Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Tunable Benzothiadiazole-Based Donor-Acceptor Materials for Two-Photon Excited Fluorescence

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Additional Figures and Tables

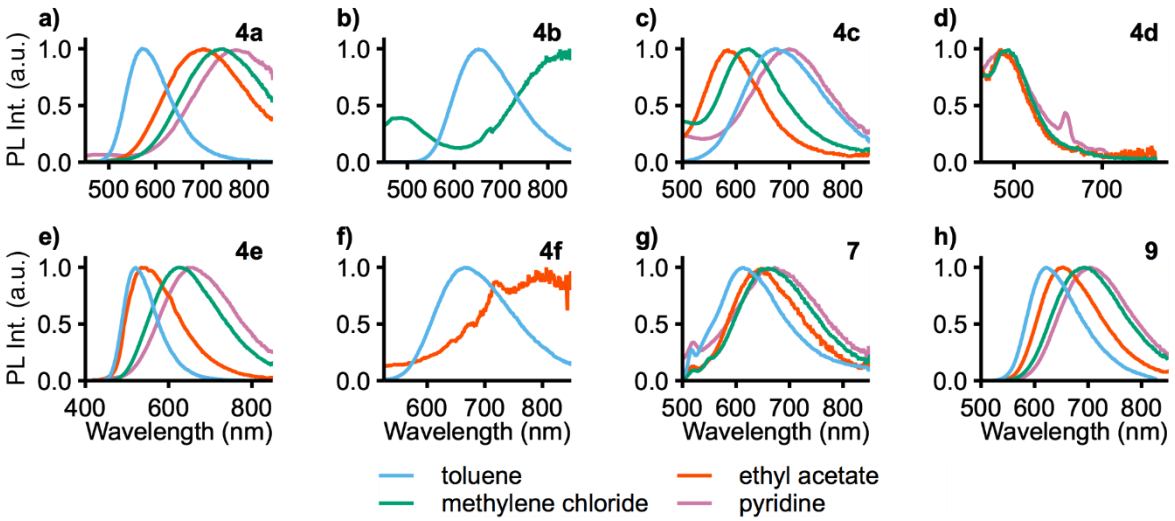

Figure S1. Normalized one-photon photoluminescence (PL) of BTD-based D-π-A-π-D and D-A-D compounds in toluene (blue), methylene chloride (green), ethyl acetate (orange), and pyridine (pink) at 0.01 mg mL^{-1}; $\lambda_{ex} = \lambda_{max,\ abs}$. Non-emissive solutions are omitted for clarity.

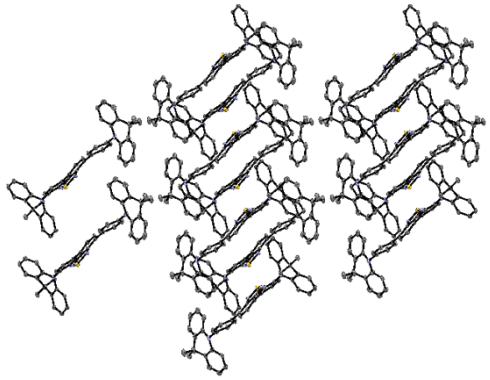

Figure S2. Molecular packing of **4a** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Carbon = grey, nitrogen = blue.

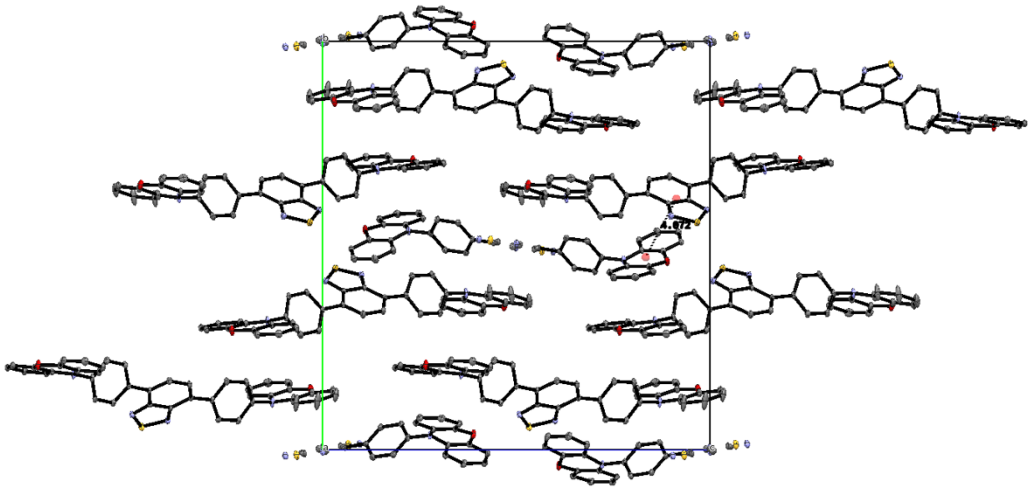

Figure S3. Molecular packing of **4b** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Carbon = grey, nitrogen = blue, oxygen = red.

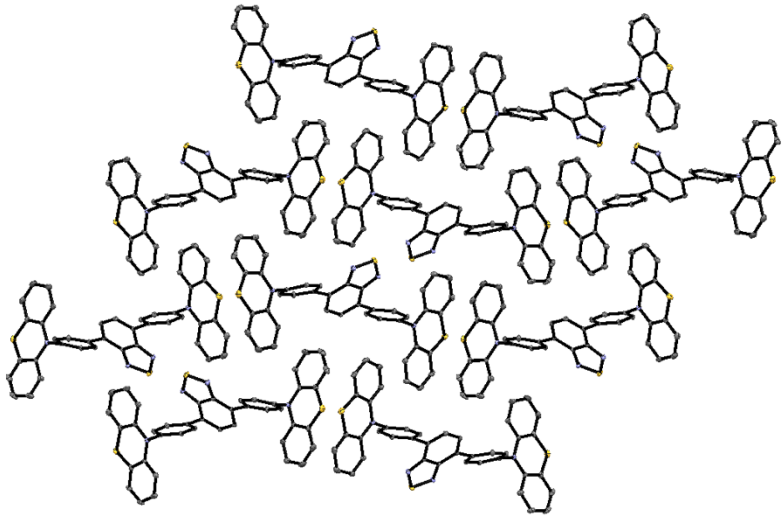

Figure S4. Molecular packing of **4c** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Carbon = grey, nitrogen = blue, sulfur = yellow.

