

Insight into the Chemoselective Aromatic vs Side-chain Hydroxylation of Alkylaromatics with H₂O₂ Catalyzed by a Non-Heme Imine Based Iron Complex

Barbara Ticconi,^a Giorgio Capocasa,^a Andrea Cerrato,^a Stefano Di Stefano,^a Andrea Lapi,^a Beatrice Marincioni,^a Giorgio Olivo^b and Osvaldo Lanzalunga^{a,*}

^aDipartimento di Chimica and Istituto CNR per i Sistemi Biologici (ISB-CNR), Sezione Meccanismi di Reazione, Università degli Studi di Roma “La Sapienza”, P.le Aldo Moro 5, 00185 Rome, Italy

^bDepartment Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus de Montilivi, 17071 Girona, Spain

*Corresponding author, email: osvaldo.lanzalunga@uniroma1.it

Electronic Supplementary Information

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Instruments and general methods

NMR spectra were recorded on a Bruker300 spectrometer and were internally referenced to the proton solvent signal. GC analyses were carried out on a gas chromatograph equipped with a capillary methylsilicone column (30 m x 0.25 mm x 25 μ m) Chrompack CP-Sil 5 CB and a capillary nitroterephthalic acid modified polyethylene glycol column (30 m x 0.25 mm x 25 μ m) Zebron ZB-FFAP. GC-MS analyses were performed with a gas chromatograph equipped with a silica capillary column (30 m x 0.2 mm x 25 μ m) OV5 (95% methylsilicone, 5% phenylsilicone) coupled with a mass detector (EI, 70eV). Oxidation products were identified by comparison of their GC retention times, GC/MS and ^1H NMR spectra with those of authentic specimens or by comparison of their spectral data with those reported in the literature. Oxidations were carried out by mixing $\text{Fe}(\text{CF}_3\text{SO}_3)_2(\text{CH}_3\text{CN})_2$ (2.50 μ mol), picolylamine (5.0 μ mol) and picolylaldehyde (5.0 μ mol) in a vial at 25 $^\circ\text{C}$. Substrate (250 μ mol) and CH_3CN were then added up to a total volume of 1 mL. A solution 1.74 M of H_2O_2 in CH_3CN was then added over 30 minutes by syringe pump under vigorous stirring, and left reacting for additional 1 hour. In the oxidation of xanthene-*d*₂, silylation of hydroxylated products was required for their quantitative analysis. Reaction crude was placed in a round bottom flask and diluted with 200 μL of toluene. *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) (1 equiv.) was added to the solution and the mixture was heated at 60 $^\circ\text{C}$ for 2 h.

After addition of an internal standard, reaction mixtures were filtered over a short pad of SiO_2 with 10 mL of AcOEt and analyzed by GC, GC-MS and ^1H NMR.

Oxidation products were identified by comparison with authentic specimens or by comparison of their spectral data with those reported in the literature.

1-Hydroxydihydroanthracene, 2-hydroxydihydroanthracene, were isolated by column chromatography from the crude reaction mixture of dihydroanthracene oxidation carried out

under the same reaction conditions reported above using 25 μmol of $\text{Fe}(\text{CF}_3\text{SO}_3)_2(\text{CH}_3\text{CN})_2$, 50 μmol of picolylamine and picolylaldehyde, 2.5 mmol of dihydroanthracene and 0.5 mmol of H_2O_2 in 10 mL of CH_3CN . Products were characterized as follows:

1-hydroxy-9,10-dihydroanthracene:

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.34-7.18 (*m*, 2H), 7.09-7.04 (*t*, $J = 7.6$ Hz, 2H), 6.91- 6.89 (*d*, $J = 7.6$ Hz, 2H), 6.88-6.86 (*d*, $J = 7.6$ Hz, 2H), 4.86 (*br s*, 1H), 3.96 (*s*, 4H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 138.3, 136.0, 135.5, 128.8, 127.8, 127.4, 126.6, 126.1, 126.0, 120.1, 112.4, 35.6, 28.5. GC-MS m/z (rel. intensity): M^+ 196 (100), 195 (86), 194 (17), 181 (11), 179 (20), 178 (16), 177 (18), 167 (29), 166 (14), 165 (42), 152 (14). HRMS (ESI $^+$, m/z): calcd for $(\text{C}_{14}\text{H}_{13}\text{O})^+$ ($\text{M}+\text{H})^+$: 197.0966; found 197.0972.

2-hydroxy-9,10-dihydroanthracene:

$^1\text{H-NMR}$ (300 MHz, CDCl_3) δ : 7.29-7.27 (*m*, 2H), 7.23-7.19 (*m*, 2H), 7.15 (*d*, $J = 8.1$ Hz, 2H), 6.80 (*d*, $J = 2.5$ Hz, 2H), 6.68 (*dd*, $J = 8.1, 2.5$ Hz, 2H), 4.86 (*br s*, 1H), 3.89 (*s*, 4H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ : 153.7, 138.1, 136.9, 136.2, 128.8, 128.3, 127.3, 126.0, 125.9, 114.1, 112.9, 36.1, 35.1. GC-MS m/z (rel. intensity): M^+ 196 (100), 195 (70), 194 (17), 181 (14), 179 (39), 178 (19), 177 (17), 167 (23), 166 (13), 165 (44), 152 (17). HRMS (ESI $^+$, m/z): calcd for $(\text{C}_{14}\text{H}_{13}\text{O})^+$ ($\text{M}+\text{H})^+$: 197.0966; found 197.0977.

