

Supporting Information

Chiral Carbon Nanodots Can Act as Molecular Catalysts in Chemical and Photochemical Reactions

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1. General information

Microwave. MW synthesis was performed on a CEM Discover-SP, using 10 mL glass microwave vials. Nuclear magnetic resonance. ¹H, and ¹³C-NMR spectra were obtained on Varian Inova spectrometer (500 MHz ¹H and 126 MHz ¹³C) or Varian 400 MHz NMR spectrometer (400 MHz ¹H and 101 MHz ¹³C). Chemical shifts were reported in ppm according to tetramethylsilane using the solvent residual signal as an internal reference $(CDCl_3: \delta H = 7.26 \text{ ppm}, \delta C = 77.16 \text{ ppm})$. Coupling constants (J) were given in Hz and were averaged. Resonance multiplicity was described as s (singlet), d (doublet), t (triplet), m (multiplet), br (broad signal), dd (doublet of doublets), dt (doublet of triplets). Carbon spectra were acquired with a complete decoupling for the proton, unless specified. All spectra were recorded at 25 °C unless specified. ESI-High resolution mass spectrometry. ESI-HRMS was performed at University of Trieste Chemistry department, high resolution mass spectra (HRMS) were obtained on Bruker micrOTOF-Q (ESI-TOF). Photophysical analysis. All the spectra were recorded at room temperature using 10 mm path-length quartz cuvettes. Absorption spectra of compounds were recorded with an Agilent Cary 5000 UV-Vis spectrophotometer. Emission measurements were performed on an Edinburgh instruments FS5 spectrofluorometer using a 150 W CW Ozone-free xenon arc lamp as source and a Photomultiplier R928P (spectral coverage 200 nm – 900 nm, cooled and stabilised) as detector. Quantum yields were performed using the integrating sphere setup SC-30. Luminescence lifetimes were measured with an Edinburgh Instruments FS5 time-correlated single-photon counting spectrofluorimeter, exciting the sample at 375 nm with a picosecond pulsed diode laser (EPL-375 Edimburgh Instruments). Electronic Circular Dichroism (ECD) spectra were recorded using Jasco J-810 at room temperature (20 °C). Conditions were as follows: scanning rate 50 nm/min, data pitch 1 nm, Digital Integration Time (D.I.T.) 2 s, 4 accumulations. Atomic force microscopy. AFM images were obtained with a Nanoscope IIIa, VEECO Instruments. As a general procedure, AFM analyses were performed using tapping mode with a HQ:NSC19/ALBS probe (80 kHz; 0.6 N/m) (MikroMasch) from drop cast of samples in methanol diluted solution (concentration in the order of $\mu g/mL$) on an exfoliated mica substrate. The obtained AFM images were analyzed in S3 Gwyddion 2.58, using Profile extraction tool and Find peaks function. Statistical analysis was carried out on one hundred nanoparticles. Chemical characterization. ATR-Fourier-transform infrared spectroscopy was performed on a Shimadzu IRAffinity1S equipped with a QATR-10 with diamond crystal. X-Ray Photoelectron Spectroscopy experiments were performed on a Kratos Axis Ultra XPS, sample was prepared depositing the CND powder on copper support. CasaXPS software (version 2.3.16 PR1.6) was used for data analysis. Survey spectra were employed to calculate relative atomic composition of all elements present in the samples. Cyclic voltammetry. The electrochemical characterizations were carried out in dichloromethane (DCM)/0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) (solution saturated with CNDs), at room temperature, on a Autolab 302 N electrochemical workstation (Metrohm, The Netherlands) in a glass cell from CH Instruments (10 mL, CHI220). A typical three-electrode cell was employed, which was composed of glassy carbon (GC) working electrode (3 mm diameter), a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode (RE). RE was connected to the glass cell through a salt bridge in 0.1 M TBAPF₆ DCM solution. Oxygen was removed by purging the DCM solution with Argon. The GC electrode was polished twice before use with 0.05 and 0.1 colloidal silica polishing suspension and ultrasonically rinsed with deionized water for 15 minutes. HPLC. Enantiomeric excess (ee) values were determined by Agilent Infinity II, employing a Phenomenex chiral stationary phase column (specified in the individual description compound) and a detector operating at 220 and 254 nm. Racemic samples were prepared using the same reaction protocol but employing pyrrolidine (20 mol%) as the organocatalyst.

Materials. Commercial reagents and solvents were purchased from Sigma-Aldrich, Apollo scientific or VWR and used without further purification, unless otherwise stated. MilliQ water was obtained from a Millipore Milli-Q Plus 185 apparatus and presented a resistivity of 18.2 MΩcm. MilliQ water was always used unless otherwise specified.

2. CNDs

2.1 Synthesis of CNDs

(S)- or (R)-2-(Aminomethyl)-1-Boc-pyrrolidine (100 mg, 0.5 mmol) and citric acid (192 mg, 1 mmol) were dissolved in Milli-Q water (100 μ L) and then heated at 240 °C, and 150 W for 180 seconds. In the process of microwave heating, the solution changes color from pale yellow to brown as a result of formation of CNDs. The solution was diluted with chloroform (CHCl₃) and washed with water (3 times). The organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The solid was suspended in the minimum amount of chloroform and then precipitated with diethyl ether (10 mL) to induce the CND precipitation. The precipitate was collected though centrifugation (6000 rpm, 10 min). The precipitation process was repeated twice. After drying, the final material is obtained as a brownish powder (CNDs: 60 mg).



Figure S1. Photographs of the vials (a) before and (b) after microwave-heating process and (c) the final CNDs.





Figure S2. ¹H NMR spectrum (D₂O, 400 MHz, rt) of Pyr.



Figure S3. Size histogram of AFM height data of (*S*)-CNDs, with distribution fit (red curve) based on a Gaussian distribution.



Figure S4. PLQY of (S)-CNDs in chloroform upon changing the excitation wavelength.



Figure S5. Fluorescence decay curve of (*S*)-CNDs in chloroform. The yellow curve corresponds to the sample fluorescence decay, the blue curve corresponds to the instrument response function and the magenta curve corresponds to the best fit, with their respective residuals (green line).

