Supplementary Material

Synthesis of the new porphyrinoid dyads linked with butenyne bridge via Sonogashira reaction

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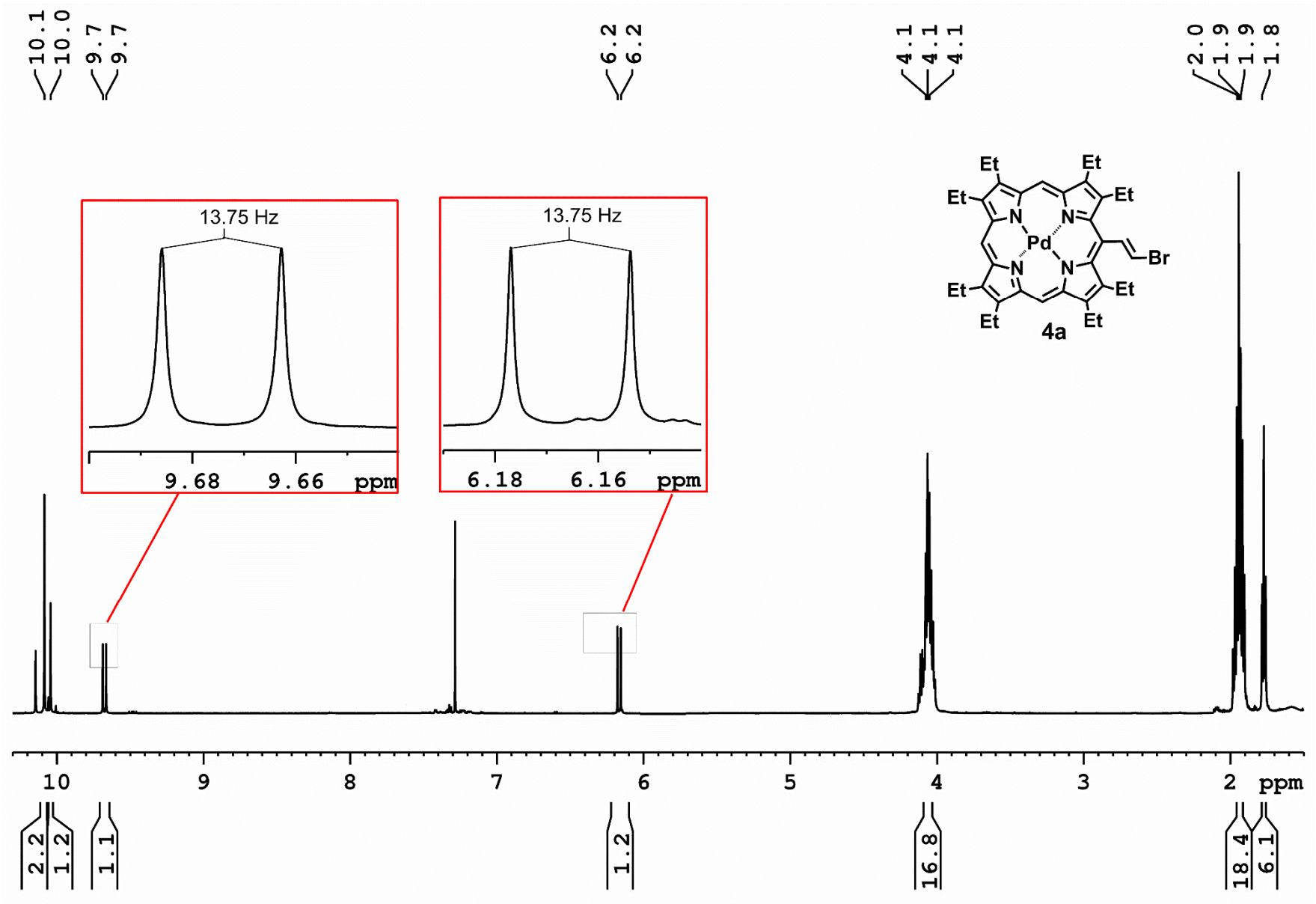

Figure S1. ^{1}H NMR spectrum of the **4a**.

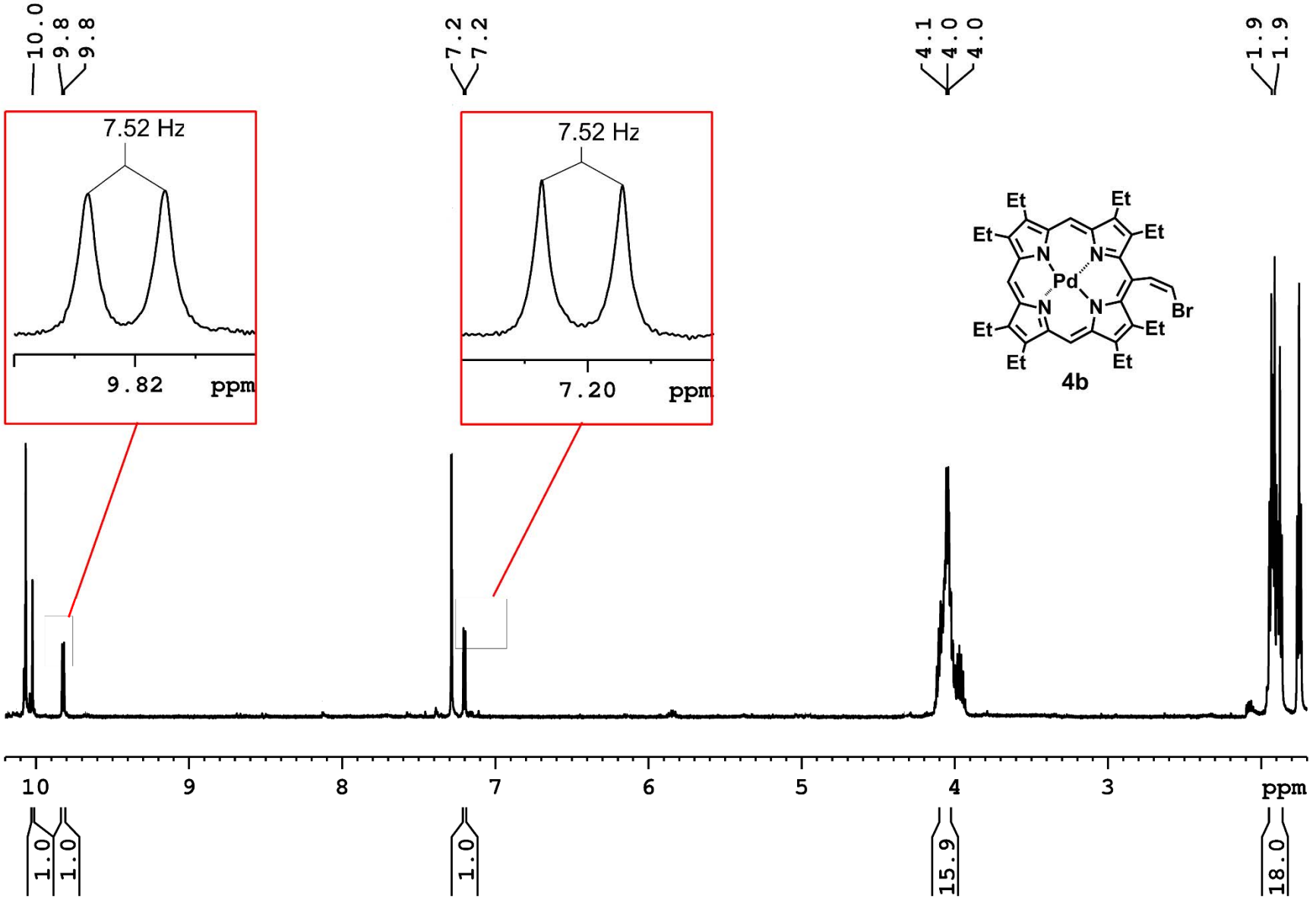

Figure S2. ^{1}H NMR spectrum of the **4b**.

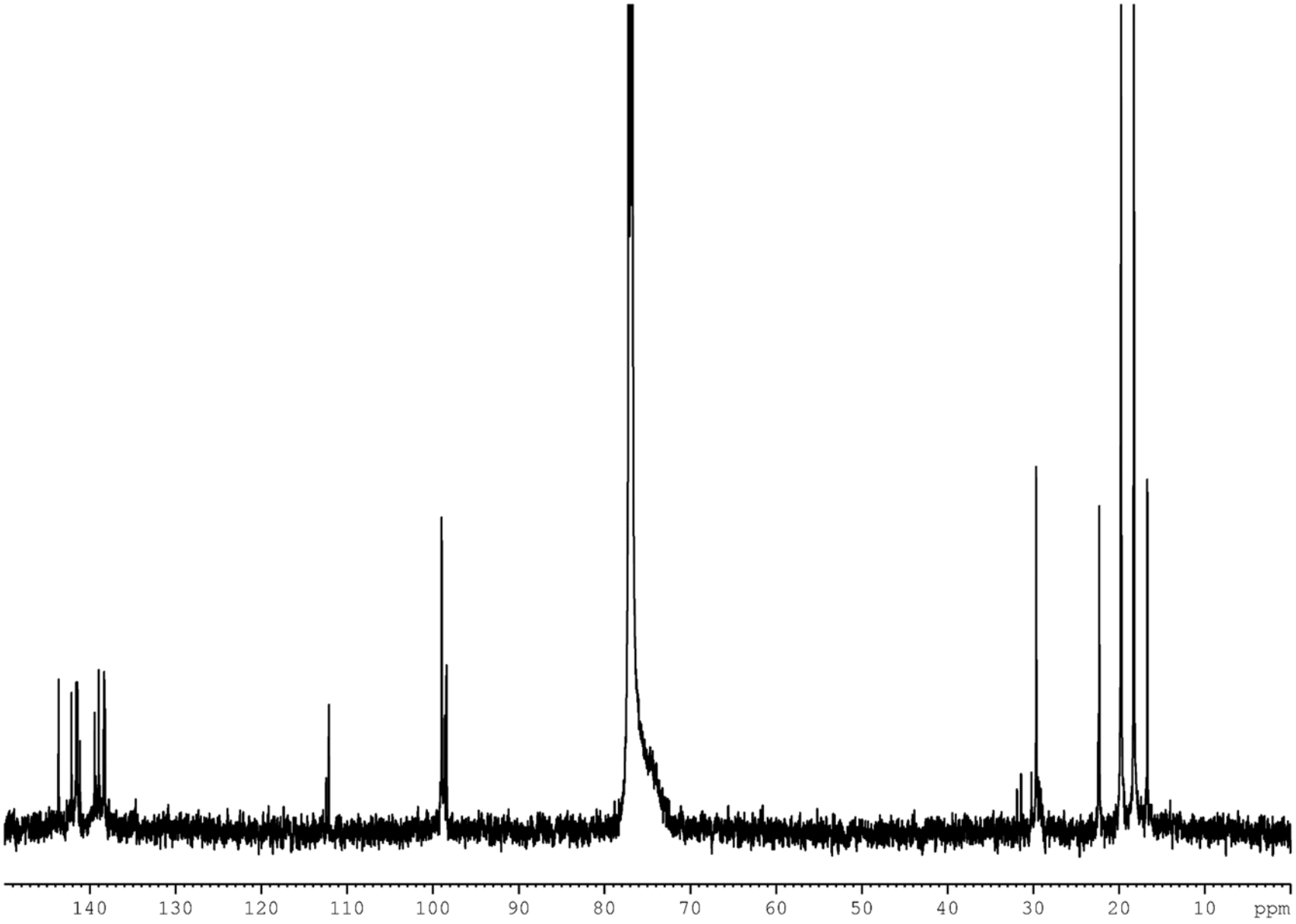

Figure S3. ^{13}C NMR spectrum of the **4a**.

