

Supplementary Material

C₈H₆ Thermal Chemistry. 7-Methylenecyclohepta-1,3,5-dienyne (Heptafulvyne) by Flash Vacuum Thermolysis–Matrix Isolation. Chemical Activation in the Rearrangements of Phenylenedicarbenes and of Benzocyclobutadiene to Phenylacetylene

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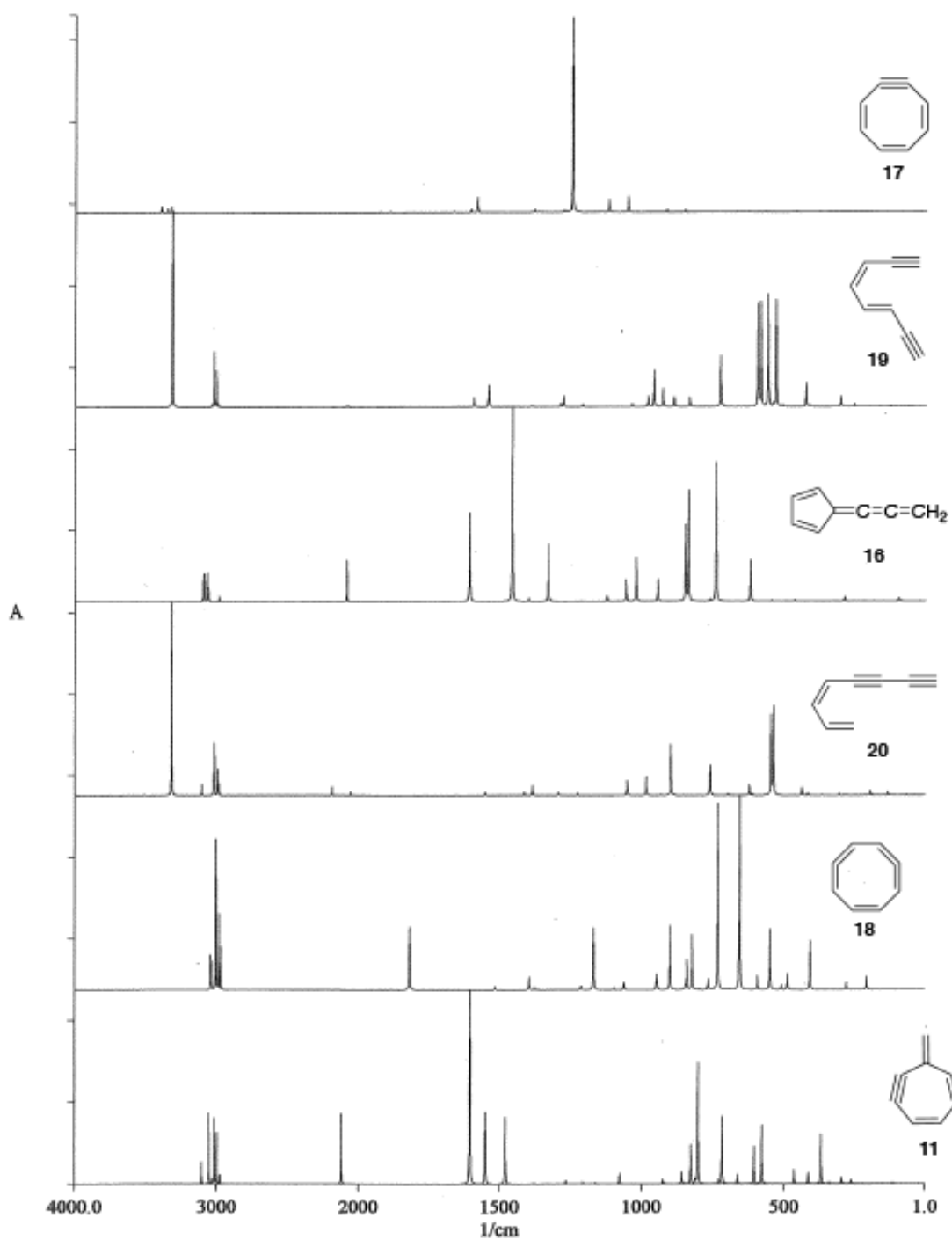


Figure S1. Calculated IR spectra of compounds **11** and **16-20** (B3LYP/6-31G*); wavenumbers scaled by a factor 0.95.

