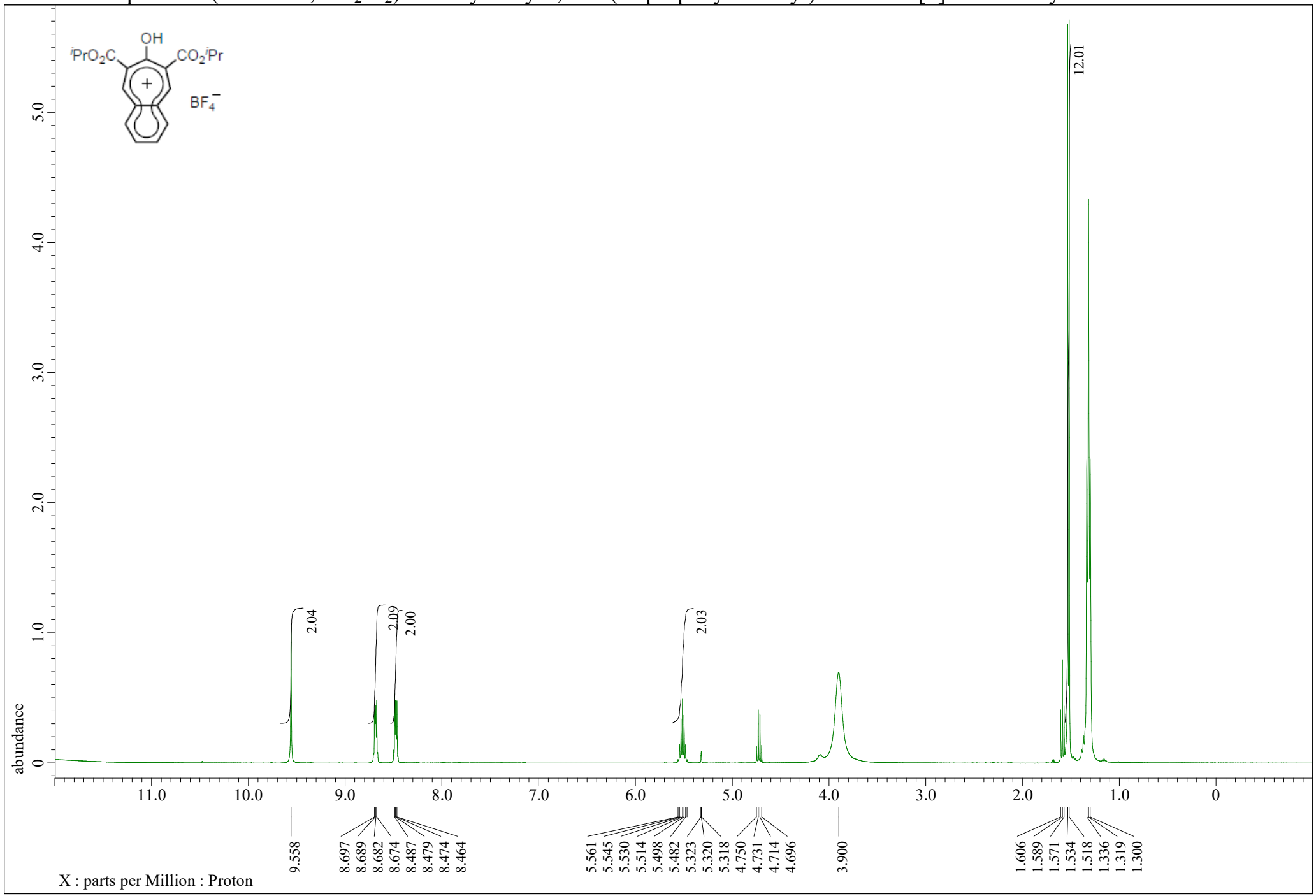
^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of 6,8-Bis(4-(*tert*-butyl)phenyl)-7-hydroxy-7*H*-benzo[7]annulen-7-ylium tetrafluoroborate



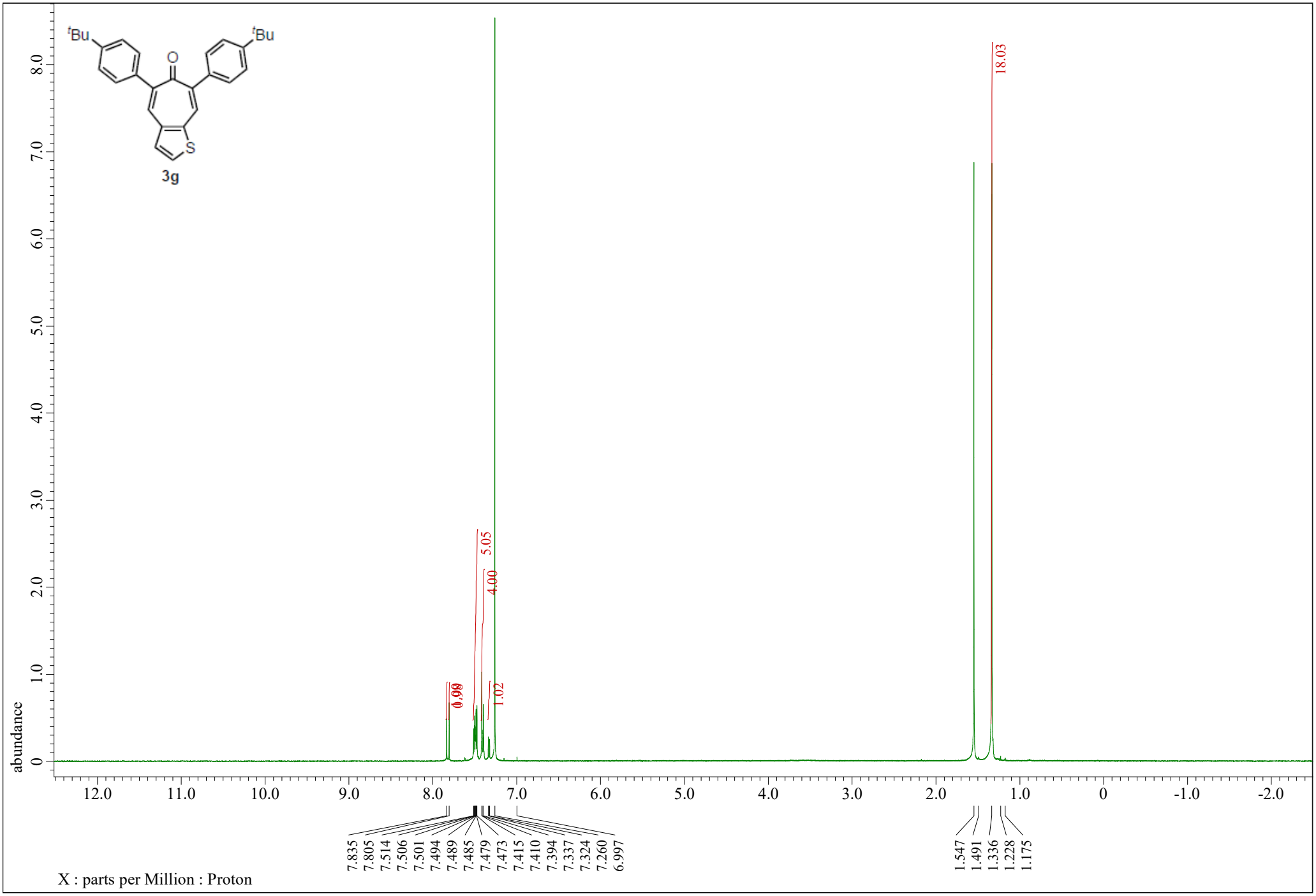
^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of 7-Hydroxy-6,8-diisopropyl-7*H*-benzo[7]annulen-7-ylium tetra-fluoroborate