	A1	$\tau_1 \pm 0.1$ / ns	A ₂	$\tau_2 \pm 0.1 / ns$	τ _{av} / ns
(S)-CNDs	0.22	1.1	0.41	11.6	7.9

Table S1. Fitting parameters of the fluorescence decay curve.



Figure S6. FT-IR spectra of CA, Pyr, and (S)-CNDs.



Figure S7. XPS survey of (S)-CNDs showing the C1s, N1s and O1s peaks.



Figure S8. Deconvoluted C1s, O1s, N1s spectra of (S)-CNDs.

С%	78,8
C-C/C=C	57,2
C-O/C-N	24,2
C=O	7,1
0-C=0	11,5
0%	13,4
O=C	83,9
0-C	16,1
N%	7,8
NH ₂ /C-N-C	81,3
N-C ₃	18,7

Table S2. XPS percentage of C, O, and N atoms and their deconvoluted components.



Figure S9. Cyclic voltammograms of (*S*)-CNDs in 0.1 M TBAPF₆ DCM solution. Scan rate: 0.025 V/s, potential referred to SCE at room temperature.



Figure S10. Emission spectra of (S)-CNDs (0.01 mg/mL in chloroform, excitation at λ =456 nm) in the presence of increasing amounts of BrCCl₃.

2.3 Reductive amination for the quantification of surface amines

A solution of NaBH₃CN (10.5 mg), (*S*)-CNDs (25.0 mg), 3,5-bis(trifluoromethyl)benzaldehyde (28 μ L) and acetic acid (10 μ L) in MeCN/MeOH (1:1 v/v, 2.0 mL) was stirred at rt, for 36 h. The resulting mixture was extracted with water and the organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. The solid was suspended in the minimum amount of chloroform and then precipitated with diethyl ether (10 mL) to induce the CND precipitation. The precipitate was collected though centrifugation (6000 rpm, 10 min). The precipitation process was repeated twice. After drying, the final product is obtained (15 mg). The concentration of fluorinated moieties was quantified through ¹⁹F-NMR and using 1-fluoro-2-nitrobenzene as internal standard.



Figure S11. ¹H NMR (top) and ¹⁹F NMR (bottom) spectra (CDCl₃, 400 MHz, rt) of (*S*)-CNDs after the reductive amination.

3. Use of CNDs in organocatalyzed transformations

3.1 General Procedures A for the CNDs-catalyzed aldol reaction

A 2 mL vial, equipped with a magnetic stirring bar, was charged with **(S)-CNDs** (38 mg), cyclohexanone **1a** (0.25 mmol, 5 eq), 4-NO₂-benzaldehyde **2** (0.05 mmol, 1 eq), benzoic acid (20 mol%, 0.01 mmol) and 1,2-DCE (200 μ L). The reaction mixture was stirred for 3 days and then quenched by dropping the organic solvent into 10 mL of cold Et₂O to precipitate the CNDs. After centrifugation (6000 rpm, 10 min), the organic phase was separated while **(S)-CNDs** were suspended in the minimum amount of CH₂Cl₂, precipitated again into 10 mL of cold Et₂O and centrifugated (6000 rpm, 10 min) to separate the organic phase from the precipitate. The combined organic phases were concentrated under reduced pressure to give the crude product. The residue was purified by flash column chromatography (mixtures of EtOAc/cyclohexane) to afford the desired product.

Anti-2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one, anti-3



Following the General Procedure A, cyclohexanone **1a** and 4-NO₂-benzaldehyde **2** were employed and the reaction was stirred for 3d and ¹H NMR analysis on the crude mixture showed that the desired product was formed in a 3:1 d.r.. Purification by FC on silica gel (10% EtOAc in cyclohexane) afforded **3** as a white solid (10 mg, 0.041 mmol, 81% combined yield). Further purification by FC on silica

gel (5 to 15% EtOAc in cyclohexane) enabled the isolation of the two separate diastereomers.

The characterization of the compound matches with the data reported in the literature.¹

¹**H NMR** (400 MHz, CDCl₃): δ [ppm] 8.24 – 8.18 (m, 2H), 7.54 – 7.48 (m, 2H), 4.90 (d, *J*=8.4, 1H), 2.63 – 2.55 (m, 1H), 2.53 – 2.45 (m, 1H), 2.42 – 2.32 (m, 1H), 2.18 – 2.08 (m, 1H), 1.89 – 1.79 (m, 1H), 1.75 – 1.50 (m, 3H), 1.45 – 1.32 (m, 1H).

HPLC: Phenomenex Cellulose-5; *n*-hexane/iPrOH, 80:20 isocratic; flow-rate 0.75 mL/min; t_{major} = 24.6 min; t_{minor} = 25.6 min.

Syn-2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one, syn-3



The characterization of the compound matches with the data reported in the literature. $^{\rm 2}$

NO₂ ¹**H NMR** (400 MHz, CDCl₃): δ [ppm] 8.24 – 8.18 (m, 2H), 7.52 – 7.46 (m, 2H), 5.51 – 5.46 (m, 1H), 2.67 – 2.59 (m, 1H), 2.53 – 2.45 (m, 1H), 2.45 – 2.34 (m, 1H), 2.12 (ddt, *J*=12.5, 5.9, 3.0, 1H), 1.86 (d, *J*=13.5, 1H), 1.77 – 1.48 (m, 4H).

HPLC: Phenomenex Cellulose-5; *n*-hexane/iPrOH, 80:20 isocratic; flow-rate 0.75 mL/min; $t_{major} = 15.2$ min; $t_{minor} = 17.2$ min.

¹ Z. Tang, Z.-H. Yang, X.-H. Chen, L.-F. Cun, A.-Q. Mi, Y.-Z. Jiang, L.-Z. Gong J. Am. Chem. Soc. **2005**, 127, 9285–9289.

² G.-F. Wen, R. Zhang, C.-Y. Zhang, C.-S. Da Synthesis **2023**, 55, 670–682.

