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Supporting Information

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Synergistic Effect of Ketone and Hydroperoxide in Brønsted Acid Catalyzed Oxidative Coupling Reactions**

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Supporting Information

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1 Experimental details

Unless otherwise indicated, all reagents and solvents were purchased from commercial distributors and used as received.

Solvents (toluene, hexanes, ethyl acetate, dichloromethane, methanol) used for column chromatography were of technical grade and used after distillation in a rotary evaporator.

TLC was used to check the reactions for full conversion and was performed on Macherey-Nagel Polygram Sil G/UV_{254} thin layer plates. TLC spots were visualized by UV-light irradiation.

Routine GC-MS analyses were performed with an Agilent Technologies 7890A GC System equipped with a MN Optima® 5 Accent capillary column (0.32 mm × 30 m × 0.25 μm) and coupled with an Agilent Technologies 5975C VL MSD mass detector.

Flash column chromatography was carried out using Merck Silica Gel 60 (40-63 μm). Yields refer to pure isolated compounds.

^{1}H and ^{13}C NMR spectra were measured with Bruker AV 600, AV 500 and AV 400 spectrometers. All chemical shifts are given in ppm downfield relative to TMS and were referenced to the solvent residual peaks.[1] ^{1}H NMR chemical shifts are designated using the following abbreviations as well as their combinations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, app. = apparent. For ^{13}C NMR data the following abbreviations are used: p = primary (CH_3), s = secondary (CH_2), t = tertiary (CH), q = quaternary (C).

High resolution mass spectra were recorded with a Bruker APEX III FTICR-MS or a Finnigan SSQ 7000 quadrupole MS or a Finnigan MAT 95 double focusing sector field MS instrument.

Abbreviations:
Cbz: benzyloxycarbonyl; CHP: cumyl hydroperoxide; DCM: dichloromethane; DTBP: di-*tert*-butyl hydroperoxide; Et_2O: diethyl ether; EtOAc: ethyl acetate; MeOH: methanol; MsOH: methanesulfonic acid; TBHP: *tert*-butyl hydroperoxide; TCA: trichloroacetic acid; TFA: trifluoroacetic acid; TfOH: trifluormethanesulfonic acid; T-HYDRO: *tert*-butyl hydroperoxide in water.

Warning:

Although we never experienced any problem in working with or handling the compounds described in this work, precautions should be taken when working with peroxides. In particular, it should be avoided as much as possible to expose neat peroxides to heat or to mix them with metals or metal salts. Performing such reactions behind a blast shield is recommended.

Special care should be taken when mixing ketones, hydrogen peroxide and acids since this combination is known to be capable of generating explosive compounds.[2]

2 Mechanistic studies

2.1 Determination of NMR yields for xanthene autoxidation and coupling reaction

Unless otherwise noted, all yields refer to ^{1}H NMR yields. In order to determine these NMR yields, a sample of the reaction mixture (~100µL) was taken and dissolved in d6-DMSO and directly analyzed. All products could be distinguished from the spectrum of a reaction mixture and ratio of products was directly determined by integration of reference peaks (Table S1).

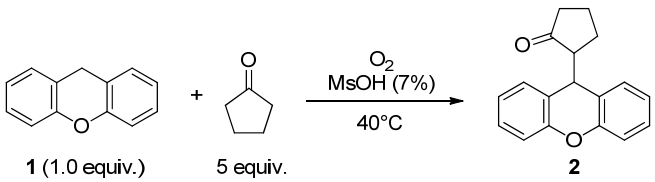
In the case of autoxidation reactions, xanthene hydroperoxide **3** decomposes in DMSO to xanthydrol **6** and xanthone **5**. However, if all oxygenated products are considered, the conversion of xanthene remains the same for a given sample and the values are reproducible.

Although the autoxidation of xanthene in DMSO is feasible at 40°C (vide infra), at room temperature and under the dilution of an NMR sample, we never saw any further autoxidation of the samples measured. In order to minimize all these effects, we measured our samples as quickly as possible. If NMR-samples had to be stored for more than a couple hours, they were frozen and kept in a fridge.

Table S1: List of signals considered for the determination of ^{1}H NMR yields.

product	signal in d6-DMSO
1	singlet (4ppm; 1H)
2	doublet (4.6ppm; 2H)
3	singlet (5.95ppm; 1H)
5	doublet (8.2ppm; 2H)
6	singlet (5.7ppm; 1H)

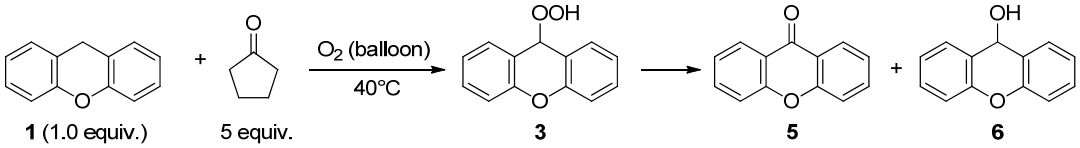
2.2 General procedure for the autoxidative coupling of xanthene



Scheme S1: Autoxidative coupling of xanthene with cyclopentanone, model reaction of the present study.

In a 4mL screw cap vial equipped with 2 silicon/Teflon septa, xanthene (91 mg; 0.5 mmol) was dissolved in cyclopentanone (0.22 mL; 2.5 mmol). Methanesulfonic acid (3.3 mg; 2.3 µl; 7 mol%) was added, the reaction vessel was flushed with O_2 and closed then connected to an O_2 balloon. The reaction mixture was heated at 40°C in an aluminum heating block and stirred at 400 rpm. If required for reaction progress monitoring, the reaction was performed on a larger scale.

2.3 General procedure for autoxidation of xanthene



Scheme S2: Autoxidation of xanthene in cyclopentanone.

In a 4mL screw cap vial equipped with 2 silicon/Teflon septa, xanthene (91 mg; 0.5 mmol) was dissolved in cyclopentanone (0.22 mL; 2.5 mmol). The reaction vessel was flushed with O_2 and closed then connected to an O_2 balloon. The reaction mixture was heated at 40°C in an aluminum heating block and stirred at 400 rpm. If required for reaction progress monitoring, the reaction was performed on a larger scale.

2.4 Xanthene autoxidation in cyclopentanone

It was found that xanthene hydroperoxide decomposes to xanthone and xanthydrol overtime under autoxidation conditions (Scheme S2). While the selectivity for xanthene hydroperoxide remained high until rather high conversions, to accurately follow conversion overtime, all the oxidized species of xanthene had to be considered. Analysis of ^{1}H NMR samples of the crude reaction mixture in d6-DMSO provided an easy way of quantifying all these species.

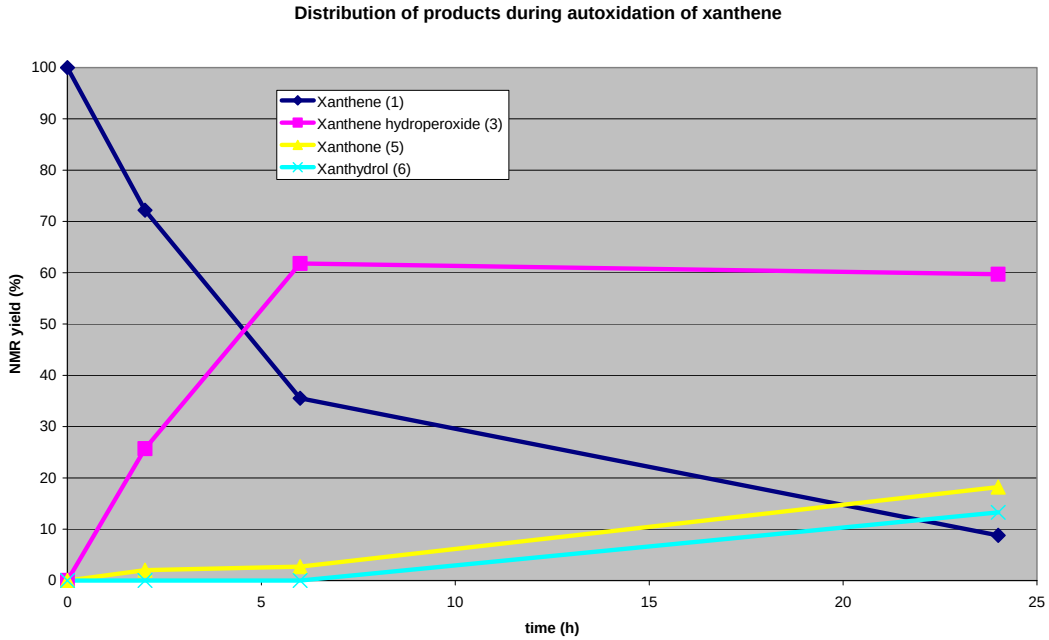
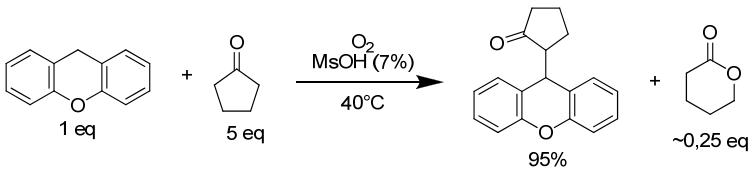


Figure S1: Distribution of oxidized products in the autoxidation of xanthene.

As can be seen on the graph of a representative example (Figure S1), xanthene hydroperoxide **3** is the only product formed at the beginning of the reaction. After further conversion is achieved, **3** starts to break down to xanthone (**5**) and xanthydrol (**6**). Because this degradation pathway is not always reproducible, following only the formation of **3** is misleading and results vary from experiment to experiment. However, if all oxidized products are monitored and only conversion of xanthene taken into account, kinetic data is reproducible.

2.5 Bayer-Villiger oxidation of cyclopentanone to valerolactone



Close examination of crude NMR of reaction mixture showed the presence of valerolactone **7** in approximately 25% yield (based on **1**, i.e. the theoretical release of 1 equivalent of H_2O_2 from hydroperoxide **3**) resulting from a Bayer-Williger oxidation of cyclopentanone (Figure S2). The presence of this oxidised product indirectly shows the presence of hydroperoxides in our reaction mixtures.

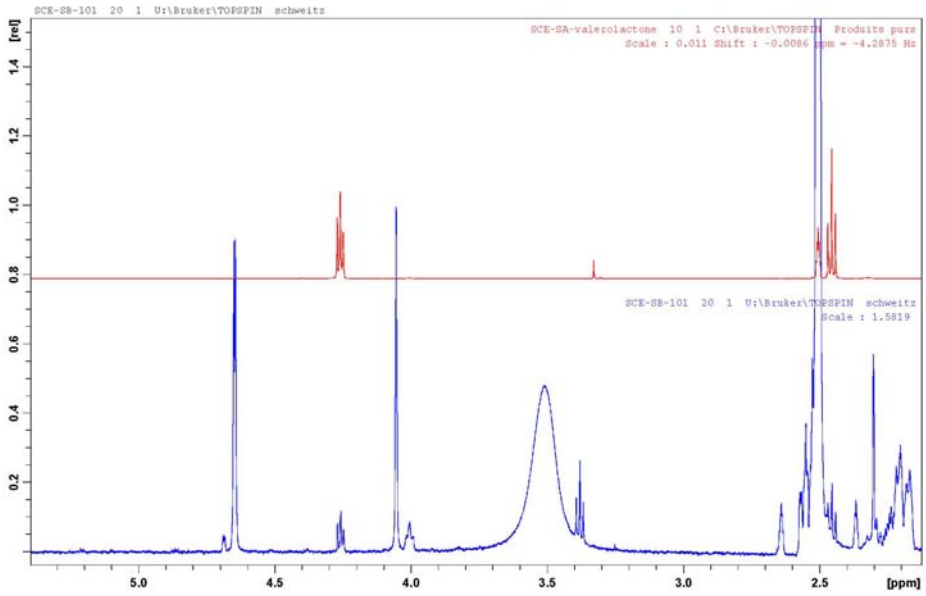


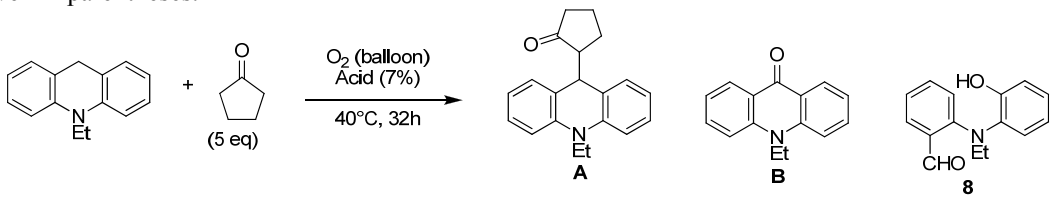
Figure S2: NMR of crude mixture (blue) and valerolactone (red) in d6-DMSO.

Both triplets of valerolactone **7** at 4.26 and 2.47 ppm are visible in the crude NMR. Doublet at 4.64 ppm is coupling product **2** while the singlet at 4.05 ppm is xanthene.

2.6 Isolation of byproduct 8 from hydroperoxide rearrangement

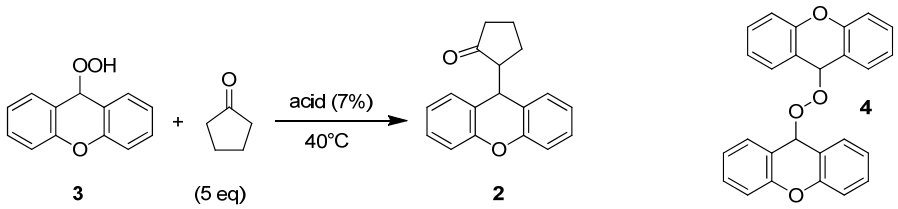
Product **8** was isolated from an oxidative coupling reaction using *N*-ethylacridane in cyclopentanone using TfOH as catalyst. Under the same reaction conditions but using MsOH as catalyst, **8** could only be observed in traces by NMR analysis (Table S3).

Table S2: Detection of byproduct **8** from hydroperoxide rearrangement. Isolated yields, NMR yields given in parentheses.



acid	GC-conversion (%)	A, yield (%)	B, yield (%)	8, yield (%)
TfOH	52	3 (2)	22 (23)	10 (8)
MsOH	70	39 (41)	0 (2)	0 (1)

2.7 Conversion of xanthene hydroperoxide 3 to coupling product 2



In a 4mL screw cap vial, xanthene hydroperoxide **3** (107 mg; 0.5 mmol) was dissolved in cyclopentanone (0.22 mL; 2.5 mmol) and acid (0.035 mmol) was added. The progress of the reaction was followed by NMR as described above.

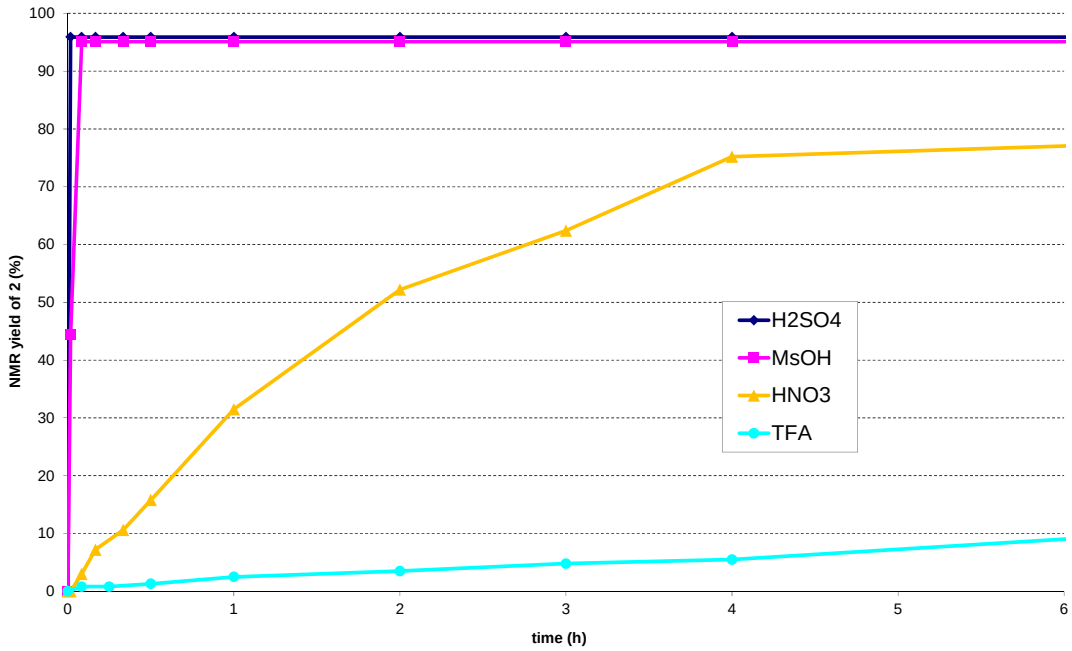


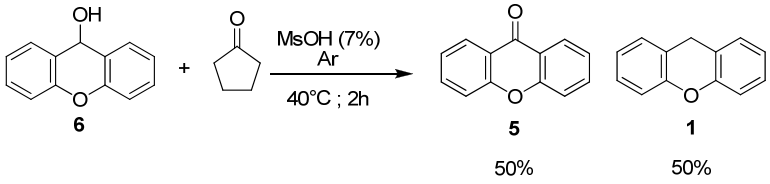
Figure S3: conversion profile of hydroperoxide 3 to 2 under acidic conditions

As can be seen from Figure S3, strong acids are needed to achieve good conversion of **3** to **2** in short reaction times. Of the acids tested, H_2SO_4 (dark blue line) is the fastest one, followed by methane sulfonic acid (magenta line), where complete conversion is observed in less than 1 and 5 minutes, respectively. Nitric acid (yellow line) gives reasonable conversion, achieving 75% in 4 hours and complete conversion overnight (93%, not shown on figure). The limit for this reaction is attained with trifluoroacetic

acid (turquoise line), giving only 5% of **2** in 4 hours. Even after prolonged reaction time (22h), complete conversion was not achieved (37% of **2**, not shown on figure**).** It is to be noted that in this last case, significant amounts of mixed peroxide **4** were observed in the reaction mixture, as noted before.[3]

2.8 Xanthydrol (6) control experiments

In a 4mL screw cap vial, xanthydrol **6** (99 mg; 0.5 mmol) was dissolved in cyclopentanone (0.11 mL; 1.25 mmol) then methane sulfonic acid (2.3 µL; 0.035 mmol; 7 mol%) was added. Xanthone **5** immediately precipitated upon addition of methane sulfonic acid. Analysis of the mixture showed xanthene **1** and xanthone **5** in a 1:1 ratio as the only detectable products by ^{1}H NMR (Scheme S3).



Scheme S3: Control experiment with xanthydrol (**6**) under standard reaction conditions.

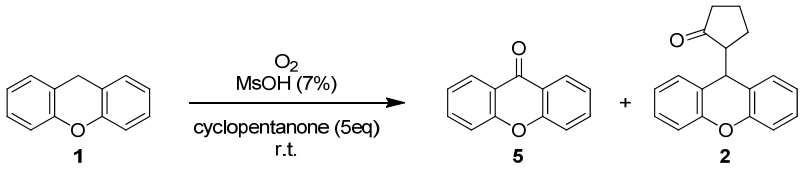
2.9 Oxygen consumption experiments:

Figure S4: Picture of experimental setup including three-necked flask and gas burette.

Xanthene (364mg; 2mmol) was charged into a 3 necked flask (see picture of the setup, Figure S4) connected to a gas burette. The whole system was flushed with oxygen 3 times through the gas burette and the gas burette filled with oxygen. A solution of methane sulfonic acid (9.2µL; 0.14 mmol) in cyclopentanone (0.88 mL; 10 mmol) was added to the flask through the septum. The septum was then wrapped in parafilm to avoid any leak. The volume read on the burette after addition of all liquids

was used as the starting reference value. As can be seen from Table S3, the amount of O_2 consumed is essentially equimolar to the amount of xanthene converted.

Table S3: Measurement of oxygen consumption in the oxidative coupling of xanthene with cyclopentanone**.**

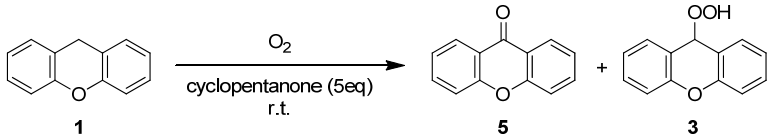


time (h)	5 (%)[a]	2 (%)[a]	conv. (%)[b]	V O_2 (mL)[c]	N°eq O_2[d]	mol% O_2
24	1,1	81,2	82,3	39,2	0,79	79
48	1,4	88,7	90,1	42,8	0,87	87

[a] ^{1}H NMR yields; [b] conversion of **1**, measured by ^{1}H-NMR; [c] volume of O_2 consumed; [d] molar equivalents relative to the initial amount of xanthene; [e] molar fraction of O_2 consumed relative to the initial amount of xanthene.

Xanthene (364mg; 2mmol) was charged into a 3 necked flask (see picture of the setup) connected to a gas burette. The whole system was flushed with oxygen 3 times through the gas burette and the gas burette filled with oxygen. Cyclopentanone (0.88 mL; 10 mmol) was added to the flask through the septum. The septum was then wrapped in parafilm to avoid any leak. The volume read on the burette after addition of all liquids was used as the starting reference value to calculate the amount of oxygen consumed (Table S4).

Table S4: Measurement of oxygen consumption by autoxidation of xanthene.



time (h)	5 (%)[a]	3 (%)[a]	conv. (%)[b]	V O_2 (mL)[c]	N°eq O_2[d]	mol% O_2
6	0	22,9	22,9	11	0,22	22
24	1,2	62,8	64	32,2	0,65	65

[a] ^{1}H NMR yields; [b] conversion of **1**, measured by ^{1}H-NMR; [c] volume of O_2 consumed; [d] molar equivalents relative to the initial amount of xanthene; [e] molar fraction of O_2 consumed relative to the initial amount of xanthene.

In both cases, NMR samples were taken to monitor the conversion of products.

In both experiments, the number of equivalents of O_2 consumed by the reaction follows almost perfectly the conversion of xanthene to the coupling product or oxygenated products, respectively (compare conversion of **1** and mol% O_2).

2.10 Autoxidation of xanthene in different solvents

The best conversions of xanthene were obtained in ketones, with cyclopentanone being better than acetone. Moderate yields and rates of autoxidation were obtained in nitromethane, DMSO and ethyl acetate while chloroform proved much less efficient for this autoxidation (Figure S5). Hexane and dichloromethane were found to be similarly or even less efficient than chloroform (data not shown). Interestingly, a strong induction period was detected in most solvents.

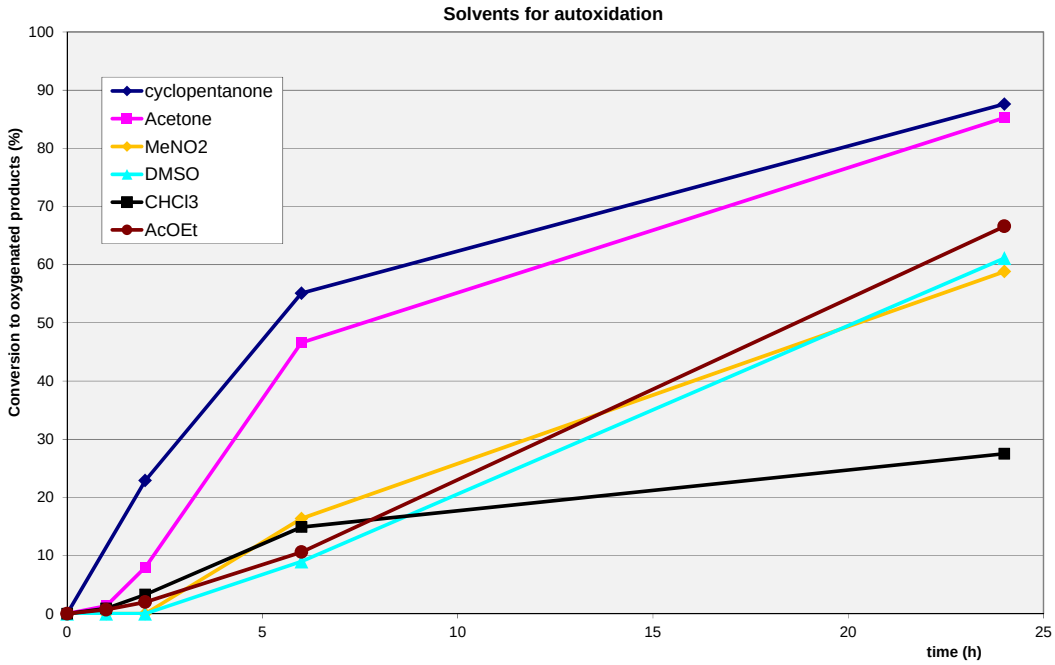


Figure S5: Autoxidation of xanthene in different solvents. Following general procedure using 0.5 mL of solvent (1 mL for $MeNO_2$) instead of cyclopentanone and 0.5 mmol xanthene, average of 3 experiments.

2.11 Acid effect on the autoxidation of xanthene

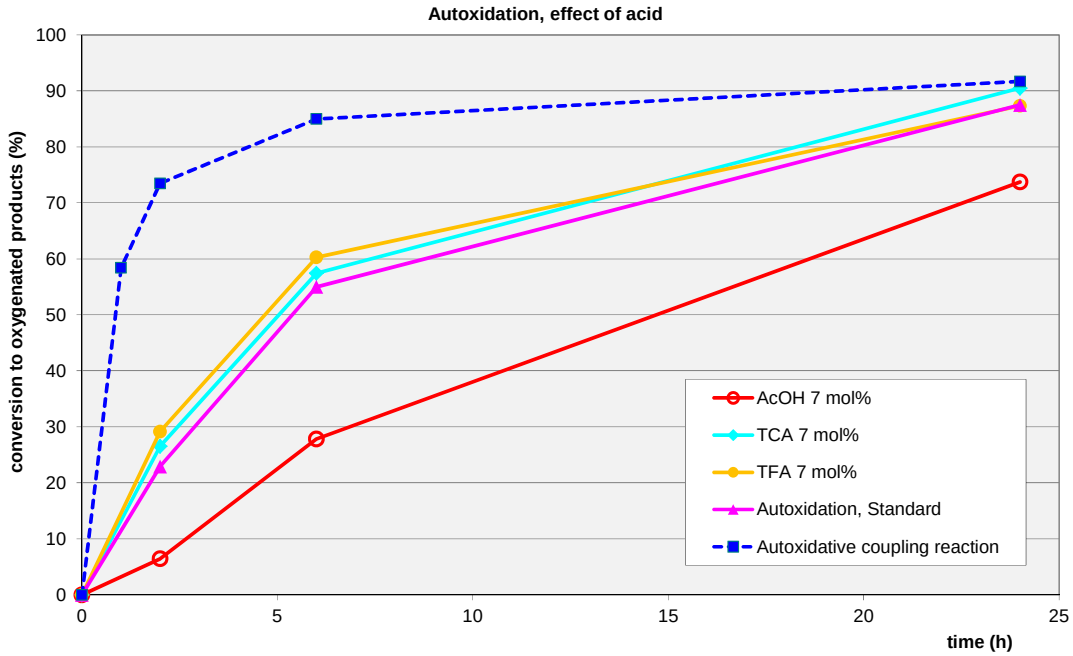


Figure S6: Reaction rates of the autoxidation of xanthene (**Scheme S2**) without (pink triangles) and with addition of 7 mol% of acids: AcOH (red hollow dots), TCA (turquoise diamonds), TFA (orange circles); standard coupling reaction (**Scheme S1**) shown for comparison (blue boxes, dashed line); average of 3 experiments.

