Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Substituted diethynyldithia[3.3]paracyclophanes—a synthetically more accessible new building blocks for molecular scaffolding

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1. Uv-Vis absorption spectra of **9a-e**, **10**, and **11**

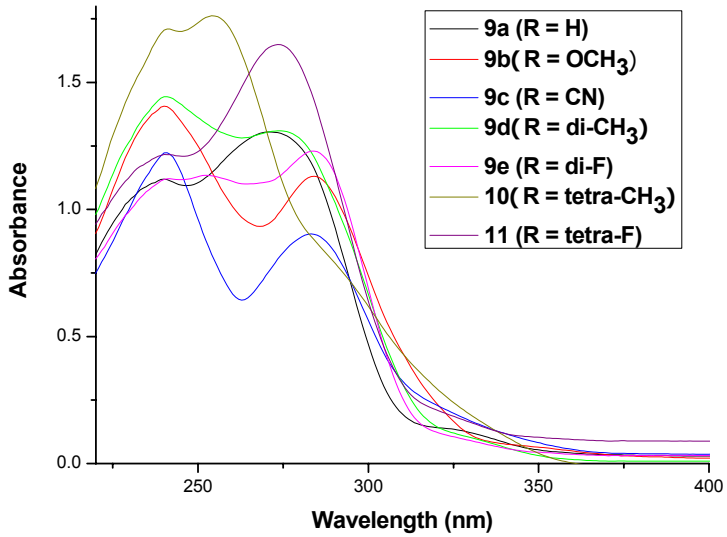

Figure S1 UV-vis absorption spectra of **9a-e**, **10**, and **11** measured in solution (CH_2Cl_2; ca. 1×10^{-5} M) at room temperature.

2. **Crystallographic data of compounds 5b.**

Table S1. Crystal data and structure refinement for **5b**.

Empirical formula	$C_{16}H_{10}Br_2F_4S_2$
Formula weight	502.18
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Fdd2
a (Å)	25.726(2)
b (Å)	28.737(3)

c (Å)	9.0939(8)
α(°)	90
β(°)	90
γ(°)	90
Volume ($Å^3$)	6723.1(11)
Z	16
D_{calcd} (Mg/m^3)	1.985
Abs. coeff. (mm^{-1})	5.107
F(000)	3904
Crystal size (mm^3)	0.20 x 0.10 x 0.10
θ range (°)	2.13 to 28.28
Index ranges	-33<=h<=33, -37<=k<=37, -12<=l<=7
Reflections collected	11877
Independent reflections	3157 [R(int) = 0.1818]
Completeness to theta = 28.28	99.2 %
Absorption correction	None
Max. and min. transmission	0.6291 and 0.4282
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3157 / 1 / 217
Goodness-of-fit on F^2	0.963
Final R indices [I>2sigma(I)]	R1 = 0.0754, wR2 = 0.1728
R indices (all data)	R1 = 0.0955, wR2 = 0.1829
Absolute structure parameter	-0.005(18)
Largest diff. peak and hole	1.459 and -0.995 $e.^{-3}$

Table S2. Bond lengths (Å) and angles (°) for **5b**.

Br(1)-C(10)	1.893(9)
Br(2)-C(13)	1.899(9)
C(1)-C(2)	1.394(12)
C(1)-C(6)	1.396(17)

C(1)-C(7)	1.478(16)
C(2)-C(3)	1.371(13)
C(2)-F(1)	1.383(12)
C(3)-F(2)	1.343(9)
C(3)-C(4)	1.364(14)
C(4)-C(5)	1.392(12)
C(4)-C(16)	1.495(13)
C(5)-C(6)	1.371(16)
C(5)-F(3)	1.375(13)
C(6)-F(4)	1.308(10)
C(7)-S(4)	1.833(13)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.507(12)
C(8)-S(4)	1.813(10)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(14)	1.374(13)
C(9)-C(10)	1.385(11)
C(10)-C(11)	1.380(12)
C(11)-C(12)	1.384(13)
C(11)-H(11)	0.9300
C(12)-C(13)	1.387(11)
C(12)-C(15)	1.519(13)
C(13)-C(14)	1.395(13)
C(14)-H(14)	0.9300
C(15)-S(3)	1.808(9)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-S(3)	1.813(11)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700

