

## **Electronic Supplementary Information**

### **Carbon dot/TiO<sub>2</sub> nanocomposites as photocatalysts for metallaphotocatalytic carbon-heteroatom cross-couplings**

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## 1. General materials and methods

All substrates, reagents, and solvents were obtained from commercial suppliers and were used without further purification unless otherwise noted. All light-emitting diode (LED) lamps were purchased from Kessil Lighting (<https://www.kessil.com/science/index.php>). Analytical thin layer chromatography (TLC) was performed on pre-coated TLC-sheets, ALUGRAM Xtra SIL G/UV<sub>254</sub> sheets (Macherey-Nagel) and visualized with 254 nm light or staining solutions followed by heating. Purification of final compounds was carried out by flash chromatography on the Reveleris X2 Flash Chromatography System from GRACE using prepacked columns with 40  $\mu\text{m}$  silica gel. Silica 60 M (0.04-0.063 mm) silica gel (Sigma Aldrich) was used for dry loading of the crude compounds on the flash chromatography system. Carbon dots (CDs) were synthesized using a domestic microwave (SEVERIN). Centrifugation of CDs and CD/titanium dioxide (TiO<sub>2</sub> P25) nanocomposites were carried out using an Eppendorf 5810R centrifuge and an Eppendorf 5430 centrifuge, respectively. NMR spectra were recorded on an Ascend<sup>TM</sup> 400 (400 MHz, Bruker) spectrometer, and are reported in ppm relative to the residual solvent peaks. Peaks are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, with coupling constants in Hz. Infrared (IR) spectra were recorded on a Perkin-Elmer FT-IR spectrometer (Spectrum 100). The morphologies of CDs were observed using transmission electron microscopy (TEM, Zeiss EM 912 $\Omega$ ). The prepared CDs were diluted with distilled water to suitable concentrations and then deposited onto carbon-coated copper grids. After drying at room temperature, the samples were imaged. The morphologies and elemental composition of CD/TiO<sub>2</sub> P25 nanocomposites were measured using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX, LEO 1550 system). The freeze-dried CD/TiO<sub>2</sub> P25 nanocomposites were suspended in distilled water and sonicated for 5 min. The resulting suspension was deposited on the silicon substrate and coated with Au. After drying at room temperature, the samples were imaged. Fluorescence spectra of CDs were measured using a microplate reader (SpectraMax M5, Molecular Devices). Absorption spectra of CDs and CD/TiO<sub>2</sub> P25 nanocomposites were collected using a Shimadzu UV-1900 (solutions), or a Shimadzu UV-2600 spectrometer equipped with an integrating sphere (solids). X-ray diffraction (XRD) spectrum was measured with a Bruker D8 Advanced X-ray diffractometer with Cu K $\alpha$  radiation. Zeta potential was

measured with a dynamic light scattering instrument (DLS, Zetasizer Nano, Malvern). Photoluminescence lifetime was measured using the time-correlated single photon counting technique (TCSPC, FluoTime 250, fluorescence lifetime spectrometer). Inductively coupled plasma - optical emission spectrometry (ICP-OES) was carried out using a Horiba Ultra 2 instrument equipped with a photomultiplier tube detection system.

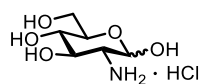
## 2. Synthesis of CDs

The carbohydrate carbon source was dissolved in ultrapure H<sub>2</sub>O (20 mL) in a conical flask (300 mL). The doping agent was added and the mixture was agitated to yield a homogenous solution. The flask was transferred into a domestic microwave in a fume hood and heated at 700 W for the respective time. The crude mixture was cooled for 10 min before ultrapure H<sub>2</sub>O (40 mL) was added. The resulting solution was filtered through a filter paper and centrifuged at 8000 rpm for 0.5 h through Amicon® Ultra-15 centrifugal filter units. The filtrate was lyophilized to yield the desired CDs.

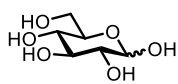
**Table S1** Summary of the conditions used for the synthesis of the CDs.

Entry	CD	Carbon source (mmol/mL)	Doping agent (mmol/mL)	Time / min
1	CD1	GlcN·HCl (0.12)	β-Ala (0.13)	3
2	CD2 <sup>a</sup>	GlcN·HCl (0.15)	1,3-Diaminobenzene (0.17)	3
3	CD3		l-Cys (0.25)	3
4	CD4	GlcN·HCl (0.23)	PEG (0.25)	9
5	CD5		Gly (0.25)	3
6	CD6	Glc (0.12)		4.5
7	CD7	GlcNAc (0.12)		4.5
8	CD8	Gal (0.12)	β-Ala (0.13)	4.5
9	CD9	Lac (0.12)		4.5
10	CD10	Pullulan (25 mg/mL)		5

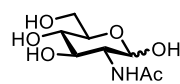
<sup>a</sup>The doping agent was first dissolved in MeOH (10 mL) and then added to the aqueous solution (20 mL) of carbon source. GlcN·HCl = glucosamine hydrochloride. Glc = glucose. GlcNAc = *N*-acetylglucosamine. Gal = galactose. Lac = D-lactose. β-Ala = β-alanine. l-Cys = l-cysteine. PEG = poly(ethylene glycol) (average *M<sub>n</sub>* 400). Gly = glycine.

**Carbon source**

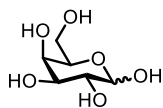
GlcN·HCl



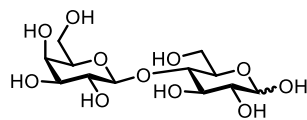
Glc



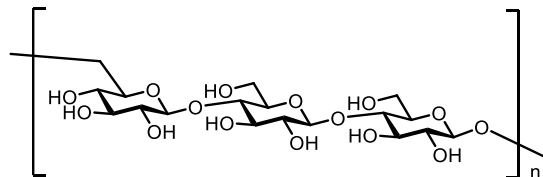
GlcNAc



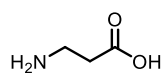
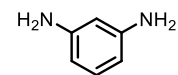
Gal



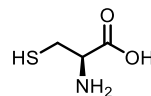
Lac



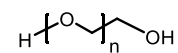
Pullulan

**Doping agent** $\beta$ -Ala

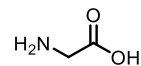
1,3-Diaminobenzene



L-Cys



PEG



Gly

**Fig. S1** Chemical structures of carbon sources and doping agents used for CD synthesis.

### 3. Preparation of CD/TiO<sub>2</sub> P25 nanocomposites

TiO<sub>2</sub> P25 (120 mg) was dispersed in ultrapure H<sub>2</sub>O (80 mL) in a round-bottom flask. The respective amount of CDs was added to prepare nanocomposites with different CD-to-TiO<sub>2</sub> P25 mass ratios. The mixture was shielded from light and stirred for 24 h at room temperature. The resulting CD/TiO<sub>2</sub> nanocomposites were centrifuged at 5000 rpm for 15 min and further washed two times with ultrapure H<sub>2</sub>O. The nanocomposites were lyophilized to afford a light brown powder. The amount of CDs immobilized on the TiO<sub>2</sub> P25 surface was determined using UV-Vis absorption spectroscopy.

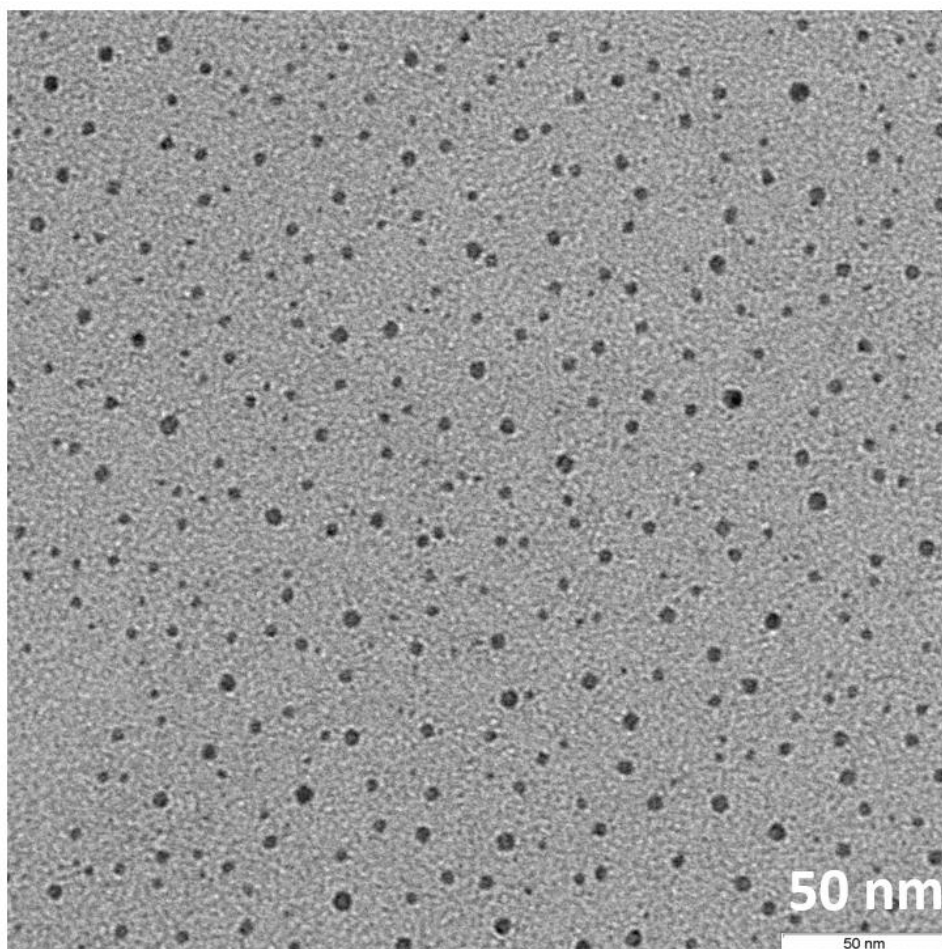
**Table S2** Conditions used for the preparation of the CD/TiO<sub>2</sub> nanocomposites.

Entry	CD	CD-to-TiO <sub>2</sub> P25 mass ratio	CD Immobilization (weight % (CD/nanocomposite))
1	<b>CD1</b>	1 : 20	1.5
2		1 : 10	1.8
3		1 : 4	2.4
4		1 : 1	5.0
5		4 : 1	8.1
6		1 : 1 (CD-to-SiO <sub>2</sub> )	1.6
7	<b>CD2</b>	1 : 1	– <sup>a</sup>
8	<b>CD3</b>	1 : 1	2.5
9	<b>CD4</b>	1 : 1	13.6
10	<b>CD5</b>	1 : 1	3.4
11	<b>CD6</b>	1 : 1	3.7
12	<b>CD7</b>	1 : 1	11.9
13	<b>CD8</b>	1 : 1	3.0
14	<b>CD9</b>	1 : 1	11.4
15	<b>CD10</b>	1 : 1	27.2

<sup>a</sup>Quantification by UV-Vis was not possible due to the formation of side-products in the solution that affected the measurements.

## 4. Characterization of CDs

### 4.1. CD1

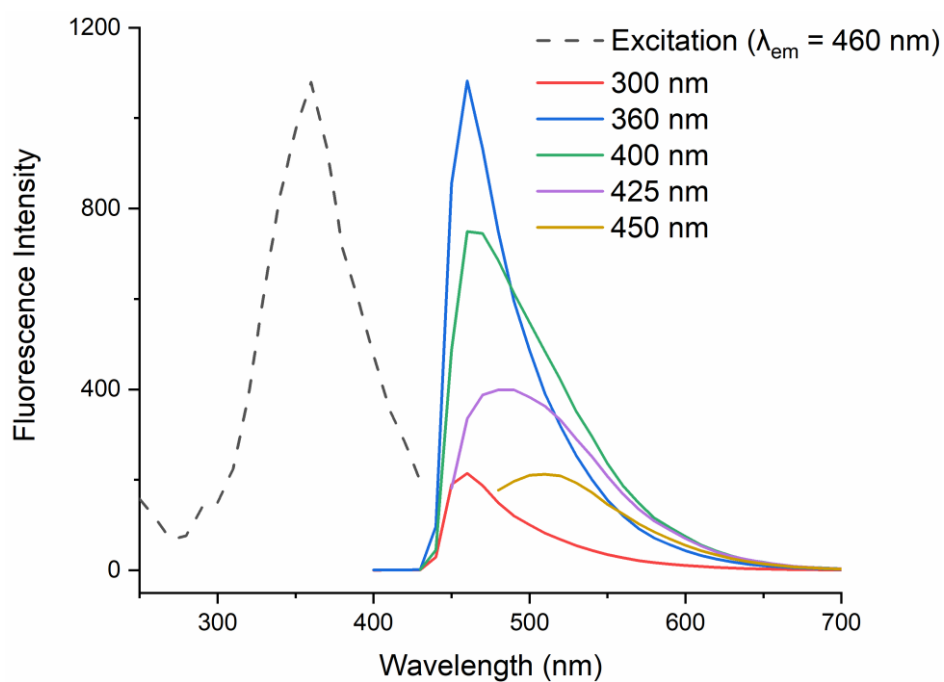


**Fig. S2** TEM image of **CD1**.

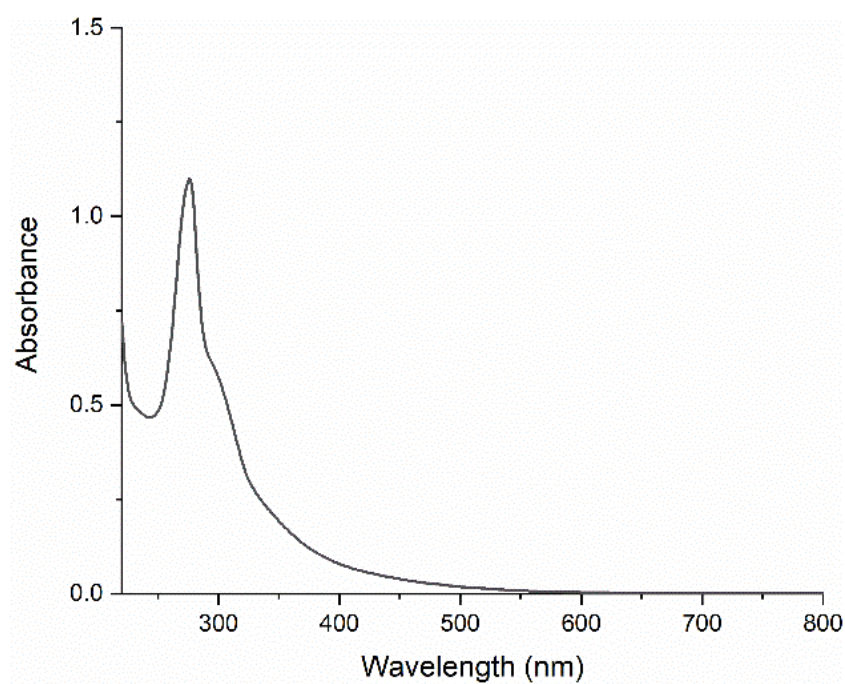


**Fig. S3** Photographs of an aqueous solution of **CD1** in daylight (left) and under UV light irradiation ( $\lambda_{\text{ex}} = 366 \text{ nm}$ , right).

