Azulene-Substituted Aromatic Amines. Synthesis and Amphoteric Redox Behavior of *N*,*N*-Di(6-azulenyl)-*p*-toluidine and *N*,*N*,*N*',*N*'-Tetra(6-azulenyl)-*p*-phenylenediamine and Their Derivatives.

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Supporting Information

Cyclic voltammograms

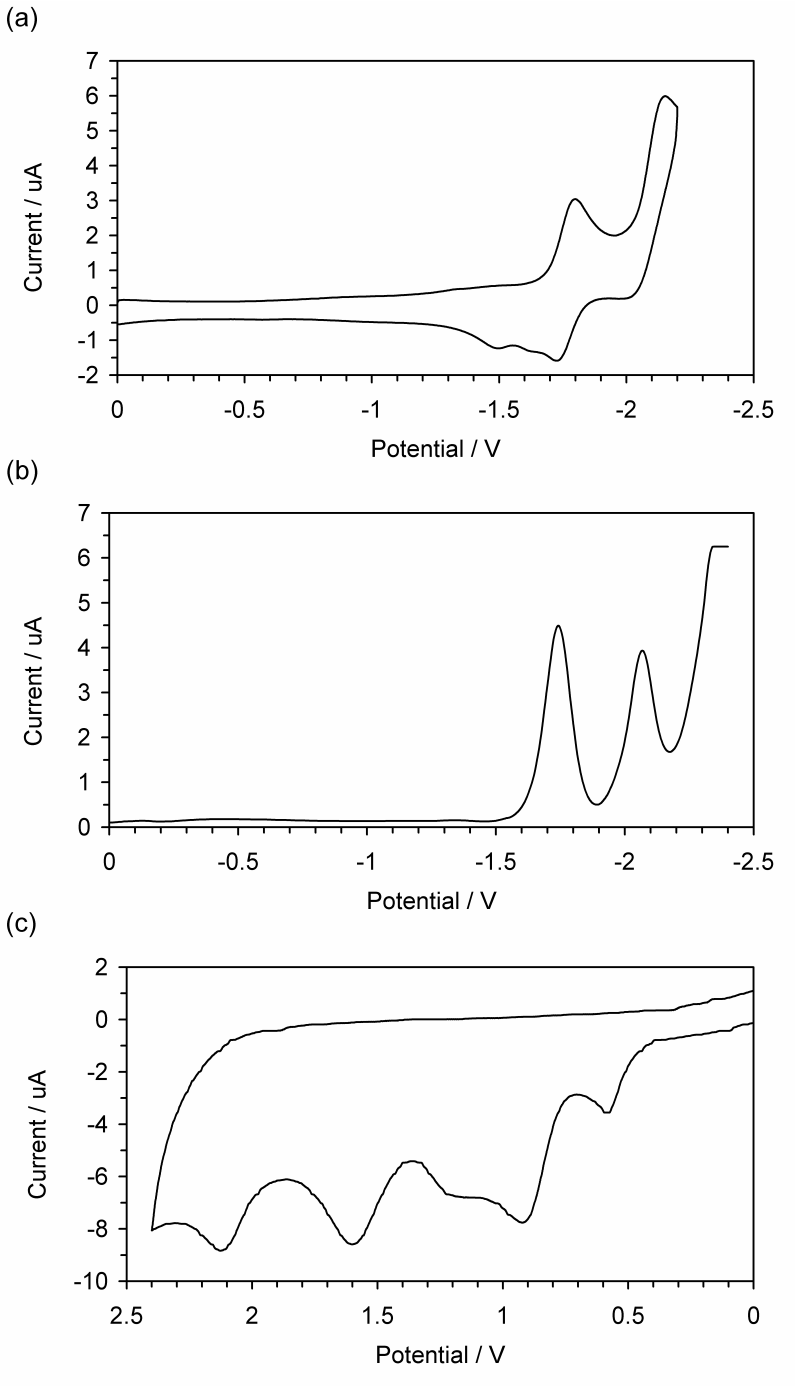

Figure S-1. (a) Reduction wave upon CV and (b) upon DPV, and (c) oxidation wave upon CV of **1a** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.

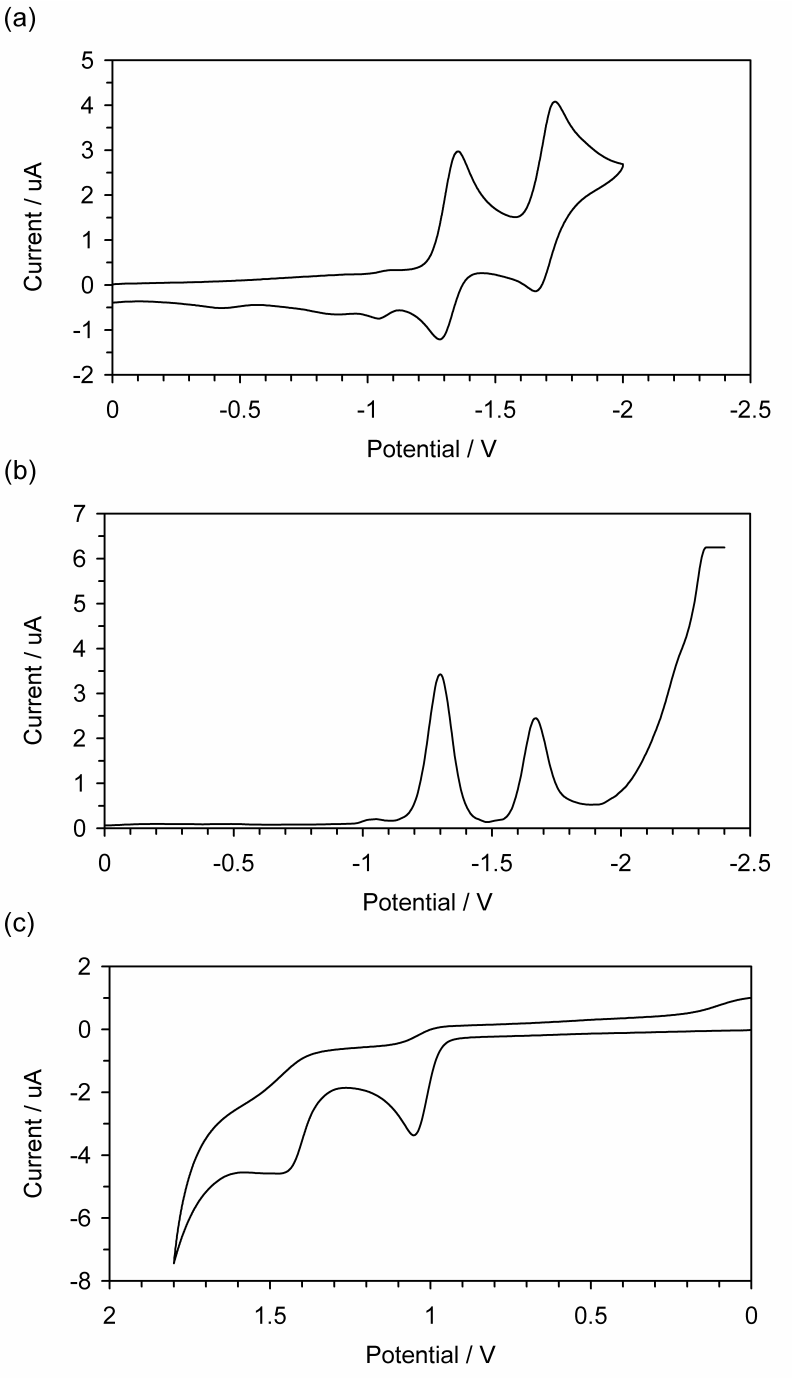

Figure S-2. (a) Reduction wave upon CV and (b) upon DPV, and (c) oxidation wave upon CV of **1b** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.

