Electronic Supplementary Information

A BODIPY-functionalized Pd^{II} Photoredox Catalyst for Sonogashira C-C Cross-coupling Reactions

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1. General information

Commercial reagents chloroform ($CHCl_3$), dichloromethane (DCM), methanol (MeOH), hexanes and triethylamine (Et_3N) from Fisher Scientific, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) from Biosynth International Inc., tetrahydrofuran (THF), dimethylformamide (DMF), deuterated chloroform ($CDCl_3$), bromobenzene, 1-chloro-4-iodobenzene, 4-iodobenzonitrile, ethyl-4-iodobenzoate, 4-iodoanisole, methyl 4-iodobenzoate, diphenylacetylene, N,N-dimethylformamide from Acros organics, 4-iododbenzonitrile, 4-(phenylethynyl)acetophenone, 3-ethynylbenzonitrile from Alfa Aser, dichloro(1,10-phenanthroline)palladium (II), 4-ethynyl-N,N-dimethylamine, o-tolunitrile from Sigma Aldrich and iodobenzene from Eastman, 48% boron trifluoride diethyl etherate ($BF_3 \cdot O(C_2H_5)_2$), 2,4 dimethylpyrrole from the TCI were used without further purification unless otherwise stated.

DCM was dried with CaH_2 under nitrogen and distilled prior to use. Chromatographic purification of products was done under gravity on silica gel (70-230 mesh Silica gel). Thin-layer chromatography (TLC) was performed on Silica plated aluminum backed TLC plates. ^1H NMR spectra were recorded on 400 MHz Bruker Avance II- NMR spectrometer and were internally

referenced to $CDCl_3$ (δ 7.26 ppm). Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), coupling constant (Hz), and integration. ^{31}P NMR spectra were recorded on 400 MHz Bruker Avance II- NMR spectrometer. UV-VIS spectra were recorded on a Cary 100 Series UV-VIS Dual Beam Spectrophotometer over a range of 200-800 nm. Fluorescence spectra were collected on a fluorimeter FS5 from Edinburgh Instruments Inc. Mass spectra were acquired on a Waters Synapt G2-Si ESI MS using 50/50 H_2O/CH_3CN as solvent with ~0.1% formic acid.

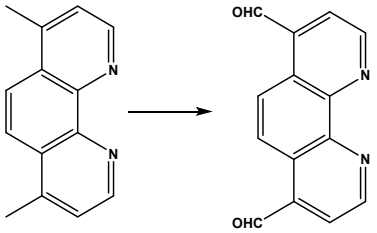
All Sonogashira cross-coupling reactions were carried out under inert atmosphere with the use of standard Schlenk techniques. Great Value LED dimmable E26 light bulb, 13W (1050 Lumens) was used as a light source. The yields of products were analyzed by GC-MS on a Shimadzu GC-MS-QP 2010 SE equipped with a SHRXI-5MS 30 m column, 0.25 μm ID.

GC-MS method: Sample injection: 1 μL. Split ratio, 30-1, although another split ratio of 5:1 was used as appropriate. Temperature program: 75 ^{0}C for 2 minutes then ramped at 20 ^{0}C per minute to 140 ^{0}C then ramped 50 ^{0}C per minute to 300 ^{0}C and held at 300 ^{0}C for 4 minutes. Solvent cut time varied depending on the split ratio used 2.4 minutes to 3.5 minutes.

Cyclic voltammetry experiments were carried out with a Potentiostat/Galvanostat Model 263 A from Princeton Applied research.

2. Synthesis

2.1 Synthesis of 4,7-diformyl-1,10-phenanthroline (YH1)



YH1

Ligand **YH1** was synthesized according to the literature method with the following modifications. 4,7-Dimethyl-1,10- phenanthroline (1.50 g, 7 mmol) was dissolved in dioxane containing 4% v/v water (100 mL) in a 250 mL round bottom flask and SeO_2 (3.75 g, 34 mmol) was added. The mixture was refluxed for 2 hours at 90 ^oC and it was filtered while hot. The filtrate was allowed to cool down to room temperature. The yellow solid was filtered out from the solution. Recrystallization from 1,4-dioxane provided the title compound (0.4725 g, 30% yield) as light-yellow powder. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.54 (s, 2H), 9.54 (d, J_{H-H} = 4.32 Hz, 2H), 9.23 (s, 2H), 8.09 (d, J_{H-H} =4.32 Hz, 2H)

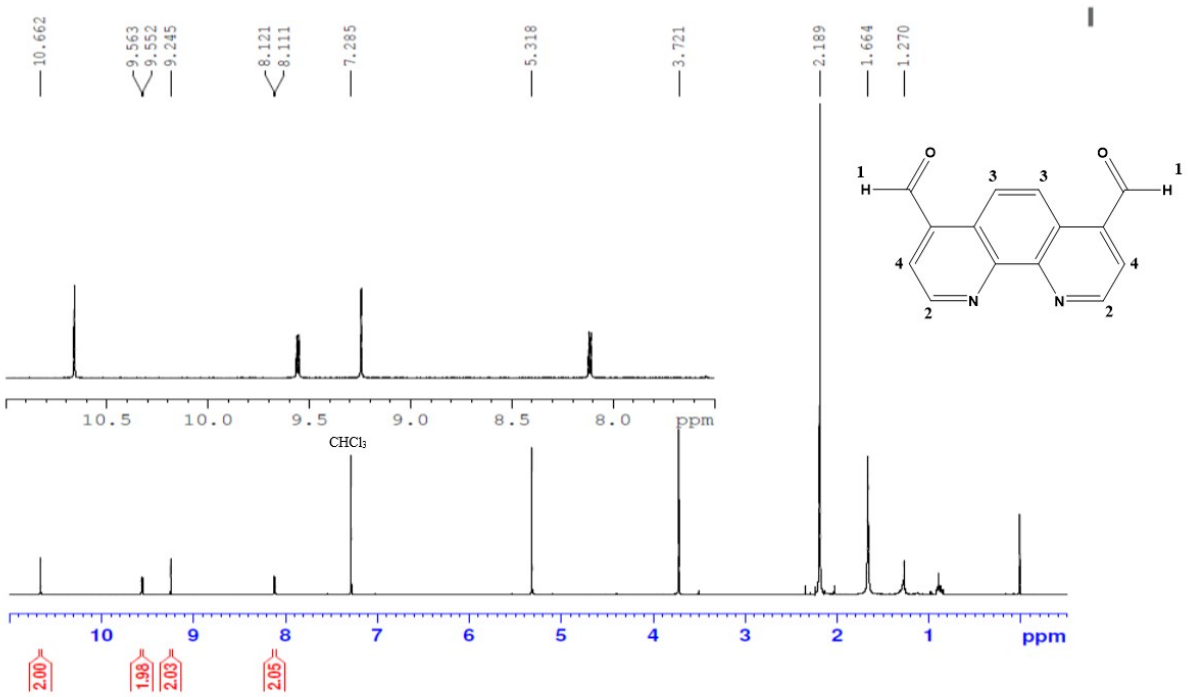
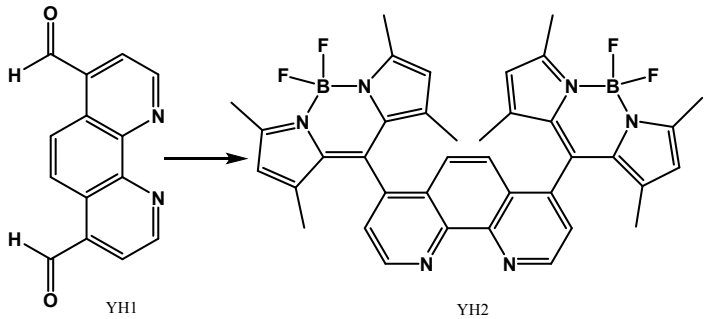


Figure S1. ^{1}H NMR of 4,7-diformyl-1,10-phenanthroline ($CDCl_3$ was used as a solvent)

2.2 Synthesis of 4,7-di(4′,4′′-difluoro-1′,3′,5′,7′-tetramethyl-4′-bora-3′a,4′a-diaza-s-indacene)-1,10-phenanthroline (YH2)



Ligand BDP was synthesized as follows. Compound **YH1** (0.476 g, 1.79 mmol) was added to distilled DCM under N_2, followed by 2,4-dimethylpyrrole (0.856 g, 9.03 mmol) and two drops of trifluoroacetic acid. The mixture was stirred overnight at room temperature. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.915 g, 4.00 mmol) was dissolved in 15 mL of DCM and was slowly

added to the reaction mixture. After stirring the mixture for one-hour triethylamine (8.0 mL, 57 mmol) was added. Stirring was continued for 30 min and afterwards 48 % $BF_3 \cdot O(C_2H_5)_2$ (8.0 mL, 31 mmol) was added to the mixture, and a strong green fluorescence was immediately observed under flash light. The reaction mixture was stirred for 3 hours at room temperature before removing the solvent under vacuum. The crude product was purified via column chromatography with DCM/MeOH (v:v, 200:5) and $CHCl_3$/MeOH (v:v, 100:1). The product containing fraction which showed green fluorescence was subjected to vacuum to remove the solvent and the recrystallization of the resultant solid with MeOH provided the title compound (0.175 g, 15% yield) as orange solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (d, *J* =4.44 Hz, 2H), 7.84 (s, 2H), 7.695 (d, *J* =4.44 Hz 2H), 5.97 (s, 2H), 2.58 (s, 3H), 1.09 (s, 3H); ESI HRMS (m^+/z, 673.3055, calcd, 673.3045).