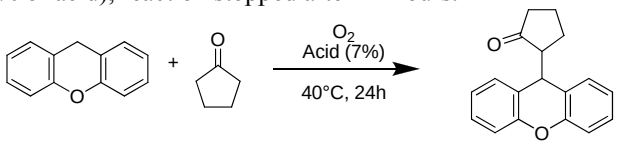
It can be seen from the curves in Figure S6 that although acetic acid slows the autoxidation process, TCA and TFA gave identical rates as the autoxidation without any acid catalyst. It is to be noted that for TCA and TFA, coupling product **2** started

to appear overtime, with xanthene hydroperoxide **3** still being the major product. After 24 hours, about 13-20% of **2** was detected by ^{1}H NMR analysis of the reaction mixture in the case of TCA and TFA.

2.12 Nature of acid in the autoxidative coupling reaction

It could be envisioned that peracids are formed in the presence of hydrogen peroxide under our reaction conditions and such peracids could act as the real oxidant in our reaction. We decided to vary the nature of the acid to test this, representative yields from repeated experiments are shown in Table S5.

Table S5: Effect of the nature of the acid in the autoxidative coupling reaction. Following general procedure (with 7 mol% of acid), reaction stopped after 24 hours.



entry	acid	NMR yield (%)
1	MsOH	88-92
2	HNO_3	84-98
3	H_2SO_4	60-79
4	HCl	21
5	TFA	13-29
6	TCA	13-21
7	AcOH	0

As long as the acid was strong enough, different types of acids could be used. Methane sulfonic acid and nitric acid behaved similarly (88% and 84% respectively), sulfuric acid was less effective (60%) and an ethereal solution of HCl showed a very reduced activity (21%) but still significant conversion. Weaker acid trifluoroacetic acid showed even lower activity (13%, entry 5) while acetic acid didn't give any coupling product (entry 6) but still allowed the autoxidation (see figure S4). Both carboxylic acids are well known to form peracids. From this we can conclude that the nature of the acid probably does not have a strong influence on the reaction and that the pKa value has to be chiefly considered to explain the different reactivities.

Kinetic measurements were also performed to investigate the role of acid strength on the rate of the autoxidative coupling (Figure S7). As HCl, TFA and TCA were shown to give very low yields of **2** and no accelerated autoxidation of xanthene, they were excluded from these further measurements.

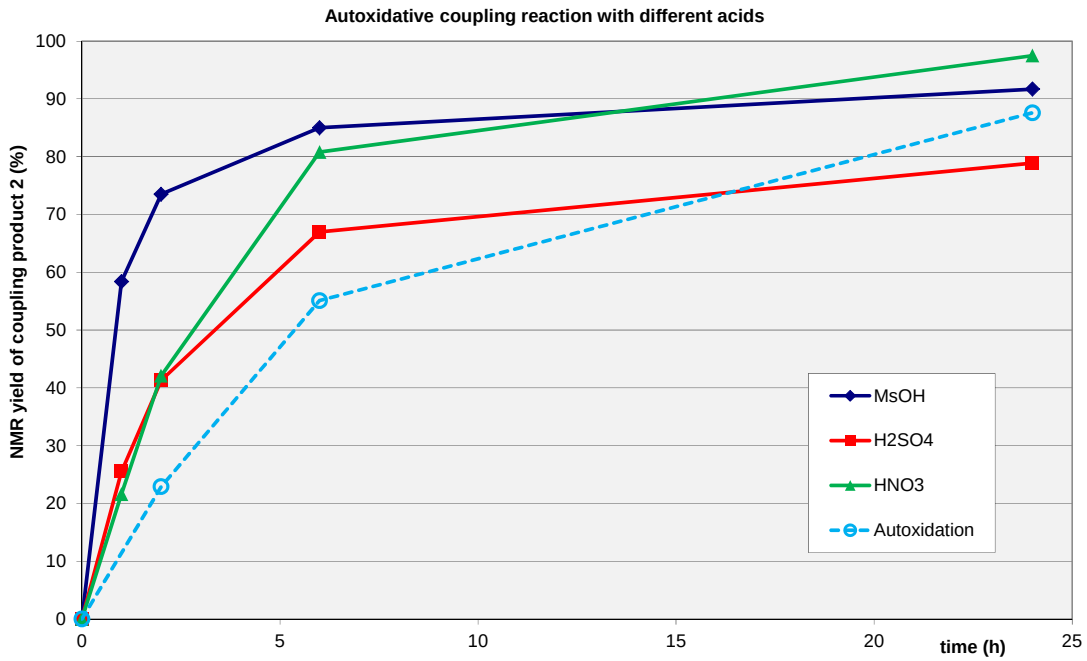


Figure S7: Autoxidative coupling of 1 to 2 using different acids at 7 mol%: MsOH (blue diamonds), H_2SO_4 (red squares), HNO_3 (green triangles); autoxidation (Scheme S2) shown for comparison (turquoise hollow circles).

Methane sulfonic acid (blue line), sulfuric acid (red line) and nitric acid (green line) all showed accelerated initial conversion over simple autoxidation in the absence of acid (dashed turquoise line). However, if an increase in acid strength is beneficial, such as from nitric acid to methane sulfonic acid (pKa = −1.3 and −2.6, respectively), there seem to be an optimal acid strength since going to stronger sulfuric acid (pKa = −3) is detrimental.

In order to detect a possible induction period in the autoxidative coupling reaction (Scheme S1) under standard conditions, kinetic measurements were performed with methane sulfonic acid in a larger scale (4 times compared to standard conditions) to allow for more data points (Figure S8).

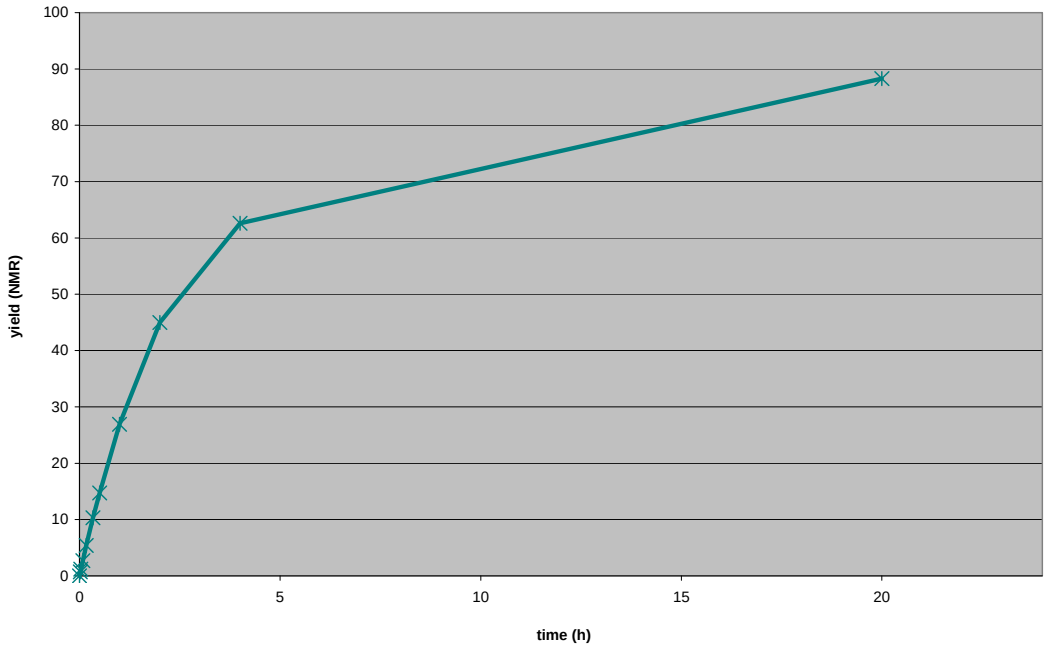
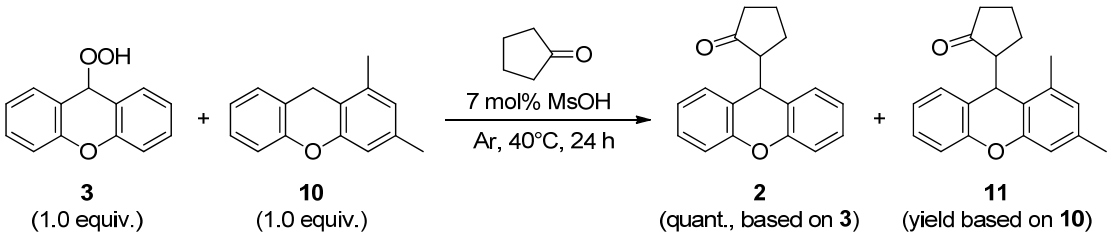


Figure S8: Attempt at detecting an induction period for the autoxidative coupling of 1 to 2 using MsOH as catalyst.

As can be seen, the reaction rate is slightly slower than previously found (see figure S6) but still larger than autoxidation of xanthene. This difference is attributed to the different exchange surface area in this large scale experiment compared to the standard conditions, as it is well known that such factors greatly influence biphasic systems. However, no induction period could be detected, contrary to the autoxidation of **1**.

2.13 In situ generated H_2O_2



Scheme S4: Cross-over experiments, oxidizing **10** by H_2O_2 formed in situ.

In a Schlenk tube, xanthene hydroperoxide **3** (53.5 mg; 0.25 mmol) and dimethyl xanthene **10** (52.5 mg; 0.25 mmol) were dissolved in cyclopentanone (0.22 mL; 2.5 mmol). The mixture was degassed (freeze, pump, thaw technique) 3 times then methane sulfonic acid (2.3 µL; 0.035 mmol) was added under a stream of argon and the reaction mixture stirred at 40°C (Scheme 4). The reaction was monitored by ^{1}H NMR (Figure S9).

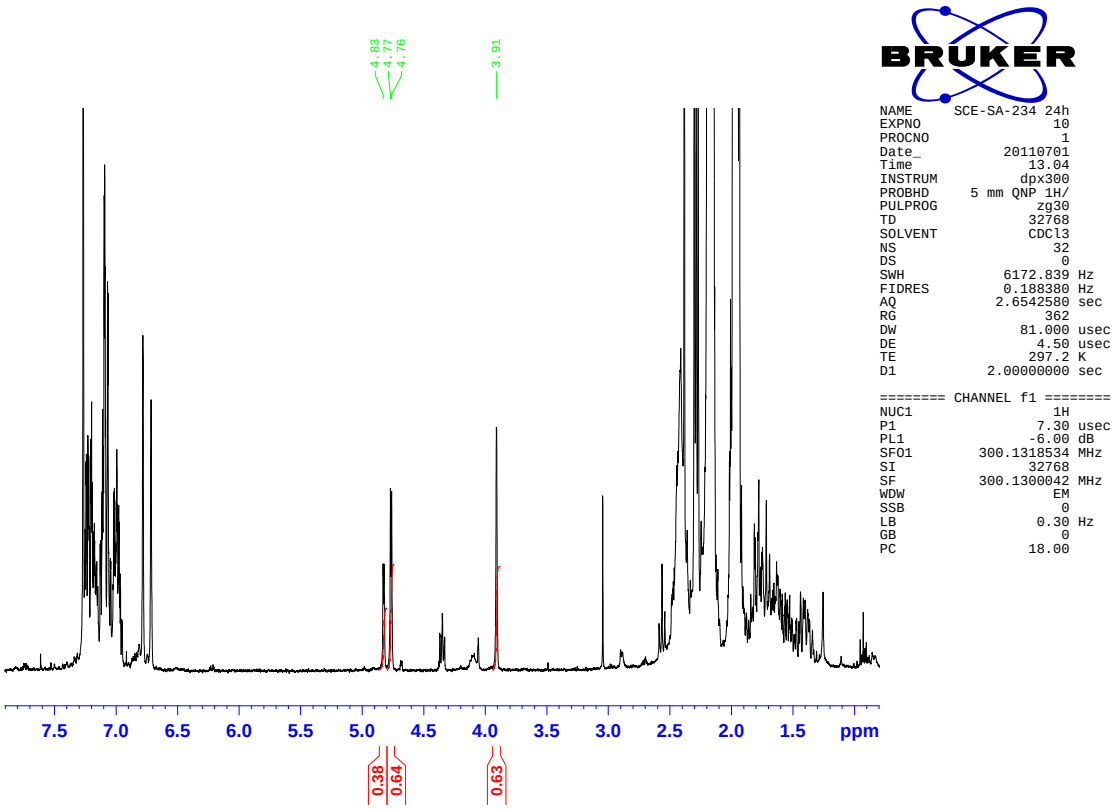


Figure S9: Crude NMR spectrum of reaction as shown in Scheme 4 after 24h.

After 24 hours, no hydroperoxide **3** is visible anymore (singlet at 6 ppm) and all of it was converted to coupling product **2** (doublet at 4.7 ppm). On the other hand, **10** is still present (singlet at 3.91 ppm) but was converted to **11** (doublet at 4.8 ppm). **10** and **11** are in a 1:1 ratio, showing a 50% yield of **11** based on **10.**

A representative conversion profile could be also obtained in a separate experiment, showing very fast conversion of **3** to **2** as seen above (dotted lines) and slower conversion of **10** to **11** in 4 to 6 hours (solid lines) (Figure S10)**.** It is also apparent that this reaction, while generally reproducible, shows varying yields of the coupling products formed by H_2O_2.

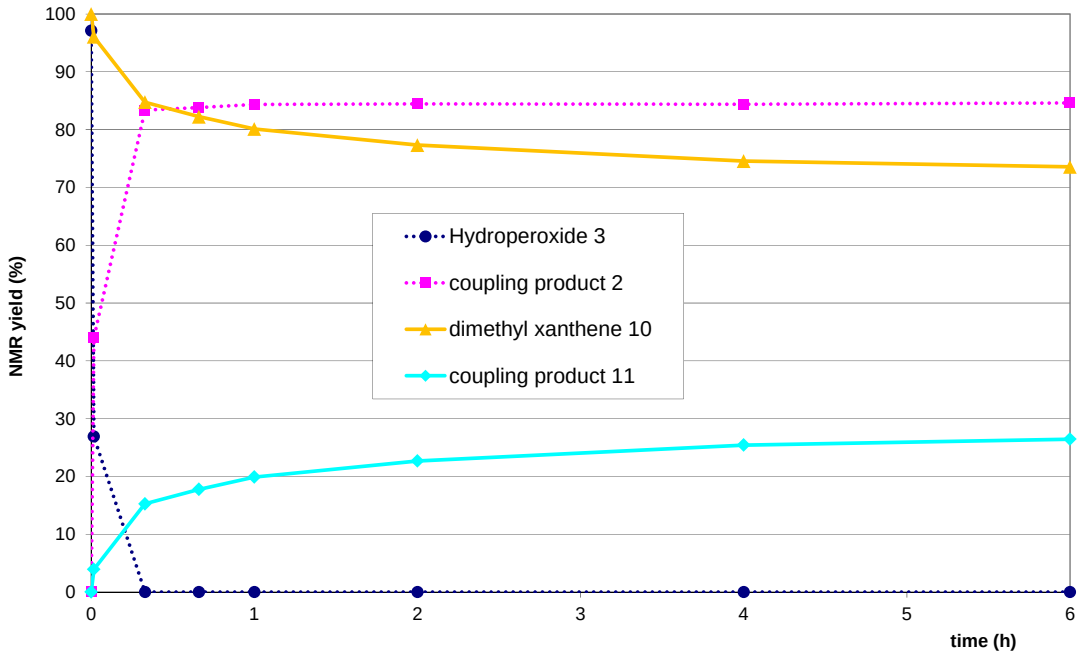
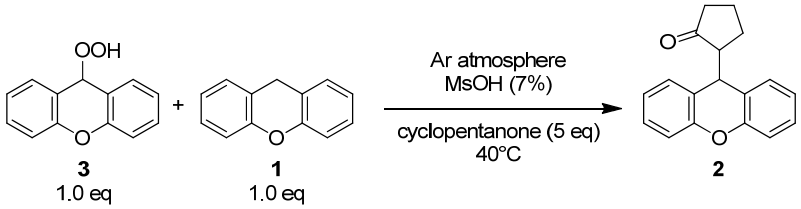


Figure S10: conversion profile for conversion of **10** to **11** using H_2O_2 generated *in situ* from **3**.

Similarly, experiments were conducted using a 1:1 mixture of xanthene hydroperoxide **3** and xanthene **1** (Scheme S5). Similar results were obtained compared with the reaction using dimethyl xanthene **10** shown in Figure S10. The general outcome of the reaction was reproducible but yields varied between 15% and 46% (based on conversion of xanthene **1**); after reaction times between 3 and 5 hours.



Scheme S5: Oxidative coupling of **1** by hydrogen peroxide generated *in situ* as byproduct in the reaction of **3** with cyclopentanone.

As can be seen from the crude NMR spectrum of a representative example (Figure S11), the reaction is as clean as when using autoxidative conditions. In the case shown, 73% of **2** is obtained (based on the initial amount of **1** + **3**). When corrected to take into account the equivalent of **3** being converted to the same product, a yield of 46% based on the conversion of **1** is obtained.

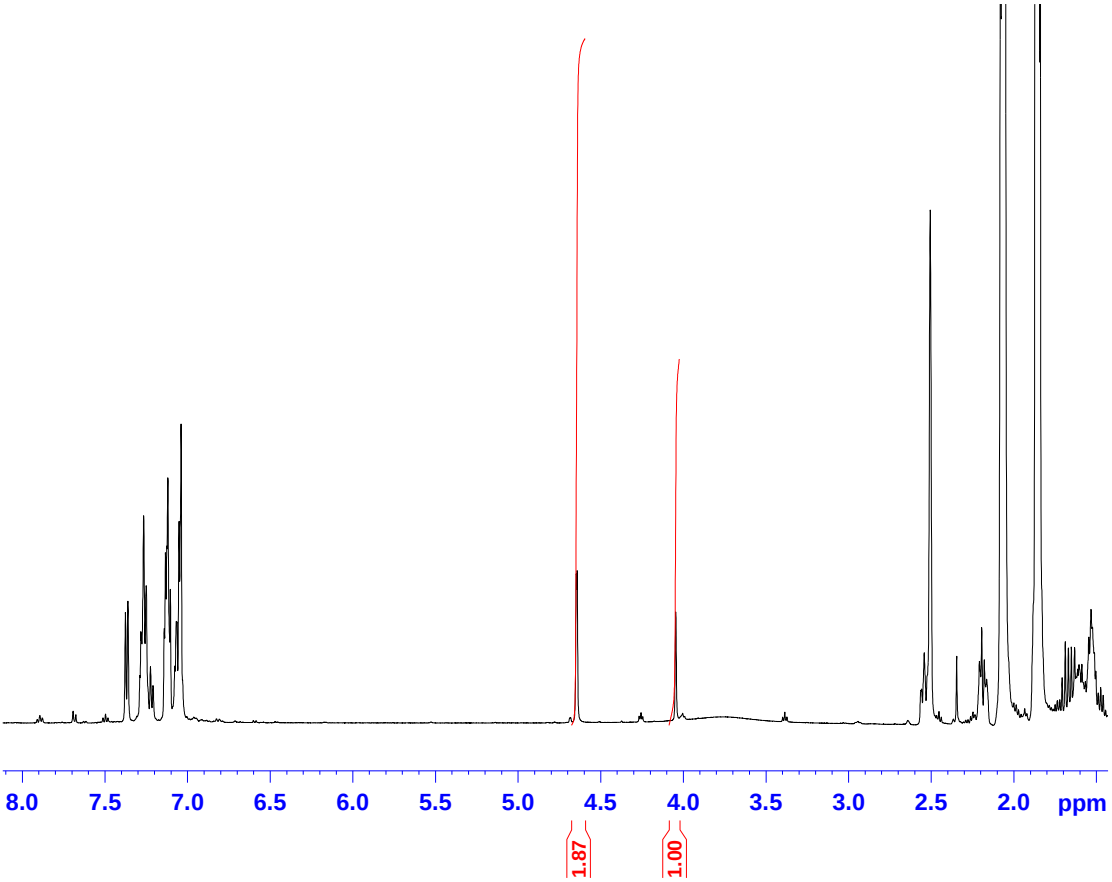


Figure S11: Crude NMR of a reaction mixture from Scheme S5 after 4 hours.

Following the progress of the reaction over time shows that this process is on a similar timescale as the crossover experiment shown in Figure S10 above. Indeed, the reaction is usually complete after 2 to 6 hours, as can be seen from representative examples (Figure S12), and no further conversion is observed after prolonged reaction times.

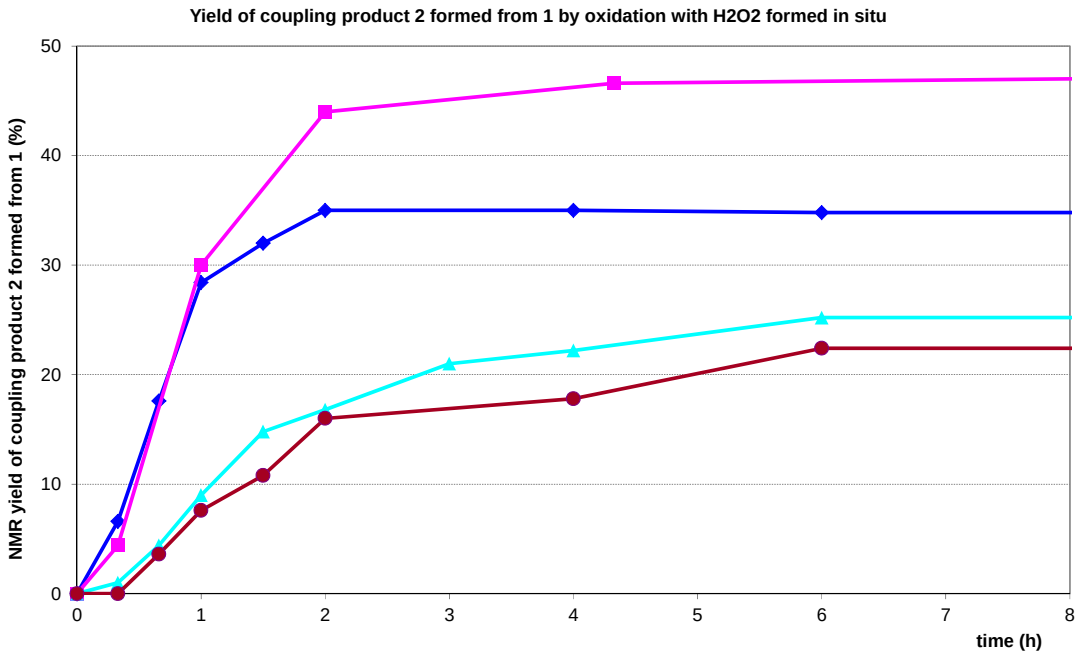
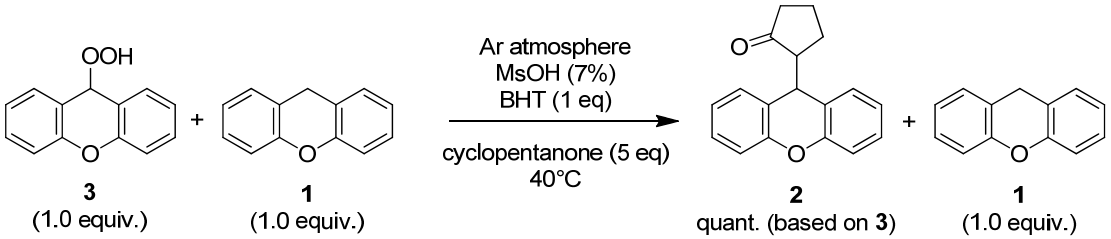


Figure S12: Representative examples of conversion of **1** to **2** using H_2O_2 generated from **3** under inert atmosphere.

The same reaction run in the presence of BHT gave a yield of 50% of **2** (quantitative if based on **3**) and even prolonged reaction times did not improve conversion and yield (Scheme S6). This shows that the conversion of hydroperoxide **3** to **2** can happen in the presence of a radical inhibitor, supporting the ionic character of this process. However, the oxidation of **1** with hydrogen peroxide does not occur when a radical inhibitor is present, suggesting a radical based mechanism for this process.



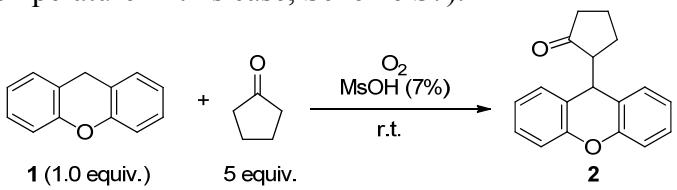
3 (1.0 equiv.) **1** (1.0 equiv.) **2** quant. (based on **3**) **1** (1.0 equiv.)

Scheme S6: Performing the experiment of Scheme S5 in the presence of the radical inhibitor BHT.

2.14 Analysis of hydrogen peroxide

H_2O_2 is used in large scale industrial processes e.g. for bleaching, disinfection or catalyst and explosives production. Furthermore, H_2O_2 determination is a relevant key for studying biological processes. Classified as a reactive oxygen species H_2O_2 indicates oxidative stress in biological tissue. From the analytical point of view, a variety of different techniques have been developed for H_2O_2 detection basing on principles[4] e.g. redox reactions, hydrolysis, photoinduced electron transfer or complexation, partially integrated in H_2O_2 sensors.[5]

In this project, the question whether an equimolar amount of H_2O_2 forms, is significant to propose a mechanism for the reaction under study shown in Scheme 1a (using ambient temperature in this case, Scheme S7).



Scheme S7: Conditions used for the analysis of hydrogen peroxide in the reaction mixture.

The reaction mixture (matrix) contains high amounts of methane sulfonic acid, which acts as a catalyst in the reaction. In addition, oxidative xanthene hydroperoxide species may be formed during the reaction which makes specific H_2O_2 detection troublesome using redox-based assays such as resorufin derivatives[6] or the oxidative condensation of 4-amino-antipyrin with phenol (Trindler´s reagent).[7]

In classical wet chemical analysis complexation methods to detect H_2O_2 are the method of choice, namely formation of orange-yellow colored TiO_2^{2+}[8] or of blue $CrO(O_2)_2$.[9] Preliminary experiments exhibited that both reactions show negligible cross sensitivities with purified xanthene hydroperoxide. Due to the slightly yellow colour of the dissolved xanthene, the chromium(VI)peroxide formation was chosen to minimize spectral interferences.

Protocol
At ambient temperature of 22.5°C 100 µL of reaction mixture was added to a test tube containing a two phase system of 1 mL $K_2Cr_2O_7$ (0.1 M), 1 mL H_2SO4 (2.5 M) and 5 mL peroxide free diethyl ether. The sample was gently mixed for 20 seconds and then 3 mL of the ether phase were transferred into a closable fused silica cuvette. UV/vis spectra between 200 and 800 nm were recorded using a double beam spectrometer (Varian Cary 5G UV vis NIR). Pure diethyl ether was used as the reference. The absorbance of the chromium(VI)peroxide complex in ether was measured in the blue spectral region at 580 nm.

A positive probe with two different initial H_2O_2 concentrations in cyclopentanone containing methane sulfonic acid is displayed in Figure S13 (generated from 35% aqueous H_2O_2 (467 µmol and 46,7 µmol, respectively, corresponding to 1.0 and 0.1 equivalents relative to the initial xanthene concentration as used in the general procedure of the autoxidative coupling reaction) cyclopentanone (0.21 ml) and MsOH (2.1 µl)). The absorbance of the concentrated hydrogen peroxide solution was

determined to be 1.92, whereas the 1:10 dilution showed an absorbance of 0.20. A calibration plot (data not shown) exhibited a linear correlation between the H_2O_2 concentration and the absorbance in the range of 467 to 6 µmol, corresponding to 1.0 and ca. 0.015 equivalents, respectively, of H_2O_2 relative to xanthene in the autoxidative coupling reaction.

