SUPPORTING INFORMATION

for

Trapping of a *tert*-adamantyl peroxyl radical in the gas phase

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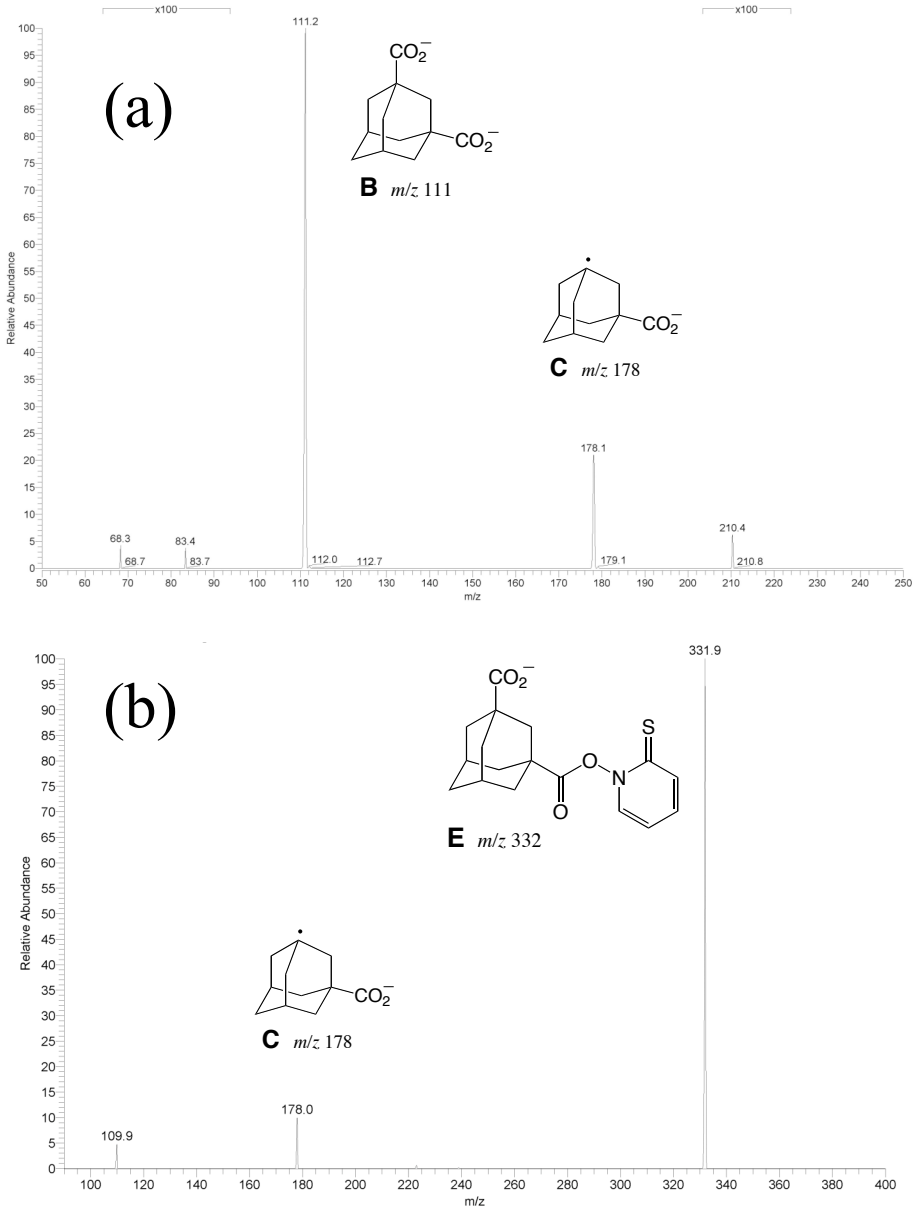
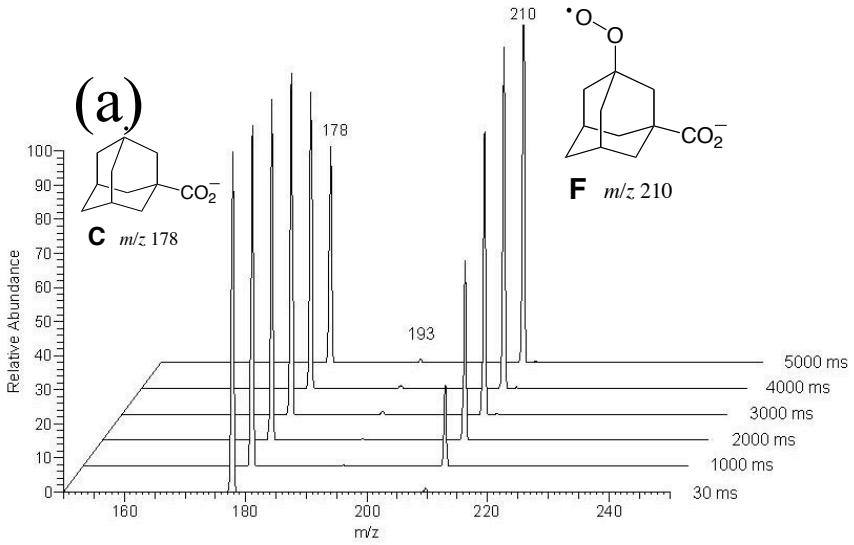
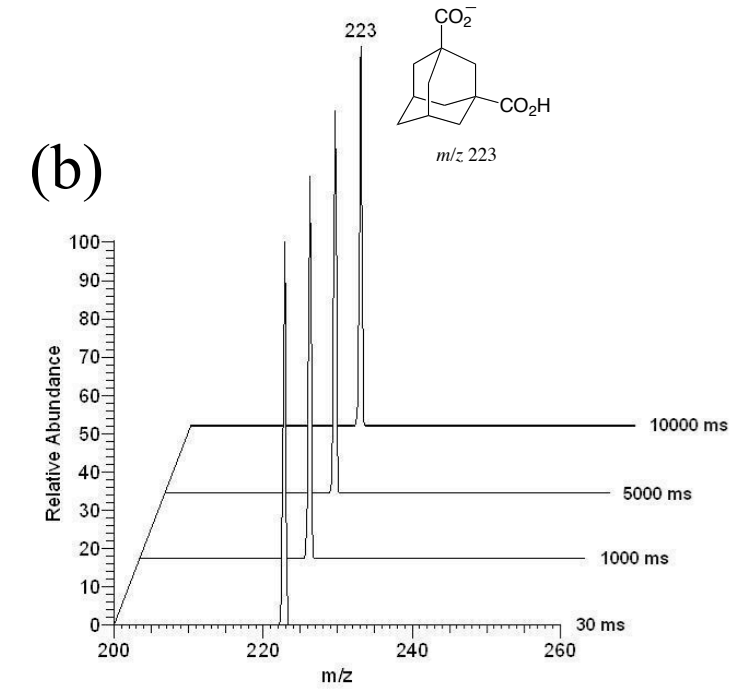
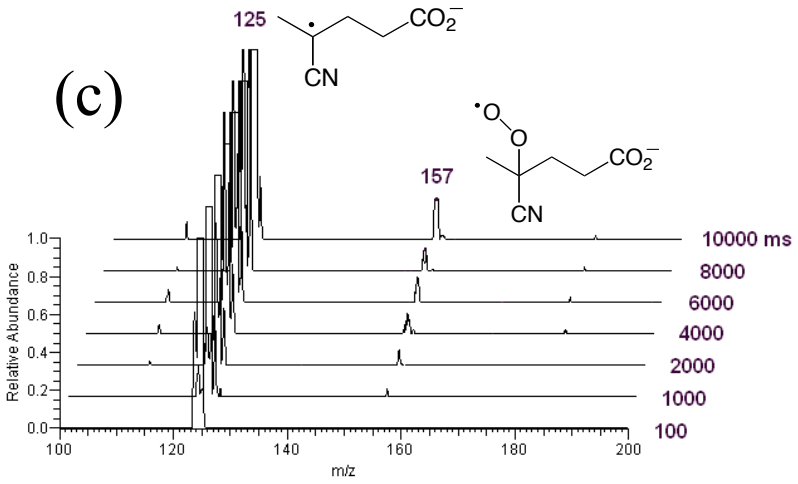
Supporting Information Figure 1. (a) The ESI-MS/MS spectrum of the $[M-2H]^{2-}$ dianion (*m/z* 111.2) formed by electrospray ionization 1,3-adamantane dicarboxylic acid (**A**, Scheme 1) and (b) The ESI-MS/MS spectrum of the $[M-H]^{-}$ anion (*m/z* 331.9) formed by electrospray ionization of 3-(*N*-oxycarbonyl-2(1*H*)-pyridinethione)-adamantane-1-carboxylic acid (**D**, Scheme 1).



