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meso-Antracenyl-BODIPY Dyad as a New Photocatalyst in Atom-Transfer Radical Addition Reactions

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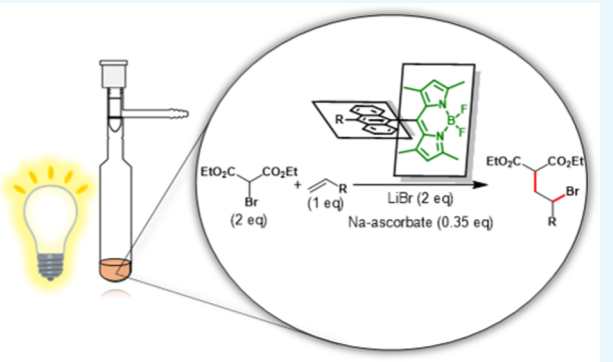
ABSTRACT: We demonstrate that because of the efficient generation of triplet excited state under UV or visible-light irradiation, *meso*-antracenyl-BODIPY donor−acceptor dyad can catalyze atom-transfer radical addition (ATRA) reactions between bromomalonate and alkenes. This finding paves the way for the design and application of the new type of heavy atom-free organic chromophores for photocatalysis.



INTRODUCTION

In the past few decades, the field of photocatalysis attracted much attention among synthetic chemists. Photocatalysis, as a method of activation of organic molecules, relies on the electron or energy transfer between photoexcited catalysts and substrates and allows bond formation and breakage under mild conditions. Though the most used photocatalysts—ruthenium or iridium polypyridyl complexes—have already proved their efficiency in multiple reactions,[1−5] their high cost, laborious synthesis, and generation of heavy-atom wastes prompted chemists toward the search and development of new photocatalytic systems.[6−15] Among them, there are several examples of the application of metal-free organic chromophores as photocatalysts in the reactions of oxidation,[16−20] reductive dehalogenation,[21] C−C bond formation,[22−26] and others.[27−30] For the majority of catalysts, either organometallic complexes or metal-free chromophores, the ability to form long-lived excited states has been postulated as a prerequisite for the efficient photocatalytic activity.[31,32] Within this context, we turned our attention to the recently reported orthogonal electron donor−acceptor (D−A) boron dipyrromethene (BODIPY)-based dyads.[33] In these dyads, BODIPY chromophores are usually substituted at the *meso*-position with another π-conjugated "dye," e.g., anthracene (Ant), so that the planes of BODIPY and the "dye" form an angle close to 90° (Figure 1a). The dyads possess long-lived triplet excited states of BODIPY, when selectively excited at either BODIPY or the "dye" unit of the dyad. Notably, in contrast to many other organic and organometallic compounds, the formation of triplet excited states in "dye"-BODIPY dyads does not require the presence of heavy atoms in the structure of chromophores. In this case, the generation of the triplet excited state of BODIPY (T_1) proceeds through the initial formation of the charge-separated state (^{1}CS) within the dyad, where BODIPY unit usually serves as an electron acceptor and the "dye" as a donor (Figure 1b). Importantly, the spin-forbidden ^{1}CS → T_1 transition, termed spin-orbit charge-transfer intersystem crossing (SOCT-ISC), is favored when the molecular orbitals of the donor ("dye") and acceptor (BODIPY) are orthogonal, creating a large enough orbital angular momentum for the spin flip.[34−36] The quantum yields of the triplet excited-state formation can reach 90% and above in the dyads with the properly matching photophysical parameters of the BODIPY and the "dye" units (e.g., reduction potentials, excitation energies, etc.). This trend of "dye"-BODIPY dyads to the efficient formation of long-lived triplet excited states encouraged us to explore the possibility of their application as photocatalysts in chemical reactions.

RESULTS AND DISCUSSION

Among various types of chemical transformations, the C−C bond formation seemed to us the most attractive, as it constitutes the fundamental basis for the creation of new organic frameworks. When choosing the reaction, we also considered the fact that catalytic cycles should include the

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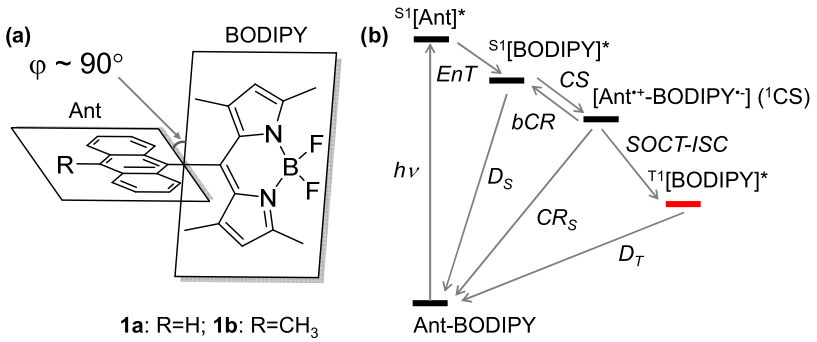

Figure 1. (a) Molecular structures and (b) photophysical scheme of catalysts upon photoexcitation of anthracene. We can also selectively photoexcite BODIPY to directly produce ^{S1}[BODIPY]*. EnT = energy transfer; CS = charge separation; bCR = back charge recombination; CR_S = singlet charge recombination; D_S = singlet decay; and D_T = triplet decay.

oxidation or reduction of the photoexcited catalyst by the substrate. While excited states of ruthenium or iridium complexes can be easily oxidized or reduced, the oxidation/reduction of the triplet excited state of BODIPY might be challenging due to the lower reduction potentials. However, this issue can be overcome if a sacrificial reductant or oxidant is used to convert the excited state of the catalyst. Based on these considerations, we chose atom-transfer radical addition (ATRA) as a model reaction to test the photocatalytic performance of "dye"-BODIPY dyad. Photoredox ATRA reactions between olefins and various halogen-containing reagents have been thoroughly studied by Stephenson group,[37] using $Ru(bpy)_3^{2+}$ as a photocatalyst and a wide range of sacrificial reductants from alkyl- and aryl-amino derivatives to sodium ascorbate. Moreover, recently it was shown that diiodo-BODIPY in combination with sodium ascorbate can also catalyze ATRA reactions.[38] Though the last finding seemed reassuring, we anticipated that the "dye"-BODIPY dyads might perform differently in ATRA reactions due to the different mechanism of the triplet state formation. Indeed, it was shown that the quantum yields of the triplet excited-state formation in various "dye"-BODIPY dyads are largely determined by the energy of ^{1}CS, which in turn depends on the polarity of the solvent. Thereby, any factors, which make up the reaction microenvironment, e.g., substrates, solvent mixtures, and additives can potentially affect the efficiency of photocatalysis.

