Steady state and transient kinetics in crystalline solids: The photochemistry of nanocrystalline 1,1,3-triphenyl-3-hydroxy-2-indanone

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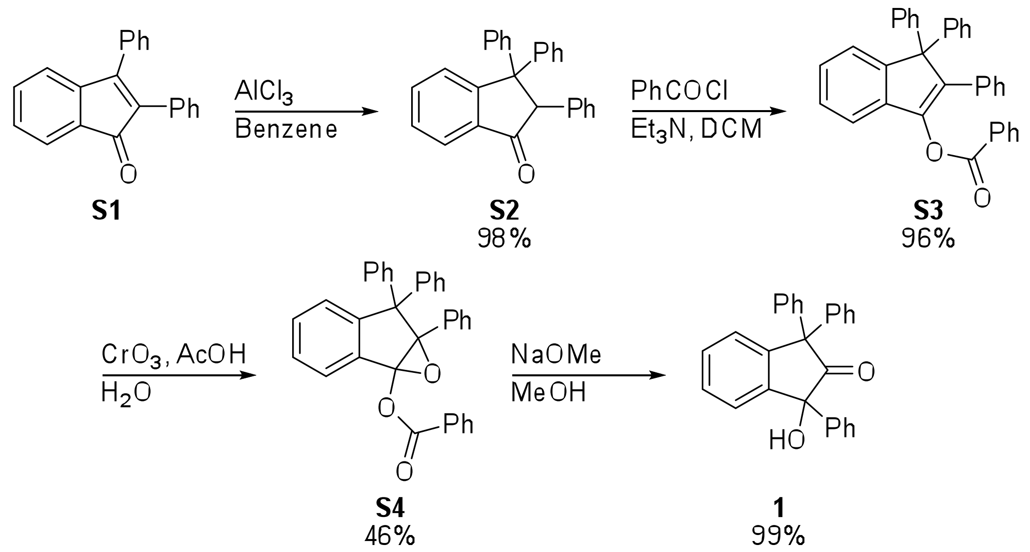
General Methods. All chemicals were purchased from Sigma-Aldrich Co. Inc. and used without further purification. Anhydrous DCM was acquired via distillation from sodium. Silica used for purification was Silica-P flash silica gel (40-62 Å), purchased from SiliCycle Inc. ^{1}H and ^{13}C NMR was acquired on a Bruker Advance AV300. IR spectra were obtained with a Perkin-Elmer Spectrum instrument equipped with a universal attenuated total reflectance (ATR) accessory. Gas chromatography data were acquired on a Hewlett-Packard 5890 series II gas chromatograph equipped with an HP3396 series II integrator and an HP-5 capillary column of dimensions 25 m × 0.2 mm with a film thickness of 0.11 mm. UV-vis spectra were taken on an Ocean Optics USB2000. Solid-state CPMAS ^{13C} NMR spectra were obtained at 75 MHz. All SEM images were recorded with a JEOL JSM-6700F field emission scanning electron microscope (Peabody, MA) on an aluminum stage.

ns Laser spectroscopy methods: A Surelite-II at 255 nm (10 mJ/pulse, ca. 6 ns pulse) was used as excitation source. In all cases, fused silica cells with a path length of 1.0 cm were used. Data were acquired with a customized LFP 111 laser-flash photolysis system (Luzchem Inc., Ottawa, Canada). All solution measurements were performed in flowing N_2 saturated solutions. All nanocrystalline suspensions were preformed in air saturated water. To minimize degradation of the sample, a gravity flow system was employed and 10 single laser shots were averaged.

fs Laser spectroscopy methods: The ultrafast UV-vis broadband absorption measurements were performed using the home-built spectrometers at The Ohio State University for Chemical and Biophysical Dynamics and have been described previously.[1]

Following a modified synthetic route by Koelsch[2] and Paul,[3] previously reported **1** was synthesized in four steps. The ^{1}H and ^{13}C NMR spectra for **S2**, **S3**, **S4**, and **1** agree well with published spectra.

Scheme S1. Synthesis of **1**.



Synthesis of S2. In a flame-dried, argon filled three-neck round bottom, **S1** (3 grams, 10 mmol) was dissolved in 30 mL of dry benzene. The solutions was cooled to 0 °C. To this, aluminum chloride (0.5 eq.) was added at 0 °C. The suspension was warmed to room temperature and allowed to stir for 8 hours. The solution was then quenched slowly with satd. ammonium chloride solution and extracted with DCM. The organic extract was then washed with brine. The solvents were removed under reduced pressure to give **S2**. The resulting crystalline solid was recrystallized from ethanol.

2,3,3-triphenyl 1-indanone (S2). Yield 98%; ^{1}H NMR (500 MHz, $CDCl_3$) δ7.91 (1H, d, J = 12 Hz), 7.58 (2H, t, J= 12 Hz), 7.47 (2H, m), 7.29 (4H, m), 6.98 (3H, m), 6.89 (2H, q, J = 13 Hz), 6.60 (2H, d, J= 12 Hz), 6.39 (2H, d, J= 13 Hz), 5.12 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.70, 158.49, 145.54, 143.44, 136.99, 135.73, 135.30, 130.63, 130.41, 128.57, 128.34, 128.27, 127.75, 127.71, 127.05, 126.84, 126.45, 123.88, 66.74, 63.35.

Synthesis of S3. In a flame-dried, argon filled three-neck round bottom, anhydrous triethyl amine (1.2 eq) was added to **S2** (2.54 g, 7 mmol) in dry dichloromethane (DCM). The solutions was allowed to stir for 15 minutes at room temperature. To this, benzoyl chloride (1.5 eq.) was added over 30 minutes. This was allowed to stir at 60 °C for 3 hour. The solution was then quenched slowly with satd. ammonium chloride solution and extracted with DCM and washed with brine. The solvents were removed under reduced pressure, and the crude material subjected to column chromatography (9:1 hexane:diethyl ether).

2,3,3-triphenyl, 1H-inden-3-yl benzoate (S3). Yield 96%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.26 (2H, d, J = 13 Hz), 7.66 (1H, t, J = 12 Hz), 7.55 (2H, d, J = 13.5 Hz), 7.48 (4H, m), 7.283 (12H, m), 7.14 (3H, m); ^{13}C (125 MHz, CDCl$_3$) δ 164.18, 151.54, 146.46, 141.48, 139.17, 137.43, 133.87, 133.10, 130.38, 129.20, 129.00, 128.85, 128.78, 128.28, 127.90, 127.58, 127.15, 127.08, 127.03, 125.04, 119.12, 67.34.

Synthesis of S4. In one-neck round bottom, chromium trioxide (66 mg, 0.66 mmol, 3 eq.) was added to **S3** (100 mg, 0.22 mmol.) in an acetic acid/water solution (4:1). The solutions was allowed to stir at 60 -70 ^{o}C for 3 hours. Decomposition occured if heated about 80 ^{o}C for an extended period. A white precipitate formed during the heating. The solution was then quenched with water, extracted with DCM, and washed with sat. ammonium chloride. The solvents were removed under reduced pressure, and subjected to column chromatography (9:1 hexane:diethyl ether).

1,2-epoxy -2,3,3-triphenyl-1 indanol beznoate (S4). Yield 46%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.08 (1H, d, J= 7.5 Hz), 7.83 (2H, d, J= 8 Hz), 7.65 (1H, t, 7.5 Hz), 7.52 (4H ,m,), 7.38 (1H, d, J= 7.5 Hz), 7.35 (2H, t, J= 8Hz), 7.21 (2H, t, J= 7.5 Hz), 7.03 (2H, dd, J= 5Hz, 7Hz), 6.97 (8H, m); ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.63, 163.29, 155.69, 142.10, 141.46, 138.23, 135.71, 135.31, 132.85, 130.63, 130.61, 129.74, 128.57, 128.55, 128.39, 128.10, 127.67, 127.62, 127.21, 126.44, 126.38, 123.91, 93.61, 67.84.

Synthesis of 1. In a flame-dried, argon filled three neck, sodium (210 mg, 9 mmol, 6 eq.) was added to **S4** (733 mg, 1 eq., 1.5 mmol) in 5 mL of dry methanol. The solutions was allowed to stir for 4 hours at room temperature. The solution was then quenched slowly with satd. ammonium chloride solution and extracted with DCM and washed with brine. The solvents were removed under reduced pressure, and the resulting solid was recrystallized from ethanol.

1-hydroxy, 1,3,3,-triphenyl-2-indanone (1). Yield 99%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (2H, m), 7.60 (4H, m), 7.58 (9H, m), 7.14 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 215.09, 144.22, 144.12, 141.41, 140.66, 139.33, 129.98, 129.29, 129.01, 128.98, 128.33, 128.30, 128.11, 127.93, 127.35, 127.31, 127.12, 126.57, 125.85, 81.84, 30.95

Photolysis of 1. Upon photolysis of **1** at 312 nm in acetonitrile, cyclohexane, or as a nanocrystalline suspension, only one product could be isolated.

2-(diphenylmethyl)benzophenone (2).[3] Yield 99%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (2H, d, J= 8 Hz), 7.49 (2H, m), 7.32 (3H, m), 7.27 (2H, m), 7.20 (3H, m), 7.12 (4H, m), 7.04 (3H, m), 5.95 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ198.67, 143.08, 139.58, 137.54, 133.08, 130.42, 130.15, 129.97, 129.71, 128.51, 128.30, 128.17, 127.93, 127.76, 127.67, 127.51, 126.80, 126.37, 125.74, 52.45.

Figure S1 and S2. ^{1}H and ^{13}C NMR spectra of **S2**.

