

Supporting Information

**Triplet State Quantum Chain Amplification in Crystalline Dewar
Benzenes by Intramolecular Sensitization**

Edris Rivera, Indrajit Paul, Javier Fajardo and Miguel Garcia-Garibay*

Department of Chemistry and Biochemistry, University of California, Los Angeles, 90095-1569,
United States

mgg@chem.ucla.edu

TABLE OF CONTENTS.

General Information.....	S2
Synthetic Procedures.....	S2-S5
¹ H, ¹³ C-NMR Spectra.....	S6-S9
IR Spectra.....	S10-S11
UV-vis.....	S12-S13
Dynamic Light Scattering (DLS).....	S14
pXRD.....	S15-S16
Transient Absorption Spectroscopy and Kinetics.....	S17-S19
Quantum Yields in Solution and in Suspension.....	S20-S26
Polycrystalline Powder Suspension vs Reprecipitated Suspension Analysis.....	S26

1. General Information: All Dewar benzene derivatives were synthesized under an inert argon atmosphere unless otherwise specified. Nuclear magnetic resonance (NMR) spectra for ^1H and ^{13}C were obtained using 500 MHz Bruker NMR spectrometer. All chemical shifts are reported in ppm using natural abundance isotopes of reference solvents. Infrared (IR) spectra was collected using the Perkin-Elmer 1000 Series FT-IR spectrometer.

2. Synthetic Procedures

Samples of tetramethyl-Dewar benzene dicarboxylate derivatives with methoxy (**DB-CO₂Me**), one (**DB-CO₂Me/CO₂H**) or two free carboxylic acids (**DB-CO₂H**), and the analogous 4-hydroxy benzophenone (**DB-CO₂BPh**) esters were prepared as indicated in Figure S1. Full and partial hydrolysis of the **DB-CO₂Me** yielded diacid **DB-CO₂H** and acid/ester **DB-CO₂Me / DB-CO₂H** as white powders. The desired sensitizer-linked Dewar benzene **DB-CO₂BPh** was obtained by EDC-mediated coupling of 4-hydroxybenzophenone with dicarboxylic acid **DB-CO₂H**. A sample of 4-acetoxy benzophenone was also prepared as a model compound to analyze the properties of the triplet sensitizer.

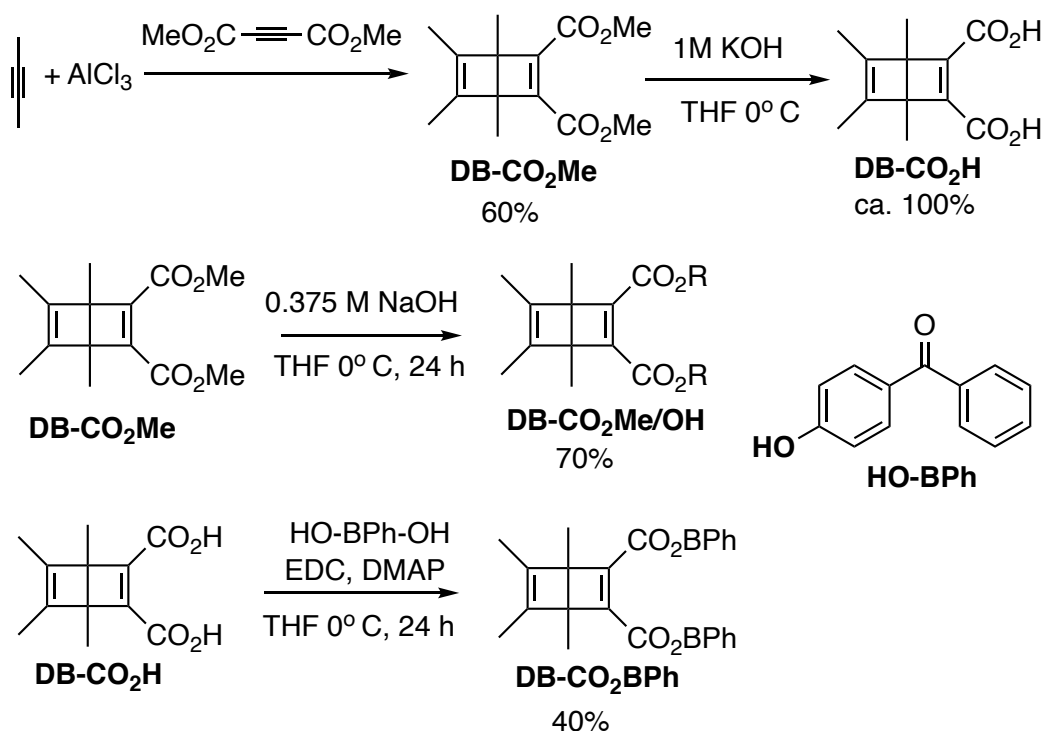
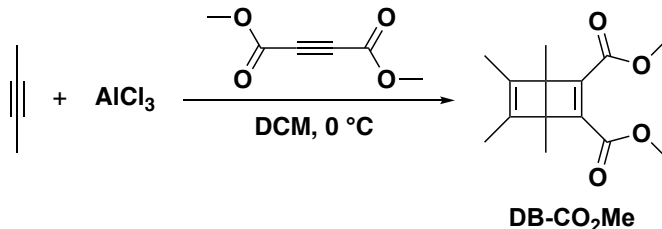


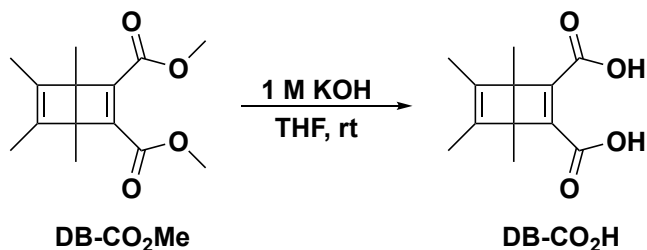
Figure S1. Synthesis of Dewar benzene derivatives

2.1 Synthesis and Characterization of DB-CO₂Me¹



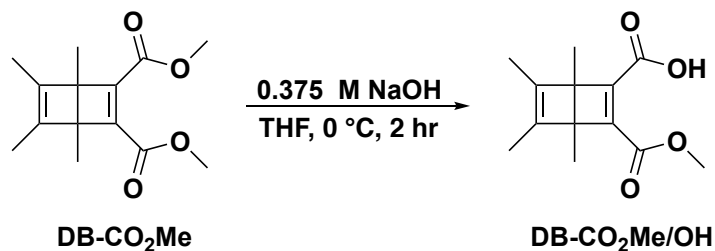
A 25 mL 3-neck round bottom flask was flame dried and charged with a stir bar and a AlCl₃ (0.090 g, 0.647 mmol, 1 equiv). This was followed by the addition of 1 mL anhydrous dichloromethane (DCM). 2-Butyne was then added dropwise (0.070 g, 101 μ L, 1.29 mmol, 2 equiv) and allowed to stir for 10 minutes at 0 °C. This was followed by the dropwise addition of dimethyl acetylene dicarboxylate (60 μ L, 0.480 mmol, 0.74 equiv). This was allowed to stir for 30 minutes at room temperature. Dimethylsulfoxide (DMSO) was then added dropwise (650 μ L), followed by the addition of anhydrous DCM (1 mL). The reaction was then washed with deionized water, brine, and then extracted in ether. The organic layer was dried over sodium sulfate, filtered, then concentrated under pressure to yield a yellow oil. The crude oil was purified using vacuum filtration between 70-75 °C and for 3 hours. The collected fraction was washed with hexanes and further purification involved precipitating the product out of hexanes at -78 °C as a white solid. The impurities within the layer of hexanes were carefully decanted, leaving a white powdery solid at -78 °C. The product **DB-CO₂Me** (72 mg, 0.288 mmol, 60%) was isolated as an oil at room temperature. ¹H NMR (500 MHz, CDCl₃): δ = 3.78 (s, 6H), 1.63 (s, 6H), 1.28 (s, 6H).

2.2 Synthesis and Characterization of DB-CO₂H²



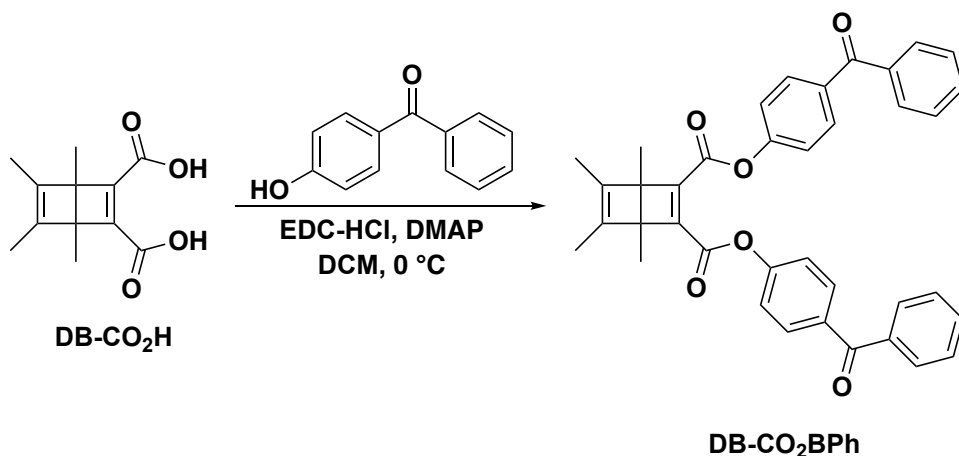
DB-CO₂Me (200 mg, 0.799 mmol, 1 equiv.) was dissolved in 20 mL THF and 20 mL 1 M KOH within a 500 mL round bottom flask. The reaction was allowed to stir overnight. Product was washed with ether and extracted in deionized water. The water layer was acidified with 1 M HCl, then extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, then concentrated under pressure to yield **DB-CO₂H** (177 mg, 0.799 mmol, 100%) a yellow solid. No further purification was required. ¹H NMR (500 MHz, CDCl₃): δ = 2.17 (s, 18H), 1.67-1.63 (m, 18H), 1.29 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ = 161.25, 152.32, 143.38, 81.21, 55.84, 41.49, 36.21, 30.86, 11.05, 9.94. m.p.: 165 °C

2.3 Synthesis and Characterization of DB-CO₂Me/OH²



DB-CO₂Me (200 mg, 0.799 mmol, 1 equiv.) was dissolved in 20 mL THF and 20 mL 0.375 M NaOH within a 500 mL round bottom flask. The reaction was allowed to stir for 2 hours cold at 0 °C. Product was washed with ether and extracted in deionized water. The water layer was acidified with 1 M HCl, then extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, then concentrated under pressure to yield a pale yellow solid. The crude product was purified using column chromatography. Utilizing a gradient solvent system composed of hexanes: ethyl acetate (50:1, 20:1, 15:1). Purified product **DB-CO₂Me** (132 mg, 0.559 mmol, 70%) was isolated as white powder. ¹H NMR (500 MHz, CDCl₃): δ = 2.17 (s, 18H), 1.67-1.63 (m, 18H), 1.29 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ = 161.25, 152.32, 143.38, 81.21, 55.84, 41.49, 36.21, 30.86, 11.05, 9.94. m.p.: 103 °C