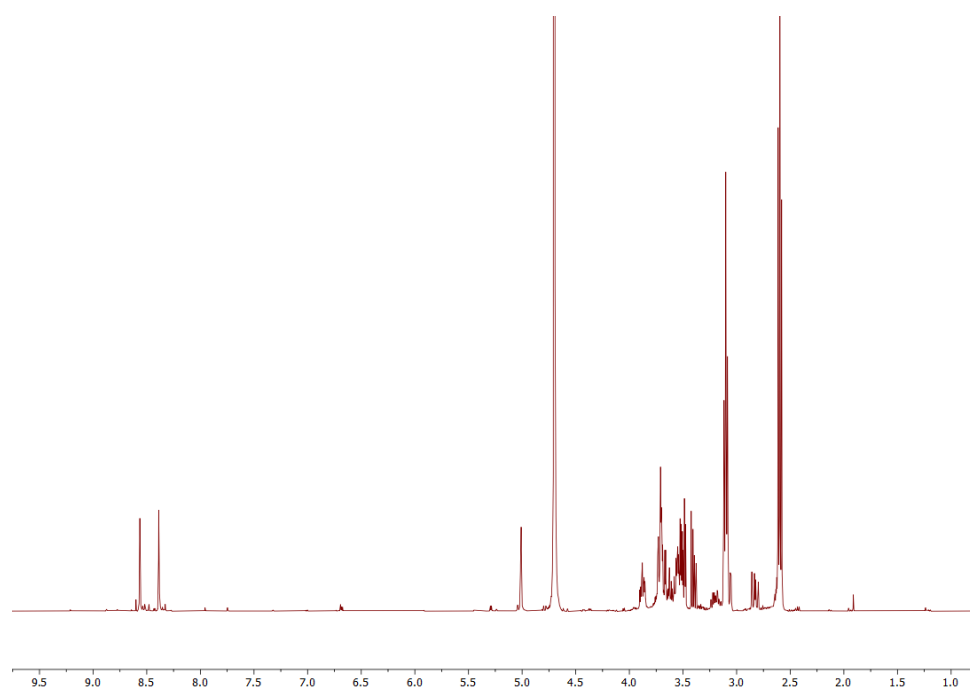




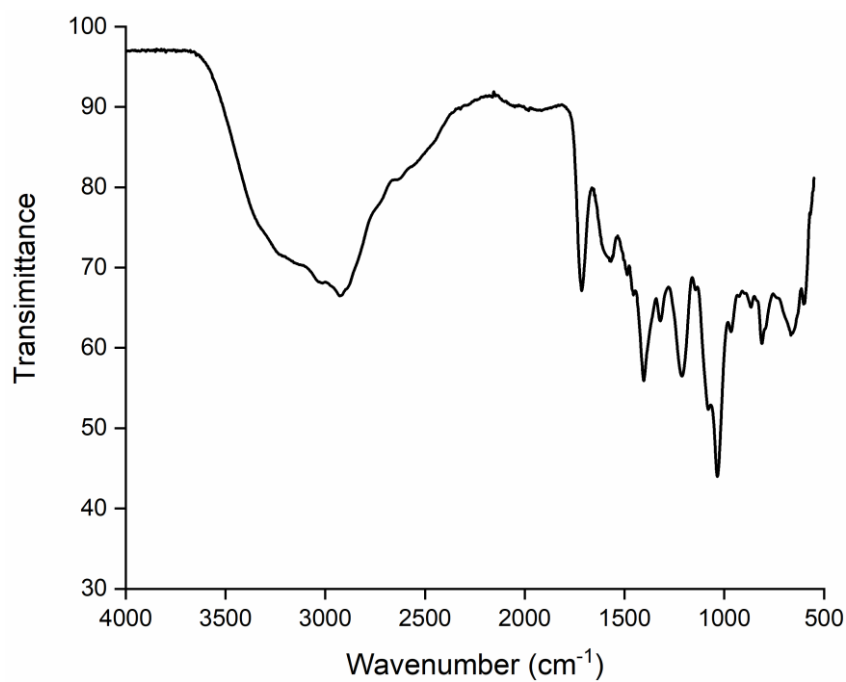
**Fig. S4** Excitation ( $\lambda_{\text{em}} = 460 \text{ nm}$ ) and emission spectra of **CD1** recorded upon excitation with different excitation wavelengths ( $\text{H}_2\text{O}$ , 298 K).



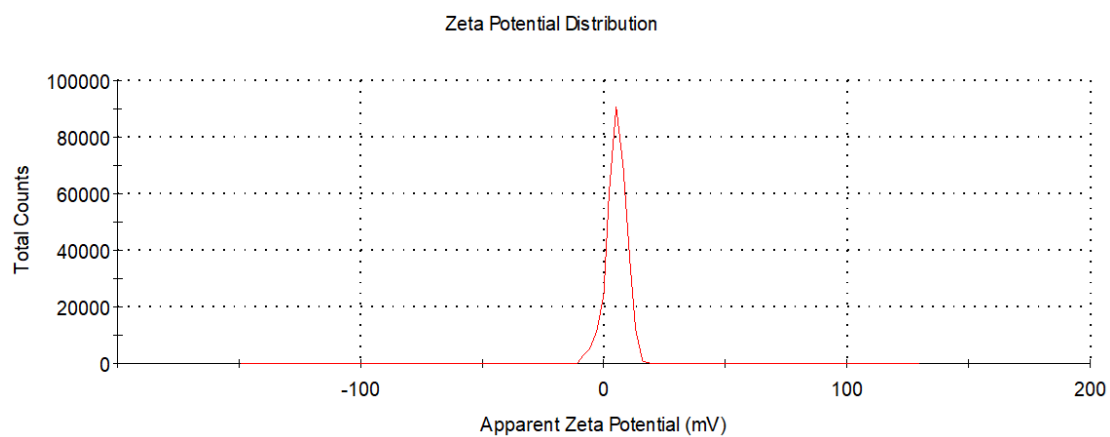
**Fig. S5** Absorption spectrum of **CD1** ( $\text{H}_2\text{O}$ , 298 K).



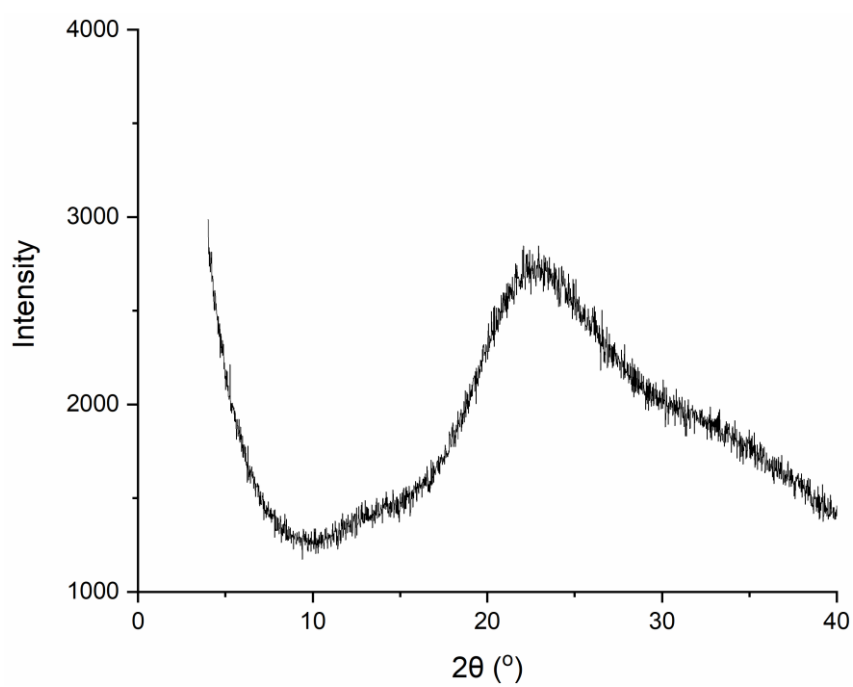
**Fig. S6**  $^1\text{H}$  NMR spectrum of **CD1** in  $\text{D}_2\text{O}$  (400 MHz). The spectrum is in agreement with previously reported data,<sup>1</sup> indicating the presence of the  $\beta$ -alanine on **CD1** surface.



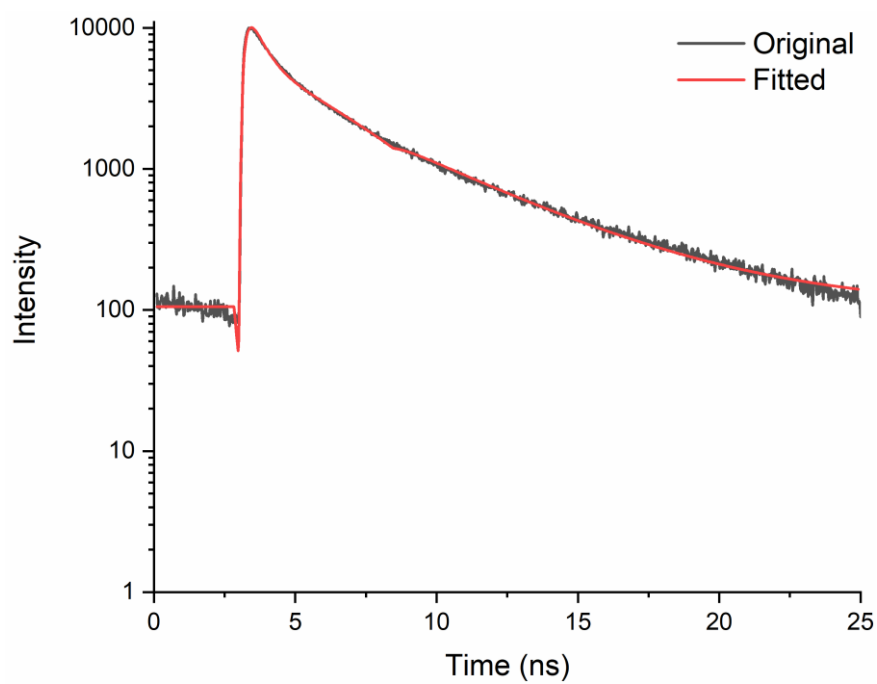
**Fig. S7** IR spectrum of **CD1**. Key features:  $2927\text{ cm}^{-1}$  (O-H);  $1715\text{ cm}^{-1}$  (C=O).



**Fig. S8** Zeta potential of **CD1** (-11.1 to +18.7 mV, H<sub>2</sub>O, 298 K).



**Fig. S9** Powder XRD profile of **CD1** confirming its amorphous nature.

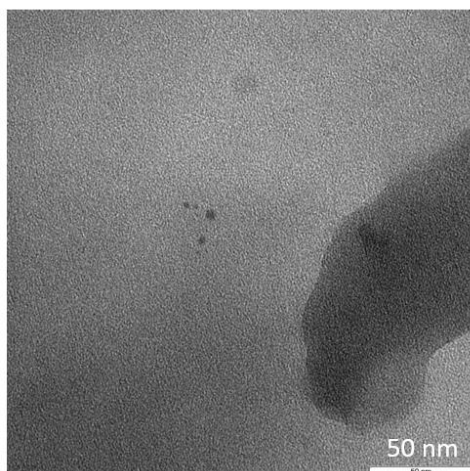


$A_1$	$A_2$	$\tau_1$ (ns)	$\tau_2$ (ns)
10.49	6.131	0.451	4.454

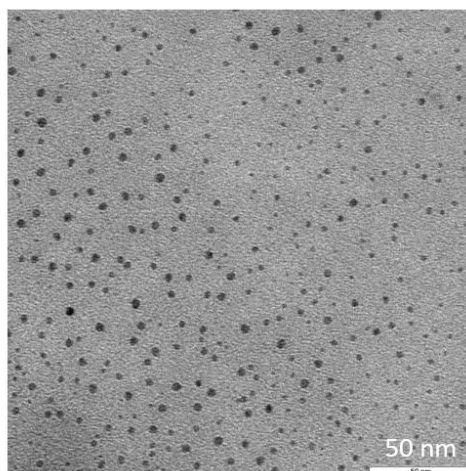
**Fig. S10** Photoluminescence lifetime of **CD1** (H<sub>2</sub>O, 298 K).