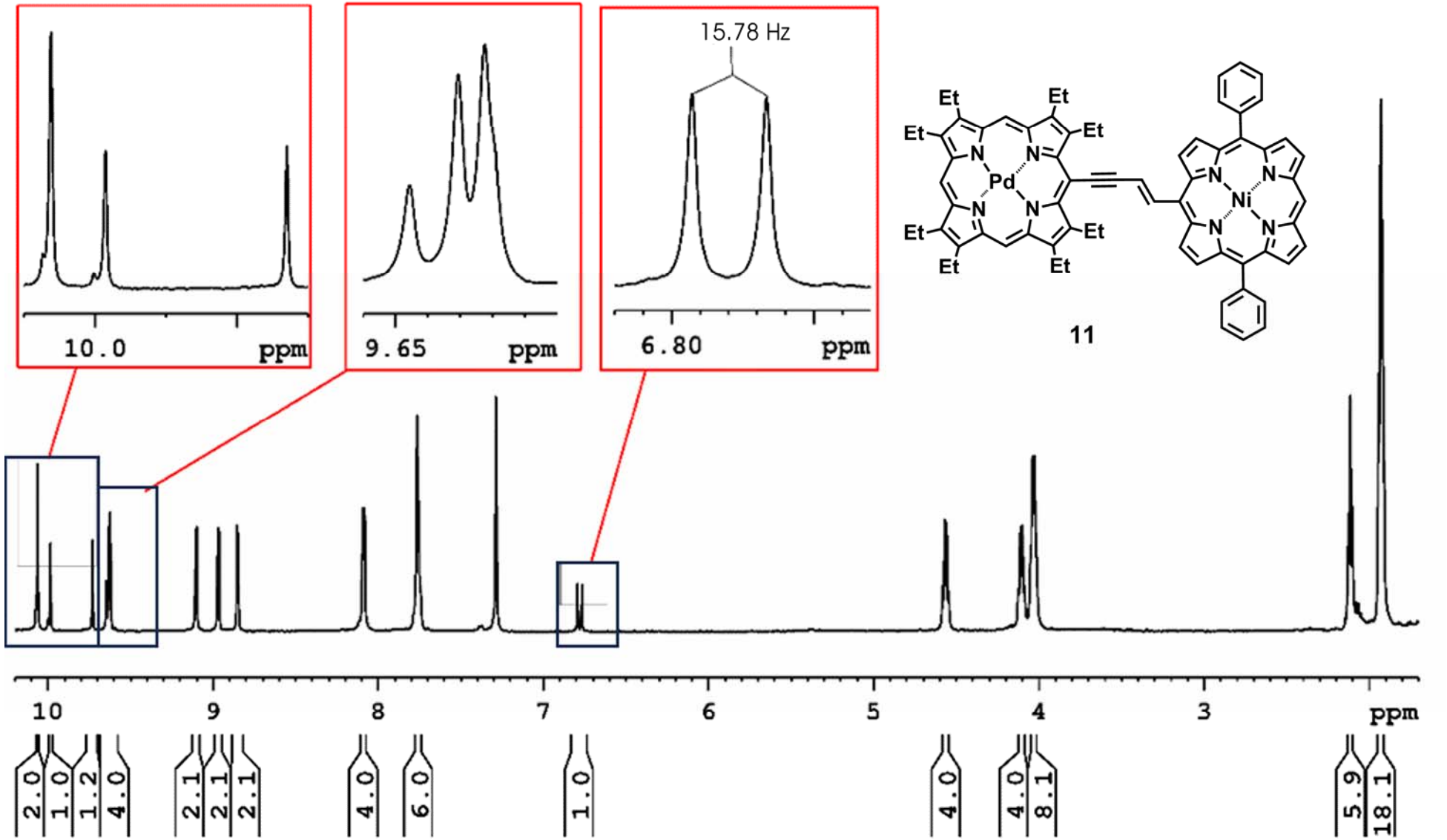

Figure S4. ^{1}H NMR spectrum of the dyad **11**.

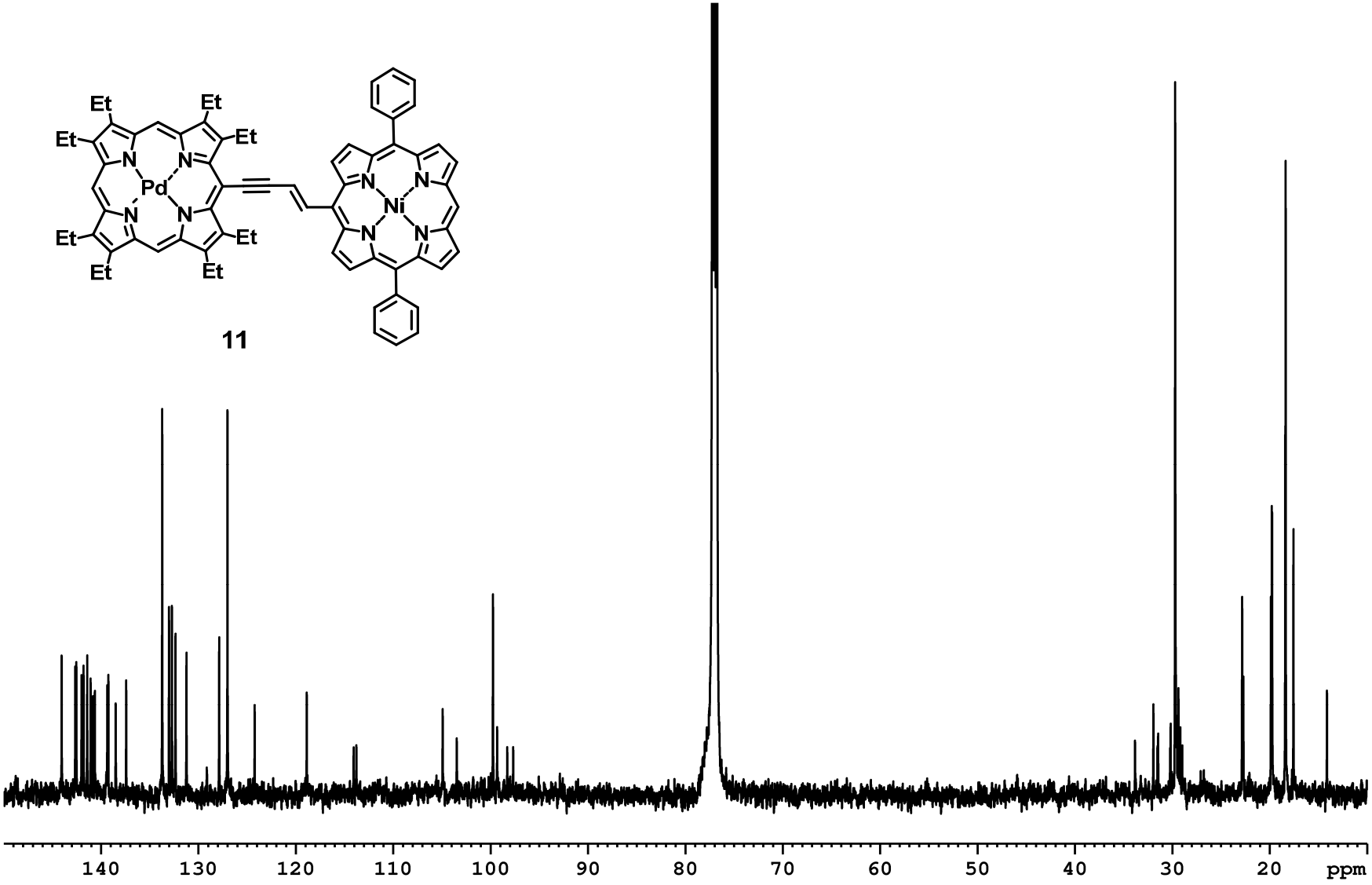

Figure S5. ^{13}C NMR spectrum of the dyad **11**.

