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Exploring Eosin Y as a Bimodular Catalyst: Organophotoacid Mediated Minisci-Type Acylation of N-Heteroarenes

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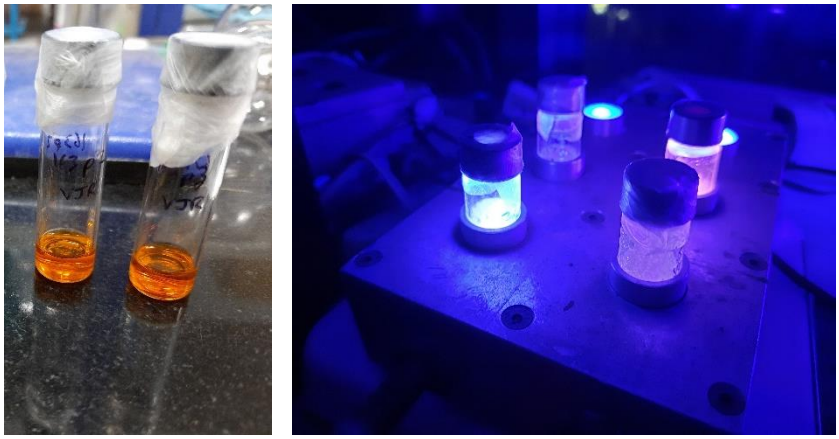
General Information:

Photochemical reactions were irradiated with blue LED (Opulant Americas make LED, 455nm, Power: 3W, Luminous Flux/Radiant Flux: 687 mW; Viewing Angle: 120 Deg) which were installed on a passive cooling system of a custom-made six vials aluminium reactor and connected with a liquid cooling system to maintain the temperature (Figure S1). Commercially available 7 mL screw cap vials fitted with PTFE/silicone septa were purchased from Sigma-Aldrich. All the reactions were performed by sealing the vials with nitrogen gas with the help of standard schlenk line techniques. The distance between the base of the glass vial and the 3W blue LED was measured to be 4 mm. Chromatographic purification of products was accomplished by Column chromatography on silica gel (230-400 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were employed, using UV light as the visualizing agent. Organic solutions were concentrated under reduced pressure on a Heidolph rotary evaporator. The products obtained were characterised using ^{1}H NMR,^{13}C NMR, ESI-HRMS. NMR spectra were recorded at 400 MHz and 500 MHz for ^{1}H, 101 MHz, 126 MHz for ^{13}C and 471 MHz for ^{19}F NMR. The chemical shift (δ) for ^{1}H and ^{13}C are given in ppm relative to internal standard/residual signals of the solvents (for ^{1}H NMR ($CHCl_3$ @ 7.26 ppm and DMSO @ 2.5 ppm), for ^{13}C NMR ($CHCl_3$ @ 77.00 ppm and DMSO @ 39.52 ppm) and tetramethylsilane @ 0 ppm). Coupling constants are given in Hertz. The following abbreviations are followed to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; ddd, doublet of doublets of doublets. High-resolution mass spectra (HRMS) were obtained from the High Resolution Mass Spectrometry unit on MicroTOF Focus with electrospray ionization. A Shimadzu, Nexis GC-2030 gas chromatography (GC) instrument was used for quantitative yield determination.

Materials: Synthesis grade solvents like tertiary butanol (^{t}BuOH) were used as purchased. Eosin Y was purchased from Sigma-Aldrich. Heterocycles, aldehydes, and all the other commercial grade reagents and solvents were purchased from Sigma-Aldrich, Spectrochem and GLR Innovations at the highest commercial quality and used without further purification, unless otherwise stated.

Reaction Setup and Photochemical Setup:

Figure S1: 3W blue LED photoreactor setup with magnetic stirring plate.



a **b**

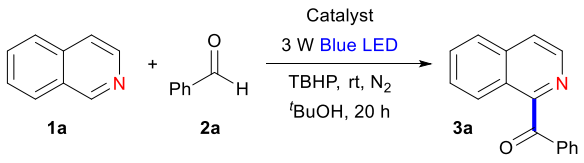
Figure S2: (a) Sealed reaction vials, (b) Vials in photoreactor

General Procedure for Photochemical Acylation of N-Heteroarenes with Aldehydes:

A 7 mL glass vial was charged with eosin Y (8 mol%), heterocycle (0.1 mmol), aldehyde (0.4 mmol), TBHP in water (0.4 mmol) and a magnetic stirring bead. ^{t}BuOH (1.0 mL) was added as the solvent. The vial was sealed with a PTFE septum, purged with N_2 by using schlenk line and coated with parafilm layer (Figure S2a). The reactions were placed in a pre-programmed temperature (25 ºC) controlled blue LED reactor (Figure S2b) and the reaction mixtures were irradiated with a 455 nm blue LED and stirred for 4 hours. After completion, the mixture was concentrated on a rotary evaporator and subjected to a workup procedure for removal of any acid residues generated due to the oxidation of aldehydes. The mixture was dissolved in EtOAc and transferred to a separating funnel wherein saturated sodium bicarbonate ($NaHCO_3$) wash was provided. The organic layer was extracted. This step was repeated twice with EtOAc as the organic layer and the combined extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was finally purified using silica gel (230-400 mesh) column chromatography using hexane/EtOAc.

Optimization of Reaction Conditions:

Table S1. Catalyst and additive optimization for Minisci-type acylation of isoquinoline with benzaldehyde[a]

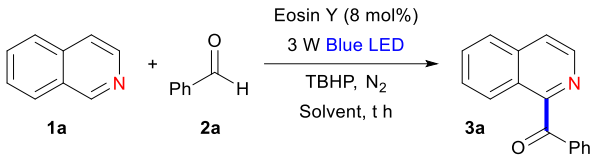


Entry	Catalyst	Deviation	Yield (%)
1	Eosin Y	None	86 (80)[b]
2	Na_2-Eosin Y	None	6
3[c]	Eosin Y	No additive	<5
4	Eosin Y	H_2O_2 (additive)	<5
5	Eosin Y	TBPB (additive)	23
6	Eosin Y	Open Air	0
7	Eosin Y	No light	0
8	None	No light	0
9[d]	Eosin Y	No additive, 60 °C	<5

[a] Optimized reaction conditions: Eosin Y (8 mol %), isoquinoline (0.1 mmol), benzaldehyde (0.4 mmol), and TBHP in H_2O (0.4 mmol) are kept under photo irradiation by blue LED (455 nm, 3 W) for 20 h using ^{t}BuOH (1 mL) as solvent under N_2 atmosphere. Yields were calculated using GC with benzophenone as internal standard. [b] Isolated yield. [c] 50 W Kessil lamp was used. [d] 40 W white light was used. TBPB: tert-butyl peroxybenzoate.

***Note*:** Initially, the experiments were conducted at room temperature (rt) using 3 W blue LED emitting at 455 nm, 8 mol % of the photocatalyst Eosin Y, and TBHP (0.4 mmol) as additive for hydrogen atom abstraction. We observed, to our delight, that under the optimized reaction conditions, the Minisci-acylated product **3a** was obtained in 86% yield (Table 1, entry 1). However, as we switched to the di-sodium salt of Eosin Y, the yield drastically reduced to 6% (Table 1, entry 2). This indicated the need for free -OH and -COOH groups in the active catalyst. In the absence of TBHP, <5% of **3a** was formed (Table 1, entry 3). Switching to H_2O_2 and TBPB led to diminished yields (Table 1, entry 4 and 5). Furthermore, the reaction does not proceed under open air conditions (Table 1, entry 6). This signifies that O_2 must be quenching the Eosin Y triplet state which hampers the process. Similarly, product formation was not observed both in the absence of light as well as when both light and photocatalyst were removed (Table 1, entry 7 and 8). This proved that the presence of visible light and photoexcitation of Eosin Y are crucial for the formation of **3a**.

Table S2. Solvent and time optimization for Minisci-type acylation of isoquinoline with benzaldehyde[a]



Entry	Solvent	Time	Yield[b] (%)
1	Acetone	20	11
2	MTBE	20	4
3	Acetonitrile	20	8
4	Hexane	20	16
5	EtOAc	20	11
6	^{t}BuOH	20	86
7	^{t}BuOH	17	64
8	^{t}BuOH	24	85

[a]Reactions conditions: Unless otherwise stated, solvent (1 mL), Eosin Y (8 mol%), **1a** (0.1 mmol), **2a** (0.4 mmol), TBHP in water (0.4 mmol) and irradiated (Blue LED, 455nm) under N_2 atmosphere. [b]Yields were determined by GC.

***Note*:** Upon completion of solvent screening, *tert*-butyl alcohol (^{t}BuOH) was chosen to be the optimal reaction medium.

Mechanistic Investigations:

1) Radical Inhibition Experiments and Trapping of Radical Intermediates:

A 7 mL glass vial was charged with eosin Y (8 mol%), **1a** (0.1 mmol), **2a** (0.4 mmol), TBHP in water (0.4 mmol), TEMPO (4 equiv.) or BHT (4 equiv.), and a magnetic stirring bead. ^{t}BuOH (1.0 mL) was added as the solvent. The vial was sealed with a PTFE septum, purged with N_2 by using schlenk line and coated with parafilm layer. The reactions were placed in a pre-programmed temperature (25 ºC) controlled blue LED reactor and the reaction mixtures were irradiated with a 455 nm blue LED and stirred for 20 hours. After completion of the reaction, the mixtures were subjected to GC for observing product formation. The desired product was not formed in both cases. Further, the TEMPO inhibited reaction mixture was detected by HRMS from which the data of TEMPO adduct of benzaldehyde (Figure S3) is given below.

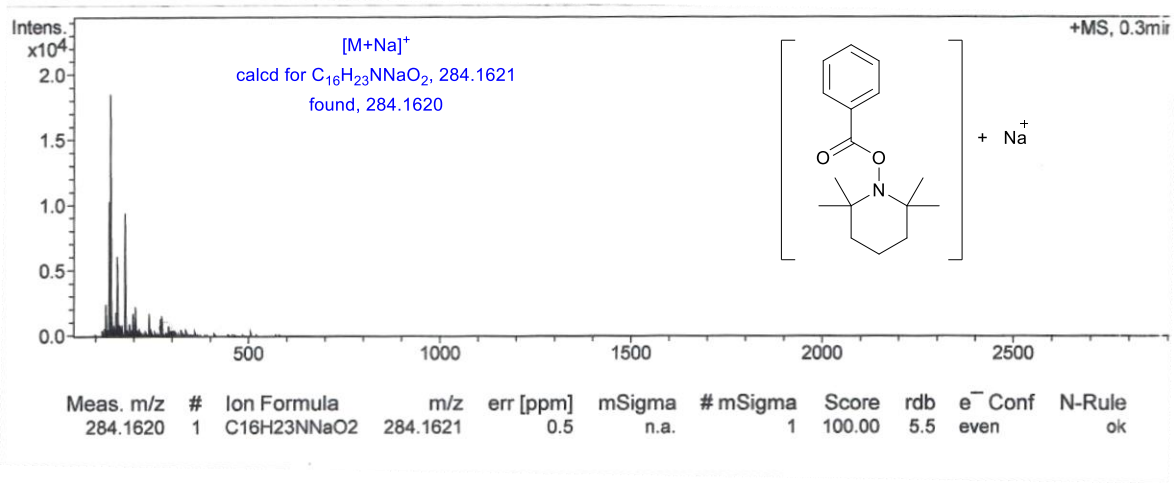


Figure S3: HRMS data of TEMPO adduct of benzaldehyde

2) Photoacid Quenching Experiment:

A 7 mL glass vial was charged with eosin Y (8 mol%), **1a** (0.1 mmol), **2a** (0.4 mmol), TBHP in water (0.4 mmol), triethylamine (4 equiv.), and a magnetic stirring bead. ^{t}BuOH (1.0 mL) was added as the solvent. The vial was sealed with a PTFE septum, purged with N_2 by using schlenk line and coated with parafilm layer. The reactions were placed in a pre-programmed temperature (25 ºC) controlled blue LED reactor and the reaction mixtures were irradiated with a 455 nm blue LED and stirred for 20 hours. After completion of the reaction, the mixtures were subjected to GC for observing product formation. No product formation was observed.

3) Normalized Emission Spectra of Eosin Y and UV-Vis Absorption Spectra of all other components:

Fluorescence measurements were carried out using a Varian Cary Eclipse fluorimeter equipped with Peltier using 1 cm path length quartz cuvette equipped with a Teflon® septum. Fluorescence emission spectrum of Eosin Y in dry acetonitrile was collected from 500 nm to 800 nm with an excitation wavelength of 450 nm. Solutions of isoquinoline (**1a**), benzaldehyde (**2a**) and TBHP in water, in dry acetonitrile, were introduced to a 1 cm path length quartz cuvette equipped with a Teflon® septum. The solutions were analyzed using a UV-Vis spectrophotometer (UV-2450, Shimadzu, Japan). The normalized absorption spectra of these components along with the emission spectrum of Eosin Y are shown below (Figure S4).

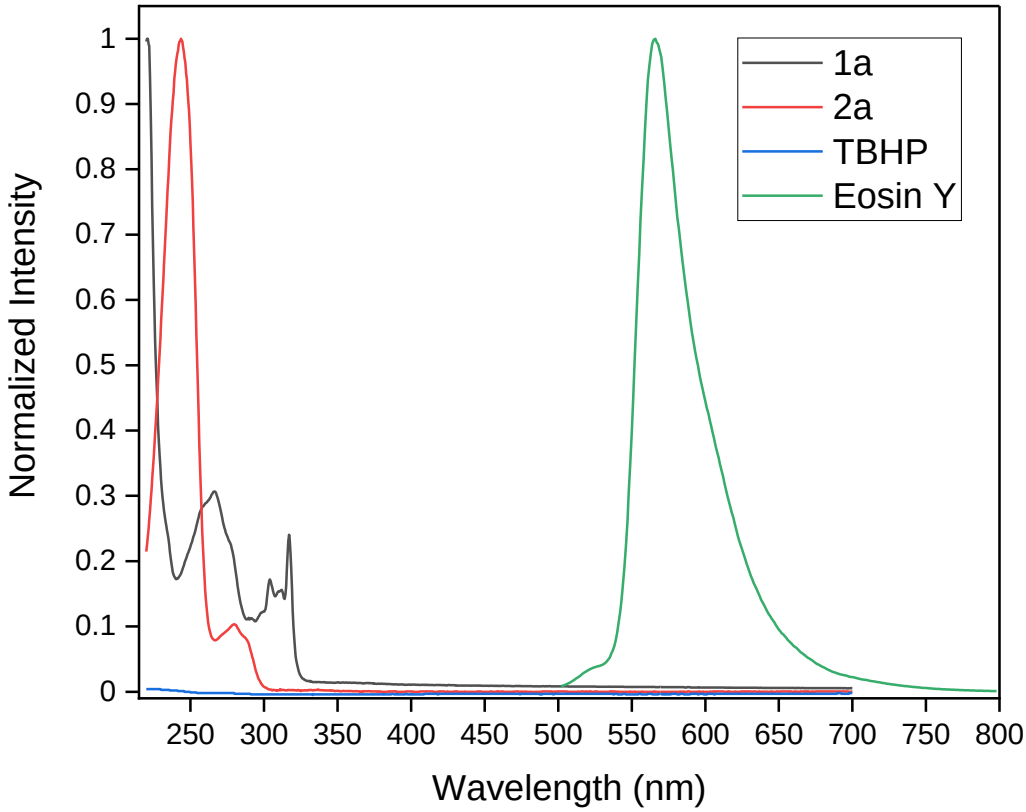


Figure S4: a) Normalized absorption spectra of isoquinoline (**1a**), benzaldehyde (**2a**), TBHP in water, and normalized emission spectra of Eosin Y (excited at 450 nm) in MeCN.

***Note*:** The absence of any overlap between the absorption spectrum of the individual reactants and the emission spectra of Eosin Y indicates that electron transfer is likely to be a more viable process than energy transfer.

4) Fluorescence Quenching Experiment:

Fluorescence measurements were carried out using a Varian Cary Eclipse fluorimeter equipped with Peltier using 1 cm path length quartz cuvette equipped with a Teflon® septum. A 0.375 mM solution was prepared by mixing Eosin Y in CH_3CN by an appropriate dilution of 0.002 M stock solution and taken in a fluorescence cuvette (filled up to 800 μL). The excitation and emission slit widths were fixed at 10 nm for data collection. Fluorescence emission spectra of Eosin Y were collected from 500 nm to 800 nm with an excitation wavelength of 450 nm. λ_{max}(emission) of Eosin Y was observed at 563 nm. For each fluorescence quenching experiment, 3 μL of 0.1 M solution of isoquinoline (**1a**) was added to Eosin Y solution (0.375 mM) taken in a fluorescence cuvette, and emission spectra were recorded after each sequential addition. Figure S5 (Figure 2a in manuscript) shows an increase in emission intensity after each addition of TBHP (0 to 3.375 mM). Relevant spectrum is shown below. *We thank Prof. Shashank Deep, IIT Delhi for providing the access to Fluorimeter and enabling us to perform the fluorescence quenching experiments.*

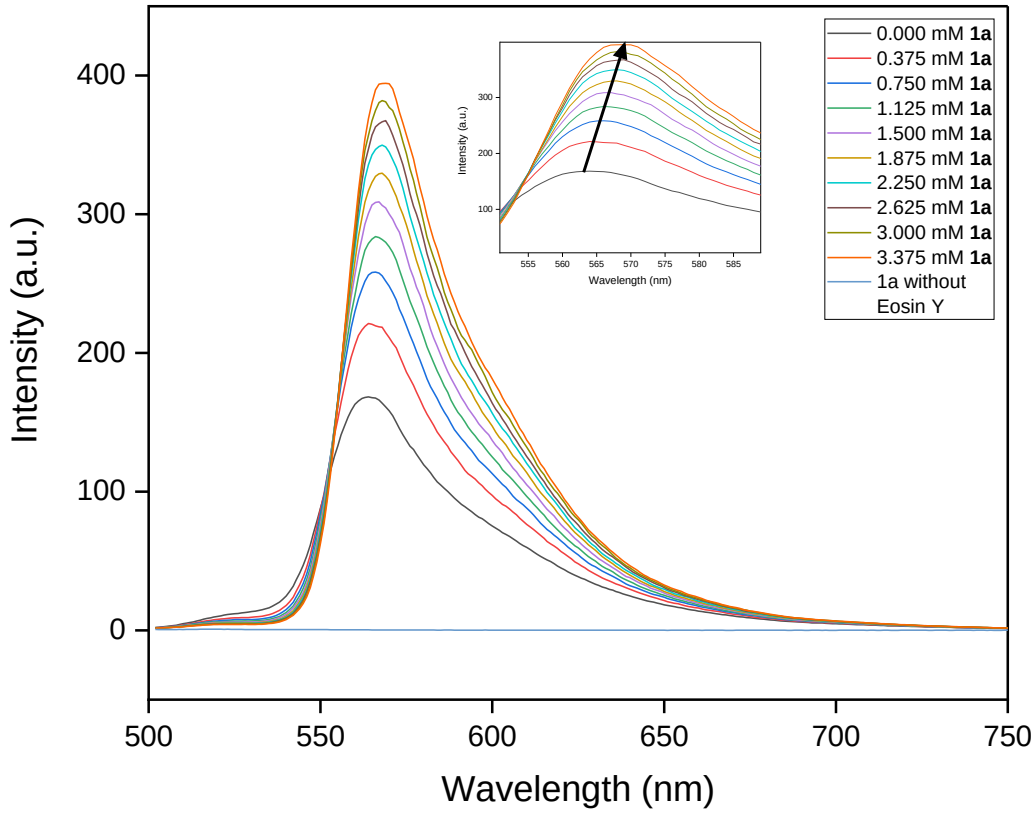


Figure S5: a) Fluorescence-quenching spectra of a 0.375 mM solution of Eosin Y in CH_3CN with isoquinoline (**1a**) as the quencher.

5) Fluorescence Lifetime Quenching Experiments:

Excited state lifetime measurements were performed using a time-correlated single photon counting (TCSPC) spectrophotometer (Fluotime 300, PicoQuant, Germany). The instrument response function (IRF) was obtained through the use of a scattering Ludox solution. The sample of neutral Eosin Y (0.375 mM) in dry acetonitrile was excited at 485 nm using a picosecond-pulsed diode laser. The picosecond fluorescence lifetime decays were deconvoluted using Fluofit software. The lifetime decay of the sample were collected at 558 nm (emission maxima) with a 5 nm emission slit width where the peak counts were normalized to 10000 counts. The lifetime decay was fit in two exponentials. *We thank Prof. Pramit Kumar Chowdhury and Harshita Rastogi, IIT Delhi for providing the access to spectrophotometer and enabling us to perform the fluorescence lifetime quenching experiments.*

A) Fluorescence lifetime quenching studies for 0.375 mM Eosin Y in dry CH_3CN with increasing concentration of isoquinoline (1a) as the quencher (addition from 0 to 3.375 mM).

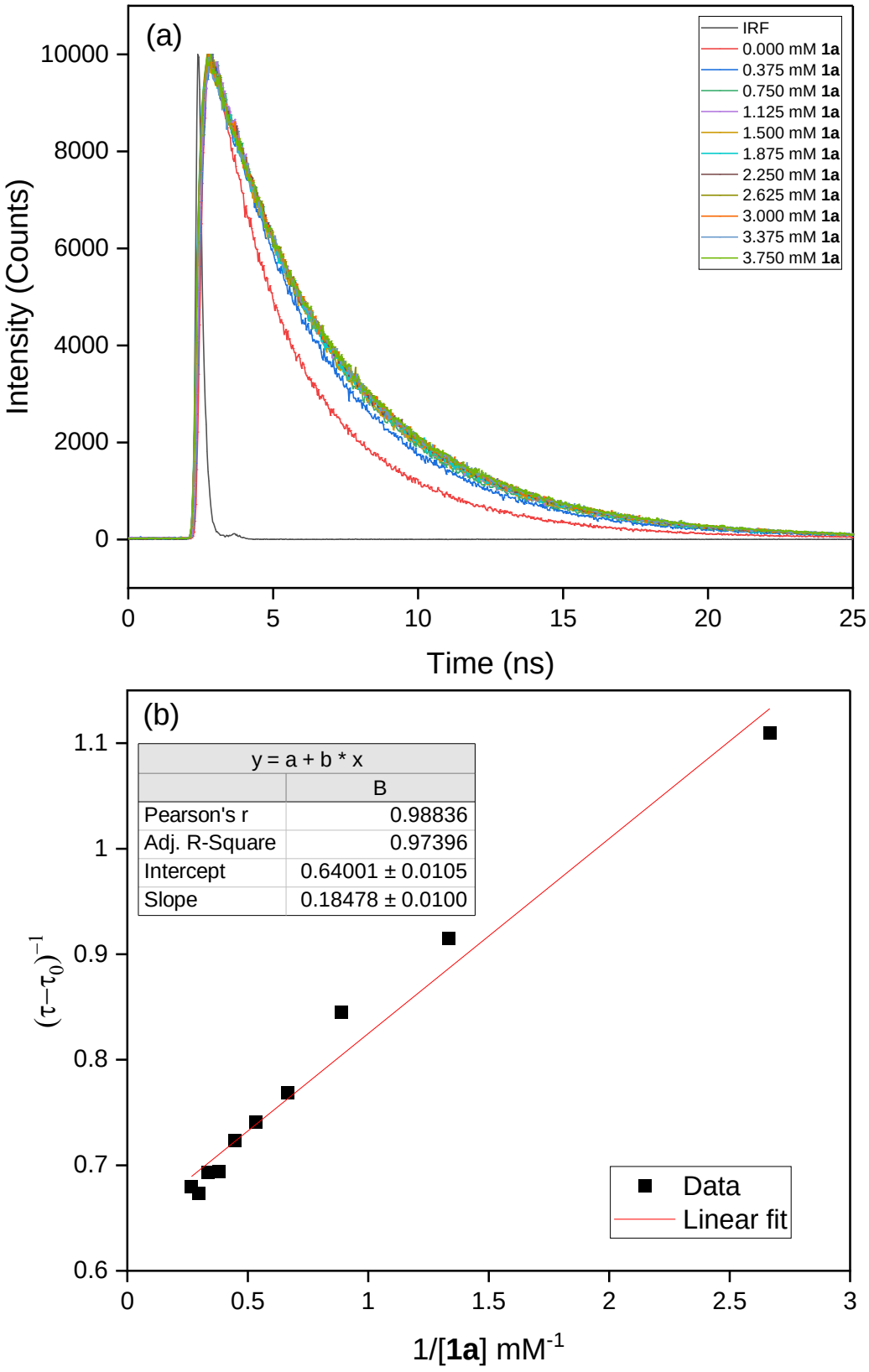
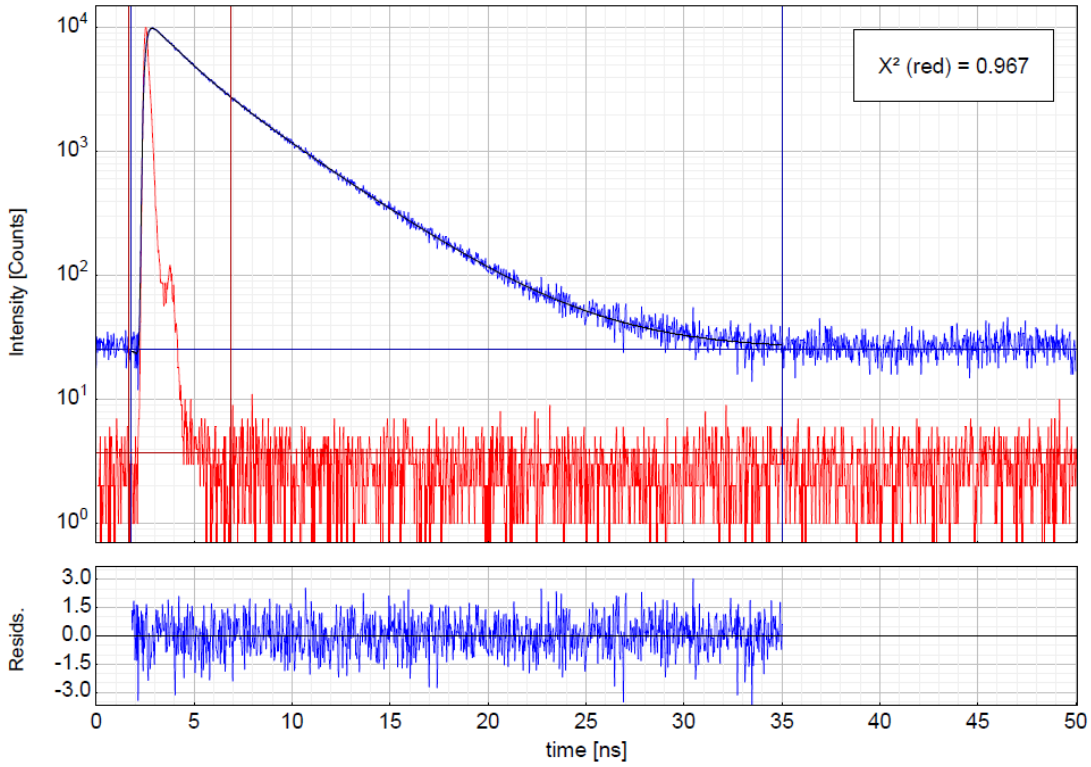


Figure S6: a) Fluorescence lifetime quenching spectra of a 0.375 mM solution of Eosin Y in CH_3CN with isoquinoline (**1a**) as the quencher; b) Benesi-Hildebrand plot (Plot of $1/[\tau-\tau_0]$ vs $1/[$**1a**$]$).

Datasets of Lifetime Decay studies with Isoquinoline (1a) as quencher:

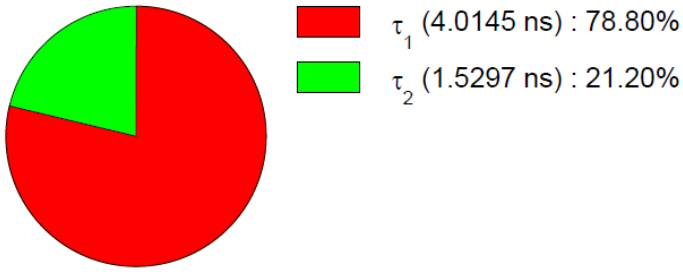


Average Lifetime:

$\tau_{Av.1}$=3.4876 ns (intensity weighted)

$\tau_{Av.2}$=2.9860 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

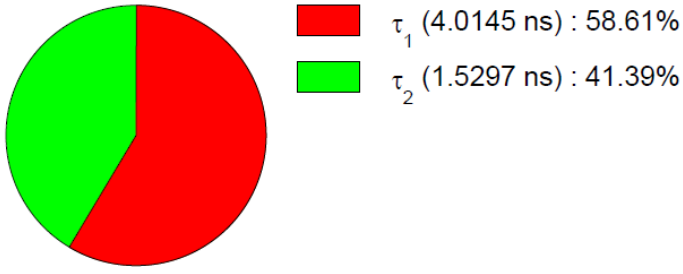
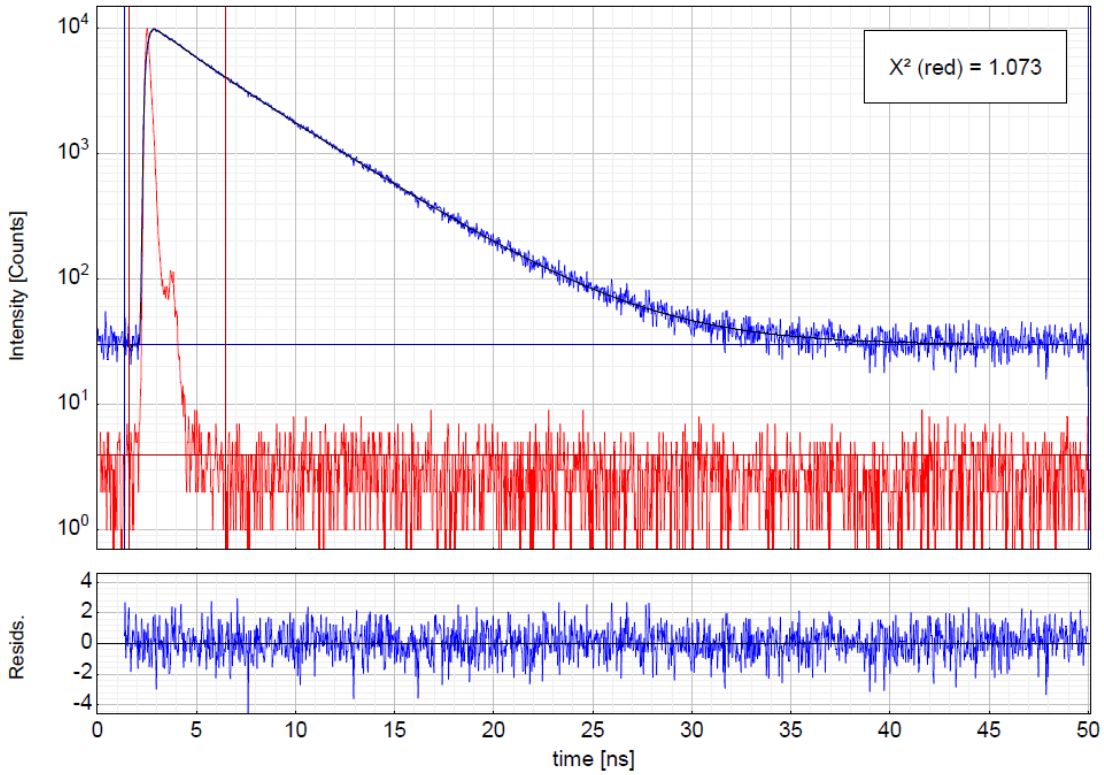


Figure S7: Lifetime dataset for 0.375 mM neutral Eosin Y

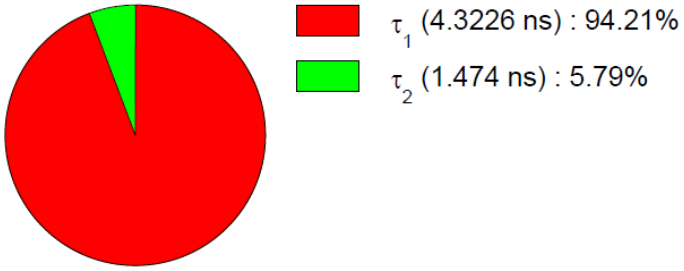


Average Lifetime:

$\tau_{Av.1}$=4.1576 ns (intensity weighted)

$\tau_{Av.2}$=3.8874 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

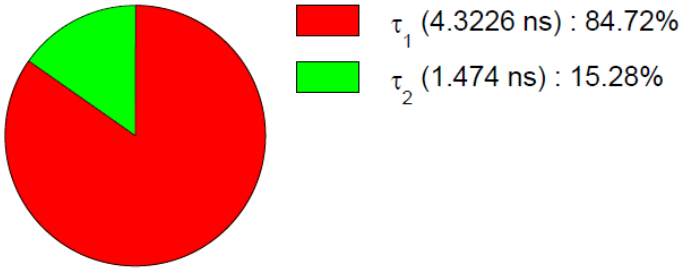
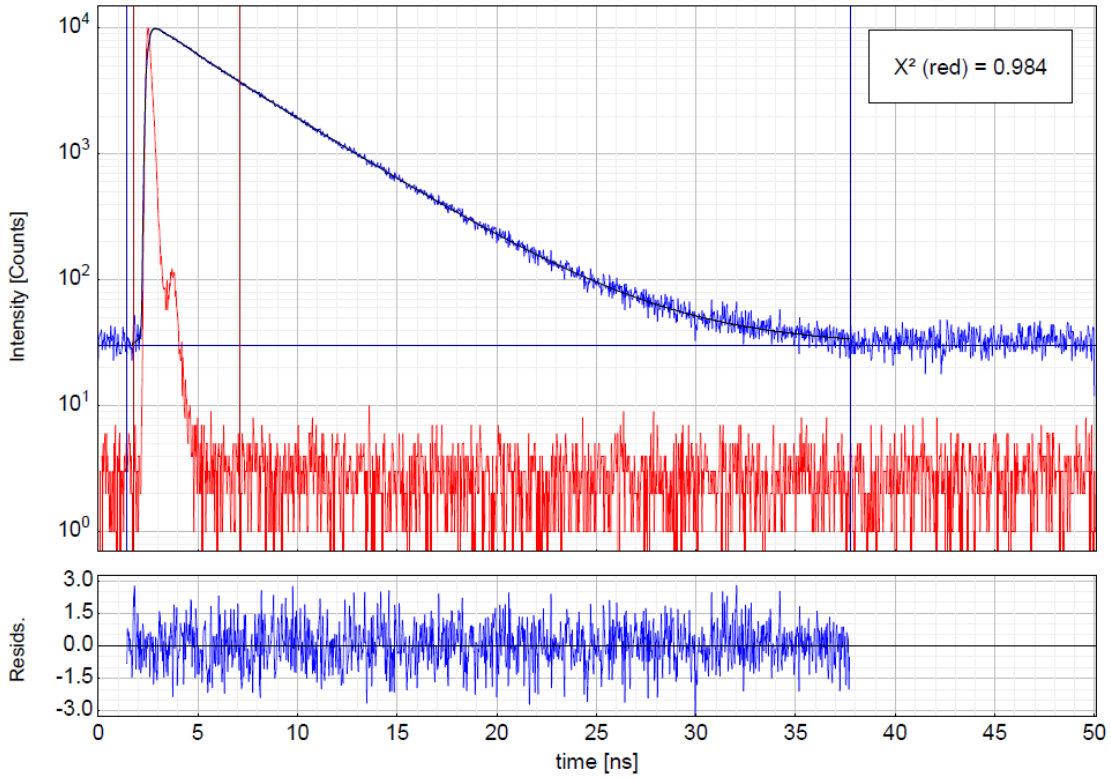


Figure S8: Lifetime dataset for 0.375 mM neutral Eosin Y + 0.375 mM **1a**.