We started the investigation with the reaction between 5-hexen-1-ol (**2**) and diethyl bromomalonate (Scheme 1) and have chosen antracenyl-BODIPY (**1a**) and 9-methylantracenyl-BODIPY (**1b**) as the catalysts, due to the high quantum yields of the triplet excited-state formation (Φ_T = 0.93 and 0.90 in acetonitrile, AcCN, respectively) and quite high reduction potentials (BODIPY/BODIPY$^{\bullet-}$ = −1.01 V vs saturated calomel electrode (SCE)).[33] All reactions were performed in deoxygenated solutions under Ar, using 350 nm excitation light source, which selectively excited anthracene unit in the dyads **1a** and **1b**. As the solvents, we have chosen *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and AcCN, since the triplet excited states in the dyads **1a** and **1b** form with the highest efficiency in polar solvents.[33] No product **12** formation was observed when the reaction was performed in DMF/H_2O, 1:1 mixture, using triethylamine or 4-methoxy-*N*,*N*-diphenylaniline as sacrificial reductants; however, the product was obtained with high yield of 87% when sodium ascorbate was used (Table 1, entry 1). Since we noticed a sufficient aggregation of the catalyst upon addition of water to the reaction mixture, the amount of water was reduced to solvent/water, 3:1 ratio. In DMF/H_2O, 3:1 mixture, the product was formed with 86% yield (Table 1, entry 3); quite good yield of 66% was obtained in DMSO/H_2O, 3:1 (Table 1, entry 4); and almost quantitative yield of 96% was obtained in AcCN/H_2O, 3:1 mixture (Table 1, entry 5). Our attempts to improve the yield in DMSO/H_2O, 3:1 by varying the reaction time were unsuccessful (Scheme S1 and Table S1, Supporting Information). In fact, the highest yield of 66% was obtained, when the reaction proceeded for 24 h, and the yield decreased to 57% and 48% in the case of longer (30 h) or shorter (18 h) reaction time, respectively. In principle, these results were not surprising, since we anticipated that the yield of the product should depend on the solvent polarity. To get more insights on our observations, we measured the quantum yields of the triplet excited-state formation for the dyad **1** in DMF/H_2O, AcCN/H_2O, and DMSO/H_2O, 3:1, and for all solvent mixtures, the obtained values were about the same and equal to $\Phi_T > 0.90$. These results do not explain why in DMSO/H_2O mixture the yield of the product is lower. Probably, other factors play a crucial role in this case, and more mechanistic studies are required to shed light onto this issue. We then performed the reaction in AcCN/H_2O, 3:1 without the addition of LiBr to check whether it affects the reaction efficiency (Scheme S2 and Table S2, Supporting Information). The obtained yield of product **12** was c.a. 2 times lower than for the case when LiBr was present in the reaction mixture. This observation is in agreement with Stephenson's hypothesis that the addition of Lewis acids facilitates the carbon−halogen bond breakage and the formation of radicals in ATRA reactions.[39]

Next, we studied the scope of the reaction in application to various functionalized alkenes (Scheme 1 and Table 1). The reaction between bromomalonate and terminal alkenes proceeded well in the presence of hydroxy-, aldehyde, cyano-, alkoxycarbonyl-, and protected amino groups. As regard solvents, the best yields were obtained in AcCN/H_2O, 3:1 mixture, as compared to DMF/H_2O, 1:1 and DMSO/H_2O, 3:1 (Table 1, entry 9 vs 10 vs 11; entry 12 vs 13 vs 14). In addition, in DMF/H_2O, we detected the formation of the oxidized byproducts in some cases (Scheme S1 and Table S1, Supporting Information), and in the case of DMSO/H_2O—the formation of a higher amount of debrominated malonic ester. This trend is similar to what we observed initially for the reaction between 5-hexen-1-ol and diethyl bromomalonate. In respect to alkene substrates, the reaction proceeded well with terminal alkenes but resulted in poor yields with secondary