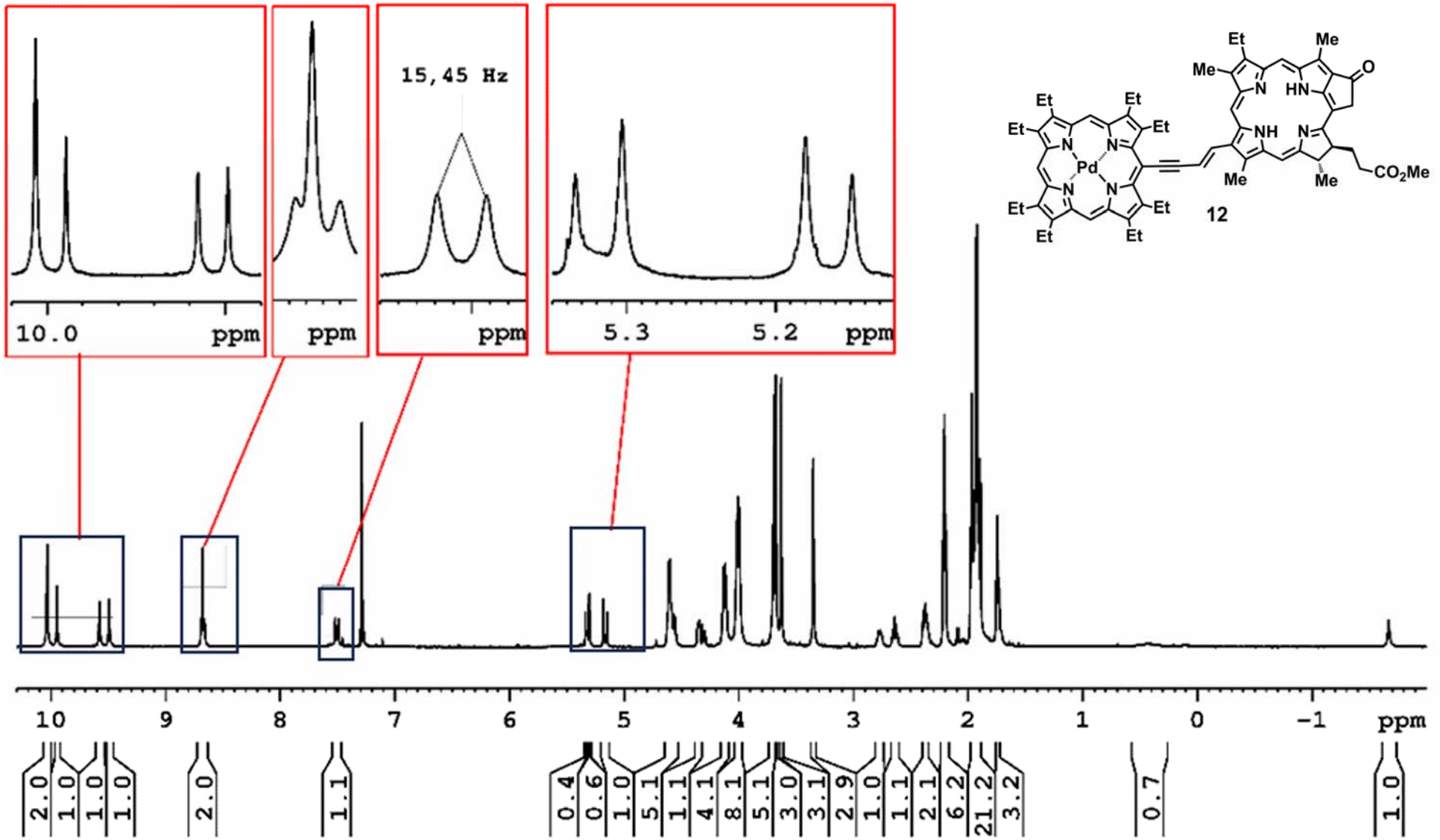

Figure S6. ^{1}H NMR spectrum of the dyad **12**.

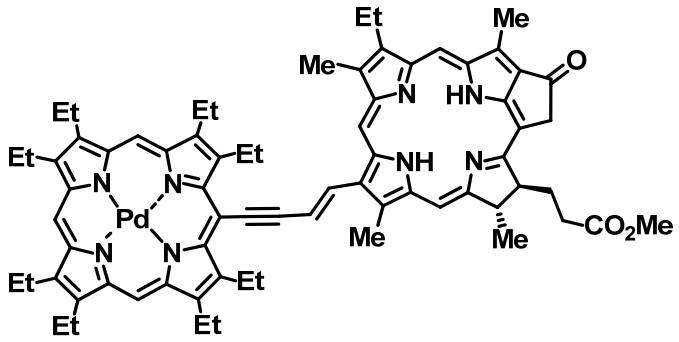

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Figure S7. ^{13}C NMR spectrum of the dyad **12**.

Mass spectra

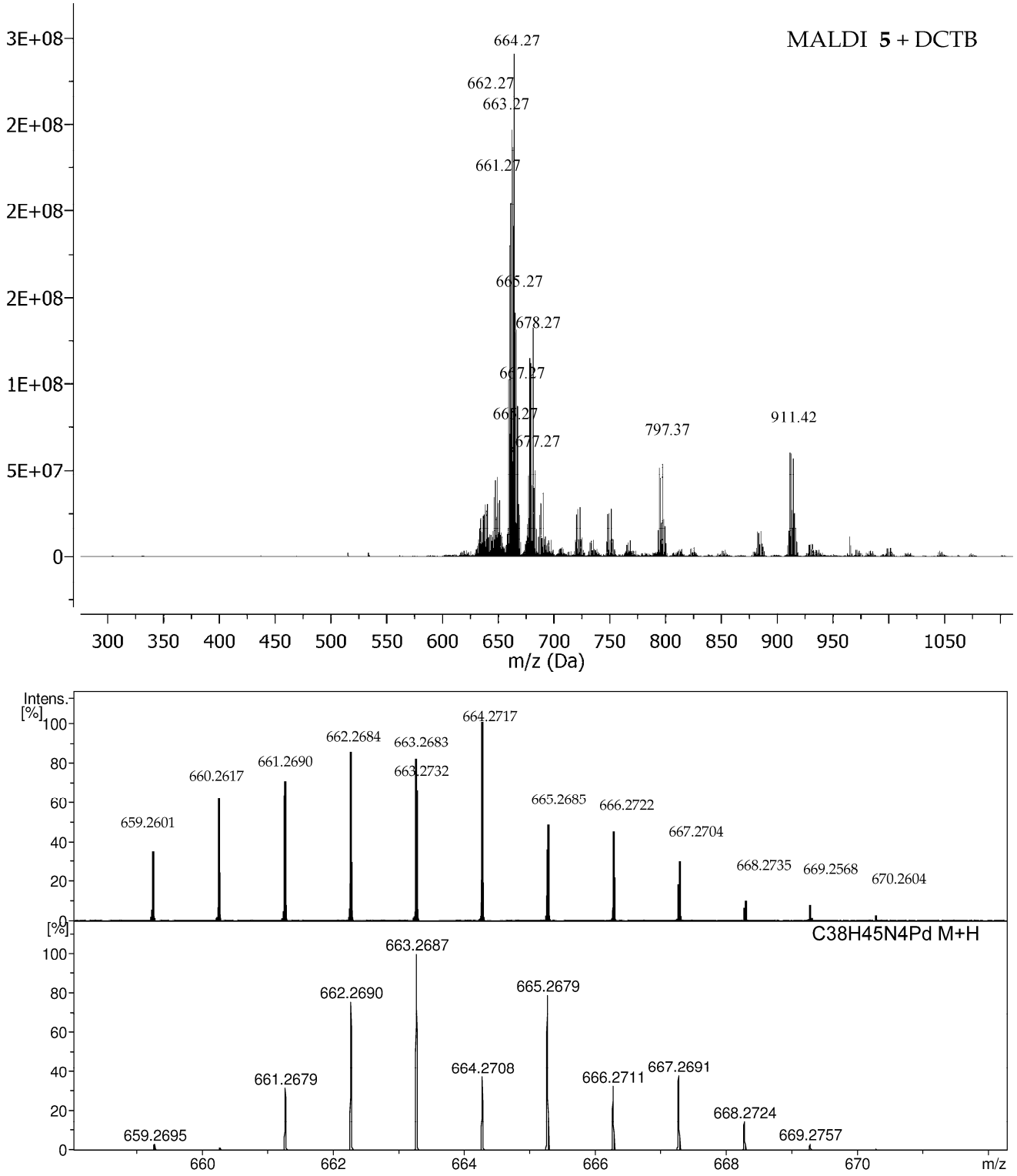


Figure S8. MALDI mass spectrum of **5** with expanded molecular ion area and simulated mass spectrum of the protonated molecule.

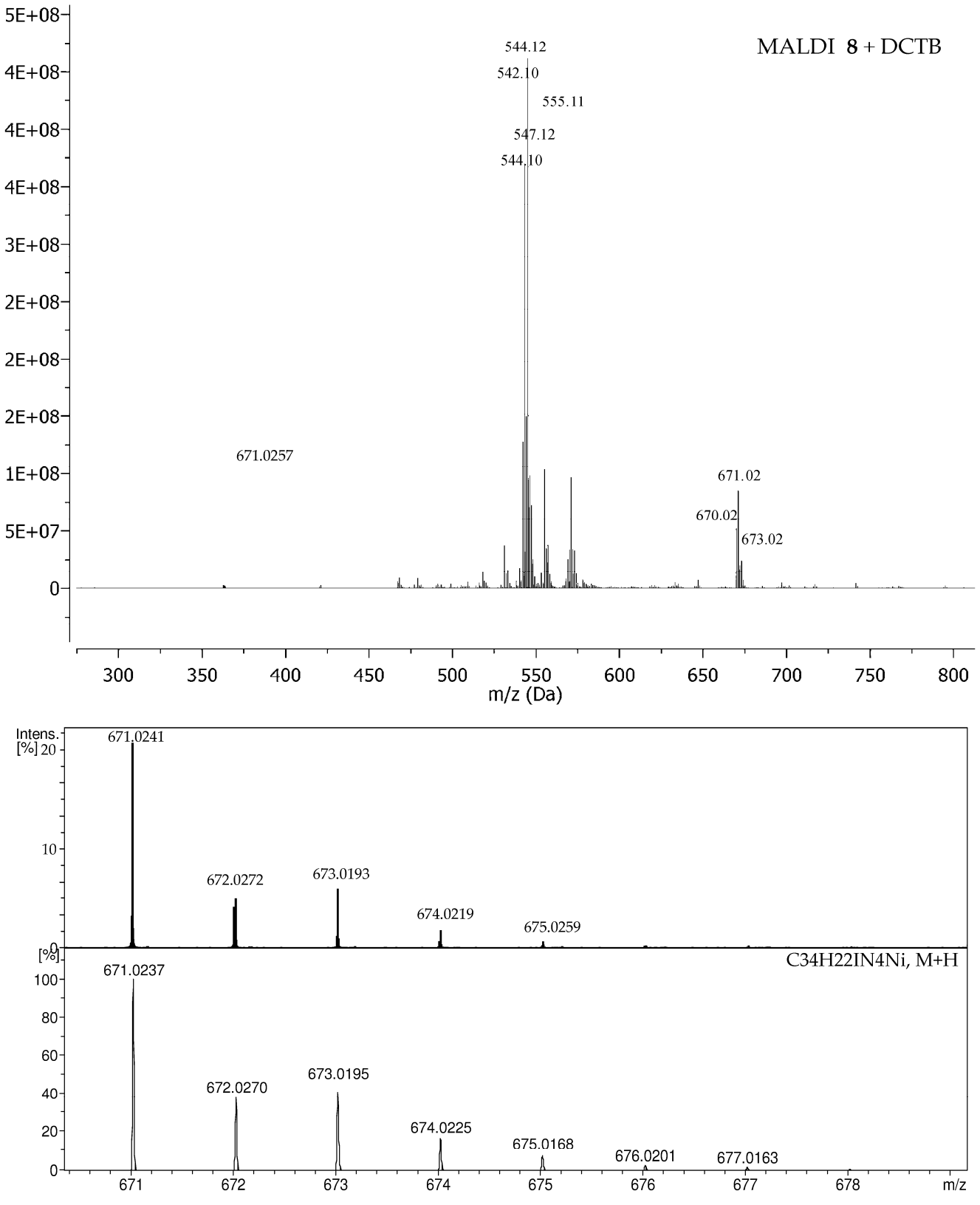


Figure S9. MALDI mass spectrum of **8** with expanded molecular ion area and simulated mass spectrum of the protonated molecule.

