

# 3D-Printed Eosin Y-Based Heterogeneous Photocatalyst for Organic Reactions

Cloé Delacourt,<sup>[a],[b]</sup> Abraham Chemtob,<sup>[b]</sup> Jean-Philippe Goddard,<sup>[a]</sup> Arnaud Spangenberg,<sup>[b]\*</sup> Morgan Cormier<sup>\*[a]</sup>

[a] Laboratoire d'Innovation Moléculaire et Applications (LIMA), UMR 7042  
Université de Haute-Alsace, Université de Strasbourg, CNRS  
3 rue Alfred Werner, 68093 Mulhouse  
E-mail: [morgan.cormier@uha.fr](mailto:morgan.cormier@uha.fr)

[b] Institut de Science des Matériaux de Mulhouse (IS2M) UMR 7361  
Université de Haute-Alsace, Université de Strasbourg, CNRS  
15 rue Jean Starcky, 68057 Mulhouse  
E-mail: [arnaud.spangenberg@uha.fr](mailto:arnaud.spangenberg@uha.fr)

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## 1. General methods

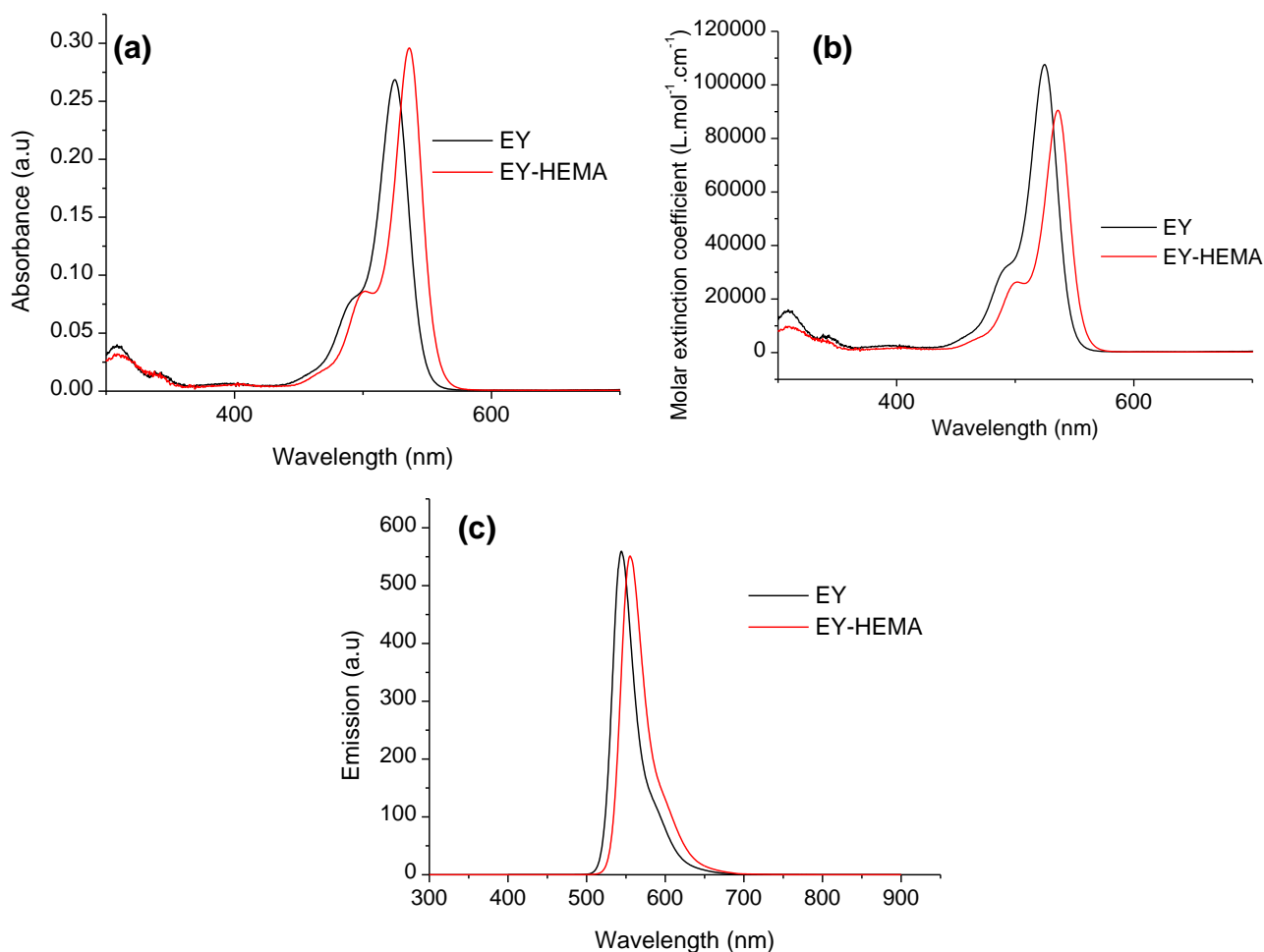
Unless otherwise stated, all the reagents were commercially available and used without further purification. Solvents were distilled and stored under N<sub>2</sub> in absence of light. Column chromatography was performed using Merck© Geduran© Si 60A silica gel (0.040–0.063 mm).

The absorption and excitation spectra of solutions were recorded using a Molecular Devices SpectraMax ID3 UV-Visible multimode microplate reader.

Liquid state <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400.16 and 100.62 MHz respectively or 500 MHz and 126 MHz on a Bruker 400 spectrometer or a Bruker 500 spectrometer, respectively. All spectra were reported in  $\delta$  (ppm) relative to TMS, with CDCl<sub>3</sub> as solvent. <sup>1</sup>H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quadruplet (q), dd (doublet of doublets), or m (multiplets).

All objects have been printed with a DLP 3D printer (Asiga Pico 2 HD 385) equipped with a 385 nm UV LED projector.

## 2. Absorption and emission spectra of EY and EY-HEMA



**Figure S1.** (a,b) UV/Vis spectroscopy (c) and fluorescence spectroscopy of EY ( $C = 2.9 \mu\text{M}$ ,  $\lambda_{exc} = 530 \text{ nm}$ ) and EY-HEMA ( $C = 2.9 \mu\text{M}$ ,  $\lambda_{exc} = 535 \text{ nm}$ ) in EtOH.

### 3. 3D Printing

#### 3.1. DLP 3D printer (Asiga Pico 2 HD 385)

The Asiga Pico 2 printer is a 3D printer that build objects from CAD data using Asiga Composer™ software. Equipped with an HD projector with a light source emitting at 385 nm, it employs the SAS (Slide And Separate) process to apply minimal forces to the model, thereby reducing the time required for the construction process. It features a print platform of 64 x 40 x 75 mm, a pixel size of 50 µm, and a printing speed of up to 40 mm/h.

#### 3.2. Configuration of printing resins with Asiga Pico 2

The Asiga Pico 2 printer is compatible with various resins, but printing an object requires an appropriate exposure time to cure each layer and ensure their adhesion to each other. Exposure times are automatically suggested by the Asiga Composer™ construction software. To do this, Composer™ collects two essential pieces of information : the LED intensity of the device and the polymerization table of the chosen material. The polymerization table is extracted from the material configuration file, typically created by measuring the thickness of the polymerized material based on the exposure time. The procedure involves depositing 250 µL of resin on a glass plate, exposed to irradiation for a specified time with a circular pattern of a 5 mm radius. Subsequently, the sample is rinsed with ethanol, and the thickness is measured using a caliper. This operation is performed for different exposure times at a given energy level.

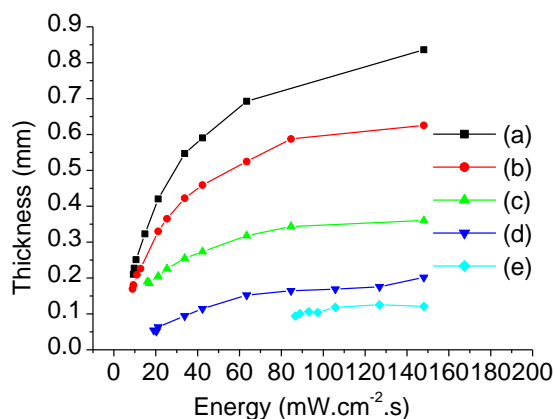
#### 3.3. Test Resin



**Figure S2.** Solubility of EY in 1g of PEGDA resin. **(a)** PEGDA<sub>250</sub>, BAPO (0.4 wt%), BBOT (0.16 wt%), EY (2 wt%), **(b)** PEGDA<sub>700</sub>, EtOH (2 wt%), BAPO (0.4 wt%), BBOT (0.16 wt%), EY (4 wt%), **(c)** PEGDA<sub>700</sub>, EtOH (10 wt%), BAPO (0.4 wt%), BBOT (0.16 wt%), EY (4 wt%)

#### 3.4. EY and EY-HEMA as a photoabsorber

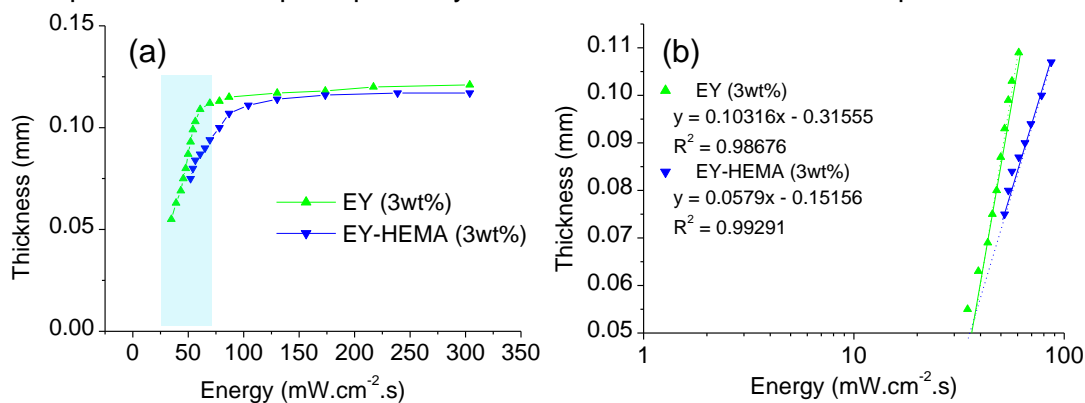
Based on the experimental measurements obtained during the resins configuration for the creation of Asiga's polymerization table, it is possible to plot the calibration curve of thickness as a function of energy for resins with different eosin compositions. Each formulation is composed of PEGDA, EtOH (10 wt%) and BAPO (0.4 wt%) with different weight percentage of EY (0.8 – 4 wt%).



**Figure S3.** Calibration curve with (a) 0.5 % of EY, (b) 0.8 % of EY, (c) 2 % of EY, (d) 3 % of EY, (e) 4 % of EY as photoabsorber (irradiance maintained at  $4.23 \text{ mW.cm}^{-2}$ ).

### 3.5. Jacobs Working Curves

For a specific combination of photopolymerizable materials and absorbers, we need to determine the Jacobs' working curve before running the DLP printing with this material. This curve illustrates the correlation between light intensity and the required exposure time to solidify a photopolymerizable material. The experimental measurements obtained during calibration enable the definition of Jacobs' working curve, encompassing all measured values before reaching the maximum thickness plateau. Using a semi-logarithmic plot of the thickness  $C_d$  as a function of the exposure energy  $E$  ( $\text{mW.cm}^{-2}\text{s}^{-1}$ ), the depth of light penetration  $D_p$  and the critical exposure energy  $E_c$  (i.e the minimum energy dose to form a film) can be determined as the slope and x-intercept respectively. Data for each formulation are reported in table S1.



**Figure S4.** (a) Calibration curve, (b) Jacobs' working curve of EY (3 wt%) and EY-HEMA (3 wt%) with an irradiance maintained at  $4.23 \text{ mW.cm}^{-2}$ .

### 3.6. Characteristics of EY and EY-HEMA resins

**Table S1.** Characteristics summary of EY and EY-HEMA resins.

Resin composition (40g)	PEGDA <sub>700</sub> , EtOH (10 wt%), BAPO (0.4 wt%), EY (3 wt%)	PEGDA <sub>700</sub> , EtOH (10 wt%), BAPO (0.4 wt%), EY-HEMA (3 wt%)
$n_{\text{EY or EY-HEMA}}$ (mmol) <sup>[a]</sup>	1.73	1.53
$\epsilon_{\text{max}}$ ( $\text{L.mol}^{-1}\text{.cm}^{-1}$ ) <sup>[b]</sup>	107 588 (525 nm)	90 386 (537 nm)
$\epsilon_{385 \text{ nm}}$ ( $\text{L.mol}^{-1}\text{.cm}^{-1}$ ) <sup>[c]</sup>	2540	1370
$\eta$ (Pa.s) <sup>[d]</sup>	$68.10^{-3}$	$72.10^{-3}$
$E$ ( $\text{mW.cm}^{-2}\text{.s}$ ) <sup>[e]</sup>	34.7	52.1
$Th_{\text{min}}$ (mm) <sup>[f]</sup>	0.050	0.075
$Dp$ (mm) <sup>[g]</sup>	0.103	0.058

<b>Ec (mW.cm<sup>-2</sup>.s)</b> <sup>[h]</sup>	36	34
<b>Rp<sub>max</sub> (%.s<sup>-1</sup>)</b> <sup>[i]</sup>	4.27	4.55
<b>Conv<sub>max</sub> (%)</b> <sup>[j]</sup>	63	66

<sup>[a]</sup> amount of material, <sup>[b]</sup> molar extinction coefficient of EY and EY-HEMA at the maximum absorption wavelength, <sup>[c]</sup> molar extinction coefficient of EY and EY-HEMA at printing wavelength <sup>[d]</sup> viscosity, <sup>[e]</sup> received energy, <sup>[f]</sup> minimum thickness, <sup>[g]</sup> light penetration, <sup>[h]</sup> critical energy, <sup>[i]</sup> polymerization rate, <sup>[j]</sup> maximum conversion of polymerization

### 3.7. Printing parameters with Asiga Pico 2

The 3D model for printing is created by importing a Surface Tessellation Language (.stl) file into the Composer™ software. To generate the corresponding .stl file, we used the online library *Cults3D* (<https://cults3d.com/fr>). The stl file is provided as a distinct SI. When imported in the Composer™ software, the height of the stent is fixed at 2 cm.

