

### Article

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J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.0c00055 • Publication Date (Web): 15 Mar 2020 Downloaded from pubs.acs.org on March 16, 2020

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## Visible and UV-light-induced Decarboxylative Radical Reactions of Benzoic Acids Using Organic Photoredox Catalysts

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Supporting Information Placeholder

**ABSTRACT:** Photoinduced decarboxylative radical reactions of benzoic acids with electron-deficient alkenes, diborane, and acetonitrile under organic photoredox catalysis conditions and mild heating afforded adducts, arylboronate esters, and the reduction product, respectively. The reaction is thought to involve single-electron transfer promoted generation of aryl radicals via decarboxylation. A diverse range of benzoic acids were found to be suitable substrates for this photoreaction. Only our two-molecule organic photoredox system can work well for the direct photoinduced decarboxylation of benzoic acids.

### Introduction

Photoinduced decarboxylative radical reactions of carboxylic acids in the presence of a photoredox catalyst constitute a powerful and environment-friendly method for the synthesis of polymers<sup>1,2</sup> and complex organic molecules<sup>3-9</sup>. This strategy has several advantages: (1) carboxylic acids occur widely in nature in addition to being inexpensive and easy to store and handle; (2) decarboxylation releases only CO<sub>2</sub>, which is nonflammable, nontoxic, and easily removable from the reaction medium; (3) light is a traceless reagent, and (4) harsh reaction conditions such as high temperature and pressure are not required. However, the substrates used in this transformation are limited to aliphatic carboxylic acids, which generate alkyl radicals. Aryl radicals 2 are useful reactive intermediates in reactions that introduce aryl groups. However, benzoic acids cannot be employed as substrates for generating 2 because the rate ( $k = 10^6 \text{ s}^{-1}$ ) of decarboxylation of any carboxy radical 1 is lower than that  $(k = 10^9 \text{ s}^{-1})$  of the alkyl carboxy radical (Figure 1a).<sup>10</sup> Typically, the generation of **2** requires the use of stoichiometric amounts of toxic metals (Sn, Cu, Ag) and/or sensitive substrates such as aryl halides and aryl diazonium salts, as well as harsh reaction conditions such as high temperature.<sup>11,12</sup> In particular, diazonium salts are often explosive and highly toxic, and diazonium salts bearing sensitive substituents cannot be used as substrates for generating aryl radicals. Thus, one of the recent challenges in organic chemistry is decarboxylation of benzoic acids to generate aryl radicals under mild photoredox catalysis conditions.13-15

We have previously described photoinduced decarboxylative radical reactions of aliphatic carboxylic acids, which involves decarboxylation of the alkyl carboxy radicals produced under UV light irradiation in the presence of organic photoredox catalysts such as phenanthrene (Phen) and 1,4-dicyanobenzene (DCB) via photoinduced electron transfer (PET) (Figure 1b).<sup>16-22</sup> The process is initiated by PET from Phen to DCB, generating the radical cation of Phen, which oxidizes the alkyl carboxylate ions to form alkyl carboxy radicals. These alkyl carboxy radicals are smoothly decarboxylated to generate the corresponding alkyl radicals,

**Figure 1. a**.Decarboxylation of benzoic acids using a photoredox catalyst. **b**.Photoinduced decarboxylative radical reactions of carboxylic acids (previous work 1). **c**.Photoinduced deboronative radical addition of arylboronic acids to electron-deficient alkenes (previous work 2). **d**.Decarboxylative radical reactions with BP and DCN or DCA (this work).

a. Decarboxylation of benzoic acids with photoredox catalyst



which then react with a variety of radical acceptors to provide the respective products in high yields. However, our attempts toward the decarboxylation of benzoic acids to generate aryl radicals under the same photochemical conditions failed, and the benzoic acids were almost completely recovered. This finding encouraged us to screen suitable substrates for the generation of aryl radicals under similar organic photoredox catalysis conditions. We found that arylboronic acids are promising candidates for aryl radical precursors via photoinduced deboronation (Figure 1c).<sup>23</sup> A careful reinvestigation revealed that the photoinduced decarboxylative radical reactions of benzoic acids proceeded well when using a biphenyl (BP)/1,4-dicyanonaphthalene (DCN) or BP/9,10-dicyanoanthracene (DCA) system as the organic photoredox catalyst under UV and visible-light irradiation with mild heating (30 °C) (Figure 1d).