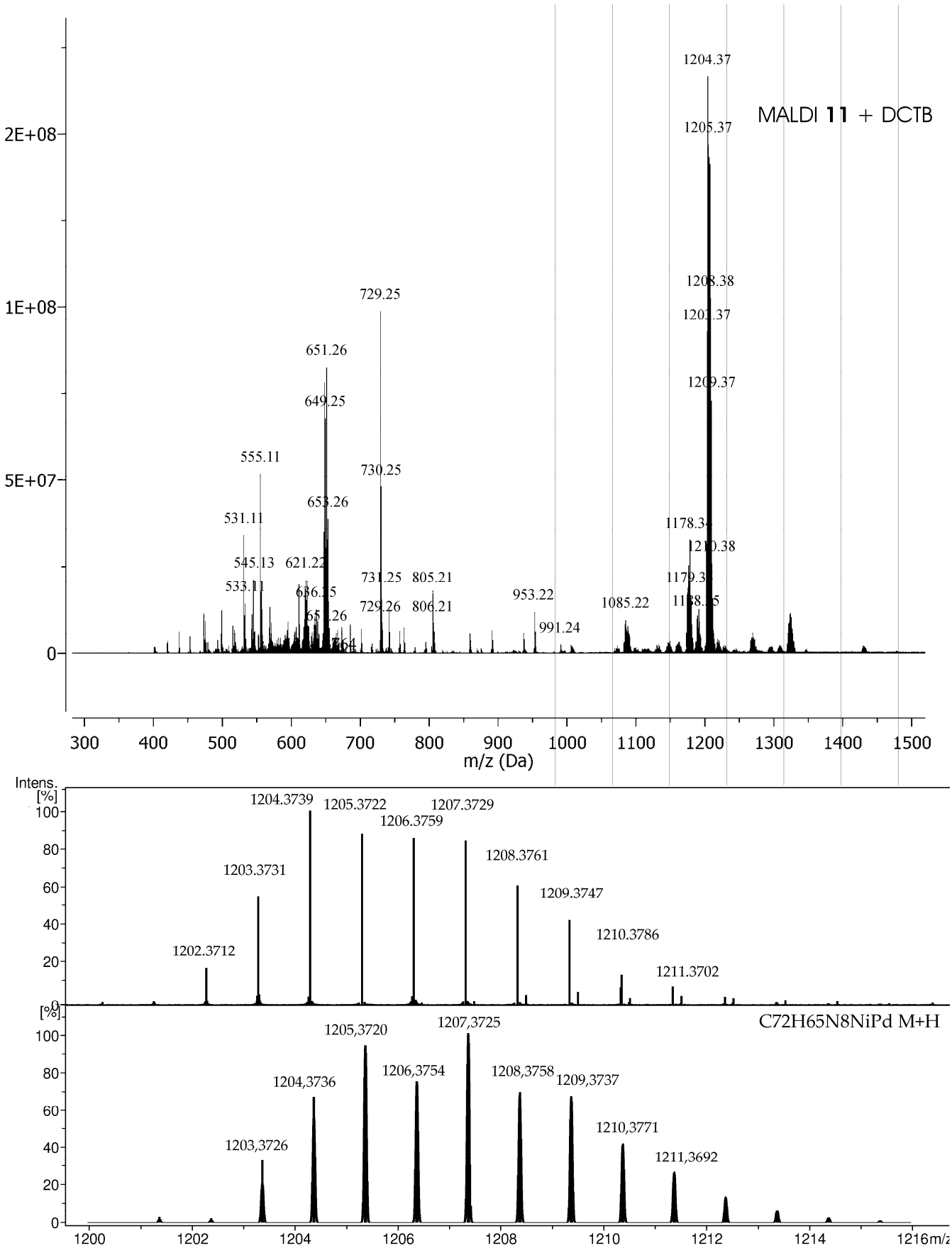
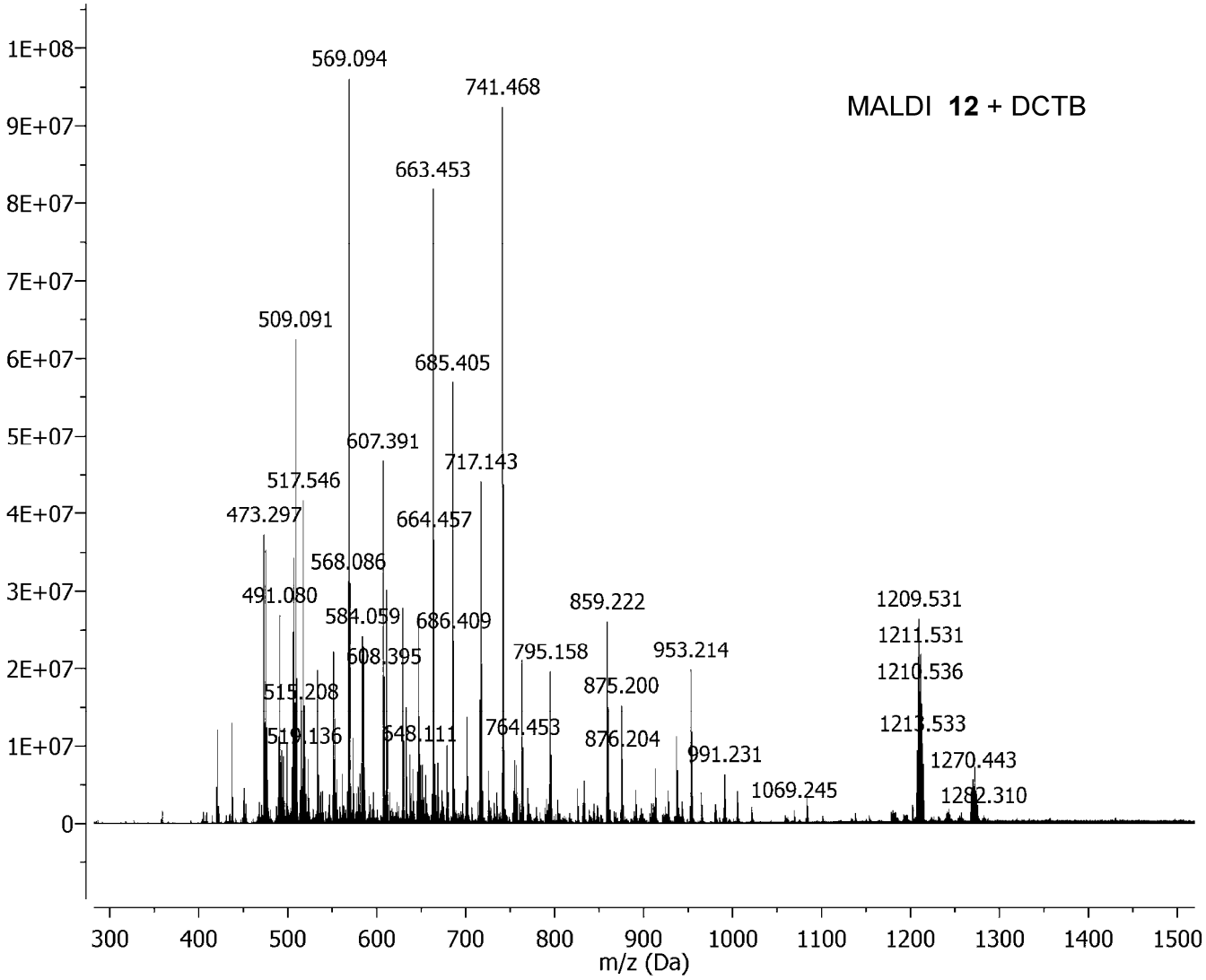


Figure S10. MALDI mass spectrum of **11** with expanded molecular ion area and simulated mass spectrum of the protonated molecule.



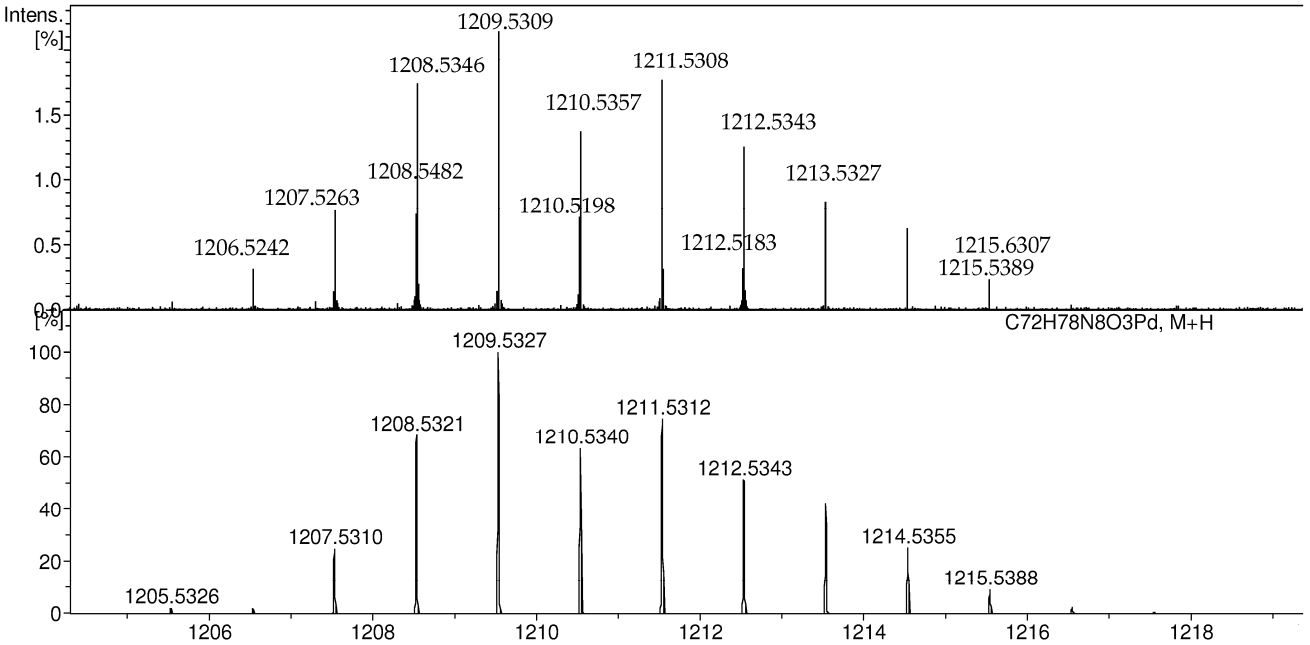


Figure S11. MALDI mass spectrum of **12** with expanded molecular ion area and simulated mass spectrum of the protonated molecule.

