Synthesis of rigidified flavin–guanidinium ion conjugates and investigation of their photocatalytic properties

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Supporting Information

Detailed experimental setups for the photocatalytic experiments

Oxidative photocleavage of dibenzyl phosphate

The photocleavage of dibenzyl phosphate was tested in small glass vials with deuterated solvents (1 mL, MeCN-d_3 or D_2O), containing the phosphate starting material (10×10^{-3} M) and flavin catalyst (2×10^{-3} M, 20 mol%). The mixture was stirred and irradiated by a LED (440 nm, 5 W) at 40 °C for 2 h (D_2O) or 4 h (MeCN-d_3), respectively. The products were identified by ^{1}H NMR and mass spectrometry and the conversion was determined by integration of the aromatic protons in the ^{1}H NMR.

Photoreduction of 4-nitrophenyl phosphate

The photocleavage of dibenzyl phosphate was tested in small glass vials in MeCN or water (5 mL), containing the 4-nitrophenyl phosphate starting material (10×10^{-3} M), triethanol amine as sacrificial electron donor (100×10^{-3} M, 10 equivalents), and flavin catalyst (1×10^{-3} M, 10 mol%). The solution was degassed by three consecutive pump and freeze circles and afterwards, the solution was stirred and irradiated by a LED (440 nm, 5 W) and a UV-lamp (370 nm) at 40 °C for 4 h. Reaction mixtures in MeCN were evaporated and dried. The mixtures of the experiments in water were lyophilized. 4-aminophenyl phosphate and 4-amino phenol as by-product were identified by ^{1}H NMR and mass spectrometry, respectively. The conversion was determined by integration of the aromatic protons in the ^{1}H NMR.

Photo Diels–Alder-reaction of anthracene with N-methyl-maleinimide

Photoinduced Diels–Alder-reactions were carried out in small glass vials in dry toluene (1.2 mL), containing anthracene (33×10^{-3} M), methyl maleinimide (83×10^{-3} M, 2.5 equivalents), and flavin catalyst (0.67×10^{-3} M, 2 mol%). The mixture was stirred and irradiated by a LED (440 nm, 5 W) at 40 °C for 8 h. Afterwards, the solvent was evaporated and the mixture was dried. The products were identified by ^{1}H NMR and mass spectrometry and the conversion was determined by integration of the aromatic protons in the ^{1}H NMR.

Calculated gas phase conformations

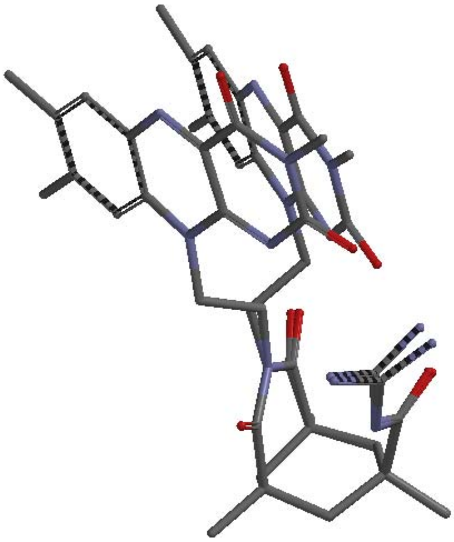


Figure S.1: Calculated conformations of **1** in the gas phase (AM1, Spartan program package).

Figure S.1 shows the two lowest energy conformations of compound **1** in the gas phase (semi-empirical AM1, Spartan program package, difference: 13.5 kJ/mol). It is possible to transform the structures into each other by rotation of the C–C single bonds of the ethane linker that are expected to rotate freely in solution.

UV/Vis and fluorescence spectra of compounds 1, 2 and 3

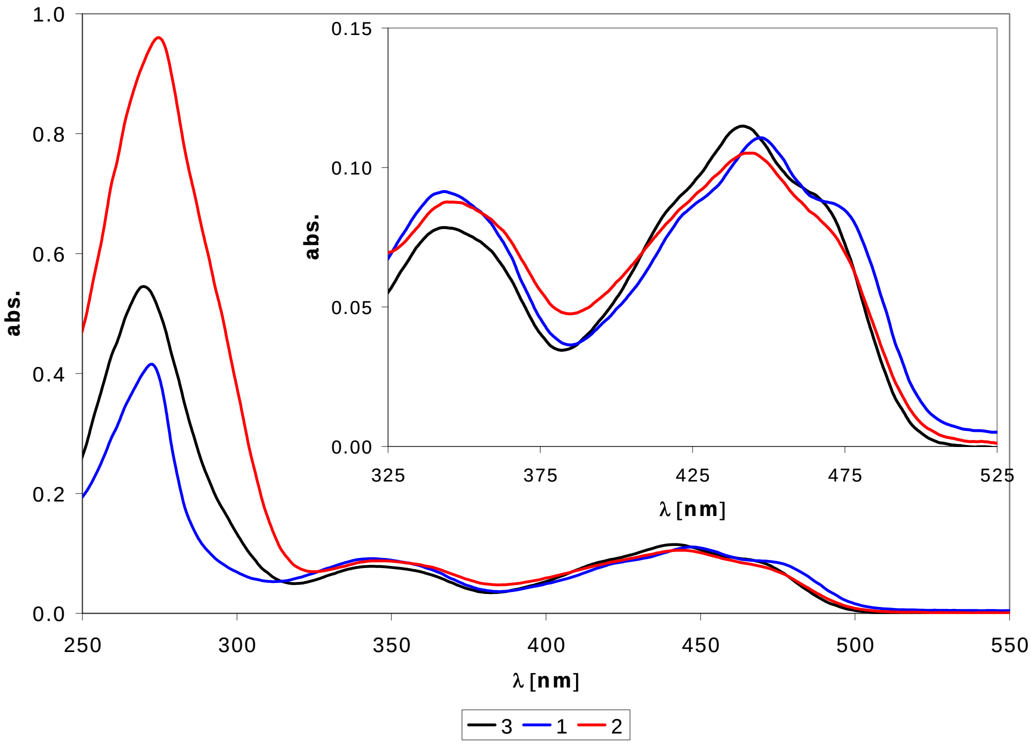


Figure S.2: Absorption spectra of **1**, **2** and **3** (MeCN + 1% DMSO, 1 × 10^{-5} M)