As for the printing parameters, we chose to print a full support plate that covers the entire build platform. The Composer™ software provides various advanced settings that are automatically filled in by the software but can be modified by the user.

**Table S2.** 3D printing parameters summary of PCat 1 and 2.

	<b>PCat 1</b>	<b>PCat 2</b>
	PEGDA <sub>700</sub>	PEGDA <sub>700</sub>
Resin composition	EtOH (10 wt%), BAPO (0.4 wt%) EY (3 wt%)	EtOH (10 wt%), BAPO (0.4 wt%) EY-HEMA (3 wt%)
Light Intensity (mW/cm <sup>2</sup> )	17.41	29.50
Wavelength (nm)	385	385
Slice Thickness (mm)	0.05	0.075
Exposure time (s)	5.00	6.00
Burn-In Exposure Times (s) <sup>[a]</sup>	8.00	10.00
Burn-In Layers <sup>[b]</sup>	2	2
Separation Velocity (mm.s <sup>-1</sup> ) <sup>[c]</sup>	4.95	4.95
Heater Temperature (°C)	25	25
Build Time (h, min, s)	1 h, 55 min, 36 s	1 h, 6 min, 43 s

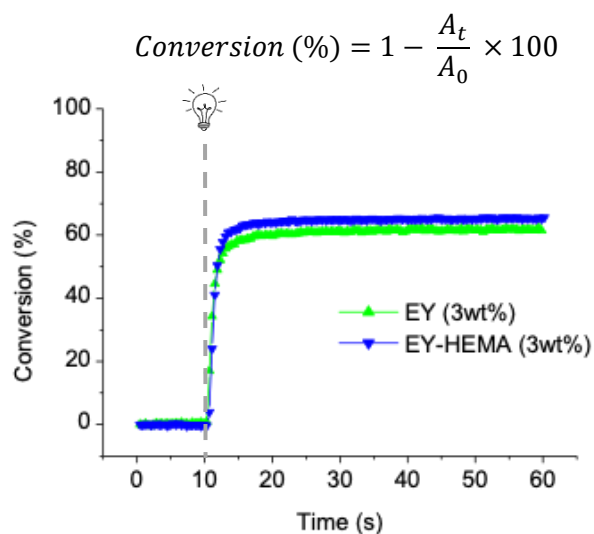
<sup>[a]</sup> Time during which the LED overexposes the resin during the creation of the support plate; <sup>[b]</sup> Number of overexposed layers during the creation of the support plate; <sup>[c]</sup> The speed at which the platform separates from the bottom of the tray.

## 4. Photopolymerization kinetics of EY and EY-HEMA based resin

We used the horizontal sampling chamber of the iS50 de Thermo Fisher Scientific spectrometer. A LED light beam with a wavelength of 365 nm (LC-L1V3, Hamamatsu) was directed into the spectrometer chamber using a flexible light guide positioned 5 cm from the

sample. To prevent solvent evaporation, the formulations were placed between a silicon wafer and a polypropylene film. On each sample, 4  $\mu\text{L}$  of the formulation were deposited on the silicon wafer.

FTIR spectra were recorded in transmission mode using an MCT detector in scan mode. This configuration allowed us to acquire 2 scans every 0.5 s, with a spectral resolution of 4  $\text{cm}^{-1}$ . The spectra were recorded in the range of 500 to 4000  $\text{cm}^{-1}$ . The conversion was calculated based on the peak area of the C=C double bond allylic stretching at 1630  $\text{cm}^{-1}$  ( $A_t$ ), with the C=O stretching of the acrylate at 1720  $\text{cm}^{-1}$  as the reference ( $A_0$ ). The conversion rate is directly calculated as follows:



**Figure S5.** Photopolymerization experiments by RT-FTIR using 3 wt% EY or 3 wt% EY-HEMA under LED 365 nm and 75  $\text{mW cm}^{-2}$  of incident irradiance

## 5. Determination of swelling index, gel content and EY-HEMA loading

- *Swelling Index*

One stent is weighed at constant weight ( $m_{\text{dry}}$ ) under vacuum pump. Then it is immersed in the solvent for 24 hours and weighed again ( $m_{\text{swell}}$ ) to determine the swelling index.

$$\text{swelling index (\%)} = \frac{m_{\text{swell}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100$$

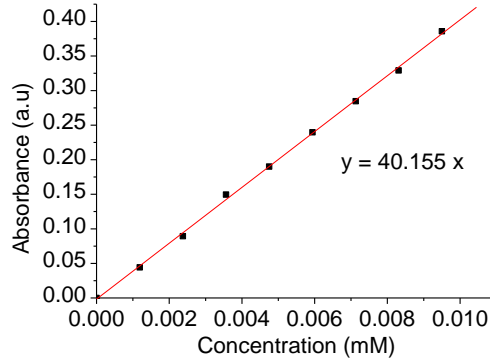
- *Gel Content*

A batch of 8 stents ( $m_i$ ) was washed by Soxhlet extraction with EtOH for 24h under reflux. After Soxhlet extraction, the batch of 8 stents is dried under the vacuum pump and then is weighed at constant weight ( $m_f$ ) to determine the gel content.

$$\text{gel content (\%)} = \frac{m_f}{m_i} \times 100$$

- *EY-HEMA loading*

The amount of EY-HEMA, before Soxhlet extraction, is estimated to 3% by weight of the batch of 8 stents (3% of  $m_i$ ). After Soxhlet extraction, the filtrate is diluted and analyzed by UV/Vis spectroscopy and the amount of EY-HEMA in the filtrate is determined ( $m_{lost}$ ).

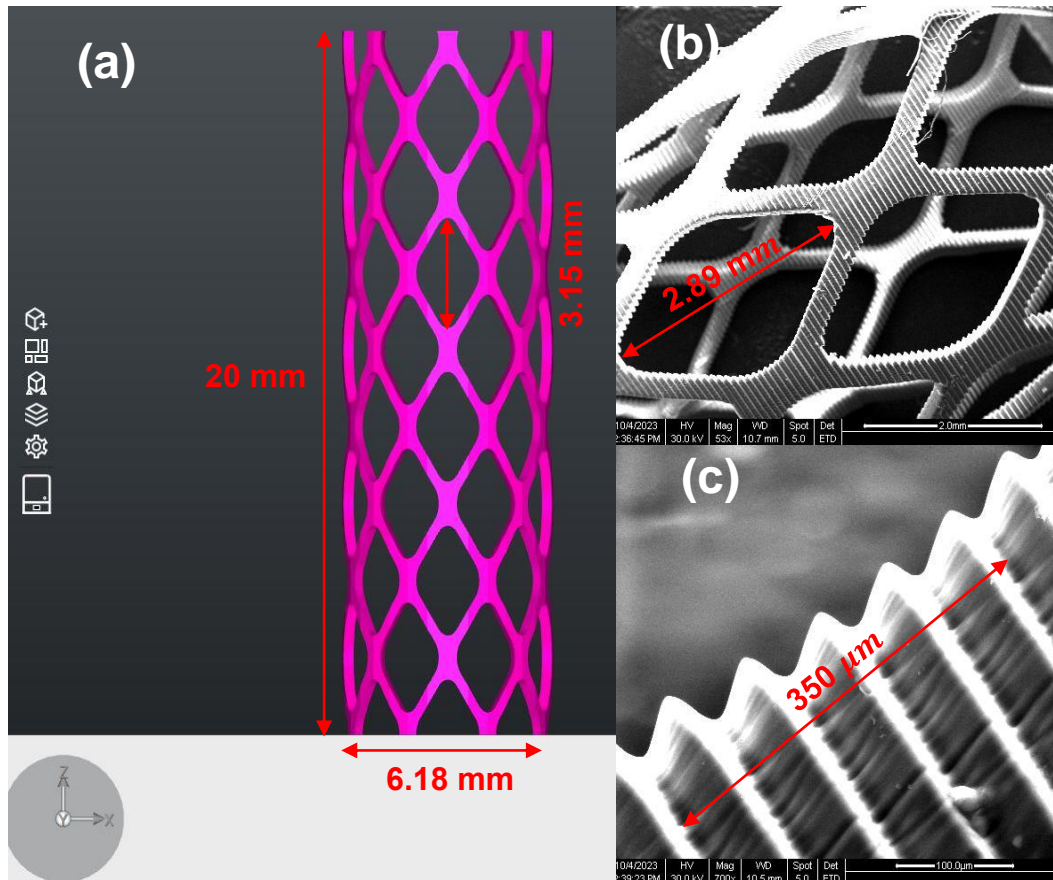


**Figure S6.** Calibration curve for the determination of the EY-HEMA amount in the filtrate ( $m_{lost}$ ).

Thus, the difference between the initial and lost mass is used to estimate the amount of EY-HEMA for each stent.

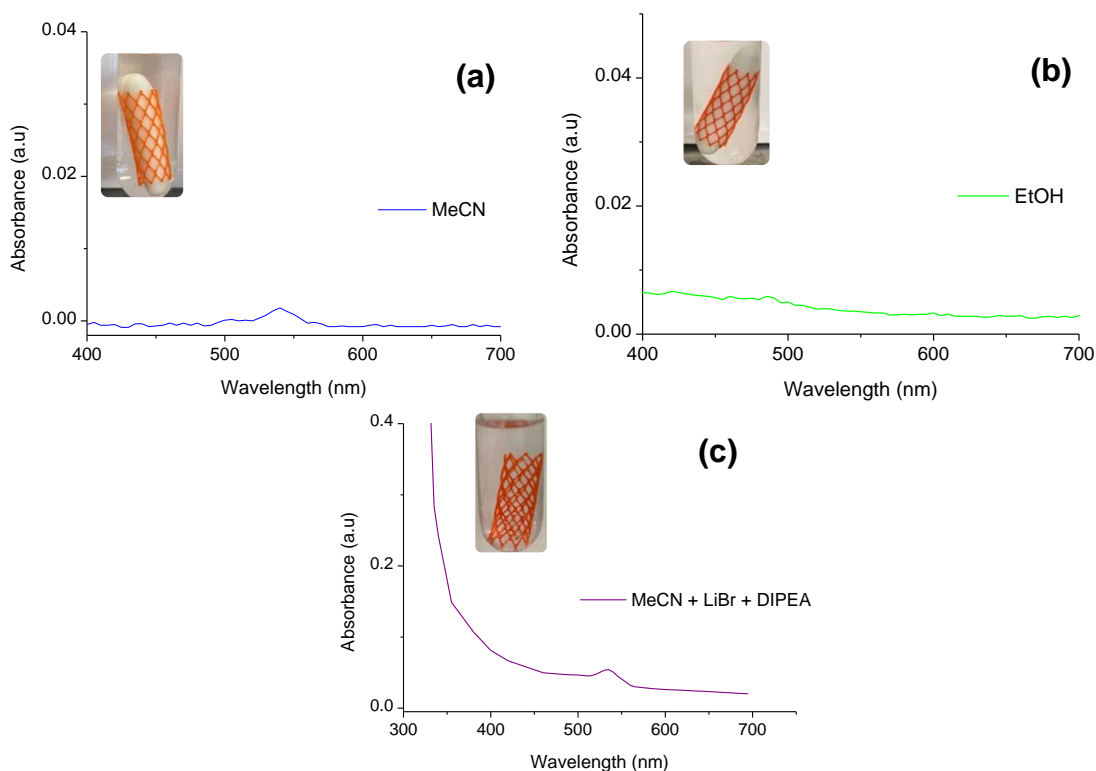
$$m_{EY-HEMA \text{ for 1 stent}} = \frac{m_i - m_{lost}}{8_{(\text{batch of 8 stents})}}$$

## 6. PCat 2 printing resolution



**Figure S7.** (a) CAD model of the stent with a height fixed at 2 cm. (b) and (c) SEM images of PCat 2 showing a close view of the stent and the staircase effect inherent to DLP process, respectively.

## 7. Analysis of PCat 2 desorption in reaction solvents

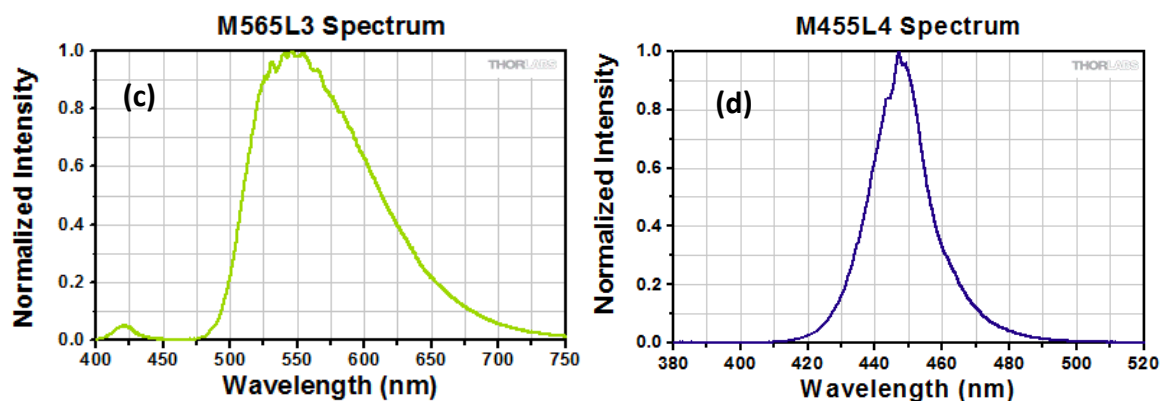


**Figure S8.** UV/Vis spectroscopic analysis of filtrate after 24 h immersion of PCat 4 in 4 mL of (a) MeCN, (b) EtOH, (c) MeCN, DIPEA (0.16 mmol), LiBr (0.25 mmol).