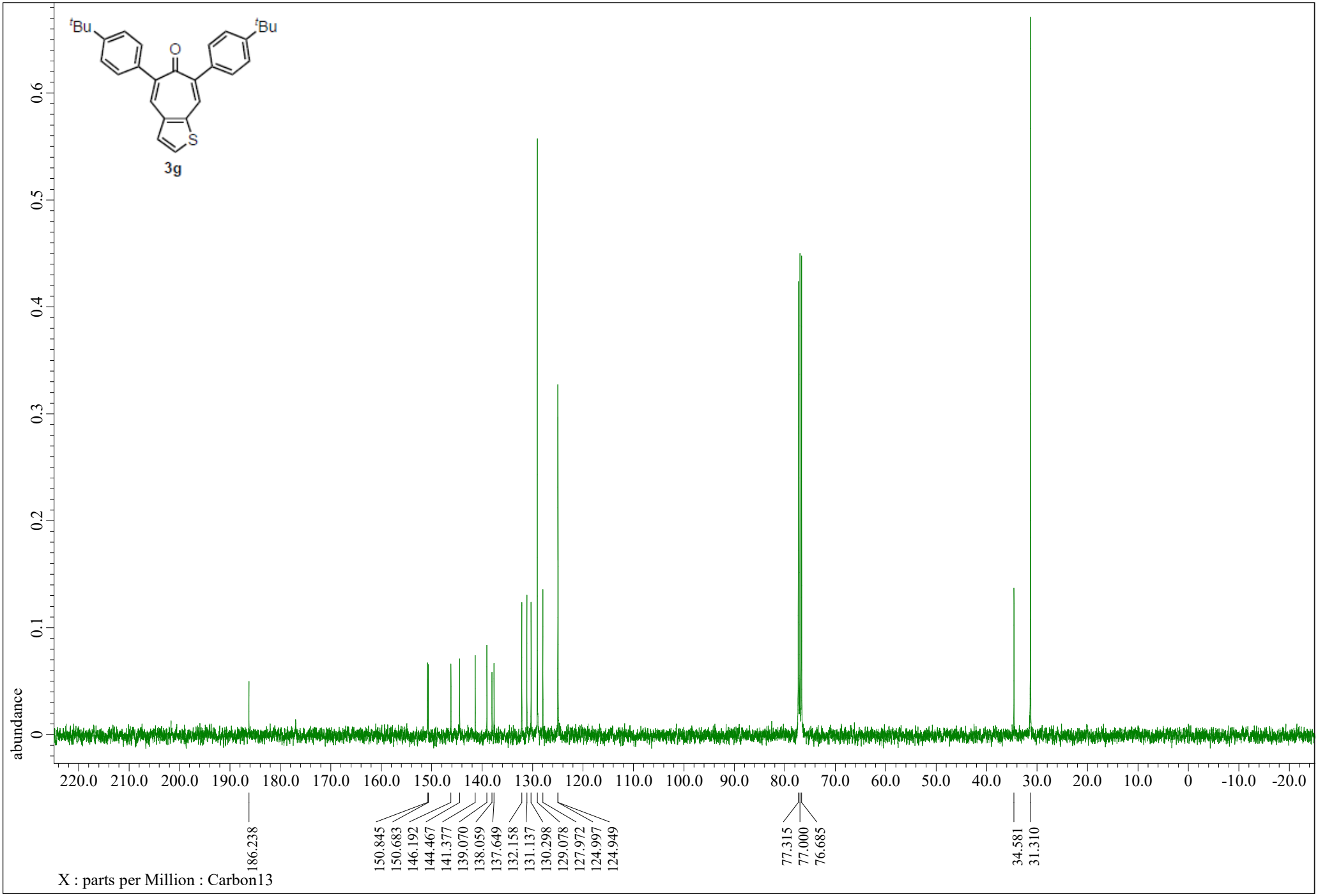
^{1}H-NMR spectrum (400 MHz, CD_2Cl_2) of 7-Hydroxy-6,8-bis(isopropoxycarbonyl)-7*H*-benzo[7]annulen-7-ylium tetrafluoroborate



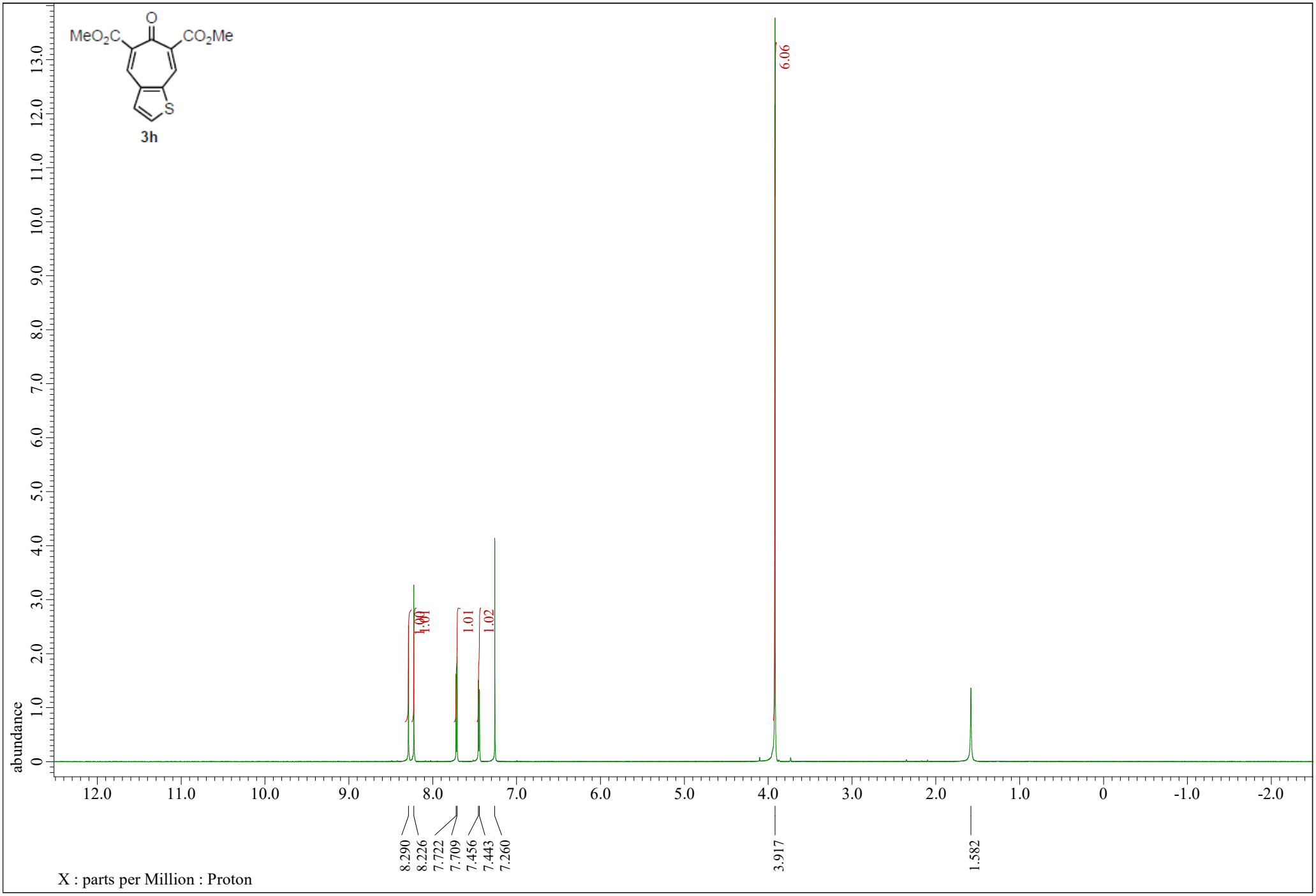
^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **3g**



