Supporting Information for

# Oxidative Deamination of Azafulleroids into $C_{60}$ by Peracids

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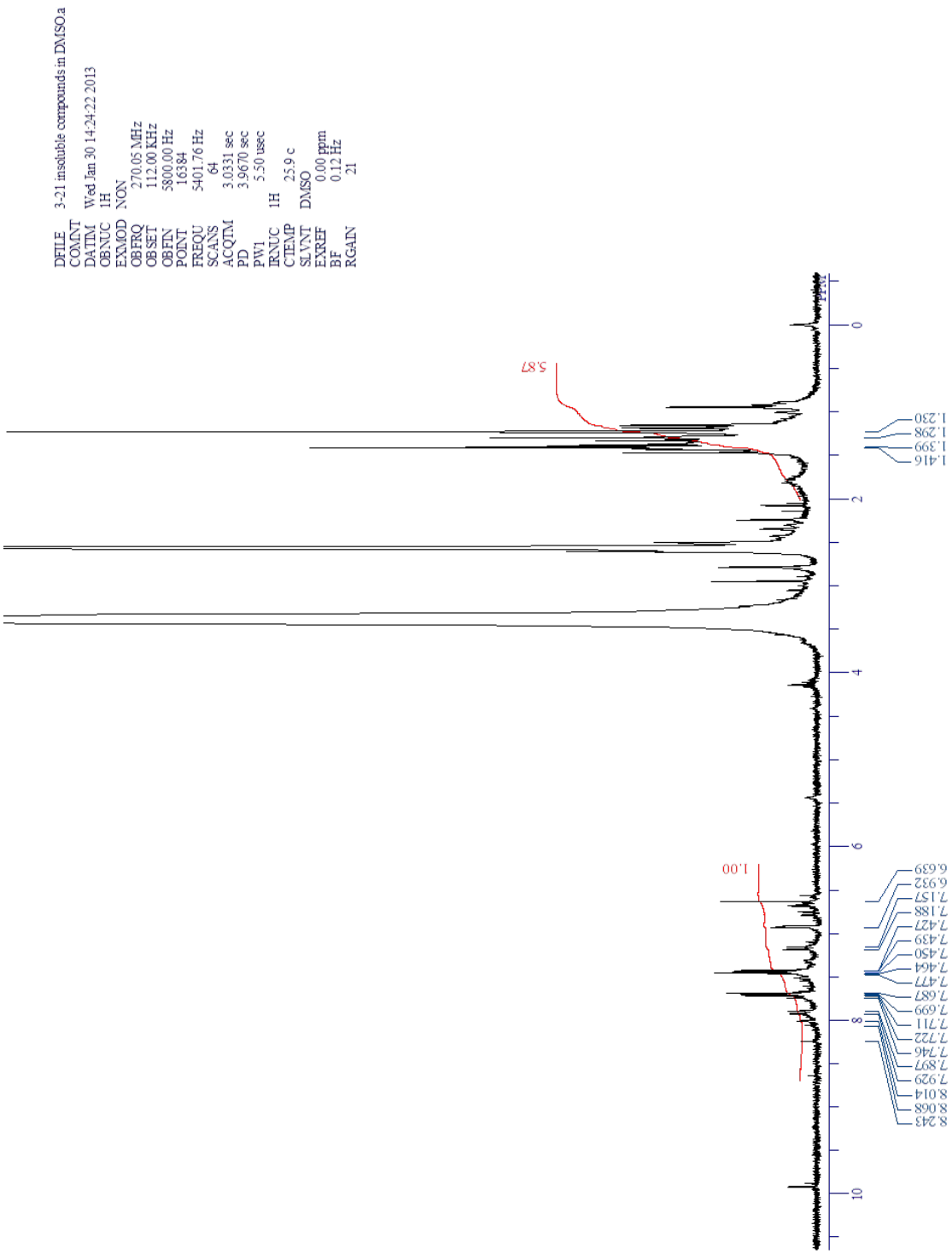



Fig. S1. $^{1}$H NMR (in DMSO-d6) of oxidized products of azafulleroid **1g**. (too low solubility of the oxidized products inhibited $^{13}$C NMR measurement)

