

Intramolecular [4+2] Cycloaddition Reactions of Diarylacetylenes: Synthesis of Benzo[*b*]fluorene Derivatives via Cyclic Allenes

David Rodríguez, Armando Navarro, Luis Castedo,
Domingo Domínguez* and Carlos Saá*

Departamento de Química Orgánica y Unidad Asociada al CSIC, Facultad de Química,
Universidad de Santiago de Compostela. 15706 Santiago de Compostela, SPAIN.

SUPPORTING INFORMATION

1-(5-Trimethylsilyl-2,4-pentadiynyl)-2-(2-phenyl-1-ethynyl)benzene (1c). To a solution of **1a**¹ (70 mg, 0.21 mmol) and Et₃SiH (71 μL, 0.45 mmol) in anhydrous CH₂Cl₂ (5 mL) TFA (81 μL, 1.06 mmol) was slowly added. The reaction mixture was stirred at room temperature for 7 h and then quenched with an aqueous saturated solution of NaHCO₃ (10 mL) and stirred for 30 min more. After dilution with CH₂Cl₂, the mixture was washed with water and brine. The organic layer was dried over anhydrous Na₂SO₄ and, after removal of solvent, the residual oil was purified by column chromatography on silica gel using a mixture of hexane/EtOAc 96:4 as eluent. to give **1c** (60 mg) in 90% yield: colorless oil; ¹H NMR (250 MHz, CDCl₃) δ: 7.63-7.56 (m, 4H), 7.43-7.38 (m, 5H), 4.00 (s, 2H), 0.27 (s, 9H); ¹³C NMR, DEPT (62.8 MHz, CDCl₃) δ: 136.9 (C), 132.0 (CH), 131.6 (2 x CH), 128.7 (CH), 128.5 (CH), 128.4 (2 x CH), 128.1 (CH), 127.0 (CH), 123.0 (C), 122.3 (C), 94.7 (C), 88.3 (C), 86.9 (C), 84.3 (C), 76.4 (C), 67.8 (C), 24.6 (CH₂), -0.4 (3 x CH₃). EI MS *m/z* (rel intens %): 312 (M⁺, 32), 297 (59), 239 (100), 73 (90).

1-[2-(2-Phenyl-1-ethynyl)phenyl]-3-(trimethylsilyl)-2-propyn-1-one (2c). A solution of **2e*** in dried CH₂Cl₂ (3 mL) was slowly added to a suspension of PCC (249 mg, 1.15 mmol) in CH₂Cl₂ (6 mL). After stirring during 4 h at room temperature, the reaction was filtered through a pad of celite and the filtrate evaporated. The resulting residue was diluted in EtOAc (25 mL) and washed successively with aqueous solutions of 5% HCl (3 x 25 mL) and brine (3 x 25 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated. Purification of the residue by column chromatography on silica gel using a mixture of hexane/EtOAc 94:6 as eluent. gave **2c** (84 mg) in 94% yield as a colorless oil. ¹H NMR (250 MHz, CDCl₃) δ: 8.18 (d, *J*= 7.3 Hz, 1H), 7.66-7.38 (m, 8H), 0.29 (s, 9H). ¹³C NMR, DEPT (62.8 MHz, CDCl₃) δ: 171.4 (CO), 138.0 (C), 134.5 (CH), 132.9 (CH), 132.3 (CH), 132.3 (2 x CH), 129.0 (CH), 128.6 (2 x CH), 128.2 (CH), 123.5 (C), 123.2 (C), 101.9 (C), 100.8 (C), 95.6 (C), 88.5 (C), -0.5 (3 x CH₃). EI MS *m/z* (rel intens %): 302 (M⁺, 50), 287 (100), 257 (49), 73 (4).

