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Photoredox catalysis using infrared light via triplet fusion upconversion

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Supplementary Materials for

Photoredox Catalysis Using Infrared Light via Triplet Fusion Upconversion

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Materials and Methods

General Comments

Unless noted, all reactions were performed in oven-dried glassware and carried out under an atmosphere of argon or nitrogen with magnetic stirring. The reactions in the general procedures section are tolerant of non flame-dried vials. All column chromatography was performed using general flash techniques on SiliCycle[®] SilicaFlash[®] P60, 40-63 μm 60 Å. For particularly difficult separations, on Teledyne Isco Combiflash using CombiFlash gold pre-packed columns. Thin layer chromatography was performed on SiliCycle[®] 250 μm 60 Å plates. Visualization was accomplished with 254 nm UV light, KMnO₄ stain, or I₂.

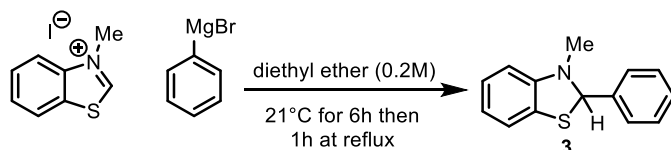
NMR spectra were recorded on Varian 300 or 400 MHz spectrometers, and Bruker 400 or 500 MHz spectrometers at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from CDCl₃ (¹H: 7.26 ppm, ¹³C: 77.16 ppm), CD₂Cl₂ (¹H: 5.32 ppm, ¹³C: 54.0 ppm), CD₃OD (¹H: 4.78, 3.31 ppm, ¹³C: 49.15 ppm) or CD₃CN (¹H: 1.94 ppm, ¹³C: 1.32 ppm) with multiplicity (*s* = singlet, br. *s* = broad singlet, *d* = doublet, *t* = triplet, *q* = quartet, and *m* = multiplet) and coupling constants (in Hz). Diastereomer ratios for all compounds were determined by ¹H NMR analysis of the unpurified reaction mixtures. Mass spectra were recorded on a Waters Acquity H UPLC-MS. Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR spectrometer. Gel permeation chromatography was performed using a Waters 1515 isocratic HPLC pump with a 2990 photodiode array detector and 2414 refractive index detector.

Solutions of FDPP, TTBP, PdPc, and PtTPTNP were prepared from anhydrous toluene in a nitrogen glovebox. Solutions were made in 1 cm x 1 cm quartz cuvettes from Spectrocell and were degassed by sparging with nitrogen for 30 seconds then sealed before removing from glovebox for measurement. Solutions were excited with a 730 nm laser diode purchased from Thorlabs, focused to a beam diameter of 0.15 mm. All upconverted PL spectra were measured with a QEPro spectrometer purchased from Ocean Optics through a 700 nm shortpass filter. Absorption spectra were obtained on an Agilent Technologies Cary 60 UV-Vis spectrophotometer.

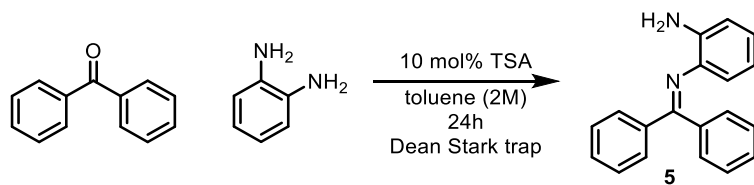
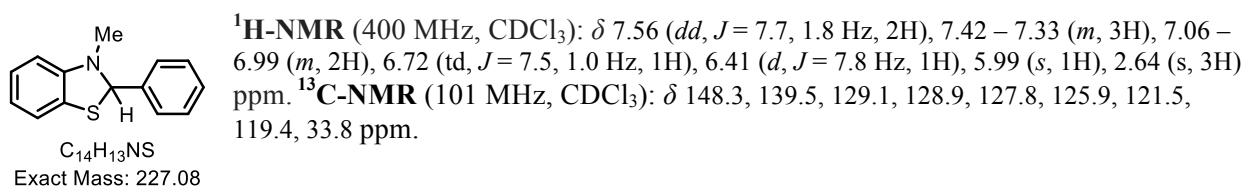
730nm and 450 nm laser diodes were purchased from Thorlabs. 700-800 nm LED lamp was purchased from powerPAR via Amazon. The Blue lamp is an H150 Kessil 35W LED lamp. Reactions were placed approximately 10 cm from lamps, and at the focal point of lasers

Unless otherwise stated, all starting materials were obtained from commercial sources including Sigma-Aldrich, TCI, Matrix, Alfa-Aesar, and Oakwood Scientific. FDPP and PtTPTNP were synthesized according to previously described procedures. PdPc was purchased from Frontier Scientific and was used without further purification. TTBP was purchased from TCI and used without further purification.

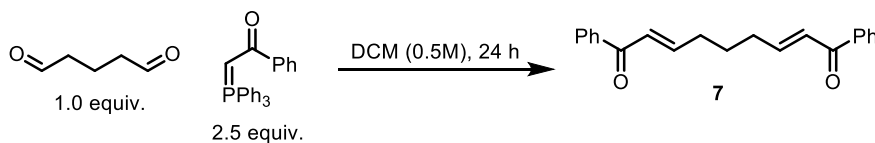
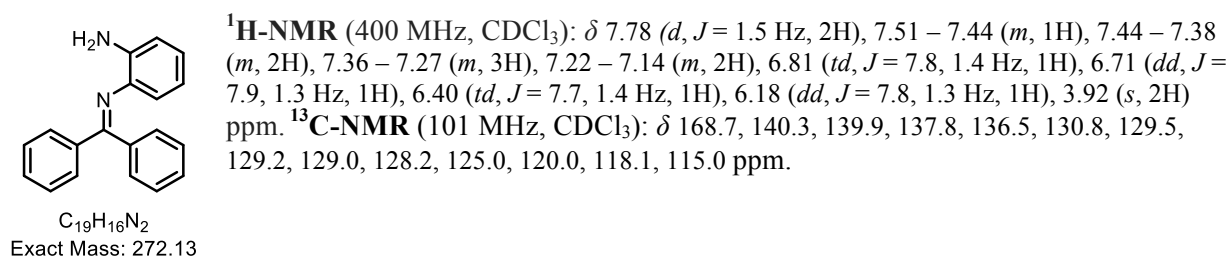
Starting Material Preparation



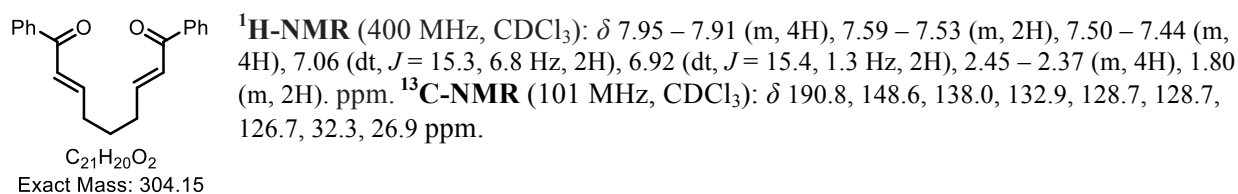
Procedure: Compound **3** was isolated according to published procedure and the product spectra are identical to the known compound (*1*).

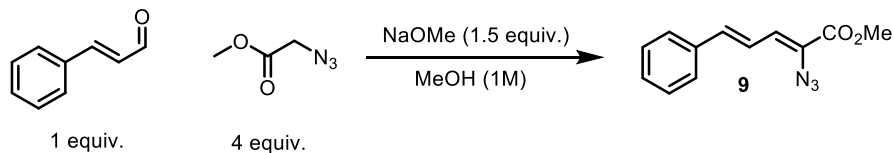


Procedure: Compound **5** was isolated according to published procedure and the product spectra are identical to the known compound (*2*).

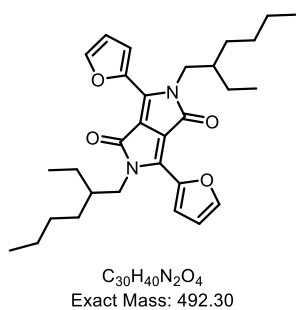
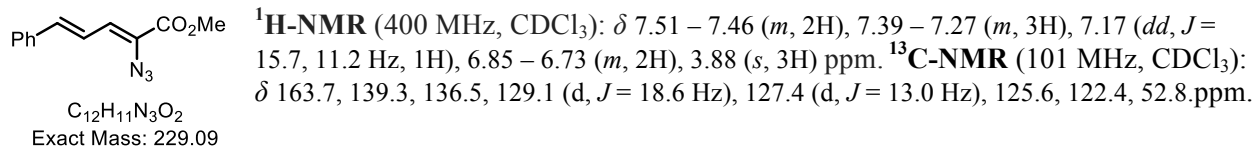


Procedure: Compound **7** was isolated according to published procedure and the product spectra are identical to the known compound (*3*).



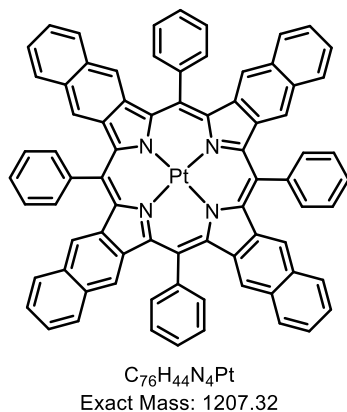


Procedure: Compound **9** was isolated according to published procedure and the product spectra are identical to the known compound (**4**).



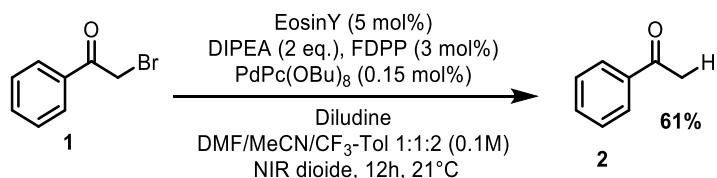
Procedure: Compound **FDPP** was isolated according to published procedure and the product spectra are identical to the known compound (**5**).

¹H-NMR (400 MHz, CDCl_3): δ 8.32 (*d*, 2H), 7.61 (*d*, 2H), 6.69 (*m*, 2H), 4.04 (*d*, 4H), 1.76 (*m*, 2H), 1.38 – 1.24 (*d*, 16H), 0.93–0.84 (*m*, 12H). ppm. **¹³C-NMR** (101 MHz, CDCl_3): δ 161.4, 145.0, 144.8, 134.1, 120.3, 113.6, 106.6, 46.3, 40.1, 30.1, 28.8, 24.0, 23.2, 14.2, 10.9 ppm.



Procedure: Compound **PtTPTNP** was isolated according to published procedure and the product spectra are identical to the known compound (**6**). The ¹H-NMR (400 MHz, CDCl_3) of the non-metallated macrocycle precursor has been provided.

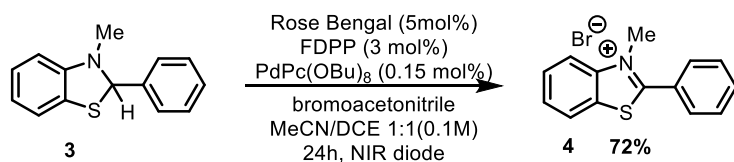
General Procedures



Control Reactions:

no Eosin Y:	3%
no DIPEA:	9%
no FDPP:	3%
no Pd(Pc):	2%
no NIR:	3%
40W Blue Lamp:	78%

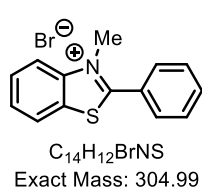
Procedure: To a flame dried 1 dram vial containing a stir-bar was added 50.0 mg **1** (0.25 mmol), 70 mg diludine (0.28 mmol), 8.1 mg Eosin Y (0.0125 mmol), and 3.5 mg FDPP (0.007 mmol). The vial was then pumped into a glove-box under argon atmosphere. After, 0.625 mL anhydrous DMF, 0.625 mL anhydrous acetonitrile, and 0.8 mL trifluorotoluene was added followed by 0.45 mg (0.000375 mmol) PdPc(OBu)₈ (stored as a 1 mg/mL solution in trifluorotoluene). Finally, 89 μ L DIPEA (0.50 mmol) was added, the reaction was sealed, and transferred to the IR light source under the shield of aluminum foil. After, the reaction was irradiated for 12 h at 21°C. Upon completion, the vial was wrapped in aluminum foil and was concentrated under reduced pressure to remove the acetonitrile. The crude mixture was subjected to column chromatography on silica gel using pentane/ethyl acetate as eluent. The combined fractions were concentrated under reduced pressure and the product spectra are identical to the known compound **2** (7).



