Electronic Supplementary Information

Luminescent Tungsten(VI) Complexes as Photocatalysts for Light-Driven C-C and C-B Bond Formation Reactions

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General information.

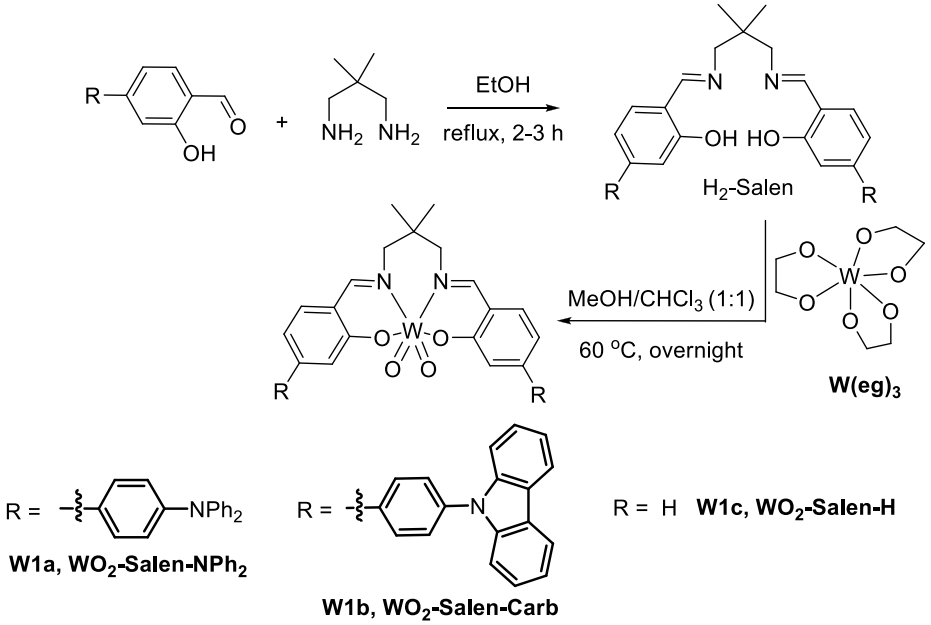
All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. All solvents for reactions and measurement were purified by standard method. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded respectively on 500 MHz, 400 MHz, 376 MHz and 101 MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{1}H NMR spectroscopy. Flash column chromatography was carried out using 300-400 mesh silica-gel at medium pressure.

High resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA). Elemental analyses were performed at the Institute of Chemistry of the Chinese Academy of Sciences, Beijing. Gas chromatography-mass spectrometry (GC-MS) analyses were performed with an Agilent Technologies 7890A Network GC System equipped with an Agilent Technologies 5975C Network Mass Selective Detector (MSD).

All absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Steady-state emission spectra were recorded on a Horiba Fluorolog-3 spectrophotometer. Solutions for photophysical studies were degassed by using a high vacuum line in a two-compartment cell with five freeze-pump-thaw cycles. The emission quantum yield was measured with [Ru(2,2'-bipyridine)$_3$](PF_6)$_2$ in degassed CH_3CN as the standard (Φ = 0.062) and calculated by: $\Phi_s = \Phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r)$, in which the subscripts s and r refer to sample and reference standard solution, respectively, n is the refractive index of the solvents, D is the integrated emission intensity and Φ is the luminescence quantum yield. The excitation intensity B is calculated by: $B = 1–10^{-AL}$, where A is the absorbance at the excitation wavelength and L is the optical path length (λ = 1 cm in all cases). The refractive indices of the solvents at room temperature were taken from standard sources. The emission lifetime measurements were performed on a Quanta Ray GCR 150-10 pulsed Nd:YAG laser system. Errors for λ values (±1 nm), τ (±10 %), and Φ (± 10 %) are estimated. Singlet oxygen quantum yield was determined with *meso*-tetraphenylporphyrin (H_2TPP) as a reference (Φ_{O_2} = 0.55 in aerated chloroform). Nanosecond time-resolved emission measurements were performed on a LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd., Livingston, UK). The excitation source was the 355 nm output (third harmonic) of a Nd:YAG laser (Spectra-Physics Quanta-Ray Lab-130 Pulsed Nd:YAG Laser). The signals were processed by a PC plug-in controller with L900 software. The preparation of samples for the measurements was the same as those for steady-state emission

measurements. Femtosecond time-resolved transient absorption (fs-TA) measurements were performed on a HELIOS setup equipped with a femtosecond regenerative amplified Ti:sapphire laser system (Spitfire Pro) in which the amplifier was seeded with the 120 fs laser pulses from an oscillator laser system (1k Hz). The laser probe pulse was produced by utilizing about 100 mW of the amplified 800 nm laser pulses to generate a white-light continuum (430-750 nm) in a sapphire crystal and then this probe beam was split into two 4 parts before traversing the sample. One part of the probe laser beam goes through the sample while the other part of the probe laser beam goes to the reference spectrometer. For the present experiments, sample solutions were excited by a 400 nm or 266 nm pump beam in a 2 mm path-length cuvette. The maximum time window is 3300 ps. Signals for each measurement were averaged for 1 s. Femtosecond time-resolved emission (fs-TRE) measurements were performed on the same setup as fs-TA. The output 800 nm laser pulse (200 mW) is used as gate pulse while the 400 nm laser pulse (10 mW) S4 (second harmonic) is used as the pump laser. After excitation by the pump laser, the sample fluorescence is focused into the nonlinear crystal (BBO) mixing with the gate pulse to generate the sum frequency signal. Broadband fluorescence spectra were obtained by changing the crystal angles and the spectra were detected by the aircooled CCD.Cyclic voltammetry was conducted on a Princeton Applied Research PMC-1000 Potentiostat. The working electrode was glassy carbon; the reference electrode was SCE; the counter electrode was a platinum wire. Scan rate: 100 mV/s. All potentials were reported versus SCE (+0.241 V vs. NHE).

Experimental Procedures



Procedure for synthesis of Schiff base ligand

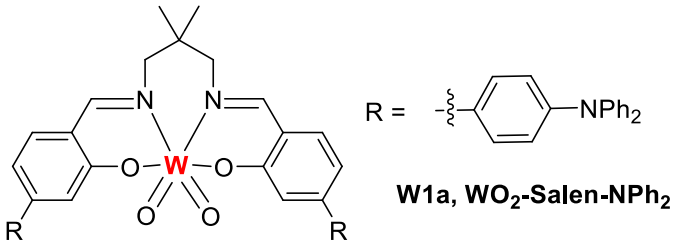
Synthesis of Salen-NPh$_2$: To a solution of 4'-(diphenylamino)-3-hydroxy-[1,1'-biphenyl]-4-carbaldehyde (2.2 g, 6.0 mmol) dissolved in 40 mL ethanol, 2,2-dimethylpropane-1,3-diamine (306 mg, 3.0 mmol) in 1 mL ethanol was added dropwise. The solution was heated to reflux for 2 h, after which the solution was cooled to room temperature. The yellow solid precipitated in the reaction mixture was filtered, washed with hexane, and used without further purification. Yield: 2.34 g (98 %, yellow crystalline solid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.71 (s, 2 H), 8.38 (s, 2 H), 7.53 (d, J = 8.6 Hz, 4 H), 7.33 (d, J = 2.7 Hz, 2 H), 7.35 – 7.30 (m, 8 H), 7.21 (d, J = 1.7 Hz, 2 H), 7.17 (d, J = 7.3 Hz, 10 H), 7.15 – 7.11 (m, 4 H), 7.07 (t, J = 7.3 Hz, 4 H), 3.54 (s, 4H), 1.13 (s, 6 H).

Synthesis of Salen-Carb: The procedure was similar to that of **Salen-NPh$_2$** except that 4'-(9*H*-carbazol-9-yl)-3-hydroxy-[1,1'-biphenyl]-4-carbaldehyde (110 mg, 0.30 mmol) was used as the aldehyde. Yield: 0.36 g (90 %, yellow solid). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 13.80 (s, 2 H), 8.47 (s, 2 H), 8.18 (dd, J = 7.8, 1.0 Hz, 4 H), 7.89 (d, J = 8.5 Hz, 4 H), 7.69 (d, J = 8.5 Hz, 4 H), 7.52 (d, J = 8.2 Hz, 4 H), 7.48 – 7.42 (m, 6 H), 7.36 – 7.31 (m, 6 H), 7.28 – 7.25 (m, 2 H), 3.1 (s, 4 H), 1.18 (s, 6 H).

Synthesis of Salen-H: To a solution of salicylaldehyde (4.88 g, 40.0 mmol) dissolved in 50 mL ethanol, 2,2-dimethylpropane-1,3-diamine (2.04 g, 20.0 mmol) in 10 mL ethanol was added dropwise. The solution was heated to reflux 3 h, after which the solution was concentrated by rotary evaporation. The crude product was purified by chromatography

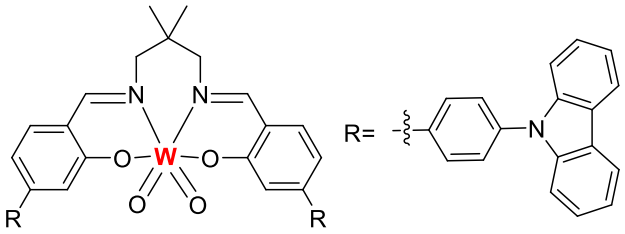
column using petroleum ether and ethyl acetate mixtures as eluting solvent. Yield: 5.04 g (81%, yellow solid). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.60 (s, 2 H), 8.36 (d, *J* = 1.3 Hz, 2 H), 7.35 (ddd, *J* = 8.4, 7.3, 1.7 Hz, 2H), 7.29 (dd, *J* = 7.6, 1.6 Hz, 2 H), 7.00 (dd, *J* = 8.3, 1.1 Hz, 2 H), 6.91 (td, *J* = 7.5, 1.1 Hz, 2 H), 3.52 (d, *J* = 1.3 Hz, 4 H), 1.11 (s, 6 H).

Procedure for synthesis of WO_2-Salen-NPh_2 complex



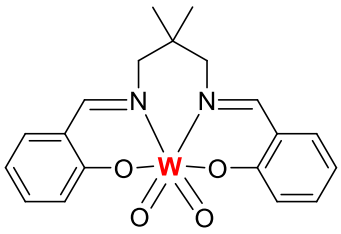
W1a, WO_2-Salen-NPh_2

Synthesis of **W1a**: A suspension of $W(eg)_3$ (0.77 g, 2.1 mmol) in 20 mL methanol, was heated to 60 ºC until all the $W(eg)_3$ dissolved completely. A $CHCl_3$ solution of the Schiff base ligand (1.7 g, 2.1 mmol) was added. The mixture turned orange and the yellow solid precipitated. The mixture was heated to 60 ºC overnight during which the whole mixture turned yellow. The reaction mixture was cooled to room temperature. The yellow solids were filtered, washed with methanol. The complex obtained was analytically pure and used without further purification. Yield: 1.9 g (89 % yellow solid). For characterization data, please refer to reference 1.



W1b, WO_2-Salen-Carb

The synthesis of **W1b** is similar to that of **W1a**, except that **Salen-Carb** was used as the ligand. Yield: 90 %, yellow solid. HR-MS (+ESI) *m/z*: 1007.2744 $[M+H]^+$ (calcd. 1007.2794). Selected IR (KBr, υ cm^{-1}): 933.55 (W=O), 896.90 (W=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (s, 1H, J_{H-W} = 11.0 Hz), 8.12–8.16 (m, 5H), 7.94 (d, 2H, *J* = 8.0 Hz), 7.77 (d, 2H, *J* = 8.5 Hz), 7.70 (d, 2H, *J* = 8.5 Hz), 7.60 (d, 2H, *J* = 8.5 Hz), 7.53–7.54 (m, 2H), 7.48 (t, 3H, *J* = 8.5 Hz), 7.37–7.44 (m, 7H), 7.27–7.31 (m, 4H), 7.09 (dd, 1H, *J* = 8.5 and 1.0 Hz), 7.01 (s, 1H), 4.96 (d, 1H, *J* = 11.0 Hz), 4.43 (d, 1H, *J* = 12.0 Hz), 3.81 (d, 1H, *J* = 11.0 Hz), 3.50 (d, 1H, *J* = 12.5 Hz), 1.22 (s, 3H), 0.86 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 168.5, 168.3, 163.6, 160.6, 150.1, 146.8, 140.7, 140.6, 138.8, 128.3, 138.1, 138.0(7), 134.0, 128.7, 128.6(6), 127.4, 127.2, 126.1, 126.0, 123.5, 123.4(9), 122.2, 121.6, 120.3, 120.2, 120.1, 119.7, 119.3, 118.8, 117.7, 109.8, 109.7(7), 73.2, 37.9, 26.1, 23.6. Elemental analysis (%) calcd. for $C_{55}H_{42}N_4O_4W \cdot CH_3OH$: C, 64.75; H, 4.46; N, 5.39; Found: C, 64.66; H, 4.20; N, 5.56.



W1c, WO_2-Salen-H

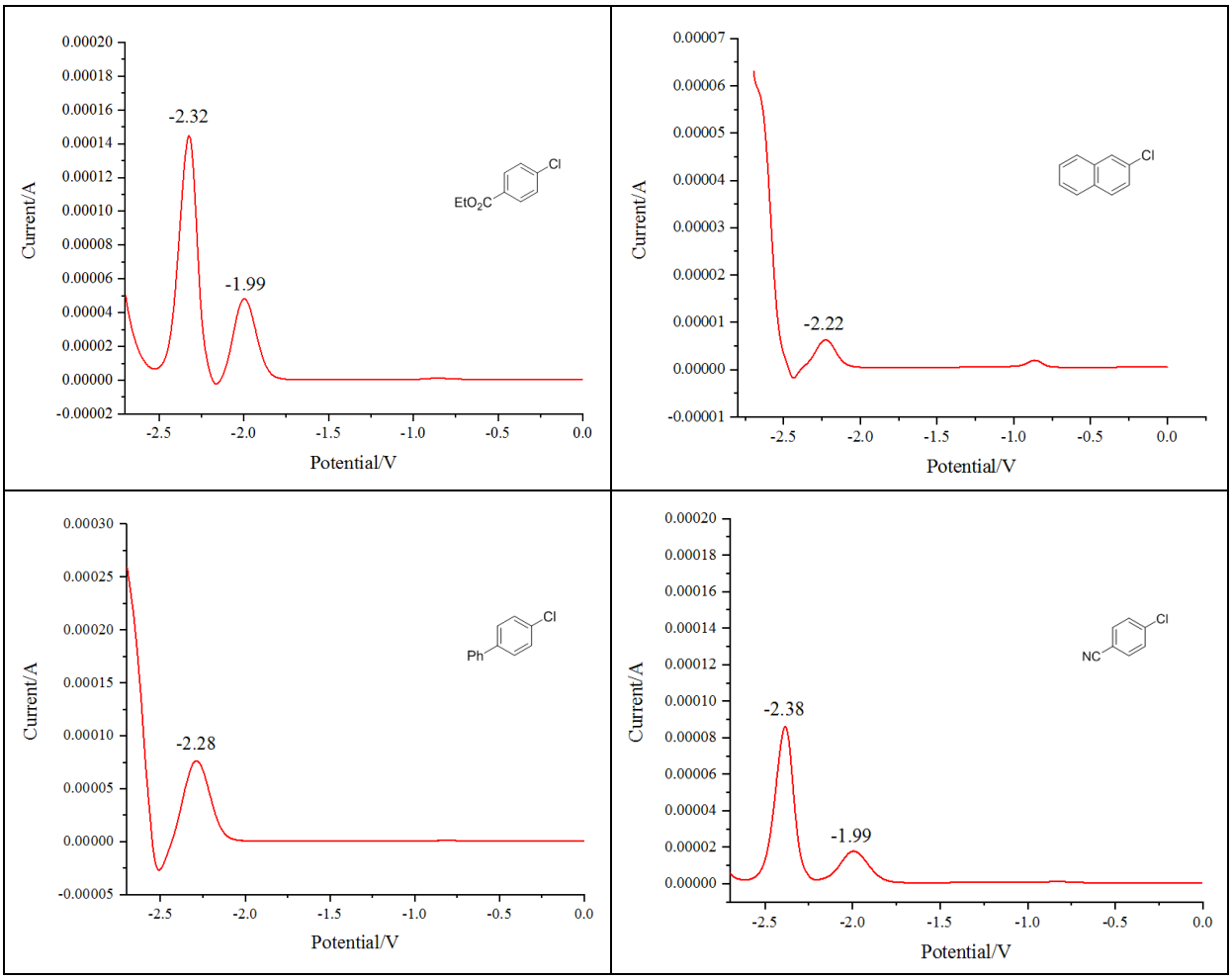
The synthesis of **W1c** is similar to that of **W1a**, except that **Salen-H** was used as the ligand. Yield: 68 %, yellow solid. For characterization data, please refer to reference 1.

