Supporting Information

A Highly Reducing Metal-free Photoredox Catalyst: Design and Application in Radical Dehalogenations

General Reagent Information

All reactions were carried out under an argon atmosphere unless otherwise noted. All commercially obtained reagents were used as received unless otherwise noted. All reactions were performed at room temperature (ca. 23 °C), unless otherwise noted. Aryl halides 5, 19, and 23 were prepared according to literature procedures.^{1,2} Aryl halides 1-4, 6-18, 20-22 were purchased from commercial sources. Acetonitrile was purchased from Fisher Scientific and used as received. Phenothiazine, chlorobenzene, sodium tertbutoxide, anhydrous dioxane, *fac*-lr(ppy)₃, tributylamine, N,N-diisopropylethylamine, Triethylamine, formic acid. RuPhos. 1,3,5-trimethoxybenzene, and 1.2.4.5tetramethylbenzene were purchased from Sigma-Aldrich and used as received. RuPhos (Chloro-(2-Dicyclohexylphosphino-2',6'-diisopropoxy-1,1'-biphenyl)[2-(2-Precatalyst aminoethyl)phenyl]palladium(II) - methyl-t-butyl ether adduct) was purchased from Strem Chemicals Inc.

General Analytical Information

Nuclear magnetic resonance spectra were recorded on a Varian 400 MHz, a Varian 500 MHz, or a Varian 600 MHz instrument. All ¹H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ¹³C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ¹H decoupling. For quantitative NMR a 15-second relaxation delay parameter and 1,3,5-trimethoxybenzene or 1,2,4,5-tetramethylbenzene was used as internal standard to monitor yields, unless otherwise stated.

Light Source

LED strips (380 nm) were bought from elemental led (see www.elementalled.com) and used as shown below (Figure S1). Reactions were placed next to the 380 nm lights under vigorous stirring while cooling with compressed air. The light intensity was measured to be $1.8 \ \mu$ W/cm².



Figure S1. Representative reaction set-up comprising reaction vial surrounded by 380 nm LEDs with a tube blowing compressed air for cooling.

Synthesis of 10-phenylphenothiazine:



The following procedure was adopted from Maiti et al.³ To a vial armed with a magnetic stir bar was added NaOtBu (134 mg, 1.4 mmol), phenothiazine (199 mg, 1 mmol),

RuPhos Precat (14 mg, .02 mmol, 2 mol %), and RuPhos (8 mg, 0.02 mmol, 2 mol %). The vial was evacuated and backfilled 3x with argon before adding anhydrous Dioxane (1 mL). Lastly, anhydrous chlorobenzene (143 μ L, 1.4 mmol) was added. The vial was then placed in an oil bath at 110 °C and let react for 5 h. The vial was then cooled to room temperature, diluted with CH₂Cl₂, washed with water, brine, dried with Mg₂SO₄, and run through a silica plug (5 % EtOAc/Hexanes). The product was then dried under reduced pressure to yield 267 mg of a white solid (97 % yield). ¹H NMR (600 MHz, CDCl₃) δ : 7.60 (t, J = 8 Hz, 2H), 7.49 (t, J = 8 Hz, 1H), 7.40 (d, J = 7 Hz, 2H), 7.02 (d, J = 8 Hz, 2H), 6.86-6.79 (m, 4 H), 6.20 (d, J = 8 Hz, 2 H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ : 144.5, 141.2, 131.1, 130.9, 128.4, 127.0, 126.9, 122.7, 120.4, 116.3 ppm. HRMS C₁₈H₁₃NS Found 275.0753, Calc'd 275.0769.

General Procedure for Table 1 using lr(ppy)₃ or PTH:



A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with iodo- or bromobenzene (0.1 mmol), PTH (5 mol %) or $Ir(ppy)_3$ (1 mol %), formic acid (19 µL, 0.5 mmol), tributylamine (119 µL, 0.5 mmol), 1,2,4,5-tetramethylbenzene (NMR standard, 13.4 mg, 0.1 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction conversion was monitored by ¹H NMR.