3.2 General Procedures B for the CNDs-catalyzed Michael addition of cyclic ketones 1 to nitroalkenes 4

A 2 mL vial, equipped with a magnetic stirring bar, was charged with **(S)-CNDs** (38 mg), ketone **1** (0.25 mmol, 5 eq), nitroalkene **4** (0.05 mmol, 1 eq), benzoic acid (20 mol%, 0.01 mmol) and 1,2-dichloroethane (100 μ L). The reaction mixture was stirred for 3-4 days and then quenched by dropping the organic solvent into 10 mL of cold Et₂O to precipitate the **(S)-CNDs**. After centrifugation (6000 rpm, 10 min), the organic phase was separated while **(S)-CNDs** were suspended in the minimum amount of CH₂Cl₂, precipitated again into 10 mL of cold Et₂O and centrifugated (6000 rpm, 10 min) to separate the organic phase from the precipitate. The combined organic phases were concentrated under reduced pressure to give the crude product. The residue was purified by flash column chromatography (mixtures of EtOAc/cyclohexane) to afford the desired product.

(S)-2-((R)-2-Nitro-1-phenylethyl)cyclohexan-1-one, 5a



Following the General Procedure B applying cyclohexanone **1a**, *trans*- β -nitrostyrene **4a** and **(S)-CNDs**, full conversion of **4a** was observed after 3 days. Purification by FC on silica gel (10 to 20% EtOAc in cyclohexane) afforded **5a** as a white solid (10 mg, 0.04 mmol, 81% yield, 20:1 d.r., 91% ee).

¹**H NMR** (CDCl₃, 400 MHz): δ [ppm] 7.35 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 7.19 – 7.14 (m, 2H), 4.94 (dd, J=12.5, 4.5, 1H), 4.63 (dd, J=12.5, 9.9, 1H), 3.76 (td, J=9.9, 4.5, 1H), 2.74 – 2.65 (m, 1H), 2.52 – 2.44 (m, 1H), 2.43 – 2.34 (m, 1H), 2.12 – 2.03 (m, 1H), 1.83 – 1.51 (m, 4H), 1.30 – 1.17 (m, 1H).

 $^{13}\textbf{C NMR} \ (\text{CDCl}_3, \ 400 \ \text{MHz}): \ \delta \ [ppm] \ 212.0, \ 137.9, \ 129.1, \ 128.3, \ 127.9, \ 79.0, \ 52.7, \ 44.1, \ 42.9, \ 33.4, \ 28.7, \ 25.2.$

HRMS (ESI+): m/z calcd. for $[C_{14}H_{17}NO_3+Na]^+$: 270.1101; found = 270.1102.

 $[\alpha]^{26}_{D}$ = -50.4 (*c* = 0.12, CHCl₃) for 91% ee.³

HPLC: Phenomenex Cellulose-5; *n*-hexane/iPrOH, gradient of iPrOH 0 to 30% in 20 minutes, flow-rate 0.75 mL/min; $t_{minor} = 29.8 \text{ min}$; $t_{major} = 31.1 \text{ min}$.

(R)-2-((S)-2-nitro-1-phenylethyl)cyclohexan-1-one, ent-5a



Following the General Procedure B applying cyclohexanone **1a**, nitroalkene **4a** and **(***R***)**-**CNDs** (38 mg), full conversion of **4a** was observed after 4 days. Purification by FC on silica gel (10 to 20% EtOAc in cyclohexane) afforded *ent*-**5a** as a white solid (11 mg, 0.044 mmol, 89% yield, 20:1 d.r., 74% ee).

¹**H NMR** (CDCl₃, 400 MHz): δ [ppm] 7.35 – 7.29 (m, 2H), 7.29 – 7.24 (m, 1H), 7.19 – 7.14 (m, 2H), 4.94 (dd, J=12.5, 4.5, 1H), 4.63 (dd, J=12.5, 9.9, 1H), 3.76 (td, J=9.9, 4.5, 1H), 2.74 – 2.65 (m, 1H), 2.52 – 2.44 (m, 1H), 2.43 – 2.34 (m, 1H), 2.12 – 2.03 (m, 1H), 1.83 – 1.51 (m, 4H), 1.30 – 1.17 (m, 1H).

 $^{13}\textbf{C}\,\textbf{NMR}\,(\text{CDCl}_3,\,400\,\,\text{MHz});\,\delta\,[\text{ppm}]\,212.0,\,137.9,\,129.1,\,128.3,\,127.9,\,79.0,\,52.7,\,44.1,\,42.9,\,33.4,\,28.7,\,25.2.$

HRMS (ESI+): m/z calcd. for $[C_{14}H_{17}NO_3+Na]^+$: 270.1101; found = 270.1102.

 $[\alpha]^{26}_{D}$ = +41.9 (*c* = 0.25, CHCl₃) for 74% ee.

HPLC: Phenomenex Cellulose-5; *n*-hexane/iPrOH, gradient of iPrOH 0 to 30% in 20 minutes, flow-rate 0.75 mL/min; $t_{major} = 29.7$ min; $t_{minor} = 31.3$ min.

³ H.-W. Zhao, H.-L. Li, Y.-Y. Yue, Z.-H. Sheng Eur. J. Org. Chem. 2013, 1740.

(S)-2-((R)-1-(4-methoxyphenyl)-2-nitroethyl)cyclohexan-1-one, 5b



Following the General Procedure B applying cyclohexanone **1a** and nitroalkene **4b**, full conversion of **4b** was observed after 4 days. Purification by FC on silica gel (10 to 20% EtOAc in cyclohexane) afforded **5b** as a white solid (10 mg, 0.036 mmol, 72% yield, 20:1 d.r., 91% ee).

¹**H NMR** (CDCl₃, 400 MHz): δ [ppm] 7.10 – 7.06 (m, 2H), 6.88 – 6.82 (m, 2H), 4.90 (dd, J=12.3, 4.6, 1H), 4.58 (dd, J=12.3, 9.9, 1H), 3.78 (s, 3H), 3.71 (td, J=9.9, 4.6, 1H), 2.69 – 2.60 (m, 1H), 2.51 – 2.43 (m, 1H), 2.42 – 2.32 (m, 1H), 2.13 – 2.02 (m, 1H), 1.83 – 1.50

(m, 4H), 1.29 – 1.17 (m, 1H).

