Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Evidence for Diffusing Atomic Oxygen Uncovered by Separating Reactants with a Semi-Permeable Nanocapsule Barrier

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I. Additional Experimentation Details

Materials. Monomers, butyl methacrylate (BMA), t-butyl methacrylate (t-BMA), and ethylene glycol dimethacrylate (EGDMA) were purchased from Sigma Aldrich, and prior to synthesis, purified over aluminum oxide (neutral, ~2.5 mL). Sodium dodecylbenzenesulfonate (SDBS, an anionic surfactant), cetyltrimethylammonium p-toluenesulfonate (CTAT, a cationic surfactant), 2,2'- azobis(2-methylproprionamidine)dihydrochloride (V-50, thermal initiator) and dyes were purchased from Sigma Aldrich and used without further purification. V-50 was selected as the photoinitiator for its water-solubility, relatively low initiation temperature (65 °C), and commercial availability. HPLC grade solvents were used unless otherwise noted.

Instrumentation for nanocapsules. Extrusion was performed using a Nucleopore membrane (Sterlytech) with 0.2 μm pore and an Avanti mini extruder. Dynamic light scattering (DLS) measurements were taken on a Malvern Nano-ZS zetasizer (Malvern Instruments Ltd., Worcestershire, U.K.). Samples (80 μL) were taken from reaction solutions and placed in disposable cuvettes (Malvern, ZEN0040) without dilution. SEM images were obtained with a FEI SEM Inspect F instrument. Samples were coated with a ~5 nm gold layer using EMS 590 X sputter prior to analysis. HPLC was performed on a Agilent 1200 series equipped with a diode array detector (DAD), a quaternary pump, and either an Agilent Eclipse XDB-C18 column (5 μm particles, 150 x 4.6mm) or a Higgins Analytical Phalanx C18 column (3 μm particles, 150 x 3.0 mm). Mobile phases composed of varying concentrations of 0.1% trifluoroacetic acid (TFA) in water and acetonitrile (HPLC grade). Fluorescence spectroscopy was performed using an Olis DM 45 instrument. GC-MS was performed on a Shimadzu instrument equipped with a Shimadzu GCMS-QP2010S mass spectrometer and a 30 m RDX column (0.25 mm ID, 0.25 μm film thickness).

Instrumentation for Small Molecule Characterization. UV-Vis analysis was performed on a Shimadzu UV-1800 using a 10 mm quartz cuvette. GC-MS was performed on a Shimadzu instrument equipped with a Shimadzu GCMS-QP2010S mass spectrometer and a 30 m RDX column (0.25 mm ID, 0.25 μm film thickness). NMR was performed with a Bruker 400 MHz instrument. High Resolution Mass Spectrometry (HRMS) was recorded on a JEOL MStation Mass Spectrometer.

Preparation of 1a, 1b, and 3 Solutions. **1a** and **1b** were dissolved in water, which resulted in a very acidic solution (pH <1). The pH was increased by adding sodium bicarbonate ($NaHCO_3$) until the pH read between 4 and 7 using pH paper. Aqueous stock solutions of **1a** and **1b** were prepared with concentrations of ~10 and ~4 mM, respectively. **3** was found to be poorly soluble at neutral pH but very soluble at high pH. However, vesicle templated nanocapsules would not form at high pH. Thus, dissolution of **3** in water was aided with sonication (1 – 2 h), and the maximum concentration of **3** achieved in water was ~1 mM.

General Protocol for the Synthesis of Nanocapsules. Nanocapsules were prepared in 10-, 20-, 30-, or 40-mL batches, where the batch volume is equal to the volume of water (or other aqueous solution) used. For a 20-mL batch, SDBS (156 mg) and CTAT (44 mg) were dissolved in water, dye solution, or **1a**, **1b**, or **3** in solution, followed by brief vortex mixing. The solution was kept

at ~35 °C for 2 h. BMA (22 μL), t-BMA (24 μL), and EGDMA (24 μL) were added. After brief vortex mixing, the solution was kept at ~30 °C for 30 min. The headspace of the reaction vessel was purged with N_2 (g) for ~10 min. 2,2'-Azobis(2-methylpropionamidine)dihydro-chloride (aka V-50) (0.4 mL of a 50 mM aqueous stock solution) was added. After brief vortex mixing, the solution was heated at ~70 °C for at least 20 h. Following polymerization, methanol (20 mL) was added to the reaction mixture to precipitate the nanocapsules. As needed, an aqueous NaCl (3 M) solution was added drop-wise to facilitate precipitation of the nanocapsules. Following centrifugation, the solvent above the condensed nanocapsules was removed, and the nanocapsules were purified by repeated centrifugations, solvent removal, and resuspension in methanol-water mixtures (methanol: water ratios from 4:1, 3:1, 1:1, 1:3, 1:4 to 100% water). In a similar fashion, nanocapsules were resuspended in acetonitrile by washing with the desired solvent at least ten times.

Preparation of Dye Solutions. Procion Red MX-5B (PR), 4-(phenylazo)benzoic acid (PBA), or Nile Blue A (NBA) was dissolved in either a $NaHCO_3$ solution (aq, 10 mM; for PR and PBA), or a TRIS buffer (aq, 10 mM; for NBA), to give concentrations of 4 mM, 12 mM, and 0.2 mM, respectively. PR solutions were prepared a day prior to use, and allowed to stir overnight. PBA and NBA solutions were prepared fresh on the day of use. NBA solutions were filtered using filter paper prior to use.

Photoreactions. Solutions were prepared in 5- or 10-mL volumetric flasks. **2a** was weighed in the volumetric flask to prepare a 20 ± 2 mM solution. Acetonitrile was added to **1a**-loaded, **1b**-loaded, or "empty" nanocapsules (stored in a small amount of acetonitrile) and transferred to the volumetric flask containing **2a**. For consistency in the amount of nanocapsules used, the ratio of the batch volume used in the preparation of the nanocapsules to the volume of photolysis solution was set at 4:1. For example, if 20 mL of water were used to synthesize the nanocapsules, then 5 mL of acetonitrile was used to reconstitute the nanocapsules in solution for photolysis.
Solutions containing **1b**-loaded or "empty" nanocapsules served as two different types of photocontrols. Prior to photolysis, solutions were either degassed by argon-sparging or by freeze-pump-thaw. The prepared solutions (4 mL) were added to either quartz test tubes (~1 cm x 10 cm) for argon-sparging or quartz cells (1 cm x 1 cm x ~4.75 cm) equipped with freeze-pump-thaw capabilities. All photolyses were carried out in a Luzchem LZC-4C photoreactor using 14-broadly emitting fluorescent bulbs centered at 350 nm (fwhm: 325-375 nm; primarily UVA and some UVB and visible light), unless otherwise noted. Before and after photolysis, 0.5 - 0.75 mL of each solution was removed, nanocapsules were filtered off, and the supernatant was analyzed by HPLC. All experimental and photocontrol solutions were analyzed after photolysis for leakage of **1a** or **1b**.

Argon-Sparging. Quartz test tubes were sealed with a Suba seal wrapped with Parafilm. The Suba seal was punctured with a 6-inch 22 gauge stainless steel syringe needle (argon in) and a 1-inch disposable 22 gauge metal needle (argon out). The longer needle was pushed to the bottom of tube, and argon was bubbled through the solution for 45 min. Needles were removed while argon continued to flow, and an additional Suba seal was inverted and placed atop the other seal and parafilmed. These added measured were used to ensure minimal exposure of oxygen to the solution.

Freeze-Pump-Thaw. Freeze-pump-thaw tubes were custom built by Mr. Matt Reinsch at Washington University in St. Louis. The following procedure was followed for each freeze-pump-thaw cycle: (1) froze with liquid nitrogen, (2) placed under vacuum for 20 s, and (3) thawed by placing the tube in a beaker of room temperature water. Seven freeze-pump-thaw cycles were performed for each solution. Upon completing the cycles, the vacuum adapter on the freeze-pump-thaw tube was sealed with a Suba seal and parafilm and then was purged with nitrogen for 10 min.

Calibration Curves. All stock and standard solutions were prepared fresh daily. For **2b,** standard solutions were prepared in 10-mL volumetric containing 1 – 100 μM of **2b**. Calibration curves for **2b** were performed on an HPLC, and the peak area were recorded using an absorbance wavelength of 255 nm and plotted against concentration. R^2 values were found to be 0.999 or better.

Photodegradation of 2a. Solutions were prepared with **2a** (20 ± 2 mM) alone or in the presence of "empty" nanocapsules. Dodecane (1 mM) was added to solutions and used as an internal standard. Following photolysis, solutions were analyzed by HPLC and GC-MS. Products of degradation were identified as thiophenol, diphenyl disulfide, 2,2-bis((phenylthio)methyl)-propane (4a), and 2,2-bis((phenylthio)methyl)-cyclopropane. The products were analogous to those observed in the photochemically induced C-S homolytic cleavage of benzyl alkyl/aryl sulfides (1-3), suggesting that the observed photodegradation of **2a** occurs by a similar mechanism.

Purity of 2a. Due to oxidation of **2a** in ambient air, very pure **2a** (>99.998%) containing no detectable **2b** (LOD, 0.5 μM) was only achieved after multiple purifications by normal phase column chromatography. Purity could be maintained via storage under nitrogen at 4 °C.