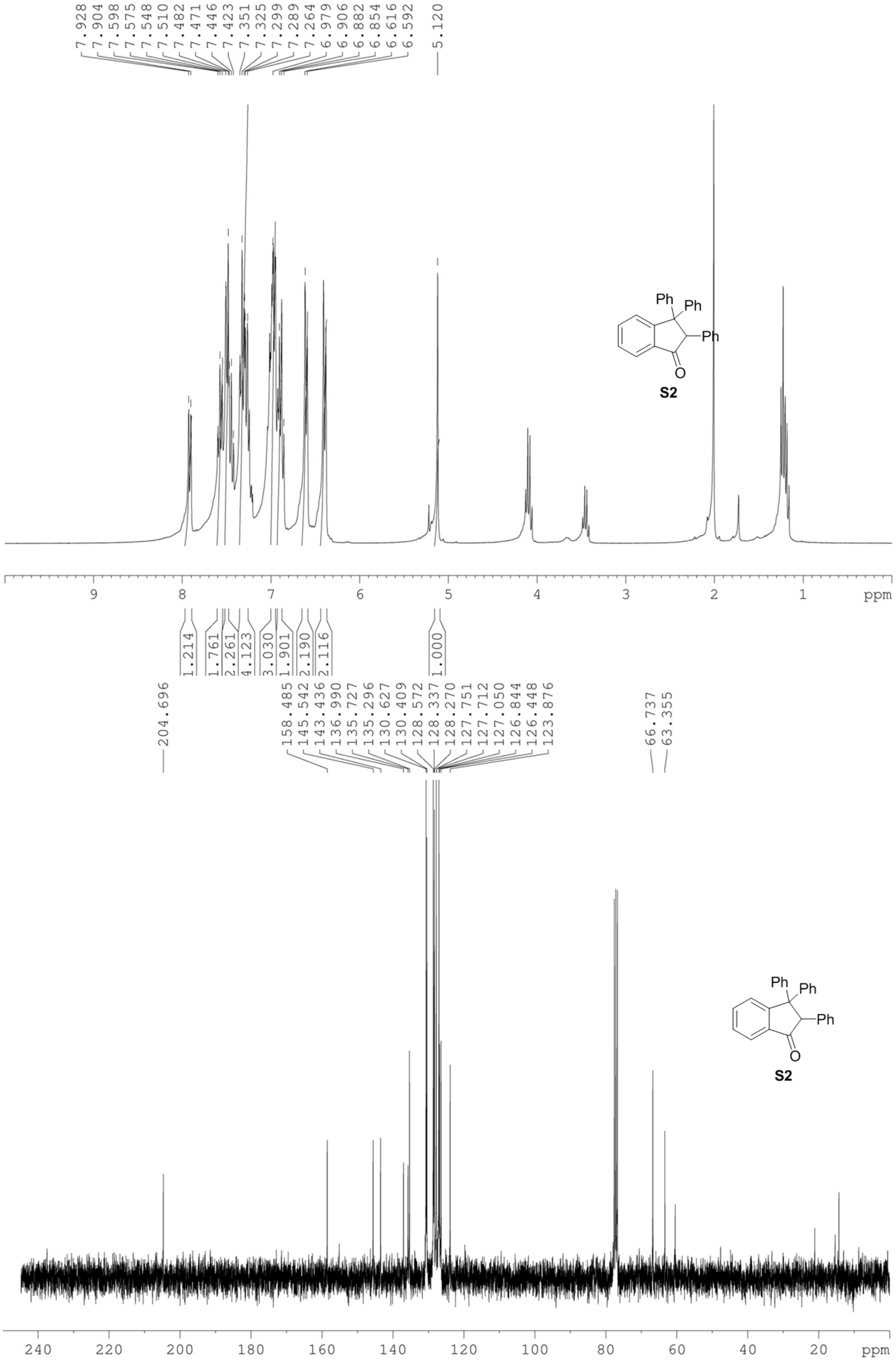
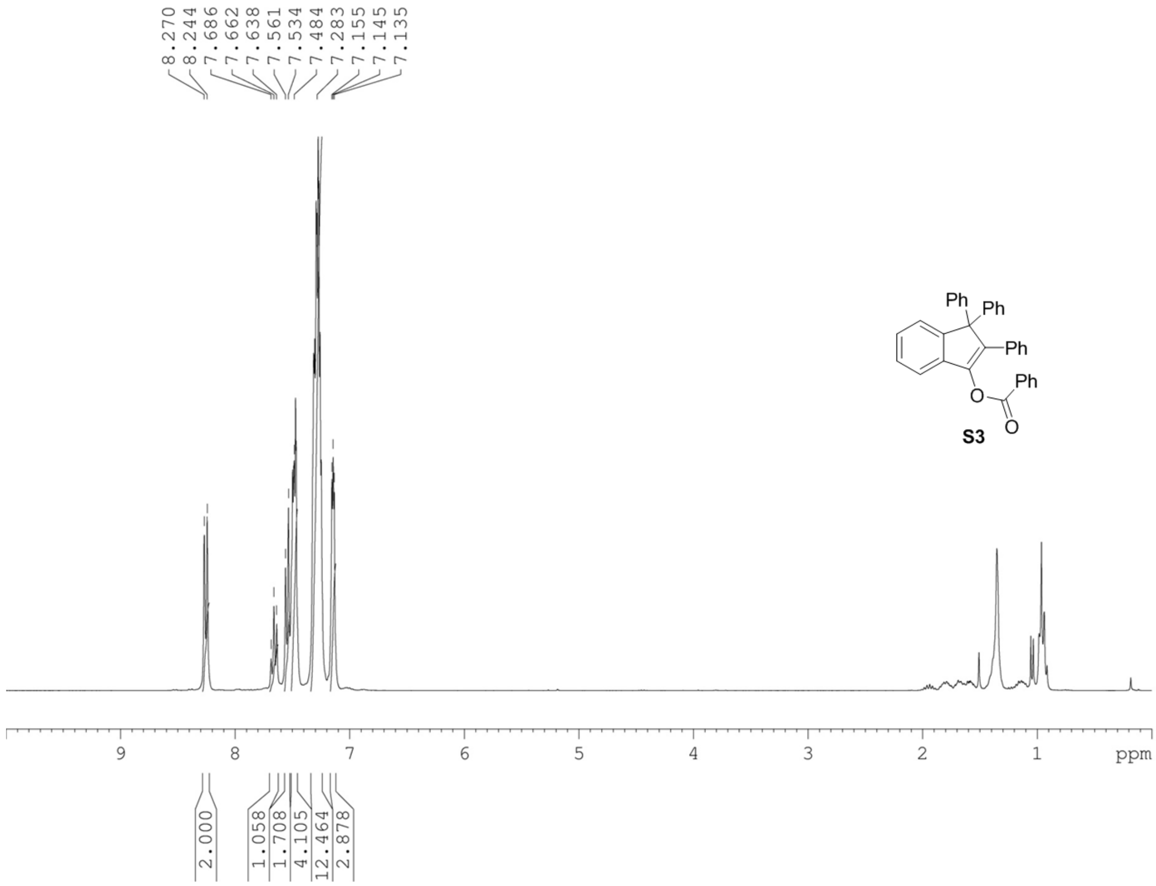


Figure S3 and S4. ^{1}H and ^{13}C NMR spectra of **S3**.