C(2)-C(1)-C(6)	115.4(9)
C(2)-C(1)-C(7)	120.0(11)
C(6)-C(1)-C(7)	124.5(9)
C(3)-C(2)-F(1)	118.0(7)
C(3)-C(2)-C(1)	122.5(10)

F(1)-C(2)-C(1)	119.4(9)
F(2)-C(3)-C(4)	119.5(8)
F(2)-C(3)-C(2)	118.0(8)
C(4)-C(3)-C(2)	122.5(7)
C(3)-C(4)-C(5)	115.2(9)
C(3)-C(4)-C(16)	121.3(8)
C(5)-C(4)-C(16)	123.5(9)
C(6)-C(5)-F(3)	118.9(8)
C(6)-C(5)-C(4)	123.4(9)
F(3)-C(5)-C(4)	117.6(9)
F(4)-C(6)-C(5)	118.4(12)
F(4)-C(6)-C(1)	120.8(11)
C(5)-C(6)-C(1)	120.7(7)
C(1)-C(7)-S(4)	114.4(8)
C(1)-C(7)-H(7A)	108.7
S(4)-C(7)-H(7A)	108.7
C(1)-C(7)-H(7B)	108.7
S(4)-C(7)-H(7B)	108.7
H(7A)-C(7)-H(7B)	107.6
C(9)-C(8)-S(4)	114.7(7)
C(9)-C(8)-H(8A)	108.6
S(4)-C(8)-H(8A)	108.6
C(9)-C(8)-H(8B)	108.6
S(4)-C(8)-H(8B)	108.6
H(8A)-C(8)-H(8B)	107.6
C(14)-C(9)-C(10)	117.7(8)
C(14)-C(9)-C(8)	120.9(7)
C(10)-C(9)-C(8)	121.4(9)
C(11)-C(10)-C(9)	119.9(8)
C(11)-C(10)-Br(1)	118.0(5)
C(9)-C(10)-Br(1)	122.1(7)
C(10)-C(11)-C(12)	123.5(6)
C(10)-C(11)-H(11)	118.2
C(12)-C(11)-H(11)	118.2
C(11)-C(12)-C(13)	115.1(8)
C(11)-C(12)-C(15)	122.4(7)
C(13)-C(12)-C(15)	122.4(9)
C(12)-C(13)-C(14)	121.9(8)

C(12)-C(13)-Br(2)	121.6(7)
C(14)-C(13)-Br(2)	116.3(6)
C(9)-C(14)-C(13)	121.0(7)
C(9)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(12)-C(15)-S(3)	113.1(6)
C(12)-C(15)-H(15A)	109.0
S(3)-C(15)-H(15A)	109.0
C(12)-C(15)-H(15B)	109.0
S(3)-C(15)-H(15B)	109.0
H(15A)-C(15)-H(15B)	107.8
C(4)-C(16)-S(3)	117.1(7)
C(4)-C(16)-H(16A)	108.0
S(3)-C(16)-H(16A)	108.0
C(4)-C(16)-H(16B)	108.0
S(3)-C(16)-H(16B)	108.0
H(16A)-C(16)-H(16B)	107.3
C(15)-S(3)-C(16)	103.7(5)
C(8)-S(4)-C(7)	104.0(6)

3. Molecular modelling coordinates of compounds 9a-e, 10, and 11.

Table S3: Atom coordinates and total energies (in Hartrees) of **9a**, according to B3LYP/6-31+G(d,p) calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.407656	-1.005798	-1.671144
2	6	0	0.804652	0.115437	-2.257759
3	6	0	-0.583605	0.239237	-2.311852
4	6	0	-1.411451	-0.751763	-1.769556
5	6	0	-0.809177	-1.921620	-1.284750
6	6	0	0.579055	-2.050157	-1.240735
7	6	0	2.901855	-1.038006	-1.445422
8	1	0	3.378889	-0.157459	-1.885269