Photophysical data

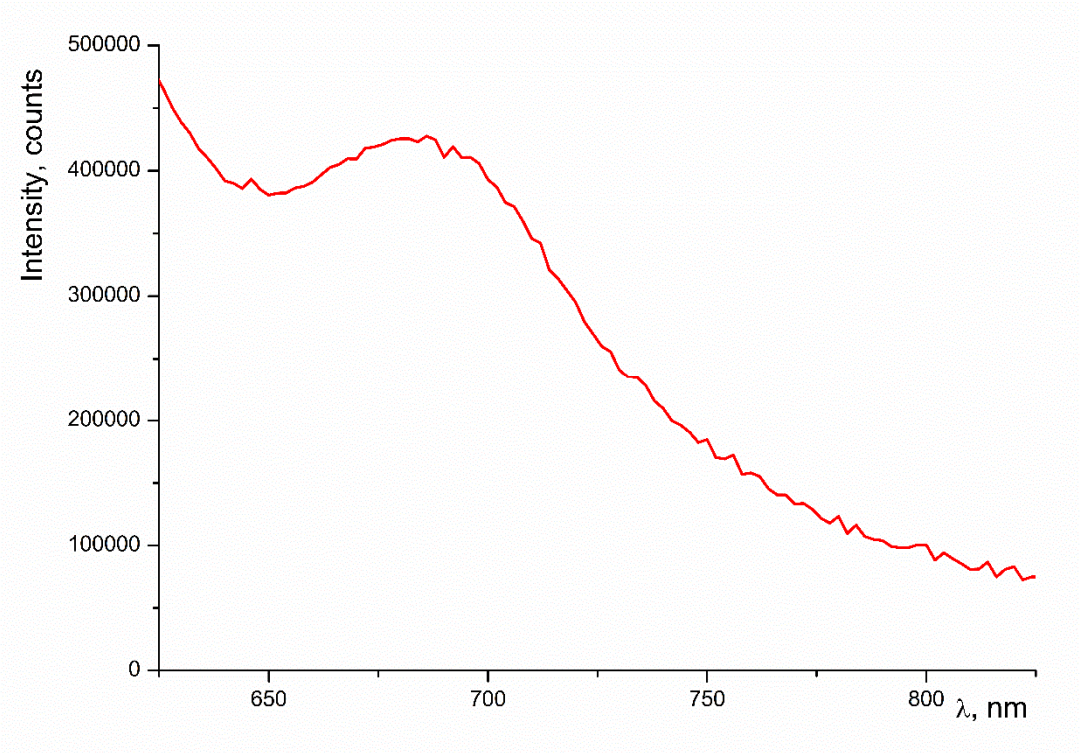


Figure S12. Steady state room temperature (298 K) luminescence spectrum of the dyad **11**, excitation at 506 nm.

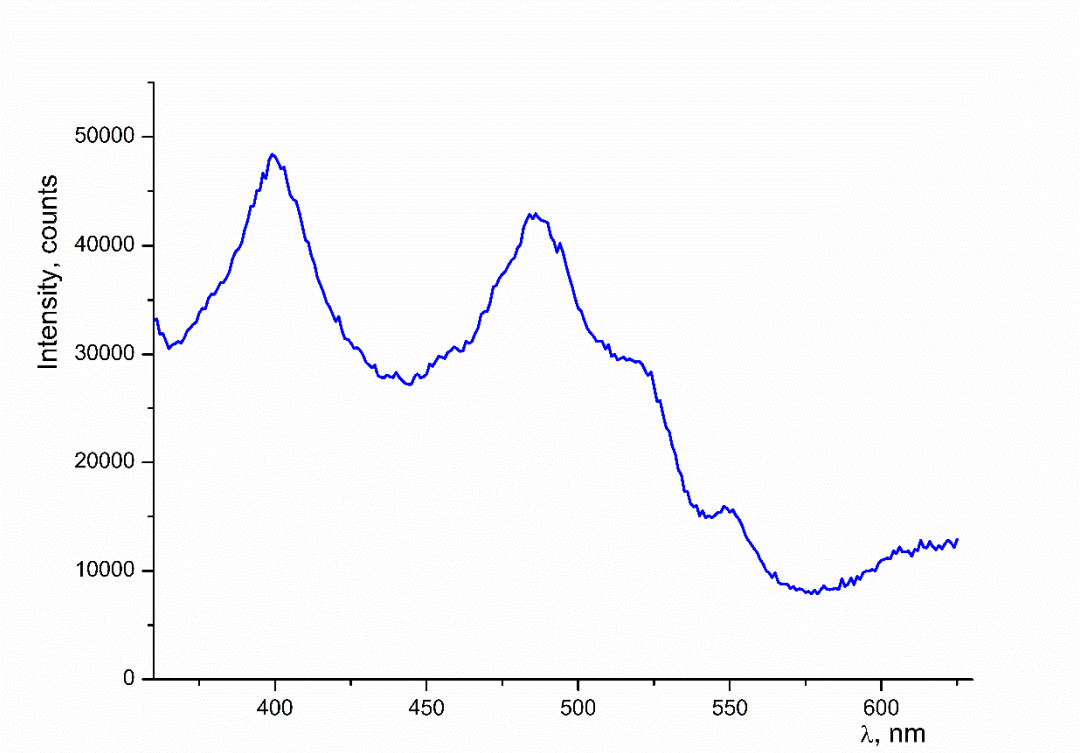


Figure S13. Room temperature (298 K) luminescence excitation spectrum of the dyad **11** at 670 nm emission.

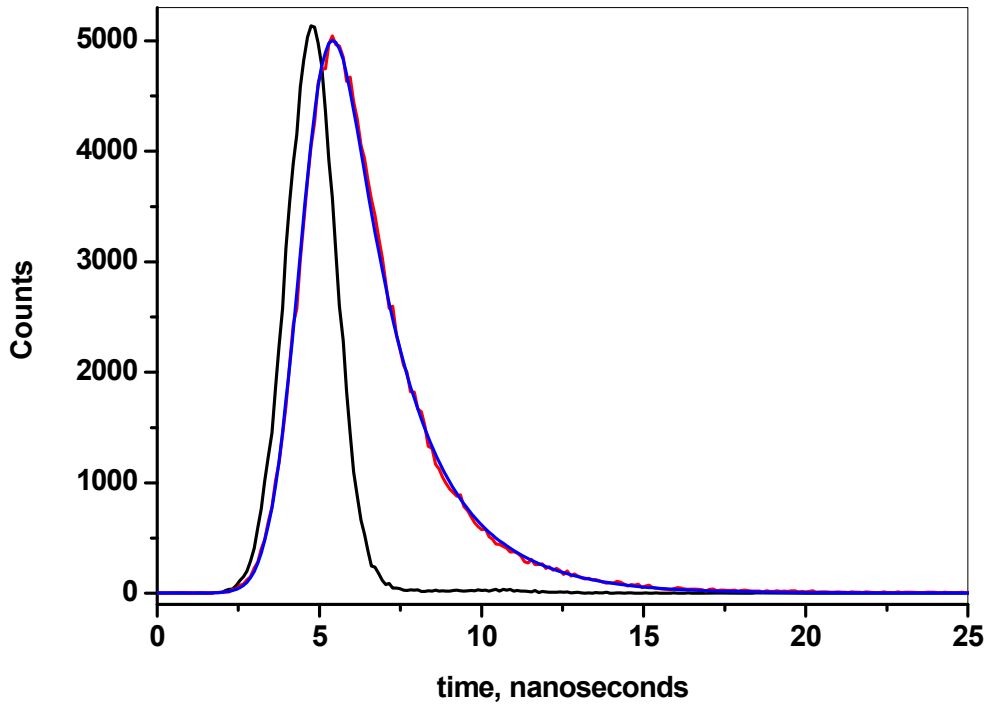


Figure S14. Fluorescence decay curve of compound **12** in air saturated CH_2Cl_2 solution (red line), prompt (black line), modelling of experimental data by DAS 6 software of Horiba (blue line). Defined life time is 1.89 nanosecond.

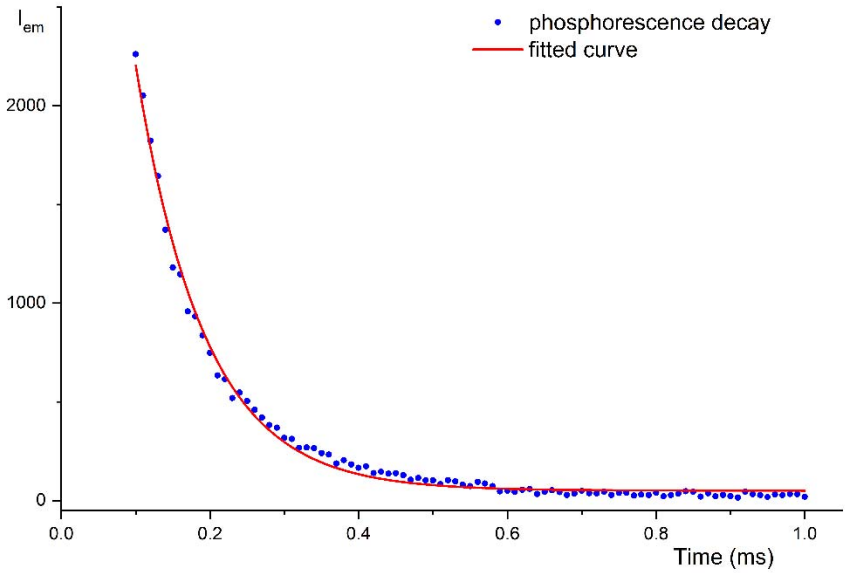


Figure S15. Phosphorescence decay (blue line) at 298K recorded at 722 nm, excitation at 410 nm and fitted exponential curve (red line), t = 92 mks. Compound **12** at concentration 10^{-6} M in CH_2Cl_2.