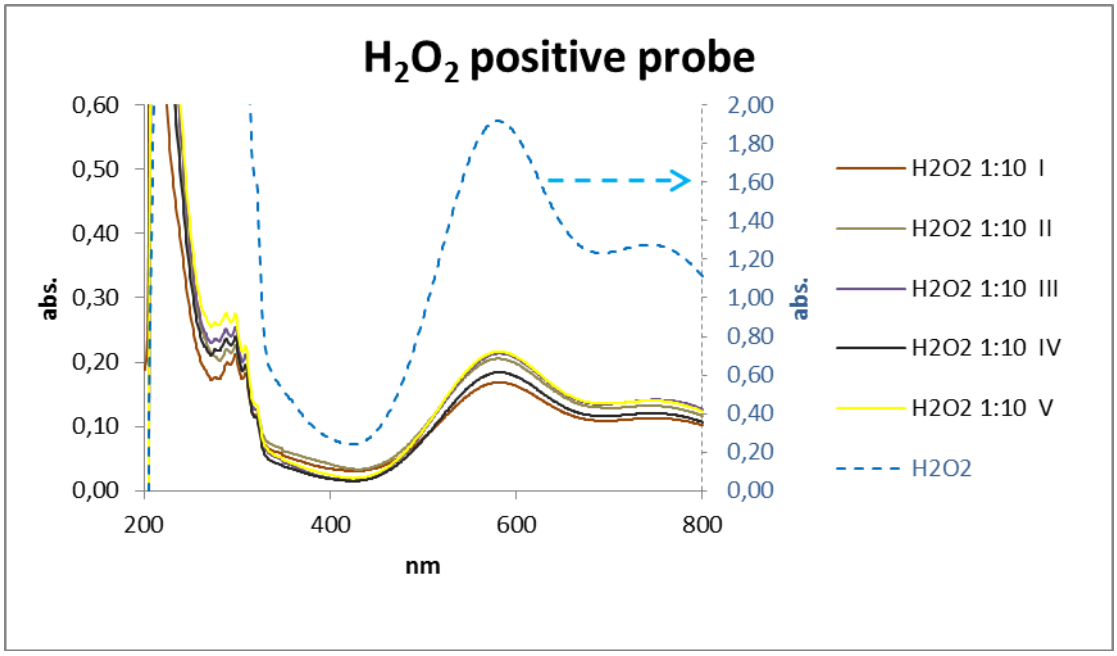


Figure S13: Positive test of H_2O_2 samples forming the blue $CrO(O_2)_2$ complex in ether. "H_2O_2" displays a positive probe prepared with 467 µmol H_2O_2. This corresponds to the initial concentration of xanthene in the reaction matrix under the general conditions of the autoxidative coupling reaction. "1:10" are repetitive measurements containing an initial concentration of 46.7 µmol H_2O_2.

In Figure S14 the same protocol with purified xanthene hydroperoxide instead of hydrogen peroxide was conducted. The undiluted xanthene hydroperoxide solution results in small amounts of $CrO(O_2)_2$ indicating a small concentration of hydrogen peroxide (absorbance 0.21) present. We assume an equilibrium hydrolysis of xanthene hydroperoxide into xanthenol and H_2O_2 during sample preparation in the presence of H_2SO_4. However, the 1:10 diluted solution of the xanthene hydroperoxide only generates minute amounts of $CrO(O_2)_2$ (absorbance 0.05). In summary, the absorbance of the xanthene hydroperoxide sample is roughly a magnitude lower compared to that of hydrogen peroxide. We conclude that the cross sensitivity of the method is marginal enough to clarify the question whether equimolar amounts of H_2O_2 are formed during the oxidative coupling reaction of xanthene and cyclopentanone in the presence of xanthene hydroperoxide or not.

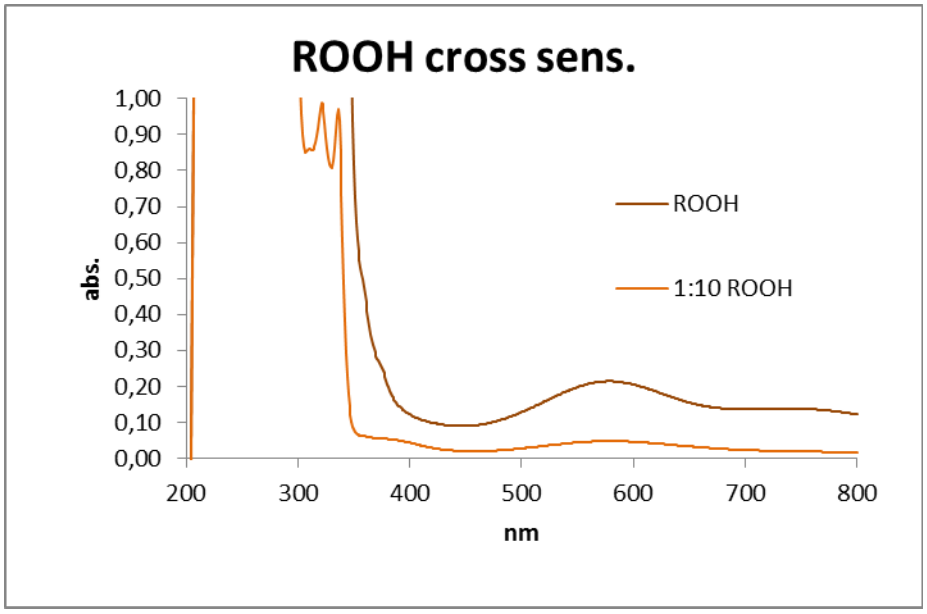
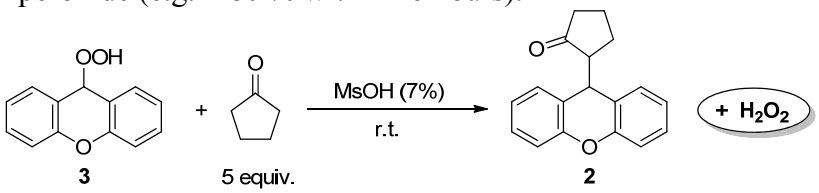


Figure S14: UV/Vis spectra of xanthene hydroperoxide in ether, prepared with 467 µmol xanthene hydroperoxide in 0.21 ml cyclopentanone, forming small amounts $CrO(O_2)_2$ out of equilibrium H_2O_2 (abs. ~ 0.2). The 1:10 dilution generates only insignificant amounts of H_2O_2 (abs. < 0.05).

Liberation of H_2O_2 from xanthenyl hydroperoxide in the presence of acid

The reaction as shown in Scheme S8 was analyzed for the amount of H_2O_2 formed by adding 7 mol% of MsOH to a solution of xanthenyl hydroperoxide **3** in cyclopentanone at ambient temperature and stirring for 2 minutes. Afterwards, a sample was analysed as described in the protocol above with the exception, that the ether/aqueous two phase system was stirred for exactly 60 seconds at 500 r.p.m.using a stirring bar. About one third equivalent of hydrogen peroxide relative to the xanthenyl hydroperoxide was clearly detected (after subtraction of the blank value, i.e. xanthenyl hydroperoxide in the absence of MsOH). Samples of xanthenyl hydroperoxide with MsOH taken after longer reaction times exhibited a slow decline of hydrogen peroxide (e.g. ~ 80 % within 16 hours).



Scheme S8: Analysis of hydrogen peroxide liberated by acid-catalyzed reaction of xanthenyl hydroperoxide **3** in cyclopentanone.

Analysis of H_2O_2 in the autoxidative coupling reaction (Scheme S7)

It is well known that the reaction rate of gaseous/liquid-phase reactions (as in Scheme S7) depend on classical parameters (reaction temperature, reaction time etc.) as well as on additional parameters e.g. surface area or stirring intensity. In another set of experiments, a kinetic monitoring regarding a possible H_2O_2 formation was performed over a time period of 50 minutes after initiating the standard reaction as shown in Scheme S7 (Figure S15). No hydrogen peroxide formation could be observed at room temperature.

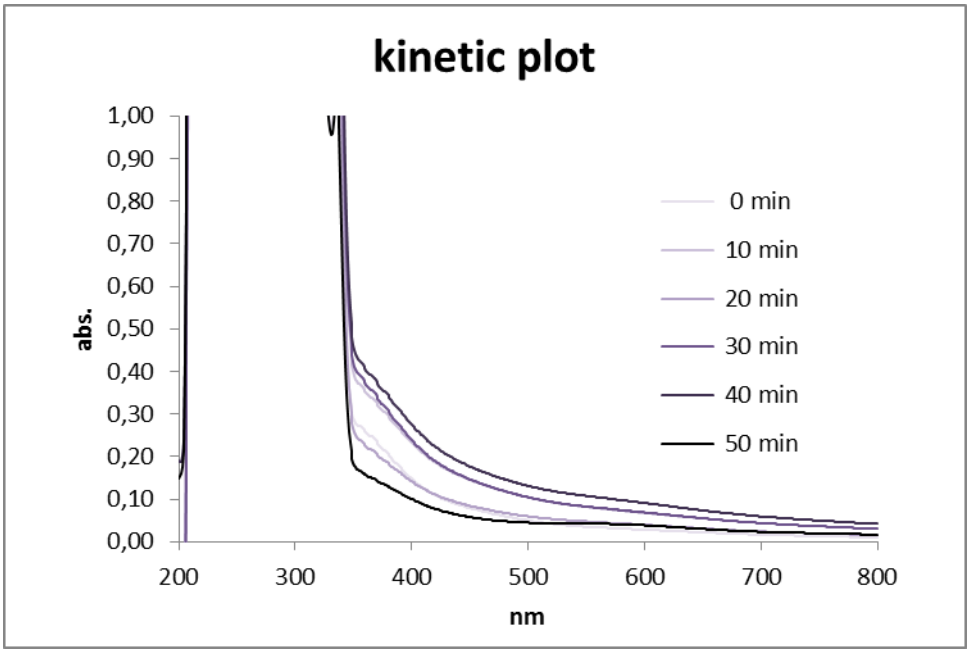


Figure S15: Kinetic plot of the reaction mixture falsifies equimolar H_2O_2 generation within 50 min. In case of a positive result the absorbance at 580 nm would be about 2.0.

A second analytical experiment was conducted in order to analyze H_2O_2 over the entire course of the reaction while verifying that the reaction was actually progressing. To this end, an elongated kinetic study was performed under oxygen atmosphere utilizing NMR spectroscopy to monitor the reaction progress and UV/vis spectroscopy to monitor H_2O_2. Samples from the reaction mixture were drawn between 0 and 96 hours. The formation of H_2O_2 in significant concentrations can clearly be excluded from the corresponding UV/vis spectra (Figure S16 and Figure S17), while the NMR data shows a steady increase in the concentration of the coupling product (data not shown, analogous to Scheme 3).

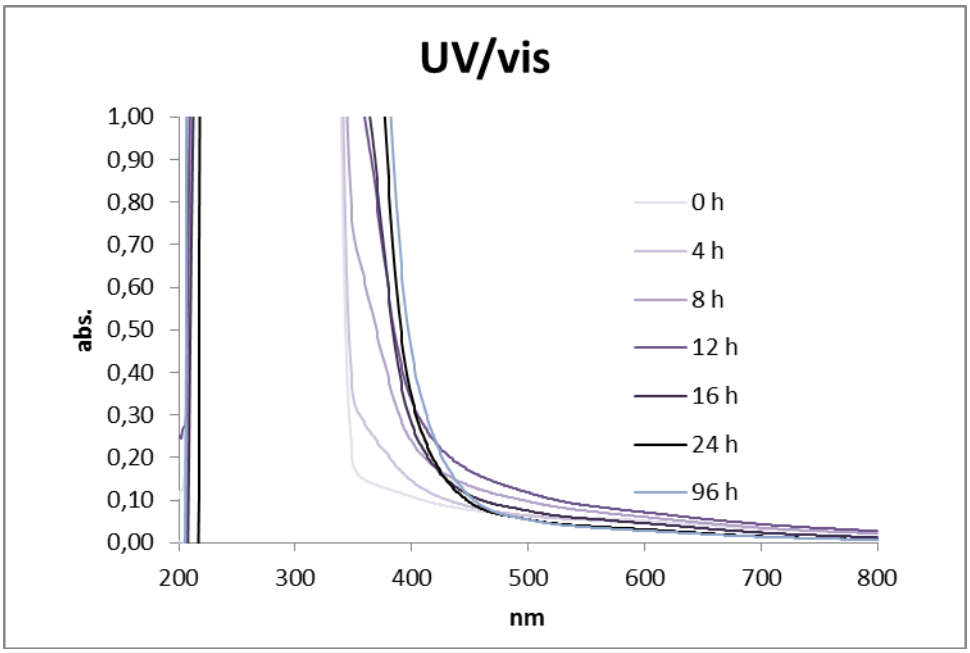


Figure S16: Long time kinetic plot conducted with extensive stirring under oxygen atmosphere. UV/vis measurements rule out the formation of equimolar hydrogen peroxide concentrations.

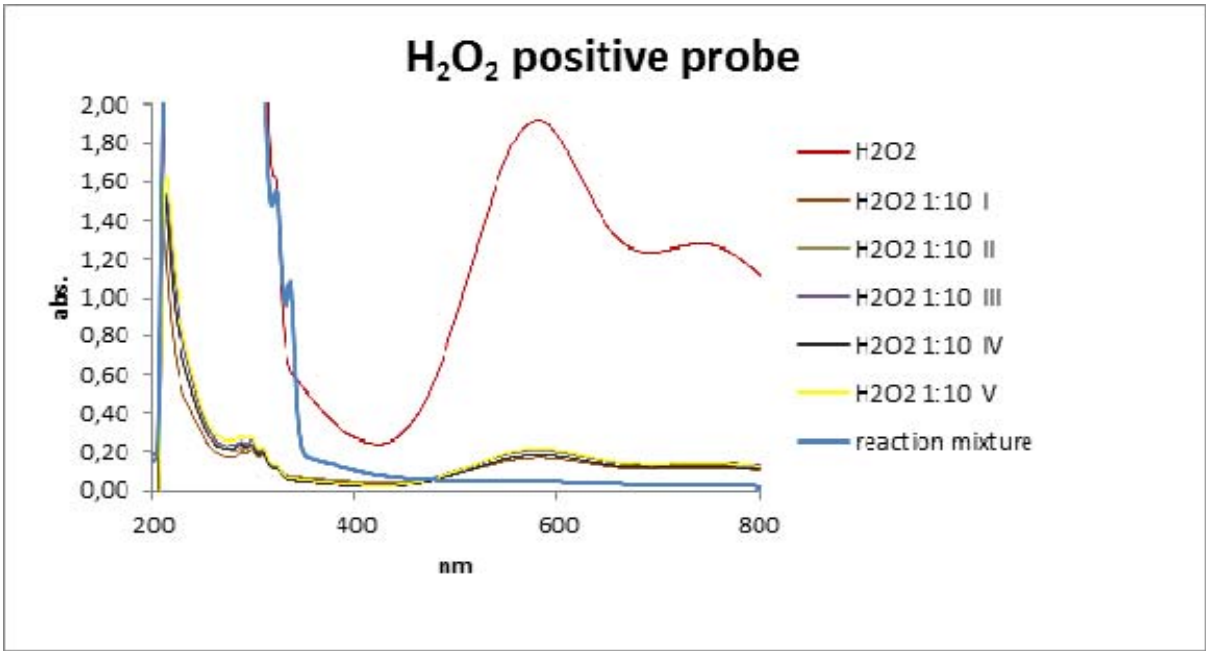


Figure S17: Comparison of the UV/vis measurement of the reaction mixture (taken after 50 min. reaction time) with reference samples prepared with 467 µmol as described above ("H_2O_2", red curve) and 46.7 µmol H_2O_2, (("H_2O_2 1-10"), respectively, corresponding to 1.0 and 0.1 equivalents of H_2O_2, respectively, being formed relative to the amount of xanthene in the reaction.

In summary, the answer to the initial question concerning equimolar H_2O_2 formation during the reaction of Scheme 1a is negative. H_2O_2 is not formed as a by-product of the reaction in significant concentrations of more than 1.5 mol% relative to the initial amount of xanthene. In contrast, H_2O_2 is formed in the reaction of xanthenyl hydroperoxide **3** with acid (Scheme 2b).

2.15 Intermediacy of *tert*-butyl peroxide 12 (Scheme 5)

In a 4 mL screw cap vial, xanthene **1** (91 mg, 0.5 mmol. 1 eq) was dissolved in cyclopentanone (0.22 ml, 2.5 mmol, 5 eq) then TBHP (182 µL, 1 mmol) and methane sulfonic acid were added (2.3 µL, 7 mol%). The vial was flushed with Argon and connected to an argon balloon. The mixture was let to react at 40°C and monitored by ^{1}H NMR (Figure S18).

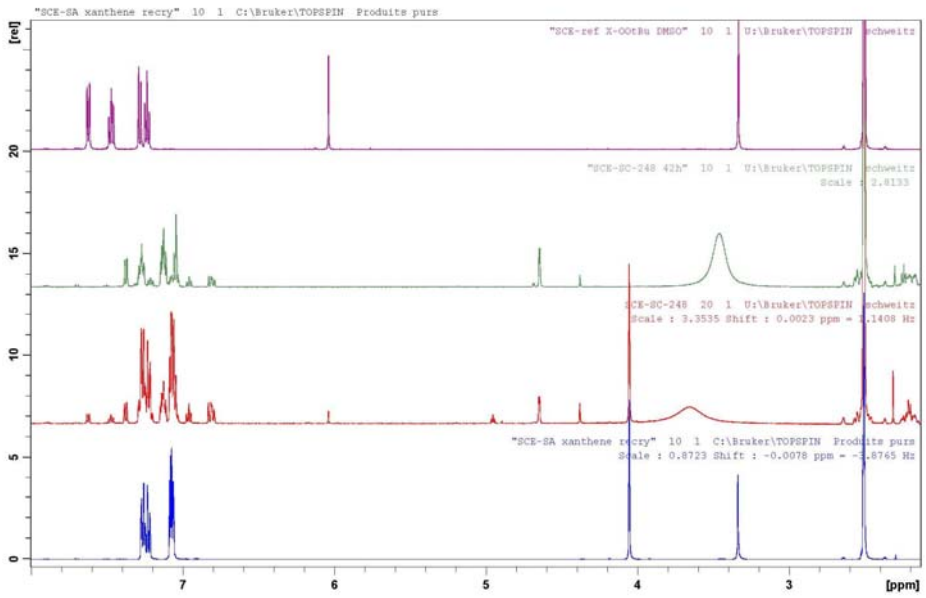
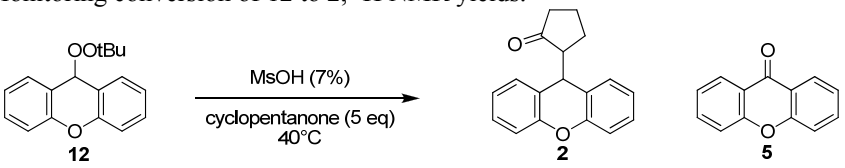


Figure S18: NMR monitoring of the reaction from Scheme 5: from bottom to top: blue: reference spectrum of xanthene; red: reaction mixture after 2 hours; green: reaction mixture after 42 hours; purple: reference spectrum of 12.

As can be seen from the NMR, after 2 hours, xanthene **1** is partially converted to the coupling product and the intermediate **12** is clearly visible (singlet at 6.03ppm). After prolonged reaction time, all xanthene (singlet at 4 ppm) and **12** have disappeared, and only the coupling product **2** is visible (doublet at 4.6 ppm) along with small amounts of xanthene dimer **13** and xanthone **5** (see also below, Table S7, entry 3).

Direct conversion of **12** was also tested (Table S6). After 2 h, only traces of peroxide **12** remain in the mixture and conversion to **2** was 92% (NMR yield). Xanthone **5** is the only other by-product, formed in 7% yield.

Table S6: Monitoring conversion of 12 to 2, ^{1}H NMR yields.



time	12 (%)	5 (%)	2 (%)
1 min	96%	4%	0
1h	11%	5%	84%
2h	1%	7%	92%

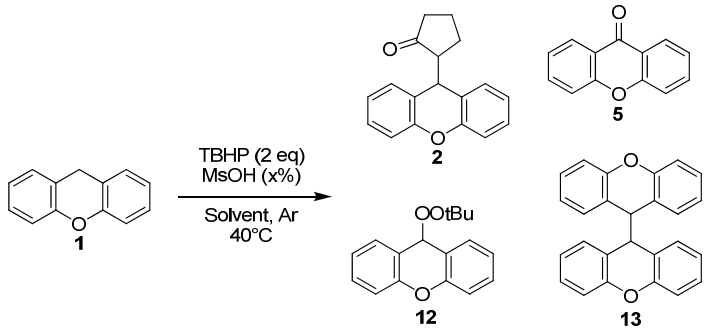
In a 4mL screw cap vial, **12** (135 mg; 0.5 mmol) was dissolved in cyclopentanone (0.22 mL; 2.5 mmol) and methane sulfonic acid (2.3µL; 0.035 mmol) was added and the mixture allowed to react at 40°C. Reaction was monitored by ^{1}H NMR as previously described.

2.16 Anaerobic reactions of xanthene without added nucleophile

In a screw cap vial, xanthene (45.5 mg; 0.25 mmol) was dissolved in solvent (0.25 mL) and TBHP (5,5 M solution in decane; 91µL, 0.5 mmol) and methanesulfonic acid (1.77 µL; 0.025 mmol) were added. The vial was then flushed with argon and connected to an argon balloon and the mixture then stirred at 40°C for the indicated times. Triethylamine (17.4 µL; 0.125 mmol) was added to the mixture to quench the acid and degrade remaining tBuOOH. Solvent was evaporated under reduced pressure and the crude residue analysed by NMR to give a yield of product (Table S7).

Other solvents were also tested (dichloromethane, ethyl acetate, nitromethane, toluene and methyl tert-butyl ester). In all cases, conversion of xanthene was observed by TLC and ^{1}H NMR, but identification of the products was not possible.

Table S7: Solvent effects on the anaerobic conversion of xanthene in the presence of TBHP and MsOH.



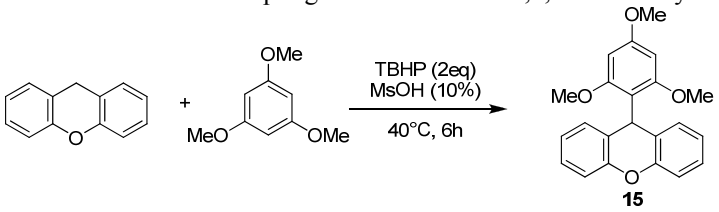
entry	solvent	time	MsOH (%)	1	2	5	12	13
1	DCM	5 d	7	~99	0	trace	trace	trace
2	cyclopentanone	42 h	0	84	0	trace	7	9
3	cyclopentanone	42 h	7	0	91	2	0	7
4[a]	cyclopentanone	24 h then overnight	7	0	88	2	0	8
5[b]	cyclopentanone	overnight	7	5	81 (75)	2	0	14 (3)

a) TBHP was added in 2 portions of 0.5mmol; b) performed on a 1mmol scale; isolated yields in parentheses.

2.17 Solvent effects in anaerobic reactions of xanthene with 14

In a screw cap vial, xanthene (45.5 mg; 0.25 mmol) was dissolved in solvent (0.25 mL) and 1,3,5 trimethoxybenzene (**14**, 42 mg, 0.25 mmol), TBHP (5,5 M solution in decane; 91µL, 0.5 mmol) and methanesulfonic acid (1.77 µL; 0.025 mmol) were added. Under an air atmosphere, the vial was closed and the mixture then stirred at 40°C for 6 hours. Triethylamine (17.4 µL; 0.125 mmol) was added to the mixture to quench the acid and degrade remaining TBHP. Solvent was evaporated under reduced pressure and the crude residue analysed by NMR to give a yield of product (Table S8).

Table S8: Solvent effects in anaerobic coupling of xanthene with 1,3,5 trimethoxybenzene (**14**).



entry	Solvent	1	13	5	15 (%)
1	acetone	7	<1	1	92
2	cyclopentanone	52	<1	0	48
3	AcOEt	79	1	3	17
4	MeNO2	83	1	1	15
5	toluene	90	1	1	8
6	MTBE	93	1	1	5
7	MeOH	78	1	<1	21
8	CHCl3	80	1	<1	18
9	d6 DMSO	90	0	3	7
10	MeCN	73	<1	<1	27
11	MeCN[a]	77	<1	<1	23

a) reaction mixture was degassed before MsOH was added.

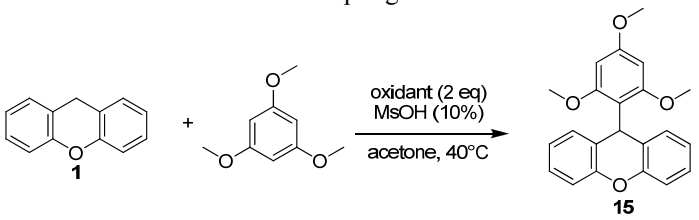
As can be seen, of all solvent tested, acetone (entry 1) is the only one to give full conversion of the coupling product in 6 hours. Cyclopentanone (entry 2) is less efficient but still gives high conversion (48%) and yields (47%) compared to all other solvents. All other solvents (entries 3-10) are inferior but do give conversion, probably due to acid promoted degradation of tBuOOH under slightly elevated temperature. Degassing the mixture does not have any beneficial influence on the reaction (entry 10 vs entry 11).

2.18 Effect of oxidants in the oxidative coupling of xanthene with 14

As previously reported, molecular oxygen is not sufficient to promote oxidative coupling of xanthene to **15** (Table S9, entry 1), elevated temperatures and partial pressure of oxygen are required for this reaction.[10] On the other hand, after one night of reaction, xanthene is converted in almost quantitative yield to **15** when 2 equivalents of TBHP are used as oxidant in acetone as solvent (entry 2, 96%). T-HYDRO, an aqueous solution of tBuOOH, is also competent in this reaction, albeit in lower yields and conversions (entry 3, 68%). Cumene hydroperoxide (CHP) is still a competent oxidant and gives **15** in 20% yield (entry 4). To further investigate if the

hydroperoxide character of the oxidant is crucial, di-*tert*-butyl peroxide (DTBP) was used, giving only traces of product under our reaction conditions (entry 5).

Table S9: Influence of oxidant in the oxidative coupling of xanthene with **14**.



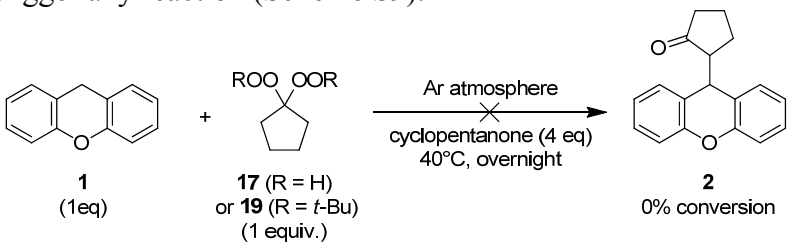
entry	Time	oxidant	Conversion	yield
1	48h	O_2	0%	0%
2	18h	TBHP	Full	96%[a]
3	48h	T-HYDRO	74%[a]	68%[a]
4	18h	CHP	21%[b]	20%[b]
5	18h	DTBP	0%	trace[b]

TBHP: 5.5M solution of tBuOOH in decane; T-HYDRO: 70% aqueous tBuOOH; CHP: 80% solution of cumene hydroperoxide; DTBP: di-*tert*-butyl peroxide; a) determined by isolation b) determined by analysis of crude ^{1}H NMR spectrum.

