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Atom Transfer Radical Addition via Dual Photoredox/Manganese Catalytic System

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Abstract: Atom transfer radical addition of bromonitromethane and 1,2-dibromotetrafluoroethane to alkenes is described. The reaction is performed under blue light irradiation using two catalysts: 4CzIPN and manganese (II) bromide. The cyanoarene photocatalyst serves for the redox activation of starting organic bromide, while the manganese salt facilitates the trapping of the alkyl radical with the formation of the carbon–bromine bond.

Keywords: atom transfer; radical reactions; organofluorine; photocatalysis

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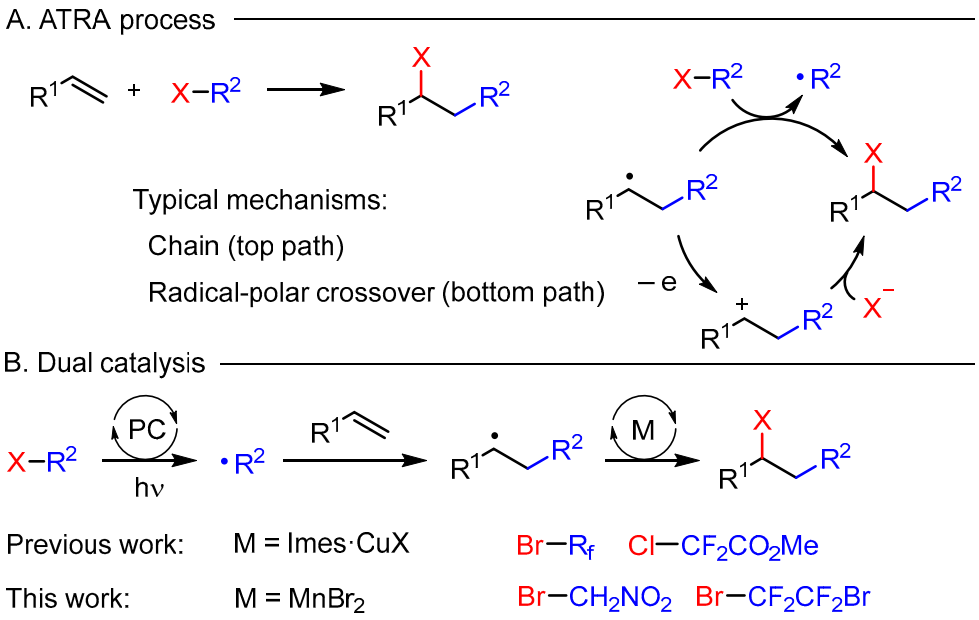
1. Introduction

Atom transfer radical addition (ATRA) constitutes a valuable way of functionalization of alkenes [1–6]. However, despite intrinsic efficiency, the method has a limited scope, which is associated with a delicate balance of reaction parameters needed for the realization of the sequence of bond-breaking and bond-forming steps. The advent of visible light photocatalysis has offered new opportunities for the generation of free radicals, which have been applied for the cleavage of the carbon–halogen bond [7–11] and successfully used for performing ATRA reactions [2,12]. The best substrates for these processes include perfluorinated alkyl iodides [13–17], bromides bearing an adjacent electron withdrawing group [18–20], and carbon tetrahalides [12,21,22].

The ATRA process may proceed via different mechanisms (Scheme 1A). In a classic chain mechanism, the addition radical abstracts halogen from the starting alkyl halide via a direct halogen transfer step. Alternatively, the addition radical may be oxidized to carbocation followed by capturing halide anion. In 2021 we developed the ATRA reaction of fluorinated alkyl bromides based on the synergistic use of two catalytic cycles—a photoredox cycle responsible for the radical generation and a copper cycle responsible for the carbon–bromine bond formation [23,24] (Scheme 1B). However, such readily available halides as bromonitromethane [25] and 1,2-dibromotetrafluoroethane (Halon 2402, Freon 114B2) [26] could not be involved under these conditions, which may be associated with the propensity of used copper complexes towards oxidation by these halides. Recently, Reiser has demonstrated a protocol for the ATRA reaction with bromonitromethane using $[Cu(dap)_2]Cl$ as a photocatalyst [27]. Earlier examples of iridium-catalyzed reactions of α-substituted bromonitro compounds involved only styrenes [28]. However, for 1,2-dibromotetrafluoroethane, the ATRA process is known only using reducing systems based on sodium dithionite [29] and Fe/Cp_2TiCl_2 [30]. It should be noted that the ability to use this fluorinated bromide in combination with alkenes would allow facile synthesis of various organofluorine compounds bearing tetrafluorinated fragments [31] by using subsequent transformations of carbon–bromine bonds.

Herein, we report a method for performing the ATRA reaction of these problematic bromides and unactivated alkenes using dual catalytic system involving manganese (II) salt for effecting carbon–bromine bond formation. In contrast to copper (I), manganese (II) is not prone to facile single electron oxidation, and it would be better suitable as a

carrier of the halogen atom to facilitate the carbon–halogen bond formation upon trapping of the alkyl radical. An opportunity of manganese (II) salts to serve for the transfer of a terminating component in a radical alkene difunctionalization process has been recently demonstrated [32].



