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Supplementary Information

Synthesis of Unstable Cyclic Peroxides for Chemiluminescence Studies

Fernando H. Bartoloni,[#] Marcelo A. de Oliveira, Felipe A. Augusto, Luiz Francisco M. L. Ciscato,[#] Erick L. Bastos and Wilhelm J. Baader*

Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, 05508-000 São Paulo-SP, Brazil

Supplementary Information

2-Adamantenecarboxylic acid (**1s**) preparation

The chosen procedure[1] consists in the reaction of NaH with trimethylsulfoxonium iodide (**2s**) generating an ylide, which then reacts with 2-adamantanone to give the epoxide **3s**; this epoxide is subsequently transformed in the corresponding aldehyde **4s**, which is oxidized to 2-adamantanecarboxylic acid (**1s**). The first step, namely the epoxide formation, is apparently favored since that 2-adamantanone has a low tendency to undergo enolization.[2] Total yields of 50 to 70% were achieved for the preparation of **1s** from 2-adamantanone (Scheme S1).

Trimethylsulfoxonium iodide (**2s**)[3]

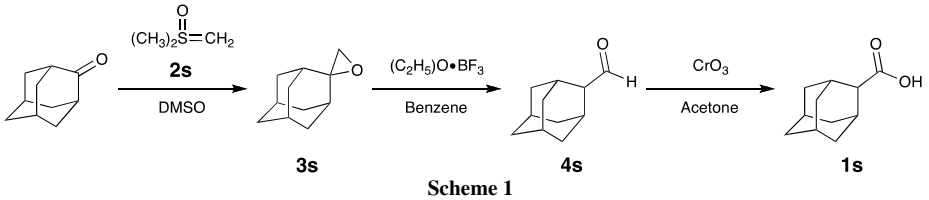
A 125 mL round-bottomed flask, equipped with a condenser and drying tube, was charged with 50 mL (55 g, 0.70 mol) of DMSO and 92 mL (210 g, 1.48 mL) of methyl iodide. This mixture was refluxed for 90 h, filtered under low-pressure on a Büchner funnel and the resulting solid washed with $CHCl_3$. The solid **2s** was transferred to a 50 mL round-bottomed flask and left dry under vacuum (25 °C, 1 mmHg) during 2 h. Following that, **2s** was dried over P_2O_5 during one day under vacuum and stored in an amber flask at 4 °C. The melting point could not be determined since **2s** decomposes above 200 °C. The substance was identified by its IR spectra, compared to reported literature data.

Yield 63.4 g (45%); IR (KBr) ν/cm^{-1} 3700-3300, 2972, 2879, 1406, 1230, 1038, 952 and 756.

2-Epoxymethyleneadamantane (**3s**)[1]

A vacuum-flamed 250 mL three-necked round-bottomed flask, equipped with reflux condenser, septum, magnetic stirring and argon flow, was charged with 4.1 g of a 60% NaH suspension in mineral oil (2.46 g of NaH, 0.103 mol). The mineral oil was removed by washing the slurry three times with pentane and drying the solid with an argon flow. After that, 120 mL of dry DMSO (stored over molecular sieves) were added, followed by 15.5 g (0.071 mol) of **2s**, added in small portions during 10 min, observing a gentle evolution of gas. 30 min after the gas evolution had ceased, 9.44 g (0.0628 mol) of solid 2-adamantanone were added in small portions during 5 min, the reaction mixture was stirred for 1 h at room temperature and another 1.5 h at 60 °C, assuming a dark orange coloration. The mixture was poured in 300 mL of cold water and extracted with hexane (6 × 50 mL); the combined organic phases dried over $MgSO_4$, filtered and concentrated at reduced pressure below 25 °C. The obtained colorless powder was dried under vacuum (1 mmHg) at room temperature and stored in a vacuum desiccator over P_2O_5.

Yield 9.62 g (93%); mp 180-184.4 °C (in a sealed tube, partial sublimation); anal. found (calc.) % for $C_{11}H_{16}O$ (164.2) C 80.66 (80.44), H 10.13 (9.83), N 0.06 (0.00); IR (CS_2) ν/cm^{-1} 3680-3150, 2909, 2851, 1723, 1450, 917,



Scheme 1

*e-mail: wjbaader@iq.usp.br
[#]Current address: Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, 09210-170 Santo André-SP, Brazil

875 and 530; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.35 (bs, 2H), 1.5-2.3 (m, 12 H), 2.46 (s, 2H, O–CH_2); LR-MS (70 eV) *m/z* 164 (M^+, 95%), 149 (13), 135 (22), 122 (100), 109 (14), 93 (38), 91 (83), 77 (48), 53 (22), 39 (59).

2-Adamantanecarboxaldehyde (**4s**)[1]

In a separatory funnel, 7 mL of boron trifluoride etherate (freshly distilled from CaH_2, b.p. 49–52 °C) were added through a syringe to a solution of 12.2 g (0.0743 mol) of **3s** in 135 mL of benzene while the reaction mixture warmed up and became yellow. Vigorous stirring was applied during 2 min; the mixture was allowed to stand for an additional 1 min and was then washed with cold water (3 × 50 mL). The combined aqueous phases were extracted with benzene (5 × 30 mL), and the combined organic layer dried over Na_2SO_4. The product was not isolated due to its instability[4] and its benzene solution was used directly in the next preparation.

2-Adamantanecarboxylic acid (**1s**)[1]

The benzene solution of **4s** was concentrated under reduced pressure at a temperature below 25 °C and transformed into an acetone solution by successive acetone addition and evaporation cycles. 116 mL of Jones reagent[5] were added in portions during 50 min at 17-21 °C, under stirring, to 90 mL of the obtained **4s** acetone solution and the mixture stirred for another 2h at 17-21 °C. Various portions of acetone were added during this period to wash the flask walls (total volume 80 mL). The mixture was then poured in water (1 L) and the aqueous layer extracted with $CHCl_3$ (6 × 30 mL); the combined organic layer had its volume reduced under vacuum at a temperature below 27 °C. The obtained residue was heated at 50 °C for 30 min with 500 mL of 1.0 mol L^{-1} NaOH and then diluted with 1.5 L of 0.5 mol L^{-1} NaOH. The basic solution was filtered and slowly acidified, to cause the precipitation of **1s** in a very exothermic process. This mixture was partitioned in four portions of 500 mL and **1s** was extracted from each one of them with $CHCl_3$ (3 × 50 mL). The combined organic layer was dried over Na_2SO_4, concentrated under reduced pressure below 30 °C and the obtained solid dried under vacuum (1 mmHg).

