

Supplementary Information

Quantum dots in visible light photoredox catalysis: Reductive dehalogenations and C–H arylation reactions using aryl bromides

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Materials and Methods

Aryl halides were commercially available and used without further purification unless otherwise stated. Thin-layer chromatography was performed using silica gel plates 60 F254. Standard flash chromatography was performed on an IsoleraTM Spektra Systems automated with high performance flash purification system using silica gel of particle size 40–63 μm . ¹H and ¹³C NMR spectra were recorded on Bruker Avance spectrometers (300 MHz and 75 MHz) in CDCl₃ and DMSO-*d*₆ solution with internal solvent signal as reference (7.26 and 77.2, 2.50 and 39.5 respectively). Proton NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, dd = doublet of doublets, m = multiplet, br. s. = broad singlet), coupling constants (Hz) and numbers of protons. Data for ¹³C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. Gas chromatography (GC) and gas chromatography coupled to low resolution mass spectrometry (GC–MS) analysis were performed using a capillary column (length: 30 m; diam. 0.25 mm; film: 0.25 μm) using He gas as carrier. GC was equipped with an FID detector. GC–MS was performed on 5975 MSD single quadrupole detector. Reduction products were identified by comparing with authentic samples (GC/FID and GC–MS). Quantification of reduction products was performed by GC/FID analysis using internal standards. UV–Vis and fluorescence measurements were performed with Varian Cary 50 UV/Vis spectrophotometer and FluoroMax-4 spectrofluorometer, respectively. Photoreduction and C–H arylation reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs (λ = 455 nm (\pm 15 nm), 3.5 V, 700 mA).

General procedure for the photoreduction of aryl halides:

In a 5 mL snap vial with magnetic stirring bar the respective aryl halide (0.05 mmol, 1.0 equiv) and QDs (0.32 μmol , 0.006 equiv) were dissolved in hexane (total volume of the solution 2 mL) and the resulting mixture was degassed by "pump-freeze-thaw" cycles (\times 3) via a syringe needle. DIPEA (0.40 mmol, 8.0 equiv) was added under N₂ and the reaction mixture was photoirradiated through the plane bottom side of the snap vial using 455 nm LEDs. The reaction progress was

monitored by GC analysis. Photoreduction yields were calculated from GC measurements using internal standards.

General procedure for C–H arylation reactions:

In a 5 mL snap vial with magnetic stirring bar the aryl halide (0.05 mmol, 1.0 equiv) and QDs (0.32 μ mol, 0.006 equiv) were dissolved in hexane (total volume of the solution 2 mL), and the resulting mixture was degassed by "pump-freeze-thaw" cycles (\times 3) via a syringe needle. DIPEA (0.40 mmol, 8.0 equiv) and the corresponding pyrrole (1.5 mmol) were added under N₂ and the reaction mixture was photoirradiated through the plane bottom side of the snap vial using a 455 nm LED. The reaction progress was monitored by GC analysis. Hexane was removed under reduced pressure, and the purification of the crude reaction mixture was achieved by flash column chromatography using petrol ether/ethyl acetate as eluents on silica gel.



Figure S1. Photograph of the photochemical reaction setup. The reaction vials (5 mL crimp cap vials) were illuminated from the bottom side with blue LEDs ($\lambda_{\text{ex}} = 455 (\pm 15)$ nm) and cooled (to maintain the reaction temperature of 25 °C) from the side using custom-made aluminum cooling blocks connected to a thermostat. Photograph reproduced with permission of Burkhard König.