9	1	0	3.359436	-1.921115	-1.905443
10	6	0	2.916355	0.367075	1.144302
11	1	0	3.401056	0.291793	2.124273
12	1	0	3.366453	1.216687	0.627660
13	6	0	1.421844	0.559399	1.291327
14	6	0	0.779081	1.733006	0.825180
15	6	0	-0.625691	1.792820	0.804044
16	1	0	-1.099234	2.665301	0.365363
17	6	0	-1.419390	0.731949	1.233461
18	6	0	-0.775767	-0.380951	1.827882
19	6	0	0.628979	-0.444003	1.841952
20	1	0	1.102359	-1.342341	2.224504
21	6	0	-2.913962	0.748967	1.004487
22	1	0	-3.377908	1.607628	1.502104
23	1	0	-3.380006	-0.151654	1.407711
24	6	0	-2.905974	-0.552254	-1.642440
25	1	0	-3.372171	-1.422601	-1.171788
26	1	0	-3.377750	-0.422519	-2.623327
27	16	0	-3.454473	0.979876	-0.753758
28	16	0	3.453106	-1.201515	0.319443
29	1	0	1.426045	0.928015	-2.626013
30	1	0	-1.024432	1.150271	-2.707053
31	1	0	1.020205	-2.937945	-0.795705
32	1	0	-1.430274	-2.718417	-0.883258
33	6	0	1.521056	2.845913	0.317426
34	6	0	-1.516840	-1.479946	2.366360
35	6	0	-2.122338	-2.421253	2.834552
36	1	0	-2.653906	-3.244410	3.255138
37	6	0	2.127445	3.804338	-0.113426
38	1	0	2.660412	4.650658	-0.483181

HF=-1568.05769898

Table S4: Atom coordinates and total energies (in Hartrees) of **9b**, according to B3LYP/6-31+G(d,p) calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	1.353483	0.418472	-1.596883
2	6	0	0.307523	1.349067	-1.644705
3	6	0	-1.032137	0.947959	-1.676828

4	6	0	-1.353134	-0.419464	-1.596826
5	6	0	-0.307166	-1.350081	-1.644151
6	6	0	1.032496	-0.948995	-1.676312
7	6	0	2.776222	0.887722	-1.434742
8	1	0	2.834817	1.970584	-1.575221
9	1	0	3.434210	0.415532	-2.170966
10	6	0	2.639363	1.245513	1.491638
11	1	0	3.288718	1.143573	2.368949
12	1	0	2.535685	2.314729	1.296255
13	6	0	1.284294	0.613375	1.737173
14	6	0	0.109184	1.399121	1.824286
15	6	0	-1.149287	0.771535	1.812761
16	1	0	-2.038017	1.392609	1.774862
17	6	0	-1.284670	-0.612275	1.737394
18	6	0	-0.109547	-1.398004	1.824665
19	6	0	1.148906	-0.770427	1.812895
20	1	0	2.037647	-1.391504	1.775129
21	6	0	-2.639762	-1.244470	1.492061
22	1	0	-3.289281	-1.141662	2.369160
23	1	0	-2.536153	-2.313880	1.297679
24	6	0	-2.775894	-0.888641	-1.434684
25	1	0	-2.834458	-1.971582	-1.574563
26	1	0	-3.433743	-0.416850	-2.171290
27	16	0	-3.641794	-0.456295	0.155831
28	16	0	3.641759	0.456319	0.156212
29	1	0	0.558554	2.403368	-1.618649
30	1	0	-0.558203	-2.404372	-1.617676
31	6	0	0.164167	2.828475	1.859170
32	6	0	-0.164557	-2.827349	1.859961
33	6	0	-0.188036	-4.040003	1.900652
34	1	0	-0.212150	-5.104516	1.957905
35	6	0	0.187625	4.041158	1.899021
36	1	0	0.211718	5.105698	1.955765
37	8	0	-2.091389	1.813149	-1.743609
38	8	0	2.091757	-1.814192	-1.742684
39	6	0	-1.832439	3.210175	-1.798325
40	1	0	-2.810457	3.689455	-1.861306
41	1	0	-1.314491	3.557167	-0.896222
42	1	0	-1.241805	3.471964	-2.686067
43	6	0	1.832860	-3.211270	-1.796395
44	1	0	2.810905	-3.690562	-1.858859
45	1	0	1.314764	-3.557611	-0.894130
46	1	0	1.242395	-3.473738	-2.684051