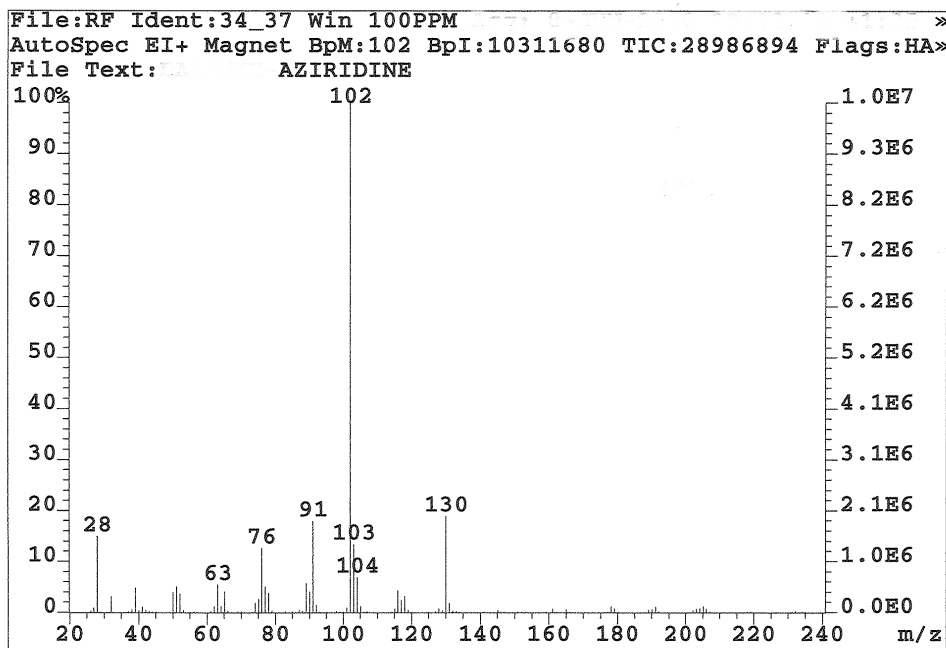


Figure S2. Mass spectrum of diazobenzocyclobutene **2** (m/z 130) obtained by FVT of aziridine **8** at 200 °C (70 eV EI)