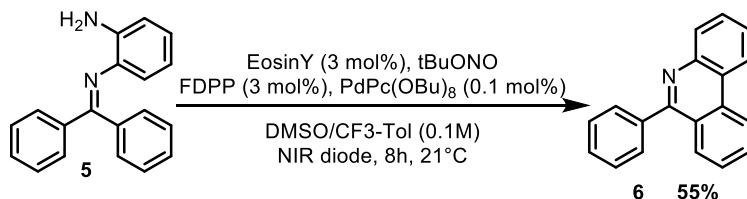
Control Reactions:

No IR laser:	4%
No RB:	7%
No FDPP:	4%
No PdPc(OBu) ₈ :	4%
40W Blue Lamp:	82%

Procedure: To a flame dried 1 dram vial containing a stir-bar was added 57.0 mg **3** (0.25 mmol), 12.2 mg Rose Bengal (0.0125 mmol), and 3.5 mg FDPP (0.007 mmol). The vial was then pumped into a glove-box under argon atmosphere. After, 1.03 mL anhydrous DCE, 20 μ L bromoacetonitrile (0.28 mmol), and 1.03 mL anhydrous MeCN were added followed by 0.45 mg (0.0004 mmol) PdPc(OBu)₈ (stored as a 1 mg/mL solution in trifluorotoluene). Afterward, the reaction was sealed, and transferred to the IR light source under a shield of aluminum foil. After, the reaction was irradiated for 24 h at 21°C. Upon completion, the vial was wrapped in aluminum foil and was concentrated under reduced pressure to remove all solvent. To the crude mixture was added 3 mL diethyl ether which produced a white precipitate. The solid was filtered and washed with 5 mL diethyl ether. Then, the solid was washed with acetonitrile and the filtrate was concentrated and re-precipitated with diethyl ether. This process was repeated 4 times to remove Rose Bengal to yield 72% product **4**.



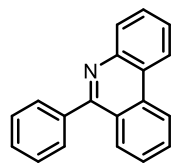
¹H-NMR (400 MHz, CD₃CN): δ 8.44 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.98 (ddd, J = 8.5, 7.3, 1.1 Hz, 1H), 7.91 – 7.83 (m, 4H), 7.82 – 7.72 (m, 2H), 4.23 (s, 3H). ppm.
¹³C-NMR (101 MHz, CD₃OD): δ 176.4, 144.1, 135.3, 131.5, 131.5, 131.4, 131.1, 130.3, 126.7, 125.2, 118.6, 38.6. ppm. **IR** (neat): ν 3397 (s), 3061 (s), 2924 (s), 1630 (s), 1596 (s), 1446 (s), 1334 (m), 1246 (s), 760 (s) cm⁻¹. **HRMS-ASAP** (positive): M = C₁₄H₁₂BrNS; expected (M)⁺ m/z 226.0690, observed (M +H)⁺ m/z 226.0695; expected (NaBr₂)⁻ m/z 180.8264, observed (NaBr₂)⁻ m/z 180.8287.


Controls Reactions:

No IR laser:	2%
No Eosin Y:	2%
No FDPP:	1%
No PdPc(OBu) ₈ :	2%
40W Blue Lamp:	78%

Procedure: To a flame dried 1 dram vial containing a stir-bar was added 68.8 mg **5** (0.25 mmol), 5.2 mg Eosin Y (0.008 mmol), and 3.5 mg FDPP (0.007 mmol). The vial was then pumped into a glove-box under argon atmosphere. After, 0.95 mL anhydrous trifluorotoluene and 1.25 mL anhydrous DMSO were added followed by 0.30 mg (0.0003 mmol) PdPc(OBu)₈ (stored as a 1 mg/mL solution in trifluorotoluene) and 45 μ l tert-butyl nitrite (0.38 mmol). Afterward, the reaction was sealed, and transferred to the IR light source under the shield of aluminum foil. After, the reaction was irradiated for 8 h at 21°C. Upon completion, the vial was wrapped in aluminum foil and was concentrated under reduced pressure to remove all solvent. The product was purified via column chromatography of silica eluting 20% ethyl acetate in hexanes. The combined fractions were concentrated revealing a yellow solid product. The product spectra are

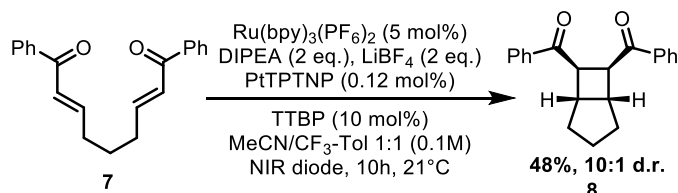
identical to the known compound **6** (8).



C₁₉H₁₃N

Exact Mass: 255.10

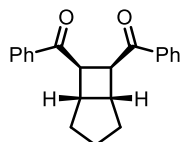
¹H-NMR (400 MHz, CDCl₃): δ 8.72 (*d*, *J* = 8.3 Hz, 1H), 8.63 (*dd*, *J* = 8.1, 1.4 Hz, 1H), 8.25 (*dd*, *J* = 7.9, 1.2 Hz, 1H), 8.13 – 8.09 (*m*, 1H), 7.87 (*ddd*, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.81 – 7.67 (*m*, 4H), 7.65 – 7.52 (*m*, 4H) ppm. ¹³C-NMR (101 MHz, CDCl₃): δ 161.4, 144.0, 140.0, 133.6, 130.7, 130.5, 129.9, 129.1, 129.0, 128.8, 128.6, 127.3, 127.1, 125.4, 123.9, 122.4, 122.1 ppm.


Controls Reactions:

No IR laser:	2%
No Ru(bpy) ₃ (PF ₆) ₂ :	38%
No TTBP:	1%
No PtTPTNP:	1%
40W Blue Lamp:	63%

Procedure: To a flame dried 1 dram vial containing a stir-bar was added 76.0 mg **7** (0.25 mmol), 46.9 mg LiBF₄ (0.50 mmol), 10.7 mg Ru(bpy)₃(PF₆)₂ (0.0125 mmol), and 11.9 mg TTBP (0.0025 mmol). The vial was then pumped into a glove-box under argon atmosphere. After, 1.25 mL anhydrous MeCN and 0.89 mL anhydrous trifluorotoluene were added followed by 0.36 mg (0.0003 mmol) PtTPTNP (stored as a 1 mg/mL solution in trifluorotoluene). Finally, 87 μ l DIPEA (0.50 mmol) was added to the reaction mixture. Afterward, the reaction was sealed, and transferred to the IR light source under the shield of aluminum foil. After, the reaction was irradiated for 2 h at 21°C. Upon completion, the vial was wrapped in aluminium foil and was concentrated under reduced pressure to remove all solvent. The product was purified via column

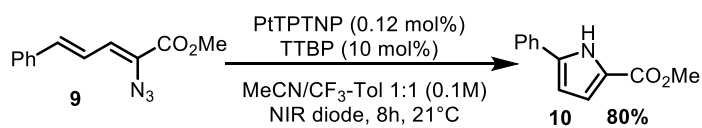
chromatography of silica eluting 20% ethyl acetate in hexanes. The combined fractions were concentrated revealing a white crystalline product. The product spectra are identical to the known compound **8** (9).



C₂₁H₂₀O₂

Exact Mass: 304.15

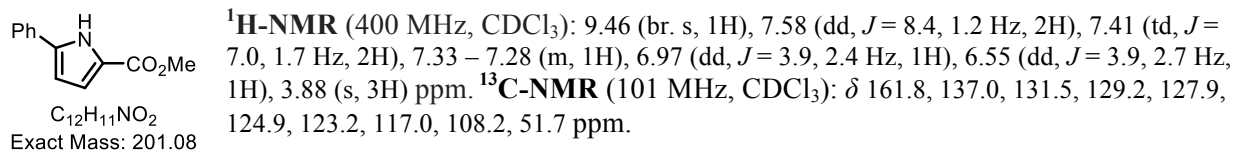
¹H-NMR (400 MHz, CDCl₃): 7.76 (*dt*, *J* = 8.5, 1.6 Hz, 4H), 7.47 – 7.41 (*m*, 2H), 7.38 – 7.32 (*m*, 4H), 3.87 (*d*, *J* = 4.1 Hz, 2H), 3.21 (*dq*, *J* = 4.2, 2.5 Hz, 2H), 2.09 – 1.99 (*m*, 2H), 1.89 – 1.82 (*m*, 2H), 1.76 – 1.65 (*m*, 2H) ppm. ¹³C-NMR (101 MHz, CDCl₃): δ 198.7, 136.5, 132.6, 128.6, 127.9, 48.4, 39.2, 32.6, 25.4 ppm.



Controls:

No IR laser:	2%
No TTBP:	1%
No PtTPTNP:	1%
40W Blue Lamp:	88%

Procedure: To a flame dried 1 dram vial containing a stir-bar was added 57.3 mg **9** (0.25 mmol) and 11.9 mg TTBP (0.0025 mmol). The vial was then pumped into a glove-box under argon atmosphere. After, 1.25 mL anhydrous MeCN and 0.89 mL anhydrous trifluorotoluene were added followed by 0.36 mg (0.0003 mmol) PtTPTNP (stored as a 1 mg/mL solution in trifluorotoluene). Afterward, the reaction was sealed, and transferred to the IR light source under the shield of aluminum foil. After, the reaction was irradiated for 24 h at 21°C. Upon completion, the vial was wrapped in aluminum foil and was concentrated under reduced pressure to remove all solvent. The product was purified via column chromatography with silica eluting 20% ethyl acetate in hexanes. The combined fractions were concentrated revealing a white, solid product. The product spectra are identical to the known compound (**10**). Note: We propose the mechanism involves TTBP's ¹[An]^{*} reducing the dienyl azide to the radical-anion which subsequently releases nitrogen gas and cyclizes onto the pendant alkene. The resulting radical can be oxidized by the radical cation, ²A⁺⁺, to turn the photocatalyst over and yield product. Notably, the ³[An]^{*} (~35 kcal/mol, E_{1/2}(PC⁺⁺/PC^{*}) = -0.78 V) is too low energy to perform energy transfer or SET with the substrate (³Sub^{*} ~45 kcal/mol, E_{1/2}(Sub/Sub^{•-}) = -1.55 V vs Ag/AgCl in MeCN), which justifies the requirement of TF upconversion for catalysis.¹⁰



Controls:

No IR laser:	No rxn
No TTBP:	No rxn
No PtTPTNP:	No rxn

Procedure: To a flame dried 1 dram vial containing a stir-bar was added 8 mg TTBP (0.017 mmol). The vial was then pumped into a glove-box under argon atmosphere. After, 1 mL methyl methacrylate **11** (9.35 mmol), 200 μL amethyl α-bromophenyl acetate **13** (1.27 mmol) and 0.36 mg (0.0003 mmol) PtTPTNP (stored as a 1 mg/mL solution in trifluorotoluene) were added to the vial. Afterward, the reaction was sealed, and transferred to the IR light source under the shield of aluminum foil. After, the reaction was irradiated for 2 h at 21°C. Upon completion, the reaction solution was precipitated from methanol. The product was collected as a white solid. GPC analysis reveals the molecular weight and dispersity of our polymer **12**. Note: the (E_{1/2}(13/13^{•-}) = -1.58 V vs Ag/AgCl in MeCN).

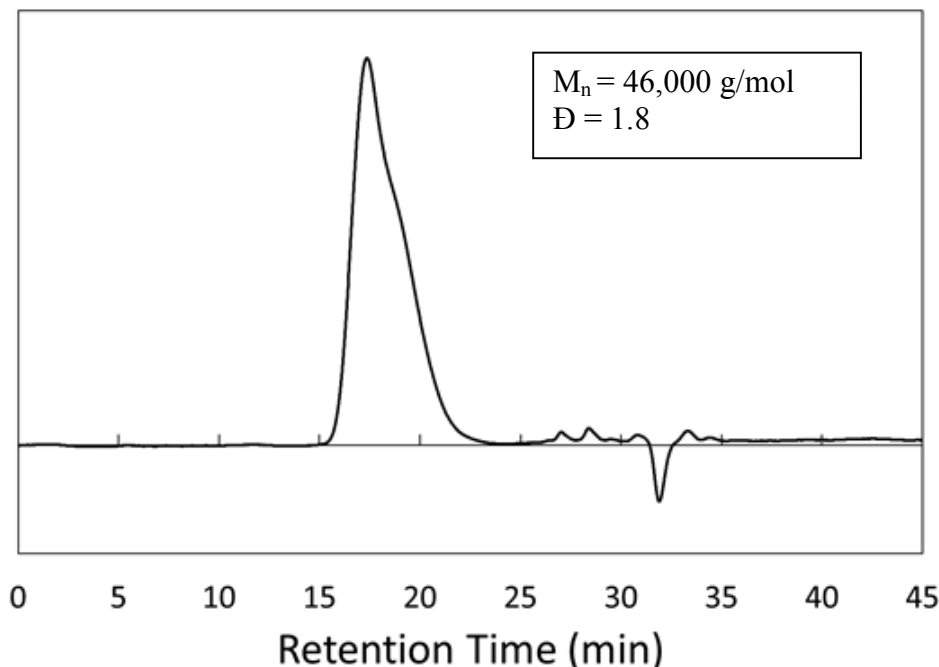
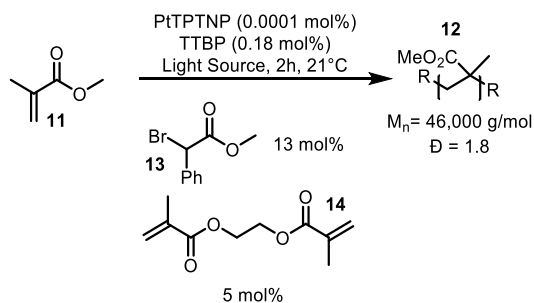


Figure S1. Gel permeation chromatograph of methyl methacrylate polymer generated.