¹³C NMR (CDCl₃, 101 MHz): δ [ppm] 212.2, 159.2, 129.7, 129.3, 114.5, 79.2, 55.4, 52.8, 43.4, 42.9, 33.3, 28.7, 25.1.

HRMS (ESI+): m/z calcd. for $[C_{15}H_{19}NO_4+Na]^+$: 300.1206; found = 300.1208.

 $[\alpha]^{26}_{D} = -5.4$ (*c* = 0.25, CHCl₃) for 91% ee.

HPLC: Phenomenex Amylose-3; *n*-hexane/iPrOH, 70:30 isocratic, flow-rate 0.75 mL/min; $t_{minor} = 14.0$ min; $t_{major} = 15.0$ min.

(S)-2-((R)-2-nitro-1-(p-tolyl)ethyl)cyclohexan-1-one, 5c



Following the General Procedure B applying cyclohexanone **1a** and nitroalkene **4c**, full conversion of **1a** was observed after 4 days. Purification by FC on silica gel (10 to 20% EtOAc in cyclohexane) afforded **4c** as a white solid (9.5 mg, 0.037 mmol, 73% yield, 20:1 d.r., 90% ee).

¹**H NMR** (CDCl₃, 400 MHz): δ [ppm] 7.15 – 7.09 (m, 2H), 7.07 – 7.02 (m, 2H), 4.91 (dd, J=12.4, 4.5, 1H), 4.61 (dd, J=12.3, 9.9, 1H), 3.72 (td, J=9.9, 4.6, 1H), 2.71 – 2.61 (m, 1H),

2.52 – 2.44 (m, 1H), 2.43 – 2.34 (m, 1H), 2.31 (s, 3H), 2.12 – 2.03 (m, 1H), 1.83 – 1.50 (m, 4H), 1.32 – 1.16 (m, 1H).

¹³**C NMR** (CDCl₃, 101 MHz): δ [ppm] 212.2, 137.6, 134.7, 129.8, 128.1, 79.2, 52.7, 43.7, 42.9, 33.3, 28.7, 25.2, 21.2.

HRMS (ESI+): m/z calcd. for $[C_{15}H_{19}O_3+Na]^+$: 284.1257; found = 284.1257.

 $[\alpha]^{26}_{D} = -38.3 \ (c = 0.25, \text{CHCl}_3) \ \text{for } 90\% \ \text{ee.}$

HPLC: Phenomenex Amylose-3; *n*-hexane/iPrOH, 70:30 isocratic, flow-rate 0.75 mL/min; $t_{minor} = 10.4$ min; $t_{major} = 11.4$ min.

(S)-2-((R)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexan-1-one, 5d



Following the General Procedure B applying cyclohexanone **1a** and nitroalkene **4d**, full conversion of **4d** was observed after 4 days. Purification by FC on silica gel (10 to 20% EtOAc in cyclohexane) afforded **5d** as a white solid (14 mg, 0.049 mmol, 99% yield, 20:1 d.r., 93% ee).

¹**H NMR** (CDCl₃, 400 MHz): δ [ppm] 7.32 – 7.27 (m, 2H), 7.14 – 7.09 (m, 2H), 4.93 (dd, J=12.6, 4.6, 1H), 4.60 (dd, J=12.6, 10.0, 1H), 3.76 (td, J=9.8, 4.5, 1H), 2.70 – 2.60 (m, 1H), 2.53 – 2.43 (m, 1H), 2.43 – 2.31 (m, 1H), 2.15 – 2.04 (m, 1H), 1.85 – 1.51 (m, 4H), 1.31 –

1.16 (m, 1H).

¹³**C NMR** (CDCl₃, 101 MHz): δ [ppm] 211.6, 136.4, 133.8, 129.7, 129.3, 78.7, 52.6, 43.5, 42.9, 33.3, 28.6, 25.2.

HRMS (ESI+): *m*/*z* calcd. for $[C_{14}H_{16}^{35}CINO_3+Na]^+$: 304.0711; found: 304.0710; calcd. for $[C_{14}H_{16}^{37}CINO_3+Na]^+$: 306.0682; found: 306.0681.

 $[\alpha]^{26}_{D} = -19.6 \ (c = 0.25, CHCl_3) \ for 93\% \ ee.$

HPLC: Phenomenex Cellulose-5; *n*-hexane/iPrOH, gradient of iPrOH 0 to 30% in 20 minutes, flow-rate 0.75 mL/min; $t_{minor} = 26.3 \text{ min}$; $t_{major} = 26.9 \text{ min}$.

(R)-3-((R)-2-nitro-1-phenylethyl)tetrahydro-4H-pyran-4-one, 5e



Following the General Procedure B applying tetrahydro-4*H*-pyran-4-one **1b** and nitroalkene **4a**, full conversion of **4a** was observed after 4 days and ¹H NMR analysis on the crude mixture showed that the desired product was formed in a 20:1 d.r. Purification by FC on silica gel (10 to 20% EtOAc in cyclohexane) afforded **5e** as a white solid (7 mg,

0.035 mmol, 61% yield, d 5:1 d.r., 92% ee).

¹**H NMR** (CDCl₃, 400 MHz): δ [ppm] 7.37 – 7.28 (m, 3H), 7.21 – 7.16 (m, 2H), 4.93 (dd, J=12.7, 4.5, 1H), 4.65 (dd, J=12.7, 10.1, 1H), 4.18 – 4.11 (m, 1H), 3.88 – 3.74 (m, 2H), 3.70 (ddd, J=11.5, 5.4, 1.3, 1H), 3.27 (dd, J=11.5, 8.8, 1H), 2.88 (dddd, J=10.2, 8.8, 5.5, 1.2, 1H), 2.67 (dddd, J=13.8, 9.6, 6.2, 1.2, 1H), 2.61 – 2.53 (m, 1H).