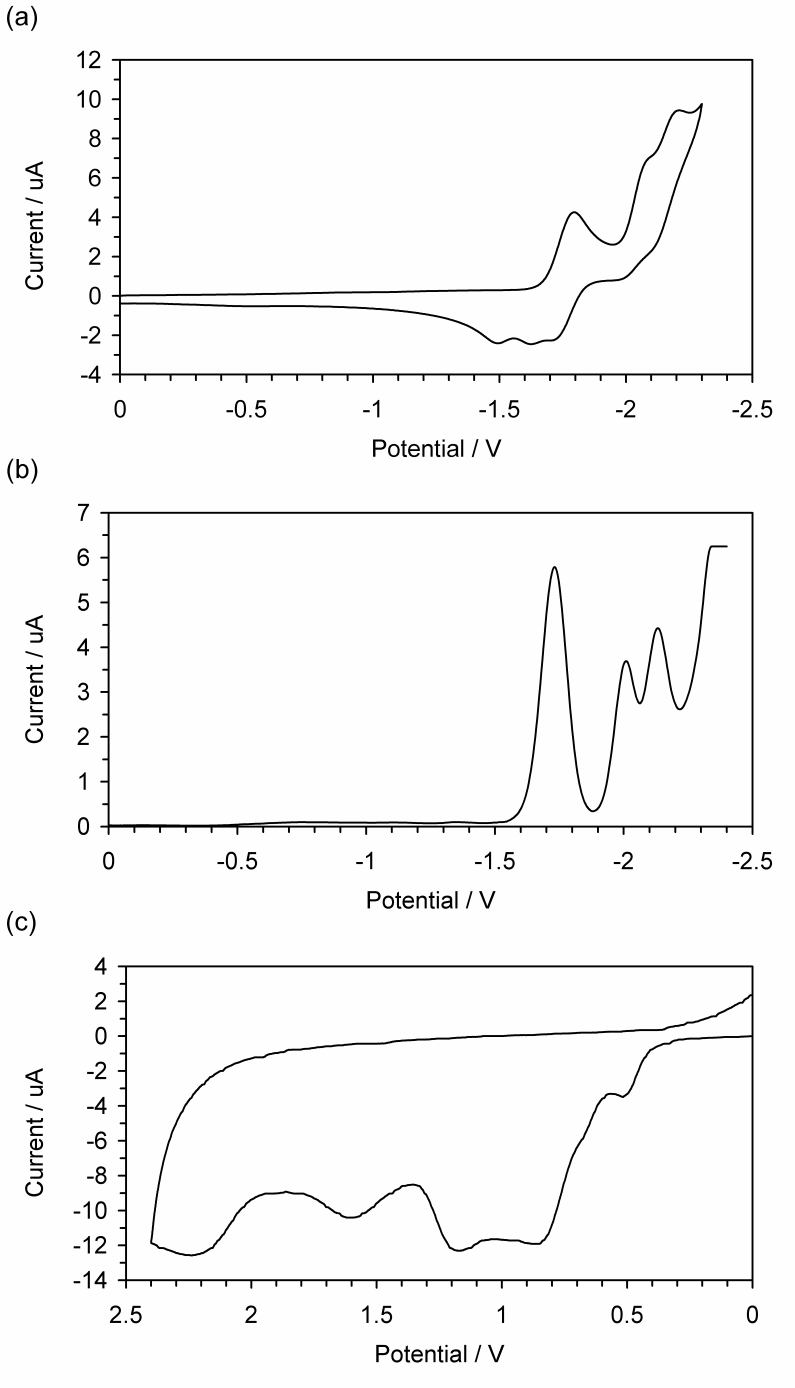

Figure S-3. (a) Reduction wave upon CV and (b) upon DPV, and (c) oxidation wave upon CV of **2a** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.

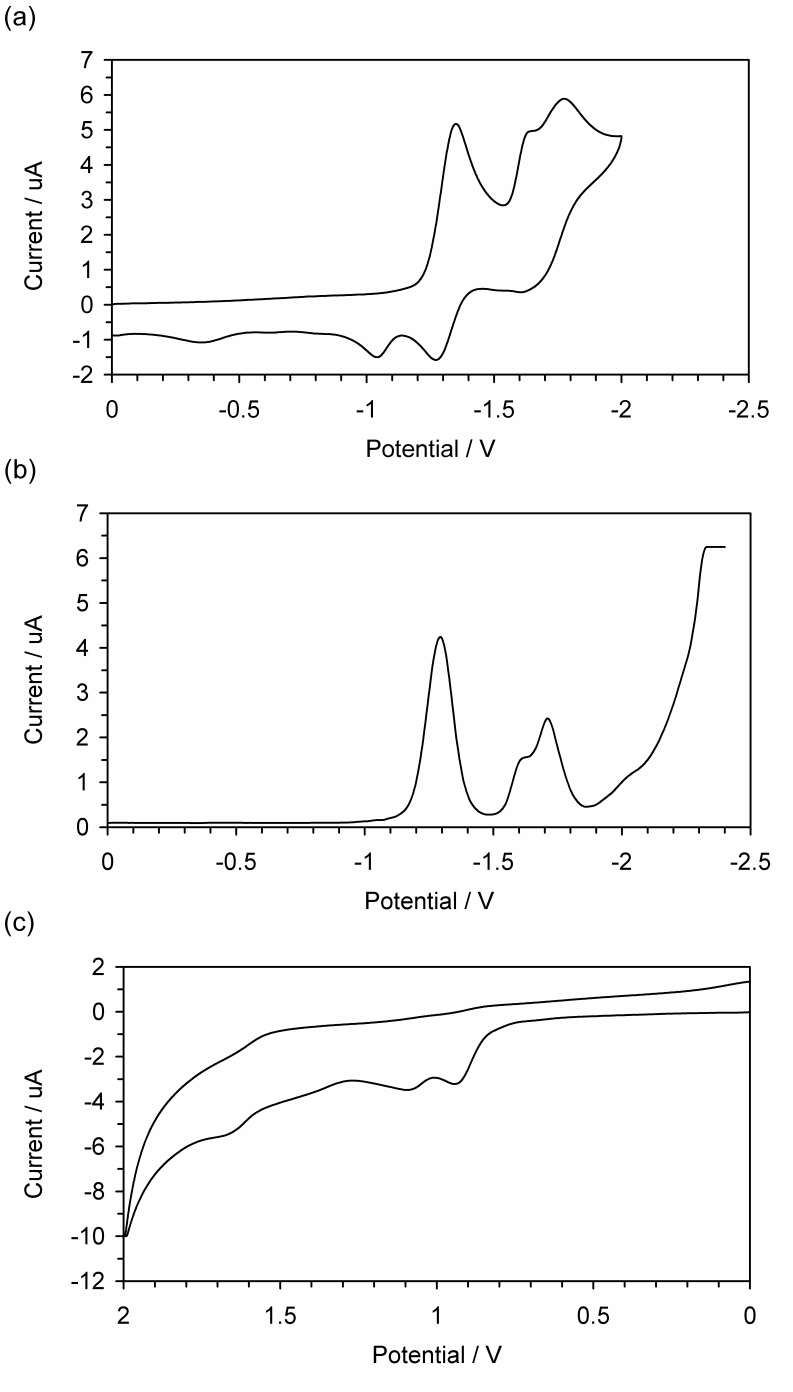

Figure S-4. (a) Reduction wave upon CV and (b) upon DPV, and (c) oxidation wave upon CV of **2b** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.

