

## Supporting Information

# Protecting Triplet Excited State in Sterically Congested Platinum Porphyrin

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### Synthetic Procedures

**2-Bromo-1,3,5-triethylbenzene.**<sup>1</sup> To 50 mL three neck round bottom flask fitted with dropping funnel and magnetic stir bar was charged with 1,3,5-triethylbenzene (4.0 g, 24.7 mmol) and iron fillings (0.125 g, 2.2 mmol) in carbon tetrachloride (50 mL). Resulted solution was cooled to 0°C and protected against the light. Solution of bromine (4.0 g, 25 mmol) in carbon tetrachloride (5 mL) was added dropwise over 2 hours. Then bath was removed and reaction mixture was stirred 12 hours at room temperature. Reaction mixture was washed two times with water, 10 % sodium hydroxide and water again. Organic phase was separated and dried over magnesium sulfate. Solvent was removed under reduced pressure to afford colorless oil (5.3 g, 89 %) which was used without further purification for the next step. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.94 (m, 2H), 2.80 (m, 4H), 2.61(m, 2H), 1.26 (m, 9H).

**2,4,6-Triethylbenzaldehyde.** 2,4,6-Triethylbenzaldehyde was synthesized similarly to 2,4,6-trimethylbenzaldehyde.<sup>2</sup> A 100 mL three neck round bottom flask fitted with a reflux condenser, stirring bar and nitrogen inlet was charged with 2-bromo-1,3,5-triethylbenzene (5.3 g, 22 mmol) in dry THF (50 mL). The resulted solution was cooled down -78°C and 2.5 M *n*-BuLi in hexanes (11.1 mL, 27.7 mmol) added dropwise via syringe over 20 minutes. The reaction mixture was stirred for additional 20 minutes and DMF (2.3 mL, 30 mmol) was added dropwise via syringe while maintaining the temperature below -73°C. The reaction mixture was stirred for additional 15 minutes and then was warmed up to -10°C. Water was added and the resulted solution was extracted with diethyl ether. Organic phase was separated and dried over sodium sulfate. Solvent was removed under reduced pressure and crude product was purified by column chromatography (silica, hexanes/ethyl acetate) to afford the product (purity established by GC-MS) as a yellowish oil (1.69 g, 40 %). The spectroscopic data are in agreement with the previous report.<sup>3</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 10.55 (s, 1H), 6.95 (s, 2H), 2.97(q, *J* = 7.8 Hz, 4H), 2.64 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 9H); GC/MS (EI) m/z (%) = 190.1 (M<sup>+</sup>, 80).

**Platinum 5,19,15,20-tetrakisphenyl-21H,23H-porphyrin (PtTPP).** A 10 mL one-neck round bottom flask fitted with magnetic stir bar, nitrogen inlet and reflux condenser was charged with H<sub>2</sub>TPP (0.011 g, 0.018 mmol), PtCl<sub>2</sub> (12 mg, 0.045 mmol) and benzonitrile (10 g). The resulting solution was reflux overnight when the UV-vis spectroscopy confirmed complete conversion of the free base porphyrin. Benzonitrile was evaporated under reduced pressure to afford dark solid, which was purified by chromatography (silica, hexane/DCM = 2/1), collecting the reddish fraction that gave the desired product as a purple solid (10 mg, 69 %). NMR spectrum is in a good agreement with literature.<sup>4</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.75 (m, 8H), 8.16 (d, *J* = 7.2 Hz, 8H), 7.74 (m, 12H). The product was recrystallized from ethanol/chloroform for photophysical measurements.

<sup>1</sup> R. C. Fuson and J. Corse *J. Am. Chem. Soc.* 1938, **60**, 2063.

<sup>2</sup> S. Fergus, S. J. Eustace and A. F. Hegarty, *J. Org. Chem.* 2004, **69**, 4663.

<sup>3</sup> S. Andersson, R. E. Carter and T. Drakenberg, *Acta Chem. Scand. B* 1984, **38**, 579.

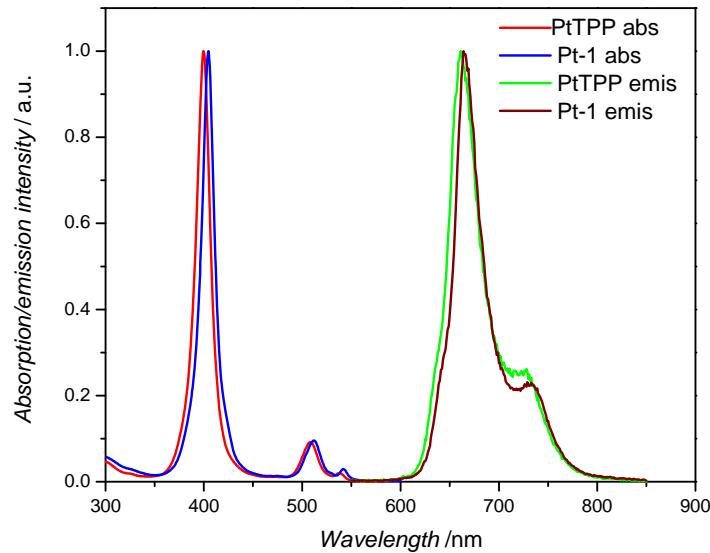
<sup>4</sup> W. Wu, W. Wu, S. Ji, H. Guo, X. Wang and J. Zhao, *Dyes and Pigments* 2011, **89**, 199.

*X-ray crystallographic analysis* was performed

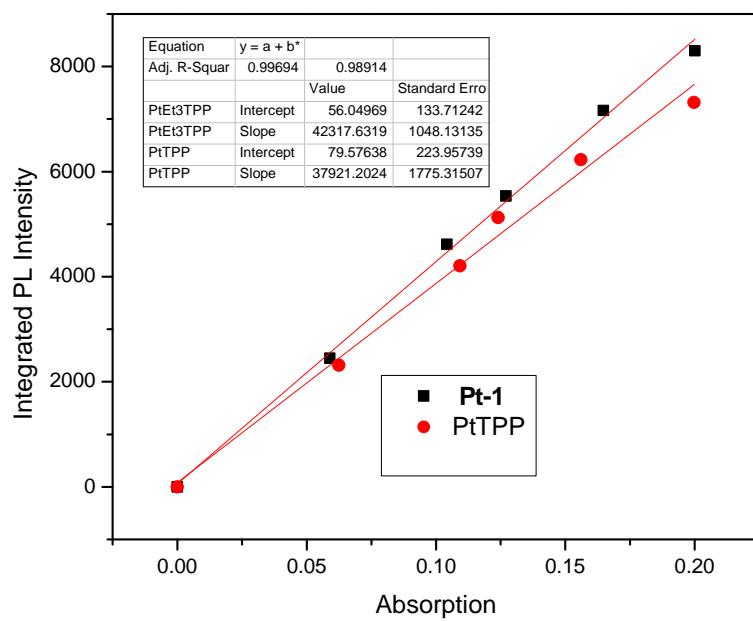
**Table 1.** Crystal data and structure refinement for **Pt-1**.

Identification code	pere28
Empirical formula	C72 H88 N4 O2 Pt
Formula weight	1236.55
Temperature	100K
Wavelength	1.54178 Å
Crystal system	Tetragonal
Space group	I41/a
Unit cell dimensions	$a = 28.8481(5)$ Å $\alpha = 90^\circ$ $b = 28.8481(5)$ Å $\beta = 90^\circ$ $c = 14.8117(3)$ Å $\gamma = 90^\circ$
Volume	12326.5(4) Å <sup>3</sup>
Z	8
Density (calculated)	1.333 g/cm <sup>3</sup>
Absorption coefficient	4.623 mm <sup>-1</sup>
F(000)	5136
Crystal size	0.08 x 0.04 x 0.02 mm
Theta range for data collection	3.06 to 71.05°
Index ranges	$-35 \leq h \leq 35$ , $-35 \leq k \leq 35$ , $-17 \leq l \leq 15$
Reflections collected	122150
Independent reflections	5936 [R <sub>int</sub> = 0.034]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9117 and 0.7293
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5936 / 99 / 477
Goodness-of-fit on F <sup>2</sup>	1.037
Final R indices [I>2sigma(I)]	R <sub>1</sub> = 0.0298, wR <sub>2</sub> = 0.0854
R indices (all data)	R <sub>1</sub> = 0.0326, wR <sub>2</sub> = 0.0890
Largest diff. peak and hole	0.888 and -0.486 e/Å <sup>3</sup>