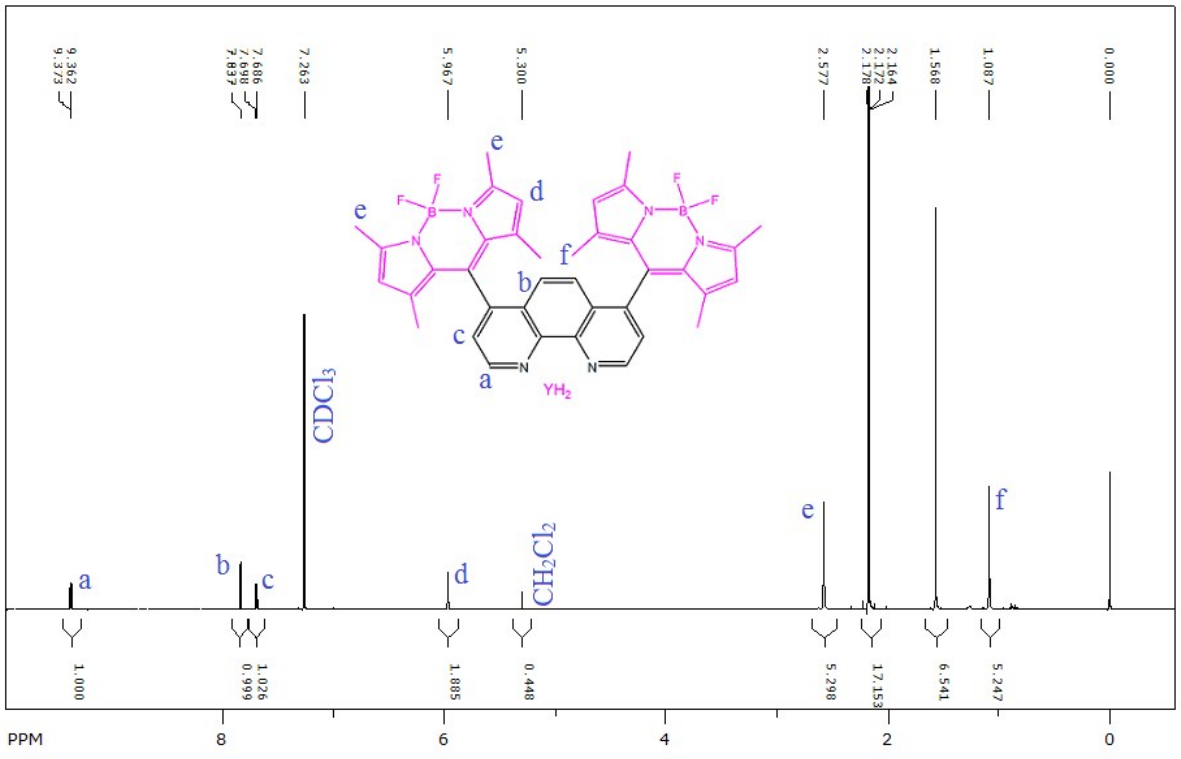


Figure S2. ^{1}H NMR in $CDCl_3$ spectrum of YH2

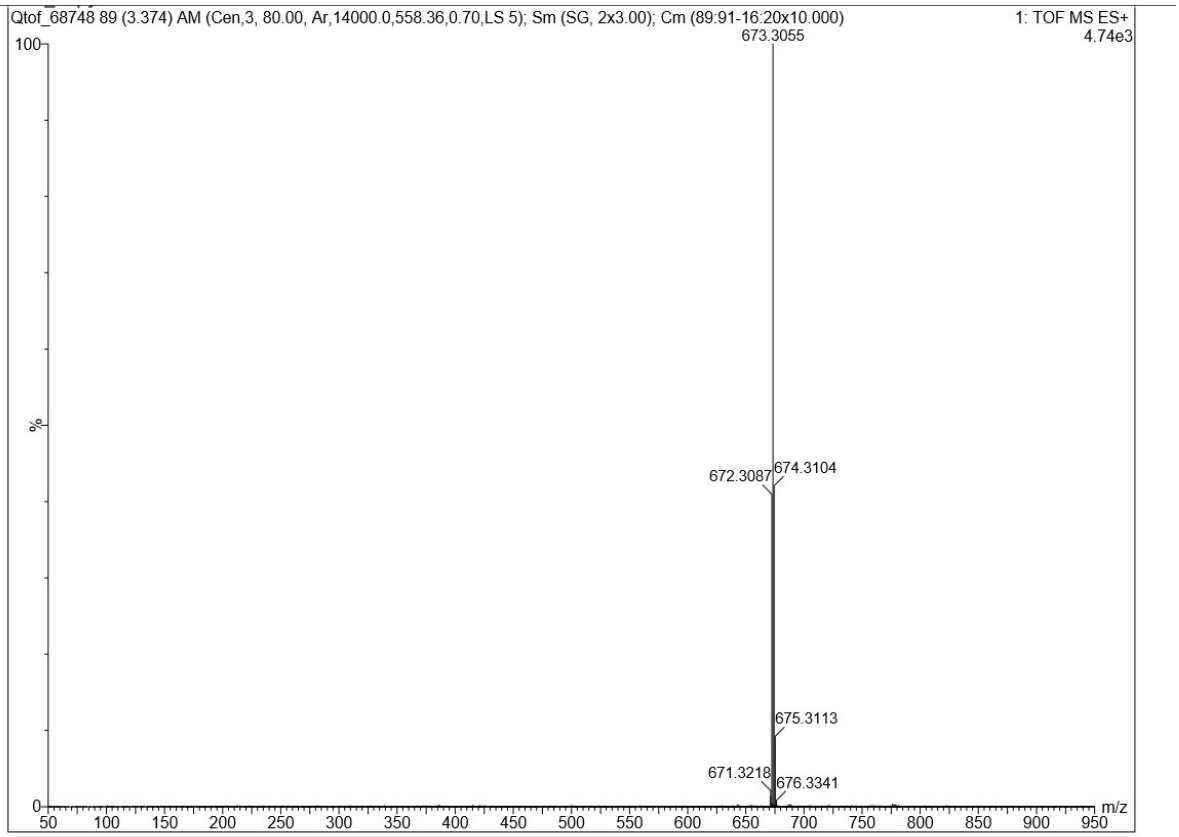
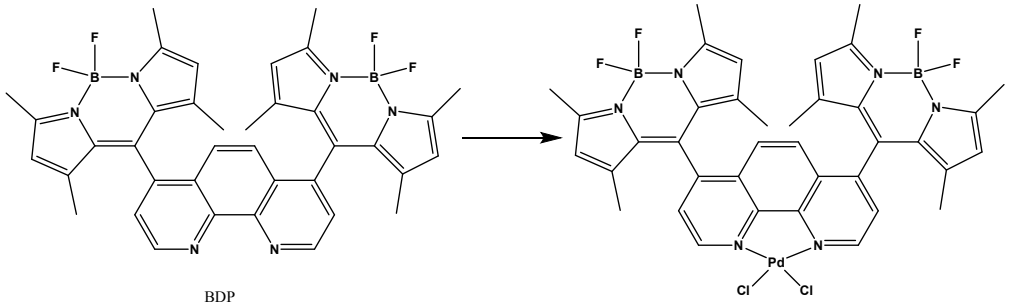


Figure S3. ESI HR-MS spectra of YH2

2.3 Synthesis of dichloro(4,7-di(4′,4′′-difluoro-1′,3′,5′,7′-tetramethyl-4′-bora-3′a,4′a-diaza-s-indacene)-1,10-phenanthroline)palladium(II) (**1**)



