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 $\delta$ 0.0 ppm and $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ as internal standard. Chemical shifts ($\delta$) 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$_3$CN as the standard ($\Phi = 0.062$) and calculated by: $\Phi_s = \Phi_r (B_r/B_s)(D_s/D_r)$, 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 $\Phi$ is the luminescence quantum yield. The excitation intensity $B$ is calculated by: $B = 1-10^{-A_L}$, where $A$ is the absorbance at the excitation wavelength and $L$ is the optical path length ($\lambda = 1$ 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 $\lambda$ values ($\pm 1$ nm), $\tau$ ($\pm 10 \%$), and $\Phi$ ($\pm 10 \%$) are estimated. Singlet oxygen quantum yield was determined with meso-tetraphenylporphyrin (H$_2$TPP) as a reference ($\Phi_{O_2} = 0.55$ 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-NPh₂: 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). ¹H NMR (400 MHz, CDCl₃) 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, 4 H), 1.13 (s, 6 H).

Synthesis of Salen-Carb: The procedure was similar to that of Salen-NPh₂ except that 4’-(9H-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). ¹H 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\(_3\)) \(\delta\) 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**

![Diagram of W1a, WO\(_2\)-Salen-NPh\(_2\)](image)

Synthesis of **W1a**: A suspension of W(eg)\(_3\) (0.77 g, 2.1 mmol) in 20 mL methanol, was heated to 60 °C 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 °C 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.

![Diagram of W1b, WO\(_2\)-Salen-Carb](image)

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, \(\nu\) cm\(^{-1}\)): 933.55 (W=O), 896.90 (W=O). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.28 (s, 1H, \(J_{W-H} = 11.0\) 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, \(J = 12.0\) Hz), 3.50 (d, 1H, \(J = 1.0\) Hz), 3.50 (d, 1H, \(J = 12.5\) Hz), 1.22 (s, 3H), 0.86 (s, 3H). \(^{13}\)C\({}^1\)H NMR (125 MHz, CDCl\(_3\)): \(\delta\) 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\(_{12}\)N\(_4\)O\(_4\)W·CH\(_3\)OH: C, 64.75; H, 4.46; N, 5.39; Found: C, 64.66; H, 4.20; N, 5.56.
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

| Complex | Medium  | $\lambda_{\text{abs}}$ [nm] | $\lambda_{\text{em}}$ [nm] | $\tau$ [μs] | $k_r$ $[10^3 \text{ s}^{-1}]$ | $\Phi_{\text{em}}$ $^b$ |
|---------|---------|-----------------------------|-----------------------------|-------------|-------------------------------|---------------------|
| W1a     | CH$_2$Cl$_2$ | 297 (43.7), 407 (34.6) | 608 | 4.6 | 23.9 | 0.11 |
|         | CHCl$_3$  | 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$_2$Cl$_2$ | 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$_2$Cl$_2$ | 270 (26.2), 299 (18.2), 402 (5.5) | 582 | 83.6 | 0.4 | 0.03 |
|         | CHCl$_3$  | 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 ($\Phi$) were estimated with [Ru(2,2‘-bipyridine)$_3$](PF$_6$)$_2$ in degassed CH$_3$CN as the standard ($\Phi = 0.062$). $^c$ 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 N₂. Potentials versus SCE.
**Table S3:** Photo-dehydrogenation reactions catalysed by W1a

![Catalyst Reaction Scheme](image)

| 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$_2$CO$_2$H | 365 nm | MeCN    | 60%$^b$      |
| 7     | W1a         | - - - - - | 365 nm     | MeCN    | 0%$^c$       |
| 8     | H$_2$TPP$^d$| - - - - - | 365 nm     | MeCN    | 15%          |
| 9     | - - - - -   | H$_2$O$_2$ | 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-1H-inden-1-yl 2,2-difluoroacetate A was obtained in 26% yield.