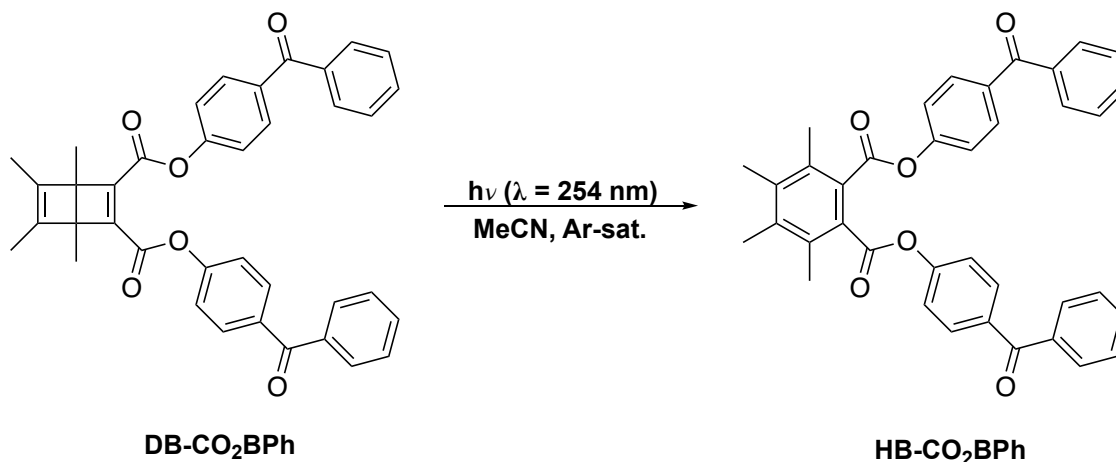
2.4 Synthesis and Characterization of DB-CO₂BPh



A 25 mL 3-neck flask round bottom flask was flame dried and charged with compound diacid **DB-CO₂H** (0.050 g, 0.225 mmol, 1 equiv.), 4-hydroxybenzophenone (0.054g, 0.270 mmol, 1.2 equiv), a catalytic amount of 4-(dimethylamino)pyridine (0.003 g, 0.023 mmol, 0.1 equiv) and a stir bar. This was followed by the addition of 2 mL anhydrous DCM and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) stirring at 0 °C. The reaction was allowed to stir cold for at least 2 hours. The reaction was subjected to column chromatography without workup utilizing a gradient solvent system composed of hexanes: ethyl acetate (100:0, 50:1, 25:1, 20:1). The purified product **DB-CO₂BPh** (52 mg, 0.04 mmol, 40%) was isolated as a

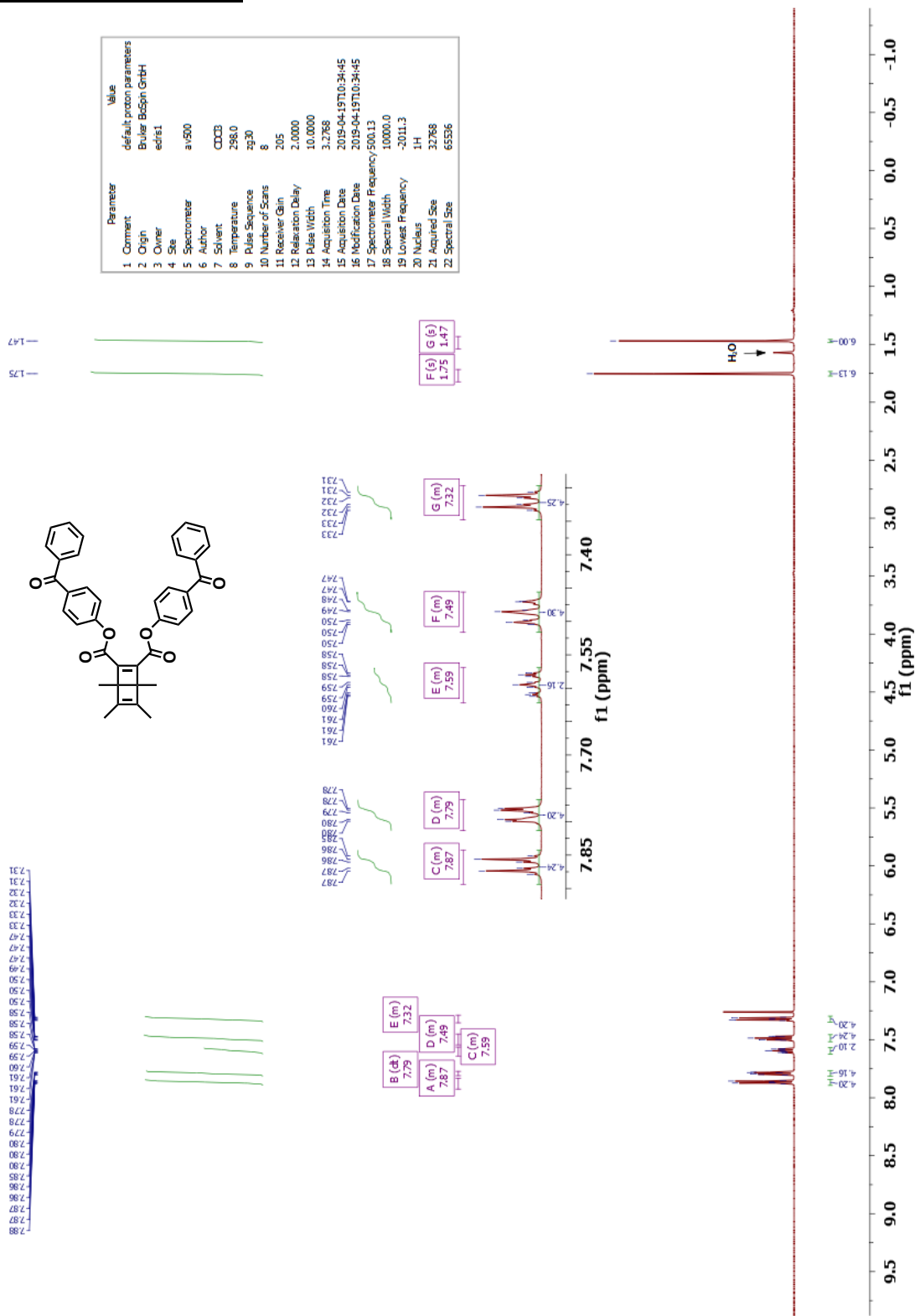
white. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.93 - 7.83$ (m, 4H), 7.79 (dt, $J = 8.4, 1.5$ Hz, 4H), 7.64 – 7.56 (m, 2H), 7.54 – 7.45 (m, 4H), 7.35 – 7.29 (m, 4H), 1.75 (s, 6H), 1.47 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 195.50, 159.59, 153.45, 152.74, 143.44, 137.42, 135.32, 132.55, 131.74, 129.98, 128.37, 121.34, 57.06, 11.24, 10.04$. HRMS (DART) calcd for $\text{C}_{38}\text{H}_{30}\text{O}_6$ $[\text{M}+\text{H}]^+$ 582.20131, found 582.20113. $R_f = 0.4$ in hexanes: ethyl acetate (5:1). m.p.: 109 °C

2.5 Synthesis and Characterization of HB-CO₂BPh



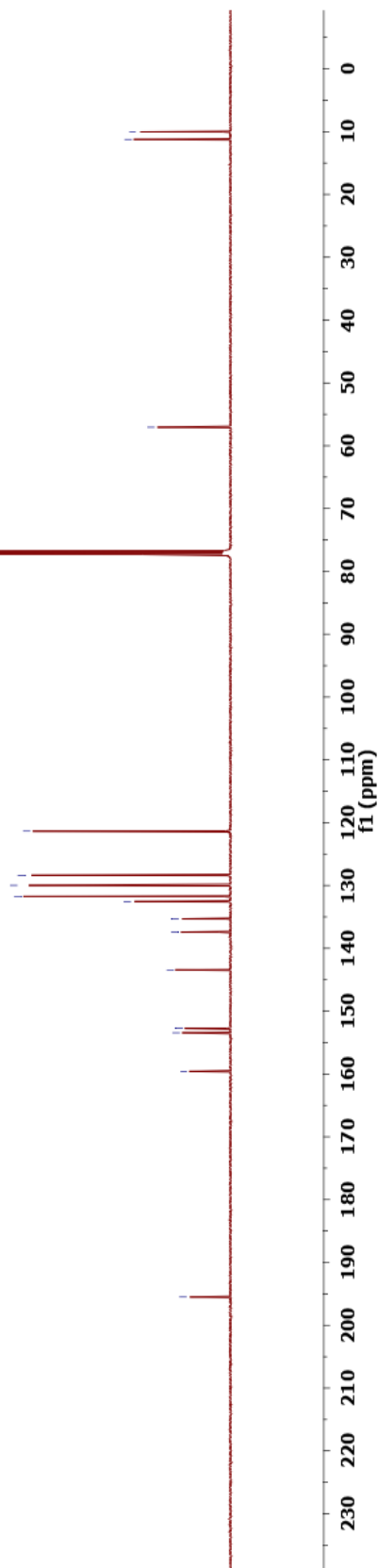
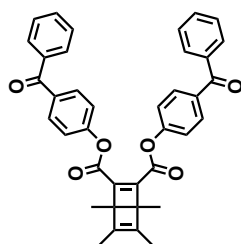
A 25 mg sample of **DB-CO₂BPh** (0.010 mg, 0.017 mmol) was irradiated at 254 nm light in Argon-saturated MeCN for 1.5 hours. The product was purified by recrystallization to give **HB-OBPh** in quantitative yield. ^1H NMR (500 MHz, CDCl_3): $\delta = 7.86 - 7.81$ (m, 4H), 7.78 (dt, $J = 8.4, 1.5$ Hz, 4H), 7.60 – 7.56 (m, 2H), 7.50 – 7.45 (m, 4H), 7.30 – 7.26 (m, 4H), 2.50 (s, 6H), 2.36 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3) $\delta = 195.50, 167.12, 153.84, 139.39, 137.39, 135.38, 132.69, 132.56, 131.75, 129.97, 129.01, 128.38, 121.49, 17.88, 16.89$. $R_f = 0.4$ in hexanes: ethyl acetate (5:1). HRMS (DART) calcd for $\text{C}_{38}\text{H}_{30}\text{O}_6$ $[\text{M}+\text{H}]^+$ 582.20413, found 582.20424. m.p.: 142 °C