## 4.2. Characterization of CD2-CD10

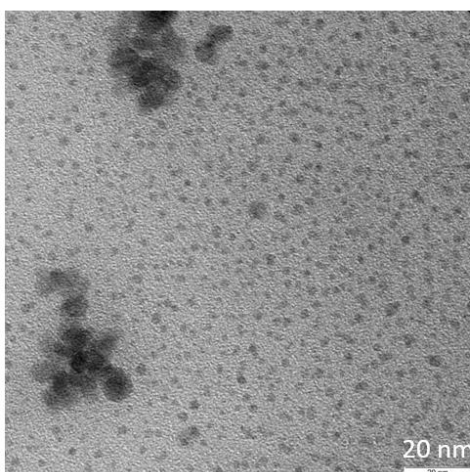
**CD2**



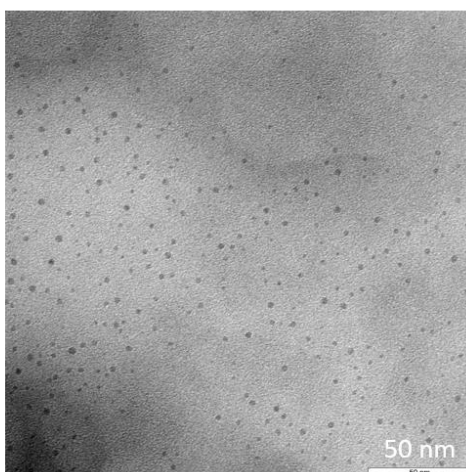
**CD3**



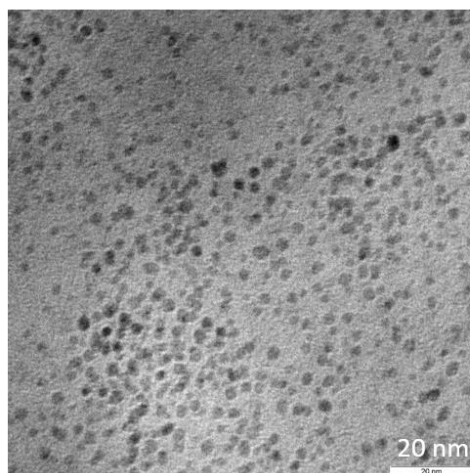
**CD4**



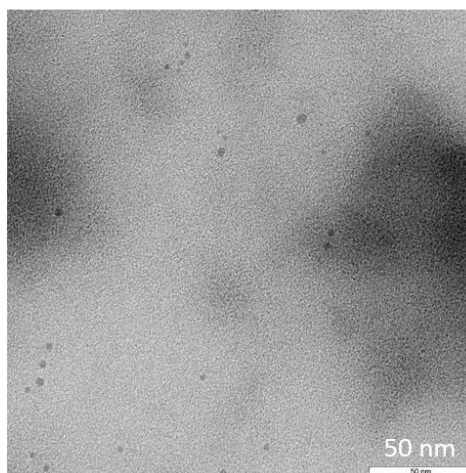
**CD5**



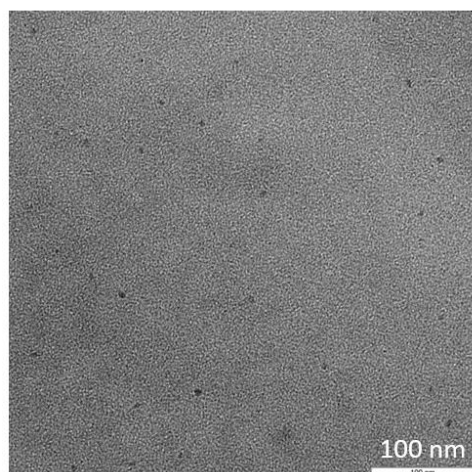
**CD6**



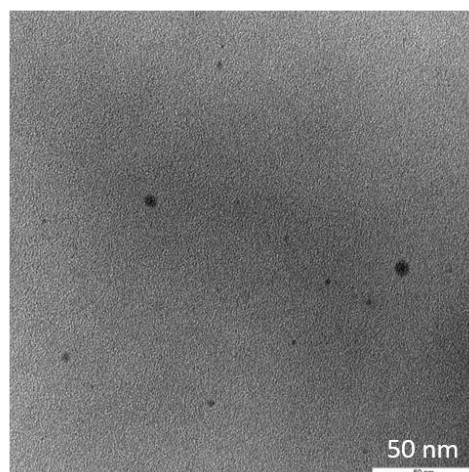
**CD7**



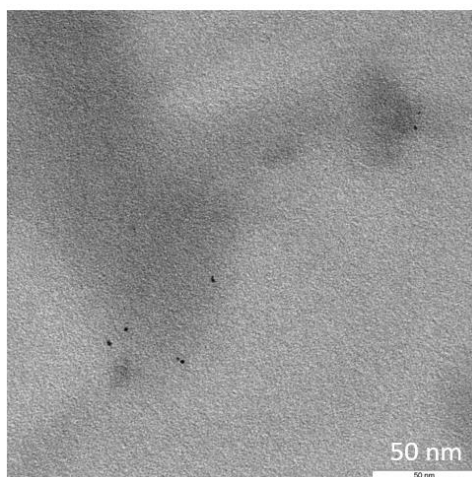
**CD8**



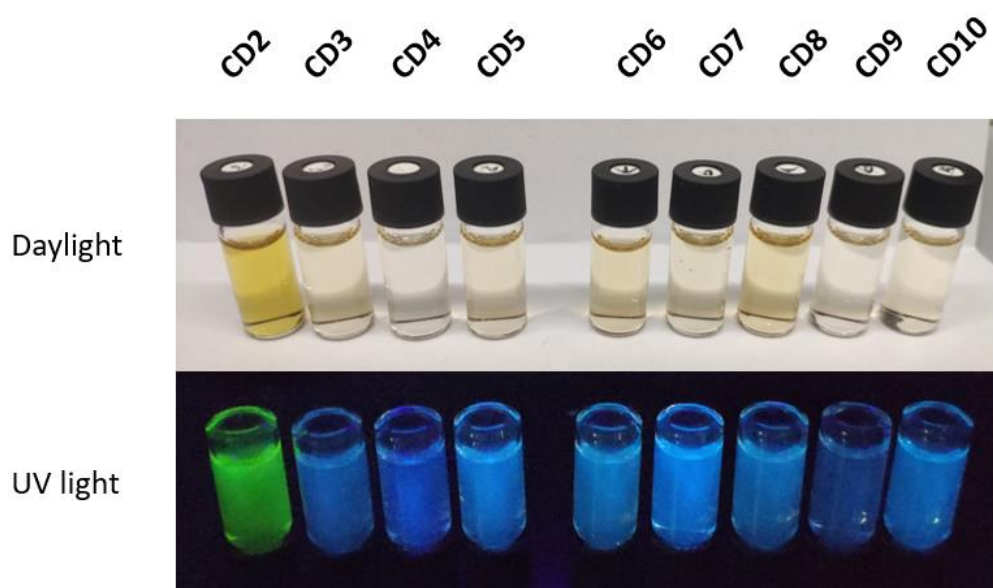
**CD9**



**CD10**

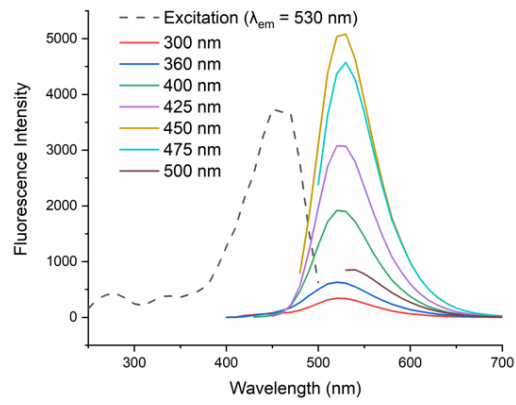


**Fig. S11** TEM images of **CD2**, **CD3**, **CD4**, **CD5**, **CD6**, **CD7**, **CD8**, **CD9** and **CD10**.

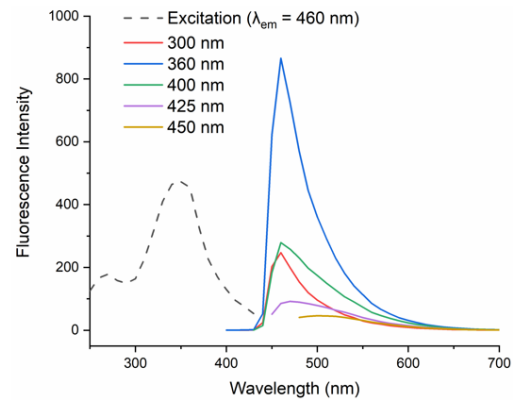


**Fig. S12** Photographs of aqueous solutions of **CD2**, **CD3**, **CD4**, **CD5**, **CD6**, **CD7**, **CD8**, **CD9** and **CD10** in daylight and under UV light irradiation ( $\lambda_{\text{ex}} = 366 \text{ nm}$ ).