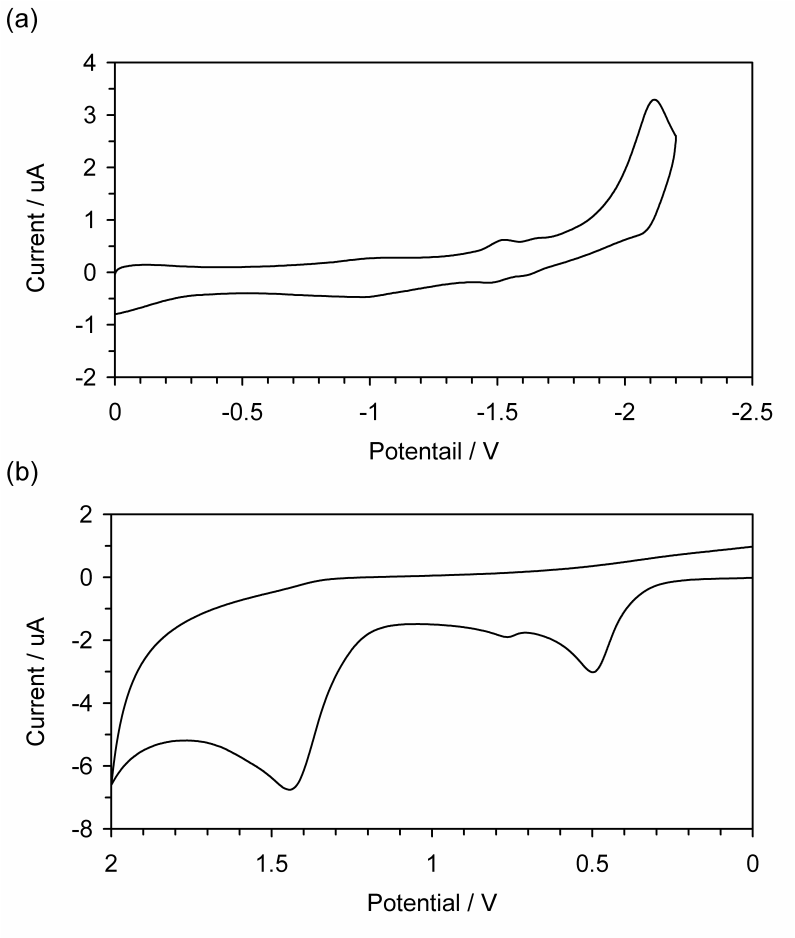

Figure S-5. (a) Reduction wave upon CV and (b) oxidation wave upon CV of **5a** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.

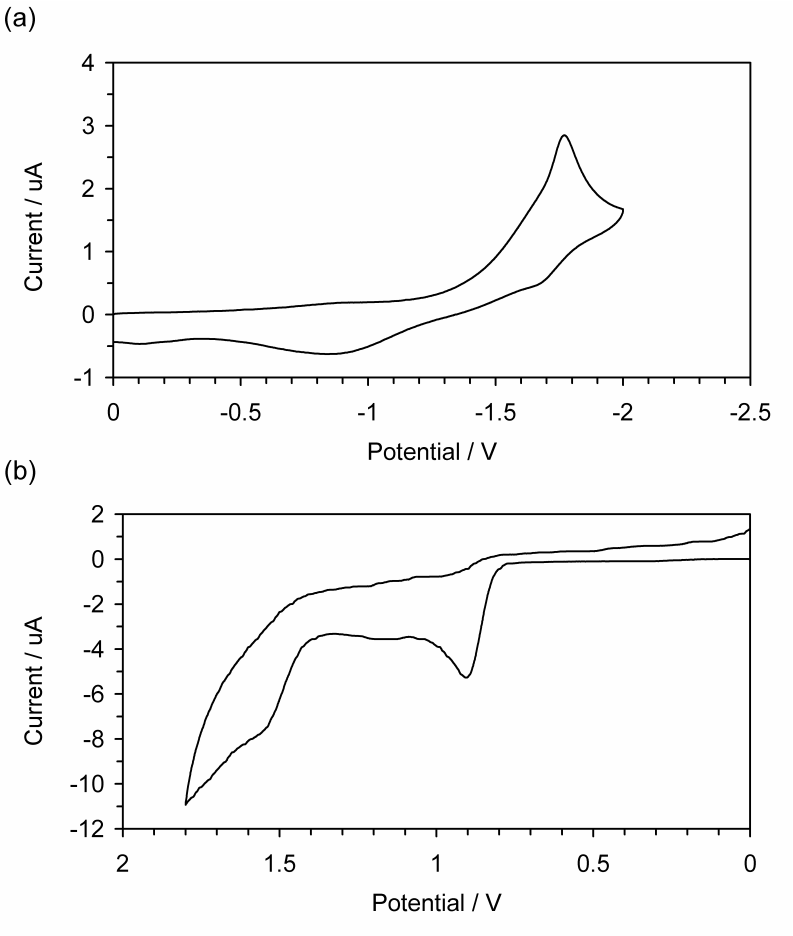

Figure S-6. (a) Reduction wave upon CV and (b) oxidation wave upon CV of **5b** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.

