Synthesis and redox reactions of bis(verdazyl)palladium complexes

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Supporting Information

Contents:

Table S1. Crystallographic data for **4, 5, 6,** and **7**

	4	**5**	**6**	**7**
Empirical Formula	$C_{28}H_{42}B_2F_8N_{10}O_3PdS$	$C_{26}H_{36}N_{10}O_2Pd$	$C_{26}H_{36}ClN_{10}O_2Pd$	$C_{13}H_{20}Cl_2N_5OPd_{0.5}$
Formula Weight	878.79	627.05	662.50	386.44
a (Å)	9.2988(4)	9.7686(5)	18.4316(5)	14.3982(19)
b (Å)	22.7666(9)	10.5532(5)	8.8810(2)	8.6271(12)
c (Å)	18.2185(7)	14.0846(7)	18.9892(5)	14.4349(19)
α (deg)	90	77.023(2)	90	90
β (deg)	92.149(3)	77.476(2)	108.3960(10)	107.688(3)
γ (deg)	90	77.674(2)	90	90
V (Å^3)	3854.2(3)	1360.35(12)	2949.52(13)	1708.3(4)
Z	4	2	4	4
space group	$P2_1/n$	P-1	$P2_1/n$	$P2_1/c$
T (K)	90	100	90	90
λ (Å)	1.54178	0.71073	0.71073	0.71073
D_{calcd} (g cm^{-3})	1.514	1.531	1.492	1.503
μ (mm^{-1})	5.129	0.727	0.762	0.896
R [all data] [a]	0.0998	0.0398	0.0422	0.0288
R_w [all data][b]	0.1904	0.0611	0.0642	0.0584
CCDC#	1415460	1415461	1415462	1415463

[a] $R = \sum|F_{obs}-F_{calc}|/\sum|F_{obs}|$. [b] $R_w = [\sum(|w||F_{obs}-F_{calc}|)^2/\sum|wF_{obs}^2|]^{1/2}$.

Figure S1. ^{1}H NMR of **5** ($CDCl_3$, 360 MHz)