* Prepared in 99% yield by addition of lithium trimethylsilylacetylide to 2-(2-phenyl-1-ethynyl)benzaldehyde.¹

1-[2-(2-Phenyl-1-ethynyl)phenyl]- 2-propyn-1-one (2d). To a solution of benzodiynone **2c** (240 mg, 0.79 mmol) in MeOH (10 mL) was added a 10 mM aqueous solution of borax (1 mL). After stirring for 30 min at room temperature, a 5% aqueous solution of HCl (15 mL) was added and the mixture was extracted with EtOAc. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated. Purification of the residue by column chromatography on silica gel using a mixture of hexane/EtOAc 90:10 as eluent yielded 155 mg of **2d** (85%) as a yellowish oil. ¹H NMR (250 MHz, CDCl₃) δ: 8.15 (d, *J* = 7.8 Hz, 1H), 7.63-7.59 (m, 3H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42-7.32 (m, 4H), 3.46 (s, 1H). ¹³C NMR, DEPT (62.8 MHz, CDCl₃) δ: 176.3 (CO), 136.8 (C), 134.2 (CH), 132.8 (CH), 132.2 (CH), 131.7 (2 x CH), 128.6 (CH), 128.2 (2 x CH), 127.8 (CH), 122.9 (C), 122.9 (C), 95.3 (2 x C), 88.0 (C), 80.9 (CH). EI MS *m/z* (rel intens %): 230 (M⁺, 100), 202 (87), 201 (58), 200 (64).

10-[2-(Trimethylsilyl)-1-ethynyl]-11H-benzo[*b*]fluorene (3c). A solution of **1c** (55 mg, 0.18 mmol) in dry and degassed toluene (8 mL) was heated in a sealed tube at 130 °C for 20 h. After evaporation of the solvent, the crude residue was purified by column chromatography on silica gel using a mixture of hexane/EtOAc 96:4 as eluent to give **3c** (22 mg) in 40% yield as a pale yellow oil. ¹H NMR (250 MHz, CDCl₃) δ: 8.39 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 1H), 7.95-7.89 (m, 2H), 7.66-7.33 (m, 5H), 4.16 (s, 2H), 0.41 (s, 9H); ¹³C NMR, DEPT (62.8 MHz, CDCl₃) δ: 145.9 (C), 143.5 (C), 140.9 (C), 139.7 (C), 132.9 (C), 132.8 (C), 131.7 (C), 128.6 (CH), 128.2 (CH), 127.1 (CH), 126.3 (CH), 126.0 (CH), 125.9 (CH), 125.4 (CH), 120.7 (CH), 118.8 (CH), 103.5 (C), 101.3 (C), 37.1 (CH₂), 0.4 (3 x CH₃). EI MS *m/z* (rel intens %): 312 (M⁺, 100), 297 (59), 269 (47), 239 (36), 73 (11).

10-[2-(Trimethylsilyl)-1-ethynyl]-11H-benzo[*b*]fluoren-11-one (3d). A solution of **1a**¹ (76 mg, 0.23 mmol) in CH₃CN (2 mL) was slowly added to a mixture of Dess-Martin periodinane (147 mg, 0.35 mmol) and ^tBuOH (25 μL, 0.27 mmol) in dried CH₃CN (5

mL). While stirring the mixture at room temperature two new products appeared besides starting material remaining (TLC monitoring). This mixture of three products finally converge to only one final product after stirring for 3. The mixture was diluted with ether (25 mL) and washed with aqueous mixtures of saturated NaHCO₃ and 10% Na₂S₂O₅ (3 x 25 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated. Purification of the residue by column chromatography on silica gel using a mixture of hexane/EtOAc 95:5 as eluent gave **3d** (75 mg) in 98% yield as yellow crystals, mp 115-117 °C (EtOH). ¹H NMR (250 MHz, CDCl₃) δ: 8.38-8.35 (m, 1H), 7.72-7.24 (m, 8H), 0.44 (s, 9H); ¹³C NMR, DEPT (62.8 MHz, CDCl₃) δ: 191.5 (CO), 143.6 (C), 138.5 (C), 136.4 (2 x C), 135.1 (CH), 134.4 (C), 133.7 (C), 129.7 (CH), 129.5 (CH), 129.3 (CH), 128.8 (CH), 127.9 (CH), 124.6 (CH), 121.1 (CH), 120.0 (C), 119.6 (CH), 108.8 (C), 99.4 (C), 0.4 (3 x CH₃). EI MS *m/z* (rel intens %): 326 (M⁺, 39), 311 (100), 296 (8), 281 (49).