Catalyst **1** was synthesized as follows. Bis(benzonitrile)dichloropalladium(II) (0.844 mg, 2.20 mmol) was dissolved in $CHCl_3$ in a 250 mL RBF. Ligand **BDP** (0.138 g, 2.01 mmol) was added

to the mixture. The mixture was stirred at room temperature under dark for 3 hours. Upon completion of the reaction, the solvent was removed under vacuum. The crude product was purified via column chromatography with DCM/MeOH (v:v, 200:5). The product containing fraction was subjected to vacuum to remove the solvent and the recrystallization of the resultant solid with MeOH provided the title compound (0.155 g, 91% yield) as an orange solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.865 (d, J = 5.36 Hz, 2H), 7.98 (s, 2H), 7.97 (s, 2H), 6.01 (s, 2H), 2.57 (s, 3H), 1.07 (s, 3H)

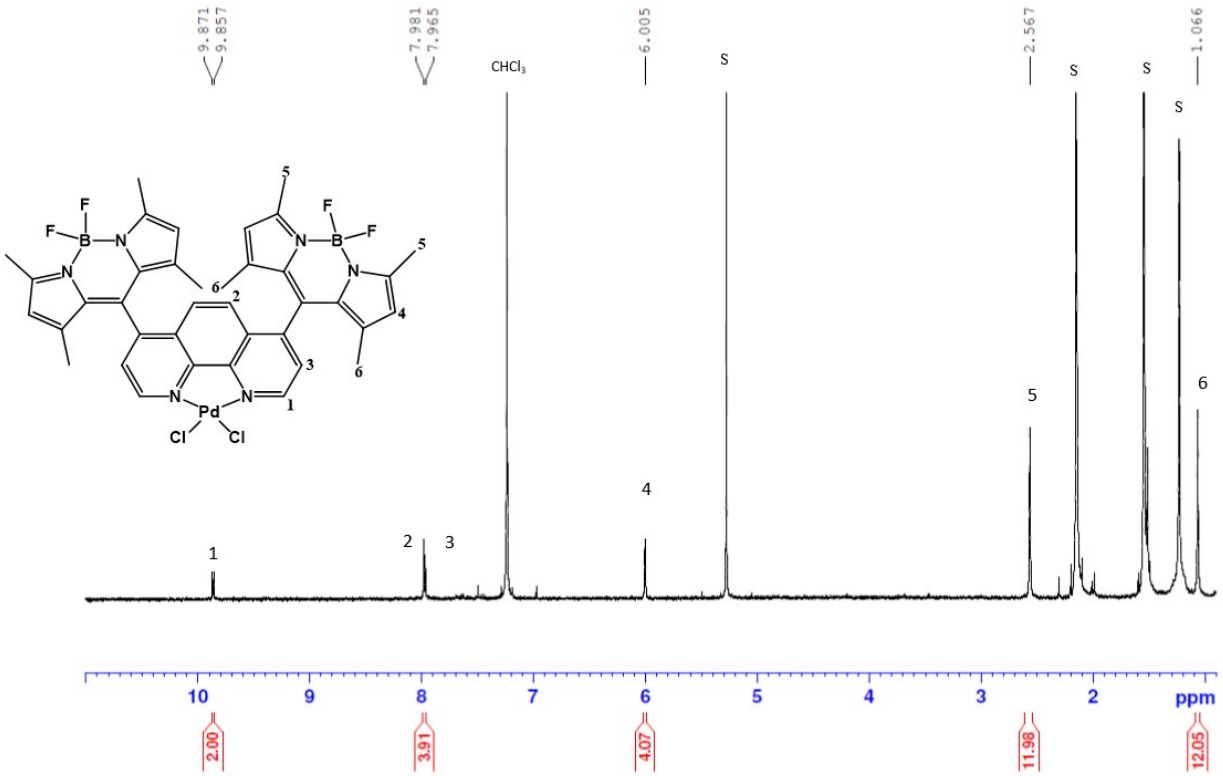


Figure S4. ^{1}H NMR spectrum of YH2-Pd in $CDCl_3$.

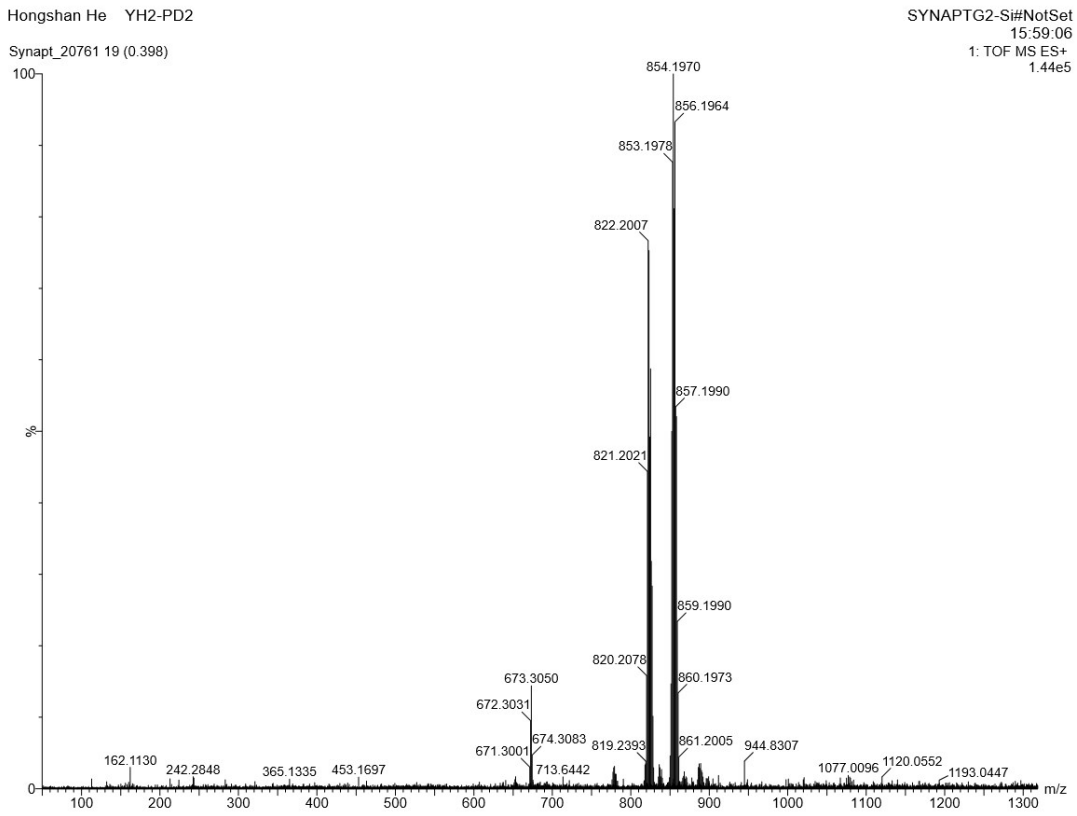


Figure S5. ESI-MS of YH2-Pd (CH_3CN and formic acid were used during data acquisition). The 854.1970 and 822.2007, and 673. 3050 corresponded to $[M\text{-}Cl+CH_3CN]^+$, $[M - 2Cl + COOH^-]^+$ and $[M\text{-}Pd – 2Cl + H^+]^+$ fragments.

3. Spectral and electrochemical measurements

Solutions of **BDP** (4×10^{-6} mol/L), **1** (5×10^{-6} mol/L) and a supernatant of a saturated solution of a dichloro(1,10-phenanthroline) palladium (II) in DCM were used to obtain UV-VIS spectra for the preceding compounds. To monitor the reaction, catalyst **1** (4.2 mg, 0.005 mmol, 0.005 equiv) was added to a Schlenk flask (50 mL) fitted with a rubber stopper. The vessel was degassed and filled with N_2. All the manipulations hereafter was carried under Ar conditions inside the glove box. DMF (4 mL) was added to the flask followed by Et_3N (1 mL, 7.11 mmol, 7.11 equiv) and

PPh_3 (0.5 mL of a 0.01M solution in DMF, 0.05 mmol, 0.05 equiv). The stirred mixture was irradiated using a 13 W LED lamp. UV-VIS spectra were obtained in 0, 10, 60, 120, 240 min time intervals after irradiation. Samples for UV-VIS were prepared by diluting 15 µL of the reaction mixture in a 2.5 mL DCM solution in a quartz cuvette at each time interval.

