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In Situ-Generated Halogen-Bonding Complex Enables Atom-Transfer Radical Addition (ATRA) Reactions of Olefins

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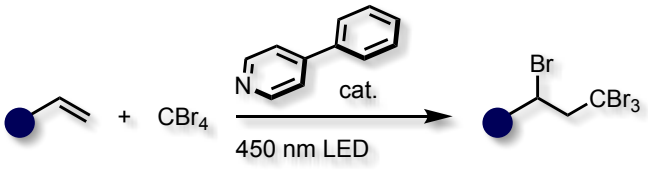
Keywords; photocatalysis, CT complex, halogen bonding, atom transfer radical addition, carbon radical



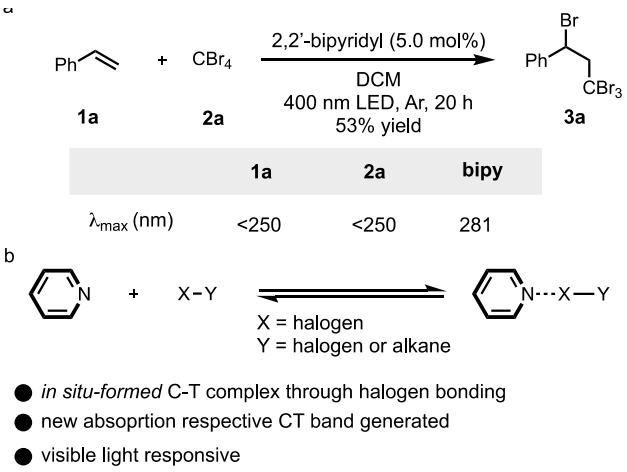
ABSTRACT: Although organic based photocatalysts provide an inexpensive, environmentally friendly alternative, many are incapable of absorption within the visible wavelength range; this ultimately influences their effectiveness. Photocatalytic reactions usually proceed via single electron transfer (SET) or energy transfer (ET) processes from the photoexcited molecules to the various substrates. In our study, the carbohalogenation of olefins was accomplished by combining CBr_4 and 4-Ph-pyridine under irradiation. The atom transfer radical addition reaction of olefins was catalyzed by an in situ formed photocatalyst *via* halogen bonding to afford a variety of products in moderate to good yields. Essential to the reaction is the formation of a CT complex with the haloalkene, which triggers charge separation processes and, ultimately, leads to the formation of the C-centered radical. While taking advantage of relatively inexpensive, readily available, and environmentally friendly reagents, the indirect activation of the substrate via the photoexcited catalyst paves the way for more efficient routes, especially for otherwise challenging chemical syntheses.

Introduction

Over the past decade, visible light photocatalysis has been extensively researched for the activation of small molecules. This process is often used to synthesize or functionalize a myriad of organic molecules that were previously difficult to access due to challenging or even impossible chemical transformations.[1–3] Most of the photocatalysts that have been developed so far are expensive and often use rare transition metals (e.g., ruthenium $[Ru(bpy)_3]^{2+}$ or iridium $[Ir(bpy)(ppy)_2]^{+}$ complexes); in a few cases, several other metal-based photocatalysts that incorporate heavy metals such as copper and bismuth have been reported.[4–6] Indeed, transition metal-based photocatalysts possess a long-lived metal-to-ligand charge transfer (MLCT) state, making them ideal as chemical reagents.[7,8] On the other hand, alternative and complementary methods of the above-mentioned methodology based on utilizing an organic photocatalyst have been actively developed.[9] Transition metal-based or organic photocatalyst undergo photocatalytic reactions via single electron transfer (SET) or energy-transfer (ET) processes from the photoexcited catalyst to the various substrates/reactants.[10,11] In these cases, the photoexcited catalyst can indirectly activate the substrate/reactant. Therefore, the development of photocatalysts that enable direct substrate/reactant activation is expected to lead to the creation of more efficient catalysts for chemical synthesis.

In this context, we have reported copper based photoredox complex catalyzed an atom-transfer radical addition (ATRA) reaction.[12,13] In the course of our study, we have found that combining CBr_4 with a catalytic amount of 2,2-bipyridyl under 400 nm LED irradiation furnished the 1,2-addition product through ATRA reaction with styrene (Scheme 1a).[14]

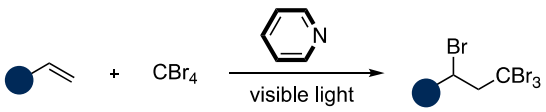
Scheme 1. (a) Preliminary results for the ATRA reaction between styrene and CBr_4. (b) In situ-formed CT complex via halogen bonding between pyridine and haloalkane/halogen.



Since the reagents employed for this reaction did not show any absorption capabilities around the visible region, we hypothesized that the *in situ*-formed active species may have acted as a photocatalyst under these light conditions. From that point of view, we focused on developing a in situ-generated photocatalyst based on halogen bonding which is relatively stable nonbonding interaction between the electrophilic region of the halogen atom and the nucleophilic region of the reacting molecules.[15–20] It is known that complexation between an amine or pyridine and a halogen atom results in the formation of charge-transfer complexes that respond to visible light, thus generated complex triggers photoinitiated charge separation, thus leading to the formation of *C*-centered radicals (Scheme 1b).[21] On the other hand, the use of halogen bonding for photocatalysis is unreliable due to the instability of the cations or cation radical species that are generated during the charge separation state by the photoexcitation of the CT complex; in the case of using amine as a halogen bonding acceptor, decomposition often occurs immediately under the reaction conditions.[21a] In 2019, Czekelius et al. performed photocatalytic perfluoroalkylation of alkenes mediated via the in situ-formed phosphine–alkyl iodide EDA complex.[22,23] However, a photocatalysis through halogen bonding employing a catalytic amount of amine has not been developed, and the methodology has long been desired.

Herein, we report the use of an in situ-generated photocatalyst that utilizes halogen bonding to enable the photocatalytic transformation of olefins via ATRA reactions (Scheme 2).

Scheme 2. This work



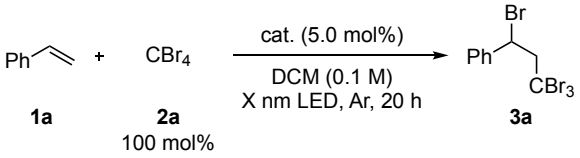
- Metal-free photocatalysis
- *in situ*-formed photocatalyst through halogen bonding
- visible light responsive