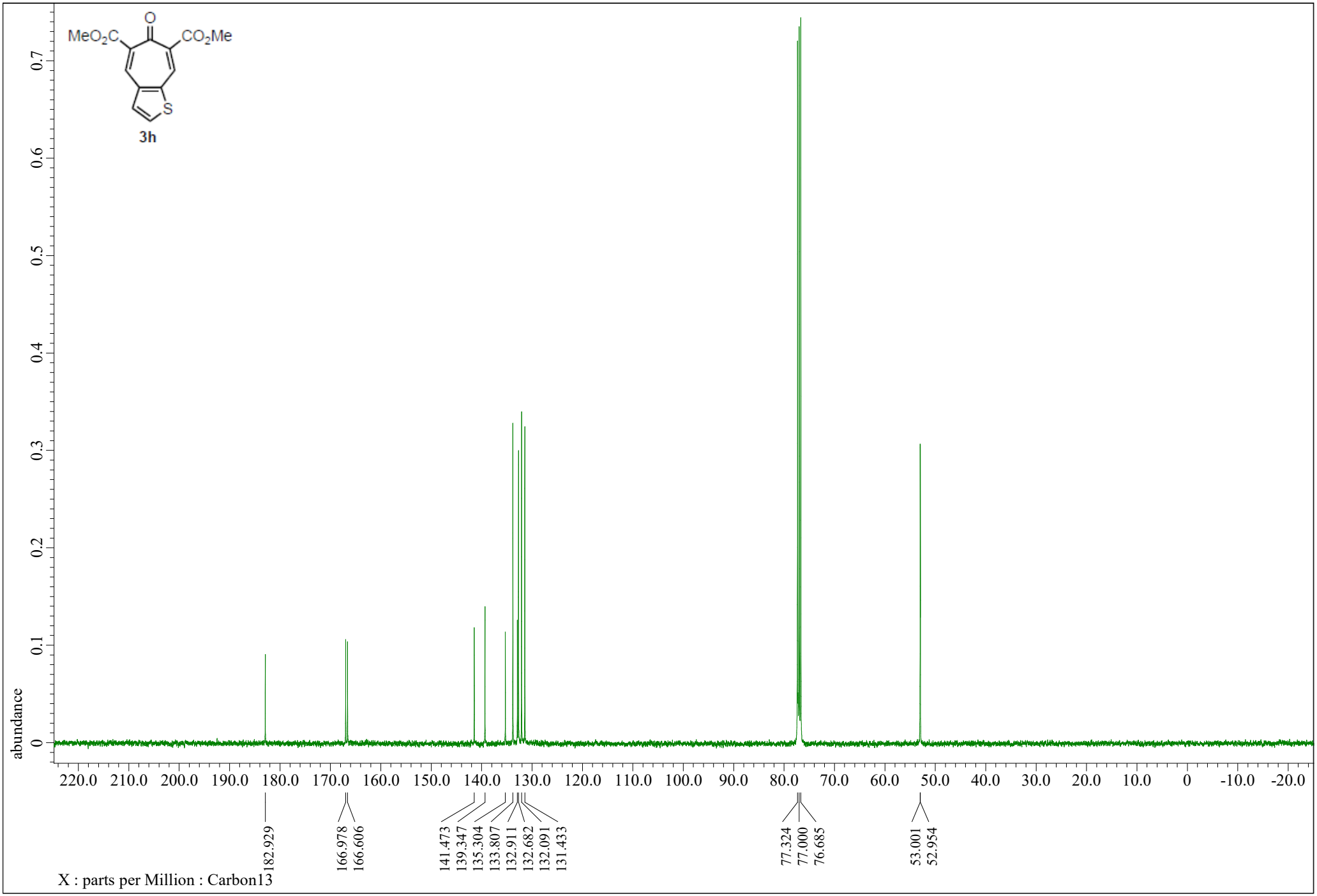
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, $CDCl_3$) of **3g**



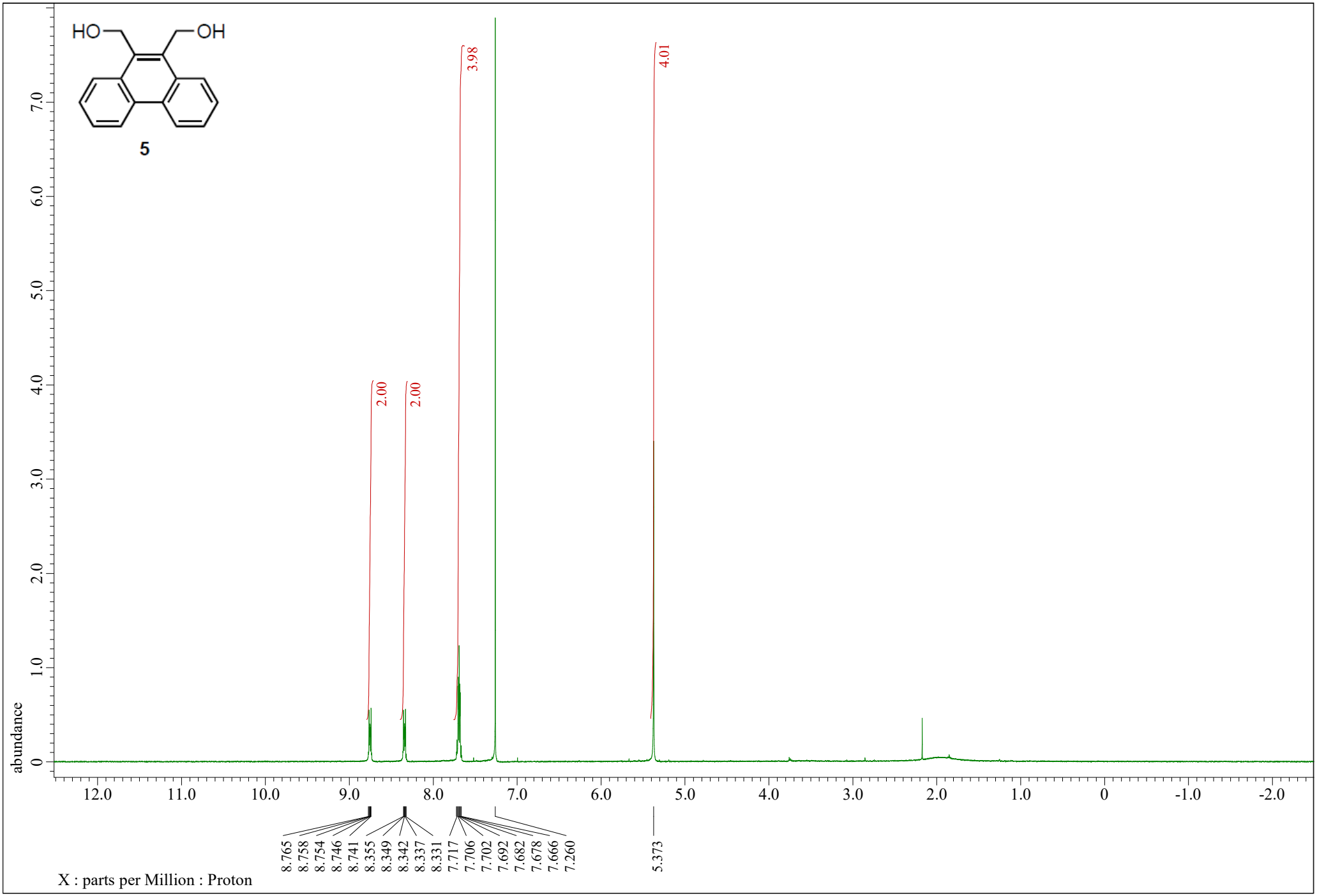
^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **3h**



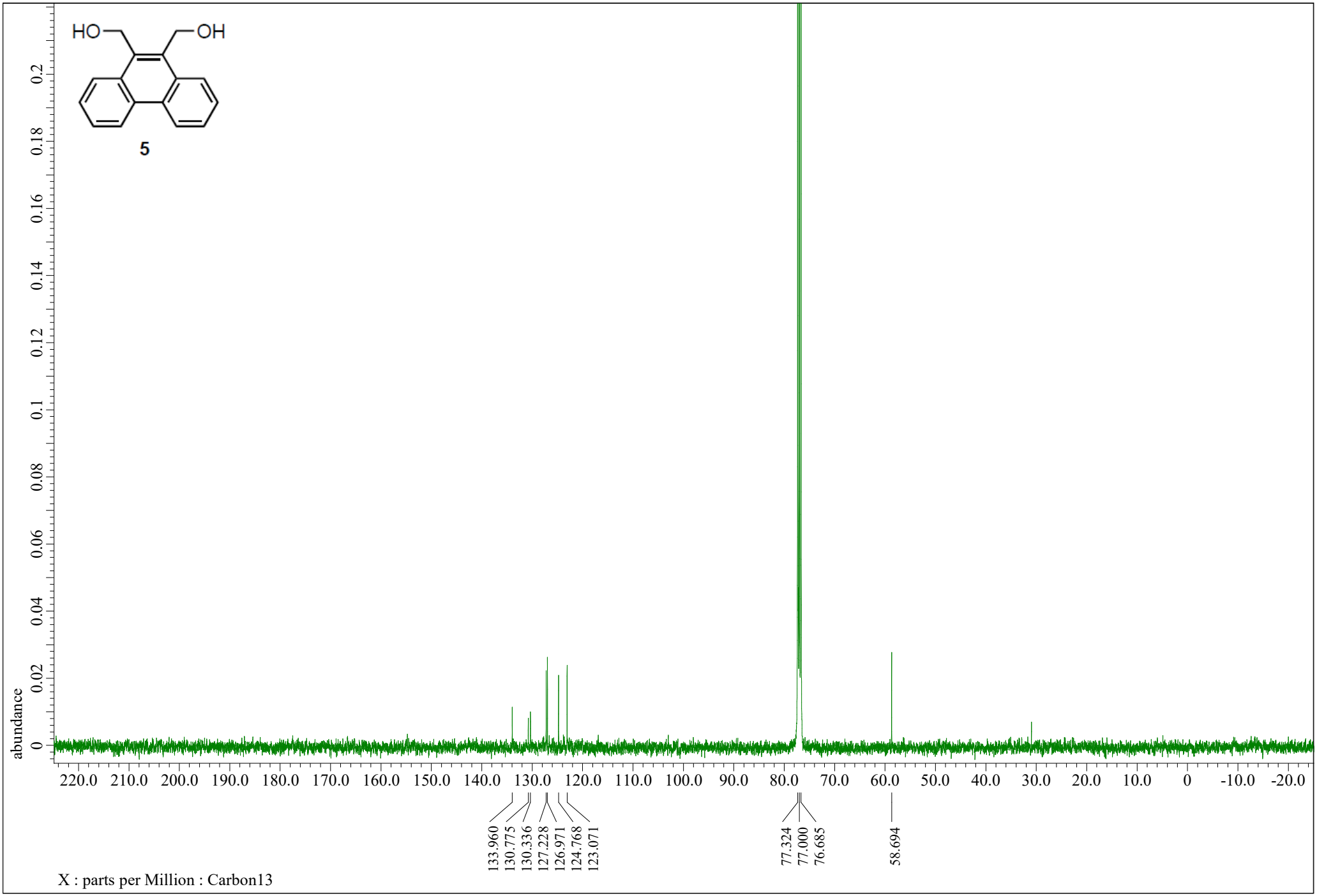
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, $CDCl_3$) of **3h**



