

Efficient Photocatalytic Chemoselective and Stereoselective C-C Bond Formation over AuPd@N-rich Carbon Nitride

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1. Experimental Section

1.1 Materials

All chemicals used were purchased directly without further purification. Melamine (CP), Sodium hydroxide (AR), NaBH_4 (AR) and reaction solvents (AR) were purchased from Chengdu Kelong Chemical Reagent Factory. Ammonia solution (AR) was purchased from Chongqing Chuandong Chemical. $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ and PdCl_2 was purchased from Kunming Institute of Precious Metals, China. L-lysine (98%), aryl halides and olefins were purchased from Aladdin or Macklin. The water used in all experiments was prepared by being passed through an ultra-purification system.

1.2 Preparation of NRCN

Bulk carbon nitride was prepared by condensation of 10 g melamine in a crucible with a cover at 550 °C for 4 h with a ramping rate of 5 °C min^{-1} in the air in a muffle furnace. The product was well grinded in an agate mortar and denoted as CN. NRCN was prepared according to literature method and the process was partially modified.^{S1} 2.0 g CN and 25 mL saturated ammonia solution were mixed in a 50 mL Teflon-lined stainless-steel autoclave. The autoclave was heated at 150 °C for 2 hours. The product was collected after the reaction and washed with deionized water to neutral. The solid was dried in vacuum at 60 °C.

1.3 Preparation of AuPd@NRCN

AuPd@NRCN (1.5 wt % Au-1.5 wt % Pd supported on NRCN, Au/Pd molar ratio of 1/1.86) were prepared by the impregnation-reduction method. NRCN powder (0.5 g) was dispersed into a HAuCl_4 and PdCl_2 aqueous solution under magnetic stirring at room temperature. A lysine aqueous solution was added to the mixture and the mixture was vigorously stirred for 30 min, then the pH was adjusted to 8-9 by NaOH aqueous and stirred for 12 hours.^{S2} A freshly prepared aqueous NaBH_4 solution was added dropwise to this suspension with stirring in 20 min. The mixture was standing for 24 h, and then the solid was separated by centrifugation, washed with water (three times) and ethanol (once), and dried at 60 °C in vacuum for 24h. The dried powder was used directly as a catalyst. Pure Au NPs (3 wt %) and Pd NPs (3 wt %) were prepared *via* a similar method but using different quantities of HAuCl_4 and PdCl_2 aqueous solutions. The Au and Pd loading of photocatalysts were confirmed by ICP-OES.

1.4 Characterization of Catalysts

Fourier transform infrared (FT-IR) spectras were obtained on the IRPrestige-21 instrument. Scanning electron microscopy (SEM) was carried out on the SU1510 (Hitachi, Japan). Transmission electron microscopy (TEM) measurements were carried out on the FEI corporation Tecnai G2 TF30 S-Twin field transmission electron microscopy with an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a LynxEye array detector/Bruker D8 Advance running at 40kV and 40mA with Cu $\text{K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) spectra was conducted on Thermo Scientific Escalab 250Xi and all binding energy (BE) values were referenced to C1s line at 284.8 eV. Transient photocurrent responses and electrochemical impedance spectroscopy (EIS) were measured using an electrochemical system (CHI-660B, Chinehwa, Shanghai, China). Photoluminescence (PL) spectra were obtained using the Hitachi F-7000. UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained for the dry-pressed disk samples using a scanning UV-vis spectrophotometer (UV-vis DRS, UV-2450, Shimadzu, Japan) equipped with an integrating sphere assembly to investigate the optical properties of the samples.

1.5 In situ DRIFTS

In situ DRIFTS measurements were conducted using a TENSOR II FT-IR spectrometer (Bruker) equipped with an in situ diffuse reflectance cell (Harrick) and a high-temperature reaction chamber (HVC). The reaction chamber was equipped with three gas ports and two coolant ports. High-purity He, high-purity O_2 , and high-purity N_2 mixtures could be fed into the reaction system and a three-way ball valve was used to switch between the N_2 and the He. The total gas flow rate was 100 mL/min, and the air atmosphere was simulated by N_2 with O_2 . The chamber was enclosed with a dome having three windows, two for IR light entrance and detection, and one for illuminating the photocatalyst. The observation window was made of UV quartz and the other two windows were made of ZnSe. A Xe lamp (MVL-210, Japan) was used as the irradiation light source.

1.6 Photocatalytic Reactions

A 25 ml glass tube was used as the reaction container, reactants and catalyst were added and the reactor was sealed with rubber diaphragm cap. The glass tube with magnetic agitation using a LED lamp as the visible light source, and the measured light intensity including 0.15 W cm^{-2} or 0.75 W cm^{-2} . The reaction system under light and the corresponding reaction system in the dark were carried out to clarify the significance of comparison. Liquid phase products were analyzed by Agilent 7820A gas chromatography (GC) with HP-5 column, and the change of reactants and product concentrations was determined. The products were identified by GC-MS (Agilent HP5975), NMR and compared to known compounds. The solid catalyst was collected by centrifugation and then thoroughly washed with deionized water and ethanol, and the solid was dried at $60 \text{ }^\circ\text{C}$ under vacuum for the next cycle.

1.6.1 Ullmann Reactions ^{S3}

The Ullmann homo-coupling reaction conditions as follows: Aryl iodide (0.15 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol), 3 mL MeOH with irradiation at 460 nm (0.15 W cm^{-2}) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

The Ullmann cross-coupling reaction conditions as follows: Aryl iodide **1** (0.15 mmol), Aryl iodide **2** (0.2 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH with irradiation at 460 nm (0.15 W cm^{-2}) and 520 nm (0.15 W cm^{-2}) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

1.6.2 Heck Cross-Coupling Reactions

Aryl iodide (0.2 mmol), olefins (0.4 mmol), photocatalysts (15 mg), and Et_3N (0.5 mmol) in 2 mL DMF with visible light irradiation (0.75 W cm^{-2}) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

2. Figures and Tables

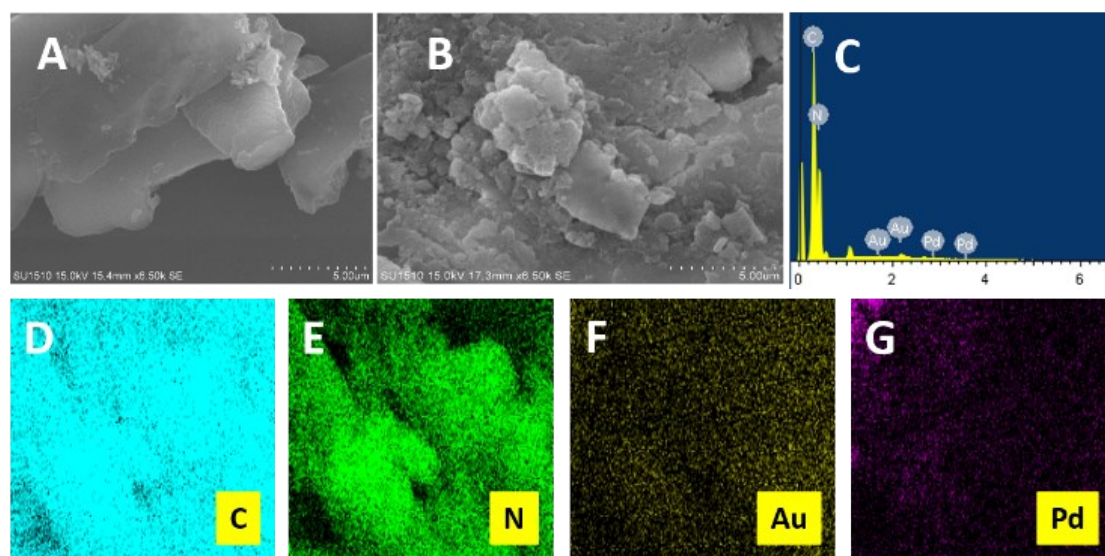


Figure S1. (A and B) SEM images of the CN and NRCN. (C) EDS of the AuPd@NRCN. (D-G) The EDS elemental mappings of C, N, Au and Pd.