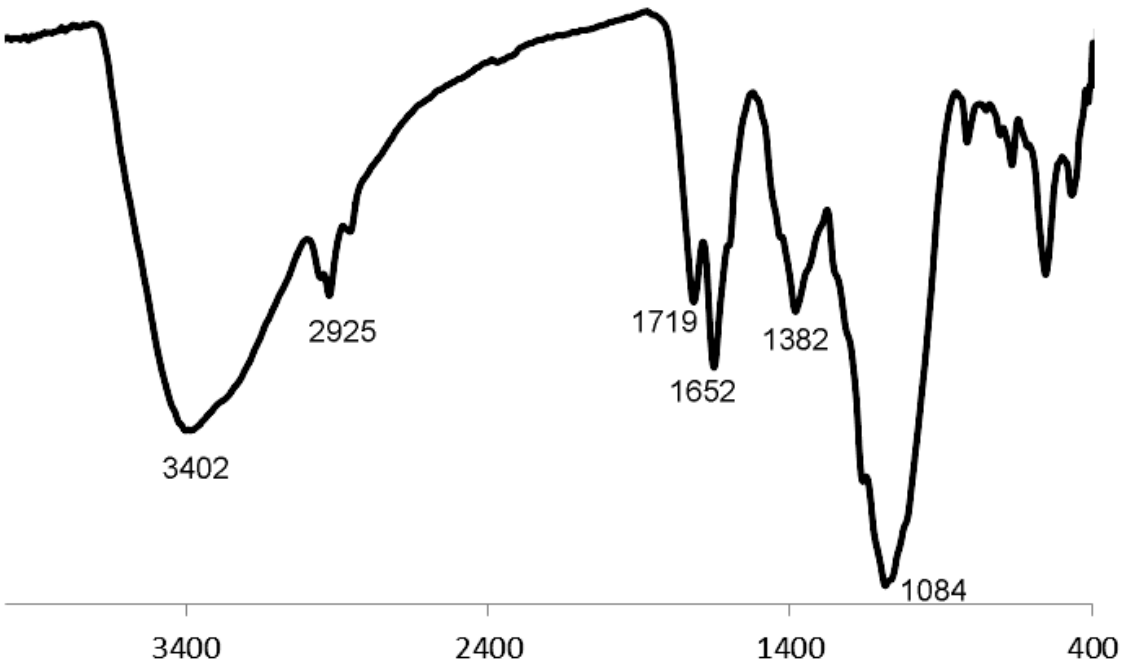
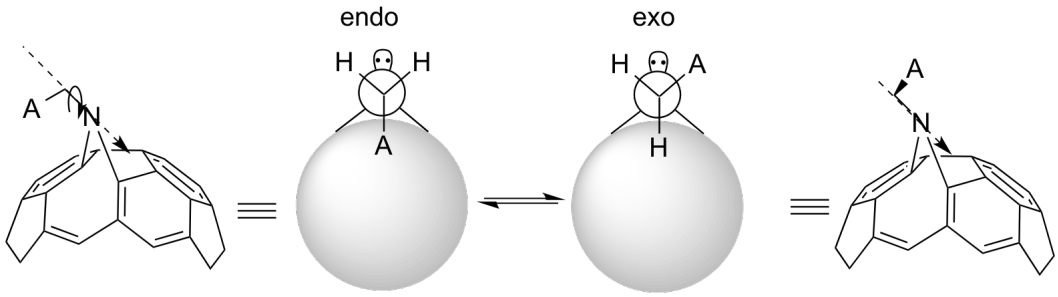



Fig. S2. IR of the insoluble product of **1g** with *m*CPBA.




Scheme S1. Endo/exo definition for substituted azafulleroid.

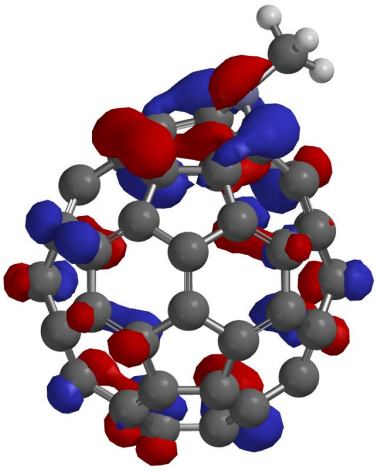
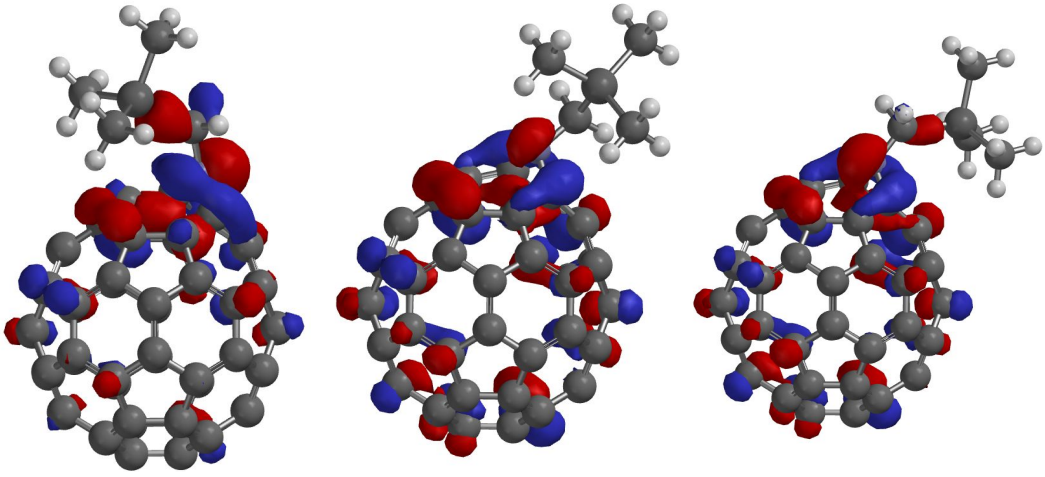
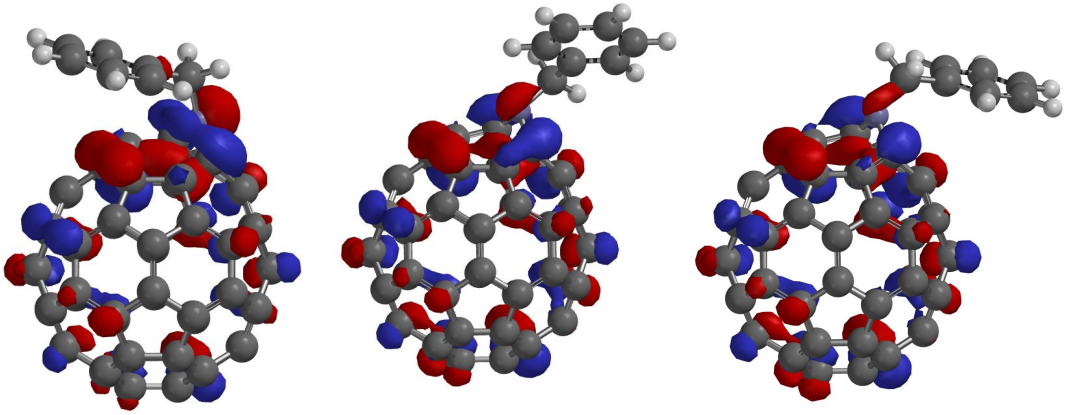