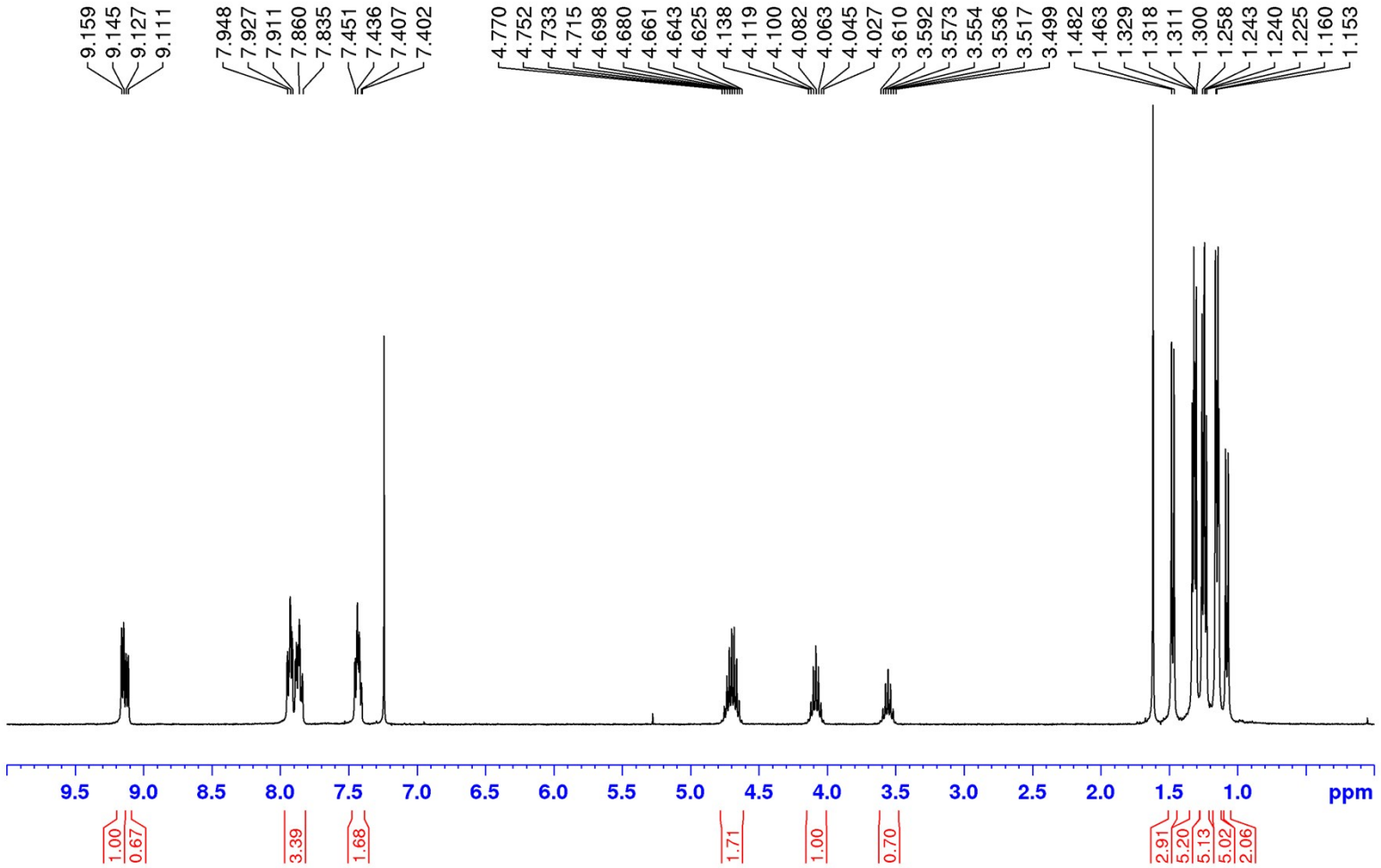

Figure S2. ^{1}H NMR of **5** ($CDCl_3$, 360 MHz) - *Expansions*

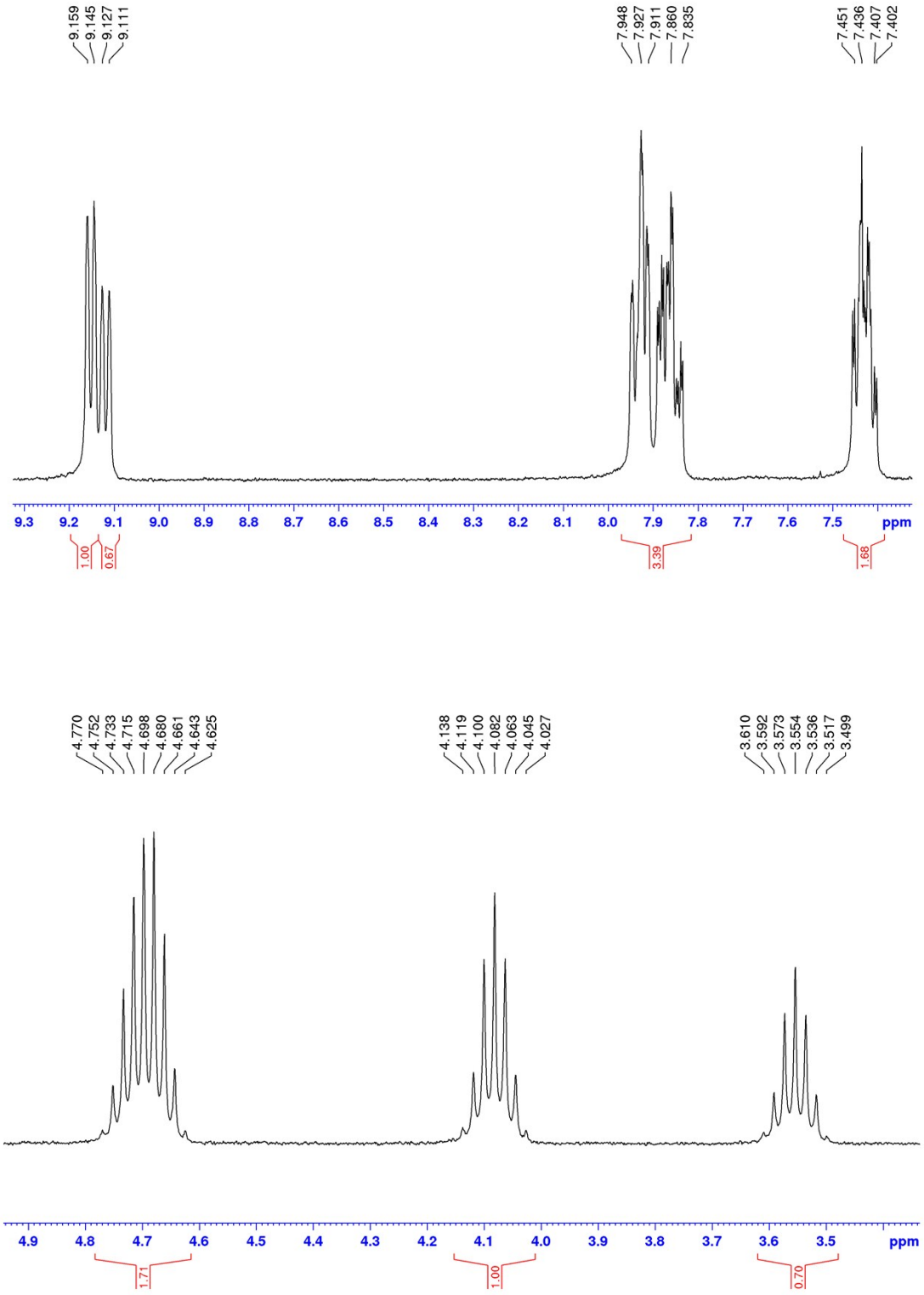

Figure S3: ^{1}H NMR of **5** ($CDCl_3$, 360 MHz) – *Expansions*

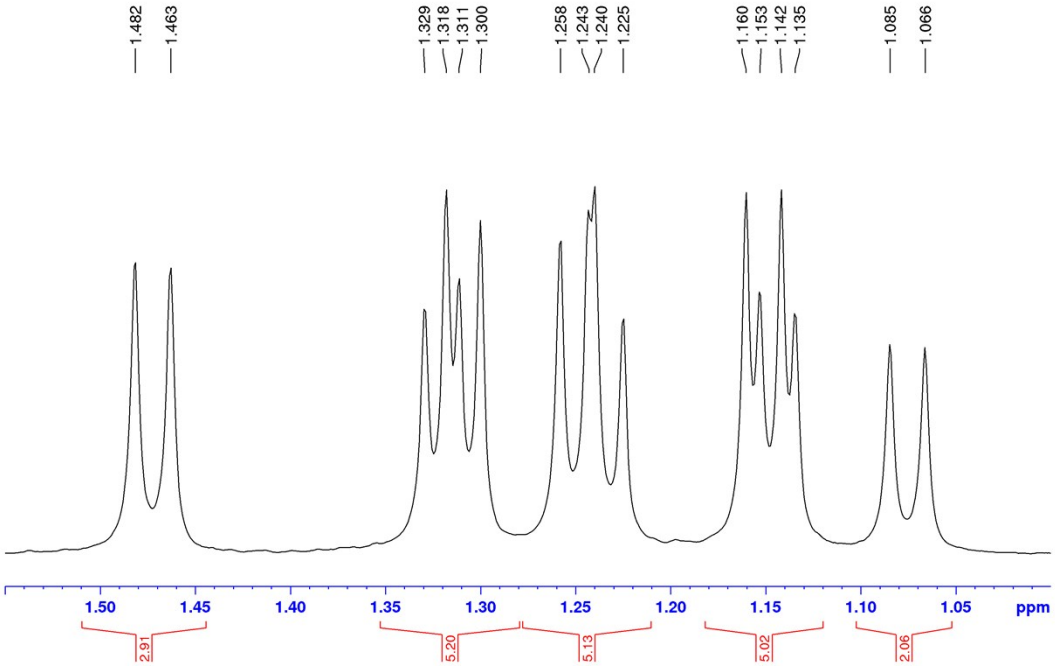

Figure S4. COSY of **5** ($CDCl_3$, 360 MHz)