HF=-1797.11057760

Table S5: Atom coordinates and total energies (in Hartrees) of **9c**, according to B3LYP/6-31+G(d,p) calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.377173	-0.389689	1.647975
2	6	0	0.370757	-1.355424	1.695256
3	6	0	-0.989213	-1.007261	1.724115
4	6	0	-1.387936	0.346287	1.653067
5	6	0	-0.381735	1.310721	1.723732
6	6	0	0.978199	0.962012	1.748115
7	6	0	2.817316	-0.807380	1.465345
8	1	0	2.900242	-1.895709	1.523447
9	1	0	3.452594	-0.385084	2.251444
10	6	0	2.744906	-0.991222	-1.475273
11	1	0	3.389137	-0.753693	-2.329533
12	1	0	2.750496	-2.076842	-1.361997
13	6	0	1.337619	-0.477364	-1.692511
14	6	0	0.235741	-1.364122	-1.771924
15	6	0	-1.072191	-0.846202	-1.764032
16	1	0	-1.903106	-1.543811	-1.739442
17	6	0	-1.326420	0.521128	-1.682799
18	6	0	-0.224529	1.409230	-1.747039
19	6	0	1.083360	0.891298	-1.749381
20	1	0	1.914304	1.588413	-1.712947
21	6	0	-2.733769	1.032002	-1.457257
22	1	0	-3.373679	0.824265	-2.322484
23	1	0	-2.736339	2.113564	-1.309925
24	6	0	-2.827560	0.767374	1.474771
25	1	0	-2.912316	1.853607	1.562499
26	1	0	-3.466572	0.322467	2.245185
27	16	0	-3.661692	0.211153	-0.084220
28	16	0	3.662207	-0.209432	-0.072287
29	1	0	0.637520	-2.407320	1.678982
30	1	0	-0.648549	2.362713	1.730406
31	6	0	0.412024	-2.783628	-1.791872
32	6	0	-0.401000	2.828842	-1.741742
33	6	0	-0.521579	4.035745	-1.738001
34	1	0	-0.618027	5.097987	-1.743194

35	6	0	0.532109	-3.990452	-1.809920
36	1	0	0.628175	-5.052470	-1.833928
37	6	0	-1.958091	-2.062755	1.811657
38	6	0	1.946354	2.015576	1.862763
39	7	0	-2.715403	-2.938200	1.932407
40	7	0	2.702358	2.889067	2.004069

HF=-1752.54002534

Table S6: Atom coordinates and total energies (in Hartrees) of **9d**, according to B3LYP/6-31+G(d,p) calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.424635	-0.072771	1.748810
2	6	0	-0.693565	1.119267	1.843077
3	6	0	0.704535	1.162250	1.870952
4	6	0	1.402324	-0.057717	1.754050
5	6	0	0.670864	-1.253333	1.771608
6	6	0	-0.727157	-1.297744	1.792326
7	6	0	-2.923717	0.008185	1.582061
8	1	0	-3.269578	1.030948	1.754637
9	1	0	-3.449545	-0.637852	2.294088
10	6	0	-2.874023	0.498744	-1.333834
11	1	0	-3.464722	0.249433	-2.223019
12	1	0	-3.074831	1.546557	-1.102614
13	6	0	-1.394954	0.281649	-1.578708
14	6	0	-0.492527	1.372186	-1.630225
15	6	0	0.892034	1.126828	-1.632920
16	1	0	1.567342	1.974504	-1.581521
17	6	0	1.415395	-0.162934	-1.591709
18	6	0	0.513059	-1.248212	-1.707970
19	6	0	-0.871638	-1.003058	-1.696664
20	1	0	-1.546994	-1.852151	-1.695832
21	6	0	2.893312	-0.393020	-1.355879
22	1	0	3.489054	-0.063678	-2.215067
23	1	0	3.099412	-1.455343	-1.212957