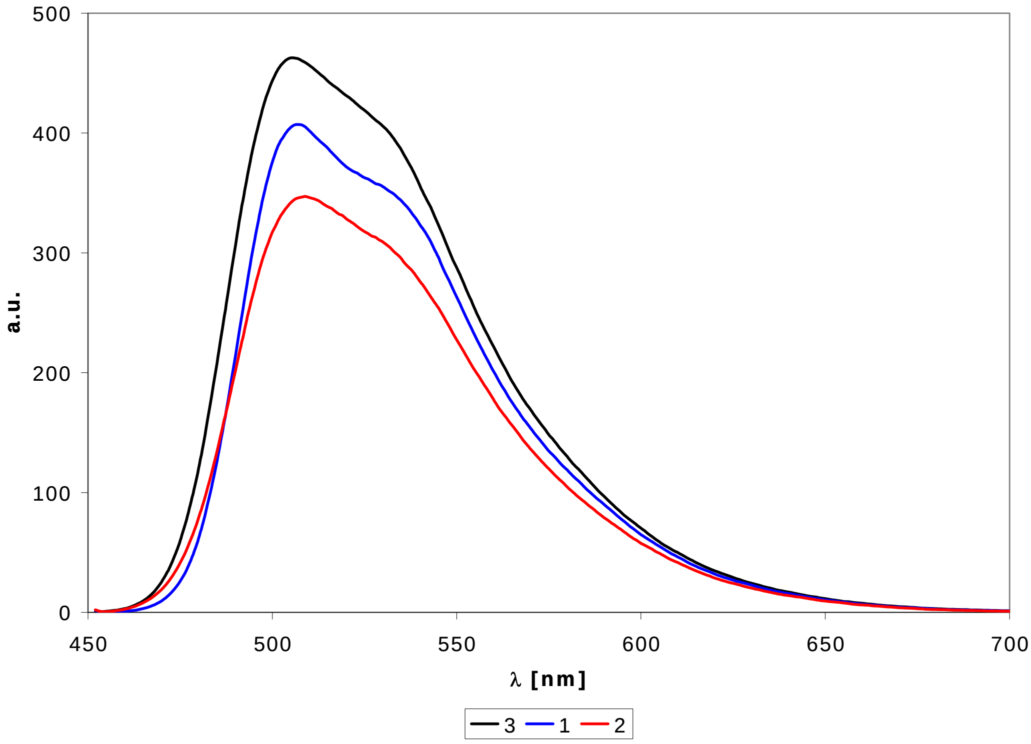
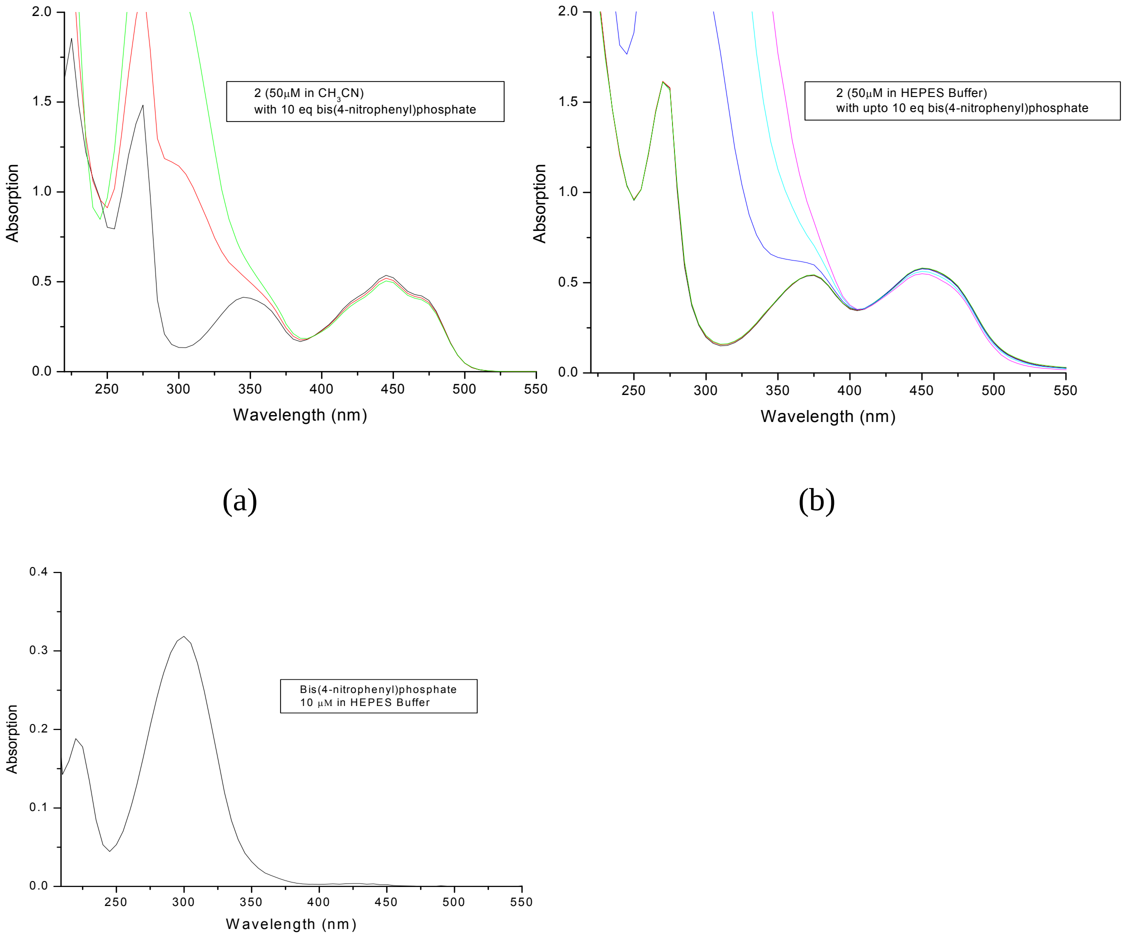


