

Supporting Information

Generation, Characterization, and Rearrangements of 4,5-Benzocyclohepta-1,2,4,6-tetraene

Paul A. Bonvallet and Robert J. McMahon*

Department of Chemistry, University of Wisconsin,

Madison, Wisconsin 53706-1396

Methods Section

Computational Methods. Calculations were performed with the Becke three parameter gradient-corrected exchange functional¹ with the correlation functional of Lee, Yang, and Parr² (referred to as B3LYP) as implemented in the Gaussian 98 package.³ The 6-31G* basis set was employed for geometry optimizations as well as single point energy and harmonic vibrational frequency calculations. The frequency calculations give the zero-point vibrational energy correction and verify each structure as a true minimum or transition state on the potential energy surface. Transition states were characterized by following atomic motion along the imaginary frequency. Reported computed vibrational frequencies are unscaled.

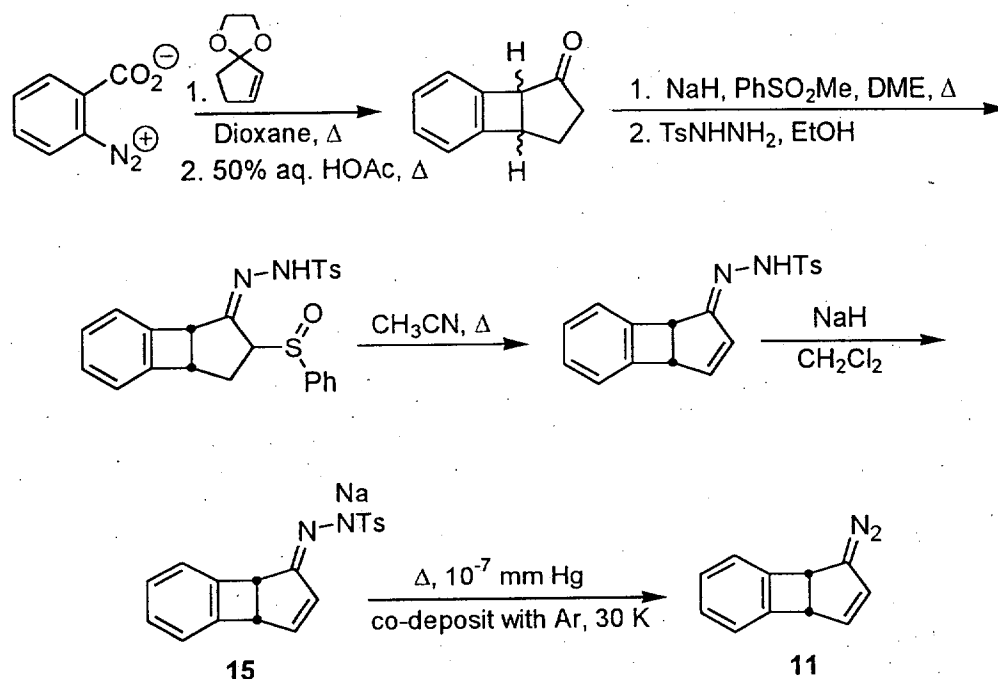
General Experimental Methods. Compounds from commercial sources gave acceptable ¹H NMR spectra and were used without further purification. Dichloromethane and DME were distilled over CaH₂ and Na/benzophenone respectively. Uncorrected melting points were measured in open capillaries with a Thomas-Hoover Unimelt apparatus. Routine NMR spectra were obtained with a 300 MHz Bruker AC 300 spectrometer, with CDCl₃ as the solvent and chemical shifts reported in parts per million downfield from TMS. One-dimensional NOE

experiments were conducted on a Varian Unity INOVA 500 MHz NMR spectrometer. Mass spectra were obtained from a Kratos MS-80RFA spectrometer with a DS55/DS90 detector.

GC/MS measurements were carried out with a Shimadzu QP-5000 mass spectrometer coupled to a Shimadzu GC-17A gas chromatograph.

Matrix Isolation Spectroscopy. Techniques and apparatus for low-temperature matrix isolation spectroscopy are described elsewhere.^{4,5} Generally, the same deposition temperature of the sample and argon flow rate are used regardless of the particular instrumental technique employed. The matrix thickness (i.e. the amount of sample) is identical for ESR and IR experiments, while a UV/visible matrix is thinner. Photolysis times differ depending on the instrumental technique employed. IR spectra were recorded on a Nicolet 740 FT-IR spectrometer equipped with a MCT-B detector. Ultraviolet/visible spectra were acquired with a Hitachi U-3210 spectrophotometer. ESR experiments were conducted on a Bruker ESP 300 spectrometer with a Bruker ER 042 MRH E microwave bridge and an EIP Model 625A microwave frequency counter. Zero-field splitting parameters were assigned by a best fit of the observed spectrum to the spin Hamiltonian (assuming $g_x = g_y = g_z = g_e$).

6,7-Benzobicyclo[3.2.0]hept-6-en-2-one.⁶ In a typical preparation, a slurry of benzenediazonium-2-carboxylate⁷ (prepared from 34.22 g, 250 mmol anthranilic acid; Aldrich) in dioxane is added to a solution of 2-cyclopenten-1-one ethylene ketal⁸ (90.00 g, 0.71 mol) in 400 mL dioxane. The mixture is stirred under N₂ and maintained at 50 °C for 5 h. The resultant



brown liquid is cooled and diluted with 600 mL 5% aq. NaHCO₃. The mixture is extracted with 5 × 300 mL hexane and the combined organic extracts washed successively with 300 mL 5% aq. NaHCO₃, water, and brine. Drying of the organic layer with MgSO₄ followed by evaporation of solvent affords a dark brown oil. Excess ketal is removed by vacuum distillation (35–44 °C / 3 mmHg). The crude mixture is stirred with 60 mL 50% aq. acetic acid under N₂ at 50 °C for 4 h and then diluted with 100 mL water. The product is extracted with 5 × 100 mL ether, washed with 7 × 100 mL 5% aq. NaHCO₃, and dried over MgSO₄. Concentration followed by column chromatography (silica gel, 5% ether in hexane, R_f = 0.10) affords a crude yellow oil which is purified by distillation (63–65 °C / 0.1 mmHg) to afford a 3:2 mixture of *cis* and *trans* fused tricyclic ketones respectively as a colorless oil (1.90 g, 5% total yield from anthranilic acid). The isomers are separable to some extent on a chromatographic column (silica gel, 1:1 ether/hexane, *trans* isomer R_f = 0.36, *cis* isomer R_f = 0.46). The relative stereochemistry of the protons on the