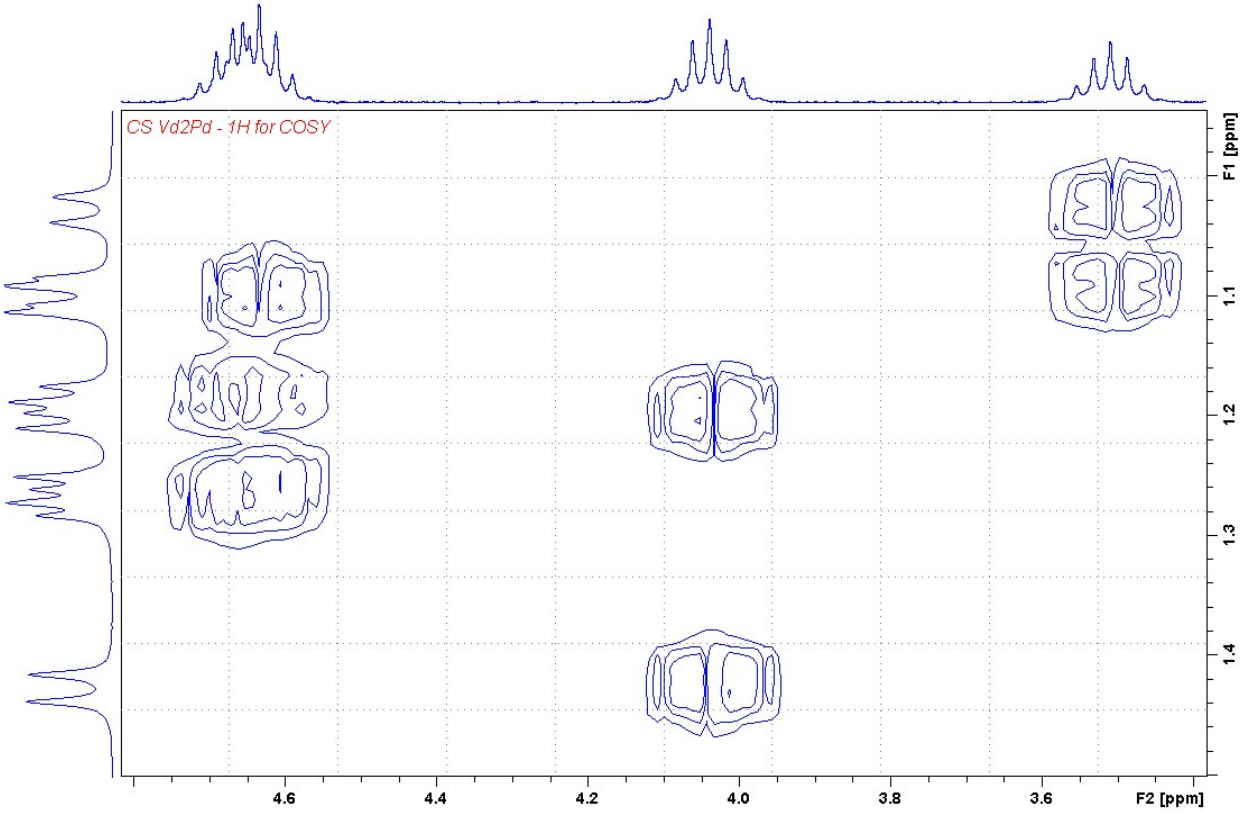

Figure S5. ^{13}C NMR of **5**($CDCl_3$, 90.6 MHz)

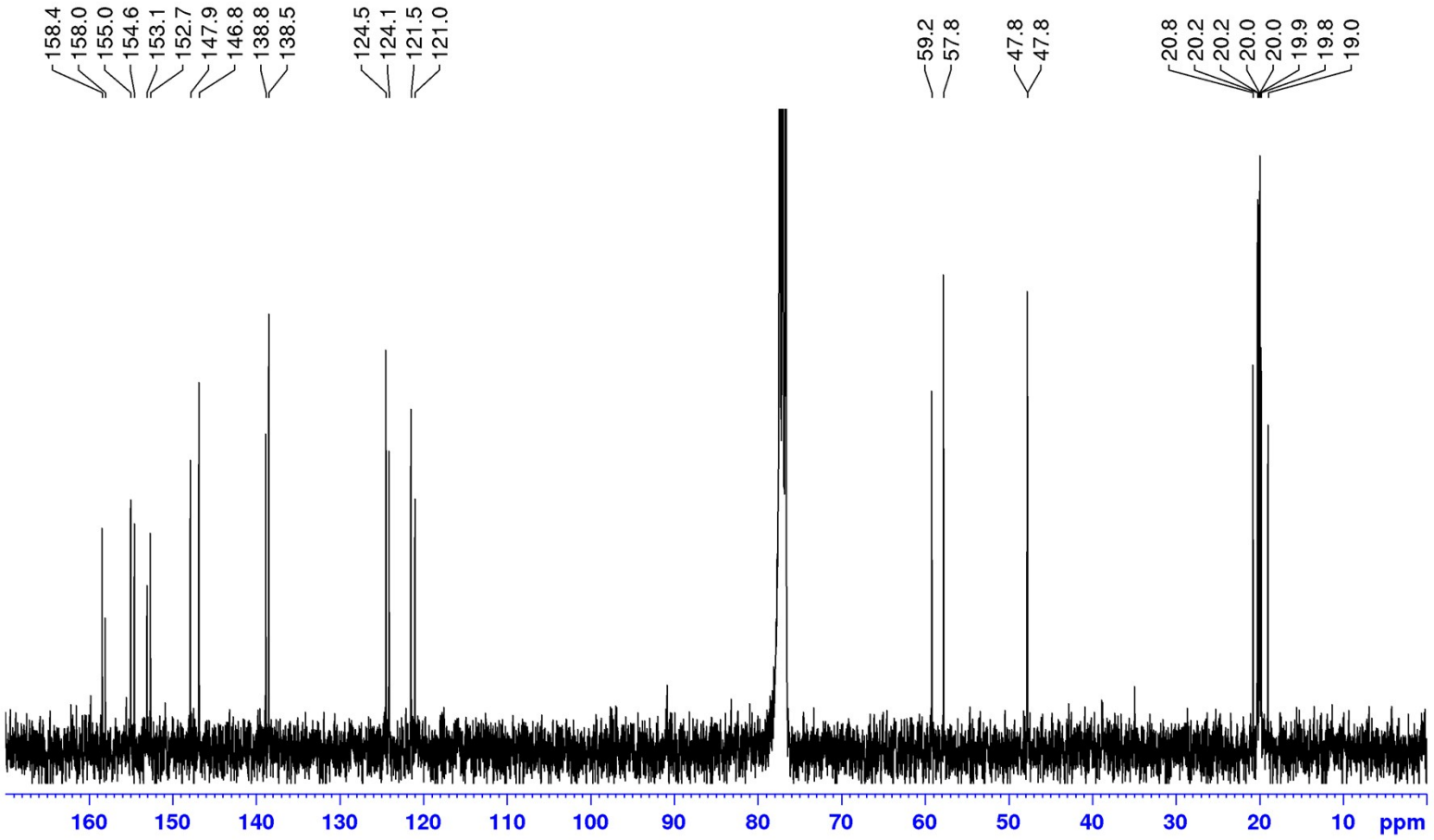

Figure S6 ^{1}H NMR of **7** (DMSO-d_6, 300 MHz, 298 K)