GC traces for selected oxidations of alkylaromatics with H₂O₂ catalyzed by the non-heme imine based iron complex **1**

Oxidation of toluene

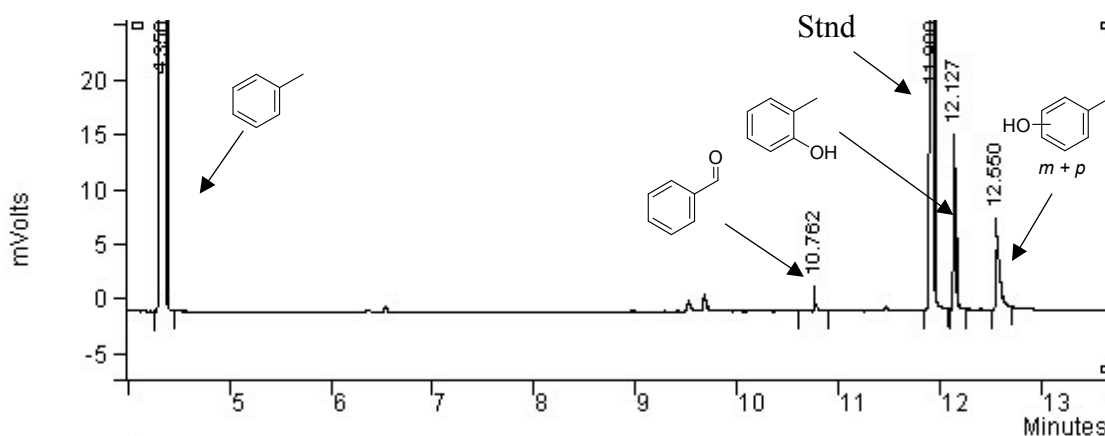


Figure S1: GC trace for toluene oxidation

Oxidation of ethylbenzene

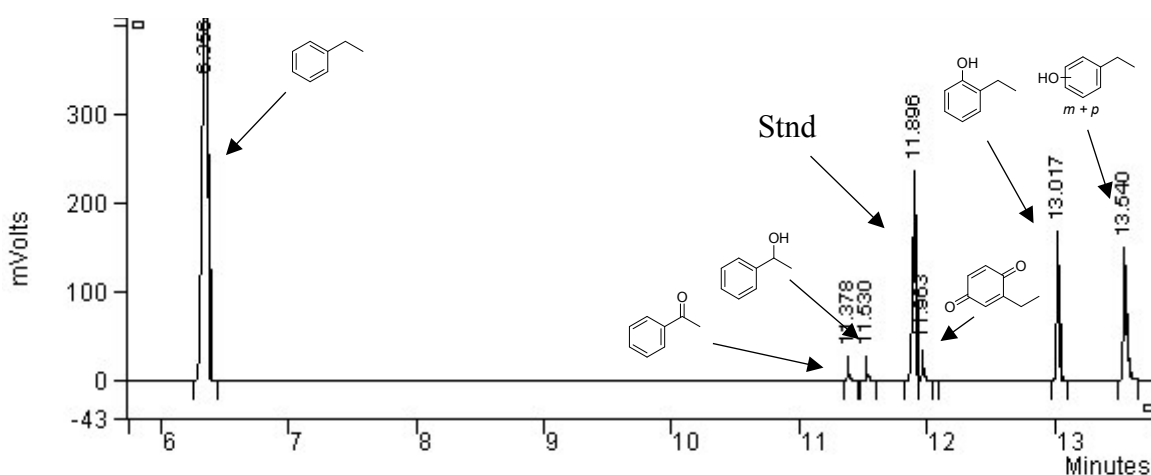


Figure S2: GC trace for ethylbenzene oxidation

Oxidation of diphenylmethane

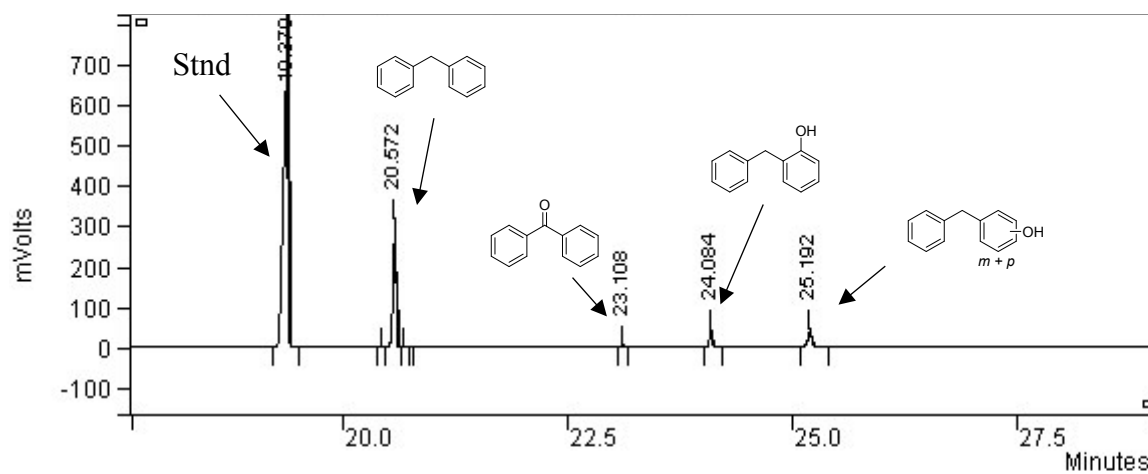


Figure S3: GC trace for diphenylmethane oxidation

Oxidation of fluorene

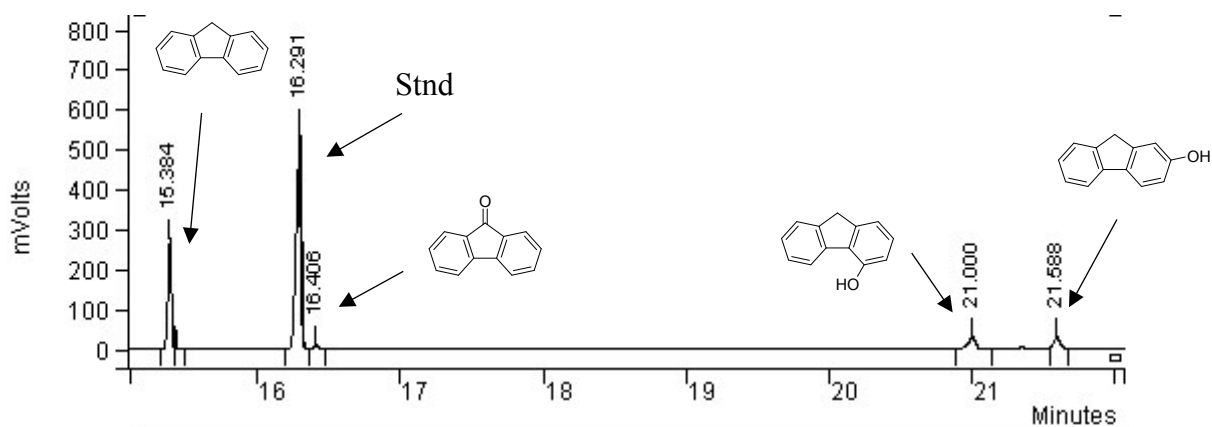


Figure S4: GC trace for fluorene oxidation

Oxidation of dihydroanthracene