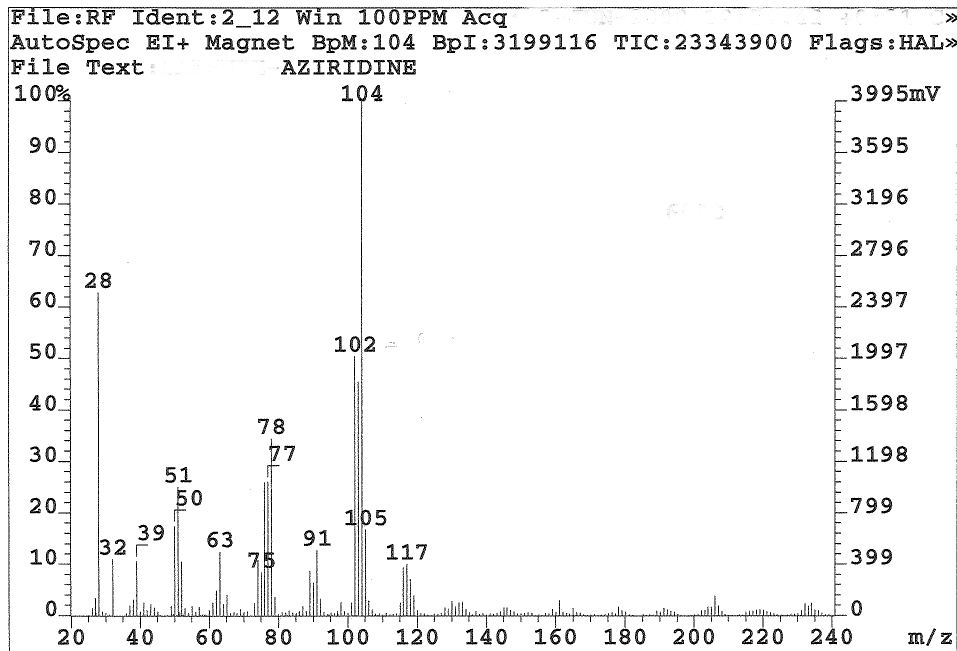


Figure S3. Mass spectrum of products of FVT of aziridine **8** at 400 °C; m/z 104 = styrene; m/z 102 = **11/12/13**

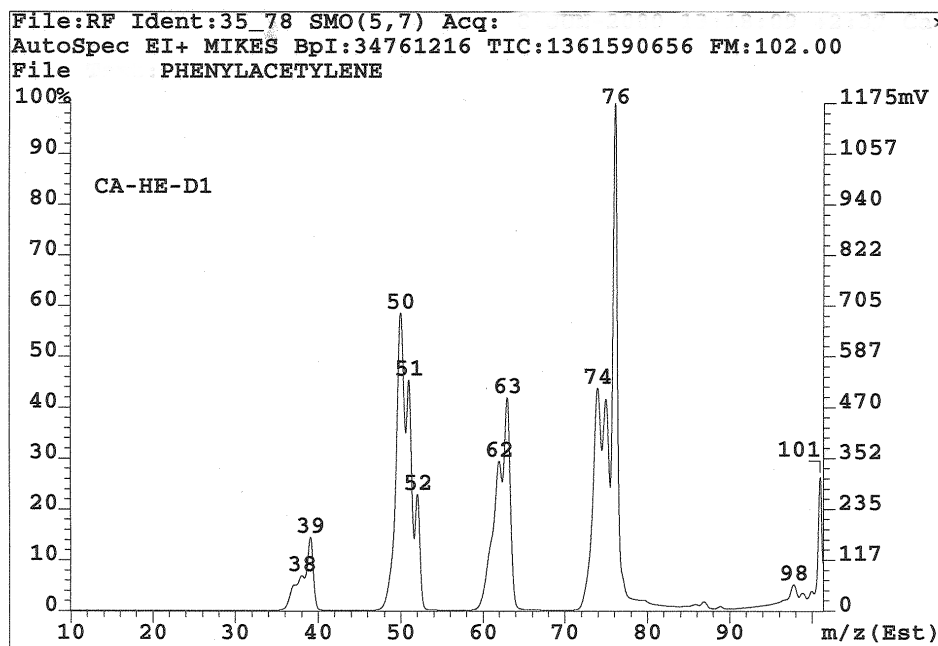


Figure S4. CAMS of m/z 102 from phenylacetylene (He as collision gas)

