Radical Benzylation of Quinones via C–H Abstraction

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ABSTRACT: Herein we report the development of radical benzylation reactions of quinones using Selectfluor and catalytic Ag(I) initiators. The reaction is believed to proceed via a C–H abstraction mechanism after Ag(I)-mediated reduction of Selectfluor. This reaction occurs under mild conditions and is effective for a variety of quinones and radical precursors bearing primary benzylic carbons. The use of pre-formed $Ag(4\text{–}OMePy)_2NO_3$ as a catalyst proved effective in improving reaction efficiency by reducing unwanted degradation pathways available to Selectfluor.

Functionalized quinones are well-established as oxidants for organic and organometallic transformations, but are also important structural motifs in biologically active molecules.[1a] Even very simple quinone structures have shown potent biological activity and have been utilized by pharmaceutical and agrochemical industries.[1b-d] Specifically, benzylated quinones have demonstrated enzyme inhibition[1e], antitumor[1f], anticancer[1g], and antifeedant[1h] properties (Figure 1). A benzylated adduct of menadione is responsible for the high potency and antimalarial properties of Plasmidione towards blood-stage parasites.[1j-k]

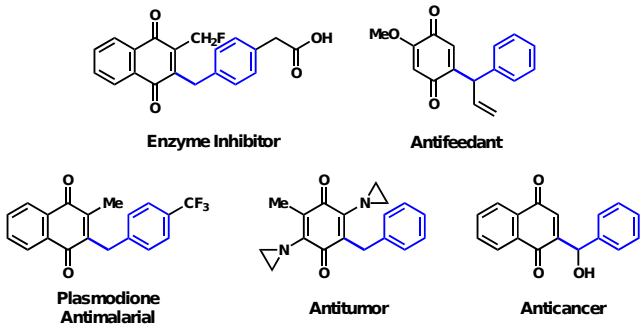
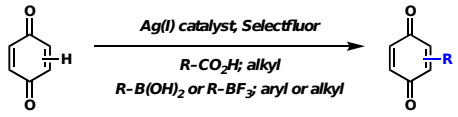


Figure 1. Biologically active quinones bearing benzylic substitution.

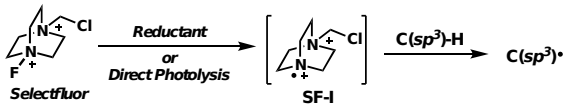
Several methods are known for the synthesis of functionalized quinones including palladium-catalyzed coupling reactions[2], alkylation/oxidation of hydroquinones and phenols[3], and direct radical functionalization.[4] In the context of radical functionalizations, several methods have been reported that utilize Minisci-type conditions for radical functionalization of quinones, typically involving pre-functionalized radical precursors and strong oxidants.[5] Oxidative radical processes leading to quinone substitution from unfunctionalized reagents often require air and moisture free conditions, large excess of the radical precursor, and elevated temperatures to circumvent unfavorable radical pathways.

Previously, our group had shown that quinones and aromatic heterocycles could be directly alkylated or arylated via carboxylic or boronic acid radical precursors using Selectfluor and catalytic $AgNO_3$ (Figure 2A).[5] Others have demonstrated that diazabicyclo radical cation **SF-I**, formed after single-electron reduction or direct photolysis of Selectfluor, is a suitable hydrogen atom transfer (HAT) agent to generate carbon centered radicals leading to C–F and C–C bond formation (Figure 2B).[6] We sought to combine mechanistic features of these two protocols to develop a quinone benzylation reaction that operates via C–H abstraction from **SF-I** after single-electron transfer between a Ag(I) source and Selectfluor (Figure 2C).

A) Silver-Catalyzed Minisci Reactions Using Selectfluor as a Mild Oxidant



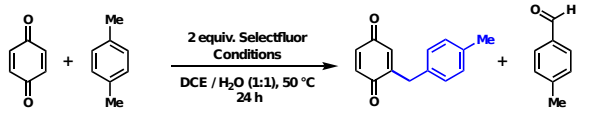
B) Hydrogen Atom Abstraction of sp^3 C-H Bonds via Selectfluor



C) C-H Benzylation of Quinones Using Selectfluor and Methyl Arenes (This Work)

Figure 2. Selectfluor as an oxidant and/or HAT precursor.

