

Supplementary Material

Development of a Tethered Palladium–BODIPY Dual Catalyst for Enhanced Photo- and Transition Metal Catalysis, and for Promoting Sequential Reactivity

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Supplementary Material

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General Information

Reagents and solvents

In general, all compounds were commercially available (Sigma Aldrich/Merck, Alfa Aesar and Combi Blocks) and used as received, unless otherwise stated. For all air- or moisture-sensitive procedures acetonitrile, dichloromethane, tetrahydrofuran and pentane were dispensed from a LC Technology solvent purification system and stored under an inert atmosphere in glass ampoules fitted with a J. Young's Teflon valve. *t*-Amyl alcohol was purchased from Sigma Aldrich and saturated with air before use. Solvents for extractions and columns such as dichloromethane, methanol, *n*-hexane and ethyl acetate were technical grade. Deuterated solvents were purchased from Cambridge Stable Isotopes and used as received. The compressed argon gas (> 99.999%) was obtained from Air Liquide and used as received. The nitrogen gas for the Schlenk line is from in-house liquid nitrogen boil-off.

Experimental techniques

Whether an inert or air atmosphere was used for a reaction is specified in the experimental section. All manipulations that were performed under an inert atmosphere were done so using standard Schlenk techniques or in a glovebox (LC Technology Solutions Inc.). Unless otherwise stated, all reaction work-ups were carried out in air. The term 'under reduced pressure' refers to use of a rotary evaporator, and '*in vacuo*' indicates use of a high vacuum pump attached to a Schlenk line.

The photocatalysis experiments were performed using a green LED light strip (12 V green 5 M 3528 SMD 300 LED strips). The spectra of the green LED had a maximum wavelength of 510 nm.

Characterisation

All ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B , ^{31}P and ^{19}F NMR spectra were recorded on either a Bruker 400 or 500 MHz (^1H) spectrometer. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts were referenced internally using the residual solvent resonance. Unless otherwise stated, spectra were recorded at 298 K, and chemical shifts (δ), are quoted in parts per million (ppm). Multiplicity is abbreviated as: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet) and br (broad). The annotations of the Pd-BDP **4** were determined by two-dimension NMR spectroscopy experiments, including homonuclear correlation spectroscopy (COSY), nuclear overhauser effect spectroscopy (NOESY), heteronuclear single-quantum correlation spectroscopy (HSQC) or heteronuclear multiple-bond correlation spectroscopy (HMBC).

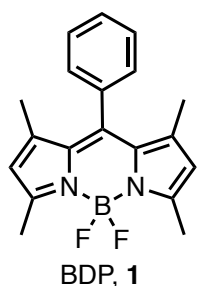
High Resolution Mass Spectrometric (HRMS) analyses were performed on a Q ExactiveTM Plus (Thermo Scientific), spray voltage: 4.5 kV.

UV-Vis measurements were carried out on a Cary 8458 UV-Vis spectrophotometer from Agilent Technologies, using a step size of 1 nm. Emission spectra were acquired on an Edinburgh FLS980 spectrophotometer using 450 W Xenon lamp for excitation, using $\lambda_{\text{ex}} = 371$ nm, step size = 1 nm, integration time = 0.3 s. Absolute quantum yields were measured using an integrating sphere from Edinburgh Instruments, using an integration time of 0.3 s. The quantum yield was measured once for each sample, with an estimated instrumental error of $\pm 5\%$.

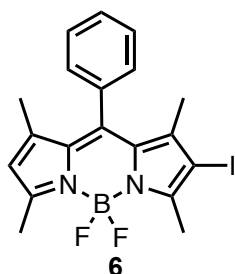
Fluorescence (τ_{F}) and phosphorescence (τ_{P}) lifetimes in solution were measured with an EPL-VIS Picosecond Pulsed Diode Laser ($\lambda_{\text{max}} = 371.8$ nm) from Edinburgh Instruments, either under an air or nitrogen atmosphere (as stated). All data was tail fit, or reconvolution fit, to a mono-exponential term, with all fitting having χ^2 between 1.0 and 1.3, resulting in a maximum standard deviation of 0.004 ns. Sample

Pd-BDP **4** with low fluorescence quantum yield was measured by using a neutral density filter. LUDOX HS-40 colloidal silica (40 wt. % suspension in H₂O) was used to measure the instrument response function (IRF).

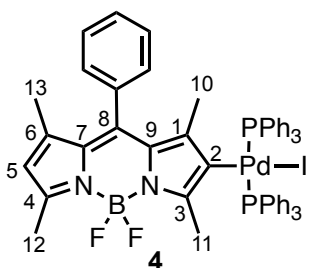
Synthetic Procedures



BDP **1** was synthesised according to a reported procedure.^[1] ¹H NMR (400 MHz, Methylene Chloride-*d*₂) δ 7.54 – 7.43 (m, 3H), 7.34 – 7.22 (m, 2H), 5.99 (s, 2H), 2.49 (s, 6H), 1.37 (s, 6H) ppm. ¹¹B NMR (128 MHz, Methylene Chloride-*d*₂) δ 0.72 (t, *J* = 33.0 Hz) ppm. ¹⁹F NMR (376 MHz, Methylene Chloride-*d*₂) δ -146.29 (q, *J* = 32.7 Hz) ppm. The data matches that reported in the literature (in Chloroform-*d*).^[1]



Compound **6** was synthesised according to a reported procedure.^[2] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.40 (m, 3H), 7.28-7.25 (m, 2H), 6.04 (s, 1H), 2.63 (s, 3H), 2.57 (s, 3H), 1.38 (s, 6H) ppm. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 0.67 (t, *J* = 32.8 Hz) ppm. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -145.99 (q, *J* = 32.6 Hz) ppm. The data matches that reported in the literature.^[2]



Pd-BDP **4** was synthesised by reacting to the iodo substituted BDP compound **6** (23 mg, 0.05 mmol) with Pd(PPh₃)₄ **3** (58 mg, 0.05 mmol) in the presence of K₂CO₃ (76 mg, 0.25 mmol) in THF-H₂O (9:1, v/v, 5 mL) under a nitrogen atmosphere at 85 °C for 18 hours. The reaction mixture was filtered through Celite and washed thoroughly with CH₂Cl₂. The combined organic extractions were dried over anhydrous Na₂SO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by using flash column chromatography on silica gel eluting with CH₂Cl₂-hexane (1:1, v/v, R_f = 0.5) to afford a deep-red solid in 83% yield (45 mg). ¹H NMR (400 MHz, Methylene Chloride-*d*₂) δ 7.57 – 7.48 (m, 12H, P-*ortho*-CH), 7.42 (t, *J* = 7.3 Hz, 6H, P-*p*-CH), 7.37 – 7.25 (m, 15H, P-*meta*-CH overlapped with *ortho*- and *para*-CH of ph), 6.78 – 6.72 (m, 2H, *meta*-CH of ph), 5.80 (s, 1H, **H5**), 2.35 (s, 3H, **H12**), 2.24 (s, 3H, **H11**), 1.18 (s, 3H, **H13**), 0.76 (s, 3H, **H10**) ppm. ¹³C{¹H} NMR (101 MHz, Methylene Chloride-*d*₂) δ 159.9 (s, **C3**), 150.5 (s, **C2**), 150.0 (s, **C4**), 145.7 (s, **C1**), 139.5 (s, **C7**), 137.4 (s, **C8**), 136.2 (s, *ipso* C of Ph), 135.4 (t, ²*J*_{PC} = ⁴*J*_{PC} = 6.1 Hz, P-*ortho*-C), 133.9 (s, **C9**), 132.7 (t, ¹*J*_{PC} = 25.0 Hz, P-C), 131.1 (s, P-*para*-C), 129.5 (s, **C6**), 129.2 (s, *ortho*-C of Ph), 128.9 (s, *meta*-C of Ph), 128.9 (s, *para*-C of Ph), 128.7 (t, ³*J*_{PC} = ⁵*J*_{PC} = 5.2 Hz, P-*meta*-C), 119.6 (s, **C5**), 18.4 (s, **C11**), 17.8 (s, **C10**), 14.7 (s, **C12**), 14.5 (s, **C13**) ppm. ¹¹B NMR (128 MHz, Methylene Chloride-*d*₂) δ 0.26 (t, *J* = 33.6 Hz) ppm. ¹⁹F NMR (376 MHz, Methylene Chloride-*d*₂) δ -146.92 (q, *J* = 32.6 Hz) ppm. ³¹P NMR (162 MHz, Methylene Chloride-*d*₂) δ 22.67 ppm. HRMS (ESI⁺, MeOH) calculated for [C₅₅H₄₈BF₂N₂PdIP₂+H]⁺: 1081.15062 [M+H]⁺, found 1081.14903.