In a screw cap vial, xanthene (91 mg; 0.5 mmol) was dissolved in acetone (0.5 mL) and 1,3,5 trimethoxybenzene (84 mg, 0.5 mmol), oxidant (1 mmol) and methanesulfonic acid (3.55 µL; 0.05 mmol) were added. Under an air atmosphere, the vial was closed and the mixture then stirred at 40°C for the night. Triethylamine (35 µL; 0.25 mmol) was added to the mixture to quench the acid and degrade remaining peroxide. Solvent was evaporated under reduced pressure and the crude residue subjected to column chromatography (hexanes/DCM 6/4) to afford coupling product **15** or directly analyzed by ^{1}H NMR.

2.19 Oxidative coupling reactions with preformed perketals or derivatives

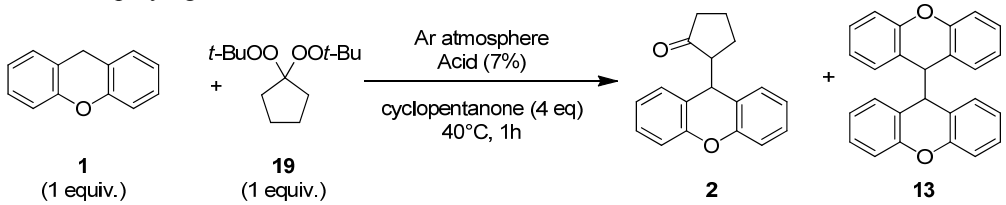
Peroxy derivatives **17** and **19** were synthesized from cyclopentanone (vide infra) and evaluated as oxidants/initiators. In the absence of acid and under an atmosphere of argon (freeze-pump-thaw-degassed solution), both compounds were stable at 40°C and did not trigger any reaction (Scheme S9).



Scheme S9: Employing peroxy ketals as oxidants in the absence of acid.

The behaviour of **19** was very different in the presence of acids (
Table S10).

Table S10: Employing **19** as initiator for the anaerobic conversion of xanthene.



entry	acid	2 (%)	13 (%)
1	H2SO4	18	38
2	MsOH	25	35
3	HNO3	0	0
4	TFA	0	0

NMR yields given.

Sulfuric and methane sulfonic acid promoted decomposition of **19** and formation of coupling product **2** together with large amounts of dimer **13** (entries 1 and 2). Apparently, there is a pKa value threshold for this phenomenon to take place, since the weaker acids nitric acid and TFA (entries 3 and 4) were completely ineffective and **19** was stable for 24 hours with no conversion observed.

In the case of methane sulfonic acid, a conversion profile was taken, which showed that all of **19** was decomposed after one hour, while coupling product **2** and dimer **13** were formed during this time (Figure S19). The reaction profile using sulfuric acid was similar, but faster, so that all of **19** was decomposed in less than 30 minutes.

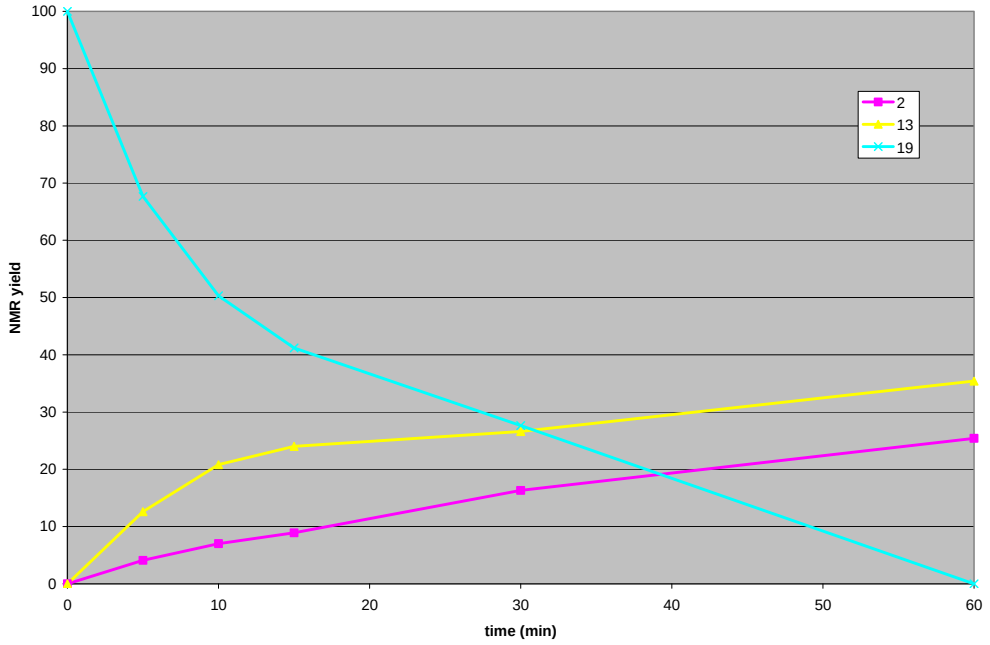
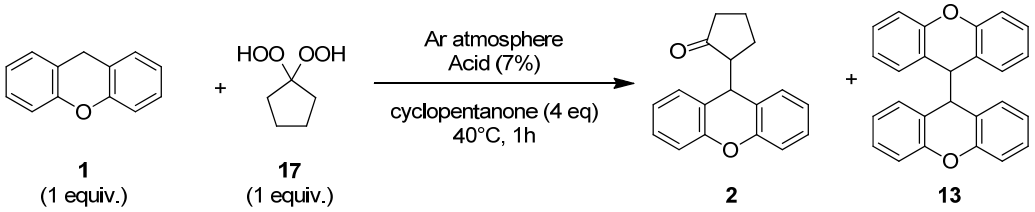


Figure S19: Conversion profile of the reaction of Table **S10** catalyzed by MsOH: **19** (turquoise), coupling product **2** (magenta) and xanthene dimer **13** (yellow).

The high yields of dimer **13** point to a purely radical mechanism for the activation of xanthene by this process. Similarly, the anaerobic coupling reaction could be triggered when using compound **17** in the presence of a strong acid (Table S11). Products **2** and **13** were formed in low but clearly detectable yields using methane

sulfonic acid (entry 1), while being completely ineffective with the weaker acid TFA (entry 3). Contrary to compound **19**, gem-bishydroperoxide **17** could be activated by nitric acid (entry 2).

Table S11: 17 as initiator for conversion of xanthene.



1 (1 equiv.) + **17** (1 equiv.) → **2** + **13**

entry	acid	2	13
1	MsOH	4	5
2	HNO3	2	1
3	TFA	0	0

NMR yields given.

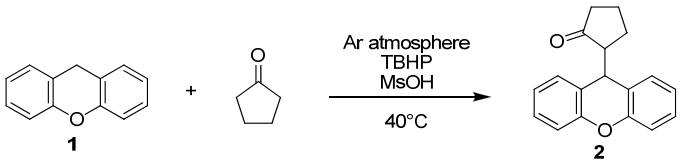
These experiments show that compounds **17** and **19** are stable to purely thermal decomposition under standard reaction conditions in the absence of acid but that they generate radicals in the presence of Brønsted acids of a certain strength. These or related compounds are most likely formed under standard reaction conditions by combination of hydro(gen)peroxide and ketone under acid catalysis, as the synthesis of these compounds is reported under similar conditions (see chapter 3.8 and 3.9 below).[11] Thus, the acid is not only needed to generate such peroxy-derivatives but also to promote their decomposition to radicals.

2.20 Concluding remarks: the choice of acid catalyst

The yields using compound **17** (Table S11) are very low, indicating it might not be the actual active species in our system. However, the difference in behaviour between **17** and **19** (Chapter 2.19) together with the other experiments comparing different acids as described above nicely illustrate the role of acid strength. In the case of methane sulfonic acid and sulfuric acid, the conversion of hydroperoxide **3** to coupling product **2** (see Figure S3) as well as the radical formation by decomposition of compounds like **17** and **19** is favored, leading to an efficient rate and yield of the autoxidative coupling reaction. Sulfuric acid, while being more acidic than MsOH, is obviously less efficient, which could be due to additional side reactions or decomposition of product. In the case of nitric acid, being close to the threshold in pK_a value for an efficient conversion of xanthene hydroperoxide **3** to coupling product **2**, and also to the threshold in pK_a for the radical generation from compounds like **17** and **19**, the acceleration of reaction compared to the autoxidation is more modest, but good yields are eventually achieved (see Figure S3 and Figure S7). By contrast, weaker acids such as TFA or TCA, are very inefficient to convert **3** to **2** (see Figure S3), only liberating H_2O_2 in low amounts. Additionally, they are too weak to enter the second activation pathway via compounds like **17** and **19**. Therefore, the rate of conversion of xanthene using TFA and TCA follows the one observed in the absence of any acid (Figure S6).

3 Synthesis of products

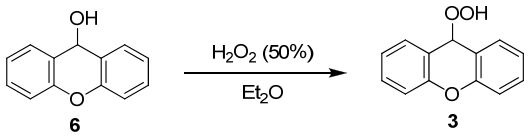
3.1 2-(9H-Xanthen-9-yl)cyclopentanone (2)



In a 4 mL screw cap vial, xanthene (91 mg, 0.5 mmol. 1 eq) was dissolved in cyclopentanone (0.22 ml, 2.5 mmol, 5 eq) then TBHP (182 µL, 1 mmol, solution in decane) and methane sulfonic acid was added (2.3 µL, 7 mol%). The vial was flushed with Argon and connected to an argon balloon. The mixture was let to react at 40°C for 24h then the whole reaction mixture was subjected to column chromatography (toluene) to afford coupling product **2** (122 mg, 93% yield) as a slightly yellow solid.

^{1}H NMR: (d6-DMSO; 500 MHz): 7.39-7.34 (m, 1H); 7.30-7.23 (m, 2H); 7.15-7.08 (m, 3H); 7.08-7.01 (m, 2H); 4.64 (d, 1H, *J*=3 Hz); 2.58-2.50 (m, 1H; overlaps with d6-DMSO residual peak); 2.23-2.13 (m, 1H); 1.73-1.46 (m, 4H); 1.29-1.17 (m, 1H)
^{13}C NMR: (d6-DMSO; 125 MHz): 217.72 (C); 152.42 (Ar q); 151.72 (Ar q); 128.90 (Ar CH); 128.63 (Ar CH); 128.36 (Ar CH); 127.90 (Ar CH); 124.12 (Ar q); 123.79 (Ar CH); 123.47 (Ar CH); 121.75 (Ar q); 116.04 (Ar CH); 115.89 (Ar CH); 58.75 (CH); 38.52 (CH_2); 37.07 (CH); 23.72 (CH_2); 19.55 (CH_2)
MS (EI): 264 (1.6); 181 (100)
HRMS (ESI): Calculated for $[C_{18}H_{16}O_2Na]^+$ ($M+Na^+$): 287.104249; found: 287.104020

3.2 Xanthene hydroperoxide (3)

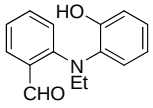


Synthesized as a reference compound.

Xanthydrol (3 g, 15.15 mmol) was dissolved in Et_2O (50 mL) then aqueous hydrogen peroxide was added (25 mL). The mixture was allowed to stir overnight at room temperature. Phases were separated and the ethereal phase washed with distilled water (3x 25 mL). Solvent was removed under reduced pressure to afford **3** as a white solid (3.099 g, 14.48 mmol; 95% yield)

^{1}H NMR: (d6-DMSO; 500 MHz): 11.41 (s; 1H); 7.62 (dd; 2H; *J*=7.6, 1.2 Hz); 7.45 (td; 2H; *J*=7.7, 1.5 Hz); 7.28-7.20 (m; 4H); 5.97 (s, 1H)
^{13}C NMR: (d6-DMSO; 125 MHz): 151.94 (Ar q); 131.19 (AR CH); 130.07 (Ar CH); 123.12 (Ar CH); 119.17 (Ar q); 116.10 (Ar CH); 75.00 (CH)
MS (EI): 214 (2.6); 181 (100)
HRMS (ESI): Calculated for $[C_{13}H_{10}O_3Na]^+$ ($M+Na^+$): 237.052218; found: 237.052294

3.3 2-(Ethyl(2-hydroxyphenyl)amino)benzaldehyde (8)

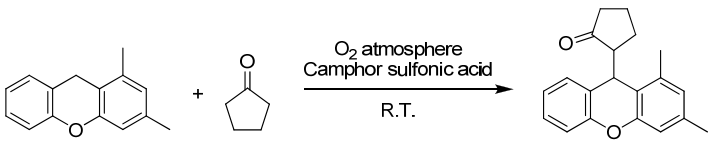


8

Isolated from reaction mixtures using *N*-ethyl acridane as described above.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.96 (s, 1H); 7.72 (dd, J_1 = 7.6 Hz, J_2 = 1.7 Hz, 1H); 7.48 (m, 1H); 7.13 (m, 3H); 6.98 (m, 2H), 6.84 (dd, J_1 = 7.6 Hz, J_2 = 1.5 Hz, 1H); 6.6 (br s, ca. 1H); 3.55 (q, J = 7.1 Hz, 2H); 1.21 (t, J = 7.1 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$): δ 191.1 (t), 152.7 (q), 150.7 (q), 136.2 (q), 134.7 (t), 133.6 (t), 129.0 (q), 127.4 (t), 127.4 (t), 126.8 (t), 122.6 (t), 122.0 (t), 120.7 (t), 116.5 (t), 49.9 (s), 13.6 (p)
HRMS-(EI) (m/z): M+ calcd for $C_{15}H_{15}NO_2$: 241.110277; found 241.110399.

3.4 2-(1,3-Dimethyl-9H-xanthen-9-yl)cyclopentanone (11)



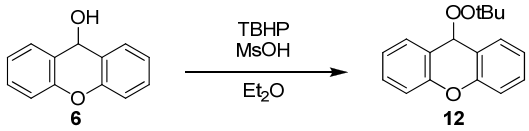
10 **11**

Synthesized as a reference compound.

In a 4mL screw cap vial, dimethyl xanthene[12] **10** (52.5 mg; 0.25 mmol) was dissolved in cyclopentanone (0.11 mL; 1.25 mmol) and camphor sulfonic acid (4 mg; 0.0175 mmol) was added. The vial was flushed with oxygen and connected to an oxygen balloon. The mixture was allowed to react at room temperature for 6 days then the whole mixture was subjected to column chromatography to afford coupling product **11** (46 mg; 63% yield) as a white solid.

^{1}H NMR: (d6-DMSO; 500 MHz): 7.29-7.22 (m; 1H); 7.10 (d, 1H; *J*=7.7 Hz); 7.06-6.96 (m; 2H); 6.82 (s, 1H); 6.79 (s, 1H); 4.69 (d, 1H, *J*=2.1 Hz); 2.5-2.42 (m, 1H, overlaps with residual d6 DMSO peak); 2.33 (s, 3H); 2.25 (s, 3H); 2.21-2.19 (m, 1H); 1.68-1.44 (m, 4H); 1.21-1.11 (m, 1H)
^{13}C NMR: (d6-DMSO; 125 MHz): 218.05 (C); 152.74 (Ar q); 152.15 (Ar q); 136.76 (Ar q); 135.56 (Ar q); 128.71 (Ar CH); 128.23 (Ar CH); 126.29 (Ar CH); 123.29 (Ar CH); 122.59 (Ar q); 119.72 (Ar q); 115.77 (Ar CH); 114.21 (Ar CH); 55.84 (CH); 38.36 (CH_2); 34.35 (CH); 23.73 (CH_2); 20.52 (CH_3); 19.58 (CH_2); 17.75 (CH_3)
MS (EI): 292 (2.7); 209 (100)
HRMS (ESI): calculated for $[C_{20}H_{20}O_2Na]^+$ $(M+Na)^+$: 315.135552; found: 315.135285

3.5 9-(*tert*-Butylperoxy)-9H-xanthene (12)

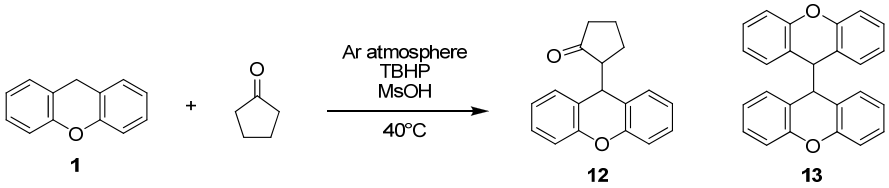


Synthesized as a reference compound.

Xanthydrol **6** (198 mg, 1 mmol) was dissolved in Et_2O (3 mL) and TBHP (450 µL, 10mmol, solution in decane) added. Methane sulfonic acid (7.11 µL, 0.1 mmol) was added and the mixture allowed to stir for 5 minutes. Distilled water was added and the aqueous phase extracted 3 times with AcOEt. Solvent was removed under reduced pressure to afford peroxide **12** (248 mg, 0.918 mmol, 91% yield) as a clear oil crystallising upon standing at room temperature or cooling.

^{1}H NMR: ($CDCl_3$; 500 MHz): 7.63 (dd; 2H; *J*=7.6, 1 Hz); 7.41 (td; 2H; *J* = 7.8, 1.5 Hz); 7.24 (br d; 2H; *J*=8 Hz); 7.18 (br t; 2H; *J*=7.3 Hz); 5.99 (s, 1H); 1.10 (s, 9H)
^{1}H NMR: (d6-DMSO; 500 MHz): 7.61 (br d; 2H; *J*=7.5 Hz); 7.46 (br t; 2H; *J*=7.6 Hz); 7.27 (br d; 2H; J=8 Hz); 7.23 (br t; 2H; *J*=7.5 Hz); 6.02 (s; 1H); 0.99 (s; 9H)
^{13}C NMR: ($CDCl_3$; 125 MHz): 152.65 (Ar q); 131.41 (Ar CH); 130.01 (Ar CH); 122.81 (Ar CH); 119.05 (Ar q); 116.68 (Ar CH); 80.38 (C); 75.44 (CH); 26.35 (CH_3)
MS (ESI): 293(M + Na); 563 (2xM + Na)
HRMS (ESI): Calculated for $[C_{17}H_{18}O_3Na]^+$ ($M+Na^+$): 293.114811; found: 293.114559

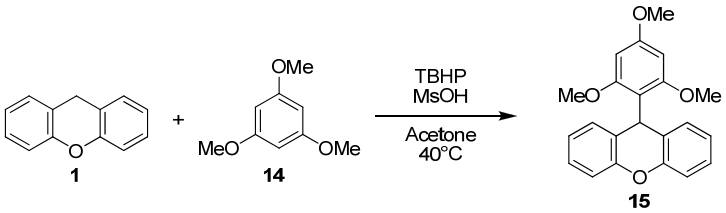
3.6 9H,9'H-9,9'-Bixanthene (13)



In a schlenck tube, xanthene (182 mg; 1 mmol) was dissolved in cyclopentanone (0.44 mL; 5 mmol) and TBHP (364 µL; 2 mmol, solution in decane) was added. The mixture was degassed 3 times and then methane sulfonic acid (4.6 µL; 7 mol%) added under a stream of argon. The tube was closed and the reaction mixture allowed to react at 40°C overnight. After the night, the whole reaction mixture was subjected to column chromatography (toluene). Bixanthene **13** was first isolated (13 mg; 0.0359 mmol; 7% yield) as a white solid and coupling product **2** next.

^{1}H NMR: ($CDCl_3$; 500 MHz): 7.12 (m, 4H); 6.85 (td; 4H; *J*=7.45, 1 Hz); 6.79 (dd; 4H; *J*=8.1, 0.8 Hz); 6.58 (dd; 4H; *J*=7.5, 1.5 Hz); 4.12 (s, 2H)
^{13}C NMR: ($CDCl_3$; 125 MHz): 153.05 (Ar q); 129.16 (Ar CH); 128.13 (Ar CH); 122.64 (Ar CH); 121.86 (Ar q); 115.86 (Ar CH); 49.54 (CH)
MS (EI): 181 (100); 152 (7)
HRMS (ESI): Calculated for $[C_{26}H_{18}O_2]^+$ (M^+): 362.1306802; found: 632.130338

3.7 9-(2,4,6-Trimethoxyphenyl)-9H-xanthene (15)

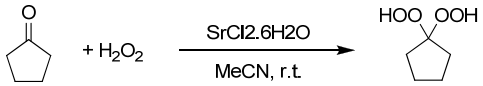


In a 4mL screw cap vial, xanthene (91 mg, 0.5 mmol) was dissolved in acetone (0.5 mL) then 1,3,5-trimethoxybenzene (84 mg; 0.5 mmol), TBHP (182µL; 1 mmol, solution in decane) and methane sulfonic acid (2.3 µL; 7 mol%) were added. The reaction mixture was stirred at 40°C for the night in a screw cap vial without exclusion of air. The whole reaction mixture was then subjected to column chromatography (hexanes/DCM 6/4) to afford coupling product **15** (165 mg; 0.4741 mmol; 94%) as a white solid.

^{1}H NMR: ($CDCl_3$; 500 MHz): 7.01 (br t; 2H; *J*=7.5 Hz); 6.91 (br d; 2H; *J*=7.8 Hz); 6.85 (br d; 2H; *J*=7.5 Hz); 6.77 (br t; 2H; *J*=7.3 Hz); 6.00 (br s; 2H); 5.84 (s, 1H); 3.82 (br s; 3H); 3.68 (s; 3H); 3.21 (br s; 3H)
^{13}C NMR: ($CDCl_3$; 125 MHz): 160.14 (Ar q); 151.57 (Ar q); 128.67 (Ar CH); 126.90 (Ar CH); 124.77 (Ar q); 122.32 (Ar CH); 116.59 (Ar q); 115.45 (Ar CH); 55.27 (CH); 31.76 (CH_3)
MS (EI): 348; 317; 181
HRMS (ESI): Calculated for $[C_2H_{20}O_{4Na}]^+$ ($M+Na^+$): 371.125378; found: 371.125286

3.8 1,1-Dihydroperoxycyclopentane (17)

Synthesized according to a reported method.[11a]



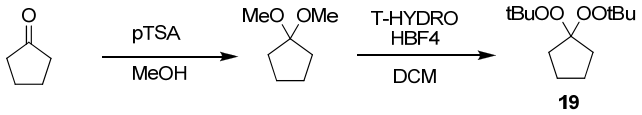
Cyclopentanone (795 µL, 9 mmol) was dissolved in acetonitrile (35 mL), aqueous hydrogen peroxide (35% solution, 27 mL) and strontium chloride (240 mg, 0.9 mmol) were added. The mixture was let to react overnight and then diluted with water (45 mL) and extracted with ether (3x45 mL). Combined organic phases were washed with brine (2x50 mL) and distilled water (50 mL), dried over sodium sulphate and concentrated to afford an essentially pure product (272 mg, 20% yield) as a clear oil. The desired product could be further purified by chromatography on silica (pentane/Et_2O 7:3). Spectral data matched literature reports.[11a]

Note: yields were irreproducible and randomly much lower than the one reported here. In all cases, we could never achieve the yields reported in the literature.

^{1}H NMR: ($CDCl_3$; 300 MHz): 9.5 (br s, 2H); 1.95-1.88 (m, 4H); 1.7-1.65 (m, 4H)
^{13}C NMR: ($CDCl_3$; 75 MHz):122.44 (q); 33.06 (CH_2); 24.51 (CH_2)

3.9 1,1-Bis(tert-butylperoxy)cyclopentane (19)

Adapted from a literature reported method.[11b]

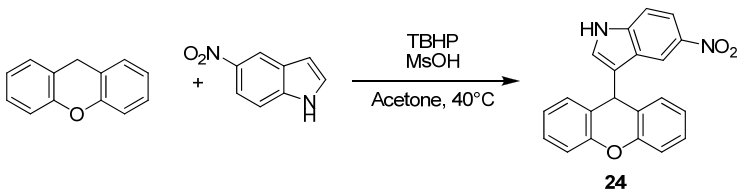


19

Cyclopentanone (883 µL, 10 mmol) was dissolved in methanol (100 mL), para-toluene sulfonic acid (190mg, 1mmol) was added and the mixture let to reat overnight. The mixture was diluted with dichloromethane (100 mL) and washed with distilled water (3x 75 mL). The organic phase was dried over sodium sulphate and concentrated to dryness to afford 567mg of a clear oil. The residue was dissolved in pentane (12 mL), tBuOOH (70% aqueous solution, 1.47mL) and HBF4 (40% aqueous solution, 210 µL) were added. The mixture was let to react for 2 hours, K2CO3 (750 mg) was added and stirring was continued for 10 more minutes. The mixture was diluted with Et2O (20 mL) and washed with distilled water (3x 20 mL). Organic phase was dried, concentrated and subjected to column chromatography (Eluant: pentane/Et_2O 99/1) to afford product **19** as a clear oil (800 mg, 3,25 mmol).

Analytical data as reported in the literature:
^{1}H NMR: (d6-DMSO; 300 MHz): 1.92-1.80 (m, 4H); 1.66-1.56 (m, 4H); 1.20 (s, 18H)
^{13}C NMR: (d6-DMSO; 75 MHz):117.67 (q); 78.89 (q); 33.25 (CH_2); 26.43 (CH_3); 23.92 (CH_2)
MS (ESI positive): 269 (M+Na); 515 (2xM+Na)
HRMS (ESI): Calculated for $[C_{13}H_{26}O_4Na]^+$ ($M+Na^+$): 269.172331; found: 269.172384

3.10 5-Nitro-3-(9H-xanthen-9-yl)-1H-indole (24)



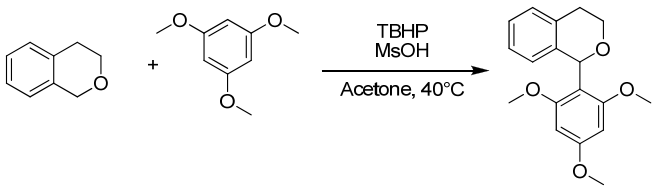
24

In a 4mL screw cap vial, xanthene (91 mg, 0.5 mmol) was dissolved in acetone (0.5 mL) then 5-nitroindole (162 mg; 1 mmol), TBHP (273 µL; 1.5 mmol, solution in decane) and methane sulfonic acid (3.55 µL; 10 mol%) were added. The reaction mixture was stirred at 40°C for the night, in a closed vial without strict exclusion of air. The whole reaction mixture was then subjected to column chromatography (hexanes/acetone 8/2) to afford coupling product **24** (106 mg; 0.3099 mmol; 62%) as a yellow solid.