Preliminary studies using *p*-xylene as a radical precursor in a biphasic solvent system (see *Supporting Information* solvent effect on reaction) showed that benzoquinone could be directly alkylated in moderate yield using a $AgNO_3$ / Selectfluor reagent system (Table 1, entry 1) with minor oxidized and fluorinated side-products observed. In our previous studies on radical fluorination via C–H abstraction, we found that pyridine additives lowered the onset oxidation potential of Ag(I) to facilitate single-electron transfer to Selectfluor.[7] Within the context of quinone functionalization we have also extended ligand additives and their effects on the shift in onset oxidation potential of silver. Guided by those results, we examined the effect of pyridine additives to develop a catalyst that would be more effective towards this benzylation reaction. We began with 4-methoxypyridine hypothesizing that electron rich pyridines would have the greatest effect in lowering the onset oxidation potential of silver, thus allowing for greater concentrations of the desired product. Interestingly, although one equivalent of 4-methoxypyridine had a deleterious effect on the reaction (Table 1, entry 2); catalytic amounts led to a slight increase in conversion (Table 1, entry 3). Examining order of the addition (Table 1, entry 4) of reagents used led us to observe an increase yield when Selectfluor is added last. Because the synthesis of Ag(I) $[pyridine]_2$ salts is straightforward[8], we examined their efficacy as catalysts for the benzylation reaction. A series of conditions were screened, and we discovered that 20 mol % of $Ag(4\text{-}OMePy)_2NO_3$ was optimum to produce **1** in good yield (73%, Table 1, entry 5). Catalysts with different pyridines led to diminished conversion (Table 1, entries 6 and 7), suggesting the electron-rich nature of 4-methoxypyridine was important for electron transfer. We examined Ag–complexes with bidentate ligands (Table 1, entries 8 and 9) with high reactivity observed when phenanthroline was the ligand, but no product formation when 2,2′-bipyridine was used. Interestingly, although a control reaction without Ag(I) yielded no product (Table 1, entry 10), one equivalent of 4-methoxypyridine was capable of promoting radical alkylation without a metal initiator (Table 1, entry 11), suggesting that electron transfer between the pyridine and Selectfluor was occurring.[8] Reaction with the standard oxidant for Minisci reactions, $(NH_4)_2S_2O_8$, led to a mixture of benzylated products (Table 1, entry 12).



1 equiv. 10 equiv. **1** **A1**

Entry	Deviation from standard conditions	Yield of 1[a]	Yield of A1[a]
1	20 mol % $AgNO_3$	49%	11%
2	20 mol % $AgNO_3$, 1 equiv. 4-methoxypyridine	32%	3%
3	20 mol % $AgNO_3$, 40 mol % 4-methoxypyridine	60%	11%
4[b]	20 mol % $AgNO_3$, 40 mol % 4-methoxypyridine	69%	10%
5	20 mol % $Ag(OMePy)_2NO_3$	73% (71%)	15%
6	20 mol % $Ag(Py)_2NO_3$	62%	20%
7	20 mol % $Ag(4\text{-}t\text{-}BuPy)_2NO_3$	47%	14%
8	20 mol % $Ag(Phen)_2NO_3$	68%	13%
9	20 mol % $Ag(ByPy)_2NO_3$	0%	30%
10	No Silver	no reaction	no reaction
11	No Silver, 1 equiv. 4-methoxypyridine	17%	5%
12	$(NH_4)_2S_2O_8$ instead of Selectfluor	38% + 14% Bis	10%

Table 1. Optimization of quinone functionalization. Reaction conditions: 1,4-benzoquinone (0.2 mmol), *p*-xylene (2.0 mmol), Selectfluor (0.4 mmol), $Ag(4\text{-}OMePy)_2NO_3$ (0.04 mmol), 2 mL of DCE/H_2O (1:1). [a] ^{1}H-NMR yields to 1,3,5-trimethoxybenzene, values in parentheses indicate isolated yield. [b] Selectfluor was added last to the reaction.

With the optimized conditions established, we examined the scope of the benzylation reaction with a variety of quinones and methyl arene reaction partners (Figure 3). Para substituted toluenes with electron donating groups (**2–3**) benzylated benzoquinone in moderate to good yield. Electron-withdrawing methylarene (**4**) was less effective resulting in poor yields with the isolation of unreacted benzoquinone accounting for mass balance. Ortho-substituted arenes with methyl substitution (**5**) furnished product in moderate yield. Meta-methylated (**6**) and tetramethylated (**7**) arenes were also effective partners in

generating desired products. A variety of quinones were screened to determine the scope of electrophiles suitable for this reaction. Benzylated 1,4-benzoquinone (**8**) was synthesized in moderate yield. It is interesting to note that using solvent quantities of the radical precursor results in largely similar reaction conversions. An increase in yield is also observed when the equivalents of Selectfluor are raised from 2 to 5 equivalents. Both methylated (**9–10**) and halogenated (**11–12**) benzoquinones were effective coupling partners and resulted in moderate yields of benzylated products with no bis-benzylated products observed. Finally, functionalized naphthaquinone (**13**) and associated analogs such as juglone (**14**) and menadione (**15**) can also be accessed. Efforts to extend this method towards other C–H radical precursors and heterocyclic substrates resulted in poor yields (see *Supporting Information* for details).