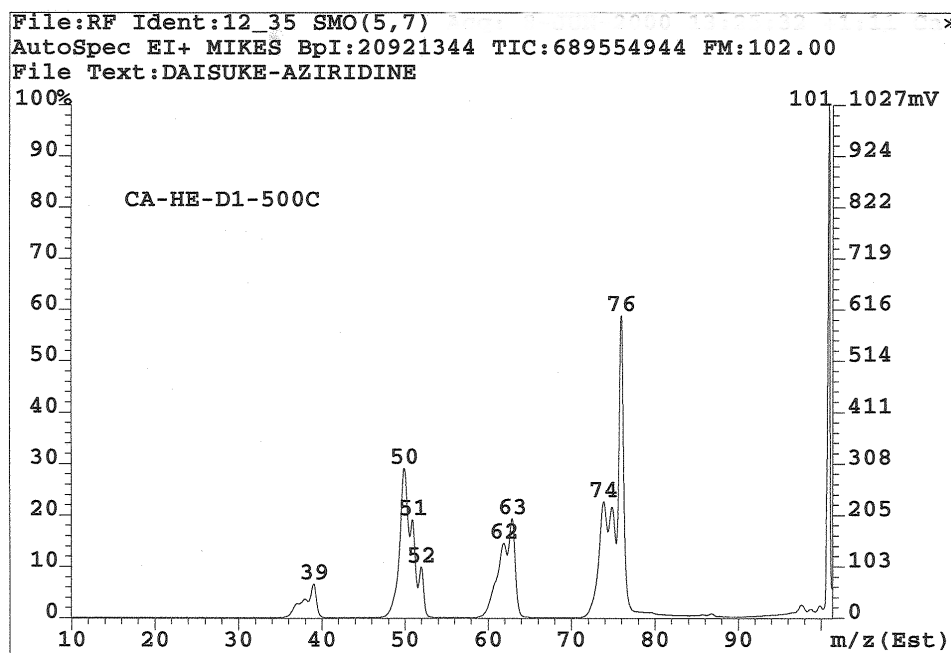


Figure S5. CAMS of m/z 102 from the FVT of aziridine **8** at 500 °C.

