# **Table of Contents**

Section S1.	General methods	S2
Section S2.	Photoirradiation system	S3
Section S3.	Synthesis of photosensitizers	S4
Section S4.	Spectroscopic analysis of the deprotonation of the PSs	S7
Section S5.	Computational study of the PS molecules	S12
Section S6.	Cyclic voltammetric measurements	S14
Section S7.	Measurement of fluorescence lifetime and quantum yield	S15
Section S8.	Photochemical reactions using the developed PSs	S17
Section S9.	Fluorescence quenching experiments	S25
Section S10.	Exploration of electron donor-acceptor (EDA) complex and exciplex between PS1 and 1a	S28
Section S11.	Exploration of EDA complex and exciplex between PS1 and 3a	S29
Section S12.	Deuterium labelling experiments	<b>S</b> 31
Section S13.	Study on the formation of dimsyl anion from DMSO and Cs <sub>2</sub> CO <sub>3</sub>	S32
Section S14.	Calculation of BDEs	S35
Section S15.	Determination of reaction quantum yields	S36
Section S16.	Possible chain propagation mechanism in the hydrodefluorination	S38
Section S17.	Effect of water on the photochemical Birch-type reaction	S38
Section S18.	Calculated molecular structures	S39
Section S19.	NMR spectra	S53
Section S20.	GC spectra	S66
Section S21.	Reference	S68

# Section S1. General methods

Unless otherwise noted, all reactions were conducted in well cleaned glasswares with magnetic stirring. Operations were performed under an atmosphere of argon using Schlenk and vacuum techniques, unless otherwise noted. All starting materials were purchased from commercial sources or were synthesized using standard procedures. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} NMR spectra (400 and 100 MHz, respectively) were recorded on a Bruker Avance III HD 400. Residual solvent peak(s) for <sup>1</sup>H NMR analysis (CDCl<sub>3</sub> (7.26 ppm), DMSO-d<sub>6</sub> (2.50 ppm), (CD<sub>3</sub>)<sub>2</sub>CO (2.05 ppm)) and deuterated solvent peak(s) for  $^{13}C{^{1}H}$  NMR analysis (CDCl<sub>3</sub> (77.2 ppm), DMSO- $d_6$  (39.5 ppm), (CD<sub>3</sub>)<sub>2</sub>CO (29.8 ppm)) were used as internal references. The following abbreviations are used in connection with NMR; s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, and m = multiplet. Mass spectra were measured using LTQ Orbitrap XL (Thermo Fisher Scientific, Brehmen, Germany) with an electrospray ionization (ESI) ion source and an atmospheric pressure chemical ionization (APCI). Preparative column chromatography was performed using Kanto Chemical silica gel 60 N (spherical, neutral). Analytical thin layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F<sub>254</sub> aluminium sheets. The photocatalytic hydrodefluorination and Birch-type reduction reactions with visible light were performed under self-manufactured LED lamp sets  $(\lambda_{max} = 440 \text{ nm or } 480 \text{ nm})$ . At the end of the reaction, the temperature of reaction mixture was determined to be  $45 \pm 5$  °C by an electronic thermometer when more than 2 mol% of photosensitizer (PS) was used. Photoluminescence spectra were recorded on a spectrofluorometer (JASCO FP-6500) with a 1 cm  $\times$  1 cm quartz absorption cuvette (light path: 1 cm). UV-vis spectra were recorded on a JASCO V-670 spectrophotometer with a 1 cm  $\times$  1 cm quartz absorption cuvette (light path: 1 cm). GC analyses were performed using a Shimazu GC-2025 gas chromatograph equipped with GL Science Inertcap 5 and flame ionization detector. Cyclic voltammetric measurements were performed at 298 K on an ALS CHI606S electrochemical analyzer, using a solvent deaerated by argon bubbling for 10 min before each measurement. The supporting electrolyte was 0.10 Μ tetrabutylammonium hexafluorophosphate or tetrabutylammonium perchlorate. A conventional three-electrode cell with a glassy carbon working electrode and platinum wire as the counter electrode was employed. The cyclic voltammograms were recorded with respect to the Ag/AgNO<sub>3</sub> (10 mM) reference electrode at a sweep rate of 100 mV/s. The oxidation potentials were corrected to the SCE scale based on the measurement of the Fc/Fc<sup>+</sup> couple redox potential as the standard (0.38 V vs SCE).<sup>1</sup> The water content in DMSO was determined by Karl-Fischer titration (model: CA-21, Mitsubishi Chemical Analytech Co. Ltd.). The DMSO used in this study contains 800 ppm w/w of water, unless otherwise noted.

# Section S2. Photoirradiation system

Visible-light irradiation of reactions was performed using a self-manufactured LED lamp (Hontiey, 50 W, 50 LED chips on a plate,  $\lambda_{max} = 440$  nm or 480 nm) with fan cooling. The reaction set up is shown in Figure S1. Irradiation intensity of LED lamp was 250–280 mW/cm<sup>2</sup> at the distance of 3 cm from the light, determined by a power meter (Newport, 843-R with a photodiode sensor 818-UV/DB).



**Figure S1.** Photoirradiation system ( $\lambda_{max} = 440 \text{ nm or } 480 \text{ nm}$ ).

Section S3. Synthesis of photosensitizers



**3,6-Dimethoxy-9***H***-carbazole**: Under argon atmosphere, sodium (21.1 g, 923 mmol, 20.0 eq.) was dissolved in 250 mL MeOH and stirred for 1 hour at 0 °C in the flamedried three-neck flask. Then 3,6-dibromocarbazole (15 g, 46.2 mmol, 1.0 eq.), copper (I) iodide (17.6 g, 92.3 mmol, 2.0 eq.) and 500 mL DMF were added. The reaction was stirred at 80 °C for 48 hours. After cooled to room temperature, the reaction mixture was filtered with celite and washed by ethyl acetate. The organic phase was washed with brine four times, dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to afford 3,6-dimethoxy-9*H*-carbazole. (9.89 g, 43.5 mmol, 94% yield).

**3,6-Dimethoxy-9-phenyl-9***H***-carbazole (PS2):**<sup>2</sup> Pd<sub>2</sub>(dba)<sub>3</sub> (20.2 mg, 0.022 mmol, 1 mol%), *t*BuXPhos (46.7 mg, 0.11 mmol, 5 mol%) and 5 mL toluene were added in the flame-dried Schlenk tube under argon atmosphere, and stirred for 5 minutes to synthesize the complex in the first step. 3,6-Dimethoxy-9*H*-carbazole (500 mg, 2.2 mmol, 1.0 eq.), LiHMDS (1.84 g, 11 mmol, 5.0 eq.) and 5 mL toluene were added in this sequence. Then bromobenzene (0.47 g, 6.6 mmol, 3.0 eq.) was added dropwise in the mixture via syringe and the reaction was stirred at 100 °C for 5 hours. The reaction was quenched with excess water. The water phase was extracted with ethyl acetate three times. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to give crude product. The crude product was purified by column chromatography on SiO<sub>2</sub> (hexane : ethyl acetate = 9 : 1) to afford **PS2** (463.3 mg, 1.53 mmol, 69% yield) as white solid.



**9-Phenyl-9***H***-carbazol-3,6-diol (PS3):** 3,6-Dimethoxy-9-phenyl-9*H*-carbazole (300 mg, 0.99 mmol, 1.0 eq.) and pyridine hydrochloride (1.714 g, 14.83 mmol, 15.0 eq.) were added into a Schlenk tube under argon atmosphere. The reaction was stirred at 160 °C for 23 hours. After cooled to room temperature, excess water was added. The mixture was extracted with ethyl acetate three times, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give crude product. The crude product was purified by column chromatography on SiO<sub>2</sub> (hexane : ethyl acetate =1 : 1) to give **PS3** (259.1 mg, 0.94 mmol, 95% yield) as white solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  = 9.09 (s, 2H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.57–7.54 (m, 2H), 7.46–7.40 (m, 3H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 2H) ppm. <sup>13</sup>C NMR (100 MHz,

DMSO- $d_6$ )  $\delta = 151.6, 138.3, 135.0, 130.4, 127.1, 126.4, 123.8, 115.7, 110.5, 105.5 ppm. IR (neat): 3372, 1592, 1498, 1315, 1193, 1155, 816, 755, 700 cm<sup>-1</sup>. Mp 231.4–232.3 °C. HRMS m/z (ESI) calcd. for C<sub>18</sub>H<sub>12</sub>NO<sub>2</sub><sup>-</sup> (M – H)<sup>-</sup> 274.0874, found 274.0873.$ 



**6-Methoxy-9-phenyl-9***H***-carbazol-3-ol (PS1):<sup>3</sup>** 3,6-Dimethoxy-9-phenyl-9*H*-carbazole (100 mg, 0.33 mmol, 1.0 eq.) and pyridine hydrochloride (571 mg, 4.94 mmol, 15.0 eq.) were added into a Schlenk tube under argon atmosphere. The reaction was stirred at 160 °C for 1 hour. After cooled to room temperature, excess water was added. The mixture was extracted with ethyl acetate three times, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give crude product. The crude product was purified by column chromatography on SiO<sub>2</sub> (hexane : ethyl acetate =4 : 1) to give **PS1** (43.9 mg, 0.152 mmol, 46% yield) as white solid.



**9H-Carbazol-3,6-diol (PS5)**:<sup>4</sup> 3,6-Dimethoxy-9*H*-carbazole (400 mg, 1.76 mmol, 1.0 eq.) and pyridine hydrochloride (3.05 g, 26.40 mmol, 15.0 eq.) were added into a Schlenk tube under argon atmosphere. The reaction was stirred at 160 °C for 21 hours. After cooled to room temperature, excess water was added. The mixture was extracted with ethyl acetate three times, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give crude product. The crude product was purified by column chromatography on SiO<sub>2</sub> (hexane : ethyl acetate =1 : 1) to give **PS5** (306.6 mg, 1.54 mol, 87% yield).