Yield 9.82 g (78%, calculated from **3s**); mp 131-140 °C; anal. found (calc.) % for $C_{11}H_{16}O_2$ (180.25) C 73.58 (73.3), H 8.77 (8.95), N 0.30 (0.00); IR (KBr) ν/cm^{-1} 1697; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.60-1.97 (m, 12H, H-Ad), 2.36 (bs, 2H, H-Ad), 2.67 (bs, 1H, H-Ad); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 181.2 (C=O); LR-MS (70 eV) *m/z* 180 (M^+, 30%), 163 (6, M^+–OH), 162 (48), 135 (47, M^+–CO_2H), 134 (100), 91 (47), 79 (81), 41 (52).

References

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2. Corey, E. J.; Chaykovsky, M.; *J. Am. Chem. Soc.* **1962**, *84*, 867.
3. Kuhn, R.; Trischmann, H.; *Liebigs Ann. Chem.* **1958**, *611*, 117.
4. Scharp, J.; Wynberg, H.; Strating, J.; *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 18.
5. Armarego, W. L. F.; Perrin, D. D.; *Purification of Laboratory Chemicals*; Butterworth Heineman: Oxford, UK, 1998, p. 529.

IR, ^{1}H and ^{13}C NMR spectra

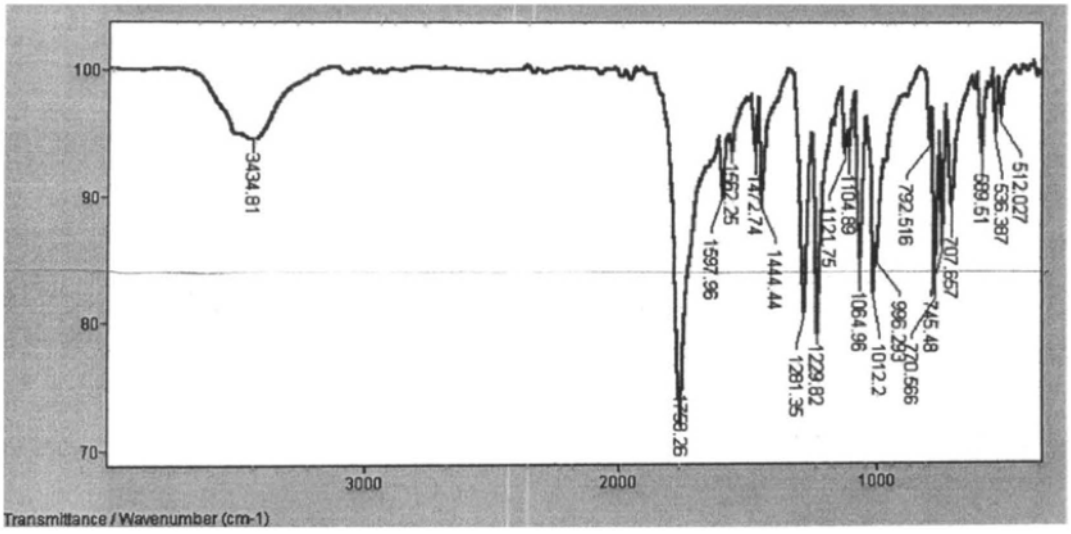

Figure S1. IR spectrum of diphenoyl peroxide (**3**) in KBr

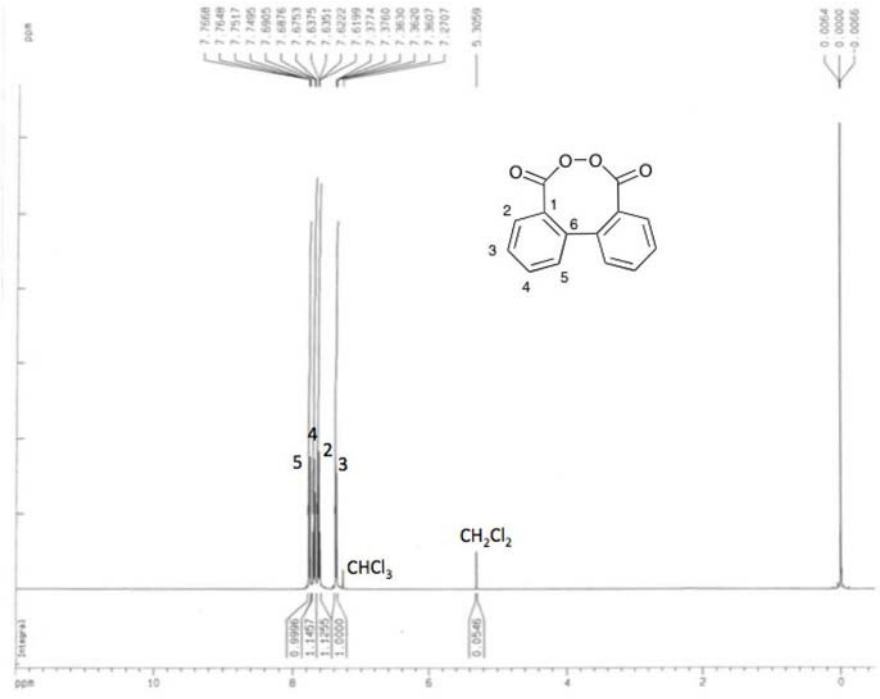

Figure S2. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, −10 °C) of diphenoyl peroxide (**3**).