$^c$under inert atmosphere without O$_2$

$^d$H$_2$TPP stands for tetraphenylporphyrin
Table S4. Optimization of reaction conditions for borylation of aryl iodine

![Reaction Scheme]

| Entry | Catalyst | Base       | solvent | DIPEA (equiv) | conversion (%) | Yield (%)\(^a\) |
|-------|----------|------------|---------|---------------|---------------|-----------------|
| 1     | W1a      | \(^t\)BuONa | MeCN    | 2.5 eq        | 100\%          | 31\%            |
| 2     | W1a      | K\(_2\)CO\(_3\) | MeCN    | 2.5 eq        | 100\%          | 52\%            |
| 3     | W1a      | Cs\(_2\)CO\(_3\) | MeCN    | 2.5 eq        | 88\%           | 40\%            |
| 4     | W1a      | Na\(_2\)CO\(_3\) | MeCN    | 2.5 eq        | 78\%           | 32\%            |
| 5     | W1a      | NaHCO\(_3\) | MeCN    | 2.5 eq        | --             | 31\%            |
| 6     | W1a      | Na\(_2\)HPO\(_4\) | MeCN    | 2.5 eq        | --             | 43\%            |
| 7     | W1a      | NaOAc      | MeCN    | 2.5 eq        | 60\%           | 31\%            |
| 8     | W1a      | KH\(_2\)PO\(_4\) | MeCN    | 2.5 eq        | --             | 21\%            |
| 9     | W1a      | K\(_2\)CO\(_3\) | MeCN    | 0.5 eq        | 52\%           | 24\%            |
| 10    | W1a      | K\(_2\)CO\(_3\) | MeCN    | 1 eq          | 87\%           | 41\%            |
| 11    | W1a      | K\(_2\)CO\(_3\) | MeCN    | 2 eq          | 100\%          | 50\%            |
| 12    | W1a      | K\(_2\)CO\(_3\) | MeCN    | 5 eq          | 100\%          | 40\%            |
| 13    | W1a      | . . . . . . | MeCN    | 2.5 eq        | 0\%            | 0\%             |
| 14    | W1a      | K\(_2\)CO\(_3\) | MeCN    | - - - -        | 32\%           | 12\%            |
| 15    | W1a      | K\(_2\)CO\(_3\) | MeCN    | DABCO         | 38\%           | 30\%            |
| 16    | W1a      | K\(_2\)CO\(_3\) | MeCN    | DBU           | 100\%          | 50\%            |
| 17    | W1a      | K\(_2\)CO\(_3\) | MeCN    | TEA           | 32\%           | 32\%            |
| 18    | W1a      | K\(_2\)CO\(_3\) | DCE     | 2.5 eq        | 0\%            | 0\%             |
| 19    | W1a      | K\(_2\)CO\(_3\) | acetone | 2.5 eq        | 40\%           | 20\%            |
| 20    | W1a      | K\(_2\)CO\(_3\) | THF     | 2.5 eq        | 0\%            | 0\%             |
| 21    | W1a      | K\(_2\)CO\(_3\) | toluene | 2.5 eq        | 0\%            | 0\%             |
| 22    | W1a      | K\(_2\)CO\(_3\) | ACN/H\(_2\)O | 2.5 eq       | 100\%          | 60\%            |
| 23    | W1a      | K\(_2\)CO\(_3\) | MeCN\(^b\) | 2.5 eq       | 100\%          | 50\%            |
| 24    | . . . . . . | K\(_2\)CO\(_3\) | MeCN    | 2.5 eq        | 0\%            | 0\%             |

\(^a\)Yields were determined by \(^1\)H NMR using dibromomethane as internal standard

\(^b\)The solvent was anhydrous
Table S5. Optimization of conditions for C-B bond formation from aryl chloride

![Chemical structures](image)

| entry | catalyst | additive   | conversion | yield (%)<sup>a</sup> | 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      | dimethylaniiline | 100% | 0%                    | 79%|     |
| 7     | W1a      | tetrahydrothiophene | 90% | 58%                    | 26%|     |
| 8     | W1a      | AllylPhS   | 75%        | 46%                    | 25%|     |
| 9     | W1a      | 1 eq Me₂S | 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/H₂O| 10%        | 0%                     | 8% |     |
| 14    | W1a      | PPh₃       | 5%         | 0%                     | 5% |     |
| 15    | W1a      | 1 eq TBAB  | 100%       | 89%                    | 9% |     |
| 16    | W1a      | TBAB/KI    | 100%       | 90%                    | 8% |     |
| 17    | -------  | TBAB       | 25%        | 20%                    | 0% |     |
| 18<sup>b</sup> | W1a | ------   | 0%         | 0%                     | 0% |     |
| 19    | W1a      | TBAB       | 100%       | 50%                    | 10%|     |
| 20    | W1c      | TBAB       | 20%        | 14%                    | 0% |     |
| 21    | W1b      | TBAB       | 36%        | 30%                    | 3% |     |
| 22<sup>c</sup> | ------- | TBAB      | 100%       | 68%                    | 10%|     |