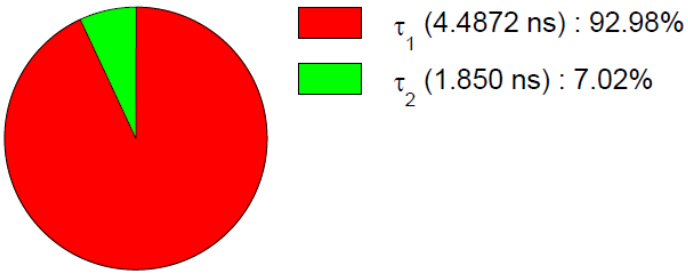


Average Lifetime:

$\tau_{Av.1}$=4.3020 ns (intensity weighted)

$\tau_{Av.2}$=4.0788 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

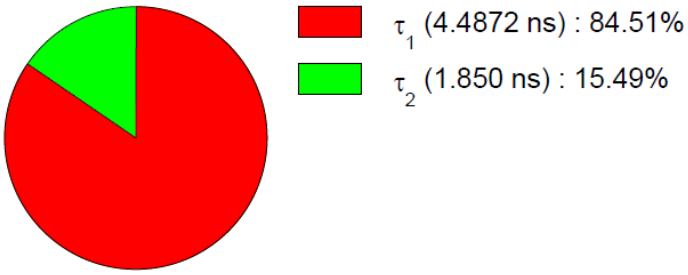
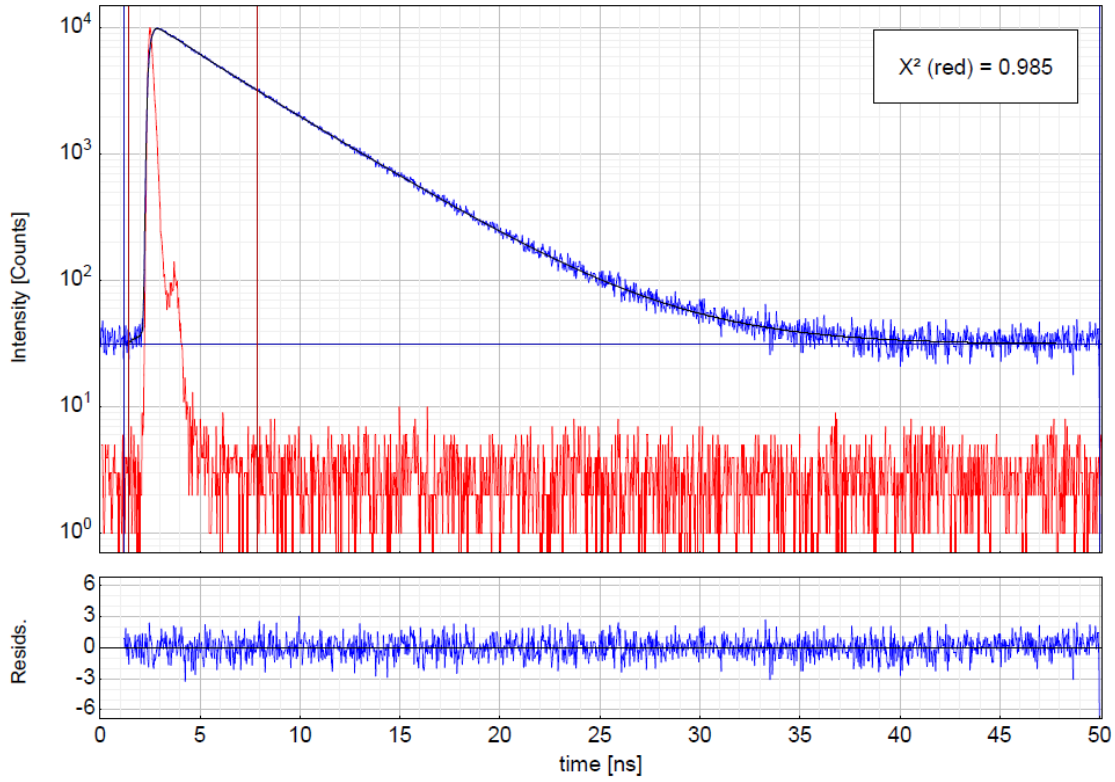


Figure S9: Lifetime dataset for 0.375 mM neutral Eosin Y + 0.750 mM **1a**.

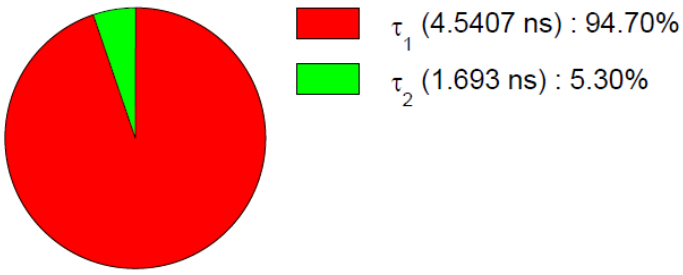


Average Lifetime:

$\tau_{Av.1}$=4.3897 ns (intensity weighted)

$\tau_{Av.2}$=4.1688 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

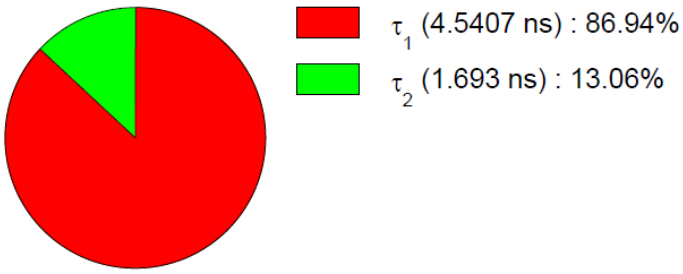
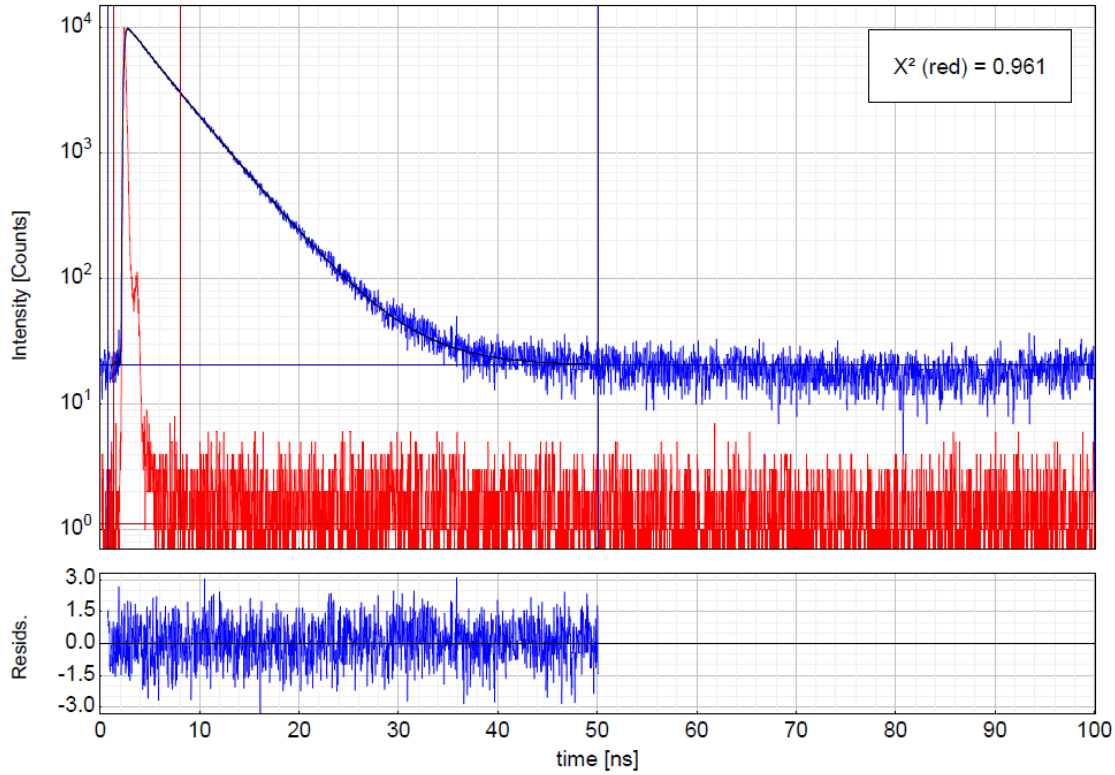


Figure S10: Lifetime dataset for 0.375 mM neutral Eosin Y + 1.125 mM **1a**.

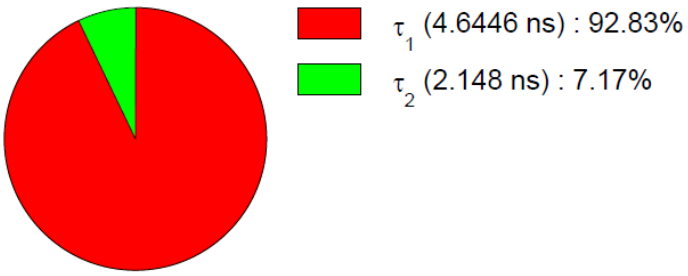


Average Lifetime:

$\tau_{Av.1}$=4.4656 ns (intensity weighted)

$\tau_{Av.2}$=4.2873 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

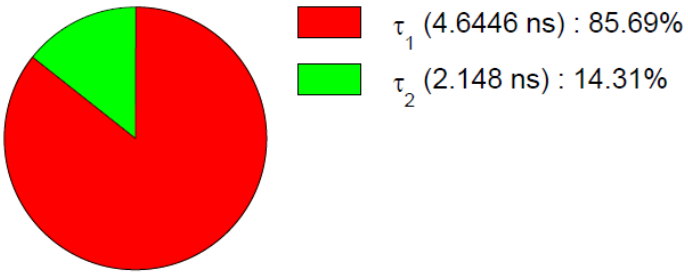
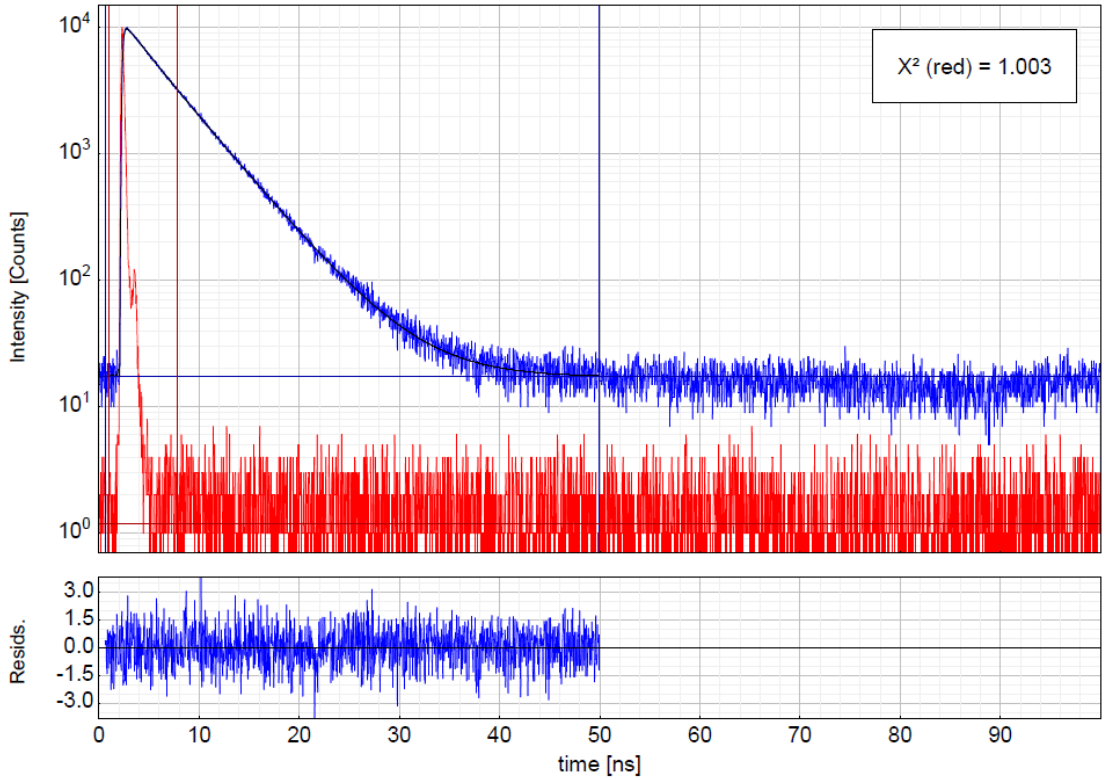


Figure S11: Lifetime dataset for 0.375 mM neutral Eosin Y + 1.500 mM **1a**.

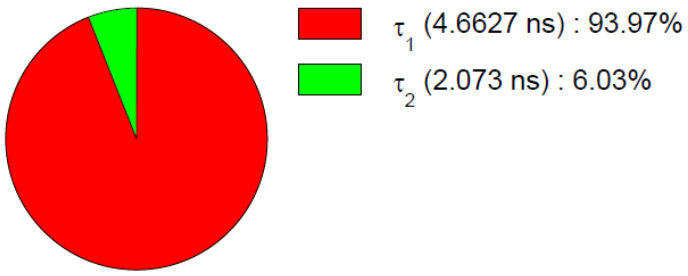


Average Lifetime:

$\tau_{Av.1}$=4.5065 ns (intensity weighted)

$\tau_{Av.2}$=4.3360 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

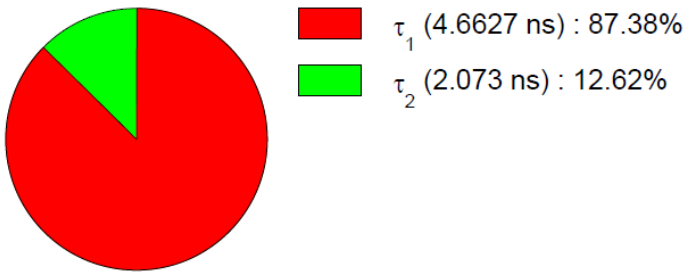
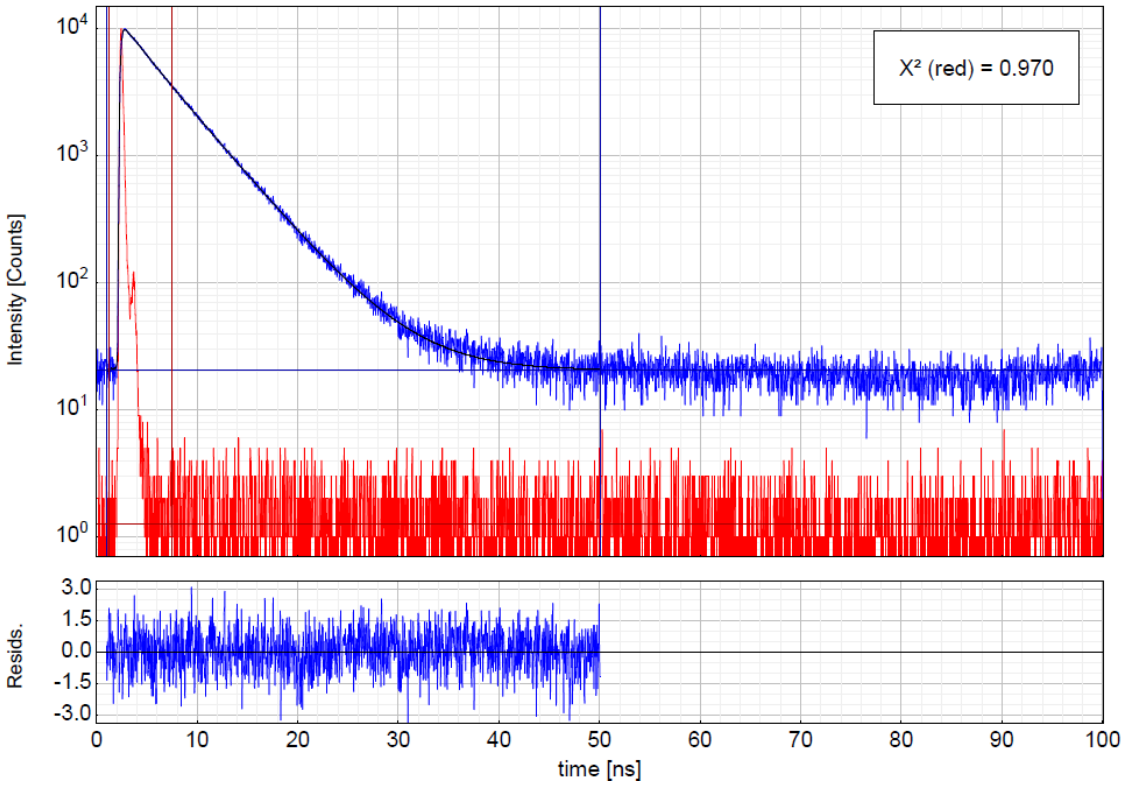


Figure S12: Lifetime dataset for 0.375 mM neutral Eosin Y + 1.875 mM **1a**.

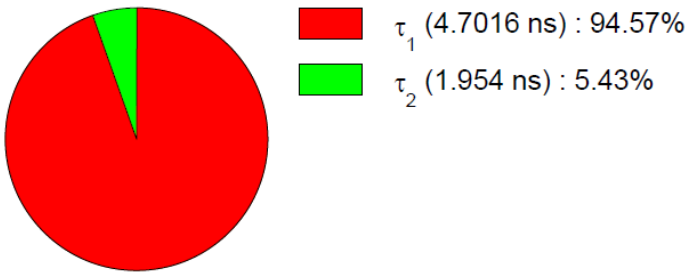


Average Lifetime:

$\tau_{Av.1}$=4.5524 ns (intensity weighted)

$\tau_{Av.2}$=4.3680 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

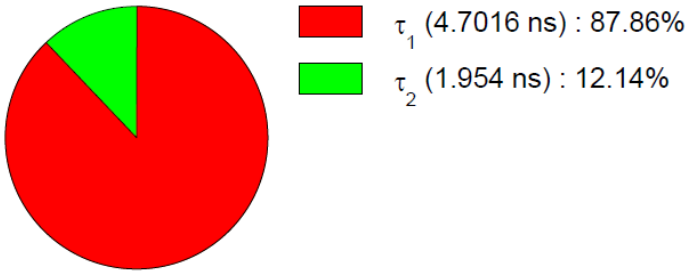
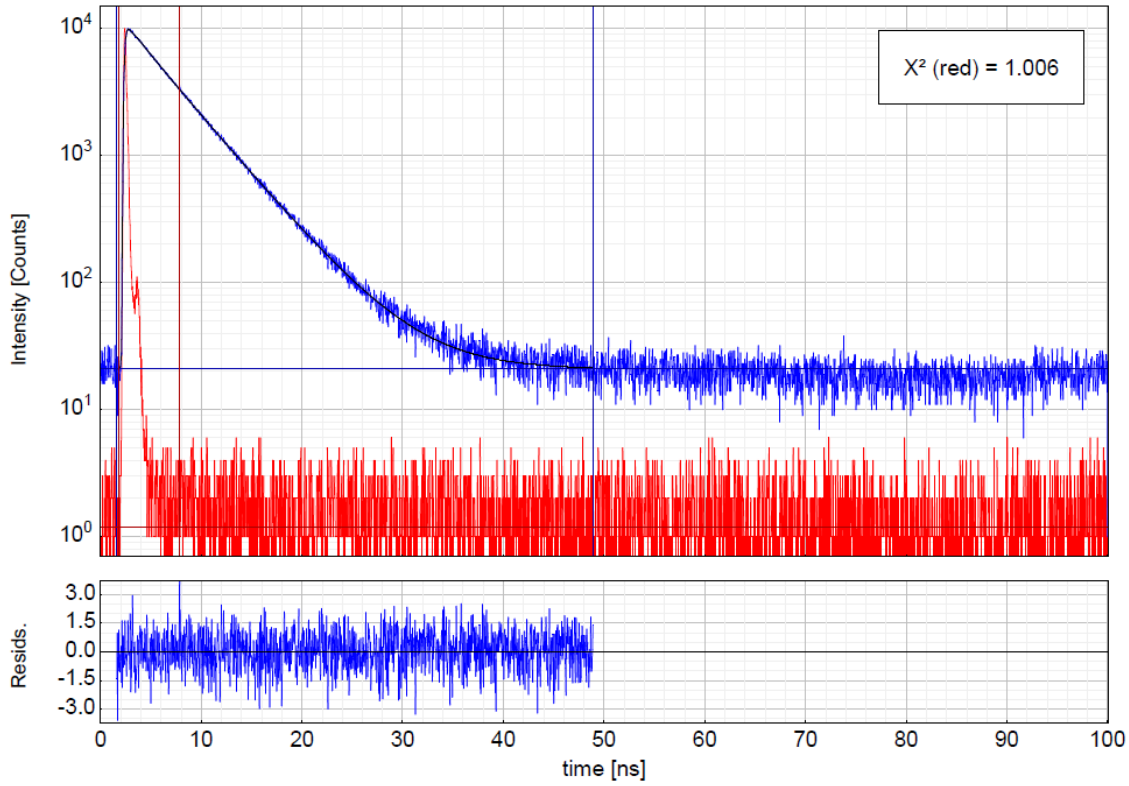


Figure S13: Lifetime dataset for 0.375 mM neutral Eosin Y + 2.250 mM **1a**.

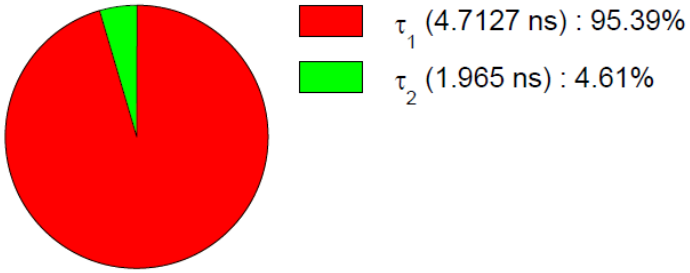


Average Lifetime:

$\tau_{Av.1}$=4.5860 ns (intensity weighted)

$\tau_{Av.2}$=4.4273 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

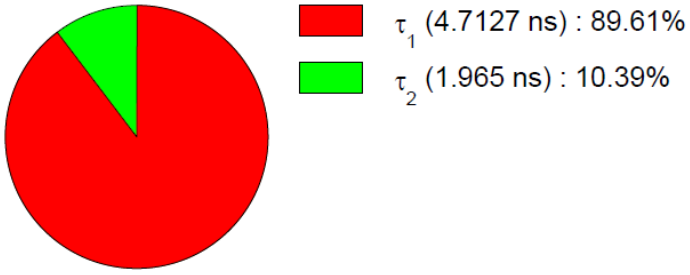
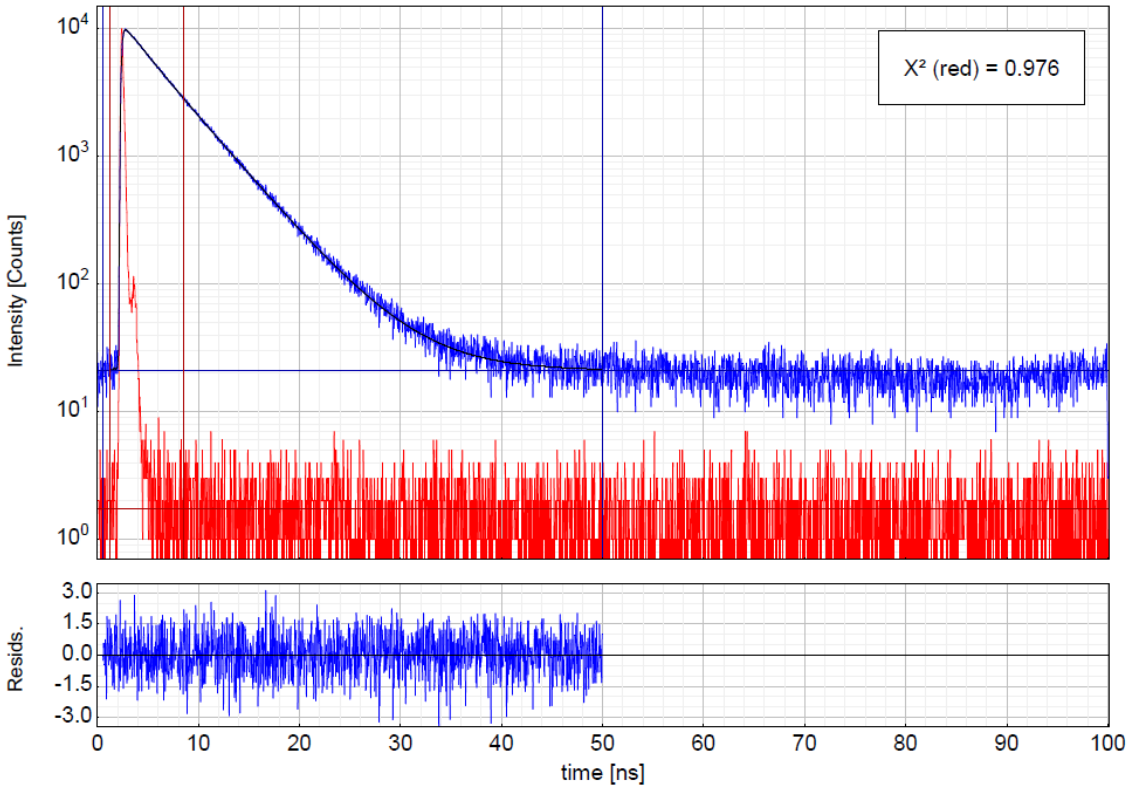


Figure S14: Lifetime dataset for 0.375 mM neutral Eosin Y + 2.625 mM **1a**.

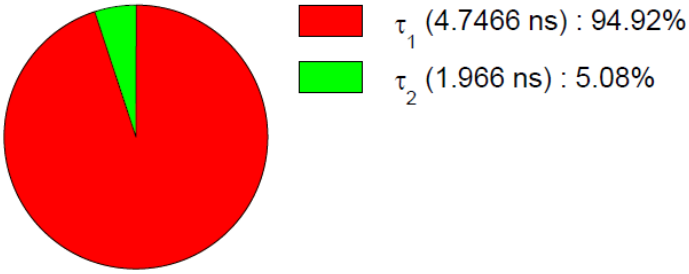


Average Lifetime:

$\tau_{Av.1}$=4.6053 ns (intensity weighted)

$\tau_{Av.2}$=4.4282 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

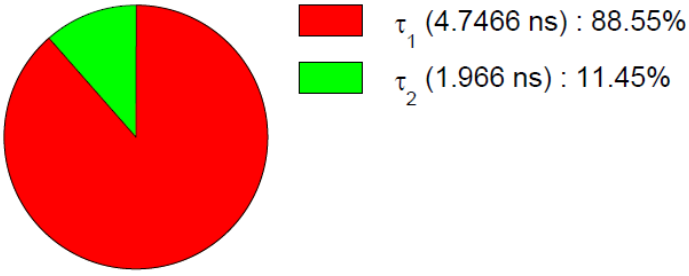
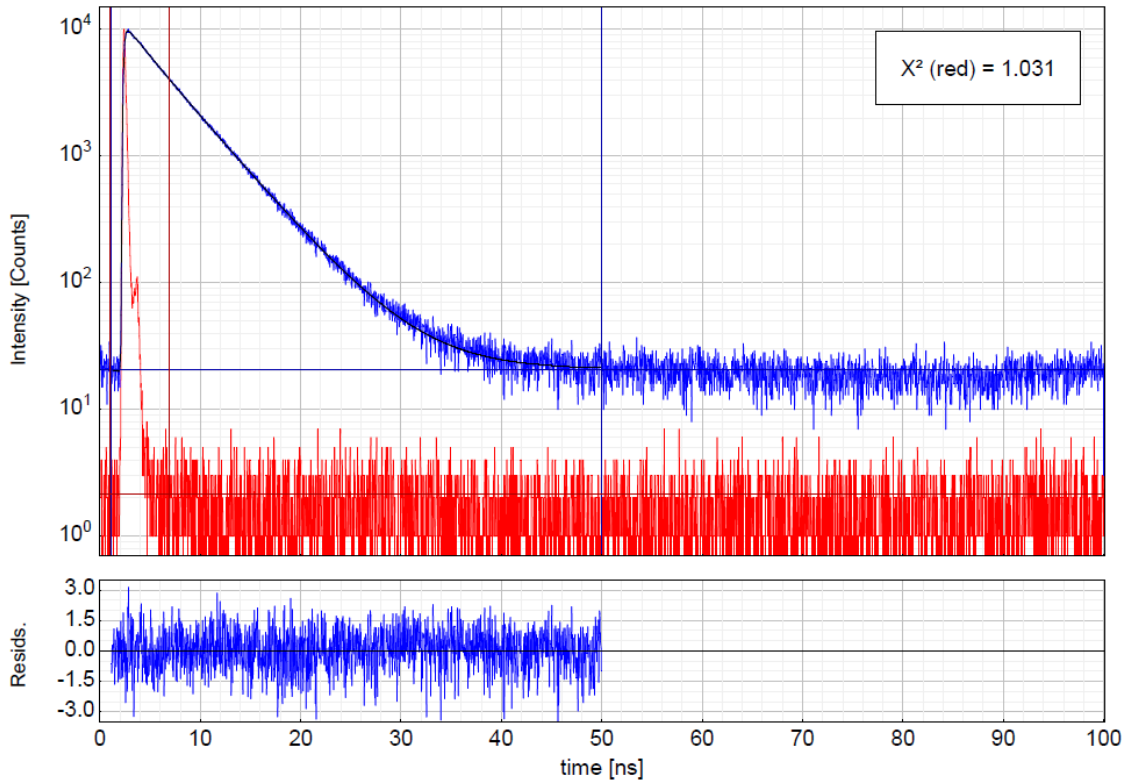


Figure S15: Lifetime dataset for 0.375 mM neutral Eosin Y + 3.000 mM **1a**.