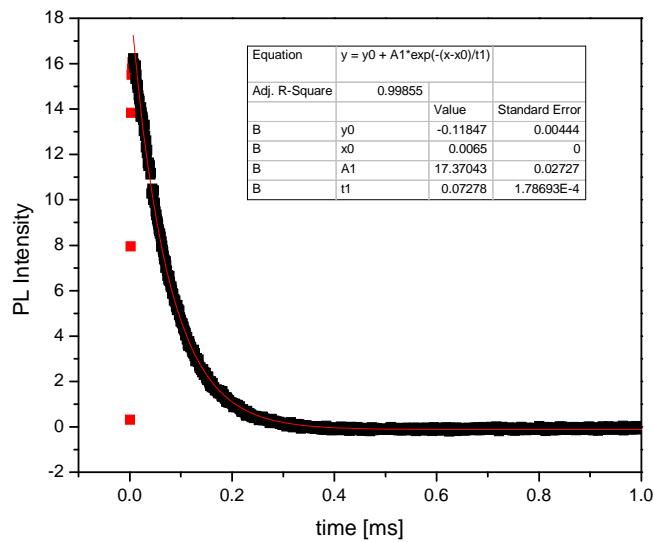
### Photophysical measurements



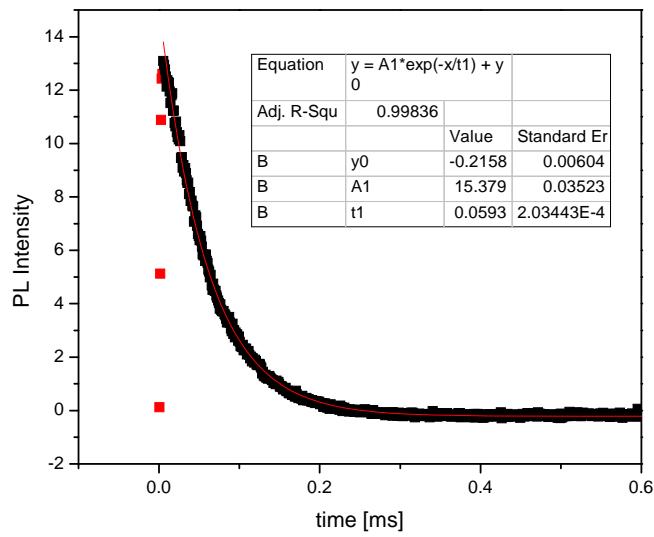
**Figure S1.** Absorption and emission spectra ( $\lambda_{\text{exc}} = 510$  nm) of **PtTPP** and **Pt-1** in Ar-saturated toluene at room temperature.



**Figure S2.** Quantum yield measurements in Ar-saturated toluene ( $\lambda_{\text{exc}} = 510$  nm).

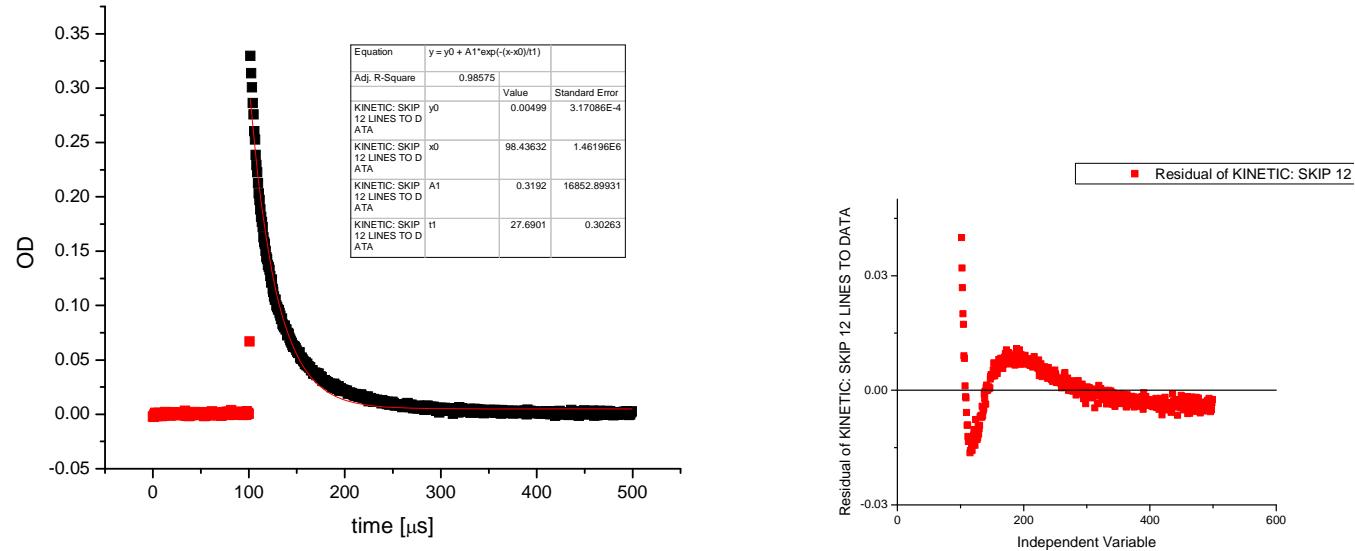


**Figure S3.** Time decay of phosphorescence emission of **Pt-1** ( $A_{510\text{nm}} = 0.1$ ) in Ar saturated toluene solution at room temperature ( $\lambda_{\text{exc}} = 510$  nm, emission monitored at 665 nm).

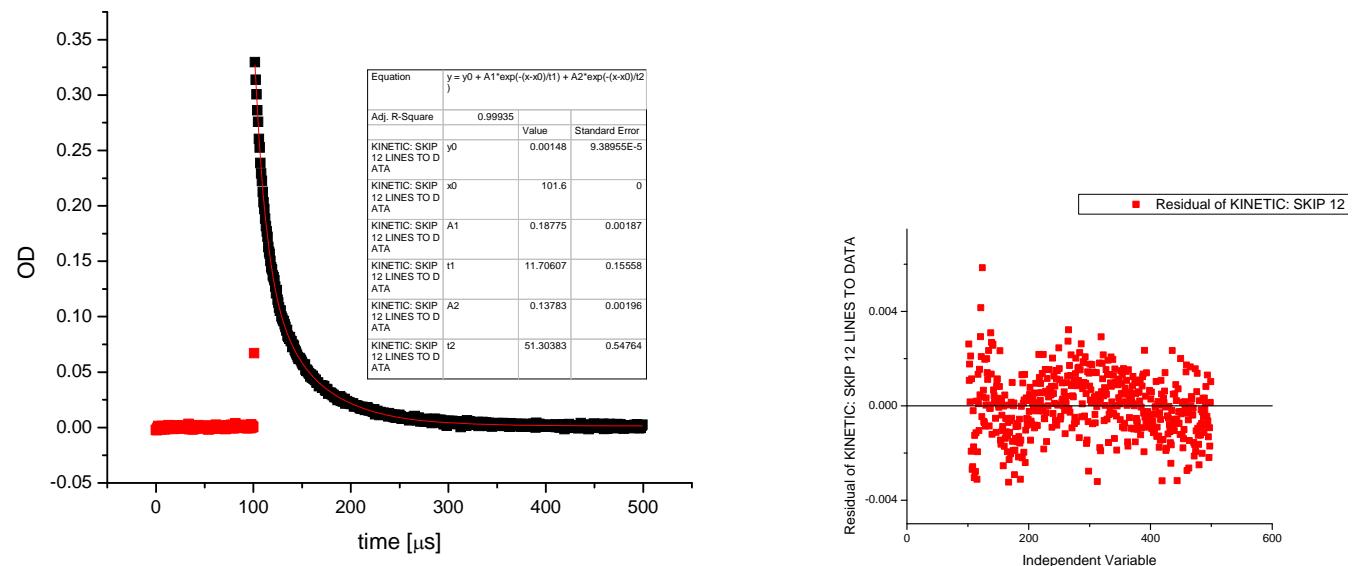


**Figure S4.** Time decay of phosphorescence emission of PtTPP ( $A_{510} = 0.1$ ) in Ar saturated toluene solution at room temperature ( $\lambda_{\text{exc}} = 510$  nm, emission monitored at 665 nm).

