Functional Group-Directed Photochemical Reactions of Aromatic Alcohols, Amines, and Thiols Triggered by Excited-State Hydrogen Detachment: Additive-free Oligomerization, Disulfidation, and C(sp²)–H Carboxylation with CO₂

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of great interest in the field of synthetic chemistry. Although excited-state hydrogen detachment (ESHD) represents a promising prospective template for additive-free photochemical reactions, applications of ESHD in a synthetic context remains scarce. Herein, we demonstrate the expansion of this photochemical reaction toward oligomerization, disulfidation, and regioselective $C(sp^2)$ -H carboxylation of aromatic alcohols, thiols, and amines. In the absence of any radical initiators in tetrahydrofuran upon irradiation with UV light ($\lambda = 280$ or 300 nm) under an atmosphere of N₂ or CO₂, thiols and catechol afforded disulfides and oligomers, respectively, as main products. Especially, the photochemical disulfidation proceeded highly selectively with the



NMR and quantum yields of up to 69 and 0.46%, respectively. In stark contrast, the photolysis of phenylenediamines and aminophenols results in photocarboxylation in the presence of CO_2 (1 atm). *p*-Aminophenol was quantitatively carboxylated by photolysis for 17 h with a quantum yield of 0.45%. Furthermore, the photocarboxylation of phenylenediamines and aminophenols proceeds in a highly selective fashion on the aromatic $C(sp^2)$ -H bond next to a functional group, which is directed by the site-selective ESHD of the functional groups for the formation of aminyl and hydroxyl radicals.

INTRODUCTION

Molecular conversion by using light energy represents a major challenge in the context of energy- and atom-economic chemical synthesis.^{1,2} For instance, the conversion of the attractive C1 feedstock carbon dioxide (CO₂) into benzoic acid derivatives^{3–5} and carbonate,^{6,7} which are important precursors for the synthesis of pharmaceuticals so far, relies on the reaction between CO₂ and activated aryl halides^{8,9} or alkali phenoxide (Kolbe–Schmitt reaction).¹⁰ However, these reactions generally require high temperatures and/or pressure, as well as strong bases and suffer from the inevitable production of waste.^{8–10}

In 1975, Tazuke and Ozawa reported the first photochemical carboxylation of aromatics using CO₂ at room temperature.¹¹ In this reaction, the photoreduction of phenanthrene by amines under irradiation with UV light (λ = 365 nm) induces the addition of CO₂ to phenanthrene to generate 9,10-dehydrophenanthrene-9-carboxylic acid. Since the discovery of redox photocatalysis,² several light-driven CO₂-fixation reactions onto carboxylic acid derivatives have been reported.^{12–19} The previously reported photochemical carboxylation reactions can be classified into four types: (a) addition reactions of CO₂ onto double or triple C–C bonds, exemplified by Tazuke's report (Scheme 1a),^{11,20–27} (b) carboxylation of alkenes in the presence of a photosensitizer (Scheme 1b),^{28,29} (c) carboxylation of C–X (X = halogen or OTf) bonds (Scheme 1c),^{30–34} and (d) direct C(sp³)–H activation with CO₂ (Scheme 1d).^{35–38} Although direct C–H activation is a more atom- and step-economic approach than C–X activation,¹² the direct photocarboxylation of aromatic C(sp²)–H bonds has not been reported yet to the best of our knowledge. In addition, precious metal-based catalysts, sacrificial reagents, and/or preactivated substrates are necessary for most of the aforementioned photochemical carboxylation reactions using CO₂.^{11,19–38} Hence, further exploring

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Scheme 1. (a-d) Previously Reported and (e) Present Photochemical Carboxylation Using CO2



Scheme 2. Plausible Mechanism for the Photoinduced Direct Carboxylation via the ESHD of o-Phenylenediamine (opda)⁴⁹



potential photochemical reactions is strongly desirable, especially with a view to their versatile synthetic application.

The excited-state hydrogen detachment (ESHD) of simple aromatics represents a promising prospective process for the photochemical activation of E-H bonds (E = O, S, and N).^{39,40} Specific E–H bonds of aromatic alcohols,^{41–43} thiols,^{41,44,45} and amines^{46–48} have been reported to dissociate via $\pi - \pi^*$ excitation, followed by internal conversion to the $\pi - \sigma^*$ state at the conical intersection, which results in formation of radical species such as the hydrogen radical. If the generated radical species could be employed for the formation of new bonds, radical initiator-free photochemical synthetic routes would be accessible. Although the ESHD processes themselves have widely been studied by means of spectroscopies and theoretical calculations in the gas phase³⁹ and even in solution,⁴⁰ the number of examples where such ESHD processes of these aromatic compounds have been applied for synthetic purposes in solution at room temperature remains scarce.