Fig. S3. HOMO of metastable methyl azafulleroid **1a**/5.



6-endo (+38.1) 5-exo (+4.3) 5-endo (+33.2)

Fig. S4. HOMO of metastable TMS-methyl azafulleroid **1b** conformers. The values in parenthesis are relative energy (kJ/mol) to the most stable 6-exo isomer (Fig. 1b).



6-endo (+22.4)  5-exo (+3.9)  5-endo (+18.4)

Fig. S5. HOMO of metastable conformers of benzylic azafulleroid **1e**. The values in parenthesis are relative energy (kJ/mol) to the most stable 6-exo isomer (Fig. 1c).

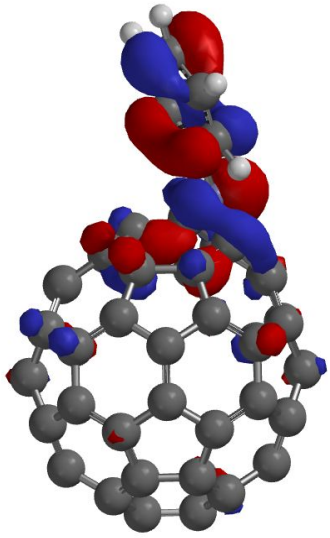
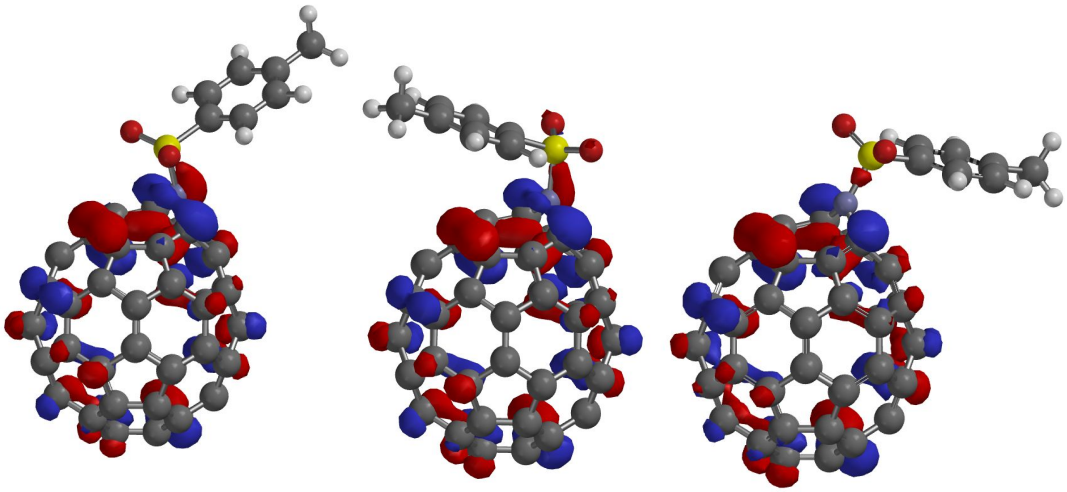


Fig. S6. HOMO of metastable phenyl azafulleroid **1f**/6.



6-exo (+5.2) 6-endo (+8.3) 5-endo (+2.1)

Fig. S7. HOMO and relative energies (kJ/mol) of metastable conformers of tosyl azafulleroid **1g.** The values in parenthesis are relative energy (kJ/mol) to the most stable 5-exo isomer (Fig. 1e)