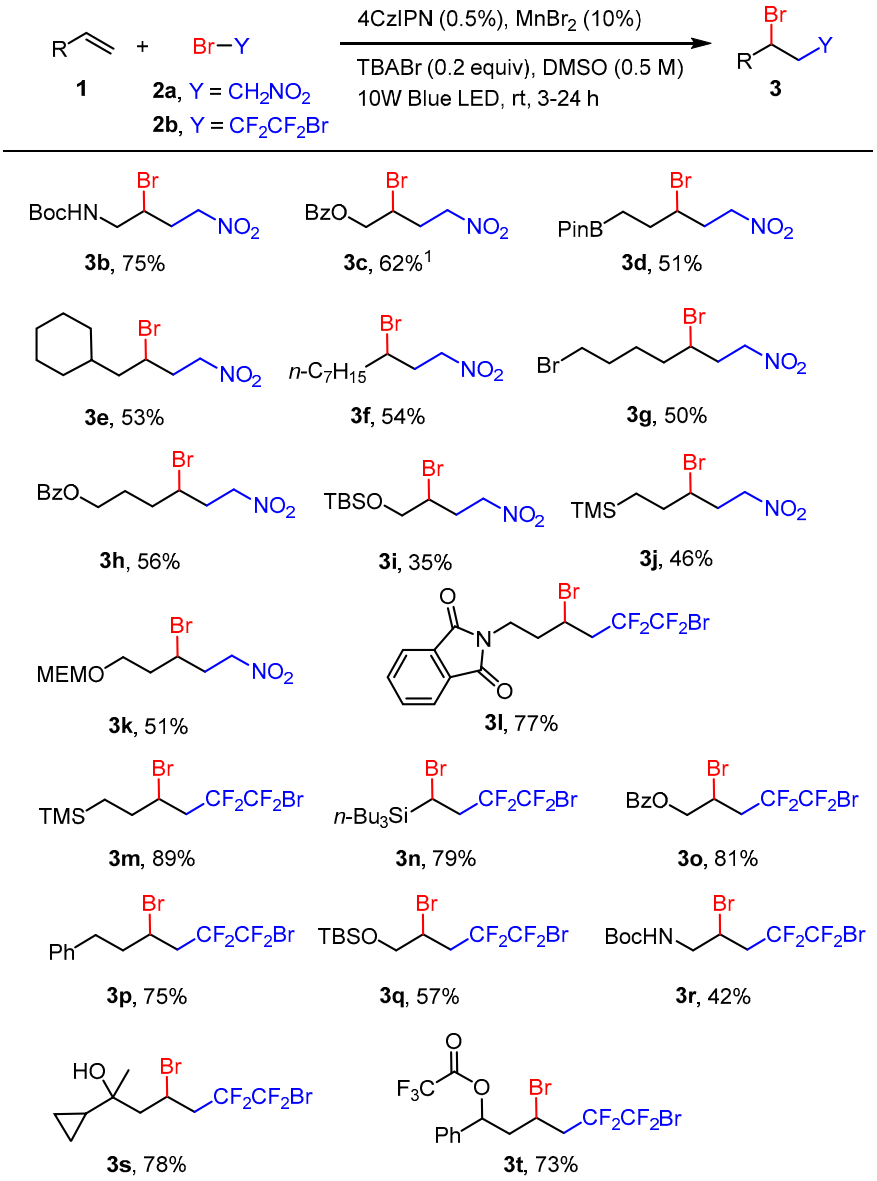
Scheme 1. ATRA reaction mechanism.

2. Results

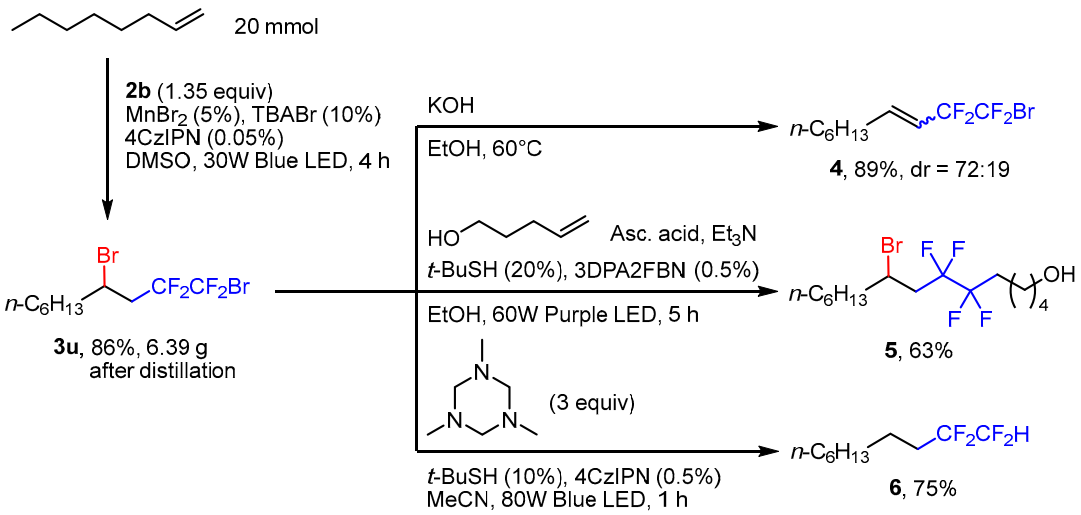
A reaction of 4-phenylbut-1-ene (**1a**) with bromonitromethane (**2a**) was performed employing manganese dibromide (10%) along with tetrabutylammonium bromide (TBABr, 20 mol %) in DMSO under 10 W blue LED irradiation, and 4CzIPN was used as a typical carbazolyl based organic photocatalyst [33,34] (Table 1). The desired atom transfer product **3a** was isolated in 60% yield, while by-product **4a** resulting from the addition of two bromine atoms at the double bond of the alkene was also observed (entry 1). Other solvents and catalysts were less efficient. The decrease in the concentration (from 0.5 to 0.125 M), as well as the use of a more powerful light source, did not lead to a yield increase (entries 5 and 6). The addition of supportive ligands had virtually no effect. In the presence of a copper complex bearing an imidazolium carbene type ligand (Imes·CuBr), the reaction did not proceed at all (entry 12).

Under the optimized conditions, a series of alkenes were subjected to the atom transfer reaction with bromonitromethane **2a** and 1,2-dibromotetrafluoroethane **2b** (Scheme 2). The reaction tolerates the ester group, N-Boc protected amino fragment, MEM, and TBS protective groups, as well as phthalimide and pinacol boryl fragments. Alkenes having unprotected hydroxyl group, as well as base sensitive trifluoroacetoxy substituent, gave expected products in good yields (compounds **3s** and **3t**, respectively). In the reaction of styrene with bromonitromethane, a complex mixture was formed containing small amounts of the product (less than 5%). It should also be noted that the amount of dibromide byproducts (similar to **4a**) depends on the nature of alkyl bromide, but not on the alkene. Thus, in reactions of bromonitromethane **2a**, about 20% of dibromides were formed for most substrates, while in the case of **2b**, dibromides were observed only in amounts of less than 5%.

The reaction may be readily scaled-up. Thus, starting from 20 mmol of 1-octene, target product **3u** was obtained in multigram amount (Scheme 3). Importantly, the product was isolated without chromatographic separation simply by vacuum distillation of the crude material. It is also worthy of note that in this experiment the loading of the photocatalyst was decreased ten times up to 0.05 mol %, thereby highlighting the reaction efficiency.

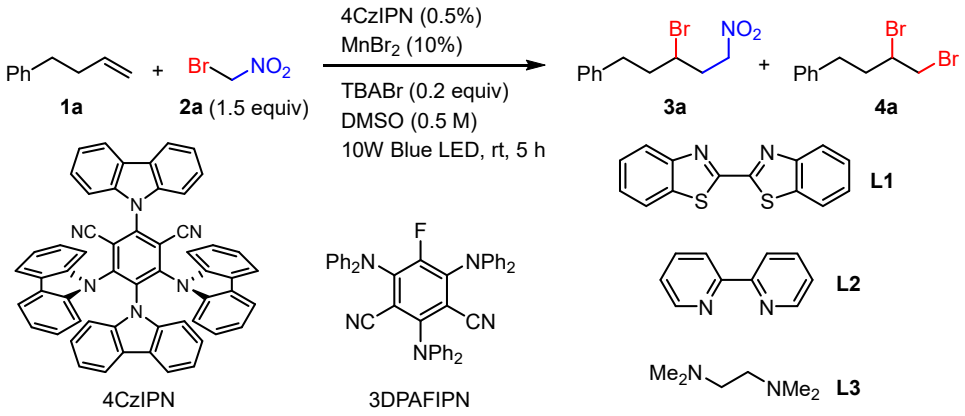


Scheme 2. Synthesis of compounds **3**. Isolated yields are shown. [1] 60 W LED was used.



