

# Electronic Supplementary Information

## Non-symmetrical aryl- and arylolethynyl-substituted thio- porphyrazines for electronic materials: Synthesis, properties, and computational studies.

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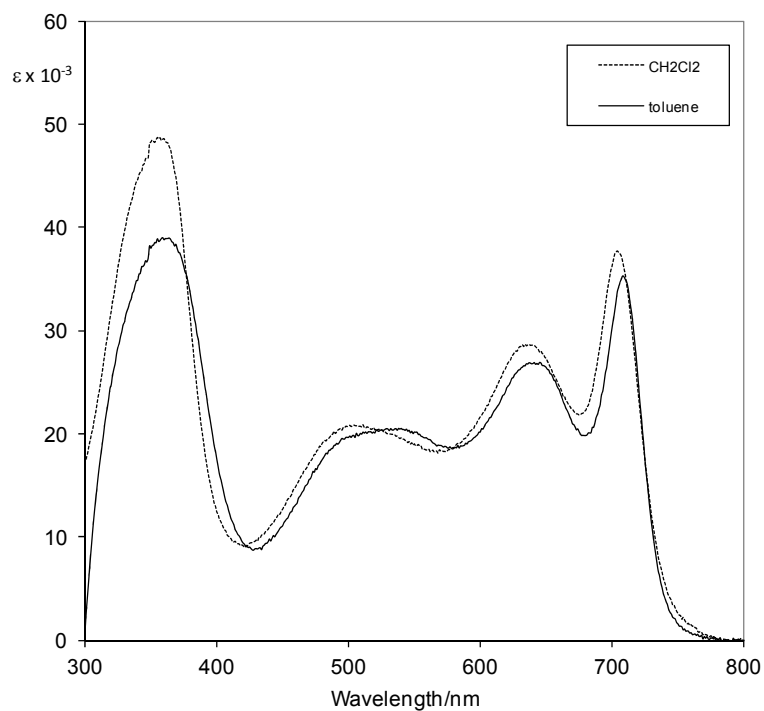
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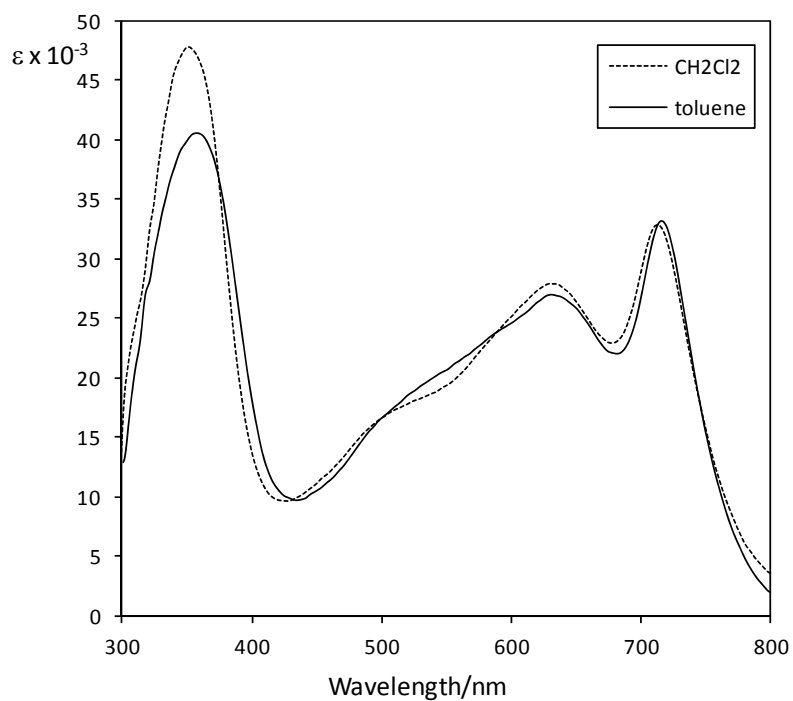
**Table S1. UV-VIS spectroscopic data for the studied compounds.**

Compound	Solvent	Absorption, RT
		$\lambda_{max}/nm$ (log $\epsilon/M^{-1}cm^{-1}$ ) $cm^{-1}$ (log $\epsilon/M^{-1}cm^{-1}$ )
1a a	CH <sub>2</sub> Cl <sub>2</sub>	354 (4.66) Soret; 498 (4.31); 637 (4.45); 714 (4.59) Q bands
		28250 (4.66) Soret; 20080 (4.31); 15700 (4.45); 14006 (4.59) Q bands
2a a	CH <sub>2</sub> Cl <sub>2</sub>	354 (4.42) Soret; 472 (3.97); 608 <sup>b</sup> (4.09); 636 (4.21); 704 (4.34) Q bands
		28250 (4.42) Soret; 21190 (3.97); 16450 <sup>b</sup> (4.09); 15720 (4.21); 14230 (4.34) Q bands
3a	CH <sub>2</sub> Cl <sub>2</sub>	359 (4.69) Soret; 511 (4.32); 637 (4.46); 704 (4.57) Q bands
		27860 (4.69) Soret; 19570 (4.32); 15700 (4.46); 14210 (4.57) Q bands
3a	Toluene	359 (4.59) Soret; 502 <sup>b,c</sup> (4.29); 544 <sup>b,c</sup> (4.31); 645 (4.43); 708 (4.55) Q bands
		27860 (4.59) Soret; 19920 <sup>b,c</sup> (4.29); 18382 <sup>b,c</sup> (4.31); 15500 (4.43); 14124 (4.55) Q bands
4a	CH <sub>2</sub> Cl <sub>2</sub>	327 (4.49) Soret; 477 (4.07); 655 (4.46) Q bands
		30581 (4.49) Soret; 20960 (4.07); 15270 (4.46) Q bands
4a	Toluene	330 (4.36) Soret; 486 (4.01); 660 (4.38) Q bands
		30300 (4.36) Soret; 20580 (4.01); 15150 (4.38) Q bands
5	CH <sub>2</sub> Cl <sub>2</sub>	358 (4.64) Soret; 497 (4.23); 639 (4.39); 705 (4.54) Q bands
		27930 (4.64) Soret; 20120 (4.23); 15650 (4.39); 14280 (4.54) Q bands
5	Toluene	355 (4.56) Soret; 498 (4.21); 641 (4.38); 711 (4.52) Q bands
		28170 (4.56) Soret; 20080 (4.21); 15600 (4.38); 14070 (4.52) Q bands
6	CH <sub>2</sub> Cl <sub>2</sub>	359 (4.63) Soret; 494 (4.26); 637 (4.42); 704 (4.55) Q bands
		27860 (4.63) Soret; 20240 (4.26); 15700 (4.42); 14210 (4.55) Q bands
6	Toluene	360 (4.63) Soret; 498 (4.23); 640 (4.39); 710 (4.54) Q bands
		27780 (4.63) Soret; 20080 (4.23); 15630 (4.39); 14090 (4.54) Q bands
7	CH <sub>2</sub> Cl <sub>2</sub>	350 (4.68) Soret; 511 <sup>b,c</sup> (4.17); 555 <sup>b,c</sup> (4.24); 630 (4.45); 713 (4.52) Q bands
		28570 (4.68) Soret; 19570 <sup>b,c</sup> (4.17); 18018 <sup>b,c</sup> (4.24); 15870 (4.45); 14030 (4.52) Q bands
7	Toluene	356 (4.61) Soret; 512 <sup>b,c</sup> (4.25); 555 <sup>b,c</sup> (4.32); 631 (4.44); 717 (4.52) Q bands
		28090 (4.61) Soret; 19530 <sup>b,c</sup> (4.25); 18020 <sup>b,c</sup> (4.32); 15850 (4.44); 13950 (4.52) Q bands
8	CH <sub>2</sub> Cl <sub>2</sub>	323 (4.45) Soret; 509 (3.99); 620 <sup>b,c</sup> (4.26); 665 (4.40) Q bands
		30960 (4.45) Soret; 19650 (3.99); 16130 <sup>b,c</sup> (4.26); 15040 (4.40) Q bands
8	Toluene	325 (4.32) Soret; 511 (3.99); 616 <sup>b,c</sup> (4.20); 667 (4.36) Q bands
		30770 (4.32) Soret; 19570 (3.99); 16230 <sup>b,c</sup> (4.20); 14990 (4.36) Q bands
9a	CH <sub>2</sub> Cl <sub>2</sub>	341 (4.48) Soret; 489 (4.04); 669 (4.32) Q bands
		29330 (4.48) Soret; 20450 (4.04); 14950 (4.32) Q bands
9a	Toluene	348 (4.20) Soret; 492 (3.95); 671 (4.25) Q bands
		28740 (4.20) Soret; 20330 (3.95); 14900 (4.25) Q bands
9b	CH <sub>2</sub> Cl <sub>2</sub>	325 (4.74) Soret; 499 (4.41); 674 (4.73) Q bands
		30770 (4.74) Soret; 20040 (4.41); 14840 (4.73) Q bands
9b	Toluene	328 (4.66) Soret; 498 (4.36); 674 (4.68) Q bands
		30490 (4.66) Soret; 20080 (4.36); 14840 (4.68) Q bands
10	CH <sub>2</sub> Cl <sub>2</sub>	344 (4.42) Soret; 381 <sup>b,c</sup> (4.10); 486 (4.03); 668 (4.30) Q bands
		29070 (4.42) Soret; 26250 <sup>b,c</sup> (4.10); 20580 (4.03); 13970 (4.30) Q bands
10	Toluene	350 (4.32) Soret; 489 (4.00); 671 (4.32) Q bands
		28570 (4.32) Soret; 20450 (4.00); 14900 (4.32) Q bands
11	CH <sub>2</sub> Cl <sub>2</sub>	329 (4.86) Soret; 511 (4.40); 621 <sup>b,c</sup> (4.63); 665 (4.75) Q bands
		30400 (4.86) Soret; 19570 (4.40); 16100 <sup>b,c</sup> (4.63); 15040 (4.75) Q bands
11	Toluene	322 (4.73) Soret; 510 (4.34); 623 <sup>b,c</sup> (4.58); 668 (4.69) Q bands
		31060 (4.73) Soret; 19610 (4.34); 16050 <sup>b,c</sup> (4.58); 14970 (4.69) Q bands
12	CH <sub>2</sub> Cl <sub>2</sub>	325 (4.40) Soret; 484 (4.00); 660 (4.37) Q bands
		30770 (4.40) Soret; 20660 (4.00); 15150 (4.37) Q bands
12	Toluene	320 (4.33) Soret; 487 (4.00); 661 (4.36) Q bands
		31250 (4.33) Soret; 20530 (4.00); 15130 (4.36) Q bands

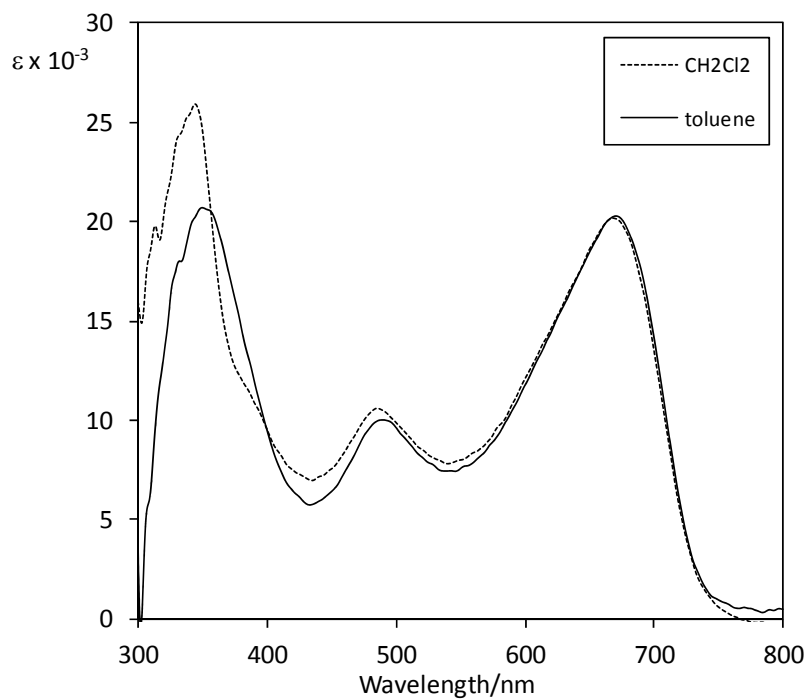
<sup>a</sup> Previously published data [ref.11]; <sup>b</sup> shoulder; <sup>c</sup> wavelength taken through spectral deconvolution.



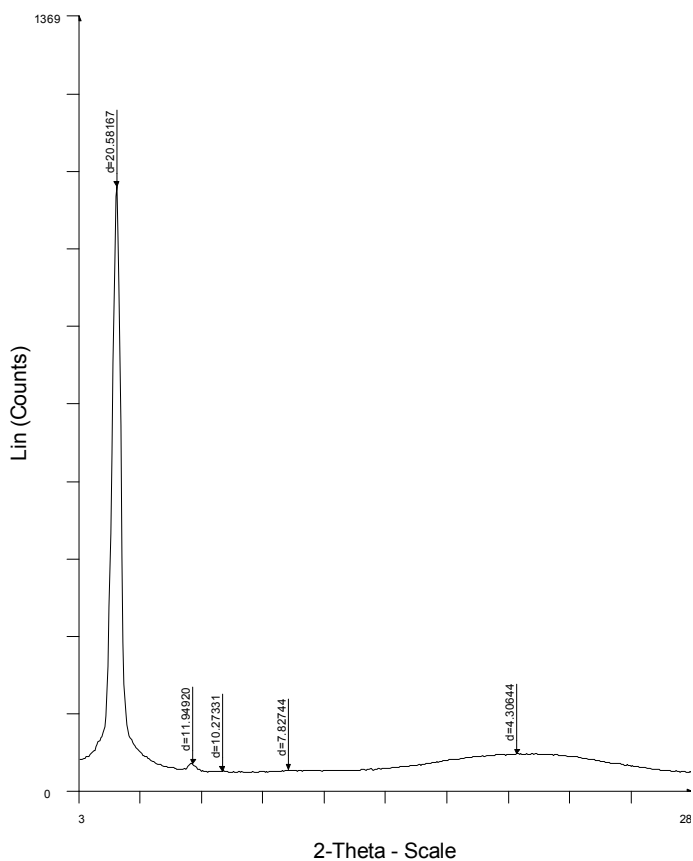
**Figure S1.** UV spectra in CH<sub>2</sub>Cl<sub>2</sub> and toluene of porphyrazine **3a**.



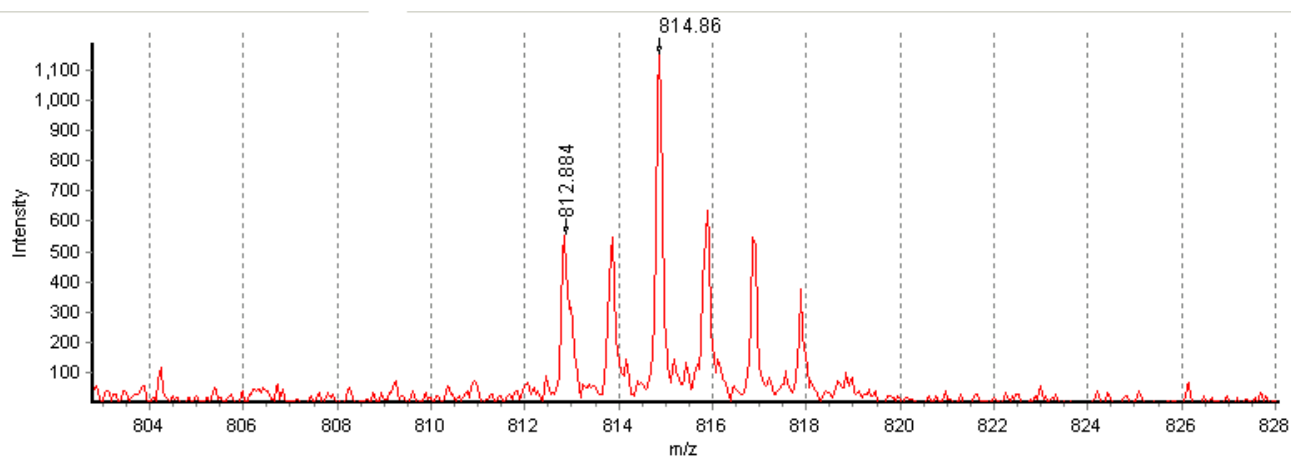
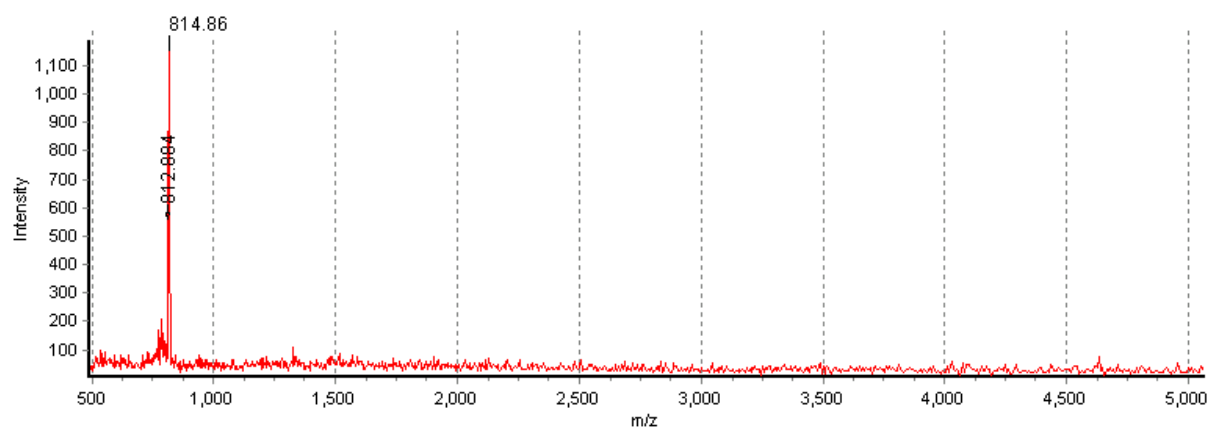
**Figure S2.** UV spectra in CH<sub>2</sub>Cl<sub>2</sub> and toluene of porphyrazine **7**.