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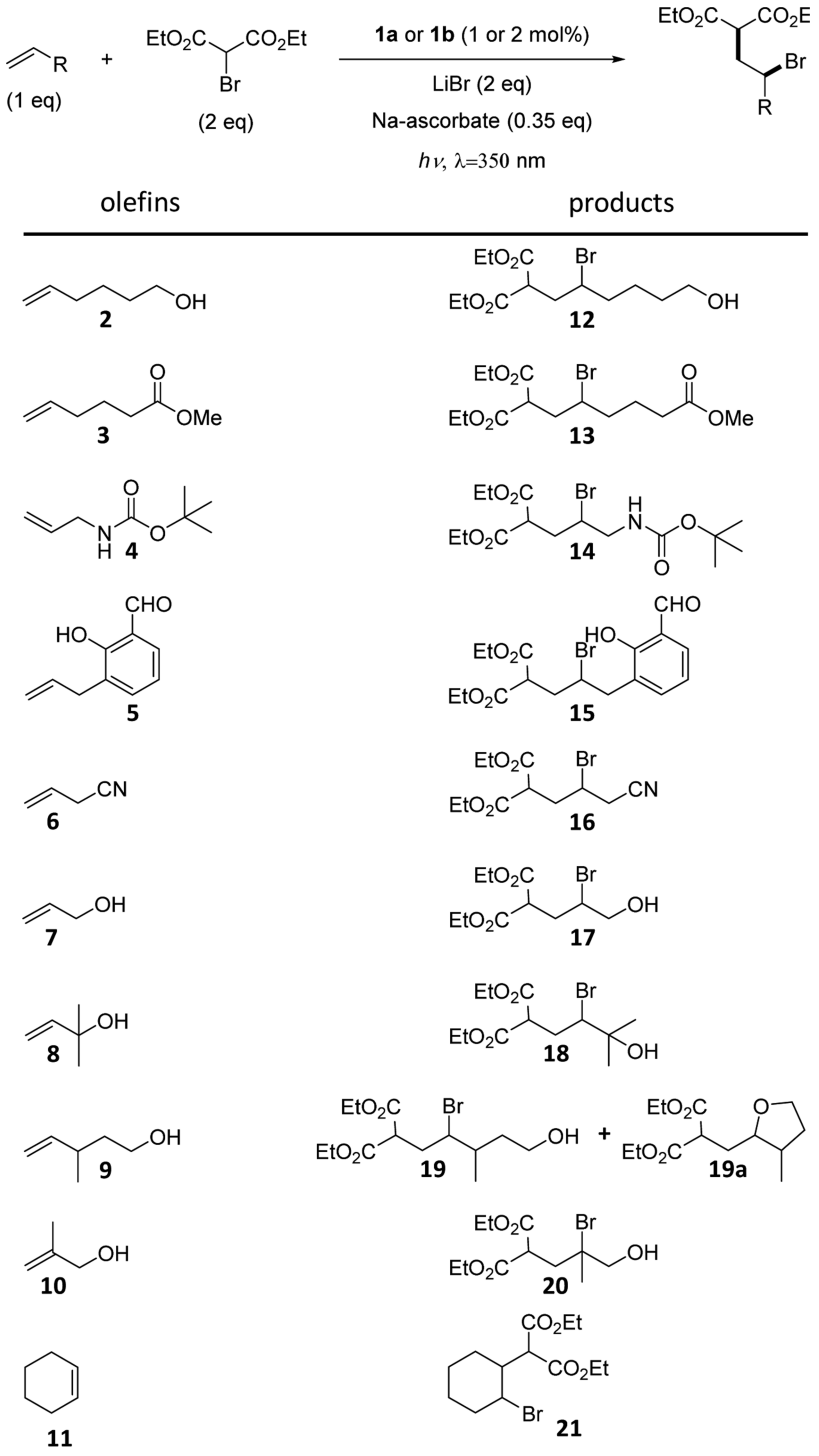
Scheme 1. ATRA Reactions between Diethyl Bromomalonate and Various Olefins



alkenes, e.g., only 10% yield was obtained for cyclohexene (Table 1, entry 19). For terminal alkenes, almost quantitative yields were obtained when the functional groups were distant from the alkene fragment (Table 1, entries 5 and 6). The presence of functional groups and/or alkyl substituents in the vicinity of the alkene resulted in lower, yet good yields. In addition, a longer reaction time was required in the case of bulky substrates. We assume that in this case, both steric and electronic factors come to interplay. Thereby, the presence of highly electron-withdrawing cyanosubstituent at α-position to alkene group led to a moderate 15% yield of the product (Table 1, entry 14).

For the substrate **7** with the less electron-withdrawing hydroxy group at α-position, the yield was 62% (Table 1, entry 15), and for the substrate **5** with electron-withdrawing aryl substituent at α-position, 40% yield was obtained (Table 1 entry 11). Methyl groups at α-position to the alkene fragment in substrates **8** and **9** led to 56% and 46% yields, respectively (Table 1, entries 16 and 17). Interestingly, a high yield of 82% was obtained for the substrate **10**, despite the presence of the electron-withdrawing OH group at α-position to alkene, and a

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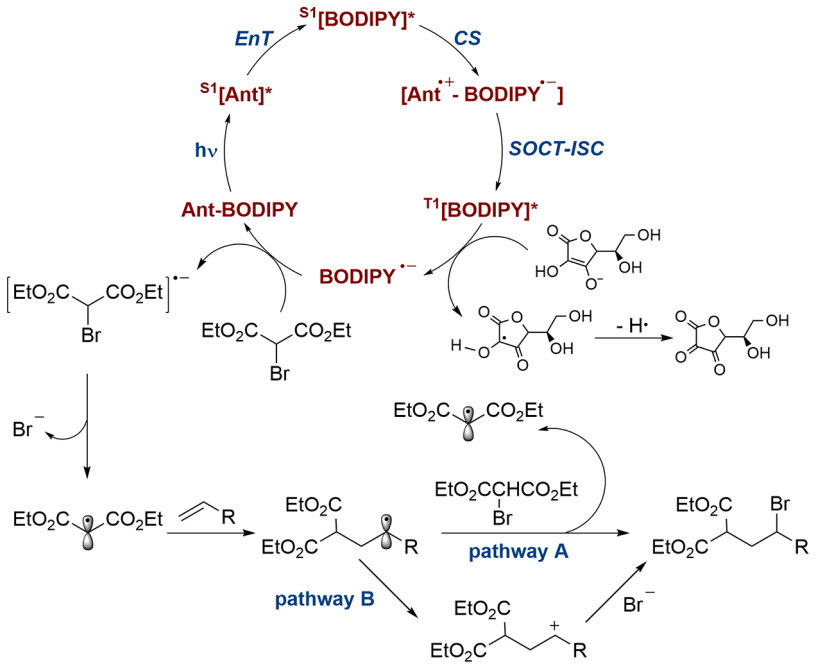
Table 1. ATRA Reactions of Various Olefins under Different Conditions