Estimation of 1a in nanocapsules. To estimate the approximate concentration of **1a** in the experimental solution, all washes from the preparation of **1a**-loaded nanocapsules were concentrated, and free **1a** was purified by reverse phase high performance flash chromatography using a C18 column in two sequential purifications and then weighed. The difference between added and recovered **1a** was used to estimated the maximum amount of encapsulated **1a**.

Statistical Analysis. The error in the concentration of **2b** was calculated using a t-based confidence interval at a 95% confidence level (one trail; see below for t-values used) where error = t[stdev/sqrt(n)]. Table S2 gives the averages associated error for the change in **2b** concentration for all experiments (both argon-sparged and freeze-pump-thaw, with and without **2b** at t = 0 h). Table S3 and S4 below give the data shown in Figure 4A & 4B from the main text as well as statistical information used to calculate the error.

Isolation Experiment of 2a. To investigate the mechanism of photodeoxyenation of **1a**, an isolation experiment was performed by immobilizing **1a** in a dilute EPA glass solution and irradiating it with UV-A light to monitor photoproduct formation. 0.20 mM solution of **1a** was prepared in Ether (5.0ml), Pentane (5.0ml) and Ethanol (2.0ml) solution. The solution was transferred in a quartz NMR tube and was then degassed using argon sparging for 10 minutes.

The EPA solution was then frozen using liquid nitrogen, forming a clear glass, and irradiated for 1 hour in a photoreactor with 12 UV-A bulbs. Fluorescence spectroscopy, using Photon Technology International Fluorometer, was performed at 0 and 1 hour to monitor the photodeoxygenation of **1a.** A reference spectrum for 97uM EPA glass solution of **1b** was also obtained to analyze the data. The fluorescence spectrum after 1 hour photolysis of **1a** in EPA glass showed the formation of **1b** supporting the unimolecular mechanism of photodeoxygenation.

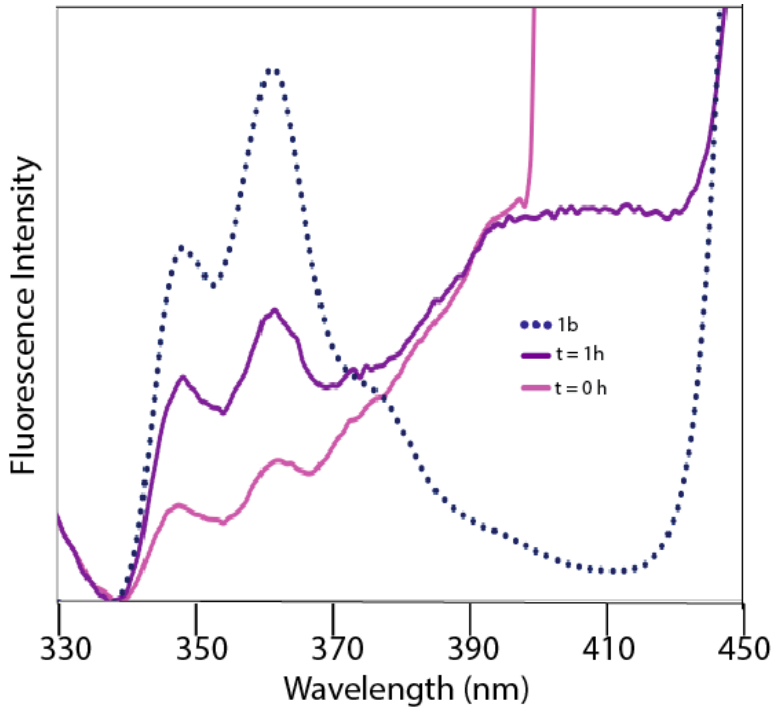


Figure S1. Fluorescence spectra (λ_{ex}, 270 nm) showing formation of **1b** after photolysis of **1a** in frozen EPA glass for 1 hour. Note: t=0 contains some **1b and** the increase in intensity at 400 nm is due to an artifact.

Table S1. Toluene fingerprint tests for dibenzothiophene *S*-oxide (DBTO), 2,8-diphenyldibenzothiophene *S*-oxide, and 5-oxodibenzothiophene-2,8-bis(phenyl-4-sulfonylneopentylester).

	% yield relative to sulfide formation				
	Benzaldehyde	Benzyl alcohol	o-cresol	M- & p-cresol	Oxidation CH3:ring
DBTO [a]	14	10	25	24	2.0
DBTO [b]	17	13	26	22	1.6
Derivatives A [c]	11	14	20	22	1.7
Derivatives B [d]	13	11	24	18	1.8

A common intermediate test, whereby a reactive oxygen species (ROS) generator is used to oxidize a given reactant, can be implemented to allow for the comparison of ROS generators as a function of the oxidized products. Toluene is a popular reactant for use in the common intermediate test because of its multitude of oxidation products, including

benzaldehyde, benzyl alcohol, o-cresol, m-cresol, and p-cresol, although, the latter two are often reported together (*4-5*). The relative yields of oxidation products form a sort of fingerprint of the responsible oxidant. The common intermediat test using toluene is known as a toluene fingerprint test. [a] Ref 6. [b] Ref 5. [c] Derivative A is 2,8-diphenyl-dibenzothiophene *S*-oxide. [d] DBTO derivative B is 5- oxodibenzo-thiophene-2,8-bis(phenyl-4-sulfonylneopentylester).

Table S2. Data and statistical information for all photolysis experiments.

	change in concentration of **2b** (μM)	
	photocontrol	experimental
confidence interval	0.5 – 3.1	8.1 – 10.6
average	1.8	9.3
standard deviation	2.1	2.4
calculated error (95%) [a]	1.3	1.2
no. of trials [b]	9	12
critical value [c]	1.860	1.796

[a] Error was calculated using a one tail t-test with critical values (95%) listed in the table, unless noted (n.a.). [b] For each trial 2 – 4 HPLC injections were performed; error of injections was found to be insignificant relative to the error between trials. [c] The t-values listed are for a single sided t-test at 95% confidence.

Table S3. Data and statistical information for Figure 4A from the main text.

concentration of **2b** (μM):	photocontrol		experimental	
	t = 0 h	t = 5 h	t = 0 h	t = 5 h
average	0.6	3.3	0.8	11.3
standard deviation	0.9	2.2	1.3	2.14
calculated error (95%) [a]	0.7	1.8	0.9	1.6
no. of trials [b]	6	6	7	7
critical value [c]	2.015	2.015	1.943	1.943

[a] Error was calculated using a one tail t-test with critical values (95%) listed in the table, unless noted (n.a.). [b] For each trial 2 – 4 HPLC injections were performed; error of injections was found to be insignificant relative to the error between trials. [c] The critical values listed are for a single sided t-test at 95% confidence.

Table S4. Data and statistical information for Figure 4B from the main text.

concentration of **2b** (μM):	photocontrol		experimental	
	t = 0 h	t = 5 h	t = 0 h	t = 5 h
average	0	0	0	8.4
standard deviation	0	0	0	1.9
calculated error (95%) [a]	0.5 [d]	0.5 [d]	0.5 [d]	3.2
no. of trials [b]	3	3	3	3
critical value [c]	n.a. [d]	n.a. [d]	n.a. [d]	2.920

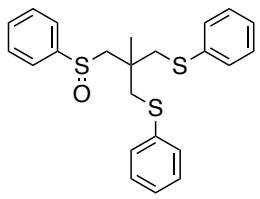
[a] Error was calculated using a one tail t-test with critical values (95%) listed in the table, unless noted (n.a.). [b] For each trial 2 – 4 HPLC injections were performed; error of injections was found to be insignificant relative to the error between trials. [c] The critical values listed are for a single sided t-test at 95% confidence. [d] The value is given as the limit of detection for **2b**.

II. Synthesis Methods

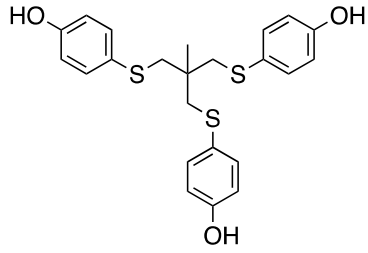
For synthesis procedures and characterization data including ^{1}H NMR, ^{13}C NMR, HRMS, IR, and HPLC Purity Analysis for 5-oxodibenzothiophene-2,8-bis(phenyl-4-sulfonic acid) [**1a**] and dibenzothiophene-2,8-bis(phenyl-4-sulfonic acid) [**1b**], we refer the reader to our recent report.[7]

2,2,2-tris((phenylthio)methyl)-ethane (2a). Prepared according to the procedure given by Dornan and coworkers.[8] UV/Vis: λ_{max} 257 nm.