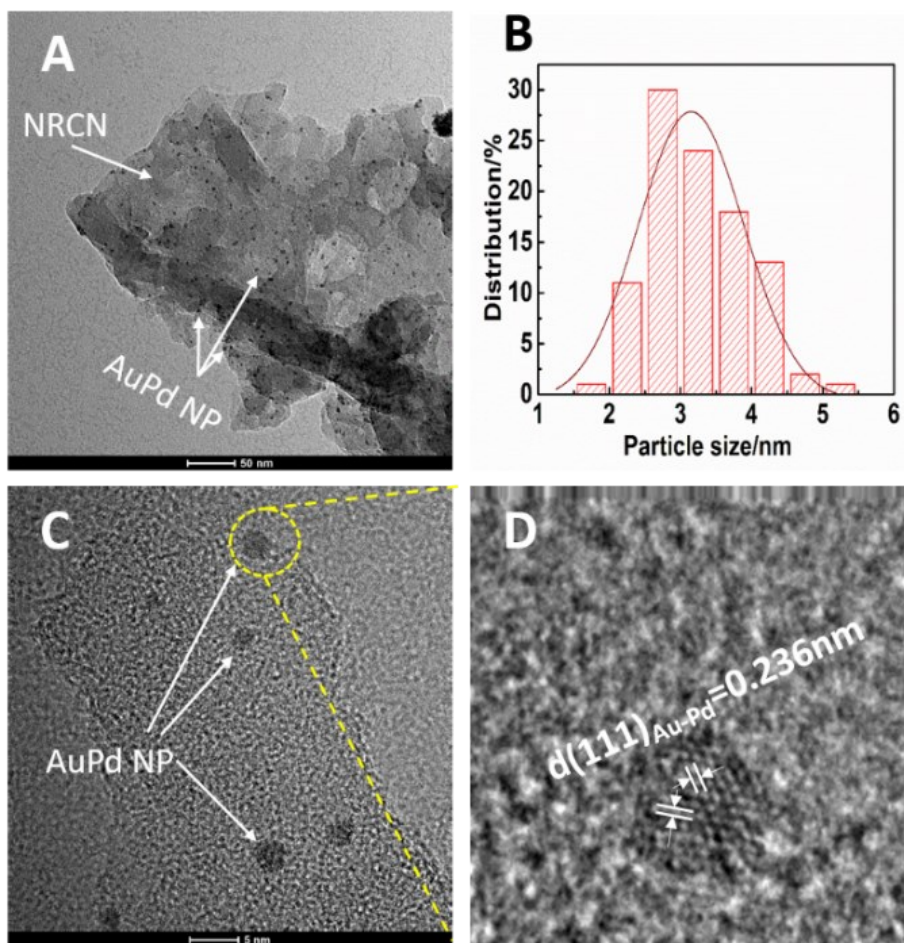


Figure S2. (A) TEM image of the AuPd@NRCN. (B) Particle size distribution of the AuPd NPs. (C and D) High-resolution TEM (HRTEM) images of the AuPd NPs.

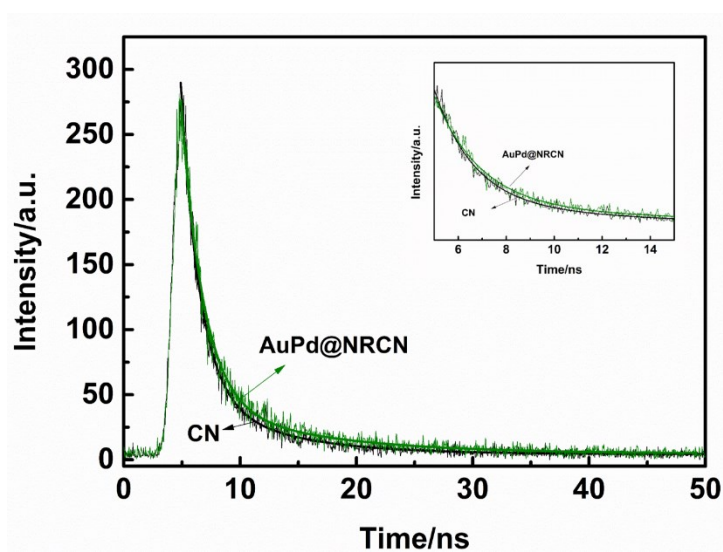


Figure S3. Time-resolved fluorescence spectra of CN and AuPd@NRCN monitored at 450 nm under a 360 nm laser irradiation at room temperature.

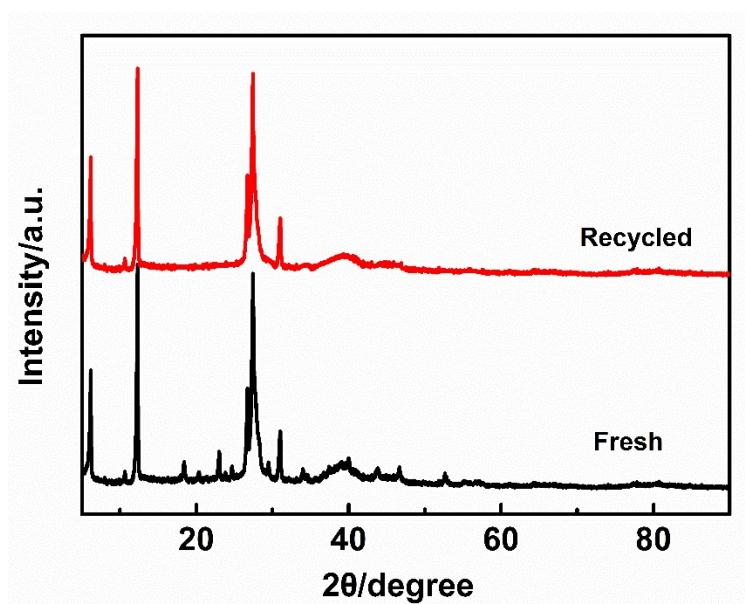


Figure S4. XRD patterns of fresh AuPd@NRCN and recycled AuPd@NRCN.

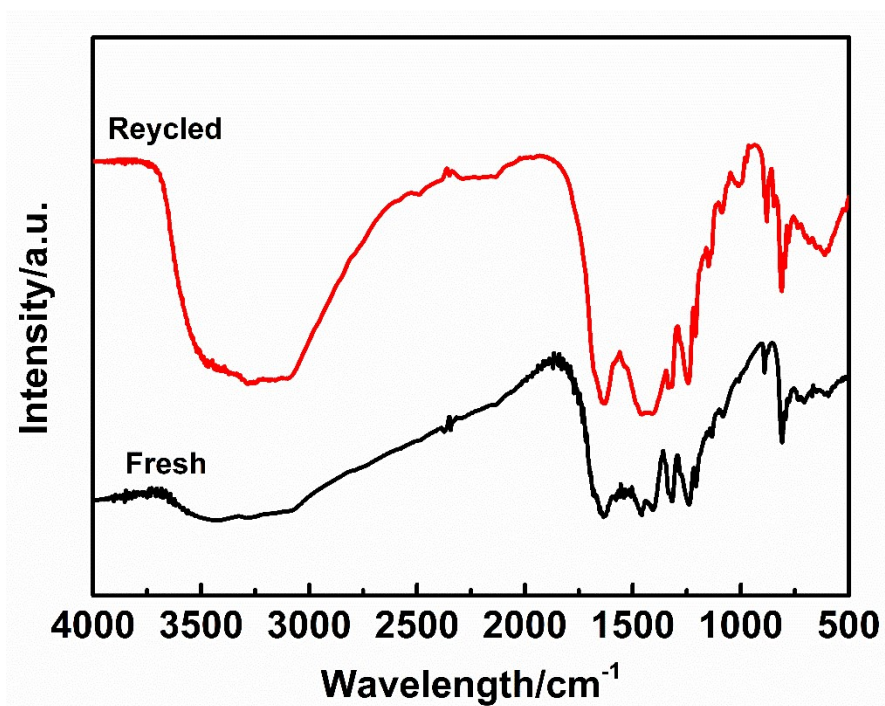


Figure S5. FT-IR spectra of fresh AuPd@NRCN and recycled AuPd@NRCN.

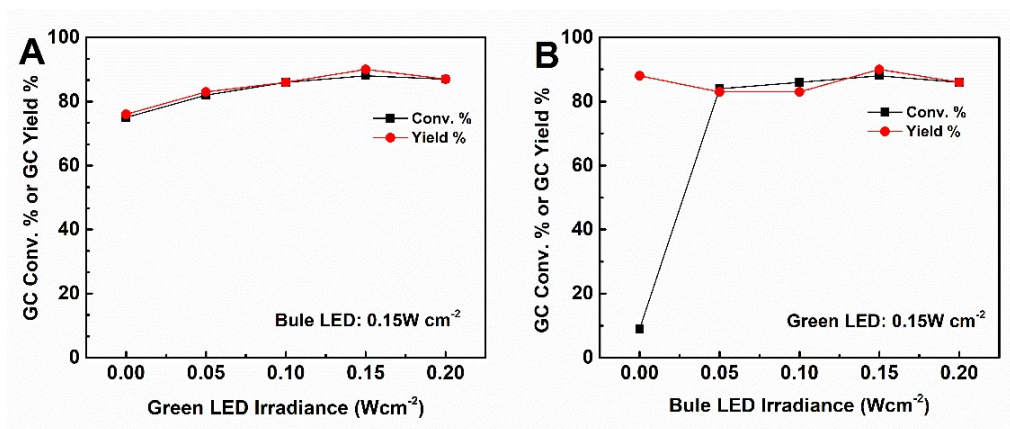


Figure S6. Conversion (blue) and yield (red) of the Ullmann cross-coupling product **3** obtained after 24 h irradiation as a function of the (A) Green LED irradiance and (B) Blue LED irradiance.