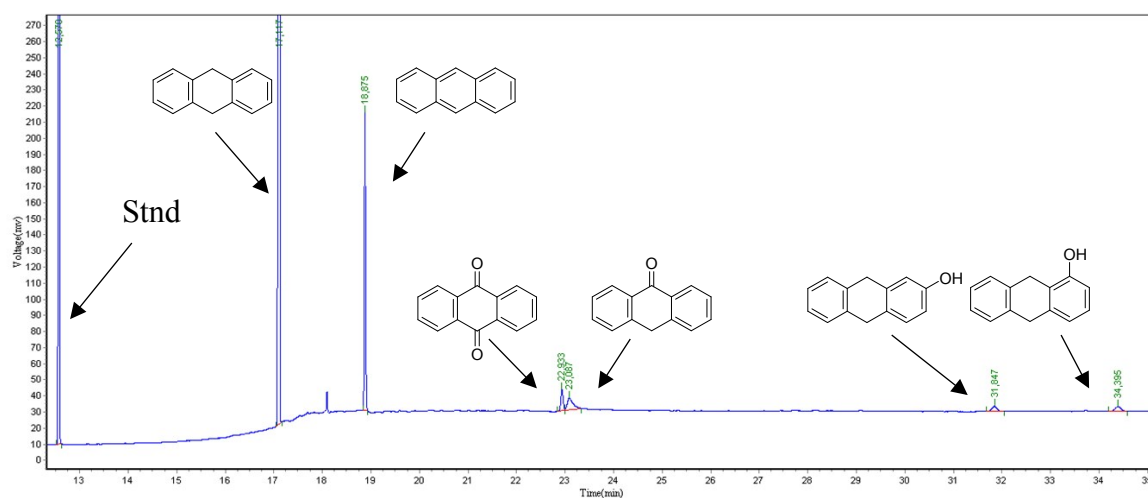


Figure S5: GC trace for dihydroanthracene oxidation

Oxidation of dihydroanthracene-*d*4

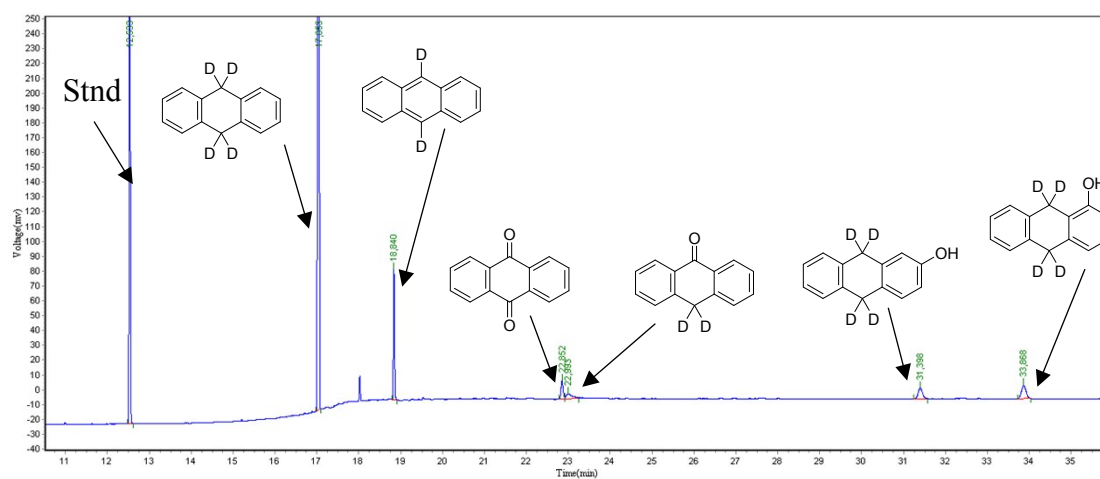


Figure S6: GC trace for dihydroanthracene-*d*4 oxidation

Oxidation of xanthene

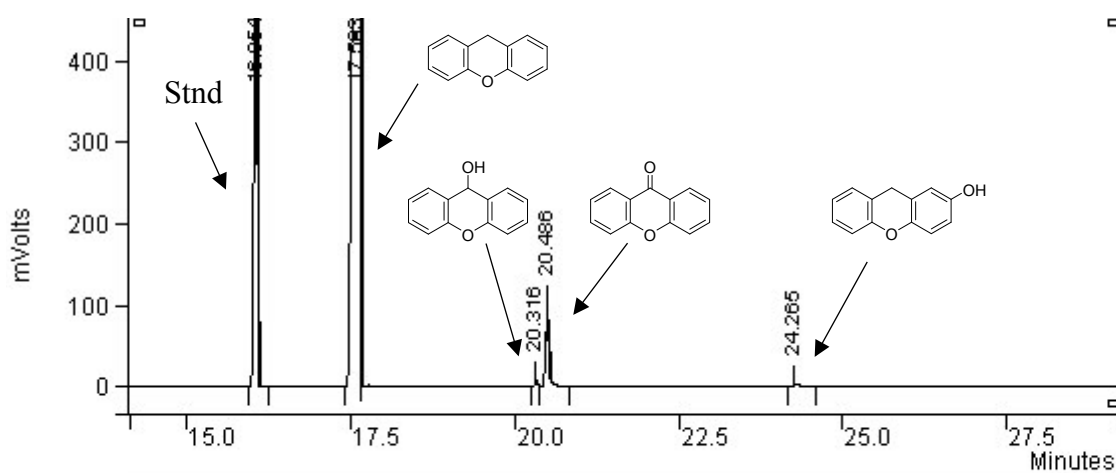


Figure S7: GC trace for xanthene oxidation

Oxidation of xanthene-d2

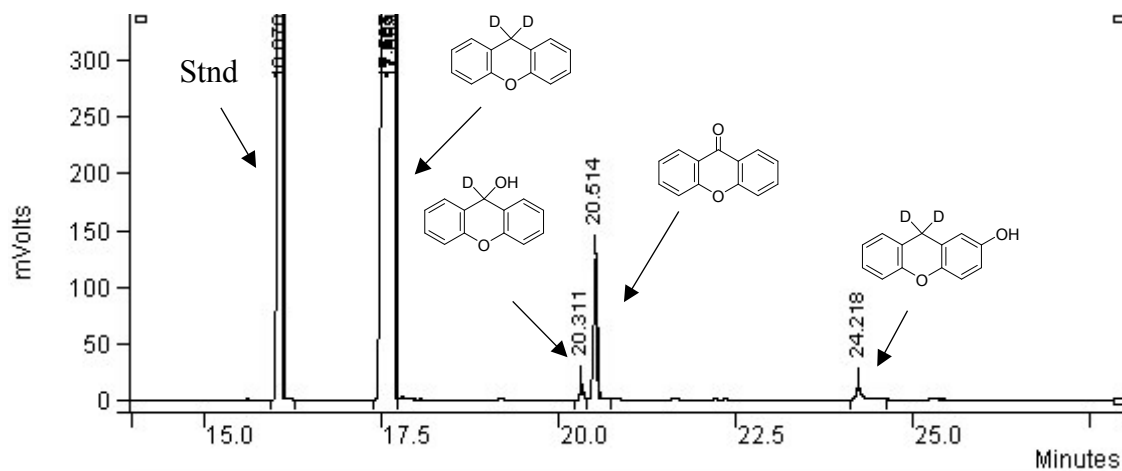


Figure S8: GC trace for xanthene-d2 oxidation

^1H NMR spectra for selected oxidations of alkylaromatics with H_2O_2 catalyzed by the non-heme imine based iron complex **1**

Oxidation of dihydroanthracene (DHA)