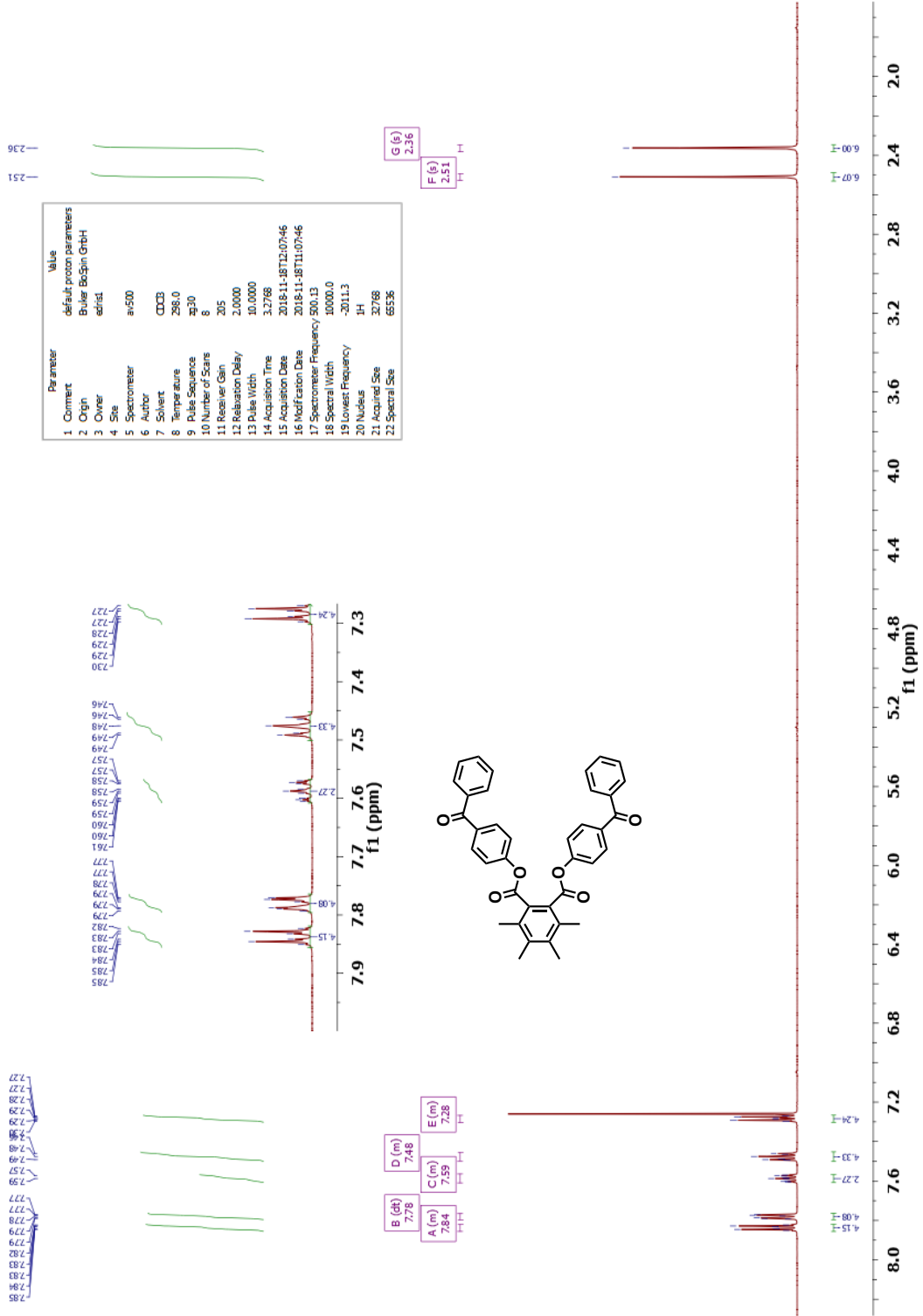
¹H, ¹³C NMR Spectra



195.50
 152.74
 152.45
 152.74
 143.44
 137.42
 135.32
 132.55
 131.74
 129.98
 128.37
 121.34
 57.06
 10.94
 11.24

Parameter	Value
1. Comment	default carbon parameters
2. Origin	Bruker BioSpin GmbH
3. Owner	edris1
4. Site	
5. Spectrometer	av500
6. Author	
7. Solvent	CDCl3
8. Temperature	298.0
9. Pulse Sequence	zgpg30
10. Number of Scans	72
11. Receiver Gain	205
12. Relaxation Delay	2.0000
13. Pulse Width	10.5000
14. Acquisition Time	1.0486
15. Acquisition Date	2019-04-19T10:42:52
16. Modification Date	2019-04-19T10:42:52
17. Spectrometer Frequency	125.76
18. Spectral Width	31150.0
19. Lowest Frequency	-1183.1
20. Nucleus	13C
21. Acquired Size	32768
22. Spectral Size	65536





1699
1788

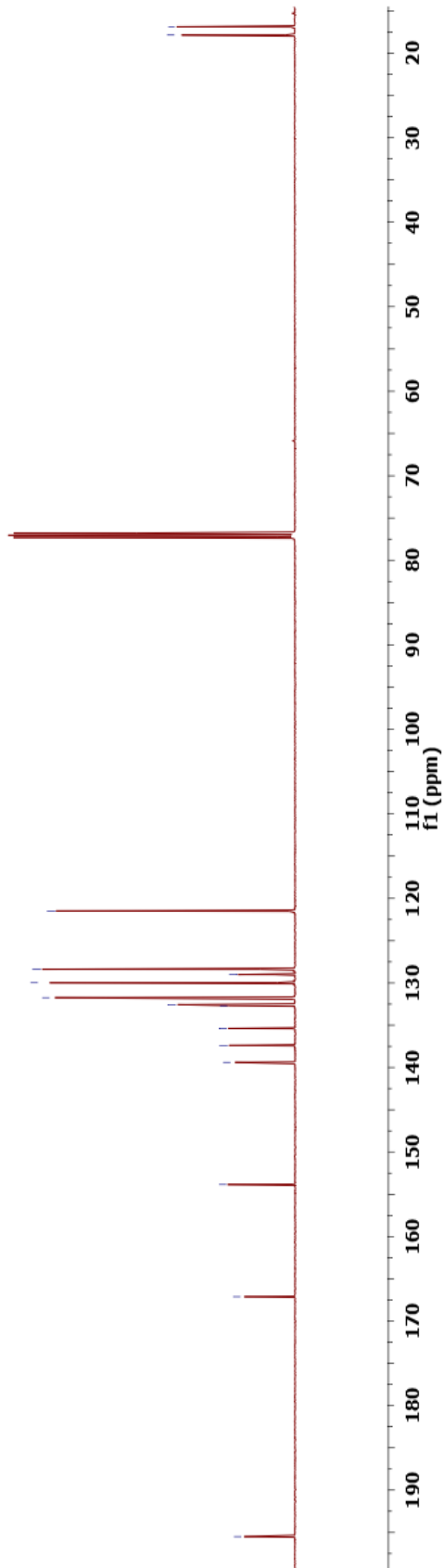
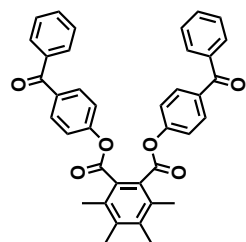
Parameter	Value
1 Comment	default carbon parameters
2 Origin	Bruker Biospin GmbH
3 Owner	edris1
4 Site	
5 Spectrometer	a-500
6 Author	
7 Solvent	CDCl3
8 Temperature	298.0
9 Pulse Sequence	zgpg30
10 Number of Scans	72
11 Receiver Gain	205
12 Relaxation Delay	2.0000
13 Pulse Width	10.5000
14 Acquisition Time	1.0486
15 Acquisition Date	2019-05-01T09:55:44
16 Modification Date	2019-05-01T09:55:44
17 Spectrometer Frequency	125.76
18 Spectral Width	31250.0
19 Lowest Frequency	-1163.1
20 Nucleus	¹³ C
21 Acquired Size	32768
22 Spectral Size	65536