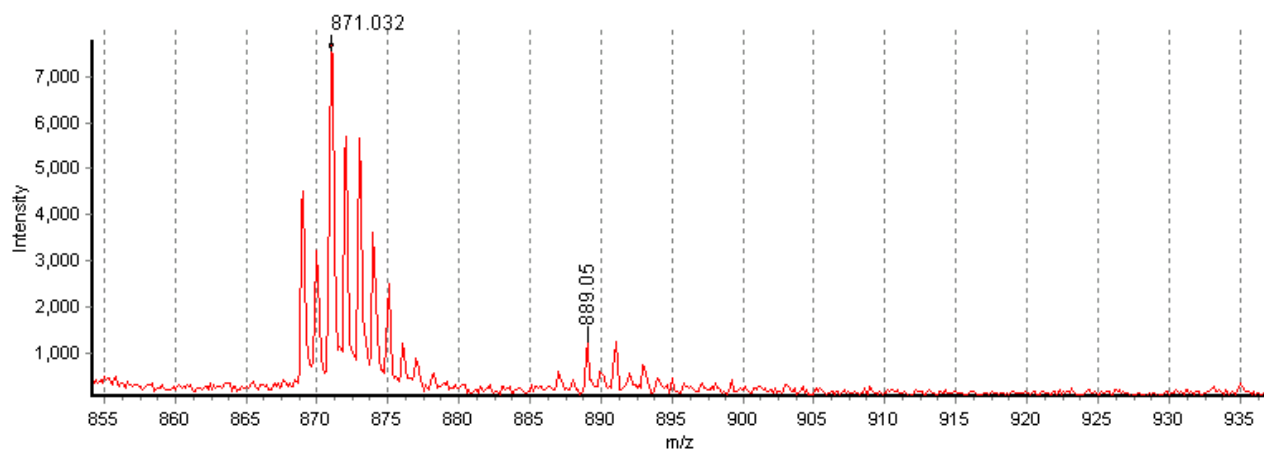
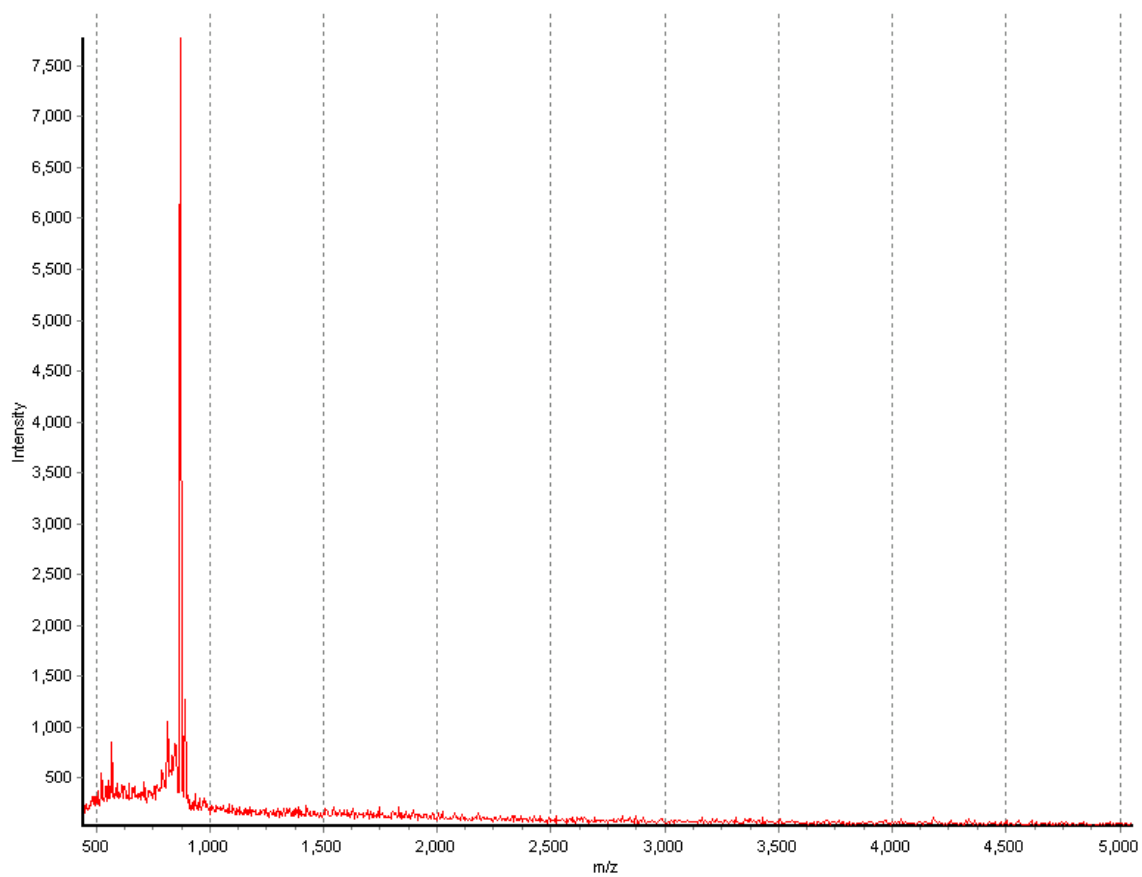
**Figure S3.** UV spectra in CH<sub>2</sub>Cl<sub>2</sub> and toluene of porphyrazine **10**.



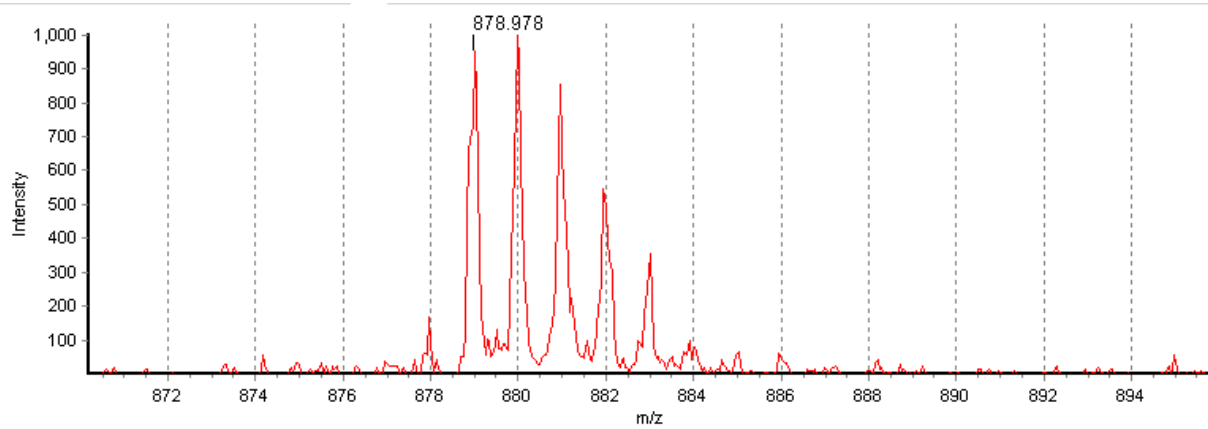
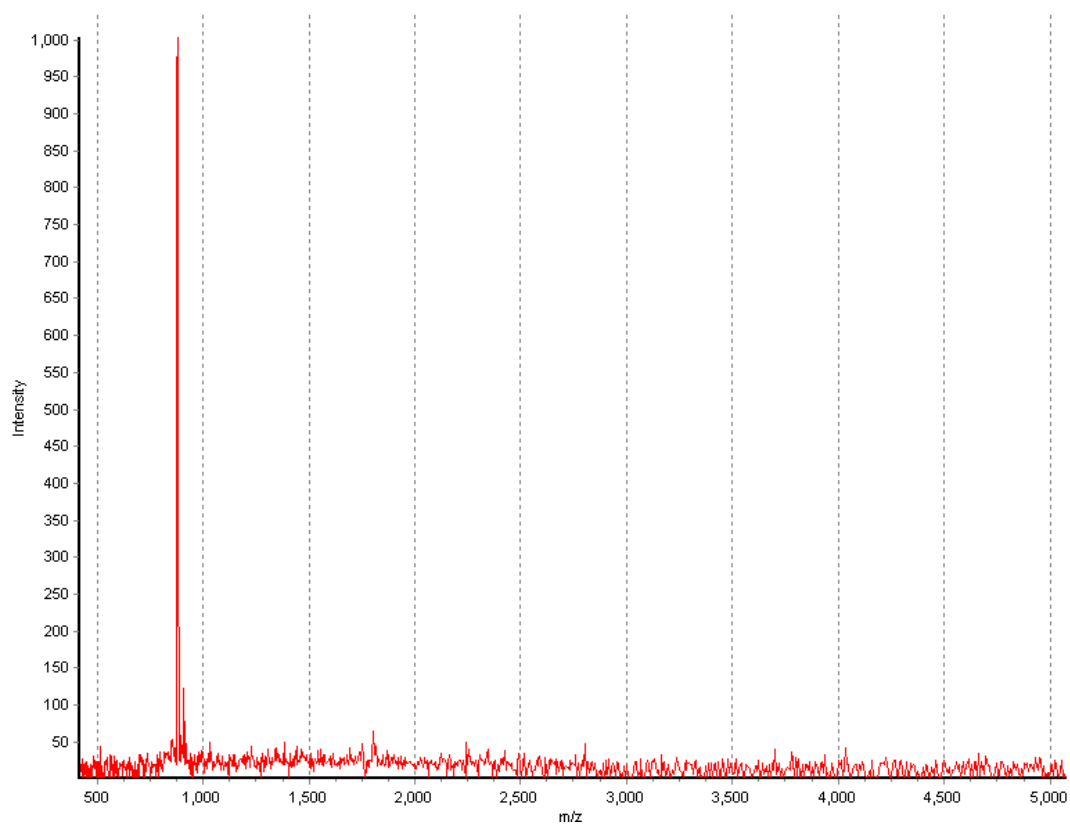
**Figure S4.** PXRD diffraction pattern of compound **9b** recorded at 110 °C on cooling.



**Figure S5.** MALDI-MS spectrum of compound **3a**.

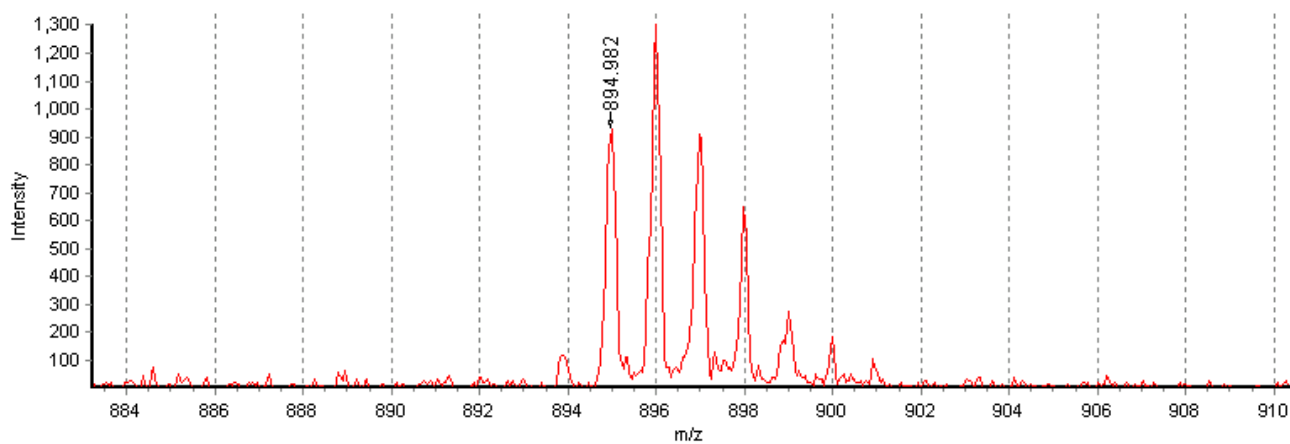
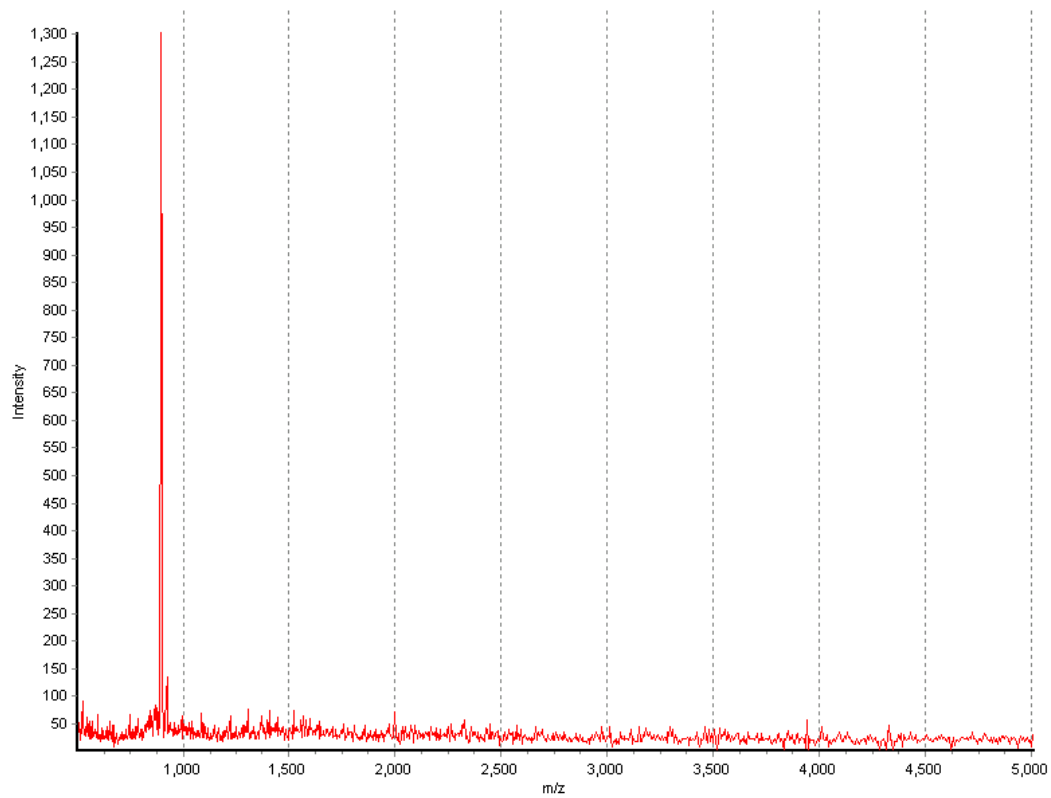


**Figure S6.** MALDI\_MS spectrum of compound **4a**.

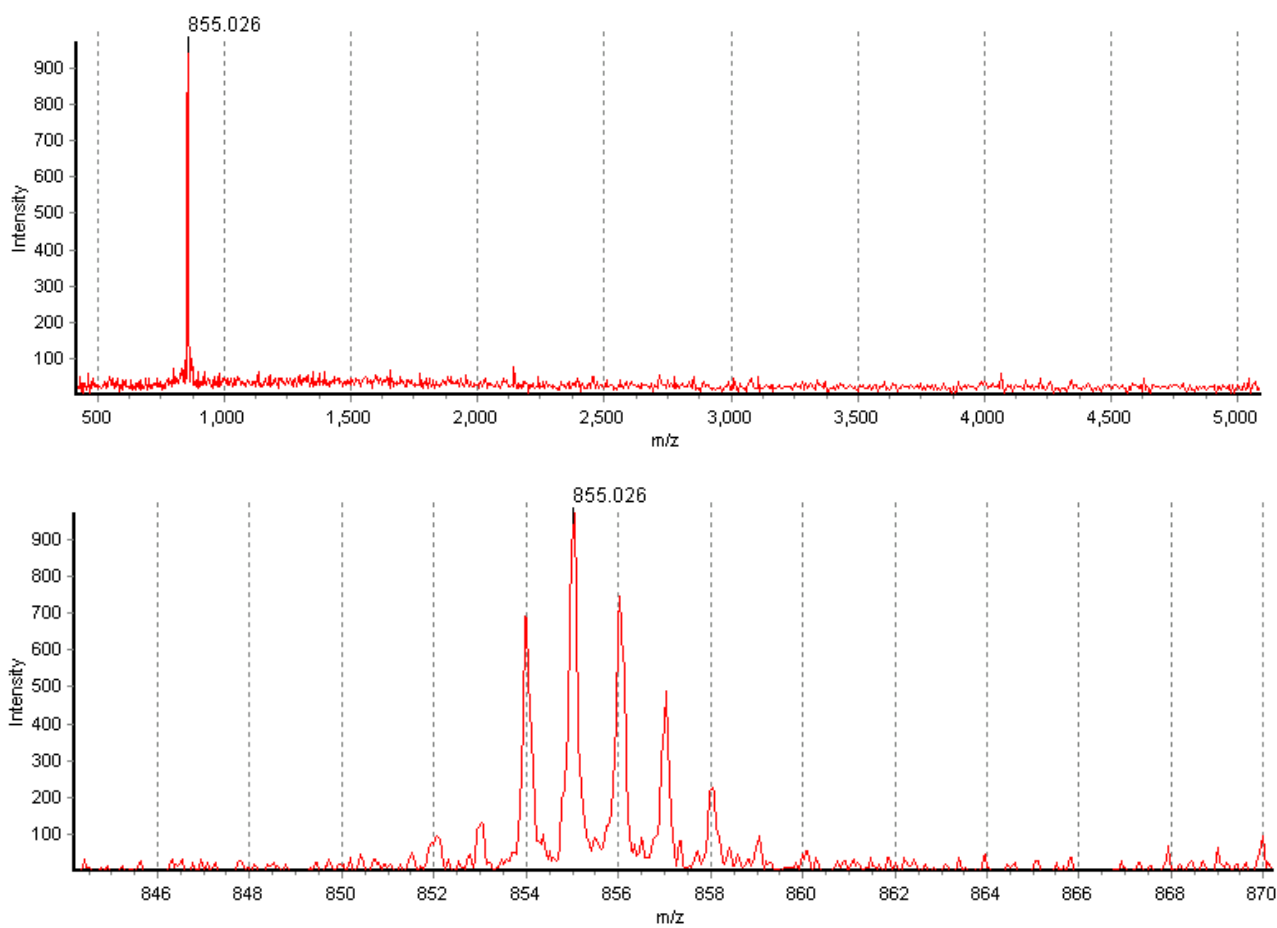


**Figure S7.** MALDI-MS spectrum of compound **5**.

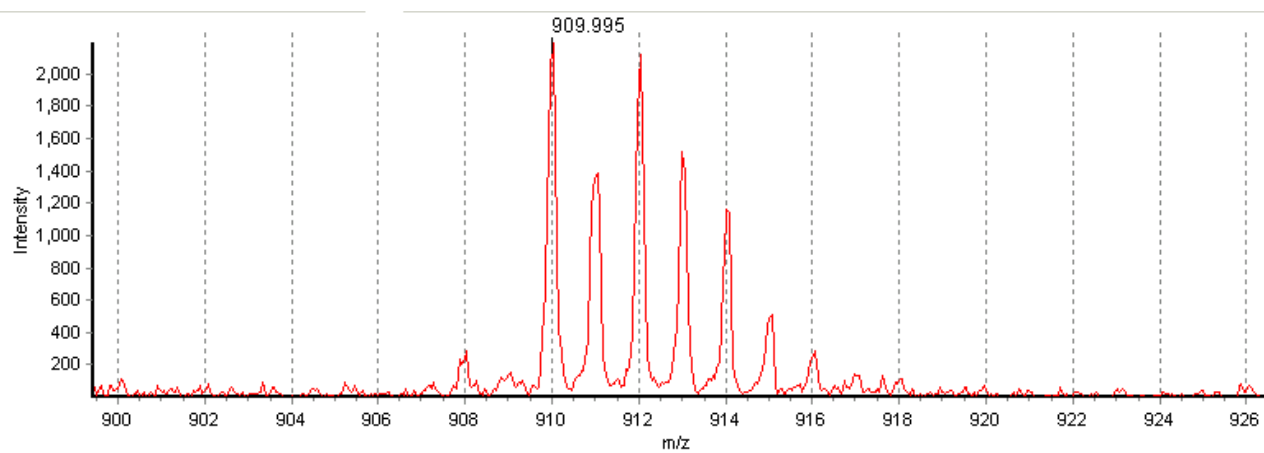
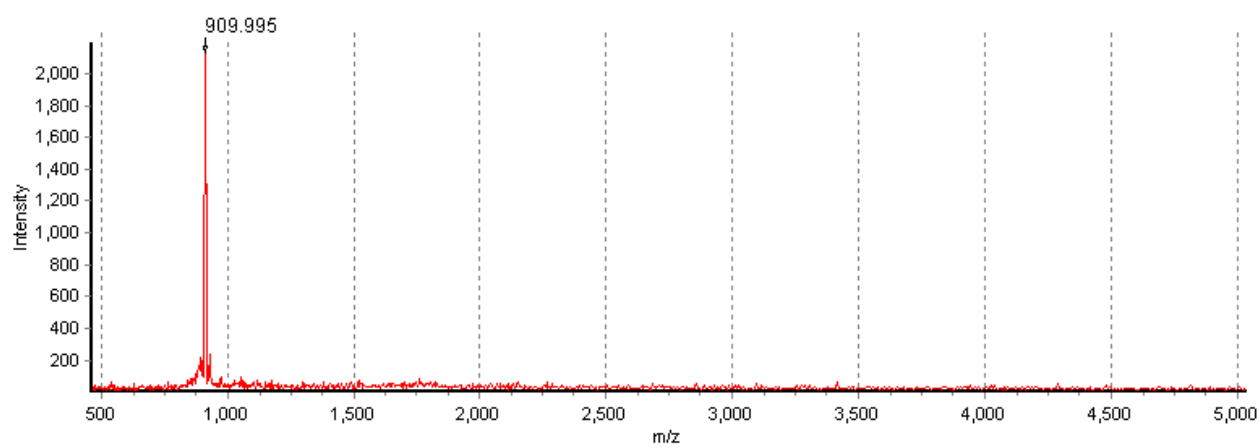