#	olefin	product	solvent	cat./load	time (h)	yield (%)
1	**2**	**12**	DMF/H_2O, 1:1	**1a**, 1 mol %	24	87
2	**2**	**12**	DMF/H_2O, 1:1	**1b**, 1 mol %	24	88
3	**2**	**12**	DMF/H_2O, 3:1	**1b**, 1 mol %	24	86
4	**2**	**12**	DMSO/H_2O, 3:1	**1a**, 1 mol %	24	66
5	**2**	**12**	AcCN/H_2O, 3:1	**1a**, 1 mol %	24	96
6	**3**	**13**	AcCN/H_2O, 3:1	**1a**, 1 mol %	24	99
7	**3**	**13**	AcCN/H_2O, 3:1	**1b**, 1 mol %	24	99
8	**4**	**14**	AcCN/H_2O, 3:1	**1b**, 2 mol %	48	94
9	**4**	**14**	DMF/H_2O, 1:1	**1b**, 2 mol %	48	90
10	**4**	**14**	DMSO/H_2O, 3:1	**1a**, 1 mol %	24	15
11	**5**	**15**	AcCN/H_2O, 3:1	**1a**, 2 mol %	48	40
12	**5**	**15**	DMF/H_2O, 1:1	**1b**, 2 mol %	48	19
13	**5**	**15**	DMSO/H_2O, 3:1	**1a**, 2 mol %	48	0
14	**6**	**16**	AcCN/H_2O, 3:1	**1a**, 1 mol %	48	15
15	**7**	**17**	AcCN/H_2O, 3:1	**1a**, 2 mol %	48	62
16	**8**	**18**	AcCN/H_2O, 3:1	**1a**, 2 mol %	72	56
17	**9**	**19** + **19a**	AcCN/H_2O, 3:1	**1b**, 2 mol %	48	46
18	**10**	**20**	AcCN/H_2O, 3:1	**1a**, 2 mol %	48	82
19	**11**	**21**	AcCN/H_2O, 3:1	**1a**, 2 mol %	48	10

Scheme 2. Proposed Mechanism for ATRA Reaction Catalyzed by Ant-BODIPY Dyad



methyl substituent at the double bond. This result can be attributed to the intermediate formation of stable tertiary radical or tertiary carbocation during the reaction and is in a good agreement with the proposed mechanism.

We hypothesized that the mechanism of the ATRA reaction, catalyzed by the dyads **1a** and **1b** should be similar to the one proposed for diiodo-BODIPY,[38] except that the triplet excited state of BODIPY in the dyads **1a** and **1b** forms from the ^{1}CS state (Scheme 2). The participation of the triplet excited state in the reaction is supported by the fact that the reaction did not proceed in the presence of oxygen, which quenches the triplet states. Thereby, upon excitation of anthracene unit at λ_{ex} = 350 nm, ultrafast energy transfer from ^{S1}[Ant]* to ^{S1}[BODIPY]* occurs, which is followed by an electron transfer within the dyad **1a** or **1b**, resulting in the formation of ^{1}CS state [Ant$^{\bullet+}$-BODIPY$^{\bullet-}$]. Then, ^{T1}[BODIPY]* forms as a result of the SOCT-ISC process. In principle, ^{T1}[Ant]* could also form. However, as it was shown earlier for the dyad **1a**, the majority of the triplet excitation energy is on BODIPY, and the contribution of ^{T1}[Ant]* is small.[40] Single electron transfer (SET) from the sacrificial reductant—sodium ascorbate—converts the triplet excited-state ^{T1}[BODIPY]* into radical-anion BODIPY$^{\bullet-}$, which has high enough reduction potential (BODIPY/BODIPY$^{\bullet-}$ = −1.01 V vs SCE)[33] to convert bromomalonate into malonic radical. Malonic radical further undergoes the addition of alkenes with the formation of the corresponding radical. The ATRA product could form through the abstraction of halogen from another equivalent of bromomalonate (radical propagation pathway, A), or through single-electron oxidation to carbocation with subsequent

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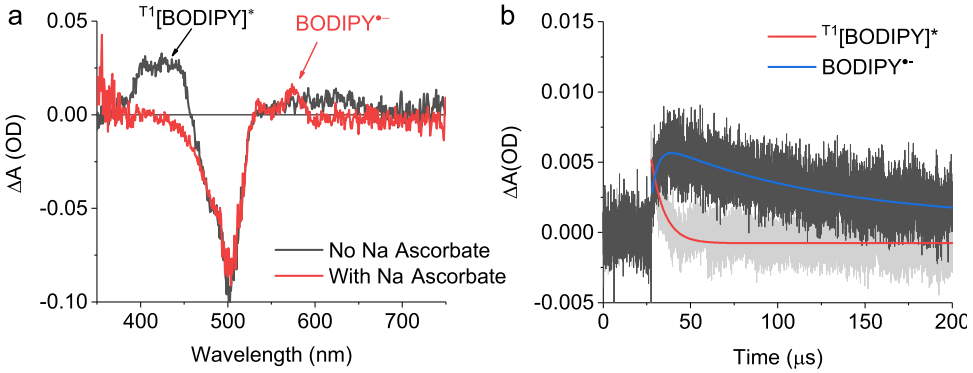

Figure 2. (a) Transient absorption spectra of **1a** at 10 μs after the ns laser pulse (λ_{ex} = 355 nm) in AcCN/H_2O = 3:1 in the presence and absence of sodium ascorbate. (b) Decay kinetics of 1a in AcCN/H_2O = 3:1 in the presence of sodium ascorbate at the ^{T1}[BODIPY]* absorption band (430 nm) and the BODIPY$^{\bullet-}$ absorption band (570 nm).

trapping by bromine anion (radical-polar crossover pathway, B), as proposed by Stephenson.[37]

Hypothetically, the malonic radical could form through the SET from the ^{1}CS state [Ant$^{\bullet+}$-BODIPY$^{\bullet-}$], followed by the reduction of Ant$^{\bullet+}$ unit with sodium ascorbate. However, transient absorption spectroscopy studies eliminated this possibility by showing that the lifetime of the ^{1}CS state is too short to undergo intermolecular reactions (more details in the SI), and further confirming that BODIPY$^{\bullet-}$ is produced by the reduction of ^{T1}[BODIPY]* by sodium ascorbate (Figure 2).