**6-Methoxy-9***H***-carbazol-3-ol (PS4):** 3,6-Dimethoxy-9*H*-carbazole (220 mg, 0.97 mmol, 1.0 eq.) and pyridine hydrochloride (1.72 g, 14.9 mmol, 15.0 eq.) were added into Schlenk tube under argon atmosphere. The reaction was stirred at 160 °C for 2 hours. After cooled to room temperature, excess water was added. The mixture was extracted with ethyl acetate three times, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure to give crude product. The crude product was purified by column chromatography on SiO<sub>2</sub> (hexane : ethyl acetate =1 : 1) to give **PS4** (69.6 mg, 0.326 mol, 34% yield) as white solid. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>)  $\delta$  =

9.77 (s, 1H), 7.81 (s, 1H), 7.56–7.48 (m, 2H), 7.36–7.28 (m, 2H), 7.01–6.93 (m, 2H), 3.86 (s, 3H) ppm. <sup>13</sup>C NMR (100 MHz, acetone- $d_6$ )  $\delta = 153.3$ , 150.4, 135.9, 135.3, 123.8, 123.3, 115.0, 114.8, 111.4, 111.3, 104.9, 102.7, 55.2 ppm. IR (neat): 3418, 1504, 1455, 1359, 1203, 1187, 1025, 758, 700 cm<sup>-1</sup>. Mp 141.0–142.0 °C. HRMS m/z (ESI) calcd. for C<sub>13</sub>H<sub>10</sub>NO<sub>2</sub><sup>-</sup> (M – H)<sup>-</sup> 212.0717, found 212.0719.

## Section S4. Spectroscopic analysis of the deprotonation of the PSs

> <sup>1</sup>H NMR spectroscopic analysis of the deprotonation of **PS1** using Cs<sub>2</sub>CO<sub>3</sub>



Figure S2. <sup>1</sup>H NMR spectra of PS1 in the presence (A) and absence (B) of  $Cs_2CO_3$ . Solvent: DMSO- $d_6$ .

The sample solution for <sup>1</sup>H NMR spectroscopic analysis was prepared using **PS1** (2.9 mg, 0.01 mmol),  $Cs_2CO_3$  (10 mg, 0.03 mmol), and 0.5 mL of degassed DMSO-*d*<sub>6</sub>. The peak attributed to the proton of the hydroxy group disappeared and the other peaks shifted, suggesting that **PS1** was deprotonated.



<sup>1</sup>H NMR spectroscopic analysis of the deprotonation of PS3 using Cs<sub>2</sub>CO<sub>3</sub> or <sup>7</sup>BuOK

Figure S3. <sup>1</sup>H NMR spectra of PS3 with  $Cs_2CO_3$  (A), with 'BuOK (B), and without base (C). Solvent: DMSO- $d_6$ .

The sample solution for the <sup>1</sup>H NMR spectroscopic analysis was prepared using **PS3** (2.8 mg, 0.01 mmol),  $Cs_2CO_3$  (10 mg, 0.03 mmol) or 'BuOK (3.4 mg 0.03 mmol), and 0.5 mL of degassed DMSO-*d*<sub>6</sub>. The NMR spectra presented in Figures S2A and S3A exhibit similar chemical shifts. In contrast, the NMR spectrum shown in Figure S3B displays several peaks that are significantly shielded, with shifts up to 6.0 ppm, distinguishing it from the spectra in Figures S2A and S3A. These observations suggest that the species formed in Figure S3A is a mono-deprotonated species, while the species in Figure S3B corresponds to a bis-deprotonated form. The spectrum in Figure S3A shows a C<sub>2</sub>-symmetrical signal pattern, likely due to the exchangeable proton on the remaining hydroxy group within the NMR timescale.

> Absorption and fluorescence spectra of **PS3** in the presence and absence of base



**Figure S4.** Absorption spectra of **PS3** (green line), **PS3** and  $Cs_2CO_3$  (orange line), and **PS3** and 'BuOK (blue line) at 293 K. Solvent: DMSO, concentration of **PS3** solution: 100  $\mu$ M. The sample named "**PS3** +  $Cs_2CO_3$ " was prepared as follows; 10 mL of **PS3** solution (100  $\mu$ M in DMSO) was treated with 1.0 mmol of  $Cs_2CO_3$ , then the supernatant solution was transferred to the quartz cell. The sample named "**PS3** + 'BuOK' was prepared as follows; 10 mL of **PS3** solution (100  $\mu$ M in DMSO) was treated with 0.03 mmol of 'BuOK.



Figure S5. Fluorescence spectra of PS3 (green line), PS3 and Cs<sub>2</sub>CO<sub>3</sub> (orange line), and PS3 and 'BuOK (blue line) at 293 K. Solvent: DMSO, concentration of PS3: 10  $\mu$ M. The sample named "PS3 + Cs<sub>2</sub>CO<sub>3</sub>" was prepared as follows; 10 mL of PS3 solution (10  $\mu$ M in DMSO) was treated with 1.0 mmol of Cs<sub>2</sub>CO<sub>3</sub>, then the supernatant solution was transferred to the quartz cell. The sample named "PS3 + 'BuOK" was prepared as follows; 10 mL of PS3 solution (10  $\mu$ M in DMSO) was treated with 0.03

mmol of 'BuOK.

Carbazol-3,6-diol **PS3** in the presence of  $Cs_2CO_3$  showed the absorption and fluorescence spectra (Figures S4 and S5) similar to those of the deprotonated **PS1** (Figures 1c and 1d), which indicates that only one hydroxy group of the two in **PS3** was deprotonated by  $Cs_2CO_3$ . On the other hand, the absorption and fluorescence spectra of **PS3** in the presence of 'BuOK are distinct from those of the deprotonated **PS1**, suggesting that bis-deprotonated species of **PS3** is formed in the presence of 'BuOK. These observations are consistent with the results of <sup>1</sup>H NMR spectroscopic analysis (Figures S2 and S3).

# Comparison of absorption and fluorescence spectra of PS1 - PS5



**Figure S6.** Absorption spectra of PSs at 293 K. Solvent: DMSO, concentration: 100  $\mu$ M. The PS samples treated with Cs<sub>2</sub>CO<sub>3</sub> were prepared as follows; 10 mL of PS solution (100  $\mu$ M in DMSO) was treated with 1.0 mmol of Cs<sub>2</sub>CO<sub>3</sub>, then the supernatant solution was transferred to the quartz cell.



**Figure S7.** Normalized fluorescence spectra of **PS1**, **PS2**, and **PS3** at 293 K. Solvent: DMSO, concentration: 10  $\mu$ M, except the sample named "**PS1** + Cs<sub>2</sub>CO<sub>3</sub>" (100  $\mu$ M). The sample named "**PS1** + Cs<sub>2</sub>CO<sub>3</sub>" was prepared as follows; 10 mL of **PS3** solution (100  $\mu$ M in DMSO) was treated with 1.0 mmol of Cs<sub>2</sub>CO<sub>3</sub>, then the supernatant solution was transferred to the quartz cell. The sample named "**PS3** + Cs<sub>2</sub>CO<sub>3</sub>" was prepared as follows; 10 mL of **PS3** solution (10  $\mu$ M in DMSO) was treated with 0.1 mmol of Cs<sub>2</sub>CO<sub>3</sub>, then the supernatant solution was transferred to the supernatant solution (10  $\mu$ M in DMSO) was treated with 0.1 mmol of Cs<sub>2</sub>CO<sub>3</sub>, then the supernatant solution was transferred to the quartz cell.



**Figure S8.** Fluorescence spectra of **PS4** and **PS5** at 293 K. Solvent: DMSO, concentration: 10  $\mu$ M. The PS samples treated with Cs<sub>2</sub>CO<sub>3</sub> were prepared as follows; 10 mL of PS solution (10  $\mu$ M in DMSO) was treated with 0.1 mmol of Cs<sub>2</sub>CO<sub>3</sub>, then the supernatant solution was transferred to the quartz cell.

#### Section S5. Computational study of the PS molecules

**DFT calculations** All density functional theory (DFT) calculations were performed with the Gaussian 09 and 16 packages.<sup>5</sup> Geometry optimization and analytical vibrational frequency analysis for the ground state were performed by the B3LYP/6-31++G(d,p) DFT method and conductor-like polarizable continuum solvation model (CPCM, DMSO).<sup>6</sup> The excitation energies were calculated by the time-dependent (TD) DFT method using B3LYP functional with 6-31++G(d,p) basis set and conductor-like polarizable continuum solvation model (CPCM, DMSO) based on the optimized geometries of the ground states (for the prediction of absorption) and lowest-lying singlet excited states (for the prediction of fluorescence). Frequency analyses were also carried out to identify the stationary points (no imaginary frequency was confirmed for the optimized states). The calculated structures are shown in Section S14. Using the DFT results, the radiative decay rates were calculated based on the harmonic approximation with the FCclasses 3 packages.<sup>7</sup> The adiabatic Hessian model, the Frank-Condon-Herzberg-Teller method, the time-dependent formalism were employed.



Figure S9. Calculated lowest energy vertical excitation of PS2 and "PS1 +  $Cs_2CO_3$ " based on the ground-state geometries. The composition (contribution), excitation energy, and oscillator strength (*f*) are presented. The calculated orbital energy levels are presented in units of electron volts.



Figure S10. Absorption (dotted lines) and calculated oscillator strength (solid bars) of "PS1 +  $Cs_2CO_3$ " (orange) and PS2 (blue).



**Figure S11.** Calculated lowest energy vertical excitation of **PS2** and "**PS1** +  $Cs_2CO_3$ " based on the optimized geometries of the lowest-lying singlet excited states. The composition (contribution), excitation energy, and oscillator strength (*f*) are presented. The calculated orbital energy levels are presented in units of electron volts.

# Section S6. Cyclic voltammetric measurements

Refer to the description in Section S1 for details. Tetrabutylammonium hexafluorophosphate (3.87 g, 10 mmol) was dissolved in 100 mL of DMSO to prepare a 0.1 M electrolyte solution. The solutions made by mixing photosensitizers (0.1 mmol),  $Cs_2CO_3$  (325 mg), and 10 mL of the electrolyte solution were bubbled with argon gas for 10 min prior to measurement.



