Supporting information for:

Strongly emitting fluorophores based on 1-azaperylene scaffold

Daniel T. Gryko, Joanna Piechowska and Michał Gałęzowski

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1. General experimental:

All chemicals were used as received unless otherwise noted. Reagent grade solvents (MeCN, CH_2Cl_2, hexane, toluene) were distilled prior to use. All reported NMR spectra were recorded on 400 MHz or 500 MHz spectrometer unless otherwise noted. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. UV-vis absorption spectra were recorded in THF. Chromatography was performed on neutral alumina (act. 1). Mass spectra were obtained via EI or electrospray MS. A spectrophotometer and a spectrofluorimeter were used to acquire absorption and emission spectra. Spectrophotometric grade solvents were used without further purification.

2. Synthesis

8-(1-Naphthyl)-isoquinoline (**6**): PEG-400 (20 mL) was added to the mixture of 8-bromoisoquinoline (624 mg, 3.0 mmol), 1-naphthaleneboronic acid (824 mg, 4.5 mmol), $Pd(OAc)_2$ (13.2 mg, 0.06 mmol) and K_2CO_3 (6 mmol, 828 mg). The reaction mixture was stirred at 45 °C overnight, added to water and extracted four times with CH_2Cl_2. After drying (Na_2SO_4) the solvent was removed *in vacuo* and product was isolated by chromatography on a silica gel (hexanes, then hexanes:EtOAc, 95:5, 9:1). 693 mg (91%) of compound **6** was obtained as colorless crystals. mp 95-96 ^oC; ^1H NMR (600 MHz, $CDCl_3$, δ) 7.31-7.37 (m, 2H), 7.49-7.51 (m, 2H), 7.59-7.62 (m, 2H), 7.76 (d, 1H, *J*=5.6), 7.80-7.83 (m, 1H), 7.92-8.00 (m, 3H), 8.53 (d, 1H, *J*=5.8), 8.83 (s, 1H); ^{13}C NMR (600 MHz, $CDCl_3$, δ) 120.7, 125.2, 126.0, 126.1, 126.37, 126.41, 127.9, 128.1, 128.3, 128.6, 129.3, 130.1, 123.7, 133.5, 136.05, 136.09, 129.4, 142.5, 151.3; EI-HR obsd 255.1037 [$M^{\cdot+}$], calcd exact mass 255.1048;

12-Cyano-1-azaperylene (**7**): Under air, a reaction tube was charged with 1-azaperylene (**2**) (50.6 mg, 0.2 mmol), CuCN (21.5 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), $CuBr_2$ (17.9 mg, 0.08 mmol) and dry DMF (1 mL). The mixture was kept stirring at 130 ^oC for 24 h. After the completion of the reaction, as monitored by TLC, the solvent was evaporated under reduced pressure and the residue was purified by dry column vacuum chromatography column chromatography on a neutral Al_2O_3 (eluting with

CH_2Cl_2:hexanes 4:96 then 1:9). The crystallization from cyclohexane afforded pure product **7** as a orange crystals (34 mg, 61%). mp (dec) 200-230°C; ^{1}H NMR (600 MHz, $CDCl_3$, δ) 7.45-7.52 (m, 2H), 7.55-7.60 (m, 2H), 7.64 (d, 2H, *J*=8.4), 7.67 (d, 1H, *J*=8.4), 8.02 (dd, 1H, J_1=1.4, J_2=6.8), 8.08 (d, 1H, *J*=7.3), 8.59 (d, 1H, *J*=5.4); ^{13}C NMR (600 MHz, $CDCl_3$, δ) 106.8, 120.9, 121.3, 121.4, 122.5, 123.1, 126.6, 128.3, 128.62, 128.63, 129.69, 129.71, 130.4, 130.8, 131.6, 134.4, 135.0, 136.6, 142.9, 148.5; EI-HR obsd 278.0853 [$M^{\cdot+}$], calcd exact mass 278.0844; λ_{abs} (acetonitrile) 430, 458 nm; λ_{em} (cyclohexane) 457, 487, 520 nm;

1-Azaperylene (**2**): *Method B*: Compound **6** (42 mg, 0.16 mmol) was dissolved in dry toluene (1 mL), subsequently potassium (12 mg, 1,6 mmol) was added under argon atmosphere. Reaction was stirred at 95 °C for 2 h, quenched with EtOH under Ar, filtrated through Celite and evaporated under reduced pressure. The residue was chromatographed (dry column vacuum chromatography column chromatography on Al_2O_3, hexanes/AcOEt, 95:5). The crystallization (CH_2Cl_2/petroleum ether) afforded pure product **2** as a yellow crystals, (13.7 mg, 34%), R_f =0.32 (silica, CH_2Cl_2/acetone 99:1). The purity of 1-azaperylene prepared by method B is compared to that prepared by method A.