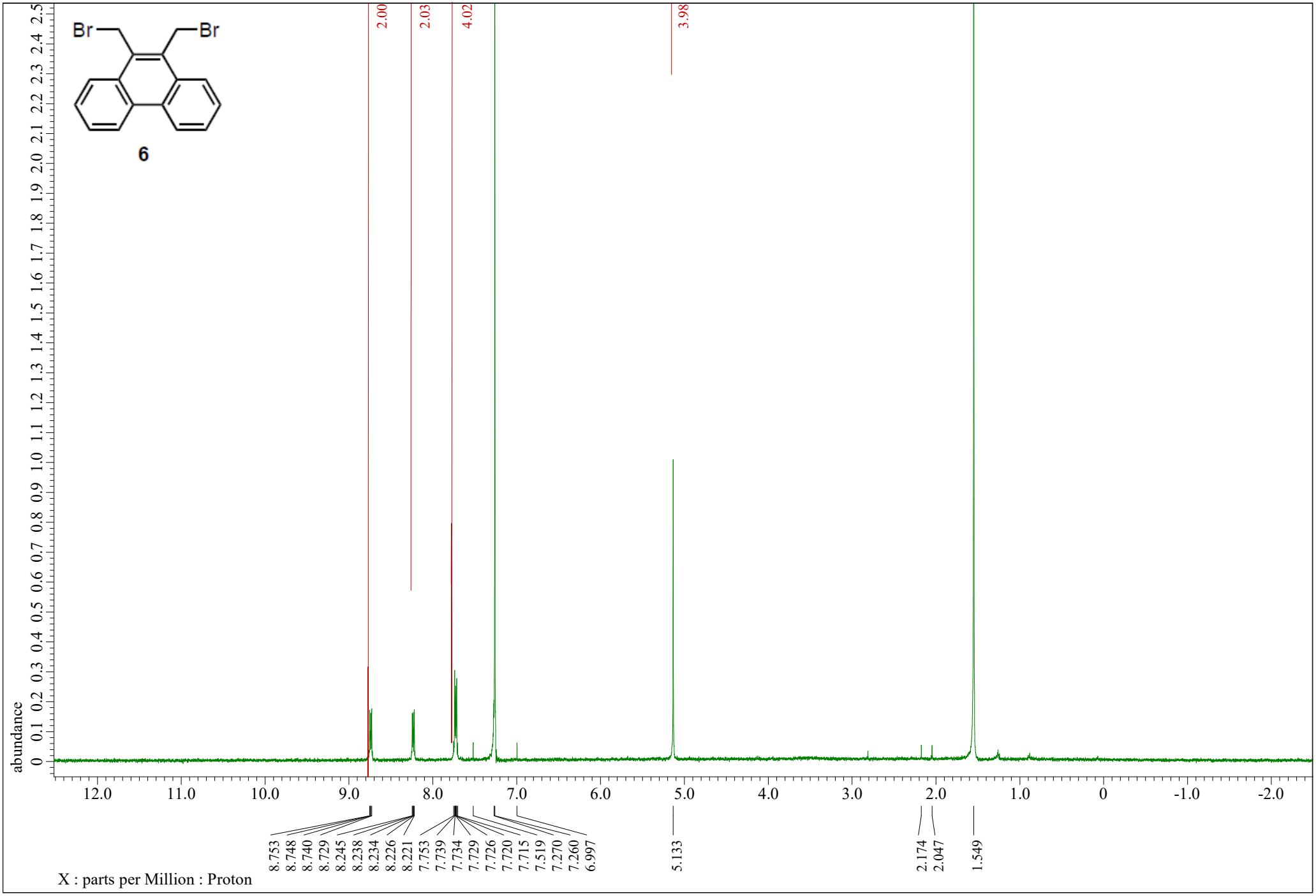
^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **5**



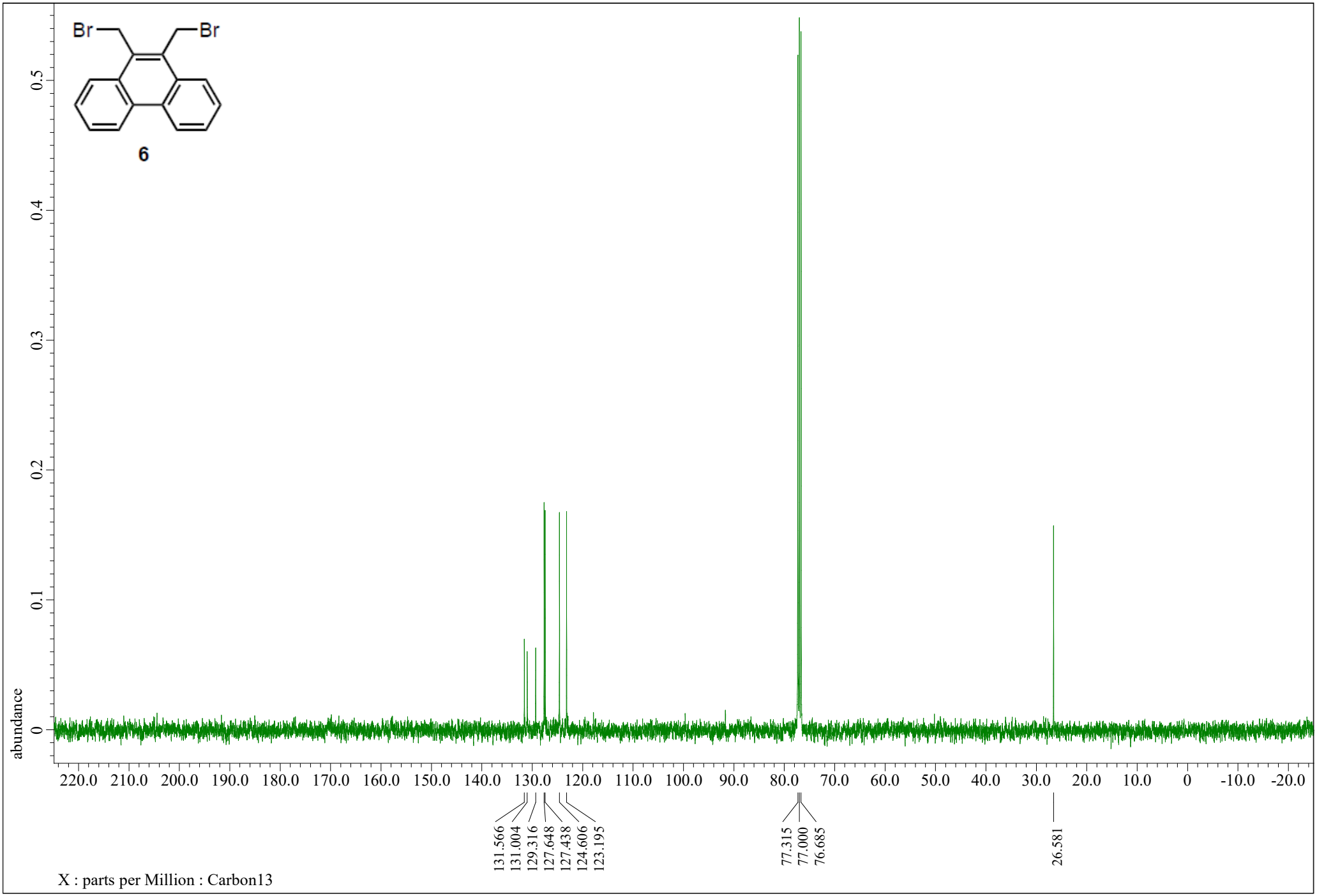
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, $CDCl_3$) of **5**



