Electronic supplementary information

for

Catalyst-free aerobic photooxidation of sensitive benzylic alcohols with chemoselectivity controlled by DMSO solvent

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Content:

S1. General procedures

Materials and Instrumentation: chemicals were purchased at Sigma-Aldrich and Fluorochem. The solvents were purified and dried using standard procedures. Commercially obtained reagents were used as received without further purification unless otherwise stated. Thin layer chromatography (TLC) analyses were carried out on DC Alufolien Kieselgel 60 F254 (Merck). The compounds were visualised with UV light (254 and 366 nm). Compound structures were drawn and named using ChemDraw. **Nuclear magnetic resonance** (NMR) spectra were recorded on a Agilent 400-MR DDR2 (399.94 MHz for ^{1}H, 100.58 MHz for ^{13}C), or JNM-ECZL400S spectrometer (JEOL Ltd., (399.94 MHz for ^{1}H, 100.58 MHz for ^{13}C) at 298 K. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad etc.), coupling constant (Hz), and integration. All NMR spectra were processed and assigned using MestreNova. **Mass spectra** were obtained on single quadrupol DSQ II mass spectrometer equipped with an electron ionization (EI+ 70eV) ion source with Trace Ultra gas chromatograph (Thermo Scientific). Agilent JW DB-5 30 m x 0.25 mm, film 0.25 um GC column was used. **The melting points** were measured on a Boetilus melting point apparatus and are uncorrected. **Cyclic voltammetry measurements** were performed on PGSTAT204 (Autolab-Metrohm) (see Chapter S7 for details on cyclic voltammetry measurements).

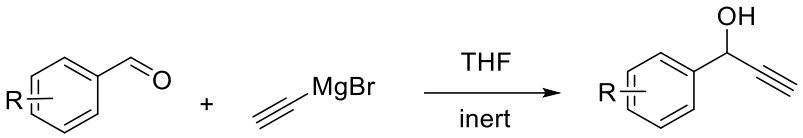
Photophysical measurements: **UV-Vis absorption spectra** were recorded on the SHIMADZU UV-2550-230V spectrophotometer. **Fluorescence emission spectra and quantum yields** were measured using the Horiba Jobin Yvon Fluorolog-322 spectrofluorometer. The quantum yields of flavins were determined by preparing a series of dilutions with optical density ranging from 0.02 to 0.07 and excited at their respective absorption maxima, λ_{abs} Lumichrome (LC) has been used as a standard for fluorescence quantum yield (Φ_F = 0.028, λ_{exc} = 380nm). Radiative and non-radiative decay constants for the lowest excited singlet state were calculated as $k_r = \Phi_F/\tau_F$, and $\Sigma_{knr} = (1- \Phi_F)/\tau_F$. **The singlet oxygen quantum yields** also were determined using the gradient method by preparing a series of dilutions. Measurements were taken on the Pico Quant-Fluo Time 300- fluorescence lifetime spectrometer equipped with an H10220B-45 NIR-PMT module, sensitive in the 950-1400 NIR range, with excitation (λ_{exc} = 408nm or 378nm) using perinaphthenone as standard, (Φ_Δ = 0.95, λ_{exc} = 408nm). The excitation source for steady-state emission spectra was a xenon lamp with monochromator. Phosphorescence decays were measure at around 1270nm using a pulsed laser diode head λ_{exc} = 408nm or 378nm. **Femtosecond UV-vis transient absorption spectra** were obtained using a commercially available system (Ultrafast Systems, Helios).[1] Experiments were performed at the excitation wavelength 365nm (**1a**) or 350 nm (**2a**), with 1 or 2 μJ energy per pulse, respectively. The pump diameter (FWHM) at the sample was ≈250 μm. Probing white light continuum pulse (330−660 nm) was generated in a CaF2 plate and the residual presence of the residual 800 nm pulse was reduced using CG-BG-38 Shott filter in front of the sample. Sample solution in 2 mm thick quartz cell was stirred by a Teflon-coated bar. The recorded transient absorption spectra were corrected for the chirp using Surface Xplorer software. Convolution with the instrument response function (ca. 150 fs FWHM) was included into the fitting procedure. **Nanosecond laser flash photolysis** was performed with a home-built setup described previously[2] using third harmonic (355 nm, 8 ns FWHM) of Q-switched Nd:YAG laser (Continuum Surelite II) and 150 W xenon arc lamp (Applied Photophysics) operating in the pulsed mode. A Pellin Broca prism was used for the laser beam to ensure selective sample excitation with only 355 nm pulses. Energy of laser pulses was set at 1 mJ. 1 cm × 1 cm fused silica cell without stirring was used. The cell was equipped with a Rotaflo valve to perform argon bubbling upon sample deaeration prior to the experiment.

Photochemical Setup: Reactions were performed in vessels from borosilicate glass using commercial LED(s) as a light source: LED Engine, 1.35 W@700 mA, 400 nm (dominant wavelengths 385-410 nm). For details, see Chapter S5.

S2. Preparation of benzylic alcohols with multiple bond

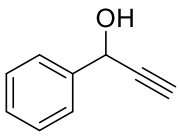
Preparation of 1-phenylpropargyl alcohols

General procedure



A solution of aldehyde (1 equiv.) in dry THF was cooled in ice bath to 0 °C under argon atmosphere. Ethynylmagnesium bromide (1.2 - 1.3 equiv.) was added dropwise to the solution. The cooling bath was removed, and the reaction mixture was stirred at room temperature for several hours and monitored by TLC. The reaction was quenched with saturated NH_4Cl (20 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with water (100 mL) saturated brine (100 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give pure propargylic alcohol **1**.

*1-Phenylprop-2-yn-1-ol **(1a)***



Alkyne **1a** was prepared according to a general procedure from benzaldehyde (1.06 g, 10.0 mmol) and ethynylmagnesium bromide (0.5 M in THF; 26.0 mL, 13.0 mmol) in dry THF (20 mL). The solution was stirred 2.5 hours and monitored by TLC (hexan-EtOAc, 3:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 3:1). Following the procedure, alkyne **1a** was prepared in an isolated yield of 77% (1.02 g) as a yellow oil.

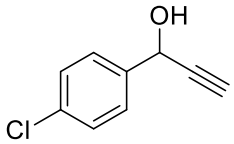
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.51 – 7.43 (m, 2H), 7.41 – 7.33 (m, 2H), 7.30 (d, *J* = 7.3 Hz, 1H), 6.06 (d, *J* = 5.5 Hz, 1H), 5.39 – 5.33 (m, 1H), 3.50 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 141.9, 128.3, 127.7, 126.4, 85.8, 75.9, 62.4.

HR-MS (EI) calculated for C_9H_8O [M^+]: 132.057; **observed**: 132.058.

Spectral data are in agreement with previously published characterization data.[3]

*1-(4-Chlorophenyl)prop-2-yn-1-ol **(1b)***



Alkyne **1b** was prepared according to a general procedure from 4-chlorbenzaldehyde (0.70 g, 5.0 mmol) and ethynylmagnesium bromide (0.5 M in THF; 12.0 mL, 6.0 mmol) in dry THF (10 mL). The solution was stirred for 3 hours and monitored by TLC (hexan-EtOAc, 3:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 3:1). Following the procedure, alkyne **1b** was prepared in an isolated yield of 77% (0.64 g) as a brown oil.

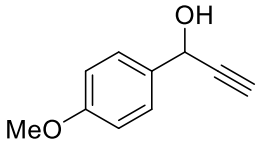
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.51 – 7.45 (m, 2H), 7.45 – 7.39 (m, 2H), 6.17 (d, *J* = 5.9 Hz, 1H), 5.41 – 5.34 (m, 1H), 3.53 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 141.0, 132.2, 128.3, 128.3, 85.1, 76.2, 61.7.

HR-MS (EI) calculated for C_9H_7ClO [M^+]: 166.019; **observed**: 166.017.

Spectral data are in agreement with previously published characterization data.[3]

1-(4-Methoxyphenyl)prop-2-yn-1-ol ***(1c)***



Alkyne **1c** was prepared according to a general procedure from 4-anisaldehyde (1.36 g, 10.0 mmol) and ethynylmagnesium bromide (0.5 M in THF; 24.0 mL, 12.0 mmol) in dry THF (10 mL). The solution was stirred for 3 hours and monitored by TLC (hexan-EtOAc, 2:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 2:1). Following the procedure, alkyne **1c** was prepared in isolated yield of 74% (1.20 g) as a yellow oil.

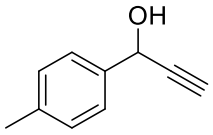
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.43 – 7.34 (m, 2H), 6.96 – 6.88 (m, 2H), 5.94 (d, *J* = 5.9 Hz, 1H), 5.30 (dd, *J* = 5.9, 2.3 Hz, 1H), 3.74 (s, 3H), 3.47 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 158.8, 134.0, 134.1, 127.8, 113.6, 85.8, 75.6, 62.0.

HR-MS (EI) calculated for $C_{10}H_{10}O_2$ [M^+]: 162.068; **observed**: 162.068.

Spectral data are in agreement with previously published characterization data.[3]

1-(p-Tolyl)prop-2-yn-1-ol ***(1d)***



Alkyne **1d** was prepared according to a general procedure from *p*-tolualdehyde (1.40 g, 12.0 mmol) and ethynylmagnesium bromide (0.5 M in THF; 30.0 mL, 15.0 mmol) in dry THF (10 mL). The solution was stirred for 3 hours and monitored by TLC (hexan-EtOAc, 2:1). Following the procedure (without column chromatography), alkyne **1d** was prepared in isolated yield of 87% (1.49 g) as a brown oil.

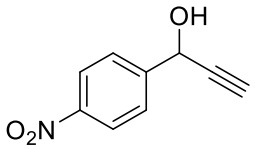
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.37 – 7.28 (m, 2H), 7.20 – 7.11 (m, 2H), 5.96 (d, *J* = 5.9 Hz, 1H), 5.29 (dd, *J* = 6.0, 2.3 Hz, 1H), 3.47 (d, *J* = 2.3 Hz, 1H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 139.0, 136.7, 128.7, 126.4, 85.7, 75.6, 62.2, 20.7.

HR-MS (EI) calculated for $C_{10}H_{10}O$ [M^+]: 146.073; **observed**: 146.074.

Spectral data are in agreement with previously published characterization data.[4]

1-(4-Nitrophenyl)prop-2-yn-1-ol ***(1e)***



Alkyne **1e** was prepared according to a general procedure from *p*-nitrobenzaldehyde (1.03 g, 6.8 mmol) and ethynylmagnesium bromide (0.5 M in THF; 16.0 mL, 8.0 mmol) in dry THF (10 mL). The solution was stirred for 1.5 hours and monitored by TLC (hexan-EtOAc, 2:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 2:1). Following the procedure, alkyne **1e** was prepared in isolated yield of 54% (0.65 g) as a yellow solid, m.p.: 55-56 °C.

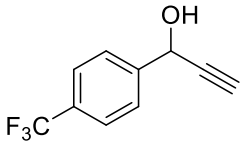
^{1}H NMR (400 MHz, DMSO-D6) δ 8.29 – 8.21 (m, 2H), 7.77 – 7.68 (m, 2H), 6.42 (d, J = 6.0 Hz, 1H), 5.54 (dd, J = 5.8, 2.3 Hz, 1H), 3.62 (d, J = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 149.3, 146.9, 127.5, 123.6, 84.5, 76.8, 61.6.

HR-MS (APCI) calculated for $C_9H_7NO_3$ [M^+]: 177.04259; **observed**: 177.04240.

Spectral data are in agreement with previously published characterization data.[3]

1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol ***(1f)***



Alkyne **1f** was prepared according to a general procedure from *p*-trifluoromethylbenzaldehyde (1.5 g, 8.6 mmol) and ethynylmagnesium bromide (0.5 M in THF; 18 mL, 9.5 mmol) in dry THF (10 mL). The solution was stirred for 3 hours and monitored by TLC (hexan-EtOAc, 4:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 4:1). Following the procedure, alkyne **1f** was prepared in isolated yield of 71% (1,23 g) as an orange oil.

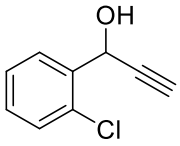
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.77 – 7.72 (m, 2H), 7.70 – 7.65 (m, 2H), 6.29 (d, *J* = 6.0 Hz, 1H), 5.48 (ddt, *J* = 6.7, 2.2, 0.7 Hz, 1H), 3.60 – 3.54 (m, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 147.0 (q, J_{CF} = 1.4 Hz), 128.7 (q, J_{CF} = 46. Hz), 127.6, 125.8 (q, J_{CF} = 5.9 Hz, 85.4, 76.9, 62.3.

HR-MS (EI) calculated for $C_{10}H_7F_3O$ [M^+]: 200.045; **observed**: 200.047.

Spectral data are in agreement with previously published characterization data.[4]

1-(2-Chlorophenyl)prop-2-yn-1-ol ***(1g)***



Alkyne **1g** was prepared according to a general procedure from 2-chlorbenzaldehyde (1.40 g, 10.0 mmol) and ethynylmagnesium bromide (0.5 M in THF; 24.0 mL, 12.0 mmol) in dry THF (10 mL). The solution was stirred for 3 hours and monitored by TLC (hexan-EtOAc, 3:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 3:1). Following the procedure, alkyne **1g** was prepared in isolated yield of 71% (1.18 g) as a pale yellow oil.

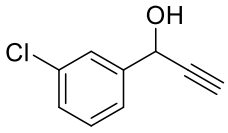
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.74 – 7.66 (m, 1H), 7.45 – 7.41 (m, 1H), 7.39 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.34 (td, *J* = 7.5, 1.8 Hz, 1H), 6.31 – 6.25 (m, 1H), 5.56 (dd, *J* = 5.7, 2.3 Hz, 1H), 3.49 (d, *J* = 2.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 139.1, 131.2, 129.5, 129.3, 127.9, 127.4, 84.1, 75.7, 59.5.

HR-MS (EI) calculated for C_9H_7ClO [M^+]: 166.019; **observed**: 166.019.

Spectral data are in agreement with previously published characterization data.[5]

1-(3-Chlorophenyl)prop-2-yn-1-ol ***(1h)***



Alkyne **1h** was prepared according to a general procedure from 3-chlorbenzaldehyde (0.70 g, 5.0 mmol) and ethynylmagnesium bromide (0.5 M in THF; 12.0 mL, 6.0 mmol) in dry THF (10 mL). The solution was stirred for 3 hours and monitored by TLC (hexan-EtOAc, 3:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 3:1). Following the procedure, alkyne **1h** was prepared in an isolated yield of 79% (0.66 g) as a yellow oil.

^{1}H NMR (400 MHz, DMSO-D_6) δ 7.48 (tt, *J* = 1.4, 0.9 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.39 – 7.34 (m, 1H), 6.22 (d, *J* = 6.1 Hz, 1H), 5.39 (ddt, *J* = 6.1, 2.3, 0.7 Hz, 1H), 3.56 (d, *J* = 2.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D6) δ 144.3, 132.7, 130.1, 127.4, 125.9, 124.9, 84.7, 75.5, 61.5.

HR-MS (EI) calculated for C_9H_7ClO [M^+]: 166.019; **observed**: 166.017.

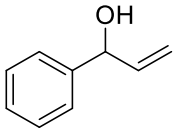
Spectral data are in agreement with previously published characterization data.[6]

Preparation of 1-phenylallyl alcohols

General procedure

A solution of aldehyde (1 equiv.) in dry THF was cooled in an ice bath to 0 °C under argon atmosphere. Vinylmagnesium bromide (1.1 - 1.3 equiv.) was added dropwise to the solution. The cooling bath was removed, and the reaction mixture was stirred at room temperature for several hours and monitored by TLC. The reaction was quenched with saturated NH_4Cl (20 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with water (100 mL) saturated brine (100 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give pure allylic alcohol **1**.

*1-Phenylprop-2-en-1-ol **(6a)***



Alkene **6a** was prepared according to a general procedure from benzaldehyde (2.08 g, 19.6 mmol) and vinylmagnesium bromide (0.7 M in THF; 34.0 mL, 23.5 mmol) in dry THF (20 mL). The solution was stirred 4 hours and monitored by TLC (hexan-EtOAc, 3:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 3:1). Following the procedure, alkene **6a** was prepared in isolated yield of 71% (1.85 g) as a pale yellow oil.

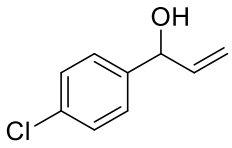
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.32 (dq, *J* = 3.9, 1.9 Hz, 2H), 7.23 (qdd, *J* = 4.8, 3.9, 2.0 Hz, 2H), 5.94 (ddddd, *J* = 13.8, 8.6, 6.0, 3.7, 2.7 Hz, 1H), 5.55 – 5.46 (m, 1H), 5.30 – 5.19 (m, 1H), 5.05 (ddtt, *J* = 9.3, 6.3, 3.2, 1.6 Hz, 1H), 3.42 – 3.31 (m, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 144.3, 142.1, 128.1, 126.9, 126.2, 113.3, 73.4.

HR-MS (EI) calculated for $C_9H_{10}O$ [M^+]: 134.073; **observed**: 134.073.

Spectral data are in agreement with previously published characterization data.[7]

*1-(4-Chlorophenyl)prop-2-en-1-ol **(6b)***



Alkene **6b** was prepared according to a general procedure from 4-chlorbenzaldehyde (1.06 g, 7.6 mmol) and vinylmagnesium bromide (0.7 M in THF; 12.0 mL, 8.3 mmol) in dry THF (15 mL). The solution was stirred for 3 hours and monitored by TLC (hexan-EtOAc, 10:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 7:1). Following the procedure, alkene **6b** was prepared in isolated yield of 74% (0.94 g) as a pale yellow oil.

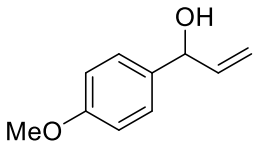
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.43 – 7.28 (m, 4H), 5.98 – 5.85 (m, 1H), 5.61 (d, *J* = 4.5 Hz, 1H), 5.25 (ddd, *J* = 17.1, 1.9, 1.5 Hz, 1H), 5.13 – 5.01 (m, 1H), 3.37 (m, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 143.3, 141.7, 131.4, 128.1, 128.0, 113.8, 72.7.

HR-MS (EI) calculated for C_9H_9ClO [M^+]: 168.034; **observed**: 168.035.

Spectral data are in agreement with previously published characterization data.[7]

1-(4-Methoxyphenyl)prop-2-en-1-ol ***(6c)***



Alkene **6c** was prepared according to a general procedure from anisaldehyde (0.82 g, 6.0 mmol) and vinylmagnesium bromide (0.7 M in THF; 10.3 mL, 7.2 mmol) in dry THF (10 mL). The solution was stirred for 3 hours and monitored by TLC (hexan-EtOAc, 3:1). After extraction, the product was purified by column chromatography (hexan-EtOAc, 3:1). Following the procedure, alkene **6c** was prepared in isolated yield of 68% (0.67 g) as a pale-yellow oil.

^{1}H NMR (400 MHz, DMSO-D_6) δ 7.28 – 7.18 (m, 2H), 6.94 – 6.83 (m, 2H), 6.00 – 5.86 (m, 1H), 5.38 (dd, *J* = 4.5, 0.5 Hz, 1H), 5.21 (ddd, *J* = 17.1, 2.1, 1.4 Hz, 1H), 5.06 – 4.96 (m, 2H), 3.73 (d, *J* = 0.5 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 158.2, 142.3, 136.3, 127.4, 113.5, 113.0, 73.0, 55.0.

HR-MS (EI) calculated for $C_{10}H_{12}O_2$ [M^+]: 164.084; **observed**: 164.082.

Spectral data are in agreement with previously published characterization data.[7]

S3. UV/Vis spectra of alcohols

UV/Vis spectra were recorded on a UV-VIS HP8454 (Hewlet Packard) spectrophotometer at 25 °C in analytical-grade solvents. Spectra were processed by using Microsoft Excel and Origin 2018 (OriginLab). The were recorded at different concentrations: "analytical" concentration (given in Figures) and concentration c = 0.25 mol L^{-1}, which is the same as concentration in photooxidation reaction mixtures.

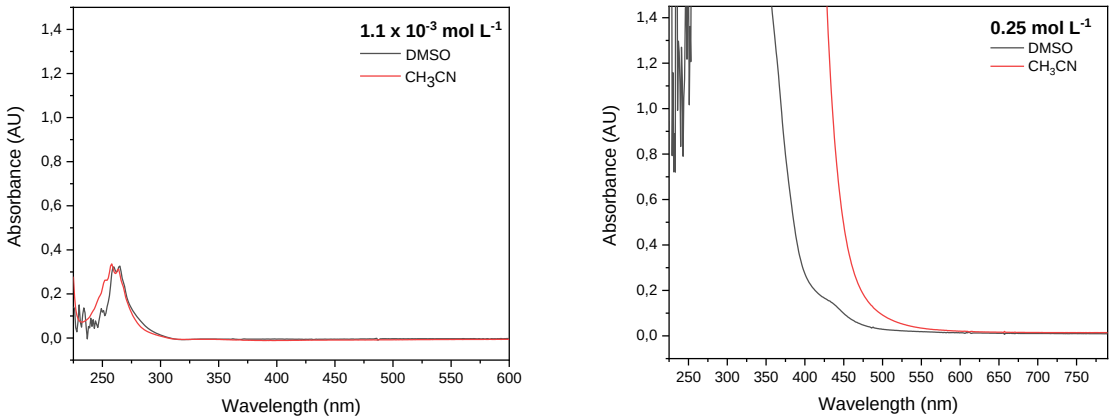


Figure S1. UV/Vis spectrum of 1-phenylprop-2-yn-1-ol (**1a**) in DMSO and acetonitrile.

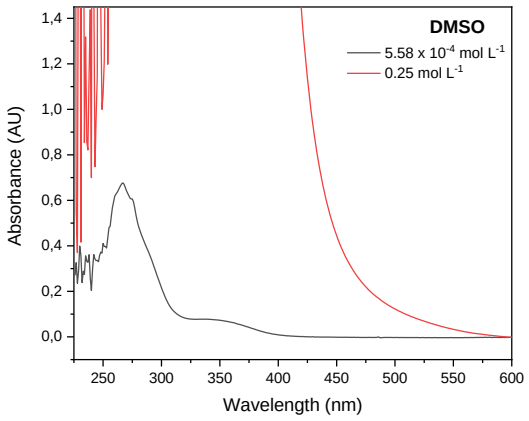


Figure S2. UV/Vis spectrum of 1-(4-chlorophenyl)prop-2-yn-1-ol (**1b**).

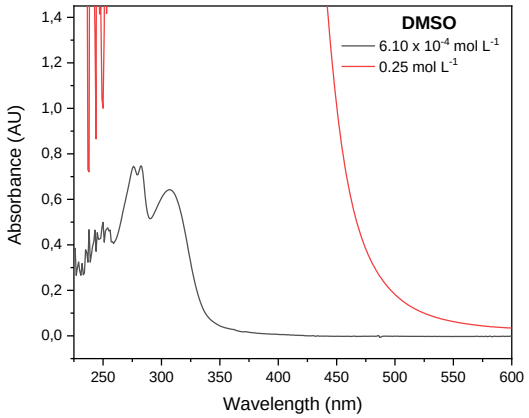


Figure S3. UV/Vis spectrum of 1-(4-methoxyphenyl)prop-2-yn-1-ol (**1c**).

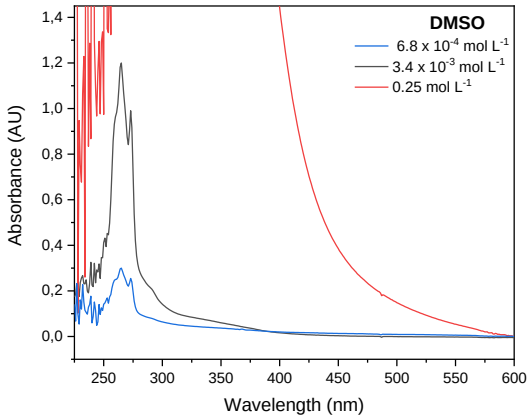


Figure S4. UV/Vis spectrum of 1-(*p*-tolyl)prop-2-yn-1-ol (**1d**).

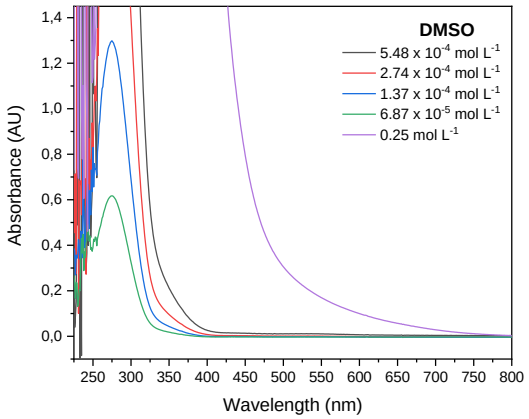


Figure S5. UV/Vis spectrum of 1-(4-nitrophenyl)prop-2-yn-1-ol (**1e**).

