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Supplementary Material

Mass Spectrometry of Cyclopentadienylideneketene. Differentiation of Isomeric Ion Structures by Means of Ion-Molecule Reactions.

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Contents:

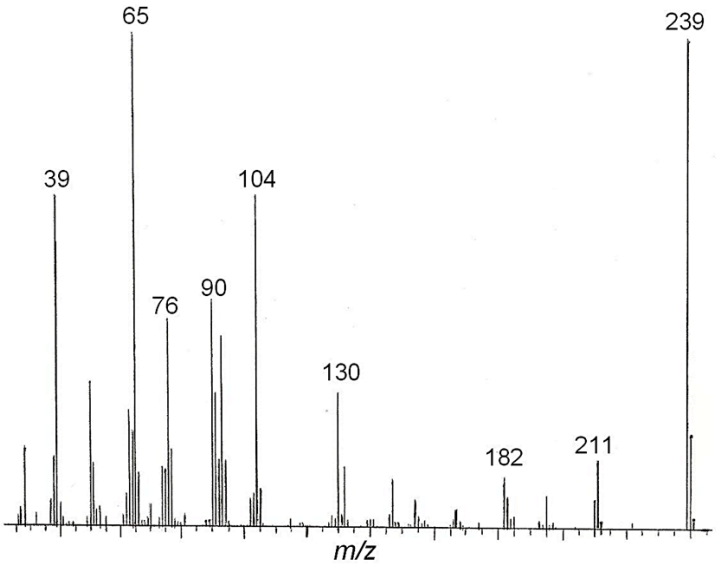


Figure S1. EI-MS of *N*-phenoxyphthalimide (MW 239 u); *m/z* 104 ions are derived from the loss of PhONCO from the molecular ion (*m/z* 239); *m/z* 76 corresponds to benzyne or a ring-opened isomer thereof, $C_6H_4^{+\bullet}$.

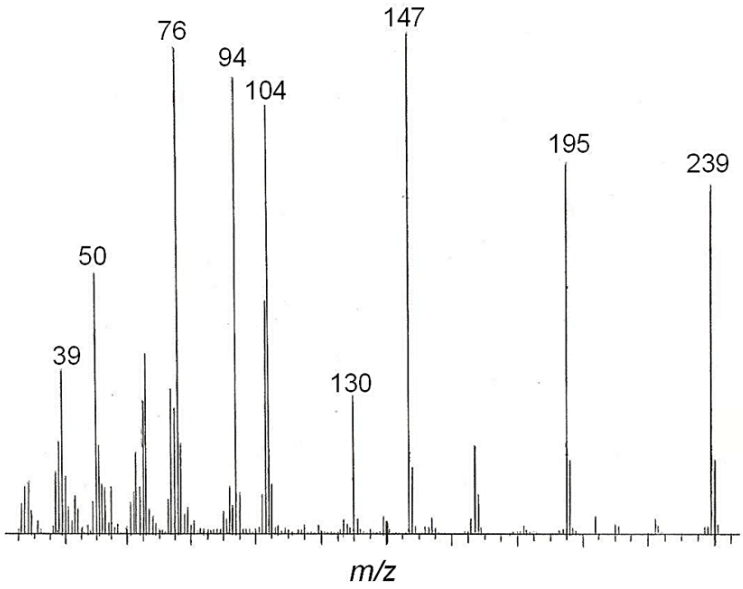


Figure S2. FVT-EI-MS of *N*-phenoxyphthalimide at 500 ^{o}C; *m/z* 195 is derived from the loss of CO_2 from the molecular ion (*m/z* 239); *m/z* 94 corresponds to PhOH molecular ions, and *m/z* 147 to ionized phthalimide. Phenol and phthalimide are formed as neutrals by FVT; *m/z* 104 and 76 as in Figure S1.