Procedure: To a flame dried 1 dram vial containing a stir-bar was added 8 mg TTBP (0.017 mmol). The vial was then pumped into a glove-box under argon atmosphere. After, 1 mL methyl methacrylate **11** (9.35 mmol), 200 μ L methyl α -bromophenyl acetate **13** (1.27 mmol), 88 μ L ethylene glycol dimethacrylate **14** (0.47 mmol) and 0.36 mg (0.0003 mmol) PtTPTNP (stored as a 0.1 mg/mL solution in trifluorotoluene) were added to the vial. Afterward, the reaction was sealed, and transferred to the light source under the shield of aluminum foil. After, the reaction was irradiated for 4 h at 21°C. Upon completion, the reaction solution became a freestanding gel, indicative of the formation of a crosslinked PMMA if the light source is able to penetrate the barrier. The reaction mixture remaining as a liquid is indicative of a failed reaction.

Light sources used were:

Thorlabs 730 nm 40 mW laser diode (NIR)
 Thorlabs 450 nm 1.6 W laser diode (Blue)
 powerPAR 700-800 nm 15W LED lamp (NIR)
 H150 Kessil 35W LED lamp (400-520 nm, Blue).

LEDs were used when the barrier could be physically wrapped around the reaction vial, otherwise lasers were used in order to fix the barrier in the path of the incident light. The NIR light source was not capable of forming a gel with either a spinach leaf or tripe as a barrier.

Table S1. Barrier Penetration

Barrier	LED or Laser	Blue Result	NIR-Result
Air	Laser	Gel	Gel
Water (1 cm path length cuvette)	Laser	Gel	Gel
Amber Glass Vial	Lamp	No Gel	Gel
Bacon (3.2 mm thick)	Laser	No Gel ^a	Gel
Ru(bpy) ₃ (PF ₆) ₂ solution (1.5 mM in DCM) (1 cm path length cuvette)	Laser	No Gel	Gel
700 nm long pass filter	Laser	No Gel	Gel
3 Sheets white printer paper	LED	No Gel	Gel
Silicone Sheet (7 mm thick)	Lamp	No Gel	Gel
Spinach leaf	Lamp	No Gel	No Gel
Hemoglobin (0.2mM) ^b	Laser	No Gel	Gel
Tripe (14.3 mm thick)	Laser	No Gel	No Gel
Pig Skin (6.4 mm thick)	Laser	No Gel	Gel

^aReaction halted due to bacon burning where laser was focused.

^b In addition to the gelation reaction, the [2+2] in Fig. 2D was performed under the shield of 0.2 mM hemoglobin solution. The yield with the NIR laser is 46% while the blue laser provides 1% yield.

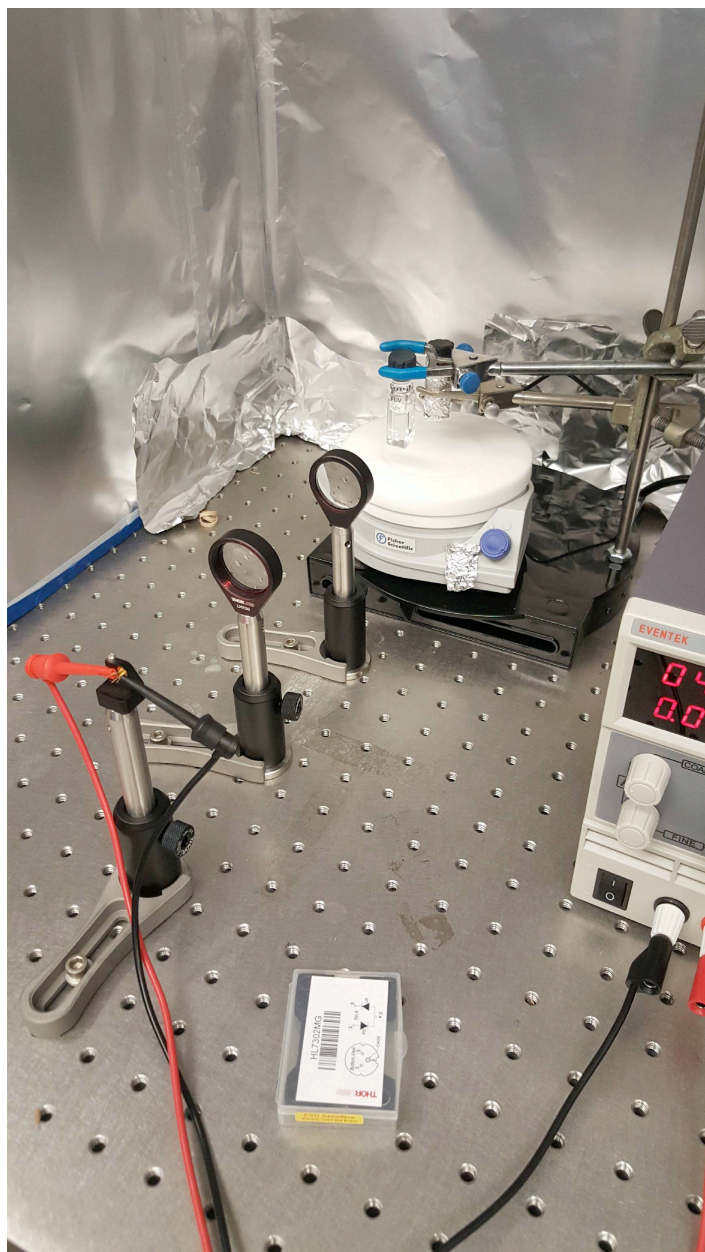


Figure S2. Experimental set up for materials barrier penetration. Shown here with 730 nm laser on, with 1 cm path length quartz cuvette filled with water as the barrier. Reaction wrapped with foil to prevent visible light excitation while taking picture

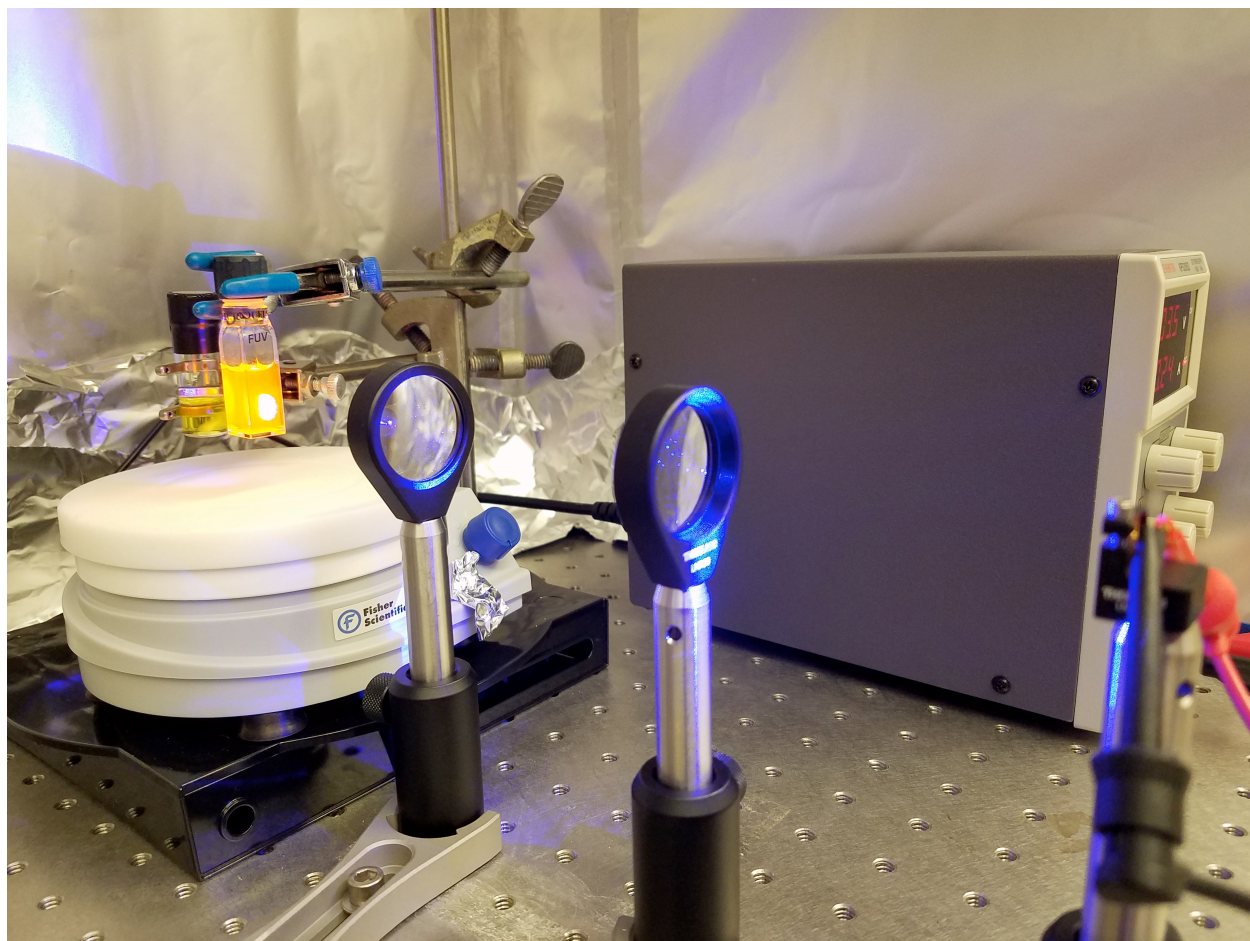


Figure S3. Experimental set up for materials barrier penetration. Shown here with 450 nm laser on, with 1.5mM $\text{Ru}(\text{bpy})_3 (\text{PF}_6)_2$ solution in DCM as the barrier. Note that the barrier completely blocks the reaction vial behind it from absorbing any visible light.



Figure S4. Silicone mold filled with gel reaction mixture, irradiated with NIR lamp through silicone barrier, yielded defined X and O PMMA gels.

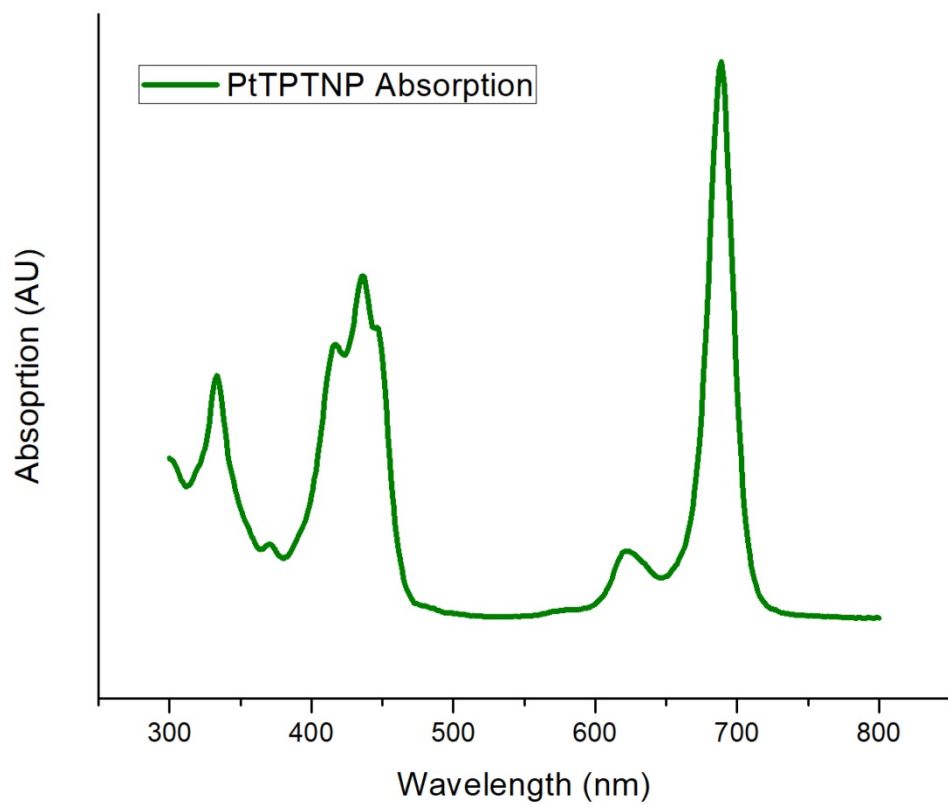
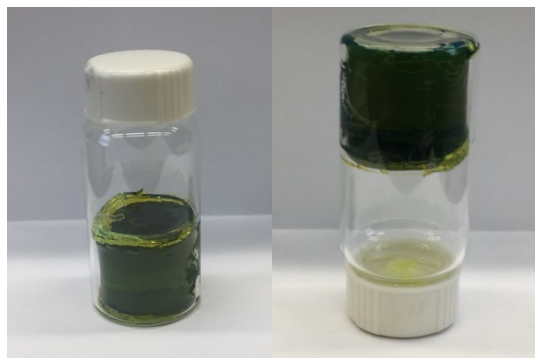


Figure S5. Full absorption spectrum of PtTPTNP in toluene.