We have recently reported that the photochemical aromatic $C(sp^2)$ -H carboxylation of *o*-phenylenediamine (opda) under atmospheric pressure of CO₂ in tetrahydrofuran (THF) affords the corresponding carboxylic acid, for example, 2,3-diaminobenzoic acid (Scheme 1e).⁴⁹ In the presence of Fe(II), synthetic and quantum yield values of 58 and 0.47%, respectively, were obtained, while 28 and 0.22% were observed for opda alone. The proposed reaction mechanism of the photocarboxylation in the present study is different from that of the aforementioned photochemical reactions (Scheme 1ad): a hydrogen radical-trapping experiment for opda strongly suggested that the ESHD from an amino N-H bond initiates the carboxylation of aromatic C-H bonds *via* the migration of the radical in the aminyl radical species (Scheme 2).⁴⁹ It should be noted here that this direct photocarboxylation does not require any potentially reactive sacrificial reagents, preactivated substrates, or strong bases (Scheme 1e). Although the concept of photochemical reactions based on ESHD can be expected to expand the scope with regard to synthetic chemistry by utilizing light energy, the photochemical reactivity has so far been documented only for carboxylation of phenylenediamines.⁴⁹ Against this background, we have unveiled the photochemical reactivity of other organic substrates (Figure 1), with the aim to develop diverse applications for ESHD in photochemical synthesis.

Herein, we report substituent effects of aromatic compounds with hydroxyl, amino, and thiol groups, including monosubstituted (aniline, phenol, and thiophenol) and disubstituted aromatics, such as catechol (o-bdH₂), resorcinol (m-bdH₂), hydroquinone (p-bdH₂), o-aminothiophenol (atpH₂), oaminophenol (o-apH₂), m-aminophenol (m-apH₂), and paminophenol (p-apH₂), on their photoreactivity in the presence of CO₂. The present study highlights the distinctly unique reactivity of these compounds, that is, their reactivity depends on the number, position, and combination of substituents. Specifically, these compounds engage not only in carboxylation (Scheme 1e) but also in oligomerization and



Figure 1. Aromatic compounds with hydroxyl, amino, and thiol groups used in this study.

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disulfidation. Spectroscopic analyses of the photoreactions coupled with theoretical calculations have provided guidelines for the selective photochemical carboxylation with CO_2 and disulfidation.

RESULTS AND DISCUSSION

Photophysical Properties of Substituted Aromatic Compounds under N₂ and CO₂. Figures 2 and S1 show the UV-vis absorption spectra of aniline, phenol, thiophenol, opda, o-bdH₂, atpH₂, o-apH₂, m-apH₂, and p-apH₂ under an atmosphere of CO2 or N2. All compounds exhibited two characteristic absorption bands between 200 and 400 nm, and peaks in the visible region were not observed. The absorption spectra are consistent, regardless of the atmospheres $(CO_2 \text{ or}$ N_2), which suggests negligible interactions between the substrates and CO₂ in the ground state. Density functional theory (DFT) calculations were carried out to assign the observed absorption bands, which indicated that the HOMO, LUMO, and LUMO+1 exhibit a π character that arises from the aromatic rings including heteroatomic substituents, whereas the LUMO+2 is located around the E-H (E = N, O, and S) σ -bond(s) for all compounds (Figure S2). Accordingly, the experimentally observed absorption bands shown in Figures 2 and S1 were attributed to two distinct $\pi - \pi^*$ transitions.

The wavelengths of the absorption maxima of the two $\pi - \pi^*$ absorption bands vary depending on the types and positions of the substituents (Table S1). The spectra of the monosubstituted compounds phenol and thiophenol exhibit similar absorption maxima, while the absorption maximum of aniline is bathochromically shifted approximately by 20 nm. The aminophenols exhibit absorption maxima that are shifted by 16-39 nm bathochromically relative to that of phenol, whereas the shift in the case of o-bdH₂ relative to phenol was much smaller (5 nm). A similar trend was observed for thiophenol and aminothiophenol. These results suggest that the amino group tends to red-shift the $\pi - \pi^*$ absorption. The absorption maxima of o- and m-apH₂ (~292 nm) are shifted by ca. 20 nm hypsochromically to that of p-apH₂. A similar trend has been observed for the regioisomers of phenylenediamine⁴⁹ and ascribed to the degree of solvent effects, which is different for each regioisomer.⁵⁰ The observed shifts in the experimental absorption bands are comparable to the calculated energy gaps