Finally, we confirmed that the ATRA reactions proceed with the same efficiency under visible-light irradiation. Thereby, the reaction between diethyl bromomalonate and substrates **2** and **3** in AcCN/H_2O, 3:1 mixture, and using catalyst **1b** and 470 nm excitation light source led to products **12** and **13** with 98 and 99% yields, respectively (Scheme S3 and Table S3, Supporting Information). In this case, a BODIPY unit was selectively excited at λ_{ex} = 470 nm to produce ^{S1}[BODIPY]*. The remaining steps of the mechanism are analogous to the described above for 350 nm excitation.

CONCLUSIONS

In conclusion, we demonstrated that BODIPY-based donor–acceptor dyads can efficiently catalyze light-driven ATRA reactions. The dyads can be excited with UV and visible light. Given the ease of the synthesis, availability of synthetic precursors, and readily tunable photophysical and redox properties, these dyads can become a new inexpensive environmentally friendly alternative to classical organometallic photocatalysts.

EXPERIMENTAL SECTION

General Experimental Procedures. All solvents and reagents were purchased from commercial sources and used as received. Column chromatography was performed on silica gel (pore size 60 Å, particle size 40–63 μm, Sigma-Aldrich). Analytical thin-layer chromatography (TLC) was carried out using aluminum plates covered with silica gel and containing a fluorescent indicator (layer thickness 200 μm, particle size 25 μm, Sigma-Aldrich). NMR spectra were recorded on the AVANCE III HD Bruker 500 spectrometer operating at 500 MHz (^{1}H) and 125 MHz (^{13}C). Photoreactions were carried out using an RPR-100 photochemical reactor (The Southern New England Co. Inc.), equipped with eight lamps (λ_{ex} = 350 or 470 nm) and a stirring plate. Prior each reaction, the reaction mixtures were degassed by three to five freeze–pump–thaw cycles and filled with Ar, using the standard Schlenk technique.

Optical Measurements. UV–vis absorption spectra were recorded on a Cary 50 Scan UV–vis spectrophotometer (Varian). Fluorescence measurements were performed on an FLS1000 spectrofluorometer (Edinburgh Instruments, U.K.). The femtosecond and nanosecond transient absorption (fsTA and nsTA) setups were described elsewhere.[33] In short, we used 355 nm, a third harmonic of Nd:YAG (adjusted to 1–4 mJ), and 500 nm (output from an optical parametric amplifier, adjusted to 0.5 μJ) as an excitation pump for nsTA and fsTA, respectively. The samples for nsTA measurements were degassed by three to five freeze–pump–thaw cycles. Quantum yields of triplets were measured using a relative actinometry method compared with the formation of triplets of benzophenone in acetonitrile (MeCN) (Φ_T = 1.0).[41] Data sets were analyzed using OriginPro 2017 (OriginLab Corporation).

General Procedure for Photocatalytic ATRA Reactions. A 15 mL Schlenk tube was equipped with a Rotaflo stopcock, magnetic stir bar, and was charged with photocatalyst **1a** or **1b** (1–2 mol %, 1.2–2.5 mg, 0.0028–0.0057 mmol), sodium ascorbate (19.41 mg, 0.098 mmol, 0.35 equiv), LiBr (48.63 mg, 0.56 mmol, 2 equiv), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol, 2 equiv), olefin **2–11** (0.28 mmol, 1 equiv), and water (0.15 mL). The heterogeneous reaction mixture was degassed (freeze–pump–thaw cycle × 3–5), and the vessel was refilled with Ar. The reaction mixture was tightly sealed and positioned approximately (5–7 cm) away from the light source (λ = 350 nm), where it vigorously stirred for 24–72 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL), washed with brine (1 mL), and dried over Na_2SO_4. The solvent was removed in vacuum, and the residue was purified by column chromatography on silica gel, using the solvent system indicated, to obtain the desired products in the stated yields.

Experimental Procedures. *Diethyl 2-(2-Bromo-6-hydroxyhexyl)malonate (**12**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (1.2 mg, 1 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol), 5-hexen-1-ol (**2**) (28.04 mg, 0.28 mmol), and water (0.15 mL). The reaction mixture was stirred for 24 h. The residue was purified by column

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chromatography (silica gel, hexanes/ethyl acetate (AcOEt), gradient from 2:1 to 1:1) to give the title compound **12** as orange oil. Yield 91 mg (96%). All characterizations are consistent with those reported in literature.[39] NMR ^{1}H ($CDCl_3$), δ, ppm: 1.25 (3H, t, ^3J = 7.2 Hz, $-CH_3-$), 1.26 (3H, t, ^3J = 7.0 Hz, $-CH_3-$), 1.45−1.68 (5H, m, $-CH_2-$), 1.83−1.91 (2H, m, $-CH_2-$), 2.23 (1H, ddd, J_1 = 14.8, J_2 = 10.7, J_3 = 4.2 Hz, $-CH_2-$), 2.44 (1H, ddd, J_1 = 13.4, J_2 = 10.2, J_3 = 3.2 Hz, $-CH_2-$), 3.63 (2H, t, ^3J = 6.2 Hz, $-CH_2-$), 3.76 (1H, dd, $^3J_1$ = 10.3, $^3J_2$ = 4.2 Hz, $-CH-$), 3.95−4.03 (1H, m, $-CHBr-$), and 4.14−4.26 (4H, m, $-CH_2CH_3$). NMR ^{13}C ($CDCl_3$), δ, ppm: 13.97, 14.01, 23.7, 31.9, 37.8, 39.1, 50.5, 54.6, 61.62, 61.69, 168.8, and 169.0.

