Electron Accepting Naphthalene Bisimide Ligand Architectures for Modulation of π-π Stacking Nanocrystal Hybrid Materials

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Techniques

NMR. ^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on Bruker UNI500 or BIODRX500 NMR spectrometer. ^{1}H and ^{13}C chemical shifts (δ) are reported in ppm while coupling constants (J) are reported in Hertz (Hz). The multiplicity of signals in ^{1}H NMR spectra is described as "s" (singlet), "d" (doublet), "t" (triplet), "q" (quartet), "p" (pentet), "dd" (doublet of doublets) and "m" (multiplet). All spectra were referenced using solvent residual signals ($CDCl_3$: ^{1}H, δ 7.27 ppm; ^{13}C, δ 77.2 ppm).[1] Heteronuclear single quantum coherence (^{1}H-^{13}C HSQC) experiments were used to confirm NMR peak assignments. Reaction progress was monitored by thin-layer chromatography using silica gel coated plates or ^{1}H NMR. Compounds were purified by filtration, precipitation, crystallization or flash column chromatography using silica gel (Acros Organics, 90 Å, 35-70 μm) as indicated in corresponding procedures.

Mass Spectroscopy. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry was performed on Bruker Ultraflex III (Maldi-Tof-Tof) mass spectrometer using dithranol as the matrix.

Optical Extinction Spectra. Optical extinction spectra were collected using a Cary 5000 UV-VIS-NIR. Spectral band-pass was set to 2 nm and integration time to 0.5 s. Fluorescence spectra were acquired with an Edinburgh Instruments FLS1000 fluorescence spectrometer.

Electron Microscopy. TEM micrographs were collected using a JEOL 1400 microscope operated at 120 kV. The TEM was calibrated using a MAG*I*CAL® TEM calibration standard.

Cyclic Voltammetry. CVs were recorded on a Epsilon, Bioanalytical Systems Inc. workstation using a Ag/AgCl electrode as the reference electrode. 0.1 M solution tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane was used as the supporting electrolyte. The LUMO energy levels can be estimated by taking Fc/Fc^+ energy level to be 4.8 eV below the vacuum level and using the formula $E_{LUMO} = -4.8 - E_{1/2}{}^{1}{}_{red}$

Transient Absorption Measurements. Femtosecond transient absorption measurements were conducted using a Helios spectrometer. The output of regeneratively amplified Ti:sapphire laser (Coherent Libra, 50 fs, 1 kHz, 3.5 W) was split to generate the pump and probe beams. The pump beam wavelength was selected using an optical parametric amplifier. A broad-band white light continuum (WLC) probe from 340 - 700 nm was generated by focusing and attenuating an 800 nm pulse into an CaF_2 crystal window. The WLC was then split to detector and reference channels to correct for any fluctuations. The pump and probe beams were spatially overlapped at the sample position and the transient absorption signal was measured using a synchronized chopper (500 Hz) at a sequence of pump-probe time delays controlled by an optical delay stage. The FWHM at the

sample position were 150 μm for 535 nm pump, 190 μm for 400 nm pump, and ~90 μm for the probe. The QD solution was contained in 1 mm quartz cuvette for all the measurements.

Materials

Potassium Iodide (99 %) and p-toluenesulfonyl chloride (≥ 98 %) were purchased from Sigma-Aldrich and used without further purification. Methyl 3,4,5-trihydroxybenzoate (98 %), 1-bromodecane (97 %), 4-dimethylaminopyridine (≥ 99 %), naphthalene diimide (98 %), and lithium aluminum hydride (95 %) were purchased from Aldrich and used without further purification. 3,5-dihydroxybenzoate (97 %) and 2,2-dimethoxypropane (98 %) were purchased from Acros Organics. Thionyl chloride (> 98 %) was purchased from TCI and used without further purification. All chemicals were used as received. Sodium sulfate (anhydrous, reagent grade), silica gel (230-400 mesh, grade 60), triethyl amine (reagent grade), dimethylfomamide, tetrahydrofuran, methanol, hexanes, and ethyl acetate were purchased from Fisher Scientific and used without further purification. All solvents were ACS grade or higher. Dichloromethane was purchased from Fisher Scientific and was dried with activated molecular sieves (3A, 4 to 8 mesh, purchased from Acros Organics) before use.

Synthesis of QDs

CdSe Synthesis

Wurtzite CdSe nanocrystals were synthesized following a modified hot-injection literature procedure.[2] Briefly, 120 mg cadmium oxide (CdO), 560 mg octadecylphosphonic acid (ODPA), and 6 g of trioctylphosphonic acid (TOPO) were combined in a 50 ml flask and degassed at 150°C under vacuum for 20 min. The solution was then put under nitrogen and heated to 340°C to

facilitate the dissolution of CdO. Once clear and colorless, the flask was cooled back down to 150°C and kept under vacuum for an additional 45 minutes. Under nitrogen, the flask was heated to 360°C, during which 3 mL of trioctylphosphine (TOP) were injected. Once the temperature recovered to 360°C, 1 mL of a TOP-Se solution (700 mg Se in 5 mL TOP) was swiftly injected and the nanocrystals allowed to grow before the reaction was quenched and the solution rapidly cooled. The nanocrystals were washed by precipitation in ethanol and redispersion in toluene, followed by an additional wash with ethanol and isopropanol before a final redispersion in toluene.

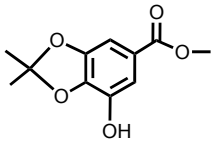
CdSe/CdSe Core/Shell Synthesis

The CdS shell was grown following a known literature procedure.[3] 100 nmol of CdSe seeds in toluene were mixed with 3 mL of 1-octadecene (ODE) and 3 mL oleylamine (OAm) and the solution was degassed under vacuum for 1 hour at room temperature and for an additional 20 minutes at 120°C. The flask was then put under nitrogen and heated to 310°C. Once the temperature reached 240°C, a dropwise injection of cadmium oleate and octanethiol in ODE was started at a rate of 3 ml/hr. The amount of Cd-oleate and octanethiol (1.2 molar equivalents) needed to grow the desired shell thickness was diluted in ODE for a total of 6 mL each. After the injections finished, 1 mL of oleic acid was rapidly injected and the solution kept at 310°C for an additional hour before the heating mantle was removed and the solution cooled and washed. The washing procedure was similar to that of the QDs, with two washes in ethanol and one in isopropanol, followed by redispersion in toluene.

Ligand Exchange with NBI Ligands

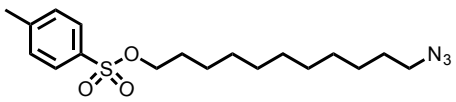
A solution of 10 mg of ligands dissolved in 3mL of chloroform was added to a 1 mL solution of 10 mg/mL oleic acid-capped NCs (QD@OA) in hexanes. The resulting mixture was stirred at 50 °C for 12 hours, after which it was quenched by addition of ethanol. The resulting precipitate was collected by centrifugation (8000 rpm, 3 min) and the supernatant liquid was discarded. The solid was redispersed in hexanes under ultrasonic irradiation (2 min) and precipitated by addition of ethanol. This step was repeated at least twice to remove any excess ligands.

Ligand Synthesis

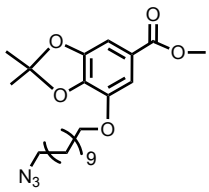


Methyl 7-hydroxy-2,2-dimethylbenzo[*d*][1,3]dioxole-5-carboxylate 1. A stirred solution of methyl gallate (5.00 g, 27.15 mmol) and 2,2-dimethoxypropane (10 g, 96.02 mmol) in dry toluene (35 mL) was fitted with a dean stark trap under nitrogen atmosphere. A catalytic amount of p-toluene sulfonic acid was added to the reaction solution, and the reaction was refluxed for 24 hours. After being cooled to room temperature, the reaction mixture was filtered, using $CHCl_3$ to rinse the remaining methyl gallate, and the filtrate was concentrated under reduced pressure. The crude product was purified with column chromatography (hexanes → 50% hexanes:EtOAc) to afford pure **1** as a red solid (2.97 g, 44 %). ^{1}H NMR (DMSO-d_6) δ 9.98 (s, 1H), 7.12 (d, J = 1.6 Hz, 1H), 6.87 (d, J = 1.6 Hz, 1H), 3.77 (s, 3H), 1.65 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 165.75, 148.12, 140.63, 138.11, 122.82, 119.32, 113.05, 101.04, 51.94, 25.50; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{11}H_{12}O_5Na$, 247.06; found 248.475.

11-azidoundecan-1-ol 2. Compound **2** was syntheized following previously reported literature.[5] ^{1}H NMR ($CDCl_3$) δ 3.49 – 3.41 (m, 2H), 3.14 (t, J = 6.8 Hz, 2H), 1.49 (t, J = 7.5 Hz, 2H), 1.43 (t, J = 7.1 Hz, 2H), 1.20 (d, J = 16.2 Hz, 14H); ^{13}C NMR ($CDCl_3$) δ 77.23, 62.39, 62.37, 51.32, 32.58, 29.48, 29.38, 29.36, 29.04, 28.72, 26.60, 25.70.

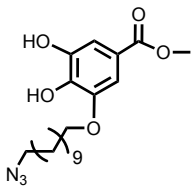


11-Azidoundecyl 4-methylbenzenesulfonate 3. Compound **3** was synthesized following previously reported literature.[6] ^{1}H NMR ($CDCl_3$) δ 7.67 (d, J = 6.9 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 3.91 (t, J = 6.5 Hz, 2H), 3.15 (t, J = 7.0 Hz, 2H), 2.34 (s, 3H), 1.56 – 1.44 (m, 4H), 1.25 (t, J = 8.2 Hz, 2H), 1.20 – 1.11 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 144.52, 133.23, 129.70, 127.72, 70.56, 51.32, 29.28, 29.23, 29.21, 29.00, 28.77, 28.72, 28.70, 26.58, 25.21, 20.81, 14.07.



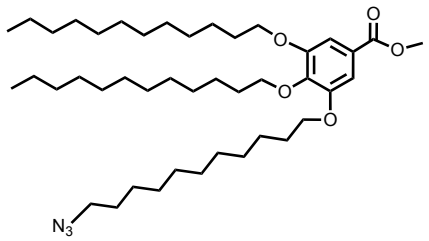
Methyl 7-((11-azidoundecyl)oxy)-2,2-dimethylbenzo[*d*][1,3]dioxole-5-carboxylate 4. To a stirred solution of **1** (0.70 g, 3.12 mmol) and **3** (1.72 g, 4.68 mmol) in DMF (45 mL) was added K_2CO_3 (1.29 g, 9.37 mmol) and KI (0.05 g, catalytic). The resulting mixture was stirred at 80 °C for 12 h, then cooled to room temperature, diluted with $CHCl_3$ (200 mL) and then washed with H_2O (2 x 100 mL) and 1 M HCl (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The product was utilized in the

subsequent step without further purification. For analysis purposes, a small amount of the crude product was purified with column chromatography (hexanes → 50% hexanes:EtOAc) to afford pure **4** as a red powder. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (s, 1H), 7.07 (s, 1H), 4.05 (t, *J* = 6.1 Hz, 2H), 3.83 (d, *J* = 1.7 Hz, 3H), 3.22 (t, *J* = 7.0 Hz, 2H), 1.78 (p, *J* = 6.8 Hz, 2H), 1.68 (d, *J* = 1.5 Hz, 6H), 1.55 (p, *J* = 7.6, 6.9 Hz, 2H), 1.41 (p, *J* = 7.4 Hz, 2H), 1.33 – 1.25 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.67, 148.39, 142.65, 139.69, 123.51, 119.86, 110.59, 103.70, 69.56, 52.10, 51.53, 29.57, 29.53, 29.41, 29.27, 29.22, 28.92, 26.79, 25.94; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{22}H_{33}O_5N_3Na$, 442.23; found 444.382.

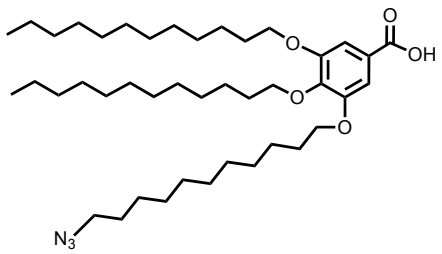


Methyl 3-((11-azidoundecyl)oxy)-4,5-dihydroxybenzoate 5. To a stirred solution of the crude product **4** (estimated 3.12 mmol), in CH_2Cl_2 (15 mL) was added trifluoroacetic acid dropwise until the solution maintained a dark red-brown color. This resulting mixture was stirred for 4 hours at room temperature before being concentrated under reduced pressure. The residue was dispersed in MeOH (35 mL) and concentrated under reduced pressure. This step was repeated twice more before the product crystallized out of MeOH. The crystals were obtained through filtration and washed with hexanes, resulting in pure **5** as red crystals (1.1 g, 93 %). ^{1}H NMR ($CDCl_3$) *δ* 7.32 (s, 1H), 7.19 (s, 1H), 4.08 (t, *J* = 6.6 Hz, 2H), 3.87 (s, 3H), 3.25 (t, *J* = 6.9 Hz, 2H), 1.81 (p, *J* = 6.5 Hz, 2H), 1.59 (p, *J* = 6.7 Hz, 2H), 1.44 (dt, *J* = 14.6, 7.2 Hz, 2H), 1.35 – 1.28 (m, 12H); ^{13}C NMR ($CDCl_3$) *δ* 167.19, 146.03, 143.60, 137.21, 121.89, 110.99, 105.86, 69.61, 52.29, 51.68, 29.65,

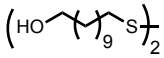
29.60, 29.47, 29.31, 29.30, 29.01, 26.88, 26.10; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{19}H_{29}O_5N_3Na$, 402.20; found 404.352.



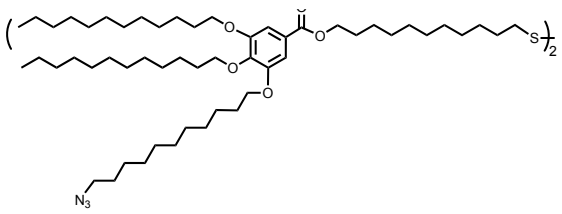
Methyl 3-((11-azidoundecyl)oxy)-4,5-bis(dodecyloxy)benzoate 6. To a stirred solution of **5** (1.20 g, 3.16 mmol) and 1-bromo dodecane (1.97 g, 7.91 mmol) in DMF (45 mL) was added K_2CO_3 (1.71 g, 12.65 mmol) and KI (0.05 g, catalytic). The resulting mixture was stirred at 80 °C for 12 h, then cooled to room temperature, diluted with $CHCl_3$ (200 mL) and then washed with H_2O (2 x 100 mL) and 1 M HCl (2 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The resulting oil was dissolved in the smallest amount of $CHCl_3$ (~2 mL), and the product was precipitated out of solution with cold MeOH, and subsequently filtered and dried to afford pure **6** as a yellow powder (1.43 g, 63%). ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 2H), 4.01 (q, J = 6.2 Hz, 6H), 3.87 (s, 3H), 3.24 (t, J = 7.0 Hz, 2H), 1.80 (p, J = 6.8 Hz, 4H), 1.73 (p, J = 7.0 Hz, 2H), 1.58 (p, J = 6.8 Hz, 2H), 1.47 (t, J = 7.7 Hz, 6H), 1.37 – 1.23 (m, 44H), 0.87 (t, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 167.03, 152.98, 152.97, 142.56, 124.82, 108.19, 108.17, 73.61, 69.31, 52.20, 51.63, 32.11, 32.10, 30.51, 29.92, 29.89, 29.86, 29.83, 29.80, 29.73, 29.68, 29.65, 29.56, 29.54, 29.52, 29.49, 29.47, 29.33, 29.02, 26.90, 26.26, 26.23, 22.86, 14.26; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{43}H_{77}O_5N_3Na$, 738.58; found 739.938.



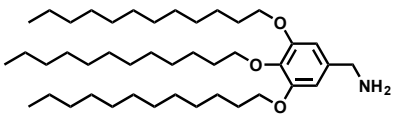
3-((11-Azidoundecyl)oxy)-4,5-bis(dodecyloxy)benzoic acid 7. To a stirred solution of **6** (0.5 g, 0.70 mmol) in THF (10 mL) was added KOH (0.12 g, 2.09 mmol), H_2O (2 mL), and MeOH (2 mL). The reaction mixture was stirred at 80 °C for 4 h. The solvents were evaporated under reduced pressure, and the resulting product was acidified with 1 M HCl before being extracted with chloroform (3 x 75 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure to yield **7** as a pure yellow powder (0.45 g, 92 %). ^{1}H NMR ($CDCl_3$) δ 7.33 (s, 2H), 4.03 (dt, J = 13.2, 6.5 Hz, 6H), 3.24 (t, J = 7.0 Hz, 2H), 1.82 (p, J = 6.7 Hz, 4H), 1.74 (p, 2H), 1.59 (p, J = 7.0 Hz, 2H), 1.48 (p, J = 7.5, 7.0 Hz, 6H), 1.37 – 1.24 (m, 44H), 0.88 (t, J = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 172.04, 153.00, 152.97, 143.30, 123.94, 108.74, 73.68, 69.33, 51.62, 32.11, 32.10, 30.51, 29.92, 29.90, 29.89, 29.87, 29.84, 29.81, 29.73, 29.65, 29.57, 29.54, 29.52, 29.47, 29.45, 29.33, 29.02, 26.90, 26.26, 26.22, 22.86, 14.26; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{42}H_{75}O_5N_3Na$, 724.56; found 726.849.