Figure 2. UV–vis spectra of THF solutions (6.0 mM) of aniline (light blue), phenol (light green), thiophenol (orange), opda (blue), *o*-bdH₂ (green), atpH₂ (brown), *o*-apH₂ (red), *m*-apH₂ (black), and *p*-apH₂ (purple) immediately after preparation of each solution under CO₂ at room temperature.

for the $\pi-\pi^*$ transitions (HOMO–LUMO and HOMO– LUMO+1; Figure S2 and Table S2). Importantly, the lowest $\pi-\pi^*$ transitions are found between 270 and 315 nm for all compounds used in this study, which showed luminescence upon $\pi-\pi^*$ excitation, albeit that the luminescence intensities were relatively low for phenol and thiophenol (Figure S3). Hence, the photoirradiation at 280 or 300 nm used in the following experiments is able to induce $\pi-\pi^*$ transitions of the aromatic compounds.

Photochemical Reactivity of Monosubstituted Aromatic Compounds under N₂ and CO₂. Initially, we attempted the photochemical reactions of monosubstituted aromatic compounds with amino, hydroxyl, and thiol groups. According to our previous report,⁴⁹ aniline showed hardly any reactivity after photoirradiation at $\lambda_{ex} = 300 \pm 10$ nm for 8 h under N₂ or CO₂, and the starting materials were recovered in 98 and 96%, respectively (Figure S4 and run 1 in Table 1). On the other hand, the $\pi - \pi^*$ absorption band of phenol broadened after photoirradiation ($\lambda_{ex} = 280 \pm 10$ nm) under both N₂ and CO₂ (Figure S5a). The ¹H NMR spectrum after photoirradiation revealed phenol as the major species together with multiple signals in the high-magnetic field region, regardless of the presence of CO_2 (Figure S5b-d). Although 72% of the introduced phenol was consumed, which was estimated based on the integral ratio of ¹H NMR signals using dimethyl sulfoxide (DMSO) as an internal standard, the ¹H NMR signals of the products were relatively low, indicating an unselective formation of multiple products. In fact, an electrospray ionization (ESI) mass spectrum of the solution after photoirradiation for 8 h under N₂ showed multiple signals that were attributed to oligomeric phenol-based products (Figure S5e). Although the mass spectrum of the products under CO₂ showed the parent peak at m/z 137 and 275, which is consistent with [phenol + CO_2-H^+]⁻ and [2 phenol + 2 $CO_2 - H^+$]⁻, respectively (Figure S5f), these species were not prominent in the ¹H NMR spectrum (Figure S5d). Based on these results, we concluded that phenol is photoreactive but gives trace amounts of CO₂ adducts and oligomers (run 2 in Table 1).

In the case of thiophenol, a new strong absorption band emerged in the UV region after photoirradiation ($\lambda_{ex} = 280 \pm$ 10 nm) for 8 h, regardless of the atmosphere (Figure 3a). The ¹H NMR spectrum of the photochemical products under N₂ atmosphere showed that the main signals were assignable to diphenyl disulfide (DPD) (Figure 3b-d). The ¹H NMR yield and quantum yield (Φ) of DPD were estimated to be 52 and 0.37%, respectively, based on the amount of thiophenol used (run 3 in Table 1). The photochemical coupling of thiols to afford a disulfide has already been reported, albeit that a photocatalyst that acts as a photochemical radical initiator is required.⁵¹⁻⁵⁵ To the best of our knowledge, this is the first example of a direct photochemical disulfidation of thiophenol in the absence of any additives. In the presence of CO_{2} , the same photoreactivity was observed as under N₂ (Figures 3a and S6), indicating that thiophenol selectively engages in disulfidation rather than reacting with CO₂ upon photoirradiation.

As mentioned above, the monosubstituted aromatic compounds showed distinct photoreactions upon $\pi - \pi^*$ excitation in THF, depending on the functional groups (runs 1–3 in Table 1). According to previous studies on the ESHD of these aromatic compounds, the homolytic cleavage of the E–H bonds (E = N, O, or S) of these compounds *via* $\pi - \pi^*$

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Table 1. Photochemical Products of Substituted Aromatics under CO₂