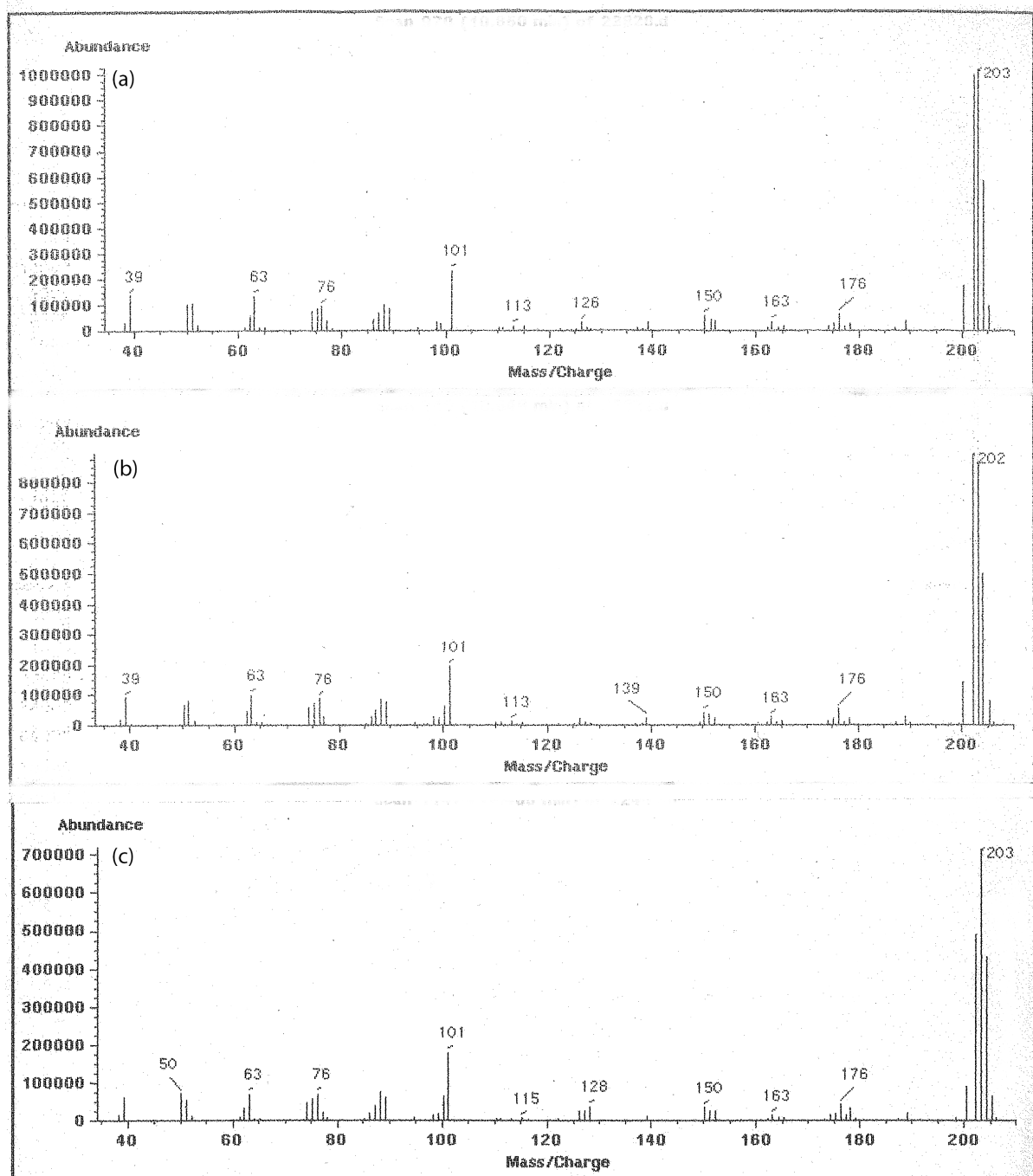


Figure S6. Mass spectra of (a) Frimer's dimer **5**, (b) Frimer's dimer **4**, and (c) benzocyclobutadiene dimer **14** (70 eV, EI).

Calculated Vibrational Spectra (B3LYP/6-31G*); wavenumbers scaled by 0.95

Cycloocta-1,3,5-trien-7-yne 17

Moden-Nr.	Frequenz	abs.Int.	rel. Int.	Scale :0.95
1	486.584	.6962	0	462
2	555.1261	.0274	0	527
3	606.6233	.8416	0	576
4	785.7664	.0094	0	746
5	866.8966	.1825	0	823
6	898.6178	2.2771	1	853
7	944.9197	.3281	0	897
8	968.124	2.282	1	919
9	970.5162	.4347	0	921
10	1072.071	.208	0	1018
11	1108.73	13.2389	8	1053
12	1122.429	.4575	0	1066
13	1180.919	10.9037	6	1121
14	1314.624	164.3997	100	1248
15	1317.819	1.9398	1	1251
16	1345.475	1.9693	1	1278
17	1393.23	.002	0	1323
18	1395.947	.0603	0	1326
19	1423.919	.0205	0	1352
20	1429.488	.3034	0	1358
21	1440.845	.4348	0	1368
22	1455.693	2.5224	1	1382
23	1590.86	.0616	0	1511
24	1668.239	12.8739	7	1584
25	1692.808	2.7454	1	1608
26	1754.813	.7751	0	1667
27	1957.478	.0421	0	1859
28	1993.689	.9062	0	1894
29	2031.254	.6113	0	1929
30	2640.214	.2164	0	2508
31	3495	1.2685	0	3320
32	3500.284	5.5716	3	3325
33	3528.286	2.6072	1	3351
34	3528.926	2.6559	1	3352
35	3574.74	5.1846	3	3396
36	3574.914	5.4384	3	3396