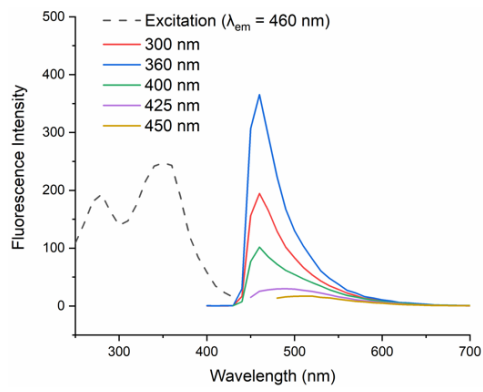
## CD2



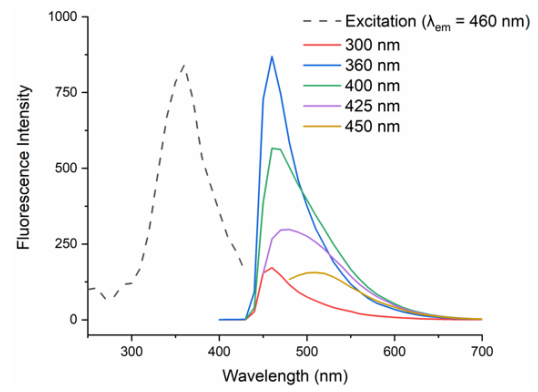
## CD3



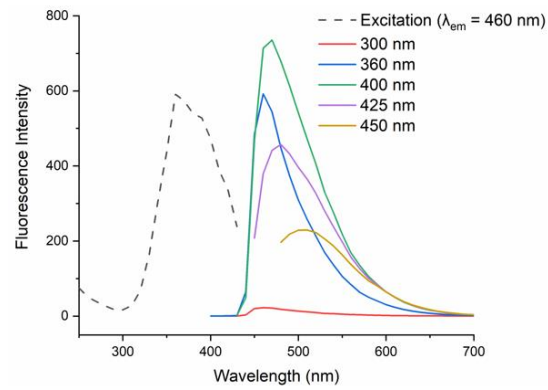
## CD4



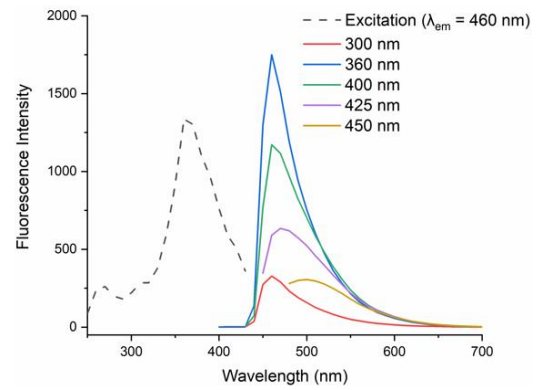
## CD5



## CD6

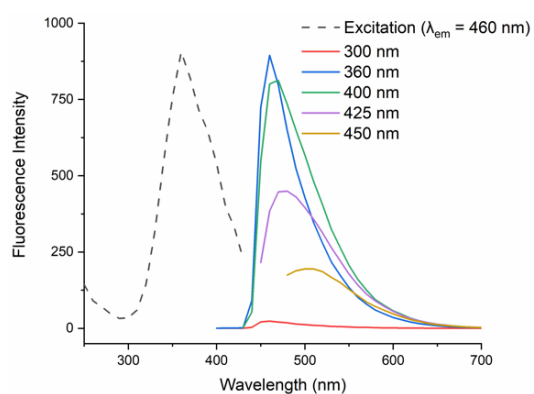


## CD7

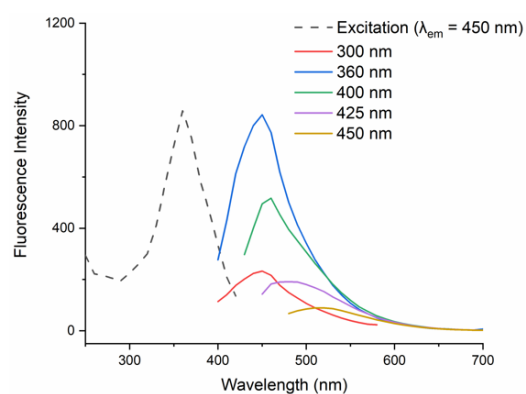




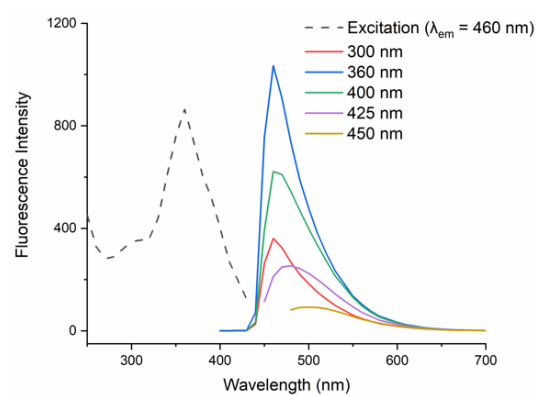
### CD8



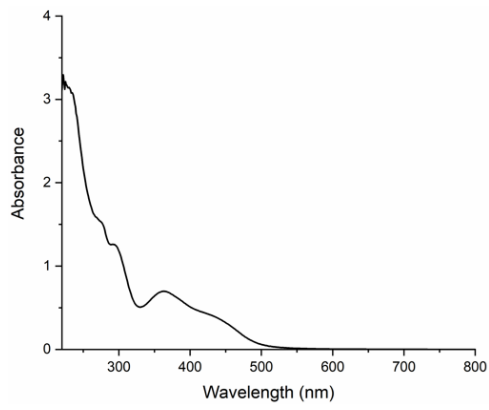
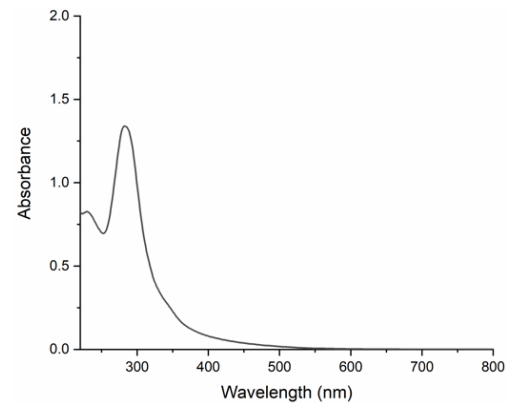
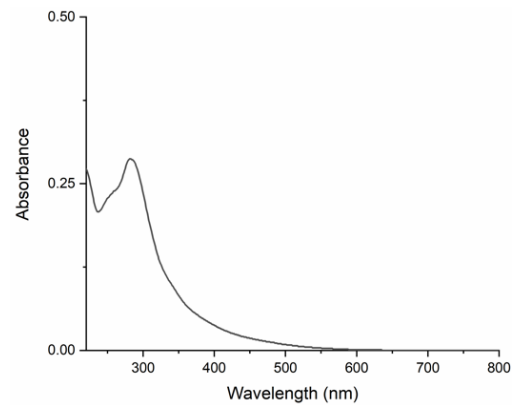
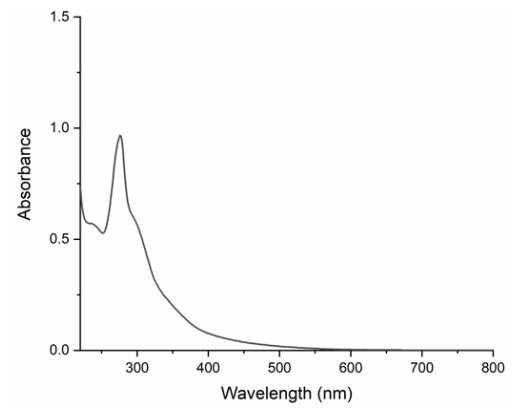
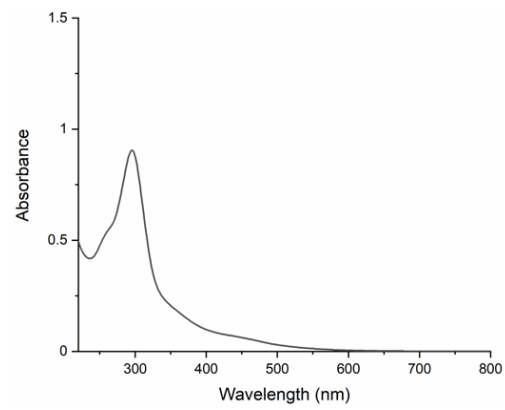
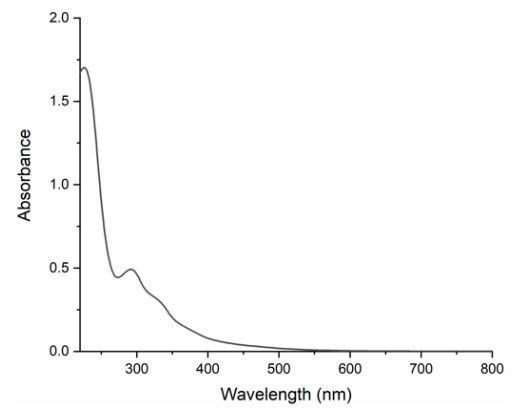
### CD9

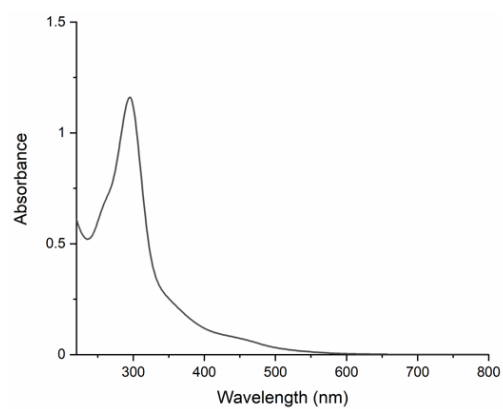
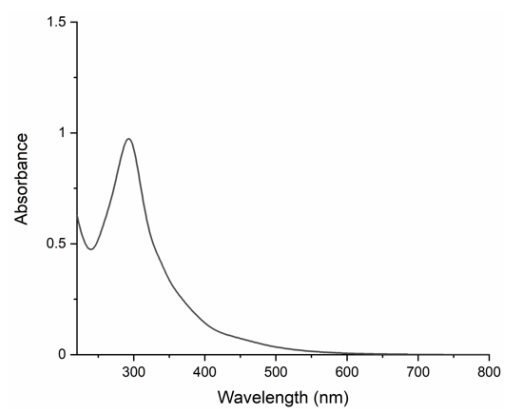
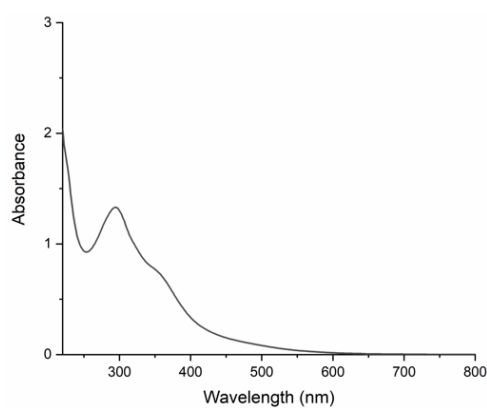


### CD10



**Fig. S13** Excitation and emission spectra of **CD2**, **CD3**, **CD4**, **CD5**, **CD6**, **CD7**, **CD8**, **CD9** and **CD10** recorded upon excitation with different excitation wavelengths ( $H_2O$ , 298 K).

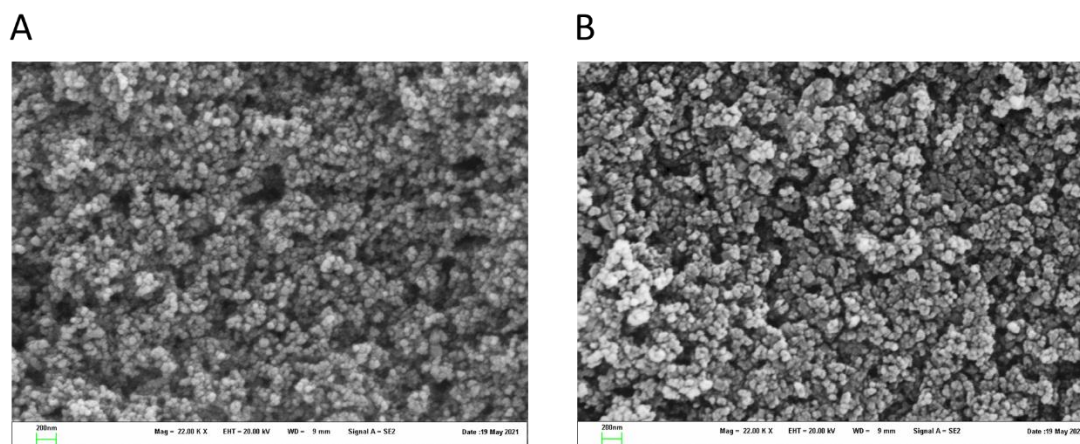
**CD2****CD3****CD4****CD5****CD6****CD7**

**CD8****CD9****CD10**

**Fig. S14** Absorption spectra of **CD2**, **CD3**, **CD4**, **CD5**, **CD6**, **CD7**, **CD8**, **CD9** and **CD10** (H<sub>2</sub>O, 298 K).

## 5. Characterization of CD/TiO<sub>2</sub> nanocomposites

### 5.1. CD1/TiO<sub>2</sub>

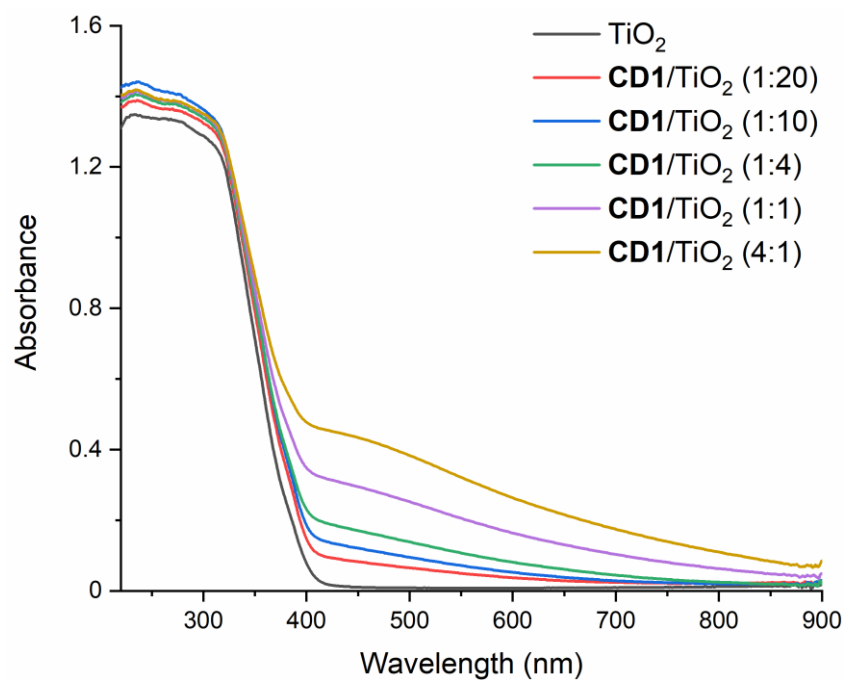


Sample	C	O	Ti	Ni
CD1/TiO <sub>2</sub>	23.86	59.04	17.15	0
CD1/TiO <sub>2</sub> (after)	32.75	60.79	6.26	0.23

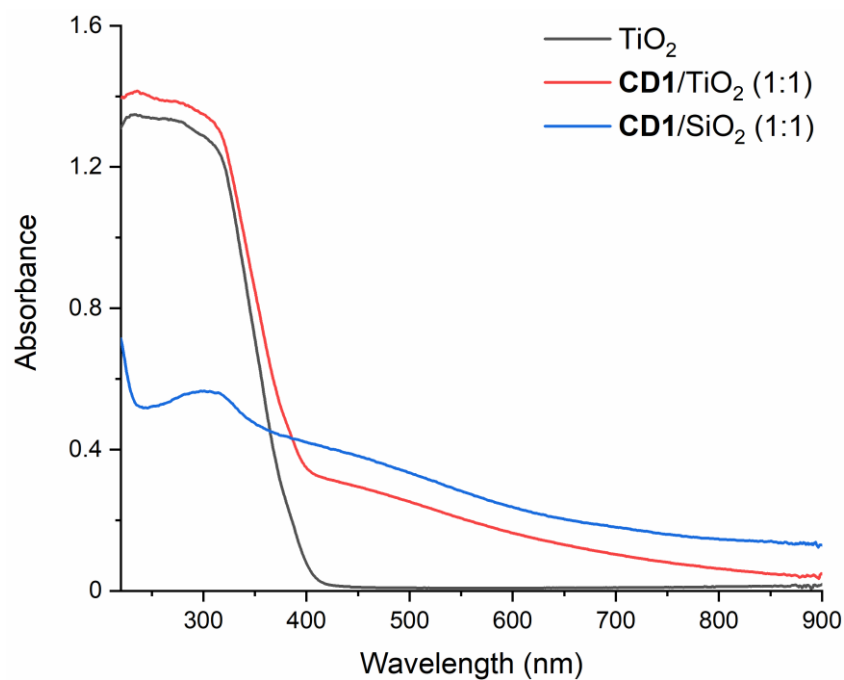
**Fig. S15** SEM image and elemental composition of **CD1/TiO<sub>2</sub>** P25 nanocomposite (A) and **CD1/TiO<sub>2</sub>** P25 nanocomposite after the catalytic reaction (B). All values are given as atomic %.

**Table S3** ICP-OES measurements of the nickel content of **CD1/TiO<sub>2</sub>** P25 nanocomposite and **CD1/TiO<sub>2</sub>** P25 nanocomposite after the catalytic reaction.

