JOC The Journal of Organic Chemistry

pubs.acs.org/joc Article

Bimetallic Photoredox Catalysis: Visible Light-Promoted Aerobic Hydroxylation of Arylboronic Acids with a Dirhodium(II) Catalyst

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Cite This: J. Org. Chem. 2020, 85, 2040−2047 Read Online

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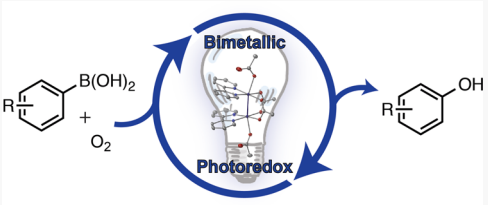
ABSTRACT: We report the use of a rhodium(II) dimer in visible light photoredox catalysis for the aerobic oxidation of arylboronic acids to phenols under mild conditions. Spectroscopic and computational studies indicate that the catalyst $Rh_2(bpy)_2(OAc)_4$ (**1**) undergoes metal−metal to ligand charge transfer upon visible light irradiation, which is responsible for catalytic activity. Further reactivity studies demonstrate that **1** is a general photoredox catalyst for diverse oxidation reactions.



INTRODUCTION

Photoredox catalysis has been a major focus for organic reaction method development in the past decade.[1] While organic catalysts in photoredox reactions have recently emerged as a promising strategy,[2] a majority of methods were established based on the archetypal ruthenium(II) catalyst $Ru(bpy)_3Cl_2$ and its various derivatives (bpy = 2,2′-bipyridine).[3] Among metal-catalyzed photoredox reactions, oxidation reactions that use molecular oxygen provide a mild and environmentally benign route for chemical synthesis.[4] Such reactions often proceed via generation of the superoxide radical anion in the photoredox cycle.[5]

Dirhodium(II) complexes have long been a privileged class of catalysts and are perhaps the most widely used bimetallic catalysts due to their well-known utility in nitrene and carbene transfer reactions.[6,7] Only recently, however, rhodium dimers have been studied for electron-transfer reactions in their excited states, an area of research pioneered by the Dunbar and Turro groups.[8] Inspired by this work, we envisioned that the reactivity of bimetallic rhodium(II) complexes could be expanded to include photoredox catalysis for organic synthesis. Here, we report the first examples of visible light-promoted aerobic oxidation reactions with a dirhodium catalyst. Our work suggests that dirhodium complexes are a promising and highly tunable platform for the development of new photoredox catalysts.

RESULTS AND DISCUSSION

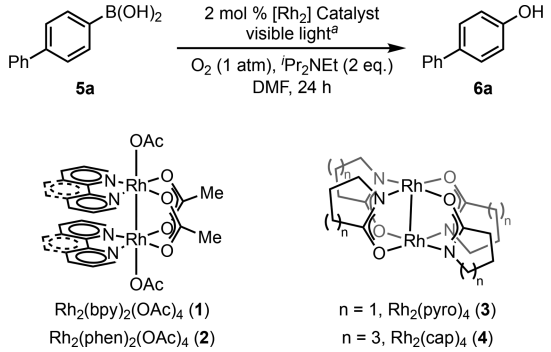
Our investigations began with the visible light-promoted aerobic hydroxylation of arylboronic acids, a transformation originally reported by Jørgenson and Xiao. using $Ru(bpy)_3Cl_2$ and subsequently by Scaiano et al. using methylene blue.[9] As polypyridyl ligands such as bpy are typically key features of photoredox catalysts, with low-lying π^* orbitals that create strong metal-to-ligand charge transfer (MLCT) bands in the visible region,[10] we targeted the complex $Rh_2(bpy)_2(OAc)_4$ (**1**).[11] As shown in Table 1, complex **1** is a highly effective catalyst for the aerobic hydroxylation reaction, along with the related 1,10-phenanthroline complex **2**. In comparison, dirhodium(II) complexes lacking polypyridyl ligands, such as lactamate complexes **3** and **4**, showed substantially reduced photoredox activity; carboxylate complexes $Rh_2(OAc)_4$ and $Rh_2(esp)_2$ were completely ineffective catalysts (entries 3−6).[12] Catalyst **1** can be conveniently generated in situ from a mixture of $Rh_2(OAc)_4$ and bpy (entry 7). The reaction can also proceed in an open flask under air, albeit in a reduced yield as compared to using an O_2 balloon (entry 8). Control experiments clearly establish that both O_2 and light are required for this transformation (entries 9 and 10). When the light source was intermittently turned on and off during the course of the reaction, product generation plateaued during dark periods and resumed when the light was switched back on (Figure 1). This further demonstrates that light is required to sustain catalytic turnover, although we note that the involvement of light-initiated radical chain processes cannot be ruled out.[13,14]

Exploration of the substrate scope showed that a wide range of arylboronic acids and pinnacol boronic esters can undergo aerobic hydroxylation using catalyst **1**, as shown in Table 2. Gram-scale synthesis of **6a** was accomplished in 99% isolated yield. Arenes with both electron-donating (alkoxy, **6b−6d**) and electron-withdrawing (nitro, **6g,m**) substituents gave yields of >80%. Protected and free amino groups were well tolerated (**6e,f**), along with a range of other substituents including cyano

Received: October 13, 2019
Published: December 30, 2019

https://dx.doi.org/10.1021/acs.joc.9b02777
J. Org. Chem. 2020, 85, 2040−2047

Table 1. Reactivity of Rh(II) Dimers in the Hydroxylation of Arylboronic Acids with O_2 and Visible Light



entry	[Rh_2] catalyst	yield (%)[b]
1	**1**	94
2	**2**	91
3	**3**	38
4	**4**	21
5	$Rh_2(OAc)_4$	trace
6	$Rh_2(esp)_2$	trace
7	$Rh_2(OAc)_4$ + bpy[c]	82
8	**1** (air)	65
9	**1** (Ar)	n.d.[d]
10	**1** (dark reaction)	trace

[a]10.5 W white LED. [b]Isolated yield. [c]2 mol% $Rh_2(OAc)_4$, 4 mol % bpy, 36 h. [d]n.d. = not detected.

