Dye-sensitized photocatalytic hydrogen production: distinct activity in a glucose derivative of a phenothiazine dye

By N. Manfredi, B. Cecconi, V. Calabrese, A. Minotti, F. Peri, R. Ruffo, M. Monai, I. Romero-Ocaña, T. Montini, P. Fornasiero* and A. Abbotto*

Electronic Supplementary Information (ESI)

Experimental Section

General information

NMR spectra were recorded with a Bruker AMX-500 spectrometer operating at 500.13 MHz (^1H) and 125.77 MHz (^{13}C). Coupling constants are given in Hz. Absorption spectra were recorded with a V-570 Jasco spectrophotometer. Flash chromatography was performed with Merck grade 9385 silica gel 230–400 mesh (60 Å). Reactions performed under inert atmosphere were done in oven-dried glassware and a nitrogen atmosphere was generated with Schlenk technique. Conversion was monitored by thin-layer chromatography by using UV light (254 and 365 nm) as a visualizing agent. All reagents were obtained from commercial suppliers at the highest purity grade and used without further purification. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Extracts were dried with Na_2SO_4 and filtered before removal of the solvent by evaporation.

Electrochemical characterization

Test solutions were prepared by dissolving 2.3 and 2.2 mg of PTZ-TEG and PTZ-GLU, respectively, in the electrolyte (0.1 M $TBAClO_4$ in DMSO). DPV and CV were carried out at scan rate of 20 and 50 mV/s, respectively, using a PARSTA2273 potentiostat in a two-compartment, 3-electrode electrochemical cell in a glove box filled with N_2 ($[O_2]$ and $[H_2O] \leq 0.1$ ppm). The working, counter, and the pseudo-reference electrodes were a glassy carbon pin, a Pt flag and an Ag/AgCl wire, respectively. The working electrodes discs were well polished with alumina 0.1 μm suspension, sonicated for 15 min in deionized water, washed with 2-propanol, and cycled for 50 times in 0.5 M H_2SO_4 before use. The Ag/AgCl pseudo-reference electrode was calibrated, by adding ferrocene (10^{-4} M) to the test solution after each measurement. Energy levels were calculated using the absolute value of 5.2 V vs. vacuum for the ferrocene reference couple.

Preparation of Pt/TiO_2 nanocomposite

Deposition of Pt nanoparticles on TiO_2 Degussa P25 was done through a photodeposition method known in literature.[1-4] 32.7 mg of $Pt(NO_3)_2$ was dissolved in 300 mL of a solution of water/methanol 1:1 by volume. 2.0 g of TiO_2 Degussa P25 was suspended in the Pt solution in order to reach a final metal loading of 1.0 wt%. After stirring for 1 h in the dark, the suspension was irradiated with a 450 W medium pressure lamp for 4 h. The Pt/TiO_2 nanocomposites were collected by centrifugation, washed 3 times with water and finally dried at 80 °C overnight.

Characterization of Pt/TiO_2 nanocomposite

Phase composition has been determined by Powder X-ray Diffraction (PXRD) using a Philips X'Pert diffractometer using a Cu Kα ($\lambda = 0.154$ nm) X-ray source in the range $10° < 2\theta < 100°$ and data were analyzed by using the PowderCell 2.0 software. Mean crystallite sizes were calculated applying the Scherrer's equation to the principal reflection of each phase [(101) for anatase and (110) for rutile].

Textural properties of the catalyst have been analyzed by N_2 physisorption at the liquid nitrogen temperature using a Micromeritics ASAP 2020 automatic analyzer. The samples were previously degassed under vacuum at 200°C overnight. Specific surface area has been determined applying the BET method to the adsorption isotherm in the range $0.10 < p/p^0 < 0.35$. Pore size distribution has been evaluated applying the BJH theory to the desorption branch of the isotherm.[5]

The morphology of the composite materials and the distribution of the supported Pt nanoparticles were evaluated by High Resolution Transmission Electron Microscopy (HR-TEM) and High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) images recorded by a JEOL 2010-FEG microscope operating at the acceleration voltage of 200 kV. The microscope has 0.19 nm spatial resolution at Scherzer defocus conditions in HR-TEM mode and a probe of 0.5 nm was used in HAADF-STEM mode.

Adsorption of dyes on Pt/TiO_2

200 mg of Pt/TiO_2 nanocomposite were suspended in 10 mL of dye solution in ethanol for 24 h in the dark. The concentration of the dye was adjusted in order to obtain the desired loading, between

1.0 and 30.0 μmol g^{-1}. The obtained materials were recovered by centrifugation, washed 2 times with 10 mL of EtOH each and dried under vacuum at room temperature overnight. UV-vis spectra of the solutions after dye adsorption showed that the amount of residual dyes is negligible, confirming the quantitative adsorption of the dyes on Pt/TiO_2.

Photocatalytic hydrogen production

The **PTZ-TEG**/Pt/TiO_2 and **PTZ-GLU**/Pt/TiO_2 nanomaterials have been tested for H_2 production following a procedure previously described.[6] The required amount of the photocatalyst was suspended into 60 mL of 10% v/v aqueous solution of triethanolamine (TEOA) previously neutralized with HCl. After purging with Ar (15 mL min^{-1}) for 30 min, the suspension was irradiated using a 150 W Xe lamp with a cut-off filter at 420 nm. Irradiance was ~ 6 x 10^{-3} W m^{-2} in the UV-A range and ~ 180 W m^{-2} in the visible range (400 – 1000 nm). The concentration of H_2 in gas stream coming from the reactor has been quantified using a Agilent 7890 gaschromatograph equipped with a TCD detector, connected to a Carboxen 1010 column (Supelco, 30 m x 0.53 mm ID, 30 μm film) using Ar as carrier. Notably, the amount of catalyst has been optimized following the indications recently presented by Kisch and Bahnenmann.[7] The optimization has been performed using the **PTZ-GLU**/Pt/TiO_2 photocatalyst qith a loading of 30 μmol g^{-1}, increasing the amount of catalyst employed until the optimal H_2 production rate has been obtained (further addition of catalyst did not afford increased production of H_2). The optimum amount of photocatalyst has been found to be 60 mg as illustrated in Figure S4.

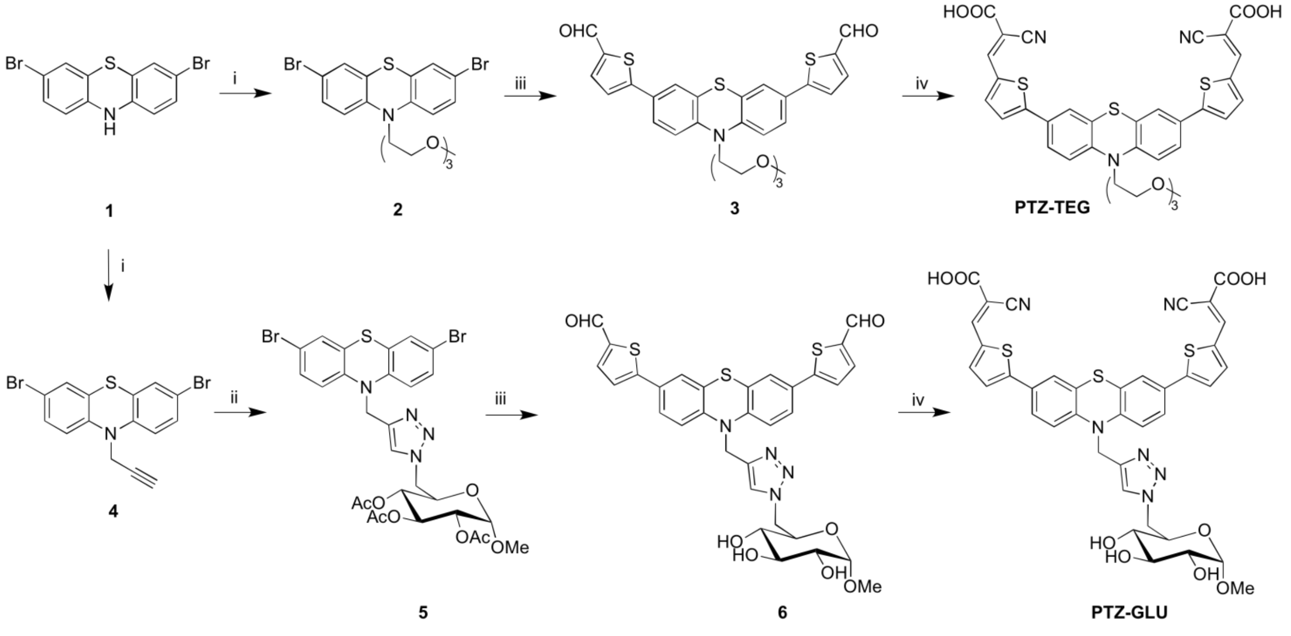
The performances of the sensitized photocatalysts have been reported in terms of H_2 production rate and overall H_2 productivity. Turn-Over Numbers (TON) were calculated as (2 x overall H_2 amount) / (dye loading). Light-to-Fuel Efficiency (LFE) was calculated as:

$$\mathrm{LFE} = \frac{F_{H_2} * \Delta H^0_{H_2}}{S * A_{irr}}$$

where F_{H2} is the flow of H_2 produced (expressed in mol s^{-1}), ΔH^0_{H2} is the enthalpy associated with H_2 combustion (285.8 kJ mol^{-1}), S is the total incident light irradiance, as measured by adequate radiometers in 400 – 1000 nm ranges (expressed in W cm^{-2}) and A_{irr} is the irradiated area (expressed in cm^2).

UV-vis spectra of the aqueous solutions recovered at the end of the photocatalytic runs highlighted that no desorption of the dyes took place during the experiments.

Scheme S1: Synthesis of PTZ-TEG and PTZ-GLU.



Reagents and conditions: (i) a. NaH 60%, DMF, 0°C, b. TEG-OTs for **2** and propargyl bromide for **4**, rt, 4 h; (ii) methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside, $Cu_2SO_4 \cdot 5H_2O$, sodium ascorbate, THF/H_2O, rt, 4 h; (iii) 5-formyl-2-thienylboronic acid, $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene], K_2CO_3, DME/MeOH, microwave, 70 °C, 90 min; (iv) cyanoacetic acid, piperidine, $CHCl_3$, reflux, 5 h.

The synthetic procedure for achieving **PTZ-TEG** is similar to the one used for **PTZ2**,[6] the alkylating reagent was prepared according to a known procedure starting from triethylene glycol monomethyl ether and *p*-TsOH.[8] Phenothiazine was brominated with Br_2 following the reported procedure,[9] then the anilinic nitrogen was deprotonated with NaH 60% in DMF followed by addition of the prepared tosylate. A following Suzuki-Miyaura cross coupling to introduce the π portion and a Knoevenagel condensation to introduce the anchoring and accepting unit enabled to afford **PTZ-TEG** with satisfactory yields.[6]

To obtain the glucose-functionalized dye **PTZ-GLU** we adopted the Cu-assisted azide-alkyne cycloaddition (CuAAC) “click” reaction,[10,11] using the methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside, which was synthetized as reported in literature,[12] and the alkyne-functionalized dye **4**. The advantage of azide–alkyne cycloadditions is their high chemoselectivity, which makes these reactions particularly attractive to conjugate highly functional molecules as for example carbohydrates.[13] The triple bond has been introduced on the phenothiazine moiety through nucleophilic substitution in an analogous way as for **PTZ-TEG**, using NaH as base to deprotonate the nitrogen and propargyl bromide as alkylating reagent. Butynyl bromide has been tested as well for alkylation but the strong basic conditions precluded the achievement of the desired product because of likely side-reactions taking place on the butynyl chain. Anyway the presence of a sp^3 carbon on the propargyl chain guarantees that no π conjugation of the molecule with the triazole ring will be present in the dye. Click reaction has been performed in standard conditions using $CuSO_4$ as copper source and sodium ascorbate as reducing agent in a THF and water mixture. The thienyl group was introduced with a Suzuki-Miyaura cross-coupling, during such reaction step the basic conditions due to K_2CO_3 brought to the formation of the desired product with the simultaneous cleavage of the three acetate groups on the glucose. Such side reaction was not forecast but since the protecting groups were introduced to perform the previous steps there had been no problem in performing the final Knoevenagel condensation in basic conditions to afford the desired product.