### Monoexponential fit

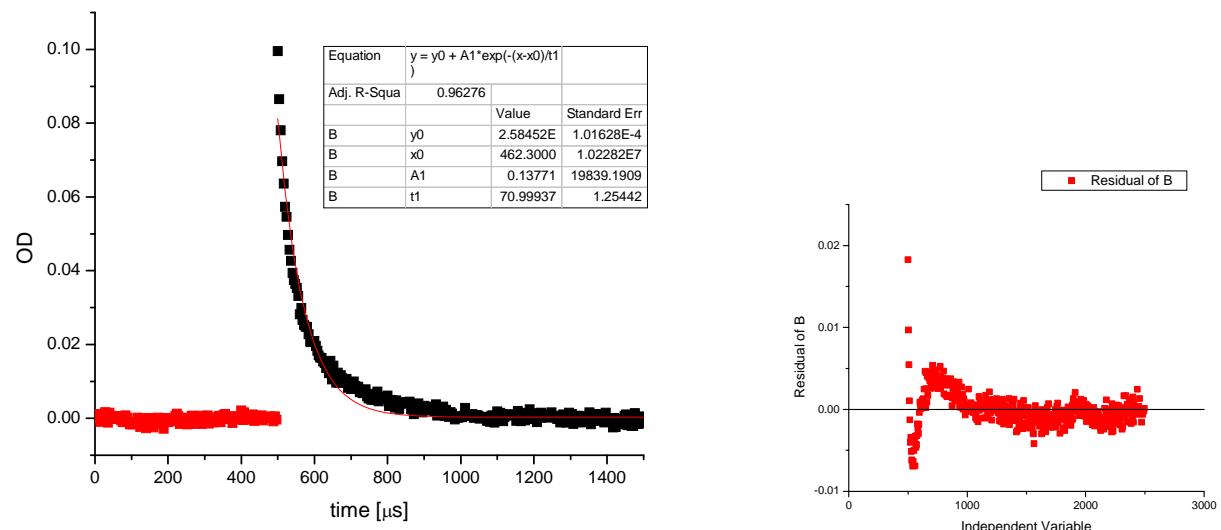


### Biexponential fit

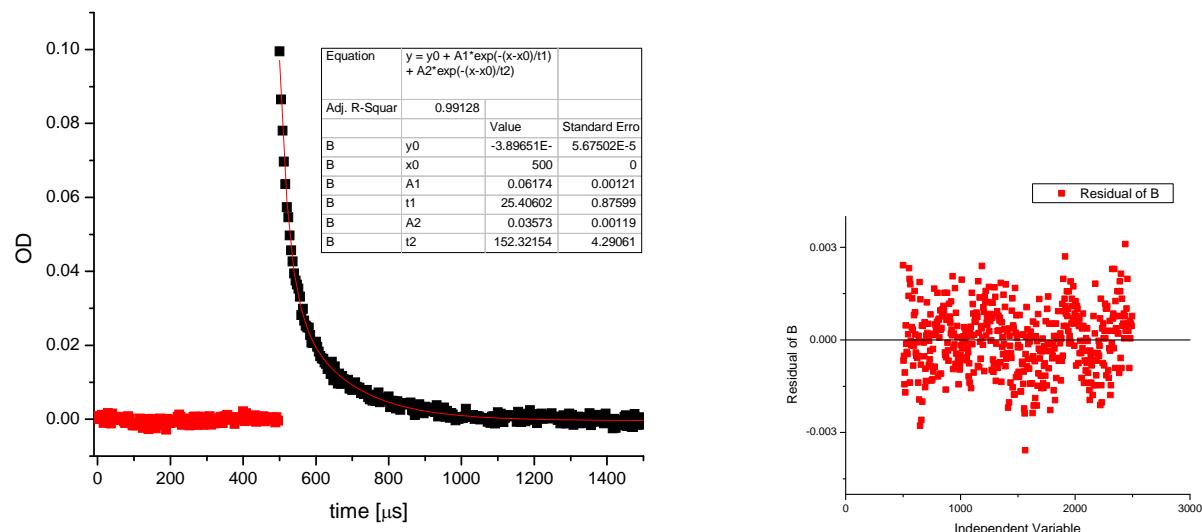


**Figure S5.** Decay of the transient absorption of **Pt-1** in Ar saturated toluene, after 532 nm laser excitation (monitored at 450 nm), analyzed with monoexponential (top) and biexponential (bottom) fits.

Monoexponential

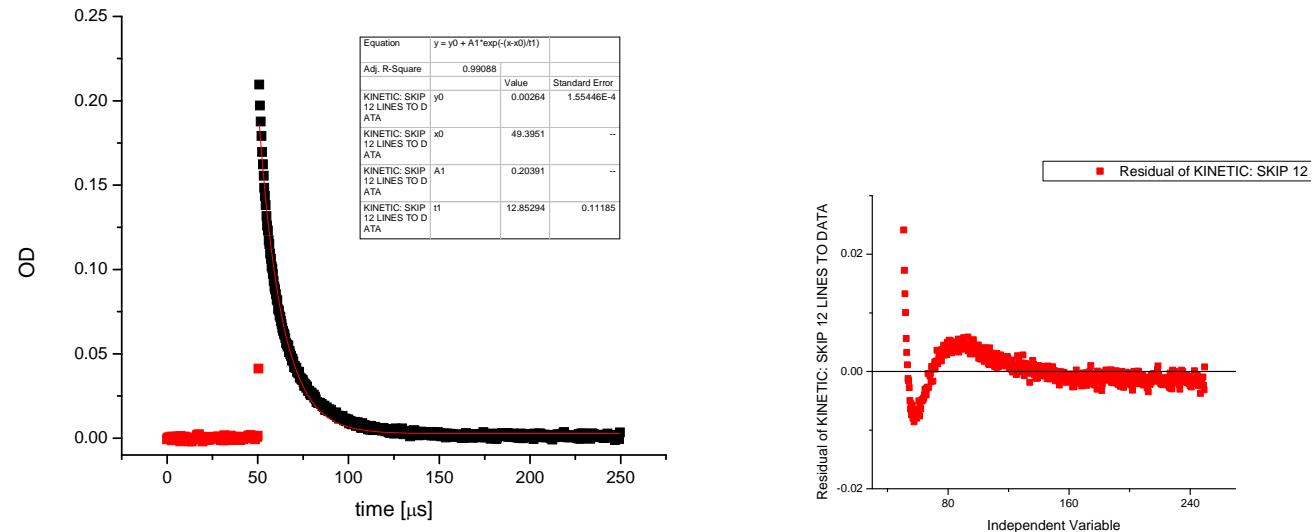


### Bi-exponential

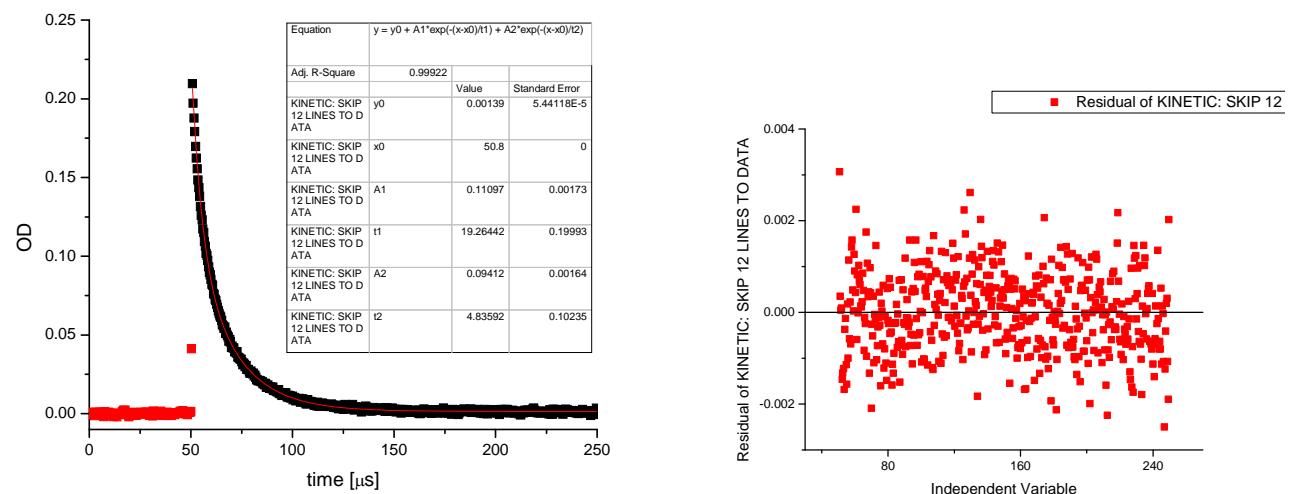


**Figure S6.** Decay of the transient absorption of **1** in Ar saturated dichloromethane, after 532 nm laser excitation (monitored at 440 nm), analyzed with biexponential fit.

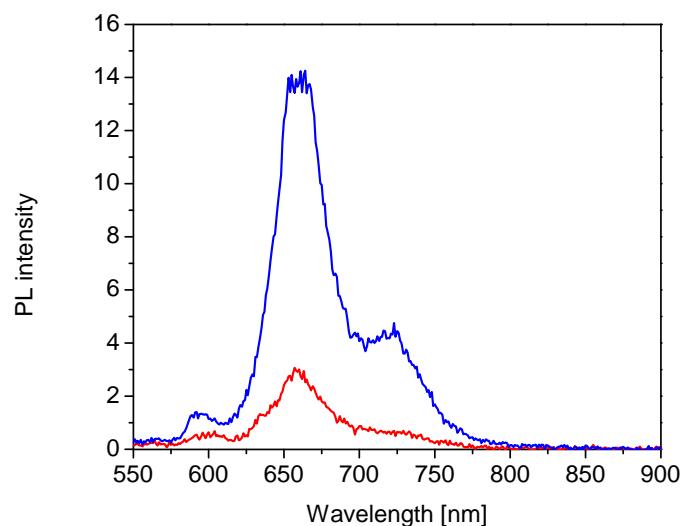
Monoexponential fit



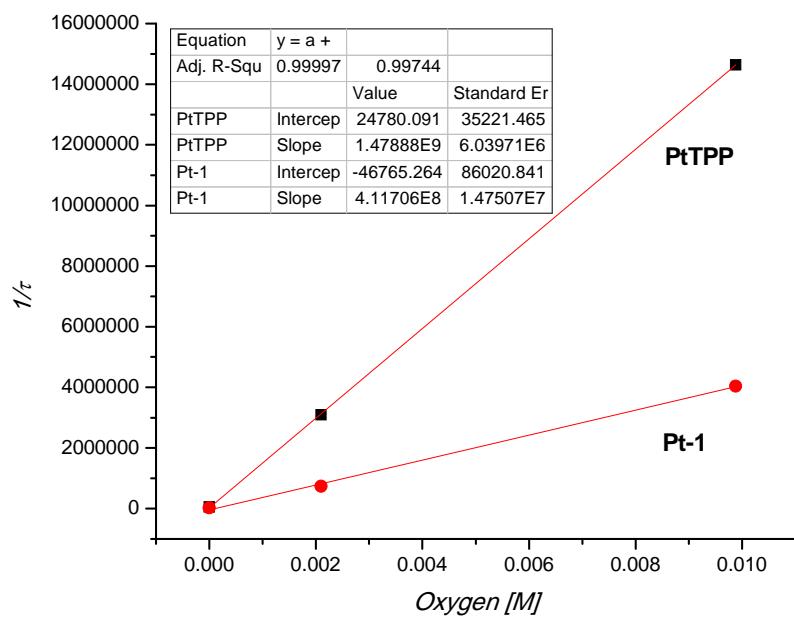
Biexponential fit



**Figure S7.** Decay of the transient absorption of PtTPP in Ar saturated toluene, after 532 nm laser excitation (monitored at 450 nm), analyzed with monoexponential (top) and biexponential (bottom) fits.