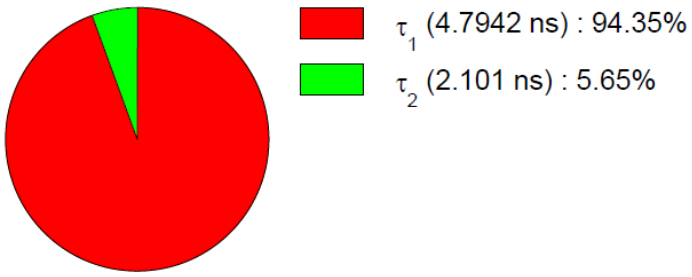


Average Lifetime:

$\tau_{Av.1}$=4.6421 ns (intensity weighted)

$\tau_{Av.2}$=4.4705 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

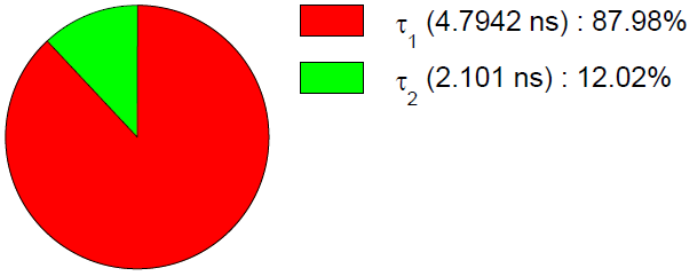
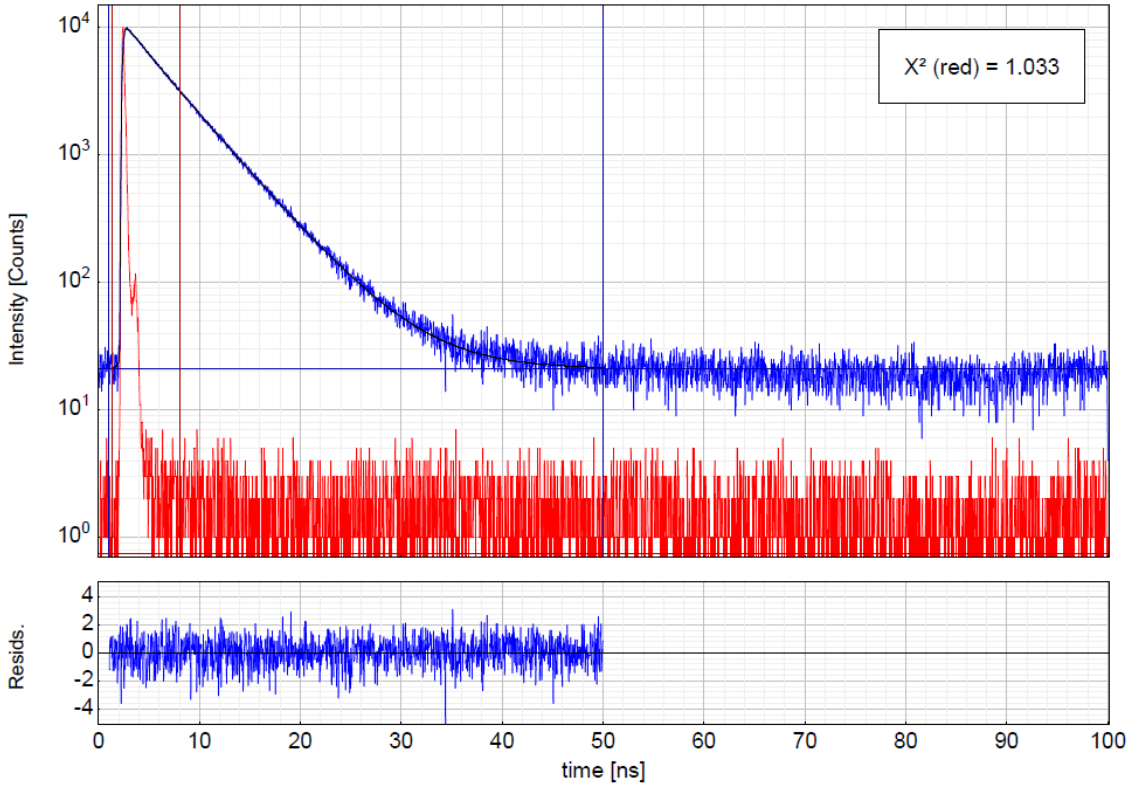


Figure S16: Lifetime dataset for 0.375 mM neutral Eosin Y + 3.375 mM **1a**.

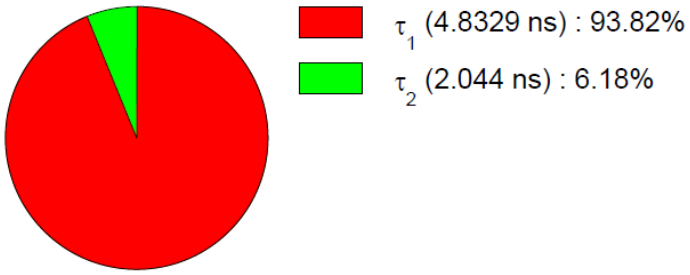


Average Lifetime:

$\tau_{Av.1}$=4.6605 ns (intensity weighted)

$\tau_{Av.2}$=4.4570 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

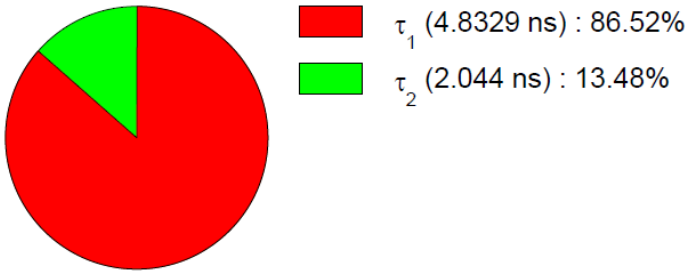


Figure S17: Lifetime dataset for 0.375 mM neutral Eosin Y + 3.750 mM **1a**.

A) Fluorescence lifetime quenching studies for 0.375 mM Eosin Y in dry CH_3CN with increasing concentration of TBHP as the quencher (addition from 0 to 3.375 mM).

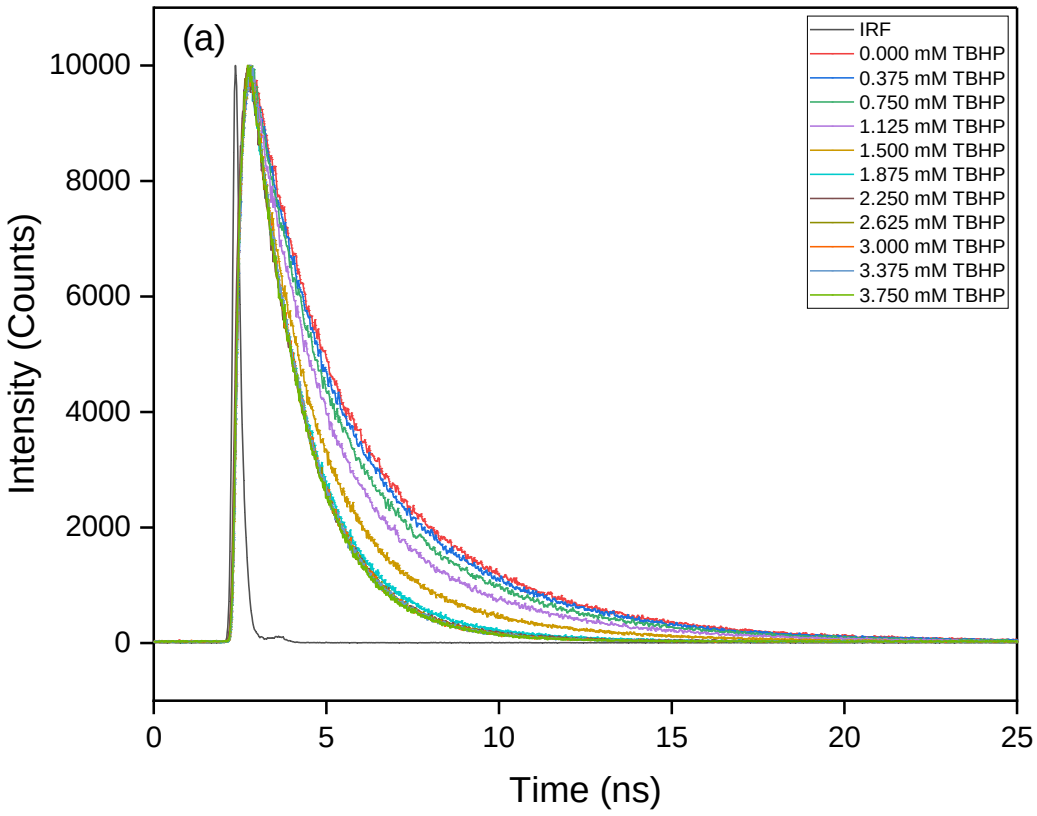
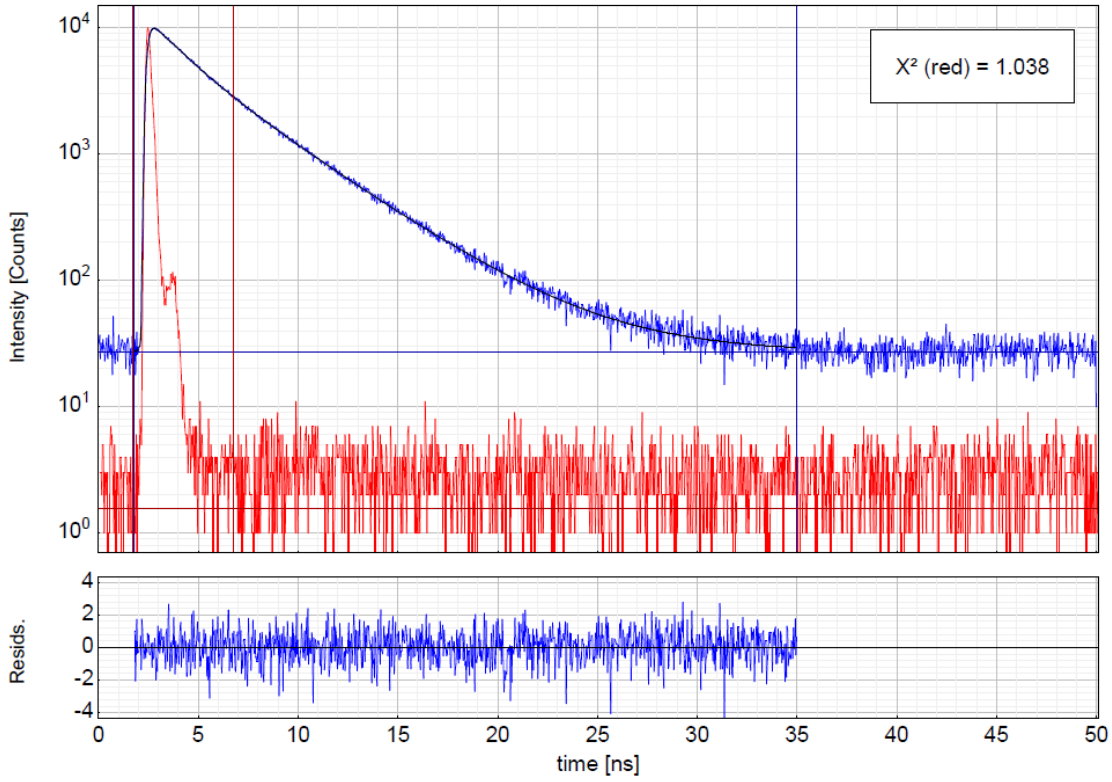


Figure S18: a) Fluorescence lifetime quenching spectra of a 0.375 mM solution of Eosin Y in CH_3CN with TBHP as the quencher.

Datasets of Lifetime Decay studies with TBHP as quencher:

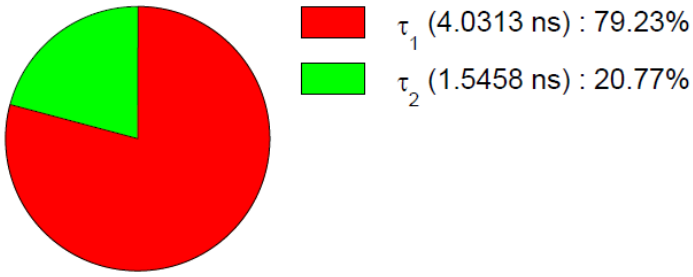


Average Lifetime:

$\tau_{Av.1}$=3.5150 ns (intensity weighted)

$\tau_{Av.2}$=3.0220 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

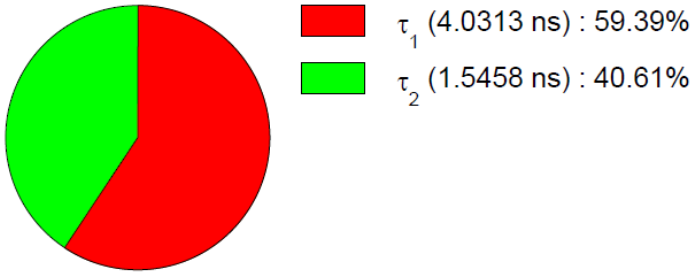
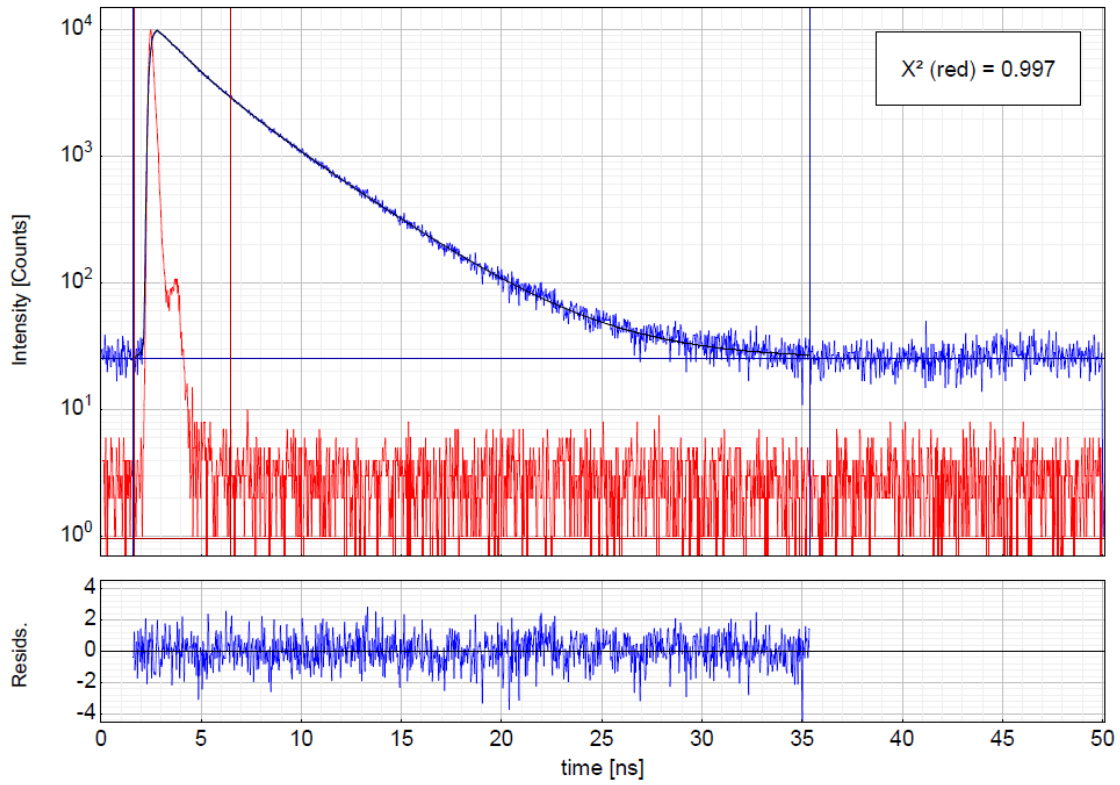


Figure S19: Lifetime dataset for 0.375 mM neutral Eosin Y

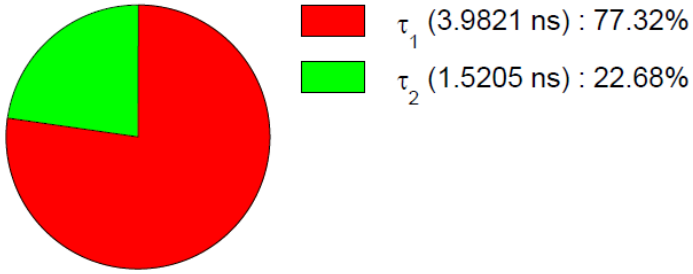


Average Lifetime:

$\tau_{Av.1}$=3.4238 ns (intensity weighted)

$\tau_{Av.2}$=2.9126 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

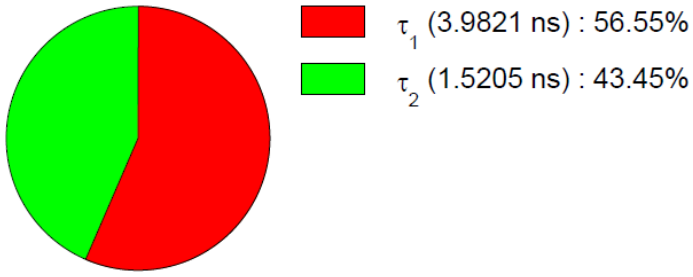
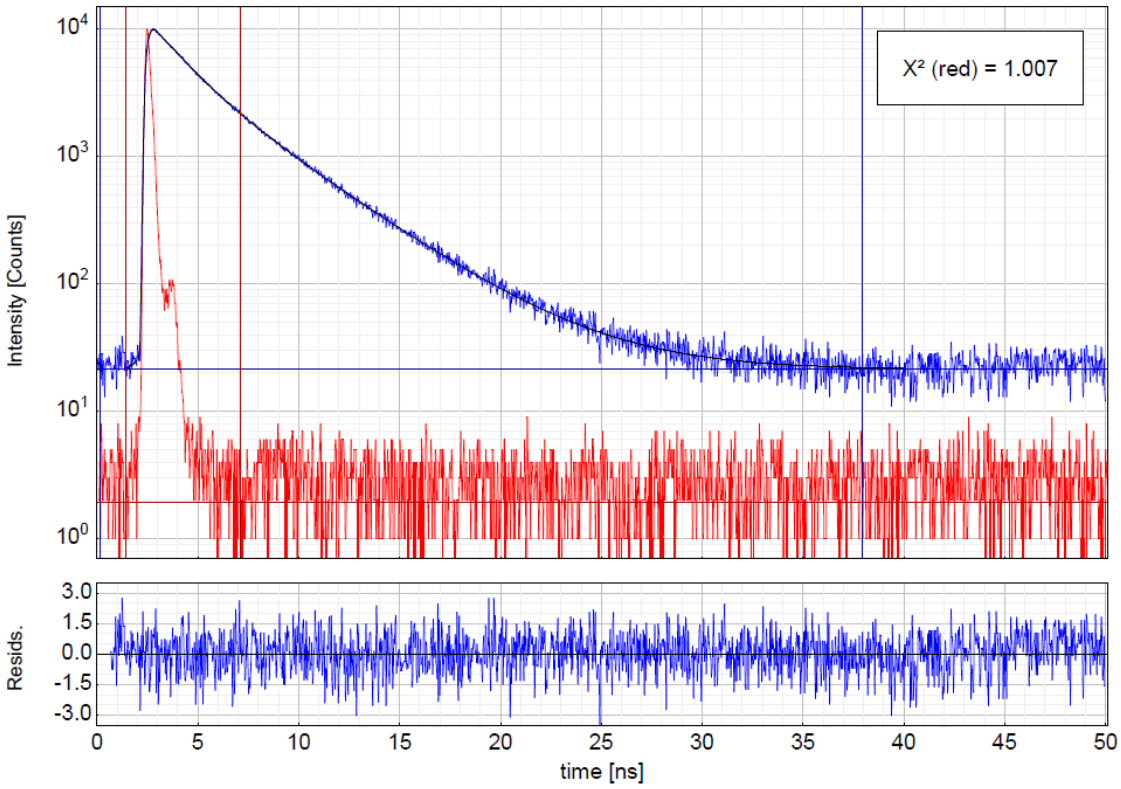


Figure S20: Lifetime dataset for 0.375 mM neutral Eosin Y + 0.375 mM TBHP.

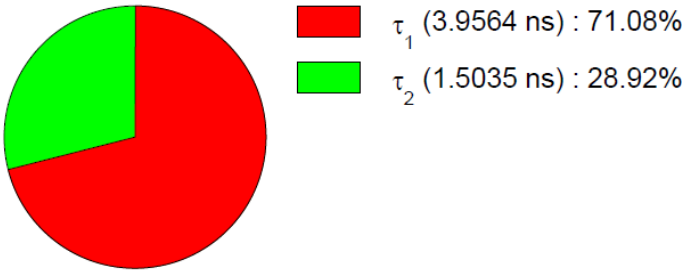


Average Lifetime:

$\tau_{Av.1}$=3.2470 ns (intensity weighted)

$\tau_{Av.2}$=2.6881 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

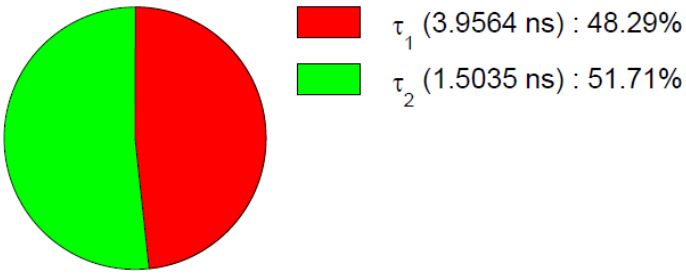
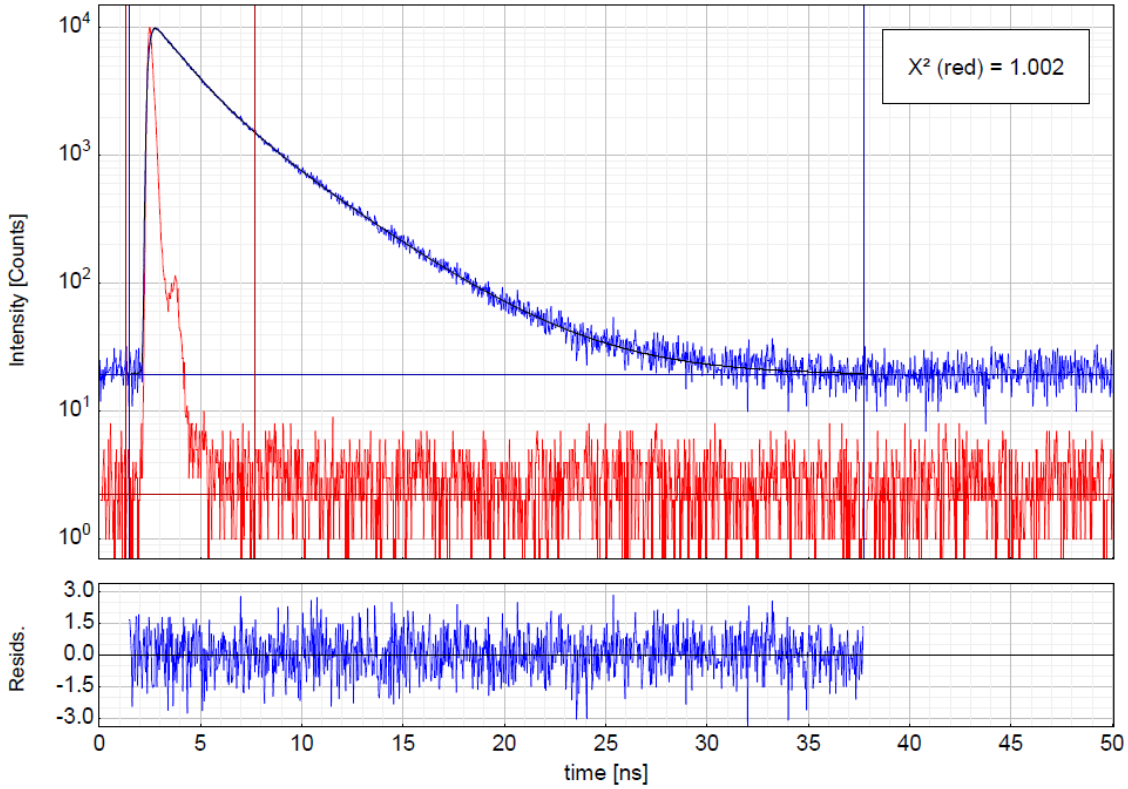


Figure S21: Lifetime dataset for 0.375 mM neutral Eosin Y + 0.750 mM TBHP.

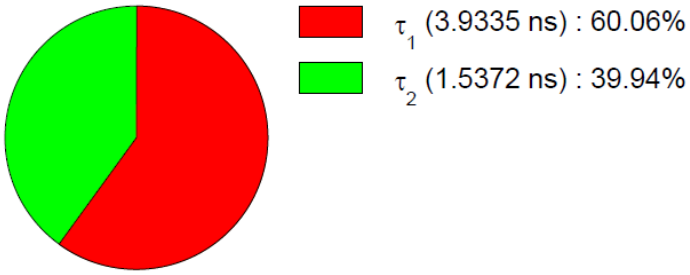


Average Lifetime:

$\tau_{Av.1}$=2.9764 ns (intensity weighted)

$\tau_{Av.2}$=2.4242 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

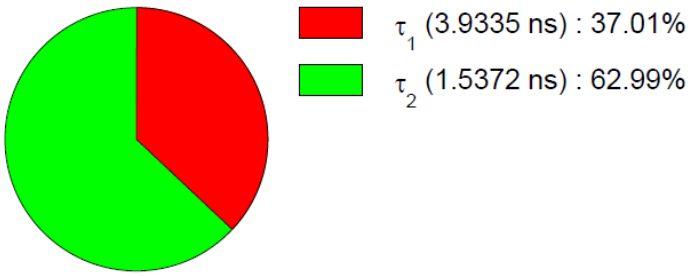
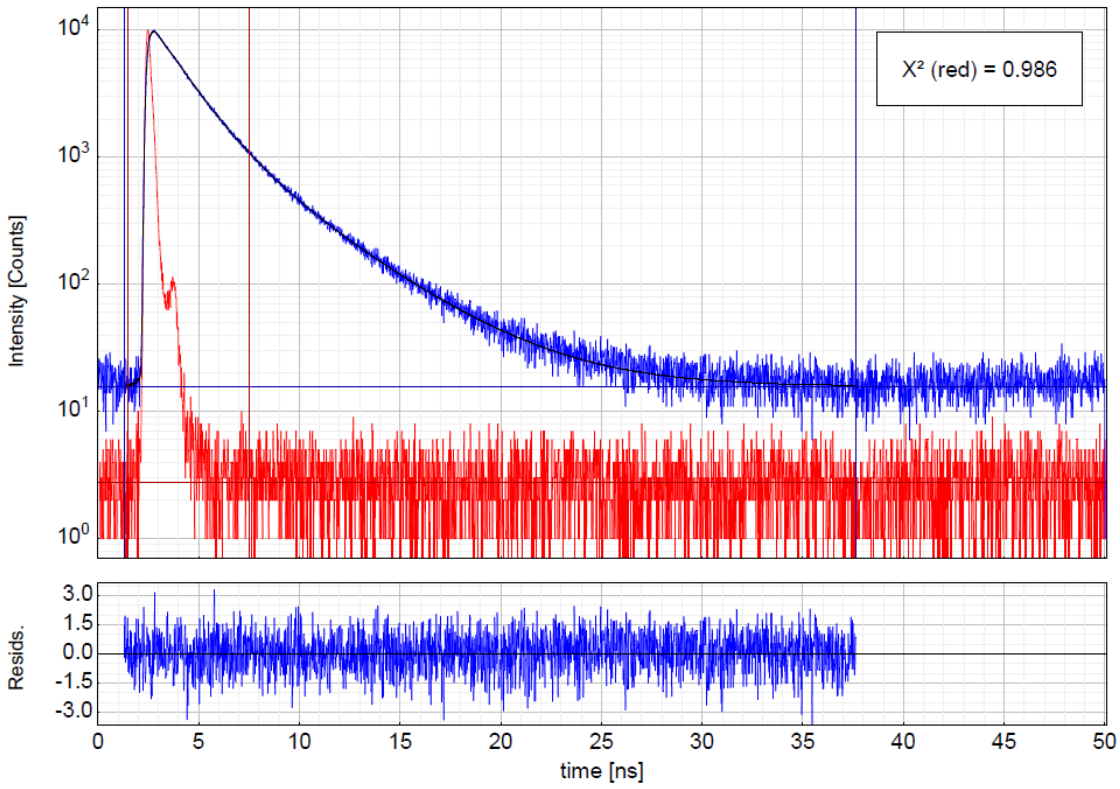


Figure S22: Lifetime dataset for 0.375 mM neutral Eosin Y + 1.125 mM TBHP.

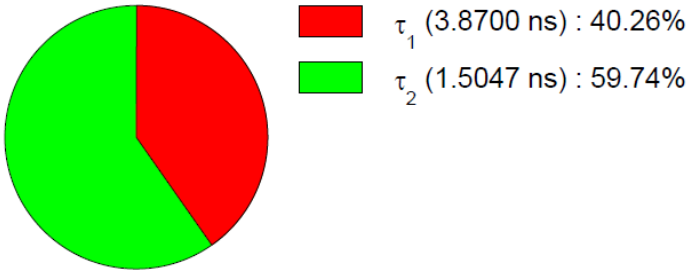


Average Lifetime:

$\tau_{Av.1}$=2.4570 ns (intensity weighted)

$\tau_{Av.2}$=1.9958 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

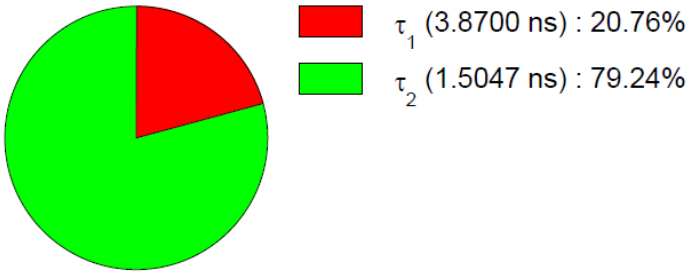
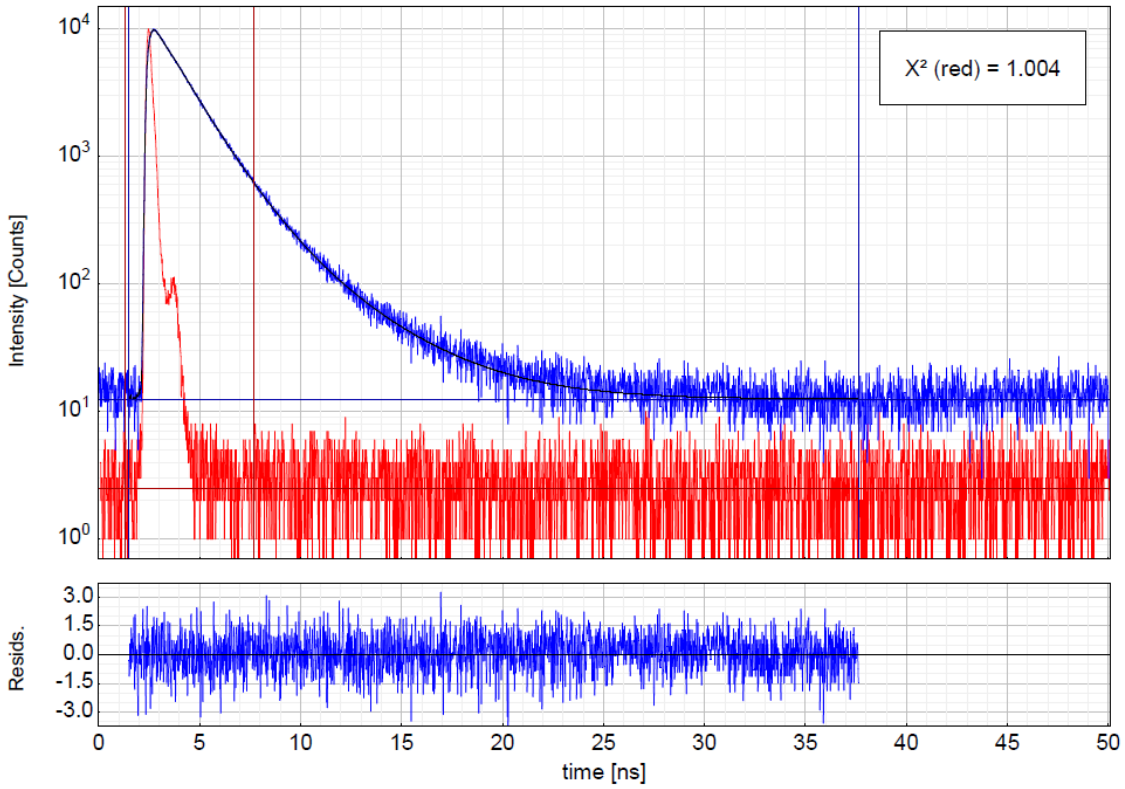


Figure S23: Lifetime dataset for 0.375 mM neutral Eosin Y + 1.500 mM TBHP.