**Figure S8.** MALDI-MS spectrum of compound 6.



**Figure S9.** MALDI-MS spectrum of compound 7.



**Figure S10.** MALDI-MS spectrum of compound **8**.

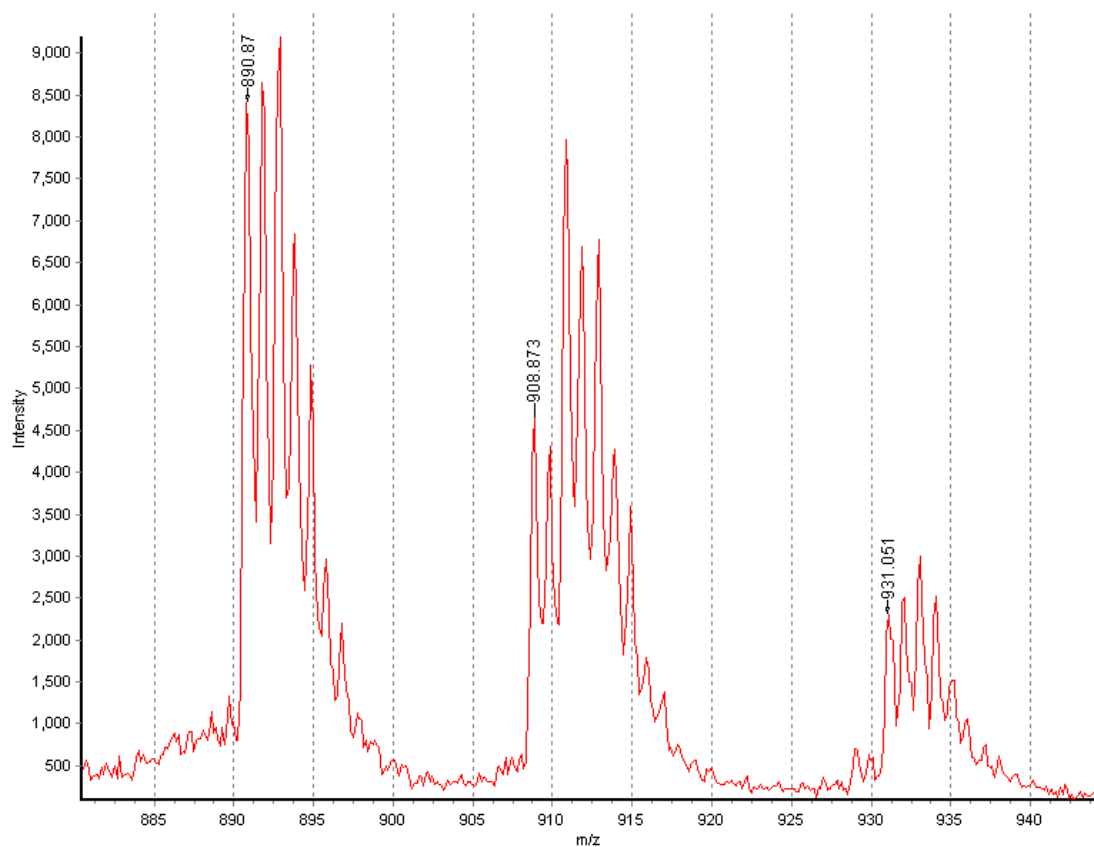
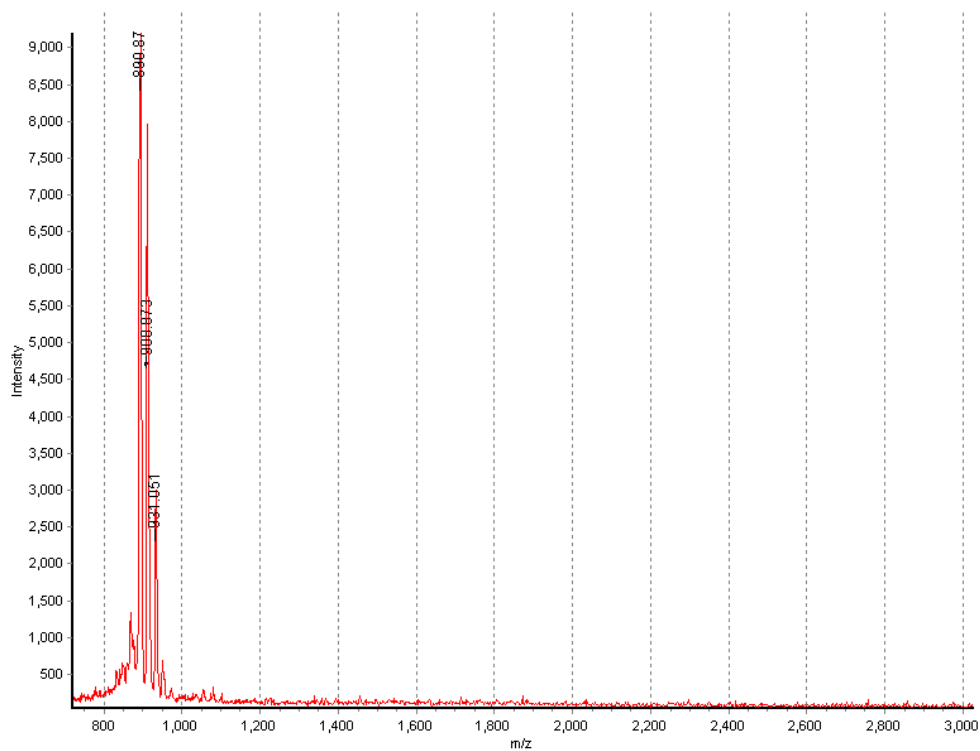
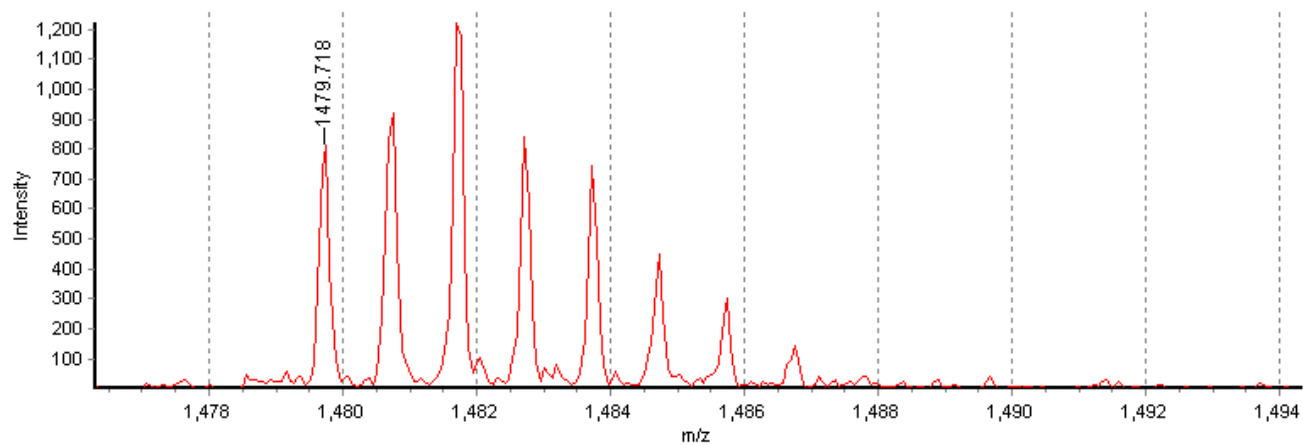
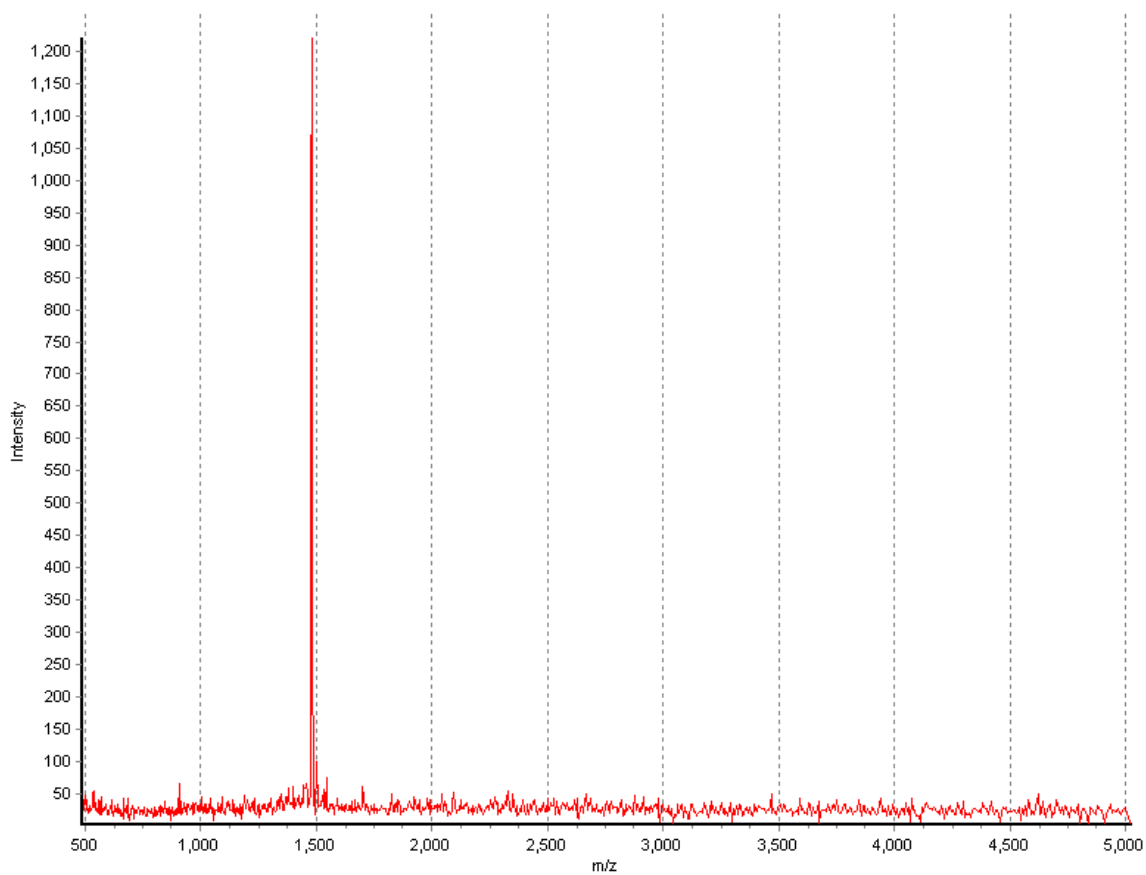
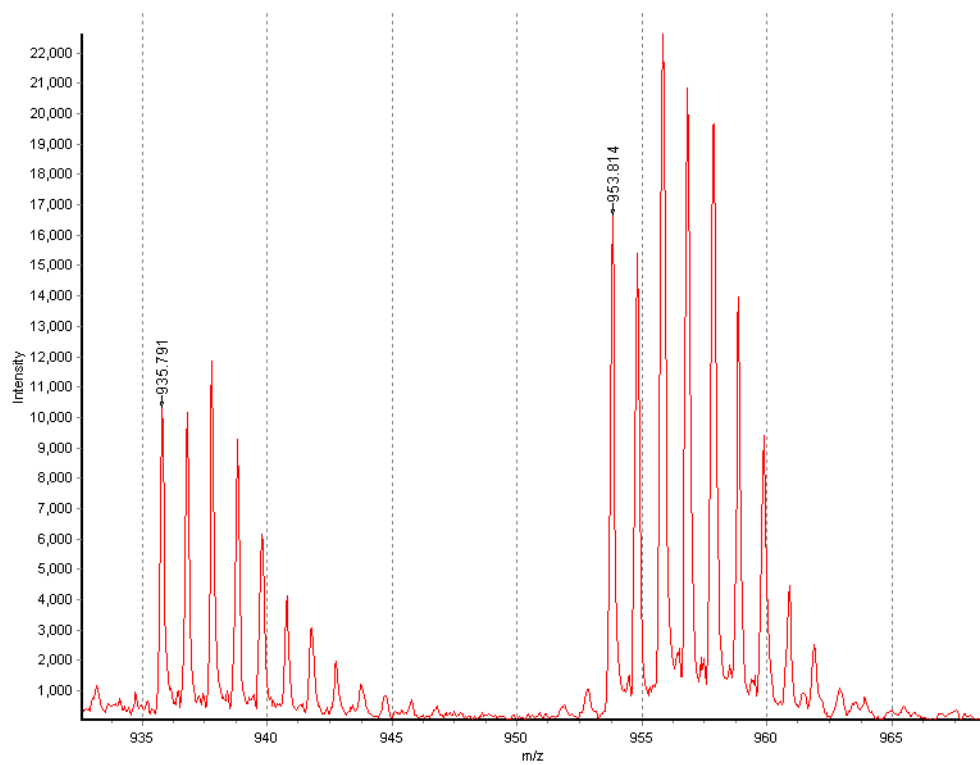
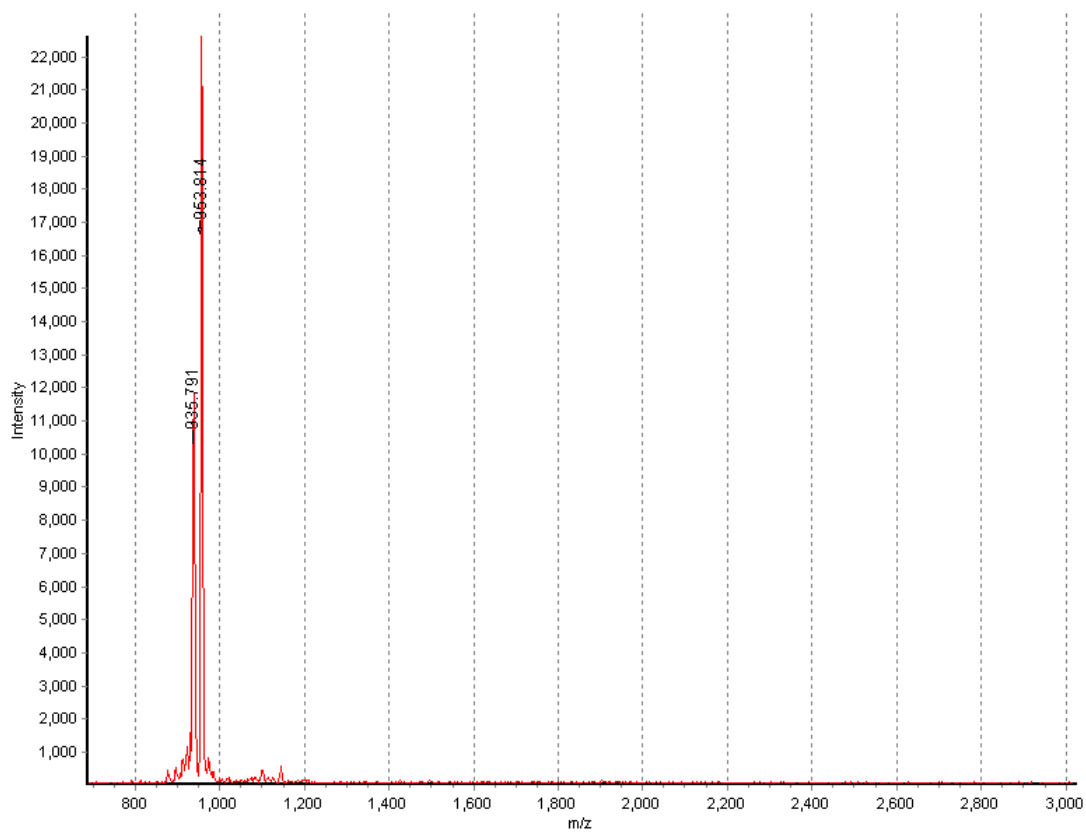


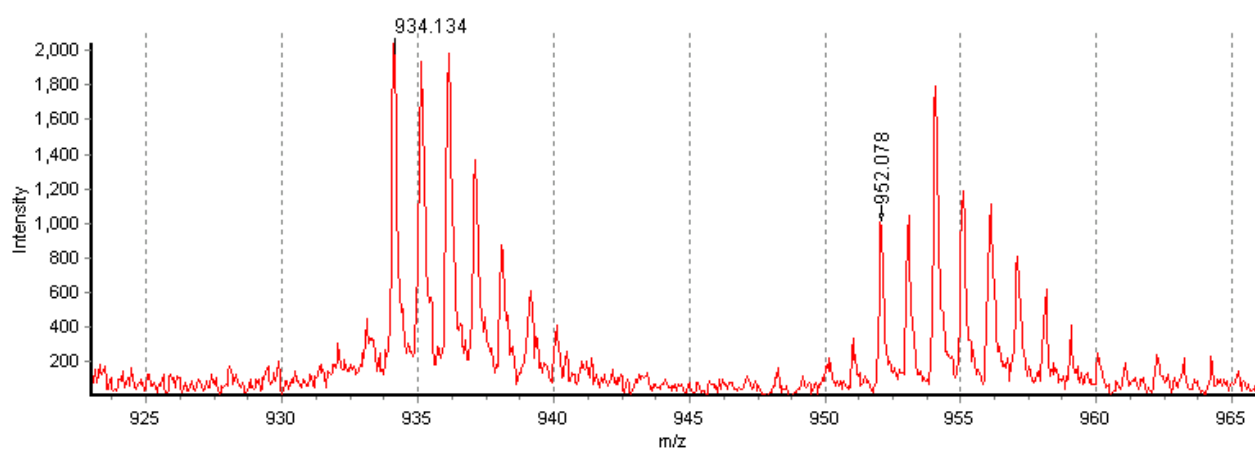
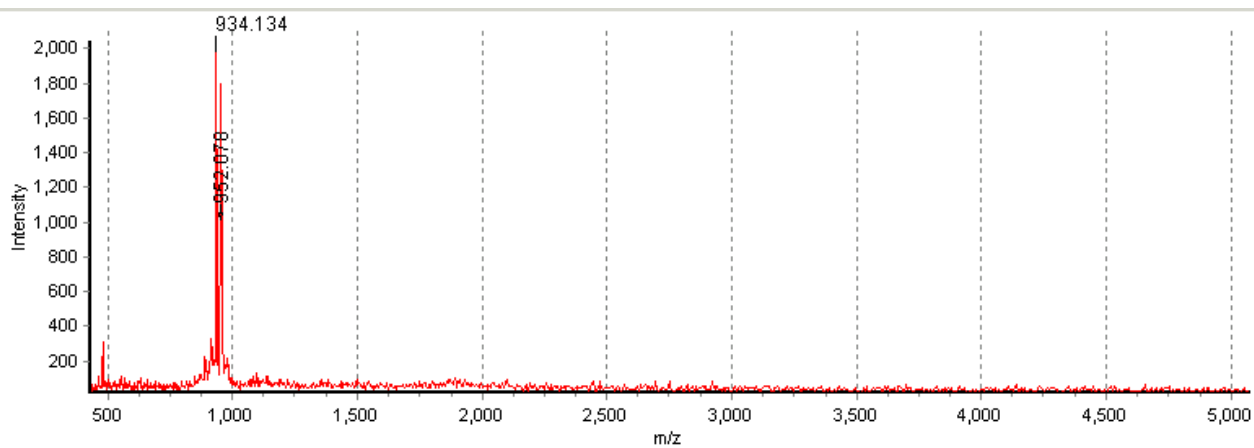
Figure S11. MALDI-MS spectrum of compound 9a.