Table S1. Results of DFT and TDA-DFT calculations for **4a-f**, **7**, **9**.

Cmpd	ω ($Bohr^{-1}$)	HOMO[a] (eV)	LUMO[a] (eV)	E_{gap} (eV)	Dipole[b] (Debye)	E_{S1}[c] (eV)	f[c]
4a	0.1448	-6.58	-1.35	5.23	1.12	3.48	0.0251
4b	0.1457	-6.50	-1.43	5.06	0.69	3.37	0.0001
4c	0.1490	-6.74	-1.41	5.33	0.24	3.53	0.6384
4d	0.1479	-6.09	-1.29	4.79	1.51	3.13	0.0001
4e	0.1375	-6.86	-1.67	5.19	0.73	3.37	0.8772
4f	0.1343	-6.00	-1.39	4.60	1.11	3.10	0.7409
7	0.1375	-6.11	-1.51	4.60	0.77	2.75	0.0223
9	0.1293	-6.10	-1.13	4.97	1.32	2.73	0.6843

a) Calculated at the ωB97XD*/6-31+G(d) level. b) Ground state dipole calculated at the ωB97XD*/6-31+G(d) level.

c) Calculated using TDA-DFT at the ωB97XD*/6-31+G(d) level in toluene using PCM.

Table S2. Crystallography data for solid-state structure of compound **4a**.

Formula	$C_{52}H_{46}N_4OS$
$D_{calc.}$/ g cm^{-3}	1.299
μ/mm^{-1}	0.128
Formula Weight	774.99
Colour	yellow
Shape	plate
Size/mm^3	0.40×0.30×0.03
T/K	90(2)
Crystal System	triclinic
Space Group	P-1
a/Å	9.1767(11)
b/Å	12.3849(14)
c/Å	18.948(2)
α/°	84.388(4)
β/°	80.102(4)
γ/°	69.216(4)
V/Å^3	1981.7(4)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	1.092
Θ_{max}/°	22.656
Measured Refl.	17258
Independent Refl.	5187
Reflections with I > 2(I)	3422
R_{int}	0.0716
Parameters	558
Restraints	195
Largest Peak	0.412
Deepest Hole	-0.326
GooF	1.097
wR_2 (all data)	0.1881
wR_2	0.1733
R_1 (all data)	0.1290
R_1	0.0850

Table S3. Crystallography data for solid-state structure of compound **4b**.

Formula	$C_{69}H_{44}ClN_6O_3S_{1.5}$
$D_{calc.}$/ g cm^{-3}	1.410
μ/mm^{-1}	0.196
Formula Weight	1088.64
Colour	orange
Shape	prism
Size/mm^3	0.28×0.26×0.14
T/K	90(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	9.0449(6)
b/Å	24.4570(16)
c/Å	23.2721(14)
α/°	90
β/°	95.117(2)
γ/°	90
V/Å^3	5127.5(6)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	1.665
Θ_{max}/°	30.547
Measured Refl.	80125
Independent Refl.	15663
Reflections with I > 2(I)	11562
R_{int}	0.0498
Parameters	806
Restraints	570
Largest Peak	0.449
Deepest Hole	-0.529
GooF	1.023
wR_2 (all data)	0.1201
wR_2	0.1076
R_1 (all data)	0.0716
R_1	0.0464

Table S4. Crystallography data for solid-state structure of compound **4c**.

Formula	$C_{42}H_{26}N_4S_3$
$D_{calc.}$/ g cm^{-3}	1.411
μ/mm^{-1}	0.270
Formula Weight	682.85
Colour	red
Shape	needle
Size/mm^3	0.54×0.11×0.06
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	7.1069(5)
b/Å	29.8434(19)
c/Å	15.2458(10)
α/°	90
β/°	96.180(2)
γ/°	90
V/Å^3	3214.8(4)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK_α
Θ_{min}/°	1.915
Θ_{max}/°	30.550
Measured Refl.	44276
Independent Refl.	9823
Reflections with I > 2(I)	7248
R_{int}	0.0587
Parameters	442
Restraints	0
Largest Peak	0.456
Deepest Hole	-0.412
GooF	1.021
wR_2 (all data)	0.1097
wR_2	0.0988
R_1 (all data)	0.0725
R_1	0.0455

Table S5. Cartesian coordinates (Å) for the optimized ground-state structure of **4a**.

Atom	x	y	z
C	1.464927	-0.041500	-0.015075
C	0.724149	1.188027	-0.010582
C	0.712466	-1.193138	-0.008364
C	-0.724151	1.188026	0.010580
C	-0.712464	-1.193139	0.008353
H	1.220322	-2.153485	-0.030343
C	-1.464926	-0.041502	0.015068
H	-1.220318	-2.153487	0.030328
N	1.249321	2.419274	-0.012716
N	-1.249325	2.419271	0.012719
S	-0.000003	3.461689	0.000003
C	-2.946240	-0.073462	0.012090
C	-3.625405	-0.979067	-0.816494
C	-3.697804	0.773263	0.840516
C	-5.015922	-1.043853	-0.813942
H	-3.061214	-1.620080	-1.488465
C	-5.087519	0.705717	0.846854
H	-3.193196	1.483839	1.485719
C	-5.750604	-0.200887	0.019282
H	-5.541163	-1.737680	-1.463570
H	-5.669877	1.357007	1.491779
C	2.946241	-0.073457	-0.012097
C	3.697803	0.773272	-0.840520
C	3.625407	-0.979064	0.816484
C	5.087518	0.705729	-0.846858
H	3.193194	1.483850	-1.485720
C	5.015924	-1.043848	0.813931
H	3.061217	-1.620080	1.488453
C	5.750604	-0.200877	-0.019290
H	5.669876	1.357022	-1.491781
H	5.541166	-1.737675	1.463557
C	-7.891384	0.563327	-0.869851
C	-7.828957	-1.134269	0.898280
C	-7.193020	1.429913	-1.731875
C	-9.297228	0.529319	-0.906582