cyclobutane ring was assigned by 1-D NOE experiments. *Cis* isomer: ^1H NMR δ 7.26 (t, $J = 8$ Hz, 1H), 7.21 (t, $J = 8$ Hz, 1H), 7.17 (d, $J = 7$ Hz, 1H), 7.09 (d, $J = 7$ Hz, 1H), 4.13 (dt, $J = 4, 3$ Hz, 1H), 3.88 (d, $J = 4$ Hz, 1H, strong NOE with proton at 4.13 ppm), 2.60-2.45 (m, 1H), 2.23-2.13 (m, 3H); ^{13}C NMR δ 215.5, 147.7, 142.0, 128.5, 128.0, 122.5, 122.1, 54.5, 44.9, 34.8, 24.2. *Trans* isomer: ^1H NMR δ 7.29-7.24 (m, 2H), 7.15 (td, $J = 8, 1$ Hz, 1H), 7.10 (td, $J = 8, 2$ Hz, 1H), 3.65 (m, 1H), 3.56 (d, $J = 1$ Hz, 1H, no NOE with proton at 3.65 ppm), 2.47-2.42 (m, 1H), 2.33-1.94 (ABX, 3H); ^{13}C NMR δ 213.4, 148.5, 139.7, 127.3, 126.6, 123.5, 121.5, 57.9, 50.7, 41.6, 40.2. Both isomers: mass spectrum m/z (relative intensity) 158 (M^+ , 28), 129 (100), 115 (92), 102 (45); HRMS calcd for $\text{C}_{11}\text{H}_{10}\text{O}$ 158.0732, found 158.0721.

2-Benzenesulfinyl-6,7-benzobicyclo[3.2.0]hept-6-en-2-one.⁹ A dry 3-neck round bottom flask is filled with NaH (60% dispersion in oil, 1.16 g, 29 mmol; Aldrich), methyl benzenesulfinate¹⁰ (2.22 g, 14 mmol), and 13 mL DME and then fitted with an addition funnel, reflux condenser, and gas inlet. The slurry is stirred under N_2 and refluxed for 5 min. Dropwise addition of a 3:2 mixture of *cis* and *trans* 6,7-benzobicyclo[3.2.0]hept-6-en-2-one (1.90 g, 12 mmol) in 7 mL DME is carried out over 15 min. The dark purple reaction mixture is refluxed for an additional 15 min then cooled, quenched with ca. 1 mL ethanol, and poured into 70 mL 5% aq. NaOH. The solution is washed with 3×70 mL ether and the dark aqueous layer is acidified to Congo Red with 6 N H_2SO_4 . The aqueous solution is extracted with 3×70 mL ether, dried over MgSO_4 , and the solvent is removed to afford a dark brown oil. At this point only the stereoisomer with a *cis* fusion of cyclobutyl and cyclopentyl rings is recovered. Purification of the crude product by column chromatography (silica gel, 10% CH_3CN in CH_2Cl_2 , $R_f = 0.46$) affords a sticky yellow oil

(1.00 g, 30%): ^1H NMR δ 7.55-7.46 (m, 5H), 7.27-7.23 (m, 2H), 7.16-7.06 (m, 2H), 4.15-4.09 (m, 2H, *cis* fused ring), 3.63 (dd, $J = 11, 9$ Hz, 1H), 2.90-2.85 (m, 1H), 1.80 (dd, $J = 14, 9$ Hz, 1H); ^{13}C NMR δ 206.9, 147.5, 141.6, 140.1, 130.9, 129.2, 129.0, 128.6, 123.8, 122.7, 122.6, 69.0, 55.3, 42.3, 19.7; mass spectrum m/z (relative intensity) 282 (M^+ , 6), 156 (71), 128 (100); HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}$ 282.0715, found 282.0721.

2-Benzenesulfinyl-6,7-benzobicyclo[3.2.0]hept-6-en-2-one tosylhydrazone. A slurry of 2-benzenesulfinyl-6,7-benzobicyclo[3.2.0]hept-6-en-2-one (1.00 g, 3.6 mmol), *p*-toluenesulfonylhydrazide (662 mg, 3.6 mmol; Aldrich), and 5 mL EtOH is heated briefly until a clear orange solution is obtained. After stirring overnight at room temperature, a powdery white solid (1.15 g, 72%) is isolated by vacuum filtration and washed with cold ethanol until the filtrate is colorless. The product is suitably clean without additional purification: mp 143–144 °C (dec.); ^1H NMR δ 10.79 (s, 1H), 8.00 (d, $J = 8$ Hz, 2H), 7.53 (t, $J = 7$ Hz, 1H), 7.42 (d, $J = 8$ Hz, 2H), 7.33 (t, $J = 8$ Hz, 2H), 7.27-7.25 (m, 2H), 7.15-7.08 (m, 3H), 6.91 (t, $J = 3$ Hz, 1H), 5.02 (dd, $J = 8, 4$ Hz, 1H), 3.19-3.13 (m, 1H), 2.99 (d, $J = 5$ Hz, 1H), 2.52 (s, 3H), 2.31-2.25 (m, 2H); ^{13}C NMR δ 154.8, 147.2, 143.6, 143.4, 137.6, 136.1, 132.8, 129.4, 129.3, 128.5, 128.4, 128.3, 125.2, 123.0, 121.7, 68.7, 52.1, 44.0, 26.3, 21.7; mass spectrum m/z (relative intensity) 450 (M^+ , not detected), 324 (elimination product, 55), 169 (88), 140 (100), 139 (91), 128 (52), 115 (72).

6,7-Benzobicyclo[3.2.0]hepta-3,6-dien-2-one tosylhydrazone. A slurry of 2-benzenesulfinyl-6,7-benzobicyclo[3.2.0]hept-6-en-2-one tosylhydrazone (1.15 g, 2.6 mmol) and 50 mL CH_3CN is refluxed under N_2 for 90 min. Removal of solvent affords a crude yellow solid which is

recrystallized twice from ether/ CH_2Cl_2 to afford white crystals (300 mg, 36%): mp 192-193 °C (dec.); ^1H NMR δ 7.88 (d, J = 8 Hz, 2H), 7.51 (s, 1H), 7.32 (d, J = 8 Hz, 2H), 7.21-7.17 (m, 2H), 7.09-7.04 (m, 2H), 6.79 (dd, J = 6, 3 Hz, 1H), 6.17 (d, J = 6 Hz, 1H), 4.65 (t, J = 3 Hz, 1H), 4.41 (d, J = 3 Hz, 1H), 2.42 (d, 1H); ^{13}C NMR δ 161.9, 149.9, 147.3, 143.8, 143.7, 135.2, 129.4, 127.7, 127.5, 127.4, 123.4, 122.8, 121.8, 52.3, 49.6, 21.4; mass spectrum m/z (relative intensity) 324 (M^+ , 32), 169 (72), 140 (97), 139 (100), 128 (41), 115 (61); HRMS calcd for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$ 324.0933, found 324.0933.