**Figure S12.** Cyclic voltammograms of PSs for the measurement of their oxidation potentials. Temp: 293 K, solvent: DMSO, WE: glassy carbon, RE:  $Ag/Ag^+$  with 0.1 M tetrabutylammonium perchlorate in MeCN, CE: platinum wire, electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate, sweep rate: 100 mV/s.

	$E_S$	$E_{\rm ox}$	${}^{1}E_{\mathrm{ox}}*$
	/eV	(vs SCE)	(vs SCE)
$\mathbf{PS1} + \mathbf{Cs_2CO_3}$	2.61	- 0.31	- 2.92
PS2	3.34	0.96	- 2.38
$\mathbf{PS3} + \mathbf{Cs}_2\mathbf{CO}_3$	2.67	- 0.38	- 3.05

Table S1. Optoelectronic data of PSs.

 $E_{\rm s}$ : singlet state energies approximated as the high-energy onset of fluorescence spectra, where the emission intensity is 10% of the obtained at the maximum emission wavelength.

 $E_{\text{ox}}$ : oxidation potentials of the ground state of molecules obtained from cyclic voltammetry analysis. When reversible cyclic voltammograms were obtained, standard reduction penitential ( $E^0$ ) were calculated by averaging the forward and reverse peak potentials. When irreversible cyclic voltammograms were obtained, half-peak potentials ( $E_{1/2}$ ), corresponding to the potential at half the maximum current of the cyclic voltammogram, were used as an estimate of  $E^0$ .

 ${}^{1}E_{\text{ox}}^{*}$ : oxidation potential of the singlet exited states of molecules, calculated from the ground state oxidation potential and the singlet state energy according to the following equation.<sup>8</sup>

 ${}^{1}E_{\mathrm{ox}} * = E_{\mathrm{ox}} - E_{\mathrm{s}}$ 

# Section S7. Measurement of fluorescence lifetime and quantum yield

Measurement of fluorescence lifetime

Time-resolved fluorescence measurements were performed using a streak scope Streak Scope C4334 with Imaging Spectrograph C5094 (Hamamatsu photonics, Ltd.). For the light excitation, a ps light pulser (C10196) of 403 nm and third harmonics (355 nm) of Nd:YAG laser (Continuum, Minilite II) were used. The pulse lengths were 46 ps (403 nm) and 5 ns (355 nm), respectively. The time profiles of the fluorescence data were fit by using single exponential decay functions with deconvoluting the profiles of the excitation pulses. The fittings were performed using an HPD-TA software (Hamamatsu photonics, Ltd.). The instrument response functions were measured using a DMSO solvent in a quartz cell with laser pulses. The time profiles were averaged from 493 nm to 563 nm (PS1) and from 378 nm to 432 nm (PS2) of the fluorescence data, respectively. A 10 mL DMSO solution of **PS1** (10  $\mu$ M) was treated with 1 mmol Cs<sub>2</sub>CO<sub>3</sub>, followed by argon bubbling for 10 minutes and ultrasonic treatment for 5 minutes. The supernatant solution (3 mL) was placed in a 1 cm × 1 cm quartz cell.



**Figure S13.** Time profile of the fluorescence together with the fitting data (red line) of **PS1**<sup>-</sup>. The decay was fit using the function of  $A_1 \exp(-t/\tau_1)$  with  $A_1 = 493.6$  and  $\tau_1 = 24.3$  ns.



**Figure S14.** Time profile of the fluorescence together with the fitting data (red line) of **PS2**. The decay was fit using the function of  $A_1 \exp(-t/\tau_1)$  with  $A_1 = 1540.0$  and  $\tau_1 = 6.4$  ns.

#### Measurement of fluorescence quantum yield

To derive fluorescence quantum yields, fluoresce spectra were recorded at 298 K on a spectrofluorometer equipped with an integrating sphere (JASCO FP-6600/ILFC-543L). The excitation wavelength was 420 nm and 350 nm for **PS1** +  $Cs_2CO_3$  (Sample 1) and **PS2** (Sample 2), respectively.

Sample 1 was prepared as follows: **PS1** (2.9 mg, 0.01 mmol) was dissolved in 10 mL of DMSO. Then, 1 mL of the resulting **PS1** solution (1 mM) was mixed with  $Cs_2CO_3$  (325 mg, 1 mmol) and diluted to a final volume of 5 mL with DMSO (deaerated by argon bubbling for 10 minutes). Next, 0.15 mL of the supernatant was transferred into a 5-mm diameter NMR tube. The final concentration of the sample was 0.2 mM.

Sample 2 was prepared as follows: **PS2** (3.0 mg, 0.01 mmol) was dissolved in 10 mL of DMSO. Then, 1 mL of the resulting **PS2** solution (1 mM) was diluted to a final volume of 5 mL with DMSO (deaerated by argon bubbling for 10 minutes). Then, 0.15 mL of the supernatant was transferred into a 5-mm diameter NMR tube. The final concentration of the sample was 0.2 mM.

# Section S8. Photochemical reactions using the developed PSs

#### Hydrodefluorination of aryl fluorides

#### **General procedure A**

**PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.), substrates (if solid, 0.2 mmol, 1.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.) and 2 mL DMSO were added into a Schlenk tube under argon atmosphere. After bubbling with argon for 10 min, substrates (if liquid, 0.2 mmol, 1.0 eq.) was added into the Schlenk tube via syringe. The reaction was stirred under irradiation with a 440 nm LED light for 24 hours. Typically, the internal temperature of the reaction solution during the reaction ranged from 40 to 50 °C with fan cooling. After the reaction, 33.6 mg of 1,3,5-trimethoxybenzene and 1 mL DMSO were added into the Schlenk tube (solution **A**).

To determine the product yield by <sup>1</sup>H NMR spectroscopic analysis, solution **A** was subjected to the analysis and the product yield was quantified using 1,3,5-trimethoxybenzene as an internal standard. Large signals derived from DMSO did not affect the analysis except **2h**.

To determine the product yield by GC analysis, 0.3 mL of solution **A** was diluted to 2 mL with acetone, and the resulting solution was subjected to the analysis. The yield was quantified using 1,3,5-trimethoxybenzene as an internal standard, with reference to a calibration curve established prior to the analysis.

For product **2h**, to avoid the overlap of the signals derived from solvent DMSO and the product, after the reaction, 0.7 mL CDCl<sub>3</sub>, 1 mL brine, 3 mL H<sub>2</sub>O and 33.6 mg 1,3,5-trimethoxybenzene were added. The CDCl<sub>3</sub> layer of the resulting solution was analyzed by <sup>1</sup>H NMR spectroscopy.

Table S2. Complete list of investigations into hydrodefluo	rınat	ion of	4-t	luoroanısol	e
--	-------	--------	-----	-------------	---



Entry	Variation from "standard condition"	Yield [%]
1	None	95
2	No light	0
3	Without Cs <sub>2</sub> CO <sub>3</sub>	< 5
4	Without <b>PS1</b>	< 5
5	Without HCOOK	12
6	PS2 instead of PS1	9
7	PS3 instead of PS1	83
8	PS4 instead of PS1	80
9	PS5 instead of PS1	78
10	PS6 instead of PS1	71
11	<i>i</i> Pr <sub>2</sub> NEt instead of HCOOK	45
12	K <sub>2</sub> CO <sub>3</sub> instead of Cs <sub>2</sub> CO <sub>3</sub>	10
13	DMF instead of DMSO	< 5 <sup>a</sup>
14	Cs <sub>2</sub> CO <sub>3</sub> (1.0 equiv)	27
15	Cs <sub>2</sub> CO <sub>3</sub> (2.0 equiv)	69
16	HCOOK (2.0 equiv)	80
17	HCOOK (3.0 equiv)	85
18	6 h instead of 24 h	43
19	<b>PS3</b> instead of <b>PS1</b> , 6 h instead of 24 h	66
20	γ-terpinene instead of HCOOK, 6 h instead of 24 h	20

Standard conditions: **PS1** (0.004 mmol, 2 mol%), potassium formate (0.8 mmol, 4.0 equiv),  $Cs_2CO_3$  (0.6 mmol, 3.0 equiv), 4-fluoroanisole (0.2 mmol, 1.0 equiv) and DMSO (2 mL), argon atmosphere, 24 h, NMR yield shown. <sup>a</sup>GC yield.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 4-fluoroanisole (25.2 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 95% determined by <sup>1</sup>H NMR spectroscopy.<sup>9</sup>



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 3-fluoroanisole (25.2 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 55% determined by <sup>1</sup>H NMR spectroscopy.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 2-fluoroanisole (25.2 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 75% determined by <sup>1</sup>H NMR spectroscopy.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), fluorobenzene (19.2 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 95% determined by <sup>1</sup>H NMR spectroscopy.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 4-fluorotoluene (22.0 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 98% determined by GC analysis.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 2-fluorotoluene (22.0 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 74% determined by GC analysis.



The general procedure A was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 4-fluorobiphenyl (34.4mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 45% determined by <sup>1</sup>H NMR spectroscopy.



The general procedure A was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 2-fluoro*m*-xylene (24.8 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 90% determined by <sup>1</sup>H NMR spectroscopy.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), methyl 4-fluorobenzoate (30.8 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 28% determined by GC analysis.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), methyl

4-fluorobenzonitrile (24.2 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 40% determined by GC analysis.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 1-fluoronaphthalene (29.2 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 10% determined by <sup>1</sup>H NMR spectroscopy.



The general procedure A was followed with **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.),  $Cs_2CO_3$  (195.5 mg, 0.6 mmol, 3.0 eq.), 3-fluoropyridine (19.4 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 36% determined by <sup>1</sup>H NMR spectroscopy.