Table S1. Photophysical data of complexes **W1a**–**W1c**[a]

Complex	Medium	λ_{abs} [nm] (ε [10^3 mol^{-1} dm^3 cm^{-1}])	λ_{em} [nm]	τ [μs]	k_r [10^3 s^{-1}]	Φ_{em}[b]
W1a	CH_2Cl_2[c]	297 (43.7), 407 (34.6)	608	4.6	23.9	0.11
	$CHCl_3$[c]	299 (45.2), 410 (36.7)	583	22.1	12.7	0.28
	THF[c]	292 (49.7), 392 (42.9)	572	117.8	2.3	0.27
	Toluene[c]	297 (sh, 55.2), 402 (40.8)	510, 552 (sh)	67.6	0.6	0.04
	EtOAc[c]	297 (sh, 56.3), 402 (41.9)	570	45.6	2.4	0.11
	MeCN	293 (44.2), 392 (37.0)	635	0.4	7.5	0.003
W1b	CH_2Cl_2	261 (57.1), 285 (45.9), 292 (49.8), 327 (30.4), 341 (31.9), 365 (sh, 25.0), 420 (sh, 10.6)	553	74.9	1.7	0.13
	$CHCl_3$	286 (50.1), 293 (54.2), 315 (29.7), 328 (31.7), 342 (32.7), 368 (25.9), 420 (11.4)	555	98.7	1.5	0.15
	THF	283 (49.8), 292 (55.2), 327 (35.6), 341 (39.2), 415 (10.2)	556	82.0	1.3	0.11
	Toluene	293 (64.0), 327 (32.5), 342 (34.2), 368 (28.1), 420 (11.3)	560	97.3	2.1	0.21
	EtOAc	283 (49.1), 291 (54.3), 326 (36.2), 340 (39.8), 415 (10.1)	556	99.0	1.3	0.13
	MeCN	283 (47.6), 291 (51.6), 326 (35.1), 340 (37.5), 415 (10.4)	560	11.8	1.3	0.020
W1c	CH_2Cl_2[c]	270 (26.2), 299 (18.2), 402 (5.5)	582	83.6	0.4	0.03
	$CHCl_3$[c]	270 (22.4), 398 (15.5), 405 (4.4)	578	37.4	1.2	0.046
	Toluene[c]	301 (11.1), 405 (3.8)	579	83.0	0.5	0.042
	MeCN	270 (20.6), 297 (14.4), 398 (4.6)	575	47.1	0.4	0.019

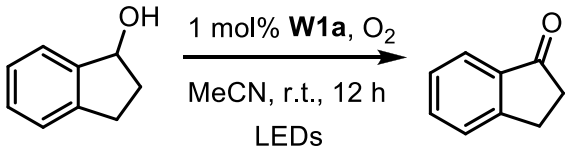
[a] Measurements were performed at 298 K unless specified. [b] All emission quantum yields (Φ) were estimated with $[Ru(2,2'\text{-bipyridine})_3](PF_6)_2$ in degassed CH_3CN as the standard (Φ = 0.062). [c] Value taken from reference 1.

Table S2. Differential pulse voltammograms of some aryl halides



Measured in DMF containing 0.1 M tetrabutylammonium hexafluorophosphate and under N_2. Potentials versus SCE.

Table S3: Photo-dehydrogenation reactions catalysed by **W1a**



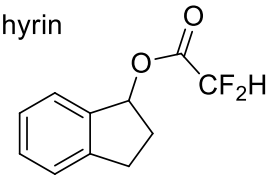
entry	catalyst(%)	additives	LEDs light	Solvent	yield (%)[a]
1	**W1a**	- - - - - -	450 nm	DMF	18%
2	**W1a**	- - - - - -	450 nm	MeCN	15%
3	**W1a**	- - - - - -	410 nm	MeCN	23%
4	**W1a**	- - - - - -	300 W Xe lamp	DMF	4%
5	**W1a**	- - - - - -	365 nm	MeCN	52%
6	**W1a**	HCF_2CO_2H	365 nm	MeCN	60%[b]
7	**W1a**	- - - - - -	365 nm	MeCN	0%[c]
8	**H_2TPP**[d]	- - - - - -	365 nm	MeCN	15%
9	- - - - - -	H_2O_2	365 nm	MeCN	45%

[a]yields were determined by ^{1}H NMR using 2,2-difluoroacetic acid or methyl 4-bromobenzoate as internal standard

[b]2,3-dihydro-1*H*-inden-1-yl 2,2-difluoroacetate **A** was obtained in 26% yield.

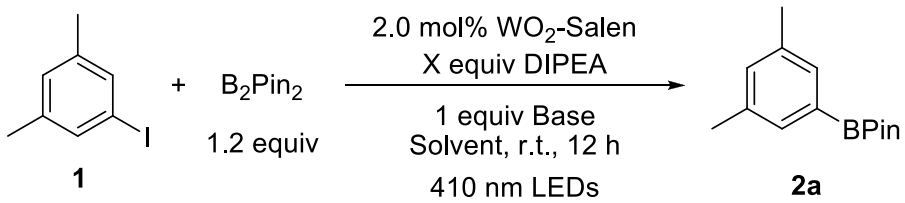
[c]under inert atomsphere without O_2

[d] H_2TPP stands for tetraphenylporphyrin



A

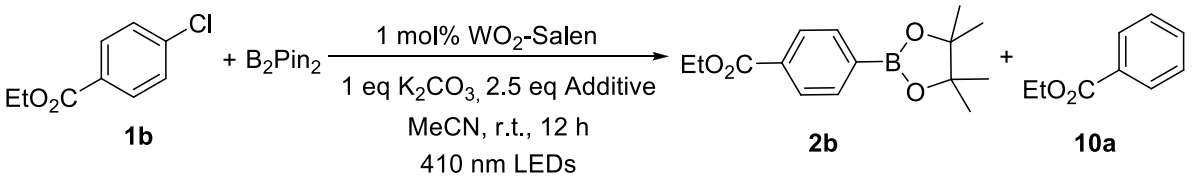
Table S4. Optimization of reaction conditions for borylation of aryl iodine



Entry	Catalyst	Base	solvent	DIPEA (equiv)	conversion (%)	Yield (%)[a]
1	**W1a**	^{t}BuONa	MeCN	2.5 eq	100%	31%
2	**W1a**	K_2CO_3	MeCN	2.5 eq	100%	52%
3	**W1a**	Cs_2CO_3	MeCN	2.5 eq	88%	40%
4	**W1a**	Na_2CO_3	MeCN	2.5 eq	78%	32%
5	**W1a**	$NaHCO_3$	MeCN	2.5 eq	--	31%
6	**W1a**	Na_2HPO_4	MeCN	2.5 eq	--	43%
7	**W1a**	NaOAc	MeCN	2.5 eq	60%	31%
8	**W1a**	KH_2PO_4	MeCN	2.5 eq	--	21%
9	**W1a**	K_2CO_3	MeCN	0.5 eq	52%	24%
10	**W1a**	K_2CO_3	MeCN	1 eq	87%	41%
11	**W1a**	K_2CO_3	MeCN	2 eq	100%	50%
12	**W1a**	K_2CO_3	MeCN	5 eq	100%	40%
13	**W1a**	----	MeCN	2.5 eq	0%	0%
14	**W1a**	K_2CO_3	MeCN	----	32%	12%
15	**W1a**	K_2CO_3	MeCN	DABCO	38%	30%
16	**W1a**	K_2CO_3	MeCN	DBU	100%	50%
17	**W1a**	K_2CO_3	MeCN	TEA	32%	32%
18	**W1a**	K_2CO_3	DCE	2.5 eq	0%	0%
19	**W1a**	K_2CO_3	acetone	2.5 eq	40%	20%
20	**W1a**	K_2CO_3	THF	2.5 eq	0%	0%
21	**W1a**	K_2CO_3	toluene	2.5 eq	0%	0%
22	**W1a**	K_2CO_3	ACN/H_2O	2.5 eq	100%	60%
23	**W1a**	K_2CO_3	MeCN[b]	2.5 eq	100%	50%
24	-------	K_2CO_3	MeCN	2.5 eq	0%	0%

[a]yields were determined by ^{1}H NMR using dibromomethane as internal stantard
[b]the solvent was anhydrous

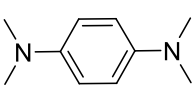
Table S5. Optimization of conditions for C-B bond formation from aryl chloride



1b **2b** **10a**

entry	catalyst	additive	conversion	yield (%)[a] 2b	10a
1	**W1a**	DIPEA	100%	53%	41%
2	**W1a**	TMBDA	70%	41%	20%
3	**W1a**	DM-DMF	100%	51%	45%
4	**W1a**	TMDMA	75%	53%	20%
5	**W1a**	TBBDMM	85%	50%	30%
6	**W1a**	dimethylaniline	100%	0%	79%
7	**W1a**	tetrahydrothiophene	90%	58%	26%
8	**W1a**	AllylPhS	75%	46%	25%
9	**W1a**	1 eq Me_2S	89%	64%	22%
10	**W1a**	p-toluenethiol	100%	33%	41%
11	**W1a**	L-Ascorbic acid	40%	26%	5%
12	**W1a**	1 eq KI	100%	53%	43%
13	**W1a**	1 eq KI/H_2O	10%	0%	8%
14	**W1a**	PPh_3	5%	0%	5%
15	**W1a**	1eq TBAB	100%	89%	9%
16	**W1a**	TBAB/KI	100%	90%	8%
17	- - - - - -	TBAB	25%	20%	0%
18[b]	**W1a**	TBAB	0%	0%	0%
19	**W1a**	- - - - -	100%	50%	10%
20	**W1c**	TBAB	20%	14%	0%
21	**W1b**	TBAB	36%	30%	3%
22[c]	- - - - - -	TBAB	100%	68%	10%

[a] Reaction conditions: **1b**(0.2 mmol), B_2Pin_2(0.22 mmol), WO_2-Salen (1 mol%), K_2CO_3 (0.2 mmol), in MeCN at room temperature for 12 h. yields were determined by ^1H NMR using dibromomethane as internal standard.[b]no light. [c] Reaction time = 48 hours.



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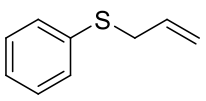
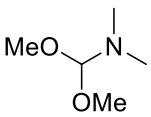


AllyPhS



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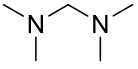

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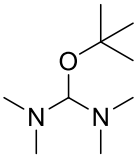

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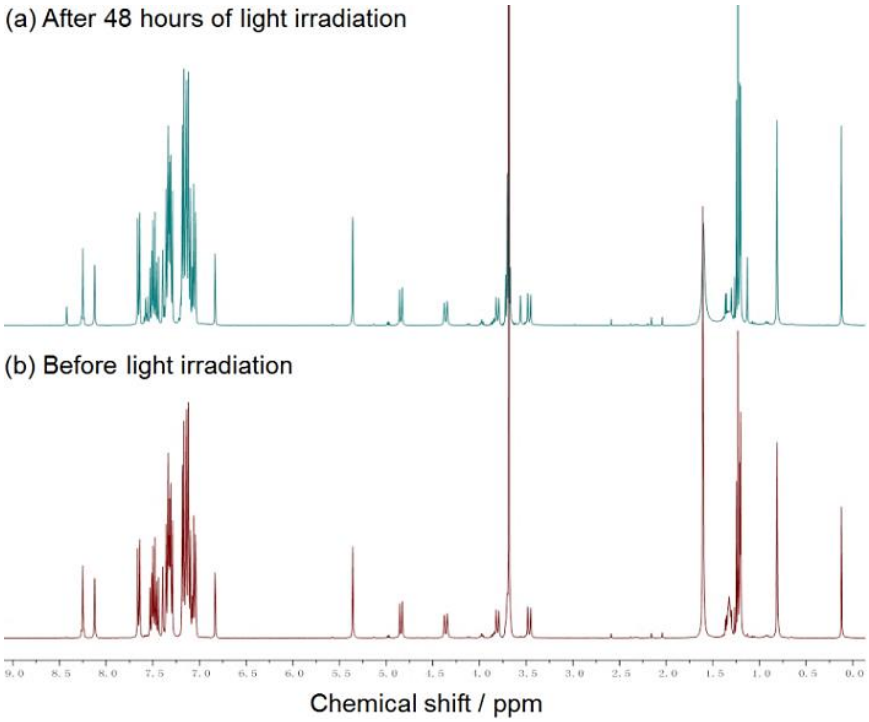


Figure S1. ^{1}H NMR spectral traces of **W1a** in degassed CD_2Cl_2 upon 450 nm LEDs irradiation.

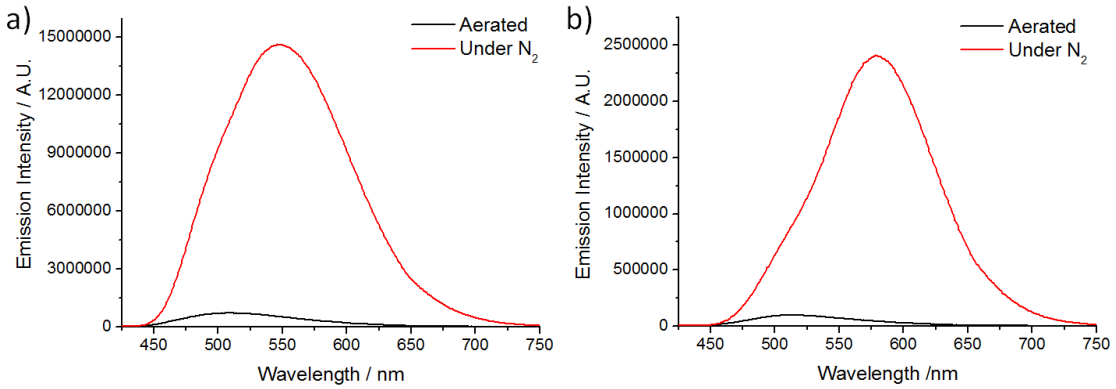


Figure S2. Emission spectra of a) **W1b** and b) **W1c** in CH_2Cl_2 under aerated condition and under N_2.

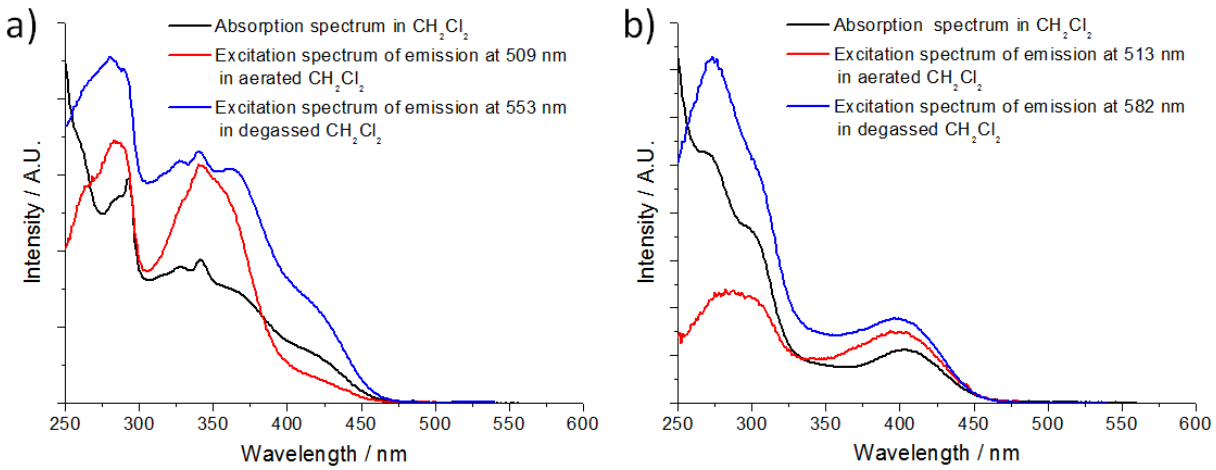


Figure S3. Excitation spectra of a) **W1b** and b) **W1c** in CH_2Cl_2 under aerated and degassed condition.

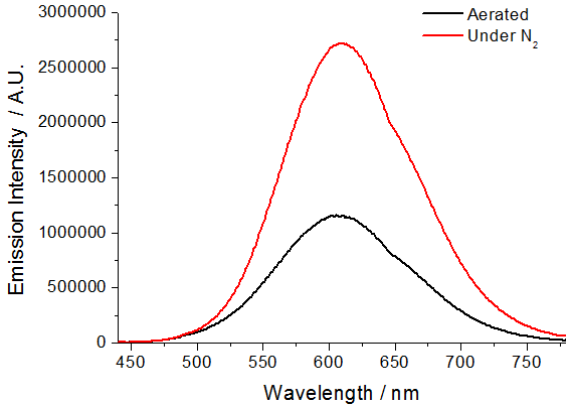


Figure S4. Emission spectra of **W1a** in CH_2Cl_2 under aerated condition and under N_2.

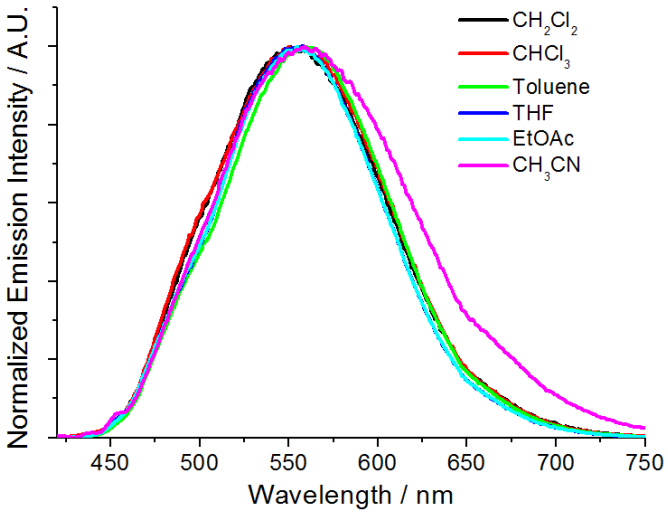


Figure S5. Emission spectra of **W1b** in different degassed solvents at room temperature.