Scheme 3. Gram-scale synthesis and reactions of **3u**.

Table 1. Optimization studies.



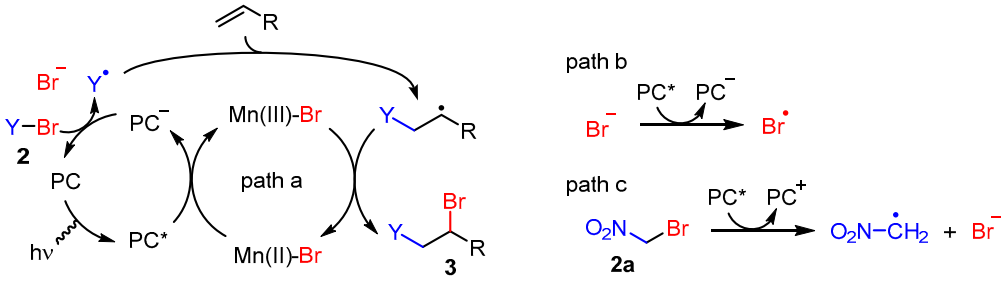
Entry	Deviation from Stand. Cond.	Conv. of 1a, % [1]	Y. of 3a, % [2]	Y. of 4a, % [2]
1	None	>99	70 (60) [3]	20
2	MeCN as solv., 24 h	>99	56	19
3	DMF as solv., 24 h	97	64	21
4	3DPAFIPN as PC, 24 h	91	32	25
5	Conc. 0.125 M	>99	61	13
6	60 W LED, 2 h	>99	68	14
7	1.2 equiv. of **2a**, 8 h	>99	68	17
8	**L1** (11%)	>99	71	18
9	**L2** (11%)	85	57	20
10	**L3** (11%)	95	48	22
11	no $MnBr_2$	>99	42	13
12	Imes·CuBr instead of $MnBr_2$	1	n.d.	n.d.

[1] Determined by GC-MS analysis. [2] Determined by NMR analysis. [3] Isolated yield.

Products **3** obtained from 1,2-dibromotetrafluoroethane **2b** contain two carbon–bromine bonds, which provide opportunities for subsequent functionalization. Given the different nature of these C-Br fragments (secondary or perfluorinated), their selective transformations can be carried out. For example, the treatment of dibromide **3u** with potassium hydroxide in ethanol affected the elimination of one bromide leading to alkene **4** as a mixture of geometric isomers in 89% yield. On the other hand, the fluorinated moiety of **3u** is apparently more susceptible to single electron reduction and may be preferentially involved in radical reactions. Thus, the interaction of compound **3u** with another alkene was performed under photocatalytic conditions. Here, the ascorbic acid under basic conditions was used as stoichiometric reducing agent furnishing hydrofluoroalkylation product **5**. The latter example demonstrates that 1,2-dibromotetrafluoroethane **2b** may serve as a template for the synthesis of tetrafluorinated products starting from two different alkenes. Finally, both C-Br bonds can be reduced using the halogen atom transfer (XAT) methodology. In this regard, we applied a triazinane-type reagent recently developed in our group [35] for the conversion of dibromide **3u** into tetrafluoroalkane **6** in good yield.

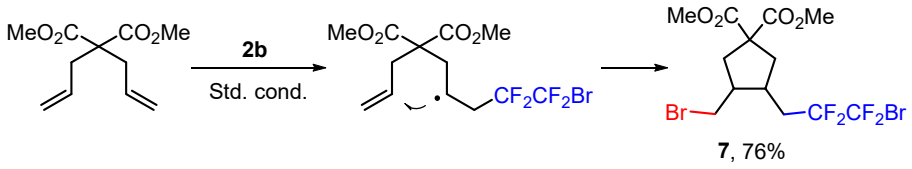
The proposed mechanism is shown in Scheme 4. The photoexcited catalyst may oxidize manganese (II), likely existing in a complex form with bromide anion to manganese (III). The reduced form of the photocatalyst then performs the single electron reduction of organic bromide **2** to generate the radical, which adds to the double bond. At the final step, manganese (III) promotes the bromine transfer leading to product **3**. This mechanism was supported by Stern–Volmer analysis (see Supplementary Materials for details). Thus,

both manganese (II) bromide and bromide anion, as well as their combination, effectively quench the fluorescence of the photocatalyst (paths a and b). It is worth noting that oxidation of bromide anion would generate bromine radical, which itself can oxidize Mn (II) to Mn (III) or recombine with the addition radical leading to product **3**. Moreover, bromine radical can add at the double bond eventually affording dibrominated byproduct **4**. 1,2-Dibromotetrafluoroethane **2b** does not quench the fluorescence of 4CzIPN [36], and the reduced form of the photocatalyst is needed. At the same time, bromonitromethane **2a** is an effective quencher thereby suggesting that it can be directly reduced by the photoexcited 4CzIPN (path c). The mechanism of the formation of dibromides in reactions of bromonitromethane **2a** is not clear at present. It may be tentatively proposed that radical intermediates attack **2a** at the oxygen atom followed by the expulsion of bromine radical with its subsequent addition at the double bond, though other pathways cannot be excluded.



Scheme 4. Proposed mechanism.

To support the radical character of the reaction, a radical clock experiment was performed (Scheme 5). The reaction of diallylmalonate gave dibromide **7** containing a five-membered cycle, which results from the rapid intramolecular trapping of the radical intermediate generated from the initial addition of the fluorinated radical.



Scheme 5. Radical clock experiment.

3. Materials and Methods

3.1. General Information

All reactions were performed under an argon atmosphere. DMSO was distilled from CaH_2 and stored over MS 4 Å. Column chromatography was carried out employing silica gel (230–400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. $KMnO_4$ solution. High-resolution mass-spectra (HRMS) were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer (Bruker MicrOTOF II). The measurements were conducted in a positive-ion mode (interface capillary voltage −4500 V) or in a negative-ion mode (3200 V); the mass ranged from m/z 50 to m/z 3000. Photo-induced reactions were performed in Duran culture tubes (Roth cat. no K248.1, outside diameter = 12 mm). For irradiation, a strip of 455 nm light-emitting diodes (SMD 2835 − 120 LED 1 M Blue, 12 V, 24 W/m; 50 cm strip length) or 455 nm COB LED matrix Hontiey (29–32 V, 3000 mA, 100 W; operated at 60 W) were used. The distance between the reaction vessel and diodes was about 5 mm. The reaction tube was placed in a glass jacket and cooled with water at room temperature. The reaction setup was used as previously described: for LED strip [37] and for LED matrix [38].

