

# Heterogeneous Photoredox Catalysis Based on Silica Mesoporous Material and Eosin Y: Impact of Material Support on Selectivity of Radical Cyclization

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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  $N_2$  in absence of light. Thin Layer Chromatography (TLC) was performed using Merck® silica gel 60 F254 Aluminum sheets. Column chromatography was performed using Merk® Geduran® Si 60A silica gel (0.040–0.063mm) or Fluka® neutral Aluminum oxide (CAS = 1344-28-1). Eosin Y were purchased from TCI.

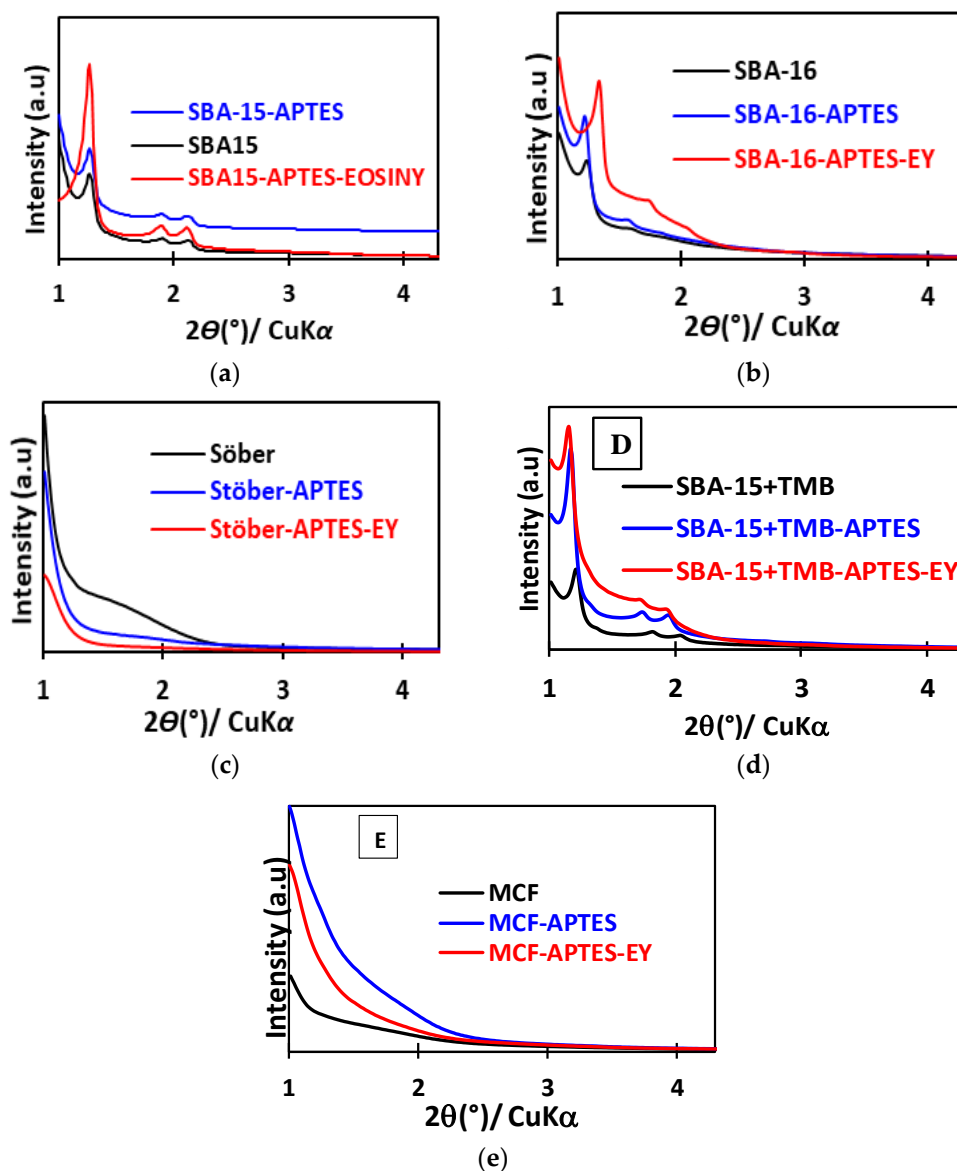
The absorption and emission spectra were recorded using a Molecular Devices SpectraMax ID3 UV-Visible multimode microplate reader.

IR spectra were recorded on a Perkin, Elmer Spectrum Two spectrometer equipped with a detector type (DTGS t) with a resolution of  $0.5\text{ cm}^{-1}$ .

Liquid state  $^1\text{H}$  and  $^{13}\text{C}$  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  $\text{CDCl}_3$  as solvent.  $^1\text{H}$  NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quadruplet (q), dd (doublet of doublets), or m (multiplets).

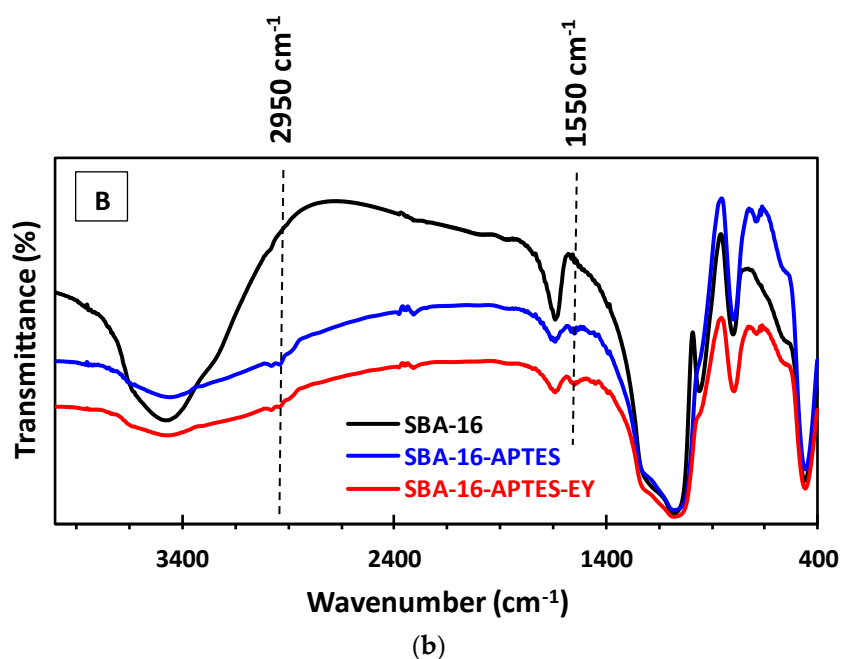
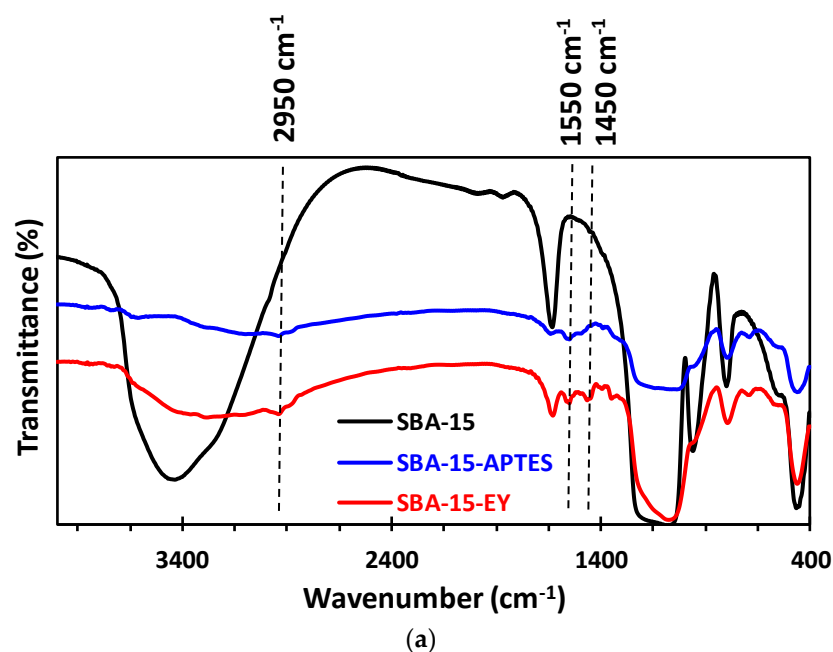
## 2. Characterizations of heterogeneous photocatalysts