6,7-Benzobicyclo[3.2.0]hepta-3,6-dien-2-one tosylhydrazone sodium salt (15). Under nitrogen, NaH (60% dispersion in oil, 40 mg, 1.0 mmol; Aldrich) is added to a solution of 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one tosylhydrazone (159 mg, 0.49 mmol) in 5 mL CH_2Cl_2 . The resulting white mixture is stirred for 1.5 h. The solution is poured into 100 mL dry hexane, forming a fine white precipitate that is isolated by vacuum filtration and dried *in vacuo* (rt, $\leq 10^{-6}$ mmHg) before use.

Matrix isolation of 6,7-Benzo-2-diazobicyclo[3.2.0]hepta-3,6-diene (11). Tosylhydrazone sodium salt 15 is placed in a round-bottom flask which is affixed to the matrix isolation apparatus. The salt is heated to 130-140 °C at 1×10^{-7} mmHg and the pyrolysate co-condensed with argon onto a spectroscopic window at 30 K. The matrix is cooled to 10 K after deposition is complete. The sole product of the pyrolysis is diazo compound 11: IR (Ar, 10 K) 3085 m, 3075 m, 2053 vs, 2033 m, 1605 w, 1559 m, 1460 m, 1458 m, 1395 w, 1274 w, 1220 w, 1186 w, 1175 w, 1131 w, 983 w, 884 w, 763 w, 738 s, 705 s, 608 m cm^{-1} ; UV/visible (Ar, 10 K) λ_{max} 294, 284, 271, 267,

261, 218 nm.

4,5-Benzocyclohepta-1,2,4,6-tetraene (6) and Subsequent Photochemistry. Irradiation ($\lambda > 237$, $\lambda > 472$, or $\lambda > 571$ nm) of diazo compound **11** results in the complete formation of allene **6** (100% conversion). IR (Ar; 10K) 3060 m, 3030 m, 1842 w, 1600 w, 1476 w, 1445 w, 1374 w, 1290 w, 1248 w, 1159 w, 891 w, 834 m, 805 m, 792 m, 759 s, 735 w, 713 w, 697 m, 630 s, 574 m, 500 m cm^{-1} ; UV/visible (Ar, 10 K) 230 nm. Prolonged irradiation ($\lambda > 237$ nm) causes **1** to disappear¹¹ and 2-naphthylcarbene (**8**) to emerge.^{12b} UV/visible (Ar, 10 K) λ_{max} 359, 342, 279, 269, 240, 221 nm; ESR (Ar, 14 K) *s*-E isomer $|D/hc| = 0.4758 \text{ cm}^{-1}$, $|E/hc| = 0.0254 \text{ cm}^{-1}$, $Z_1 = 1668 \text{ G}$, $X_2 = 4841 \text{ G}$, $Y_2 = 5875 \text{ G}$, $Z_2 = 8479 \text{ G}$; *s*-Z isomer $|D/hc| = 0.4964 \text{ cm}^{-1}$, $|E/hc| = 0.0220 \text{ cm}^{-1}$, $Z_1 = 1896 \text{ G}$, $X_2 = 4974 \text{ G}$, $Y_2 = 5875 \text{ G}$, $Z_2 = 8703 \text{ G}$; microwave frequency = 9.530 GHz. Bandpass irradiation ($\lambda = 290 \pm 10$ nm) of the matrix affords a greater concentration of **8**.

Flash vacuum pyrolysis of sodium salt 15. An unpacked 60 cm quartz tube is affixed with a vacuum adapter, cold trap, and 100 mL round-bottom flask containing tosylhydrazone sodium salt **15** (420 mg, 1.25 mmol). The apparatus is evacuated to 2×10^{-2} mmHg as the quartz tube is heated to 600 °C in a furnace. The cold trap is immersed in dry ice/acetone and the salt is heated to 90-110 °C with a heating mantle. After 18 h, all glassware is cooled to rt and the system vented to dry nitrogen as the cold trap warms. The colorless oil collected from the cold trap, as determined by ¹H NMR and GC/MS, is a mixture of cyclobuta[*de*]naphthalene (**4**, 51%), 1-methylnaphthalene (23%), 2-methylnaphthalene (9%), and naphthalene (17%).

Notes and References

(1) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

(2) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

(3) *Gaussian 98, Revision A.6*, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1998.

(4) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597-7606.

(5) Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183-7189.

(6) Ohkita, M.; Nishida, S.; Tsuji, T. *J. Am. Chem. Soc.* **1999**, *121*, 4589-4597.

(7) Logullo, F. M.; Seitz, A. H.; Friedman, L. *Org. Synth.* **1973**, Coll. Vol. 5, 54-59.

