Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting information

On-Demand Guest Release from MOF-5 Sealed with Nitrophenylacetic Acid Photocapping Groups

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General Procedures. All reagents were purchased and used without further purification, and reactions were carried out under an inert atmosphere. Previously reported procedures were used to prepare 1-bromomethyl-3-nitro-benzene (**1**)[1] and methyl (2S) aminophenyl ethanoate (**2**).[2] The photocapping group 3-nitrophenylacetic acid (**PC2**, **PhotoCap-2)** was purchased from Acros Organics. MOF-5 was synthesized following established procedures,[3] and its PXRD pattern was compared to simulated patterns from single crystal to confirm the uniformity of the crystalline sample. Acetonitrile (CH_3CN), diethylether (Et_2O) and tetrahydrofuran (THF) were sparged with argon and dried by passing through alumina-based drying columns. All chromatography and thin-layer chromatography (TLC) were performed on silica (200-400 mesh). TLCs were developed by using CH_2Cl_2 or solvent mixtures containing CH_2Cl_2, hexanes, or diethyl ether (Et_2O). ^1H and ^{13}C NMR spectra were recorded with a 500 MHz Bruker Biospin NMR instrument. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS). FT-IR spectra were recorded using Bruker Vertex70 Optics FT-IR spectrometer equipped with a Specac Golden Gate attenuated total reflection (ATR) accessory by collecting 256 scans over a scan range from 4000 to 600 cm^{-1} at 4 cm^{-1} resolution. LC/MS was carried on a Single Quadruple, Agilent Technologies 1200 series LC system. GC/MS spectra were obtained from a Single Quadruple, Agilent Technologies 7890B GC system. Thermogravimetric analysis (TGA) measurements were carried out on a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer from room temperature to 800 °C under nitrogen atmosphere at a heating rate of 10 °C/min. High resolution

mass spectra were obtained at the University of Notre Dame mass spectrometry facility using microTOF instrument operating in positive ionization mode. Melting-point information was obtained using a Hydrothermal Mel-Temp instrument.

[Bis-(3-nitro-benzyl)-amino]-phenyl-acetic acid methyl ester (3). Methyl (2S) aminophenyl ethanoate (**2**) (0.490 g, 2.95 mmol) was combined with 1-bromomethyl-3-nitro-benzene (1.29 g, 5.97 mmol), potassium carbonate (0.410 g, 2.97 mmol) and sodium iodide (0.134 g, 0.894 mmol) in dry CH_3CN (9 mL). After refluxing for 1 h, additional 1-bromomethyl-3-nitro-benzene (0. 642 g, 2.97 mmol) and potassium carbonate (0.410 g, 2.97 mmol) was added to the reaction before refluxing for another 6 h, and stirred for an additional 16 h at 45 °C. Removal of precipitates by filtration and solvent removal provided the crude product as a yellow oil. Flash chromatography on silica (5:4 CH_2Cl_2/hexanes) yielded light yellow oil (0.675 g, 52.2%). TLC R_f = 0.57 (silica, 5:2 DCM/Hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 2 H), 8.07 (d, *J* = 8.12 Hz, 2 H), 7.63 (d, *J* = 7.7 Hz, 2 H), 7.46 (t, *J* = 7.9 Hz, 2 H), 7.32-7.42 (m, 5 H), 4.60 (s, 1 H), 3.94 (d, *J* = 14.5 Hz, 2 H), 3.85 (d, *J* = 14.4 Hz, 2H), 3.81 (s, 3 H); ^{13}C NMR (125 MHz) δ 172.1, 148.4, 141.4, 135.5, 134.6, 129.4, 128.9, 128.6, 123.5, 122.4, 66.91, 54.38, 51.9. FT-IR (diamond-ATR, cm^{-1}) 3084.4, 3065.6, 3032.4, 2957.0, 2928.8, 2849.0, 1738.6, 1602.4, 1527.1, 1498.8, 1456.8, 1437.9, 1353.2, 1282.3, 1207.5, 1169.9, 1136.6, 1075.7, 1004.8, 915.7, 854.2, 746.2, 699.1, 638.2. HRMS (+ESI) calculated for MH^+ 436.1503 and observed 436.1524.

[Bis-(3-nitro-benzyl)-amino]-phenyl-acetic acid (4). Compound **3** (0.100 g, 230 μmol) was dissolved in a mixture of MeOH (5 mL) and THF (2 mL), and sonicated for 5 min. Potassium hydroxide (KOH, 0.129 g, 2.30 mmol) was dissolved in MeOH (0.5 mL) and deionized water (0.5 mL). The KOH solution was added to the solution of compound **3** solution dropwise over 10 min at room temperature, and the sealed reaction vessel was placed in the dark for 36 h. After solvent removal, 2 g of crushed ice was added, and the pH was adjusted to ~5 with dilute HCl. The product was extracted into EtOAc (2×25 mL), washed with saturated NaCl, and dried over Na_2SO_4. Solvent removal yielded a brown powder without additional purification (66.0 mg, 68.1%). TLC R_f = 0.68 (silica, 5:2 Et_2O/hexanes); mp = 143-144 °C. ^{1}H NMR (500 MHz, CD_3CN) δ 8.12 (s, 2 H), 7.97 (d, *J* = 8.2 Hz, 2 H), 7.67 (d, *J* = 7.6 Hz, 2 H), 7.50 (d, *J* = 7.3 Hz, 2 H), 7.43 (t, *J* = 7.9 Hz, 2 H), 7.38 (t, *J* = 7.5 Hz, 2 H), 7.30 (m, 1 H), 4.55 (s, 1 H), 4.00 (d, *J* = 14.6 Hz, 2 H), 3.83 (d, *J* = 14.6 Hz, 2 H); ^{13}C NMR (125 MHz) δ 173.6, 149.6, 143.3, 137.4, 136.4, 130.7, 130.6, 130.0, 129.7, 127.8, 123.3, 69.0, 56.0. FT-IR (diamond-ATR, cm^{-1}) 3078.3, 3036.5, 2921.3, 2851.7, 1711.7, 1587.3, 1522.6, 1448.7, 1347.1, 1213.5, 1185.8, 1135.2, 1089.0, 1028.7, 982.5, 927.1, 890.2, 858.1, 802.7, 733.7, 696.7, 669.0. HRMS (+ESI) calculated for MH^+ 422.1347 and observed 422.1325.

[Bis-(3-nitro-benzyl)-amino]-(3-nitro-phenyl)-acetic acid (5, PC1). Compound **4** (66.0 mg, 0.157 mmol) was dissolved in concentrated sulfuric acid (3.00 mL, 55.2 mmol) using sonication. Concentrated nitric acid (0.100 mL, 1.17 mmol) was added drop wise to the mixture at 0 °C, and the sealed reaction vessel was placed in the dark

for 1 h at 0 °C. The resultant reaction mixture was added dropwise to ice (50 g), and the product was extracted into EtOAc (2×50 mL). The combined organics were washed with saturated NaCl (15 mL), dried over Na_2SO_4, and the solvent was removed to yield an orange powder without additional purification (66.7 mg, 91.3 % yield). TLC R_f = 0.27 (silica, 5:2 Et_2O/hexanes); mp 117-118 °C dec. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1 H), 8.24 (d, *J* = 8.2 Hz, 1 H), 8.17 (s, 2 H), 8.12 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 1 H), 7.61-7.69 (m, 3 H), 7.53 (t, *J* = 7.9 Hz, 2 H), 4.74 (s, 1 H), 4.00 (d, *J* = 14.4 Hz, 2 H), 3.87 (d, *J* = 14.3 Hz, 2 H); ^{13}C NMR (125 MHz) δ 173.2, 148.5, 140.2, 137.0, 135.0, 135.6, 130.0, 129.8, 123.8, 123.6, 123.5, 122.9, 65.7, 54.4. FT-IR (diamond-ATR, cm^{-1}) 3087.5, 2925.6, 2851.7, 1739.4, 1619.9, 1531.9, 1458.0, 1347.1, 1310.2, 1273.2, 1227.6, 1195.0, 1167.2, 1135.2, 1098.3, 1042.9, 1010.3, 908.6, 839.6, 807.6, 728.8, 687.5, 673.4. HRMS (+ESI) calculated for MH^+ 467.1197 and observed 467.1174.

Powder X-ray Diffraction. PXRD data were collected on a Bruker-AXS D8-Advance diffractometer using Cu-Kα radiation with X-rays generated at 40 kV and 40 mA. Freshly prepared MOF-5 crystals were washed with a few drops of ethanol (EtOH) and blotted dry with a filter paper. A layer of parafilm was placed on the sample holder before the crystals were placed, a few drops of EtOH were added to prevent crystals from degradation. The sample was scanned at RT from 3° to 50° (2θ) in 0.05° steps at a scan rate of 2°/min. Simulated PXRD patterns from single crystal data were compared to PXRD patterns of MOF-5, to confirm the uniformity of the crystalline sample.

General Spectroscopic Methods. All aqueous solutions were prepared from Millipore BiopakTM Ultrafiltration Cartridge purified water. All organic solutions were prepared using spectroscopic grade solvents. UV-vis absorption spectra were obtained by taking sample solutions in 1.0 cm quartz cuvette at 23 °C with total volumes kept at 2 mL or 3 mL and recorded on Thermo Scientific Evolution 300 UV-vis spectrometer with inbuilt Cary winUV software. Photolysis was carried at 23 °C in 1.0 cm quartz cuvette illuminated by 3 W UV LED (Mouser Electronics, 365 nm, 200 mW) powered by a 700 mA LuxDrive FlexBox using a variable DC source set at 12 VDC. Rate of photolysis and photoproducts were analyzed using LC/MS (Single Quadrupole, Agilent Technologies) by monitoring at changes at 277 nm. GC/MS spectra were obtained from a Single Quadruple, Agilent Technologies 7890B GC system.