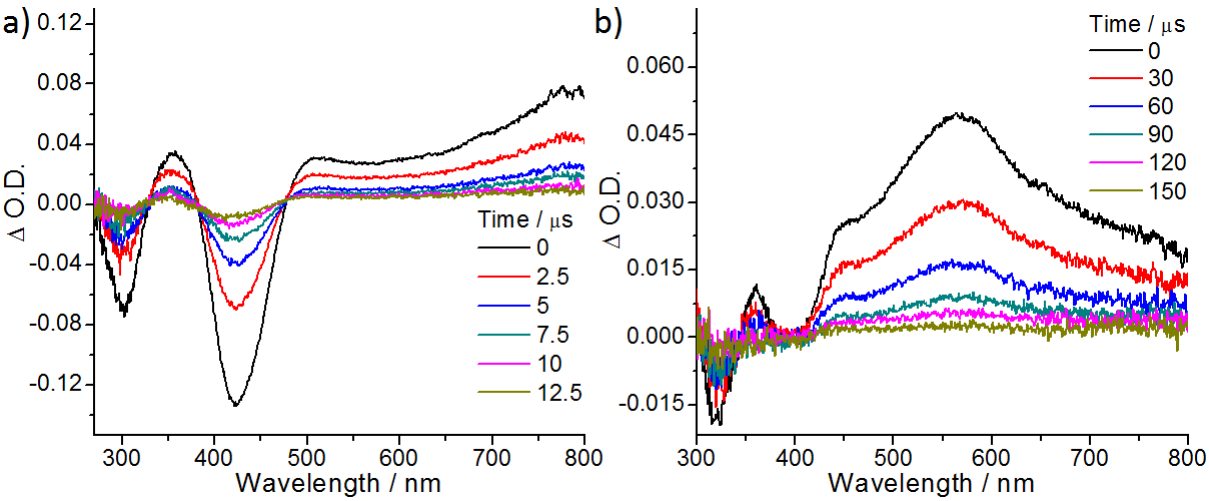


Figure S6. ns-TA spectra of **W1a** and **W1b** in CH_2Cl_2 at room temperature.

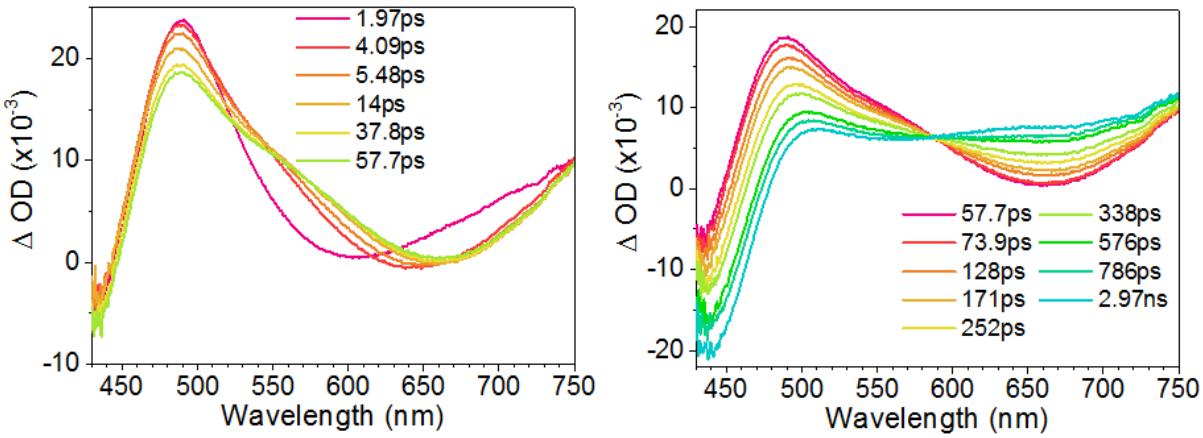


Figure S7. fs-TA spectra of **W1a** in CH_2Cl_2 at room temperature with 266 nm excitation.

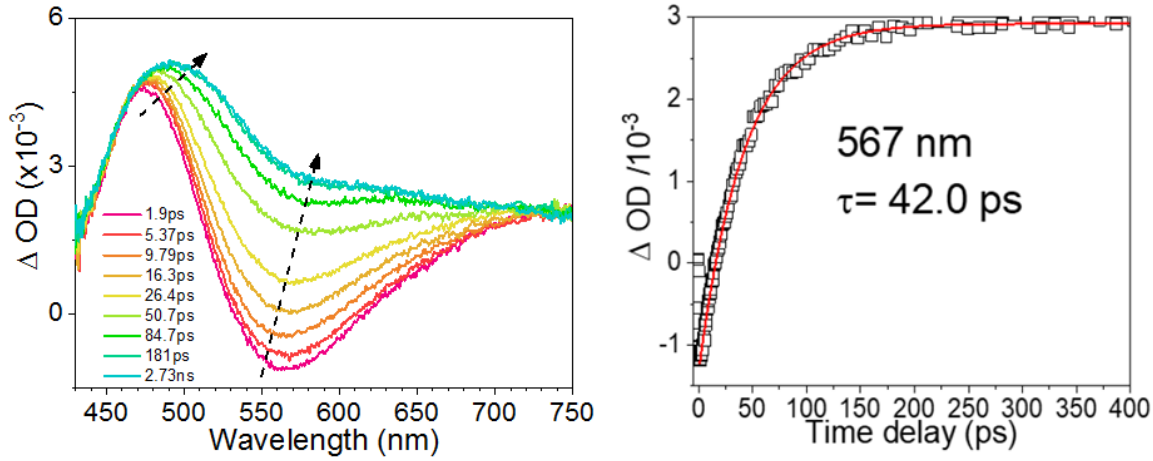


Figure S8. fs-TA spectra of **W1c** in CH_2Cl_2 at room temperature with 400 nm excitation.[1]

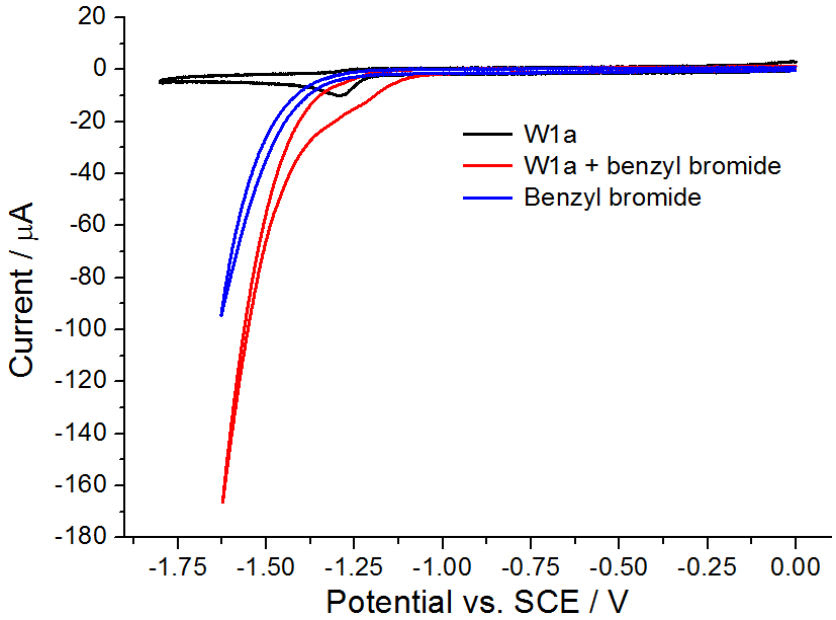


Figure S9. Cyclic voltammogram of **W1a**, a mixture of **W1a** and benzyl bromide (0.01 M), and benzyl bromide only (0.01 M) in DMF under N_2.

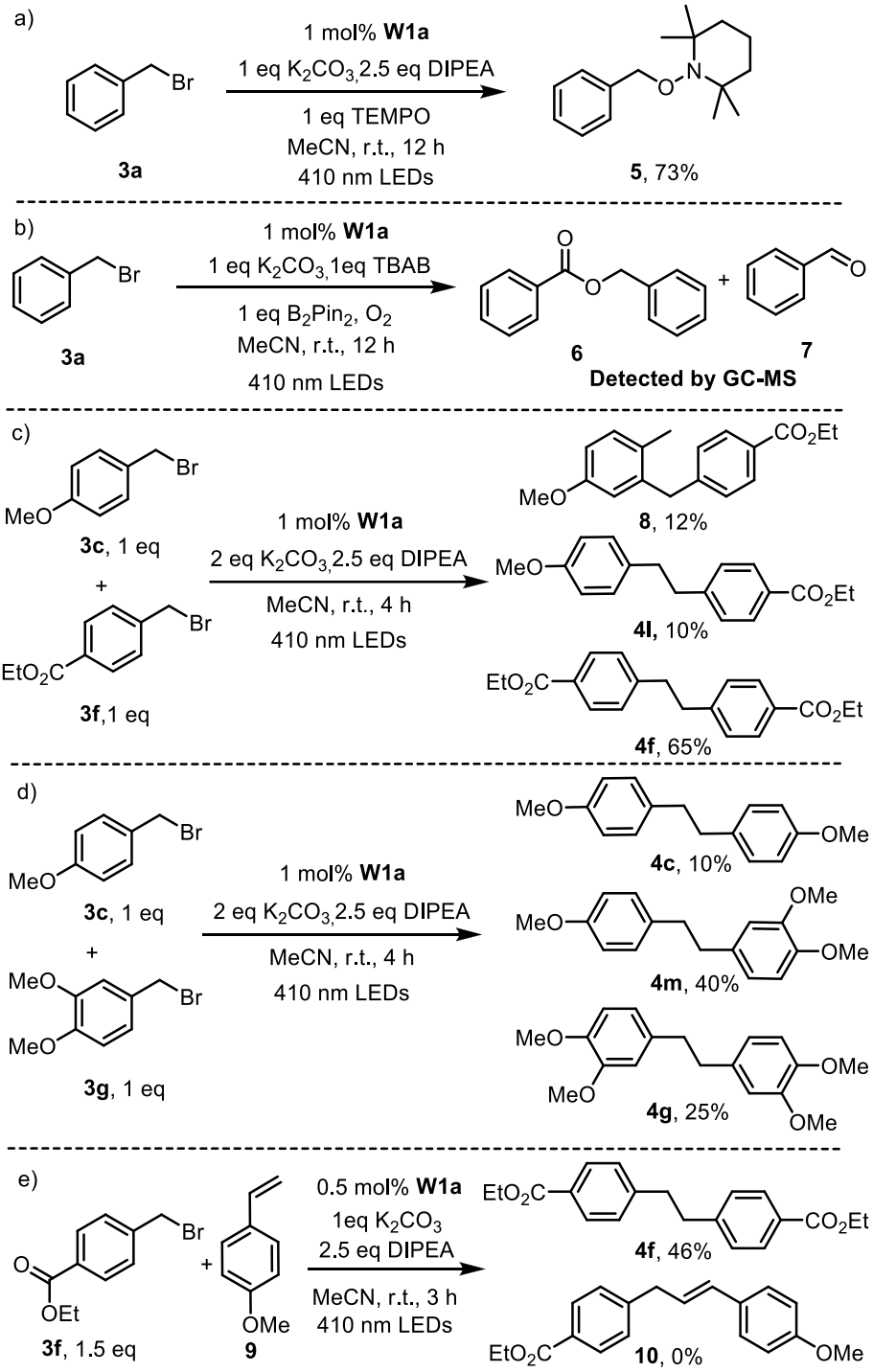


Figure S10. Mechanistic experiments.

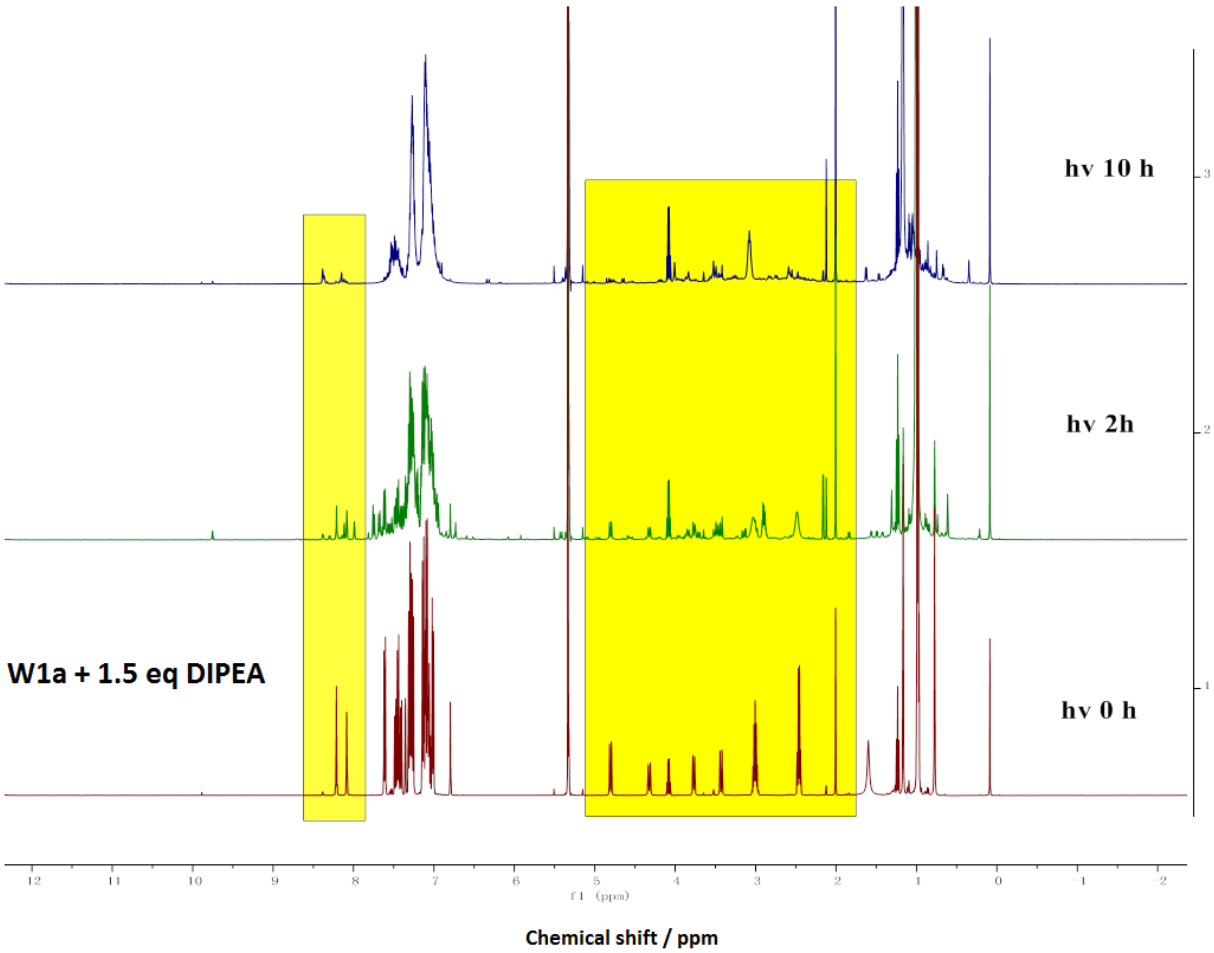


Figure S11. ^{1}H NMR spectral traces of **W1a** and 1.5 molar equivalent of DIPEA in degassed CD_2Cl_2 upon 410 nm LEDs irradiation for 2 and 10 hours.