3. Calculation Methodology

All calculations were performed using the Gaussian 03 program.[1] The ground state geometries of hydroxyazapenantrene and hydroxyazaperylene and its proton-transfer tautomer were optimized using DFT theory with a 6-311++G(d, p) basis set.[2] Time-dependent DFT (TDB3LYP) calculations were then performed with the same basis set at the optimized geometry to obtain electronic transition energies and the corresponding orbital configuration.[3]

Table S1. The calculated energy levels of the lowest singlet states of enol and keto tautomer forms (Gaussian 03 DFT/6-311++G(d,p))

State	Excitation	E_{cal} (eV)	λ_{cal} (nm)	Oscillator strength
10-hydroxybenzo[*h*]quinoline				
enol				
S_1	HOMO → LUMO	3.38	366.24	0.1272
keto				
S_1	HOMO → LUMO	2.51	493.89	0.1351
12-hydroxy-1-azaperylene				
enol				
S_1	HOMO → LUMO	2.79	443.90	0.3262
keto				

S_1	HOMO → LUMO	2.73	453.38	0.2811

Cartesian Coordinates and Energies

10-hydroxybenzo[*h*]quinoline

Enol form

E(HF) = -630.972902408

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	6	-3.460207	0.127163	-0.000177
2	6	-2.682375	1.272116	-0.000113
3	6	-1.279185	1.167928	0.000000
4	6	-0.657125	-0.115872	0.000038
5	6	-1.486393	-1.278403	0.000040
6	6	-2.871276	-1.138913	-0.000096
7	6	-0.455785	2.345275	0.000072
8	6	0.787116	-0.189687	0.000008
9	6	1.563544	1.004395	0.000077
10	6	0.899914	2.274179	0.000135
11	6	2.963527	0.876794	0.000058
12	1	3.577633	1.771578	0.000126
13	6	3.544081	-0.377072	-0.000074
14	6	2.704514	-1.497827	-0.000228
15	1	-0.950943	3.310465	0.000073
16	1	-4.541635	0.207889	-0.000258
17	1	-3.141718	2.253782	-0.000157
18	1	-3.474055	-2.038906	-0.000077
19	1	1.502949	3.175983	0.000179
20	1	4.619590	-0.503248	-0.000106
21	1	3.120315	-2.500825	-0.000374
22	7	1.381469	-1.411028	-0.000199
23	8	-0.977044	-2.522911	0.000345
24	1	0.011838	-2.436687	0.000788

Keto form

E(HF) = -630.951924962

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	6	-3.512682	-0.377681	-0.000152
2	1	-4.579224	-0.485717	-0.000224
3	6	-2.706841	-1.476138	0.000130
4	1	-3.084534	-2.480476	0.000220
5	6	-2.902926	0.884148	0.000041
6	1	-3.516589	1.768135	-0.000065
7	6	-1.535043	1.017491	-0.000126
8	6	-0.740374	-0.161948	-0.000207
9	6	0.670961	-0.120337	-0.000053
10	6	1.311592	1.152887	0.000091
11	6	0.484081	2.348877	0.000119

12	6	-0.849764	2.292409	0.000069
13	1	-1.442159	3.190000	0.000230
14	6	2.681679	1.234711	-0.000058
15	6	3.434598	0.044773	-0.000188
16	1	4.509351	0.116312	-0.000036
17	1	0.983523	3.301304	0.000253
18	6	2.858267	-1.190433	-0.000077
19	1	3.451919	-2.085873	0.000033
20	1	3.173031	2.190134	0.000173
21	8	0.887106	-2.467174	0.000139
22	1	-0.724078	-2.143178	-0.000313
23	6	1.437638	-1.347350	0.000144
24	7	-1.379314	-1.348815	0.000030

12-hydroxy-1-azaperylene

Enol form

E(HF) = -860.894075028

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	6	3.567387	0.760122	0.000071
2	6	2.786179	-0.430455	-0.000005
3	6	1.361669	-0.321018	-0.000019
4	6	0.754100	0.972138	-0.000048
5	6	1.570384	2.120533	-0.000006
6	6	2.983519	1.994050	0.000073
7	6	0.570779	-1.511810	-0.000053
8	6	-0.695903	1.078735	-0.000120
9	6	-1.495273	-0.106490	-0.000029
10	6	-0.896763	-1.402485	0.000017
11	6	-2.914652	0.041755	0.000005
12	6	-3.447665	1.359752	-0.000024
13	6	-2.593113	2.428064	-0.000065
14	1	4.648686	0.670833	0.000131
15	1	3.569932	2.904763	0.000146
16	1	-4.520429	1.512092	-0.000015
17	1	-2.966181	3.446686	-0.000091
18	7	-1.244804	2.299263	-0.000120
19	8	1.074404	3.357588	0.000123
20	1	0.069624	3.263583	0.000104
21	6	-3.140660	-2.360480	0.000103
22	1	-3.762836	-3.248776	0.000157
23	6	2.618692	-2.845206	-0.000053
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26	1	4.475134	-1.769932	-0.000011
27	6	1.222091	-2.743752	-0.000068
28	1	0.645843	-3.659683	-0.000078
29	6	-1.746195	-2.507290	0.000077
30	1	-1.339630	-3.509675	0.000111
31	6	-3.726962	-1.112387	0.000070