10-(Trimethylsilyl)-11H-benzo[*b*]fluoren-11-one (4c). A solution of **2c** (155 mg, 0.51 mmol) in dry and degassed toluene (15 mL) was heated in a sealed tube at 150 °C for 13 h. After evaporation of the solvent, the crude residue was purified by column chromatography on silica gel using a mixture of hexane/EtOAc 90:10 as eluent to give **4c** (132 mg) in 85% yield as yellow crystals, mp 113-114 °C (EtOH). ¹H NMR (250 MHz, CDCl₃) δ: 8.40 (d, *J*= 8.3 Hz, 1H), 7.85 (s, 1H), 7.78 (dd, *J*= 8.8, 1.5 Hz, 1H), 7.70-7.65 (m, 2H), 7.55-7.39 (m, 3H), 7.31 (dt, *J*= 7.5, 0.7 Hz, 1H), 0.59 (s, 9H). ¹³C NMR, DEPT (62.8 MHz, CDCl₃) δ: 194.5 (CO), 144.6 (C), 144.2 (C), 139.9 (C), 138.4 (C), 138.3 (C), 135.8 (C), 135.7 (C), 134.8 (CH), 131.3 (CH), 129.4 (CH), 129.0 (CH), 128.1 (CH), 126.1 (CH), 124.0 (CH), 120.5 (CH), 120.4 (CH), 2.9 (3 x CH₃). EI MS *m/z* (rel intens %): 302 (M⁺, 6), 287 (100), 257 (22), 73 (3).

11H-Benzo[*b*]fluoren-11-one (4d). A solution of **2d** (135 mg, 0.58 mmol) in dry and degassed toluene (18 mL) was heated in a sealed tube at 150 °C for 13 h. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel using a mixture of hexane/EtOAc 90:10 as eluent to give **4d** (100 mg) in 74% yield as yellow crystals, mp 146-147 °C (EtOH) (lit⁹ 152 °C). ¹H NMR (250 MHz,

CDCl₃) δ : 8.16 (s, 1H), 7.89-7.69 (m, 5H), 7.58-7.31 (m, 4H). ¹³C NMR, DEPT (62.8 MHz, CDCl₃) δ : 193.5 (CO), 145.3 (C), 138.8 (C), 137.3 (C), 136.6 (C), 135.4 (CH), 134.1 (C), 133.2 (C), 131.2 (CH), 129.6 (CH), 129.4 (CH), 129.2 (CH), 127.3 (CH), 126.1 (CH), 124.9 (CH), 121.4 (CH), 119.5 (CH). EI MS *m/z* (rel intens %): 230 (M⁺, 100), 202 (24), 101 (22), 58 (87).

Deuteration experiments

A solution of **1a** (45 mg, 0.14 mmol) in toluene (8 mL) was heated in a sealed tube at 100 °C for 10 h. After evaporation of the solvent, the residual oil was purified by column chromatography on silica gel using a mixture of hexane/EtOAc 90:10 as eluent to give benzo[*b*]fluorene **3a** (25 mg) in 56% yield as yellow crystals, mp 108-110 °C (EtOH). ¹H NMR (250 MHz, CDCl₃) δ : 8.31 (d, *J* = 7.5 Hz, 1H), 8.01 (s, 1H), 7.89 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7 Hz, 1H), 7.72 (dd, *J* = 7, 0.9 Hz, 1 H), 7.60-7.36 (m, 4H), 6.01 (s, 1H), 3.30 (br s, OH), 0.41 (s, 9H). ¹³C NMR, DEPT (75.47 MHz, CDCl₃) δ : 147.9 (C), 145.1 (C), 139.6 (C), 138.3 (C), 134.3 (C), 132.1 (C), 129.7 (CH), 129.2 (CH), 129.1 (CH), 127.2 (CH), 127.1 (CH), 126.4 (CH), 126.1 (CH), 121.0 (CH), 119.6 (CH), 117.2 (C), 105.8 (C), 100.7 (C), 74.8 (CH), 0.5 (3 x CH₃). EI MS *m/z* (rel intens %): 328 (M⁺, 77), 327 (42), 239 (100), 73 (55).