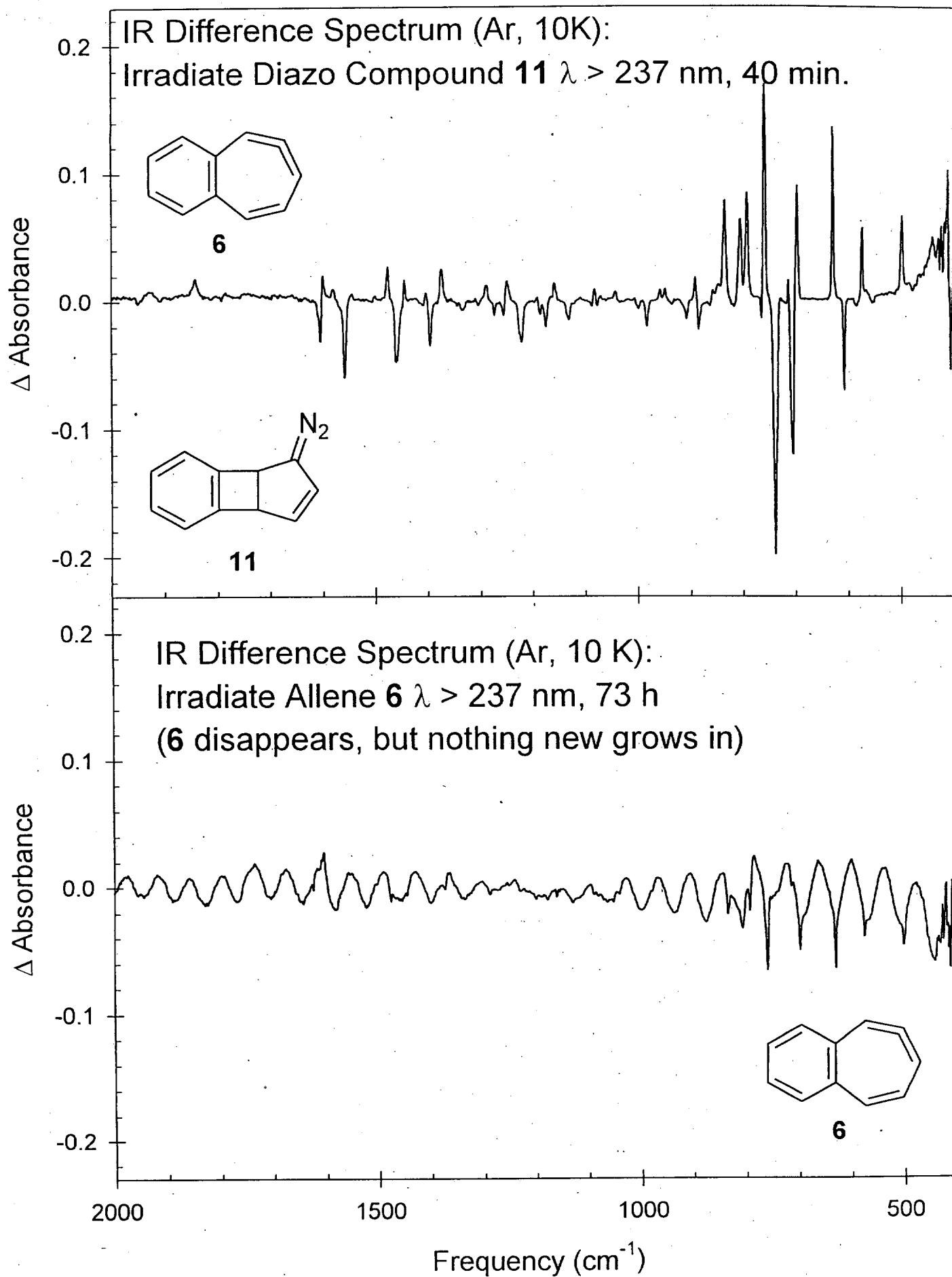
(8) Garbisch, E. W., Jr. *J. Org. Chem.* **1965**, *30*, 2109-2120.

(9) Chapman, O. L.; Abelt, C. J. *J. Org. Chem.* **1987**, *52*, 1218-1221.

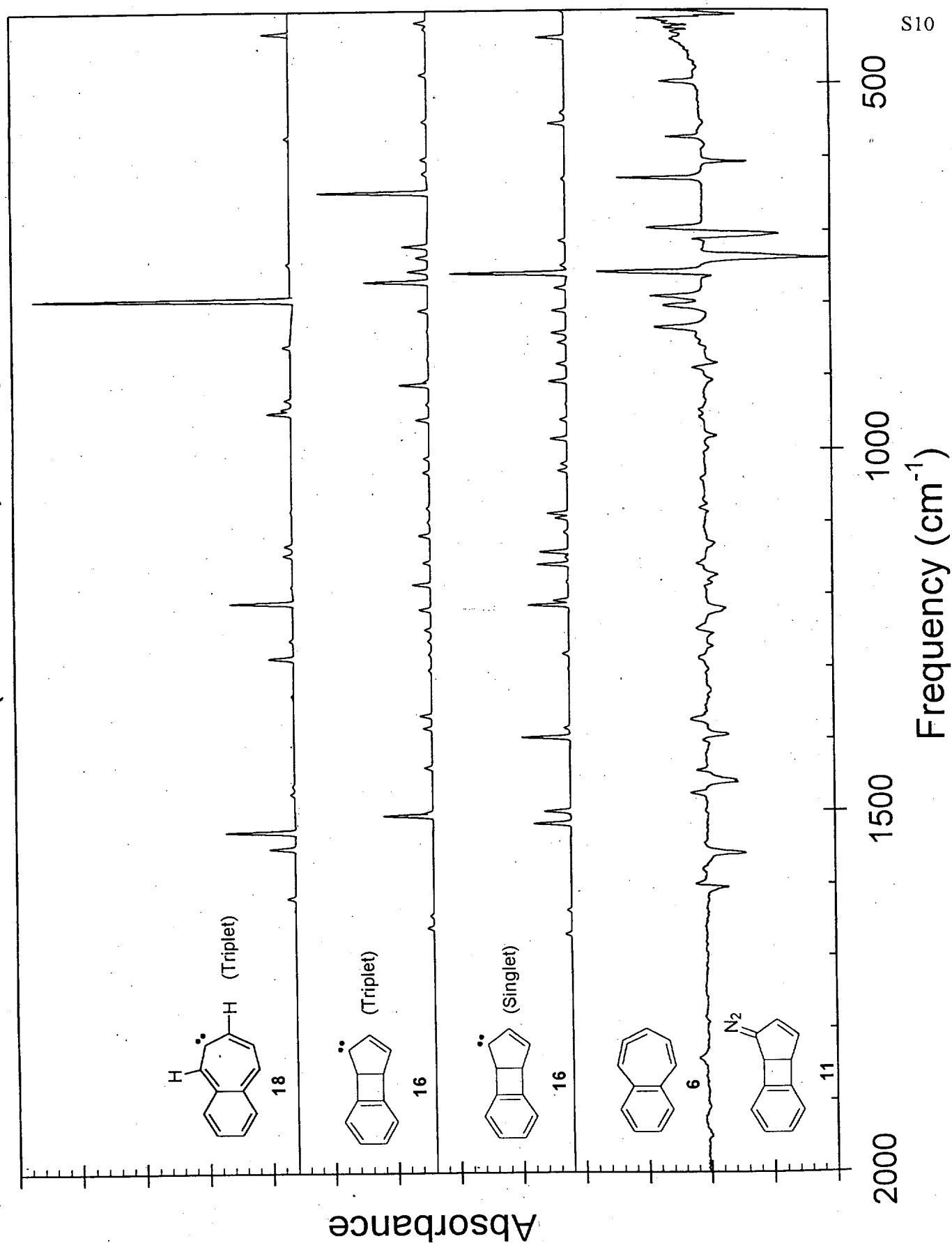
(10) Field, L.; Locke, J. M. *Org. Synth.* **1973**, Coll. Vol. 5, 723-726.

(11) The disappearance of benzocycloheptatetraene **6** is highly sensitive to matrix thickness. The IR bands for **6** (thick matrix) decrease only slightly under these conditions, with no new absorptions appearing. In a UV/visible experiment (thin matrix), **6** disappears completely.