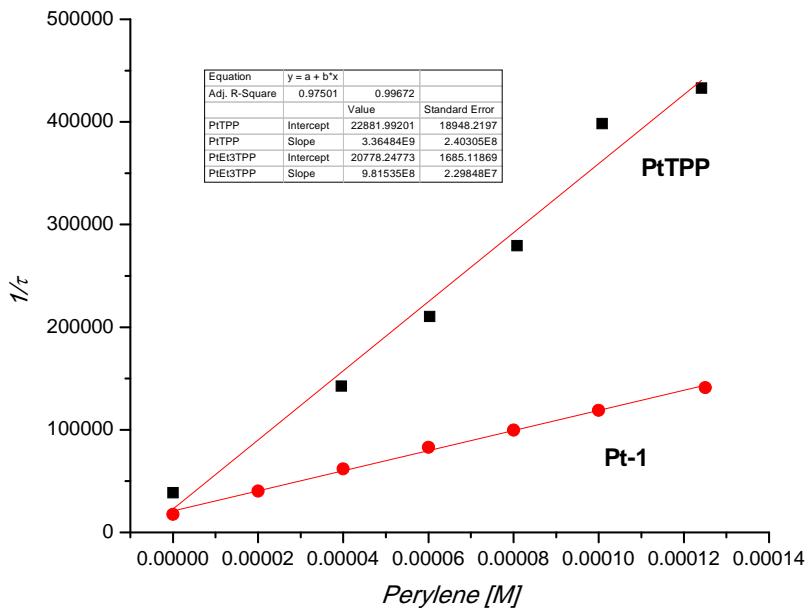


**Figure S8.** Emission ( $\lambda_{\text{exc}} = 532 \text{ nm}$ ) of PtTPP (red,  $A_{532} = 0.238$ ) and **Pt-1** (blue,  $A_{532} = 0.253$ ) in air saturated toluene, showing stronger quenching of PtTPP.



**Figure S9.** First order fitting of quenching of PtTPP and **Pt-1** triplet absorption (at 470 nm) by oxygen (concentrations correspond to saturated oxygen concentration in toluene at room temperature, in air and in pure oxygen). Concentrations of oxygen at 0.21 atm (air) and 1.0 atm (pure oxygen) in toluene at 25°C are  $2.1 \times 10^{-3} \text{ M}$  and  $9.9 \times 10^{-3} \text{ M}$ , respectively.<sup>5</sup>

<sup>5</sup> S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry* Marcel Dekker, Inc.; 1993.



**Figure S10.** First order fitting of perylene quenching of PtTPP and **Pt-1** (phosphorescence lifetime measured at 665 nm).

**DFT calculations** were performed using B3LYP hybrid functional and split basis set (LanDZ2 for Pt, 6-31G(d) for all other atoms), as implemented in Gaussian 03W program.<sup>6</sup> The optimized geometries are given below:

**Pt-1 (HF=-2975.3989825 Hartree)**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	78	0	0.000004	-0.000009	0.012071
2	6	0	4.236490	0.679526	-0.002337
3	6	0	4.236477	-0.679623	-0.002475
4	6	0	2.858235	-1.109199	0.002797
5	6	0	2.858256	1.109127	0.002991
6	7	0	2.039838	-0.000028	0.008086
7	6	0	2.447593	-2.447660	0.011261
8	6	0	2.447640	2.447594	0.011596
9	6	0	1.109200	2.858281	0.020569
10	6	0	1.109146	-2.858320	0.020389
11	7	0	-0.000015	-2.039883	0.015902
12	6	0	-1.109191	-2.858298	0.020560
13	6	0	0.679539	-4.236556	0.024899
14	6	0	-0.679610	-4.236542	0.025015
15	6	0	-2.447632	-2.447613	0.011554
16	6	0	-2.858248	-1.109146	0.002937
17	6	0	-4.236483	-0.679544	-0.002422
18	6	0	-4.236469	0.679604	-0.002551
19	6	0	-2.858225	1.109180	0.002743
20	7	0	-2.039829	0.000009	0.008051
21	6	0	-2.447586	2.447640	0.011205
22	6	0	-1.109137	2.858302	0.020353
23	7	0	0.000023	2.039864	0.015898
24	6	0	0.679618	4.236525	0.025010
25	6	0	-0.679531	4.236537	0.024863
26	6	0	3.513688	-3.513002	0.009911
27	6	0	3.513758	3.512914	0.010549
28	6	0	-3.513754	-3.512928	0.010469
29	6	0	-3.513679	3.512984	0.009832
30	6	0	4.098441	3.932909	1.226924
31	6	0	3.930048	4.098807	-1.206646
32	6	0	4.915438	5.092392	-1.180198
33	6	0	5.089044	4.921364	1.198837
34	6	0	5.513183	5.516957	0.008762
35	6	0	-3.929765	4.098678	-1.207528
36	6	0	-4.098535	3.933207	1.226047
37	6	0	-5.089116	4.921672	1.197635
38	6	0	-5.513069	5.517060	0.007387
39	6	0	-4.915146	5.092284	-1.181404
40	6	0	-3.930030	-4.098779	-1.206745
41	6	0	-4.098476	-3.932938	1.226826
42	6	0	-5.089096	-4.921369	1.198694
43	6	0	-5.513225	-5.516925	0.008591

<sup>6</sup> Gaussian 03W, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

44	6	0	-4.915446	-5.092346	-1.180342
45	6	0	3.929785	-4.098707	-1.207444
46	6	0	4.098550	-3.933201	1.226129
47	6	0	5.089140	-4.921661	1.197730
48	6	0	5.513095	-5.517063	0.007494
49	6	0	4.915173	-5.092302	-1.181307
50	6	0	3.671262	3.379911	2.575770
51	6	0	3.370906	3.674827	-2.553935
52	1	0	5.222780	5.547585	-2.120933
53	1	0	5.536751	5.238295	2.139982
54	6	0	6.612276	6.558590	0.003203
55	6	0	-3.370402	3.674471	-2.554651
56	6	0	-3.671556	3.380452	2.575055
57	1	0	-5.536952	5.238789	2.138656
58	6	0	-6.612150	6.558704	0.001494
59	1	0	-5.222337	5.547317	-2.122266
60	6	0	-3.370856	-3.674777	-2.554011
61	6	0	-3.671320	-3.379967	2.575690
62	1	0	-5.536827	-5.238319	2.139821
63	6	0	-6.612354	-6.558519	0.003002
64	1	0	-5.222787	-5.547502	-2.121095
65	6	0	3.370436	-3.674501	-2.554575
66	6	0	3.671577	-3.380426	2.575132
67	1	0	5.536983	-5.238755	2.138755
68	6	0	6.612177	-6.558705	0.001601
69	1	0	5.222367	-5.547345	-2.122162
70	6	0	2.679786	-4.294960	3.317501
71	6	0	8.015509	-5.945235	-0.153862
72	6	0	4.279317	-2.679996	-3.300303
73	6	0	2.679209	4.294226	3.318058
74	6	0	4.280046	2.680663	-3.299802
75	6	0	8.015612	5.945145	-0.152327
76	6	0	-4.279243	2.679934	-3.300385
77	6	0	-8.015520	5.945191	-0.153453
78	6	0	-2.679835	4.295038	3.317448
79	6	0	-4.279941	-2.680562	-3.299875
80	6	0	-8.015719	-5.944960	-0.151810
81	6	0	-2.679323	-4.294314	3.318011
82	1	0	3.226401	2.387752	2.458098
83	1	0	4.565169	3.248893	3.199461
84	1	0	2.377843	3.232704	-2.433805
85	1	0	3.240761	4.569753	-3.176312
86	1	0	6.438607	7.270375	-0.813911
87	1	0	6.574271	7.137517	0.934734
88	1	0	-3.240377	4.569271	-3.177233
89	1	0	-2.377259	3.232583	-2.434307
90	1	0	-4.565576	3.249339	3.198567
91	1	0	-3.226487	2.388360	2.457601
92	1	0	-6.573967	7.138120	0.932717
93	1	0	-6.438625	7.270059	-0.816023
94	1	0	-2.377781	-3.232689	-2.433850
95	1	0	-3.240724	-4.569690	-3.176410
96	1	0	-3.226425	-2.387820	2.458041
97	1	0	-4.565244	-3.248923	3.199354
98	1	0	-6.438988	-7.269990	-0.814448
99	1	0	-6.574056	-7.137814	0.934295
100	1	0	3.240390	-4.569303	-3.177150
101	1	0	2.377307	-3.232583	-2.434239
102	1	0	4.565594	-3.249382	3.198661
103	1	0	3.226576	-2.388305	2.457678
104	1	0	6.574227	-7.137871	0.932988
105	1	0	6.438448	-7.270280	-0.815682
106	1	0	2.425292	-3.873319	4.296768
107	1	0	1.751917	-4.414548	2.748578
108	1	0	3.106068	-5.292077	3.477978
109	1	0	8.786389	-6.724597	-0.154001
110	1	0	8.097037	-5.385535	-1.092442
111	1	0	8.233132	-5.251428	0.665992
112	1	0	4.398787	-1.752060	-2.731438
113	1	0	5.276875	-3.103633	-3.465016
114	1	0	3.853027	-2.426171	-4.277728