### **Results and Discussion**

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Initially, we attempted to optimize the reaction conditions by using benzoic acid 3a and acrylonitrile 4A with organic photoredox catalysts for the decarboxylation (Table 1). An aqueous acetonitrile solution (CH<sub>3</sub>CN/H<sub>2</sub>O = 9:1, v/v) containing 3a (20 mM), 4A (100 mM), Phen (10 mM, 50 mol%), DCB (10 mM, 50 mol%), and NaOH (20 mM) under an argon atmosphere for 3 h at room temperature was irradiated (100 W high-pressure mercury lamp with a Pyrex glass filter;  $\lambda > 280$  nm, organic photocatalysts such as Phen or DCN mainly absorb at 313 nm) to give no formation of adduct 5aA (entry 1). However, when the solution was heated to 60 °C, excitation occurred under the same photochemical conditions to give 5aA, albeit in a low yield (9%), along with some oligomeric materials (entry 2). The low rate of decarboxylation of 1 necessitates high-temperature conditions, which promoted radical polymerization. Fortunately, the use of BP and DCN as photocatalysts improved the yield of 5aA (20%, entry 3) even at room temperature, and heating at 30 °C gave the best yield of 5aA (69%, entry 4; photochemical conditions with UV irradiation are illustrated in Method I). A further increase in temperature accelerated the polymerization and decreased the vield of **5aA** (entries 5–7). The effect of the concentrations of **4A**. BP, and DCN as well as the type of solvent and base in the photoreaction of 3a (see Table S1 in SI) followed a similar trend in the photoreaction of phenylboronic acid,<sup>23</sup> wherein a phenyl radical is the reactive intermediate. The formation of 5aA in the photoreaction using BP and DCN in the presence of 3 equiv. of 2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO; 60 mM) under similar conditions was completely disturbed to give a complex mixture. Nonetheless, the corresponding TEMPO coupling product, as reported in our previous photoreaction of phenylboronic acid,23 was not isolated because it was unstable under the photochemical conditions using DCN.<sup>24</sup> These results suggested the generation of a phenyl radical from 3a via photoinduced decarboxylation for addition to alkene 4A. Competitive phenyl radical H-abstraction from CH<sub>3</sub>CN and addition to 4A occur during the photoreaction, thereby entailing a high concentration (100 mM) of alkene for the latter process. The use of a high alkene concentration makes oligomerization more efficient, and requires high concentrations of photocatalysts for preventing oligomerization.<sup>23</sup> In the absence of a base (NaOH), the photoreaction furnished 5aA in a decreased yield (entry 8, 42%). When using naphthalene (oxidation potential: +1.70 V vs. SCE in acetonitrile),<sup>25</sup> 1-methylnaphthalene (+1.43 V),<sup>25</sup> and Phen  $(+1.50 \text{ V})^{25}$  instead of BP  $(+1.95 \text{ V})^{26}$  as the photocatalyst, 5aA was not formed (entries 9-11), with almost 100% recovery of 3a. This result indicated that a high oxidation potential of the arene is required for the decarboxylation of 3a, although the oxidation potential of the benzoate ion is +1.40 V vs. SCE in acetonitrile.<sup>27</sup> In the absence of BP, the photoinduced decarboxylation of 3a did not proceed (entry 12). The reaction of 3a (5 mM) with NaOH (5

mM) and 5 equiv. of **4A** (25 mM) with BP (2 mM, 40 mol%) and DCA (2 mM, 40 mol%) for 3 h at 30 °C under irradiation by a blue LED (405 nm, 18 W) also afforded **5aA** in a decreased yield (42%, entry 13; the photochemical conditions under visible-light irradiation are illustrated in **Method II**). The low yield of **5aA** was attributed to the low solubility of DCA in the aqueous acetonitrile solution, but the visible light-induced decarboxylation of **3a** using BP and DCA was successful. Similar photoreactions with typical visible light-induced redox catalysts such as Ir(ppy)<sub>3</sub>, Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)<sup>+</sup>, and Fukuzumi catalyst<sup>5-6,8,28</sup> by **Method II** failed to provide **5aA** and **3a** was recovered almost completely (entries 14–16), although the Fukuzumi catalyst has a higher oxidation potential (+2.06 V)<sup>28</sup> than BP. Thus, only our two-molecule photoredox system is suited for the photoinduced decarboxylation of benzoic acid.

 Table 1. Photoinduced decarboxylative radical addition of 3a to

 4A.

3a	(20 m	CO <sub>2</sub> H PI + CN 4A (100 mM)	hv, 3 h hotocatalyst (10 m <u>NaOH (20 mM)</u> CH <sub>3</sub> CN/H <sub>2</sub> O = 9:	IM) 1	CN 5aA
_	Entry	Photocatalyst	Temperature/ºC	Yield of 5a	<b>A</b> /%
_	1	Phen, DCB	r.t.	0	
	2	Phen, DCB	60	9	
	3	BP, DCN	r.t.	20	
	4	BP, DCN	30	69	(Method I)
	5	BP, DCN	40	50	
	6	BP, DCN	50	35	
	7	BP, DCN	60	33	
	8 <sup>a</sup>	BP, DCN	30	42	
	9	Naphthalene, DCN	I 30	0	
	10	1-Methyl- naphthalene, DCN	30	0	
	11	Phen, DCN	30	0	
	12	DCN	30	0	
	13 <sup>b</sup>	BP, DCA	30	37	(Method II)
	14 <sup>b</sup>	lr(ppy) <sub>3</sub>	30	0	
	15 <sup>b</sup>	Ir[dF(CF <sub>3</sub> )ppy] <sub>2</sub> (dtbb	ру)+ 30	0	
-	16 <sup>b</sup>	Fukuzumi catalyst	30	0	

<sup>a</sup>In the absence of NaOH. <sup>b</sup>Photoreaction of **3a** (5 mM), **4A** (25 mM), NaOH (5 mM), and photocatalyst (2 mM) was carried out under blue LED (405 nm, 18 W) irradiation for 3 h at 30  $^{\circ}$ C.