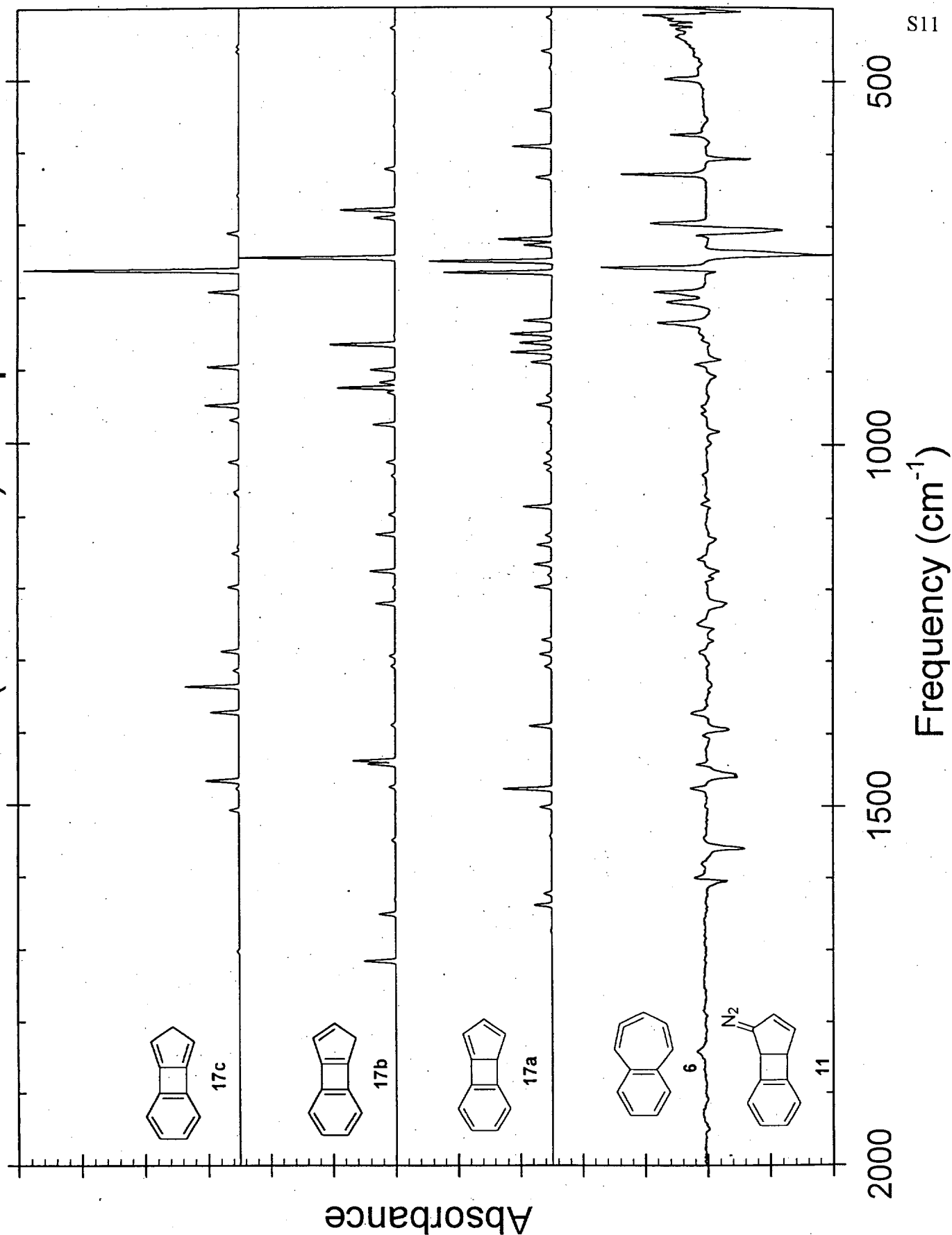
(12) (a) West, P. R.; Mooring, A. M.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem.* **1986**, *51*, 1316-1320. (b) Albrecht, S. W.; McMahon, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 855-859. (c) Bonvallet, P. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 10496-10503.



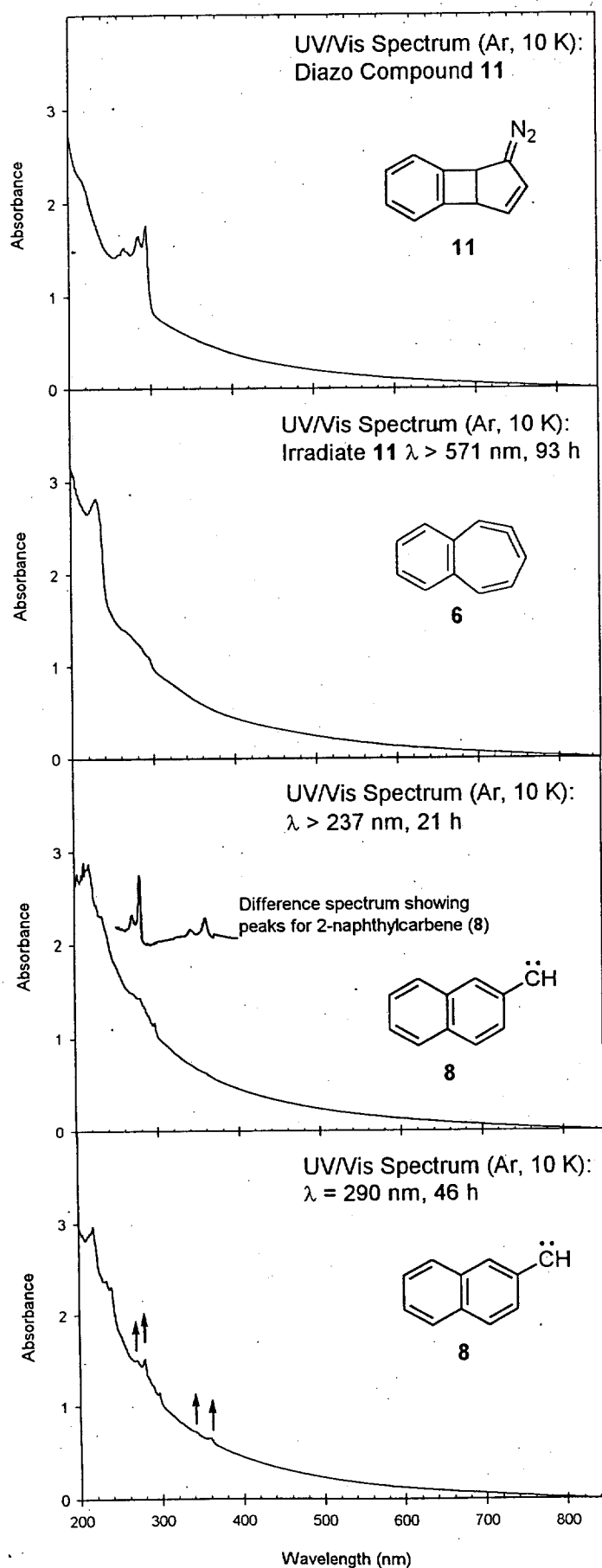
Experimental Spectrum vs. B3LYP/6-31G* Calculated (Unscaled) IR Spectra