2-methyl-1-(phenylsulfinyl)-3-(phenylthio)-2-[(phenylthio)-methyl]propane (2b). 2a (1.078 g, 2.72 mmol) was dissolved in CH_2Cl_2 (30 mL), and the solution was cooled to -65 °C. The reaction flask was sealed and a nitrogen atmosphere was introduced. To an addition funnel, mCPBA (0.11 M) in CH_2Cl_2 (25.0 mL, 2.76 mmol) was added. Over a period of 45 min, the mCPBA solution was added to the reaction flask. The reaction was allowed to stir for 3 h at -10 °C and then was allowed to warm to room temperature. A saturated aqueous $NaHCO_3$ solution (50 mL) was added to the reaction mixture, drop-wise, over a period of 20 min. The aqueous layer was removed, and the organic layer was washed a second time with saturated aqueous $NaHCO_3$ solution (50 mL), and again, with water (75 mL). The solution was dried with $MgSO_4$, and the solvent was removed under vacuum. The resulting liquid was purified by silica chromatography using a 4:1 hexane/EtOAc solution as the eluent. This afforded **2b** (514 mg, 46% yield) as a clear, viscous liquid. IR (NaCl): 1582, 1479, 1439, 1377, 1088, 1038, 1024, 851, 741, 691 cm^{-1}; λ_{max} = 253-254 nm; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.54-7.50 (m, 3H), 7.42-7.37 (m, 4H), 7.31-7.26 (m, 4H), 7.23-7.19 (m, 2H), 3.444 (d, J=13.0 Hz, 1H), 3.391 (d, J=13.0 Hz, 1H), 3.368 (d, J=12.9 Hz, 1H), 3.321 (d, J=12.9 Hz, 1H), 3.051 (d, J=13.8 Hz, 1H), 2.923 (d, J=13.8 Hz, 1H), 1.428 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 136.7, 136.7, 131.1, 130.2, 130.2, 129.5, 129.3, 129.2, 126.7, 126.6, 124.0, 67.7, 44.6, 44.5, 41.2, 24.8 ppm; HRMS (m/z) calcd. for $[C_{23}H_{24}OS_3]^+$, 412.099; found, 412.100.

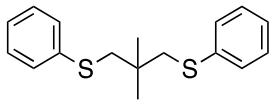


2,2,2-tris((4-hydroxyphenylthio)methyl)ethane (3). Under an argon atmosphere, sodium iodide (346.0 mg, 2.31 mmol), sodium hydroxide (480.4 mg, 12.01 mmol), and DMF (anhydrous, 10 mL) were gently heated and stirred. In a vial, 4-mercaptophenol (1027.1 mg, 8.14 mmol) was dissolved in DMF (anhydrous, 3 mL) and then was added to the reaction flask. 1,3-dichloro-2-(chloromethyl)-2-methylpropane (250 μL, 1.81 mmol) was added to the reaction flask and heated for two days at 100 °C, and then was allowed to cool to room temperature. CH_2Cl_2 (100 mL) and 0.1% TFA in water (50 mL) were added to the reaction mixture and stirred for ~30 min. The aqueous layer was removed, and then, the organic layer was washed twice with water (75 mL) and then dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting oil was purified via column chromatography using a Biotage Flash Chromatography System (stationary phase = silica; mobile phase: solvent A = pentane, solvent B = 2:1 EtOAc: isopropanol, from 2%B to 70%B). This afforded **3** (370.9 mg, 46% yield) as a white powder. IR (NaCl): 3552, 2361, 2342, 2129, 1998, 1599, 1584, 1493, 1427, 1234, 1169, 1094, 1009, 826 cm^{-1}; λ_{max} = 258 nm; ^{1}H NMR



(400 MHz, CD_3OD): δ 7.227 (dt, J_1=9.3 Hz, J_2=2.0 Hz, 6H), 6.721 (dt, J_1=9.3 Hz, J_2=2.6 Hz, 6H), 3.022 (s, 6H), 1.073 (s, 3H) ppm; ^{13}C NMR (100 MHz, CD_3OD): δ 158.2, 134.8, 127.4, 117.1, 46.9, 43.0, 24.4 ppm; HRMS (m/z) calcd. for $[C_{23}H_{24}O_3S_3]^+$, 444.089; found, 444.089.

2,2-bis((phenylthio)methyl)propane (4a). Sodium iodide (1.20 g, 8.0 mmol), sodium hydroxide (1.3 g, 32.7 mmol), 2,2-dimethyl-1,3-dichloropropane (974.9 mg, 6.9 mmol), and DMF (anhydrous, 15 mL) were added to a flask. The solution was placed under an argon atmosphere and gently heated (40-55 °C). After a few minutes, thiophenol (2 mL, 19.5 mmol) was added to the reaction flask. The solution was heated (~100 °C) for two days, before allowing it to cool to room temperature. EtOAc (50 mL) and water (50 mL) were then added. The aqueous layer was removed, and the organic layer was washed twice with water (100 mL), twice with 0.1 M HCl (50 mL), and again with water (100 mL). The solvent was removed under reduced pressure. The resulting liquid was purified by silica chromatography using pentane as the eluent. This afforded **4a** (1.53 g, 77% yield) as a clear, viscous liquid. IR (NaCl): 3073, 2959, 2913, 2868, 1942, 1871, 1788, 1724, 1584, 1479, 1466, 1437, 1383, 1366, 1090, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 4H), 7.30-7.25 (m, 4H), 7.182 (tt, J_1=7.3 Hz, J_2=1.8 Hz, 2H), 3.085 (s, 4H), 1.156 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 129.6, 129.0, 126.1, 46.2, 37.2, 26.9 ppm; HRMS (m/z) calcd. for $[C_{17}H_{20}S_2]^+$, 288.101; found, 288.098.



III. Characterization of Nanocapsules

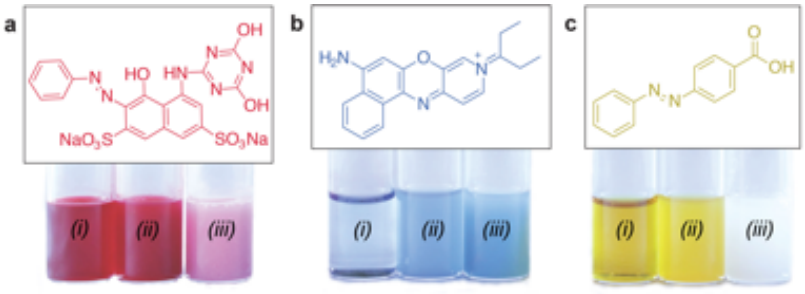


Figure S2. Measuring the nanocapsule pore size using dyes as probes. Pore size probes; **a**, Procion Red, 1.1 nm; **b**, Nile Blue A, 1.0 nm; and **c**, 4-(phenylazo)benzoic acid, 0.6 nm. Photographs of each size probe as (i) dye alone, (ii) dye in nanocapsules before washing, (iii) dye in nanocapsules after washing >15 times with methanol and water; all using water as the solvent. Dye is shown to be retained in (iii) for Procion Red and Nile Blue A, and not retained for 4-(phenylazo)benzoic acid. Prior to washing, the dyes are both inside and outside of the nanocapsules; therefore, after washing, some loss in color intensity is expected even when the dyes are retained as observed in **a** and **b**.

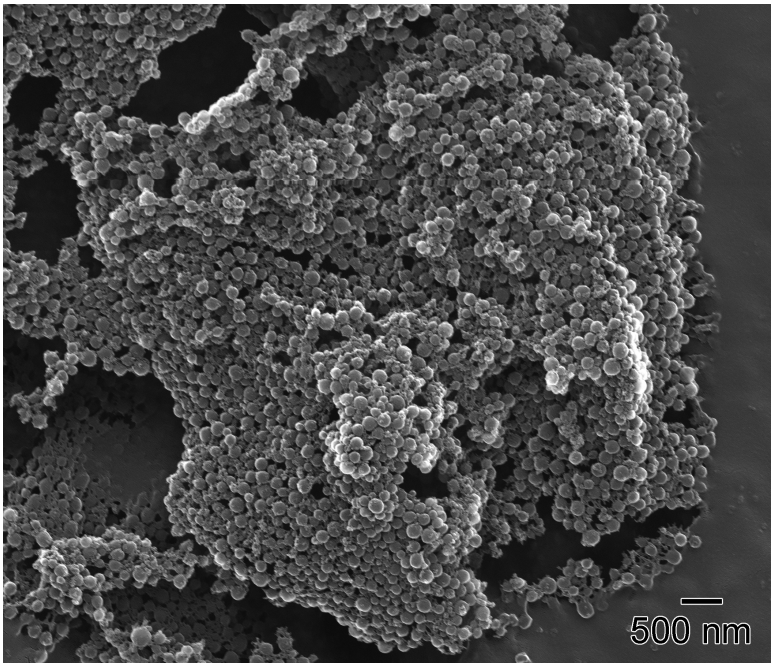


Figure S3. Characterization of "empty" nanocapsules by SEM.