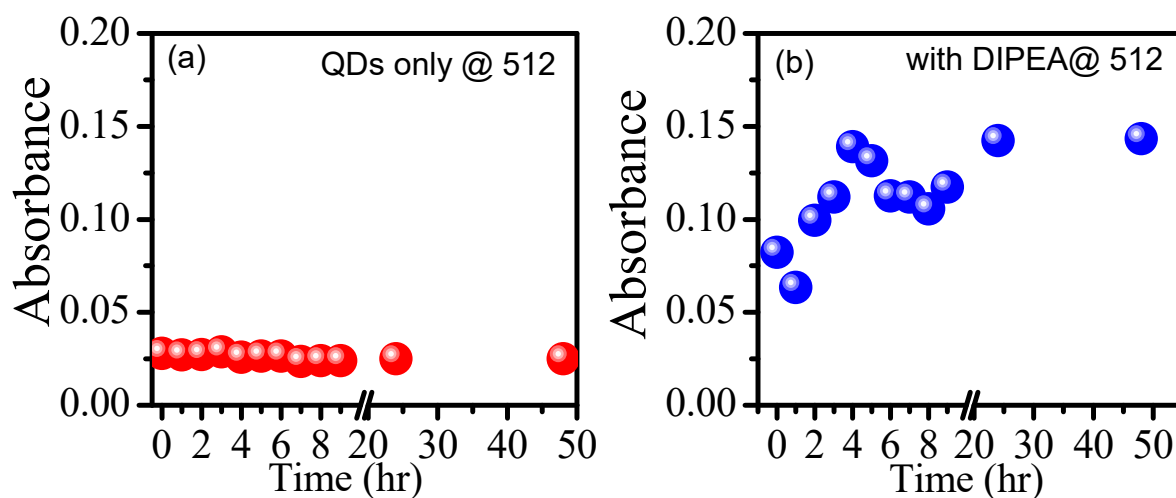


Figure S2. Changes in the absorbance (at 512 nm) of QDs upon photoirradiation with blue LEDs ($\lambda_{\text{Ex}} = 455 (\pm 15)$ nm) with time in the absence (a) and in the presence (b) of DIPEA.

Determination of the concentration of QDs:

The concentration of ZnSe core QDs has been calculated by using the extinction coefficient reported by Banin and coworkers (Small, **2008**, 4, 1319-1323) and Lambert Beer law. Notably, the absorbance of QDs scale quite linearly at low concentrations. Core/shell was synthesized by SILAR method, and an assumption was made that the concentration of core/shell QDs would remain same as core QDs.

Characterization of C–H arylated products:

4-(1-Methyl-1H-pyrrol-2-yl)benzonitrile¹

The compound was prepared according to the general procedure using 9.1 mg of 4-bromobenzonitrile, 0.32 μmol of QDs, 132 μL of *N*-methylpyrrole, and 68 μL of DIPEA. The crude product was purified using chromatography on silica gel.

¹H NMR (300 MHz, CDCl₃) δ 7.75 – 7.59 (m, 2H), 7.60 – 7.37 (m, 2H), 6.78 (dd, *J* = 2.4, 2.0 Hz, 1H), 6.35 (dd, *J* = 3.7, 1.8 Hz, 1H), 6.23 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.72 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 137.7, 132.6, 132.2, 128.3, 125.8, 119.0, 110.7, 109.6, 108.6, 35.5.