Synthesis of PDI Photocatalyst:



The following procedure was adopted from Ghosh et al.⁴ To a dry 100 mL round bottomed flask equipped with a magnetic stir bar was added perylene-3,4,9,10tetracarboxylic dianhydride (392 mg, 1 mmol), 2,6-diisoprpylaniline (785 μL, 4.16 mmol), and imidazole (2.9 g). The flask was immersed in an oil bath at 190 °C for 20 h. The reaction was then stopped by cooling the flask to room temperature and adding EtOH (25 mL) and 2 M HCl (25 mL), sonicating, and filtering. The filtrate was washed with 1:1 EtOH/HCI (2 M) and 1:1 EtOH/H₂O mixtures before purifying by silica column chromatography using hexanes/dichloromethane (1:1 to 30:70 hexanes/dichloromethane). PDI was obtained as a red solid (35 mg). ¹H NMR (600 MHz, $CDCl_3$) δ : 8.80 (d, J = 7.9 Hz, 4H), 8.75 (d, J = 8.0 Hz, 4H), 7.51 (t, J = 7.8 Hz, 2H), 7.36 (d, J = 7.7 Hz, 4H), 2.82 – 2.70 (m, 4H), 1.19 (d, J = 6.8 Hz, 24H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ: 163.7, 145.9, 135.3, 132.3, 130.8, 130.4, 129.9, 127.1, 124.3, 123.7, 123.6, 29.5, 24.2 ppm. HRMS C₄₈H₄₂N₂O₄ Found 710.3129, Calc'd 710.3145.

General Procedure for Table 1 using PDI:

A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with iodo- or bromobenzene (0.05 mmol), PDI (1.8 mg, 0.0025 mmol, 5 mol %), 1,2,4,5-tetramethylbenzene (NMR standard, 6.7 mg, 0.05 mmol) and *N*,*N*-dimethylformamide (3 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and triethylamine (56 µL, 0.4 mmol) was added under argon before vigorously stirring in front of blue LEDs (λ_{max} = 465 nm, 5 μ W/cm²) while cooling with compressed air to maintain 40 °C. The reaction yields were monitored by ¹H NMR.

General Procedure for Table 2:

A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with substrate (0.1 mmol), PTH (1.4 mg, 5 mol %), formic acid (19 μ L, 0.5 mmol), tributylamine (119 μ L, 0.5 mmol), 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.

General Procedure for Isolation of Dehalogenated Products of 5, 8, and 19:

A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with substrate (0.2 mmol), PTH (2.8 mg, 5 mol %), formic acid (38 μ L, 1 mmol), tributylamine (238 μ L, 1 mmol), and acetonitrile (2 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction conversion was monitored by ¹H NMR, and stopped by opening the reaction to air. The acetonitrile was removed *in vacuo* before redissolving in ethyl acetate and washing with 2 M HCI. The aqueous layer was washed again with ethyl acetate, and the organic layers were combined and washed with 1 M NaCO₃, brine, and dried over Mg₂SO₄. The solvent was removed *in vacuo* and the resulting mixture was purified by silica gel column chromatography eluting with 99:1 hexane:ethyl acetate.



Benzyl benzoate (5): Spectral data matched that of commercially available reagents (see Sigma-Aldrich). ¹H NMR (600 MHz, CDCl₃) δ : 8.09 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (m, 4H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 5.37 (s, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ : 166.6, 136.3, 133.2, 130.4, 129.9, 128.8, 128.6, 128.5, 128.4, 66.9 ppm. HRMS C₁₄H₁₂O₂ Found 212.0830, Calc'd 212.0837.



Dimethyl Isophthalate (8): Spectral data matched that of commercially available reagents (see Sigma-Aldrich). ¹H NMR (600 MHz, CDCl₃) δ : 8.69 (s, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 3.95 (s, 6H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ : 166.5, 134.0, 131.0, 130.8, 128.8, 52.6 ppm. HRMS C₁₀H₁₀O₄ Found 194.0573, Calc'd 194.0579.



Benzyl benzoate (19): Spectral data matched that of commercially available reagents (see Sigma-Aldrich). ¹H NMR (600 MHz, CDCl₃) δ : ¹H NMR (600 MHz, CDCl₃) δ : 8.09 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.45 (m, 4H), 7.40 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.3 Hz, 1H), 5.37 (s, 2H) ppm.