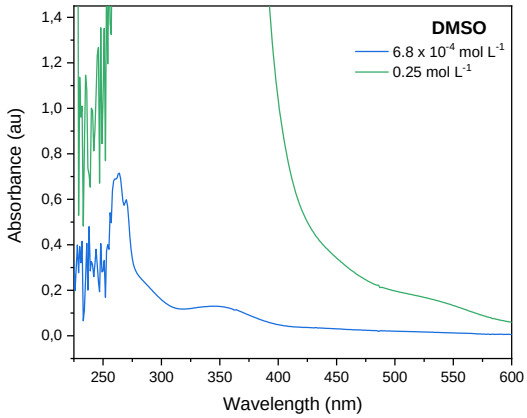


Figure S6. UV/Vis spectrum of 1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol **(1f).**

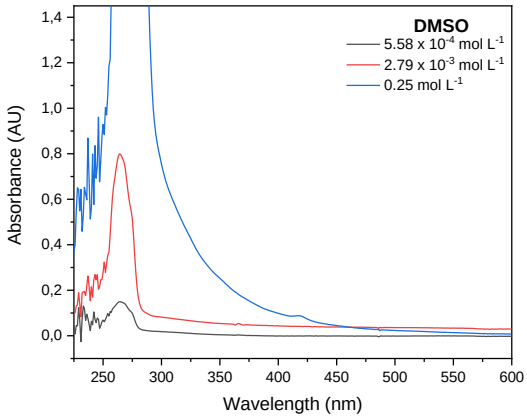


Figure S7. UV/Vis spectrum of 1-(2-chlorophenyl)prop-2-yn-1-ol (**1g**).

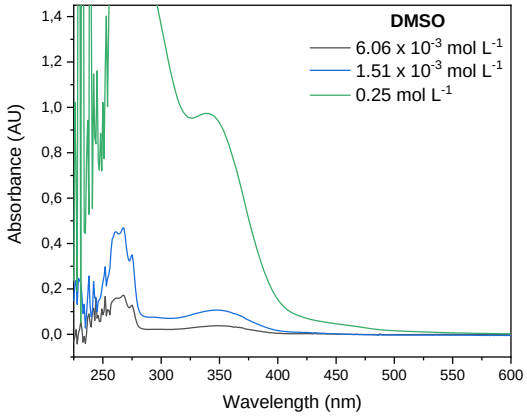


Figure S8. UV/Vis spectrum of 1-(3-chlorophenyl)prop-2-yn-1-ol (**1h**).

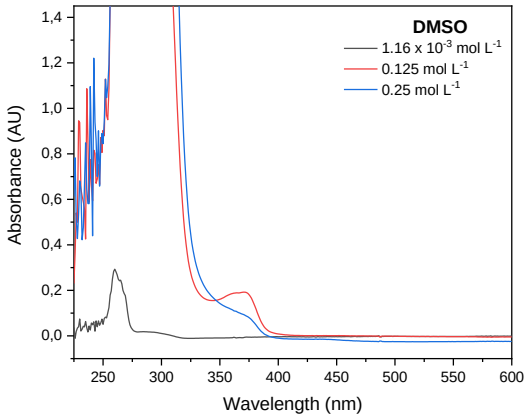


Figure S9. UV/Vis spectrum of 1-phenylprop-2-en-1-ol (**6a**).

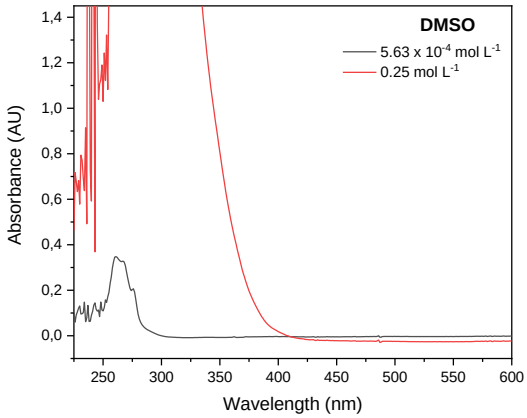


Figure S10. UV/Vis spectrum of 1-(4-chlorophenyl)prop-2-en-1-ol (**6b**).

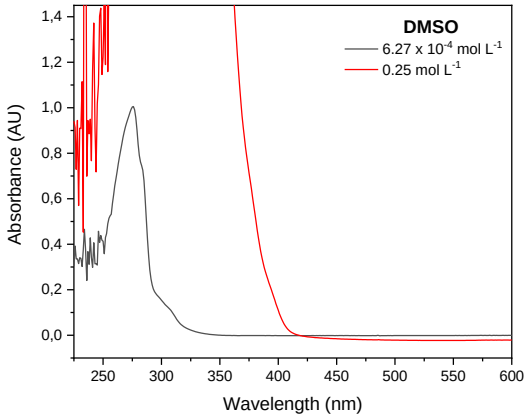


Figure S11. UV/Vis spectrum of 1-(4-methoxyphenyl)prop-2-en-1-ol (**6c**).

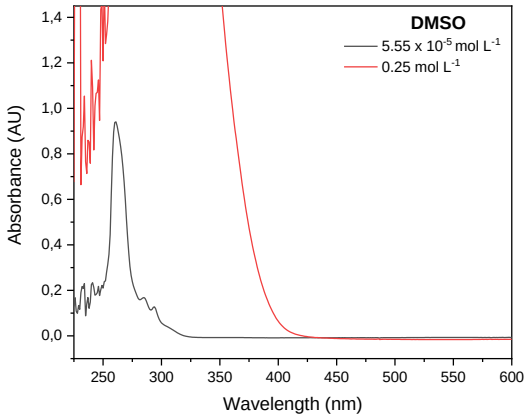


Figure S12. UV/Vis spectrum of cinnamyl alcohol (**8**).

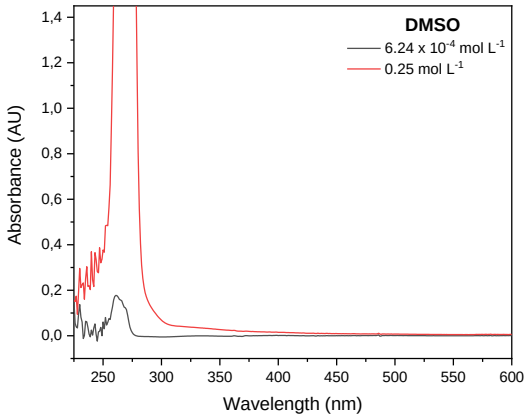


Figure S13. UV/Vis spectrum of diphenylmethanol (**10**).

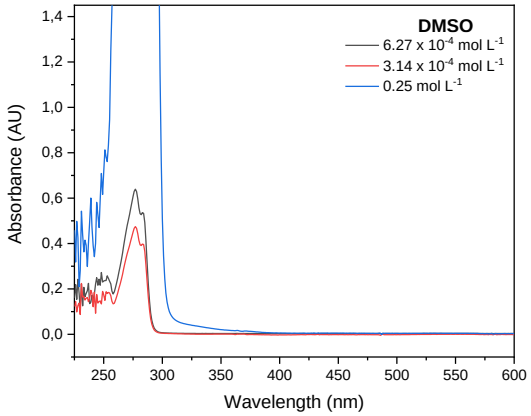
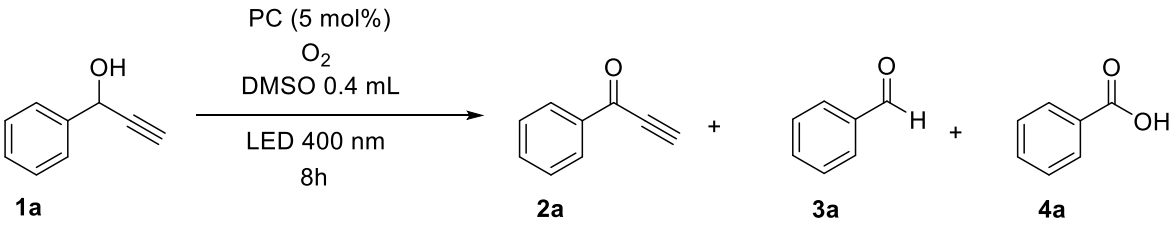
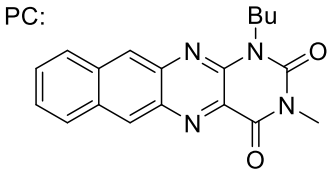


Figure S14. UV/Vis spectrum of 1-(4-methoxyphenyl)ethanol (**12**).

S4. Preliminary experiments on photooxidations

Table S1. Oxidation of benzylic alcohols with flavin catalyst (for synthesis of flavin catalyst, se ref.[8]). For experimental, see Chapter S5.



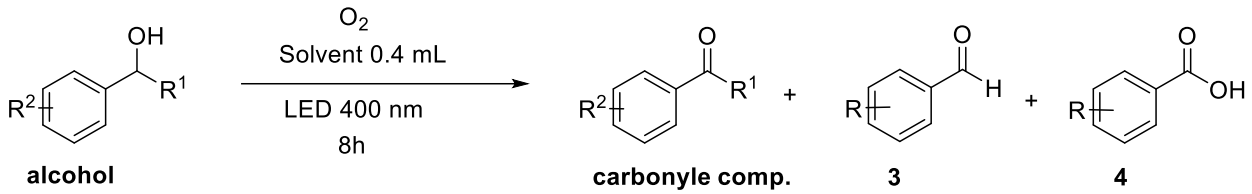


Entry	Starting compound	Conditions alternation	Conversion [%][a]			
			1a	**2a**	**3a**	**4a**
1	**1a**	-	77	21	1	1
2	**1a**	without PC	4	90	2	4

[a] Determined by GC-MS

S5. Catalyst- and additive-free photooxidations

Analytical experiments



alcohol **carbonyle comp.** **3** **4**

In a vial with septum (3 mL), an alcohol (0.1 mmol) was dissolved in dry DMSO (0.4 mL). The reaction mixture was bubbled with oxygen around 1 minute and tempered to 25 or 45 °C with aluminium block equipped Peltier unit. Then, the reaction mixture was stirred and irradiated with 400 nm LED under oxygen (balloon) at constant temperature.

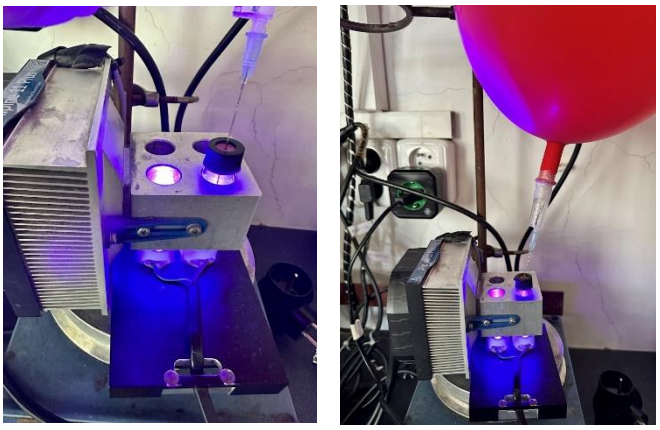
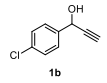
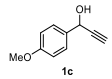
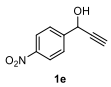
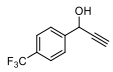
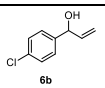
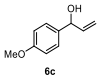
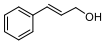
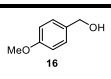


Figure S15. Experimental setup for the analytic photocatalytic oxidation of benzylic alcohols with oxygen balloon under LED irradiation (400 nm).

Table S2. Oxidation of benzylic alcohols on analytical scale – overview of all results.

Entry	Substrate	Temperature [°C]	Time [h]	Yield [%] [a]			
				carbonyle	alcohol	3	4
1	 1a	25	8	90	4	2	4
2		45	8	91	2	3	4
3	 1b	25	8	89	0	11	0
4		45	8	39	27	34	0
5	 1c	25	8	93	0	3	3
6		45	8	79	2	4	15
7	 1d	25	8	85	4	11	0
8		45	8	86	3	11	0
9	 1e	25	8	14	77	1	8
10		25	16	4	62	0	34
11		45	8	12	81	2	5
12	 1f	25	8	27	50	6	12
13		25	16	28	28	18	22
14		45	8	32	13	21	38
15	 1g	25	8	2	98	0	0
16		45	8	5	95	0	0
17	 1h	25	8	49	40	8	3
18		25	16	24	8	17	51
19		45	8	19	38	22	21
20	 6a	25	8	47	28	5	20
21		45	8	42	23	4	30
22	 6b	25	8	44	28	12	0
23		45	8	26	16	5	35
24	 6c	25	8	70	0	8	20
25		45	8	16	0	27	52
26	 8	25	8	75	0	0	17 + 9[c]
27		45	8	64	3	24	6
28	 10	25	8	45[b]	55	0	0
29		45	8	72[b]	28	0	0
30	 12	25	8	17[b]	83	0	0
31		45	8	41[b]	59	0	0
32	 14	25	8	34[b]	66	0	0
33		45	8	39[b]	61	0	0
34	 15	25	8	5[b]	95	0	0
35		45	8	30[b]	70	0	0
36	 16	25	8	39[b]	54	0	7
37		45	8	49[b]	29	0	22
38	 17	25	8	24[b]	76	0	0
39		45	8	33[b]	67	0	0
40	 18	25	8	12[b]	88	0	0
41		45	8	36[b]	64	0	0

[a]Determined by GC-MS [b]Determined by NMR [c]cinnamic acid

Preparative experiments

General method A – system without cooling

In Schlenk tube with septum (20 mL), alcohol (1 mmol) was dissolved in dry DMSO (4 mL). Schlenk tube was put into photochemical reactor equipped with 8 LEDs (400 nm). Then, the reaction mixture was irradiated and continually stirred and bubbled with oxygen. Time of the reaction was optimized to get the highest conversion of the ketone according to formation of the side product (NMR). The temperature of the reaction mixture was around 45 °C.

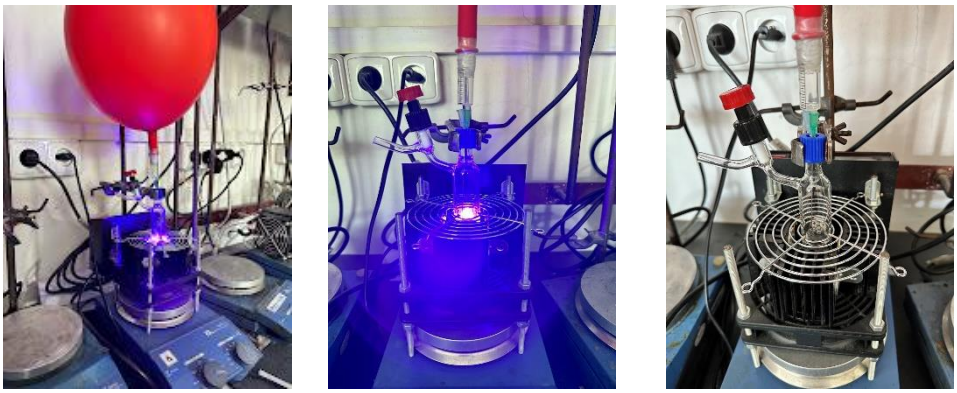


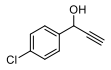
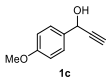
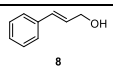
Figure S16. Experimental setup for the preparative photocatalytic oxidation of benzylic alcohols with oxygen balloon under LED irradiation (400 nm).

General method B – system with cooling

In sublimation apparatus with septum, alcohol (1 mmol) was dissolved in dry DMSO (4 mL). This apparatus was put into photochemical reactor equipped with 8 LEDs (400 nm). Then, the reaction mixture was irradiated and continually stirred and bubbled with oxygen. Time of the reaction was optimized to get the highest conversion of the ketone according to formation of the side product (NMR). During irradiation, the temperature was kept at 25 $\pm$ 1 °C by cooling water.

Figure S17. Experimental setup for the preparative photocatalytic oxidation of benzylic alcohols with oxygen balloon under LED irradiation (400 nm) and with water cooling system.

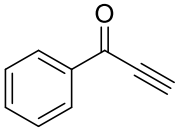
Table S3. Composition of the reaction mixtures upon oxidations on preparative scale.

Entry	Substrate	Temperature [°C]	Time [h]	Yield [%] [a]		
				carbonyle	alcohol	3+4
1	 1a	45	8	82	3	15
2	 1b	25	10	58	12	30
3	 1c	25	8	83	0	17
4	 1d	45	8	83	3	14
5	 8	25	8	58	28	14
6	 10	45	8	94	6	0
7	 12	45	8	53	47	0

[a] Determined by ^{1}H NMR

Preparation and characterization of products on 1 mmol scale

*1-Phenylprop-2-yn-1-one **(2a)***



Ketone **2a** was prepared according to a general procedure A from 1-phenylprop-2-yn-1-ole (**1a**). After 8 hours irradiation, the reaction mixture was extracted between water (250 mL) and EtOAc (100 mL). The water phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ (100 mL) and saturated brine (100 mL), dried over $MgSO_4$ and concentrated in vacuo. Following the procedure, keton **2a** was prepared in isolated yield of 62% (81 mg) as a yellow solid, m.p.: 49-50 °C.

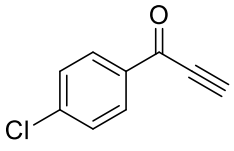
^{1}H NMR (400 MHz, DMSO-D_6) δ 8.22 – 8.12 (m, 2H), 7.88 – 7.79 (m, 1H), 7.73 – 7.63 (m, 2H), 5.21 (s, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 177.1, 135.7, 135.0, 129.2, 129.2, 85.6, 80.3.

HR-MS (EI) calculated for C_9H_6O [M^+]: 130.042; **observed**: 130.044.

Spectral data are in agreement with previously published characterization data.[9]

1-(4-Chlorophenyl)prop-2-yn-1-one ***(2b)***



Ketone **2b** was prepared according to a general procedure B from 1-(4-chlorphenyl)prop-2-yn-1-ole (**1b**). After 10 hours irradiation, the reaction mixture was extract between water (250 mL) and EtOAc (100 mL). The water phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ (100 mL) and saturated brine (100 mL), dried over $MgSO_4$ and concentrated in vacuo. After extraction, the product was purified by recrystallization (hexan-EtOAc, 5:1). Following the procedure, keton **2b** was prepared in isolated yield of 49% (80 mg) as a pale-yellow solid, m.p.: 94-95 °C.

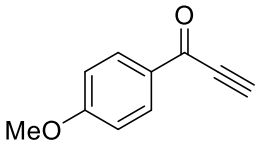
^{1}H NMR (400 MHz, DMSO-D_6) δ 8.18 – 8.01 (m, 2H), 7.71 – 7.60 (m, 2H), 5.20 (s, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 175.9, 140.03, 134.4, 131.0, 129.4, 86.2, 80.0.

HR-MS (EI) calculated for C_9H_5ClO [M^+]: 164.003; **observed**: 164.005.

Spectral data are in agreement with previously published characterization data.[9]

1-(4-Methoxyphenyl)prop-2-yn-1-one ***(2c)***



Ketone **2c** was prepared according to a general procedure B from 1-(4-methoxyphenyl)prop-2-yn-1-ole (**1c**). After 8 hours irradiation, the reaction mixture was extract between water (250 mL) and EtOAc (100 mL). The water phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ (100 mL) and saturated brine (100 mL), dried over $MgSO_4$ and concentrated in vacuo. Following the procedure, keton **2b** was prepared in isolated yield of 58% (92 mg) as a yellow solid, m.p.: 82-83 °C.

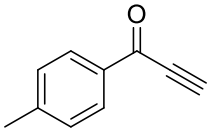
^{1}H NMR (400 MHz, DMSO-D_6) δ 8.05 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.5 Hz, 2H), 4.99 (s, 1H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 175.4, 164.6, 131.7, 129.0, 114.5, 84.5, 80.3, 55.8.

HR-MS (EI) calculated for $C_{10}H_8O_2$ [M^+]: 160.052; **observed**: 160.053.

Spectral data are in agreement with previously published characterization data.[9]

1-(p-Tolyl)prop-2-yn-1-one ***(2d)***



Ketone **2d** was prepared according to a general procedure A from 1-(*p*-tolyl)prop-2-yn-1-ole (**1d**). After 8 hours irradiation, the reaction mixture was extract between water (250 mL) and EtOAc (100 mL). The water phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with saturated $NaHCO_3$ (100 mL) and saturated brine (100 mL), dried over $MgSO_4$ and concentrated in vacuo. Following the procedure, keton **2d** was prepared in isolated yield of 76% (110 mg) as a yellow solid, m.p.: 36-38 °C.

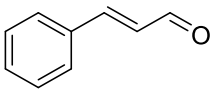
^{1}H NMR (400 MHz, DMSO-D_6) δ 8.02 – 7.94 (m, 2H), 7.44 – 7.37 (m, 2H), 5.07 (s, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 176.6, 145.9, 133.4, 129.7, 129.4, 85.0, 80.3, 21.4.

HR-MS (EI) calculated for $C_{10}H_8O$ [M^+]: 144.058; **observed**: 144.059.

Spectral data are in agreement with previously published characterization data.[9]

*Cinnamaldehyde **(9)***



Adehyde **9** was prepared according to a general procedure B from cinnamyl alcohol (**8**). After 8 hours irradiation, the reaction mixture was extract between water (250 mL) and EtOAc (100 mL). The water phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. After extraction, the product was purified by column chromatography (hexan-EtOAc, 50:1). Following the procedure, aldehyde **9** was prepared in isolated yield of 41% (54 mg) as a yellow oil.

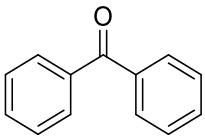
^{1}H NMR (400 MHz, DMSO-D_6) δ 9.68 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.47 (dd, *J* = 5.0, 1.9 Hz, 3H), 6.87 (dd, *J* = 16.0, 7.8 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 194.5, 153.3, 134.1, 131.3, 129.1, 128.8, 128.6.

HR-MS (APCI) calculated for C_9H_8O [M+H$^+$]: 133.06534; **observed**: 133.06479.

Spectral data are in agreement with previously published characterization data.[10]

*Benzophenone **(11)***



Ketone **11** was prepared according to a general procedure A from diphenylmethanol (**10**). After 8 hours irradiation, the reaction mixture was extract between water (250 mL) and EtOAc (100 mL). The water phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. After extraction, the product was purified by column chromatography (hexan-EtOAc, 10:1). Following the procedure, ketone **11** was prepared in isolated yield of 77% (140 mg) as a white solid, m.p.: 47-49 °C.

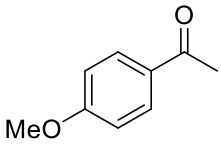
^{1}H NMR (400 MHz, DMSO-D_6) δ 7.77 – 7.72 (m, 4H), 7.70 (s, 2H), 7.60 – 7.51 (m, 4H).

^{13}C NMR (101 MHz, DMSO-D_6) δ 195.8, 137.0, 132.7, 129.6, 128.6.

HR-MS (APCI) calculated for $C_{13}H_{10}O$ [M+H$^+$]: 183.08099; **observed**: 183.08044.

Spectral data are in agreement with previously published characterization data.[11]

*1-(4-methoxyphenyl)ethan-1-one **(13)***



Ketone **13** was prepared according to a general procedure A from 1-(4-methoxyphenyl)ethan-1-ol (**12**). After 8 hours irradiation, the reaction mixture was extract between water (250 mL) and EtOAc (100 mL). The water phase was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. After extraction, the product was purified by column chromatography (hexan-EtOAc, 50:1). Following the procedure, aldehyde **13** was prepared in isolated yield of 41% (54 mg) as a white solid, m.p.: 38-39 °C.

^{1}H NMR (400 MHz, DMSO-D_6) δ 7.95 – 7.88 (m, 2H), 7.06 – 6.98 (m, 2H), 3.82 (d, *J* = 0.4 Hz, 3H), 2.50 (d, *J* = 0.5 Hz, 3H).

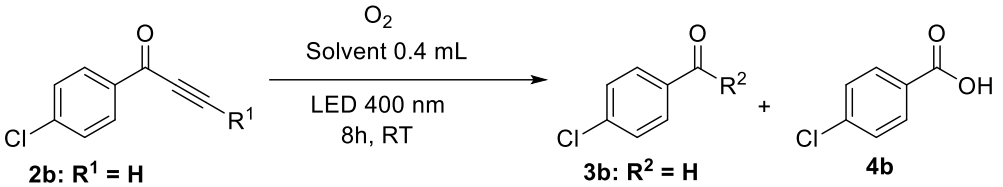
^{13}C NMR (101 MHz, DMSO-D_6) δ 196.3, 163.1, 130.5, 129.9, 113.8, 55.5, 26.4.

HR-MS (APCI) calculated for $C_9H_{10}O_2$ [M+H$^+$]: 151.07591; **observed**: 151.07536.

Spectral data are in agreement with previously published characterization data.[11]

S6. Extended analysis on photooxidations

Table S4. Experiments with deuterated substrate/solvent.