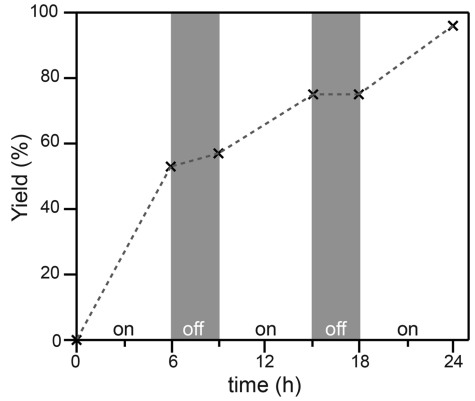
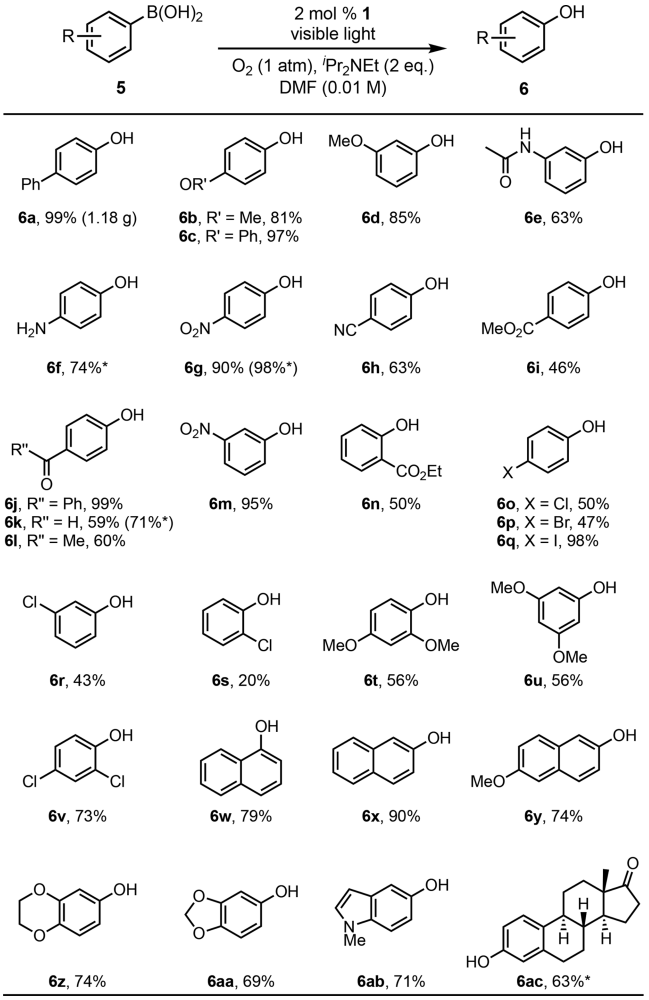


Figure 1. Light source on/off experiment for the conversion of **5a** to **6a** catalyzed by **1** (conditions as described in Table 1, entry 1), demonstrating that reaction progress pauses and resumes when light is temporarily removed.

groups, esters, acyl groups, and halogens (**6h**–**6s**). For the aryl bromide and chloride substrates shown in Table 2, we suspect that the low isolated yields may be due in part to product volatility. Disubstituted (**6t**–**6v**), polycyclic (**6w**–**6y**), and heterocyclic (**6z**–**6ab**) substrates could all be successfully hydroxylated. We were also able to obtain estrone (**6ac**) via this method in 63% yield from the corresponding pinnacol boronic ester.

Structural characterization of **1** via single crystal X-ray diffraction had not been previously reported, although the structure of the related trifluoroacetate complex was determined.[11] We have obtained single crystals of **1** from a DMF solution, confirming the expected structure as shown in Table 1 (Figure S3). Our data suggests that the axial acetate ligands remain coordinated to rhodium in DMF solution: the

Table 2. Aerobic Hydroxylation of Arylboronic Acids with Dirhodium(II) Catalyst 1[a]



[a]Yields reported are for isolated products. Asterisk (*): pinnacol boronic ester (Ar-BPin) used instead of $ArB(OH)_2$.

structurally related complex $[Rh_2(bpy)_2(OAc)_2(MeCN)_2][BF_4]_2$ (**7**)[11] in which the axial ligands are replaced with coordinated solvent molecules showed substantially decreased photoredox activity (44% isolated yield for the conversion of **5a** to **6a**). A comparison of the electronic structures of **1** and **7** shows that replacement of the axial acetate ligands with weaker L-type donors produces significant changes in the energy and relative ordering of the frontier molecular orbitals (Figure S4). Indeed, it is well-established that the ordering of the metal–metal bonding orbitals in dirhodium complexes is highly sensitive to the supporting ligand scaffold.[15] The ability to modulate both the energy and ordering of the Rh–Rh bonding orbitals provides an additional handle for tuning of the electronic structure and reactivity, as compared to mononuclear photoredox catalysts. Studies have shown that weaker axial ligand coordination at rhodium(II) dimers can lead to decreased excited state lifetimes, disfavoring excited state electron transfer processes, which may also account in part for the decreased catalytic activity of **7** compared to **1**.[8b]