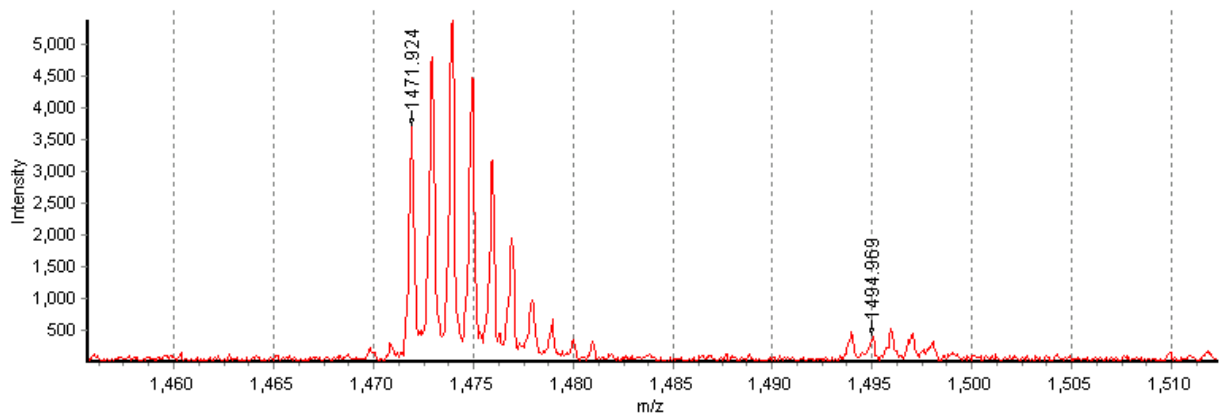
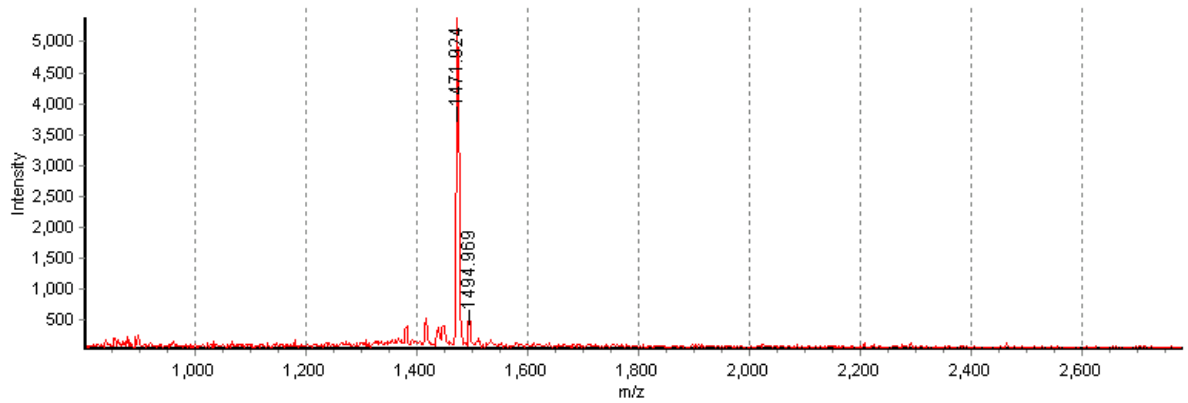
**Figure S12.** MALDI-MS spectrum of compound **9b**.



**Figure S13.** MALDI-MS spectrum of compound **10**



**Figure S14.** MALDI-MS spectrum of compound **11**



**Figure S15.** MALDI-MS spectrum of compound **12**



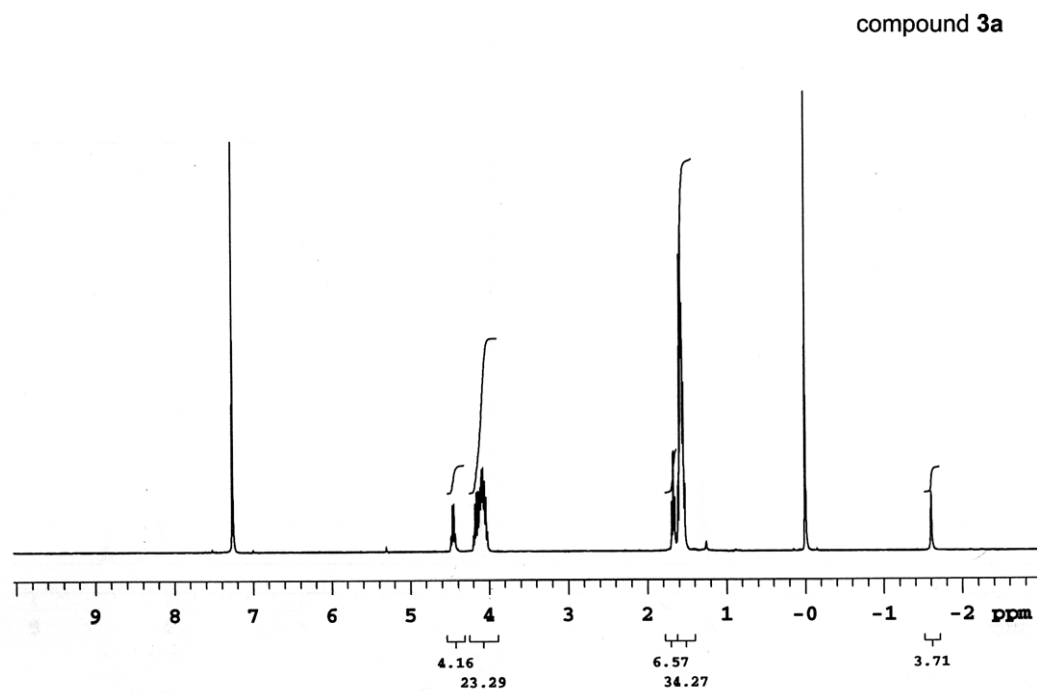


Figure S16.  $^1\text{H}$  NMR spectrum of compound 3a.

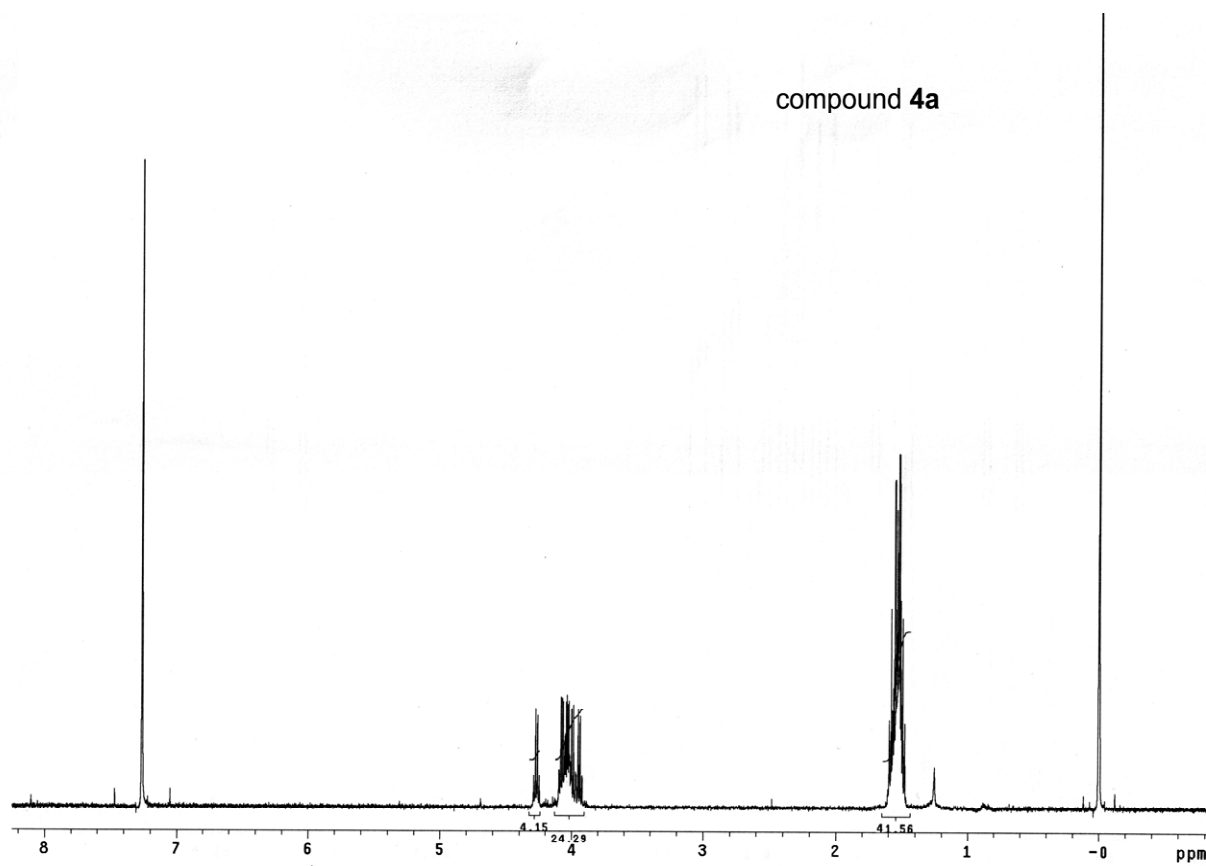
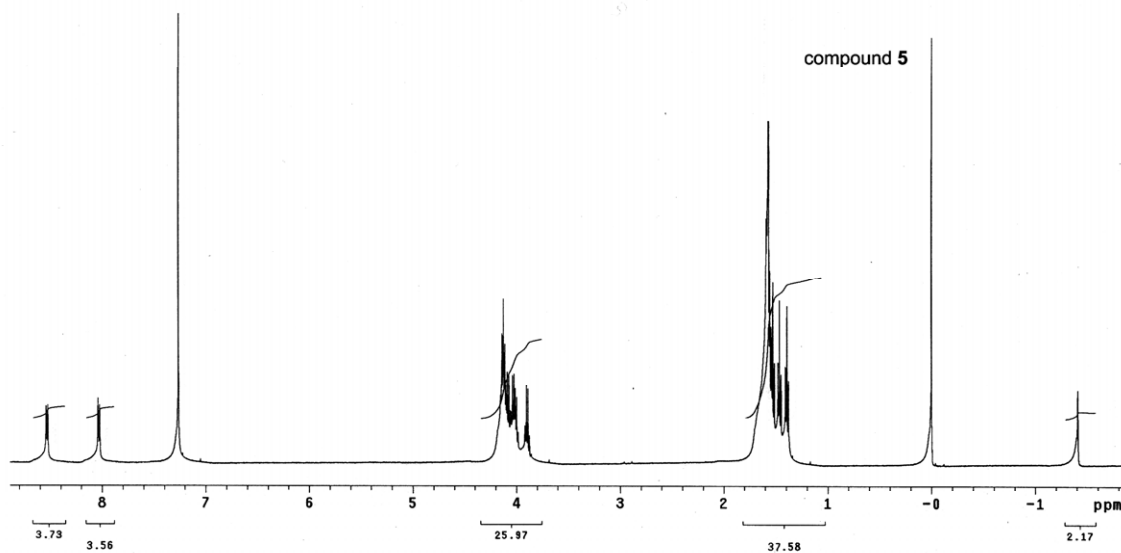
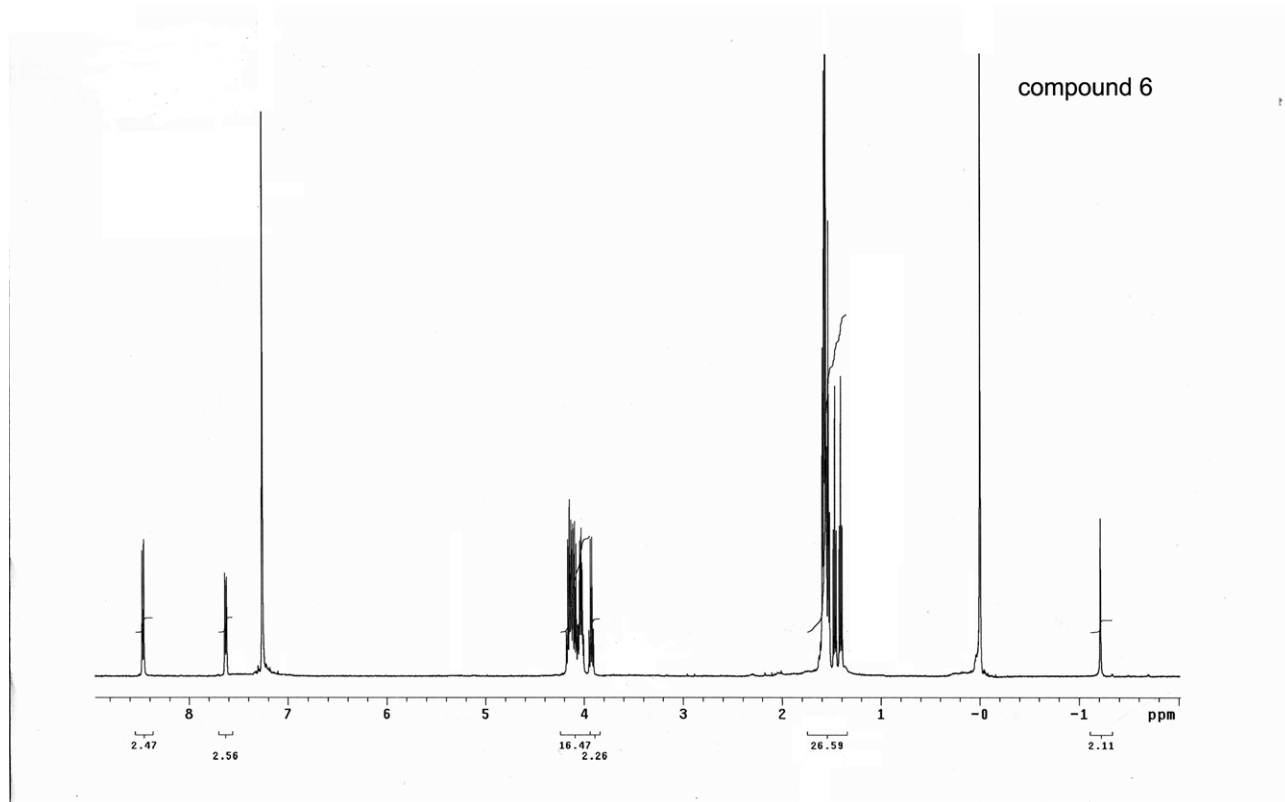


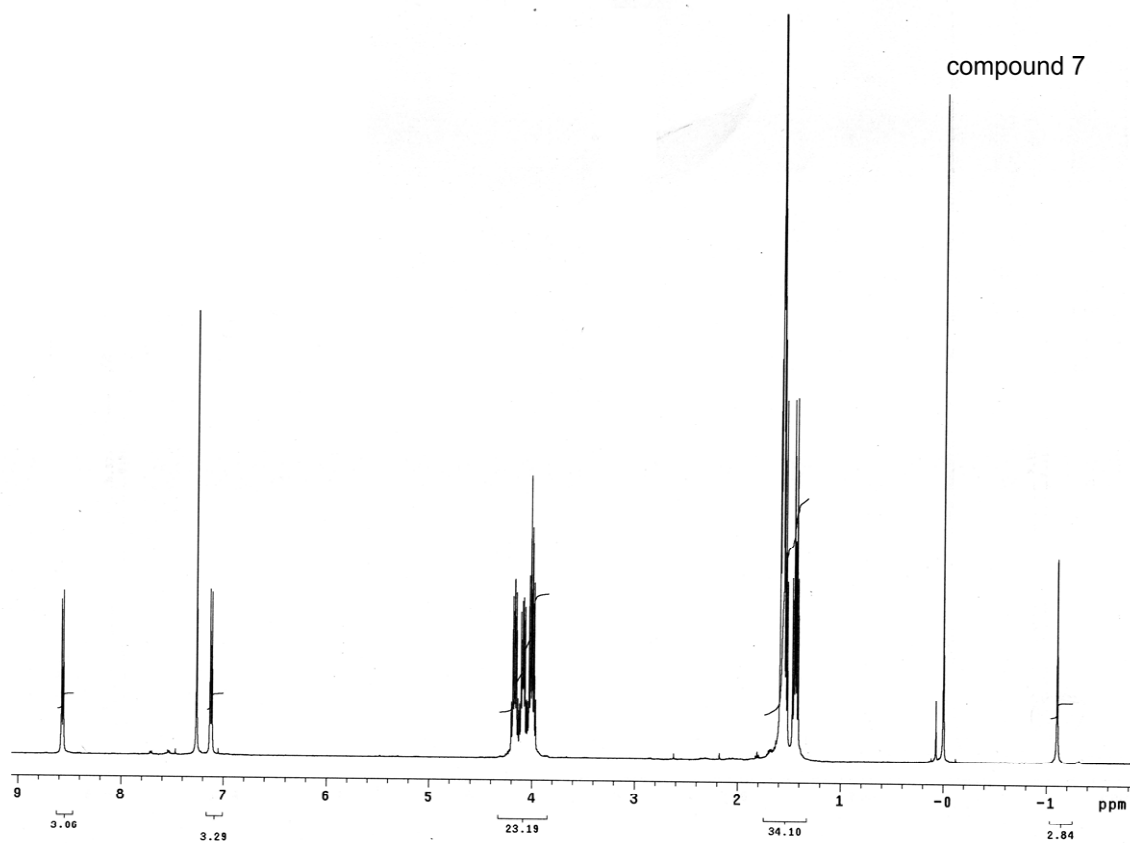
Figure S17.  $^1\text{H}$  NMR spectrum of compound 4a.