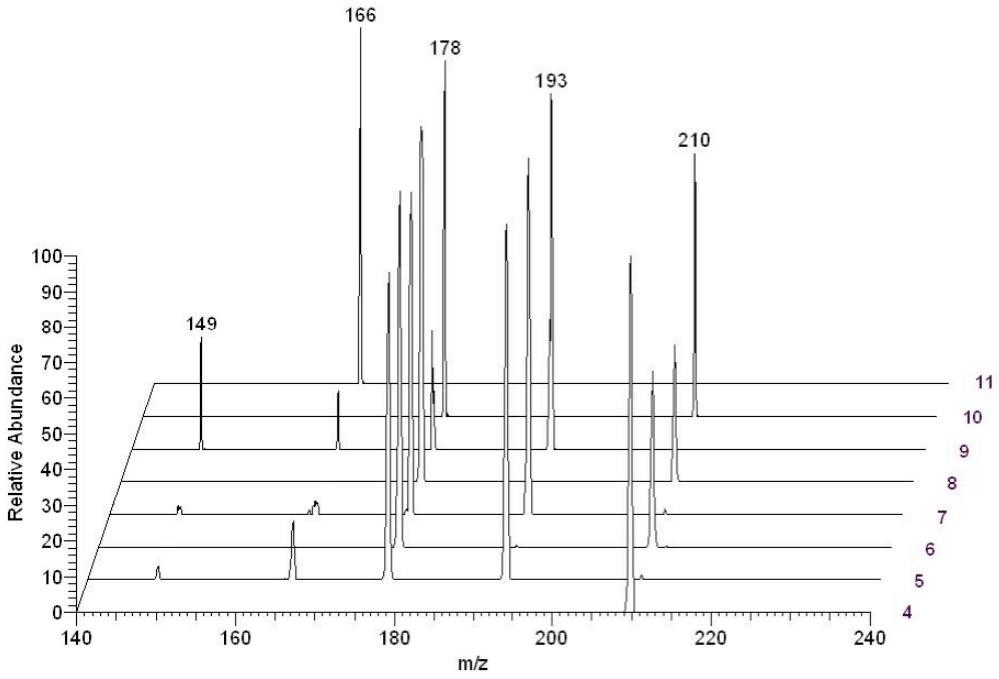
Supporting Information Figure 2. Trapping of (a) the distonic radical anion, **C**, at *m/z* 178, (b) the even electron, $[M-H]^-$ anion of 1,3-adamantane dicarboxylic acid at *m/z* 223 and (c) the 3-carboxylate-1-cyano-1-methyl-propyl radical anion formed by CID of the $[M-2H]^{2-}$ ion of 4,4'-azobis(4-cyano-pentanoic acid). All spectra shown are MS^3 experiments conducted using the ThermoFinnigan LTQ ion-trap mass spectrometer with trapping times ranging from 30 up to 10^4 ms. The radical anion, **C**, shows prominent addition of 32 Da to form *m/z* 210 while the analogous even electron anion does not form any such adduct upon trapping. The non-bridgehead 3-carboxylate-1-cyano-1-methyl-propyl radical anion at *m/z* 125 also shows addition of 32 Da to a lesser extent.