C	-9.233121	-1.221738	0.917075
C	-7.070411	-1.934077	1.774028
C	-7.872681	2.253000	-2.619952
H	-6.109906	1.460414	-1.705581
C	-9.949661	1.371984	-1.813950
C	-9.822108	-2.115557	1.818708
H	-5.988606	-1.868409	1.764547
C	-7.688098	-2.810544	2.656351
C	-9.264724	2.229886	-2.668160
H	-7.307262	2.911985	-3.272686
H	-11.035318	1.358782	-1.856205
C	-9.077333	-2.908848	2.685301
H	-10.905313	-2.196247	1.846417
H	-7.076940	-3.414880	3.320727
H	-9.809906	2.867593	-3.357195
H	-9.574582	-3.589440	3.369511
C	7.828958	-1.134255	-0.898290
C	7.891383	0.563330	0.869851
C	7.070414	-1.934050	-1.774051
C	9.233122	-1.221733	-0.917075
C	9.297227	0.529312	0.906593
C	7.193019	1.429918	1.731872
C	7.688102	-2.810514	-2.656376
H	5.988610	-1.868376	-1.764577
C	9.822110	-2.115549	-1.818712
C	9.949659	1.371968	1.813970
H	6.109906	1.460428	1.705569
C	7.872679	2.252997	2.619958
C	9.077337	-2.908828	-2.685316
H	7.076945	-3.414841	-3.320762
H	10.905314	-2.196247	-1.846412
C	9.264721	2.229872	2.668178
H	11.035315	1.358757	1.856234
H	7.307260	2.911984	3.272690
H	9.574586	-3.589418	-3.369528
H	9.809903	2.867573	3.357220
N	7.178804	-0.258249	-0.016906

N	-7.178803	-0.258260	0.016898
C	-10.126659	-0.384581	-0.001396
C	10.126658	-0.384592	0.001412
C	10.971385	-1.335795	0.884702
H	11.593099	-1.996250	0.271205
H	11.639013	-0.772603	1.545128
H	10.321378	-1.959231	1.507038
C	11.065603	0.487118	-0.868821
H	11.734276	1.090401	-0.245964
H	11.690503	-0.133560	-1.519461
H	10.482731	1.165215	-1.500393
C	-10.971408	-1.335767	-0.884681
H	-11.593124	-1.996219	-0.271180
H	-11.639038	-0.772564	-1.545095
H	-10.321418	-1.959208	-1.507029
C	-11.065582	0.487136	0.868855
H	-11.690480	-0.133540	1.519500
H	-10.482692	1.165222	1.500423
H	-11.734255	1.090431	0.246009

Table S6. Cartesian coordinates (Å) for the optimized ground-state structure of **4b**.

Atom	x	y	z
C	1.464357	0.212789	0.027724
C	0.724047	-1.016818	0.010384
C	0.712391	1.364560	0.012495
C	-0.724047	-1.016818	-0.010383
C	-0.712391	1.364560	-0.012494
H	1.220648	2.324893	0.005298
C	-1.464357	0.212789	-0.027724
H	-1.220648	2.324893	-0.005298
N	1.248981	-2.248015	0.023442
N	-1.248980	-2.248015	-0.023441
S	0.000000	-3.290460	0.000001
C	-2.945012	0.245397	-0.073495
C	-3.598972	1.151400	-0.920309
C	-3.720210	-0.601290	0.734170
C	-4.989917	1.219383	-0.955865

H	-3.015522	1.791491	-1.576398
C	-5.108603	-0.531299	0.702933
H	-3.234177	-1.312724	1.392539
C	-5.747177	0.378674	-0.142942
H	-5.497122	1.914135	-1.618343
H	-5.708154	-1.182002	1.332909
C	2.945012	0.245397	0.073497
C	3.598972	1.151401	0.920310
C	3.720210	-0.601289	-0.734169
C	4.989916	1.219383	0.955866
H	3.015521	1.791491	1.576399
C	5.108603	-0.531299	-0.702931
H	3.234178	-1.312724	-1.392538
C	5.747177	0.378675	0.142944
H	5.497122	1.914136	1.618344
H	5.708154	-1.182001	-1.332908
C	-7.860106	1.166572	0.810390
C	-7.888371	-0.510365	-0.929845
C	-7.208453	1.924785	1.786116
C	-9.264002	1.138556	0.816469
C	-9.291336	-0.494688	-0.878455
C	-7.265187	-1.466429	-1.735518
C	-7.940093	2.638878	2.738652
H	-6.124365	1.963738	1.796964
C	-9.991693	1.835905	1.767439
C	-10.046255	-1.407156	-1.597953
H	-6.182269	-1.493423	-1.794060
C	-8.024340	-2.379729	-2.471690
C	-9.330175	2.596554	2.735162
H	-7.409849	3.225560	3.482609
H	-11.075057	1.780942	1.731139
C	-9.413308	-2.355992	-2.405200
H	-11.127826	-1.355656	-1.523273
H	-7.515981	-3.109077	-3.094885
H	-9.903504	3.147560	3.473828
H	-10.007739	-3.064334	-2.973431
C	7.888371	-0.510364	0.929845

C	7.860105	1.166573	-0.810391
C	7.265188	-1.466428	1.735518
C	9.291337	-0.494687	0.878454
C	9.264002	1.138556	-0.816470
C	7.208452	1.924785	-1.786116
C	8.024342	-2.379728	2.471690
H	6.182270	-1.493422	1.794062
C	10.046256	-1.407155	1.597951
C	9.991692	1.835904	-1.767442
H	6.124364	1.963737	-1.796964
C	7.940091	2.638876	-2.738654
C	9.413310	-2.355991	2.405199
H	7.515983	-3.109076	3.094886
H	11.127826	-1.355655	1.523271
C	9.330173	2.596552	-2.735166
H	11.075056	1.780940	-1.731142
H	7.409847	3.225557	-3.482611
H	10.007741	-3.064334	2.973429
H	9.903502	3.147556	-3.473832
N	7.173177	0.450085	0.188222
N	-7.173177	0.450083	-0.188221
O	-9.971424	0.452495	-0.145338
O	9.971424	0.452496	0.145337

Table S7. Cartesian coordinates (Å) for the optimized ground-state structure of **4c**.