Sample	Ni (mg/g)
CD1/TiO <sub>2</sub>	0.016
CD1/TiO <sub>2</sub> (after)	24.8



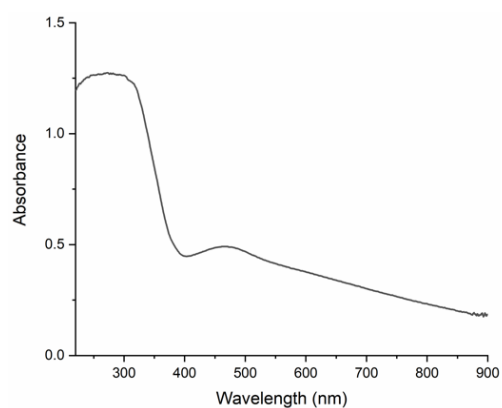
**Fig. S16** Absorption spectra (solid state) of **CD1**/ $\text{TiO}_2$  nanocomposites prepared using different **CD1**-to- $\text{TiO}_2$  P25 mass ratios.



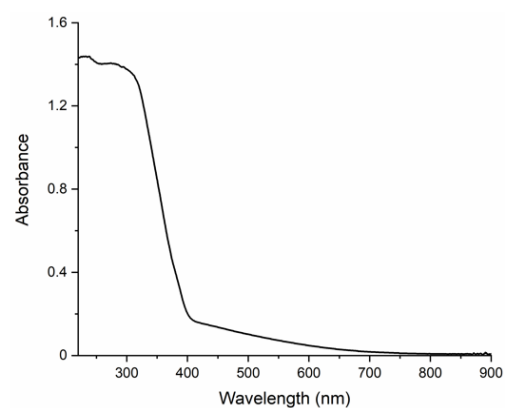
**Fig. S17** Absorption spectra (solid state) of **CD1**/ $\text{TiO}_2$  and **CD1**/ $\text{SiO}_2$  nanocomposites (mass ratio = 1:1).

## 5.2. Characterization of nanocomposites prepared using CD2-CD10

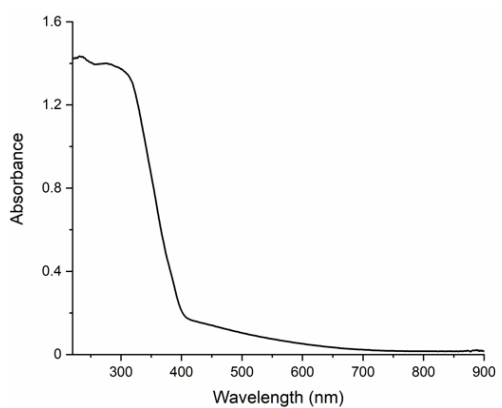
**CD2/TiO<sub>2</sub>**



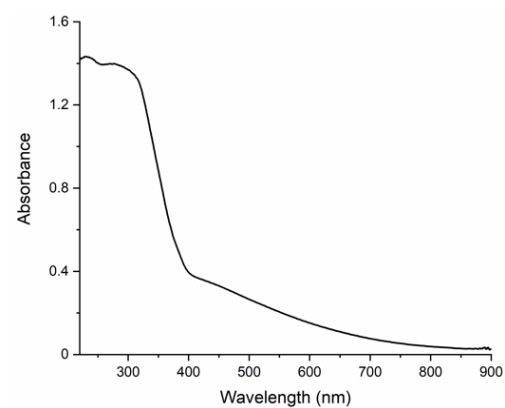
**CD3/TiO<sub>2</sub>**



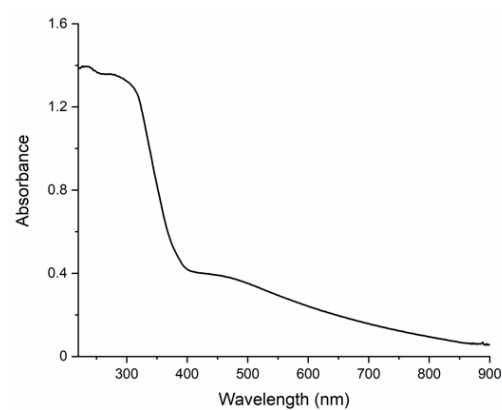
**CD4/TiO<sub>2</sub>**



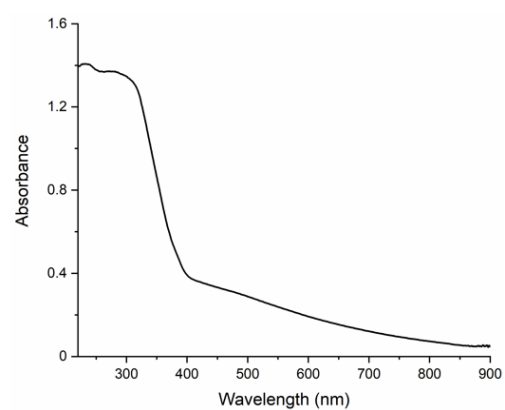
**CD5/TiO<sub>2</sub>**



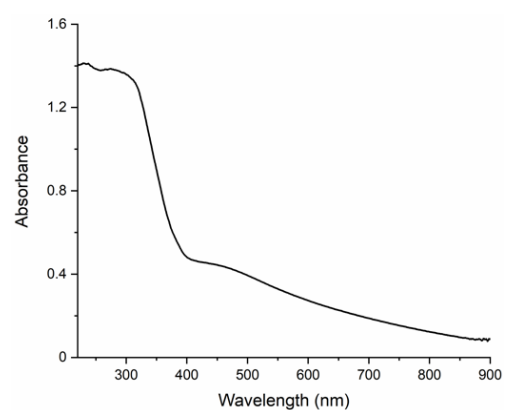
**CD6/TiO<sub>2</sub>**



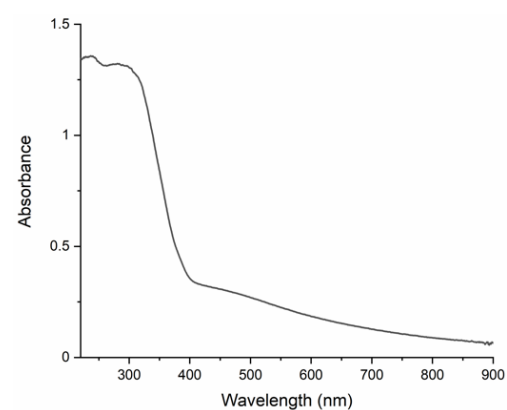
**CD7/TiO<sub>2</sub>**



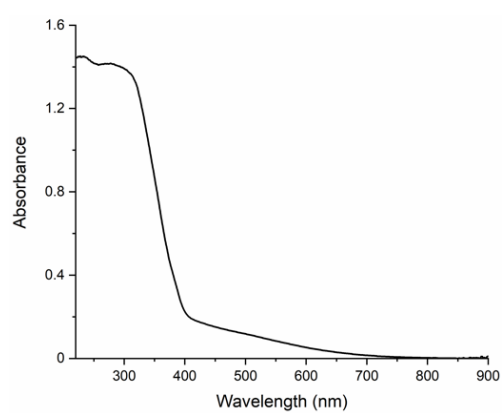
**CD8/TiO<sub>2</sub>**



**CD9/TiO<sub>2</sub>**



**CD10/TiO<sub>2</sub>**



**Fig. S18** Absorption spectra (solid state) of **CD2/TiO<sub>2</sub>**, **CD3/TiO<sub>2</sub>**, **CD4/TiO<sub>2</sub>**, **CD5/TiO<sub>2</sub>**, **CD6/TiO<sub>2</sub>**, **CD7/TiO<sub>2</sub>**, **CD8/TiO<sub>2</sub>**, **CD9/TiO<sub>2</sub>** and **CD10/TiO<sub>2</sub>** nanocomposites.

## 6. Cross-coupling reaction

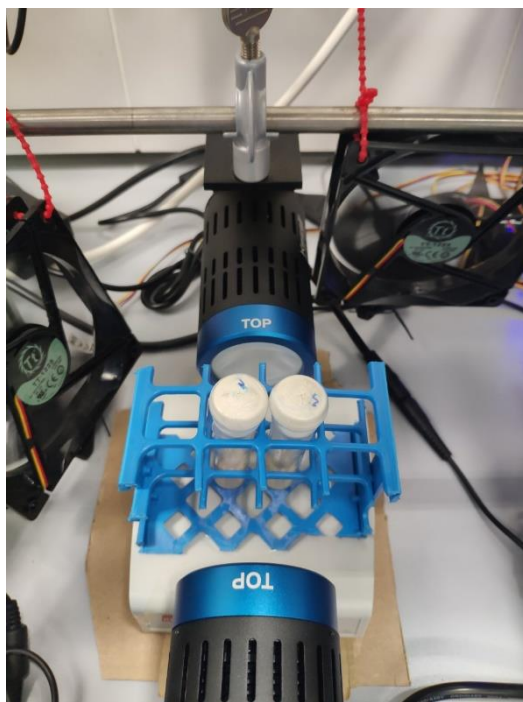
**Setup for blue light experiments.**<sup>1</sup> Two vials were placed in the middle of the stirring plate (4.5 cm away from single lamp). The reaction was irradiated with a single blue LED lamp (Kessil PR160L-440). The fan was used to avoid possible heating of the reaction mixture.



**Fig. S19** Image of the setup using a single blue LED lamp.

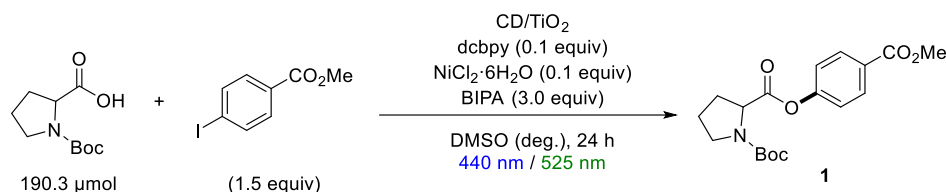


**Setup for green light experiments.**<sup>1</sup> Two vials were placed in the middle of the stirring plate (4.5 cm away from each lamp). The reaction was irradiated with two green LED lamps (Kessil PR160L-525). The fan was used to avoid the possible heating of the reaction mixture.

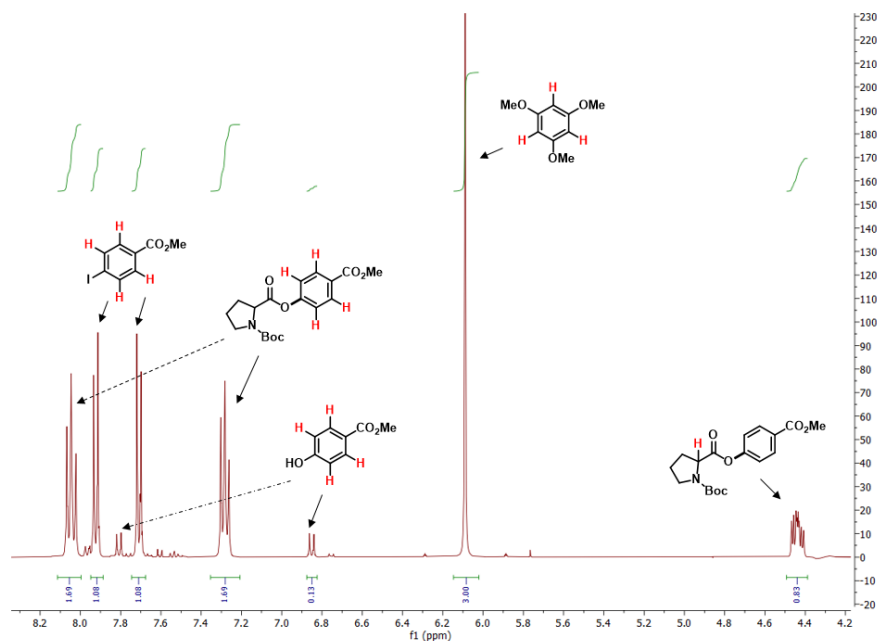


**Fig. S20** Image of the setup using two green LED lamps.

## 6.1. C-O arylation of Boc-Pro-OH



**General experimental procedure.** Boc-Pro-OH (*N*-(*tert*-butoxycarbonyl)-L-proline, 41.0 mg, 190.3  $\mu\text{mol}$ ), methyl 4-iodobenzoate (74.8 mg, 285.4  $\mu\text{mol}$ ) and the respective CD/TiO<sub>2</sub> nanocomposite (*Table S4*) were added to an oven-dried glass vial equipped with a stir bar. Subsequently, a DMSO solution (3 mL) of dcbpy (2,2'-bipyridine-4,4'-dicarboxylic acid, 4.7 mg, 19.0  $\mu\text{mol}$ ), NiCl<sub>2</sub>·6H<sub>2</sub>O (nickel(II) chloride hexahydrate, 4.5 mg, 19.0  $\mu\text{mol}$ ), and BIPA (*N*-*tert*-butylisopropylamine, 90.5  $\mu\text{L}$ , 570.8  $\mu\text{mol}$ ) were added. The glass vial was sealed with a septum and Parafilm. The reaction mixture was stirred and sonicated for 10 min to obtain a fine dispersion and subsequently degassed with Argon for 10 min. The vial was then irradiated with the respective LED lamps at room temperature for the respective time. 1,3,5-Trimethoxybenzene (32.0 mg, 190.3  $\mu\text{mol}$ ) was added as internal standard to determine NMR yields. An aliquot of the resulting mixture (~250  $\mu\text{L}$ ) was filtered through a syringe filter, diluted with DMSO-d<sub>6</sub> (~250  $\mu\text{L}$ ) and subjected to <sup>1</sup>H-NMR analysis.