Figure S.3: Fluorescence spectra of **1**, **2** and **3** [MeCN + 1% DMSO, 1 × 10^{-5} M, excitation at 445 nm (**1+2**) and 440 nm (**3**)]

UV- and emission titration of compound 2 and phosphate esters

UV-visible and emission titrations were recorded for compound **2** with sodium phenyl phosphate (dibasic dihydrate) and bis-(4-nitrophenyl) phosphate. UV–visible absorption spectroscopy was performed using a Cary 50 Bio spectrophotometer and fluorescence spectroscopy was performed using a Varian Cary Eclipse fluorescence spectrophotometer. The titration experiments with the phosphate anion species were carried out using a solution (2.5 mL) of compound **2** (50 μM in HEPES Buffer; pH 7.4 and 50 μM in CH_3CN) in a quartz cell at 25 °C. The absorption and emission spectral changes were monitored upon addition of a freshly prepared solution of the analytes (in HEPES Buffer and in CH_3CN) with a microsyringe.



(a)

(b)

(c)

Figure S.4: UV-Visible spectra of compound **2** (a) with bis (4-nitrophenyl) phosphate in CH_3CN, (b) with bis (4-nitrophenyl) phosphate in HEPES Buffer (c) UV-Visible of bis (4-nitrophenyl) phosphate in HEPES Buffer.

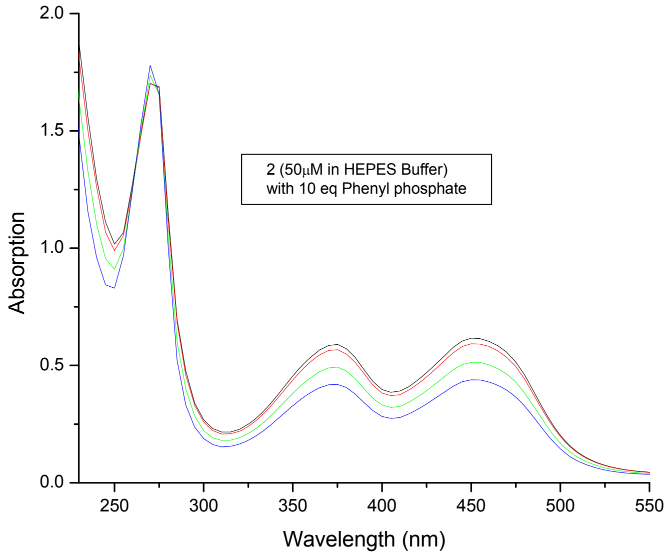


Figure S.5: UV-Visible spectra of compound **2** and sodium phenyl phosphate (dibasic dihydrate) in HEPES Buffer.

The fluorescence spectroscopic studies of compound **2** are shown below. In the presence of bis-(4-nitrophenyl) phosphate as analyte in acetonitrile the emission intensity decreases, while the change is not prominent in HEPES Buffer solution.

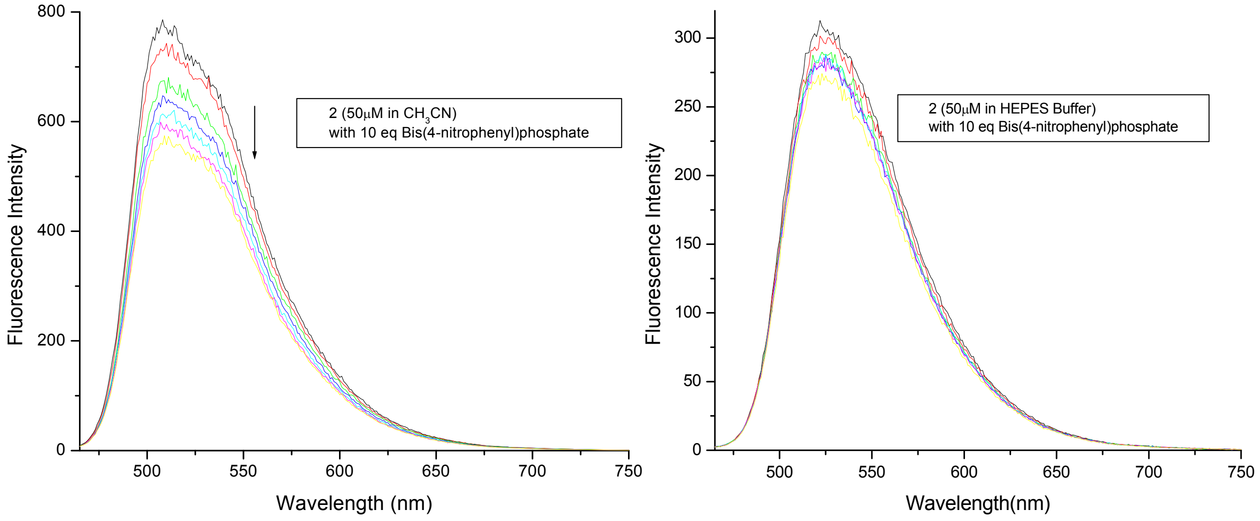


Figure S.6: Fluorescence intensity change of compound **2** with bis (4-nitrophenyl) phosphate in CH_3CN and in HEPES Buffer. λ_{ex} = 445 nm, PMT detector voltage is medium, slit width = 5.