Dehalogenation Using Commercially Available Catalyst:



A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with iodobenzene (11.2 μ L, 0.1 mmol), MePTH (1.1 mg, 5 mol %), formic acid (19 μ L, 0.5 mmol), tributylamine (119 μ L, 0.5 mmol), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.1 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.

	Conditions	
	2h, rt	
Entry	Conditions	% Yield
1	TBA(5eqv.), HCOOH(5eqv.) in ACN	94
2	TBA(5eqv.), HCOOH(5eqv.) in DMA	47
3	TBA(5eqv.), HCOOH(5eqv.) in DMF	67
4	TBA(5eqv.), HCOOH(5eqv.) in THF	10
5	TBA(5eqv.), HCOOH(5eqv.) in Hexane	12
6	TEA(5eqv.), HCOOH(5eqv.) in ACN	44
7	DIPEA(5eqv.), HCOOH(5eqv.) in ACN	93
8*	Compact Fluorescent Lamp , TBA(5eqv.), HCOOH(5eqv.) in ACN	45
9*	465 nm LED , TBA(5eqv.), HCOOH(5eqv.) in ACN	53

Table S1:	Optimization	table using	iodobenzene	and PTH ^[a]
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[a] Reaction conditions: Iodobenzene (1 equiv.), PTH (5 mol %), formic acid (5 equiv), tributylamine (5 equiv), Acetonitrile (0.08 M of substrate) at room temperature for 2 h with irradiation from 380 nm LEDs (1.8 μ W/cm²) unless otherwise stated. ¹H NMR yield determined using 1,2,4,5-tetramethylbenzene as an internal standard. *24 hour reaction time

Table S2: Control Experiments^[a]

	Conditions	
Entry	Conditions	% Yield
1	NO CATALYST, TBA(5eqv.), HCOOH(5eqv.) in ACN, 2hrs	0
2	NO LIGHT, TBA(5eqv.), HCOOH(5eqv.) in ACN, 2hrs	0
3	NO TBA, HCOOH(5eqv.) in ACN, 2hrs	0
4	TBA(5eqv.), NO HCOOH in ACN, 2hrs	71
5	NO TBA, NO HCOOH in ACN, 2hrs	0

[a] Reaction conditions: Iodobenzene (1 equiv.), PTH (5 mol %)), formic acid (5 equiv), tributylamine (5 equiv), Acetonitrile (0.08 M of substrate) at room temperature for 2 h with irradiation from 380 nm LEDs (1.8 μ W/cm²) unless otherwise stated. ¹H NMR yield determined using 1,3,5-trimethoxybenzene as an internal standard.

Table S3:	Optimization	of Catalyst	Loadings ^[a]
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'	X mol% PTH HCOOH (5 equiv) NBu ₃ (5 equiv)	
	380 nm light ACN, rt, 2h	
Entry	Catalyst loading	Yield
	(mol %)	(%)
1	5	> 95
2	1	90
3	0.5	85
4	0.1	42

[a] Reaction conditions: Iodobenzene (1 equiv.), PTH (0.1-5 mol %), Formic acid (5 equiv.), tributylamine (5 equiv.), Acetonitrile (0.08 M of iodobenzene) at room temperature with irradiation from 380 nm LEDs for 2 h. Yield tracked using 1,3,5-trimethoxybenzene as an internal standard.

Cost per reaction basis calculations for optimized PTH catalyst loading (5 mol %) and $Ir(ppy)_3$ (0.01 mol %)

Despite the fact that 5 mol % catalyst is typically used (of note, we demonstrate that as little as 0.5 mol % can be used), it is still ~ 1 order of magnitude cheaper than using 0.01 mol % of rare-earth derived $Ir(ppy)_3$. This calculation is based on the following analysis: Using prices obtained from Sigma-Aldrich, $Ir(ppy)_3$ costs \$270/250 mg or about \$1.08 per mg and the starting materials (phenothiazine and chlorobenzene) to prepare PTH (1-step synthesis) costs about \$0.00014 per mg. Thus for a 10.0 mmol reaction the price for a 0.01 mol % $Ir(ppy)_3$ reaction would be ~\$0.71 per reaction and for 5 mol % PTH it would be ~\$0.019 per reaction. In addition, as mentioned in the text of the manuscript potential applications in biological and electronic systems would benefit from a metal-free system where even trace amounts of metals can be potential hazardous.