Synthesis of PTZ-TEG and PTZ-GLU

General Procedure for Alkylation: Compound **1** (1 eq.) was dissolved in dry DMF under N_2 atmosphere, then the solution was cooled to 0°C using an ice bath and NaH 60% (2 eq.) was slowly added. After stirring at 0 °C for 1 h, the appropriate tosylate or bromide (2 eq.) was added and the solution was stirred at rt for 4 h, when TLC revealed the complete conversion of the starting material. The reaction mixture was quenched with iced water, then extracted with Et_2O and the organic phase was dried with Na_2SO_4 and concentrated. The crude was purified using flash column chromatography on silica gel.

General Procedure for Suzuki-Miyaura Cross-Coupling: Compound **2** or **5** (1 eq.) and $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (0.1 eq.) were dissolved in dimethoxyethane and stirred for 15 minutes under nitrogen atmosphere. Then 5-formyl-2-thienylboronic acid (2.4 eq.) and K_2CO_3 (10 eq.) were added as suspension in methanol. The reaction was performed with microwave irradiation (70 °C, 200 W, 90 minutes) and then quenched by pouring into a saturated solution of NH_4Cl. Filtration on Celite and extractions with organic solvent allowed to isolate the crude product, which was then purified through flash column chromatography on silica gel.

General Procedure for Knoevenagel Condensation: Compound **3** or **6** (1 eq.), cyanoacetic acid (10 eq.) and piperidine (10 eq. + catalytic) were dissolved in $CHCl_3$ and heated to reflux for 5 h. Then the solvent was evaporated and a solution of HCl 1 M (~50 mL) was added and the mixture was left under magnetic stirring for 5 h at rt. The dark red solid that precipitated was filtered and washed with water (3x30 mL) and petroleum ether (2x30 mL).

Compound **2** was synthetized according to general procedure for alkylation using product **1** (0.20 g, 0.56 mmol), NaH 60% (0.13 g, 1.12 mmol) and TEG-OTs (0.35 g, 1.12 mmol) in 5 mL of dry DMF. Extraction with Et_2O and purification with petroleum ether/AcOEt 5:1 as eluent, gave product **2** as pale yellow oil in 80% yield (0.70 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.6, 2.2 Hz, 2H), 7.17 (d, *J* = 1.7 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 3.99 (t, *J* = 6.1 Hz, 2H), 3.78 (t, *J* = 6.1 Hz, 2H), 3.67 – 3.57 (m, 6H), 3.55 – 3.48 (m, 2H), 3.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 130.2, 129.6, 126.0, 116.6, 115.0, 71.9, 70.7, 70.6 (x3), 68.1, 59.0, 47.9.

Compound **3** was synthetized according to general procedure for Suzuki-Miyaura cross-coupling using product **2** (0.24 g, 0.48 mmol), Pd(dppf)$Cl_2 \cdot CH_2Cl_2$ (0.04 g, 0.05 mmol), 5-formyl-2-thienylboronic acid (0.21 g, 1.15 mmol), K_2CO_3 (0.66 g, 4.80 mmol), DME (5 mL) and methanol (5 mL). Extractions with AcOEt and purification with petroleum ether/AcOEt 2:1 as eluent, gave product 3 as an orange solid in 75 % yield (0.19 g). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.76 (s, 2H), 7.60 (d, *J* = 3.9 Hz, 2H), 7.31 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.22 (d, *J* = 2.2 Hz, 2H), 7.19 (d, *J* = 3.9 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.99 (t, *J* = 6.0 Hz, 2H), 3.78 (t, *J* = 6.0 Hz, 2H), 3.71 – 3.51 (m, 6H), 3.50 – 3.45 (m, 2H), 3.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 182.4, 152.7, 144.6, 141.6, 137.5, 127.8, 125.7, 124.6, 123.9, 123.2, 115.5, 71.8, 70.7, 70.5, 70.4(x2), 67.9, 58.9, 47.9. HRMS (ESI) *m/z*: calcd. for $[M+Na]^+$ $C_{35}H_{29}N_3NaO_7S_3$: 588.0949; found 588.1081.

Compound **4** was synthetized according to general procedure for alkylation using product 1 (0.20 g, 0.56 mmol), NaH 60% (0.13 g, 1.12 mmol), propargyl bromide (0.04 g, 1.12 mmol) in 5 mL of dry DMF. Extraction with Et_2O and purification with petroleum ether/AcOEt 20:1 as eluent, gave product **4** as pale yellow solid in 77% yield (0.17 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.6, 2.2 Hz, 2H), 7.22 (d, *J* = 2.2 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 4.43 (d, *J* = 2.3 Hz, 2H), 2.47 (t, *J* = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 130.5, 129.5, 125.1, 116.1, 115.8, 78.2, 75.2, 38.8.

Compound **5** was synthetized by mixing compound **4** (0.12 g, 0.30 mmol) and methyl 2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-α-D-glucopyranoside (0.09 g, 0.27 mmol) in THF (6 mL), and adding a second solution of $CuSO_4 \cdot 5H_2O$ (0.08 g, 0.33 mmol) and sodium ascorbate (0.08 g, 0.41 mmol) in H_2O (2.5 mL), then the reaction mixture was stirred at rt in the dark for 4 h. TLC (petroleum ether/AcOEt 1:1) revealed the complete consumption of compound **4**, then the solvents were evaporated and the crude was dissolved in CH_2Cl_2 and washed with HCl 5% solution and brine. The crude was purified using flash chromatography (petroleum ether/AcOEt 8:2 then 4:6) affording compound **5** (0.19 g, 95%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.23 (d, *J* = 2.2 Hz, 2H), 7.15 (dd, *J* = 8.7, 2.3 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 5.42 (t, *J* = 10.0 Hz, 1H), 5.12 (s, 2H), 4.79 (d, *J* = 3.6 Hz, 1H), 4.67 – 4.58 (m, 2H), 4.51 (dd, *J* = 14.5, 2.1 Hz, 1H), 4.37 – 4.31 (m, 1H), 4.07 (td, *J* = 8.2, 4.1 Hz, 1H), 2.91 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.9, 169.7, 144.1, 143.2, 130.2, 129.6, 125.7, 123.8, 116.6, 115.5, 96.5, 70.6, 69.5, 69.4, 67.6, 55.2, 50.8, 44.6, 20.7 (x3).

Compound **6** was synthetized according to general procedure for Suzuki-Miyaura cross-coupling using product **5** (0.10 g, 0.13 mmol), Pd(dppf)$Cl_2 \cdot CH_2Cl_2$ (0.01 g, 0.01 mmol), 5-formyl-2-thienylboronic acid (0.05 g, 0.31 mmol), K_2CO_3 (0.18 g, 1.35 mmol), DME (3 mL) and methanol (3 mL). Extraction with AcOEt and purification with AcOEt/*i*PrOH 10:1 as eluent, gave product **6** as an orange solid in 74% yield (0.07 g). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.88 (s, 2H), 8.01 (d, *J* = 3.8 Hz, 2H), 7.97 (s, 1H), 7.69 (d, *J* = 3.6 Hz, 2H), 7.61 (s, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 5.33 (d, *J* = 5.8 Hz, 1H), 5.24 (s, 2H), 4.93 (d, *J* = 4.7 Hz, 1H), 4.77 (d, *J* = 6.5 Hz, 1H), 4.71 (d, *J* = 14.0 Hz, 1H), 4.46 – 4.29 (m, 2H), 3.61 (t, *J* = 9.2 Hz, 1H), 3.23 – 3.11 (m, 1H), 3.02 – 2.93 (m, 1H), 2.73 (s, 3H). ^{1}H NMR (500 MHz, DMSO-d_6 + D_2O) δ 9.83 (s, 2H), 7.96 (d, *J* = 3.8 Hz, 2H), 7.92 (s, 1H), 7.61 (d, *J* = 3.8 Hz, 2H), 7.55 (s, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 5.20 (s, 2H), 4.68 (d, *J* = 13.4 Hz, 1H), 4.35 (d, *J* = 3.6 Hz, 2H), 3.56 (s, 1H), 3.32 (s, 1H), 3.15 (dd, *J* = 9.5, 3.6 Hz, 1H), 2.97 (s, 1H), 2.70 (d, *J* = 24.2 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ ^{13}C NMR (126 MHz, DMSO) δ 184.1, 152.0, 144.5, 143.1, 141.8, 139.8, 127.9, 126.3, 125.1, 124.6, 123.1, 116.7, 100.1, 73.5, 72.2, 72.2, 71.0, 54.4, 51.6, 44.5. HRMS (ESI) *m/z*: calcd. for $[M+H]^+$ $C_{32}H_{29}N_4O_7S_3$: 677.1198; found 677.1185; calcd. for $[M+Na]^+$ $C_{32}H_{28}N_4NaO_7S_3$: 699.1018; found 699.1040.