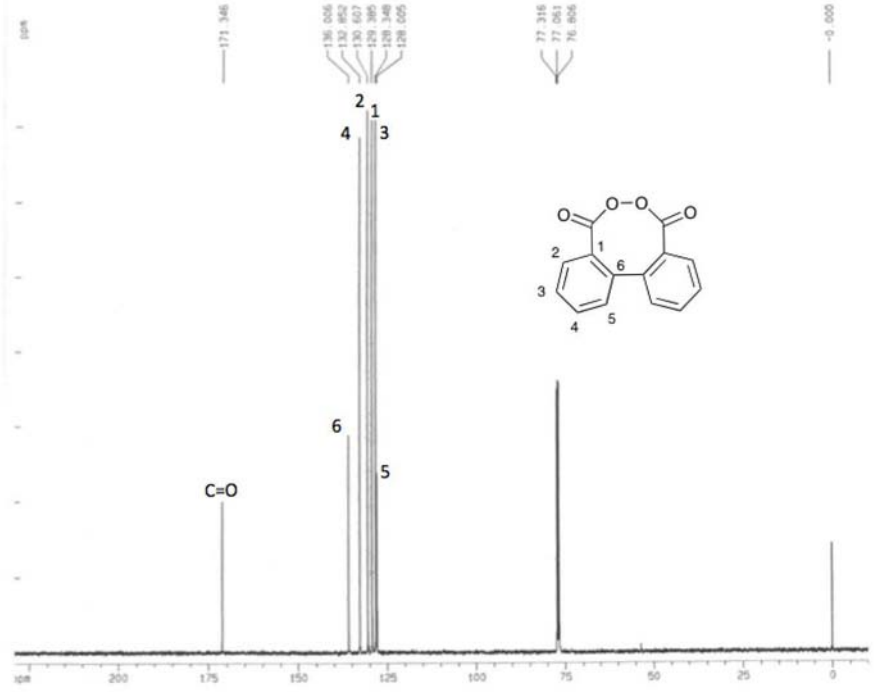

Figure S3. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, −10 °C) of diphenoyl peroxide (**3**).

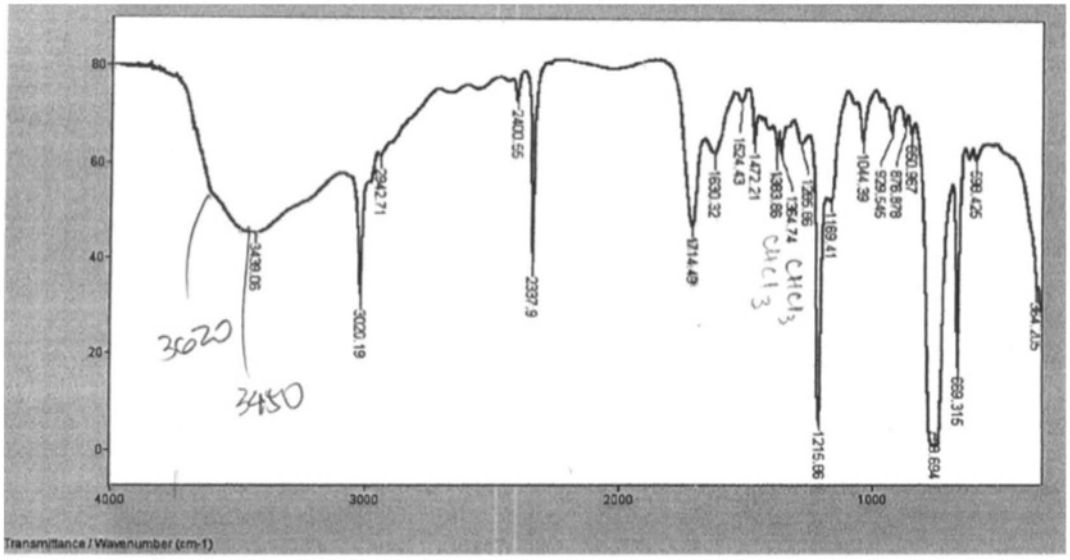

Figure S4. IR spectrum of 2-hydroperoxy-2-methylpropanoic acid (**7**) in $CHCl_3$.

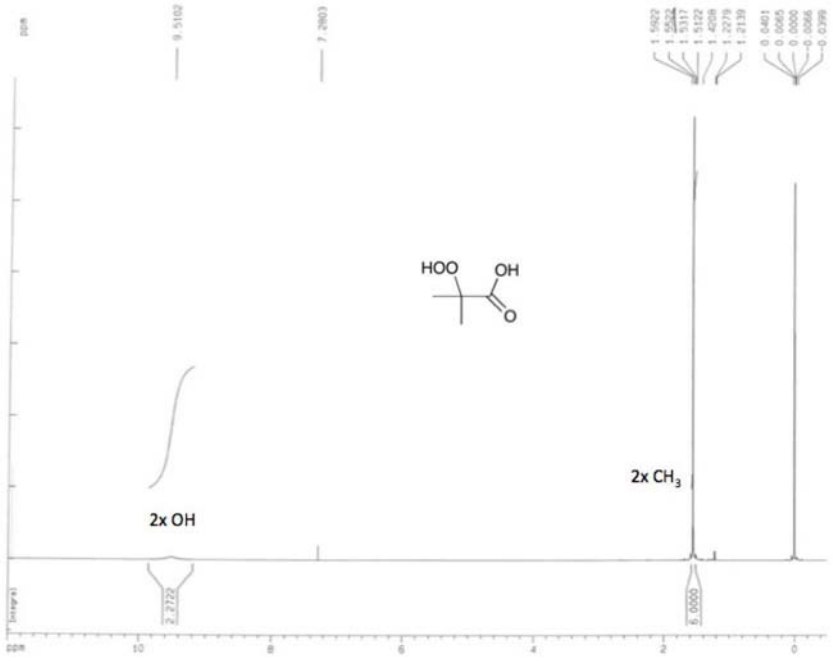

Figure S5. ^1H NMR spectrum (500 MHz, $CDCl_3$, 0 °C) of 2-hydroperoxy-2-methylpropanoic acid (**7**).