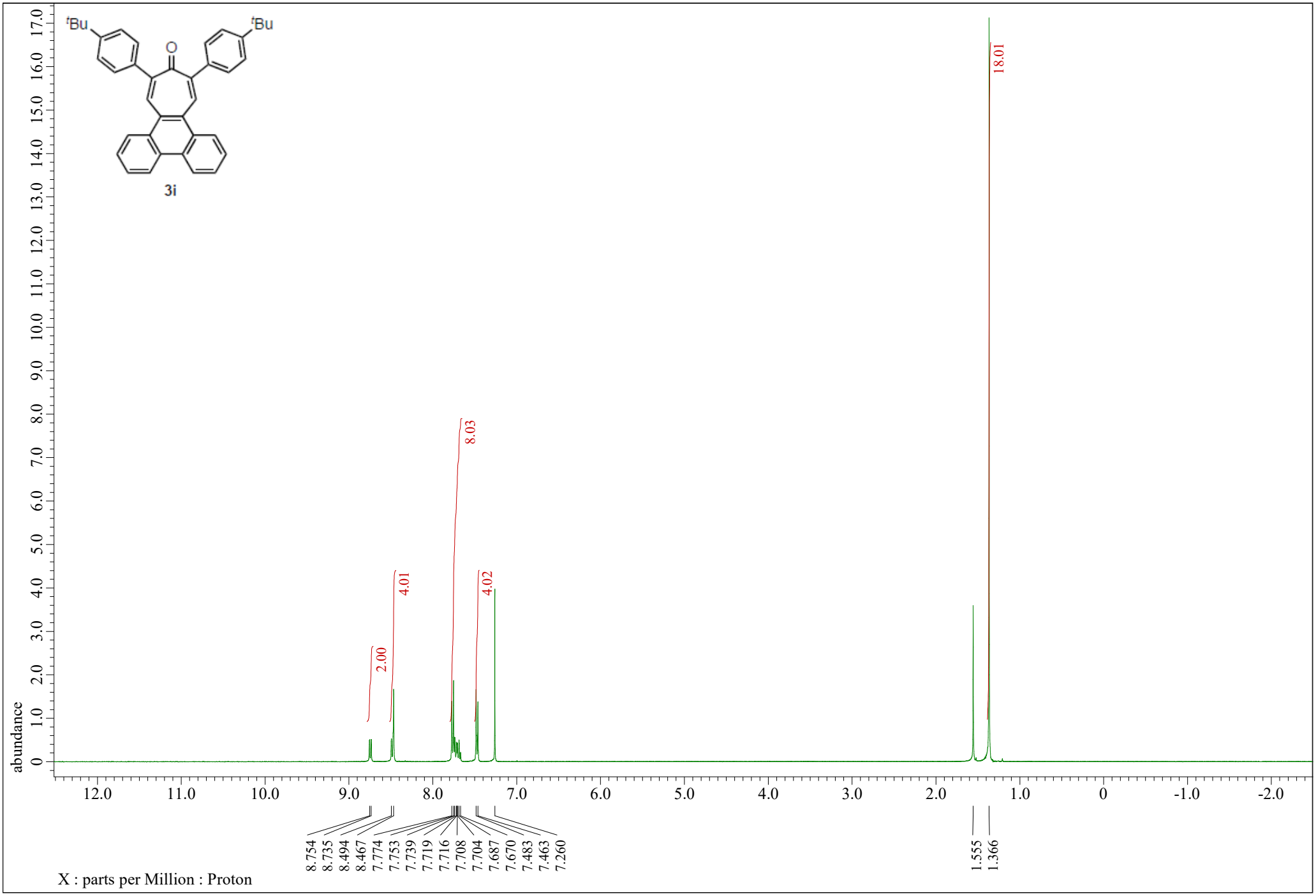
^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **6**



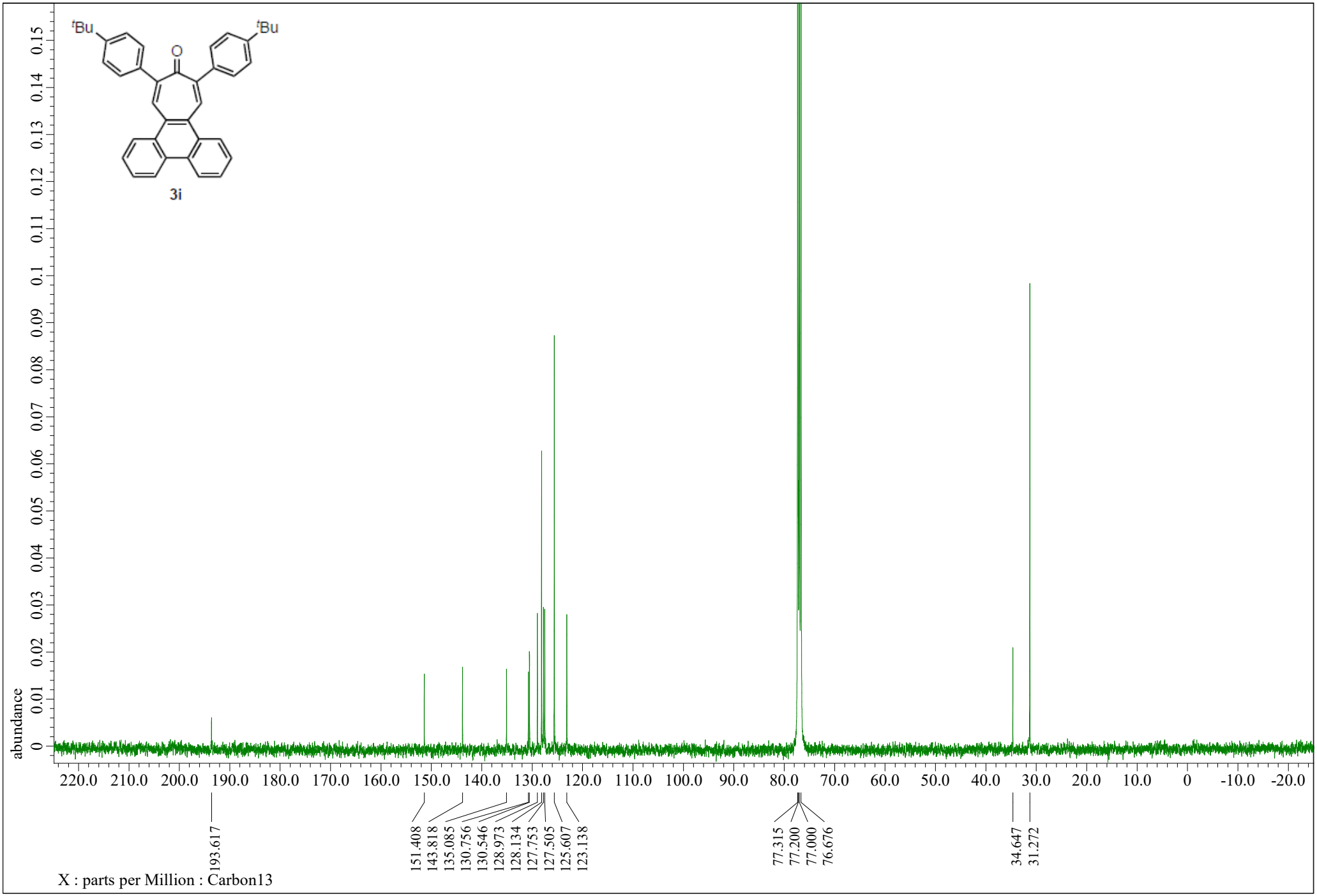
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, $CDCl_3$) of **6**