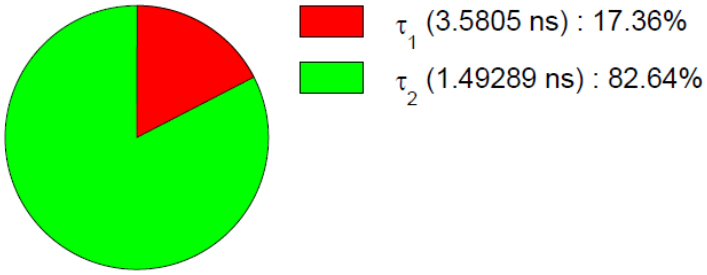


Average Lifetime:

$\tau_{Av.1}$=1.8553 ns (intensity weighted)

$\tau_{Av.2}$=1.6610 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

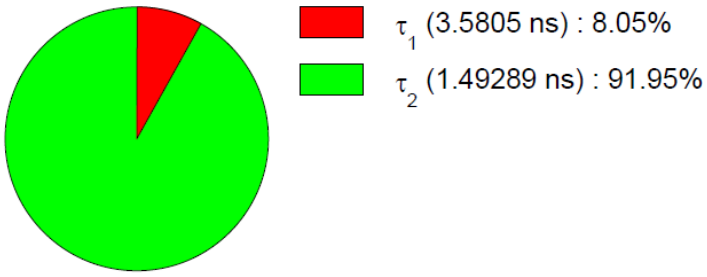
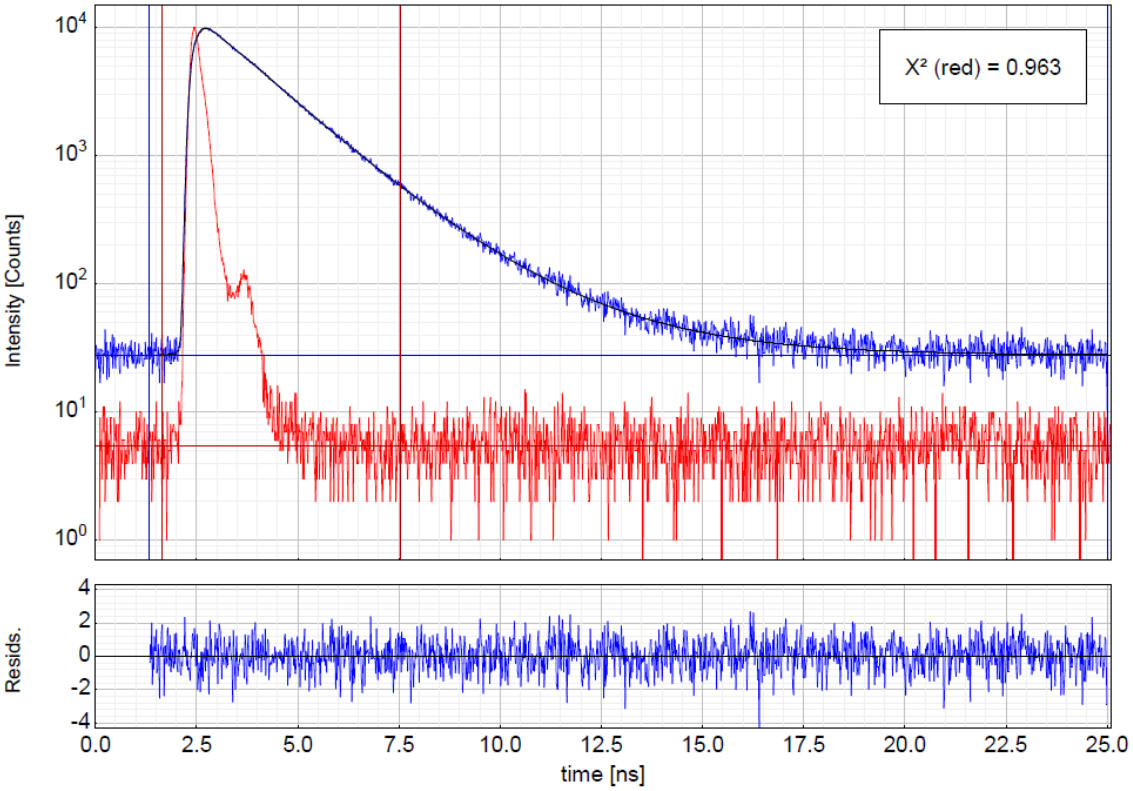


Figure S24: Lifetime dataset for 0.375 mM neutral Eosin Y + 1.875 mM TBHP.

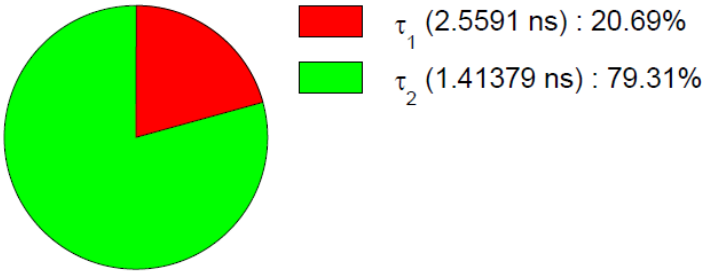


Average Lifetime:

$\tau_{Av.1}$=1.6508 ns (intensity weighted)

$\tau_{Av.2}$=1.5581 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

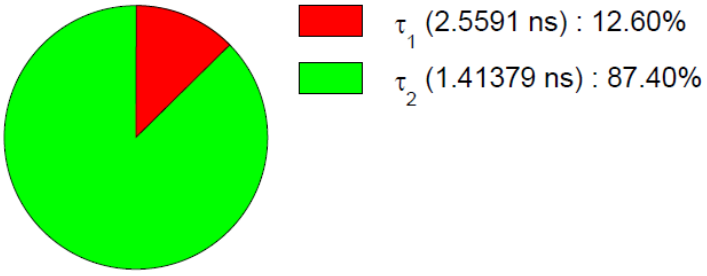
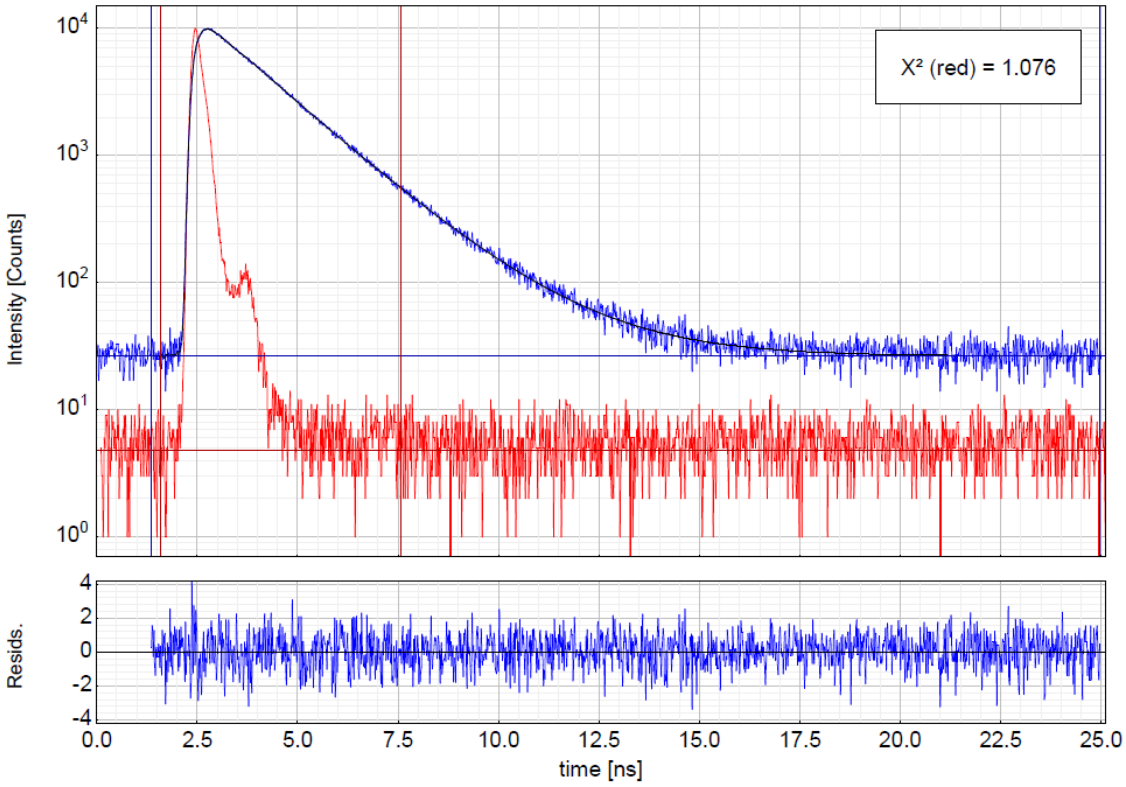


Figure S25: Lifetime dataset for 0.375 mM neutral Eosin Y + 2.250 mM TBHP.

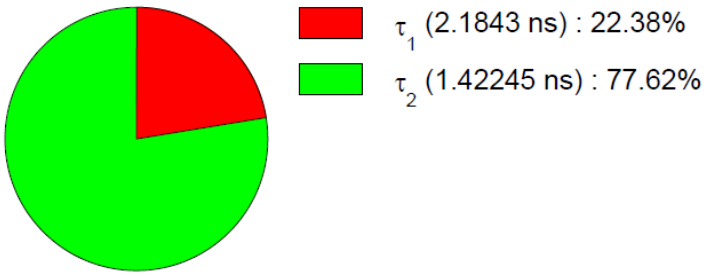


Average Lifetime:

$\tau_{Av.1}$=1.5930 ns (intensity weighted)

$\tau_{Av.2}$=1.5429 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

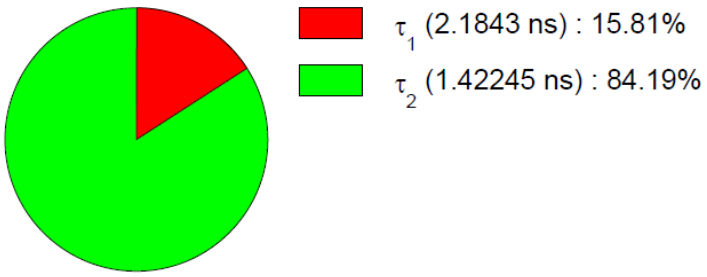
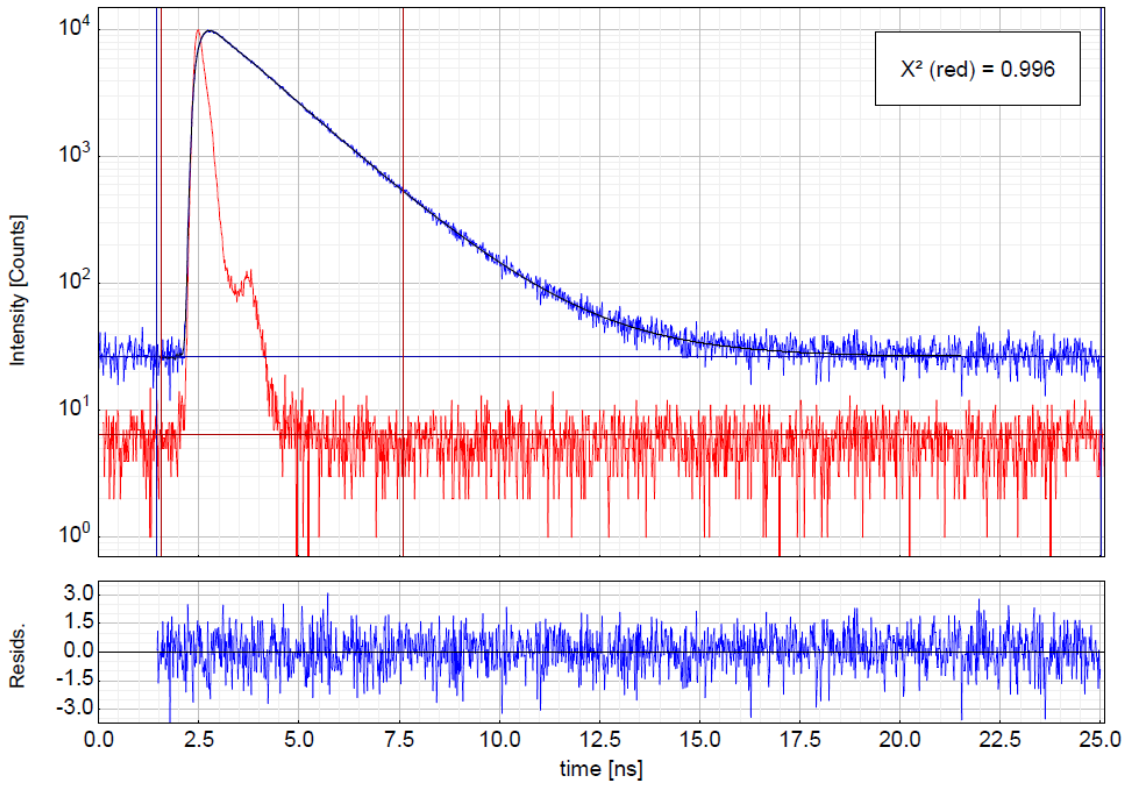


Figure S26: Lifetime dataset for 0.375 mM neutral Eosin Y + 2.625 mM TBHP.

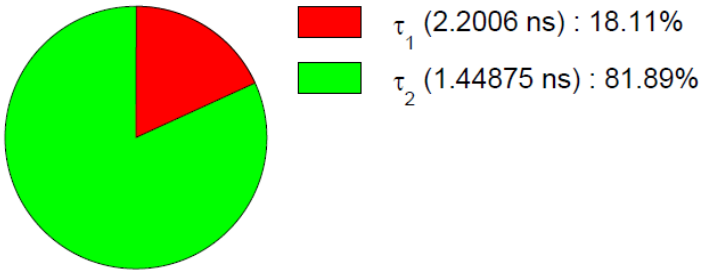


Average Lifetime:

$\tau_{Av.1}$=1.5849 ns (intensity weighted)

$\tau_{Av.2}$=1.5443 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

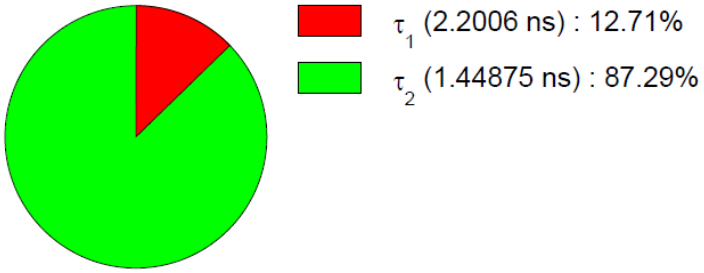
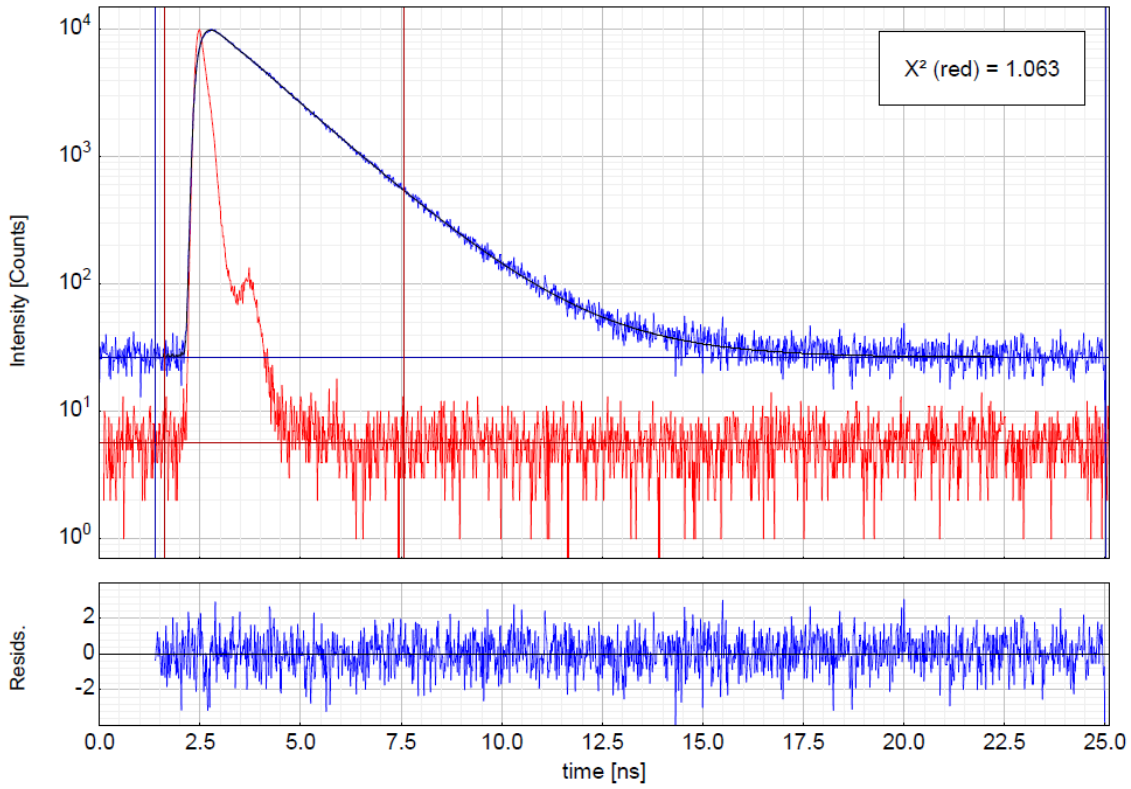


Figure S27: Lifetime dataset for 0.375 mM neutral Eosin Y + 3.000 mM TBHP.

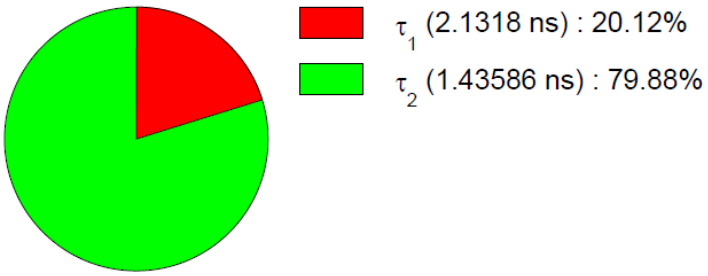


Average Lifetime:

$\tau_{Av.1}$=1.5759 ns (intensity weighted)

$\tau_{Av.2}$=1.5368 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

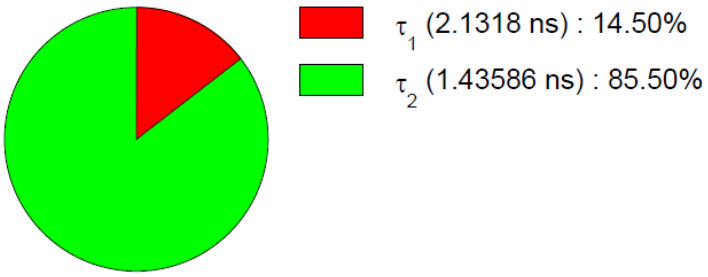
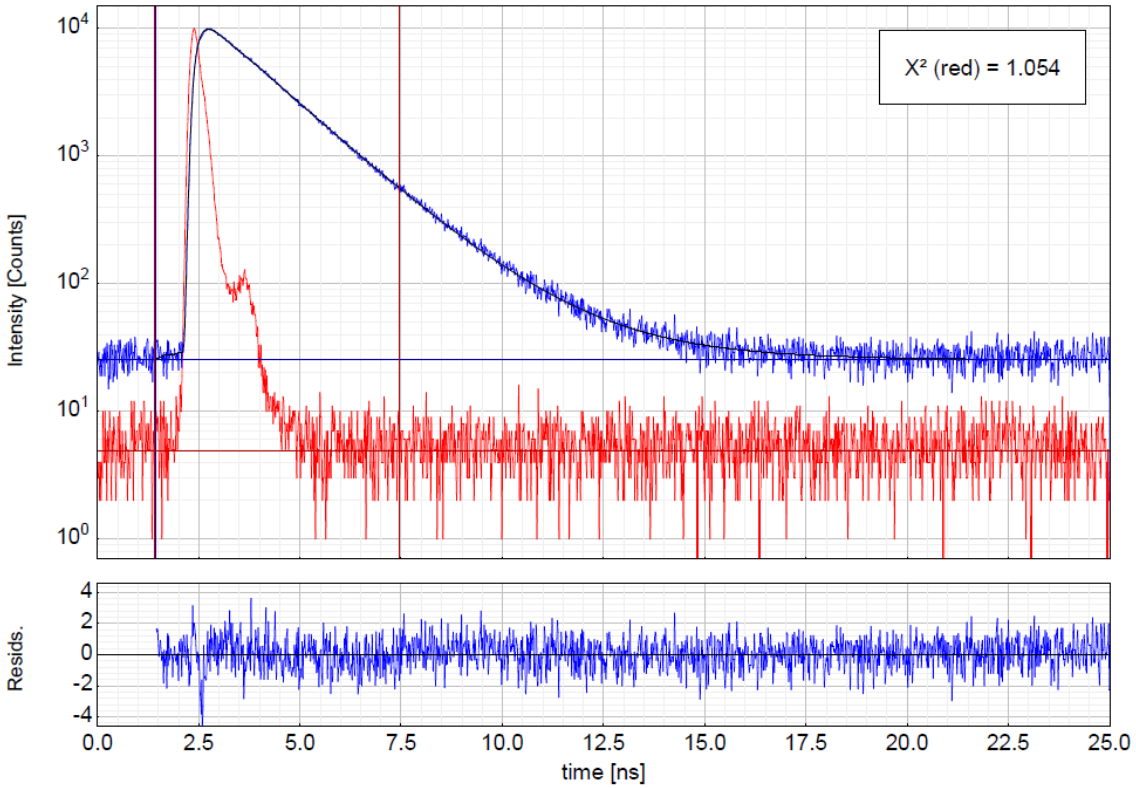


Figure S28: Lifetime dataset for 0.375 mM neutral Eosin Y + 3.375 mM TBHP.

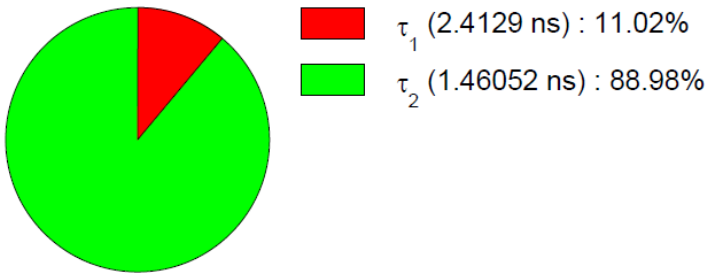


Average Lifetime:

$\tau_{Av.1}$=1.5655 ns (intensity weighted)

$\tau_{Av.2}$=1.5269 ns (amplitude weighted)

Fractional Intensities of the Positive Decay Components:



Fractional Amplitudes of the Positive Decay Components:

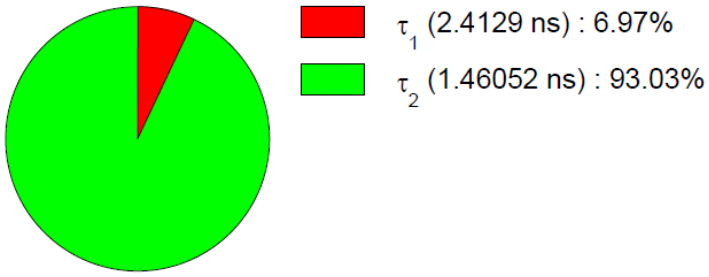
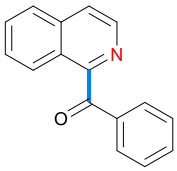


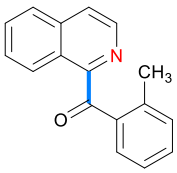
Figure S29: Lifetime dataset for 0.375 mM neutral Eosin Y + 3.750 mM TBHP.

Characterization of Products:



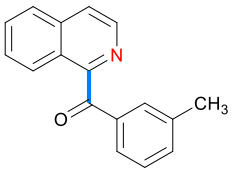
Isoquinolin-1-yl(phenyl)methanone (3a):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3a** (18.7 mg, 80% yield) was obtained as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.6 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.00 – 7.89 (m, 3H), 7.81 (d, *J* = 5.6 Hz, 1H), 7.75 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.62 (td, *J* = 7.7, 3.2 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 156.4, 141.1, 136.7, 136.6, 133.6, 130.7, 130.7, 128.4, 128.3, 127.1, 126.4, 126.1, 122.6.



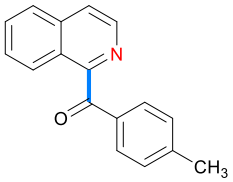
Isoquinolin-1-yl(*o*-tolyl)methanone (3b):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3b** (19.5 mg, 79% yield) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.6 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.71 (m, 2H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.42 (dd, *J* = 14.8, 7.5 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 156.9, 141.3, 139.7, 137.2, 136.7, 132.0, 131.8, 131.7, 130.6, 128.5, 127.1, 126.3, 126.2, 125.4, 122.8, 21.4.



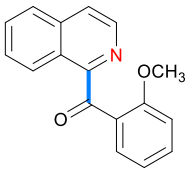
Isoquinolin-1-yl(*m*-tolyl)methanone (3c):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3c** (17.6 mg, 71% yield) was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.6 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 5.6 Hz, 1H), 7.79 – 7.69 (m, 3H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.0, 156.7, 141.2, 138.3, 136.7, 136.6, 134.5, 131.0, 130.7, 128.3, 128.2, 128.1, 127.1, 126.3, 126.2, 122.5, 21.3.



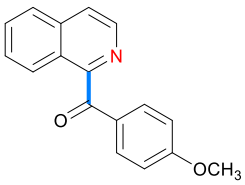
Isoquinolin-1-yl(*p*-tolyl)methanone (3d):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3d** (20 mg, 81% yield) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.7 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 5.7 Hz, 1H), 7.67 – 7.60 (m, 1H), 7.55 – 7.47 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 156.8, 144.7, 141.1, 136.6, 134.1, 130.8, 130.6, 129.1, 128.1, 127.0, 126.3, 126.2, 122.3, 21.7.



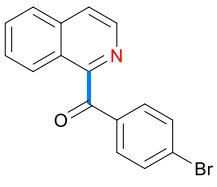
Isoquinolin-1-yl(2-methoxyphenyl)methanone (3e): The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3e** (17.1 mg, 65% yield) was obtained as a brown gum.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.6 Hz, 1H), 8.39 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 11.4, 4.3 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.9, 159.2, 157.9, 141.1, 136.6, 134.2, 131.2, 130.3, 128.3, 128.1, 126.8, 126.4, 125.5, 122.3, 120.9, 112.1, 55.6. HRMS (ESI^+) *m/z* $[M+Na]^+$ calcd for $C_{17}H_{13}NNaO_2$, 286.0838, found 286.0831.



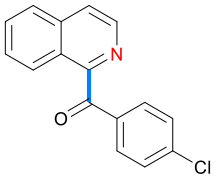
Isoquinolin-1-yl(4-methoxyphenyl)methanone (3f):[2] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3f** (19 mg, 72% yield) was obtained as a pale-brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 5.7 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 15.8, 8.6 Hz, 3H), 7.78 (d, *J* = 5.7 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 164.1, 157.0, 141.1, 136.6, 133.1, 130.6, 129.4, 128.1, 126.9, 126.2, 126.2, 122.2, 113.7, 55.5.



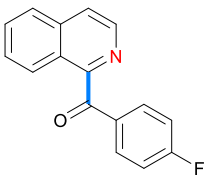
(4-bromophenyl)(isoquinolin-1-yl)methanone (3g):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3g** (10.9 mg, 35% yield) was obtained as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.6 Hz, 1H), 8.26 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.81 (m, 3H), 7.79 – 7.73 (m, 1H), 7.67 – 7.60 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.6, 155.5, 141.1, 136.8, 135.4, 132.2, 131.7, 130.8, 128.9, 128.5, 127.1, 126.4, 126.0, 122.9.



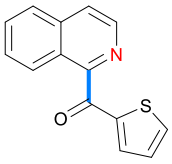
(4-chlorophenyl)(isoquinolin-1-yl)methanone (3h):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3h** (11.2 mg, 42% yield) was obtained as a pale-brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.6 Hz, 1H), 8.25 (d, *J* = 8.5 Hz, 1H), 7.93 (dd, *J* = 7.8, 5.8 Hz, 3H), 7.83 (d, *J* = 5.6 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.65 (dd, *J* = 11.4, 4.1 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 155.6, 141.1, 140.1, 136.8, 135.0, 132.1, 130.8, 128.8, 128.5, 127.1, 126.4, 126.0, 122.9.



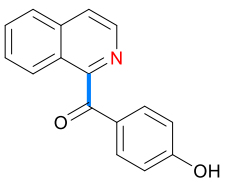
(4-fluorophenyl)(isoquinolin-1-yl)methanone (3i):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3i** (17.6 mg, 70% yield) was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.6 Hz, 1H), 8.23 (dd, *J* = 8.5, 0.6 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 5.6 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.64 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.19 – 7.12 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.0, 166.1 (d, J=256 Hz), 155.9, 141.1, 136.8, 133.5 (d, J=8.8 Hz), 133.0 (d, J=3.8 Hz), 130.8, 128.4, 127.1, 126.4, 126.1, 122.8, 115.6 (d, J=21.4 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -103.94.



Isoquinolin-1-yl(thiophen-2-yl)methanone (3j):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3j** (10.8 mg, 45% yield) was obtained as a yellow solid.

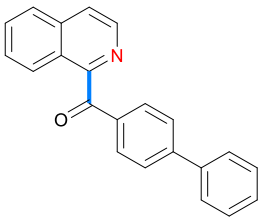
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.6 Hz, 1H), 8.55 (d, *J* = 8.6 Hz, 1H), 7.91 (dd, *J* = 4.3, 3.1 Hz, 2H), 7.84 (d, *J* = 5.6 Hz, 1H), 7.75 (ddd, *J* = 9.3, 6.6, 1.1 Hz, 2H), 7.66 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.16 (dd, *J* = 4.9, 3.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.0, 154.6, 142.6, 140.8, 136.9, 136.5, 135.9, 130.6, 128.6, 128.0, 127.0, 126.4, 126.2, 123.5.



(4-hydroxyphenyl)(isoquinolin-1-yl)methanone (3k): The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3k** (23.9 mg, 96% yield, mp 205-206°C) was obtained as a pale-yellow solid.

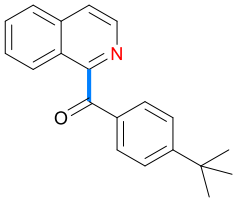
^{1}H NMR (500 MHz, DMSO) δ 10.66 (s, 1H), 8.57 (d, *J* = 5.6 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 5.6 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.77 (m, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.69 – 7.61 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (126 MHz,

DMSO) δ 192.8, 163.1, 157.3, 141.2, 136.1, 133.0, 130.9, 128.4, 127.6, 127.3, 125.5, 125.2, 122.0, 115.6. HRMS (ESI$^+$) *m/z* $[M+Na]^+$ calcd for $C_{16}H_{11}NNaO_2$, 272.0682, found 272.0674.



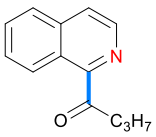
[1,1'-biphenyl]-4-yl(isoquinolin-1-yl)methanone (3l):[2] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3l** (24.7 mg, 80% yield) was obtained as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.6 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 5.6 Hz, 1H), 7.76 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 8.4, 7.3 Hz, 3H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.3, 156.5, 146.4, 141.2, 139.9, 136.7, 135.4, 131.3, 130.7, 128.9, 128.3, 128.3, 127.3, 127.2, 127.1, 126.5, 126.2, 122.6.



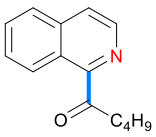
(4-(tert-butyl)phenyl)(isoquinolin-1-yl)methanone (3m):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3m** (20.8 mg, 72% yield) was obtained as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.6 Hz, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.91 (dd, *J* = 8.0, 6.0 Hz, 3H), 7.79 (d, *J* = 5.6 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 1.34 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.4, 157.6, 156.8, 141.2, 136.7, 134.0, 130.7, 130.7, 128.2, 127.1, 126.4, 126.3, 125.5, 122.4, 35.2, 31.1.



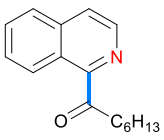
1-(isoquinolin-1-yl)butan-1-one (3o):[3] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3o** (14.3 mg, 72% yield) was obtained as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.5 Hz, 1H), 8.56 (d, *J* = 5.5 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 5.5 Hz, 1H), 7.73 – 7.61 (m, 2H), 3.29 (dd, *J* = 9.2, 5.5 Hz, 2H), 1.80 (dt, *J* = 14.7, 7.4 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8, 153.5, 141.0, 136.9, 130.3, 128.9, 126.9, 126.7, 125.7, 124.2, 42.2, 17.6, 13.9.