Results and Discussion

We first investigated the catalysis of N-heteroaromatics via the ATRA reaction between styrene (**1a**) and CBr_4 irradiated with a 3W LED light source (Table 1). When the reaction was performed using bipyridyl as the catalyst under 450 nm LED irradiation, the corresponding product **3a** was obtained in 1% yield (Entry 1). Using phenanthroline as the catalyst improved the yield to 42% (Entry 2). To our delight, **1a** could be functionalized into the corresponding **3a** at 450 nm using 5.0 mol% pyridine instead of the bidentate bipyridyl-type catalyst (Entry 3). We then examined the effect of the substituents on the pyridine ring. Here, introducing electron-donating substituents such as an *N,N*-dimethyl amino group onto the pyridine ring gave **3a** in lower yield (Entry 4). However, replacing the functional group with an electron-deficient moiety such as a cyano or an acetyl group improved the yield of the product, and these results indicated that the pyridines bearing electron withdrawing group tend to promote the desired reaction. (Entries 5 and 6). While 4-phenylpyridine showed excellent catalytic activity when compared to the aforementioned catalyst and gave the product in 57% yield (Entry 8), a significant drop in yield was noted when 2-phenylpyridine was used as the catalyst (Entry 7).[24] Additionally, the efficiency of the light source was evaluated by comparing for the ATRA reaction of **1a**. Under the optimized reaction conditions with 5.0 mol% catalyst loading, various wavelengths ranging from 400 to 500 nm were examined. We found

that when the reaction was conducted under shorter wavelengths, i.e., between 400 and 420 nm, the yield of **3a** decreased slightly (Entries 9–11). However, using longer wavelengths resulted in a significant drop in yield (Entries 12 and 13). Therefore, 450 nm was chosen as the optimal wavelength for this reaction.[25] Finally, the load of **1a** was increased to 150 mol%, which resulted in the highest reaction yield of 70 % (NMR) and 62 % (isolated yield) (Entry 14). A set of control experiments revealed that light and pyridine were necessary for reactivity (Entries 15 and 16).

Table 1. Optimization of the ATRA reaction between styrene and CBr_4



entry	**1a** (mol%)	cat.	LED (nm)	yield (%)
1	100	2,2-Bipyridyl	450	1
2	100	phenanthroline	450	42
3	100	Pyridine	450	42
4	100	DMAP	450	23
5	100	4-CN-pyridine	450	48
6	100	4-Ac-pyridine	450	49
7	100	2-Ph-pyridine	450	25
8	100	4-Ph-pyridine	450	57
9	100	4-Ph-pyridine	400	47
10	100	4-Ph-pyridine	410	51
11	100	4-Ph-pyridine	420	53
12	100	4-Ph-pyridine	470	20

13	100	4-Ph-pyridine	500	2
14	150	4-Ph-pyridine	450	70 (62)
15	150	4-Ph-pyridine	dark	NR
16	150	w/o cat.	450	NR

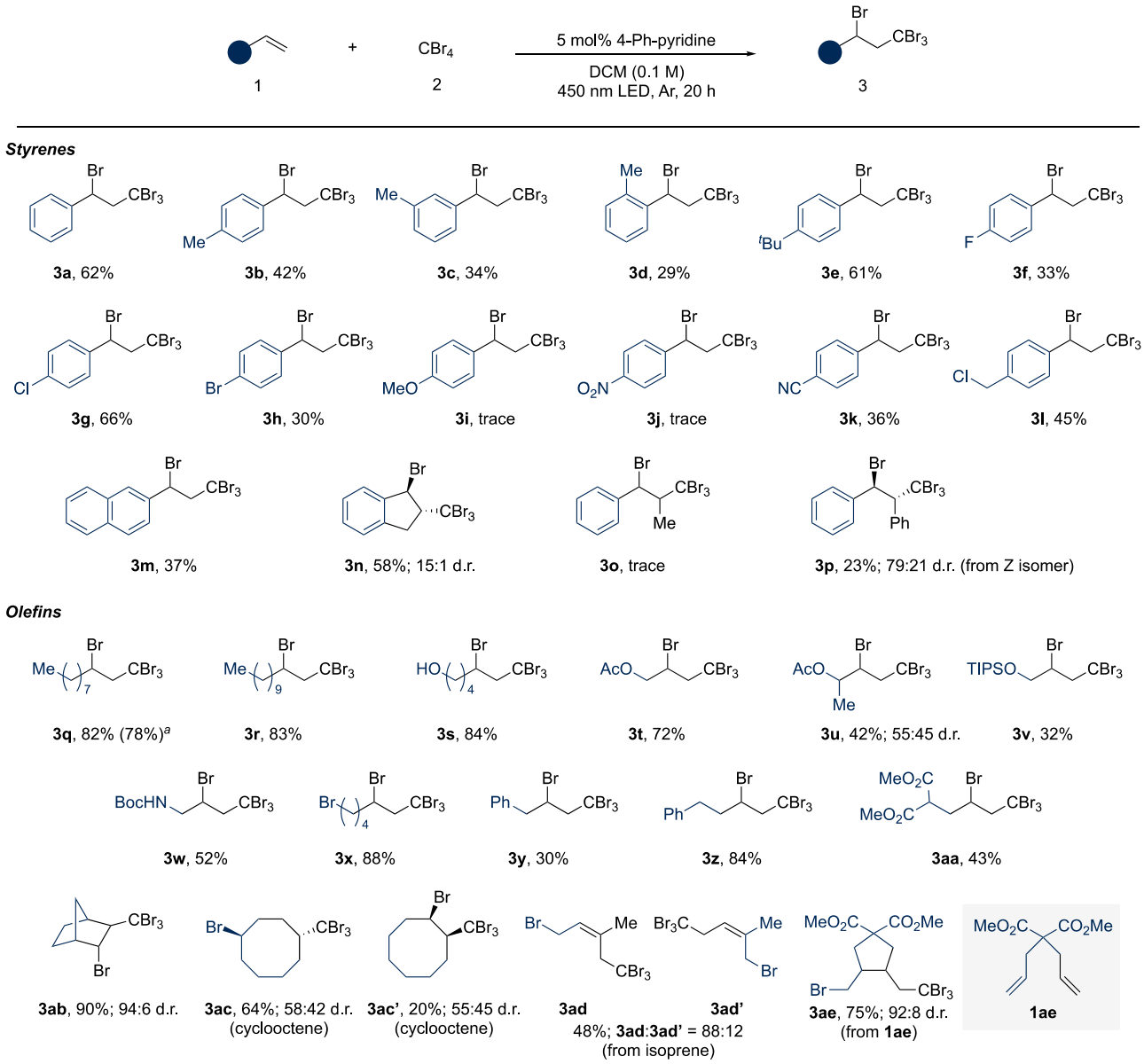
Yields were determined via ^{1}H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard. The values in parentheses are the isolated yields.

With the optimized conditions in hand, we subjected various olefins to the ATRA reaction (Table 2) and found that this reaction was applicable for a wide range of styrene-bearing alkyl (**1b–e**), halo (**1f–h**) and cyano (**1k**) groups. Under the optimal conditions, 4-nitrostyrene (**1j**) did not react with CBr_4, due to **1j** could act as a quencher for complex formed.[26] However, the use of 4-MeO-substituted styrene (**1i**) predominantly resulted in the polymerization of styrene because of the increased reactivity of the stabilized olefin radical.[27] It was also determined that 2-vinylnaphthalene was well tolerated under the aforementioned reaction conditions. Using internal olefins such as indene (**1n**) and stilbene (**1p**) resulted in low yields, whereas β-methylstyrene (**1o**) gave no product at all.