115	1	0	3.105338	5.291373	3.478755
116	1	0	1.751441	4.413777	2.748964
117	1	0	2.424568	3.872423	4.297218
118	1	0	5.277547	3.104516	-3.464300
119	1	0	4.399616	1.752614	-2.731142
120	1	0	3.853911	2.426993	-4.277335
121	1	0	8.786498	6.724502	-0.152231
122	1	0	8.233180	5.251136	0.667369
123	1	0	8.097192	5.385675	-1.091040
124	1	0	-5.276814	3.103538	-3.465108
125	1	0	-3.852934	2.426126	-4.277807
126	1	0	-4.398689	1.751994	-2.731524
127	1	0	-8.786402	6.724551	-0.153600
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129	1	0	-8.232938	5.251597	0.666636
130	1	0	-1.751954	4.414670	2.748551
131	1	0	-3.106166	5.292136	3.477911
132	1	0	-2.425348	3.873412	4.296725
133	1	0	-3.853780	-2.426903	-4.277399
134	1	0	-5.277461	-3.104363	-3.464394
135	1	0	-4.399476	-1.752513	-2.731207
136	1	0	-8.786638	-6.724284	-0.151744
137	1	0	-8.232981	-5.251253	0.668224
138	1	0	-8.097593	-5.385129	-1.090282
139	1	0	-2.424707	-3.872520	4.297181
140	1	0	-3.105488	-5.291449	3.478692
141	1	0	-1.751537	-4.413894	2.748953
142	1	0	5.085996	1.346748	-0.000777
143	1	0	5.085972	-1.346860	-0.001050
144	1	0	1.346670	-5.086137	0.022759
145	1	0	-1.346758	-5.086109	0.022992
146	1	0	-5.085990	-1.346765	-0.000882
147	1	0	-5.085963	1.346842	-0.001139
148	1	0	1.346764	5.086093	0.022995
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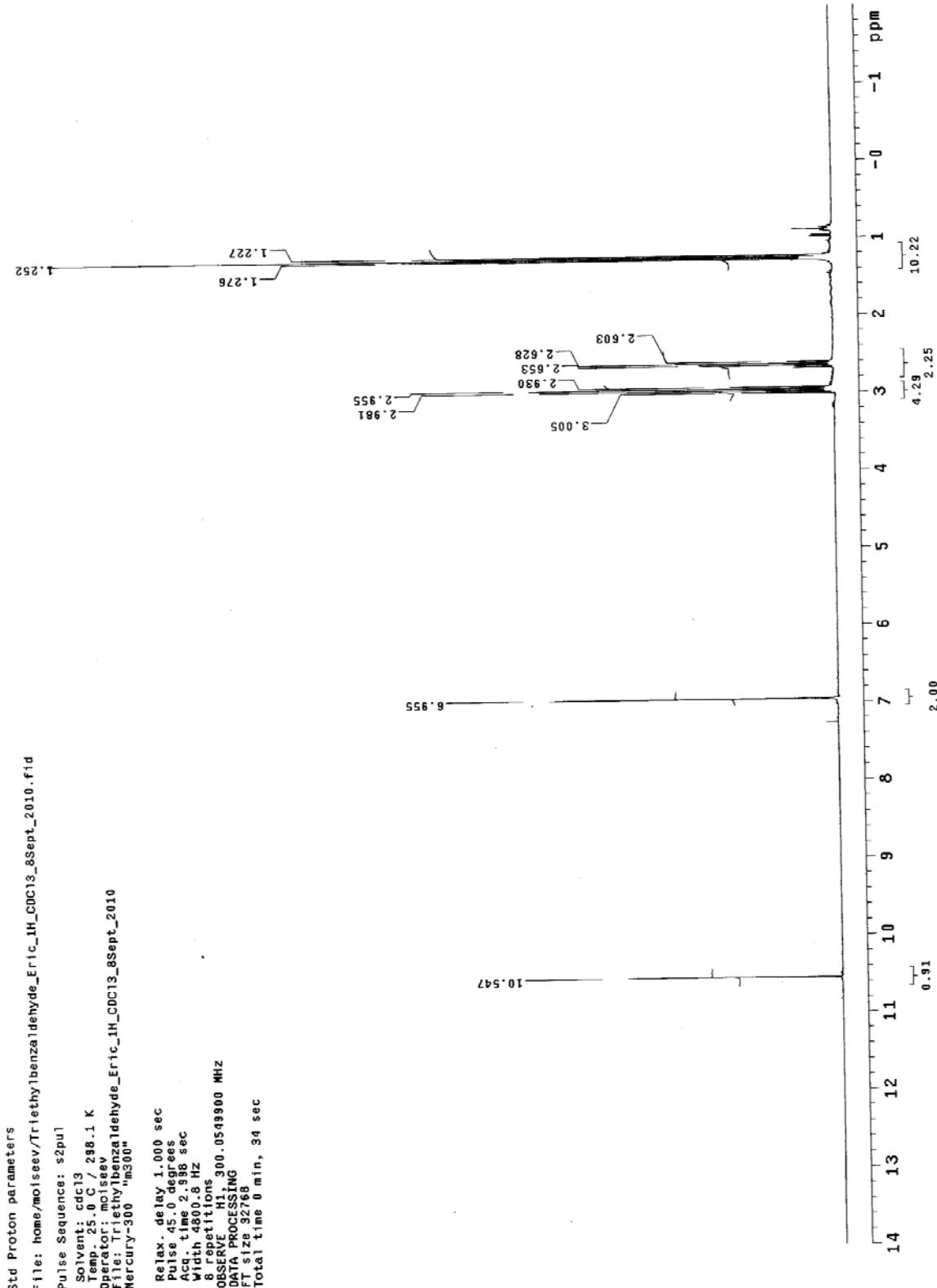
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 Rotational constants (GHZ):      0.0279557      0.0254745      0.0153045

### PtTPP (HF =-2031.8374045 Hartree)

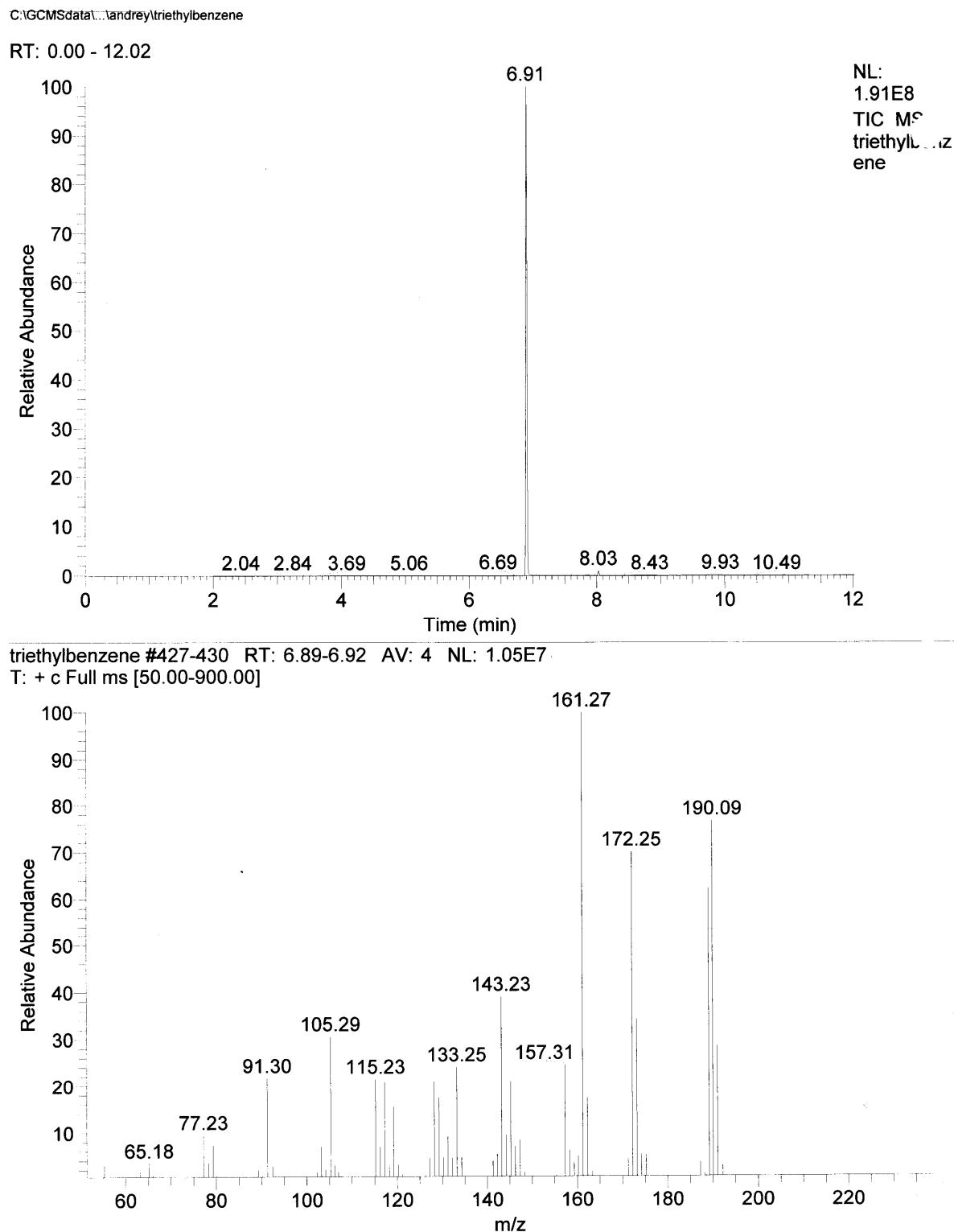
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	78	0	-0.000299	0.000010	-0.000097
2	6	0	0.850029	4.206647	0.023870
3	6	0	-0.507265	4.261956	0.023881
4	6	0	-0.991691	2.902050	0.005819
5	6	0	1.222476	2.811937	0.006041
6	7	0	0.082115	2.039030	-0.000660
7	6	0	-2.343148	2.540710	-0.000219
8	6	0	2.540408	2.342896	0.000053
9	6	0	2.901723	0.991371	-0.005932
10	6	0	-2.812246	1.222835	-0.006359
11	7	0	-2.039275	0.082514	0.000284
12	6	0	-2.902200	-0.991316	-0.006298
13	6	0	-4.206936	0.850313	-0.024227
14	6	0	-4.262137	-0.506996	-0.024308
15	6	0	-2.540962	-2.342770	-0.000222
16	6	0	-1.223171	-2.812053	0.005889
17	6	0	-0.850574	-4.206722	0.023773
18	6	0	0.506729	-4.261811	0.023926
19	6	0	0.991002	-2.901845	0.006014
20	7	0	-0.082872	-2.038991	-0.000651
21	6	0	2.342581	-2.540803	0.000121
22	6	0	2.811793	-1.222891	-0.005973
23	7	0	2.038783	-0.082521	0.000589
24	6	0	4.261652	0.506994	-0.023887
25	6	0	4.206467	-0.850296	-0.023793