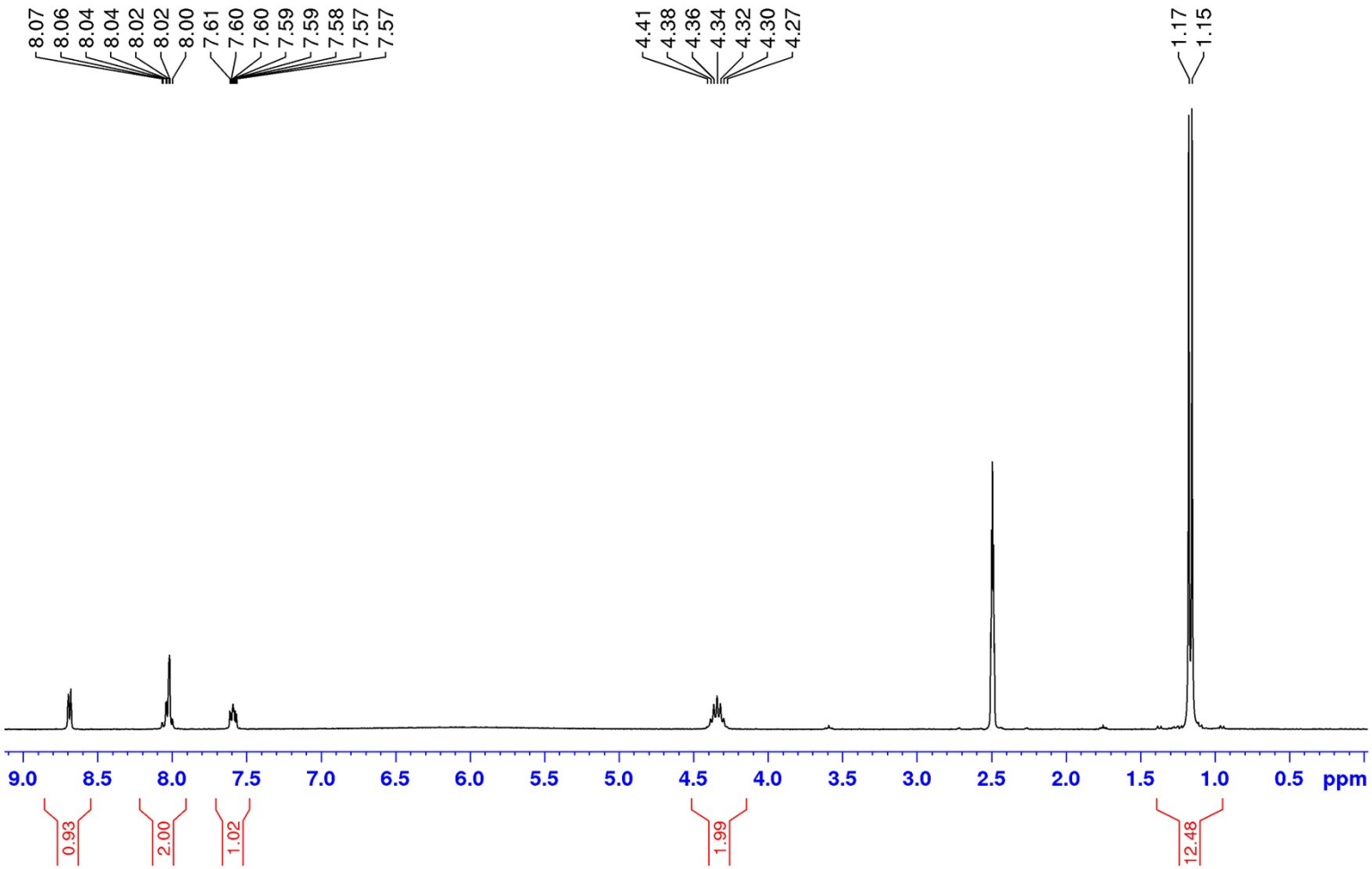

Figure S7. ^{1}H NMR of **7** (DMSO-d_6, 300 MHz, 298 K) - *Expansions*

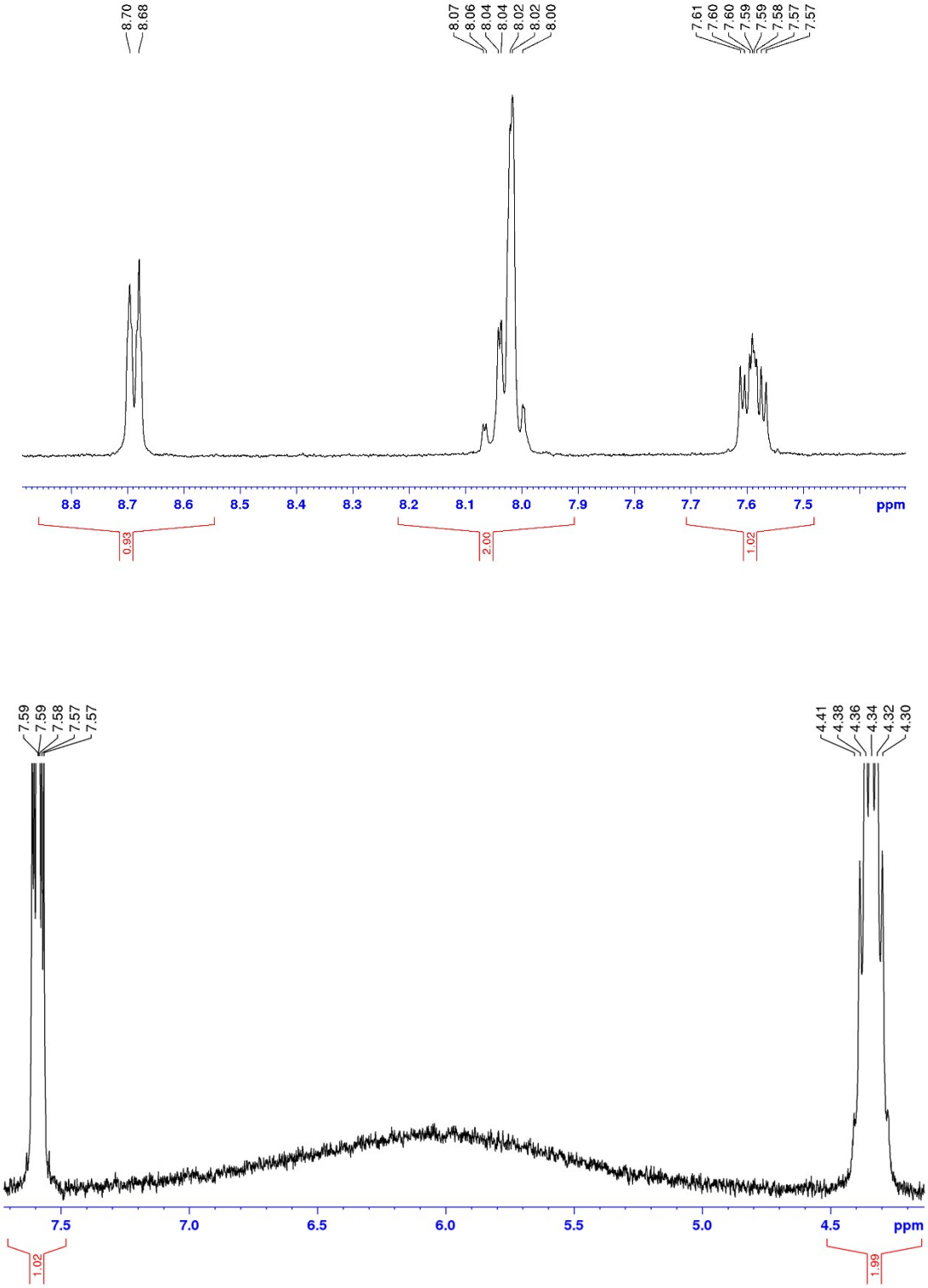

Figure S8. ^{1}H NMR of **7** (CD_3CN, 500 MHz, 233 K)