Figure S2. Absorbance spectrum of PTH (0.17 mM in ACN) recorded on a Shimadzu 3600 UV-Vis-NIR spectrometer



Figure S3. Evidence for singlet state catalysis using PTH (a) Photoluminescence spectroscopy at room temperature and 77 K suggests no triplet emission at RT (b) Reaction in the presence of air (triplet quencher) proceeds, while no reaction is observed when using a triplet sensitizing catalyst (PTH-BP).

Triplet quenching control:

A control experiment was conducted using reported optimized conditions for $Ir(ppy)_3$, but in the presence of air and, as expected, no reduction of iodobenzene was observed after 2 h.

Fluorescence quenching studies:

A Varian Cary Eclipse Fluorescence Spectrophotometer was used in the quenching studies. The PTH solutions were excited at 350 nm. The emission of a 0.17 mM solution of PTH was first measured with varying concentrations of iodobenzene. As can be seen in Figure S2, the intensity of the peak emission was decreased with increasing concentration of iodobenzene, giving evidence for the direct reduction of iodobenzene upon irradiation of PTH. Next, the emission of a 0.17 mM solution of PTH was measured with varying concentrations of tributylamine. Figure S3 shows the raw emission data, demonstrating no quenching from the amine source.



Figure S4. Stern-Volmer quenching study with iodobenzene (quencher) and PTH (0.17 mM in ACN)



Figure S5. Emission spectra of 0.17 mM PTH solution in ACN with varying concentrations of tributylamine

Lifetime measurements:

PTH (0.17 mM in ACN) lifetime measurements were performed using Time-Correlated Single Photon Counting (TCSPC) technique. Approximately 200 femtosecond (fs) excitation pulses with wavelength 380 nm and ~10 pJ energy were generated by doubling the fundamental frequency of fs Ti:Sapphire laser (Coherent Mira 900) pulses in a commercial optical harmonic generator (Inrad). The laser repetition rate was reduced to 2 MHz by a home-made acousto-optical pulse picker in order to avoid saturation of the chromophore. TCSPC system is equipped with an ultrafast microchannel plate photomultiplier tube detector (Hamamatsu R3809U-51) and electronics board (Becker & Hickl SPC-130) and has instrument response time about 60-65 picoseconds. Triggering signal for the TCSPC board was generated by sending a small fraction of the laser beam onto a fast (400 MHz bandwidth) Si photodiode (Thorlabs Inc.). Fluorescence signal was dispersed in Acton Research SPC-500 monochromator after passing through a pump blocking, long wavelength-pass, autofluorescence-free, interference filter (Omega Filters, ALP series). The monochromator is equipped with a CCD camera (Roper Scientific PIXIS-400) allowing for monitoring of the time-averaged fluorescence spectrum.

A biexponential decay of the emission at 450 nm was observed to be τ_1 = 0.81 ns (54 %) and τ_2 = 2.3 ns (46 %).

Synthesis of PTH-BP:



To a 10 mL round-bottom flask with stir bar and condenser was added phenothiazine (0.5 g, 2.5 mmol), *m*-bromobenzophenone (0.78 g, 3.0 mmol), RuPhos (5.9 mg, 0.013 mmol), RuPhos Precatalyst (10.3 mg, 0.013 mmol) and sodium *tert*-butoxide (0.29 g, 3.0 mmol). The flask was evacuated and backfilled with argon three times before 2.5 mL