Compound **PTZ-TEG** was synthetized according to general for Knoevenagel condensation using product **3** (0.19 g, 0.34 mmol), cyanoacetic acid (0.29 g, 3.40 mmol), piperidine (0.34 g, 3.4 mmol) and $CHCl_3$ (6 mL). A dark red solid (0.22 g) has been isolated as the product in 92% yield. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.45 (s, 2H), 7.98 (d, *J* = 3.8 Hz, 2H), 7.71 (d, *J* = 3.8 Hz, 2H), 7.57 (m, 4H), 7.16 (d, *J* = 9.1 Hz, 2H), 4.13 (t, *J* = 5.3 Hz, 2H), 3.79 (t, *J* = 5.3 Hz, 2H), 3.66 – 3.43 (m, 6H), 3.43 – 3.29 (m, 2H), 3.20 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 164.2, 152.0, 146.0, 145.0, 141.0, 134.5, 127.7, 126.5 125.0, 124.8, 123.8, 117.2, 116.9, 98.8, 71.7, 70.4, 70.2, 70.1, 67.8, 58.5, 44.1. HRMS (ESI) *m/z*: calcd. for $[M+H]^+$ $C_{35}H_{30}N_3O_7S_3$: 700.1246; found 700.0552; calcd. for $[M+Na]^+$ $C_{35}H_{29}N_3NaO_7S_3$: 722.1065; found 722.0307. m.p.: 206-207 °C (deg)

Compound **PTZ-GLU** was synthetized according to general for Knoevenagel condensation using product **6** (0.18 g, 0.27 mmol), cyanoacetic acid (0.11 g, 2.70 mmol), piperidine (0.22 g, 2.70 mmol) and CHCl$_3$ (5 mL). A dark red solid (0.19 g) has been isolated as the product in 90% yield. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 8.47 (s, 2H), 7.99 (m, 3H), 7.71 (d, *J* = 4.0 Hz, 2H), 7.57 (d, *J* = 2.1 Hz, 2H), 7.50 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 5.24 (s, 2H), 4.71 (d, *J* = 12.9 Hz, 1H), 4.46 – 4.29 (m, 2H), 3.61 (t, *J* = 9.5 Hz, 1H), 3.36 (t, *J* = 9.1 Hz, 1H), 3.17 (dd, *J* = 9.6, 3.6 Hz, 1H), 2.98 (t, *J* = 9.2 Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d$_6$) δ 164.1, 152.2, 147.0, 144.6, 143.0, 142.0, 134.4, 127.7, 126.3, 125.1, 124.6, 123.1, 117.0, 116.8, 100.1, 98.2, 73.5, 72.2, 72.1, 71.0, 54.4, 51.6, 44.4. HRMS (ESI) *m/z*: calcd. for $[M+H]^+$ $C_{38}H_{31}N_6O_9S_3$: 811.1315; found 811.0627; calcd. for $[M+Na]^+$ $C_{38}H_{30}N_6NaO_9S_3$: 833.1134; found 833.0417. m.p.: 283-284 °C (deg)

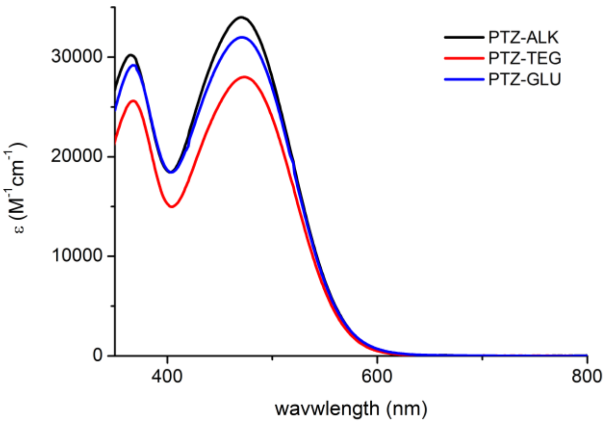


Figure S1. Absorption spectra of dyes **PTZ-ALK**, **PTZ-TEG** and **PTZ-GLU** in THF

Table S1. Optical and electrochemical characterization of dye **PTZ-ALK, PTZ-TEG** and **PTZ-GLU**.

Sample	λ_{max} [a] (nm)	ε ($M^{-1}cm^{-1}$)	V_{ox} (V vs. Fc) ± 10 mV	HOMO[b] eV ± 0.1 eV	V_{red} (V vs. Fc) ± 10 mV	LUMO[b] eV ± 0.1 eV
PTZ-ALK[c]	470	34000 ± 1000	0.15	-5.4	-	-3.3
PTZ-TEG	470	28000 ± 1000	0.33	-5.5	-1.52	-3.7
PTZ-GLU	471	32000 ± 1000	0.30	-5.5	-1.49	-3.7

[a] Dye solution 10^{-5} M in THF. [b] Vacuum potential = Fc/Fc$^+$ + 5.2 V. c Values from Ref 6; CV and DPV plots are reported in Ref 6.

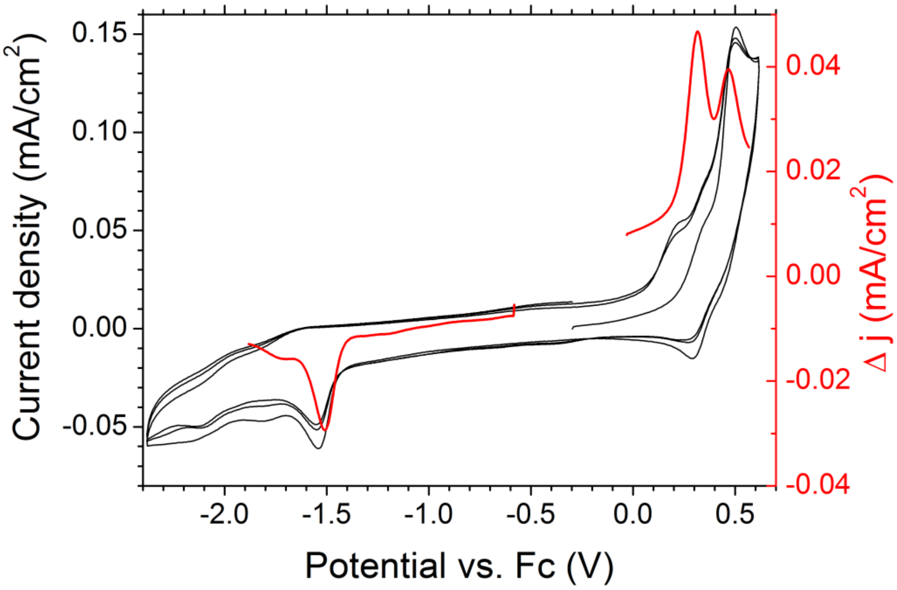


Figure S2. Electrochemistry of **PTZ-TEG:** CV (black line) and DPV (red line) measurements.

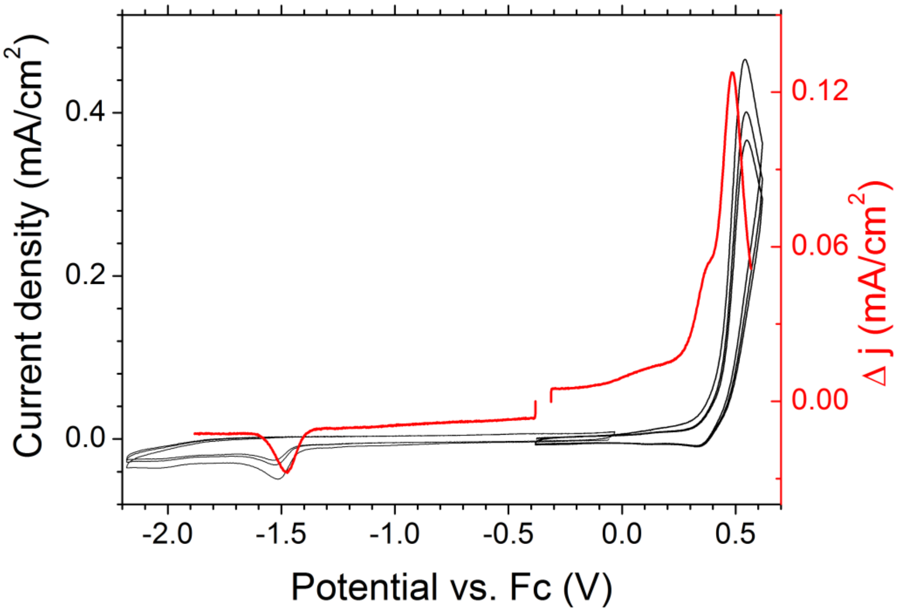


Figure S3. Electrochemistry of **PTZ-GLU:** CV (black line) and DPV (red line) measurements.

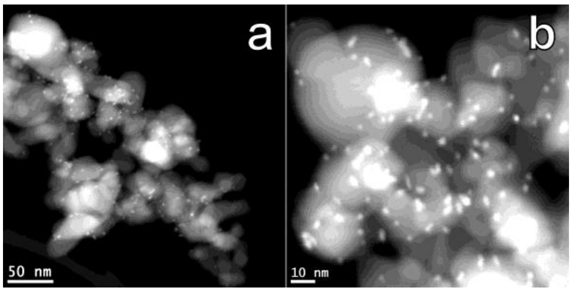


Figure S4: Representative HAADF-STEM images of the Pt/TiO_2 nanocomposite.

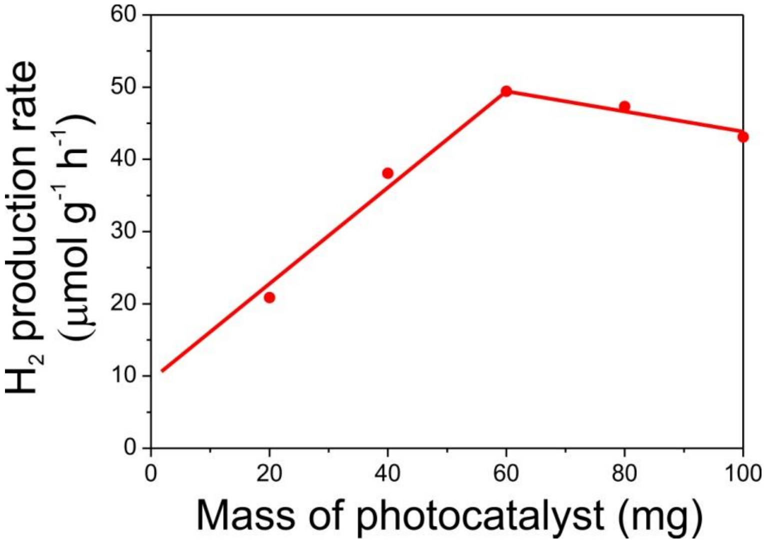


Figure S5. Optimization of the experimental conditions for photocatalytic H_2 production.

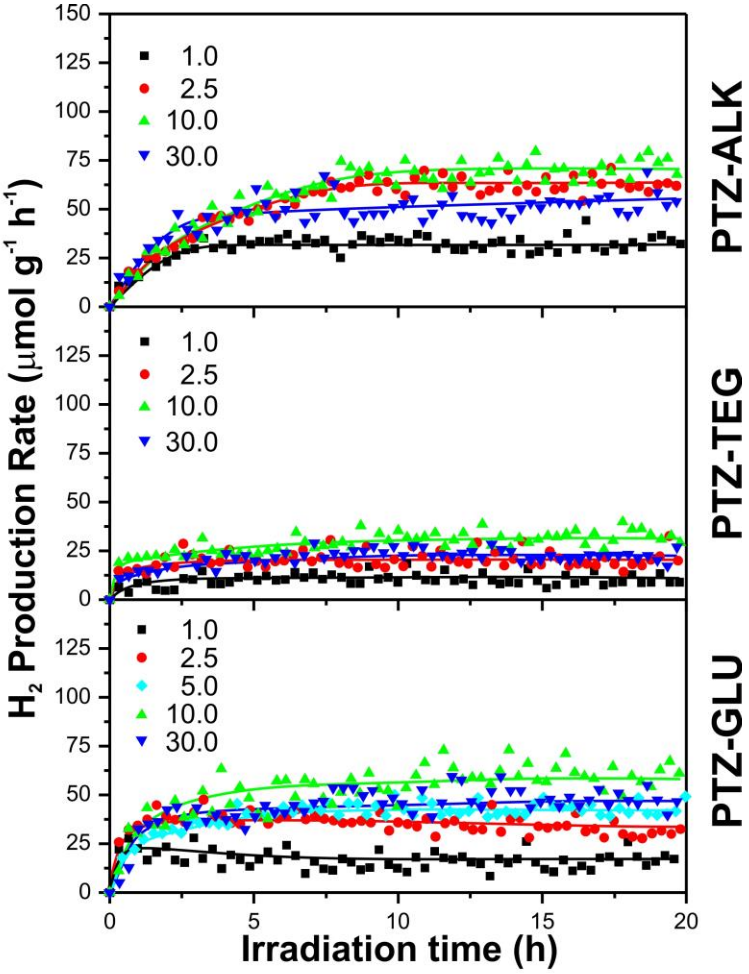


Figure S6. H_2 production rates from TEOA 10% v/v solution at pH 7.0 under irradiation with visible light ($\lambda > 420$ nm) measured using the dye/Pt/TiO_2 materials. Numbers in the legends correspond to the dye loading in μmol g^{-1}.