Quantum Efficiency and Photoproducts Determination. A 2 mL solution of **PC1** (2.50 mM) or **PC2** (4.76 mM) in MeOH containing 2.5% H_2O were prepared from 15 mM stock solutions and irradiated for 30, 60, 120, 300, 420, and 600 s. A separate 2 mL solution was used for each data collection. Samples were subjected to LC-MS analysis with ketoprofen (5 mM), as internal standard. The quantum efficiency was calculated using established procedures.[4] All samples were eluted with an isocratic mixture of 95:5 H_2O:CH_3CN containing 5 mM NH_4HCO_3 for **PC1**, or 0.5% formic acid for **PC2** at a flow rate of 0.3 mL/min. The compounds corresponding to the individual peaks in the LC of both compounds were identified by m/z values.

Guest Loading, Trapping and Release.

CVMOF. Freshly prepared MOF-5 (75.0 mg, 97.4 μmol) was washed with EtOH, blotted dry with filter paper and transferred into an EtOH solution of crystal violet (CV) (4 mL, 65.3 mM, 90% saturated). The mixture was kept in dark for 1 d at room temperature before the crystals were isolated and blotted dry with filter paper.

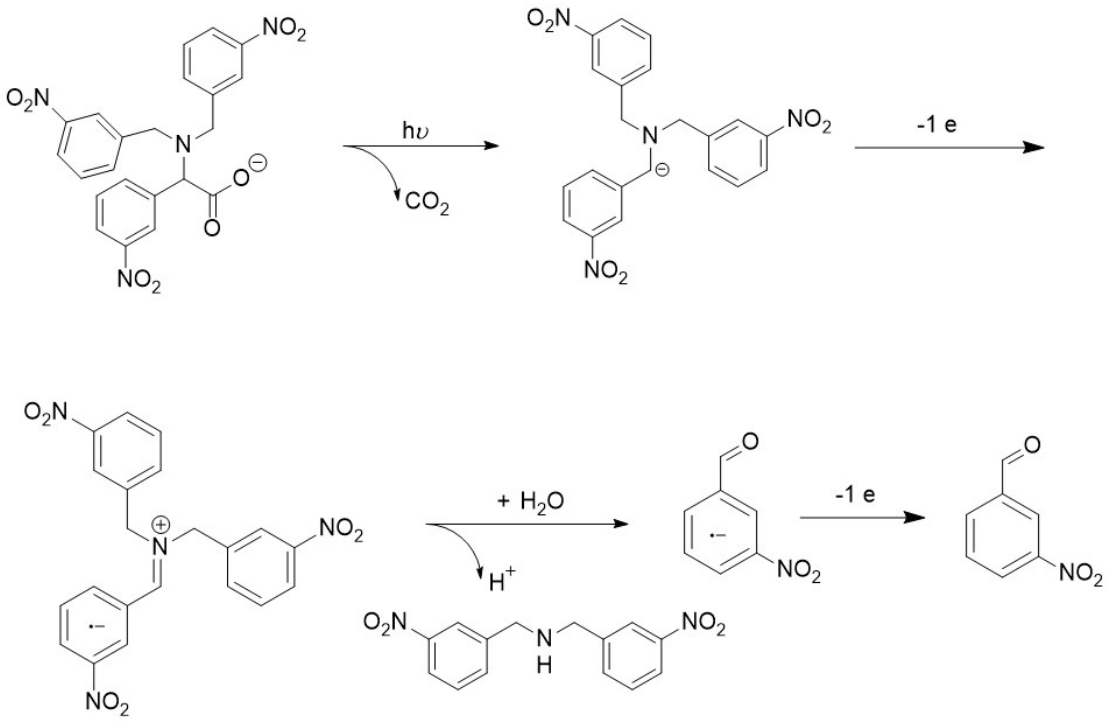
MOF Capacity Determination. The amount of CV encapsulated in CVMOF was quantified by digesting 2.0 mg of the MOF in 20 mL of EtOH with 10 μL concentrated HCl. The absorbance at 580 nm of the digested solution was recorded, and CV concentration was calculated with a calibration curve. Three trials gave an average loading capacity of 100 mg/g MOF (10 wt%).

CVMOF@PC1. CVMOF (25 mg) was added to 5 mL of DMF solution of [bis-(3-nitro-benzyl)-amino]-(3-nitro-phenyl)-acetic acid (**PC1**) (15.4 mg, 0.0330 mmol), with the addition of *N*,*N*-diisopropylethylamine (DIPEA) (6.3 μL, 0.036 mmol), zinc nitrate hexahydrate (20.0 mg, 0.0672 mmol), and CV (10.0 mg, 0.0245 mmol). The mixture was placed in dark at room temperature for 48 h, before the crystals were blotted dry with filter paper, quickly washed with small amount of EtOH, and transferred into EtOH solution for future use.

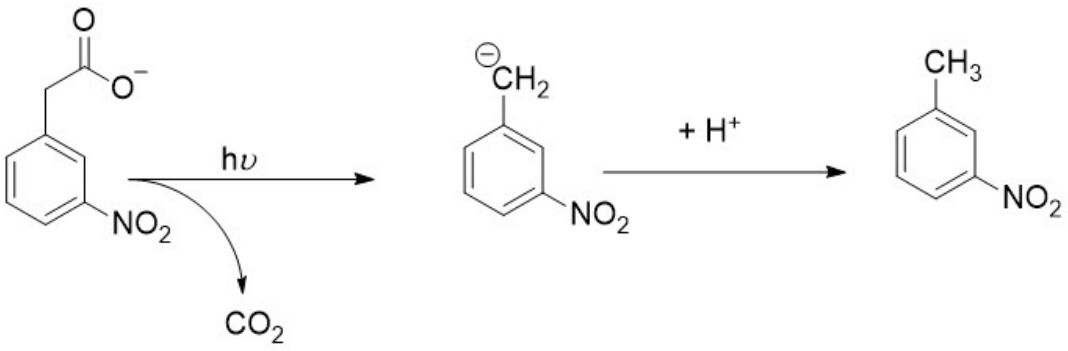
CVMOF@PC2. Guest loading and trapping with 3-nitrophenylacetic acid (**PC2**) (6.00 mg, 0.0331 mmol) was carried out analogously as **CVMOF@PC1** except the mixture was heated to 100 ºC at 1 ºC/min, kept at 100 ºC for 48 h, and cooled to room temperature at 0.25 ºC/min, and without the addition of DIPEA.

CVMOF@TPAA and CVMOF@DBA. Guest loading and trapping with TPAA (9.54 mg, 0.0331 mmol) and dibenzylamine (DBA) (6.53 mg, 0.0331 mmol) were carried out analogously to **CVMOF@PC2**.

CV Release from Capped Systems. Capped crystals (0.7 mg) were dispersed in 2.5 mL EtOH and the absorbance (450–650 nm) was recorded at 10 min increments for 90 min in the dark, and then at 10 min increments while continuously irradiating for 90 min. The supernatant was decanted and replaced with 2.5 mL EtOH and irradiation was continued for 30 min and the absorbance recorded. Under continuous irradiation, the decanting and replenishment procedure were repeated three times until no further absorbance increase was observed. Experiments were performed in triplicate.



Scheme S1. Proposed mechanism for the photolysis of **PC1**. There are two major products after decarboxylation and hydrolysis, bis(*m*-nitrobenzyl)amine and *m*-nitrobenzaldehyde. The probable oxidant is dissolved oxygen.



Scheme S2. Proposed mechanism of photolysis of **PC2**. The major photolysis product is 3-nitrotoluene.

