Supporting Information

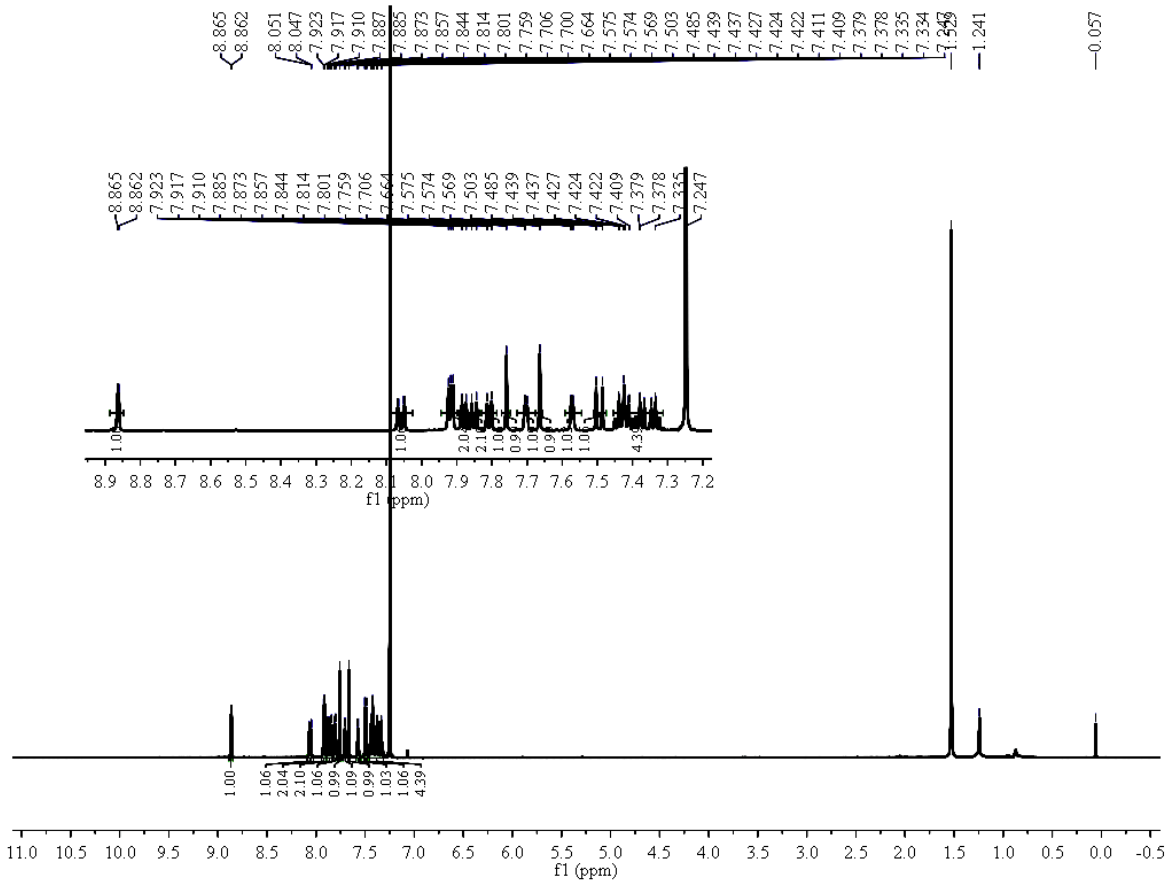
Conjugated Oligomers Incorporating Azulene Building Blocks – Seven- vs Five-Membered Ring Connectivity

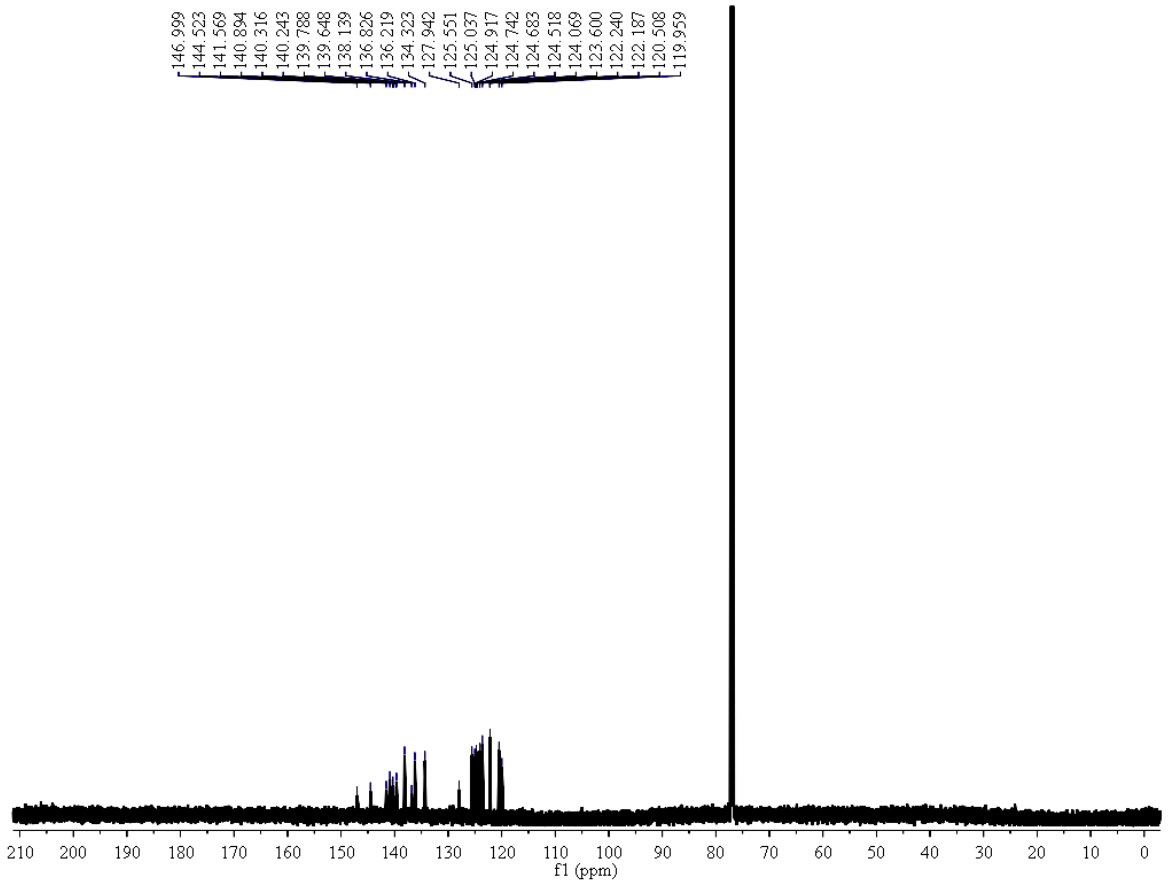
Elizabeth Amir, Masahito Murai, Roey J. Amir, John S. Cowart Jr., Michael L. Chabinyc, and Craig J. Hawker

General. Chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. All materials were characterized by nuclear magnetic resonance (NMR) spectroscopy using Varian 400, 500 and 600 MHz spectrometers as indicated. Chemical shifts are reported in ppm and referenced to the solvent (proton and carbon). Microwave-assisted reactions were conducted on a Biotage Microwave reactor at a frequency of 2.5 GHz. VG70 Magnetic Sector and Waters GCT Premier TOF instruments were used for low and high resolution mass analysis by electron ionization (EI). Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer was used for high-resolution mass analysis using electrospray ionization (ESI). UV-Vis spectra were recorded on an Agilent 8453 spectrophotometer using quartz cuvettes and dichloromethane as a solvent. Geometry optimizations were carried out using the Gaussian 09 quantum chemistry program package at the B3LYP functional. All compounds were fully optimized with the 6-31G* basis set. Plot of molecular orbital were constructed using the MOLEKEL program 4.1.

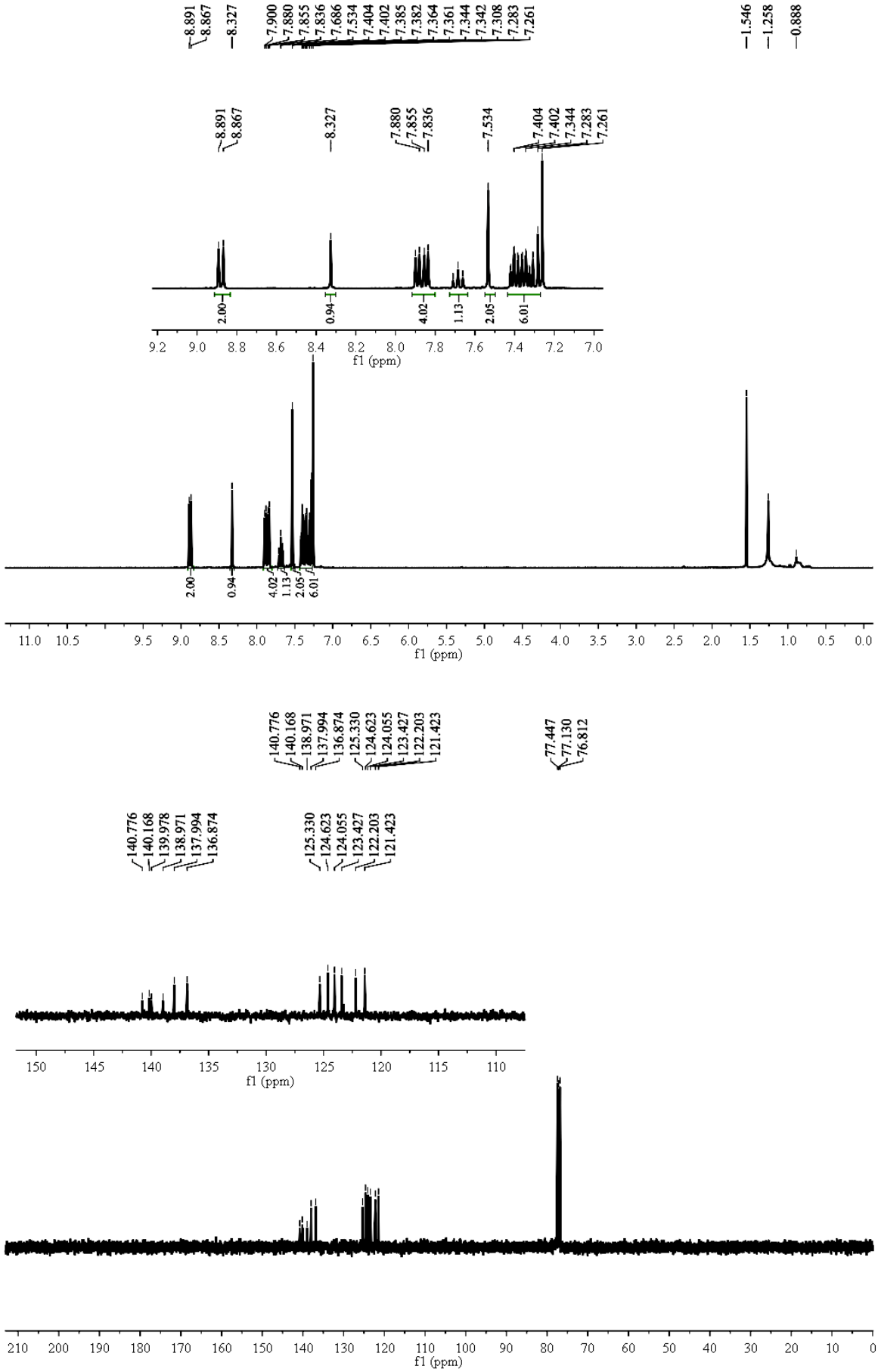
^{1}H-NMR and ^{13}C-NMR spectra.