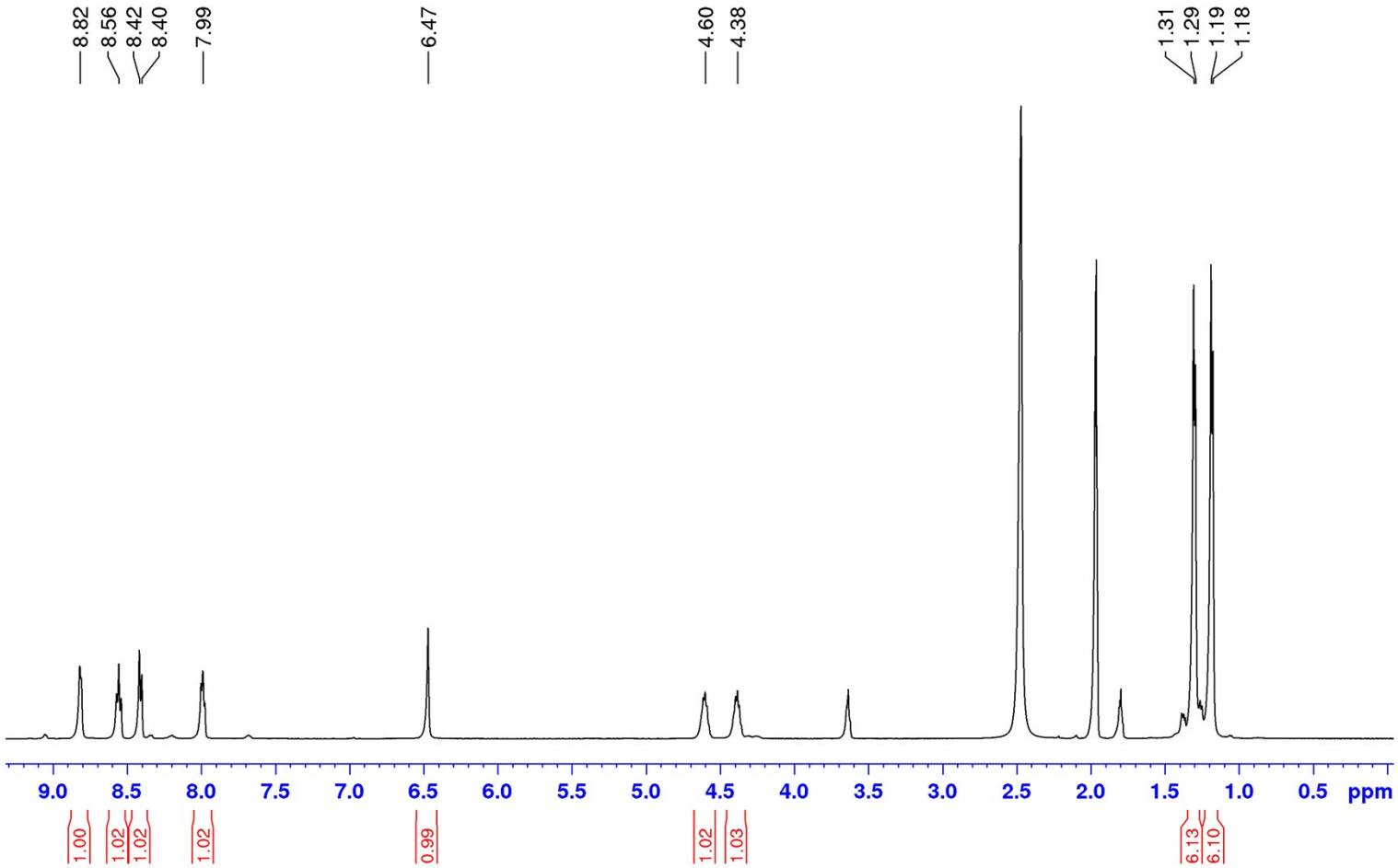

Figure S9. ^{13}C NMR of **7** (DMSO-d_6, 75.5 MHz, 298 K)