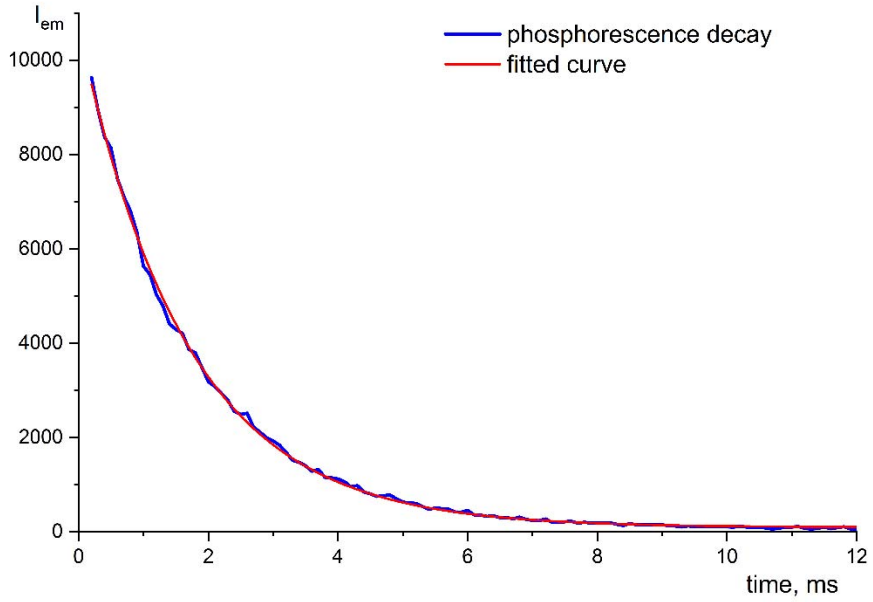


Figure S16. Phosphorescence decay (blue line) at 77K recorded at 662 nm, excitation at 397 nm and fitted exponential curve (red line), t=1.67 ms. Compound **12** at concentration 10^{-6} M in CH_2Cl_2.

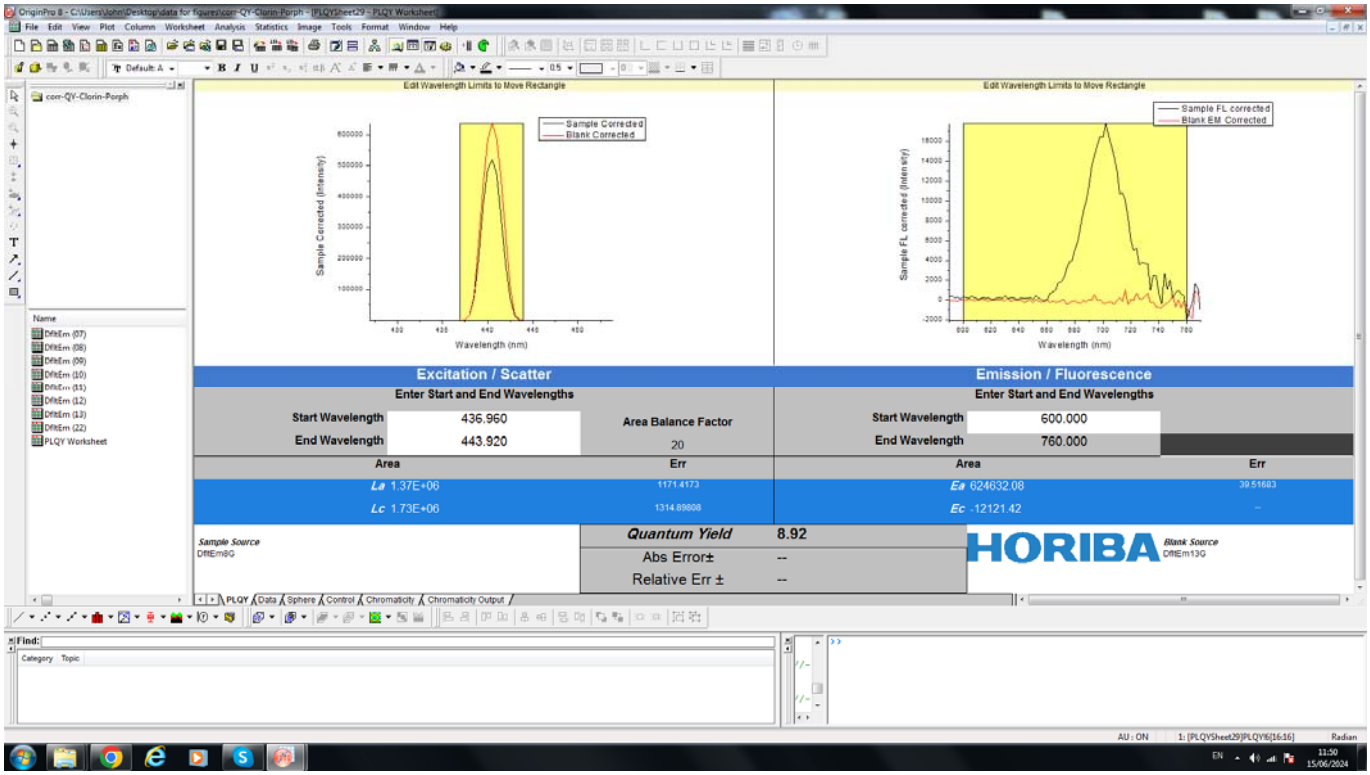


Figure S17. Quantum yield measurement. Compound **12** at concentration 10^{-6} M in CH_2Cl_2.

Results of DFT calculations

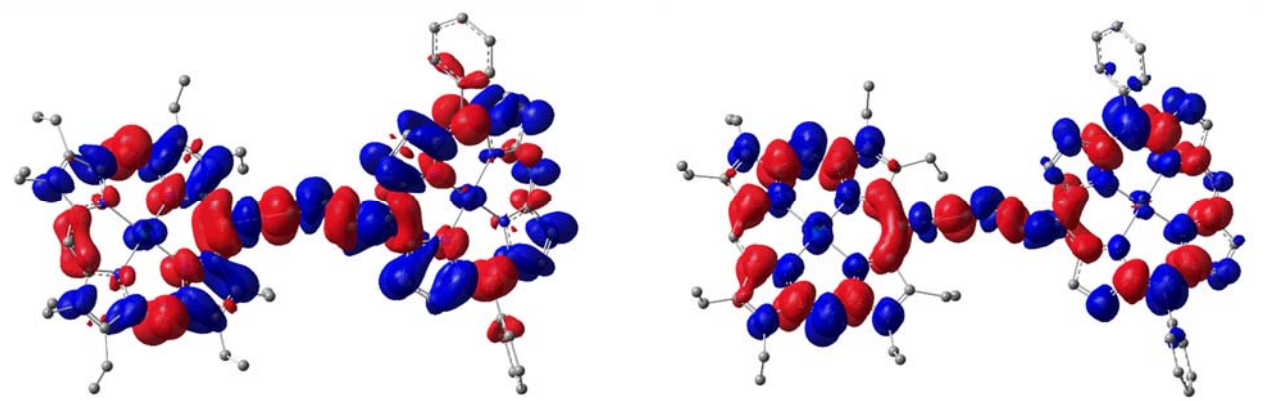


Figure S18. Electron density difference maps for the lowest wavelength (Q-band) (left) and most intense (B-band) (right) transitions of **11**. Increased and decreased densities are marked red and blue, respectively.

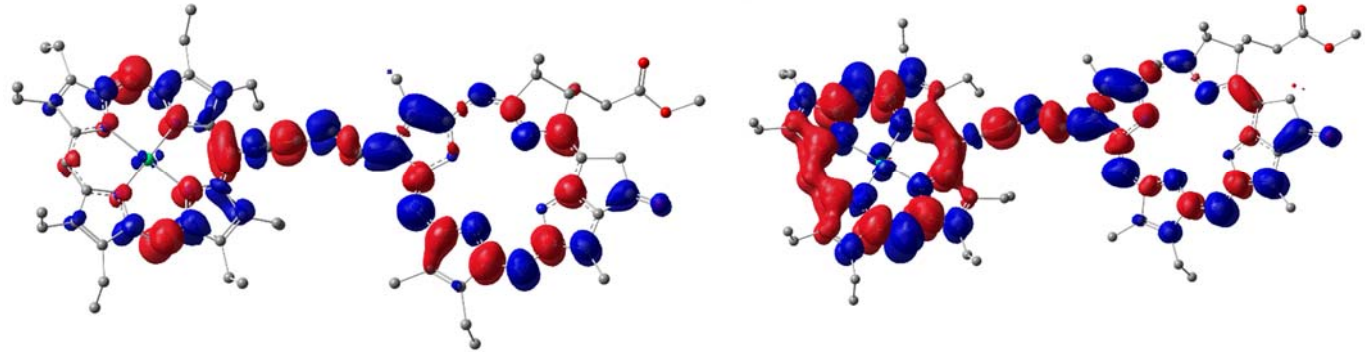


Figure S19. Electron density difference maps for the lowest wavelength (Q-band) (left) and most intense (B-band) (right) transitions of **12**. Increased and decreased densities are marked red and blue, respectively.

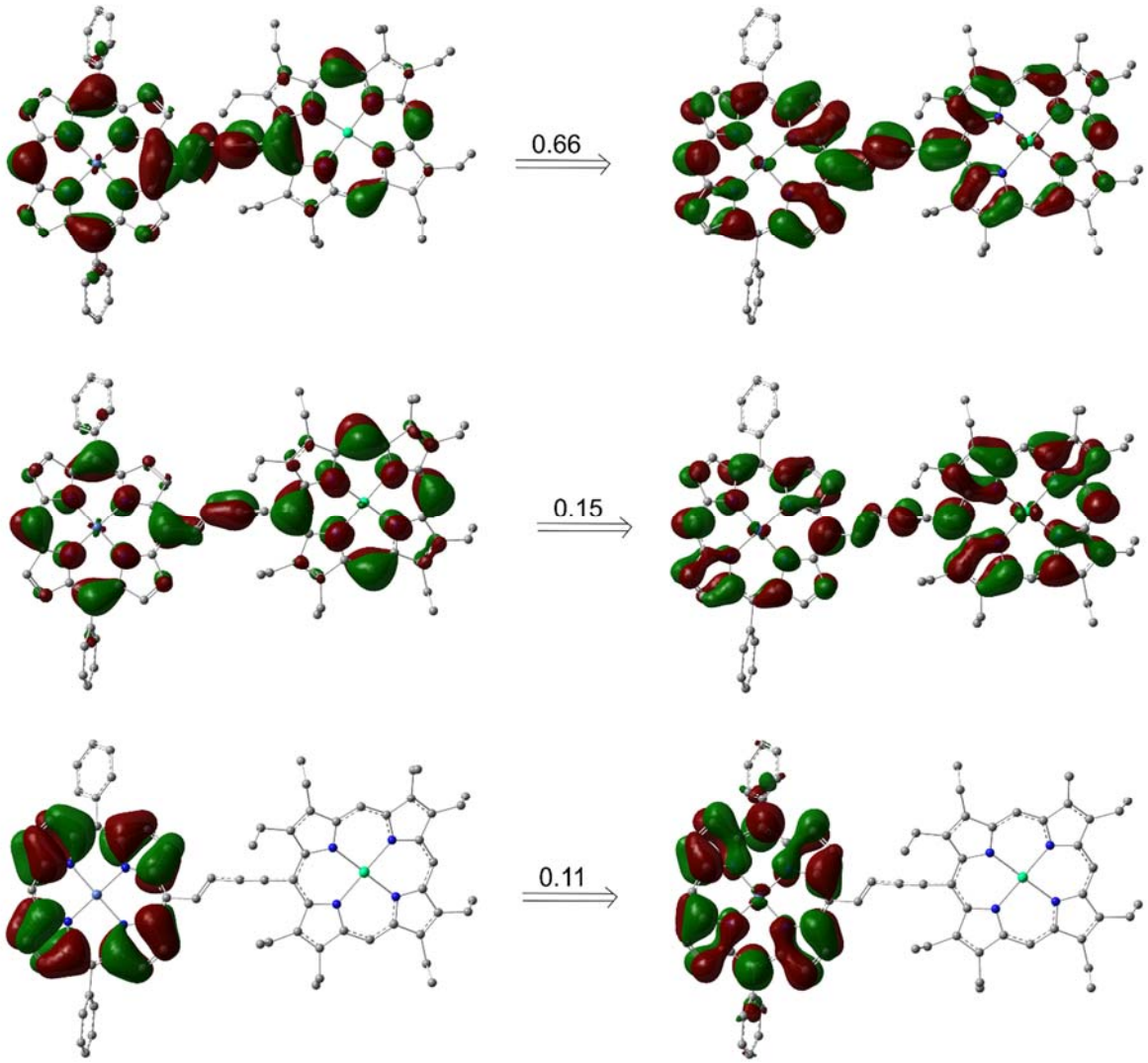


Figure S20. Natural transition orbitals of **11** composing the excited state 1 (615 nm band), calculated with wB97XD/DGDZVP. The coefficients of the transition components are above the arrows.