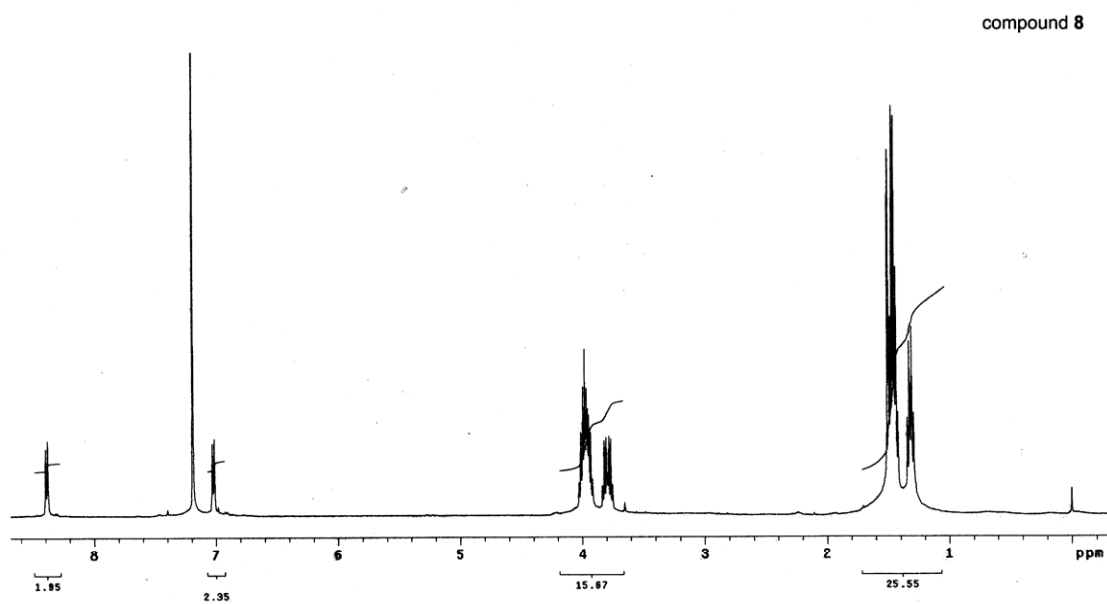
**Figure S18.**  $^1\text{H}$  NMR spectrum of compound 5.



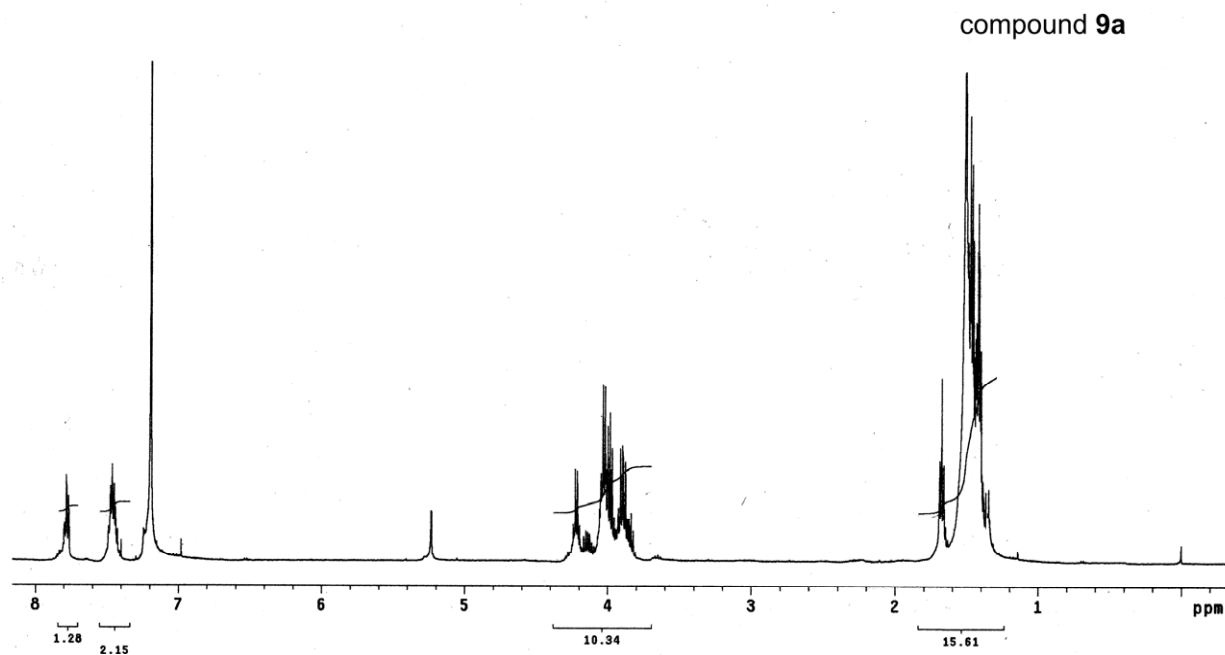
**Figure S19.**  $^1\text{H}$  NMR spectrum of compound 6.



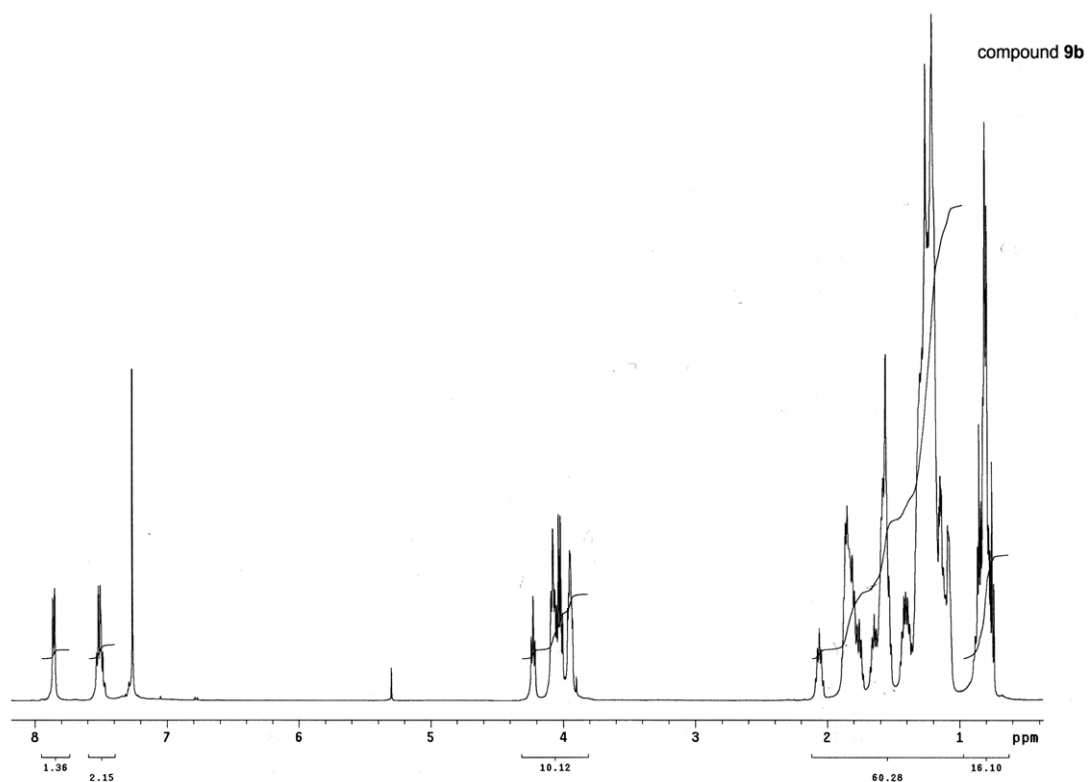
**Figure S20.** <sup>1</sup>H NMR spectrum of compound 7.



**Figure S21.** <sup>1</sup>H NMR spectrum of compound 8.



**Figure S22.**  $^1\text{H}$  NMR spectrum of compound **9a**.



**Figure S23.**  $^1\text{H}$  NMR spectrum of compound **9b**.

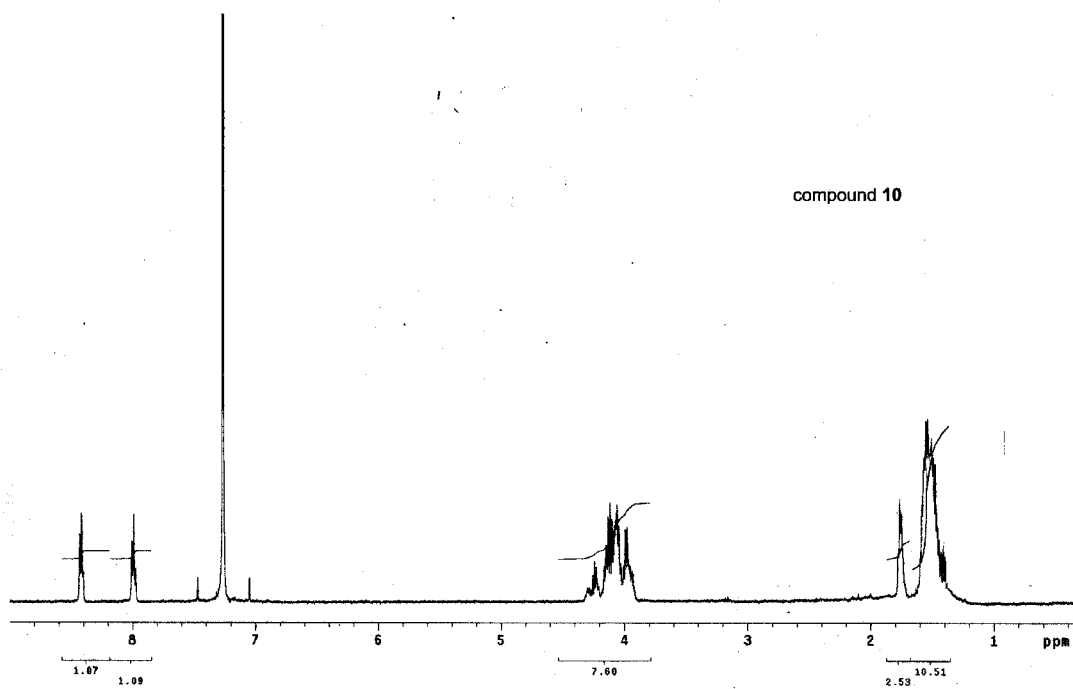


Figure S24. <sup>1</sup>H NMR spectrum of compound 10.

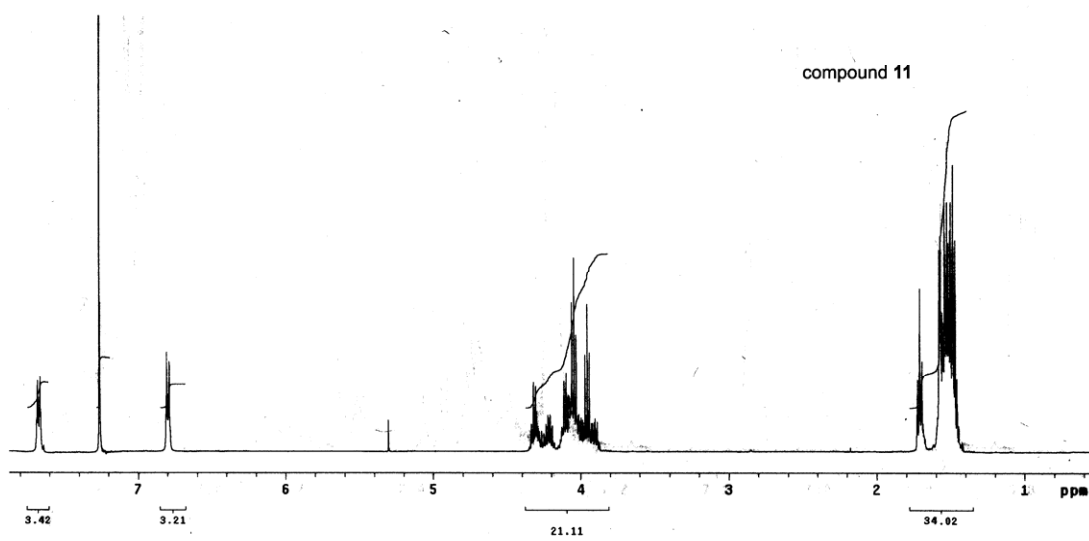
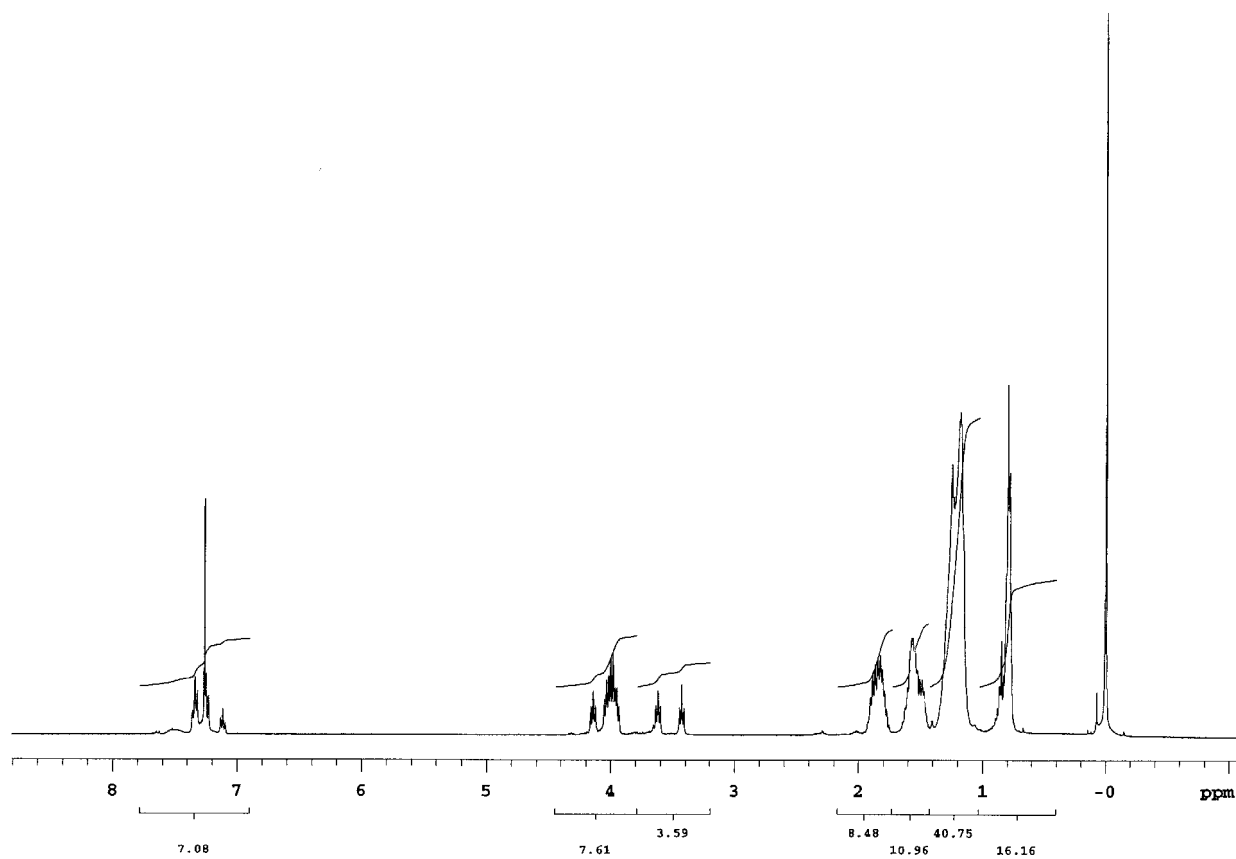
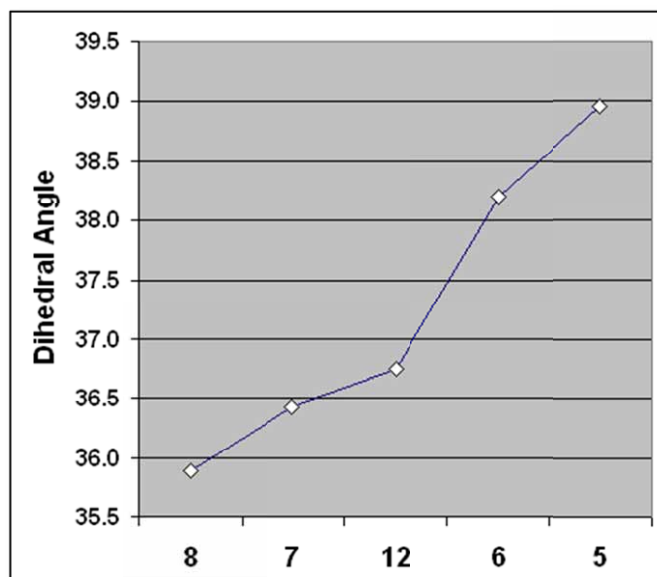


Figure S25. <sup>1</sup>H NMR spectrum of compound 11.



**Figure S26.** <sup>1</sup>H NMR spectrum of compound **12**.

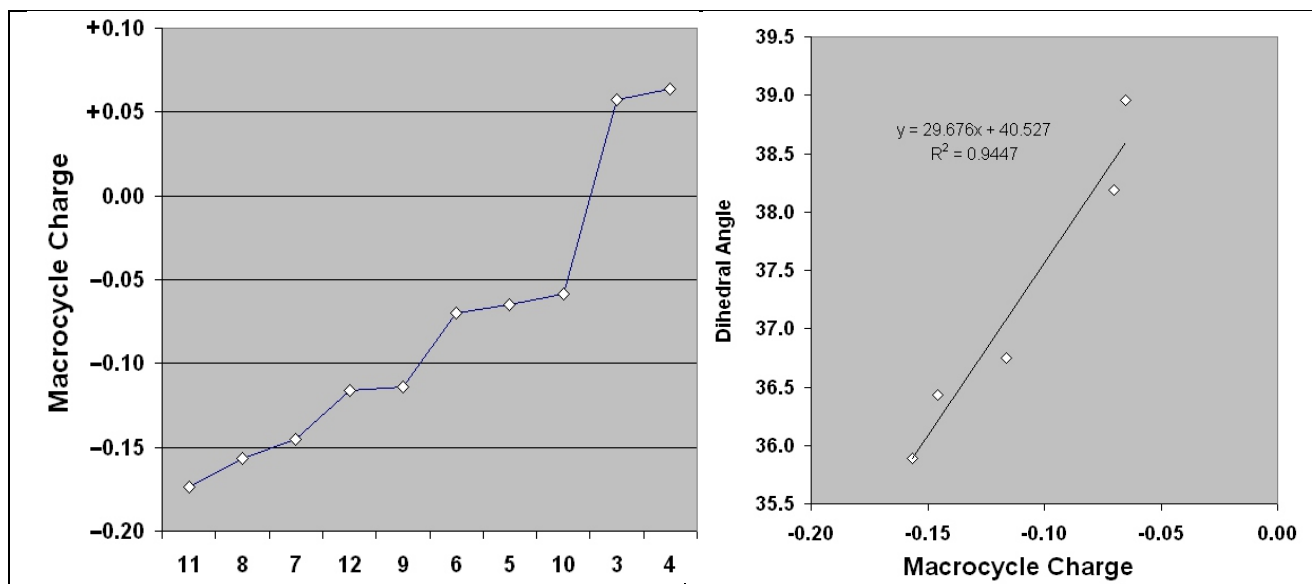
## Computational Results: Structures and Mulliken Atomic Charges



**Figure S27.** Computed dihedral angle between the average planes of the phenyl group and porphyrazine macrocycle. The thioalkyl chains were not included in the computation of the macrocycle average plane. The reported angles are degrees. Structure optimization at the B3LYP/6-31G\* level of approximation (in vacuum computations).