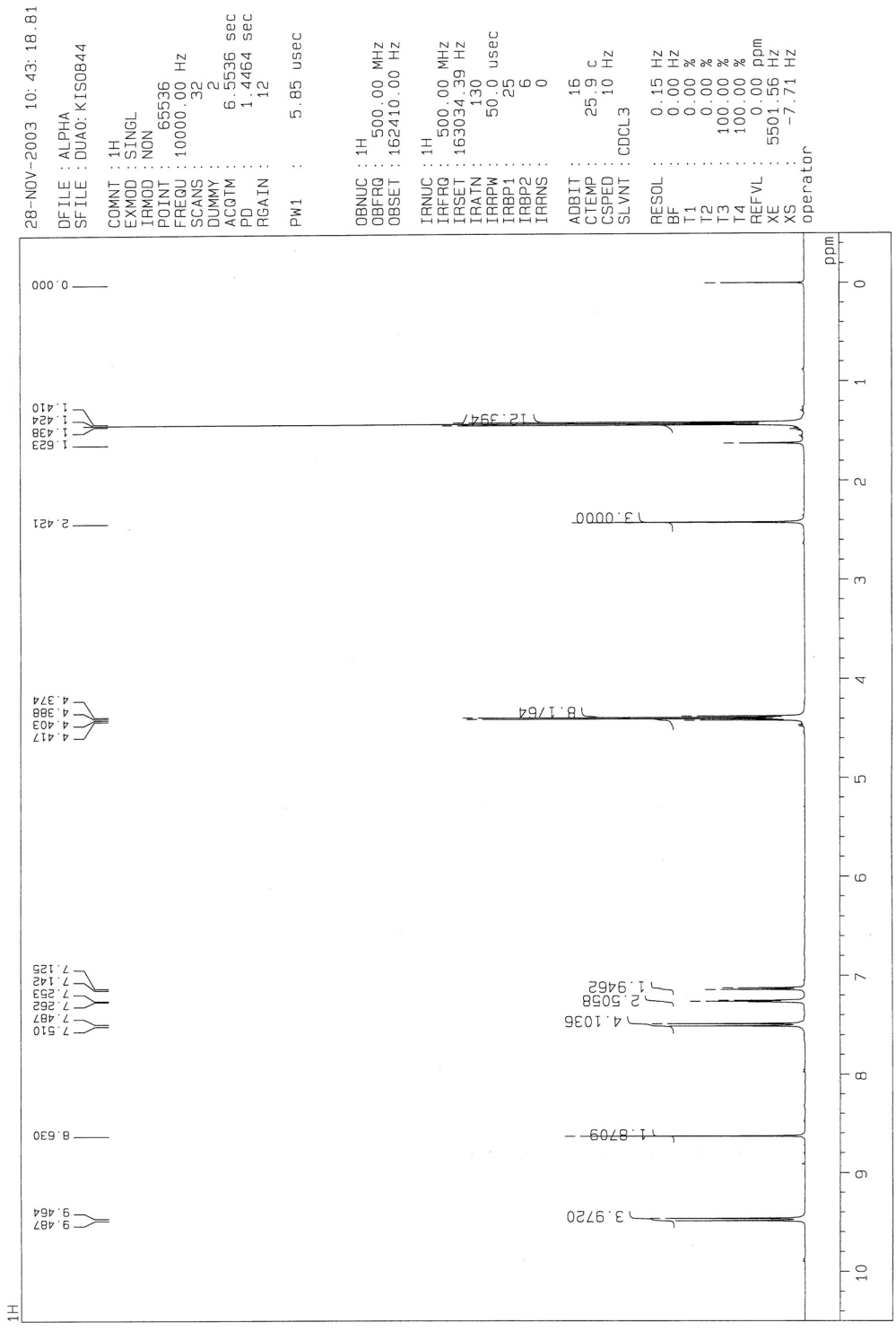

Figure S-7. ^{1}H NMR (500 MHz) spectrum of **1b** in $CDCl_3$ at room temperature.

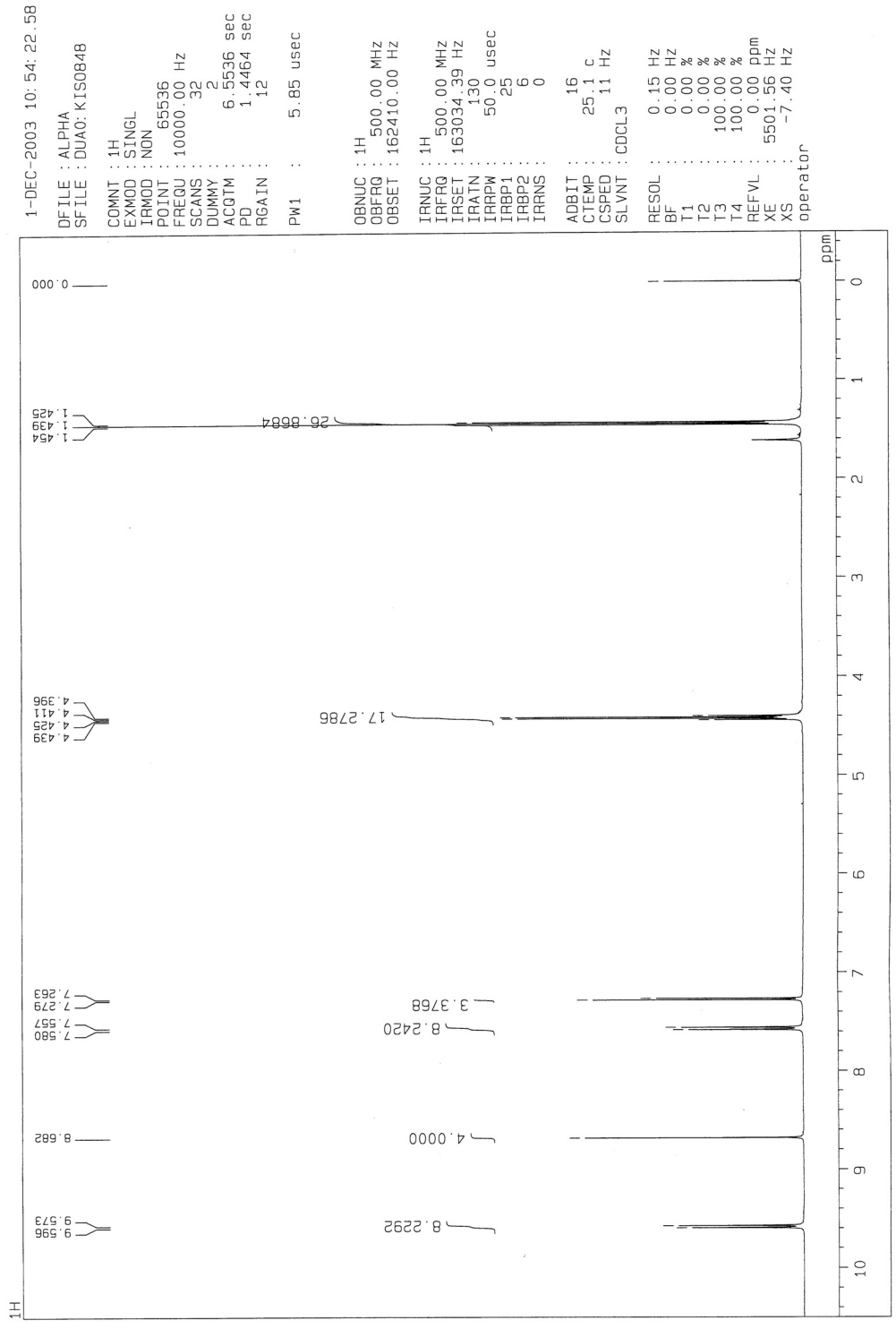

Figure S-8. ^{1}H NMR (500 MHz) spectrum of **2b** in $CDCl_3$ at room temperature.