32	1	-4.805721	-1.004543	0.000095

Keto form

E(HF) = -860.893128344

Center Number	Atomic Number	Coordinates(Angstroms)		
		X	Y	Z
1	6	3.564640	0.803190	0.000000
2	6	2.788239	-0.407737	0.000000
3	6	1.364413	-0.312373	0.000000
4	6	0.747694	0.977818	0.000000
5	6	1.547405	2.194273	0.000000
6	6	2.989795	2.029535	0.000000
7	6	0.587428	-1.507705	0.000000
8	6	-0.664267	1.049406	0.000000
9	6	-1.480693	-0.124173	0.000000
10	6	-0.872328	-1.412127	0.000000
11	6	-2.903139	0.018880	0.000000
12	6	-3.459241	1.343522	0.000000
13	6	-2.635091	2.419013	0.000000
14	1	4.646689	0.709945	0.000000
15	1	3.579187	2.938819	0.000000
16	1	-4.532632	1.480013	0.000000
17	1	-2.990224	3.440877	0.000000
18	7	-1.278699	2.265535	0.000000
19	8	1.037030	3.347029	0.000000
20	1	-0.597935	3.054851	0.000001
21	6	-3.106158	-2.386337	0.000000
22	1	-3.728486	-3.274467	0.000000
23	6	2.641793	-2.825808	0.000000
24	1	3.123967	-3.796163	0.000000
25	6	3.403984	-1.663530	0.000000
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27	6	1.253706	-2.742460	0.000000
28	1	0.684683	-3.662834	0.000000
29	6	-1.721482	-2.529189	0.000000
30	1	-1.307206	-3.528007	0.000000
31	6	-3.701672	-1.131741	0.000000
32	1	-4.781159	-1.033079	0.000000

4. References

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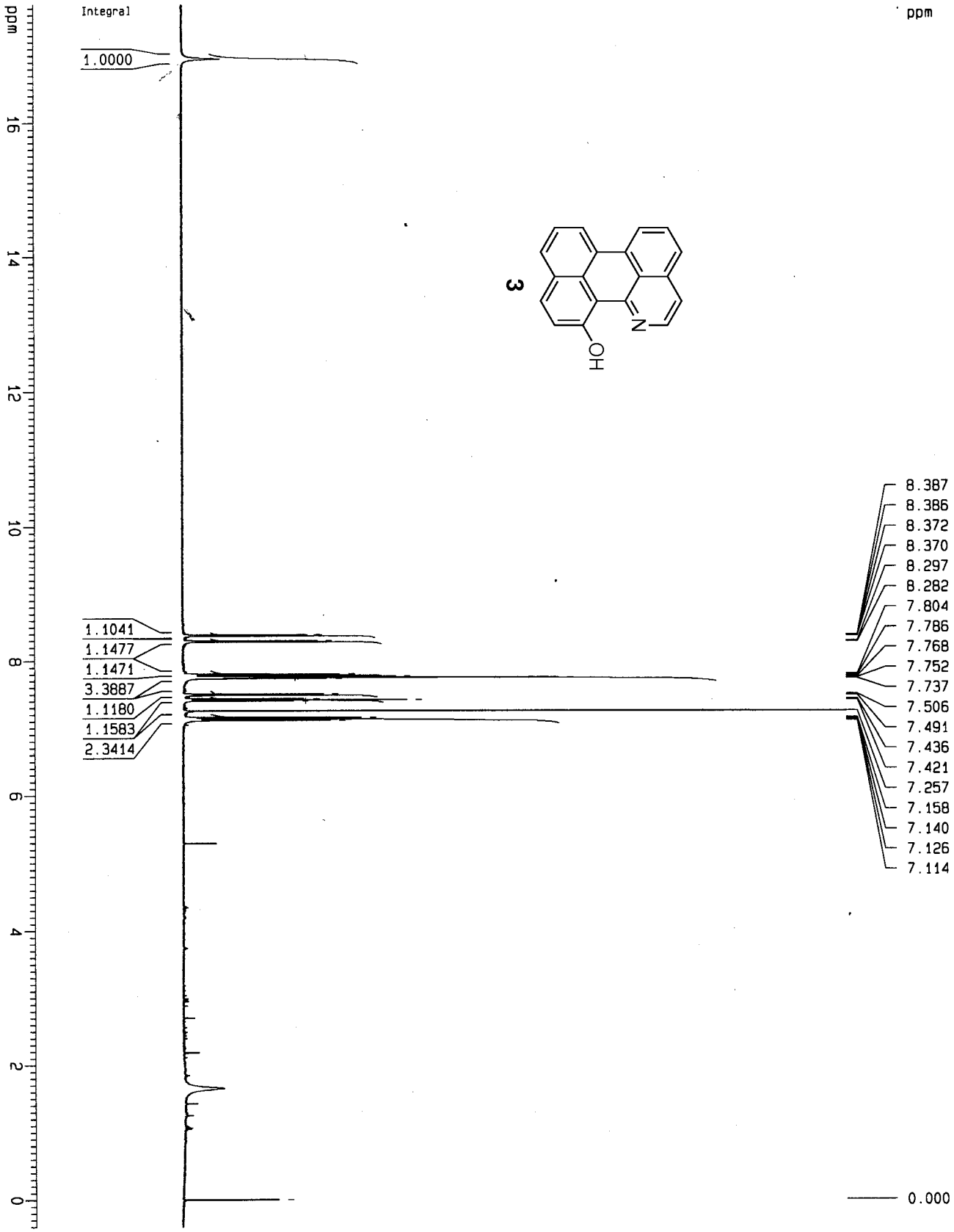
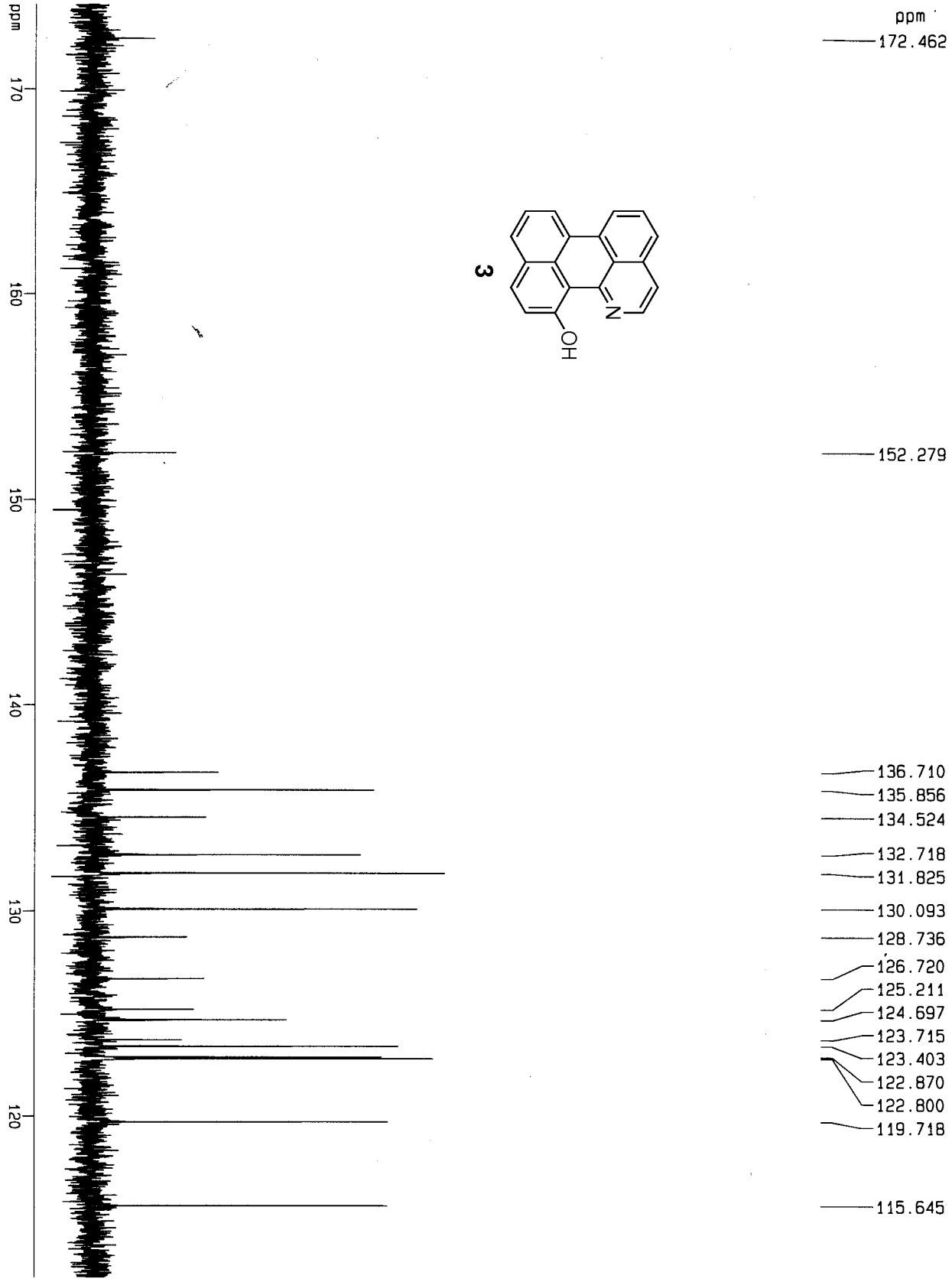
3. R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett*. 1996, **256**, 454.