Next, the scope of benzoic acids and alkenes in the photoreaction was evaluated under the optimized conditions (Method I and II). The results are summarized in Table 2. Because of the poor solubility of substrates **3e**,**f**,**n**,**o** in the reaction medium, the ratio of water in the solvent had to be increased. The photoreactions of benzoic acids **3b-f** bearing alkyl groups proceeded efficiently to afford the corresponding adducts 5bA-fA in moderate yields. Benzoic acids with strongly electron-donating groups such as the (4-methoxybenzoic acid methoxy group and 2.4dimethoxybenzoic acid) were unfavorable for PET, and adducts 3 were not formed. However, the introduction of an appropriate protecting group such as acetyl or Boc onto the phenolic hydroxyl group of benzoic acids 3g,h facilitated PET-promoted decarboxylative radical addition to furnish 5gA,hA. Similar photoreactions of halogenated benzoic acids 3i-k provided the corresponding adducts 5iA-kA in moderate yields. Moreover, photoreactions of benzoic acids 31-n substituted with a paraelectron-withdrawing group (CN, CF<sub>3</sub>, and CO<sub>2</sub>CH<sub>3</sub>) gave slightly decreased yields because of the low rate of addition of the

electron-deficient aryl radicals to the electron-deficient alkene 4A. In addition, 4-phenylbenzoic acid **30** underwent the photoredox catalyzed reaction to generate the corresponding adduct **50A**. The use of 3 equiv. of low electron-deficient alkenes such as t-butyl acrylate 4B, acrylamide 4C, and phenyl vinyl sulfone 4D instead of 5 equiv. of 4A led to the formation of the corresponding adducts 5aB-aD along with oligomeric materials in low yields. Visible-light-induced reactions (Method II) of 3a,b,j,l with 4A,B furnished the corresponding adducts **5bA**, **jA**, **IA**, **aB**. In particular, the reaction of 31 gave 51A (44%) in improved yield after prolonged irradiation (6 h). The combined results showed that a wide variety of benzoic acids and alkenes can participate in C-C bond formation under UV and visible-light irradiation via photoinduced decarboxylation, and that the yields of the adducts depend on the electronic nature of the arene ring and alkene substituents.

**Table 2**. Scope of benzoic acid and alkene in the photoinduced decarboxylative radical addition.



<sup>a</sup>Yields of **5** in parentheses correspond to the reactions by **Method II**. <sup>b</sup>CH<sub>3</sub>CN/H<sub>2</sub>O = 8:2. <sup>c</sup>CH<sub>3</sub>CN/H<sub>2</sub>O = 17:3. <sup>d</sup>Irradiation time is 6 h.  $^{e}$ [**4**] = 60 mM. <sup>f</sup>[**4B**] = 15 mM.

To demonstrate the synthetic utility of the photoinduced decarboxylation of benzoic acids, borylation of benzoic acids with bis(pinacolato)diboron  $6^{29-31}$  under similar conditions was investigated, as the resulting arylboronate esters are frequently used in Suzuki–Miyaura coupling reactions.<sup>32</sup> The optimal conditions for the photoinduced borylation of **3a** with **6** were 3

equiv. of **6**, 1.5 equiv. of BP and DCN, without NaOH (Table S2 in SI). This is possibly because back electron transfer (BET) from the generated radical anion of DCN did not occur to decompose DCN during the borylation. The photoreactions of benzoic acids **3** bearing an electron-donating or electron-withdrawing substituent under UV irradiation and the optimized conditions provided arylboronate esters **7** in moderate yields (Table 3). Visible-light induced reaction of **1a** (2 mM) and **6** (6 mM) with BP (2 mM, 100 mol%) and DCA (2 mM, 100 mol%) also provided **7a** in a 38% yield. A similar trend in the substituent effect was observed for the photoreaction with **4**. A secondary photoreaction of halogenated arylboronate ester **7i** took place to decrease the yield of **7i**. Thus, commercially available benzoic acids are proven to be suitable precursors of synthetically useful arylboronate esters.



 Table 3. Photoinduced decarboxylative radical borylation of 3 with 6.

<sup>a</sup>Photoreaction of **3a** (2 mM) and **6** (6 mM) with BP (2 mM) and DCA (2 mM) was carried out under blue LED (405 nm, 18 W) for 3 h at 30 °C. <sup>b</sup>Irradiation time is 8 h. <sup>c</sup>CH<sub>3</sub>CN/H<sub>2</sub>O = 8:2. <sup>d</sup>CH<sub>3</sub>CN/H<sub>2</sub>O = 17:3.

To extend this methodology to other reactions and elucidate the reaction mechanism, photoinduced decarboxylative reduction and deuteration of **3** were carried out (Scheme 1). The photoreaction of **3f** in the presence of a catalytic amount of BP (5 mM) and DCN (5 mM) in CH<sub>3</sub>CN/H<sub>2</sub>O = 8:2 gave the reduction product **8** in 72% yield. The similar reaction of **3f** in CD<sub>3</sub>CN/H<sub>2</sub>O = 8:2 afforded the deuteration product *d*-**8** with approximately 91% *d*-content, as in the case of arylboronic acids.<sup>23</sup> These findings indicate that in the absence of an electron-deficient alkene and diboron, the aryl radical intermediate abstracts a hydrogen and deuteration products, respectively, and catalytic amounts of BP and DCN (25 mol%) is sufficient for the photoinduced decarboxylation of benzoic acids.