**Table S2.** Macrocycle charges (sum of atomic Mulliken charges) in all the studied complexes. B3LYP/6-31G\* (in vacuum computations).

Compound	Charge
11	-0.174
8	-0.156
7	-0.146
12	-0.116
9	-0.114
6	-0.070
5	-0.065
10	-0.059
3	0.058
4	0.064



**Figure S28.** Graphical view of the macrocycle charges of Table S1 (left) and correlation chart between dihedral angles (Figure S27) and macrocycle charges (right).



**Table S3.** Computed molecular structures.

In all the cases, thiomethyl chains replaced the thioethyl and thiooctyl chains of the synthesized compounds. Structure optimizations at the B3LYP/6-31G(d) level of approximation. The reported structures are cartesian coordinates in angstrom.

**2 (free base, -H substituent)**

C	0.154877283905	-0.165194302166	-0.215414543551
C	0.064450237136	-0.118650511016	1.225788444393
N	1.347449410541	-0.071550355797	1.707431458953
C	2.263447159190	-0.053152630250	0.681426421245
C	1.500416649717	-0.113260119353	-0.561772148983
N	-1.060840174802	-0.116784702087	1.923717155245
C	-1.107259854195	-0.079638991599	3.253587127152
N	-0.054314808966	-0.070313886198	4.117642247805
C	-0.599343133026	-0.090608487647	5.363716509130
C	-2.078414145306	-0.054883754022	5.308089873911
C	-2.398989672376	-0.048804628702	3.976747271103
N	0.047315532030	-0.140718322585	6.528527601345
C	1.365618294497	-0.151349123095	6.636179147986
N	2.288509884281	-0.103383561976	5.623624579080
C	3.572697302302	-0.093845069460	6.118369691141
C	3.457523762719	-0.169685060864	7.573540761537
C	2.103563398625	-0.212736142923	7.879219329889
N	4.689439069617	-0.040390328756	5.423836694527
C	4.727591665131	-0.003778436008	4.082908243426
N	3.663645976366	-0.030743203734	3.225137532892
C	4.204813702748	0.009095483191	1.980888657450
C	5.680184467028	0.068997486804	2.045227943645
C	5.993842597841	0.061028428173	3.372586038397
S	6.667204980718	0.131782486901	0.604969150627
C	8.334933018077	0.212898023082	1.341742399619
N	3.575051694868	-0.007406197744	0.801804302153
S	1.409183850291	-0.210891535280	9.498405973879
C	0.330630280675	-1.698622566349	9.451958638975
S	4.704045767301	-0.176449389509	8.802572780356
C	6.291432663192	-0.363578412836	7.912386370533
S	-4.014340153788	-0.146984412350	3.289715108307
C	-3.995217477211	1.166237052729	2.004006564004
S	-3.204126311617	-0.160135719304	6.655005591332
C	-2.599339757257	1.147011721684	7.796698489144
S	2.046143506602	-0.115989746542	-2.223983093381
C	3.873258671044	-0.161189851419	-2.161785986930
S	-1.203204929144	-0.164915946652	-1.338839356055
C	-2.108992500820	-1.682606400756	-0.834473357346
H	8.442599253595	1.106249498047	1.962780032363
H	9.039937295600	0.266434690065	0.508883776705
H	8.544667486872	-0.681948783603	1.933895259657
H	4.237434050914	-1.043445785113	-1.635446555536
H	4.284030568056	0.734366862549	-1.696927201825
H	4.169886128753	-0.206314003377	-3.213576024275
H	-2.987097655637	-1.735285686370	-1.483813183255
H	-2.423733400323	-1.610293216119	0.207016761296
H	-1.490181551894	-2.568710998927	-0.992376529567
H	-4.985192190531	1.133650016187	1.540721742117
H	-3.847819629024	2.146504973620	2.463567036200
H	-3.225943723590	0.971493266841	1.257740890953
H	-1.574205771653	0.949855030126	8.108021524611
H	-2.677085617916	2.129847975823	7.325736264321
H	-3.268049924380	1.110659389424	8.661140569468
H	-0.148390948034	-1.748861535789	10.433522072804
H	0.927532257968	-2.599890550578	9.295705836027
H	-0.427374558933	-1.596668777216	8.674933140518
H	6.306174209737	-1.271990097468	7.309460900150
H	6.502153338550	0.497459156020	7.280053777322
H	7.034562846283	-0.436644923723	8.711622162117
H	6.960746787392	0.091557220604	3.853365383611
H	1.598031013631	-0.056335037035	2.689350858457
H	2.061812771678	-0.079933339172	4.636140106266

**3 (free base, -Br substituent)**

C	0.034728000844	-0.067450361900	0.023511616169
C	0.029786685113	-0.037309414937	1.467361379285
N	1.339454617597	-0.002196104506	1.873283213341
C	2.193504080712	0.028958789076	0.795329979069

C	1.357667240284	-0.011310505083	-0.401523004184
N	-1.052882084936	-0.030190862818	2.229672483101
C	-1.023644342648	-0.013043405983	3.560196493713
N	0.076673148188	-0.052434036041	4.362772336328
C	-0.397273177314	-0.079790207595	5.637243729741
C	-1.874136492625	0.005429179109	5.667672169238
C	-2.270530994459	0.045182437419	4.357315227121
N	0.313215324998	-0.176121253240	6.762582794507
C	1.633449486196	-0.233577181847	6.790634632600
N	2.490740911590	-0.192974475730	5.721887115765
C	3.802112263914	-0.218802389457	6.135666938822
C	3.780315340210	-0.340212028657	7.590898761432
C	2.449408270538	-0.348925176881	7.985545790249
N	4.874577035298	-0.142260828876	5.378536560248
C	4.837637992602	-0.043633501997	4.047428537379
N	3.739198318916	-0.036613492857	3.243812964954
C	4.211745778301	0.053538992692	1.974863636737
C	5.691093937822	0.118814032999	1.940511301502
C	6.061893185160	0.055297366353	3.254097356883
S	6.487463109797	0.237121147568	0.386895897252
C	8.261830256854	0.490212381962	0.753064115577
N	3.510181207384	0.070751242044	0.838371235841
S	1.862861561200	-0.358927110517	9.645120229666
C	0.645124960206	-1.735956587993	9.618724930353
S	5.134801098890	-0.351169020662	8.701357271773
C	6.501529391730	-1.146117852207	7.771355860992
S	-3.925964052171	0.010504342322	3.767224006416
C	-3.936726721584	1.325011802234	2.482967243931
S	-2.920411911082	-0.086723533419	7.078301499917
C	-2.223778577268	1.205059932460	8.184830101018
S	1.800328456230	0.010668160710	-2.093207082630
C	3.627369648073	-0.025455287174	-2.144568459745
S	-1.387904069526	-0.054416170188	-1.016373640501
C	-2.274436383941	-1.565209711713	-0.459360209566
H	8.421581926465	1.386668478906	1.353344549887
H	8.723530127800	0.624333988522	-0.228986511092
H	8.702959883908	-0.375015626018	1.247770410377
H	4.027166350969	-0.920577107433	-1.668057035579
H	4.062900264027	0.858159117194	-1.679678689663
H	3.858692869849	-0.038804834848	-3.213511914691
H	-3.186972254546	-1.613055396656	-1.059733955639
H	-2.531139194622	-1.489722756133	0.597759447359
H	-1.670881883281	-2.455432333334	-0.649779752104
H	-4.954466488962	1.330682743209	2.083205195292
H	-3.723909414424	2.297894570493	2.932429671777
H	-3.224114671634	1.103272998853	1.689763577312
H	-1.184777949017	0.989276036712	8.431622828396
H	-2.313631628112	2.191104536472	7.722957613839
H	-2.837458452713	1.176376600221	9.089384137313
H	0.219449373003	-1.771292870198	10.625145607884
H	1.145461034952	-2.683447657352	9.406324731565
H	-0.140718028037	-1.540848702495	8.889107272438
H	6.208957866496	-2.145525891876	7.441574220427
H	6.816629294262	-0.551118188078	6.916723150407
H	7.311678970576	-1.231232361642	8.500913281051
Br	7.766098258354	0.059849012965	4.056406540840
H	1.646374516319	0.000606943105	2.838656222387
H	2.195096818725	-0.143149538912	4.754157844993

#### 4 (Ni complex, -Br substituent)

C	1.740788223909	3.883512411144	0.231257868844
C	1.833579226937	2.441000186077	0.104707369084
N	0.588197098495	1.866104007109	0.063931091759
C	-0.307863315255	2.916427205998	0.093077323286
C	0.400784150705	4.193468933639	0.217496055535
N	3.000572268803	1.821352068032	0.015125409947
C	3.075224178417	0.512463156443	-0.089172887808
N	2.031567519664	-0.382871214455	-0.051516757454
C	2.608980479182	-1.629708862364	-0.106132640960
C	4.061014216696	-1.524652844282	-0.259642407100
C	4.353404737740	-0.185146649182	-0.247677349048
N	1.997693319280	-2.791912604893	-0.017081334508
C	0.680215993369	-2.870377199854	0.080480057314
N	-0.211727515533	-1.829401603556	0.055432930583
C	-1.462782414775	-2.412865089717	0.090067380344
C	-1.352529624835	-3.867011488148	0.212844876807
C	-0.007397701203	-4.147810312491	0.206601240822
N	-2.618893311265	-1.796033879379	0.005482775396

C	-2.690383665842	-0.478429668141	-0.066409890891
N	-1.654291433556	0.422588043898	-0.021105529966
C	-2.233747906989	1.668421301386	-0.062054361706
C	-3.685117938091	1.567726477745	-0.156478202569
C	-3.948558390033	0.225473305686	-0.149563034005
S	-4.765763602933	2.956784819258	-0.186885295185
C	-5.769289060551	2.629050635308	-1.689215261108
N	-1.616934665547	2.835916324518	0.010328174611
S	0.737591762852	-5.742502264723	0.189200884351
C	1.934984500551	-5.630650015699	1.579012033935
S	-2.632782777815	-5.064267121992	0.213742416325
C	-4.018863351535	-4.275129064736	1.121689494135
S	5.956769840821	0.533200440766	-0.255978282702
C	5.802078715097	1.893779240805	-1.481848455585
S	5.216498176922	-2.848919111818	-0.290592835963
C	4.524404481571	-3.973763151516	-1.568862202053
S	-0.219726457198	5.829399280777	0.241512122953
C	-1.969252169054	5.704861513858	0.768231362034
S	3.087815956123	5.018355507841	0.243847035448
C	4.045443201533	4.456331659407	1.708115125291
H	-5.136114252780	2.626618039852	-2.579174815894
H	-6.480265437167	3.456997135752	-1.752767628202
H	-6.313120184637	1.687329475531	-1.606588172718
H	-2.055862543265	5.167772947908	1.714504557376
H	-2.590128617120	5.223691064986	0.015219301609
H	-2.277323519069	6.744498316874	0.911930840976
H	4.910949459223	5.121485985700	1.772017862810
H	4.380601969612	3.427162525114	1.575108501724
H	3.448127130471	4.555334156589	2.617301779043
H	6.792383650936	2.355441083895	-1.523221609588
H	5.554125882446	1.491438302608	-2.466838507105
H	5.060070730350	2.625658483788	-1.165547224915
H	3.538483148998	-4.336399596958	-1.280837526436
H	4.484037059077	-3.469950511393	-2.537383407701
H	5.228448501804	-4.808191206745	-1.628988586121
H	2.440172975753	-6.599776662054	1.612105218499
H	1.410541638046	-5.466880462601	2.523179666338
H	2.662709422088	-4.839602298216	1.397981659706
H	-3.694877495494	-3.959732310406	2.116173586512
H	-4.433190973548	-3.429398068841	0.576982991643
H	-4.764958364800	-5.068175887581	1.223596176452
Br	-5.608344787127	-0.639990140036	-0.169454353223
Ni	0.187636859546	0.019306253486	0.017365389023

### 5 (free base, -Ph-CF<sub>3</sub> substituent)

C	-0.003747879835	-0.003116423273	0.001038807460
C	-0.001931097964	0.000457789673	1.446616365588
N	1.309637277461	0.006978679265	1.847543371196
C	2.159793087831	0.053186944096	0.766908173531
C	1.317674831578	0.039063428449	-0.427748724953
N	-1.080481167885	0.009646530456	2.213736640863
C	-1.041992932696	0.007784203140	3.544678024165
N	0.063728028202	-0.050193290916	4.337613995471
C	-0.400709112963	-0.089143597288	5.615325125463
C	-1.876280697333	0.005772890237	5.658513575470
C	-2.282379829537	0.065328578615	4.351798717290
N	0.318952998334	-0.203571777069	6.732617267292
C	1.638881495325	-0.266007717936	6.749970748428
N	2.491559539673	-0.204429314211	5.678787347597
C	3.805368373244	-0.239248971657	6.085476629080
C	3.789704078425	-0.398067717052	7.536010346734
C	2.462513066212	-0.411200882848	7.939426562549
N	4.876845854301	-0.134807350902	5.326463258668
C	4.838933645937	-0.006766175864	3.994111617424
N	3.730934173977	-0.022184150026	3.203536508203
C	4.189611235007	0.081608474871	1.930237995462
C	5.661356358958	0.171913075804	1.896371621888
C	6.079103326402	0.107575957144	3.204661031197
S	6.505820955800	0.364378194005	0.364395859095
C	7.913061995784	1.464692300288	0.770221559805
N	3.474848591398	0.099476949280	0.799981465455
S	1.888020881645	-0.458622124596	9.601855395450
C	0.625543801905	-1.793792113444	9.549050351229
S	5.168212876683	-0.431940741001	8.622303661984
C	6.371427318642	-1.518187489036	7.759734005628
S	-3.941818772931	0.051878519230	3.772553575608
C	-3.951334052674	1.389390787582	2.511919321038
S	-2.910313637838	-0.093930822285	7.078015647843

C	-2.204245146135	1.196959316916	8.179694958179
S	1.761600709126	0.105331596975	-2.117909274415
C	3.570131604572	-0.160950438527	-2.178339388978
S	-1.428807434878	0.061862052181	-1.032731749065
C	-2.354961727017	-1.432637168795	-0.496548693270
H	7.563399154020	2.333654899232	1.331992147383
H	8.305713876374	1.794772777848	-0.195170922737
H	8.699015949240	0.952389727501	1.326540139383
H	3.846777408618	-1.111284491584	-1.720037887372
H	4.118163008228	0.647561255273	-1.697487803185
H	3.795771639801	-0.189165613140	-3.248164795053
H	-3.273679112528	-1.441180959081	-1.089215039596
H	-2.599901466036	-1.370543711637	0.564164930015
H	-1.779917341594	-2.336341378528	-0.710151237243
H	-4.971199772447	1.408655958930	2.118026402069
H	-3.730056088419	2.352604263418	2.977819573774
H	-3.244351447021	1.178166968477	1.710649984214
H	-1.160096691960	0.985918082340	8.408461954255
H	-2.307421152192	2.184546808998	7.723971209684
H	-2.802077730487	1.160432021161	9.094483519052
H	0.222383861989	-1.852775240501	10.563642670804
H	1.091503971371	-2.747846901683	9.292229494598
H	-0.170001105548	-1.550584045417	8.845376855728
H	5.935934415174	-2.504699391105	7.585288396666
H	6.704672901302	-1.074702206484	6.823814492524
H	7.211658589422	-1.614862144457	8.452583539165
C	7.436601772065	0.054720792998	3.771046279957
C	8.407155199888	-0.796246280677	3.211429550239
C	9.688977875623	-0.871493311252	3.748297760544
C	10.027295869962	-0.093532976828	4.859271119839
C	9.074333989789	0.754497130141	5.429420330944
C	7.791828964076	0.826026926734	4.892121687220
H	8.145057426497	-1.409246825723	2.354109578942
H	10.427063068913	-1.532443845704	3.305411350433
C	11.394449382580	-0.216940293732	5.473731691217
H	9.338946117718	1.365948518553	6.285821840242
H	7.057499686132	1.486055143490	5.339593539210
H	2.194627547235	-0.133054660752	4.712784836003
H	1.619236936193	-0.010812024993	2.811850930660
F	11.770234053756	0.918684027254	6.102523123510
F	11.441406625454	-1.208781892164	6.395214811938
F	12.337953332208	-0.500874629040	4.547662266962

## 6 (free base, -Ph-OCF<sub>3</sub> substituent)

C	-0.038764237194	0.024100446286	-0.001257729447
C	-0.026600745559	0.009795800861	1.444479808637
N	1.288117491836	0.017924591118	1.835629989493
C	2.129851326077	0.080298894500	0.749589384819
C	1.279252576858	0.075663561113	-0.439026140247
N	-1.099246789080	0.001903662609	2.219408205149
C	-1.051050297548	-0.017132783801	3.550102797165
N	0.060577285868	-0.075164061596	4.334320870979
C	-0.394249498482	-0.134249685411	5.614937242996
C	-1.870012431692	-0.054068916469	5.669431751436
C	-2.285941625072	0.018618886839	4.366405337141
N	0.335068070905	-0.254590892998	6.725470093218
C	1.655686194109	-0.303467694121	6.732075048100
N	2.499217482920	-0.220344657714	5.655094256587
C	3.816222735776	-0.245697550557	6.051076170270
C	3.813824398234	-0.420153330220	7.499341644416
C	2.490231938049	-0.453706926659	7.913339272395
N	4.881569843009	-0.123817221662	5.285458277108
C	4.833410833511	0.013997161931	3.954833245126
N	3.719574701276	-0.004380375392	3.172269601858
C	4.169205912007	0.111018622243	1.896538595895
C	5.639826028641	0.213229881527	1.853216683637
C	6.067958940067	0.144898377272	3.157737672124
S	6.478425784728	0.418737286344	0.318609235688
C	7.850820864745	1.564182369809	0.720709052967
N	3.444943578045	0.133222731138	0.772303678004
S	1.928992491743	-0.529953449157	9.579060425519
C	0.669810347888	-1.867835727363	9.514506915533
S	5.203768194527	-0.448517950346	8.571827877137
C	6.399032201572	-1.533144362968	7.696022830505
S	-3.948930613617	-0.002388902115	3.797530409061
C	-3.978865254862	1.353552203974	2.557099850349
S	-2.892886058713	-0.178978752745	7.095368615750
C	-2.194858119793	1.112774420195	8.201034841417