121.49
129.38
129.01
129.97
131.75
132.56
132.69
133.38
132.39
139.39

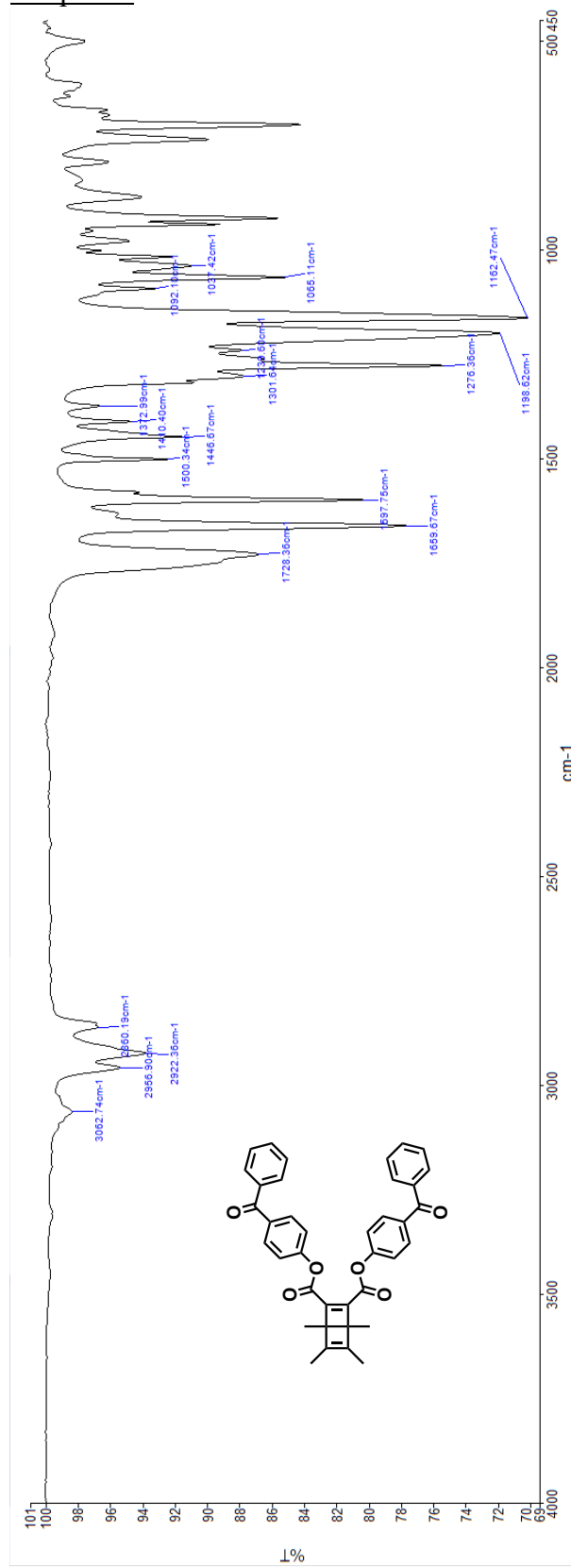
153.84

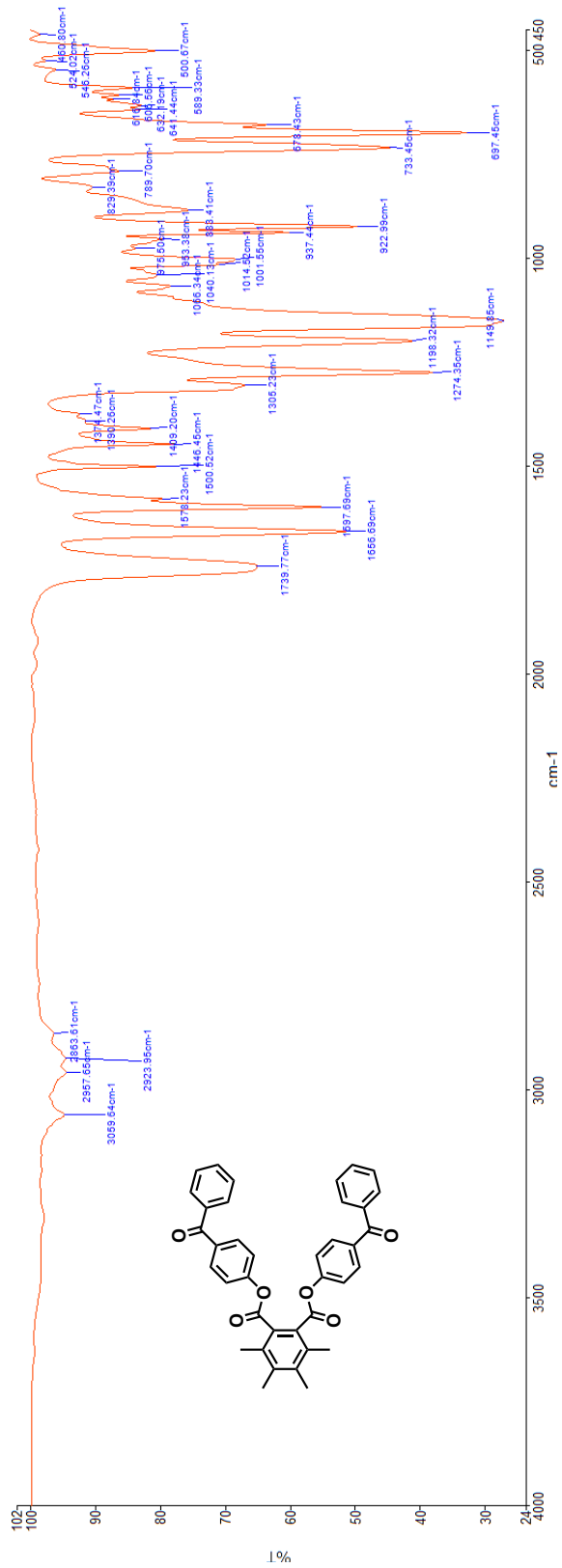
167.12

195.50

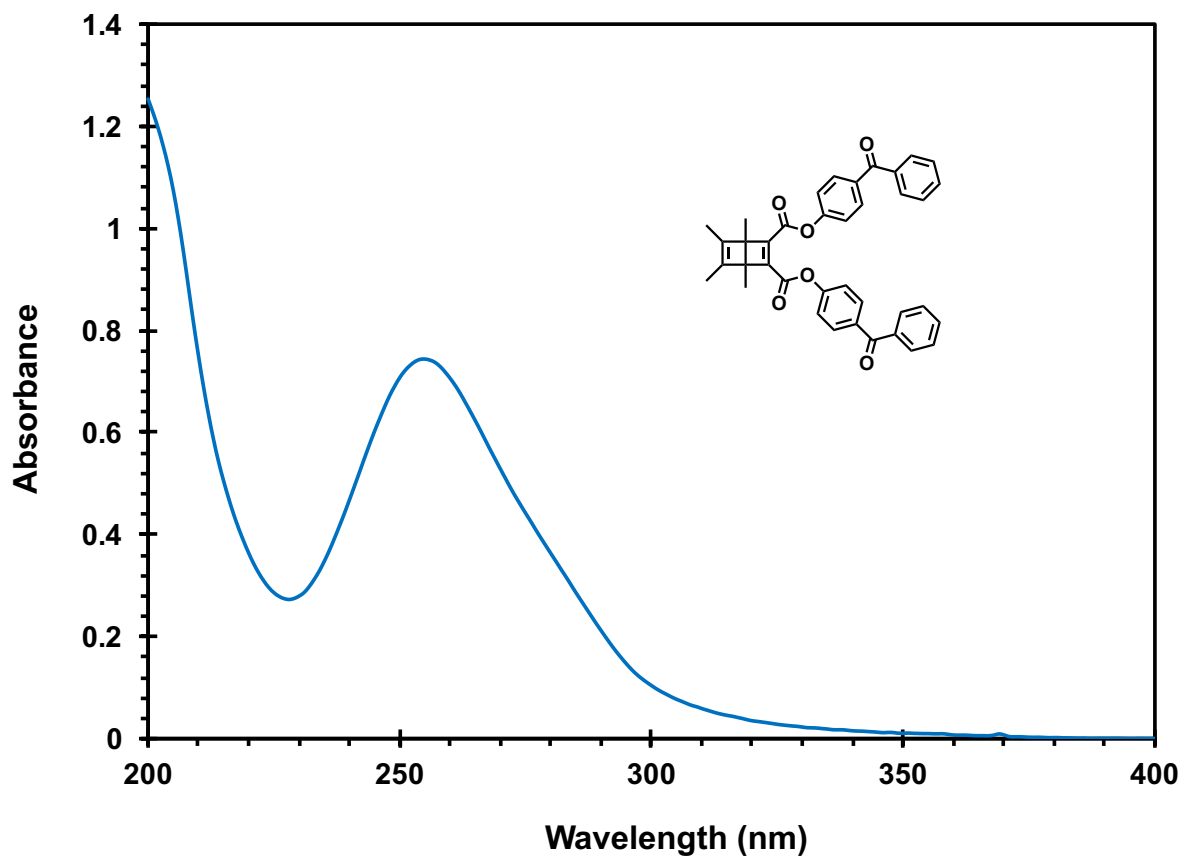


IR spectra

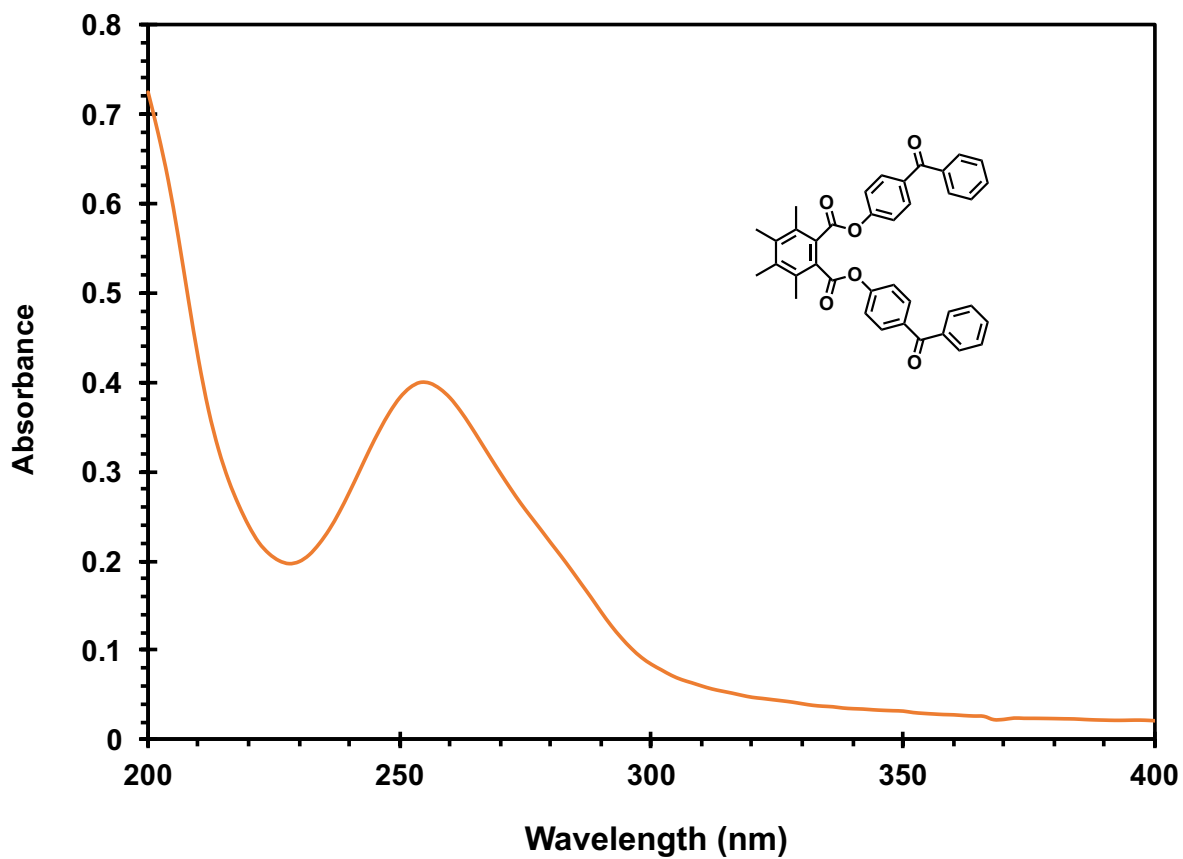




UV-vis spectra



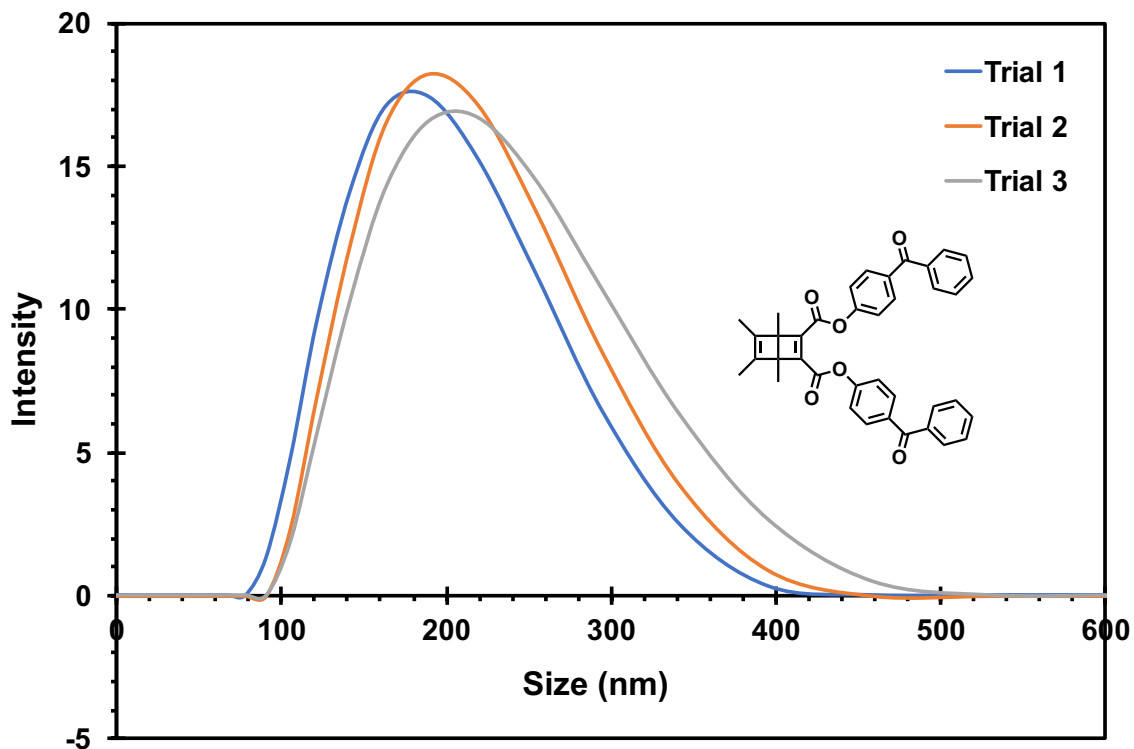
UV-vis spectra of DB-CO₂BPh (1.65×10^{-5} M) in MeCN