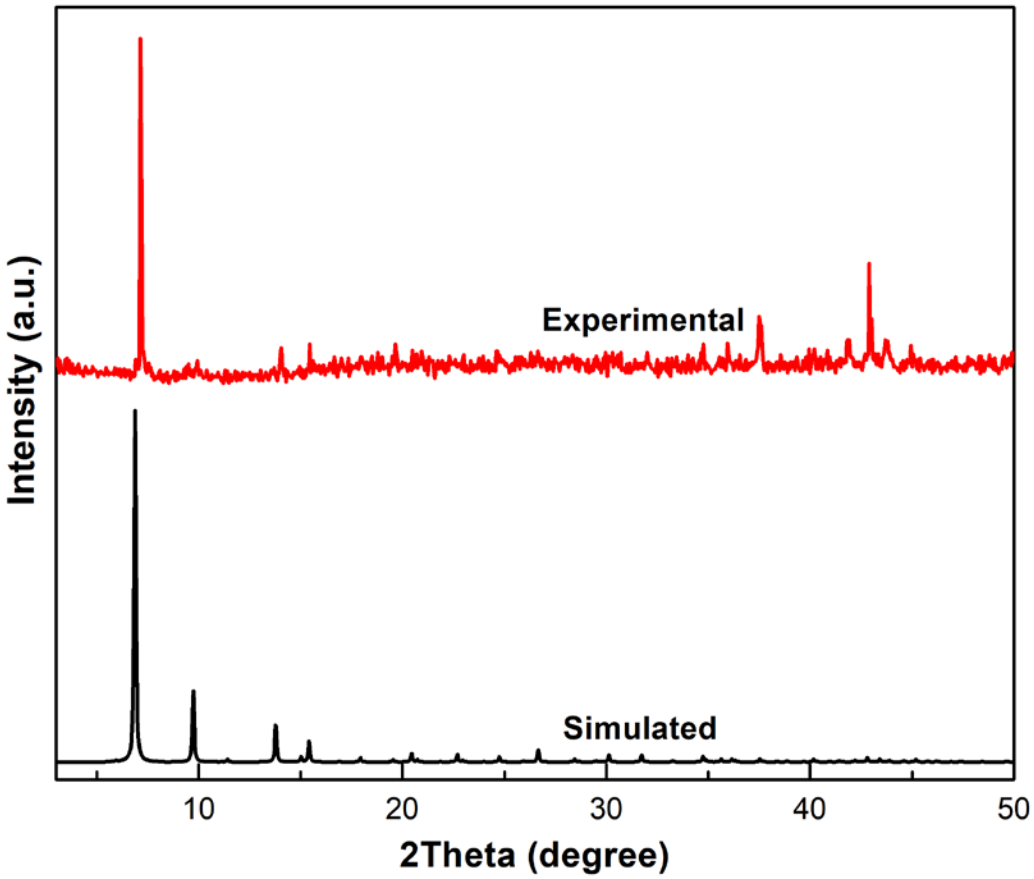


Figure S1. Powder X-ray diffraction patterns of MOF-5. Both experimental and simulated patterns from single crystal structures[3] are shown to confirm the phase purity. Details: freshly prepared MOF-5 crystals were washed with a few drops of ethanol and blotted dry with a filter paper. A layer of parafilm was placed on the sample holder before the crystals were placed, a few drops of ethanol were added to prevent crystals from degradation. The sample was scanned at RT from 3° to 50° (2θ) in 0.05° steps at a scan rate of 2°/min.

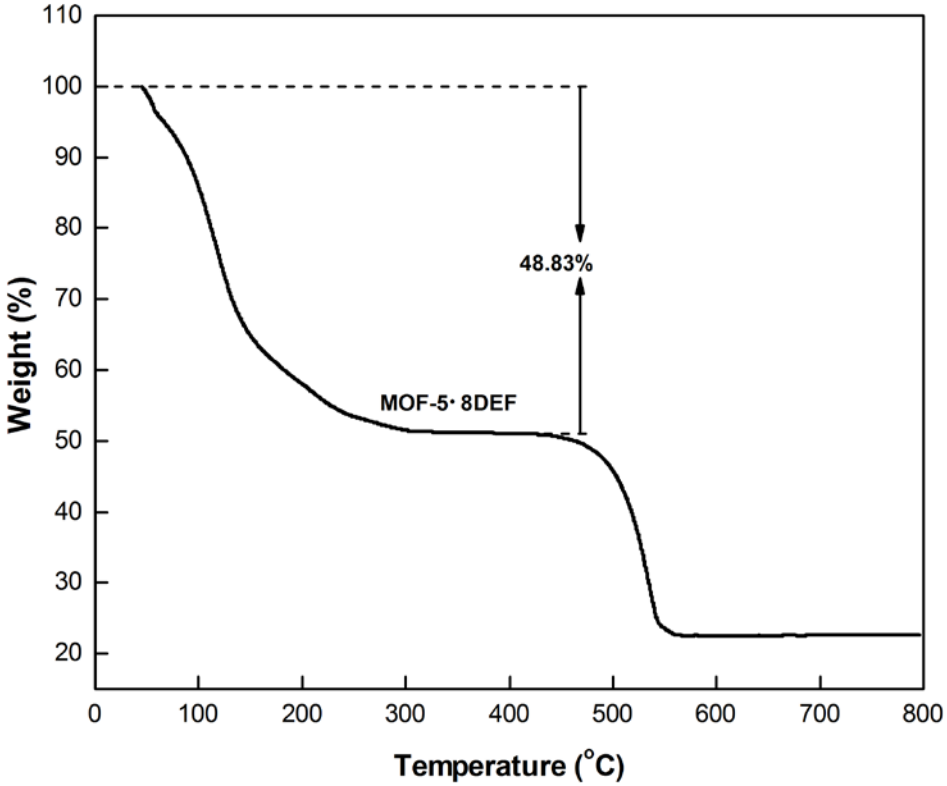


Figure S2. The thermogravimetric analysis (TGA) diagram of fresh prepared MOF-5. The solvent weight loss is calculated to 48.83%, and by using the formula $Zn_4O(C_8H_4O_4)_3 \cdot X(C_5H_{11}O)$, X can be calculated to be 8, meaning there are 8 DEF molecules per MOF unit cell. The curve also suggests MOF-5 can persist to 400 °C, which is a typical range for MOF-5.[5]

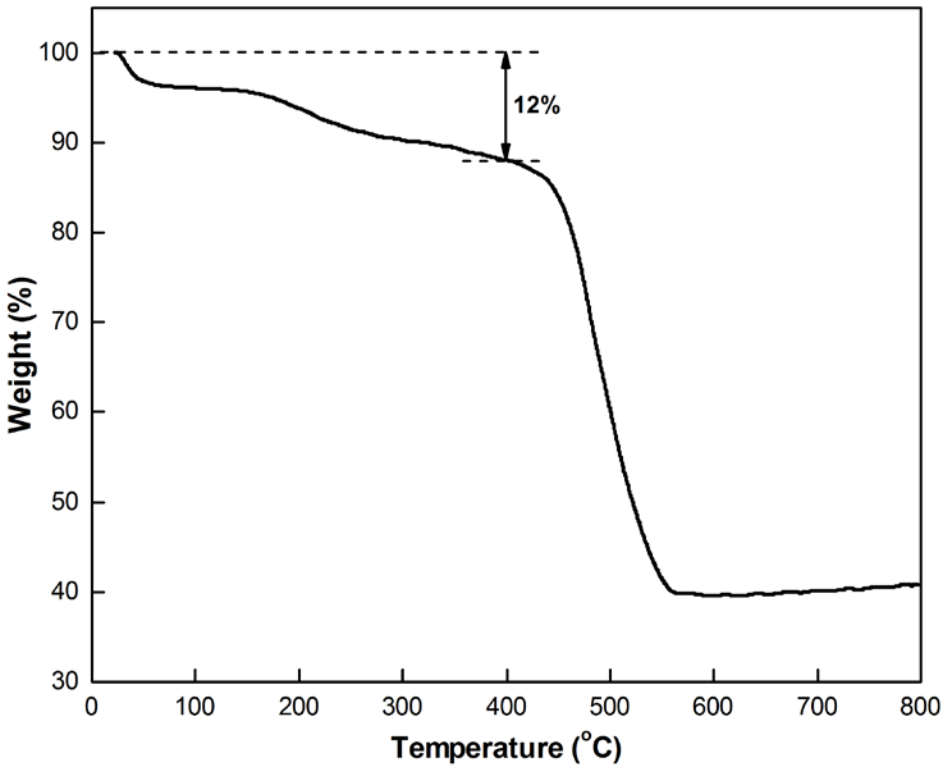


Figure S3. The thermogravimetric analysis (TGA) diagram of CVMOF after heated in 60 °C oven for 1 h. The weight loss before 400 °C can be attributed to the weight of loaded CV, which is 12%.

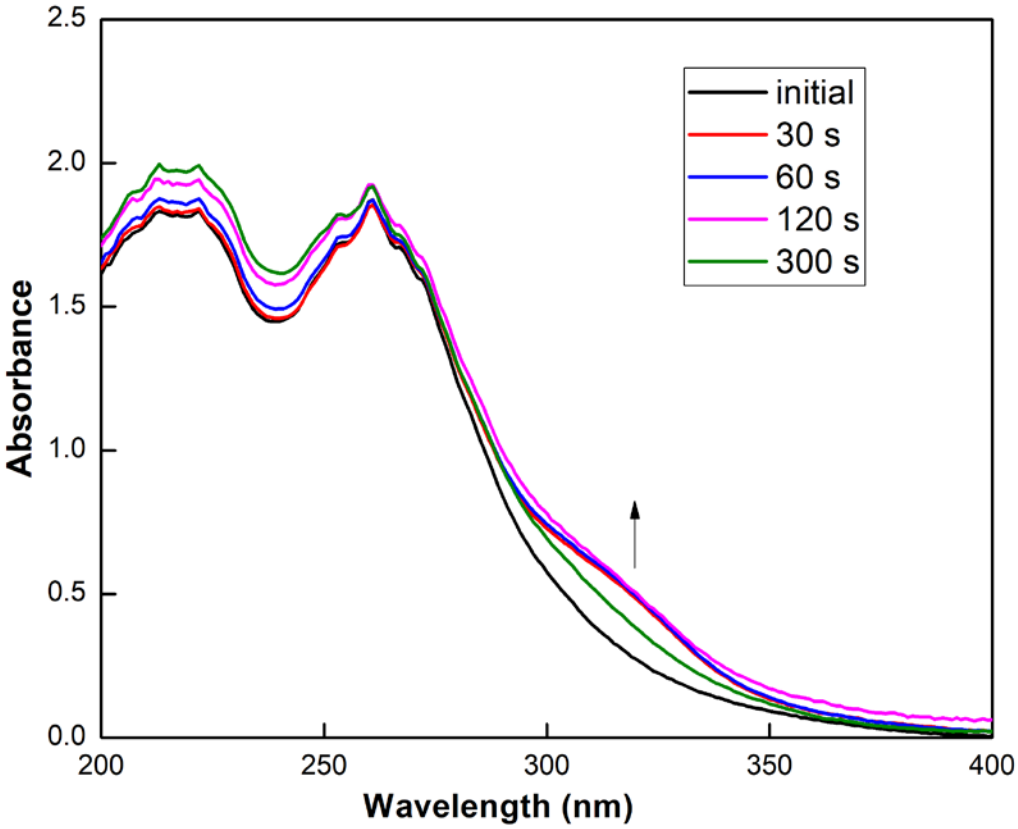


Figure S4. UV-Vis absorbance spectra showing photolysis of **PC1** (100 μM) in MeOH (2.5% water). Irradiation at 365 nm leads to the new bands forming in the absorption range from 300 to 350 nm, indicating the forming of photoproducts.