The same result was obtained when toluene-*d*₈ was used as solvent. However, when mixtures of toluene + CD₃OD or toluene + CH₃OD 80:20 (v/v) were used as solvents, the isolated benzo[*b*]fluorene, in each case, was labelled at position C-5, **3a-d**₁, and the yield of the reaction increased to 85% and 84%, respectively. Finally, when a mixture of toluene + CD₃OH 80:20 (v/v) was used, the isolated benzo[*b*]fluorene **3a** was not labelled at C-5 and the yield was 81%.

3a-d₁: pale yellow crystals, mp 121-123 °C (EtOH); ¹H NMR (250 MHz, CDCl₃) δ : 8.31 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.3 Hz, 1H), 7.78 (d, *J* = 7 Hz, 1H), 7.72 (dd, *J* = 7, 0.9 Hz, 1 H), 7.60-7.36 (m, 4H), 6.01 (d, *J* = 3.5 Hz, 1H), 3.30 (d, *J* = 3.5 Hz, OH), 0.41 (s, 9H). EI MS *m/z* (rel intens %): 329 (M⁺, 95), 328 (53), 240 (100), 73 (26).

Cartesian coordinates of optimized structures (b3lyp/6-31g*) as xyz files

2d

28

scf done: -728.922221

C	4.015077	-1.781830	0.000000
C	3.002095	-2.744814	0.000000
C	1.668119	-2.354711	0.000000
C	1.301464	-0.992454	0.000000
C	2.336179	-0.013586	0.000000
C	3.675331	-0.433516	0.000000
C	2.020944	1.442092	0.000000
O	0.884916	1.896860	0.000000
C	3.150924	2.373143	0.000000
C	4.027543	3.206613	0.000000
C	-0.083961	-0.681105	0.000000
C	-1.292213	-0.538247	0.000000
C	-2.680921	-0.227968	0.000000
C	-3.092761	1.121177	0.000000
C	-4.447670	1.438290	0.000000
C	-5.409426	0.423736	0.000000
C	-5.010356	-0.915405	0.000000
C	-3.657408	-1.243342	0.000000
H	5.059244	-2.080140	0.000000
H	3.252201	-3.802257	0.000000
H	0.878499	-3.099220	0.000000
H	4.455932	0.320239	0.000000
H	4.791878	3.951565	0.000000
H	-2.334882	1.898311	0.000000
H	-4.755954	2.480292	0.000000
H	-6.466448	0.675885	0.000000
H	-5.756122	-1.705793	0.000000
H	-3.341440	-2.282174	0.000000

2d reactive conformer

28

scf done: -728.919450

C	-4.360872	-1.358622	-0.085716
C	-3.437050	-2.402152	0.030198
C	-2.076815	-2.125142	0.079936
C	-1.596649	-0.798131	0.031812
C	-2.539718	0.259681	-0.064627
C	-3.907596	-0.046354	-0.139568
C	-2.205342	1.718416	-0.098177
O	-2.991066	2.535070	-0.566127
C	-0.975904	2.202191	0.512807
C	-0.035999	2.733247	1.058775
C	-0.186061	-0.609969	0.023079
C	1.028607	-0.561919	-0.018689
C	2.443816	-0.414299	-0.066633
C	3.014533	0.809203	-0.474049
C	4.397867	0.957063	-0.520207
C	5.232821	-0.105344	-0.163894
C	4.676554	-1.321932	0.239827
C	3.294435	-1.479960	0.289017
H	-5.425342	-1.569356	-0.131535
H	-3.777425	-3.433085	0.074697
H	-1.353710	-2.931709	0.145621
H	-4.603741	0.780212	-0.233203
H	0.809804	3.166181	1.544522
H	2.359220	1.628202	-0.753701
H	4.827045	1.903469	-0.837992
H	6.312127	0.013633	-0.202313
H	5.322540	-2.150584	0.516831
H	2.858249	-2.423384	0.602749