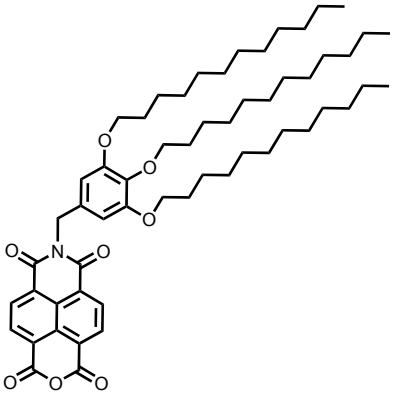
11,11'-disulfanediylbis(undecan-1-ol), 8. **8** was prepared following previously reported literature, the product is a white powder.[7] ^{1}H NMR ($CDCl_3$) δ 3.64 (t, J = 6.6 Hz, 2H), 2.68 (t, 2H), 1.67 (p, J = 7.3 Hz, 2H), 1.56 (p, 2H), 1.40 – 1.23 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 77.47, 77.22, 76.97, 63.29, 39.41, 33.00, 29.78, 29.72, 29.69, 29.63, 29.43, 28.72, 25.94.



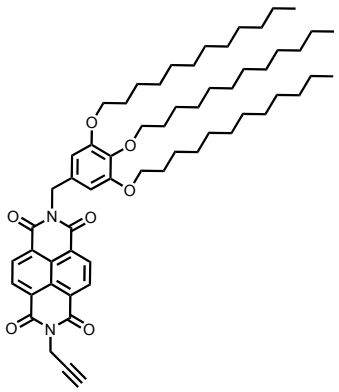
11-(Methylthio)undecyl 3-((11-azidoundecyl)oxy)-4,5-bis(dodecyloxy)benzoate 9. To an oven dried round bottom flask was added **7** (1.0 g, 1.42 mmol) and dry CH_2Cl_2 (20 mL). The solution was stirred for 10 min under nitrogen atmosphere before thionyl chloride (0.51 g, 4.27 mmol) was added, then the reaction mixture was stirred at room temperature for 3 h under nitrogen. The reaction mixture was then concentrated under reduced pressure, and the crude product was dissolved in dry CH_2Cl_2 (20 mL) and cooled to -10 °C. To the stirred solution was added **8** (0.26 g, 0.64 mmol), Et3N (0.62 g, 5.67 mmol, 0.85 mL), and DMAP (0.05 g, catalytic amount). The reaction mixture was allowed to warm up to room temperature and stirred overnight, then was washed with 1 M HCl (2 x 50 mL). The organic layer was dried over anhydrous Na2SO4, filtered, and the filtrate was concentrated under reduced pressure. The crude product was purified with column chromatography (100:1 hexanes:ethyl acetate) to afford pure **9** as a white solid (1.09 g, 96%). ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 2H), 4.28 (t, J = 6.8 Hz, 2H), 4.01 (t, J = 6.5 Hz, 6H), 3.25 (t, J = 7.0 Hz, 2H), 2.67 (t, 2H), 1.80 (p, 4H), 1.77 – 1.70 (m, 4H), 1.66 (p, 2H), 1.63 – 1.54 (m, 4H), 1.51 – 1.44 (m, 6H), 1.38 – 1.25 (m, 54H), 0.88 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 166.72, 152.98, 142.50, 125.27, 108.21, 73.70, 69.37, 65.36, 51.69, 39.33, 32.16, 32.15, 30.54, 29.97, 29.95, 29.94, 29.93, 29.91, 29.89, 29.86, 29.79, 29.76, 29.73, 29.72, 29.63, 29.61, 29.59, 29.52, 29.48, 29.43, 29.39, 29.06, 28.97, 28.76, 26.95, 26.31, 26.29, 26.28, 26.23, 22.92, 14.34; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{106}H_{192}O_{10}N_6S_2Na$,1796.40; found 1798.858.



(3,4,5-Tris(dodecyloxy)phenyl)methanamine 10. Compound **10** was synthesized following previously reported literature.[8] ^{1}H NMR ($CDCl_3$) δ 6.48 (s, 2H), 3.97 – 3.88 (m, 6H), 3.75 (s, 2H), 1.80 – 1.69 (m, 6H), 1.45 (p, J = 7.7, 7.1 Hz, 6H), 1.33 – 1.24 (m, 46H), 0.86 (t, J = 6.7 Hz, 9H); ^{13}C NMR ($CDCl_3$) δ 153.30, 138.50, 137.07, 105.49, 77.43, 73.46, 69.15, 46.83, 32.07, 32.05, 30.47, 29.89, 29.87, 29.83, 29.79, 29.77, 29.75, 29.58, 29.55, 29.52, 29.50, 26.28, 26.24, 22.81, 14.21; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{43}H_{81}O_3N_1Na$, 682.61; found 682.850.

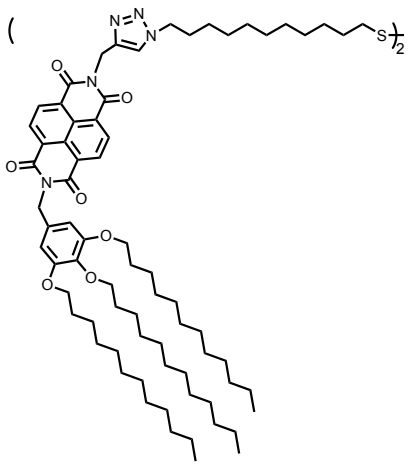


7-(3,4,5-Tris(dodecyloxy)benzyl)-1*H*-isochromeno[6,5,4-*def*]isoquinoline-1,3,6,8(7*H*)-tetraone 11.[9] To a microwave reaction vial was added naphthalene diimide (0.61 g, 2.27 mmol), **10** (0.50 g, 0.76 mmol), and dry DMF (3 mL). The suspension was sonicated until it became a homogeneous solution, and was then put under microwave irraditation for 5 minutes at 75 °C, followed by 15 minutes at 140 °C. The resulting reaction mixture was then suspended in acetone (10 mL), and a precipitate was formed upon the addition of 1 M HCl (5 mL). This precipitate was filtered and washed with H_2O (20 mL) followed by drying under vacuum. The resulting crude product was used without further purification, while mass spectrometry was used to confirm the product: MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{57}H_{83}NO_8Na$, 932.60; found 933.605.

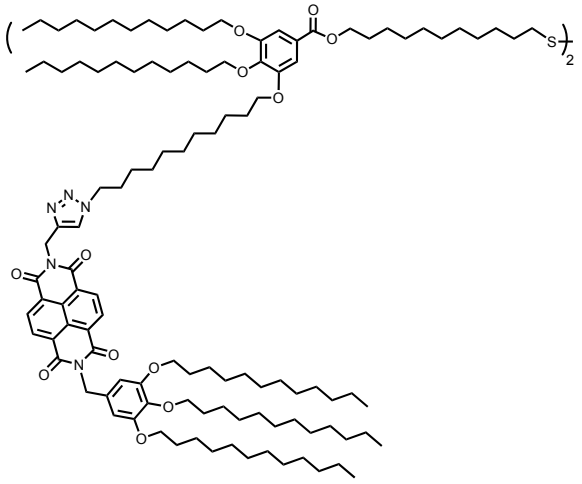


2-(Prop-2-yn-1-yl)-7-(3,4,5-tris(dodecyloxy)benzyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone 12. As for **11**. **11** (0.5 g, 0.55 mmol), propargyl amine (0.04 mL, 0.66 mmol), dry DMF (3 mL). The crude product was purified by column chromatography (hexanes → hexanes:CH_2Cl_2 1:1) to afford pure **12** as a red powder (0.41 g, 79 %). ^{1}H NMR ($CDCl_3$) δ 8.83 (s, 1H), 8.79 (d, J = 1.7 Hz, 3H), 6.80 (s, 2H), 5.27 (s, 2H), 4.99 – 4.97 (m, 2H), 3.96 (t, J = 6.5 Hz, 4H), 3.88 (t, J = 6.6 Hz, 2H), 2.23 (t, J = 2.6 Hz, 1H), 1.80 – 1.74 (m, 4H), 1.72 – 1.66 (m, 2H), 1.47 – 1.40 (m, 6H), 1.31 – 1.24 (m, 46H), 0.89 – 0.85 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 162.94, 162.24, 153.26, 138.30, 131.63, 131.60, 131.55, 131.37, 127.25, 127.02, 126.98, 126.83, 126.53, 108.60, 69.41, 44.47, 32.15, 30.54, 30.16, 30.12, 29.96, 29.93, 29.91, 29.89, 29.87, 29.83, 29.68, 29.66, 29.59, 26.34, 22.91, 14.33; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{60}H_{86}N_2O_7Na$, 969.63; found 971.104.

(11-azidoundecyl) disulfide 13. 13 was prepared following previously reported literature, the product is a white powder.[10] ^{1}H NMR ($CDCl_3$) δ 3.24 (t, J = 7.0 Hz, 2H), 2.66 (t, J = 7.4 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.62 – 1.53 (m, 2H), 1.38 – 1.31 (m, 4H), 1.30 – 1.25 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 77.23, 51.64, 39.34, 29.61, 29.37, 29.30, 29.00, 28.67, 26.87.



2-((1-(11-(Methylthio)undecyl)-1*H*-1,2,3-triazol-4-yl)methyl)-7-(3,4,5-tris(dodecyloxy)benzyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone 14. To a stirred solution of **13** (0.048 g, 0.11 mmol), **12** (0.25 g, 0.26 mmol), and a catalytic amount of $CuSO_4 \cdot 5H_2O$, in THF (3 mL) was added a catalytic amount of sodium ascorbate and H_2O (0.5 mL). The reaction mixture was stirred under microwave irradiation at 75 °C for 14 hours. The crude product was then diluted in $CHCl_3$ (100 mL), and washed with 6 M HCl (2 x 50 mL) then 1 M HCl (2 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The resulting product was precipitated out of cold MeOH to afford pure **15** as an orange solid (0.17 g, 67 % yield). ^{1}H NMR ($CDCl_3$) δ 8.67 (s, 4H), 7.24 (s, 1H), 6.44 (s, 2H), 5.36 (s, 2H), 5.22 (s, 2H), 3.91 (q, J = 7.0 Hz, 6H), 2.64 (t, J = 7.4 Hz, 2H), 1.79 – 1.71 (m, 8H), 1.65 – 1.59 (m, 4H), 1.49 – 1.41 (m, 8H), 1.33 – 1.25 (m, 54H), 0.87 (t, J = 6.7 Hz, 9H); ^{13}C NMR ($CDCl_3$) δ 162.94, 162.24, 153.26, 138.30, 131.63, 131.60, 131.55, 131.37, 130.70, 127.25, 127.02, 126.98, 126.83, 126.53, 122.90, 108.60, 73.67, 69.48, 54.85, 46.20, 39.32, 32.14, 30.55, 30.35, 30.22, 29.96, 29.95, 29.92, 29.90, 29.88, 29.86, 29.82, 29.65, 29.60, 29.58, 29.40, 29.18, 29.04, 29.00, 28.90, 27.08, 26.33, 26.32, 25.96, 25.46, 22.90, 22.40, 22.36, 14.31; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{142}H_{216}N_{10}O_{14}S_2Na$, 2372.58; found 2377.885.



11-(Methylthio)undecyl 3,4-bis(dodecyloxy)-5-((11-(4-((1,3,6,8-tetraoxo-7-(3,4,5-tris(dodecyloxy)benzyl)-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)methyl)-1*H*-1,2,3-triazol-1-yl)undecyl)oxy)benzoate 15. To a stirred solution of **9** (0.25 g, 0.14 mmol), **12** (0.28 g, 0.3 mmol), and a catalytic amount of $CuSO_4 \cdot 5H_2O$, in THF (3 mL) was added a catalytic amount of sodium ascorbate and H_2O (0.5 mL). The reaction mixture was stirred under microwave irradiation at 75 °C for 14 hours. The crude product was then diluted in $CHCl_3$ (100 mL), and washed with 6 M HCl (2 x 50 mL) then 1 M HCl (2 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and the filtrate was concentrated under reduced pressure. The resulting product was precipitated out of cold MeOH to afford pure **15** as an orange solid (0.51 g, 98 % yield). ^{1}H NMR ($CDCl_3$) δ 8.67 (s, 4H), 7.67 (s, 1H), 7.20 (s, 2H), 6.78 (s, 2H), 5.46 (s, 1H), 5.22 (s, 2H), 4.25 (t, J = 6.8 Hz, 4H), 4.01 – 3.91 (m, 10H), 3.85 (t, J = 6.6 Hz, 2H), 2.64 (t, J = 7.4 Hz, 2H), 1.86 (s, 1H), 1.82 – 1.70 (m, 12H), 1.68 – 1.61 (m, 4H), 1.47 – 1.38 (m, 14H), 1.33 – 1.22 (m, 102H), 0.86 (t, J = 6.8 Hz, 15H); ^{13}C NMR ($CDCl_3$) δ 166.45, 162.72, 162.43, 153.03, 152.77, 142.24, 137.91, 131.53, 131.13, 131.06, 126.75, 126.69, 126.64, 126.49, 125.06, 108.26, 107.95, 107.91, 73.47, 73.38, 69.14, 69.11, 65.17, 44.23, 39.14, 32.00, 30.38, 29.82, 29.79,

29.76, 29.74, 29.72, 29.68, 29.63, 29.60, 29.58, 29.53, 29.49, 29.45, 29.37, 29.32, 29.26, 29.08, 28.81, 28.59, 26.20, 26.18, 26.13, 26.09, 22.77, 14.20; MALDI-TOF (m/z): $[M+Na]^+$ calcd. for $C_{226}H_{364}N_{10}O_{24}S_2Na$, 3689.69; found 3694.997.

Additional Figures

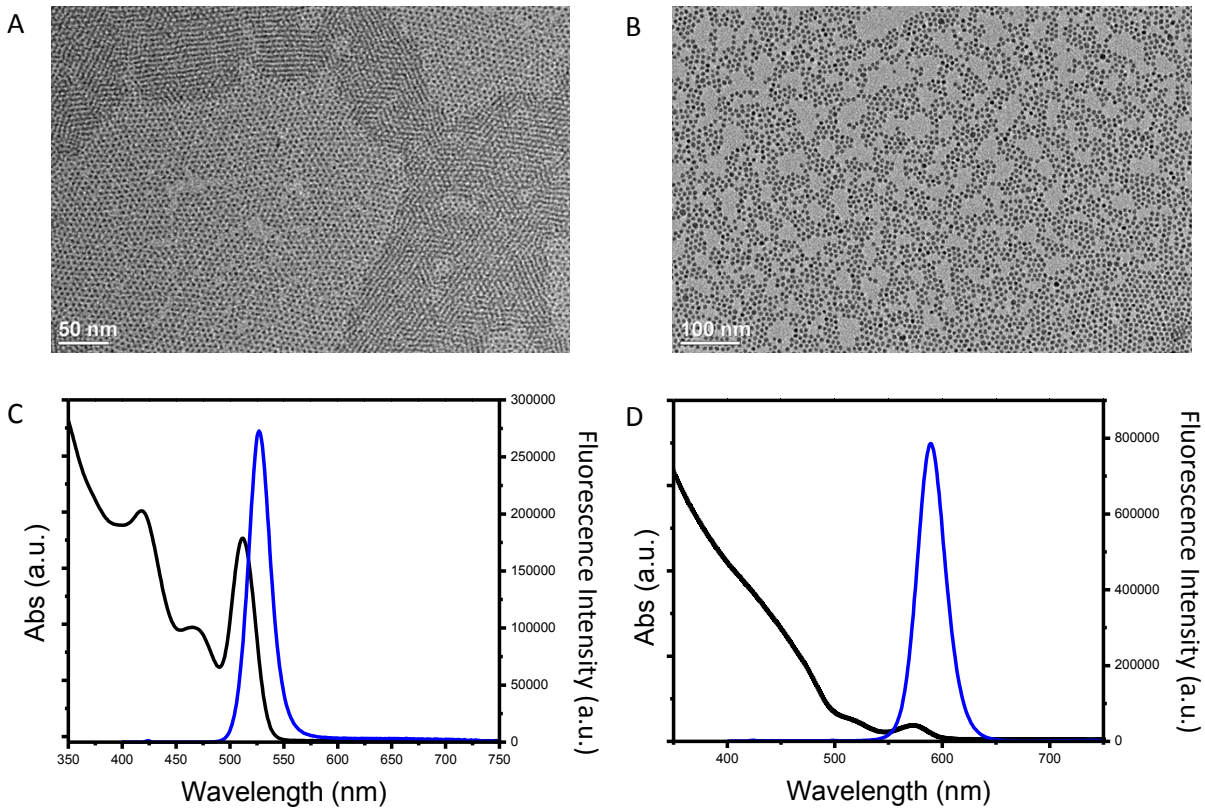


Figure S1. TEM images of as-synthesized (a) CdSe and (b) CdSe/CdS QDs; with associated absorbance and fluorescence spectra for as-synthesized (c) CdSe and (d) CdSe/CdS.

