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Radical Benzylation of Quinones via C−H Abstraction

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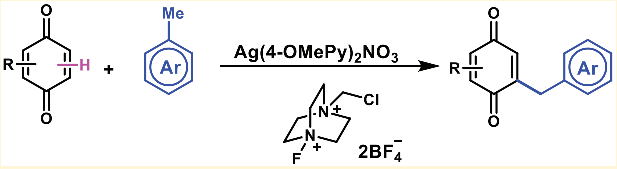
Supporting Information

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 preformed Ag(4-OMePy)$_2$NO$_3$ as a catalyst proved effective in improving the 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 toward blood-stage parasites.[1j]

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.[5] In the context of radical functionalizations, several methods have been reported that utilize Minisci-type conditions for radical functionalization of quinones, typically involving prefunctionalized radical precursors and strong oxidants.[6] 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).[6] 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).[7] 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).

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 a 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.[8] 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 toward 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 1 equiv 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 the 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,[9] 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-OMePy)$_2$NO$_3$ was optimum to produce **1** in a 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

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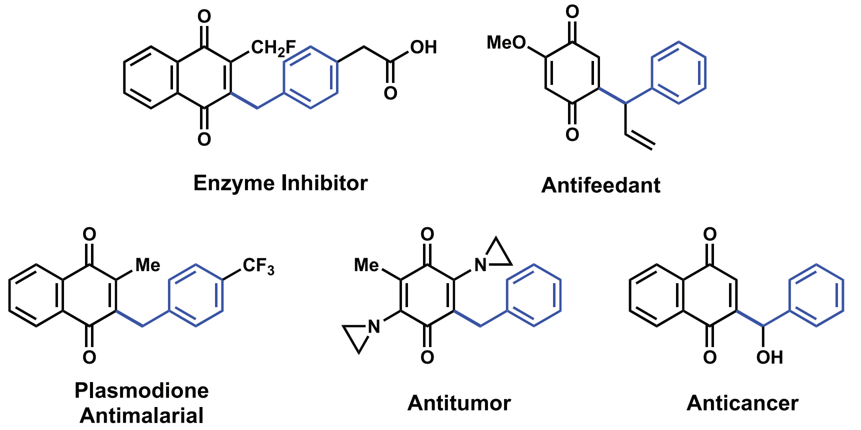


Figure 1. Biologically active quinones bearing benzylic substitution.

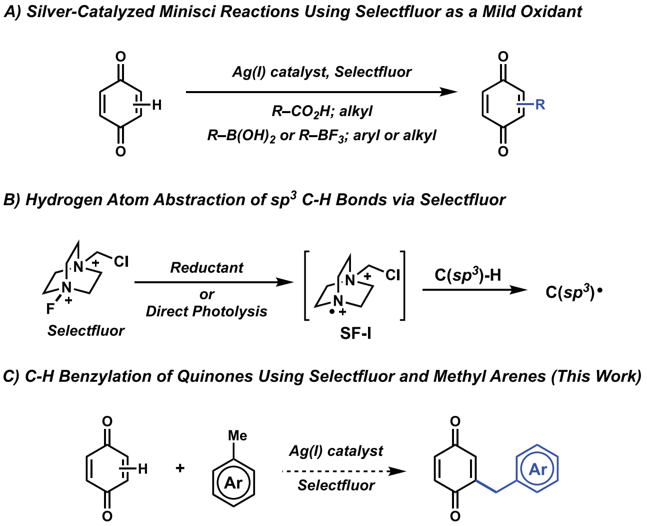


Figure 2. Selectfluor as an oxidant and/or HAT precursor.