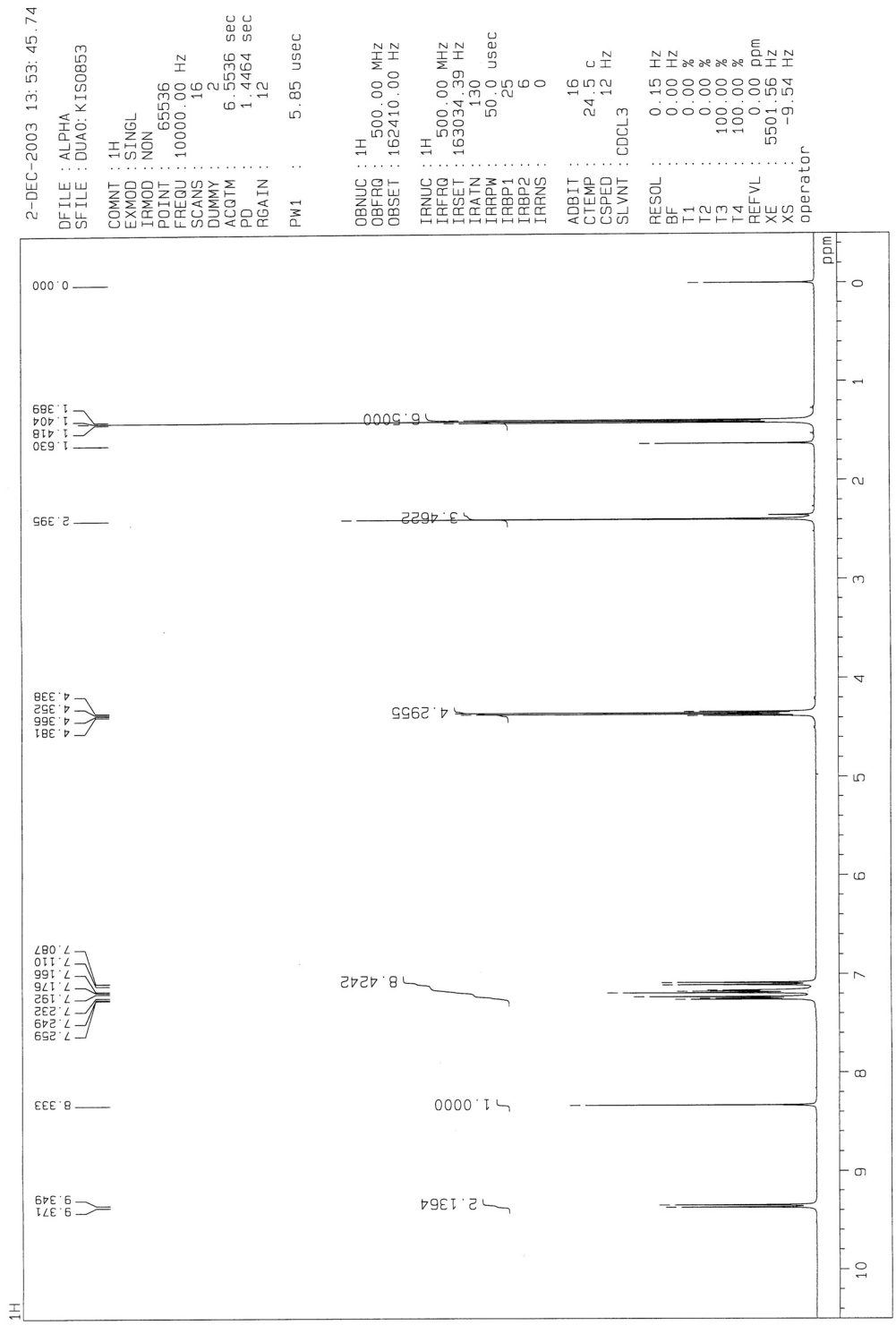

Figure S-9. ^{1}H NMR (500 MHz) spectrum of **5b** in $CDCl_3$ at room temperature.

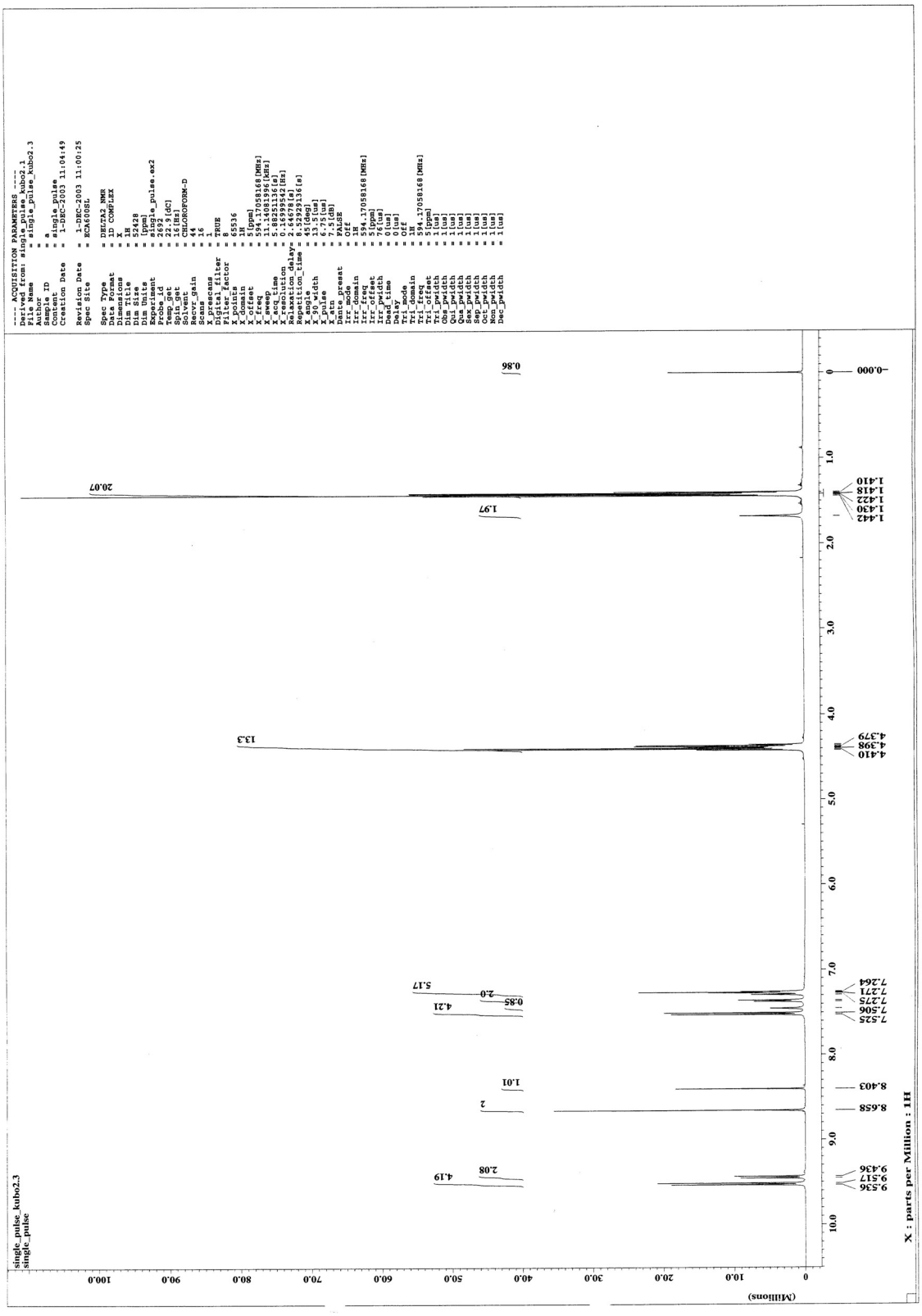

Figure S-10. ^{1}H NMR (600 MHz) spectrum of **7** in $CDCl_3$ at room temperature.