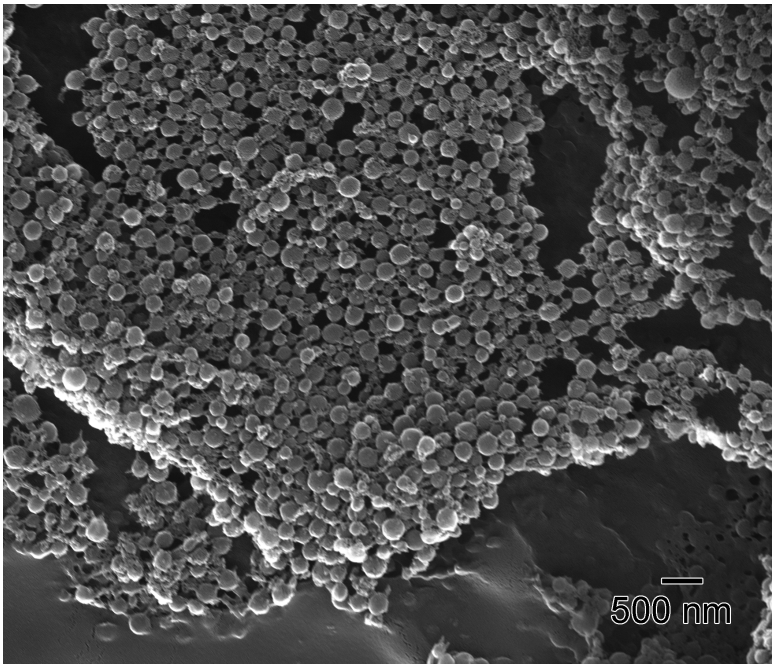


Figure S4. Characterization of **3**-loaded nanocapsules by SEM.

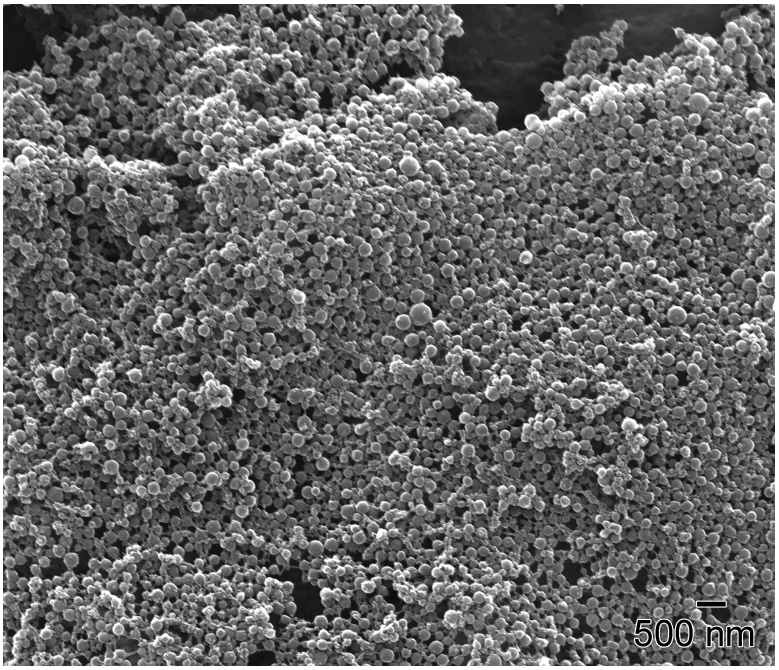
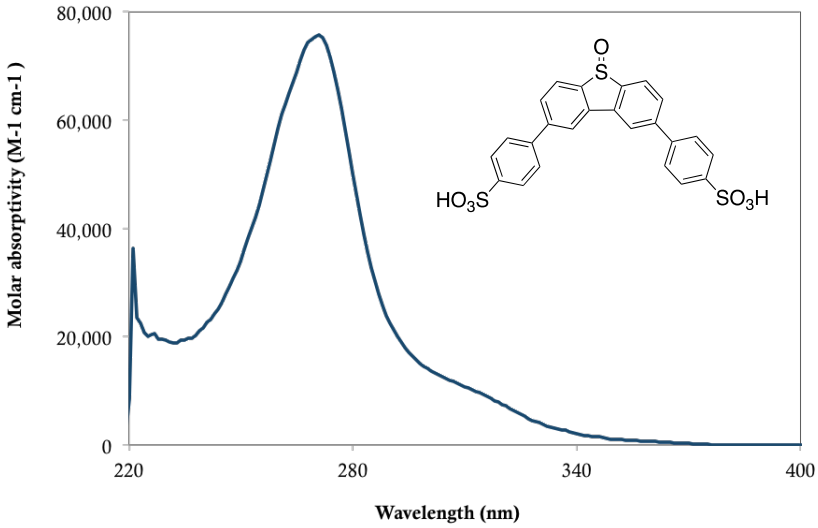


Figure S5. Characterization of **1a**-loaded nanocapsules by SEM.

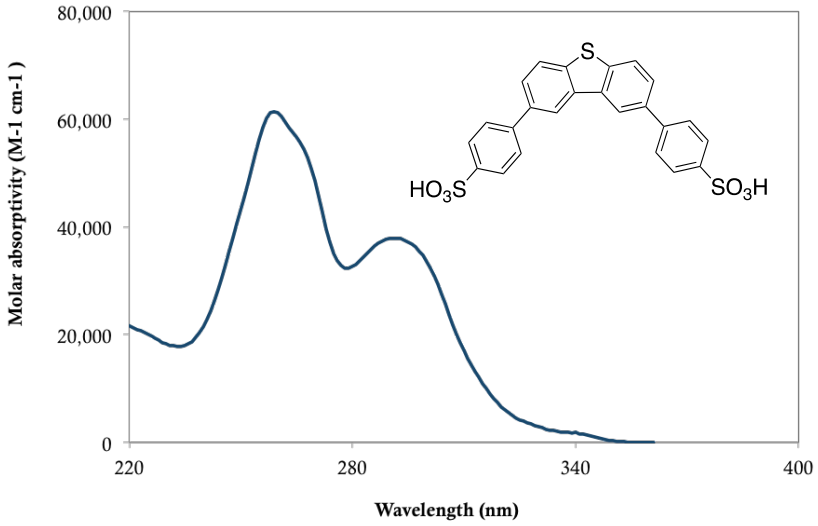
IV. Characterization of Small Molecules

UV-Vis (in water) **(1a)**

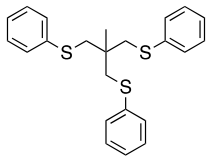


λ_{max} = *271 nm*

UV-Vis (in Methanol) **(1b)**



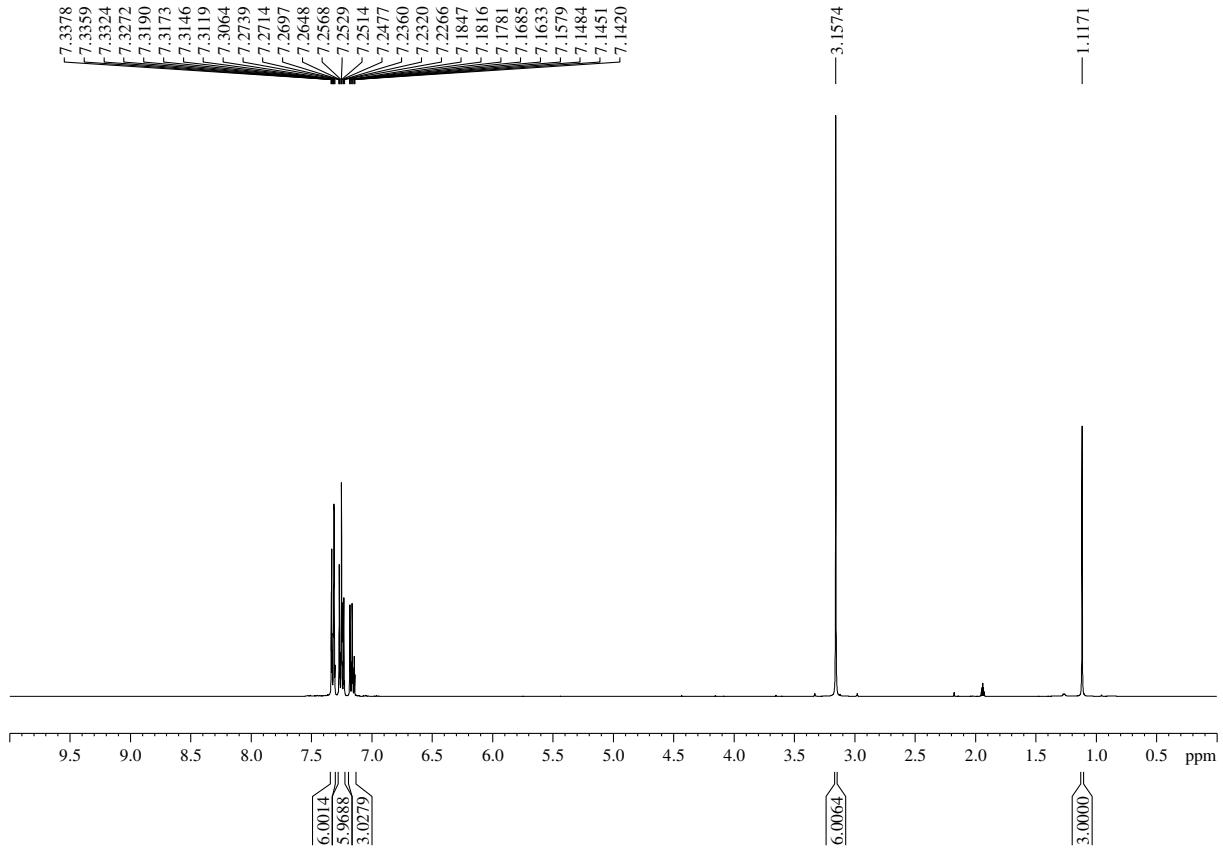
λ_{max} = *259 nm; (second band at 291-292 nm)*