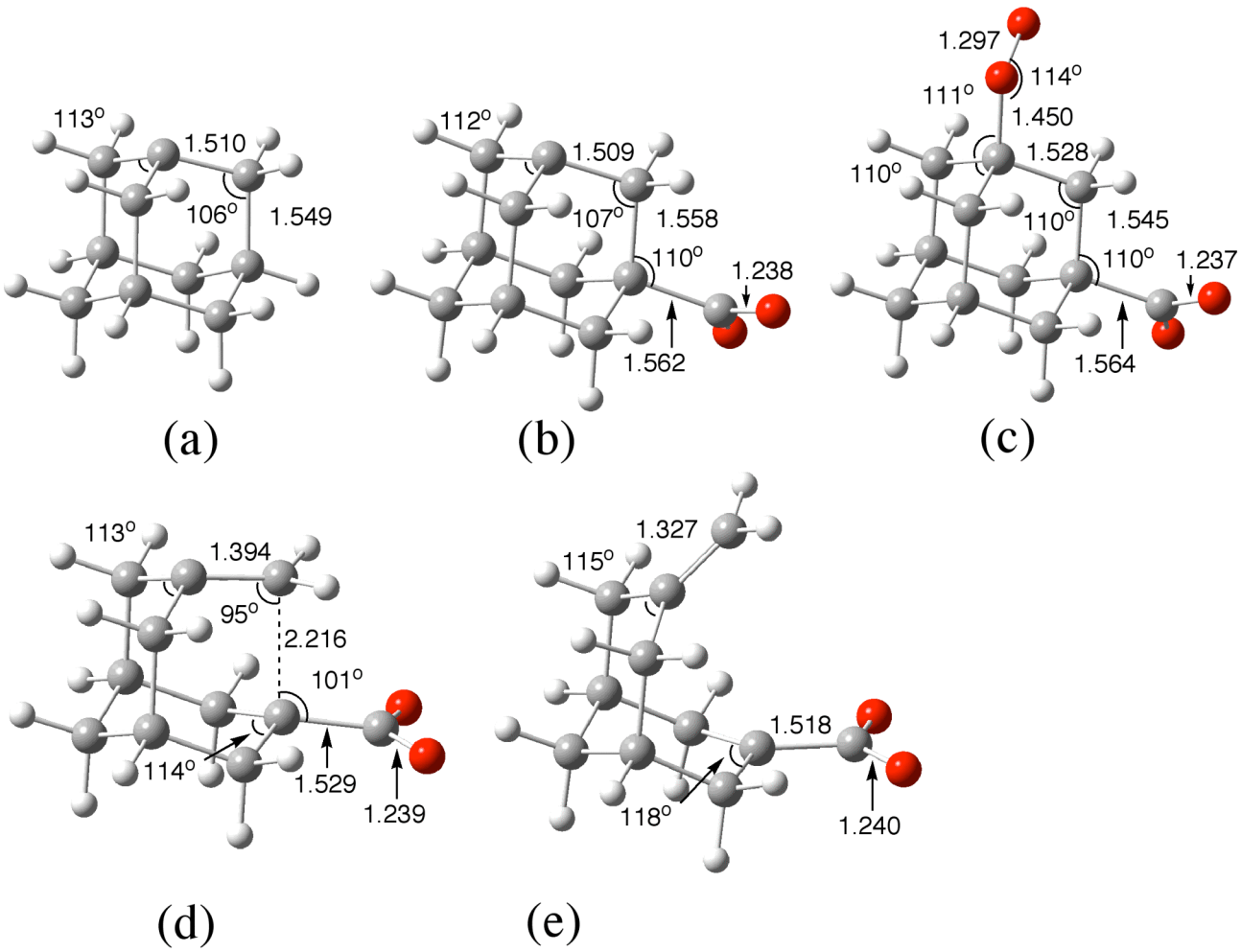

(b)
223
CO_2^-
CO_2H
m/z 223
Relative Abundance
m/z
10000 ms
5000 ms
1000 ms
30 ms


(c)
125
CO_2^-
CN
157
CO_2^-
CN
Relative Abundance
m/z
10000 ms
8000
6000
4000
2000
1000
100

Supporting Information Figure 3. ESI-MS^n spectra obtained from *m/z* 332 (**E**, Scheme 1) formed by ESI of 3-(*N*-oxycarbonyl-2(1*H*)-pyridinethione)-adamantane-1-carboxylic acid (**D**, Scheme 1). The spectrum labelled 4 was obtained from the sequence *m/z* 332 (CID, MS^2) → 178 (+ O_2, MS^3) → 210 (isolation, MS^4). The spectrum labelled 5 corresponds to CID of *m/z* 210 (MS^5) resulting in regeneration of *m/z* 178, isolation of which (MS^6) produces *m/z* 210. The spectra shown demonstrate that this sequence may be repeated up to MS^{11} with addition and removal of O_2 repeated 3 times.



Supporting Information Figure 4. Molecular structures calculated at the HF/6-31+G(d) level of theory for: (a) the 1-adamantyl radical, (b) the charge tagged *tert*-adamantyl radical **C**, (c) the charge tagged *tert*-adamantyl peroxyl radical **F**, (d) the transition state for unimolecular ring opening of **C**, and (e) the ring opened isomer of **C**. The single point electronic energies of these structures were calculated at the B3LYP/6-31+G(d) level of theory and are presented in Supporting Information Table 1.