¹³C NMR (CDCl₃, 101 MHz): δ [ppm] 207.5, 136.4, 129.4, 128.5, 128.1, 78.8, 71.7, 69.1, 53.4, 43.1, 41.5.

HRMS (ESI+): *m*/*z* calcd. for [C₁₃H₁₅NO₄+Na]⁺: 272.0893; found: 272.0894.

HPLC: Phenomenex Amylose-3; *n*-hexane/iPrOH, gradient of iPrOH 0 to 30% in 20 minutes, flow-rate 0.75 mL/min; $t_{minor} = 13.5$ min; $t_{major} = 23.6$ min.

(R)-3-((R)-2-nitro-1-phenylethyl)tetrahydro-4H-pyran-4-one, 5f



Following the General Procedure B applying tetrahydro-4H-thiopyran-4-one **1c** and nitroalkene **4a**, full conversion of **4a** was observed after 4 days and ¹H NMR analysis on the crude mixture showed that the desired product was formed in a 10:1 d.r. Purification by FC on silica gel (10 to 20% EtOAc in cyclohexane) afforded **5f** as a white solid (12 mg,

0.045 mmol, 90% yield, 10:1 d.r., 87% ee).

¹**H NMR** (CDCl₃, 400 MHz): δ [ppm] 7.38 – 7.28 (m, 3H), 7.22 – 7.17 (m, 2H), 4.74 (dd, *J*=12.6, 4.6, 1H), 4.63 (dd, *J*=12.6, 9.7, 1H), 3.98 (td, *J*=10.2, 4.6, 1H), 3.09 – 3.01 (m, 1H), 3.01 – 2.96 (m, 2H), 2.90 – 2.77 (m, 2H), 2.62 (ddd, *J*=13.9, 4.2, 1.7, 1H), 2.46 (ddd, *J*=13.8, 9.3, 0.8, 1H).

¹³C NMR (CDCl₃, 101 MHz): δ [ppm] 209.6, 136.6, 129.5, 128.5, 128.3, 78.8, 55.1, 44.7, 43.6, 35.3, 31.7.

HRMS (ESI+): m/z calcd. for $[C_{13}H_{15}NO_3S+Na]^+$: 272.0893; found = 272.0894.

HPLC: Phenomenex Amylose-1; *n*-hexane/iPrOH, 70:30 isocratic, flow-rate 0.75 mL/min; $t_{minor} = 10.4$ min; $t_{major} = 22.0$ min.

(S)-4,4-dimethyl-2-((R)-2-nitro-1-phenylethyl)cyclohexan-1-one, 5g



Following the General Procedure B applying 4,4-dimethylcyclohexanone **1d** and nitroalkene **4a**, full conversion of **4a** was observed after 4 days. Purification by FC on silica gel (10% EtOAc in cyclohexane) afforded **5g** as a colorless oil (10 mg, 0.037 mmol, 73% yield, 20:1 d.r., 90% ee).

¹**H NMR** (CDCl₃, 400 MHz): δ [ppm] 7.35 – 7.24 (m, 4H), 7.17 – 7.11 (m, 2H), 4.99 (dd, *J*=12.3, 4.6, 1H), 4.64 (dd, *J*=12.4, 9.6, 1H), 3.70 (td, *J*=9.6, 4.6, 1H), 2.92 – 2.82 (m, 1H), 2.55 (tdd, *J*=13.7, 6.2, 1.0, 1H), 2.31 (ddd, *J*=13.5, 4.6, 2.8, 1H), 1.79 – 1.71 (m, 1H), 1.63 (td, *J*=13.7, 4.7, 1H), 1.37 (ddd, *J*=13.4, 5.1, 3.4, 1H), 1.27 – 1.17 (m, 1H), 1.13 (s, 3H), 0.88 (s, 3H).

¹³**C NMR** (CDCl₃, 101 MHz): δ [ppm] 212.7, 137.9, 129.1, 128.3, 127.9, 79.2, 47.8, 46.0, 44.0, 40.8, 39.2, 31.21, 31.18, 24.5.

HRMS (ESI+): m/z calcd. for $[C_{16}H_{21}NO_3+Na]^+$: 298.1414; found = 298.1412.

 $[\alpha]^{26}_{D} = -58.2 \ (c = 0.27, \text{CHCl}_3) \ \text{for } 90\% \ \text{ee.}$

HPLC: Phenomenex Cellulose-5; *n*-hexane/iPrOH, 70:30 isocratic, flow-rate 0.75 mL/min; $t_{minor} = 16.6$ min; $t_{major} = 18.9$ min.

4. Use of CNDs in photoredox reactions

4.1 General Procedures C for the CNDs-promoted atom transfer radical addition between alkenes 6 and radical precursors

A Schlenk tube (10 mL), equipped with a magnetic stirring bar, was charged with (*S*)-CNDs (6 mg), olefine **6** (0.1 mmol, 1 eq), radical precursor **7** (0.3 mmol, 3 eq) and CH_2Cl_2 (400 µL). The reaction mixture was degassed via freeze pump thaw (3 cycles) and the vessel filled with argon. Then, the Schlenk tube was located 4-5 cm away from the Kessil lamp (456 nm)and stirred overnight (16 h). The reaction was quenched by dropping the organic solvent into 10 mL of cold Et₂O to precipitate the CNDs. After centrifugation (6000 rpm, 10 min), the organic phase was separated while (*S*)-CNDs were suspended in the minimum amount of CH_2Cl_2 , precipitated again into 10 mL of cold Et₂O and centrifugated (6000 rpm, 10 min) to separate the organic phase from the precipitate. The combined organic phases were concentrated under reduced pressure to give the crude product. The residue was purified by flash column chromatography (mixtures of EtOAc/cyclohexane) to afford the desired product.

5-Bromo-7,7,7-trichloroheptyl acetate, 8a

CI Br O Following the General Procedure C and applying olefine **6a** and bromotrichloromethane **7a**, the reaction was stirred for 16h. Purification by FC on silica gel (5 to 10% EtOAc in cyclohexane) afforded **8a** as a colorless oil (30.6 mg, 0.09 mmol, 90% yield).