## Birch-type reduction

Table S3. Optimization of Birch-type reduction reaction



Entry	Variation from "standard condition"	Yield of <b>4a</b> [%]	Yield of <b>4a'</b> [%]
1	None	<5	16
2	PS3 instead of PS1	6	0
3	NMP instead of DMSO	<5	0
4	HCOOK (6.0 eq.)	9	22
5	HCOOK (6.0 eq.), Cs <sub>2</sub> CO <sub>3</sub> (1.0 eq.)	<5	7
6	γ-terpinene instead of HCOOK	9	0
7	NEt <sub>3</sub> instead of HCOOK	44	<5
8	<i>i</i> Pr <sub>2</sub> NEt instead of HCOOK	63	5
9	<i>i</i> Pr <sub>2</sub> NEt (6.0 eq.)	74	11

10	<i>i</i> Pr <sub>2</sub> NEt (8.0 eq.)	68	14
11	<i>i</i> Pr <sub>2</sub> NEt (6.0 eq.), Cs <sub>2</sub> CO <sub>3</sub> (1.0 eq.)	74	11
12	<i>i</i> Pr <sub>2</sub> NEt (6.0 eq.), Cs <sub>2</sub> CO <sub>3</sub> (1.0 eq.), 12 h	74	13

#### **General procedure B**

**PS1** (2.9 mg, 0.01 mmol, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol, 1.0 eq.), substrates (if solid, 0.2 mmol, 1.0 eq.) and 2 mL DMSO were added into a Schlenk tube under argon atmosphere. After bubbling with argon for 10 min, substrates (if liquid, 0.2 mmol, 1.0 eq.) and *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.) were added into the Schlenk tube via syringe. The reaction was stirred under irradiation with a 440 nm LED light for 12 hours. Typically, the internal temperature of the reaction solution during the reaction ranged from 40 to 50 °C with fan cooling. After the reaction, 33.6 mg of 1,3,5-trimethoxybenzene, 1 mL brine, 3 mL water and 0.7 mL CDCl<sub>3</sub> were added into Schlenk tube. The CDCl<sub>3</sub> layer was analyzed by <sup>1</sup>H NMR spectroscopy to determine the product yield using 1,3,5-trimethoxybenzene as the internal standard.

For product **4i**, to avoid the overlap of the signals derived from  $iPr_2NEt$  and the product, after the reaction excess water was added, and the reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Then 33.6 mg 1,3,5-trimethoxybenzene, 1 mL brine, 3 mL water and 0.7 mL CDCl<sub>3</sub> were added (the phase separation was conducted to eliminate the residual DMSO that interfered the analysis). The yield of products was analyzed via <sup>1</sup>H NMR of CDCl<sub>3</sub> layer.



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), naphthalene (25.6 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 74%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>9</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), 1-methylnaphthalene (28.4 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 63%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>9</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), 2-methylnaphthalene (28.4 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield of **4c**: 56%, yield of **4c**': 28%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>10</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), 1-methoxynaphthalene (31.6 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 69%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>9</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), 2-methoxynaphthalene (31.6 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield of **4e**: 63%, yield of **4e**': 15%, yield of **4**": 12%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>11-12</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), 1-(dimethylamino)naphthalene (34.2 mg, 0.2 mmol, 1.0 eq.), and 2 mL DMSO. Yield: 58%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>11</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), 1-fluoronaphthalene (29.2 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield of **4g**: 35%, yield of **4a**: 32%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>11</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), phenanthrene (35.6 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 74%. The <sup>1</sup>H NMR spectrum matched the reported data. <sup>9</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), 2,3-benzofuran (23.6 mg, 0.2 mmol, 1.0 eq.), 2 mL DMSO, except that the reaction time was 24 hours. Yield: 45%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>13</sup>



The general procedure B was followed with **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), benzo[b]thiophene (26.8 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO. Yield: 27%. The <sup>1</sup>H NMR spectrum matched the reported data.<sup>14</sup>



**Figure S15.** Low reactive substrates for Birch-type reduction reactions (product yield < 5%).

# Section S9. Fluorescence quenching experiments

> Fluorescence quenching experiments of deprotonated PS1 with 1a as a quencher

Procedure: Solutions of **PS1** (20  $\mu$ M) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO in the presence of **1a** of various concentrations (0, 98, 207, 339, and 459 mM) were made in the glovebox. Then, 3 mL of the supernatant of each sample was transferred into 1 cm × 1 cm quartz cuvettes. The fluorescence spectroscopy of the above solutions was measured with the following measurement parameters: excitation wavelength: 440 nm; start wavelength: 445 nm; end wavelength: 700 nm; band width of excitation: 5 nm; band width of emission: 10 nm; response: medium; sensitivity: low. The above procedure of experiment was performed twice under the same conditions and the averaged data were applied.





**Figure S16.** Fluorescence quenching of deprotonated **PS1** in the presence of varying concentrations of **1a** as quenchers. Solvent: DMSO. The concentration of **PS1**:  $2.0 \times 10^{-5}$  mol L<sup>-1</sup>. (top) Fluorescence spectra. (bottom) The ratios of fluorescence intensities at 524 nm ( $I_0/I$ ) in the presence (I) and absence ( $I_0$ ) of the quenchers are represented by the function of the quencher concentrations.

The quenching rate constant  $(k_q)$  can be calculated based on the Stern–Volmer equation,

$$I_o/I = 1 + k_q \tau_s[Q]$$

where *I* and  $I_0$  represent the fluorescence intensities in the presence and absence of the quenchers, respectively;  $k_q$  and  $\tau_s$  represent the quenching rate constant and the fluorescence lifetime of the **PS1** anion, respectively. According to Figure S16,  $k_q \tau_s$  is calculated as 0.852. Given that the fluorescence lifetime of the **PS1** anion is 24.3 ns, the value of  $k_q$  can be calculated as  $3.4 \times 10^7$  L mol<sup>-1</sup> s<sup>-1</sup>.

> Fluorescence quenching experiments of deprotonated PS1 with 3a as a quencher

Procedure: Solutions of **PS1** (20  $\mu$ M) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO in the presence of **3a** of various concentrations (0, 4, 8, 12, and 16 mM) were made in the glovebox. Then, 3 mL of the supernatant of each sample was transferred into 1 cm × 1 cm quartz cuvettes. The fluorescence spectroscopy of the above solutions was measured with the following measurement parameters: excitation wavelength: 440 nm; start wavelength: 445 nm; end wavelength: 700 nm; band width of excitation: 10 nm; band width of emission: 10 nm; response: medium; sensitivity: low. The above procedure of experiment was performed twice under the same conditions and the averaged data were applied.



Figure S17. Fluorescence quenching of deprotonated PS1 in the presence of varying concentrations of **3a** as quenchers. Solvent: DMSO. The concentration of PS1:  $2.0 \times 10^{-5}$  mol L<sup>-1</sup>. (top) Fluorescence spectra. (bottom) The ratios of fluorescence intensities at 524 nm ( $I_0/I$ ) in the presence (I) and absence ( $I_0$ ) of the quenchers are represented by the function of the quencher concentrations.

According to Figure S17,  $k_q \tau_s$  is calculated as  $1.47 \times 10^2$ . Given that the fluorescence lifetime of the **PS1** anion is 24.3 ns, the value of  $k_q$  can be calculated as  $5.9 \times 10^9$  L mol<sup>-1</sup> s<sup>-1</sup>.



Section S10. Exploration of electron donor-acceptor (EDA) complex and exciplex between PS1 and 1a

**Figure S18.** The steady-state absorption spectra. (A) **1a** (2 mM) in DMSO (blue line); a mixture of **PS1** (100  $\mu$ M) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO (orange line); a mixture of **PS1** (100  $\mu$ M), Cs<sub>2</sub>CO<sub>3</sub> (saturated), and **1a** (2 mM) in DMSO (green line). Temperature: 293 K. (B) **1a** (100 mM) in DMSO (blue line); a mixture of **PS1** (5 mM) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO (orange line); a mixture of **PS1** (5 mM), Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO (green line). Temperature: 293 K. (B) **1a** (100 mM) in DMSO (blue line); a mixture of **PS1** (5 mM) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO (orange line); a mixture of **PS1** (5 mM), Cs<sub>2</sub>CO<sub>3</sub> (saturated), and **1a** (100 mM) in DMSO (green line). Temperature: 293 K. Orange and green spectra are almost identical, suggesting that no EDA complex was generated.



**Figure S19.** The normalized fluorescence spectra. A mixture of **PS1** (100  $\mu$ M) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO (orange line); a mixture of **PS1** (100  $\mu$ M), Cs<sub>2</sub>CO<sub>3</sub> (saturated), and **1a** (2 mM) in DMSO (green line). Temperature: 293 K. Excitation wave length: 440 nm. Both spectra are almost identical, suggesting that no exciplex was generated under this condition.



Section S11. Exploration of EDA complex and exciplex between PS1 and 3a



**Figure S20.** The steady-state absorption spectra. (A) **3a** (2 mM) in DMSO (blue line); a mixture of **PS1** (100  $\mu$ M) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO (orange line); a mixture of **PS1** (100  $\mu$ M), Cs<sub>2</sub>CO<sub>3</sub> (saturated), and **3a** (2 mM) in DMSO (green line). Temperature: 293 K. (B) **3a** (100 mM) in DMSO (blue line); a mixture of **PS1** (5 mM) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO (orange line); a mixture of **PS1** (5 mM), Cs<sub>2</sub>CO<sub>3</sub> (saturated), and **3a** (100 mM) in DMSO (green line). Temperature: 293 K. Orange and green spectra are almost identical, suggesting that no EDA complex was generated.



**Figure S21.** The normalized fluorescence spectra. A mixture of **PS1** (100  $\mu$ M) and Cs<sub>2</sub>CO<sub>3</sub> (saturated) in DMSO (orange line); a mixture of **PS1** (100  $\mu$ M), Cs<sub>2</sub>CO<sub>3</sub> (saturated), and **3a** (2 mM) in DMSO (green line). Temperature: 293 K. Excitation wave length: 440 nm. Both spectra are almost identical, suggesting that no exciplex was generated under this condition.

# Section S12. Deuterium labelling experiments

	$\begin{array}{c} \text{LED } (\lambda_{\text{max}} = 440 \text{ nm}) \\ \textbf{PS1} (2 \text{ mol}\%) \\ \textbf{Cs}_2 \text{CO}_3 (3.0 \text{ eq.}) \\ \textbf{HCOONa} (4.0 \text{ eq.}) \\ \textbf{DMSO}, 24 \text{ h} \end{array} \xrightarrow[\textbf{F}]{}$	Me	OMe D D-2a
Entry	Variation from "standard condition"	Yield [%]	2a:D-2a
1	None	20	_
2	DCOONa instead of HCOONa	47	42:58
3	DMSO-d <sub>6</sub> instead of DMSO	38	100:0
4	DCOONa instead of HCOONa, DMSO-d6 instead of DMSO	51	30:70

 Table S4. Deuterium labelling experiments

 "standard condition"

# Discussion

In entry 2, deuterated product **D-2a** was obtained, indicating that the HAT from formate to 7 is operative. The partial formation of **2a** suggested the presence of an alternative pathway, namely ET followed by protonation, in which the main proton source is likely to be residual water.