24	6	0	2.903015	-0.130419	1.593725
25	1	0	3.243801	-1.164637	1.691728
26	1	0	3.423345	0.457035	2.358794
27	16	0	3.637610	0.574440	0.033020
28	16	0	-3.635735	-0.576447	-0.037901
29	1	0	-1.237636	2.061485	1.867363
30	1	0	1.215019	-2.195178	1.738422
31	6	0	-0.951315	2.727143	-1.616861
32	6	0	0.971158	-2.601797	-1.775536
33	6	0	1.336609	-3.756815	-1.841464
34	1	0	1.657351	-4.771457	-1.909289
35	6	0	-1.318887	3.883363	-1.613445
36	1	0	-1.641018	4.899807	-1.620385
37	6	0	1.414189	2.490485	1.986975
38	1	0	0.699486	3.296146	2.175264
39	1	0	2.138423	2.488649	2.811026
40	1	0	1.971243	2.732894	1.075983
41	6	0	-1.438580	-2.629848	1.824879
42	1	0	-0.722617	-3.448991	1.933174
43	1	0	-2.140735	-2.689013	2.665952
44	1	0	-2.019786	-2.801638	0.912858

HF = -1646.69519707

Table S7: Atom coordinates and total energies (in Hartrees) of **9e**, according to B3LYP/6-31+G(d,p) calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.448985	-0.306258	1.721171
2	6	0	-0.719833	0.868503	1.953416
3	6	0	0.667148	0.842170	1.973368
4	6	0	1.413137	-0.312028	1.720820
5	6	0	0.683671	-1.501677	1.581452
6	6	0	-0.703228	-1.482130	1.606406
7	6	0	-2.945690	-0.273851	1.548239
8	1	0	-3.331862	0.711475	1.822266
9	1	0	-3.434050	-1.014623	2.189075

10	6	0	-2.890639	0.521887	-1.285973
11	1	0	-3.455416	0.336971	-2.207089
12	1	0	-3.157165	1.524764	-0.946801
13	6	0	-1.398696	0.418183	-1.528895
14	6	0	-0.560446	1.557170	-1.439513
15	6	0	0.836160	1.393828	-1.463095
16	1	0	1.461454	2.265726	-1.300750
17	6	0	1.432467	0.140293	-1.582107
18	6	0	0.593836	-0.975587	-1.821885
19	6	0	-0.803128	-0.814109	-1.785547
20	1	0	-1.428293	-1.695964	-1.878531
21	6	0	2.923326	-0.024936	-1.382722
22	1	0	3.487072	0.505508	-2.158559
23	1	0	3.210039	-1.076554	-1.439505
24	6	0	2.912481	-0.294924	1.558210
25	1	0	3.287338	-1.317818	1.467755
26	1	0	3.397825	0.161382	2.427115
27	16	0	3.597217	0.726659	0.167625
28	16	0	-3.597346	-0.734166	-0.128824
29	1	0	-1.227025	1.819407	2.081474
30	1	0	1.190971	-2.445363	1.408792
31	6	0	-1.096071	2.871558	-1.260534
32	6	0	1.128271	-2.285124	-2.036829
33	6	0	1.557604	-3.403899	-2.225509
34	1	0	1.929534	-4.387913	-2.400408
35	6	0	-1.528189	3.995397	-1.112785
36	1	0	-1.902397	4.986556	-0.991344
37	9	0	-1.362278	-2.662000	1.454763
38	9	0	1.323931	2.010861	2.198522

HF = -1766.53464582

Table S8: Atom coordinates and total energies (in Hartrees) of **10**, according to B3LYP/6-31+G(d,p) calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.410867	0.152153	1.765778
2	6	0	0.804752	-1.123196	1.875994
3	6	0	-0.597216	-1.226267	1.852659
4	1	0	-1.044345	-2.214735	1.836688