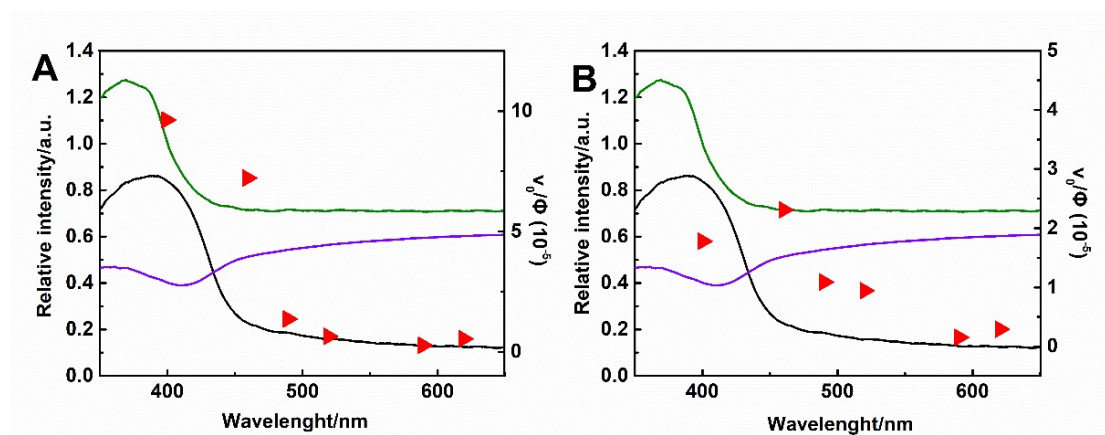


Figure S7. Comparison of the acquired action spectrum (red dots) and the diffuse reflectance spectra of NRCN (black) and AuPd@NRCN (green), along with the difference spectrum (purple). (A) Ullmann cross-coupling and (B) Heck reactions. (Conditions see supporting information Table S15 and Table S16).

Table S1. The fluorescence decay lifetimes and percentages of photo-induced carriers in CN and AuPd@NRCN.

Samples	τ_1 (ns)	Rel (%)	τ_2 (ns)	Rel (%)	τ_A (ns)
CN	1.3473	39.44	5.4881	60.56	4.9173
AuPd@NRCN	1.6236	43.87	7.8085	56.13	6.9438

Table S2. Fitting results of the impedance plots based on the equivalent circuit for CN and AuPd@NRCN

Samples	R_s (Ω)	R_{ct} (Ω)	CPE (F)
CN	0.92265	102150	3.2124×10^{-5}
NRCN	0.64445	1.145×10^{12}	3.9280×10^{-5}
AuPd@NRCN	0.71336	224540	6.4906×10^{-5}

Table S3. Condition control of Ullmann and Heck reactions.

Entry	Change condition	Reaction Conversion %	
		Ullmann ^[a]	Heck ^[b]
1	No catalyst	0	0
2	CN	0	0
3	NRCN	0	0
4	No base	<1	1
5	No light	22 ^[c]	7 ^[d]
6	None	99	97
7	AuPd@CN	16	3
8	Au@NRCN	4	6
9	Pd@NRCN	2	52
10	AuPd@PVP ^[e]	5	1
11	AuPd@NRCN ^[f]	99	96

[a] Reaction conditions: iodobenzene (0.15 mmol), photocatalysts (15 mg), and base (0.6 mmol), 3 mL MeOH with blue LED irradiation (460 nm, 0.15 W cm^{-2}) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

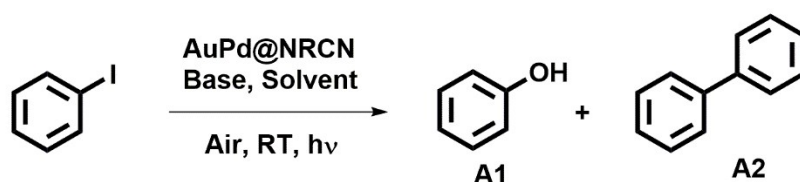
[b] Reaction conditions: iodobenzene (0.2 mmol), styrene (0.4 mmol), photocatalysts (15 mg), and Et_3N (0.5 mmol) in 2 mL DMF with white LED irradiation (0.75 W cm^{-2}) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

[c] The reaction temperature was 50 °C.

[d] The reaction temperature was 80 °C.

[e] AuPd@PVP was prepared with the similar method as in reference S4 and the same amount of reduced AuPd was employed as the catalyst.

[f] The catalyst was after four cycles.

Table S4. Optimization of base and solvent in Ullmann reaction.^[a]

Entry	Base	Solvent	Time(h)	Conv. %	A1(Sel. %)	A2(Sel. %)
1	NaOH	Acetone	24	6	7	93
2	NaOH	Ethanol	24	41	1	99
3	NaOH	Methanol	24	99	1	99
4	NaOH	DMF	24	6	26	74

5	LiOH	Methanol	24	63	1	99
6	KOH	Methanol	24	70	1	99
7	K ₂ CO ₃	Methanol	24	40	4	96
8	Cs ₂ CO ₃	Methanol	24	28	3	97
9 ^[b]	NaOH	Methanol	24	86	2	98
10 ^[c]	NaOH	Methanol	24	99	1	99

[a] Reaction conditions: iodobenzene (0.15 mmol), photocatalysts (15 mg), and base (0.6 mmol) in 3 mL solvent with blue LED irradiation (460 nm, 0.15 W cm⁻²) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

[b] N₂ instead of air.

[c] fourth cycles.

Table S5. Optimization of base and solvent in Heck reaction.^[a]

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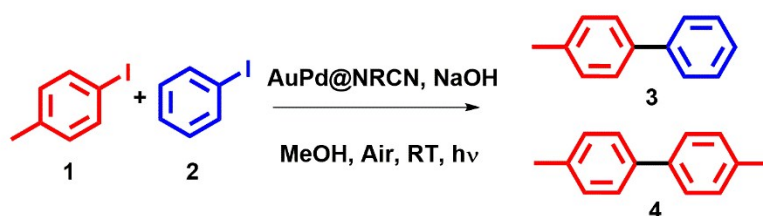
Entry	Base	Solvent	Time(h)	5(Conv. %)	B1(Sel. %)	B2(Sel. %[Z:E])	B3(Sel. %)
1	Et ₃ N	DMF	24	98	2	98[86:14]	ND
2	Et ₃ N	DMA	24	62	2	98[80:20]	ND
3	Et ₃ N	Methanol	24	54	83	17[91:9]	ND
4	K ₂ CO ₃	Methanol	24	100	100	ND	ND
5	K ₂ CO ₃	DMF	24	14	98	2[100:1]	ND
6	DBU	DMF	24	15	66	34[90:10]	ND
7	NaOH	DMF	24	13	100	ND	ND
8 ^[b]	Et ₃ N	DMF	24	58	4	96[86:14]	ND
9 ^[c]	Et ₃ N	DMF	24	95	4	96[88:12]	ND

[a] Reaction conditions: iodobenzene (0.2 mmol), olefins (0.4 mmol), photocatalysts (15 mg), and base (0.5 mmol) in 2 mL solvent with white LED irradiation (0.75 W cm⁻²) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

[b] N₂ instead of air.

[c] fourth cycles.

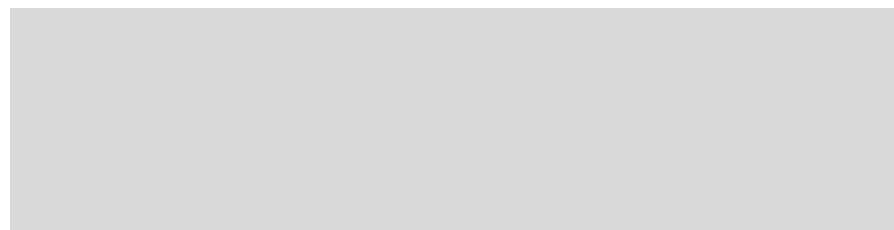
Table S6. Photocatalytic Ullmann cross-coupling with light working at 0.15 W cm⁻².^{[a] S3}



Entry	λ	1(Conv. %)	3(Sel. %)	4(Sel. %)
1	400nm	85	76	24
2	460nm	75	76	24
3	490nm	14	85	15
4	520nm	9	88	12
5	590nm	4	86	14
6	620nm	9	89	11

[a] Reaction conditions: **1** (0.15 mmol), **2** (0.2 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH with irradiation in air. The reaction temperature was room temperature, with a reaction time of 24 h.

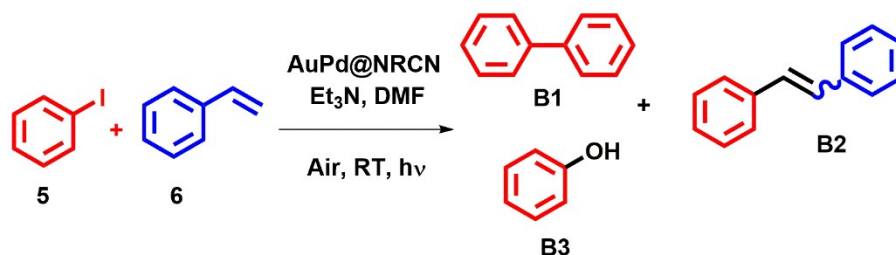
Table S7. Photocatalytic Ullmann cross-coupling between 4-iodotoluene and iodobenzene with two-color light working at 0.15 W cm⁻².^[a]



Entry	λ_1	λ_2	1(Conv. %)	3(Sel. %)	4(Sel. %)
1	460nm	400nm	94	63	37
2	460nm	460nm	75	76	24
3	460nm	490nm	82	85	15
4	460nm	520nm	88	90	10
5	460nm	590nm	90	85	15
6	460nm	620nm	90	85	15

[a] Reaction conditions: **1** (0.15 mmol), **2** (0.2 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH with irradiation in air. The reaction temperature was room temperature, with a reaction time of 24 h.