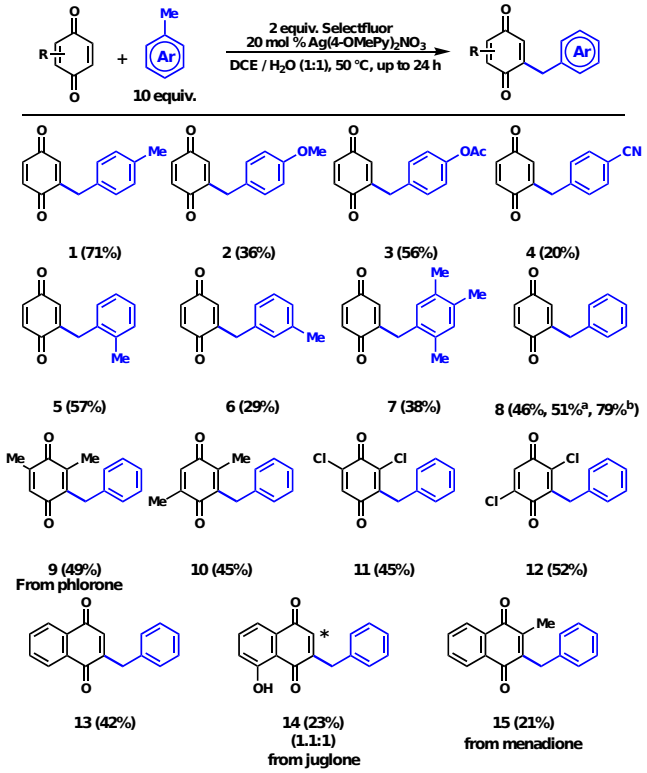


Figure 3. Scope of quinone benzylation. Yields refer to chromatographically pure compounds. [a]Toluene was used instead of DCE as organic solvent. [b]5 equivalents of Selectfluor used instead of 2 equivalents.

To better understand the effect of 4-methoxypyridine as a ligand for Ag(I), we tracked the concentration of Selectfluor by ^{19}F-NMR over the course of a typical experiment. Due to the biphasic nature of the reaction, *in situ* reaction monitoring posed a challenge. Instead, small aliquots were removed from the aqueous phase of the reaction to determine Selectfluor concentration against an external standard over the course of 24 hours (see *Supporting Information* for details). Entry 2 from Table 1 suggested that excess 4-methoxypyridine had a negative effect on reaction conversion, and previous work in our group had established that electron-rich pyridines can directly consume Selectfluor in an unproductive manner, an observation that is now extended to this biphasic solvent system.[9a]

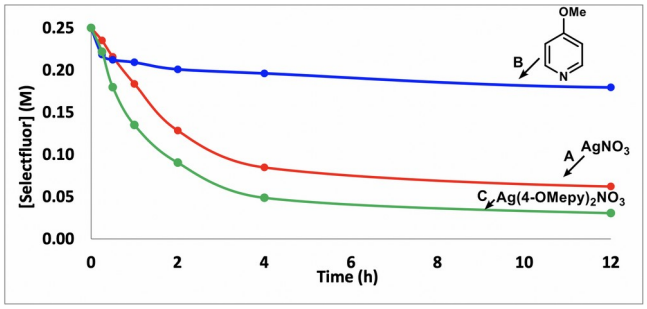


Figure 4. ^{19}F-NMR monitoring of the consumption of Selectfluor (1.0 mmol) with either (**A**) 0.1 mmol of $AgNO_3$, (**B**) 0.2 mmol of 4-methoxypyridine, or (**C**) 0.1 mmol of Ag(4-OMePy)$_2$NO$_3$. Reaction conditions: Selectfluor (1.0 mmol) in DCE/H_2O (4 mL, 1:1) at 50 ºC for up to 24 h. Using a glass microsyringe, 200 µL aliquots were taken from the aqueous phase at specified time points. Conversions were determined by ^{19}F-NMR using trifluorotoluene as an external standard.

We were interested, however, in comparing the use of $AgNO_3$ and catalytic 4-methoxypyridine to Ag(4-OMePy)$_2$NO$_3$ to establish the benefit of the pre-formed catalyst. A catalytic amount of $AgNO_3$ consumed approximately 80% of Selectfluor within 24 hours, confirming that a nitrogen additive is not required for the Ag(I)/(II) redox cycle under these conditions (Figure 4A). A Ag(I)/(II) redox cycle is proposed because following the oxidation of Ag(I) by Selectfluor to generate Ag(II); aqueous solutions of Ag(II) are unstable and readily oxidize water to oxygen at room temperature regenerating Ag(I).[10] A catalytic amount of 4-methoxypyridine consumes Selectfluor in an apparent 1:1 stoichiometry with an initial rate that is on par with the $AgNO_3$-mediated reaction (Figure 4B). Under these conditions only trace amounts of product are formed, confirming that free 4-methoxypyridine has a deleterious effect on the desired transformation even in catalytic quantities. Finally, reaction with pre-formed Ag(4-

$OMePy)_2NO_3$ produces the highest overall reaction rate for consumption of Selectfluor, while providing the desired product in the highest overall conversion (Figure 4C). These data suggest that the pre-formed catalyst circumvents unfavorable interactions between 4-methoxypyridine and Selectfluor, presumably because strong association to Ag(I) precludes the occurrence of free pyridine in solution.