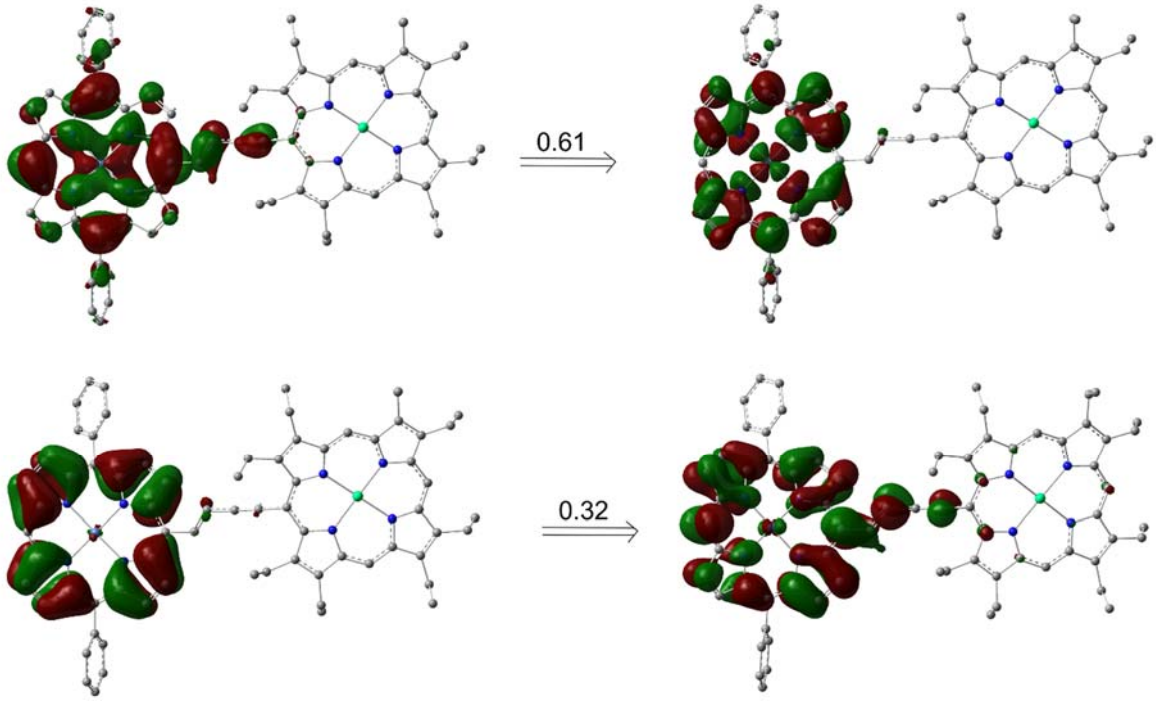


Figure S21. Natural transition orbitals of **11** composing the excited state 4 (615 nm band), calculated with wB97XD/DGDZVP. The coefficients of the transition components are above the arrows.

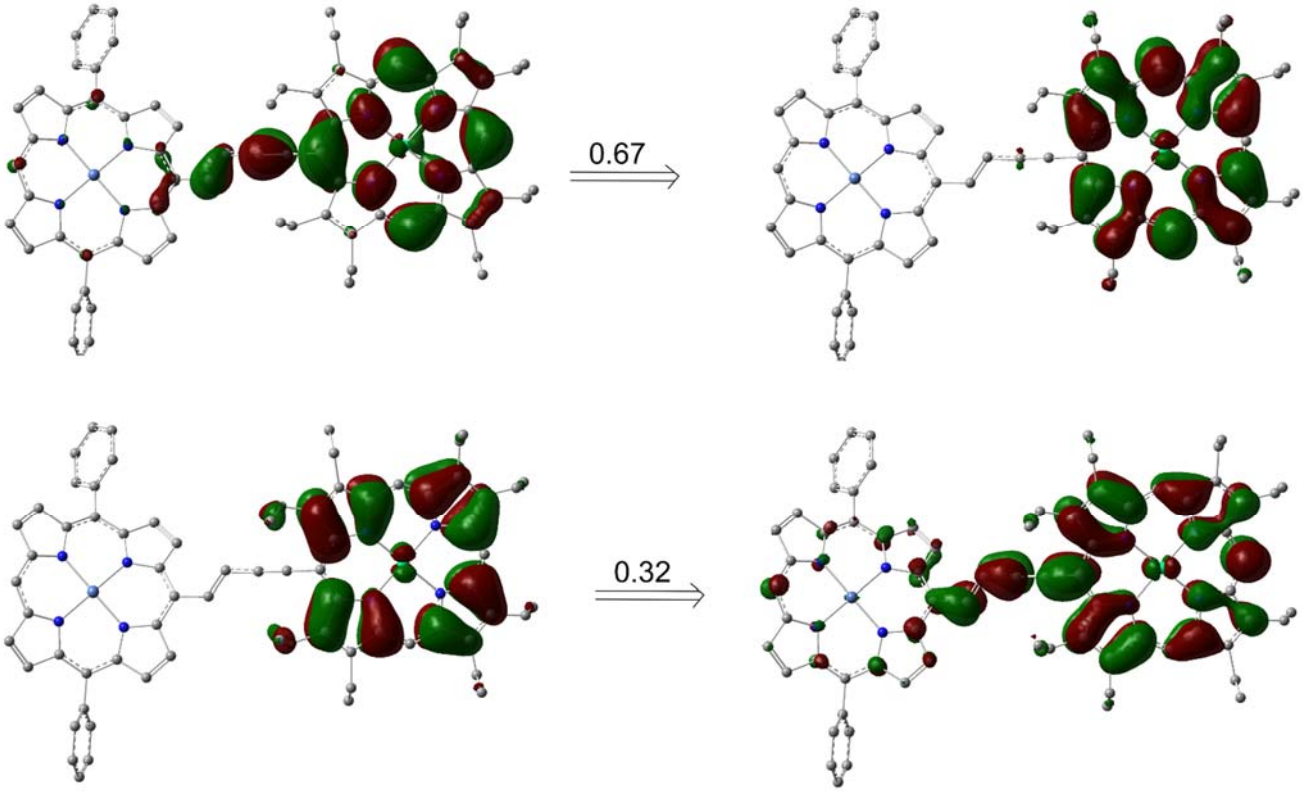


Figure S22. Natural transition orbitals of **11** composing the excited state 6 (615 nm band), calculated with wB97XD/DGDZVP. The coefficients of the transition components are above the arrows.

Table S1. Cartesian coordinates and energy of the dyad **11** in chloroform.
RB3LYP/(6-31G(d,p) for C,H,N; LanL2DZ for P,Ni) E= -3516.495153 a.u.

Atom	x	y	z
N	4.558866	1.263197	0.913058
N	7.409064	1.25251	0.192245
N	7.222101	-1.52801	-0.49468
N	4.374061	-1.51315	0.230217
C	3.204679	1.135483	1.093614
C	4.908598	2.537697	1.290238
C	7.320193	2.537456	0.654534
C	8.694799	1.074069	-0.25011
C	8.532786	-1.32841	-0.84499
C	6.958383	-2.85871	-0.67563
C	4.551334	-2.8523	-0.02374
C	3.043878	-1.31639	0.501743
C	2.674229	2.384456	1.650025
C	2.466897	-0.04442	0.785317
C	3.743527	3.236692	1.781032
C	6.168745	3.113857	1.177955
C	8.59723	3.212752	0.495743
C	9.45182	2.302943	-0.074
C	9.210209	-0.11782	-0.74757
C	9.122945	-2.58322	-1.28235
C	8.143812	-3.53798	-1.17075
C	5.730459	-3.46356	-0.43435
C	3.297753	-3.5496	0.145827
C	2.349227	-2.60677	0.459513
C	1.281473	2.715322	2.124586
C	3.744847	4.650044	2.299334
C	8.893043	4.62452	0.92189
C	10.88526	2.505408	-0.48185
H	10.2501	-0.11255	-1.05256
C	10.53089	-2.75224	-1.7835

C	8.246791	-5.01152	-1.45431
H	5.677173	-4.53046	-0.61532
C	3.109625	-5.03292	-0.02812
C	0.919731	-2.9412	0.801987
H	0.543317	2.48199	1.356546
H	1.22738	3.797976	2.275935
C	0.895447	2.018221	3.442888
H	4.685987	4.850488	2.823776
H	2.959648	4.76431	3.053582
C	3.542441	5.706582	1.195482
H	8.044693	5.273338	0.672501
H	9.739829	5.006252	0.341701
C	9.20987	4.75738	2.424532
H	11.47415	1.61657	-0.22479
H	11.31411	3.325678	0.103439
C	11.05742	2.812325	-1.98255
H	10.83528	-3.79671	-1.65782
H	11.2193	-2.16476	-1.16388
C	10.70737	-2.34913	-3.26072
H	9.052958	-5.18457	-2.17512
H	7.329662	-5.36083	-1.94394
C	8.5056	-5.86081	-0.19426
H	2.302287	-5.379	0.62532
H	4.007725	-5.56139	0.311022
C	2.795317	-5.44352	-1.48014
H	0.722106	-3.96222	0.46061
H	0.230918	-2.29904	0.252528
C	0.60959	-2.85932	2.308602
H	-0.11068	2.316782	3.756105
H	0.905425	0.930249	3.337248
H	1.59386	2.286084	4.242499
H	3.560752	6.717139	1.616766
H	4.328107	5.639732	0.436223