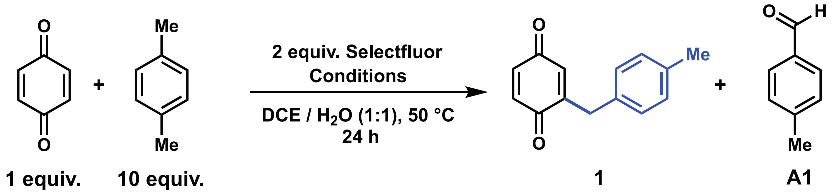
when 2,2′-bipyridine was used. Interestingly, although a control reaction without Ag(I) yielded no product (Table 1, entry 10), 1 equiv of 4-methoxypyridine was capable of promoting radical alkylation without a metal initiator (Table 1, entry 11), suggesting that electron transfer between the pyridine and Selectfluor was occurring.[9] Reaction with the standard oxidant for Minisci reactions, $(NH_4)_2S_2O_8$, led to a mixture of benzylated products (Table 1, entry 12).

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 the product in a 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 a 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 equiv. 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 analogues such as juglone (**14**) and menadione (**15**) can also be accessed. Efforts to extend this method toward other C−H radical precursors and heterocyclic substrates resulted in poor yields (see Supporting Information for details).

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 the Selectfluor concentration against an external standard over the course of 24 h (see Supporting Information for details). Entry 2 from Table 1 suggested that excess 4-methoxypyridine had a negative effect on the 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.[10a]

We were interested, however, in comparing the use of $AgNO_3$ and catalytic 4-methoxypyridine to Ag(4-OMe-Py)$_2$NO$_3$ to establish the benefit of the preformed catalyst. A catalytic amount of $AgNO_3$ consumed approximately 80% of Selectfluor within 24 h, 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, 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).[11] 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 preformed Ag(4-OMePy)$_2$NO$_3$ 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 preformed catalyst circumvents unfavorable interactions between 4-methoxypyridine and

Table 1. Optimization of Quinone Functionalization[a]



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-*t*-BuPy)$_2$NO$_3$	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%

[a] Reaction conditions: 1,4-benzoquinone (0.2 mmol), *p*-xylene (2.0 mmol), Selectfluor (0.4 mmol), Ag(4-OMePy)$_2$NO$_3$ (0.04 mmol), 2 mL of DCE/H_2O (1:1). [b] ^{1}H NMR yields to 1,3,5-trimethoxybenzene; values in parentheses indicate isolated yield. [c] Selectfluor was added last to the reaction.