Experimental Spectrum vs. B3LYP/6-31G* Calculated (Unscaled) IR Spectra



S12



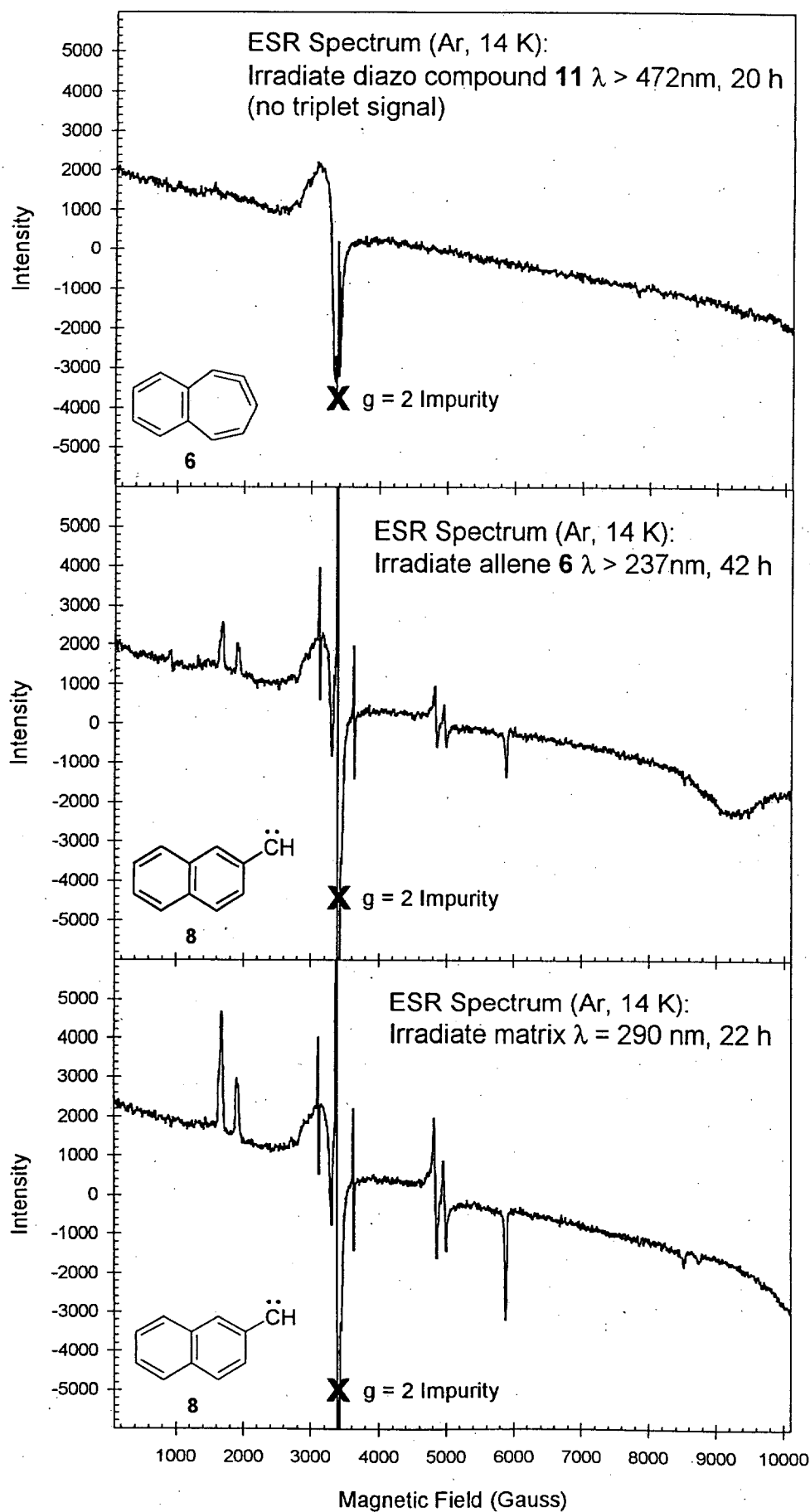


Table S1. B3LYP/6-31G* Cartesian Coordinates (Å) for Computed Structures

Cyclobuta[de]naphthalene (4)

C	0.000000	2.312038	0.000000
C	-1.049131	1.140868	0.000000
C	-2.326029	0.630872	0.000000
C	-2.415000	-0.806185	0.000000
C	-1.330216	-1.683364	0.000000
C	0.000000	-1.161255	0.000000
C	1.330216	-1.683364	0.000000
C	2.415000	-0.806185	0.000000
C	2.326029	0.630872	0.000000
C	1.049131	1.140868	0.000000
C	0.000000	0.225134	0.000000
H	0.000000	2.949578	-0.890879
H	0.000000	2.949578	0.890879
H	-3.236070	1.224847	0.000000
H	-3.412184	-1.240614	0.000000
H	-1.516330	-2.754701	0.000000
H	1.516330	-2.754701	0.000000
H	3.412184	-1.240614	0.000000
H	3.236070	1.224847	0.000000

4,5-Benzocyclohepta-1,2,4,6-tetraene (6)

C	-0.852133	-1.623914	-0.439028
C	-1.982365	-1.236831	0.126032
C	-2.697304	-0.220310	0.584657
C	-2.381357	1.060495	-0.047022
C	-1.096030	1.386413	-0.350296
C	0.157967	0.640114	-0.148386
C	1.323331	1.426687	0.004975
C	2.577675	0.863356	0.188102
C	2.721218	-0.529797	0.198635
C	1.602449	-1.334379	0.029704
C	0.321780	-0.781855	-0.144114
H	-0.775775	-2.441084	-1.154872
H	-3.377991	-0.278803	1.432467
H	-3.160327	1.806043	-0.208480
H	-0.935319	2.395717	-0.729199
H	1.222739	2.509465	-0.009697
H	3.446385	1.504012	0.312838
H	3.703169	-0.978762	0.321695
H	1.705738	-2.416468	0.015691

6,7-Benzo-2-diazobicyclo[3.2.0]hepta-3,6-diene (11)