2b: R^1 = H
2ba: R^1 = D

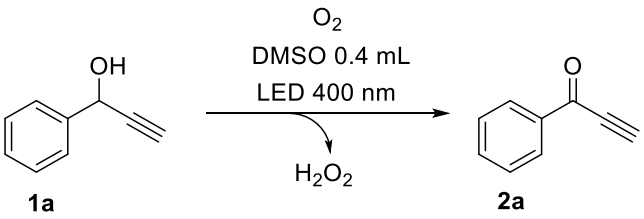
3b: R^2 = H
3ba: R^2 = D

4b

Entry	Solvent	Starting compound	Conditions alternation	Conversion [%][b]				% of deuterated aldehyde in **3b** [%][b]
				2b	**2ba**	**3b**	**4b**	**3ba**
1	*d*[6] DMSO	**2b**	-	65	-	5	24	3
2	DMSO	**2b**	D_2O (10 µl)	68	-	9	16	36
3	DMSO	**2ba**	-	-	34	6	43	3

[a] Conditions: **2b** (0.1 mmol), solvent (0.4 mL), 400 nm, oxygen (balloon), 8h. [b] Determined by GC-MS

Determination of peroxide



1a **2a**

Hydrogen peroxide was determined iodometry.[12]

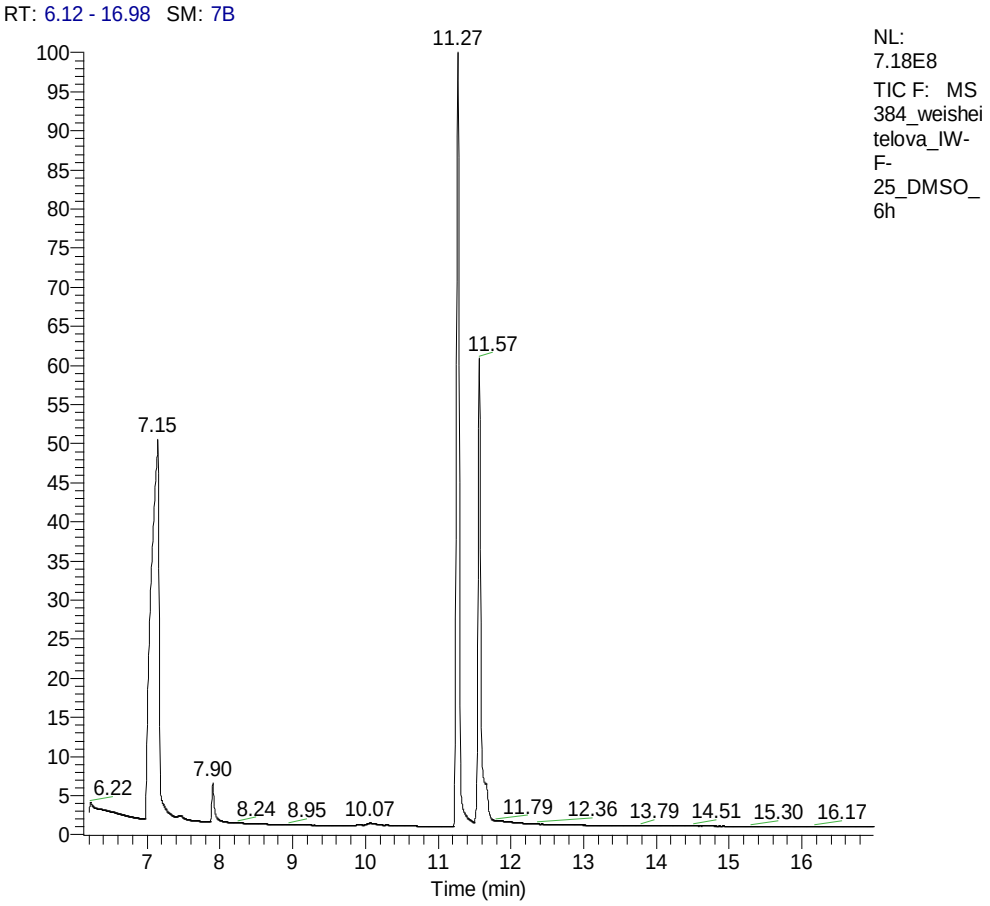
Table S5. Concentration of H_2O_2 during photooxidation in different time.

Time [h]	Concentration of H_2O_2 [mM]
2	0.01419
4	0.03223
8	0.05202

Table S6. Amount of H_2O_2 and ketone **2a** during photooxidation in different time in the reaction mixture (0.4 mL).

Time [h]	H_2O_2 [mmol]	**2a** [mmol]
2	0.071	0.078
4	0.161	0.110
8	0.260	0.225

Proof of dimethylsulfone



PEAK LIST

384_weisheitelova_IW-F-25_DMSO_6h.raw

RT: 0.00 - 23.57

Number of detected peaks: 4

Apex RT	Start RT	End RT	Area	%Area		MW Da
7.15	6.94	7.36	2758894983	46.29	dimethylsulfone	94
7.9	7.85	8	116667267	1.96	benzaldehyde	106
11.27	11.16	11.46	1954868282	32.8	2-Propyn-1-one, 1-phenyl-	130
11.57	11.52	11.77	1129317017	18.95	Benzenemethanol, α-ethynyl-	122+ 132
			976392391	16.38	Benzenemethanol, α-ethynyl-	132
			152924626	2.57	benzoic acid	122

Figure S18. Mass spectrum of the reaction mixture of the alcohol **1a**.

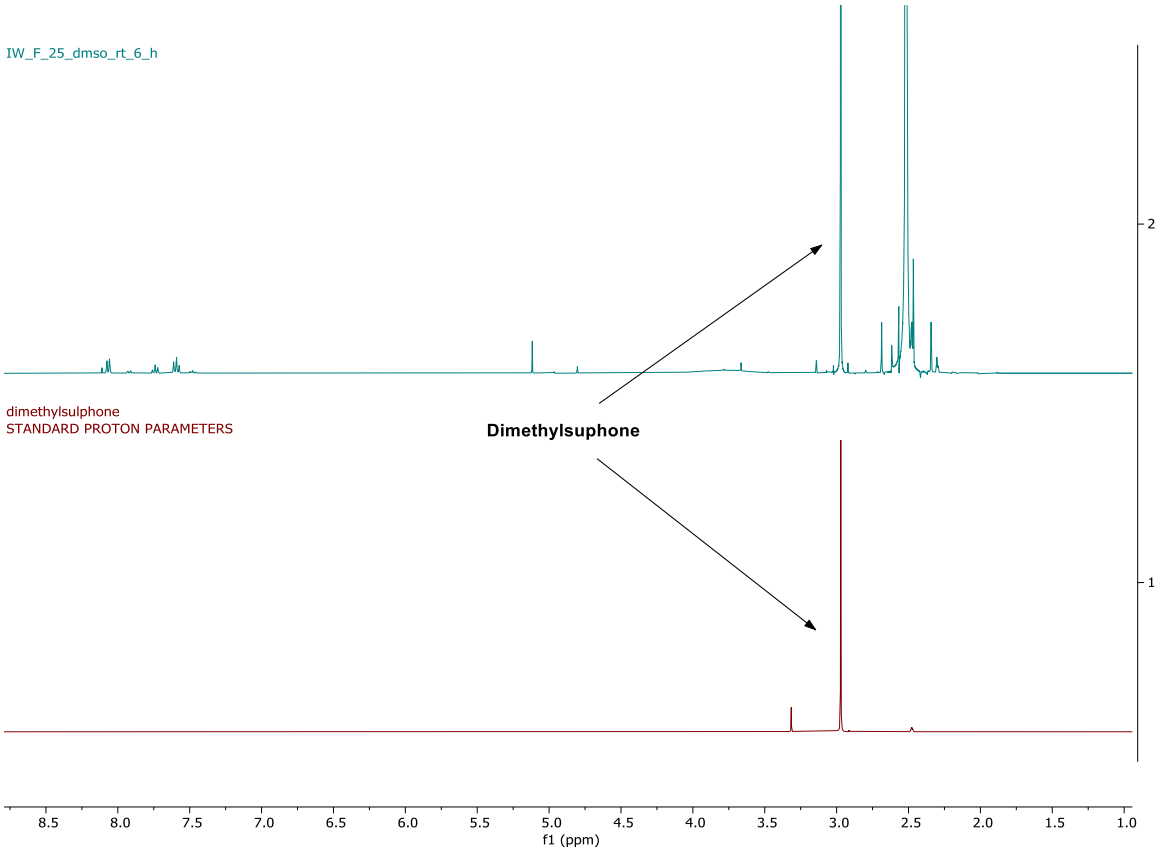


Figure S19. NMR spectra of the reaction mixture of the alcohol **1a** (up) and the dimethylsulfone (down).

S7. Cyclic voltammetry measurements

Electrochemical measurements were performed with a PGSTAT204 (Autolab-Metrohm) using a standard three-electrode system with a stationary classy carbon electrode. Saturated calomel reference electrode was separated from the investigated aprotic solution by a glass frit and a salt bridge filled with the same electrolyte. A platinum wire served as an auxiliary electrode. The cyclic voltammetry measurements were carried out in acetonitrile containing alcohol **1a** or ketone **2a** (c = 1.9×10^{-3}) and tetrabutylammonium hexafluorophosphate (c = 0.1M) as supporting electrolyte under argon atmosphere. The scan rate was 100 mV s^{-1}.

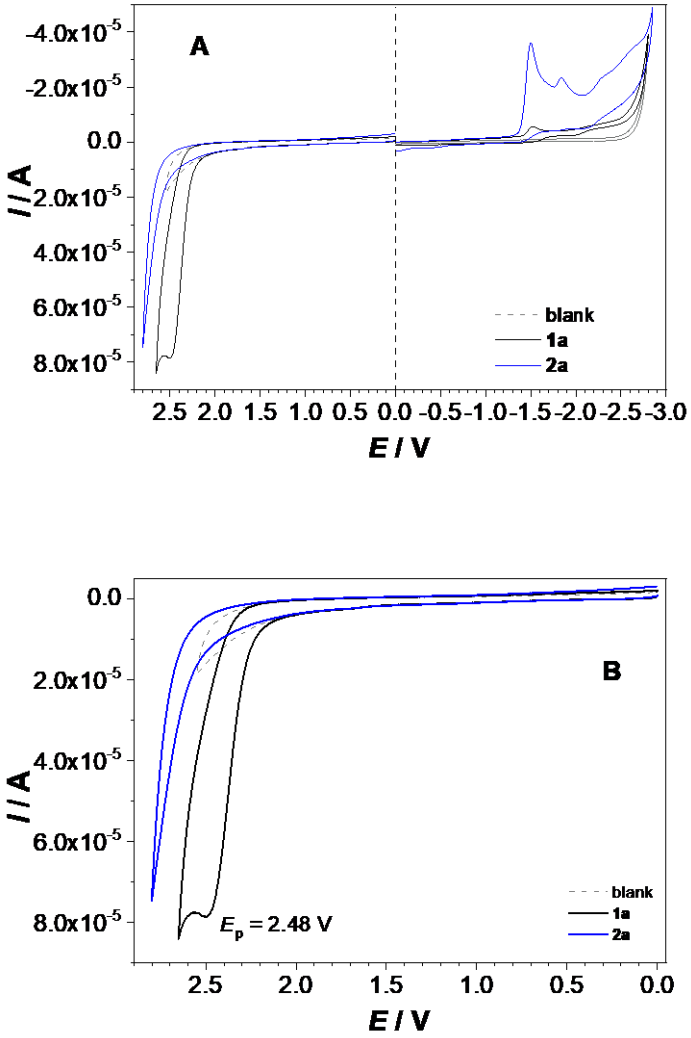


Figure S20. Comparison of (**A**) cyclic voltammogram (CV) and (**B**) oxidative part of CV for alcohol **1a** (black) and ketone **2a** (blue) in acetonitrile.

S8. Photophysical measurements on 1a and 2a

1a in DMSO

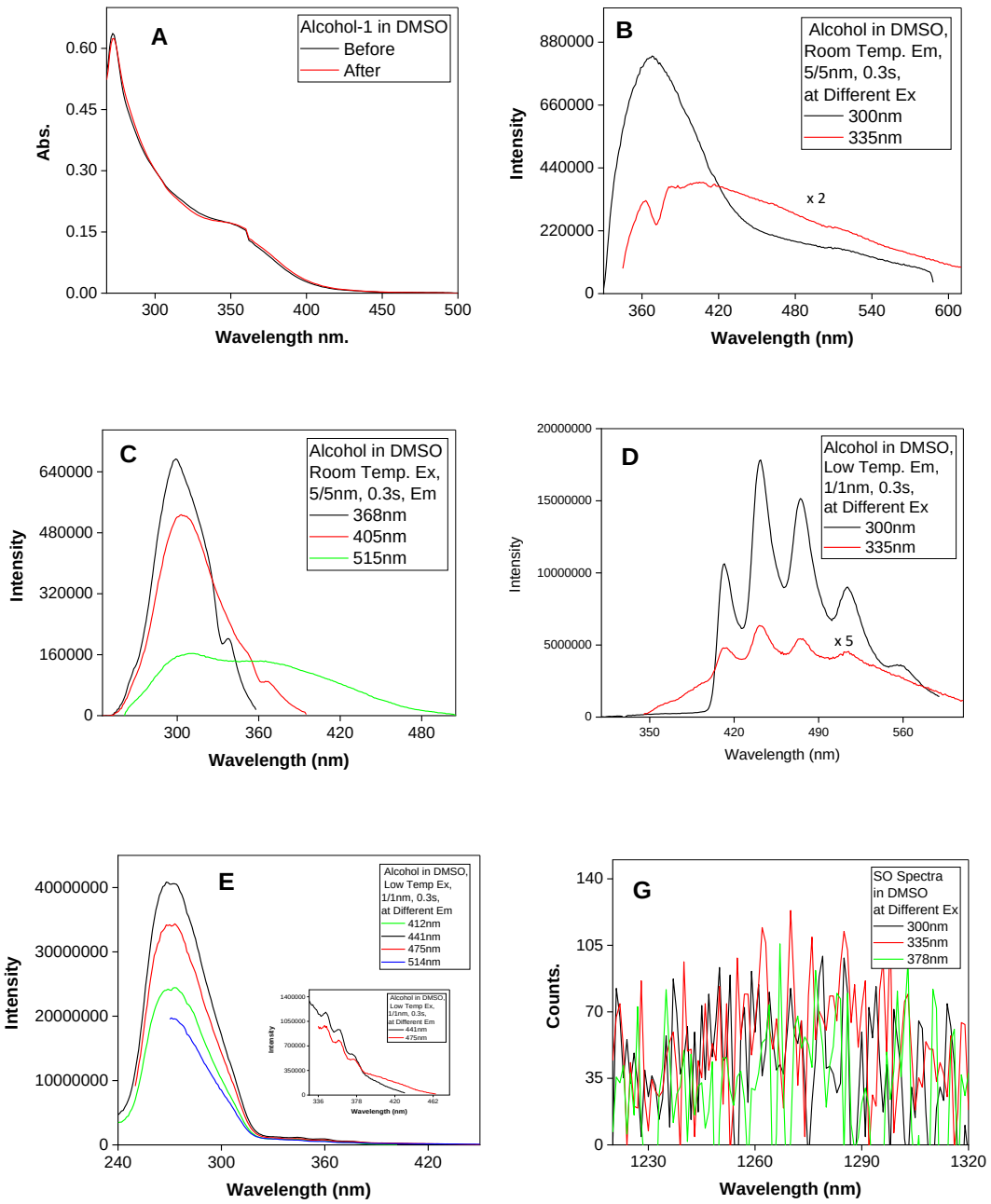


Figure S21. Panel **(A)** absorption spectra recorded on Spectrophotometer UV-2550-230V/SHIMADZU, Panel **(B)** Fluorescence spectra recorded on a Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer at room temp. slit width 5/5nm, integration time 0.3s, A Xe lamp with a monochromator was used for excitation. Panel **(C)** Excitation spectra were recorded using the Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer, slit width 5/5nm, integration time 0.3s, Panel **(D)** Low Temperature (77K) emission spectra, slit width 1/1nm, integration time 0.3s and Panel **(E)** Low temperature (77K) excitation spectra, slit width 1/1nm, integration time 0.3s were recorded using the Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer., Panel **(F)** The steady-state emission spectra of singlet oxygen were measured using Lamp at Ex-335nm, excitation slit 5nm, integration time 0.5s, were recorded on fluorescence lifetime spectrometer/ FluoTime 300-Pico Quant, having HAMAMATSU- NIR-PMT detector-module controller Max 800 V.

2a in DMSO

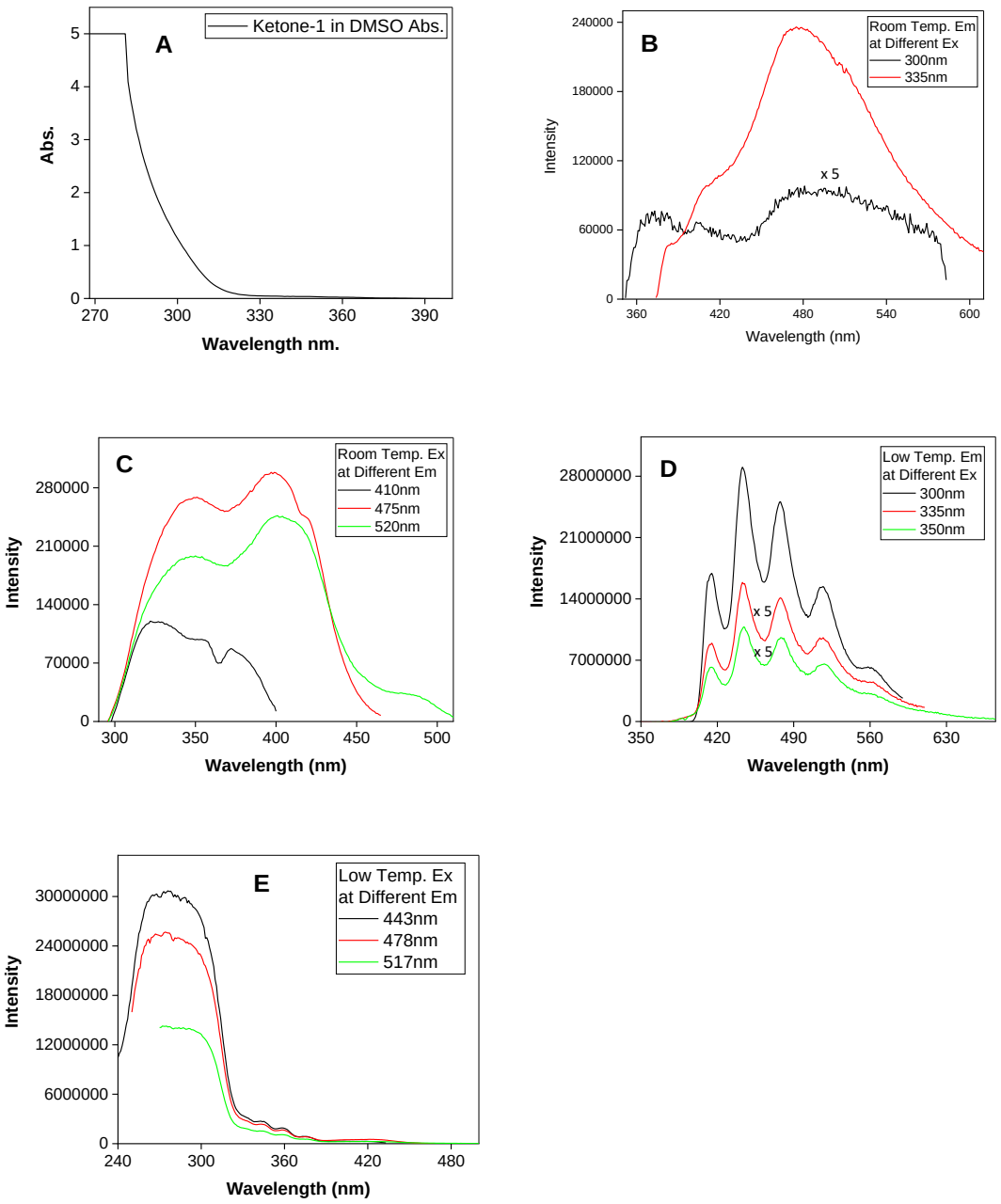


Figure S22. Panel **(A)** absorption spectra recorded on Spectrophotometer UV-2550-230V/SHIMADZU, Panel **(B)** Fluorescence spectra recorded on a Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer at room temp. slit width 5/5nm, integration time 0.3s, A Xe lamp with a monochromator was used for excitation. Panel **(C)** Excitation spectra were recorded using the Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer, slit width 5/5nm, integration time 0.3s, Panel **(D)** Low Temperature (77K) emission spectra, slit width 1/1nm, integration time 0.3s and Panel **(E)** Low temperature (77K) excitation spectra, slit width 1/1nm, integration time 03s were recorded using the Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer.

1a in acetonitrile

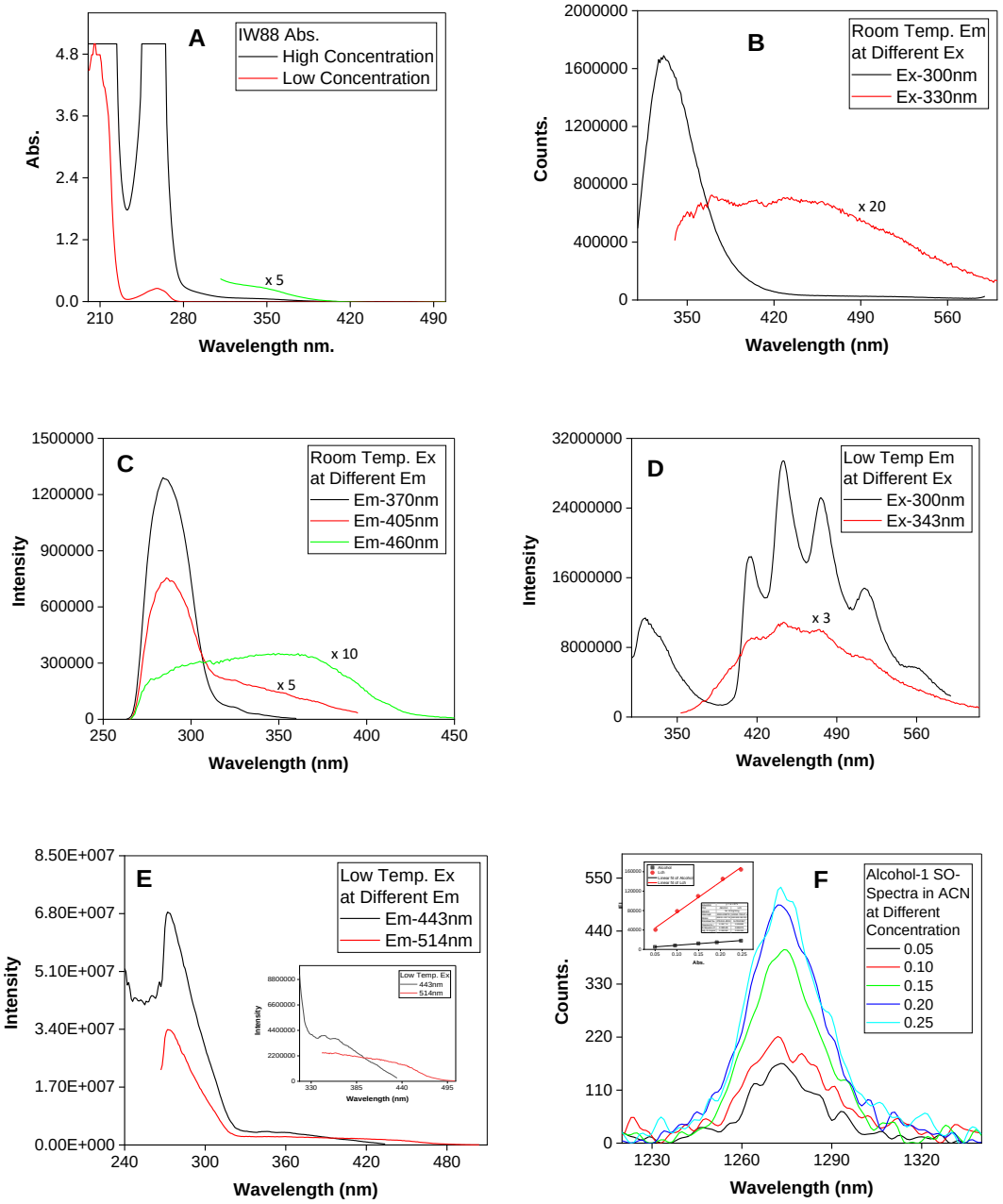


Figure S23. Panel **(A)** absorption spectra recorded on Spectrophotometer UV-2550-230V/SHIMADZU, Panel **(B)** Fluorescence spectra recorded on a Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer at room temp. slit width 3/1nm, integration time 0.3s, A Xe lamp with a monochromator was used for excitation. Panel **(C)** Excitation spectra were recorded using the Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer, slit width 3/1nm, integration time 0.3s, Panel **(D)** Low Temperature (77K) emission spectra, slit width 0.6/0.6nm, integration time 0.1s and Panel **(E)** Low temperature (77K) excitation spectra, slit width 1/1nm, integration time 0.1s were recorded using the Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer., Panel **(F)** The steady-state emission spectra of singlet oxygen were measured using Lamp at Ex-335nm, excitation slit 5nm, integration time 0.5s, were recorded on fluorescence lifetime spectrometer/ FluoTime 300-Pico Quant, having HAMAMATSU- NIR-PMT detector-module controller Max 800V, Inside: integrated phosphorescence intensity vs. Abs. plot using a linear fit method for calculating singlet oxygen quantum yield.