Atom	x	y	z
C	1.464644	0.122877	0.003935
C	0.724087	-1.106756	-0.001050
C	0.712506	1.274374	0.000592
C	-0.724087	-1.106756	0.001050
C	-0.712506	1.274374	-0.000625
H	1.220518	2.234729	-0.015471
C	-1.464644	0.122877	-0.003951
H	-1.220518	2.234729	0.015425
N	1.248999	-2.337930	0.003790
N	-1.248999	-2.337929	-0.003775
S	0.000000	-3.380296	0.000013

C	-2.945668	0.155993	-0.024924
C	-3.614305	1.065689	-0.855463
C	-3.707875	-0.693530	0.791687
C	-5.005434	1.135353	-0.865809
H	-3.042501	1.708749	-1.518896
C	-5.096360	-0.622302	0.784281
H	-3.211897	-1.408791	1.438469
C	-5.750976	0.292701	-0.044976
H	-5.523913	1.833858	-1.515360
H	-5.683094	-1.277226	1.422376
C	2.945668	0.155994	0.024910
C	3.614301	1.065700	0.855442
C	3.707878	-0.693535	-0.791690
C	5.005430	1.135367	0.865790
H	3.042494	1.708766	1.518867
C	5.096364	-0.622305	-0.784280
H	3.211904	-1.408802	-1.438468
C	5.750976	0.292708	0.044968
H	5.523906	1.833880	1.515335
H	5.683100	-1.277236	-1.422365
C	-7.825701	1.099400	0.958232
C	-7.886830	-0.581617	-0.842165
C	-7.143352	1.499186	2.115771
C	-9.182381	1.447736	0.834192
C	-9.249096	-0.387713	-1.131519
C	-7.260496	-1.730842	-1.344492
C	-7.797888	2.210994	3.120073
H	-6.091156	1.267531	2.232039
C	-9.840882	2.121810	1.861482
C	-9.967359	-1.343156	-1.848833
H	-6.205739	-1.899036	-1.161449
C	-7.975368	-2.660719	-2.098158
C	-9.151090	2.516690	3.006564
H	-7.238881	2.515872	3.999910
H	-10.895729	2.355344	1.747335
C	-9.333325	-2.480884	-2.345327
H	-11.024765	-1.177597	-2.035199

H	-7.459051	-3.535339	-2.482776
H	-9.666365	3.058392	3.793498
H	-9.894997	-3.210696	-2.919900
C	7.886822	-0.581588	0.842194
C	7.825708	1.099370	-0.958258
C	7.260481	-1.730795	1.344553
C	9.249087	-0.387680	1.131550
C	9.182390	1.447701	-0.834223
C	7.143366	1.499125	-2.115811
C	7.975345	-2.660650	2.098253
H	6.205726	-1.898992	1.161505
C	9.967342	-1.343103	1.848900
C	9.840901	2.121735	-1.861534
H	6.091168	1.267476	-2.232075
C	7.797912	2.210894	-3.120135
C	9.333300	-2.480812	2.345427
H	7.459022	-3.535257	2.482896
H	11.024747	-1.177541	2.035268
C	9.151116	2.516582	-3.006632
H	10.895749	2.355265	-1.747390
H	7.238910	2.515748	-3.999984
H	9.894966	-3.210607	2.920028
H	9.666399	3.058252	-3.793582
N	7.180751	0.381463	0.078945
N	-7.180752	0.381455	-0.078949
S	-10.033052	1.141272	-0.691652
S	10.033052	1.141286	0.691635

Table S8. Cartesian coordinates (Å) for the optimized ground-state structure of **4d**.

Atom	x	y	z
C	-1.464781	-0.180766	-0.021317
C	-0.724150	1.048799	-0.007438
C	-0.712472	-1.332184	-0.009167
C	0.724150	1.048799	0.007438
C	0.712472	-1.332184	0.009167
H	-1.220858	-2.292459	0.000581
C	1.464781	-0.180765	0.021317

H	1.220858	-2.292459	-0.000581
N	-1.249073	2.279933	-0.018441
N	1.249073	2.279933	0.018441
S	0.000000	3.322283	0.000000
C	2.945508	-0.213856	0.060447
C	3.603329	-1.120314	0.903163
C	3.717749	0.632344	-0.750606
C	4.994498	-1.189554	0.931212
H	3.022738	-1.760357	1.561959
C	5.105908	0.560699	-0.726400
H	3.229129	1.344710	-1.406199
C	5.749442	-0.350383	0.115599
H	5.505127	-1.884917	1.590309
H	5.702040	1.211484	-1.359691
C	-2.945507	-0.213856	-0.060446
C	-3.717749	0.632344	0.750606
C	-3.603329	-1.120315	-0.903162
C	-5.105908	0.560699	0.726400
H	-3.229129	1.344710	1.406198
C	-4.994498	-1.189555	-0.931211
H	-3.022738	-1.760357	-1.561958
C	-5.749442	-0.350383	-0.115599
H	-5.702040	1.211485	1.359691
H	-5.505127	-1.884917	-1.590309
C	7.886326	0.566581	0.866352
C	7.845054	-1.107376	-0.886194
C	7.256130	1.620985	1.523211
C	9.292389	0.447506	0.931124
C	9.251731	-1.210794	-0.804969
C	7.174615	-1.698955	-1.954345
C	8.003750	2.566402	2.234722
H	6.175128	1.702375	1.497469
C	10.029033	1.420007	1.606034
C	9.948178	-1.857614	-1.825101
H	6.093012	-1.642691	-2.007574
C	7.881715	-2.383906	-2.949350
C	9.386854	2.472924	2.268534

H	7.490152	3.372018	2.750437
H	11.111801	1.361817	1.628262
C	9.265287	-2.455353	-2.891157
H	11.031111	-1.908263	-1.794636
H	7.337016	-2.849174	-3.765257
H	9.979388	3.208570	2.803889
H	9.826949	-2.970183	-3.664681
C	-7.845054	-1.107376	0.886194
C	-7.886326	0.566581	-0.866352
C	-7.174616	-1.698955	1.954345
C	-9.251731	-1.210794	0.804969
C	-9.292389	0.447506	-0.931124
C	-7.256130	1.620985	-1.523211
C	-7.881716	-2.383907	2.949350
H	-6.093012	-1.642692	2.007575
C	-9.948178	-1.857614	1.825101
C	-10.029032	1.420007	-1.606034
H	-6.175127	1.702375	-1.497469
C	-8.003749	2.566402	-2.234722
C	-9.265288	-2.455353	2.891156
H	-7.337016	-2.849174	3.765257
H	-11.031112	-1.908263	1.794635
C	-9.386854	2.472924	-2.268535
H	-11.111801	1.361817	-1.628262
H	-7.490152	3.372018	-2.750437
H	-9.826950	-2.970183	3.664680
H	-9.979387	3.208570	-2.803890
N	-7.176199	-0.431632	-0.159879
N	7.176199	-0.431631	0.159879
N	9.879589	-0.684300	0.337665
N	-9.879589	-0.684300	-0.337666
C	11.273845	-0.973114	0.580771
H	11.463842	-2.027211	0.363235
H	11.958766	-0.357522	-0.024570
H	11.494162	-0.806943	1.638288
C	-11.273845	-0.973114	-0.580771
H	-11.463842	-2.027210	-0.363235

H	-11.958766	-0.357521	0.024570
H	-11.494162	-0.806943	-1.638288

Table S9. Cartesian coordinates (Å) for the optimized ground-state structure of **4e**.