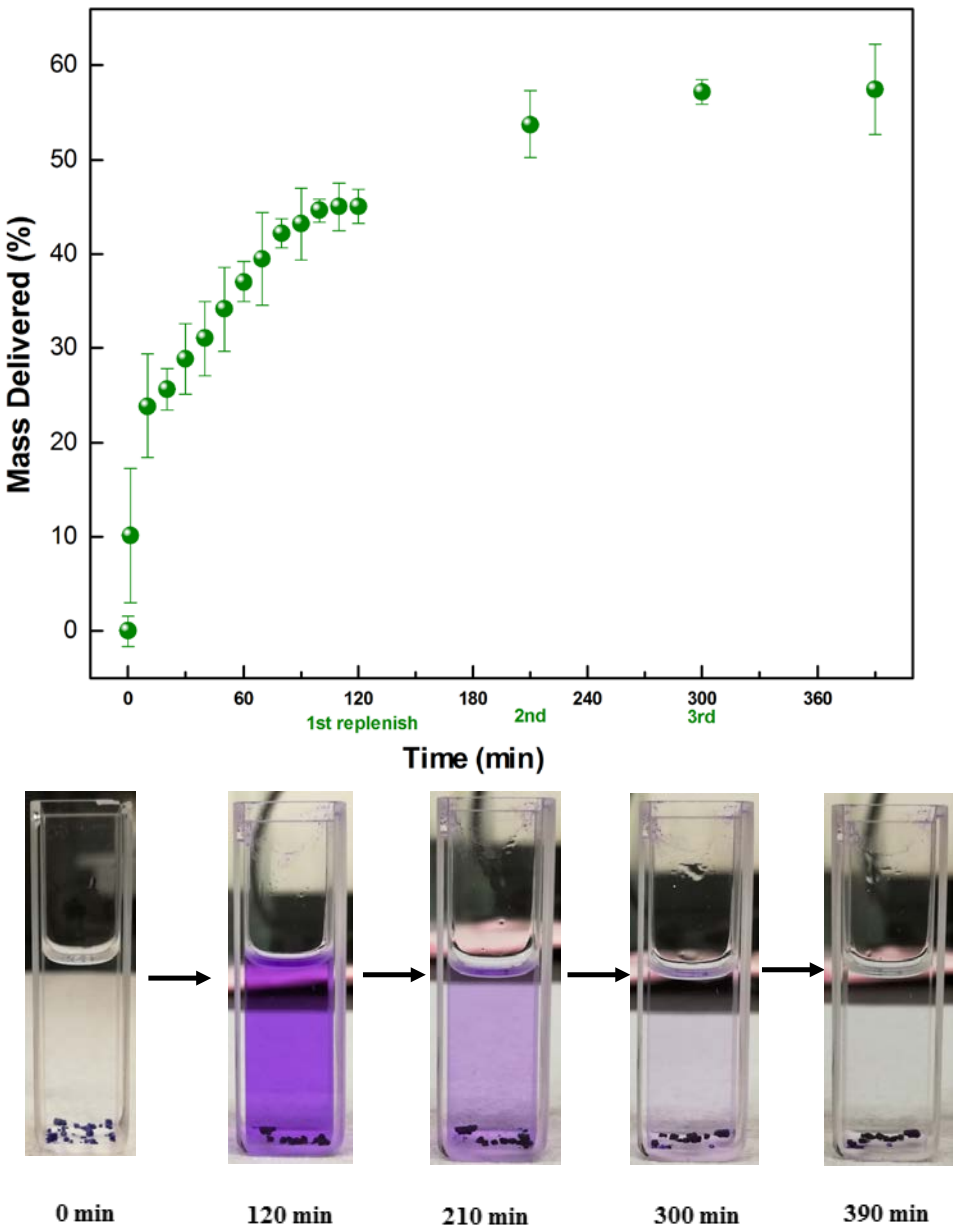


Figure S5A. CV release profile from CVMOF without capping. Details: cuvette was charged with 0.7 mg of crystals and filled with 2.5 mL EtOH. The absorbance was monitored by UV-Vis instrument at 580 nm. The system was kept in dark for 120 min until equilibrium reached, and supernatant was decanted and replenished with 2.5 mL fresh EtOH with absorbance recorded after 90 min. Three replenishment cycles were conducted until no further releasing was observed. **S5B**. Photos taken during the CV release process. Error bars represent standard deviation over three trials.

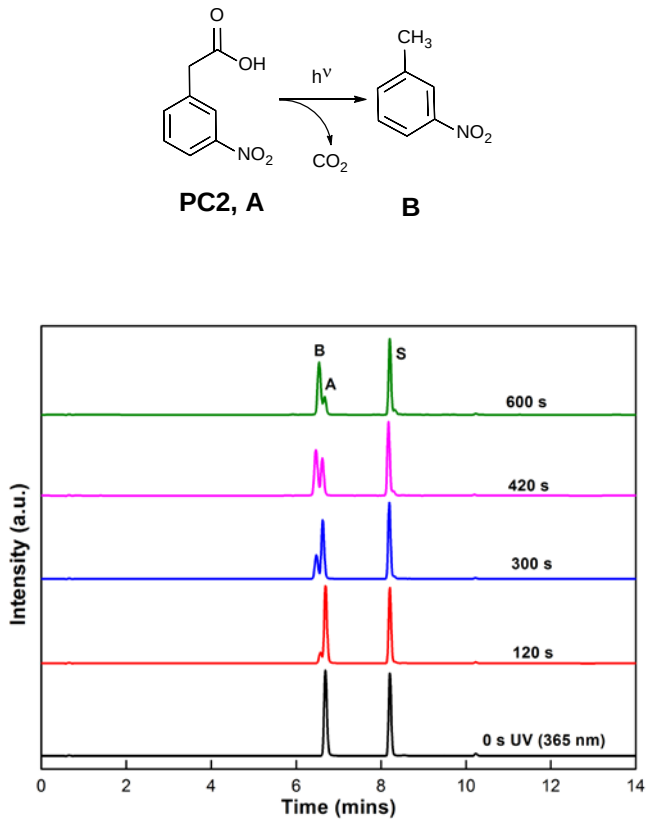


Figure S6. Photodecarboxylation of **PC2** in MeOH (2.5% water) with 365 nm light as measured by HPLC. Ketoprofen was used as internal standard (**S**). A decrease in the intensity of **PC2** (**A**) was accompanied by an increase in the intensity of the 3-nitrotoluene (**B**) photoproduct peak**.**

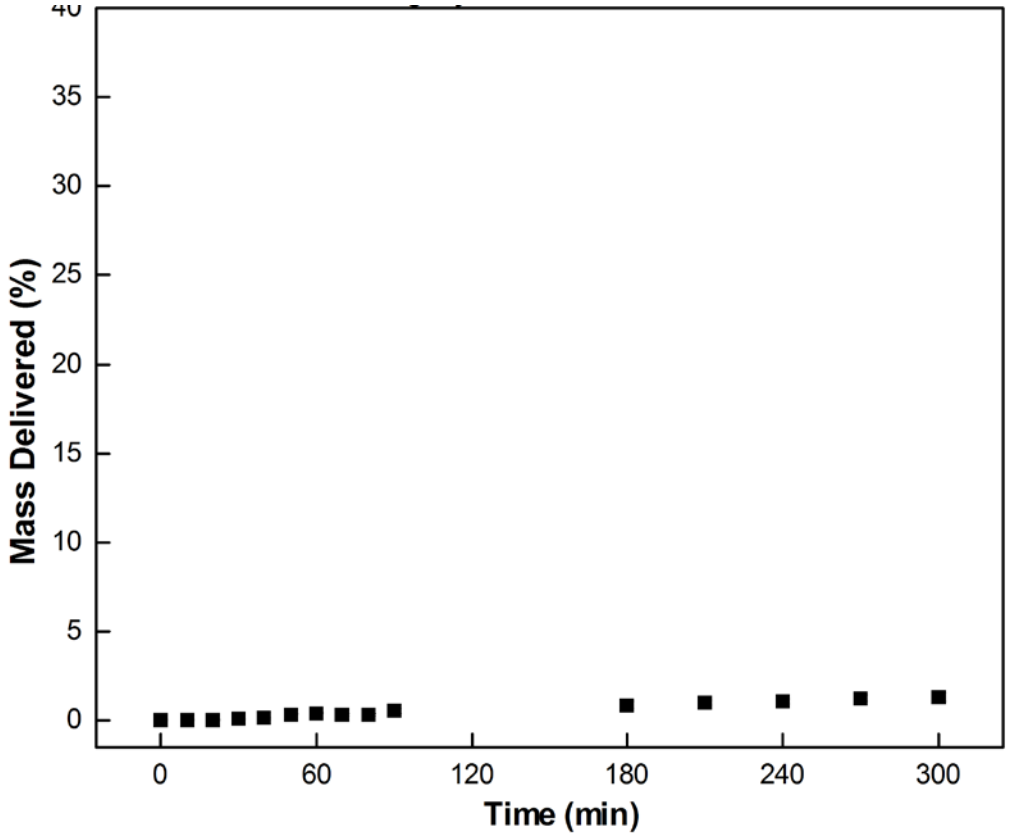


Figure S7. CV release profile from CVMOF@DBA. Details: UV cuvette was charged with 0.7 mg of capped crystals and filled with 2.5 mL EtOH. The absorbance was monitored by UV-Vis at 580 nm.