A.



B. NIR

Blue



Figure S6. (A) 10g scale cross-linked polymerization flip-experiment with IR lamp; (B) Resulting plastic obtained from IR lamp irradiation (left) and blue lamp irradiation (right).

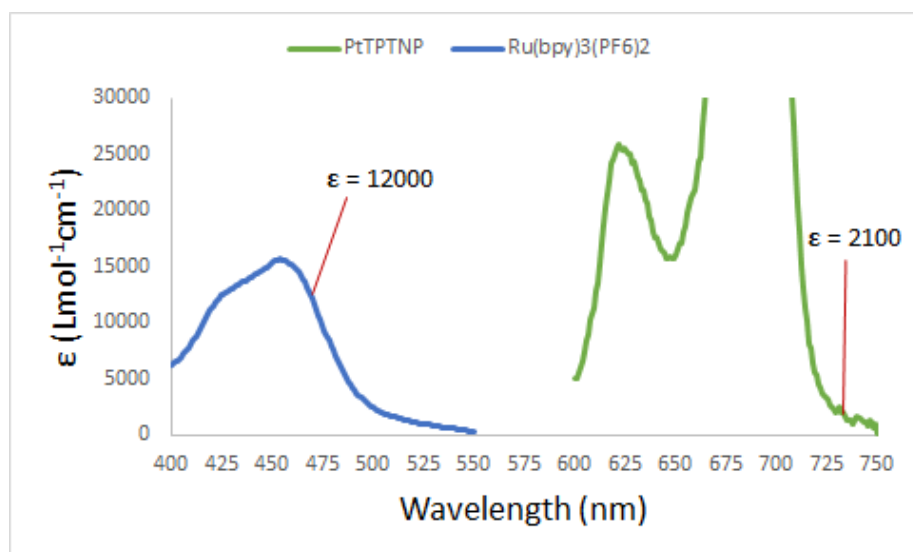


Figure S7. Absorbance depth penetration for IR vs Blue light

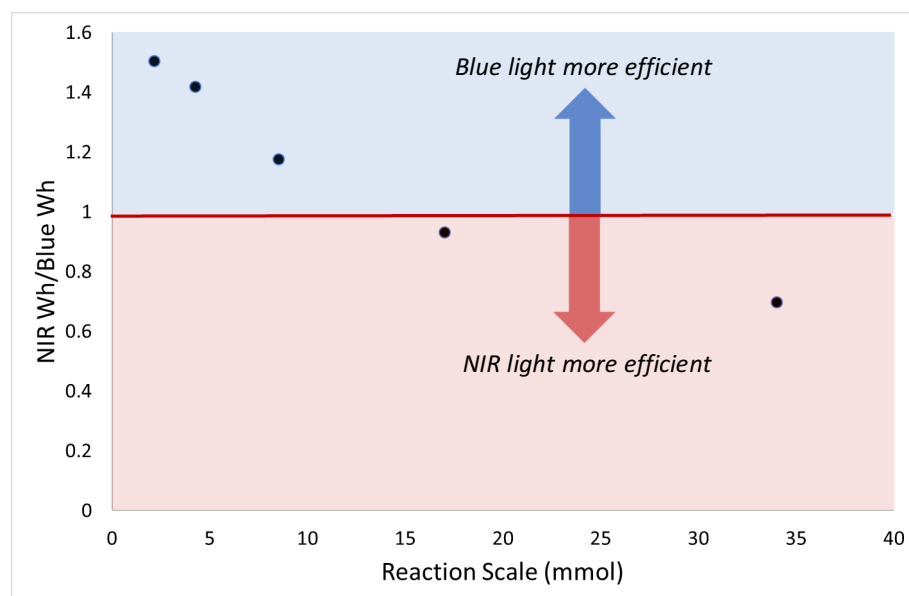


Figure S8. A comparison of power efficiency with reaction scale (Procedure: See procedure for Fig. 2F. The reaction was monitored by GCMS with mesitylene as a standard. The time of the reaction to reach 50% monomer conversion at various scales was measured. Multiplying the reaction time (h) by the power (W) of the beam provides the Wh necessary to perform the reaction. The NIR Wh/Blue Wh is >1 at lower scales and <1 at larger scales.)

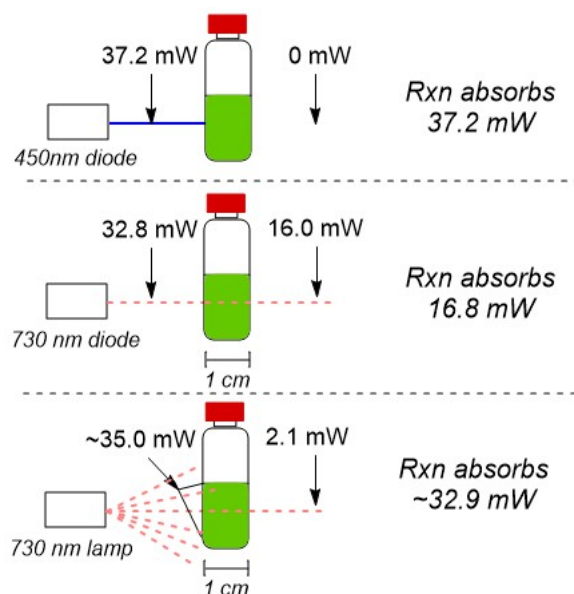


Figure S9. Schematic of how laser power was measured. Reactions were conducted in 1 cm path length quartz cuvettes. Laser power was measured using a Newport 818-SL Si photodetector, which was placed directly in front of and behind the cuvette in order to measure the amount of power absorbed by the reaction. In the case of the 450 nm blue laser diode, no photocurrent was measured by the Si diode behind the cuvette, indicating full absorption of 37.2 mW. In the case of the 730 nm NIR diode, we measured significant photocurrent penetrating the cuvette, with only 16.8 mW absorbed. The laser fluence was measured periodically throughout the experiment and remained constant. 450 nm 80 mW diode was attenuated to achieve a similar power to the 730 nm 40 mW diode. The NIR lamp delivers 35 mW of relatively diffuse photons. As a quantitative comparison of the two light sources, the polymerization in Fig. 2F was performed with each light source and the energy required to reach 50% monomer conversion was measured. The NIR laser requires 0.168 Wh while the NIR lamp requires 0.1925 Wh, indicating comparable reaction efficiencies.

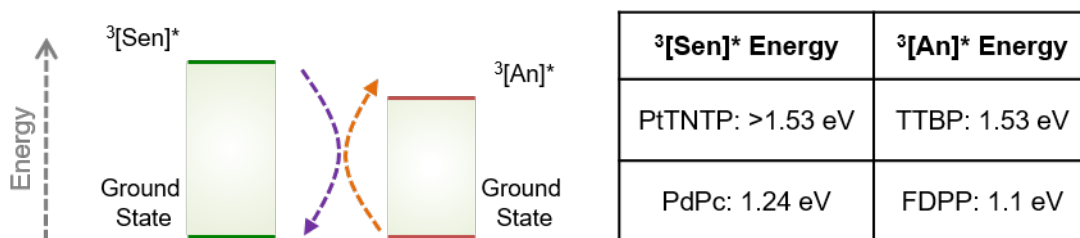


Figure S10. Simplified Jablonski diagram of the triplet energy transfer (TET) step from triplet excited sensitizer $^3[\text{Sen}]^*$ to triplet excited state annihilator $^3[\text{An}]^*$, as well as these triplet energies for the sensitizers and annihilators used in this work. It is necessary that the energy of $^3[\text{Sen}]^*$ be greater than that of $^3[\text{An}]^*$ in order for TET to occur. These energies informed our choice of sensitizer and annihilator pairs. Triplet energies for PdPc¹¹ and FDPP¹² have been reported. We denote the triplet energy of PtTNP as greater than 1.53 eV, because in the past it

has been reported as lower¹³, but the observation of optical upconversion when combined with TTBP indicates that it must have a higher triplet energy than the reported 1.53 eV of TTBP.¹⁴ Previous studies have shown it is possible to use TTBP as an annihilator with 730 nm excitation.¹⁴

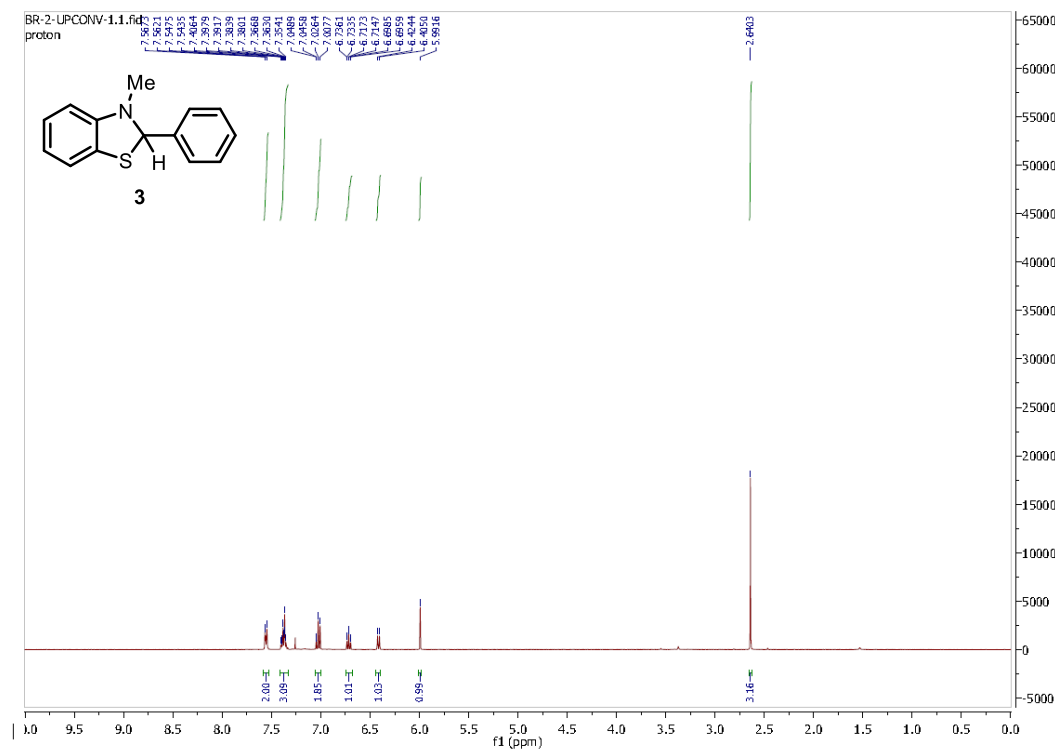
Upconversion Yield Measurements. Upconversion yield (upconversion yield is defined as the percentage of absorbed photons that participate in generating a singlet on the annihilator) measurements were taken following the procedure below:

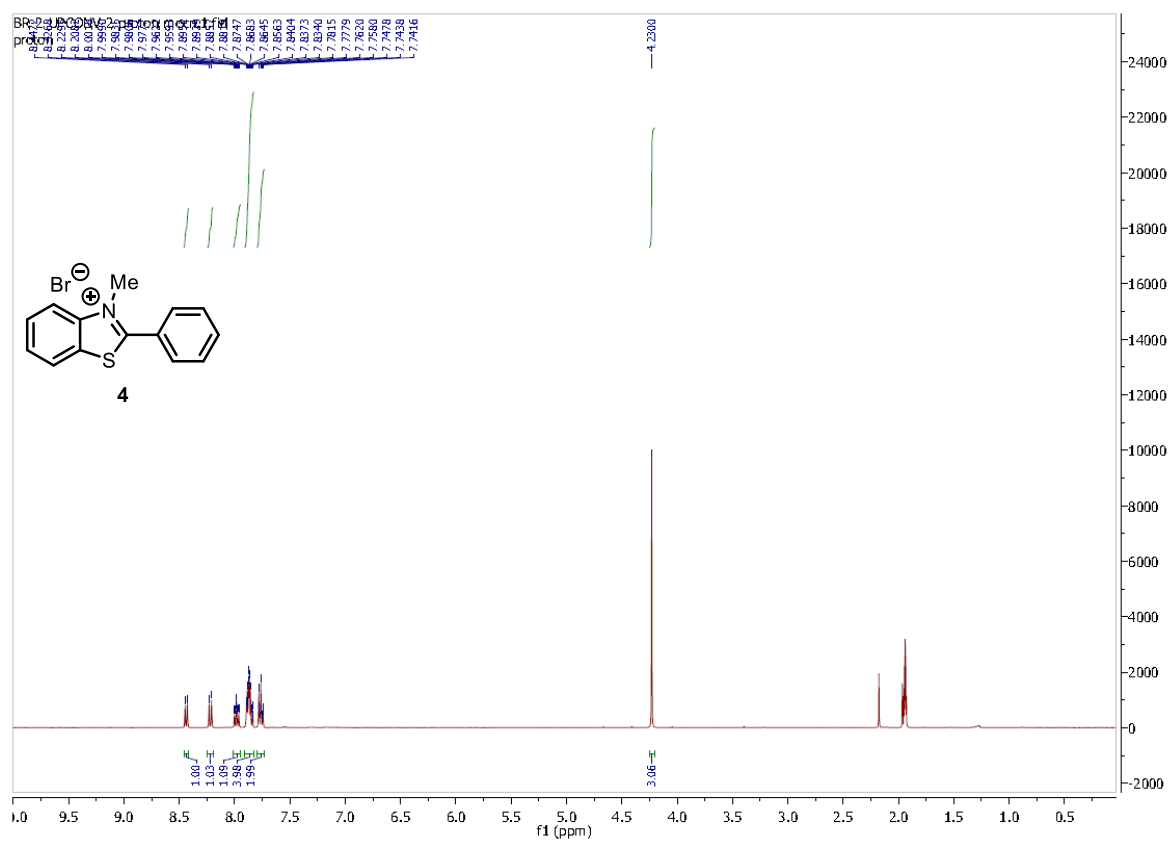
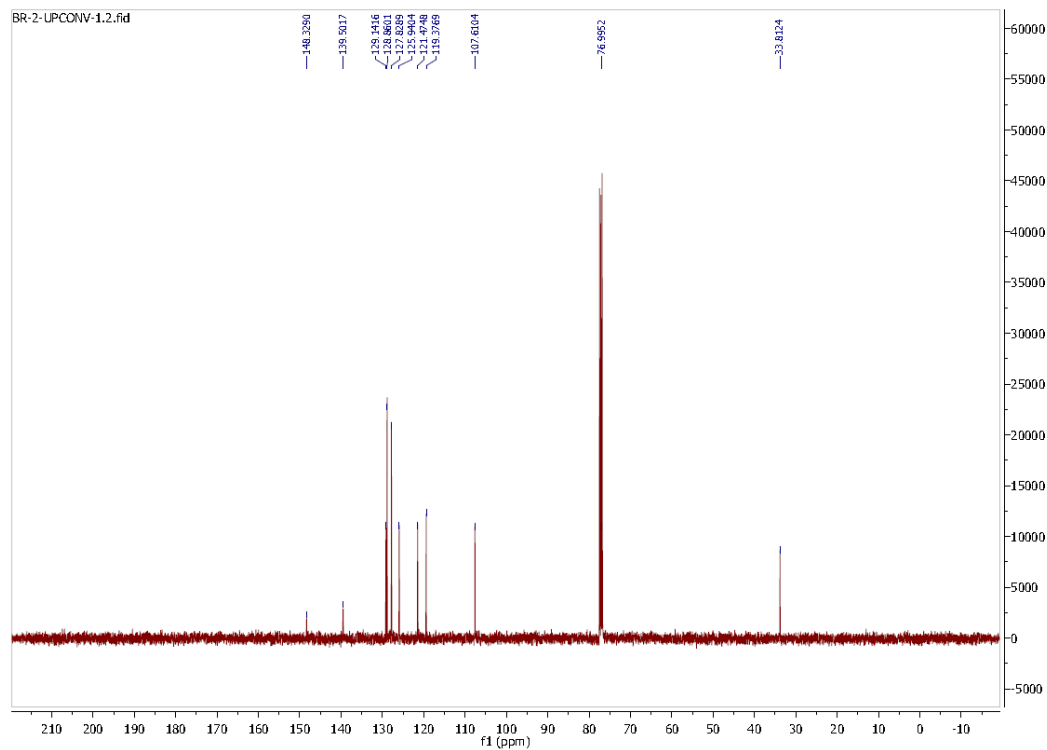
Samples were mixed in an air and moisture-free glovebox and bubbled with N₂ for 60 seconds before being tightly sealed and transferred to an integrating sphere. The upconversion yields were measured following de Mello,¹⁵ where the luminescence with the sample in the beam, out of the beam, and out of the sphere were measured. With this information, the upconversion yield can be calculated. The measurement was performed with both blue 445 nm excitation and NIR excitation; two times the ratio of these two measurements gives the upconversion yield.¹⁶

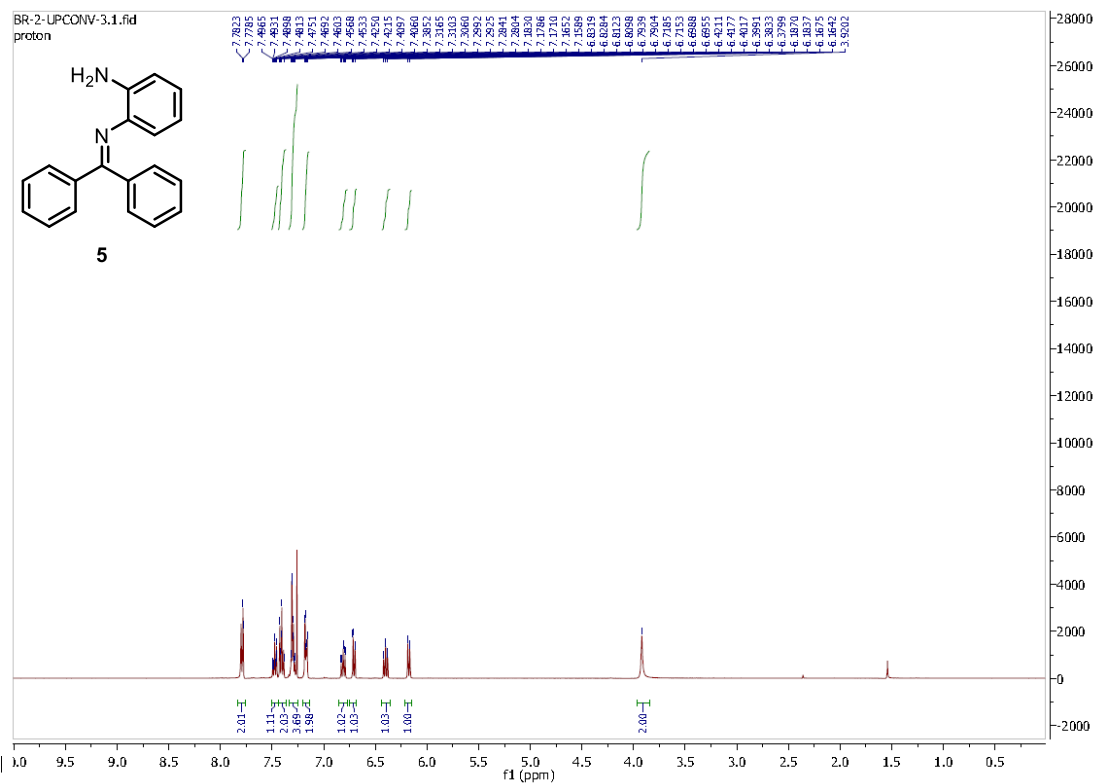
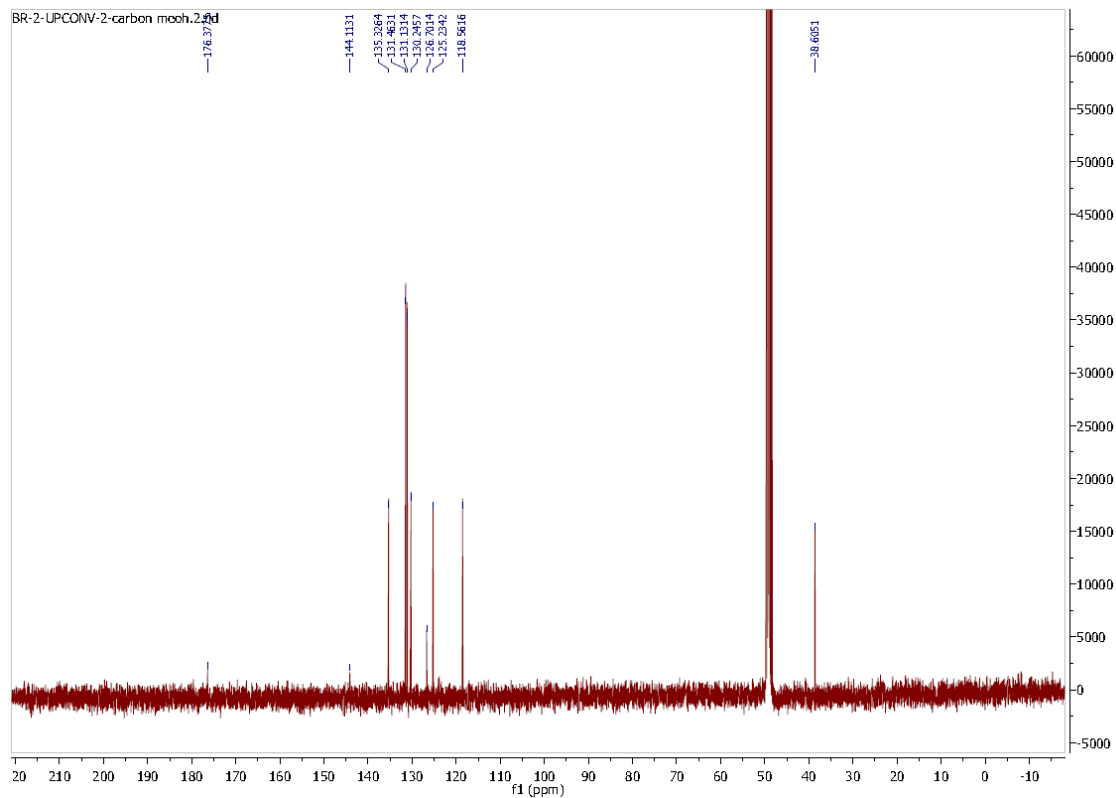
15 mg/mL TTBP, 0.01 mg/mL PtTPTNP excited at 690 nm in toluene → 2.0% upconversion yield.