All commercially available reagents were purchased from Acros Organics, ABCR, or P&M Invest. Alkenes were distilled prior to use. *tert*-Butyl allylcarbamate [39], allyl benzoate [40], 2-(but-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [41], allylcyclohexane [42], 6-bromohex-1-ene [43], pent-4-en-1-yl benzoate [44], (allyloxy)(tert-butyl)dimethylsilane [45], but-3-en-1-yltrimethylsilane [46], 4-((2-methoxyethoxy)methoxy)but-1-ene [47], 2-(but-3-en-1-yl)isoindoline-1,3-dione [48], 4CzIPN [49], 3DPA2FBN [50], and dimethyl diallylmalonate [51] were synthesized according to literature procedures.

3.1.1. Synthesis of 2-Cyclopropylpent-4-en-2-ol (**1s**) [52]

A two-neck flask, containing magnesium turnings (40 mmol, 972 mg) was equipped with a magnetic stirring bar, pressure-equalizing dropping funnel, and a condenser with a calcium chloride drying tube. Anhydrous ether (7 mL) and a crystal of iodine (ca. 11 mg) were added. After 5 min of intense stirring, the ether became colorless. The dropping funnel was charged with a solution of allyl bromide (40 mmol, 3.46 mL) and cyclopropyl methyl ketone (20 mmol, 1.87 mL) in anhydrous ether (2 mL), and this solution was added to the suspension of magnesium with intense stirring at such a rate that gentle reflux was maintained (ca. 40 min). The reaction mixture was stirred for 3 h at room temperature, then water (20 mL), and 2M HCl (20 mL) were slowly added, and the resulting mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was washed with ether (2 × 10 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated at atmospheric pressure. The residue was distilled under reduced pressure using Hickmann distilling head (bp 62–68 °C, 18 Torr) to give colorless liquid. Yield 2.27 g, 90%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.03–5.83 (m, 1H), 5.15–5.02 (m, 2H), 2.38–2.17 (m, 2H), 1.39 (s, 1H), 1.09 (s, 3H), 0.97–0.82 (m, 1H), 0.43–0.22 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 134.4, 118.4, 70.5, 47.8, 26.0, 21.0, 0.61, 0.55.

3.1.2. Synthesis of 1-Phenylbut-3-en-1-yl 2,2,2-Trifluoroacetate (**1t**) [53]

A solution of 1-phenylbut-3-en-1-ol (10 mmol, 1.48 g) and pyridine (12 mmol, 1.05 mL) in dichloromethane (4 mL) was cooled to 5 °C (water/ice bath) and trifluoroacetic acid anhydride (12 mmol, 1.67 mL) was slowly added. The cooling bath was removed, and the mixture was stirred for 30 min allowing to warm up to room temperature. Then, the reaction was quenched with saturated aqueous solution of $NaHCO_3$ (dropwise, under intense stirring, until evolution of gas has stopped) and transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with pentane (2 × 5 mL). The combined organic layers were washed with brine (15 mL), dried with Na_2SO_4, filtered, and concentrated at atmospheric pressure. The residue was distilled under reduced pressure using Hickmann distilling head (bp 91–96 °C, 13 Torr) to give pale-yellow liquid. Yield 1.94 g, 79%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47–7.25 (m, 5H), 5.95 (dd, *J* = 8.1, 5.7 Hz, 1H), 5.81–5.61 (m, 1H), 5.22–5.10 (m, 2H), 2.87–2.61 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 156.9 (q, *J* = 42.5, 41.9 Hz), 137.8, 132.0, 129.1, 128.9, 126.67, 119.5, 114.7 (q, *J* = 286.2 Hz), 79.8, 40.5. ^{19}F NMR (282 MHz, Chloroform-*d*) δ −76.00.

3.2. ATRA Reaction of Bromides **2a-b** *with Alkenes (General Procedure)*

A test tube was evacuated and filled with argon. Then, DMSO (1 mL), TBABr (32 mg, 0.1 mmol), alkene (0.5 mmol), bromide **2** (0.75 mmol, 105 mg for **2a**, 89 μL for **2b**), $MnBr_2$ (11 mg, 0.05 mmol), and 4CzIPN (2 mg, 0.0025 mmol) were added. The tube was screw-capped and irradiated with 455 nm (10 W) strip for 3–24 h. The reaction was quenched with water (5 mL) and extracted (for **3a-l**, with methyl *tert*-butyl ether; for **3m-r**, hexane; 3 × 1.5 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography.

*(3-Bromo-5-nitropentyl)benzene (**3a**).* Irradiation time 8 h. Yield 82 mg (60%). Colorless oil. Chromatography: hexane/EtOAc, 15/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47–7.20 (m, 5H), 4.64 (t, *J* = 6.8 Hz, 2H), 4.10–3.95 (m, 1H), 2.97 (ddd, *J* = 13.9, 8.0, 6.1 Hz, 1H), 2.82 (dt, *J* = 13.9, 7.9 Hz, 1H), 2.73–2.56 (m, 1H), 2.52–2.34 (m, 1H), 2.34–2.11 (m, 2H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ 140.3, 128.8, 128.6, 126.5, 73.6, 51.8, 40.8, 36.2, 33.6. HRMS (ESI-TOF): calcd for $C_{11}H_{14}[^{81}Br]NO_2Na$ [M+Na]: 296.0080; found 296.0074.

*tert-Butyl (2-bromo-4-nitrobutyl)carbamate (**3b**)* [27]. Irradiation time 8 h. Yield 111 mg (75%). Yellow solid. Mp 68–72 °C. Chromatography: hexane/EtOAc, 3/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.06 (t, *J* = 6.4 Hz, 1H), 4.70–4.48 (m, 2H), 4.19–4.06 (m, 1H), 3.63–3.41 (m, 2H), 2.70–2.53 (m, 1H), 2.40–2.21 (m, 1H), 1.42 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 80.2, 73.2, 51.2, 47.0, 33.0, 28.4.

*2-Bromo-4-nitrobutyl benzoate (**3c**).* Modified general procedure: irradiation using 455 nm 60W LED matrix. Irradiation time 8 h. Yield 94 mg (62%). Pale-yellow oil. Chromatography: hexane/EtOAc, 6/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.64–7.53 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 4.70–4.59 (m, 3H), 4.53 (dd, *J* = 12.0, 6.1 Hz, 1H), 4.39–4.26 (m, 1H), 2.86–2.69 (m, 1H), 2.51–2.32 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 133.6, 129.8, 129.3, 128.67, 73.0, 67.4, 46.4, 32.6. HRMS (ESI-TOF): calcd for $C_{11}H_{12}[^{81}Br]NO_4Na$ [M+Na]: 325.9822; found 325.9830.