2a in acetonitrile

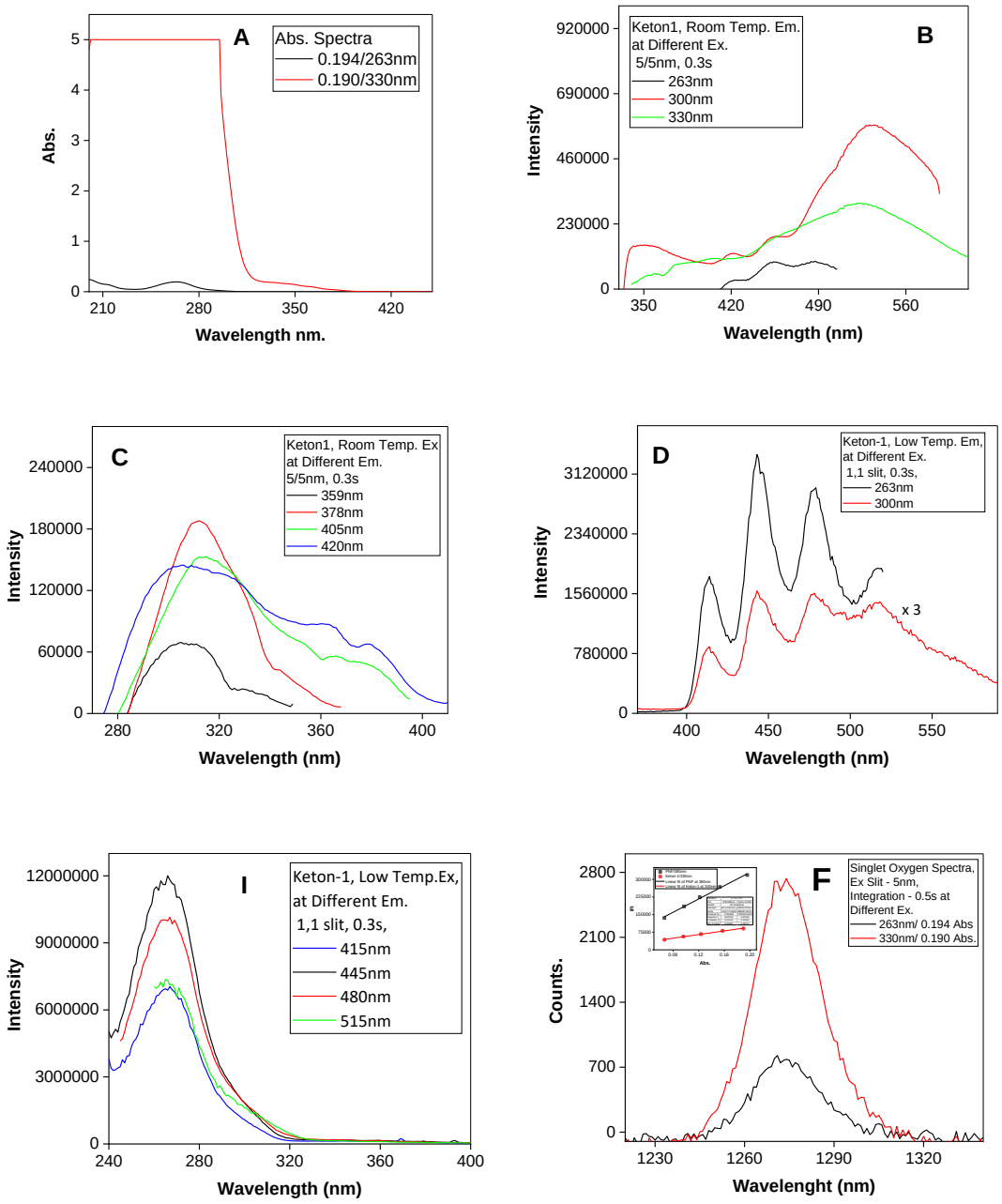


Figure S24. Panel **(A)** absorption spectra λ_{abs}.(nm) 264nm (2435.59/log Ɛ = 3.39), recorded on Spectrophotometer UV-2550-230V/SHIMADZU, Panel **(B)** Fluorescence spectra recorded on a Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer at room temp. slit width 3/1nm, integration time 0.3s, A Xe lamp with a monochromator was used for excitation. Panel **(C)** Excitation spectra were recorded using the Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer, slit width 3/1nm, integration time 0.3s., Panel **(D)** Low Temperature (77K) emission spectra, slit width 0.6/0.6nm, integration time 0.1s and Panel **(E)** Low temperature (77K) excitation spectra, slit width 1/1nm, integration time 0.1s were recorded using the Horiba Jobin Yvon 221 – Fluorolog 3 spectrofluorometer., Panel **(F)** The steady-state emission spectra of singlet oxygen were measured using Lamp at Ex-263nm and 330nm, excitation slit 5nm, integration time 0.5s, was recorded on fluorescence lifetime spectrometer/ FluoTime 300-Pico Quant, having HAMAMATSU- NIR-PMT detector-module controller Max 800V; Inside: integrated phosphorescence intensity vs. Abs. plot using a linear fit method for calculating singlet oxygen quantum yield. (Using standard as a lumichrome - λ_x 263nm).

S9. Singlet oxygen lifetime in DMSO/DMSO-d_6

Singlet oxygen lifetimes were measured using perinaphthenone sensitizer.[13]

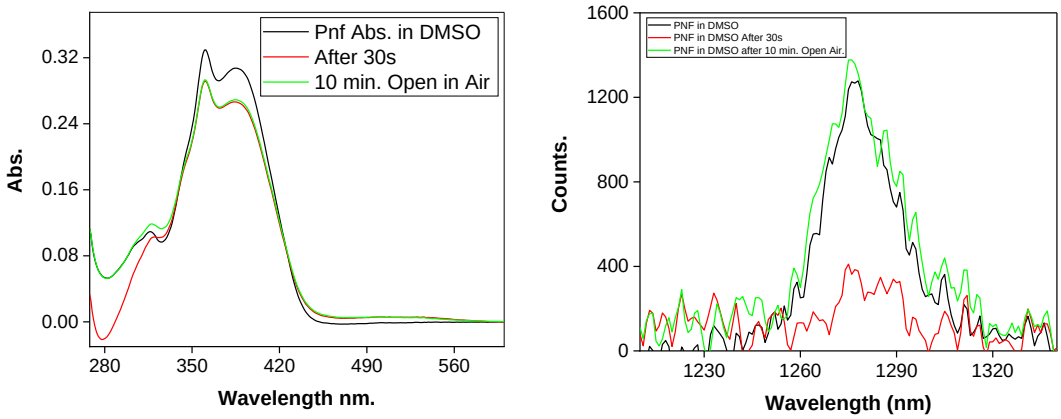


Figure S25. Perinaphthenone as singlet oxygen photosensitizers in DMSO. Panel on the left presents absorption spectra, while panel on the right displays singlet oxygen spectra before and after the respective sample treatments. The two spectra, for singlet oxygen absorption and singlet oxygen emission, were captured (back and red line) respectively before and after exposure to 396 nm light for 30 seconds in a closed, airtight cuvette, initially containing the perinaphthenone solution in DMSO in equilibrium with air. The last spectra (green lines, absorption and singlet oxygen emission) were recorded under conditions of re-equilibrium with air, observed 10 minutes after opening the cuvette.

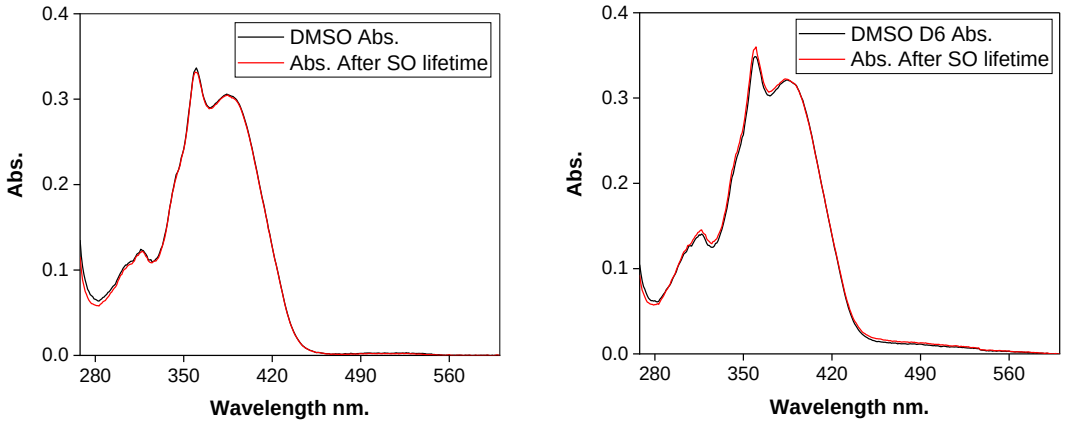


Figure S26. Absorption spectra control measurements of perinaphthenone absorption before and after measurements of singlet oxygen.

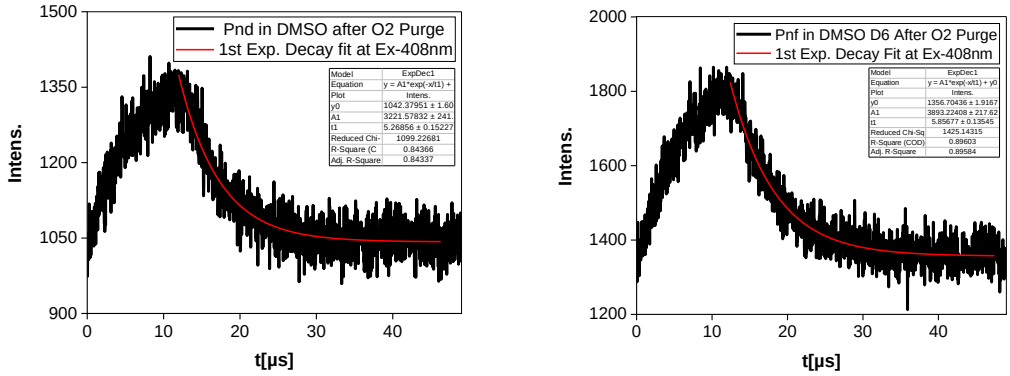


Figure S27. Singlet oxygen lifetime in DMSO (left panel) and DMSO-d^6 (right panel).

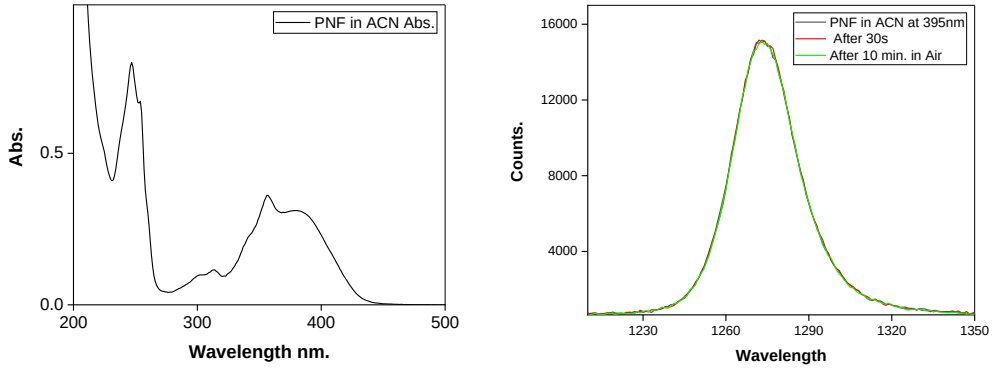
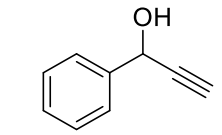
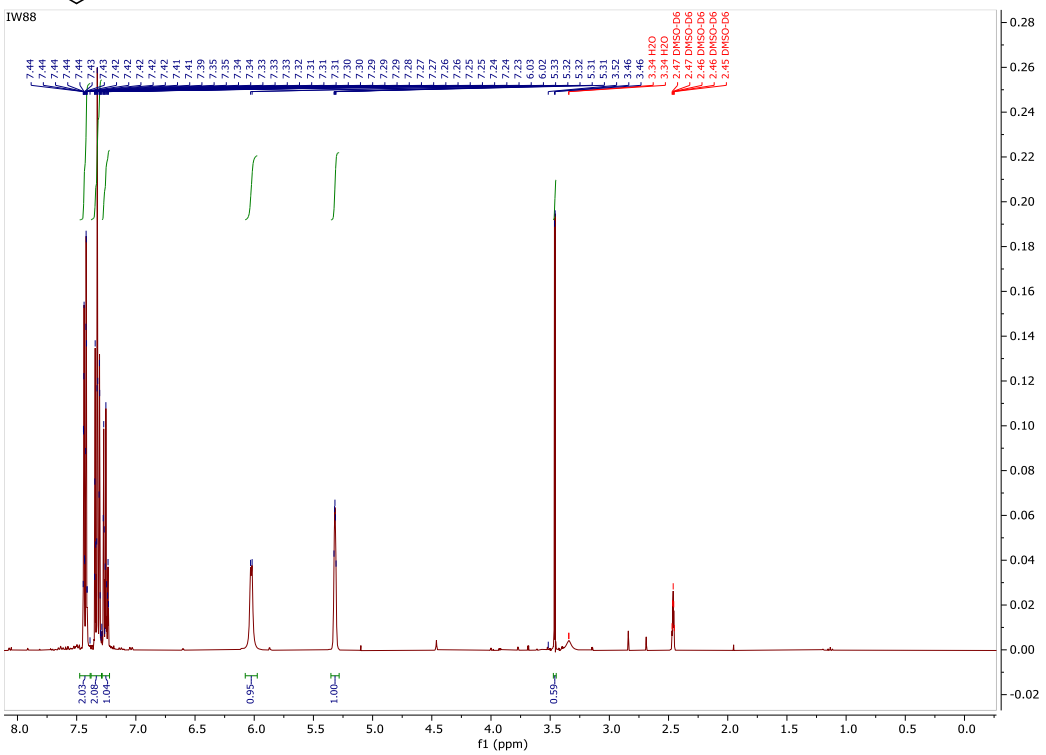
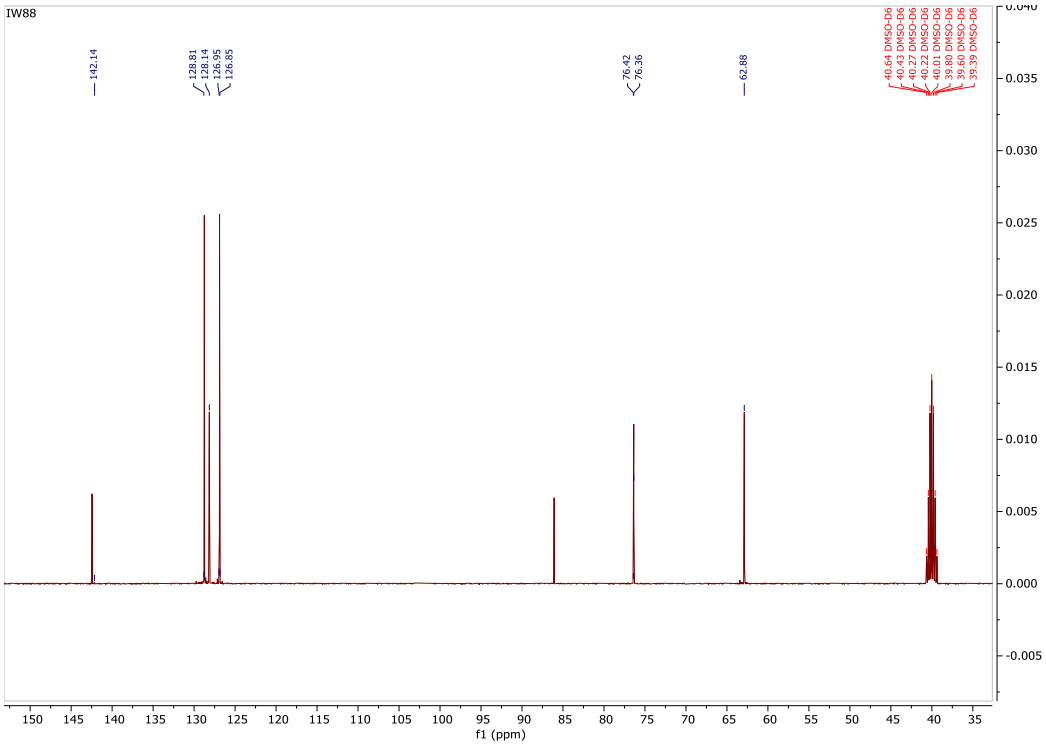


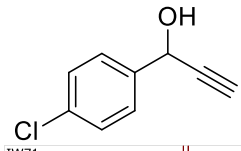
Figure S28. Perinaphthenone as singlet oxygen photosensitizers in acetonitrile. Panel on the left presents absorption spectra, while panel on the right displays singlet oxygen spectra before and after the respective sample treatments. The two spectra, for singlet oxygen absorption and singlet oxygen emission, were captured (back and red line) respectively before and after exposure to 396 nm light for 30 seconds in a closed, airtight cuvette, initially containing the perinaphthenone solution in acetonitrile in equilibrium with air. The last spectra (green lines, absorption and singlet oxygen emission) were recorded under conditions of re-equilibrium with air, observed 10 minutes after opening the cuvette.

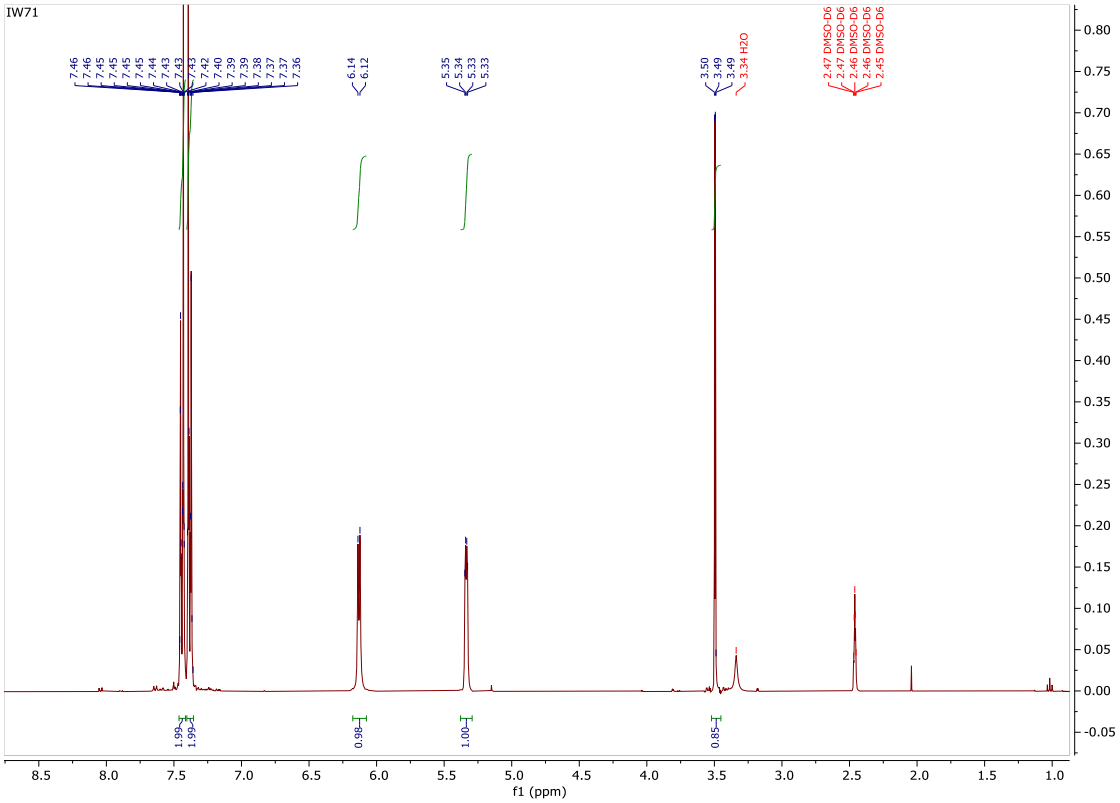
S10. Copies of NMR spectra








OH
Cl


IW71
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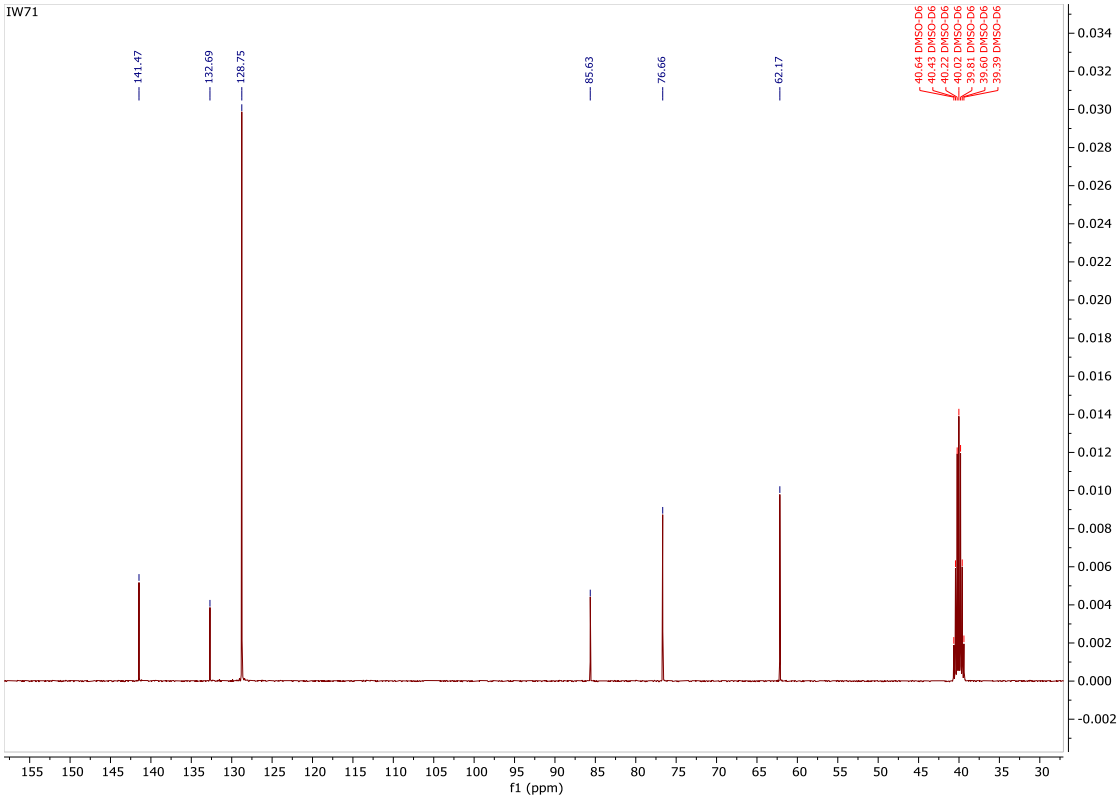
7.46
7.45
7.45
7.45
7.45
7.44
7.43
7.43
7.42
7.40
7.39
7.39
7.38
7.37
7.37
7.36
6.14
6.12
5.35
5.34
5.33
5.33
3.50
3.49
3.49
3.34 H2O
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
1.99
1.99
0.98
1.00
0.85
f1 (ppm)


IW71
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132.69
128.75
85.63
76.66
62.17
40.64 DMSO-D6
40.43 DMSO-D6
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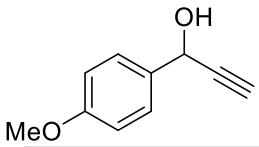
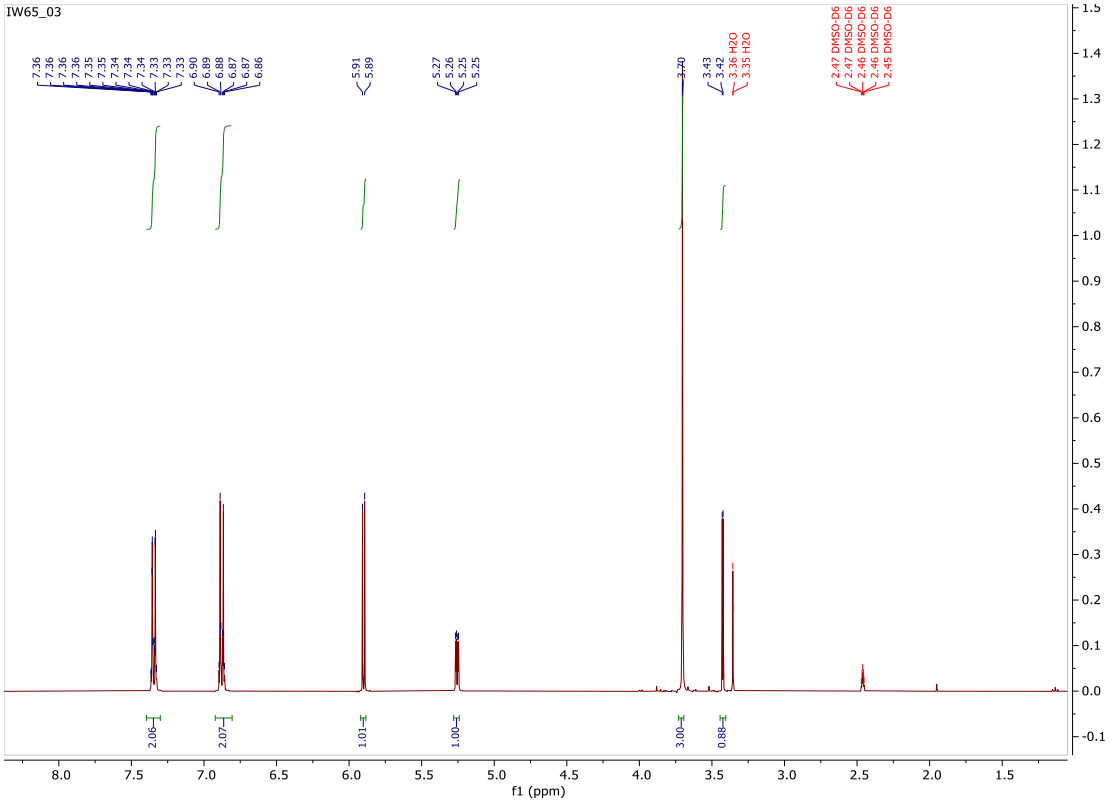
40.02 DMSO-D6
39.81 DMSO-D6
39.60 DMSO-D6
39.39 DMSO-D6
f1 (ppm)