Table S8. Photocatalytic Heck coupling with light working at 0.75 W cm⁻².^[a]



Entry	λ	5(Conv%)	B1(Sel. %)	B2(Sel. %[Z:E])	B3(Sel. %)
1	400nm	50	12	88[89:11]	ND
2	460nm	73	2	98[89:11]	ND
3	490nm	35	2	98[82:18]	ND
4	520nm	33	2	98[78:22]	ND
5	590nm	5	12	88[49:51]	ND
6	620nm	13	5	95[22:78]	ND

[a] Reaction conditions: iodobenzene (0.2 mmol), styrene (0.4 mmol), photocatalysts (15 mg), and Et₃N (0.5 mmol) in 2 mL DMF with irradiation in air. The reaction temperature was room temperature, with a reaction time of 24 h.

Table S9. The recyclability of photocatalysts in Ullmann and Heck reactions.^[a]

Photocatalysts	Ullmann homo-coupling ^[a]		Ullmann cross-coupling ^[b]		Heck reaction ^[c]	
	Conv. %	Sel. %	Conv. %	Sel. %	Conv. %	Sel. %[Z:E]
Fresh	99	99	88	90	98	98[86:14]
Fourth cycles	99	99	84	90	95	96[88:12]

[a] Reaction conditions: iodobenzene (0.15 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH with blue LED irradiation (460 nm, 0.15 W cm⁻²) in air. The reaction temperature was room temperature, with reaction time

of 24 h.

[b] Reaction conditions: *p*-iodotoluene (0.15 mmol), iodobenzene (0.2 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH with blue LED (460 nm, 0.15 W cm⁻²) and green LED (520 nm, 0.15 W cm⁻²) irradiation in air. The reaction temperature was room temperature, with a reaction time of 24 h. *p*-Iodotoluene as quantitative reagent.

[c] Reaction conditions: iodobenzene (0.2 mmol), styrene (0.4 mmol), photocatalysts (15 mg), and Et₃N (0.5 mmol) in 2 mL DMF with white LED irradiation (0.75 W cm⁻²) in air. The reaction temperature was room temperature, with a reaction time of 24 h. Iodobenzene as quantitative reagent.

Table S10. Ullmann homo-coupling reaction of different substrates.^[a]

Entry	X	R	Time(h)	Light	Conv. %
1	I	-H	24	0.15W cm ⁻²	99
2	I	- <i>p</i> -CH ₃	24	0.15W cm ⁻²	93
3	I	- <i>m</i> -CH ₃	24	0.15W cm ⁻²	100
4	I	- <i>o</i> -OCH ₃	24	0.15W cm ⁻²	100
5	I	- <i>m</i> -OCH ₃	24	0.15W cm ⁻²	100
6	I	- <i>p</i> -OCH ₃	24	0.15W cm ⁻²	100
7	I	- <i>m</i> -Cl	24	0.30W cm ⁻²	100
8	I	- <i>p</i> -NO ₂	24	0.30W cm ⁻²	ND
9	I	- <i>p</i> -CN	24	0.30W cm ⁻²	ND
10	Br	-H	48	0.75W cm ⁻²	96
11	Br	- <i>p</i> -OCH ₃	24	0.75W cm ⁻²	100
12	Cl	-H	48	0.75W cm ⁻²	89

[a] Reaction conditions: Aryl iodide (0.15 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH with blue LED irradiation (460nm) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

Table S11. Scope of Ullmann cross-coupling reaction.^[a]

Entry	R ₁	R ₂	Time(h)	1(Conv. %)	3(Sel. %)	4(Sel. %)
R ₁ =EWG & R ₂ =EDG						
1	- <i>m</i> -Cl	-H	24	96	84	16
2	- <i>m</i> -Cl	- <i>m</i> -CH ₃	24	95	70	30
3	- <i>m</i> -Cl	- <i>p</i> -CH ₃	24	100	75	25
4	- <i>m</i> -Cl	- <i>o</i> -OCH ₃	24	99	35	65
5	- <i>m</i> -Cl	- <i>m</i> -OCH ₃	24	97	75	25
6	- <i>m</i> -Cl	- <i>p</i> -OCH ₃	24	100	65	35
7 ^[b]	- <i>p</i> -NO ₂	-H	24	85 ^b	8	92
8 ^[b]	- <i>p</i> -CN	-H	24	51 ^b	30	70
9	- <i>p</i> -NO ₂	- <i>p</i> -OCH ₃	24	0	-	-
10	- <i>p</i> -CN	- <i>p</i> -OCH ₃	24	0	-	-
11 ^[c]	- <i>p</i> -CF ₃	- <i>p</i> -OCH ₃	24	0	-	-
R ₁ =EDG & R ₂ =EDG						
12	- <i>o</i> -OCH ₃	-H	24	43	99	1
13	- <i>m</i> -OCH ₃	-H	24	97	96	4

14	- <i>p</i> -OCH ₃	-H	24	99	99	1
15	- <i>m</i> -CH ₃	-H	24	88	84	16
16	- <i>p</i> -CH ₃	-H	24	88	90	10
17	- <i>p</i> -OCH ₃	- <i>p</i> -CH ₃	24	99	99	1
18 ^[d]	-H	- <i>p</i> -OCH ₃	24	0	-	-
R ₁ =EWG & R ₂ =EWG						
19	- <i>m</i> -Cl	- <i>p</i> -NO ₂	24	100	ND	100
20	- <i>m</i> -Cl	- <i>p</i> -CN	24	100	ND	100

[a] Reaction conditions: **1** (0.15 mmol), **2** (0.2 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH with blue LED (460 nm, 0.15 W cm⁻²) and green LED (520 nm, 0.15 W cm⁻²) irradiation in air. The reaction temperature was room temperature, with a reaction time of 24 h.

[b] Conversion calculated on **2**.

[c] Substrate are *p*-bromobenzotrifluoride and *p*-bromoanisole.

[d] Substrate are bromobenzene and *p*-bromoanisole.

Table S12. Heck reaction of different substrates.^[a]

Entry	R ₁	R ₂	Time(h)	5(Conv. %)	7(Sel. %[Z:E])
1	-H	-Ph	24	78	98 [90:10]
			48	100	99 [90:10]
2	-H	-COOEt	24	53	93 [95:5]
			34	73	88 [99:1]
3	- <i>m</i> -CH ₃	-Ph	24	74	99 [26:74]
			48	90	98 [38:62]
4	- <i>p</i> -CH ₃	-Ph	24	57	99 [99:1]
			48	83	96 [95:5]
5	- <i>o</i> -OCH ₃	-Ph	24	26	97 [70:30]
			48	58	99 [84:16]
6	- <i>m</i> -OCH ₃	-Ph	24	65	99 [40:60]
			48	73	84 [86:14]
7	- <i>p</i> -OCH ₃	-Ph	24	14	99 [89:11]
			48	100	98 [96:4]
8	- <i>m</i> -Cl	-Ph	48	55	91 [94:6]
			48	85	98 [86:14]
9	- <i>p</i> -CH ₃	-COOEt	48	85	98 [86:14]
			48	6	99 [99:1]
10 ^[b]	-H	-Ph	24	6	99 [99:1]
11 ^[b]	-H	-COOEt	24	0	-

[a] Reaction conditions: aryl halide (0.2 mmol), olefins (0.4 mmol), photocatalysts (15 mg), and Et₃N (0.5 mmol) in 2 mL DMF with blue LED irradiation (460nm, 0.75 W cm⁻²) in air. The reaction temperature was room temperature, with a reaction time of 24 h.

[b] Aryl halide is bromobenzene.

Table S13. Mechanism study: light activation of different substrates in Ullmann cross-coupling reaction.^[a]

Entry	Substrate <i>p</i> -iodoanisole/ iodobenzene	Blue and green LEDs	Time	Conv.%	Sel. %	
					Homo-coupling ^[b]	Cross-coupling
1	-/+	-	2h	0.0	0.0	0.0
2	-/+	+	2h	15.0	15.0	0.0
3	+/-	+	2h	0.0	0.0	0.0

4 ^[c]	entry 2 + entry 3	-	6h	19.6	18.0	1.6
5 ^[d]	entry 1 + entry 3	-	6h	0.0	0.0	0.0

[a] Reaction conditions: iodobenzene (0.15mmol), *p*-iodoanisole (0.2mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH in air, +/- means with/without.

[b] Conversion calculated on iodobenzene.

[c] Indicated that the reaction after mixing entry 2 and entry 3.