26	6	0	-3.360845	3.645205	0.001191
27	6	0	3.644808	3.360673	-0.001151
28	6	0	-3.645260	-3.360732	-0.001294
29	6	0	3.360438	-3.645110	0.001414
30	6	0	5.303870	4.675477	1.193310
31	6	0	5.095277	4.898062	-1.201381
32	6	0	4.677650	-5.302069	-1.193218
33	6	0	4.901221	-5.092217	1.201338
34	6	0	-5.093699	-4.900837	-1.200786
35	6	0	-5.302367	-4.677818	1.193623
36	6	0	-4.676450	5.303937	-1.193002
37	6	0	-4.898619	5.095267	1.201570
38	1	0	5.782126	4.953354	2.128981
39	1	0	5.411242	5.348774	-2.138628
40	1	0	4.957438	-5.779233	-2.128875
41	1	0	5.354790	-5.405993	2.137940
42	1	0	-5.407433	-5.352007	-2.138585
43	1	0	-5.778644	-4.955545	2.130368
44	1	0	-4.954663	5.780813	-2.129290
45	1	0	-5.349701	5.409488	2.139239
46	1	0	1.549829	5.029414	0.037349
47	1	0	-1.137948	5.138788	0.037235
48	1	0	-5.029765	1.550039	-0.037667
49	1	0	-5.138916	-1.137788	-0.037775
50	1	0	-1.550214	-5.029610	0.037050
51	1	0	1.137613	-5.138520	0.037337
52	1	0	5.138438	1.137736	-0.037310
53	1	0	5.029315	-1.549957	-0.037168
54	6	0	5.716897	5.260585	-0.005129
55	1	0	6.522549	5.989726	-0.007243
56	6	0	4.066353	3.954554	-1.199400
57	1	0	3.580526	3.674728	-2.130081
58	6	0	4.274796	3.732247	1.195392
59	1	0	3.948847	3.281269	2.128603
60	6	0	-5.261421	5.717195	0.005489
61	1	0	-5.990007	6.523274	0.007849
62	6	0	-3.954780	4.066587	1.199325
63	1	0	-3.676099	3.582332	2.131183
64	6	0	-4.274697	-3.732874	1.195053
65	1	0	-3.956317	-3.278475	2.129236
66	6	0	-4.066311	-3.955559	-1.199028
67	1	0	-3.587711	-3.672581	-2.132518
68	6	0	-5.714445	-5.264706	-0.004352
69	1	0	-6.518394	-5.995596	-0.006057
70	6	0	3.732490	-4.274741	-1.195158
71	1	0	3.274713	-3.954074	-2.126868
72	6	0	5.264500	-5.713181	0.004971
73	1	0	5.995038	-6.517601	0.006988
74	6	0	3.955755	-4.065154	1.199570
75	1	0	3.668960	-3.584152	2.130620
76	6	0	-3.732961	4.275026	-1.195111
77	1	0	-3.283948	3.950210	-2.129684

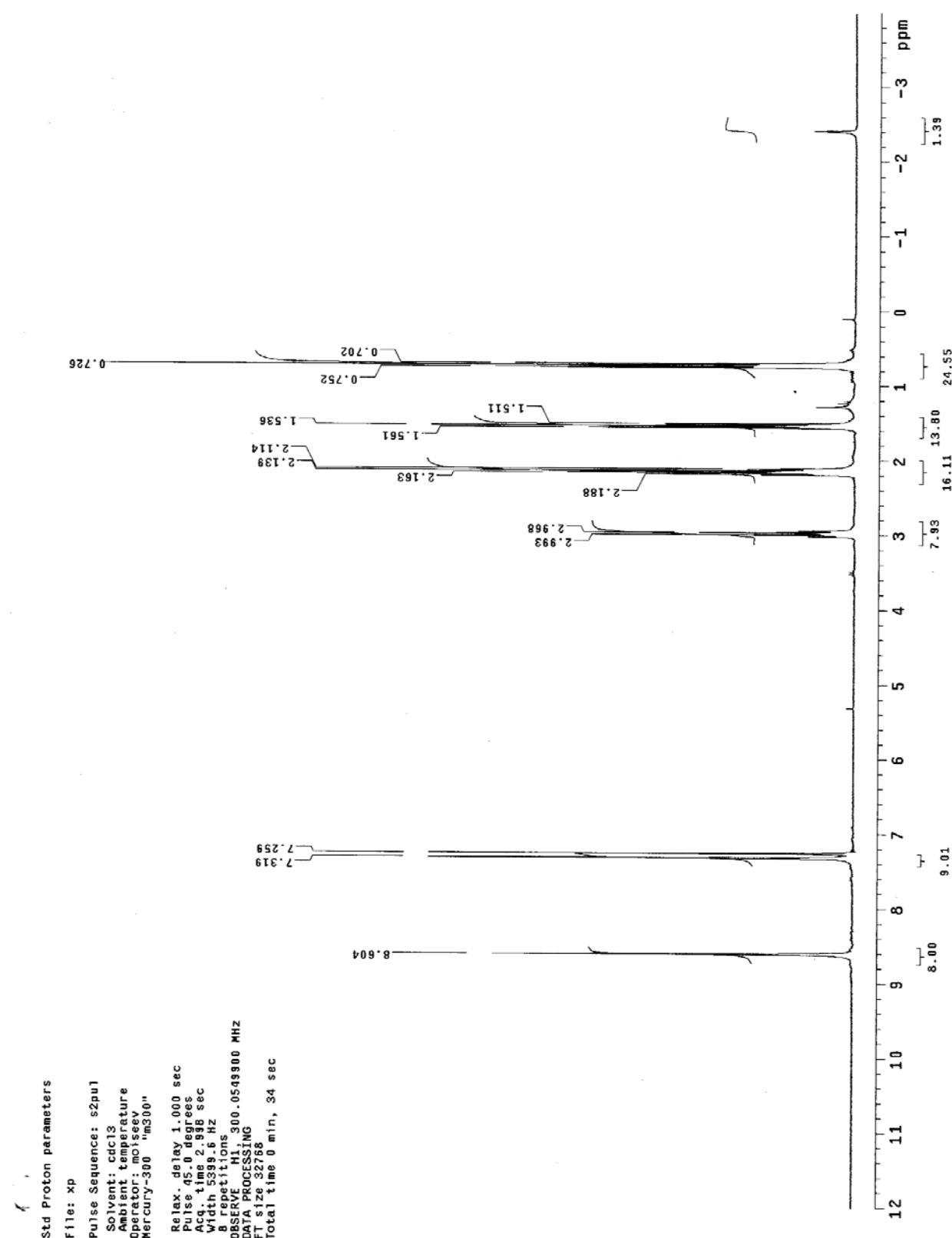
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Rotational constants (GHZ):      0.0582287      0.0582231      0.0303311