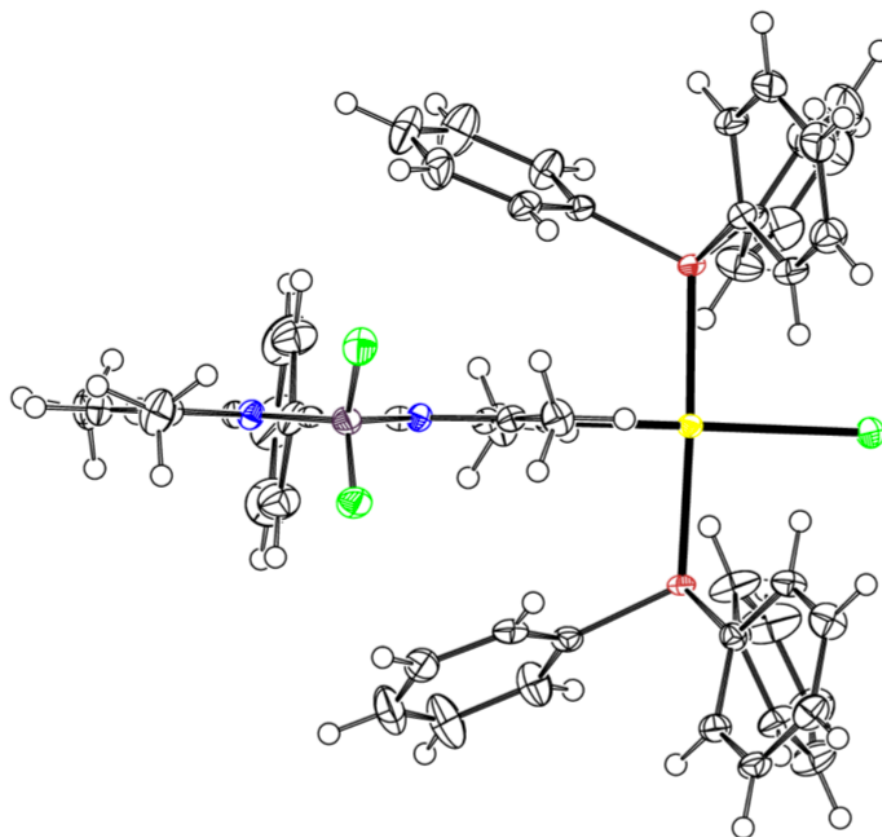
X-ray Crystallographic Data

Table S1: Crystallography data of Pd-BDP 4

Complex	Pd-BDP 4
CCDC number	1961608
Empirical formula	C ₅₅ H ₄₈ BF ₂ IN ₂ P ₂ Pd
Formula weight	1081.00
Temperature / K	149.15
Crystal system	Monoclinic
Space group	P2 ₁
a / Å	11.3987(7)
b / Å	16.6855(10)
c / Å	13.7811(8)
α / °	90.00
β / °	108.703(2)
γ / °	90.00
Volume / Å ³	2482.7(3)
Z	2
ρ_{calc} / cm ³	1.446
μ / mm ⁻¹	1.105
F(000)	1088.0
Crystal size / mm ³	0.6 × 0.3 × 0.17
Radiation	MoK α (λ = 0.71073)
2 Θ range / °	3.78 to 55.18
Index ranges	-14 ≤ h ≤ 14, -21 ≤ k ≤ 21, -17 ≤ l ≤ 16
Reflections collected	58140
Independent reflections	11462 [R _{int} = 0.0538, R _{sigma} = 0.0356]
Data/restraints/parameters	11462/1/582
Goodness-of-fit on F ²	1.144
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0312, wR ₂ = 0.0684
Final R indexes [all data]	R ₁ = 0.0367, wR ₂ = 0.0734
Largest diff. peak/hole / e Å ⁻³	1.23/-0.80
Flack parameter	0.00(13)

Table S2: Summary of selected distances between atoms and bond angles for complex Pd-BDP 4

Atoms	Bond lengths (Å)	Atoms	Bond angles (°)
Pd-I	Pd1-I1: 2.6732(3)	P-Pd-I	P1-Pd1-I1: 91.35(2) P2-Pd1-I1: 90.86(2)
Pd-C	Pd1-C17: 2.015(4)	P-Pd-C	P1-Pd-C17: 89.08(10) P2-Pd-C17: 88.70(10)
Pd-P	Pd1-P1: 2.3339(9) Pd1-P2: 2.3153(9)	N-B-N	N1-B1-N2: 107.6(3)
B-N	B1-N1: 1.545(4) B1-N2: 1.544(6)	F-B-F	F1-B1-F2: 109.7(2)
B-F	B1-F1: 1.393(5) B1-F2: 1.399(5)	F-B-N	F1-B1-N1: 110.3(3) F1-B1-N2: 110.0(3) F2-B1-N1: 109.6(3) F2-B1-N2: 110.3(3)
Pd-B	Pd1-B1: 5.652(4)		

**Figure S1:** The molecular structure of Pd-BDP 4 generated using the ORTEP program.^[3] The ellipsoids are drawn at a 50% probability level.

Measurement of the Singlet Oxygen Quantum Yields

The singlet oxygen quantum yields (Φ_{Δ}) were determined using the chemical trapping method, as frequently used in the literature.^[4] *t*-Amyl alcohol was saturated with air by bubbling air through the solvent for 1 hour before use. A mixture of 1,3-diphenylisobenzofuran **7** (DPBF) (3×10^{-5} mol/L) and the respective photocatalyst (1×10^{-5} mol/L) was dissolved in 2 mL of air saturated *t*-amyl alcohol, and was irradiated under green LED light (max wavelength = 510 nm). The photooxidation of DPBF **7** was monitored over time, ranging from 5 seconds to 1 minute depending to the efficiency of the photocatalyst. The time dependent absorption graphs showing the decrease in the DPBF **7** signal at 410 nm, and the corresponding linear regression (natural log of the absorbance against time) from which the rate constant was calculated, are shown in Figures S2 to S6.

The Φ_{Δ} data was obtained according to Equation 1 using methylene blue ($\Phi_{\Delta}^{ref} = 0.52$ in ethanol)^[5] as the reference:

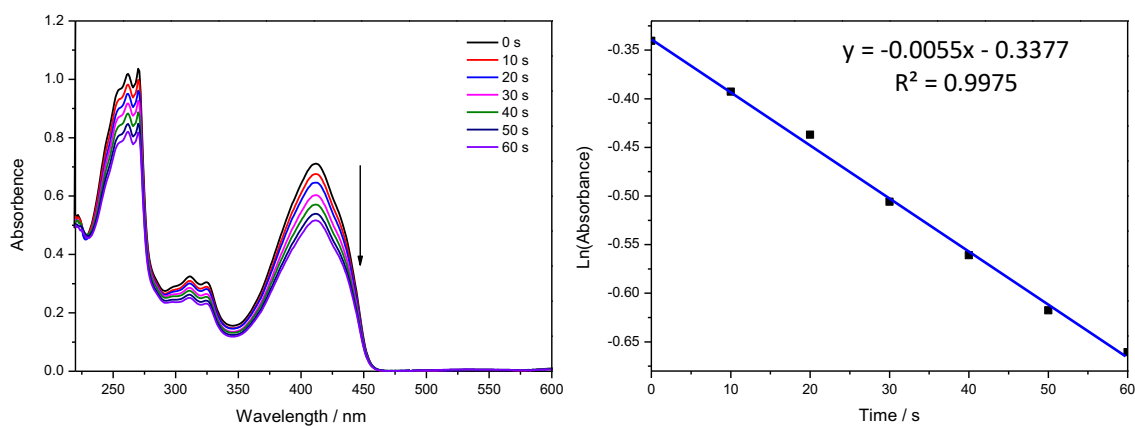
$$\Phi_{\Delta} = \Phi_{\Delta}^{ref} \frac{k}{k^{ref}} \frac{I_a^{ref}}{I_a} \quad (1)$$

where k and k^{ref} are the DPBF **7** photobleaching rate constants in the presence of the either the corresponding photocatalyst or methylene blue reference (calculated from the natural log of the absorbance at 410 nm), respectively; I_a and I_a^{ref} are the absorption correction factors at the irradiation of 510 nm by the samples and the standard, respectively. I_a and I_a^{ref} were calculated according to Equation 2, where A_{510} is the absorption of the species at 510 nm.

$$\frac{I_a^{ref}}{I_a} = \frac{1 - 10^{-A_{510}^{ref}}}{1 - 10^{-A_{510}}} \quad (2)$$

Methylene blue reference

Repeat 1



Repeat 2

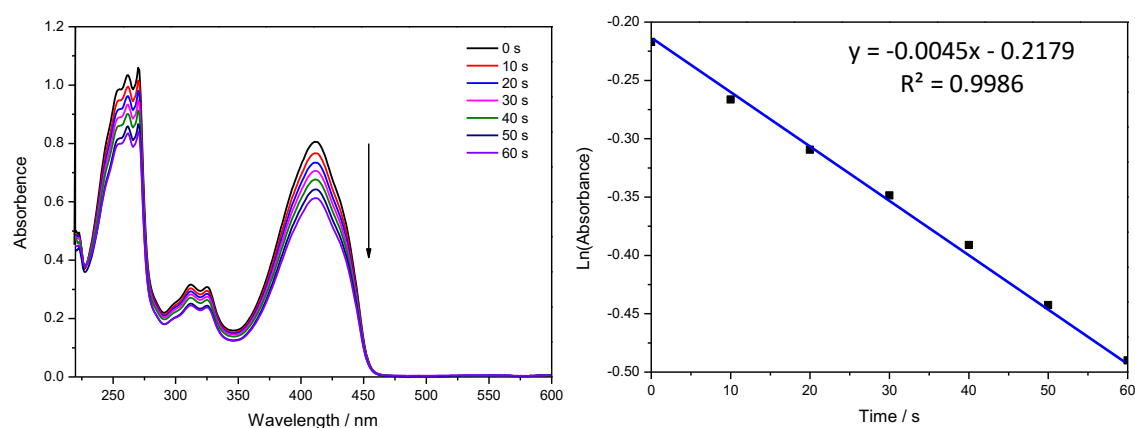


Figure S2. Left: the decay in the DPBF 7 signal in the absorption spectra over time, as a mixture of methylene blue (5×10^{-6} mol/L) and DPBF 7 (5×10^{-5} mol/L) in air saturated *t*-amyl alcohol was irradiated with a green LED (max wavelength = 510 nm). Right: The change in the natural log of the absorbance at 410 nm over time, showing the linear regression from which the rate constant was calculated. Experiments were performed in duplicate.

BDP 1

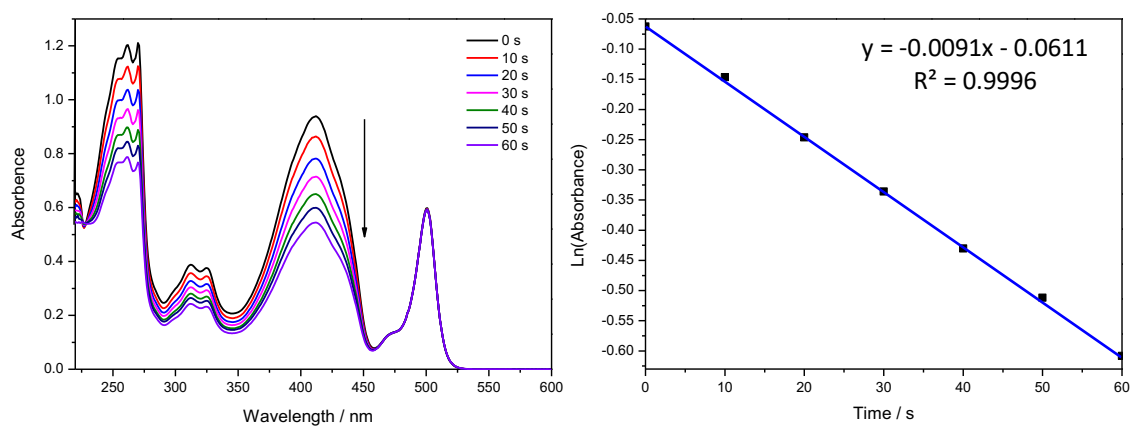
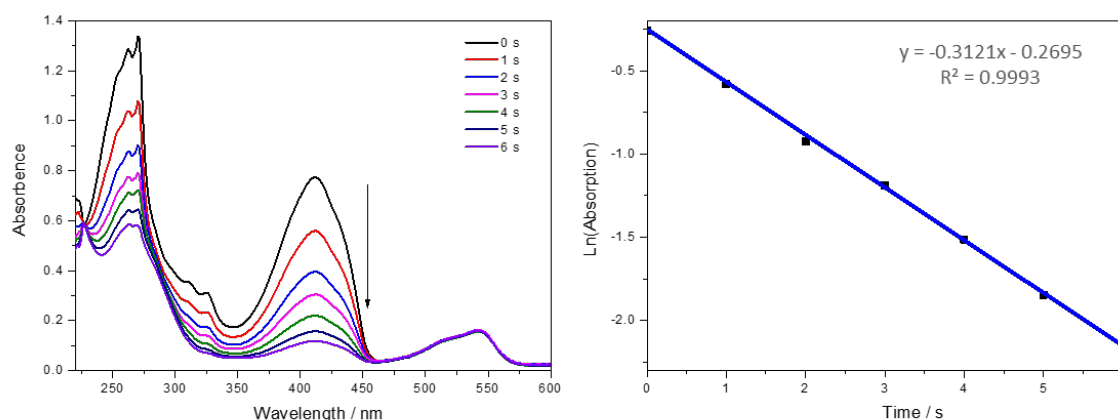