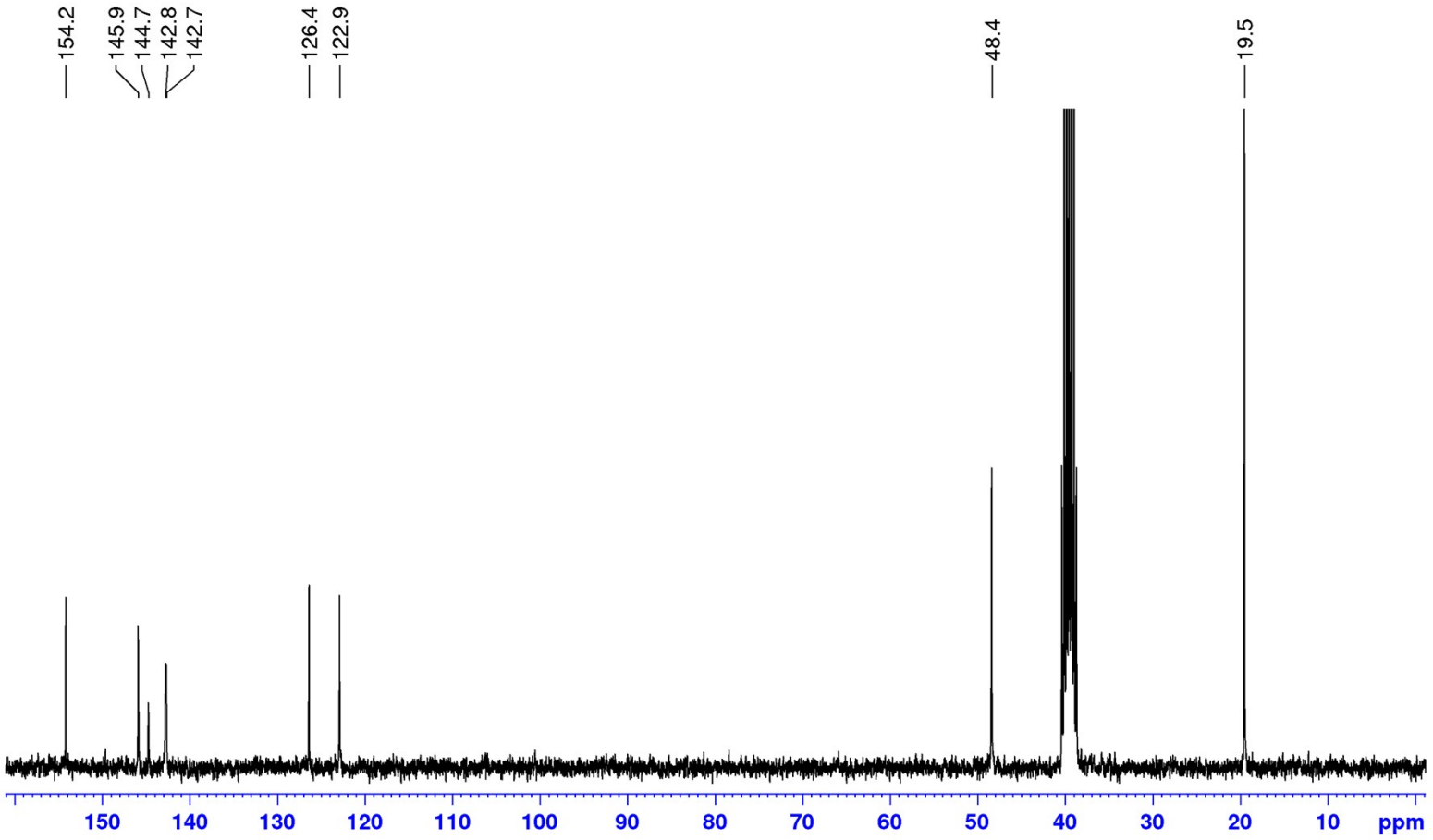

Figure S10. Electronic spectra of **3** (black dotted line) and **4** (black solid line) in dichloromethane

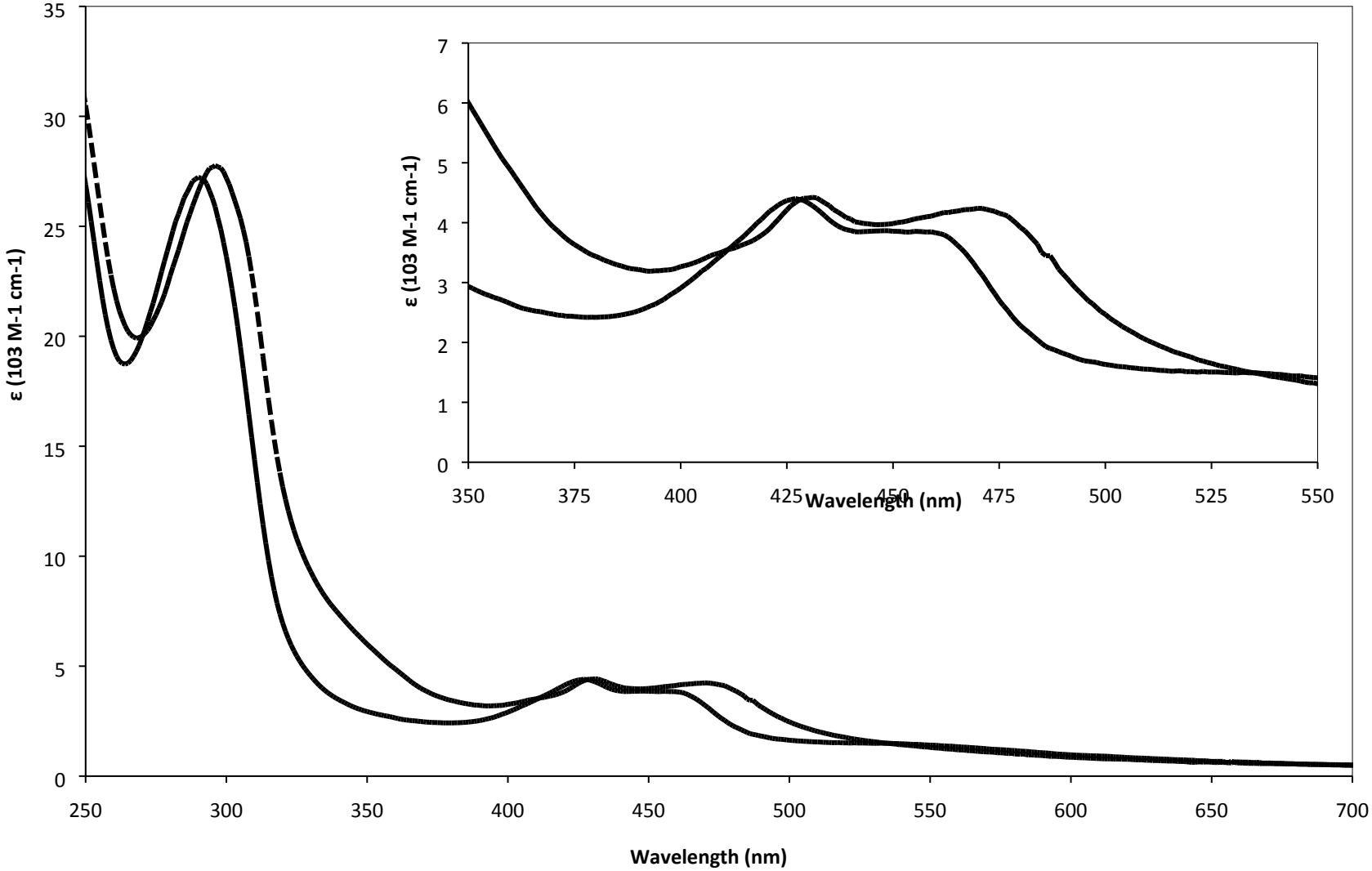

Figure S11. Electronic spectra of **5** (red line, dichloromethane), **6** (blue line, dichloromethane), and **7** (green line, acetonitrile). The inset contains bis-radical complex **4** for comparison (black line) and **7** has been omitted from the inset for clarity.