*Diethyl 2-(2-Bromo-6-hydroxyhexyl)malonate (**12***).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (1.2 mg, 1 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), DMF (0.3 mL), diethyl bromomalonate (134 mg, 0.56 mmol), 5-hexen-1-ol (**2**) (28.04 mg, 0.28 mmol), and water (0.3 mL). The reaction mixture was stirred for 24 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt, gradient from 2:1 to 1:1) to give the title compound **12** as orange oil and compound **12a** as red oil. **12:** Yield 83 mg (87%). NMR ^{1}H ($CDCl_3$), δ, ppm: 1.25 (3H, t, ^3J = 7.2 Hz, $-CH_3-$), 1.26 (3H, t, ^3J = 7.0 Hz, $-CH_3-$), 1.45−1.68 (5H, m, $-CH_2-$), 1.83−1.91 (2H, m, $-CH_2-$), 2.23 (1H, ddd, J_1 = 14.8, J_2 = 10.7, J_3 = 4.2 Hz, $-CH_2-$), 2.44 (1H, ddd, J_1 = 13.4, J_2 = 10.2, J_3 = 3.2 Hz, $-CH_2-$), 3.63 (2H, t, ^3J = 6.2 Hz, $-CH_2-$), 3.76 (1H, dd, $^3J_1$ = 10.3, $^3J_2$ = 4.2 Hz, $-CH-$), 3.95−4.03 (1H, m, $-CHBr-$), and 4.14−4.26 (4H, m, $-CH_2CH_3$). NMR ^{13}C ($CDCl_3$), δ, ppm: 13.97, 14.01, 23.7, 31.9, 37.8, 39.1, 50.5, 54.6, 61.62, 61.69, 168.8, and 169.0. **12a:** Yield 4.5 mg (5%). NMR ^{1}H ($CDCl_3$), δ, ppm: 1.23−1.29 (6H, m, $-CH_2CH_3$), 1.44−1.96 (5H, m, $-CH_2-$), 2.18−2.29 (1H, m, $-CH_2-$), 2.40−2.50 (2H, m, $-CH_2-$), 3.74−3.79 (1H, m, $-CH-$), 3.95−4.02 (1H, m, $-CHBr-$), 4.14−4.30 (4H, m, $-CH_2CH_3$), and 9.76−9.78 (1H, m, $-CHO$).

*1,1-Diethyl 6-Methyl 3-bromohexane-1,1,6-tricarboxylate (**13**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (1.2 mg, 1 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol), methyl 5-hexenoate (**3**) (35.89 mg, 0.28 mmol), and water (0.15 mL). The reaction mixture was stirred for 24 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt = 3:1), to give the title compound **13** as yellow oil. Yield 101.5 mg (99%). All characterizations are consistent with those reported in literature.[39] NMR ^{1}H ($CDCl_3$), δ, ppm: 1.22−1.29 (6H, m, $-CH_2CH_3$), 1.70−1.81 (1H, m, $-CH_2-$), 1.81−1.94 (3H, m, $-CH_2-$), 2.23 (1H, ddd, J_1 = 14.8, J_2 = 10.7, J_3 = 4.1 Hz, $-CH_2-$), 2.28−2.36 (2H, m, $-CH_2-$), 2.43 (1H, ddd, J_1 = 13.6, J_2 = 10.3, J_3 = 3.1 Hz, $-CH_2-$), 3.65 (3H, s, broad, $-OCH_3$), 3.75 (1H, dd, $^3J_1$ = 10.2, $^3J_2$ = 4.1 Hz, $-CH-$), 3.93−4.01 (1H, m, $-CHBr-$), and 4.14−4.28 (4H, m, $-CH_2CH_3$). NMR ^{13}C ($CDCl_3$), δ, ppm: 13.87, 13.91, 22.7, 33.0, 37.6, 38.4, 50.4, 51.4, 53.8, 61.5, 61.6, 168.6, 168.7, and 173.3.

*Diethyl 2-(2-Bromo-3-((tert-butoxycarbonyl)amino)-propyl)malonate (**14**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1b** (2.5 mg, 2 mol %), sodium ascorbate (19.02 mg, 0.096 mmol), LiBr (47.76 mg, 0.55 mmol), AcCN (0.45 mL), diethyl bromomalonate (131.48 mg, 0.55 mmol), *tert*-butyl allylcarbamate (**4**) (43.08 mg, 0.274 mmol), and water (0.15 mL). The reaction mixture was stirred for 48 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt = 5:1), to give the title compound **14** as orange oil. Yield 101.5 mg (94%). All characterizations are consistent with those reported in literature.[39] NMR ^{1}H ($CDCl_3$), δ, ppm: 1.26 (3H, t, ^3J = 7.2 Hz, $-CH_3-$), 1.27 (3H, t, ^3J = 7.2 Hz, $-CH_3-$), 1.43 (9H, s, broad, $-C(CH_3)_3-$), 2.21−2.29 (1H, m, $-CH_2-$), 2.46 (1H, ddd, J_1 = 13.3, J_2 = 9.5, J_3 = 3.7 Hz, $-CH_2-$), 3.45−3.57 (2H, m, $-CH_2-$), 3.73 (1H, dd, $^3J_1$ = 9.5, $^3J_2$ = 5.0 Hz, $-CH-$), 4.07−4.15 (1H, m, $-CHBr-$), 4.15−4.26 (4H, m, $-CH_2CH_3$), and 4.91−4.99 (1H, m, broad, $-NH-$). NMR ^{13}C ($CDCl_3$), δ, ppm: 13.9, 14.0, 28.2, 34.6, 47.0, 50.1, 53.2, 61.65, 61.71, 79.8, 155.6, 168.4, and 168.8.