In entry 3, **D-2a** was not detected, suggesting that the HAT process proceeds more rapidly than the ET + protonation pathway under these conditions.

In entry 4, a higher ratio of **D-2a** to **2a** was observed compared to entry 2. In this case,  $D_2O$  or DHO, generated from DMSO-d<sub>6</sub> and residual water, may serve as a deuterium source in the ET + protonation pathway, thereby increasing the ratio of **D-2a** to **2a** relative to entry 2.

The reason why higher product yields were obtained with DCOONa or DMSO-d<sub>6</sub> compared to HCOONa remains unclear.



Section S13. Study on the formation of dimsyl anion from DMSO and Cs<sub>2</sub>CO<sub>3</sub>





**Figure S22.** H–D exchange experiments of DMSO. <sup>1</sup>H NMR spectra of (a) **Sample A**, (b) **Sample B**, and (c) **Sample C**, and <sup>13</sup>C NMR spectra of (d) **Sample A**, (e) **Sample B**, and (f) **Sample C**. Red arrows indicated the new peaks.

Samples A–C were prepared as follows.

### Sample A:

A mixture of DMSO (1.5 mL) and DMSO-d<sub>6</sub> (1.5 mL) was stirred at room temperature for 1 minute. Then, 0.6 mL of the solution was transferred to an NMR tube.

# Sample B:

Sample A was left to stand at 25 °C for 3 hours.

# Sample C:

To the remaining 2.4 mL of DMSO–DMSO-d<sub>6</sub> mixture from the preparation of **Sample A**, 30 mg of  $Cs_2CO_3$  was added. The mixture was bubbled with argon for 10 minutes, after which the suspension was stirred in a 6-mL screw-cap vial at 50 °C for 1 hour. The suspension was then filtered through a 0.45 µm membrane filter, and 0.6 mL of the resulting solution was transferred to an NMR tube.

# Discussion

In **Sample C**, new peaks (indicated by red arrows) were observed, which are attributed to DMSO- $d_1$ ,  $d_2$ ,  $d_3$ ,  $d_4$ , and  $d_5$ . In contrast, no new peaks appeared in **Sample B**. These results suggest that Cs<sub>2</sub>CO<sub>3</sub> deprotonated the methyl protons of DMSO, facilitating H–D exchange (as shown in Figure S23), and indicate that dimsyl anion can be generated under the present photoreaction conditions.



Figure S23. Mechanism of H–D exchange between DMSO and DMSO-d<sub>6</sub>.

The formation of dimsyl anion from DMSO and Cs<sub>2</sub>CO<sub>3</sub> was studied using UV-Vis absorption spectroscopy (Figure S24). A broad tailing absorption spectrum, extending smoothly from 325 to 500 nm, was observed, consistent with previous reports.<sup>15</sup>



**Figure S24.** Absorption spectrum of DMSO and  $Cs_2CO_3$  at 293K. Sample preparation: 5 mL of DMSO was treated with 0.5 mmol of  $Cs_2CO_3$ , then the supernatant solution was transferred to a quartz cell.

# Section S14. Calculation of BDEs

BDEs of specific O–H bonds can be computationally estimated as follows. The BDE of the phenol O–H bond is reported to be 88.3 kcal mol<sup>-1</sup>.<sup>16</sup> The driving force ( $\Delta G^0$ ) of hydrogen atom exchange reaction between phenol and the specific molecules can be calculated based on the following equation.

phenol +  $RO^{\bullet} \longrightarrow PhO^{\bullet}$  + ROH $\Delta G^{0}$ 

 $\Delta G^0 = \text{BDE}(\text{PhO}-\text{H}) - \text{BDE}(\text{RO}-\text{H}) = G(\text{PhO}^{\bullet}) + G(\text{ROH}) - G(\text{phenol}) - G(\text{RO}^{\bullet})$ 

BDE(RO-H) in kcal mol<sup>-1</sup> = 88.3 - { $G(PhO^{\bullet}) + G(ROH) - G(PhoO) - G(RO^{\bullet})$ } × 627.5



Table S5 Calculated Gibbs energies (298.15 K, 1 atm)<sup>a</sup>

Chemical Species	Gibbs energy (hartree)
Phenol	-307.425732

PhO•	-306.796737
PS1	-938.081797
6	-937.464855
11	-370.851555
12	-370.218351

<sup>a</sup>(U)B3LYP/6-31G++(d,p)/CPCM(DMSO).

Based on the above results, the BDEs of PS1 and 11 were calculated.

BDE (O–H in **PS1**) = 80.7 kcal mol<sup>-1</sup> BDE (C–H in **11**) = 90.9 kcal mol<sup>-1</sup>

# Section S15. Determination of reaction quantum yields

The photon flux of the employed LED lamp was determined by standard ferrioxalate actinometry.<sup>17-19</sup> In the dark, 1.473 g of ferrioxalate was dissolved in 15 mL of preprepared 0.05 M H<sub>2</sub>SO<sub>4</sub> solution. Upon complete dissolution of the solid ferrioxalate, the solution was topped up to 20 mL with 0.05 M H<sub>2</sub>SO<sub>4</sub>, obtaining 0.15 M ferrioxalate solution. The buffer solvent was prepared by dissolving 20 mg of phenanthroline and 4.5 g of sodium acetate in 10 mL of 0.5 M H<sub>2</sub>SO<sub>4</sub>, and the volume was adjusted to 20 mL Then, 2 mL of 0.15 M ferrioxalate prepared above was placed in a fluorescence cell (1cm × 1cm) and irradiated for 30 s using LED lamp ( $\lambda_{max} = 440$  nm) with a 0.8 cm × 0.8 cm square-shaped slit made of aluminum foil. After irradiation, 0.35 mL phenanthroline buffer prepared above was added to the reaction solution, and the solution was left for 1 h. As a control, 0.35 mL of the phenanthroline buffer solution was also left for 1 h. The absorbance of the ferrioxalate was measured at 510 nm, and the average of the three absorbance differences was obtained as 0.785 ( $\Delta A$ ). The number of moles of Fe<sup>2+</sup> was then calculated as follows :

nol Fe<sup>2+</sup> = (V • 
$$\Delta A$$
) / (1 •  $\epsilon$ )

where V is the volume of the ferrioxalate solution,  $\Delta A$  is the absorbance difference, l is the path length, and  $\epsilon$  is the molar absorption coefficient. The value of  $\epsilon_{510 \text{ nm}} = 11,100 \text{ M}^{-1} \text{cm}^{-1}$ .<sup>19</sup> Using this equation, the number of moles of Fe<sup>2+</sup> (mol Fe<sup>2+</sup>) is calculated; mol Fe<sup>2+</sup> = (0.00235L • 0.785) / (1.000 cm • 11100 mol<sup>-1</sup> cm<sup>-1</sup>) = 1.66 × 10<sup>-7</sup> mol.

The photon flux was calculated as follows :

photon flux = mol Fe<sup>2+</sup> / ( $\Phi \bullet t \bullet f$ )

where  $\Phi$  is the quantum yield of the ferrioxalate actinometer, t is the irradiation time, and f is the fraction of light absorption. The absorbance of the 0.15 M ferrioxalate solution was determined to be 2.556 at 440 nm. The fraction of light absorption of the ferrioxalate actinometer can be calculated using the equation,  $f = 1 - 10^{-A} = 1 - 10^{-2.556}$ 

= 0.997. The reaction quantum yield  $\Phi$  is known to be 1.01 at 436 nm.<sup>17</sup> Photon flux =  $1.66 \times 10^{-7}$  mol/(1.01 • 30 s • 0.997) =  $5.50 \times 10^{-9}$  einstein s<sup>-1</sup>.

Determination of quantum yield of hydrodefluorination of 4-fluoroanisole: **PS1** (1.1 mg, 0.004 mmol, 2 mol%), HCOOK (67.3 mg, 0.8 mmol, 4.0 eq.), Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol, 3.0 eq.) and 2 mL DMSO were added to a Schlenk tube under an argon atmosphere. After bubbling with argon for 10 min, 4-fluoroanisole (25.1 mg, 0.2 mmol, 1.0 eq.) was added to the Schlenk tube via syringe. The reaction was stirred for 2 hours under a 440 nm LED light with a 0.8 cm × 0.8 cm square-shaped slit. After the reaction, 33.6 mg of 1,3,5-trimethoxybenzene and 1 mL DMSO were added into the Schlenk tube. The yield was determined to be 18% by <sup>1</sup>H NMR spectroscopic analysis. The reaction quantum yield can be calculated as follows:  $\Phi = \text{mol product / (flux • t • f)}$ , where flux is the photon flux, t is reaction time, f is the fraction of light absorption of **PS1**. The measured absorbance of 2 mM **PS1** with excess Cs<sub>2</sub>CO<sub>3</sub> in DMSO was 2.836 at 440 nm. In the present setup combining the Schlenk tube and slit, the optical path length at all illuminated positions exceeds 1.5 cm, and thus the light absorption efficiency was calculated to be nearly unity.

 $\Phi = 0.2 \text{ mmol} \bullet 0.18 / (5.50 \times 10^{-9} \text{ einstein s}^{-1} \bullet 7200 \text{ s} \bullet 1) = 0.91.$ 

Determination of quantum yield of Birch-type reduction of naphthalene:

**PS1** (2.9 mg, 0.01 mmol, 5 mol%), naphthalene (25.6 mg, 0.2 mmol, 1.0 eq.),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.) and 2 mL DMSO were added to a Schlenk tube under an argon atmosphere. After bubbling with argon for 10 min, *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.) was added to the Schlenk tube via syringe. The reaction was stirred for 4 hours under a 440 nm LED light with a 0.8 cm × 0.8 cm square-shaped slit. After the reaction, 33.6 mg of 1,3,5-trimethoxybenzene and 1 mL DMSO were added to the Schlenk tube. The yield was determined to be 5.8% by <sup>1</sup>H NMR spectroscopic analysis.