Run	Substrate	λ_{\max} (nm)	$\lambda_{\mathrm{ex}} (\mathrm{nm})$	Major Product	Yield (%) ^a	$arPsi(\%)^b$
10	NH ₂	291	300 ± 10	N. D. ^{<i>d</i>}	_	_
2	ОН	273	280 ± 10	CO ₂ adducts, oligomers, etc.	traces	traces
3	SH	274	280 ± 10	S's	52	0.37
4 ^{<i>c</i>}	NH ₂ NH ₂	298	300 ± 10	CO ₂ H NH ₂ NH ₂	28	0.22
5	ОН	278	280 ± 10	oligomers	trace	trace
6	OH OH	276	280 ± 10	oligomers	trace	trace
7	но	296	300 ± 10	oligomers	trace	trace
8	SH NH ₂	302	300 ± 10	H ₂ N S NH ₂	69	0.46
9	OH NH ₂	292	300 ± 10	CO ₂ H OH NH ₂	25	0.34
10	H ₂ N OH	312	300 ± 10	H ₂ N CO ₂ H OH	34	0.45
11	NH ₂ OH	289	300 ± 10	N. D. ^{<i>d</i>}	_	_

^{*a*1}H NMR yield (%). ^{*b*}External quantum yield (%). ^{*c*}Reference 49. ^{*d*}N.D. = not detected.

excitation and subsequent π^*/σ^* internal conversion at a conical intersection is possible even in solution.⁴⁰ Hence, the ESHD efficiency should be one of the determining factors for the photochemical reactivity of these aromatic compounds. It has been reported that phenol^{41,43} and thiophenol^{41,44} show E–H bond cleavage, whereas the $\pi-\pi^*$ excitation of aniline does not induce N–H bond cleavage in the gas phase on account of the high activation energy in the π^*/σ^* conical intersection.⁴⁷ The lack of photoreactivity of aniline in THF (Figure S4 and run 1 in Table 1) is consistent with the aforementioned trend observed for the ESHD in the gas phase. Furthermore, a photochemically generated radical counterpart

after ESHD would delocalize over the E atom (E[•]) to the aromatic carbons (Ph[•]), as depicted in Scheme S1, which would promote oligomerization (E = O) and dimerization (E = S) *via* intermolecular E[•]/Ph[•] and E[•]/E[•] coupling, respectively. Whereas phenol furnished multiple products including oligomers and byproducts that could not be assigned, thiophenol engaged efficiently in disulfidation. These results can be, at least in part, rationalized in terms of the larger atomic radius of sulfur relative to oxygen and nitrogen, which leads to weak electronic interactions between the S 3p and the aromatic π orbitals, as reported by Ashfold *et al.*⁴¹ Consequently, a counterpart radical generated *via* ESHD



Figure 3. (a) UV-vis absorption spectra of thiophenol in THF (6.0 mM) before irradiation under N₂ (black dashed line) or CO₂ (blue) and after irradiation at $\lambda_{ex} = 280 \pm 10$ nm for 8 h under N₂ (green) or CO₂ (red) at room temperature (the black and blue lines overlap each other). ¹H NMR (CDCl₃, 400 MHz) spectra of thiophenol (b) before and (c) after the photoirradiation for 8 h and (d) commercial DPD at room temperature under a N₂ atmosphere. The symbols "#", "*", and "‡" indicate the signals from residual protons of H₂O, CHCl₃, and THF, respectively. The full ¹H NMR spectra are shown in Figure S6.

predominantly localizes on the E atom only in the case of thiophenol (E = S) but not in the case of aniline (E = NH) and phenol (E = O); the preferable coupling of thiyl radicals is also supported by the results of spin density calculations (Figure S7). Moreover, the S–S bond energy (264 kJ mol⁻¹) is higher than that of O–O (146 kJ mol⁻¹),⁵⁶ which makes the disulfide bond substantially more stable than the peroxide bond.

Photochemical Reactivity of Disubstituted Aromatic Compounds under N₂ and CO₂. In contrast to monosubstituted aromatics, that is, aniline, phenol, and thiophenol, which exhibit limited photoreactivity toward carboxylation, our previous study demonstrated the successful photocarboxylation of opda with CO₂ (run 4 in Table 1).⁴⁹ Furthermore, Pino *et al.* have reported that the introduced amino group in *o*-apH₂ drastically enhances the mixing of the π^*/σ^* excited states compared to phenol, leading to efficient ESHD.⁴⁸ These facts motivated us to investigate the effects of the presence of a second functional group in such aromatic compounds on their photoreactivity toward carboxylation.