<sup>a</sup> Reaction conditions: 1b(0.2 mmol), B₂Pin₂(0.22 mmol), WO₂-Salen (1 mol%), K₂CO₃ (0.2 mmol), in MeCN at room temperature for 12 h. yields were determined by ¹H NMR using dibromomethane as internal standard.<sup>a</sup>no light. <sup>c</sup> Reaction time = 48 hours.
Figure S1. $^1$H NMR spectral traces of W1a in degassed CD$_2$Cl$_2$ upon 450 nm LEDs irradiation.

Figure S2. Emission spectra of a) W1b and b) W1c in CH$_2$Cl$_2$ under aerated condition and under N$_2$.

Figure S3. Excitation spectra of a) W1b and b) W1c in CH$_2$Cl$_2$ under aerated and degassed condition.
Figure S4. Emission spectra of W1a in CH₂Cl₂ under aerated condition and under N₂.

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

Figure S6. ns-TA spectra of W1a and W1b in CH₂Cl₂ at room temperature.
Figure S7. fs-TA spectra of W1a in CH₂Cl₂ at room temperature with 266 nm excitation.

Figure S8. fs-TA spectra of W1c in CH₂Cl₂ at room temperature with 400 nm excitation.\textsuperscript{[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 N₂.
**Figure S10. Mechanistic experiments.**
**Figure S11.** $^1$H NMR spectral traces of W1a and 1.5 molar equivalent of DIPEA in degassed CD$_2$Cl$_2$ 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$_2$Cl$_2$ 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 different 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 \( \eta = 1.4969 \)). 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. \( \text{NImag} = 0 \)). 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).

![Figure S15. Simulated absorption spectra of W1a and W1c at their respective optimized S0 geometry.](image)

W1a

W1c
Table S6. $S_0 \rightarrow S_n$ Absorption energies of complex $W1a$ at the optimized $S_0$ geometry in toluene solution.

| n | $\lambda$ (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%) |
Table S7. $S_0 \rightarrow S_n$ Absorption energies of complex W1c at the optimized $S_0$ geometry in toluene solution.