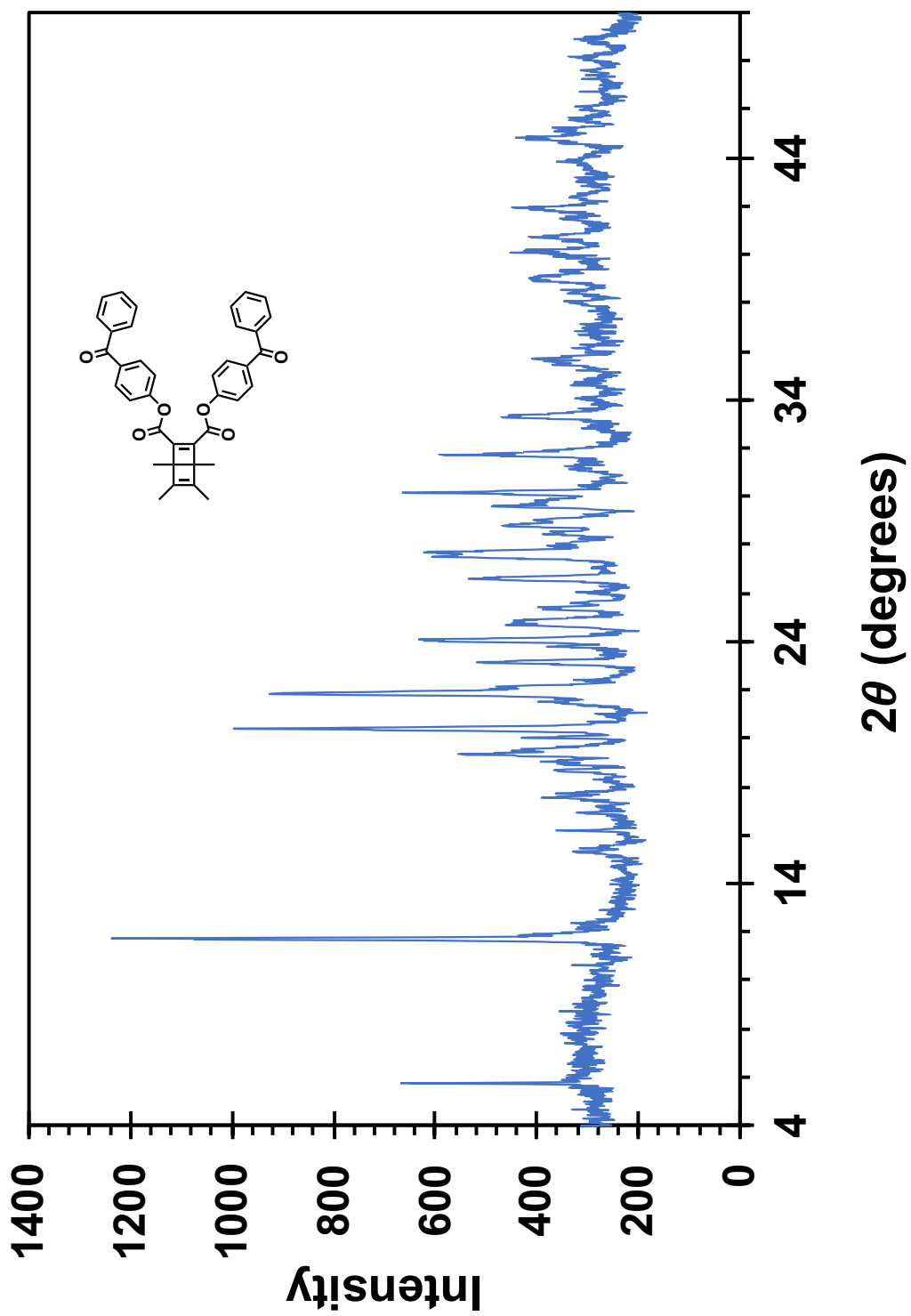


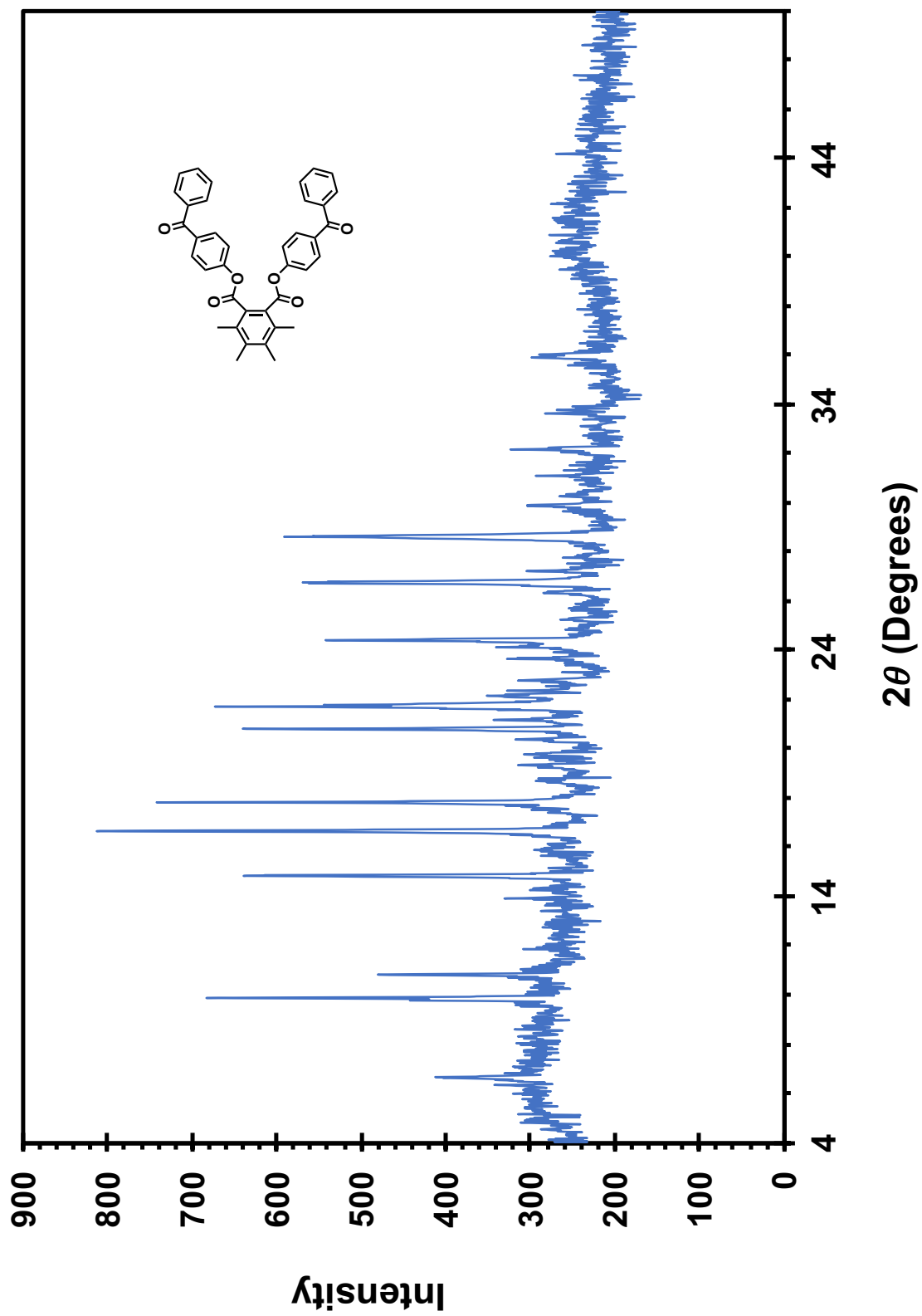
UV-vis spectra of **HB-CO₂BPh** (1.30×10^{-5} M) in MeCN

Dynamic Light Scattering (DLS)

Record	Z-Ave (d.nm)	Pdl	Mean (d.nm)	Area (Percent)	Scattering Angle (°)	Size Peak (d.nm)	Size Analysis Version
Trial 1	174.2	0.068	189.9	100	173	58.12	1.2
Trial 2	187.9	0.066	203.7	100	173	60.24	1.2
Trial 3	198.7	0.072	217.9	100	173	69.4	1.2





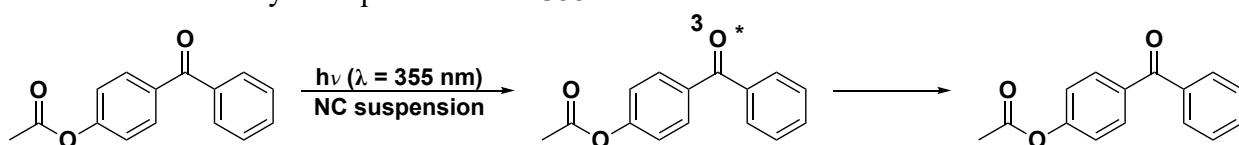


Transient Absorption Spectroscopy

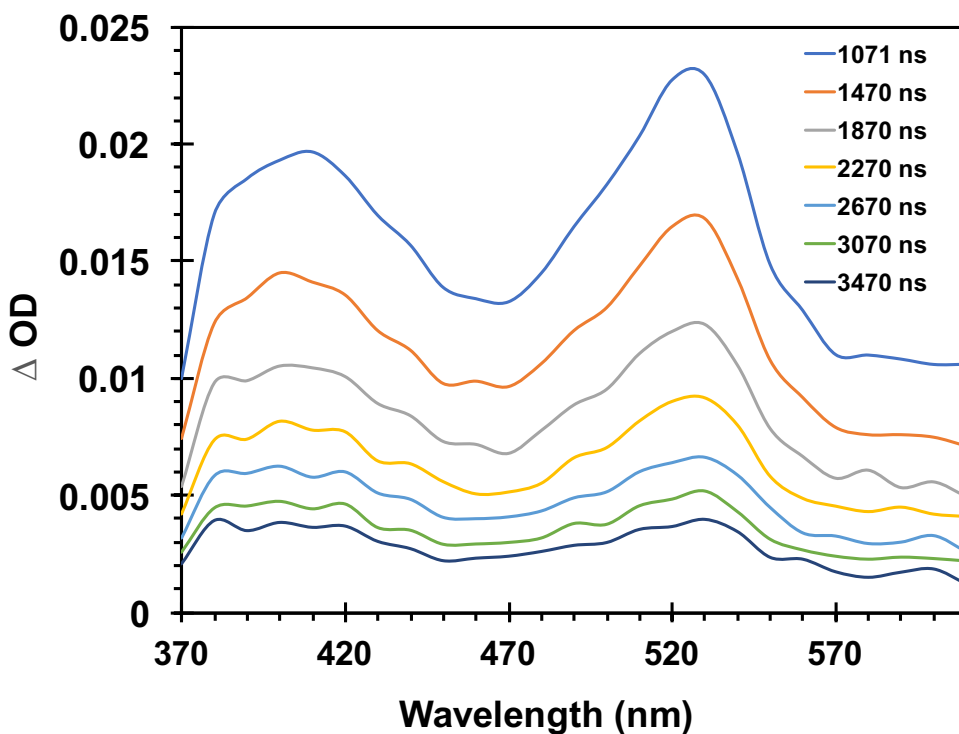
4-Acetoxybenzophenone NC suspension

Preparation: A 33 mg/mL stock solution was utilized to prepare a stock aqueous crystalline suspension of 4-acetoxybenzophenone based on the reprecipitation method. A 100 μL aliquot of the stock suspension was then resuspended in 12 mL of 0.1932 mM CTAB solution and introduced to the sample cell of the laser through a flow cell.