With sodium phenyl phosphate (dibasic dihydrate) as the analyte, compound **2** did not show any significant change in its emission intensity.

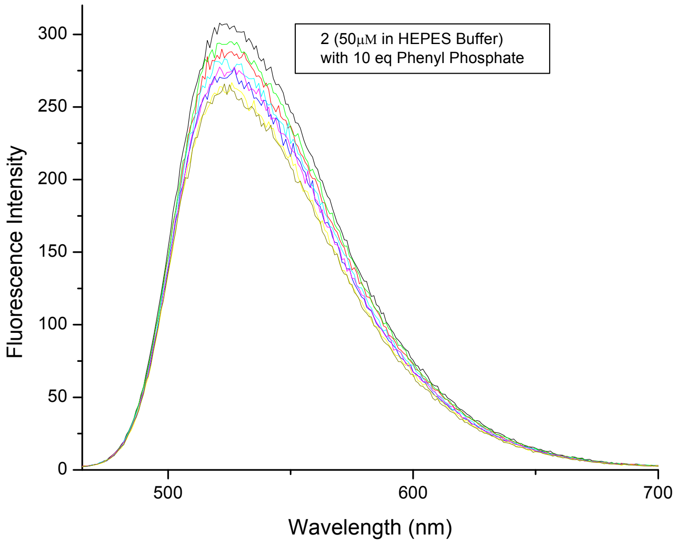
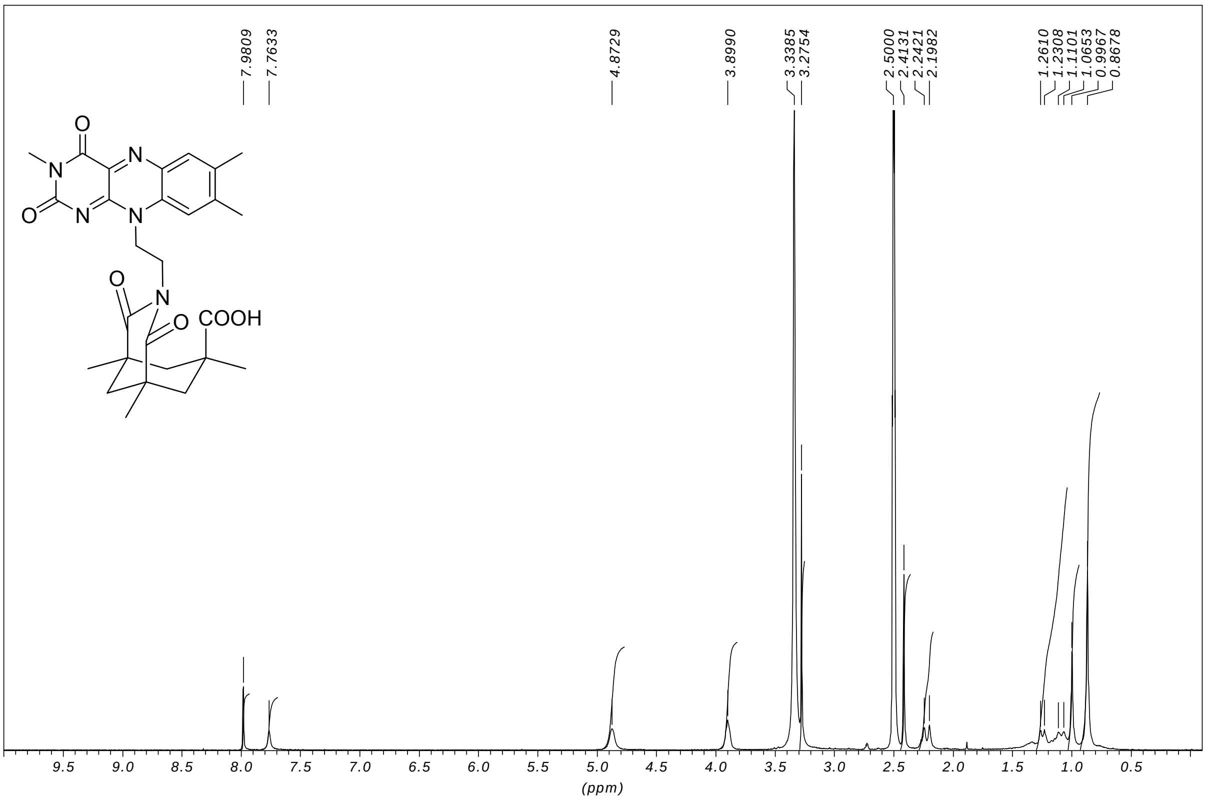
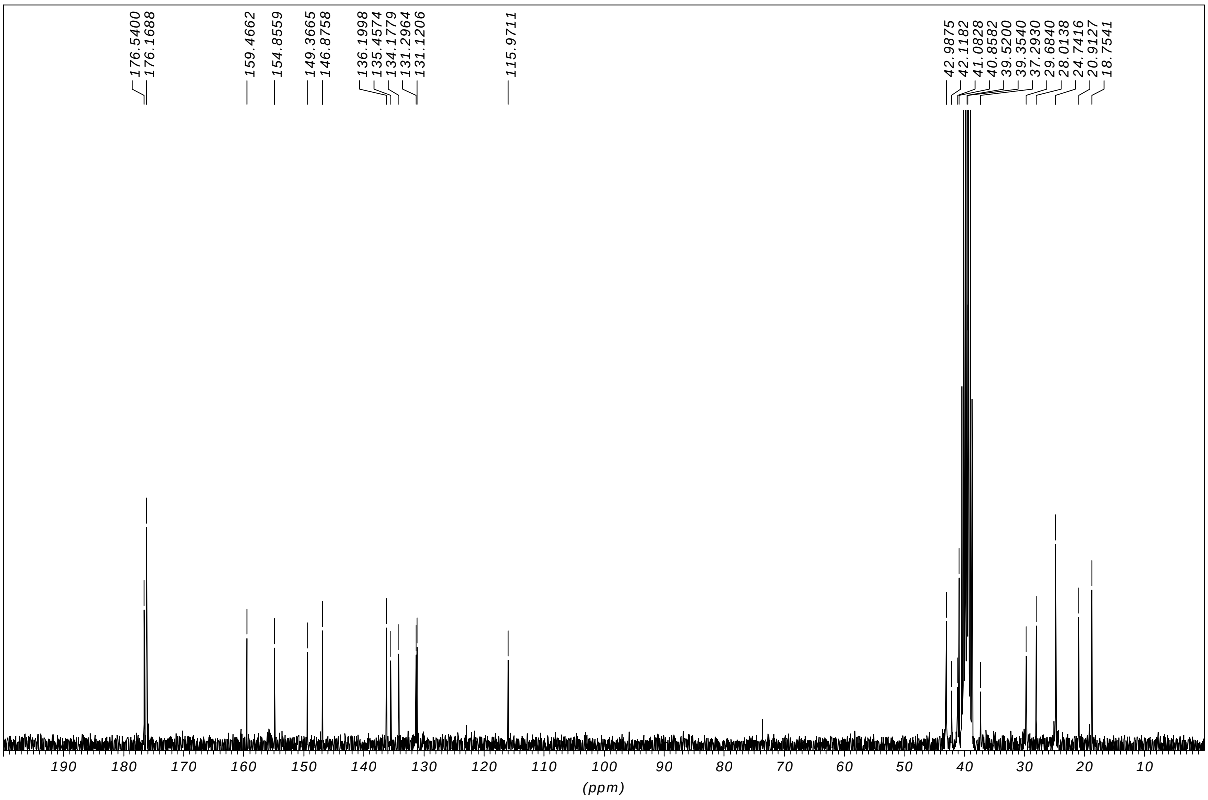