Next, aliphatic olefins were subjected to this optimized ATRA reaction. As noted, aliphatic olefins tended to give better yields than their styrene counterparts. Moreover, the gram scale reaction of **1q** gave corresponding product in 78% yield, although prolonged reaction time to 40 h was required. A linear, alkene-bearing, unprotected alcohol (**1s**), an acetate (**1t**), a branched (**1u**), a TIPS-protected alcohol (**1v**), an amine (**1w**), and an ester (**1aa**) were all tolerated under these reaction conditions and gave the corresponding product in moderate to good yields. Interestingly, the primary alkyl bromide (**1x**) was a good substrate and gave the product in 88% yield without any decomposition of the C–Br bond. Although the use of an allylbenzene (**1y**) as a substrate resulted in reduced yield, the phenyl butene (**1z**) furnished the product in high yield. Notably, a cyclic alkene such as norbornene (**1ab**) smoothly furnished the product with excellent selectivity. On the other hand, while the reaction proceeded using cyclooctene as the starting material, the 1,2-addition and 1,4-addition products were obtained in 64% and 20%,

respectively. Previous reports on ATRA reactions between cyclooctene and CBr_4 revealed that the formation of the 1,4-addition product proceeded through a 1,5-hydrogen shift before the radical had been trapped.[28,29] When a conjugated diene such as isoprene (**1ad**) was used as the substrate, two regioisomers, namely, **3ad** and **3ad'**, were generated in moderate yield with a regioisomeric ratio of 88:12. The radical addition/cyclization trapping experiments were conducted using diallyl malonate (**1ae**).[30] The reaction between **1ae** and CBr_4 gave the product **3ae** in 75% yield with high diastereoselectivity. These experiments revealed that the ATRA reaction was initiated through a radical addition to olefins.

Table 2. Substrate scope for the atom-transfer radical addition of styrenes and CBr_4.

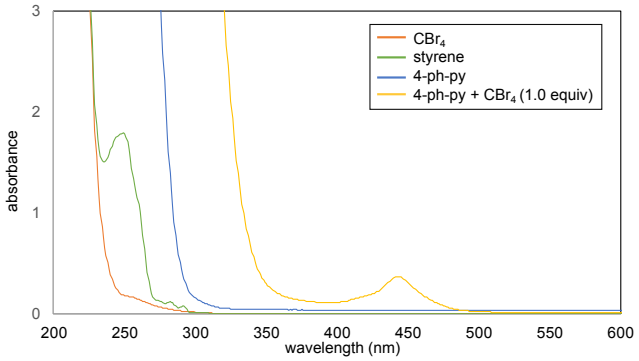


The diastereomeric ratio was determined via 1H NMR analysis of the crude reaction mixture.

[a] 4 mmol of **2** was used.

Further experiments were conducted to gain mechanistic insight into the catalyst's mode of action. At first, UV–Vis spectra of the solution containing 4-phenylpyridine, styrene, and CBr_4 alone as well as an

equimolar mixture of 4-phenylpyridine with CBr_4 were obtained. Styrene, 4-phenylpyridine, and CBr_4 did not show any absorption bands around the visible region (Figure 1 top). In contrast, the UV–Vis spectrum of the equimolar mixture of 4-phenylpyridine and CBr_4 had a new absorption band at 444 nm, which indicated that charge-transfer absorption had occurred between pyridine and CBr_4 via halogen bonding. Moreover, the newly formed absorption band was also measured using 4-phenylpyridine with various concentrations of CBr_4 (Figure 1 bottom).[31] The broad band between 400 and 500 nm was concentration dependent on CBr_4, indicating pronounced halogen bonding interactions between CBr_4 and 4-phenylpyridine. Thus, catalysis could have been initiated through the formation of the CT complex between pyridine and CBr_4, followed by photoexcitation to generate the active species.



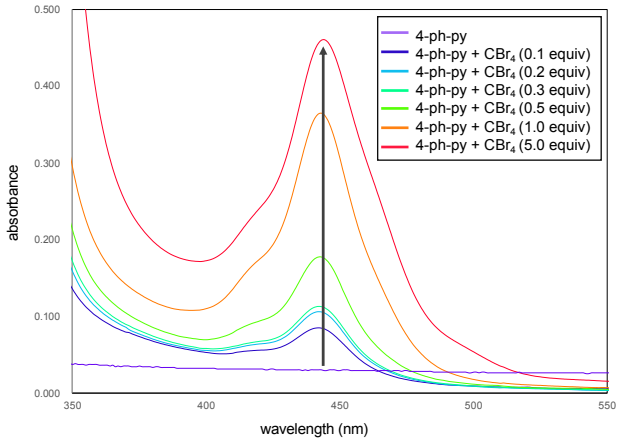


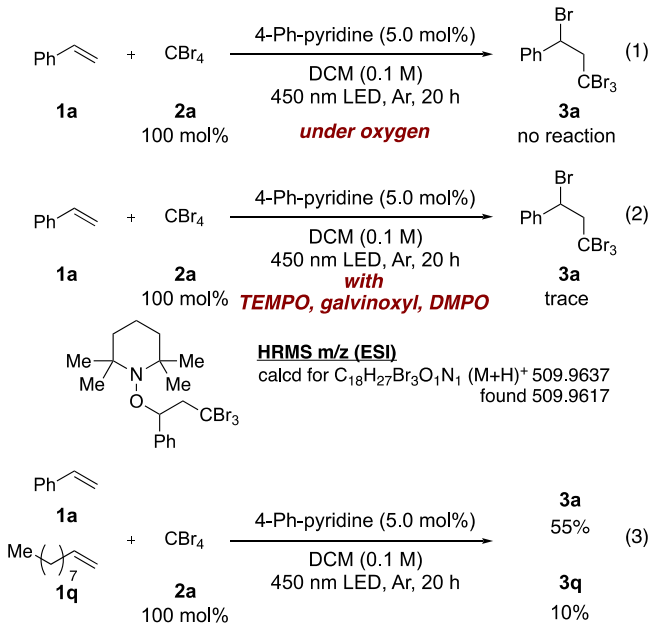
Figure 1. Study of the halogen-bond adduct. top) UV–Vis spectra of styrene (**1a**), CBr_4 (**2**), 4-ph-py, and a 1:1 mixture of **2** with 4-ph-py. The concentration of **1a**, **2**, and 4-ph-py in DCM was 1.0 mM each, whereas the mixture of 2 and 4-ph-py was 0.1 M. bottom) UV–Vis spectra of 4-ph-py (0.1 M in DCM) with different equivalents of CBr4 in DCM after irradiation at 450 nm for 1 h.

Further mechanistic investigations were also conducted (Scheme 3). The reaction between **1a** and **2a** under the optimized conditions in oxygen resulted in no reaction (Eq. 1). This result indicated that the photoexcited active species was quenched by a triplet oxygen molecule.[32] Furthermore, radical trapping experiments gave no desired product, whereas the use of TEMPO, galvinoxyl, and DMPO under the optimized conditions proceeded via the radical intermediate (Eq. 2). In the case of using TEMPO as a radical scavenger, TEMPO adduct was determined by ESI-MS. Finally, competition experiments using styrene (**1a**) and decene (**1q**) were conducted (Eq. 3); the products obtained from styrene **3a** and decene **3q** were obtained in 55% and 10% yield, respectively. This result was consistent with previous reports in