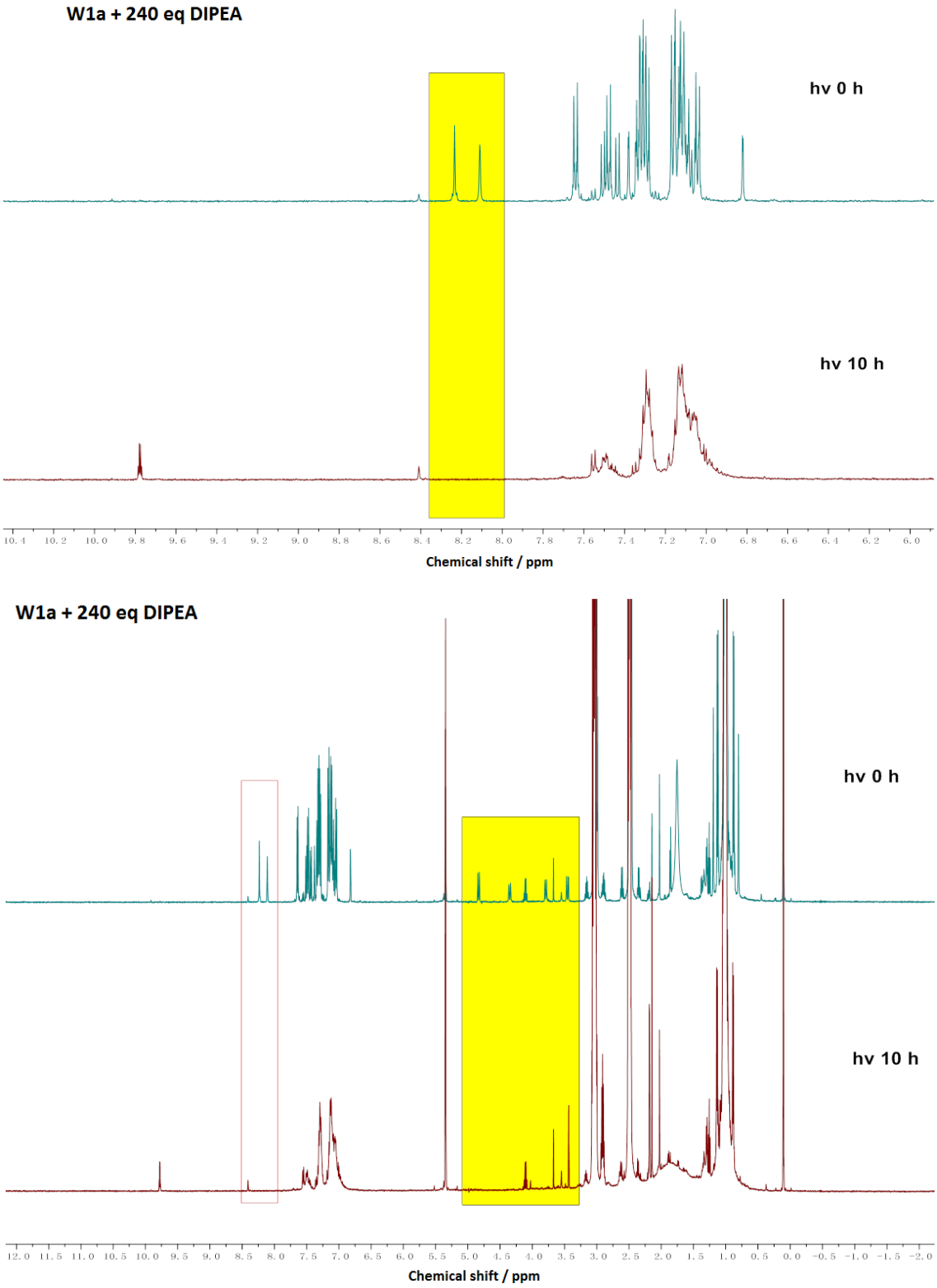


Figure S12. ^{1}H NMR spectral traces of **W1a** and 240 molar equivalent of DIPEA in degassed CD_2Cl_2 upon 410 nm LEDs irradiation for 10 hours. Upper: chemical shift range: 5.9 to 10.4 ppm. Lower: chemical shift range: -2 to 12 ppm.

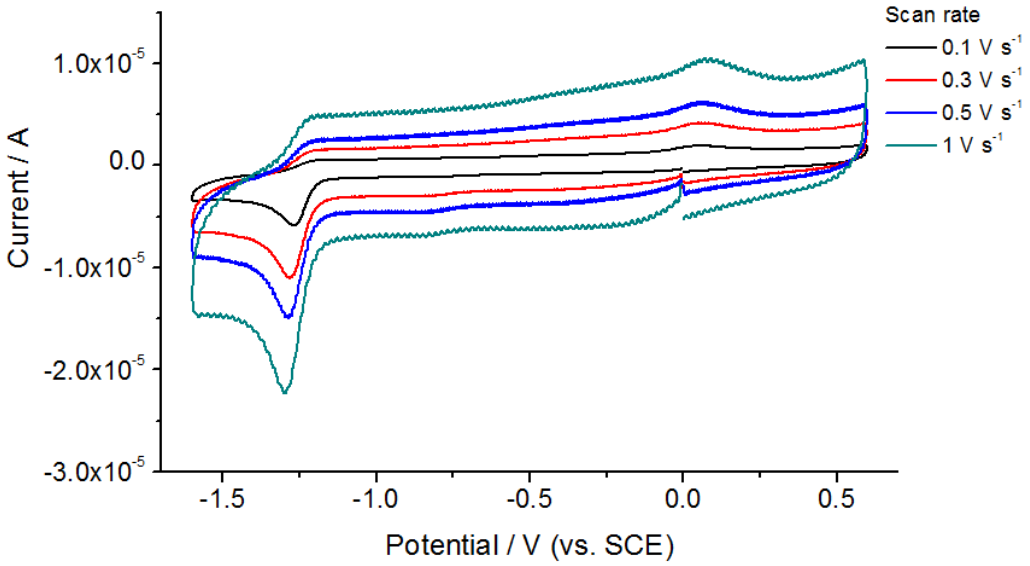


Figure S13. Cyclic voltammogram of **W1a** at difference scan speeds.

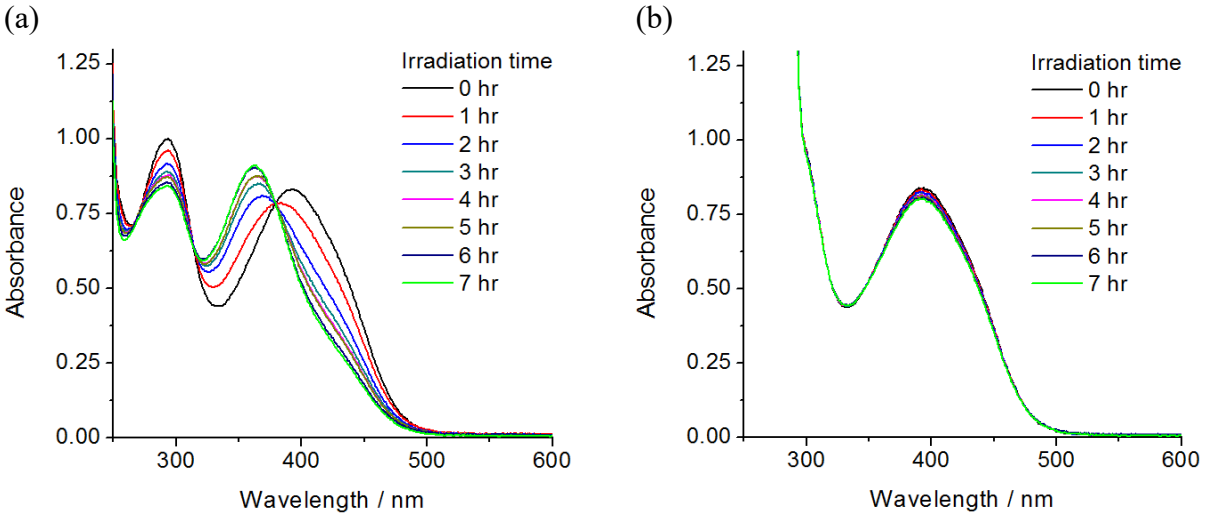
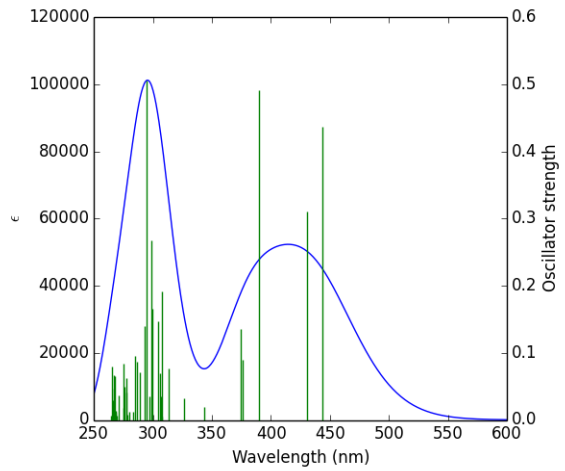


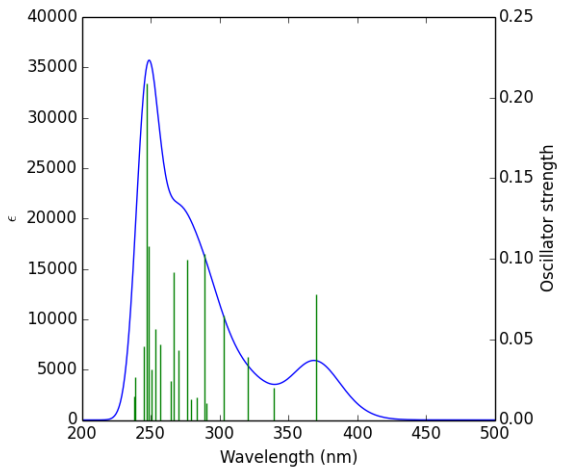
Figure S14. UV-vis absorption spectral change of mixtures of (a) **W1a** and TBAB (0.1 M) and (b) **W1a** and ethyl 4-chlorobenzoate (0.1 M) upon blue LED irradiation.

Computational details

In this work, the hybrid density functional, M06,[2] was employed for all calculations using the program package G09.[3] The 6-31G* basis set[4] is used for all atoms except W, which is described by the Stuttgart relativistic pseudopotential and its accompanying basis set (ECP60MWB).[5] Solvent effect was also included by means of the polarizable continuum model (PCM)[6] and default parameters are used for the solvent, toluene (refractive index η = 1.4969). No symmetry constraints were applied in geometry optimizations. For the singlet ground state (S_0), the restricted density functional theory (RDFT) formalism was employed. Frequency calculations were performed on the optimized structures to ensure that they are minimum energy structures by the absence of imaginary frequency (i.e. NImag = 0). Stability calculations were also performed for all the optimized structures to ensure that all the wavefunctions obtained are stable. The absorption energies were computed using TDDFT within the Tamm-Dancoff approximation (TDA)[7] to avoid the triplet instability problems.[8] The simulated absorption spectra were created using the software, gausssum 3.0.[9] CCD maps, NTOs, orbital overlap, the transition dipole moment density (TDMD), and fragment TDM were computed using the program Multiwfn.[10] Details about these calculations could be found in the Multiwfn manual (version 3.6).



W1a



W1c

Figure S15. Simulated absorption spectra of **W1a** and **W1c** at their respective optimized S_0 geometry.

Table S6. $S_0 \rightarrow S_n$ Absorption energies of complex **W1a** at the optimized S_0 geometry in toluene solution.

n	λ (nm)	*f*	Major contribs
1	**443**	**0.4363**	**H-1->LUMO (86%)**
2	**430**	**0.3101**	**H-1->LUMO (10%), HOMO->LUMO (86%)**
3	**390**	**0.4909**	**HOMO->L+1 (92%)**
4	**376**	**0.0899**	**H-1->L+1 (95%)**
5	**374**	**0.1351**	**H-2->LUMO (90%)**
6	**344**	**0.0187**	**H-3->LUMO (86%)**
7	**326**	**0.0317**	**H-2->L+1 (92%)**
8	**313**	**0.0763**	**H-3->L+1 (35%), HOMO->L+2 (43%)**
9	**308**	**0.0054**	**H-3->L+1 (34%), HOMO->L+2 (38%)**
10	**308**	**0.1921**	**H-4->LUMO (19%), H-1->L+2 (47%), H-1->L+5 (12%)**
11	**306**	**0.0349**	**HOMO->L+6 (59%), HOMO->L+7 (20%)**
12	**306**	**0.0699**	**H-1->L+5 (60%), H-1->L+7 (11%)**
13	**305**	**0.1464**	**H-4->LUMO (54%), H-1->L+2 (27%)**
14	**299**	**0.1651**	**H-1->L+3 (55%)**
15	**298**	**0.2676**	**H-5->LUMO (45%), HOMO->L+3 (16%)**
16	**297**	**0.0348**	**H-5->LUMO (25%), HOMO->L+3 (52%)**
17	**295**	**0.5056**	**H-1->L+9 (63%), HOMO->L+10 (19%)**
18	**293**	**0.1405**	**H-1->L+9 (21%), HOMO->L+10 (53%)**
19	**289**	**0.0706**	**H-2->L+2 (76%)**
20	**286**	**0.0864**	**HOMO->L+3 (14%), HOMO->L+6 (10%), HOMO->L+7 (15%), HOMO->L+10 (14%)**
21	**285**	**0.095**	**H-14->LUMO (14%), H-1->L+3 (15%), H-1->L+8 (17%)**
22	**283**	**0.0115**	**H-16->LUMO (13%), H-15->LUMO (15%), H-14->LUMO (10%), H-1->L+8 (12%)**
23	**280**	**0.0129**	**H-11->LUMO (15%), H-9->LUMO (20%), H-7->LUMO (28%)**
24	**278**	**0.0085**	**HOMO->L+4 (77%)**
25	**278**	**0.0618**	**H-5->L+1 (29%), H-2->L+3 (25%)**
26	**278**	**0.0414**	**H-5->L+1 (22%), H-2->L+3 (16%), H-1->L+4 (10%)**
27	**276**	**0.0498**	**H-17->LUMO (14%), H-15->LUMO (12%), H-1->L+4 (21%)**
28	**275**	**0.018**	**HOMO->L+13 (32%)**
29	**275**	**0.0843**	**H-2->L+3 (22%), H-1->L+4 (38%), H-1->L+8 (11%)**
30	**271**	**0.0365**	**H-4->L+1 (53%)**
31	**269**	**0.0059**	**HOMO->L+5 (81%)**
32	**269**	**0.013**	**H-9->LUMO (13%), H-7->LUMO (18%), H-4->L+1 (11%)**
33	**268**	**0.0108**	**H-8->LUMO (35%), H-6->LUMO (14%), HOMO->L+13 (12%)**
34	**268**	**0.0649**	**H-3->L+2 (29%)**
35	**268**	**0.0023**	**H-1->L+6 (66%), H-1->L+7 (27%)**

36	**267**	**0.0463**	**H-6->LUMO (23%), H-1->L+7 (11%), HOMO->L+16 (14%)**
37	**267**	**0.0664**	**H-6->LUMO (14%), H-3->L+2 (12%), H-1->L+12 (11%)**
38	**266**	**0.0287**	**H-9->LUMO (11%), H-1->L+7 (16%)**
39	**265**	**0.0791**	**H-8->LUMO (19%), H-3->L+2 (13%), HOMO->L+8 (20%), HOMO->L+9 (10%)**
40	**265**	**0.006**	**H-8->LUMO (12%), H-1->L+14 (10%), HOMO->L+16 (28%)**

Table S7. $S_0 \rightarrow S_n$ Absorption energies of complex **W1c** at the optimized S_0 geometry in toluene solution.

n	λ / nm	*f*	Major contributions
1	**370**	**0.078**	**HOMO->LUMO (93%)**
2	**339**	**0.0201**	**H-1->LUMO (89%)**
3	**320**	**0.039**	**HOMO->L+1 (92%)**
4	**303**	**0.0646**	**H-1->L+1 (87%)**
5	**291**	**0.0106**	**HOMO->L+2 (82%)**
6	**289**	**0.1031**	**H-5->LUMO (14%), H-3->LUMO (63%)**
7	**283**	**0.0139**	**H-4->LUMO (40%), H-2->LUMO (27%)**
8	**279**	**0.0127**	**HOMO->L+3 (74%)**
9	**276**	**0.0992**	**H-4->LUMO (34%), H-2->LUMO (43%)**
10	**270**	**0.0432**	**H-2->LUMO (10%), H-2->L+1 (10%), H-1->L+2 (54%)**
11	**267**	**0.0919**	**H-5->LUMO (39%), H-3->LUMO (13%), H-1->L+3 (21%)**
12	**265**	**0.024**	**H-5->LUMO (11%), H-1->L+3 (58%)**
13	**257**	**0.0468**	**H-6->LUMO (10%), H-4->L+1 (16%), H-4->L+2 (20%), H-1->L+2 (10%)**
14	**253**	**0.0567**	**H-4->L+2 (17%), H-3->L+1 (10%), H-2->L+1 (25%)**
15	**250**	**0.0316**	**H-3->L+1 (23%), HOMO->L+4 (39%), HOMO->L+5 (17%)**
16	**248**	**0.1077**	**H-6->LUMO (12%), H-3->L+1 (37%), HOMO->L+4 (25%)**
17	**247**	**0.209**	**H-2->L+1 (26%), H-1->L+5 (13%)**
18	**245**	**0.0456**	**HOMO->L+4 (15%), HOMO->L+5 (70%)**
19	**239**	**0.0267**	**H-6->LUMO (16%), H-4->L+1 (36%), H-4->L+3 (18%)**
20	**238**	**0.0149**	**H-1->L+4 (58%), H-1->L+5 (11%)**

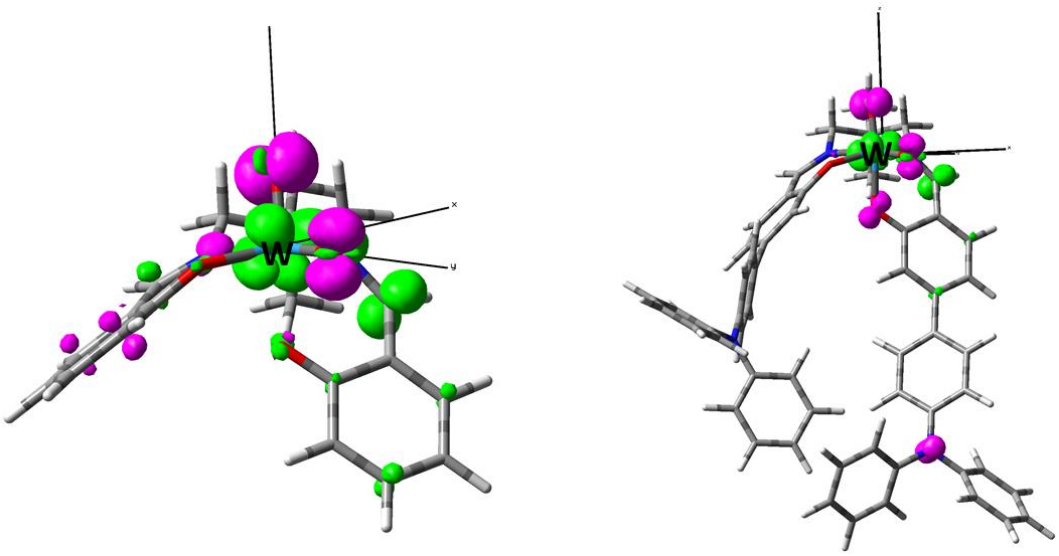


Figure S16. The charge density difference (CCD) maps for the ^{1}LMCT excited state computed at 283 nm.