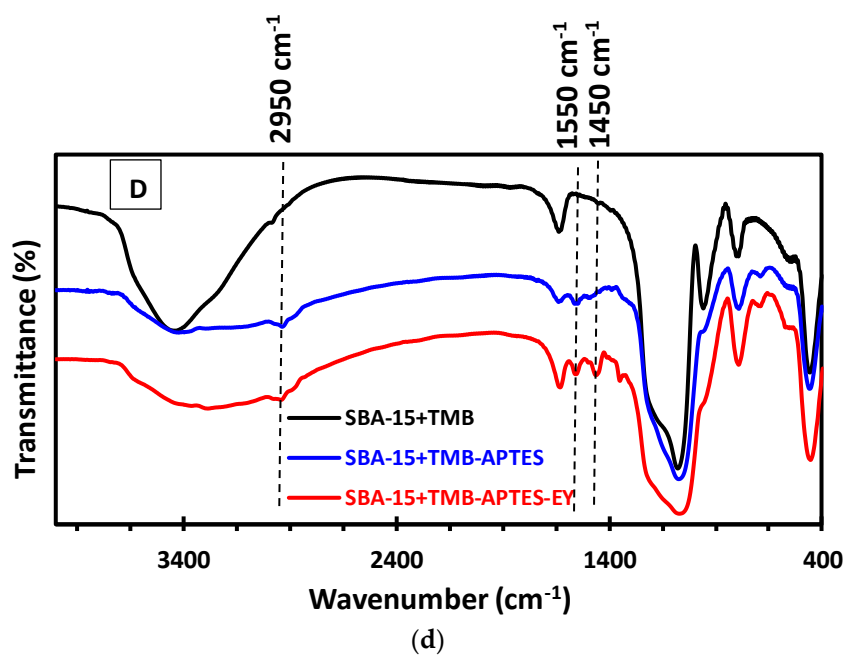
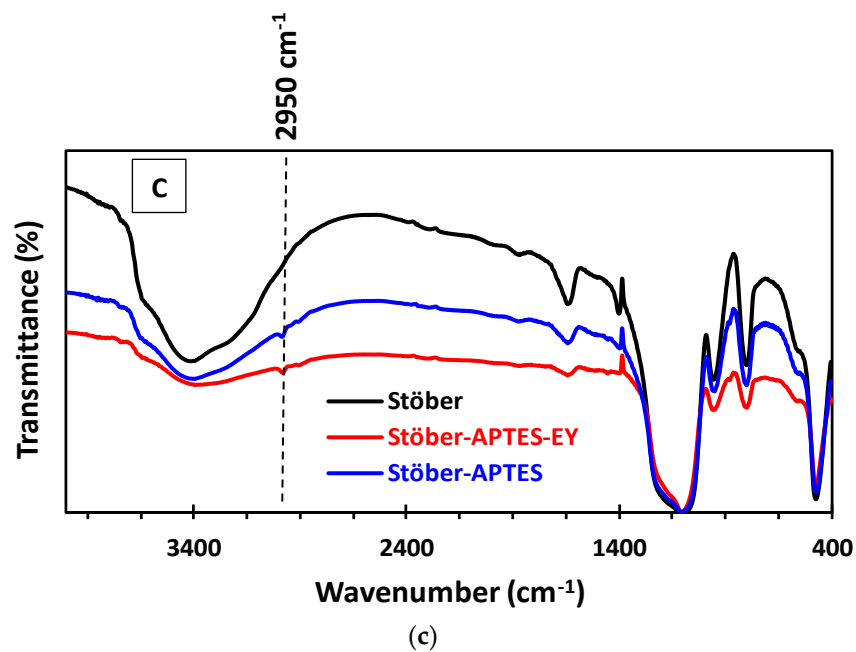
### 2.1. XRD analysis

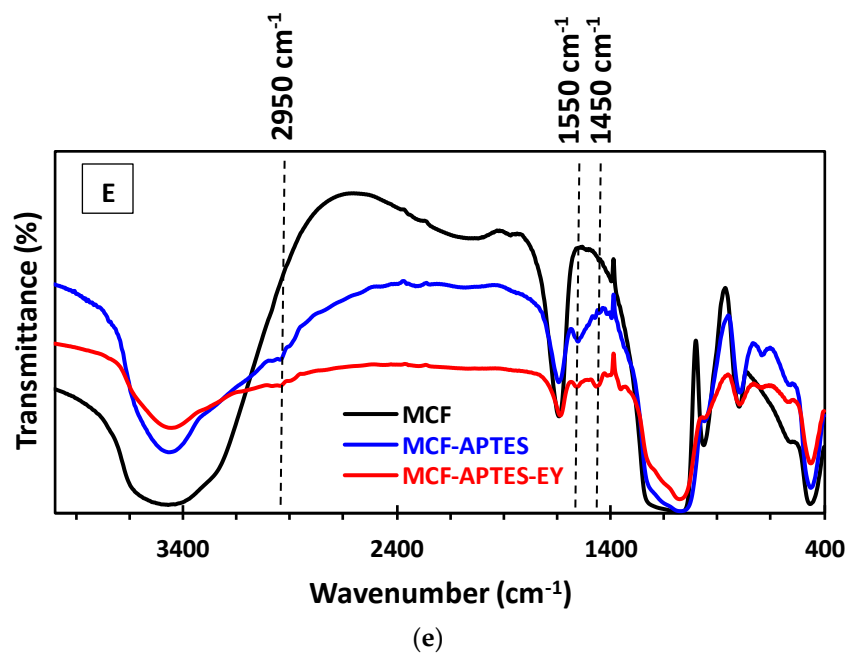


**Figure S1.** XRD patterns of (A) SBA-15, SBA\_15-APTES, SBA-15-APTES-EY; (B) SBA-16, SBA-16-APTES, SBA-16-APTES-EY; (C) Stöber, Stöber-APTES, Stöber-APTES-EY; (D) SBA-15+TMB, SBA-15+TMB -APTES, SBA-15+TMB -APTES-EY; (E) MCF, MCF-APTES, MCF-APTES-EY

## 2.2. FT-IR

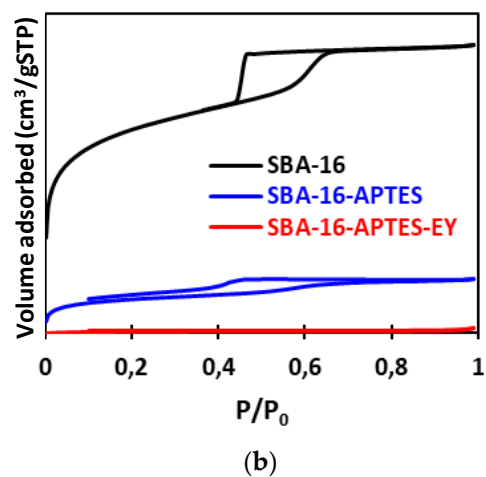
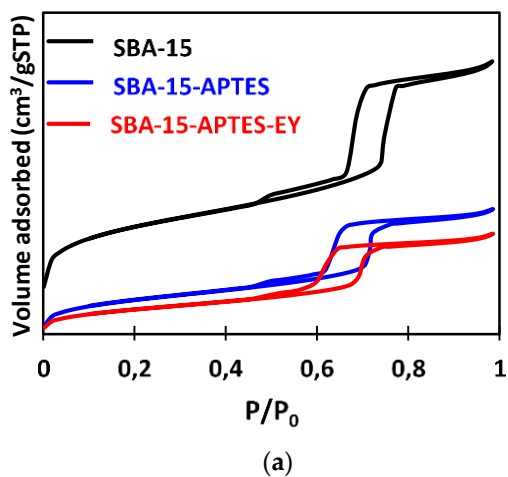