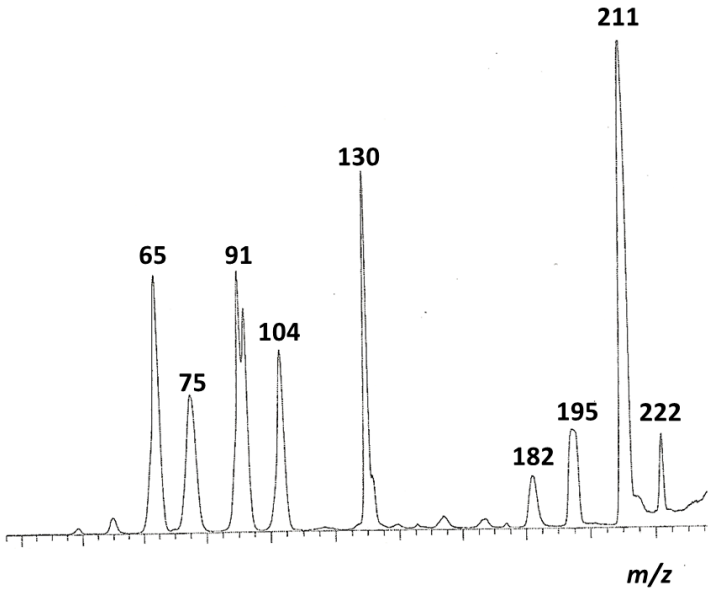


Figure S3. EI-MS of *N*-phenoxyphthalimide at 150 °C: collisional activation mass spectrum (He, 8 kV) of the *m/z* 239 molecular ions.

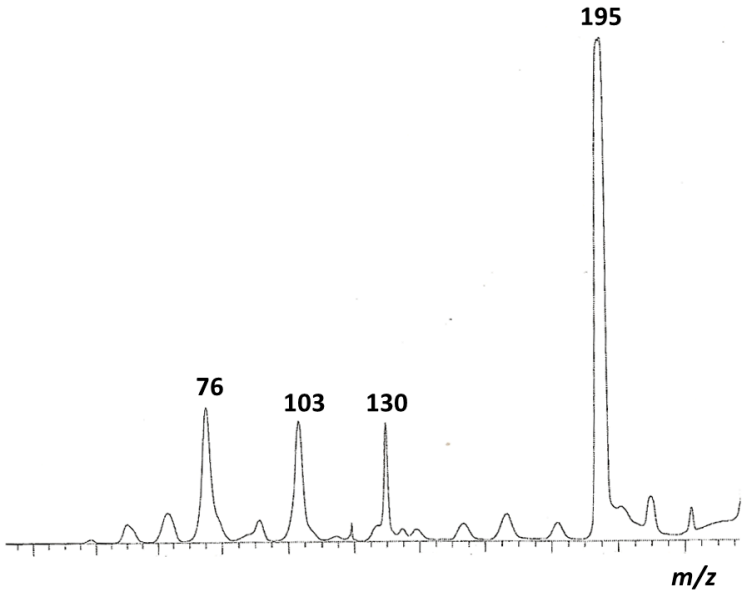


Figure S4. FVT-EI-MS of *N*-phenoxyphthalimide at 500 °C: collisional activation mass spectrum (He, 8 kV) of the *m/z* 239 molecular ions.