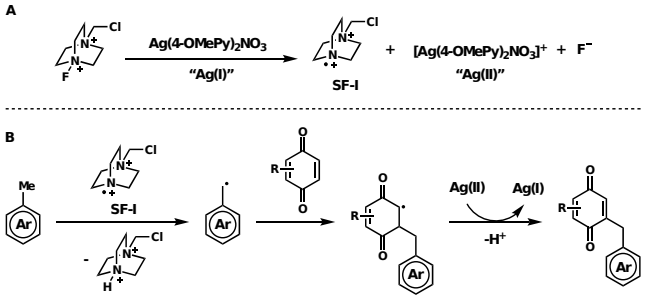


Figure 5. Proposed mechanism for quinone benzylation.

A plausible mechanism for the benzylation of quinone is shown in Figure 5. Single-electron transfer between $Ag(4\text{-}OMePy)_2NO_3$ and Selectfluor generates **SF-I** and the Ag(II) complex with concomitant generation of fluoride anion (Figure 5A**)**. Hydrogen atom abstraction of a methylarene via **SF-I** leads to a nucleophilic benzyl radical that is trapped by an electrophilic quinone substrate. The resulting radical intermediate is then oxidized, either by Selectfluor or Ag(II), and deprotonated to produce the expected C–H benzylated product (Figure 5B**)**.

In summary, we have developed a robust catalyst system for generating benzylic radicals via C–H abstraction, and combining these radicals with various electrophilic quinones.[11] A pre-formed Ag(I)/pyridine catalyst was found to be optimum for reducing Selectfluor via single-electron transfer to generate diazabicyclo radical cation **SF-I** as hydrogen atom transfer agent. The quinone benzylation reaction is simple to perform and operates under mild reaction conditions without pre-functionalized substrates. Efforts are ongoing to identify new catalyst systems to make the reaction more compatible with alternative radical precursors or electrophilic partners such as aromatic heterocycles.

General Considerations

Reagents and solvents were purchased at the highest commercial quality and used without purification. Yields refer to chromatographically and spectroscopically (^{1}H NMR, ^{13}C NMR, ^{19}F NMR) homogenous material, unless otherwise noted. Reactions were monitored by GCMS (Agilent Technologies 5975 Series MSD GC MS) and thin-layer chromatography using 0.25 mm E. Merck silica gel plates (60F-254) using UV light. HRMS data were collected on a
Thermo Fisher Scientific Exactive Plus Oribitrap Mass Spectrometer. Melting points were recorded from a Electrothermal IA9100. NMR spectra were recorded on a Bruker-INOVA 400 MHz or 500 MHz spectrometer and calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$ – ^{1}H NMR 7.26 ppm, ^{13}C NMR 77.16 ppm). The following abbreviations were used to explain multiplicities (s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet).

General Reaction Procedures

General Procedure

The threads of a 3 mL borosilicate scintillation vial were thoroughly taped with Teflon tape. To this vial containing a stir bar was added quinone (0.2 mmol, 1 equiv), benzylic arene (2.0 mmol, 10 equiv) and Selectfluor (141.7 mg, 0.4 mmol, 2 equiv). Dichloroethane (1 mL) and H_2O (1 mL) were then added and stirred for approximately 1 min at room temperature. A solid amount of $Ag(4\text{-methoxypyridine})_2NO_3$ (15.5 mg, 0.04 mmol, 20 mol %) was added in one portion. The reaction was capped with a teflon screw cap and rubber septum (24/40). The reaction was heated to 50 °C until reaction was completed as judged by GCMS (up to 24 hours).

Upon completion, the reaction was diluted with ethyl acetate (1 mL) and transferred to a test tube containing H_2O (3 mL). The aqueous phase was extracted with ethyl acetate (3 x 3 mL) and the combined organic layers were dried over $MgSO_4$, filtered and carefully concentrated *in vacuo*. The crude material was purified by silica gel chromatography (ethyl acetate:hexanes) to yield the desired product.