5. Spectral data

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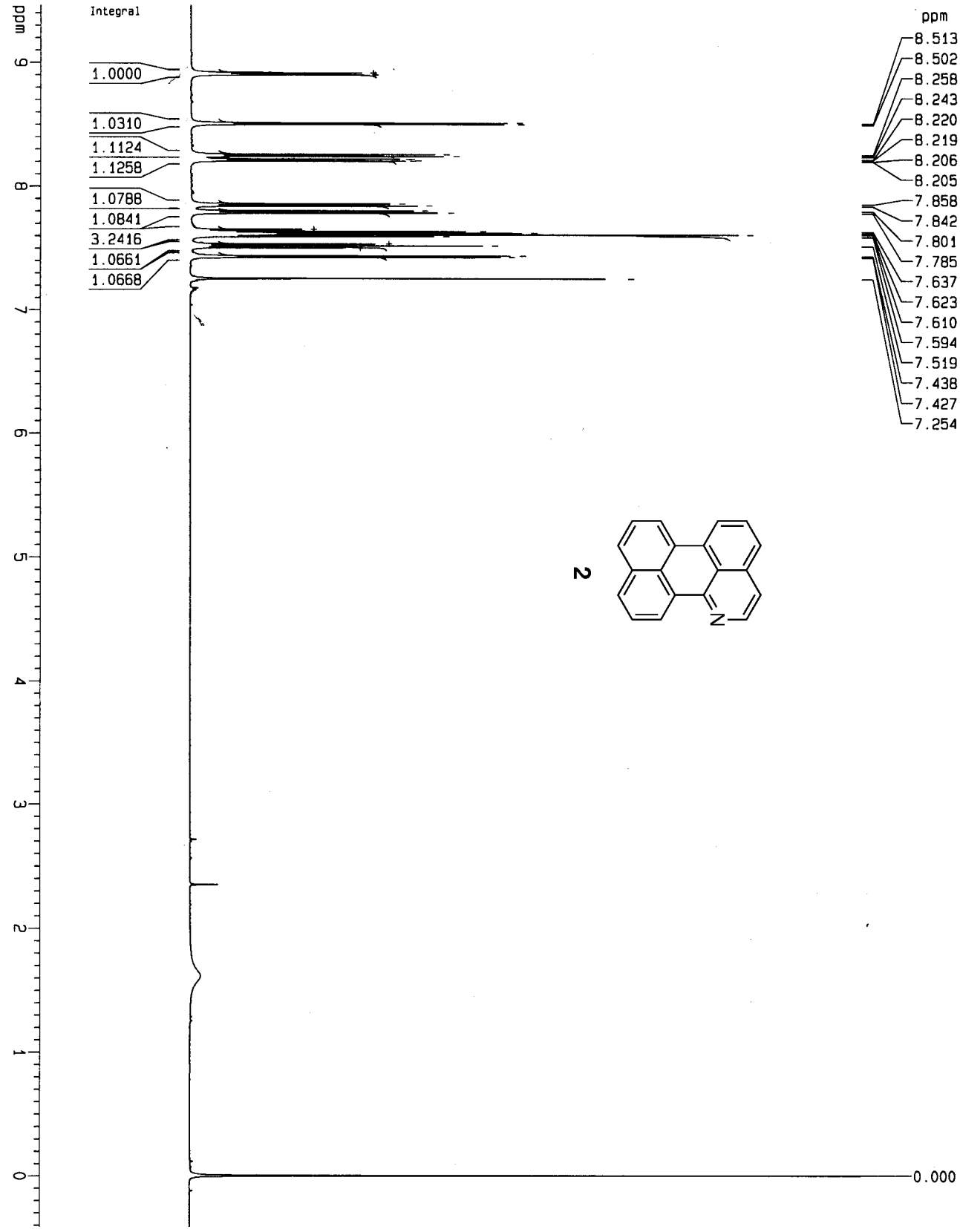
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