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H	3.596506	-5.13577	-2.15952
H	-0.43161	-3.13773	2.503364
H	1.255005	-3.53819	2.875521
H	0.764099	-1.84786	2.693451
H	6.254059	4.142368	1.507635
C	1.058335	0.080647	0.671396
C	-0.14235	0.212226	0.483581
C	-8.43158	-5.33427	1.225789
C	-8.10163	-4.57959	0.088116
C	-8.03269	-5.23085	-1.15426
C	-8.29688	-6.5975	-1.25823
C	-8.62936	-7.33655	-0.12076
C	-8.69394	-6.70129	1.121525
H	-8.47052	-4.84728	2.195571
H	-7.7772	-4.65795	-2.04088
H	-8.94275	-7.27036	2.012669
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C	-5.7509	2.571949	-1.16386
N	-5.67536	1.317239	-0.58095
C	-4.3605	0.933484	-0.68169
C	-5.36675	-3.57174	-0.08012
C	-4.24962	-2.7961	-0.0856
C	-4.69045	-1.42497	-0.12119
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C	-6.49694	-2.68196	-0.03664
C	-3.83727	-0.31624	-0.28762
C	-10.74	-1.49221	1.483188
C	-10.1239	-2.62168	1.040244
C	-8.81612	-2.22869	0.570546
N	-8.66953	-0.86038	0.666243
C	-9.8431	-0.39963	1.218134
C	-7.80945	-3.11596	0.179728
C	-9.04694	4.014868	-0.02211
C	-9.92954	3.335739	0.759959
C	-9.45628	1.979516	0.835599
N	-8.26683	1.844355	0.155208
C	-8.00548	3.083386	-0.38621
C	-6.85651	3.426016	-1.10707
C	-10.1814	0.934092	1.383505
H	-2.5648	1.849075	-1.66346
H	-4.27073	3.8268	-2.28403
H	-5.42709	-4.64949	-0.06589
H	-3.22565	-3.13712	-0.09499
H	-11.7266	-1.38749	1.914642
H	-10.5011	-3.633	1.046532
H	-9.07332	5.054177	-0.31355
H	-10.8366	3.697825	1.225522
C	-5.87882	5.750345	-1.30421
C	-6.78868	4.775419	-1.74572
C	-7.65918	5.097223	-2.80023

C	-7.61411	6.35504	-3.40342
C	-6.70204	7.31457	-2.95842
C	-5.83626	7.009025	-1.90577
H	-5.21182	5.521424	-0.4786
H	-8.36697	4.351884	-3.15092
H	-5.12987	7.752372	-1.54755
H	-8.24464	-7.08319	-2.22839
H	-8.83403	-8.40015	-0.20113
H	-11.1274	1.165026	1.861215
H	-8.29018	6.583354	-4.22234
H	-6.66755	8.293864	-3.42681
C	-2.40273	-0.50859	-0.12651
H	-2.0116	-1.50342	-0.30957
C	-1.52241	0.433146	0.31316
H	-1.88639	1.424478	0.577755
Pd	5.88622	-0.12773	0.197055
Ni	-7.16915	0.233535	0.049161

Table S2. Cartesian coordinates and energy of the dyad **12** in chloroform.
RB3LYP/(6-31G(d,p) for C,H,N,O; LanL2DZ for P,Ni) E= -3581.257522 a.u.

Atom	x	y	z
N	5.623729	-1.74748	-0.5925
N	8.418073	-1.30638	0.205994
N	7.920694	1.515236	0.378313
N	5.129112	1.069591	-0.42382
C	4.274317	-1.79889	-0.8357
C	6.117542	-3.02305	-0.7256
C	8.482149	-2.65385	-0.02444
C	9.655853	-0.91674	0.649385
C	9.224505	1.520936	0.80309
C	7.516383	2.820987	0.312155
C	5.15856	2.443612	-0.40686
C	3.840656	0.687037	-0.69858
C	3.899767	-3.1753	-1.17621

C	3.408427	-0.66904	-0.76785
C	5.054131	-3.91764	-1.12013
C	7.421905	-3.43245	-0.47342
C	9.811397	-3.14985	0.290507
C	10.54065	-2.06862	0.716925
C	10.02363	0.391598	0.943921
C	9.662604	2.888368	1.032297
C	8.600489	3.698889	0.719826
C	6.248334	3.23971	-0.07327
C	3.851851	2.962326	-0.73882
C	3.019451	1.883071	-0.91014
C	2.571988	-3.73147	-1.62565
C	5.223104	-5.3909	-1.37909
C	10.26904	-4.57339	0.128142
C	11.96538	-2.04131	1.198019
H	11.04208	0.550615	1.278449
C	11.0181	3.290154	1.545291
C	8.540036	5.201625	0.742868
H	6.079714	4.309807	-0.08644
C	3.508119	4.424469	-0.83872
C	1.583537	1.996784	-1.35495
H	1.777507	-3.44466	-0.93584
H	2.63289	-4.82334	-1.57914
C	2.184875	-3.32456	-3.06006
H	6.203458	-5.57599	-1.83254
H	4.490034	-5.71828	-2.12333
C	5.077317	-6.25602	-0.1118
H	9.47883	-5.25793	0.459536
H	11.11951	-4.75695	0.793252
C	10.67334	-4.92557	-1.31701
H	12.47265	-1.15087	0.807244
H	12.50385	-2.89812	0.779383
C	12.09361	-2.06587	2.733882

H	11.22065	4.32673	1.255829
H	11.7938	2.687568	1.057239
C	11.15804	3.156317	3.074469
H	9.284611	5.58168	1.450365
H	7.567395	5.528552	1.130134
C	8.780042	5.845663	-0.63688
H	2.704536	4.56278	-1.56927
H	4.365017	4.978936	-1.2377
C	3.081032	5.046062	0.505531
H	1.267461	3.03464	-1.20985
H	0.933906	1.390658	-0.72303
C	1.362636	1.618881	-2.8318
H	1.2299	-3.77888	-3.34525
H	2.08257	-2.24025	-3.15375
H	2.944946	-3.65469	-3.77572
H	5.216853	-7.31631	-0.34701
H	5.816311	-5.97495	0.645202
H	4.084863	-6.13325	0.333208
H	10.99293	-5.97049	-1.3872
H	9.838379	-4.77812	-2.00922
H	11.49977	-4.29279	-1.65572
H	13.14571	-2.04042	3.036121
H	11.58872	-1.20715	3.187457
H	11.64159	-2.9725	3.14841
H	12.16044	3.452979	3.400176
H	10.43029	3.791301	3.589511
H	10.98611	2.125315	3.399315
H	8.72072	6.937057	-0.57157
H	9.768884	5.580552	-1.02419
H	8.037396	5.507837	-1.36654
H	2.851361	6.110032	0.386149
H	2.19079	4.547364	0.901566
H	3.873847	4.950713	1.254187

H	0.310234	1.743837	-3.10834
H	1.964882	2.253774	-3.48984
H	1.638704	0.578499	-3.02269
H	7.625948	-4.48735	-0.61256
C	2.014853	-0.92169	-0.67747
C	0.826011	-1.14485	-0.50289
C	-1.5112	-0.57366	-0.0525
H	-1.21262	0.468636	0.022705
C	-0.53241	-1.47792	-0.33358
H	-0.78111	-2.52853	-0.46055
Pd	6.767847	-0.11902	-0.09457
C	-12.0839	1.170966	0.955443
C	-10.8537	1.908907	0.671326
C	-11.6848	-0.33239	1.007894
C	-10.3484	3.194092	0.464118
C	-9.78796	0.977069	0.580027
C	-10.1775	-0.36791	0.750555
C	-8.94201	3.019233	0.244671
C	-11.0987	4.489492	0.46981
N	-8.65562	1.658102	0.330499
C	-9.3138	-1.45237	0.759433
C	-7.94149	3.959392	-0.02385
H	-7.70358	1.322442	0.209334
N	-7.96119	-1.27861	0.674793
C	-9.6811	-2.92918	0.884338
C	-6.5859	3.665997	-0.20531
C	-7.35661	-2.44277	0.964174
C	-8.34858	-3.5124	1.417892
C	-10.0172	-3.58845	-0.48046
N	-6.04913	2.404244	-0.10173
C	-5.54968	4.654533	-0.51133
C	-5.97796	-2.67247	0.918896
C	-8.32445	-3.68434	2.947341

C	-11.294	-3.1248	-1.18309
C	-4.71993	2.554311	-0.32011
C	-4.37588	3.953813	-0.59007
C	-5.77948	6.124406	-0.72782
C	-4.96311	-1.7681	0.58997
C	-12.5603	-3.52805	-0.45284
C	-3.76142	1.521026	-0.26658
C	-2.99753	4.466452	-0.88287
C	-6.25427	6.468631	-2.15339
N	-5.14271	-0.43797	0.29954
C	-3.55228	-2.03786	0.501669
O	-12.6431	-4.40825	0.381589
O	-13.615	-2.79526	-0.86505
C	-3.94252	0.180048	0.035837
H	-6.04305	0.022379	0.299116
C	-2.91718	-0.84825	0.146631
C	-2.92389	-3.36473	0.797357
C	-14.8852	-3.12833	-0.26972
H	-12.2853	-0.87016	0.267273
H	-11.9564	-0.7433	1.988441
H	-10.7211	5.168591	1.242811
H	-12.1579	4.308633	0.661967
H	-11.0079	5.010828	-0.49009
H	-8.25172	4.996465	-0.09637
H	-10.512	-3.09389	1.577407
H	-8.1234	-4.47849	0.952511
H	-10.0925	-4.66753	-0.31034
H	-9.17214	-3.43008	-1.16021
H	-5.65374	-3.67998	1.155392
H	-9.06302	-4.42895	3.261326
H	-8.55586	-2.74	3.45134
H	-7.33927	-4.01596	3.289912
H	-11.3493	-3.58989	-2.17644

H	-11.3013	-2.04678	-1.36373
H	-4.85425	6.672603	-0.51784
H	-6.51623	6.495273	-0.00437
H	-2.73946	1.819305	-0.47082
H	-2.99007	5.554895	-0.98192
H	-2.60018	4.050423	-1.81702
H	-2.28921	4.202998	-0.08824
H	-7.19359	5.959344	-2.39106
H	-5.51248	6.159254	-2.89647
H	-6.4153	7.546516	-2.26048
H	-2.73123	-3.94304	-0.11536
H	-3.56174	-3.97635	1.439949
H	-1.96522	-3.23565	1.309147
H	-14.8452	-2.99769	0.813788
H	-15.1544	-4.16222	-0.49763
H	-15.6049	-2.43983	-0.71043
O	-13.2193	1.594794	1.123036