OH
MeO


IW65_03
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7.36
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6.90
6.89
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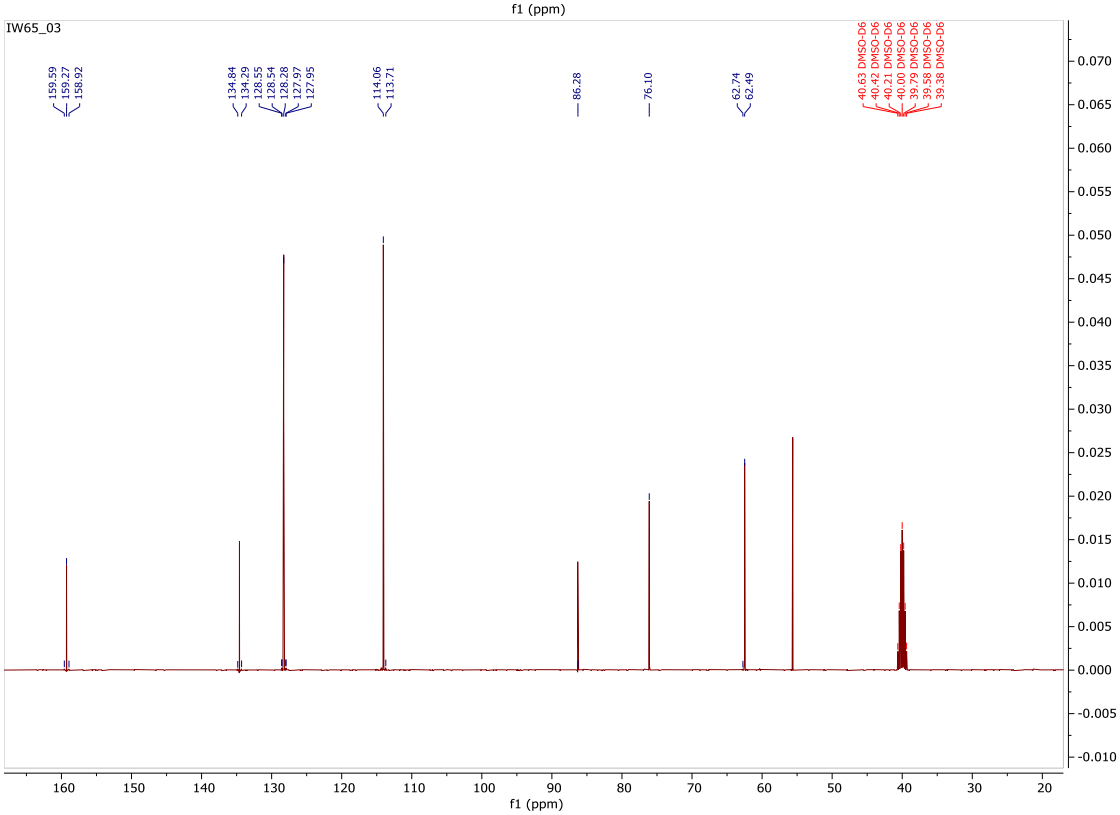
6.87
6.86
5.91
5.89
5.27
5.26
5.25
5.25
3.40
3.43
3.42
3.36 H2O
3.35 H2O
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
2.06
2.07
1.01
1.00
3.00
0.88
f1 (ppm)


IW65_03
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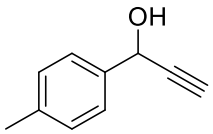
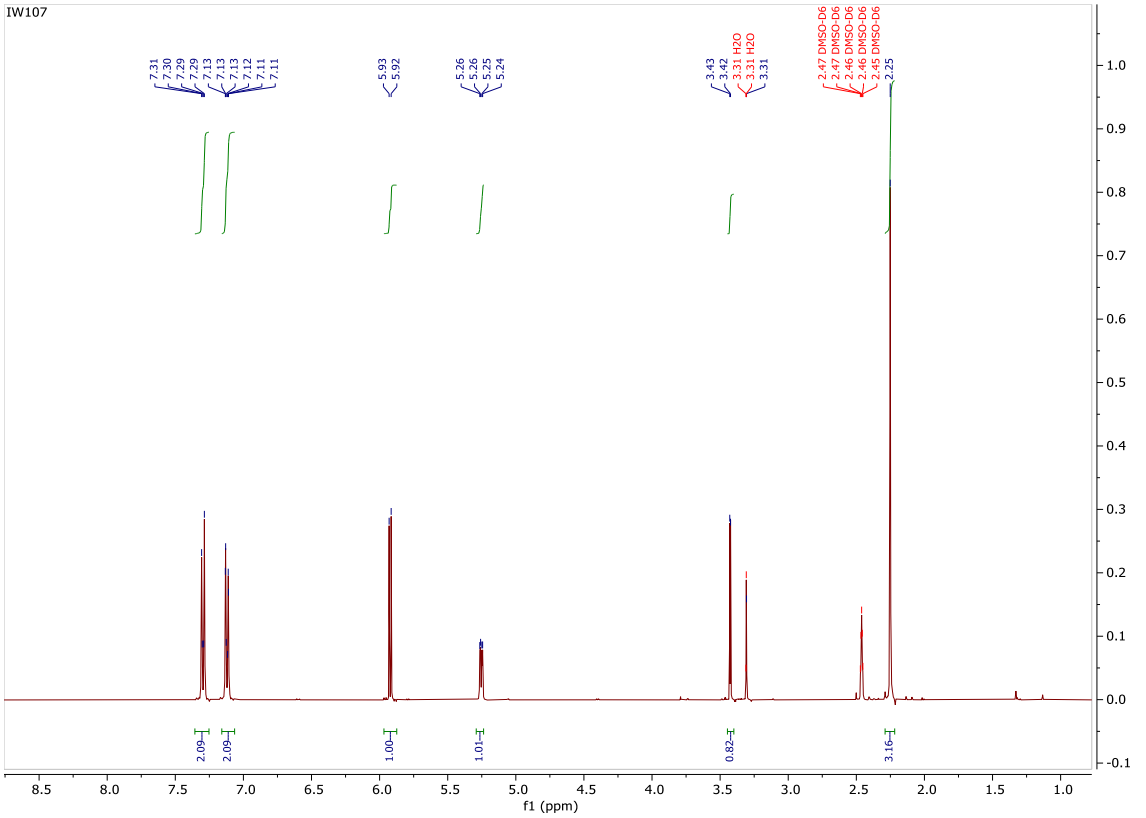
158.92
134.84
134.29
128.55
128.54
128.28
127.97
127.95
114.06
113.71
86.28
76.10
62.74
62.49
40.63 DMSO-D6
40.42 DMSO-D6
40.21 DMSO-D6
40.00 DMSO-D6
39.79 DMSO-D6
39.58 DMSO-D6
39.38 DMSO-D6
f1 (ppm)


OH


IW107
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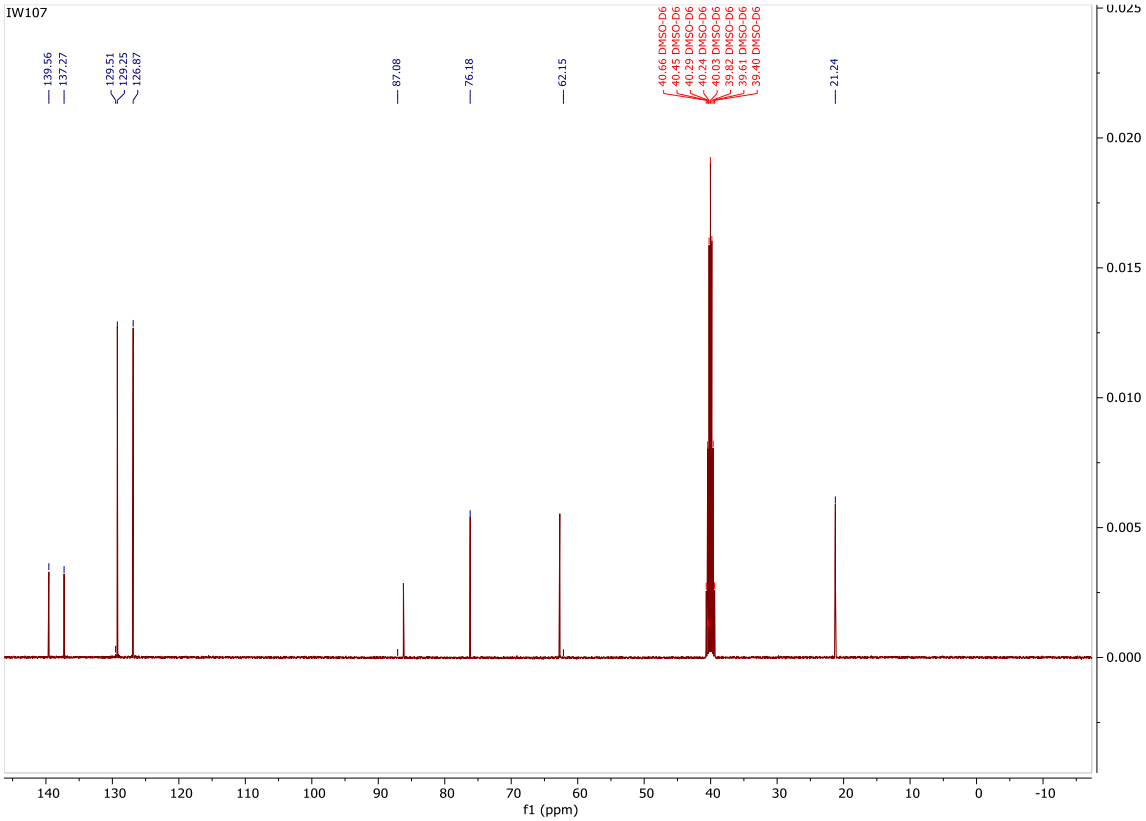
7.13
7.12
7.11
7.11
5.93
5.92
5.26
5.26
5.25
5.24
3.43
3.42
3.31 H2O
3.31 H2O
3.31
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
2.25
2.09
2.09
1.00
1.01
0.82
3.16
f1 (ppm)


IW107
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129.51
129.25
126.87
87.08
76.18
62.15
40.66 DMSO-D6
40.45 DMSO-D6
40.29 DMSO-D6
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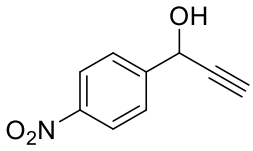
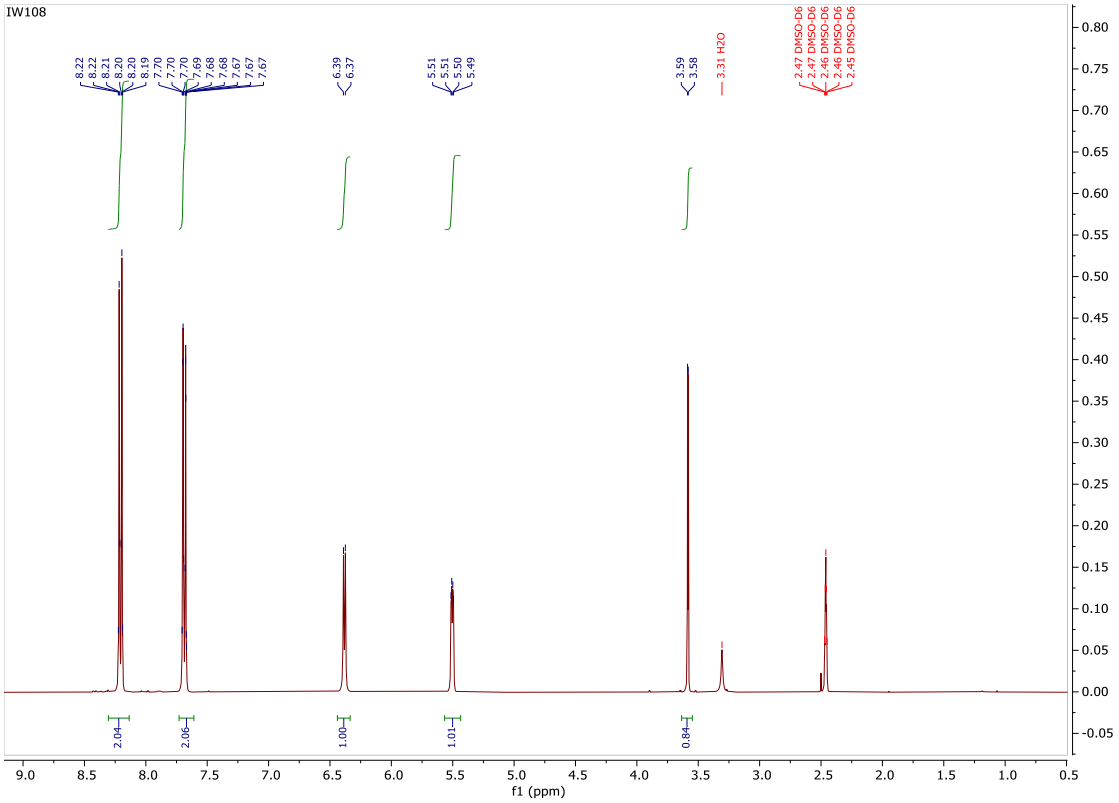
21.24
f1 (ppm)


OH
O2N


IW108
8.22
8.22
8.21
8.20
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7.70
7.70
7.69
7.68
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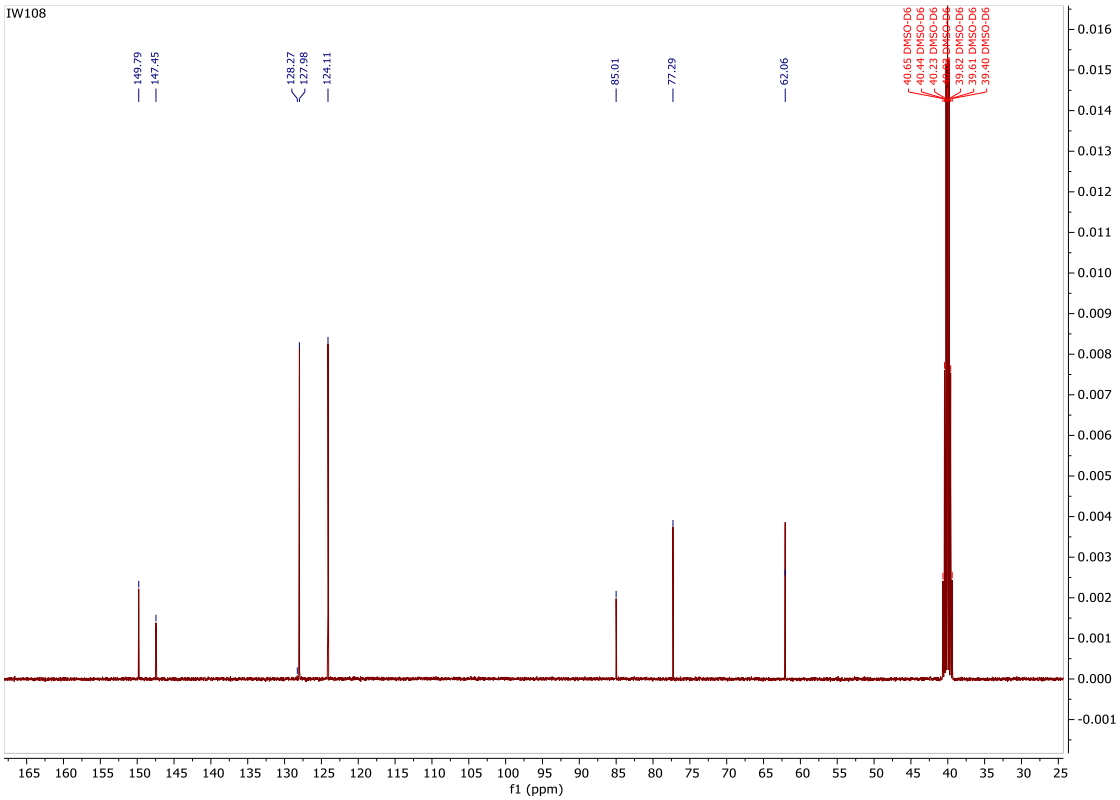
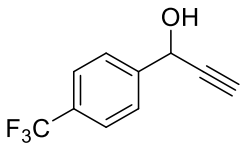
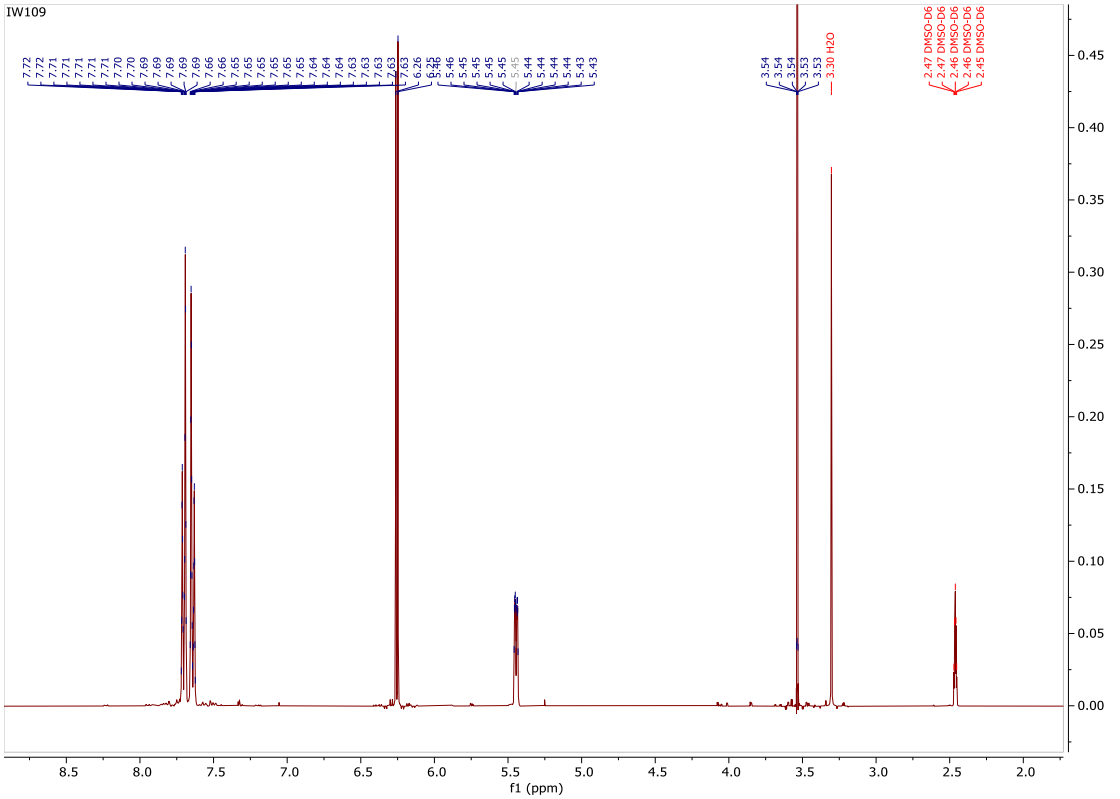
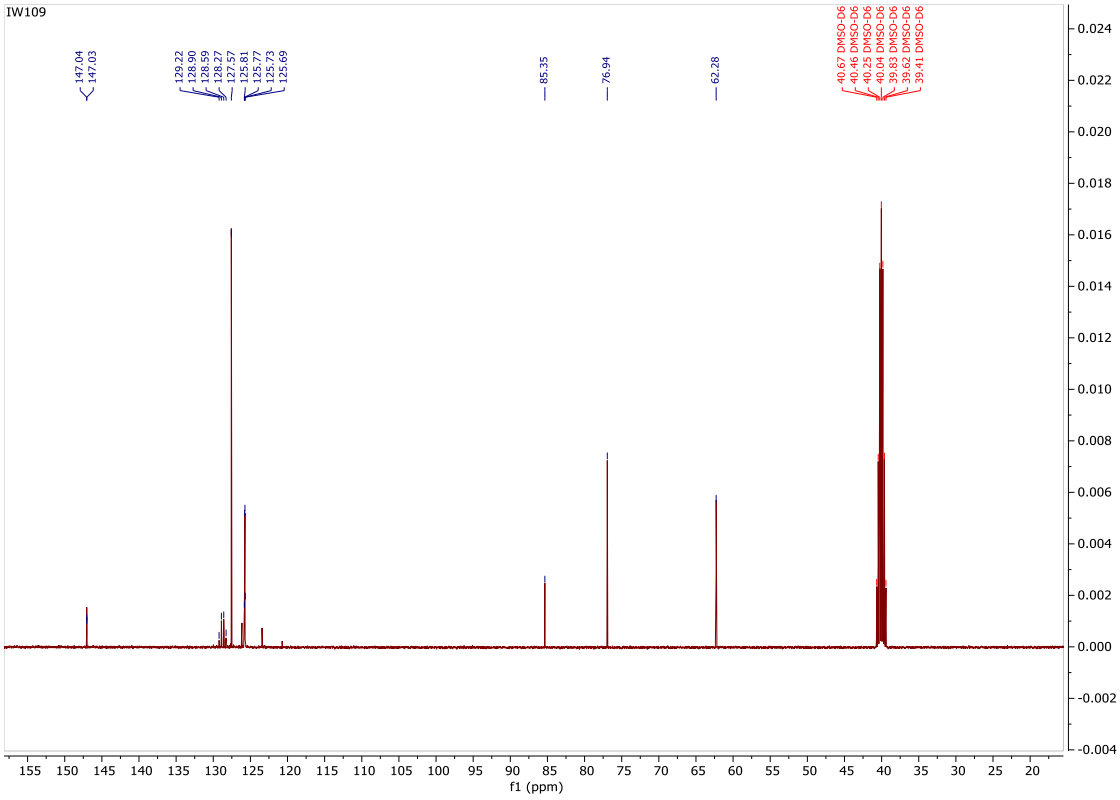
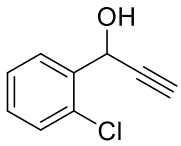
7.67
7.67
7.67
7.67
6.39
6.37
5.51
5.51
5.50
5.49
3.59
3.58
3.31 H2O
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
2.04
2.06
1.00
1.01
0.84
f1 (ppm)

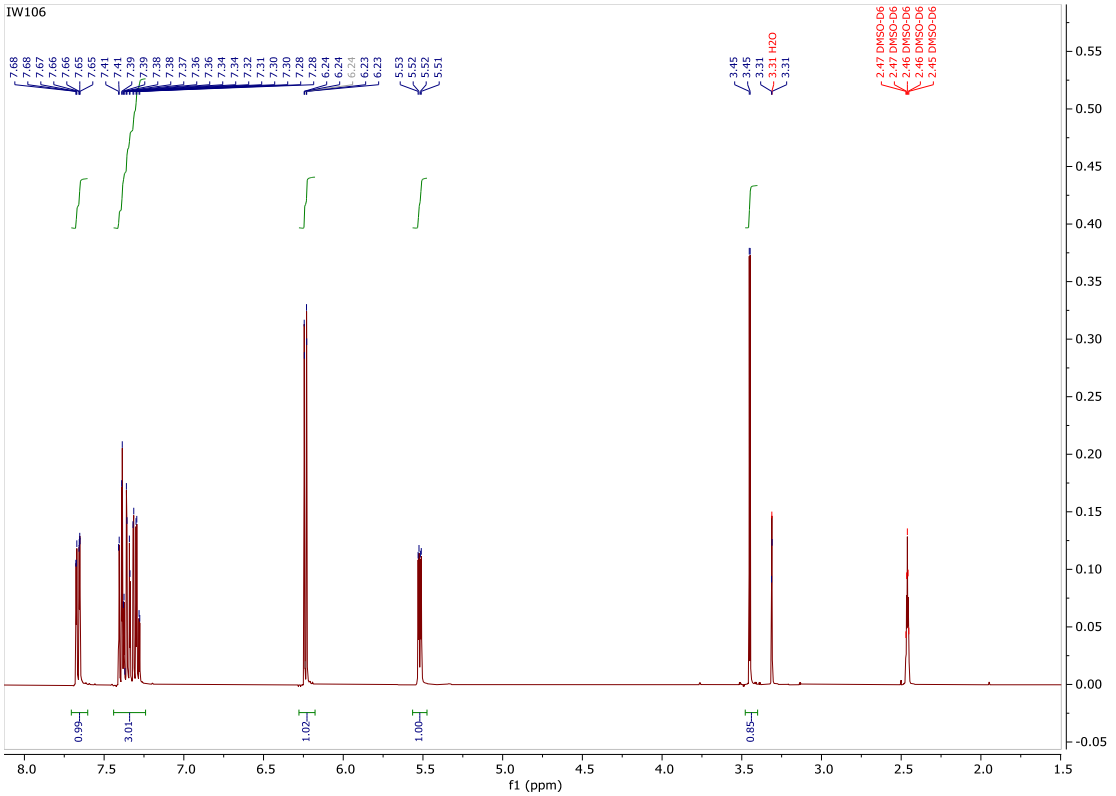

IW108
149.79
147.45
128.27
127.98
124.11
85.01
77.29
62.06
40.65 DMSO-D6
40.44 DMSO-D6
40.23 DMSO-D6
39.82 DMSO-D6
39.61 DMSO-D6
39.40 DMSO-D6
f1 (ppm)