2f

30

scf done: -730.118481

C	-4.230919	-0.429793	-1.746029
C	-4.069040	-1.165298	-0.571726
C	-2.859932	-1.114671	0.115803
C	-1.791120	-0.333152	-0.362316
C	-1.957085	0.416546	-1.553410
C	-3.178851	0.354567	-2.222882
C	-0.836899	1.300129	-2.107256
O	-0.393674	2.284129	-1.178111
C	0.279796	0.494926	-2.640678
C	1.196944	-0.147566	-3.093899
C	-0.563871	-0.308279	0.364875
C	0.483763	-0.296425	0.985391
C	1.729395	-0.282670	1.678940
C	2.884870	0.222182	1.048637
C	1.825913	-0.770873	2.996879
C	3.047827	-0.752343	3.663573
C	4.187759	-0.248325	3.032133
C	4.101400	0.237524	1.724814
H	-5.172473	-0.460138	-2.287120
H	-4.882444	-1.775419	-0.189251
H	-2.723049	-1.681640	1.031468
H	-3.310289	0.932711	-3.134454
H	-1.257624	1.880068	-2.936933
H	0.007934	1.805294	-0.432130
H	2.001874	-0.727883	-3.484564
H	2.812417	0.591044	0.029842
H	0.937271	-1.159518	3.484618
H	3.110995	-1.131276	4.679994
H	5.139243	-0.234432	3.556530
H	4.985795	0.629254	1.229818

2g

29

scf done: -654.913416

C	4.527643	-0.930250	-0.020730
C	3.745008	-2.016577	-0.415068
C	2.357622	-1.915463	-0.390805
C	1.728746	-0.725803	0.025659
C	2.523923	0.374145	0.431429
C	3.913332	0.251048	0.398712
C	1.878194	1.668812	0.906988
C	1.390531	2.520688	-0.184135
C	0.993647	3.230377	-1.076809
C	0.306638	-0.638708	0.036263
C	-0.905959	-0.542124	0.037563
C	-2.323376	-0.395309	0.032100
C	-2.900974	0.890699	0.047000
C	-4.285063	1.038383	0.042341
C	-5.114544	-0.086081	0.022218
C	-4.551188	-1.364538	0.005175
C	-3.167996	-1.522787	0.009966
H	5.611719	-1.000952	-0.035950
H	4.213836	-2.941241	-0.740048
H	1.738756	-2.753789	-0.695563
H	4.524921	1.095054	0.708879
H	2.605899	2.232430	1.504762
H	1.039460	1.433143	1.574862
H	0.650300	3.845170	-1.877313
H	-2.249666	1.759481	0.054790
H	-4.718965	2.034667	0.053131
H	-6.194560	0.033325	0.018863
H	-5.192386	-2.241781	-0.011490
H	-2.726468	-2.514594	-0.002133