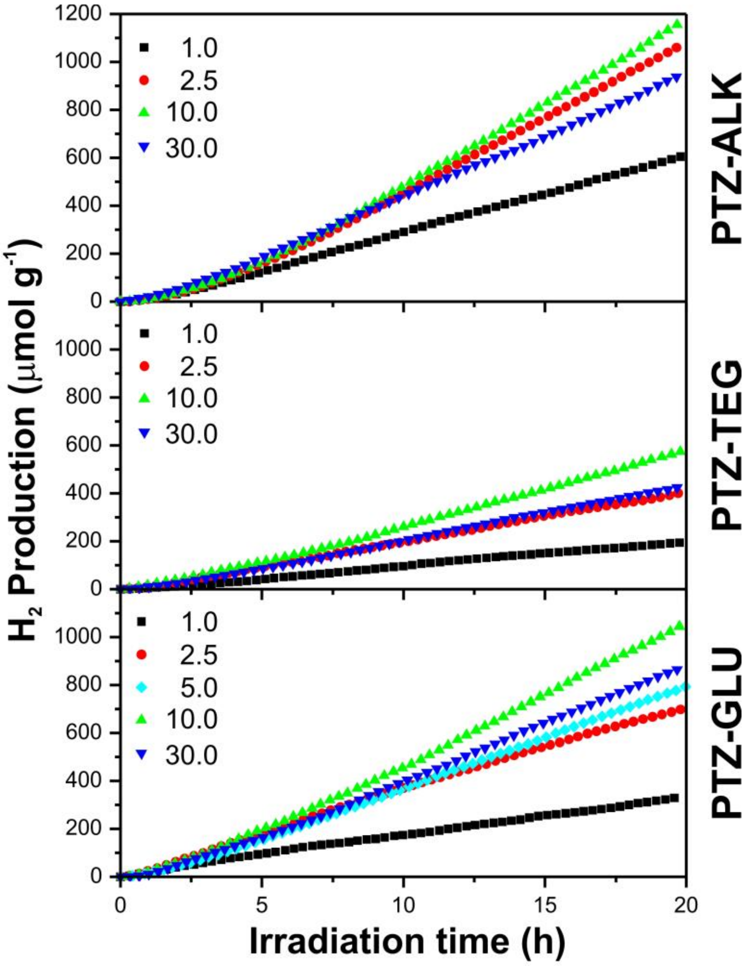


Figure S7. H_2 production from TEOA 10% v/v solution at pH 7.0 under irradiation with visible light ($\lambda > 420$ nm) measured using the dye/Pt/TiO$_2$ materials. Numbers in the legends correspond to the dye loading in μmol g^{-1}.

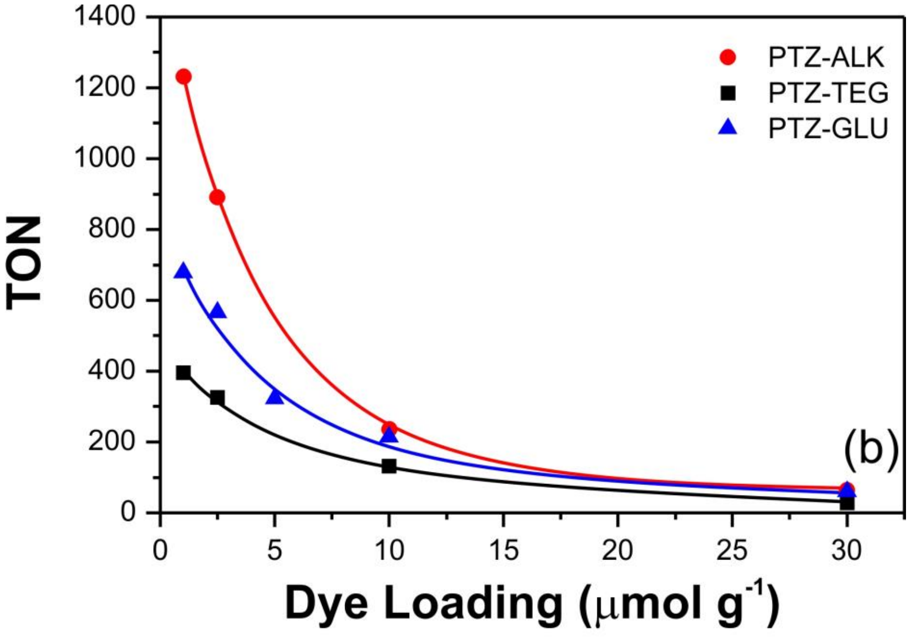


Figure S8: TON in H_2 evolution from TEOA 10% v/v solution at pH = 7.0 under irradiation with visible light ($\lambda > 420$ nm) using the Pt/TiO$_2$ materials sensitized with PTZ-ALK, PTZ-TEG and PTZ-GLU.

Table S2. TON values and Light-to-Fuel Efficiencies (LFE) of dye **PTZ-ALK**, **PTZ-TEG** and **PTZ-GLU**.

Dye Loading (μmol g^{-1})	**TON**			**LFE (%)**		
	PTZ-ALK	**PTZ-TEG**	**PTZ-GLU**	**PTZ-ALK**	**PTZ-TEG**	**PTZ-GLU**
1.0	1232	396	678	0.017	0.005	0.008
2.5	892	326	566	0.034	0.011	0.016
5.0	-	-	323	-	-	0.023
10.0	236	132	213	0.040	0.017	0.031
30.0	64	29	59	0.029	0.013	0.026

References

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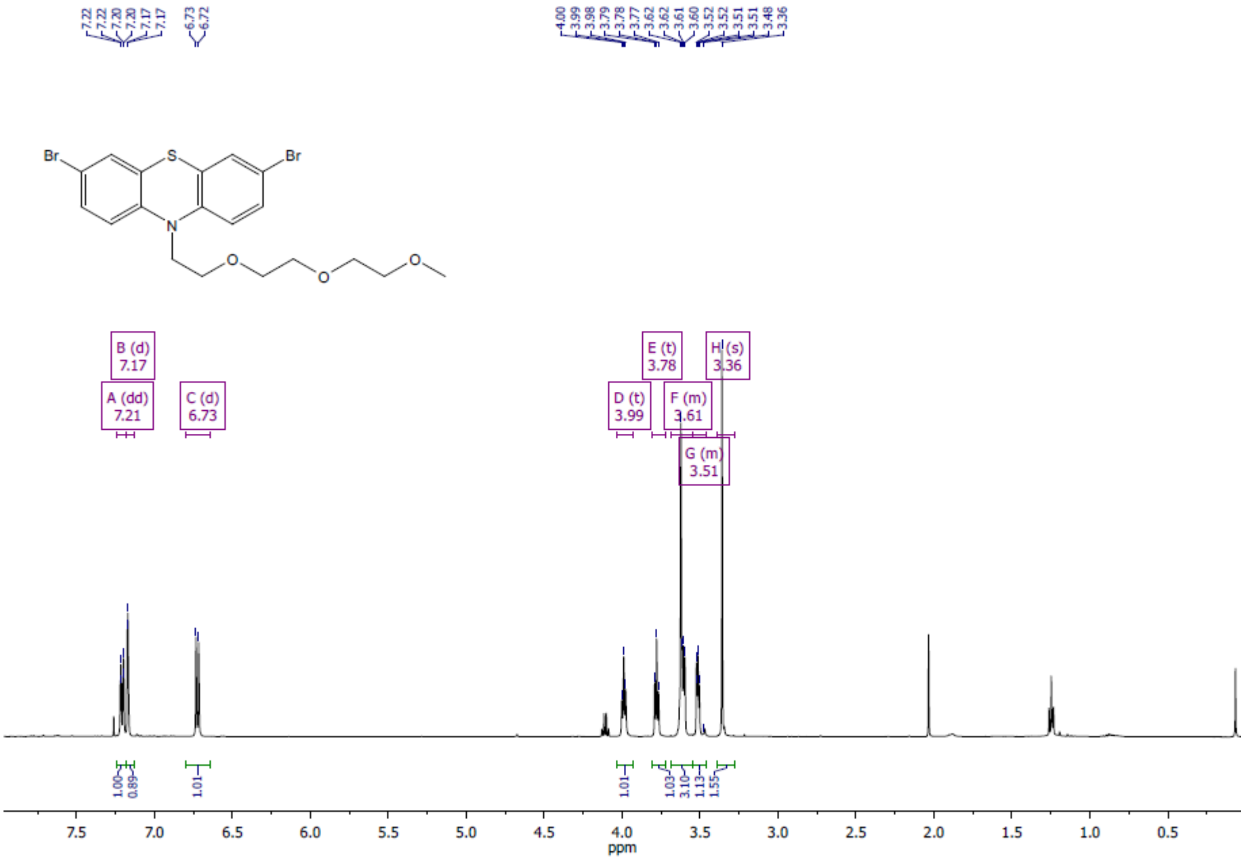
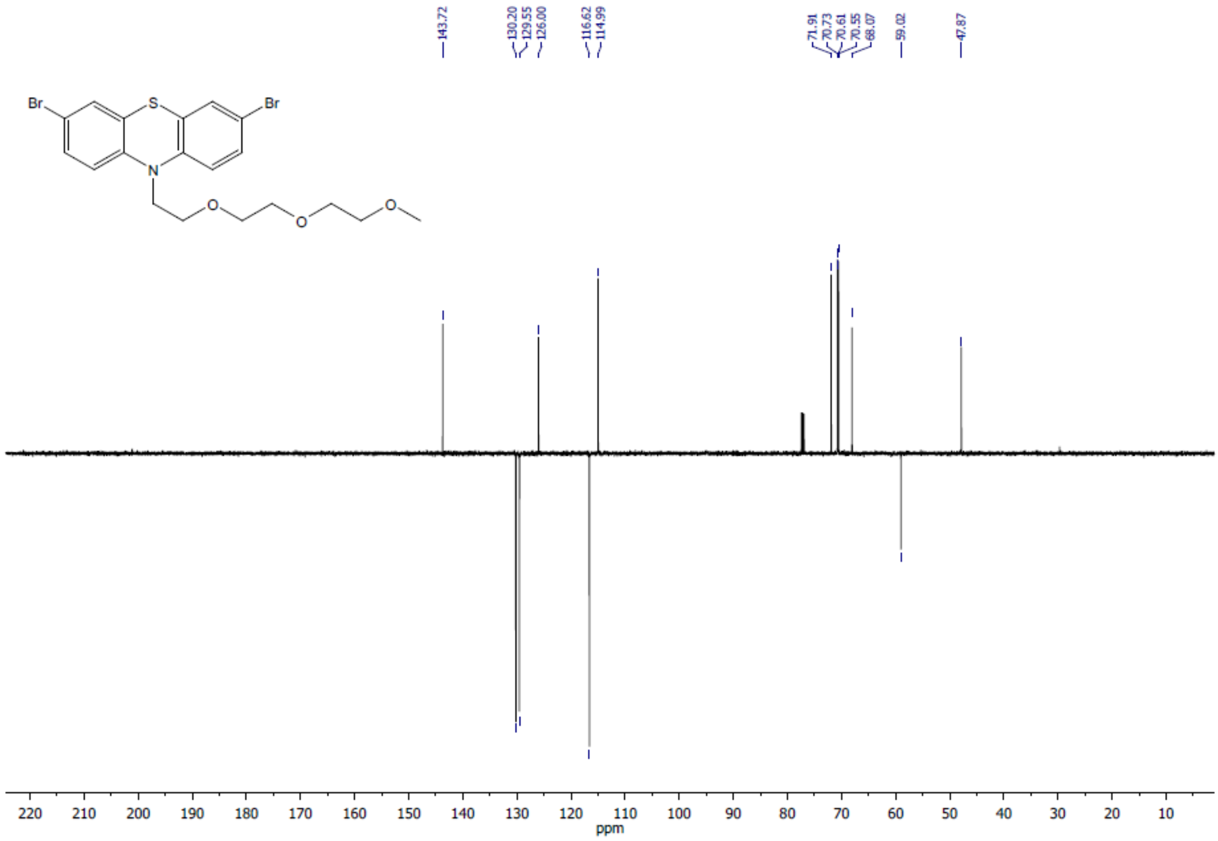
^{1}H NMR and ^{13}C NMR spectra