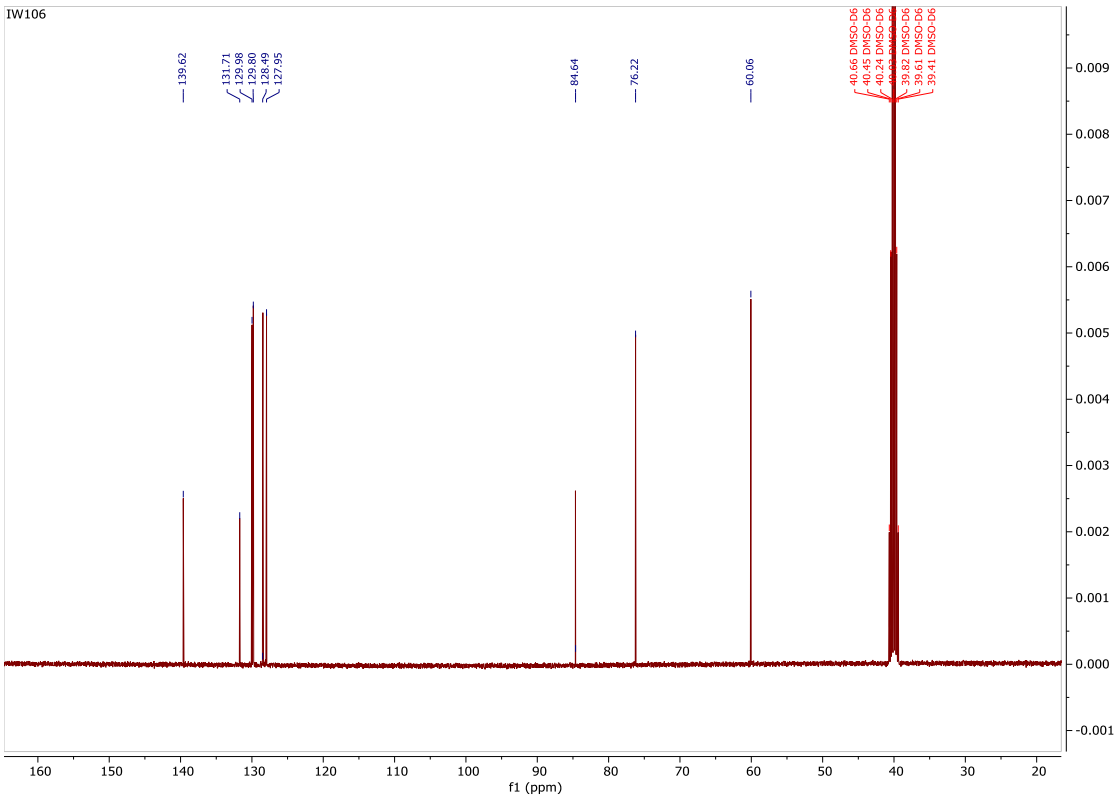

OH
F3C

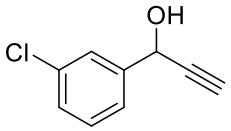

IW109
f1 (ppm)

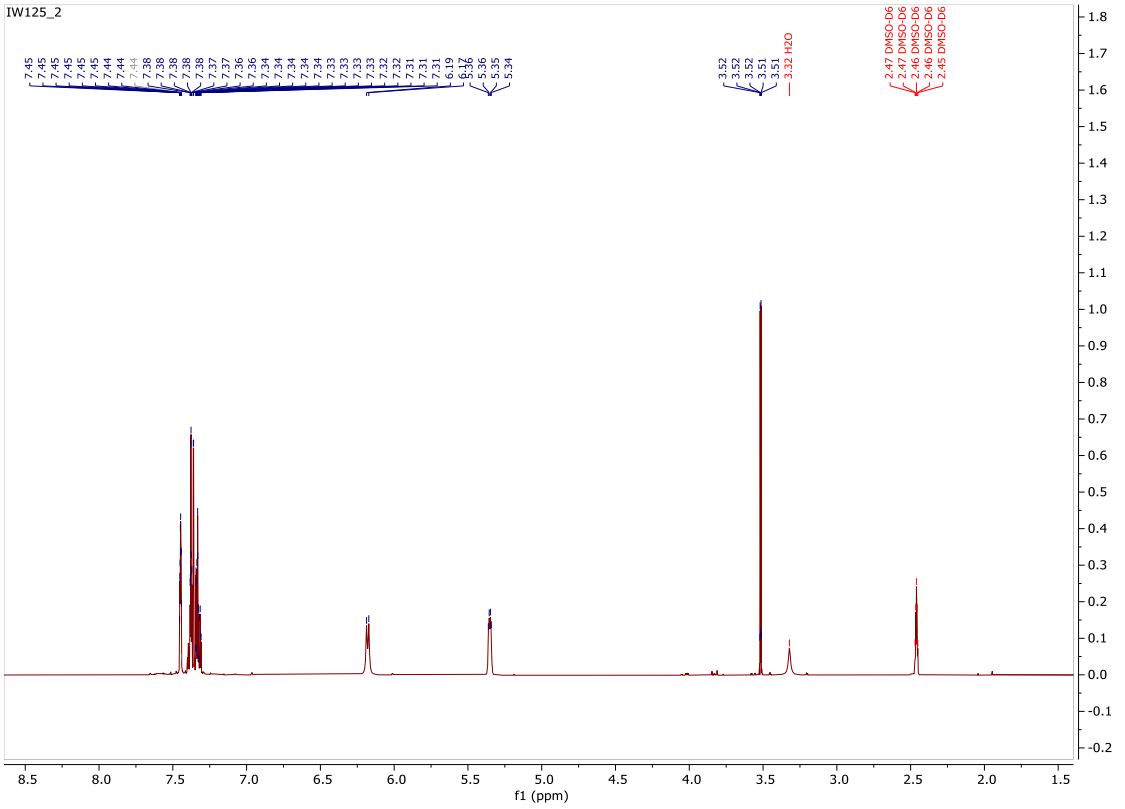

IW109
f1 (ppm)

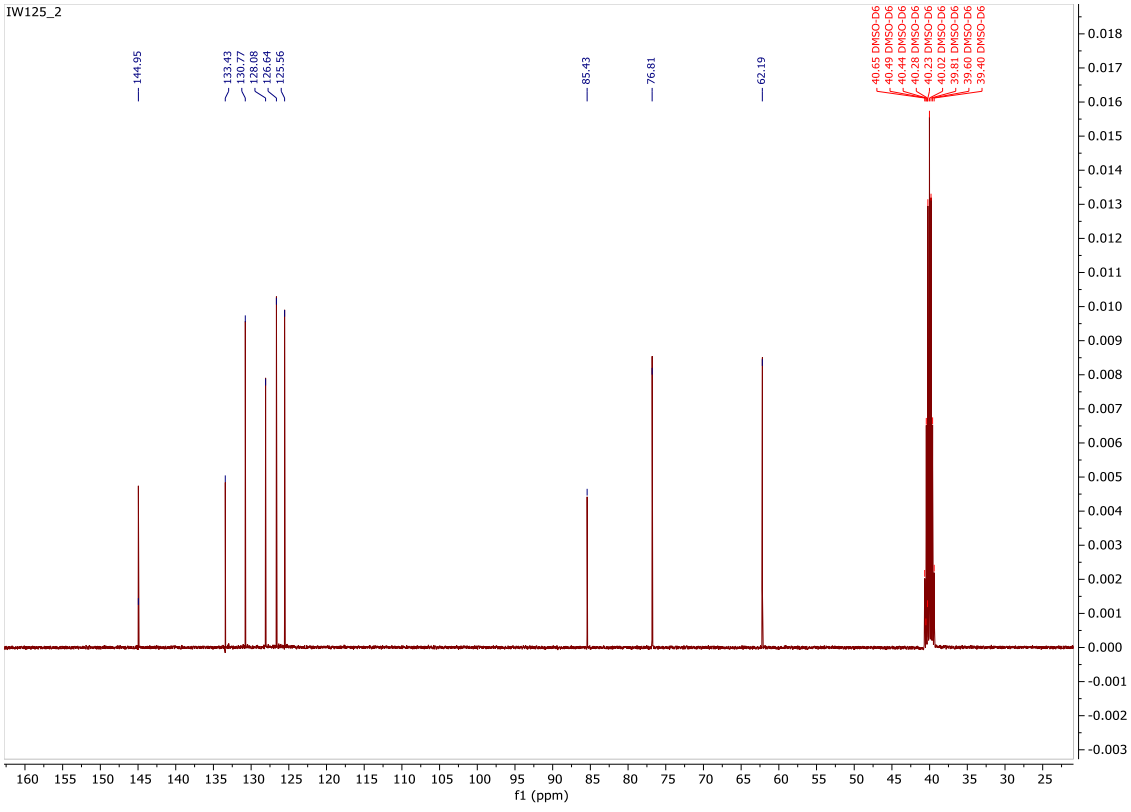

OH
Cl

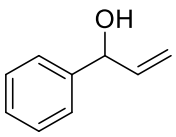

IW106
7.68
7.68
7.67
7.66
7.66
7.65
7.65
7.41
7.41
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.34
7.34
7.32
7.31
7.30
7.30
7.28
7.28
6.24
6.24
6.24
6.23
6.23
5.53
5.52
5.52
5.51
3.45
3.45
3.31
3.31 H2O
3.31
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
2.45 DMSO-D6
0.99
3.01
1.02
1.00
0.85
f1 (ppm)

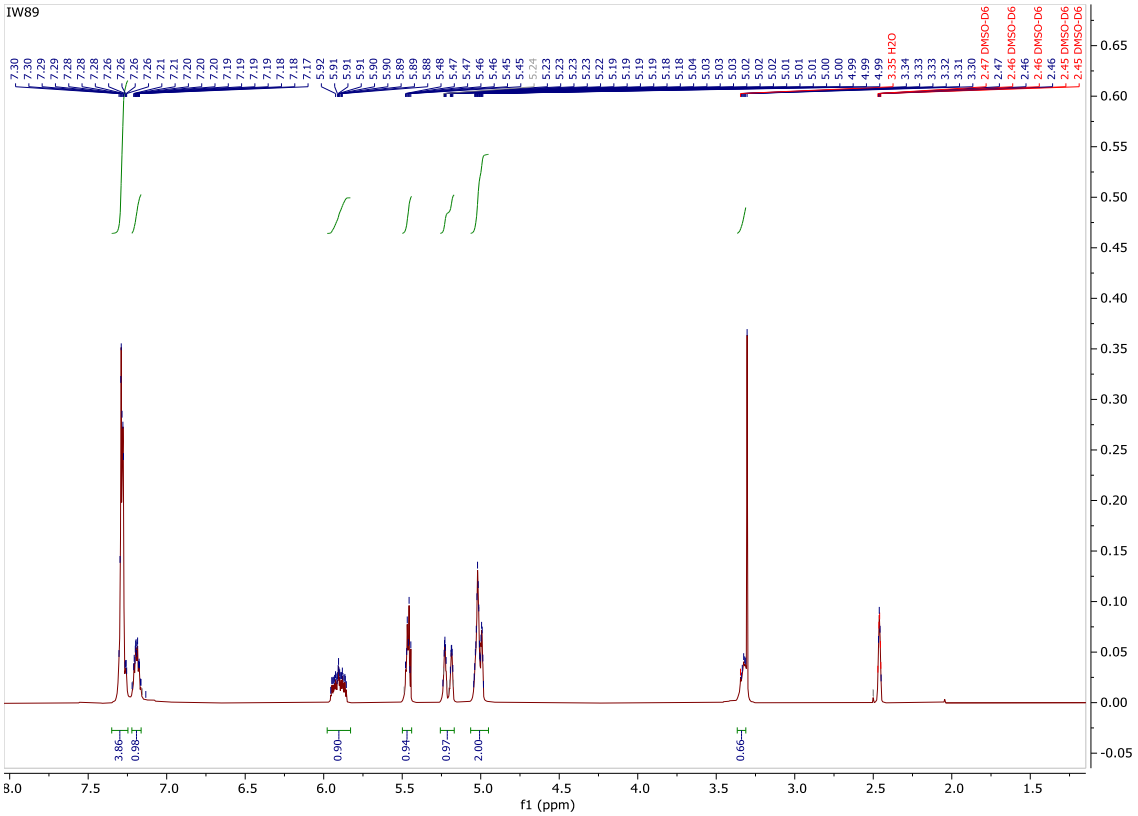

IW106
139.62
131.71
129.98
129.80
128.49
127.95
84.64
76.22
60.06
40.66 DMSO-D6
40.45 DMSO-D6
40.24 DMSO-D6
40.03 DMSO-D6
39.82 DMSO-D6
39.61 DMSO-D6
39.41 DMSO-D6
f1 (ppm)

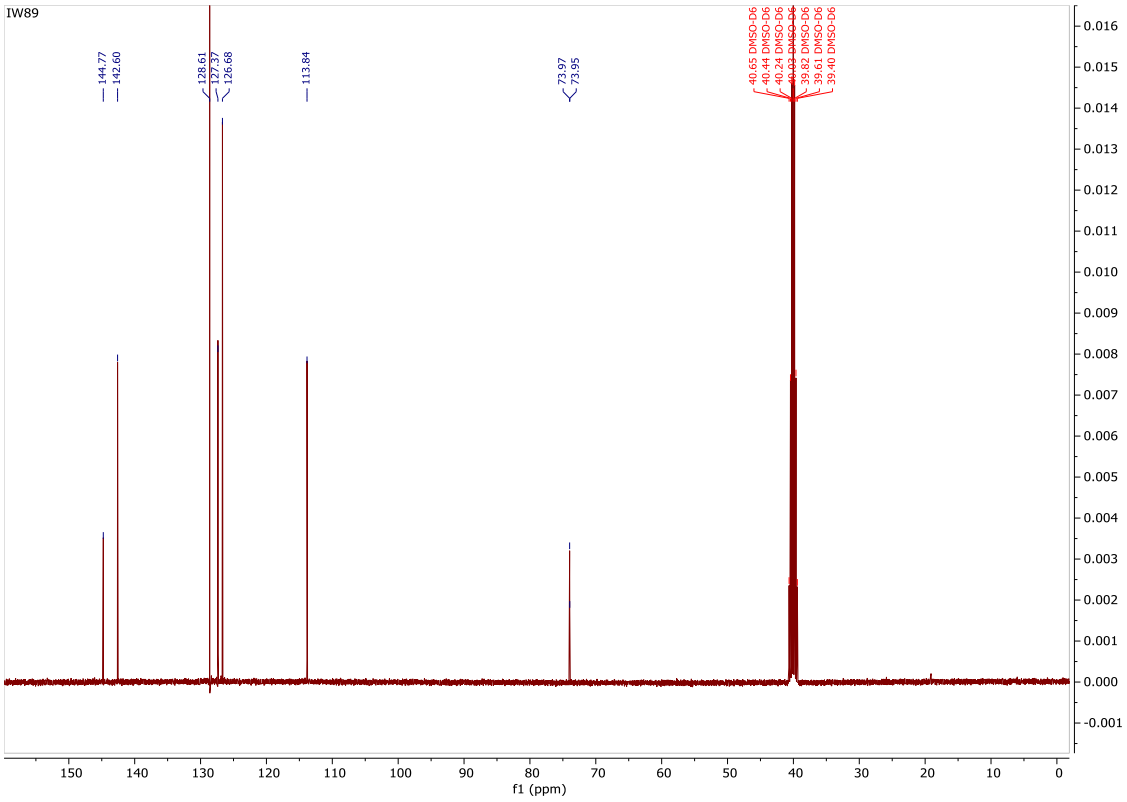

OH
Cl

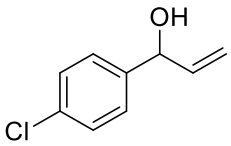

IW125_2
7.45
7.45
7.45
7.45
7.45
7.44
7.44
7.38
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.34
7.34
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.31
6.19
5.36
5.36
5.35
5.34
3.52
3.52
3.52
3.51
3.51
3.32 H2O
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
f1 (ppm)

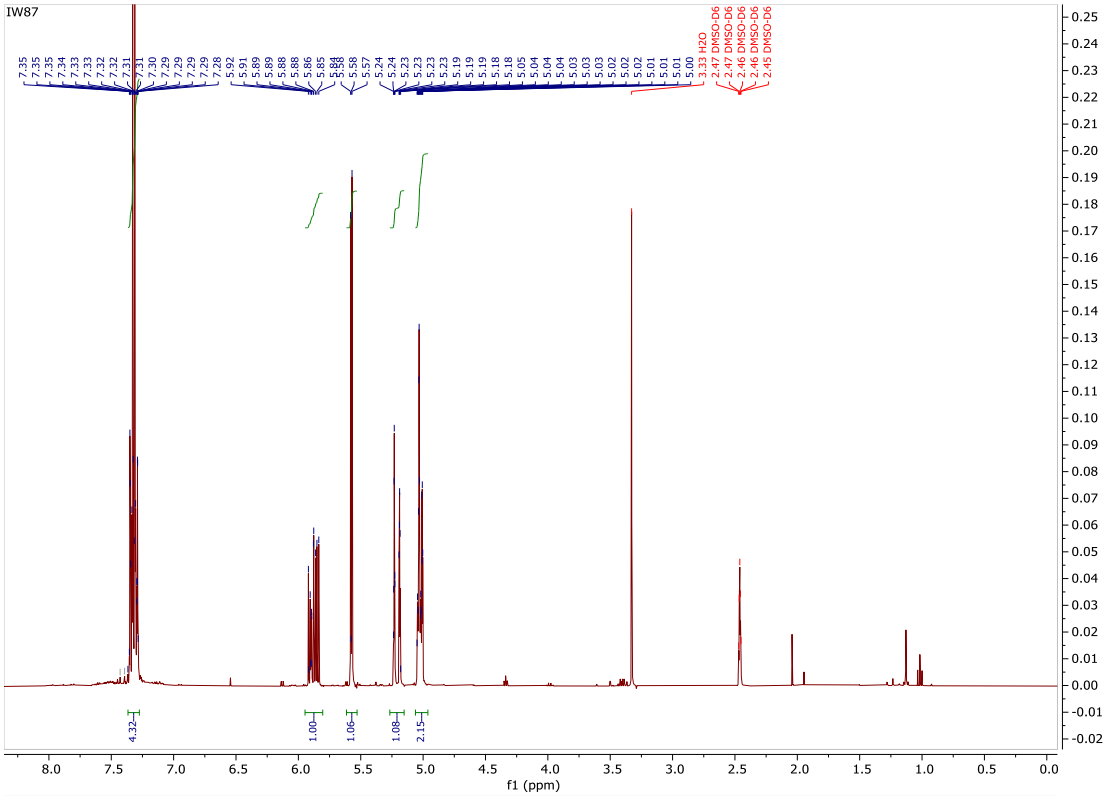

IW125_2
144.95
133.43
130.77
128.08
126.64
125.56
85.43
76.81
62.19
40.65 DMSO-D6
40.49 DMSO-D6
40.44 DMSO-D6
40.28 DMSO-D6
40.23 DMSO-D6
40.02 DMSO-D6
39.81 DMSO-D6
39.60 DMSO-D6
39.40 DMSO-D6
f1 (ppm)

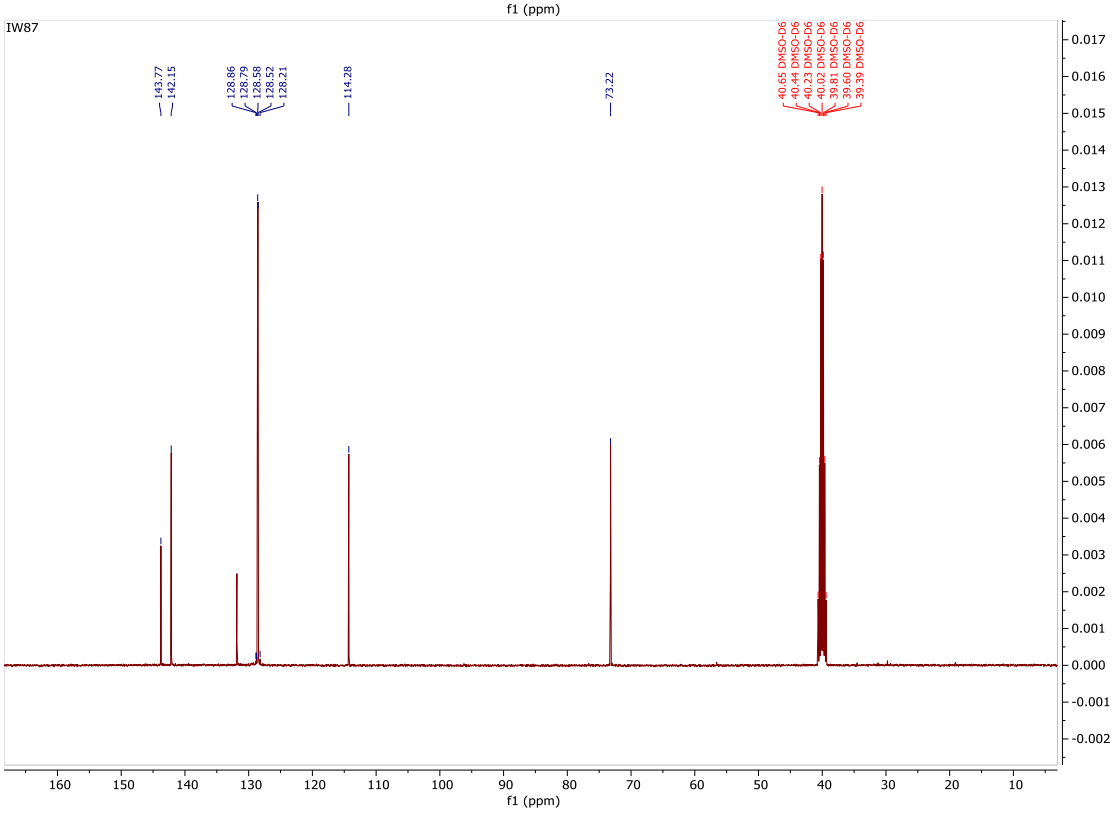

OH

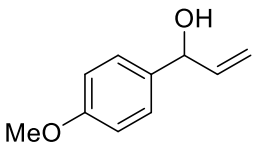

IW89
f1 (ppm)

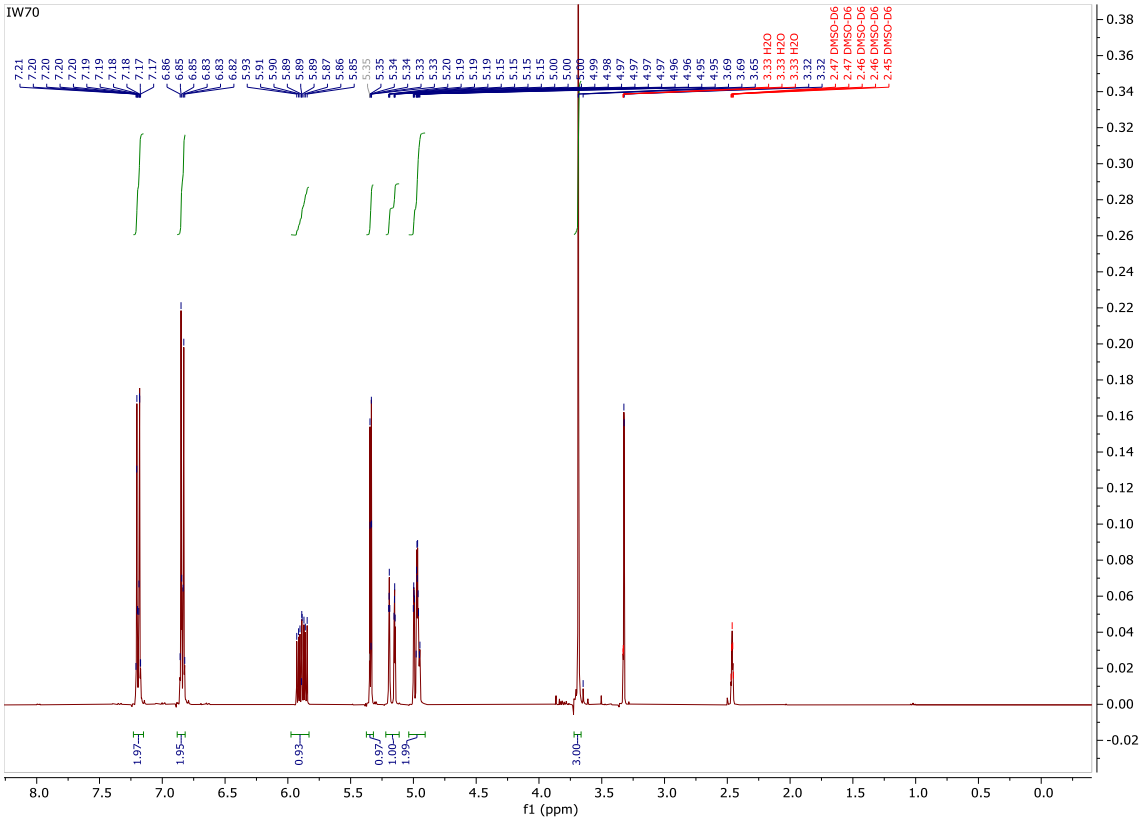

IW89
f1 (ppm)