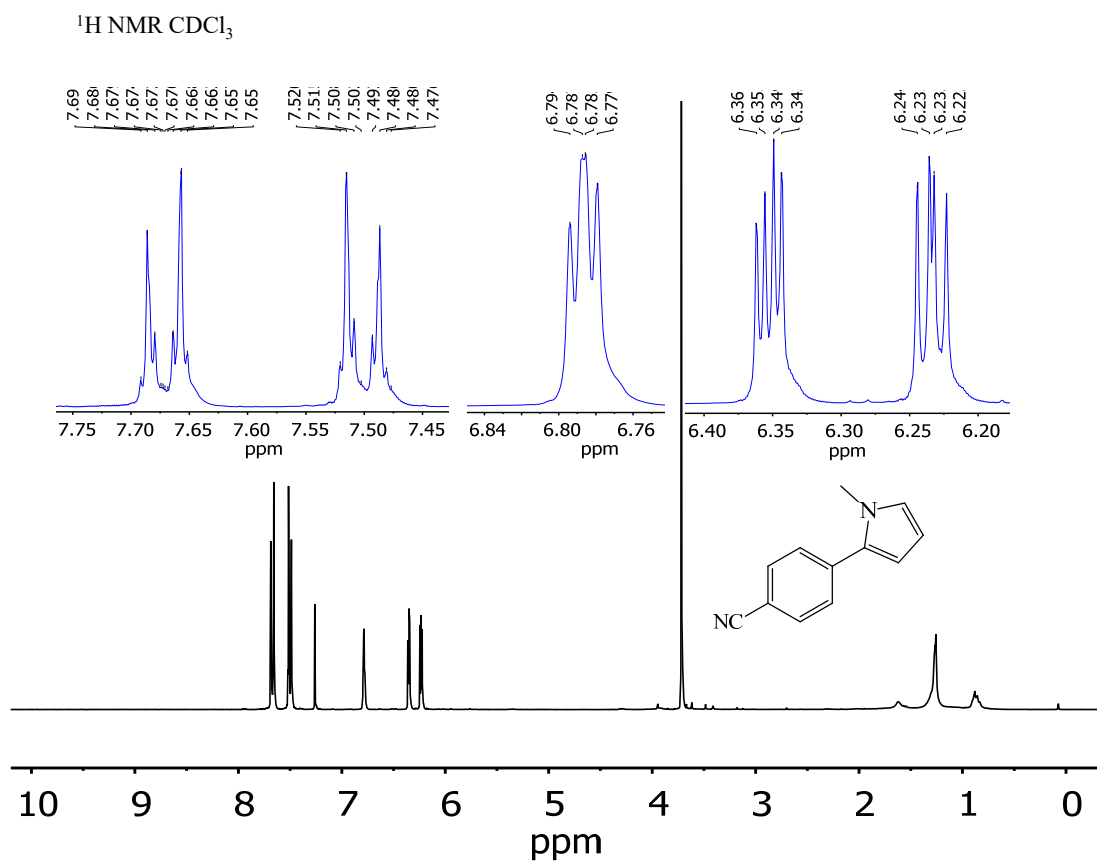


Figure S3: Proton NMR spectra of 4-(1-methyl-1H-pyrrol-2-yl)benzonitrile. Inset shows a magnified view of selected resonances.

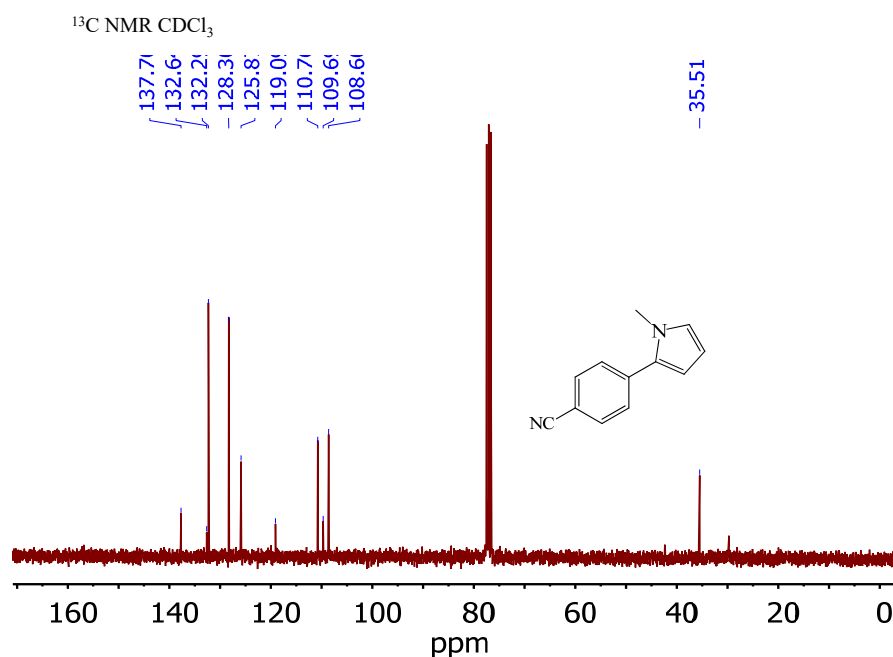


Figure S4: Carbon NMR spectra of 4-(1-Methyl-1H-pyrrol-2-yl)benzonitrile.