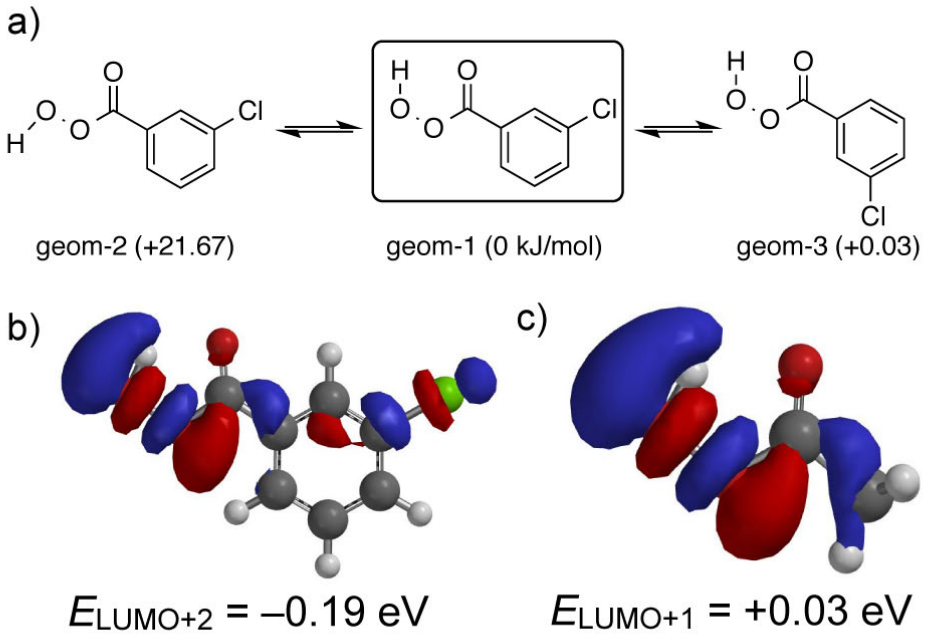



Fig. S8. (a) Three plausible conformer of *m*CPBA with B3LYP/6-31G(d) energy. (b) LUMO+2 of *m*CPBA (geom-1). (c) LUMO+1 of PAA.

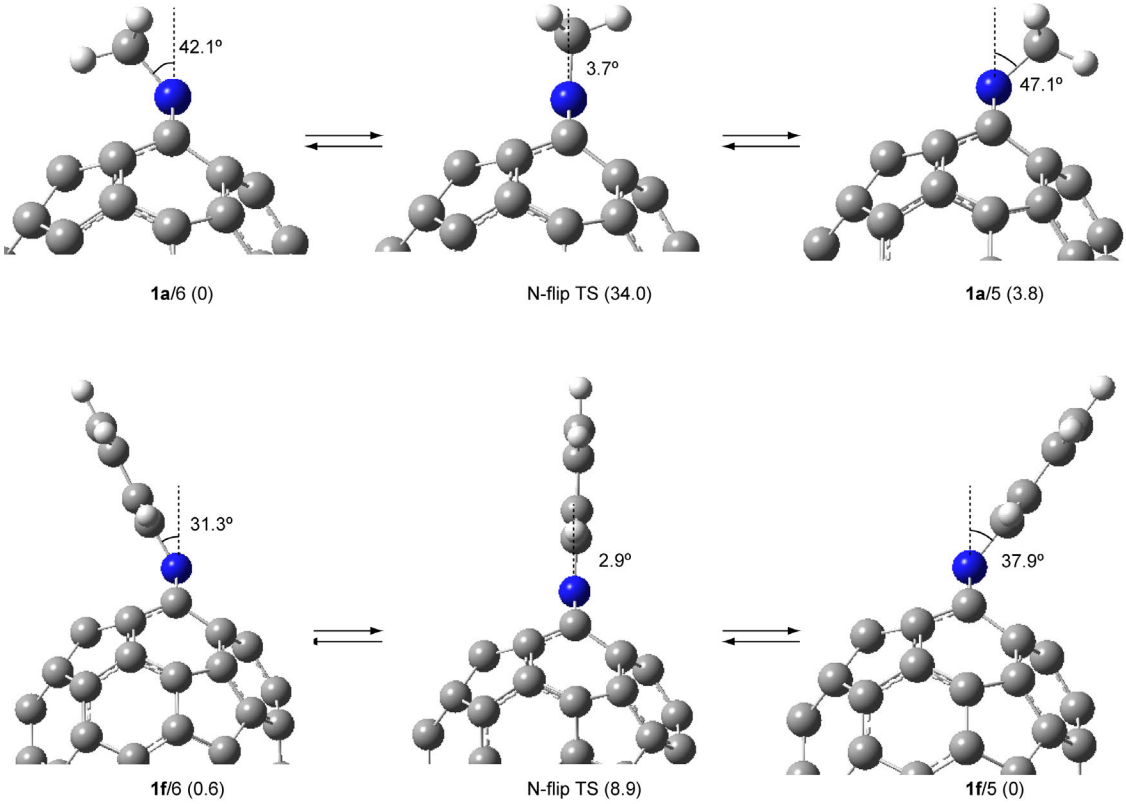
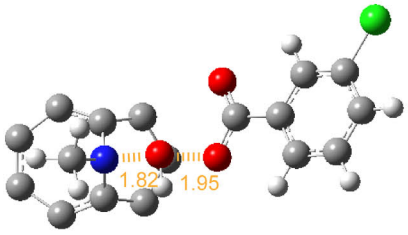
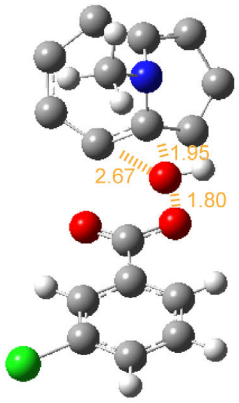


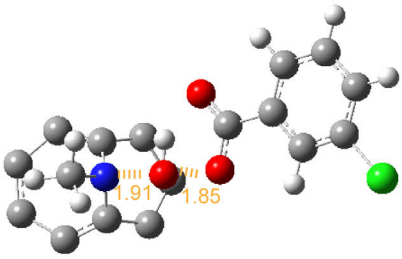

Fig. S9. N-flipping transition states of **1a** (top) and **1f** (bottom) (B3LYP/6-31G(d) with IEFPCM (*o*-DCB)). The values in parentheses are relative energies (kJ/mol).