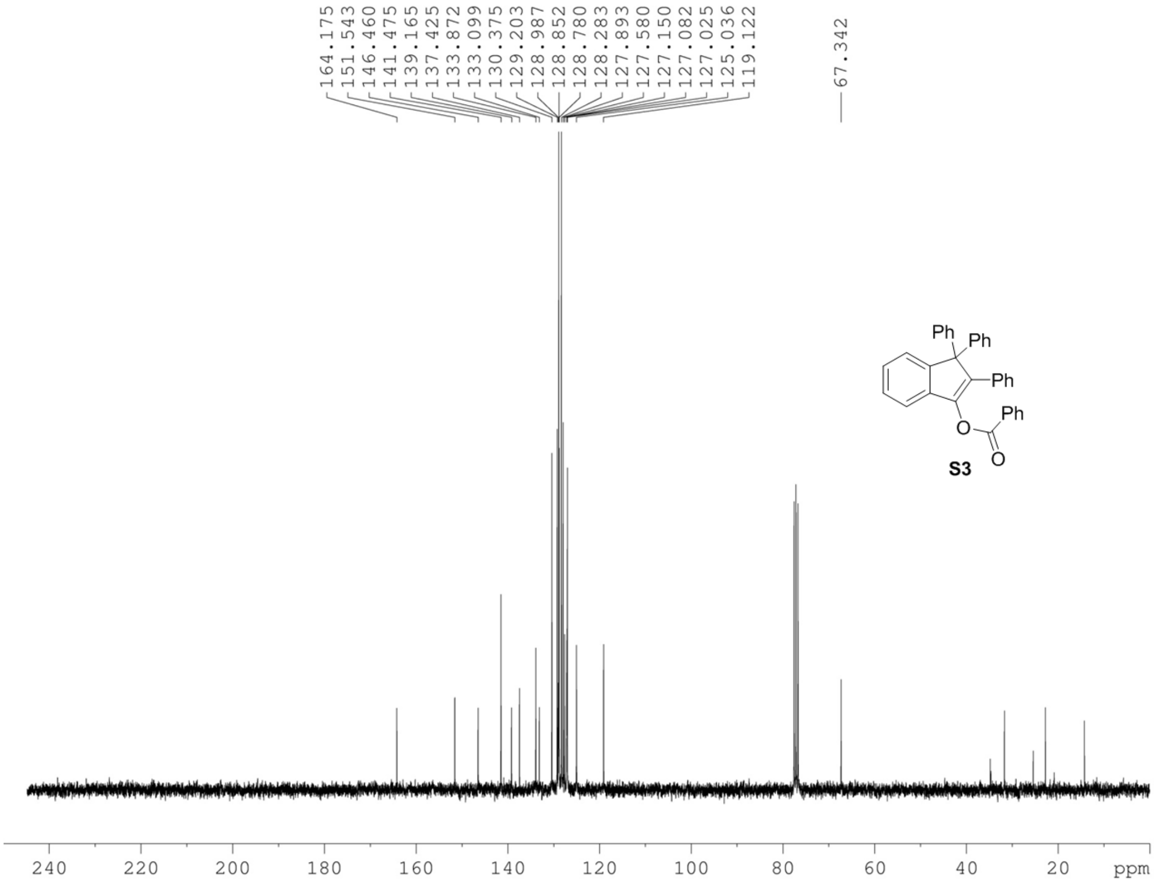
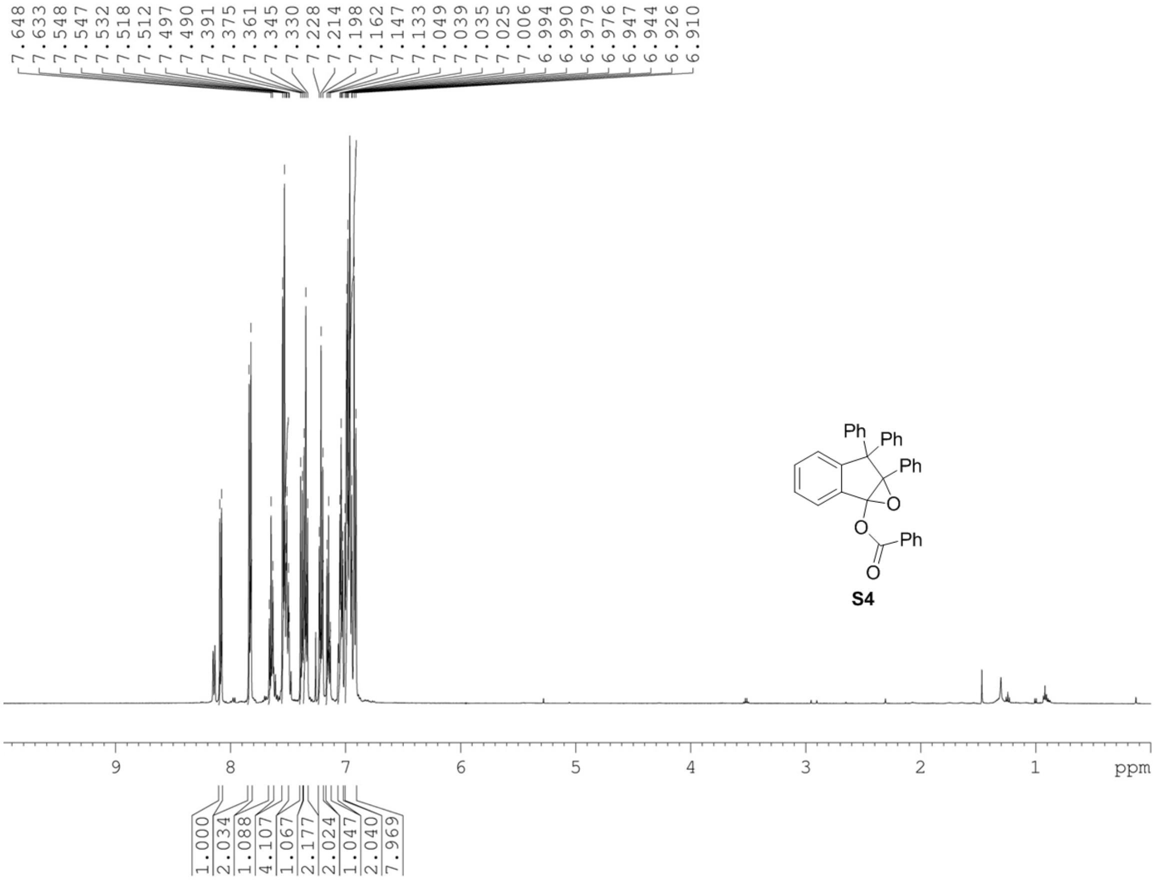


Figure S5 and S6. ^{1}H and ^{13}C NMR spectra of **S4**.



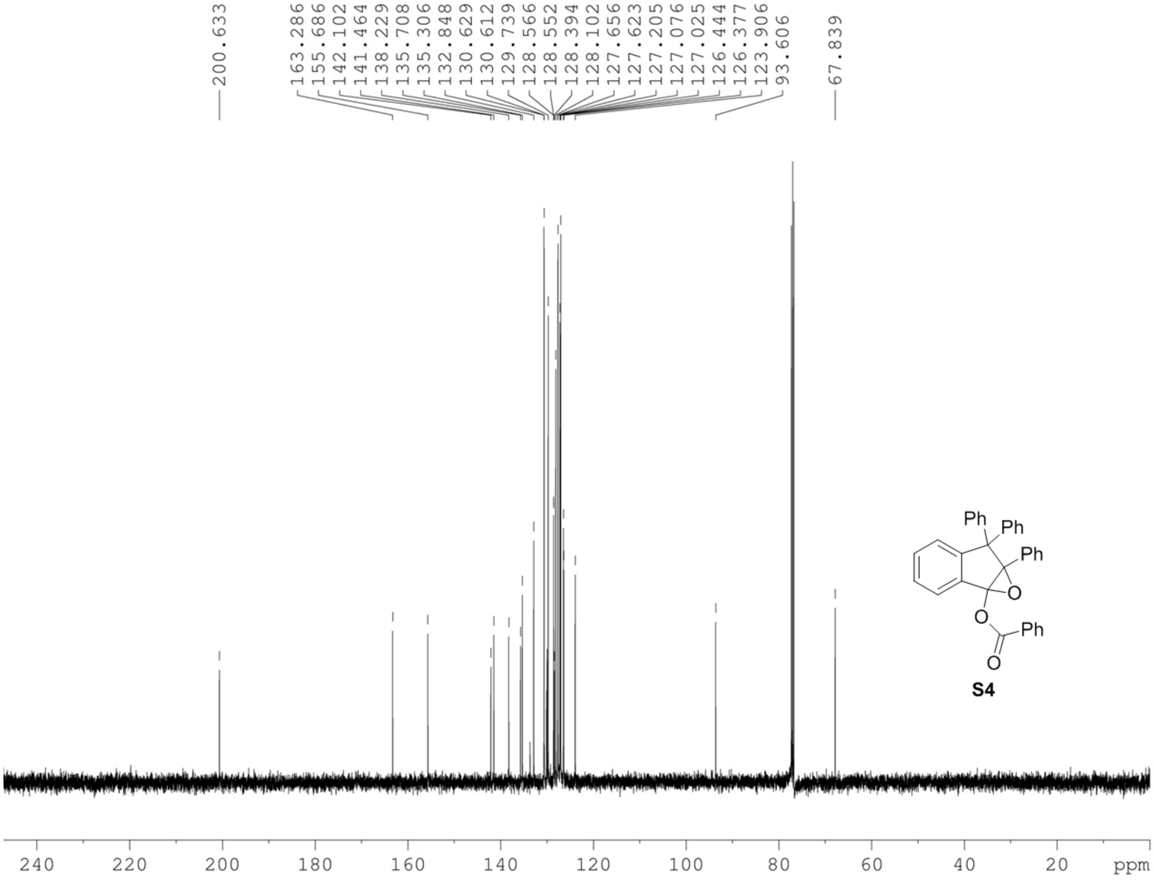


Figure S7 and S8. ^{1}H and ^{13}C NMR spectra of **1**.