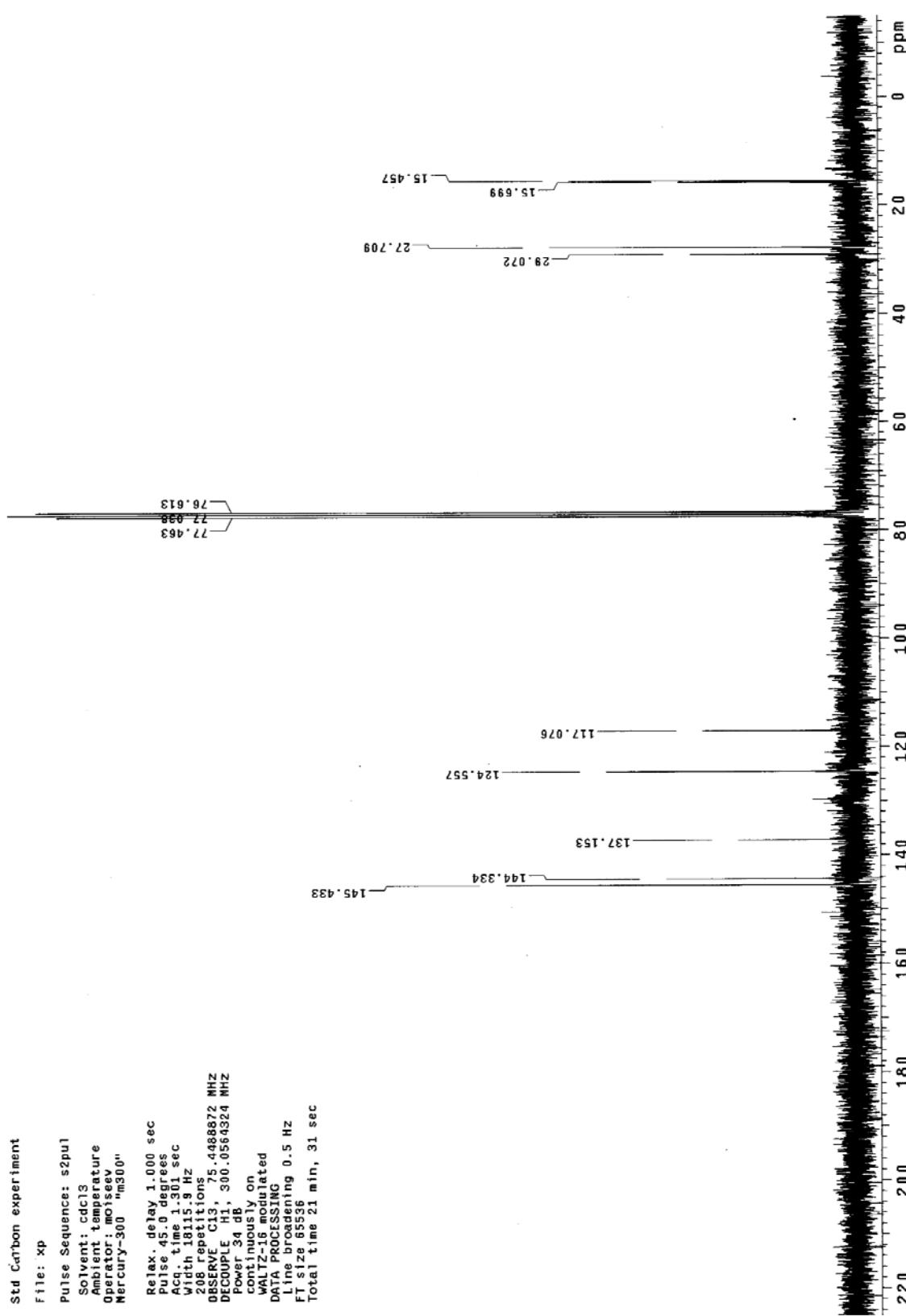
**Figure S11.** 300 MHz  $^1\text{H}$  NMR spectrum of 2,4,6-triethylbenzaldehyde in  $\text{CDCl}_3$ .



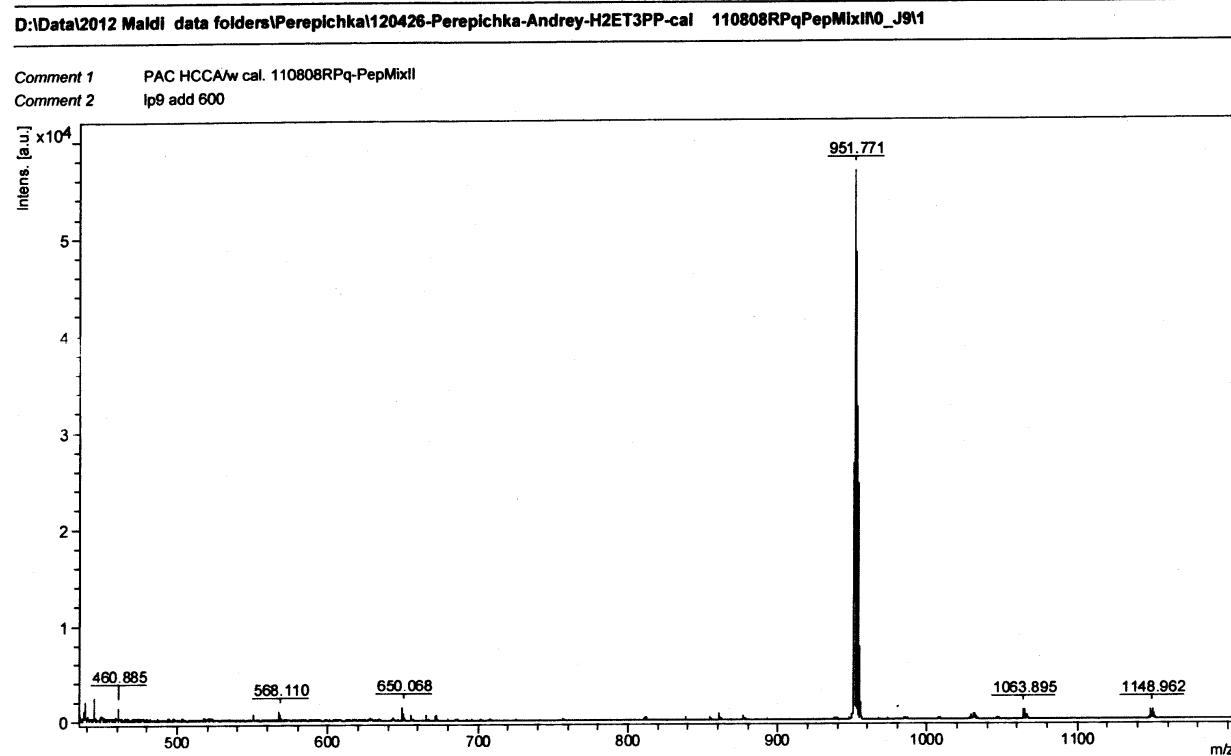
**Figure S12.** GC/MS (EI) of 2,4,6-triethylbenzaldehyde.



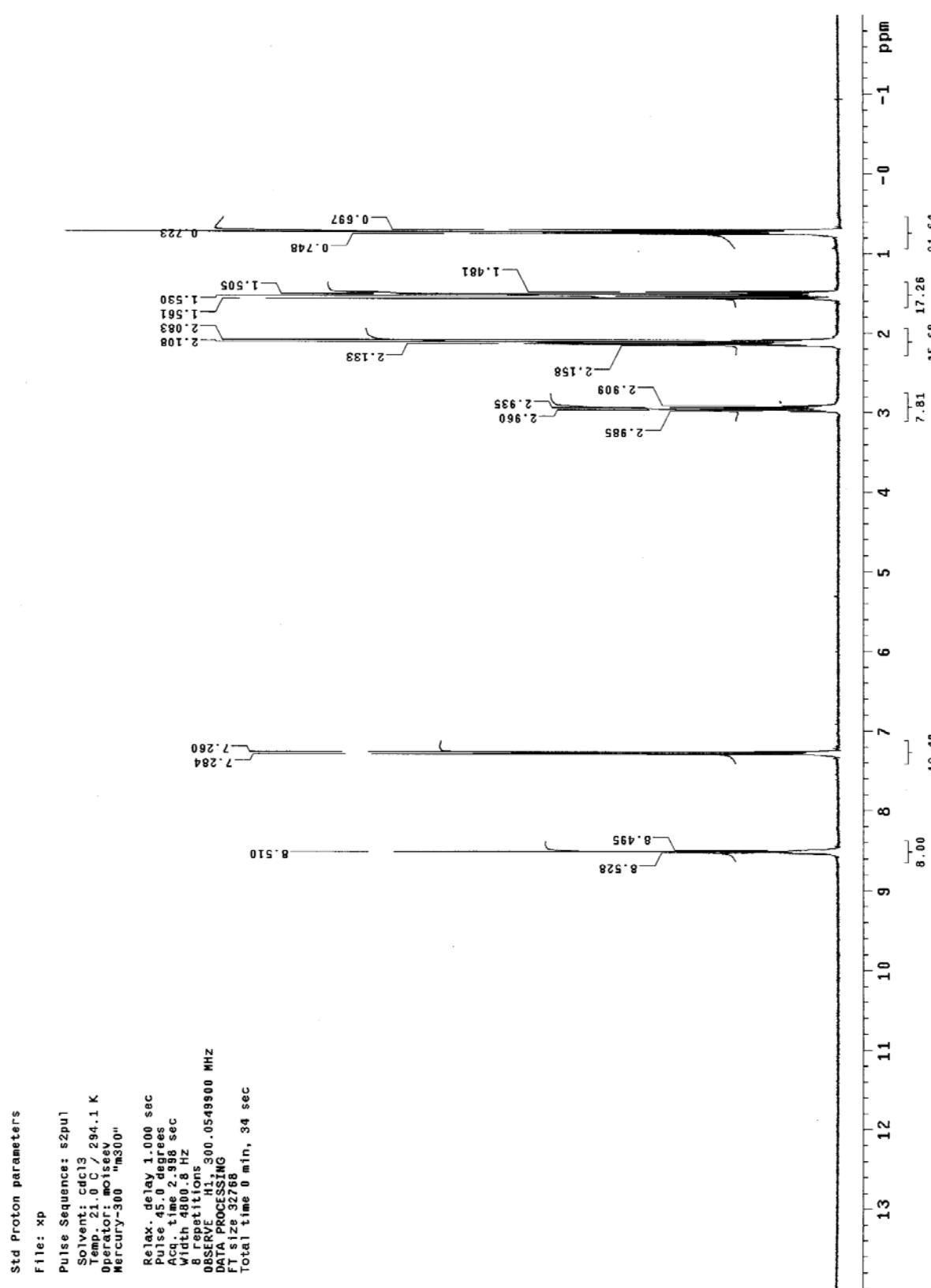
**Figure S13.** 300 MHz  $^1\text{H}$  NMR spectrum of porphyrin **1** in  $\text{CDCl}_3$ .