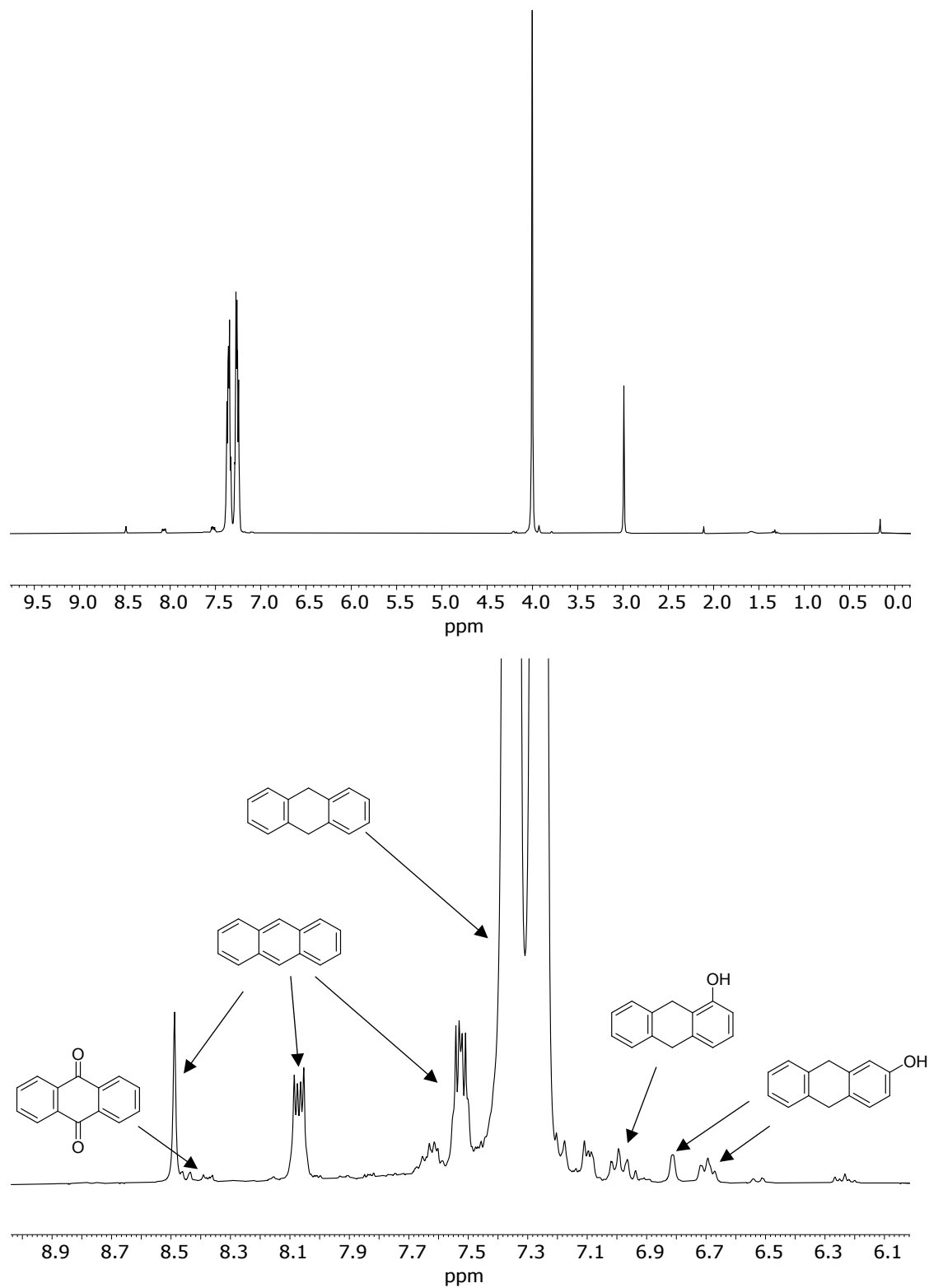


Figure S9: ^1H -NMR spectrum for DHA oxidation

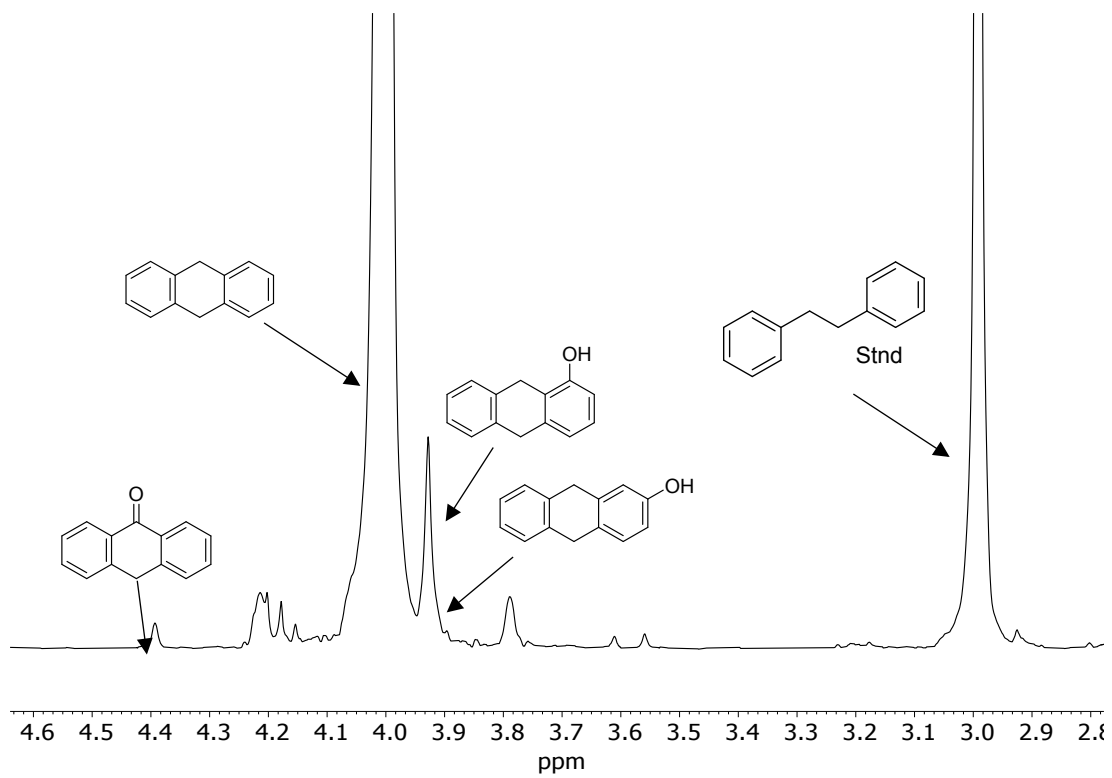


Figure S9: ¹H-NMR spectrum