Experimental Procedures and Characterization Data

General Conditions for the synthesis of bis(pyridine) silver complexes

To a round bottom containing a stir bar was added $AgNO_3$ (1 – 3.0 mmol) and pyridine (2.1 equiv.) which were mixed in MeCN (0.15M) and stirred at room temperature overnight protected from light. The reaction mixture was filtered through Celite, and the solvent removed from the filtrate under vacuum. The resulting residue was washed with diethyl ether.

bis(pyridine)silver(I) nitrate complex ($Ag(Py)_2NO_3$). The general procedure was employed using $AgNO_3$ (169 mg, 1.0 mmol) and pyridine (170 μL, 2.1 mmol). The reaction

afforded **Ag(Py)$_2$NO$_3$** (259.0 mg, 79% yield) as a white solid (m.p. 80−84 °C). **^{1}H NMR** (400 MHz, CD_3CN): 8.62 – 8.54 (m, 2H), 7.89 (tt, *J* = 7.7, 1.7 Hz, 1H), 7.48 (ddd, *J* = 7.7, 4.7, 1.4 Hz, 2H). **^{13}C{^{1}H} NMR** (100 MHz, CD_3CN): 151.8, 138.9, 125.7. **HRMS (ESI-TOF) m/z:** [M – NO_3]+ Calcd for $C_{10}H_{10}AgN_2$ 264.9889; Found 264.9878.

bis(4-(tert-butyl)pyridine)silver(I) nitrate complex (Ag(4-*t*BuPy)$_2$NO$_3$). The general procedure was employed using $AgNO_3$ (169 mg, 1.0 mmol) and 4-tert-Butylpyridine (308 μL, 2.1 mmol). The reaction afforded **Ag(4-*t*BuPy)$_2$NO$_3$** (380.6 mg, 86% yield) as a white solid (m.p. 138−139 °C). **^{1}H NMR** (400 MHz, CD_3CN): 8.49 (dd, *J* = 4.9, 1.6 Hz, 2H), 7.50 (dd, *J* = 4.9, 1.7 Hz, 2H), 1.31 (s, 9H). **^{13}C{^{1}H} NMR** (100 MHz, CD_3CN): 163.3, 151.7, 122.8, 35.6, 30.4. **HRMS (ESI-TOF) m/z:** [M – NO_3]+ Calcd for $C_{18}H_{26}AgN_2$ 377.1141; Found 377.1126.

bis(4-methoxypyridine)silver(I) nitrate complex (Ag(OMePy)$_2$NO$_3$). To a round bottom containing a stir bar was added $AgNO_3$ (510 mg, 3.0 mmol) and 4-methoxypyridine (640 μL, 6.3 mmol) which were mixed in MeCN (20 mL) and stirred at room temperature overnight protected from light. The reaction mixture was filtered through Celite, and the solvent removed from the filtrate under vacuum. The resulting residue was washed with diethyl ether to afford **Ag(OMePy)$_2$NO$_3$** (1,094.5 mg, 94% yield) as a white solid(m.p. 141−143 °C). **^{1}H NMR** (500 MHz, CD_3CN): 8.40 (dd, *J* = 5.1, 1.5 Hz, 2H), 7.02 (dd, *J* = 5.1, 1.5 Hz, 2H), 3.88 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, CD_3CN): 167.7, 153.3, 111.8, 56.5. **HRMS (ESI-TOF) m/z:** [M – NO_3]+ Calcd for $C_{12}H_{14}AgN_2O_2$ 325.0101; Found 325.0106.

bis(phenathroline)silver(I) nitrate complex (Ag(phen)$_2$NO$_3$). The general procedure was employed using $AgNO_3$ (169 mg, 1.0 mmol) and phenanthroline (378 mg, 2.1 mmol). The reaction afforded **Ag(phen)$_2$NO$_3$** (498.5 mg, 94% yield) as a yellow solid solid (m.p. 351−357 °C). **^{1}H NMR** (500 MHz, CD_3CN): 9.07 (dd, *J* = 4.5, 1.6 Hz, 4H), 8.64 (dd, *J* = 8.1, 1.6 Hz, 4H), 8.12 (s, 4H), 7.93 (dd, *J* = 8.1, 4.5 Hz, 4H).**^{13}C{^{1}H}NMR** (125 MHz, CD_3CN): 152.1, 143.7, 139.3, 130.4, 128.2, 125.7. **HRMS (ESI-TOF) m/z:** [M – NO_3]+ Calcd for $C_{24}H_{16}AgN_4$ 467.0420; Found 467.0403.

bis(2,2′-bipyridine)silver(I) nitrate complex (Ag(byp)$_2$NO$_3$). The general procedure was employed using $AgNO_3$ (169 mg, 1.0 mmol) and 2,2′-bipyridine (328 mg, 2.1 mmol). The reaction afforded **Ag(bypy)$_2$NO$_3$** (429.2 mg, 89% yield) as a yellow solid solid (m.p. 154−157 °C). **^{1}H NMR** (500 MHz, CD_3CN): 8.67 (ddd, *J* = 4.8, 1.6, 0.9 Hz, 1H), 8.35 (dt, *J* = 8.1, 0.9 Hz, 1H), 8.01 (td, *J* = 7.8, 1.7 Hz, 1H), 7.52 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H). **^{13}C{^{1}H}NMR** (125 MHz, CD_3CN): 154.5, 151.1, 139.3, 125.9, 122.8. **HRMS (ESI-TOF) m/z:** [M – NO_3]+ Calcd for $C_{20}H_{16}AgN_4$ 419.0420; Found 419.0412.