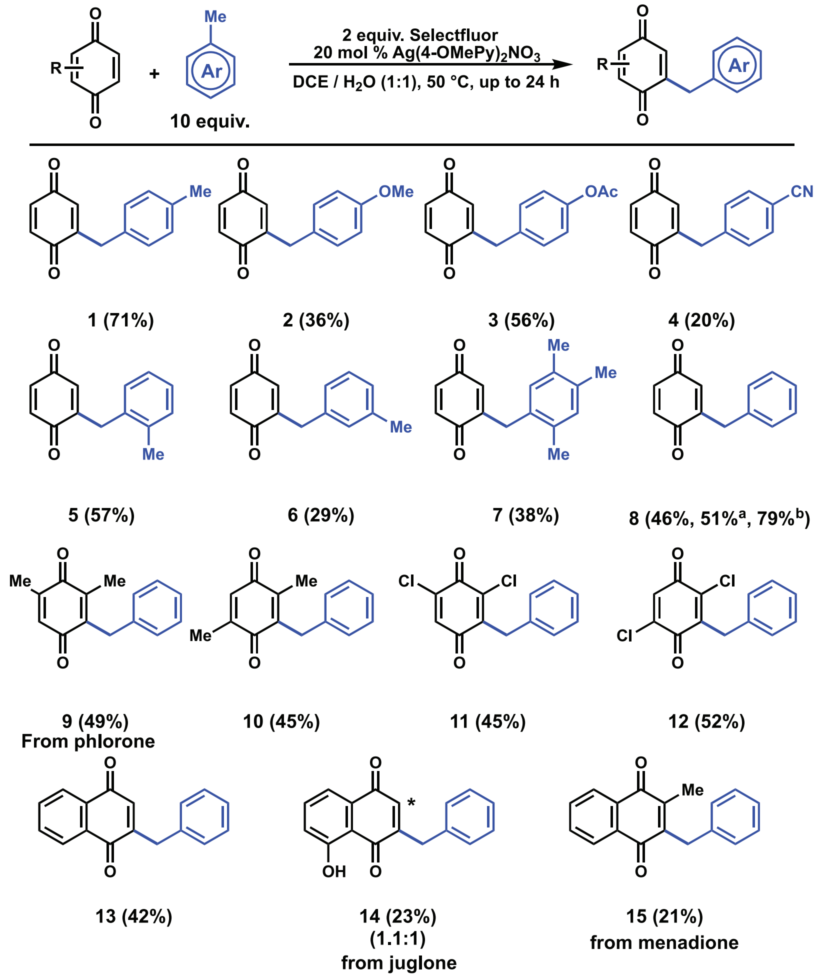


Figure 3. Scope of quinone benzylation. Yields refer to chromatographically pure compounds. (a) Toluene was used instead of DCE as an organic solvent. (b) 5 equiv of Selectfluor was used instead of 2 equiv.

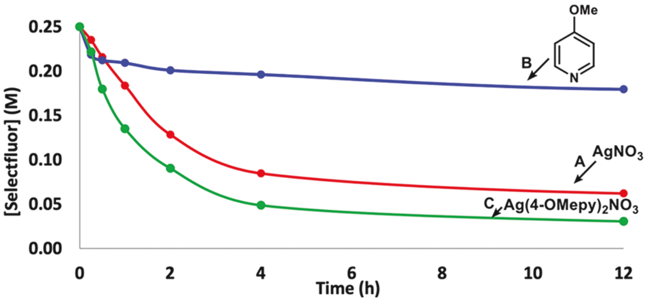


Figure 4. ^{19}F NMR monitoring of the consumption of Selectfluor (1.0 mmol) with either (**A**) 0.1 mmol of $AgNO_3$, (**B**) 0.2 mmol of 4-methoxypyridine, or (**C**) 0.1 mmol of Ag(4-OMePy)$_2$NO$_3$. Reaction conditions: Selectfluor (1.0 mmol) in DCE/H_2O (4 mL, 1:1) at 50 °C for up to 24 h. Using 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.

Selectfluor, presumably because strong association to Ag(I) precludes the occurrence of free pyridine in solution.

A plausible mechanism for the benzylation of quinone is shown in Figure 5. Single-electron transfer between Ag(4-OMePy)$_2$NO$_3$ and Selectfluor generates **SF-I** and the Ag(II) complex with concomitant generation of a 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.[12] A preformed 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 prefunctionalized 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) homogeneous materials, unless otherwise noted. Reactions were monitored by GC−MS (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 using a Electrothermal IA9100 instrument. NMR spectra were recorded on a Bruker-INOVA 400 or 500 MHz spectrometer and calibrated using a 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 were 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-methoxypyridine)$_2$NO$_3$ (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 the reaction was completed as judged by GC−MS (up to 24 h).

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 × 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 flask containing a stir bar were added $AgNO_3$ (1−3.0 mmol) and pyridine (2.1 equiv), which were mixed in MeCN (0.15 M) and stirred at room temperature overnight protected from light. The reaction mixture was filtered through Celite,