## 8. Set-up for photoredox reaction, blue LED (455 nm) and green LED (565 nm) emission spectrum.

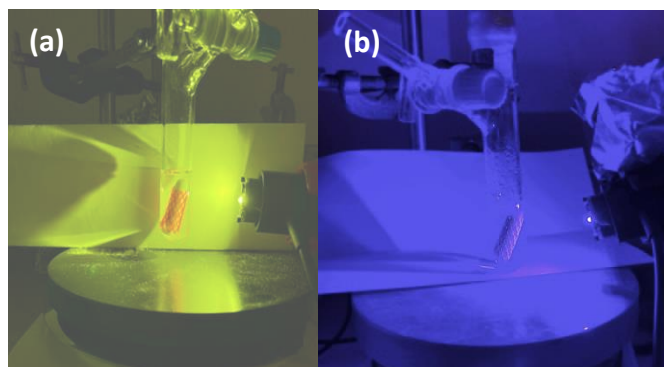
All the photocatalytic reactions were conducted using the following LED from Thorlabs:

- M565L3, light-emitting diode (LED, nominal wavelength: 565 nm, output power: 979 mW, irradiance:  $11.7 \mu\text{W}/\text{mm}^2$ )
- M455L4, light-emitting diode (LED, nominal wavelength: 455 nm, output power: 1445 mW, irradiance:  $32 \mu\text{W}/\text{mm}^2$ )



The reactions were carried out as represented in the picture bellow, LED was placed at 4 cm to the reaction tube.





**Figure S9.** (a-b) LED was placed at 4 cm to the reaction tube. (c) M565L3, light-emitting diode (LED, nominal wavelength: 565 nm, output power: 979 mW, irradiance:  $11.7 \mu\text{W}/\text{mm}^2$ ). (d) M455L4, light-emitting diode (LED, nominal wavelength: 455 nm, output power: 1445 mW, irradiance:  $32 \mu\text{W}/\text{mm}^2$ ).

## 9. Materials and methods

### 9.1. Materials

Eosin Yellowish (Eosin Y, 97%), N, N-Diisopropylethylamine (DIPEA, 99%), Potassium phosphate anhydrous (97%) and Copper(I) iodide (98%) were purchased from Alfa Aesar. EDC.HCl, Iodobenzene and triethylamine was purchased from Acros Organics. 1,2,3,4-Tetrahydroisoquinoline, 9,10-Dimethylantracene, 2-Hydroxyethylmethacrylate (HEMA) and 2-bromoacetophenone was purchased from TCI. Ethylene glycol was purchased from Riedel-de Haën, Honeywell. Nitromethane, N,N-dimethylformamide anhydrous, polyethylenglycol diacrylate (PEGDA<sub>700</sub>), Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) was purchased from Sigma Aldrich. All solvents were purchased from VWR.

### 9.2. Preparation of EY-HEMA <sup>[1]</sup>

The synthesis of EY-HEMA is realized. Eosin Y (1.0 eq., 535.0 mg, 0.77 mmol), DMAP (0.2 eq., 22.0 mg, 0.18 mmol), and EDC·HCl (2.4 eq., 350.9 mg, 1.83 mmol) were combined in a 50 mL round bottom flask under N<sub>2</sub>. At 0 °C, dry DMF (4 mL) was added together with HEMA (2.3 eq, 0.23 mL, 1.79 mmol), and TEA (0.7 eq., 0.08 mL, 0.57 mmol). Then the reaction was warmed up to room temperature and was stirred overnight under N<sub>2</sub> without light. Upon dilution with DCM, the crude mixture was washed with aqueous HCl (1 M), NaHCO<sub>3</sub> (saturated), water and brine. After drying the organic extract with MgSO<sub>4</sub>, the solvent was evaporated. Then, solid was washed with Et<sub>2</sub>O and filtered to remove non react HEMA. Finally, the compound was purified by short large flash column chromatography on silica gel with DCM/MeOH (90/10) to give EY-HEMA (pink solid) in 51% yield. Data are conformed to the literature: <sup>[1]</sup> <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.19 (d, *J* = 7.8 Hz, 1H), 7.81 (m, 1H), 7.78 (m, 1H), 7.48 (d, *J* = 7.3 Hz, 1H), 6.90 (s, 2H), 5.81 (s, 1H), 5.53 (s, 1H), 4.28 (m, 2H), 4.09 (m, 2H), 1.75 (s, 3H) <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>)  $\delta$  165.8, 164.3, 152.5, 152.2, 134.7, 133.3, 132.8, 130.4, 130.3, 129.7, 129.0, 128.7, 125.6, 118.1, 108.8, 99.2, 62.5, 61.9, 17.5.

### 9.3. Aza-Henry Photocatalyzed Reaction

### 9.3.1. Preparation of N-Aryl-tetrahydroisoquinoline derivatives (**1**)<sup>[2]</sup>

Copper(I) iodide (0.1 eq., 98.0 mg, 0.51 mmol) and potassium phosphate (2.0 eq., 1393.3 mg, 10.39 mmol) were put into a Schlenk tube (25 mL). The tube was evacuated and back filled with nitrogen. 2-Propanol (5 mL), ethylene glycol (2.0 eq., 0.56 mL, 10.04 mmol), 1,2,3,4-tetrahydro-isoquinoline (1.5 eq., 1.0 mL, 7.56 mmol) and the nucleophile (1 eq.) were added successively by micro-syringe at room temperature. The reaction mixture was heated at 90 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted by diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the product was purified by column chromatography on silica gel with petroleum ether and ethyl acetate (95/5).

*2-phenyl-1,2,3,4-tetrahydroisoquinoline (1a)*<sup>[2]</sup>: Light yellow oil, 51 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33–7.28 (m, 2H), 7.21–7.15 (m, 4H), 7.00 (dd, *J* = 8.8, 0.9 Hz, 2H), 6.89–6.79 (tt, *J* = 7.3, 1.0 Hz, 1H), 4.42 (s, 2H), 3.56 (t, *J* = 5.9 Hz, 2H), 3.00 (t, *J* = 5.8 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.7, 135.0, 134.6, 129.3 (2C), 128.6, 126.7, 126.5, 126.2, 118.8, 115.3 (2C), 50.9, 46.6, 29.3.

*2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (1b)*<sup>[3]</sup>: White solid, 31 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 – 7.10 (m, 4H), 7.01 – 6.95 (m, 2H), 6.90 – 6.84 (m, 2H), 4.30 (s, 2H), 3.78 (s, 3H), 3.45 (t, *J* = 5.9 Hz, 2H), 2.99 (t, *J* = 5.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.7, 145.6, 134.8, 134.8, 128.9, 126.7, 126.5, 126.1, 118.2, 114.8, 55.9, 52.9, 48.7, 29.3.

*2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (1c)*<sup>[3]</sup>: White solid, 41 % yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18 (ddt, *J* = 17.2, 11.9, 4.7 Hz, 4H), 7.00 (t, *J* = 8.7 Hz, 2H), 6.97 – 6.91 (m, 2H), 4.34 (s, 2H), 3.50 (t, *J* = 5.9 Hz, 2H), 3.00 (t, *J* = 5.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.0 (d, *J* = 237.9 Hz), 147.6 (d, *J* = 2.1 Hz), 134.6 (d, *J* = 31.2 Hz), 127.8 (d, *J* = 267.7 Hz), 126.6, 126.2, 117.4, 117.3, 115.9, 115.7, 52.1, 48.0, 29.2.

### 9.3.2. Photocatalyzed Aza-Henry reaction with **PCat 2**<sup>[2]</sup>

N-Aryl-tetrahydroisoquinoline (1 eq., 0.2 mmol) and nitromethane (10 eq., 0.11 mL, 2 mmol) in EtOH (4 mL) were charged in a tube Schlenk (10 mL) with magnetic stirring bar under **PCat 2** (0.6 mol %). The reaction mixture was stirred under blue LED (455 nm) irradiation (approximately 4 cm away from the LED lamp) at room temperature for 16h. The setup of the whole reaction was covered with aluminum foil. After the reaction, the solvent was evaporated under vacuum and **PCat 2** was rinsed with EtOH. The crude product was directly loaded onto a short silica gel column. The filtration was performed using pentane/diethyl ether (90/10) to obtain the desired product.

#### **PCat 2 Recycling :**

**PCat 2** is removed from the reaction mixture and immersed in 5 mL of ethanol. Subsequently, **PCat** in EtOH is placed in ultrasound bath for approximately 1 minute to eliminate any potential residues from the reaction mixture. This operation is repeated three times, with each rinse performed using a fresh ethanol solution. Finally, **PCat 2** is dried under vacuum for 10 minutes.

Control:

*N*-Aryl-tetrahydroisoquinoline (1 eq., 0.2 mmol) and nitromethane (10 eq., 0.11 mL, 2 mmol) in EtOH (4 mL) were charged in a tube Schlenk (10 mL) **with/without PCat 2** (0.6 mol %). The reaction mixture was stirred **under irradiation/without irradiation** at room temperature for 16h. The setup of the whole reaction was covered with aluminum foil. After the reaction, the solvent was evaporated under vacuum and the conversion is determined by <sup>1</sup>H-NMR on the crude. (**PCat 2**, no irradiation: 3 % // No **PCat 2**, under irradiation: 16 %)

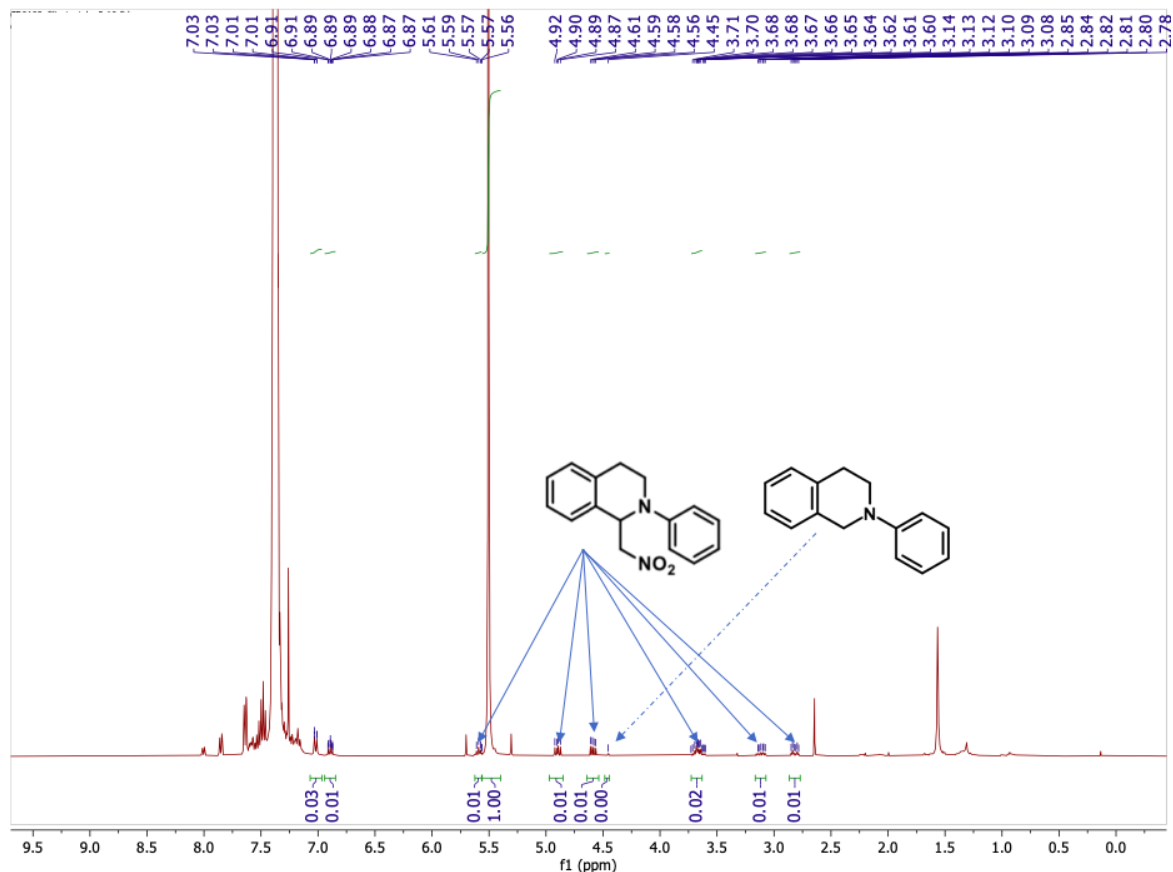
1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**2a**)<sup>[2]</sup>: yellow oil, 78 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.33–7.10 (m, 6H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.86 (td, *J* = 7.3, 0.7 Hz, 1H), 5.56 (t, *J* = 7.2 Hz, 1H), 4.88 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.57 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.77–3.47 (m, 2H), 3.17–2.95 (m, 1H), 2.80 (dt, *J* = 16.3, 4.9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.5, 135.5, 133.1, 130.1 (2C), 129.4, 129.2, 128.1, 127.1, 126.7, 116.0 (2C), 79.0, 58.5, 42.4, 26.4, 20.5.