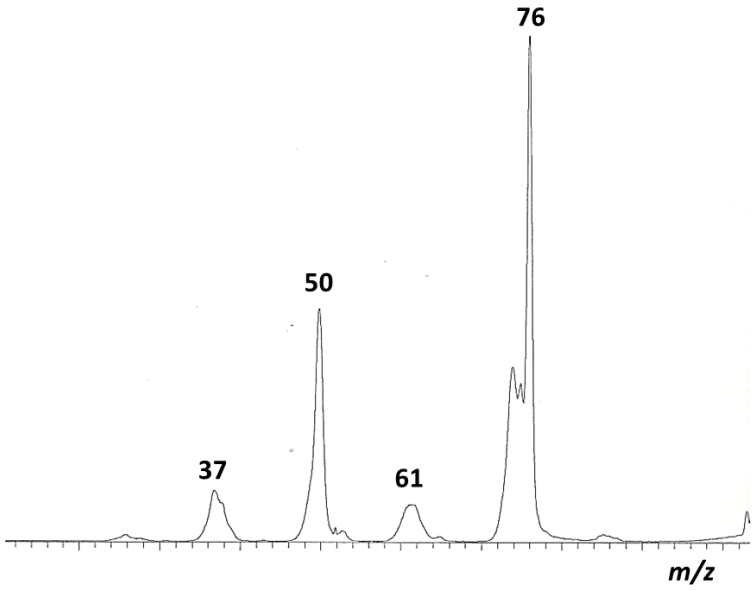


Figure S5. FVP-MSMS of *N*-phenoxyphthalimide at 150 °C: Collisional activation mass spectrum (He, 8 kV) of the *m/z* 104 radical cations from **9**.

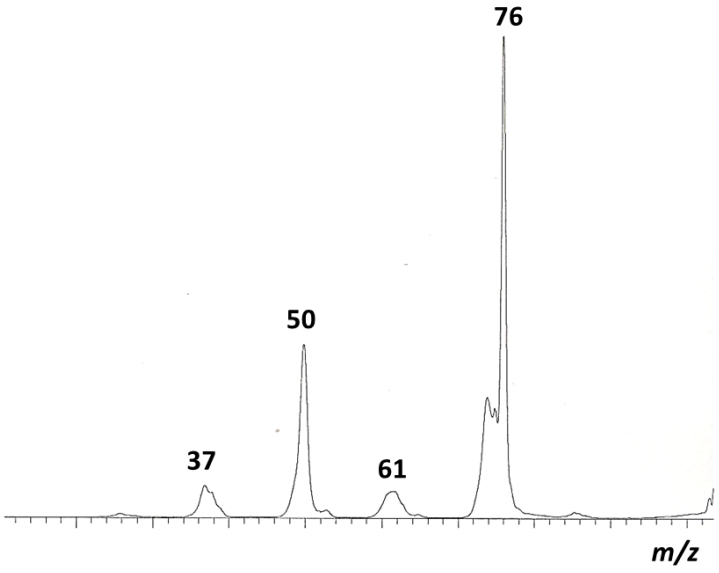


Figure S6. FVP-MSMS at 510 °C: Collisional activation mass spectrum (He, 8 kV) of the *m/z* 104 radical cations from **9** or **10**.

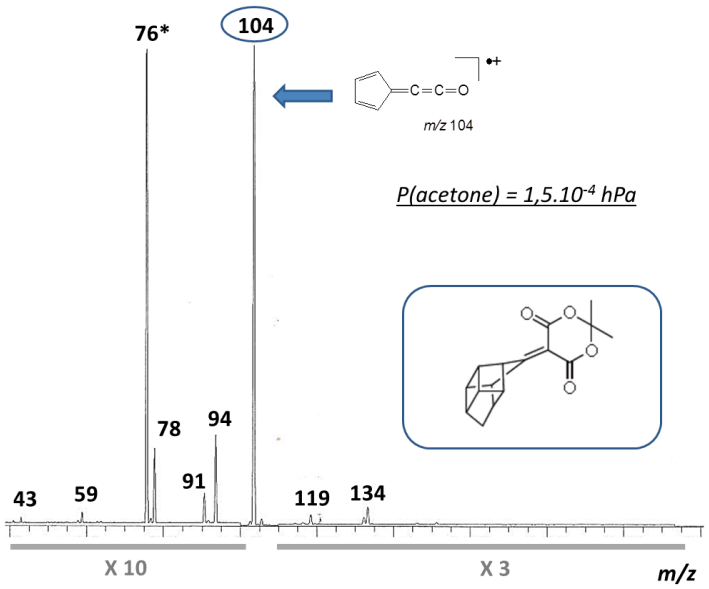


Figure S7. Associative ion-molecule reaction between acetone and *m/z* 104 radical cations prepared by EI-MS (150 °C) of the cage compound (**3**).