*2-(3-Bromo-5-nitropentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**).* Irradiation time 8 h. Yield 82 mg (51%). Colorless oil. Chromatography: hexane/EtOAc, 6/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.70–4.50 (m, 2H), 4.12–3.97 (m, 1H), 2.68–2.51 (m, 1H), 2.41–2.22 (m, 1H), 2.05–1.86 (m, 2H), 1.23 (s, 12H), 1.12–0.82 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.5, 73.8, 55.1, 35.8, 33.7, 24.9, 24.9, 11.3–7.3 (m). HRMS (ESI-TOF): calcd for $C_{11}H_{21}B$ $[^{81}Br]NO_4Na$ [M+Na]: 346.0620; found 346.0612.

*(2-Bromo-4-nitrobutyl)cyclohexane (**3e**).* Irradiation time 8 h. Yield 70 mg (53%). Colorless oil. Chromatography: hexane/EtOAc, 20/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73–4.49 (m, 2H), 4.20–4.05 (m, 1H), 2.68–2.51 (m, 1H), 2.40–2.23 (m, 1H), 1.92–1.49 (m, 8H), 1.37–1.06 (m, 3H), 1.04–0.73 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.7, 50.5, 46.9, 36.5, 35.7, 33.5, 32.2, 26.5, 26.2, 26.0. HRMS (ESI-TOF): calcd for $C_{10}H_{18}[^{81}Br]NO_2Na$ [M+Na]: 288.0393; found 288.0399.

*3-Bromo-1-nitrodecane (**3f**).* Irradiation time 8 h. Yield 72 mg (54%). Colorless oil. Chromatography: hexane/EtOAc, 25/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.72–4.51 (m, 2H), 4.11–3.96 (m, 1H), 2.69–2.52 (m, 1H), 2.43–2.26 (m, 1H), 1.98–1.74 (m, 2H), 1.63–1.38 (m, 2H), 1.36–1.22 (m, 8H), 0.93–0.83 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.7, 52.8, 39.3, 36.2, 31.8, 29.2, 28.9, 27.5, 22.7, 14.2. HRMS (ESI-TOF): calcd for $C_{10}H_{20}[^{79}Br]NO_2Na$ [M+Na]: 288.0570; found 288.0567.

*3,7-Dibromo-1-nitroheptane (**3g**).* Irradiation time 8 h. Yield 76 mg (50%). Yellow oil. Chromatography: hexane/EtOAc, 6/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73–4.52 (m, 2H), 4.11–3.96 (m, 1H), 3.42 (t, *J* = 6.6 Hz, 2H), 2.70–2.53 (m, 1H), 2.44–2.25 (m, 1H), 2.00–1.51 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.6, 52.1, 38.3, 36.1, 33.12, 32.0, 26.2. HRMS (ESI-TOF): calcd for $C_7H_{13}[^{81}Br]_2NO_2Na$ [M+Na]: 327.9165; found 327.9172.

*4-Bromo-6-nitrohexyl benzoate (**3h**).* Irradiation time 8 h. Yield 92 mg (56%). Colorless oil. Chromatography: hexane/EtOAc, 6/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.73–4.52 (m, 2H), 4.45–4.27 (m, 2H), 4.17–4.04 (m, 1H), 2.72–2.55 (m, 1H), 2.46–2.28 (m, 1H), 2.18–1.83 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 133.2, 130.2, 129.7, 128.5, 73.5, 64.0, 51.9, 36.2, 35.9, 27.0. HRMS (ESI-TOF): calcd for $C_{13}H_{16}[^{81}Br]_2NO_4Na$ [M+Na]: 354.0135; found 354.0132.

*(2-Bromo-4-nitrobutoxy)(tert-butyl)dimethylsilane (**3i**).* Irradiation time 8 h. Yield 55 mg (35%). Colorless oil. Chromatography: hexane/EtOAc, 25/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.61 (dd, *J* = 7.6, 6.2 Hz, 2H), 4.10–3.97 (m, 1H), 3.93 (dd, *J* = 10.7, 4.5 Hz, 1H), 3.77 (dd, *J* = 10.7, 7.3 Hz, 1H), 2.77 (dtd, *J* = 15.4, 7.6, 3.5 Hz, 1H), 2.34 (ddt, *J* = 15.4, 9.5, 6.2 Hz, 1H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.5, 67.3, 50.4, 32.7, 25.9, 18.4, −5.2, −5.3. HRMS (ESI-TOF): calcd for $C_{10}H_{22}[^{81}Br]_2NO_3SiNa$ [M+Na]: 336.0424; found 336.0432.

*(3-Bromo-5-nitropentyl)trimethylsilane (**3j**).* Irradiation time 8 h. Yield 62 mg (46%). Colorless oil. Chromatography: hexane/EtOAc, 25/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.72–4.52 (m, 2H), 4.00 (dtd, *J* = 9.5, 6.8, 3.0 Hz, 1H), 2.64 (dtd, *J* = 15.2, 7.6, 3.0 Hz, 1H), 2.40–2.27 (m, 1H), 1.98–1.74 (m, 2H), 0.74 (ddd, *J* = 14.1, 10.2, 7.0 Hz, 1H), 0.61 (ddd, *J* = 14.1,

10.5, 6.9 Hz, 1H), 0.01 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.9, 56.1, 35.4, 34.2, 14.7, −1.7. HRMS (ESI-TOF): calcd for $C_8H_{18}[^{81}Br]NO_2SiNa$ [M+Na]: 292.0162; found 292.0165.

*3-Bromo-1-((2-methoxyethoxy)methoxy)-5-nitropentane (**3k**).* Irradiation time 8 h. Yield 77 mg (51%). Yellow oil. Chromatography: hexane/EtOAc, 1/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (s, 2H), 4.60 (dd, *J* = 7.6, 6.1 Hz, 2H), 4.21 (tt, *J* = 9.3, 3.5 Hz, 1H), 3.77–3.61 (m, 4H), 3.61–3.48 (m, 2H), 3.35 (s, 3H), 2.62 (dtd, *J* = 15.1, 7.6, 3.5 Hz, 1H), 2.45–2.27 (m, 1H), 2.22–1.95 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 95.7, 73.6, 71.8, 67.0, 65.0, 59.0, 49.3, 39.0, 36.1. HRMS (ESI-TOF): calcd for $C_9H_{18}[^{81}Br]NO_5Na$ [M+Na]: 324.0241; found 324.0242.