^{1}H NMR: (d6-DMSO; 500 MHz): 11.76 (s, 1H); 8.11 (d, 1H, *J*=2 Hz); 7.90 (dd, 1H, *J*= 9; 2 Hz); 7.63 (d, 1H, *J*=2 Hz); 7.5 (d, 1H, *J*=9 Hz); 7.27-7.20 (m, 4H); 7.16 (br d; 2H); 7.02-6.96 (m, 2H); 5.75 (s, 1H)
^{13}C NMR: (d6-DMSO; 125 MHz): 150.52 (Ar q); 140.20 (Ar q); 139.85 (Ar q); 129.54 (Ar CH); 128.09 (Ar CH); 127.26 (Ar CH); 124.26 (Ar q); 123.83 (Ar q); 123.43 (Ar CH); 122.06 (Ar q); 116.56 (Ar CH); 116.15 (Ar CH); 115.52 (Ar CH); 112.20 (Ar CH); 34.28 (CH)

MS (EI): 342 (100); 295 (37); 265 (19); 181 (48)
HRMS (ESI): Calculated for $[C_{21}H_{14}N_2O_3Na]^+$ ($M+Na^+$): 365.089662; found: 365.090166

3.11 1-(2,4,6-Trimethoxyphenyl)isochromane (25)

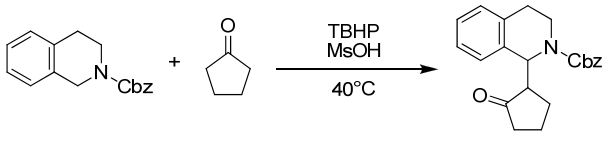


25

In a 4mL screw cap vial, isochromane (63.2 µL; 0.5 mmol) was dissolved in acetone (0.5mL) then 1,3,5-trimethoxybenzene (84 mg; 0.5 mmol), TBHP (182 µL; 1 mmol, solution in decane) and methane sulfonic acid (3.55 µL; 10 mol%) were added and the mixture allowed to react overnight, in a closed vial without strict exclusion of air. The whole mixture was then subjected to column chromatography (hexane/AcOEt 9/1) to afford a mixture of coupling product and isochromanone which was then separated by preparative TLC (DCM as eluant) to afford coupling product **25** (59 mg, 0.1966 mmol, 39% yield) as a white solid. Spectroscopic data matches previous report. [13]

^{1}H NMR: ($CDCl_3$; 500 MHz): 7.14-7.06 (m, 2H); 7.05-6.98 (, 1H); 6.7 (d, 1H, *J*=7.7 Hz); 6.32 (s, 1H); 6.14 (s, 2H); 4.32 (ddd, 1H, *J*=11, 5.5, 2 Hz); 3.95 (dt , 1H, *J*=11, 2.8 Hz); 3.82 (s, 3H); 3.63 (br s, 6H); 3.29-3.19 (m, 1H); 2.69 (br d, 1H, *J*=16 Hz)
^{13}C NMR: ($CDCl_3$; 125 MHz): 161.26 (Ar q); 159.97 (Ar q); 139.76 (Ar q); 133.88 (Ar q); 127.86 (Ar CH); 125.60 (Ar CH); 125.19 (Ar CH); 124.27 (Ar CH); 111.75 (Ar q); 91.44 (broad, Ar q); 70.30 (CH); 65.42 (CH_2); 55.95 (CH_3); 55.29 (CH_3); 29.08 (CH_2)
MS (EI): 300 (100); 269 (45); 239 (54); 195 (39); 168 (40); 132 (24)
HRMS (ESI): Calculated for $[C_{18}H_{20}O_4Na]^+$ ($M+Na^+$): 323.125378; found: 323.125264.

3.12 *N*-Cbz-1-(2-oxocyclopentyl)-3,4-dihydroisoquinoline-2(1H) (26)



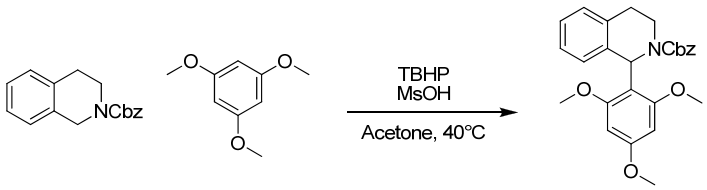
26

In a 4mL screw cap vial, N-Cbz tetrahydroisoquinoline (67.5 mg; 0.25 mmol) was dissolved in cyclopentanone (0.22 mL; 2.5 mmol). TBHP (136.5 µL; 0.75 mmol, solution in decane) and methane sulfonic acid (1.77 µL; 0.025 mmol) were added and the reaction stirred for 22 hours in a closed vial without strict exclusion of air. The whole mixture was then subjected to column chromatography (hexane/AcOEt 85/15) to afford coupling product **26** (60 mg; 0.1719 mmol; 68%). From the reaction mixture was also reisolated the starting material (13 mg; 0.0486 mmol; 19%)

^{1}H NMR: (80°C d6-DMSO; 400 MHz): 7.41-7.25 (m, 5H); 7.22-7.10 (m, 3H); 7.05-6.94 (m, 1H); 5.45 (d, 1H, *J*=5.1 Hz, major); 5.26 (d, 1H, *J*=5.7 Hz, minor); 5.15-5.06

(m, 2H); 4.02-3.74 (m, 1H); 3.59-3.25 (m, 1H); 2.89-2.78 (m, 2H); 2.60-2.43 (m, 1H; overlaps with d6-DMSO signal); 2.22-2.11 (m, 1H); 2.10-1.77 (m, 3H); 1.77-1.43 (m, 2H)
^{13}C NMR: (80°C d6-DMSO; 100 MHz): 216.56 (q, minor); 216.45 (q, major); 154.47 (q, major); 154.26 (q, minor); 137.22(Ar q); 136.55 (Ar q); 136.45 (Ar q); 134.79 (Ar q); 134.29 (Ar q); 133.41 (Ar q); 128.19 (Ar H); 127.85 (ArH); 127.35 (ArH); 127.24 (ArH); 127.16 (ArH); 126.95 (ArH); 126.69 (ArH); 126.57 (ArH); 126.11 (ArH); 126.02 (ArH); 125.64 (ArH); 66.04 (CH_2, minor)65.96 (CH_2, major); 55.67 (CH); 54.09 (CH); 53.84 (CH); 52.70 (CH); 37.47 (CH_2, major); 36.52 (CH_2, minor); 27.23 (CH_2, major); 27.14 (CH_2, minor); 26.02 (CH_2, major); 25.84 (CH_2, minor); 19.39 (CH_2, major); 19.25 (CH_2, minor)
MS (ESI): m/z=349
HRMS (ESI): Calculated for $[C_{22}H_{23}NO_3Na]^+$: 372.157012; found: 372.156920

3.13 *N*-Cbz-1-(2,4,6-trimethoxyphenyl)-3,4-dihydroisoquinoline-2(1H) (27)

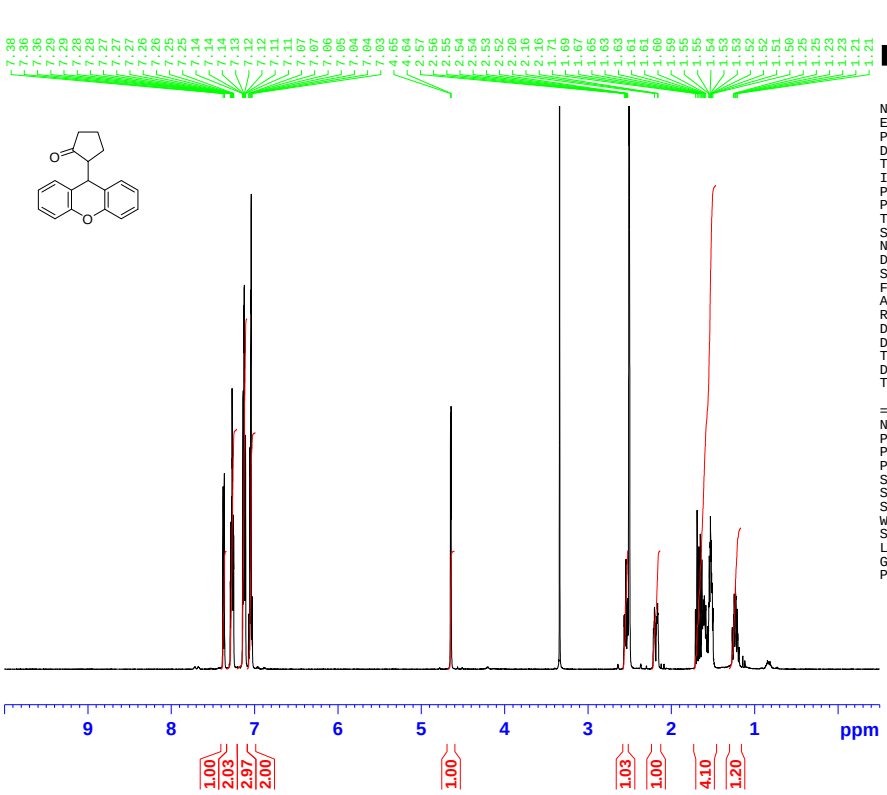


27

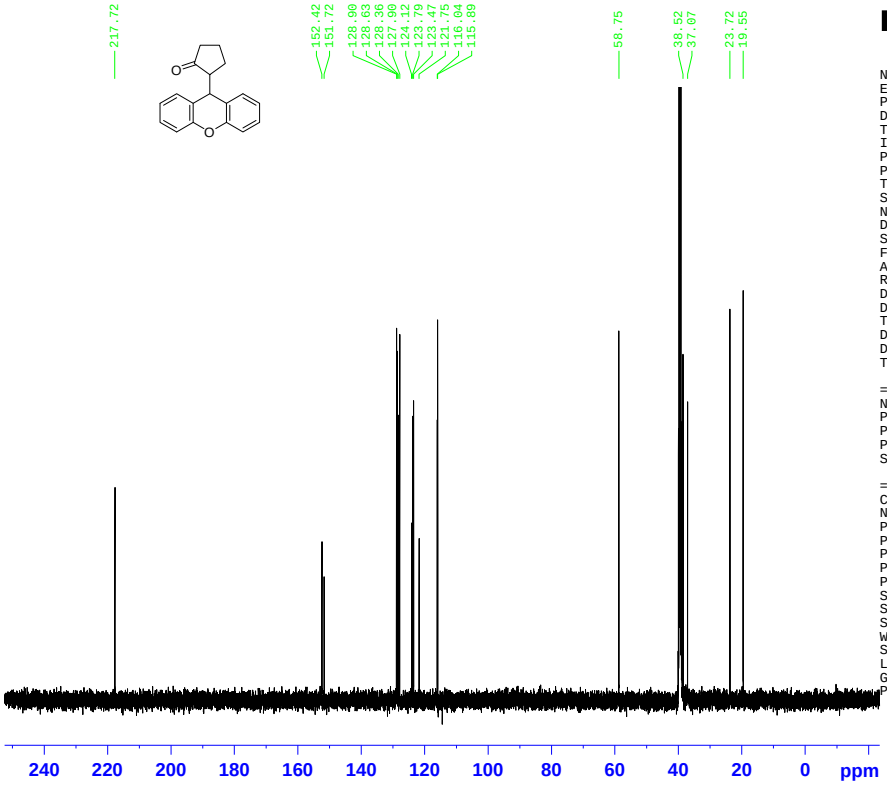
In a 4mL screw cap vial, N-Cbz tetrahydroisoquinoline (133.5 mg; 0.5 mmol) was dissolved in acetone (0.5mL) then trimethoxybenzene (84 mg; 0.5 mmol), TBHP (182 µL; 1mmol, solution in decane) and methane sulfonic acid (2.3 µL; 7 mol%) were added and the mixture allowed to react overnight, in a closed vial without strict exclusion of air. The whole mixture was then subjected to column chromatography (hexane/AcOEt 85/15) to afford coupling product **27** (108 mg, 0.2494 mmol, 49% yield) as a clear oil which upon standing at room temperature or cooling often gives a white solid.
Spectroscopic data matches previous report.[14]

^{1}H NMR: (80°C; d6-DMSO; 400 MHz): 7.31-7.22 (m, 3H); 7.17-7.10 (m, 3H); 7.06 (tt, 1H, *J*=2, 7.2Hz); 7.00 (td, 1H, *J*=2, 7.7Hz); 6.69 (d, 1H, *J*=7.7Hz); 6.46 (s, 1H); 6.19 (s, 2H); 5.05-4.95 (m, 2H); 4.24 (ddd, 1H, J=3, 5, 12.6Hz); 3.77 (s, 3H); 3.58-3.49 (m, 7H); 2.90-2.75 (m, 2H)
^{13}C NMR: (80°C; d6-DMSO; 100 MHz): 159.89 (Ar q); 158.41 (Ar q); 154.46 (q); 136.79 (Ar q); 136.53 (Ar q); 134.08 (Ar q); 127.67 (ArH); 127.52 (ArH); 126.97 (ArH); 126.80 (ArH); 125.42 (ArH); 125.32 (ArH); 125.05 (ArH); 113.06 (Ar q); 91.62 (ArH); 65.59 (CH^2); 55.33 (CH_3); 54.81 (CH_3); 48.75 (CH); 39.28 (CH_2); 29.19 (CH_2)
MS (EI): 433 (5); 342 (4); 298 (100); 91 (27)
HRMS (ESI): calculated for $[C_{26}H_{27}NO_5Na]^+$ ($M+Na^+$): 456.178527; found: 456.178146

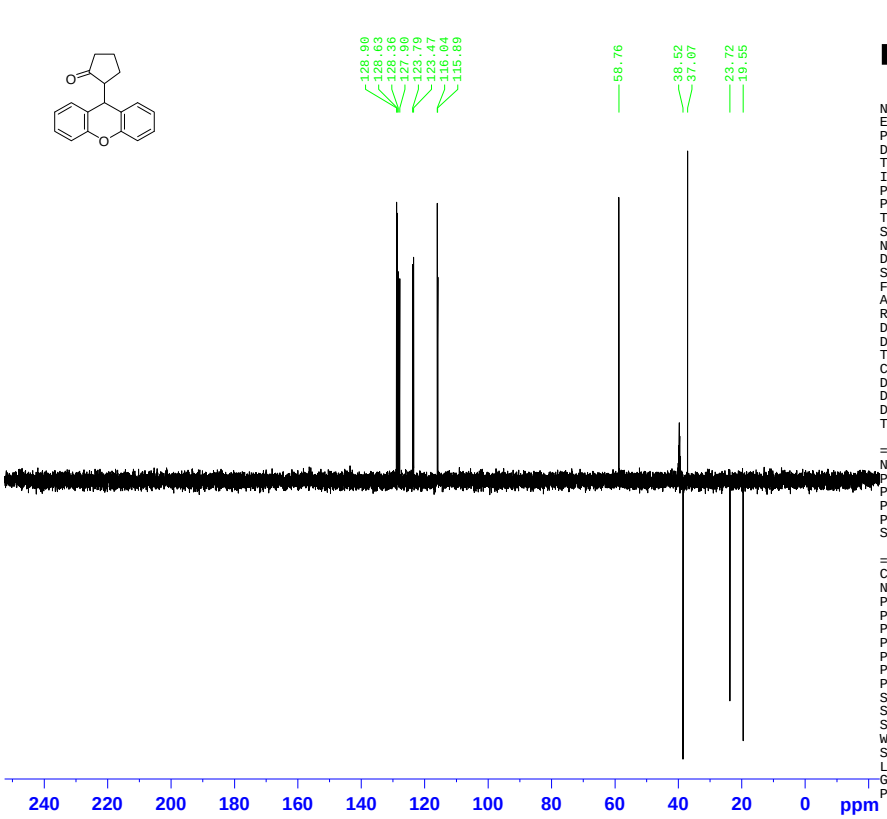
4 NMR-spectra



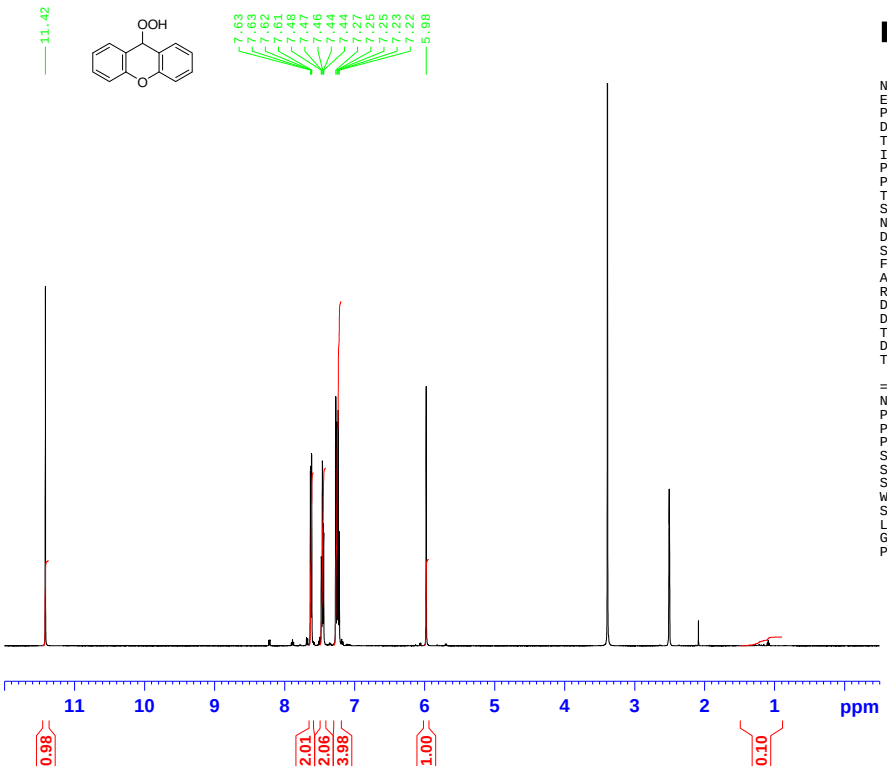

```
NAME          SCE-SD-087 carac
EXPNO                   10
PROCNO                   1
Date_             20130114
Time                  9.52
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT               DMSO
NS                      16
DS                       2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ                3.1719923 sec
RG                     161
DW                  48.400 usec
DE                   6.50 usec
TE                  296.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.05 usec
PL1                   0.00 dB
PL1W           26.62599564 W
SFO1           500.3530899 MHz
SI                   32768
SF             500.3500000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



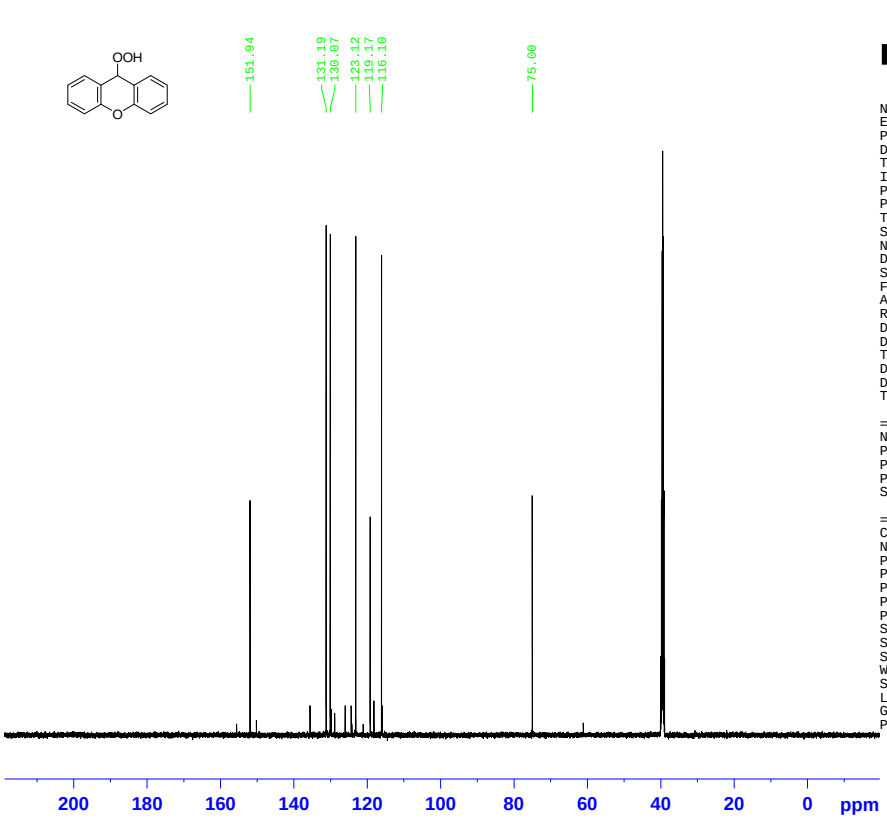

```
NAME          SCE-SD-087 carac
EXPNO                   11
PROCNO                   1
Date_             20130115
Time                  0.45
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgdc30
TD                   65536
SOLVENT               DMSO
NS                    1500
DS                       4
SWH              34722.223 Hz
FIDRES            0.529819 Hz
AQ                0.9437684 sec
RG                   32800
DW                  14.400 usec
DE                  10.00 usec
TE                  296.0 K
D1              0.01000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    6.78 usec
PL1                   0.00 dB
PL1W           83.14344025 W
SFO1           125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL2W           26.62599564 W
PL12W           0.50385541 W
SFO2           500.3520014 MHz
SI                   32768
SF             125.8131709 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



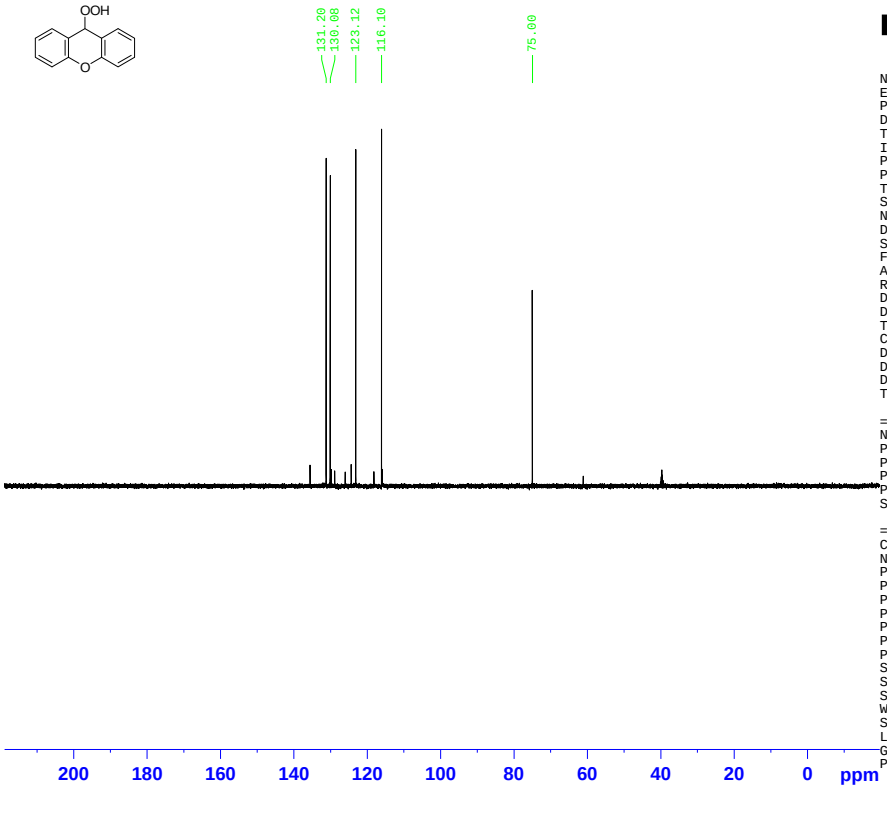

```
NAME          SCE-SD-087 carac
EXPNO                      12
PROCNO                      1
Date_               20130115
Time                    0.59
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG              dept135
TD                     65536
SOLVENT                DMSO
NS                       256
DS                         4
SWH                34722.223 Hz
FIDRES              0.529819 Hz
AQ                  0.9437684 sec
RG                      16400
DW                     14.400 usec
DE                     10.00 usec
TE                     296.0 K
CNST2              145.0000000
D1                   2.00000000 sec
D2                   0.00344828 sec
D12                  0.00002000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                        6.78 usec
P2                       13.55 usec
PL1                       0.00 dB
PL1W               83.14344025 W
SFO1               125.8275765 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
P3                       11.05 usec
P4                       22.10 usec
PCPD2                    80.00 usec
PL2                       0.00 dB
PL12                     17.23 dB
PL2W               26.62599564 W
PL12W               0.50385541 W
SFO2               500.3520014 MHz
SI                       32768
SF                 125.8131709 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```



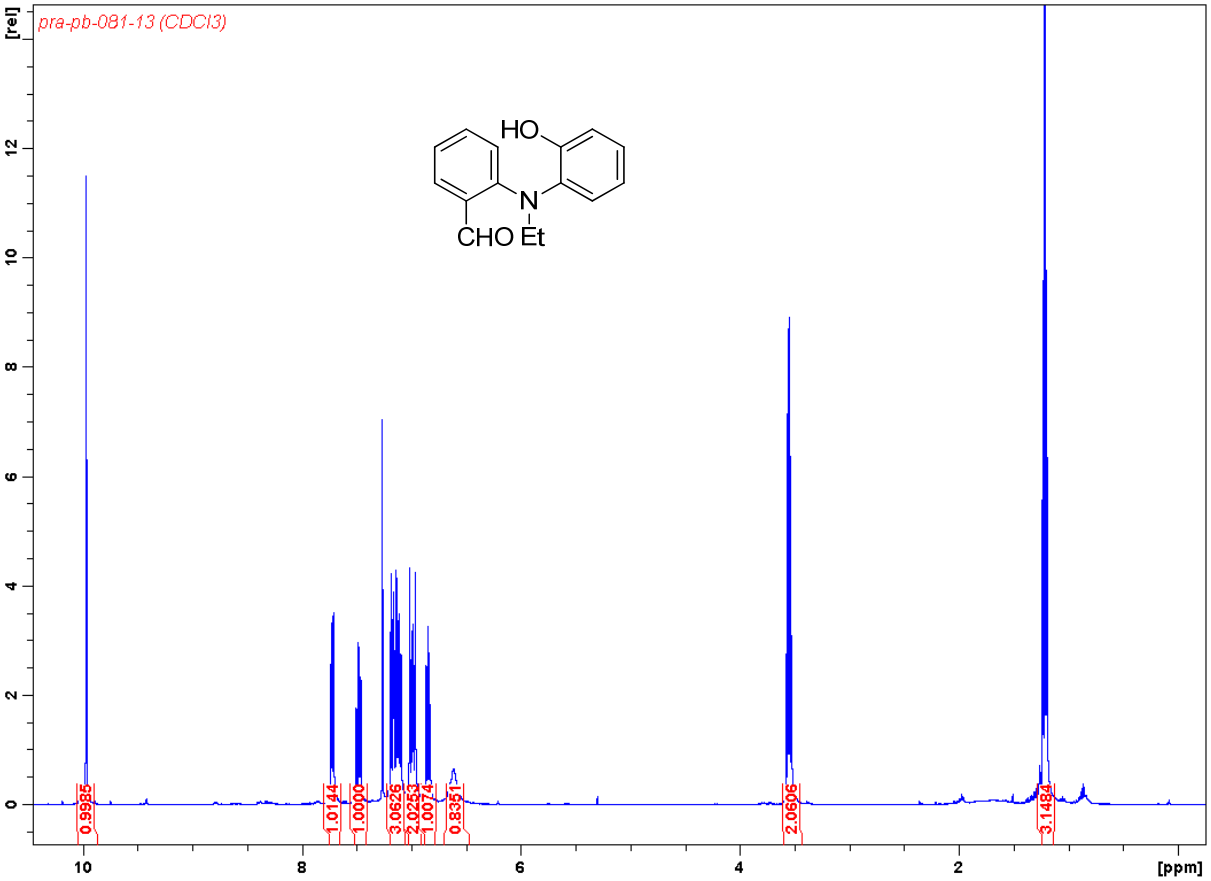