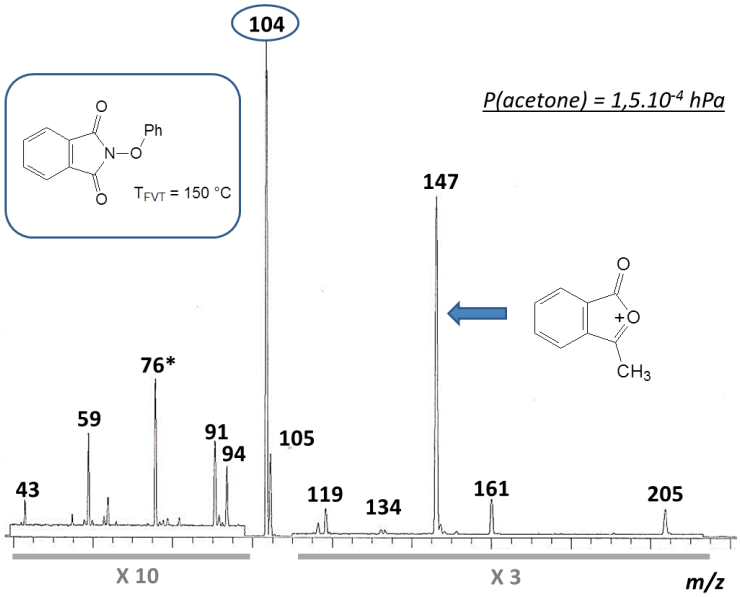


Figure S8. Associative ion-molecule reaction between acetone and *m/z* 104 radical cations prepared by EI-MS (150 °C) of the *N*-phenoxyphthalimide (**9**).

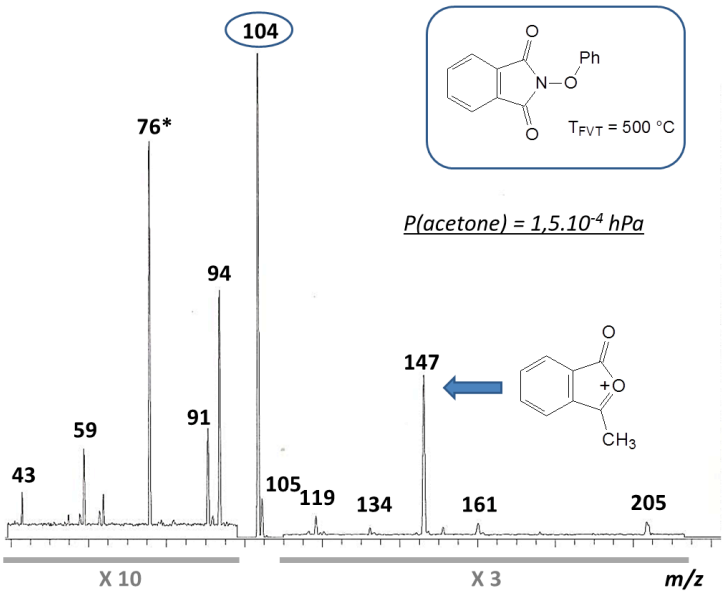


Figure S9. Associative ion-molecule reaction between acetone and *m/z* 104 radical cations prepared by FVT-EI-MS (510 °C) of the *N*-phenoxyphthalimide (**9**).