C	-0.638905	-0.513363	0.439319
C	-1.192371	0.757103	0.279085
C	-2.487903	0.948256	-0.178750
C	-3.213295	-0.217426	-0.473128
C	-2.655868	-1.494510	-0.313681
C	-1.342908	-1.673460	0.150286
C	0.701206	0.020194	0.944493
C	0.078988	1.479774	0.737742
C	1.874865	0.022095	-0.019932
C	1.909728	1.277345	-0.754081
C	0.932986	2.107297	-0.338694
N	2.718016	-0.950372	-0.147279
N	3.455982	-1.830078	-0.244962
H	0.974681	-0.261978	1.967158
H	-0.025798	2.098368	1.638037
H	-2.934532	1.930861	-0.307459
H	-0.924063	-2.669158	0.271467
H	0.751213	3.099091	-0.737907
H	-4.235258	-0.131710	-0.833861
H	-3.259662	-2.365809	-0.554389
H	2.636306	1.483664	-1.533311

Singlet 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-ylidene (16)

C	2.623836	-0.681504	-0.333956
C	2.611421	0.720224	-0.332023
C	1.454960	1.449081	-0.004337
C	0.336094	0.691304	0.304708
C	-1.138815	0.797408	0.742217
C	-2.163376	1.040236	-0.307412
C	-2.703396	-0.125099	-0.790139
C	-1.998271	-1.302813	-0.343739
C	-1.117847	-0.801161	0.754570
C	0.355401	-0.696130	0.321312
C	1.483077	-1.432629	-0.002987
H	1.503483	-2.518434	-0.000687
H	3.542789	-1.198635	-0.597970
H	3.520128	1.255329	-0.595749
H	1.459445	2.535959	-0.002570
H	-1.303955	1.380760	1.658228
H	-2.409628	2.037238	-0.673516
H	-3.479877	-0.144773	-1.552855
H	-1.290881	-1.300957	1.715839

Table S1 Continued

Triplet 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-ylidene (16)

C	0.375256	-0.732138	0.308942
C	0.323170	0.659763	0.351584
C	1.418259	1.451958	0.038403
C	2.589021	0.766749	-0.325126
C	2.640164	-0.633830	-0.368468
C	1.523073	-1.422952	-0.049764
C	-1.082609	-0.910644	0.741388
C	-1.146915	0.707472	0.783315
C	-2.084676	-1.204160	-0.318602
C	-2.658403	-0.079402	-0.889491
C	-2.167240	1.068923	-0.269147
H	-1.242354	-1.437454	1.689476
H	-1.334436	1.157907	1.766446
H	1.394033	2.538276	0.069349
H	1.575397	-2.507960	-0.086050
H	-2.440524	2.088461	-0.520692
H	3.480952	1.334050	-0.579162
H	3.570257	-1.118182	-0.655114
H	-3.377924	-0.085523	-1.702468

6,7-Benzobicyclo[3.2.0]hepta-1,3,6-triene (17a)

C	-0.383838	-0.681050	0.230335
C	-0.459734	0.720541	0.328413
C	-1.640837	1.417492	0.115519
C	-2.760161	0.633452	-0.210667
C	-2.678880	-0.759614	-0.338970
C	-1.470884	-1.453535	-0.134236
C	1.108749	-0.732295	0.652600
C	1.011236	0.786592	0.481251
C	2.335474	-1.079558	-0.138490
C	2.923776	0.080133	-0.539117
C	2.076124	1.235621	-0.233072
H	-1.712233	2.499525	0.178894
H	-3.717004	1.120814	-0.380014
H	-3.575231	-1.317741	-0.596775
H	-1.419422	-2.533442	-0.244885
H	1.200455	-1.077042	1.692721
H	2.193459	2.214604	-0.686486
H	2.787775	-2.064687	-0.186779
H	3.876046	0.151286	-1.058057

H-shift product (17b)

C	-0.513212	-0.709276	-0.000080
C	-0.525168	0.725823	-0.000055
C	-1.678464	1.447487	0.000022
C	-2.895247	0.682004	0.000080
C	-2.885057	-0.696353	0.000054
C	-1.660284	-1.446209	-0.000031
C	1.002446	-0.662177	-0.000166
C	1.002321	0.693957	-0.000136
C	2.404896	-1.178312	0.000081
C	3.190233	0.132034	0.000164
C	2.360533	1.210492	-0.000051
H	-1.707444	2.533410	0.000054
H	-3.844885	1.210348	0.000140
H	-3.827704	-1.237347	0.000091
H	-1.676209	-2.532389	-0.000047
H	2.666610	2.250216	0.000113
H	2.648655	-1.792432	0.879384
H	2.648968	-1.792568	-0.879032
H	4.274029	0.163947	-0.000002

6,7-Benzobicyclo[3.2.0]hepta-1,4,6-triene (17c)

C	0.490647	-0.713553	0.000105
C	0.490562	0.713556	0.000055
C	1.664010	1.447427	0.000114
C	2.857082	0.700571	-0.000036
C	2.857126	-0.700502	-0.000101
C	1.664090	-1.447420	-0.000008
C	-1.000906	-0.738149	0.000049
C	-1.000916	0.737818	0.000069
C	-2.254551	-1.214651	-0.000055
C	-3.188493	0.000168	0.000066
C	-2.254428	1.214674	-0.000222
H	1.683836	2.533468	0.000126
H	3.809363	1.224490	-0.000096
H	3.809440	-1.224364	-0.000243
H	1.683954	-2.533457	0.000091
H	-2.610451	2.238839	-0.000518
H	-2.611027	-2.238666	-0.000399
H	-3.855653	0.000026	-0.876965
H	-3.854804	0.000041	0.877788

Table S1 Continued

Triplet 3,4-benzocycloheptatrienyliene (18)

C	-2.309182	1.562899	0.000000
C	-2.804900	0.259426	0.000000
C	-0.932977	1.771383	0.000000
C	-1.912096	-0.808896	0.000000
C	-0.517228	-0.625620	0.000000
C	0.000000	0.713542	0.000000
C	0.305178	-1.835521	0.000000
C	1.404205	1.108844	0.000000
C	1.652826	-1.890737	0.000000
C	2.739540	-1.029657	0.000000
C	2.571244	0.375650	0.000000
H	-2.295091	-1.826365	0.000000
H	-3.875355	0.073812	0.000000
H	-2.986482	2.412316	0.000000
H	-0.552067	2.789675	0.000000
H	1.541429	2.188079	0.000000
H	3.490955	0.960722	0.000000
H	-0.251771	-2.772840	0.000000
H	3.748723	-1.433283	0.000000