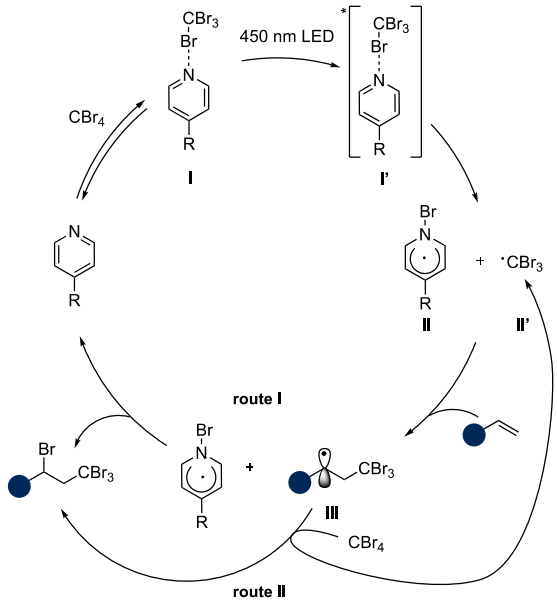
which the electron-deficient radical tended to react faster with the styrene analogs than with their aliphatic counterparts.[33]

Based on the literature reports and our experimental evidence, it was postulated that the reaction between CBr_4 and 4-phenylpyridine proceeded via the formation of the charge-transfer complex, **I**, before photoexcitation at 450 nm (Scheme 4). The photoexcitation of **I** led to a homolysis of C–Br bond that generated the radical, **II**, and the tribromomethyl radical, **II'**. The resulting *C*-centered radical, **II'**, was then reacted with the olefins to generate the radical intermediate, **III**, which subsequently reacted with **II** to furnish the desired ATRA product (route I). Another possibility is a radical chain mechanism where the generated **III** reacts with CBr_4 to give ATRA product and regenerate **II'** (route 2).

Scheme 3. Controlled experiments for mechanistic studies



Scheme 4. Possible mechanism for the ATRA reaction of olefins



Conclusion

ATRA reactions of olefins catalyzed by an in situ-formed photocatalyst via halogen bonding were investigated. Carbohalogenation of olefins with carbon tetrabromide afforded a variety of products in moderate to good yields when irradiated at 450 nm. The photocatalysts from our study revealed that a CT complex between pyridines and CBr_4 was a crucial intermediate in the subsequent charge separation processes that led to the formation of the *C*-centered radical.

The activation of the substrate via halogen bonding to form the CT complex is a novel activation method that can be used for challenging synthetic routes since halogen bond acceptors such as pyridine are relatively inexpensive and readily available. Continued efforts are focused on extending this new methodology to other classes of compounds for photocatalysis, including alkyl halides with amines or phosphines.

■Experimental Section General considerations

General Information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received.

Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F_{254}). Flash column chromatography was performed with Kanto silica gel 60N (Spherical, Neutral, 40-50 mm). Visualization of the developed chromatogram was performed by UV lamp (254 nm) and vanillin or basic potassium permanganate stain. NMR spectra were recorded on a JEOL ECA 500 spectrometer (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR and 470 MHz for ^{19}F NMR), and are internally referenced to residual protio solvent signals or TMS (note: $CDCl_3$ referenced at δ 7.26

and 77.0 ppm respectively, TMS referenced at δ 0 and 0 ppm respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets), coupling constant (Hz), integration, and assignment. Data for $^{13}C\{^{1}H\}$ NMR are reported in terms of chemical shifts (δ ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD (TOF Mass Analyzer) and are reported as *m*/*z* ($M+H^{+}$, relative intensity). Melting points were measured on a Yanagimoto micro melting point apparatus without correlation.

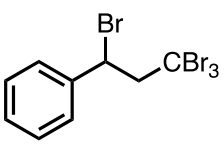
General Procedure for Atom-Transfer Radical Addition

A Pyrex® test tube (12.5 cm × 1.6 cm) containing a mixture of alkene **1** (1.5 equiv, 0.15 mmol), carbontetrabromide **2** (1.0 equiv, 0.1 mmol) and 4-phenylpyridine (0.05 equiv, 0.005 mmol) in dichloromethane (1.0 mL) was degassed *via* FPT cycling for three times and backfilled with Ar. The tube was placed ca. 0.5 cm from 3W 450 nm LED. The resulting solution was stirred at ambient temperature for 20 h. The residue was filtrated through Celite, washed with $CHCl_3$, concentrated *in vacuo*. The resulting mixture was purified by flash column chromatography on silica gel (*n*-hexane) to give desired product **3**.

Scale up reaction of 1q

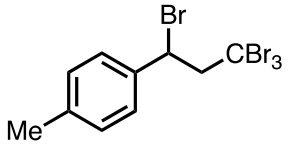
100 mL flask containing a mixture of alkene **1q** (1.5 equiv, 6.0 mmol), carbontetrabromide **2** (1.0 equiv, 4.0 mmol) and 4-phenylpyridine (0.05 equiv, 0.2 mmol) in dichloromethane (40 mL) was degassed *via* FPT cycling for three times and backfilled with Ar. The tube was placed ca. 0.5 cm from 3W 450 nm LED x 4. The resulting solution was stirred at ambient temperature for 40 h. The residue was filtrated through Celite, washed with $CHCl_3$, concentrated *in vacuo*. The resulting mixture was purified by flash column chromatography on silica gel (*n*-hexane) to give desired product **3q** (78% yield, 1.46 g, 3.12 mmol) as a coloress oil.

Characterization Data

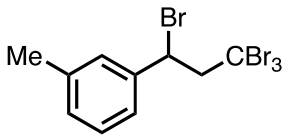


1,3,3,3-Tetrabromopropyl)benzene (**3a**): Following the general procedure, **3a** was obtained from a flash column chromatography (*n*-hexane) as a white crystalline solid

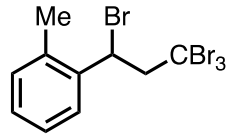
(62% yield, 26.8 mg, 0.062 mmol). **TLC (SiO_2)**: R_f = 0.54 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 5.33 (dd, *J* = 7.5 Hz, 4.0 Hz, 1H), 4.12 (dd, *J* = 15.5 Hz, 4.0 Hz, 1H), 4.06 (dd, *J* = 15.5 Hz, 7.5 Hz, 1H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 140.8, 128.94, 128.87, 128.1, 66.4, 50.0, 35.0. NMR spectra of the **3a** were consistent with the reported one.[14j]



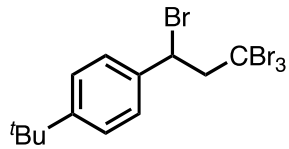
1-Methyl-4-(1,3,3,3-Tetrabromopropyl)benzene (**3b**): Following the general procedure, **3b** was obtained from a flash column chromatography (*n*-hexane) as a colorless oil (42% yield, 18.7 mg, 0.042 mmol). **TLC (SiO_2)**: R_f = 0.59 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 5.32 (dd, *J* = 7.5 Hz, 4.0 Hz, 1H), 4.11 (dd, *J* = 15.5 Hz, 4.0 Hz, 1H), 4.05 (dd, *J* = 15.5 Hz, 7.5 Hz, 1H), 2.34 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 139.0, 137.8, 130.0, 128.0, 66.4, 50.3, 35.2, 21.3. NMR spectra of the **3b** were consistent with the reported one.[13c]