Atom	x	y	z
C	1.465438	-0.147619	-0.002010
C	0.724386	-1.377252	0.001437
C	0.712234	1.004460	0.000556
C	-0.724375	-1.377257	-0.002278
C	-0.712240	1.004455	-0.001401
H	1.218916	1.965355	0.019114
C	-1.465436	-0.147629	0.001177
H	-1.218929	1.965346	-0.019953
N	1.249246	-2.608914	-0.003046
N	-1.249225	-2.608924	0.002202
S	0.000014	-3.651909	-0.000424
C	-2.945991	-0.115125	0.021776
C	-3.616766	0.810310	0.835690
C	-3.709854	-0.981803	-0.774484
C	-5.006776	0.871110	0.858130
H	-3.046414	1.464387	1.489264
C	-5.098872	-0.911473	-0.771803
H	-3.215472	-1.704176	-1.413846
C	-5.751991	0.011188	0.048797
H	-5.518460	1.568678	1.514336
H	-5.683088	-1.567424	-1.410096
C	2.945993	-0.115104	-0.022557
C	3.709826	-0.981776	0.773739
C	3.616798	0.810343	-0.836432
C	5.098843	-0.911422	0.771138
H	3.215419	-1.704160	1.413067
C	5.006810	0.871166	-0.858793
H	3.046472	1.464416	-1.490033
C	5.751992	0.011257	-0.049418
H	5.683032	-1.567366	1.409462
H	5.518520	1.568746	-1.514966
C	-8.017555	-0.977409	0.425905

C	-7.946310	1.166644	-0.283592
C	-7.697943	-2.262343	0.871760
C	-9.358256	-0.544581	0.306707
C	-9.312750	0.828282	-0.149228
C	-7.543462	2.425307	-0.736982
C	-8.748623	-3.119664	1.173889
H	-6.667593	-2.587564	0.973472
C	-10.400514	-1.412807	0.638526
C	-10.295136	1.774060	-0.449914
H	-6.494265	2.674291	-0.859263
C	-8.535578	3.345574	-1.052212
C	-10.088166	-2.701370	1.062013
H	-8.544701	-4.133406	1.504770
H	-11.438836	-1.101099	0.576065
C	-9.899061	3.028631	-0.904271
H	-11.351523	1.547580	-0.340477
H	-8.266758	4.328674	-1.426433
C	7.946251	1.166755	0.283212
C	8.017618	-0.977296	-0.426280
C	7.543327	2.425411	0.736556
C	9.312714	0.828400	0.149063
C	9.358299	-0.544463	-0.306867
C	7.698084	-2.262235	-0.872176
C	8.535390	3.345676	1.051959
H	6.494110	2.674390	0.858674
C	10.295049	1.774176	0.449920
C	10.400613	-1.412691	-0.638501
H	6.667751	-2.587460	-0.974053
C	8.748816	-3.119558	-1.174118
C	9.898897	3.028738	0.904234
H	8.266507	4.328769	1.426153
H	11.351454	1.547699	0.340652
C	10.088339	-2.701262	-1.062018
H	11.438925	-1.100982	-0.575865
H	8.544951	-4.133306	-1.505016
N	7.169401	0.066752	-0.067683
N	-7.169400	0.066642	0.067167

C	11.083105	5.211339	0.587610
C	11.793595	3.900185	2.285637
C	10.420009	5.734057	-0.525364
C	12.141560	5.904808	1.220425
C	11.953554	2.874892	3.220916
C	12.597918	5.063646	2.307943
C	10.830131	6.979729	-0.991897
H	9.618496	5.186417	-1.011778
C	12.534568	7.154862	0.731695
C	12.949041	3.029773	4.181225
H	11.322787	1.991406	3.201646
C	13.591686	5.194695	3.283439
C	11.874327	7.687560	-0.371196
H	10.333298	7.411059	-1.856312
H	13.345747	7.700964	1.205204
C	13.763867	4.175051	4.214312
H	13.096953	2.248086	4.920884
H	14.219175	6.081112	3.314568
H	12.169261	8.657315	-0.760708
H	14.532685	4.263340	4.976008
N	10.880146	3.999109	1.239888
C	12.078036	-4.110699	-0.498369
C	11.373216	-4.151311	-2.645363
C	12.220018	-3.865021	0.869534
C	12.943210	-4.988293	-1.193016
C	10.697206	-3.924035	-3.846638
C	12.490656	-5.015414	-2.568862
C	13.259168	-4.509476	1.534495
H	11.543353	-3.198397	1.395399
C	13.979737	-5.623567	-0.501406
C	11.154930	-4.592307	-4.978552
H	9.849690	-3.247262	-3.896953
C	12.930828	-5.674717	-3.721149
C	14.134066	-5.378648	0.859490
H	13.394425	-4.336389	2.598342
H	14.653793	-6.299974	-1.019639
C	12.258170	-5.461822	-4.920429

H	10.648922	-4.434854	-5.926826
H	13.787592	-6.341611	-3.680634
H	14.935666	-5.863934	1.408153
H	12.589088	-5.967837	-5.822406
C	-11.083210	5.211225	-0.587403
C	-11.793995	3.900107	-2.285334
C	-10.419918	5.733916	0.525466
C	-12.141774	5.904709	-1.220020
C	-11.954112	2.874833	-3.220605
C	-12.598320	5.063570	-2.307478
C	-10.829953	6.979580	0.992097
H	-9.618321	5.186263	1.011727
C	-12.534692	7.154755	-0.731194
C	-12.949762	3.029734	-4.180742
H	-11.323342	1.991346	-3.201459
C	-13.592252	5.194640	-3.282803
C	-11.874256	7.687427	0.371593
H	-10.332967	7.410891	1.856434
H	-13.345952	7.700869	-1.204548
C	-13.764592	4.175014	-4.213668
H	-13.097800	2.248062	-4.920392
H	-14.219746	6.081058	-3.313809
H	-12.169118	8.657174	0.761177
H	-14.533537	4.263320	-4.975234
C	-12.077994	-4.110801	0.498791
C	-11.372753	-4.151353	2.645648
C	-12.220243	-3.865170	-0.869092
C	-12.943054	-4.988347	1.193642
C	-10.696503	-3.924045	3.846783
C	-12.490231	-5.015429	2.569400
C	-13.259543	-4.509622	-1.533822
H	-11.543666	-3.198583	-1.395117
C	-13.979736	-5.623618	0.502262
C	-11.154023	-4.592262	4.978813
H	-9.848961	-3.247291	3.896908
C	-12.930193	-5.674677	3.721799
C	-14.134330	-5.378745	-0.858611