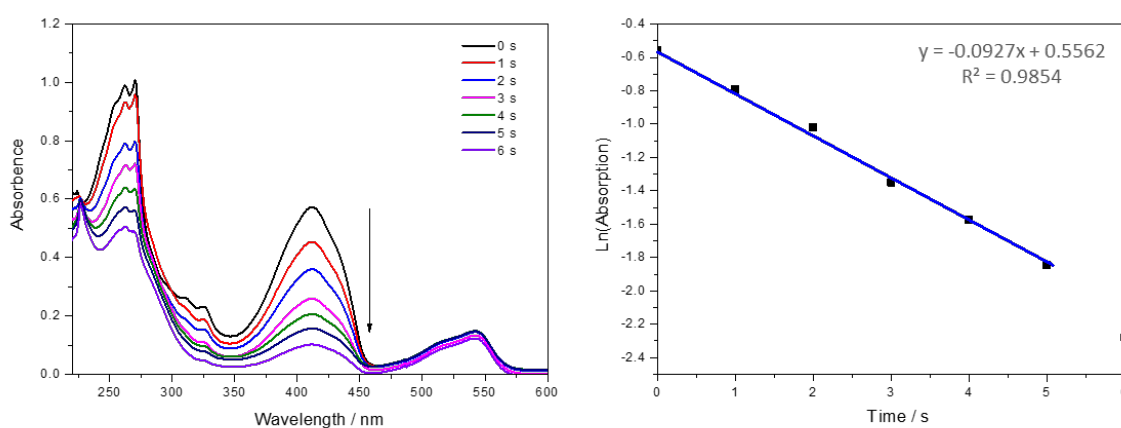
Figure S3. Left: the decay in the DPBF 7 signal in the absorption spectra over time, as a mixture of BDP 1 (5×10^{-6} mol/L) and DPBF 7 (5×10^{-5} mol/L) in air saturated *t*-amyl alcohol was irradiated with a green LED (max wavelength = 510 nm). Right: The change in the natural log of the absorbance at 410 nm over time, showing the linear regression from which the rate constant was calculated.

Pd-BDP 4

Repeat 1



Repeat 2



Repeat 3

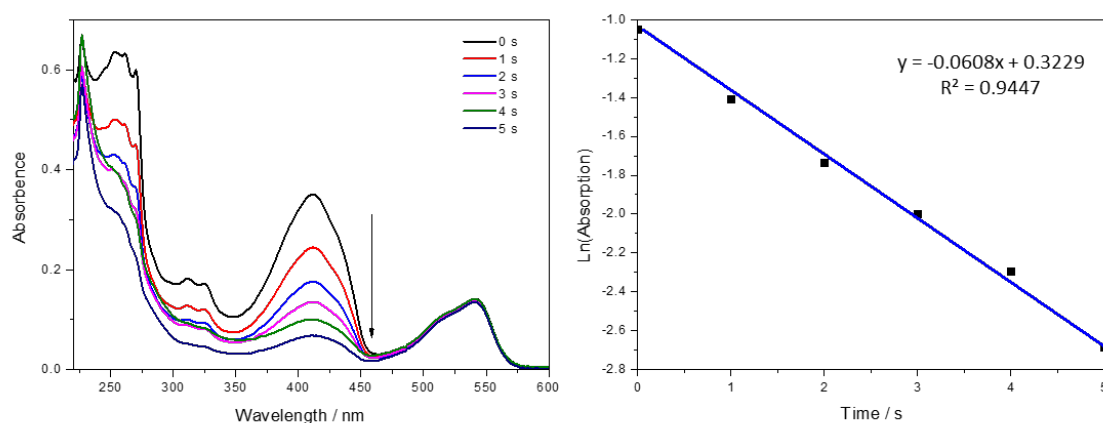
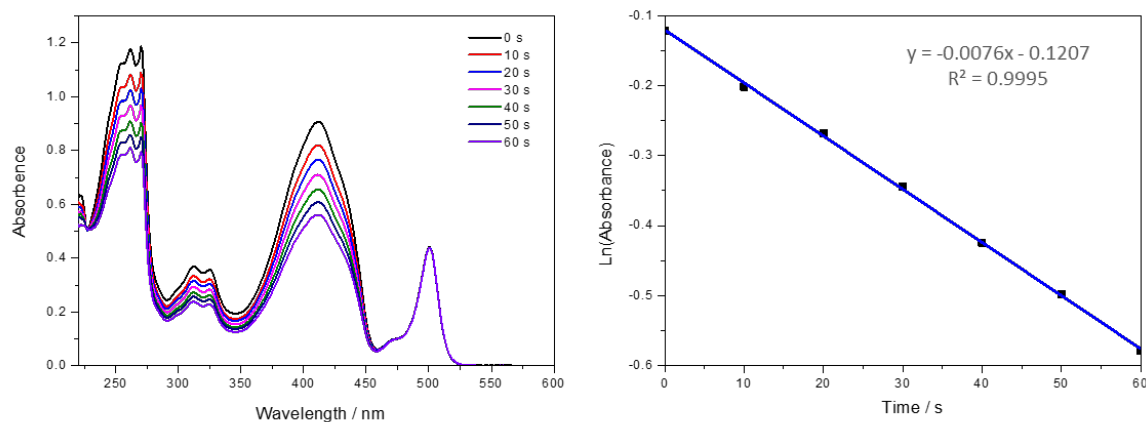


Figure S4. Left: the decay in the DPBF 7 signal in the absorption spectra over time, as a mixture of Pd-BDP 4 (5×10^{-6} mol/L) and DPBF 7 (5×10^{-5} mol/L) in air saturated *t*-amyl alcohol was irradiated with a green LED (max wavelength = 510 nm). Right: The change in the natural log of the absorbance at 410 nm over time, showing the linear regression from which the rate constant was calculated. Experiments were performed in triplicate.

BDP 1 and Pd(PPh₃)₂Cl₂ 2 (1:1 mixture)

Repeat 1



Repeat 2

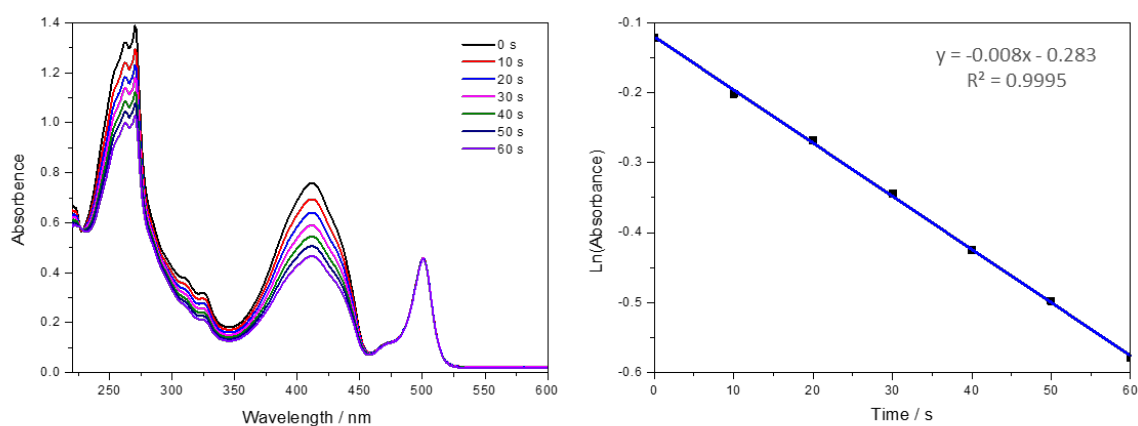


Figure S5. Left: the decay in the DPBF 7 signal in the absorption spectra over time, as a mixture of BDP 1 and Pd(PPh₃)₂Cl₂ 2 (1:1 ratio of 5×10^{-6} mol/L) and DPBF 7 (5×10^{-5} mol/L) in air saturated *t*-amyl alcohol was irradiated with a green LED (max wavelength = 510 nm). Right: The change in the natural log of the absorbance at 410 nm over time, showing the linear regression from which the rate constant was calculated. Experiments were performed in duplicate.

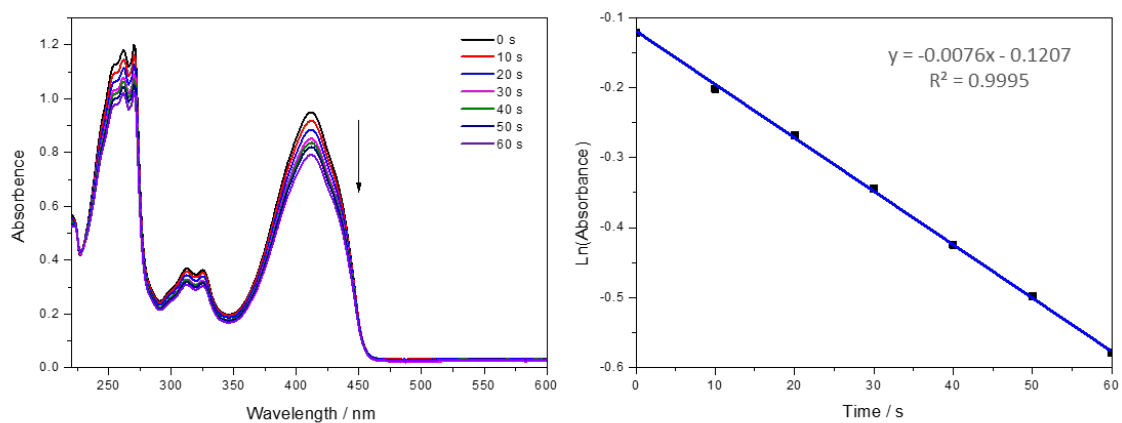


Figure S6. Left: the decay in the DPBF **7** signal in the absorption spectra over time, as a mixture of $Pd(PPh_3)_2Cl_2$ **2** (5×10^{-6} mol/L) and DPBF **7** (5×10^{-5} mol/L) in air saturated *t*-amyl alcohol was irradiated with a green LED (max wavelength = 510 nm). Right: The change in the natural log of the absorbance at 410 nm over time, showing the linear regression from which the rate constant was calculated.