Figure 4 Compounds (1–15)

2-(4-methylbenzyl)cyclohexa-2,5-diene-1,4-dione (1). The general procedure was employed using 1,4-benzoquinone (22 mg, 0.2 mmol) and *p*-xylene (247 μL, 2.0 mmol). The reaction afforded **1** (30.1 mg, 71% yield) as a yellow oil separated by silica gel (3 to 10% ethyl acetate in hexanes). . **^{1}H NMR** (500 MHz, $CDCl_3$): 7.13 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 10.1 Hz, 1H), 6.69 (dd, *J* = 10.1, 2.5 Hz, 1H), 6.38–6.35 (m, 1H), 3.70 (s, 2H), 2.33 (s,3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 187.9, 187.4, 149.0, 136.8, 136.4, 133.3, 133.3, 129.7, 129.4, 34.9, 21.2. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{14}H_{13}O_2$ 213.0910; Found 213.0901.

2-(4-methoxybenzyl)cyclohexa-2,5-diene-1,4-dione (2). The general procedure was employed using 1,4-benzoquinone (22 mg, 0.2 mmol) and 4-methylanisole (252 μL, 2.0 mmol). The reaction afforded **2** (16.3 mg, 36% yield) as a yellow oil separated by silica gel (3 to 10% ethyl acetate in hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.10 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 10.1 Hz, 1H), 6.69 (d, *J* = 10.0 Hz, 1H), 6.35 (s, 1H), 3.79 (s, 3H), 3.68 (s, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 187.9, 187.5, 158.8, 149.2, 136.8, 136.5, 133.2, 130.5, 128.3, 114.4, 55.4, 34.5. **HRMS (ESI-TOF) m/z:** [M + H] + Calcd for $C_{14}H_{13}O_3$ 229.0859; Found 229.0853.

4-((3,6-dioxocyclohexa-1,4-dien-1-yl)methyl)phenyl acetate (3). The general procedure was employed using 1,4-benzoquinone (22 mg, 0.2 mmol) and *p*-tolyl acetate (287 μL, 2.0 mmol). The reaction afforded **3** (28.6 mg, 56% yield) as a pale yellow oil separated by silica gel (3 to 10% ethyl acetate in hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.19 (d, *J* = 8.5 Hz, 2H), 7.06–7.00 (m, 2H), 6.75 (d, *J* = 10.1 Hz, 1H), 6.69 (dd, *J* = 10.1, 2.5 Hz, 1H), 6.40 (dt, *J* = 2.6, 1.5 Hz, 1H), 3.72 (d, *J* = 1.0 Hz, 2H), 2.27 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 187.7, 187.1, 169.5, 149.7, 148.3, 136.7, 136.4, 134.0, 133.3, 130.4, 122.0, 34.7, 21.2. **HRMS (ESI-TOF) m/z:** [M + H] + Calcd for $C_{15}H_{13}O_4$ 257.0808; Found 257.0798.

4-((3,6-dioxocyclohexa-1,4-dien-1-yl)methyl)benzonitrile (4). The general procedure was employed using 1,4-benzoquinone (22 mg, 0.2 mmol) and p-tolunitrile (234 mg, 2.0 mmol). The reaction afforded **4** (8.9 mg, 20% yield) as a yellow resin separated by silica gel (3 to 25% ethyl acetate in hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.62 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 10.1 Hz, 1H), 6.75 (dd, *J* = 10.1, 2.4 Hz, 1H), 6.46–6.40 (m, 1H), 3.80 (s, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 187.3, 186.8, 147.2, 142.2, 136.8, 136.7, 133.8, 132.8, 130.2, 118.7, 111.3, 35.6. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{14}H_9NO_2$ 224.0706; Found 224.0698.

2-(2-methylbenzyl)cyclohexa-2,5-diene-1,4-dione (5). The general procedure was employed using 1,4-benzoquinone (22 mg, 0.2 mmol) and *o*-xylene (241 μL, 0.4 mmol). The reaction afforded **5** (24.3 mg, 57% yield) as a yellow oil separated by silica gel (5% ethyl acetate in

hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.22–7.14 (m, 3H), 7.12–7.06 (m, 1H), 6.81 (d, *J* = 10.1 Hz, 1H), 6.71 (dd, *J* = 10.1, 2.6 Hz, 1H), 6.11 (dd, *J* = 4.4, 2.0 Hz, 1H), 3.75 (d, *J* = 1.9 Hz, 2H), 2.21 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 187.8, 187.5, 148.4, 136.8, 136.7, 136.5, 134.4, 133.1, 130.8, 130.5, 127.6, 126.6, 32.7, 19.5. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{14}H_{13}O_2$ 213.0910; Found 213.0902.