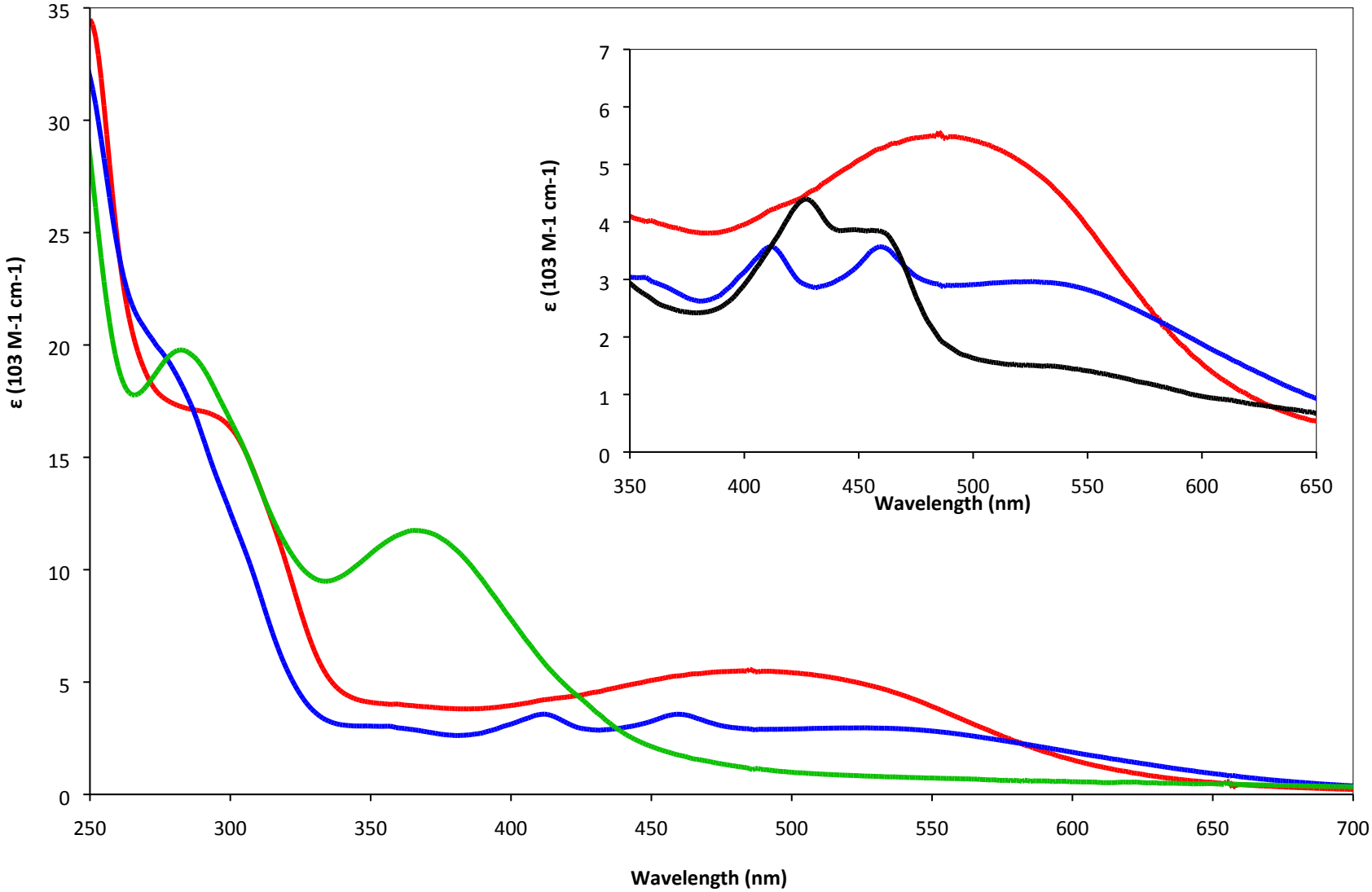

Figure S12. EPR spectra of **3** (red line), **4** (black line), and **6** (blue line) in dichloromethane. The bold lines represent the experimental spectra and the thin lines represent simulated spectra.

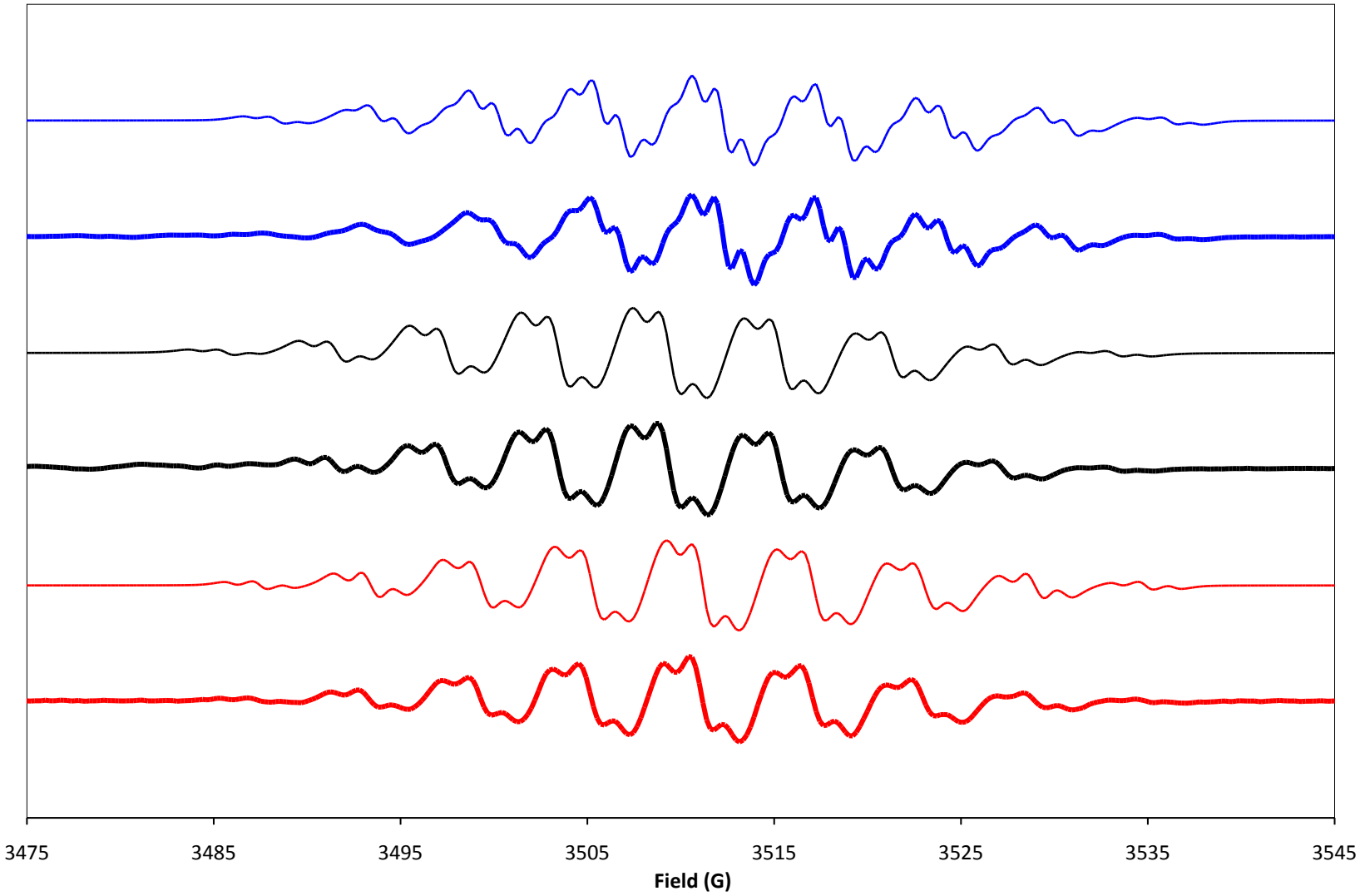

Table S2. EPR Parameters

Compound	**3**	**4**	**6**
Frequency (GHz)	9.8458	9.8438	9.8528
g	2.0047	2.0046	2.0049
a(N)[a] (G)	5.7	5.8	5.4
a(N)[a] (G)	6.1	6.1	6.6
a(H)[b] (G)	1.5	1.5	1.4

a) Two equivalent ^{14}N nuclei

b) C<u>H</u> of isopropyl groups (two equivalent ^{1}H nuclei)