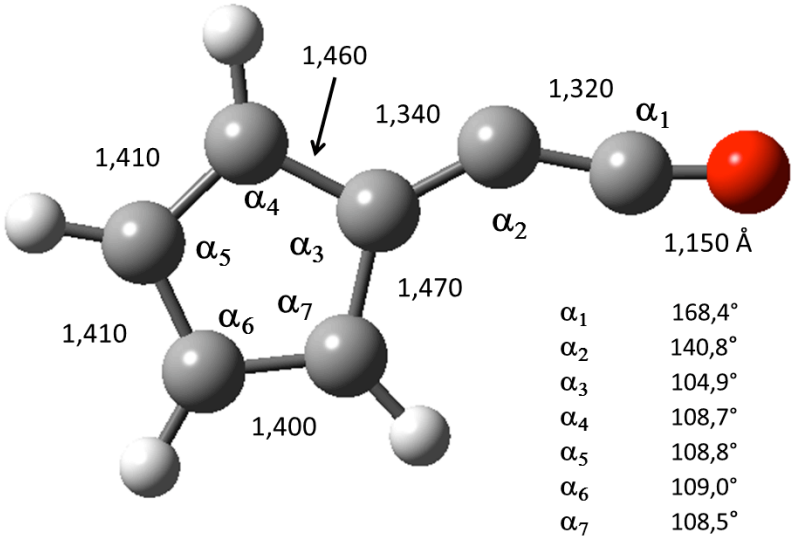


Figure S10. Radical cations $\mathbf{1}^{\bullet+}$: geometrical parameters of the optimized structure at the B3LYP/6-31+G(d,p) level of theory.

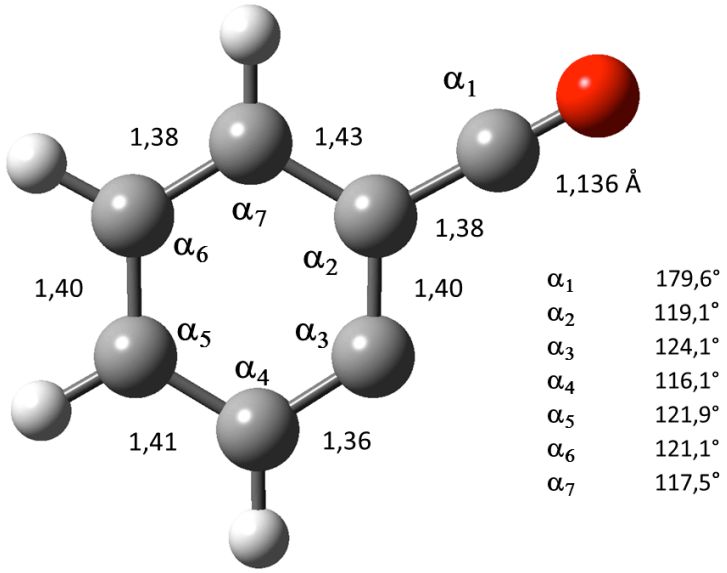
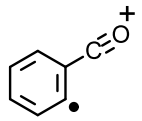
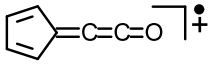
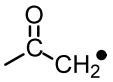
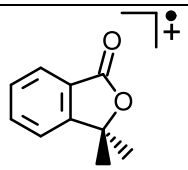
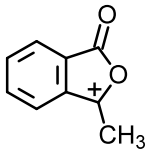
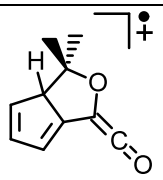
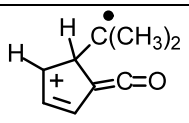


Figure S11. Radical cations $\mathbf{8}^{\bullet+}$: geometrical parameters of the optimized structure at the B3LYP/6-31+G(d,p) level of theory.

Table S1. Electronic energy (Hartree) and ZPE (kJ/mol) for the molecules and ions relevant to the associative io,/molecule reactions between ions $\mathbf{1}^{\bullet+}$ and $\mathbf{8}^{\bullet+}$ and acetone: energies obtained at the B3LYP/6-31+G(d,p) level of theory

	Electronic energy (Hartree)	Zero-point vibrational energy (kJ/mol)
	-344,00877100	225,7654
	-343,9697841	220,162
	-193,17450180	219,1845
CO	-113,3173231	13,1738
	-192,5134375	184,4676
$CH_3^{\bullet}$	-39,8473347	78,2923
	-344,7046118	260,3391
	-537,25783330	457,6659
	-497,3835442	359,4715
	-537,2123857	458,1599
	-423,8852233	429,1598