S	1.712360966322	0.165083232865	-2.130823306517
C	3.517487359201	-0.122627289305	-2.207548896467
S	-1.471491467069	0.095505274077	-1.024193707372
C	-2.381065418405	-1.416015900657	-0.508271468560
H	7.472582589414	2.427128222061	1.273109439038
H	8.238960027304	1.897374160627	-0.245467957312
H	6.648339078356	1.079996374343	1.285768594404
H	3.784480035503	-1.083606683890	-1.765714967261
H	4.079426813000	0.670785293682	-1.717715816939
H	3.735733395144	-0.137931526497	-3.279166973353
H	-3.302939907821	-1.423292917429	-1.096070370477
H	-2.620875273149	-1.373834970260	0.554529419622
H	-1.799025348981	-2.310766767123	-0.739843874585
H	-5.000487740240	1.367277603528	2.167533944713
H	-3.766437875590	2.312170962819	3.036440685726
H	-3.272856881866	1.162089404890	1.750016638644
H	-1.146518562613	0.912990991610	8.420798205038
H	-2.313279245146	2.102164636381	7.752975801911
H	-2.785327578214	1.062836047242	9.119991491352
H	0.274688124895	-1.943996218804	10.531120132424
H	1.136680906240	-2.816336876461	9.239313211104
H	-0.131676203103	-1.616322604165	8.820471251648
H	5.965740883596	-2.522659076611	7.533219642249
H	6.715362178266	-1.092198624296	6.752865503648
H	7.250629330946	-1.622421107829	8.375960806895
C	7.429666154402	0.104421601955	3.713591315832
C	8.410054845548	-0.722560552307	3.140166755460
C	9.701617565552	-0.799164978798	3.659834266374
C	10.024630793926	-0.021130802183	4.771408809369
C	9.073966987687	0.806322722744	5.366344812512
C	7.785745513585	0.862161240777	4.844195399949
H	8.152802318879	-1.333065266069	2.279539963020
H	10.428750609579	-1.462203229752	3.208749443376
O	11.272665290057	-0.023714477817	5.401286579021
H	9.356993503398	1.400292491288	6.229173425543
H	7.048494022509	1.503917509587	5.312787666118
C	12.390297077356	-0.396624016757	4.731568736749
H	2.192717641926	-0.140477268639	4.692743219334
H	1.606170562942	-0.009693802413	2.796959134923
F	13.434519872919	-0.111506644495	5.506901453402
F	12.416532983205	-1.720717210574	4.463375517843
F	12.529985892567	0.248483077964	3.559205208689

### 7 (free base, -Ph-N(CH<sub>3</sub>)<sub>2</sub> substituent)

C	-0.036740694252	0.061388295278	-0.039112912823
C	-0.065438624594	0.005230663173	1.406250056871
N	1.237803884486	0.032143935500	1.834649776746
C	2.108149957071	0.146226210494	0.775984953571
C	1.290888233503	0.156117751368	-0.436521065074
N	-1.158253537964	-0.049700801804	2.148781948234
C	-1.145435512588	-0.110334364506	3.480383833459
N	-0.054651846539	-0.171721924535	4.291503919408
C	-0.541223324413	-0.283935434020	5.557541217493
C	-2.018442378817	-0.234478947313	5.574383435704
C	-2.401144921461	-0.126136529344	4.263287860796
N	0.161529424583	-0.430494720145	6.681398856433
C	1.482557043848	-0.452827595297	6.721229270803
N	2.352429432921	-0.305480661313	5.671625515371
C	3.658609843410	-0.323564546517	6.100535207230
C	3.622502683926	-0.563496928546	7.538033041899
C	2.289412175013	-0.639170978561	7.915449581184
N	4.742177090264	-0.144973870264	5.370716274340
C	4.727804030387	0.047665676865	4.046971257219
N	3.635675265536	0.024866231676	3.234822220338
C	4.118961211368	0.191944221390	1.975108450686
C	5.582877490983	0.335337693812	1.974240437526
C	5.984190031404	0.242689594226	3.287950375409
S	6.474495775665	0.614365656561	0.476674516381
C	7.653945045879	1.940422954471	0.937389000750
N	3.420032118808	0.229200081694	0.834373509386
S	1.687618599411	-0.800934957613	9.561439781200
C	0.462931719899	-2.162927826656	9.405147536441
S	4.986341883455	-0.621766403585	8.643155557891
C	6.226476020324	-1.631842603533	7.740563935577

S	-4.048093932695	-0.158836301867	3.647902792389
C	-4.070609022055	1.243827644673	2.460442650227
S	-3.075676390365	-0.427444219013	6.967832632879
C	-2.429232100102	0.835700909762	8.136158585451
S	1.773211599189	0.312486992215	-2.110987142085
C	3.579797779517	0.023361170324	-2.145710975687
S	-1.442050242253	0.130173786834	-1.099518663427
C	-2.341684585274	-1.404499248741	-0.636982704983
H	7.119847464549	2.781500648792	1.385097193192
H	8.111342815914	2.262570558170	-0.002102870419
H	8.429132462024	1.584501390163	1.617747010310
H	3.831322949252	-0.953932595681	-1.731150831358
H	4.128728254294	0.796002903317	-1.610498217321
H	3.829035852952	0.045057213518	-3.210527649859
H	-3.248092864662	-1.413640809338	-1.248395170933
H	-2.608480623965	-1.387083039413	0.420097006498
H	-1.740220344305	-2.285728309880	-0.871034688799
H	-5.080755161162	1.254173618605	2.041790976250
H	-3.890237260650	2.186872100047	2.982037384475
H	-3.338184849378	1.096828046138	1.667549173047
H	-1.383099021874	0.645998664488	8.374578019000
H	-2.554279199382	1.838453869119	7.720657757607
H	-3.040920737846	0.742669929089	9.03776573182
H	0.043008643816	-2.293361126397	10.406250224396
H	0.959022974530	-3.087481057093	9.100899204575
H	-0.325689466414	-1.898466347608	8.701225617129
H	5.808639934340	-2.608959028411	7.487469057008
H	6.578713802522	-1.121468222419	6.846392815225
H	7.049116466305	-1.767123036718	8.448227413529
C	7.327799838465	0.244263014558	3.872787212026
C	8.389462694883	-0.440811616370	3.252927154673
C	9.666131510552	-0.466004956001	3.797301328382
C	9.959791770512	0.215194619366	5.003349566698
C	8.891011055881	0.896082735312	5.633517642324
C	7.617240670928	0.905848710215	5.080684208237
H	8.202272217175	-0.982486070433	2.329994499278
H	10.436728229587	-1.027951417609	3.283152628880
N	11.236271825720	0.221055503920	5.538443849967
H	9.053121283612	1.429274455229	6.562579478023
H	6.827813046731	1.441281505030	5.596364370050
C	11.461641679196	0.789493391174	6.856802381804
C	12.269557160594	-0.613243281625	4.948864530904
H	13.208393276658	-0.448867484394	5.480741857053
H	12.029139137357	-1.686813546940	4.999519007413
H	12.435219709216	-0.352772203925	3.896278129510
H	12.522937360186	0.716834551129	7.100908623718
H	11.186828982371	1.851236927759	6.882757110850
H	10.891599440313	0.272166936275	7.644097185874
H	2.072084374040	-0.192067376102	4.704685638868
H	1.529831856143	-0.020194793095	2.803202406076

### 8 (Ni complex, -Ph-N(CH<sub>3</sub>)<sub>2</sub> substituent)

C	1.740788223909	3.883512411144	0.231257868844
C	1.833579226937	2.441000186077	0.104707369084
N	0.588197098495	1.866104007109	0.063931091759
C	-0.307863315255	2.916427205998	0.093077323286
C	0.400784150705	4.193468933639	0.217496055535
N	3.000572268803	1.821352068032	0.015125409947
C	3.075224178417	0.512463156443	-0.089172887808
N	2.031567519664	-0.382871214455	-0.051516757454
C	2.608980479182	-1.629708862364	-0.106132640960
C	4.061014216696	-1.524652844282	-0.259642407100
C	4.353404737740	-0.185146649182	-0.247677349048
N	1.997693319280	-2.791912604893	-0.017081334508
C	0.680215993369	-2.870377199854	0.080480057314
N	-0.211727515533	-1.829401603556	0.055432930583
C	-1.462782414775	-2.412865089717	0.090067380344
C	-1.352529624835	-3.867011488148	0.212844876807
C	-0.007397701203	-4.147810312491	0.206601240822
N	-2.618893311265	-1.796033879379	0.005482775396
C	-2.690383665842	-0.478429668141	-0.066409890891
N	-1.654291433556	0.422588043898	-0.021105529966
C	-2.233747906989	1.668421301386	-0.062054361706
C	-3.685117938091	1.567726477745	-0.156478202569
C	-3.948558390033	0.225473305686	-0.149563034005
S	-4.765763602933	2.956784819258	-0.186885295185
C	-5.769289060551	2.629050635308	-1.689215261108
N	-1.616934665547	2.835916324518	0.010328174611

S	0.737591762852	-5.742502264723	0.189200884351
C	1.934984500551	-5.630650015699	1.579012033935
S	-2.632782777815	-5.064267121992	0.213742416325
C	-4.018863351535	-4.275129064736	1.121689494135
S	5.956769840821	0.533200440766	-0.255978282702
C	5.802078715097	1.893779240805	-1.481848455585
S	5.216498176922	-2.848919111818	-0.290592835963
C	4.524404481571	-3.973763151516	-1.568862202053
S	-0.219726457198	5.829399280777	0.241512122953
C	-1.969252169054	5.704861513858	0.768231362034
S	3.087815956123	5.018355507841	0.243847035448
C	4.045443201533	4.456331659407	1.708115125291
H	-5.136114252780	2.626618039852	-2.579174815894
H	-6.480265437167	3.456997135752	-1.752767628202
H	-6.313120184637	1.687329475531	-1.606588172718
H	-2.055862543265	5.167772947908	1.714504557376
H	-2.590128617120	5.223691064986	0.015219301609
H	-2.277323519069	6.744498316874	0.911930840976
H	4.910949459223	5.121485985700	1.772017862810
H	4.380601969612	3.427162525114	1.575108501724
H	3.448127130471	4.555334156589	2.617301779043
H	6.792383650936	2.355441083895	-1.523221609588
H	5.554125882446	1.491438302608	-2.466838507105
H	5.060070730350	2.625658483788	-1.165547224915
H	3.538483148998	-4.336399596958	-1.280837526436
H	4.484037059077	-3.469950511393	-2.537383407701
H	5.228448501804	-4.808191206745	-1.628988586121
H	2.440172975753	-6.599776662054	1.612105218499
H	1.410541638046	-5.466880462601	2.523179666338
H	2.662709422088	-4.839602298216	1.397981659706
H	-3.694877495494	-3.959732310406	-2.116173586512
H	-4.433190973548	-3.429398068841	0.576982991643
H	-4.764958364800	-5.068175887581	1.223596176452
Br	-5.608344787127	-0.639990140036	-0.169454353223
Ni	0.187636859546	0.019306253486	0.017365389023

### 9 (Ni complex, -CC-Ph substituent)

N	1.576137866986	1.625640672603	-0.028565451104
C	0.972422981329	2.856131104008	0.059888039459
C	2.924328434941	1.878771399407	-0.050444962811
C	1.960702586138	3.924770527708	0.140046380414
C	3.190948418795	3.311652875269	0.069905479960
N	-0.324112660559	3.107382758000	0.028026812805
N	3.901759966634	1.001277391552	-0.176085498117
C	-1.210426883827	2.135332679228	-0.044676150709
C	3.659072281720	-0.292212287278	-0.253332922797
C	-2.641312331934	2.391138011215	-0.108093349939
C	4.718336353783	-1.288533949921	-0.414015438831
C	-3.256032977438	1.156100243424	-0.078385389239
C	4.093817366279	-2.515920940653	-0.385219060030
C	-2.179666760742	0.167080287934	-0.022341494110
C	2.677338392633	-2.255699710137	-0.232493543412
N	2.427417818723	-0.904963377328	-0.175245243865
N	-0.954675084080	0.778557972157	-0.028967304347
N	-2.435400842593	-1.126038958879	0.033485937612
N	1.790277033032	-3.233666786560	-0.146779051540
C	0.503938962055	-2.990359166240	-0.033335824162
C	-1.458471327634	-2.012413372758	0.050262988584
C	-0.486194162564	-4.061649703829	0.093043297349
C	-1.712985941208	-3.445182450102	0.146126610469
N	-0.108838746769	-1.756042697239	-0.021088112080
Ni	0.736233850483	-0.064893804304	-0.061507624109
S	1.559664582004	5.642576591649	0.102082748496
S	4.856445333755	3.864549726632	0.056500723579
S	6.448074303630	-1.105524178892	-0.593388231537
S	-3.454666488007	3.945895360676	-0.069820822164
S	4.808443647736	-4.120384424605	-0.555004519369
S	-3.270517141046	-4.258805974228	0.153750039243
S	-0.241150076454	-5.796281348777	0.027619587847
C	4.834260095781	5.453116633189	0.963855020001
C	0.536900537470	5.844361822033	1.615180987281
H	5.889404389078	5.700116253441	1.110856607081
H	4.341068146044	6.244894229801	0.401493898931
H	4.353836002934	5.334297510812	1.937237140135
H	0.245685546489	6.898101417256	1.641680506860
H	-0.353110254993	5.217369912691	1.557168871371
H	1.118078731191	5.609000557410	2.510199944592
C	-2.578152987082	4.907148556298	-1.367719811924

H	-3.064138250623	5.886573079373	-1.380993524792
H	-1.521530402475	5.016502857731	-1.126047825056
H	-2.704391952331	4.431081884656	-2.342905381376
C	-4.249212125379	-3.305114836221	1.380115568776
C	1.368031606051	-6.083037752514	0.861121608118
H	-5.198245072008	-3.841361715301	1.468477744101
H	-3.749408427727	-3.303444024989	2.351629303725
H	-4.418542055571	-2.286200016086	1.034974444447
H	1.446675363538	-7.171326967468	0.936295457205
H	2.196604324055	-5.677451687677	0.283533386587
H	1.360307051179	-5.654320626363	1.865956874385
C	5.748405100454	-4.277437151281	1.017696304524
C	6.788287379637	0.681125648404	-0.770548893314
H	6.242601293074	-5.251967757685	0.974068233697
H	6.505880035078	-3.496443626473	1.111994179362
H	5.072095130230	-4.253729756233	1.875273636281
H	7.867151531932	0.725269444417	-0.945798288688
H	6.259831007074	1.103483722428	-1.625558795348
H	6.528742785053	1.236996781745	0.128709938569
C	-4.625158253983	0.846288411827	-0.104040893024
C	-5.815652344236	0.591391245206	-0.134509115462
C	-7.208676144188	0.308533862328	-0.176143063117
C	-7.669013502007	-1.018580124351	-0.299505196104
C	-9.034090535427	-1.286345153588	-0.338861711642
C	-9.959843993037	-0.242694594092	-0.256628792369
C	-9.513392299306	1.076110303518	-0.135826663603
C	-8.150661092628	1.355085565596	-0.095987386294
H	-6.945547970914	-1.824973731254	-0.368079198791
H	-9.377850023626	-2.312550121646	-0.435669279065
H	-11.024749636846	-0.456101041450	-0.288026284758
H	-10.230551202178	1.889997253915	-0.073126115824
H	-7.796999300602	2.377211268292	-0.003578080311

## 10 (Ni complex, -CC-Ph-NO<sub>2</sub> substituent)

N	2.216867893224	1.598900772823	-0.021804502745
C	1.644582882517	2.845093504022	0.071934680417
C	3.569226531334	1.818971936297	-0.051370517939
C	2.659347538636	3.888594987875	0.151610010965
C	3.873450997119	3.245107564354	0.071622598974
N	0.355102724602	3.127143935255	0.045223108214
N	4.525027229793	0.918268129438	-0.186674246278
C	-0.555081978263	2.176646817457	-0.023366526020
C	4.250458885532	-0.368008396073	-0.266285455707
C	-1.979824518122	2.467297931409	-0.076585937868
C	5.284259906577	-1.389837394552	-0.441584636942
C	-2.622061480843	1.244966913304	-0.035737785814
C	4.629838543196	-2.601297077414	-0.414096613344
C	-1.572405131633	0.231298784441	0.014897702844
C	3.221328839801	-2.306749786063	-0.246211982578
N	3.004882370845	-0.950580601731	-0.179848314710
N	-0.334173649514	0.814072391866	-0.004689671901
N	-1.859345433037	-1.055873851146	0.077167651133
N	2.311962576653	-3.262953605690	-0.154261354629
C	1.033073038584	-2.988654050955	-0.025120812639
C	-0.904482710887	-1.965106939212	0.083653315518
C	0.018944406991	-4.037160930837	0.111111727671
C	-1.191715173429	-3.391479308238	0.180949409511
N	0.450809841624	-1.740642240229	-0.003410817140
Ni	1.335903362921	-0.070258955643	-0.049908480107
S	2.292580980471	5.615006512648	0.134936903929
S	5.555611355887	3.739980586257	0.050715484750
S	7.014644103022	-1.248581920604	-0.643430747228
S	-2.764801472239	4.033974251044	-0.039526520824
S	5.300154334234	-4.222661833083	-0.600987317559
S	-2.769677362157	-4.164461520760	0.207391496967
S	0.220346992059	-5.776455178029	0.040130417146
C	5.586392557759	5.386540011771	0.845582656233
C	1.313953920885	5.822856416636	1.676187057137
H	6.650061968960	5.606754314378	0.972683116631
H	5.119530171477	6.153506266222	0.228969924845
H	5.106090453807	5.354521314790	1.825366119316
H	1.043265911518	6.881492869472	1.719401045357
H	0.410564422623	5.213540324288	1.636895837000
H	1.913229586224	5.568632992747	2.553866274860
C	-1.834655920864	5.010425889375	-1.287648794870
H	-2.308592427699	5.995696196155	-1.291896400190
H	-0.784512025191	5.098822708928	-1.013077295579
H	-1.938857873738	4.557888228518	-2.276434754056



C	-3.687189244709	-3.211949337185	1.481134295550
C	1.837439773029	-6.105514509304	0.842024640964
H	-4.652297686501	-3.717012590496	1.578566585252
H	-3.165936096884	-3.253268876293	2.440386789336
H	-3.828396358714	-2.178939195122	1.165972893545
H	1.887217610086	-7.195474825393	0.917073385124
H	2.665690183198	-5.723759616695	0.248119556097
H	1.861006945488	-5.676063003540	1.846236732044
C	6.269252965661	-4.407370171799	0.950866568882
C	7.403440289911	0.532047258949	-0.773332000090
H	6.736226184978	-5.394512874185	0.894278611449
H	7.049064376338	-3.647074180250	1.030266218383
H	5.612245433005	-4.368172734871	1.822688009434
H	8.482345536561	0.550560358423	-0.952581389688
H	6.883114597017	0.993244361260	-1.612935660564
H	7.164442580602	1.069111223693	0.143029560317
C	-3.998954516720	0.972198647594	-0.055155474780
C	-5.196352401358	0.751692656745	-0.081199546856
C	-6.593573030365	0.507454130885	-0.119263034659
C	-7.089888218504	-0.810990452039	-0.219750628460
C	-8.456665055058	-1.049126328323	-0.255476391085
C	-9.332420001911	0.035196584327	-0.190761890868
C	-8.874484713310	1.349664050785	-0.093514392138
C	-7.507009699385	1.583210821099	-0.058379010453
H	-6.390173242576	-1.638214053884	-0.273659630604
H	-8.855817281163	-2.052816880088	-0.333498789803
N	-10.778825311116	-0.214129273681	-0.226215773408
H	-9.590089270345	2.161162719621	-0.047135623731
H	-7.127080006180	2.596582637849	0.016143688639
O	-11.529229220942	0.761119513757	-0.172592402491
O	-11.156383294393	-1.383686015289	-0.306738940984