Scheme 1. Photoinduced decarboxylative reduction and deuteration of 3f.

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Additional information about the photoreaction mechanism was obtained by the fluorescence quenching. The fluorescence of DCN and DCA in the aqueous CH<sub>3</sub>CN solution (CH<sub>3</sub>CN/H<sub>2</sub>O = 9:1) excited at 310 and 400 nm were quenched by BP (Figures S2 and S4), 3a with 1 equiv. of NaOH (Figures S3 and S5), and 4methoxybenzoic acid with 1 equiv. of NaOH (Figure S6), respectively. The rate constants for fluorescence quenching (kg) of DCN by BP, 3a with NaOH, and 4-methoxybenzoic acid with NaOH were calculated as  $6.77 \times 10^9$ ,  $3.31 \times 10^9$ , and  $7.69 \times 10^9$  $M^{-1}$  s<sup>-1</sup>, respectively. The higher rate of fluorescence quenching by 4-methoxybenzoic acid with NaOH than that by BP indicates that PET between DCN and BP is prevented by 4methoxybenzoic acid with NaOH. Similarly, the rate constant of DCA by BP was calculated as  $4.55 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>; however, the interaction between the excited state of DCA and 3a with NaOH was not observed in these concentrations (Detailed method of the calculation is shown in Experimental Section).

Based on the abovementioned results and our previous report,<sup>23</sup> we suggest that the generation of aryl radicals 2 from benzoic acids 3 using organic photoredox catalysts via photoinduced decarboxylation leads to the radical reactions, as depicted in Figure 2. PET between BP and DCN or DCA under UV or visible-light irradiation affords the radical cation of BP and the radical anion of DCN or DCA. The radical cation of BP oxidizes the aryl carboxylate ion to generate aryl carboxy radical 1, which undergoes sequential decarboxylation upon heating to give 2. In addition, PET between the aryl carboxylate ion and the excited state of DCN generates the carboxy radical 1 and the radical anion of DCN, although PET between the aryl carboxylate ion and the excited state of DCA did not occur. As shown in entry 12 in Table 1, the photoreaction through the direct PET between the aryl carboxylate ion and DCN did not proceed, probably because BET between 1 and the radical anion of DCN was faster than the decarboxylation of 1. In the case of 4-methoxybenzoic acid, the similar PET between DCN and 4-methoxybenzoate ion took place, and the fast BET led to non-decarboxylation and the recovery of starting material. This means that products are primarily obtained through the formation of the BP/DCN or BP/DCA radical ion pair as shown in Figure 2. Photoinduced decarboxylation of benzoic acids using Ir and Fukuzumi photocatalysts was unsuccessful and the starting material was regenerated, probably because of the low rate of decarboxylation of 1 and the high rate of BET between 1 and the reductant part of Ir and Fukuzumi photocatalysts. In contrast, the low efficiency of BET in our two-molecule photoredox system led to the successful decarboxylation of 1. According to Glorius et al., the high rates of non-decarboxylative pathways, such as hydrogen abstraction of 1, disturb the photoinduced decarboxylation of benzoic acids.<sup>14</sup> However, we have suggested that the low rate of the BET to 1 is essential for a successful photoinduced decarboxylation. Addition of the resulting aryl radicals 2 to electron-deficient alkenes 4 gave the radical intermediates, and subsequent reduction via BET from the radical anion of DCN or DCA and protonation furnished adducts 5. In the presence of diboron 6, aryl radicals 2 attacked the

diboron to furnish the corresponding arylboronate esters 7. As mentioned, the absence of BET from the radical anion of DCN led to the decomposition of DCN; hence, 1.5 equiv. of DCN was required for the reaction. In the absence of radical acceptors, abstraction of the hydrogen and deuterium atom from CH<sub>3</sub>CN and CD<sub>3</sub>CN by 2 occurred to yield reduction and deuteration products 8 and cyanomethyl radical (•CH<sub>2</sub>CN). BET from the radical anion of DCN to the resulting cyanomethyl radical generated a cyanomethyl anion, followed by protonation to regenerate CH<sub>3</sub>CN, as previously reported by us.<sup>23,33</sup> Although the direct photoinduced decarboxylation of benzoic acids proceeded with catalytic amounts of BP and DCN, increasing the yield of adducts 5 and arylboronate esters 7 required higher concentrations of BP, DCN, DCA, alkene, and 6.

#### Conclusion

In conclusion, the direct photoinduced decarboxylation of benzoic acids using BP and DCN or DCA with slight heating was achieved. The resulting aryl radicals react with electron-deficient alkenes, diboron, and acetonitrile to furnish adducts, arylboronate esters, and the reduction product, respectively. Further investigation into improvement of product yields with visible light-irradiation using the modified organic photoredox catalyst is in progress.

Figure 2. Plausible mechanism underlying decarboxylative radical reactions of **3**.