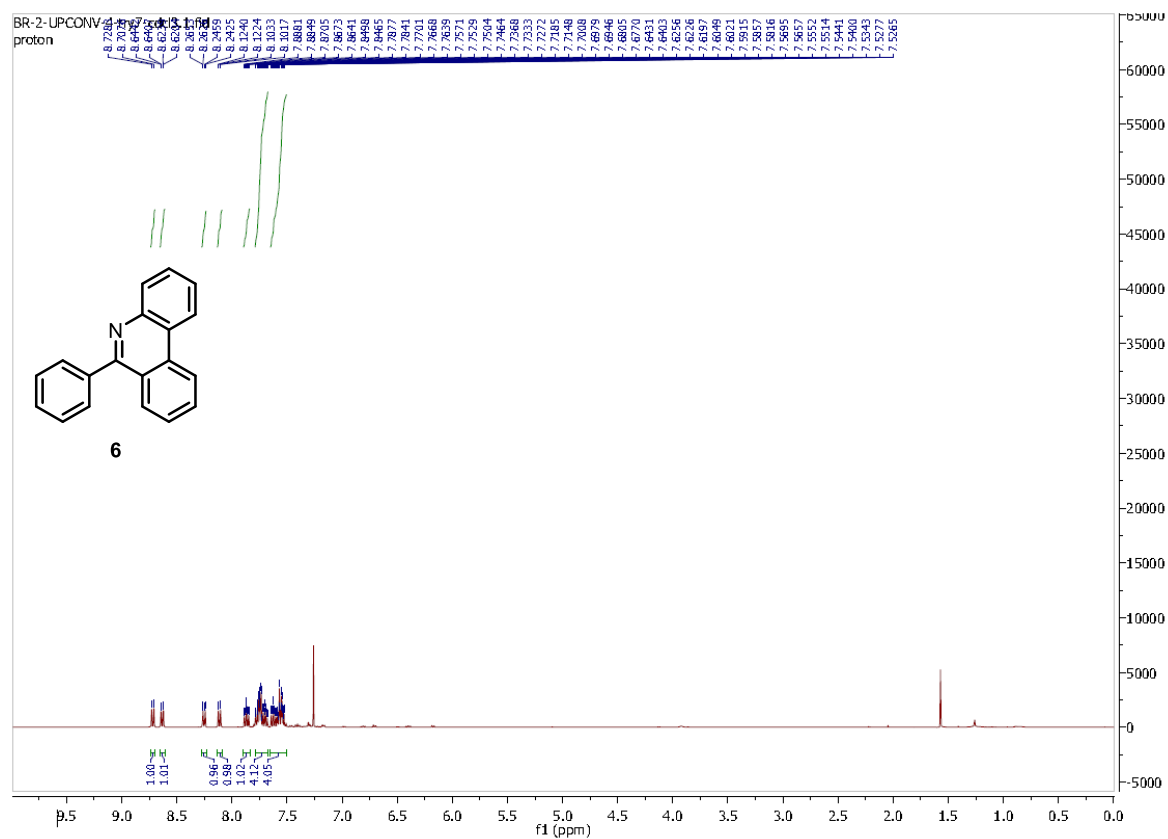
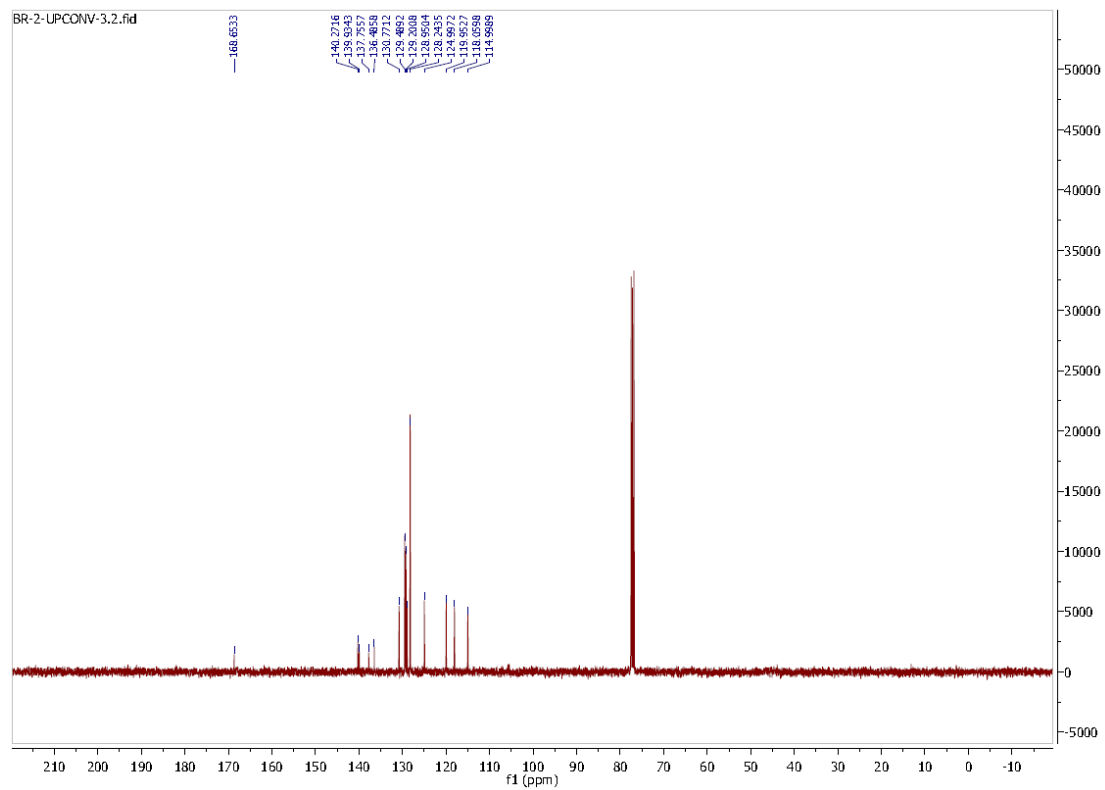
2 mg/mL FDPP, 0.03 mg/mL PdPc excited at 730 nm in toluene → 3.2% upconversion yield.

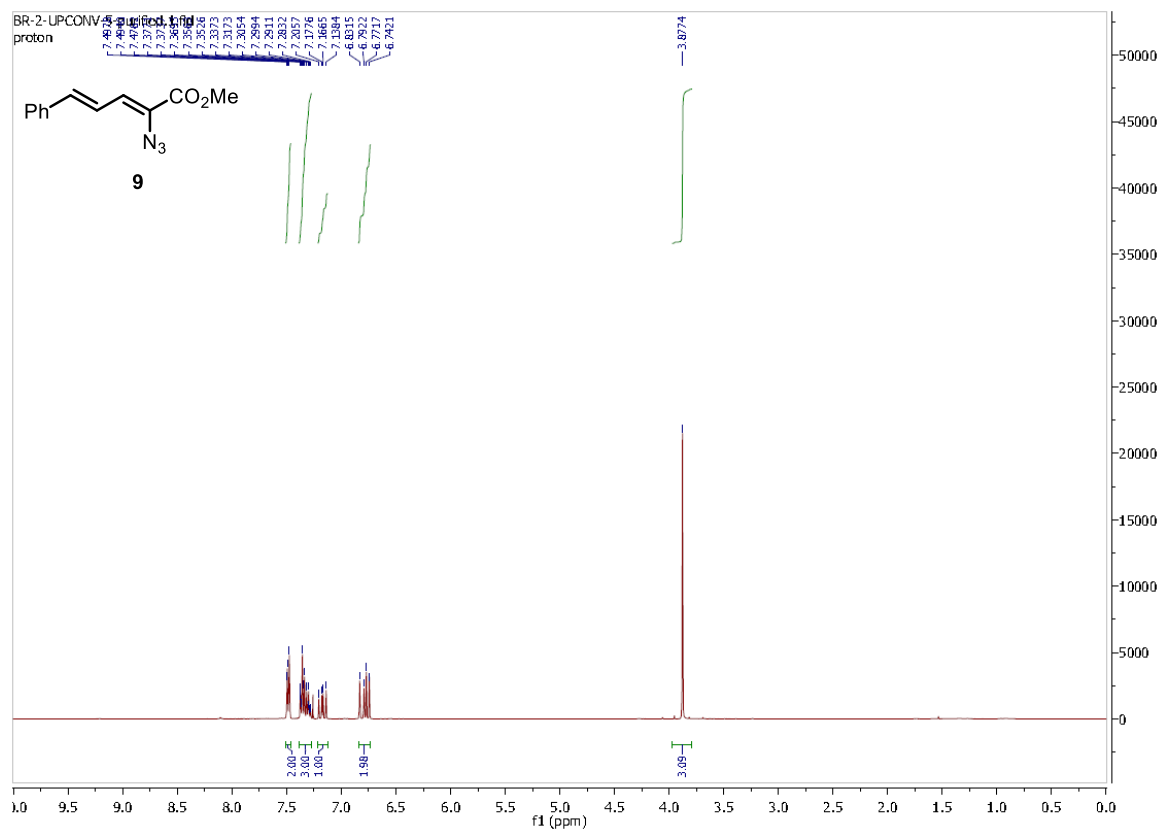
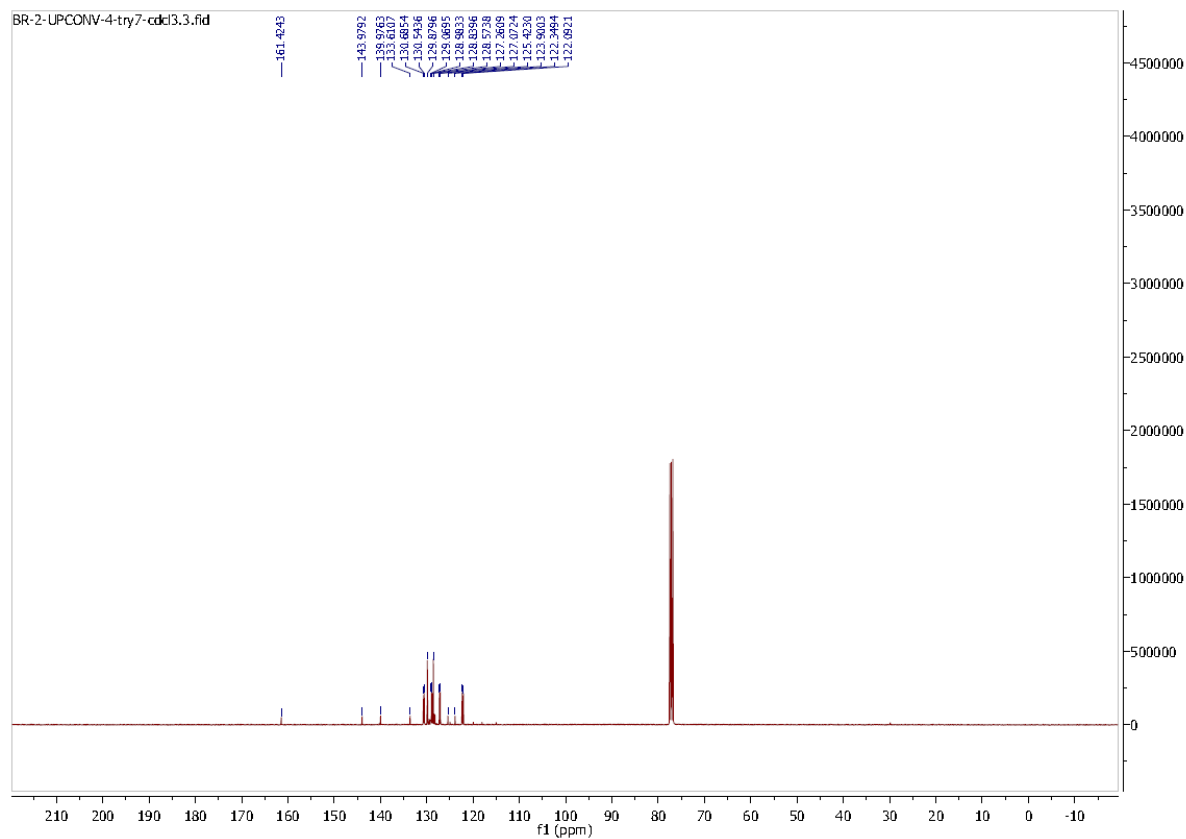
NMR Spectra