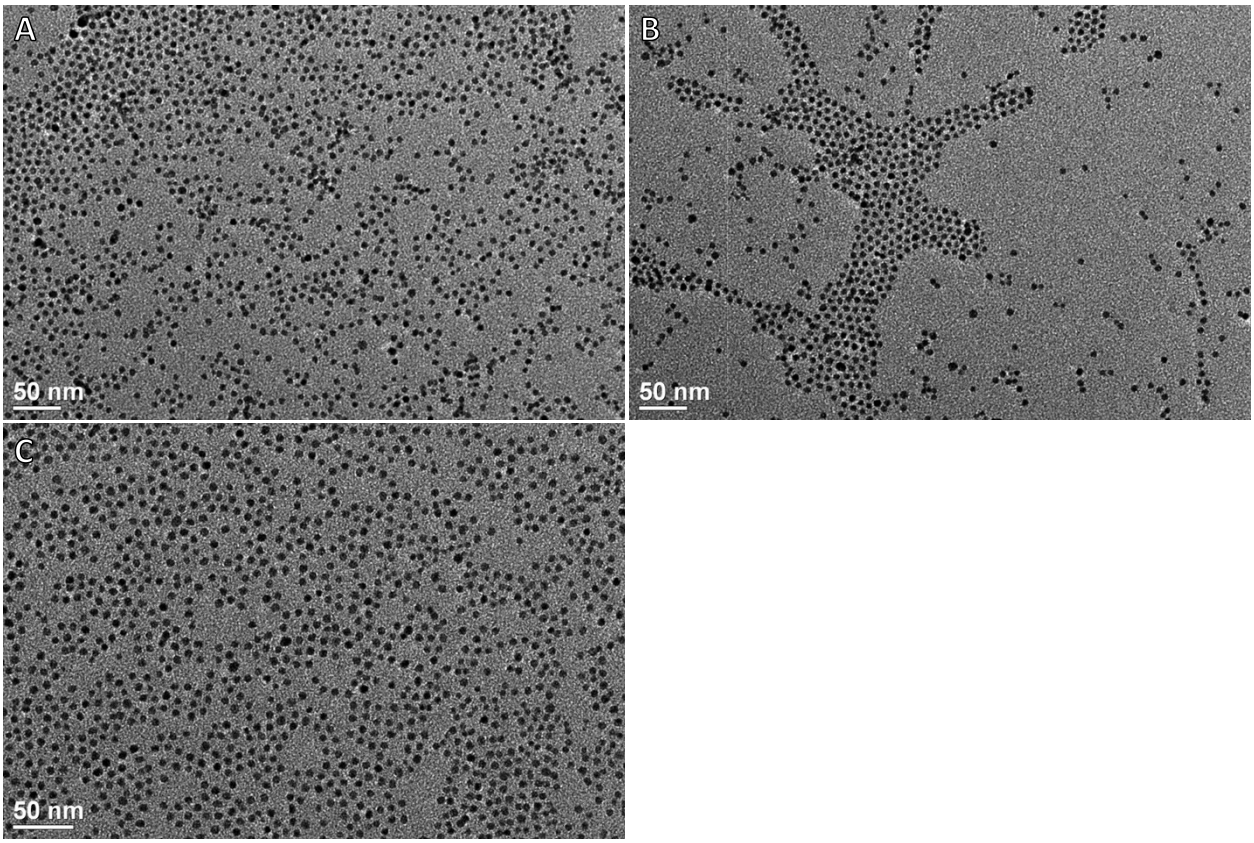


Figure S2. TEM images of CdSe/CdS after ligand exchange: (a) QD@CD, (b) QD@NBI1, (c) QD@NBI2.

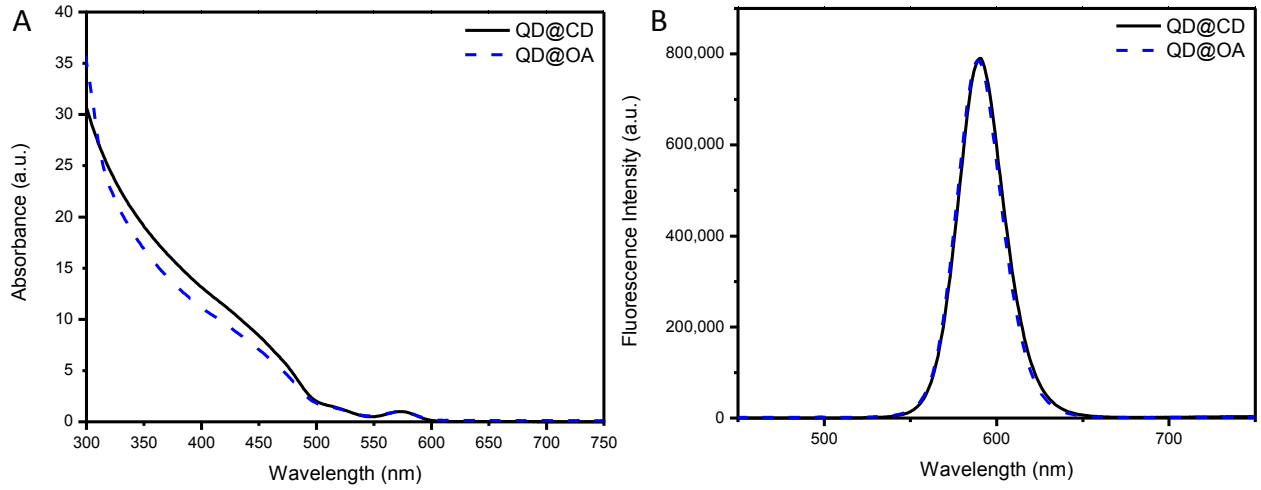


Figure S3. (a) Normalized absorbance and (b) fluorescence spectra of QD@CD and QD@OA.

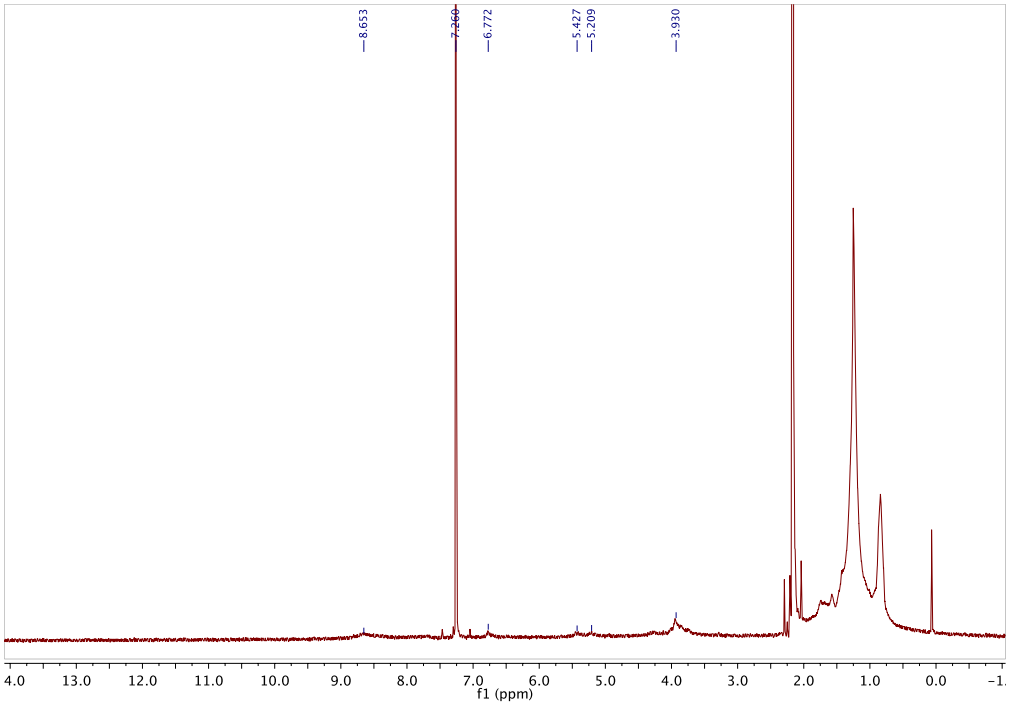


Figure S4. ^{1}H NMR of QD@NBI1-50%, highlighting the OA peak at 5.427 ppm, and signature peaks from the NBI1 ligand at 8.653, 6.772, 5.209, and 3.930 ppm.

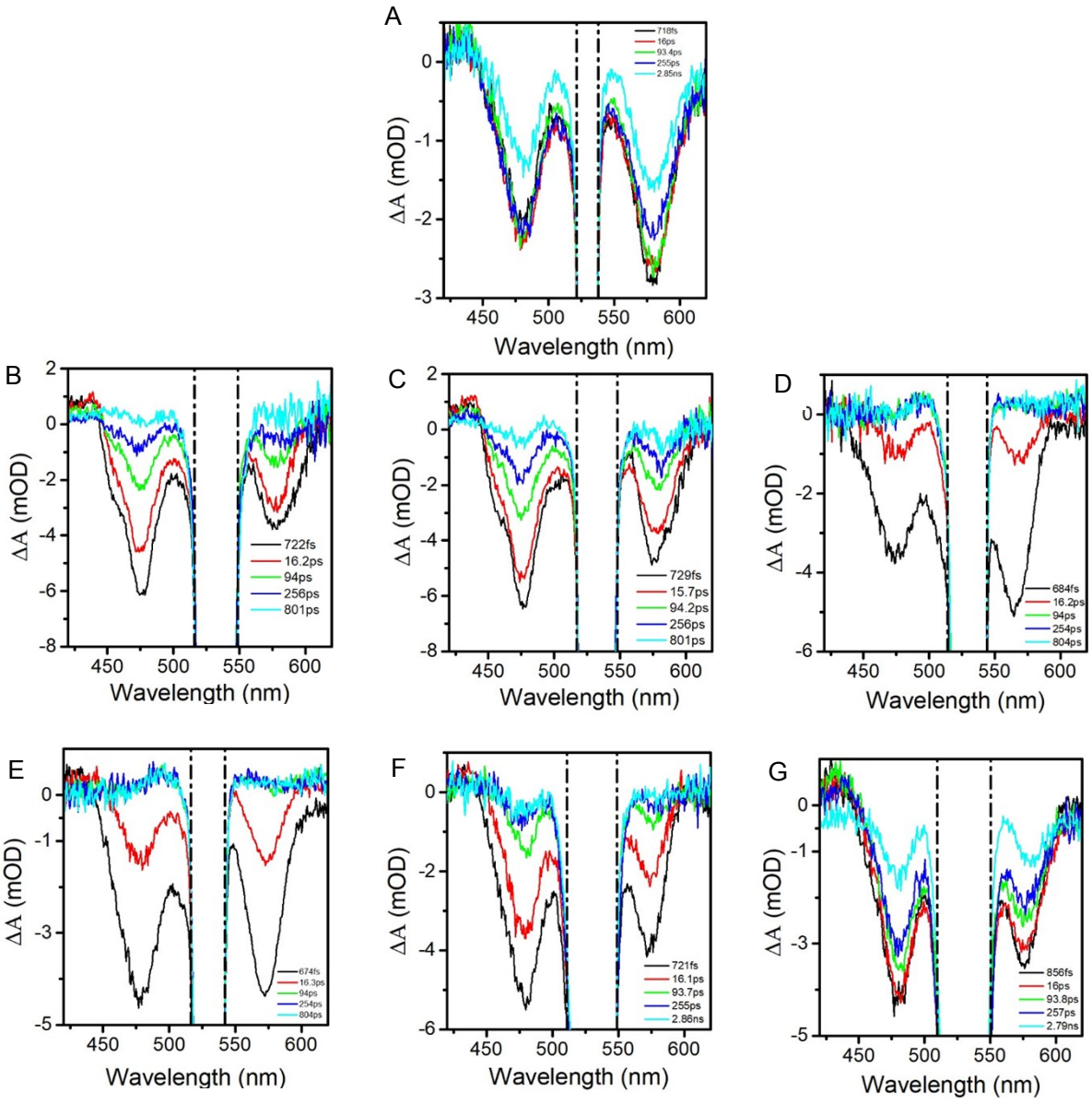


Figure S5. Transient absorption spectra of A) QD@CD, B) QD@NBI1-15%, C) QD@NBI1-19%, D) QD@NBI1-32%, E) QD@NBI1-53%, F) QD@NBI1-100%, and G) QD@NBI2-100% photoexcited with 535nm pump. The gap around 535nm corresponds to the scattered light from the pump.

Estimation of average exciton per QD

We estimate the average number of excitons per QD following a previously reported approach.[4] In short, we measure the pump fluence dependence of the exciton bleach amplitudes (~570 nm in Figure S4a; denoted as 1S in the main text) at long delay times (~3 ns) by which all multiexcitons have decayed. The QD@CD was used so that no effects from charge transfer are expected. We assume that the amplitude of the bleach scales with the excitons present, and can be governed by Poisson statistics:

$$P(n) = \frac{< N >^{n} e^{-< N >}}{n!}$$

Where <N> is the average excitons per QD which is proportional to the pump fluence: <N> = σI, where σ is the absorption cross section and I is the pump fluence. At long delay times, the exciton bleach amplitude is proportional to the number of excitons and can be estimated as follow:

$$\left|\Delta A_{3ns}(\lambda)\right| = \alpha(\lambda) P_1 = \alpha(\lambda)\left[1 - P_0\right] = \alpha(\lambda)[1 - e^{-< N >}]$$

Where $\alpha(\lambda)$ is a scaling factor and P_1 and P_0 are the Poisson probabilities of finding 1 and 0 excitons. By fitting the $\left|\Delta A_{3ns}(\lambda)\right|$ data to the above equation, we can obtain the absorption cross section for the 535 nm pump and use that to calculate the average excitons per QD for any given pump fluence.

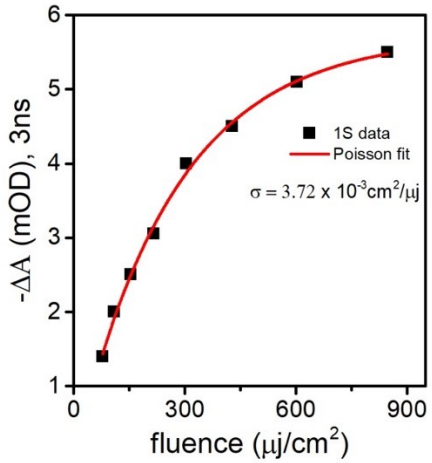


Figure S6. Exciton bleach amplitudes at long delay time as a function of 535nm pump fluence for QD@CD.

The fluence was measured using an effective area of the overlap of the pump and the probe, using the following equation:

$$A_{eff} = \frac{\pi}{\ln(2)}(FWHM_{pump}^{2} + FWHM_{probe}^{2})$$

A FLIR Blackfly photodiode camera was used to capture the pump and probe profile and a Gaussian function was used to extract the FWHM of the pump and probe beams.

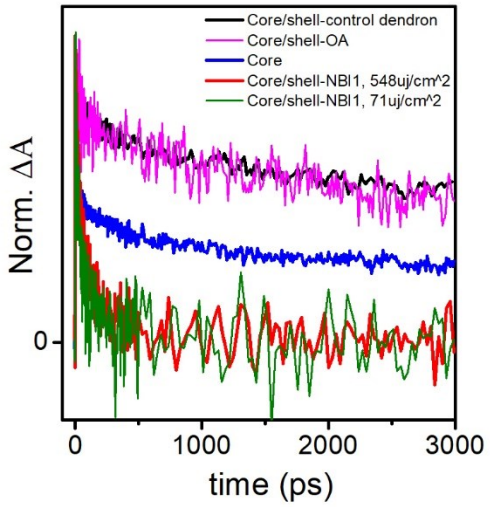


Figure S7. Normalized kinetic at the 1S state for different structures. Enhanced carrier lifetime for the core/shell-control dendron structure compared to just the core structure by passivating the surface defects using CdS shell. Also, for all the experiments we are making sure that the excitation condition is in the linear regime (<N> <1) where the Auger recombination is minimized, as we can see, the dynamics for core/shell-NBI1 for two different fluence conditions remain invariant, but faster than the control sample due to charge transfer from QD into NBI1.

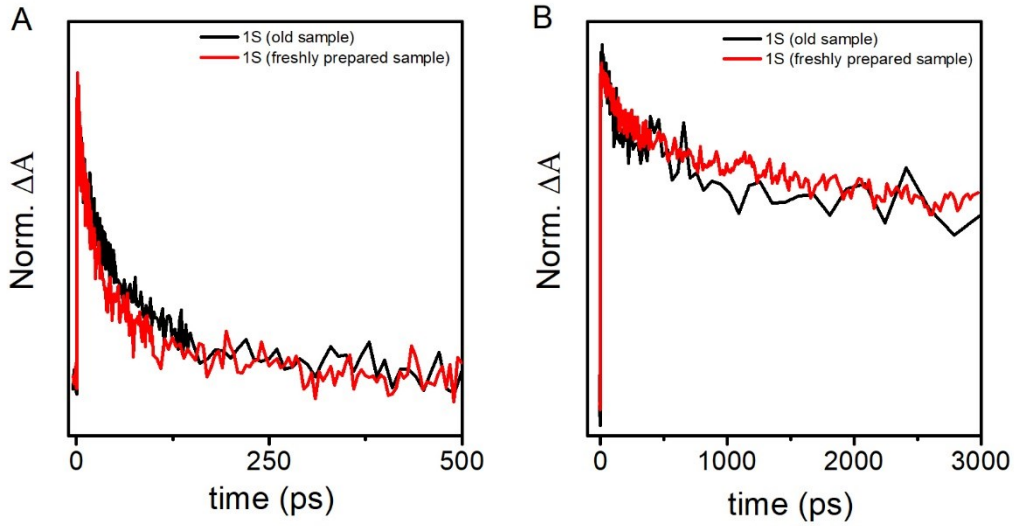


Figure S8. 1S kinetic for A) QD@NBI1-100% and B) QD@CD old vs freshly prepared solution. The dried-out solution (After 1 month for QD@NBI1-100% and 5 months for QD@CD) was redispersed in chloroform and was tested under the same experimental condition. The 1S kinetic for both old and freshly prepared solution showed no significant difference in dynamics, which indicates the sample stability over 1 month.

Table S1. Time constants (τ_i) and their corresponding coefficients (α_i) extracted from multi-exponential fit of 1S kinetic (Figure 4a) of QD@CD, QD@NBI2 (100%) and QD@NBI1 (100%).

Sample	τ_1 (α_1)	τ_2 (α_2)	τ_3 (α_3)	$\tau^*_{average}$
QD@CD	251.6 ps ±15.5 ps (0.21 ± 0.006)	11.1ns ± 0.6 ns (0.79 ± 0.006)	-	11 ns
QD@NBI2 (100%)	24.3 ps ± 12.3 ps (0.14 ± 0.046)	207 ps ± 69 ps (0.3 ± 0.04)	4.3 ns ± 0.7 ns (0.56 ± 0.038)	4.2 ns
QD@NBI1 (100%)	18.2 ps ± 1.4 ps (0.63 ± 0.03)	144.2 ps ± 15.5 ps (0.37 ± 0.03)	-	122 ps
QD@NBI1 (53%)	3 ps ± 0.7 ps (0.17 ± 0.02)	16.6 ps ± 0.3 ps (0.83 ± 0.02)	-	16 ps
QD@NBI1 (32%)	3.8 ps ± 0.6 ps (0.35 ± 0.05)	12.9 ps ± 0.6 ps (0.65 ± 0.06)	-	12 ps
QD@NBI1 (19%)	36.4 ps ± 3.4 ps (0.49 ± 0.04)	217.6 ps ± 18.5 ps (0.51 ± 0.04)	-	192 ps
QD@NBI1 (15%)	75.6 ps ± 4.9 ps (0.59 ± 0.03)	562.5 ps ± 40.8 ps (0.41 ± 0.03)	-	483 ps

*The average time constant is calculated as: $$\tau_{average} = \frac{\sum_{i=1}^{n} \alpha_i \tau_i^2}{\sum_{i=1}^{n} \alpha_i \tau_i}$$.