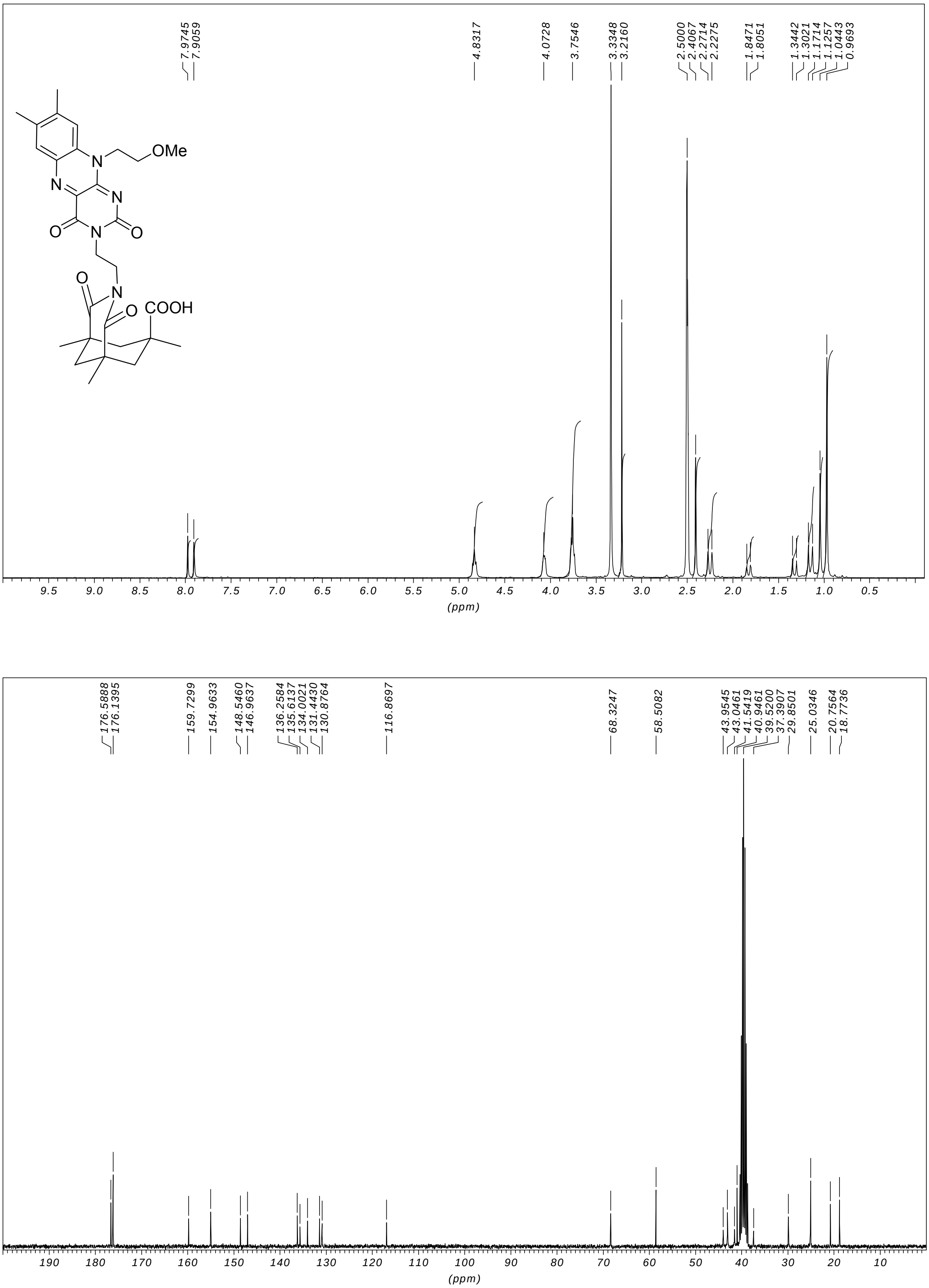
Figure S.7: Fluorescence intensity change of compound **2** with sodium phenyl phosphate (dibasic dihydrate) in HEPES Buffer. λ_{ex} = 445 nm, PMT detector voltage is medium, slit width = 5.