6d

28

scf done: -728.886456

C	-3.027613	-0.319568	-1.222888
C	-2.294531	-0.332017	0.000000
C	-3.027613	-0.319568	1.222888
C	-4.413790	-0.278644	1.212253
C	-5.116307	-0.258673	0.000000
C	-4.413790	-0.278644	-1.212253
C	-0.902889	-0.403582	0.000000
C	0.305314	0.114872	0.000000
C	1.592006	-0.620125	0.000000
C	2.673565	0.271533	0.000000
C	2.191131	1.671553	0.000000
C	0.658454	1.587546	0.000000
C	3.995337	-0.176548	0.000000
C	4.225565	-1.549958	0.000000
C	3.144777	-2.448798	0.000000
C	1.825184	-1.997338	0.000000
O	2.861160	2.685153	0.000000
C	-0.120585	2.642891	0.000000
H	5.242244	-1.932650	0.000000
H	3.342186	-3.517648	0.000000
H	0.994498	-2.697240	0.000000
H	4.809743	0.541999	0.000000
H	0.034613	3.713310	0.000000
H	-2.481100	-0.334979	2.160669
H	-4.956783	-0.260069	2.153438
H	-6.202092	-0.228516	0.000000
H	-4.956783	-0.260069	-2.153438
H	-2.481100	-0.334979	-2.160669

6f

30

scf done: -730.072661

C	-4.165225	-1.627780	0.023156
C	-3.074702	-2.500779	0.139311
C	-1.768266	-2.016187	0.105574
C	-1.564834	-0.641422	-0.047971
C	-2.653538	0.227721	-0.174821
C	-3.958616	-0.256004	-0.135248
C	-0.283934	0.098277	-0.094149
C	-0.668320	1.581988	-0.265433
C	-2.211513	1.659347	-0.335445
C	0.111769	2.627497	-0.337987
C	0.929238	-0.389224	-0.019705
C	2.320819	-0.332782	0.011024
C	3.088220	-0.438581	-1.186773
C	4.474132	-0.405599	-1.142331
C	5.144599	-0.277150	0.081473
C	4.409509	-0.179746	1.270503
C	3.023001	-0.209855	1.246694
O	-2.790372	2.453880	0.693884
H	-5.177278	-2.021908	0.057694
H	-3.249453	-3.566658	0.260290
H	-0.920058	-2.687965	0.202272
H	-4.799236	0.427239	-0.216855
H	-2.503730	2.056873	-1.320530
H	1.164597	2.870519	-0.301399
H	2.566743	-0.540697	-2.133472
H	5.042238	-0.480116	-2.065876
H	6.230284	-0.255238	0.108496
H	4.927377	-0.078687	2.220668
H	2.451303	-0.136242	2.166627
H	-2.377676	3.330905	0.631829

6g

29

scf done: -654.866506

C	1.615835	-2.109903	0.000000
C	1.662111	-0.712671	0.000000
C	2.889654	-0.037439	0.000000
C	4.084568	-0.754395	0.000000
C	4.041829	-2.150865	0.000000
C	2.813117	-2.823582	0.000000
C	2.692193	1.459354	0.000000
C	1.168264	1.646550	0.000000
C	0.531439	0.243017	0.000000
C	-0.748467	-0.041740	0.000000
C	-2.117965	0.201390	0.000000
C	-2.847384	0.306958	-1.222689
C	-4.217677	0.519734	-1.211993
C	-4.913235	0.627525	0.000000
C	-4.217677	0.519734	1.211993
C	-2.847384	0.306958	1.222689
C	0.549102	2.800518	0.000000
H	0.658761	-2.624193	0.000000
H	5.040494	-0.235715	0.000000
H	4.968240	-2.718997	0.000000
H	2.793101	-3.910200	0.000000
H	3.143837	1.935217	-0.879772
H	3.143837	1.935217	0.879772
H	-2.307691	0.220954	-2.160753
H	-4.754279	0.604021	-2.153458
H	-5.986939	0.791993	0.000000
H	-4.754279	0.604021	2.153458
H	-2.307691	0.220954	2.160753
H	-0.467355	3.169866	0.000000