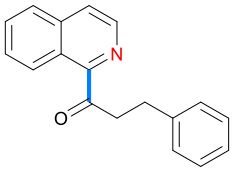
1-(isoquinolin-1-yl)pentan-1-one (3p):[3] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3p** (15.6 mg, 73% yield) was obtained as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 5.3 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 5.4 Hz, 1H), 7.68 (dt, *J* = 15.2, 7.1 Hz, 2H), 3.32 (t, *J* = 7.3 Hz, 2H), 1.76 (td, *J* = 15.0, 7.6 Hz, 2H), 1.51 – 1.40 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.9, 153.6, 141.0, 136.9, 130.3, 128.9, 126.9, 126.7, 125.7, 124.1, 40.1, 26.3, 22.5, 13.9.



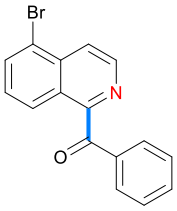
1-(isoquinolin-1-yl)heptan-1-one (3q):[4] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3q** (19.3 mg, 80% yield) was obtained as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 8.5 Hz, 1H), 8.57 (d, *J* = 5.5 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 5.5 Hz, 1H), 7.75 – 7.62 (m, 2H), 3.31 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.47 – 1.31 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0, 153.6, 141.0, 136.9, 130.3, 128.9, 126.9, 126.7, 125.7, 124.2, 40.4, 31.7, 29.0, 24.1, 22.5, 14.0.



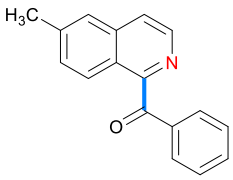
1-(isoquinolin-1-yl)-3-phenylpropan-1-one (3r):[3] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3r** (14.6 mg, 56% yield) was obtained as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.5 Hz, 1H), 8.57 (d, *J* = 5.5 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 5.5 Hz, 1H), 7.75 – 7.64 (m, 2H), 7.33 – 7.27 (m, 4H), 7.19 (ddd, *J* = 8.5, 5.7, 3.0 Hz, 1H), 3.74 – 3.67 (m, 2H), 3.14 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.6, 152.9, 141.3, 141.0, 136.9, 130.3, 128.9, 128.5, 128.4, 126.9, 126.7, 125.9, 125.7, 124.4, 41.8, 30.1.



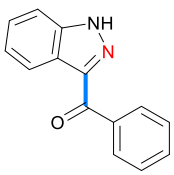
(5-bromoisoquinolin-1-yl)(phenyl)methanone (3aa):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3aa** (28.7 mg, 92% yield) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.4 Hz, 1H), 8.18 (t, *J* = 6.0 Hz, 2H), 8.03 (d, *J* = 7.3 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.51 – 7.42 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 156.8, 142.6, 136.3, 135.7, 134.4, 133.9, 130.7, 128.6, 128.5, 127.4, 125.9, 122.0, 121.4.



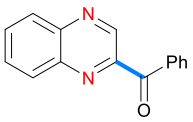
(6-methylisoquinolin-1-yl)(phenyl)methanone (3ab):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3ab** (13.8 mg, 56% yield) was obtained as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.6 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.99 – 7.89 (m, 2H), 7.77 – 7.66 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.46 (ddd, *J* = 7.5, 6.8, 4.6 Hz, 3H), 2.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.9, 156.0, 141.2, 137.0, 136.7, 133.6, 130.7, 130.6, 128.4, 125.9, 125.9, 124.9, 122.1, 21.9.



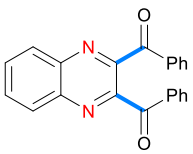
(1*H*-indazol-3-yl)(phenyl)methanone (3ac):[5] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3ac** (15.8 mg, 71% yield) was obtained as a yellow solid.

^{1}H NMR (500 MHz, DMSO) δ 14.01 (s, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 8.28 – 8.22 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.50 (dd, *J* = 11.3, 4.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, DMSO) δ 188.2, 142.1, 140.7, 137.7, 132.4, 130.1, 128.2, 127.0, 123.5, 122.9, 121.8, 111.0.



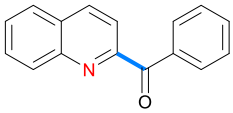
Phenyl(quinoxalin-2-yl)methanone (3ad):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3ad** (10.5 mg, 45% yield) was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.26 – 8.22 (m, 2H), 8.22 – 8.18 (m, 2H), 7.87 (dtd, *J* = 16.5, 7.0, 1.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.3, 148.6, 145.3, 143.1, 140.4, 135.5, 133.6, 131.9, 131.2, 130.7, 130.4, 129.4, 128.3.



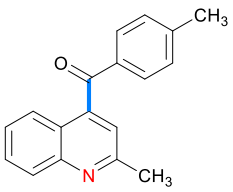
Quinoxaline-2,3-diylbis(phenylmethanone) (3ae):[1] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3ae** (5 mg, 15% yield) was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 6.4, 3.4 Hz, 2H), 8.15 – 8.09 (m, 4H), 7.95 (dt, *J* = 6.4, 3.1 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.6, 152.0, 140.2, 135.2, 133.9, 132.1, 130.9, 129.9, 128.5.



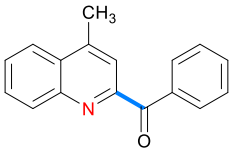
Phenyl(quinolin-2-yl)methanone (3af):[4] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3af** (10.7 mg, 46% yield) was obtained as a red solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.5 Hz, 1H), 8.22 (dd, *J* = 18.3, 8.0 Hz, 3H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 7.3 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.52 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.8, 154.7, 146.7, 137.1, 136.1, 133.0, 131.4, 130.5, 130.1, 128.9, 128.4, 128.1, 127.6, 120.8.



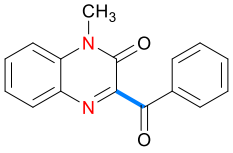
(2-methylquinolin-4-yl)(*p*-tolyl)methanone (3ag):[6] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3ag** (18.3 mg, 70% yield) was obtained as a yellow gum.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.5 Hz, 1H), 7.75 (dt, *J* = 8.4, 4.5 Hz, 4H), 7.49 – 7.43 (m, 1H), 7.29 (dd, *J* = 6.6, 3.9 Hz, 3H), 2.81 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 158.2, 148.0, 145.3, 145.2, 134.1, 130.3, 129.9, 129.4, 128.9, 126.6, 125.2, 123.3, 120.2, 25.2, 21.7.



(4-methylquinolin-2-yl)(phenyl)methanone (3ah):[4] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3ah** (10.1 mg, 41% yield) was obtained as a pale-yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 15.2, 8.0 Hz, 3H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.94 (s, 1H), 7.77 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 2.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.1, 154.4, 146.6, 145.6, 136.2, 133.0, 131.4, 131.1, 129.7, 128.9, 128.1, 128.1, 123.7, 121.3, 18.9.



3-benzoyl-1-methylquinoxalin-2(1*H*)-one (3ai):[7] The crude mixture was purified by column chromatography on silica gel (Hexane/EtOAc as eluent). Product **3ai** (19.0 mg, 72% yield) was obtained as a pale-yellow solid.

^{1}H NMR (500 MHz, DMSO) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (126 MHz, DMSO) δ 192.2, 154.8, 152.8, 134.6, 134.4, 133.9, 131.9, 131.7, 129.9, 129.7, 128.9, 123.9, 115.2, 28.9.

References:

1 R. Chang, J. Fang, J.-Q. Chen, D. Liu, G.-Q. Xu and P.-F. Xu, *ACS Omega*, 2019, **4**, 14021–14031.

2 K. Matcha and A. P. Antonchick, *Angew. Chemie Int. Ed.*, 2013, **52**, 2082–2086.

3 S. Paul, M. Bhakat and J. Guin, *Chem. – An Asian J.*, 2019, **14**, 3154–3160.

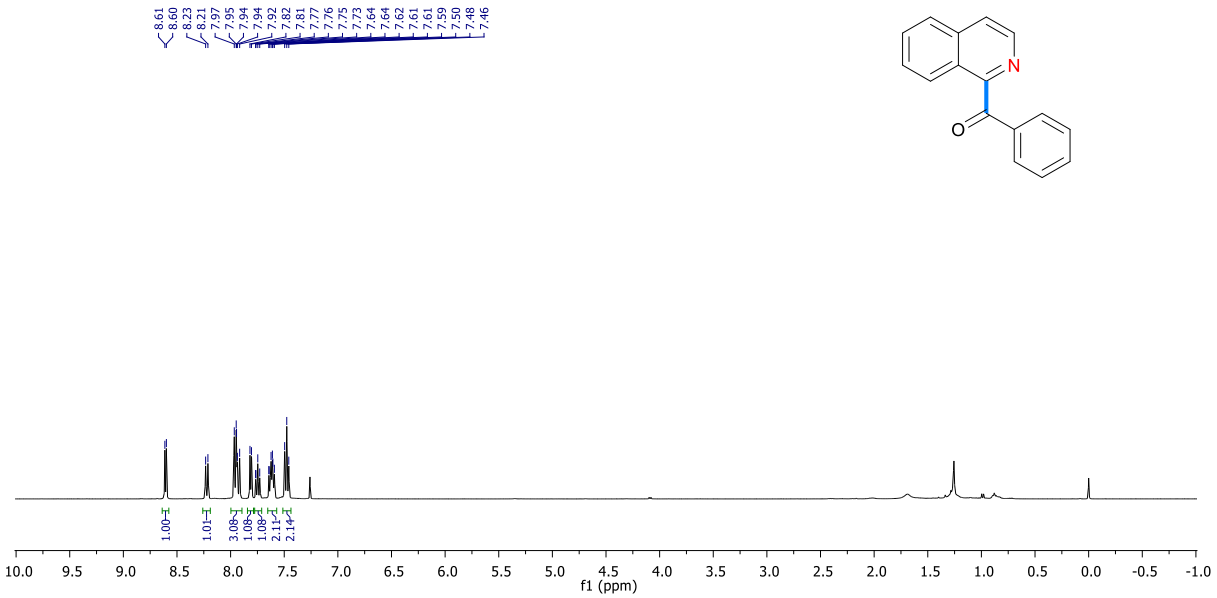
4 J. Chen, M. Wan, J. Hua, Y. Sun, Z. Lv, W. Li and L. Liu, *Org. Biomol. Chem.*, 2015, **13**, 11561–11566.

5 C.-D. Wang and R.-S. Liu, *Org. Biomol. Chem.*, 2012, **10**, 8948–8952.

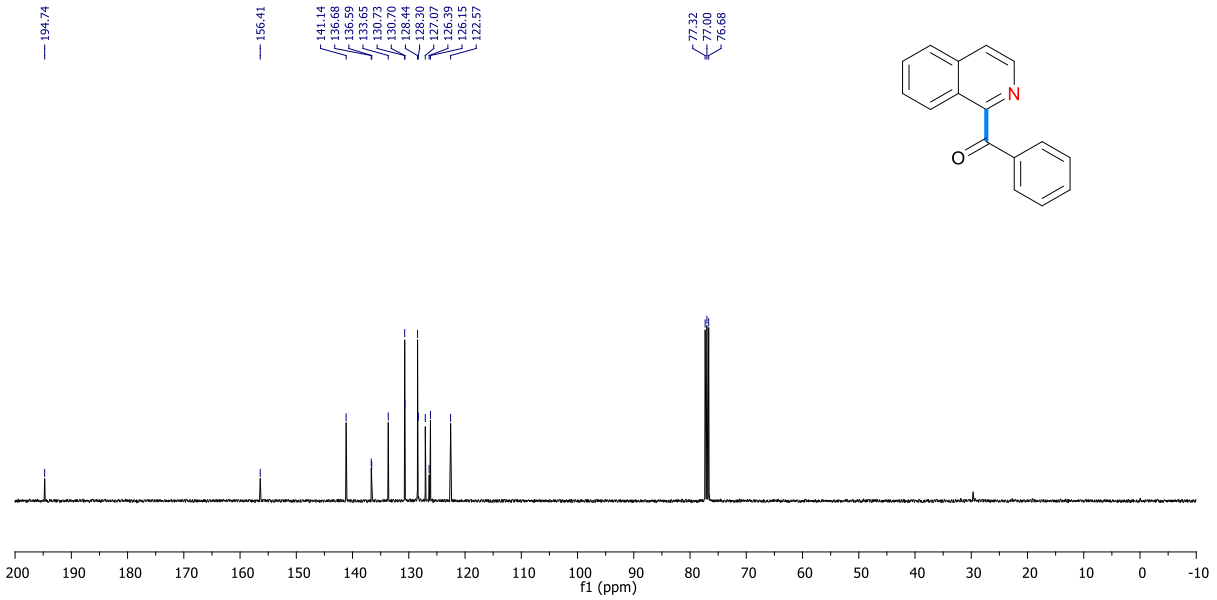
6 L. Zhang, G. Zhang, Y. Li, S. Wang and A. Lei, *Chem. Commun.*, 2018, **54**, 5744–5747.

7 L.-Y. Xie, Y.-S. Bai, X.-Q. Xu, X. Peng, H.-S. Tang, Y. Huang, Y.-W. Lin, Z. Cao and W.-M. He, *Green Chem.*, 2020, **22**, 1720–1725.

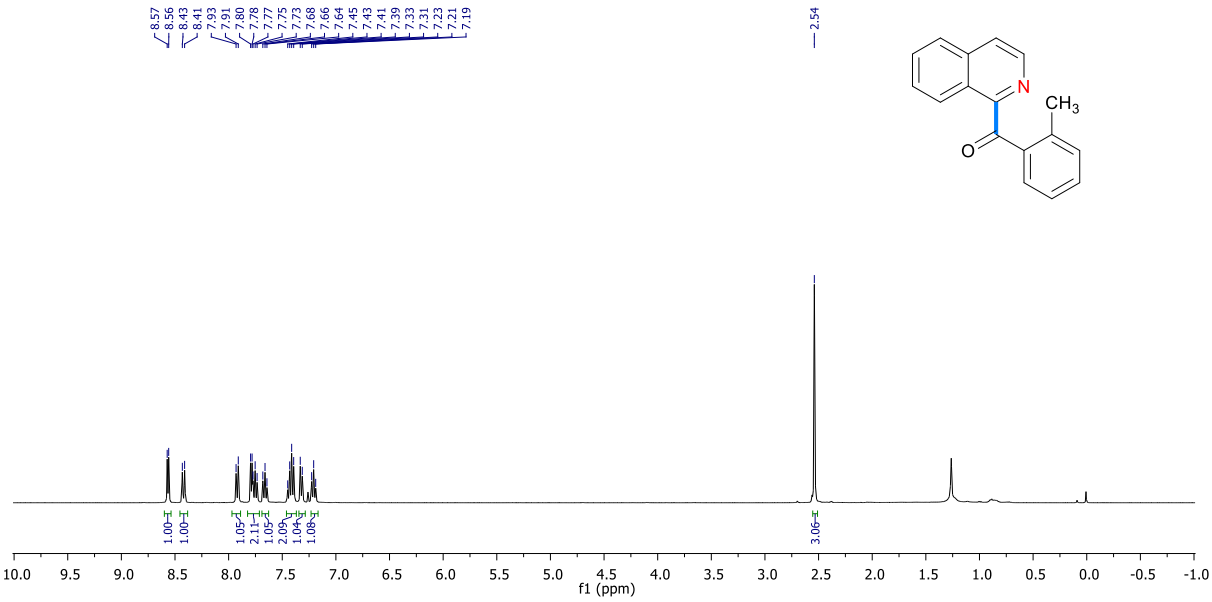
^{1}H and ^{13}C NMR Spectra:



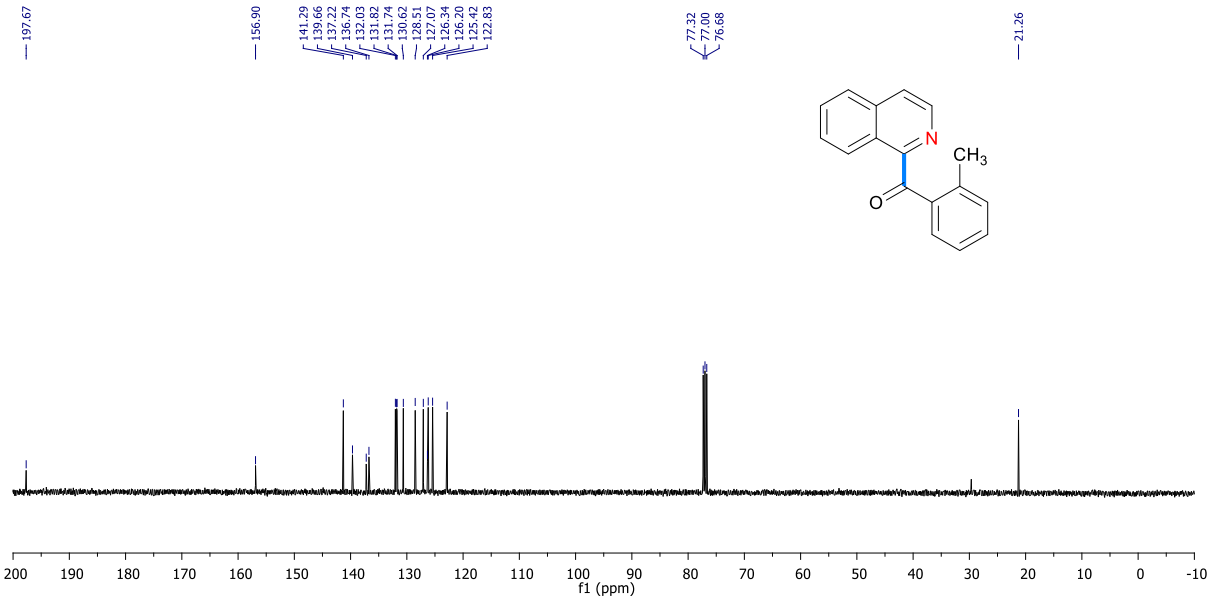
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**



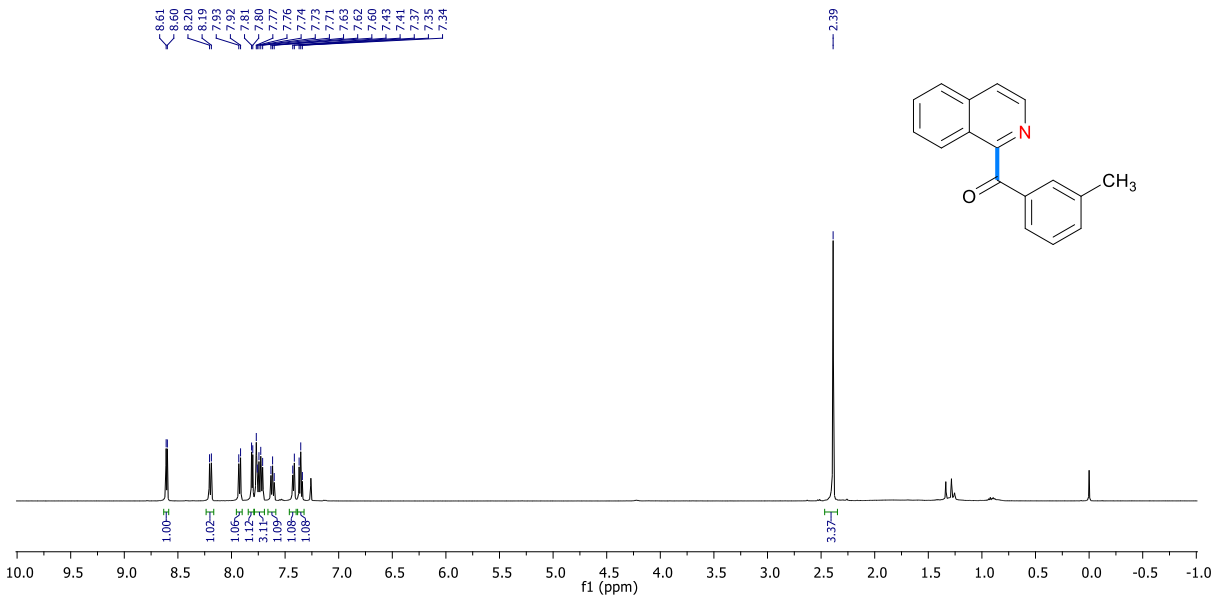
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3a**



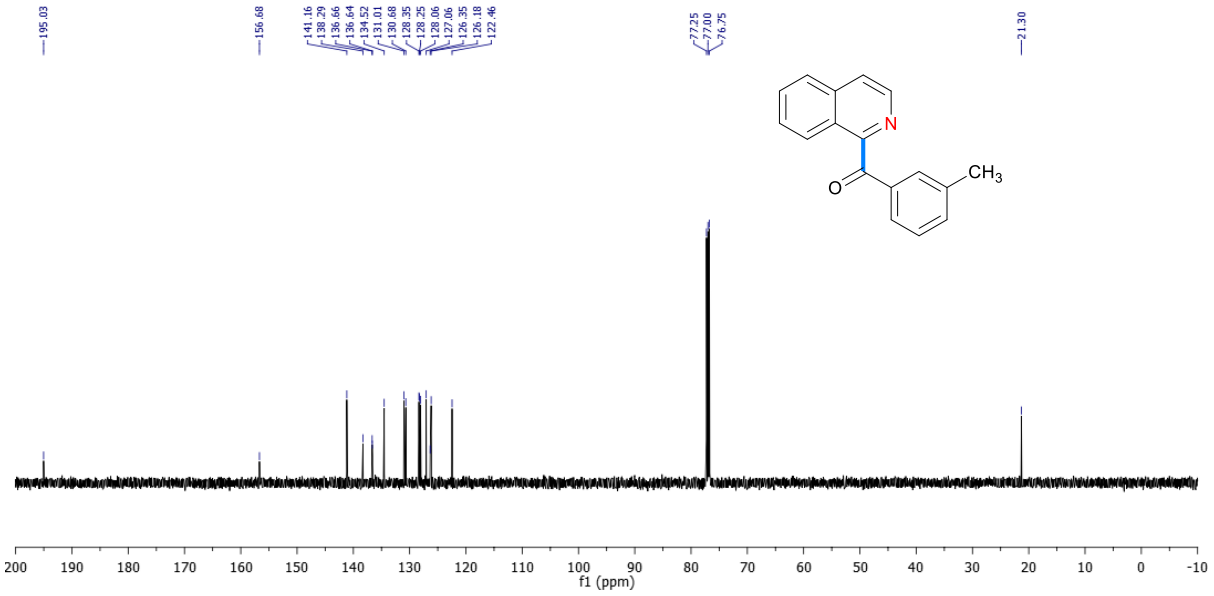
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**



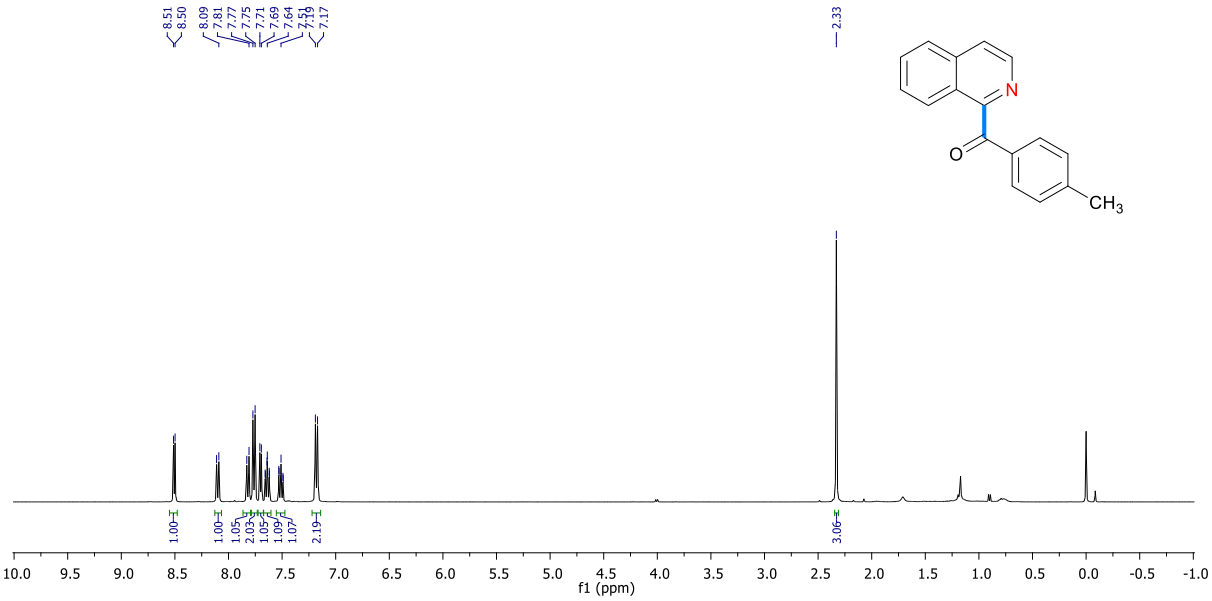
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3b**



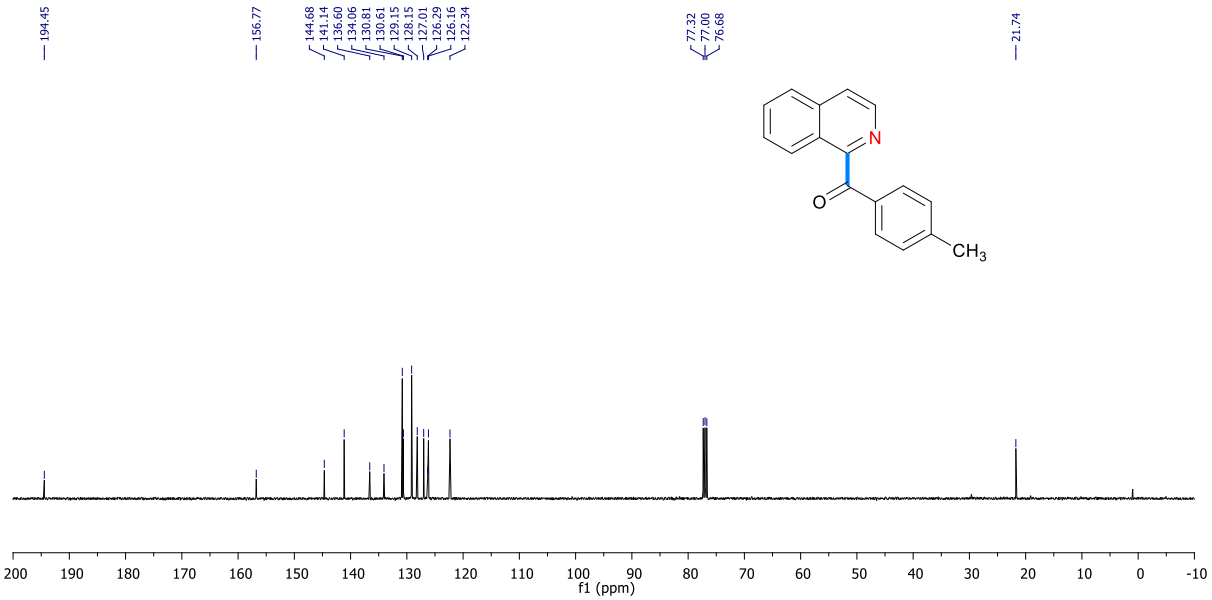
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**



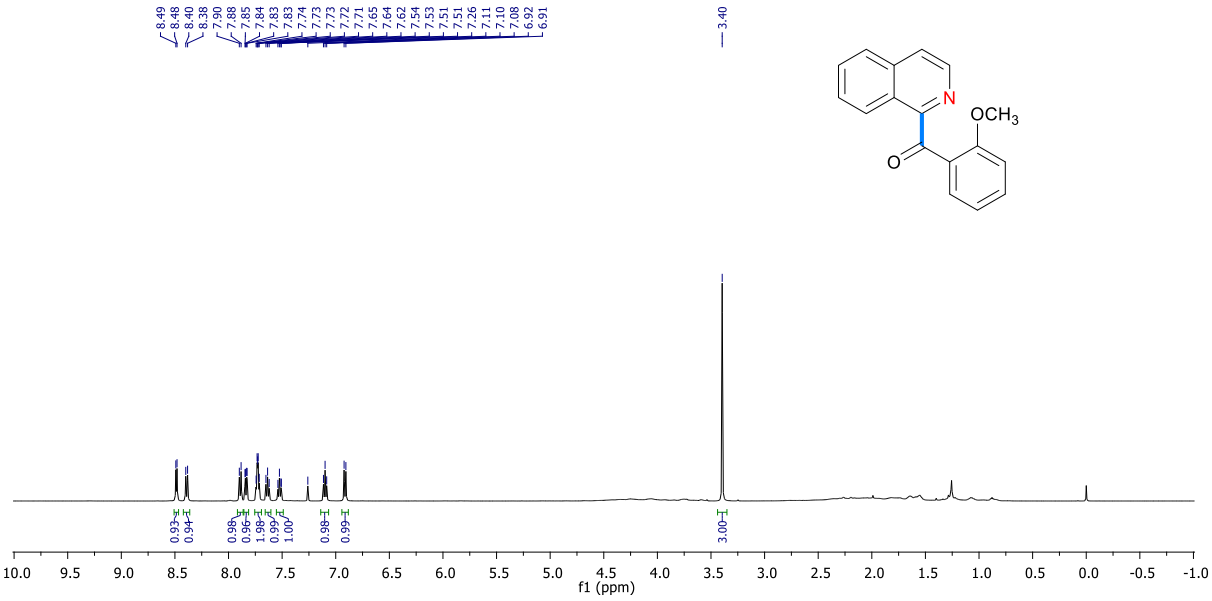
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3c**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3d**



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3d**



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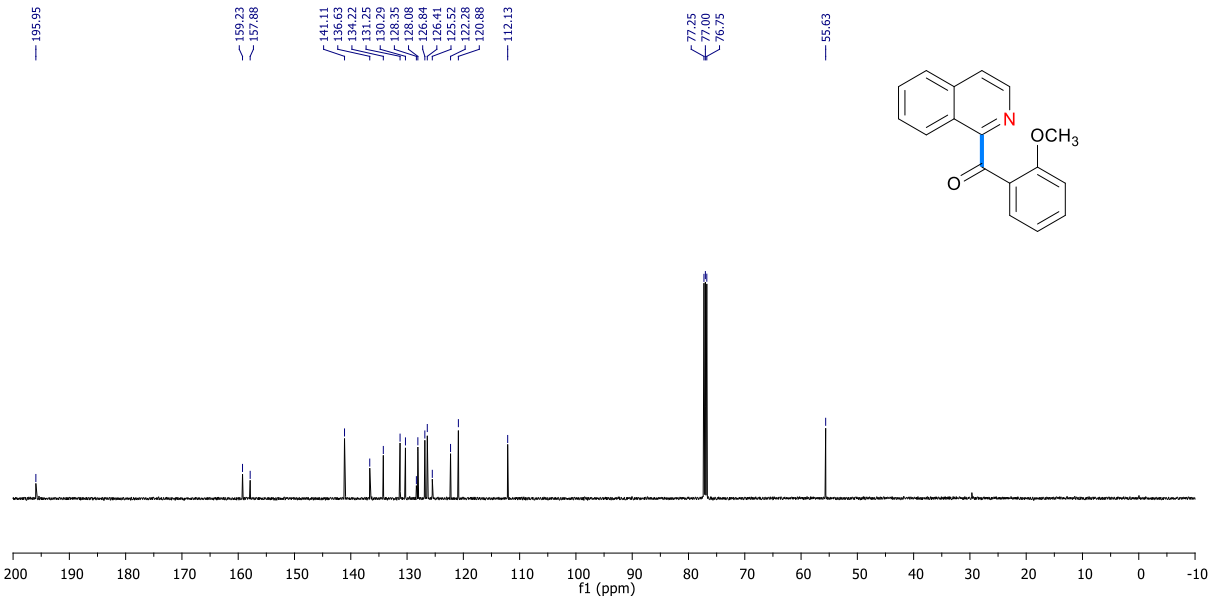
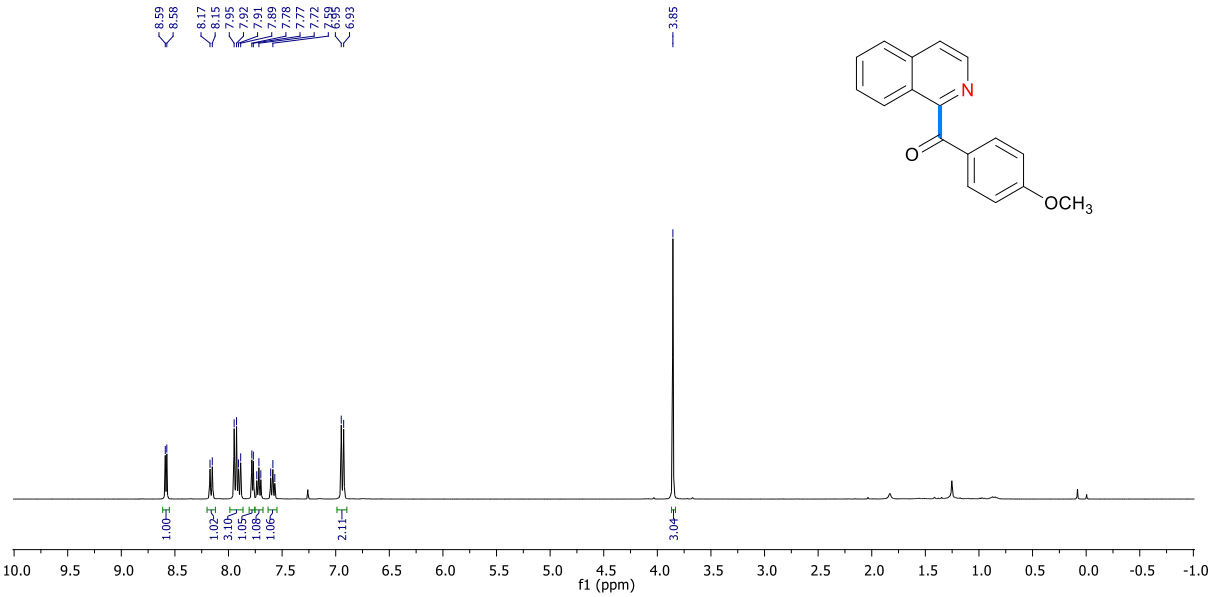
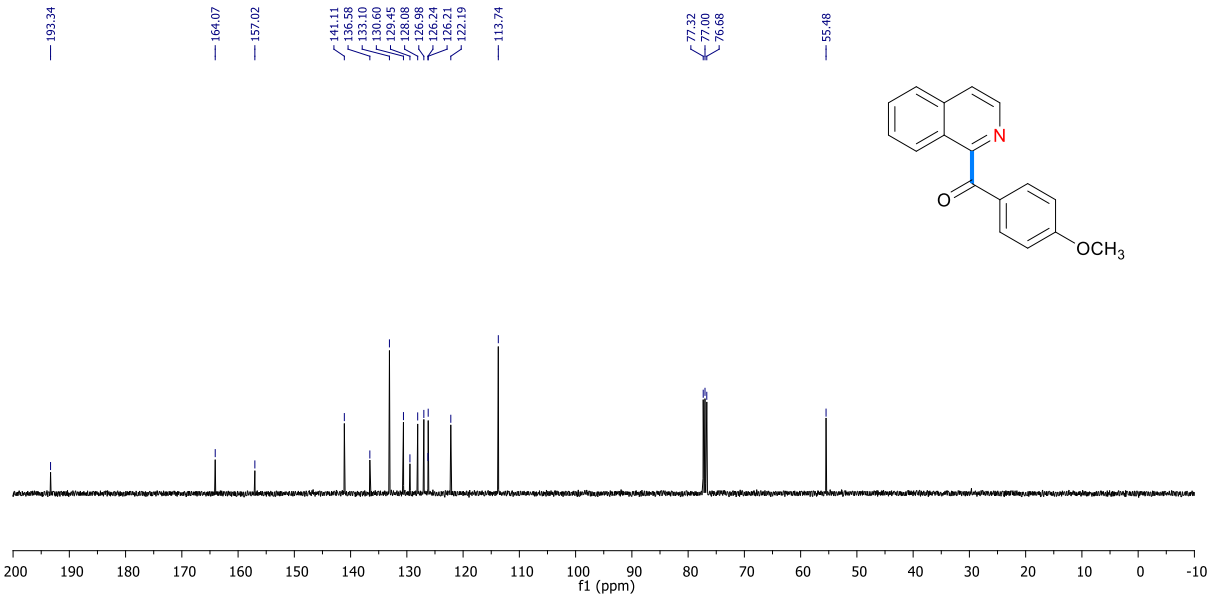