degassed 1,4-dioxane was added. The mixture was heated to 110 °C for 1 hour, then cooled to room temperature and partitioned between EtOAc and water. The EtOAc layer was washed twice more with water and once with brine, then the organic layer was dried with MgSO₄, filtered, and concentrated. The product was recrystallized from EtOAc/hexanes to give 727 mg PTH-BP as a yellow solid (76% yield) ¹H NMR (600 MHz, CDCl₃) δ 7.92 (d, J = 7.6 Hz, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.72 (t, J = 7.6 Hz, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 8.2 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 6.93 (t, J = 8.2 Hz, 2H), 6.87 (t, J = 7.6 Hz, 2H), 6.34 (d, J = 8.2 Hz, 2H) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 195.6, 143.8, 141.5, 140.2, 137.1, 134.0, 132.7, 131.3, 130.7, 130.0, 129.2, 128.4, 127.1, 129.9, 123.0, 121.6, 116.9 ppm; HRMS (ESI) calculated for C₂₅H₁₇NNaOS [M+Na]⁺: 402.0923, found 402.0919.

PTH-BP Photoluminescence at Room Temperature and 77 K:



Figure S6. Comparison of photoluminescence between PTH (0.17 mM in ACN) and BP-PTH (0.17 mM in ACN), giving evidence for no singlet state emission



Figure S7. Photoluminescence of PTH-BP (0.17 mM in ACN) at 77 K, showing triplet emission

Dehalogenation Procedure in the Presence of Air:

A vial equipped with a magnetic stir bar and fitted with a screw cap was charged with substrate (0.1 mmol), PTH (1.4 mg, 5 mol %), formic acid (19 μ L, 0.5 mmol), tributylamine (119 μ L, 0.5 mmol), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.1 mmol) and acetonitrile (1 mL). Without degassing, the reaction mixture was vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.

Note: lodobenzene was first tested using the above procedure, observing 90 % yield in 16 h with a capped vial. To be sure that the catalyst could operate in an "infinite" amount of oxygen, the reaction was also run continuously open to air and 90 % yield was observed after 15 h.

Procedure for Radical Cyclization:



A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with **23** (0.1 mmol), PTH (1.4 mg, 5 mol %), formic acid (19 μ L, 0.5 mmol), tributylamine (119 μ L, 0.5 mmol), 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.

Mechanistic Investigations:

The following tentative mechanism is proposed (Scheme S1). Upon absorption of a photon, PTH enters a highly reducing excited state, and an oxidative quenching cycle ensues. The excited catalyst preferentially reduces the carbon-halide bond, subsequently transforming the catalyst to an oxidized radical cation before it is reduced back to its native form by tributylamine, completing the catalytic cycle. To provide evidence that the reaction indeed occurs through the oxidative quenching cycle rather than reductive quenching, Stern-Volmer studies were conducted (Figures S4-5). Upon addition of iodobenzene to a solution of PTH, dynamic quenching was observed, implying a reductive process between the catalyst and substrate. However, when tributylamine was added to a solution of PTH, no decrease in photoluminescence occurred. This suggests that PTH is not reduced by tributylamine, and further supports that the oxidative quenching cycle is the mechanism for generation of the reactive intermediate.

Lastly, we were also interested in understanding subsequent steps of our proposed mechanism, including the primary source of the H-atom that eventually replaces the halide. In a series of control experiments with PTH/iodobenzene in the presence and absence of formic acid and tributylamine, reactions conducted with no formic acid, a reagent generally reported as a source for H-atom abstraction, did indeed lead to reduction of iodobenzene (71 % yield after 2 h).

This suggests that in addition to serving as reducing agent for the oxidized PTH, tributylamine may be the primary source of labile H-atoms. Subsequent experiments with deuterated NEt₃, HCOOH, and MeCN provided additional evidence suggesting that the tertiary amine served as the primary H-atom source. Interestingly, when deuterated formic acid was employed under the optimized conditions, deuterium incorporation was observed in the alpha and beta positions of tributylamine, indicating that an imine/enamine equilibrium was occurring in the reaction, with the formic acid playing a role in regenerating the amine (Figures S8-9).



Scheme S1 Proposed mechanism for metal-free photoredox radical dehalogenations

Deuterated Studies:



D₁₅-**TEA**: A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl 4-iodobenzoate (0.1mmol), PTH (5 mol %), formic acid (19 μ L, 0.5 mmol), D₁₅-triethylamine (80 μ L, 0.5 mmol), 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.