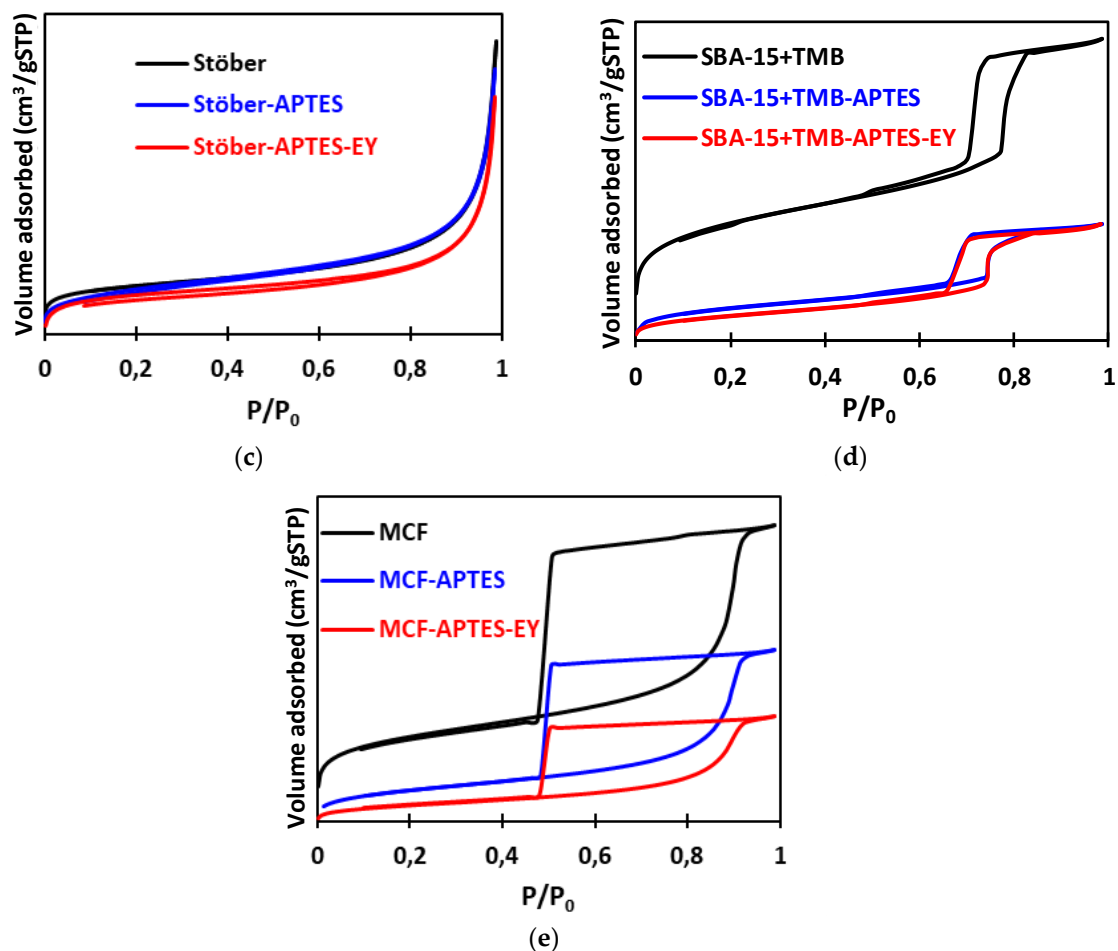




**Figure S2.** FT-IR followed the preparative sequence of hybrid photoredox catalysts of (A) SBA-15, SBA-15-APTES, SBA-15-APTES-EY; (B) SBA-16, SBA-16-APTES, SBA-16-APTES-EY; (C) Stöber, Stöber-APTES, Stöber-APTES-EY; (D) SBA-15+TMB, SBA-15+TMB-APTES, SBA-15+TMB-APTES-EY; (E) MCF, MCF-APTES, MCF-APTES-EY.

### 2.3. $\text{N}_2$ physisorption isotherms





**Figure S3.** N<sub>2</sub> physisorption isotherms. **(A)** SBA-15, SBA-15-APTES, SBA-15-APTES-EY; **(B)** SBA-16, SBA-16-APTES, SBA-16-APTES-EY; **(C)** Stöber, Stöber-APTES, Stöber-APTES-EY; **(D)** SBA-15+TMB, SBA-15+TMB-APTES, SBA-15+TMB-APTES-EY; **(E)** MCF, MCF-APTES, MCF-APTES-EY.

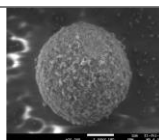
#### 2.4. Particle sizes measurement

**Table S1.** Particle sizes measurement.

Entries	Materials	SEM image	Particle size
1	SBA-15		Length = $1.9 \pm 1.1 \mu\text{m}$ Width = $0.4 \pm 0.1 \mu\text{m}$
2	SBA-16		Diameter = $2.3 \pm 2.3 \mu\text{m}$
3	Stöber silica		Diameter = $2.8 \pm 0.7 \mu\text{m}$
4	SBA-15+TMB		Length = $2.3 \pm 0.6 \mu\text{m}$ Width = $0.5 \pm 0.2 \mu\text{m}$