In the case of *o*-bdH₂, which contains two hydroxy groups at the *o*-position relative to each other, photoirradiation ($\lambda_{ex} = 280 \pm 10 \text{ nm}$) for 8 h led to a slight decrease of the absorption band at 278 nm coupled with a growth of a broad absorption in the UV region under both N₂ and CO₂ (Figure S8a). In the ¹H NMR spectrum after photoirradiation under both N₂ and CO₂, several new signals were observed, which suggested the formation of multiple products, while *ca.* 30% of *o*-bdH₂ remained unreacted (Figure S8b-d). ESI mass spectra showed several peaks associated with *o*-bdH₂, oligomers, and THFincorporated compounds (Figure S8e-g). Considering that similar photoreactivity was observed both under both N₂ and CO₂ without any evidence for CO₂ incorporation, it seems feasible to conclude that *o*-bdH₂ does not react with CO₂ upon photoirradiation. Photolysis of the regioisomers (*m*-bdH₂ and *p*-bdH₂) also gave oligomers (Figures S9 and S10, runs 6 and 7 in Table 1). Although the reaction of *o*-bdH₂ with THF is characteristic, *o*-bdH₂ (run 5 in Table 1) shows a behavior that is essentially comparable to that of phenol (run 2), while it is distinctly different from that of opda,⁴⁹ which engages in photocarboxylation (run 4).

Disubstituted aromatics with two different substituents were also investigated with respect to their photoreactivity. In the case of $atpH_2$, we observed that the formation of disulfides is favorable even in the presence of CO₂ (Figure S11), similar to the case of thiophenol (Figure 3). The ¹H NMR yield and quantum yield (Φ) of bis-2-aminophenyl-disulfide were estimated to be 69 and 0.46%, respectively (run 8 in Table 1). As discussed for the photoreactivity of thiophenol, the relatively high S–S bond energy and localization of the radical on the sulfur atom likely causes the preferred formation of the S–S bond relative to the carboxylation, even in the presence of an amino group.

In contrast, o-apH₂ showed drastic changes of its absorption spectrum upon photoirradiation ($\lambda_{ex} = 300 \pm 10$ nm), when under a N₂ or CO₂ atmospheres (Figure 4a). As opposed to the initial absorption maximum at 292 nm, which is attributable to the $\pi - \pi^*$ transition, the photolysis of *o*-apH₂ induced a broadening of the $\pi - \pi^*$ absorption under N₂. Conversely, a new characteristic absorption band emerged at $\lambda_{\rm max}$ = 341 nm under a concomitant decrease of the original $\pi - \pi^*$ absorption at $\lambda_{max} = 292$ nm after photolysis in the presence of CO₂, which strongly suggests a progressing photochemical reaction that involves CO₂ fixation. The ¹H NMR spectrum of the photochemical product is substantially different from that of o-apH₂ (Figure 4b) but corresponds to that of 3-amino-2-hydroxybenzoic acid (3A2H) (Figure 4c,d). The carboxylation of o-apH₂ was further supported by the negative ESI mass signal of the product at m/z 152, which corresponds to $[o-apH_2 + CO_2 - H^+]^-$ (Figure 4e,f). The ¹H NMR yield and quantum yield (Φ) of 3A2H were calculated to be 25 and 0.34%, respectively (run 9 in Table 1). Conversely, the ¹H NMR signals assignable to other regioisomers, for example, 2-amino-3-hydroxybenzoic acid (2A3H) (Figure S13a), 3-amino-4-hydroxybenzoic acid (3A4H) (Figure S13b), or 4-amino-3-hydroxybenzoic acid (4A3H) (Figure S13c) were not obtained in detectable amounts. Hence, we can conclude that the photoirradiation of o-apH₂ under CO₂ leads to regioselective carboxylation of the $C(sp^2)$ -H bond that is ortho position-relative to the hydroxy group. Notably, the photocarboxylation reaction does not require any electron donors or bases; the photoreactivity of o-apH2 became negligible when the base TBAOH was added to the reaction solution (Figure S14). Therefore, the present photochemical reaction is characteristically distinct from previously reported conventional photocarboxylation reactions.^{11–38}

Effects of Functional Groups on the Selectivity of the Photocarboxylation. Notably, *o*-apH₂ shows photocarboxylation selectively on the aromatic carbon next to the hydroxy group (run 9 in Table 1), while an orthoselective carboxylation relative to the amino group occurs in opda,⁴⁹ indicating that



Figure 4. (a) UV–vis spectra of o-apH₂ in THF (6.0 mM) before irradiation under N₂ (black dashed line) or CO₂ (blue) and after irradiation at $\lambda_{ex} = 300 \pm 10$ nm for 8 h under N₂ (green) or CO₂ (red) at room temperature (the black and blue lines overlap each other). ¹H NMR (CD₃OD, 400 MHz) spectra of o-apH₂ (b) before and (c) after the photoirradiation for 8 h, and of (d) commercial 3A2H at room temperature under a CO₂ atmosphere. The symbols "#", "*", and "‡" indicate the signals from residual protons of H₂O, CD₂HOD, and THF. The full ¹H NMR spectra are shown in Figure S12. (e,f) Negative ESI-MS spectrum of the reaction solution of o-apH₂ (e) before and (f) after photoirradiation for 8 h under a CO₂ atmosphere.