2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**2b**)<sup>[3]</sup>: yellow oil, 60 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 – 7.10 (m, 4H), 6.89 (dt, *J* = 9.0, 2.9 Hz, 2H), 6.79 (dt, *J* = 9.0, 2.9 Hz, 2H), 5.37 (dd, *J* = 8.5, 5.9 Hz, 1H), 4.80 (dd, *J* = 11.9, 8.6 Hz, 1H), 4.53 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.73 (s, 3H), 3.56 - 3.52 (m, 2H), 2.99 (ddd, *J* = 16.2, 9.1, 6.8 Hz, 1H), 2.67 (dt, *J* = 16.5, 3.9 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.1, 143.2, 135.6, 133.0, 129.6, 128.0, 127.0, 126.7, 119.0 (2C), 114.8 (2C), 79.1, 59.0, 55.7, 43.3, 25.9.

2-(4-fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**2c**)<sup>[3]</sup>: yellow oil, 68 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 – 7.14 (m, 4H), 6.99 – 6.89 (m, 4H), 5.43 (dd, *J* = 8.6, 5.9 Hz, 1H), 4.84 (dd, *J* = 12.0, 8.7 Hz, 1H), 4.58 (dd, *J* = 12.0, 5.9 Hz, 1H), 3.60 (dd, *J* = 9.0, 4.3 Hz, 2H), 3.10 – 2.96 (m, 1H), 2.73 (dt, *J* = 16.5, 4.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.3 (d, *J* = 239.2 Hz), 145.4 (d, *J* = 2.2 Hz), 135.4, 132.7, 129.6, 128.2, 127.1, 126.9, 118.1 (d, *J* = 7.7 Hz), 116.0 (d, *J* = 22.2 Hz), 79.0, 58.9, 43.0, 25.9

### 9.3.3. <sup>1</sup>H NMR spectra of 2a in **PCat 2**

After photocatalyzed Aza Henry reaction with **PCat 2** (and 0.2 mmol of **1**, 2 mmol of nitromethane and 4 mL of EtOH), **PCat 2** is placed in a Schlenk tube (10 mL) without rinsing with 4 mL EtOH. **PCat 2** is remained immersed for 24h and the filtrate was analyzed by <sup>1</sup>H NMR using diphenylethylene (0.2 mmol) as an internal reference.



**Figure S10.** <sup>1</sup>H NMR (CDCl<sub>3</sub>) of the filtrate after 24h desorption of **PCat 2** in EtOH (0.2 mmol of diphenylethylene as internal reference).

## 9.4. [2+2] Cycloaddition Photocatalyzed Reaction

### 9.4.1. Preparation of (2*E*,7*E*)-Diphenylnona-2,7-diene-1,9-dione (**3**)<sup>[4]</sup>

A solution of PPh<sub>3</sub> (1.01 eq., 6.4 mmol, 1.69 g) and 2-bromoacetophenone (1.0 eq., 6.3 mmol, 2.27 g) in 13 mL of THF was heated under reflux and stirred for 4 hours. Then, the reaction mixture was cooled to room temperature and the crude phosphonium bromide was filtered and washed with THF (3 × 20 mL). Then, 25 mL of CH<sub>2</sub>Cl<sub>2</sub> and aqueous NaOH (20 wt %, 25 mL) were added, and the mixture was stirred for 10 minutes. The organic phase was separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure to give the corresponding phosphonium ylide. The ylide (1.0 eq., 3.8 mmol, 1.44 g) was dissolved in THF and mixed with glutaric dialdehyde solution (1.0 eq., 3.8 mmol, 1.5 mL) and MgSO<sub>4</sub>. The mixture was stirred at room temperature for 2 days. Then, the sample was filtered and the reaction solvent was evaporated. Silica gel chromatography was used to purify the bis(enone) with diethylether and petroleum ether (60/40). Yellow oil, 28 % yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.94 - 7.92 (dt, *J* = 8.5, 1.7 Hz, 4H), 7.57–7.54 (m, 2H), 7.54–7.44 (m, 4H), 7.08-7.02 (dt, *J* = 15.3, 6.8 Hz, 2H), 6.94 - 6.90 (dt, *J* = 15.4, 1.3 Hz, 2H), 2.37 – 2.42 (td, *J* = 8.0, 1.2 Hz, 4H), 1.82–1.73 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.6, 148.5, 137.8, 132.7, 128.5, 128.5, 126.5, 32.2, 26.7.

### 9.4.2. [2+2] Cycloaddition Photocatalyzed Reaction with **PCat 2**<sup>[5]</sup>

In a Schlenk tube (10 mL), (2E, 7E) -Diphenylnona-2,7-diene-1,9-dione (1.0 eq., 0.08 mmol, 24.3 mg) was added with **PCat 2** (1 mol%), N, N-Diisopropylethylamine (2.0 eq., 0.16 mmol, 30.0  $\mu$ L) and LiBr (3 eq., 0.25 mmol, 21.5 mg). A measure of 4 mL of the degassed MeCN were added under nitrogen then the reaction medium was stirred and irradiated by a blue LED. The setup of the whole reaction was covered with aluminum foil while continuing the agitation for 16 h. After the reaction, the solvent was evaporated under vacuum. The products obtained by the cycloaddition reaction were quantified by  $^1\text{H}$  NMR (NMR yield) using 1 equiv. of diphenylethylene as an internal standard.

#### PCat 2 Recycling :

**PCat 2** is removed from the reaction mixture and immersed in 5 mL of ethanol. Subsequently, **PCat** in EtOH is placed in ultrasound bath for approximately 1 minute to eliminate any potential residues from the reaction mixture. This operation is repeated three times, with each rinse performed using a fresh ethanol solution. Finally, **PCat 2** is dried under vacuum for 10 minutes.

#### Control:

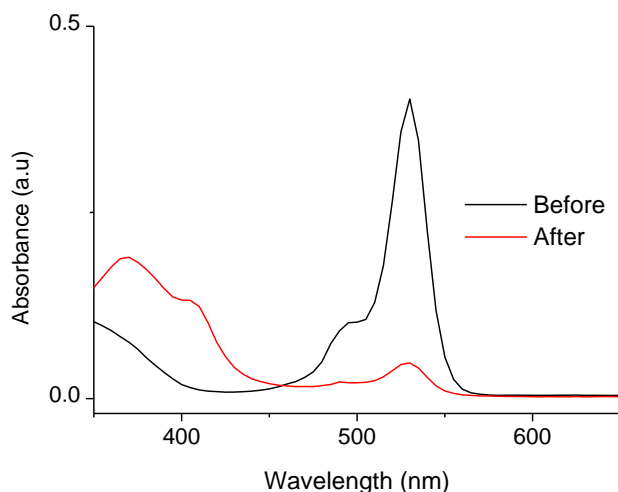
In a schlenk tube (10 mL), (2E, 7E) -Diphenylnona-2,7-diene-1,9-dione (1.0 eq., 0.08 mmol, 24.3 mg) was added **with/without PCat 2** (1 mol%), N, N-Diisopropylethylamine (2 eq., 0.16 mmol, 30.0  $\mu$ L) and LiBr (3 eq., 0.25 mmol, 21.5 mg). A measure of 4 mL of the degassed MeCN were added under nitrogen then the reaction medium was stirred **with/without blue LED**. The setup of the whole reaction was covered with aluminum foil while continuing the agitation for 16 h. After the reaction, the solvent was evaporated under vacuum and the conversion is quantified by  $^1\text{H}$  NMR (NMR yield) using 1 equiv. of diphenylethylene as an internal standard. (**PCat 2**, no irradiation: 0 % // No **PCat 2**, under irradiation: 15 %)

Cis-Bicyclo[3.2.0]heptane-6,7-diylbis(phenylmethanone) (**4a**)<sup>[6]</sup>:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85–7.66 (m, 4H), 7.45 (tt,  $J$  = 7.4 Hz, 2H), 7.39–7.31 (m, 4H), 3.86 (d,  $J$  = 4.0 Hz, 2H), 3.25–3.15 (m, 2H), 2.09–1.99 (m, 2H), 1.90–1.81 (m, 2H), 1.76–1.60 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  198.6, 136.4, 132.5, 128.5, 127.8, 48.3, 39.1, 32.5, 25.2.

Trans-Bicyclo[3.2.0]heptane-6,7-diylbis(phenylmethanone) (**4b**)<sup>[6]</sup>:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (m, 2H), 7.94 (m, 2H), 7.58–7.53 (m, 2H), 7.53–7.45 (m, 4H), 4.57 (dd,  $J$  = 10.3, 7.9 Hz, 1H), 4.26 (t, 1H), 3.26 (m, 1H), 3.05 (q,  $J$  = 6.9 Hz, 1H), 1.85 (m, 3H), 1.52 (m, 1H), 1.39 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  200.4, 198.1, 136.2, 135.7, 133.2, 133.1, 128.7, 128.7, 128.6, 128.3, 43.1, 43.0, 40.5, 40.4, 32.1, 28.5, 25.5.

#### 9.4.3. UV/Vis Spectra of EY degradation

[2+2] cycloaddition photocatalyzed reaction was performed with eosin (as homogeneous catalysis). The UV/Vis spectra of the reaction mixture were analyzed before irradiation and after 16h of irradiation with blue LED (455 nm).



**Figure S11.** UV/Vis spectroscopy of homogeneous photocatalysts (EY) before and after [2+2] cycloaddition photocatalyzed reaction.

## 9.5. Photosensitization Photocatalyzed Reaction <sup>[7]</sup>

### 9.5.1. Photosensitization Photocatalyzed Reaction with **PCat 2**

9,10-Dimethylantracene (1 eq., 10.3 mg, 49.9  $\mu\text{mol}$ ) and **PCat 2** (2 mol %) was charged in 10-mL tube Schlenk with MeCN (4 mL). After two freeze pump  $\text{N}_2$  purge thaw cycles,  $\text{O}_2$  (1 atm.) was injected into the vial using a gas-tight syringe. The reaction was stirred and irradiated with green LED (565 nm) for 1 hour. Then **PCat 2** was rinsed with EtOH and the concentration by rotary evaporation afforded 9,10-endoperoxide as a white solid, 99% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 – 7.41 (m, 4 H), 7.26 – 7.29 (m, 4 H), 2.15 (s, 6 H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.6, 127.2, 120.5, 79.3, 13.5.

#### PCat 2 Recycling :

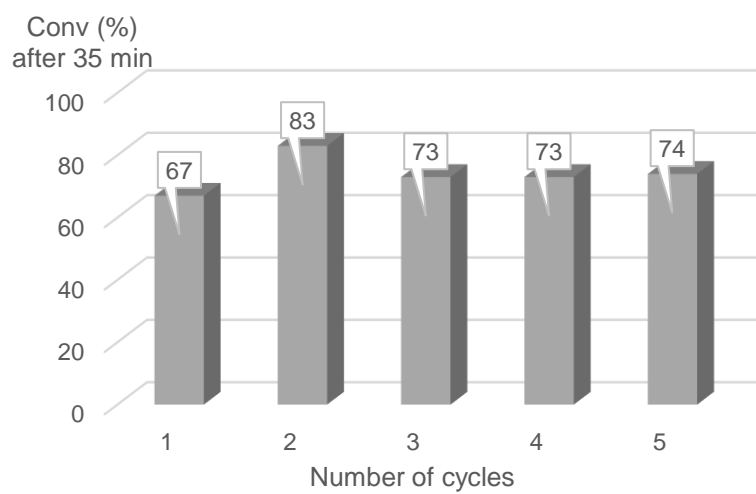
**PCat 2** is removed from the reaction mixture and immersed in 5 mL of ethanol. Subsequently, PCat in EtOH is placed in ultrasound bath for approximately 1 minute to eliminate any potential residues from the reaction mixture. This operation is repeated three times, with each rinse performed using a fresh ethanol solution. Finally, **PCat 2** is dried under vacuum for 10 minutes.

#### Control:

9,10-Dimethylantracene (1 eq., 10.3 mg, 49.9  $\mu\text{mol}$ ) **with/without PCat 2** (2 mol %) was charged in 10-mL tube Schlenk with MeCN (4 mL). After two freeze pump  $\text{N}_2$  purge thaw cycles,  $\text{O}_2$  (1 atm.) was injected into the vial using a gas-tight syringe. The reaction was stirred **with/without** green LED (565 nm) irradiation for 1 hour. After solvent evaporation, the conversion is determined by  $^1\text{H}$ -NMR on the crude. (**PCat 2**, no irradiation: 0 % // No **PCat 2**, under irradiation: 17 %)

### 9.5.2. **PCat 2** recycling ( $t = 35$ min)

Following the procedure (8.5.1), the reaction is stopped after 35 min and the conversion is monitored by  $^1\text{H}$  NMR.