[d] Indicated that the reaction after mixing entry 1 and entry 3.

Table S14. Mechanism study: light activation of different substrates in Heck reaction.^[a]

Entry	Substrate		Blue LED	Time	Conv. %	GC yield %	
	Iodobenzene	Styrene				Homo-coupling ^[b]	Stilbene[Z:E]
1	+	-	+	2h	4.6	4.6	0.0
2	-	+	+	2h	0.0	0.0	0.0
3	-	+	-	2h	0.0	0.0	0.0
4 ^[c]	entry 1+ entry 2		-	6h	7.5	5.4	2.1[86:14]
5 ^[d]	entry 1+ entry 3		-	6h	9.3	7.9	1.4[86:14]

[a] Reaction conditions: iodobenzene (0.2 mmol), styrene (0.4 mmol), photocatalysts (15 mg), and Et₃N (0.5 mmol) in 2 mL DMF in air, +/- means with/without.

[b] Conversion calculated on iodobenzene.

[c] Indicated that the reaction after mixing entry 1 and entry 2.

[d] Indicated that the reaction after mixing entry 1 and entry 3.

Table S15. Experimental and calculated data for the construction of the Ullmann cross-coupling action spectrum.^[a]

λ (nm)	Conversion (%)	v_0 (10^{-7} mol/min)	ϕ (mol/m ² min)	v_0/Φ (10^{-5})
400	23	2.90	3.01×10^{-3}	9.63
460	20	2.50	3.46×10^{-3}	7.22
490	4	0.50	3.68×10^{-3}	1.36
520	2	0.25	3.90×10^{-3}	0.64
590	1	0.12	4.43×10^{-3}	0.27
620	2	0.25	4.66×10^{-3}	0.54

[a] Reaction conditions: *p*-iodotoluene (0.15 mmol), iodobenzene (0.2 mmol), photocatalysts (15 mg), and NaOH (0.6 mmol) in 3 mL MeOH with LED (0.15 W cm⁻²) irradiation in air. The reaction temperature was room temperature, with a reaction time of 2 h. *p*-Iodotoluene as quantitative reagent. Conversion was determined by GC-FID using *t*-butylbenzene as an external standard.

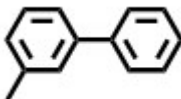
Table S16. Experimental and calculated data for the construction of the Heck action spectrum.^[a]

λ (nm)	Conversion (%)	v_0 (10^{-7} mol/min)	ϕ (mol/m ² min)	v_0/Φ (10^{-5})
400	16	2.67	1.50×10^{-2}	1.78
460	24	4.00	1.73×10^{-2}	2.31
490	12	2.00	1.84×10^{-2}	1.09
520	11	1.83	1.95×10^{-2}	0.94
590	2	0.33	2.22×10^{-2}	0.15

[a] Reaction conditions: iodobenzene (0.2 mmol), styrene (0.4 mmol), photocatalysts (15 mg), and Et₃N (0.5 mmol) in 2 mL DMF with LED irradiation (0.75 W cm⁻²) in air. The reaction temperature was room temperature, with a reaction time of 2 h. Iodobenzene as quantitative reagent. Conversion was determined by GC-FID using t-butylbenzene as an external standard.

3. Reaction Products Characterization

3.1



3-Phenyltoluene (3c): MS calculated for C₁₃H₁₂: 168, found:168.

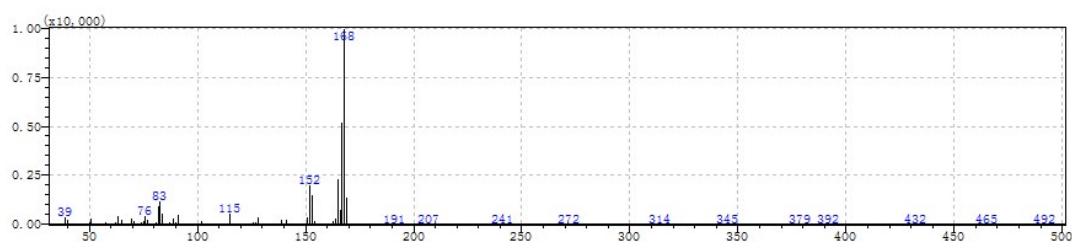
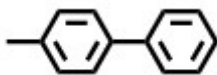


Figure S8. MS spectrum of 3-Phenyltoluene.

3.2



4-Phenyltoluene (3d): MS calculated for C₁₃H₁₂: 168, found 168.

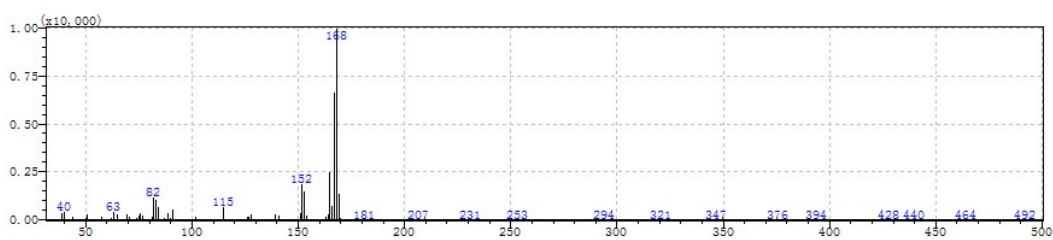
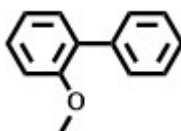


Figure S9. MS spectrum of 4-Phenyltoluene.

3.3



2-Methoxybiphenyl (3e): MS calculated for C₁₃H₁₂O: 184, found 184.

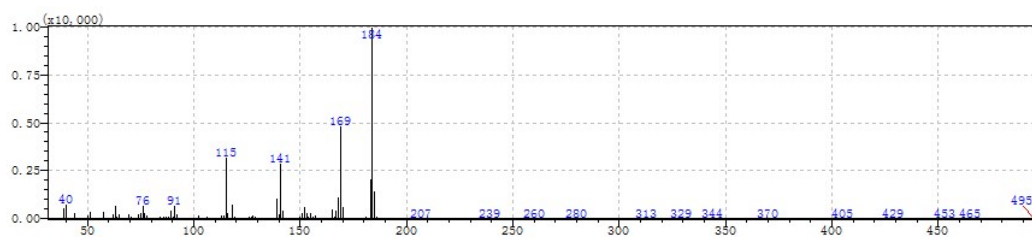
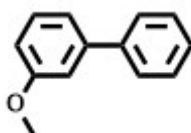


Figure S10. MS spectrum of 2-Methoxybiphenyl.

3.4



3-Methoxybiphenyl (3f): MS calculated for $C_{13}H_{12}O$: 184, found 184.

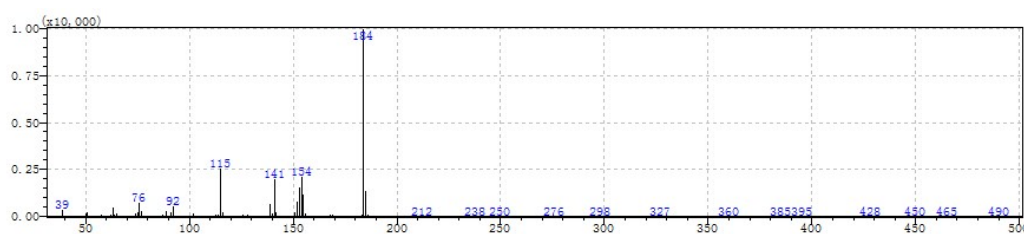
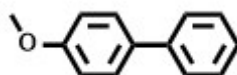


Figure S11. MS spectrum of 3-Methoxybiphenyl.

3.5



4-Methoxybiphenyl (3g): MS calculated for $C_{13}H_{12}O$: 184, found 184.

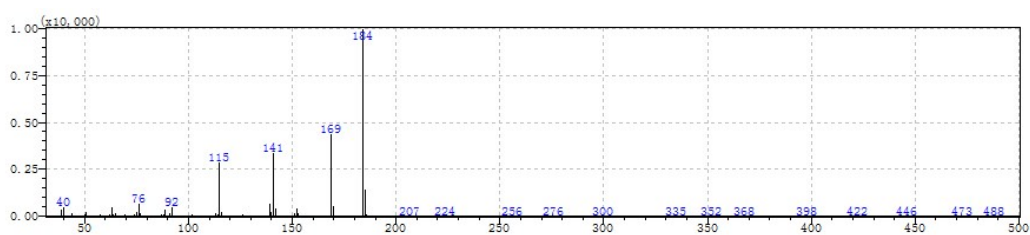
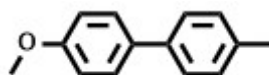


Figure S12. MS spectrum of 4-Methoxybiphenyl.

3.6



1-methoxy-4-(4-methylphenyl)benzene (3h): MS calculated for $C_{14}H_{14}O$: 198, found 198.