The reaction quantum yield can be calculated as follows:  $\Phi = \text{mol product / (flux • t • f)}$ , where flux is the photon flux, t is reaction time, f is the fraction of light absorption of **PS1**. The measured absorbance of 5 mM **PS1** with excess Cs<sub>2</sub>CO<sub>3</sub> at 440 nm in DMSO was 1.887. In the present setup combining the Schlenk tube and slit, the optical path length at all illuminated positions exceeds 1.5 cm, and thus the light absorption efficiency was calculated to be nearly unity.

 $\Phi = 0.2 \text{ mmol} \bullet 0.058 / (5.50 \times 10^{-9} \text{ einstein s}^{-1} \bullet 14400 \text{ s} \bullet 1) = 0.15.$ 

## Section S16. Possible chain propagation mechanism in the hydrodefluorination



Considering the redox potentials of  $CO_2^{\bullet-}(E_{ox} = -2.2 \text{ V vs SCE})$  and **1a** ( $E_{red} = ca. -3.1 \text{ V vs SCE}$ ), the ET from  $CO_2^{\bullet-}$  to **1a** is uphill in energy. The coordination of a cesium cation to the fluoride atom of **1a** may play a role in enhancing the electron-accepting ability of **1a**, enabling this chain propagation mechanism.

# Section S17. Effect of water on the photochemical Birch-type reaction



Figure S25. Photochemical Birch-type reactions using DMSO with different water contents

To investigate the effect of water on the photochemical Birch-type reaction, reactions were performed using DMSO containing 16 ppm w/w of water ("Dry condition") and 800 ppm w/w of water ("Wet condition"), and the resulting yields were compared. To assess the reaction rate, the reaction time was set to 3 hours, and yields were measured at an intermediate stage before the reaction reached completion. As shown in Figure S25, the reaction using DMSO with a higher water content exhibited a faster rate. This observation aligns with the hypothesis that water acts as a proton source, facilitating the reaction progress.

# "Dry condition"

Inside a glove box, **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), naphthalene (25.6 mg, 0.2 mmol, 1.0 eq.) and 2 mL of anhydrous DMSO (16 ppm w/w water content) were added into a Schlenk tube. The tube was then removed from the glove box, and under an argon atmosphere, *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.), dried over 4 Å molecular sieves, was added via syringe. The reaction was stirred under 440 nm LED light irradiation for 3 hours. After the reaction, 33.6 mg of 1,3,5-trimethoxybenzene, 1 mL of brine, 3 mL of water and 0.7 mL of CDCl<sub>3</sub> were added to the Schlenk tube. The CDCl<sub>3</sub> layer was analyzed using <sup>1</sup>H NMR spectroscopy to determine the product yield, with 1,3,5-trimethoxybenzene used as the internal standard. The product yield was 26%.

### "Wet condition"

Under an argon atmosphere, **PS1** (2.9 mg, 0.01 mmol, 5 mol%),  $Cs_2CO_3$  (65.2 mg, 0.2 mmol, 1.0 eq.), naphthalene (25.6 mg, 0.2 mmol, 1.0 eq.) and 2 mL of DMSO (800 ppm w/w water content) were added to a Schlenk tube. The mixture was bubbled with argon for 10 minutes, after which *i*Pr<sub>2</sub>NEt (155 mg, 1.2 mmol, 6.0 eq.) was added to the Schlenk tube via syringe. The reaction mixture was stirred under 440 nm LED light irradiation for 3 hours. Following the reaction, 33.6 mg of 1,3,5-trimethoxybenzene, 1 mL of brine, 3 mL of water, and 0.7 mL of CDCl<sub>3</sub> were added to the Schlenk tube. The CDCl<sub>3</sub> layer was analyzed using <sup>1</sup>H NMR spectroscopy to determine the product yield, with 1,3,5-trimethoxybenzene used as the internal standard. The product yield was 46%.

## Section S18. Calculated molecular structures

For the calculation procedure, see Section S5 and S14 for the details. The Cartesian coordinates of the optimized structures are given below. The molecular structures were depicted by using the CYLview v1.0.561  $\beta$ .<sup>20</sup> NIMAG stands for the number of imaginary frequencies.

> Optimized geometry of the ground state of "**PS1**+Cs<sub>2</sub>CO<sub>3</sub>"



# *E* = -937.844373576, G = -937.610443, NIMAG = 0

Center	Atomic	Atomic	Coord	dinates (Ang	stroms)
Number	Number	Туре	Х	Y	Z
1	6	0	-1. 475262	-0. 196479	-0. 289641
2	6	0	-0.092363	-0.067516	-0. 033272
3	6	0	0.658329	0.951748	-0. 612754
4	6	0	0.009450	1.860243	-1. 460464
5	6	0	-1.375705	1.727939	-1.737671
6	6	0	-2. 124281	0.694691	-1.144909
7	1	0	0. 380477	-0. 785223	0. 629908
8	1	0	1.720319	1.025974	-0. 405974
9	1	0	-3. 181587	0.602630	-1.364195
10	6	0	-0. 540075	3.500530	-2.933086
11	6	0	-0.564600	4.615202	-3. 781063
12	6	0	-1.774446	4.977295	-4. 369812
13	6	0	-3.017383	4. 272170	-4. 151956
14	6	0	-2.945418	3. 152872	-3. 269893
15	6	0	-1. 730233	2.778212	-2. 673893
16	1	0	0. 332676	5. 193719	-3. 980746
17	1	0	-1.802598	5.839623	-5.032900
18	1	0	-3.856641	2.595150	-3.061686
19	7	0	0. 522500	2.940004	-2. 185780
20	6	0	1.868077	3. 380108	-2. 188337
21	6	0	2. 549745	3. 569117	-3. 401732
22	6	0	2. 533252	3. 636953	-0. 978257
23	6	0	3.873799	4.013539	-3. 400763

24	1	0	2.044063	3.358402	-4. 338168
25	6	0	3.863751	4.062497	-0. 985141
26	1	0	2.004117	3. 514400	-0. 038920
27	6	0	4. 539202	4. 257501	-2. 194426
28	1	0	4. 389312	4. 156527	-4. 346093
29	1	0	4.367013	4. 255672	-0. 042147
30	1	0	5. 570654	4. 596528	-2. 196940
31	8	0	-2.093369	-1.246098	0.355057
32	8	0	-4. 122111	4. 652944	-4. 727094
33	6	0	-3. 488737	-1. 441684	0. 134817
34	1	0	-3.700942	-1.642984	-0. 922130
35	1	0	-3.767581	-2. 310251	0. 732341
36	1	0	-4.069950	-0. 571496	0.462905

> Optimized geometry of the ground state of **PS2** 



E = -977.630226079, G = -977.356984, NIMAG = 0

Center	Atomic	Atomic	Coordinates (Angstroms)		troms)
Number	Number	Туре	Х	Y	Z
1	6	0	0. 506982	-3. 275802	1. 885443
2	6	0	1.894710	-3. 148553	2. 127310
3	6	0	2.640640	-2. 128612	1. 548325
4	6	0	1.979199	-1.217606	0.713457
5	6	0	0. 592169	-1. 342452	0. 455083
6	6	0	-0. 153826	-2. 378897	1.047147
			S41		

7	1	0	2. 372101	-3.871857	2. 780757
8	1	0	3. 704563	-2.051166	1.743633
9	1	0	-1.214208	-2. 467281	0.843621
10	6	0	1. 429341	0. 448038	-0. 716572
11	6	0	1. 418538	1. 573245	-1. 552167
12	6	0	0. 211732	1. 949261	-2. 130229
13	6	0	-0.979373	1.226367	-1.886901
14	6	0	-0.976352	0. 112537	-1.048334
15	6	0	0.240339	-0. 276721	-0. 457224
16	1	0	2.319706	2.143670	-1.748638
17	1	0	0. 164859	2.814314	-2. 784111
18	1	0	-1.881102	-0. 447332	-0. 844207
19	7	0	2. 485603	-0. 127105	-0. 001812
20	6	0	3. 837191	0. 319952	-0. 000610
21	6	0	4. 551829	0.397026	-1. 204045
22	6	0	4. 454932	0. 683565	1. 204042
23	6	0	5.875005	0.845492	-1.200100
24	1	0	4. 073943	0. 100746	-2. 132332
25	6	0	5. 784460	1.112834	1. 202456
26	1	0	3.893202	0. 635751	2. 131433
27	6	0	6. 496619	1. 199823	0. 001757
28	1	0	6. 422474	0.905870	-2. 135947
29	1	0	6. 258384	1. 390412	2. 139228
30	1	0	7. 527366	1. 540893	0. 002649
31	8	0	-0.099480	-4. 328730	2. 528390
32	8	0	-2. 093941	1.712009	-2. 528609
33	6	0	-3. 335482	1.037624	-2. 326441
34	1	0	-3.631075	1.057580	-1. 270792
35	1	0	-4. 070875	1. 581483	-2. 919821
36	1	0	-3. 283838	-0.001679	-2. 671857
37	6	0	-1. 499330	-4. 523943	2. 329896
38	1	0	-1. 727889	-4. 716785	1. 275049
39	1	0	-1. 766314	-5.397690	2. 924852
40	1	0	-2.074396	-3.656889	2. 675838

> Optimized geometry of the lowest-lying singlet excited state of "**PS1**+Cs<sub>2</sub>CO<sub>3</sub>"