ar10 COen3yn B3LYP/6-31G* 0.95

Gaussian 94

Octa-3,5-dien1,7-diyne 19

Moden-Nr.	Frequenz	abs.Int.	rel. Int.	Scale :0.95
1	77.8303	.0373	0	73
2	103.0309	.0821	0	97
3	136.0134	.409	0	129
4	175.8623	.1722	0	167
5	273.3064	1.4209	1	259
6	322.2337	4.7247	5	306
7	442.6093	1.0041	1	420
8	453.1529	10.5246	13	430
9	539.2293	.9882	1	512
10	562.9812	47.3588	58	534
11	573.1314	2.1097	2	544
12	592.0884	49.6935	61	562
13	619.1794	46.3276	57	588
14	631.4419	45.9457	56	599
15	764.4948	5.3898	6	726
16	768.3681	22.4409	27	729
17	881.6789	4.2861	5	837
18	938.2308	4.3045	5	891
19	980.1419	8.2581	10	931
20	1012.898	16.4162	20	962
21	1034.276	4.7701	5	982
22	1093.237	1.3786	1	1038
23	1277.288	1.1261	1	1213
24	1347.947	4.7536	5	1280
25	1358.394	1.5834	1	1290
26	1464.488	.5535	0	1391
27	1626.052	9.5782	11	1544
28	1680.542	4.1183	5	1596
29	2201.305	.8199	1	2091
30	2209.726	.0115	0	2099
31	3157.858	1.1149	1	2999
32	3171.542	16.3294	20	3012
33	3186.72	24.5798	30	3027
34	3204.655	1.1726	1	3044
35	3492.732	70.1633	87	3318
36	3495.159	80.6241	100	3320

ar15 1,7diyne B3LYP/6-31G* 0.95

Gaussian 94

Propadienylidenecyclopentadiene 16

Moden-Nr.	Frequenz	abs.Int.	rel. Int.	Scale :0.95
1	102.0318	.8897	1	96
2	105.3572	1.4367	1	100
3	275.4543	.0281	0	261
4	307.1777	1.9536	2	291
5	452.2313	0	0	429
6	492.2185	.5923	0	467
7	522.655	.2194	0	496
8	577.8613	.3763	0	548
9	601.3479	0	0	571
10	656.1969	17.306	21	623
11	727.8228	0	0	691
12	784.1115	58.4235	71	744
13	804.3563	1.0652	1	764
14	884.5212	46.3337	56	840
15	894.9798	32.3351	39	850
16	917.9902	.1469	0	872
17	930.9057	0	0	884
18	997.8605	9.0891	11	947
19	1046.029	.005	0	993
20	1076.984	18.5088	22	1023
21	1113.704	8.8528	10	1058
22	1166.456	.0012	0	1108
23	1184.907	2.3874	2	1125
24	1323.364	.0051	0	1257
25	1402.51	24.1716	29	1332
26	1475.365	1.3088	1	1401
27	1536.579	81.5292	100	1459
28	1620.165	.0542	0	1539
29	1695.077	37.2841	45	1610
30	2199.165	17.2783	21	2089
31	3147.523	2.2259	2	2990
32	3222.517	3.3015	4	3061
33	3224.237	5.8446	7	3063
34	3236.293	12.0467	14	3074
35	3261.575	10.3836	12	3098
36	3264.986	11.5357	14	3101

ar5 Cp=C=C=CH2 B3LYP/6-31G* 0.95

Gaussian 94

Cycloocta-1,3-dien-5,7-diyne 20

Moden-Nr.	Frequenz	abs.Int.	rel. Int.	Scale :0.95
1	48.1871	.0066	0	45
2	73.4358	.4411	0	69
3	143.4695	2.694	2	136
4	208.573	3.2631	2	198
5	308.9729	.3247	0	293
6	327.244	1.1195	0	310
7	443.1991	1.4255	1	421
8	464.3445	4.9815	4	441
9	569.9318	54.2641	45	541
10	578.9214	49.9525	42	549
11	649.4958	.9357	0	617
12	658.2414	6.6991	5	625
13	679.6495	.1909	0	645
14	736.5621	.9677	0	699
15	803.5148	18.6303	15	763
16	806.4646	1.9932	1	766
17	946.6689	6.4744	5	899
18	949.2693	31.2976	26	901
19	985.8771	.328	0	936
20	1038.079	11.6765	9	986
21	1108.48	9.3571	7	1053
22	1194.151	.0671	0	1134
23	1291.333	1.4102	1	1226
24	1362.426	1.6422	1	1294
25	1459.966	6.4254	5	1386
26	1489.163	2.3398	1	1414
27	1635.131	1.9969	1	1553
28	1701.301	.0807	0	1616
29	2167.422	2.1734	1	2059
30	2306.575	5.4951	4	2191
31	3148.647	7.1121	5	2991
32	3155.495	16.226	13	2997
33	3178.726	32.2026	27	3019
34	3184.877	13.5361	11	3025
35	3273.849	6.8978	5	3110
36	3495.554	118.901	100	3320