2-(1-Methyl-1H-pyrrol-2-yl)benzonitrile^{1, 2}

The compound was prepared according to the general procedure using 9.1 mg of 2-bromobenzonitrile, 0.32 μ mol of QDs, 132 μ L of *N*-methylpyrrole, and 68 μ L of DIPEA. The crude product was purified using chromatography on silica gel.

¹H NMR (300 MHz, CDCl₃): δ 7.74 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.68 – 7.56 (m, 1H), 7.50 – 7.36 (m, 2H), 6.80 (dd, *J* = 2.5, 1.9 Hz, 1H), 6.41 (dd, *J* = 3.7, 1.7 Hz, 1H), 6.25 (dd, *J* = 3.7, 2.7 Hz, 1H), 3.62 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 136.9, 133.5, 132.3, 130.8, 129.9, 127.4, 124.8, 118.6, 112.8, 111.4, 108.3, 34.9.

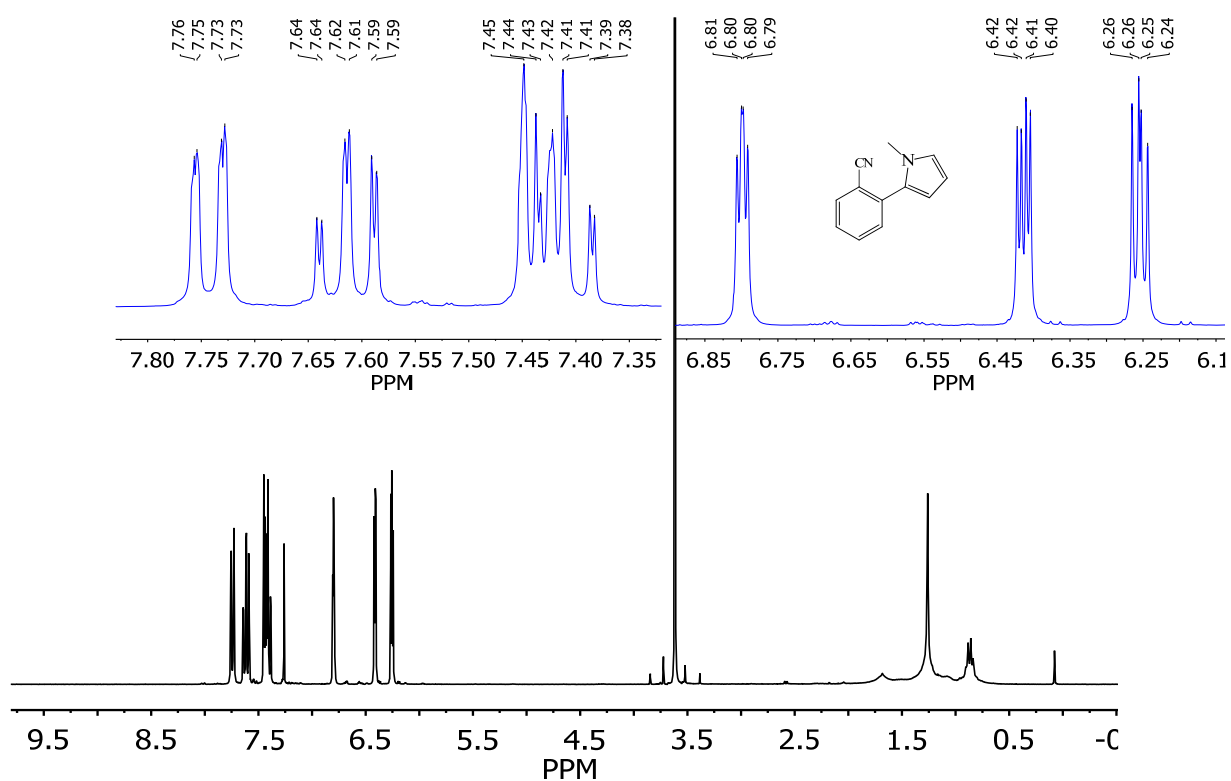


Figure S5. Proton NMR spectra of 2-(1-methyl-1H-pyrrol-2-yl)benzonitrile. Inset shows a magnified view of selected resonance signals.