*E* = -937.837464630, G = -937.519858, NIMAG = 0

Center	Atomic	Atomic	Coor	dinates (Ang	stroms)
Number	Number	Туре	Х	Y	Z
1	6	0	2. 973960	-1. 744454	0. 078153
2	6	0	1.923015	-2.669849	0.091437
3	6	0	0.554400	-2.227095	0.057356
4	6	0	0. 340391	-0. 852613	0.000068
5	6	0	1. 392353	0.090146	-0. 007977
6	6	0	2. 754399	-0.353389	0. 032844
7	1	0	2. 157276	-3. 728655	0. 127829
8	1	0	-0. 259748	-2.941230	0.076686
9	1	0	3.566563	0.361483	0. 034924
10	6	0	-0.631693	1.219967	-0. 037130
11	6	0	-1.524542	2.305399	-0. 092416
12	6	0	-1.005580	3. 598491	-0. 122087
13	6	0	0. 424080	3.836151	-0. 104413
14	6	0	1. 314441	2. 692884	-0. 062757
15	6	0	0. 799236	1.398089	-0. 033468
16	1	0	-2.596981	2. 138555	-0. 112593
17	1	0	-1.662717	4. 461791	-0. 161185
18	1	0	2.383996	2.884816	-0. 064287
19	7	0	-0.890744	-0. 136542	-0. 021631
20	6	0	-2. 180161	-0. 737346	-0. 001345
21	6	0	-3.085185	-0. 427356	1.023460
22	6	0	-2.543907	-1.643218	-1.008022
			0.40		

23	6	0	-4. 353201	-1.013861	1.031764
24	1	0	-2.791187	0. 261574	1.808514
25	6	0	-3.808891	-2. 234439	-0. 985376
26	1	0	-1.840617	-1.873043	-1.801464
27	6	0	-4. 717778	-1.920374	0. 031044
28	1	0	-5.051107	-0. 768552	1.826735
29	1	0	-4.086705	-2. 934075	-1.768105
30	1	0	-5. 701875	-2.378895	0.043011
31	8	0	4. 242900	-2. 300282	0. 115545
32	8	0	0.897610	5. 026678	-0. 130328
33	6	0	5. 369891	-1. 429570	0. 102316
34	1	0	5.376087	-0. 766793	0.976116
35	1	0	6. 248956	-2. 075316	0. 133376
36	1	0	5. 397815	-0. 822416	-0. 810594

> Optimized geometry of the lowest-lying singlet excited state of **PS2** 



E = -977.625947227, G = -977.239009, NIMAG = 0

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	Х	Y	Z
1	6	0	-1. 716288	-3. 047779	-0. 079925
2	6	0	-0.368179	-3. 458372	-0. 097057
3	6	0	0.667562	-2. 489224	-0. 067415
4	6	0	0.301779	-1.148463	-0. 008277
5	6	0	-1.062285	-0. 716501	-0. 006692
6	6	0	-2.090871	-1.680508	-0. 039293
			S44		

7	1	0	-0. 140362	-4. 516989	-0. 134646
8	1	0	1. 705543	-2. 798381	-0. 096378
9	1	0	-3. 130203	-1.378703	-0. 044733
10	6	0	0. 301773	1. 148462	0. 008281
11	6	0	0.667558	2. 489219	0.067433
12	6	0	-0. 368187	3. 458369	0.097066
13	6	0	-1.716293	3.047777	0. 079912
14	6	0	-2.090876	1.680507	0. 039268
15	6	0	-1.062285	0.716499	0. 006677
16	1	0	1. 705539	2.798376	0. 096415
17	1	0	-0.140368	4. 516986	0. 134667
18	1	0	-3. 130207	1.378700	0. 044680
19	7	0	1. 107513	-0.000004	0.00008
20	6	0	2. 526263	0.000000	0.00003
21	6	0	3. 224145	0.750256	-0. 959475
22	6	0	3. 224155	-0. 750251	0.959478
23	6	0	4. 618895	0. 744549	-0.955199
24	1	0	2. 676210	1.308400	-1. 710381
25	6	0	4. 618905	-0. 744537	0.955194
26	1	0	2.676228	-1. 308395	1.710390
27	6	0	5. 319690	0. 000008	-0. 000005
28	1	0	5. 157545	1.316418	-1. 704220
29	1	0	5. 157563	-1.316403	1. 704212
30	1	0	6. 405110	0.000011	-0. 000008
31	8	0	-2. 627255	-4. 059283	-0. 111290
32	8	0	-2.627263	4. 059283	0. 111254
33	6	0	-4. 027612	3.757159	0. 105763
34	1	0	-4. 306324	3. 172131	0.988058
35	1	0	-4. 534714	4. 721367	0. 130837
36	1	0	-4. 309229	3.216916	-0. 803688
37	6	0	-4. 027606	-3. 757164	-0. 105726
38	1	0	-4. 306368	-3. 172154	-0. 988018
39	1	0	-4. 534704	-4. 721375	-0. 130755
40	1	0	-4. 309172	-3. 216905	0.803730

> Optimized geometry of phenol



E = -307.501004592, G = -307.425732, NIMAG = 0

Center	Atomic	Atomic	Coor	dinates (Ang	stroms)
Number	Number	Туре	Х	Y	Z
1	6	0	4. 076421	-2. 388210	0. 016658
2	6	0	5. 476517	-2.394389	0.031893
3	6	0	6. 166269	-1.178990	-0.014180
4	6	0	5. 471236	0.033119	-0. 074381
5	6	0	4. 071164	0. 026239	-0. 088076
6	6	0	3. 370184	-1.185170	-0. 043046
7	1	0	3. 527609	-3.324993	0.051790
8	1	0	6. 020719	-3. 332435	0.078883
9	1	0	7. 252389	-1.166914	-0. 003415
10	1	0	6.012448	0.975202	-0. 110180
11	1	0	2.284684	-1.171764	-0. 054864
12	8	0	3. 328969	1. 180152	-0. 145700
13	1	0	3. 911376	1.952913	-0. 168222

Optimized geometry of PhO•



Center	Atomic	Atomic	Coor	dinates (Ang	stroms)
Number	Number	Туре	Х	Y	Z
1	6	0	-0. 218272	0. 046620	0. 000282
2	6	0	1. 194715	0.062524	0.014428
3	6	0	1.903768	1.283890	-0. 031613
4	6	0	1. 221642	2. 480675	-0. 090921
5	6	0	-0. 231121	2.504695	-0. 106551
6	6	0	-0. 925148	1. 228853	-0. 058659
7	1	0	-0. 742515	-0.903306	0.036218
8	1	0	1. 741457	-0. 873944	0.061124
9	1	0	2. 989224	1. 272630	-0. 019933
10	1	0	1. 741689	3. 432864	-0. 127308
11	1	0	-2.010542	1. 245483	-0. 070802
12	8	0	-0. 868351	3. 596283	-0. 160776

E = -306.858634769, G = -306.796737, NIMAG = 0

> Optimized geometry of **PS1** 



*E* = -938.328499551, G = -938.081797, NIMAG = 0

Center	Atomic	Atomic	Coor	dinates (Ang	stroms)
Number	Number	Туре	Х	Y	Z
1	6	0	-0. 492810	-0. 344072	-0. 003076
2	6	0	0.893249	-0. 214470	0. 246141
			S47		

3	6	0	1.642209	0.803362	-0. 332763
4	6	0	0. 985251	1.710340	-1. 175620
5	6	0	-0.399593	1.582580	-1. 441129
6	6	0	-1.148815	0. 548751	-0. 849617
7	1	0	1.367316	-0. 934455	0.905661
8	1	0	2. 704843	0. 882287	-0. 131299
9	1	0	-2. 207853	0. 459628	-1.059644
10	6	0	0. 444827	3.371403	-2. 616650
11	6	0	0. 439586	4. 490517	-3. 454868
12	6	0	-0.766615	4.866486	-4. 046855
13	6	0	-1.950728	4. 141127	-3. 805729
14	6	0	-1.953376	3.032710	-2. 962774
15	6	0	-0.747840	2.643944	-2. 360700
16	1	0	1. 341544	5.060847	-3. 647504
17	1	0	-0. 792475	5.732939	-4. 702725
18	1	0	-2.878067	2.493089	-2. 783212
19	7	0	1. 496220	2.798268	-1.892095
20	6	0	2.848331	3. 243711	-1. 885221
21	6	0	3. 570766	3. 311421	-3. 084568
22	6	0	3. 458912	3. 614392	-0. 679105
23	6	0	4. 894745	3.757407	-3. 075101
24	1	0	3. 098273	3. 009668	-4. 013855
25	6	0	4. 789255	4. 041199	-0. 675010
26	1	0	2.891205	3. 573638	0. 244990
27	6	0	5.509289	4. 118645	-1. 871644
28	1	0	5. 448410	3.810377	-4. 007751
29	1	0	5. 257752	4. 324061	0. 262912
30	1	0	6. 540702	4. 457650	-1.866395
31	8	0	-1. 102588	-1.394105	0. 641134
32	8	0	-3. 149615	4. 498526	-4. 387746
33	6	0	-2.501476	-1. 589991	0. 435971
34	1	0	-2.724286	-1.787923	-0. 619147
35	1	0	-2. 771883	-2. 460750	1.033718
36	1	0	-3. 078102	-0. 721094	0. 774554
37	1	0	-3.026156	5. 276311	-4. 949245

> Optimized geometry of **6** 



E = -937.699263017, G = -937.464855, NIMAG = 0

Number	Number	Type			
		Турс	Х	Y	Z
1	6	0	-0. 543818	0. 260077	-0. 037500
2	6	0	0.841838	0. 397192	0. 199525
3	6	0	1.576500	1. 429617	-0. 375454
4	6	0	0.896258	2.332645	-1. 195252
5	6	0	-0. 485383	2.203348	-1. 448190
6	6	0	-1. 220249	1.161735	-0. 867556
7	1	0	1. 328021	-0.326920	0.844840
8	1	0	2.640409	1. 519332	-0. 186795
9	1	0	-2. 280521	1.066413	-1.066149
10	6	0	0.357882	4. 023552	-2.600464
11	6	0	0. 371054	5. 172413	-3. 428965
12	6	0	-0.808815	5. 564168	-4. 011929
13	6	0	-2.060341	4.844247	-3. 802429
14	6	0	-2.032762	3.681532	-2. 937872
15	6	0	-0.847120	3. 286101	-2. 352298
16	1	0	1. 289282	5. 725643	-3. 594684
17	1	0	-0.845656	6. 438644	-4. 653856
18	1	0	-2.963899	3.148373	-2. 771608
19	7	0	1. 391245	3.447140	-1.905681
20	6	0	2.754999	3.881193	-1.911032
21	6	0	3. 491267	3.840737	-3. 100607
22	6	0	3. 340216	4. 337367	-0. 724260
23	6	0	4.820760	4. 269975	-3. 100555
24	1	0	3. 028427	3. 470637	-4. 009758