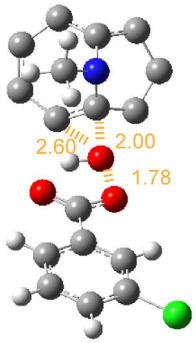

**1a**/6: N-attack of *m*CPBA (geom-2)
$\Delta E^{\ddagger}$ = +71.7 kJ/mol




**1a**/6: Cα-attack of *m*CPBA (geom-2) : $\Delta E^{\ddagger}$ = +71.4 kJ/mol




**1a**/6: N-attack of *m*CPBA (geom-3)
$\Delta E^{\ddagger}$ = +44.6 kJ/mol




**1a**/6: Cα-attack of *m*CPBA (geom-2) : $\Delta E^{\ddagger}$ = +51.7 kJ/mol

Fig. S10. Representative results of transition states of **1a** with geom-2 and geom-3 *m*CPBA.

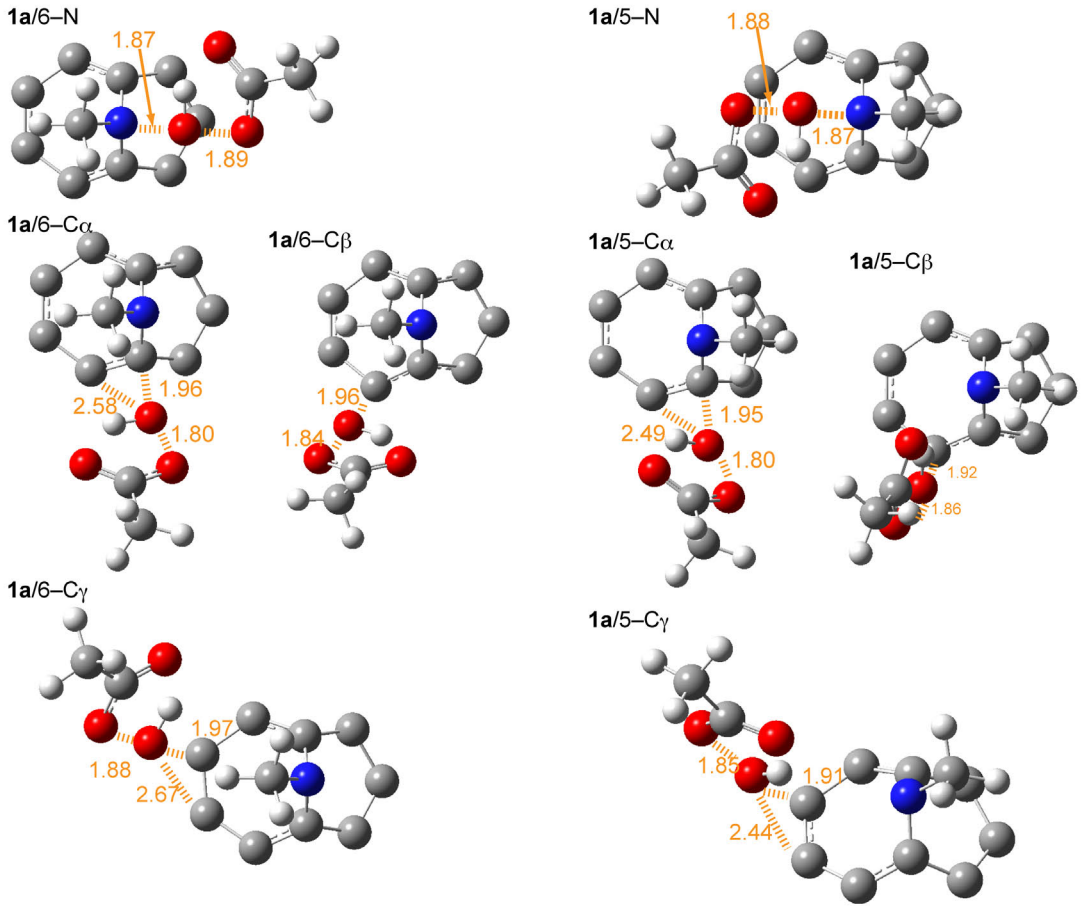



Fig. S11. Transition state geometry of **1a** with peracetic acid.