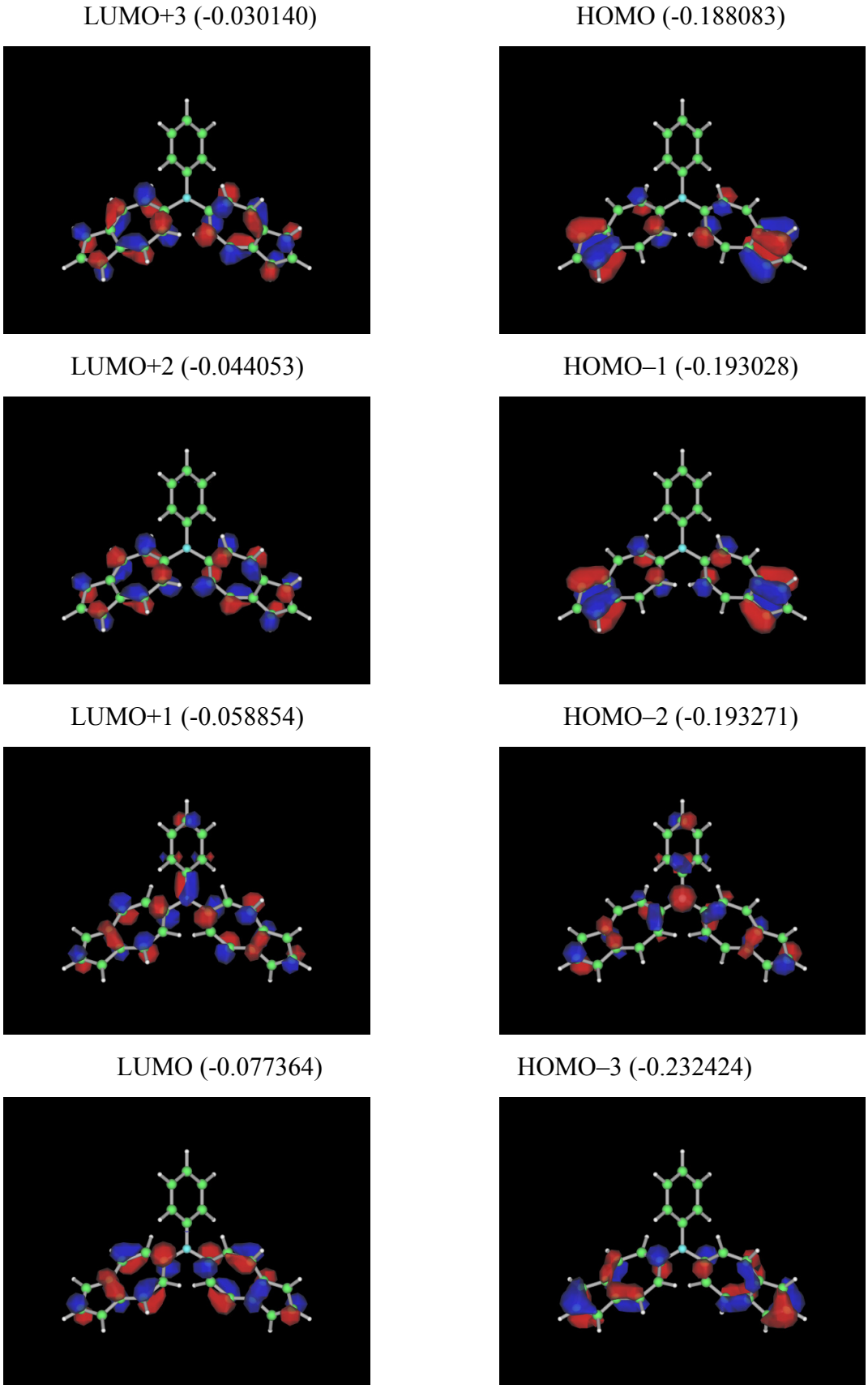

Figure S-11. Optimized structure of **1a** without 4'-methyl substituent with HOMO and LUMO orbitals calculated by B3LYP/6-31G** density functional theory.

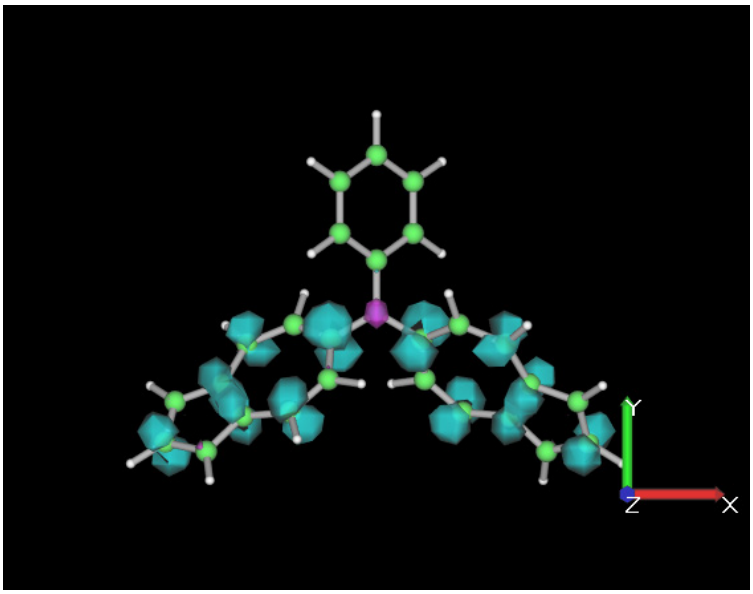

Figure S-12. Optimized structure of **1a**$^{\bullet-}$ without 4'-methyl substituent with spin density distribution calculated by B3LYP/6-31G** density functional theory. Blue: positive spin density. Red: negative spin density.

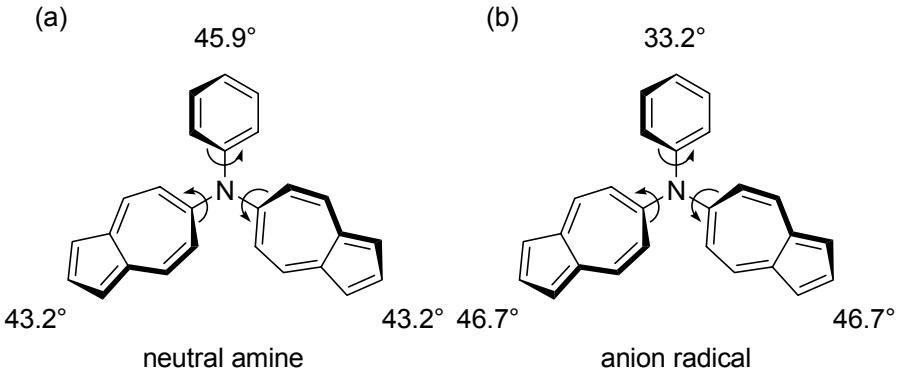

Figure S-13. Calculated dihedral angles of each ring from the central planer nitrogen atom: (a) those of neutral amine **1a** and (b) those of anion radical **1a**$^{\bullet-}$ without 4'-methyl substituent.

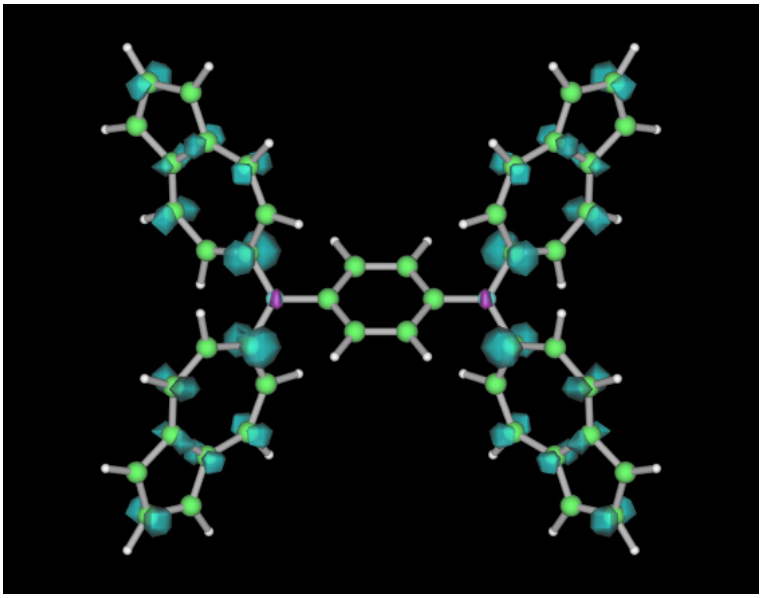

Figure S-14. Optimized structure of **2a**$^{\bullet-}$ with spin density distribution calculated by B3LYP/6-31G** density functional theory. Blue: positive spin density. Red: negative spin density.