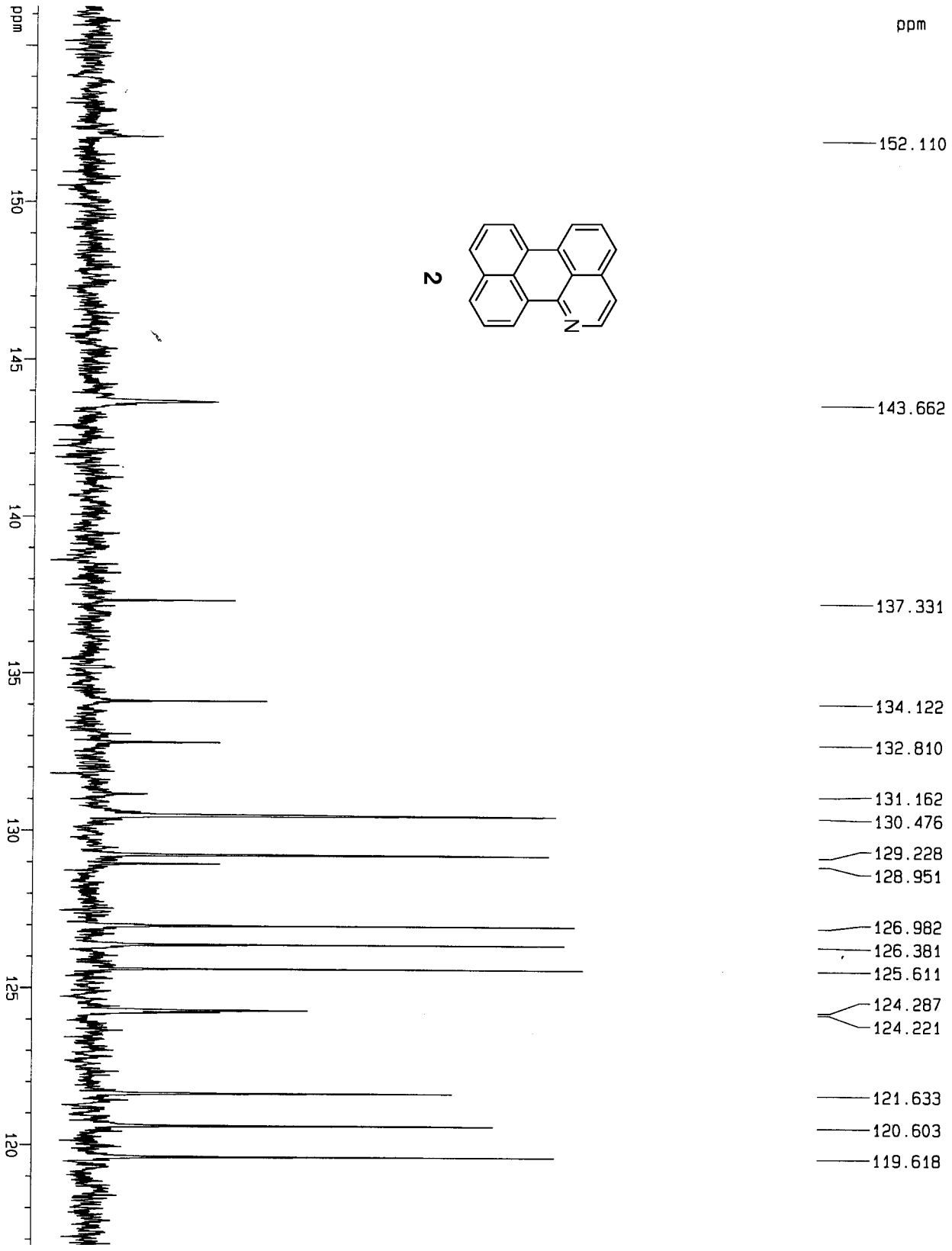
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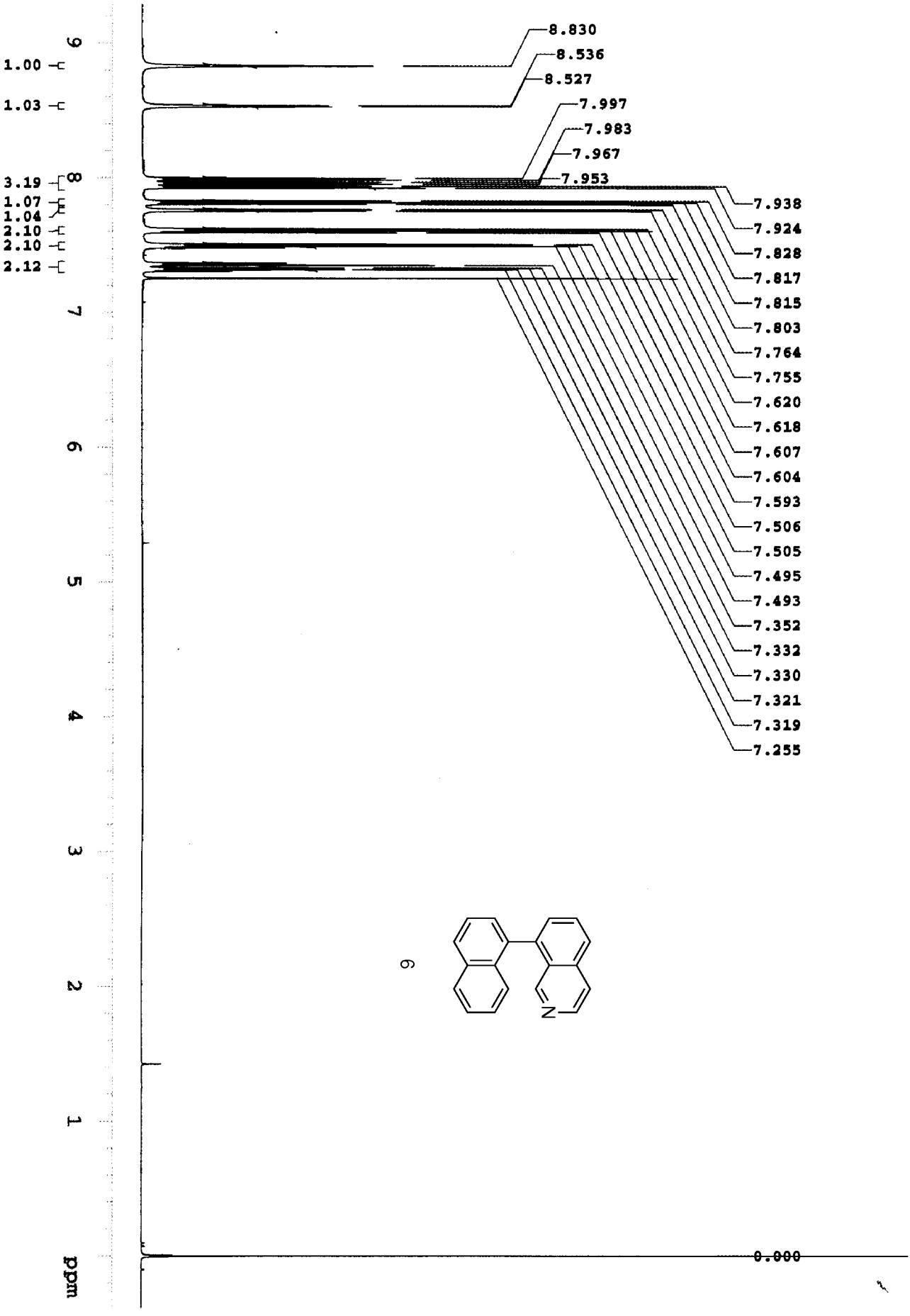