DCOOD: A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl 4-iodobenzoate (0.1 mmol), PTH (5 mol %), D₂-formic acid (19 μ L, 0.5 mmol), tributylamine(119 μ L, 0.5 mmol), 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.



D₃-ACN: A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl 4-iodobenzoate (0.1mmol), PTH (5 mol %), D₂-formic acid (19 μ L, 0.5 mmol), tributylamine (119 μ L, 0.5 mmol), 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.



DCOOD and D₃-ACN: A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl 4-iodobenzoate (0.1mmol), PTH (5 mol %), D₂-formic acid (19 μ L, 0.5 mmol), tributylamine (119 μ L, 0.5 mmol), 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) and D₃-acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.



D₁₅-TEA and DCOOD: A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with methyl 4-iodobenzoate (0.1mmol), PTH (5 mol %), D₂-formic acid (19 μ L, 0.5 mmol), D₁₅-triethylamine (80 μ L, 0.5 mmol), 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.



Figure S8. Deuterium NMR (in CH_2CI_2) of reaction mixture (see above, **DCOOD**) at 0 h and 2 h, showing deuterium incorporation at the alpha and beta position of tributylamine



2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0. fl(ppm)

Figure S9. Comparison of ¹H and deuterium NMR of reaction mixture (see above, **DCOOD**) after 2 h to confirm that deuterium is incorporated in the alpha and beta positions of tributylamine

Preparative Scale Reaction Conducted in Air:



To a 125mL Erlenmeyer flask equipped with a magnetic stir bar was added benzyl 4iodobenzoate (2.37 g, 7.0 mmol), PTH (96.4 mg, 0.35 mmol, 5 mol %), formic acid (1.32 mL, 35 mmol), tributylamine (8.32 mL, 35 mmol), and acetonitrile (70 mL). The flask was capped with a rubber septum and was stirred vigorously while irradiating with 380 nm LEDs and cooling with compressed air for 20 hours. The acetonitrile was removed *in vacuo* before redissolving in ~100mL of ethyl acetate and washing with ~100mL of 2M HCl. After extracting the aqueous layer with ethyl acetate (100 mL), the organic layer was combined and washed with 1 M NaCO₃ (100 mL) and brine before drying with Na₂SO₄. The solvent was removed *in vacuo* and the resulting mixture was purified by silica gel column chromatography eluting with 99:1 hexanes:ethyl acetate to give 1.486g of a pale yellow liquid (87%).

Recycled catalyst: 56 mg of PTH was isolated and purity was confirmed by ¹H and C¹³ NMR. ¹H NMR (600 MHz, DMSO) δ : : 6.86 (t, *J* = 6.9 Hz, 2H), 6.73 (t, *J* = 12 Hz, 1H), 6.61 (d, *J* = 7.7 Hz, 2H), 6.27 (d, *J* = 7.5 Hz, 2H), 6.12 (t, *J* = 7.8 Hz, 2H), 6.05 (t, *J* = 7.5 Hz, 2H), 5.35 (d, *J* = 8.2 Hz, 2H) ppm. ¹³C NMR (101 MHz, DMSO) δ : 143.7, 140.4, 131.2, 130.4, 128.6, 127.4, 126.8, 122.9, 119.5, 116.2 ppm.



Figure S9. ¹H NMR in DMSO of the isolated PTH after preparative scale reaction

Reductive Dehalogention Using Recycled PTH:



A vial equipped with a magnetic stir bar and fitted with a teflon screw cap septum was charged with benzyl 4-iodobenzoate (33.8 mg, 0.1 mmol), PTH (1.4 mg, 5 mol %), formic acid (19 μ L, 0.5 mmol), tributylamine (119 μ L, 0.5 mmol), 1,2,4,5-tetramethylbenzene (13.4 mg, 0.1 mmol) and acetonitrile (1 mL). The reaction mixture was degassed with three freeze-pump-thaw cycles. The vial was then backfilled with argon and vigorously stirred in front of 380 nm LEDs while cooling with compressed air to maintain ambient temperature. The reaction yield was monitored by ¹H NMR.

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