As shown in Figure 2a, catalyst **1** dissolved in DMF exhibits two broad absorption bands in the visible spectrum, with λ_{max} = 445 nm (ε = 3900 M^{-1} cm^{-1}) and 527 nm (ε = 1200 M^{-1} cm^{-1}). The experimental UV–vis spectrum is well-reproduced

https://dx.doi.org/10.1021/acs.joc.9b02777
J. Org. Chem. 2020, 85, 2040–2047

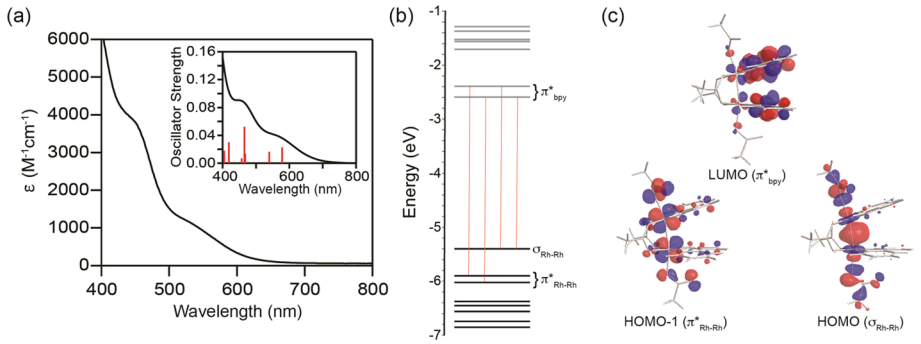


Figure 2. (a) Visible region electronic absorption spectrum of **1** in DMF (the inset shows the TD-DFT calculated spectrum); (b) calculated molecular orbital (MO) diagram for **1**, showing the primary transitions that contribute to visible light absorption; (c) visualizations of selected MOs (details of DFT calculations are given in the Supporting Information).

by time-dependent density functional theory (TD-DFT) calculations on the geometry-optimized structure of **1**. Calculations indicate that both absorption bands in the visible spectrum are due to metal−metal to ligand charge transfer (MMLCT): the lower-energy band arises from $\sigma_{Rh-Rh} \rightarrow \pi^*_{bpy}$ transitions, and $\pi^*_{Rh-Rh} \rightarrow \pi^*_{bpy}$ transitions produce the higher-energy band (Figure 2b,c). A comparison of LED sources suggests that the higher-energy $\pi^*_{Rh-Rh} \rightarrow \pi^*_{bpy}$ MMLCT transitions may be primarily responsible for photocatalytic activity (Table S1). Excitation at 440 nm produces an emission maximum of 468 nm at room temperature for **1** (Figure S5). In combination with the reduction potential measured by cyclic voltammetry (−0.49 V vs SCE; Figure S6), this provides an excited state reduction potential of approximately 2.1 V versus SCE.[16] This potential is more than sufficient to allow for reductive quenching by tertiary amines and is also consistent with the ability to use weaker reductants such as pyridine (Table S2).[17]

A plausible mechanism for the observed aerobic hydroxylation reaction with **1** is shown in Figure 3. Following visible

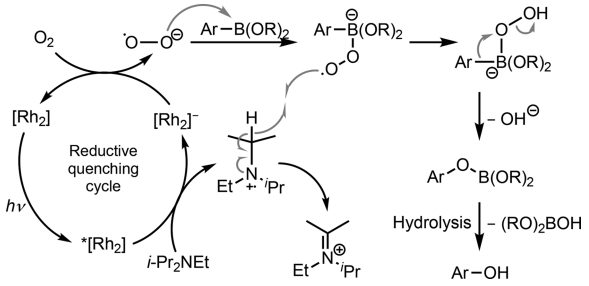


Figure 3. Plausible mechanism for aerobic hydroxylation of arylboronic acids catalyzed by **1**.

light excitation of the catalyst, reductive quenching with Hünig's base would generate an intermediate $[Rh_2]^-$. Single electron transfer with molecular oxygen would then produce the superoxide radical anion and regenerate the catalyst, and superoxide is capable of arylboronic acid hydroxylation.[9] Consistent with this mechanism, peroxide generation is observed in the absence of the arylboronic acid substrate but not in the absence of Hünig's base (Table S5), and no product is formed if Hünig's base is omitted from the reaction (Table S1).

To explore the generality of dirhodium(II) complex **1** for photoredox catalysis, we examined several other visible light-promoted oxidation reactions (Figure 4). Aerobic oxidation of

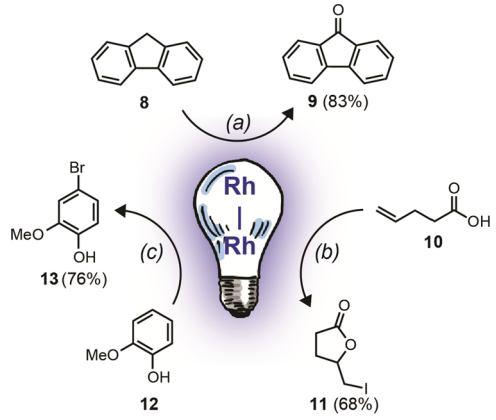


Figure 4. Demonstration of diverse oxidation reactions catalyzed by **1** in the presence of visible light (all reactions conducted with white LED light, room temp., 48 h): (a) 2 mol% **1**, O_2, DMF, $^iPr_2NEt$; (b) 2 mol % **1**, KI, O_2, MeOH, AcOH; (c) 5 mol % **1**, CBr_4, DMF.

activated C−H bonds was found to give fluorenone (**9**) from fluorene (**8**).[18] In situ oxidation of iodide could also promote iodolactonization of **10** to give **11**.[19] Finally, replacement of O_2 with CBr_4 allowed for bromination of guaiacol (**12**) to give **13**.[20] We note that these proof-of-concept reactions were conducted without optimization and that negligible background reactions were observed in the absence of either catalyst **1** or light.

In conclusion, we have presented the first use of a rhodium(II) dimer in visible light photoredox catalysis for aerobic oxidation of organic substrates. In addition to cleanly performing hydroxylation of arylboronic acid derivatives, **1** demonstrates reactivity toward a variety of other light-promoted oxidation reactions. We believe that dinuclear rhodium complexes are a promising platform for the development of new photoredox catalysts. In particular, the dirhodium core provides an additional handle for tuning the catalyst's electronic structure and excited state electron transfer reactivity, as compared to more commonly used mononuclear catalysts.