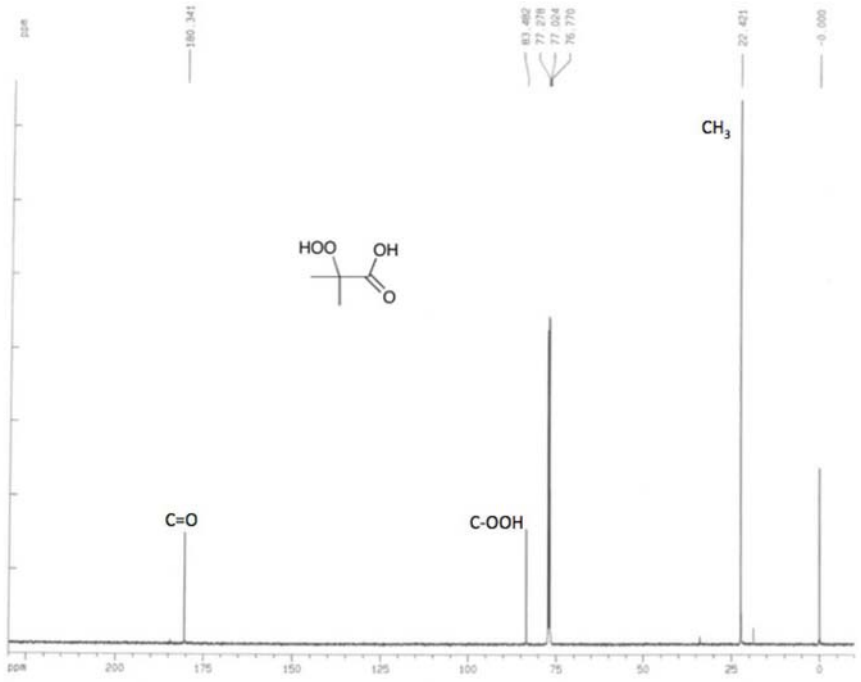

Figure S6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 0 °C) of 2-hydroperoxy-2-methylpropanoic acid (**7**).

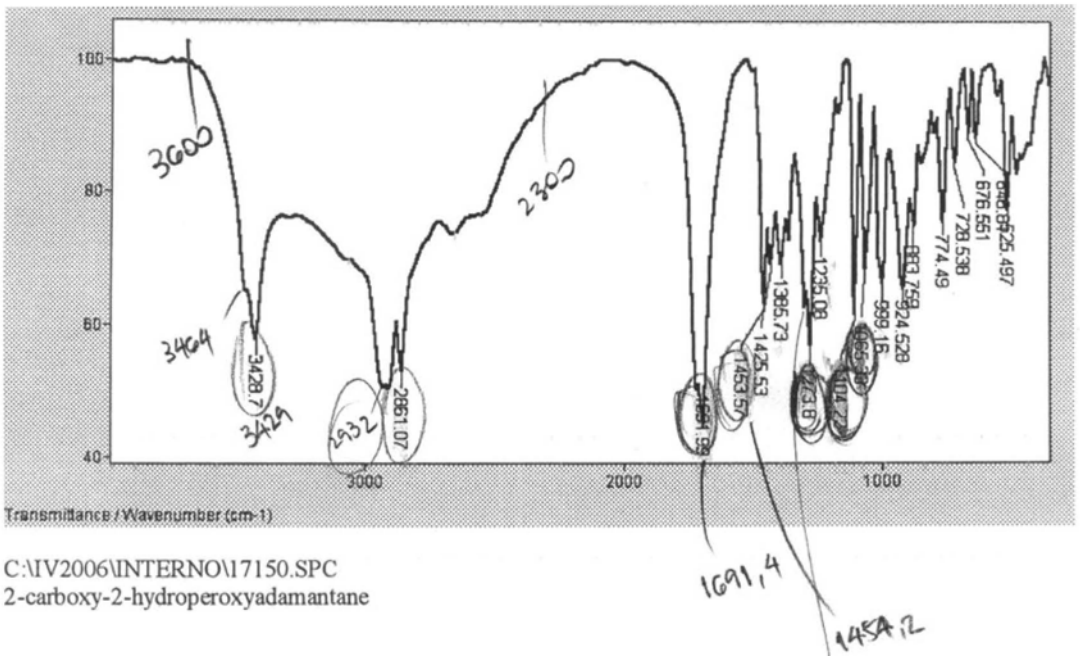

Figure S7. IR spectrum of 2-carboxy-2-hydroperoxyadamantane (**8**) in KBr.

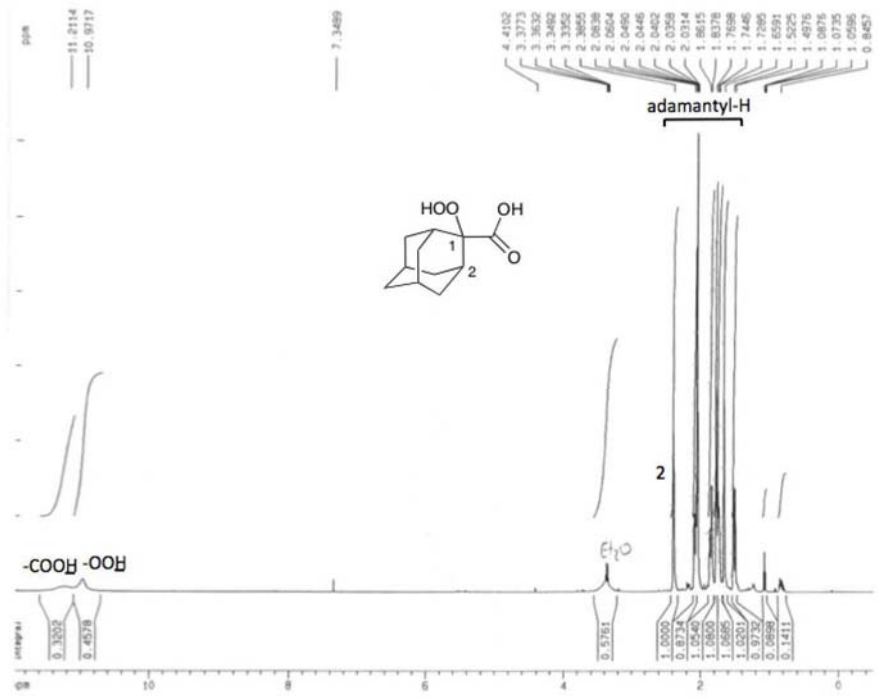

Figure S8. ^{1}H NMR spectrum (500 MHz, acetone-d_6, −20 °C) of 2-carboxy-2-hydroperoxyadamantane (**8**).