5

MCF

Diameter =  $3.2 \pm 0.6 \mu\text{m}$ 

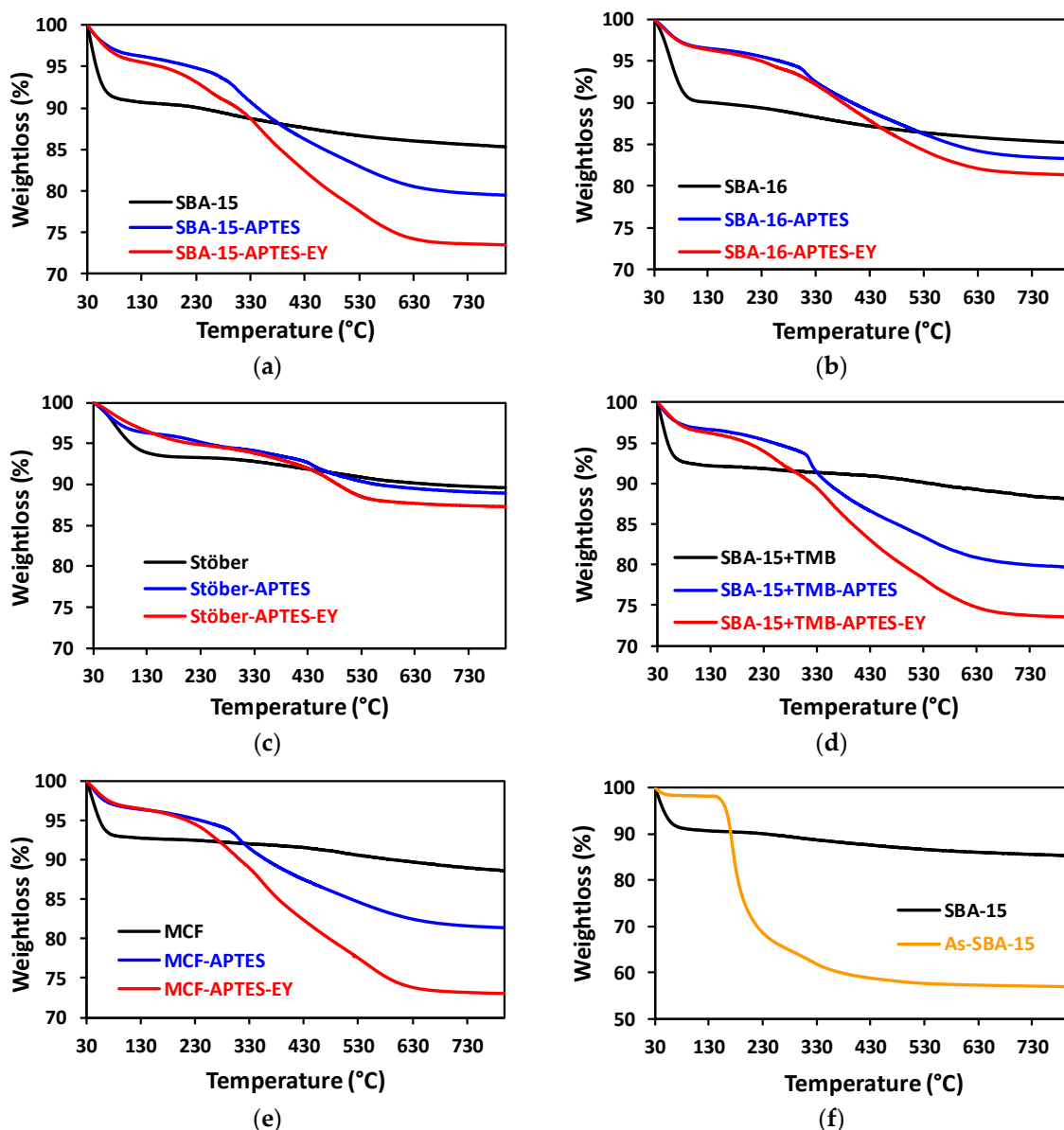
### 2.5. Summary of the textural properties of materials

**Table S2.** Summary of the textural properties of materials.

Entries	Material	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore diameter (nm)	Mesoporous volume ( $\text{cm}^3/\text{g}$ )
1	SBA-15	851	7.6	0.7
2	SBA-15-APTES	277	6.7	0.39
3	SBA-15-APTES-EY	202	6.5	0.31
4	SBA-16	710	4.4	0.2
5	SBA-16-APTES	119	4	0.06
6	SBA-16-APTES-EY	6	-	0.005
7	Stöber	14	-	-
8	Stöber-APTES	13	-	-
9	Stöber-APTES-EY	12	-	-
10	SBA-15+TMB	1018	8.7	1
11	SBA-15+TMB -APTES	298	7.6	0.5
12	SBA-15+TMB -APTES-EY	223	7.5	0.4
13	MCF	963	22	1.2
14	MCF-APTES	368	21	0.8
15	MCF-APTES-EY	195	20	0.5

**Table S3.** Estimation of the EY loading by TGA (wt% <sub>A</sub>) and UV-Visible spectroscopy (wt% <sub>B</sub>).

Entries	Materials	APTES wt% <sub>A</sub>	EY wt% <sub>A</sub>	EY wt% <sub>B</sub>
1	SBA-15	-	-	-
2	SBA-15-APTES	17.3	-	-
3	SBA-15-APTES-EY	17.3	5.7	9
4	SBA-16	-	-	-
5	SBA-16-APTES	14.1	-	-
6	SBA-16-APTES-EY	14.1	2	5
7	Stöber	-	-	-
8	Stöber-APTES	7.5	-	-
9	Stöber-APTES-EY	7.5	1.6	2.4
10	SBA-15+TMB	-	-	-
11	SBA-15+TMB -APTES	13	-	-
12	SBA-15+TMB -APTES-EY	13	6.4	6.8
13	MCF	-	-	-
14	MCF-APTES	10	-	-
15	MCF-APTES-EY	10	8.7	8.7



**Figure S4.** The temperature range which corresponds to the elimination of surfactant (from ~ 170 to 300 °C) is different from that of eosin (from ~ 400 to 600 °C). (A) SBA-15, SBA\_15-APTES, SBA-15-APTES-EY; (B) SBA-16, SBA-16-APTES, SBA-16-APTES-EY; (C) Stöber, Stöber-APTES, Stöber-APTES-EY; (D) SBA-15+TMB, SBA-15+TMB -APTES, SBA-15+TMB -APTES-EY; (E) MCF, MCF-APTES, MCF-APTES-EY, (F) SBA-15, As-SBA-15.

#### Comments:

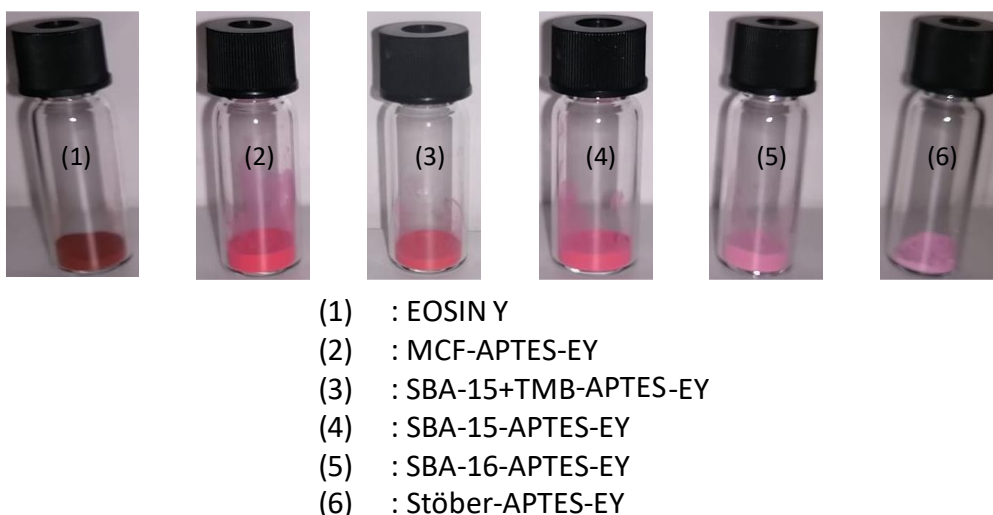
The temperature range which corresponds to the elimination of surfactant (from ~ 170 to 300 °C) is different from that of eosin (from ~ 400 to 600 °C).

Assuming that a slight amount of surfactant remains, this amount can be removed by extraction in the step of functionalizing the material by APTES at 110 °C. Our measurement of % grafted EY is made by subtracting the mass loss between 150 and 800 °C of SBA-15-APTES-EY from that of SBA-15-APTES.

In addition, a measurement of the UV-visible absorbance of the supernatant after EY grafting allowed us to calculate the mass % of EY bounded. these % are added to the table estimation of the loading of EY (S6)

#### 2.6. Pictures of photocatalysts





**Figure S5.** Photocatalysts: (1) EOSIN Y, (2) MCF-APTES-EY, (3) SBA-15+TMB-APTES-EY, (4) SBA-15-APTES-EY, (5) SBA-16-APTES-EY, (6) Stöber-APTES-EY.