**Figure S12.** Recycling of **PCat 2** for 5 cycles of 35-minute photocatalysis in photosensitization.

## 10. NMR spectra

### $^1\text{H}$ and $^{13}\text{C}$ of *EY-HEMA* in $\text{DMSO-d}_6$

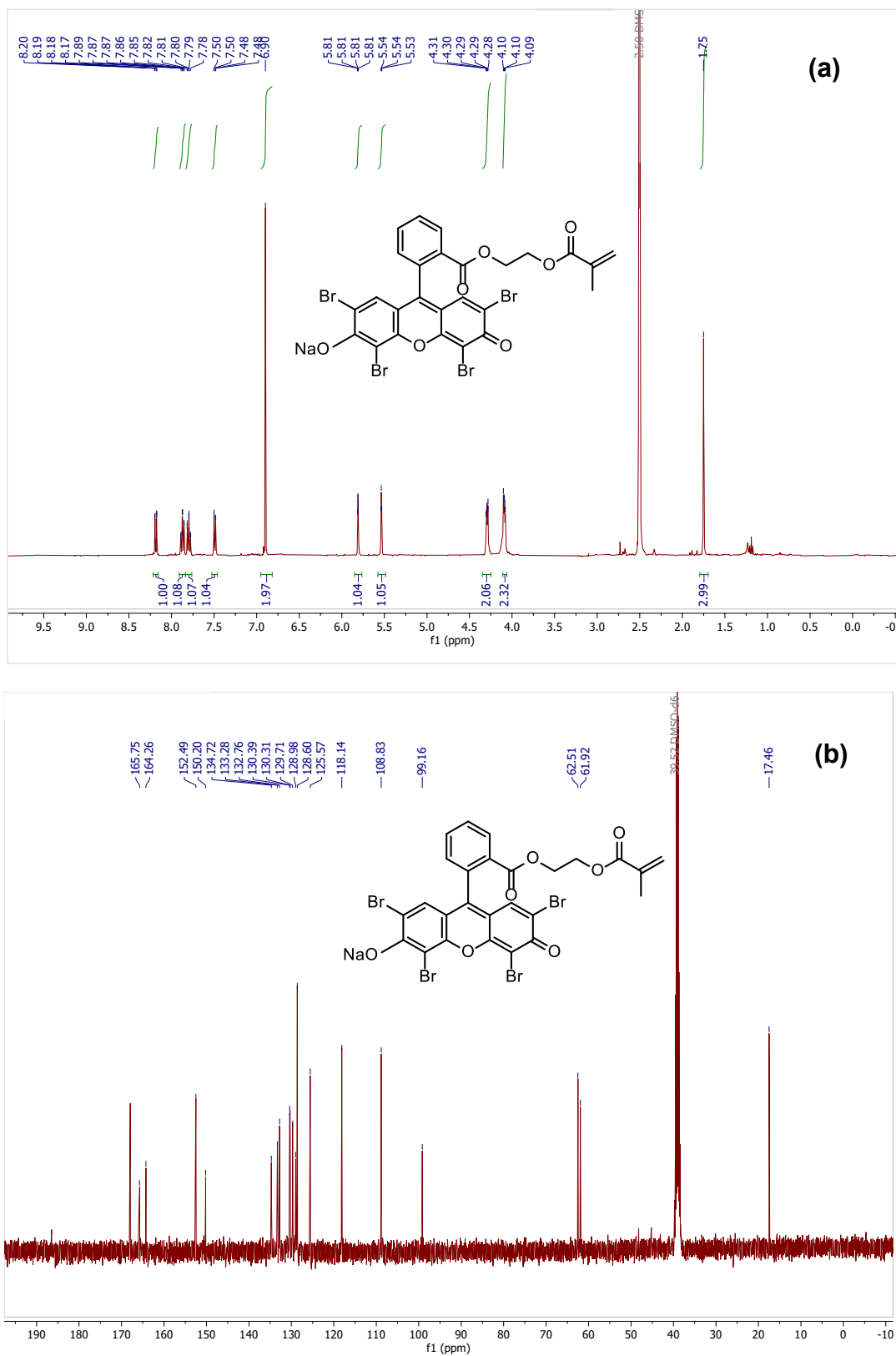
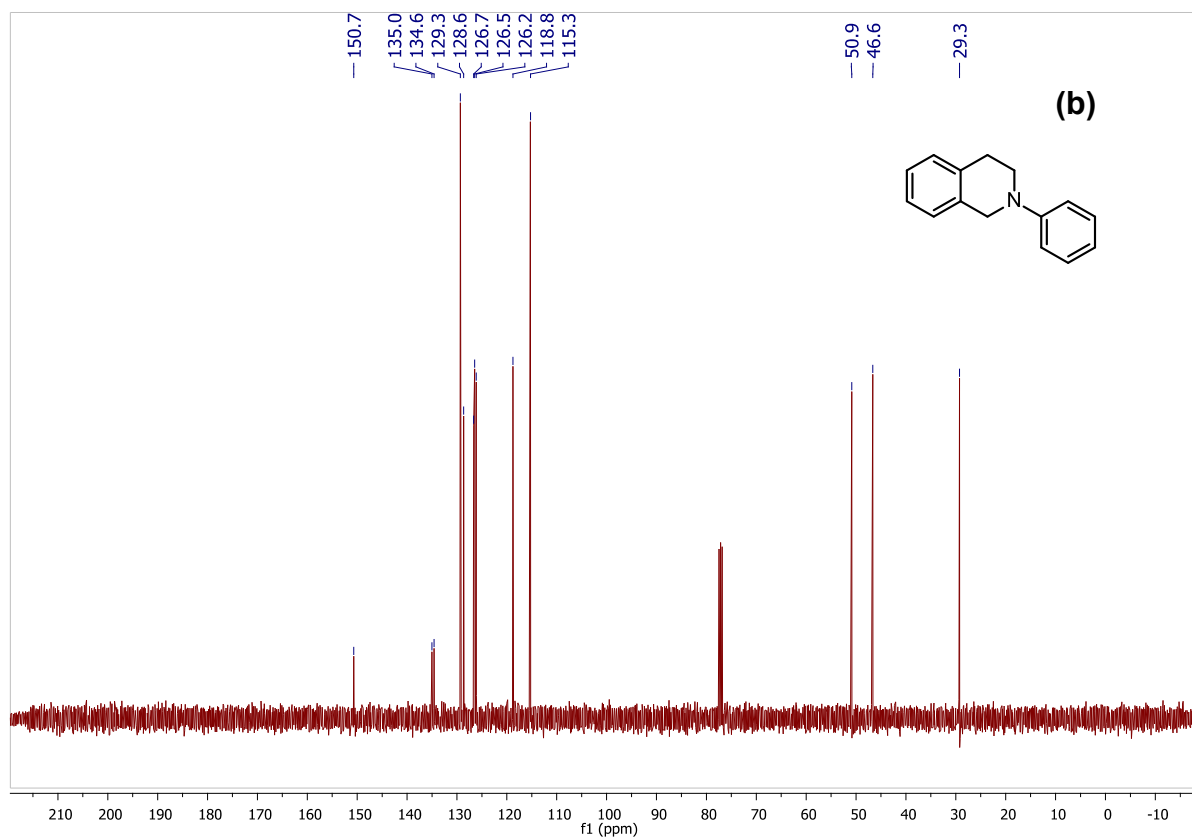
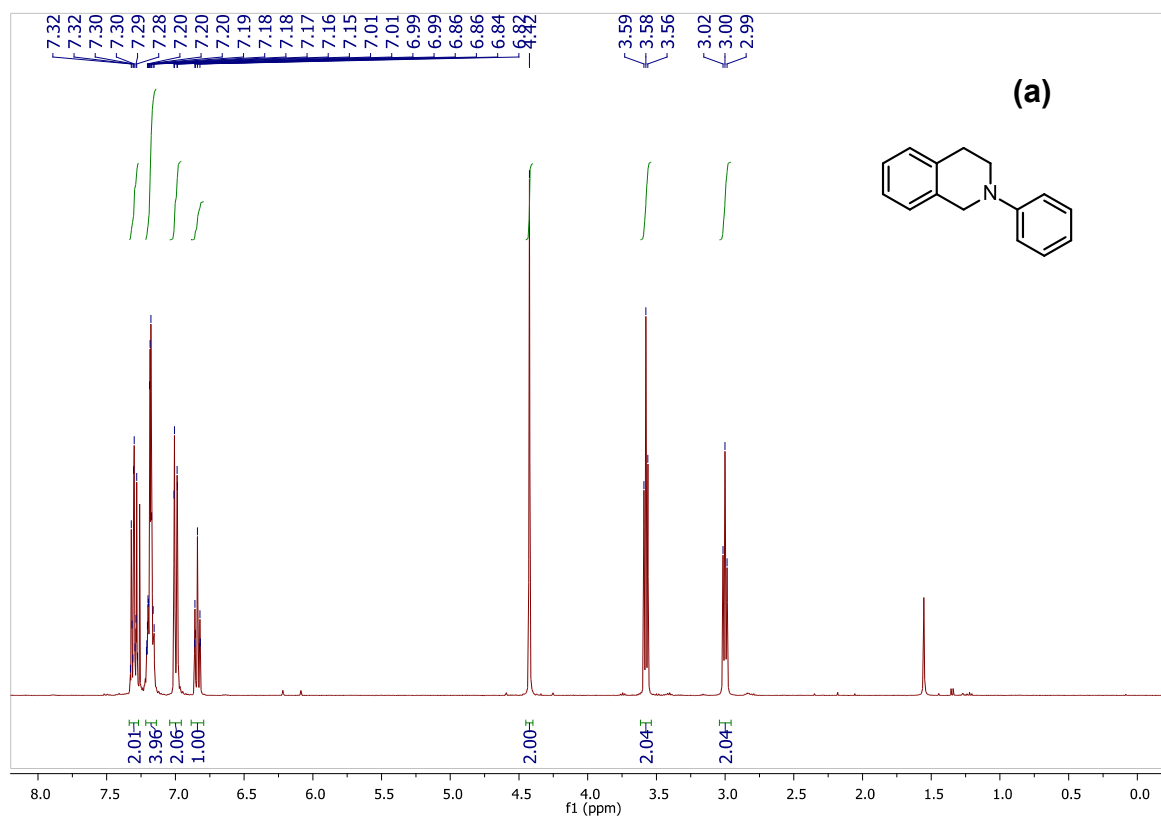


Figure S13.  $^1\text{H}$  and  $^{13}\text{C}$  of *EY-HEMA* in  $\text{DMSO-d}_6$  (a)  $^1\text{H}$ -NMR; (b)  $^{13}\text{C}$ -NMR.

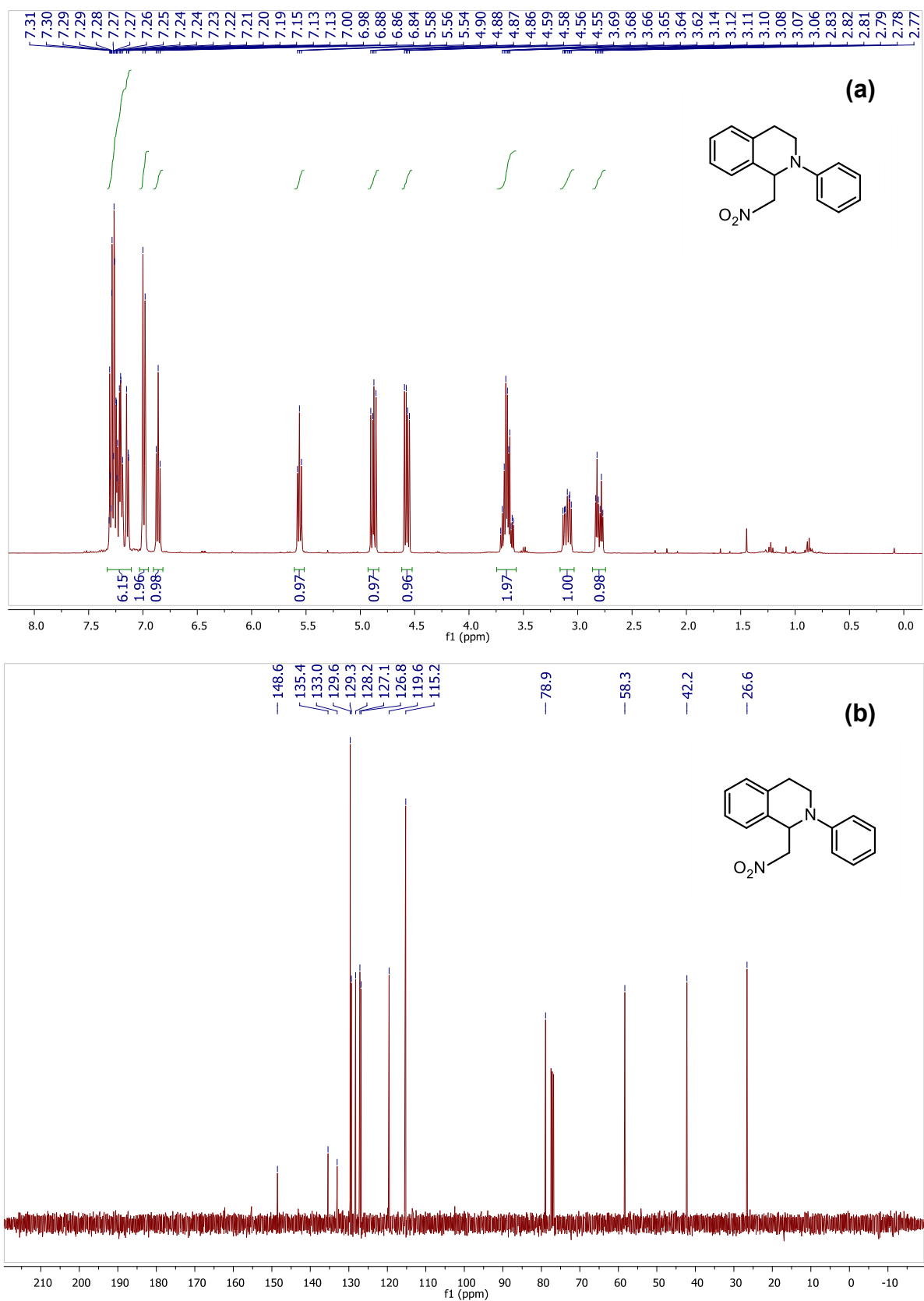


$^1\text{H}$  and  $^{13}\text{C}$  of 2-N-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**) in  $\text{CDCl}_3$