ortho-hydroxycarboxylic acid and -aminocarboxylic acid moieties can be generated from o-apH₂ and opda, respectively. The origin of the selectivity of the photocarboxylation can be interpreted in terms of a functional group-directed ESHD. As described above, both opda⁴⁶ and o-apH₂⁴⁸ have been reported to engage in ESHD in the gas phase. According to their radical resonance structures, a radical generated by ESHD on the E atom (E[•]) can migrate to its ortho and para positions (Scheme S1). In the case of o-apH₂, a photodissociation of the O–H bond is necessary for the formation of 3A2H (Scheme 3), assuming that a radical reaction between CO₂ and a radical at the ortho position relative to the hydroxy group initiates the carboxylation. This hypothesis is supported by the fact that *o*-anisidine, which contains a methoxy instead of a hydroxy group, did not afford any carboxylation product because of the absence of an O-H bond (Figure S15). The calculated molecular orbitals of *o*-apH₂ in THF indicates that the lowest-lying σ^* excited state is localized at the O-H bond (Figure S2g), which is consistent with the DFT calculations on *o*-apH₂ reported by Pino *et al.*⁴⁸ Therefore, the O-H bond preferentially dissociates *via* $\pi - \pi^*$ photoexcitation, followed by π^*/σ^* conical intersection, leading to a selective carboxylation at the ortho position relative to the hydroxy group rather than that relative to the amino group.

Effects of the Substituent Positions of Aminophenols on the Photocarboxylation. As described above, amino substitution of phenol at the ortho position allows photocarboxylation, although the amino group does not function as the source of radicals, which strongly suggests that the amino group acts as a supporting moiety. Thus, we further investigated the photochemical reactivity of the two regioisomers, m- and p-apH₂. UV-vis absorption spectra (Figure 5a), together with ¹H NMR (Figure 5b-e) and ESI mass spectra (ESI-MS) (Figure 5f,g) spectroscopic studies on the photochemical products obtained from p-apH₂ revealed that the photocarboxylation proceeds selectively on the C-H bond next to the hydroxy group to form 5-amino-2hydroxybenzoic acid (5A2H), similar to the case of o-apH₂. The synthetic yield and Φ were 34 and 0.45%, respectively (run 10 in Table 1). Furthermore, the signals of the aromatic protons derived from p-apH2 were fully converted to 5A2H after 17 h of photoirradiation (Figure 5d). On the other hand, *m*-apH₂ did not show any significant changes in the UV-vis absorption and ¹H NMR spectra after photoirradiation under CO_2 (Figure S16), which demonstrates considerable inertness toward photochemical reactions (run 11 in Table 1).

The efficiency of the ESHD should be one of the main factors to determine the photoreactivity for the carboxylation. Using resonantly enhanced multiphoton ionization spectroscopy in the gas phase, Fujii and Dedonder-Lardeux et al. have demonstrated that *m*-fluorophenol exhibits an excited-state hydrogen transfer (ESHT) to ammonia that is slow compared to that of o- and p-fluorophenol.⁵⁷ In this previous report, the position of the fluorine substituent was proposed to affect the energy of the $\pi - \sigma^*$ state and thus the rate of the ESHT *via* the π^*/σ^* conical intersection. A similar explanation may also apply to the case of aminophenols; the activation energies from the optimum structure of the $S_1(\pi - \pi^*)$ state to the $S_1(\pi - \pi^*)/$ $(\pi - \sigma^*)$ conical intersection points are shown in Table 2. Both TDDFT and ab initio CASPT2 calculations clearly show that *m*-apH₂ requires a higher activation energy than *o*- and *p*-apH₂. These results suggest that the efficiency of the ESHD should be much lower for *m*-apH₂, which is commensurate with negligible activity for photocarboxylation.

The stability of the generated radical species should also be considered as another factor in the determination of the photocarboxylation reactivity. The radical resonance structures of *o*- and *p*-apH₂ include tertiary carbon radicals bound to the amino groups, while those of *m*-apH₂ do not (Scheme 4). As tertiary carbon radicals are known to be more stable than secondary carbon radicals,⁵⁸ radical intermediates of *o*- and *p*apH₂ may be more likely to react with CO₂.