Oligoazulene 1

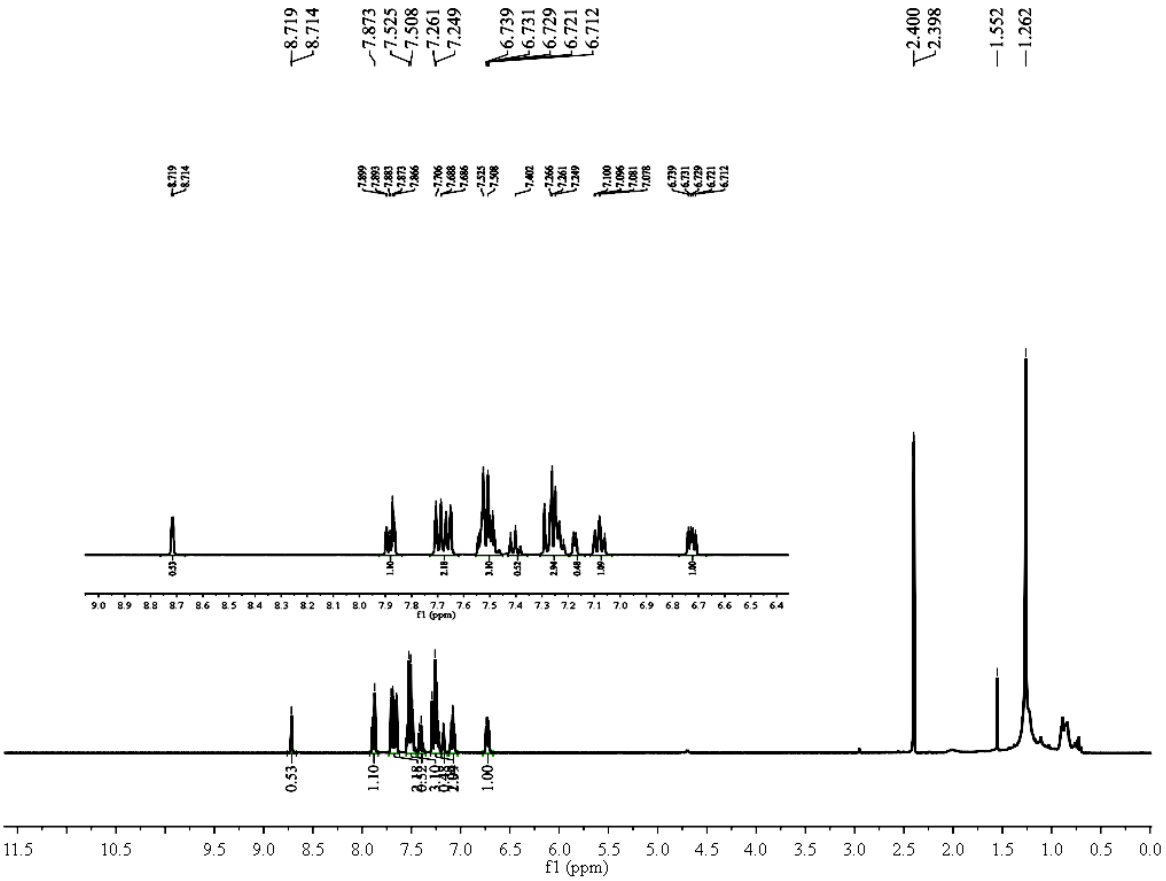


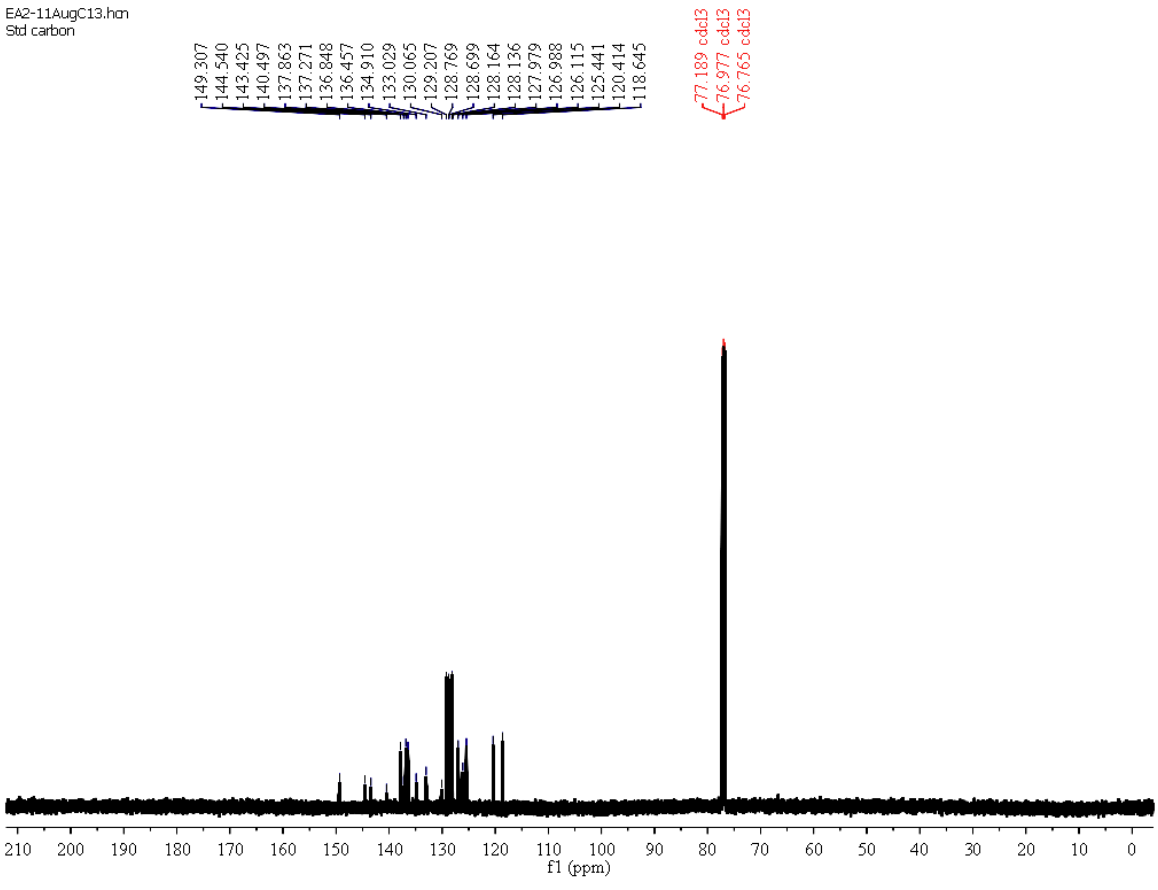


Oligoazulene 2

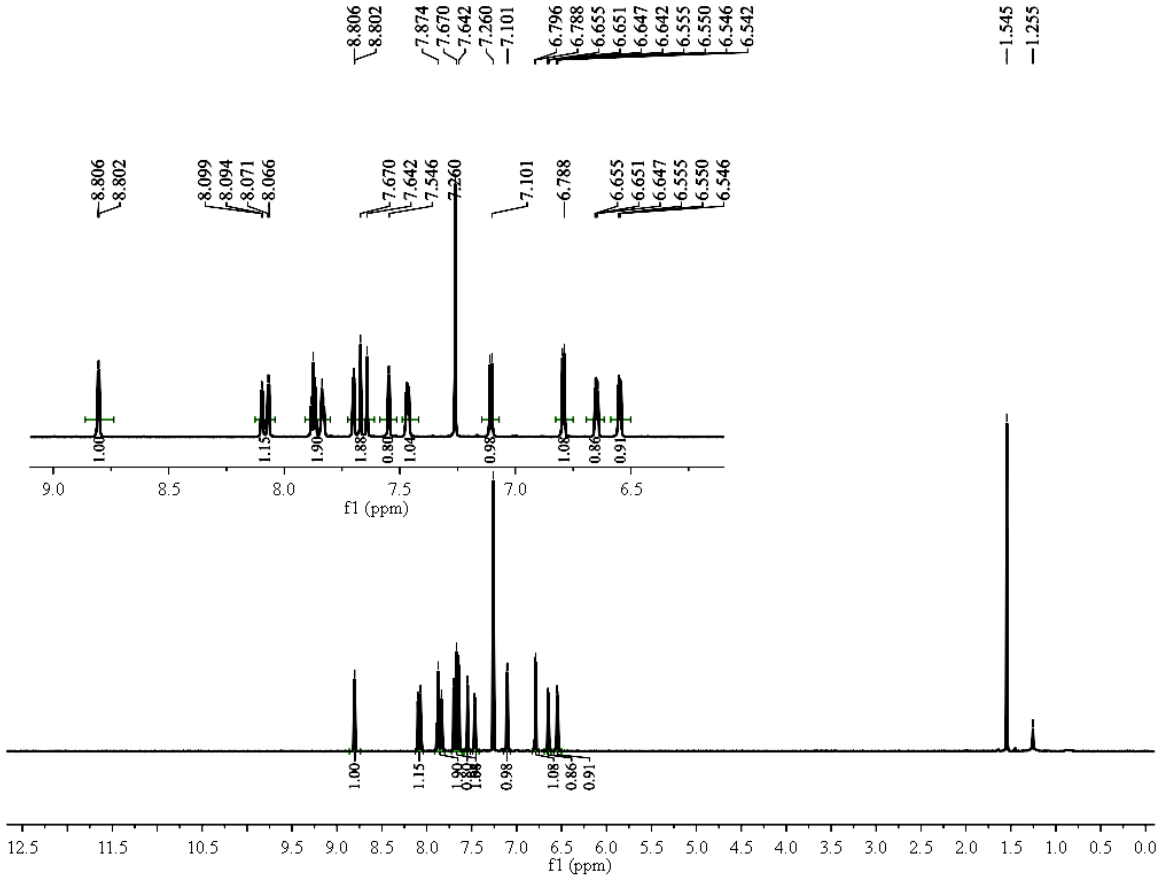


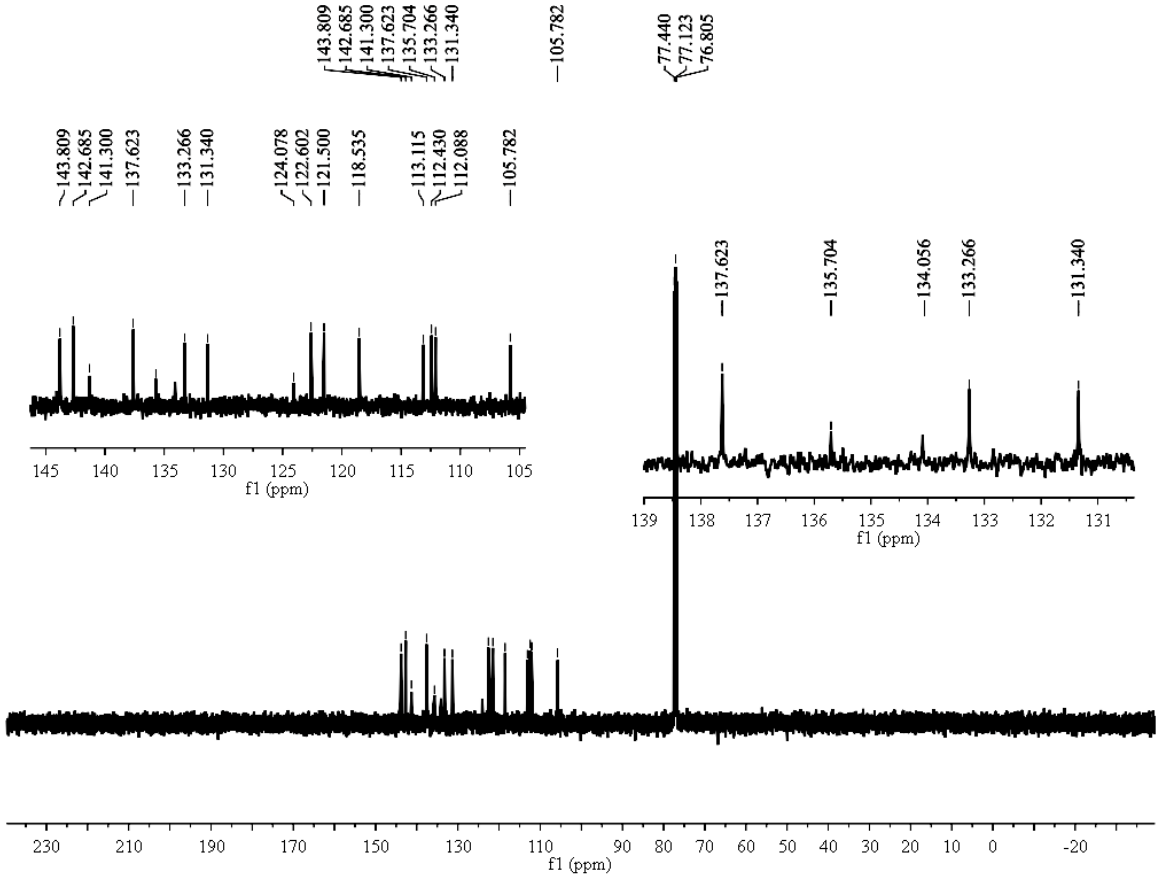
Oligoazulene 11



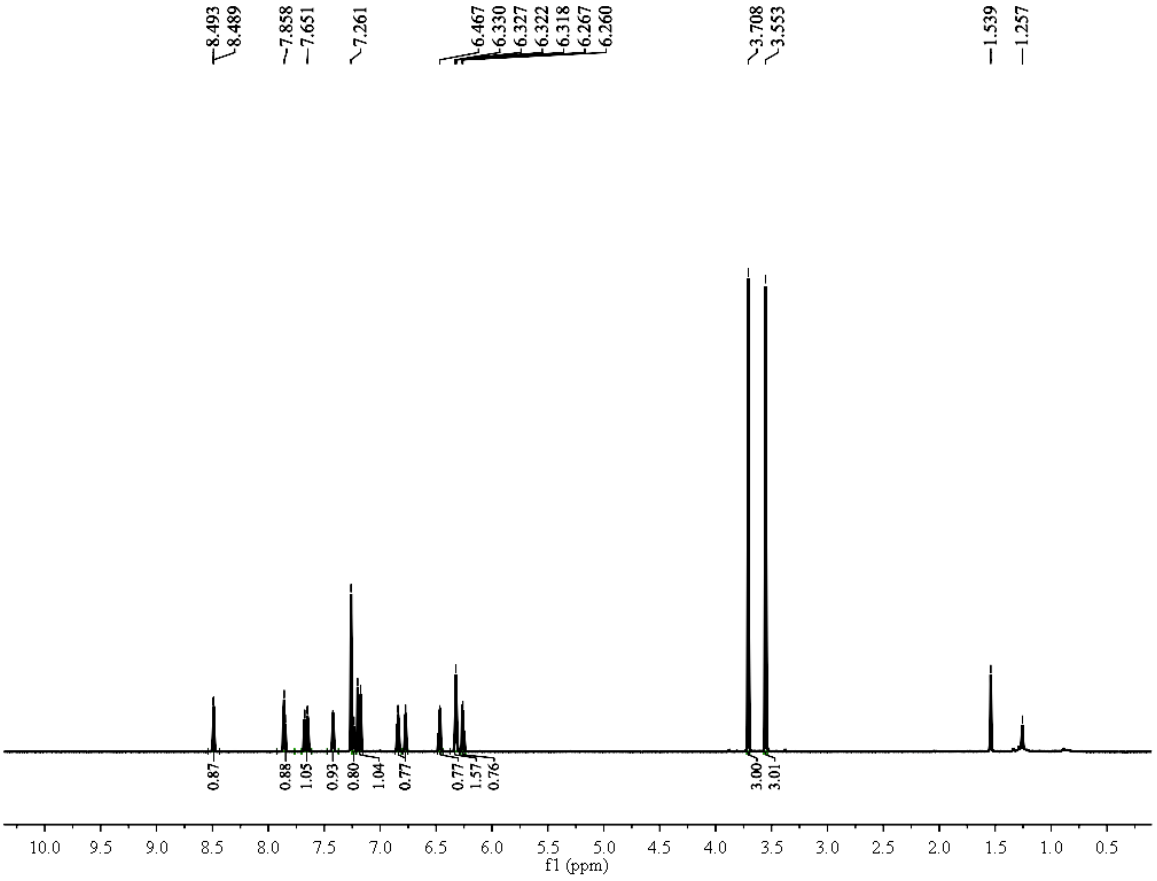