1-Methyl-3-(1,3,3,3-Tetrabromopropyl)benzene (**3c**): Following the general procedure, **3c** was obtained from a flash column chromatography (*n*-hexane) as a colorless oil (34% yield, 15.2 mg, 0.034 mmol). **TLC (SiO_2)**: R_f = 0.59 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.29-7.23 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 5.29 (dd, *J* = 7.5 Hz, 4.0 Hz, 1H), 4.11 (dd, *J* = 15.5 Hz, 4.0 Hz, 1H), 4.05 (dd, *J* = 15.5 Hz, 7.5 Hz, 1H), 2.37 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 140.8, 138.6, 129.7, 128.73, 128.72, 125.2, 66.4, 50.2, 35.2, 21.4. NMR spectra of the **3c** were consistent with the reported one.[12]

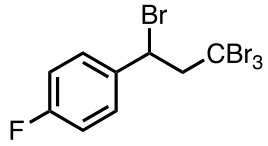


1-Methyl-2-(1,3,3,3-Tetrabromopropyl)benzene (**3d**): Following the general procedure, **3d** was obtained from a flash column chromatography (*n*-hexane) as a colorless oil (29% yield, 12.9 mg, 0.029 mmol). **TLC (SiO_2)**: R_f = 0.57 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 6.9 Hz, 1H), 7.26 (dt, *J* = 7.5 Hz, 6.9 Hz, 1H), 7.20 (dt, *J* = 7.5 Hz, 6.9 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 5.56 (br, 1H), 4.21-4.13 (m, 2H), 2.50 (s, 3H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 139.1, 135.3, 130.8, 128.6, 128.1, 126.8, 66.2, 45.9, 35.3, 19.5. NMR spectra of the **3d** were consistent with the reported one.[12]

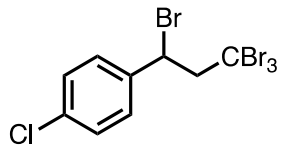


1-Methyl-4-(1,3,3,3-Tetrabromopropyl)benzene (**3e**): Following the general procedure, **3e** was obtained from a flash column chromatography (*n*-hexane) as a yellow crystalline solid (61% yield, 29.8 mg, 0.061 mmol). **TLC (SiO_2)**: R_f = 0.61 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.37

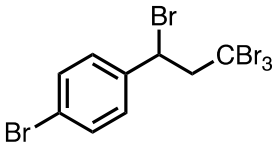
(d, *J* = 8.6 Hz, 2H), 5.32 (dd, *J* = 7.5 Hz, 4.0 Hz, 1H), 4.12 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 4.04 (dd, *J* = 7.5 Hz, 16.0 Hz, 1H), 1.31 (s, 9H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 152.2, 137.8, 127.7, 125.8, 66.5, 50.2, 35.2, 34.7, 31.3. NMR spectra of the **3e** were consistent with the reported one.[12]



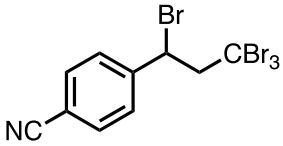
1-Fluoro-4-(1,3,3,3-Tetrabromopropyl)benzene (**3f**): Following the general procedure, **3f** was obtained from a flash column chromatography (*n*-hexane) as a colorless oil (33% yield, 14.8 mg, 0.033 mmol). **TLC (SiO_2)**: R_f = 0.56 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.48 (dd, *J* = 7.5 Hz, 5.2 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 2H), 5.34 (dd, *J* = 8.0 Hz, 3.4 Hz, 1H), 4.10 (dd, *J* = 15.5 Hz, 3.4 Hz, 1H), 4.01 (dd, *J* = 15.5 Hz, 8.0 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 163.7, 161.8, 136.6, 136.5, 130.1, 130.0, 116.0, 115.8, 66.4, 49.1, 34.7. **^{19}F NMR (100 MHz, $CDCl_3$)** δ -111.9. NMR spectra of the **3f** were consistent with the reported one.[12]



1-Chloro-4-(1,3,3,3-Tetrabromopropyl)benzene (**3g**): Following the general procedure, **3g** was obtained from a flash column chromatography (*n*-hexane) as a white crystalline solid (66% yield, 30.7 mg, 0.066 mmol). **TLC (SiO_2)**: R_f = 0.61 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 5.30 (dd, *J* = 8.3 Hz, 3.7 Hz, 1H), 4.10 (dd, *J* = 15.5 Hz, 3.4 Hz, 1H), 4.01 (dd, *J* = 15.5 Hz, 8.3 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 139.2, 134.8, 130.0, 129.1, 66.2, 48.9, 34.6. NMR spectra of the **3g** were consistent with the reported one.[12]

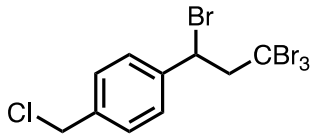


1-Bromo-4-(1,3,3,3-Tetrabromopropyl)benzene (**3h**): Following the general procedure, **3h** was obtained from a flash column chromatography (*n*-hexane) as a white crystalline solid (30% yield, 15.3 mg, 0.030 mmol). **TLC (SiO_2)**: R_f = 0.57 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 5.29 (dd, *J* = 8.3 Hz, 3.7 Hz, 1H), 4.10 (dd, *J* = 15.5 Hz, 3.7 Hz, 1H), 4.01 (dd, *J* = 15.5 Hz, 8.3 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 139.7, 132.1, 129.8, 122.9, 66.2, 48.9, 34.6. NMR spectra of the **3h** were consistent with the reported one.[12]

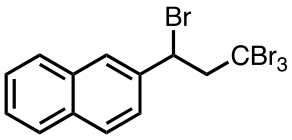


1-Cyano-4-(1,3,3,3-Tetrabromopropyl)benzene (**3k**): Following the general procedure, **3g** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil (36% yield, 16.4 mg, 0.036 mmol). **TLC (SiO_2)**: R_f = 0.10 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 5.32 (dd, *J* = 8.6 Hz, 3.4 Hz, 1H), 4.12 (dd, *J* = 15.5 Hz, 3.4 Hz, 1H), 4.02 (dd, *J* = 15.5 Hz, 8.6 Hz, 1H).

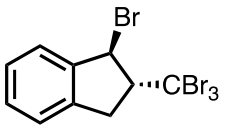
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 145.6, 132.7, 129.0, 118.2, 112.8, 65.9, 47.9, 34.1. NMR spectra of the **3k** were consistent with the reported one.[34]



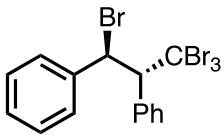
1-Chloromethyl-4-(1,3,3,3-Tetrabromopropyl)benzene (**3l**): Following the general procedure, **3l** was obtained from a flash column chromatography (*n*-hexane) as a colorless oil (45% yield, 21.6 mg, 0.045 mmol). **TLC (SiO_2)**: R_f = 0.26 (*n*-hexane). **^1H NMR (500 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 5.33-5.32 (m, 1H), 4.58 (s, 2H), 4.12 (dd, *J* = 15.5 Hz, 1.7 Hz, 1H), 4.04 (dd, *J* = 15.5 Hz, 7.5 Hz, 1H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 140.9, 138.2, 129.1, 128.5, 66.3, 49.3, 45.6, 34.8. NMR spectra of the **3l** were consistent with the reported one.[12]