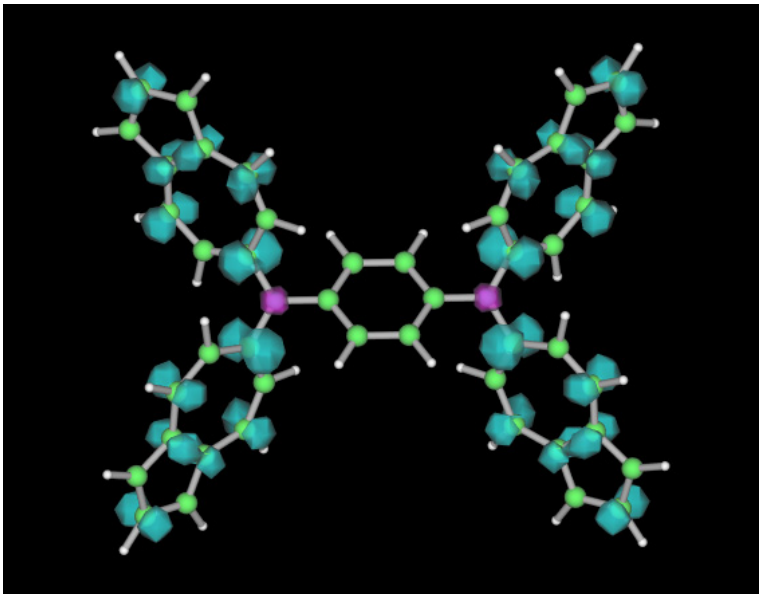

Figure S-15. Optimized structure of **2a**$^{2\bullet2-}$ with spin density distribution calculated by B3LYP/6-31G** density functional theory. Blue: positive spin density. Red: negative spin density.

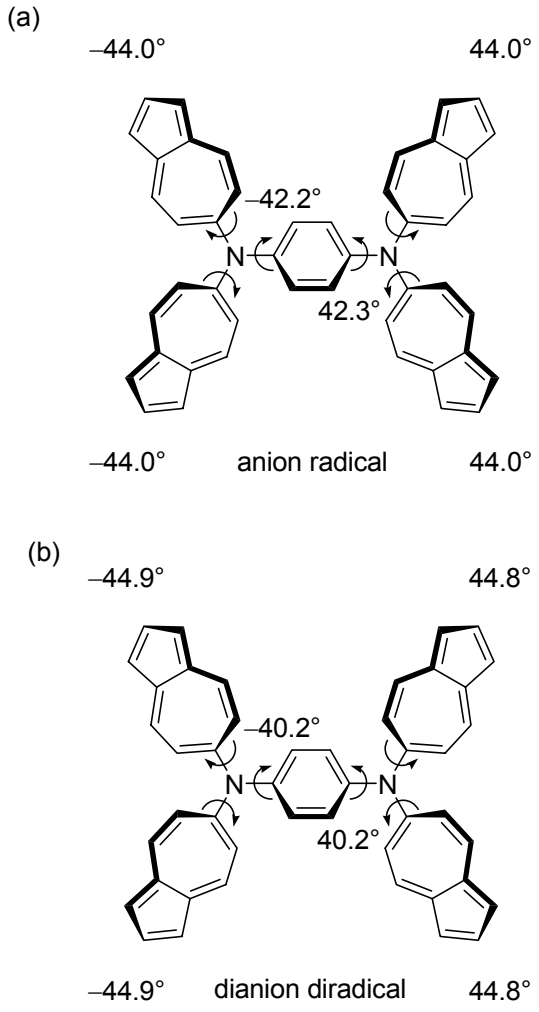

Figure S-16. Calculated dihedral angles of each ring from the central planer nitrogen atoms: (a) those of anion radical $\mathbf{2a}^{\bullet-}$ and (b) those of dianion diradical $\mathbf{2a}^{2\bullet 2-}$.

Cartesian coordinates and computed total energies

Compound 1a without 4'-methyl group

Total Energy -1.056907731724263E+03 a.u.

			Angstrom
C	4.211090	-2.176605	0.446304
C	2.372513	-3.119339	-1.098114
C	1.315079	-2.241089	-0.878632
C	1.238876	-1.130692	-0.012512
C	2.249252	-0.634033	0.835480
C	3.550766	-1.092773	1.021805
N	0.000214	-0.426270	-0.000443
C	3.653412	-3.136566	-0.548218
C	0.000824	3.805344	-0.000320
C	4.673538	-4.059738	-0.834747
C	5.806396	-3.718735	-0.076477
C	5.533234	-2.580811	0.700714
C	0.837402	3.101349	-0.868896
C	0.834412	1.707977	-0.878662
C	0.000366	1.000336	-0.000412
C	-0.833374	1.708191	0.877914
C	-0.835938	3.101547	0.868240
C	-2.372604	-3.118652	1.097824
C	-4.210800	-2.176315	-0.447266
C	-5.532928	-2.580490	-0.701752
C	-5.806351	-3.718094	0.075821
C	-4.673676	-4.058914	0.834442
C	-3.653412	-3.135941	0.547729
C	-3.550278	-1.092728	-1.023041
C	-2.248779	-0.634033	-0.836624
C	-1.238586	-1.130493	0.011734
C	-1.315033	-2.240570	0.878204
H	2.172562	-3.901962	-1.829163
H	0.420929	-2.427338	-1.464554
H	1.963745	0.223633	1.435700
H	4.135452	-0.526993	1.746384
H	0.001007	4.890869	-0.000275

H	4.589264	-4.890854	-1.523987
H	6.749359	-4.253616	-0.089188
H	6.217026	-2.089706	1.382019
H	1.487762	3.637665	-1.553604
H	1.474716	1.161041	-1.562714
H	-1.473816	1.161407	1.561966
H	-1.486100	3.638031	1.553009
H	-2.172836	-3.901031	1.829178
H	-6.216553	-2.089584	-1.383362
H	-6.749374	-4.252869	0.088547
H	-4.589584	-4.889771	1.524002
H	-4.134766	-0.527176	-1.747940
H	-1.963074	0.223343	-1.437149
H	-0.420990	-2.426727	1.464325

Anion radical 1a$^{\bullet-}$ without 4'-methyl group

Total Energy -1.056942661762114E+03 a.u.

Angstrom

C	4.148270	-2.333939	0.467087
C	2.334808	-3.088684	-1.206726
C	1.304611	-2.199249	-0.965973
C	1.229523	-1.126846	-0.038528
C	2.233276	-0.729904	0.889008
C	3.498093	-1.247253	1.096527
N	0.000000	-0.405426	0.000000
C	3.608551	-3.190491	-0.594254
C	0.000031	3.828888	0.000000
C	4.604141	-4.135452	-0.904236
C	5.724609	-3.897751	-0.082260
C	5.447632	-2.800705	0.753235
C	0.990463	3.118500	-0.682846
C	0.991257	1.726273	-0.693085
C	0.000000	1.005768	0.000000
C	-0.991241	1.726288	0.693085
C	-0.990417	3.118515	0.682846
C	-2.334824	-3.088684	1.206726
C	-4.148285	-2.333908	-0.467087

C	-5.447647	-2.800690	-0.753235
C	-5.724625	-3.897736	0.082260
C	-4.604156	-4.135437	0.904236
C	-3.608566	-3.190475	0.594254
C	-3.498108	-1.247238	-1.096527
C	-2.233292	-0.729889	-0.888992
C	-1.229538	-1.126846	0.038528
C	-1.304626	-2.199249	0.965973
H	2.146606	-3.810913	-2.001419
H	0.415894	-2.321808	-1.579254
H	1.951416	0.101868	1.529724
H	4.078812	-0.752350	1.876007
H	0.000031	4.915298	0.000000
H	4.510727	-4.915283	-1.652863
H	6.648453	-4.467377	-0.093079
H	6.112320	-2.374039	1.497360
H	1.766113	3.652405	-1.226440
H	1.755722	1.179794	-1.233871
H	-1.755707	1.179825	1.233871
H	-1.766052	3.652435	1.226440
H	-2.146622	-3.810898	2.001419
H	-6.112335	-2.374008	-1.497360
H	-6.648468	-4.467346	0.093079
H	-4.510757	-4.915268	1.652847
H	-4.078812	-0.752335	-1.876007
H	-1.951431	0.101883	-1.529724
H	-0.415894	-2.321808	1.579254

Anion radical 2a$^{\bullet-}$

Total Energy -1.881605835655465E+03 a.u.