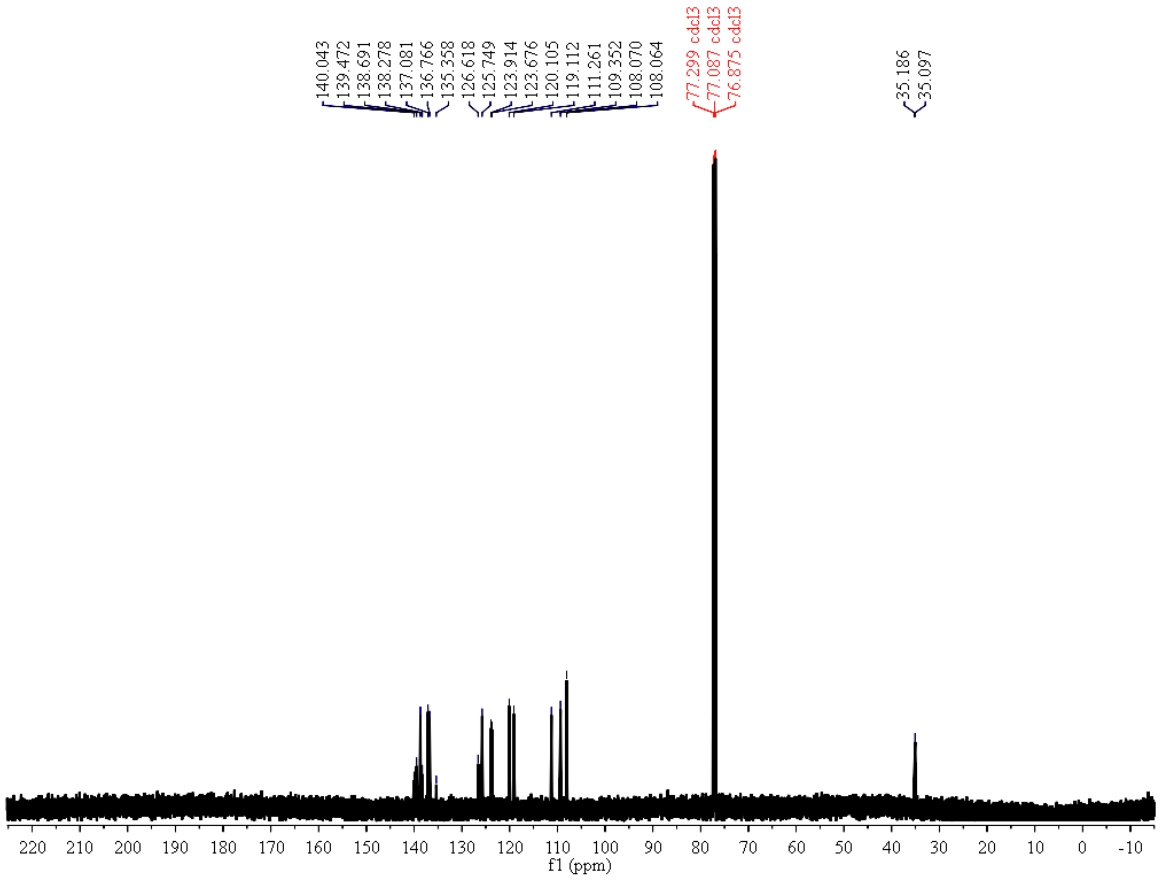
Oligoazulene 12



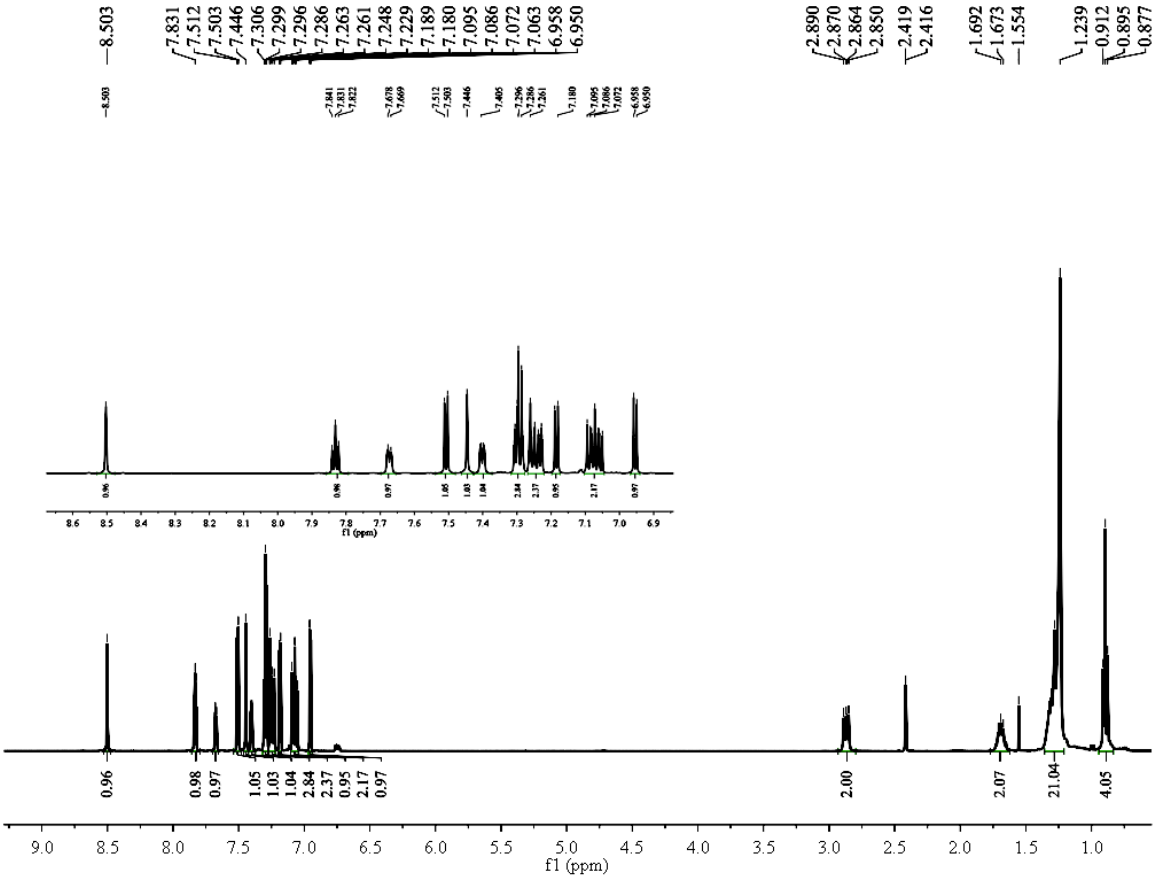


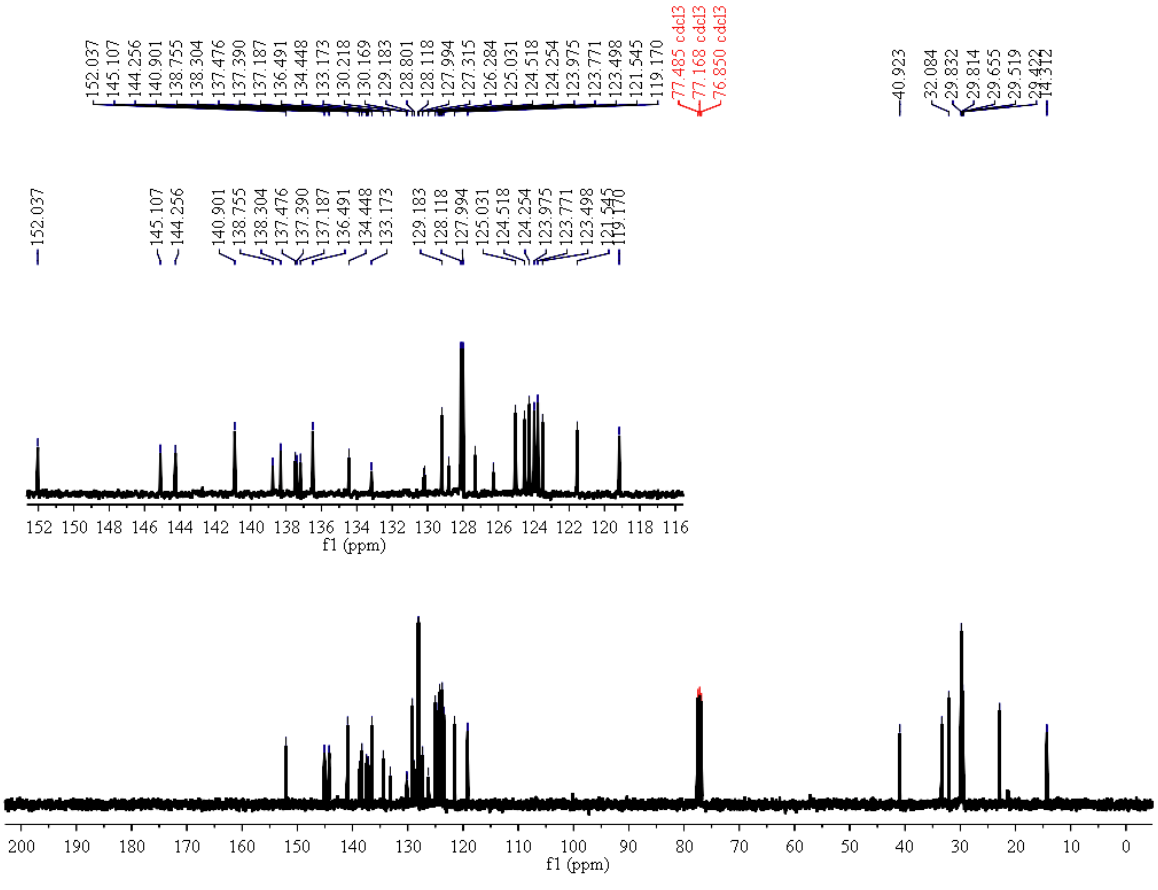
Oligoazulene 13





Oligoazulene 14





Crystallographic data.

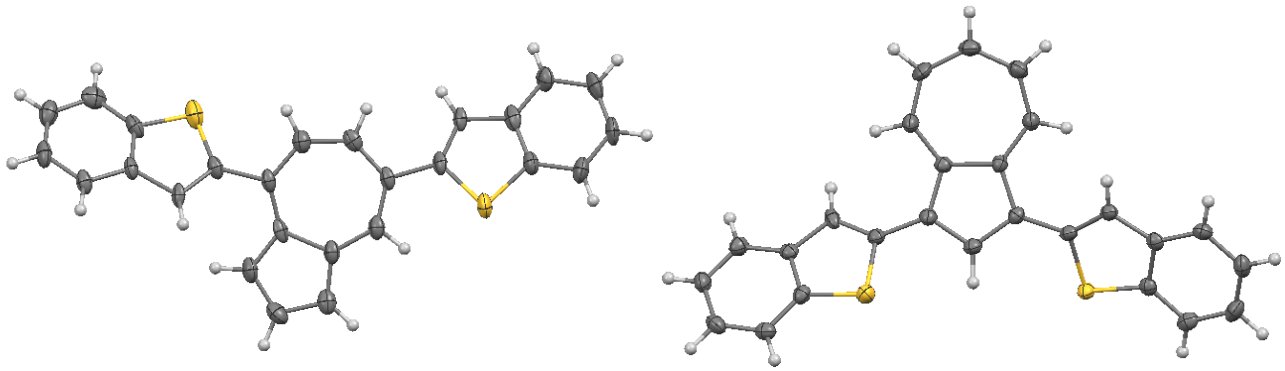


Figure S1. Crystal structures of compounds **1** and **2**.

Crystal structures were deposited at the Cambridge Crystallographic Data Centre (CCDC) and the data have been assigned the following deposition numbers: CCDC 943616 (compound **1**) and CCDC 943617 (compound **2**).