for DHA oxidation (continue)

Oxidation of dihydroanthracene-*d*4 (DHA-*d*4)

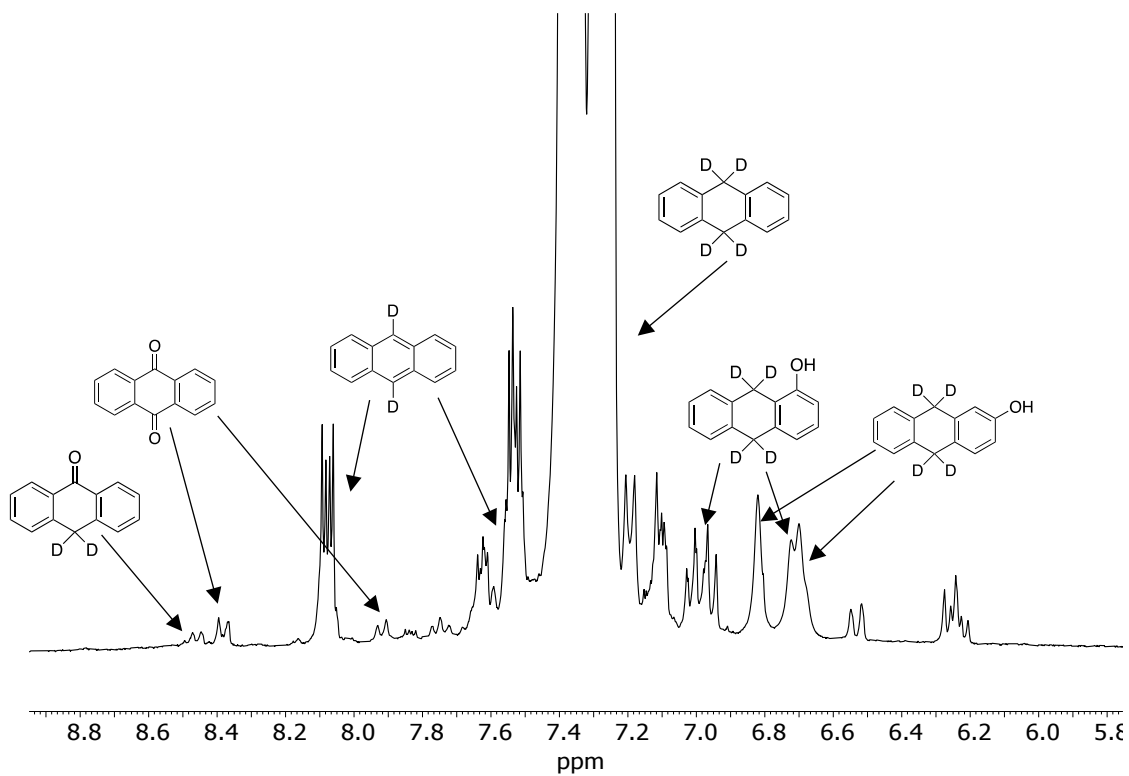
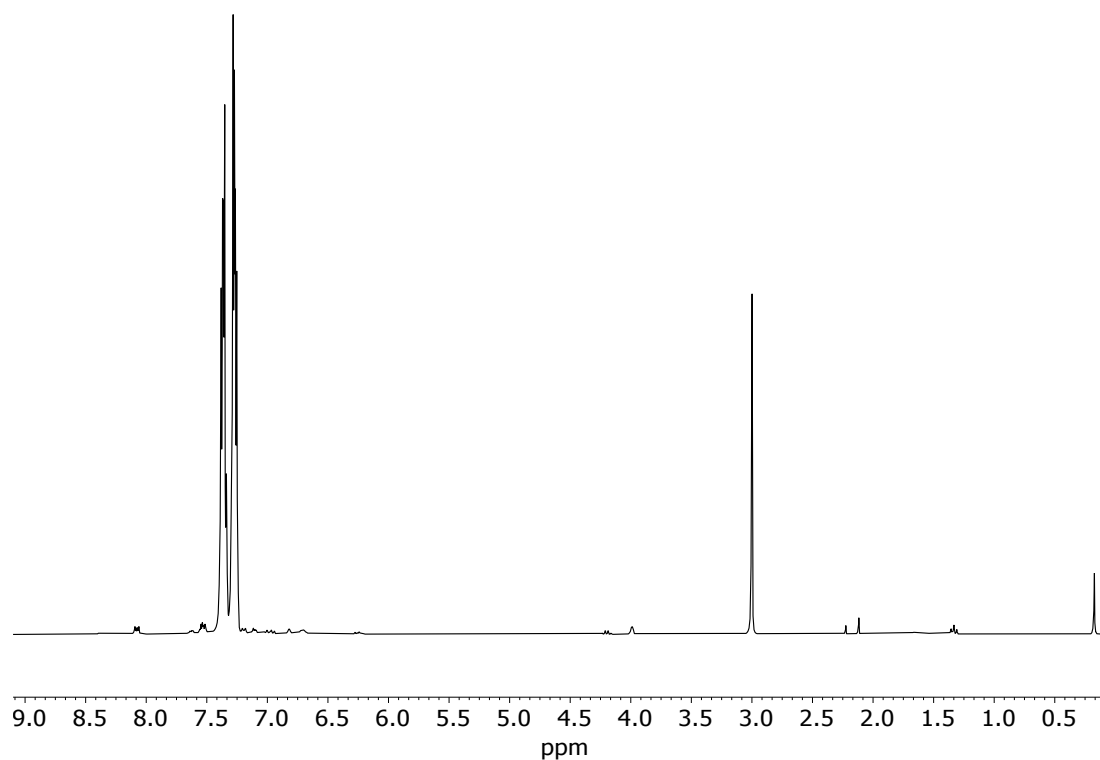