EXPERIMENTAL SECTION

General Information. Reactions were carried out under an ambient atmosphere unless otherwise specified. Methanol and dichloromethane were dried by distillation from CaH_2. THF, benzene, and toluene were dried by distillation from Na/benzophenone. Commercially obtained reagents were used as received unless otherwise specified. Visible light photoreactions

https://dx.doi.org/10.1021/acs.joc.9b02777
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were carried out using a 10.5 W white LED strip (180 × Huga 2835 SMD LEDs, luminous flux: 1300 lm) and with continuous stirring. Yields refer to purified and spectroscopically pure compounds. Thin-layer chromatography (TLC) was performed using Merck TLC aluminum sheet silica gel 60 F_{254} plates and visualized by fluorescence quenching under UV light and $KMnO_4$ stain. Flash chromatography was performed using silica gel (Chromatorex, MB 70-40/75, 40-75 μm) purchased by Fuji Silysia Chemicals. NMR spectra were recorded on a Bruker AVANCE spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C and Bruker AVANCE II operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C acquisitions. Chemical shifts are reported in ppm with the solvent resonance as the internal standard. The following solvent chemical shifts were used as reference values (ppm):[21] $CDCl_3$ = 7.26 (^{1}H), 77.16 (^{13}C); CD_3OD = 3.31 (^{1}H), 49.00 (^{13}C); DMSO-d_6 = 2.50 (^{1}H), 39.52 (^{13}C). Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. High-resolution mass spectra were obtained on JMS-700 with a TOF analyzer at the Academia Sinica. Melting points were determined by using a Büchi melting point B-540 melting point apparatus. UV−vis spectra were measured on a Varian Cary 50 spectrophotometer, using quartz cuvettes with a 1 cm path length. Rhodium(II) dimers **1**−**4**, **7**, and $Rh_2(esp)_2$ were synthesized according to the previously reported procedures.[11,12,22−24]

General Procedure for the Aerobic Hydroxylation Reaction in Table 2 (6a as a Representative Example). To a solution of 4-biphenylboronic acid (**5a**, 99 mg, 0.5 mmol) and $Rh_2(bpy)_2(OAc)_4$ (**1**, 8 mg, 0.01 mmol) in anhydrous DMF (50 mL) in a flame-dried flask was added diisopropylethylamine (170 μL, 1 mmol). The reaction mixture was stirred under an atmosphere of oxygen (1 atm) and visible light irradiation (10.5 W white LEDs). After complete consumption of the starting material (18 h, monitored by TLC), the reaction mixture was poured into ice-cold $HCl_{(aq)}$ (1%, 50 mL) and extracted with diethyl ether (5 × 50 mL). The combined organic extracts were washed with water (80 mL) and brine (80 mL), dried over $MgSO_4$, and filtered. After removal of the solvent under vacuum, the crude product was purified by column chromatography (EtOAc/hexanes = 1:8) to give **6a** (81 mg, 95% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, δ): 7.54 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.2 Hz, 2H), 4.88 (br s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 22 °C, δ): 155.2, 140.9, 134.1, 128.9, 128.5, 126.9, 115.8; HRMS (EI) m/z: [M]$^+$ calcd for $C_{12}H_{10}O$ 170.0732; found, 170.0735; FTIR (neat, cm^{-1}) 3415, 3062, 3037, 1944, 1891, 1597, 1523, 1485, 1375, 1243, 1113, 833, 759, 687.

6a from 5a at Gram Scale. To a solution of 4-biphenylboronic acid (**5a**, 1.39 g, 7.0 mmol) and $Rh_2(bpy)_2(OAc)_4$ (**1**, 112 mg, 0.14 mmol) in anhydrous DMF (700 mL) in a flame-dried flask was added diisopropylethylamine (2.4 mL, 14 mmol). The reaction mixture was stirred under an atmosphere of oxygen (1 atm) and visible light irradiation (21 W white LEDs). After complete consumption of the starting material (36 h, monitored by TLC), the reaction mixture was poured into ice-cold $HCl_{(aq)}$ (1%, 500 mL) and extracted with diethyl ether (5 × 500 mL). The combined organic extracts were washed with water (500 mL) and brine (500 mL), dried over $MgSO_4$, and filtered. After removal of the solvent under vacuum, the crude product was purified by column chromatography (EtOAc/hexanes = 1:8) to give **6a** (1.18 g, 99% yield) as a white solid.

6a from 5a Using $[Rh_2(Bpy)_2(OAc)_2(MeCN)_2][BF_4]_2$ (7) as Catalyst. To a solution of 4-biphenylboronic acid (**5a**, 99 mg, 0.5 mmol) and **7** (9 mg, 0.01 mmol) in anhydrous DMF (50 mL) in a flame-dried flask was added diisopropylethylamine (170 μL, 1 mmol). The reaction mixture was stirred under an atmosphere of oxygen (1 atm) and visible light irradiation (10.5 W white LEDs). After 18 h, the reaction mixture was poured into ice-cold $HCl_{(aq)}$ (1%, 50 mL) and extracted with ether (5 × 50 mL). The combined organic extracts were washed with water (80 mL) and brine (80 mL), dried over $MgSO_4$, and filtered. After removal of the solvent under vacuum, the crude product was purified by column chromatography (EtOAc/hexanes = 1:8) to give **6a** (38 mg, 44% yield) as a white solid.

4-Methoxyphenol 6b. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:6) to give the product **6b** (51 mg, 81% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, δ): 6.83−6.74 (m, 4H), 4.60 (s, 1H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 22 °C, δ): 153.6, 149.6, 116.2, 115.0, 56.0; HRMS (EI) m/z: [M]$^+$ calcd for $C_{12}H_{10}O_2$, 186.0681; found, 186.0680; FTIR (neat, cm^{-1}) 3349, 3034, 2924, 2834, 1860, 1607, 1510, 1455, 1375, 1231, 1102, 1031, 824, 734.