8d singlet

28

scf done: -728.922722

C	-4.561290	-0.399515	-0.013185
C	-3.974044	-1.665516	0.152225
C	-2.588639	-1.824437	0.187460
C	-1.782523	-0.688398	0.060673
C	-2.379409	0.582712	-0.109003
C	-3.762828	0.736701	-0.147710
C	-0.328786	-0.550034	0.029191
C	-0.031181	0.905087	-0.054891
C	-1.331048	1.638650	-0.213966
C	0.729224	-1.385954	0.059556
C	2.042183	-0.957349	0.092238
C	2.280215	0.403276	0.744836
C	1.171965	1.381330	0.293742
O	-1.497506	2.839878	-0.348226
C	3.102857	-1.608722	-0.596770
C	4.348464	-1.044595	-0.694909
C	4.634645	0.234319	-0.088379
C	3.684502	0.918563	0.582953
H	-5.643709	-0.310118	-0.037694
H	-4.613703	-2.538660	0.251759
H	-2.141417	-2.807224	0.304986
H	-4.194050	1.725207	-0.278167
H	2.104986	0.335000	1.839792
H	1.353390	2.448351	0.393950
H	2.889311	-2.565664	-1.064556
H	5.135842	-1.557061	-1.240022
H	5.641458	0.636443	-0.166506
H	3.922073	1.857985	1.077932

8d triplet

28

scf done: -728.917299

C	-4.551667	0.605772	-0.142402
C	-4.192694	-0.172169	0.971359
C	-2.858145	-0.457065	1.261031
C	-1.867073	0.051792	0.413509
C	-2.235576	0.834602	-0.707976
C	-3.568336	1.115343	-0.992328
C	-0.417946	-0.077790	0.455787
C	0.133430	0.672924	-0.682096
C	-1.018331	1.252332	-1.456104
C	0.467945	-0.776657	1.216439
C	1.840971	-0.844163	1.024325
C	2.451848	0.194137	0.056069
C	1.452340	0.769029	-0.921171
O	-0.955725	1.923921	-2.472816
C	2.707907	-1.769315	1.642532
C	4.005584	-1.943885	1.200601
C	4.490883	-1.238282	0.044437
C	3.753524	-0.270014	-0.549004
H	-5.600440	0.808867	-0.339438
H	-4.972556	-0.560441	1.621384
H	-2.592358	-1.059066	2.125203
H	-3.821373	1.717445	-1.860492
H	2.728333	1.058106	0.711125
H	1.819121	1.322420	-1.783019
H	2.309787	-2.401378	2.431686
H	4.640636	-2.687565	1.672629
H	5.456223	-1.517314	-0.370527
H	4.110422	0.247970	-1.436035

8f singlet

30

scf done: -730.107751

C	-4.533954	-0.217776	0.116923
C	-4.009729	-0.934405	1.201029
C	-2.631891	-1.085235	1.357482
C	-1.780333	-0.504640	0.411662
C	-2.312668	0.199358	-0.687984
C	-3.684479	0.351135	-0.838913
C	-0.322251	-0.485032	0.337723
C	0.038096	0.426092	-0.784898
C	-1.211899	0.694805	-1.614367
C	0.689977	-1.017869	1.052605
C	2.007087	-0.654047	0.889943
C	2.236692	0.759440	0.362819
C	1.219587	1.051874	-0.770158
C	3.104311	-1.559316	1.007163
C	4.374161	-1.195044	0.653856
C	4.653975	0.135322	0.159264
C	3.672507	1.049415	0.017198
O	-1.432603	2.054112	-1.979780
H	-5.610220	-0.105658	0.016502
H	-4.685233	-1.374895	1.929739
H	-2.220470	-1.637622	2.197535
H	-4.086947	0.911140	-1.678270
H	-1.198807	0.069781	-2.524434
H	1.958564	1.505839	1.136508
H	1.449510	1.878782	-1.437857
H	2.893376	-2.561863	1.369171
H	5.189777	-1.907858	0.737109
H	5.681032	0.397117	-0.083135
H	3.903186	2.062242	-0.308418
H	-0.868068	2.245632	-2.744306