Figure S10: ¹H-NMR spectrum for DHA-*d*4 oxidation.

Oxidation of xanthene

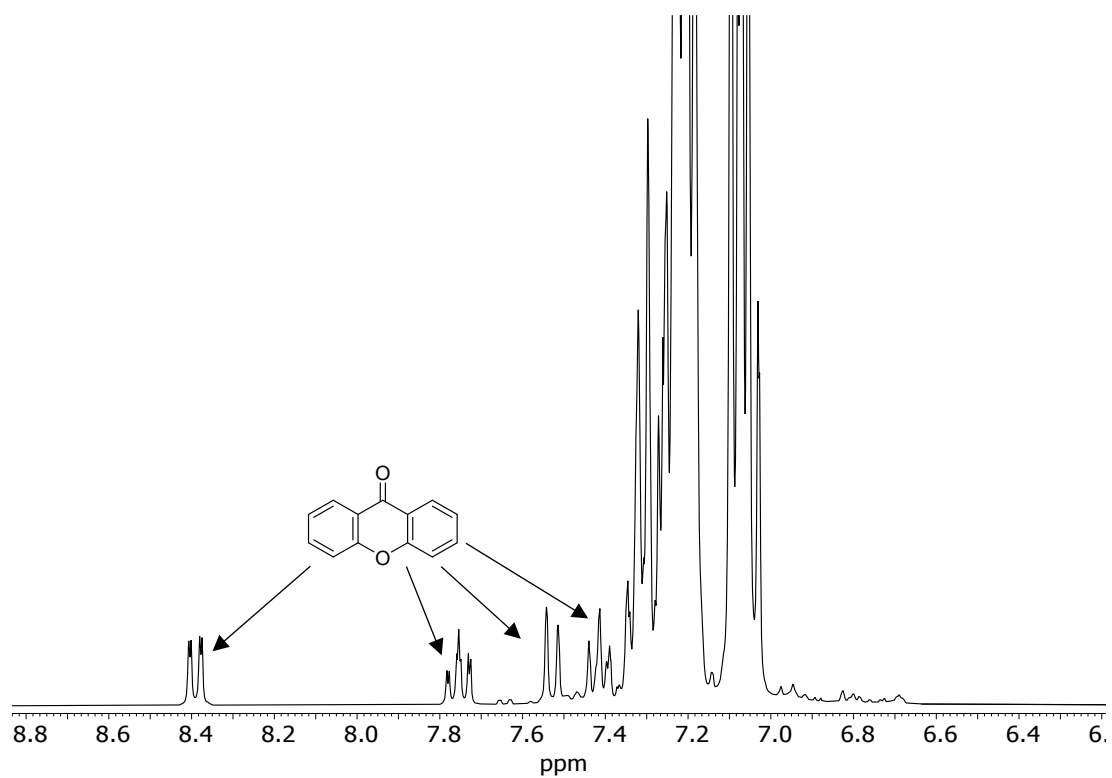
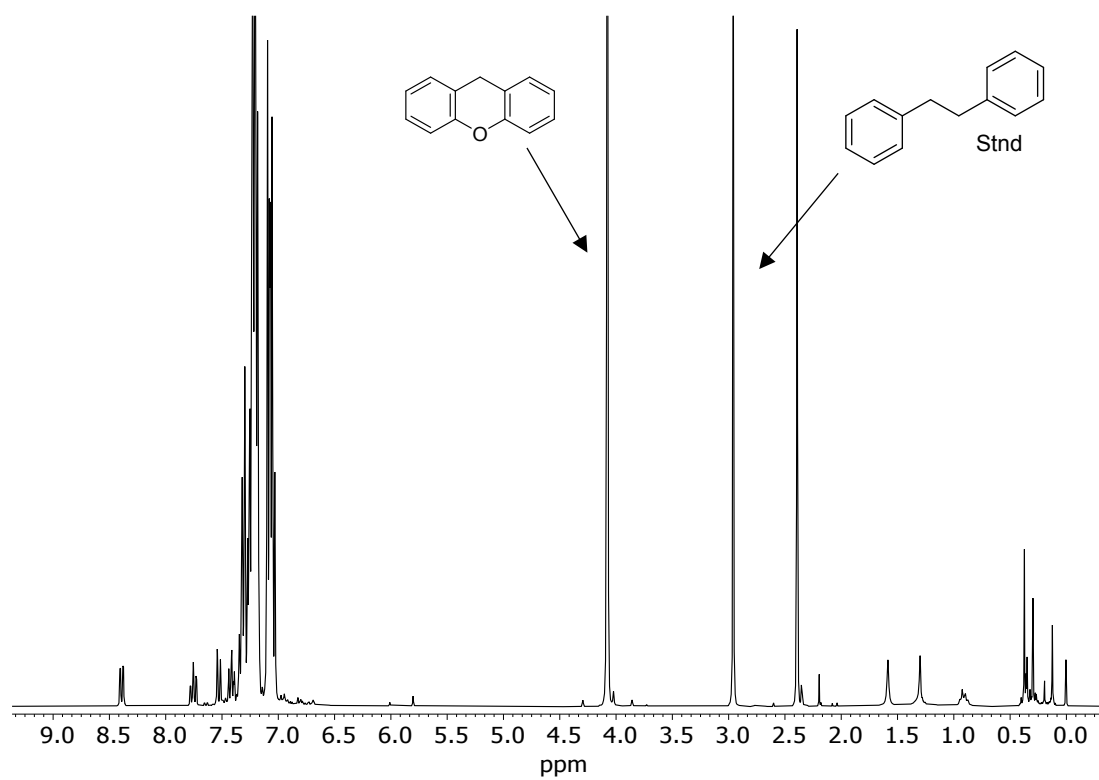