2a

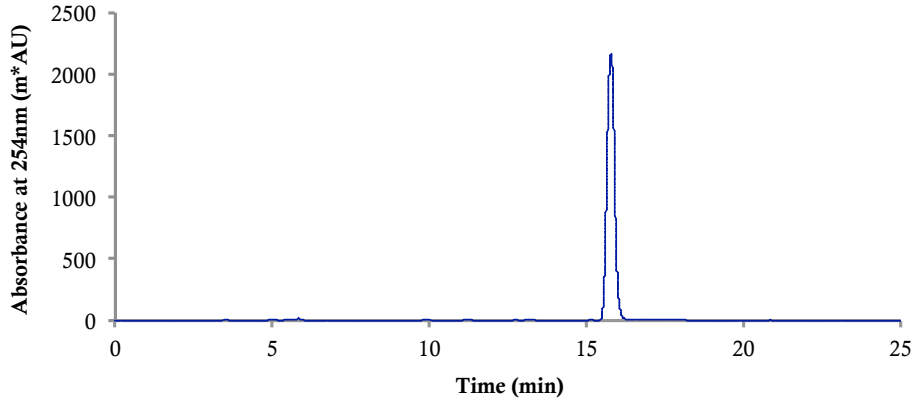
*Note: **2a** was previously reported by Dornan et. al.*

^{1}H-NMR Spectrum (400 MHz, CD_3CN) **(2a)**

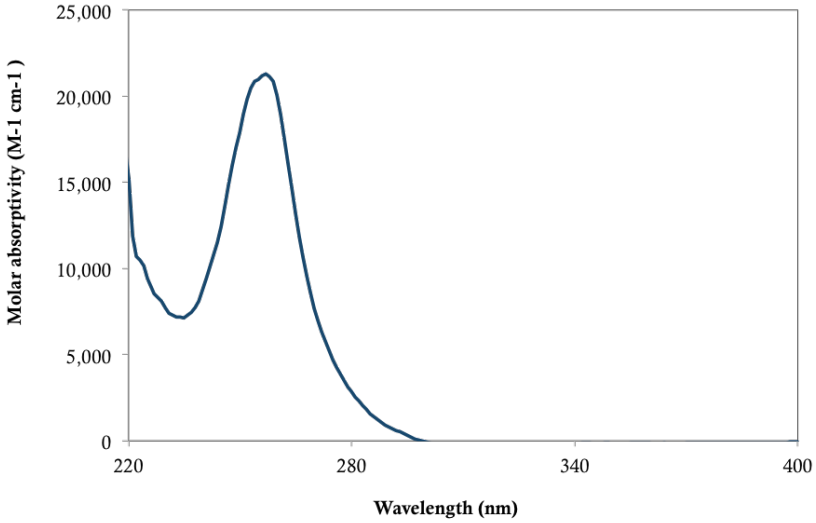


acetonitrile (1.94 ppm)