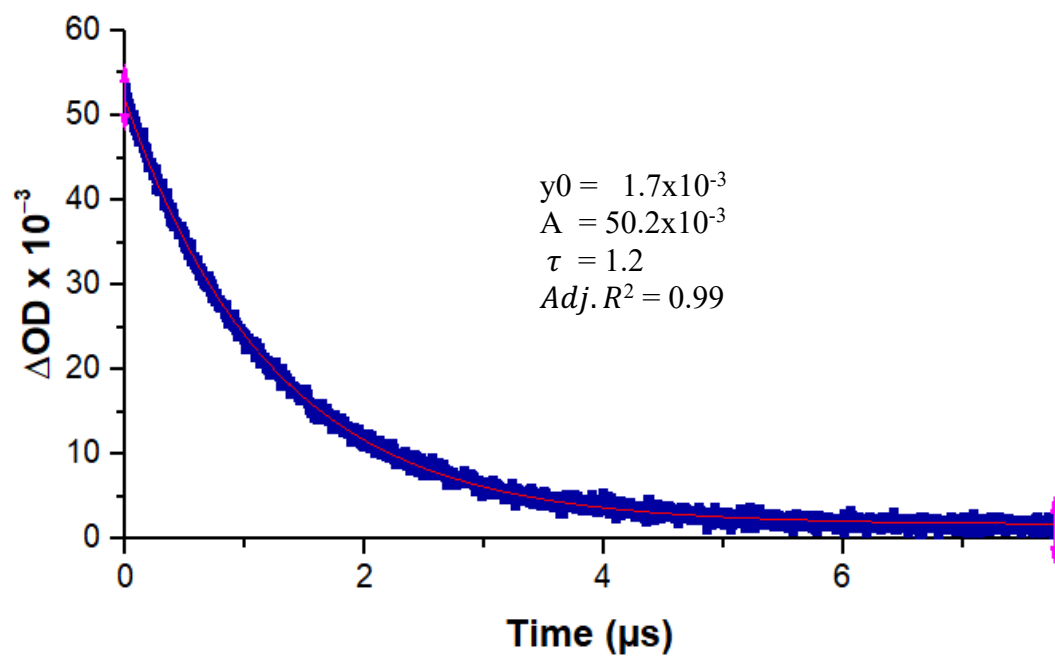
Reaction of 4-acetoxybenzophenone with 355 nm laser excitation



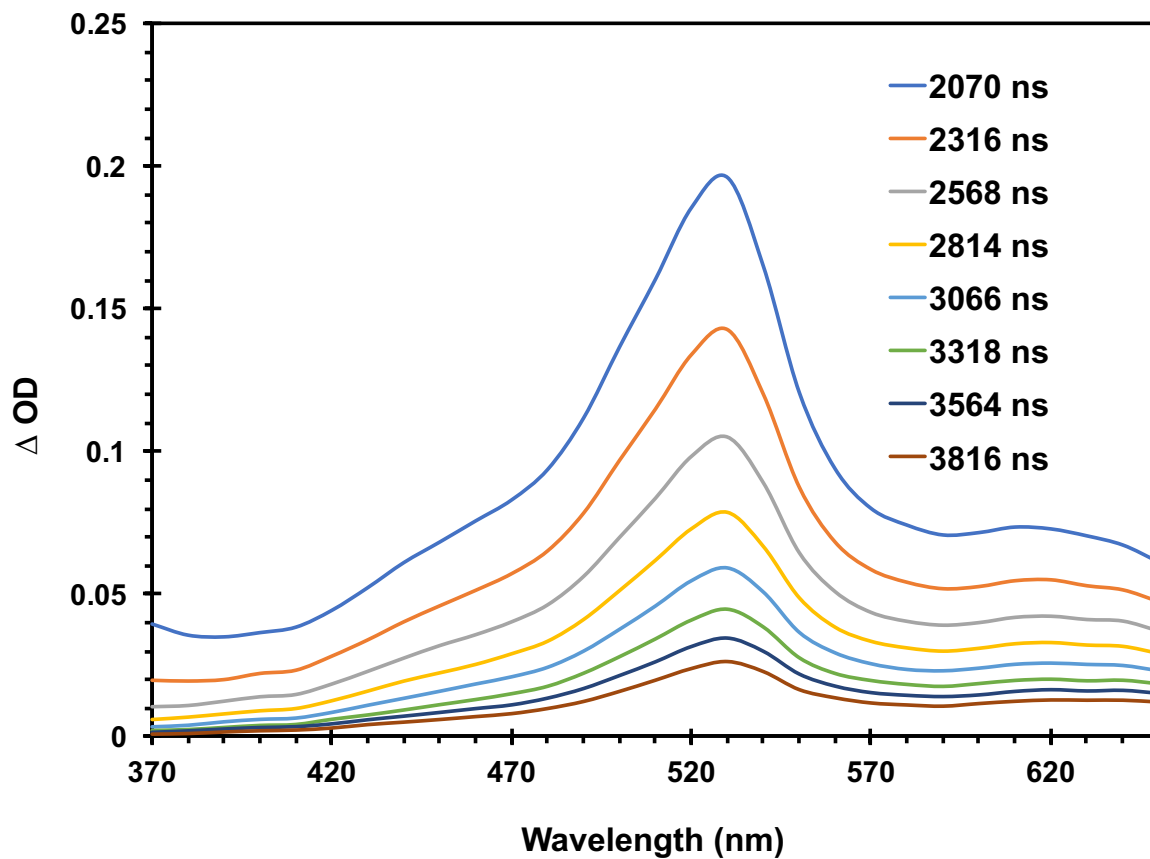
Pump-probe Absorption (370-610 nm)



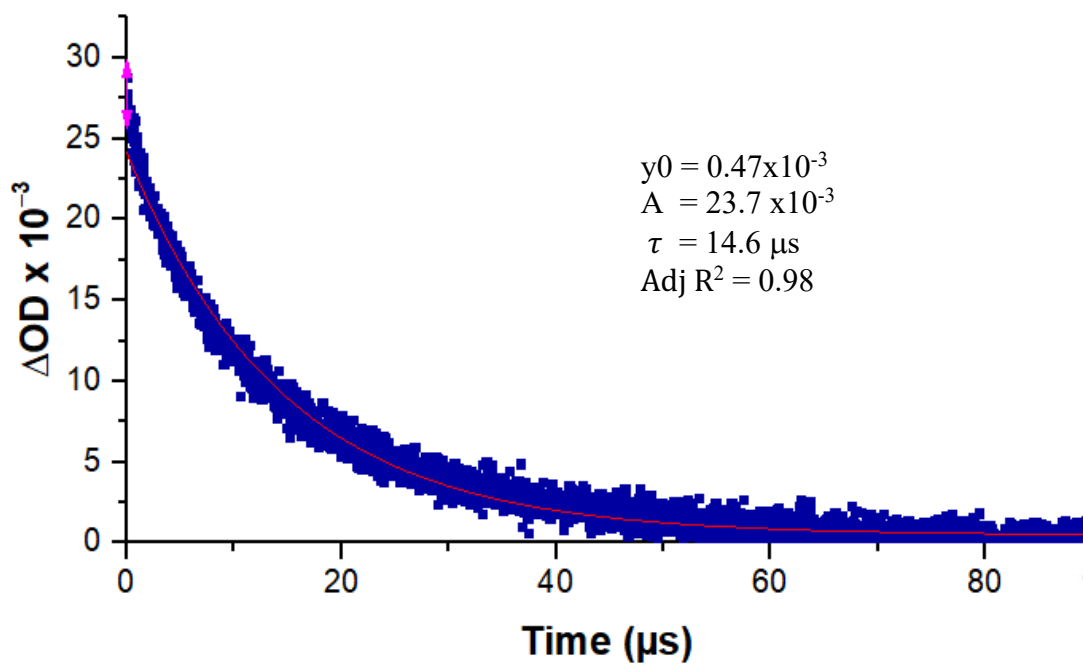
Transient Lifetime (530 nm)



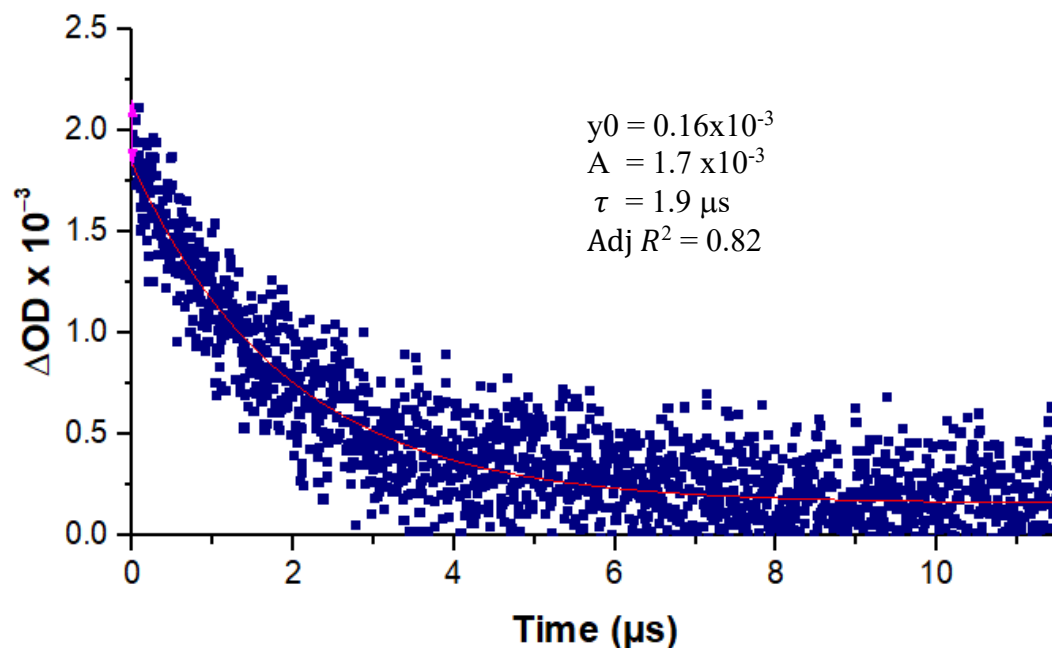
Transient Absorption of 4-Acetoxybenzophenone in Solution



Transient Decay of freeze-pump-thawed 4-Acetoxybenzophenone in acetonitrile solution detected at 530 nm



Transient Decay of freeze-pump-thawed DB-CO₂BPh in acetonitrile solution detected at 530 nm.

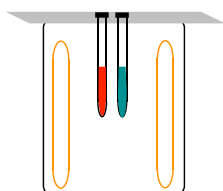


Quantum Yields in Solution and in Suspension

Quantum yield protocol

In solution

Stock solutions of **DB-CO₂BPh** (5, 10, 15, 20, 25, 35, 50 mM) and **DCK** (5, 10, 15, 20, 25, 35, 50 mM) were prepared in acetonitrile and benzene, respectively. A 1 mL aliquot of each sample was sparged with Argon in separate Pyrex tubes and sealed with a septum for 15 minutes each. Sparged samples were irradiated simultaneously for 20 seconds using the Rayonet photochemical reactor containing eight 12 inch 8W (BLE-8T312) 312 nm bulbs. All samples were optically dense and were reproduced in triplicate. A pictorial representation of the experimental setup is provided below.



Rayonet with cardboard on top (grey) to hold samples (red and green) in place while irradiated with eight 312 nm bulbs (orange).

2-methoxynaphthalene was used as an external standard to determine the number of product moles formed. ¹H NMR was used to monitor product formation from **DB-CO₂BPh** and **DCK**, respectively. An example calculation to determine quantum yields is provided below:

Quantum yield: $\Phi_{\text{DB-CO}_2\text{BPh}} = (A_{\text{DB-CO}_2\text{BP}}/A_{\text{DCK}})(\text{mol}_{\text{HB-CO}_2\text{BP}}/\text{mol}_{\text{DC}})\Phi_{\text{DCK}}$

$A_{\text{DB-CO}_2\text{BPh}}$: Absorbance of **DB-CO₂BPh** at given concentration

A_{DCK} : Absorbance of **DCK** at given concentration

$\text{mol}_{\text{HB-CO}_2\text{BPh}}$: moles of **DB-CO₂BPh** photoproduct

mol_{DC} : moles of **DC** photoproduct

Φ_{DCK} : Quantum yield of **DCK** (0.2 in benzene)

The equation was modified to consider the difference in refractive indices between actinometer (**DCK**) and analyte (**DB-CO₂BPh**) solvents:

$$\Phi_{\text{DB-CO}_2\text{BPh}} = (A_{\text{DB-CO}_2\text{BPh}}/A_{\text{DCK}})(\text{mol}_{\text{HB-CO}_2\text{BPh}}/\text{mol}_{\text{DC}})(\eta_{\text{Acetonitrile}}/\eta_{\text{Benzene}})\Phi_{\text{DCK}}$$

$\eta_{\text{Acetonitrile}}$: 1.3441

η_{Benzene} : 1.5011

A table for solvent refractive indices was provided by: <http://www.raeco.com/training/refractive-index-values.htm>

Irradiation of the analyte an actinometer can be irradiated as a mixture if both samples are prepared in the same solvent; however, we chose to irradiate them in separate vessels since the quantum yield of DCK was determined in benzene.