**Fig. S21** Representative <sup>1</sup>H-NMR spectrum of the crude reaction mixture to determine yields by <sup>1</sup>H-NMR analysis using 1,3,5-trimethoxybenzene as internal standard (DMSO-d<sub>6</sub>, 400 MHz).

**Table S4** Summary of the CD/TiO<sub>2</sub> nanocomposites used in the photocatalyzed C-O cross-coupling of Boc-Pro-OH with methyl 4-iodobenzoate.

Entry	Nanocomposite	Initial CD-to-TiO <sub>2</sub> P25 mass ratio <sup>[a]</sup>	CD Immobilization <sup>[b]</sup> (weight % (CD/nanocomposite))	Amount <sup>[c]</sup> / mg
1	TiO <sub>2</sub> P25	-	-	30.0
2	<b>CD1</b>	-	-	30.0
3	<b>CD1/TiO<sub>2</sub></b>	1 : 20	1.5	30.5
4		1 : 10	1.8	30.5
5		1 : 4	2.4	30.8
6		1 : 1	5.0	31.6
7		4 : 1	8.1	32.6
8		1 : 1 (CD-to-SiO <sub>2</sub> )	1.6	30.5
9	<b>CD2/TiO<sub>2</sub></b>	1 : 1	-	30.0
10	<b>CD3/TiO<sub>2</sub></b>	1 : 1	2.5	30.8
11	<b>CD4/TiO<sub>2</sub></b>	1 : 1	13.6	34.7
12	<b>CD5/TiO<sub>2</sub></b>	1 : 1	3.4	31.1
13	<b>CD6/TiO<sub>2</sub></b>	1 : 1	3.7	31.1
14	<b>CD7/TiO<sub>2</sub></b>	1 : 1	11.9	34.1
15	<b>CD8/TiO<sub>2</sub></b>	1 : 1	3.0	30.9
16	<b>CD9/TiO<sub>2</sub></b>	1 : 1	11.4	33.9
17	<b>CD10/TiO<sub>2</sub></b>	1 : 1	27.2	41.2

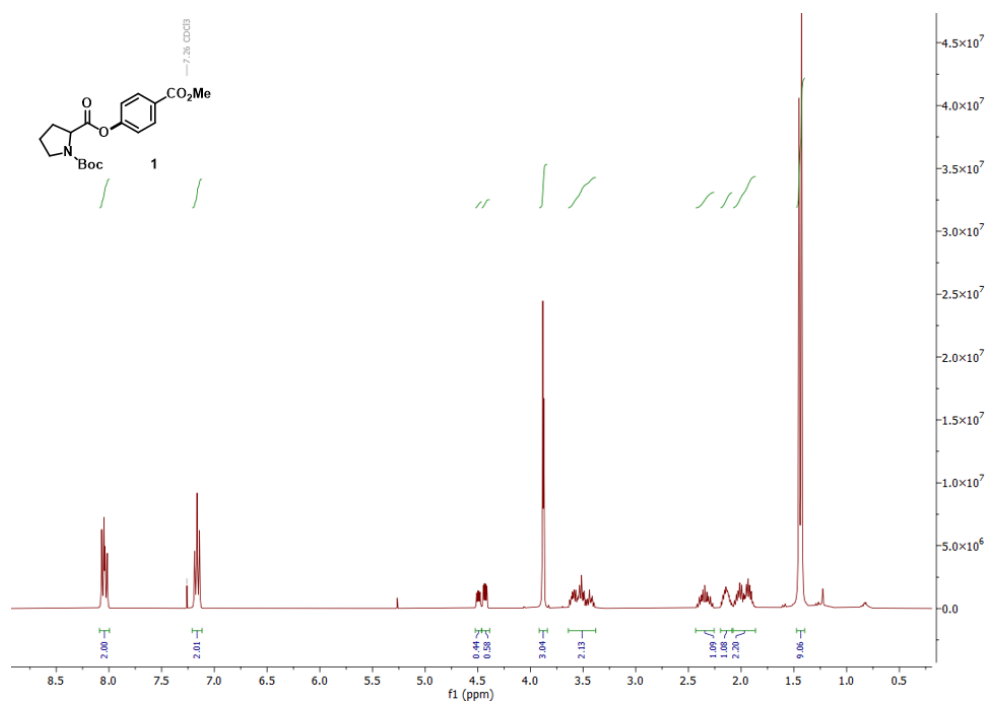
[a] CD-to-TiO<sub>2</sub> P25 mass ratio used for the preparation of the nanocomposite. [b] Weight % of CD immobilized on TiO<sub>2</sub> as calculated by UV-Vis spectroscopy. [c] Amount of nanocomposite used in the C-O arylation of Boc-Pro-OH.

**Procedure to obtain the isolated yield.** An oven-dried vial (19 x 100 mm) equipped with a stir bar was charged with **CD1**/TiO<sub>2</sub> (63.2 mg), Boc-Pro-OH (82 mg, 380.6  $\mu$ mol, 1.0 equiv), methyl 4-iodobenzoate (149.6 mg, 571  $\mu$ mol, 1.5 equiv), NiCl<sub>2</sub>·6H<sub>2</sub>O (9 mg, 38  $\mu$ mol, 10 mol%) and dcbpy (9.3 mg, 38  $\mu$ mol, 10 mol%). Subsequently, DMSO (anhydrous, 6 mL) and BIPA (180.9  $\mu$ L, 1.14 mmol, 3.0 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min to obtain a fine dispersion. The mixture was then degassed by bubbling Argon for 10 min. The mixture was irradiated using the 440 nm setup with rapid stirring (1400 rpm). After 40 h, one equivalent of 1,3,5-trimethoxybenzene (internal standard, 64 mg, 380  $\mu$ mol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~200  $\mu$ L) was filtered, diluted with DMSO-d<sub>6</sub> and subjected to <sup>1</sup>H-NMR analysis to determine the NMR yield (90%). Thereafter, the NMR sample was combined with the reaction mixture. The reaction mixture was diluted with H<sub>2</sub>O (40 mL) and extracted with dichloromethane (3 x 30 mL). The combined organic phases were washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The product was purified by flash column chromatography (SiO<sub>2</sub>, Hexane/EtOAc elution gradient of 0-20%) on a Grace Reveleris system using a 12 g cartridge. In some cases, mixed fractions containing small amounts of the phenol byproduct and the desired product were observed. These could be easily purified by a basic extraction (DCM and 0.5 M NaOH), followed by drying the organic phase over Na<sub>2</sub>SO<sub>4</sub> and solvent evaporation to maximize the reaction yield. The title compound was isolated as a yellowish solid.

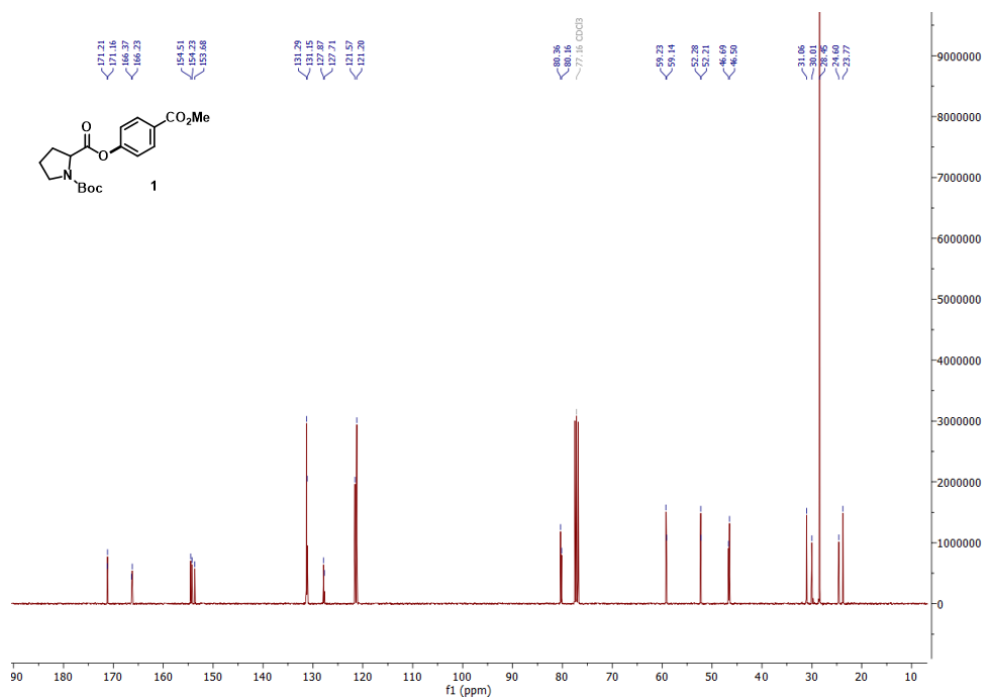
Isolated yield: 84% (111.5 mg, 319  $\mu$ mol)

**1-(tert-butyl) 2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate 1:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) rotameric mixture,  $\delta$  8.04 (m, 2H), 7.16 (m, 2H), 4.49 (dd,  $J$  = 8.6, 4.4 Hz, 0.4H), 4.43 (dd,  $J$  = 8.7, 4.3 Hz, 0.6H), 3.87 (m, 3H), 3.66 – 3.39 (m, 2H), 2.42 – 2.26 (m, 1H), 2.19 – 2.09 (m, 1H), 2.07 – 1.86 (m, 2H), 1.44 (m, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) rotameric mixture, signals for minor rotamer are enclosed in parenthesis  $\delta$  (171.21) 171.16, (166.37) 166.23, 154.51 (154.23), 153.68, 131.29 (131.15), 127.87 (127.71), (121.57) 121.20, 80.36, (80.16), 59.23 (59.14), 52.28 (52.21), (46.69) 46.50, 31.06 (30.01), 28.45, (24.60) 23.77.

The data are in full agreement with those previously published in the literature<sup>2</sup>.

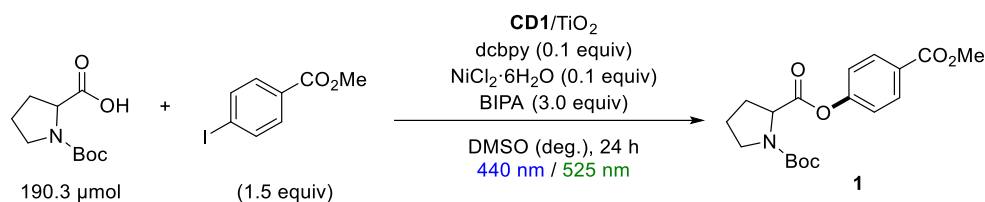


**Fig. S22** <sup>1</sup>H-NMR spectrum of compound **1** (CDCl<sub>3</sub>, 400 MHz).



**Fig. S23** <sup>13</sup>C-NMR spectrum of compound **1** (CDCl<sub>3</sub>, 151 MHz).

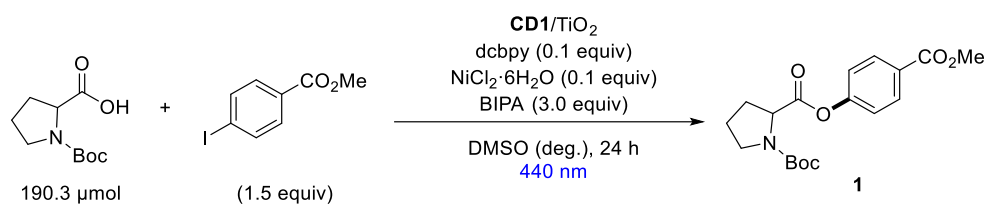
**Table S5** Screening of **CD1**/TiO<sub>2</sub> nanocomposites prepared using different **CD1**-to-TiO<sub>2</sub> P25 mass ratios for the metallaphotocatalytic C-O arylation of Boc-Pro-OH with methyl 4-iodobenzoate.



Entry	CD1-to-TiO <sub>2</sub> P25 mass ratio <sup>[a]</sup>	<b>1</b> [%] <sup>[b]</sup>	<b>1</b> [%] <sup>[c]</sup>
1	1 : 20	52	8
2	1 : 10	64	10
3	1 : 4	80	19
4	<b>1 : 1</b>	<b>83</b>	<b>22</b>
5	<b>1 : 1</b> <sup>[d]</sup>	<b>84</b>	-
6	4 : 1	70	14

[a] CD-to-TiO<sub>2</sub> P25 mass ratio used for the preparation of the nanocomposite. Reaction conditions: methyl 4-iodobenzoate (285.4 μmol), Boc-Pro-OH (190.3 μmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (19.0 μmol) and dcbpy (19.0 μmol) in DMSO (anhydrous, 3 mL), BIPA (570.8 μmol), **CD1**/TiO<sub>2</sub>, 24 h. NMR yields were determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. [b] 440 nm LED lamp (50% power). [c] 525 nm LED lamp (200% power). [d] **CD1**/TiO<sub>2</sub> stored at room temperature for 26 weeks. deg. = degassed.

**Table S6** Screening of different amount of **CD1**/TiO<sub>2</sub> nanocomposites for the metallaphotocatalytic C-O arylation of Boc-Pro-OH with methyl 4-iodobenzoate.