2-(1,3,3,3-Tetrabromopropyl)naphthalene (**3m**): Following the general procedure, **3m** was obtained from a flash column chromatography (*n*-hexane) as a white crystalline solid (37% yield, 17.9 mg, 0.037 mmol). **TLC (SiO_2)**: R_f = 0.51 (*n*-hexane). **^1H NMR (500 MHz, $CDCl_3$)** δ 7.90-7.88 (m, 2H), 7.85-7.82 (m, 2H), 7.63 (d, *J* = 8.6 Hz, 1H), 7.53-7.50 (m, 2H), 5.54 (t, *J* = 5.2 Hz, 1H), 4.18 (d, *J* = 5.2 Hz, 2H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 137.7, 133.3, 132.9, 129.1, 128.2, 127.7, 127.3, 126.9, 126.7, 125.4, 66.1, 50.7, 35.0. **FTIR (ATR)** 3391, 3054, 3024, 2928, 2163, 1913, 1709, 1632, 1600, 1509, 1470, 1440, 1416, 1371, 1271, 1220, 1201, 1174, 1158, 1126, 1089, 1050, 1018, 1002, 986, 964, 942, 907, 892, 857, 816, 772, 756, 737, 703, 660 cm^{-1}. **HRMS m/z (DART)** calcd for $C_{13}H_{11}Br_4^+$ $(M+H)^+$ 482.7589, found 482.7612. **m.p.** 84.2-86.2 ºC.

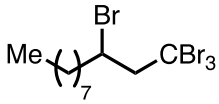


1-Bromo-2-tetrabromomethyl-2,3-dihydro-1H-inden (**3n**): Following the general procedure, **3n** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil {58% yield, 25.7 mg, 0.058 mmol (*dr* = 15 : 1)}. **TLC (SiO_2)**: R_f = 0.55 (*n*-hexane). **^1H NMR (500 MHz, $CDCl_3$)** δ 7.44 (dd, *J* = 8.3 Hz, 4.6 Hz, 1H), 7.30 (dd, *J* = 4.6 Hz, 3.7 Hz, 2H), 7.23 (dd, *J* = 8.3 Hz, 3.7 Hz, 2H), 5.65 (d, *J* = 3.1 Hz, 1H), 4.20 (ddd, *J* = 9.2 Hz, 4.0 Hz, 3.1 Hz, 1H), 3.60 (dd, *J* = 17.5 Hz, 9.2 Hz, 1H), 3.25 (dd, *J* = 17.5 Hz, 4.0 Hz, 1H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 141.9, 140.6, 129.5, 127.9, 126.0, 124.5, 71.7, 55.1, 45.5, 38.3. NMR spectra of the **3n** were consistent with the reported one.[12]

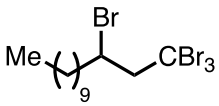


(1,3,3,3-Tetrabromo-2-phenylpropyl)benzene (**3p**): Following the general procedure, **3p** was obtained from a flash column chromatography (*n*-hexane) as a colorless oil {23% yield, 11.7 mg, 0.023 mmol, 79:21 d.r. (from Z isomer)}. **TLC**

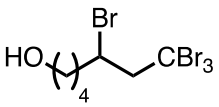
(SiO$_2$): R_f = 0.19 (*n*-hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.59 (br, 1H), 7.47-7.37 (m, 5H), 7.32-7.21 (m, 4H), 5.94 (d, *J* = 5.8 Hz, 1H), 4.38 (d, *J* = 5.8 Hz, 1H). **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 140.7, 138.1, 128.9, 128.71, 128.68, 128.4, 127.7, 71.9, 55.0, 42.9. **FTIR (ATR)** 3062, 3030, 1601, 1496, 1453, 1339, 1185, 1157, 177, 1033, 977, 915, 853, 825, 778, 761, 725, 698 cm^{-1}. **HRMS m/z (DART)** calcd for $C_{15}H_{12}Br_3$ $(M\text{-}Br)^+$ 428.8484, found 428.8479.



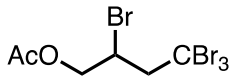
1,1,1,3-Tetrabromoundecane (**3q**): Following the general procedure, **3q** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil (82% yield, 38.4 mg, 0.082 mmol). **TLC (SiO$_2$)**: R_f = 0.64 (*n*-hexane). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 4.20 (dt, *J* = 7.2 Hz, 4.6 Hz, 1H), 3.83 (dd, *J* = 11.5 Hz, 4.6 Hz, 1H), 3.55 (dd, J = 11.5 Hz, 5.2 Hz, 1H), 2.11-1.93 (m, 2H), 1.63-1.47 (m, 2H), 1.33-1.25 (m, 11H), 0.89 (t, *J* = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 66.9, 52.1, 39.7, 36.4, 31.8, 29.4, 29.2, 28.7, 27.3, 22.6, 14.1. NMR spectra of the **3q** were consistent with the reported one.[12]



1,1,1,3-Tetrabromotridecane (**3r**): Following the general procedure, **3r** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil (83% yield, 41.2 mg, 0.083 mmol). **TLC (SiO$_2$)**: R_f = 0.64 (*n*-hexane).**^{1}H NMR (500 MHz, CDCl$_3$)** δ 4.20 (dt, *J* = 4.6 Hz, 4.0 Hz, 1H), 3.84 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 3.55 (dd, J = 16.0 Hz, 4.6 Hz, 1H), 2.11-1.93 (m, 2H), 1.63-1.56 (m, 1H), 1.54-1.47 (m, 1H), 1.37-1.27 (m, 14H), 0.88 (t, *J* = 5.7 Hz, 3H). **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 66.9, 52.1, 39.7, 36.4, 31.9, 29.6, 29.5, 29.4, 29.3, 28.7, 27.3, 22.7, 14.1. NMR spectra of the **3r** were consistent with the reported one.[35]

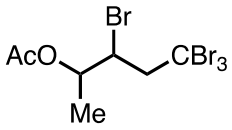


5,7,7,7-Tetrabromoheptan-1-ol (**3s**): Following the general procedure, **3s** was obtained from a flash column chromatography (*n*-hexane : ethyl acetate = 2:1) as a coloress oil (84% yield, 35.9 mg, 0.084 mmol). **TLC (SiO$_2$)**: R_f = 0.40 (*n*-hexane : ethyl acetate = 2:1). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 4.22 (dq, *J* = 4.6 Hz, 4.0 Hz, 1H), 3.85 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 3.70 (t, J = 5.2 Hz, 2H), 3.56 (dd, J = 16.0 Hz, 4.6 Hz, 1H), 2.16-1.99 (m, 2H), 1.75-1.60 (m, 4H), 1.40 (s, 1H). **^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$)** δ 66.8, 62.6, 51.7, 39.4, 36.2, 31.7, 23.7. NMR spectra of the **3s** were consistent with the reported one.[6]

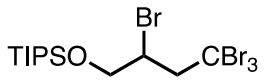


1,1,1,3-Tetrabromo-4-acetoxybutane (**3t**): Following the general procedure, **3t** was obtained from a flash column chromatography (*n*-hexane : ethyl acetate = 10:1) as a coloress oil (72% yield, 30.8 mg, 0.072 mmol). **TLC (SiO$_2$)**: R_f = 0.38 (*n*-hexane : ethyl acetate = 10:1). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 4.53 (dd, *J* = 11.5 Hz, 5.2 Hz, 1H), 4.42-4.33 (m, 2H), 3.75 (dd, *J* = 20.6