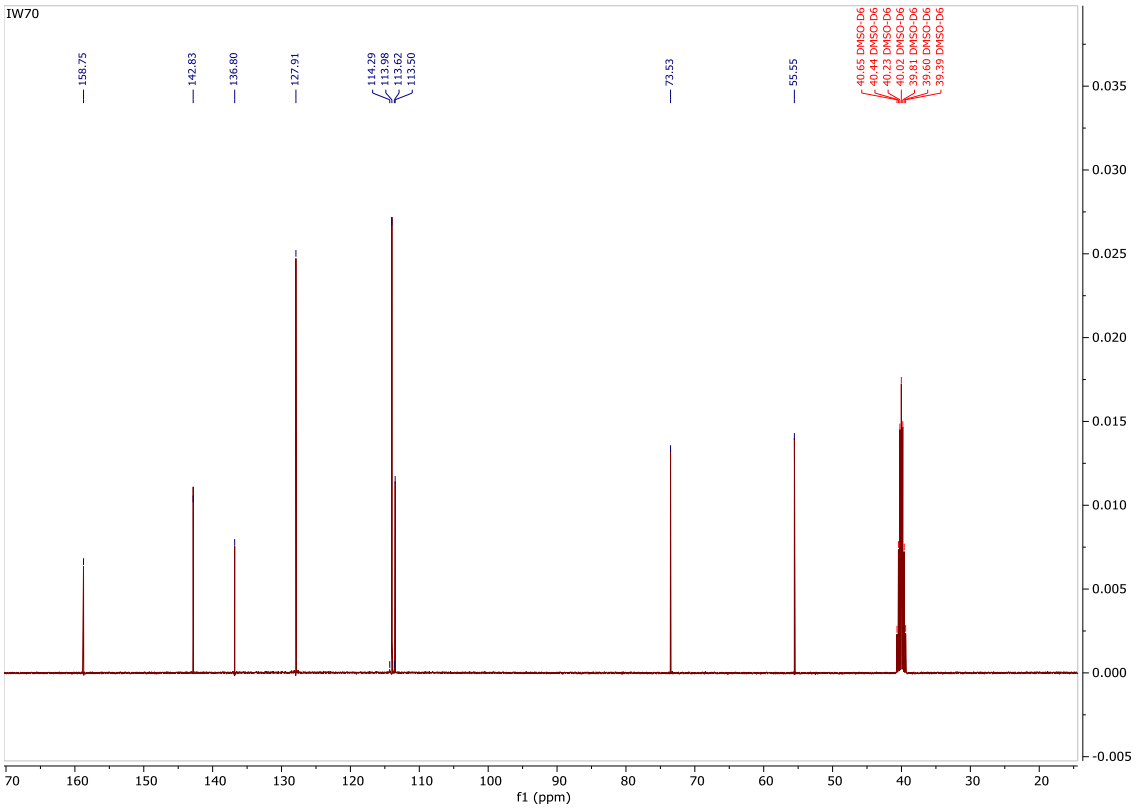

OH
Cl

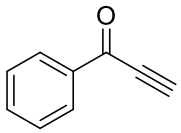

IW87
f1 (ppm)

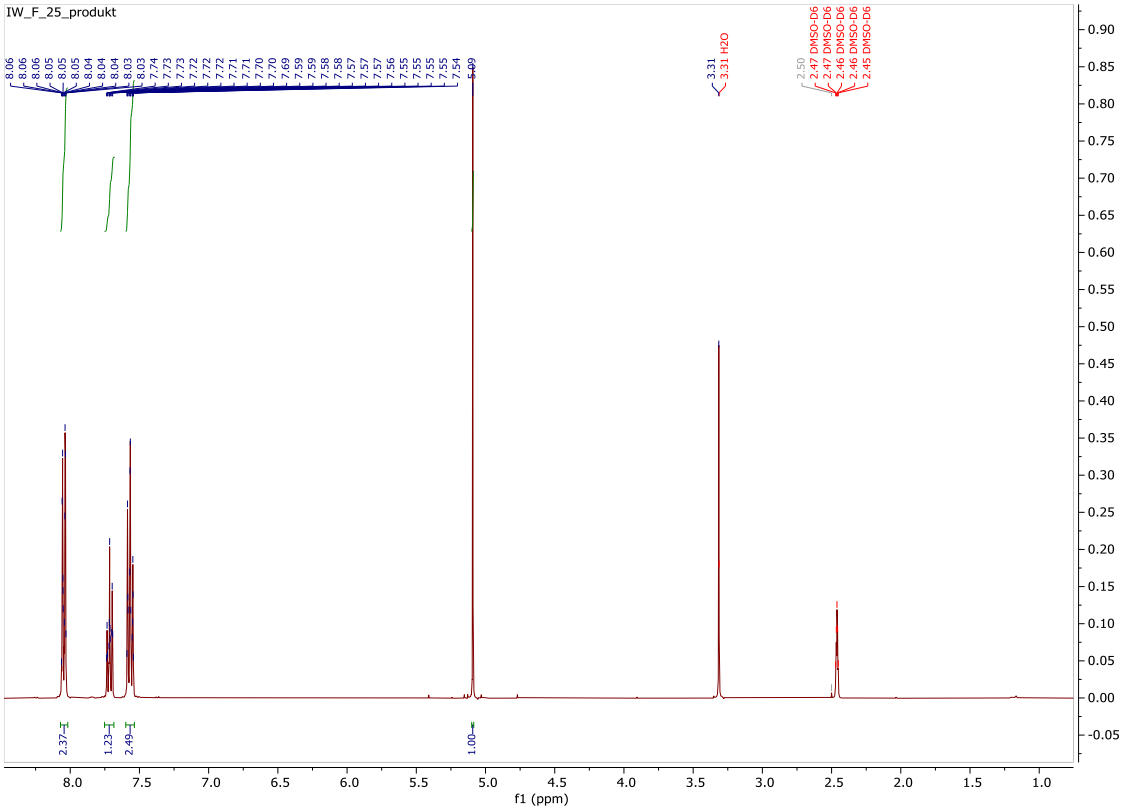

IW87
f1 (ppm)

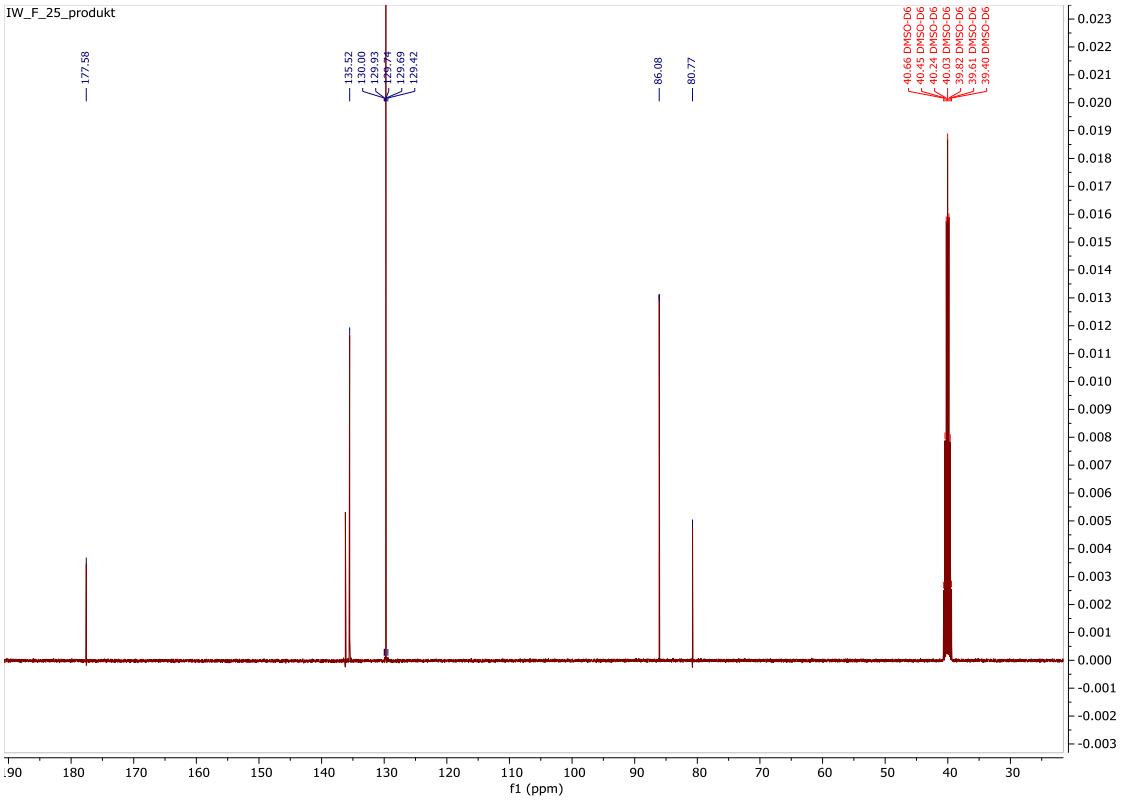

OH
MeO

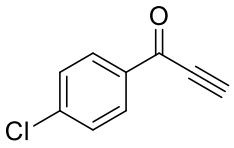

IW70
f1 (ppm)

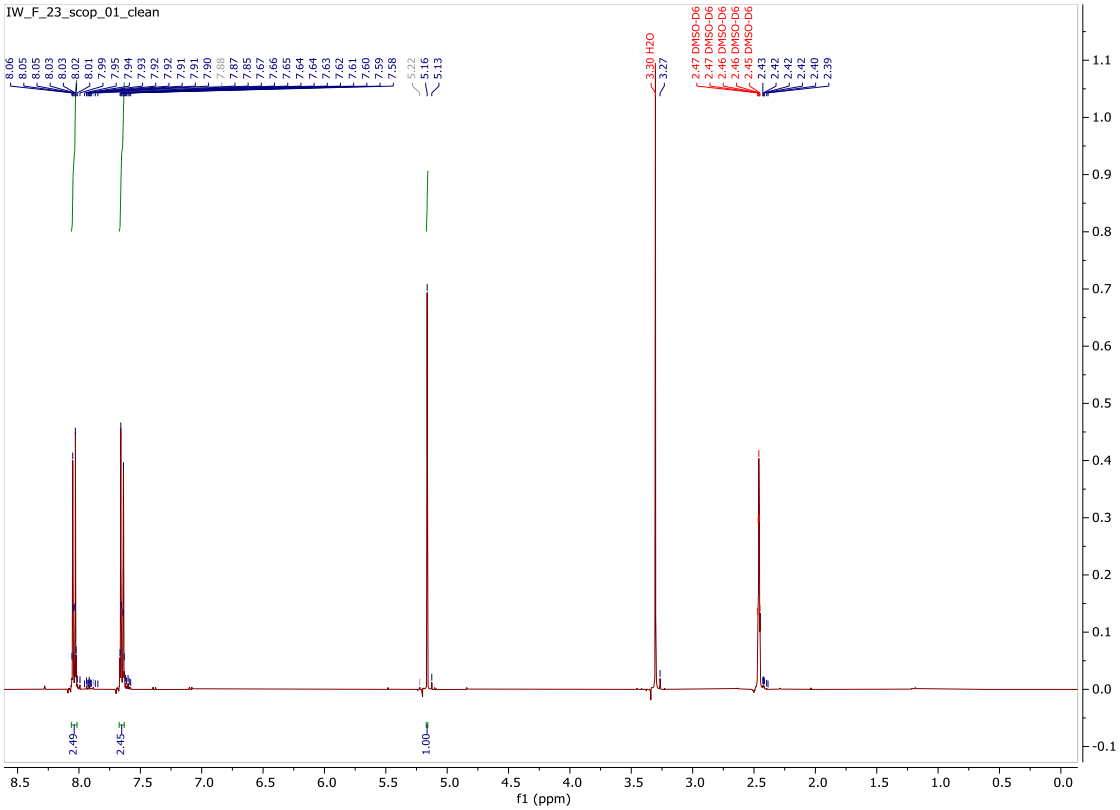

IW70
f1 (ppm)

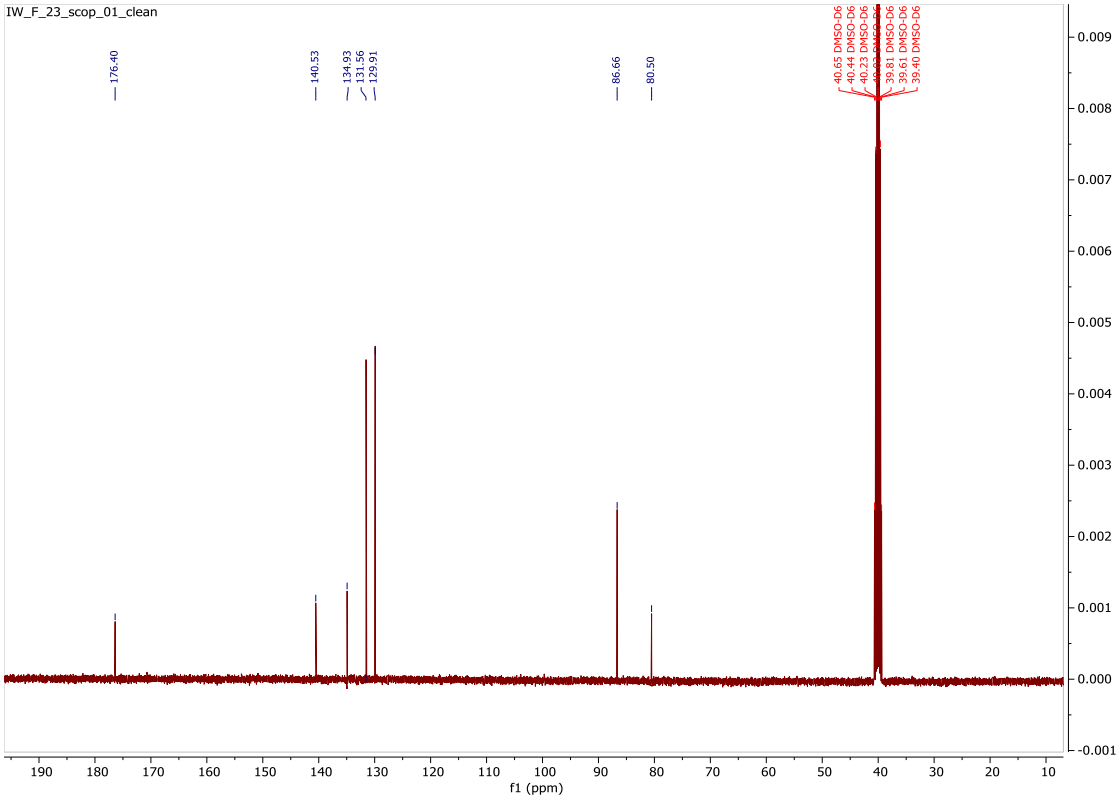


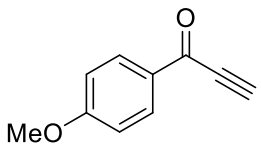

IW_F_25_produkt
3.31
3.31 H2O
2.50
2.47 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
2.37
1.23
2.49
1.00
f1 (ppm)

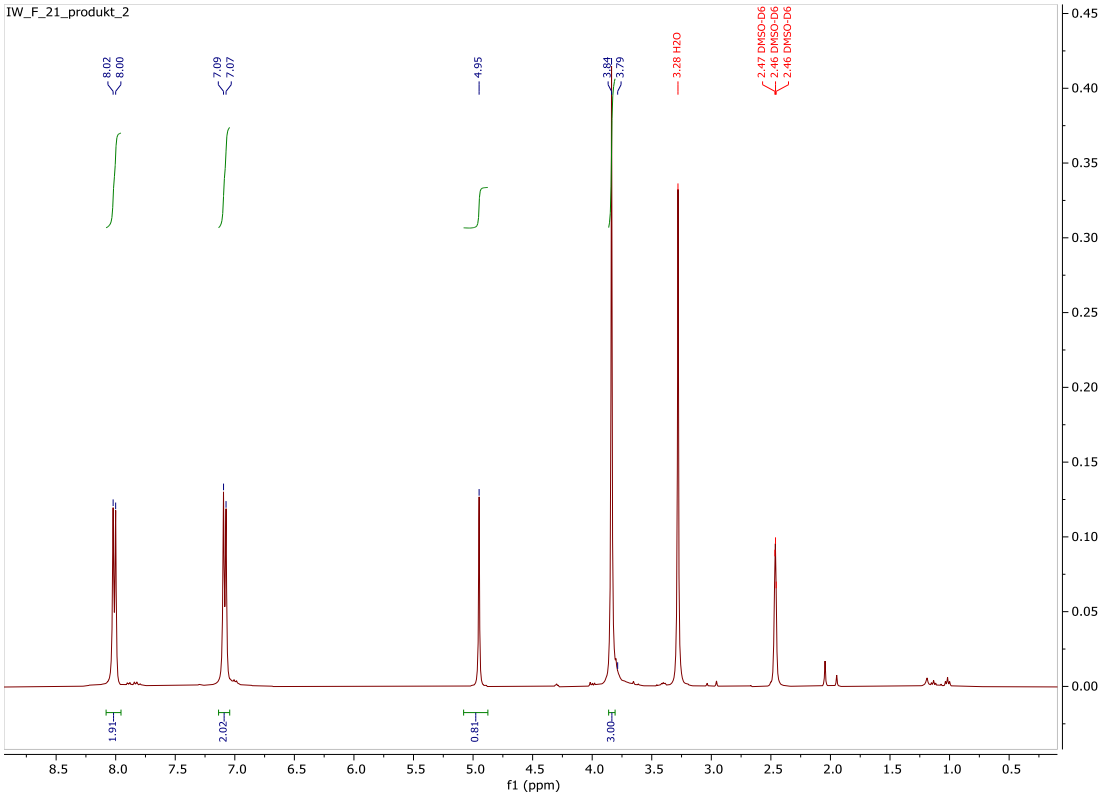

IW_F_25_produkt
177.58
135.52
130.00
129.93
129.74
129.69
129.42
86.08
80.77
40.66 DMSO-D6
40.45 DMSO-D6
40.24 DMSO-D6
40.03 DMSO-D6
39.82 DMSO-D6
39.61 DMSO-D6
39.40 DMSO-D6
f1 (ppm)

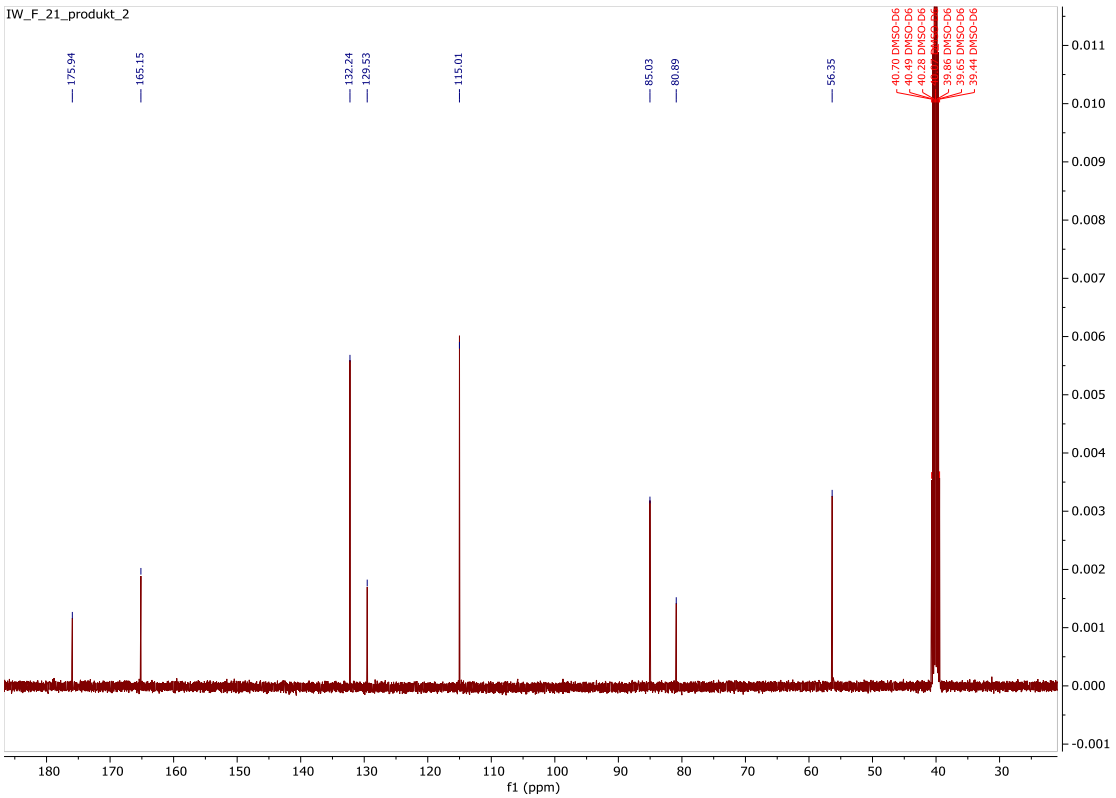

O
Cl

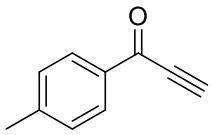

IW_F_23_scop_01_clean
8.06
8.05
8.05
8.03
8.03
8.02
8.01
7.99
7.95
7.94
7.93
7.92
7.92
7.91
7.91
7.90
7.88
7.87
7.85
7.67
7.66
7.65
7.64
7.64
7.63
7.62
7.61
7.60
7.59
7.58
5.22
5.16
5.13
3.30 H2O
3.27
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
2.43
2.42
2.42
2.42
2.40
2.39
2.49
2.45
1.00
f1 (ppm)

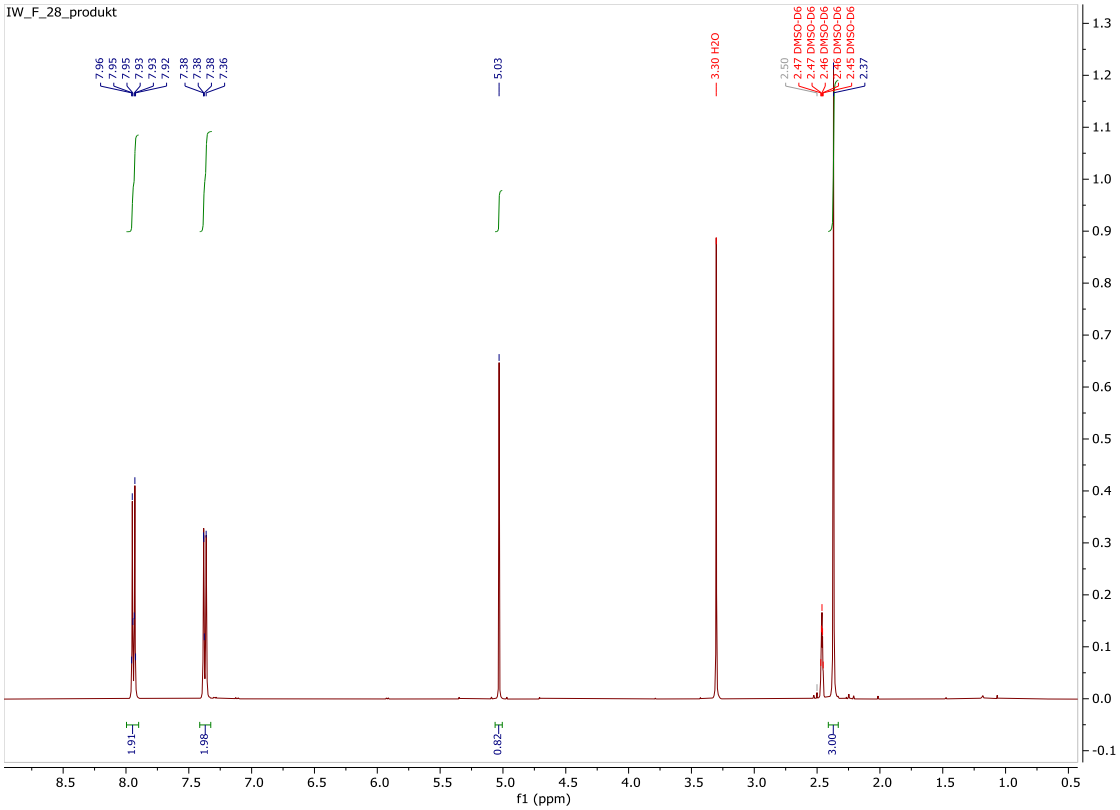

IW_F_23_scop_01_clean
176.40
140.53
134.93
131.56
129.91
86.66
80.50
40.65 DMSO-D6
40.44 DMSO-D6
40.23 DMSO-D6
39.81 DMSO-D6
39.61 DMSO-D6
39.40 DMSO-D6
f1 (ppm)