*2-(3,6-Dibromo-5,5,6,6-tetrafluorohexyl)isoindoline-1,3-dione (**3l**).* Irradiation time 5 h. Yield 177 mg (77%). Yellow oil. Chromatography: hexane/EtOAc, 5/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.27 (dtd, *J* = 10.0, 6.6, 3.5 Hz, 1H), 4.00–3.77 (m, 2H), 2.96–2.55 (m, 2H), 2.39 (dtd, *J* = 14.5, 7.2, 3.5 Hz, 1H), 2.30–2.14 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 134.2, 132.1, 123.4, 117.0 (tt, *J* = 311.9, 39.0 Hz), 116.2 (tt, *J* = 257.1, 31.7 Hz), 41.0 (t, *J* = 2.5 Hz), 39.4 (t, *J* = 21.3 Hz), 37.4, 37.4, 36.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.37 (s, 2F), −110.65 (dd, *J* = 257.2, 27.1 Hz, 1F), −112.33 (dd, *J* = 257.2, 24.5 Hz, 1F). HRMS (ESI-TOF): calcd for $C_{14}H_{11}[^{81}Br]_2F_4NO_2Na$ [M+Na]: 485.8944; found 485.8922.

*(3,6-Dibromo-5,5,6,6-tetrafluorohexyl)trimethylsilane (**3m**).* Irradiation time 5 h. Yield 173 mg (89%). Colorless oil. Chromatography: pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.35–4.20 (m, 1H), 2.93–2.59 (m, 2H), 2.04–1.74 (m, 2H), 0.76 (ddd, *J* = 13.9, 11.9, 4.9 Hz, 3H), 0.63 (ddd, *J* = 13.9, 11.9, 5.2 Hz, 3H), 0.03 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 117.8 (tt, *J* = 312.2, 39.3 Hz), 116.5 (tt, *J* = 257.3, 32.0 Hz), 48.3, 38.7 (t, *J* = 21.3 Hz), 34.1, 14.0, −1.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.09 (s, 2F), −111.01 (dm, *J* = 256.7 Hz, 1F), −112.41 (dm, *J* = 256.7 Hz, 1F). Anal. Calcd for $C_9H_{16}Br_2F_4Si$: C, 27.85; H 4.16. Found: C 27.71, H 4.25.

*Tributyl(1,4-dibromo-3,3,4,4-tetrafluorobutyl)silane (**3n**).* Irradiation time 24 h. Yield 191 mg (79%). Colorless oil. Chromatography: hexane. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.51 (dd, *J* = 10.3, 2.7 Hz, 1H), 2.79–2.49 (m, 2H), 1.47–1.22 (m, 12H), 0.91 (t, *J* = 6.8 Hz, 9H), 0.83–0.63 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 117.8 (tt, *J* = 312.0, 39.5 Hz), 116.9 (tt, *J* = 257.1, 31.1 Hz), 34.9 (t, *J* = 22.2 Hz), 26.9, 26.8, 26.0, 13.8, 11.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ −66.96 (s, 2F), −111.46 (dd, *J* = 258.2, 25.8 Hz, 1F), −114.36 (dd, *J* = 260.5, 24.6 Hz, 1F). HRMS (ESI-TOF): calcd for $C_{16}H_{30}[^{79}Br][^{81}Br]F_4SiNa$ [M+Na]: 509.0292; found 509.0309.

*2,5-Dibromo-4,4,5,5-tetrafluoropentyl benzoate (**3o**).* Irradiation time 10 h. Yield 171 mg (81%). Yellow oil. Chromatography: hexane/EtOAc, 20/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.66–7.54 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.66–4.60 (m, 2H), 4.60–4.47 (m, 1H), 3.08–2.70 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 133.6, 129.9, 129.4, 128.7, 117.0 (tt, *J* = 311.4, 39.0 Hz), 116.2 (tt, *J* = 257.2, 31.9 Hz), 67.4, 39.0 (t, *J* = 2.5 Hz), 36.6 (t, *J* = 21.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.22 (s, 2F), −111.02 (ddd, *J* = 256.6, 22.9, 11.2 Hz, 1 F), −112.07 (ddd, *J* = 257.6, 22.1, 12.9 Hz, 1F). HRMS (ESI-TOF): calcd for $C_{12}H_{10}[^{81}Br]_2F_4O_2Na$ [M+Na]: 446.8835; found 446.8832.

*(3,6-Dibromo-5,5,6,6-tetrafluorohexyl)benzene (**3p**).* Irradiation time 3 h. Yield 175 mg (75%). Colorless oil. Chromatography: hexane/EtOAc, 100/1. According to ^{1}H NMR analysis, the compound contains ca. 3% of impurity, which can be ascribed to the dibromination product **4a** [54]. ^{1}H NMR (300 MHz, $CDCl_3$), **3a**: δ 7.40–7.20 (m, 4H), 4.34–4.19 (m, 1H), 3.06–2.61 (m, 4H), 2.40–2.10 (m, 2H); **4a:** 3.88 (dd, *J* = 10.2, 4.3 Hz, 1H), 3.67 (t, *J* = 9.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.2, 128.7, 128.6, 126.5, 117.2 (tt, *J* = 311.9, 39.3 Hz), 116.3 (tt, *J* = 257.1, 257.1, 31.6, 31.6 Hz), 44.3, 40.6, 39.7 (t, *J* = 21.3 Hz), 33.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.19 (s, 2F), −110.12 (dd, *J* = 257.6 Hz, 28.0 Hz, 1F), −112.47 (dd, *J* = 257.6, 26.0 Hz, 1F). Anal. Calcd for $C_{12}H_{12}Br_2F_4$: C, 36.77; H 3.09. Found: C 36.61, H 3.25.

*tert-Butyl((2,5-dibromo-4,4,5,5-tetrafluoropentyl)oxy)dimethylsilane (**3q**).* Irradiation time 10 h. Yield 123 mg (57%). Colorless oil. Chromatography: hexane/EtOAc, 100/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.19 (tt, *J* = 7.1, 4.7 Hz, 1H), 3.93 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.75 (dd, *J* = 10.9, 7.1 Hz, 1H), 3.19–2.94 (m, 1H), 2.67–2.41 (m, 1H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 117.4 (tt, *J* = 311.3, 38.9 Hz), 116.6 (tt, *J* = 256.7, 31.6 Hz),

66.9, 42.9 (t, *J* = 2.3 Hz), 35.6 (t, *J* = 21.4 Hz), 25.9, 18.4, −5.2, −5.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.21 (s, 2F), −111.47 (dd, *J* = 258.2, 22.2 Hz, 1F), −112.52 (dd, *J* = 255.9, 19.6 Hz, 1F). HRMS (ESI-TOF): calcd for $C_{11}H_{20}[^{81}Br]_2F_4OSiNa$ [M+Na]: 456.9438; found 456.9415.