#### **Experimental Section**

**General Information.** All reagents and solvents were used as received from commercial suppliers. IR spectra were recorded on an FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> containing tetramethylsilane as an internal standard, and were acquired on either a 300 or 500 MHz spectrometers. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were acquired on a 125 MHz spectrometer. High-resolution mass spectra were obtained using double-focusing magnetic sector mass spectrometer coupled with FAB. The UV-light source was a Riko UV-100HA high-pressure (100 W) mercury arc. Pyrex vessels (18 mm × 180 mm) in the water bath were directly attached to the light source ( $\lambda > 280$  nm, DCN mainly absorbs at 313 nm light; Figure S1a). The visible-light

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source was a 18 W blue LED (EvoluChem, P206-18-1 405 nm), and Pyrex vessels (10 mm  $\times$  120 mm) in the water bath were set at a distance of 10 cm from the LED (Figure S1b).

# General procedures for the photoreaction of benzoic acids 3 and acrylonitrile $4{\rm A}$

An aqueous CH<sub>3</sub>CN solution (CH<sub>3</sub>CN 36 mL, H<sub>2</sub>O 4 mL) of benzoic acids **3** (20 mM), NaOH (20 mM, 0.0320 g), BP (10 mM, 0.0616 g), and DCN (10 mM, 0.0712 g) in Pyrex vessels (18 mm x 180 mm) was purged with argon for 10 min, and acrylonitrile **4A** (100 mM, 0.264 mL) was added under argon atmosphere. The mixture was irradiated with 100 W high-pressure mercury lamp for 3 h at 30°C, and then the solvent was removed under reduced pressure. The crude product was purified by silica-gel column chromatography using hexane/EtOAc as the eluents to yield adducts **5**. Photoreactions of **3** (5 mM) and **4A** (25 mM, 0.100 mL) with visible light-irradiation (blue LED, 405 nm) using BP (2 mM, 0.0185 g) and DCA(2 mM, 0.0276 g) for 3 h at 30°C were also carried out similarly (CH<sub>3</sub>CN 54 mL, H<sub>2</sub>O 6 mL).

### General procedures for the photoreaction of benzoic acids 3 and bis(pinacolato)diboron 6 and the photoreaction of 3g without 4 and 6

An aqueous CH<sub>3</sub>CN solution (CH<sub>3</sub>CN 18 mL, H<sub>2</sub>O 2 mL) of benzoic acids **3** (20 mM), BP (30 mM, 0.0925 g), and DCN (30 mM, 0.107 g) in Pyrex vessels (18 mm x 180 mm) was purged with argon for 10 min, and bis(pinacolato)diboron **6** (60 mM, 0.305 g) was added under argon atmosphere. The mixture was irradiated with 100 W high-pressure mercury lamp for 6 h at 30°C, and then the solvent was removed under reduced pressure. The crude product was purified by silica-gel column chromatography using hexane/EtOAc as the eluents to yield adducts **7**. Similar photoreactions of **3f** (20 mM, 0.1041 g) using BP (5 mM, 0.0148 g) and DCN (5 mM, 0.0178 g) in CH<sub>3</sub>CN/H<sub>2</sub>O = 8:2 or CH<sub>3</sub>CN/D<sub>2</sub>O = 8:2 for 6 h at 30°C without **4** and **6** were carried out. Visible-light induced reaction of **3a** (2 mM, 0.0146 g) and **6** (6 mM, 0.0914 g) with BP (2 mM, 0.0185 g) and DCA (2 mM, 0.0273 g) was conducted similarly (CH<sub>3</sub>CN 54 mL, H<sub>2</sub>O 6 mL).

### Large scale photoreaction of 3a with 4A by UV irradiation

Similar large scale photoreaction of **3a** (20 mM, 0.488 g) with **4A** (100 mM, 1.321 mL) in the presence of NaOH (20 mM, 0.160 g), BP (10 mM, 0.3084 g), and DCN (10 mM, 0.3564 g) by high-pressure (100 W) mercury arc in an aqueous CH<sub>3</sub>CN solution (CH<sub>3</sub>CN 180 mL, H<sub>2</sub>O 20 mL) using ten Pyrex vessels (18 mm x 180 mm) was carried out to furnish **5aA** (0.351 g) in a 67 % yield.

# Fluorescence quenching of DCN and DCA by BP and 3a with NaOH

The fluorescence of DCN and DCA  $(1.0 \times 10^{-4}M)$  in the aqueous CH<sub>3</sub>CN solution (CH<sub>3</sub>CN/H<sub>2</sub>O = 9:1) excited at 310 and 400 nm were quenched by BP (Figure S2 and S4), **3a** with 1 equiv. of NaOH (Figure S3 and S5), and 4-methoxybenzoic acid with 1 equiv. of NaOH (Figure S6), respectively. The rate constants for fluorescence quenching (kq) of DCN and DCA by BP, **3a** with NaOH, and 4-methoxybenzoic acid with NaOH were calculated from the Stern–Volmer plot  $I_0/I = 1+kq\tau[Q]$ . ( $I_0$ : fluorescence intensity of DCN and DCA at 386 and 437 nm, I: observed fluorescence intensity of DCN and DCA at 386 and 437 nm with BP or **3a** with 1 equiv. of NaOH or 4-methoxybenzoic acid with 1 equiv. of NaOH,  $\tau = 10.1$  and 15.1 ns (fluorescence lifetime of DCN and DCA), [Q]: concentration of BP or **3a** with 1 equiv. of NaOH or 4-methoxybenzoic acid with 1 equiv. of NaOH or 4-

### Characterization data for 5, 7, and 8

Adducts 5 have been previously reported by  $us^{23}$  except 5dA,eA,fA,gA,hA,kA,nA.