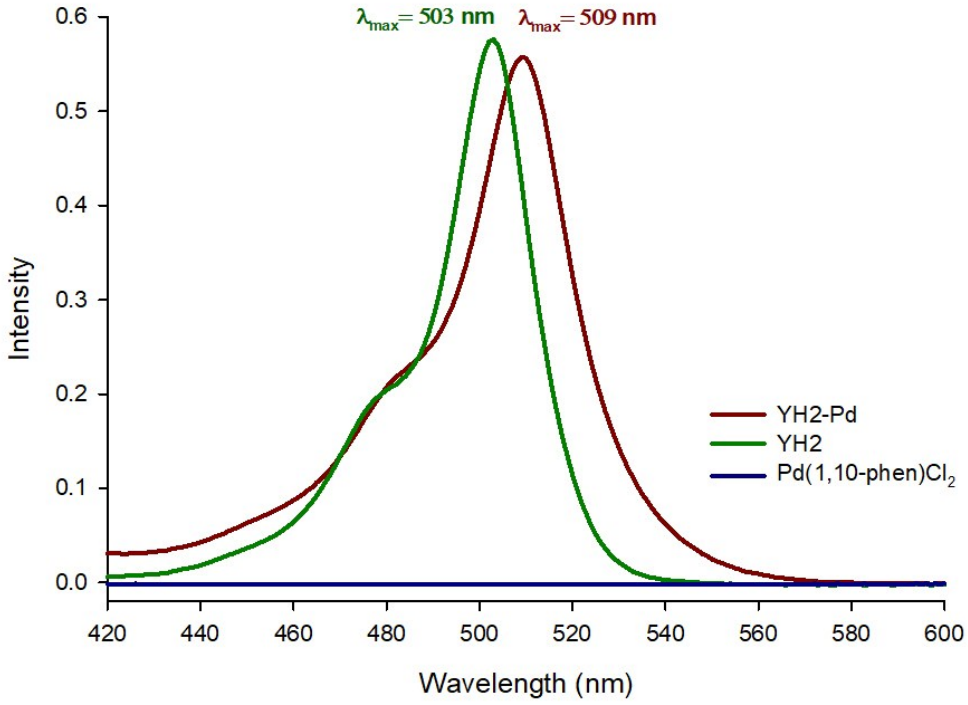
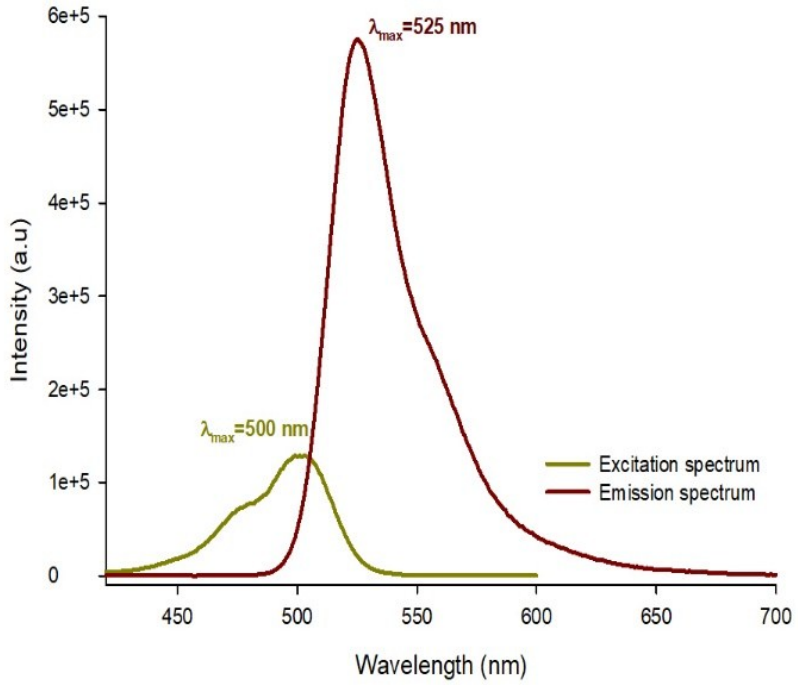


Figure S6 (Original S1). Absorption spectra for BDP (labeled as YH2) (4.2×10^{-6} mol/L), compound 1 (labeled as YH2-Pd) (2.1×10^{-6} mol/L) and [Pd(1,10-phen)Cl_2] (saturated solution) in DCM

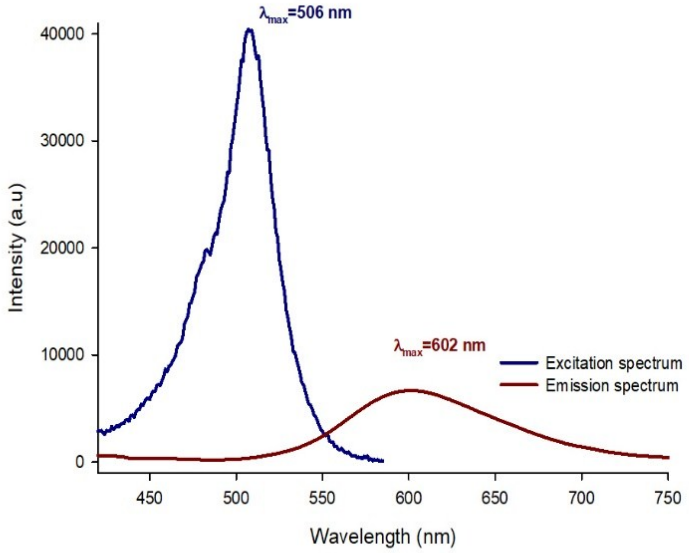
Emission and excitation spectra for ligand **BDP** and catalyst **1** were recorded. Stock solutions of ligand **BDP (**1.74×10^{-4} mol/L) and catalyst **1** (1.00×10^{-4} mol/L) were prepared and 60 µL and 50 µL from the stock solutions were diluted in 2.5 mL DCM to give 4.00×10^{-6} mol/L and 2.08×10^{-6} mol/L, respectively. Ligand **BDP** emission spectra was recorded at a fixed excitation

wavelength of 375.00 nm while scanning from 400.00 nm to 700.00 nm. Excitation spectrum was recorded with a fixed emission wavelength at 620 nm while scanning in 350-600 nm range.

Catalyst **1** emission spectrum was recorded at a fixed excitation wavelength of 371.40 nm while scanning from 400 nm to 750 nm Excitation spectrum was recorded with a fixed emission wavelength at 600 nm while scanning in 350-585 nm range.



(a)



(b)

Figure S7 (original S2) Fluorescence spectra for BDP (4 × 10^{-6} mol/L) (a) and compound **1** (2.08 × 10^{-6} mol/L) (b) in DCM. BDP with an excitation wavelength of 375.00 nm and emission wavelength at 620 nm and compound **1** with an excitation wavelength of 371.40 nm emission wavelength at 600 nm

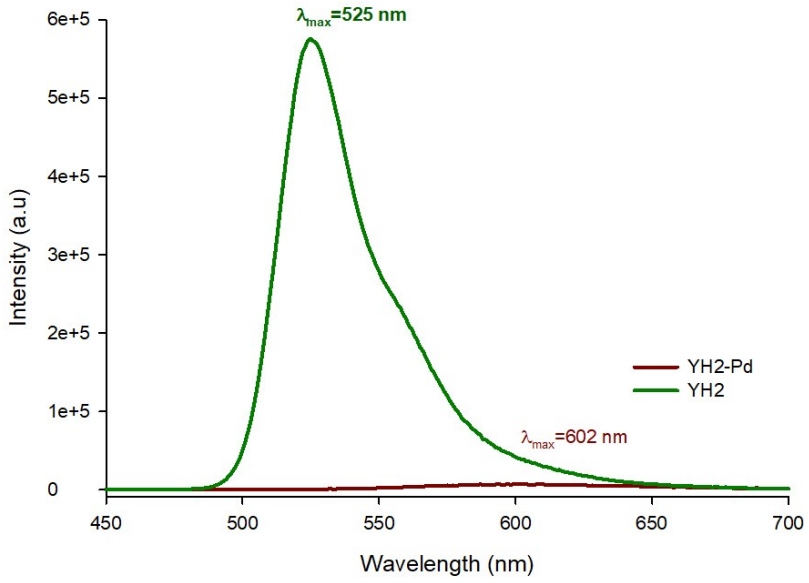


Figure S8 (original S3). Comparison of emission spectra of BDP (labeled as YH2) (4×10^{-6} mol/L) (green) and **1** (Labeled as YH2-Pd) (2.08×10^{-6} mol/L (red) in DCM. λ_{ex} = 375.00 nm