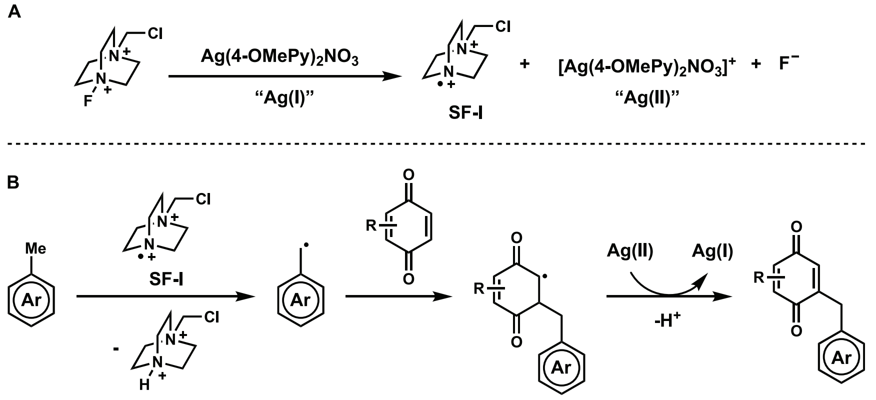


Figure 5. Proposed mechanism for quinone benzylation.

and the solvent was removed from the filtrate under a 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 $Ag(Py)_2NO_3$ (259.0 mg, 79% yield) as a white solid (mp 80−84 °C). ^1H NMR (400 MHz, CD_3CN): δ 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). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 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 ($Ag(4\text{-}tBu\text{-}Py)_2NO_3$). 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 $Ag(4\text{-}t\text{BuPy})_2NO_3$ (380.6 mg, 86% yield) as a white solid (mp 138−139 °C). ^1H NMR (400 MHz, CD_3CN): δ 8.49 (dd, *J* = 4.9, 1.6 Hz, 2H), 7.50 (dd, *J* = 4.9, 1.7 Hz, 2H), 1.31 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ 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 ($Ag(OMePy)_2NO_3$). To a round-bottom flask containing a stir bar were 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 a vacuum. The resulting residue was washed with diethyl ether to afford $Ag(OMePy)_2NO_3$ (1,094.5 mg, 94% yield) as a white solid (mp 141−143 °C). ^1H NMR (500 MHz, CD_3CN): δ 8.40 (dd, *J* = 5.1, 1.5 Hz, 2H), 7.02 (dd, *J* = 5.1, 1.5 Hz, 2H), 3.88 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN): δ 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 ($Ag(phen)_2NO_3$). The general procedure was employed using $AgNO_3$ (169 mg, 1.0 mmol) and phenanthroline (378 mg, 2.1 mmol). The reaction afforded $Ag(phen)_2NO_3$ (498.5 mg, 94% yield) as a yellow solid (mp 351−357 °C). ^1H NMR (500 MHz, CD_3CN): δ 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). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN): δ 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 ($Ag(byp)_2NO_3$). 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 $Ag(bypy)_2NO_3$ (429.2 mg, 89% yield) as a yellow solid (mp 154−157 °C). ^1H NMR (500 MHz, CD_3CN): δ 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). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN): δ 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 (3−10% ethyl acetate in hexanes).

^1H NMR (500 MHz, $CDCl_3$): δ 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). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 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 (3−10% ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 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). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 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 (3−10% ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 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). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 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 (3−25% ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 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). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 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). ^1H NMR (500 MHz, $CDCl_3$): δ 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). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 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). ^1H NMR (500 MHz, $CDCl_3$): δ 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). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 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 (3−10% ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 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). $^{13}C\{^1H\}$ 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] ^1H NMR (500 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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, $CDCl_3$): δ 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.[5c] ^{1}H NMR (400 MHz, $CDCl_3$): δ 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 (mp 96−98 °C) separated by silica gel (3% ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$): δ 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, $CDCl_3$): δ 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 (mp 93−94 °C) separated by silica gel (3% ethyl acetate in hexanes). The data matches those previously reported.[3a] ^{1}H NMR (500 MHz, $CDCl_3$): δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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 (mp 104−105 °C) separated by silica gel (10% ethyl acetate in hexanes). The data matches those previously reported.[4h] ^{1}H NMR (400 MHz, $CDCl_3$): δ 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b01004.

^{19}F NMR studies, solvent screen, analogues of featured reaction, and relevant spectral data (PDF)

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The authors declare no competing financial interest.

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