Scheme 3. Photochemical Carboxylation of o-ApH₂ via an ESHD Processes Involving (a) O-H or (b) N-H Bond Dissociation



CONCLUSIONS

In this study, we investigated the substituent effects of hydroxyl, thiol, and amino groups on the photocarboxylation reactivity of aromatic compounds in the absence and presence of CO2. We found that the functional groups direct the selectivity of the photochemical reaction; phenols and thiophenols engage in oligomerization and disulfidation even in the absence of any radical initiator, whereas o-phenylenediamine (opda) and o-aminophenol (o-apH₂) engage in the direct photocarboxylation with CO2 in the absence of any additives. Because of the characteristic localization of the lowest-lying σ^* orbitals, it was possible to construct oaminobenzoic acid and o-hydroxybenzoic acid moieties from opda and o-apH₂, respectively. Moreover, we found that the position of the amino group also influences the photoreactivity of aminophenols and that $o-/p-apH_2$ are suitable for photocarboxylation reactions with CO₂, which is supported by the results of theoretical calculations. The photoirradiation of p apH_2 leads to a complete carboxylation within 17 h with a quantum yield (Φ) of 0.45% at room temperature, suggesting sufficient potential to serve in the photochemical synthesis of aromatic carboxylic acids.

The findings of the present study suggest promising potential of ESHD in synthetic applications, even in the absence of any additives such as radical initiators, bases, or reductants/oxidants. In particular, the activation of the aromatic C–H bond generally requires higher energy than that of aliphatic $C(sp^3)$ –H bonds, and consequently, aliphatic $C(sp^3)$ –H bonds are preferentially activated relative to aromatic $C(sp^2)$ –H bonds by conventional photochemical hydrogen atom transfer systems.^{59,60} On the other hand, the present study enables the selective carboxylation of aromatic $C(sp^2)$ –H bonds *via* the ESHD of E–H bonds (E = NH and O). This photochemical reaction based on ESHD can thus be expected to provide new options for the photochemical synthesis of useful aromatics with CO₂.

EXPERIMENTAL SECTION

General Procedures. All experimental operations were performed under an atmosphere of N₂ or CO₂ using standard Schlenk-line techniques. DMSO, phenol, o-apH₂, o-bdH₂, p-bdH₂, o-anisidine, and bis-2-aminophenyldisulfide were purchased from Wako Pure Chemical Industries (Japan). Thiophenol, atpH₂, m-apH₂, p-apH₂, DPD, 2amino-3-hydroxybenzoic acid (2A3H), 3-amino-2-hydroxybenzoic acid (3A2H), 4-amino-3-hydroxybenzoic acid (4A3H), and 5amino-2-hydroxybenzoic acid (5A2H) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan). Dehydrated THF, acetonitrile- d_3 (CD₃CN), methanol- d_4 (CD₃OD), and m-bdH₂ were purchased from Kanto Chemical Co. Inc. (Japan). Chloroform-d (CDCl₃) was purchased from Sigma-Aldrich. 3-Amino-4-hydroxybenzoic acid (3A4H) was purchased from Acros Organics (Belgium). THF was degassed by at least five freeze-pump–thaw cycles and sparging with N_2 or CO_2 gas for 20 min prior to use.

Physical Measurements. UV–vis absorption and emission spectra were recorded at room temperature on a Hitachi U-4100 and a Horiba FluoroMax-4 spectrophotometer, respectively. ¹H NMR spectra were measured on Varian 400 MHz and JEOL ECA-500 spectrometers (400 and 500 MHz). ESI-MS were recorded on a Shimadzu LCMS-2020 liquid chromatograph mass spectrometer.

Photochemical Reactions. Sample solutions were prepared under an atmosphere of N2 or CO2. Degassed THF solutions (6.0 $\times 10^{-3}$ M, 4.0 mL) of phenol, thiophenol, o-bdH₂, atpH₂, o-apH₂, mapH₂, or *p*-apH₂ were placed into a handmade quartz tube (headspace = 165 mL) equipped with a Schlenk flask, which was preliminarily filled with N2 or CO2 at ambient pressure by vacuum-refill cycles. The THF solutions were irradiated for 8 h using a Hg-Xe lamp (LC-8, Hamamatsu Photonics K.K.). The photoirradiation wavelength was fixed by using LX0280 (Asahi Spectra Inc., $\lambda = 280 \pm 10$ nm, half bandwidth: 10.8 nm) or LX0300 (Asahi Spectra Inc., $\lambda = 300 \pm 10$ nm, half bandwidth: 10.4 nm) band-pass filters. The light intensity, which was measured before each experiment using a power meter (Nova, Ophir Optronics Ltd.) and a thermopile sensor (3A, Ophir Optronics Ltd.), was set to 24.8-29.3 mW. During photoirradiation, H₂ generated in the headspace was collected using a gas-tight syringe (Tokyo Glass Kikai Co. Ltd) and analyzed on a gas chromatograph (GC-2014, Shimadzu) equipped with a thermal conductivity detector and molecular sieve 5A column (3.0 m) with Ar as the carrier gas (15.0 mL/min). The temperatures of column, injector, and detector were set to 70, 100, and 200 °C, respectively.