Photophysical Measurements

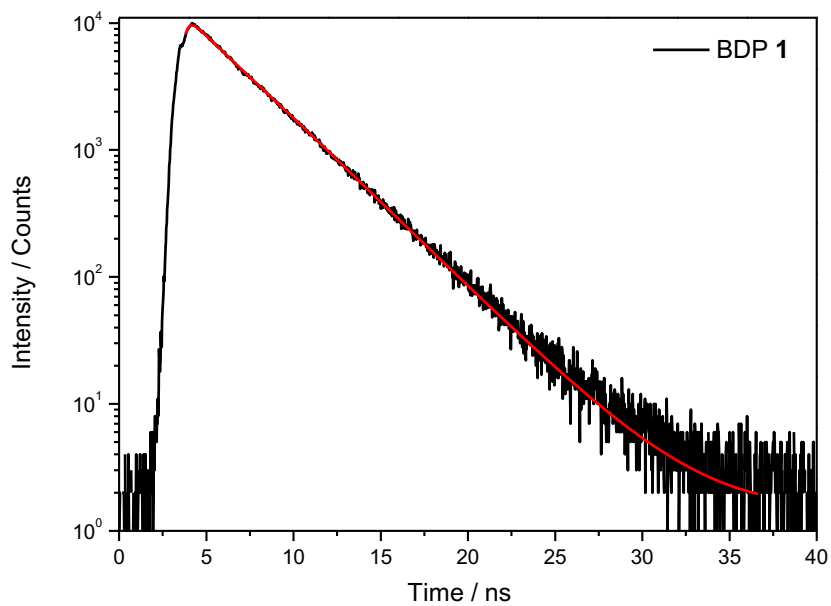


Figure S7. Emission decay profile of BDP 1.

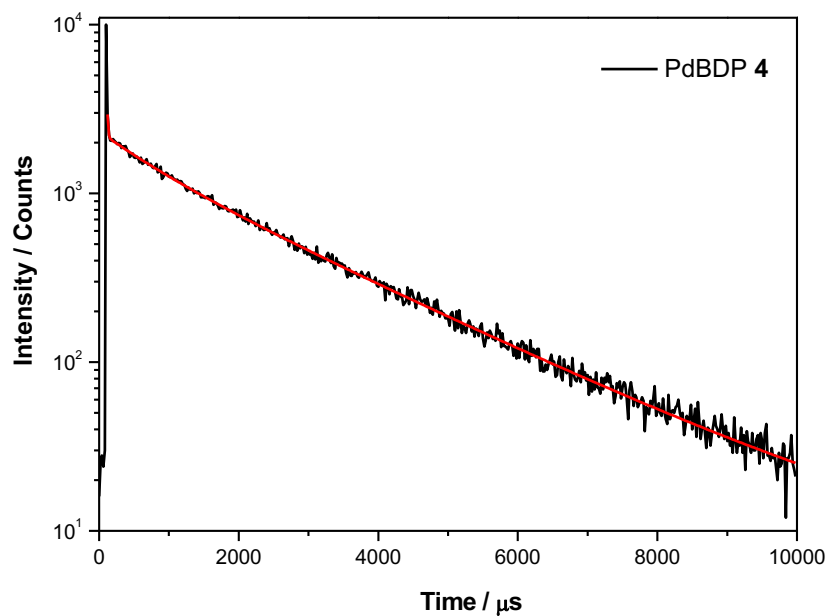


Figure S8. Emission decay profile of Pd-BDP 4.

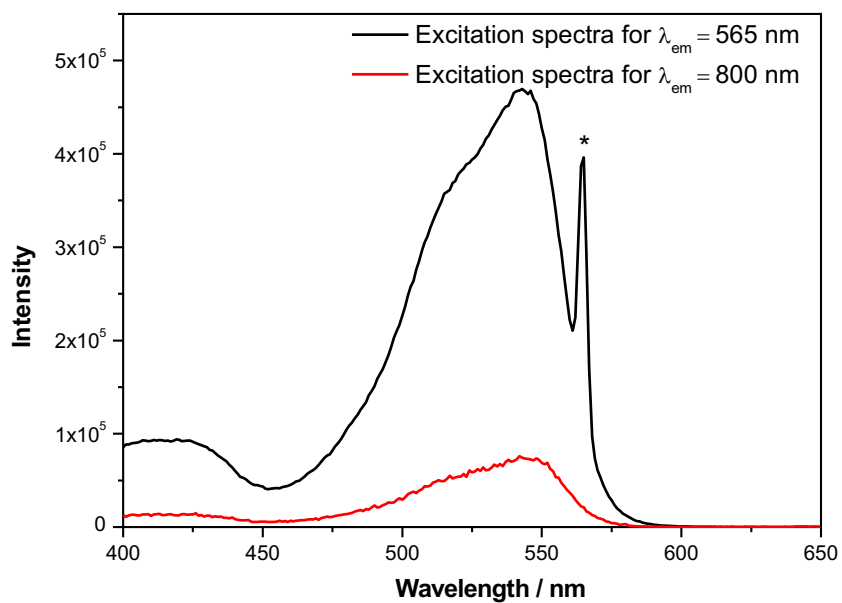


Figure S9. Comparison of excitation spectra detected at fluorescence emission wavelength and phosphorescence wavelength of Pd-BDP 4. *Artefact peak due to the excitation signal at 565 nm.

Catalytic Investigations and Control Reactions

Photocatalysis reaction set up

The reactor was simply made up by wrapping LED strip around a 150 ml crystallising dish. The reaction vials are centred in the reactor and the distance to the edge is 4 cm.

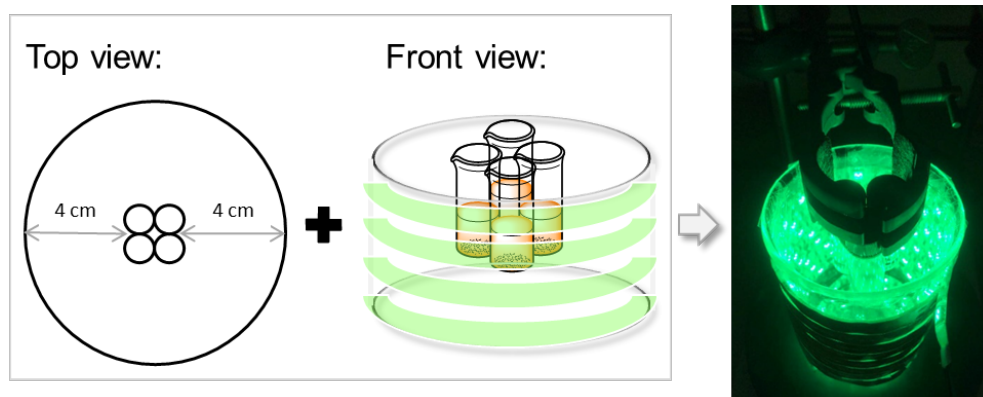
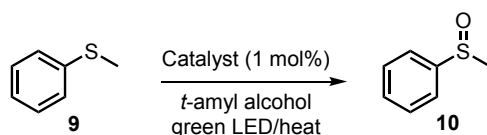


Figure S10. The set-up for the photocatalytic reactions.

Thioanisole oxidation using heat instead of light



Procedure: Thioanisole **9** (23 μ L, 0.2 mmol), catalyst (0.002 mmol), *t*-amyl alcohol (1 mL, saturated with air) were all combined in a 4 mL vial under air. The vial was sealed and was either heated at 70°C, or irradiated with a green LED, for 24 hours. Aliquots were taken and dissolved in chloroform-*d*. The samples were analysed using ^1H NMR (using a D1 value of 10 seconds). Conversion to the product **10** was calculated relative to the starting material **9**.

Note: as a sealed vial was used for the experiments at 70°C, the analogous experiments under green LED irradiation were also performed to allow direct comparison with the results at 70°C (as previous experiments using green LED were done using an open vial).

The ^1H NMR signals used to monitor the reaction progress

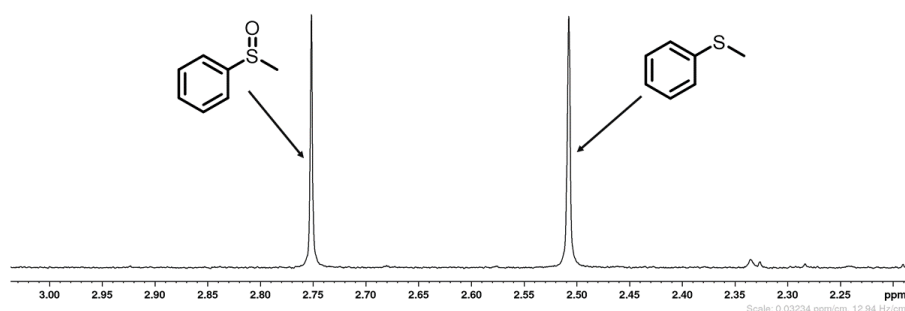


Table S3: Control reactions using either heat or light

Catalyst	Conversion to product 10 / %	
	24h, 70°C, closed vial	24h, green LED, closed vial
Pd-BDP 4	20	31
	18	41
		30
		33
BDP 1	1	17
	1	22

Testing for singlet oxygen being involved in the reaction mechanism^[6]

Reaction conditions: Thioanisole **9** (23 μ L, 0.2 mmol), catalyst (0.002 mmol), 1,4-diazabicyclo[2.2.2]octane **12** (DABCO, 24.6 mg, 0.22 mmol), *t*-amyl alcohol (1 mL, saturated with air) were all combined in a 4 mL vial under air. The vial was left open (no cap) and irradiated with green LED light for 4 or 24 hours. Aliquots were taken and dissolved in chloroform-*d*. The samples were analysed using ¹H NMR (using a D1 value of 10 seconds). Conversion to the product **10** was calculated relative to the starting material **9**.

Table S4: Control reactions using a DABCO **12** additive

Catalyst	Conversion to product 10 / %
	24h
BDP 1 + DABCO 12	0
	0
Pd(PPh ₃) ₂ Cl ₂ 2 + DABCO 12	5
	3
	4h
Pd-BDP 4 + DABCO 12	8
	7

Testing superoxide radical anion being involved in the reaction mechanism^[6]

Reaction conditions: Thioanisole **9** (23 μ L, 0.2 mmol), catalyst (0.002 mmol), *N*-tert-butyl-alpha-phenylnitron **11** (PBN, 25.8 mg, 0.22 mmol), *t*-amyl alcohol (1 mL, saturated with air) were all combined in a 4 mL vial under air. The vial was left open (no cap) and irradiated with green LED light for 4 or 24 hours. Aliquots were taken and dissolved in chloroform-*d*. The samples were analysed using ¹H NMR (using a D1 value of 10 seconds). Conversion to the product **10** was calculated relative to the starting material **9**.