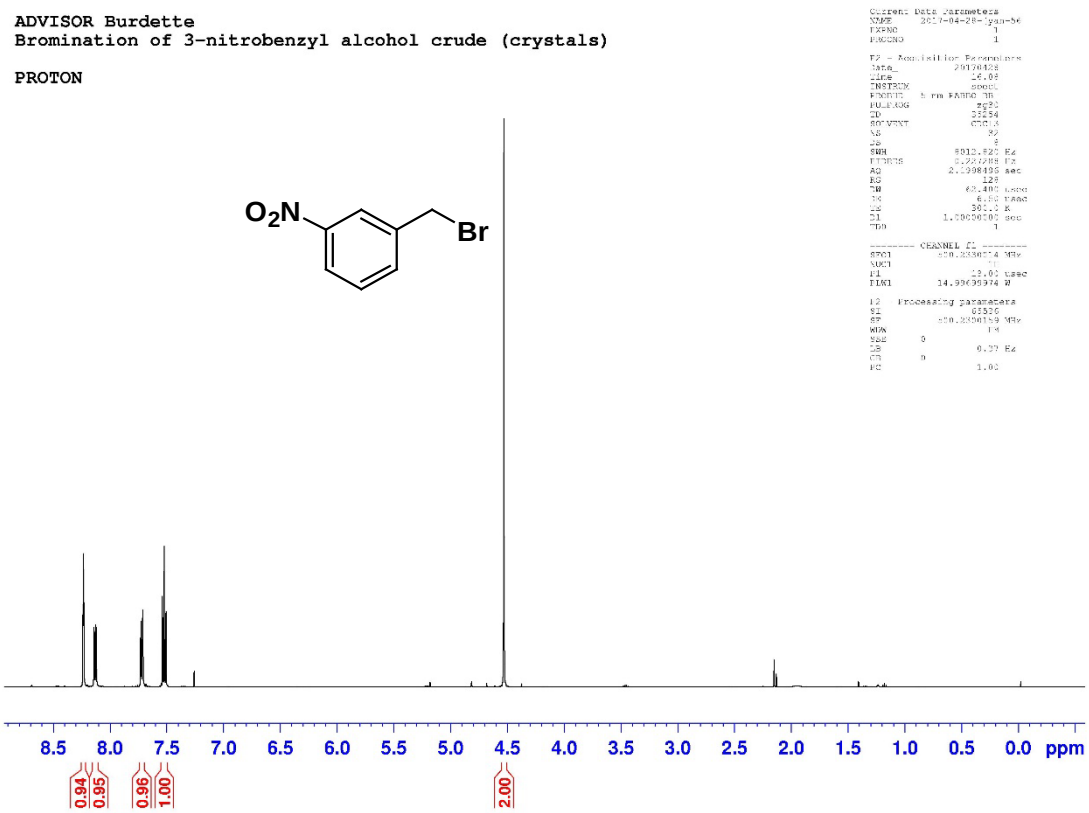


Figure S8. ^{1}H NMR of 1-bromomethyl-3-nitro-benzene (**1**).

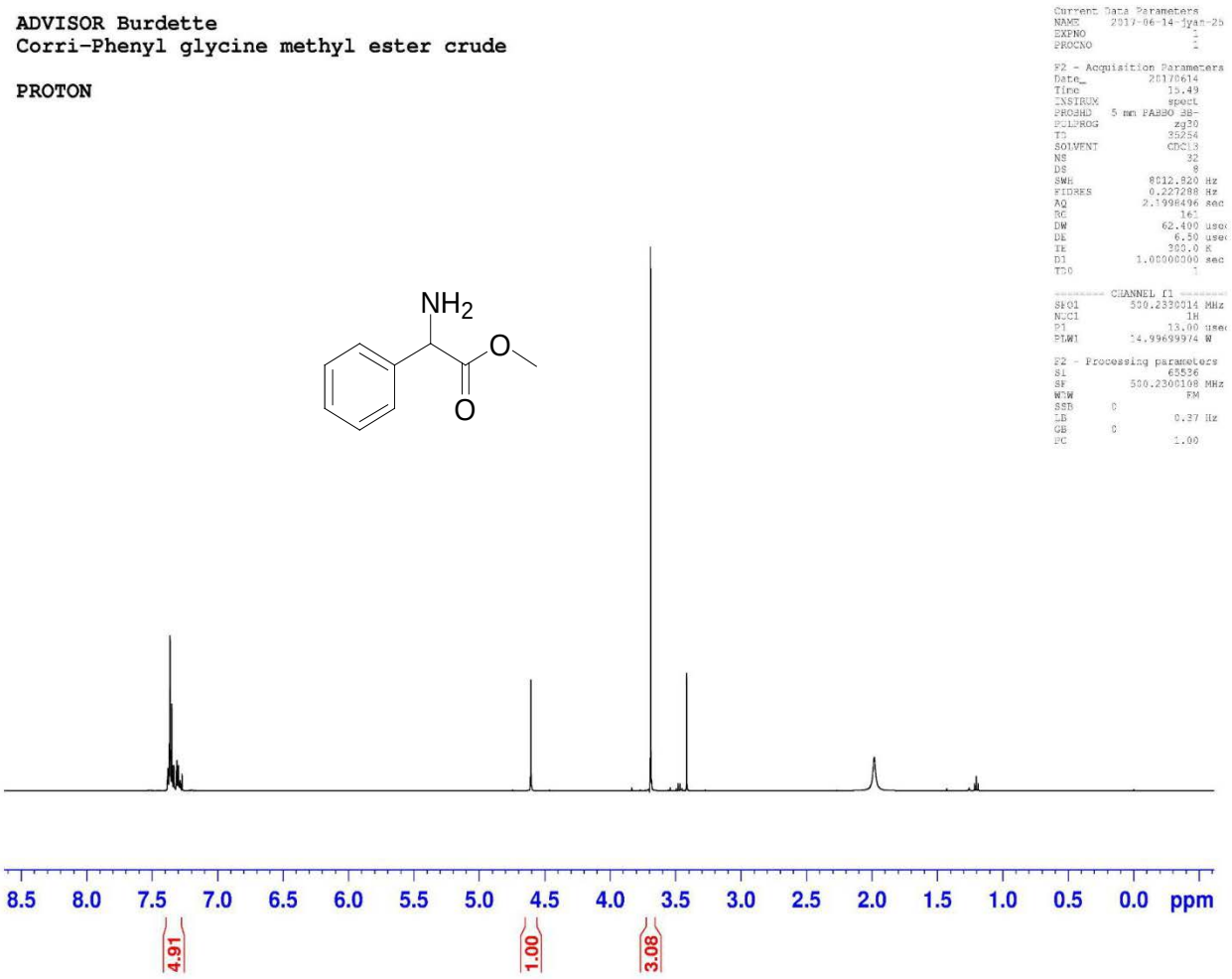


Figure S9. ^{1}H NMR of methyl (2S) aminophenyl ethanoate (**2**).