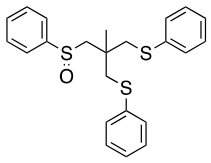
Purity Analysis by HPLC **(2a)**



UV-Vis (in Acetonitrile) **(2a)**

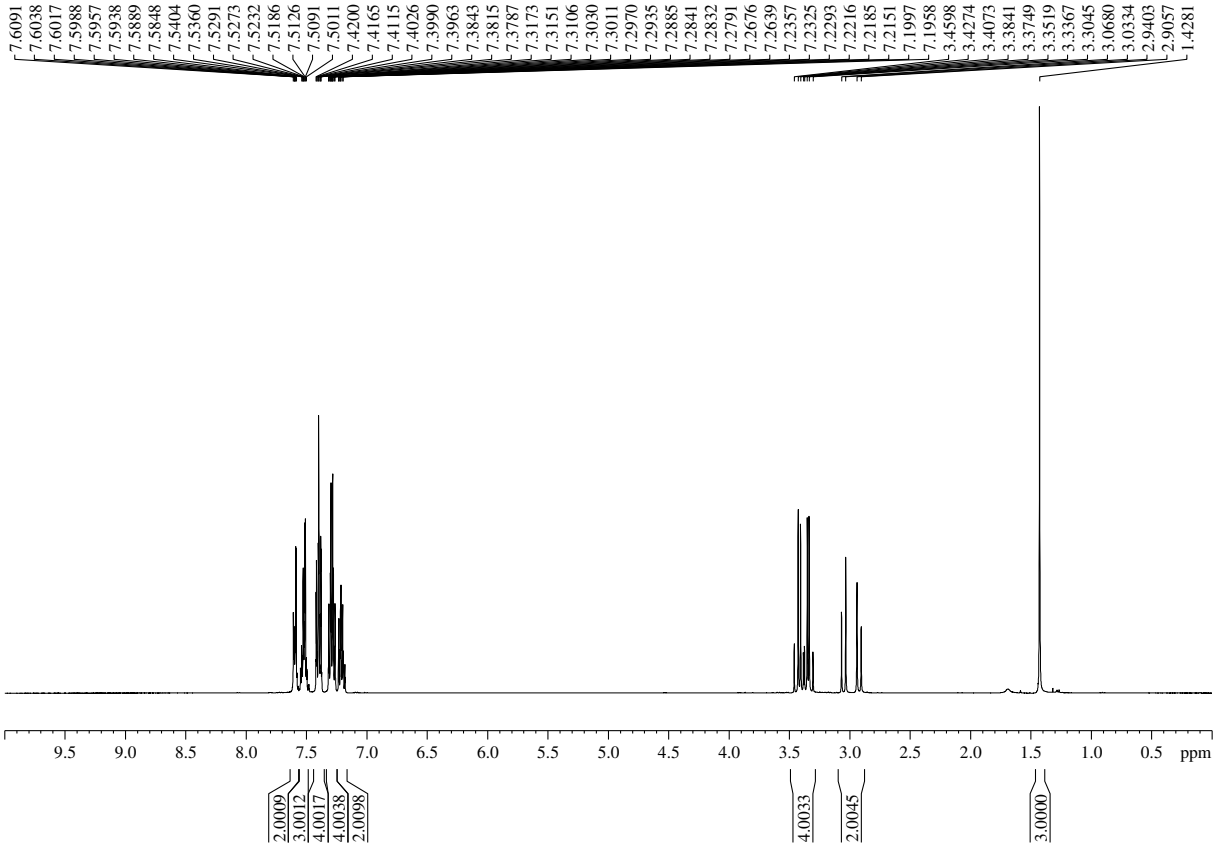


λ_{max} = *257 nm*

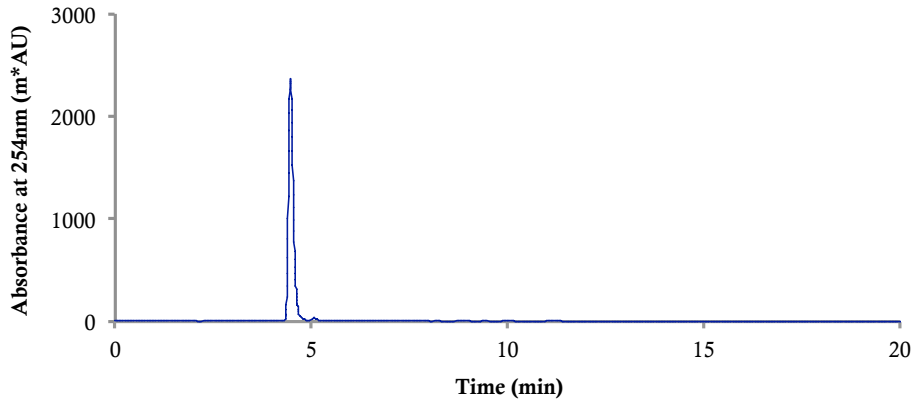


2b

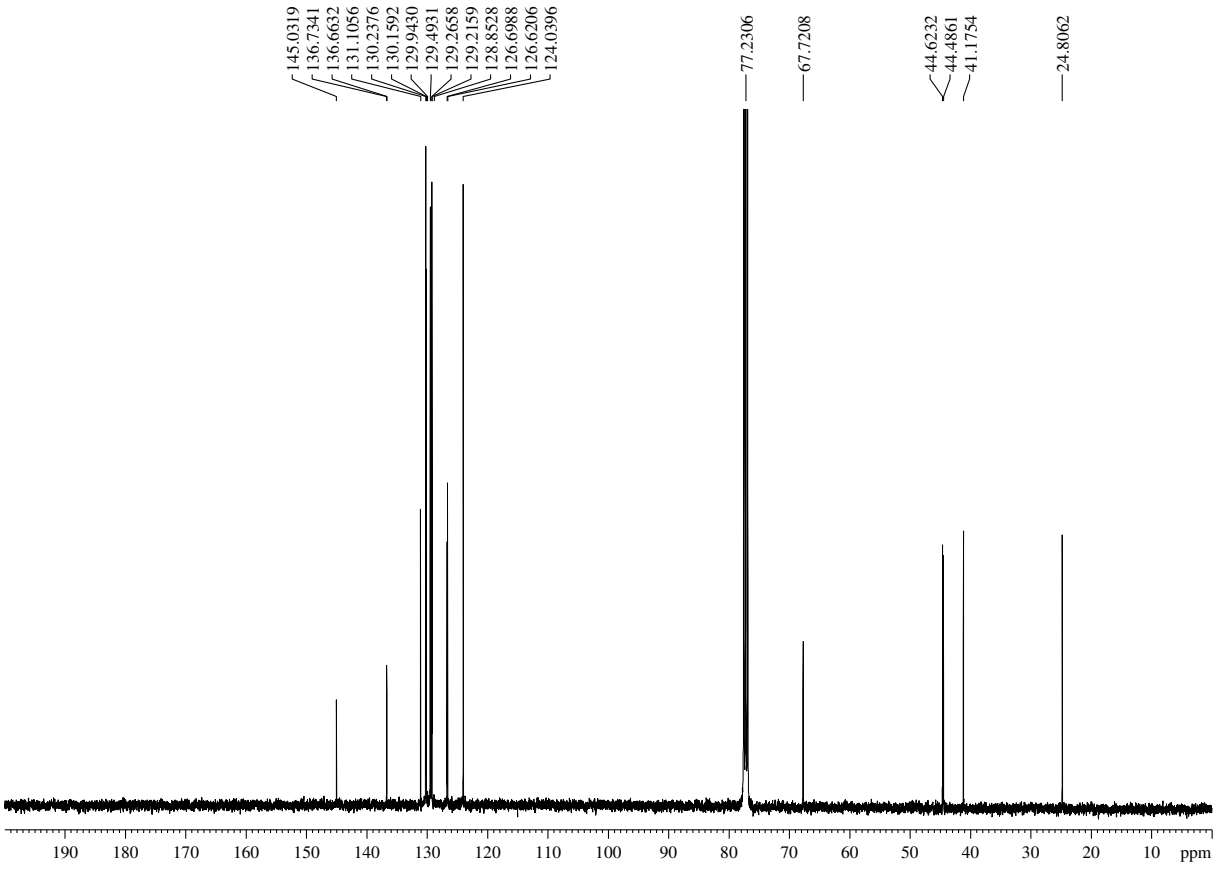
[1]H-NMR Spectrum (400 MHz, $CDCl_3$) **(2b)**



Purity Analysis by HPLC **(2b)**

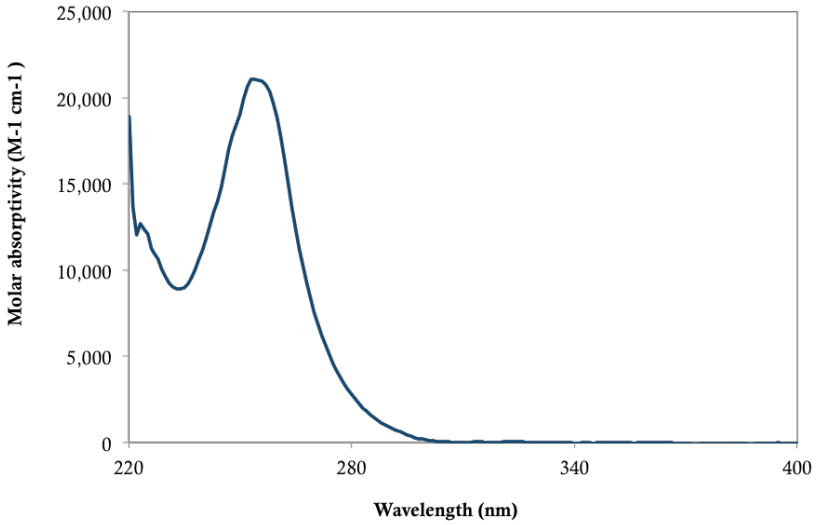


^{13}C-NMR Spectra (400 MHz, $CDCl_3$) **(2b)**



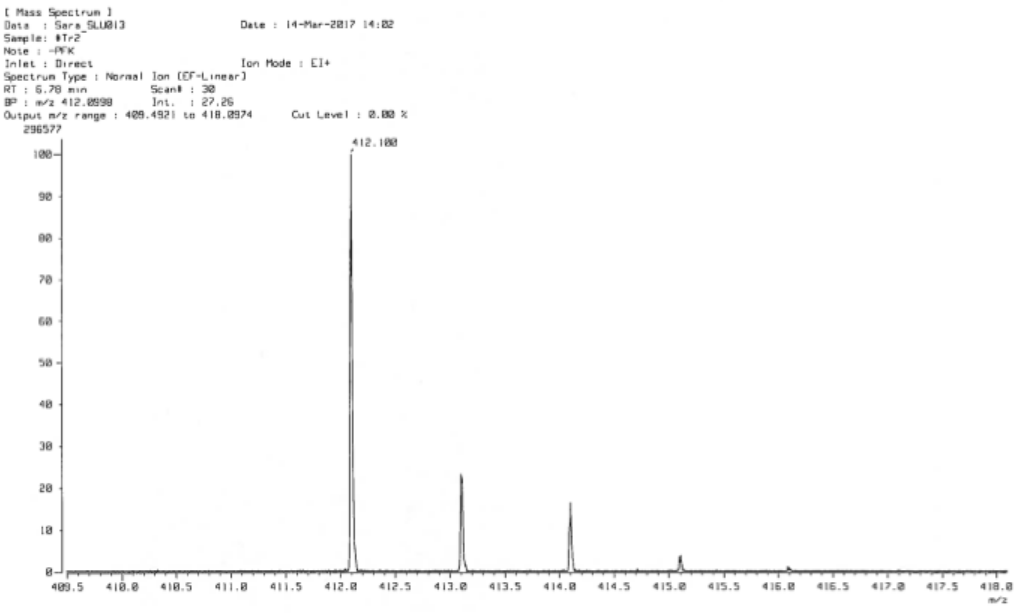
chloroform (77.2 ppm)