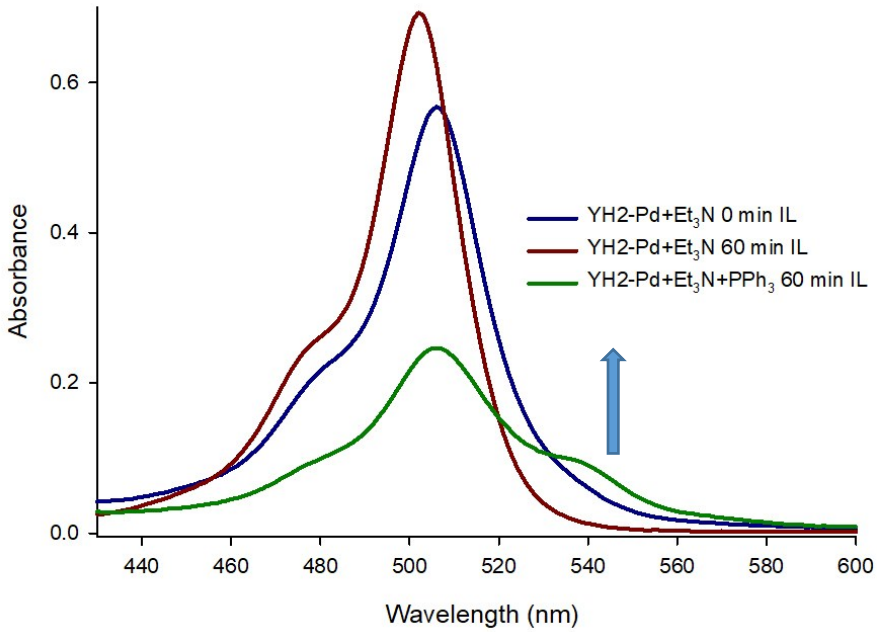


Figure S9 (Original S4). Monitoring the reaction with time upon addition of Et_3N and PPh_3 consecutively with illuminating (IL) the reaction mixture with compound **1** (3.04×10^{-6} mol/L) in DMF. The catalyst **1** was labeled as YH2-Pd.

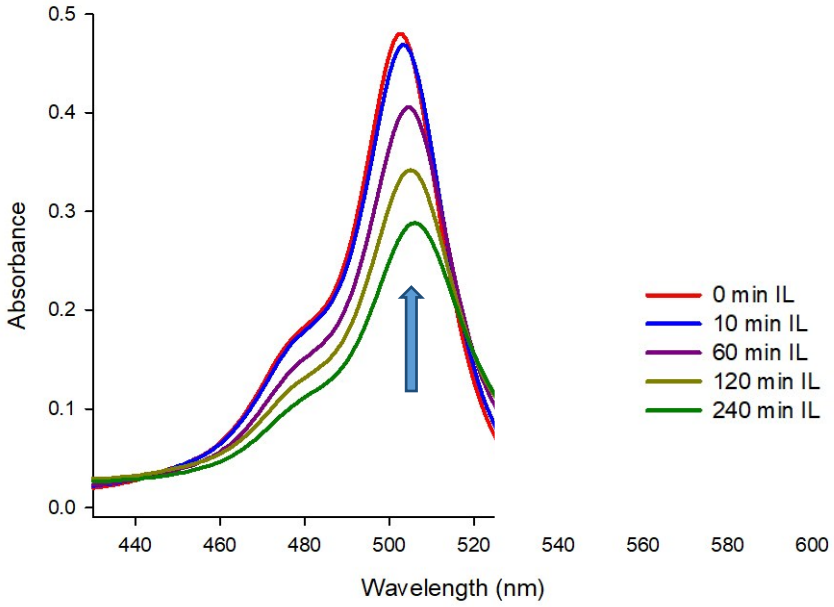


Figure S10 (original S5). Monitoring the formation of the unidentified species upon addition of Et_3N and PPh_3 with compound **1** (3.04×10^{-6} mol/L) in DMF

4. Monitoring the reduction of Pd(II) with ^{31}P NMR studies

Catalyst **1** (8.5 mg, 0.025 mmol, 0.025 equiv) was added to a Schlenk flask (50 mL) fitted with a rubber stopper. The vessel was degassed and filled with N_2 followed by the addition of DMF (4 mL). Then Et_3N (1 mL, 7.11 mmol, 7.11 equiv) and PPh_3 (x=2, 4.0 mg, 0.05 mmol, 0.05 equiv) were added respectively via syringes to the stirred reaction mixture under N_2 conditions. After irradiating the sample for four hours $CDCl_3$ (~ 0.5 mL) was added to the reaction mixture in the glove box and the NMR tube was prepared.

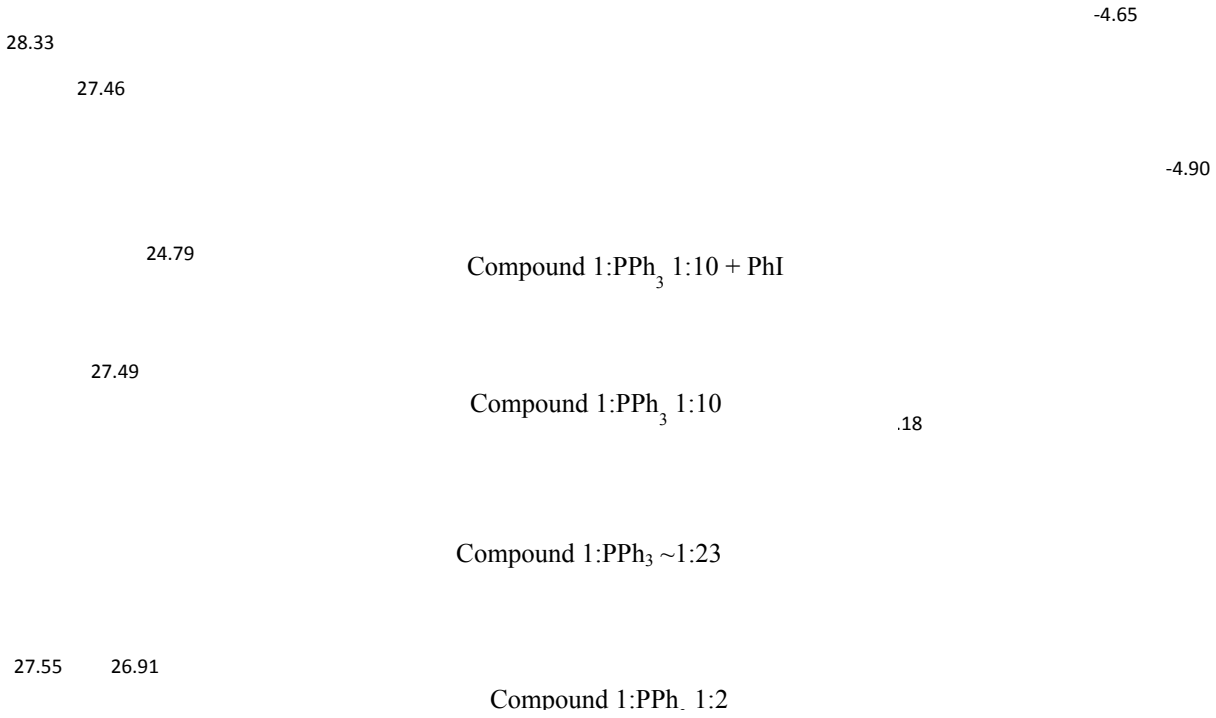


Figure S11 (Original S6). ^{31}P NMR spectra for systems with different Pd/PPh_3 molar ratios

5. Electrochemical procedure for cyclic voltammetry

Experiments were carried out in a three-electrode cell with Pt working electrode, Ag wire reference electrode at room temperature connected to a N_2 supply. All three compartments were filled with nBu_4NBF_4 (0.1 M) in acetonitrile followed by purging N_2 for 20 minutes. To the working electrode containing compartment, the compound of interest (~ 4mg) and ferrocene were introduced. Cyclic voltammetry was performed at 100 mVs^{-1}.

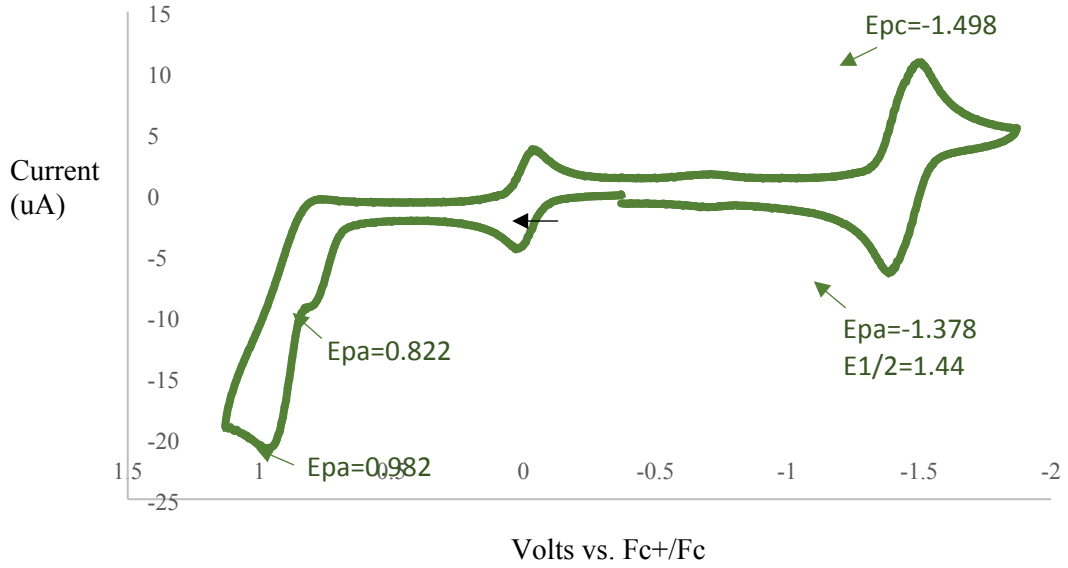


Figure S12 (Original S7). Cyclic voltammogram for BDP in MeCN / 0.1 M N-Bu_4PF_6, W: Pt disk, Aux: Pt wire, Ref: Ag wire, Scan rate = 100 mV/s