2-(3-methylbenzyl)cyclohexa-2,5-diene-1,4-dione (6). The general procedure was employed using 1,4-benzoquinone (22 mg, 0.2 mmol) and *m*-xylene (247 μL, 2.0 mmol). The reaction afforded **6** (12.2 mg, 29% yield) as a yellow oil separated by silica gel (5% ethyl acetate in hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.21 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.0 Hz, 1H), 7.01–6.96 (m, *J* = 8.2 Hz, 2H), 6.77 (dd, *J* = 10.0, 4.9 Hz, 1H), 6.70 (dd, *J* = 10.1, 2.5 Hz, 1H), 6.37 (dt, *J* = 2.4, 1.6 Hz, 1H), 3.70 (d, *J* = 1.3 Hz, 2H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 187.9, 187.4, 148.9, 138.7, 136.8, 136.5, 136.4, 133.4, 130.2, 128.9, 127.9, 126.5, 35.2, 21.5. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{14}H_{12}O_2$ 213.0910; Found 213.0907.

2-(2,4,5-trimethylbenzyl)cyclohexa-2,5-diene-1,4-dione (7). The general procedure was employed using 1,4-benzoquinone (22 mg, 0.2 mmol) and 3'-methylacetophenone (266 μL, 2.0 mmol). The reaction afforded **7** (13.6 mg, 28% yield) as a colorless oil separated by silica gel (3 to 10% ethyl acetate in hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 6.96 (s, 1H), 6.84 (s, 1H), 6.79 (d, *J* = 10.1 Hz, 1H), 6.70 (dd, *J* = 10.1, 2.5 Hz, 1H), 6.12 (d, *J* = 1.9 Hz, 1H), 3.68 (s, 2H), 2.22 (s, 3H), 2.20 (s, 3H), 2.14 (s, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): δ 187.9, 187.6, 148.8, 136.8, 136.5, 135.7, 134.6, 133.8, 133.1, 132.2, 131.8, 131.5, 32.3, 19.4, 19.3, 18.9. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{16}H_{17}O_2$ 241.1223; Found 241.1216.

2-benzylcyclohexa-2,5-diene-1,4-dione (8). The general procedure was employed using 1,4-benzoquinone (22 mg, 0.2 mmol) and toluene (213 μL, 2.0 mmol). The reaction afforded **8** (19.8 mg, 46% yield) as a yellow oil separated by silica gel (5% ethyl acetate in hexanes). The data matches those previously reported.[3a] **^{1}H NMR** (500 MHz, $CDCl_3$): 7.33 (t, *J* = 7.3 Hz, 2H), 7.29–7.23 (m, 1H), 7.19 (d, *J* = 7.1 Hz, 2H), 6.78 (d, *J* = 10.1 Hz, 1H), 6.71 (dd, *J* = 10.1, 2.5 Hz, 1H), 6.37 (dt, *J* = 2.4, 1.6 Hz, 1H), 3.75 (d, *J* = 1.3 Hz, 2H).

2-benzyl-3,5-dimethylcyclohexa-2,5-diene-1,4-dione (9). The general procedure was employed using 2,6-dimethylbenzoquinone (27 mg, 0.2 mmol) and toluene (213 μL, 2.0 mmol). The reaction afforded **9** (22.2 mg, 49% yield) as a yellow oil separated by silica gel (3% ethyl acetate in hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.29–7.23 (m, 2H), 7.21–7.15 (m, 3H), 6.59 (dd, *J* = 3.0, 1.4 Hz, 1H), 3.86 (s, 2H), 2.10 (s, 3H), 2.05 (d, *J* = 1.6 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 188.5, 187.3, 145.6, 142.9, 141.9, 138.2, 133.2, 128.7, 128.7, 126.5, 31.9, 16.1, 12.9. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{15}H_{15}O_2$ 227.1067; Found 227.1055.

3-benzyl-2,5-dimethylcyclohexa-2,5-diene-1,4-dione (10). The general procedure was employed using 2,5-dimethyl-1,4-benzoquinone (27 mg, 0.2 mmol) and toluene (213 μL, 2.0 mmol). The reaction afforded **10** (20.4 mg, 45% yield) as a yellow oil separated by silica gel (3% ethyl acetate in hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.30–7.23 (m, 2H), 7.22–7.15 (m, 3H), 6.59 (d, *J* = 1.6 Hz, 1H), 3.87 (s, 2H), 2.09 (s, 3H), 2.04 (d, *J* = 1.6 Hz, 3H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 188.0, 187.7, 145.6, 143.1, 141.8, 138.2, 133.3, 128.8, 128.7, 126.6, 32.2, 16.1, 12.6. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{15}H_{15}O_2$ 227.1067; Found 227.1067.

2-benzyl-3,5-dichlorocyclohexa-2,5-diene-1,4-dione (11). The general procedure was employed using 2,6-dichloro-1,4-benzoquinone (35 mg, 0.2 mmol) and toluene (213 μL, 2.0 mmol). The reaction afforded **11** (23.9 mg, 45% yield) as a yellow solid separated by silica gel (3% ethyl acetate in hexanes). The data matches those previously reported.[4c] **^{1}H NMR** (400 MHz, $CDCl_3$): 7.30–7.20 (m, 5H), 7.03 (s, 1H), 4.01 (s, 2H).