4-Phenoxyphenol 6c. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:6) to give the product **6c** (90 mg, 97% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, δ): 7.36−7.28 (m, 2H), 7.10−7.04 (m, 1H), 7.00−6.92 (m, 4H), 6.87−6.80 (m, 2H), 5.59 (br s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 22 °C, δ): 158.4, 151.7, 150.2, 129.8, 122.7, 121.1, 117.7, 116.5; HRMS (EI) m/z: [M]$^+$ calcd for $C_{12}H_{10}O_2$ 186.0681; found, 186.0680; FTIR (neat, cm^{-1}): 3225, 3026, 1882, 1601, 1587, 1504, 1440, 1342, 1219, 1094, 875, 850, 813, 751, 691.

3-Methoxyphenol 6d. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:10) to give the product **6d** (53 mg, 85% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.13 (t, J = 8.0 Hz, 1H), 6.51−6.44 (m, 3H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ); 160.8, 156.8, 130.3, 108.0, 106.4, 101.7, 55.4; HRMS (EI) m/z: [M]$^+$ calcd for $C_7H_8O_2$ 124.0524; found, 124.0522; FTIR (neat, cm^{-1}): 3424, 2928, 2854, 1605, 1494, 1462, 1156, 947, 837, 769, 684.

N-(3-Hydroxyphenyl)acetamide 6e. Using the general procedure, the crude mixture was purified by column chromatography (acetone/hexanes = 1:5) to give the product **6e** (47 mg, 63% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_3OD, 22 °C, δ): 7.16 (s, 1H), 7.10 (t, J = 8.10 Hz, 1H), 6.92 (d, J = 8.10 Hz, 1H), 6.52(m, 1H), 2.10 (s, 3H); ^{13}C{^{1}H}NMR (100 MHz, CD_3OD, 22 °C, δ): 171.6, 158.8, 140.9, 130.5, 112.3, 112.1, 23.8; HRMS (EI) m/z: [M]$^+$ calcd for $C_8H_9NO_2$, 151.0631; found, 151.0633; FTIR (neat, cm^{-1}): 3330, 3065, 1617, 1568, 1507, 14,663, 1377, 1284.

4-Aminophenol 6f. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6f** (40 mg, 74% yield) as a dark brown solid. ^{1}H NMR (400 MHz, CD_3OD, 21 °C, δ): 6.66 (m, 4H). ^{13}C{^{1}H}NMR (100 MHz, CD_3OD, 21 °C, δ): 151.4, 140.1, 118.6, 116.7; HRMS (EI) m/z: [M]$^+$ calcd for C_6H_7NO, 109.0527; found, 109.0527; FTIR (neat, cm^{-1}): 3341, 3281, 3177, 1860, 1615, 1509, 1474, 1386, 1092, 970, 826, 750, 646.

4-Nitrophenol 6g. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6g** (64 mg, 91% yield from 4-nitrophenylboronic acid; 68 mg, 98% yield from 4-nitrophenyl-boronic acid pinacol ester) as a pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, 21 °C, δ): 11.06 (br s, 1H), 8.08 (d, J = 8.9 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 22 °C, δ): 164.0, 139.7, 126.2, 115.8; HRMS (EI) m/z: [M]$^+$ calcd for $C_6H_5NO_3$, 139.0269; found, 139.0271; FTIR (neat, cm^{-1}): 3329, 3120, 3084, 2921, 1589, 1498, 1326, 1287, 1216, 1167, 1113, 851, 755, 629.

4-Hydroxybenzonitrile 6h. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6h** (38 mg, 63% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C, δ): 7.56 (d, J = 8.00 Hz, 2H), 6.92 (d, J = 7.80 Hz, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$, 21 °C, δ): 159.9, 134.4, 119.3, 116.5, 103.8; HRMS (EI) m/z: [M]$^+$ calcd for C_7H_5O N, 119.0372; found, 119.0371; FTIR (neat, cm^{-1}): 838, 1223, 1449, 1509, 1586, 1612, 2233, 3283.

Methyl 4-Hydroxybenzoate 6i. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6i** (35 mg, 46% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.97 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 5.29 (br, 1H), 3.89, (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 167.4, 160.2, 132.1, 122.6, 115.4, 52.2. HRMS (EI) m/z: [M]$^+$ calcd for $C_8H_8O_3$, 152.0470; found, 152.0473; FTIR (neat, cm^{-1}):3283, 2233, 1509, 1586, 1166, 838.

https://dx.doi.org/10.1021/acs.joc.9b02777
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4-Hydroxybenzophenone ***6j***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:6) to give the product **6j** (98 mg, 99% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, 21 °C, δ): 10.47 (br s, 1H), 7.69−7.63 (m, 4H), 7.60 (t, J = 7.1 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 6.94−6.88 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 22 °C, δ) 194.4, 126.1, 138.2, 132.6, 131.8, 129.2, 128.4, 128.0, 115.3; HRMS (EI) m/z: [M]$^+$ calcd for $C_{13}H_{10}O_2$ 198.0681; found, 198.0676; FTIR (neat, cm^{-1}): 3321, 3055, 1643, 1569, 1510, 1445, 1318, 1283, 1222, 1152, 939, 924, 855, 795, 748, 705, 607.

4-Hydroxybenzaldehyde ***6k***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6k** (36 mg, 59% yield from boronic acid; 43 mg, 71% yield from boronic acid pinacol ester) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C, δ): 9.88 (s, 1H), 7.82 (d, J = 8.00 Hz, 2H), 6.96 (d, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, δ): 191.5, 161.9, 132.6, 129.6, 116.1. HRMS (EI) m/z: [M]$^+$ calcd for $C_7H_6O_2$, 122.0369; found, 122.0368. FTIR (neat, cm^{-1}): 3158, 2879, 1905, 1663, 1647, 1588, 1518, 1449, 1385, 1314, 1282, 1215, 1155, 1112, 858, 831, 788.