| n | $\lambda$ / nm | $f$ | Major contributions |
|---|---|---|---|
| 1 | 370 | 0.078 | HOMO$\rightarrow$LUMO (93%) |
| 2 | 339 | 0.0201 | H-1$\rightarrow$LUMO (89%) |
| 3 | 320 | 0.039 | HOMO$\rightarrow$L+1 (92%) |
| 4 | 303 | 0.0646 | H-1$\rightarrow$L+1 (87%) |
| 5 | 291 | 0.0106 | HOMO$\rightarrow$L+2 (82%) |
| 6 | 289 | 0.1031 | H-3$\rightarrow$LUMO (14%), H-3$\rightarrow$LUMO (63%) |
| 7 | 283 | 0.0139 | H-4$\rightarrow$LUMO (40%), H-2$\rightarrow$LUMO (27%) |
| 8 | 279 | 0.0127 | HOMO$\rightarrow$L+3 (74%) |
| 9 | 276 | 0.0992 | H-4$\rightarrow$LUMO (34%), H-2$\rightarrow$LUMO (43%) |
| 10 | 270 | 0.0432 | H-2$\rightarrow$LUMO (10%), H-2$\rightarrow$L+1 (10%), H-1$\rightarrow$L+2 (54%) |
| 11 | 267 | 0.0919 | H-5$\rightarrow$LUMO (39%), H-3$\rightarrow$LUMO (13%), H-1$\rightarrow$L+3 (21%) |
| 12 | 265 | 0.024 | H-3$\rightarrow$LUMO (11%), H-1$\rightarrow$L+3 (58%) |
| 13 | 257 | 0.0468 | H-6$\rightarrow$LUMO (10%), H-4$\rightarrow$L+1 (16%), H-4$\rightarrow$L+2 (20%), H-1$\rightarrow$L+2 (10%) |
| 14 | 253 | 0.0567 | H-4$\rightarrow$L+2 (17%), H-3$\rightarrow$L+1 (10%), H-2$\rightarrow$L+1 (25%) |
| 15 | 250 | 0.0316 | H-3$\rightarrow$L+1 (23%), HOMO$\rightarrow$L+4 (39%), HOMO$\rightarrow$L+5 (17%) |
| 16 | 248 | 0.1077 | H-6$\rightarrow$LUMO (12%), H-3$\rightarrow$L+1 (37%), HOMO$\rightarrow$L+4 (25%) |
| 17 | 247 | 0.209 | H-2$\rightarrow$L+1 (26%), H-1$\rightarrow$L+5 (13%) |
| 18 | 245 | 0.0456 | HOMO$\rightarrow$L+4 (15%), HOMO$\rightarrow$L+5 (70%) |
| 19 | 239 | 0.0267 | H-6$\rightarrow$LUMO (16%), H-4$\rightarrow$L+1 (36%), H-4$\rightarrow$L+3 (18%) |
| 20 | 238 | 0.0149 | H-1$\rightarrow$L+4 (58%), H-1$\rightarrow$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 S0 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\textsubscript{0}→S\textsubscript{2} (top) and S\textsubscript{0} → S\textsubscript{3} (bottom) excitation in toluene solution at the optimized S\textsubscript{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\textsubscript{0}→S\textsubscript{2} (top) and S\textsubscript{0} → S\textsubscript{3} (bottom) excitation in toluene solution at the optimized S\textsubscript{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 |
Table S10. Cartesian coordinates of complex W1a at its optimized S0 geometry.

| Center | Atomic Number | Atomic Type | 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| -2.92270 |
|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  | -12.235773 |
| 67| 6 | 0 | 0.176288  | -0.935828 | -12.286393 |
| 68| 6 | 0 | 0.310146  | 0.016734  | -12.235773 |
| 69| 1 | 0 | 0.176288  | -0.935828 | -12.286393 |
| 70| 6 | 0 | 4.091774  | 0.750798  | -13.074637 |
| 71| 1 | 0 | 4.742229  | 0.240031  | -13.782747 |
| 72| 6 | 0 | 4.091774  | 0.750798  | -13.074637 |
| 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  | 100  | 101  | 102  | 103  | 104  | 105  | 106  | 107  | 108  | 109  | 110  |
|---|---|---|-----|------|------|------|------|------|------|------|------|------|------|------|
|   |   |   |  1  |   0  |  -1  |  -1  |  -1  |  -1  |  -0  |  0  |  1  |  6  |  6  |  6  |
|   |   |   | -2.285851 | -1.011913 | -1.405716 | -2.173973 | -0.820054 | -1.136348 | 0.151909 | 0.541323 | 1.310414 | -0.028384 | 0.286293 | 0.604574 |
|   |   |   |  -13.152403 | -7.793860 | -8.470985 | -9.239808 | -8.163489 | -8.699056 | -7.169580 | -6.491520 | -5.720835 | -6.803122 | -6.281901 | -6.924363 |
|   |   |   |    |      |      |      |      |      |      |      |      |      |      |      |
Figure S21. The energy profile for the benzyl homocoupling and the cross-coupling to W1a•−/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•− (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 SiO2 using petroleum ether and ethyl acetate mixtures as eluting solvent. For the entry with the addition of H2O2, 1 molar equivalent of aqueous H2O2 was added.

\[ \text{EtO}_2\text{C-} \quad \text{CO}_2\text{Et} \]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$Pin$_2$ (0.55 mmol), W1a (1 mol%), K$_2$CO$_3$ (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 SiO2 using petroleum ether and ethyl acetate mixtures as eluting solvent.

\[ \text{EtO}_2\text{C-} \quad \text{BO} \quad \text{O} \]

S32
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 166.69, 134.63, 132.66, 128.57, 84.17, 61.06, 24.89, 14.33 ppm.