5	6	0	-1.420877	-0.107262	1.762430
6	6	0	-0.815193	1.170277	1.847184
7	6	0	0.586914	1.272837	1.827621
8	1	0	1.034340	2.260665	1.791654
9	6	0	2.898296	0.302414	1.532151
10	1	0	3.372397	-0.672897	1.408778
11	1	0	3.385960	0.789709	2.384319
12	6	0	2.864903	0.509839	-1.427434
13	1	0	3.281380	1.166735	-2.198227
14	1	0	3.445070	-0.409068	-1.465441
15	6	0	1.384998	0.245440	-1.642867
16	6	0	0.926329	-1.089516	-1.716519
17	6	0	-0.458697	-1.357181	-1.733868
18	6	0	-1.375531	-0.287384	-1.640709
19	6	0	-0.916434	1.046055	-1.738968
20	6	0	0.468577	1.313128	-1.760786
21	6	0	1.925085	-2.234775	-1.763084
22	1	0	1.439283	-3.195165	-1.925068
23	1	0	2.486025	-2.325451	-0.826611
24	1	0	2.652722	-2.103926	-2.572112
25	6	0	-0.944410	-2.792039	-1.833486
26	1	0	-0.677956	-3.380007	-0.947912
27	1	0	-0.503277	-3.291555	-2.703160
28	1	0	-2.025146	-2.862318	-1.940894
29	6	0	0.956691	2.744416	-1.893021
30	1	0	0.496923	3.232794	-2.758999
31	1	0	2.034872	2.807271	-2.029032
32	1	0	0.715578	3.346789	-1.009768
33	6	0	-1.915206	2.190306	-1.806742
34	1	0	-1.427273	3.152218	-1.951885
35	1	0	-2.499614	2.276898	-0.884667
36	1	0	-2.622426	2.060995	-2.634296
37	6	0	-2.856621	-0.547412	-1.428344
38	1	0	-3.266319	-1.225675	-2.183970
39	1	0	-3.437650	0.369233	-1.496222
40	6	0	-2.907181	-0.262818	1.525033
41	1	0	-3.380045	0.709283	1.374458
42	1	0	-3.399752	-0.727714	2.386860
43	16	0	3.366449	1.409628	0.127263
44	16	0	-3.368643	-1.405405	0.146683
45	6	0	-1.592613	2.369455	1.921087
46	6	0	1.581694	-2.320495	1.979830
47	6	0	-2.228000	3.399047	2.011452
48	1	0	-2.785909	4.303953	2.094372

49	6	0	2.216626	-3.347824	2.095654
50	1	0	2.773764	-4.250785	2.201746

HF=-1725.31439617

Table S9: Atom coordinates and total energies (in Hartrees) of **11**, according to B3LYP/6-31+G(d,p) calculations.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.417312	0.238671	-1.621841
2	6	0	-0.883944	-1.052895	-1.667592
3	6	0	0.486485	-1.289598	-1.680273
4	6	0	1.416382	-0.248597	-1.621156
5	6	0	0.882973	1.042718	-1.672671
6	6	0	-0.487455	1.279399	-1.686137
7	6	0	-2.896645	0.476133	-1.451353
8	1	0	-3.438665	-0.465057	-1.548816
9	1	0	-3.267393	1.160552	-2.220205
10	6	0	-2.912234	0.196827	1.484063
11	1	0	-3.416358	0.642370	2.349377
12	1	0	-3.351973	-0.790349	1.330487
13	6	0	-1.418646	0.092639	1.712421
14	6	0	-0.775969	-1.167093	1.803741
15	6	0	0.629638	-1.226964	1.787642
16	1	0	1.104690	-2.202165	1.759337
17	6	0	1.419680	-0.081978	1.712307
18	6	0	0.777035	1.178282	1.796942
19	6	0	-0.628558	1.238058	1.781030
20	1	0	-1.103636	2.213073	1.747414
21	6	0	2.913127	-0.187571	1.483482
22	1	0	3.417971	-0.627562	2.351231
23	1	0	3.352712	0.798636	1.323292
24	6	0	2.895739	-0.485289	-1.450052
25	1	0	3.437974	0.455107	-1.553811
26	1	0	3.265829	-1.174732	-2.214695
27	9	0	-1.714512	-2.118470	-1.660973
28	9	0	0.918006	-2.566457	-1.699658
29	9	0	1.713549	2.108328	-1.671224
30	9	0	-0.918930	2.556113	-1.711492
31	16	0	3.419273	-1.328000	0.118511

32	16	0	-3.419572	1.328514	0.112207
33	6	0	-1.518531	-2.388077	1.867143
34	6	0	-2.126113	-3.435103	1.937193
35	1	0	-2.657297	-4.358204	1.990841
36	6	0	1.519765	2.399516	1.853411
37	6	0	2.127731	3.446677	1.917889
38	1	0	2.659027	4.369965	1.967032

HF=-1964.99602295