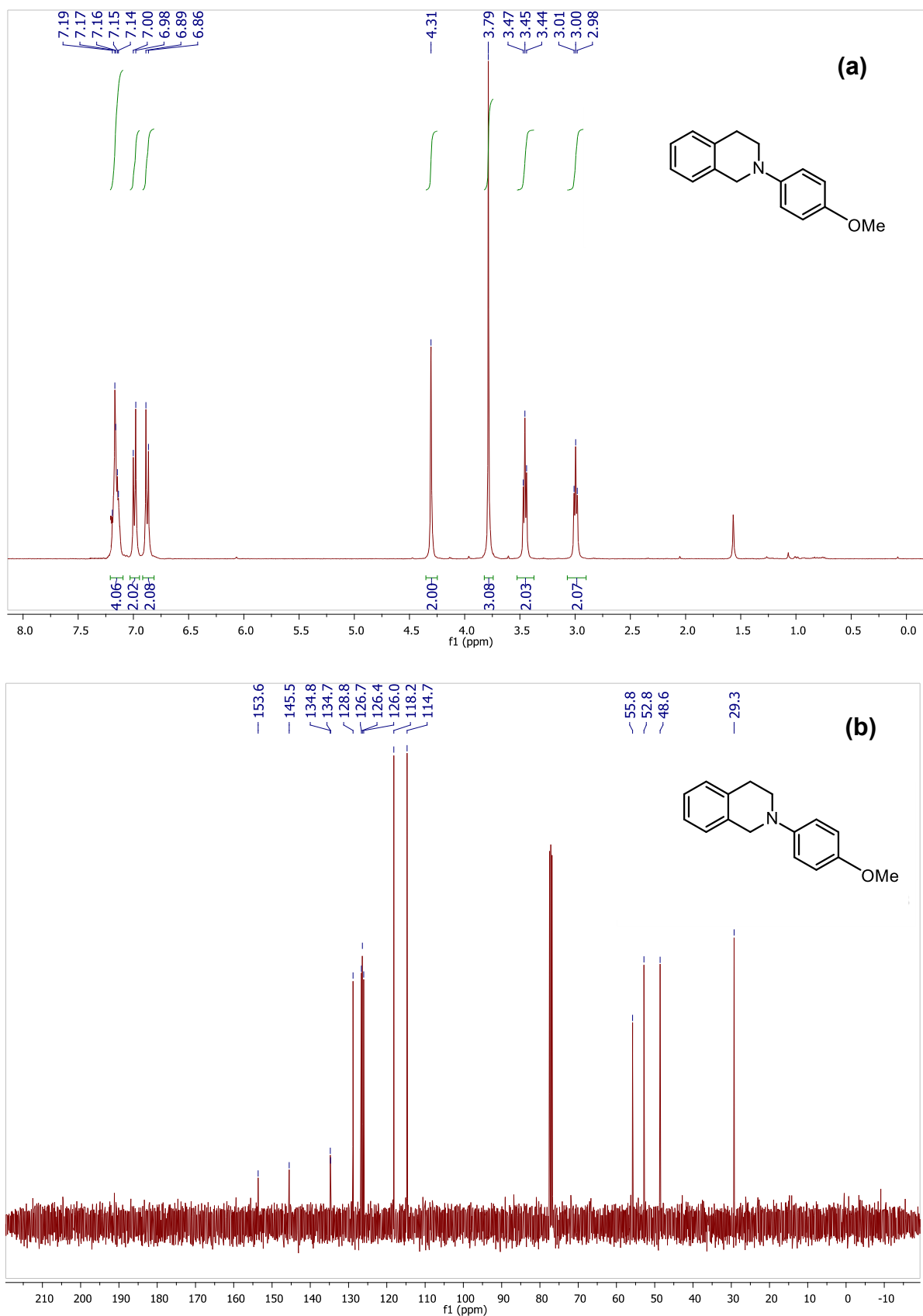
**Figure S14.**  $^1\text{H}$  and  $^{13}\text{C}$  of 2-N-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**) in  $\text{CDCl}_3$  (a)  $^1\text{H}$ -NMR; (b)  $^{13}\text{C}$ -NMR.

$^1\text{H}$  and  $^{13}\text{C}$  of 1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**2a**) in  $\text{CDCl}_3$



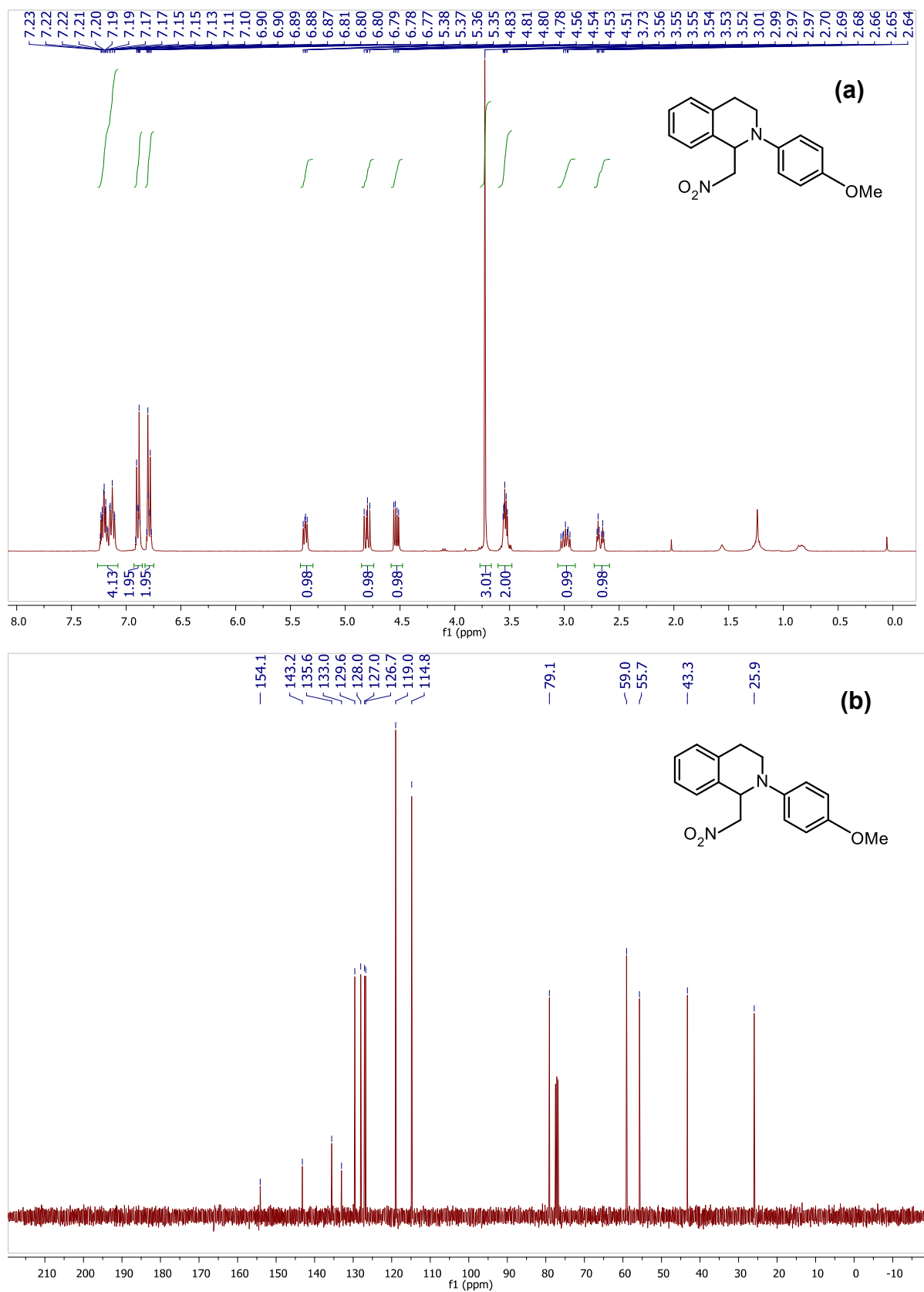
**Figure S15.**  $^1\text{H}$  and  $^{13}\text{C}$  of 1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (**2a**) in  $\text{CDCl}_3$ . **(a)**  $^1\text{H}$ -NMR **(b)**  $^{13}\text{C}$ -NMR.

$^1\text{H}$  and  $^{13}\text{C}$  of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (**1b**) in  $\text{CDCl}_3$



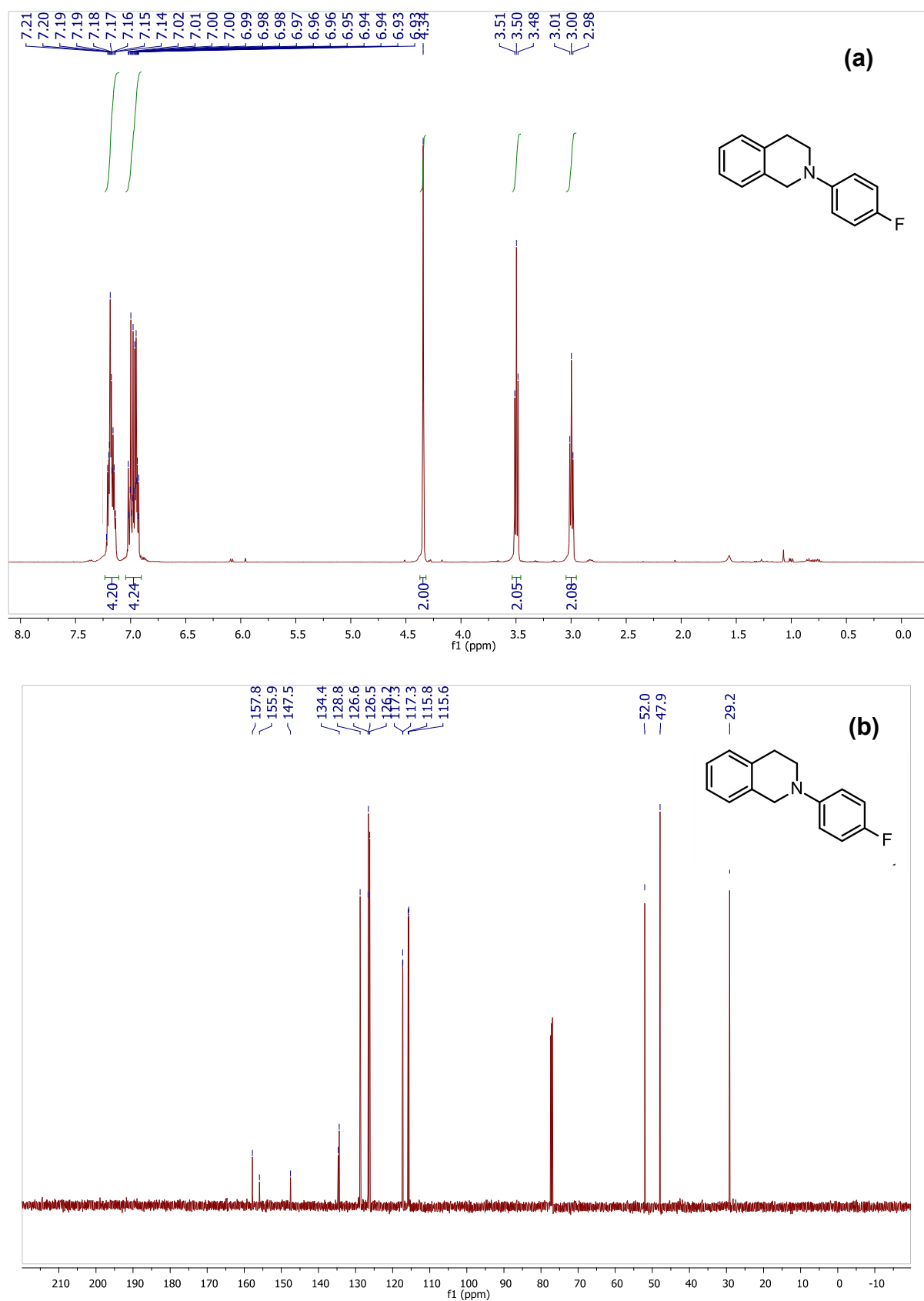
**Figure S16.**  $^1\text{H}$  and  $^{13}\text{C}$  of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (**1b**) in  $\text{CDCl}_3$ . (a)  $^1\text{H}$ -NMR (b)  $^{13}\text{C}$ -NMR.