*Diethyl 2-(2-Bromo-3-(3-formyl-2-hydroxyphenyl)propyl)-malonate (**15**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (2.5 mg, 2 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol), 3-allylsalicyaldehyde (**5**) (45.41 mg, 0.28 mmol), and water (0.15 mL). The reaction mixture was stirred for 48 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt 5:1), to give the title compound **15** as yellow oil. Yield 45 mg (40%). NMR ^{1}H ($CDCl_3$), δ, ppm: 1.23 (3H, t, ^3J = 7.0 Hz, $-CH_3-$), 1.25 (3H, t, ^3J = 7.2 Hz, $-CH_3-$), 2.31 (1H, ddd, J_1 = 15.0, J_2 = 10.7, J_3 = 4.4 Hz, $-CH_2-$), 2.52 (1H, ddd, J_1 = 13.4, J_2 = 10.2, J_3 = 3.2 Hz, $-CH_2-$), 3.16 (1H, dd, $^3J_1$ = 14.2, $^3J_2$ = 8.2 Hz, $-CH_2-$), 3.32 (1H, dd, $^3J_1$ = 14.2, $^3J_2$ = 5.7 Hz, $-CH_2-$), 3.79 (1H, dd, $^3J_1$ = 10.1, $^3J_2$ = 4.3 Hz, $-CH-$), 4.12−4.24 (4H, m, $-CH_2CH_3$), 4.37−4.44 (1H, m, $-CHBr-$), 6.98 (1H, t, ^3J = 7.6 Hz, Ar), 7.43−7.50 (2H, m, Ar), 9.87 (1H, s, $-CHO$), and 11.30 (1H, s, broad, $-OH$). NMR ^{13}C ($CDCl_3$), δ, ppm: 13.97, 13.99, 37.5, 39.6, 50.7, 52.4, 61.6, 61.7, 119.5, 120.4, 126.5, 132.8, 138.6, 159.7, 168.5, 168.9, and 196.7.

*Diethyl 2-(2-Bromo-3-cyanopropyl)malonate (**16**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (1.2 mg, 1 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol), allyl cyanide (**6**) (19.35 mg, 0.28 mmol), and water (0.15 mL). The reaction mixture was stirred for 48 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt 3:1), to give the title compound **16** as orange oil. Yield 13 mg (15%). NMR ^{1}H ($CDCl_3$), δ, ppm: 1.21−1.31 (6H, m, $-CH_2CH_3$), 2.29−2.40 (1H, m, $-CH_2-$), 2.53 (1H, ddd, J_1 = 13.6, J_2 = 10.2, J_3 = 3.2 Hz, $-CH_2-$), 3.01 (2H, dd, $^3J_1$ = 5.8, $^3J_2$ = 3.0 Hz, $-CH_2-$), 3.71 (1H, dd, $^3J_1$ = 10.4, $^3J_2$ = 4.1 Hz, $-CH-$), and 4.12−4.30 (5H, m, $-CHBr-$, $-CH_2CH_3$). NMR ^{13}C ($CDCl_3$), δ, ppm: 13.98, 14.0, 28.6, 36.9, 43.7, 50.1, 61.99, 62.04, 116.0, 168.15, and 168.18.

*Diethyl 2-(2-Bromo-3-hydroxypropyl)malonate (**17**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (2.5 mg, 2 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol), allyl alcohol (**7**) (16.26 mg, 0.28 mmol), and water (0.15 mL). The reaction mixture was stirred for 48 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt 2:1), to give the title compound **17** as orange oil. Yield 51.5 mg (62%). All characterizations are consistent with those reported in literature.[42] NMR ^{1}H ($CDCl_3$), δ, ppm: 1.26 (3H, t, ^3J = 7.0 Hz, $-CH_3-$), 1.27

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(3H, t, ^3J = 7.0 Hz, −C$\underline{H}_3$), 2.29−2.37 (2H, m, −C$\underline{H}_2$−), 2.48 (1H, ddd, J_1 = 13.3, J_2 = 9.6, J_3 = 3.7 Hz, −C$\underline{H}$−), 3.72 (1H, dd, $^3J_1$ = 9.5, $^3J_2$ = 5.0 Hz, −C$\underline{H}$Br−), 3.74−3.84 (2H, m, −C$\underline{H}_2$−), and 4.11−4.27 (4H, m, −C$\underline{H}_2$CH$_3$). NMR ^{13}C (CDCl$_3$), δ, ppm: 13.96, 14.00, 33.6, 50.0, 55.4, 61.8, 61.9, 66.9, 168.6, and 169.0.

*Diethyl 2-(2-Bromo-3-hydroxy-3-methylbutyl)malonate (**18**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (2.5 mg, 2 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol), 2-methyl-3-buten-2-ol (**8**) (24.12 mg, 0.28 mmol), and water (0.15 mL). The reaction mixture was stirred for 72 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt 3:1), to give the title compound **18** as orange oil. Yield 51 mg (56%). NMR ^{1}H (CDCl$_3$), δ, ppm: 1.26 (6H, q, ^3J = 7.0 Hz, −CH$_2$C$\underline{H}_3$), 1.35 (3H, s, broad, −C$\underline{H}_3$), 1.37 (3H, s, broad, −C$\underline{H}_3$), 2.13 (1H, s, broad, −O$\underline{H}$), 2.18 (1H, ddd, J_1 = 15.0, J_2 = 11.9, J_3 = 3.4 Hz, −C$\underline{H}_2$−), 2.58 (1H, ddd, J_1 = 13.3, J_2 = 11.2, J_3 = 2.0 Hz, −C$\underline{H}_2$−), 3.76 (1H, dd, $^3J_1$ = 11.2, $^3J_2$ = 3.3 Hz, −C$\underline{H}$−), 4.03 (1H, dd, $^3J_1$ = 11.8, $^3J_2$ = 2.0 Hz, −C$\underline{H}$Br−), and 4.14−4.28 (4H, m, −C$\underline{H}_2$CH$_3$). NMR ^{13}C (CDCl$_3$), δ, ppm: 14.00, 14.05, 25.8, 26.9, 33.3, 50.9, 61.7, 61.8, 67.3, 72.4, 168.7, and 168.9.