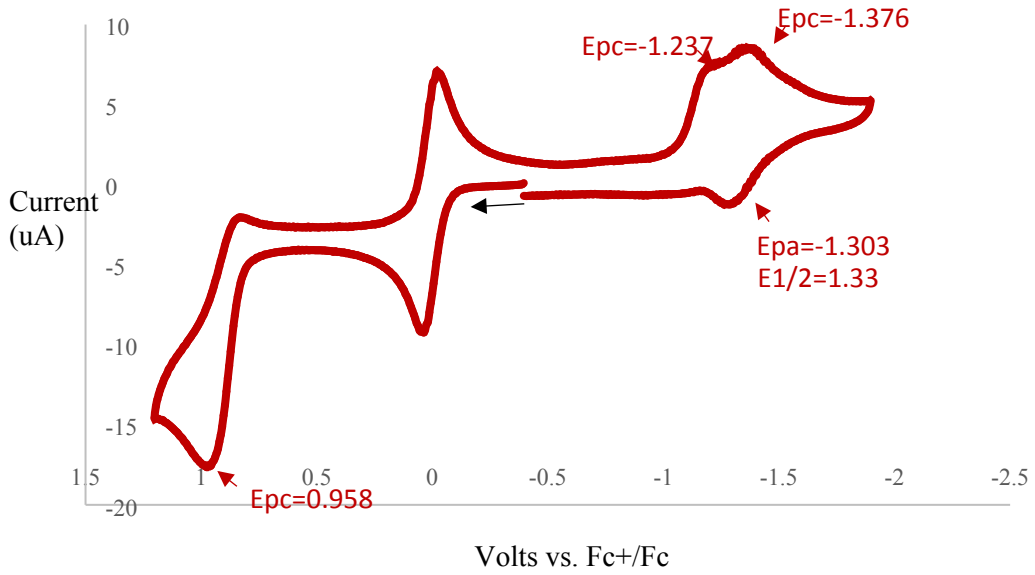


Figure S13 (Original S8). Cyclic voltammogram for 1 in MeCN / 0.1 M N-Bu_4PF_6, W: Pt disk, Aux: Pt wire, Ref: Ag wire, Scan rate = 100 mV/s

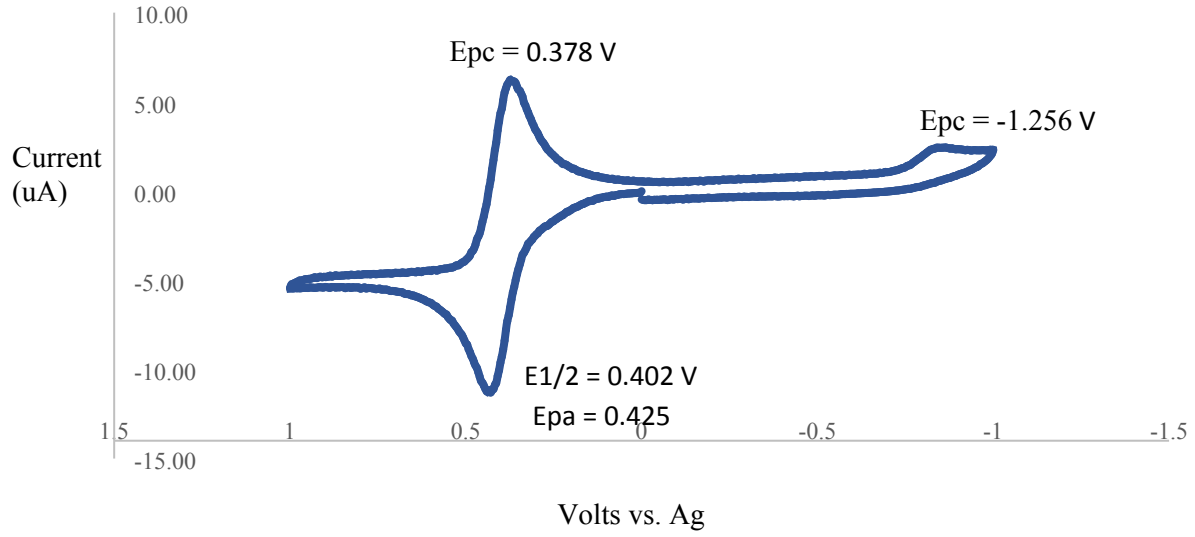


Figure S14 (Original S9) Cyclic voltammogram for [Pd(1,10-phen)Cl_2] in MeCN / 0.1 M N-Bu_4PF_6, W: Pt disk, Aux: Pt wire, Ref: Ag wire, Scan rate = 100 mV/s

Table S1: photophysical and electrochemical properties of BDP and the catalyst **1**

Compound	**λ_{max}(ab)/nm**	**ϵ*/ 10^5Lmol^{-1}cm^{-1}**	**λ_{max}(fl)/nm**	**$E_{1/2}$ (Fc/Fc+)**	
				A/A-	**A/A+**
BDP	503	1.38615	525	-1.44	0.88
1	509	1.13808	602	-1.33	0.89

6. Sonogashira C-C cross coupling reactions

Representative procedure for coupling of phenylacetylene and iodobenzene. Catalyst **1** (4.2 mg, 0.005 mmol) was added to a Schlenk flask (50 mL) with a rubber stopper. The vessel was degassed and filled with N_2 for 5 times followed by the addition of dry DMF (4 mL). Then iodobenzene (0.111 mL, 1 mmol), Et_3N (1 mL, 7 mmol), PPh_3 (0.5 mL of a 0.01M solution in DMF, 0.05 mmol)

and phenylacetylene (0.130 mL, 1.2 mmol) were added via syringes sequentially to the stirred reaction mixture. Irradiation with visible light was carried out using a 13W white light LED lamp.

Analysis of the products in 4, 17 and 24 hours were carried out using GC-MS. At each time interval two samples were prepared by mixing 10 μL of the reaction mixture in a 50-ppm solution of benzonitrile in DCM (1.5 mL) in a GC-MS vial. Calibration curves were prepared according to the equation 1 given below using 2-methylbenzonitrile as the standard. A solution series of 10, 20, 30, 40, 50 ppm iodobenzene, phenylacetylene and diphenylacetylene were prepared in 50 ppm 2-methylbenzonitrile. Area of standard signal/concentration of the standard vs plotted against the area of analyte signal/concentration of analyte to diphenylacetylene, iodobenzene and phenylacetylene to give the below equations

$$\frac{Area\ of\ the\ analyte\ signal}{Concentration\ of\ the\ analyte} = F \times \frac{Area\ of\ the\ standard\ signal}{Concentration\ of\ the\ standard}$$

A direct relationship between the standard area/ standard concentration to product area/ product concentration was used instead of calibration curves. Two samples were analyzed and the average of the results from two samples were taken.