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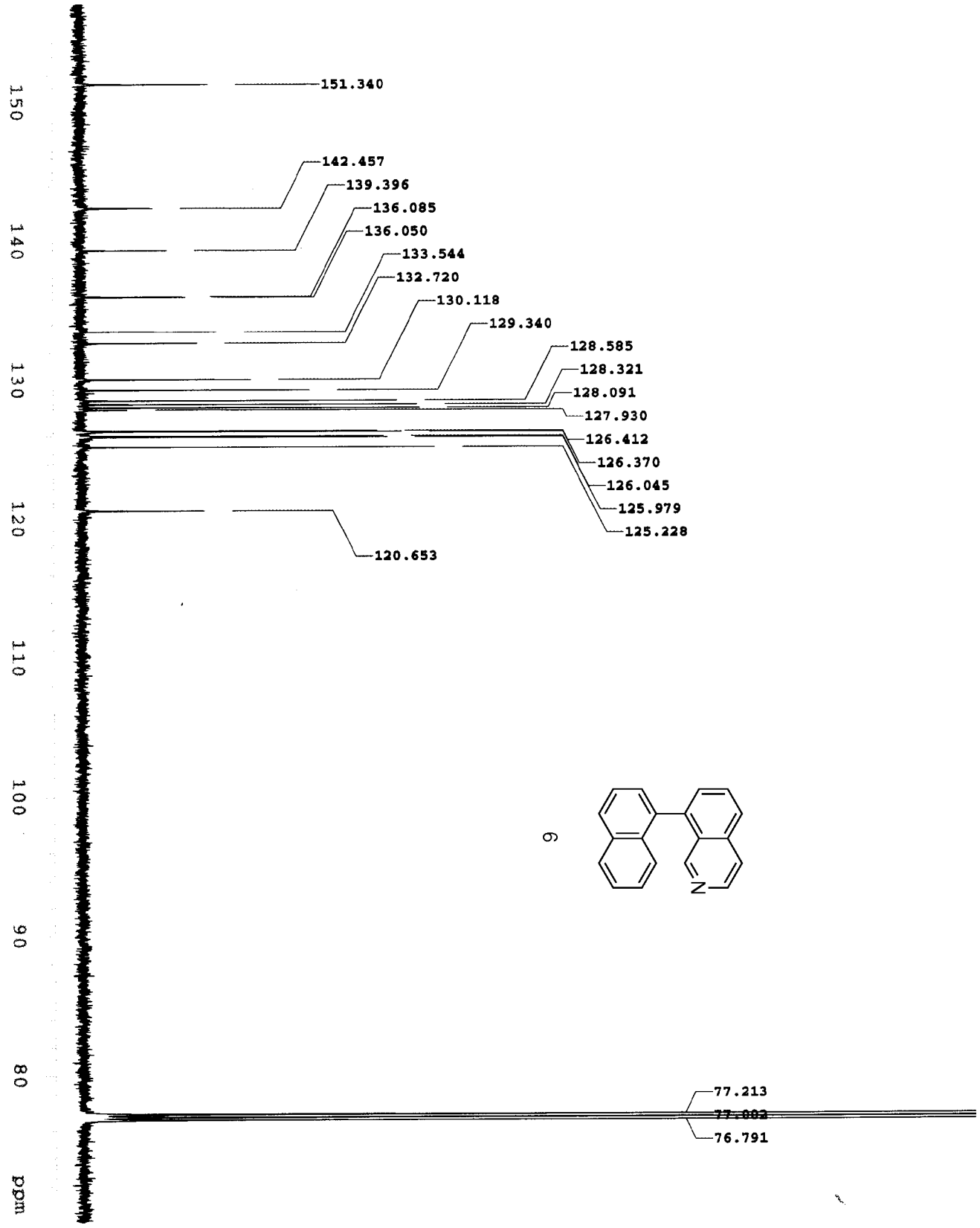
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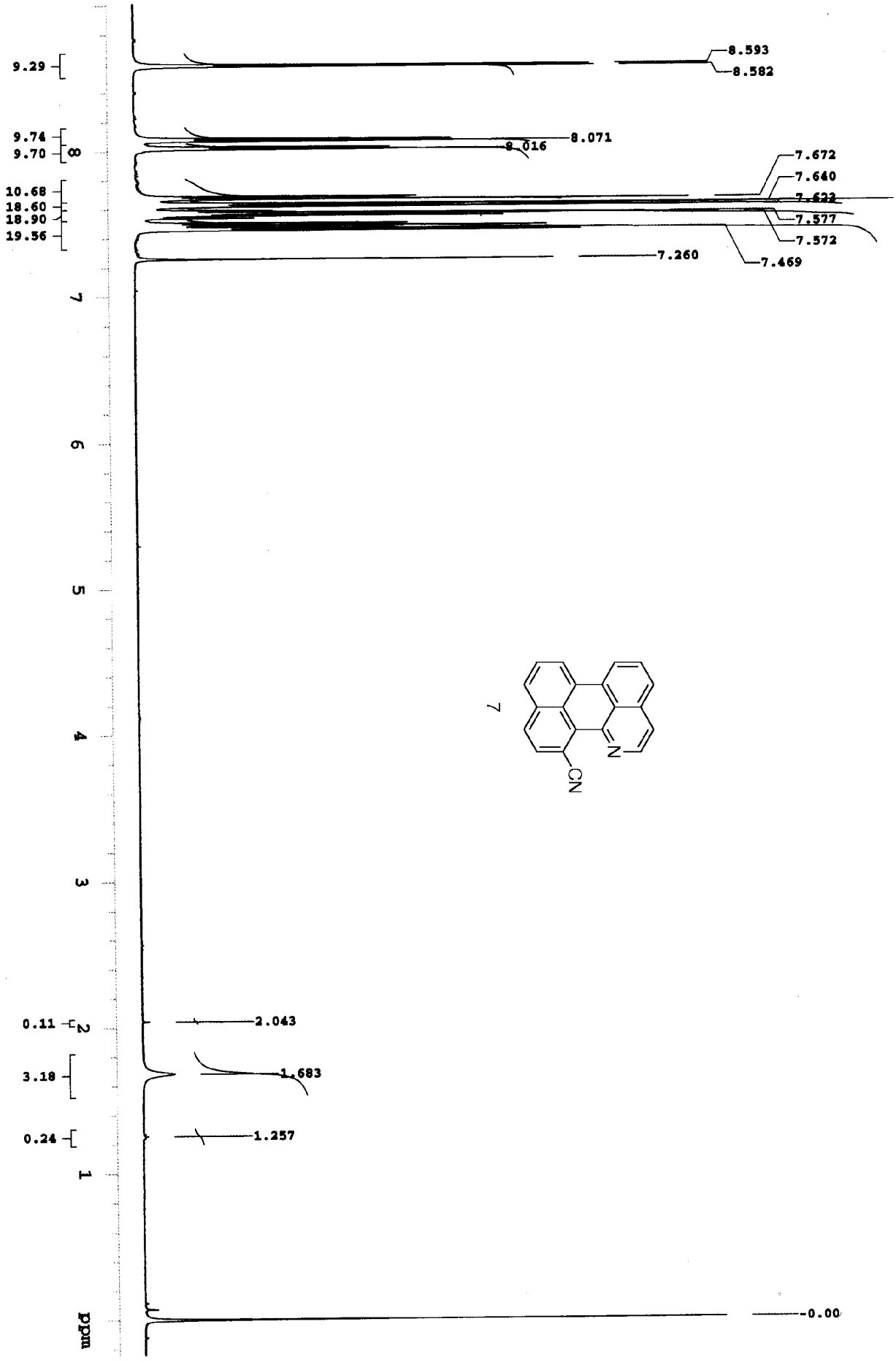