References:

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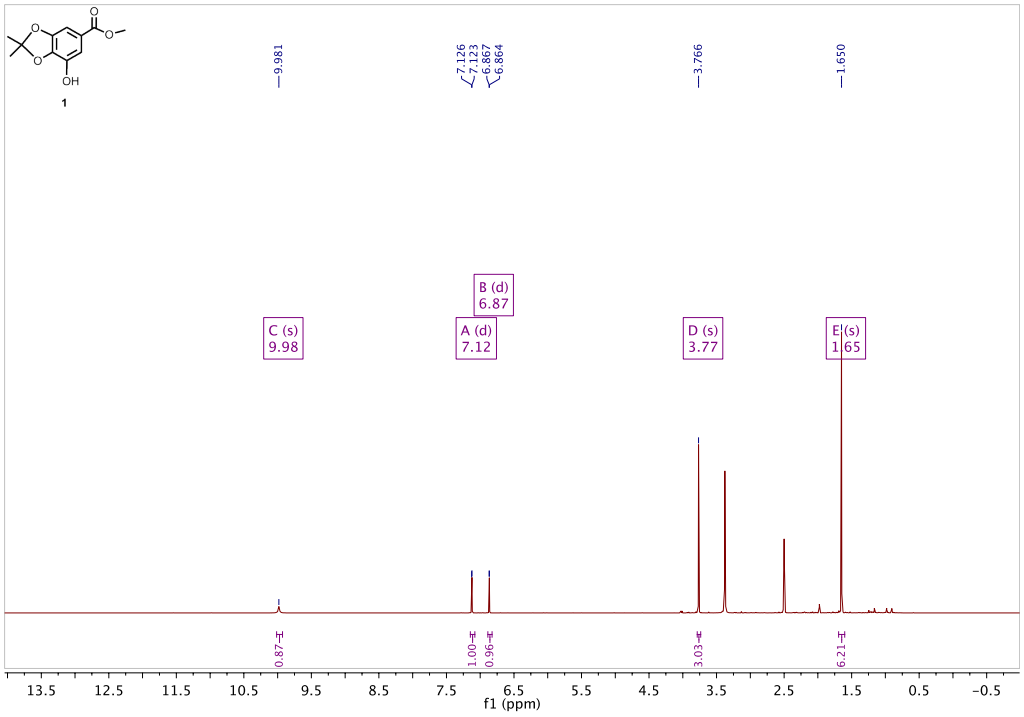
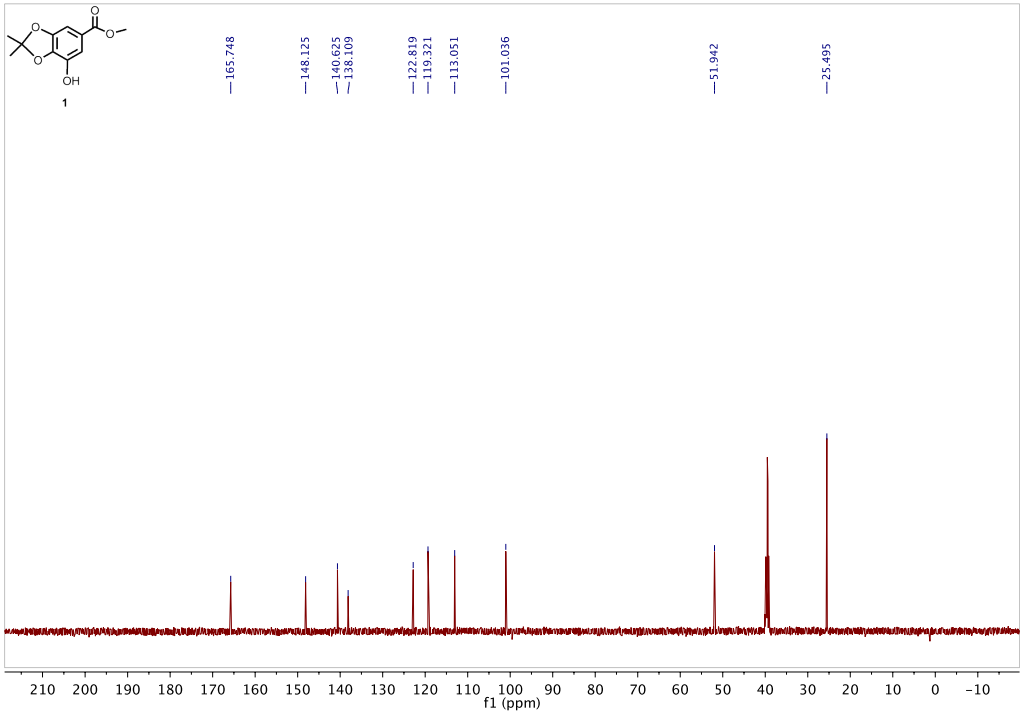
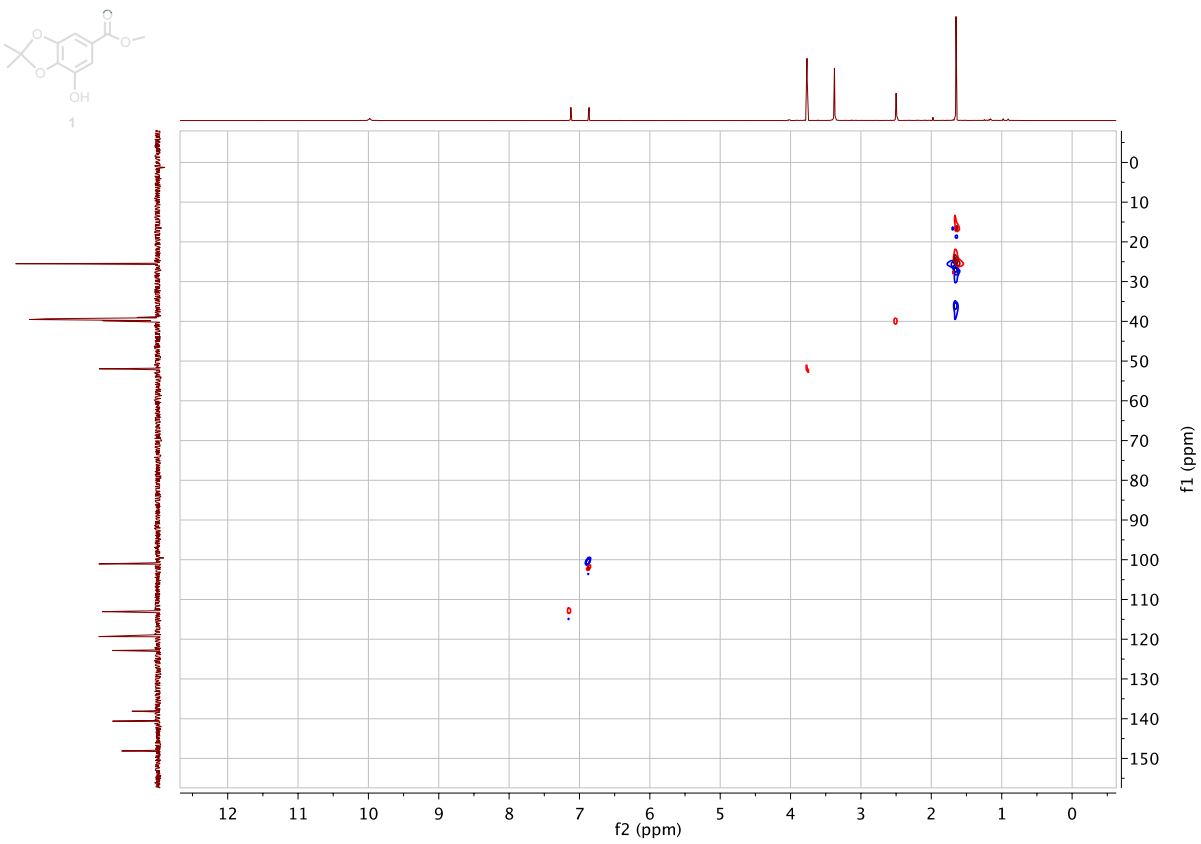
Copies of ^{1}H, ^{13}C, and HSQCs