$^1\text{H}$  and  $^{13}\text{C}$  of 2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**2b**) in  $\text{CDCl}_3$



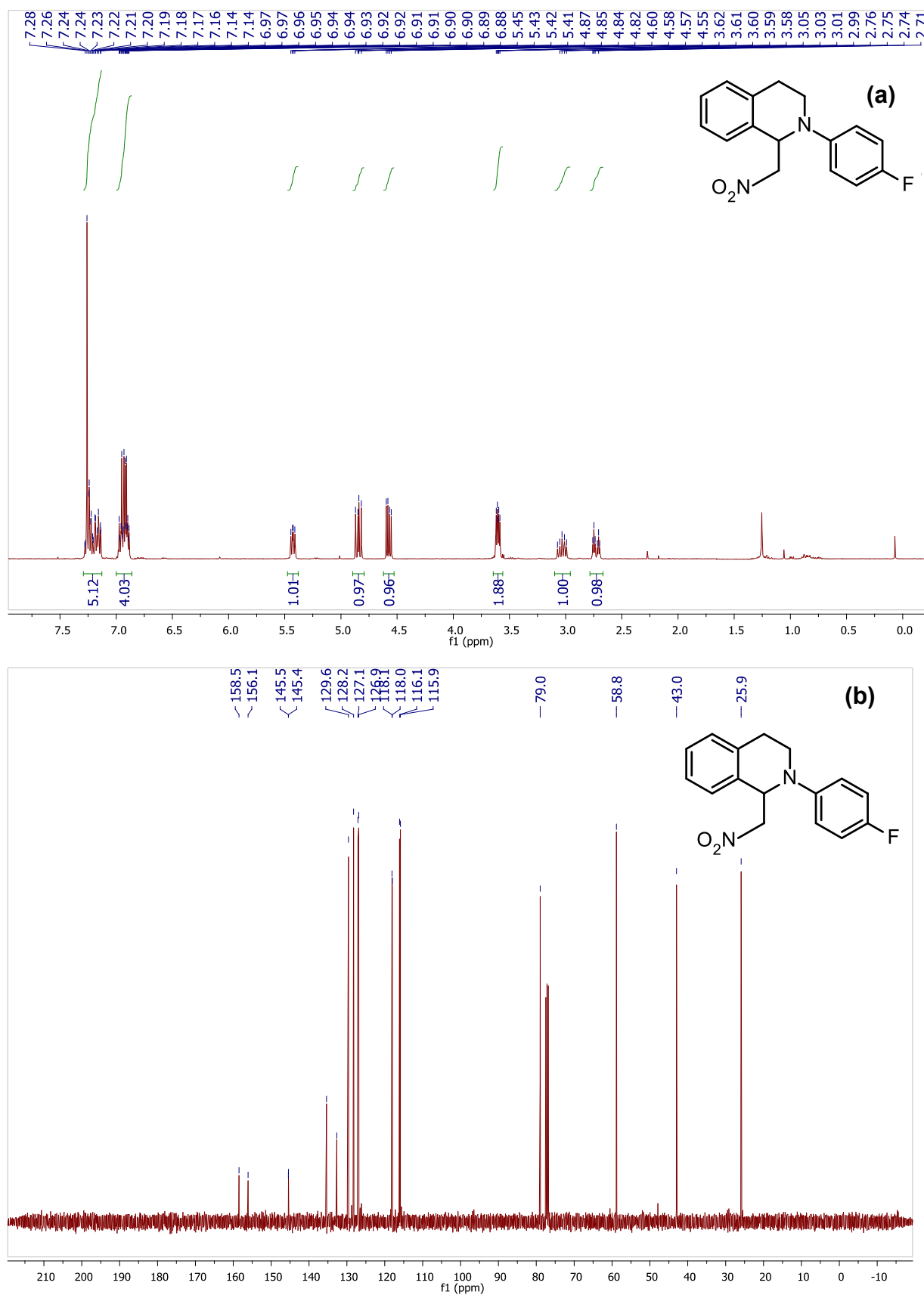
**Figure S17.**  $^1\text{H}$  and  $^{13}\text{C}$  of 1-(nitromethyl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (**2b**) in  $\text{CDCl}_3$ . (a)  $^1\text{H}$ -NMR (b)  $^{13}\text{C}$ -NMR.

$^1\text{H}$  and  $^{13}\text{C}$  of 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1c**) in  $\text{CDCl}_3$



**Figure S18.**  $^1\text{H}$  and  $^{13}\text{C}$  of 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1c**) in  $\text{CDCl}_3$ . (a)  $^1\text{H}$ -NMR (b)  $^{13}\text{C}$ -NMR.

$^1\text{H}$  and  $^{13}\text{C}$  of 2-(4-fluorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline (**2c**) in  $\text{CDCl}_3$



**Figure S19.**  $^1\text{H}$  and  $^{13}\text{C}$  of 1-(nitromethyl)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**2c**) in  $\text{CDCl}_3$ . (a)  $^1\text{H}$ -NMR (b)  $^{13}\text{C}$ -NMR.

$^1\text{H}$  and  $^{13}\text{C}$  of (2*E*,7*E*)-Diphenylnona-2,7-diene-1,9-dione (**3**) in  $\text{CDCl}_3$

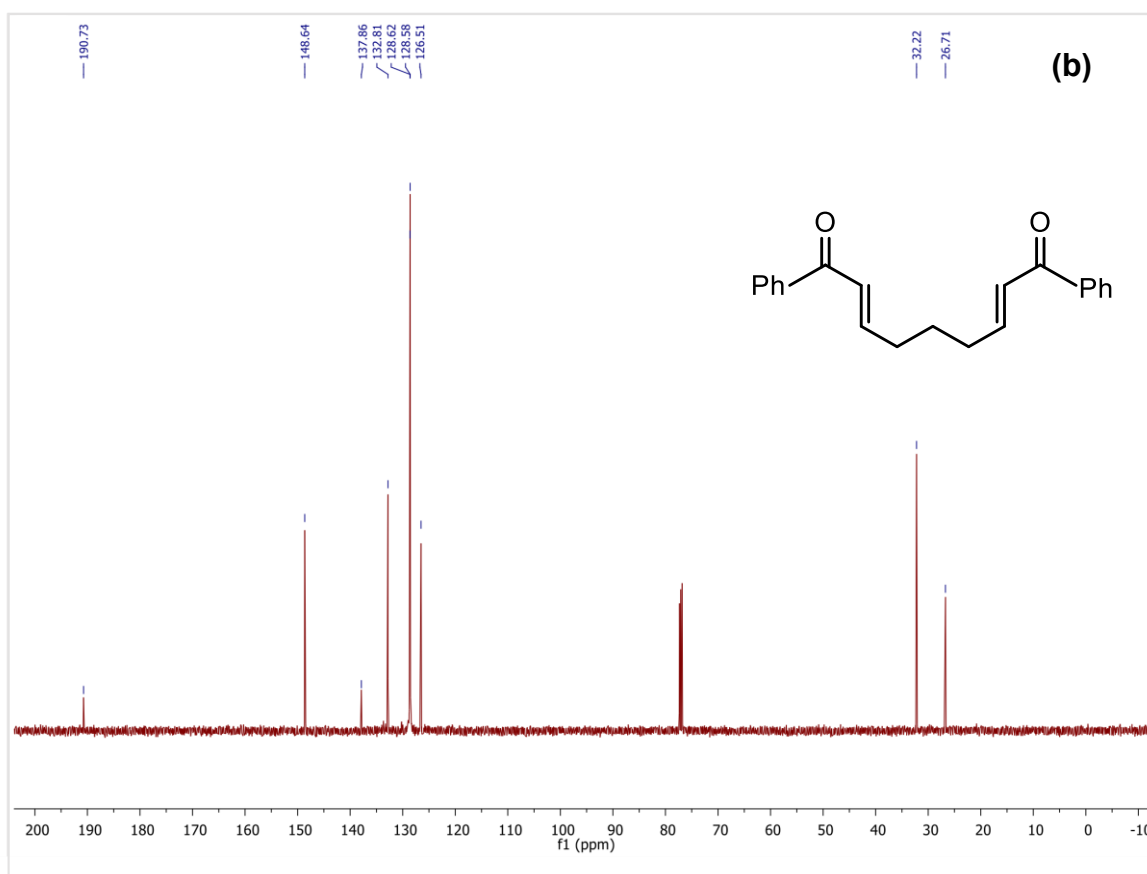
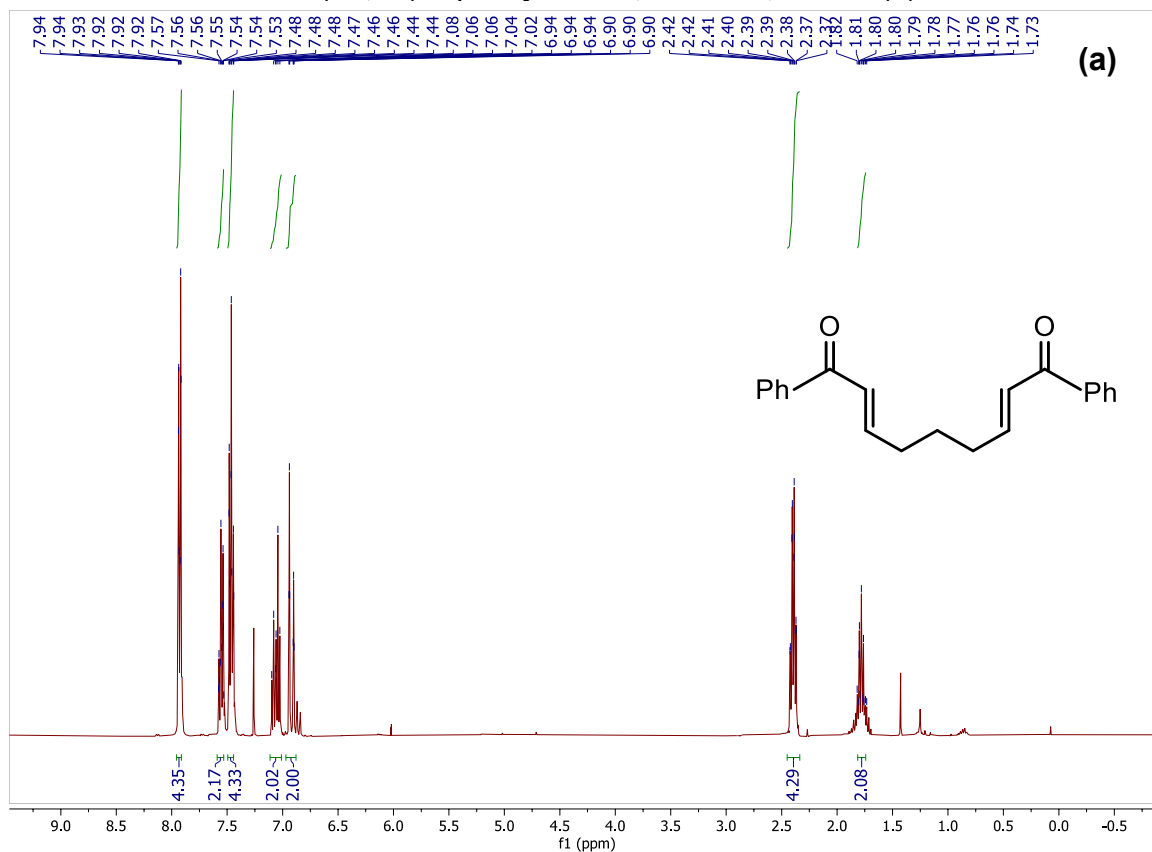
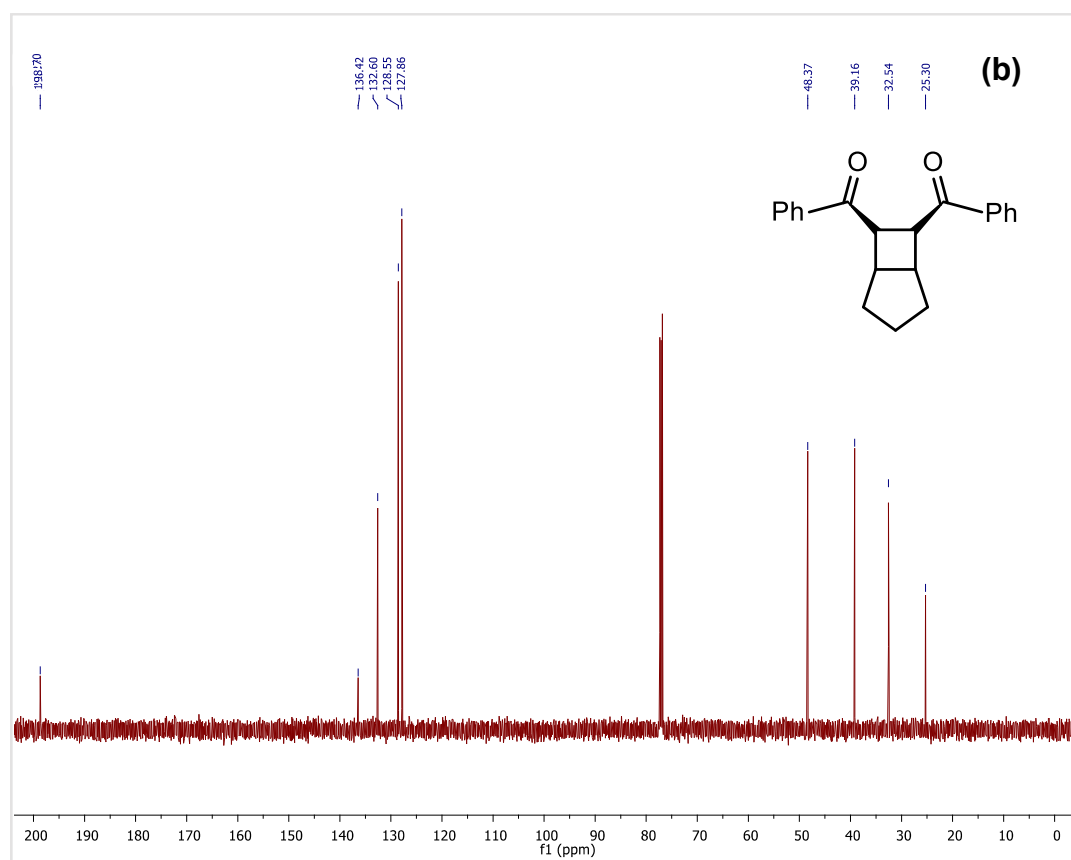
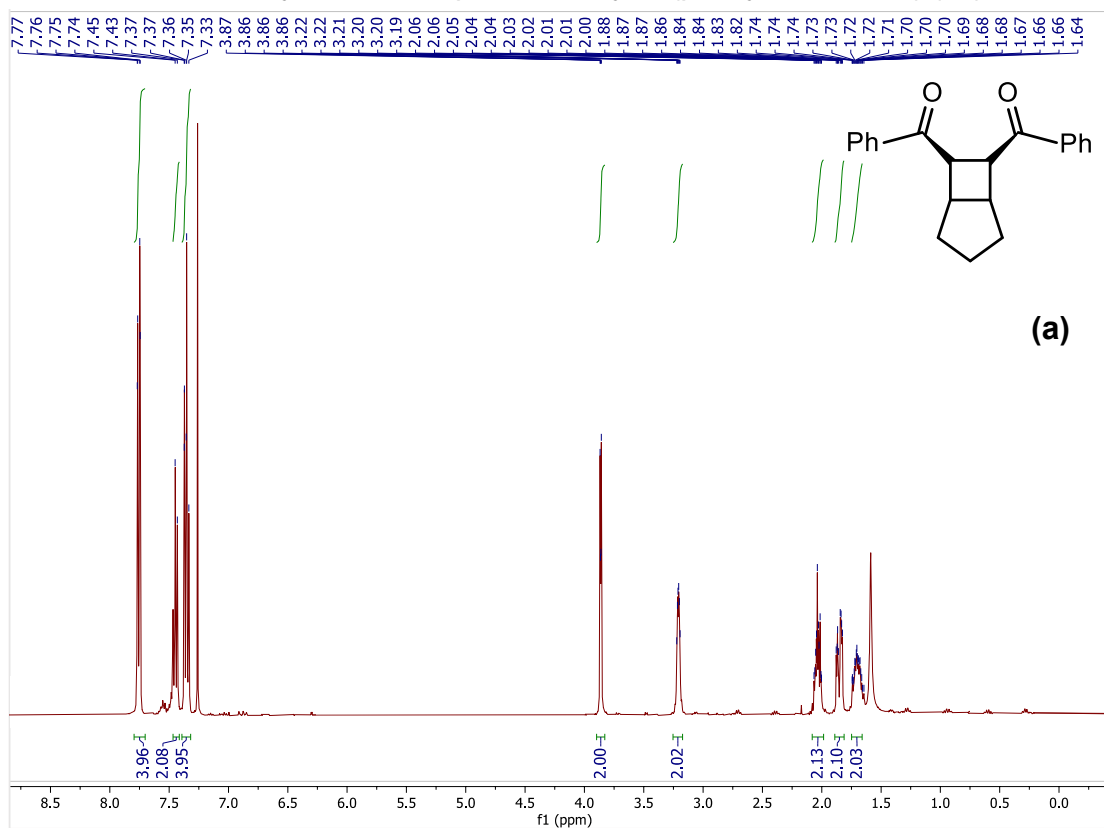