A portion of the reaction solution (0.3 mL) was transferred to a quartz cell (thickness: 1 mm) in order to measure the UV–vis absorption spectra for analysis of the products in solution after photoirradiation. The remaining solution (3.7 mL) was transferred to a Schlenk flask, where the volatiles were removed under reduced pressure. The thus-obtained residue was analyzed by ¹H NMR spectroscopy, whereby the chemical shifts were corrected using the employed solvent as an internal standard (CD₂HOD in CD₃OD: 3.31 ppm; CHCl₃ in CDCl₃: 7.26 ppm). The intensity of each peak was calibrated by integration of DMSO added to the solution (2.4 × 10⁻² M) to evaluate ¹H NMR yields.

The external quantum yield (Φ) for each product was calculated using eq 1

$$\Phi = N_{\rm products}/N_{\rm p} \tag{1}$$

where N_{products} refers to the amount of the products (mol), while N_{p} denominates the number of irradiated photons (Einstein).

Theoretical Calculations. Molecular orbitals and their energy for each compound were obtained from DFT calculations at the CAM-B3LYP/6-31G(d) level of using natural population analysis (NPA;⁶¹ solvent: THF). Solvent effects were taken into account *via* the polarizable continuum model (IEFPCM).⁶² A set of quantum chemical calculations at the time-dependent DFT (TDDFT) calculations at the TD-CAM-B3LYP⁶³/aug-cc-pVXZ (X = D, T) level of theory were performed to determine the differences in the photochemistry of *o*-, *p*-, and *m*-apH₂. Using the Tamm–Dancoff approximation, we performed geometry optimizations in order to



Figure 5. (a) UV–vis spectra of THF solutions of p-apH₂ (6.0 mM) before irradiation under N₂ (black) or CO₂ (blue) and after irradiation at $\lambda_{ex} = 300 \pm 10$ nm for 8 h under N₂ (green) or CO₂ (red) at room temperature. ¹H NMR (CD₃OD, 400 MHz) spectra of p-apH₂ (b) before and after the photoirradiation for (c) 8 h, (d) 17 h, and (e) commercial 5A2H at room temperature under a CO₂ atmosphere. The symbols "#", "*", "‡", and "+" indicate the signals from residual protons of H₂O, CD₂HOD, THF, and DMSO. The full ¹H NMR spectra are shown in Figure S17. (f,g) Negative ESI-MS spectrum of the reaction solution of p-apH₂ (f) before and (g) after photoirradiation for 8 h under a CO₂ atmosphere.

search for conical intersection points for each molecule. To confirm the accuracy of the TDDFT calculations, a set of single-point calculations at the CASPT2⁶⁴/aug-cc-pVDZ level of theory was also performed using the optimum structures obtained from the TDDFT calculations. All calculations were carried out using the Gaussian16,⁶⁵ GAMESS⁶⁶ and open OpenMOLCAS⁶⁷ quantum chemistry packages.

Table 2. Activation Energies^{*a*} for the ESHD in the $S_1(\pi - \pi^*)$ State of *o*-, *m*-, and *p*-ApH₂ (in kcal mol⁻¹)

theory	basis	o-apH ₂	m-apH ₂	p-apH ₂
CAM-B3LYP ^b	aug-cc-pVDZ	9.1	16.6	8.9
	aug-cc-pVTZ	8.5	15.6	7.7
CASPT2	aug-cc-pVDZ	7.2	13.8	7.9

^{*a*}Defined as the energy difference between the S₁ minimum and the S₁($\pi - \pi^*$)/($\pi - \sigma^*$) structures. ^{*b*}Tamm–Dancoff approximation was applied.

Scheme 4. Resonance Structures of Phenoxy Radicals Generated by ESHD Processes from (a) *o*-ApH₂, (b) *p*-ApH₂, and (c) *m*-ApH₂



ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02456.

Photophysical properties of all compounds; molecular orbitals, energy diagrams, spin densities, and optimized geometries obtained from DFT calculations; and UV–vis, ¹H NMR, and ESI-MS spectra under N_2 and CO_2 before and after photolysis (PDF)

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Notes

The authors declare no competing financial interest.

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