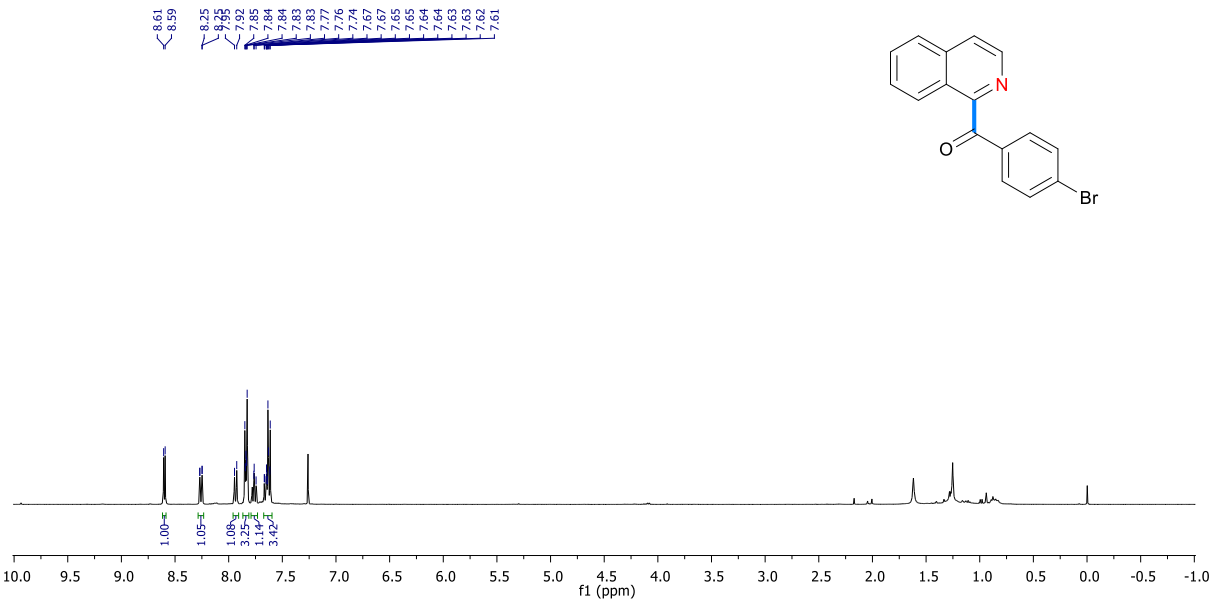
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3e**



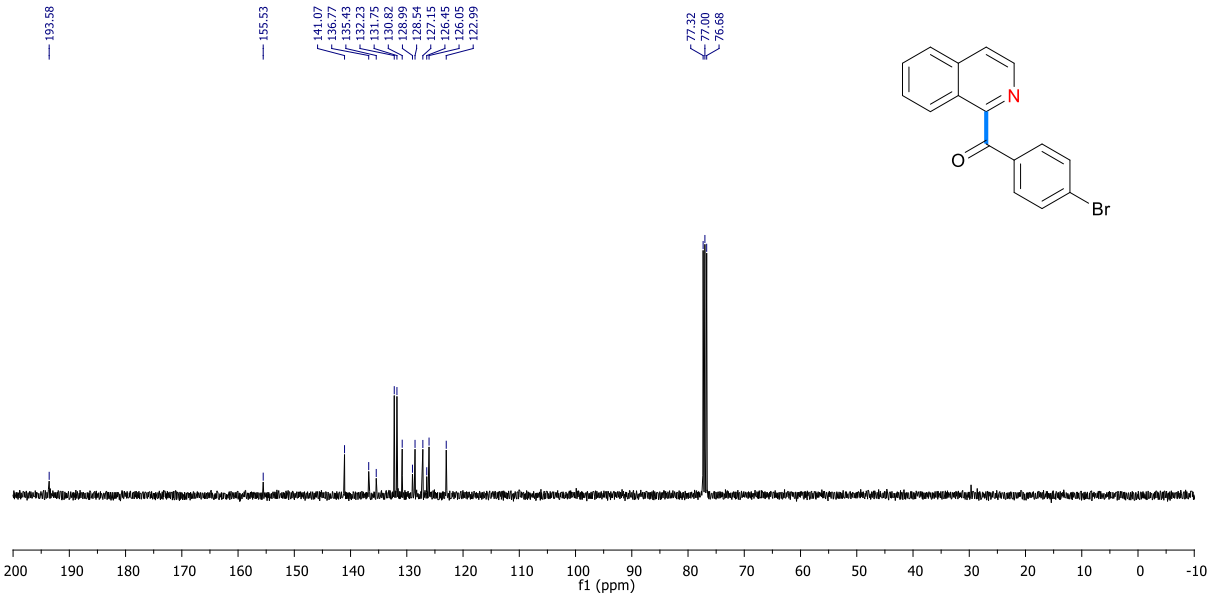
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f**



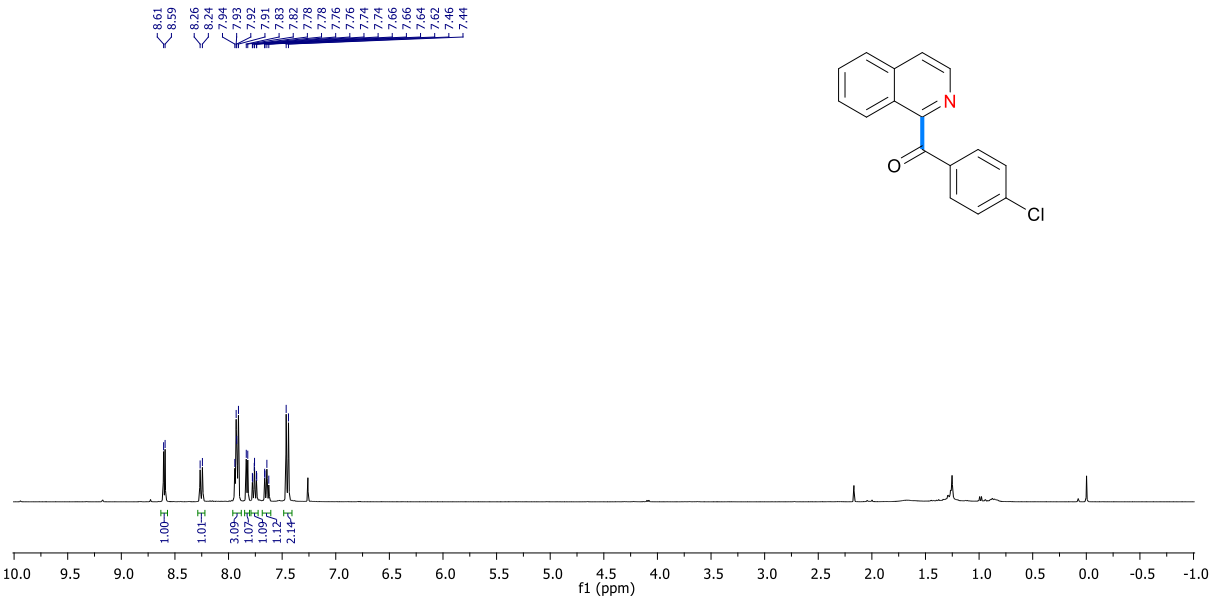
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3f**



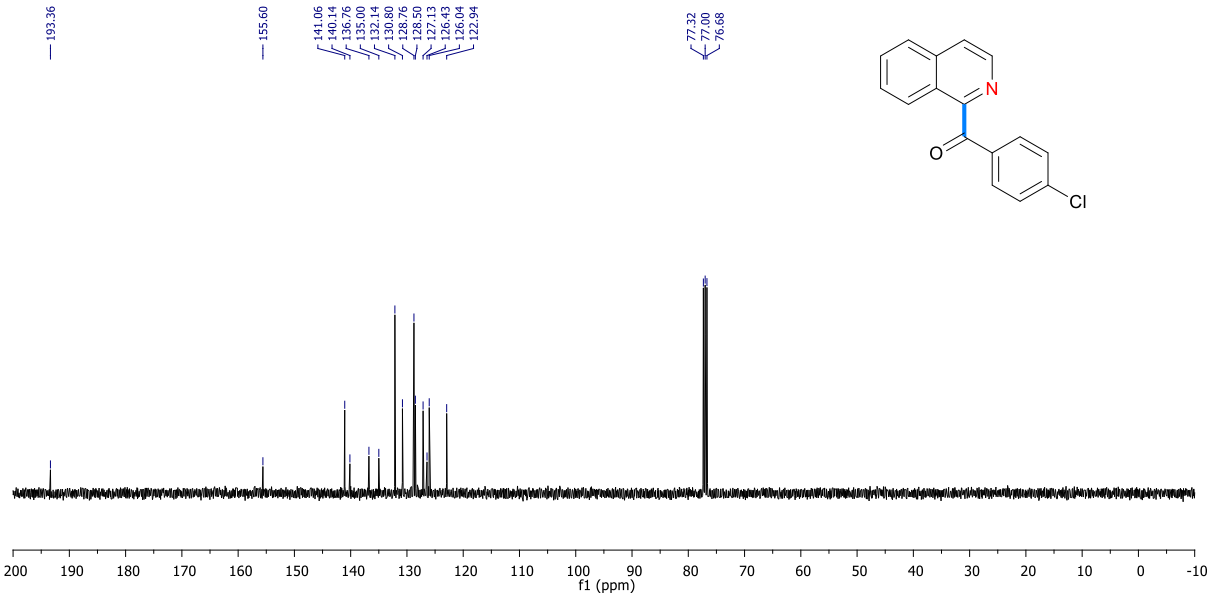
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g**



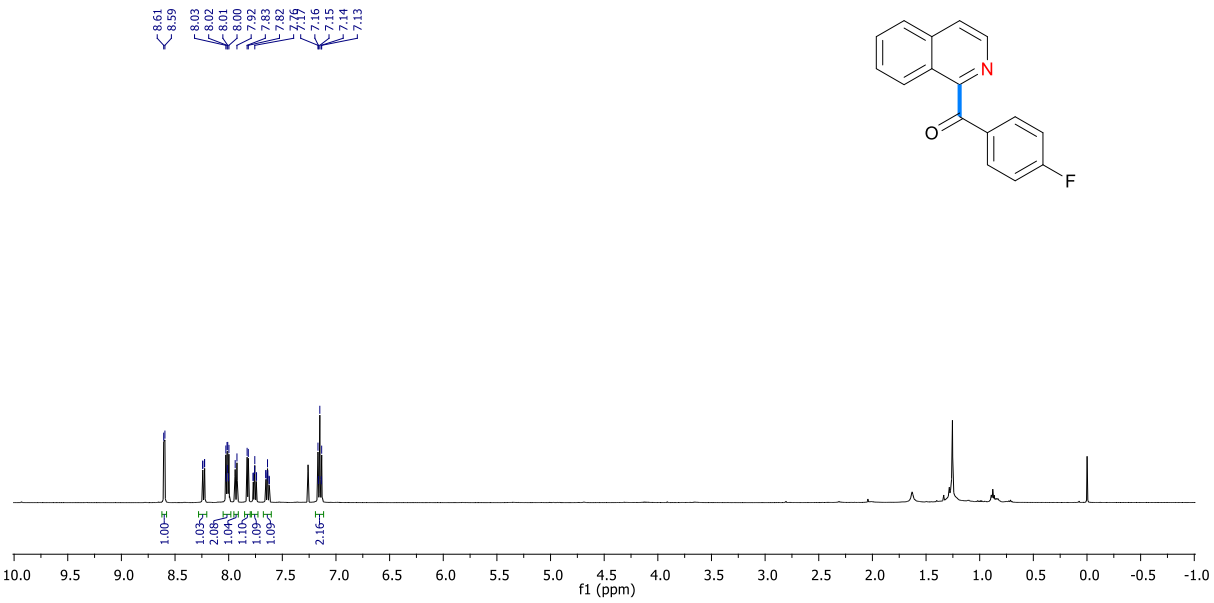
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3g**



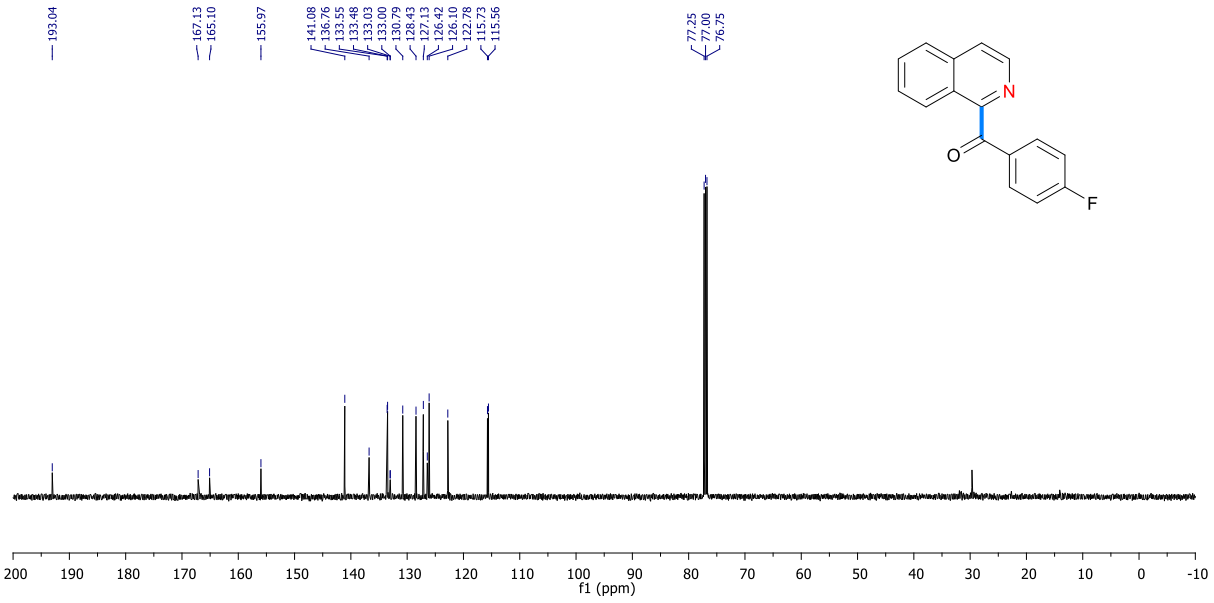
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**



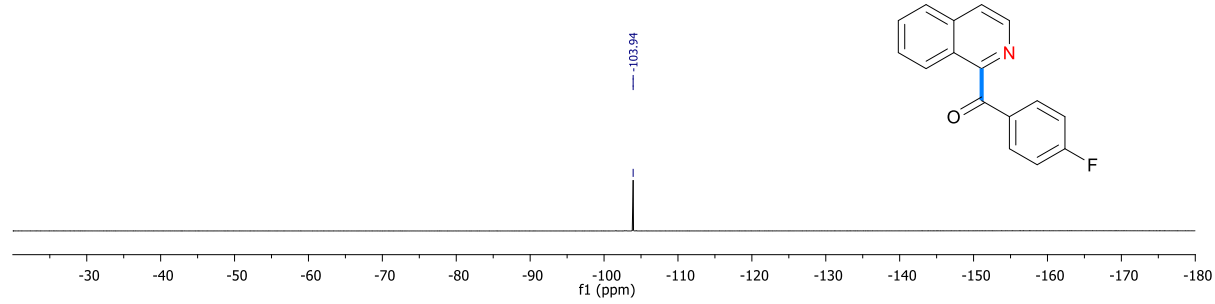
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3h**



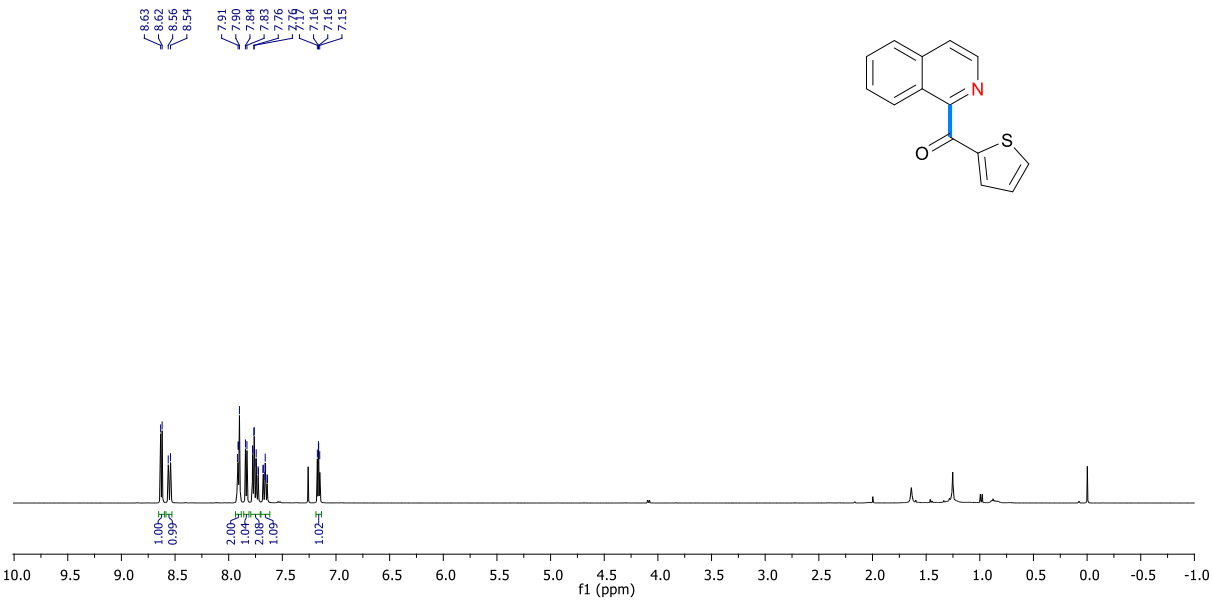
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3i**



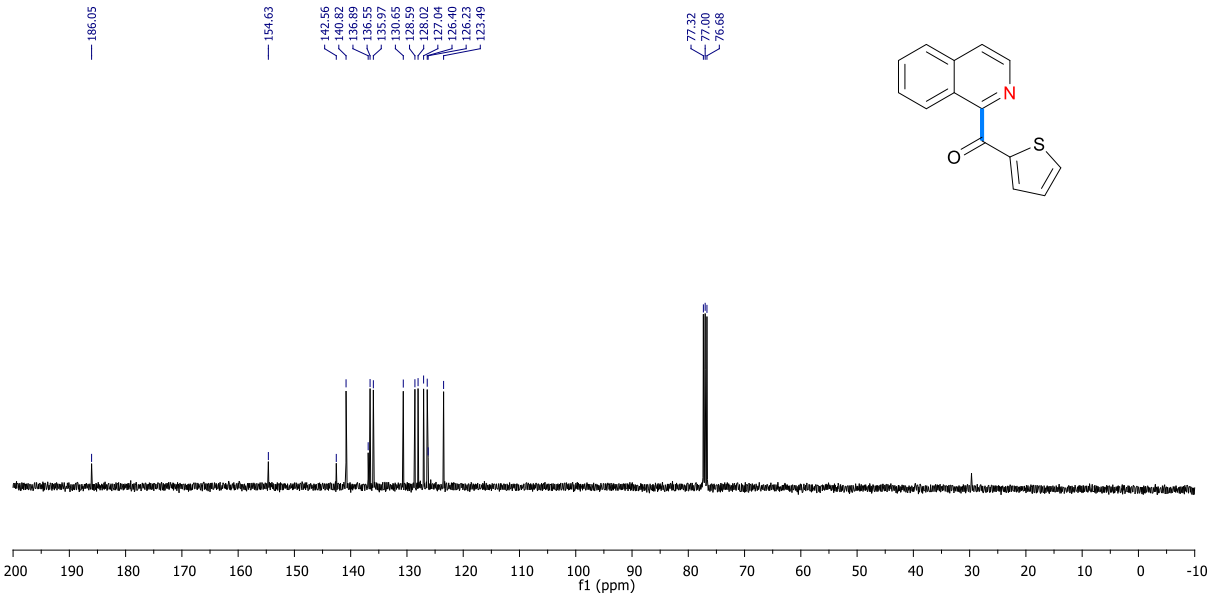
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3i**



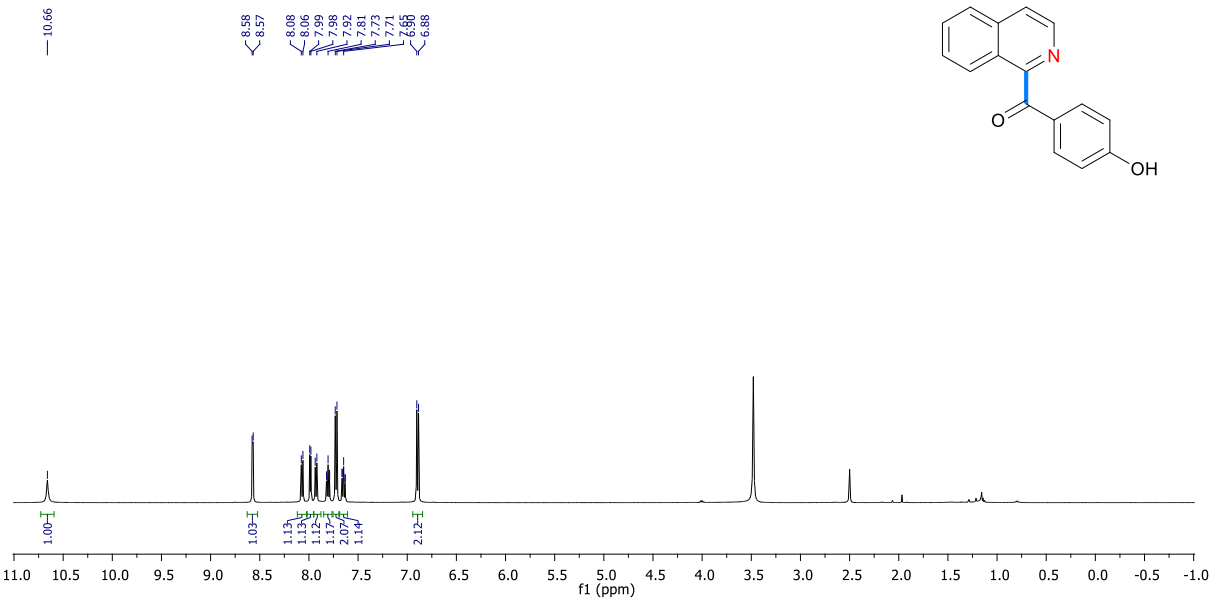
^{19}F NMR (471 MHz, $CDCl_3$) of compound **3i**



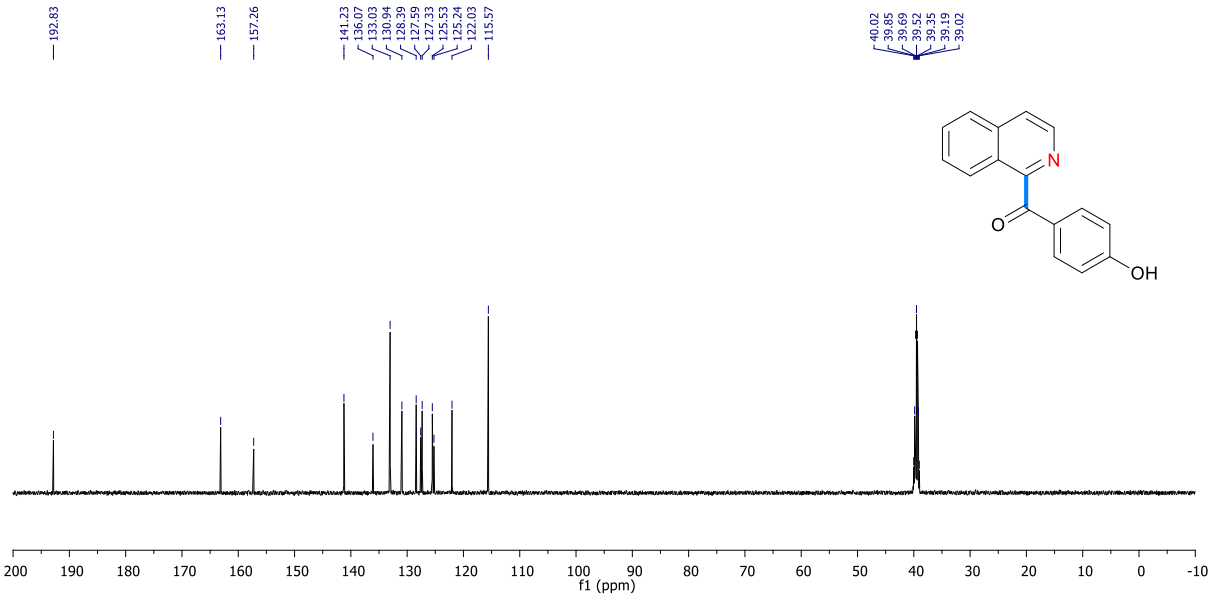
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j**



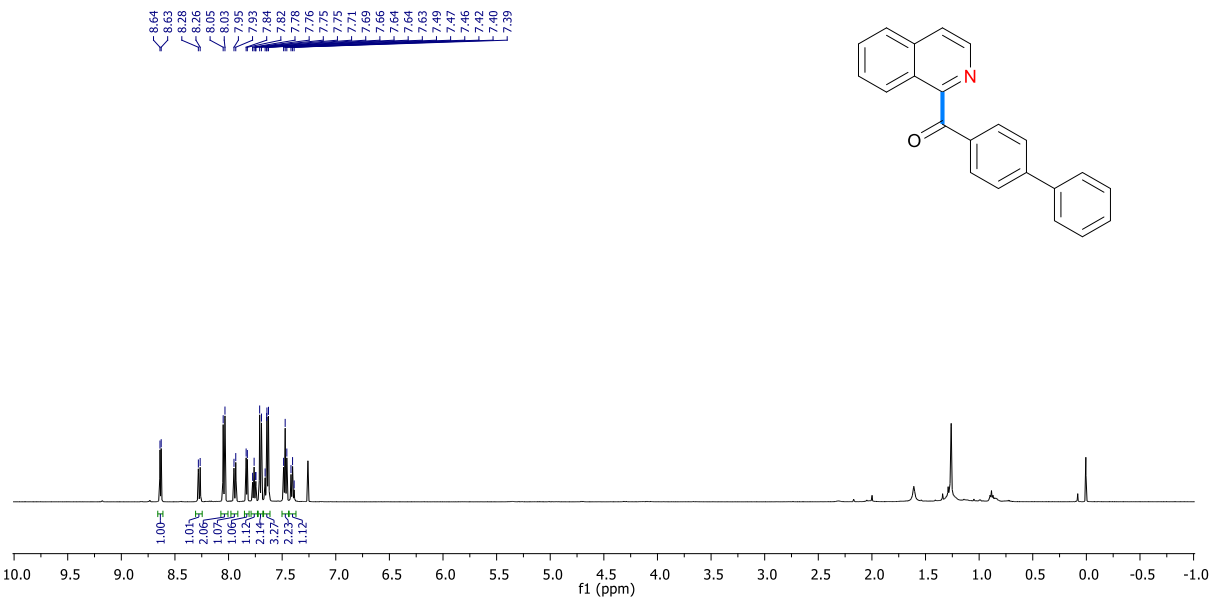
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3j**



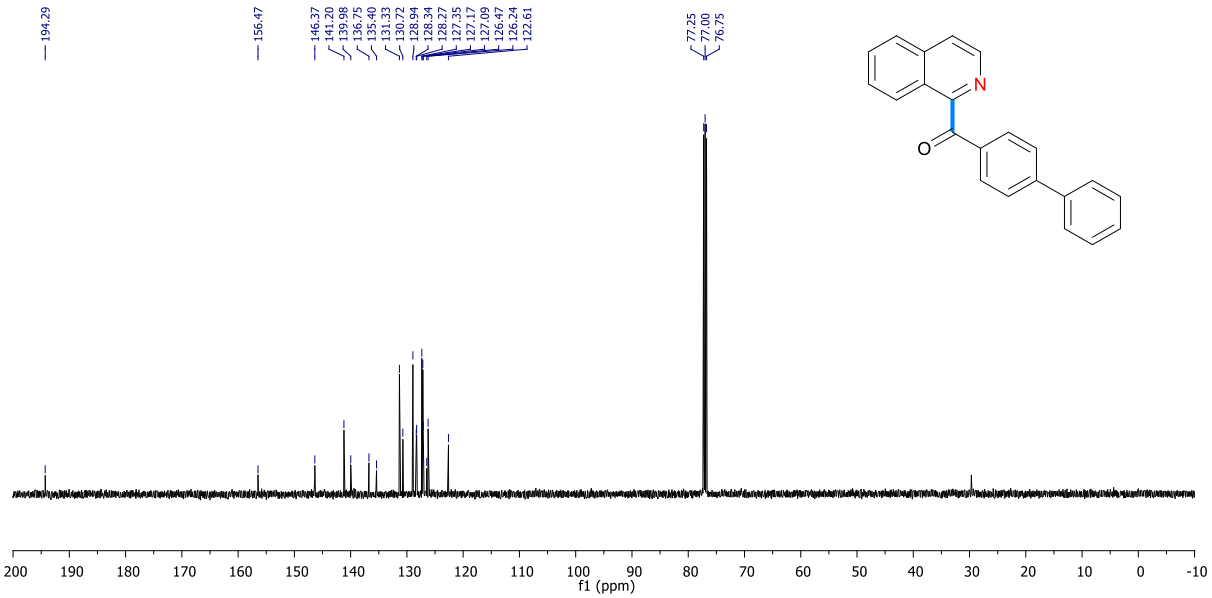
^{1}H NMR (500 MHz, DMSO) of compound **3k**