Table S5: Control reactions using a PBN **11** additive

Catalyst	Conversion to product 10 / %
	24h
BDP 1 + PBN 11	7
	10
Pd(PPh ₃) ₂ Cl ₂ 2 + PBN 11	1
	0
	4h
Pd-BDP 4 + PBN 11	2
	1

*Note: in the absence of PBN **11** or DABCO **12**, the reactions using BDP **1** reach completion in 24 hours, while reactions using Pd-BDP **4** reach completion after 4h. It seems reasonable that once all the PBN **11** or DABCO **12** has reacted with singlet oxygen, the catalyst will continue to generate singlet oxygen and hence the oxidation of thioanisole will begin. As such, it is necessary to perform the reactions in the presence of PBN **11** or DABCO **12** for the time that it took the reactions in the absence of an additive to reach completion (BDP **1** for 24 h, and Pd-BDP **4** for 4 h).*

Control reactions in the absence of oxygen

Reaction conditions: In a glove box under an argon atmosphere, thioanisole **9** (23 μ L, 0.2 mmol), Pd-BDP **4** (0.002 mmol), *t*-amyl alcohol (1 mL, degassed and stored under an argon atmosphere) were all combined in a 4 mL vial sealed with a PTFE cap and irradiated with green LED light for 24 hours. An aliquot was taken and dissolved in chloroform-*d*. The samples were analysed using ^1H NMR (using a D1 value of 10 seconds). Conversion to the product **10** was calculated relative to the starting material **9**.

Table S6: Control reactions under an inert atmosphere

Catalyst	Conversion to product 10 after 24 h / %
Pd-BDP 4	0

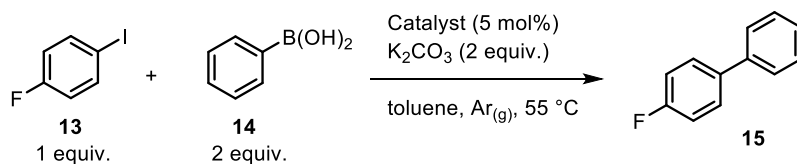
Test reactions adding an internal standard to confirm conversion

Reaction conditions: Thioanisole (23 μ L, 0.2 mmol), catalyst (0.002 mmol), *t*-amyl alcohol (1 mL, saturated with air) were all combined in a 4 mL vial under air. The vial was left open (no cap) and irradiated with green LED light for 24 hours. 1,2,4,5-Tetramethylbenzene (6.7 mg, 0.05 mmol) was then added to the reaction mixture as an internal standard, an aliquot was taken and dissolved in chloroform-*d*. The samples were analysed using ^1H NMR (using a D1 value of 10 seconds). Conversion to the product **10** was calculated relative to the internal standard.

Table S7: Conversions relative to the internal standard

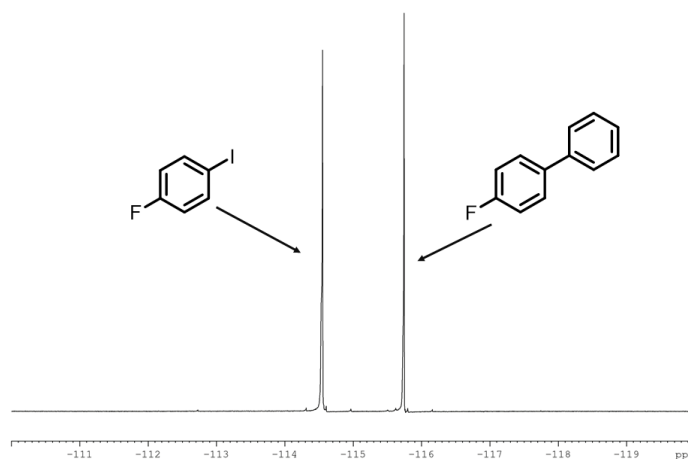
Catalyst	Conversion to product 10 after 24 h / %
BDP 1	85
Pd-BDP 4	93
$\text{Pd}^{\text{(II)}}(\text{PPh}_3)_2\text{Cl}_2$ 2	3
BDP 1 + $\text{Pd}^{\text{(II)}}(\text{PPh}_3)_2\text{Cl}_2$ 2	97

Suzuki-Miyaura cross coupling reactions

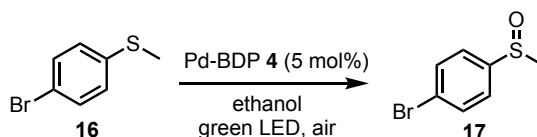


Reaction conditions: 4-fluoroiodobenzene (12 μ L, 0.1 mmol), phenylboronic acid (17 mg, 0.14 mmol), K₂CO₃ (27.6 mg, 0.2 mmol), catalyst (0.005 mmol) and toluene-*d*₈ (0.3 mL) were combined in a 4 mL vial under argon (glovebox). The vial was sealed, removed from the glovebox and heated at 55°C for the specified time. The cap was removed and the solution diluted with toluene-*d*₈, and then analysed using ¹H and ¹⁹F NMR (using a D1 value of 10 seconds). Conversion to the product **15** was calculated relative to the starting material **13**, using ¹⁹F NMR spectroscopy.

The ¹⁹F NMR signals used to monitor the reaction progress



Optimisation of the photooxidation of 4-bromo-thioanisole **16**



Reaction conditions: 4-Bromo-thioanisole **16** (101.6 mg, 0.5 mmol), Pd-BDP **4** (5.0 mg, 0.005 mmol), ethanol (2.5 mL, saturated with air) all combined in a 4 mL vial under air. The vial was left open (no cap) and irradiated with green LED light. Aliquots were taken at the specified time, dissolved in chloroform-*d*. The samples were analysed using ¹H NMR (using a D1 value of 10 seconds). Conversion to the product **17** was calculated relative to starting material **16**.

The ¹H NMR signals used to monitor reaction progress

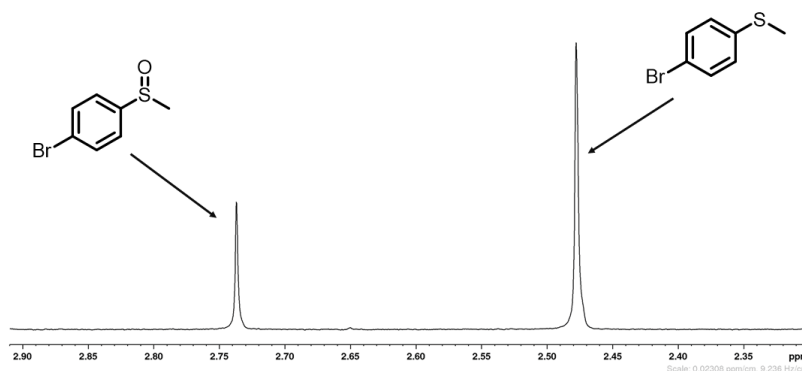
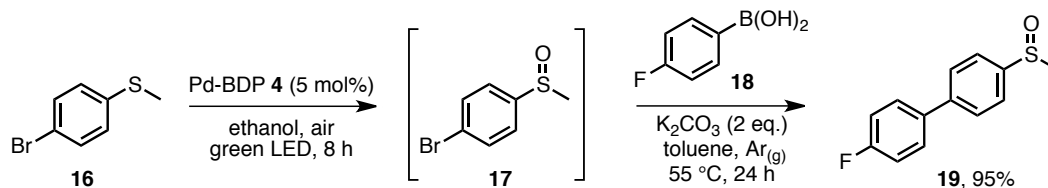


Table S8: The conversion to the product **17** at different time points.

Catalyst	Conversion to product 17 / %		
	2h	4h	8h
Pd-BDP 4	27	48	97

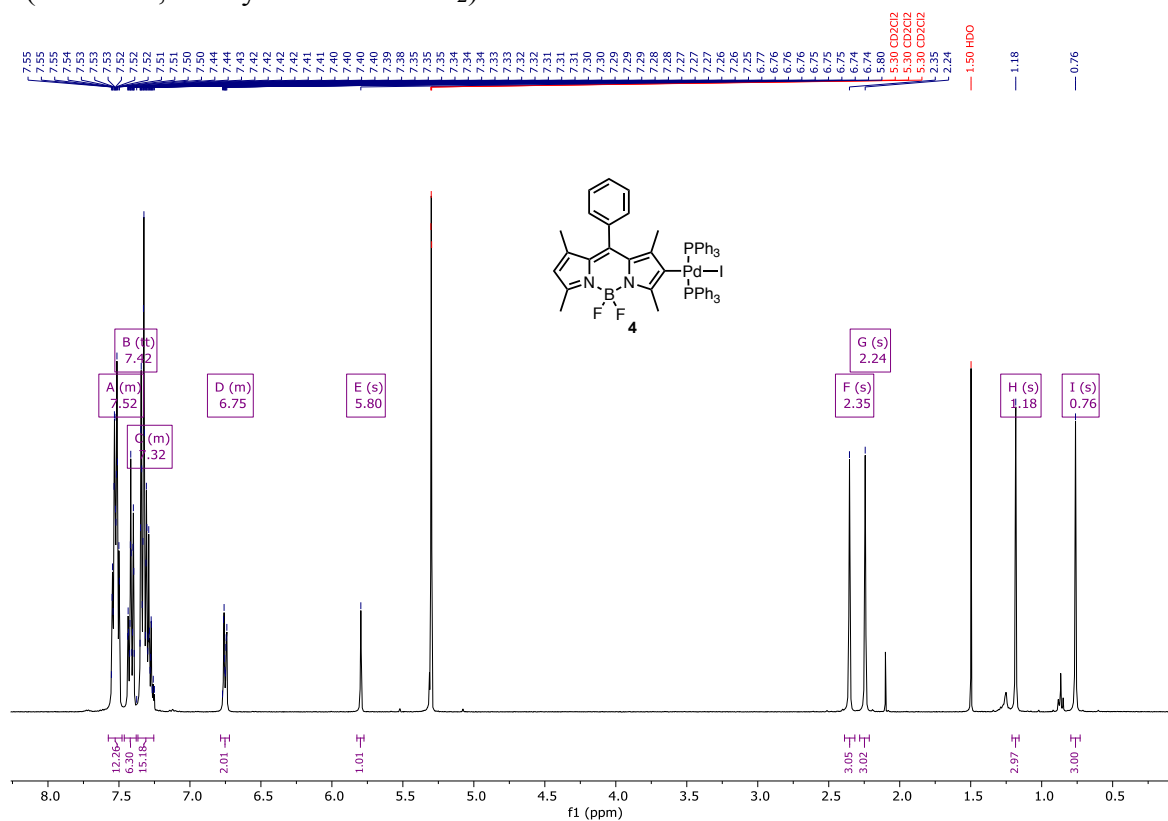
Sequential photocatalytic oxidation - Suzuki-Miyaura cross coupling reaction