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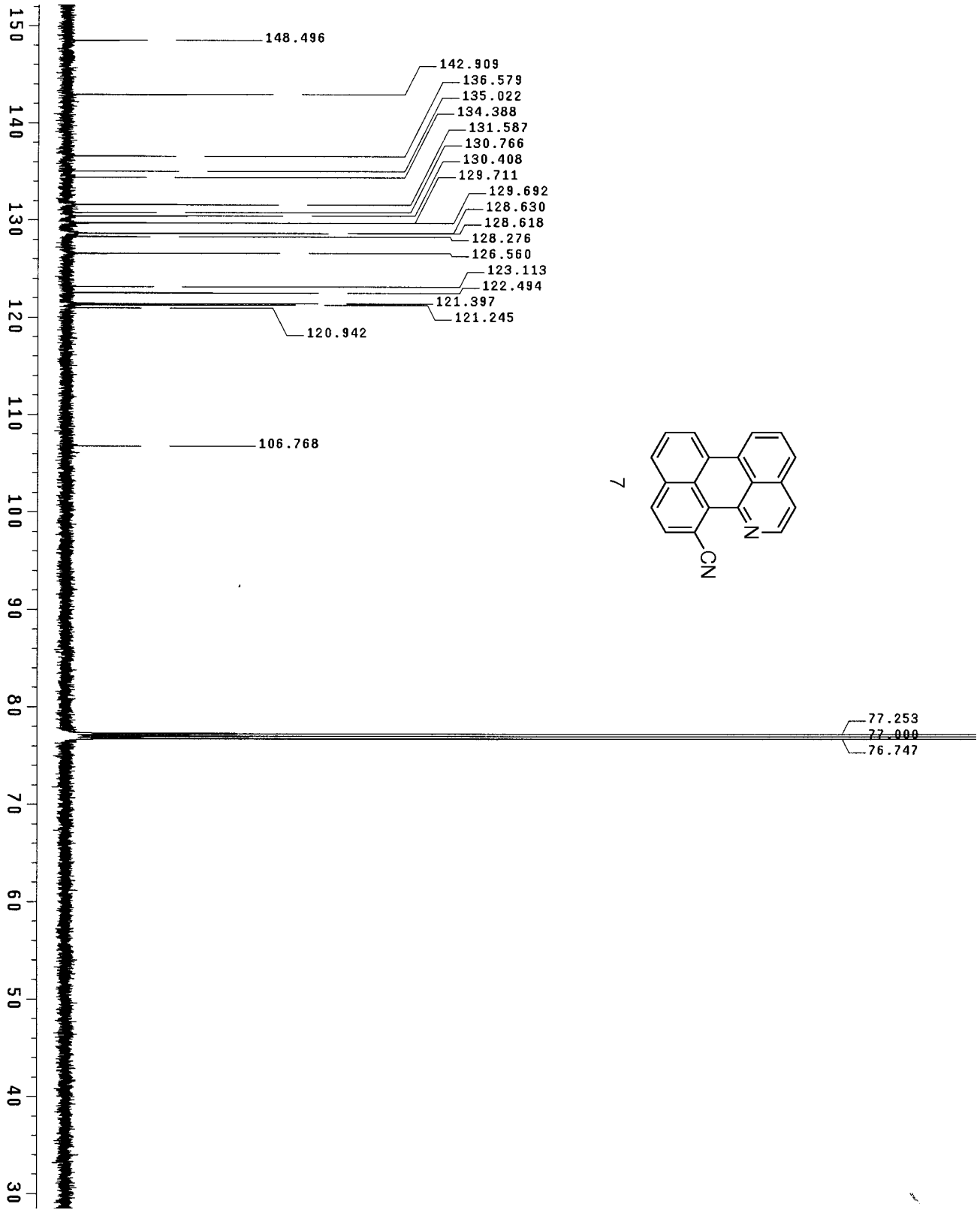
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