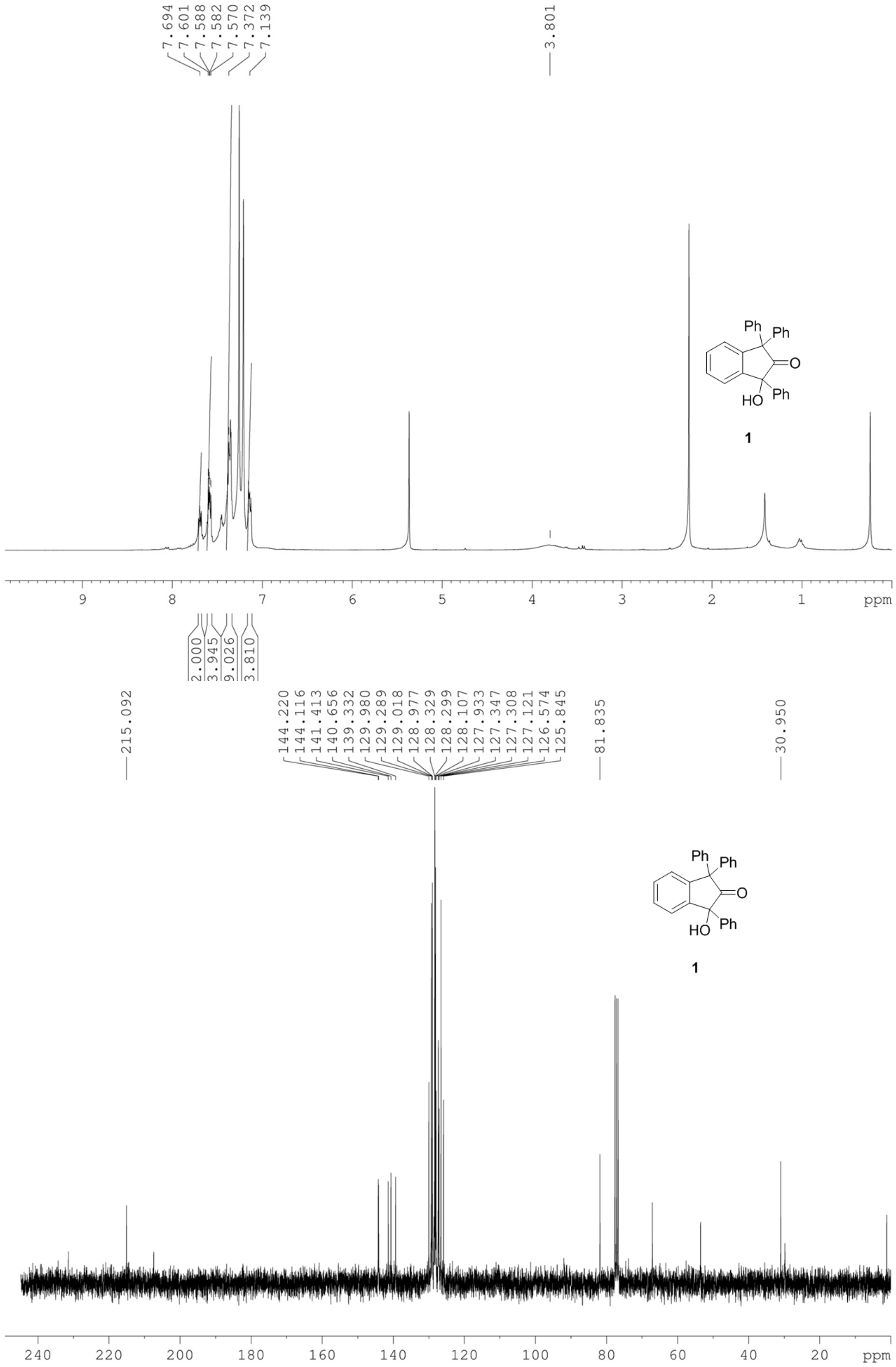
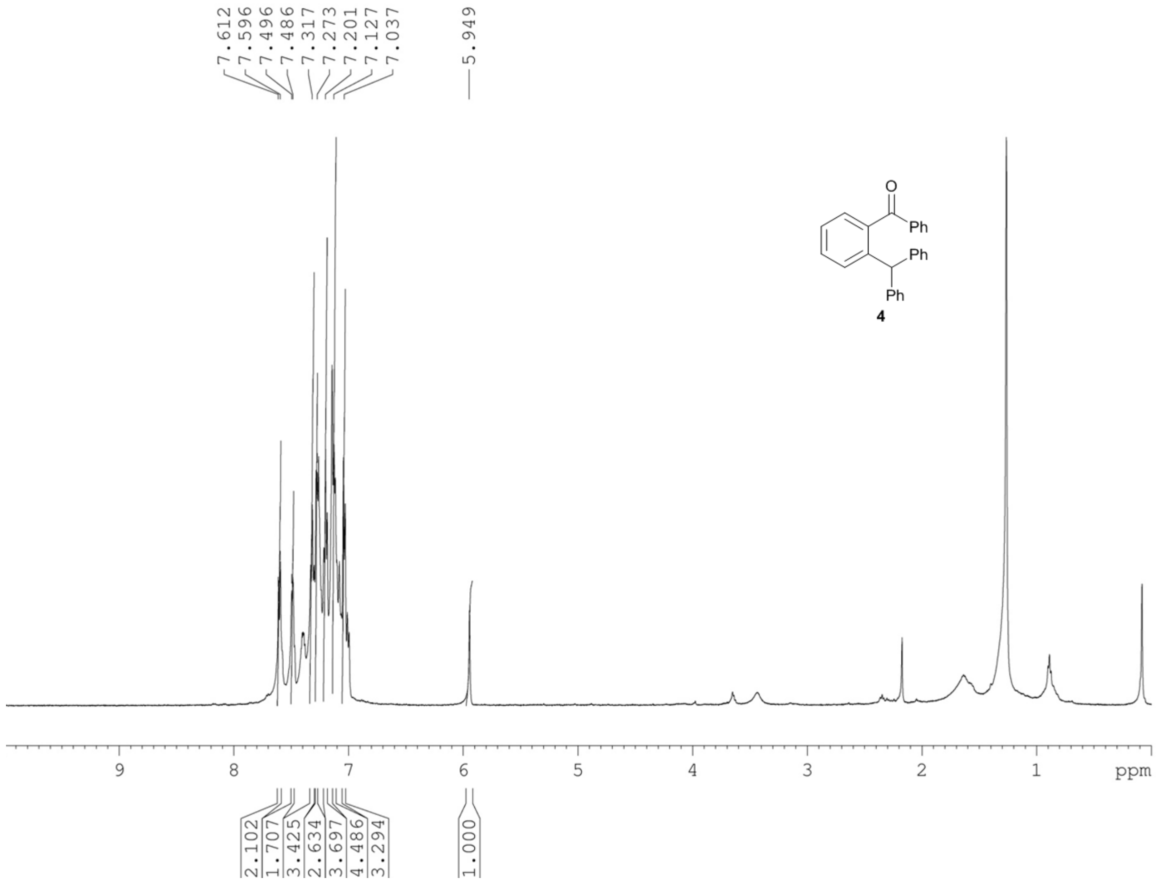
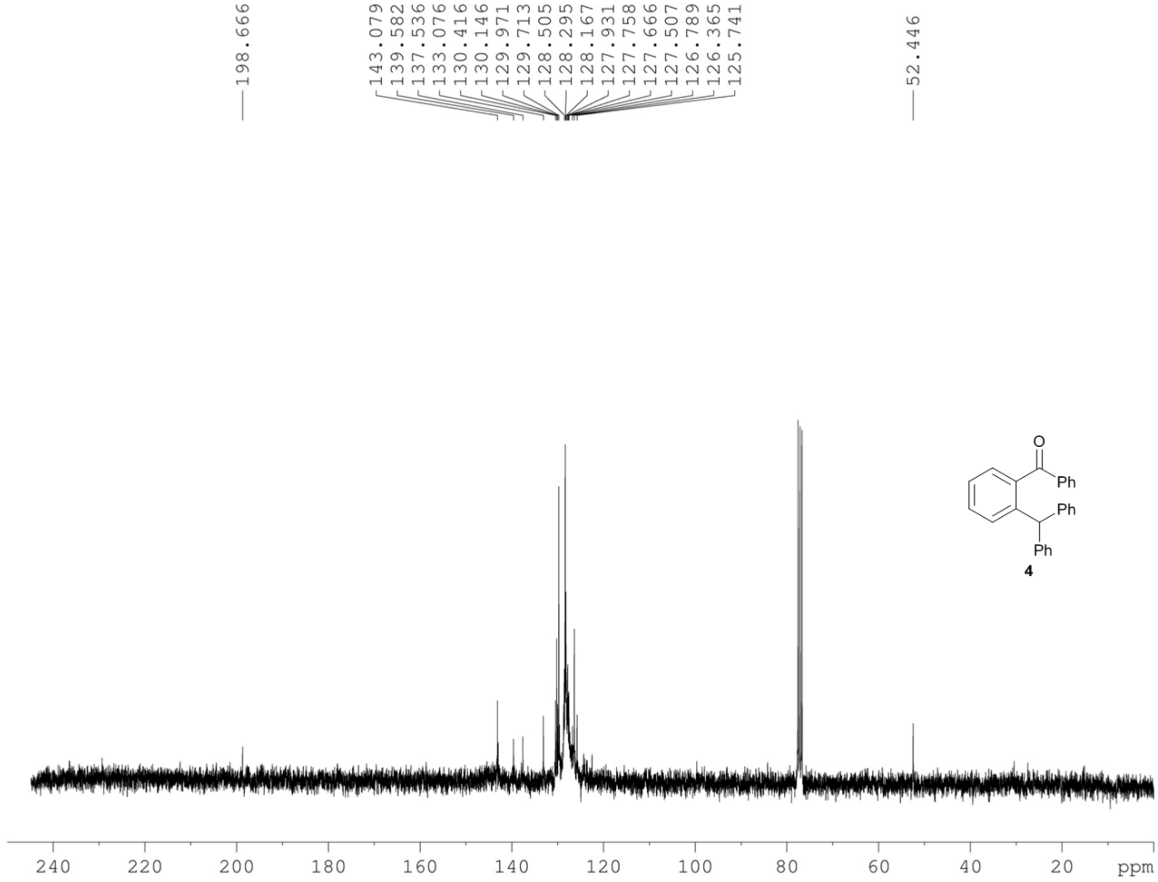