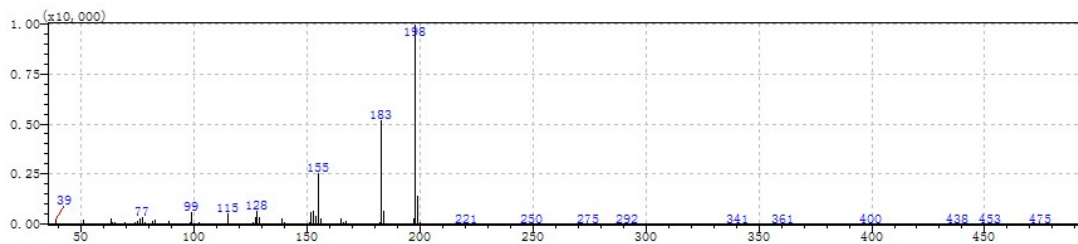
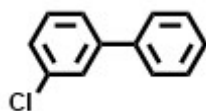


Figure S13. MS spectrum of 1-methoxy-4-(4-methylphenyl)benzene.

3.7



3-chlorobiphenyl (3i): MS calculated for $C_{12}H_9Cl$: 188, found 188.

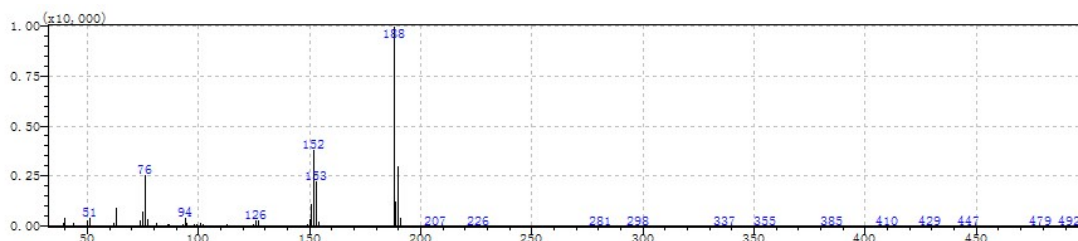
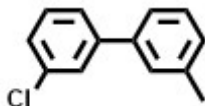


Figure S14. MS spectrum of 3-chlorobiphenyl.

3.8



3-chloro-3'-methyl-1,1'-biphenyl (3j): MS calculated for $C_{13}H_{11}Cl$: 202, found 202.

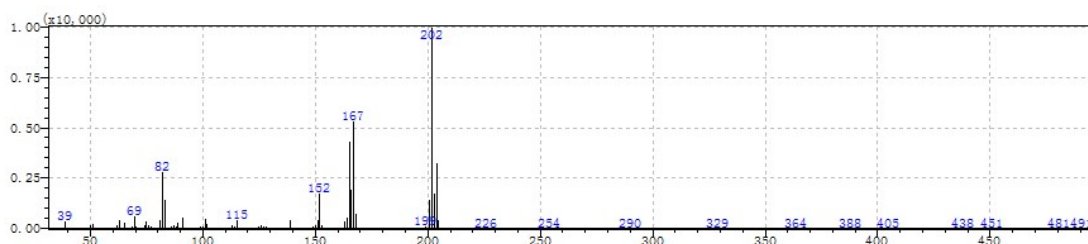
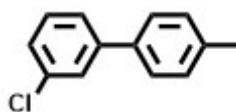


Figure S15. MS spectrum of 3-chloro-3'-methyl-1,1'-biphenyl.

3.9



3-chloro-4'-methylbiphenyl (3k): MS calculated for $C_{13}H_{11}Cl$: 202, found 202.

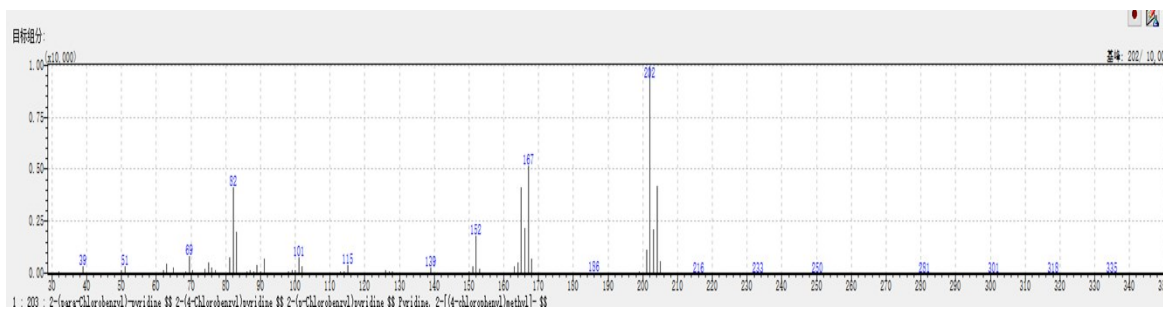
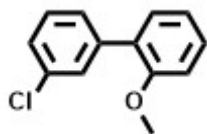


Figure S16. MS spectrum of 3-chloro-4'-methylbiphenyl

3.10



1-chloro-3-(2-methoxyphenyl)benzene (3l): MS calculated for C₁₃H₁₁ClO: 218, found 218.

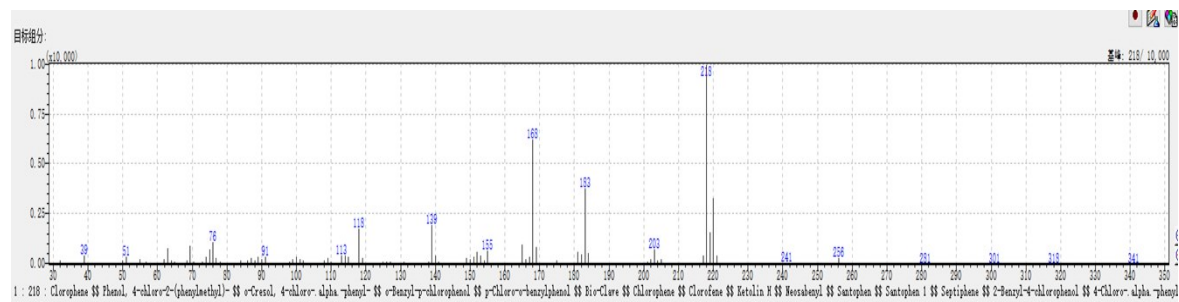
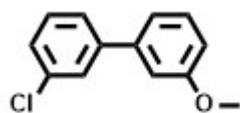


Figure S17. MS spectrum of 1-chloro-3-(2-methoxyphenyl)benzene.

3.11



1-chloro-3-(3-methoxyphenyl)benzene (3m): MS calculated for C₁₃H₁₁ClO: 218, found 218.

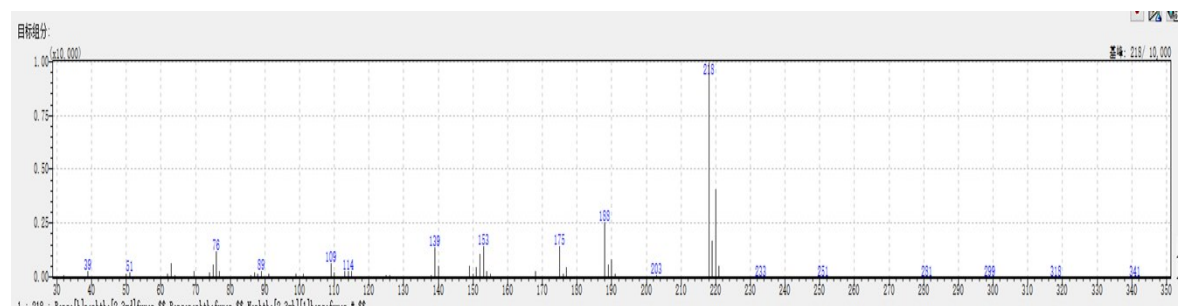
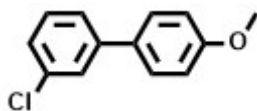


Figure S18. MS spectrum of 1-chloro-3-(3-methoxyphenyl)benzene.

3.12



1-chloro-3-(4-methoxyphenyl)benzene (3n): MS calculated for $C_{13}H_{11}ClO$: 218, found 218.

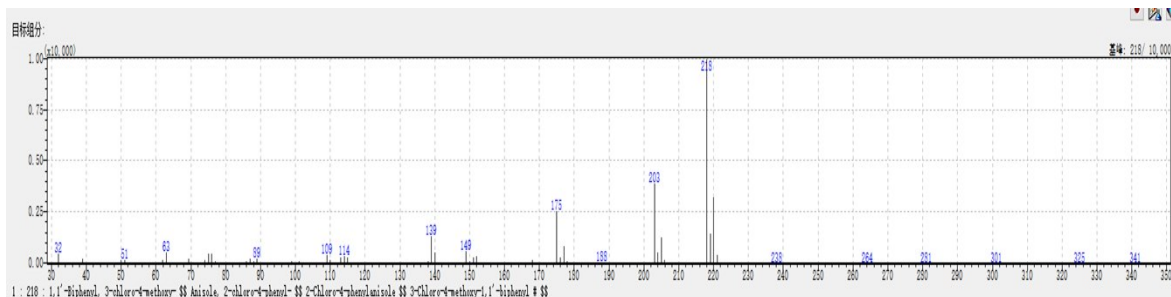
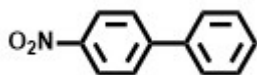


Figure S19. MS spectrum of 1-chloro-3-(4-methoxyphenyl)benzene.