Supporting Information Methods

Materials and Sample Preparation

1,3-Adamantane dicarboxylic acid was obtained from Aldrich. 1,3-dicyclohexylcarbodiimide and sodium pyridine-2-thione *N*-oxide solution were obtained from Fluka. 4,4'-Azobis(4-cyanopentanoic acid), trade name Vazo 68, was obtained from Dupont. DMF was dried over 3 Å molecular sieves. *N*-hydroxypyridine-2-thione was prepared by the treatment of a 40% aqueous solution of the sodium salt according to an established method.[1]

*Preparation of 3-(*N-*Oxycarbonyl-2(1*H*)-pyridinethione)-adamantane-1-carboxylic acid*

The desired target was prepared by adapting a procedure which produces a Barton ester from a carboxylic acid in one step.[1] A solution of 1,3-adamantane dicarboxylic acid (100 mg, 0.446 mmol) in 0.5 mL of dry DMF was stirred in the absence of light at 0°C while a solution of 1,3-dicyclohexylcarbodiimide (94 mg, 0.456 mmol) and *N*-hydroxypyridine-2-thione (55 mg, 0.43 mmol) in 1.5 mL of dry DMF was added dropwise. When the addition was complete, the solution was allowed to warm to room temperature and stirred for a further 8 hr. The resulting suspension was filtered to remove dicyclohexylurea, and the precipitate rinsed with 2 mL of DMF. The filtrate was treated with 15 mL of H_2O, which caused precipitation of a yellow crystalline solid. This was filtered, washed with 10 mL of cold water and dried under high vacuum overnight, yielding a mass of 110 mg (0.330 mmol, 77% crude). An analytical sample was obtained by flash chromatography of a small quantity on silica, eluting with 20-40% EtOAc in $CHCl_3$ (Rf 0.35, 30% EtOAc in $CHCl_3$), mp 172.5-173.5°C (dec.). ^{1}H NMR (500 MHz, CD_3SOCD_3) δ 1.76 (s, br, 2H), 2.08-2.11 (m, 8H), 2.26 (s, br, 2H), 2.44 (s, br, 2H), 6.88 (ddd, 1H), 7.43 (ddd, 1H), 7.54 (dd, 1H), 8.34 (dd, 1H), 12.20 (s, br, 1H).

Instrumentation

All experiments were performed on a ThermoFinnigan LTQ (Waltham, MA) quadrupole linear ion-trap mass spectrometer fitted with a conventional IonMax electrospray ionization source and operating Xcalibr software. Spectra were obtained by infusion (3-10 μL/min) of a standard solution (~10 μM in HPLC grade methanol or aqueous acetonitrile, 1% aqueous ammonia was added in some instances to achieve a pH ~ 10), typical settings were; spray voltages between -4-5 kV, capillary temperature 200-250 ^{o}C, sheath and auxiliary gas flow rates set at 10 and 2 (arbitrary units), respectively. For CID experiments, ions were mass selected using a window of 1-5 Da (depending upon the number of MS cycles), using a Q-parameter of 0.25, fragmentation energy was typically 15-30 (arbitrary units) and an excitation time of 30 ms. For ion-trapping and ion-molecule reaction experiments the fragmentation energy was maintained at 0 while the excitation time (or reaction time) was varied between 30 ms and 10000 ms.

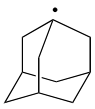
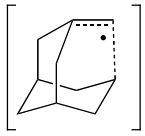
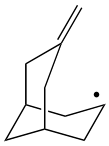
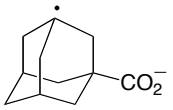
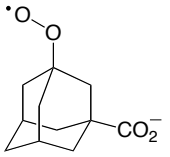
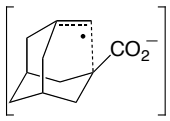
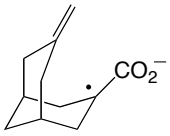
Electronic Structure Calculations

Geometry optimizations were carried out with the Hartree-Fock method using the modest 6-31+G(d) basis set within the GAUSSIAN03 suite of programs.[2] All stationary points on the potential energy surface were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures and single point energies were determined at the Becke3LYP/6-31+G(d) level.[3, 4] Frequency calculations provided zero-point energies, which were corrected by the empirical scaling factor of 0.89 and added to the calculated electronic energy.[5] The minima connected by a given transition state were confirmed by inspection of the animated imaginary frequency using the MOLDEN package[6] and by intrinsic reaction coordinate calculation.