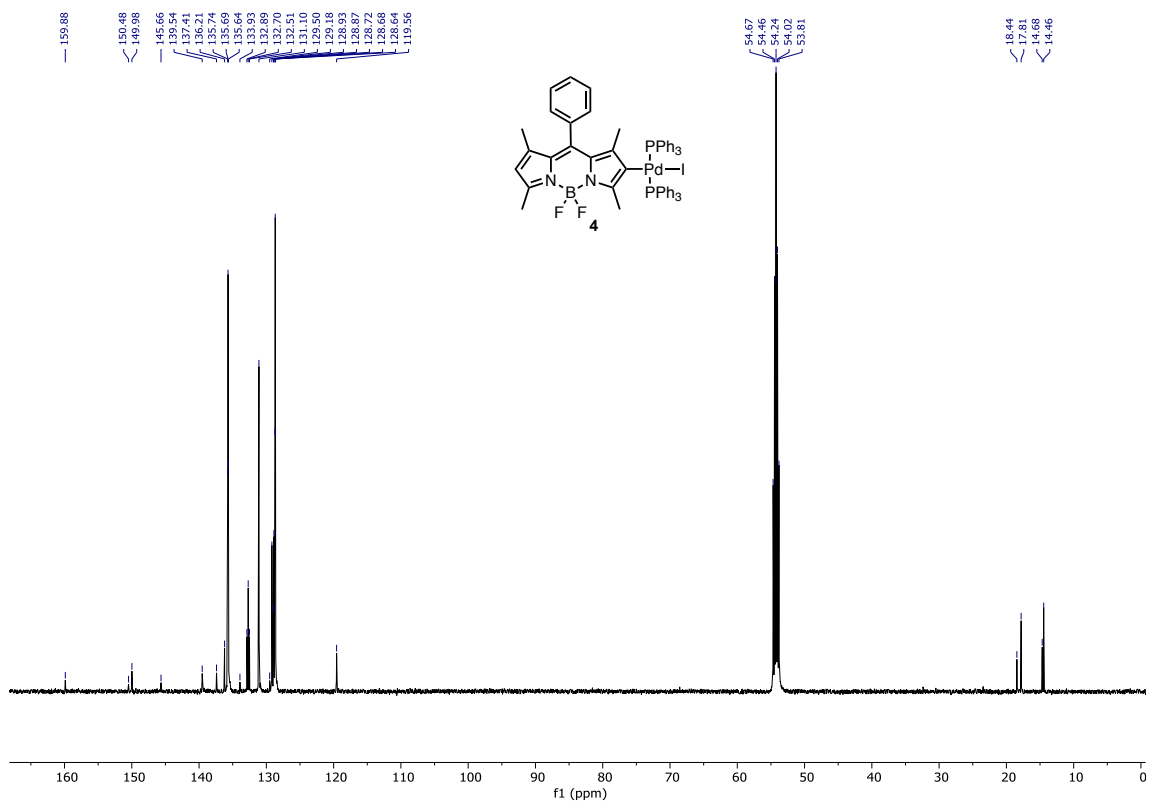
Reaction conditions: 4-bromo-thioanisole **16** (101.6 mg, 0.5 mmol), Pd-BDP **4** (5.4 mg, 0.005 mol), ethanol (2.5 mL, saturated with air) all combined in a 4 mL vial under air. The vial was left open (no cap) and irradiated with green LED light for 8 hours. The reaction mixture was transferred to a 10 mL round bottom flask and was evaporated to dryness under reduced pressure. The flask contain crude product was transferred to a glove box under an argon atmosphere, toluene (2.5 mL, degassed), K₂CO₃ (138.2 mg, 1 mmol) and 4-fluorophenylboronic acid **18** (97.9 mg, 0.7 mmol) were then added. The flask was sealed, removed from the glove box and heated at 55°C for 24 hours. The reaction mixture was allowed to cool to room temperature and the solvent removed under reduced pressure. The crude product was dissolved in methanol (5 mL) and extracted with hexane (10 mL). The solvent was removed and the residual was re-dissolved with CH₂Cl₂ (5 mL) and washed with 2M NaOH (5 mL). The organic fraction was then evaporated to dryness under reduced pressure to yield compound **19** as a brown powder in 95% yield (111.0 mg). ¹H NMR (400 MHz, Chloroform-d) δ 7.75 – 7.66 (m, 4H), 7.47 – 7.51 (m, 2H), 7.09 (t, *J* = 8.6 Hz, 2H), 2.69 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.9 (d, ¹*J*_{C-F} = 247.4 Hz), 144.7, 143.3, 136.0 (d, ⁴*J*_{C-F} = 3.0 Hz), 129.1 (d, ³*J*_{C-F} = 8.2 Hz), 128.0, 124.2, 116.1 (d, ²*J*_{C-F} = 22.1 Hz), 44.2. The data matches that reported in the literature.^[7]

NMR Spectra

^1H NMR (400 MHz, Methylene Chloride- d_2)

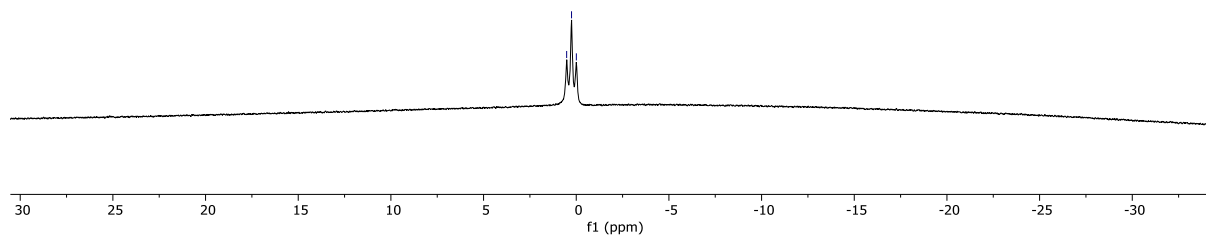
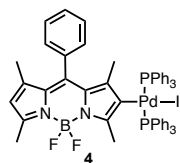


$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Methylene Chloride- d_2)



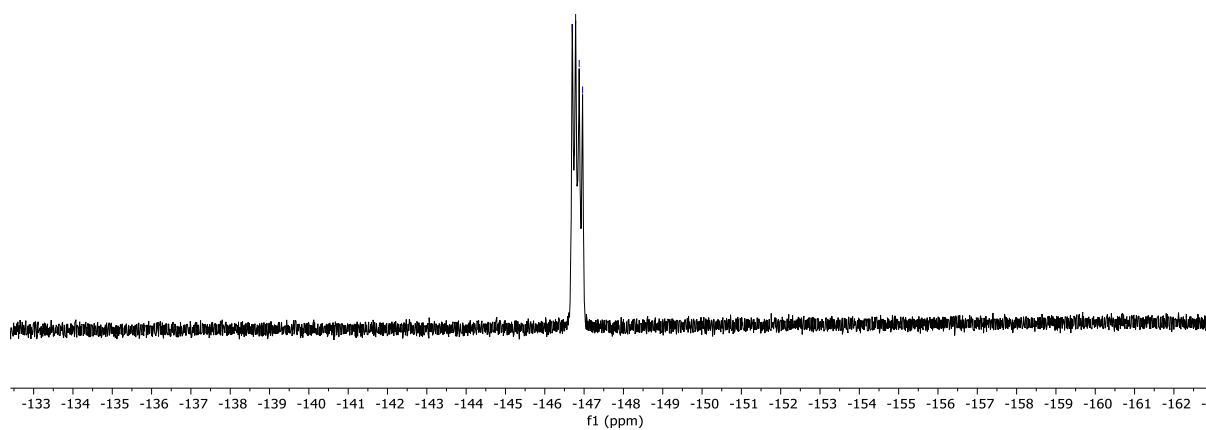
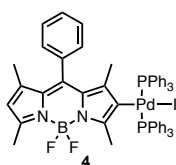
^{11}B NMR (128 MHz, Methylene Chloride- d_2)

0.52
0.26
-0.01

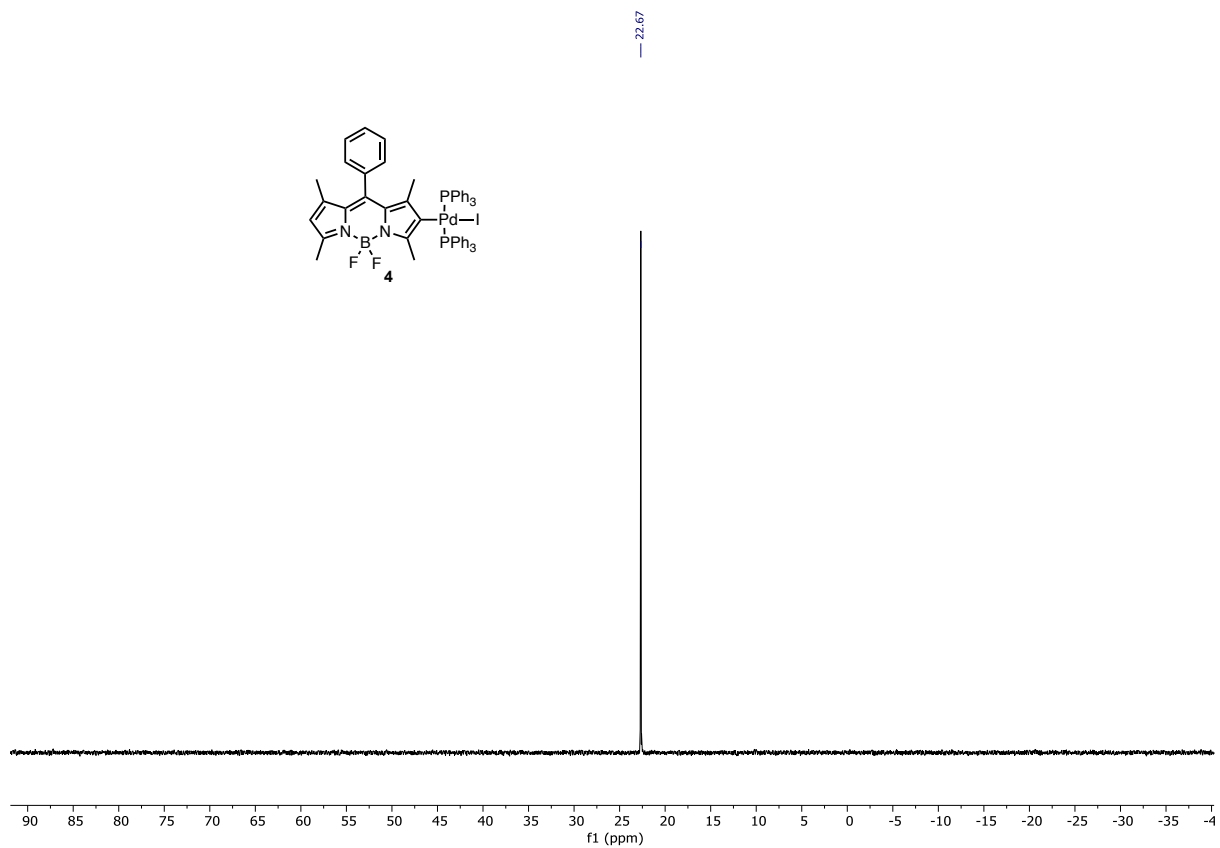


^{19}F NMR (376 MHz, Methylene Chloride- d_2)