**Figure S14.** 75 MHz <sup>13</sup>C NMR spectrum porphyrin **1** in CDCl<sub>3</sub>.



**Figure S15.** MALDI-TOF mass-spectrum of **1**.



**Figure S16.** 300 MHz <sup>1</sup>H NMR spectrum of platinum porphyrin **Pt-1** in CDCl<sub>3</sub>.

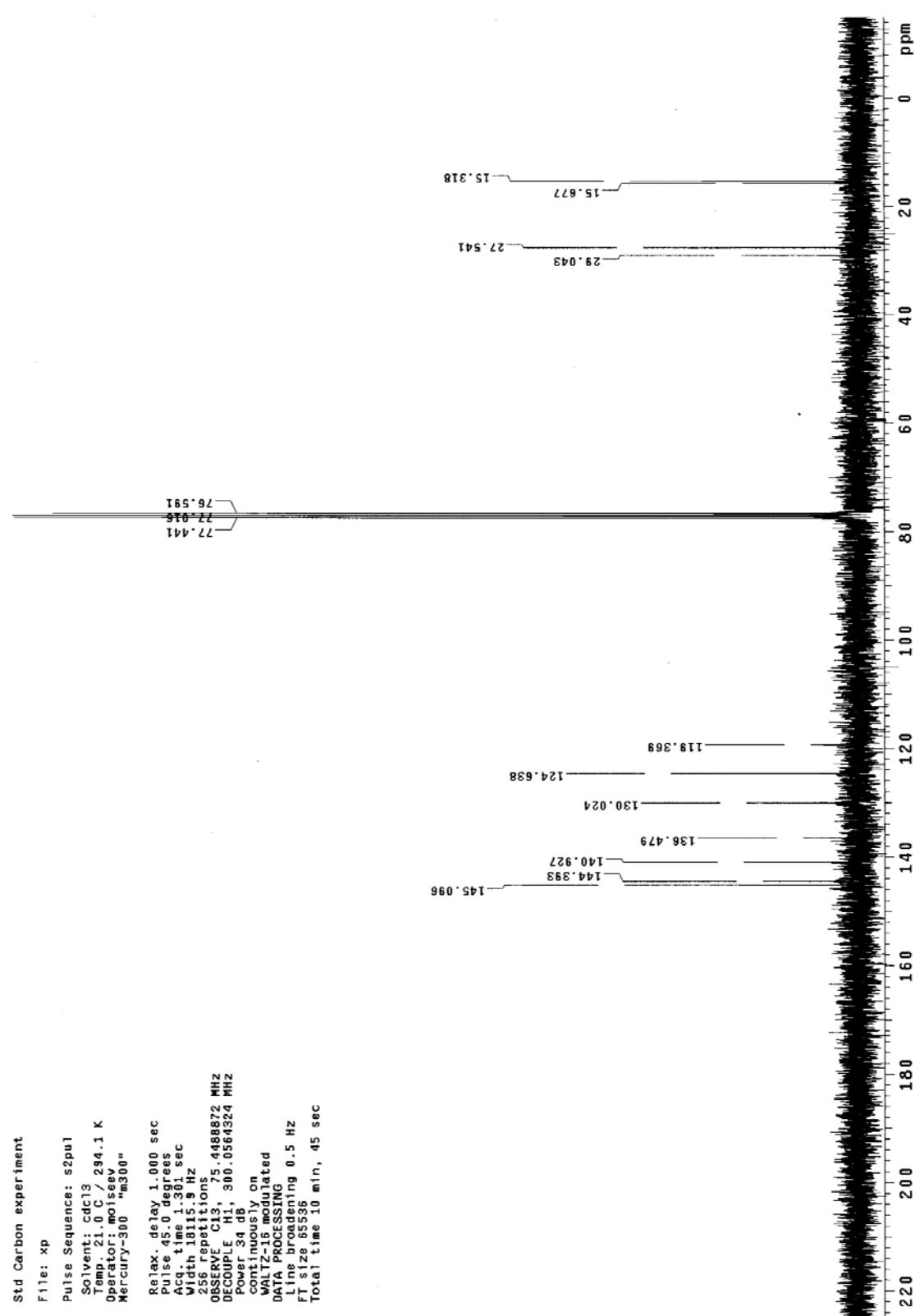
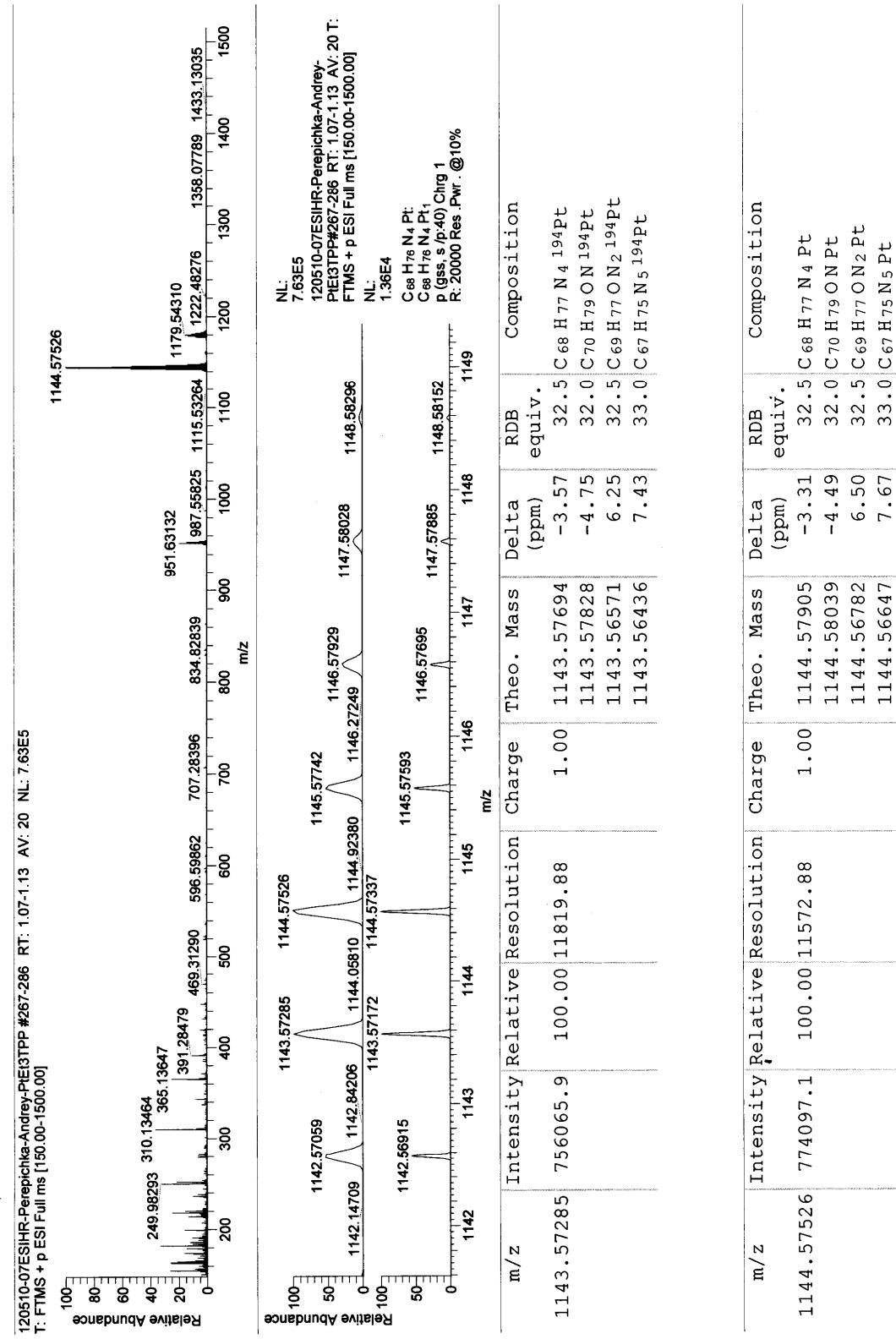


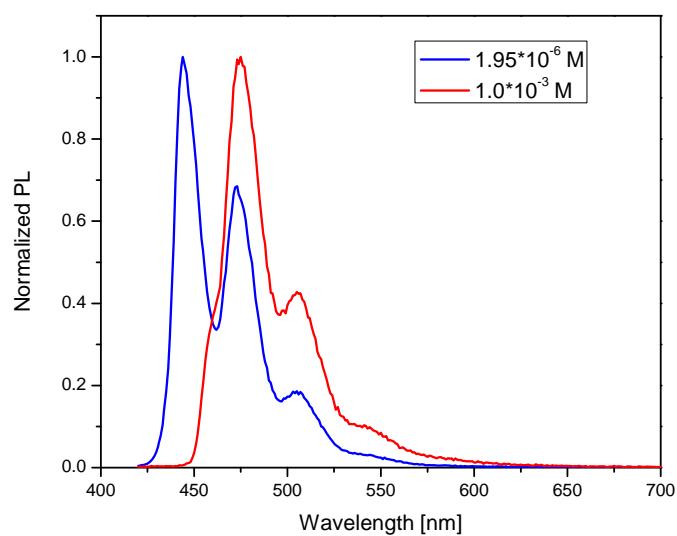
Figure S17. 75 MHz  $^{13}\text{C}$  NMR spectrum of platinum porphyrin **Pt-1** in  $\text{CDCl}_3$ .

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**Figure S18.** HRMS(ESI) mass-spectrum of Pt-1.



**Figure S19.** Emission spectra of perylene in toluene ( $\lambda_{\text{exc}} = 410$  nm). No excimer emission is observed even at very high concentration (the attenuation of the 444 nm peak in the high concentration spectrum is due to self-absorption)