Fluorescence studies.

Fluorescence spectra were recorded on Varian Cary Eclipse Fluorescence Spectrometer using quartz cuvettes.

Fluorescence studies of oligoazulenes **1**, **2**, **11** - **14** in dichloromethane revealed that all the compounds are essentially nonfluorescent in their neutral state similar to the unsubstituted azulene, which has an extremely weak S_1 - S_0 fluorescence.[S1] While protonation with TFA had no effect on the fluorescence of **1**, **2**, **11**, **13** and **14**, fluorescence of azulenium cation derived from 4,7-(bisfuran)azulene (**12**) was "switched on" accompanied by strong emission band at λ_{max} = 547 nm, Φ_f = 0.154. In concert with the switchable properties observed in the UV-vis measurements, the fluorescence of the azulenium cation **12-H**$^+$ can be "switched off" by subsequent addition of base such as triethylamine.

For the neutral oligomer **12**, the excitation wavelength was set at 307 nm and the emission was recorded from 310 nm to 800 nm with the use of excitation and emission slits of 5 nm. For the azulenium cation, **12-H**$^+$, the excitation wavelength was set at 349 nm and the emission was recorded from 350 nm to 800 nm with the use of excitation and emission slits of 5 nm.

Electrochemical studies.

Cyclic voltammetry were performed with a platinum electrode for CH_2Cl_2 solutions of the samples (ca. 1×10^{-3} M) in the presence of [Bu_4NPF_6] (0.1 M) as an electrolyte at ambient temperature under N_2 atmosphere. The scan rate was 100 mV s^{-1}. After the measurements, ferrocene was added to the mixture and the potentials were calibrated with respect to the [$FeCp_2$]/[$FeCp_2$]$^+$ redox couple. Cyclic voltammetric (CV) data and the energy levels of the frontier orbitals are summarized in Table 1.

Table 1. Electrochemical properties of oligoazulenes **1**, **11** - **14**.

Compound	Reduction Potential (vs. Ag/AgCl) $E_{p.c.}$[a] (V)	$E_{p.a.}$[b] (V)	E_g[c] (eV)	LUMO[d] (eV)	HOMO[e] (eV)
1	-2.19	-1.62	2.88	-2.90	-5.78
11	-2.31	-2.12	3.20	-2.59	-5.79
12	-2.19	-1.93	2.93	-2.74	-5.67
13	-2.12	-1.96	2.84	-2.76	-5.60
14	-2.17	-1.74	2.73	-2.85	-5.58

[a] Cathodic peak potential. [b] Anodic peak potential. [c] Optical band gap (E_g) values were calculated by the equation: $E_g = 1240/Abs\lambda_{onset}$. [d] The LUMO energy levels were calculated from cyclic voltammetry and referenced to ferrocene (-4.8 eV). [e] HOMO = LUMO + E_g.

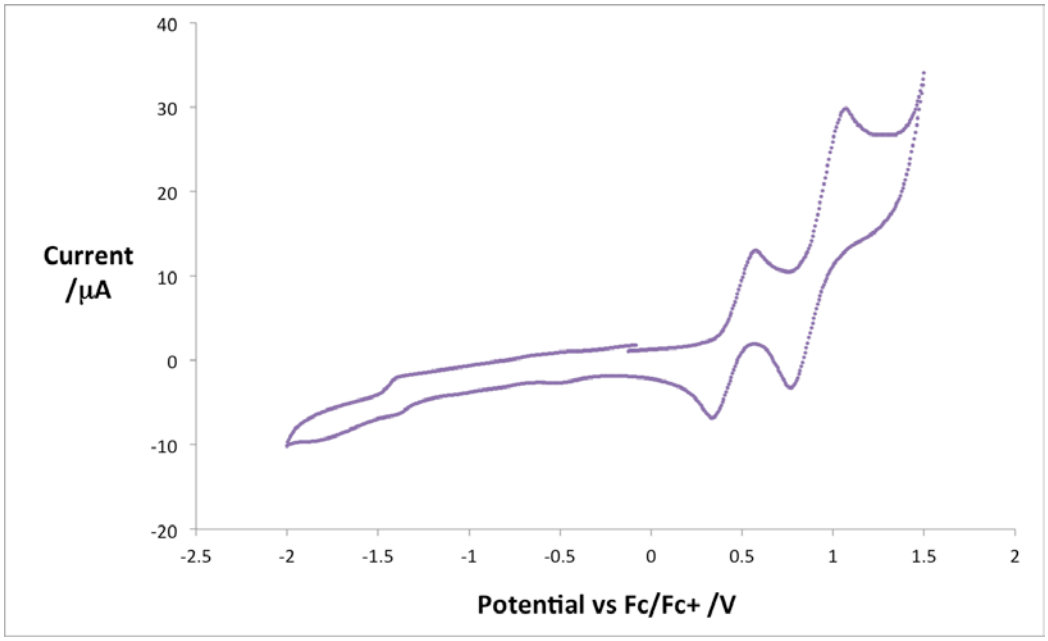
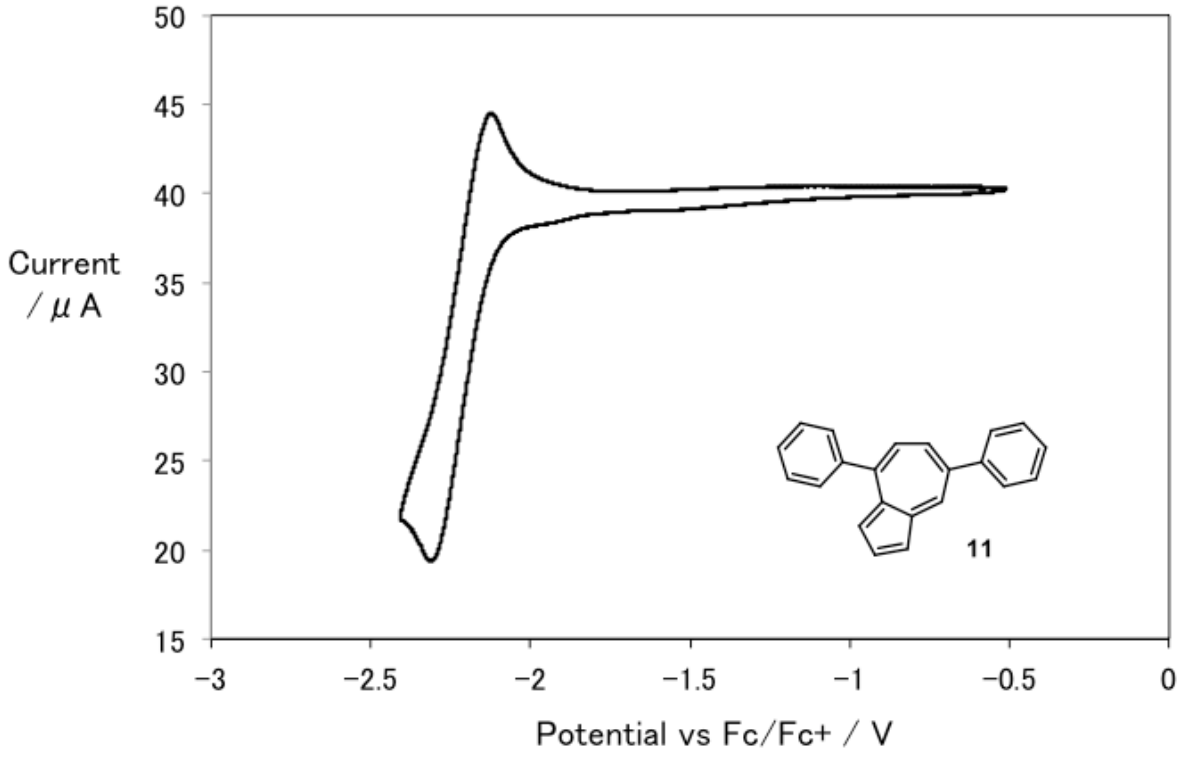
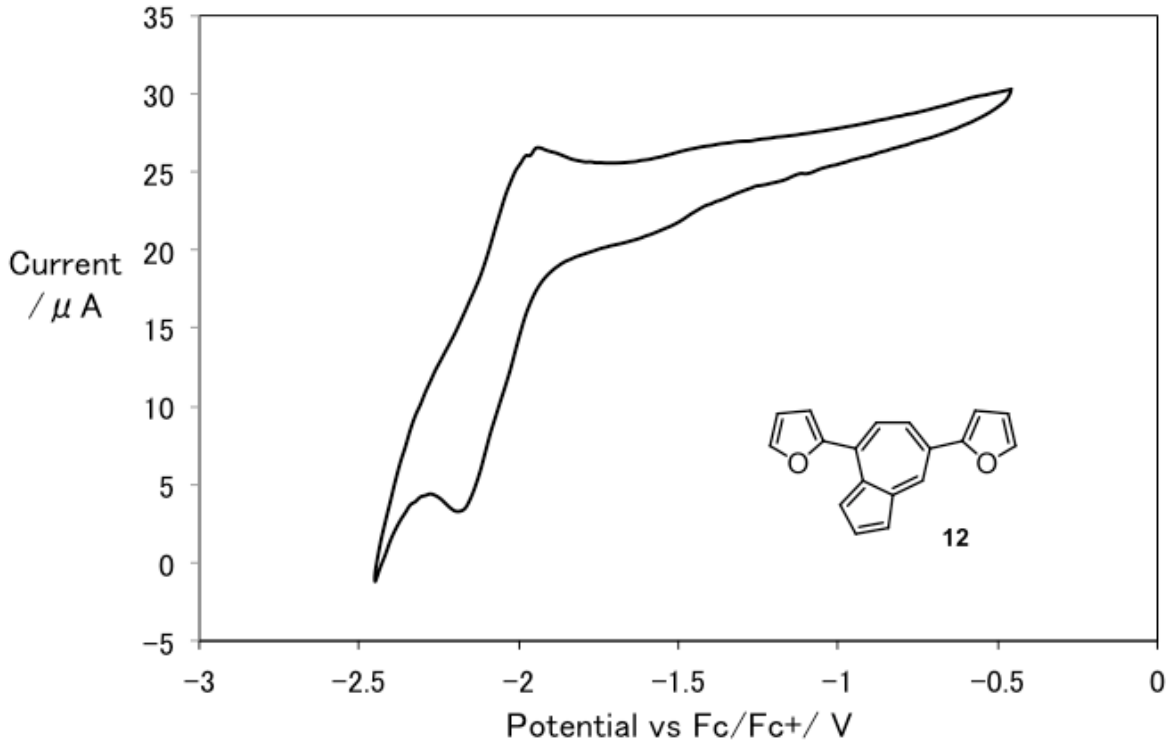
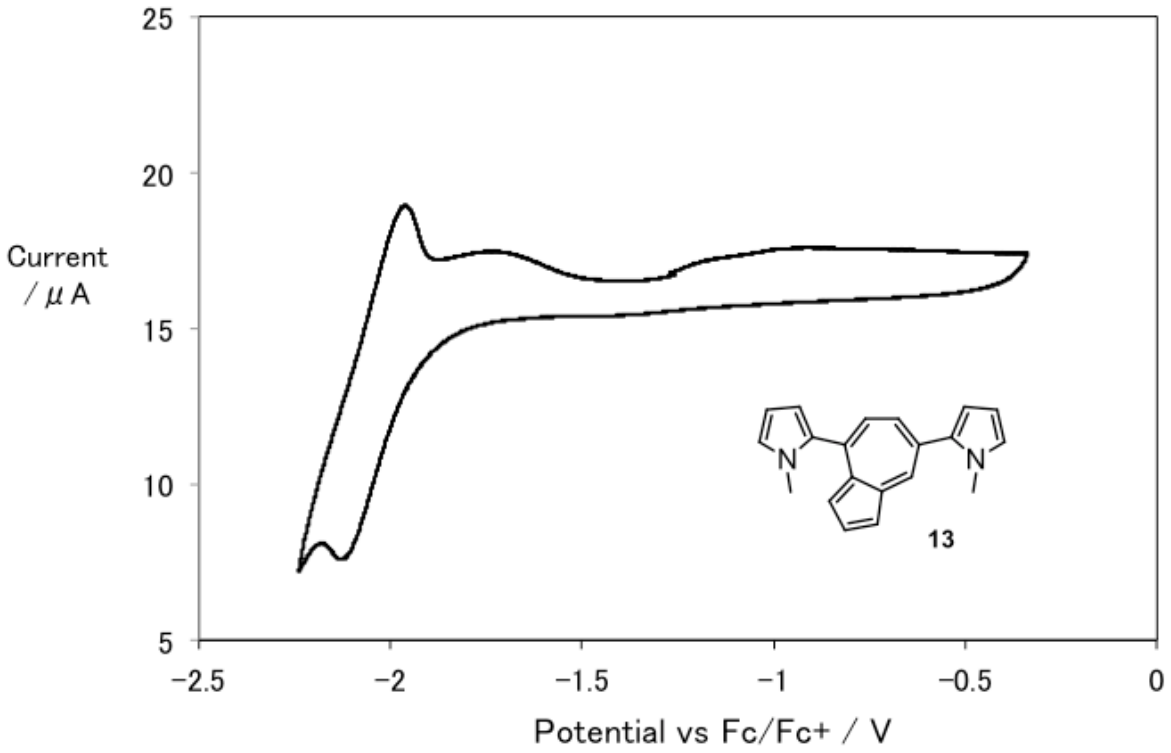