3.13



4-nitrobiphenyl (3o): MS calculated for $C_{12}H_9NO_2$: 199, found 199.

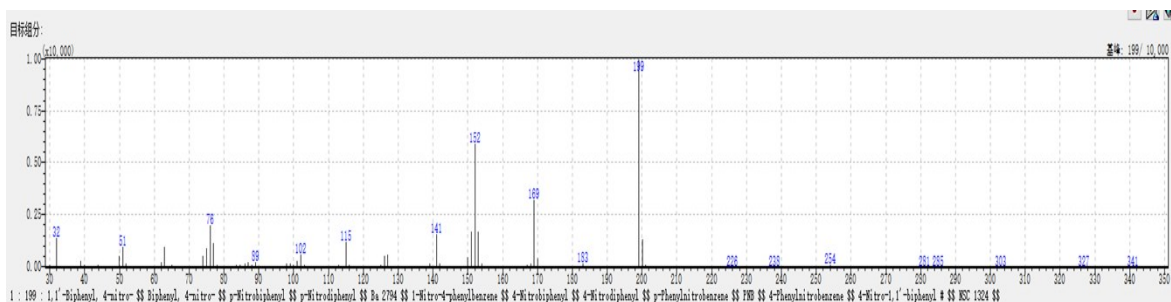
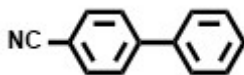


Figure S20. MS spectrum of 4-nitrobiphenyl.

3.14



4-Cyanobiphenyl (3p): MS calculated for $C_{13}H_9N$: 179, found 179.

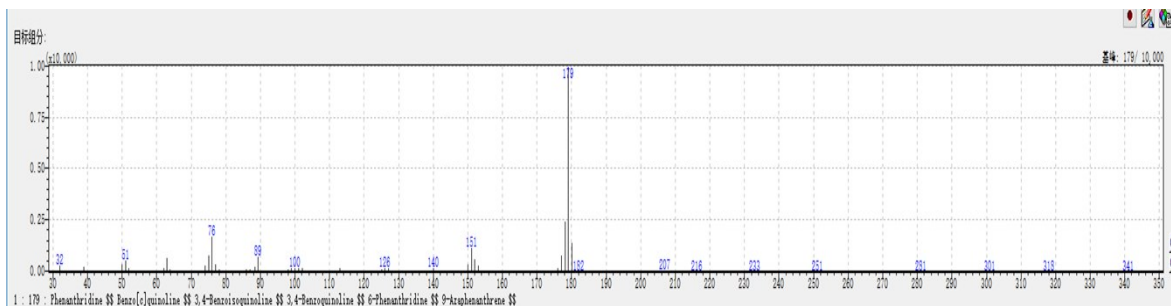
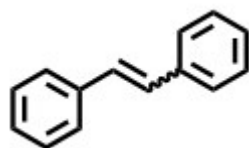


Figure S21. MS spectrum of 4-Cyanobiphenyl.

3.15



(7a)

Z:E=90:10

1,2-diphenylethene 7a, MS calculated for $C_{14}H_{12}$: 180, found:180. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.45-7.18 (m, 10H, Ph), 7.10 & 6.60 (s & s, 2H, -CH=CH-).

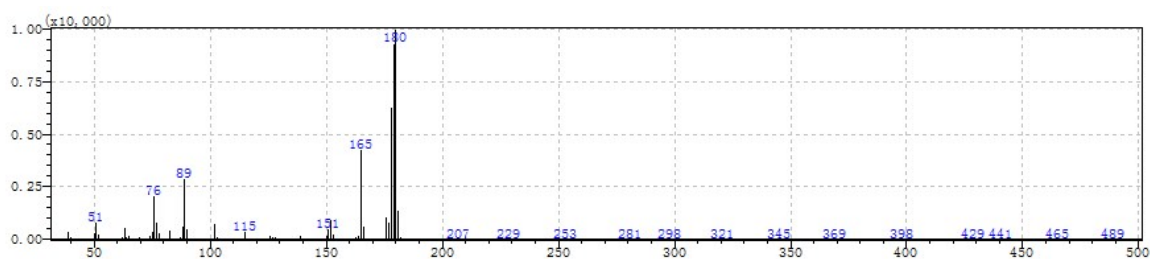
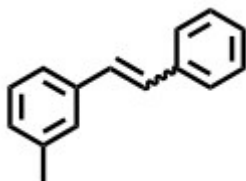


Figure S22. MS spectrum of 1,2-diphenylethene.

3.16



(7b)

Z:E=62:38

1-methyl-3-styrylbenzene 7b, MS calculated for $C_{15}H_{14}$: 194, found:194. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.41-7.20 (m, 5H, Ph), 7.15-7.05 (m, 4H, Ph), 6.96 & 6.50 (m & s, 2H, -CH=CH-), 2.31 (s, 3H, -CH₃).

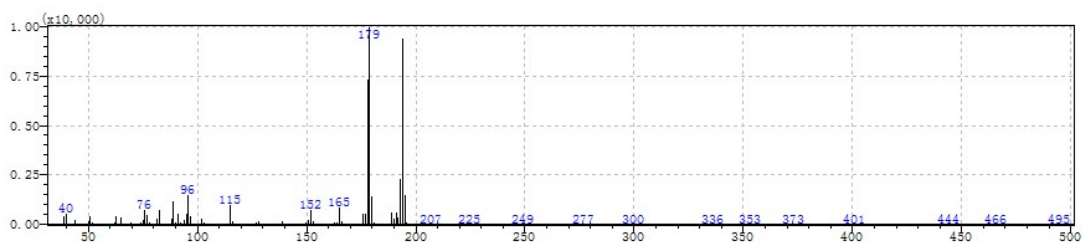
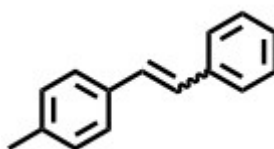


Figure S23. MS spectrum of 1-methyl-3-styrylbenzene.

3.17



(7c)

Z:E=95:5

1-methyl-4-styrylbenzene 7c, MS calculated for $C_{15}H_{14}$: 194, found:194. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.42-7.20 (m, 7H, Ph), 7.16-7.14 (m, 2H, Ph), 7.01 & 6.48 (d & s, $J = 3.0$ Hz, 2H, $-CH=CH-$), 2.30 (s, 3H, $-CH_3$).

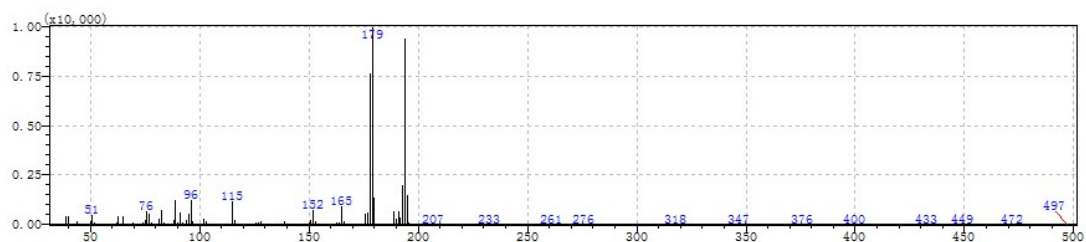
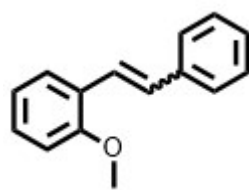


Figure S24. MS spectrum of 1-methyl-4-styrylbenzene.

3.18



Z:E=84:16

1-methoxy-2-styrylbenzene 7d, MS calculated for $C_{15}H_{14}O$: 210, found:210. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.54-7.10 (m, 9H, Ph), 7.0 & 6.69 (m & m, 2H, $-CH_2=CH_2-$), 3.89 (s, 3H, $-OCH_3$).

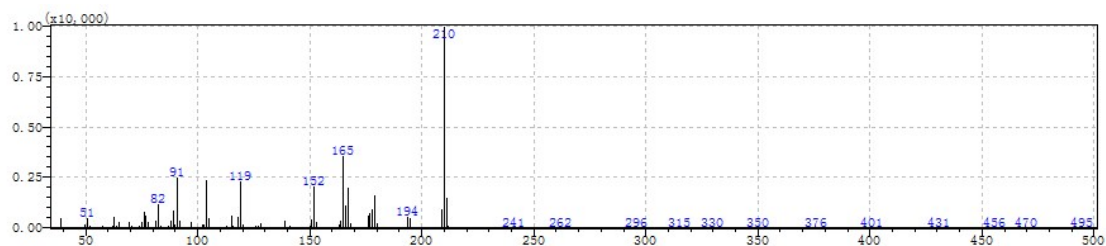
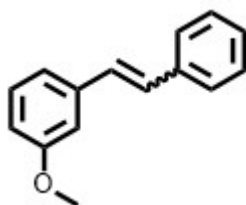


Figure S25. MS spectrum of 1-methoxy-2-styrylbenzene.