```
NAME          SCE-SD-001 carac
EXPNO                      10
PROCNO                      1
Date_               20130109
Time                   17.36
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                DMSO
NS                         16
DS                          2
SWH                10330.578 Hz
FIDRES              0.157632 Hz
AQ                  3.1719923 sec
RG                       80.6
DW                     48.400 usec
DE                      6.50 usec
TE                     296.0 K
D1                   1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                       11.05 usec
PL1                       0.00 dB
PL1W               26.62599564 W
SFO1               500.3530899 MHz
SI                       32768
SF                 500.3500000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

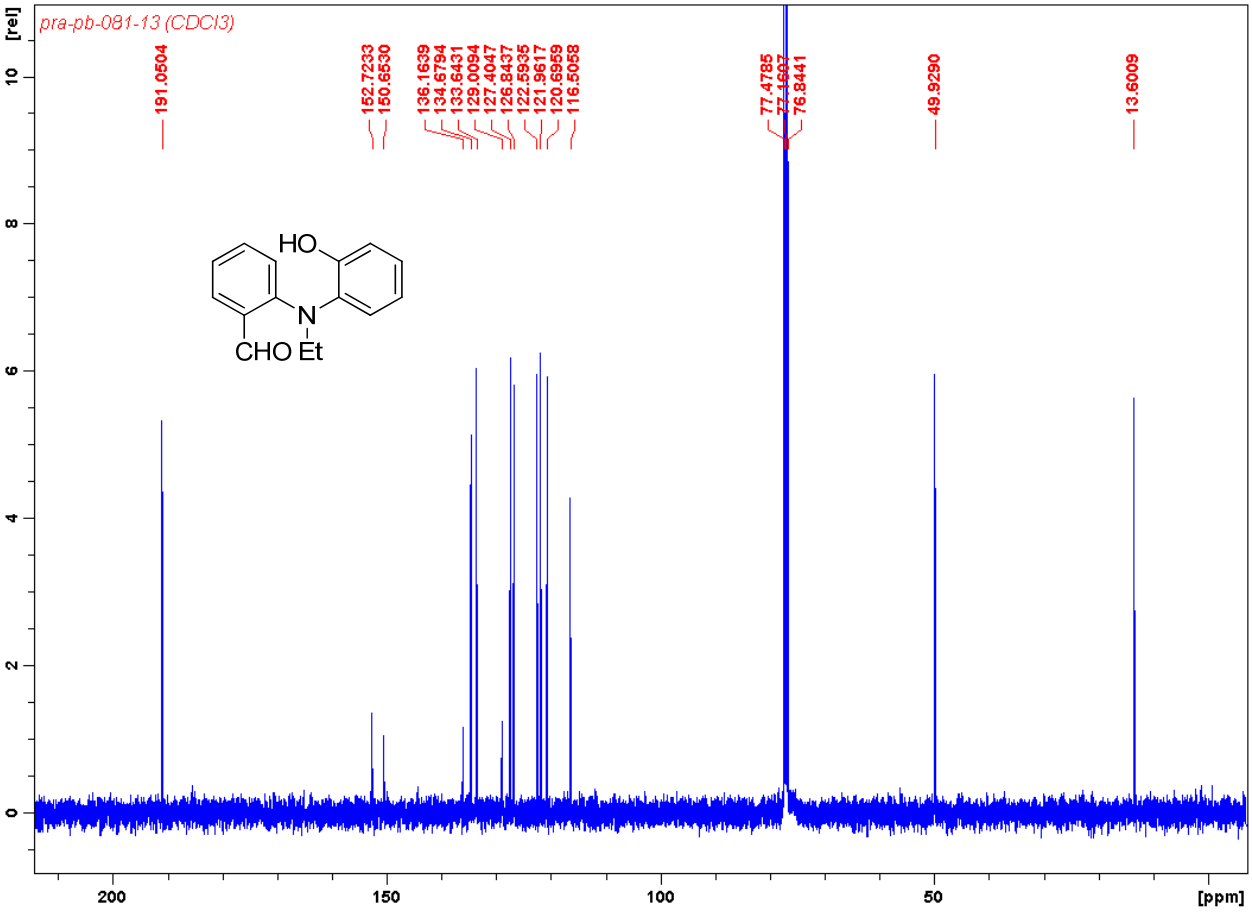


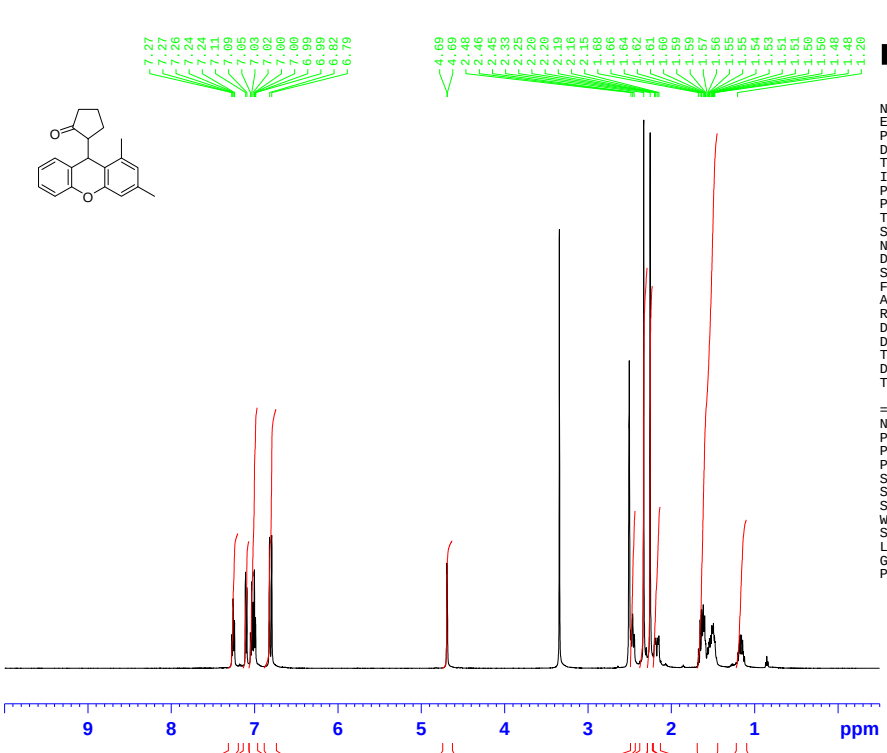

```
NAME        SCE-SD-001 carac
EXPNO                   11
PROCNO                   1
Date_             20130110
Time                  1.27
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             zgdc30
TD                   65536
SOLVENT                DMSO
NS                    1500
DS                       4
SWH              34722.223 Hz
FIDRES            0.529819 Hz
AQ               0.9437684 sec
RG                   32800
DW                  14.400 usec
DE                  10.00 usec
TE                  296.0 K
D1              0.01000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    6.78 usec
PL1                   0.00 dB
PL1W           83.14344025 W
SFO1          125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL2W           26.62599564 W
PL12W           0.50385541 W
SFO2          500.3520014 MHz
SI                   32768
SF            125.8131709 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```




```
NAME        SCE-SD-001 carac
EXPNO                   12
PROCNO                   1
Date_             20130110
Time                  1.41
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG             dept135
TD                   65536
SOLVENT                DMSO
NS                     256
DS                       4
SWH              34722.223 Hz
FIDRES            0.529819 Hz
AQ               0.9437684 sec
RG                   16400
DW                  14.400 usec
DE                  10.00 usec
TE                  296.0 K
CNST2          145.0000000
D1              2.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    6.78 usec
P2                   13.55 usec
PL1                   0.00 dB
PL1W           83.14344025 W
SFO1          125.8275765 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
P3                   11.05 usec
P4                   22.10 usec
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL2W           26.62599564 W
PL12W           0.50385541 W
SFO2          500.3520014 MHz
SI                   32768
SF            125.8131709 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

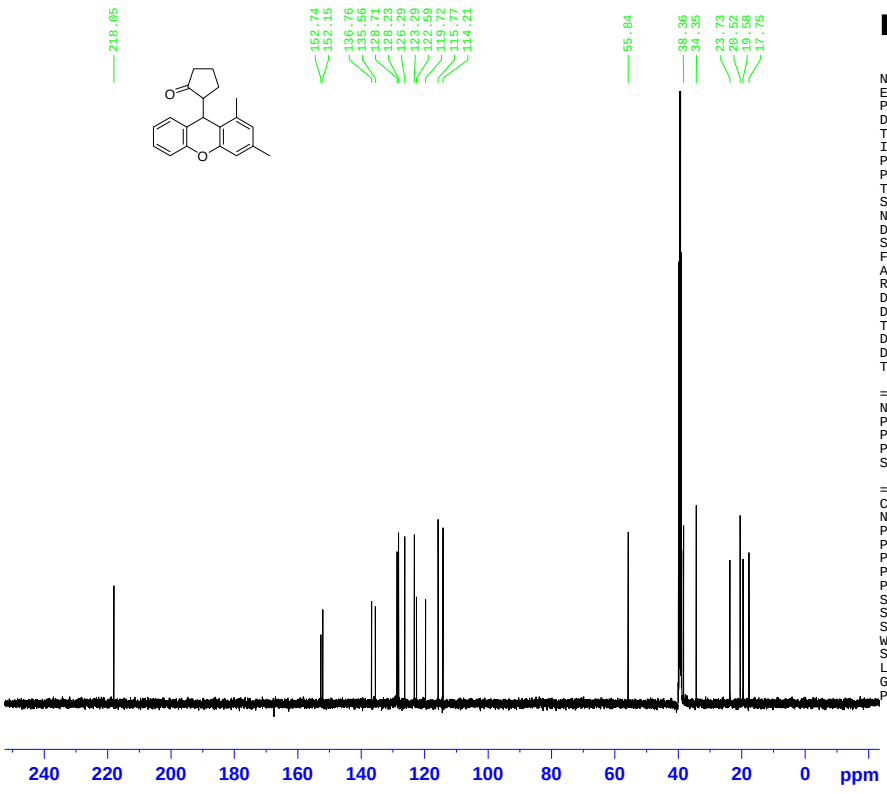

pra-pb-081-13 (CDCl3)
[rel]
HO
N
CHO Et
0.9985
1.0144
1.0000
3.0626
2.0253
1.0074
0.8351
2.0606
3.1484
[ppm]


pra-pb-081-13 (CDCl3)
[rel]
191.0504
152.7233
150.6530
136.1639
134.6794
133.8431
129.0094
127.4047
126.8437
122.5935
121.9617
120.6959
116.5058
77.4785
77.1607
76.8441
49.9290
13.6009
HO
N
CHO Et
[ppm]



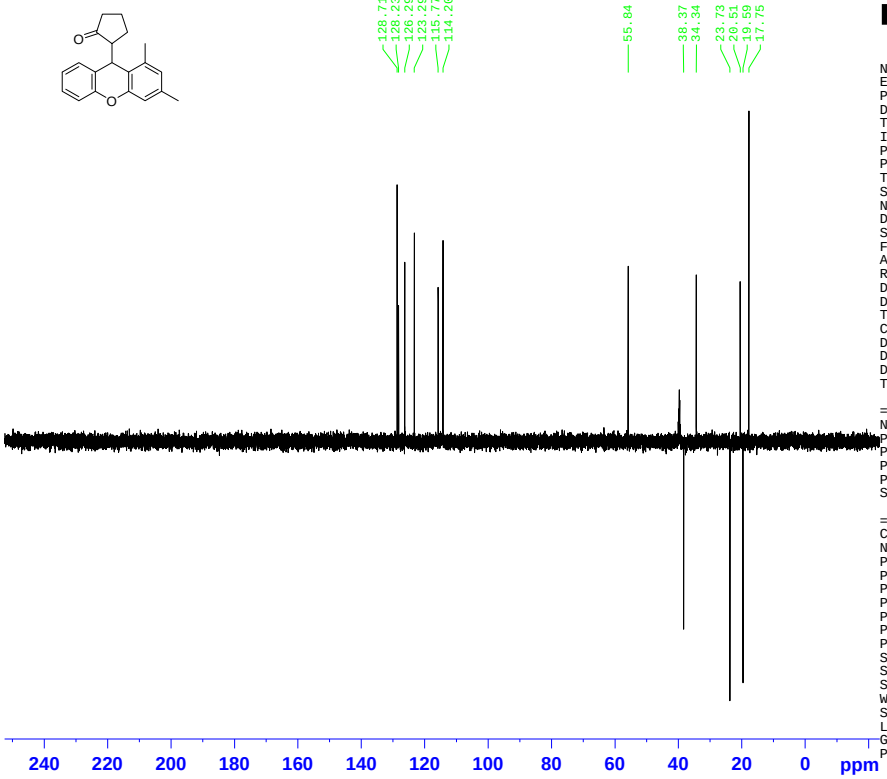
BRUKER

```
NAME          SCE BSR-BD-068 DMSO
EXPNO                     10
PROCNO                     1
Date_               20130111
Time                   13.29
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                DMSO
NS                        16
DS                         2
SWH                10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719923 sec
RG                       161
DW                    48.400 usec
DE                     6.50 usec
TE                    296.0 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     11.05 usec
PL1                     0.00 dB
PL1W             26.62599564 W
SFO1             500.3530899 MHz
SI                      32768
SF               500.3500000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

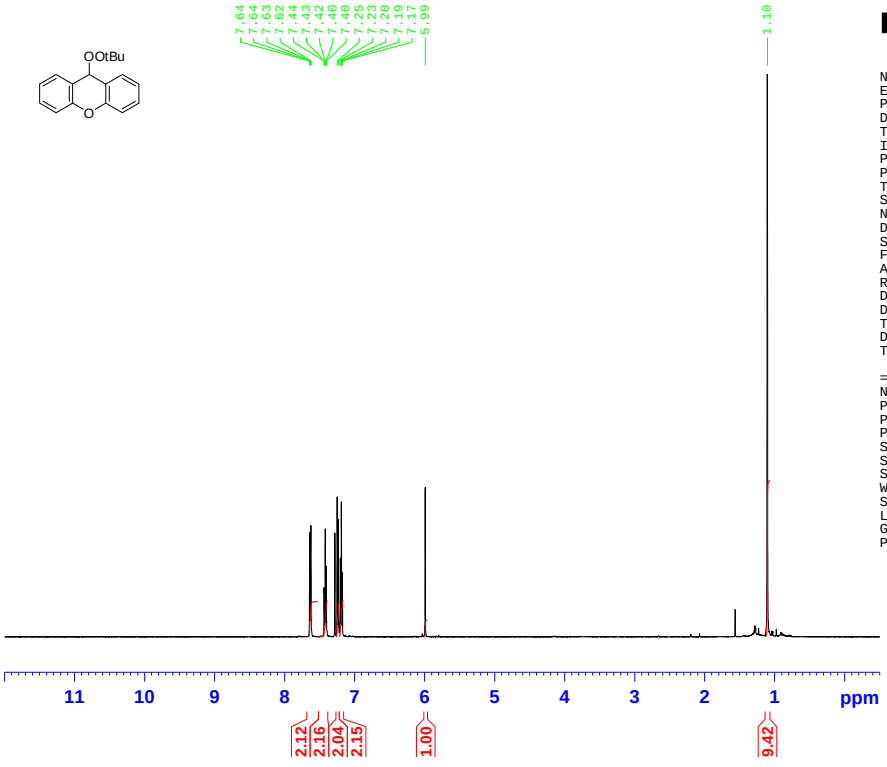


BRUKER

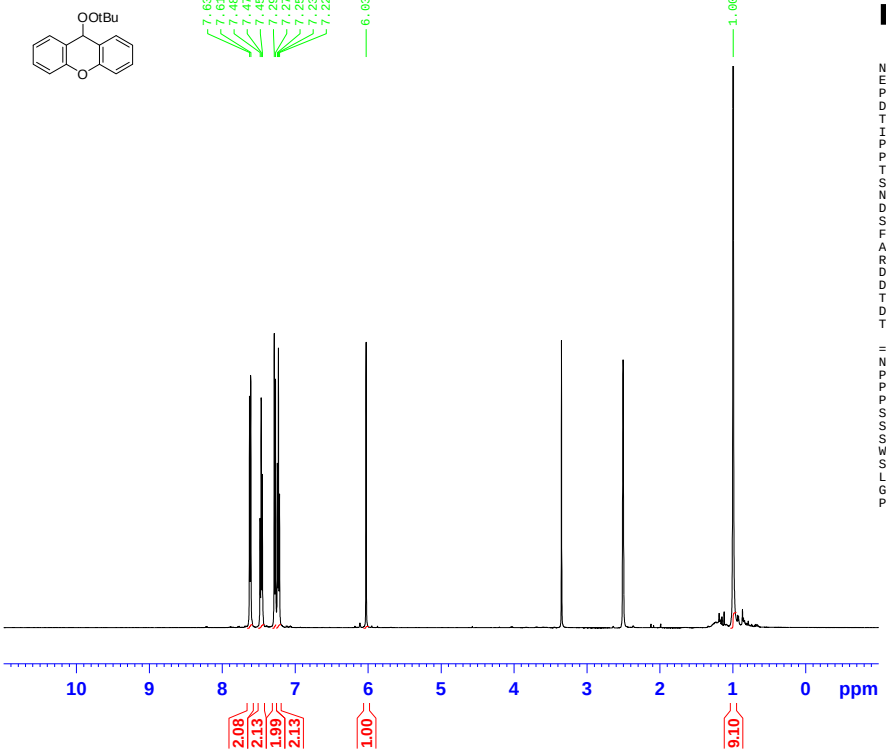
```
NAME          SCE BSR-BD-068 DMSO
EXPNO                     11
PROCNO                     1
Date_               20130115
Time                    0.01
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgdc30
TD                     65536
SOLVENT                DMSO
NS                      1500
DS                         4
SWH                34722.223 Hz
FIDRES             0.529819 Hz
AQ                 0.9437684 sec
RG                      32800
DW                    14.400 usec
DE                    10.00 usec
TE                    296.0 K
D1               0.01000000 sec
D11              0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      6.78 usec
PL1                     0.00 dB
PL1W             83.14344025 W
SFO1             125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   17.23 dB
PL2W             26.62599564 W
PL12W             0.50385541 W
SFO2             500.3520014 MHz
SI                      32768
SF               125.8131709 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



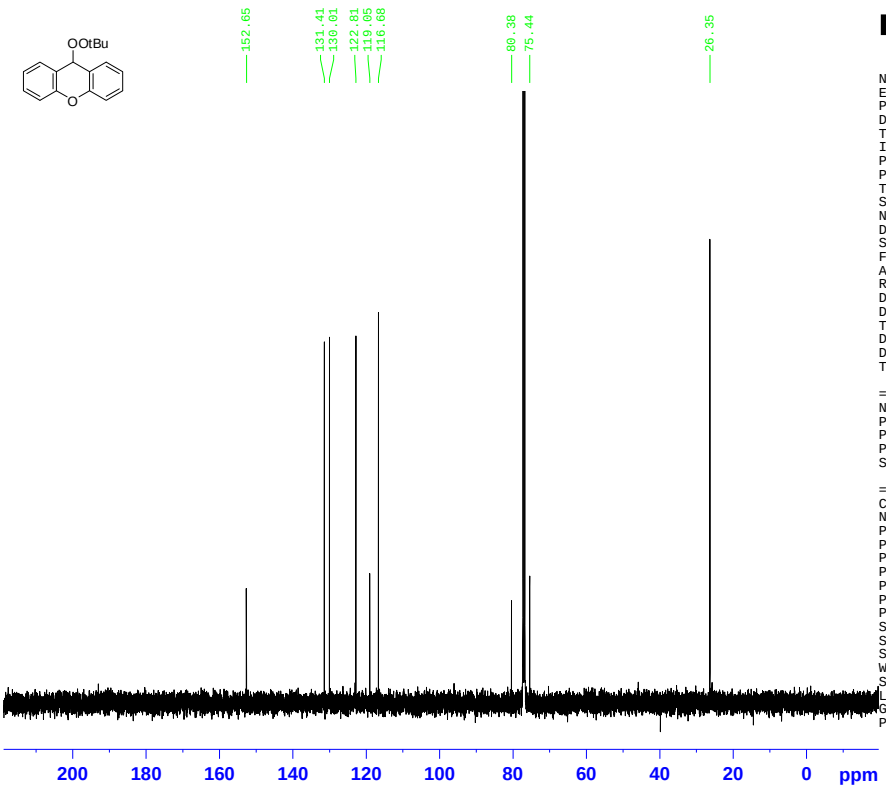

```
NAME          SCE BSR-BD-068 DMSO
EXPNO                    12
PROCNO                    1
Date_              20130115
Time                   0.16
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             dept135
TD                    65536
SOLVENT                DMSO
NS                      256
DS                        4
SWH               34722.223 Hz
FIDRES             0.529819 Hz
AQ                0.9437684 sec
RG                    16400
DW                   14.400 usec
DE                   10.00 usec
TE                   296.0 K
CNST2           145.0000000
D1                2.00000000 sec
D2                0.00344828 sec
D12               0.00002000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     6.78 usec
P2                    13.55 usec
PL1                    0.00 dB
PL1W             83.14344025 W
SFO1             125.8275765 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
P3                    11.05 usec
P4                    22.10 usec
PCPD2                 80.00 usec
PL2                    0.00 dB
PL12                  17.23 dB
PL2W             26.62599564 W
PL12W             0.50385541 W
SFO2             500.3520014 MHz
SI                     32768
SF               125.8131709 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



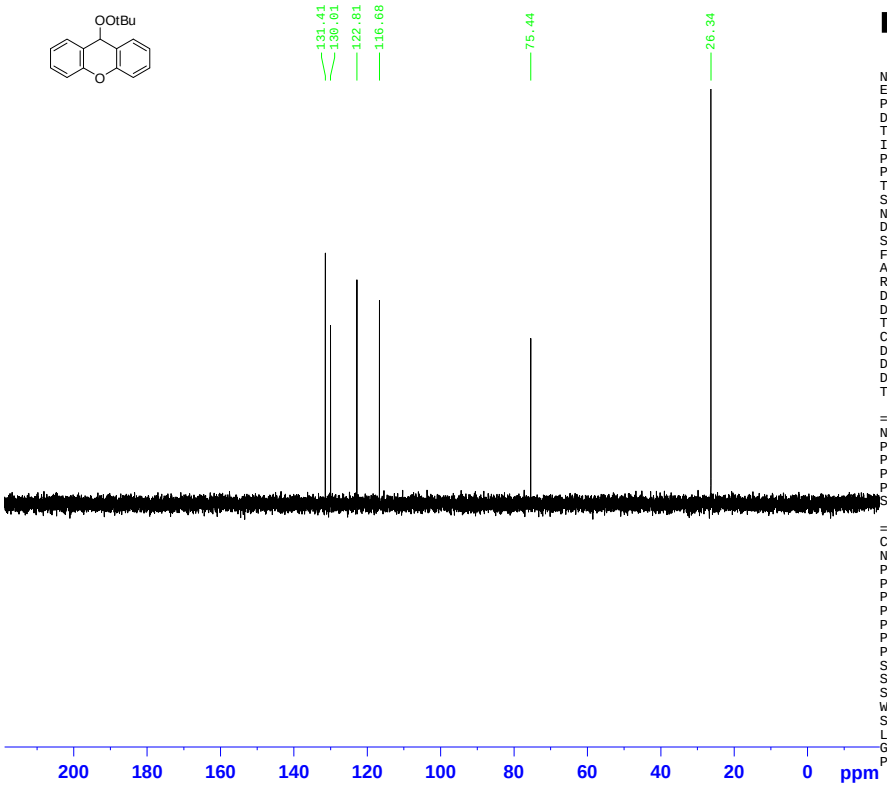

```
NAME          SCE-SC-250 A4-A5
EXPNO                    10
PROCNO                    1
Date_              20121010
Time                  11.12
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                3.1719923 sec
RG                      256
DW                   48.400 usec
DE                    6.50 usec
TE                   296.0 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                    11.05 usec
PL1                    0.00 dB
PL1W             26.62599564 W
SFO1             500.3530899 MHz
SI                     32768
SF               500.3500000 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



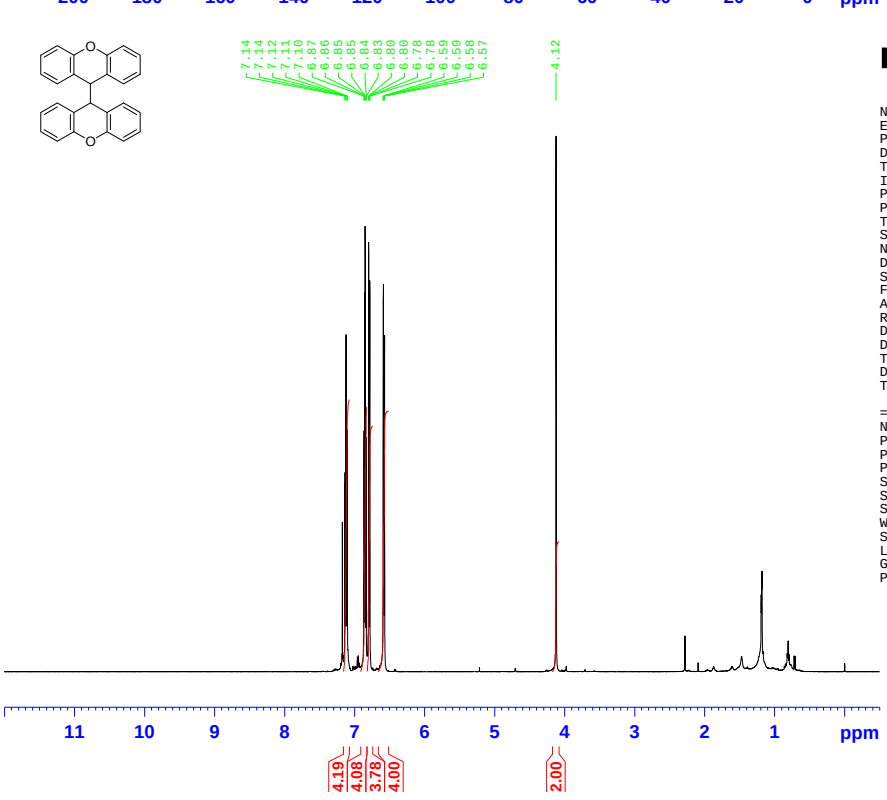

```
NAME          SCE-SC-250 A4-A5 DMSO
EXPNO                   10
PROCNO                   1
Date_             20121010
Time                 11.26
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ                3.1719923 sec
RG                     90.5
DW                   48.400 usec
DE                    6.50 usec
TE                   296.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.05 usec
PL1                   0.00 dB
PL1W           26.62599564 W
SFO1           500.3530899 MHz
SI                    32768
SF             500.3500000 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



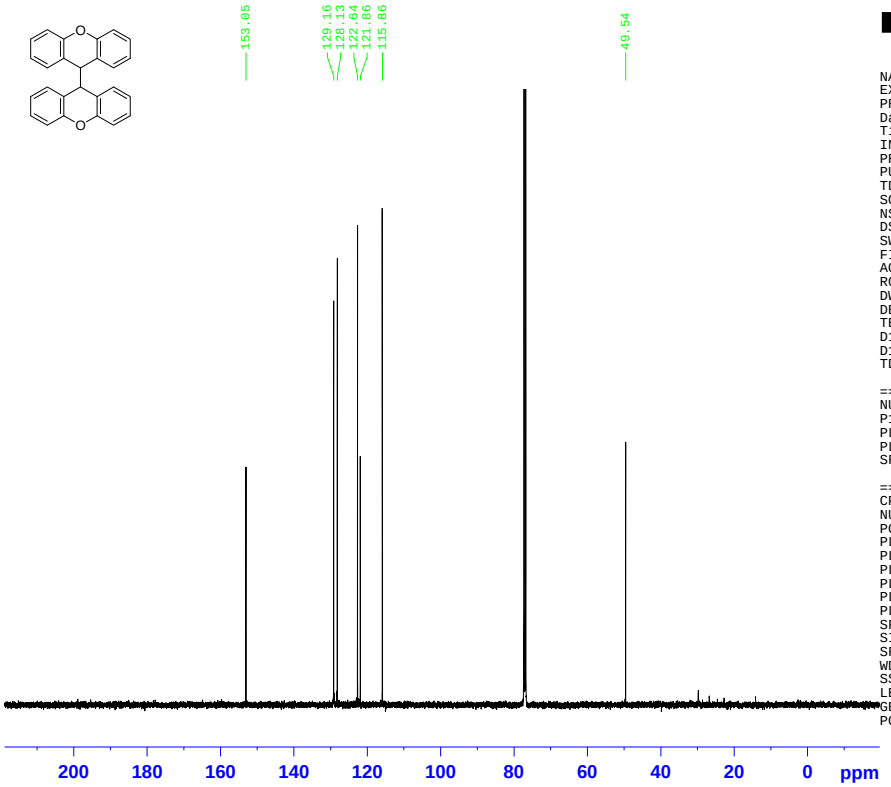