¹**H NMR** (400 MHz, CDCl₃): δ [ppm] 4.37 – 4.27 (m, 1H), 4.08 (t, *J*=6.2, 2H), 3.46 (dd, *J*=15.8, 4.9, 1H), 3.22 (dd, *J*=15.8, 5.4, 1H), 2.13 – 2.02 (m, 4H), 2.02 – 1.91 (m, 1H), 1.76 – 1.52 (m, 4H).

¹³**C NMR** (CDCl₃, 100 MHz): δ [ppm] 171.6, 97.5, 64.5, 63.1, 49.1, 39.4, 28.2, 24.3, 21.4.

HRMS (ESI+): *m*/*z* calcd. for [C₉H₁₄BrCl₃O₂+Na]⁺: 360.9135, found: 360.9134.

((5-Bromo-7,7,7-trichloroheptyl)sulfonyl)benzene, 8b



Following the General Procedure C and applying olefine **6b** and bromotrichloromethane **7a**, the reaction was stirred for 16h. Purification by FC on silica gel (5 to 10% EtOAc in cyclohexane) afforded **8b** as a colorless oil (27.4 mg, 0.064 mmol, 64% yield).

¹**H NMR** (500 MHz, CDCl₃): δ [ppm] 7.95 – 7.91 (m, 2H), 7.70 – 7.66 (m, 1H), 7.62 – 7.57 (m, 2H), 4.32 – 4.23 (m, 1H), 3.44 (dd, *J*=15.8, 4.8, 1H), 3.18 (dd, *J*=15.8, 5.6, 1H), 3.15 – 3.10 (m, 2H), 2.09 – 2.01 (m, 1H), 1.97 – 1.88 (m, 1H), 1.87 – 1.54 (m, 4H).

¹³**C NMR** (CDCl₃, 125 MHz): δ [ppm] 139.2, 133.9, 129.5, 128.2, 97.0, 62.6, 56.1, 48.3, 38.9, 26.3, 22.1.

HRMS (ESI+): *m*/*z* calcd. for [C₁₃H₁₆BrCl₃O₂S+Na]⁺: 442.9013, found 442.9012.

2-(5-Bromo-7,7,7-trichloroheptyl)isoindoline-1,3-dione, 8c



Following the General Procedure applying E olefine **6c** and bromotrichloromethane **7a**, the reaction was stirred for 16h. Purification by FC on silica gel (5 to 10% EtOAc in cyclohexane) afforded **8c** as a colorless oil (28.2 mg, 0.066 mmol, 66% yield).

¹**H NMR** (500 MHz, CDCl₃): δ [ppm] 7.89 – 7.81 (m, 2H), 7.75 – 7.69 (m, 2H), 4.33 – 4.27 (m, 1H), 3.71 (t, *J*=7.1, 2H), 3.45 (dd, *J*=15.8, 5.0, 1H), 3.21 (dd, *J*=15.9, 5.3, 1H), 2.15 – 2.07 (m, 1H), 2.02 – 1.93 (m, 1H), 1.83 – 1.62 (m, 3H), 1.61 – 1.50 (m, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ [ppm] 168.5, 134.1, 132.2, 123.4, 97.2, 62.8, 48.7, 39.0, 37.7, 27.8, 24.8.

HRMS (ESI+): *m*/*z* calcd. for [C₁₅H₂₅BrCl₃NO₂+Na]⁺: 447.9244, found 447.9250.

Diethyl 2-(2-bromohexyl)malonate, 8d



Following the General Procedure E and applying olefine **6d** and diethyl 2bromomalonate **7b**, the reaction was stirred for 16h. Purification by FC on silica gel (5% EtOAc in cyclohexane) afforded **8d** as a colorless oil (23.2 mg, 0.072 mmol, 72% yield). The characterization of the compound matches with

the data reported in the literature.⁴

¹**H NMR** (400 MHz, CDCl₃): δ [ppm] 4.15-4.22 (m, 4H), 3.95-4.0 (m, 1H), 3.75 (dd, J= 4.1, 10.2 Hz, 1H), 2.44 (ddd, J= 4.1, 10.2, 14.3 Hz, 1H), 2.22 (ddd, J= 4.2, 10.4, 14.7 Hz, 1H), 1.81-1.86 (m, 2H), 1.46-1.53 (m, 1H), 1.36-1.43 (m, 1H), 1.29-1.35 (m, 2H), 1.23-1.27 (m, 6H), 0.88 (t, J= 7.3 Hz, 3H);

HRMS (ESI+): *m*/*z* calcd. for [C₁₃H₂₃BrO₄+Na]⁺: 345.0677, found 345.0672.

⁴ A. Da Lama, B. Bartolomei, C. Rosso, G. Filippini, M. Montserrat Martínez, Luis A. Sarandeses, Maurizio Prato *Eur. J. Org. Chem.* **2022**, e202200622

4.2 General Procedures D for the CNDs-promoted photochemical cyclopropanation

A Schlenk tube (10 mL), equipped with a magnetic stirring bar, was charged with **(S)-CNDs** (19 mg), 4-phenyl-1-butene **10** (1 equiv, 0.1 mmol, 15 μ L), ethyl 2-bromo-3-oxobutanoate **9** (2 equiv, 0.2 mmol, 42 mg), 2,6-lutidine (4 equiv, 0.4 mmol, 47 μ L), LiBF₄ (1 equiv, 0.1 mmol, 9.4 mg) and DMF (250 μ L). The reaction mixture was degassed via freeze pump thaw (3 cycles) and the vessel filled with argon. Then, the Schlenk tube was located 4-5 cm away from the Kessil lamp (456 nm) and stirred overnight (19 h). The reaction was quenched by dropping the organic solvent into 10 mL of cold Et₂O to precipitate the CNDs. After centrifugation (6000 rpm, 10 min), the organic phase was separated while the CNDs were suspended in the minimum amount of CH₂Cl₂, precipitated again into 10 mL of cold Et₂O and centrifugated (6000 rpm, 10 min) to separate the organic phase from the precipitate. The combined organic phases were concentrated under reduced pressure to give the crude product. The residue was purified by flash column chromatography to afford the desired product.