8f triplet

30

scf done: -730.101903

C	-4.536497	-0.518789	-0.060780
C	-3.973908	-1.289703	0.965565
C	-2.598065	-1.286208	1.191577
C	-1.784075	-0.495613	0.370189
C	-2.352994	0.268579	-0.671493
C	-3.723579	0.266253	-0.887457
C	-0.347327	-0.283706	0.387379
C	-0.009386	0.667550	-0.676105
C	-1.286812	1.024413	-1.440435
C	0.688089	-0.826818	1.095167
C	2.031378	-0.557410	0.920804
C	2.367473	0.685037	0.067266
C	1.254804	1.080536	-0.881643
C	3.101158	-1.306373	1.465384
C	4.395734	-1.127824	1.026508
C	4.688575	-0.219132	-0.052713
C	3.737687	0.599653	-0.559019
O	-1.608475	2.415233	-1.459251
H	-5.611999	-0.530197	-0.214829
H	-4.619600	-1.894930	1.596554
H	-2.162810	-1.877022	1.992506
H	-4.157283	0.870549	-1.679351
H	-1.219901	0.647482	-2.475322
H	2.435165	1.521328	0.807639
H	1.509380	1.768562	-1.686912
H	2.869982	-2.082007	2.190533
H	5.194499	-1.740014	1.434756
H	5.688439	-0.221833	-0.480151
H	3.955655	1.269790	-1.387784
H	-0.927224	2.863777	-1.984755

8g singlet

29

scf done: -654.903798

C	-4.639904	-0.179420	-0.063314
C	-4.100081	-0.857745	1.037353
C	-2.719887	-0.933451	1.216632
C	-1.881603	-0.313465	0.282400
C	-2.425704	0.367745	-0.829219
C	-3.803481	0.433238	-1.003670
C	-0.426873	-0.255921	0.220191
C	-0.069245	0.645101	-0.908282
C	-1.324935	0.936324	-1.712642
C	0.585561	-0.801521	0.935196
C	1.910944	-0.472667	0.756809
C	2.174854	0.911471	0.171576
C	1.139588	1.224094	-0.932139
C	2.988229	-1.391870	0.930775
C	4.266248	-1.078795	0.555932
C	4.571803	0.207568	-0.030663
C	3.611291	1.134428	-0.223409
H	-5.718193	-0.131206	-0.190058
H	-4.764397	-1.330741	1.755815
H	-2.293527	-1.465041	2.062747
H	-4.231019	0.954398	-1.857255
H	-1.452925	2.007842	-1.909934
H	-1.309993	0.435484	-2.692007
H	1.958110	1.688366	0.937815
H	1.388537	2.020643	-1.629595
H	2.755599	-2.366226	1.351759
H	5.065875	-1.802916	0.683951
H	5.600596	0.424266	-0.307838
H	3.860507	2.114416	-0.626565

8g triplet

29

scf done: -654.898796

C	-4.600245	0.685096	-0.243270
C	-4.223010	-0.091798	0.859769
C	-2.879034	-0.356908	1.117190
C	-1.909169	0.168560	0.252756
C	-2.290448	0.951700	-0.861680
C	-3.632472	1.209709	-1.109503
C	-0.463251	0.051066	0.279747
C	0.087756	0.807466	-0.848880
C	-1.068754	1.394135	-1.646208
C	0.414794	-0.659626	1.054722
C	1.779799	-0.737315	0.885835
C	2.402594	0.304352	-0.068483
C	1.417054	0.890120	-1.057227
C	2.642290	-1.668635	1.516433
C	3.935383	-1.851401	1.080539
C	4.429036	-1.148323	-0.077795
C	3.702047	-0.173701	-0.670200
H	-5.652526	0.882700	-0.428777
H	-4.986744	-0.491313	1.521804
H	-2.583126	-0.958441	1.972087
H	-3.933738	1.810480	-1.964631
H	-1.001046	2.487815	-1.721862
H	-1.085695	1.010771	-2.675923
H	2.689477	1.154962	0.600830
H	1.826768	1.443087	-1.900394
H	2.236197	-2.292382	2.308266
H	4.566175	-2.597335	1.555223
H	5.391946	-1.437722	-0.492043
H	4.066062	0.340417	-1.557050