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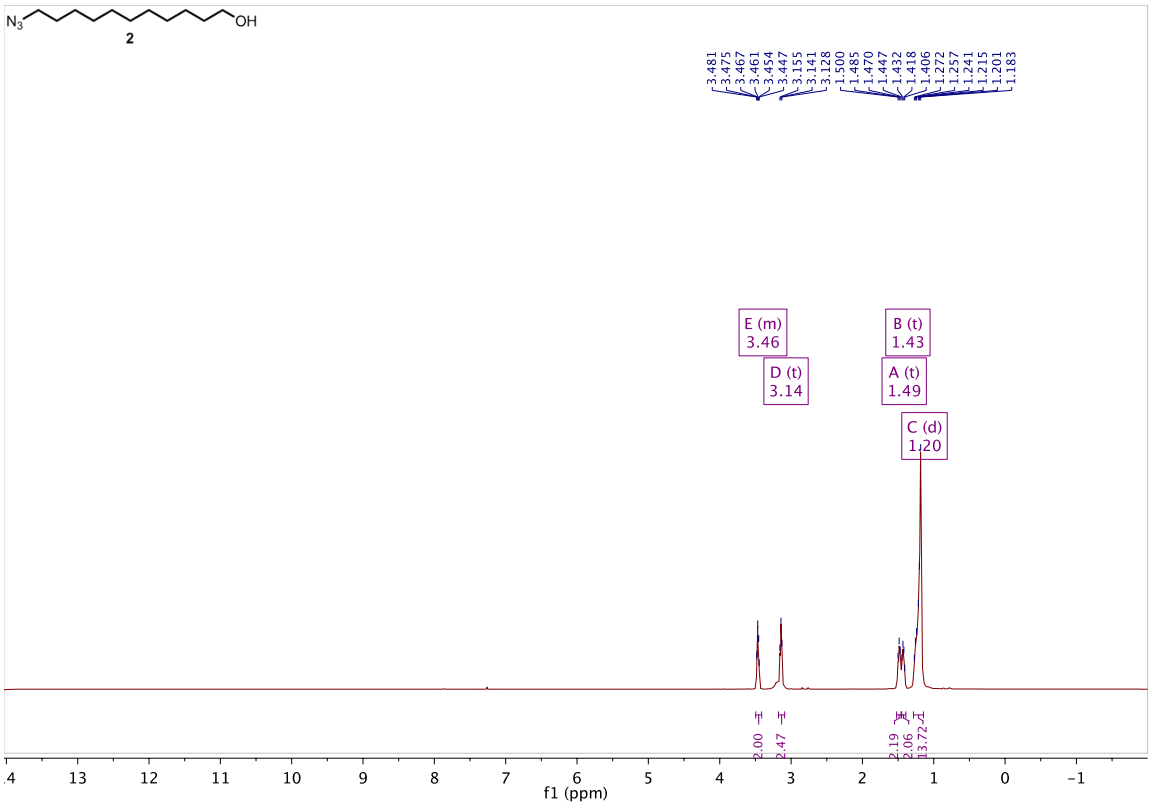
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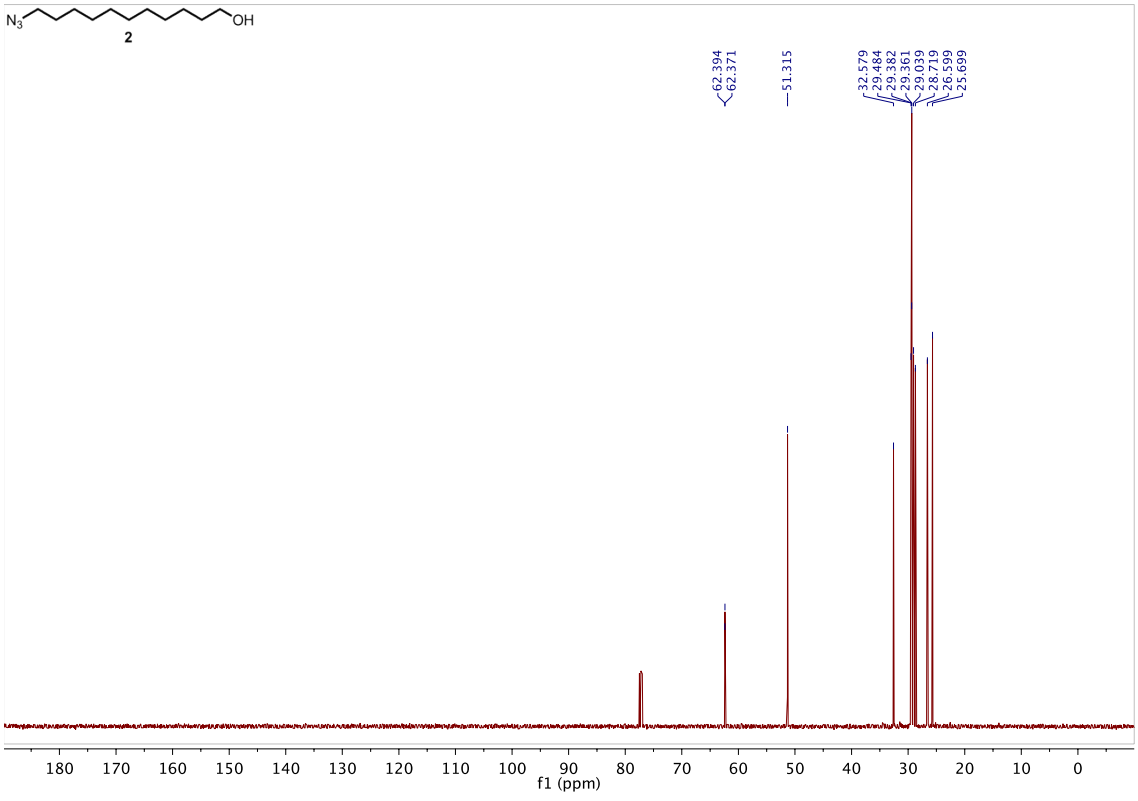
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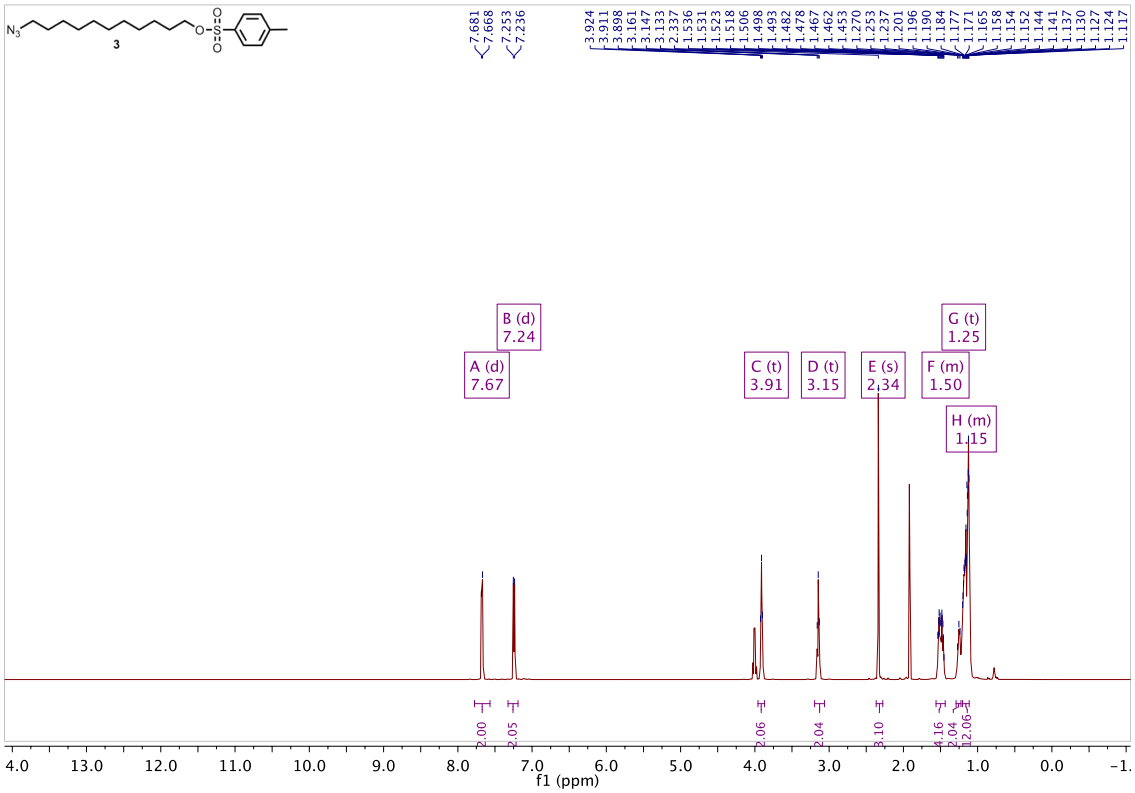
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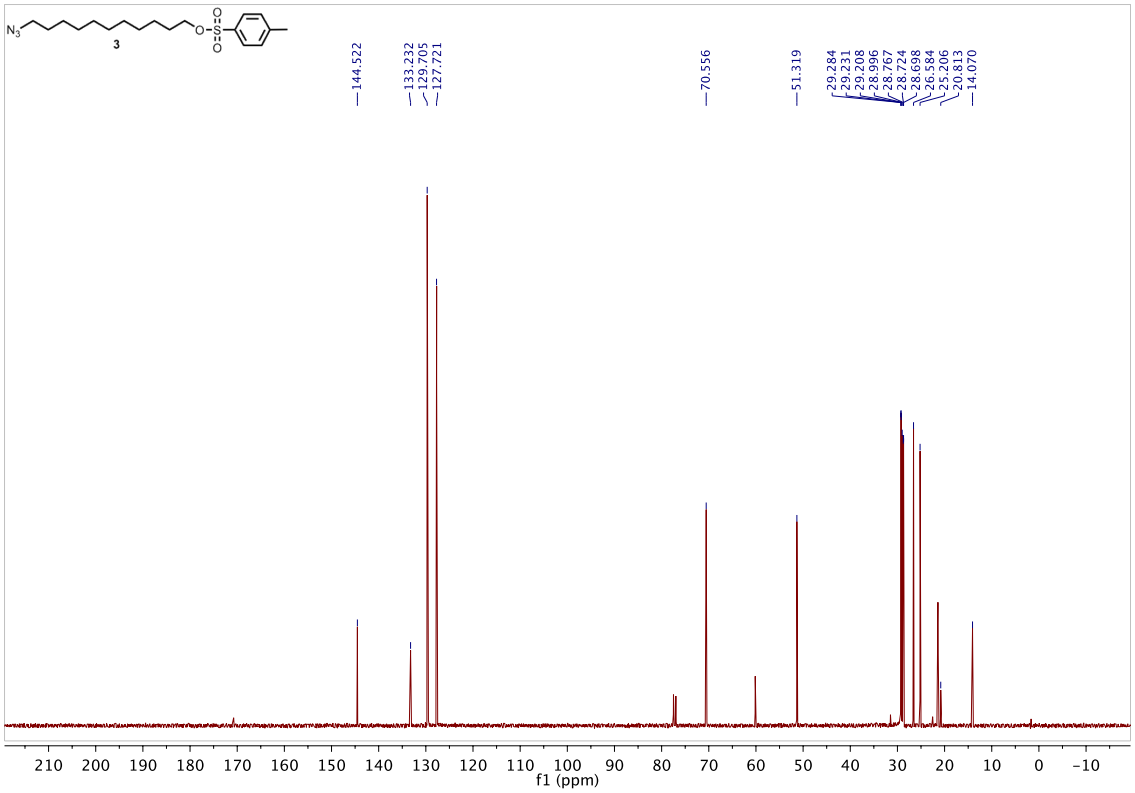
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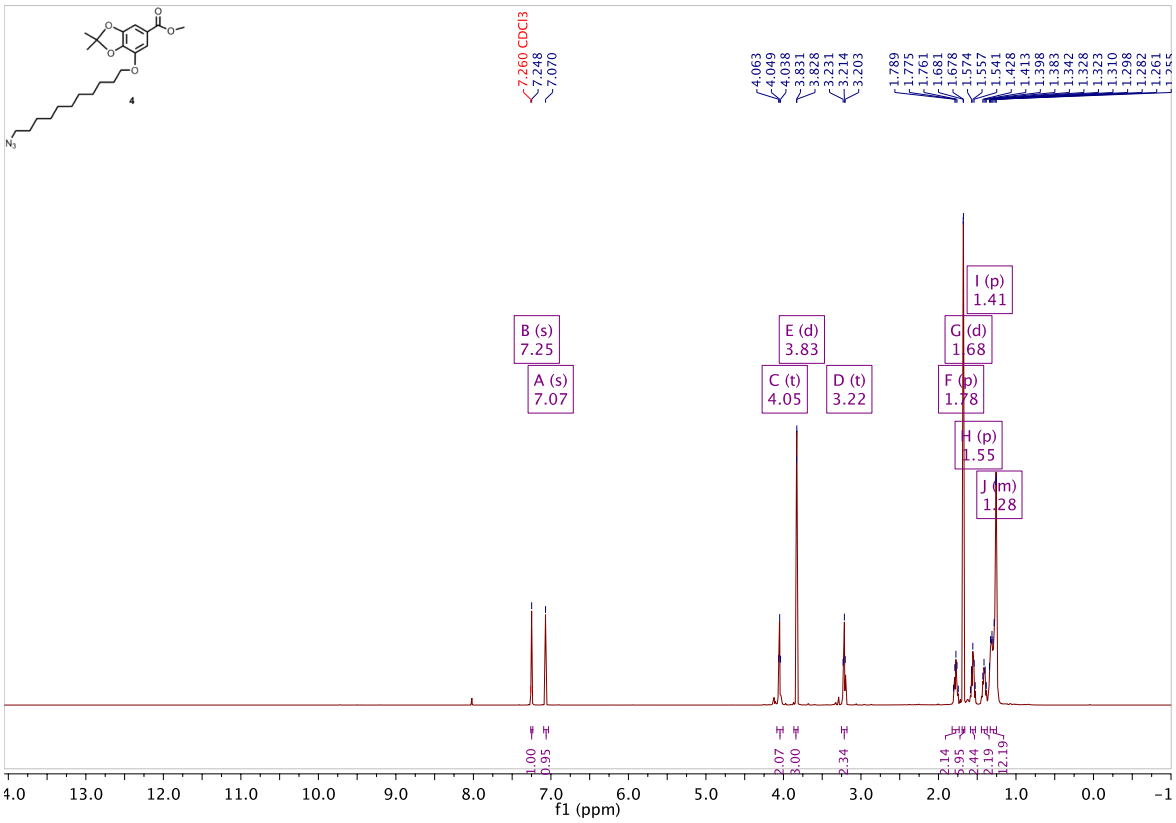
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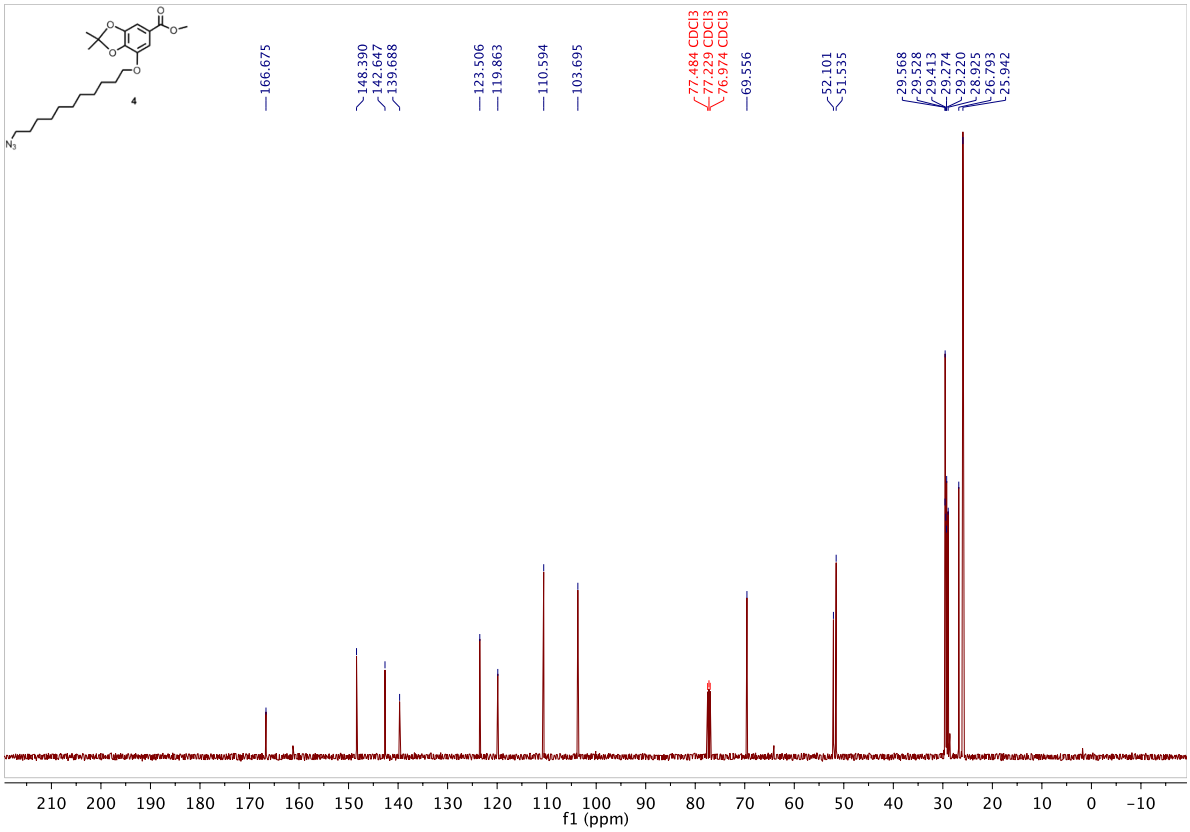
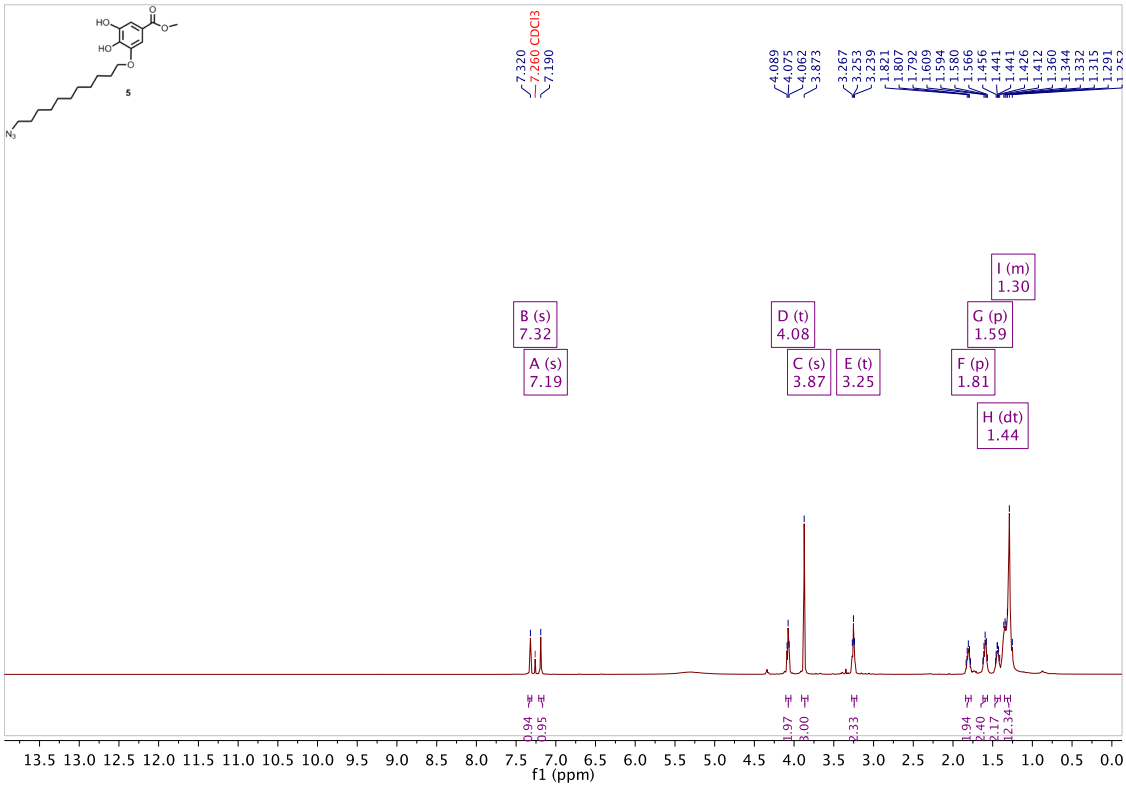
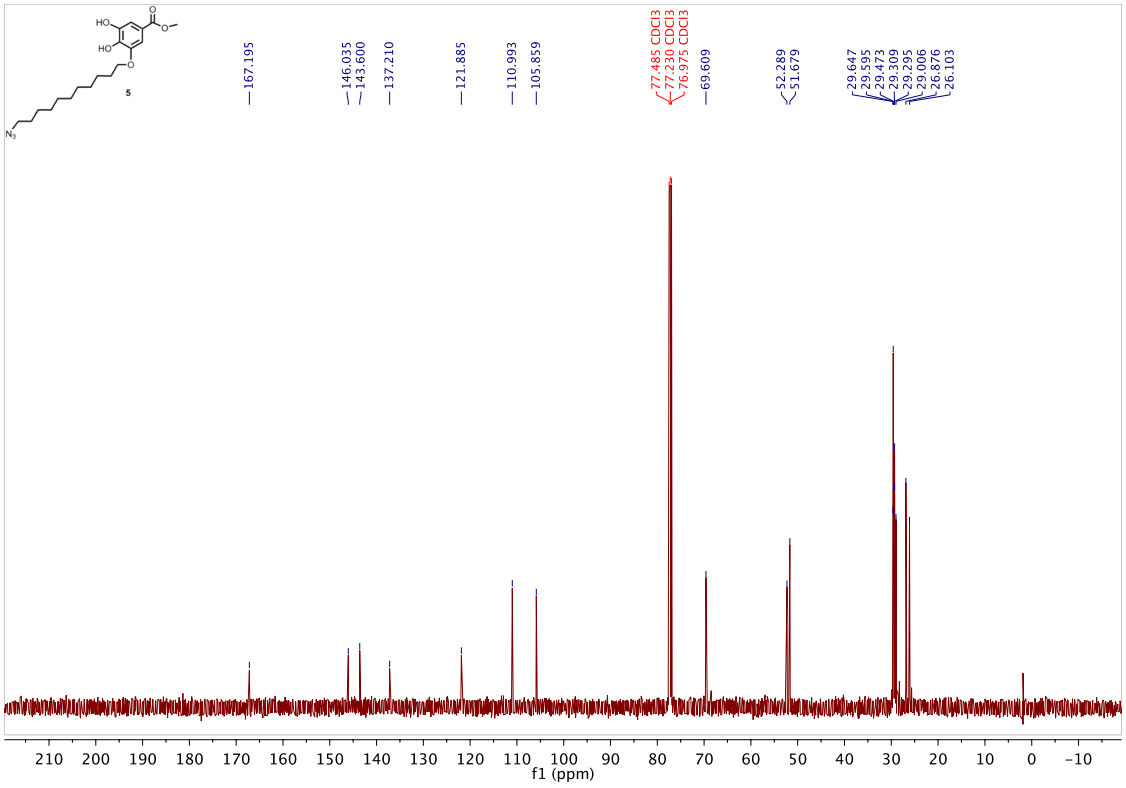
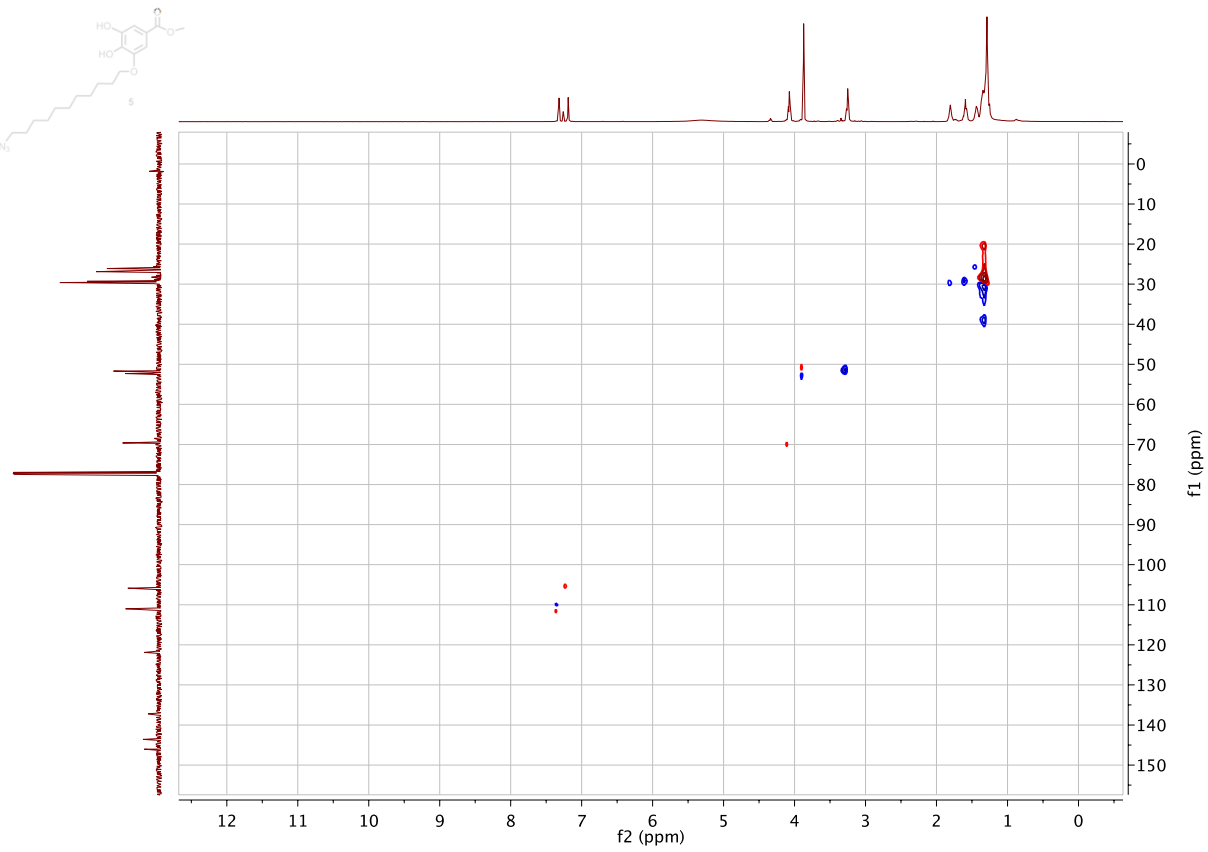
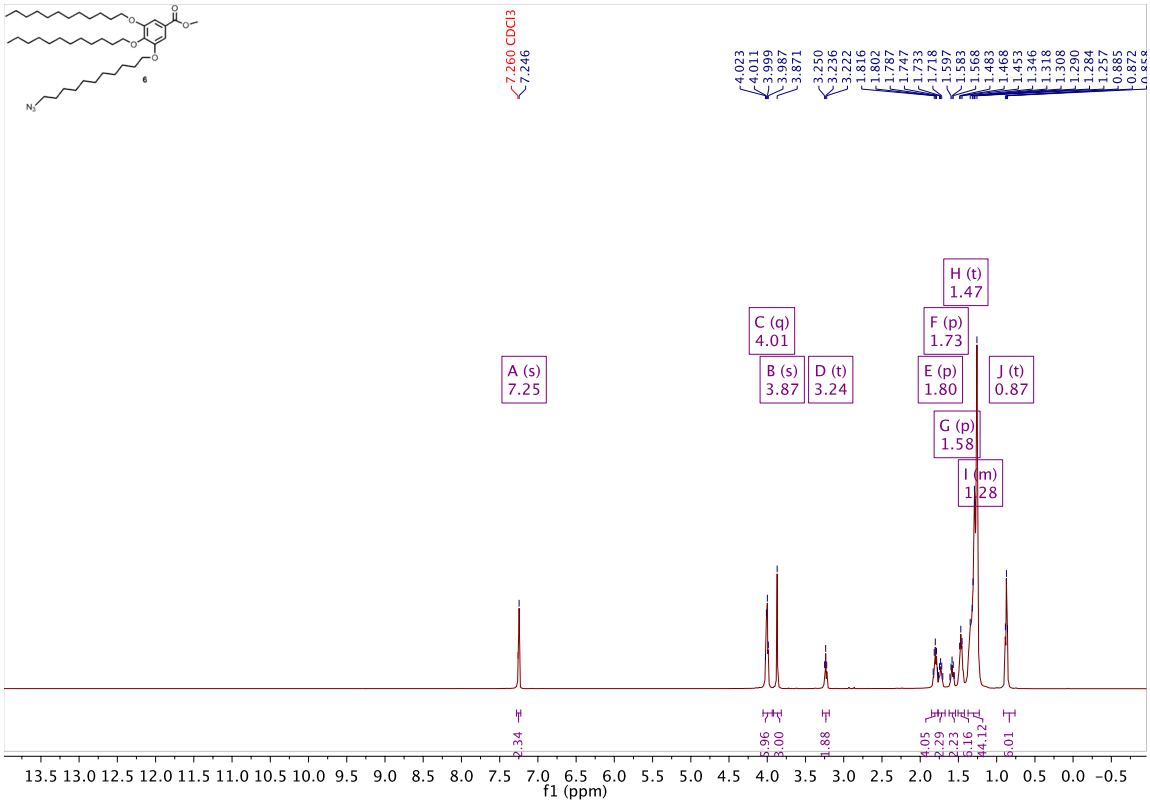
1.323
1.310
1.298
1.282
1.261
B (s)
7.25
A (s)
7.07
E (d)
3.83
C (t)
4.05
D (t)
3.22
I (p)
1.41
G (d)
1.68
F (p)
1.78
H (p)
1.55
J (m)
1.28
1.00
0.95
2.07
3.00
2.34
2.14
5.95
2.44
2.19
12.19
f1 (ppm)