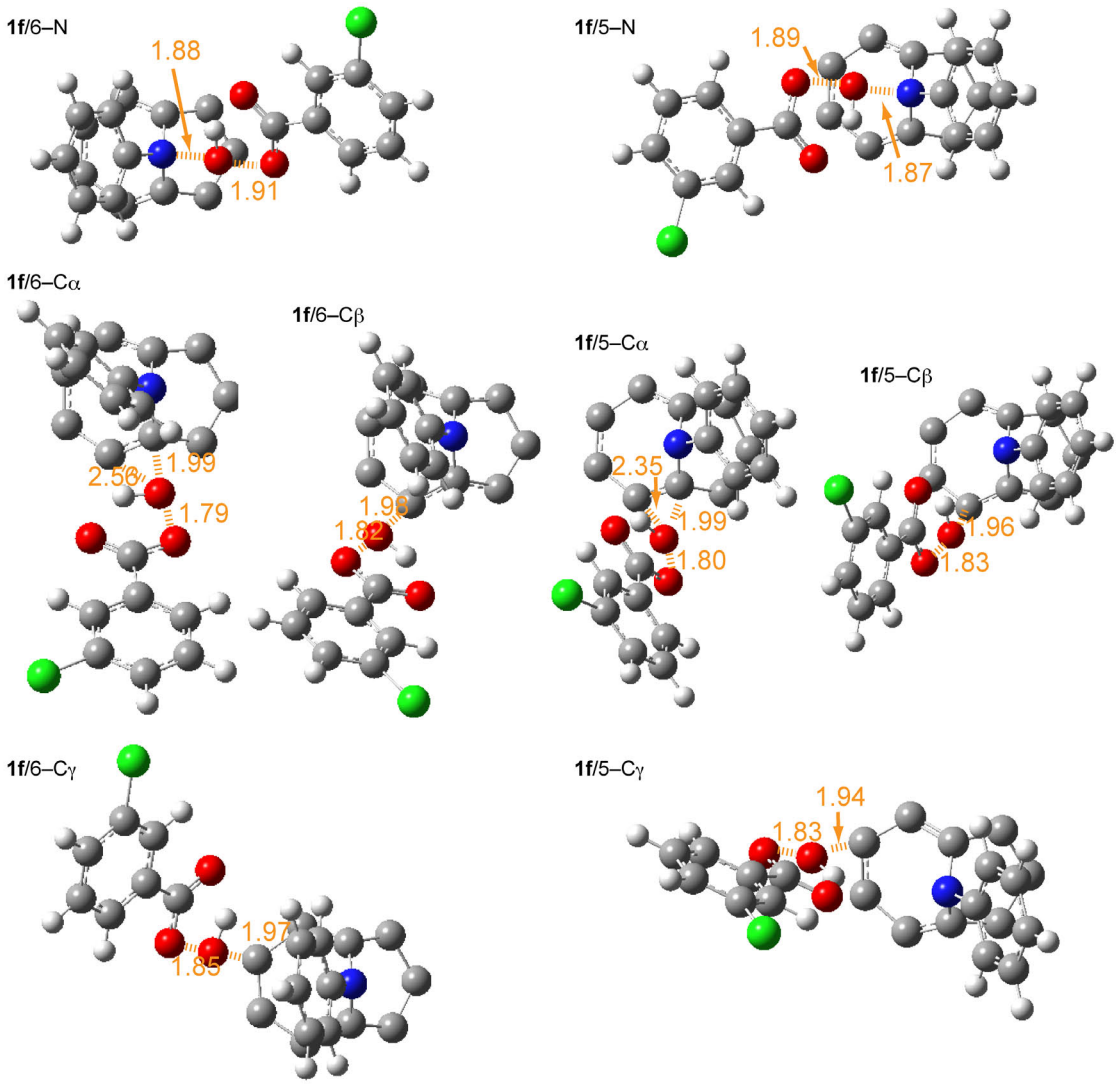
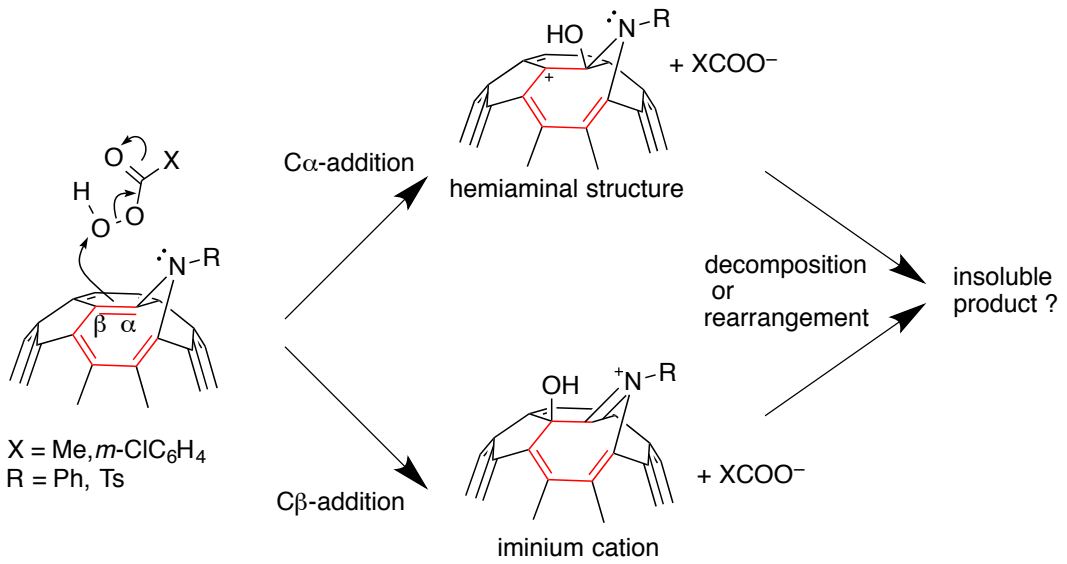
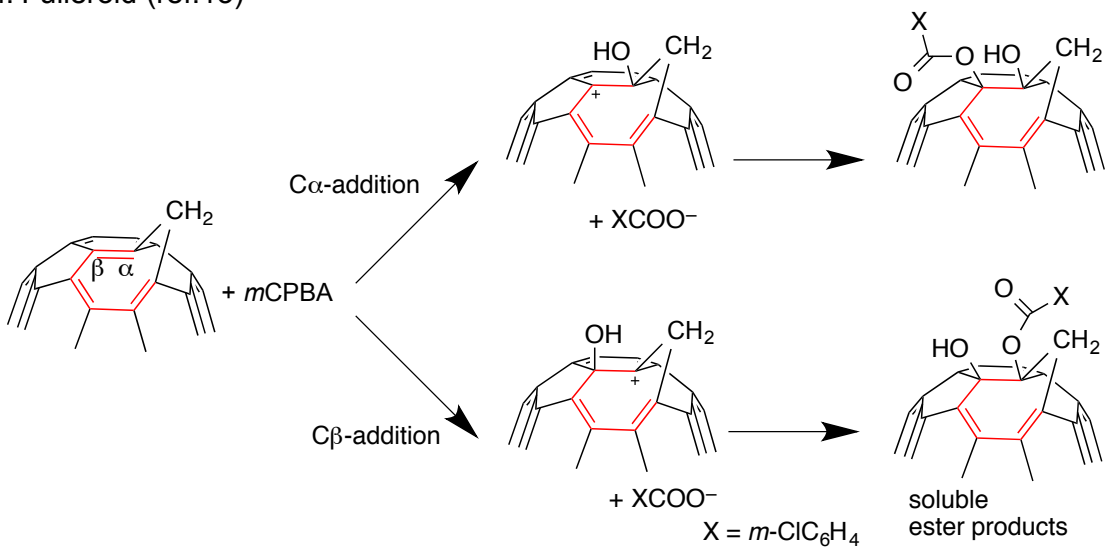