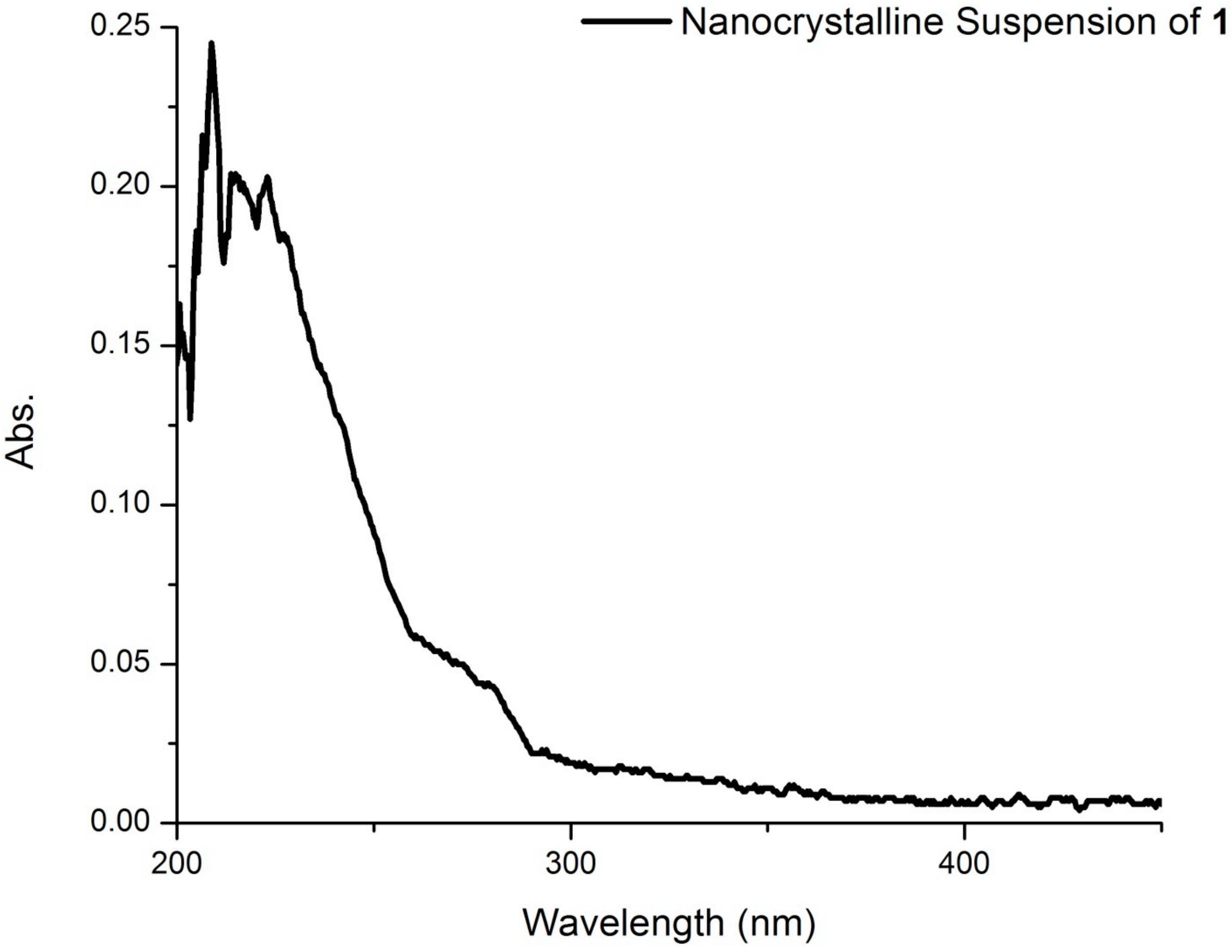
Figure S9 and S10. ^{1}H and ^{13}C NMR spectra of **4**.





Nanocrystalline Suspensions. Samples to be used for actinometry experiments were prepared by injecting a solution of **1** in acetone (ca. 10 μL of a ca. 1M) into 3 mL of vortexing water (millipore). The resulting suspension (ca. 1 * 10^{-3} M) was sonicated three times at room temperature for 4 min, allowing for 2 min rest between runs.

Figure S11. UV-Vis Spectra of **1** as a nanocrystalline suspension.



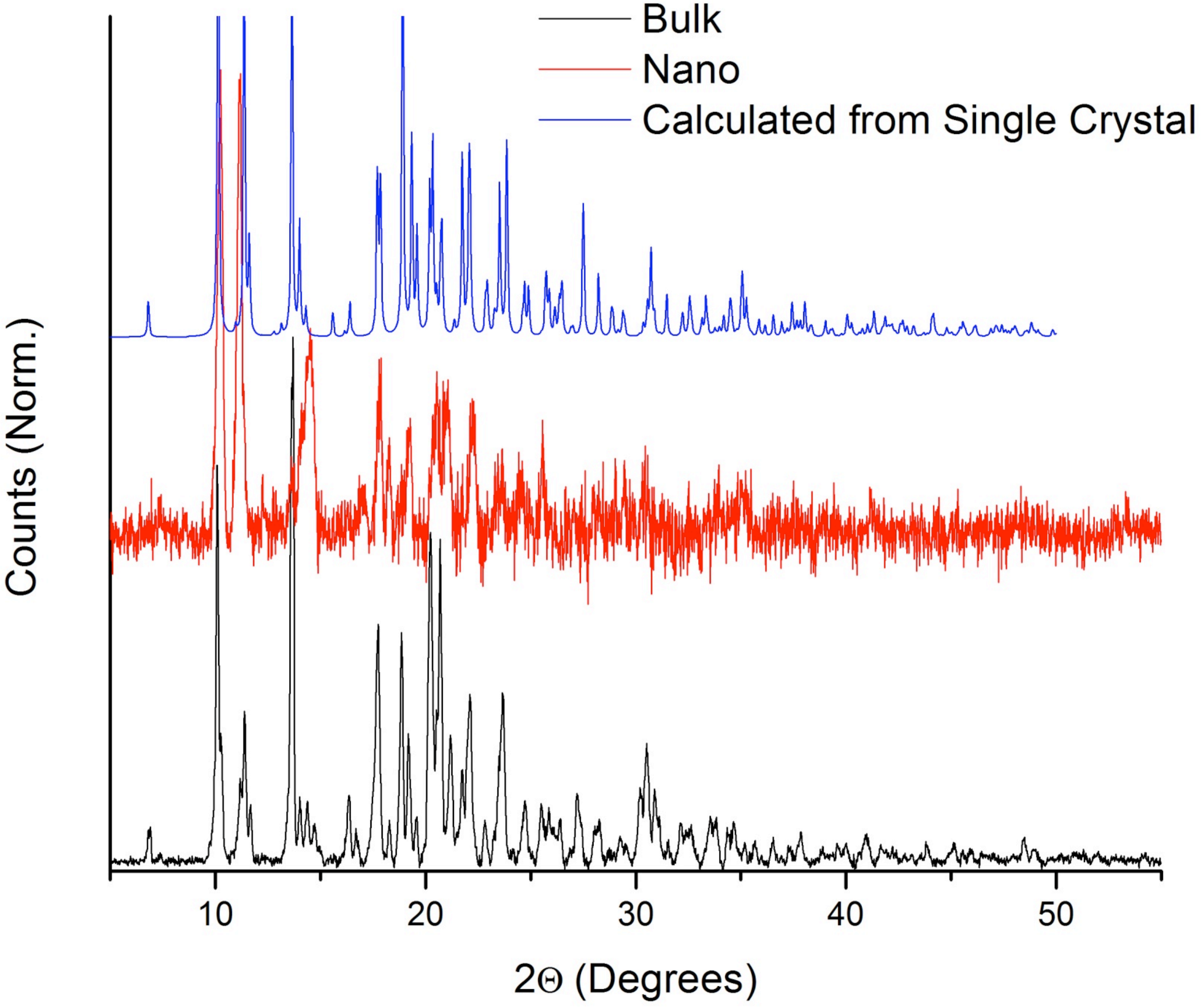
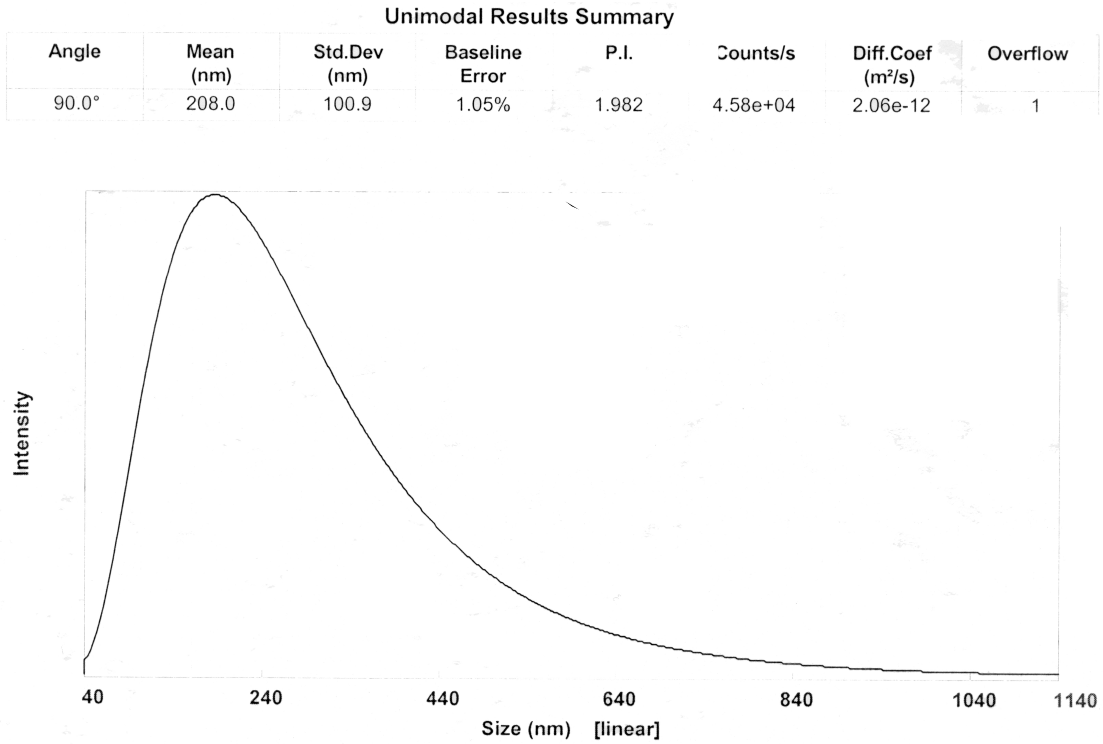


Figure S12: Powder XRD of **1** as a bulk powder (-), nanocrystalline powder (-), and calculated spectrum from single crystal X-ray (-).