```
NAME          SCE-SC-250 A4-A5
EXPNO                   11
PROCNO                   1
Date_             20121010
Time                 22.49
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT              CDCl3
NS                     512
DS                       4
SWH              34722.223 Hz
FIDRES            0.529819 Hz
AQ                0.9437684 sec
RG                     32800
DW                   14.400 usec
DE                   10.00 usec
TE                   295.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    6.78 usec
PL1                   0.00 dB
PL1W           83.14344025 W
SFO1           125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 17.23 dB
PL13                 17.23 dB
PL2W           26.62599564 W
PL12W           0.50385541 W
PL13W           0.50385541 W
SFO2           500.3520014 MHz
SI                    32768
SF             125.8131080 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



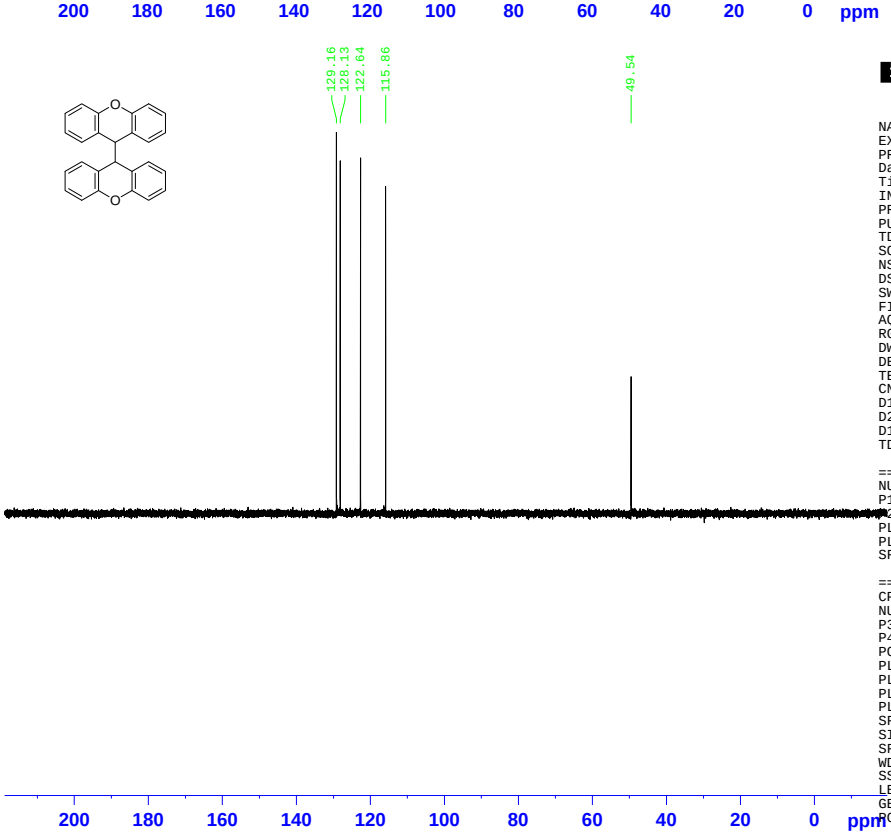

```
NAME          SCE-SC-250 A4-A5
EXPNO                     12
PROCNO                     1
Date_               20121010
Time                   23.04
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG              dept135
TD                     65536
SOLVENT                CDCl3
NS                       256
DS                         4
SWH                34722.223 Hz
FIDRES             0.529819 Hz
AQ                 0.9437684 sec
RG                     16400
DW                    14.400 usec
DE                    10.00 usec
TE                    296.0 K
CNST2             145.0000000
D1                  2.00000000 sec
D2                  0.00344828 sec
D12                 0.00002000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      6.78 usec
P2                     13.55 usec
PL1                     0.00 dB
PL1W              83.14344025 W
SFO1              125.8275765 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
P3                     11.05 usec
P4                     22.10 usec
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   17.23 dB
PL2W              26.62599564 W
PL12W              0.50385541 W
SFO2              500.3520014 MHz
SI                     32768
SF                125.8131080 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```



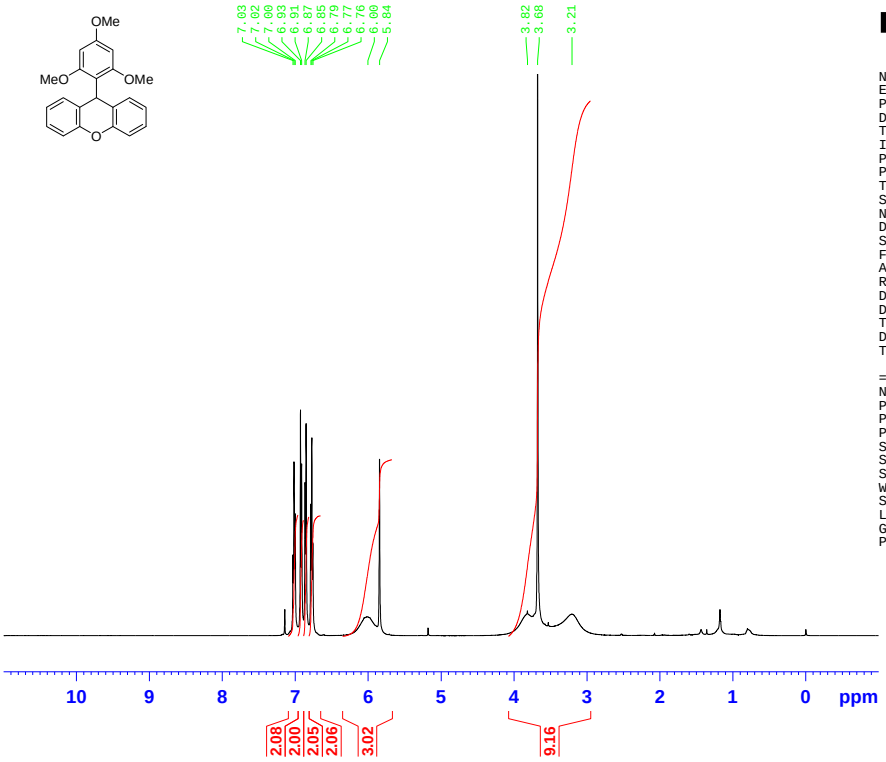

```
NAME          SCE-SD-014 A3
EXPNO                     10
PROCNO                     1
Date_               20121102
Time                   19.07
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         2
SWH                10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719923 sec
RG                       161
DW                    48.400 usec
DE                     6.50 usec
TE                    296.0 K
D1                  1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     1H
P1                     11.05 usec
PL1                     0.00 dB
PL1W              26.62599564 W
SFO1              500.3530899 MHz
SI                     32768
SF                500.3500535 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```



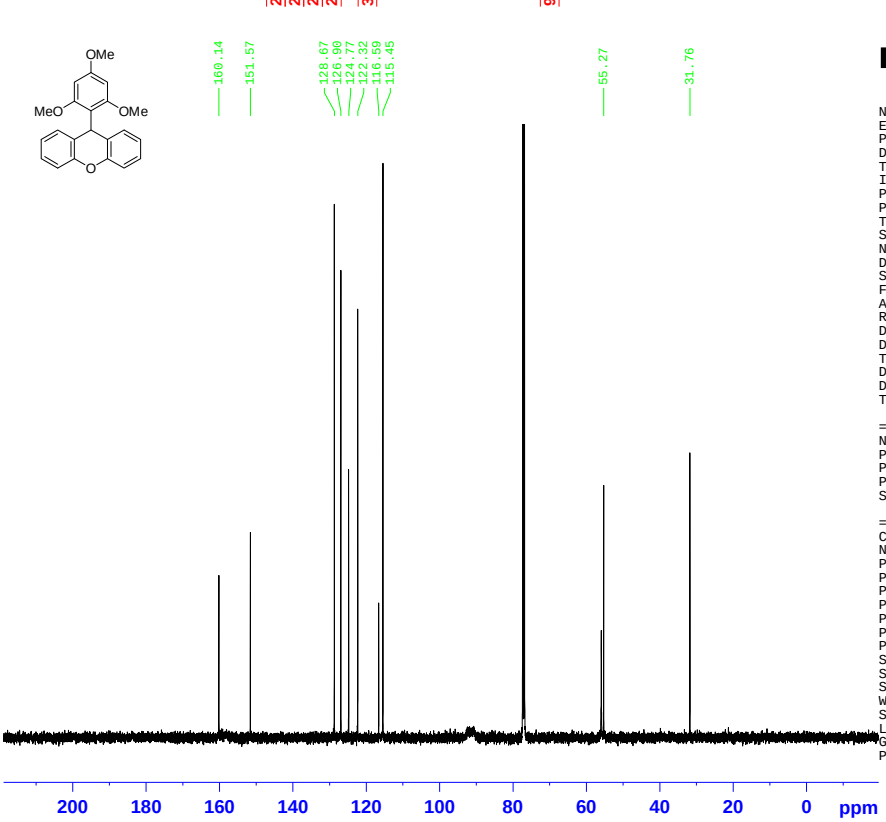

```
NAME          SCE-SD-014 A3
EXPNO                   11
PROCNO                   1
Date_           20121103
Time                 0.42
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   2048
DS                      4
SWH            34722.223 Hz
FIDRES          0.529819 Hz
AQ              0.9437684 sec
RG                  32800
DW                14.400 usec
DE                10.00 usec
TE                295.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.78 usec
PL1                  0.00 dB
PL1W         83.14344025 W
SFO1         125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                17.23 dB
PL13                17.23 dB
PL2W         26.62599564 W
PL12W         0.50385541 W
PL13W         0.50385541 W
SFO2         500.3520014 MHz
SI                  32768
SF           125.8131080 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



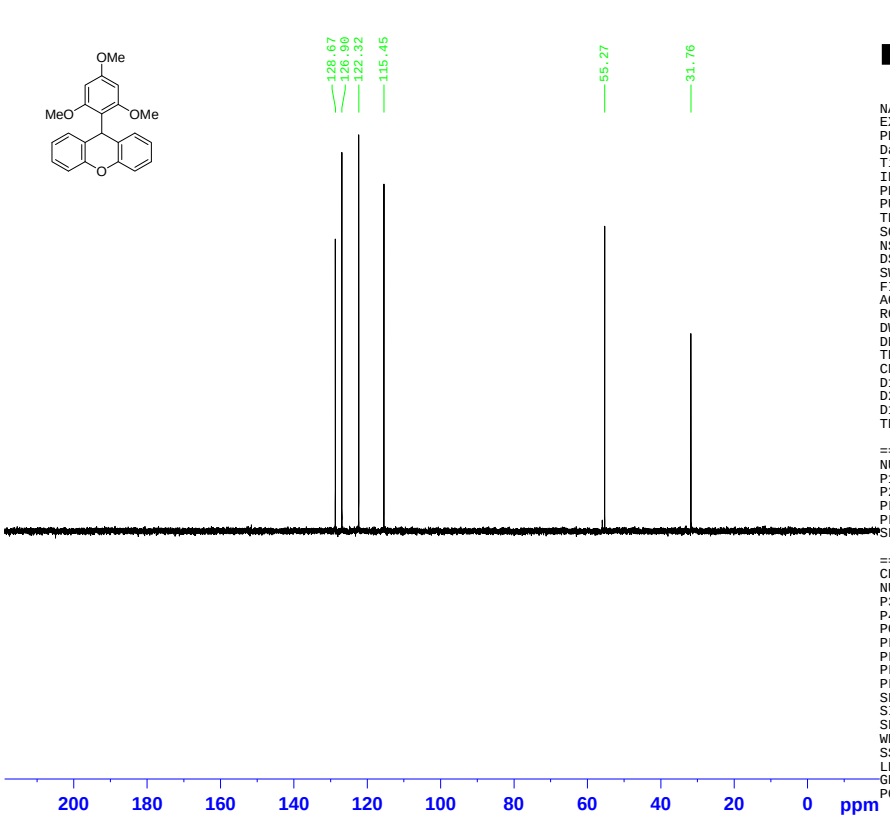

```
NAME          SCE-SD-014 A3
EXPNO                   12
PROCNO                   1
Date_           20121103
Time                 0.57
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG            dept135
TD                  65536
SOLVENT             CDCl3
NS                    256
DS                      4
SWH            34722.223 Hz
FIDRES          0.529819 Hz
AQ              0.9437684 sec
RG                  16400
DW                14.400 usec
DE                10.00 usec
TE                296.0 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.78 usec
P2                  13.55 usec
PL1                  0.00 dB
PL1W         83.14344025 W
SFO1         125.8275765 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
P3                  11.05 usec
P4                  22.10 usec
PCPD2               80.00 usec
PL2                  0.00 dB
PL12                17.23 dB
PL2W         26.62599564 W
PL12W         0.50385541 W
SFO2         500.3520014 MHz
SI                  32768
SF           125.8131080 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```



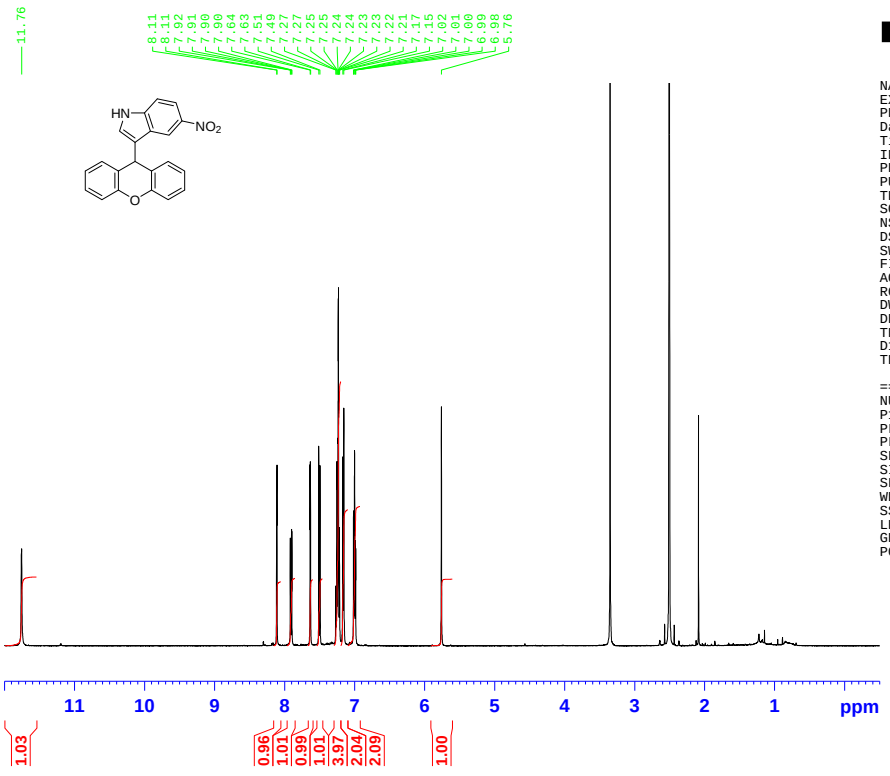

```
NAME        SCE-SD-041 A9-B3
EXPNO                 10
PROCNO                 1
Date_           20121121
Time               14.04
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                  71.8
DW                48.400 usec
DE                 6.50 usec
TE                296.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                11.05 usec
PL1                0.00 dB
PL1W        26.62599564 W
SFO1        500.3530899 MHz
SI                 32768
SF          500.3500689 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



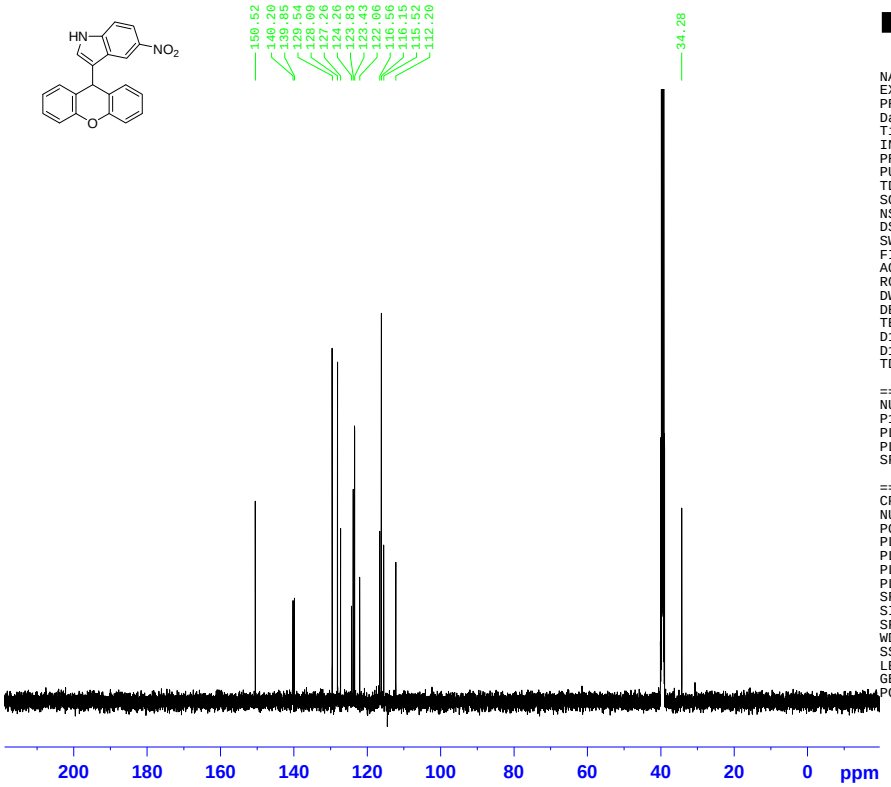

```
NAME        SCE-SD-041 A9-B3
EXPNO                 20
PROCNO                 1
Date_           20121122
Time                3.45
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH           34722.223 Hz
FIDRES         0.529819 Hz
AQ             0.9437684 sec
RG                  32800
DW                14.400 usec
DE                10.00 usec
TE                296.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 6.78 usec
PL1                0.00 dB
PL1W        83.14344025 W
SFO1        125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                0.00 dB
PL12               17.23 dB
PL13               17.23 dB
PL2W        26.62599564 W
PL12W        0.50385541 W
PL13W        0.50385541 W
SFO2        500.3520014 MHz
SI                 32768
SF          125.8131080 MHz
WDW                   EM
SSB                    0
LB                 1.00 Hz
GB                     0
PC                 1.40
```




```
NAME          SCE-SD-041 A9-B3
EXPNO                      21
PROCNO                      1
Date_              20121122
Time                    3.59
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG              dept135
TD                     65536
SOLVENT                CDCl3
NS                       256
DS                         4
SWH                34722.223 Hz
FIDRES              0.529819 Hz
AQ                  0.9437684 sec
RG                      16400
DW                     14.400 usec
DE                     10.00 usec
TE                     296.0 K
CNST2             145.0000000
D1                  2.00000000 sec
D2                  0.00344828 sec
D12                 0.00002000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       6.78 usec
P2                      13.55 usec
PL1                      0.00 dB
PL1W              83.14344025 W
SFO1              125.8275765 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
P3                      11.05 usec
P4                      22.10 usec
PCPD2                   80.00 usec
PL2                      0.00 dB
PL12                    17.23 dB
PL2W              26.62599564 W
PL12W              0.50385541 W
SFO2              500.3520014 MHz
SI                       32768
SF                125.8131080 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

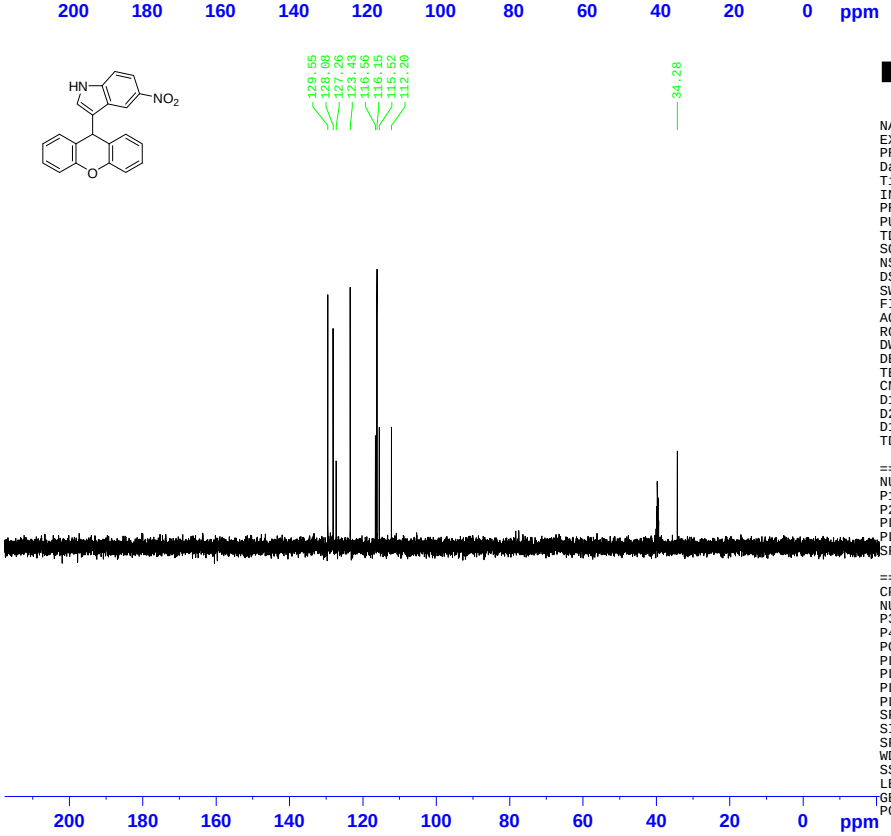



```
NAME          SCE-SD-269 C9-E2
EXPNO                      20
PROCNO                      1
Date_              20130510
Time                    9.46
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                DMSO
NS                        16
DS                         2
SWH                10330.578 Hz
FIDRES              0.157632 Hz
AQ                  3.1719923 sec
RG                        161
DW                     48.400 usec
DE                      6.50 usec
TE                     296.0 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      11.05 usec
PL1                      0.00 dB
PL1W              26.62599564 W
SFO1              500.3530899 MHz
SI                       32768
SF                500.3500000 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```



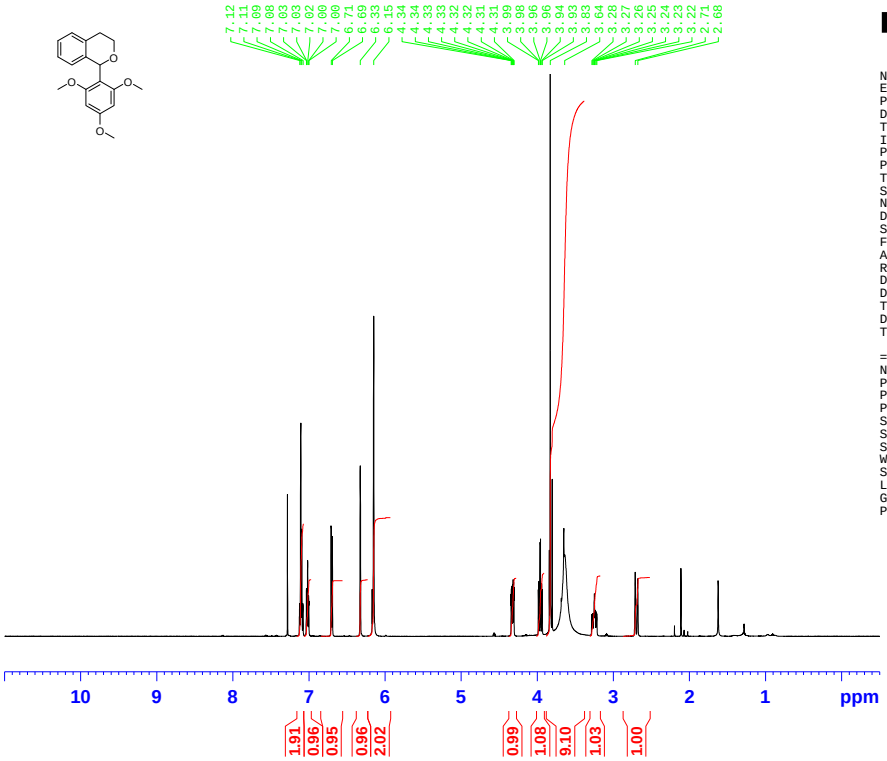
BRUKER

```
NAME        SCE-SD-269 C9-E2
EXPNO                    21
PROCNO                    1
Date_              20130510
Time                  22.49
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG              zgdc30
TD                    65536
SOLVENT                DMSO
NS                     1500
DS                        4
SWH              34722.223 Hz
FIDRES            0.529819 Hz
AQ                0.9437684 sec
RG                    32800
DW                   14.400 usec
DE                   10.00 usec
TE                   296.0 K
D1             0.01000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     6.78 usec
PL1                    0.00 dB
PL1W           83.14344025 W
SFO1          125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                    0.00 dB
PL12                  17.23 dB
PL2W           26.62599564 W
PL12W           0.50385541 W
SFO2          500.3520014 MHz
SI                    32768
SF            125.8131709 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