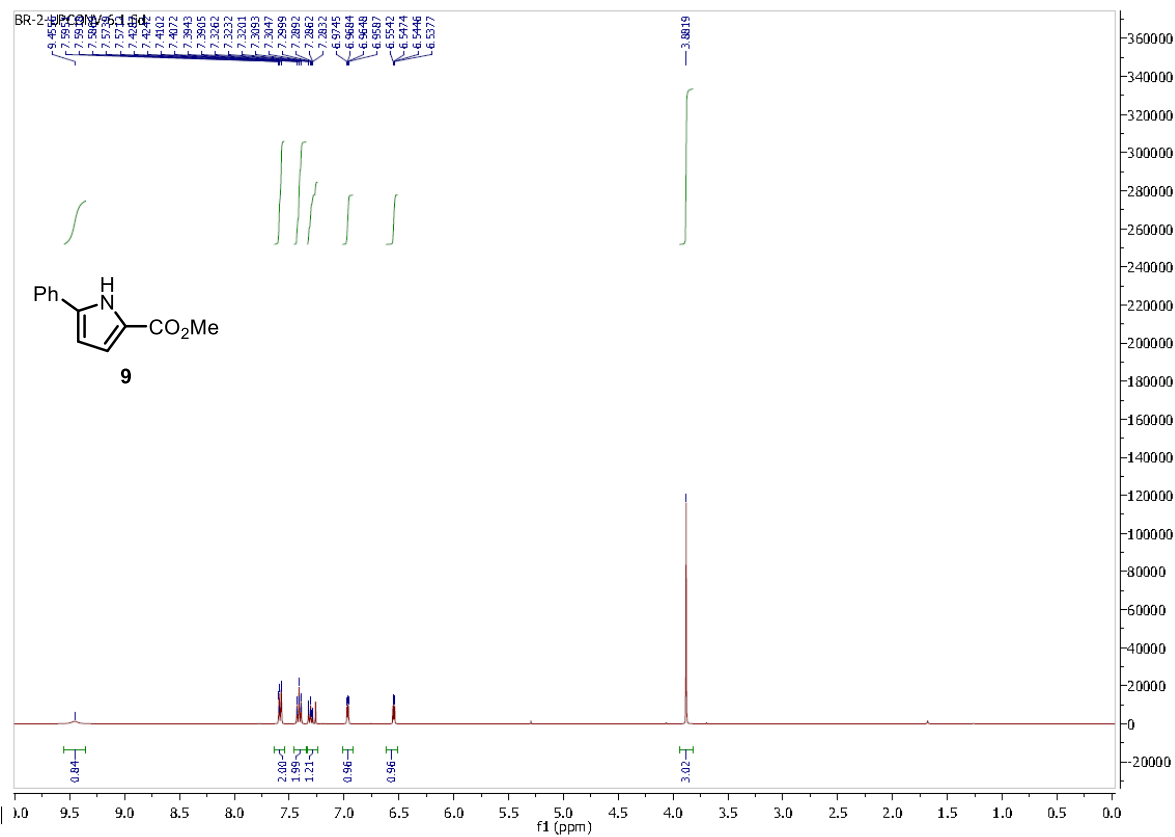
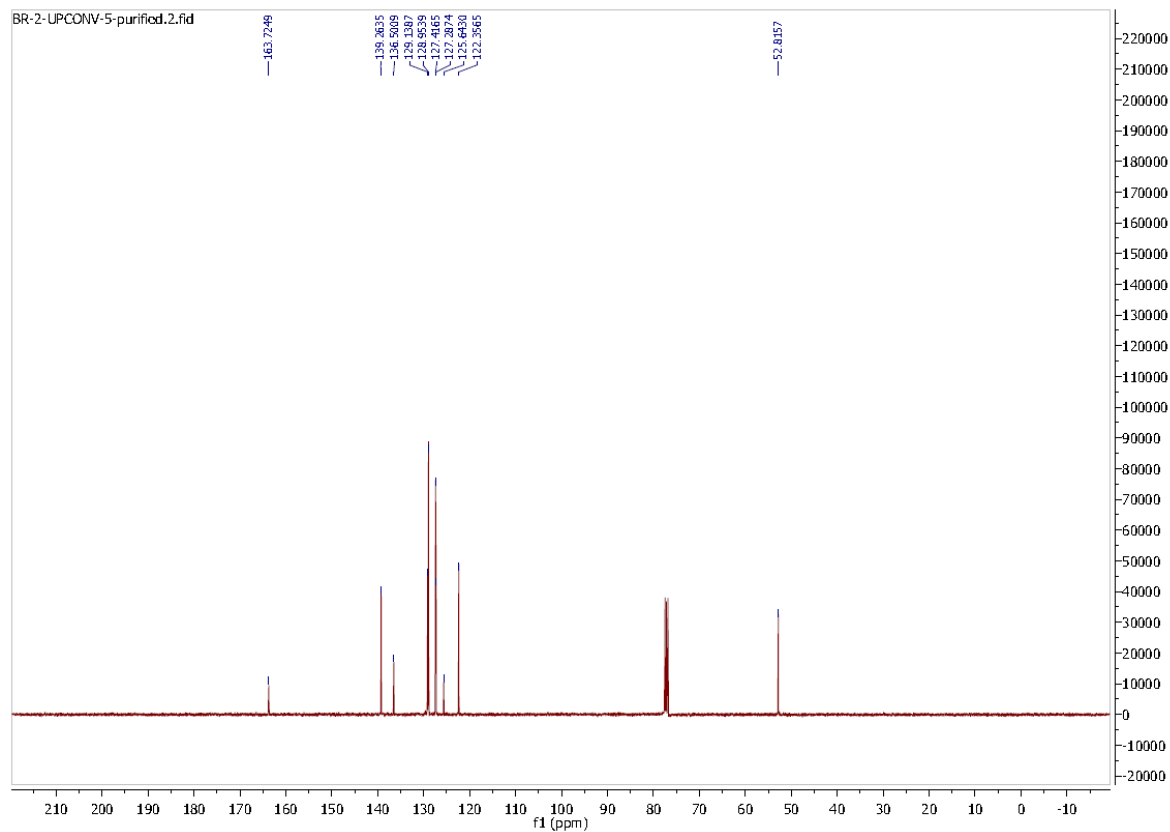


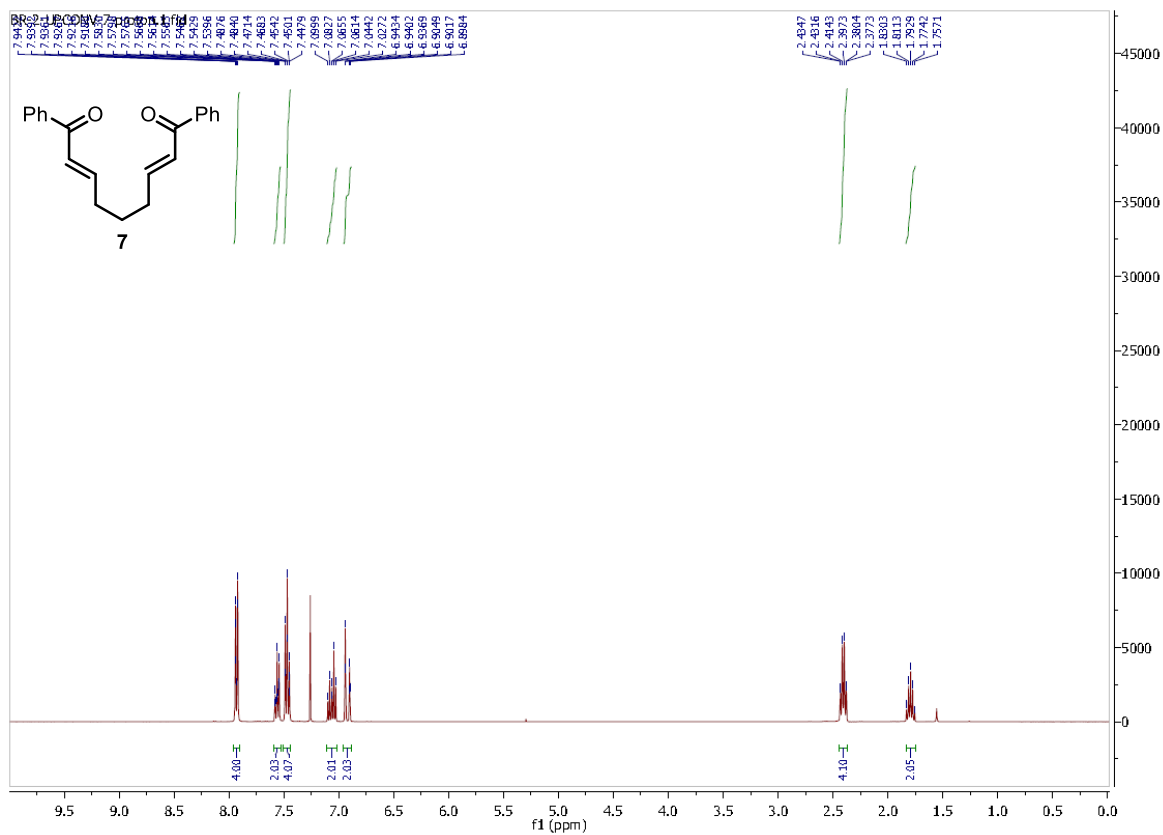
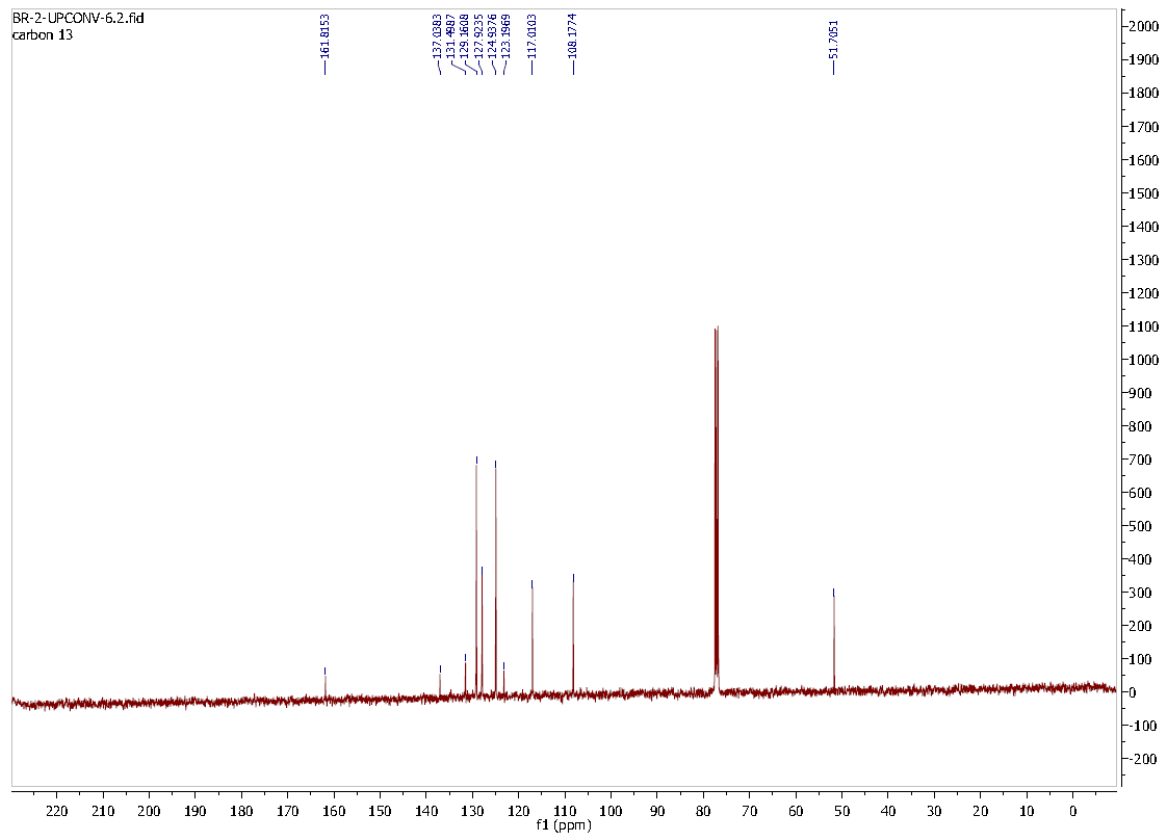


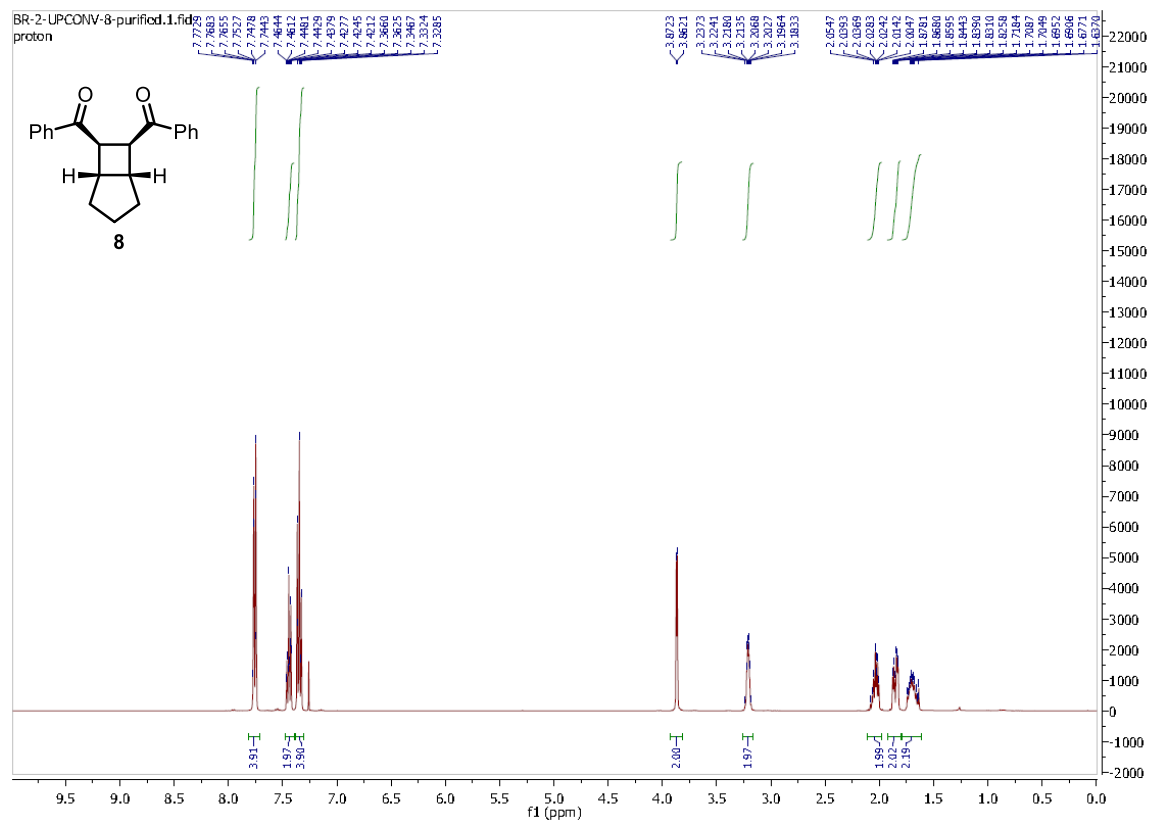
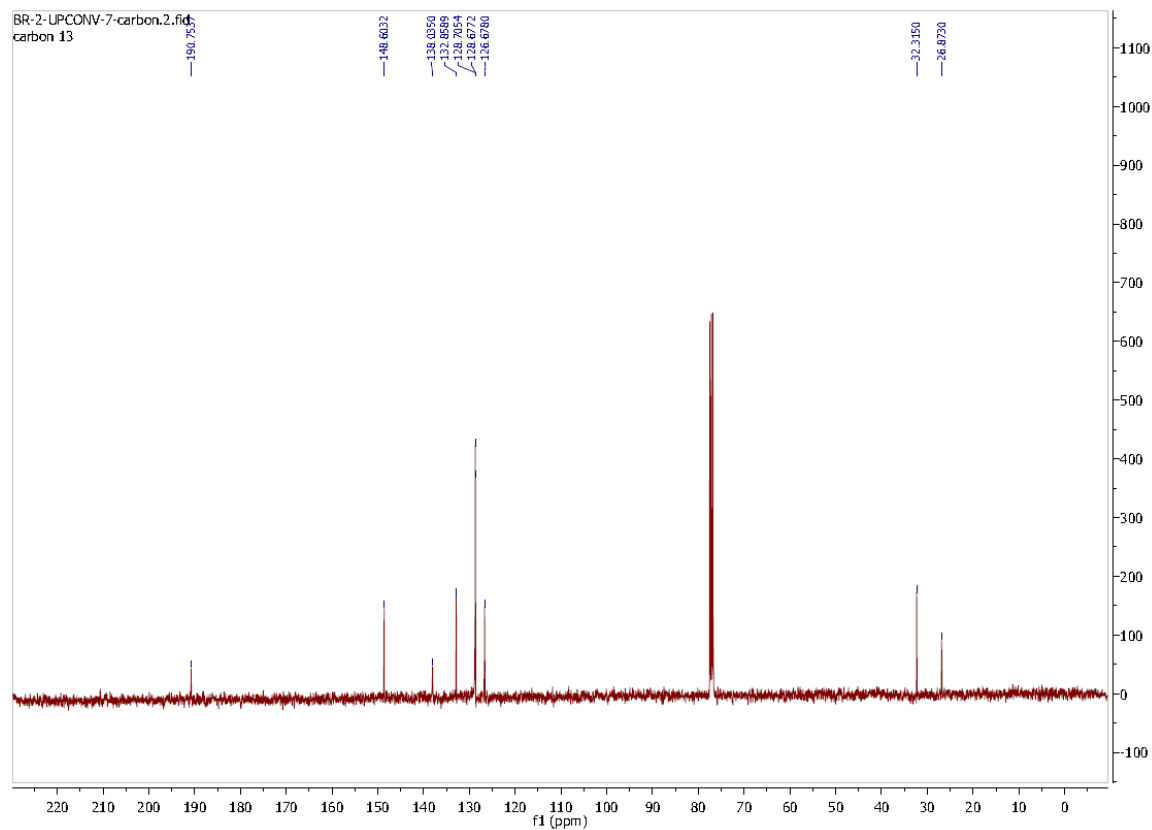