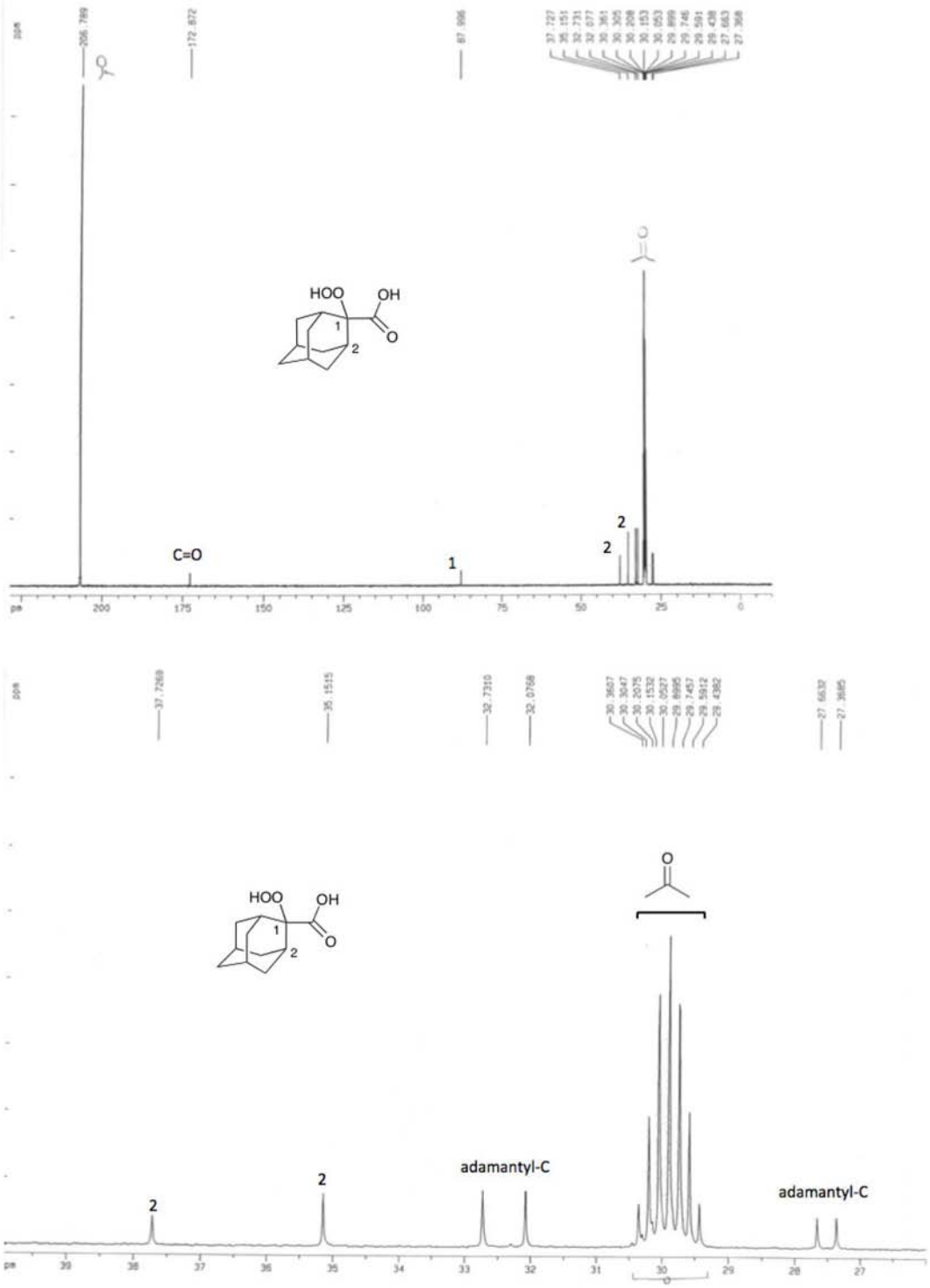

Figure S9. ^{13}C NMR spectrum (125 MHz, acetone-d_6, −20 °C) of 2-carboxy-2-hydroperoxyadamantane (**8**).

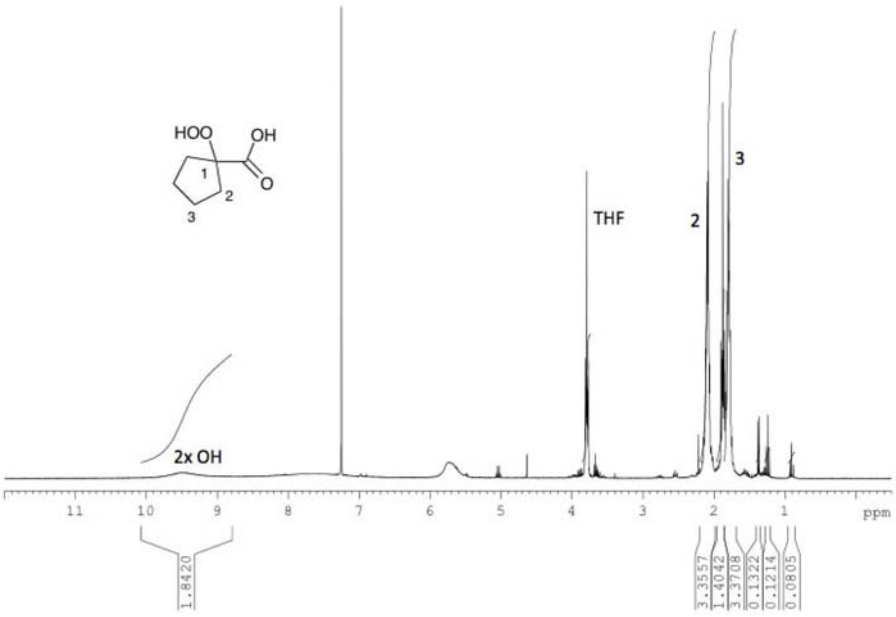

Figure S10. [1]H NMR spectrum (300 MHz, $CDCl_3$, −40 °C) of 1-carboxy-1-hydroperoxycyclopentane (**9**).