Supporting Information Additional References

1. D. H. R. Barton, J. MacKinnon, R. N. Perchet and C. L. Tse, in *Organic Syntheses, Collective Volumes*, ed. R. L. Danheiser, John Wiley & Sons, New York, 2004, vol. 10, p. 273.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision C.02*, (2004) Gaussian Inc., Wallingford CT.
3. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372-1377.
4. C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
5. A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502-16513.
6. G. Schaftenaar and J. H. Noordik, *J. Comput.-Aided Mol. Design*, 2000, **14**, 123-134.

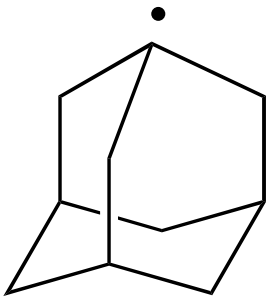
Supporting Information Table 1. The electronic energy and zero-point energy of HF/6-31+G(d) optimized structures shown in Supporting Information Figure 4. Single point electronic energies were calculated at B3LYP/6-31+G(d) level of theory. Full structural details are provided in Supporting Information Table 2.

Molecular Species	Electronic Energy (Hartrees)	Zero-point energy (Hartrees)	Relative energy (kJ mol^{-1})	Negative Frequency (cm^{-1})
	-390.06569	0.24680	0.0	-
	-390.021527	0.24133	103.2†	-482
	-390.04162	0.24104	49.7†	-
 **C** *m/z* 178	-578.09272	0.24833	0.0	-
 **F** *m/z* 210	-728.48566	0.25804	-	-
	-578.05804	0.24389	80.7‡	-493
	-578.07672	0.24410	7.7‡	-

† Energy relative to row 1, ‡ Energy relative to row 4

Supporting Information Table 2. The full Cartesian coordinates of HF/6-31+G(d) optimized geometries shown in Supporting Information Figure 4.

Molecular Species	Cartesian Coordinates of Optimized Structure



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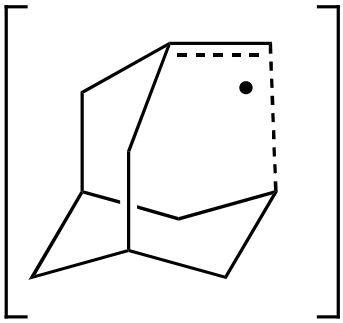

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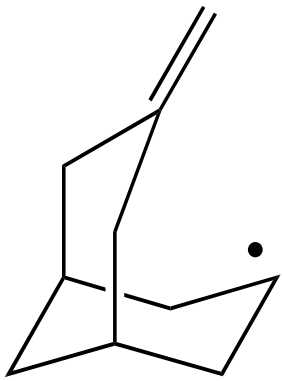

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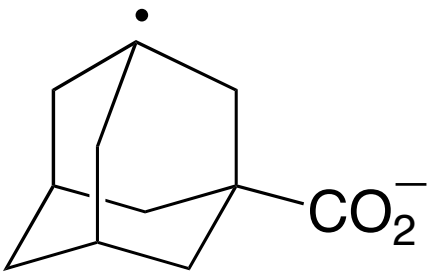

C *m/z* 178

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17	1	-1.563894	0.853824	-2.254051
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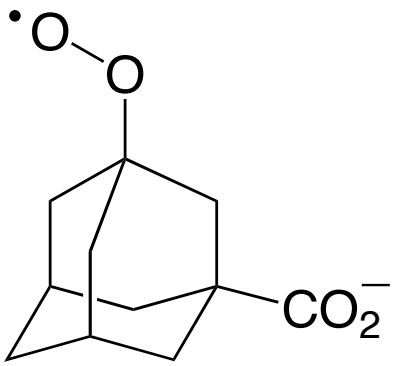