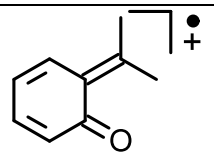
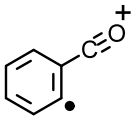
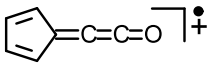
	-423,9175656	429,1661

Table S2. Optimized geometries for the prinicpal ions relevant to the associative io,/molecule reactions between ions $\mathbf{1}^{\bullet+}$ and $\mathbf{8}^{\bullet+}$ and acetone: structures obtained at the B3LYP/6-31+G(d,p) level of theory.

	Cartesian Coordinates				
	**Center Number**	**Atomic Number**	**Coordinates (Angstroms)** **X**	**Y**	**Z**
	1	**6**	**-1.339906**	**-1.467321**	**0.000000**
	2	**6**	**-1.225244**	**-0.106699**	**0.000000**
	3	**6**	**0.000000**	**0.577999**	**0.000000**
	4	**6**	**1.220512**	**-0.173428**	**0.000000**
	5	**6**	**1.124156**	**-1.553536**	**0.000000**
	6	**6**	**-0.130061**	**-2.194136**	**0.000000**
	7	**1**	**-2.302039**	**-1.970281**	**0.000000**
	8	**1**	**2.179797**	**0.334368**	**0.000000**
	9	**1**	**2.030434**	**-2.149595**	**0.000000**
	10	**1**	**-0.172992**	**-3.279991**	**0.000000**
	11	**6**	**0.014833**	**1.963005**	**0.000000**
	12	**8**	**0.034883**	**3.098775**	**0.000000**
	**Center Number**	**Atomic Number**	**Coordinates (Angstroms)** **X**	**Y**	**Z**
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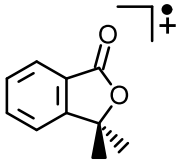
	2	**6**	**-0.776209**	**1.103510**	**-0.000063**
	3	**6**	**-0.152393**	**-0.227752**	**-0.000022**
	4	**6**	**-1.274977**	**-1.171095**	**0.000030**
	5	**6**	**-2.479271**	**-0.439507**	**0.000006**
	6	**1**	**-2.901065**	**1.746646**	**0.000099**
	7	**1**	**-0.236757**	**2.044225**	**-0.000162**

	8	1	-1.168553	-2.250100	0.000157
	9	1	-3.476144	-0.864651	0.000063
	10	6	1.146578	-0.576921	-0.000166
	11	6	2.356874	-0.033837	-0.000035
	12	8	3.488479	0.218207	0.000115



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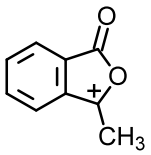
4	6	-1.948711	1.111625	0.000162
5	6	-2.877553	0.035899	-0.000101
6	6	-2.448272	-1.333376	-0.000057
7	1	-0.778223	-2.689397	0.000075
8	1	-2.278354	2.145977	0.000369
9	1	-3.942687	0.249807	-0.000423
10	1	-3.201714	-2.114432	-0.000134
11	6	0.599465	1.640218	-0.000011
12	8	0.657836	2.842492	-0.000113
13	8	1.683300	0.813853	-0.000073
14	6	1.310870	-0.590539	-0.000022
15	6	1.897747	-1.241949	-1.280423
16	1	1.672983	-2.310710	-1.301303
17	1	1.500361	-0.766296	-2.179612
18	1	2.981055	-1.102792	-1.254497
19	6	1.897706	-1.241835	1.280483
20	1	1.500399	-0.765996	2.179615
21	1	1.672790	-2.310558	1.301567
22	1	2.981026	-1.102802	1.254488



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4	6	-0.341291	0.744122	0.000092