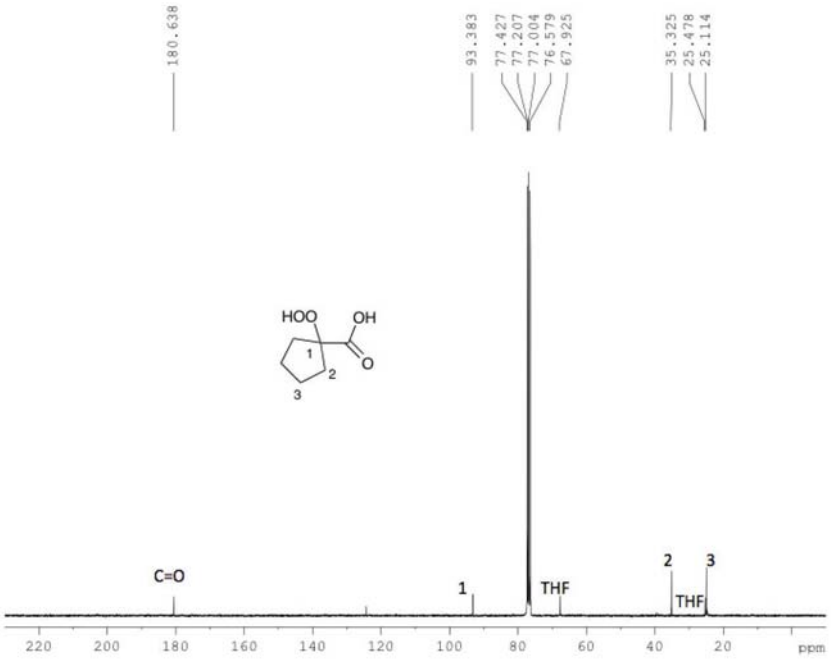

Figure S11. [13]C NMR spectrum (75 MHz, $CDCl_3$, −40 °C) of 1-carboxy-1-hydroperoxycyclopentane (**9**).

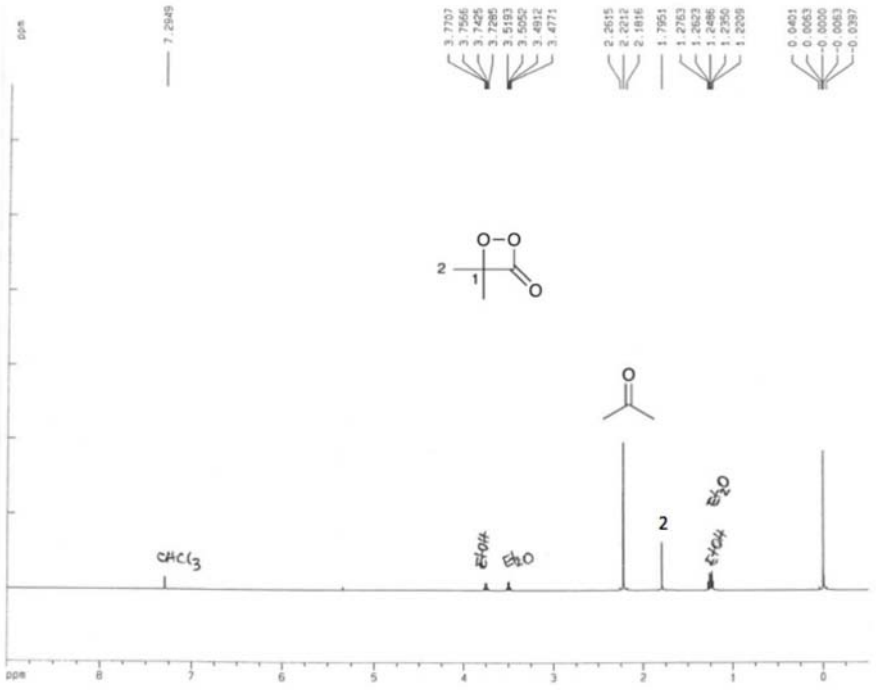

Figure S12. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, −20 °C) of 3,3-dimethyl-1,2-dioxetanone (**4**).

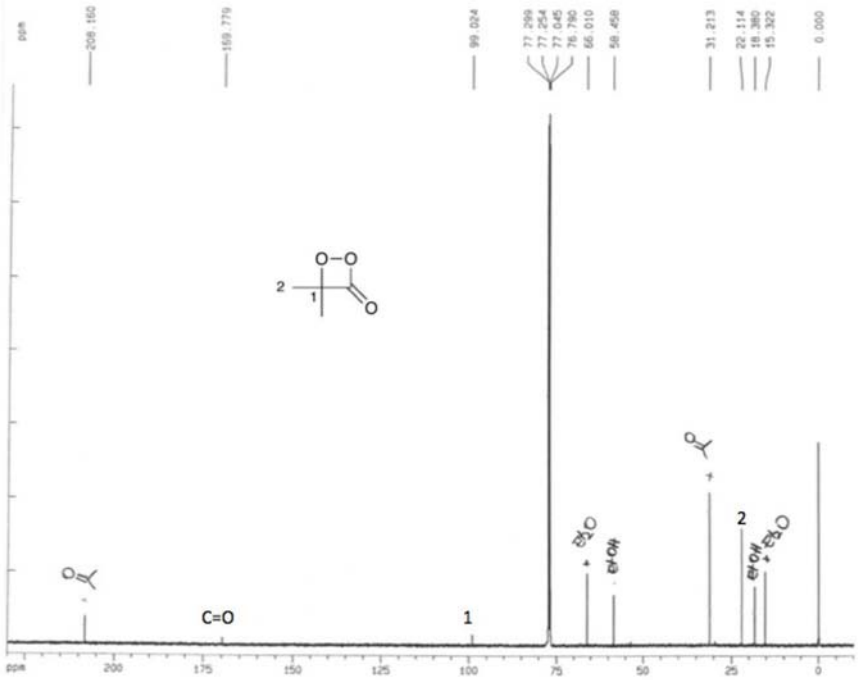

Figure S13. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, −20 °C) of 3,3-dimethyl-1,2-dioxetanone (**4**).