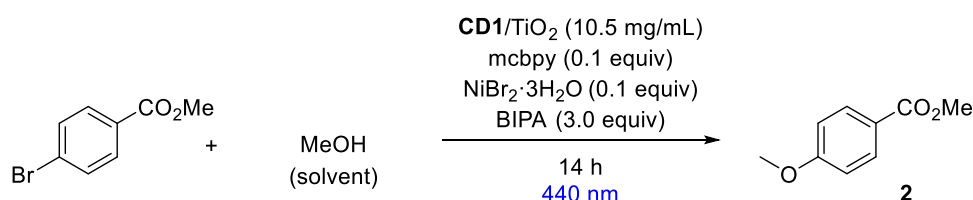
Entry	CD1/TiO <sub>2</sub> / mg	<b>1</b> [%]
1	20	85
2	10	70
3	5	63
4	1	49
5	0	7

Reaction conditions: methyl 4-iodobenzoate (285.4 μmol), Boc-Pro-OH (190.3 μmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (19.0 μmol) and dcbpy (19.0 μmol) in DMSO (anhydrous, 3 mL), BIPA (570.8 μmol), **CD1**/TiO<sub>2</sub>, 440 nm LED lamp (50% power), 24 h. NMR yields were determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. deg. = degassed.

## 6.2. C-O arylation of MeOH

An oven-dried vial (19 x 100 mm) equipped with a stir bar was charged with **CD1**/TiO<sub>2</sub> (15.8 mg), methyl 4-bromobenzoate (20.47 mg, 95.2 μmol, 1.0 equiv), NiBr<sub>2</sub>·3H<sub>2</sub>O (nickel(II) bromide trihydrate, 2.6 mg, 9.5 μmol, 10 mol%) and mcbpy (4'-methyl-2,2'-bipyridine-4-carboxylic acid, 2.1 mg, 9.5 μmol, 10 mol%). Subsequently, MeOH (anhydrous, 1.5 mL) and BIPA (45 μL, 285.6 μmol, 3.0 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min to obtain a fine dispersion. The mixture was then degassed by bubbling Argon for 10 min. The mixture was irradiated using the 440 nm LED setup with rapid stirring (1400 rpm). After 14 h, one equivalent of 1,3,5-trimethoxybenzene (internal standard, 16 mg, 95.2 μmol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~200 μL) was filtered, diluted with DMSO-d<sub>6</sub> and subjected to <sup>1</sup>H-NMR analysis. The product was identified by spiking the crude reaction mixture with a pure sample of the desired product. The data are in full agreement with those previously published in the literature.<sup>3</sup>

**Table S7** C-O arylation of methanol using **CD1**/TiO<sub>2</sub> and the 440 nm LED setup.

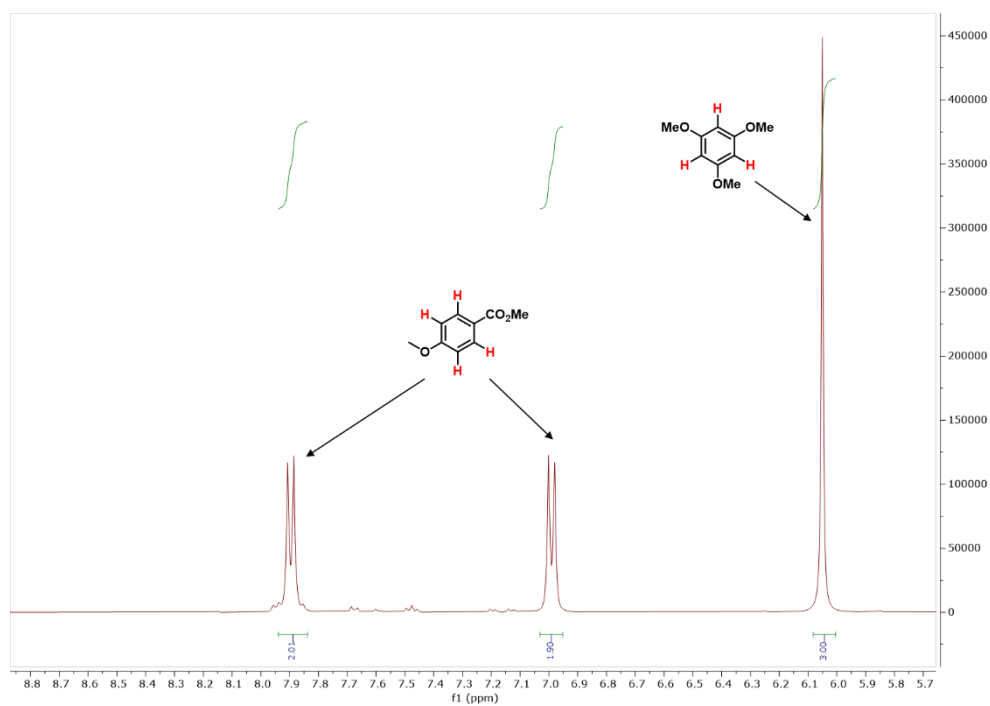


Entry	Conversion [%] <sup>[a]</sup>	<b>2</b> [%]
1	quant.	93

Reaction conditions: methyl 4-bromobenzoate (95.2 μmol), NiBr<sub>2</sub>·3H<sub>2</sub>O (9.5 μmol), mcbpy (9.5 μmol) and BIPA (285.6 μmol) in MeOH (1.5 mL), **CD1**/TiO<sub>2</sub> (15.8 mg), 440 nm LED lamp (100% power), 14 h. NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard.

[a] Conversion of methyl 4-bromobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. quant. = quantitative.





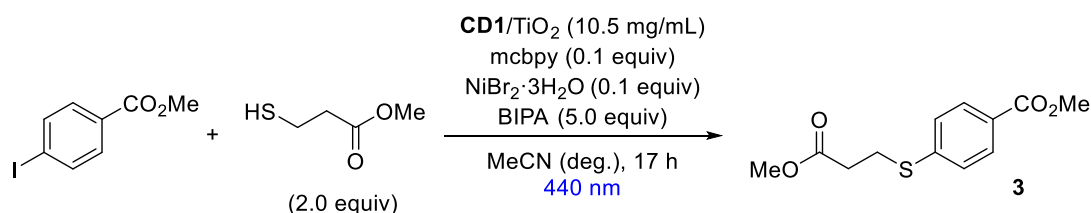
**Fig. S24** Representative  $^1\text{H}$ -NMR spectrum of a crude reaction mixture for determining NMR yields in the C-O arylation of methanol (DMSO- $\text{d}_6$ , 400 MHz).

### 6.3. C-S arylation of methyl 3-mercaptopropionate

An oven-dried vial (19 x 100 mm) equipped with a stir bar was charged with **CD1**/TiO<sub>2</sub> (31.6 mg), methyl 4-iodobenzoate (49.87 mg, 190.3  $\mu$ mol, 1.0 equiv), methyl 3-mercaptopropionate (45.2  $\mu$ L, 380.5  $\mu$ mol, 2.0 equiv), NiBr<sub>2</sub>·3H<sub>2</sub>O (5.2 mg, 19  $\mu$ mol, 10 mol%) and mcbpy (4.2 mg, 19  $\mu$ mol, 10 mol%). Subsequently, MeCN (anhydrous, 3 mL) and BIPA (150.8  $\mu$ L, 951.5  $\mu$ mol, 5.0 equiv) were added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min to obtain a fine dispersion. The mixture was then degassed by bubbling Argon for 10 min. The mixture was irradiated using the 440 nm LED setup with rapid stirring (1400 rpm). After 17 h, one equivalent of 1,3,5-trimethoxybenzene (internal standard, 32 mg, 190.3  $\mu$ mol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~200  $\mu$ L) was filtered, diluted with DMSO-d<sub>6</sub> and subjected to <sup>1</sup>H-NMR analysis. The product was identified by spiking the crude reaction mixture with a pure sample of the desired product.

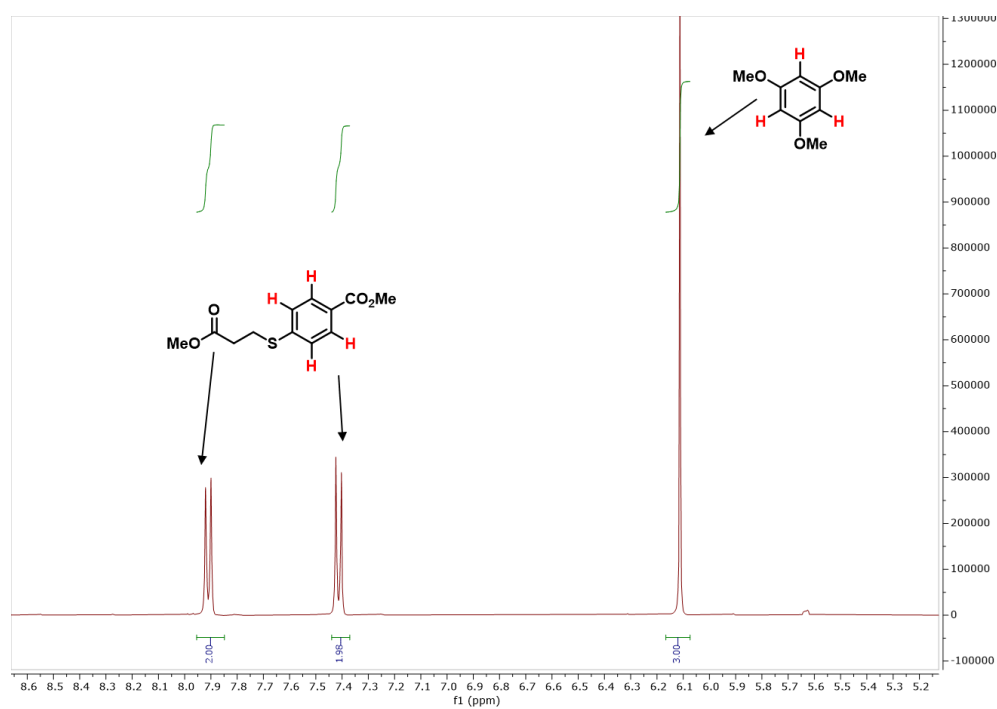
The data are in full agreement with those previously published in the literature.<sup>3</sup>

**Table S8** C-S arylation of methyl 3-mercaptopropionate using **CD1**/TiO<sub>2</sub> and the 440 nm LED setup.



Entry	Conversion [%] <sup>[a]</sup>	<b>3</b> [%]
1	quant.	98

Reaction conditions: methyl 4-iodobenzoate (190.3  $\mu$ mol), methyl 3-mercaptopropionate (380.5  $\mu$ mol), NiBr<sub>2</sub>·3H<sub>2</sub>O (19.0  $\mu$ mol), mcbpy (19.0  $\mu$ mol) and BIPA (951.5  $\mu$ mol) in MeCN (3 mL), **CD1**/TiO<sub>2</sub> (31.6 mg), 440 nm LED lamp (50% power), 17 h. NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. [a] Conversion of methyl 4-iodobenzoate determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. deg. = degassed. quant. = quantitative.



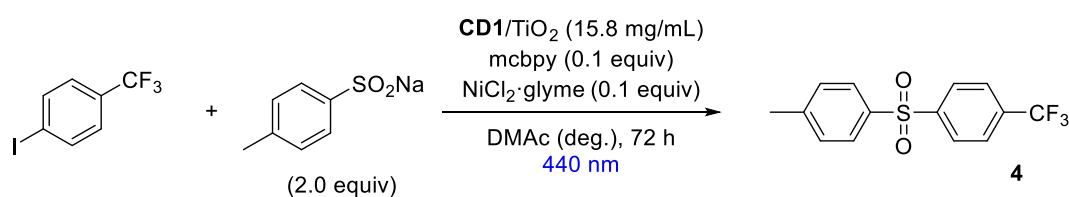
**Fig. S25** Representative  $^1\text{H}$ -NMR spectrum of a crude reaction mixture for determining NMR yields in the C-S arylation of methyl 3-mercaptopropionate (DMSO- $d_6$ , 400 MHz).

#### 6.4. C-S arylation of sodium *p*-toluensulfinate

An oven-dried vial (19 x 100 mm) equipped with a stir bar was charged with **CD1**/TiO<sub>2</sub> (31.6 mg), 4-iodobenzotrifluoride (14.7  $\mu$ L, 100  $\mu$ mol, 1.0 equiv), sodium *p*-toluensulfinate (38.8 mg, 200  $\mu$ mol, 2.0 equiv), NiCl<sub>2</sub>·glyme (nickel(II) chloride ethylene glycol dimethyl ether complex, 2.2 mg, 10  $\mu$ mol, 10 mol%) and mcbpy (2.1 mg, 10  $\mu$ mol, 10 mol%). Subsequently, DMAc (dimethylacetamide, anhydrous, 2 mL) was added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min to obtain a fine dispersion. The mixture was then degassed by bubbling Argon for 10 min. The mixture was irradiated using the 440 nm LED setup with rapid stirring (1400 rpm). After 72 h, one equivalent of 1,3,5-trimethoxybenzene (internal standard, 16.8 mg, 100  $\mu$ mol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~200  $\mu$ L) was filtered, diluted with DMSO-d<sub>6</sub> and subjected to <sup>1</sup>H-NMR analysis. The product was identified by spiking the crude reaction mixture with a pure sample of the desired product.