Figure S2. Cyclic voltammogram of oligoazulene 2 premixed with ferrocene.


50
45
40
35
30
25
20
15
Current
/ μ A
−3
−2.5
−2
−1.5
−1
−0.5
0
Potential vs Fc/Fc+ / V
11


35
30
25
20
15
10
5
0
−5
Current
/ μ A
−3
−2.5
−2
−1.5
−1
−0.5
0
Potential vs Fc/Fc+/ V
O
O
12



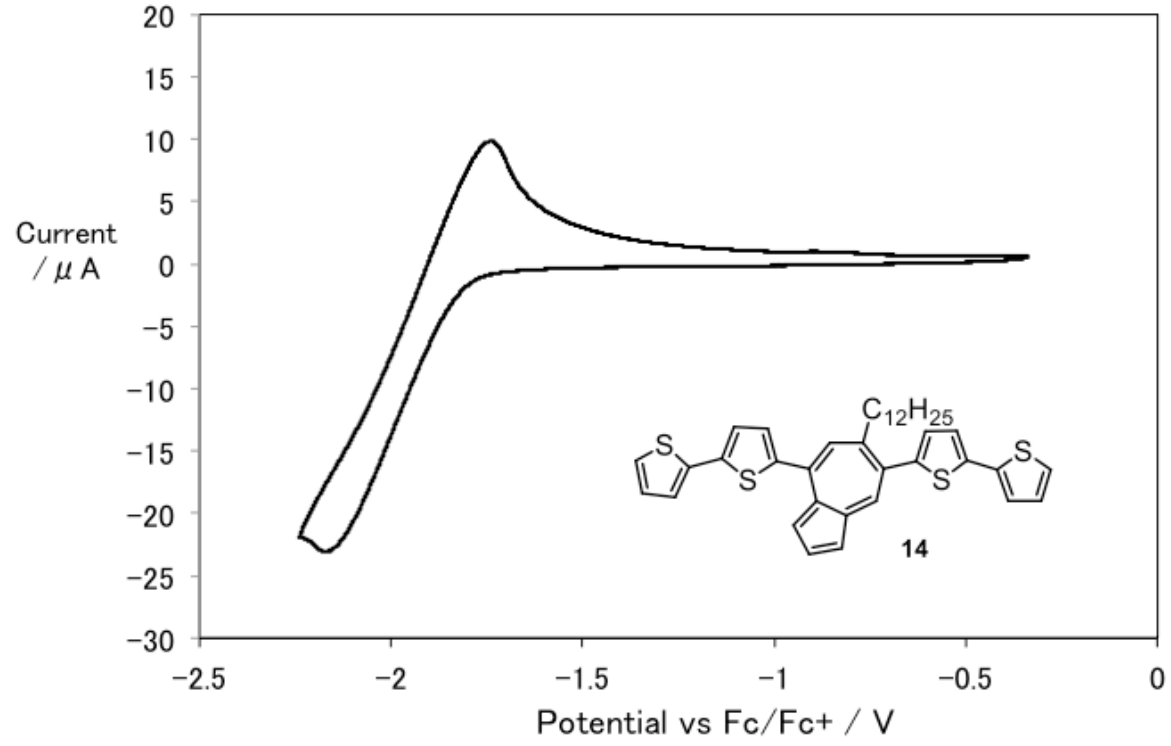


Figure S3. Cyclic voltammograms of oligoazulenes 11-14.

EPR Measurements.

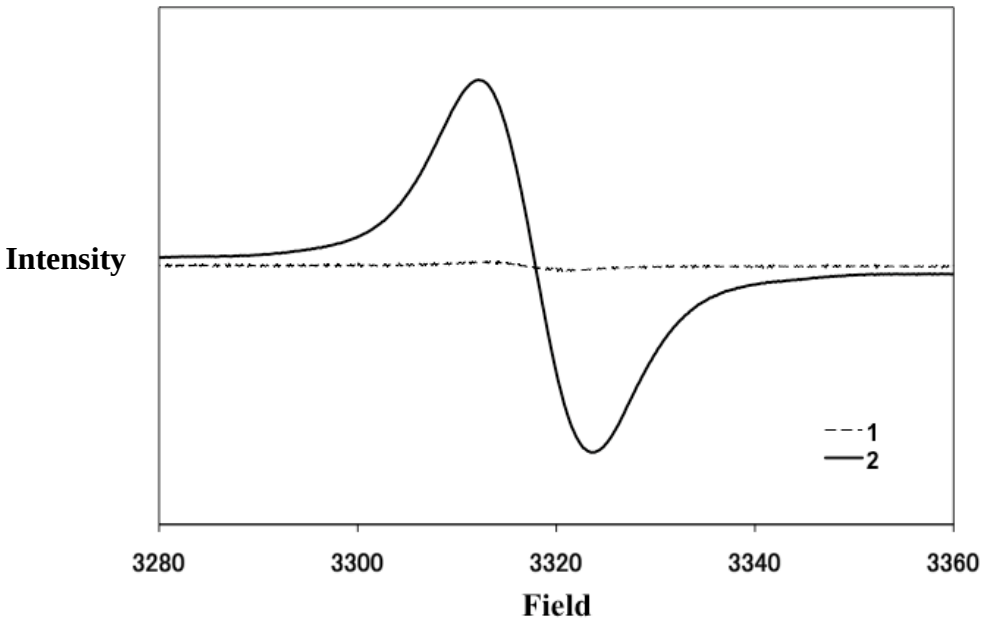


Figure S4. EPR spectra of **1** and **2** in TFA at room temperature.

Theoretical Calculations.