### 11 (Ni complex, -CC-Ph-N(CH<sub>3</sub>)<sub>2</sub> substituent)

N	2.289610717935	1.598394177009	0.002645623317
C	1.720553682050	2.845536419054	0.085992766425
C	3.646358334549	1.813021096124	-0.014329021894
C	2.739598553140	3.881245565408	0.195183184854
C	3.950191678222	3.237434252067	0.106146025613
N	0.431595779621	3.135970279186	0.062241878783
N	4.598170125589	0.906190990432	-0.119871214663
C	-0.484457837894	2.190762421632	0.000650329340
C	4.317166627508	-0.380269048084	-0.195676269584
C	-1.905483014200	2.488579858437	-0.048069704614
C	5.346709940701	-1.403860391843	-0.364004582309
C	-2.558790149413	1.272424126230	-0.020466257022
C	4.683274191372	-2.610382683458	-0.398408598421
C	-1.508087662564	0.251035835618	0.020653709665
C	3.273435590100	-2.310461619198	-0.248685787934
N	3.066424952445	-0.956122013764	-0.140183694783
N	-0.265955500030	0.825691801496	0.008792229553
N	-1.801554933006	-1.033923977489	0.065655756895
N	2.356928420501	-3.263551146848	-0.191245615324
C	1.079880268251	-2.984926108503	-0.059511407424
C	-0.850479617826	-1.949106681528	0.062977043986
C	0.058695791111	-4.027574168261	0.053126802623
C	-1.147842623210	-3.375410085104	0.133543434553
N	0.504626867856	-1.732597444446	-0.014305385874
Ni	1.399764834174	-0.066779368205	-0.030161105359
S	2.403132753999	5.608575081335	0.347978040764
S	5.622288829629	3.776312373132	0.160178331671
S	7.073205049537	-1.243532802777	-0.610697578939
S	-2.667206617005	4.070132442396	0.010956595661
S	5.336338518808	-4.234427918674	-0.632269418321
S	-2.730218579643	-4.139720324063	0.142180606314
S	0.252152198511	-5.767259570948	-0.053550117618
C	5.608553255752	5.407219853921	-0.676733370416
C	1.366536925204	5.661772040050	1.863863807424
H	6.660601143562	5.636688501434	-0.868339794458
H	5.079306005631	5.340389184920	-1.630172601400
H	5.167074996683	6.183780680272	-0.054061406993
H	1.151869676513	6.719818581550	2.038098273210
H	0.435931713814	5.115359717099	1.709584592759
H	1.916495609999	5.260463204366	2.718133489240
C	-1.796734162612	4.996424202979	-1.315822104347
H	-2.251721858799	5.990751411981	-1.325067053495
H	-0.731751207364	5.075092426899	-1.099346208375
H	-1.960297486542	4.517938844238	-2.284378733777
C	-3.668217189665	-3.173078855659	1.390126395057
C	1.848590038873	-6.118706248965	0.779984518296

H	-4.633298630161	-3.679878716591	1.479054827404
H	-3.160774210732	-3.201370493118	2.357306737972
H	-3.807149626320	-2.144370313333	1.060787655010
H	1.899631146419	-7.210282279367	0.826065370689
H	2.690046796099	-5.718831511727	0.217247007169
H	1.845921778458	-5.717246983163	1.796107473953
C	6.322393733699	-4.457675978544	0.902588979488
C	7.54055570099	0.414565100784	0.005021191199
H	6.782529205870	-5.446354795615	0.821300395708
H	7.105518487518	-3.701054970821	0.982719892414
H	5.675966516395	-4.430982981892	1.782818868636
H	8.632990982235	0.420166124237	-0.051321277747
H	7.123438088810	1.210339367648	-0.608788715866
H	7.228230305910	0.552668537786	1.041291131806
C	-3.932469494657	0.999055013627	-0.032519097537
C	-5.131363805849	0.773572917236	-0.051579009178
C	-6.525139889336	0.527761361897	-0.079884970321
C	-7.038816660584	-0.779069997117	-0.216318170781
C	-8.402148267703	-1.019995813675	-0.247475705843
C	-9.336307564267	0.040715526286	-0.137290686123
C	-8.818341197936	1.354097682033	-0.007874526942
C	-7.453422249607	1.585656233046	0.020401909649
H	-6.346966026603	-1.611101662860	-0.306383826339
H	-8.745663178131	-2.041131523220	-0.360267722634
N	-10.695655292418	-0.196283922328	-0.153045021304
H	-9.489154172965	2.201187466084	0.068310294261
H	-7.084363187108	2.602067174015	0.118959915590
C	-11.628498905949	0.917757237480	-0.121355089254
C	-11.196903756609	-1.539245986042	-0.393708474823
H	-12.287429630141	-1.525561167828	-0.360827285032
H	-10.889120493936	-1.928802129449	-1.375381054145
H	-10.847705362811	-2.241088128738	0.374847387966
H	-12.648517452569	0.530376829874	-0.112257233400
H	-11.493501090585	1.525764643956	0.782486105180
H	-11.520976135424	1.578264234391	-0.994760674777

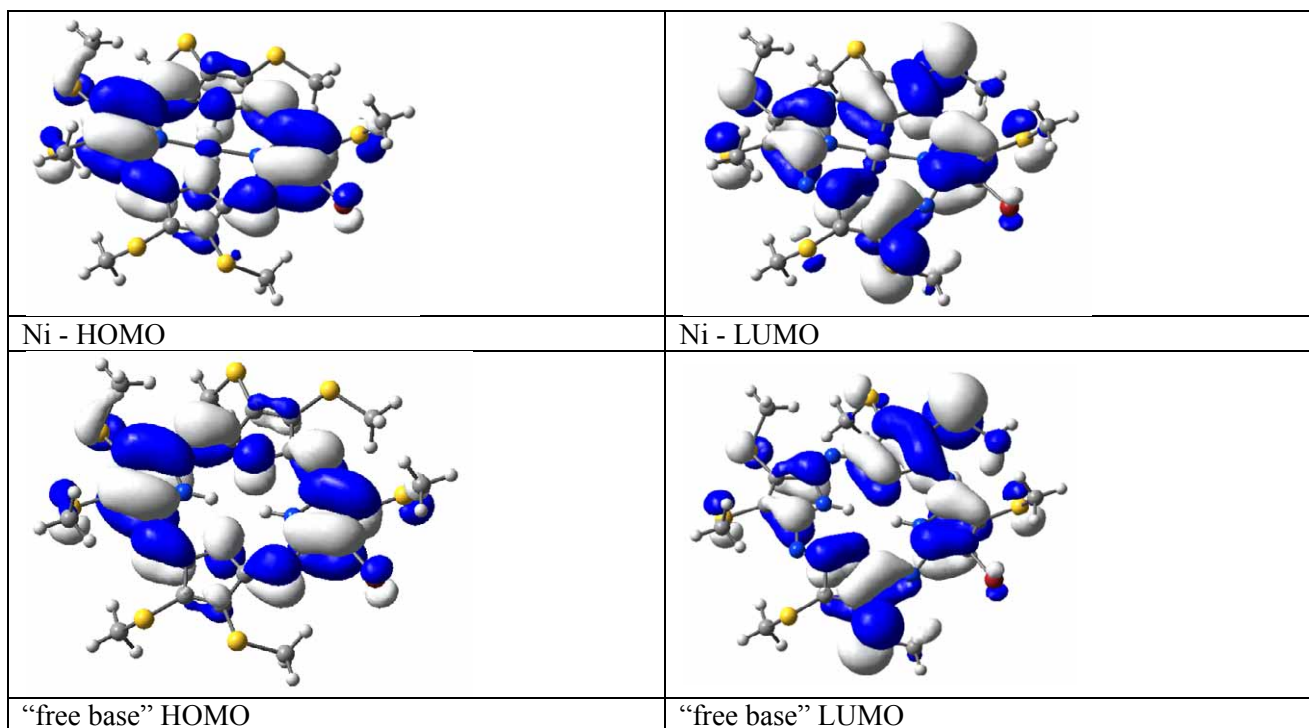
## 12 (Ni complex, -CC-Ph-OH substituent)

C	-5.929485000201	1.309450349542	0.569465474006
C	-4.967731163793	0.579637722831	-0.151328177492
C	-5.414794262747	-0.520367653563	-0.914191287235
C	-6.758541267826	-0.864242413539	-0.965390307443
C	-7.699422941247	-0.119015821002	-0.243897700512
C	-7.278101141758	0.967825533644	0.528568898948
C	-3.554627311501	0.966718196848	-0.123039631639
C	-2.985758544612	2.219577351529	-0.129476721639
C	-1.541467117891	2.028913672976	-0.051378611226
N	-1.225001764373	0.689240522049	-0.049816949909
C	-2.428109121860	0.029001303332	-0.064723214916
N	-0.703109905721	3.040979327196	0.032872970301
C	0.604703391822	2.851444407968	0.066440853987
N	1.265809953219	1.652677125738	-0.022663234471
C	2.602100070084	1.969263183827	-0.039133510870
C	2.798995739304	3.412752417097	0.083695045443
C	1.540655769306	3.966183793356	0.150820864142
Ni	0.505095767880	-0.074285290137	-0.065172335891
N	-0.259344127443	-1.801051933604	-0.032266360383
C	0.409596558793	-3.006529425073	-0.031778836315
C	-0.534546991927	-4.120956291409	0.086881011762
C	-1.787249739031	-3.557550610609	0.122310350334
C	-1.595445574614	-2.116977299086	0.026798652241
N	3.618960004164	1.138880522302	-0.160191443528
C	3.437153351895	-0.165459981259	-0.237286242001
C	4.542082817121	-1.110860961064	-0.388304134106
C	3.975460590064	-2.366457105853	-0.358178450776
C	2.548304325893	-2.172695953351	-0.214838610212
N	2.235054830971	-0.834652387371	-0.164589701306
S	1.064870371465	5.664066819198	0.104303129182
C	-0.009538201327	5.820376765400	1.586653751241
S	4.433460164167	4.053387155943	0.075485746390
C	4.332016927374	5.603701548191	1.042559491444
S	-3.806029964543	3.780193016398	-0.156414898970
C	-2.956913711289	4.664756235960	-1.525327027174
S	6.263387681711	-0.849232041408	-0.552567755987
C	6.519316466373	0.948744312393	-0.757247781768
S	4.770200133997	-3.934079038695	-0.519341108803
C	5.673307245386	-4.056925989649	1.077916116118
N	-2.613230938787	-1.275970248234	-0.001354625728
N	1.706285474286	-3.190577405402	-0.131414562198
S	-0.220192453898	-5.844267119986	0.041377757652

C	1.429233254933	-6.057201883063	0.815039647254
S	-3.317866620983	-4.425182400641	0.110346519359
C	-4.257019816039	-3.617894322305	1.466643305819
O	-9.006213222762	-0.503770707769	-0.328189439790
H	5.373081032712	5.899606732089	1.199197620666
H	3.796954889623	6.389785641149	0.511225590656
H	3.860326467603	5.422543297698	2.010712853872
H	-0.342758456049	6.861771593962	1.605175096614
H	-0.871310320423	5.158117845820	1.500983999003
H	0.554751959711	5.606753684911	2.497859323761
H	-3.476561105261	5.622481076793	-1.618452370769
H	-1.906000248782	4.830240716164	-1.290384283789
H	-3.063080333623	4.108051214846	-2.459323944462
H	-5.201746651186	-4.164435166063	1.532573690505
H	-3.719741585380	-3.714290896763	2.412979228614
H	-4.448187024742	-2.571268072234	1.233304649696
H	1.550158642971	-7.140872266111	0.900806312352
H	2.220881916485	-5.629308881496	0.203173218604
H	1.444595783600	-5.614598507511	1.813661623119
H	6.218049757391	-5.004485759112	1.042051490433
H	6.386763486958	-3.238793042922	1.197815139562
H	4.973554348363	-4.074253963576	1.916665049172
H	7.595681365822	1.041689198963	-0.928789027828
H	5.975850202683	1.331239744801	-1.621690697692
H	6.228707693640	1.506445960513	0.131273524160
H	-4.697632145966	-1.105323359795	-1.477299118210
H	-7.098911266019	-1.704016362490	-1.562736561303
H	-8.001800999711	1.543258705016	1.103082078139
H	-5.618848027913	2.139325360618	1.194873767669
H	-9.548379623973	0.098110297331	0.205495717745

## On the role of metal d orbital in the Suzuki-Miyaura reaction: “free base” vs. Ni complex

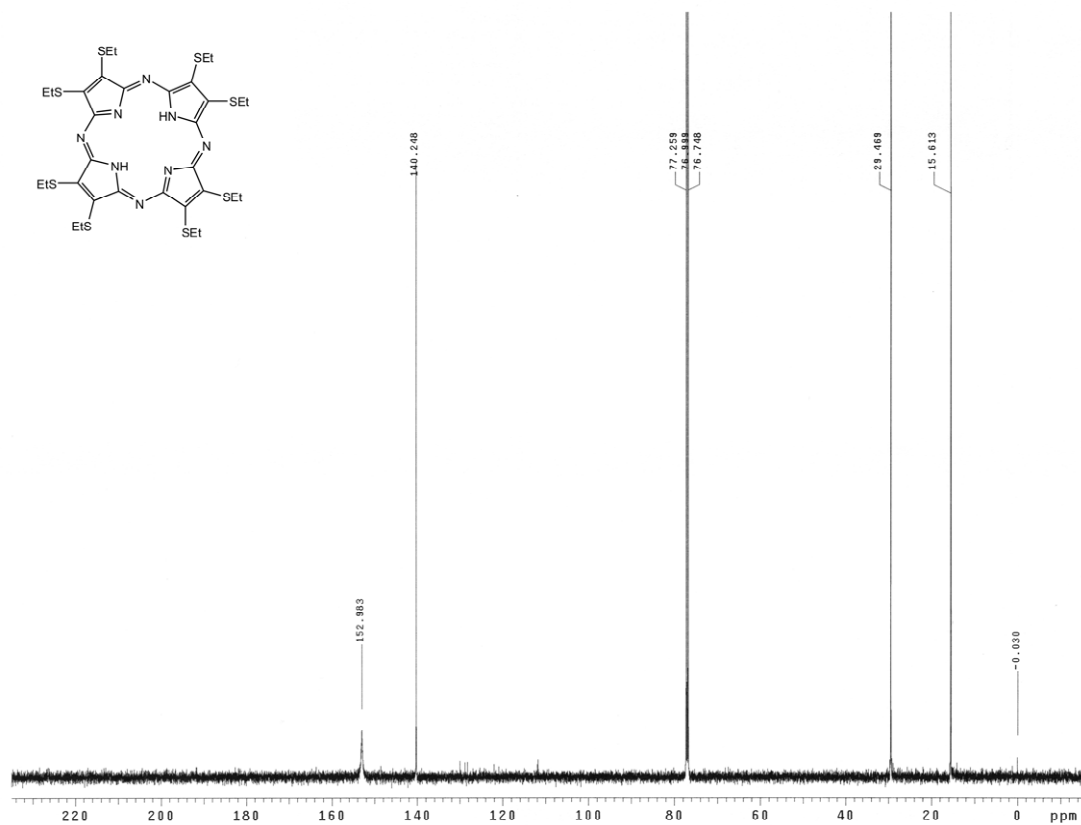
Assuming that in the Suzuki-Miyaura reaction the oxidative addition on the Pd involves both HOMO and/or LUMO of the porphyrazine and the carbon atom bearing the bromine, from the DFT calculations appears that the metal d orbitals give only a marginal contribution (see picture below) to those two. In fact, in the Ni-complex and “free base” the overall composition of both orbitals on the involved carbon atom are very similar.



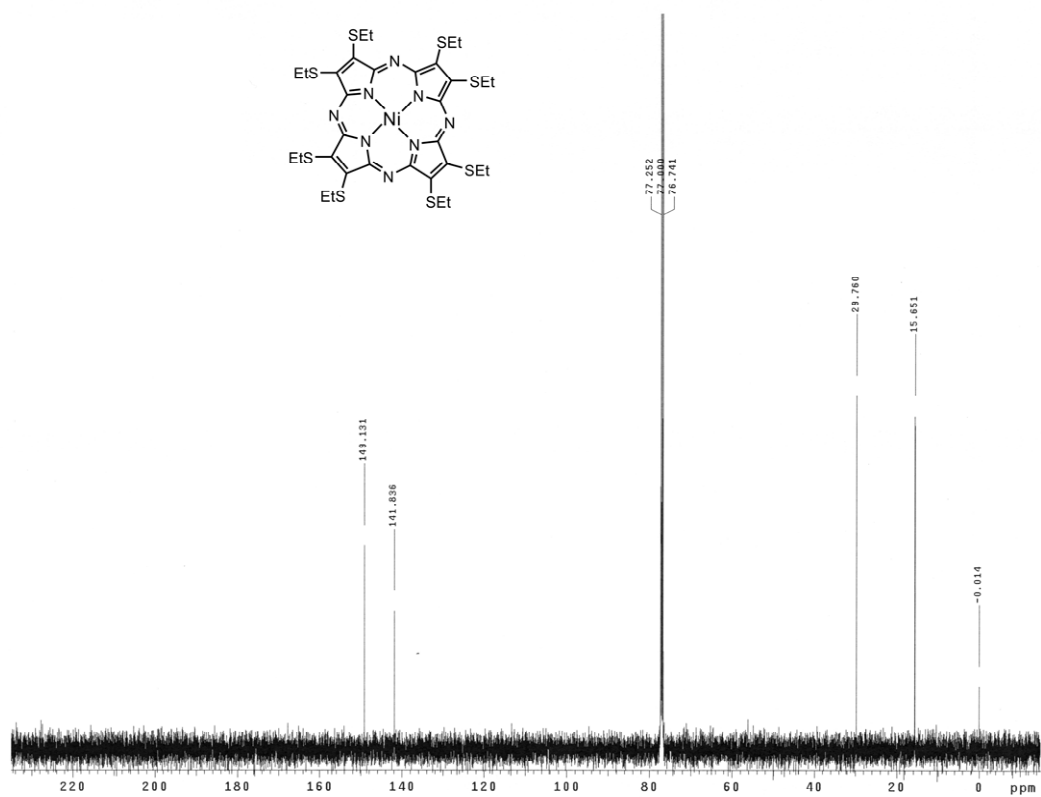
Furthermore, the Mulliken charges for the involved carbon atom are 0.018 and 0.010 |e| for “free base” and Ni complex, respectively. This is a marginal difference compared to the strongly negative charges (in the range of  $-0.130 \div -0.180|e|$ ) of all the remaining  $\beta$ -carbon atoms of the pyrrole moieties in both molecules.

Moreover, assuming  $^{13}\text{C}$  NMR chemical shifts as a good probe of the carbon atom net charge, the  $^{13}\text{C}$  NMR spectra of **1a** and of its metal complexes Ni-**1a** have been recorded to reveal the relative electron density on the  $\alpha$ - and  $\beta$ - tetrapyrrole carbon atoms. Such spectra (see Figures S29 and S30 in ESI) show that the  $\beta$ -Carbon atoms chemical shifts are only slightly affected by the presence of the metal, confirming the DFT findings.

All these observations coincide to suggest that the different behaviour of the “free bases” and the corresponding Ni-complexes cannot be ascribed to the role of the metal d orbitals. On the other hand, an effect due to the partial ionization of the two hydrogen atoms in the macrocycle cavity of the “free base” in the basic conditions of the cross-coupling reactions cannot be ruled out.



**Figure S29.** <sup>1</sup>H NMR spectrum of compound **1a**.



**Figure S30.** <sup>1</sup>H NMR spectrum of compound **Ni-1a**.