Molecule 2





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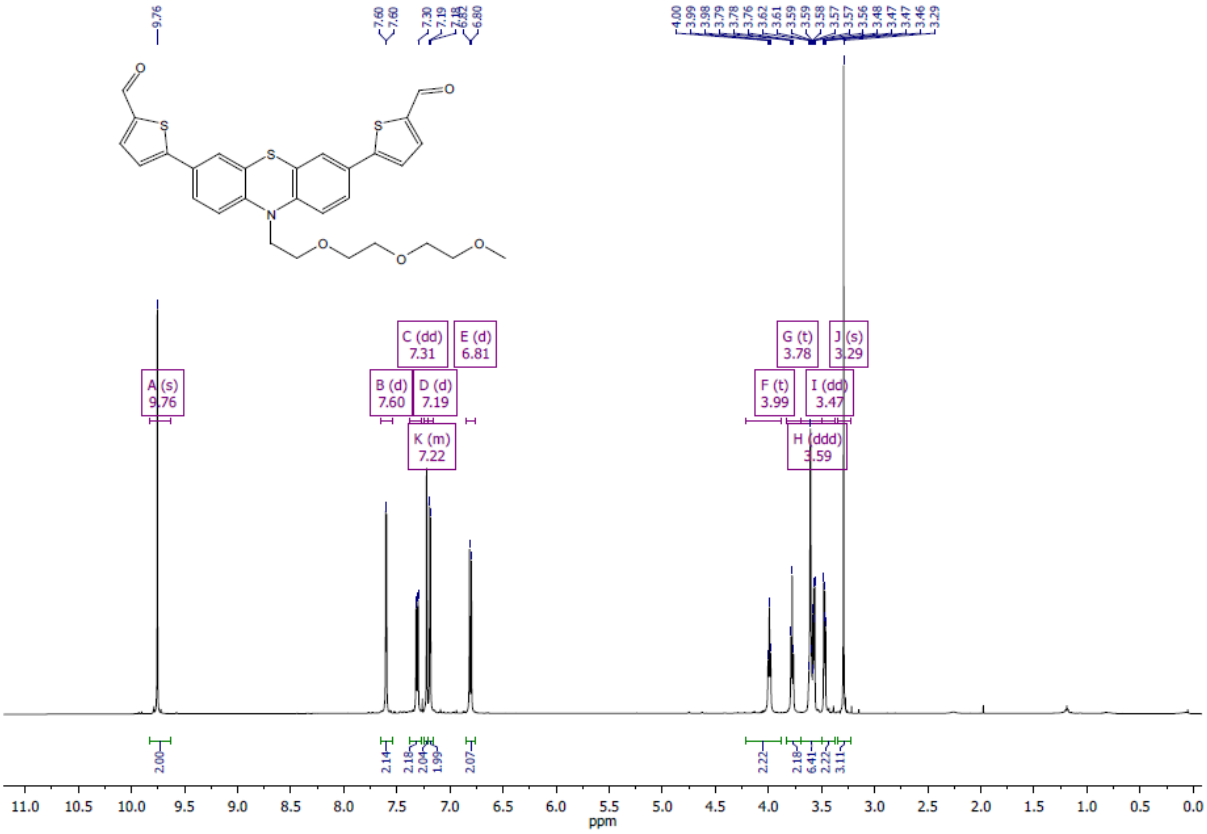
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3.59
3.58
3.57
3.57
3.56
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3.47
3.46
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S
S
O
S
N
O
O
O
A (s)
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C (dd)
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D (d)
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E (d)
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K (m)
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F (t)
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G (t)