*3-Phenylpropanenitrile* **5aA** (using hexane/EtOAc = 15:1 as the eluent), 0.07024 (UV-light) and 0.01480 (visible light) g, 69 and 37%, Colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.36–7.22 (m, 5H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  138.0, 128.9, 128.3, 127.2, 119.2, 31.6, 19.4.

3-(4-t-Butylphenyl)propanenitrile **5bA** (using hexane/EtOAc = 15:1 as the eluent), 0.09136 (UV-light) and 0.02111 (visible light) g, 61 and 38%, Colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.36 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 2.93 (t, J = 7.4 Hz, 2H), 2.60 (t, J = 7.4 Hz, 2H), 1.31 (s, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 150.1, 135.0, 128.0, 125.8, 119.3, 34.5, 31.3, 31.1, 19.3.

3-(4-Methylphenyl)propanenitrile **5cA** (using hexane/EtOAc = 15:1 as the eluent), 0.05013 g, 43%, Colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.14–7.10 (m, 4H), 2.92 (t, J = 7.4 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 2.33 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 136.9, 135.0, 129.5, 128.1, 119.2, 31.2, 21.1, 19.5.

3-(3,5-Dimethylphenyl)propanenitrile **5dA** (using hexane/EtOAc = 15:1 as the eluent), 0.06496 g, 51%, Colorless oil; IR (neat, cm<sup>-1</sup>) 2918, 2248; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  6.91 (s, 1H), 6.83 (s, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.30 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  138.5, 138.0, 128.8, 126.0, 119.3, 31.5, 21.3, 19.3; HRMS (FAB) calcd for (M+H)<sup>+</sup>C<sub>11</sub>H<sub>14</sub>N, 160.1126; found, 160.1110.

3-(4-Cyclohexylphenyl)propanenitrile **5eA** (using hexane/EtOAc = 30:1 as the eluent), 0.08940 g, 42%, Colorless oil; IR (neat, cm<sup>-1</sup>) 2969, 2249; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 7.21–7.12 (m, 4H), 2.92 (t, J = 7.4 Hz, 2H), 2.60 (t, J = 7.4 Hz, 2H), 2.52–2.44 (m, 1H), 1.87–1.73 (m, 5H), 1.47–1.21 (m, 5H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  147.1, 135.4, 128.2, 127.3, 119.3, 44.2, 34.4, 31.2, 26.9, 26.1, 19.4; HRMS (FAB) calcd for (M+H)<sup>+</sup> C<sub>15</sub>H<sub>20</sub>N, 214.1595; found, 214.1583.

3-[4-(4-Butylcyclohexyl)phenyl]propanenitrile 5fA (using hexane/EtOAc = 15:1 as the eluent), 0.09382 g, 44%, Colorless oil; IR (neat, cm<sup>-1</sup>) 2923, 2241; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.19–7.12 (m, 4H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.50–2.40 (m, 1H), 1.94–1.77 (m, 5H), 1.49–1.16 (m, 12H), 1.09–0.83 (m, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  146.9, 135.4, 128.2, 127.3, 119.3, 44.2, 37.3, 37.1, 34.3, 33.6, 31.2, 29.2, 23.0, 19.4, 14.2; HRMS (FAB) calcd for (M+H)<sup>+</sup> C<sub>19</sub>H<sub>28</sub>N, 270.2222; found, 270.2227.

3-(4-Acetoxyphenyl)propanenitrile **5gA** (using hexane/EtOAc = 15:1 to 10:1 as the eluent), 0.03413 g, 26%, Colorless oil; IR (neat, cm<sup>-1</sup>) 3039, 2251, 1759; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.24 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H), 2.95 (t, J = 7.5 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 2.29 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 169.5, 149.8, 135.6, 129.3, 122.0, 119.0, 31.0, 21.1, 19.3; HRMS (FAB) calcd for (M+H)<sup>+</sup> C<sub>11</sub>H<sub>12</sub>NO<sub>2</sub>, 190.0868; found, 190.0856.

3-(4-O-Boc-oxyphenyl)propanenitrile **5hA** (using hexane/EtOAc = 15:1 to 5:1 as the eluent), 0.09480 g, 48%, Colorless oil; IR (neat, cm<sup>-1</sup>) 2982, 2248, 1757; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.24 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 2.95 (t, J = 7.4 Hz, 2H), 2.60 (t, J = 7.4 Hz, 2H), 1.56 (s, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 151.8, 150.2, 135.5, 129.3, 121.8, 119.0,

83.7, 31.0, 27.7, 19.4; HRMS (FAB) calcd for  $(M+H)^+C_{14}H_{18}NO_3$ , 248.1287; found, 248.1280.

3-(4-Chlorophenyl)propanenitrile SiA, (using hexane/EtOAc = 15:1 to 10:1 as the eluent), 0.05864 g, 44%, Colorless oil, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.32 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 7.4 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  136.4, 133.2, 129.7, 129.1, 118.8, 30.9, 19.3.