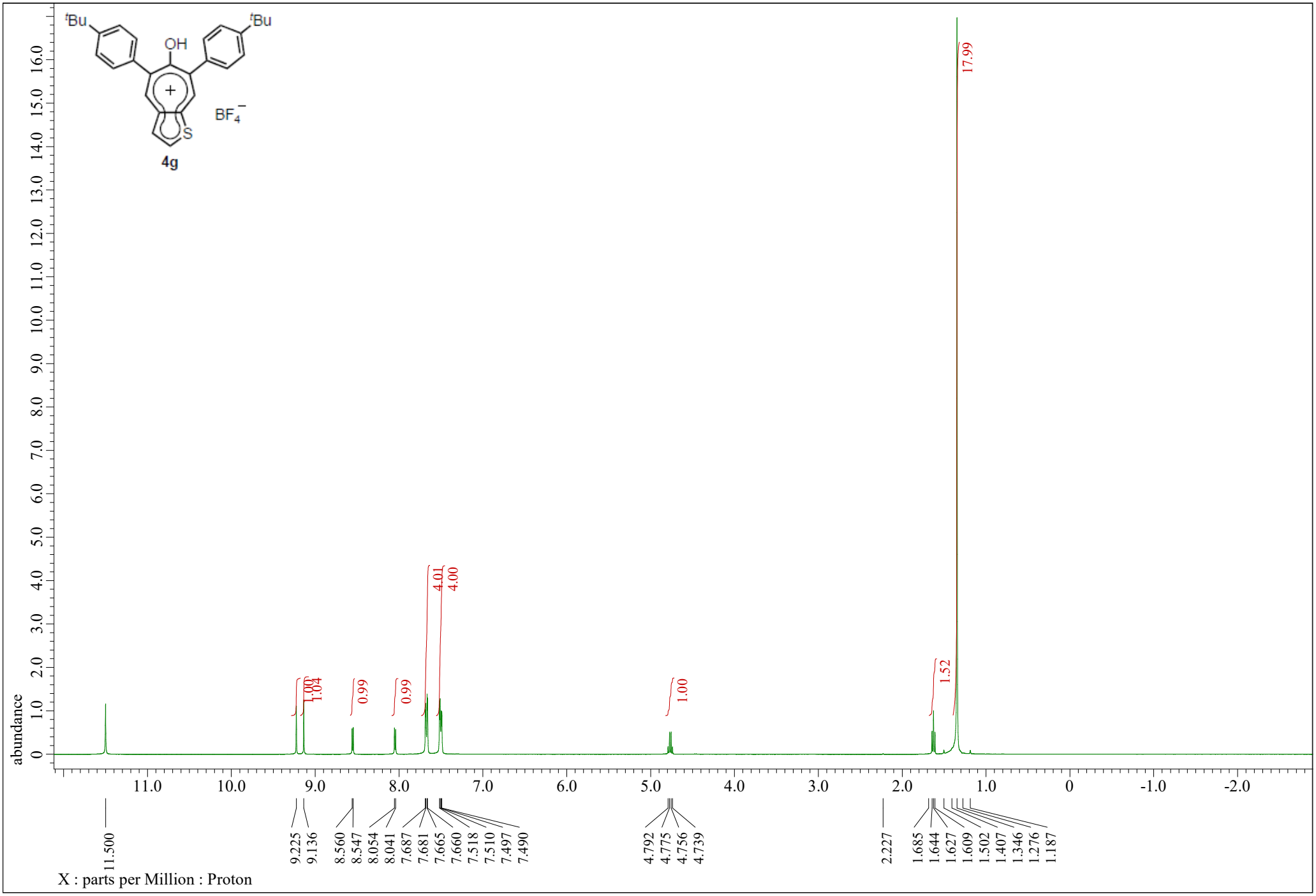
^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of **3i**



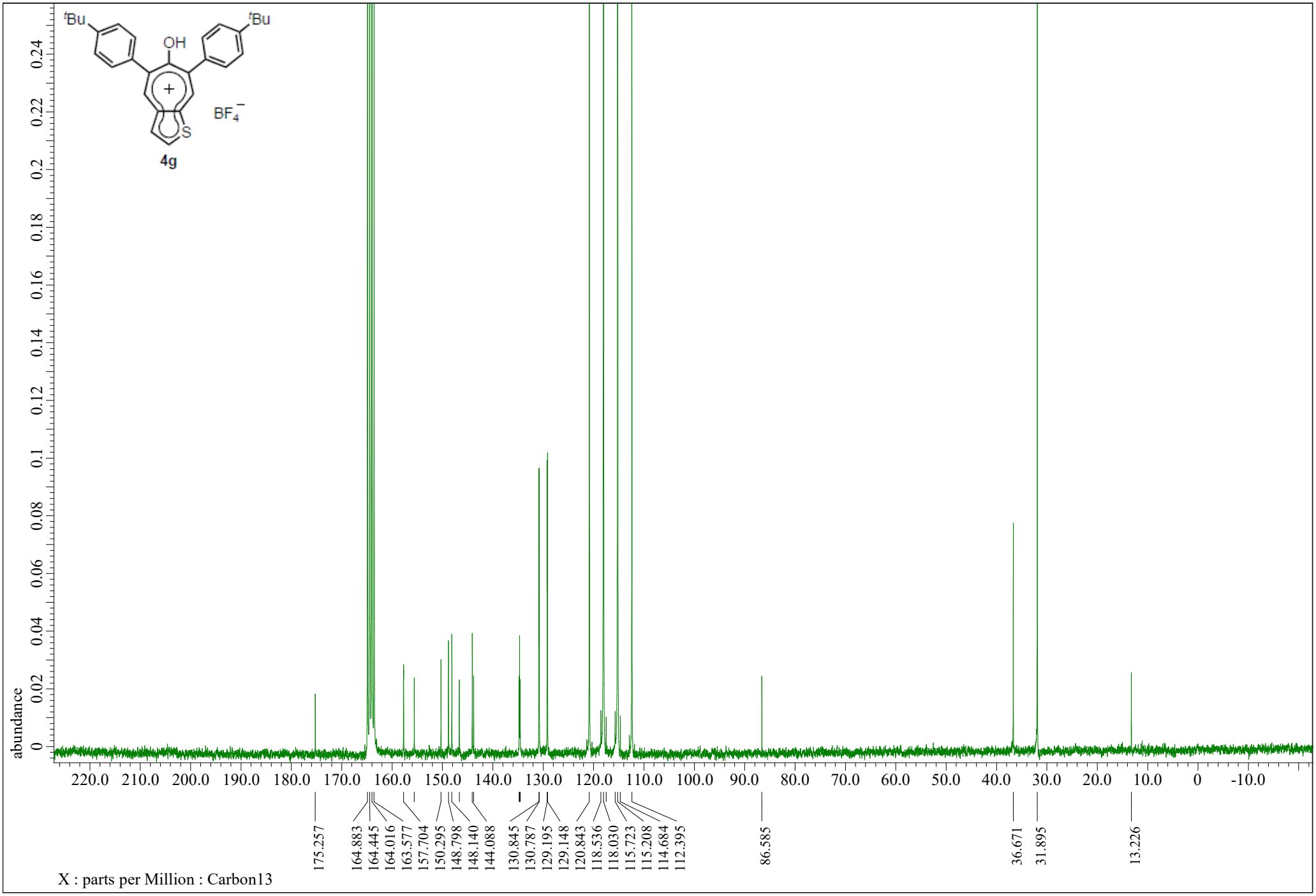
$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, $CDCl_3$) of **3i**