*tert-Butyl (2,5-dibromo-4,4,5,5-tetrafluoropentyl)carbamate (**3r**).* Irradiation time 5 h. Yield 88 mg (42%). Colorless oil. Chromatography: hexane/EtOAc, 6/1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 (s, 1H), 4.40–4.26 (m, 1H), 3.74–3.59 (m, 1H), 3.53–3.38 (m, 1H), 2.90–2.56 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8, 117.1 (tt, *J* = 311.7, 38.9 Hz), 116.3 (tt, *J* = 257.0, 31.6 Hz), 80.3, 47.6, 43.6, 36.9 (t, *J* = 21.6 Hz), 28.4. ^{19}F NMR (282 MHz, $CDCl_3$) δ −67.27 (s, 2F), −111.63 (t, *J* = 18.0 Hz, 2F). HRMS (ESI-TOF): calcd for $C_{10}H_{15}[^{81}Br]_2F_4NO_2Na$ [M+Na]: 441.9257; found 441.9258.

*4,7-Dibromo-2-cyclopropyl-6,6,7,7-tetrafluoroheptan-2-ol (**3s**).* Irradiation time 8 h. Yield 151 mg (78%). Colorless oil. Chromatography: hexane/EtOAc, 8/1. Mixture of diastereomers, 5/2. ^{1}H NMR (300 MHz, Chloroform-*d*) δ, both isomers: 4.64 (*p*, *J* = 6.6 Hz, 1H), 3.32–2.98 (m, 1H), 2.86–2.56 (m, 1H), 2.38–2.28 (m, 2H), 1.65–1.48 (m, 1H), 1.21 (s, 3H), 0.94–0.81 (m, 1H), 0.57–0.20 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ, major isomer: 71.2, 51.6, 40.5 (t, *J* = 20.8 Hz), 39.6, 27.1, 21.5, 0.9, 0.2; minor isomer: 71.4, 52.3, 40.1 (t, *J* = 20.7 Hz), 39.7, 28.1, 20.48, 1.0, 0.3; both isomers: 130.0–112.0 (m). ^{19}F NMR (282 MHz, Chloroform-*d*) δ, major isomer: −67.26 (s, 2F), −111.80 (t, *J* = 17.8 Hz, 2F); minor isomer: −67.31 (s, 2F), −110.98 (d, *J* = 17.8 Hz, 1F), −112.59 (dd, *J* = 256.4, 25.8 Hz, 1F). HRMS (ESI-TOF): calcd for $C_{10}H_{14}[^{81}Br]_2F_4ONa$ [M+Na]: 410.9199; found 410.9200.

*3,6-Dibromo-5,5,6,6-tetrafluoro-1-phenylhexyl 2,2,2-trifluoroacetate (**3t**).* Irradiation time 24 h. Yield 184 mg (73%). Colorless oil. Chromatography: hexane/EtOAc, 25/1. Mixture of diastereomers, 1/1. ^{1}H NMR (300 MHz, Chloroform-*d*) δ, both isomers: 7.50–7.33 (m, 10H), 6.26–6.11 (m, 2H), 4.48–4.32 (m, 1H), 3.87–3.72 (m, 1H), 3.05–2.53 (m, 7H), 2.34–2.19 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ, both isomers: 156.6 (q, *J* = 42.6 Hz), 156.5 (q, *J* = 42.6 Hz), 137.3, 135.7, 130.0, 129.5, 129.4, 129.2, 127.3, 126.4, 121.9–111.7 (m), 79.3, 78.7, 45.3, 45.3, 43.6, 43.6, 39.8 (t, *J* = 21.4 Hz), 39.7 (t, *J* = 21.2 Hz), 39.3. ^{19}F NMR (282 MHz, Chloroform-*d*) δ, both isomers: −67.35 (s, 2F), −67.45 (s, 2F), −75.93 (s, 3F), −75.97 (s, 3F), −109.32 (dd, *J* = 257.5, 30.0 Hz, 2F), −112.12 (dd, *J* = 104.1, 26.3 Hz, 1F), −113.09 (dd, *J* = 104.3, 26.6 Hz, 1F). HRMS (ESI-TOF): calcd for $C_{14}H_{11}[^{81}Br]_2F_7O_2Na$ [M+Na]: 528.8866; found 528.8876.

*3.3. Gram-Scale Synthesis of 1,4-Dibromo-1,1,2,2-tetrafluorodecane (**3u**)*

A 50 mL Erlenmeyer flask was charged with DMSO (15 mL), and argon was bubbled for 2 min. TBABr (512 mg, 2 mmol), alkene (2.24 g, 20 mmol), bromide **2b** (27 mmol, 3.2 mL), $MnBr_2$ (215 mg, 1 mmol), and 4CzIPN (7 mg, 0.01 mmol) were added. The flask was closed with a stopper, placed into a beaker cooled with water flow at room temperature and irradiated for 4 h with a 455 nm 30 W LED matrix placed under the bottom of the beaker. The reaction was quenched with water (30 mL) and extracted with hexane (3 × 10 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated under atmospheric pressure. The residue was distilled under vacuum using a Hickmann distilling head (bp 130–135 °C, 18 Torr) to give colorless oil. Yield 6.39 g (86%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.35–4.20 (m, 1H), 2.94–2.55 (m, 2H), 2.07–1.77 (m, 2H), 1.65–1.20 (m, 8H), 0.95–0.84 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 117.3 (tt, *J* = 311.9, 39.1 Hz), 116.4 (tt, *J* = 257.5, 256.5, 31.6, 31.1 Hz), 45.1, 39.7 (t, *J* = 21.2 Hz), 39.2 (d, *J* = 1.7 Hz), 31.7, 28.6, 27.3, 22.67, 14.2. ^{19}F NMR (282 MHz, Chloroform-*d*) δ −67.17 (s, 2F), −110.72 (ddd, *J* = 256.4, 28.3, 9.1 Hz, 1F), −112.77 (dd, *J* = 257.5, 25.8 Hz, 1F). Anal. Calcd for $C_{10}H_{16}Br_2F_4$: C, 32.28; H 4.34. Found: C 32.62, H 4.46.

*3.4. Synthesis of 1-Bromo-1,1,2,2-tetrafluorodec-3-ene (**4**)*

Potassium hydroxide (0.75 mmol, 42 mg) was added to a stirring solution of compound **3u** (0.5 mmol, 186 mg) in ethanol (1 mL) at room temperature. The mixture was heated at 60 °C for 30 min (water bath) and then allowed to cool to room temperature. The mixture was quenched with water (3 mL) and extracted with methyl *tert*-butyl ether (3 × 2 mL).