1-(4-Hydroxyphenyl)ethanone ***6l***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6 L** (41 mg, 60% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C, δ): 7.92 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.60 Hz, 2H), 2.85 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, δ): 198.5, 161.4, 131.3, 129.8, 115.7, 26.4. HRMS (EI) m/z: [M]$^+$ calcd for $C_8H_8O_2$; 136.0520; found, 136.0524; FTIR (neat, cm^{-1}): 3216, 1621, 1580, 1511, 1490, 1460, 1423, 1364, 1257, 1330, 1147, 840.

3-Nitrophenol ***6m***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6m** (66 mg, 95% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6, 21 °C, δ): 10.43 (br s, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.53 (s, 1H), 7.41 (t, J = 8.1 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 22 °C, δ): 158.4, 148.8, 130.6, 122.5, 113.9, 109.7; HRMS (EI) m/z: [M]$^+$ calcd for $C_6H_5NO_3$, 139.0269; found, 139.0270; FTIR (neat, cm^{-1}): 3379, 3110, 2923, 2853, 1624, 1522, 1350, 1299, 1214, 1078, 998, 934, 876, 818, 739, 672, 605.

Ethyl 2-Hydroxybenzoate ***6n***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6n** (41 mg, 50% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 10.58 (s, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.47 (t, J = 15.6 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 4.44 (m, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$, 23 °C, δ): 170.3, 161.7, 135.7, 130.0, 119.2, 117.6, 112.7, 61.5, 14.3; HRMS (EI) m/z: [M]$^+$ calcd for $C_9H_{10}O_3$, 166.0626; found, 166.0630; FTIR (neat, cm^{-1}): 3153, 2986, 1675, 1618, 1489, 1375, 1302, 1251, 1213, 1158, 1090, 756, 702, 668.

4-Chlorophenol ***6o***. Using the general procedure, the crude mixture was purified by column chromatography (ether/pentane = 1:10) to give the product **6o** (33 mg, 50% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.19 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 5.06 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 154.3, 129.6, 125.6, 116.8; HRMS (EI) m/z: [M]$^+$ calcd for C_6H_5ClO, 128.0029; found, 128.0032; FTIR (neat, cm^{-1}): 3351, 2928, 1590, 1495, 1433, 1369, 1240, 1095, 822.

4-Bromophenol ***6p***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:10) to give the product **6p** (41 mg, 47% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.35−7.31 (m, 2H), 6.74−6.70 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 154.8, 132.6, 117.3, 112.9; HRMS (EI) m/z: [M]$^+$ calcd for C_6H_5BrO, 171.9524; found, 171.9528; FTIR (neat, cm^{-1}) 3389, 1587, 1495, 1432, 1236, 1069, 1007, 821 cm^{-1}.

4-Iodophenol ***6q***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:9) to give the product **6q** (108 mg, 98% yield) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.52(d, J = 8.7 Hz, 2H), 6.63(d, J = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 155.2, 138.6, 117.9, 83.0; HRMS (EI) m/z: [M]$^+$ calcd for $C_7H_8O_2$ 124.0524; found, 124.0525; FTIR (neat, cm^{-1}): 3386, 2910, 1590, 1496, 1473, 1254, 1206, 830.

3-Chlorophenol ***6r***. Using the general procedure, the crude mixture was purified by column chromatography (ether/pentane = 1:9) to give the product **6r** (28 mg, 43% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.15 (t, J = 8.1 Hz, 1H), 6.92−6.89 (m, 1H), 6.86 (s, 1H), 6.72 (d, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 156.4, 135.0, 130.6, 121.1, 116.0, 113.9; HRMS (EI) m/z: [M]$^+$ calcd for C_6H_5ClO, 128.0023; found, 128.0029; FTIR (neat, cm^{-1}): 3376, 2927, 2852, 1590, 1475, 1444, 1246, 999, 886, 771, 677.

2-Chlorophenol ***6s***. Using the general procedure, the crude mixture was purified by column chromatography (ether/pentane = 1:9) to give the product **6s** (13 mg, 20% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.31 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.88 (t, J = 15.6 Hz, 1H) 5.60 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 151.7, 129.2, 128.4, 121.3, 120.1, 116.4; HRMS (EI) m/z: [M]$^+$ calcd for C_6H_5ClO, 128.0030; found, 128.0029; FTIR (neat, cm^{-1}): 3351, 2928, 2854, 1596, 1460, 1751, 1300, 1246, 1035, 845.

2,4-Dimethoxyphenol ***6t***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:10) to give the product **6t** (43 mg, 56% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.83 (d, J = 8.8 Hz, 1H), 6.49 (d, J = 2.4 Hz, 1H), 6.39 (dd, J = 8.8, 2.4 Hz, 1H), 5.23 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 153.5, 147.1, 139.8, 114.2, 104,2, 99.5, 55.9, 55.8; HRMS (EI) m/z: [M]$^+$ calcd for $C_8H_{10}O_3$, 124.0524; found, 124.0524; FTIR (neat, cm^{-1}): 3410, 2927, 2851, 1611, 1487, 1478, 1288, 1274, 1189, 1158, 947, 856.

3,5-Dimethoxyphenol ***6u***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:10) to give the product **6u** (32 mg, 41% yield) as a white solid. ^{1}NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.07 (s, 1H), 6.02 (s, 2H), 3.76 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 161.7, 157.5, 94.4, 93.2, 55.4; HRMS (EI) m/z: [M]$^+$ calcd for $C_8H_{10}O_3$, 154.0630; found, 154.0631; FTIR (neat, cm^{-1}): 3441, 2924, 2851, 1605, 1460, 1206, 1160, 1063, 823, 679 cm^{-1}.

2,4-Dichlorophenol ***6v***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:9) to give the product **6v** (59 mg, 73% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.33 (d, J = 2.5 Hz 1H), 7.15 (dd, J = 8.7, 2.4 Hz, 1H), 7.95 (d, J = 16.7 Hz, 1H), 5.56 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 150.3, 128.7, 128.6, 125.7, 120.5, 117.2; HRMS (EI) m/z: [M]$^+$ calcd for $C_6H_{4c}Cl_2O$, 161.9639; found, 161.9641; FTIR (neat, cm^{-1}): 3533, 2929, 2853, 2362, 2356, 1650, 1585, 1480, 1410, 1282, 1188, 865, 812, 723.