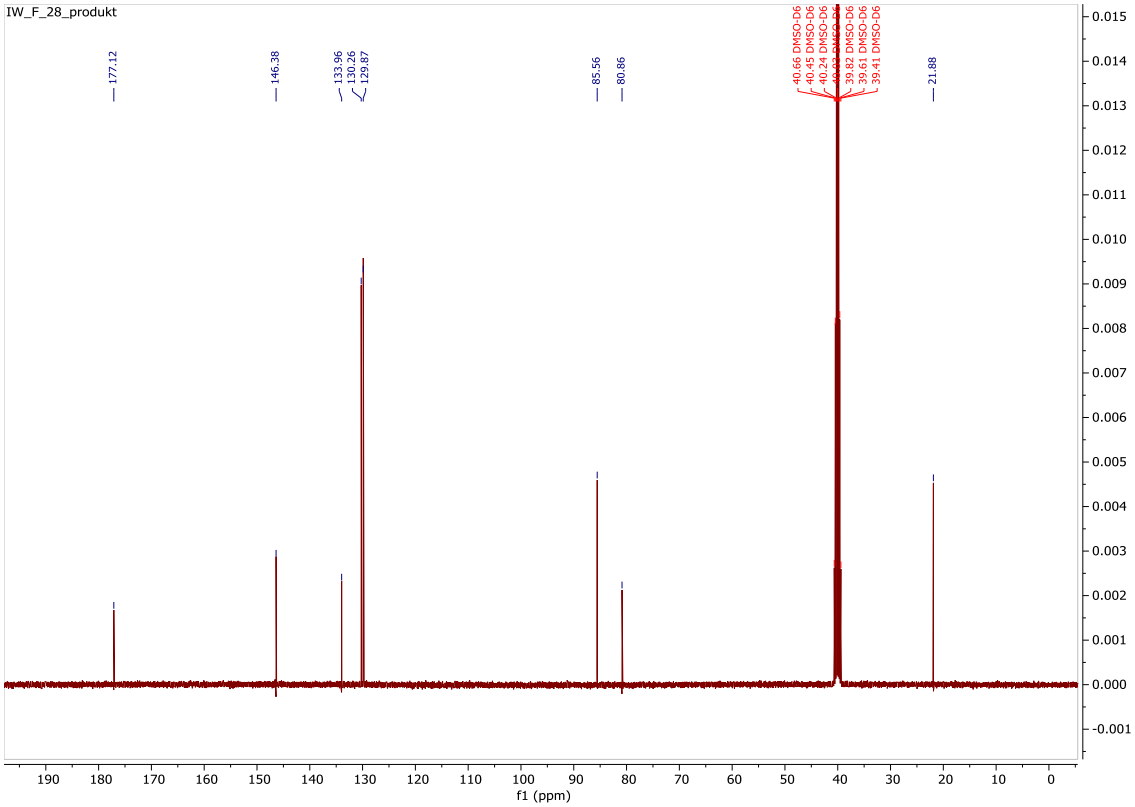

O
MeO

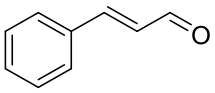

IW_F_21_produkt_2
8.02
8.00
7.09
7.07
4.95
3.84
3.79
3.28 H2O
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
1.91
2.02
0.81
3.00
f1 (ppm)

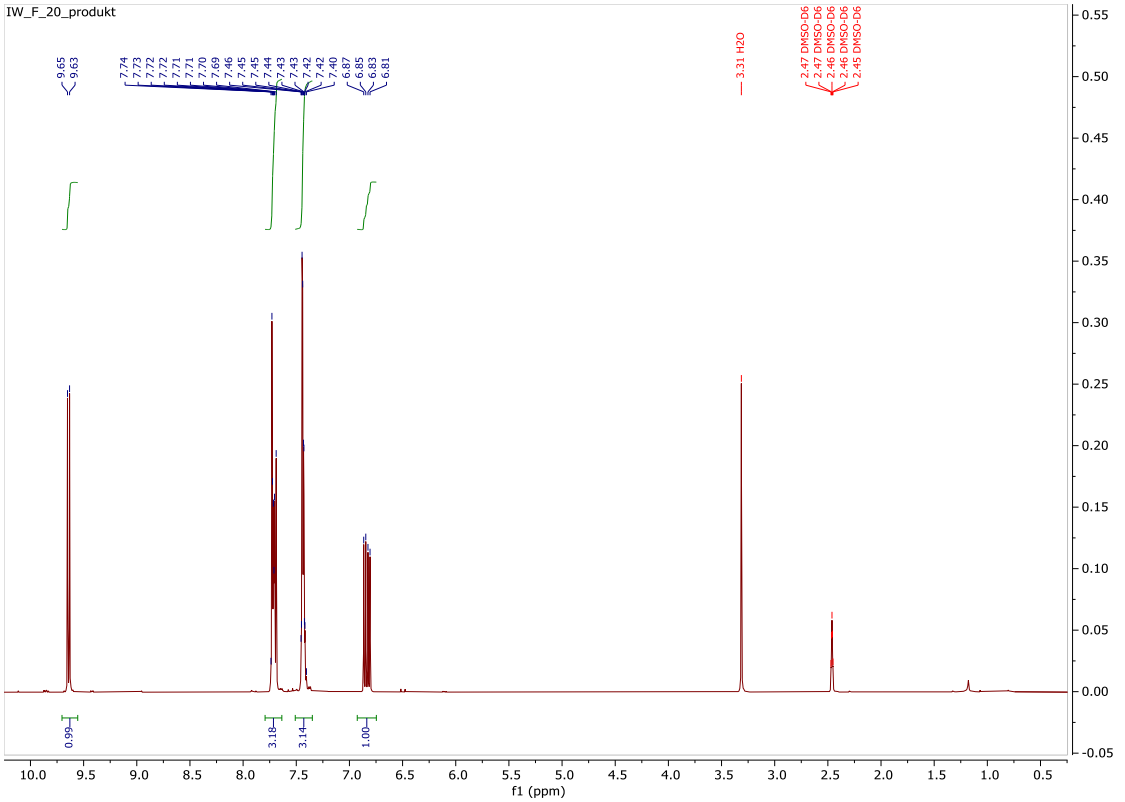

IW_F_21_produkt_2
175.94
165.15
132.24
129.53
115.01
85.03
80.89
56.35
40.70 DMSO-D6
40.49 DMSO-D6
40.28 DMSO-D6
39.86 DMSO-D6
39.65 DMSO-D6
39.44 DMSO-D6
f1 (ppm)

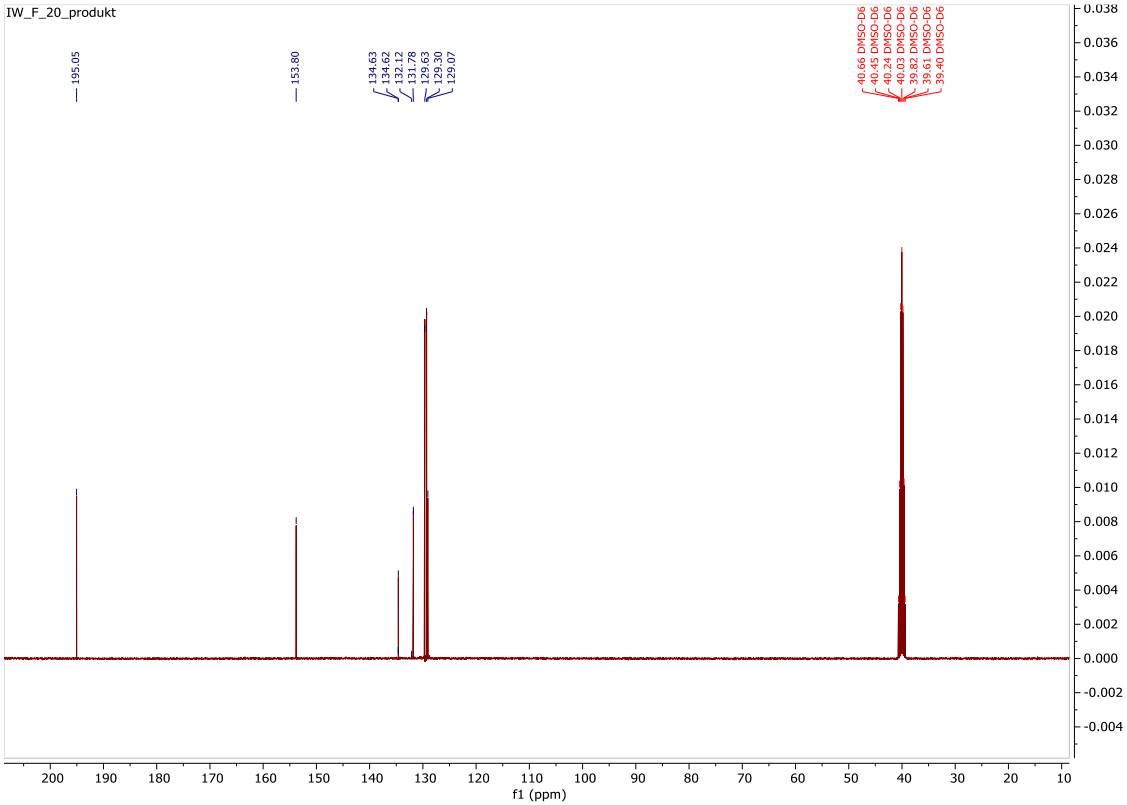


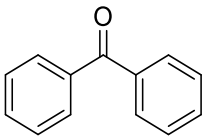

IW_F_28_produkt
7.96
7.95
7.95
7.93
7.93
7.92
7.38
7.38
7.38
7.36
5.03
3.30 H2O
2.50
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
2.37
1.91
1.98
0.82
3.00
f1 (ppm)

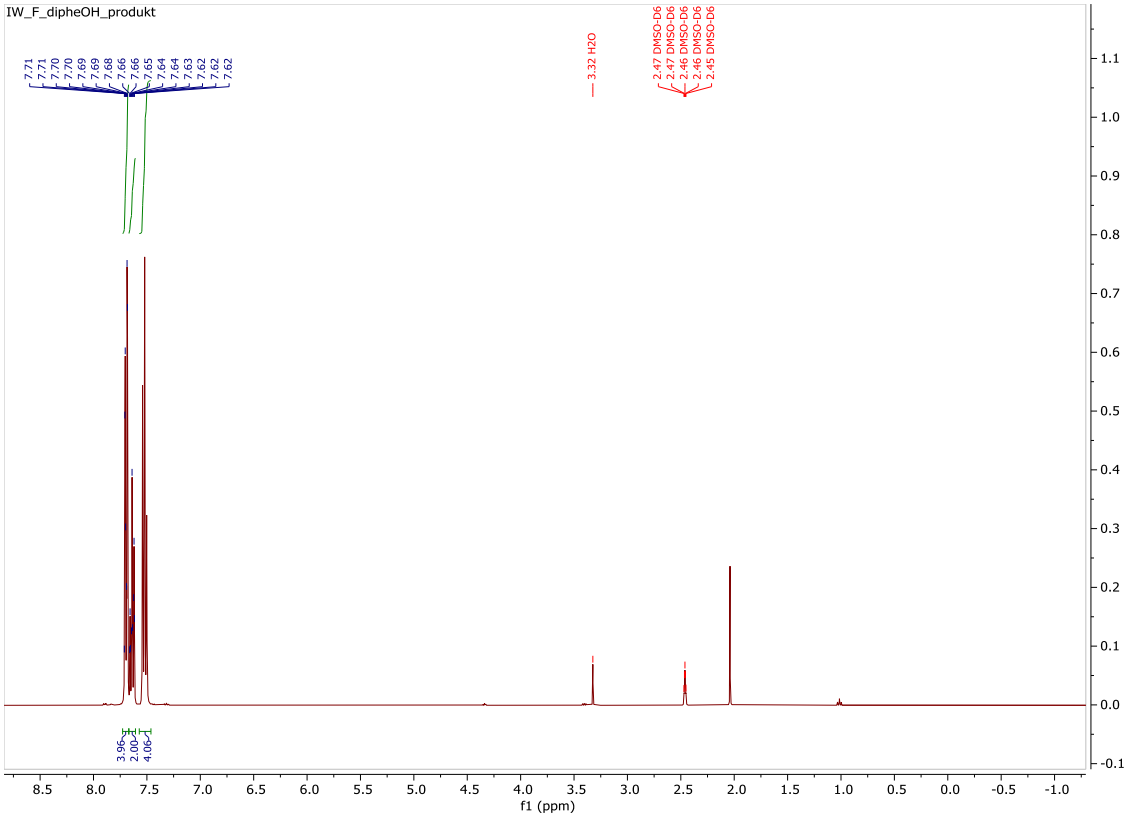

IW_F_28_produkt
177.12
146.38
133.96
130.26
129.87
85.56
80.86
40.66 DMSO-D6
40.45 DMSO-D6
40.24 DMSO-D6
39.82 DMSO-D6
39.61 DMSO-D6
39.41 DMSO-D6
21.88
f1 (ppm)

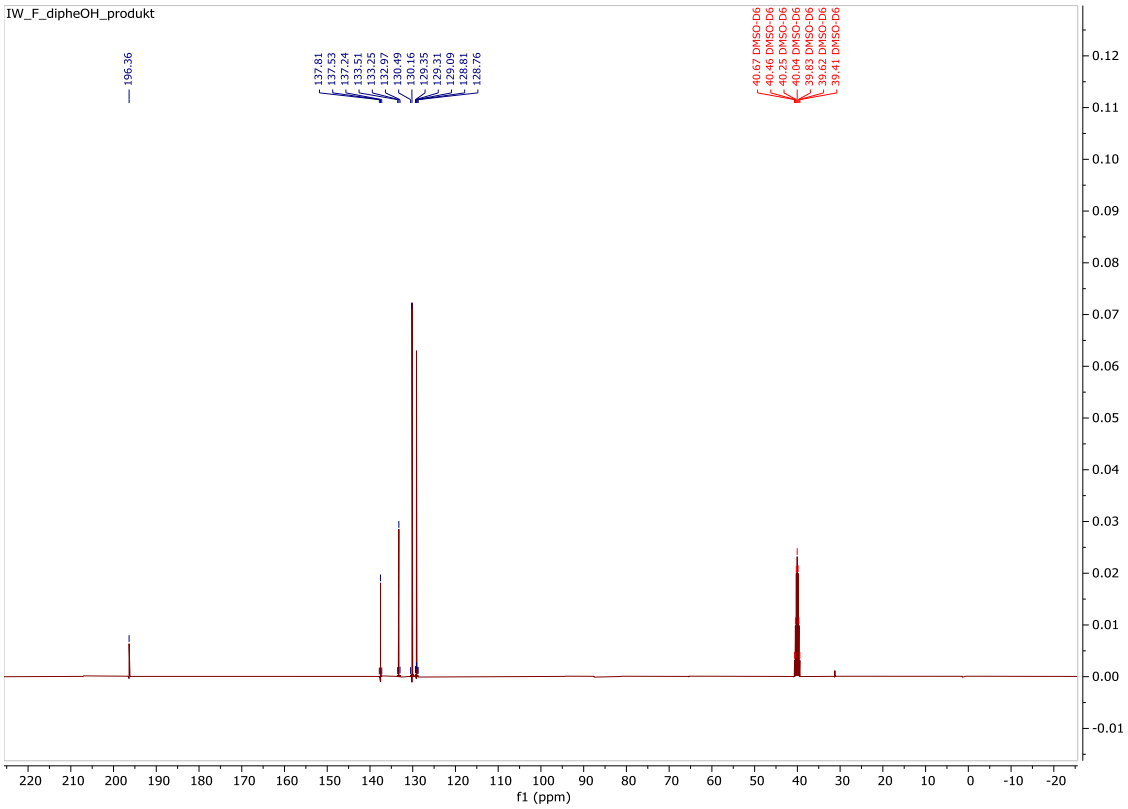

O

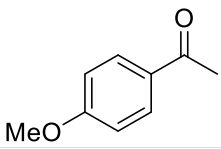

IW_F_20_produkt
9.65
9.63
7.74
7.73
7.72
7.72
7.71
7.71
7.70
7.69
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.40
6.87
6.85
6.83
6.81
3.31 H2O
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
0.99
3.18
3.14
1.00
f1 (ppm)

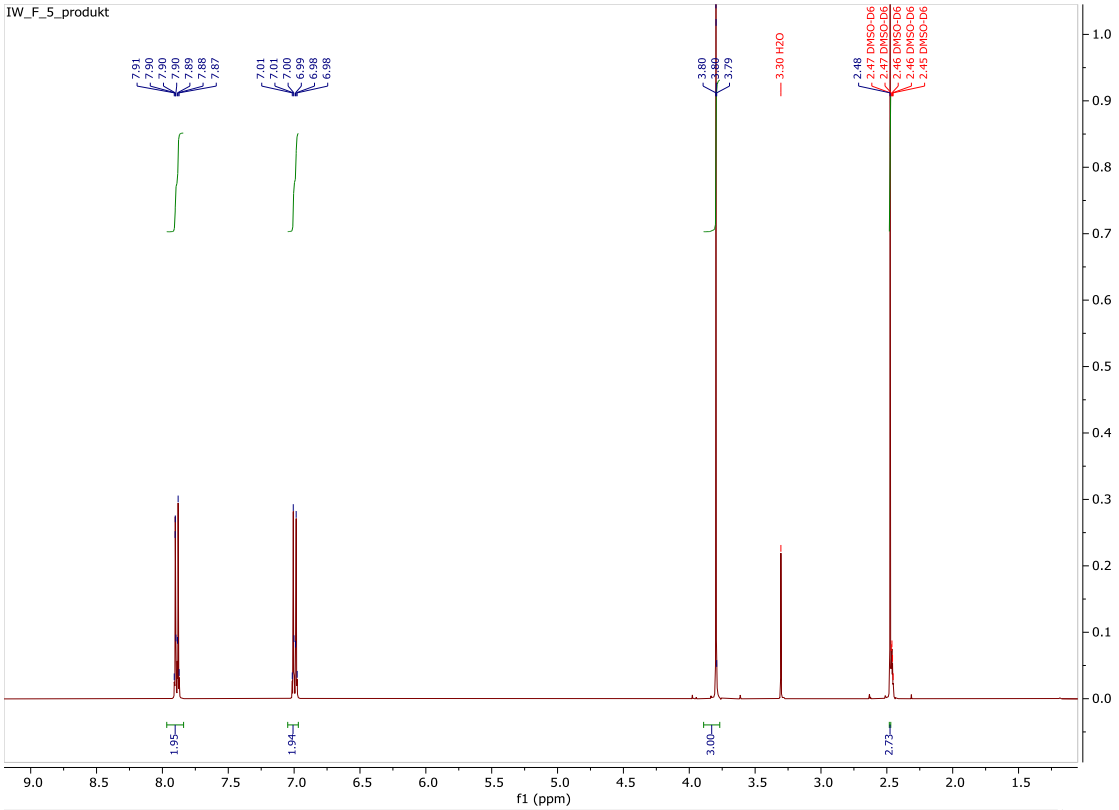

IW_F_20_produkt
195.05
153.80
134.63
134.62
132.12
131.78
129.63
129.30
129.07
40.66 DMSO-D6
40.45 DMSO-D6
40.24 DMSO-D6
40.03 DMSO-D6
39.82 DMSO-D6
39.61 DMSO-D6
39.40 DMSO-D6
f1 (ppm)

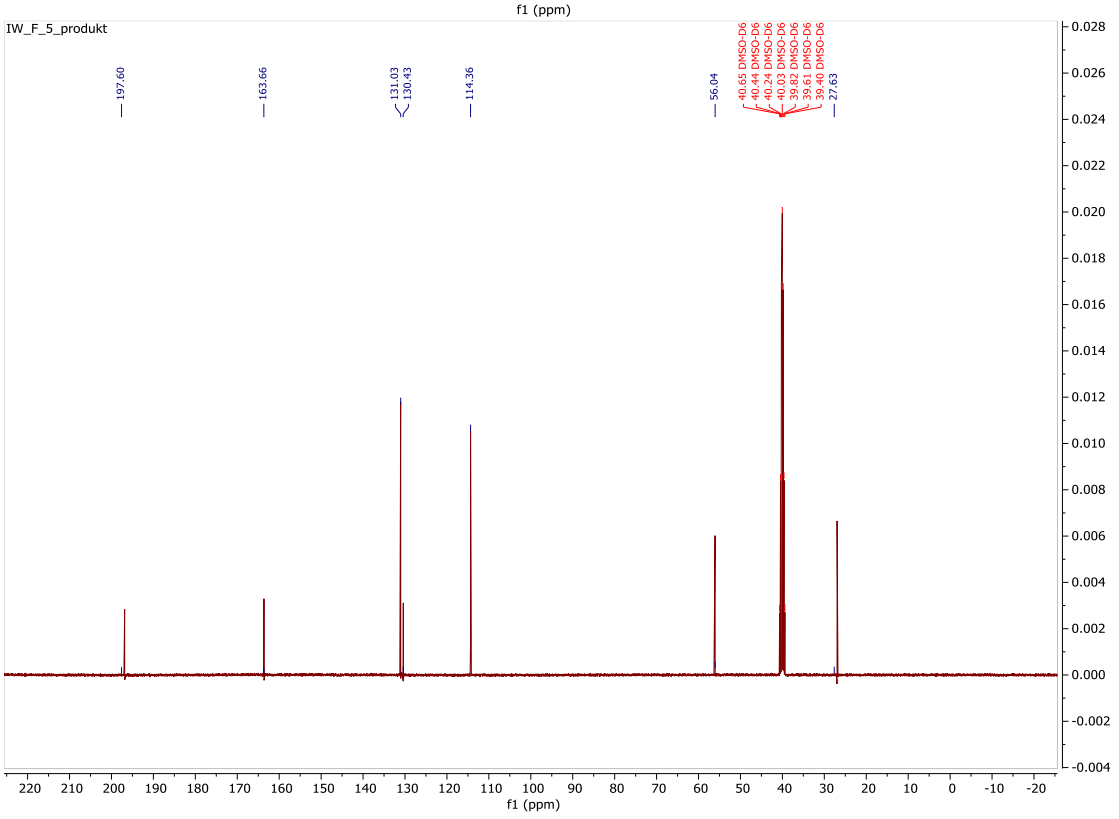



IW_F_dipheOH_produkt
7.71
7.71
7.70
7.70
7.69
7.69
7.68
7.66
7.65
7.64
7.64
7.63
7.62
7.62
7.62
3.32 H2O
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
3.96
2.00
4.06
f1 (ppm)


IW_F_dipheOH_produkt
196.36
137.81
137.53
137.24
133.51
133.25
132.97
130.49
130.16
129.35
129.31
129.09
128.81
128.76
40.67 DMSO-D6
40.46 DMSO-D6
40.25 DMSO-D6
40.04 DMSO-D6
39.83 DMSO-D6
39.62 DMSO-D6
39.41 DMSO-D6
f1 (ppm)


O
MeO


IW_F_5_produkt
7.91
7.90
7.90
7.90
7.89
7.88
7.87
7.01
7.01
7.00
6.99
6.98
6.98
3.80
3.80
3.79
3.30 H2O
2.48
2.47 DMSO-D6
2.47 DMSO-D6
2.46 DMSO-D6
2.46 DMSO-D6
2.45 DMSO-D6
1.95
1.94
3.00
2.73
f1 (ppm)


IW_F_5_produkt
197.60
163.66
131.03
130.43
114.36
56.04
40.65 DMSO-D6
40.44 DMSO-D6
40.24 DMSO-D6
40.03 DMSO-D6
39.82 DMSO-D6
39.61 DMSO-D6
39.40 DMSO-D6
27.63
f1 (ppm)

S11. References

1. M. Wendel, S. Nizinski, D. Tuwalska, K. Starzak, D. Szot, D. Prukala, M. Sikorski, S. Wybraniec and G. Burdzinski, *Phys. Chem. Chem. Phys.*, 2015, **17**, 18152-18158.
2. G. Burdzinski, M. Bayda, G. L. Hug, M. Majchrzak, B. Marciniec and B. Marciniak, J. Lumin., 2011, 131, 577-580.
3. E. Barreiro, A. Sanz-Vidal, E. Tan, S.-H. Lau, T. D. Sheppard and S. Díez-González, *Eur. J. Org. Chem.*, 2015, **2015**, 7544-7549.
4. S. Kalhor-Monfared, C. Beauvineau, D. Scherman and C. Girard, *Eur. J. Med. Chem.*, 2016, **122**, 436-441.
5. G. Ieronimo, G. Palmisano, A. Maspero, A. Marzorati, L. Scapinello, N. Masciocchi, G. Cravotto, A. Barge, M. Simonetti, K. L. Ameta, K. M. Nicholas and A. Penoni, *Org. Biomol. Chem.*, 2018, **16**, 6853-6859.
6. Sakamoto, J.; Murakami, M.; Sugata, M.; Larsen, B.; Sun, Z.; Nagorny, P.; Nagasawa, T.; Kuwahara, S.; Wang, G.; Huang, Z. *Synlett* 2020, 31 (13), 1323-1327.
7. Y.-B. Wang, B.-Y. Liu, Q. Bu, B. Dai and N. Liu, *Adv. Synth. Catal.*, 2020, **362**, 2930-2940.
8. A. Golczak, M. Insińska-Rak, A. Davoudpour, D. Hama Saeed, P. Ménová, V. Mojr, R. Cibulka, I. Khmelinskii, L. Mrówczyńska and M. Sikorski, *Spectrochim. Acta Part A: Mol. and Biomol. Spectroscopy*, 2022, 120985.
9. R. Fu, Y. Liu, T. Wu, X. Zhang, Y. Zhu, J. Luo, Z. Zhang and Y. Jiang, *Chem. Commun.*, 2022, **58**, 3525-3528.
10. B. Ardiansah, H. Tanimoto, T. Tomohiro, T. Morimoto and K. Kakiuchi, *Chem. Commun.*, 2021, **57**, 8738-8741.
11. N. Xu, X. Peng, C. Luo, L. Huang, C. Wang, Z. Chen and J. Li, *Adv. Synth. Catal.*, 2023, **365**, 142-147.
12. R. D. Mair and A. J. Graupner, *Anal. Chem.*, 1964, **36**, 194-204.
13. R. Schmidt, C. Tanielian, R. Dunsbach and C. Wolff, *J. Photochem. Photobiol., A: Chemistry*, 1994, **79**, 11-17.