ar16 1,3-diyne B3LYP/6-31G* 0.95

Gaussian 94

Cycloocta-1,2,4,5,7-pentaene 18

Moden-Nr.	Frequenz	abs.Int.	rel. Int.	Scale :0.95
1	221.6252	4.6065	7	210
2	228.8868	.0982	0	217
3	296.7242	.2182	0	281
4	297.4285	2.5464	3	282
5	433.5214	16.5111	25	411
6	516.0421	5.4679	8	490
7	538.4422	1.7129	2	511
8	581.0072	20.4815	31	551
9	626.9302	4.7427	7	595
10	692.9763	65.6008	100	658
11	772.9404	63.0431	96	734
12	807.9855	3.7079	5	767
13	836.9547	.4158	0	795
14	868.2171	18.6928	28	824
15	886.8784	10.1375	15	842
16	891.9188	1.854	2	847
17	949.8446	21.7447	33	902
18	996.8506	1.805	2	947
19	998.8929	5.2439	7	948
20	1118.155	2.4837	3	1062
21	1155.902	.7183	1	1098
22	1232.223	21.0114	32	1170
23	1276.234	1.1496	1	1212
24	1279.348	1.107	1	1215
25	1436.567	.2602	0	1364
26	1450.205	.7171	1	1377
27	1469.568	4.2903	6	1396
28	1598.228	1.1123	1	1518
29	1915.204	21.1592	32	1819
30	1982.45	.1266	0	1883
31	3131.697	14.3068	21	2975
32	3133.637	.1656	0	2976
33	3144.467	25.6077	39	2987
34	3164.102	51.0049	77	3005
35	3197.94	9.1953	14	3038
36	3202.113	11.8599	18	3042

ar17 C-oct-en5 B3LYP/6-31G* 0.95

Gaussian 94

7-Methylenecyclohepta-1,2-dien-5-yne 11 (heptafulvyne)

Moden-Nr.	Frequenz	abs.Int.	rel. Int.	Scale :0.95
1	123.0881	.5199	0	116
2	278.8877	1.6352	2	264
3	313.2849	2.6162	3	297
4	359.1429	.6772	0	341
5	389.7269	17.7379	25	370
6	438.2965	4.0401	5	416
7	489.365	5.0462	7	464
8	609.9977	21.1506	30	579
9	638.1461	13.5094	19	606
10	698.9936	3.4294	4	664
11	756.7489	24.1602	34	718
12	767.6753	1.8043	2	729
13	845.0868	43.4501	62	802
14	854.247	2.2241	3	811
15	871.5416	14.0885	20	827
16	903.8509	4.4054	6	858
17	970.4822	.0033	0	921
18	973.805	1.6982	2	925
19	1013.857	.0217	0	963
20	1134.704	3.9812	5	1077
21	1223.394	.4958	0	1162
22	1270.392	.632	0	1206
23	1333.197	1.351	1	1266
24	1418.563	.0881	0	1347
25	1451.007	.2412	0	1378
26	1484.572	.0148	0	1410
27	1557.258	24.1493	34	1479
28	1631.952	25.7218	36	1550
29	1690.454	70.0675	100	1605
30	2231.931	25.2868	36	2120
31	3135.003	3.0941	4	2978
32	3156.34	18.4486	26	2998
33	3172.68	23.771	33	3014
34	3183.206	1.9939	2	3024
35	3213.594	25.3616	36	3052
36	3270.004	7.8914	11	3106

ar18 Cyc-heptyne B3LYP/6-31G* 0.95

Gaussian 94