Angstrom

C	4.653885	4.193024	0.411758
C	5.543579	2.333710	-1.137436
C	4.655518	1.294388	-0.908890
C	3.541489	1.233963	-0.036102
C	3.067368	2.263428	0.813782
C	3.549347	3.550873	0.995377

N	2.834137	0.000015	0.000000
C	5.589569	3.622925	-0.578705
C	-1.411926	0.000015	0.000000
C	6.534195	4.623428	-0.870407
C	6.224197	5.766678	-0.110474
C	5.082855	5.508957	0.668915
C	-4.653992	4.193085	0.410690
C	-0.694794	0.869278	-0.837570
C	0.694824	0.869278	-0.837570
C	1.411942	0.000015	0.000000
C	0.694809	-0.869263	0.837555
C	-0.694794	-0.869263	0.837555
C	5.543564	-2.333725	1.137451
C	4.653854	-4.193008	-0.411758
C	5.082809	-5.508957	-0.668915
C	6.224136	-5.766693	0.110489
C	6.534149	-4.623444	0.870422
C	5.589523	-3.622925	0.578705
C	3.549332	-3.550858	-0.995392
C	3.067368	-2.263397	-0.813797
C	3.541489	-1.233948	0.036102
C	4.655502	-1.294388	0.908890
C	-5.543503	2.333420	-1.138184
C	-4.655426	1.294159	-0.909317
C	-3.541473	1.233963	-0.036438
C	-3.067459	2.263611	0.813278
C	-3.549484	3.551086	0.994568
N	-2.834106	0.000015	0.000000
C	-5.589554	3.622742	-0.579727
C	-6.534180	4.623169	-0.871735
C	-6.224289	5.766586	-0.112015
C	-5.083023	5.509064	0.667526
C	-5.543533	-2.333344	1.138184
C	-4.654053	-4.193024	-0.410690
C	-5.083100	-5.509003	-0.667526
C	-6.224380	-5.766510	0.112015
C	-6.534256	-4.623077	0.871735
C	-5.589615	-3.622665	0.579727

C	-3.549530	-3.551041	-0.994553
C	-3.067490	-2.263580	-0.813278
C	-3.541489	-1.233917	0.036438
C	-4.655441	-1.294098	0.909317
H	6.314667	2.124512	-1.878754
H	4.825485	0.391525	-1.487549
H	2.205414	1.994186	1.416748
H	2.996765	4.150513	1.718597
H	7.359512	4.518295	-1.565353
H	6.777618	6.699570	-0.124847
H	4.602859	6.198395	1.354019
H	-1.237717	1.537506	-1.497681
H	1.237747	1.537521	-1.497681
H	1.237747	-1.537506	1.497665
H	-1.237717	-1.537491	1.497681
H	6.314636	-2.124527	1.878769
H	4.602814	-6.198395	-1.354019
H	6.777557	-6.699585	0.124863
H	7.359451	-4.518311	1.565384
H	2.996750	-4.150497	-1.718613
H	2.205414	-1.994156	-1.416779
H	4.825470	-0.391525	1.487549
H	-6.314514	2.124039	-1.879517
H	-4.825317	0.391159	-1.487793
H	-2.205551	1.994522	1.416397
H	-2.996994	4.150894	1.717697
H	-7.359436	4.517853	-1.566742
H	-6.777740	6.699463	-0.126648
H	-4.603104	6.198654	1.352524
H	-6.314545	-2.123947	1.879517
H	-4.603195	-6.198608	-1.352509
H	-6.777832	-6.699371	0.126648
H	-7.359512	-4.517746	1.566742
H	-2.997040	-4.150864	-1.717682
H	-2.205566	-1.994507	-1.416382
H	-4.825317	-0.391098	1.487793

Dianion diradical $2a^{2\bullet 2-}$

Total Energy -1.881580693837958E+03 a.u.

			Angstrom
C	4.747100	4.166351	0.397568
C	5.582596	2.286026	-1.154404
C	4.675430	1.270386	-0.927856
C	3.550095	1.228470	-0.057587
C	3.096039	2.280579	0.788849
C	3.609161	3.549286	0.973557
N	2.838486	0.000015	0.000000
C	5.664093	3.580780	-0.581131
C	-1.416794	0.000015	0.000000
C	6.642059	4.554337	-0.863586
C	6.365250	5.706329	-0.099915
C	5.209579	5.470840	0.668167
C	-4.747116	4.166397	0.396851
C	-0.695145	0.883240	-0.820358
C	0.695206	0.883240	-0.820358
C	1.416855	0.000015	0.000000
C	0.695206	-0.883224	0.820343
C	-0.695145	-0.883224	0.820343
C	5.582581	-2.286026	1.154419
C	4.747086	-4.166351	-0.397568
C	5.209549	-5.470840	-0.668167
C	6.365219	-5.706345	0.099930
C	6.642029	-4.554352	0.863602
C	5.664078	-3.580780	0.581131
C	3.609161	-3.549271	-0.973572
C	3.096039	-2.280563	-0.788864
C	3.550095	-1.228470	0.057571
C	4.675430	-1.270370	0.927856
C	-5.582489	2.285828	-1.154892
C	-4.675339	1.270233	-0.928131
C	-3.550049	1.228470	-0.057800
C	-3.096054	2.280700	0.788528
C	-3.609207	3.549423	0.973022
N	-2.838425	0.000015	0.000000
C	-5.664047	3.580673	-0.581802

C	-6.641998	4.554184	-0.864471
C	-6.365250	5.706284	-0.100952
C	-5.209610	5.470917	0.667236
C	-5.582535	-2.285751	1.154892
C	-4.747192	-4.166336	-0.396851
C	-5.209717	-5.470856	-0.667236
C	-6.365356	-5.706192	0.100952
C	-6.642075	-4.554077	0.864471
C	-5.664108	-3.580597	0.581802
C	-3.609268	-3.549393	-0.973007
C	-3.096100	-2.280670	-0.788513
C	-3.550064	-1.228439	0.057800
C	-4.675354	-1.270172	0.928146
H	6.345917	2.064835	-1.901428
H	4.827866	0.360687	-1.502121
H	2.219910	2.034821	1.382919
H	3.064926	4.167068	1.688950
H	7.468018	4.424362	-1.555832
H	6.945709	6.624054	-0.105377
H	4.739777	6.167297	1.355408
H	-1.238342	1.564667	-1.466644
H	1.238403	1.564667	-1.466629
H	1.238403	-1.564651	1.466629
H	-1.238342	-1.564651	1.466629
H	6.345886	-2.064835	1.901443
H	4.739761	-6.167282	-1.355408
H	6.945679	-6.624054	0.105392
H	7.467987	-4.424377	1.555847
H	3.064926	-4.167038	-1.688965
H	2.219910	-2.034790	-1.382935
H	4.827850	-0.360687	1.502121
H	-6.345764	2.064514	-1.901932
H	-4.827713	0.360443	-1.502274
H	-2.219955	2.035034	1.382675
H	-3.065018	4.167313	1.688339
H	-7.467911	4.424088	-1.556747
H	-6.945724	6.623993	-0.106583
H	-4.739868	6.167480	1.354400

H	-6.345795	-2.064423	1.901932
H	-4.739990	-6.167419	-1.354400
H	-6.945847	-6.623886	0.106583
H	-7.468002	-4.423981	1.556747
H	-3.065094	-4.167282	-1.688339
H	-2.219986	-2.035019	-1.382660
H	-4.827713	-0.360382	1.502274