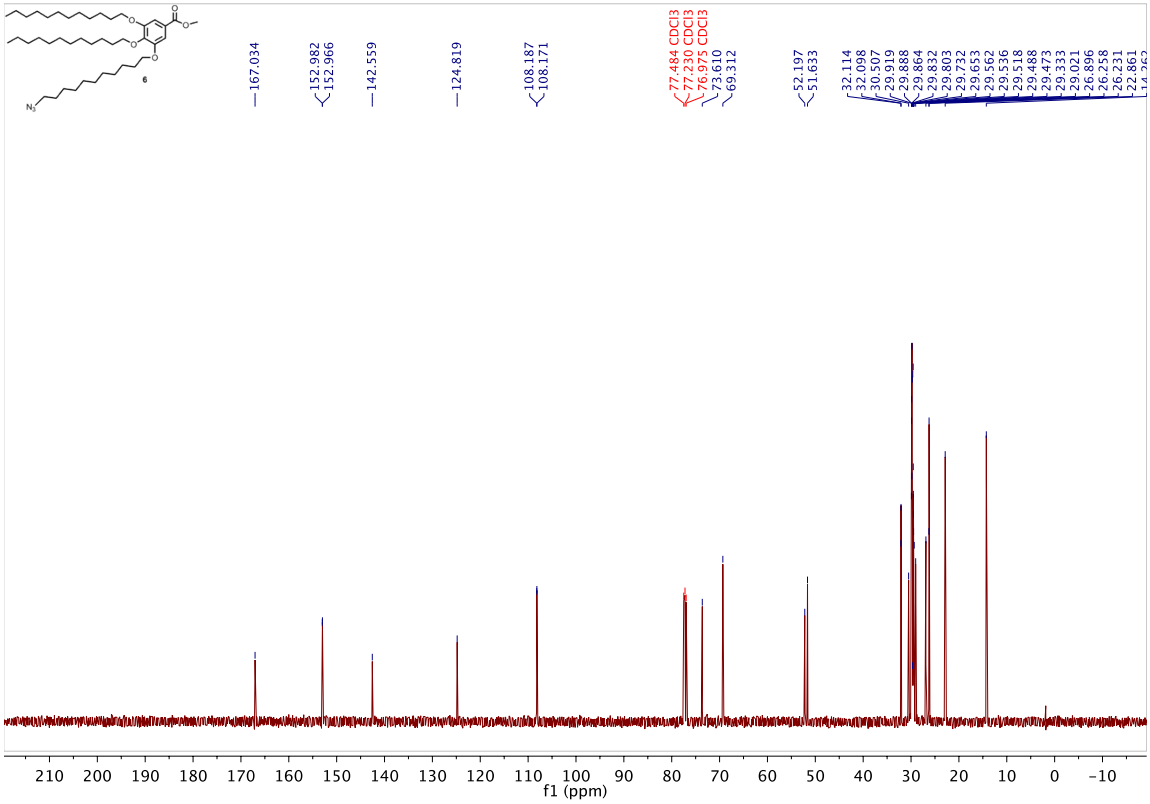

166.675
148.390
142.647
139.688
123.506
119.863
110.594
103.695
77.484 CDCl3
77.229 CDCl3
76.974 CDCl3
69.556
52.101
51.535
29.568
29.528
29.413
29.274
29.220
28.925
26.793
25.942
f1 (ppm)

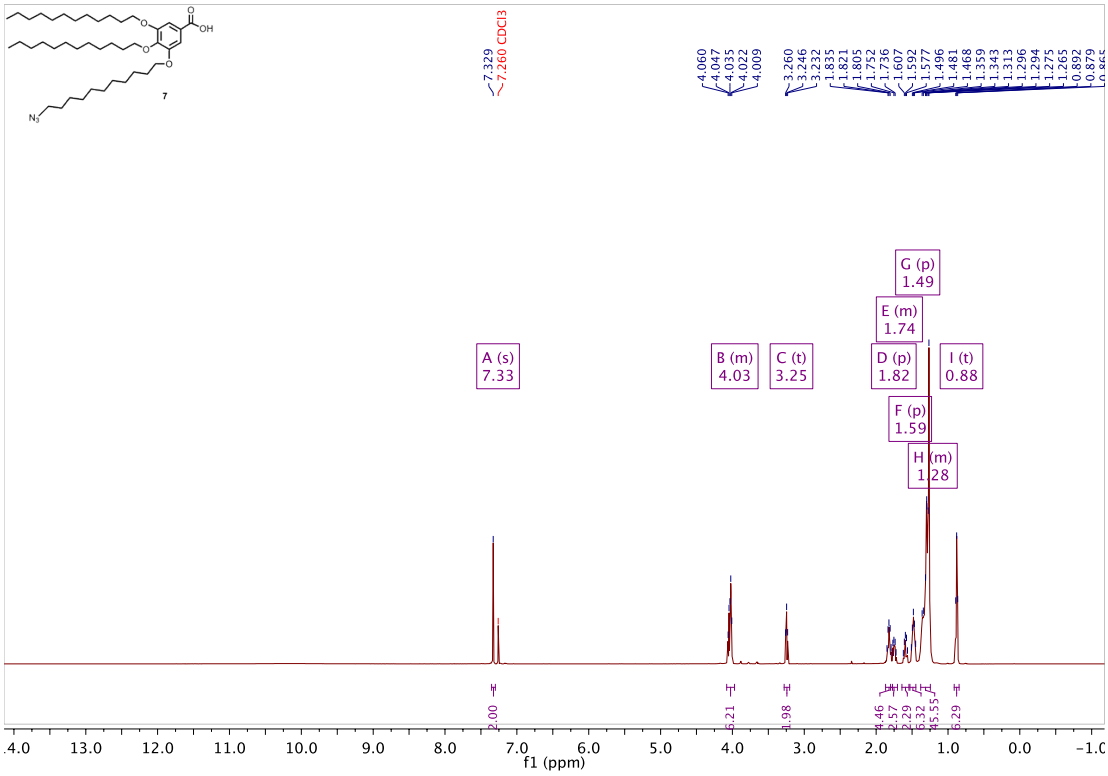

B (s)
7.32
A (s)
7.19
D (t)
4.08
C (s)
3.87
E (t)
3.25
I (m)
1.30
G (p)
1.59
F (p)
1.81
H (dt)
1.44
f1 (ppm)

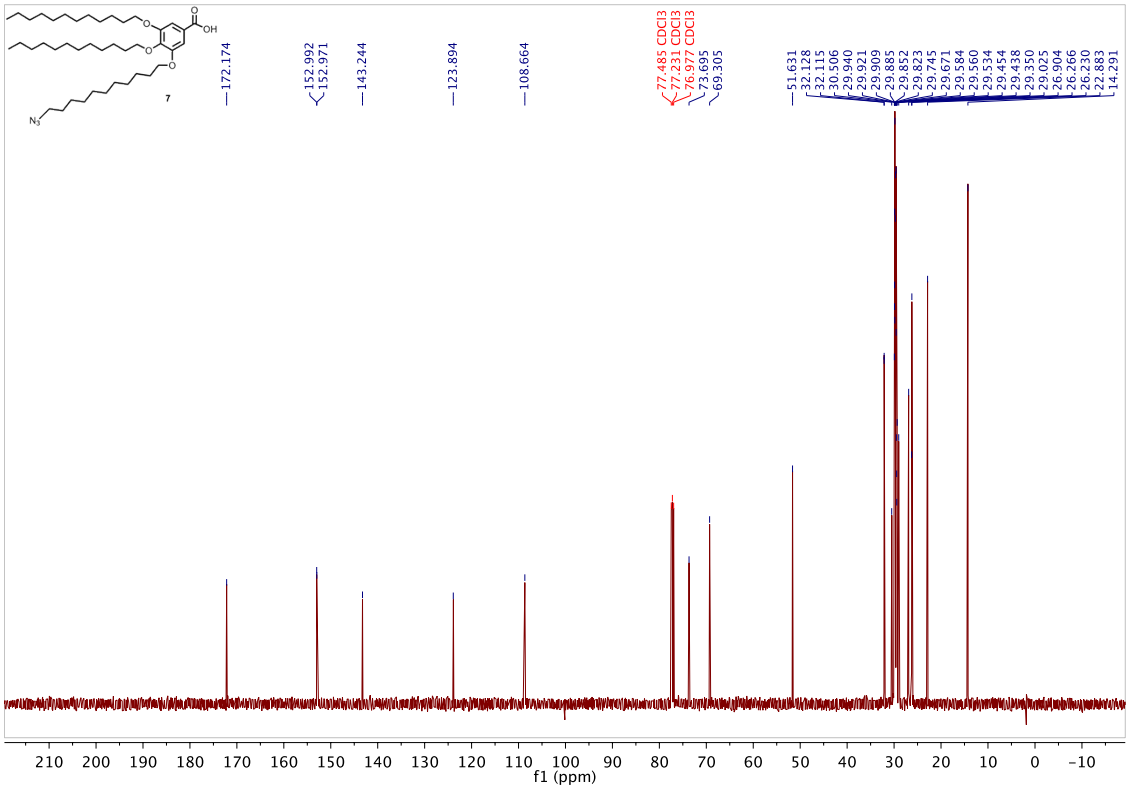

167.195
146.035
143.600
137.210
121.885
110.993
105.859
77.485 CDCl3
77.230 CDCl3
76.975 CDCl3
69.609
52.289
51.679
29.647
29.595
29.473
29.309
29.295
29.006
26.876
26.103
f1 (ppm)

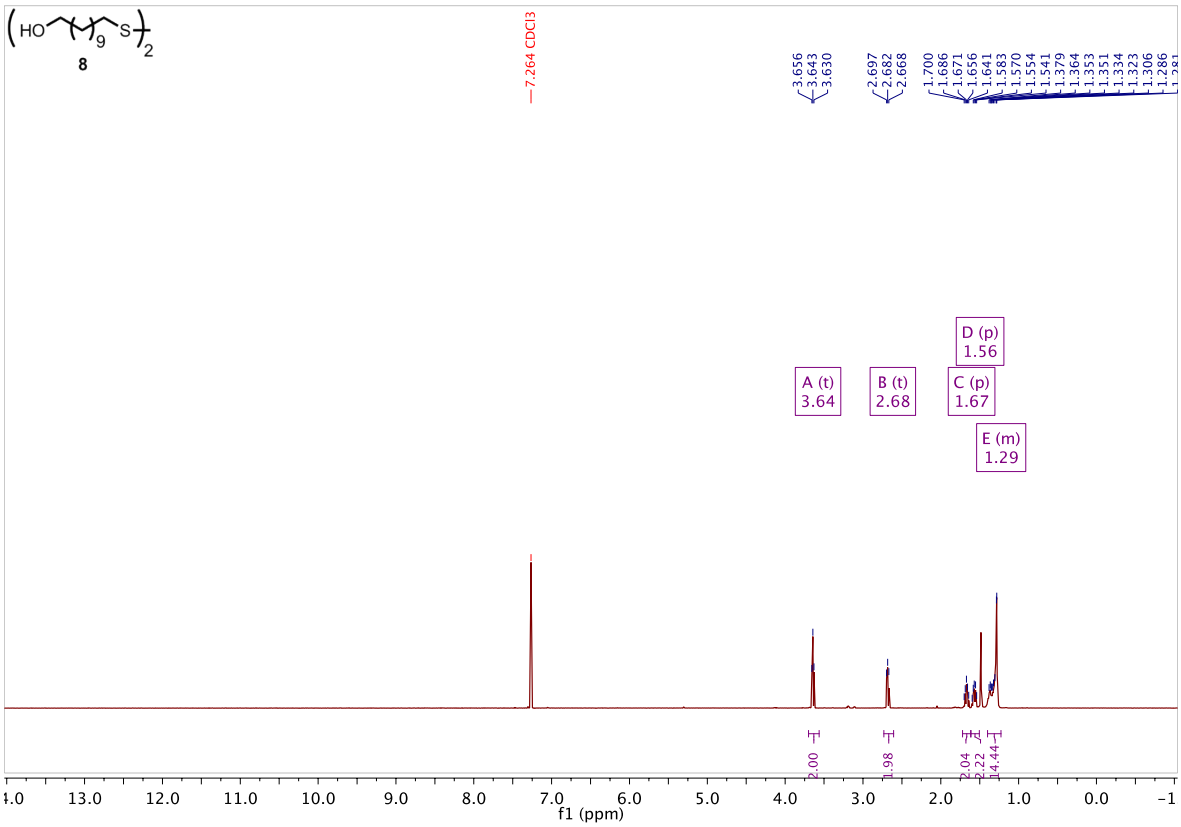

f2 (ppm)
f1 (ppm)

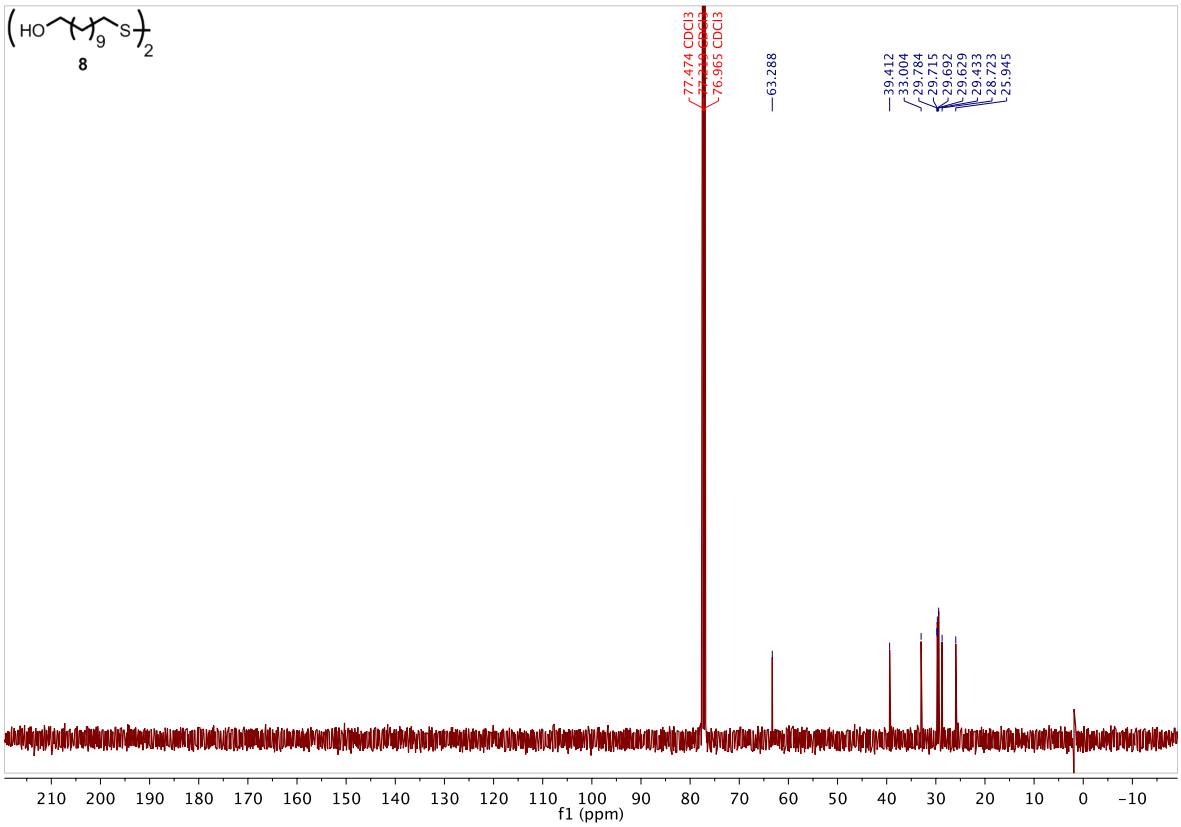

A (s)
7.25
B (s)
3.87
C (q)
4.01
D (t)
3.24
E (p)
1.80
F (p)
1.73
G (p)
1.58
H (t)
1.47
I (m)
1.28
J (t)
0.87
f1 (ppm)