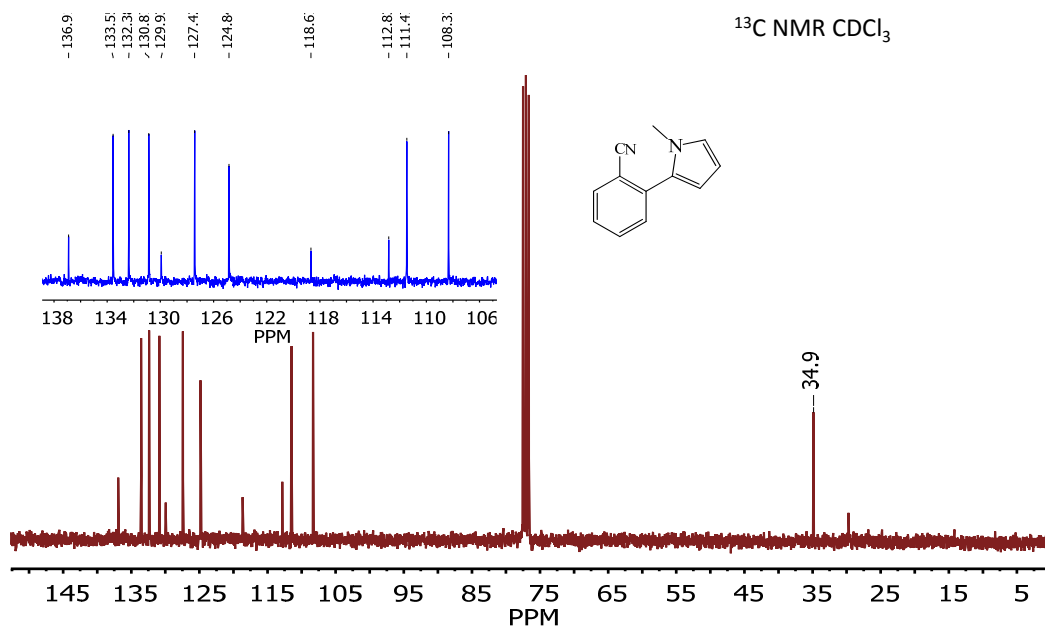


Figure S6: Carbon NMR spectra of 2-(1-methyl-1H-pyrrol-2-yl)benzonitrile. Inset shows a magnified view of selected resonance signals.

3-(1-Methyl-1H-pyrrol-2-yl)pyridine¹

The compound was prepared according to the general procedure using 7.9 mg of 3-bromopyridine, 0.32 μ mol of QDs, 132 μ L of *N*-methylpyrrole, and 68 μ L of DIPEA. The crude product was purified using chromatography on silica gel.

¹H NMR (300 MHz, CDCl₃) δ 8.69 (s, 1H), 8.54 (d, *J* = 4.1 Hz, 1H), 7.86 – 7.64 (m, 1H), 7.37 (dd, *J* = 7.8, 5.0 Hz, 1H), 6.85 – 6.67 (m, 1H), 6.31 (dd, *J* = 3.6, 1.8 Hz, 1H), 6.24 (dd, *J* = 3.5, 2.8 Hz, 1H), 3.69 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 148.4, 146.9, 136.1, 130.5, 129.6, 125.0, 123.5, 110.1, 108.4, 35.2.