3-benzyl-2,5-dichlorocyclohexa-2,5-diene-1,4-dione (12). The general procedure was employed using 2,5-dichloro-1,4-benzoquinone (35 mg, 0.2 mmol) and toluene (213 μL, 2.0 mmol). The reaction afforded **12** (27.7 mg, 52% yield) as a yellow solid (m.p. 96−98 °C) separated by silica gel (3% ethyl acetate in hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$): 7.35–7.21 (m, 5H), 7.10 (s, *J* = 3.3 Hz, 1H), 4.07 (s, 2H). **^{13}C{^{1}H} NMR** (125 MHz, $CDCl_3$): 177.5, 177.5, 144.4, 144.3, 141.6, 136.0, 133.0, 129.4, 129.0, 127.3, 34.1. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{15}H_{15}O_2$ 266.9974; Found 266.9972.

2-benzylnaphthalene-1,4-dione (13). The general procedure was employed using 1,4-naphthoquinone (32 mg, 0.2 mmol) and toluene (213 μL, 2.0 mmol). The reaction afforded **13** (21.0 mg, 42% yield) as a yellow solid (m.p. 93−94 °C) separated by silica gel (3% ethyl acetate in hexanes). The data matches those previously reported.[3a] **^{1}H NMR** (500 MHz, $CDCl_3$): 8.12 (dt, *J* = 5.5, 3.0 Hz, 1H), 8.05 (dt, *J* = 6.7, 3.1 Hz, 1H), 7.77–7.70 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.30–7.23 (m, 4H), 6.62 (t, *J* = 1.5 Hz, 1H), 3.91 (d, *J* = 1.1 Hz, 2H).

2-benzyl-5-hydroxynaphthalene-1,4-dione (14-C2) and 2-benzyl-8-hydroxynaphthalene-1,4-dione (14-C3). The general procedure was employed using 5-hydroxy-1,4-naphthoquinone (35 mg, 0.2 mmol) and toluene (213 μL, 2.0 mmol). The regioisomeric ratio of C2:C3 was determined to be 1:1.1 by crude ^{1}H NMR. The reaction afforded **14-C2** (6.0 mg, 11% yield) and **14-C3** (6.1 mg, 11% yield) as yellow solids separated by silica gel (2% DCM in hexanes). **NMR data for 14-C2 ^{1}H NMR** (500 MHz, $CDCl_3$): 11.92 (s, 1H), 7.67–7.58 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.30–7.21 (m,

4H), 6.55 (t, J = 1.5 Hz, 1H), 3.89 (d, *J* = 1.2 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): 190.5, 184.4, 161.4, 152.5, 136.6, 136.4, 135.6, 132.2, 129.6, 129.1, 127.2, 124.4, 119.6, 115.1, 35.9. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{17}H_{13}O_3$ 265.0859; Found 265.0853. **NMR data for 14-C3 ^{1}H NMR** (500 MHz, $CDCl_3$): 12.04 (s, 1H), 7.63–7.56 (m, 2H), 7.37–7.32 (m, 2H), 7.30–7.23 (m, 4H), 6.59 (t, J = 1.5 Hz, 1H), 3.89 (d, J = 1.1 Hz, 2H). **$^{13}C\{^{1}H\}$ NMR** (125 MHz, $CDCl_3$): 190.4, 184.5, 161.8, 150.9, 136.7, 136.7, 136.5, 132.3, 129.5, 129.1, 127.3, 124.5, 119.0, 115.3, 35.4. **HRMS (ESI-TOF) m/z:** [M + H]+ Calcd for $C_{17}H_{13}O_3$ 265.0859; Found 265.0849.

2-benzyl-3-methylnaphthalene-1,4-dione (15). The general procedure was employed using 2-methyl-1,4-naphthoquinone (34 mg, 0.2 mmol) and toluene (213 μL, 2.0 mmol). The reaction afforded **15** (11.1 mg, 21% yield) as a yellow solid (m.p. 104−105 °C) separated by silica gel (10% ethyl acetate in hexanes). The data matches those previously reported.[3h] **^{1}H NMR** (400 MHz, $CDCl_3$): 8.14–8.02 (m, 2H), 7.74–7.65 (m, 2H), 7.31–7.15 (m, 5H), 4.04 (s, 2H), 2.25 (s, 3H).

ASSOCIATED CONTENT

Supporting Information

^{19}F NMR studies, solvent screen, analogs of featured reaction, and relevant spectral data. This material is available free of charge via the internet at http:pubs.acs.org.

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ACKNOWLEDGMENT

J.D.G. gratefully acknowledges the National Science Foundation for receipt of a graduate fellowship (NSF Graduate Research Fellowship Program). This material is based upon work supported by the National Science Foundation under Grant No. 1752821 (R.D.B)

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