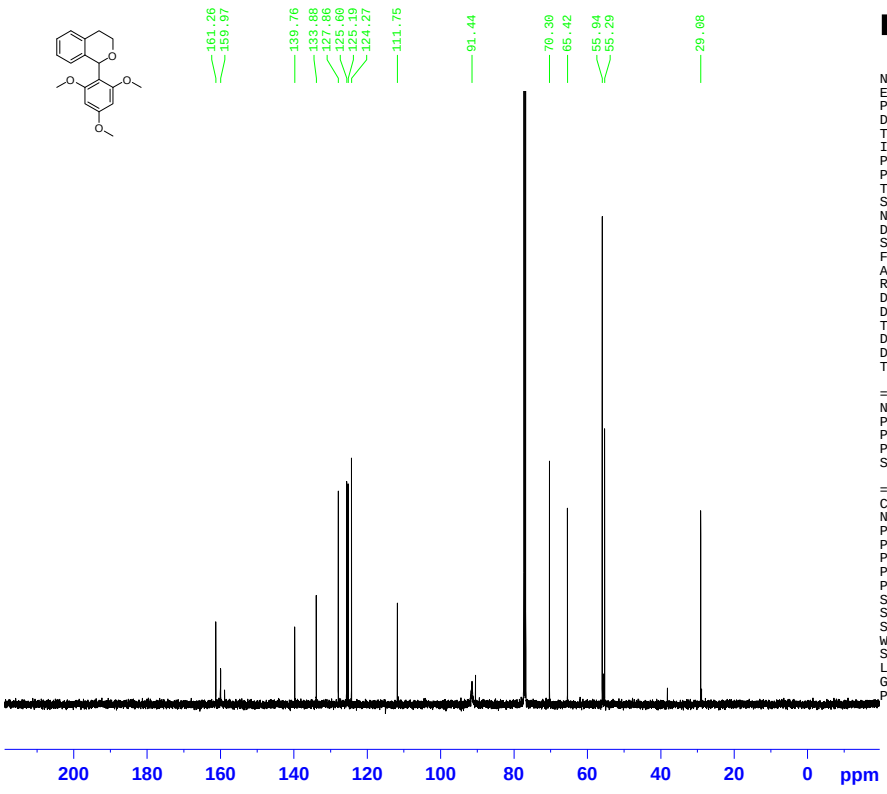


BRUKER

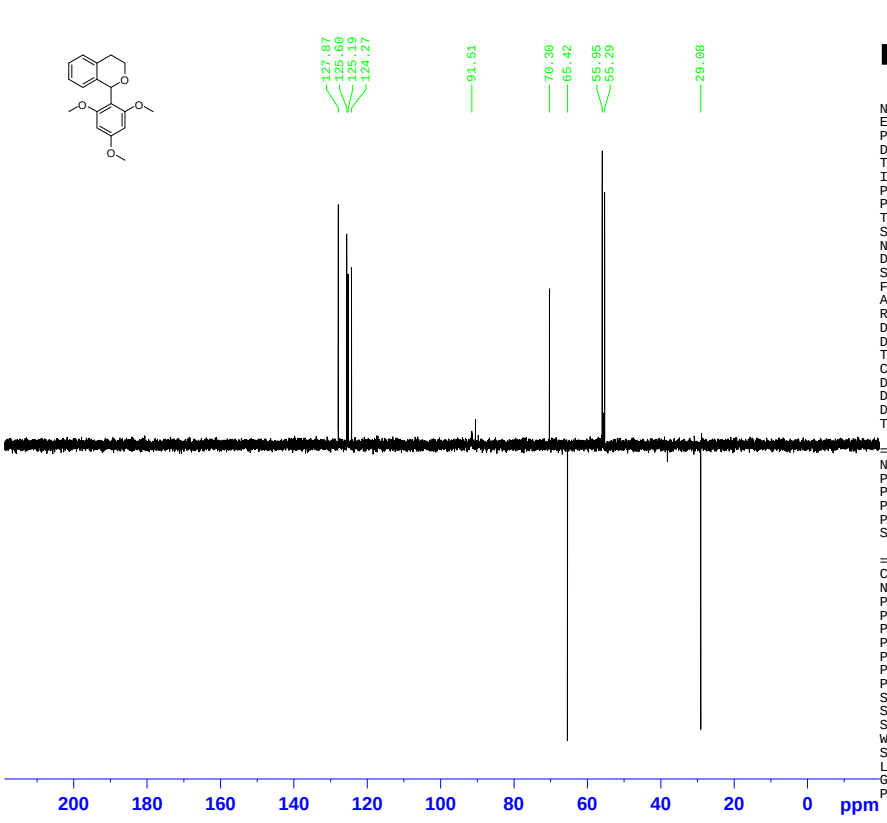
```
NAME        SCE-SD-269 C9-E2
EXPNO                    22
PROCNO                    1
Date_              20130510
Time                  23.03
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             dept135
TD                    65536
SOLVENT                DMSO
NS                      256
DS                        4
SWH              34722.223 Hz
FIDRES            0.529819 Hz
AQ                0.9437684 sec
RG                    16400
DW                   14.400 usec
DE                   10.00 usec
TE                   296.0 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     6.78 usec
P2                    13.55 usec
PL1                    0.00 dB
PL1W           83.14344025 W
SFO1          125.8275765 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
P3                    11.05 usec
P4                    22.10 usec
PCPD2                80.00 usec
PL2                    0.00 dB
PL12                  17.23 dB
PL2W           26.62599564 W
PL12W           0.50385541 W
SFO2          500.3520014 MHz
SI                    32768
SF            125.8131709 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```



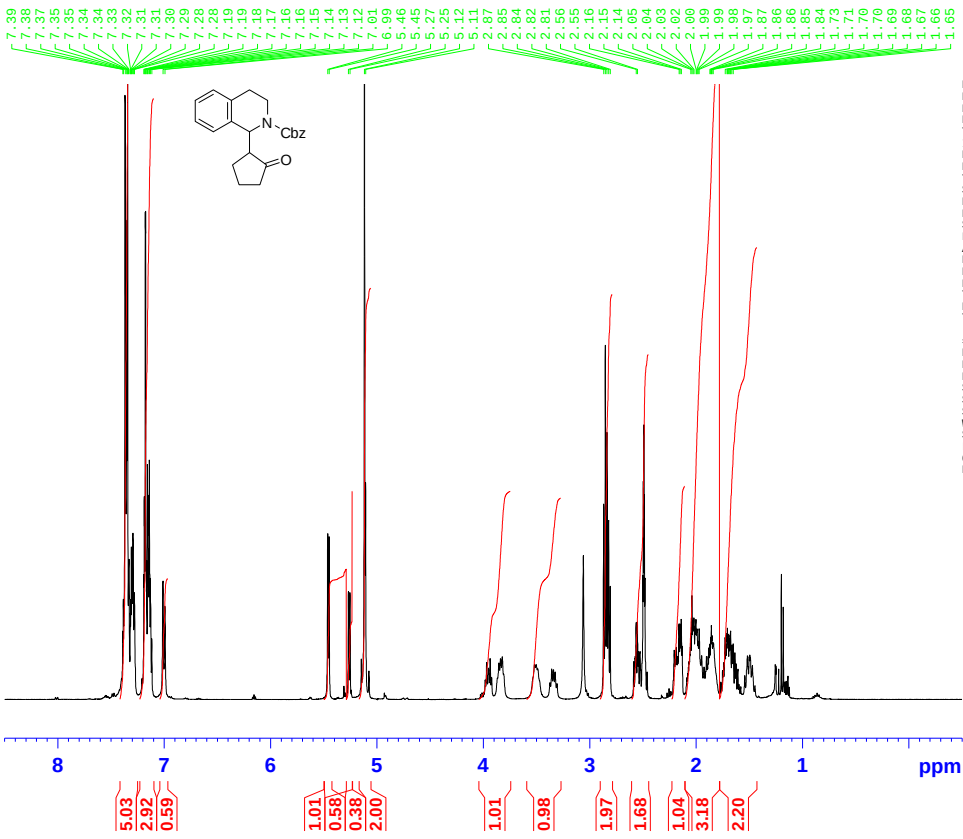

```
NAME        SCE-SE-010 prep upper
EXPNO                  10
PROCNO                  1
Date_            20130520
Time                21.21
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                    161
DW                48.400 usec
DE                 6.50 usec
TE                296.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 11.05 usec
PL1                 0.00 dB
PL1W         26.62599564 W
SFO1         500.3530899 MHz
SI                  32768
SF           500.3500000 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```




```
NAME        SCE-SE-010 prep
EXPNO                  11
PROCNO                  1
Date_            20130521
Time                 8.38
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgdc30
TD                  65536
SOLVENT             CDCl3
NS                   1991
DS                      4
SWH             34722.223 Hz
FIDRES          0.529819 Hz
AQ              0.9437684 sec
RG                  32800
DW                14.400 usec
DE                10.00 usec
TE                296.0 K
D1             0.01000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                 6.78 usec
PL1                 0.00 dB
PL1W         83.14344025 W
SFO1        125.8275761 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PL2                 0.00 dB
PL12               17.23 dB
PL2W         26.62599564 W
PL12W         0.50385541 W
SFO2         500.3520014 MHz
SI                  32768
SF           125.8131080 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

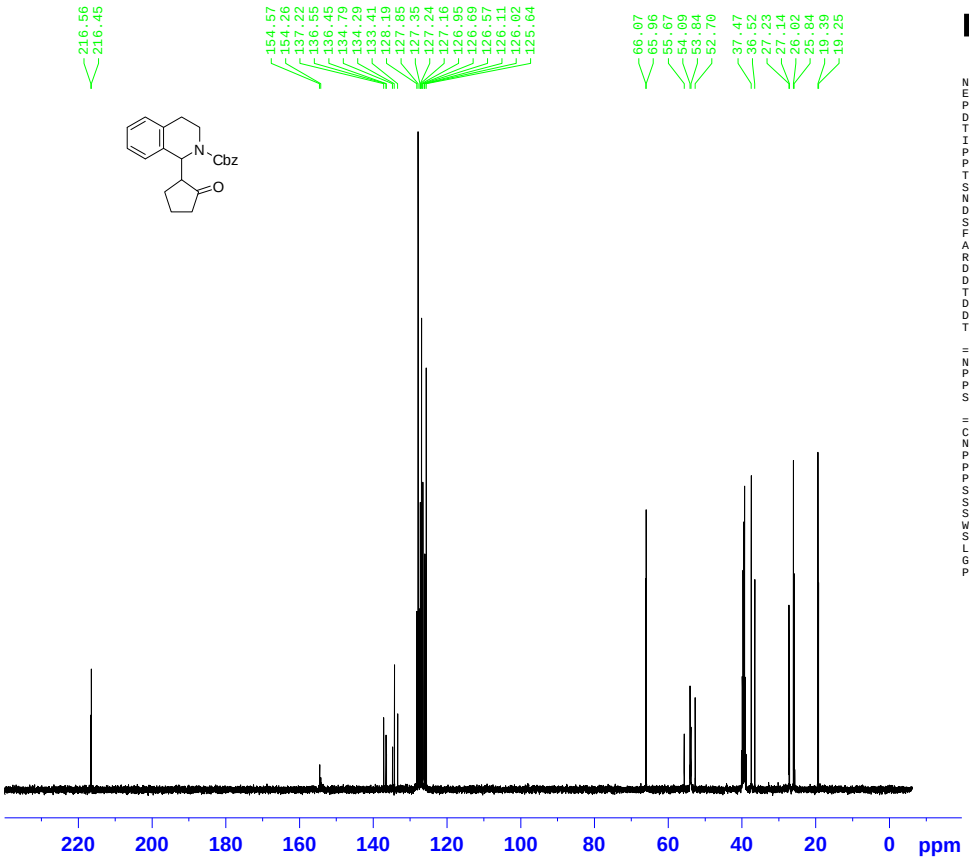



```
NAME          SCE-SE-010 prep
EXPNO                     12
PROCNO                     1
Date_               20130521
Time                   20.52
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG              dept135
TD                     65536
SOLVENT                CDCl3
NS                       256
DS                         4
SWH                34722.223 Hz
FIDRES             0.529819 Hz
AQ                 0.9437684 sec
RG                     16400
DW                    14.400 usec
DE                    10.00 usec
TE                    296.0 K
CNST2             145.0000000
D1                  2.00000000 sec
D2                  0.00344828 sec
D12                 0.00002000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                      6.78 usec
P2                     13.55 usec
PL1                     0.00 dB
PL1W              83.14344025 W
SFO1              125.8275765 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                     1H
P3                     11.05 usec
P4                     22.10 usec
PCPD2                  80.00 usec
PL2                     0.00 dB
PL12                   17.23 dB
PL2W              26.62599564 W
PL12W              0.50385541 W
SFO2              500.3520014 MHz
SI                      32768
SF                125.8131080 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```



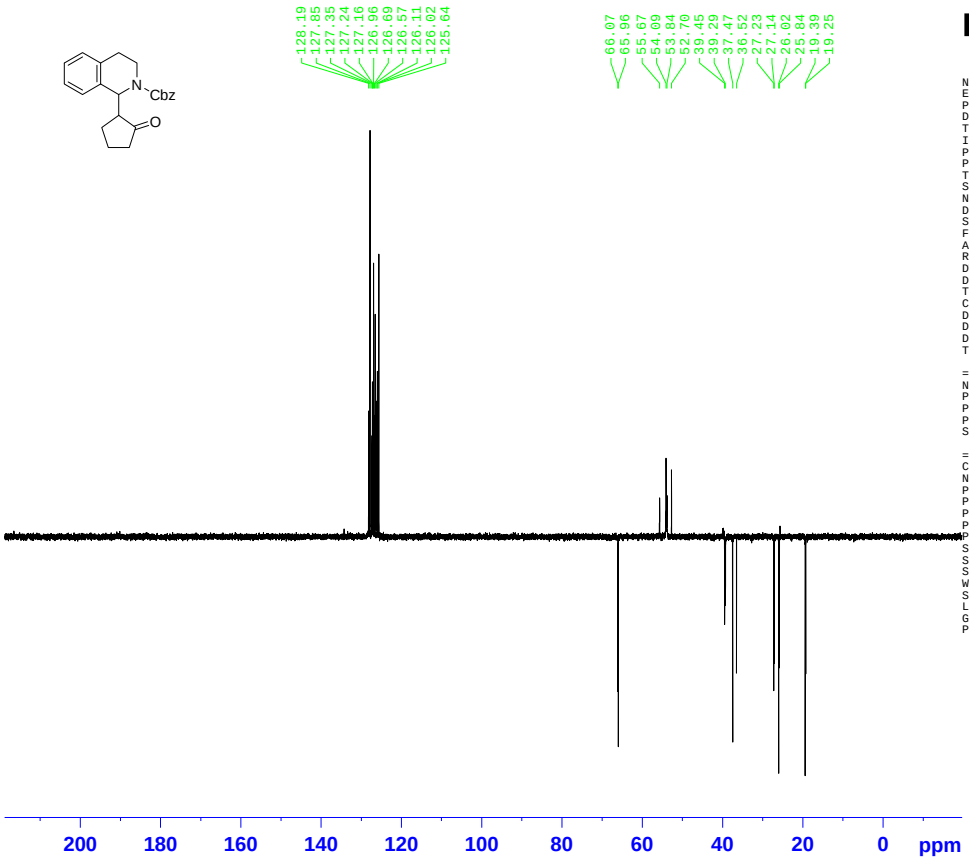

```
NAME          SCE-SC-201 (cyclopentanone)
EXPNO                      1
PROCNO                     1
Date_               20120731
Time                   13.58
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                     32762
SOLVENT                DMSO
NS                        32
DS                         2
SWH                6578.947 Hz
FIDRES             0.200810 Hz
AQ                 2.4899621 sec
RG                      71.8
DW                    76.000 usec
DE                    10.50 usec
TE                    353.0 K
D1                  2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     1H
P1                      9.50 usec
PL1                    -3.00 dB
SFO1              400.1324710 MHz
SI                      32768
SF                400.1300067 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       2.00
```

80 °C



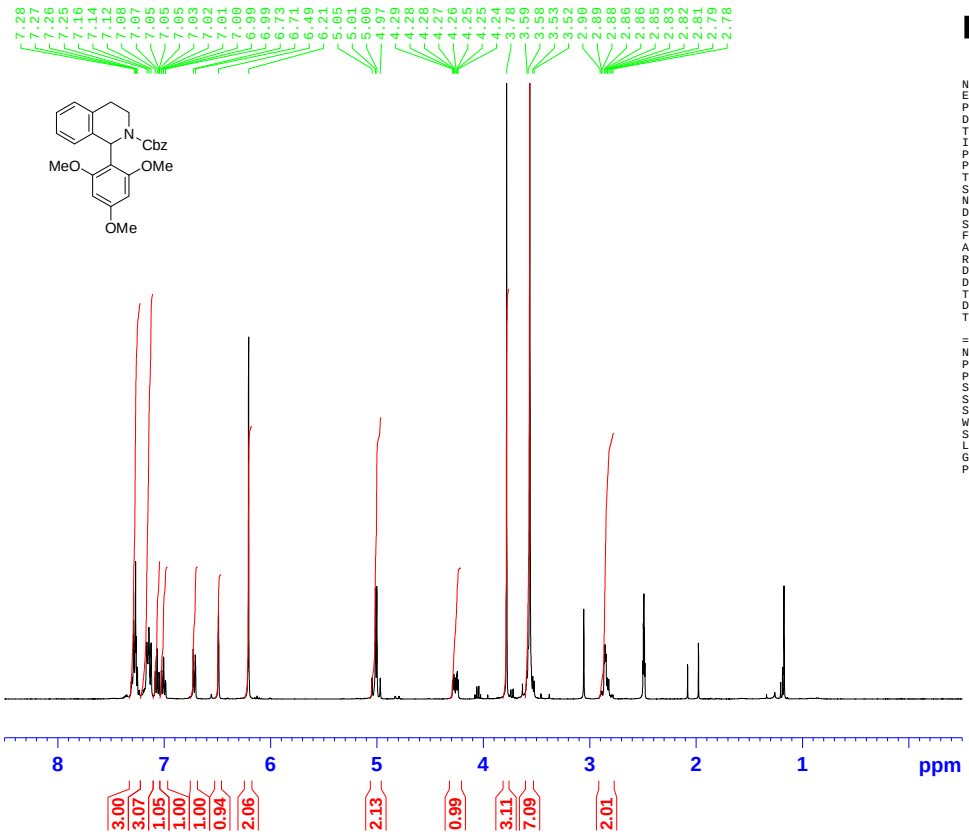

```
NAME        SCE-SC-201 (cyclopentanone)
EXPNO                 2
PROCNO                1
Date_          20120731
Time              14.01
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG         zgdc30
TD                65536
SOLVENT             DMSO
NS                 1000
DS                   12
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0486259 sec
RG                16384
DW               16.000 usec
DE                10.50 usec
TE                353.0 K
D1            0.01000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.50 usec
PL1                0.00 dB
SFO1         100.6278609 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             72.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2         400.1324710 MHz
SI                65536
SF           100.6128601 MHz
WDW                  EM
SSB                   0
LB                 0.80 Hz
GB                    0
PC                 1.40
```

80 °C




```
NAME        SCE-SC-201 (cyclopentanone)
EXPNO                 3
PROCNO                1
Date_          20120731
Time              14.40
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          dept135
TD                65536
SOLVENT             DMSO
NS                  300
DS                   16
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0486259 sec
RG                16384
DW               16.000 usec
DE                10.50 usec
TE                353.0 K
CNST2        135.0000000
D1            2.00000000 sec
D2            0.00370370 sec
D12           0.00002000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.50 usec
P2                19.00 usec
PL1                0.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
P3                10.20 usec
P4                20.40 usec
PCPD2             72.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2         400.1324710 MHz
SI                65536
SF           100.6128601 MHz
WDW                  EM
SSB                   0
LB                 0.80 Hz
GB                    0
PC                 1.40
```

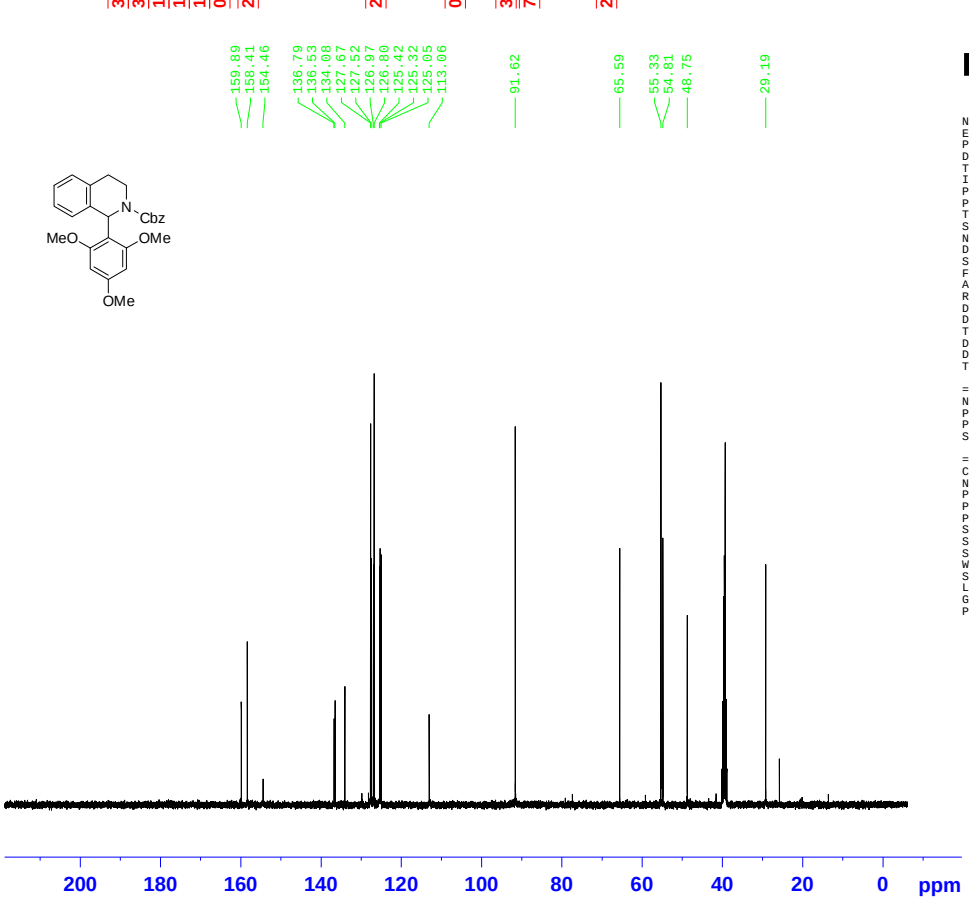
80 °C



NAME SCE-SC-095 (Cbz, TMB, HT 2)
EXPNO 10
PROCNO 1
Date_ 20120724
Time 11.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32762
SOLVENT DMSO
NS 32
DS 2
SWH 6578.947 Hz
FIDRES 0.200810 Hz
AQ 2.4899621 sec
RG 12.7
DW 76.000 usec
DE 10.50 usec
TE 353.0 K
D1 2.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 9.50 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

80 °C

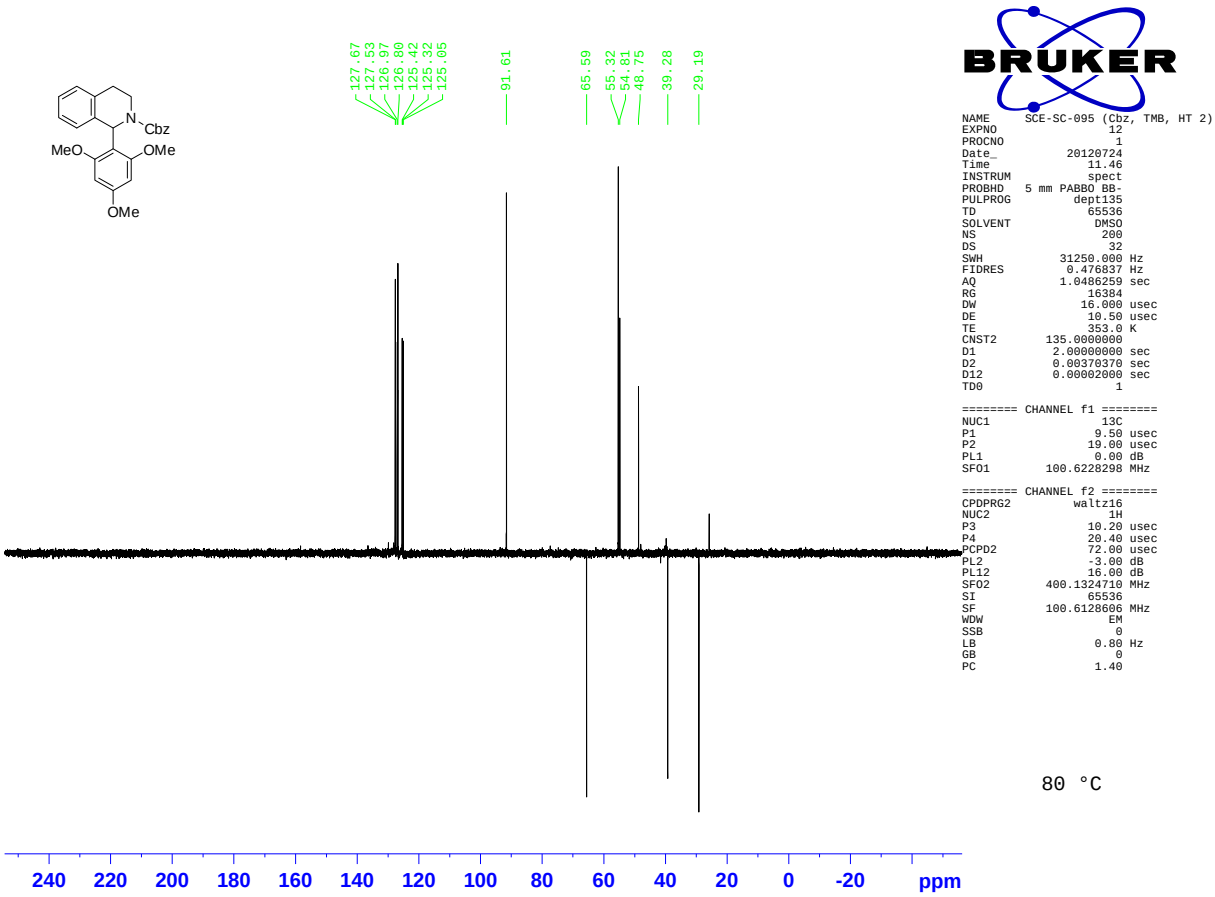


NAME SCE-SC-095 (Cbz, TMB, HT 2)
EXPNO 11
PROCNO 1
Date_ 20120724
Time 11.34
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgdc30
TD 65536
SOLVENT DMSO
NS 800
DS 12
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0486259 sec
RG 11585.2
DW 16.000 usec
DE 10.50 usec
TE 353.0 K
D1 0.01000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 100.6278609 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 72.00 usec
PL2 -3.00 dB
PL12 16.00 dB
SFO2 400.1324710 MHz
SI 65536
SF 100.6128606 MHz
WDW EM
SSB 0
LB 0.80 Hz
GB 0
PC 1.40

80 °C


127.67
127.53
126.97
126.80
125.42
125.32
125.05
91.61
65.59
55.32
54.81
48.75
39.28
29.19
N
Cbz
MeO
OMe
OMe
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
ppm
BRUKER
NAME SCE-SC-095 (Cbz, TMB, HT 2)
EXPNO 12
PROCNO 1
Date_ 20120724
Time 11.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG dept135
TD 65536
SOLVENT DMSO
NS 200
DS 32
SWH 31250.000 Hz
FIDRES 0.476837 Hz
AQ 1.0486259 sec
RG 16384
DW 16.000 usec
DE 10.50 usec
TE 353.0 K
CNST2 135.0000000
D1 2.00000000 sec
D2 0.00370370 sec
D12 0.00002000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
P2 19.00 usec
PL1 0.00 dB
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
P3 10.20 usec
P4 20.40 usec
PCPD2 72.00 usec
PL2 -3.00 dB
PL12 16.00 dB
SFO2 400.1324710 MHz
SI 65536
SF 100.6128606 MHz
WDW EM
SSB 0
LB 0.80 Hz
GB 0
PC 1.40
80 °C

5 Supplementary References

[1] H. E. Gottlieb, V. Kotlyar, A. Nudelmann, *J. Org. Chem.* **1997**, *62*, 7512-7515.

[2] R. Schulte-Ladbeck, P. Kolla, U. Karst, *Analytical Chemistry* **2003**, *75*, 731-735.

[3] Á. Pintér, A. Sud, D. Sureshkumar, M. Klussmann, *Angew. Chem. Int. Ed.* **2010**, *49*, 5004-5007.

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