H	-13.395007	-4.336569	-2.597649
H	-14.653707	-6.299987	1.020656
C	-12.257294	-5.461752	4.920939
H	-10.647825	-4.434783	5.926981
H	-13.786982	-6.341551	3.681478
H	-14.936053	-5.864029	-1.407097
H	-12.588048	-5.967724	5.823000
N	-10.880366	3.999008	-1.239741
N	-11.130638	-3.609131	1.386884
N	11.130871	-3.609034	-1.386667

Table S10. Cartesian coordinates (Å) for the optimized ground-state structure of **4f**.

Atom	x	y	z
C	-1.465914	-0.209614	-0.017502
C	-0.724407	-1.439169	-0.011617
C	-0.711932	0.942251	-0.009505
C	0.724922	-1.439174	0.012383
C	0.712455	0.942246	0.011095
H	-1.218998	1.902861	-0.033893
C	1.466433	-0.209624	0.018679
H	1.219524	1.902846	0.035809
N	-1.249625	-2.670741	-0.014722
N	1.250140	-2.670747	0.015072
S	0.000257	-3.713908	-0.000002
C	2.946662	-0.176501	0.016484
C	3.628066	0.740099	-0.798554
C	3.702444	-1.031657	0.832615
C	5.017914	0.802571	-0.803888
H	3.065594	1.385006	-1.468144
C	5.090952	-0.956680	0.850303
H	3.200848	-1.747055	1.474551
C	5.757371	-0.043612	0.027317
H	5.535349	1.490391	-1.465649
H	5.665563	-1.600171	1.509444
C	-2.946143	-0.176485	-0.015366
C	-3.701879	-1.031365	-0.831829
C	-3.627591	0.739856	0.799925

C	-5.090384	-0.956357	-0.849598
H	-3.200246	-1.746563	-1.473959
C	-5.017439	0.802351	0.805174
H	-3.065159	1.384534	1.469768
C	-5.756850	-0.043539	-0.026370
H	-5.664959	-1.599622	-1.508993
H	-5.534914	1.489959	1.467124
C	8.033108	-1.053948	-0.210919
C	7.940853	1.155090	0.266658
C	7.740209	-2.381590	-0.533172
C	9.367873	-0.599731	-0.126469
C	9.308952	0.814000	0.180322
C	7.539324	2.454498	0.586843
C	8.804083	-3.251552	-0.735553
H	6.717071	-2.734132	-0.616431
C	10.424759	-1.481046	-0.363957
C	10.288762	1.780927	0.414670
H	6.490470	2.720513	0.671373
C	8.526969	3.411035	0.785503
C	10.143692	-2.815220	-0.656730
H	8.607008	-4.292828	-0.971579
H	11.454941	-1.140854	-0.317435
C	9.898129	3.087841	0.705355
H	11.343614	1.527681	0.366712
H	8.244148	4.432823	1.019585
C	-7.940275	1.155287	-0.265614
C	-8.032643	-1.053904	0.211230
C	-7.538681	2.454794	-0.585349
C	-9.308386	0.814191	-0.179604
C	-9.367384	-0.599652	0.126631
C	-7.739835	-2.381656	0.533112
C	-8.526284	3.411401	-0.783827
H	-6.489809	2.720809	-0.669667
C	-10.288159	1.781231	-0.413680
C	-10.424344	-1.481058	0.363447
H	-6.716719	-2.734228	0.616520
C	-8.803769	-3.251684	0.734892

C	-9.897463	3.088236	-0.703846
H	-8.243452	4.433267	-1.017549
H	-11.343014	1.527965	-0.365895
C	-10.143364	-2.815356	0.655760
H	-11.454503	-1.140826	0.316727
H	-8.606777	-4.293056	0.970559
N	-7.169805	0.016542	-0.028549
N	7.170330	0.016426	0.029385
N	-11.198274	-3.742168	0.873439
N	-10.871667	4.100358	-0.917574
N	10.872527	4.099712	0.919348
N	11.198646	-3.741839	-0.875099
C	-12.319501	-3.738253	0.008754
C	-12.145859	-3.603244	-1.376928
C	-13.620416	-3.859418	0.511192
C	-13.247079	-3.581952	-2.225835
H	-11.142907	-3.509417	-1.782720
C	-14.713657	-3.857605	-0.354299
H	-13.775607	-3.959217	1.581273
C	-14.553874	-3.712947	-1.735689
H	-13.085055	-3.473957	-3.296345
H	-15.713330	-3.956363	0.062975
C	-11.165800	-4.587306	2.007802
C	-10.667219	-4.127630	3.232680
C	-11.622847	-5.911461	1.924755
C	-10.621161	-4.975587	4.338579
H	-10.312267	-3.104881	3.317411
C	-11.590176	-6.738772	3.042064
H	-12.008262	-6.285724	0.980988
C	-11.083988	-6.293087	4.271055
H	-10.227097	-4.592619	5.277366
H	-11.953801	-7.760301	2.951513
C	-11.989737	4.185686	-0.052816
C	-11.827910	4.033436	1.332501
C	-13.276336	4.412915	-0.555066
C	-12.927489	4.098815	2.181230
H	-10.836039	3.857146	1.738033