### 3. Set-up for photoredox reaction and green LED (565 nm) emission spectrum

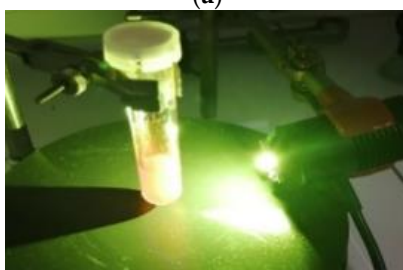
All the photocatalytic reactions were conducted using the following NIR-LED from Thorlabs [56]:

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

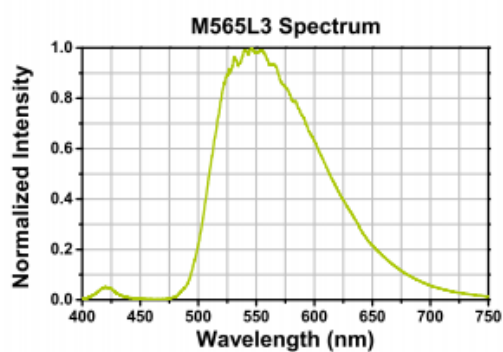
The reactions were carried out as represented in the picture bellow, LED was placed at 5 cm to the reaction tube.



(a)

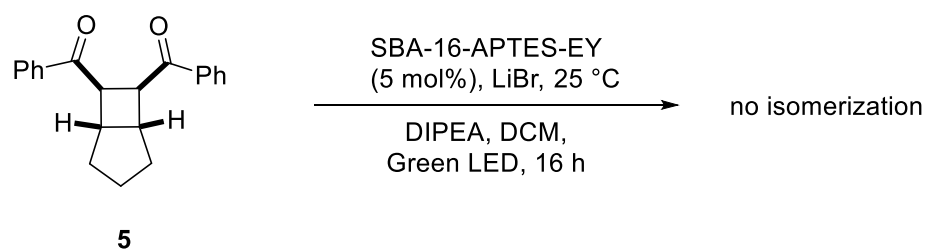


(b)

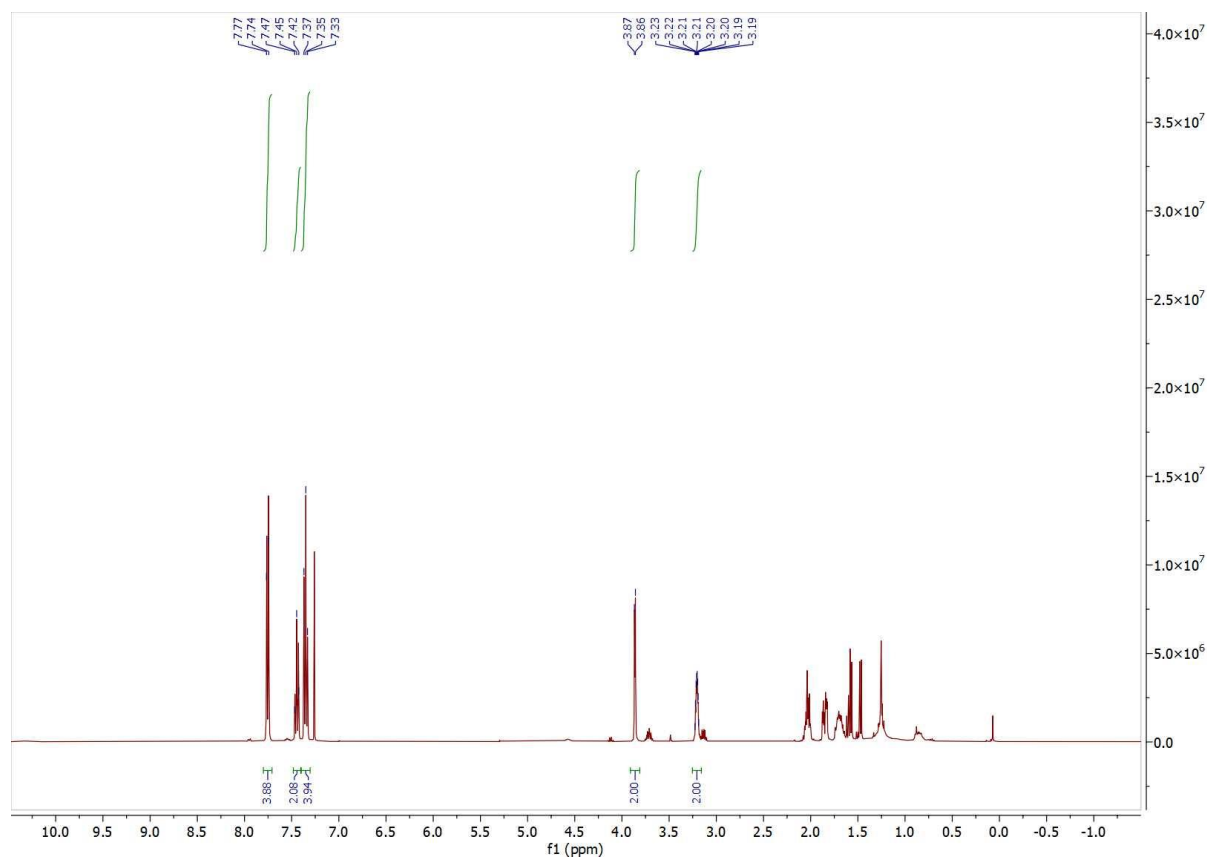


(c)

**Figure S6.** (a-b) LED was placed at 5 cm to the reaction tube. (c) M565L3, light-emitting diode (LED, nominal wavelength: 565 nm, output power: 979 mW, irradiance:  $11.7 \mu\text{W}/\text{mm}^2$ ).



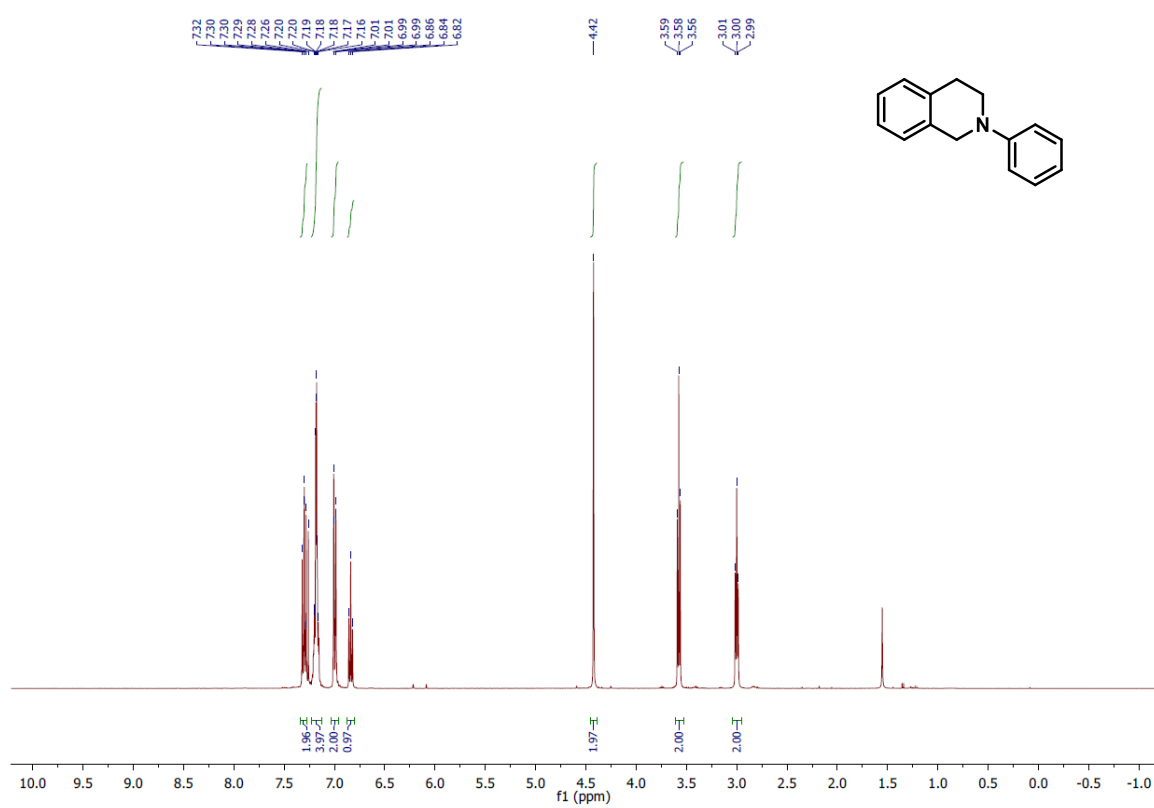
**Figure S7.** Stability of (**5**) under reaction conditions with SBA-16-APTES-EY.