*3-(4-Bromophenyl)propanenitrile* **5jA** (using hexane/EtOAc = 15:1 as the eluent), 0.08451 (UV-light) and 0.02871 (visible light) g, 48 and 45%, Colorless oil, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 7.4 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  136.9, 132.0, 130.0, 121.2, 118.8, 31.0, 19.2.

3-(2-Bromophenyl)propanenitrile **5kA** (using hexane/EtOAc = 15:1 as the eluent), 0.08469 g, 50%, Colorless oil, IR (neat, cm<sup>-1</sup>) 2947, 2246; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.57 (d, J = 7.9 Hz, 1H), 7.32–7.23 (m, 2H), 7.19–7.14 (m, 1H), 3.10 (t, J = 7.4 Hz, 2H), 2.69 (t, J = 7.4 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 137.2, 133.2, 130.8, 129.2, 128.0, 124.0, 118.8, 32.1, 17.6; HRMS (FAB) calcd for (M+H)<sup>+</sup> C<sub>9</sub>H<sub>9</sub>N<sup>79</sup>Br, 209.9919; found, 209.9916. (C<sub>9</sub>H<sub>9</sub>N<sup>81</sup>Br, 211.9898; found, 211.9911.)

3-(4-Cyanophenyl)propanenitrile **5IA** (using hexane/EtOAc = 15:1 to 5:1 as the eluent), 0.04730 (UV-light) and 0.02080 (visible light) g, 38 and 44%, White solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.65 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 2.67 (t, J = 7.4 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 143.2, 132.7, 129.2, 118.5, 118.3, 111.5, 31.5, 18.9.

 3-(4-Trifluoromethylphenyl)propanenitrile
 5mA
 (using hexane/EtOAc = 15:1 to 10:1 as the eluent), 0.06706 g, 34%, Colorless oil, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 2.66 (t, J = 7.4 Hz, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  141.9, 130.0 (q, J = 32 Hz), 128.7, 126.5, 125.9, 118.6, 31.3, 19.1.

*Methyl 4-(2-cyanoethyl)benzoate* **5nA** (using hexane/EtOAc = 15:1 to 5:1 as the eluent), 0.06801 g, 45%, White solid, mp 61 °C; IR (KBr, cm<sup>-1</sup>) 3014, 2242, 1716; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.02 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 3.91 (s, 3H), 3.01 (t, J = 7.4 Hz, 2H), 2.65 (t, J = 7.4 Hz, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  166.7, 143.1, 130.2, 129.3, 128.4, 118.7, 52.2, 31.5, 19.0; HRMS (FAB) calcd for (M+H)<sup>+</sup> C<sub>11</sub>H<sub>12</sub>NO<sub>2</sub>, 190.0868; found, 190.0856.

3-(4-Phenylphenyl)propanenitrile **50A** (using hexane/EtOAc = 15:1 to 10:1 as the eluent), 0.09214 g, 44%, White solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.59–7.30 (m, 9H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.66 (t, *J* = 7.4 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  140.6, 140.3, 137.0, 128.8, 128.7, 127.6, 127.4, 127.1, 119.1, 31.2, 19.4.

*t-Butyl 3-phenylpropanoate* **5aB** (using hexane/EtOAc = 30:1 to 8:1 as the eluent), 0.06390 (UV-light) and 0.00990 (visible light) g, 39 and 16%, Colorless oil, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.30–7.19 (m, 5H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.54 (t, *J* = 7.8 Hz, 2H), 1.42 (s, 9H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  172.3, 140.8, 128.4, 128.3, 126.1, 80.4, 37.1, 31.1, 28.1.

*3-Phenylpropanamide* **5aC** (using hexane/CHCl<sub>3</sub> = 3:1 to 0:1 as the eluent), 0.03000 g, 25%, White solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.32–7.18 (m, 5H), 2.97 (t, *J* = 7.7 Hz, 2H), 2.53 (t, *J* = 7.7 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  174.5, 140.7, 128.6, 128.3, 126.3, 37.5, 31.4.

[(2-Phenylethyl)sulfonyl]benzene **5aD** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.04488 g, 23%, Compound **5aD** has been previously reported.<sup>33</sup> Colorless oil, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.95 (d, J = 7.0 Hz, 2H), 7.70–7.56 (m, 3H), 7.29–7.20 (m, 3H), 7.11 (d, J = 6.8 Hz, 2H), 3.39–3.37 (m, 2H), 3.08–3.02 (m, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  139.0, 137.4, 133.8, 129.4, 128.8, 128.3, 128.1, 126.9, 57.5, 28.7.

*Phenylboronic acid pinacol ester* **7a** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.04381 (UV-light) and 0.00932 (visible light) g, 55 and 38%, Compound **7a** has been previously reported.<sup>35</sup> Colorless oil, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.81 (d, *J* = 6.6 Hz, 2H), 7.49–7.43 (m, 1H), 7.39–7.34 (m, 2H), 1.35 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  134.7, 131.3, 127.7, 83.8, 24.9.