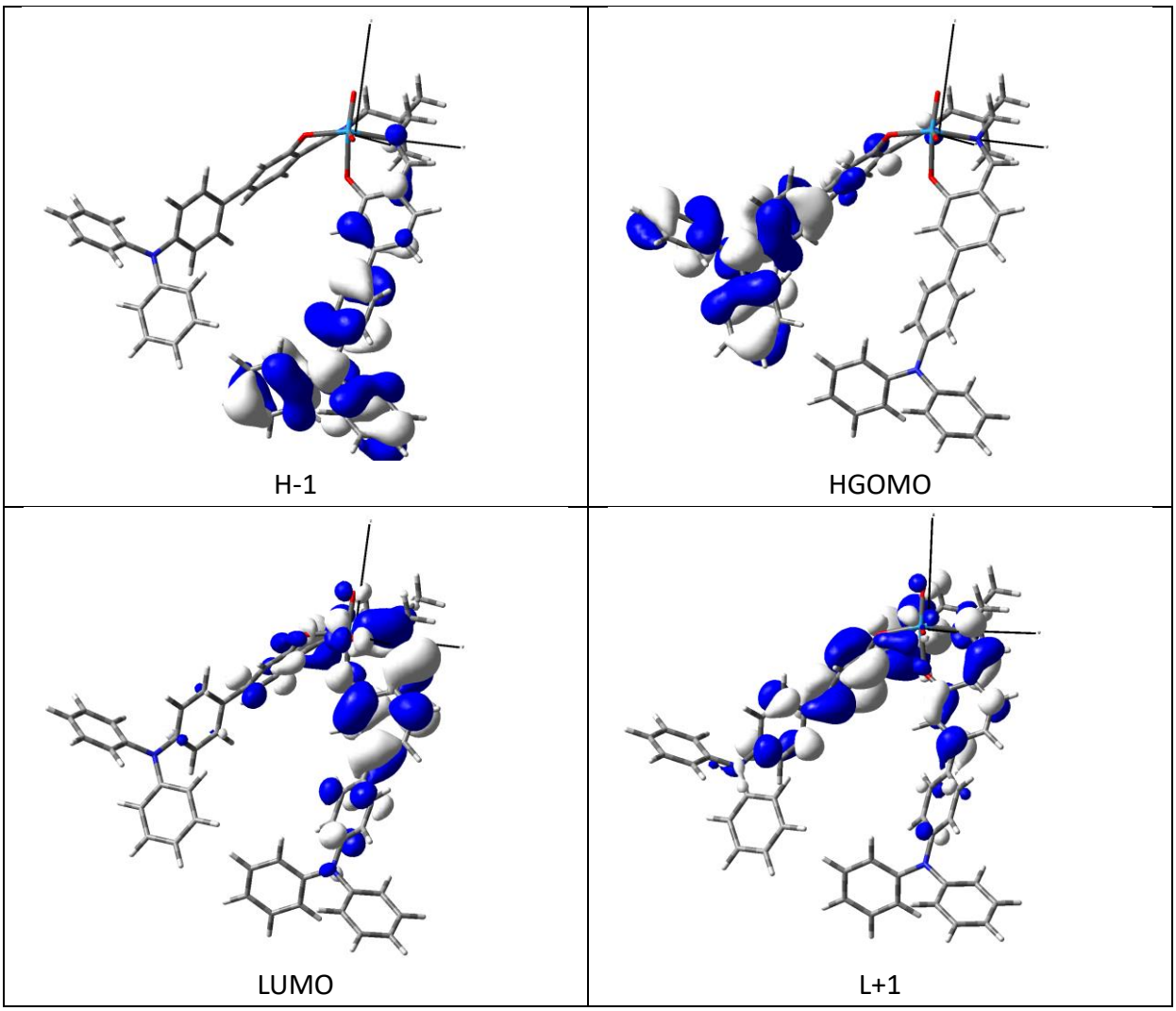


Figure S17. H-1**,** HOMO, LUMO, L+1 of **W1a** (isovalue = 0.02 a.u.)

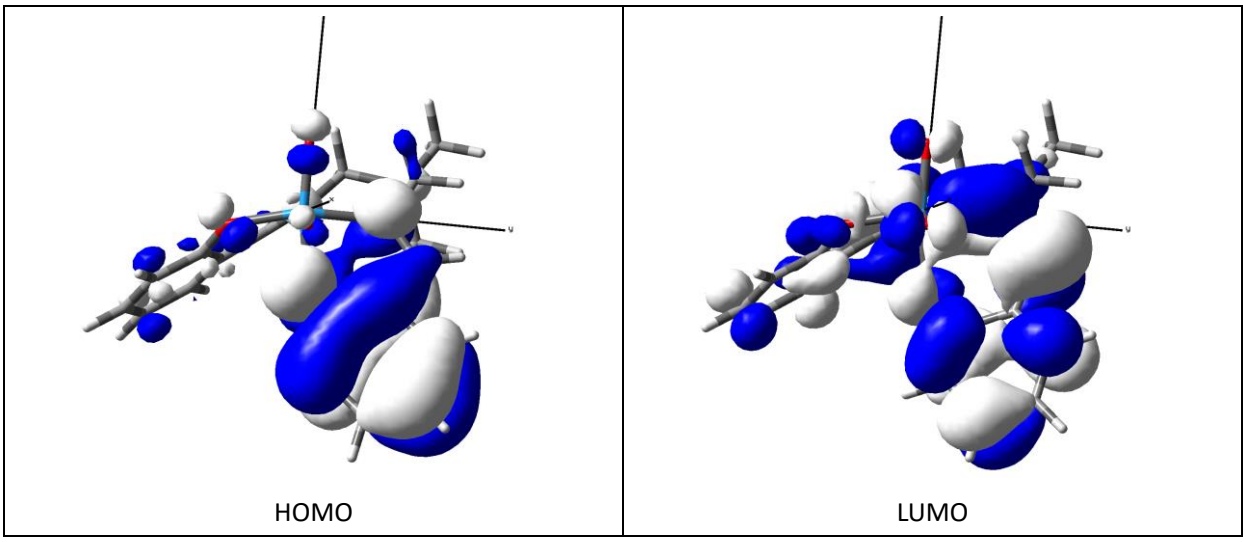


Figure S18. HOMO, LUMO of **W1c** (isovalue = 0.02 a.u.)

Table S8. orbital overlap for complexes **W1a** and **W1c** at their respective optimized S_0 geometries.

	HOMO-LUMO	H-1/L	HOMO/L+1
W1a	0.149	0.342	0.352
W1c	0.623		

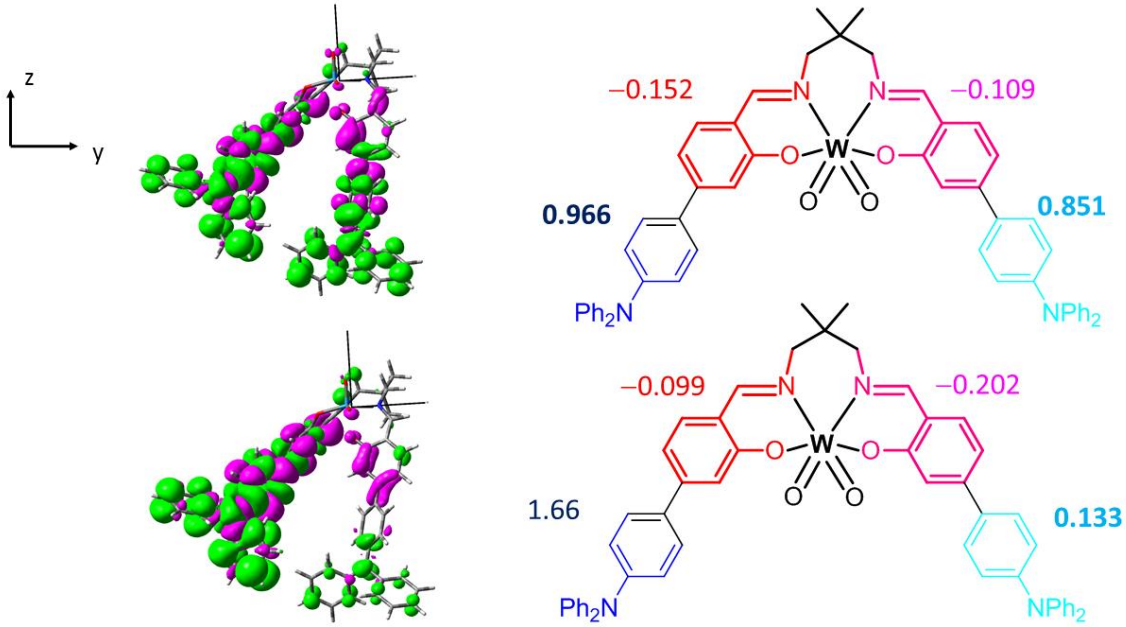


Figure S19. Transition dipole moment density and the fragment transition dipole moment along the z-direction of the $S_0 \rightarrow S_2$ (top) and $S_0 \rightarrow S_3$ (bottom) excitation in toluene solution at the optimized S_0 geometries of **W1a**. Colour code: magenta, negative; green, positive; isovalue = 0.001 a.u.)

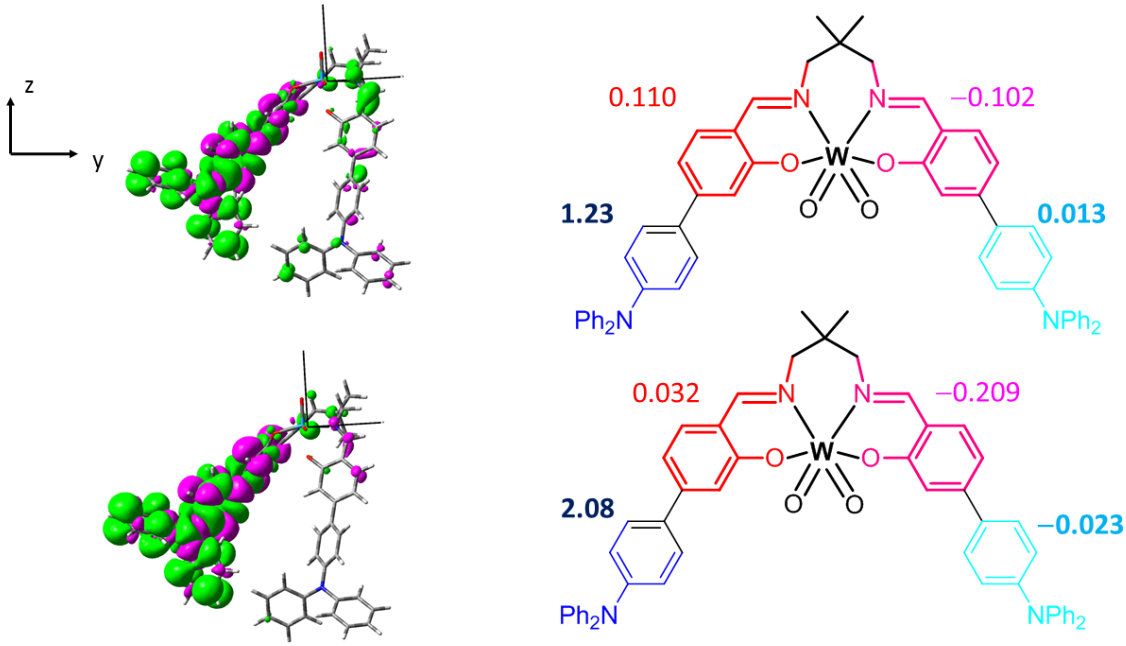


Figure S20. Transition dipole moment density and the fragment transition dipole moment along the y-direction of the $S_0 \rightarrow S_2$ (top) and $S_0 \rightarrow S_3$ (bottom) excitation in toluene solution at the optimized S_0 geometries of **W1a**. Colour code: magenta, negative; green, positive; isovalue = 0.001 a.u.)

Table S9. Cartesian coordinates of complex **W1c** at its optimized S_0 geometry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	0.072442	-0.058843	-0.046930
2	8	0	0.060045	-0.070375	1.677781
3	8	0	1.737501	-0.094797	-0.454443
4	8	0	-0.449428	0.345761	-2.062732
5	8	0	-0.553289	-1.850549	-0.496825
6	7	0	-0.095073	2.084593	-0.029979
7	7	0	-2.276181	0.218935	0.198411
8	6	0	-0.774752	2.743395	1.082961
9	1	0	-0.507291	3.812999	1.082162
10	1	0	-0.431752	2.298925	2.025279
11	6	0	-2.304882	2.622555	0.974012
12	6	0	-2.772205	1.176780	1.178638
13	1	0	-2.428623	0.828276	2.165185
14	1	0	-3.876988	1.165252	1.187733
15	6	0	-2.895916	3.452298	2.112669
16	1	0	-2.529515	3.109938	3.090826
17	1	0	-3.992219	3.383349	2.118753
18	1	0	-2.628940	4.512144	2.001787
19	6	0	-2.808459	3.151314	-0.364710
20	1	0	-3.907640	3.153132	-0.380122
21	1	0	-2.466113	2.538842	-1.209856
22	1	0	-2.474777	4.186067	-0.532231
23	6	0	0.342661	2.840187	-0.999264
24	1	0	0.394593	3.919569	-0.797629
25	6	0	0.679126	2.428989	-2.315724
26	6	0	0.179508	1.191043	-2.823512
27	6	0	0.340688	0.934635	-4.203636
28	1	0	-0.054049	-0.001747	-4.593062
29	6	0	1.005598	1.831253	-5.011781
30	6	0	1.508348	3.047433	-4.509394
31	1	0	2.021556	3.743500	-5.168249
32	6	0	1.321478	3.343538	-3.181285
33	1	0	1.673767	4.289764	-2.768492
34	6	0	-3.134436	-0.532440	-0.391394

35	1	0	-4.207393	-0.335923	-0.230751
36	6	0	-2.837686	-1.676360	-1.222742
37	6	0	-3.882724	-2.246099	-1.967941
38	1	0	-4.861219	-1.765060	-1.939350
39	6	0	-3.688929	-3.385741	-2.725566
40	1	0	-4.505616	-3.807936	-3.306311
41	6	0	-2.431157	-3.996159	-2.720763
42	6	0	-1.387995	-3.471196	-1.974673
43	1	0	-0.408082	-3.943336	-1.953971
44	6	0	-1.569316	-2.304121	-1.224802
45	1	0	-2.264906	-4.899906	-3.304784
46	1	0	1.139781	1.595333	-6.066859

Table S10. Cartesian coordinates of complex **W1a** at its optimized S_0 geometry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	74	0	-0.133774	-0.296372	0.124437
2	8	0	-0.305270	-0.206781	1.838611
3	8	0	1.534185	-0.609649	-0.123339
4	8	0	-0.434706	0.050413	-1.945076
5	8	0	-0.999171	-1.992435	-0.306810
6	7	0	0.034381	1.837464	0.011965
7	7	0	-2.426428	0.341744	0.120265
8	6	0	-0.628507	2.656567	1.023867
9	1	0	-0.203486	3.673748	0.994254
10	1	0	-0.434394	2.225892	2.014278
11	6	0	-2.146937	2.757612	0.782680
12	6	0	-2.853584	1.413705	1.006930
13	1	0	-2.657700	1.076228	2.036424
14	1	0	-3.942589	1.572583	0.907060
15	6	0	-2.696064	3.734491	1.820957
16	1	0	-2.471928	3.402301	2.844489
17	1	0	-3.786345	3.831943	1.728059
18	1	0	-2.259605	4.733490	1.684946
19	6	0	-2.446938	3.276250	-0.620102
20	1	0	-3.527113	3.444209	-0.738153

21	1	0	-2.134642	2.569475	-1.400471
22	1	0	-1.942198	4.236388	-0.803823
23	6	0	0.662072	2.456765	-0.954689
24	1	0	0.877476	3.523075	-0.795328
25	6	0	1.002496	1.928233	-2.224408
26	6	0	0.327486	0.766805	-2.712259
27	6	0	0.455828	0.447361	-4.078070
28	1	0	-0.067271	-0.440567	-4.430336
29	6	0	1.257244	1.192442	-4.930565
30	6	0	1.958885	2.317286	-4.422330
31	1	0	2.564066	2.921772	-5.095076
32	6	0	1.806430	2.683735	-3.110372
33	1	0	2.297183	3.580864	-2.730847
34	6	0	-3.319720	-0.283769	-0.559076
35	1	0	-4.360437	0.080027	-0.532372
36	6	0	-3.091948	-1.465042	-1.357846
37	6	0	-4.064288	-1.853905	-2.292270
38	1	0	-4.966850	-1.248547	-2.385591
39	6	0	-3.891775	-2.962832	-3.096062
40	1	0	-4.659324	-3.243064	-3.815090
41	6	0	-2.737028	-3.755202	-2.962230
42	6	0	-1.791390	-3.411823	-1.995618
43	1	0	-0.875945	-3.989321	-1.879255
44	6	0	-1.942433	-2.274858	-1.203355
45	7	0	1.588300	-0.117351	-10.473863
46	6	0	1.352288	0.843139	-6.355946
47	6	0	0.241124	0.344282	-7.049163
48	6	0	0.306405	0.036556	-8.397153
49	1	0	-0.581764	-0.316674	-8.917579
50	6	0	1.506675	0.191832	-9.104602
51	6	0	2.628205	0.677080	-8.416823
52	1	0	3.573648	0.786656	-8.945080
53	6	0	2.543612	1.008819	-7.074818
54	1	0	3.436193	1.364475	-6.560495
55	1	0	-0.710885	0.240065	-6.529617
56	6	0	0.787873	-1.137790	-11.044680
57	6	0	0.608140	-2.360032	-10.387501
58	1	0	1.089633	-2.527300	-9.424631
59	6	0	-0.184279	-3.349434	-10.956779