![Structure 1]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 167.14, 134.67, 132.30, 128.60, 84.18, 52.16, 24.89 ppm.

![Structure 2]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 135.21, 133.99, 131.76, 129.35, 127.62, 126.67, 125.94, 124.76, 82.90, 23.89 ppm.

![Structure 3]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 142.84, 139.94, 134.22, 127.72, 126.51, 126.18, 125.42, 82.77, 23.83 ppm.

![Structure 4]

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 198.53, 138.99, 134.93, 128.59, 128.33, 127.31, 84.23, 26.79, 24.89 ppm.

![Structure 5]

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 134.07, 130.13, 117.87, 113.50, 83.48, 23.84 ppm.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 166.97, 134.65, 132.04, 128.68, 84.22, 66.63, 60.81, 24.83 ppm.

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 140.39, 133.77, 127.50, 82.59, 23.82, 20.71 ppm.

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 141.08, 137.89, 126.41, 82.43, 23.92, 21.16, 20.21 ppm.

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$Pin$_2$ (0.55 mmol), K$_2$CO$_3$ (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$_3$) $\delta$ 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$_3$) $\delta$ 146.17, 132.27, 129.28, 118.84, 110.11, 37.16 ppm.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 157.80, 133.99, 129.76, 129.40, 113.86, 113.72, 55.27, 37.32 ppm.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ -62.32 (s, 6 F); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 197.83, 146.74, 135.30, 128.73, 128.59, 37.32, 26.60 ppm.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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.
**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 SiO₂ using petroleum ether and ethyl acetate mixtures as eluting solvent.

\[ ^1H \text{ NMR (500 MHz, CDCl}_3 \delta 7.19 \ (d, J = 8.0 \text{ Hz}, 4 \text{ H}), 7.16 \ (d, J = 8.0 \text{ Hz}, 4 \text{ H}), 7.00 \ (d, J = 8.1 \text{ Hz}, 4 \text{ H}), 6.97 \ (d, J = 8.1 \text{ Hz}, 4 \text{ H}), 2.95 \ (dt, J = 6.6, 5.0 \text{ Hz}, 2 \text{ H}), 2.82 \ (dt, J = 6.2, 4.0 \text{ Hz}, 2 \text{ H}), 2.54 \ (d, J = 7.2 \text{ Hz}, 4 \text{ H}), 2.46 \ (d, J = 7.2 \text{ Hz}, 4 \text{ H}), 1.94 \ (dt, J = 13.5, 6.8 \text{ Hz}, 2 \text{ H}), 1.87 \ (dt, J = 13.5, 6.8 \text{ Hz}, 2 \text{ H}), 1.34 \ (d, J = 6.6 \text{ Hz}, 6 \text{ H}), 1.09 \ (d, J = 6.3 \text{ Hz}, 6 \text{ H}), 0.99 \ (d, J = 6.6 \text{ Hz}, 12 \text{ H}), 0.93 \ (dd, J = 6.6, 1.4 \text{ Hz}, 12 \text{ H}); ^13C \text{ NMR (126 MHz, CDCl}_3 \delta 143.88, 143.18, 139.29, 138.88, 129.01 (, 128.46, 127.57, 127.34, 47.03, 46.36, 45.17, 45.07, 30.35, 30.30, 22.50, 22.40. 21.15, 17.49 ppm.} \]
1H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ -117.27 (tt, $J = 8.4$, 5.4 Hz, 2 F), -117.57 (tt, $J = 8.3$, 5.5 Hz, 2 F) ppm.

1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 8.3$ Hz, 4 H), 7.31 (d, $J = 8.5$ Hz, 4 H), 7.05 (d, $J = 8.4$ Hz, 4 H), 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$_3$) $\delta$ 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.

1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (t, $J = 7.4$ Hz, 4 H), 7.30 – 7.26 (m, 2 H), 7.26 – 7.22 (m, 4 H), 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 (dt, $J = 13.5$, 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$_3$) $\delta$ 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.
132.36, 131.84, 131.75, 130.06, 129.98, 129.41, 128.30, 128.24, 128.03, 127.82, 46.96, 46.85, 20.67, 19.09 ppm.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 146.84, 128.67, 126.68, 125.53, 43.68, 25.25 ppm.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 142.59, 128.44, 128.28, 125.67, 35.85, 31.13 ppm.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 139.20, 114.16, 33.81, 28.99, 28.89 ppm.