Fig. S12. Transition state geometry of **1f** with *m*CPBA.



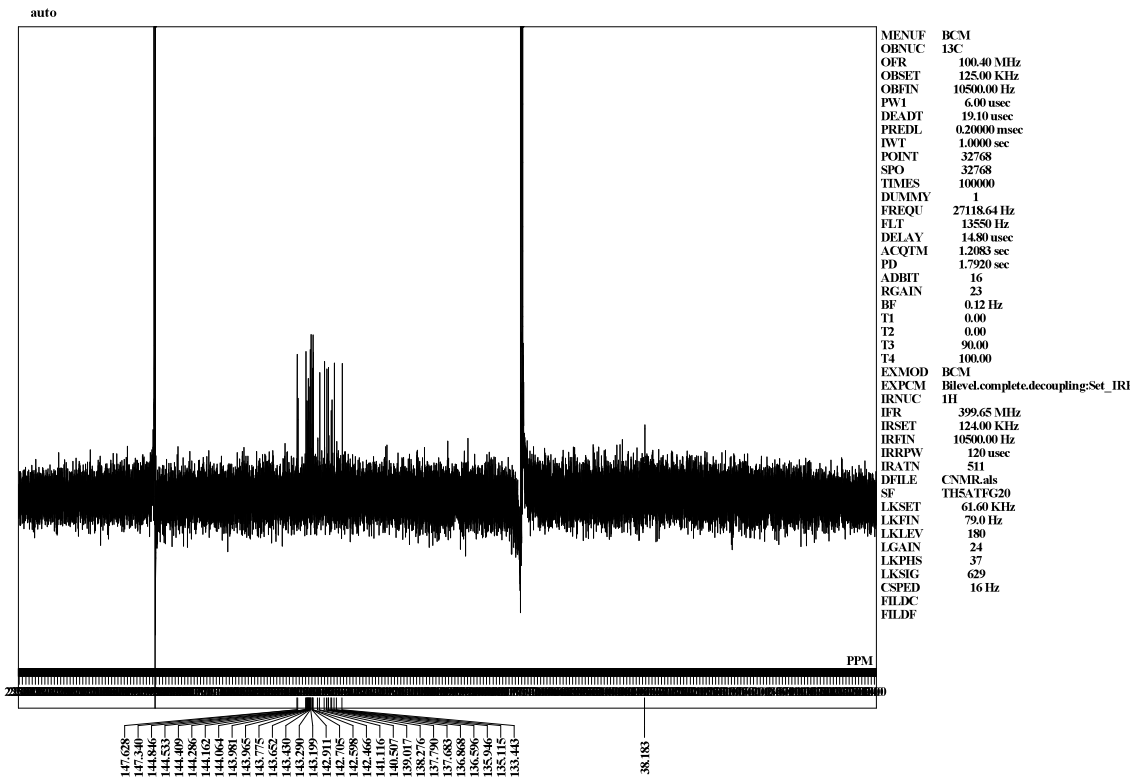

cf. Fulleroid (ref.13)




Scheme S2. Expected intermediates from Cα/Cβ attack to azafulleroid, in comparison with those of fulleroid.