60	1	0	-0.325015	-4.292669	-10.429423
61	6	0	-0.783330	-3.150226	-12.197875
62	6	0	-0.593140	-1.940558	-12.859959
63	1	0	-1.059803	-1.767976	-13.828684
64	6	0	0.176288	-0.935828	-12.286393
65	1	0	-1.394622	-3.932467	-12.643916
66	1	0	0.310146	0.016734	-12.797169
67	6	0	2.434974	0.645220	-11.321361
68	6	0	3.274056	0.003116	-12.235773
69	1	0	3.274906	-1.084946	-12.282605
70	6	0	4.091774	0.750798	-13.074637
71	1	0	4.742229	0.240031	-13.782747
72	6	0	4.093837	2.141399	-13.001694
73	6	0	3.260937	2.781479	-12.087440
74	1	0	3.247835	3.868510	-12.027549
75	6	0	2.427928	2.041339	-11.257339
76	1	0	1.766709	2.536961	-10.547875
77	1	0	4.740554	2.724318	-13.654774
78	7	0	-1.601439	-8.105008	-6.470580
79	6	0	-2.499136	-4.908679	-3.847227
80	6	0	-1.875495	-6.071627	-3.377170
81	6	0	-1.591091	-7.129411	-4.226255
82	1	0	-1.097011	-8.021480	-3.844843
83	6	0	-1.925363	-7.055258	-5.582813
84	6	0	-2.569606	-5.907567	-6.058069
85	1	0	-2.831980	-5.844845	-7.113061
86	6	0	-2.848651	-4.854145	-5.202377
87	1	0	-1.608324	-6.148255	-2.323696
88	1	0	-3.321290	-3.956000	-5.598961
89	6	0	-1.779210	-9.451641	-6.078488
90	6	0	-2.907526	-9.825584	-5.340190
91	1	0	-3.647547	-9.070545	-5.078907
92	6	0	-3.079485	-11.146435	-4.946629
93	1	0	-3.962655	-11.420547	-4.371485
94	6	0	-2.144066	-12.117121	-5.295690
95	6	0	-1.025392	-11.747864	-6.037710
96	1	0	-0.280998	-12.493931	-6.311699
97	6	0	-0.834982	-10.425995	-6.420498
98	1	0	0.048900	-10.139151	-6.988046

99	1	0	-2.285851	-13.152403	-4.991683
100	6	0	-1.011913	-7.793860	-7.719938
101	6	0	-1.405716	-8.470985	-8.878821
102	1	0	-2.173973	-9.239808	-8.809598
103	6	0	-0.820054	-8.163489	-10.100718
104	1	0	-1.136348	-8.699056	-10.994508
105	6	0	0.151909	-7.169580	-10.189118
106	6	0	0.541323	-6.491520	-9.035968
107	1	0	1.310414	-5.720835	-9.089870
108	6	0	-0.028384	-6.803122	-7.807561
109	1	0	0.286293	-6.281901	-6.904673
110	1	0	0.604574	-6.924363	-11.148637

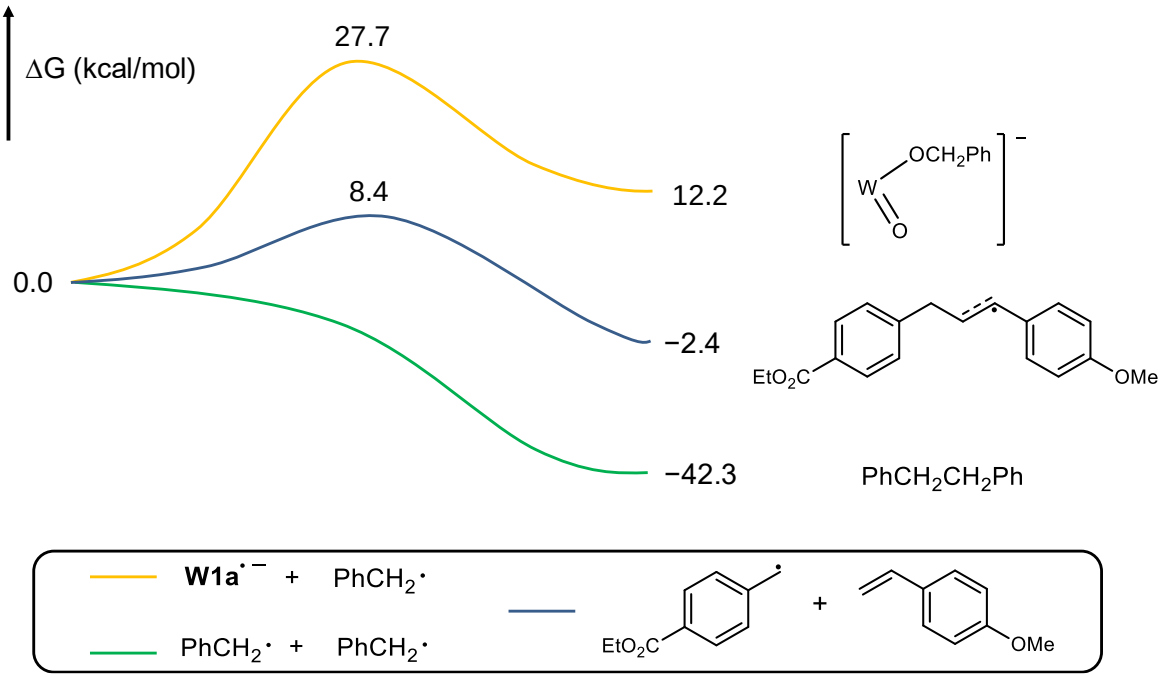


Figure S21. The energy profile for the benzyl homocoupling and the cross-coupling to **W1a**$^{\cdot-}$/styrene calculated at the B3LYP/SDD−6-311G**/PCM//B3LYP/LANL2DZ−6-31G* /PCM level.

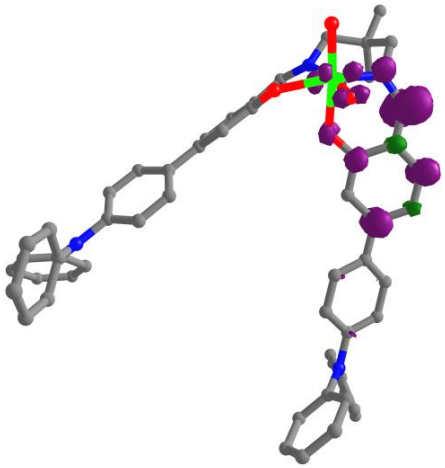
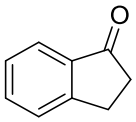


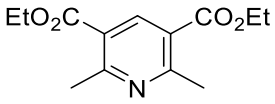
Figure S22. Spin density plot (contour value: 0.006) for one-electron reduced **W1a**$^{\cdot-}$ (12% on W, 5% on oxo, 83% on ligand). Hydrogen atoms are not shown for clarity.

General procedure for dehydrogenation reactions catalysed by tungsten photocatalyst

To a test tube (10 mL) equipped with a magnetic stir bar were added substrates (0.5 mmol), **W1a** (1 mol%), acetonitrile (5 mL). The mixture was purged with oxygen bubble for 15 min The reaction was stirred at room temperature under oxygen and 365 or 410 nm LEDs irradiation for 12 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers was washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent. For the entry with the addition of H_2O_2, 1 molar equivalent of aqueous H_2O_2 was added.



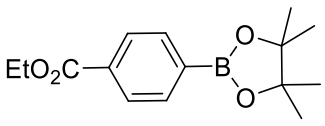
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1 H), 7.62 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.51 (d, *J* = 7.7 Hz, 1 H), 7.40 (t, *J* = 7.8 Hz, 1 H), 3.17 (t, *J* = 6.0 Hz, 2 H), 2.87 – 2.67 (m, 2 H) ppm.



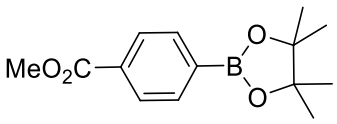
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1 H), 4.38 (q, *J* = 7.1 Hz, 4 H), 2.83 (s, 6 H), 1.40 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.83, 162.15, 141.06, 123.16, 61.44, 24.73, 14.25 ppm.

General procedure for visible light photo-redox borylation of aryl halides catalysed by tungsten photocatalyst

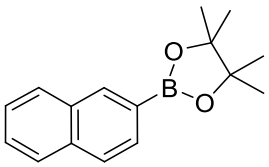
To a test tube (10 mL) equipped with a magnetic stir bar were added aryl halide (0.5 mmol), B_2Pin_2 (0.55 mmol), **W1a** (1 mol%), K_2CO_3 (0.5 mmol), TBAB (0.5 mmol) and acetonitrile (5 mL). The reaction was stirred at room temperature under argon and 410 nm LEDs irradiation for 12 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers was washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent.



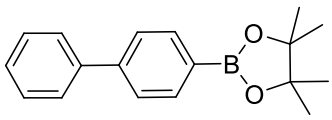
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2 H), 7.88 (d, *J* = 8.2 Hz, 2 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 1.41 (t, *J* = 7.1 Hz, 3 H), 1.37 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.69, 134.63, 132.66, 128.57, 84.17, 61.06, 24.89, 14.33 ppm.



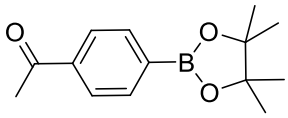
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 2 H), 7.89 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3 H), 1.37 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.14, 134.67, 132.30, 128.60, 84.18, 52.16, 24.89 ppm.



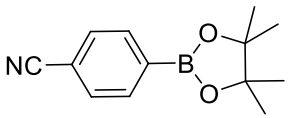
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.78 – 7.73 (m, 3 H), 7.43 (t, *J* = 7.3 Hz, 1 H), 7.39 (t, *J* = 7.4 Hz, 1 H), 1.32 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.21, 133.99, 131.76, 129.35, 127.62, 126.67, 125.94, 124.76, 82.90, 23.89 ppm.



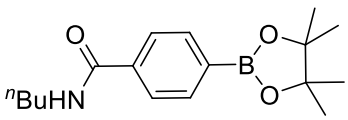
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2 H), 7.55 – 7.49 (m, 4 H), 7.34 (t, *J* = 7.6 Hz, 2 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 1.27 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.84, 139.94, 134.22, 127.72, 126.51, 126.18, 125.42, 82.77, 23.83 ppm.



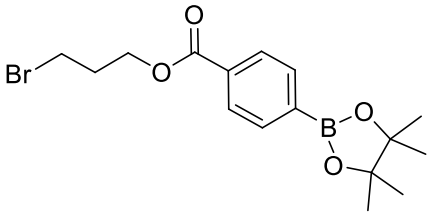
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2 H), 7.91 (d, *J* = 8.2 Hz, 2 H), 2.64 (s, 3 H), 1.38 (s, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.53, 138.99, 134.93, 128.59, 128.33, 127.31, 84.23, 26.79, 24.89 ppm.



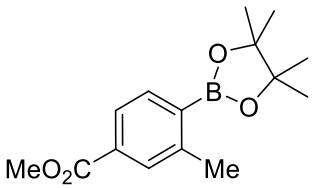
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 1.38 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.07, 130.13, 117.87, 113.50, 83.48, 23.84 ppm.



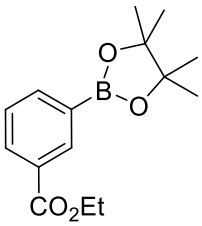
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2 H), 7.76 (d, *J* = 8.2 Hz, 2 H), 6.23 (b, 1 H), 3.47 (dd, *J* = 13.0, 7.1 Hz, 2 H), 1.66 – 1.57 (m, 2 H), 1.43 (dt, *J* = 15.0, 7.3 Hz, 2 H), 1.37 (s, 12 H), 0.97 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.44, 137.07, 134.94, 125.97, 84.12, 39.85, 31.74, 24.89, 20.18, 13.81 ppm.



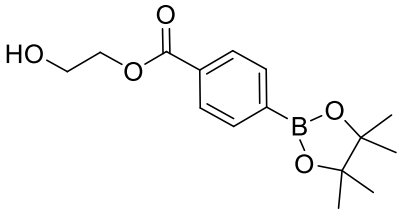
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2 H), 7.80 (d, *J* = 8.2 Hz, 2 H), 4.39 (t, *J* = 6.0 Hz, 2 H), 3.47 (t, *J* = 6.5 Hz, 2 H), 2.25 (p, *J* = 6.3 Hz, 2 H), 1.28 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.39, 133.67 131.09, 127.55, 83.17, 61.74, 30.77, 28.44, 23.85 ppm.



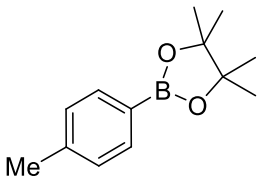
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1 H), 7.82 (s, 2 H), 3.93 (s, 3 H), 2.59 (s, 3 H), 1.37 (s, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.32, 144.90, 135.75, 131.77, 130.44, 125.57, 83.83, 52.08, 24.90, 22.10 ppm.



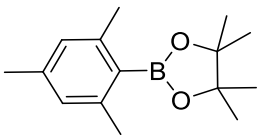
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1 H), 8.15 (dd, *J* = 7.8, 1.4 Hz, 1 H), 8.00 (d, *J* = 7.4 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 1.42 (t, *J* = 7.1 Hz, 3 H), 1.38 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.75, 139.10, 135.73, 132.32, 129.92, 127.78, 84.11, 60.96, 24.88, 14.41 ppm.



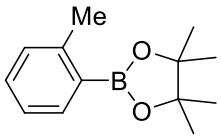
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2 H), 7.83 (d, *J* = 8.0 Hz, 2 H), 4.40 (t, *J* = 5.0 Hz, 2 H), 3.89 (t, *J* = 5.0 Hz, 2 H), 1.31 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.97, 134.65, 132.04, 128.68 , 84.22, 66.63, 60.81, 24.83 ppm.



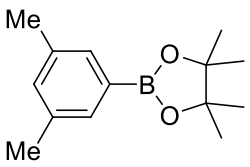
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2 H), 7.21 (d, *J* = 7.6 Hz, 2 H), 2.39 (s, 3 H), 1.36 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.39, 133.77, 127.50, 82.59, 23.82, 20.71 ppm.



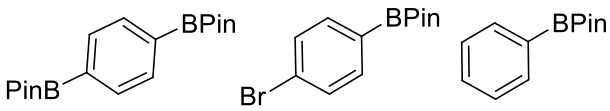
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.70 (s, 2 H), 2.29 (s, 6 H), 2.17 (s, 3 H), 1.30 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.08, 137.89, 126.41, 82.43, 23.92, 21.16, 20.21 ppm.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.0 Hz, 1 H), 7.34 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.18 (t, *J* = 6.5 Hz, 2 H), 2.56 (s, 3 H), 1.37 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.85, 135.86, 130.81, 129.79, 124.72, 83.42, 24.91, 22.24 ppm.

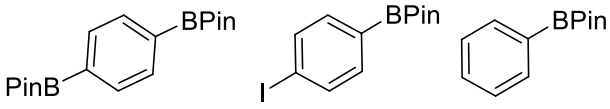


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 2 H), 7.13 (s, 1 H), 2.35 (s, 6 H), 1.37 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.19, 133.02, 132.41, 83.70, 24.87, 21.16 ppm.



3.2 : 2.5 : 1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 4 H), 7.69 (d, *J* = 8.1 Hz, 1.74 H), 7.53 (d, *J* = 8.1 Hz, 1.74 H), 7.48 (t, *J* = 7.4 Hz, 0.31 H), 7.39 (t, *J* = 7.5 Hz, 0.64 H), 1.37 (s, 24 H), 1.36 (s, 10 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.32), 134.75, 133.90, 131.27, 130.96), 127.72, 126.25, 84.04, 83.86, 83.77, 24.89), 24.88 ppm.

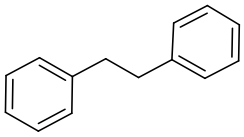


20 : 8.4: 1

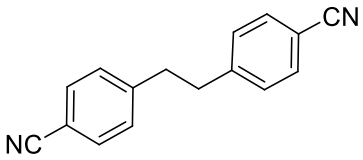
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 4 H), 7.75 (d, *J* = 8.0 Hz, 0.84 H), 7.54 (d, *J* = 8.0 Hz, 0.84 H), 7.48 (t, *J* = 7.4 Hz, 0.05 H), 7.39 (t, *J* = 7.4 Hz, 0.10 H), 1.37 (s, 24 H), 1.36 (s, 5.57 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.92, 136.29, 134.74, 133.90, 131.27, 127.72, 98.85, 84.04, 83.86, 24.89, 24.87 ppm.