Ethyl 1-acetyl-2-phenethylcyclopropane-1-carboxylate, 11



Following the General Procedure D, purification by FC on silica gel (5 to 10% EtOAc in cyclohexane) afforded **11** as a colorless oil (9.0 mg, 0.035 mmol, 35% yield).

Ph ¹H NMR (500 MHz, CDCl₃): δ [ppm] 7.29 – 7.25 (m, 2H), 7.21 – 7.16 (m, 1H), 7.16 – 7.13 (m, 2H), 4.30 – 4.21 (m, 2H), 2.69 (t, *J*=7.8, 2H), 2.36 (s, 3H), 2.02 – 1.95 (m, 1H), 1.83 – 1.73 (m, 1H), 1.69 – 1.61 (m, 1H), 1.45 – 1.37 (m, 2H), 1.31 (t, *J*=7.1, 3H).

 $^{13}\textbf{C}$ NMR (CDCl₃, 125 MHz): δ [ppm] 203.0, 169.8, 141.5, 128.6, 128.5, 126.1, 61.6, 41.9, 35.3, 31.1, 30.4, 29.5, 23.9, 14.4.

HRMS (ESI+): m/z calcd. for $[C_{16}H_{20}O_3+Na]^+$: 283.1305, found 283.1306.

5. Use of CNDs in photo-organocatalyzed transformations

5.1 General Procedures E for the CNDs-promoted cross-dehydrogenative reaction

A Schlenk tube (10 mL), equipped with a magnetic stirring bar, was charged with **(S)-CNDs** (19 mg), xanthene **12** (9.1 mg, 0.05 mmol, 1 eq), Na₃PO₄ (12.3 mg, 0.075 mmol, 1.5 eq), the corresponding aldehyde or ketone (0.15 mmol, 3 eq), BrCCl₃ (7.4 μ L, 0.075 mmol, 1.5 eq) and 1,2-DCE (500 μ L). The reaction mixture was degassed via freeze pump thaw (3 cycles) and the vessel filled with argon. Then, the Schlenk tube was located 4-5 cm away from the Kessil lamp (456 nm)and stirred overnight (16 h). The reaction was quenched by dropping the organic solvent into 10 mL of cold Et₂O to precipitated the CNDs. After centrifugation (6000 rpm, 10 min), the organic phase was separated while the CNDs were suspended in the minimum amount of CH₂Cl₂, precipitated again into 10 mL of cold Et₂O and centrifugated (6000 rpm, 10 min) to separate the organic phase from the precipitate. The combined organic phases were concentrated under reduced pressure to give the crude product. The residue was purified by flash column chromatography (mixtures of EtOAc/cyclohexane) to afford the desired product.

2-(9H-Xanthen-9-yl)butan-1-ol, 14a



Following the General Procedure E, applying xanthene **12** and butyraldehyde **13**, the reaction was stirred for 16 h. Then, MeOH (1 mL) was then added to the reaction mixture, followed by portion-wise addition of NaBH₄ (18.5 mg, 0.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h and subsequently quenched with HCl (1 M). The organic phase was extracted three times with CH_2Cl_2 , dried over Na_2SO_4 and

concentrated under reduced pressure. The residue was suspended in the minimum amount of CH_2Cl_2 to follow the procedure to remove the CNDs. Purification by FC on silica gel (5 to 10% EtOAc in cyclohexane) afforded **14a** as a colorless oil (3.3 mg, 0.013 mmol, 26% yield).

The characterization of the compound matches with the data reported in the literature.⁵

¹**H NMR** (400 MHz, CDCl₃): δ [ppm] 7.26 – 7.20 (m, 4H), 7.12 – 7.05 (m, 4H), 4.28 (d, *J*=4.3, 1H), 3.62 – 3.48 (m, 2H), 1.81 - 1.68 (m, 1H), 1.41 - 1.29 (m, 1H), 1.16 - 1.00 (m, 1H), 0.82 (t, *J*=7.4, 3H).

2-(9H-Xanthen-9-yl)cyclohexan-1-one, 14b



Following the General Procedure E, applying xanthene **12** and cyclohexanone **1a**, the reaction was stirred for 16 h. Purification by FC on silica gel (5 to 10% EtOAc in cyclohexane) afforded **14b** as a colorless oil (7.0 mg, 0.025 mmol, 50% yield).

¹**H NMR** (400 MHz, CDCl₃): δ [ppm] 7.41 (d, *J*=7.6, 1H), 7.25 – 7.17 (m, 3H), 7.10 – 7.00 (m, 4H), 4.94 (d, *J*=3.2, 1H), 2.51 (dddd, *J*=12.9, 5.7, 3.2, 1.2, 1H), 2.46 – 2.39 (m, 1H), 2.31 – 2.20 (m, 1H), 1.98 – 1.89 (m, 1H), 1.81 – 1.67 (m, 2H), 1.54 – 1.37 (m, 2H), 1.17 – 1.05

(m, 1H).

 $^{13}\textbf{C}$ NMR (CDCl₃, 100 MHz): δ [ppm] 210.9, 153.5, 153.2, 130.6, 128.9, 127.9, 127.8, 125.7, 123.6, 123.4, 123.0, 116.4, 116.2, 60.8, 42.2, 36.8, 27.8, 26.8, 24.9.

HRMS (ESI+): *m*/*z* calcd. for [C₁₉H₁₈O₂+Na]⁺: 301.1199, found 301.1197.

⁵ E. Larionov, M. M. Mastandrea, M. A. Pericàs ACS Catal. **2017**, *7*, 7008.

3-(9H-xanthen-9-yl)tetrahydro-4H-pyran-4-one, 14c



Following the General Procedure E, applying xanthene **12**, tetrahydro-4*H*-pyran-4-one **1b** and **(S)-CNDs** (38 mg), the reaction was stirred for 22h. Purification by FC on silica gel (5 to 10% EtOAc in cyclohexane) afforded **14c** as a colorless oil (8.0 mg, 0.029 mmol, 57% yield).