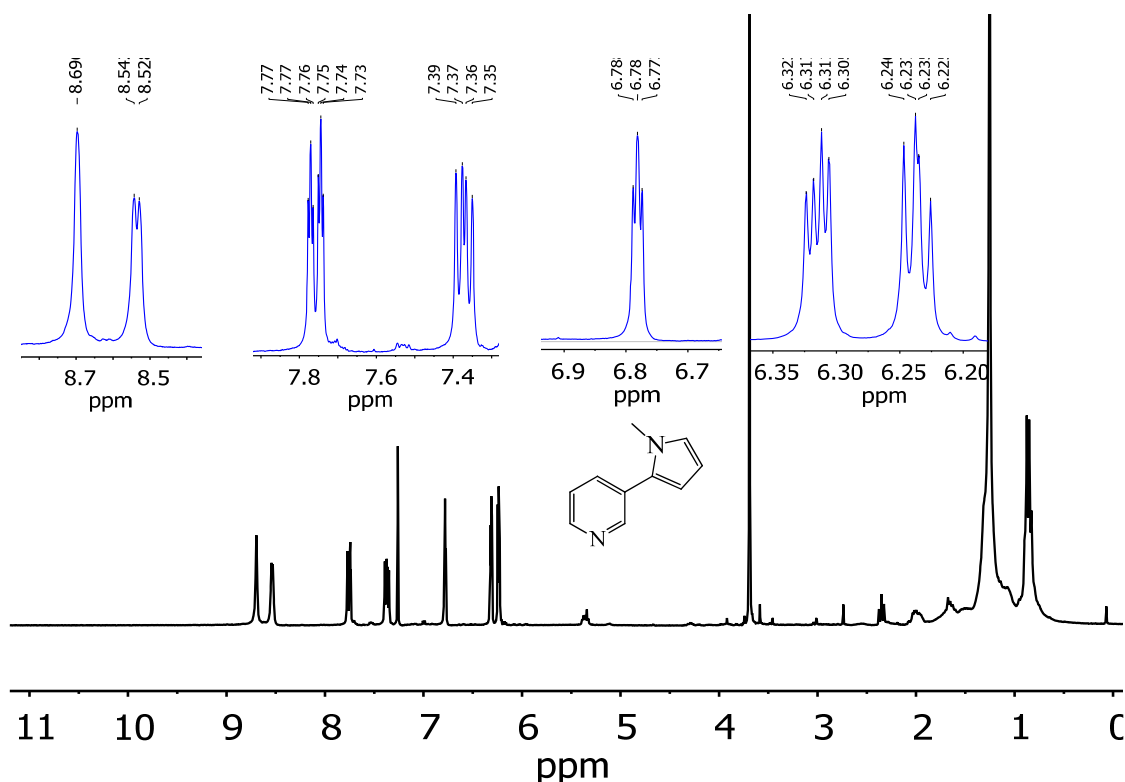


Figure S7: Proton NMR spectra of 3-(1-methyl-1H-pyrrol-2-yl)pyridine. Inset shows a magnified view of selected resonance signals.