Singlet 3,4-benzocycloheptatrienyliene (18);
One Imaginary Frequency

C	-2.323070	1.539625	0.000000
C	-2.780652	0.197686	0.000000
C	-0.976940	1.800951	0.000000
C	-1.875434	-0.832026	0.000000
C	-0.458825	-0.614404	0.000000
C	0.000000	0.755362	0.000000
C	0.360138	-1.784336	0.000000
C	1.353070	1.161820	0.000000
C	1.744019	-2.069831	0.000000
C	2.665907	-0.992761	0.000000
C	2.516486	0.407728	0.000000
H	-2.223159	-1.861344	0.000000
H	-3.847174	-0.009594	0.000000
H	-3.038581	2.356986	0.000000
H	-0.624293	2.828973	0.000000
H	1.496756	2.241704	0.000000
H	3.439803	0.990289	0.000000
H	-0.275132	-2.680623	0.000000
H	3.723595	-1.285264	0.000000

Transition State Between Singlet Carbene 16
and Allene 6; One Imaginary Frequency

C	-1.887630	-1.296547	-0.365255
C	-2.727380	-0.238754	-0.732154
C	-2.281383	0.992119	-0.241791
C	-1.140148	0.961235	0.647407
C	0.300490	0.672685	0.246853
C	1.418552	1.449310	-0.048306
C	2.603378	0.756724	-0.330697
C	2.661222	-0.645112	-0.296058
C	1.537844	-1.414370	0.035465
C	0.378216	-0.708700	0.326536
C	-1.063838	-0.914936	0.731576
H	3.554838	-0.318397	-1.434461
H	-2.791576	1.927743	-0.477173
H	-1.204960	1.721753	1.438448
H	1.382133	2.535197	-0.079694
H	3.498659	1.315699	-0.590816
H	3.601475	-1.141130	-0.522085
H	1.587936	-2.498455	0.075604
H	-1.314760	-1.224338	1.748712

Transition State Between Singlet Carbene 16
and 6,7-Benzobicyclo[3.2.0]hepta-1,3,6-triene
(17a); One Imaginary Frequency

C	0.675714	0.238834	-0.373195
C	-0.723387	0.306056	-0.457649
C	-1.416758	0.081604	-1.635916
C	-0.625653	-0.218796	-2.756322
C	0.770485	-0.315046	-2.672713
C	1.457353	-0.100623	-1.465179
C	0.744720	0.655942	1.120190
C	-0.778868	0.420839	1.029260
C	1.052534	-0.150864	2.346569
C	-0.110869	-0.536229	2.940659
C	-1.290425	-0.415078	2.040410
H	-2.499453	0.122881	-1.704290
H	-1.108058	-0.394112	-3.714254
H	1.335508	-0.556976	-3.569053
H	2.539625	-0.181162	-1.413682
H	1.101665	1.690339	1.216567
H	-1.780142	0.802465	1.802375
H	2.045470	-0.263759	2.772321
H	-0.163689	-1.019507	3.913336

Table S2. B3LYP/6-31G* + ZPVE Corrected Energies for Selected Species

<u>Compound</u>	<u>HF Energy^a</u>	<u>ZPVE^b</u>	<u>Rel Energy +ZPVE^c</u>
4	-423.922539	0.153208	0
6	16.6	-1.2	15.4
16 triplet	73.8	-2.0	71.8
16 singlet	73.2	-2.1	71.1
TS connecting singlet 16 to 6	78.5	-3.0	75.5
TS connecting singlet 16 to 17a	100.2	-4.6	95.6
17a	25.9	-0.9	25.0
17b	41.1	-1.5	39.6
17c	24.2	-0.9	23.3
18 triplet	35.5	-2.1	33.4
18 singlet (TS)	47.0	-2.0	45.0

^a Absolute energy for 4 in hartrees, energies relative to 4 in kcal/mol. ^b Total zero-point vibrational energy for 4 in hartrees (unscaled), ZPVE relative to 4 in kcal/mol. ^c In kcal/mol.

Table S3. B3LYP/6-31G* Calculated IR Frequencies (Unscaled) and Intensities (KM/mol)

Allene 6		Diazo Compound 11	
ν	I	ν	I
3210.1738	28.8732	3236.3862	15.2482
3197.2964	31.5471	3215.0447	0.9280
3185.2753	3.1807	3206.7410	29.9902
3178.8904	8.6722	3198.7759	32.9857
3167.8275	42.4074	3189.5825	5.9326
3160.9487	14.2969	3179.1261	0.0409
3160.1254	36.0389	3080.0500	34.8968
3140.5977	6.2953	3057.3833	32.1476
1934.8350	7.7665	2171.9888	833.6595
1655.0451	3.8643	1659.4122	3.1473
1637.3798	4.9791	1646.8503	1.0158
1598.6865	3.7747	1634.7655	22.1706
1518.5915	6.8349	1507.1711	13.7822
1486.3052	2.0691	1504.0942	2.7570
1448.7473	4.9391	1454.9113	21.5037
1424.4228	13.9397	1387.3136	5.8610
1356.9545	1.2297	1348.1793	0.8348
1331.8867	2.8201	1307.9309	1.7215
1286.3462	6.1139	1292.8651	1.2421
1253.7247	0.3282	1273.6108	12.5765
1225.4474	3.2108	1246.1226	6.2215
1198.3516	0.2639	1225.0610	4.1846
1188.0446	4.3888	1211.8281	3.6747
1142.6861	0.1016	1186.4442	0.5511
1115.3676	3.7716	1160.4954	4.0850
1072.2238	1.4978	1157.6033	1.6446
1030.2223	1.2898	1111.6512	1.5000
991.0015	0.5676	1105.7987	1.1010
982.4719	2.5415	1032.3289	1.8037
957.7956	2.8687	1002.6711	4.4598
910.2219	4.3323	984.4164	0.0108
874.6291	3.0977	943.7408	1.8396
864.8871	13.3825	939.5890	1.2213
827.5877	28.1435	920.0675	0.6271
815.0422	23.2074	901.4519	7.7299
776.3861	27.9110	880.4856	1.2438
754.8896	5.5491	837.8973	2.5552
727.1222	5.7617	826.7000	2.9652
717.3485	19.6370	778.4325	7.1130
639.4602	27.4705	754.7210	17.5730
584.8324	4.4852	752.1377	25.2402
582.5421	5.2122	726.2274	31.9679
508.4482	12.1969	650.3546	0.2984
456.7221	1.4276	626.6117	10.9815
433.8351	1.3674	599.2299	2.0341
423.0169	7.7948	565.0923	1.3441
359.0391	4.9677	510.6470	2.5408
327.3525	3.0800	500.6331	4.2804
314.6236	1.1039	473.6433	0.8140
147.7779	0.3849	418.2829	4.1040
131.6776	0.7081	406.2651	0.7554
		310.5580	2.0204
		269.7946	1.0973
		188.1787	1.8071
		122.2161	0.2647
		108.5404	1.3003
		56.7461	0.3001