3.19



Z:E=86:14

1-methoxy-3-styrylbenzene 7e, MS calculated for $C_{15}H_{14}O$: 210, found:210. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.38-7.27 (m, 5H, Ph), 7.10-7.05 (m, 4H, Ph), 6.83 & 6.74 (d & d, $J = 7.2$ Hz, 8.2 Hz, 2H, $-CH=CH-$), 3.85 (s, 3H, $-OCH_3$).

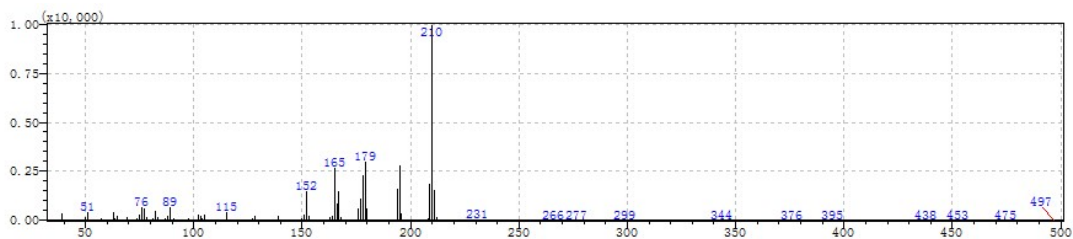
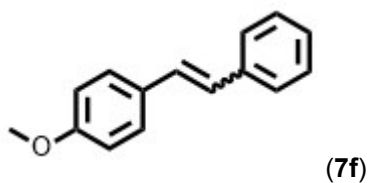


Figure S26. MS spectrum of 1-methoxy-3-styrylbenzene.

3.20



Z:E=96:4

1-methoxy-4-styrylbenzene 7f, MS calculated for $C_{15}H_{14}O$: 210, found: 210. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.45- 6.99 (m, 9H, Ph), 6.83 & 6.67 (d & d, $J=10.9$ Hz, 11.0 Hz, 2H, $-CH=CH-$), 3.75 (s, 3H, $-OCH_3$).

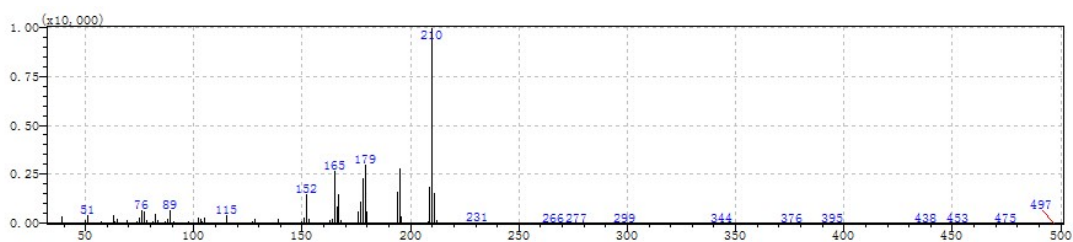
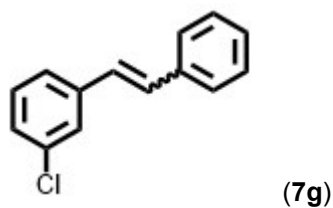


Figure S27. MS spectrum of 1-methoxy-4-styrylbenzene.

3.21



Z:E=94:6

1-chloro-3-styrylbenzene 7g, MS calculated for $C_{15}H_{14}O$: 214, found: 214. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.48-7.11 (m, 9H), 7.10 & 6.65 (d & d, $J = 4.9$ Hz, 12.2 Hz, 2H, $-CH=CH-$).

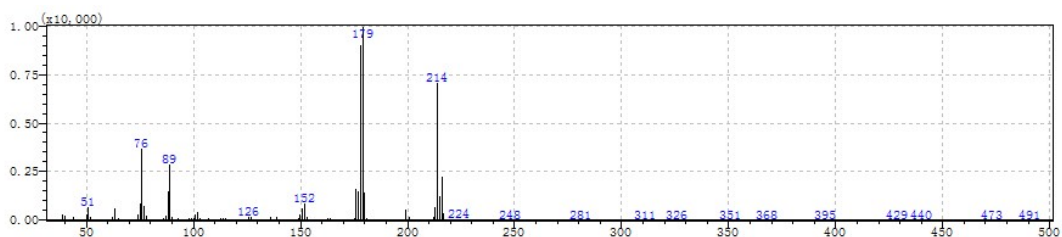
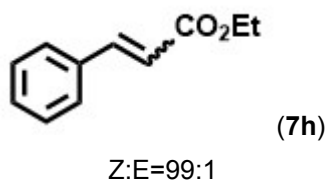


Figure S28. MS spectrum of 1-chloro-3-styrylbenzene

3.22



Ethyl cinnamate 7h, MS calculated for $C_{11}H_{12}O_2$: 176, found: 176. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.66-7.36 (m, 5H, Ph), 7.03 & 6.01 (d & d, $J=15.9$ Hz, 13.2 Hz, 2H, $-CH=CH-$), 4.27-4.15 (dd, $J=7.0$ Hz, 7.2 Hz, 2H, $-CH_2-$), 1.35-1.18 (m, 3H, CH_3).

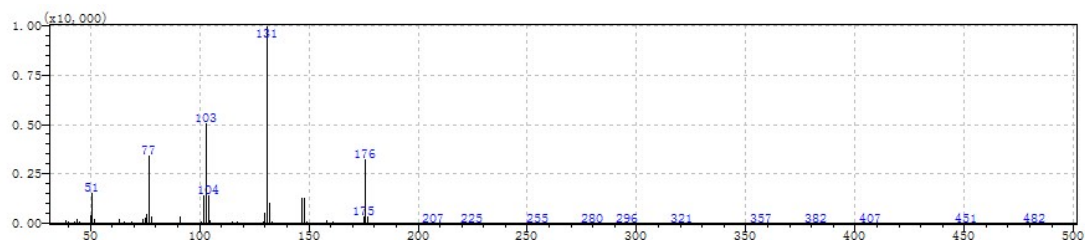
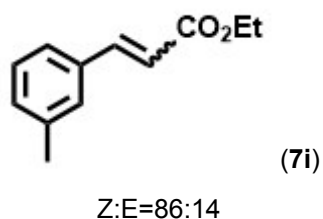


Figure S29. MS spectrum of ethyl cinnamate

3.23



ethyl 3-(3-methylphenyl)prop-2-enoate 7i, MS calculated for $C_{12}H_{14}O_2$: 190, found: 190. Z:E was analyzed with GC and 1H NMR. 1H NMR (500 MHz, $CDCl_3$): δ 7.66-7.15 (m, 4H, Ph), 6.32 & 5.83 (d & d, $J=15.9$ Hz, $J=12.7$ Hz, 2H, $-CH=CH-$), 4.23-4.10 (m, 2H, $-CH_2-$), 2.37-2.20 (m, 3H, $-CH_3$), 1.33-1.15 (m, 3H, $-CH_3$).

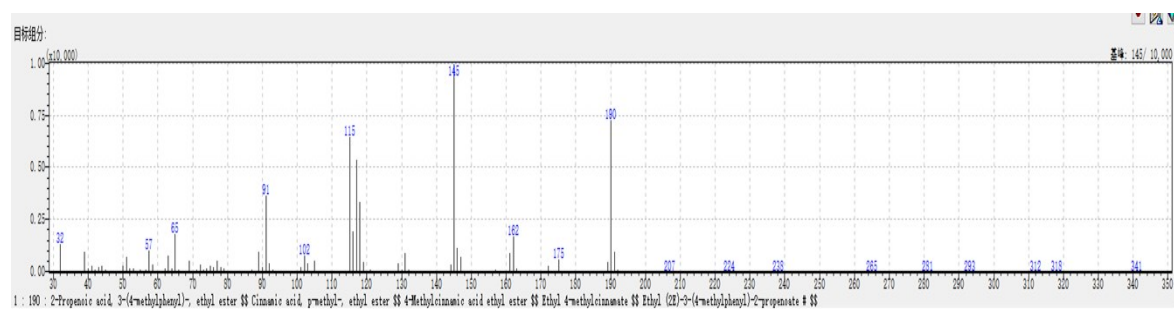


Figure S30. MS spectrum of ethyl 3-(3-methylphenyl)prop-2-enoate

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- S2 Q. Xiao, Z. Liu, A. Bo, S. Zavahir, S. Sarina, S. Bottle, J. D. Riches and H. Zhu, *J. Am. Chem. Soc.*, 2015, **5**, 1956-1966.

- S3 N. Marina, A. E. Lanterna and J. C. Scaiano, Expanding the color space in the two-color heterogeneous photocatalysis of Ullmann C-C coupling reactions, *ACS Catal.*, 2018, **8**, 7593-7597.
- S4 S. J. Freakley, N. Agarwal, R. U. McVicker, S. Althahban, R. J. Lewis, D. J. Morgan, N. Dimitratos, C. J. Kielybc and G. J. Hutchings, *Catal. Sci. Technol.*, 2020, **10**, 5935–5944.