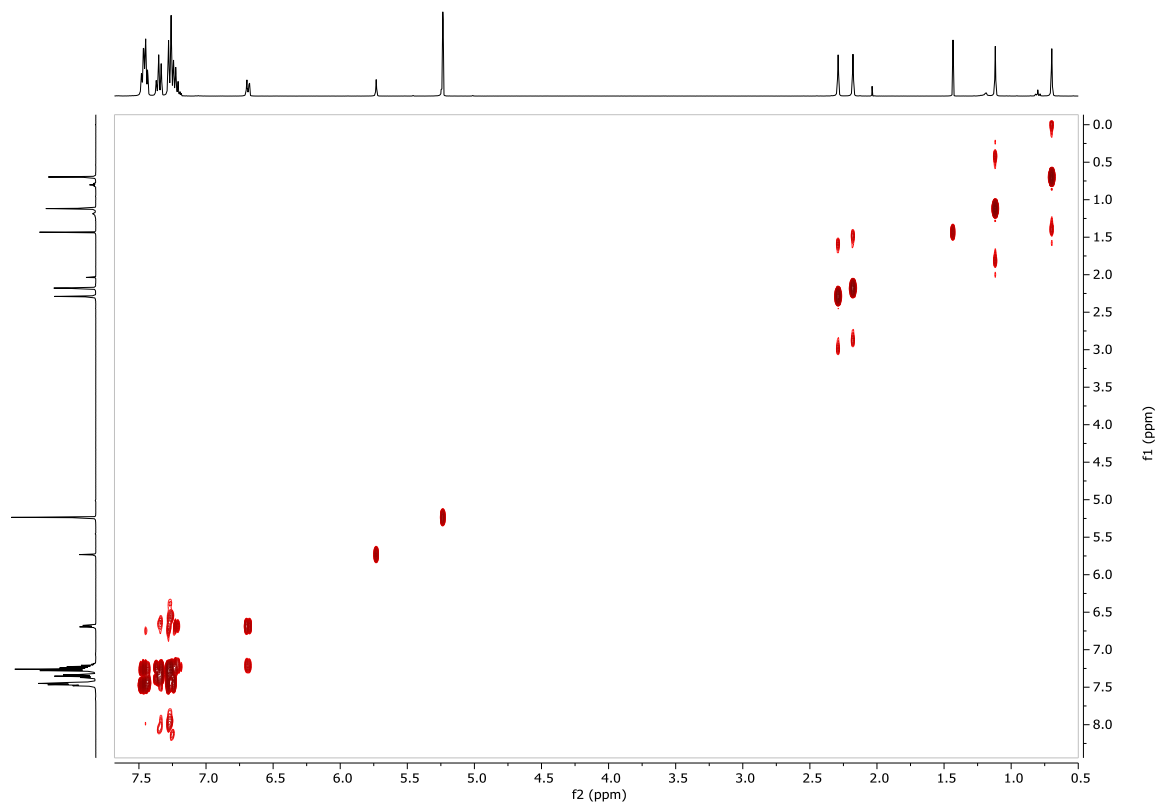
-146.70
-146.78
-146.88
-146.96



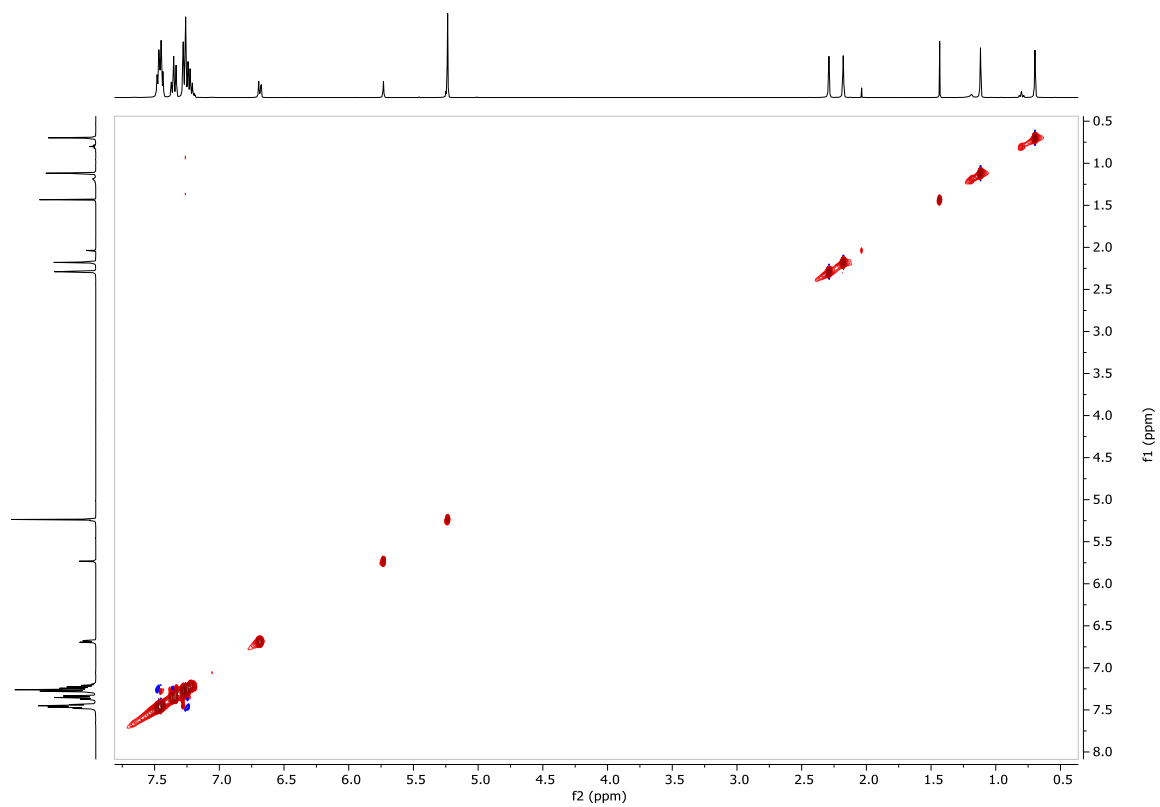
^{31}P NMR (162 MHz, Methylene Chloride- d_2)