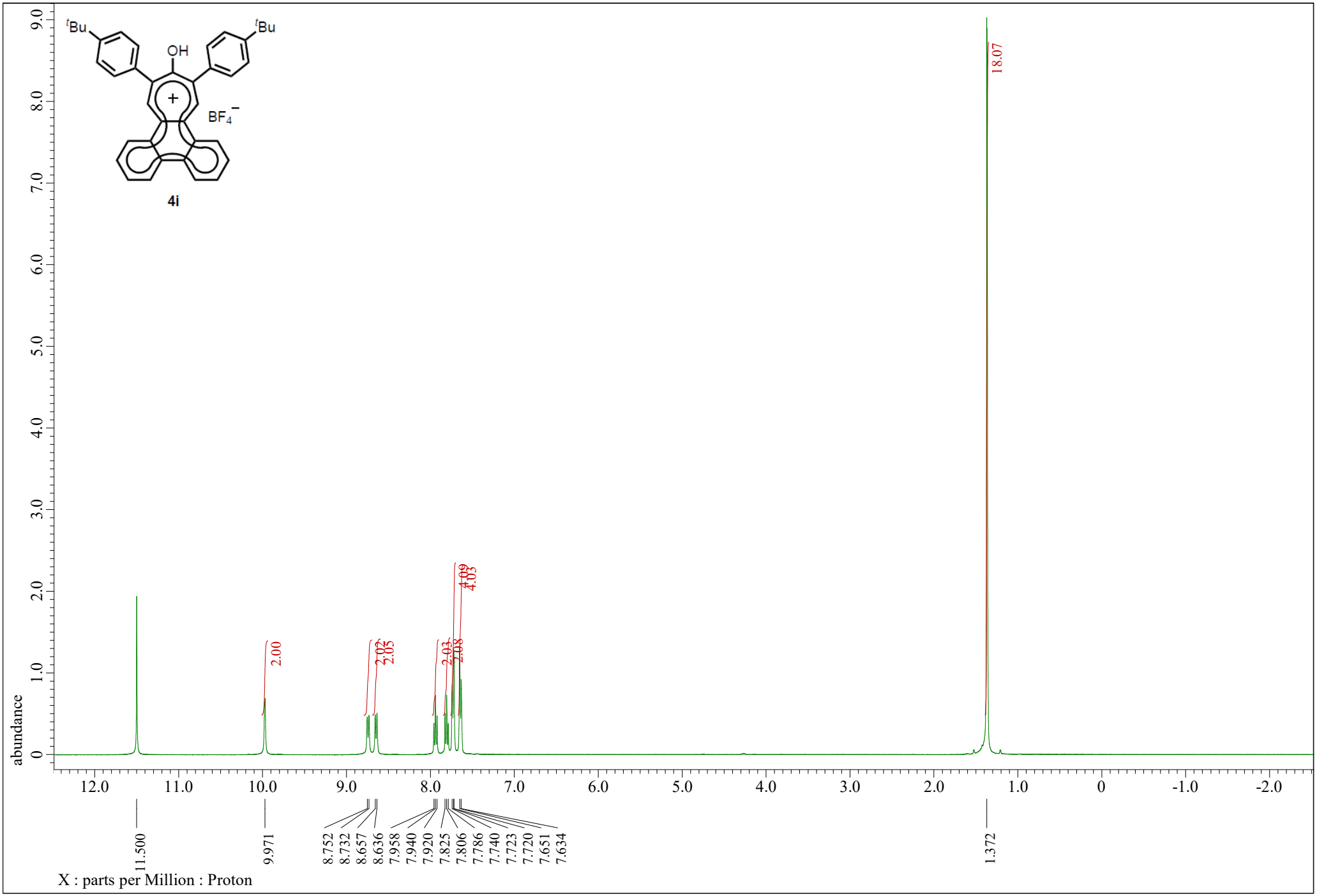
^{1}H-NMR spectrum (400 MHz, TFA-*d*) of **4g**



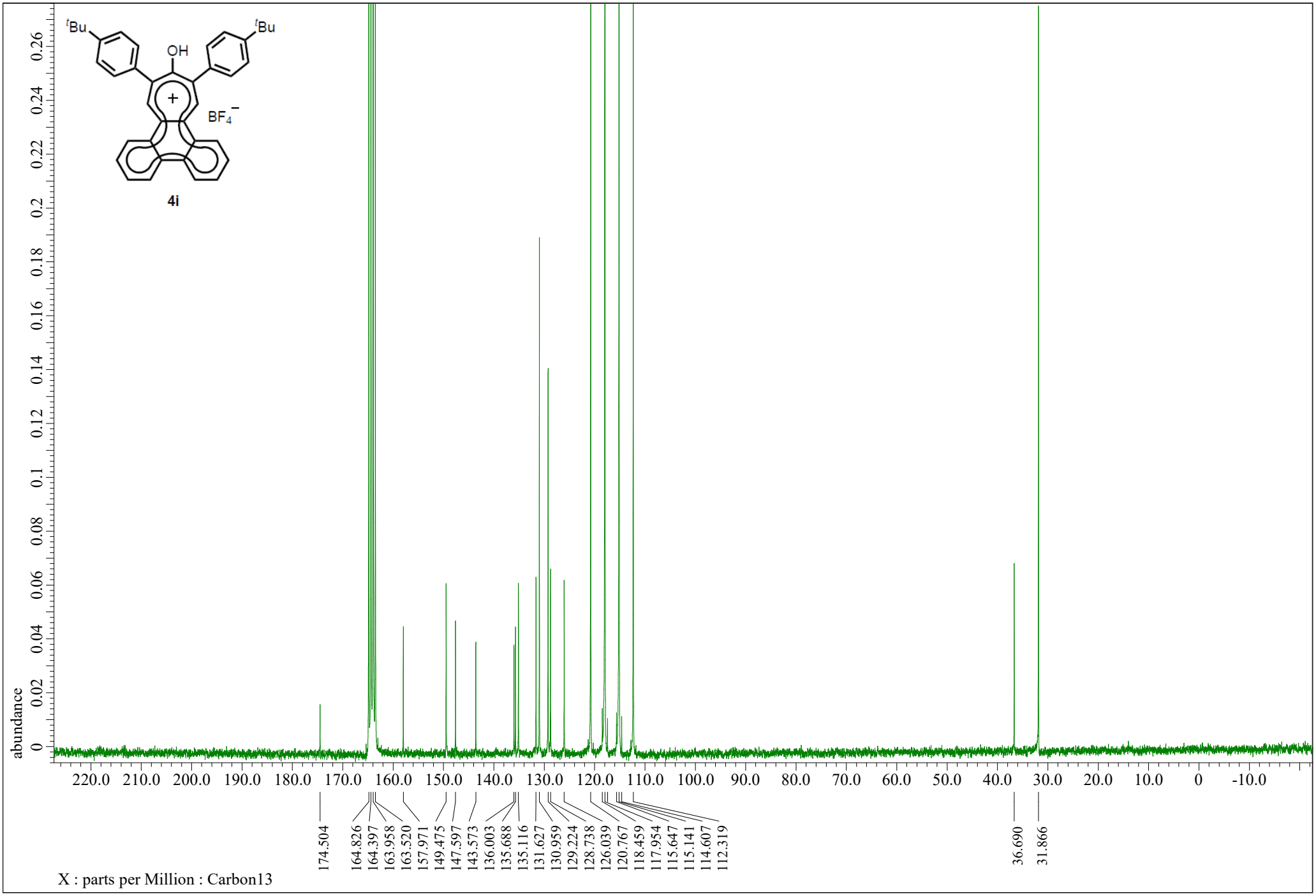
^{13}C-NMR spectrum (101 MHz, TFA-*d*) of **4g**



^{1}H-NMR spectrum (400 MHz, TFA-*d*) of **4i**



$^{13}C\{^{1}H\}$-NMR Spectrum (101 MHz, TFA-*d*) of **4i**



V. Cartesian Coordinates and Energies of Optimized Structures.

4,5-Benzotropone

6	0.000000000	0.707982712	-0.655613871
6	0.000000000	-0.707982712	-0.655613871
6	0.000000000	-1.559566878	0.525245658
6	0.000000000	-1.286520186	1.842156355
6	0.000000000	0.000000000	2.557085127
6	0.000000000	1.286520186	1.842156355
6	0.000000000	1.559566878	0.525245658
8	0.000000000	0.000000000	3.782661377
6	0.000000000	-1.376518075	-1.894308096
6	0.000000000	-0.697484624	-3.098059520
6	0.000000000	0.697484624	-3.098059520
6	0.000000000	1.376518075	-1.894308096
1	0.000000000	-2.620329942	0.279906644
1	0.000000000	-2.127459020	2.530368608
1	0.000000000	2.127459020	2.530368608
1	0.000000000	2.620329942	0.279906644
1	0.000000000	-2.462637006	-1.895281835
1	0.000000000	-1.247008214	-4.033417472
1	0.000000000	1.247008214	-4.033417472
1	0.000000000	2.462637006	-1.895281835