	5	6	-0.097031	-0.643670	-0.006325
	6	6	-1.149470	-1.562595	-0.008059
	7	1	-3.296830	-1.728594	-0.002027
	8	1	-3.707282	0.701017	0.009167
	9	1	-1.806972	2.332309	0.010480
	10	1	-0.978084	-2.633889	-0.014695
	11	6	0.946010	1.447020	-0.001094
	12	8	1.341439	2.552586	0.001765
	13	8	1.975019	0.293875	-0.009118
	14	6	1.335653	-0.831835	-0.009402
	15	6	2.111999	-2.083204	0.007633
	16	1	1.493595	-2.954741	-0.205909
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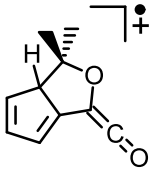
	18	1	2.559333	-2.198401	1.006137



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4	6	-0.251574	2.224451	0.060321
5	1	-1.057442	2.901681	0.319094
6	6	1.910733	1.437909	-0.173747
7	1	2.992734	1.408638	-0.227563
8	6	1.149944	2.548059	0.109625
9	1	1.537438	3.529296	0.357669
10	6	-2.584541	-0.204994	-0.014107
11	8	-3.730807	-0.162694	0.067326
12	8	-0.567722	-1.398012	-0.154454
13	6	0.921042	-1.109158	0.044899
14	1	1.111111	0.195441	-1.670241
15	6	1.652946	-2.193453	-0.723285
16	1	2.731983	-2.022717	-0.654540
17	1	1.438368	-3.176166	-0.296417
18	1	1.366583	-2.198122	-1.778060
19	6	1.184700	-1.140006	1.544704
20	1	2.251692	-0.976659	1.726887

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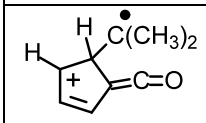

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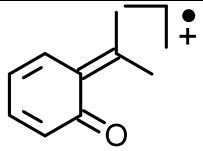
4	6	0.149044	-0.213791	-0.846760
5	6	-1.143849	0.213952	-0.224334
6	6	1.336019	-0.427660	0.097420
7	6	-2.238302	-0.582972	-0.103850
8	8	-3.162007	-1.263016	-0.030502
9	1	1.826704	1.263263	-1.353375
10	1	0.638654	2.962386	0.332734
11	1	-1.796335	2.068793	0.836699
12	6	1.199894	-0.559517	1.594204
13	1	2.122222	-0.230639	2.082672
14	1	0.370123	0.006276	2.019584
15	1	1.057916	-1.616739	1.847125
16	6	2.505118	-1.177163	-0.499497
17	1	3.445231	-0.843417	-0.047934
18	1	2.402617	-2.247587	-0.284038
19	1	2.577336	-1.053937	-1.583253
20	1	0.139143	-0.785329	-1.771346



Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
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3	6	-0.204966	-0.230438	-0.004755
4	6	0.519083	-1.439252	0.024551
5	6	1.924940	-1.480033	0.039083
6	6	2.690897	-0.297952	0.019244
7	1	2.602880	1.865265	-0.035981
8	1	-0.003503	-2.387163	0.062289
9	1	2.421344	-2.444743	0.071140

	10	**1**	**3.774938**	**-0.356479**	**0.033292**
	11	**6**	**-1.626845**	**-0.220668**	**0.010902**
	12	**6**	**-2.441548**	**-1.460812**	**-0.095711**
	13	**1**	**-3.049481**	**-1.557273**	**0.815743**
	14	**1**	**-3.170871**	**-1.322568**	**-0.905927**
	15	**1**	**-1.901731**	**-2.388381**	**-0.266755**
	16	**6**	**-2.420257**	**1.029197**	**0.127465**
	17	**1**	**-2.083549**	**1.646395**	**0.967479**
	18	**1**	**-2.241054**	**1.665376**	**-0.751486**
	19	**1**	**-3.486508**	**0.817529**	**0.211483**
	20	**8**	**0.074279**	**2.158324**	**-0.083650**