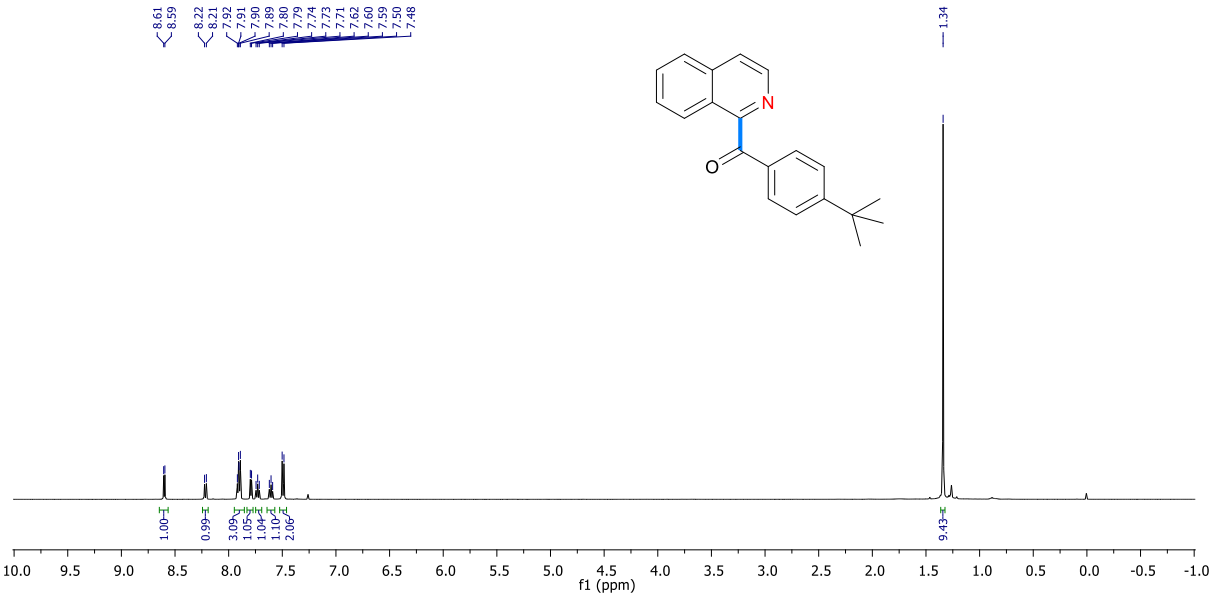
^{13}C{^{1}H} NMR (126 MHz, DMSO) of compound **3k**



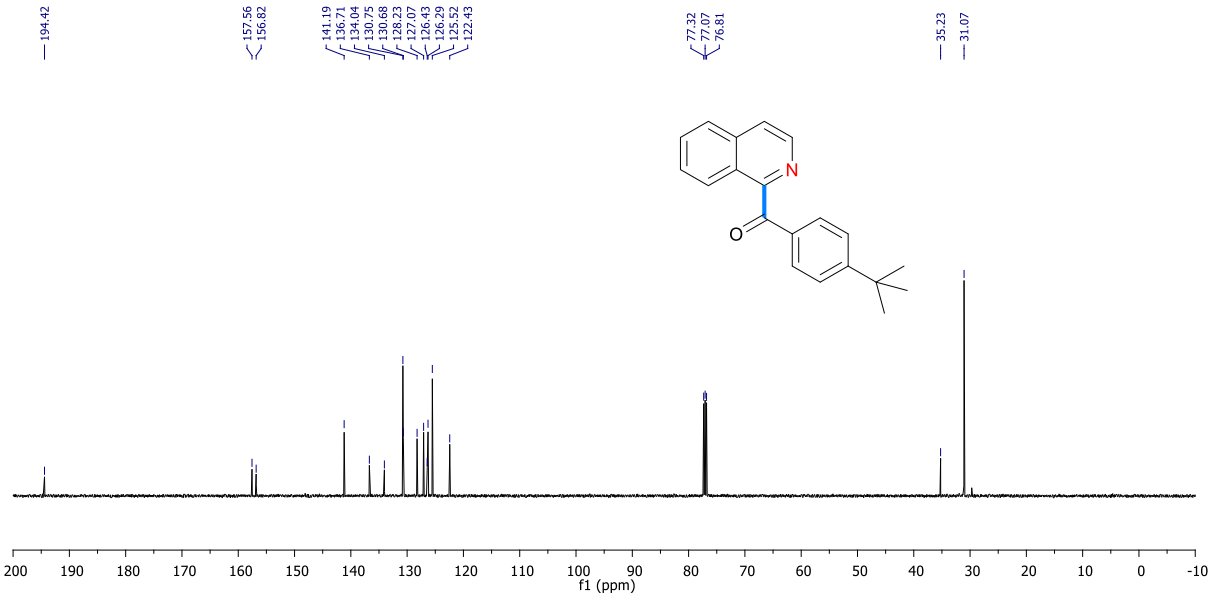
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3l**



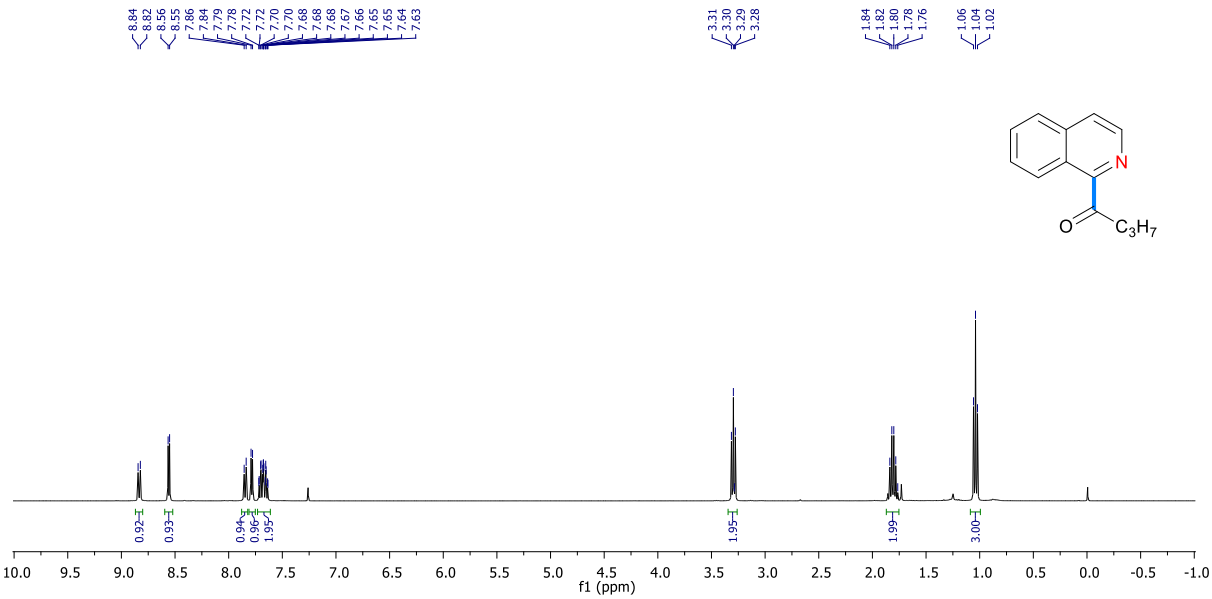
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3l**



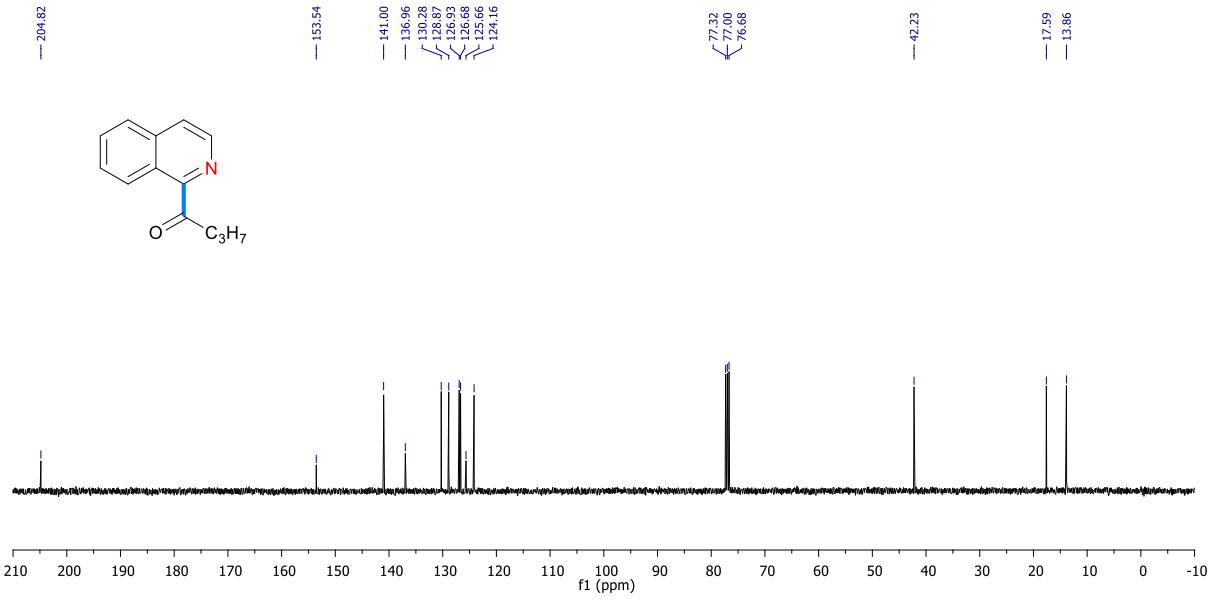
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3m**



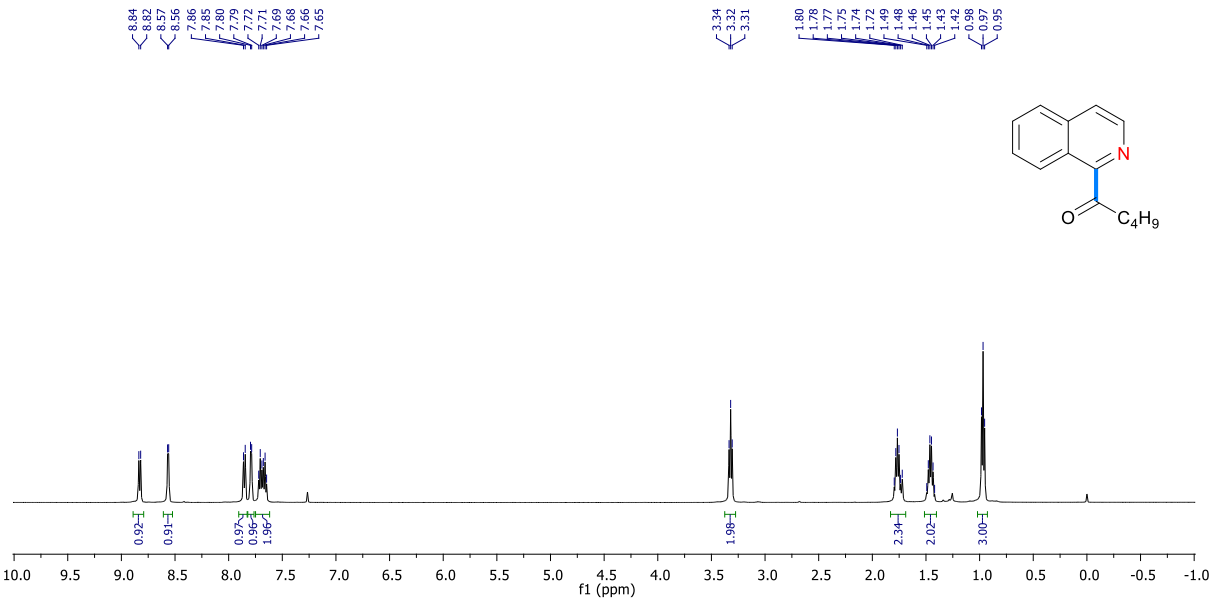
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3m**



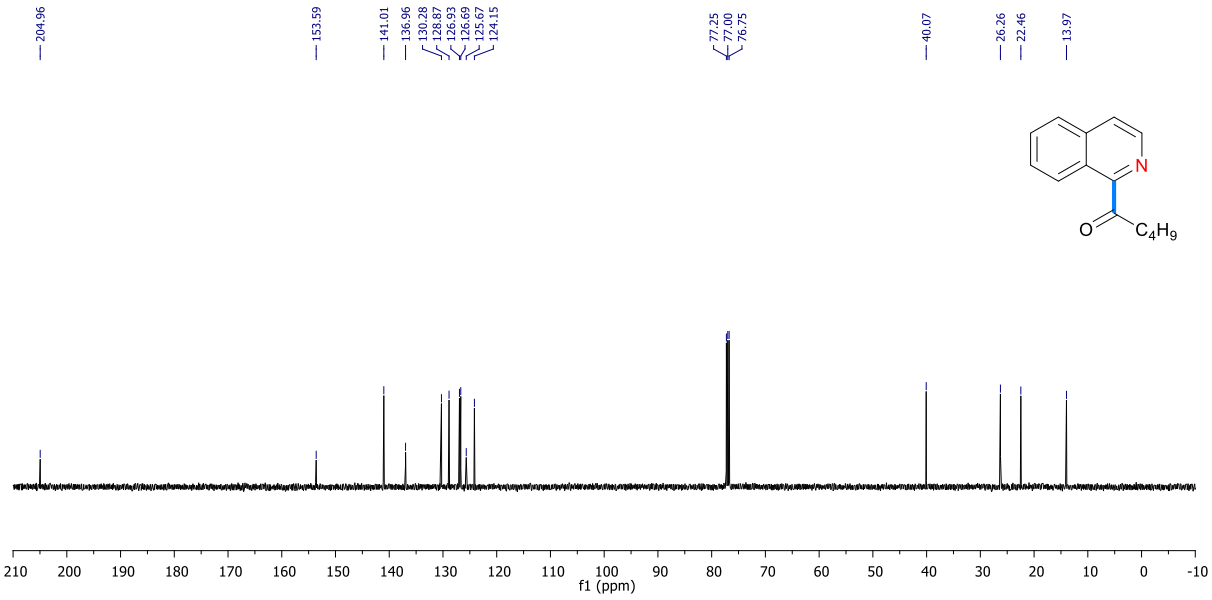
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o**



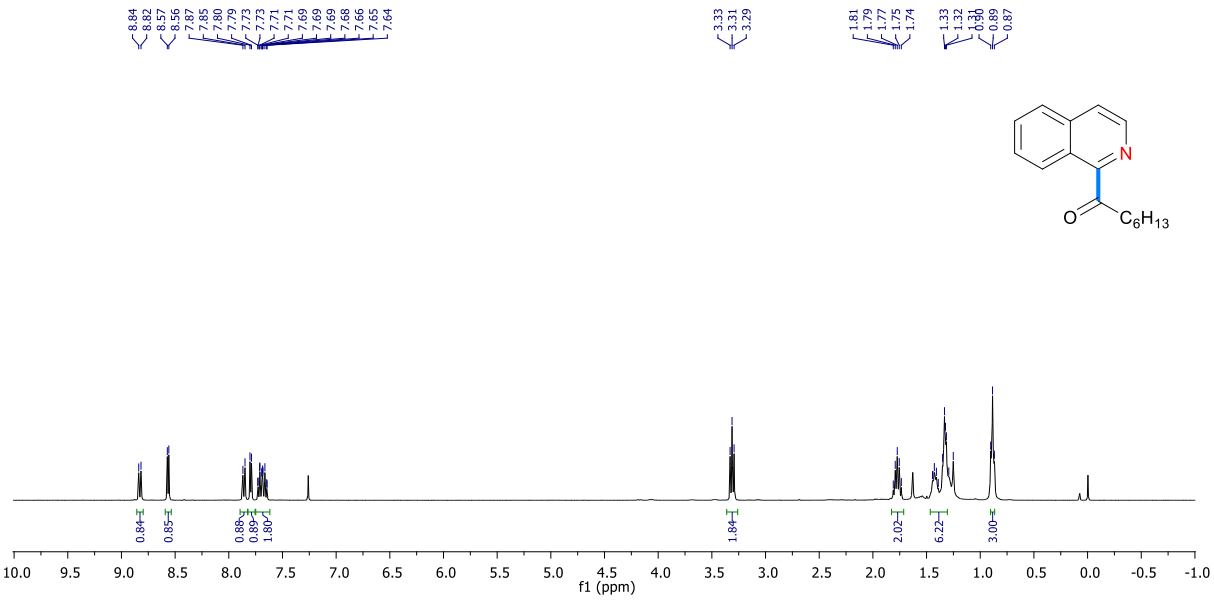
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3o**



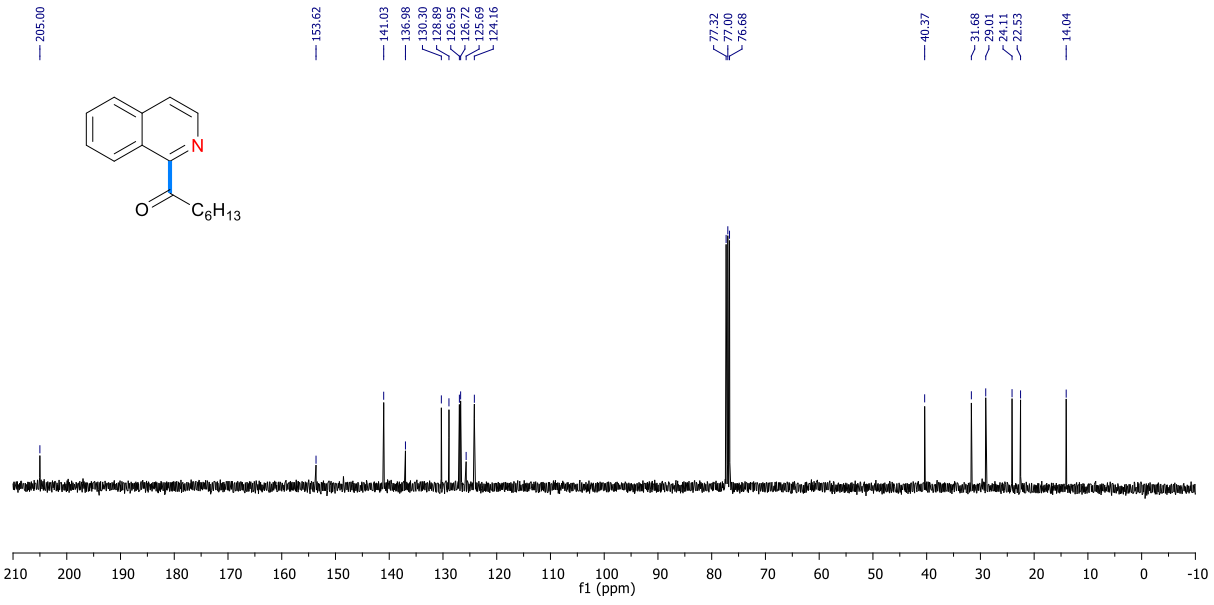
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3p**



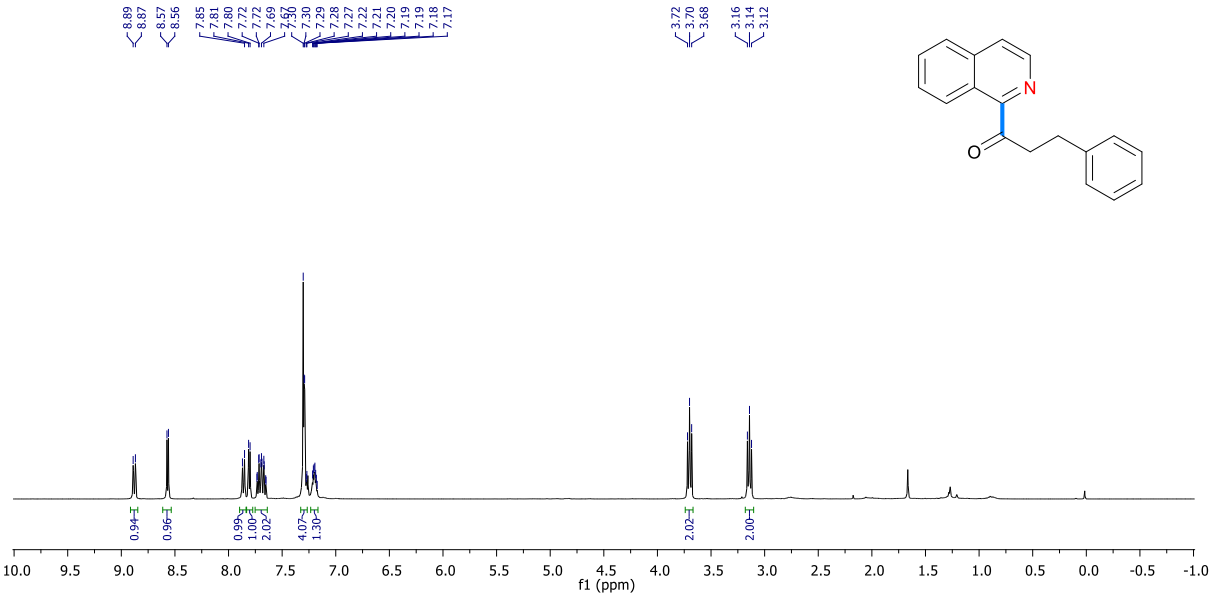
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3p**



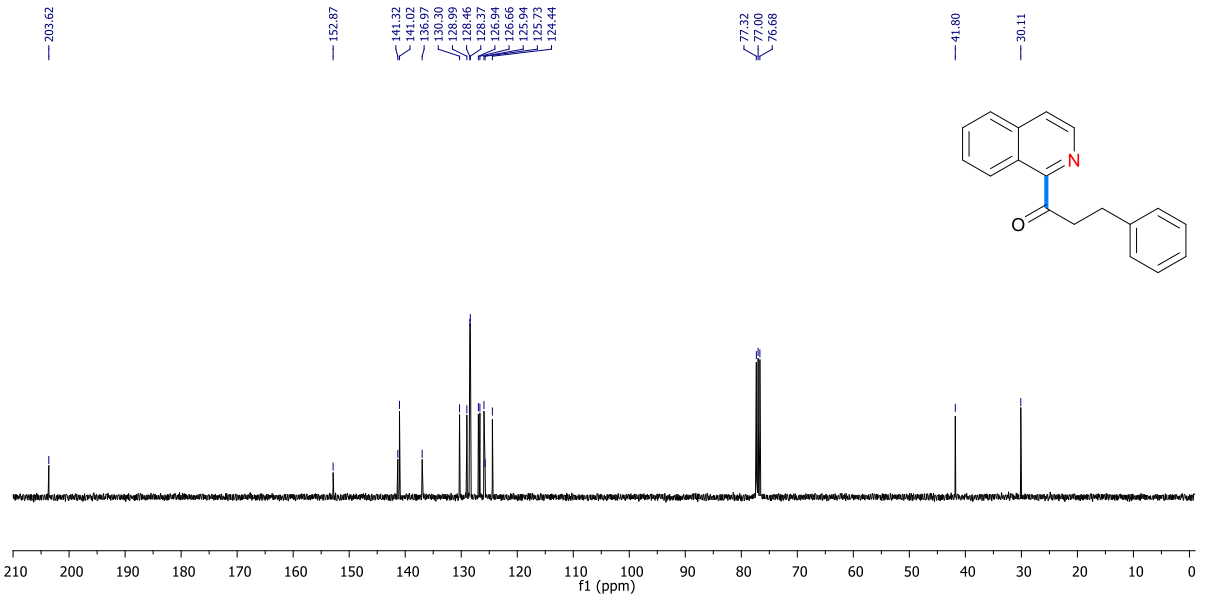
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q**



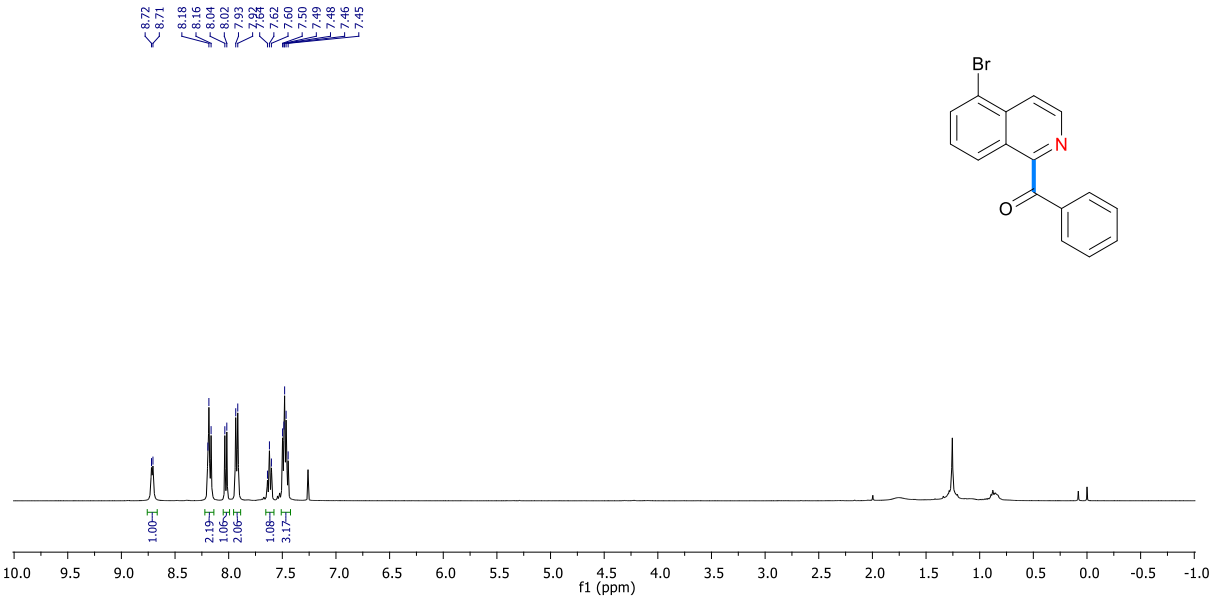
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3q**



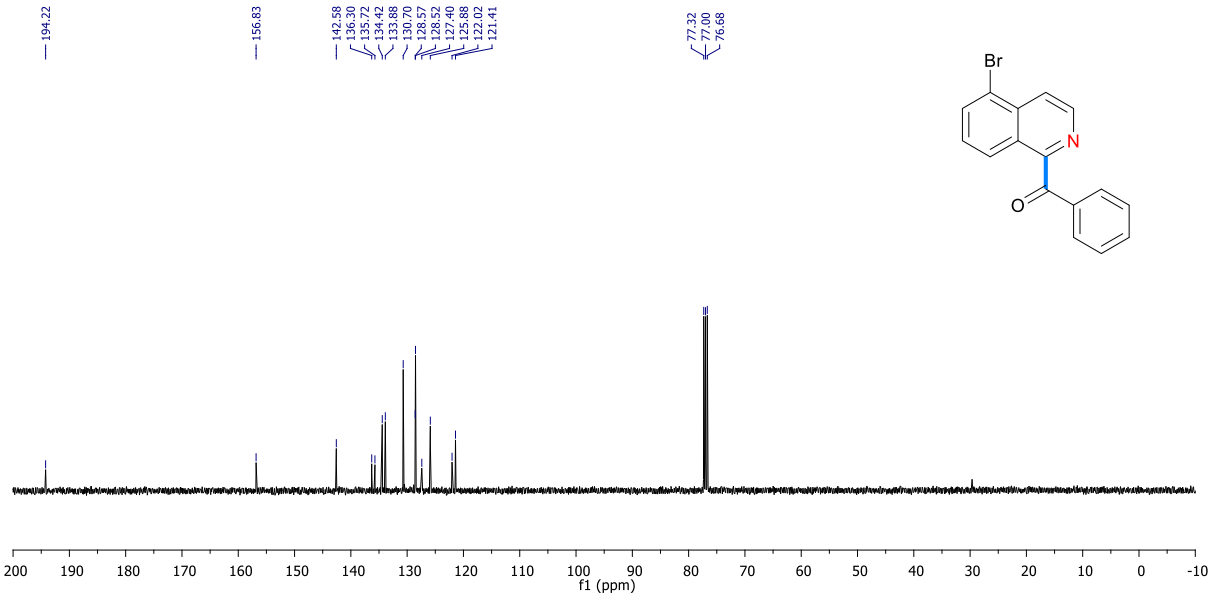
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r**



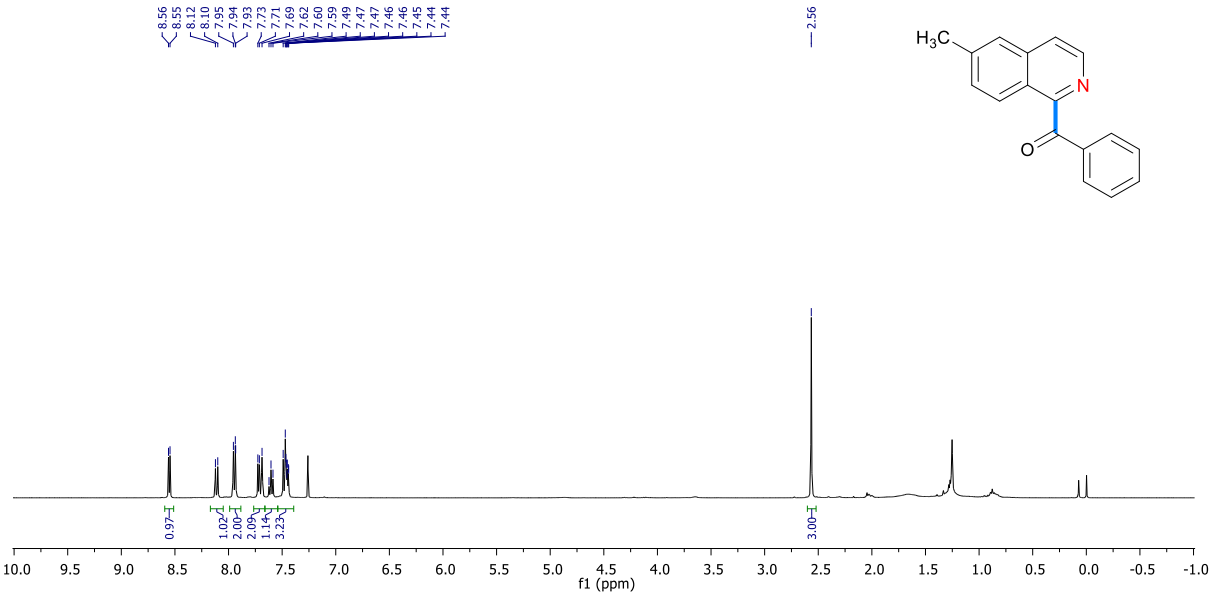
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3r**



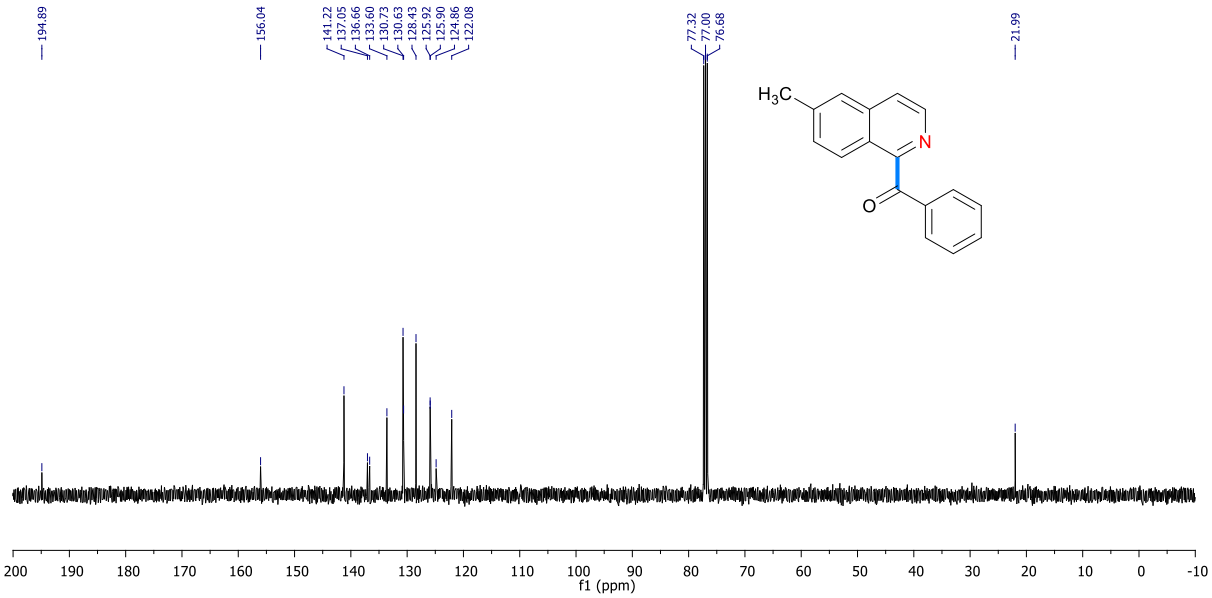
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa**