*Diethyl 2-(2-Bromo-5-hydroxy-3-methylpentyl)malonate (**19**) and Diethyl [(3-Methyltetrahydrofuran-2-yl)methyl]-malonate (**19a**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1b** (2.5 mg, 2 mol %), sodium ascorbate (19.02 mg, 0.096 mmol), LiBr (47.76 mg, 0.55 mmol), AcCN (0.45 mL), diethyl bromomalonate (131.48 mg, 0.55 mmol), 3-methylpent-4-en-1-ol (**9**) (27.44 mg, 0.274 mmol), and water (0.15 mL). The reaction mixture was stirred for 48 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt 2:1), to give the mixture of the title compounds **19** and **19a** as pink oil. Yield 43 mg (46%). NMR ^{1}H (CDCl$_3$), δ, ppm (mixture of **19** and **19a**): 0.98−1.08 (3H, m, −C$\underline{H}_3$), 1.22−1.29 (6H, m, −CH$_2$C$\underline{H}_3$), 1.46−1.61 (1H, m, −C$\underline{H}_2$−), 1.69−2.10 (2H, m, −C$\underline{H}_2$−), 2.18−2.44 (2H, m, −C$\underline{H}_2$−, −C$\underline{H}$−), 2.98−3.08 (1H, m, broad, −O$\underline{H}$), 3.62−3.85 (3H, m, −C$\underline{H}_2$−, −C$\underline{H}$−), 4.03−4.13 (1H, m, −C$\underline{H}$Br−), and 4.13−4.28 (4H, m, −C$\underline{H}_2$CH$_3$). NMR ^{13}C (CDCl$_3$), δ, ppm: 13.97, 14.01, 15.0, 17.0, 34.4, 35.70, 35.76, 35.83, 36.8, 38.0, 50.56, 50.59, 60.1, 60.5, 61.31, 61.34, 61.63, 61.70, 168.8, 168.9, 168.97, and 168.99.

*Diethyl 2-(2-Bromo-3-hydroxy-2-methylpropyl)malonate (**20**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (2.5 mg, 2 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol), β-methallyl alcohol (**10**) (20.20 mg, 0.28 mmol), and water (0.15 mL). The reaction mixture was stirred for 48 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt 3:1), to give the title compound **20** as orange oil. Yield 71.5 mg (82%). NMR ^{1}H (CDCl$_3$), δ, ppm: 1.21−1.30 (6H, m, −CH$_2$C$\underline{H}_3$) 1.72 (3H, s, broad, −C$\underline{H}_3$), 2.35 (1H, dd, $^3J_1$ = 15.6, $^3J_2$ = 4.9 Hz, −C$\underline{H}_2$−), 2.61 (1H, dd, $^3J_1$ = 15.6, $^3J_2$ = 7.0 Hz, −C$\underline{H}_2$−), 2.72−2.81 (1H, m, broad, −O$\underline{H}$), 3.51−3.61 (2H, m, −C$\underline{H}_2$−), 3.72 (1H, dd, $^3J_1$ = 6.9, $^3J_2$ = 4.9 Hz, −C$\underline{H}$−), and 4.13−4.27 (4H, m, −C$\underline{H}_2$CH$_3$). NMR ^{13}C (CDCl$_3$), δ, ppm: 13.9, 14.0, 28.7, 39.3, 49.8, 61.9, 62.1, 70.5, 70.6, 169.3, and 170.1.

*Diethyl 2-(2-Bromocyclohexyl)malonate (**21**).* In accordance with the General Procedure, the reaction was performed using photocatalyst **1a** (2.5 mg, 2 mol %), sodium ascorbate (19.41 mg, 0.098 mmol), LiBr (48.63 mg, 0.56 mmol), AcCN (0.45 mL), diethyl bromomalonate (134 mg, 0.56 mmol), cyclohexene (**11**) (23 mg, 0.28 mmol), and water (0.15 mL). The reaction mixture was stirred for 48 h. The residue was purified by column chromatography (silica gel, hexanes/AcOEt, gradient from 5:1 to 10:1), to give the title compound **15** as yellow oil. Yield 9 mg (10%). All characterizations are consistent with those reported in literature.[38] NMR ^{1}H (CDCl$_3$), δ, ppm (mixture of *cis*- and *trans*-isomers): 1.23−1.30 (6H, m, −CH$_2$C$\underline{H}_3$), 1.30−1.58 (4H, m, −C$\underline{H}_2$−), 1.69−2.01 (3H, m, −C$\underline{H}_2$−, −C$\underline{H}$−), 2.10−2.44 (2H, m, −C$\underline{H}_2$−), 3.47 (1H, d, ^3J = 10.8 Hz, −C$\underline{H}$−), 4.14−4.25 (4H, m, −C$\underline{H}_2$CH$_3$), 4.70−4.75 (1H, m, -C$\underline{H}$Br-). NMR ^{13}C (CDCl$_3$), δ, ppm (mixture of *cis*- and *trans*-isomers): 14.05, 14.08, 14.13, 20.2, 24.7, 25.3, 25.4, 27.2, 28.5, 34.8, 38.8, 42.0, 46.3, 54.3, 56.4, 57.4, 58.4, 61.1, 61.4, 61.50, 61.53, 167.9, 168.1, 168.4, and 169.1.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04724.

Experimental details and spectral characterizations of the catalysts and obtained compounds; optical properties of the dyads **1** and **2**; and photocatalytic ATRA reaction: controls/optimization (PDF)

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Notes

The authors declare no competing financial interest.

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