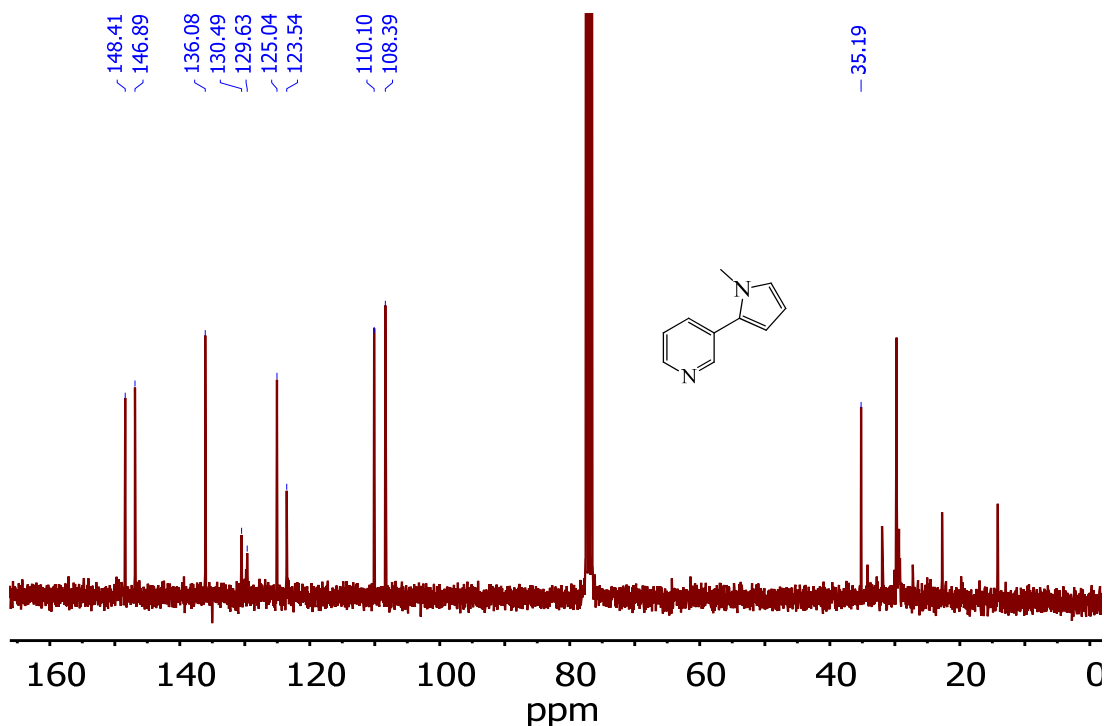


Figure S8: Proton NMR spectra of 3-(1-methyl-1H-pyrrol-2-yl)pyridine. Inset shows a magnified view of selected resonance signals.

2-(1H-Pyrrol-2-yl) benzonitrile^{1, 2}

The compound was prepared according to the general procedure using 9.1 mg of 2-bromobenzonitrile, 0.32 μ mol of QDs, 104 μ L of pyrrole, and 68 μ L of DIPEA. The crude product was purified using chromatography on silica gel.

¹H NMR (300 MHz, DMSO-*d*₆) δ 11.53 (s, 1H), 7.88 – 7.77 (m, 1H), 7.77 – 7.61 (m, 2H), 7.45 – 7.26 (m, 1H), 7.07 – 6.96 (m, 1H), 6.92 – 6.77 (m, 1H), 6.29 – 6.14 (m, 1H).

^{13}C NMR (75 MHz, DMSO- d_6) δ 135.4, 134.3, 133.2, 127.1, 126.3, 125.9, 121.1, 119.4, 109.5, 109.3, 106.3.