F *m/z* 210

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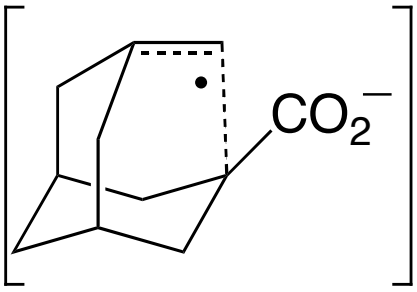
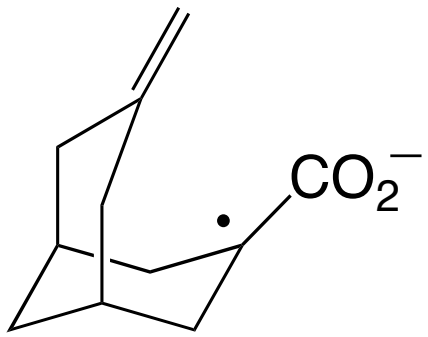
17	6	-1.104774	-0.053406	-0.025873
18	1	-1.196454	0.352279	2.09075
19	1	-1.635856	1.492375	-1.435079
20	1	-0.030201	-1.80737	-0.717435
21	1	-0.147378	-1.685978	1.023898
22	1	-0.926073	0.092493	-2.174372
23	1	-1.791858	1.662368	1.101062
24	6	-2.500375	-0.758199	-0.013716
25	8	-3.242909	-0.527035	-0.972265
26	8	-2.709904	-1.469455	0.976208
27	8	2.441071	-1.383684	0.381026
28	8	2.556919	-2.264328	-0.563406
29	6	1.374114	-0.427853	0.155093



	atomic number	x	y	z
1	8	2.896233	-1.116037	0.022755
2	8	2.896342	1.116001	0.022753
3	6	2.365618	0.00001	-0.06652
4	6	0.853638	0.000063	-0.290972
5	6	0.125347	-0.000267	1.801988
6	6	-1.223903	-0.000235	1.450426
7	1	0.613953	0.909165	2.105366
8	1	0.614014	-0.909773	2.105046
9	6	-1.760722	1.260184	0.813593
10	6	-1.329945	1.256888	-0.672371
11	6	0.206185	1.273292	-0.798345
12	6	-1.892682	0.000209	-1.354249
13	6	-1.32992	-1.256679	-0.67278
14	6	0.206208	-1.273013	-0.798755
15	6	-1.76069	-1.26046	0.813184
16	1	-1.371509	-2.145173	1.310863
17	1	-2.848688	-1.30221	0.879651
18	1	-2.84872	1.301889	0.880069
19	1	-1.371561	2.144745	1.311558
20	1	-1.734518	-2.144713	-1.159594
21	1	-2.982941	0.000191	-1.307043
22	1	-1.623529	0.000384	-2.409885
23	1	-1.734559	2.145071	-1.158901
24	1	0.465951	1.404415	-1.853603
25	1	0.630339	2.125525	-0.282023
26	1	0.630386	-2.125399	-0.28271
27	1	0.465975	-1.403781	-1.854061



	atomic number	x	y	z
1	6	-1.700535	0.565024	1.273492
2	6	-1.404714	1.326138	-0.000026
3	6	-1.700474	0.564993	-1.273521
4	6	-1.149877	-0.874456	-1.251784
5	6	-1.665437	-1.595328	0.000017
6	6	-1.149888	-0.87442	1.251802
7	6	0.388045	-0.923378	1.288473
8	6	1.032044	-0.4879	0.000001
9	6	0.388058	-0.923433	-1.288461
10	6	2.421679	0.121788	0.000009
11	8	2.916027	0.336359	-1.116926
12	6	-0.932378	2.565905	-0.000025
13	8	2.916026	0.336339	1.116947
14	1	-0.706239	3.084307	-0.916171
15	1	-0.706501	3.084384	0.916142
16	1	-1.309122	1.105562	2.129919
17	1	-2.784655	0.51063	1.39829
18	1	-2.784592	0.510656	-1.398395
19	1	-1.308978	1.105481	-2.129943
20	1	-1.531079	-1.380696	2.138807
21	1	-2.756331	-1.624631	0.000021
22	1	-1.3219	-2.628778	0.000021
23	1	-1.531109	-1.38072	-2.138778
24	1	0.682446	-1.956141	-1.510066
25	1	0.780037	-0.322642	-2.099417
26	1	0.780004	-0.32253	2.099397
27	1	0.682457	-1.956067	1.510138