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I (dd)
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J (s)
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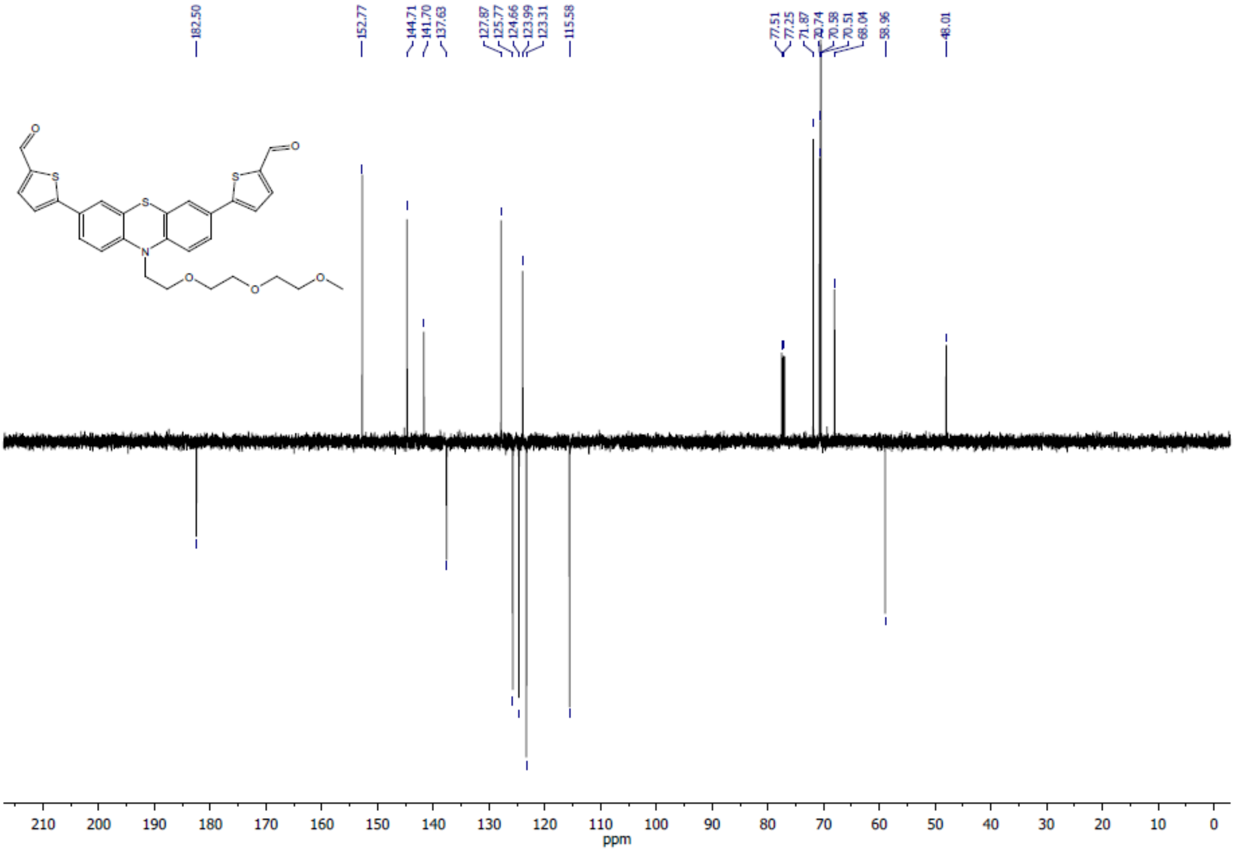
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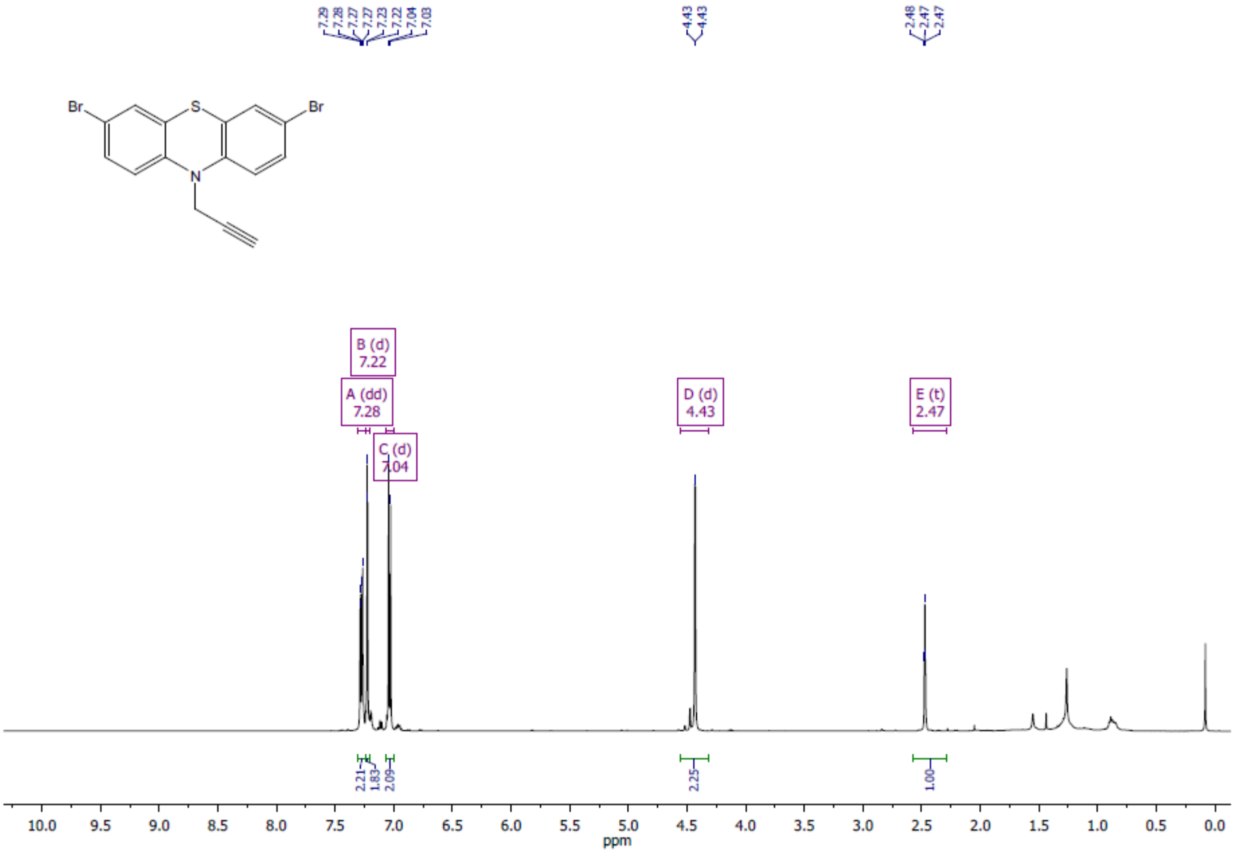
Molecule 4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Br
N
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A (dd)
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C (d)
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D (d)
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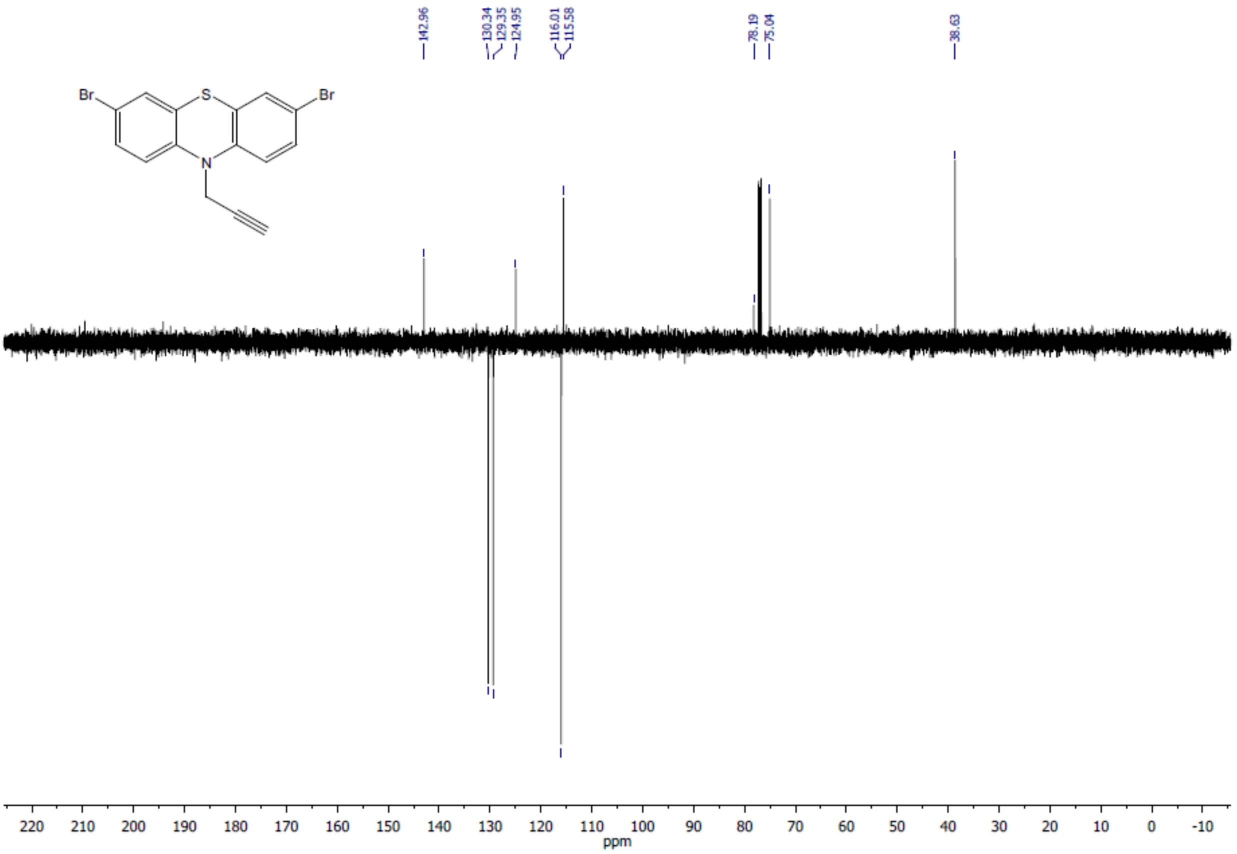