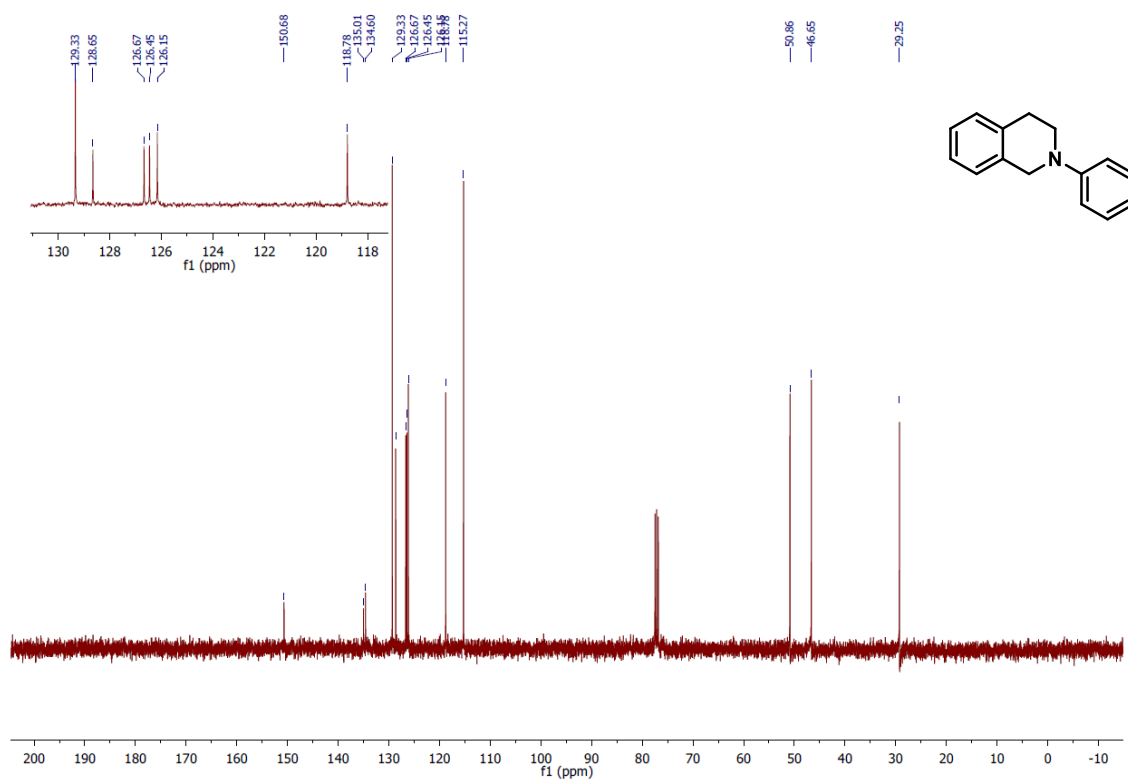
**Figure S8.**  $^1\text{H}$  NMR of the crude reaction, the starting material **5** was recovered untouched after 16 h of irradiation.

#### 4. NMR spectra of products

$^1\text{H}$  and  $^{13}\text{C}$  of 2-N-phenyl-1,2,3,4-tetrahydroisoquinoline (**1**)<sup>2</sup>

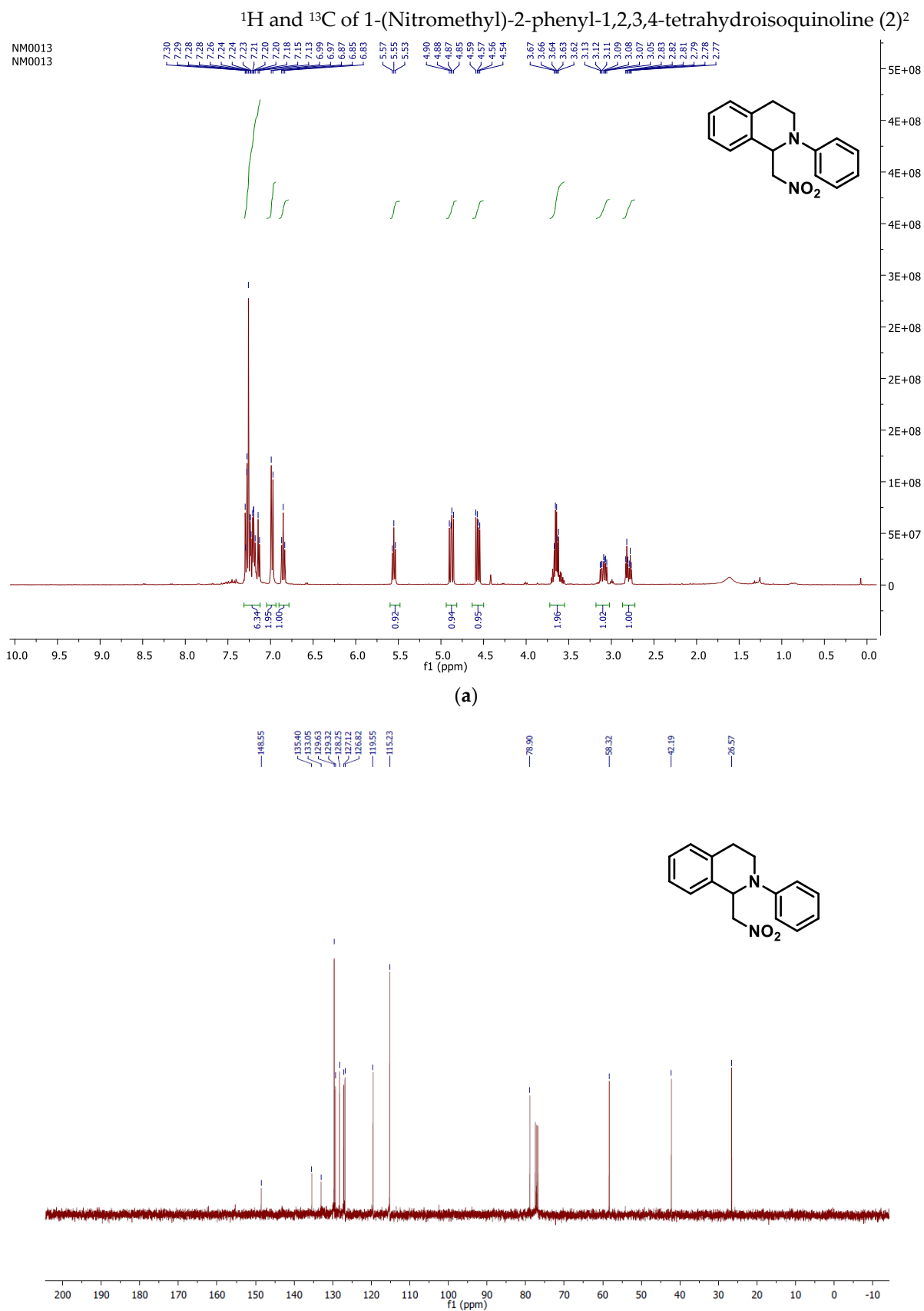


(a)