General procedure of photoassisted C-C coupling of benzylic halides catalysed by W1a

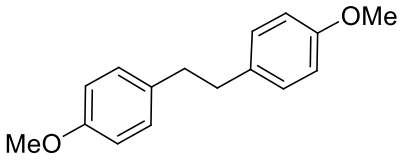
To a test tube (10 mL) equipped with a magnetic stir bar were added benzyl bromide (0.5 mmol), **W1a** (1 mol%), B_2Pin_2 (0.55 mmol), K_2CO_3 (0.5 mmol), TBAB (0.5 mmol) and acetonitrile (5 mL). The reaction was stirred at room temperature under argon and 410 nm LEDs irradiation for 12 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers was washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent



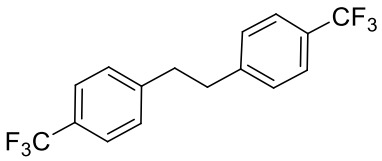
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.28 (m, 4 H), 7.23 (d, *J* = 7.3 Hz, 6 H), 2.97 (s, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.82, 128.48, 128.37, 125.95, 37.99 ppm.



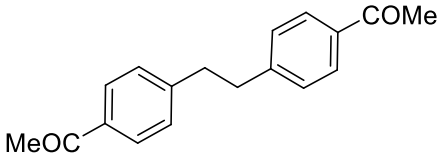
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 4 H), 7.20 (d, *J* = 8.1 Hz,4 H), 2.97 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.17, 132.27, 129.28, 118.84, 110.11, 37.16 ppm.



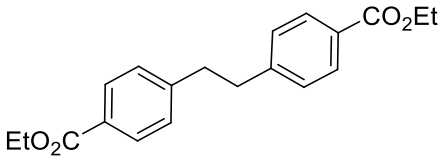
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.4 Hz, 4 H), 6.86 (d, *J* = 8.4 Hz, 4 H), 3.82 (s, 6 H), 2.86 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.80, 133.99, 129.76, 129.40, 113.86, 113.72, 55.27, 37.32 ppm.



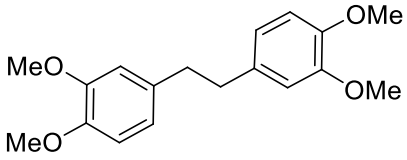
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 4 H), 7.28 (d, *J* = 7.9 Hz, 4 H), 3.02 (s, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.32 (s, 6 F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.03, 128.78, 128.58 (q, *J* = 32.3 Hz), 125.38 (q, *J* = 3.7 Hz), 124.29 (q, *J* = 271.8 Hz) 37.25 ppm.



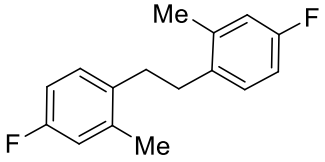
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.9 Hz, 4 H), 7.15 (d, *J* = 7.9 Hz, 4 H), 2.92 (s, 4 H), 2.50 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.83, 146.74, 135.30, 128.73, 128.59, 37.32, 26.60 ppm.



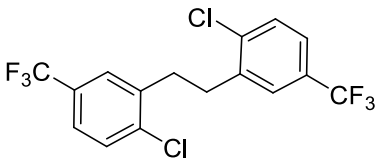
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 4 H), 7.10 (d, *J* = 8.0 Hz, 4 H), 4.27 (q, *J* = 7.1 Hz, 4 H), 2.90 (s, 4 H), 1.30 (t, *J* = 7.1 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.62, 146.41, 129.71, 128.51, 128.44, 60.87, 37.44, 14.36 ppm.



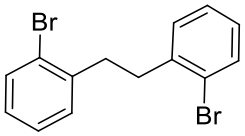
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (d, *J* = 8.1 Hz, 2 H), 6.73 (dd, *J* = 8.1, 1.7 Hz, 2 H), 6.68 (d, *J* = 1.7 Hz, 2 H), 3.88 (s, 6H), 3.86 (s, 6 H), 2.87 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.68, 147.21, 134.41, 120.34, 111.88, 111.13), 77.31, 77.06, 76.81, 55.93, 55.80; 37.75 ppm.



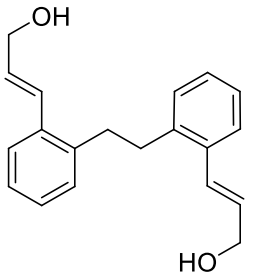
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 8.3, 6.0 Hz, 2 H), 6.89 (dd, *J* = 9.8, 2.5 Hz, 2 H), 6.84 (td, *J* = 8.4, 2.7 Hz, 2 H), 2.82 (s, 4 H), 2.29 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.79 – -117.88 (m, 2 F); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.21 (d, *J* = 243.4 Hz), 138.04 (d, *J* = 7.4 Hz), 135.38 (d, *J* = 3.1 Hz), 130.24 (d, *J* = 8.1 Hz), 116.73 (d, *J* = 20.8 Hz), 112.55 (d, *J* = 20.7 Hz), 33.44, 19.39 (d, *J* = 1.5 Hz) ppm.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2 H), 7.45 (dd, *J* = 8.4, 1.8 Hz, 2 H), 7.35 (d, *J* = 1.5 Hz, 2 H), 3.13 (s, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.18, 137.77), 130.12, 129.33 (q, *J* = 32.9 Hz), 127.43 (q, *J* = 3.7 Hz), 124.67 (q, *J* = 3.7 Hz,), 123.66 (q, *J* = 272.7 Hz), 33.46 ppm.



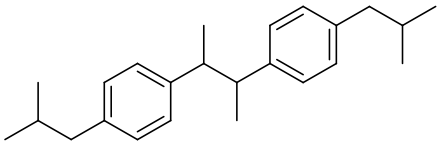
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.9 Hz, 2 H), 7.27 – 7.19 (m, 4 H), 7.12 – 7.07 (m, 2 H), 3.07 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.59, 132.82, 130.66, 127.85, 127.47, 124.50, 36.47 ppm.



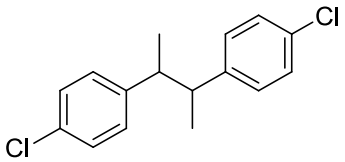
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2 H), 7.25 – 7.16 (m,6 H), 6.87 (d, *J* = 15.7 Hz, 2 H), 6.24 (dt, *J* = 15.7, 5.2 Hz, 2 H), 4.32 (d, *J* = 5.1 Hz, 4 H), 2.95 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.23, 135.69, 130.49, 129.86, 127.73, 127.69, 126.48, 126.15, 63.49, 35.11 ppm.

General procedure of decarboxylative coupling reaction of redox-active esters by W1a

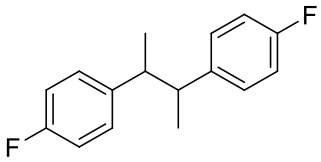
To a test tube (10 mL) equipped with a magnetic stir bar were added N-hydroxyphthalimide ester (0.5 mmol), **W1a** (1 mol%), DIPEA (1.25 mmol, 2.5 eq.), and acetonitrile (5 mL). The reaction was stirred at room temperature under argon and 450 nm LEDs irradiation for 3 h. the reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers is washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent.



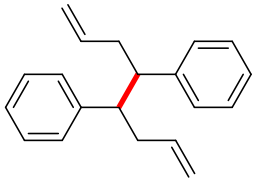
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 4 H), 7.16 (d, *J* = 8.0 Hz, 4 H), 7.00 (d, *J* = 8.1 Hz, 4 H), 6.97 (d, *J* = 8.1 Hz, 4 H), 2.95 (dt, *J* = 6.6, 5.0 Hz, 2 H), 2.82 (dt, *J* = 6.2, 4.0 Hz, 2 H), 2.54 (d, *J* = 7.2 Hz, 4 H), 2.46 (d, *J* = 7.2 Hz, 4 H), 1.94 (dt, *J* = 13.5, 6.8 Hz, 2 H), 1.87 (dt, *J* = 13.5, 6.8 Hz, 2 H), 1.34 (d, *J* = 6.6 Hz, 6 H), 1.09 (d, *J* = 6.3 Hz, 6 H), 0.99 (d, *J* = 6.6 Hz, 12H), 0.93 (dd, *J* = 6.6, 1.4 Hz, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.88, 143.18, 139.29, 138.88, 129.01 (, 128.46, 127.57, 127.34, 47.03, 46.36, 45.17, 45.07, 30.35, 30.30, 22.50, 22.40. 21.15, 17.49 ppm.



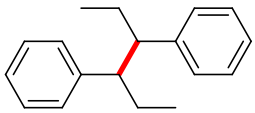
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 4 H), 7.15 (d, *J* = 8.6 Hz, 4 H), 7.13 (d, *J* = 6.2 Hz, 4 H), 6.91 (d, *J* = 8.5 Hz, 4 H), 2.93 – 2.85 (m, 2 H), 2.82 – 2.72 (m, 2 H), 1.30 (d, *J* = 6.7 Hz, 6 H), 1.03 (d, *J* = 6.3 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.40, 143.89, 131.78, 131.47, 129.11, 128.94, 128.47, 128.03, 46.56, 46.03, 20.60, 18.74 ppm.



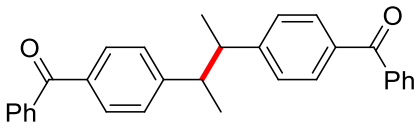
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 8.5, 5.5 Hz, 4 H), 7.03 (t, *J* = 8.7 Hz, 4 H), 6.93 (dd, *J* = 8.6, 5.6 Hz, 4 H), 6.88 (t, *J* = 8.7 Hz, 4 H), 2.94 – 2.85 (m, 2 H), 2.85 – 2.75 (m, 2 H), 1.32 (d, *J* = 7.2 Hz, 6 H), 1.05 (d, *J* = 6.3 Hz, 6 H)；^{13}C NMR (126 MHz, $CDCl_3$) δ 161.35 (d, *J* = 243.7 Hz), 161.08 (d, *J* = 243.4 Hz)，129.06 (d, *J* = 7.7 Hz), 128.87 (d, *J* = 7.7 Hz), 115.03 (d, *J* = 20.9 Hz), 114.55 (d, *J* = 20.9 Hz), 46.56, 46.09, 20.73, 18.81；^{19}F NMR (376 MHz, $CDCl_3$) δ -117.27 (tt, *J* = 8.4, 5.4 Hz, 2 F), -117.57 (tt, *J* = 8.3, 5.5 Hz, 2 F) ppm.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 4H), 7.31 (d, *J* = 8.5 Hz, 4H), 7.05 (d, *J* = 8.4 Hz, 4H), 6.73 (d, *J* = 8.3 Hz, 4 H), 5.68 – 5.53 (m, 2 H), 5.49 – 5.34 (m, 2 H), 5.08 – 4.91 (m, 4 H), 4.89 – 4.72 (m, 4 H), 2.98 (q, *J* = 6.0 Hz, 2 H), 2.84 – 2.78 (m, 2 H), 2.61 – 2.49 (m, 2 H), 2.38 (td, *J* = 14.6, 14.2, 7.2 Hz, 4 H), 2.20 – 2.08 (m, 4 H)；^{13}C NMR (101 MHz, $CDCl_3$) δ 141.94, 140.23, 136.38, 136.06, 131.51, 131.38, 131.24, 130.93, 130.88, 130.79, 130.20, 129.57, 120.12, 116.80, 116.41, 51.15, 49.36, 38.32, 37.61 ppm.

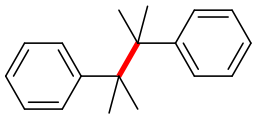


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.4 Hz, 4 H), 7.30 – 7.26 (m, 2 H), 7.26 – 7.22 (m, 4H), 7.20 – 7.15 (m, 4 H), 7.14 – 7.09 (m, 2 H), 6.94 – 6.90 (m, 4 H), 2.83 – 2.74 (m, 2 H), 2.64 (dt, *J* = 5.9, 2.3 Hz, 2 H), 2.00 – 1.88 (m, 2 H), 1.65 (dtd, *J* = 13.5, 7.4, 2.4 Hz, 2 H), 1.49 – 1.35 (m, 4 H), 0.79 (t, *J* = 7.3 Hz, 6 H), 0.58 (t, *J* = 7.4 Hz, 6 H)；^{13}C NMR (101 MHz, $CDCl_3$) δ 144.59, 143.04, 129.09, 128.44, 128.24, 127.48, 126.01, 125.65, 54.29, 53.29, 27.49, 25.84, 12.45, 12.26 ppm.

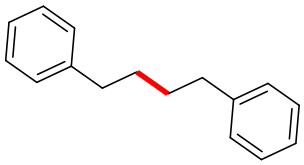


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 4 H), 7.76 – 7.37 (m, 27 H), 7.37 – 7.23 (m, 5 H), 3.14 – 2.79 (m, 4 H), 1.39 (d, *J* = 5.0 Hz, 6 H), 1.12 (d, *J* = 4.7 Hz, 6 H)；^{13}C NMR (101 MHz, $CDCl_3$) δ 196.92, 196.84, 146.23, 146.02, 137.71, 137.65, 137.61, 137.30, 132.43,

132.36, 131.84, 131.75, 130.06, 129.98, 129.41, 129.14, 128.30, 128.24, 128.03, 127.82, 46.96, 46.85, 20.67, 19.09 ppm.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.06 (m, 6 H), 6.98 (d, *J* = 7.5 Hz, 4 H), 1.23 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.84, 128.67, 126.68, 125.53, 43.68, 25.25 ppm.

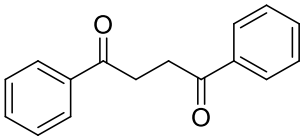


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.17 (m, 4 H), 7.11-7.08 (m, 6 H), 2.55 (t, *J* = 6.8 Hz, 4 H), 1.59 (t, *J* = 6.9 Hz, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.59, 128.44, 128.28, 125.67, 35.85, 31.13 ppm.

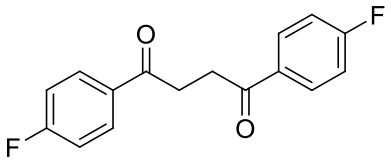
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 2 H), 5.02 (dq, *J* = 17.1, 1.6 Hz, 2 H), 4.96 (d, *J* = 10.2 Hz, 2 H), 2.07 (q, *J* = 6.9 Hz, 4 H), 1.41 (p, *J* = 7.3, 6.8 Hz, 4 H), 1.33 (dt, *J* = 7.6, 3.5 Hz, 4 H)；^{13}C NMR (126 MHz, $CDCl_3$) δ 139.20, 114.16, 33.81, 28.99, 28.89 ppm.

General procedure of photoinduced C-C bond coupling reaction of arylacyl bromides by W1a

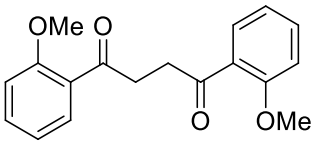
To a test tube (10 mL) equipped with a magnetic stir bar were added bromide α-bromoacetophenone (0.5 mmol), B_2Pin_2 (0.55 mmol), **W1a** (1 mol%), K_2CO_3 (0.5 mmol), TBAB (0.5 mmol) and acetonitrile (5 mL). The reaction was stirred at room temperature under argon and 410 nm LEDs irradiation for 12 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers was washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent.



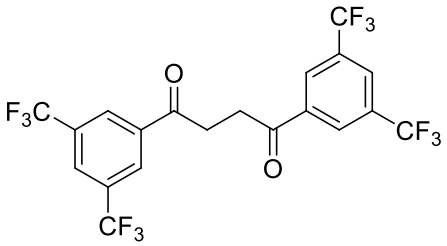
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.6 Hz, 4 H), 7.58 (t, *J* = 7.4 Hz, 2 H), 7.49 (t, *J* = 7.7 Hz, 4 H), 3.47 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.69, 136.75, 133.17, 128.61, 128.13, 32.58 ppm.



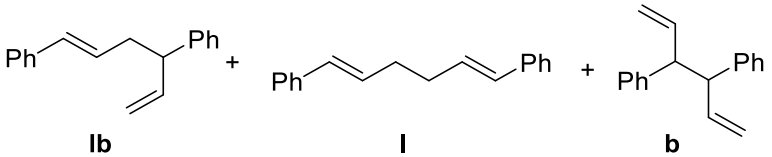
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.8, 5.4 Hz, 4 H), 7.17 (t, *J* = 8.6 Hz, 4 H), 3.45 (s, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.07; ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.00, 165.83 (d, *J* = 254.8 Hz), 133.13 (d, *J* = 3.1 Hz), 130.76 (d, *J* = 9.2 Hz), 115.72 (d, *J* = 21.8 Hz), 32.43 ppm.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.7, 1.8 Hz, 2 H), 7.48 (ddd, *J* = 8.3, 7.3, 1.8 Hz, 2 H), 7.03 (d, *J* = 7.4 Hz, 2 H), 6.99 (d, *J* = 8.6 Hz, 2 H), 3.94 (s, 6 H), 3.43 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.16, 158.69, 133.37, 130.45, 128.16, 120.60, 111.51, 55.53, 38.33 ppm.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 1.6 Hz, 4 H), 8.09 (s, 2 H), 3.55 (s, 4 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.97 (s, 12 F) ppm.