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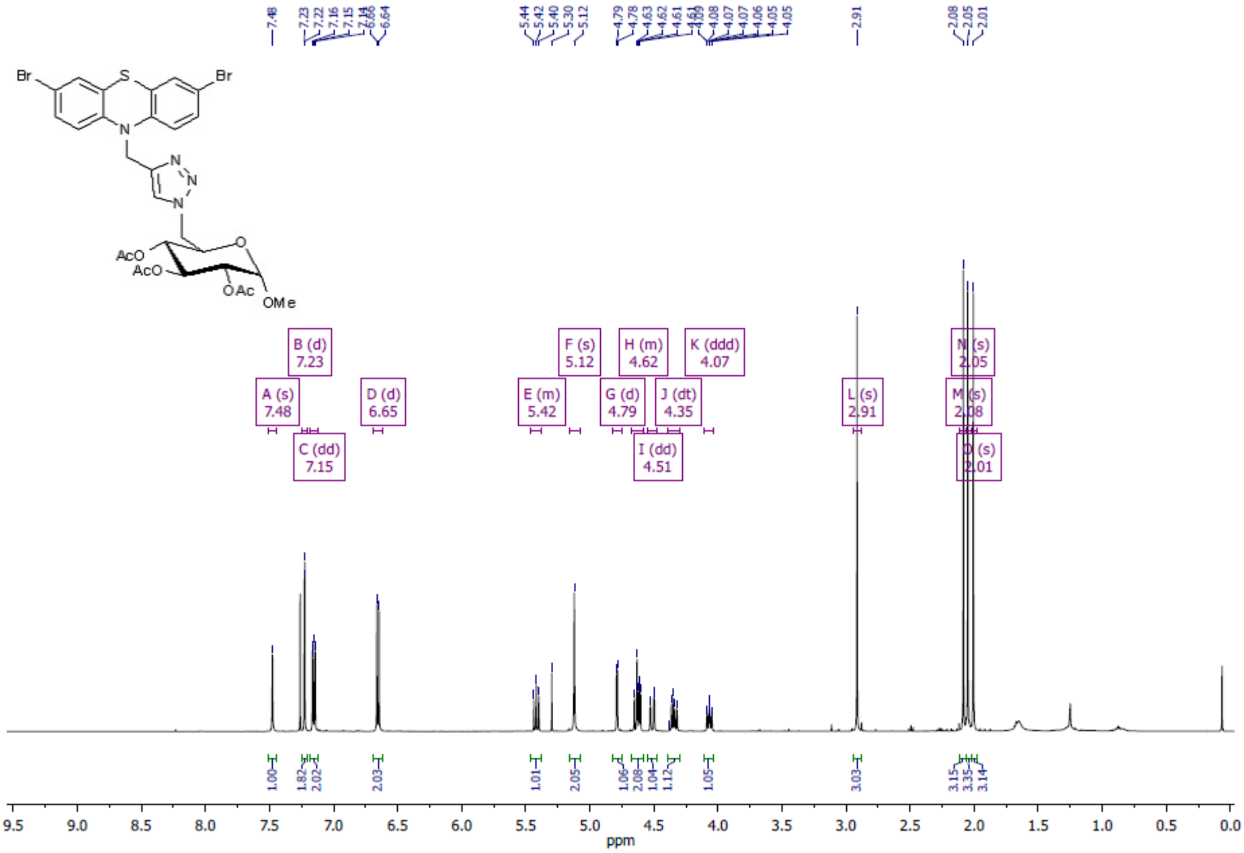
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C (dd)
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F (s)
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G (d)
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H (m)
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J (dt)
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O (s)
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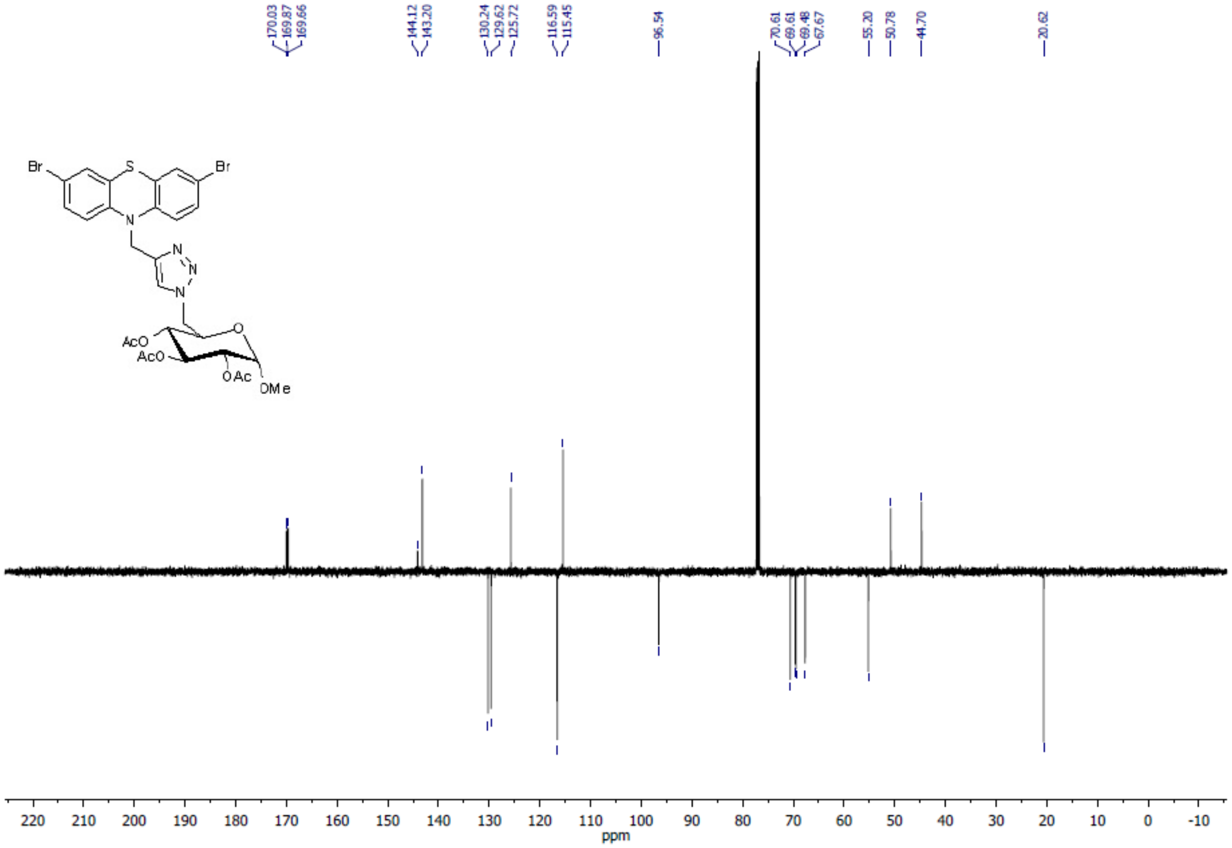
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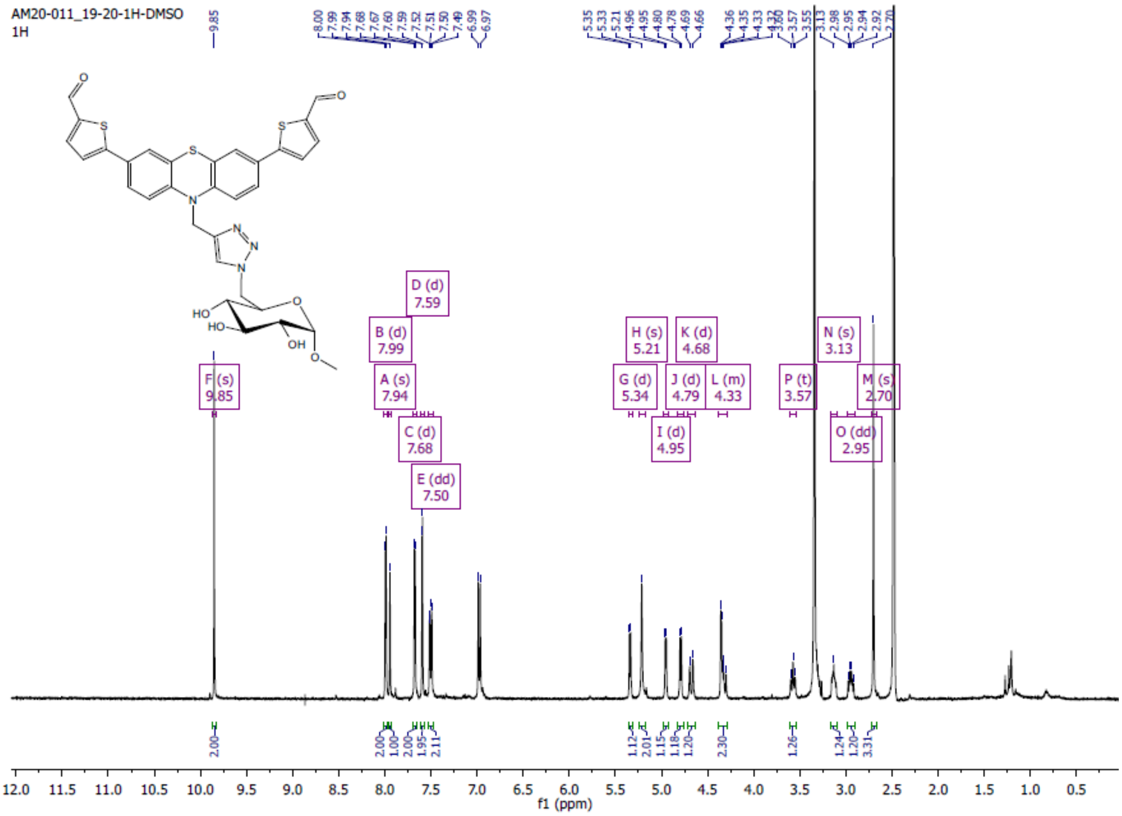
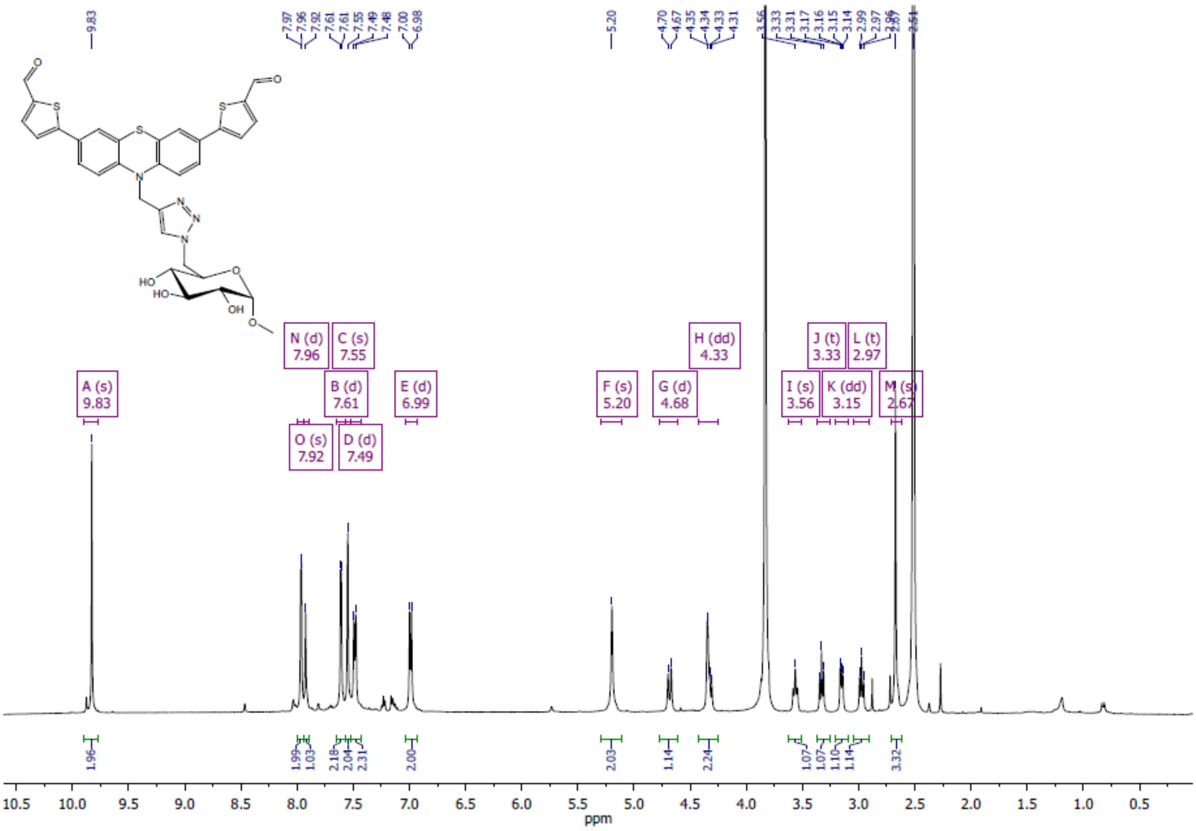
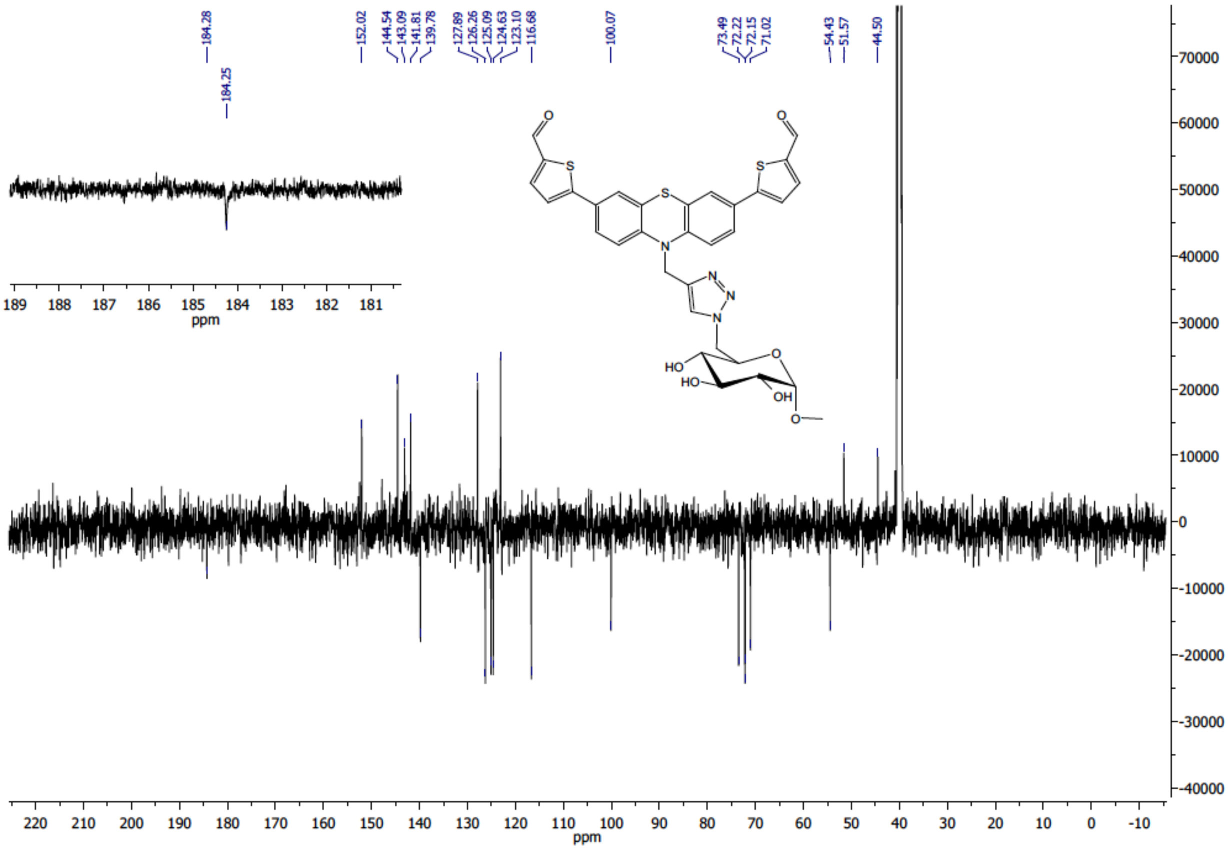
Molecule 6