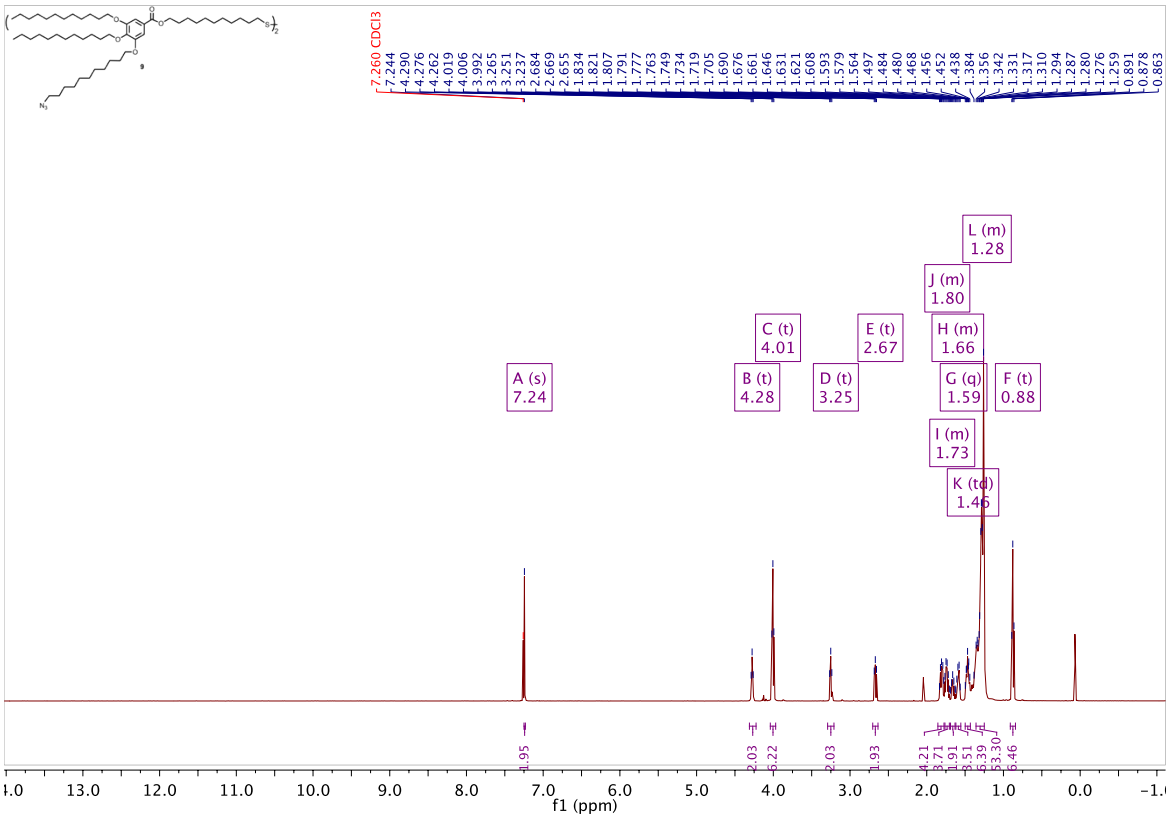

f1 (ppm)

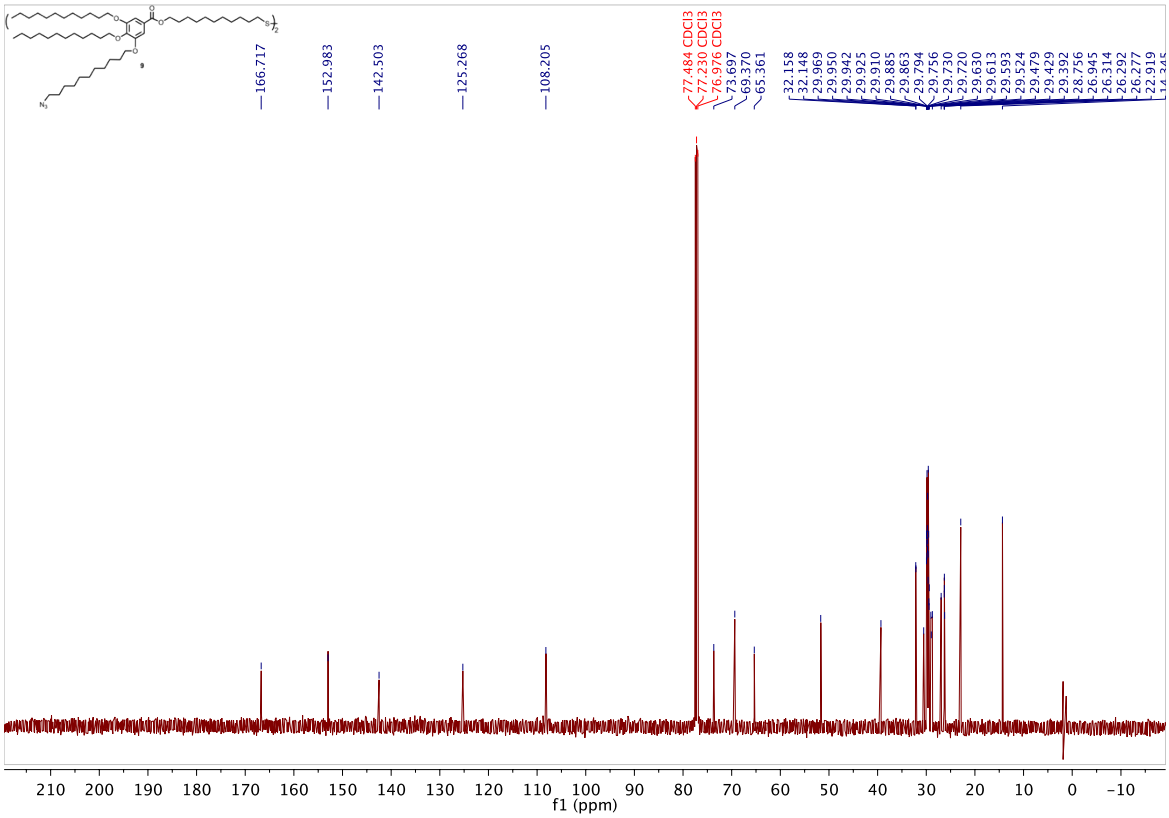

7.329
7.260 CDCl3
A (s)
7.33
B (m)
4.03
C (t)
3.25
D (p)
1.82
E (m)
1.74
F (p)
1.59
G (p)
1.49
H (m)
1.28
I (t)
0.88
f1 (ppm)

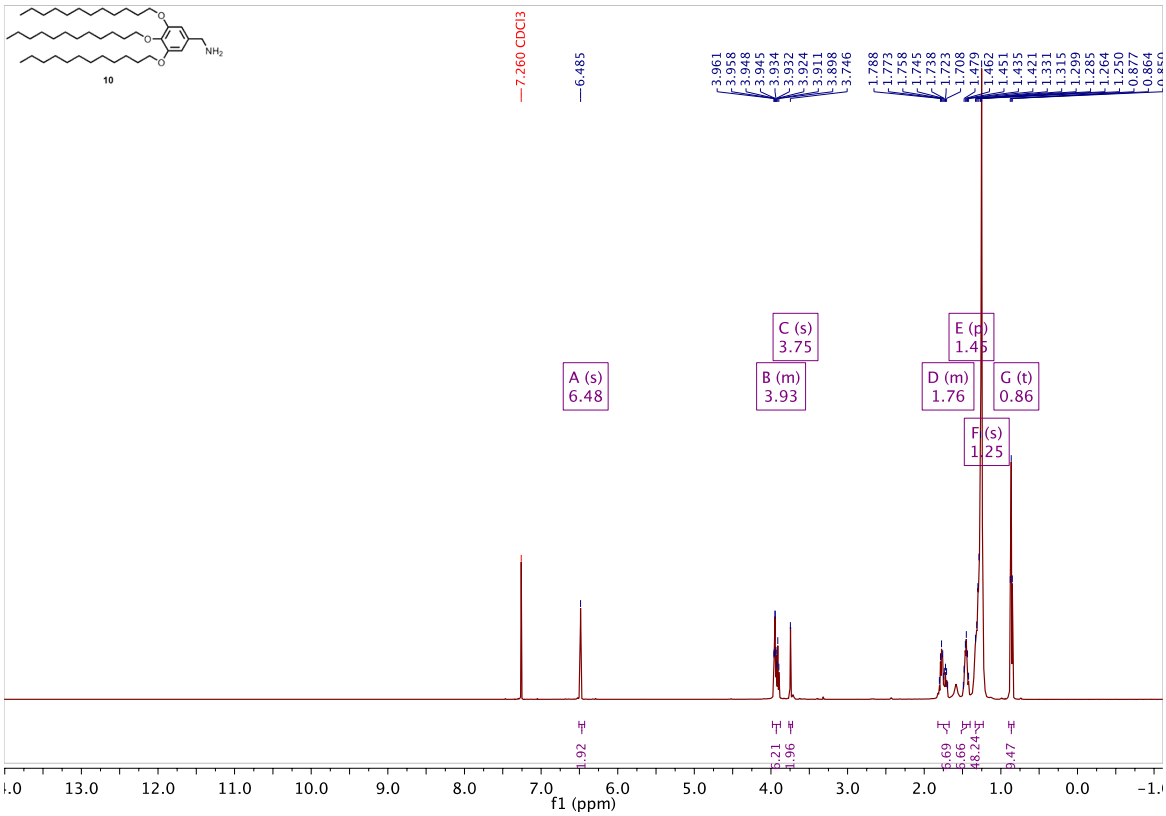

172.174
152.992
152.971
143.244
123.894
108.664
77.485 CDCl3
77.231 CDCl3
76.977 CDCl3
73.695
69.305
51.631
f1 (ppm)

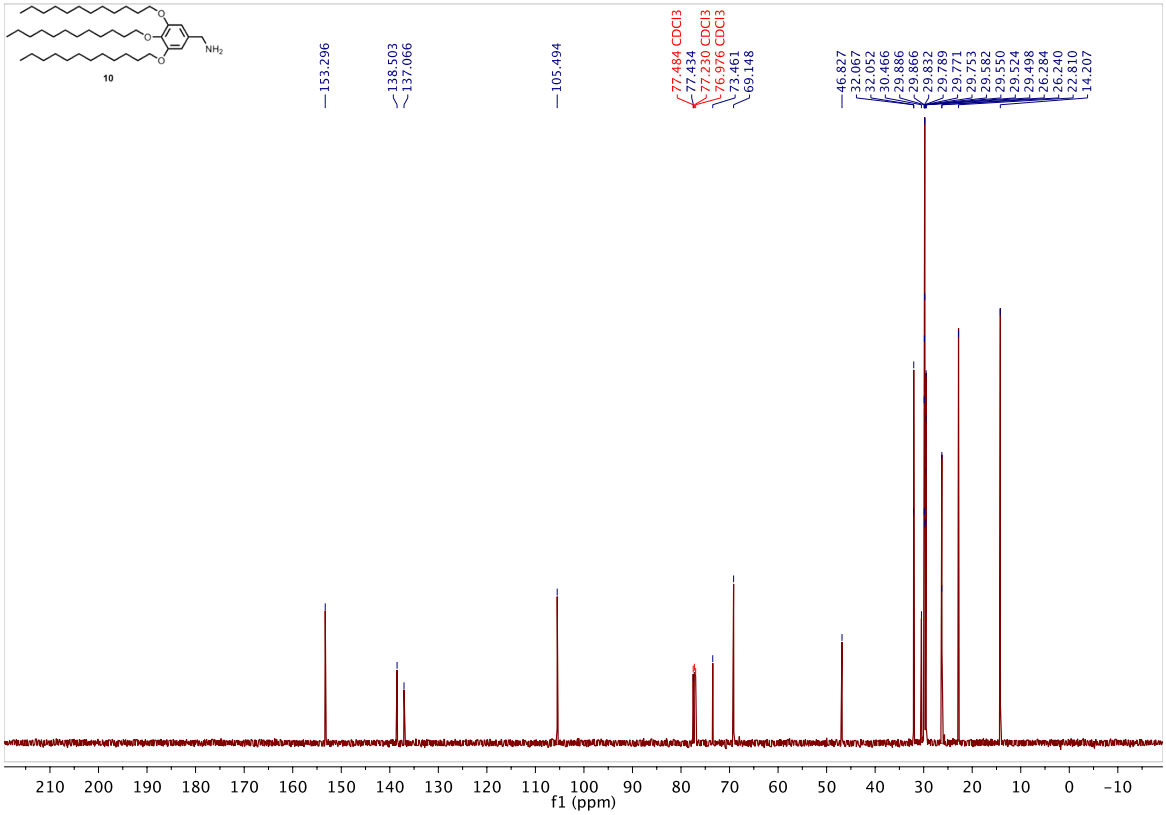

8
7.264 CDCl3
3.656
3.643
3.630
2.697
2.682
2.668
1.700
1.686
1.671
1.656
1.641
1.583
1.570
1.554
1.541
1.379
1.364
1.353
1.351
1.334
1.323
1.306
1.286
D (p)
1.56
A (t)
3.64
B (t)
2.68
C (p)
1.67
E (m)
1.29
2.00
1.98
2.04
2.22
4.44
f1 (ppm)

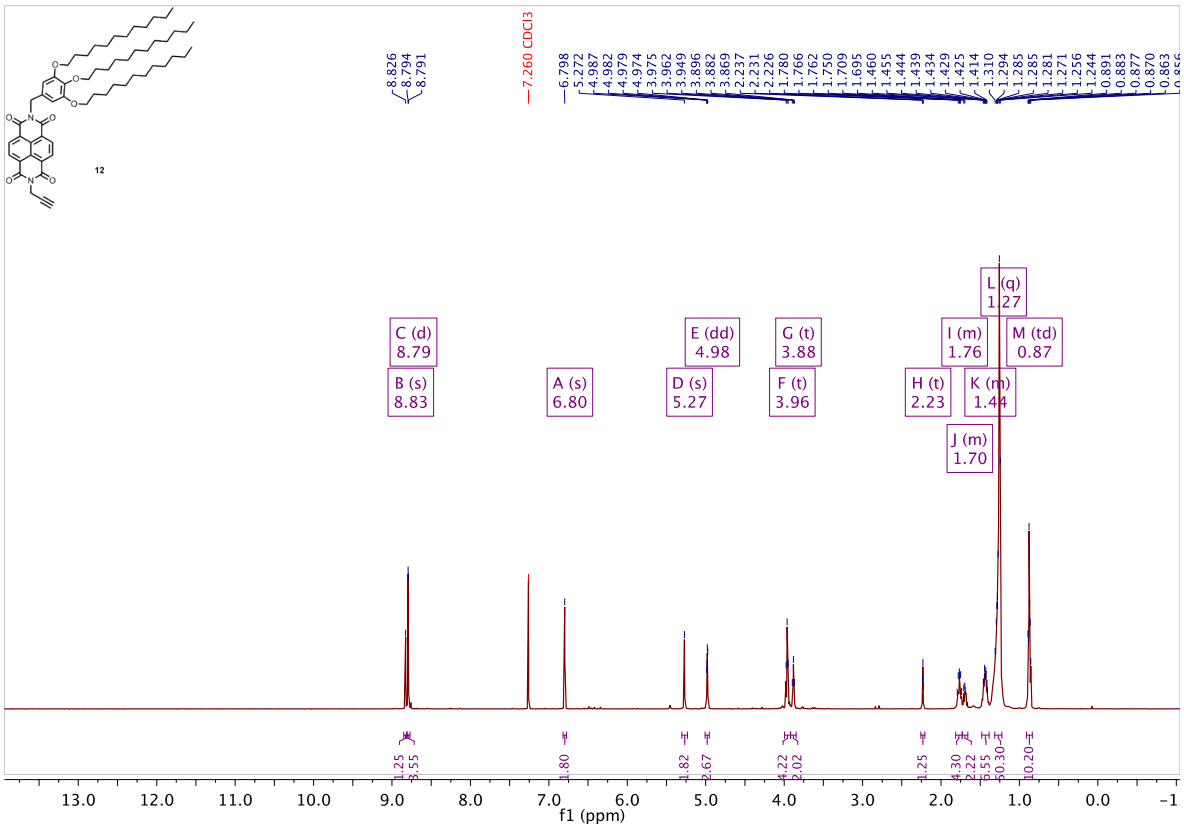

8
77.474 CDCl3
77.156 CDCl3
76.965 CDCl3
63.288
39.412
33.004
29.784
29.715
29.692
29.629
29.433
28.723
25.945
f1 (ppm)