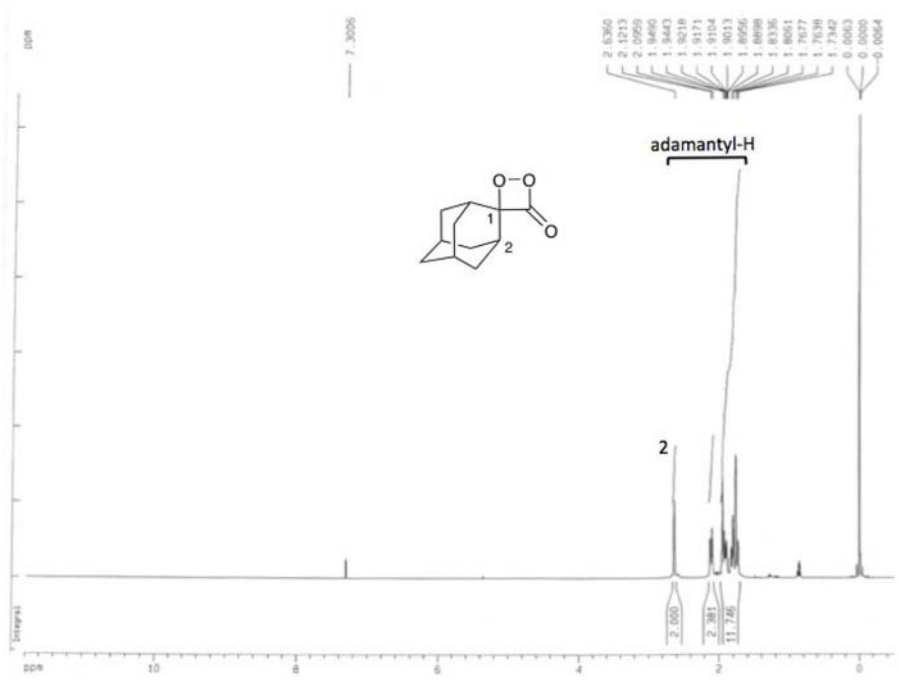

Figure S14. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, −38 °C) of *spiro*-adamantyl-1,2-dioxetanone (**5**).

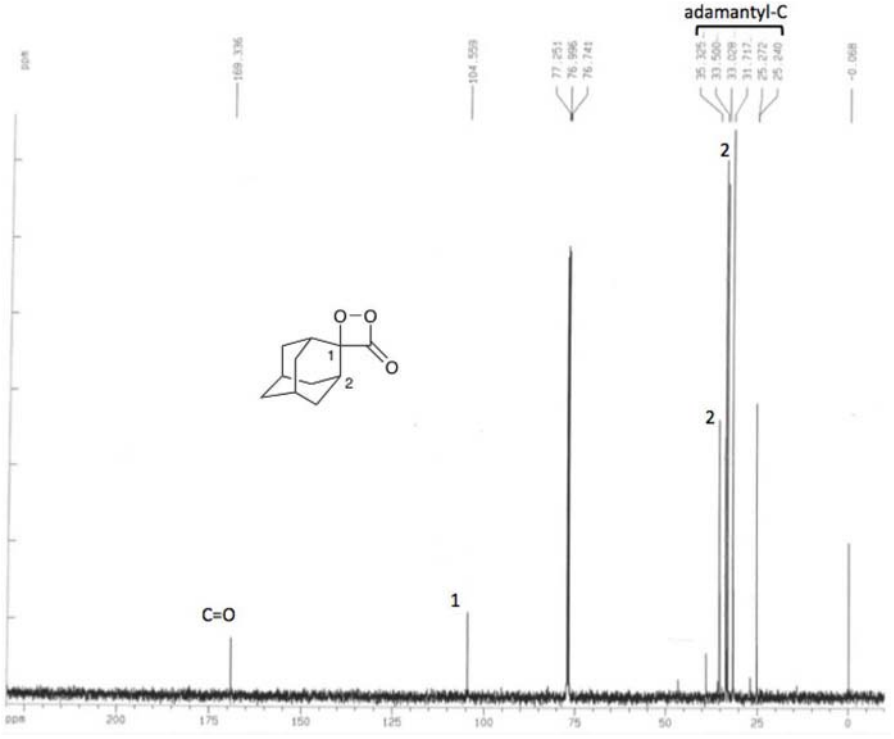

Figure S15. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, −38 °C) of *spiro*-adamantyl-1,2-dioxetanone (**5**).

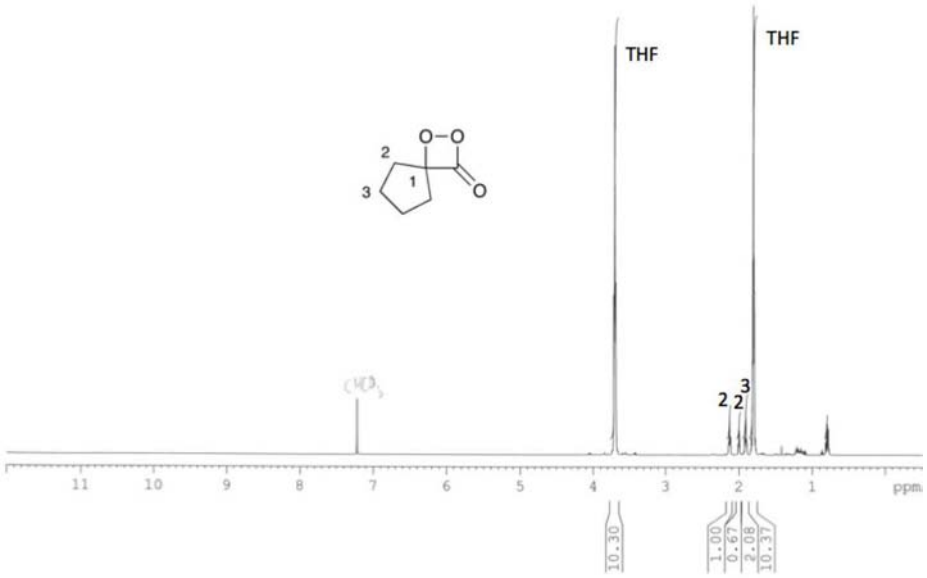

Figure S16. [1]H NMR spectrum (500 MHz, $CDCl_3$, –40 °C) of *spiro*-cyclopentyl-1,2-dioxetanone (**6**).