^{1}H NMR spectrum (300 MHz, DMSO-d_6) (top) and ^{13}C NMR (75 MHz, DMSO-d_6) of compound **6**.

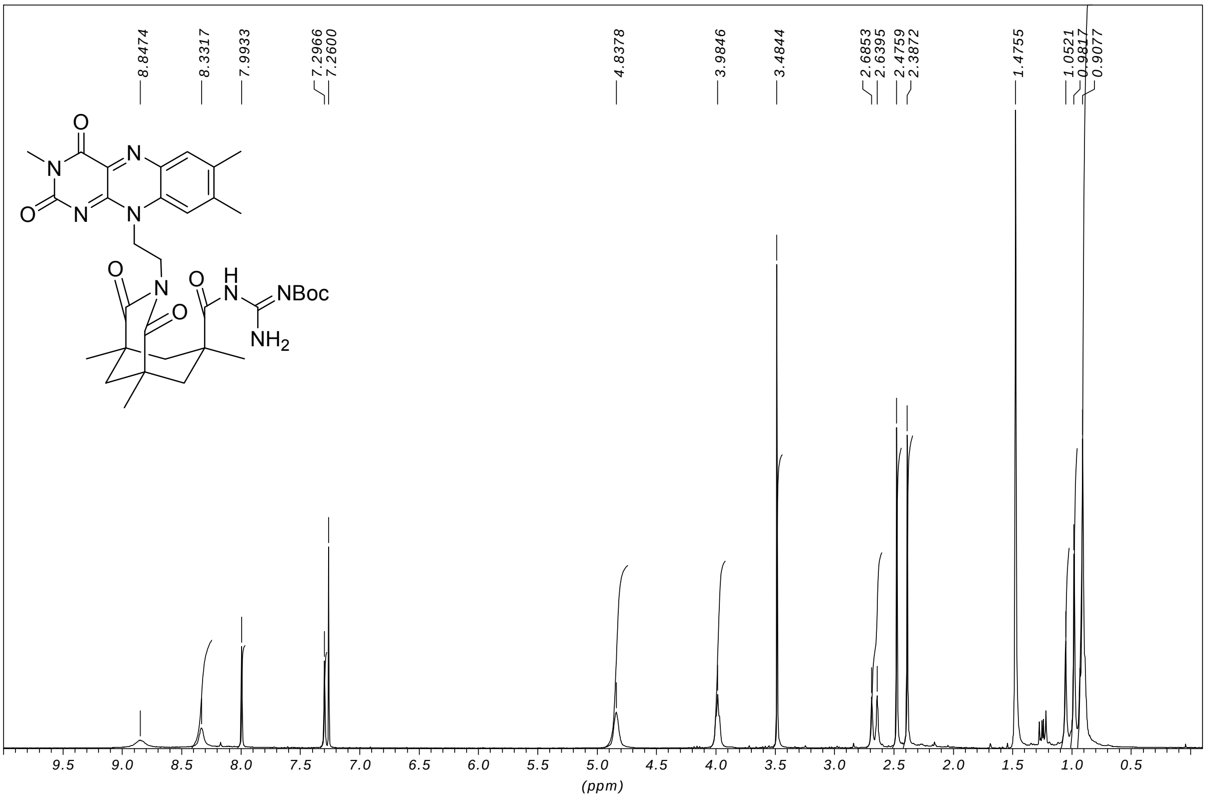


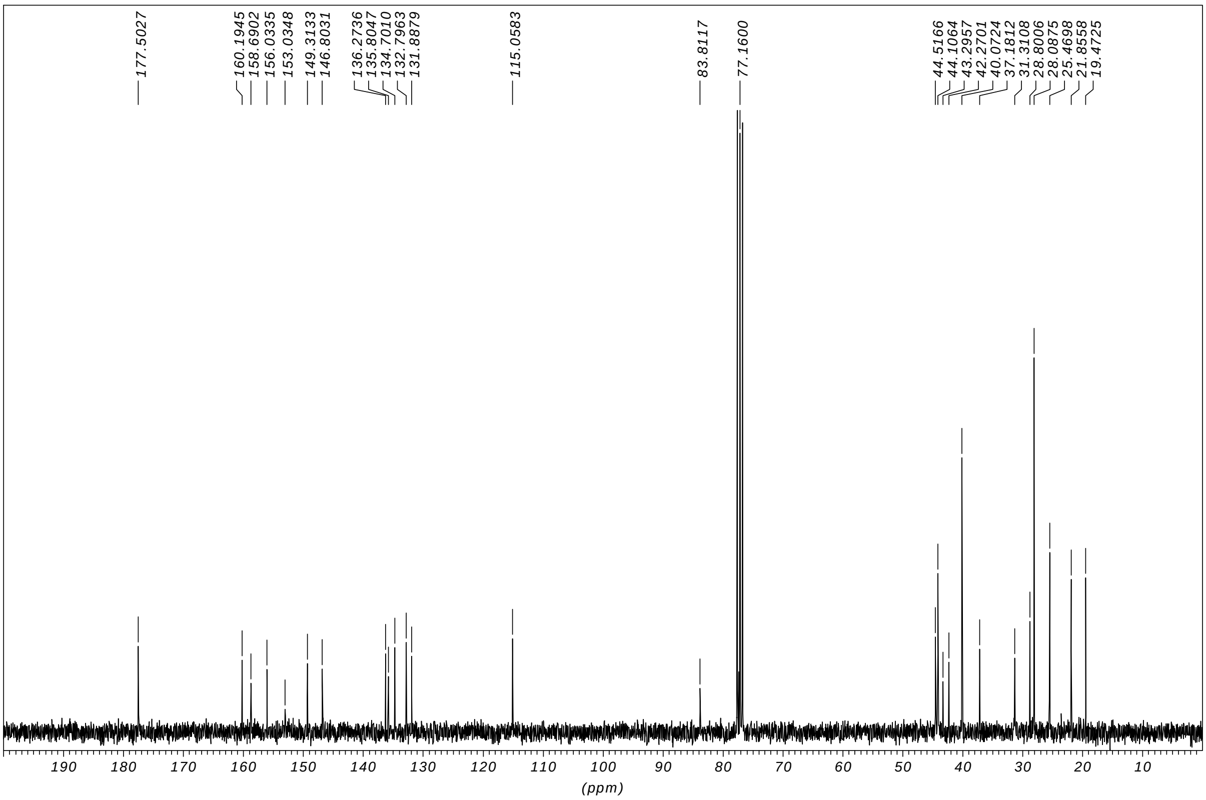


^{1}H NMR spectrum (300 MHz, DMSO-d_6) (top) and ^{13}C NMR (75 MHz, DMSO-d_6) of compound **9**.