Geometry optimizations were carried out using the Gaussian 09 quantum chemistry program package at the B3LYP level.[S2] All compounds were fully optimized with the 6-31+G* basis set. The HOMO and LUMO energies were determined by using minimized singlet geometries to approximate the ground state. Plots of molecular orbitals and spin densities were constructed using the MOLEKEL program 4.1.[S3]

11

	X	Y	Z
C	-1.021987	-1.446887	-0.006638
C	0.347256	-1.446887	-0.006638
C	1.267486	-0.377467	-0.006638
H	2.328113	-0.70811	0.000201
C	1.066672	0.977588	-0.006358
C	-0.184384	1.648895	-0.030627
C	-0.386212	3.025903	-0.07079
H	0.386581	3.792391	-0.096557
C	-1.805093	3.295363	-0.080752
H	-2.235293	4.295568	-0.110014
C	-2.489628	2.098448	-0.048887
H	-3.567009	1.948329	-0.045141
C	-1.522287	1.005274	-0.024492
C	-1.870512	-0.30449	-0.012838
H	-2.958575	-0.528463	-0.00534
H	0.832089	-2.447424	-0.007221
C	-1.707885	-2.750991	-0.002229
C	-1.332039	-3.745464	0.911063
C	-2.740863	-3.011493	-0.913256
C	-3.384093	-4.247536	-0.910162
C	-1.981013	-4.978769	0.912661
C	-3.0068	-5.232597	0.002535
H	-3.037486	-2.239043	-1.638822
H	-4.190886	-4.445664	-1.631147
H	-0.526731	-3.546411	1.634082
H	-1.682725	-5.752457	1.635436
H	-3.517116	-6.206689	0.004495
C	2.278404	1.821619	0.018343
C	3.25721	1.669486	-0.972877
C	2.473792	2.759437	1.040859
C	3.633894	3.531187	1.070181
C	4.411508	2.450059	-0.943524
C	4.602893	3.379758	0.078274
H	1.706411	2.882079	1.820583
H	3.78338	4.262012	1.878532
H	3.107331	0.935588	-1.778944
H	5.172399	2.330514	-1.728711
H	5.515759	3.99254	0.101818

12

	X	Y	Z
C	-2.898311	0.403063	-0.044967
C	1.73105	0.403062	-0.044966
C	0.756402	1.36964	-0.044967
C	-0.648019	1.259095	-0.029076
H	-1.167361	2.241384	-0.067282
C	-1.463543	0.156468	0.017916
C	-1.051249	-1.2007	0.109072
C	-1.869807	-2.316511	0.252671
H	-2.95451	-2.320867	0.345291
C	-1.048895	-3.505587	0.281861
H	-1.443704	-4.515477	0.385077
C	0.274541	-3.139676	0.162107
H	1.146903	-3.789711	0.147004
C	0.352654	-1.683736	0.066926
C	1.52347	-1.006635	-0.006296
H	2.449012	-1.621864	-0.024101
H	1.112492	2.422318	-0.076766
C	-3.956668	-0.221446	-0.685323
O	-3.367	1.546458	0.62929
H	-3.917071	-1.116391	-1.301418
C	3.11083	0.855734	-0.076713
O	4.098435	-0.098375	-0.378883
C	3.711179	2.088098	0.138364
H	3.226118	3.024797	0.397769
C	-5.139845	0.554929	-0.397815
C	-4.738226	1.607676	0.399572
H	-6.142818	0.334776	-0.751759
C	5.320302	0.569991	-0.347201
C	5.131903	1.901099	-0.036699
H	5.88916	2.673442	0.062749
H	6.177999	-0.058946	-0.567253
H	-5.235078	2.446531	0.878393

13

	X	Y	Z
C	-2.931791	0.33292	-0.021242
C	1.706541	0.332918	-0.021242
C	0.738302	1.302748	-0.021242
C	-0.668301	1.198477	0.000326
H	-1.178566	2.184879	-0.022771
C	-1.485088	0.097861	0.016599
C	-1.073491	-1.262173	0.047408
C	-1.904741	-2.37717	0.101816
H	-2.993939	-2.369197	0.119295
C	-1.091785	-3.570984	0.136796
H	-1.495219	-4.581745	0.181862
C	0.23858	-3.20924	0.106632
H	1.106445	-3.864772	0.124082
C	0.328122	-1.752782	0.051083
C	1.500861	-1.07435	0.021895
H	2.426235	-1.687908	0.048999
H	1.10746	2.351417	-0.048552
C	-3.860567	-0.18413	-0.945946
N	-3.626057	1.169139	0.868915
H	-3.630748	-0.858749	-1.765389
C	3.096107	0.792131	-0.026051
N	4.089414	0.34011	-0.90882
C	3.673906	1.75599	0.823379
H	3.164152	2.287777	1.620378
C	-5.144524	0.348667	-0.610479
C	-4.972313	1.170374	0.512336
H	-6.078355	0.154157	-1.127971
C	5.276082	1.009503	-0.615957
C	5.048898	1.888206	0.452066
H	5.780559	2.545013	0.911336
H	6.185792	0.816034	-1.184011
H	-5.703742	1.746676	1.078612
C	-3.076463	1.870631	1.982186
C	3.929833	-0.620023	-1.950948
H	-2.074873	1.439063	2.249514
H	-2.947427	2.958334	1.72789
H	-3.765049	1.785016	2.864958
H	4.295029	-1.627646	-1.610322
H	2.845715	-0.702863	-2.231903
H	4.523167	-0.306582	-2.851125

14

	X	Y	Z
C	-3.027508	-2.856761	-0.380762
C	1.591118	-2.85676	-0.380762
C	0.590032	-1.821949	-0.380762
C	-0.764718	-1.97972	-0.364497
H	-1.368678	-1.046256	-0.386152
C	-1.597157	-3.140914	-0.337199
C	-1.183813	-4.440229	-0.27015
C	-2.040281	-5.61719	-0.180749
H	-3.127407	-5.572479	-0.145414
C	-1.245358	-6.744971	-0.132374
H	-1.580862	-7.77848	-0.060082
C	0.140375	-6.344591	-0.188358
H	0.984842	-7.030266	-0.169106
C	0.203731	-4.954528	-0.265538
C	1.39663	-4.209321	-0.334233
H	2.312178	-4.841062	-0.348097
C	1.161377	-0.431189	-0.413906
C	-3.944663	-3.423773	-1.251829
S	-3.770599	-1.749589	0.643196
H	-3.698183	-4.164998	-2.016713
C	2.988961	-2.429871	-0.446414
S	3.971399	-2.321357	0.913791
C	3.690331	-2.10945	-1.595508
H	3.270211	-2.113498	-2.603968
C	-5.258675	-2.920497	-1.042411
C	-5.299274	-1.986971	-0.015271
H	-6.123963	-3.244697	-1.625024
C	5.329329	-1.844533	0.04013
C	5.04436	-1.767917	-1.315595
H	5.75999	-1.478176	-2.088277
C	6.583328	-1.574386	0.659638
C	6.788882	-1.177764	1.973557
S	8.05279	-1.713798	-0.157515
C	8.961552	-1.264311	1.162741
C	8.173956	-0.999185	2.263202
H	10.048013	-1.195573	1.134508
H	5.996824	-1.012527	2.707088
H	8.543296	-0.688069	3.242447
C	-6.451509	-1.292501	0.453027
S	-7.799403	-1.002661	-0.518862
C	-6.639531	-0.764033	1.722673
C	-7.910006	-0.128816	1.849543
C	-8.63354	-0.201272	0.677609
H	-5.915885	-0.826061	2.538374
H	-8.249425	0.347757	2.77141
H	-9.631764	0.207627	0.5278
H	1.867443	-0.329335	0.458119
H	1.781659	-0.340387	-1.350177
C	0.184723	0.723365	-0.371735
H	-0.501429	0.683281	-1.258781
H	-0.447408	0.662405	0.553271
C	0.927482	2.044886	-0.37949
H	1.61356	2.097536	0.506633
H	1.568027	2.111901	-1.298123
C	-0.035736	3.212057	-0.345756
H	-0.72181	3.159871	-1.23199
H	-0.676641	3.144875	0.572688
C	0.703219	4.533085	-0.353268
H	1.389615	4.585252	0.532697
H	1.343928	4.600414	-1.271834
C	-0.259213	5.700845	-0.319131
H	-0.945888	5.648385	-1.204862
H	-0.89964	5.633746	0.599645
C	0.479516	7.021944	-0.327332
H	1.166584	7.07421	0.558103
H	1.119579	7.089212	-1.246349
C	-0.482717	8.189838	-0.29259
H	-1.170147	8.137259	-1.17772
H	-1.122402	8.122887	0.626712
C	0.25591	9.510983	-0.301592
H	0.943843	9.56327	0.583172
H	0.895137	9.57813	-1.221203
C	-0.706074	10.678919	-0.266022
H	-1.394587	10.626497	-1.150291
H	-1.344762	10.61254	0.653982
C	0.031393	12.001081	-0.276142
H	0.720837	12.050835	0.607848
H	0.67049	12.065063	-1.196311
C	-0.922515	13.166912	-0.240364
H	-1.601756	13.148113	-1.126781
H	-1.551163	13.133979	0.682234
H	-0.358539	14.130673	-0.248578

1

	X	Y	Z
C	2.531839	-0.148385	-0.006907
C	-1.251389	4.163133	0.174043
C	0.000019	4.757241	-0.00002
C	1.251421	4.163118	-0.174073
H	2.082322	4.847623	-0.317128
C	1.583793	2.805575	-0.159535
C	0.749532	1.705008	-0.01957
C	1.160997	0.338647	-0.001222
C	-0.000006	-0.464402	0.00003
H	-0.000011	-1.545314	0.000041
C	-1.161001	0.338657	0.001252
C	-0.749523	1.705015	0.019582
C	-1.583774	2.805593	0.159529
H	-2.639125	2.572105	0.277715
H	0.000024	5.844821	-0.00003
C	3.60787	0.315525	0.702543
S	2.971028	-1.53674	-1.030001
H	3.533129	1.119061	1.422557
C	-2.531848	-0.148361	0.006937
S	-2.97106	-1.536683	1.030067
C	-3.607873	0.315554	-0.702519
H	-3.533122	1.119083	-1.42254
C	4.825603	-0.41523	0.460403
C	4.63587	-1.478359	-0.465383
C	6.102865	-0.220513	1.019157
C	7.147794	-1.059162	0.653323
C	5.689194	-2.322222	-0.830862
C	6.943594	-2.103959	-0.267386
H	6.262204	0.58189	1.730804
H	8.132484	-0.910804	1.080766
H	5.534336	-3.129473	-1.536911
H	7.77138	-2.747702	-0.540523
C	-4.63588	-1.478345	0.465379
C	-4.825605	-0.415211	-0.460403
C	-5.689199	-2.322229	0.830821
C	-6.943588	-2.103981	0.267313
C	-6.102855	-0.22051	-1.019191
C	-7.147781	-1.059179	-0.653392
H	-5.534349	-3.129479	1.536873
H	-7.771371	-2.747738	0.540425
H	-6.262187	0.581894	-1.730839
H	-8.132462	-0.910833	-1.080861
H	2.639142	2.572075	-0.277716
H	-2.082283	4.847648	0.317086