2	5 6	0	4. 673616	4. 753483	-0. 731868
20	6 1	0	2. 754037	4. 372674	0. 188324
2	7 6	0	5. 414104	4. 723469	-1.918185
28	3 1	0	5. 392859	4. 241065	-4. 022674
29	) 1	0	5. 129220	5. 108092	0. 187434
30	) 1	0	6. 448930	5.051545	-1. 920904
3	1 8	0	-1. 138439	-0. 797747	0. 593570
32	2 8	0	-3.135800	5. 228652	-4. 355721
33	3 6	0	-2.540365	-1.006206	0. 403930
34	4 1	0	-2.772918	-1. 193217	-0. 650420
3	5 1	0	-2.790743	-1.887699	0.993920
30	6 1	0	-3.119526	-0. 148246	0.763396

> Optimized geometry of 11



E = -371.076631284, G = -370.851555, NIMAG = 0

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	Х	Y	Z
1	7	0	2. 006789	0. 955251	-0. 267195
2	6	0	2. 209478	1.860898	-1. 424953
3	1	0	3. 292808	1.985849	-1.622219
4	6	0	1.616579	3. 260121	-1. 201604
5	1	0	1.677902	3. 827158	-2. 135864
6	1	0	0.559927	3. 194880	-0. 915449
7	1	0	2. 147146	3.836014	-0. 439014
8	6	0	1.581635	1. 261273	-2.694796
9	1	0	1.772622	1. 920894	-3. 548008
			S50		

10	1	0	1.989801	0. 278768	-2. 943926
11	1	0	0. 496884	1.159333	-2. 572831
12	6	0	2. 274145	1.555347	1.064393
13	1	0	1. 694149	2. 480853	1.097693
14	6	0	3. 749470	1.927100	1. 327206
15	1	0	4. 142415	2.589622	0. 548858
16	1	0	3.840708	2.449468	2. 286208
17	1	0	4. 392411	1.040941	1. 372074
18	6	0	1.717025	0.672728	2. 191231
19	1	0	1.807089	1. 196729	3. 148930
20	1	0	0.659263	0. 448556	2. 020237
21	1	0	2. 256623	-0. 275736	2. 286211
22	6	0	2.652510	-0.362657	-0. 459129
23	1	0	3. 334396	-0. 325788	-1. 319645
24	1	0	3. 290636	-0. 594155	0. 400054
25	6	0	1.655548	-1.512952	-0. 643715
26	1	0	1.011769	-1.612402	0. 236236
27	1	0	1.011528	-1.348216	-1. 512810
28	1	0	2. 188050	-2. 461667	-0. 786403

> Optimized geometry of **12** 



E = -370.428958066, G = -370.218351, NIMAG = 0

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Туре	Х	Y	Z
1	7	0	-0. 294796	-0. 925748	-0. 002602
2	6	0	-0. 357550	-0.065212	-1. 118799
3	6	0	-0. 833152	1. 348387	-0. 905400
4	1	0	-0.811088	1.882753	-1.859656
			S51		

5	1	0	-1.877166	1.396488	-0. 537041
6	1	0	-0. 220254	1.921171	-0. 201585
7	6	0	-0. 758109	-0.672699	-2. 439368
8	1	0	-0. 570733	0.039633	-3. 248694
9	1	0	-0. 221056	-1. 592533	-2. 684489
10	1	0	-1.839319	-0. 917433	-2. 470424
11	6	0	-0.083222	-0. 337798	1.340565
12	1	0	-0. 671081	0. 581266	1.363343
13	6	0	1. 387129	0. 038574	1. 608835
14	1	0	1. 768472	0. 698449	0. 822945
15	1	0	1. 476916	0. 559518	2. 568456
16	1	0	2.029800	-0.847906	1.650698
17	6	0	-0.650085	-1.232769	2. 452578
18	1	0	-0. 574936	-0. 709467	3. 411612
19	1	0	-1.704385	-1. 462396	2.269710
20	1	0	-0. 104093	-2. 176641	2. 551927
21	6	0	0. 272852	-2. 272195	-0. 204587
22	1	0	0.946143	-2.260266	-1.069386
23	1	0	0.904009	-2. 517947	0.653790
24	6	0	-0. 780291	-3. 373384	-0. 374730
25	1	0	-1. 418672	-3. 445298	0.511255
26	1	0	-1. 423162	-3. 183019	-1. 239173
27	1	0	-0. 288973	-4. 342932	-0. 521523

# Section S19. NMR spectra

TMB stands for 1,3,5-trimethoxybenzene used as the internal standard.













![](_page_58_Figure_0.jpeg)

![](_page_59_Figure_0.jpeg)

![](_page_60_Figure_0.jpeg)

![](_page_61_Figure_0.jpeg)

![](_page_62_Figure_0.jpeg)

![](_page_63_Figure_0.jpeg)

![](_page_64_Figure_0.jpeg)

Section S20. GC spectra

![](_page_65_Figure_1.jpeg)

![](_page_66_Figure_0.jpeg)

# Section S21. Reference

- V. V. Pavlishchuk and A. W. Addison, Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C, *Inorganica Chim. Acta* 2000, **298**, 97-102.
- 2 Z. Teng, H. Lv, Y. Zhang, Y. Zhang, J. Guan and W. Chengyin, Development of a Fluorescent Labeling Reagent for Determination of Proline and Hydroxyproline in Myeloma Patient Plasma by HPLC-FLD, J. Chromatogr. Sci. 2016, 54, 1743-1751.
- 3 K. Kasama, Y. Koike, H. Dai and T. Yakura, Bismuth(III)-Catalyzed Oxidative Cross-Coupling of 3-Hydroxycarbazoles with Arenols under an Oxygen Atmosphere, *Org. Lett.* 2023, **25**, 6501-6505.
- 4 J.-B. Harlé, S. Mine, T. Kamegawa, V. T. Nguyen, T. Maeda, H. Nakazumi and H. Fujiwara, Deep Blue Asymmetrical Streptocyanine Dyes: Synthesis, Spectroscopic Characterizations, and Ion-Specific Cooperative Adsorption at the Surface of TiO<sub>2</sub> Anatase Nanoparticles, *J. Phys. Chem. C* 2017, **121**, 15049-15062.
- 5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Startmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox *Gaussian 09*, Gaussian, Inc., Wallingford, CT, 2009.
- 6 J. Tomasi, B. Mennucci and R. Cammi, Quantum Mechanical Continuum Solvation Models, *Chem. Rev.* 2005, **105**, 2999-3094.
- 7 J. Cerezo and F. Santoro, FCclasses3: Vibrationally-resolved spectra simulated at the edge of the harmonic approximation, *J. Comput. Chem.* 2023, **44**, 626-643.
- 8 N. A. Romero and D. A. Nicewicz, Organic Photoredox Catalysis, *Chem. Rev.* 2016, 116, 10075-10166.
- 9 S. Wu, F. Schiel and P. Melchiorre, A General Light-Driven Organocatalytic Platform for the Activation of Inert Substrates, *Angew. Chem. Int. Ed.* 2023, **62**, e202306364.
- 10 C. Pétrier and K. Suslick, Ultrasound-enhanced reactivity of calcium in the reduction of aromatic hydrocarbons, *Ultrason. Sonochem.* 2000, 7, 53-61.
- 11 H. Li, Y. Li, J. Chen, L. Lu, P. Wang, J. Hu, R. Ma, Y. Gao, H. Yi, W. Li and A. Lei, Scalable and Selective Electrochemical Hydrogenation of Polycyclic Arenes, *Angew. Chem. Int. Ed.* 2024, **63**, e202407392.
- 12 A. Banerjee, T. Hattori and H. Yamamoto, Regio- and Stereoselective (S<sub>N</sub>2) *N*-, *O*-, *C* and *S*-Alkylation Using Trialkyl Phosphates, *Synthesis* 2021, **55**, 315-332.
- 13 P. Ji, K. Manna, Z. Lin, A. Urban, F. X. Greene, G. Lan and W. Lin, Single-Site

Cobalt Catalysts at New  $Zr_8(\mu_2-O)_8(\mu_2-OH)_4$  Metal-Organic Framework Nodes for Highly Active Hydrogenation of Alkenes, Imines, Carbonyls, and Heterocycles, *J. Am. Chem. Soc.* 2016, **138**, 12234-12242.

- 14 S. Urban, B. Beiring, N. Ortega, D. Paul and F. Glorius, Asymmetric Hydrogenation of Thiophenes and Benzothiophenes, *J. Am. Chem. Soc.* 2012, **134**, 15241-15244.
- 15 Y. Huang, Q. Zhang, L.-L. Hua, L.-W. Zhan, J. Hou and B.-D. Li, A versatile catalyst-free redox system mediated by carbon dioxide radical and dimsyl anions, *Cell Rep. Phys. Sci.* 2022, **3**, 100994.
- 16 M. Lucarini, P. Pedrielli, G. F. Pedulli, S. Cabiddu and C. Fattuoni, Bond Dissociation Energies of O-H Bonds in Substituted Phenols from Equilibration Studies, J. Org. Chem. 1996, 61, 9259-9263.
- 17 C. G. Hatchard, C. A. Parker and E. J. Bowen, A new sensitive chemical actinometer
  II. Potassium ferrioxalate as a standard chemical actinometer, *Proc. Roy. Soc.* (London) 1956, A235, 518-536.
- 18 M. A. Cismesia and T. P. Yoon, Characterizing chain processes in visible light photoredox catalysis, *Chem. Sci.* 2015, **6**, 5426-5434.
- 19 S. P. Pitre, C. D. McTiernan, W. Vine, R. DiPucchio, M. Grenier and J. C. Scaiano, Visible-Light Actinometry and Intermittent Illumination as Convenient Tools to Study Ru(bpy)<sub>3</sub>Cl<sub>2</sub> Mediated Photoredox Transformations, *Sci. Rep.* 2015, 5, 16397.
- 20 CYL view, 1.0b, C. Y. Legault Université de Sherbrooke, 2009.