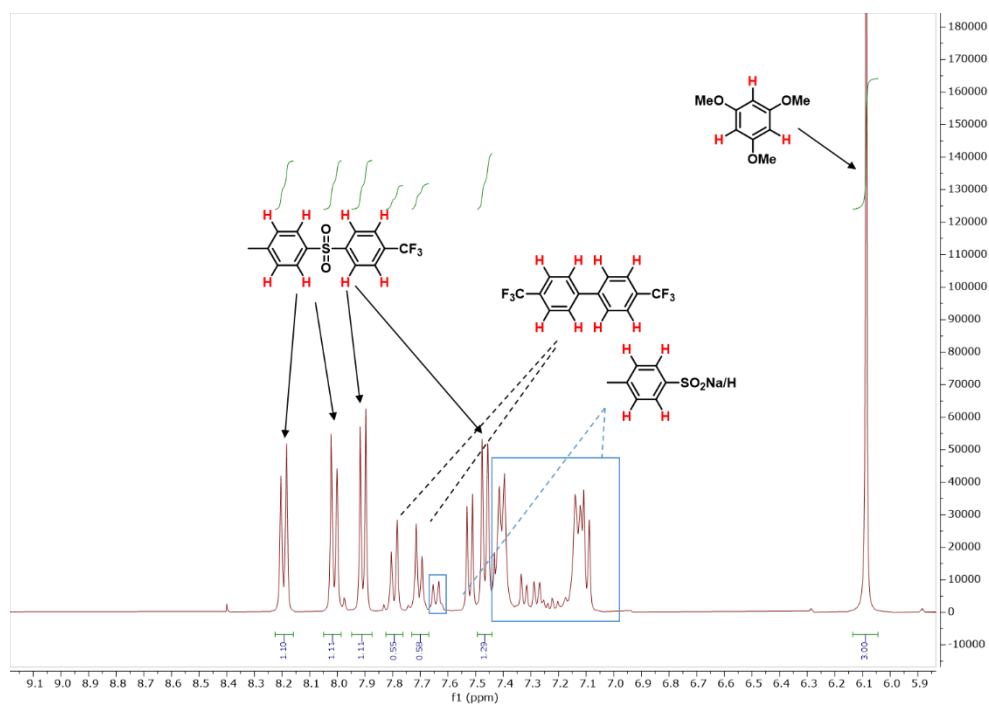
The data are in full agreement with those previously published in the literature.<sup>4</sup>

**Table S9** C-S arylation of sodium *p*-toluensulfinate using **CD1**/TiO<sub>2</sub> and the 440 nm LED setup.



Entry	Conversion [%] <sup>[a]</sup>	<b>4</b> [%]
1	quant.	55

Reaction conditions: 4-iodobenzotrifluoride (100  $\mu$ mol), sodium *p*-toluensulfinate (200  $\mu$ mol), NiCl<sub>2</sub>·glyme (10  $\mu$ mol) and mcbpy (10  $\mu$ mol) in DMAc (2 mL), **CD1**/TiO<sub>2</sub> (31.6 mg), 440 nm blue LED lamp (100% power), 72 h. NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. [a] Conversion of 4-iodobenzotrifluoride determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. deg. = degassed. quant. = quantitative.

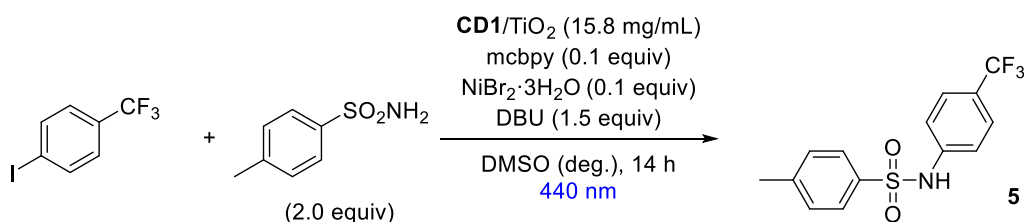


**Fig. S26** Representative  $^1\text{H}$ -NMR spectrum of a crude reaction mixture for determining NMR yields in the C-S arylation of sodium *p*-toluenesulfonate (DMSO- $\text{d}_6$ , 400 MHz).

## 6.5. C-N arylation of *p*-toluensulfonamide

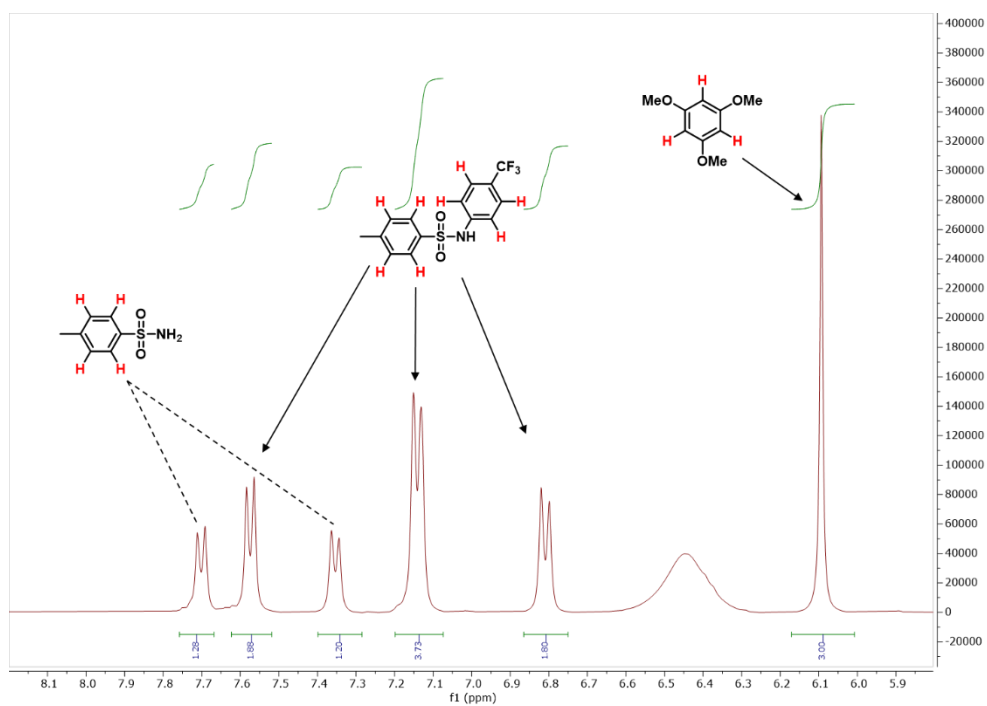
An oven-dried vial (19 x 100 mm) equipped with a stir bar was charged with **CD1**/TiO<sub>2</sub> (31.6 mg), 4-iodobenzotrifluoride (14.7  $\mu$ L, 100  $\mu$ mol, 1.0 equiv), *p*-toluensulfonamide (34.2 mg, 200  $\mu$ mol, 2.0 equiv), NiBr<sub>2</sub>·3H<sub>2</sub>O (2.7 mg, 10  $\mu$ mol, 10 mol%), mcbpy (2.1 mg, 10  $\mu$ mol, 10 mol%) and DBU (1,8-diazabicyclo[5.4.0]undec-7-en, 22.4  $\mu$ L, 150  $\mu$ mol, 1.5 equiv). Subsequently, DMSO (anhydrous, 2 mL) was added and the vial was sealed with a septum and Parafilm. The reaction mixture was sonicated for 5-10 min followed by stirring for 5 min to obtain a fine dispersion. The mixture was then degassed by bubbling Argon for 10 min. The mixture was irradiated using the 440 nm LED setup with rapid stirring (1400 rpm). After 14 h, one equivalent of 1,3,5-trimethoxybenzene (internal standard, 16.8 mg, 100  $\mu$ mol) was added and the mixture was stirred for 5 min. An aliquot of the reaction mixture (~200  $\mu$ L) was filtered, diluted with DMSO-d<sub>6</sub> and subjected to <sup>1</sup>H-NMR analysis. The product was identified by spiking the crude reaction mixture with a pure sample of the desired product. The data are in full agreement with those previously published in the literature.<sup>5</sup>

**Table S10** C-N arylation of *p*-toluensulfonamide using **CD1**/TiO<sub>2</sub> and the 440 nm LED setup.



Entry	Conversion [%] <sup>[a]</sup>	5 [%]
1	quant.	90

Reaction conditions: 4-iodobenzotrifluoride (100  $\mu$ mol), *p*-toluensulfonamide (200  $\mu$ mol), NiBr<sub>2</sub>·3H<sub>2</sub>O (10  $\mu$ mol), mcbpy (10  $\mu$ mol) and DBU (150  $\mu$ mol) in DMSO (2 mL), **CD1**/TiO<sub>2</sub> (31.6 mg), 440 nm blue LED lamp (100% power), 14 h. NMR yields determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. [a] Conversion of 4-iodobenzotrifluoride determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as internal standard. deg. = degassed. quant. = quantitative.



**Fig. S27** Representative  $^1\text{H}$ -NMR spectrum of a crude reaction mixture for determining NMR yields in the C-N arylation of *p*-toluenesulfonamide (DMSO- $\text{d}_6$ , 400 MHz).

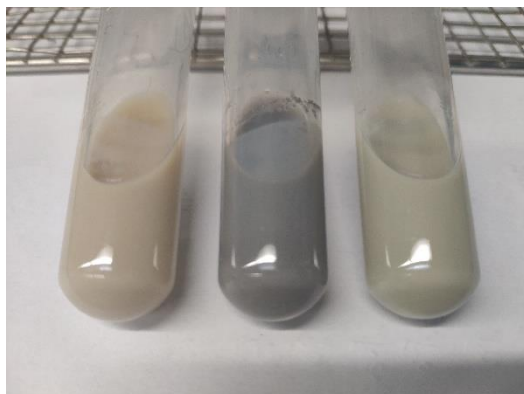
## 7. Photobleaching experiments

The photocatalyst (**CD1**/TiO<sub>2</sub>, 31.6 mg; Fluo (fluorescein)/TiO<sub>2</sub>, 0.54 mg of Fluo and 30 mg of TiO<sub>2</sub>) was added to an oven-dried glass vial equipped with a stir bar.<sup>2</sup> DMSO (1.5 mL) was added and the reaction mixture was stirred and sonicated for 10 min to obtain a fine dispersion. The vial equipped with an air balloon was then transferred into a dark fume hood and irradiated with a blue LED lamp (440 nm LED lamp, 50% power) at room temperature. After the respective time, Boc-Pro-OH (41.0 mg, 190.3  $\mu$ mol), methyl 4-iodobenzoate (74.8 mg, 285.4  $\mu$ mol), a DMSO solution (1.5 mL) of dcbpy (4.7 mg, 19.0  $\mu$ mol), NiCl<sub>2</sub>·6H<sub>2</sub>O (4.5 mg, 19.0  $\mu$ mol), and BIPA (90.5  $\mu$ L, 570.8  $\mu$ mol) were added. The glass vial was sealed with a septum and Parafilm. The reaction mixture was stirred and sonicated for 10 min to obtain a fine dispersion and subsequently degassed with Argon for 10 min. The vial was then irradiated with a blue LED lamp (440 nm LED lamp, 50% power) at room temperature for 24 h. 1,3,5-Trimethoxybenzene (32.0 mg, 190.3  $\mu$ mol) was added as internal standard to determine NMR yields. An aliquot of the resulting mixture (~250  $\mu$ L) was filtered through a syringe filter, diluted with DMSO-d<sub>6</sub> (~250  $\mu$ L) and subjected to <sup>1</sup>H-NMR analysis.



## 8. Recycling experiments

Boc-Pro-OH (41.0 mg, 190.3  $\mu\text{mol}$ ), methyl 4-iodobenzoate (74.8 mg, 285.4  $\mu\text{mol}$ ) and **CD1**/TiO<sub>2</sub> nanocomposite (31.6 mg) were added to an oven-dried glass vial equipped with a stir bar. Subsequently, a DMSO solution (3 mL) of dcbpy (4.7 mg, 19.0  $\mu\text{mol}$ ), NiCl<sub>2</sub>·6H<sub>2</sub>O (4.5 mg, 19.0  $\mu\text{mol}$ ), and BIPA (90.5  $\mu\text{L}$ , 570.8  $\mu\text{mol}$ ) were added. The glass vial was sealed with a septum and Parafilm. The reaction mixture was stirred and sonicated for 10 min to obtain a fine dispersion and subsequently degassed with Argon for 10 min. The vial was then irradiated with a blue LED lamp (440 nm LED lamp, 50% power) at room temperature. After 24 h, the reaction mixture was centrifuged and washed twice with DMSO (3 mL). The remaining nanocomposite was lyophilized overnight and reused in the next reaction. For the controlled studies, NiCl<sub>2</sub>·6H<sub>2</sub>O (4.5 mg, 19.0  $\mu\text{mol}$ ) or NiCl<sub>2</sub>·6H<sub>2</sub>O (4.5 mg, 19.0  $\mu\text{mol}$ )/dcbpy (4.7 mg, 19.0  $\mu\text{mol}$ ) were added to the new reaction mixture.



**Fig. S28** Photograph of the reaction mixture (+ none group, left; + NiCl<sub>2</sub>·6H<sub>2</sub>O group, middle; + NiCl<sub>2</sub>·6H<sub>2</sub>O/dcbpy, right) after C-O cross-coupling reaction (cycle 4).

## 9. References

1. S. A. Hill, D. Benito-Alifonso, S. A. Davis, D. J. Morgan, M. Berry and M. C. Galan, *Sci. Rep.*, 2018, **8**, 12234.
2. S. Reischauer, V. Strauss and B. Pieber, *ACS Catal.*, 2020, **10**, 13269.
3. C. Cavedon, A. Madani, P. H. Seeberger and B. Pieber, *Org. Lett.*, 2019, **21**, 5331.
4. H. Yue, C. Zhu and M. Rueping, *Angew. Chem. Int. Ed.*, 2018, **57**, 1371.
5. F. Ye, F. Berger, H. Jia, J. Ford, A. Wortman, J. Börgel, C. Genicot and T. Ritter, *Angew. Chem. Int. Ed.*, 2019, **58**, 14615.