1-Naphthol ***6w***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:8) to give the product **6w** (59 mg, 79% yield) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, δ): 8.23−8.15 (m, 1H), 7.86−7.79 (m, 1H), 7.54−7.47 (m, 2H), 7.45 (d, J = 8.3 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 7.4 Hz, 1H), 5.38 (br s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 22 °C, δ): 151.5, 134.9, 127.8, 126.6, 126.0, 125.4, 124.5, 121.7, 120.8, 108.7; HRMS (EI) m/z: [M]$^+$ calcd for $C_{10}H_8O$, 144.0575; found, 144.0573; FTIR (neat, cm^{-1}): 3257, 3052, 2926, 1699, 1674, 1633, 1598, 1518, 1457, 1386, 1269, 1082, 1043, 1014, 875, 790, 766.

2-Naphthol ***6x***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:8) to give the product **6x** (65 mg, 90% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C, δ): 7.77 (t, J = 8.2 Hz, 2H), 7.68 (d, J = 8.2 Hz, 1H), 7.44 (t, J = 7.5, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 7.12 (dd, J = 8.8, 2.5 Hz, 1H), 5.40 (br s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 21 °C, δ): 153.5, 134.7, 130.0, 129s.0, 127.9, 126.7, 126.5, 123.7, 117.9, 109.6; HRMS (EI) m/z: [M]$^+$ calcd for $C_{10}H_8O$ 144.0575; found, 144.0576; FTIR (neat, cm^{-1}): 3231,

https://dx.doi.org/10.1021/acs.joc.9b02777
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3050, 2922, 2851, 1630, 1601, 1512, 1467, 1407, 1277, 1216, 959, 844, 814, 741.

2-Methoxy-6-naphthol ***6y***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:8) to give the product 6y (64 mg, 74% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.65 (d, J = 11.6 Hz, 1H), 7.58 (d, J = 11.6 Hz, 1H), 7.14−7.05 (m, 4H), 3.90 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 156.2, 151.9, 129.9, 129.8, 128.6, 127.9, 119.4, 118.2, 109.8, 106.1, 55.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{11}H_{10}O_2$, 174.0681; found, 174.0686; FTIR (neat, cm^{-1}): 3307, 2922, 2849, 1624, 1487, 1382, 1379, 1217, 1031, 920, 859, 825, 691.

3,4-Ethylenedioxyphenol ***6z***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:9) to give the product **6z** (56 mg, 74% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24, °C, δ): 6.72 (d, J = 8.3 Hz, 1H), 6.39 (d, J = 10.6 Hz, 1H), 6.33 (d, J = 8.6 Hz, 1H), 4.24−4.20 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 150.1, 143.8, 137.6, 117.6, 108.5, 104.4, 64.7, 64.2; HRMS (EI) m/z: $[M]^+$ $C_8H_8O_3$ calcd for 152.0473; found, 152.0473; FTIR (neat, cm^{-1}): 3436, 1612, 1508, 1313, 1202, 1158, 1067, 912, 759.

3,4-(Methylenedioxy)phenol ***6aa***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:9) to give the product **6aa** (30 mg, 43% yield) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.65 (d, J = 8.3 Hz, 1H), 6.43 (d, J = 2.4 Hz, 1H), 6.25 (dd, J = 2.4, 2.5 Hz 1H), 5.91 (s, 2H); ^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$, 24 °C, δ): 150.7, 148.4, 141.6, 108.3, 106.8, 101.3, 96.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_7H_6O_3$, 138.0317; found, 138.0313; FTIR (neat, cm^{-1}): 3410, 2911, 1653, 1633, 1475, 1189, 1135, 1096, 1040, 934.

1-Methyl-1H-indol-5-ol ***6ab***. Using the general procedure, the crude mixture was purified by column chromatography (EtOAc/hexanes = 1:5) to give the product **6ab** (52 mg, 71% yield) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C, δ): 7.19 (d, J = 8.7 Hz, 1H), 7.03 (t, J = 4.5 Hz, 1H), 6.80 (d, J = 8.7 Hz, 1H), 6.35 (br, 1H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C, δ): 129.8, 111.5, 111.3, 109.9, 105.3, 100.1, 33.1. HRMS (EI) m/z: $[M]^+$ calcd for C_9H_9NO, 147.0684; found, 147.0684. FTIR (neat, cm^{-1}): 3316, 1523, 1482, 883, 791, 733.

Estrone ***6ac***. To a solution of estrone-3-boronic acid pinacol ester (**5ac**, 152 mg, 0.4 mmol) and $Rh_2(bpy)_2(OAc)_4$ (**1**, 6 mg, 0.008 mmol) in anhydrous DMF (40 mL) in a flame-dried flask was added diisopropylethylamine (140 μL, 0.8 mmol). The reaction mixture was stirred under an atmosphere of oxygen (1 atm) and visible light irradiation (10.5 W white LEDs). After complete consumption of the starting material (24 h, monitored by TLC), the reaction mixture was poured into ice-cold $HCl_{(aq)}$ (1%, 40 mL) and extracted with EtOAc (5 × 40 mL). The combined organic extracts were washed with water (2 × 60 mL) and brine (60 mL), dried over $MgSO_4$, and filtered. After removal of the solvent under vacuum, the crude product was purified by column chromatography (EtOAc/hexanes = 1:4; dry-loaded) to give **6ac** (68 mg, 63% yield) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, 21 °C, δ): 9.03 (s, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1H), 6.45 (s, 1H), 2.85−2.64 (m, 2H), 2.41 (dd, J = 18.8, 8.4 Hz, 1H), 2.35−2.22 (m, 1H), 2.18−1.83 (m, 4H), 1.80−1.66 (m, 1H), 1.61−1.12 (m, 6H), 0.80 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 21 °C, δ): 219.7 (C), 155.1 (C), 137.1 (C), 129.9 (C), 126.1 (CH), 115.0 (CH), 112.8 (CH), 49.6 (CH), 47.4 (C), 43.5 (CH), 38.0 (CH), 35.4 (CH_2), 31.4 (CH_2), 29.1 (CH_2), 26.2 (CH_2), 25.6 (CH_2), 21.2 (CH_2), 13.5 (CH_3); HRMS (EI) m/z: $[M]^+$ calcd for $C_{18}H_{22}O_2$, 270.1620; found, 270.1612; FTIR (neat, cm^{-1}): 3292, 2936, 2859, 1720, 1620, 1579, 1497, 1454, 1355, 1288, 1248, 1055, 817.