Figure S11: ¹H-NMR spectrum for xanthene oxidation after derivatization with BSTFA.

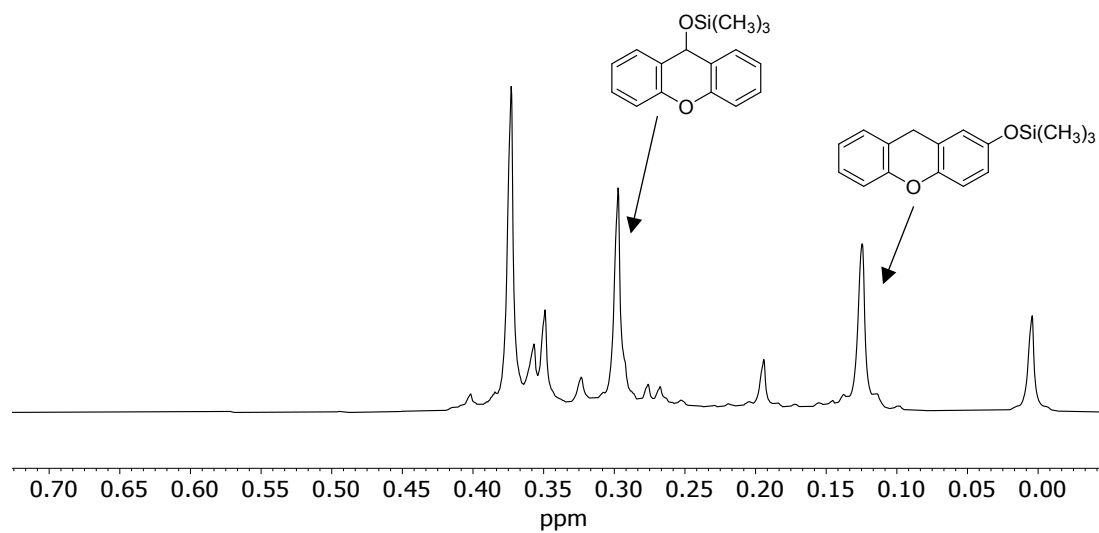


Figure S11: ¹H-NMR spectrum for xanthene oxidation after derivatization with BSTFA.
(continue)