4-t-Butylphenylboronic acid pinacol ester **7b** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.04524 g, 44%, Compound **7b** has been previously reported.<sup>36</sup> White solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.77 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 1.34–1.26 (m, 21H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ 154.5, 134.7, 124.7, 83.6, 34.9, 31.2, 24.8.

4-Methylphenylboronic acid pinacol ester **7c** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.04612 g, 53%, Compound **7c** has been previously reported.<sup>35</sup> Colorless oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.70 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 2.36 (s, 3H), 1.34 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  141.4, 134.8, 128.5, 83.6, 24.8, 21.7.

3,5-Dimethylphenylboronic acid pinacol ester **7d** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.04548 g, 49%, Compound **7d** has been previously reported.<sup>35</sup> White solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 (s, 2H), 7.10 (s, 1H), 2.32 (s, 6H), 1.34 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  137.3, 133.1, 132.5, 83.8, 24.9, 21.2.

4-Cyclohexylphenylboronic acid pinacol ester 7e, (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.05112 g, 45%, White solid; mp 91 °C; IR (KBr, cm<sup>-1</sup>) 2965, 2926, 1392, 1361; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.53–2.48 (m, 1H), 1.95–1.80 (m, 4H), 1.77–1.70 (m, 1H), 1.42–1.26 (m, 18H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  151.5, 134.9, 126.3, 83.6, 44.9, 34.2, 26.9, 26.1, 24.8; HRMS (FAB) calcd for (M+H)<sup>+</sup> C<sub>18</sub>H<sub>28</sub>BO<sub>2</sub>, 287.2183; found, 287.2174.

4-Acetoxyphenylboronic acid pinacol ester **7g** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.03796 g, 36%, Compound **7g** has been previously reported.<sup>37</sup> White solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.83 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 2.29 (s, 3H), 1.33 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.3, 153.2, 136.2, 121.0, 83.9, 24.8, 21.2.

4-Chlorophenylboronic acid pinacol ester 7i (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.01587 g, 17%, Compound 7i has been previously reported.<sup>34</sup> White solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.73 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 1.34 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>):  $\delta$  137.5, 136.1, 128.0, 84.0, 24.9.

4-Cyanophenylboronic acid pinacol ester **71** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.03461 g, 38%, Compound **71** has been previously reported.<sup>37</sup> White solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 1.35 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  135.1, 131.1, 118.9, 114.5, 84.5, 24.9.

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*4-Trifluoromethylphenylboronic acid pinacol ester* **7m** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.03769 g, 34%, Compound **7m** has been previously reported.<sup>38</sup> White solid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.91 (d, *J* = 7.9 Hz, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 1.36 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  135.0, 133.0 (q, *J* = 32 Hz), 124.3, 124.3, 84.3, 24.9.

4-Methoxycarbonylphenylboronic acid pinacol ester **7n** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.04505 g, 43%, Compound **7n** has been previously reported.<sup>36</sup> White solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.02 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 12H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  167.1, 134.6, 132.2, 128.5, 84.1, 52.1, 24.8.

4-Phenylphenylboronic acid pinacol ester **70** (using hexane/EtOAc = 30:1 to 10:1 as the eluent), 0.06279 g, 56%, Compound **70** has been previously reported.<sup>39</sup> White solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.89 (d, J = 8.0 Hz, 2H), 7.59–7.65 (m, 4H), 7.44 (m, 2H), 7.36 (m, 1H), 1.37 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  143.8, 141.0, 135.2, 128.7, 127.5, 127.20, 126.4, 83.8, 24.9.

(4-Butylcyclohexyl)benzene **8** (using hexane as the eluent), 0.06247 g, 72%, Colorless oil, IR (neat, cm<sup>-1</sup>) 2923, 2858; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD):  $\delta$  7.27–7.10 (m, 5H), 2.49–2.30 (m, 1H), 1.95–1.70 (m, 4H), 1.51–0.86 (14H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>3</sub>OD):  $\delta$  147.6, 128.0, 126.5, 125.5, 44.8, 37.3, 37.1, 34.3, 33.5, 29.1, 22.82, 13.2; HRMS (FAB) calcd for (M+H)<sup>+</sup> C<sub>16</sub>H<sub>25</sub>, 217.1957; found, 217.1938.

4-(4-Butylcyclohexyl)-1-d-benzene d-8 (using hexane as the eluent), 0.03985 g, 46%, Colorless oil, IR (neat, cm<sup>-1</sup>) 2924, 2852; <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD): δ 7.23–7.10 (m, 4H), 2.49–2.32 (m, 1H), 1.88–1.71 (m, 4H), 1.51–0.85 (m, 14H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>3</sub>OD): δ 147.6, 127.9, 126.4, 125.5, 44.8, 37.3, 37.0, 34.3, 33.5, 29.1, 22.8, 13.2; HRMS (FAB) calcd for (M+H)<sup>+</sup> C<sub>16</sub>H<sub>24</sub>D, 218.2019; found, 218.2003.

### ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publication website

Experimental procedures, and <sup>1</sup>H and <sup>13</sup>C $\{^{1}H\}$  NMR spectra (PDF).

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### Notes

The authors declare no competing financial interests.

### ACKNOWLEDGMENT

This work was supported by the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid no. 17K05779, for scientific research.

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