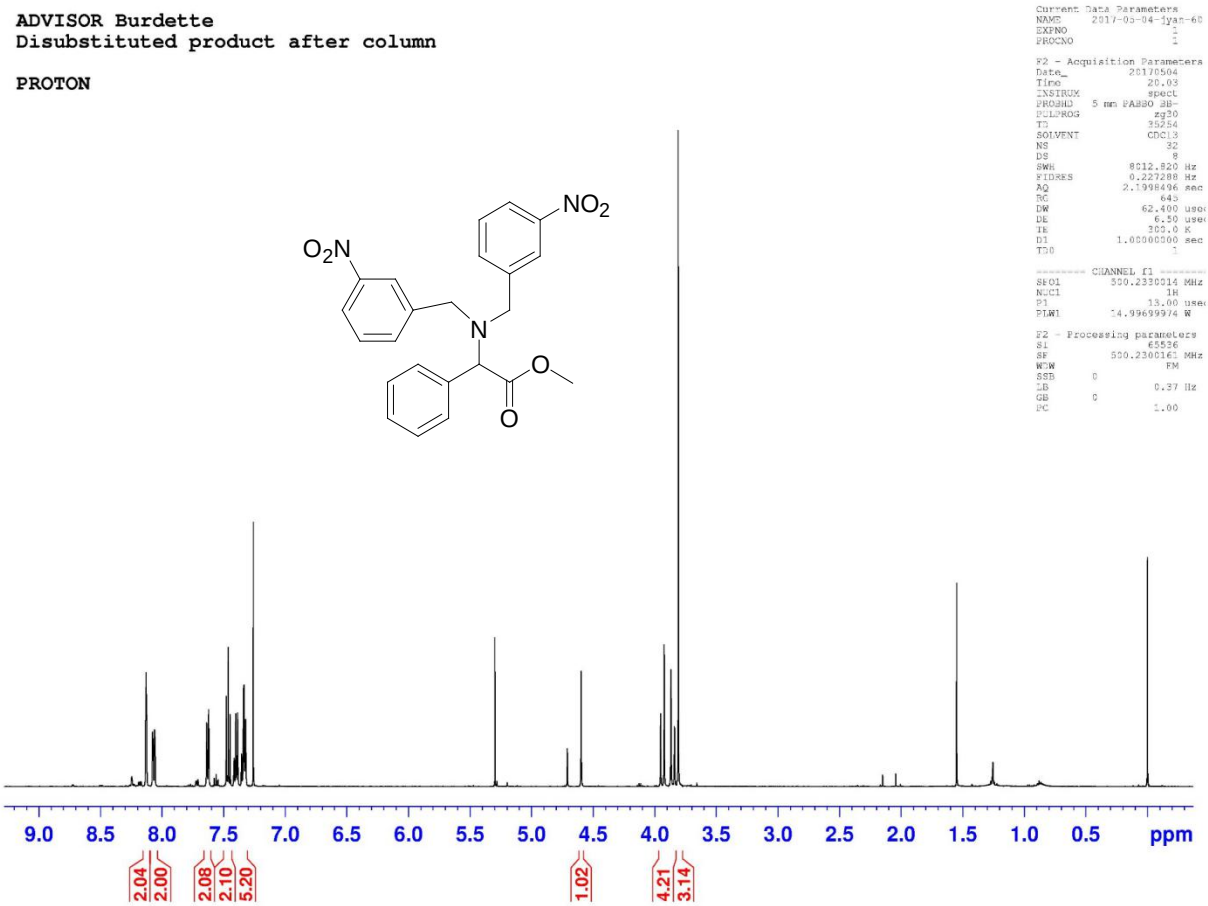


Figure S10. ^{1}H NMR of [bis-(3-nitro-benzyl)-amino]-phenyl-acetic acid methyl ester (**3**).

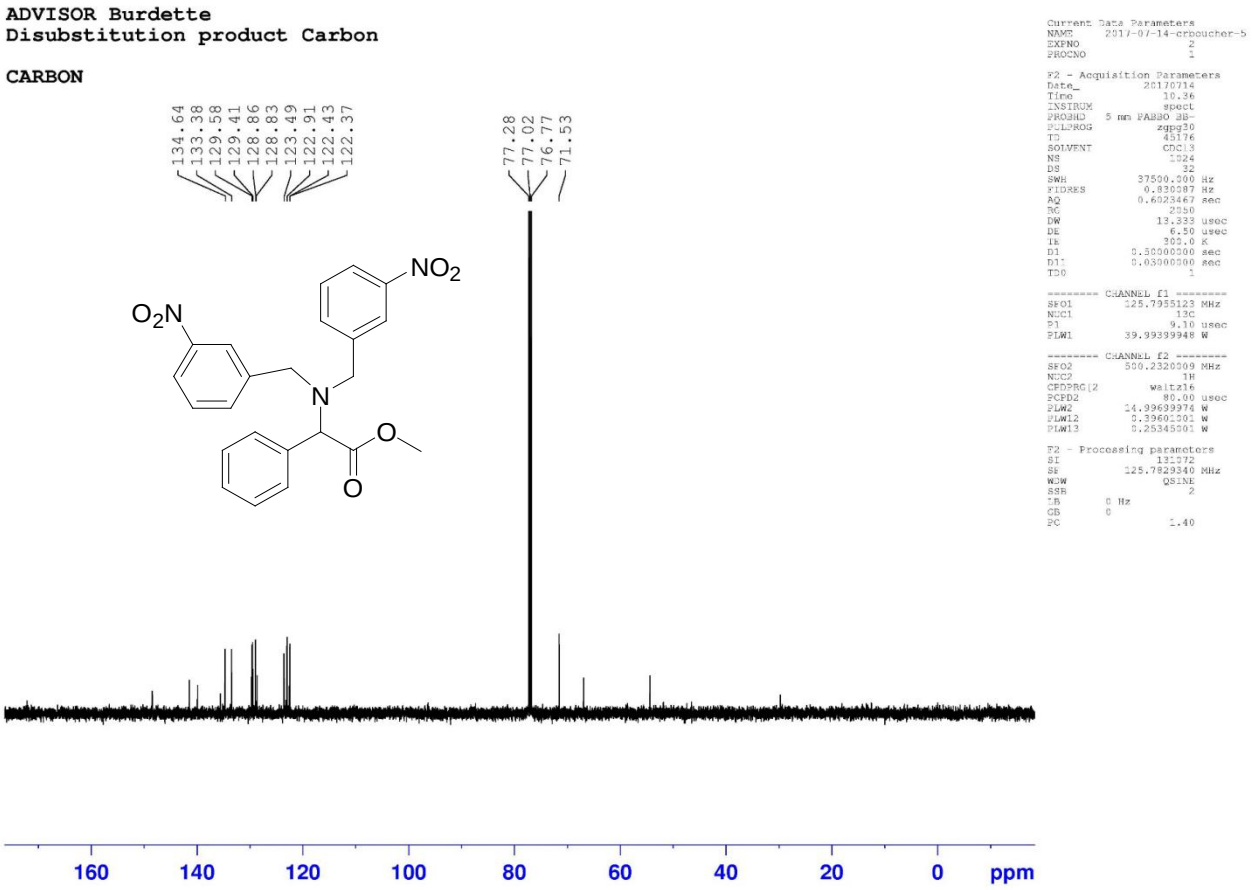


Figure S11. ^{13}C NMR of [bis-(3-nitro-benzyl)-amino]-phenyl-acetic acid methyl ester (**3**).

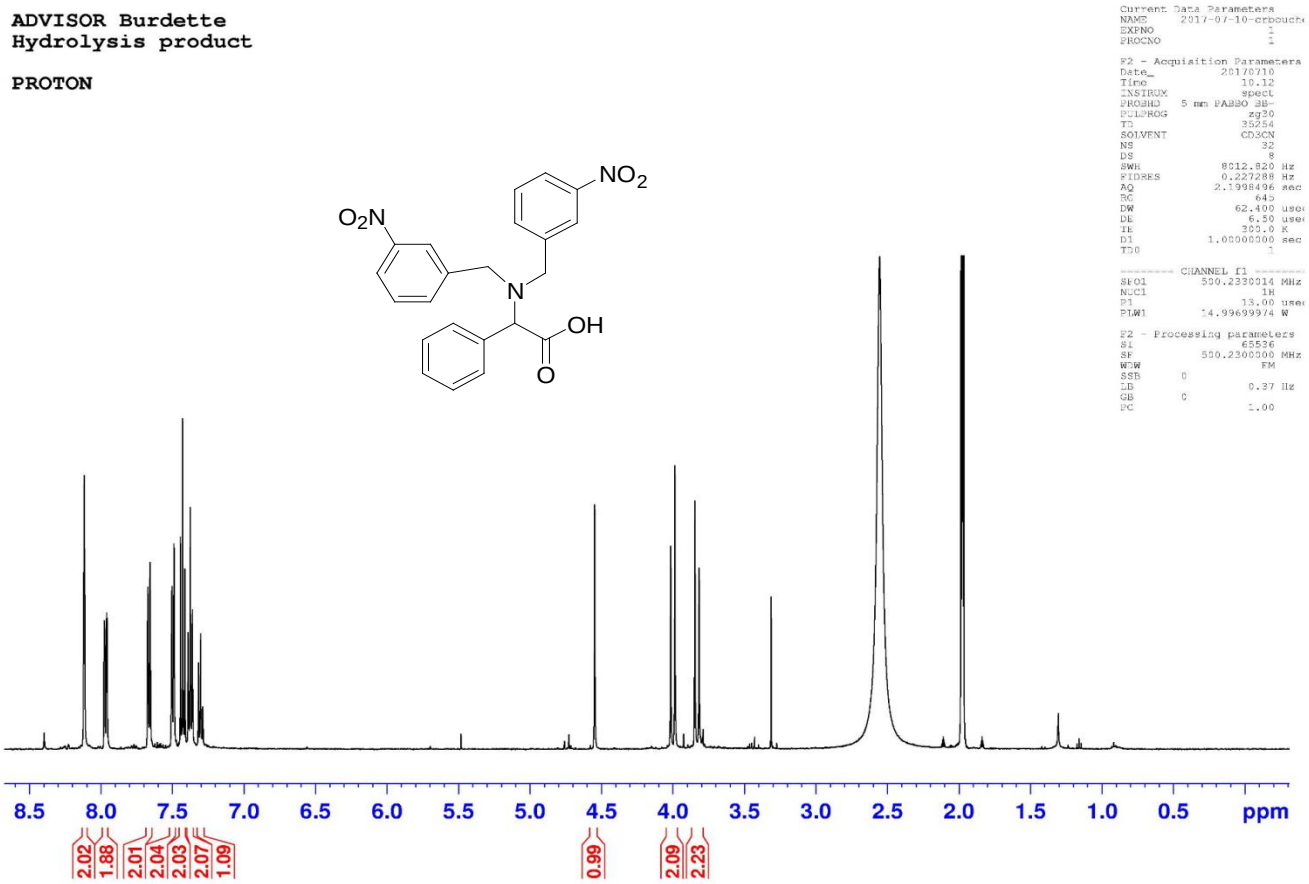


Figure S12. ^{1}H NMR of [bis-(3-nitro-benzyl)-amino]-phenyl-acetic acid (**4**).