Oxidation of xanthene-d2

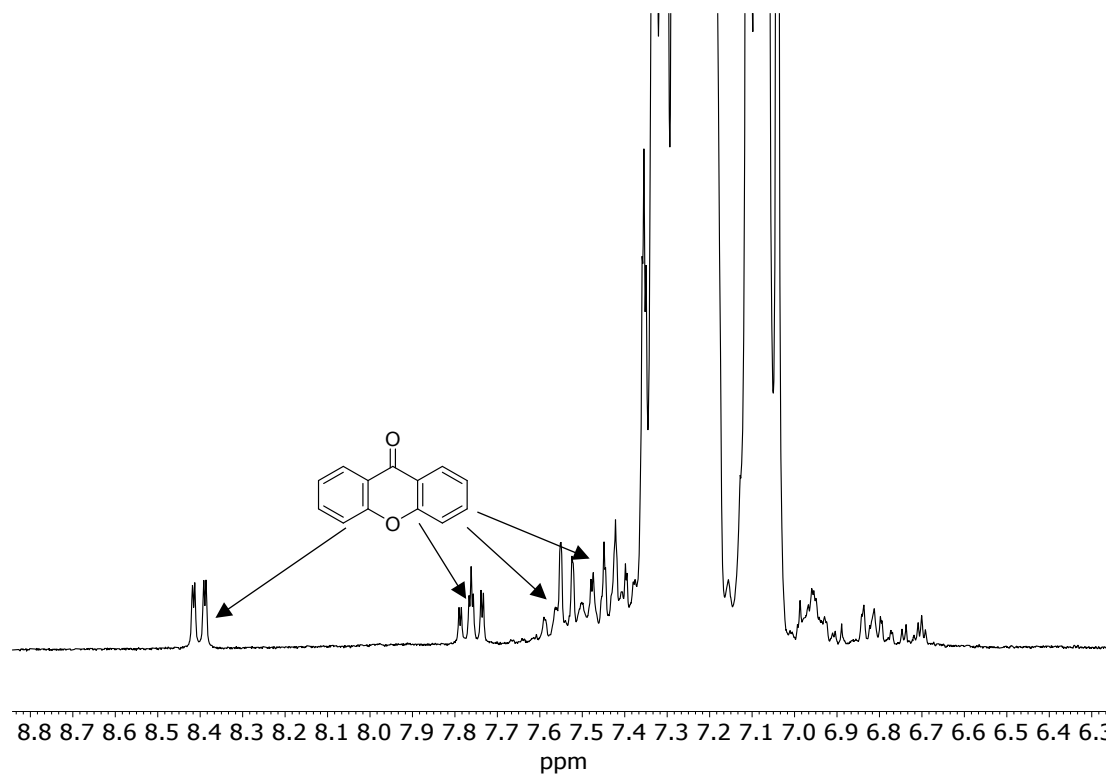
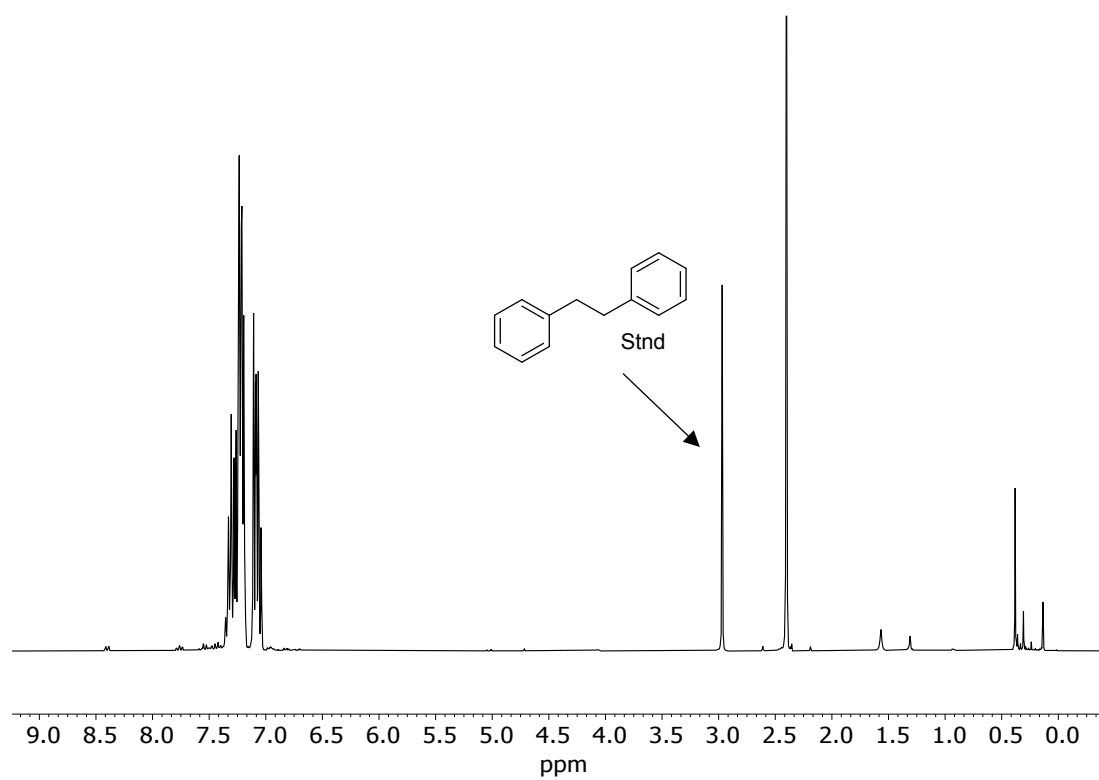


Figure S12: $^1\text{H-NMR}$ spectrum for xanthene- d_2 oxidation after derivatization with BSTFA.

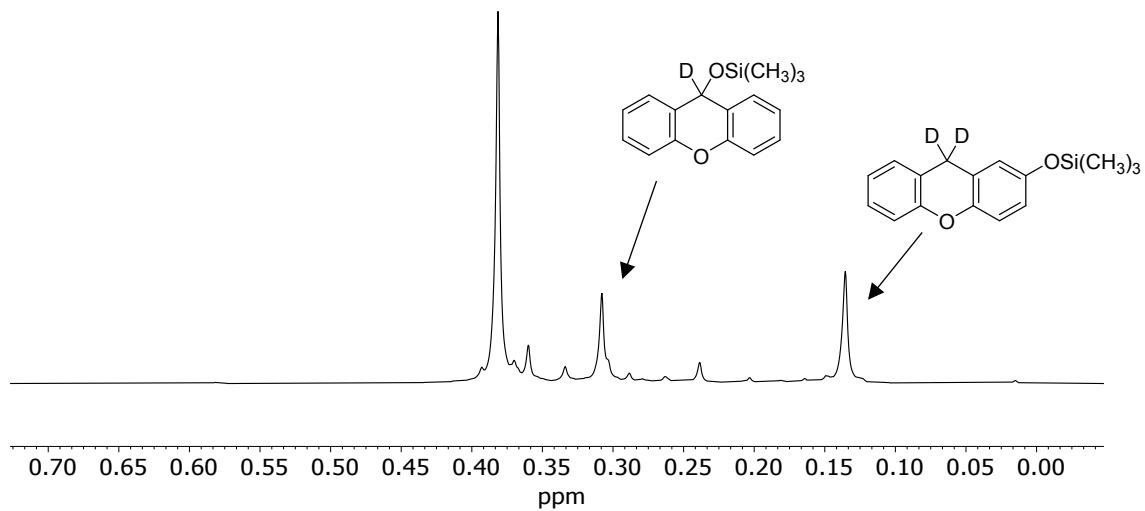


Figure S12: $^1\text{H-NMR}$ spectrum for xanthene-*d*2 oxidation after derivatization with BSTFA.
(continue).