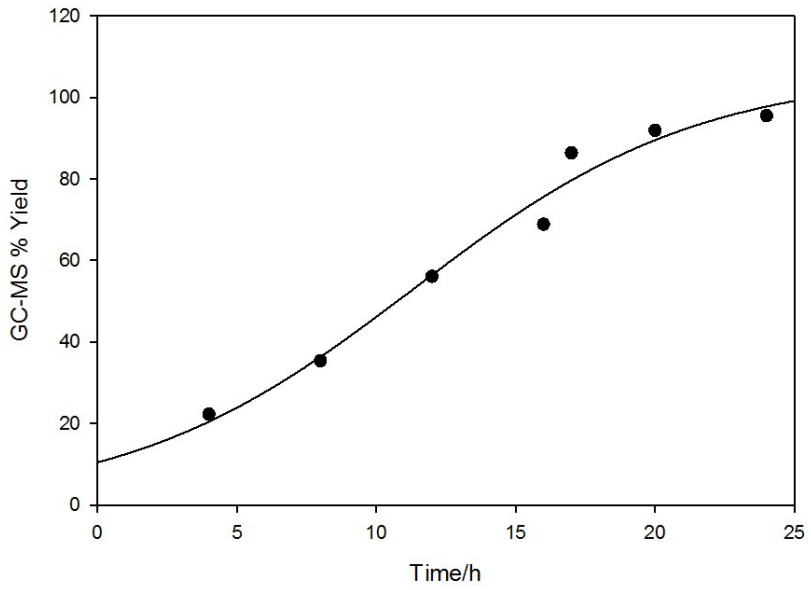
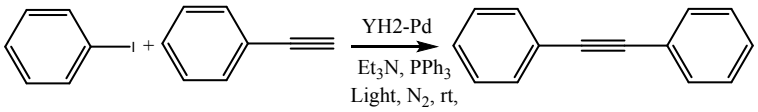


Figure S15 (Original S10). Reaction progress of a reaction between iodobenzene and phenylacetylene with time monitored with GC-MS



Sample Information

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Sample ID	: KC027_R_a_4h
Vial #	: 2
Injection Volume	: 1.00
Data File	: C:\GCMSsolution\Data\He group\KC027_R_aa_4h.qgd
Method File	: C:\GCMSsolution\Data\He group\hp inj 30-1 split 75o start slow then fast ramp.q
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Comment	

KC 024-R2-a-4h

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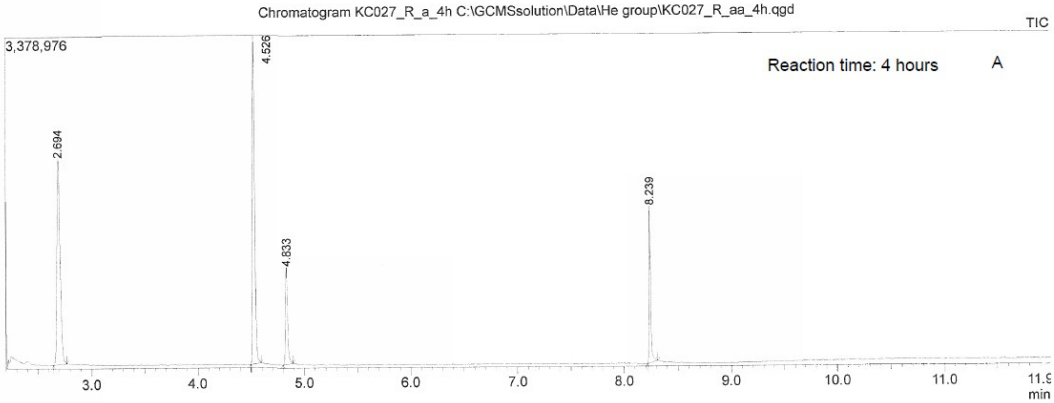

Peak Report TIC

Peak#	R.Time	Area	Area%	Name
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2	4.526	4540514	38.32	Benzene, iodo-
3	4.833	1320102	11.14	Benzonitrile, 2-methyl-
4	8.239	1621363	13.68	Diphenylacetylene
		11848925	100.00	

Sample Information

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Sample ID	: KC027_R_b_4h
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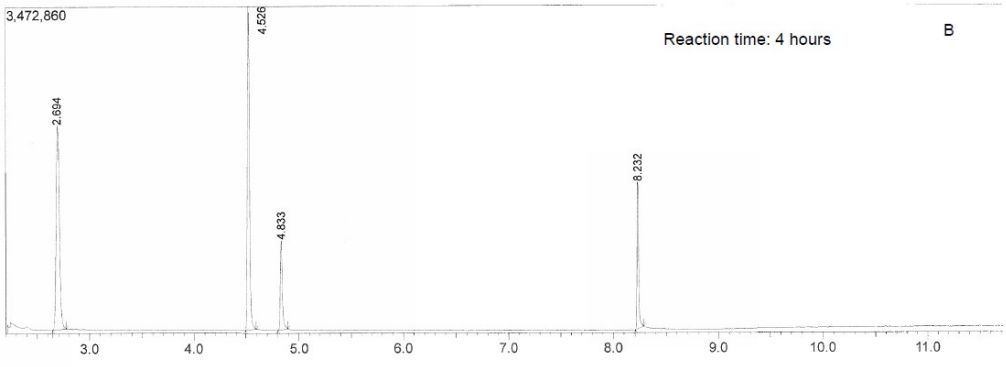
Comment	

KC024-R2-b-4h

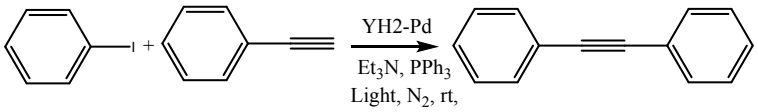
Chromatogram KC027_R_b_4h C:\GCMSsolution\Data\He group\KC027_R_bb_4h.qgd



Peak Report TIC

Peak#	R.Time	Area	Area%	Name
1	2.694	4537337	37.61	Phenylethyne
2	4.526	4655160	38.59	Benzene, iodo-
3	4.833	1274269	10.56	Benzonitrile, 2-methyl-
4	8.232	1597532	13.24	Diphenylacetylene
		12064298	100.00	

Figure S16. GC-MS results for the reactions between iodobenzene and phenylacetylene in DMF for 4 hr.



Sample Information

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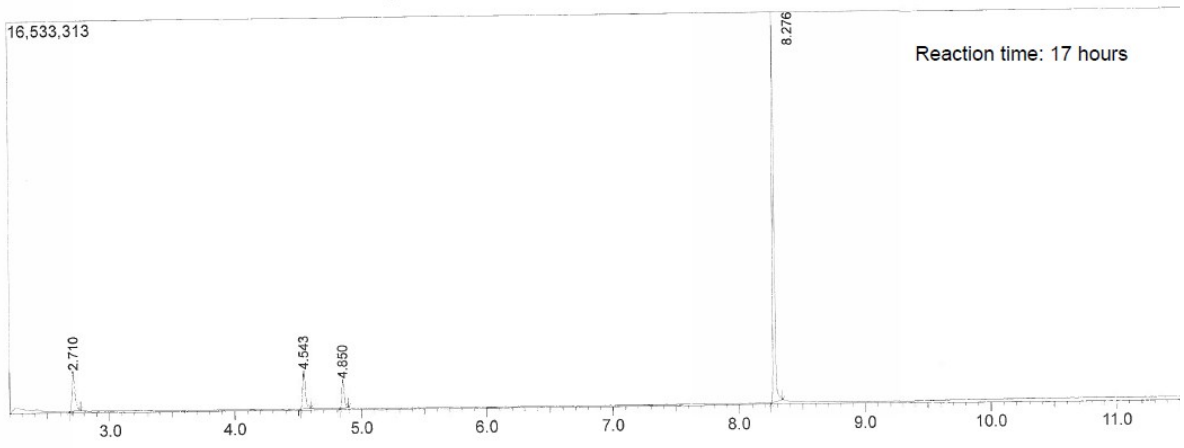
Comment	

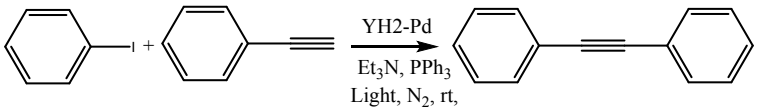
Chromatogram KC024R_17hR C:\GCMSsolution\Data\He group\KC024R_17hR.qgd



Peak Report TIC

Peak#	R.Time	Area	Area%	Name
1	2.710	3767712	15.66	Phenylethyne
2	4.543	2390450	9.94	Benzene, iodo-
3	4.850	1578989	6.56	Benzonitrile, 2-methyl-
4	8.276	16322444	67.84	Phenanthrene
		24059595	100.00	

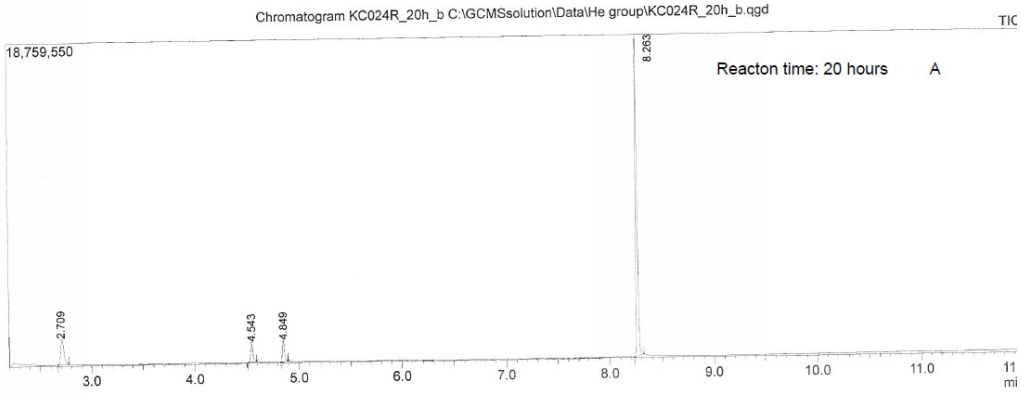
Figure S17. GC-MS results for the reaction between iodobenzene and phenylacetylene in DMF for 17 hr.