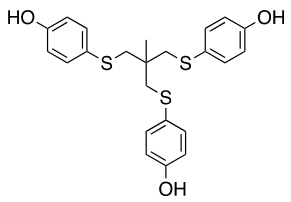
UV-Vis (in Acetonitrile) **(2b)**



λ_{max} *= 253-254 nm*

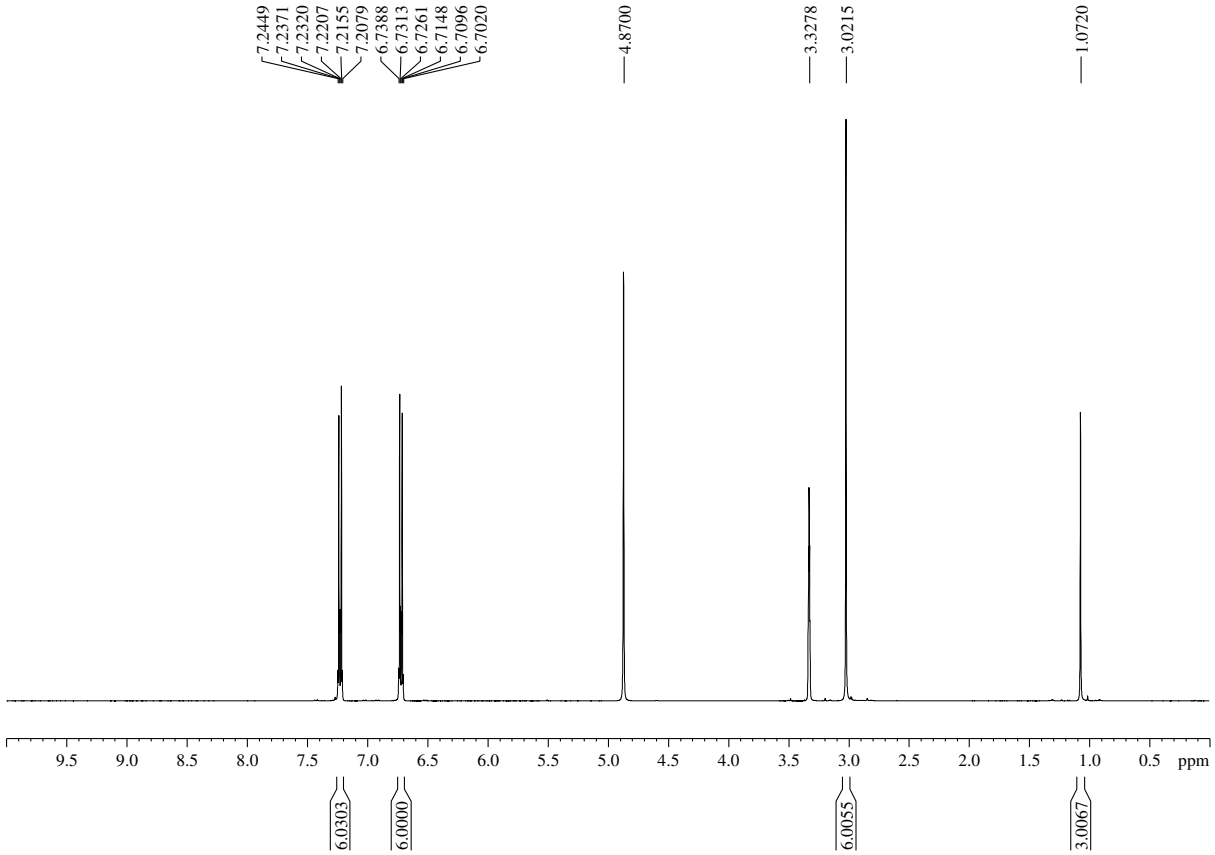
High Resolution MS Spectrum **(2b)**





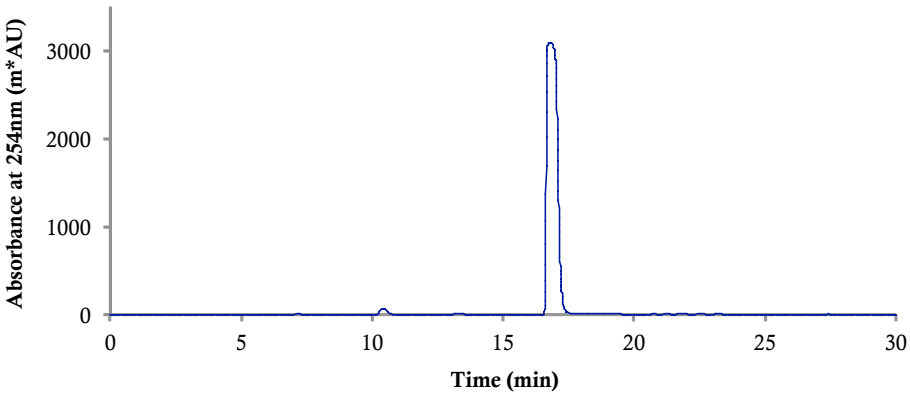
3

^{1}H-NMR Spectrum (400 MHz, CD_3OD) **(3)**

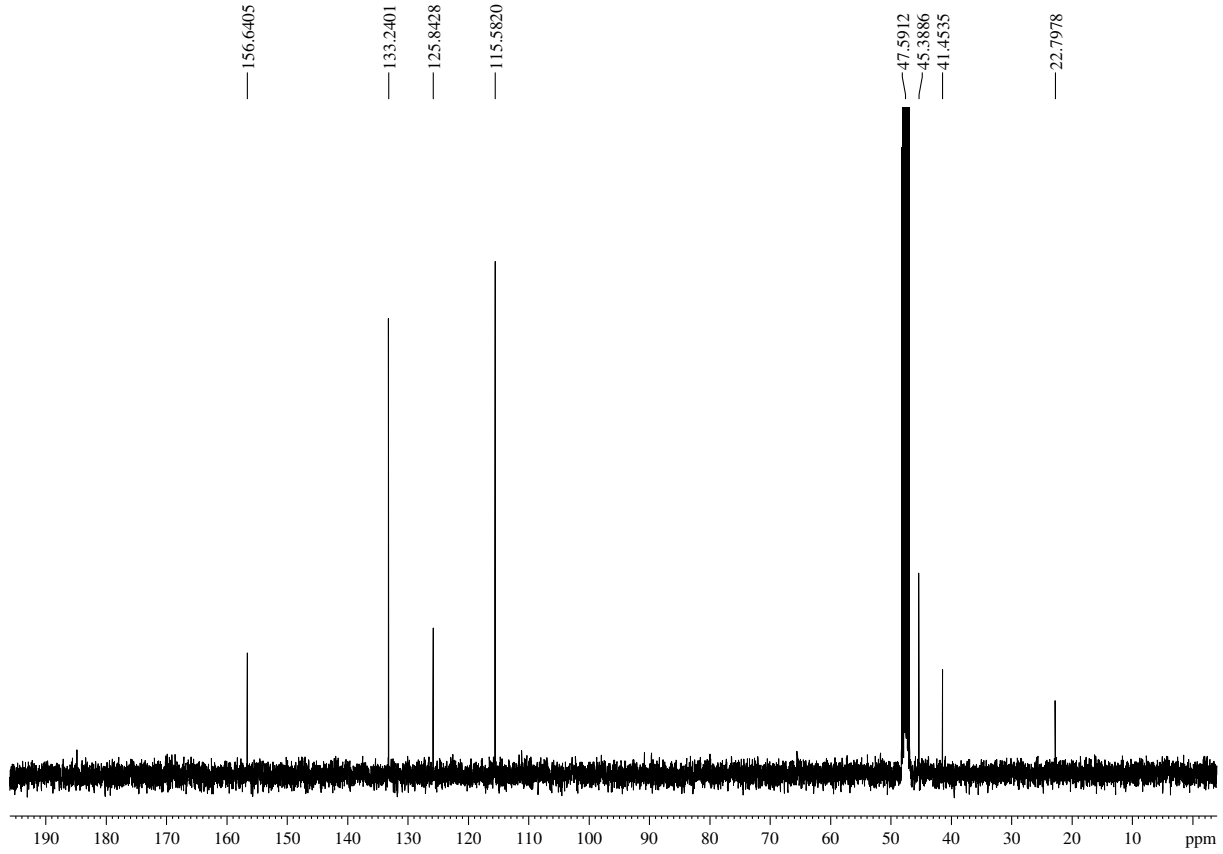


methanol (4.87, 3.33 ppm)

Purity Analysis by HPLC **(3)**

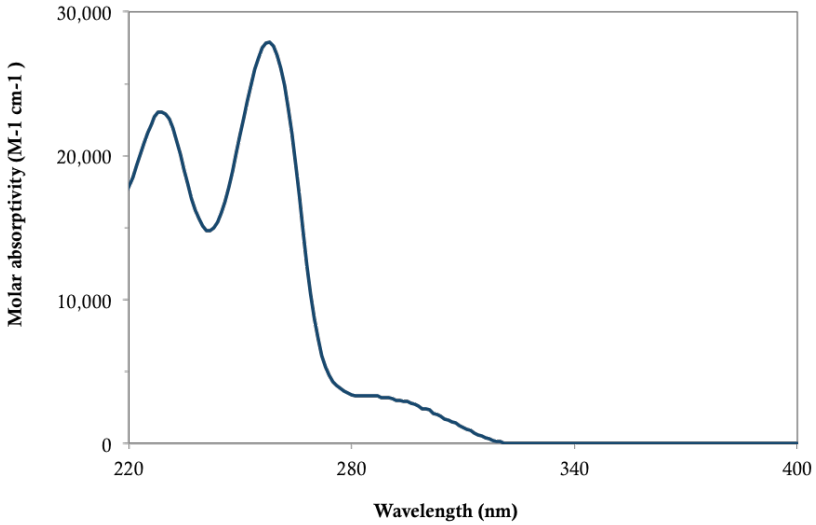


^{13}C-NMR Spectra (400 MHz, CD_3OD) **(3)**



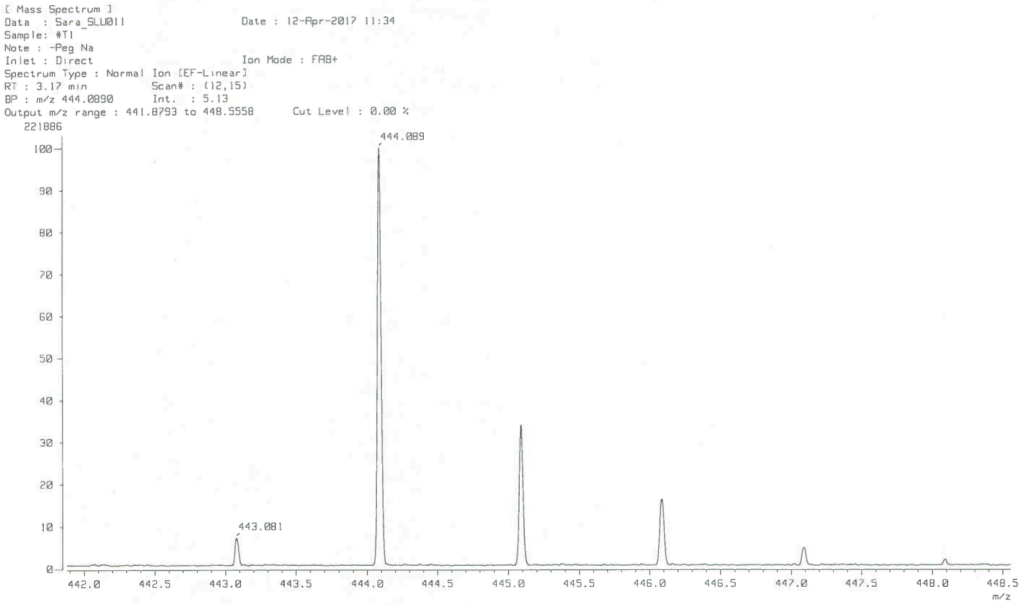
methanol (49.15 ppm)