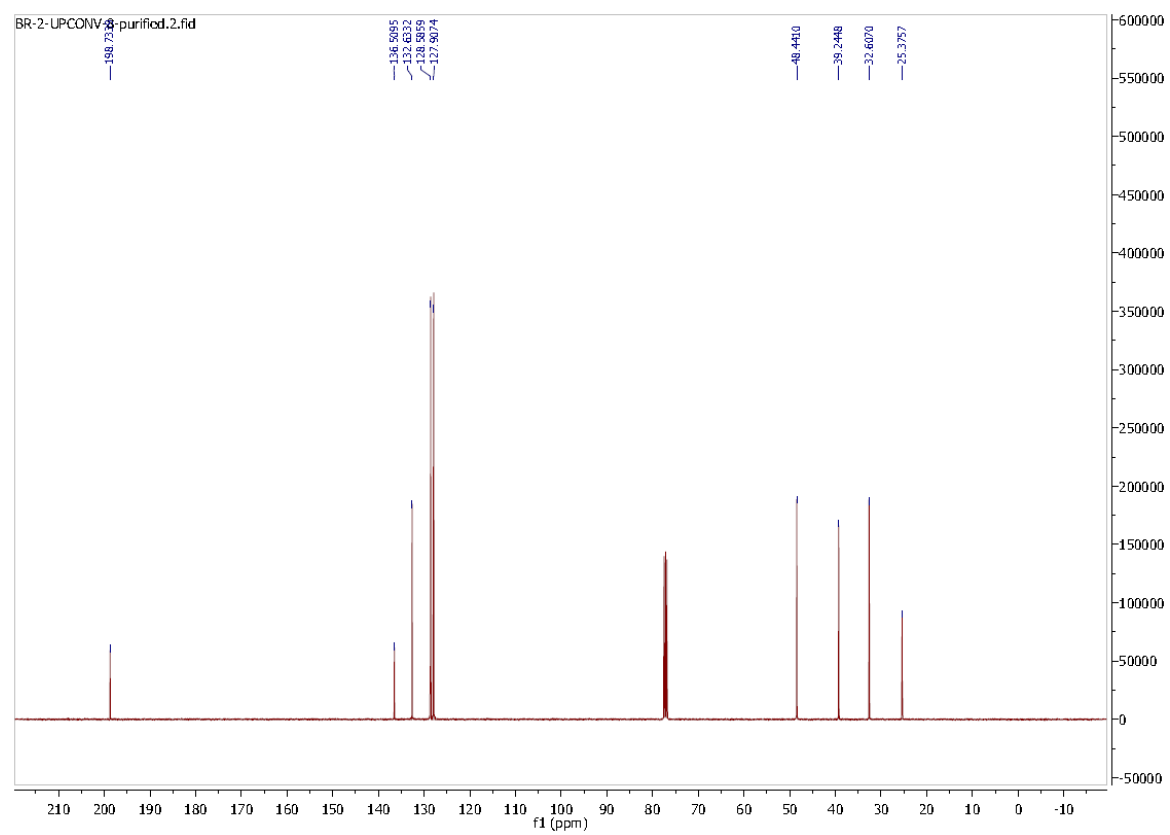


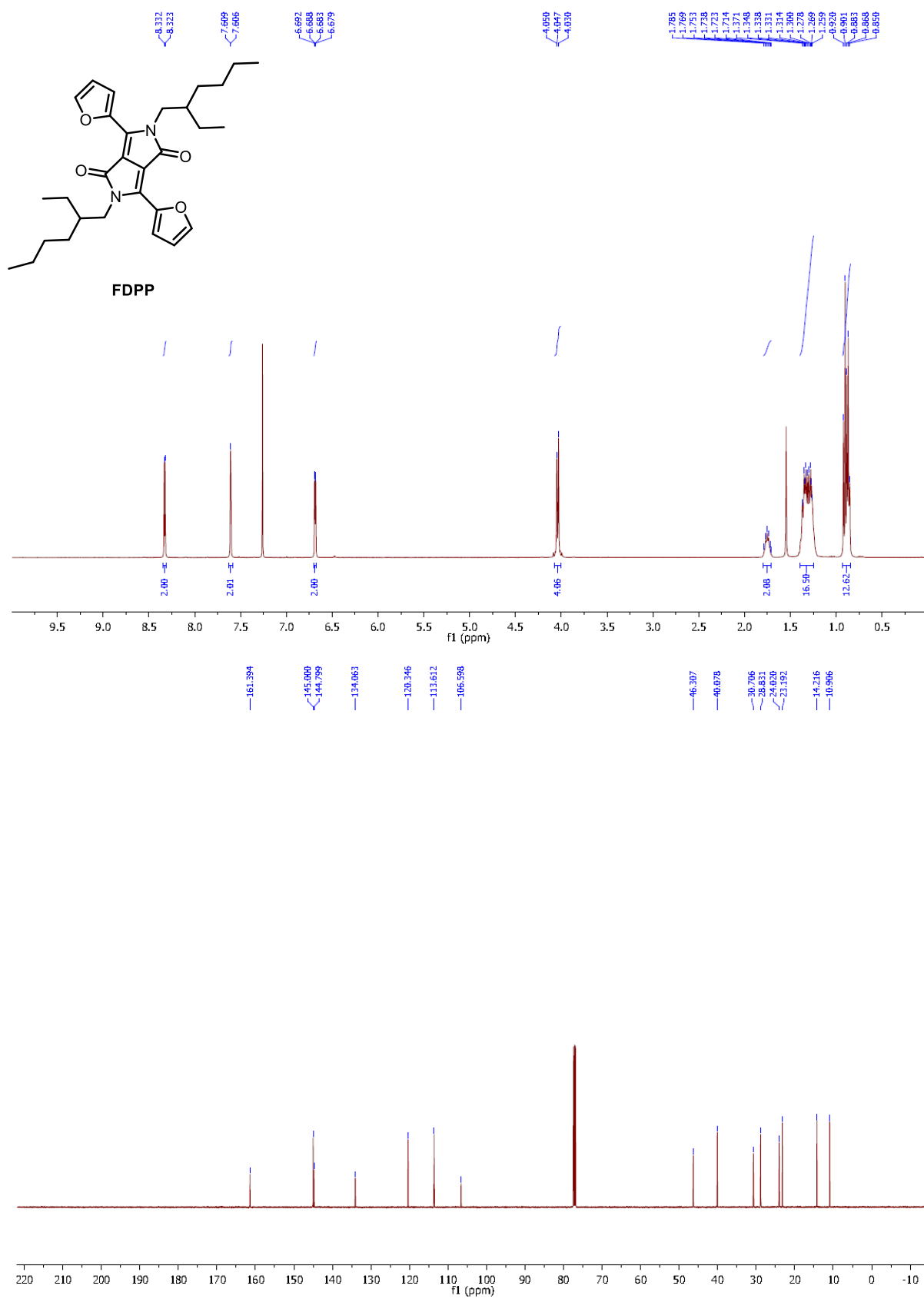


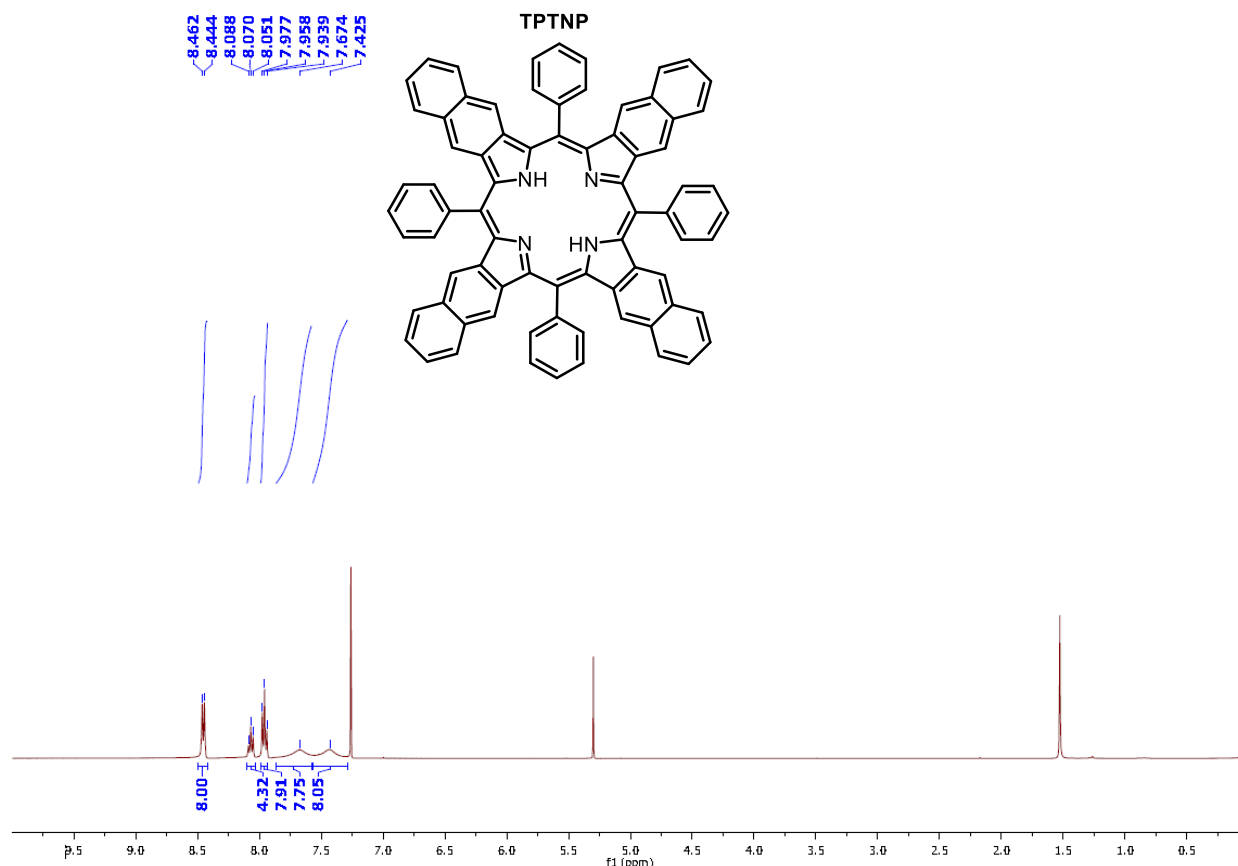












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