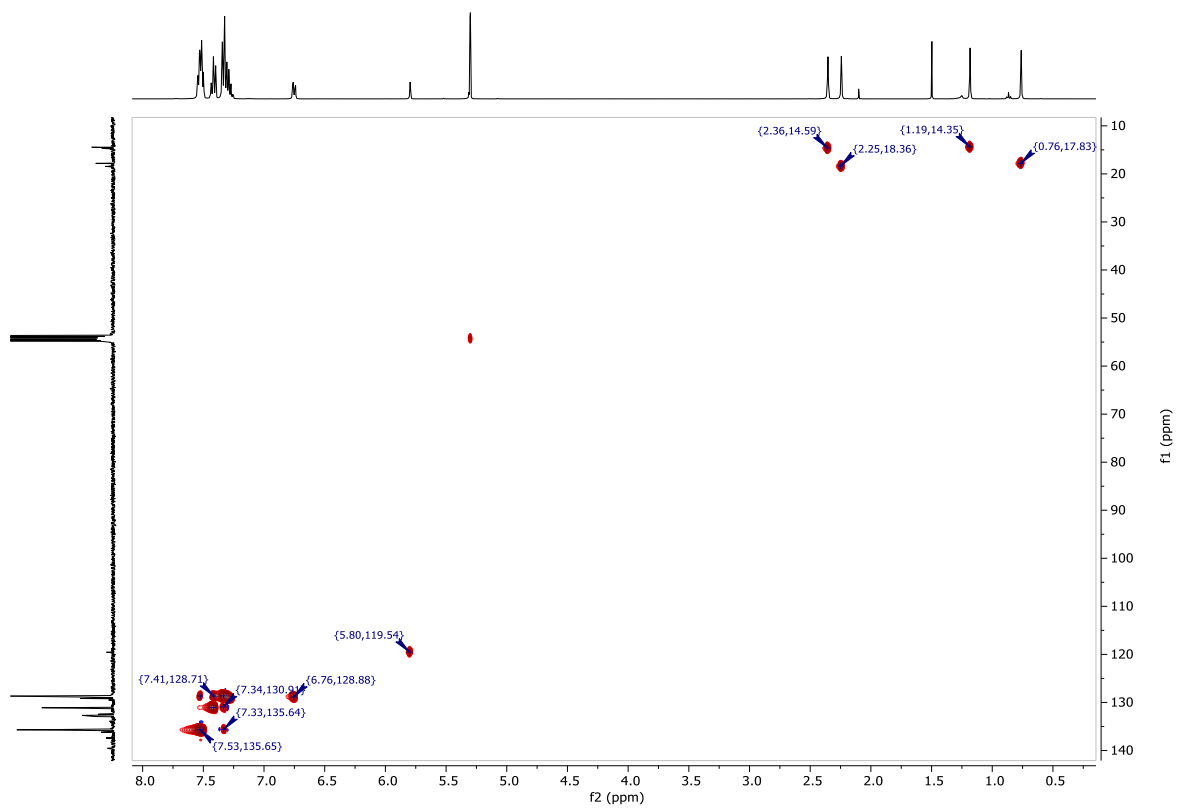
COSY



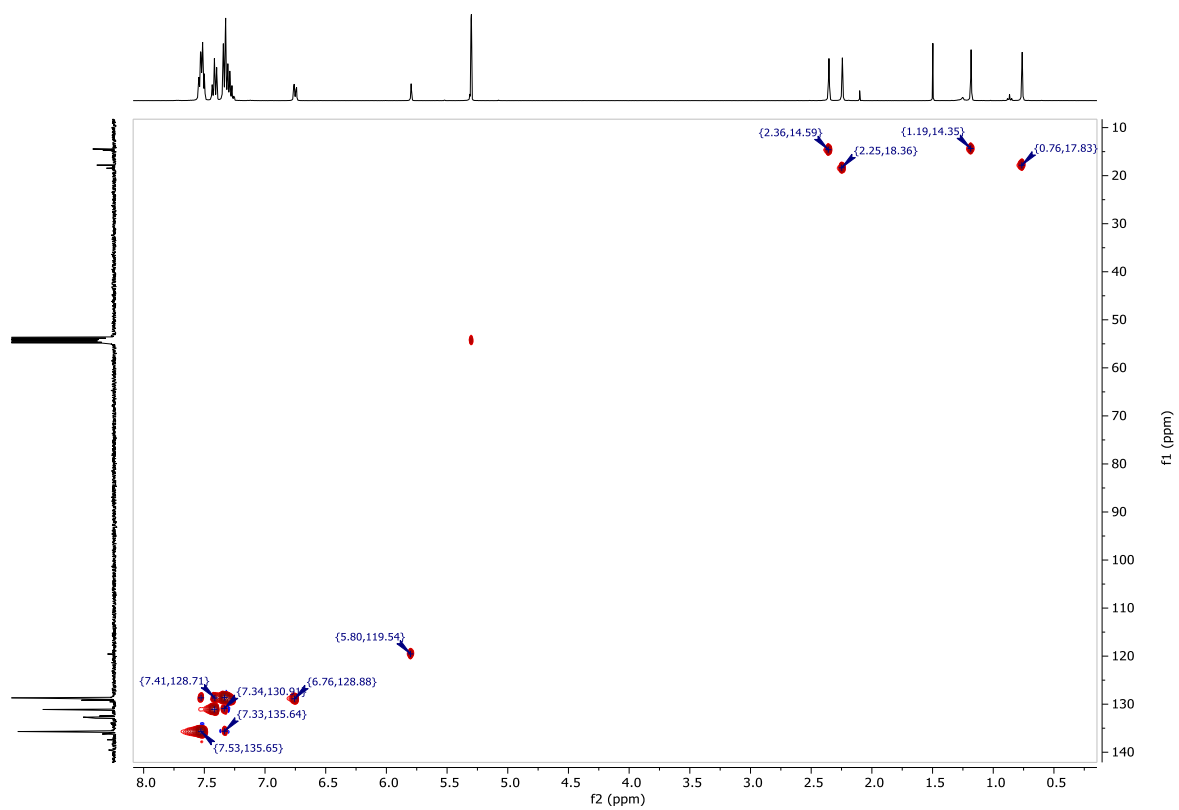
NOESY



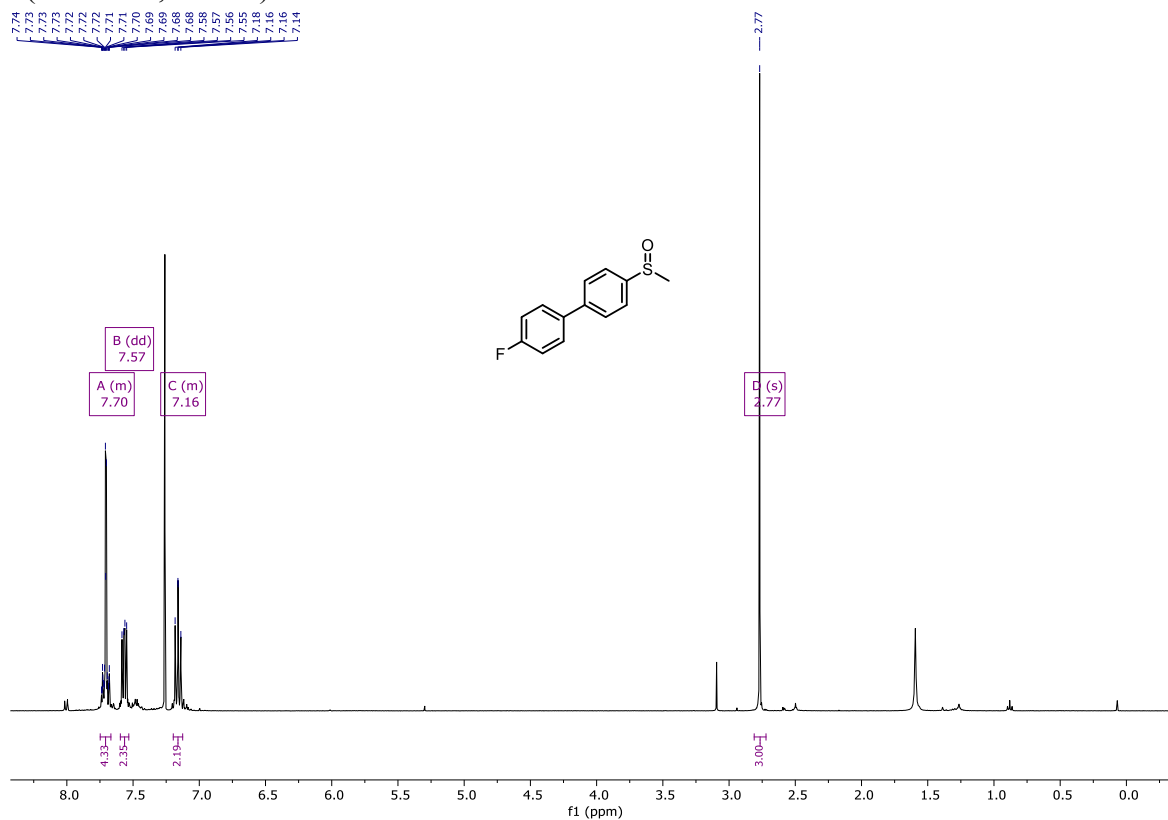
HSQC



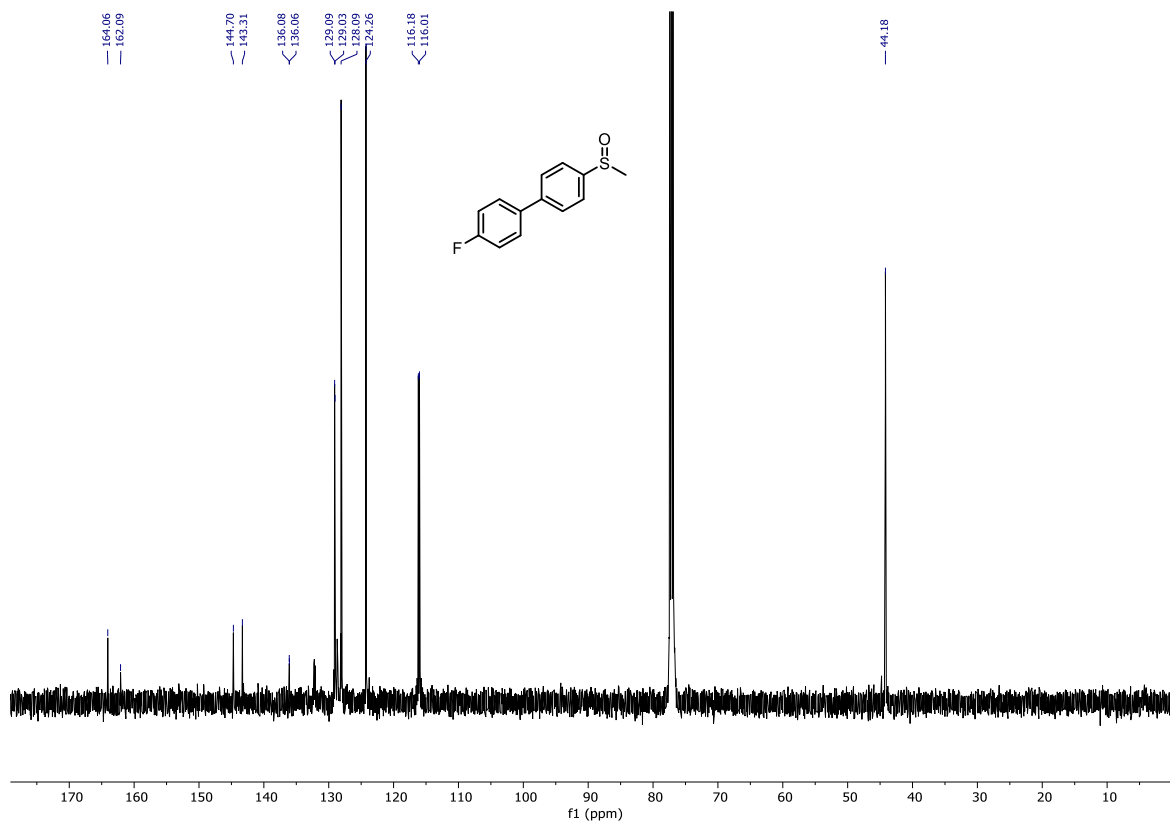
HMBC



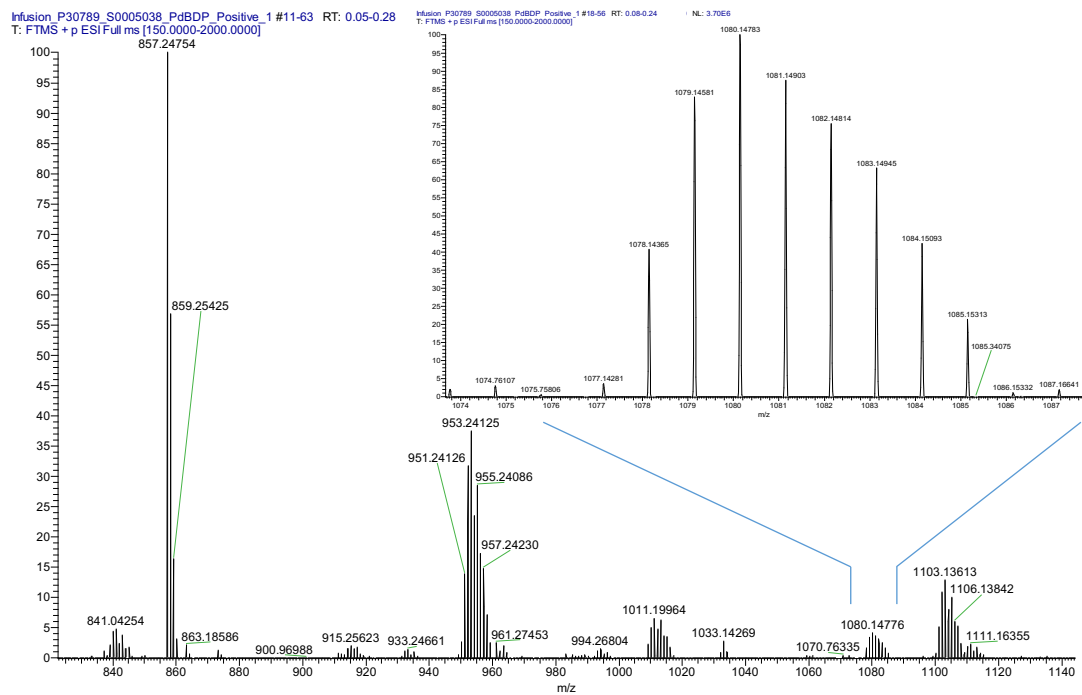
^1H NMR (400 MHz, CDCl_3)



$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3)



HRMS



References

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