Unimodal Results Summary

Angle	Mean (nm)	Std.Dev (nm)	Baseline Error	P.I.	Counts/s	Diff.Coef (m²/s)	Overflow
90.0°	208.0	100.9	1.05%	1.982	4.58e+04	2.06e-12	1

Figure S4. Dynamic light scattering results of **1** suspension showing an average size of 208 nm ± 101 nm.

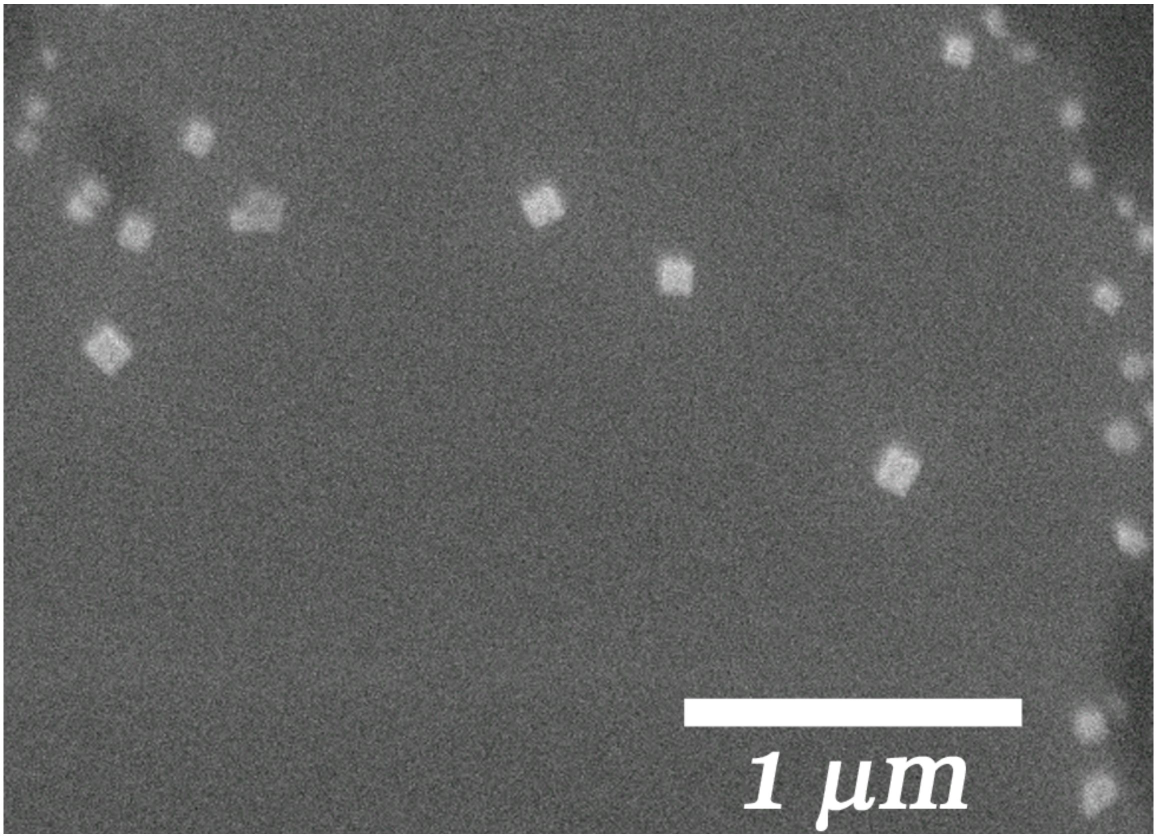


Figure S14. SEM micrograph showing nanocrystals of **1** prepared by the reprecipitation method and deposited onto a silicon substrate, showing particles that are facetted and ca. 100 – 300 nm in size.

Quantum Yield Determination in Benzene. Using both optically matched (3 experiments), and equimolar (3 experiments) solutions of **1** relative quantum yield determinations were performed with valerophenone (φ = 0.33) as an internal standard in a Rayonet photochemical reactor using 312 nm lamps (BLE-8T312).[4] These experimental yields were reproduced at least in triplicate. High conversion data were not used to avoid potential problems caused by the absorption of the products.

Quantum Yield Determination for Nanocrystalline Suspension. Relative quantum yield determinations were performed with dicumyl ketone (φ = 0.2) as an internal standard in a Rayonet photochemical reactor using either 312 nm lamps (BLE-8T312). Quantum yields were determined with equimolar, optically dense suspensions. Two independent suspensions of actinometer and substrate were independently synthesized. The samples were then combined immediately prior to irradiation in a 50 mL quartz Erlenmeyer flask and irradiated for 10 min. Every 2 minutes, an aliquot was removed (approximately one-twentieth of the suspension). The aliquots were extracted with deuterated chloroform (2 mL), washed with brine (2 × 2 mL), and dried over magnesium sulfate. ^{1}H NMR spectra were taken immediately to determine the extent of product formation. After ^{1}H NMR the same samples were then subjected to gas chromatography to determine the extent of dicumyl formation. These experimental yields were reproduced at least in triplicate. High conversion data were not used to avoid potential problems caused by the absorption of the products.

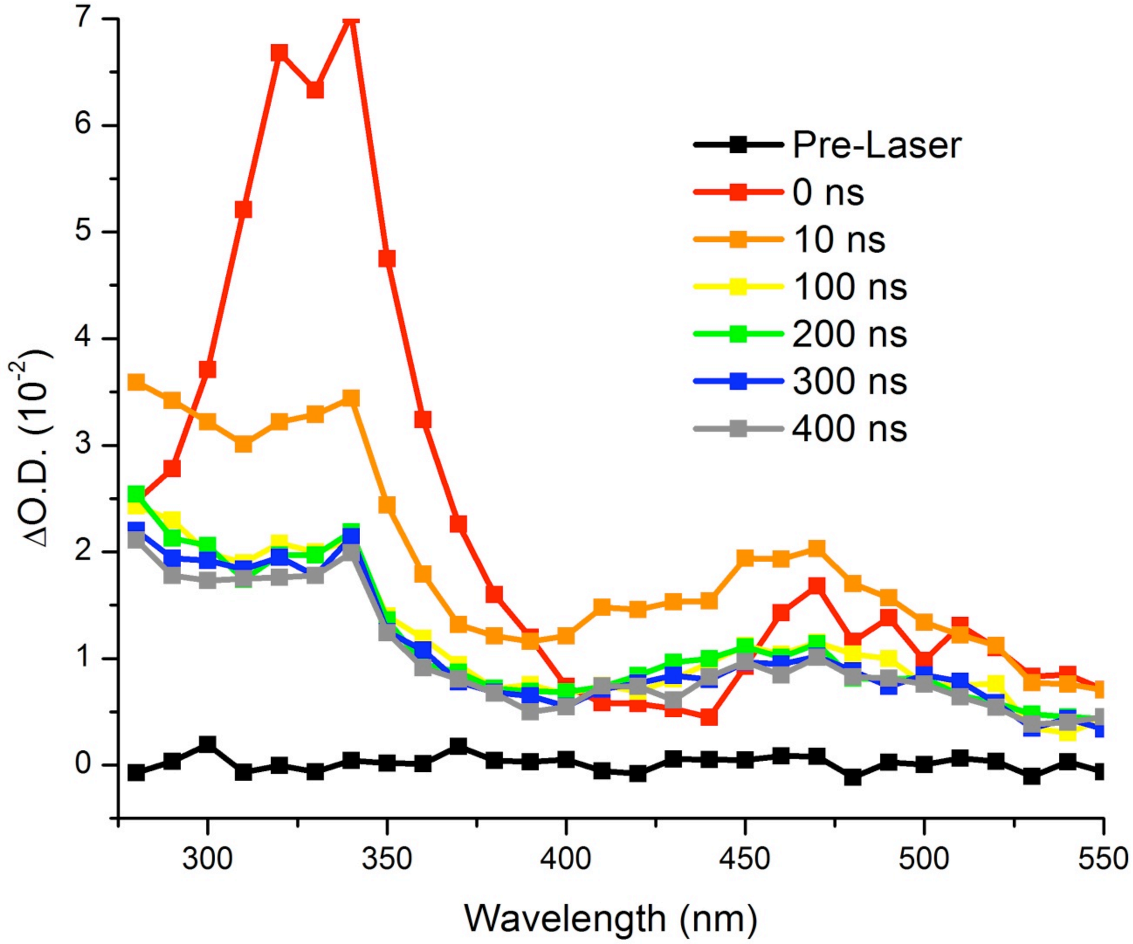


Figure S15: Transient absorption spectra of **1** dissolved in N_2 purged ACN, with λ_{max} = 330 nm.