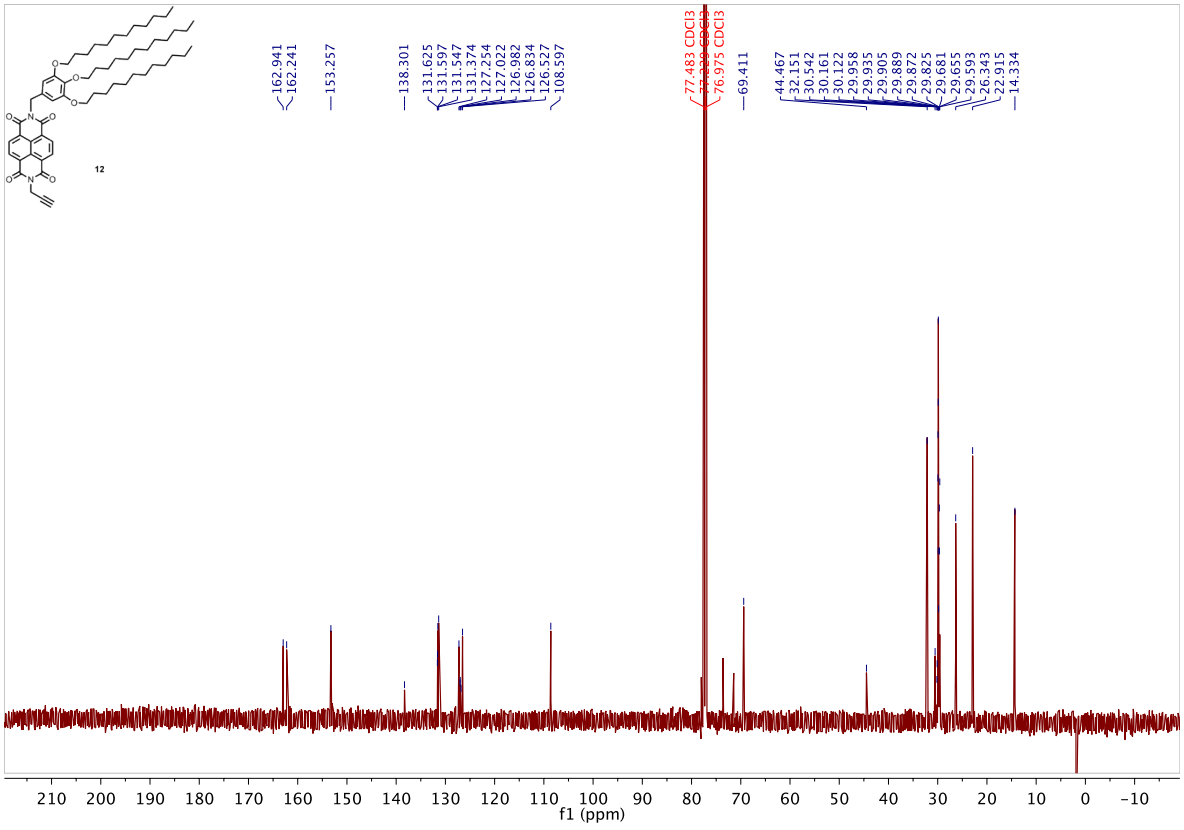

A (s)
7.24
B (t)
4.28
C (t)
4.01
D (t)
3.25
E (t)
2.67
F (t)
0.88
G (q)
1.59
H (m)
1.66
I (m)
1.73
J (m)
1.80
K (td)
1.46
L (m)
1.28
f1 (ppm)

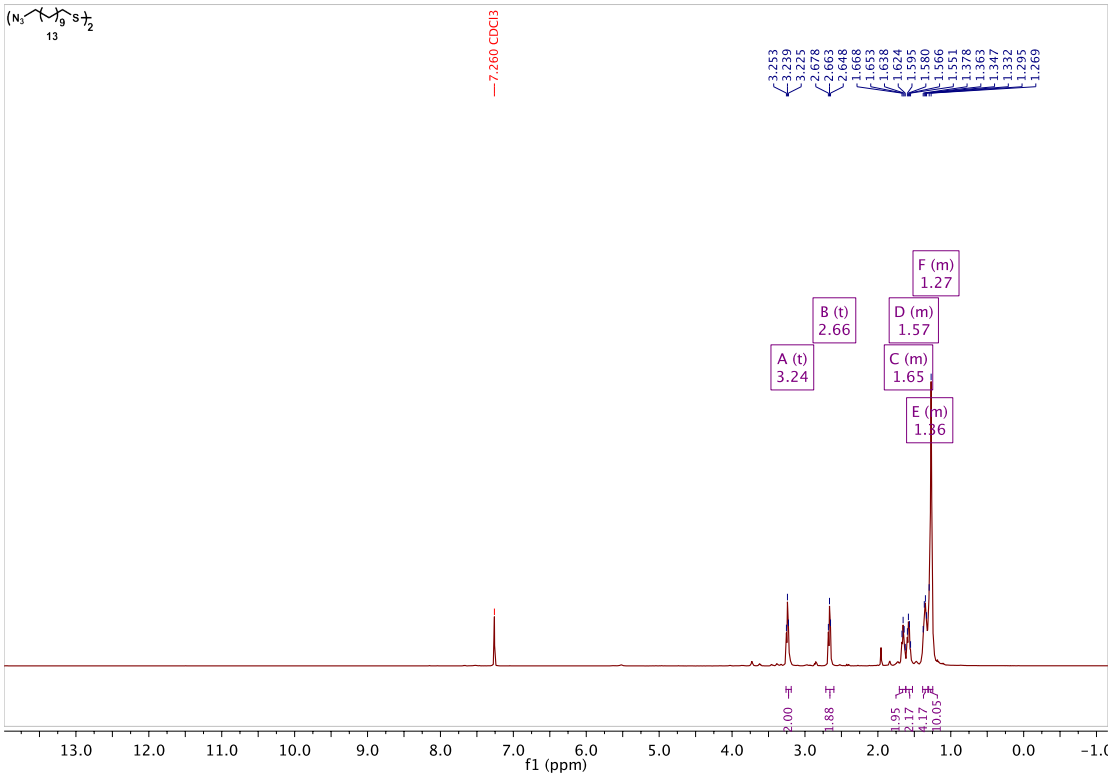

166.717
152.983
142.503
125.268
108.205
77.484 CDCl3
77.230 CDCl3
76.976 CDCl3
f1 (ppm)

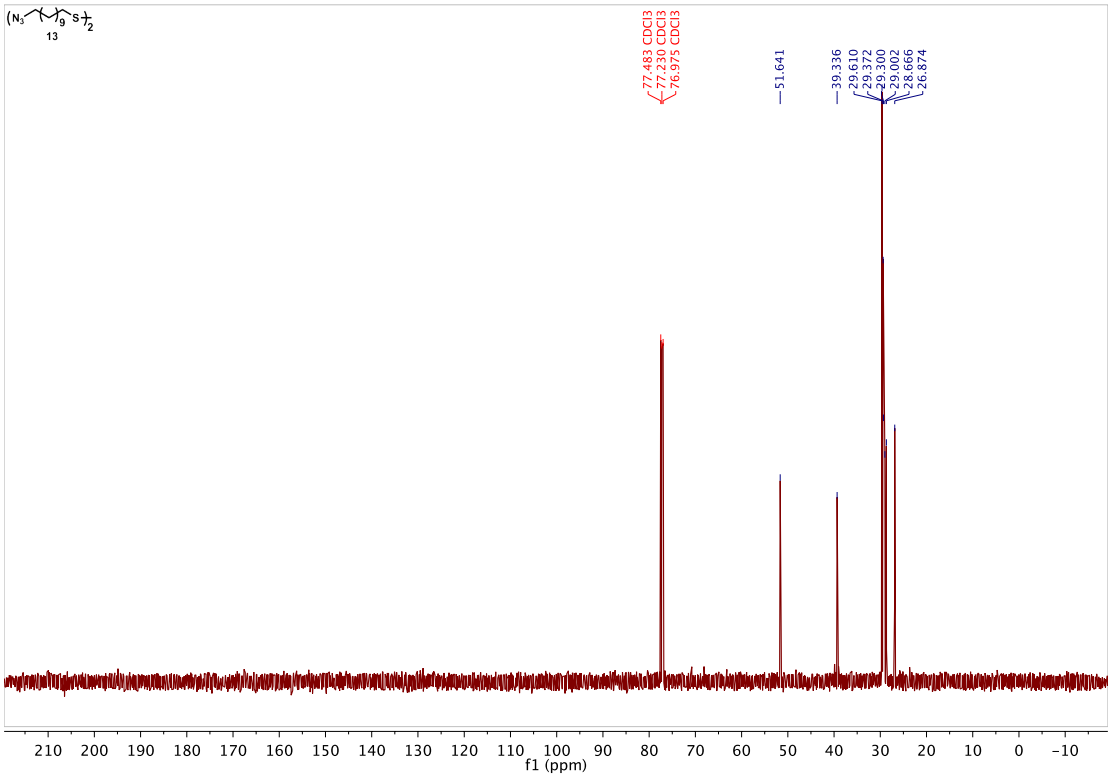

10
7.260 CDCl3
6.485
3.961
3.958
3.948
3.945
3.934
3.932
3.924
3.911
3.898
3.746
1.788
1.773
1.758
1.745
1.738
1.723
1.708
1.479
1.462
1.451
1.435
1.421
1.331
1.315
1.299
1.285
1.264
1.250
0.877
0.864
A (s)
6.48
B (m)
3.93
C (s)
3.75
D (m)
1.76
E (p)
1.45
F (s)
1.25
G (t)
0.86
1.92
6.21
1.96
5.69
6.66
48.24
9.47
f1 (ppm)

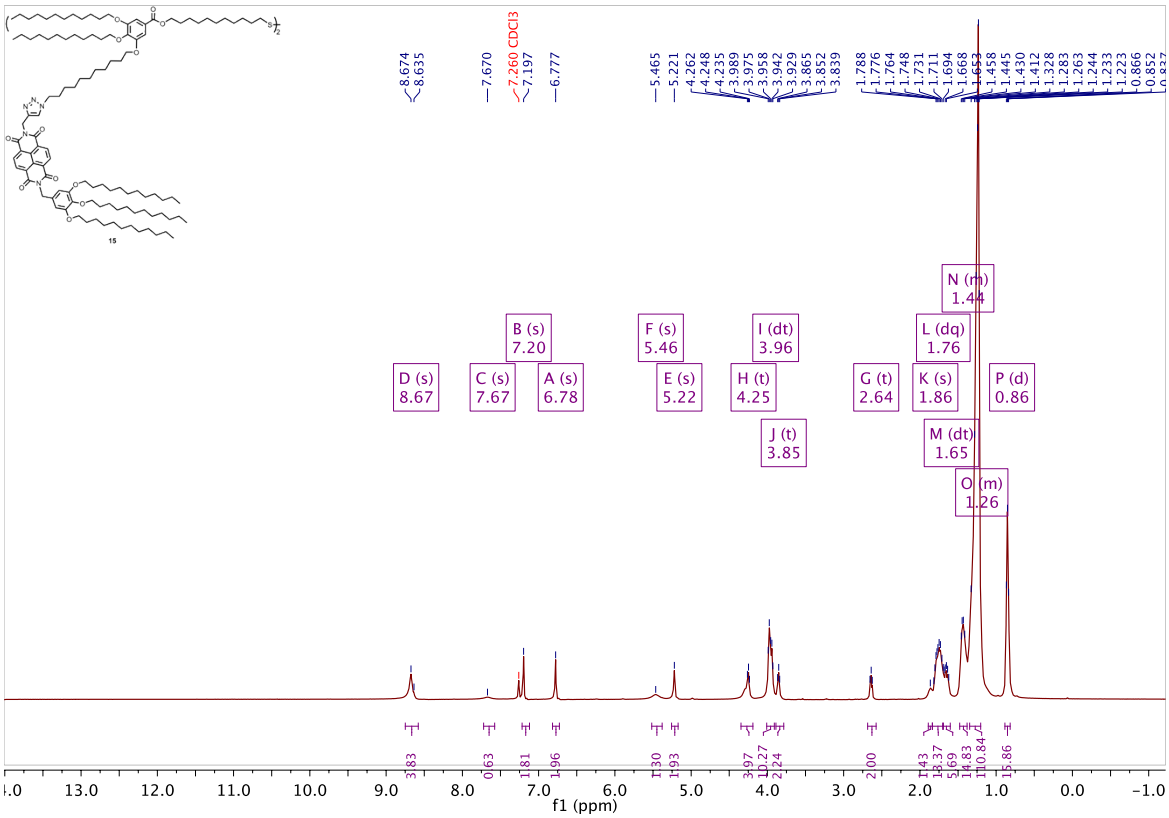

10
153.296
138.503
137.066
105.494
77.484 CDCl3
77.434
77.230 CDCl3
76.976 CDCl3
73.461
69.148
46.827
32.067
32.052
30.466
29.886
29.866
29.832
29.789
29.771
29.753
29.582
29.550
29.524
29.498
26.284
26.240
22.810
14.207
f1 (ppm)

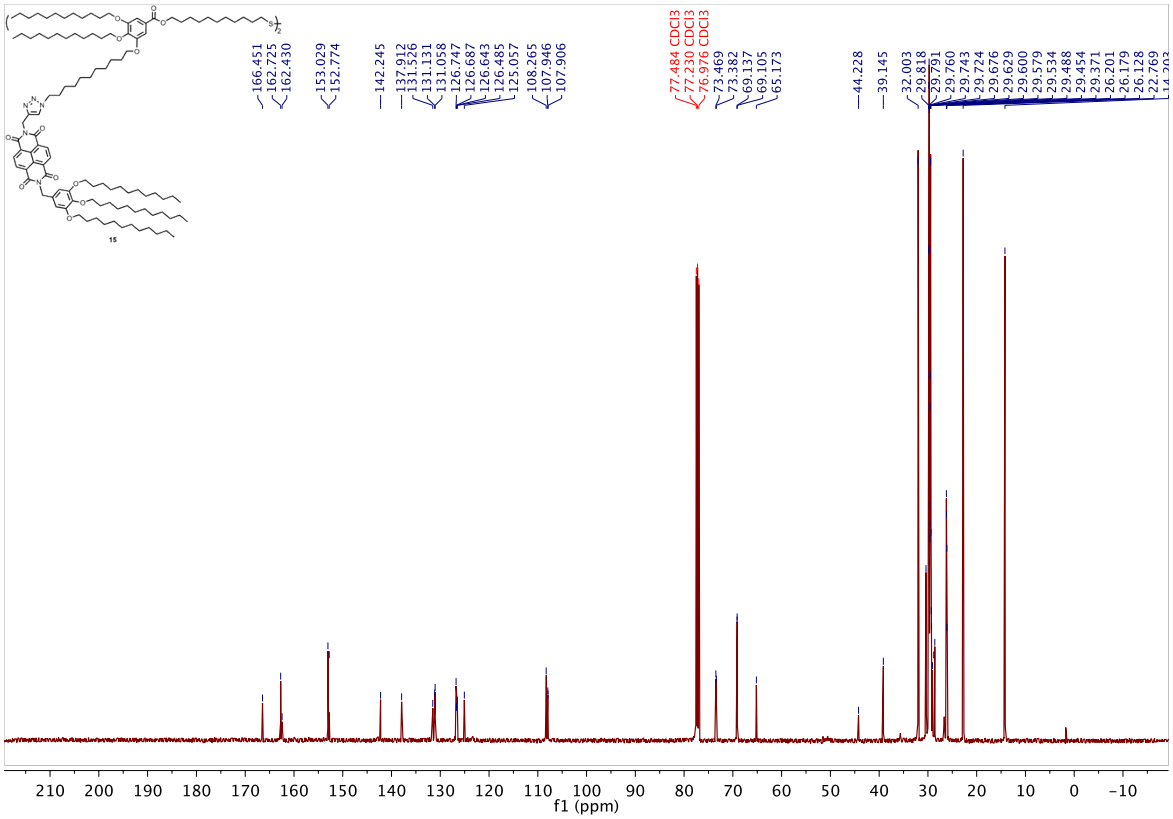

12
8.826
8.794
8.791
7.260 CDCl3
6.798
5.272
4.987
4.982
4.979
4.974
3.975
3.962
3.949
3.896
3.882
3.869
2.237
2.231
2.226
1.780
1.766
1.762
1.750
1.709
1.695
1.460
1.455
1.444
1.439
1.434
1.429
1.425
1.414
1.310
1.294
1.285
1.285
1.281
1.271
1.256
1.244
0.891
0.883
0.877
0.870
0.863
C (d) 8.79
B (s) 8.83
A (s) 6.80
E (dd) 4.98
D (s) 5.27
G (t) 3.88
F (t) 3.96
L (q) 1.27
I (m) 1.76
M (td) 0.87
H (t) 2.23
K (m) 1.44
J (m) 1.70
1.25
3.55
1.80
1.82
2.67
4.22
2.02
1.25
4.30
2.22
6.55
50.30
10.20
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1
f1 (ppm)


12
162.941
162.241
153.257
138.301
131.625
131.597
131.547
131.374
127.254
127.022
126.982
126.834
126.527
108.597
77.483 CDCl3
76.975 CDCl3
69.411
44.467
32.151
30.542
30.161
30.122
29.958
29.935
29.905
29.889
29.872
29.825
29.681
29.655
29.593
26.343
22.915
14.334
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.260 CDCl3
3.253
3.239
3.225
2.678
2.663
2.648
1.653
1.638
1.624
1.595
1.580
1.566
1.551
1.378
1.363
1.347
1.332
1.295
1.269
A (t)
3.24
B (t)
2.66
C (m)
1.65
D (m)
1.57
E (m)
1.36
F (m)
1.27
2.00
1.88
1.95
2.17
4.17
10.05
f1 (ppm)


77.483 CDCl3
77.230 CDCl3
76.975 CDCl3
51.641
39.336
29.610
29.372
29.300
29.002
28.666
26.874
f1 (ppm)


D (s) 8.67
C (s) 7.67
B (s) 7.20
A (s) 6.78
F (s) 5.46
E (s) 5.22
H (t) 4.25
I (dt) 3.96
J (t) 3.85
G (t) 2.64
N (m) 1.44
L (dq) 1.76
K (s) 1.86
M (dt) 1.65
O (m) 1.26
P (d) 0.86
f1 (ppm)


f1 (ppm)