Table S3. Initial coordinates for computational study of **5**

C	3.497601	-0.568662	9.299248
C	5.982665	-1.015187	8.361314
C	4.696071	1.343547	10.193960
H	3.922522	1.298791	10.824607
C	5.915422	0.779943	10.920778
H	5.777648	-0.174133	11.097451
H	6.038892	1.254714	11.768755
H	6.711867	0.896184	10.361313
C	4.907285	2.803632	9.831969
H	5.629213	2.876600	9.174037
H	5.145638	3.308558	10.636858
H	4.080498	3.168478	9.450933
C	3.219534	-3.021622	9.335988
H	2.309855	-2.740767	9.642734
C	3.850179	-3.865373	10.438709
H	4.713255	-4.211748	10.131692
H	3.257061	-4.613865	10.657119
H	3.984329	-3.312811	11.236575
C	3.056277	-3.819887	8.052001
H	2.628056	-3.259659	7.370836
H	2.497129	-4.606604	8.224486
H	3.936599	-4.108365	7.732827
C	7.390170	-1.132443	7.949887
C	9.131838	-0.044507	6.856620
H	9.443297	0.673128	6.317281
C	10.026407	-1.020388	7.268723
H	10.947679	-0.949798	7.048016
C	9.564302	-2.099340	8.006076
H	10.160529	-2.787187	8.277164
C	8.223461	-2.161641	8.341323
H	7.882111	-2.900127	8.832307
N	4.011654	-1.805351	9.086241
N	5.381636	-2.052456	8.853378
N	5.461288	0.213271	8.167486
N	4.338417	0.533541	8.981561
N	7.834683	-0.091505	7.204564
O	2.374494	-0.369563	9.744173
Pd	6.411413	1.285042	6.753561
C	9.325224	3.138745	4.207874
C	6.840160	3.585270	5.145808
C	8.126754	1.226536	3.313162
H	8.900303	1.271292	2.682514
C	6.907403	1.790140	2.586344
H	7.045177	2.744216	2.409671
H	6.783933	1.315369	1.738367
H	6.110958	1.673899	3.145809
C	7.915540	-0.233549	3.675153
H	7.193612	-0.306517	4.333085
H	7.677187	-0.738475	2.870263
H	8.742327	-0.598395	4.056189
C	9.603291	5.591705	4.171134
H	10.512970	5.310850	3.864388
C	8.972646	6.435456	3.068413
H	8.109570	6.781831	3.375430
H	9.565764	7.183948	2.850003
H	8.838496	5.882894	2.270547
C	9.766548	6.389970	5.455121
H	10.194769	5.829742	6.136285
H	10.325696	7.176687	5.282635
H	8.886226	6.678448	5.774295
C	5.432655	3.702526	5.557235
C	3.690987	2.614590	6.650502
H	3.379528	1.896955	7.189841
C	2.796418	3.590471	6.238399
H	1.875146	3.519882	6.459106
C	3.258523	4.669423	5.501046
H	2.662296	5.357270	5.229958
C	4.599364	4.731724	5.165799

H	4.940714	5.470210	4.674815
N	8.811171	4.375434	4.420881
N	7.441189	4.622539	4.653744
N	7.361537	2.356812	5.339635
N	8.484408	2.036542	4.525561
N	4.988142	2.661588	6.302558
O	10.448331	2.939646	3.762949

Table S4. Initial coordinates for computational study of **6**

Pd	10.57860000	3.79950000	5.94890000
Cl	10.39110000	5.03760000	4.00050000
O	12.13120000	2.21820000	10.72520000
O	9.32620000	6.96350000	10.94120000
N	9.95860000	2.65100000	10.18780000
N	8.91320000	2.32950000	9.27500000
N	10.55690000	2.62560000	7.57550000
N	11.60490000	2.48800000	8.52490000
N	8.71890000	2.99750000	5.82080000
N	11.43530000	6.27800000	10.41040000
N	12.34720000	5.81340000	9.50490000
N	10.66070000	5.97660000	7.81310000
N	9.80860000	6.46810000	8.76580000
N	12.48210000	4.50670000	6.20530000
C	11.28050000	2.42100000	9.87160000
C	9.30090000	2.43960000	8.04500000
C	12.67840000	1.61280000	7.98050000
H	12.72680000	1.80200000	7.00030000
C	12.31680000	0.14560000	8.11620000
H	12.29070000	-0.09770000	9.06530000
H	12.98910000	-0.39960000	7.65800000
H	11.43700000	-0.01240000	7.71390000
C	14.05250000	1.93340000	8.54990000
H	14.18310000	2.90500000	8.56250000
H	14.74170000	1.51870000	7.99130000
H	14.11750000	1.58350000	9.46350000
C	9.53280000	2.57190000	11.59460000
H	10.31440000	2.83480000	12.15910000
C	9.15420000	1.16700000	11.97870000
H	8.32330000	0.91560000	11.52300000
H	9.02160000	1.11720000	12.94830000
H	9.87010000	0.55150000	11.71580000
C	8.42460000	3.57190000	11.86250000
H	8.71770000	4.46630000	11.58970000
H	8.21320000	3.57550000	12.81860000
H	7.62640000	3.31970000	11.35190000
C	8.29510000	2.42010000	6.96540000
C	7.89200000	3.04620000	4.76450000
H	8.19660000	3.44410000	3.95690000
C	6.61190000	2.53370000	4.82080000
H	6.04710000	2.56930000	4.05780000
C	6.15800000	1.96710000	5.99990000
H	5.27440000	1.62610000	6.05970000
C	7.00830000	1.90590000	7.08910000
H	6.71890000	1.51870000	7.90670000
C	10.12720000	6.58790000	10.10260000
C	11.87210000	5.68300000	8.26670000
C	8.45570000	6.84370000	8.29860000
H	8.08840000	7.52580000	8.93190000
C	8.52430000	7.47340000	6.92120000
H	9.13950000	8.23710000	6.94080000
H	7.63250000	7.77890000	6.65620000
H	8.84700000	6.81080000	6.27420000
C	7.53980000	5.63140000	8.33320000
H	7.81090000	4.99730000	7.63820000
H	6.61550000	5.91650000	8.17330000
H	7.60110000	5.20070000	9.21120000
C	11.94490000	6.48310000	11.78200000

H	11.24880000	6.97600000	12.30320000
C	12.19380000	5.17230000	12.46000000
H	11.34800000	4.68740000	12.55370000
H	12.57910000	5.33130000	13.34650000
H	12.81660000	4.64030000	11.92300000
C	13.24150000	7.35880000	11.74830000
H	13.92510000	6.91120000	11.20590000
H	13.57790000	7.48140000	12.66000000
H	13.03490000	8.23270000	11.35550000
C	12.87870000	5.24780000	7.26010000
C	13.40410000	4.15630000	5.28080000
H	13.12940000	3.64030000	4.53170000
C	14.72920000	4.52310000	5.38690000
H	15.35450000	4.25580000	4.72450000
C	15.13880000	5.28420000	6.46480000
H	16.04690000	5.54970000	6.55520000
C	14.19560000	5.65190000	7.41310000
H	14.45070000	6.17670000	8.16250000