Fluoren-9-one 9. To a solution of fluorene (**10**, 83 mg, 0.5 mmol) and $Rh_2(bpy)_2(OAc)_4$ (**1**, 8 mg, 0.01 mmol) in anhydrous DMF (50 mL) in a flame-dried flask was added diisopropylethylamine (170 μL, 1 mmol). The reaction mixture was stirred under an atmosphere of oxygen (1 atm) and visible light irradiation (10.5 W white LEDs). After complete consumption of the starting material (48 h, monitored by TLC), the reaction mixture was poured into ice-cold $HCl_{(aq)}$ (1%, 50 mL) and extracted with diethyl ether (5 × 50 mL). The combined organic extracts were washed with water (80 mL) and brine (80 mL), dried over $MgSO_4$, and filtered. After removal of the solvent under vacuum, the crude product was purified by column chromatography (EtOAc/hexanes = 1:5) to give **11** (75 mg, 83% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 7.62(d, J = 8.0 Hz, 2H), 7.53−7.47(m, 4H), 7.29(t, J = 7.3 Hz, 2H) ; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 194.1, 144.6, 134.8, 134.3, 129.2, 124.5, 120.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_{13}H_8O$, 180.0575; found, 180.0574; FTIR (neat, cm^{-1}): 3050, 1710, 1605, 1600, 1475, 1377, 1298, 1013, 720.

5-(Iodmethyl)dihydro-2(3*H*)-furanone 11. To a solution of KI (183 mg, 1.1 mmol) and AcOH (380 mg, 5 mmol) in CH_3CN (50 mL) in a flame-dried flask were added pent-4-enoic acid (**12**, 100 mg, 1 mmol) and $Rh_2(bpy)_2(OAc)_4$ (**1**, 16 mg, 0.02 mmol). The reaction mixture was stirred under an atmosphere of oxygen (1 atm) and visible light irradiation (10.5 W white LEDs). After complete consumption of the starting material (48 h, monitored by TLC), sat. $Na_2S_2O_3$(aq) (10 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$, and filtered. After removal of the solvent under vacuum, the crude product was purified by column chromatography (EtOAc/hexanes = 1:10) to give **13** (153 mg, 68% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 4.58−4.52 (m, 1H), 3.42 (dd, J = 10.5, 4.24 Hz, 1H), 3.30 (dd, J = 10.5, 4.24 Hz, 1H), 2.70−2.55 (m, 2H), 2.54−2.44 (m, 1H), 2.05−1.95 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 176.3, 78.5, 28.9, 28.2, 7.4; HRMS (EI) m/z: $[M]^+$ calcd for $C_5H_7O_2I$, 225.9491; found, 225.9487; FTIR (neat, cm^{-1}): 2954, 1761, 1456, 1415, 1335, 1208, 1151, 1011, 979, 906, 873, 609.

4-Bromo-2-methoxyphenol 13. To a solution of 2-methoxyphenol (55.4 μL, 0.5 mmol) in anhydrous DMF (50 mL) in a flame-dried flask was added $Rh_2(bpy)_2(OAc)_4$ (**1**, 20 mg, 0.025 mmol) and CBr_4 (332 mg, 1.0 mmol). The reaction mixture was stirred under an atmosphere of oxygen (1 atm) and visible light irradiation (10.5 W white LEDs). After complete consumption of the starting material (48 h, monitored by TLC), H_2O (50 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (80 mL), dried over $MgSO_4$, and filtered. After removal of the solvent under vacuum, the crude product was purified by column chromatography (EtOAc/hexanes = 1:5) to give **15** (77 mg, 76% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, δ): 6.98 (d, J = 10.5 Hz, 2H), 6.79 (d, J = 8.3 Hz, 1H), 5.56 (s, 1H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 24 °C, δ): 147.7, 142.6, 127.0, 113.6, 111.8, 108.8, 56.7; HRMS (EI) m/z: $[M]^+$ calcd for $C_7H_7BrO_2$, 201.9629; found, 201.9630; FTIR (neat, cm^{-1}): 3521, 2967, 2946, 2842, 1608, 1505, 1445, 1360, 1258, 1224, 1118, 1026, 859, 839, 810, 781.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.9b02777.

Visible light photoreaction setup and reaction optimization, spectroscopic data, and details of DFT calculations (PDF)

Crystallographic data for **1** (CIF)

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https://dx.doi.org/10.1021/acs.joc.9b02777
J. Org. Chem. 2020, 85, 2040−2047

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Christian Rojas for helpful comments during manuscript preparation. M.G.C. gratefully acknowledges the NSF (CHE-1827936) for an MRI award in support of a 400 MHz NMR spectrometer at Barnard College. E.M.-S. and M.G.C. thank the Department of Chemistry and the Office of the Provost at Barnard for additional financial Support. G.J.C. gratefully acknowledges the Ministry of Science and Technology (MOST) of Taiwan for financial support (108-2113-M-033-007). SCXRD was performed at the Shared Materials Characterization Laboratory at Columbia University.

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https://dx.doi.org/10.1021/acs.joc.9b02777
J. Org. Chem. 2020, 85, 2040−2047