Sample Information

Analyzed	: 6/23/2017 11:06:21 AM
Sample Name	: KC024R_20h_b
Sample ID	: KC024R_20h_b
Vial #	: 3
Injection Volume	: 1.00
Data File	: C:\GCMSsolution\Data\He group\KC024R_20h_b.qgd
Method File	: C:\GCMSsolution\Data\He group\hp inj 30-1 split 75o start slow then fast ramp.q
Tuning File	: C:\GCMSsolution\System\Tune1\autotune 06_23_17._1.qgt
Comment	

Chromatogram KC024R_20h_b C:\GCMSsolution\Data\He group\KC024R_20h_b.qgd



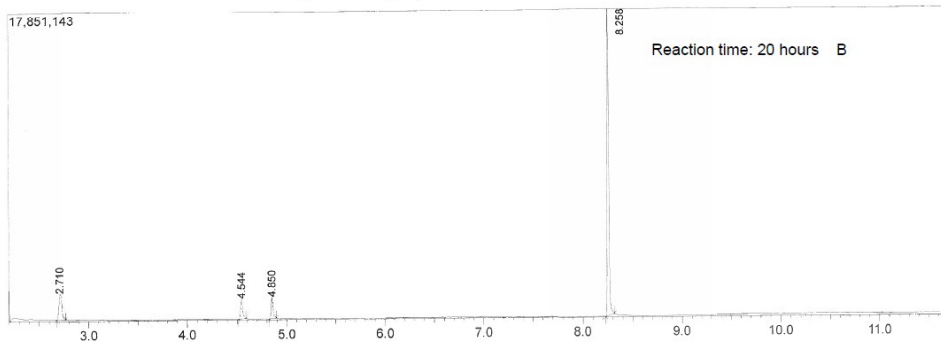
Peak Report TIC

Peak#	R.Time	Area	Area%	Name
1	2.709	3203674	12.56	Phenylethyne
2	4.543	1706379	6.69	Benzene, iodo-
3	4.849	1624524	6.37	Benzonitrile, 2-methyl-
4	8.263	18967653	74.38	Diphenylacetylene
		25502230	100.00	

Sample Information

Analyzed	: 6/23/2017 10:35:54 AM
Sample Name	: KC024R_20h_a
Sample ID	: KC024R_20h_a
Vial #	: 2
Injection Volume	: 1.00
Data File	: C:\GCMSsolution\Data\He group\KC024R_20h_a.qgd
Method File	: C:\GCMSsolution\Data\He group\hp inj 30-1 split 75o start slow then fast ramp.q
Tuning File	: C:\GCMSsolution\System\Tune1\autotune 06_23_17._1.qgt
Comment	

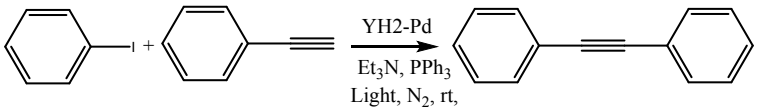
Chromatogram KC024R_20h_a C:\GCMSsolution\Data\He group\KC024R_20h_a.qgd



Peak Report TIC

Peak#	R.Time	Area	Area%	Name
1	2.710	3173549	12.52	Phenylethyne
2	4.544	1659980	6.55	Benzene, iodo-
3	4.850	1614646	6.37	Benzonitrile, 2-methyl-
4	8.258	18892699	74.55	Diphenylacetylene
		25340874	100.00	

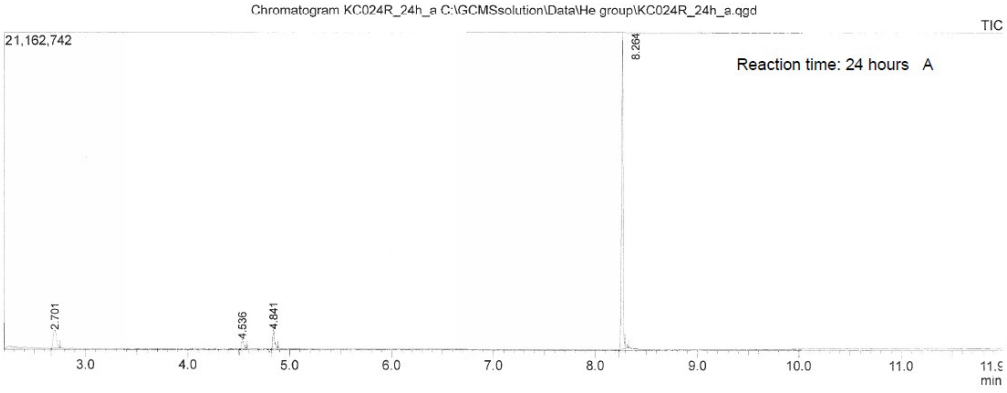
Figure S18. GC-MS results for the reaction between iodobenzene and phenylacetylene in DMF for 20 hr.



Sample Information

Analyzed	: 6/23/2017 2:27:19 PM
Sample Name	: KC024R_24h_a
Sample ID	: KC024R_24h_a
Vial #	: 1
Injection Volume	: 1.00
Data File	: C:\GCMSsolution\Data\He group\KC024R_24h_a.qgd
Method File	: C:\GCMSsolution\Data\He group\hp inj 30-1 split 75o start slow then fast ramp.q
Tuning File	: C:\GCMSsolution\System\Tune1\autotune 06_23_17._1.qgt
Comment	

Chromatogram KC024R_24h_a C:\GCMSsolution\Data\He group\KC024R_24h_a.qgd



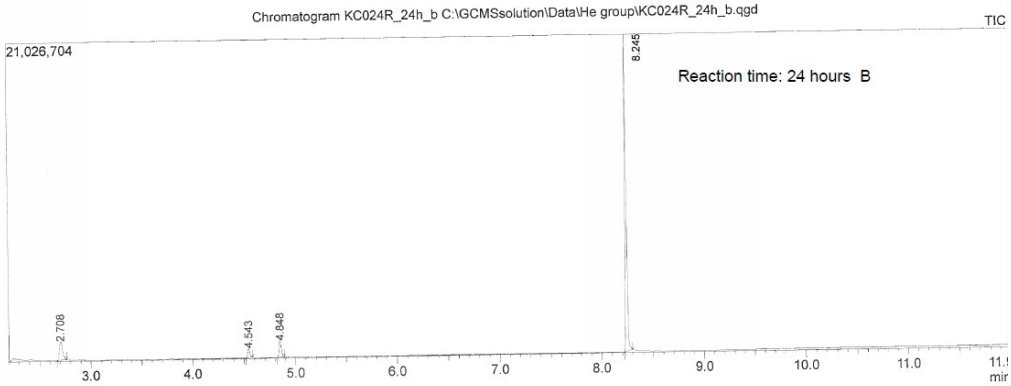
Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Name
1	2.701	2.665	2.755	2615991	9.86	Phenylethyne
2	4.536	4.510	4.575	906190	3.42	Benzene, iodo-
3	4.841	4.815	4.885	1663866	6.27	Benzonitrile, 2-methyl-
4	8.264	8.235	8.325	21332643	80.44	Diphenylacetylene
				26518690	100.00	

Sample Information

Analyzed	: 6/23/2017 2:43:27 PM
Sample Name	: KC024R_24h_b
Sample ID	: KC024R_24h_b
Vial #	: 2
Injection Volume	: 1.00
Data File	: C:\GCMSsolution\Data\He group\KC024R_24h_b.qgd
Method File	: C:\GCMSsolution\Data\He group\hp inj 30-1 split 75o start slow then fast ramp.q
Tuning File	: C:\GCMSsolution\System\Tune1\autotune 06_23_17._1.qgt
Comment	

Chromatogram KC024R_24h_b C:\GCMSsolution\Data\He group\KC024R_24h_b.qgd



Peak Report TIC

Peak#	R.Time	Area	Area%	Name
1	2.708	2516318	9.99	Phenylethyne
2	4.543	855522	3.40	Benzene, iodo-
3	4.848	1452506	5.77	Benzonitrile, 2-methyl-
4	8.245	20351556	80.84	Diphenylacetylene
		25175902	100.00	

Figure S19. GC-MS results for the reaction between iodobenzene and phenylacetylene in DMF for 24 hr.