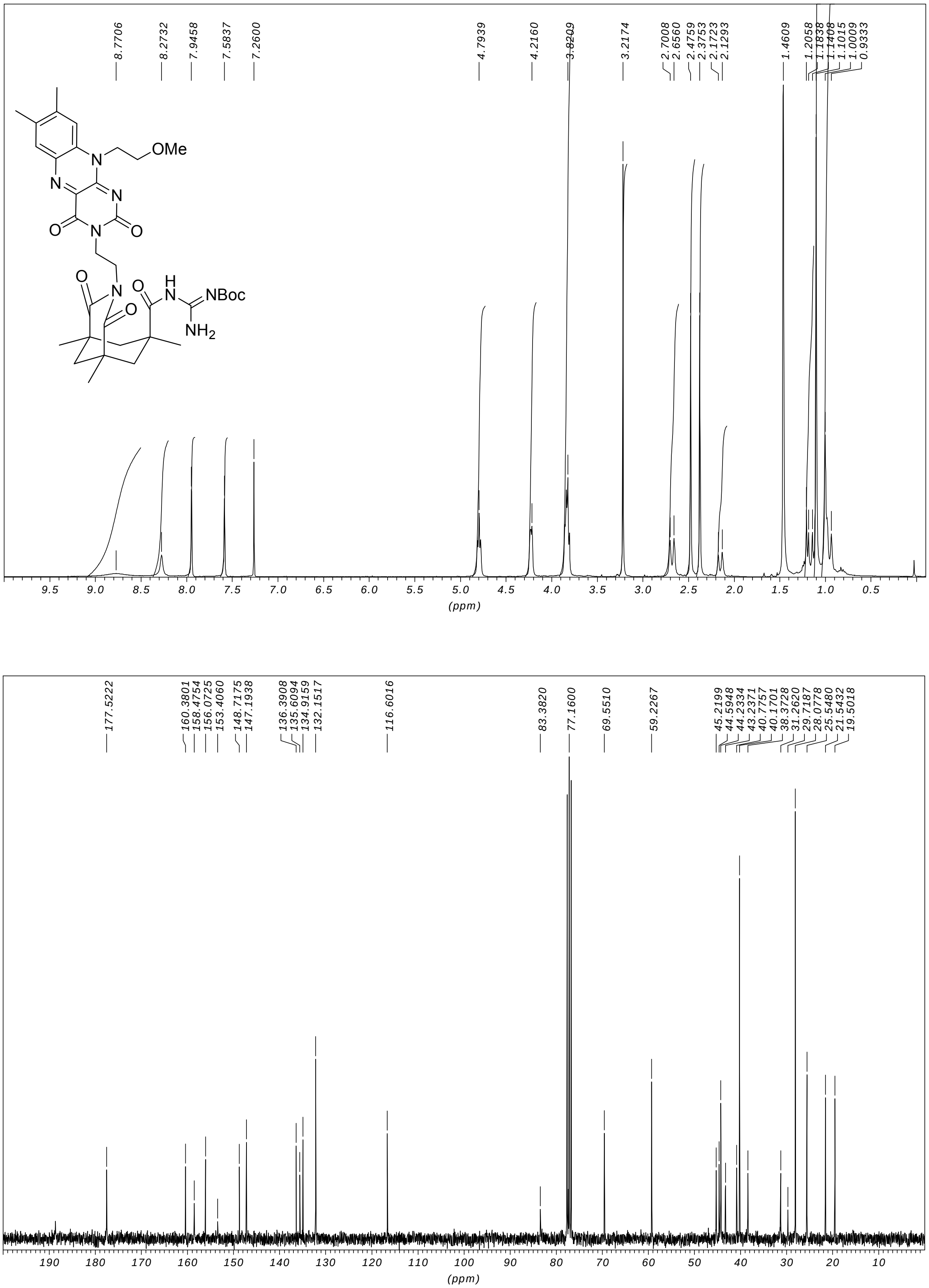


^1H NMR spectrum (300 MHz, $CDCl_3$) (top) and ^{13}C NMR (75 MHz, $CDCl_3$) of compound **7**.

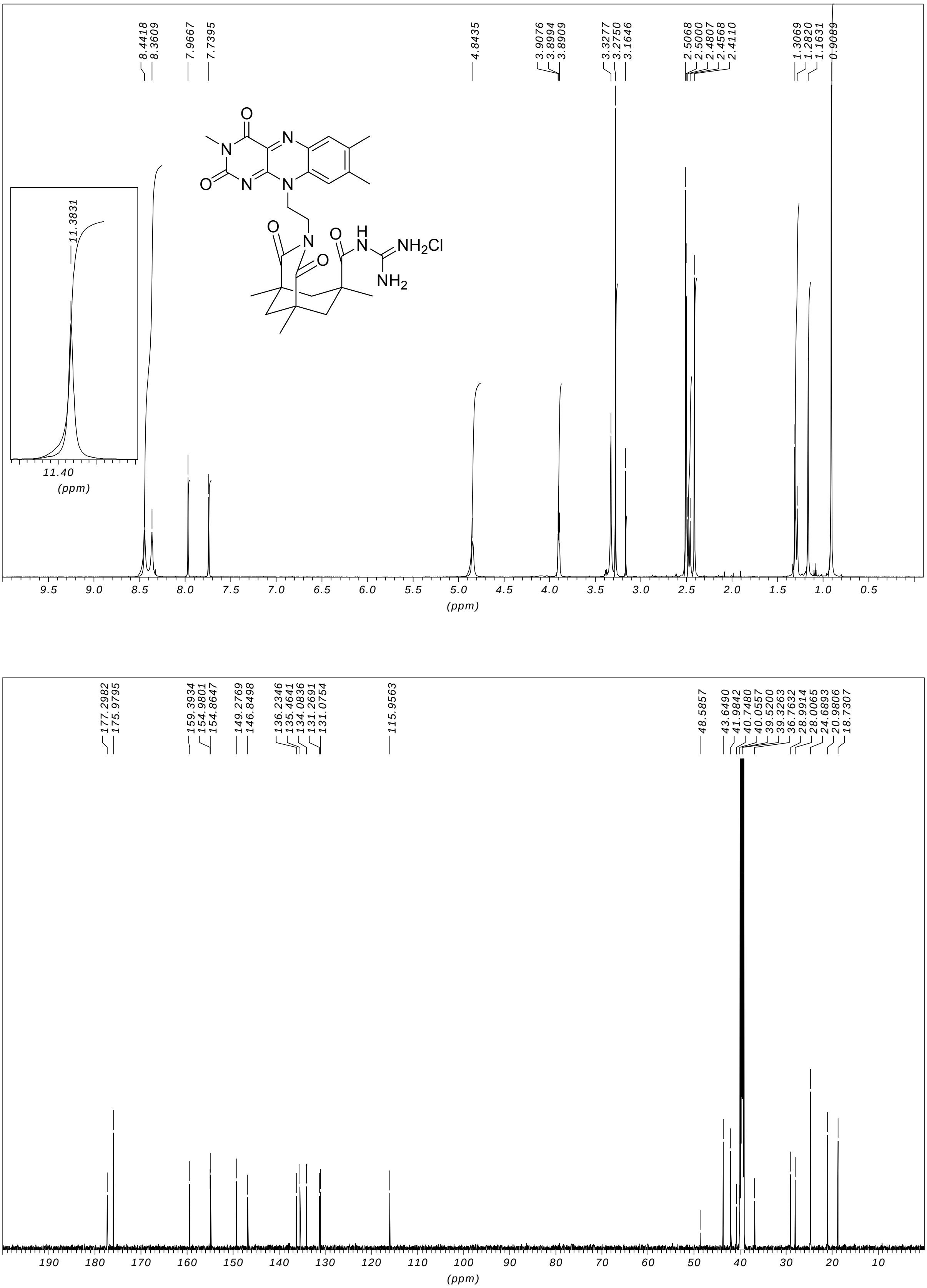




^{1}H NMR spectrum (300 MHz, CDCl$_3$) (top) and ^{13}C NMR (75 MHz, CDCl$_3$) of compound **10**.



^1H NMR spectrum (600 MHz, DMSO-d_6) (top) and ^{13}C NMR (150 MHz, DMSO-d_6) of compound **1**.



^{1}H NMR spectrum (600 MHz, DMSO-d_6) (top) and ^{13}C NMR (150 MHz, DMSO-d_6) of compound **2**.