Veerman, M.; Resendiz, M.; Garcia-Garibay, M.A. *Org Lett*, **2006**, *12*, 2615-2617.

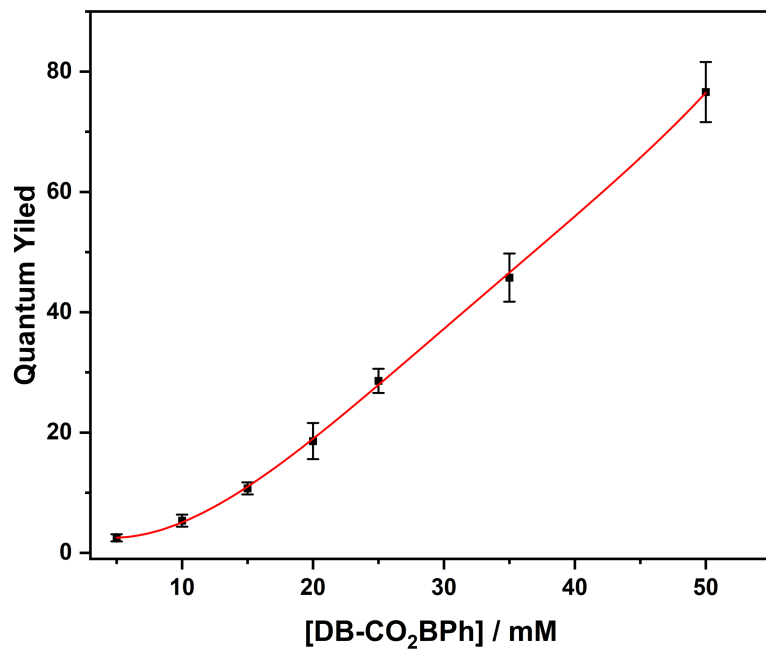
<https://pubs.acs.org/doi/full/10.1021/ol060978m>

Thoroughly degassed (15 min with Argon) samples were irradiated on a maximum time scale of 20 seconds. Experiments were run directly in deuterated solvents. Once irradiation was completed, a known concentration of 2-methoxynaphthalene was added to the reaction as an external standard. Quantum yields for DB-CO₂BPh were determined using ¹H NMR integrations.

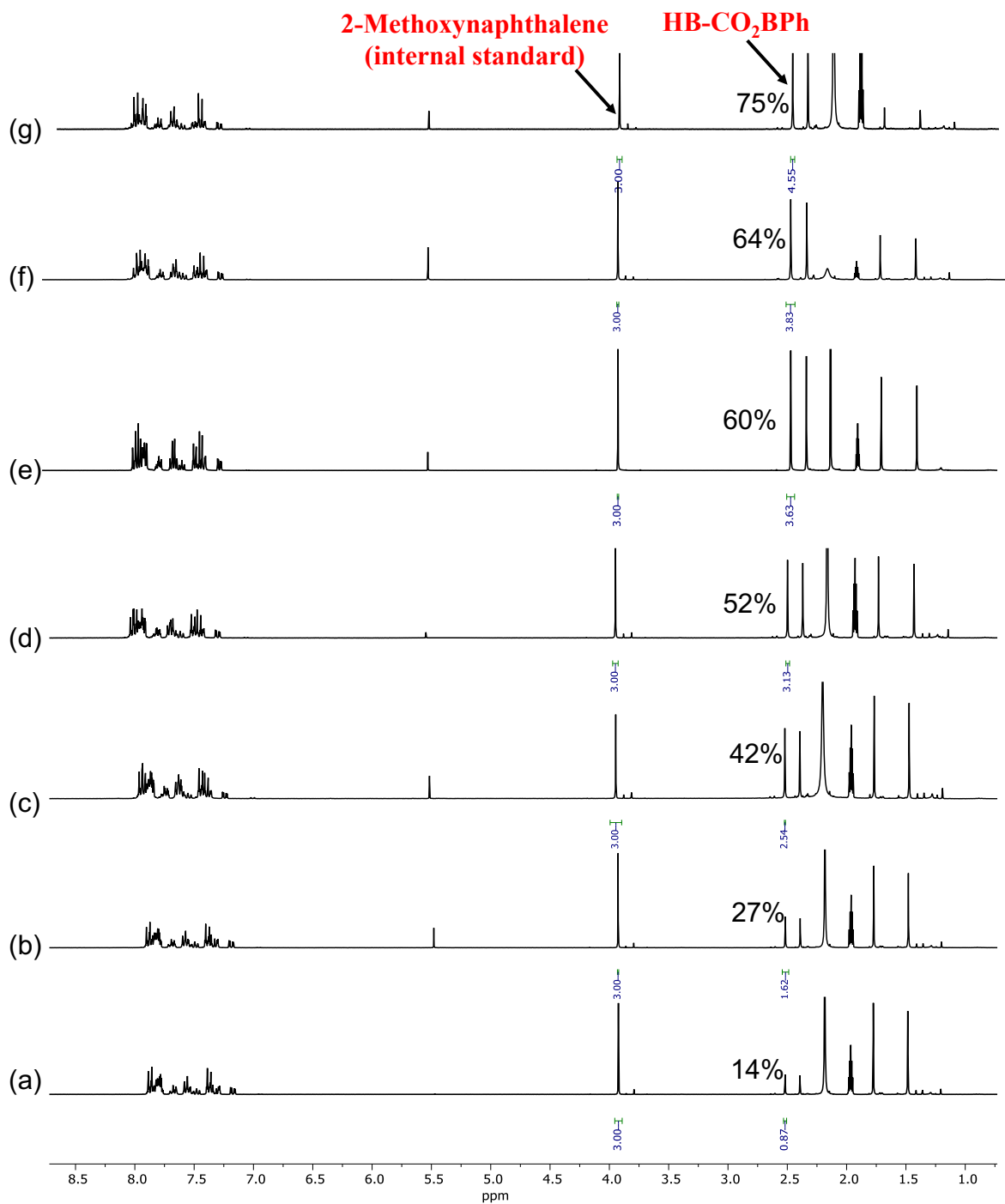
Conc. of DB-CO₂BPh / (mM)	5	10	15	20	25	35	50
Trial 1 / Yield %	14	26	42	50	59	67	79
Trial 2 / Yield %	13	27	44	52	62	64	75
Trial 3 / Yield %	15	29	41	51	60	62	77

Conc. of DCK / (mM)	5	10	15	20	25	35	50
Trial 1 / Yield %	40	36	29	20	15	10	7
Trial 2 / Yield %	39	37	30	18	14	9	6
Trial 3 / Yield %	42	35	28	22	16	11	8

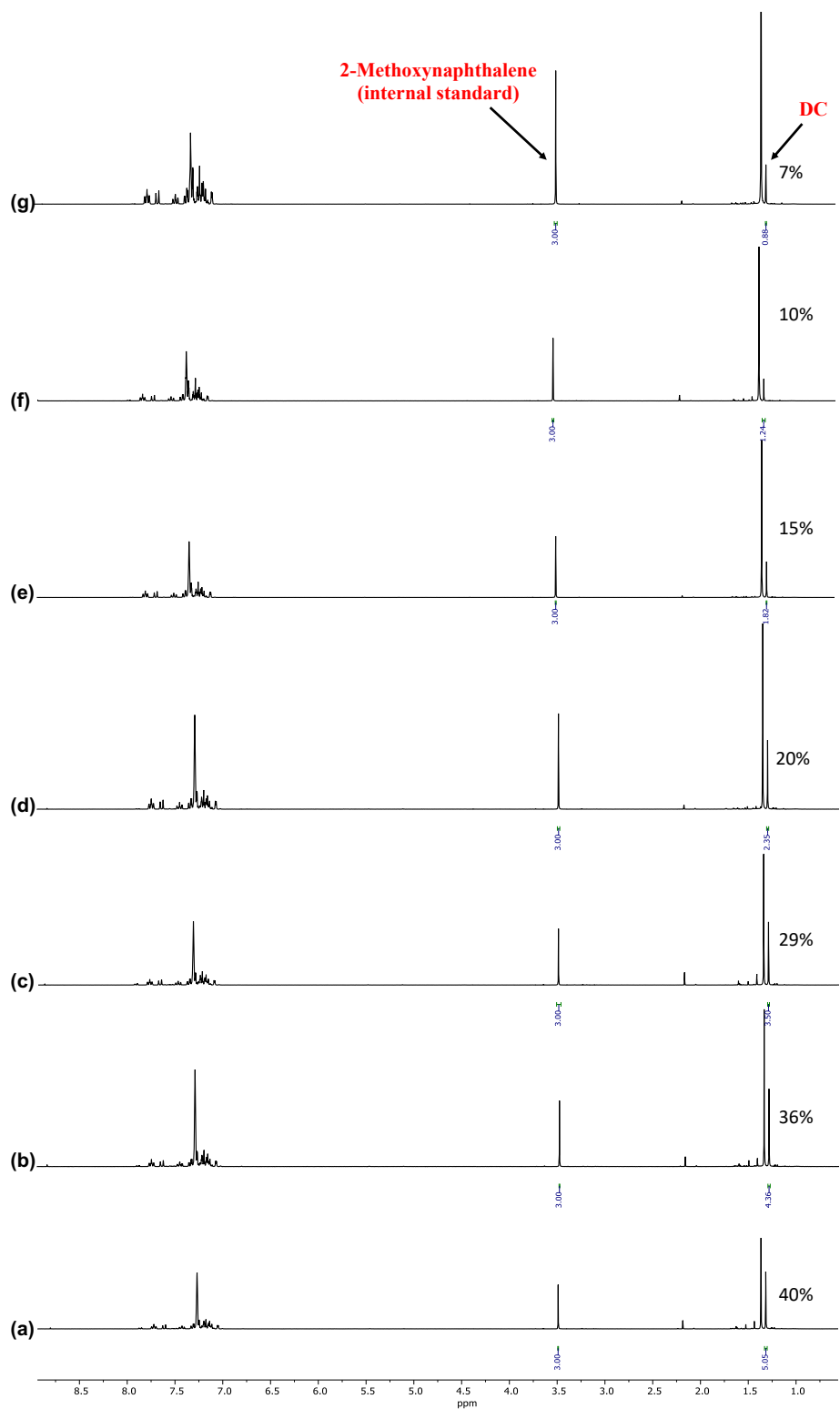
The moles of product formed was then determined as a ratio between the integrations of the analyte and internal standard. Explicit information for this reasoning can be found on this website: <http://www.organ.su.se/bo/Gruppfiler/NMR%20yield%20calculation.pdf>



Quantum yield values of **DB-CO₂BPh** at 5, 10, 15, 20, 25, 35, 50 mM in MeCN solution.