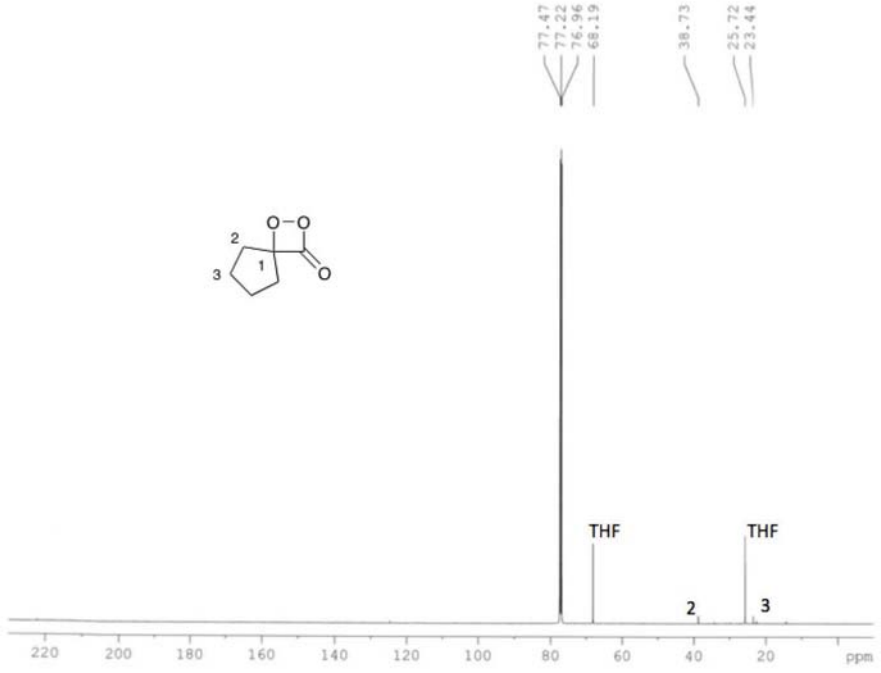

Figure S17. [13]C NMR spectrum (125 MHz, $CDCl_3$, –40 °C) of *spiro*-cyclopentyl-1,2-dioxetanone (**6**).

Pictures from the preparation of peroxides

Figure S18. Addition of the cyclopentanecarboxylic acid dianion solution (left) to oxygen-saturated THF (right) in the preparation of 1-carboxy-1-hydroperoxycyclopentane (**9**).

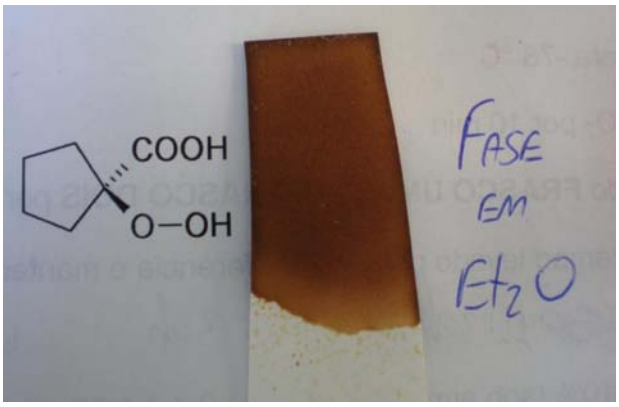

Figure S19. Qualitative detection of 1-carboxy-1-hydroperoxycyclopentane (**9**) by the KI peroxide test applied to the organic phase from the extraction of the reaction mixture.

Figure S20. Crystallization of 1-carboxy-1-hydroperoxycyclopentane (**9**) from pentane at –25 °C.

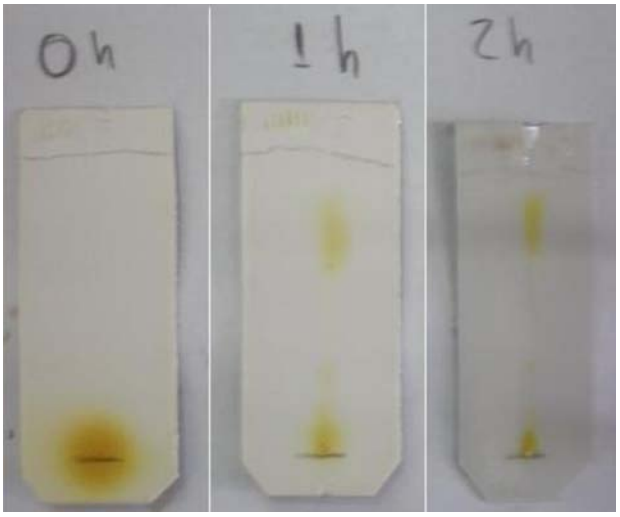

Figure S21. Thin layer chromatograms obtained at low temperature during the preparation of *spiro*-cyclopentyl-1,2-dioxetanone (**6**, Rf = 0.7) from 1-carboxy-1-hydroperoxycyclopentane (**9**, Rf = 0).

Figure 22. Bulb-to-bulb distillation of *spiro*-cyclopentyl-1,2-dioxetanone (**6**) in CH_2Cl_2, from the reaction flask at –30 °C (left) to the collection flask at –198 °C (right).