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

To a test tube (10 mL) equipped with a magnetic stir bar were added bromide α-bromoacetophenone (0.5 mmol), B$_2$Pin$_2$ (0.55 mmol), **W1a** (1 mol%), K$_2$CO$_3$ (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.

\[
\text{\includegraphics{image1}}
\]

$^1$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.

\[
\text{\includegraphics{image2}}
\]

$^1$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.

\[
\text{\includegraphics{image3}}
\]

$^1$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.

\[
\text{\includegraphics{image4}}
\]

$^1$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 (ddd, 2.42) ppm.
\( J = 7.2, 3.1, 1.4 \text{ Hz}, 2 \text{ H} \), 2.55 – 2.37 (m, 2.3 H) ; **\(^1\)C NMR (101 MHz, CDCl\(_3\)) \( \delta 141.50, 137.74, 131.43, 130.41, 128.54, 128.50, 128.40, 127.72, 127.01, 126.98, 126.39, 126.07, 126.04, 114.70, 50.05, 39.09, 32.97 \text{ ppm}.\)

**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\(_3\)N (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.

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\begin{align*}
\text{MeO} & \quad \text{CN} \\
\text{H NMR (500 MHz, CDCl} & _3\text{)} \, \delta 7.82 – 7.72 \text{ (m, 3 H)}, 7.41 \text{ (dd, } J = 8.4, 1.9 \text{ Hz, 1 H}), 7.21 \text{ (dd, } J = 8.9, 2.5 \text{ Hz, 1 H}), 7.16 \text{ (d, } J = 2.4 \text{ Hz, 1 H}), 4.04 \text{ (q, } J = 7.3 \text{ Hz, 1H}), 3.94 \text{ (s, 3 H), 1.73 \text{ (d, } J = 7.3 \text{ Hz, 3 H}); \, ^1\text{C NMR (126 MHz, CDCl} & _3\text{)} \, \delta 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 \text{ ppm.}\]
\end{align*}
\]

\[
\begin{align*}
\text{F} & \quad \text{CN} \\
\text{H NMR (500 MHz, CDCl} & _3\text{)} \, \delta 7.26 \text{ (dd, } J = 8.4, 5.2 \text{ Hz, 2 H}), 7.00 \text{ (t, } J = 8.5 \text{ Hz, 2 H}), 3.82 \text{ (q, } J = 7.3 \text{ Hz, 1 H), 1.56 \text{ (d, } J = 7.4 \text{ Hz, 3 H}); \, ^1\text{C NMR (126 MHz, CDCl} & _3\text{)} \, \delta 161.31 \text{ (d, } J = 247.2 \text{ Hz), 131.80 \text{ (d, } J = 3.3 \text{ Hz), 127.40 \text{ (d, } J = 8.3 \text{ Hz), 120.37, 115.07 \text{ (d, } J = 21.8 \text{ Hz), 29.56, 20.49 \}; \, ^19\text{F NMR (376 MHz, CDCl} & _3\text{)} \, \delta -113.93 \text{ (tt, } J = 8.6, 5.2 \text{ Hz, 1 F) ppm.}\]
\end{align*}
\]
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 134.48, 133.03, 128.31, 127.07, 120.10, 29.71, 20.36 ppm.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 135.76, 129.03, 128.02, 127.31, 120.79, 38.93, 29.24, 11.51 ppm.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_2$CO$_3$ (0.5 mmol, 1 eq.) in 5 mL CH$_3$CN 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$_2$Cl$_2$/H$_2$O. The residue was purified by silica-gel column chromatography to give the product.

$\text{O} \quad \text{OEt}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 166.67, 132.83, 130.50, 129.54, 128.33, 60.98, 14.35 ppm

$\text{NC} \quad \text{H}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 132.83, 132.15, 129.15, 118.88, 112.41 ppm.