¹H NMR (500 MHz, CDCl₃): δ [ppm] 7.40 – 7.37 (m, 1H), 7.26 – 7.20 (m, 3H), 7.12 – 7.02 (m, 4H), 4.93 (d, *J*=4.0, 1H), 4.11 – 4.04 (m, 1H), 3.89 (ddd, *J*=11.6, 6.2, 1.5, 1H), 3.57 (td, *J*=11.1, 3.6, 1H), 3.23 (dd, *J*=11.5, 10.1, 1H), 2.79 – 2.74 (m, 1H), 2.57 (dddd, *J*=15.0, 10.9, 6.9, 1.3, 1H), 2.45

(ddd, *J*=15.0, 3.6, 2.8, 1H). ¹³C NMR (CDCl₃, 125 MHz): δ [ppm] 206.4, 153.3, 153.0, 130.3, 128.6, 128.3, 128.2, 124.5, 123.9, 123.6, 122.1, 116.7, 116.6, 68.8, 68.0, 60.4, 42.5, 35.1.

HRMS (ESI+): *m*/*z* calcd. for [C₁₈H₁₆O₃+Na]⁺: 303.0992 ; found 303.0994.

2-(9H-xanthen-9-yl)cyclopentan-1-one, 14d



Following the General Procedure E, applying xanthene **12** and cyclopentanone **1e**, the reaction was stirred for 22h. Purification by FC on silica gel (5 to 10% EtOAc in cyclohexane) afforded **14d** as a colorless oil (5.0 mg, 0.019 mmol, 38% yield).

¹**H NMR** (500 MHz, CDCl₃): δ [ppm] = 7.26 - 7.19 (m, 3H), 7.13 - 7.07 (m, 4H), 6.99 (t, *J*=7.5, 1H), 4.77 (d, *J*=2.9, 1H), 2.48 - 2.42 (m, 1H), 2.30 - 2.22 (m, 1H), 1.82 - 1.75 (m, 2H), 1.68 - 1.61 (m, 1H), 1.59 - 1.51 (m, 1H), 1.46 - 1.36 (m, 1H).

¹³**C NMR** (CDCl₃, 125 MHz): δ [ppm] 219.3, 153.3, 152.6, 129.3, 128.33, 128.31, 127.9, 124.6, 123.8, 123.6, 122.0, 116.54, 116.46, 60.0, 39.4, 38.1, 24.1, 20.5.

HRMS (ESI+): *m*/*z* calcd. for [C₁₈H₁₆O₂+Na]⁺: 287.1043, found 287.1044.

6. NMR Spectra

Anti-2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one, anti-3



Syn-2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one, syn-3



(S)-2-((R)-2-Nitro-1-phenylethyl)cyclohexan-1-one, 5a



120 110 100 f1 (ppm) . 170

(S)-2-((R)-1-(4-methoxyphenyl)-2-nitroethyl)cyclohexan-1-one, 5b



(S)-2-((R)-2-nitro-1-(p-tolyl)ethyl)cyclohexan-1-one, 5c



(S)-2-((R)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexan-1-one, 5d



23

(R)-3-((R)-2-nitro-1-phenylethyl)tetrahydro-4H-pyran-4-one, 5e



(R)-3-((R)-2-nitro-1-phenylethyl)tetrahydro-4H-pyran-4-one, 5f



(S)-4,4-dimethyl-2-((R)-2-nitro-1-phenylethyl)cyclohexan-1-one, 5g



5-Bromo-7,7,7-trichloroheptyl acetate, 8a



((5-Bromo-7,7,7-trichloroheptyl)sulfonyl)benzene, 8b



28





Diethyl 2-(2-bromohexyl)malonate, 8d



Ethyl 1-acetyl-2-phenethylcyclopropane-1-carboxylate, 11



2-(9H-Xanthen-9-yl)butan-1-ol, 14a



2-(9H-Xanthen-9-yl)cyclohexan-1-one, 14b



3-(9H-Xanthen-9-yl)tetrahydro-4H-pyran-4-one, 14c



2-(9H-Xanthen-9-yl)cyclopentan-1-one, 14d



7. HPLC chromatograms

Anti-2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one, anti-3





Syn-2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one, syn-3

(S)-2-((R)-2-Nitro-1-phenylethyl)cyclohexan-1-one, 5a



38





RT [min] Type	Width [min]	Area	Height	Area%
29.660 MM	0.4347	15475.6846	593.3307	86.8540
31.278 MM	0.5014	2342.3672	77.8567	13.1460
	Sum	17818.0518		





nal:	VWD1	Β,	Wavelength=220 nm
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RT [min] Type	Width [min]	Area	Height	Area%
14.006 MM	0.3439	728.5383	35.3064	4.6179
15.024 MM	0.3500	15047.8027	716.5395	95.3821
	Sum	15776.3411		

(S)-2-((R)-2-nitro-1-(p-tolyl)ethyl)cyclohexan-1-one, 5c



0.2750	21189.6816	1284.1577

Sum 22265.4154



(S)-2-((R)-1-(4-chlorophenyl)-2-nitroethyl)cyclohexan-1-one, 5d

400 300

200-100-0-

2 4 6 8

10

16

18

12 14



→ 26.359

28

Time [min]

30 32 34 36 38 40

20 22 24 26

NO₂

42 44 46 48

50 52

54 56 58

60

(R)-3-((R)-2-nitro-1-phenylethyl)tetrahydro-4H-pyran-4-one, 5e



Signal: VWD1 B, Wavelength=220 nm

RT [min] Type	Width [min]	Area	Height	Area%
13.474 MM	0.4225	758.9697	29.9411	4.0433
23.587 MM	1.1774	18012.0938	254.9667	95.9567
	Sum	18771.0635		



10.357 BB

11.995 BB

17.945 MM

22.000 BB

0.2877

0.3415

0.6234

0.7611

Sum

155.9744

233.6670

53.2246

2251.9768

2726.8652

8.2812

10.5046

1.4229

44.9044

5.7199

8.5691

1.9519

82.5848



4	4





Sum 8062.7640