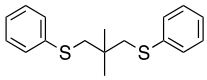
UV-Vis (in Acetonitrile) **(3)**



λ_{max} *= 258 nm; (second band at 228-229 nm)*

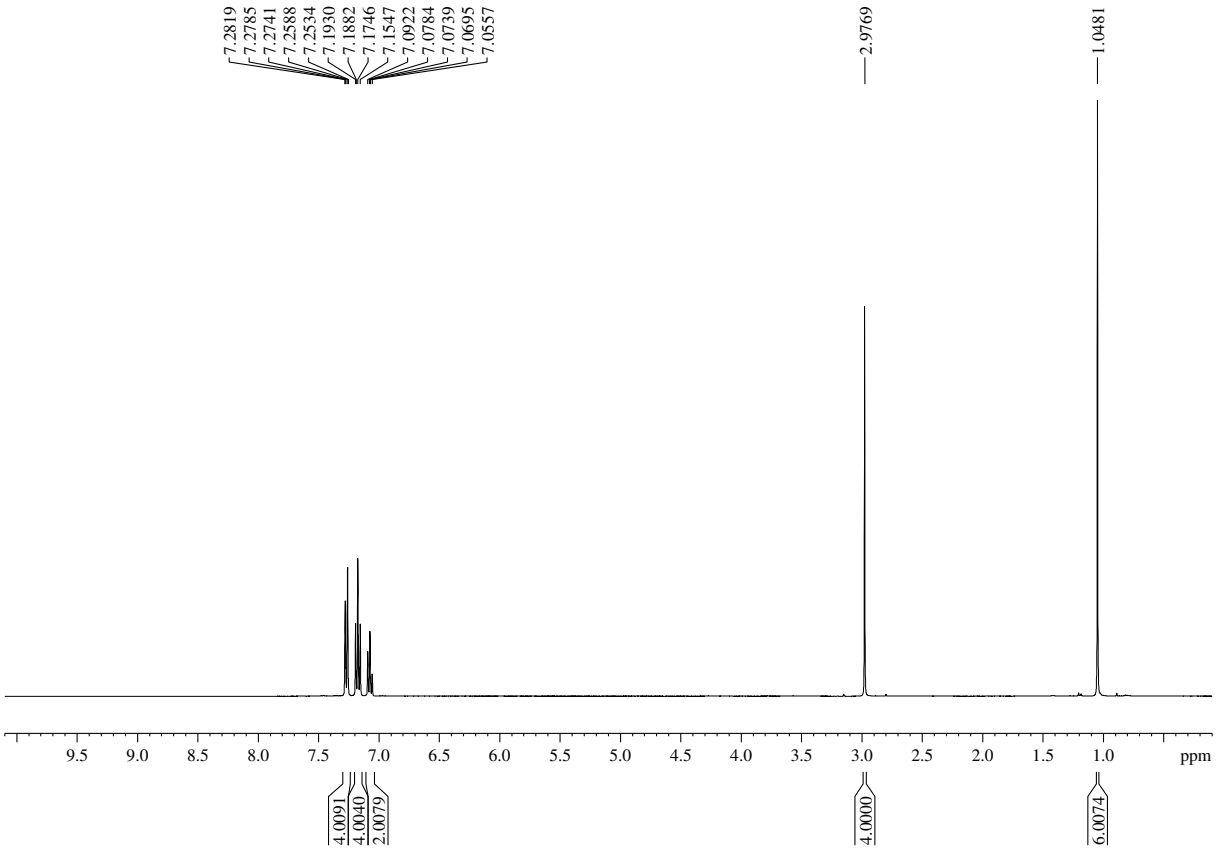
High Resolution MS Spectrum **(3)**



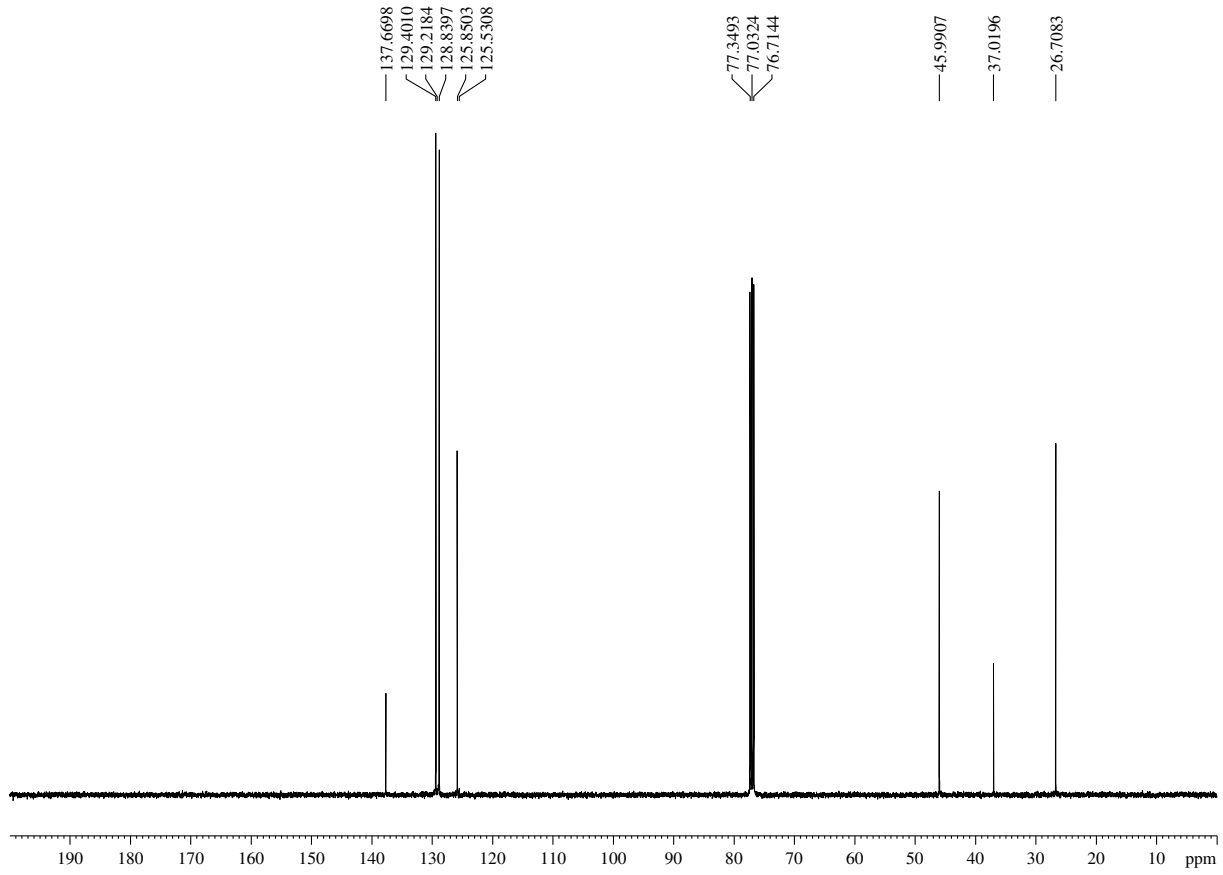


4a

^{1}H-NMR Spectrum (400 MHz, $CDCl_3$) **(4a)**

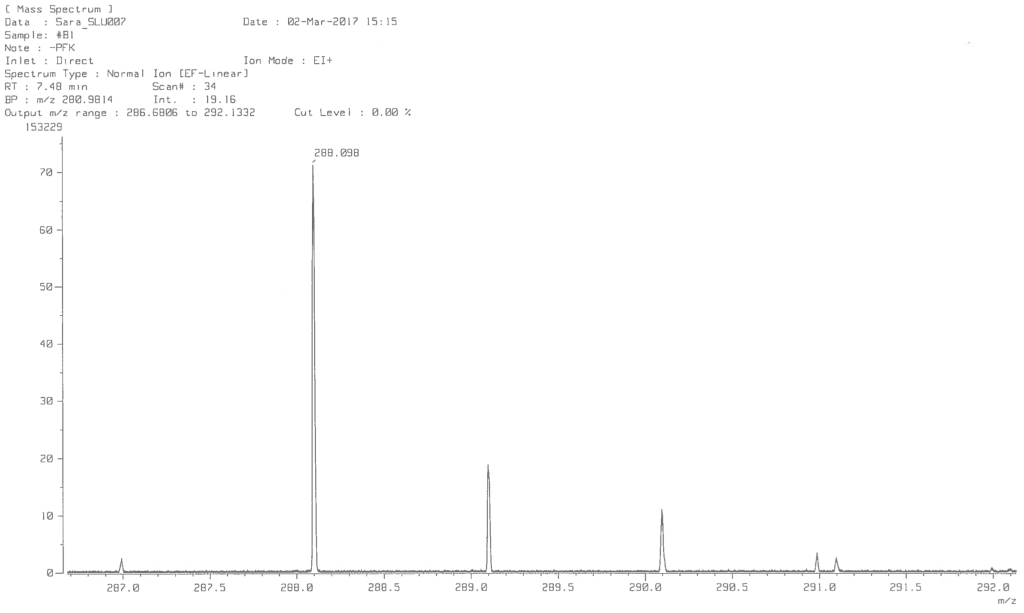


^{13}C-NMR Spectra (400 MHz, $CDCl_3$) **(4a)**



chloroform (77.2 ppm)

High Resolution MS Spectrum **(4a)**



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