C	-14.366511	4.497042	0.310329
H	-13.422620	4.527046	-1.624967
C	-14.219295	4.336374	1.691294
H	-12.775196	3.974580	3.251401
H	-15.354878	4.676710	-0.106798
C	-10.770028	4.944081	-2.048807
C	-10.311751	4.449931	-3.275868
C	-11.115544	6.301397	-1.959850
C	-10.196039	5.296024	-4.378312
H	-10.042275	3.401801	-3.365163
C	-11.014841	7.127893	-3.073549
H	-11.467656	6.702285	-1.013995
C	-10.548416	6.646823	-4.305074
H	-9.835179	4.885726	-5.318892
H	-11.291957	8.175801	-2.978341
C	12.319207	-3.739608	-0.009601
C	12.144913	-3.604653	1.376011
C	13.620277	-3.862539	-0.511238
C	13.245643	-3.585140	2.225600
H	11.141863	-3.509488	1.781243
C	14.712980	-3.862490	0.354925
H	13.775981	-3.962295	-1.581246
C	14.552553	-3.717903	1.736249
H	13.083102	-3.477150	3.296032
H	15.712768	-3.962588	-0.061753
C	11.165695	-4.587371	-2.009138
C	10.665686	-4.128732	-3.233625
C	11.620739	-5.912345	-1.924982
C	10.617035	-4.978089	-4.338568
H	10.309116	-3.106559	-3.318452
C	11.585485	-6.740861	-3.041093
H	12.004119	-6.286792	-0.980459
C	11.079735	-6.295419	-4.270552
H	10.220051	-4.596316	-5.276581
H	11.945601	-7.763551	-2.949304
C	11.989308	4.186843	0.053157
C	11.826252	4.034076	-1.331959

C	13.276062	4.416537	0.553933
C	12.924796	4.101333	-2.181906
H	10.834282	3.855938	-1.736431
C	14.365121	4.502516	-0.312657
H	13.423284	4.531154	1.623652
C	14.216695	4.341322	-1.693442
H	12.771541	3.976658	-3.251888
H	15.353611	4.684089	0.103354
C	10.770143	4.944686	2.049564
C	10.310926	4.451838	3.276832
C	11.112973	6.302533	1.958679
C	10.192536	5.299499	4.377737
H	10.040509	3.404012	3.366825
C	11.009613	7.130692	3.070946
H	11.462801	6.703099	1.011841
C	10.544163	6.650477	4.303115
H	9.829345	4.890541	5.318000
H	11.282910	8.179425	2.973777
C	-15.401379	4.405794	2.628802
H	-15.245190	5.157021	3.411892
H	-16.319769	4.667110	2.093862
H	-15.568962	3.443999	3.128328
C	-10.426864	7.564409	-5.498590
H	-9.679865	8.348107	-5.323034
H	-10.126114	7.013883	-6.395504
H	-11.378165	8.063871	-5.716008
C	15.397668	4.412528	-2.632217
H	15.238500	5.161818	-3.416553
H	16.315792	4.677552	-2.098646
H	15.567637	3.450298	-3.130109
C	10.440158	7.564564	5.500947
H	9.937333	7.069684	6.337752
H	11.432130	7.878689	5.848024
H	9.875950	8.473328	5.261340
C	11.045208	-7.211827	-5.470634
H	12.057369	-7.495054	-5.783835
H	10.501535	-8.137801	-5.249321

H	10.555001	-6.732837	-6.323976
C	15.736197	-3.692739	2.674033
H	15.621182	-4.425952	3.480803
H	16.667914	-3.919654	2.146449
H	15.850464	-2.707594	3.142411
C	-11.030573	-7.214181	5.466846
H	-11.998929	-7.696359	5.642834
H	-10.290881	-8.011093	5.321218
H	-10.757062	-6.670632	6.376693
C	-15.738059	-3.685899	-2.672736
H	-15.624574	-4.419087	-3.479746
H	-16.669770	-3.911621	-2.144630
H	-15.851221	-2.700486	-3.140816

Table S11. Cartesian coordinates (Å) for the optimized ground-state structure of **7**.

Atom	x	y	z
C	-0.741529	2.381510	-0.177355
C	-0.762705	0.003235	-0.082034
C	0.702434	2.364135	-0.030533
C	0.648122	-0.013302	0.069429
H	-1.269394	-0.957317	-0.107796
H	1.123793	-0.984092	0.176130
N	-1.240234	3.618007	-0.277561
N	1.241443	3.587746	-0.030918
S	0.017674	4.647480	-0.197122
C	2.882405	1.084866	0.227420
C	3.739080	2.072400	0.665899
S	3.769330	-0.361471	-0.176931
C	5.099918	1.667406	0.692962
H	3.395663	3.055305	0.958739
C	5.284365	0.378351	0.269177
H	5.922141	2.298521	1.011440
C	-2.960978	1.153749	-0.340362
C	-3.787138	2.136005	-0.839366
S	-3.885241	-0.247188	0.142975
C	-5.160124	1.767573	-0.852906
H	-3.415669	3.090410	-1.186456

C	-5.388131	0.513992	-0.360582
H	-5.963187	2.400134	-1.212858
C	7.304725	-0.165121	-0.982544
C	7.034722	-0.970934	1.298923
C	7.076709	0.833902	-1.924090
C	8.380257	-1.062359	-1.156015
C	8.113337	-1.858475	1.096992
C	6.544670	-0.756861	2.583696
C	7.908030	0.958808	-3.042598
H	6.236242	1.507344	-1.795832
C	9.228808	-0.899311	-2.252062
C	8.701148	-2.473739	2.203259
H	5.703642	-0.087850	2.730211
C	7.114038	-1.414250	3.679890
C	8.986545	0.100163	-3.201288
H	7.704427	1.733792	-3.774943
H	10.082639	-1.555415	-2.380126
C	8.195023	-2.263694	3.491034
H	9.554903	-3.128935	2.069846
H	6.707520	-1.247217	4.672476
H	9.648714	0.195749	-4.056369
H	8.656241	-2.768133	4.334578
C	-7.256402	-0.168712	1.036068
C	-6.987816	-1.114137	-1.195156
C	-6.692113	0.420614	2.164195
C	-8.516900	-0.797270	1.133094
C	-8.251557	-1.730911	-1.068225
C	-6.160616	-1.453548	-2.262424
C	-7.352634	0.380395	3.396837
H	-5.739883	0.932592	2.083385
C	-9.145537	-0.868092	2.377472
C	-8.619685	-2.718161	-1.983950
H	-5.205233	-0.955103	-2.381112
C	-6.559802	-2.413509	-3.198682
C	-8.571699	-0.272481	3.505926
H	-6.898845	0.856806	4.260144
H	-10.092600	-1.386633	2.476975

C	-7.781979	-3.053280	-3.053260
H	-9.567720	-3.232647	-1.873047
H	-5.903223	-2.653215	-4.029173
H	-9.087902	-0.327002	4.459483
H	-8.097965	-3.812801	-3.761759
N	6.476461	-0.349398	0.153489
N	-6.628868	-0.128264	-0.237771
C	-1.503485	1.161166	-0.202681
C	1.425359	1.126467	0.094223
N	-9.104445	-1.289628	-0.043636
N	8.521090	-2.107102	-0.225420
C	9.448680	-3.182391	-0.495224
H	10.495929	-2.919032	-0.277152
H	9.172238	-4.052357	0.105551
H	9.369340	-3.467434	-1.547181
C	-10.489356	-1.702938	-0.035319
H	-10.876567	-1.677622	-1.056892
H	-10.639376	-2.713700	0.375869
H	-11.071343	-0.992372	0.556784

Table S12. Cartesian coordinates (Å) for the optimized ground-state structure of **9**.