The solvent was removed under reduced pressure to give colorless oil. Yield 10 mg, 89%. Mixture of diastereomers, 72:19. ^{1}H NMR (300 MHz, Chloroform-*d*) δ, major isomer: 6.50–6.34 (m, 1H), 2.25–2.11 (m, 2H); minor isomer: 6.20–6.03 (m, 1H), 2.38–2.26 (m, 2H); both isomers: 5.71–5.35 (m, 1H), 5.30 (s, 1H), 1.54–1.17 (m, 11H), 0.94–0.84 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ, major isomer: 143.5 (t, *J* = 8.4 Hz), 32.2, 31.7, 28.8, 28.1 (t, *J* = 1.4 Hz), 22.7, 14.1; minor isomer: 145.6 (t, *J* = 5.3 Hz), 31.73, 29.2 (d, *J* = 1.6 Hz), 29.0; both isomers: 122.7–109.7 (m). ^{19}F NMR (282 MHz, Chloroform-*d*) δ, major isomer: −66.67 (t, *J* = 6.6 Hz, 2F), −110.01 (s, 2F); minor isomer: −67.03 (t, *J* = 6.6 Hz, 2F), −105.19 (s, 2F). Anal. Calcd for $C_{10}H_{15}BrF_4$: C, 41.26; H 5.19. Found: C 41.17, H 5.26.

*3.5. Synthesis of 9-Bromo-6,6,7,7-tetrafluoropentadecan-1-ol (**5**)*

The reaction tube containing ascorbic acid (132 mg, 0.75 mmol) was evacuated and filled with argon. Then, ethanol (1 mL), triethylamine (104 µL, 0.75 mmol), pent-4-en-1-ol (0.5 mmol, 43 mg), compound **3u** (0.75 mmol, 279 mg), 2-methylpropane-2-thiol (12 µL, 0.1 mmol) and 3DPA2FBN (1.6 mg, 0.0025 mmol) were added. The tube was screw-capped and irradiated with 400 nm 60W LED matrix for 5 h. The mixture was quenched with water (5 mL) and extracted with methyl *tert*-butyl ether (3 × 1.5 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography (hexane/EtOAc, 3/1) to give pale-yellow oil. Yield 119 mg, 63%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.29 (dtd, *J* = 10.7, 6.7, 4.1 Hz, 1H), 3.73–3.63 (m, 2H), 2.87–2.47 (m, 2H), 2.16–1.74 (m, 5H), 1.73–1.18 (m, 14H), 0.94–0.83 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 119.0 (tt, *J* = 249.2, 35.9, 35.1 Hz), 118.2 (tt, *J* = 251.9, 250.6, 36.1 Hz), 62.5, 46.3, 39.4, 39.3 (t, *J* = 21.6), 32.3, 31.7, 29.6 (t, *J* = 22.7 Hz), 28.6, 27.3, 22.7, 17.2 (t, *J* = 3.7 Hz), 14.2. ^{19}F NMR (282 MHz, Chloroform-*d*) δ −114.04 (dd, *J* = 264.3, 26.5 Hz, 1F), −115.10−−116.49 (m, 3F). HRMS (ESI-TOF): calcd for $C_{14}H_{25}[^{81}Br]F_4ONa$ [M+Na]: 389.0897; found 389.0906.

*3.6. Synthesis of 1,1,2,2-Tetrafluorodecane (**6**)*

The reaction tube containing 4CzIPN (2 mg, 0.0025 mmol) was evacuated and filled with argon. Then, acetonitrile (1 mL), 1,3,5-trimethyl-1,3,5-triazinane (194 mg, 1.5 mmol), compound **3u** (0.5 mmol, 186 mg) and 2-methylpropane-2-thiol (6 µL, 0.05 mmol) were added. The tube was screw-capped and irradiated with 455 nm 80W LED matrix for 1 h. The mixture was quenched with water (5 mL) and extracted with methyl *tert*-butyl ether (3 × 1.5 mL). The combined organic phases were filtered through a short pad of Na_2SO_4 and concentrated under atmospheric pressure. The residue was purified by column chromatography (dichloromethane) to give colorless oil. Yield 80 mg, 75%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.70 (tt, *J* = 54.1, 3.1 Hz, 1H), 1.95 (tt, *J* = 18.5, 7.8 Hz, 2H), 1.64–1.51 (m, 2H), 1.47–1.24 (m, 11H), 0.89 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 117.8 (tt, *J* = 245.7, 28.8 Hz), 110.5 (tt, *J* = 249.1, 41.5 Hz), 31.9, 30.0 (t, *J* = 22.4 Hz), 29.1, 29.3, 29.2, 22.7, 20.5 (t, *J* = 3.9 Hz), 14.1. ^{19}F NMR (282 MHz, Chloroform-*d*) δ −117.07 (t, *J* = 18.5 Hz), −136.39 (d, *J* = 54.1 Hz). Anal. Calcd for $C_{10}H_{18}F_4$: C, 56.06; H 8.47. Found: C 56.18, H 8.61.

*3.7. Radical Clock Experiment, Synthesis of Dimethyl 3-(3-Bromo-2,2,3,3-tetrafluoropropyl)-4-(bromomethyl)cyclopentane-1,1-dicarboxylate (**7**)*

The reaction was performed the general procedure using dimethyl diallylmalonate and bromide **2b**. Irradiation time 5 h. Yield 179 mg (76%). Colorless solid. Mp 60–72 °C. Chromatography: hexane/EtOAc, 10/1. Mixture of diastereomers, 13/1. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.73 (s, 6H), 3.42–3.20 (m, 2H), 2.68–2.46 (m, 4H), 2.40–1.96 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.7, 172.5, 117.56 (tt, *J* = 311.6, 39.7 Hz), 117.4 (tt, *J* = 255.4, 31.3 Hz), 58.3, 53.2, 44.4, 39.0 (d, *J* = 2.5 Hz), 38.3, 35.3, 34.9, 32.9, 29.5 (t, *J* = 22.1 Hz). ^{19}F NMR (282 MHz, Chloroform-*d*) δ, major isomer: −66.87 (s, 2F), −110.58 (dd, *J* = 256.3, 30.1 Hz, 1F), −113.26 (dd, *J* = 256.3, 28.7 Hz, 1F); minor isomer: −66.74 (s, 2F), −109.88 (dd,

J = 254.6, 32.0 Hz, 1F), −112.67 (dd, J = 254.6, 26.1 Hz, 1F). HRMS (ESI-TOF): calcd for $C_{13}H_{16}[^{81}Br]_2F_4O_4Na$ [M+Na]: 496.9203; found 496.9185.

4. Conclusions

In summary, a method for the atom transfer radical addition of alkenes with readily oxidizable bromonitromethane and Halon 2402 is described. The reaction is performed under blue light irradiation, with readily available manganese (II) salt serving as a key co-catalyst, which facilitates the trapping of the radical intermediate with the formation of the carbon–bromine bond.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13071126/s1, Stern–Volmer plots, Copies of NMR spectra.

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