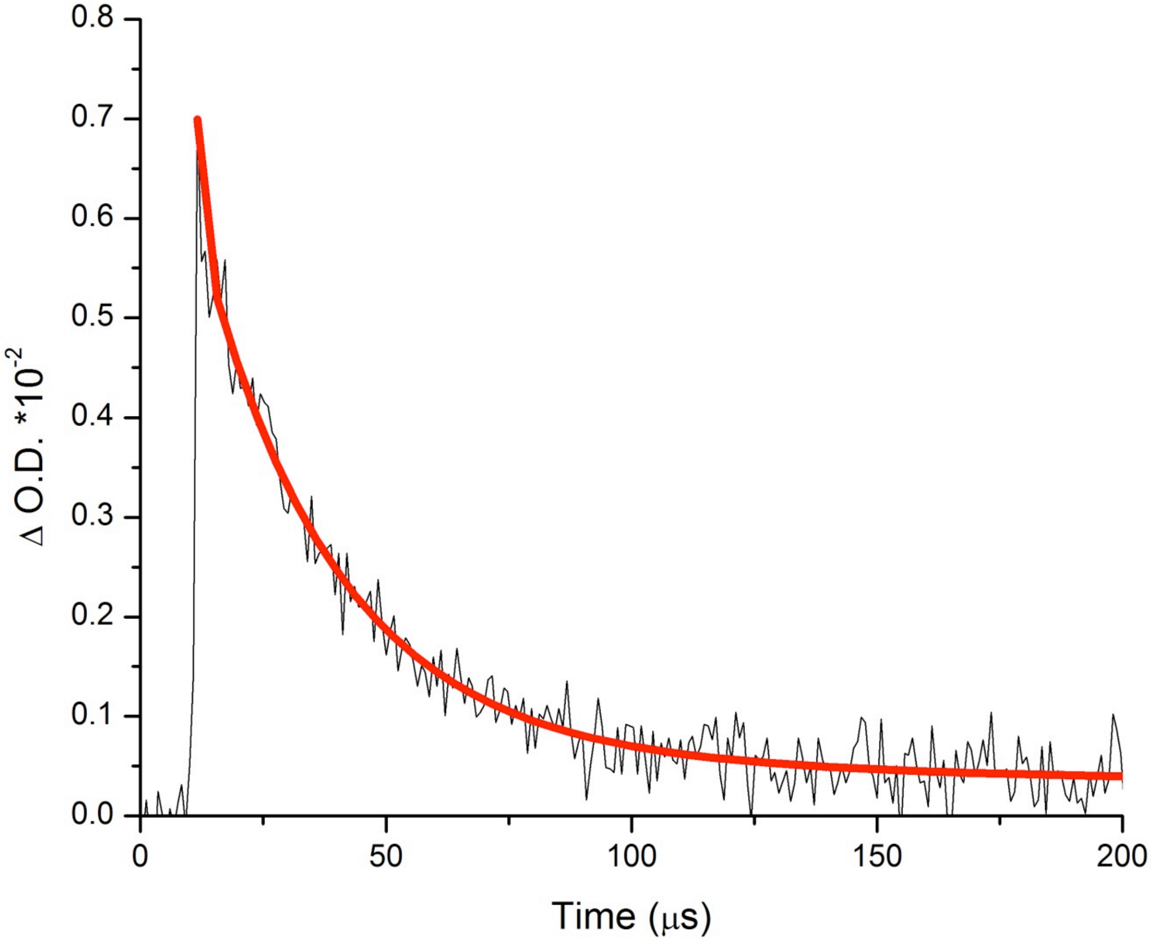


Figure S16: Decay of transient absorption spectra of **1** in N_2-purged ACN monitored at 330 nm could be fit with a biexponential with a lifetimes of τ= 300 ns and 30 μs assigned to *Z*-**2** and *E*-**2**, respectively.

fs Transient Absorption Spectroscopy of 1 in cyclohexane.

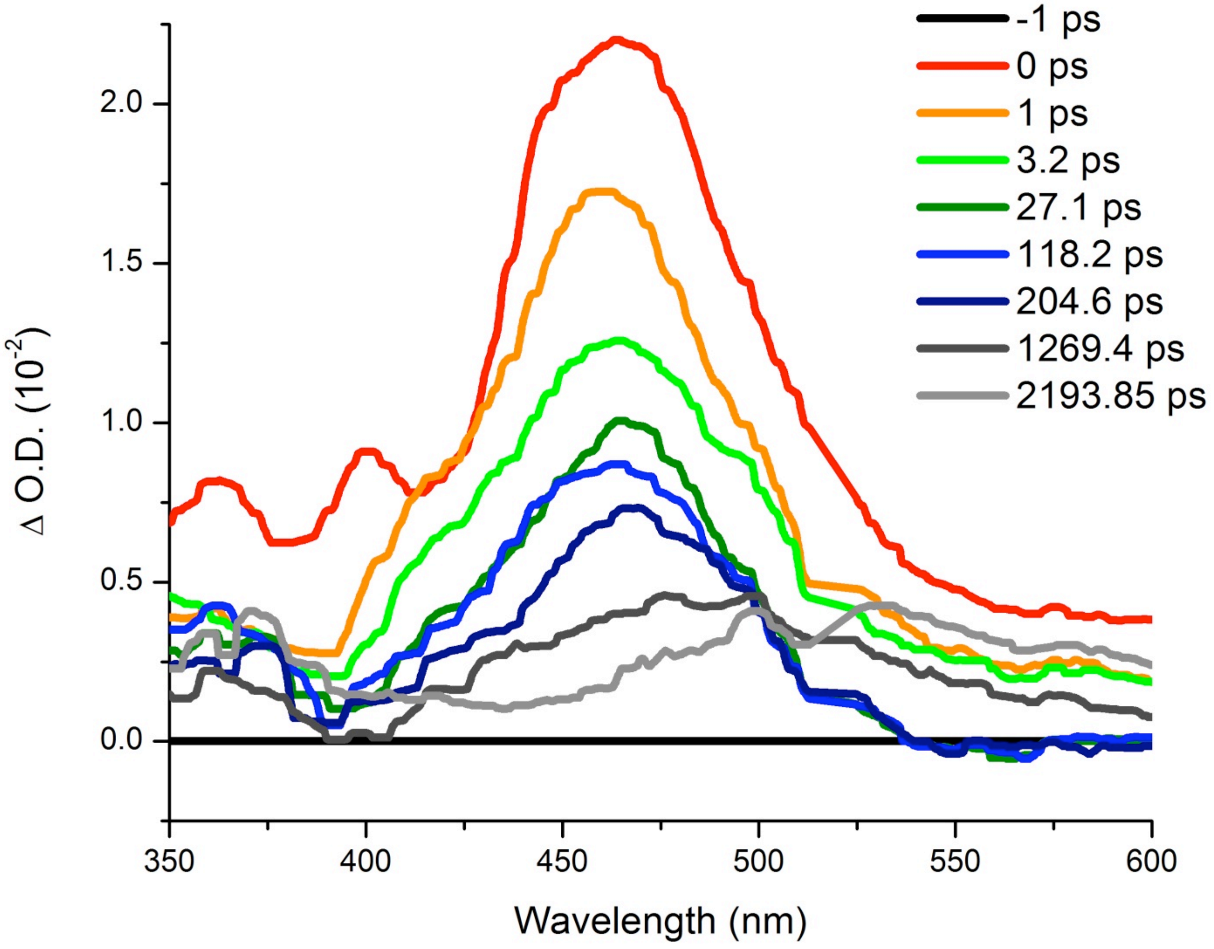


Figure S17: Transient absorption spectra of **1** dissolved in N_2 purged cyclohexane, $\lambda_{Ex.} = 255$ nm.

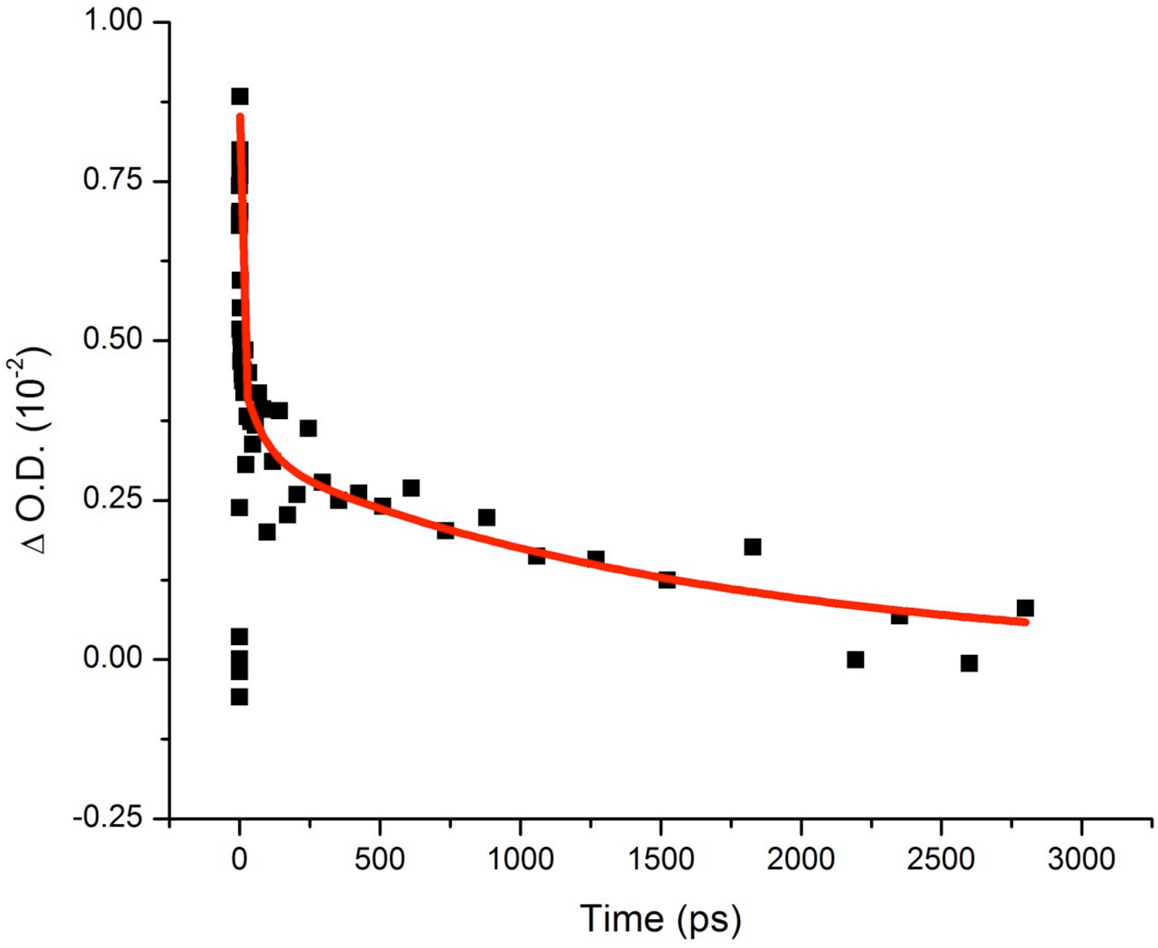


Figure S8: Decay of transient absorption spectra of **1** in Ar-purged cyclohexane monitored at 465 nm could be fit with a triexponential with a lifetimes of τ= 1.4 ps, 77 ps and 1.4 ns assigned to vibrational relaxation of $^{1}\mathbf{1}_{\mathbf{BR\text{-}2}}$, intersystem crossing to $^{3}\mathbf{1}_{\mathbf{BR\text{-}1}}$, and then decarbonylation to give $^{3}\mathbf{1}_{\mathbf{BR\text{-}2}}$.