Figure S20.  $^1\text{H}$  and  $^{13}\text{C}$  of (2*E*,7*E*)-Diphenylnona-2,7-diene-1,9-dione (**3**) in  $\text{CDCl}_3$ . (a)  $^1\text{H}$ -NMR (b)  $^{13}\text{C}$ -NMR.

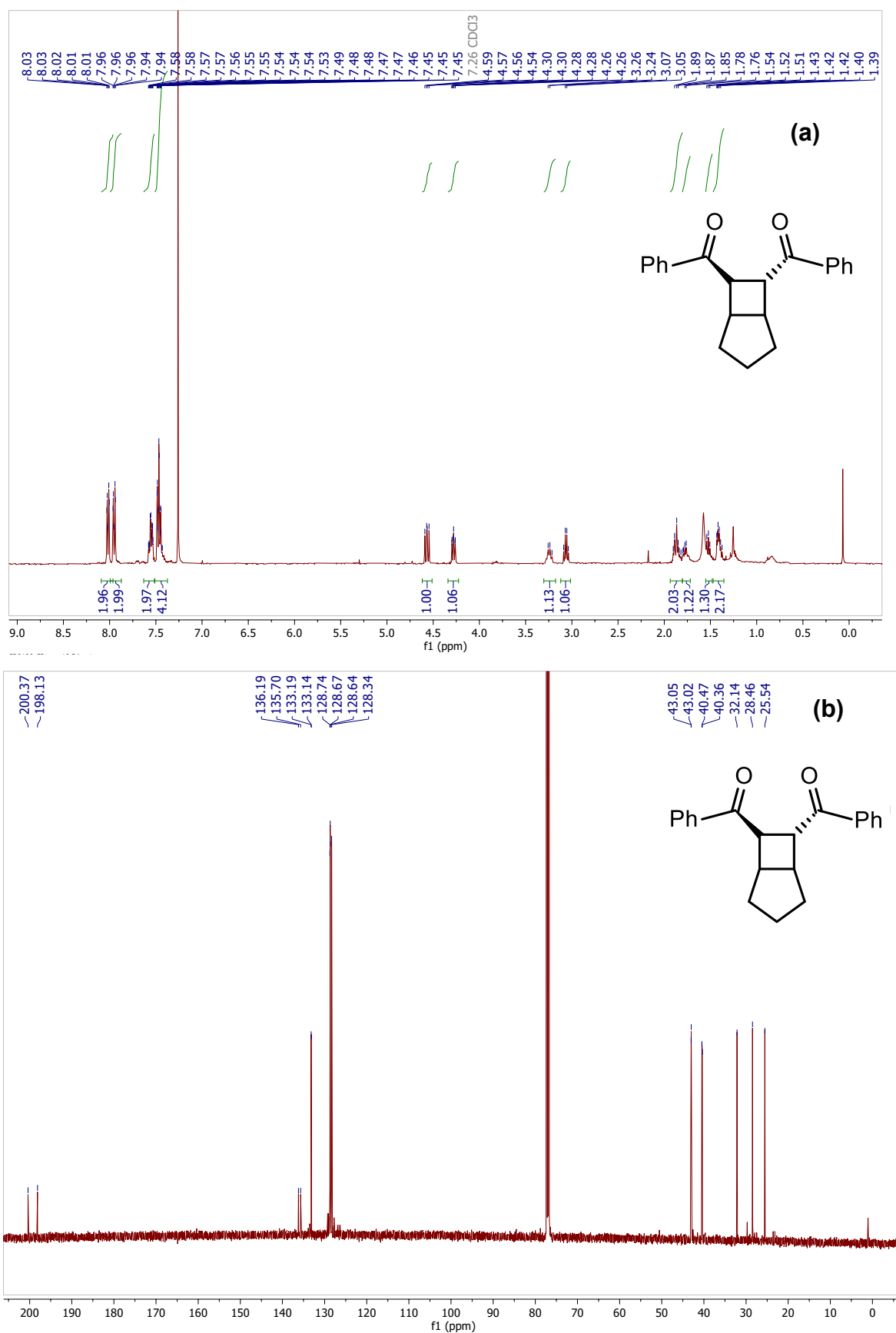
$^1\text{H}$  and  $^{13}\text{C}$  of *Cis*-Bicyclo [3.2.0]heptane-6,7-diylbis(phenylmethanone) (**4a**) in  $\text{CDCl}_3$



**Figure S21.**  $^1\text{H}$  and  $^{13}\text{C}$  of *Cis*-Bicyclo [3.2.0]heptane-6,7-diylbis(phenylmethanone)(**4a**) in  $\text{CDCl}_3$ . **(a)**  $^1\text{H}$ -NMR **(b)**  $^{13}\text{C}$ -NMR.

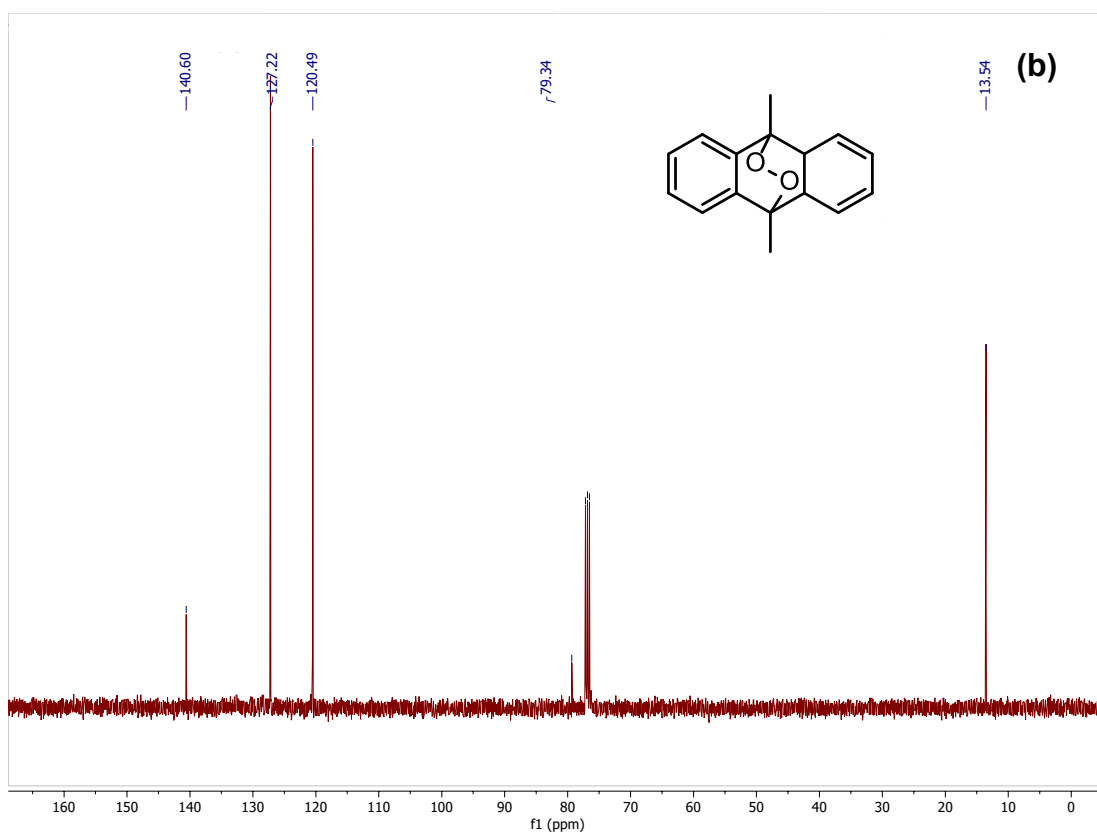
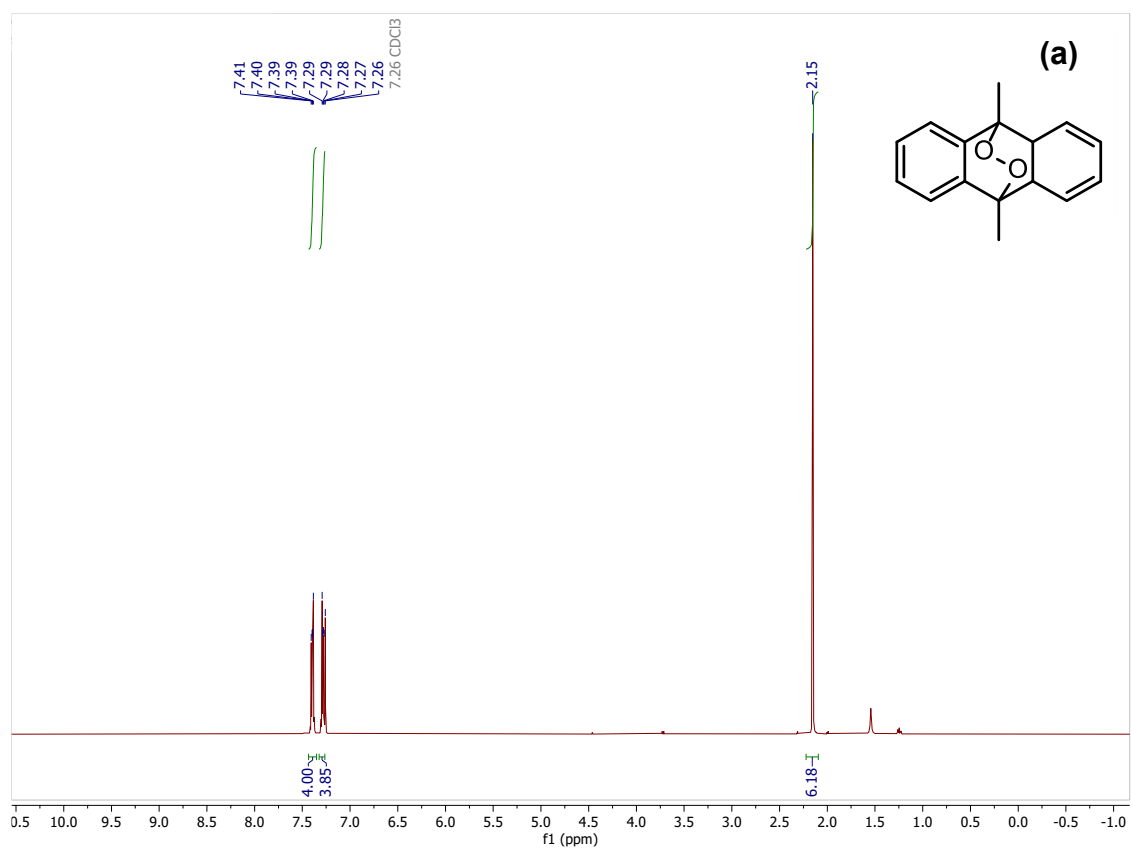


$^1\text{H}$  and  $^{13}\text{C}$  of *trans*-Bicyclo [3.2.0]heptane-6,7-diylbis(phenylmethanone) (**4b**) in  $\text{CDCl}_3$



**Figure S22.**  $^1\text{H}$  and  $^{13}\text{C}$  of *Trans*-Bicyclo [3.2.0]heptane-6,7-diylbis(phenylmethanone)(**4b**) in  $\text{CDCl}_3$  (a)  $^1\text{H}$ -NMR (b)  $^{13}\text{C}$ -NMR.

$^1\text{H}$  and  $^{13}\text{C}$  of 1,8-dimethyl-15,16-dioxanthracene (**5**) in  $\text{CDCl}_3$



**Figure S23.**  $^1\text{H}$  and  $^{13}\text{C}$  of 1,8-dimethyl-15,16-dioxanthracene (**5**) in  $\text{CDCl}_3$ . (a)  $^1\text{H}$ -NMR (b)  $^{13}\text{C}$ -NMR.

## 11. References

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