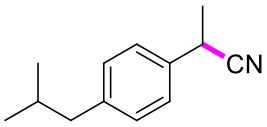


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 3 H), 7.38 – 7.31 (m, 9 H), 7.30 – 7.21 (m, 6 H), 6.60 – 6.43 (m, 1 H), 6.42 (d, *J* = 1.5 Hz, 1 H), 6.37 – 6.28 (m, 1 H), 6.25 – 5.99 (m, 2 H), 5.14 (d, *J* = 1.2 Hz,1 H), 5.11 (dt, *J* = 8.1, 1.5 Hz, 1 H), 4.92 (dd, *J* = 10.3, 1.7 Hz, 0.2 H), 4.84 (dd, *J* = 17.1, 1.6 Hz, 0.2 H), 3.76 – 3.60 (m, 0.2 H), 3.48 (q, *J* = 7.4 Hz, 1 H), 2.69 (tdd,

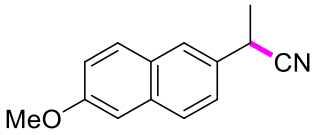
J = 7.2, 3.1, 1.4 Hz, 2 H), 2.55 – 2.37 (m, 2.3 H)； ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.50, 137.74, 131.43, 130.41, 130.04, 128.54, 128.50, 128.40, 127.72, 127.01, 126.98, 126.39, 126.07, 126.04, 114.70, 50.05, 39.09, 32.97 ppm.

General procedure of photoinduced decarboxylative cyanation reaction of redox-active esters by W1a

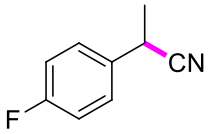
To a test tube (10 mL) equipped with a magnetic stir bar are added N-hydroxyphthalimide ester (0.5 mmol), **W1a** (0.1 mol%), CuBr (5 mol%), 1,10-phenanthroline (5 mol%) and acetonitrile (5 mL). Et_3N (0.5 mmol,) and TMSCN (0.75 mmol) were added. The reaction was stirred at room temperature under argon and 450 nm LEDs irradiation for 3 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer is extracted with DCM. The combined organic layers was washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent.



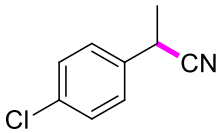
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.8 Hz, 2 H), 7.07 (d, *J* = 7.8 Hz, 2 H), 3.79 (q, *J* = 7.3 Hz, 1 H), 2.39 (d, *J* = 7.1 Hz, 2 H), 1.77 (dp, *J* = 13.5, 6.7 Hz, 1 H), 1.54 (d, *J* = 7.3 Hz, 3 H), 0.82 (d, *J* = 6.7 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.58, 133.25, 128.77, 125.39, 120.79, 43.90, 29.84, 29.15, 21.28, 20.41 ppm.



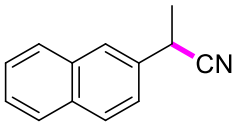
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 3 H), 7.41 (dd, *J* = 8.4, 1.9 Hz, 1 H), 7.21 (dd, *J* = 8.9, 2.5 Hz, 1 H), 7.16 (d, *J* = 2.4 Hz, 1 H), 4.04 (q, *J* = 7.3 Hz, 1H), 3.94 (s, 3 H), 1.73 (d, *J* = 7.3 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.11, 134.03, 132.03, 129.33, 128.78, 127.93, 125.40, 124.96, 121.82, 119.60, 105.68, 55.36, 31.24, 21.46 ppm.



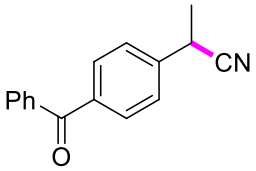
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.4, 5.2 Hz, 2 H), 7.00 (t, *J* = 8.5 Hz, 2 H), 3.82 (q, *J* = 7.3 Hz, 1 H), 1.56 (d, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.31 (d, *J* = 247.2 Hz), 131.80 (d, *J* = 3.3 Hz), 127.40 (d, *J* = 8.3 Hz), 120.37, 115.07 (d, *J* = 21.8 Hz), 29.56, 20.49 ; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.93 (tt, *J* = 8.6, 5.2 Hz, 1 F) ppm.



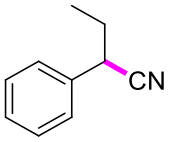
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.3 Hz, 2 H), 7.22 (d, *J* = 8.4 Hz, 2 H), 3.81 (q, *J* = 7.3 Hz, 1 H), 1.56 (d, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.48, 133.03, 128.31, 127.07, 120.10, 29.71, 20.36 ppm.



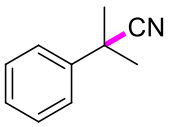
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 1 H), 7.94 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 8.2 Hz, 1 H), 7.73 (d, *J* = 7.2 Hz, 1 H), 7.62 (t, *J* = 7.5 Hz, 1 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.53 (t, *J* = 7.7 Hz, 1 H), 4.66 (q, *J* = 7.2 Hz, 1 H), 1.82 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.02, 132.66, 129.80, 129.34, 128.98, 126.95, 126.15, 125.59, 124.73, 122.09, 121.84, 28.29, 20.61 ppm.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 3 H), 7.75 (d, *J* = 7.7 Hz, 1 H), 7.66 – 7.61 (m, 2 H), 7.53 (q, *J* = 8.1 Hz, 3 H), 4.02 (t, *J* = 7.3 Hz, 1 H), 1.70 (d, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.02, 138.52, 137.55, 137.11, 132.82, 130.60, 130.06, 129.87, 129.19, 128.46, 128.19, 31.18, 21.34 ppm.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2 H), 7.36 (d, *J* = 7.1 Hz, 3 H), 3.77 (t, *J* = 7.2 Hz, 1 H), 1.97 (p, *J* = 7.3 Hz, 2 H), 1.10 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.76, 129.03, 128.02, 127.31, 120.79, 38.93, 29.24, 11.51 ppm.

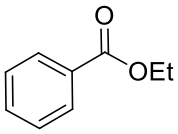


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13-7.08 (m, 3 H), 6.98 (d, *J* = 7.5 Hz, 2 H), 1.23 (s, 26 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.84, 128.67, 126.68, 125.53, 43.68, 25.25 ppm.

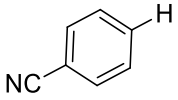
General procedure for visible-light induced dehalogenation of aryl halides:

In a 15 × 125 mm pyrex test tube equipped with a septum and magnetic stir bar, a mixture of aryl halide (0.5 mmol), **W1a** (1 mol%), DIPEA (2.5 mmol, 2.5 eq.) and K_2CO_3 (0.5 mmol, 1 eq.) in 5 mL CH_3CN was degassed by bubbling nitrogen for 10 minutes. The mixture was irradiated under a blue LED (Power = 12 W, 410 nm) for 12 hours. After that, organic

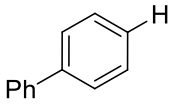
solvents were removed under reduced pressure. The crude was extracted with CH_2Cl_2/H_2O. The residue was purified by silica-gel column chromatography to give the product.



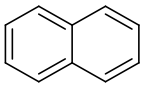
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.1 Hz, 2 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 1.42 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.67, 132.83, 130.50, 129.54, 128.33, 60.98, 14.35 ppm



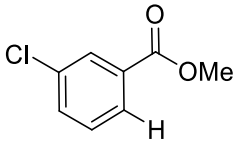
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2 H), 7.62 – 7.58 (m, 1 H), 7.49-7.48 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 132.83, 132.15, 129.15, 118.88, 112.41 ppm.



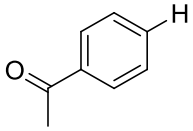
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 4H), 7.52 (t, *J* = 7.6 Hz, 4 H), 7.42 (t, *J* = 7.4 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.26, 128.79, 127.28, 127.20 ppm.



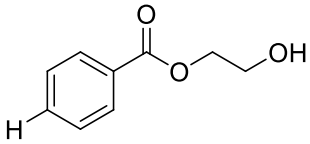
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 6.1, 3.2 Hz,4 H), 7.60 (dd, *J* = 6.2, 3.2 Hz, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.60, 128.05, 125.99 ppm.



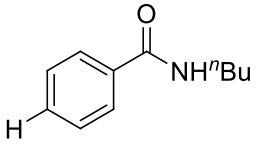
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1 H), 7.87 (d, *J* = 7.5 Hz, 1 H), 7.48 (d, *J* = 7.5 Hz, 1 H), 7.34 (t, *J* = 7.7 Hz, 1 H), 3.88 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.78, 134.42, 132.89, 131.79, 129.67, 129.57, 127.64, 52.34 ppm.



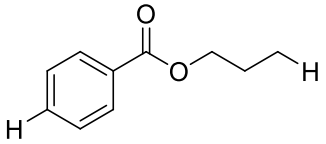
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.4 Hz, 1 H), 7.56 (t, *J* = 6.8 Hz, 1 H), 7.46 (t, *J* = 7.1 Hz, 2 H), 2.60 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.19, 137.08, 133.12, 128.57, 128.30, 26.62 ppm.



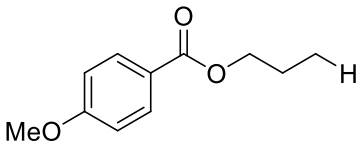
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 2 H), 7.51 (t, *J* = 7.0 Hz, 1 H), 7.38 (t, *J* = 7.3 Hz, 2 H), 4.40 (s, 2 H), 3.90 (d, *J* = 3.8 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.98, 133.14, 129.65, 128.37, 66.58, 60.93 ppm.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (t, *J* = 11.8 Hz, 2 H), 7.42 (t, *J* = 7.1 Hz, 1 H), 7.34 (t, *J* = 7.5 Hz, 2 H), 6.78 (b, 1 H), 3.38 (dd, *J* = 13.2, 6.7 Hz, 2 H), 1.54 (dd, *J* = 14.6, 7.4 Hz, 2 H), 1.35 (dd, *J* = 14.8, 7.4 Hz, 2 H), 0.90 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.67, 134.82, 131.25, 128.46, 126.91, 39.83, 31.71, 20.16, 13.80 ppm.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 8.2, 1.1 Hz, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.44 (t, *J* = 7.7 Hz, 2 H), 4.30 (t, *J* = 6.7 Hz, 2 H), 1.86 – 1.75 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.66, 132.81, 130.52, 129.53, 128.32, 66.51, 22.13, 10.54 ppm.

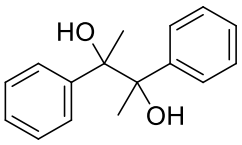


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 4.25 (t, *J* = 6.7 Hz, 2 H), 3.85 (s, 3 H), 1.84 – 1.70 (m, 2 H), 1.03 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.44, 163.25, 131.52, 122.93, 113.54, 66.22, 55.38, 22.16, 10.55 ppm.

General procedure for photo-induced homocoupling reaction of silyl enol ethers catalyzed by W1a:

To a test tube (10 mL) equipped with a magnetic stir bar were added **silyl enol ether** (0.5 mmol), **W1a** (1 mol%), DIPEA (1.25 mmol, 2.5 eq.), K_2CO_3 (0.5 mmol) and acetonitrile (5 mL). The reaction was stirred at room temperature under argon and 410 nm LEDs irradiation for 12 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers is washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2. An approximate *dl*:*meso* ratio is given for each product.

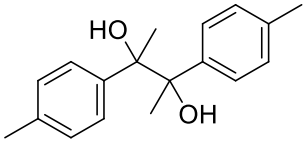
2,3-diphenylbutane-2,3-diol[11]



dl:*meso* = 5:3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 - 7.10 (m, 0.6 × 8H), 7.69 - 7.10 (m, 8 H), 7.24 -7.21 (m 0.6 × 2 H), 7.24 -7.21 (m, 2 H), 2.63 (s, 0.6 × 2 H), 2.58 (b, 2H), 1.61 (s, 0.6 × 6 H), 1.53 (s, 6 H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.78, 143.42, 127.39, 127.31, 127.18, 127.08, 126.94, 78.87, 78.61, 25.14, 24.98 ppm.

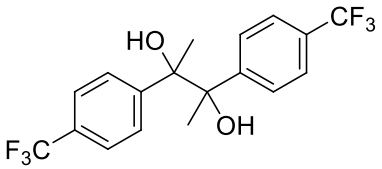
2,3-di-p-tolylbutane-2,3-diol[11a,12]



dl:*meso* = 1.2:1

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.2 Hz, 4 H), 7.14 (d, *J* = 8.4 Hz, 4 H), 7.09 (dd, *J* = 8.4, 2.4 Hz, 7 H), 2.38 (s, 5 H), 2.37 (s, 6 H), 1.58 (s, 5 H), 1.50 (s, 6 H) ppm.

2,3-bis(4-(trifluoromethyl)phenyl)butane-2,3-diol[13]

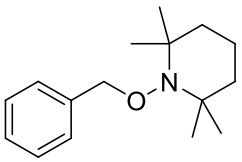


dl:*meso* = 5:2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 0.4 × 4 H), 7.53 (d, *J* = 8.4 Hz, 4 H) , 7.46 (d, *J* = 8.3 Hz, 0.4 × 4 H), 7.31 (d, *J* = 8.2 Hz, 4 H), 1.59 (s, 0.4 × 6 H), 1.55 (s, 6 H)； ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.47 (s) ppm.

Mechanistic Experiment

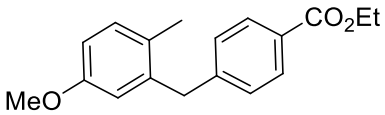
To a test tube (10 mL) equipped with a magnetic stir bar were added benzyl bromide (0.5 mmol), **W1a** (1 mol%), K_2CO_3 (0.5 mmol), DIPEA (1.25 mmol), TEMPO (0.5 mmol) and acetonitrile (5 mL). The reaction was stirred at room temperature under argon and 410 nm LEDs irradiation for 12 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers was washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent.



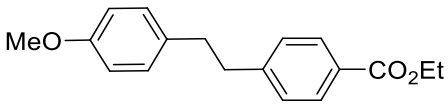
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 4 H), 7.37 – 7.30 (m, 1 H), 4.91 (s, 2 H), 1.69 – 1.50 (m, 5 H), 1.42 (d, *J* = 11.3 Hz, 1 H), 1.34 (s, 6 H), 1.23 (s, 6 H).

Cross Experiment

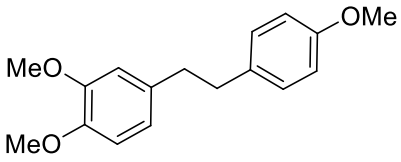
To a test tube (10 mL) equipped with a magnetic stir bar were added 1-(bromomethyl)-4-methoxybenzene (0.5 mmol), ethyl 4-(bromomethyl)benzoate (0.5 mmol), **W1a** (1 mol%), K_2CO_3 (1.0 mmol), DIPEA (1.25 mmol) and acetonitrile (5 mL). The reaction was stirred at room temperature under argon and 410 nm LEDs irradiation for 12 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers was washed in brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 4.39 (q, *J* = 7.1 Hz, 2 H), 3.81 (s, 3 H), 2.85 (s, 2 H), 2.43 (s, 3 H), 1.41 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.74, 157.83, 143.40, 133.99, 129.72, 129.57, 129.36, 129.01, 127.82, 113.73, 60.74, 55.25, 37.25, 21.61, 14.33.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2 H), 7.23 (d, *J* = 8.1 Hz, 2 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 6.84 (d, *J* = 8.5 Hz, 2 H), 4.39 (dd, *J* = 14.2, 7.1 Hz, 2 H), 3.81 (s, 3 H), 3.02 – 2.93 (m, 2 H), 2.92 – 2.81 (m, 2 H), 1.41 (t, *J* = 7.1 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ165.69, 156.87, 146.12, 132.21, 128.58, 128.34, 127.50, 127.16, 112.73, 59.78, 54.21, 37.12, 35.56, 13.32.



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 6.81 (d, *J* = 8.1 Hz, 1 H), 6.74 (dd, *J* = 8.1, 1.7 Hz, 1 H), 6.67 (d, *J* = 1.6 Hz, 1 H), 3.89 (s, 3 H), 3.86 (s, 3 H), 3.81 (s, 3 H), 2.86 (s, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.83, 148.65, 147.17, 134.49, 133.88, 129.44, 120.27, 113.71, 111.87, 111.12, 55.91, 55.78, 55.28, 37.79, 37.25.

Procedure for reaction of substrate 3f in the presence of styrene:

To a test tube (10 mL) equipped with a magnetic stir bar were added ethyl 4-(bromomethyl)benzoate (0.75 mmol, 1.5 eq), **W1a** (1 mol%), K_2CO_3 (0.50 mmol), 4-methoxystyrene (0.5 mmol, 1.0 eq), DIPEA (1.25 mmol, 2.5 eq) and acetonitrile (5 mL). the mixture was purged with argon for 15 min. Then the reaction was stirred at room temperature under argon and 410 nm LEDs irradiation for 12 h. The reaction mixture was partitioned between dichloromethane and water. The aqueous layer was extracted with DCM. The combined organic layers was washed with brine and dried over sodium sulfate. The organic solvent was removed by reduced pressure. The desired product was purified by chromatography column on SiO_2 using petroleum ether and ethyl acetate mixtures as eluting solvent.

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