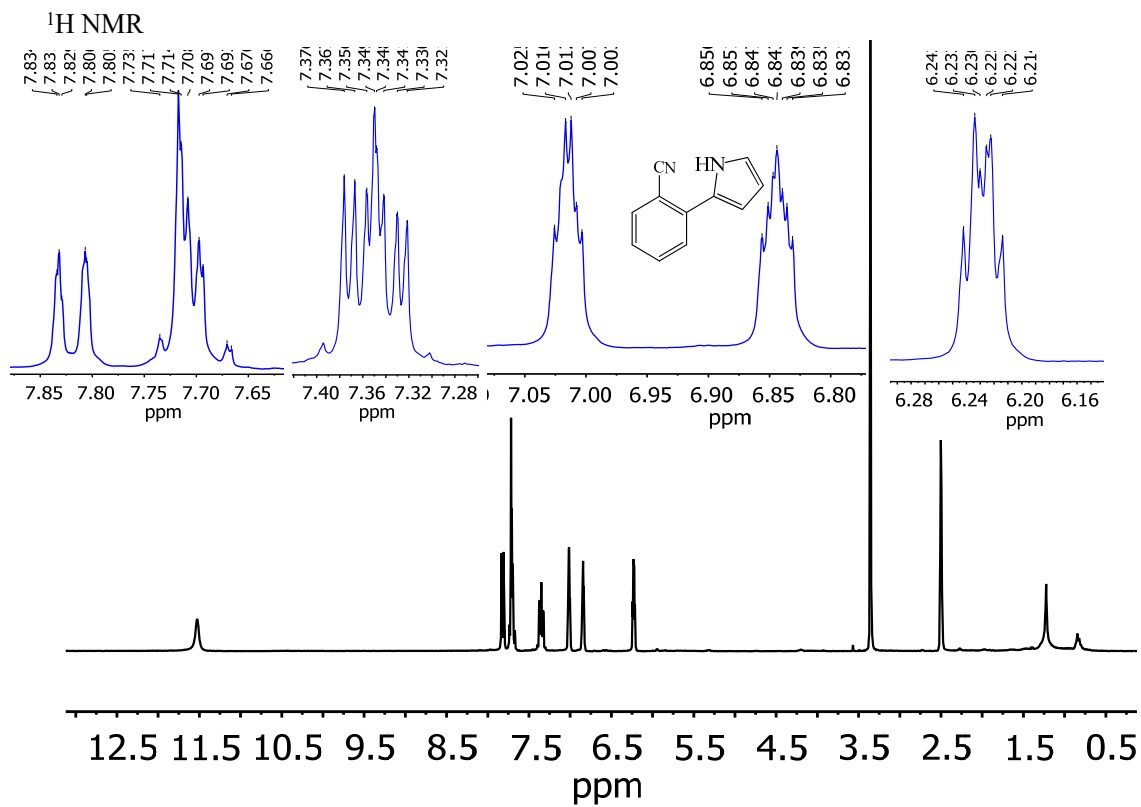


Figure S9. Proton NMR spectra of 2-(1H-pyrrol-2-yl) benzonitrile. Inset shows a magnified view of selected resonance signals.

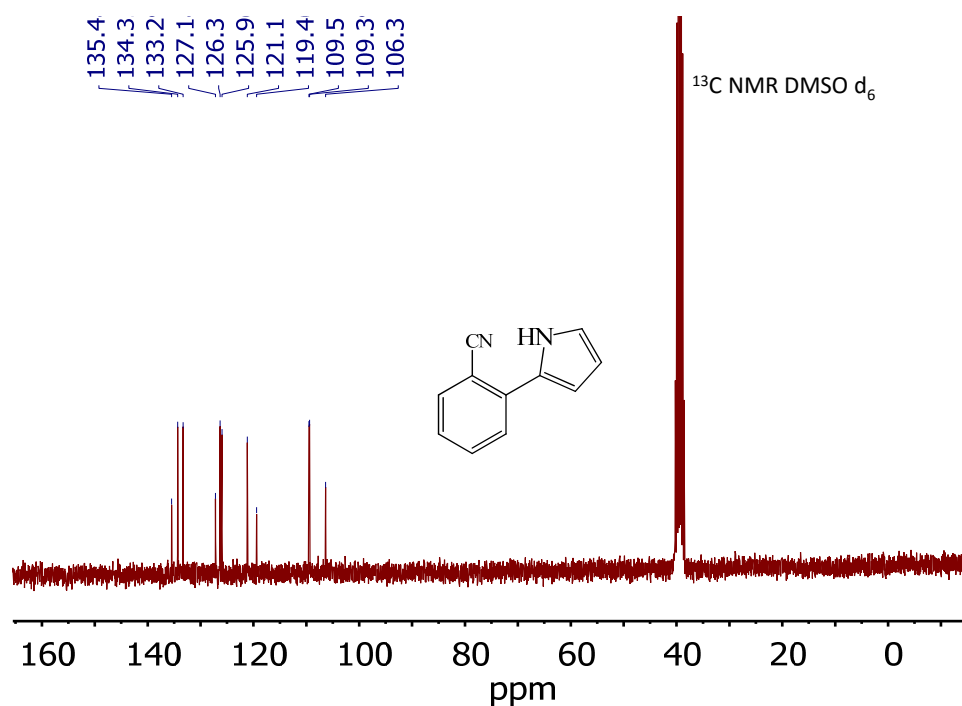


Figure S10. Carbon NMR spectra of 2-(1H-Pyrrol-2-yl) benzonitrile

References:

1. Ghosh, I.; Konig, B. Chromoselective Photocatalysis: Controlled Bond Activation through Light-Color Regulation of Redox Potentials. *Angewandte Chemie-International Edition* 2016, 55, 7676-7679.
2. Ghosh, I.; Ghosh, T.; Bardagi, J. I.; Konig, B. Reduction of aryl halides by consecutive visible light-induced electron transfer processes. *Science* 2014, 346, 725-728.