Atom	x	y	z
C	1.470108	0.028669	-0.000771
C	0.725797	1.257789	-0.002739
C	0.711723	-1.121760	-0.004132
C	-0.725797	1.257789	0.002741
C	-0.711723	-1.121760	0.004133
H	1.217393	-2.083177	-0.027470
C	-1.470108	0.028669	0.000772
H	-1.217392	-2.083177	0.027471
N	1.250392	2.490151	0.001240
N	-1.250392	2.490151	-0.001239
S	0.000000	3.534298	0.000001
C	-2.946859	-0.007525	-0.018262
C	-3.631616	-0.957119	-0.770739
C	-3.727004	0.875686	0.721033
C	-5.021593	-1.051873	-0.791473

H	-3.054290	-1.634801	-1.391370
C	-5.118764	0.823288	0.735160
H	-3.226720	1.633135	1.310888
C	-5.797352	-0.154801	-0.024682
C	-5.617950	-2.130818	-1.679413
C	-5.824650	1.863921	1.587310
N	-7.212562	-0.229900	-0.022221
C	-7.134682	-2.135138	-1.584454
C	-5.078763	-3.513341	-1.226080
C	-5.205941	-1.858484	-3.150297
C	-7.332327	1.687879	1.522611
C	-5.361152	1.711099	3.060094
C	-5.455121	3.275079	1.058420
C	-7.971368	0.687094	0.757020
C	-7.872032	-1.225325	-0.793780
C	-7.807399	-3.100542	-2.337064
H	-3.987451	-3.556579	-1.294839
H	-5.364030	-3.711251	-0.187908
H	-5.476007	-4.320646	-1.848461
H	-5.608757	-2.622083	-3.822933
H	-5.582363	-0.883766	-3.476510
H	-4.117480	-1.858899	-3.264999
C	-8.101095	2.581420	2.271936
H	-5.614640	0.715306	3.437833
H	-4.279417	1.846514	3.152379
H	-5.839785	2.452680	3.706712
H	-5.796307	3.394322	0.025096
H	-5.919786	4.059698	1.663749
H	-4.373156	3.435848	1.078061
C	-9.381827	0.619379	0.783214
C	-9.280851	-1.328157	-0.790174
C	-9.187610	-3.208160	-2.335003
H	-7.231560	-3.790216	-2.945310
C	-9.483945	2.521078	2.300462
H	-7.599973	3.349328	2.851865
C	-10.103954	1.534320	1.553318
C	-10.188881	-0.411061	0.011635

C	-9.904420	-2.316028	-1.556104
H	-9.691319	-3.966992	-2.925421
H	-10.063323	3.224354	2.890311
H	-11.187031	1.472033	1.568018
C	-11.147134	0.325162	-0.961973
C	-11.007760	-1.264569	1.015881
H	-10.986929	-2.387955	-1.543031
H	-10.575615	0.929561	-1.673538
H	-11.758784	-0.382324	-1.529901
H	-11.830044	0.988595	-0.422842
H	-11.687428	-0.641567	1.605323
H	-11.614414	-2.014080	0.498365
H	-10.337802	-1.786150	1.706839
C	2.946859	-0.007525	0.018262
C	3.631617	-0.957118	0.770739
C	3.727004	0.875686	-0.721032
C	5.021593	-1.051873	0.791474
H	3.054291	-1.634800	1.391371
C	5.118764	0.823288	-0.735160
H	3.226719	1.633135	-1.310887
C	5.797352	-0.154801	0.024682
C	5.617951	-2.130818	1.679413
C	5.824650	1.863920	-1.587311
N	7.212562	-0.229900	0.022221
C	7.134683	-2.135138	1.584454
C	5.078763	-3.513340	1.226081
C	5.205941	-1.858483	3.150298
C	7.332327	1.687879	-1.522612
C	5.361151	1.711098	-3.060095
C	5.455122	3.275078	-1.058421
C	7.971368	0.687094	-0.757020
C	7.872032	-1.225324	0.793780
C	7.807400	-3.100541	2.337065
H	3.987452	-3.556579	1.294840
H	5.364030	-3.711251	0.187909
H	5.476008	-4.320645	1.848462
H	5.608757	-2.622083	3.822933

H	5.582363	-0.883765	3.476510
H	4.117481	-1.858899	3.265000
C	8.101095	2.581418	-2.271937
H	5.614639	0.715305	-3.437833
H	4.279416	1.846513	-3.152379
H	5.839784	2.452679	-3.706713
H	5.796308	3.394322	-0.025097
H	5.919786	4.059697	-1.663750
H	4.373156	3.435848	-1.078062
C	9.381827	0.619378	-0.783215
C	9.280851	-1.328157	0.790174
C	9.187611	-3.208159	2.335004
H	7.231560	-3.790215	2.945311
C	9.483945	2.521076	-2.300465
H	7.599973	3.349327	-2.851867
C	10.103954	1.534319	-1.553320
C	10.188881	-0.411061	-0.011636
C	9.904420	-2.316027	1.556104
H	9.691319	-3.966990	2.925423
H	10.063322	3.224353	-2.890314
H	11.187031	1.472033	-1.568020
C	11.147134	0.325163	0.961972
C	11.007760	-1.264569	-1.015881
H	10.986929	-2.387954	1.543032
H	10.575615	0.929563	1.673537
H	11.758784	-0.382323	1.529900
H	11.830043	0.988596	0.422841
H	11.687429	-0.641567	-1.605323
H	11.614414	-2.014080	-0.498365
H	10.337803	-1.786151	-1.706839