2

	X	Y	Z
C	-2.957683	-0.11676	-0.00238
C	1.717438	0.303843	-0.045811
C	0.79529	-0.748512	0.115112
C	-0.59374	-0.763265	0.092949
H	-1.035819	-1.734109	0.295574
C	-1.52919	0.275736	-0.09842
C	-1.233587	1.622478	-0.349271
C	-2.145298	2.664541	-0.618781
H	-3.213335	2.549176	-0.693689
C	-1.427602	3.86431	-0.80399
H	-1.872879	4.821449	-1.033375
C	-0.05178	3.623697	-0.662541
H	0.739303	4.351707	-0.761543
C	0.145713	2.249926	-0.392434
C	1.388442	1.653733	-0.260052
H	2.232925	2.331158	-0.370608
H	1.249011	-1.712209	0.329317
C	-3.929793	0.44605	0.774905
S	-3.567104	-1.503835	-0.928452
H	-3.740775	1.285896	1.428962
C	3.149583	-0.058863	0.01514
S	4.328914	1.027531	0.784892
C	3.745545	-1.19752	-0.45383
H	3.20493	-1.968601	-0.986522
C	-5.209029	-0.208098	0.6666
C	-5.172248	-1.304005	-0.238806
C	-6.417908	0.09526	1.321016
C	-7.546521	-0.671391	1.06433
C	-6.311556	-2.073163	-0.497909
C	-7.494777	-1.748668	0.158999
H	-6.45954	0.924922	2.017574
H	-8.479773	-0.440673	1.564141
H	-6.275001	-2.904497	-1.191772
H	-8.387008	-2.334491	-0.027781
C	5.643152	-0.089477	0.441768
C	5.166198	-1.251301	-0.225137
C	6.996484	0.067486	0.755808
C	7.882882	-0.945194	0.399289
C	6.084987	-2.25736	-0.57899
C	7.428634	-2.100105	-0.265151
H	7.349485	0.956532	1.264733
H	8.935334	-0.841424	0.635296
H	5.737931	-3.147192	-1.091971
H	8.138477	-2.873436	-0.533932

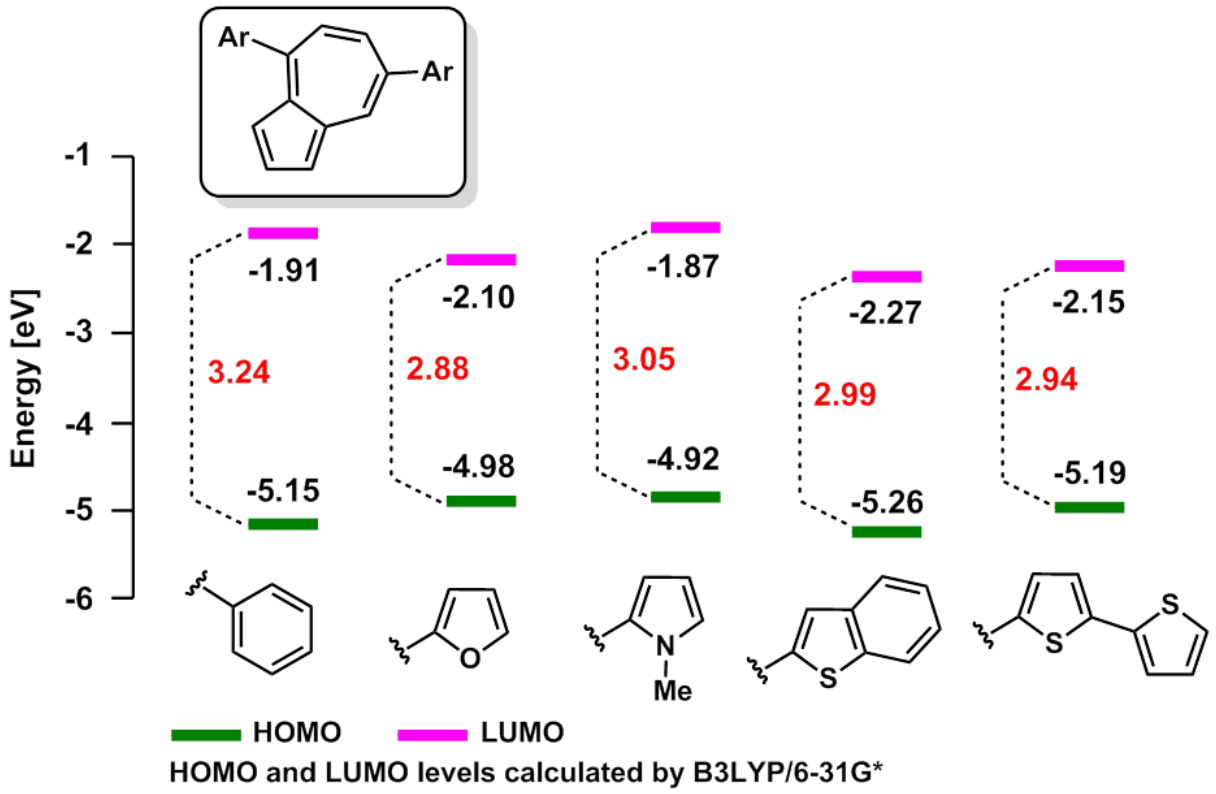


Figure S5. Energy Diagrams for oligoazulenes **11**–**14**.

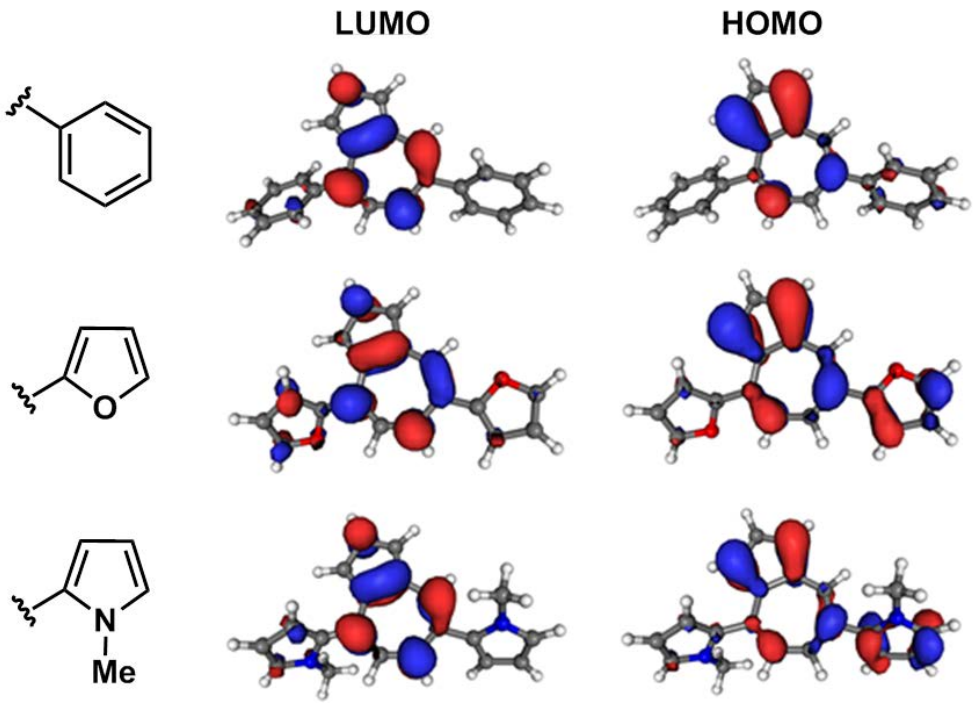


Figure S6. (Continued)

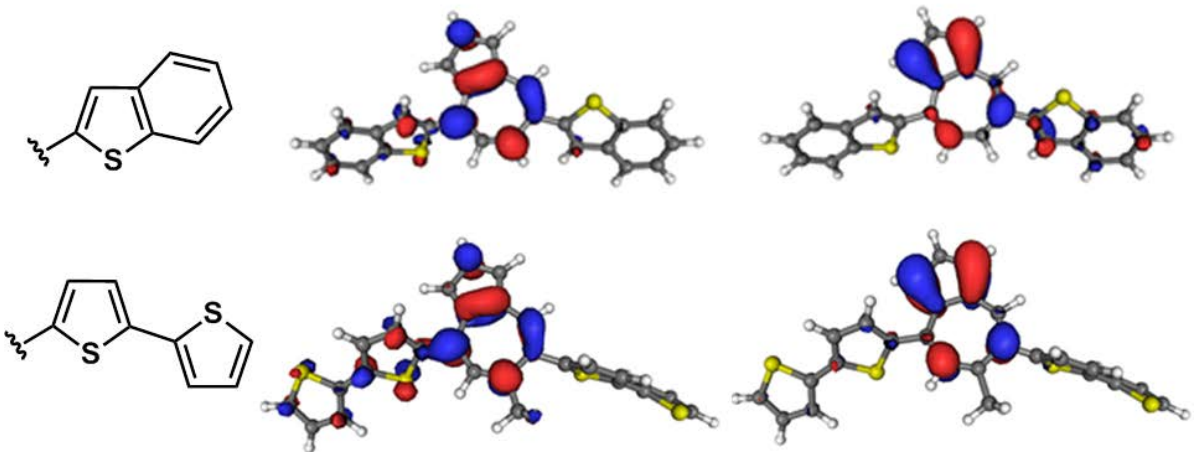


Figure S6 . Orbital plots for oligoazulenes **11**–**14**.

References

S1. (a) Beer, M.; Longuet-Higgins, H. C. *J. Chem. Phys*. **1955**, *23*, 1390-1391. (b) Rentzepis, P. M. *Chem. Phys. Lett*. **1969**, *3*, 717-720.

S2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.02; Gaussian Inc.: Pittsburgh, PA, 2009.

S3. Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. Molekel 4.3, Swiss Center for Scientific Computing: Manno, 2000-2002; http://www.cscs.ch/molkel.