# NMR Chart

1H and 13C NMR spectra of **1a** (N-Methyl azafulleroid)



**Calculations: Energy summary**

Calculated energy table of transition states for **1a** with *m*CPBA (Fig. 2, B3LYP/6-31G(d), with IEFPCM (*o*-DCB)

| Initial State /au | | Transition State (with $\nu$i) /au | | $\Delta E^0$, $\Delta E^{\ddagger}$, /kJ/mol |
|---|---|---|---|---|
| **1a**/6 | -2380.803978 | | | 0 |
| **1a**/5 | -2380.802525 | | | 3.81 |
| | | 5/6-fliping (154.1i) | -2380.791043 | 34.0 |
| *m*CPBA (geom-1) | -955.5466729 | | | |
| | | N-attack/6 (374.0i) | -3336.333707 | 44.5[a] |
| | | Cα-attack/6 (554.5i) | -3336.331084 | 51.4[a] |
| | | Cβ-attack/6 (530.7i) | -3336.328487 | 58.2[a] |
| | | Cγ-attack/6 (525.5i) | -3336.325792 | 65.3[a] |
| | | N-attack/5 (366.9i) | -3336.331931 | 49.1[a] |
| | | Cα-attack/5 (531.5i) | -3336.329781 | 54.8[a] |
| | | Cβ-attack/5 (515.6i) | -3336.327064 | 61.9[a] |
| | | Cγ-attack/5 (508.2i) | -3336.325568 | 65.8[a] |
| *m*CPBA (geom-2) | | | | |
| | | N-attack/6 (333.6i) | -3336.323323 | 71.7[a] |
| | | Cα-attack/6 (565.2i) | -3336.323450 | 71.4[a] |
| *m*CPBA (geom-3) | | | | |
| | | N-attack/6 (368.3i) | -3336.333644 | 44.6[a] |
| | | Cα-attack/6 (555.7i) | -3336.330954 | 51.7[a] |
| *m*-CBA[b] | -880.4230826 | | | |
| **2** | -2455.933987 | | | –16.9[c] |
| **4** | -2455.944849 | | | –45.4[c] |
| Nitroso methane | -169.7979863 | | | |
| C60 | -2286.174951 | | | –119.1[d] |

[a] $\Delta E^{\ddagger} = E(\text{TS}) - E(\mathbf{1a}/6) - E(m\text{CPBA, geom-1})$

[b] *m*-chlorobenzoic acid

[c] $\Delta E^{o} = E(\mathbf{2} \text{ or } \mathbf{4}) + E(m\text{-CBA}) - E(\mathbf{1a}/6) - E(m\text{CPBA, geom-1})$

[d] $\Delta E^{o} = E(C_{60}) + E(m\text{-CBA}) + E(\text{nitrosomethane}) - E(\mathbf{1a}/6) - E(m\text{CPBA, geom-1})$

Calculated energy table of transition states for **1a** with PAA (Fig. 3, B3LYP/6-31G(d), with IEFPCM (o-DCB)

| Initial State /au | | Transition State (with $\nu$i) /au | | $\Delta E^{\ddagger}$ /kJ/mol |
|---|---|---|---|---|
| PAA | -304.2136119 | | | |
| | | N-attack/6 (368.4i) | -2684.996978 | 54.1 [a] |
| | | Cα-attack/6 (550.6i) | -2684.996111 | 56.4 [a] |
| | | Cβ-attack/6 (526.8i) | -2684.992887 | 64.8 [a] |
| | | Cγ-attack/6 (523.6i) | -2684.989543 | 73.6 [a] |
| | | N-attack/5 (366.3i) | -2684.994791 | 59.8 [a] |
| | | Cα-attack/5 (532.1i) | -2684.994757 | 59.9 [a] |
| | | Cβ-attack/5 (510.6i) | -2684.990592 | 70.9 [a] |
| | | Cγ-attack/5 (510.4i) | -2684.989855 | 72.8 [a] |

[a] $\Delta E^{\ddagger} = E(\text{TS}) - E(\textbf{1a}/6) - E(\text{PAA})$

Calculated energy table of transition states for **1f** with *m*CPBA (Fig. 3, B3LYP/6-31G(d), with IEFPCM (o-DCB)

| Initial State /au | | Transition State (with $\nu$i) /au | | $\Delta E^{0}$, $\Delta E^{\ddagger}$, /kJ/mol |
|---|---|---|---|---|
| **1f**/6 | -2572.545125 | | | 0.61 |
| **1f**/5 | -2572.545358 | | | 0 |
| | | 5/6-fliping (32.8i) | -2572.541745 | 8.87 |
| *m*CPBA (geom-1) | -955.5466729 | | | |
| | | N-attack/6 (359.7i) | -3528.068000 | 63.1 [a] |
| | | Cα-attack/6 (549.2i) | -3528.062003 | 78.8 [a] |
| | | Cβ-attack/6 (552.3i) | -3528.064189 | 73.1 [a] |
| | | Cγ-attack/6 (541.5i) | -3528.064241 | 72.9 [a] |
| | | N-attack/5 (371.7i) | -3528.067831 | 63.5 [a] |
| | | Cα-attack/5 (509.7i) | -3528.067755 | 63.7 [a] |
| | | Cβ-attack/5 (519.7i) | -3528.068467 | 61.9 [a] |
| | | Cγ-attack/5 (516.7i) | -3528.067347 | 64.8 [a] |

[a] $\Delta E^{\ddagger} = E(\text{TS}) - E(\textbf{1f}/5) - E(m\text{CPBA, geom-1})$

**Reference in ESI and full citation of software.**

**Gaussian 09:** M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

**Spartan'08**: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3172.