^{1}H NMR (DMSO + D_2O)

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N
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HO
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OH
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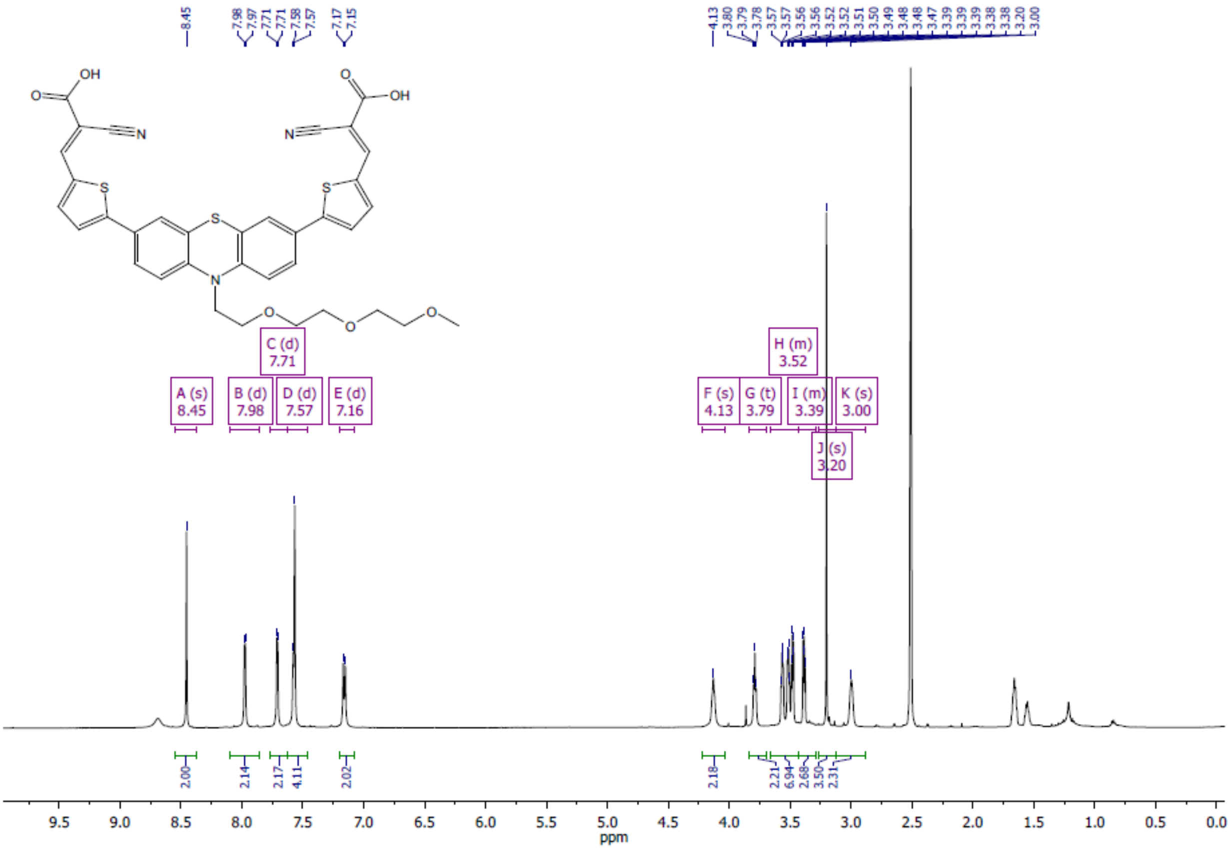
PTZ-TEG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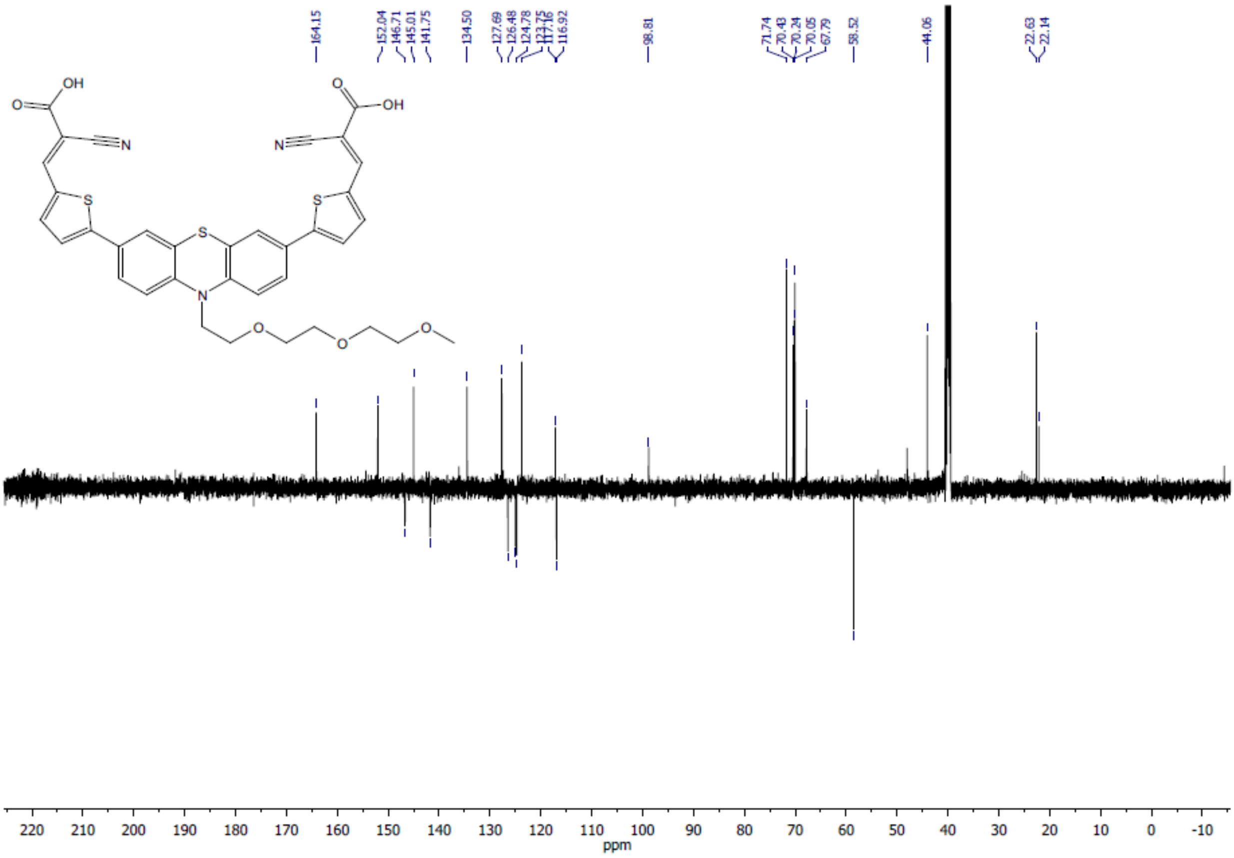
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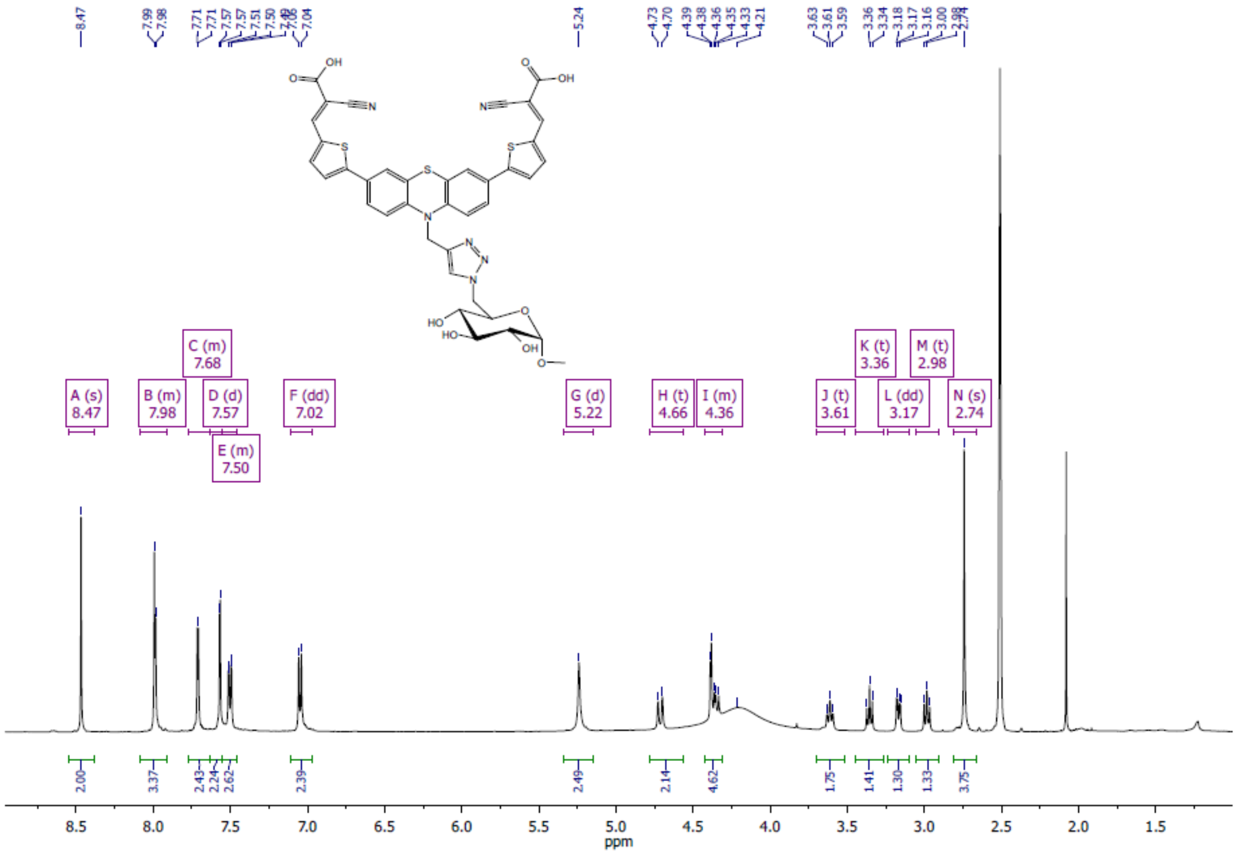
PTZ-GLU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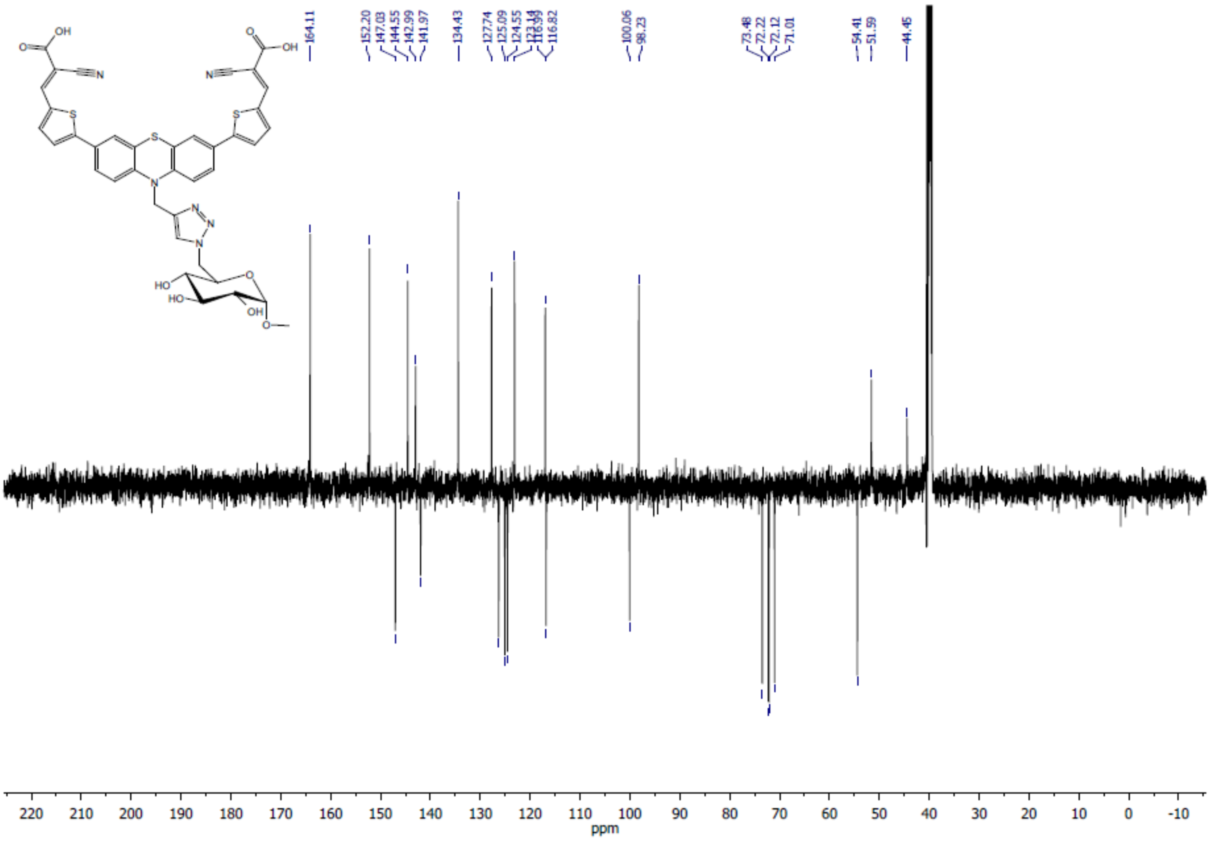
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