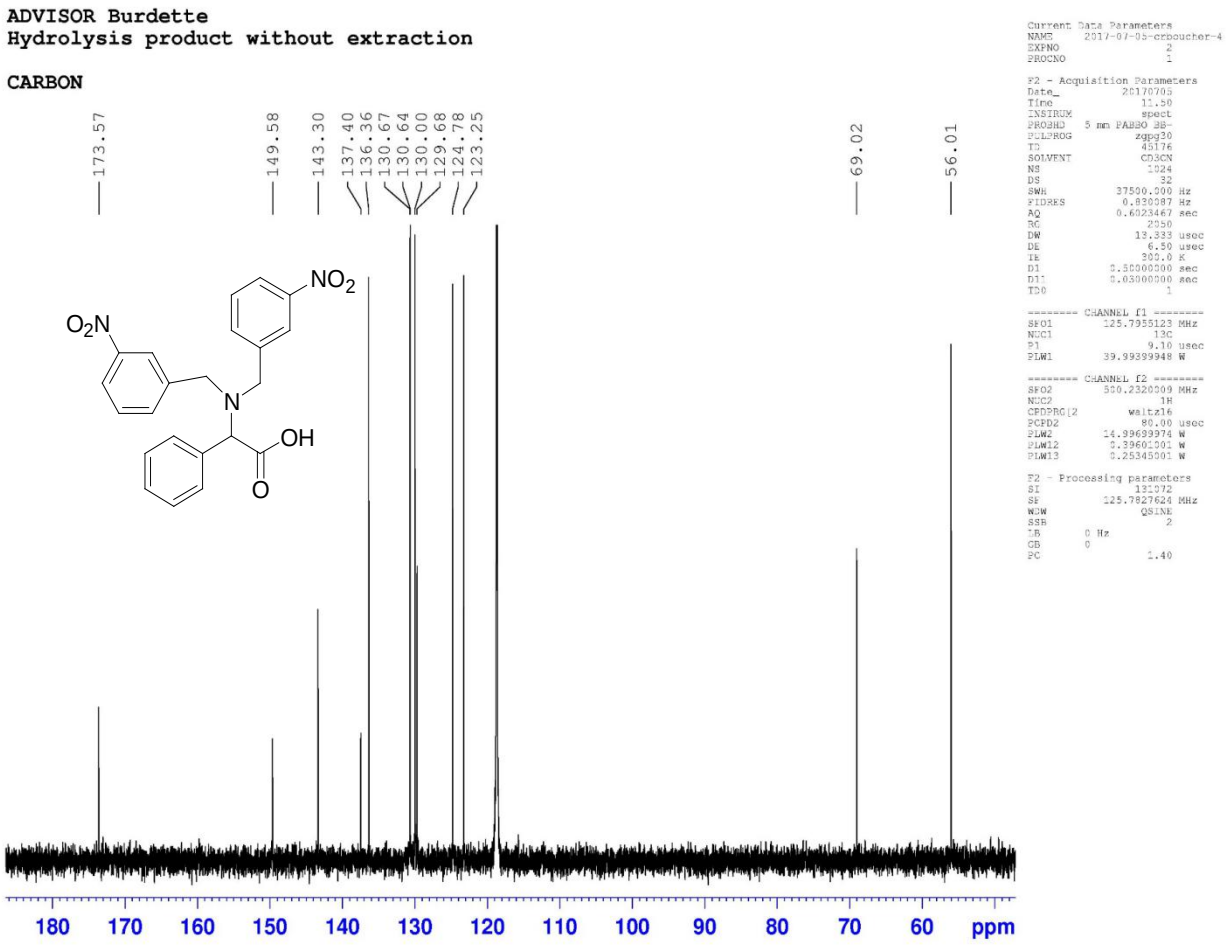


Figure S13. ^{13}C NMR of [bis-(3-nitro-benzyl)-amino]-phenyl-acetic acid (**4**).

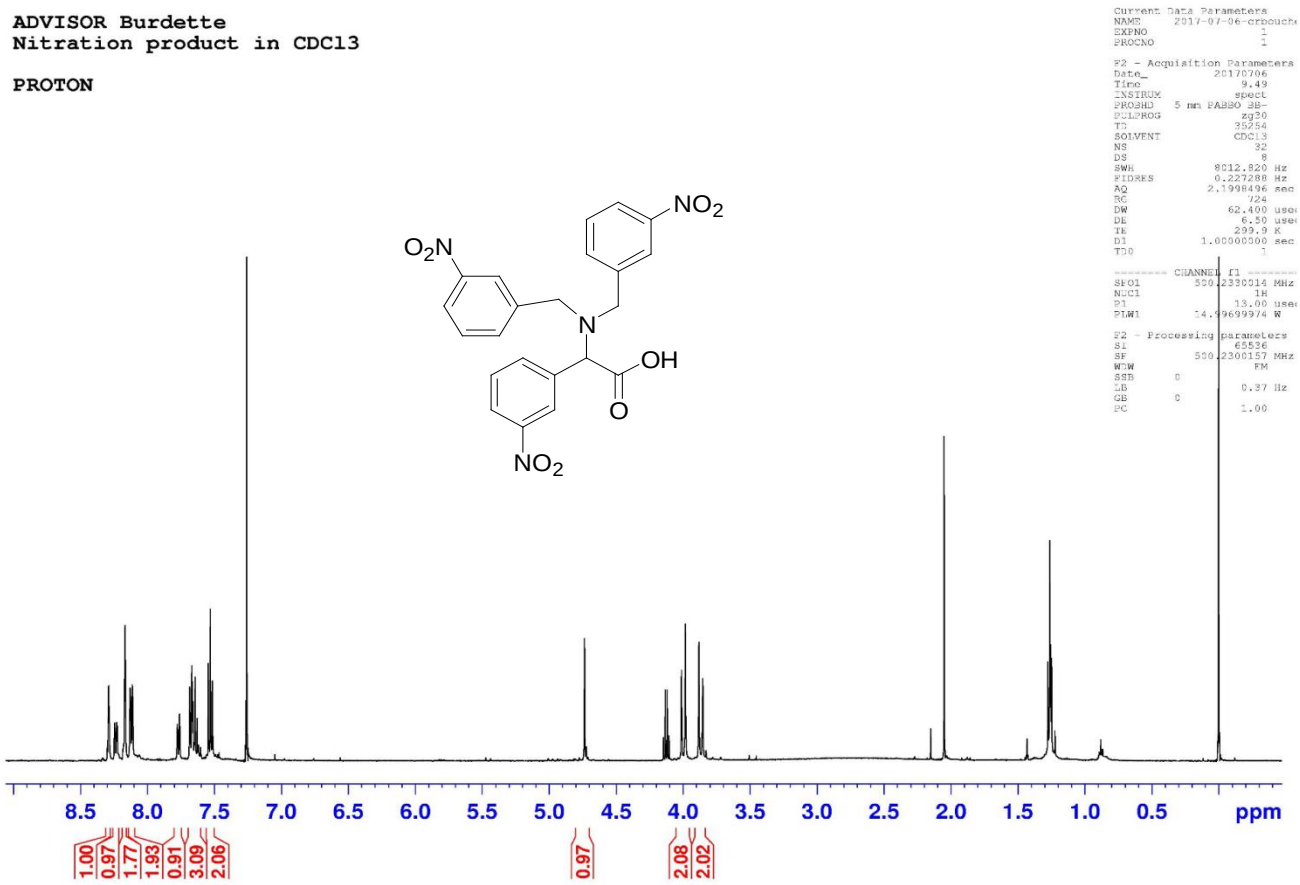


Figure S14. ^{1}H NMR of [bis-(3-nitro-benzyl)-amino]-(3-nitro-phenyl)-acetic acid (**PC1**).