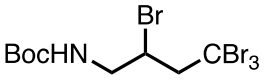
Hz, 5.2 Hz, 1H), 3.70 (dd, *J* = 20.6 Hz, 11.8 Hz, 1H), 2.14 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 170.3, 66.8, 63.1, 45.5, 35.1, 20.8. NMR spectra of the **3t** were consistent with the reported one.[12]



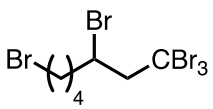
1,1,1,3-Tetrabromo-4-acetoxy-4-methylbutane (**3u**): Following the general procedure, **3u** was obtained from a flash column chromatography (*n*-hexane : ethyl acetate = 10:1) as a coloress oil (42% yield, 18.6 mg, 0.042 mmol, 55:45 d.r.). **TLC (SiO_2)**: R_f = 0.25 (*n*-hexane : ethyl acetate = 10:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.20 (dq, *J* = 9.2 Hz, 6.3 Hz, 1H), 4.23 (ddd, *J* = 9.2 Hz, 5.5 Hz, 3.7 Hz, 1H), 3.68 (dd, *J* = 16.3 Hz, 3.7 Hz, 1H), 3.63 (dd, *J* = 16.3 Hz, 5.5 Hz, 1H), 2.11 (s, 3H), 1.43 (d, 3H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 170.1, 71.7, 62.3, 51.1, 35.9, 21.2, 17.2. **FTIR (ATR)** 2927, 2847, 1742, 1372, 1231, 1058, 946 cm^{-1}. **HRMS m/z (DART)** calcd for $C_7H_{11}Br_4O_2$ $(M+H)^+$ 442.7487, found 442.7471.



1,1,1,3-Tetrabromo-4-((triisopropylsilyl)oxy)butane (**3v**): Following the general procedure, **3v** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil (32% yield, 17.3 mg, 0.032 mmol). **TLC (SiO_2)**: R_f = 0.60 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.23-4.19 (m, 1H), 4.10 (dd, *J* = 10.9 Hz, 5.7 Hz, 1H), 3.95 (dd, *J* = 10.9 Hz, 5.7 Hz, 1H), 3.91 (dd, *J* = 10.9 Hz, 2.9 Hz, 1H), 3.58 (dd, *J* = 10.9 Hz, 5.7 Hz, 1H), 1.13-1.07 (m, 21H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 67.2, 62.6, 50.2, 36.4, 18.0, 12.0. **FTIR (ATR)** 2943, 2866, 1740, 1462, 1370, 1229, 1217, 1111, 1065, 999, 945, 882, 791, 685 cm^{-1}. **HRMS m/z (DART)** calcd for $C_{13}H_{27}Br_4OSi$ $(M+H)^+$ 542.8559, found 542.8555.

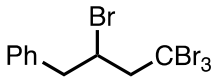


1,1,1,3-Tetrabromo-4-((tert-butoxycarbonyl)amino)butane (**3w**): Following the general procedure, **3w** was obtained from a flash column chromatography (*n*-hexane : ethyl acetate = 10:1) as a coloress oil (52% yield, 25.2 mg, 0.052 mmol). **TLC (SiO_2)**: R_f = 0.22 (*n*-hexane : ethyl acetate = 10:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 5.03 (br, 1H), 4.29-4.28 (m, 1H), 3.78-3.57 (m, 1H), 1.46 (s, 9H). **$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)** δ 155.6, 80.2, 63.9, 50.4, 47.5, 35.5, 28.3. **FTIR (ATR)**: 3348, 2977, 1694, 1511, 1392, 1367, 1252, 1166, 1076, 942, 720 cm^{-1}. **HRMS m/z (DART)** calcd for $C_9H_{16}Br_4NO_2^+$ $(M+H)^+$ 485.7909, found 485.7923.

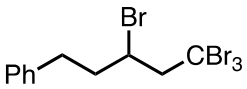


1,1,1,3,7-Pentabromoheptane (**3x**): Following the general procedure, **3x** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil (88% yield, 43.1 mg, 0.088 mmol). **TLC (SiO_2)** R_f = 0.35 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.21 (dq, *J* = 4.6 Hz, 4.0 Hz, 1H), 3.85 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 3.55 (dd, *J* = 16.0 Hz, 4.6 Hz, 1H), 3.44 (t, *J* = 6.3 Hz, 2H), 2.17-2.10 (m, 1H), 2.05-1.87 (m, 3H), 1.84-1.76 (m, 1H), 1.73-1.64 (m, 1H). **$^{13}C\{^{1}H\}$**

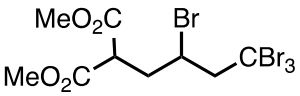
NMR (125 MHz, $CDCl_3$) δ 66.7, 51.3, 38.7, 36.0, 33.1, 31.7, 26.0. **FTIR (ATR)** 2940, 2864, 1733, 1455, 1430, 1248, 1187, 1005, 939, 721 cm^{-1}. **HRMS m/z (DART)** calcd for $C_7H_{11}Br_4$ $(M-Br)^+$ 410.7589, found 410.7574.



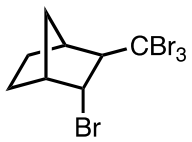
(2,4,4,4-Tetrabromobutyl)benzene (**3y**): Following the general procedure, **3y** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil (30% yield, 13.4 mg, 0.030 mmol). **TLC (SiO_2)**: R_f = 0.38 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34-7.26 (m, 5H), 4.39-4.35 (m, 1H), 3.85 (dd, *J* = 4.6 Hz, 4.0 Hz, 1H), 3.67 (dd, *J* = 11.5 Hz, 4.6 Hz, 1H), 3.53 (dd, *J* = 9.2 Hz, 5.2 Hz, 1H), 3.23 (dd, *J* = 9.2 Hz, 5.2 Hz, 1H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 137.4, 129.4, 128.6, 127.3, 65.8, 51.5, 46.0, 35.9. NMR spectra of the **3y** were consistent with the reported one.[6]



(3,5,5,5-Tetrabromopentyl)benzene (**3z**): Following the general procedure, **3z** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil (84% yield, 38.6 mg, 0.084 mmol). **TLC (SiO_2)** R_f = 0.40 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.32-7.20 (m, 5H), 4.18 (ddt, *J* = 9.7 Hz, 4.6 Hz, 4.0 Hz, 1H), 3.88 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 3.57 (dd, *J* = 16.0 Hz, 4.6 Hz, 1H), 2.98 (ddd, *J* = 13.8 Hz, 9.2 Hz, 4.6 Hz, 1H), 2.82 (ddd, *J* = 13.8 Hz, 8.0 Hz, 5.7 Hz, 1H), 2.44 (dddd, *J* = 13.8 Hz, 9.2 Hz, 6.9 Hz, 4.0 Hz, 1H), 2.28 (dddd, *J* = 14.3 Hz, 9.7 Hz, 5.2 Hz, 4.6 Hz, 1H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 140.2, 128.6, 126.3, 66.8, 51.3, 41.1, 35.9, 33.6. NMR spectra of the **3z** were consistent with the reported one.[6]