$\text{Ph} \quad \text{H}$

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J$ = 7.8 Hz, 4 H), 7.52 (t, $J$ = 7.6 Hz, 4 H), 7.42 (t, $J$ = 7.4 Hz, 2 H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 141.26, 128.79, 127.28, 127.20 ppm.

$\text{Cl} \quad \text{O} \quad \text{OMe} \quad \text{H}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 165.78, 134.42, 132.89, 131.79, 129.67, 129.57, 127.64, 52.34 ppm.

$\text{O} \quad \text{H}$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 198.19, 137.08, 133.12, 128.57, 128.30, 26.62 ppm.
1H NMR (500 MHz, CDCl3) 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); 13C NMR (126 MHz, CDCl3) δ 166.98, 133.14, 129.65, 128.37, 66.58, 60.93 ppm.

\[
\text{N} \quad \text{Bu} \\
\text{H} \\
\text{H}
\]

1H NMR (500 MHz, CDCl3) 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); 13C NMR (126 MHz, CDCl3) δ 167.67, 134.82, 131.25, 128.46, 126.91, 39.83, 31.71, 20.16, 13.80 ppm.

\[
\text{O} \\
\text{Me} \\
\text{H}
\]

1H NMR (400 MHz, CDCl3) 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); 13C NMR (101 MHz, CDCl3) δ 166.66, 132.81, 130.52, 129.53, 128.32, 66.51, 22.13, 10.54 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.), K2CO3 (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 SiO2. An approximate dl:meso ratio is given for each product.

2,3-diphenylbutane-2,3-diol\textsuperscript{[11]}
$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.69 - 7.10 (m, 0.6 $\times$ 8H), 7.69 - 7.10 (m, 8 H), 7.24 -7.21 (m 0.6 $\times$ 2 H), 7.24 -7.21 (m, 2 H), 2.63 (s, 0.6 $\times$ 2 H), 2.58 (b, 2H), 1.61 (s, 0.6 $\times$ 6 H), 1.53 (s, 6 H); $^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 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-tolybutane-2,3-diol$^{[11a,12]}$

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 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$^{[13]}$

$^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.53 (d, $J$ = 8.4 Hz, 0.4 $\times$ 4 H), 7.53 (d, $J$ = 8.4 Hz, 4 H), 7.46 (d, $J$ = 8.3 Hz, 0.4 $\times$ 4 H), 7.31 (d, $J$ = 8.2 Hz, 4 H), 1.59 (s, 0.4 $\times$ 6 H), 1.55 (s, 6 H); $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -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$_2$CO$_3$ (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.
\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \delta 7.47 \text{– 7.37 (m, 4 H), 7.37 \text{– 7.30 (m, 1 H), 4.91 (s, 2 H), 1.69 \text{– 1.50 (m, 5 H), 1.42 (d, } J = 11.3 \text{ 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$_2$CO$_3$ (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.

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \delta 7.96 (d, \( J = 8.2 \text{ Hz, 2 H}), 7.26 (d, J = 8.0 \text{ Hz, 2 H}), 7.10 (d, J = 8.6 \text{ Hz, 2 H}), 6.84 (d, J = 8.6 \text{ Hz, 2 H}), 4.39 (q, J = 7.1 \text{ Hz, 2 H}), 3.81 (s, 3 H), 2.85 (s, 2 H), 2.43 (s, 3 H), 1.41 (t, J = 7.1 \text{ Hz, 3 H).} \]

13C NMR (101 MHz, CDCl$_3$) \( \delta 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 \].

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \] \delta 7.97 (d, \( J = 8.1 \text{ Hz, 2 H}), 7.23 (d, J = 8.1 \text{ Hz, 2 H}), 7.08 (d, J = 8.5 \text{ Hz, 2 H}), 6.84 (d, J = 8.5 \text{ Hz, 2 H}), 4.39 (dd, J = 14.2, 7.1 \text{ 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 \text{ Hz, 2 H);} \]

13C NMR (126 MHz, CDCl$_3$) \( \delta 165.69, 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 \].
1H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 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); 13C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 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\textsubscript{2}CO\textsubscript{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\textsubscript{2} using petroleum ether and ethyl acetate mixtures as eluting solvent.

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