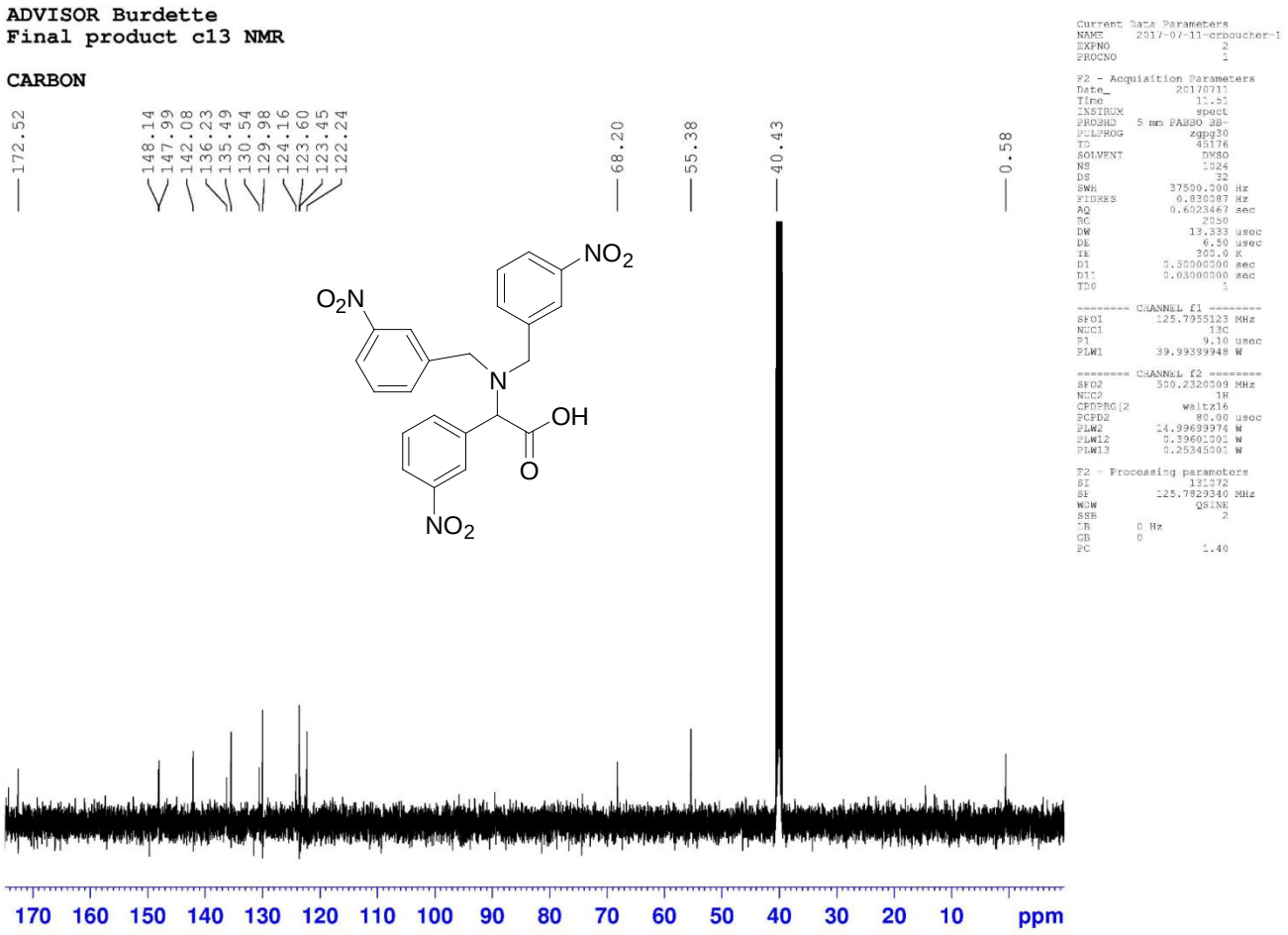


Figure S15. ^{13}C NMR of [bis-(3-nitro-benzyl)-amino]-(3-nitro-phenyl)-acetic acid (**PC1**).

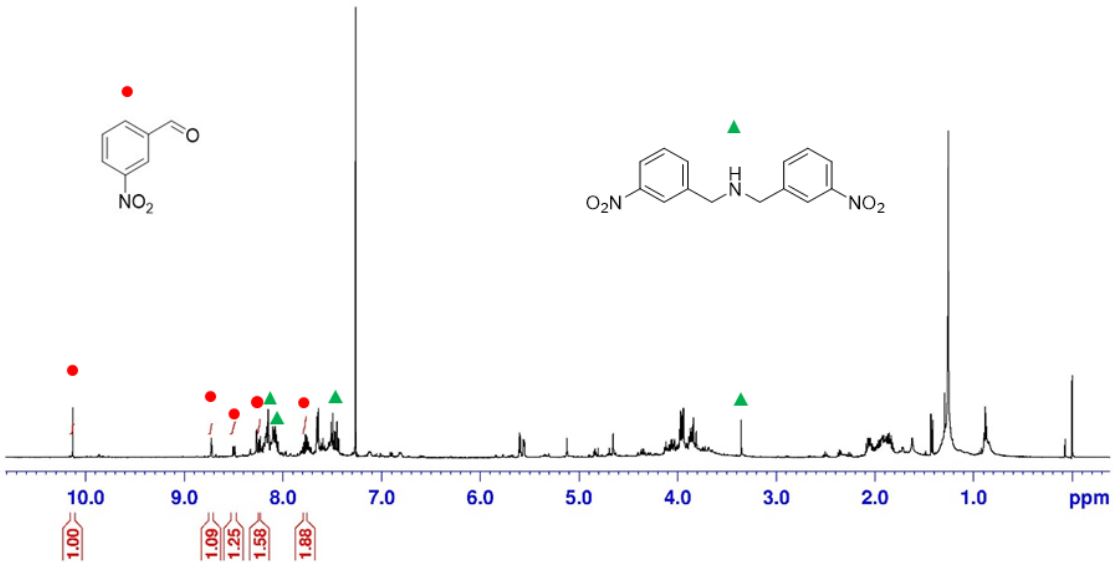


Figure S16. ^{1}H NMR spectroscopy of **PC1** in MeOH containing 2.5% H_2O (2 mL, 15 mM) after irradiation with 365 nm (LED, 3 Wcm^{-2}) for 20 mins. Solvent removal and NMR in $CDCl_3$ shows photoproducts *m*-nitrobenzaldehyde (**6**) and bis(*m*-nitrobenzyl)amine (**7**).

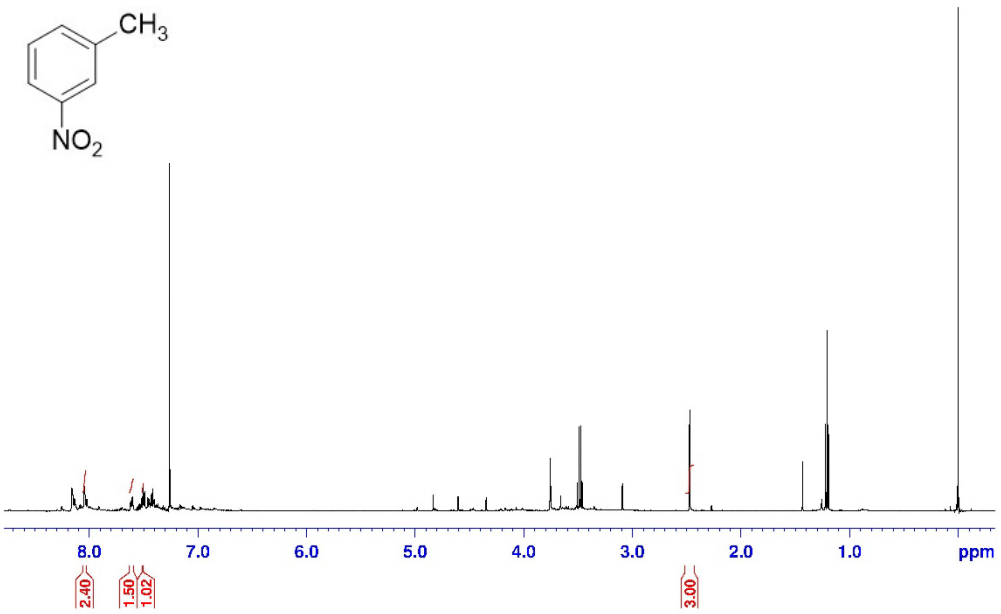


Figure S17. ^{1}H NMR of photoproducts after **PC2** photolysis. The major product 3-nitrotoluene can be clearly observed.

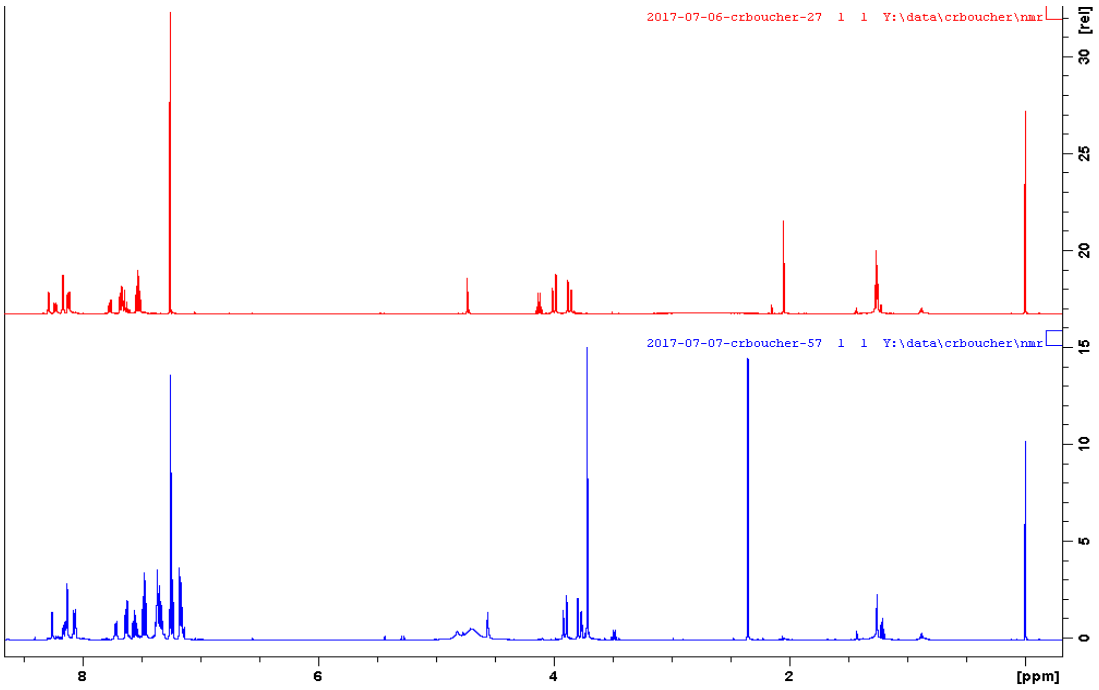


Figure S18. ^{1}H NMR spectroscopy showing thermal decomposition of compound **PC1**. Upper (red) spectrum is the original compound, and lower (blue) spectrum is after heating at 80 °C for 24 h. New peaks coming out after heating could belong to **PC1** degradation products.

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