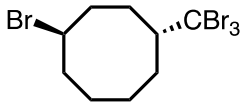


1,1,1,3-Tetrabromo-4,4-bis(carboxymethoxy)butane (**3aa**): Following the general procedure, **3aa** was obtained from a flash column chromatography (*n*-hexane : ethyl acetate = 10:1) as a coloress oil (43% yield, 21.5 mg, 0.043 mmol). **TLC (SiO_2)**: R_f = 0.12 (*n*-hexane : ethyl acetate = 10:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.27-4.22 (m, 1H), 3.92 (dd, *J* = 16.0 Hz, 4.0 Hz, 1H), 3.86 (dd, *J* = 10.9 Hz, 4.0 Hz, 1H), 3.80 (s, 1H), 3.77 (s, 1H), 3.59 (dd, *J* = 16.0 Hz, 10.9 Hz, 1H), 2.89-2.83 (m, 1H), 2.45-2.38 (m, 1H). **^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$)** δ 168.9, 168.6, 67.0, 53.0, 52.9, 50.3, 48.7, 38.4, 35.0. NMR spectra of the **3aa** were consistent with the reported one.[12]

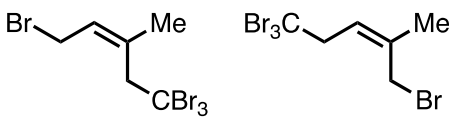


2-Bromo-3-(tribromomethyl)bicyclo[2.2.1]heptane (**3ab**): Following the general procedure, **3ab** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil (90% yield, 38.0 mg, 0.090 mmol, 94:6 d.r.) **TLC (SiO_2)**: R_f = 0.50 (*n*-hexane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.11 (ddd, *J* = 9.7 Hz, 5.7 Hz, 1.2 Hz, 1H), 2.88 (d, *J* = 5.7 Hz, 1H), 2.67 (d, *J* = 1.2 Hz, 2H), 2.34 (d, *J* = 10.9 Hz, 1H), 2.09 (dd, *J* = 12.6 Hz, 10.9 Hz, 1H), 1.63 (dd, *J*

= 12.6 Hz, 9.2 Hz, 2H), 1.44 (t, *J* = 10.9 Hz, 1H), 1.34 (d, *J* = 10.9 Hz, 1H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 74.0, 56.7, 46.0, 44.2, 44.1, 35.3, 30.2, 24.2. NMR spectra of the **3ab** were consistent with the reported one.[14j]

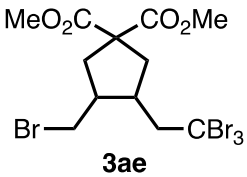


1-Bromo-4-(tribromomethyl)cyclooctane (**3ac**): Following the general procedure, **3ac** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil {64% yield, 28.0 mg, 0.064 mmol, 58:42 d.r. (from 1-octene)}. **TLC (SiO_2)**: R_f = 0.49 (*n*-hexane). **^1H NMR (500 MHz, $CDCl_3$)** δ 4.49-4.44 (m, 1H, H_2 (*trans*)), 4.42-4.37 (m, 1H, H_1 (*cis*)), 2.75-2.70 (m, 1H), 2.66-2.54 (m, 2H), 2.49-2.32 (m, 5H), 2.25-2.12 (m, 4H), 2.09-1.96 (m, 3H), 1.93-1.88 (m, 1H), 1.86-1.56 (m, 8H), 1.53-1.38 (m, 2H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 60.4, 60.2, 55.8, 55.7, 55.3, 54.9, 37.9, 36.5, 34.8, 33.0, 32.13, 32.07, 31.3, 29.8, 28.3, 27.8, 25.6, 23.0. **FTIR (ATR)**: 3412, 2963, 2921, 2849, 2695, 2163, 1981, 1721, 1460, 1443, 1436, 1423, 1373, 1361, 1347, 1328, 1281, 1245, 1229, 1208, 1175, 1155, 1119, 1099, 1073, 1043, 1005, 975, 944, 913, 856, 833, 820, 774, 762, 697, 673 cm^{-1}. **HRMS m/z (DART)** calcd for $C_9H_{14}Br_3$ $(M-Br)^+$ 358.8640, found 358.8627. NMR spectra of the **3ac** were consistent with the reported one.[29]



3ad **3ad'**

1,1,1,5-Tetrabromo-3-methyl-3-pentene (**3ad, 3ad'**): Following the general procedure, **3ad** and **3ad'** was obtained from a flash column chromatography (*n*-hexane) as a coloress oil {48% yield, 19.0 mg, 0.048 mmol, **3ad**:**3ad'** = 88:12 (from isoprene)}. **TLC (SiO_2)**: R_f = 0.44 (*n*-hexane). **^1H NMR (500 MHz, $CDCl_3$)** δ 5.97 (t, *J* = 8.6 Hz, 1H), 4.04 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 2H), 2.08 (s, 3H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 137.1, 130.3, 67.0, 39.2, 27.5, 17.8. **FTIR (ATR)**: 2922, 2853, 1736, 1650, 1437, 1377, 1306, 1229, 1203, 1090, 1020, 981, 935, 871, 788, 700 cm^{-1}. **HRMS m/z (DART)** calcd for $C_6H_9Br_4$ $(M+H)^+$ 396.7432, found 396.7443.



3ae

3-(Bromomethyl)-4-(2,2,2-tribromoethyl)-dimethylcyclopentene-1,1-carboxylate (**3ae**): Following the general procedure, **3ae** was obtained from a flash column chromatography (*n*-hexane : ethyl acetate = 10:1) as a coloress oil {75% yield, 40.5 mg, 0.075 mmol, 92:8 d.r. (from **1ae**)}. **TLC (SiO_2)**: R_f = 0.11 (*n*-hexane : ethyl acetate = 10:1). **^1H NMR (500 MHz, $CDCl_3$)** δ 3.77 (s, 6H), 3.57 (dd, *J* = 5.7 Hz, 4.6 Hz, 1H), 3.35 (dd, *J* = 10.9 Hz, 4.6 Hz, 1H), 3.30 (dd, *J* = 10.3 Hz, 9.5 Hz, 1H), 3.09 (dd, *J* = 9.5 Hz, 6.3 Hz, 1H), 2.80-2.74 (m, 2H), 2.61 (dd, *J* = 7.5 Hz, 6.9 Hz, 1H), 2.57-2.51 (m, 1H), 2.40 (dd, *J* = 14.3 Hz, 9.2 Hz, 1H), 2.37 (dd, *J* = 14.3 Hz, 5.7 Hz, 1H). **$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)** δ 172.6, 172.5, 58.6, 57.8, 53.1, 44.4,

43.3, 39.5, 39.4, 38.3, 33.6. **FTIR (ATR)**: 3461, 3001, 2952, 2844, 1727, 1434, 1369, 1257, 1244, 1199, 1165, 1111, 1068, 1028, 964, 937, 912, 875, 854, 822, 722, 690, 669, cm^{-1}. **HRMS m/z (DART)** calcd for $C_{12}H_{17}Br_4O_4$ $(M+H)^+$ 540.7855, found 540.7861.

■ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0000. ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra, UV/Vis and FL and PL spectra, and full detailed optimization study experiments (PDF).

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Competing interests

The authors declare no competing interests.

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(25) Full results for optimization study of light source were detailed in supporting information.

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