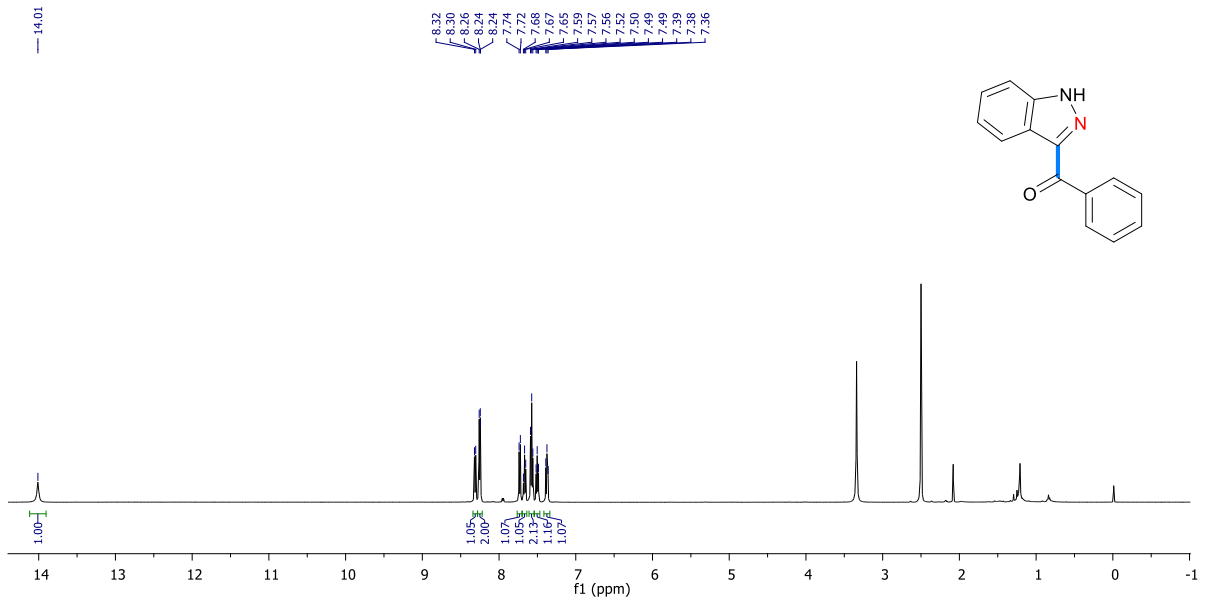
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3aa**



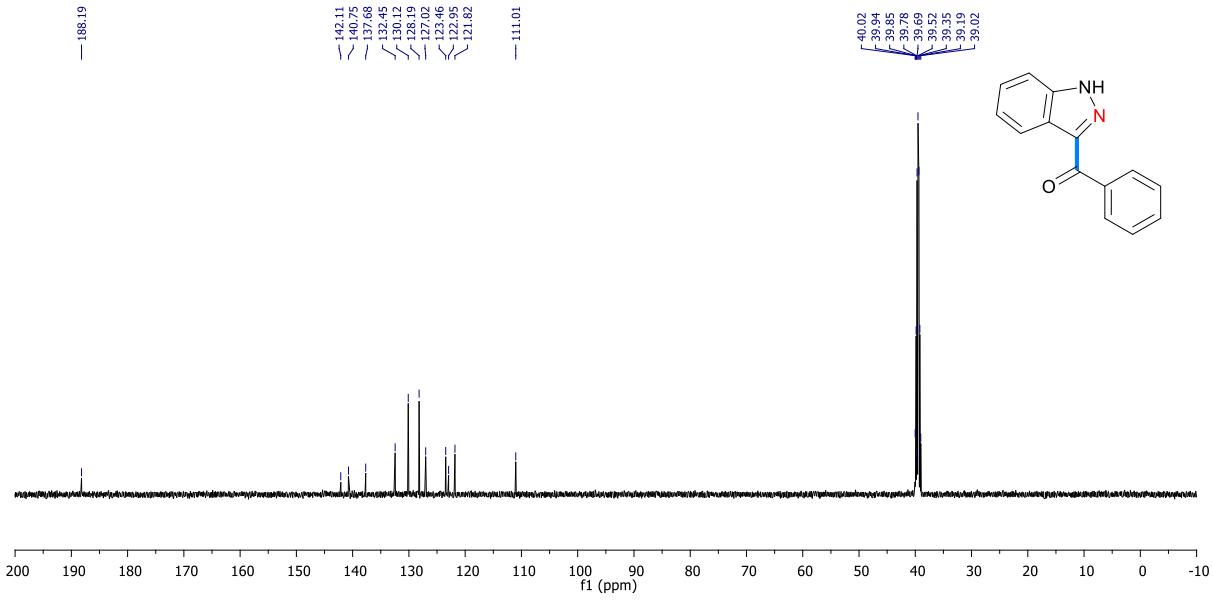
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ab**



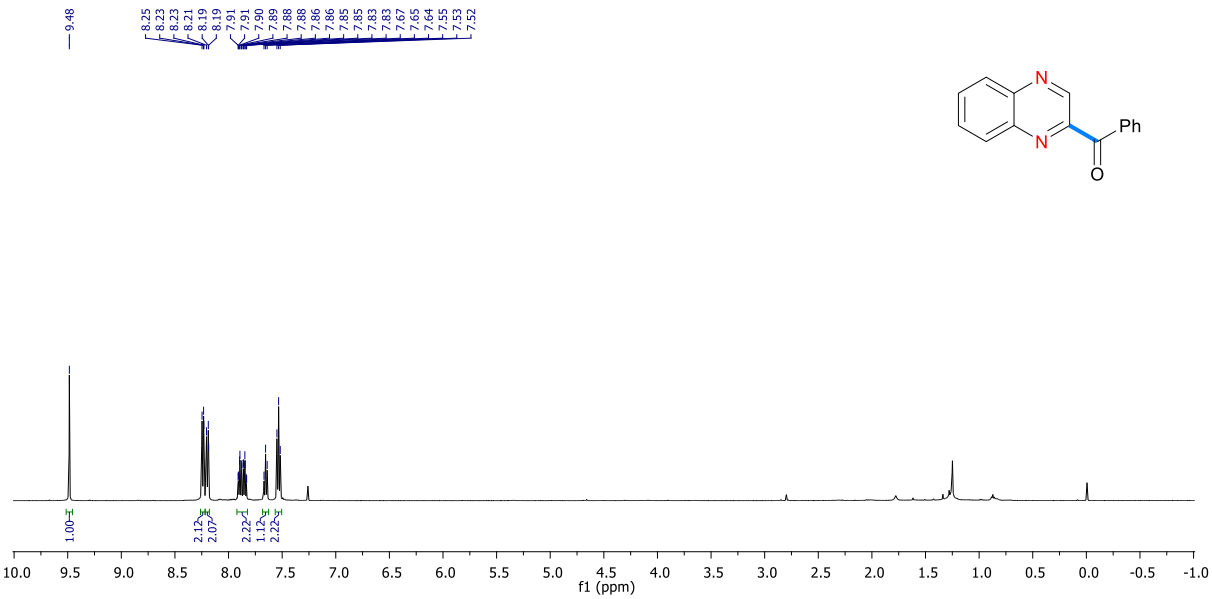
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of compound **3ab**



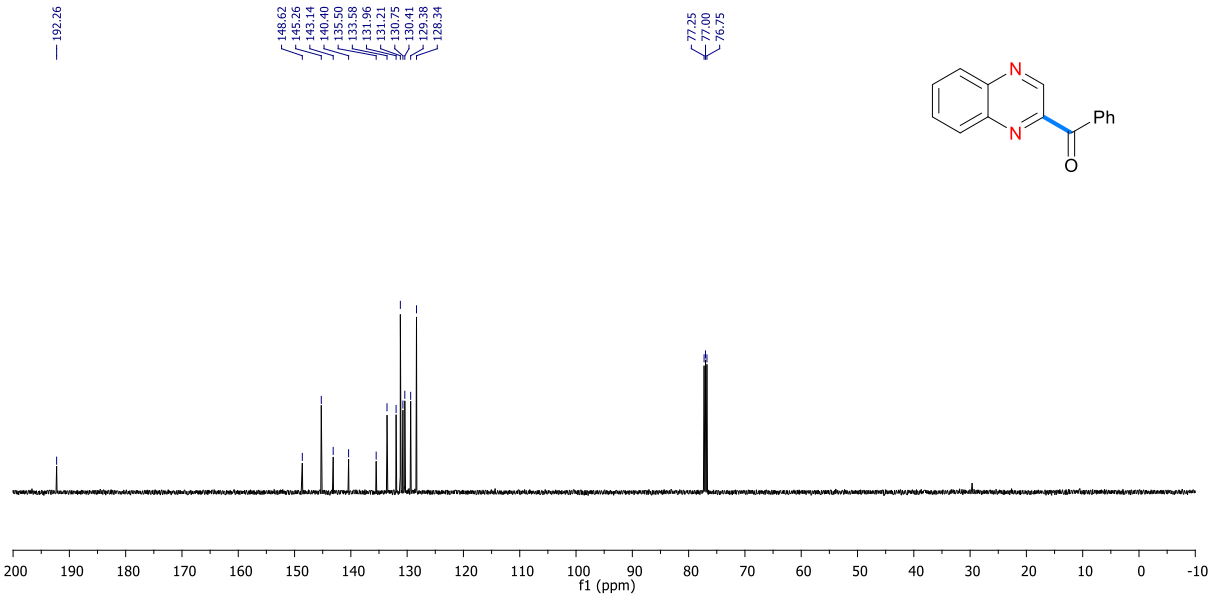
^{1}H NMR (500 MHz, DMSO) of compound **3ac**



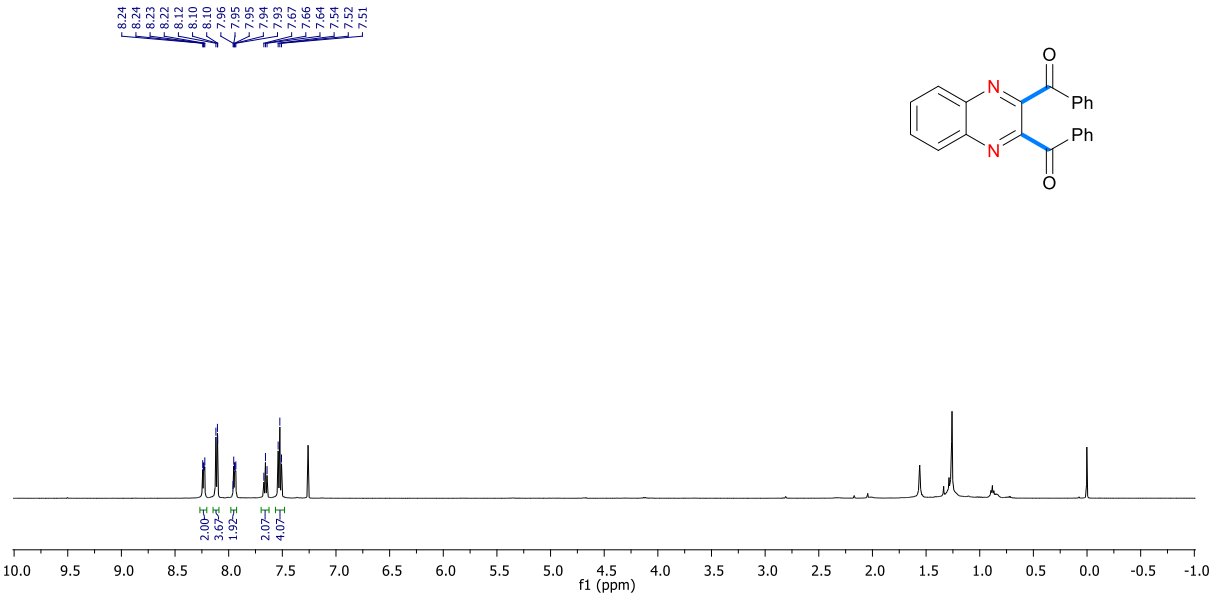
^{13}C{^{1}H} NMR (126 MHz, DMSO) of compound **3ac**



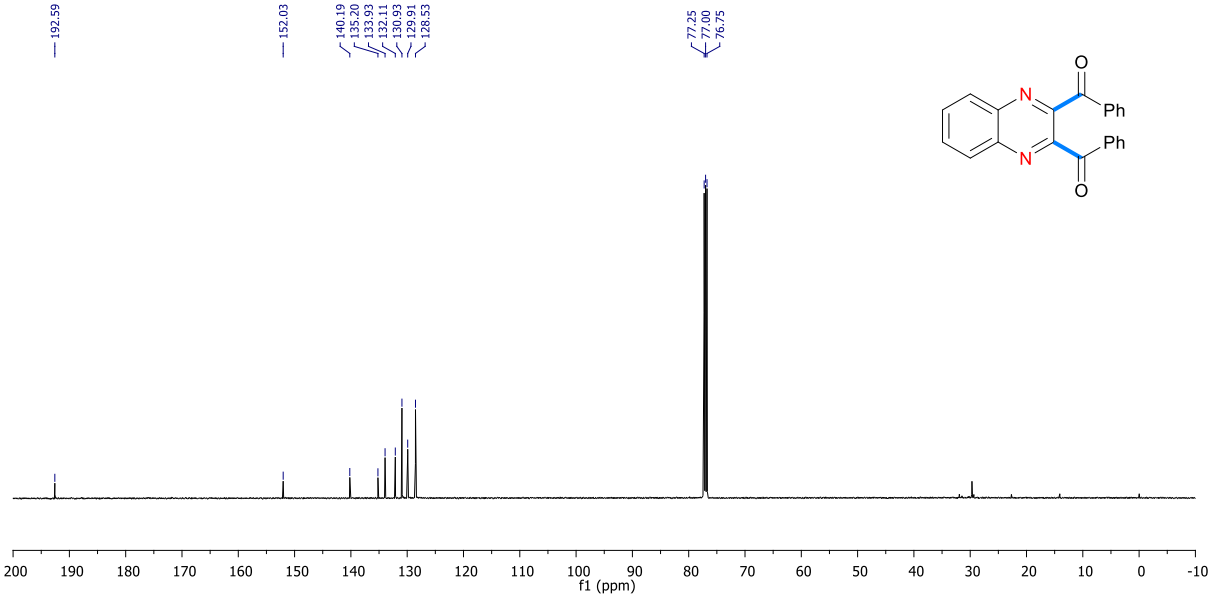
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ad**



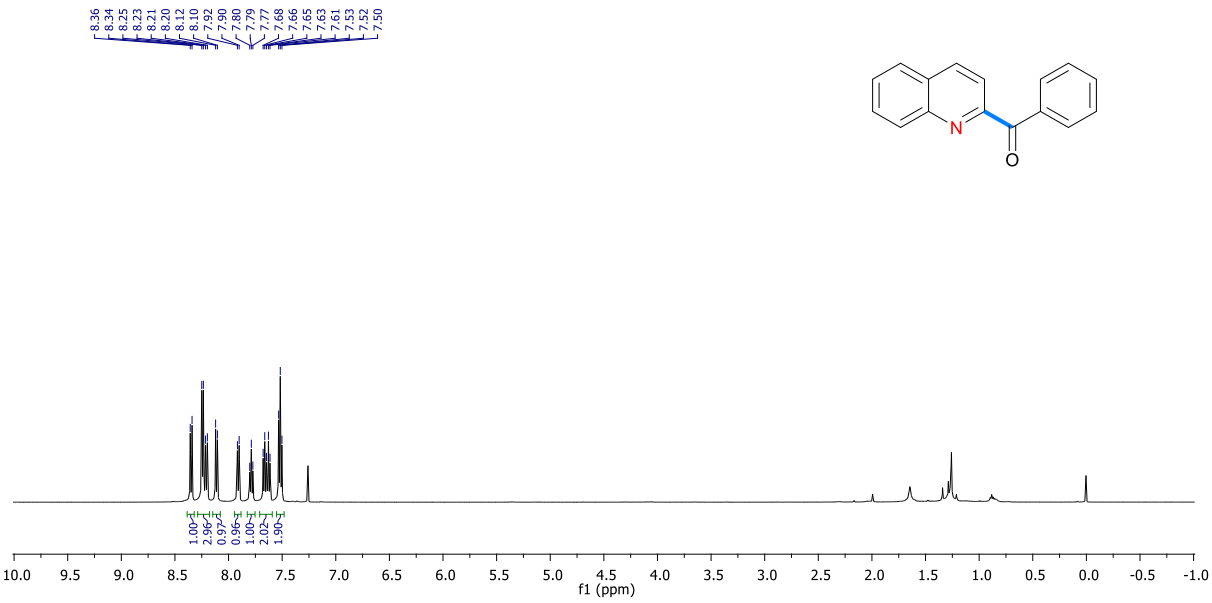
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3ad**



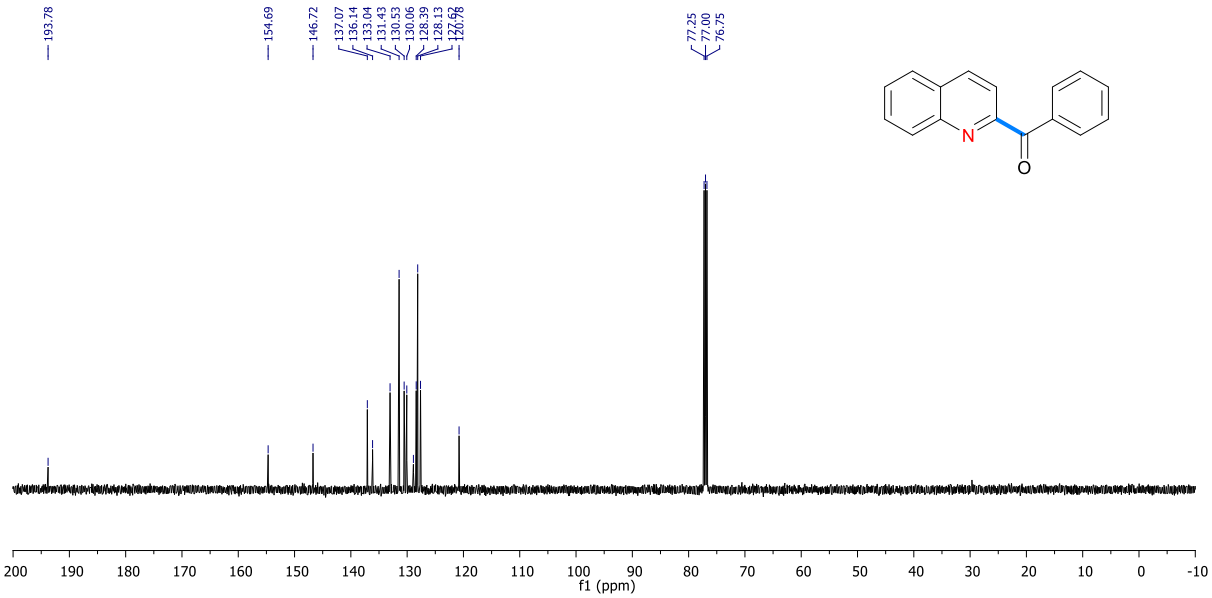
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ae**



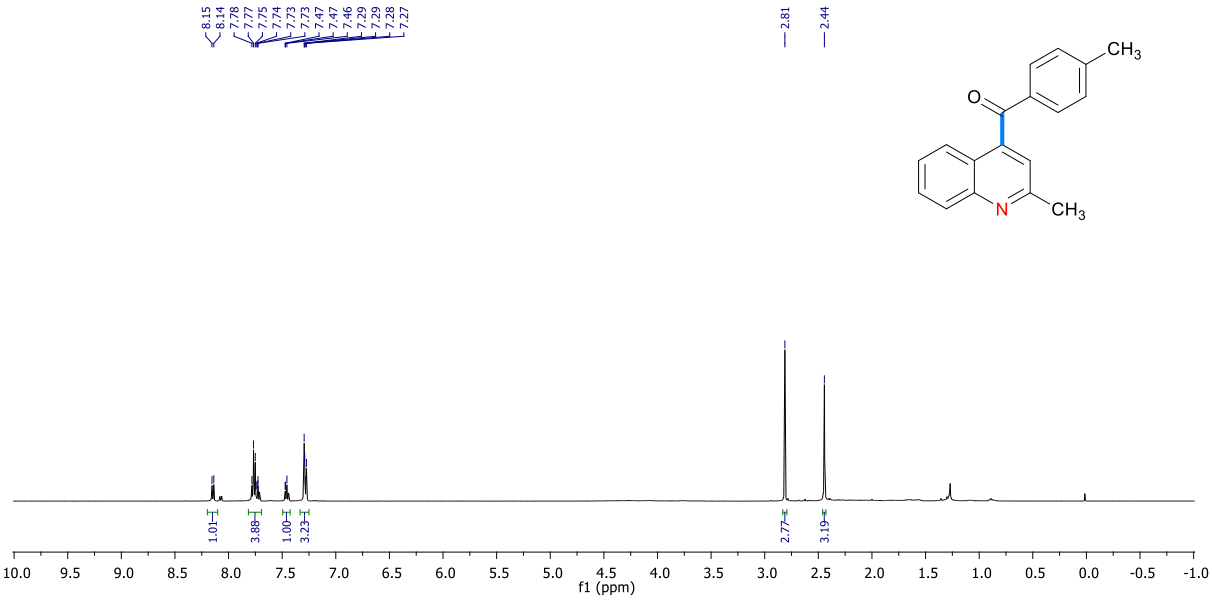
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3ae**



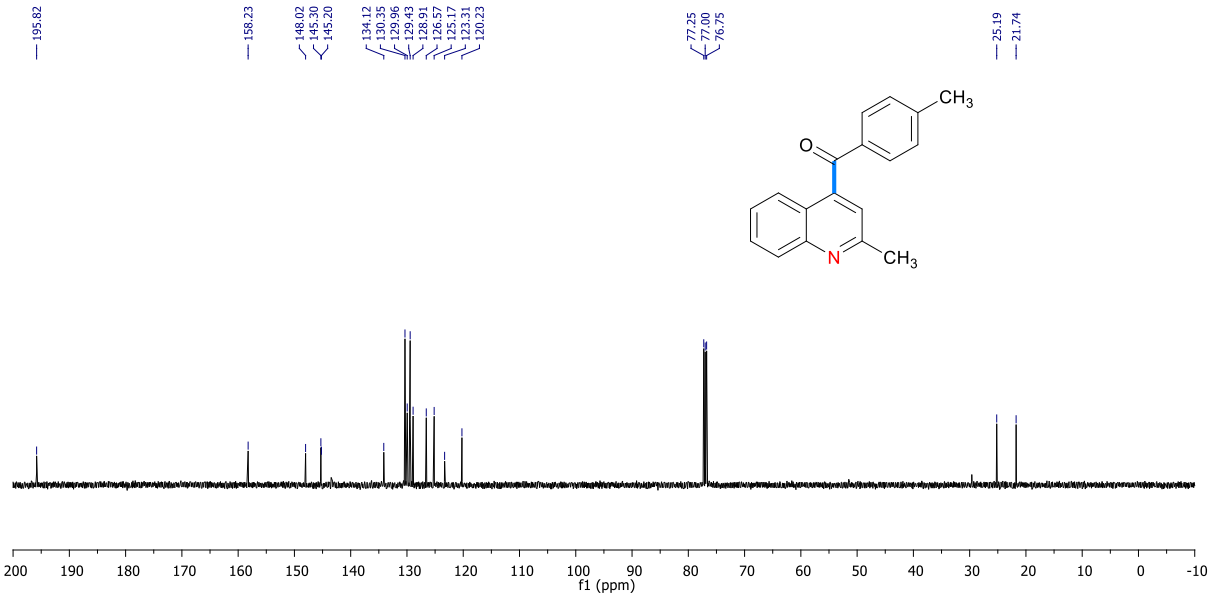
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3af**



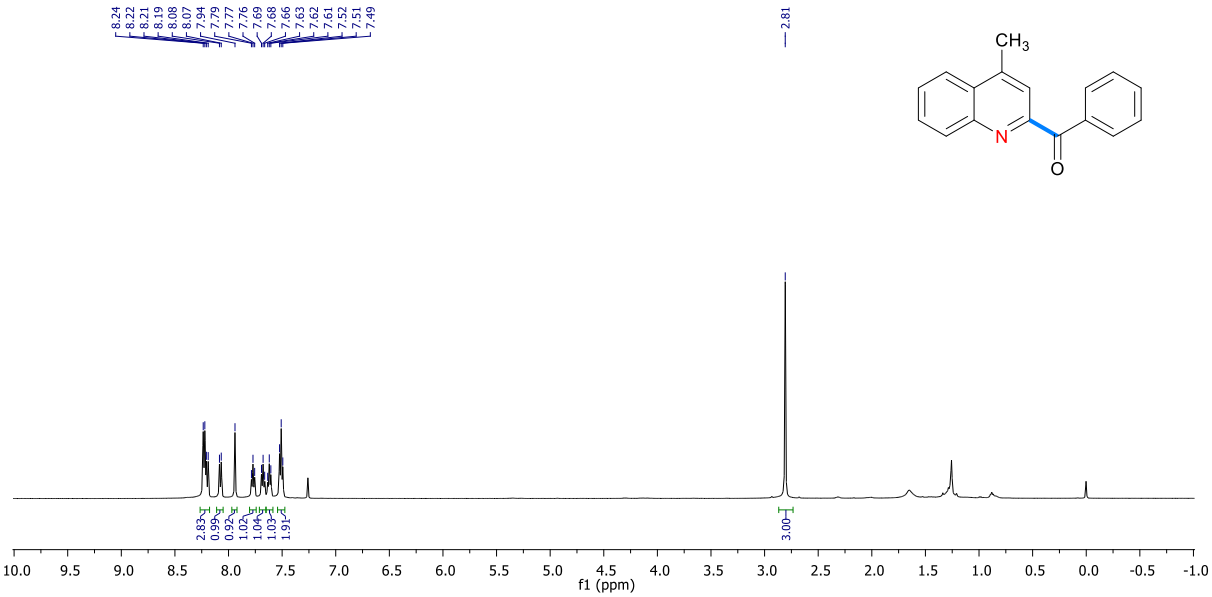
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3af**



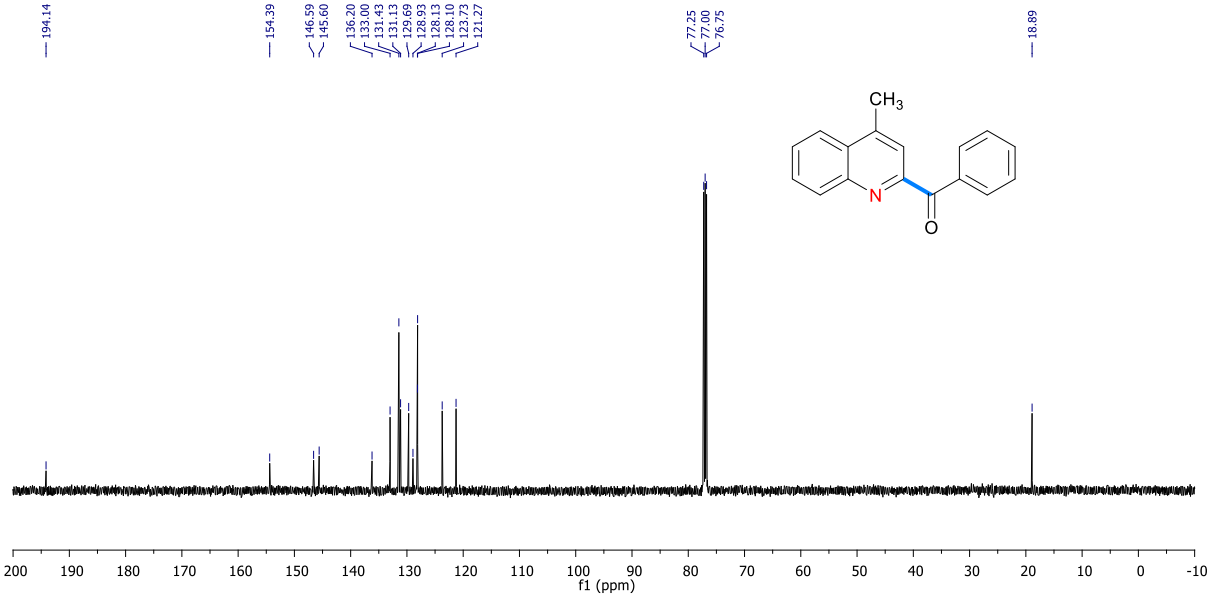
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ag**



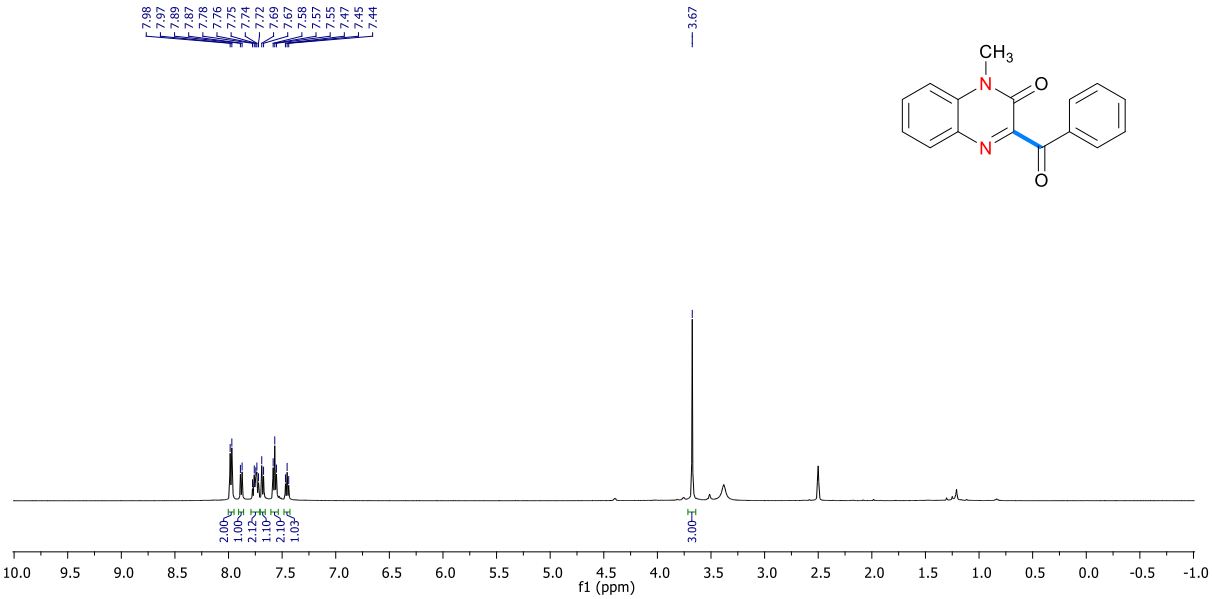
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3ag**



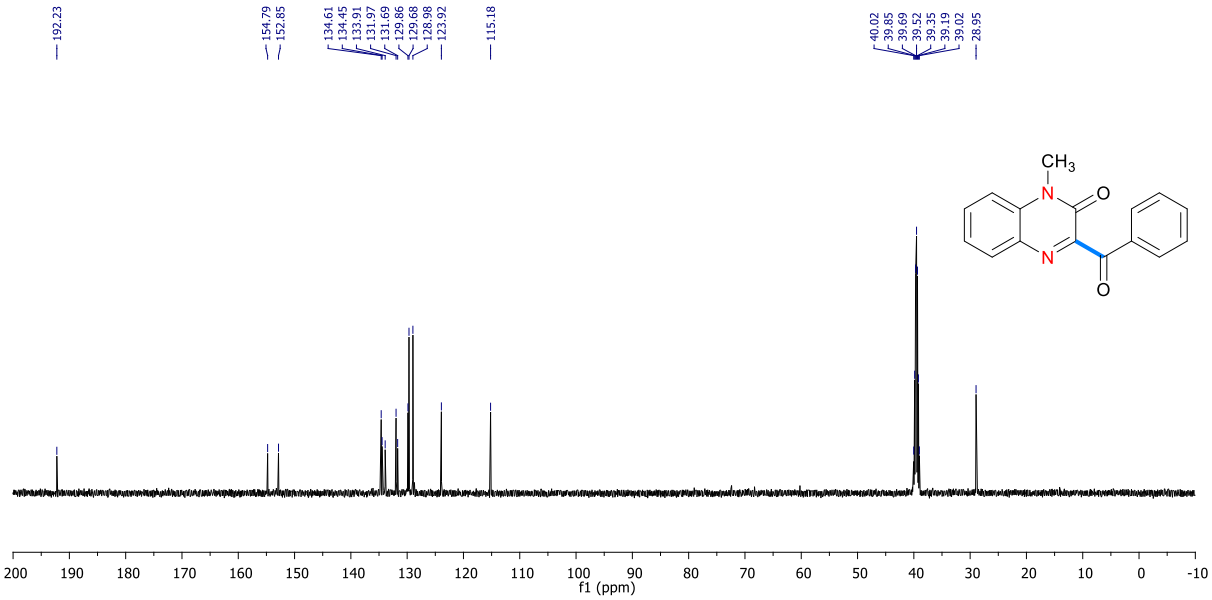
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ah**



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of compound **3ah**



^{1}H NMR (500 MHz, DMSO) of compound **3ai**



^{13}C{^{1}H} NMR (126 MHz, DMSO) of compound **3ai**