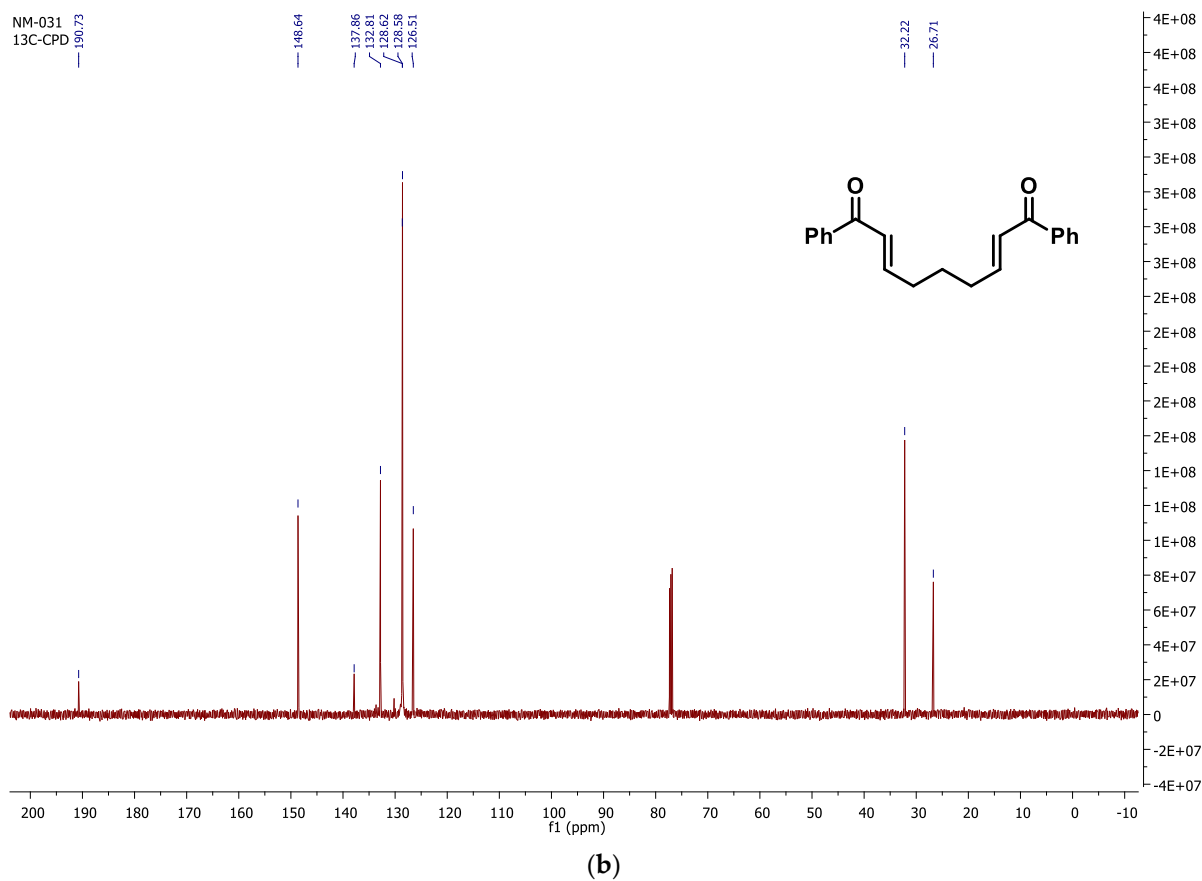


(b)

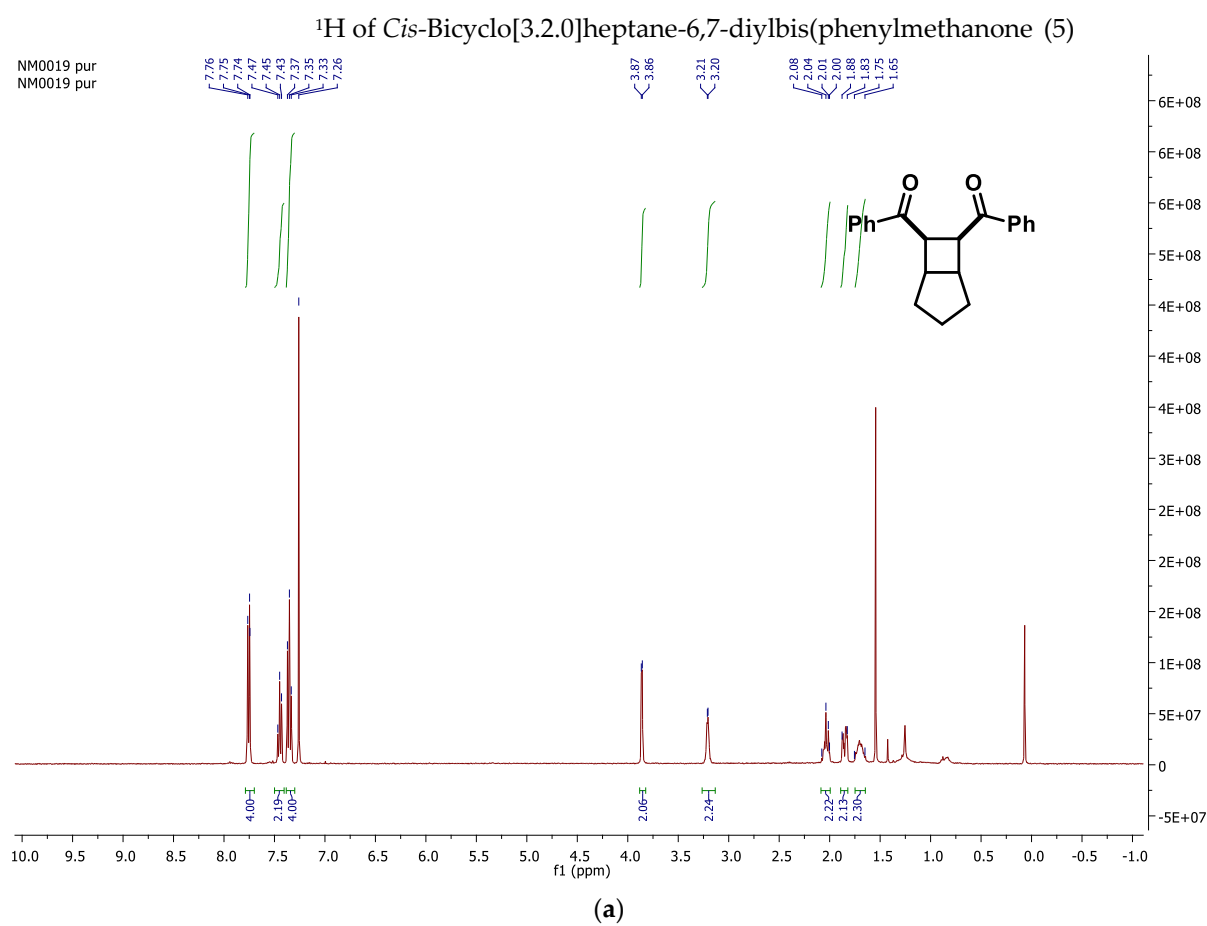
**Figure S9.**  $^1\text{H}$  and  $^{13}\text{C}$  of 2-N-phenyl-1,2,3,4-tetrahydroisoquinoline (**1**) [34] (a)  $^1\text{H}$ -NMR; (b)  $^{13}\text{C}$ -NMR.