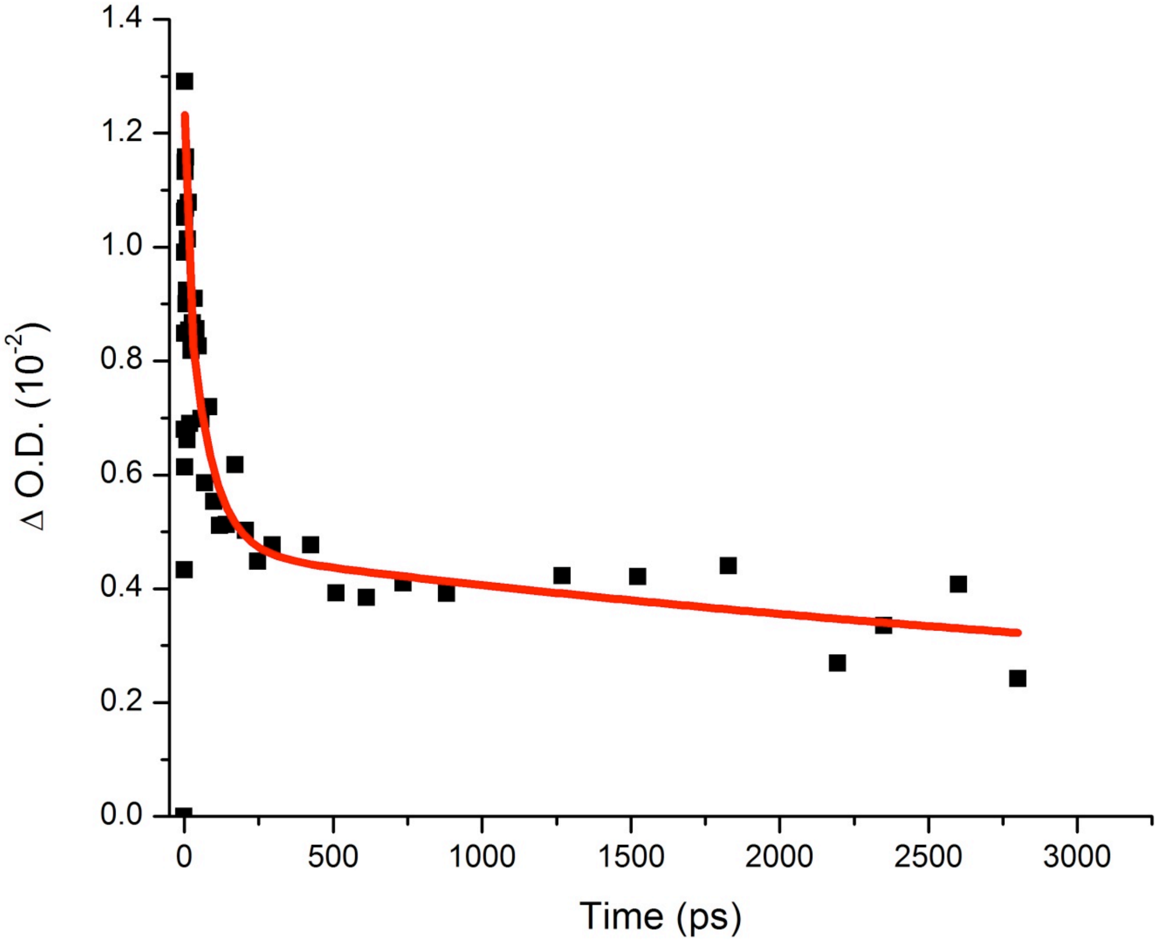


Figure S19: Decay of transient absorption spectra of **1** as a nanocrystalline suspension could be fit with a triexponential with a lifetimes of τ= 2 ps, 104 ps and 4.5 ns assigned to vibrational relaxation of $^{1}\mathbf{1}_{\mathbf{BR\text{-}2}}$, intersystem crossing to $^{3}\mathbf{1}_{\mathbf{BR\text{-}1}}$, and then decarbonylation to give $^{3}\mathbf{1}_{\mathbf{BR\text{-}2}}$.

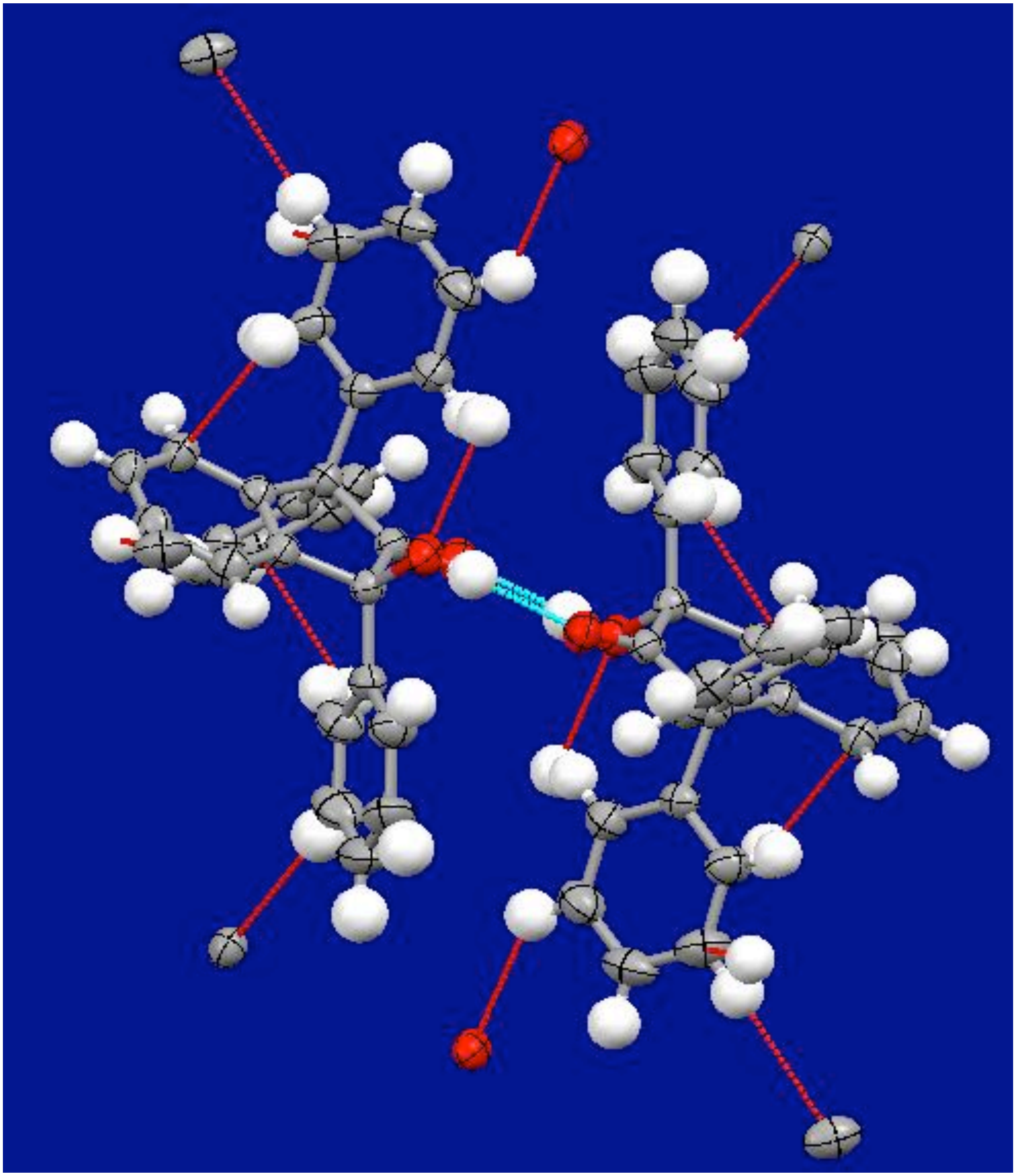


Figure S20. X-Ray Crystal structure of **1** showing dimerization and hydrogen bonding in the solid as well as intermolceular edge-to-face interactions with between phenyl rings.

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[1] Burdzinski, G.; Hackett, J. C.; Wang, J.; Gustafson, T. L.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 13402-13411.

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[4] Kuhn, J. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **2004**, *76*, 2105.