Method: ωB97XD/6-31G(d,p) Key word: opt freq pop=full
imaginary frequencies: 0 Energy: –498.901132 Hartree

1-Hydroxy-4,5-Benzotropylium

6	-0.414866123	2.349911086	0.000000000
6	-1.747772180	2.693563422	0.000000000
6	-2.729633159	1.690823055	0.000000000
6	-2.360452969	0.364026237	0.000000000
6	-1.001552840	-0.025083350	0.000000000
6	0.000000000	0.997147481	0.000000000
6	-0.753856902	-1.432309735	0.000000000
6	0.398732180	-2.165218764	0.000000000
6	1.733700902	-1.701406574	0.000000000
6	2.170143754	-0.358260280	0.000000000
6	1.409610677	0.779534032	0.000000000
8	2.619977309	-2.677919228	0.000000000
1	0.340553399	3.128572727	0.000000000
1	-2.038056688	3.738150225	0.000000000
1	-3.780055063	1.959595805	0.000000000
1	-3.124765667	-0.405790683	0.000000000
1	-1.659218272	-2.034729042	0.000000000
1	0.305599728	-3.246571549	0.000000000
1	3.247348752	-0.208775590	0.000000000
1	1.992121171	1.697970235	0.000000000
1	3.532334153	-2.361428031	0.000000000

Method: ωB97XD/6-31G(d,p) Key word: opt freq pop=full
imaginary frequencies: 0 Energy: –499.266806 Hartree

3b

6	0.000000000	0.706566406	-1.132678131
6	0.000000000	-0.706566406	-1.132678131
6	0.000000000	-1.554944504	0.042772882
6	0.000000000	-1.311758131	1.371792268
6	0.000000000	0.000000000	2.064526992
6	0.000000000	1.311758131	1.371792268
6	0.000000000	1.554944504	0.042772882

8	0.000000000	0.000000000	3.293164611
6	0.000000000	-1.376394591	-2.373604055
6	0.000000000	-0.698514355	-3.575726196
6	0.000000000	0.698514355	-3.575726196
6	0.000000000	1.376394591	-2.373604055
1	0.000000000	-2.612788134	-0.216872555
1	0.000000000	2.612788134	-0.216872555
1	0.000000000	-2.462577616	-2.374350248
1	0.000000000	-1.248195825	-4.511070542
1	0.000000000	1.248195825	-4.511070542
1	0.000000000	2.462577616	-2.374350248
6	0.000000000	-2.475337567	2.328769719
1	-0.873388798	-2.430375016	2.985408098
1	0.000000000	-3.429290542	1.797278791
1	0.873388798	-2.430375016	2.985408098
6	0.000000000	2.475337567	2.328769719
1	-0.873388798	2.430375016	2.985408098
1	0.873388798	2.430375016	2.985408098
1	0.000000000	3.429290542	1.797278791

Method: ωB97XD/6-31G(d,p) Key word: opt freq pop=full
imaginary frequencies: 0 Energy: –577.471685 Hartree

4b

6	0.071295918	2.778537588	0.000000000
6	1.276386780	3.436516108	0.000000000
6	2.476763461	2.702756231	0.000000000
6	2.443183497	1.329513758	0.000000000
6	1.217470815	0.617511230	0.000000000
6	0.000000000	1.361756570	0.000000000
6	1.320657008	-0.800953281	0.000000000
6	0.403173655	-1.824574669	0.000000000
6	-1.013448660	-1.668881012	0.000000000
6	-1.797018261	-0.479846359	0.000000000
6	-1.306869983	0.805479958	0.000000000
8	-1.640326248	-2.835052104	0.000000000
1	-0.852779435	3.347355441	0.000000000
1	1.303556359	4.520378680	0.000000000
1	3.428808054	3.221455717	0.000000000
1	3.372414450	0.769443040	0.000000000
1	2.351394169	-1.147750146	0.000000000
1	-2.084868734	1.565161631	0.000000000
1	-2.600711584	-2.743056603	0.000000000
6	0.910144661	-3.246187663	0.000000000
1	0.547880310	-3.786875739	0.878320582
1	0.547880310	-3.786875739	-0.878320582
1	1.999804661	-3.271559537	0.000000000
6	-3.300149645	-0.662859800	0.000000000
1	-3.644074946	-1.199360227	-0.892865818
1	-3.644074946	-1.199360227	0.892865818
1	-3.812154187	0.298848578	0.000000000

Method: ωB97XD/6-31G(d,p) Key word: opt freq pop=full
imaginary frequencies: 0 Energy: –577.837943 Hartree

3c

6	-1.958173000	-0.064599000	0.707712000
6	-1.958173000	-0.064599000	-0.707712000
6	-0.776885000	-0.151751000	-1.554570000
6	0.518136000	0.097252000	-1.282006000

6	1.037668000	0.650748000	0.000000000
6	0.518136000	0.097252000	1.282006000
6	-0.776885000	-0.151751000	1.554570000
8	1.867390000	1.534005000	0.000000000
6	-3.194044000	-0.031840000	-1.378485000
6	-4.395455000	0.034119000	-0.697522000
6	-4.395455000	0.034119000	0.697522000
6	-3.194044000	-0.031840000	1.378485000
1	-0.991622000	-0.422590000	-2.584887000
1	-0.991622000	-0.422590000	2.584887000
1	-3.194314000	-0.050839000	-2.464267000
1	-5.330249000	0.074216000	-1.246359000
1	-5.330249000	0.074216000	1.246359000
1	-3.194314000	-0.050839000	2.464267000
6	1.556243000	-0.112777000	-2.343093000
8	2.718173000	-0.339751000	-2.118385000
8	1.036466000	-0.062393000	-3.583765000
6	1.969574000	-0.323128000	-4.632186000
1	2.766411000	0.423405000	-4.626371000
1	2.414819000	-1.313671000	-4.515177000
1	1.398896000	-0.265287000	-5.557933000
6	1.556243000	-0.112777000	2.343093000
8	2.718173000	-0.339751000	2.118385000
8	1.036466000	-0.062393000	3.583765000
6	1.969574000	-0.323128000	4.632186000
1	2.414819000	-1.313671000	4.515177000
1	2.766411000	0.423405000	4.626371000
1	1.398896000	-0.265287000	5.557933000

Method: ωB97XD/6-31G(d,p) Key word: opt freq pop=full
imaginary frequencies: 0 Energy: –954.431805 Hartree

4c

6	-3.326845822	1.501281412	0.228877472
6	-4.550741802	0.870779907	0.162274900
6	-4.612477514	-0.517023430	-0.025060449
6	-3.450676114	-1.254873577	-0.131660142
6	-2.185169355	-0.637737491	-0.067639383
6	-2.120316874	0.774535763	0.108022718
6	-1.052969611	-1.503202791	-0.148203026
6	0.297119115	-1.289359243	-0.140349922
6	0.992718781	-0.038179104	-0.195637858
6	0.410006420	1.258991607	0.000327707
6	-0.926587839	1.545327136	0.151229091
8	2.261214497	-0.162952330	-0.456307343
1	-3.279647641	2.575938802	0.370432705
1	-5.464413234	1.447045834	0.253451407
1	-5.574557033	-1.013686885	-0.082306152
1	-3.505779653	-2.329901423	-0.266745526
1	-1.307233840	-2.557385546	-0.238240079
1	-1.094136977	2.610146365	0.302590509
1	2.707289454	0.715228053	-0.462389613
6	1.104737731	-2.580969749	-0.169318686
8	0.761237184	-3.528237972	-0.831207445
8	2.124078387	-2.552087588	0.672053646
6	2.912518668	-3.755429222	0.733010012
1	2.286119557	-4.600625341	1.021580595
1	3.366314243	-3.952319080	-0.239303215
1	3.674460976	-3.562315463	1.484311190
6	1.261000343	2.518481589	0.059560504
8	0.814072156	3.603790381	0.314092162
8	2.561313465	2.306030322	-0.206256990
6	3.430340890	3.465970971	-0.166102335

1	3.112068493	4.181137899	-0.923785777
1	3.382905653	3.919595790	0.823146334
1	4.425342420	3.083235810	-0.377718239

Method: ωB97XD/6-31G(d,p) Key word: opt freq pop=full
imaginary frequencies: 0 Energy: –954.804542 Hartree