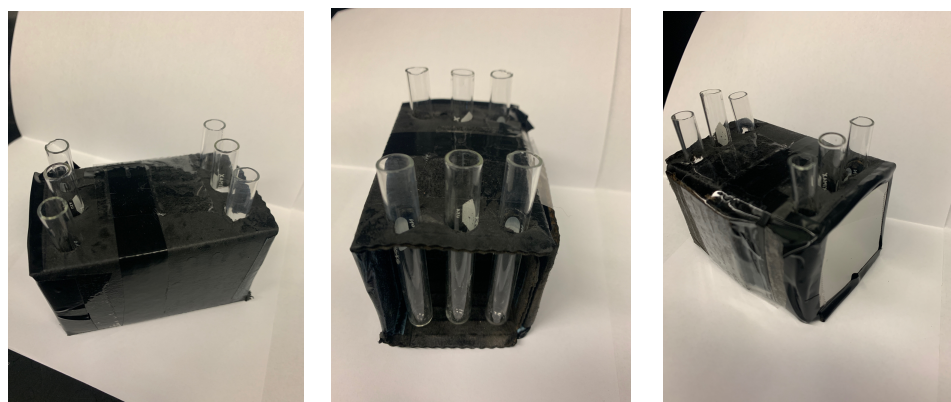
¹H NMR spectra (400 MHz, CD₃CN, 298 K) of the photolysis reaction with maximum irradiation time 20 seconds of substrate **DB-CO₂BPh** in different concentration (a) 5 mM (b) 10 mM (c) 15 mM (d) 20 mM (e) 25 mM (f) 35 mM (g) 50 mM. Product **HB-CO₂BPh** shows up at 2.48 ppm in the spectrum.



^1H NMR spectra (400 MHz, C_6D_6 , 298 K) of the photolysis reaction with maximum irradiation time 20 seconds of substrate DCK in different concentration (a) 5 mM (b) 10 mM (c) 15 mM (d) 20 mM (e) 25 mM (f) 35 mM (g) 50 mM. Product DC shows up at 1.15 ppm in the spectrum.

Quantum yields in suspension

Suspensions of **DB-CO₂BPh** and **DCK** were made by the reprecipitation method (Kasai, H.; Nalwa, H. S.; Oikawa, H.; Okada, S.; Matsuda, H.; Minami, N.; Kakuta, A.; Ono, K.; Mukoh, A.; Nakanishi, H. *Jpn. J. Appl. Phys.* 2, **1992**, 31, L1132-L1134.). Stock solutions of **DB-CO₂BPh** (0.0345 M) and **DCK** (0.0807 M) were made in acetonitrile and acetone, respectively. A 110 μ L aliquot of **DB-CO₂BPh** stock solution was added to 12 mL vortexing 0.1932 mM CTAB solution. A 120 μ L aliquot of **DCK** stock solution was added to 12 mL vortexing 4.2 mM SDS solution. Optically dense suspensions of **DB-CO₂BPh** and **DCK** were added into separate Pyrex tubes since the conversion rate of **DB-CO₂BPh** OBPh was much greater than that of **DCK**. The conversion rate of **DB-CO₂BPh** in suspension was so fast that **DB-CO₂BPh** suspension samples were irradiated behind a 5x5 cm neutral density filter (2 OD, 1% T). Suspensions were irradiated within the black box setup (shown below) in the Rayonet photochemical reactor containing eight 12 inch 8W (BLE-8T312) 312 nm bulbs. Samples were irradiated for 10, 15, and 20 seconds in triplicate.



Suspension setup for irradiation. There is a divider in the middle of the black box that does not allow light to travel through from either side.

After irradiation, samples were dried in large culture by sparging with air. Dry samples of **DB-CO₂BPh** were redissolved in deuterated chloroform (700 μ L) for ¹H NMR. Dry samples of **DCK** were redissolved in DCM (950 μ L) for GC-MS. 50 μ L of a 4.5 mM stock solution 2-methoxynaphthalene (external standard) was added to each sample before analytical analysis.

Quantum yields for suspensions were calculated similarly to the solution protocol described above. Below is an example calculation for 0.313 mM **DB-CO₂BPh** (A = 2.22) and 0.800 mM **DCK** (A = 2.00) suspensions based on ¹H NMR and GC-MS integrations

Integrations and product moles for 0.313mM **DB-CO₂BPh**

Time (sec)	10	15	20
Trial 1	0.39	0.61	0.72
Trial 2	0.45	0.59	0.70
Trial 3	0.42	0.55	0.77

Time	10	15	20
------	----	----	----

ES integration	1	1	1
ES protons	3	3	3
DB-CO ₂ BPh (H-int)	6	6	6
rA/ES	0.195 0.225 0.21	0.305 0.295 0.275	0.36 0.35 0.385
nES (mmol)	0.000252845	0.000252845	0.000252845
nES*(rA/ES)	4.93x10 ⁻⁵ 5.69x10 ⁻⁵ 5.31x10 ⁻⁵	7.71x10 ⁻⁵ 7.46x10 ⁻⁵ 6.95x10 ⁻⁵	9.10x10 ⁻⁵ 8.85x10 ⁻⁵ 9.73x10 ⁻⁵

Integrations and product moles for 0.800mM DCK

Time (sec)	ES integration	DC integration	mmol DC
10	2302860	198117	1.30x10 ⁻⁵
	1913072	14421	1.15x10 ⁻⁵
	2422266	190871	1.19x10 ⁻⁵
15	1856272	227164	1.78x10 ⁻⁵
	1846016	226475	1.78x10 ⁻⁵
	2227453	163082	1.12x10 ⁻⁵
20	1829953	224681	1.78x10 ⁻⁵
	1733605	169636	1.46x10 ⁻⁵
	1781779	197158	1.63x10 ⁻⁵

ES mass = 0.0016g

Stock conc (M) = (0.0016g/(158.2g/mol))/0.002L = 0.00505689mol/L

Conc in GC vial (M) = (0.00505689mol/L)*(50/1000) = 0.000252845mol/L

ES mass in GC vial = (0.000252845mol/L)*0.001L*158.2g/mol = 0.00004g

Quantum yields in suspension

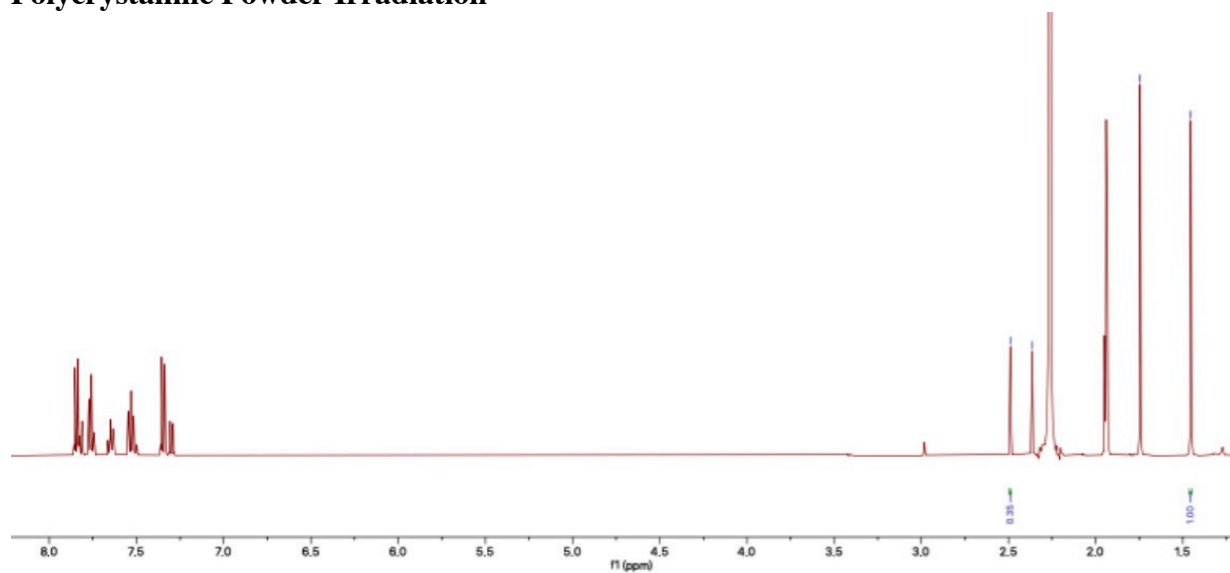
Time	10	15	20
	0.809	0.921	1.08
	1.05	0.889	1.29
	0.944	1.32	1.27
Ave	0.934	1.04	1.22
Ave*99	92.5	103.4	120.4
Std	0.12	0.24	0.11

Polycrystalline Powder Suspension vs. Reprecipitated Suspension Conversion

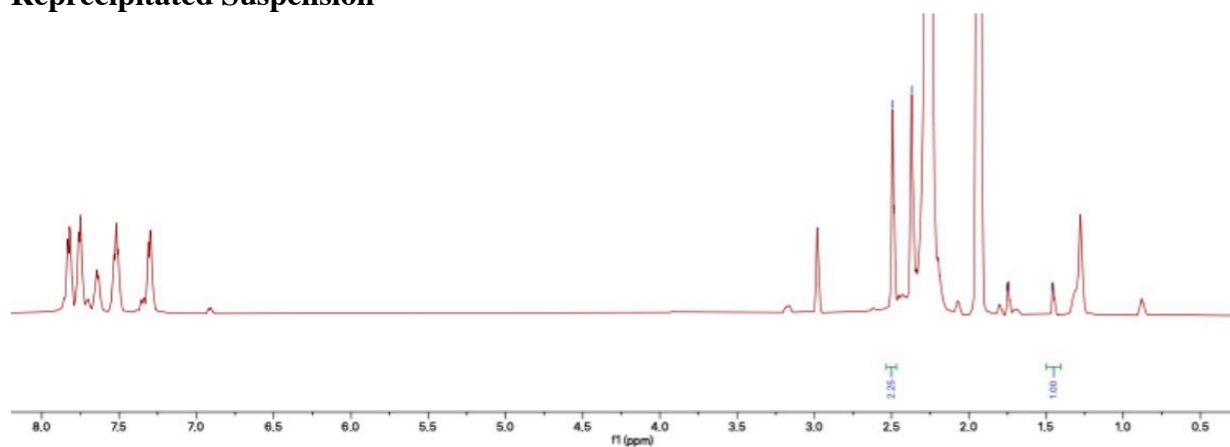
The polycrystalline suspension was prepared by suspending **DB-CO₂BPh** polycrystalline powder (11mg) into 3 mL of vortexing 0.2mM CTAB solution. The reprecipitated suspension was

prepared by dissolving **DB-CO₂BPh** (15mg) in 250 μ L MeCN and adding 30 μ L of the stock into 3 mL vortexing 0.2mM CTAB. Both samples were irradiated with 312 nm light for 6 minutes and the conversion was monitored by ¹H NMR.

Polycrystalline Powder Irradiation



Reprecipitated Suspension



Trial	Polycrystalline P product (mg)	Reprecipitated Susp product (mg)
1	2.9 (27)	1.8 (70)
2	4.18 (38)	1.82 (72)
3	3.63 (33)	1.98 (95)

(Values in parentheses denote %conversion of sample)

References

1. Koster, J. B.; Timmermans, G. J.; Bekkum, H. V. *Synthesis* **1971**, *19*, 139–140.
2. Ferrar, L.; Mis, M.; Dinnocenzo, J. P.; Farid, S.; Merkel, P. B.; Robello, D. R. *J. Org. Chem.* **2008**, *73*, 5683–5692.