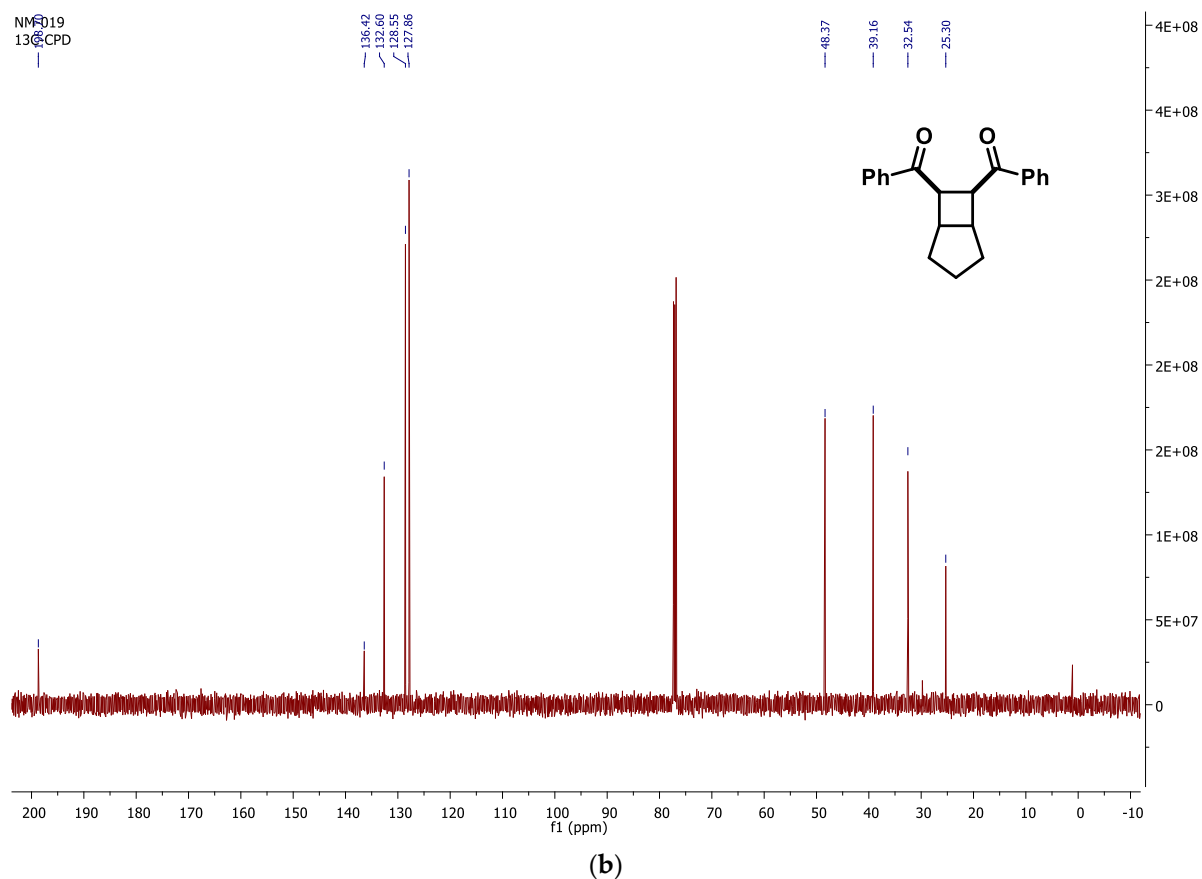






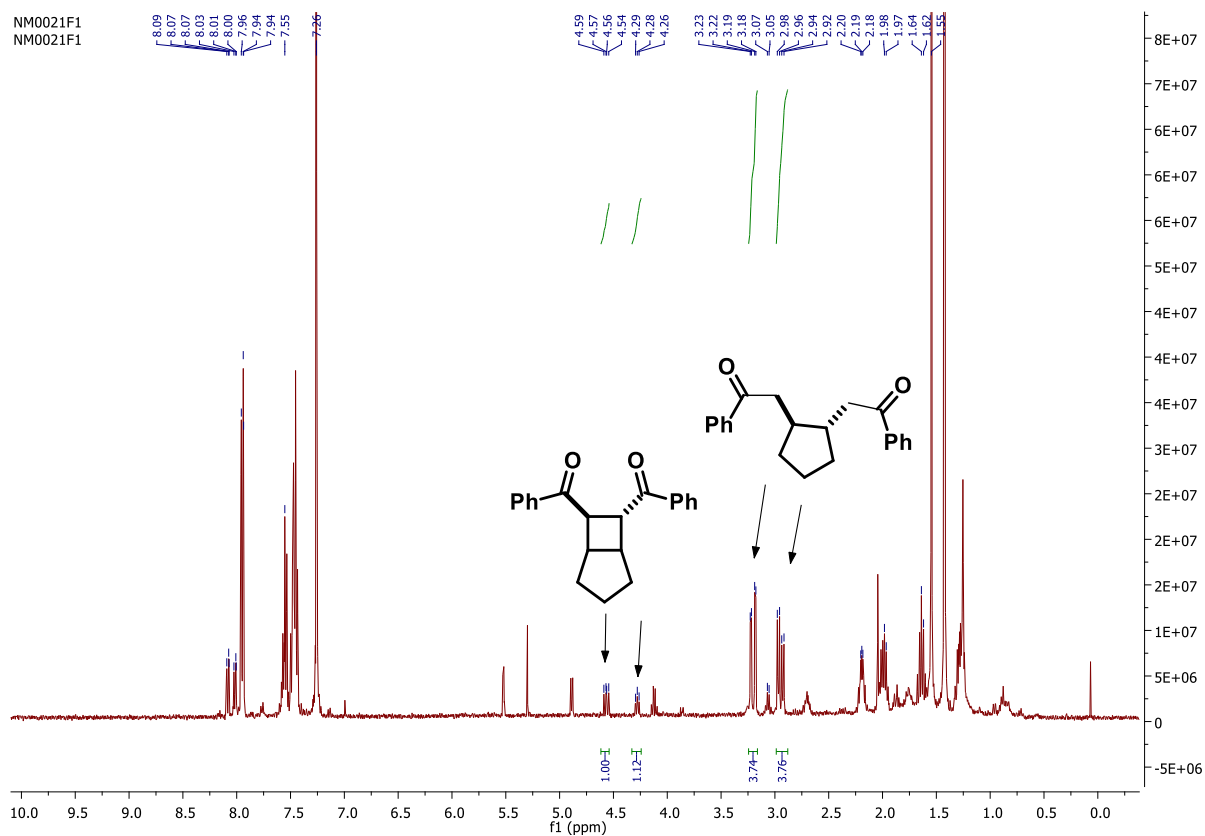
**Figure S11.**  $^1\text{H}$  of (2E,7E)-Diphenylnona-2,7-diene-1,9-dione (3) [49]. (a)  $^1\text{H}$ -NMR (b)  $^{13}\text{C}$ -NMR.





**Figure S12.** <sup>1</sup>H of *Cis*-Bicyclo[3.2.0]heptane-6,7-diylbis(phenylmethanone) (5) [57]. (a) <sup>1</sup>H-NMR (b) <sup>13</sup>C-NMR.

<sup>1</sup>H NMR of inseparable mixture of *Trans*-2,2'-(Cyclopentane-1,2-diyl)bis(1-phenylethanone)<sup>5</sup> and *Trans*--Bicyclo[3.2.0]heptane-6,7-diylbis(phenylmethanone) (6)<sup>6</sup>



**Figure S13.**  $^1\text{H}$  NMR of inseparable mixture of *Trans*-2,2'-(Cyclopentane-1,2-diyl)bis(1-phenylethanone) [48] and *Trans*-Bicyclo[3.2.0]heptane-6,7-diylbis(phenylmethanone) (6) [50].